

BULLETIN OF MAGNETIC RESONANCE

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University of Illinois at Chicago

BULLETIN OF MAGNETIC RESONANCE

*The Quarterly Review Journal of the
International Society of Magnetic Resonance*

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The aims of the International Society of Magnetic Resonance are to advance and diffuse knowledge of magnetic resonance and its applications in physics, chemistry, biology, and medicine, and to encourage and develop international contacts between scientists.

The Society sponsors international meetings and schools in magnetic resonance and its applications and publishes the quarterly review journal, *The Bulletin of Magnetic Resonance*, the house journal of ISMAR.

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**Proceedings of the Eighth Meeting of the International
Society of Magnetic Resonance
August 22 - 26, 1983
Chicago, Illinois, U.S.A.
(PART II)**

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PREFACE

This year stands as one which has been of great loss to the scientific community. We have learned that Felix Bloch died on September 10, 1983. This loss makes us very sad, indeed. We hope that in his memory lectures will be presented at several institutions around the world.

Felix Bloch shared the 1952 Nobel Prize for physics with Edward M. Purcell in recognition of their observation of the nuclear magnetic resonance phenomena and for introducing and developing nuclear magnetic resonance. He maintained a continuous interest in nuclear magnetic resonance and its applications; and was very impressed to see the utmost important applications of NMR in biology and medicine. He actively participated in the activities of ISMAR and also served as a council member.

A memorial lecture for Vaino T. Hovi was given at the 8th ISMAR Meeting by Matti Punkkinen. Professor Hovi, who died in 1982, founded the Wihuri Physical Laboratory at the University of Turku in Finland. Those of us who knew him admired his friendliness and warmth, and his concern for promoting the objectives of ISMAR.

This issue contains the second part of the Proceedings of the 8th Meeting and the ISMAR Prize Lecture by Brebis Bleaney. He was unanimously recommended for this honor in 1983 by the Prize Committee in recognition of his pioneering work in developing electron spin resonance and his many important contributions to its application in solid state physics. A second ISMAR Prize was given to Anatole Abragam in recognition of his outstanding contributions to the development and fundamental understanding of nuclear magnetism, nuclear polarization and nuclear ordering.

About 500 scientists from 28 countries participated in the 8th Meeting. The program included the most recent advances in magnetic resonance, such as multiple quantum spectroscopy, zero field nuclear magnetic resonance, magnetization and coherence transfer, microwave induced optical nuclear polarization, magnetic resonance in incommensurate and chaotic systems, spin physics in disordered semiconductors, rotating helical magnetic ordering,

highly advanced studies of three dimensional structures of polypeptides, studies of protein and nucleic acids, membranes, antibodies, liquid crystals and advances in closely related fields as laser induced spin coupling phenomena, neutron magnetic resonance, geonium spectra of the finer structure of the electron, and infrared spectra of molecular ion beams at dissociation.

For their help in making the 8th Meeting a great success, I wish to thank again the Council, National Advisory Committee and Local Organizing Committee of ISMAR.

I was pleased to hear from John Bjorkstam, Chairman of the Election Committee, that the newly revised Constitution of ISMAR was endorsed by an absolute majority of the voting members. Again, I wish to thank the Ad Hoc Committee for putting together a Constitution that is acceptable to members of our society.

We have included in this issue of the bulletin, a letter from the Election Committee detailing the results of the election. (See page 92.) I would like to thank members of the Nominating and the Election Committees for their important undertaking in service of the magnetic resonance community. Also, my thanks to the editor of the bulletin, D. Gorenstein, for excellent editorial work. I congratulate the newly elected officers and council members whose term of office begins January 1, 1984 and look forward to productive cooperation. I also wish to express my appreciation to those who recently completed their term in office.

My thanks and gratitude to ISMAR members for the honor of serving a lifetime as "The Founding Chairman of ISMAR." I hope that I shall be worthy of this privilege and be able to serve well the society and magnetic resonance community in this unusual capacity. I appreciate the personal recognition I was given by election to the Council and to the office of Secretary-General.

Looking forward to our next meeting in Brazil, I would like to inform you that Dr. N. Vugman of the Physics Institute of the Federal University of Rio de Janeiro has agreed to chair the 9th Meeting scheduled for 1986.

Daniel Fiat

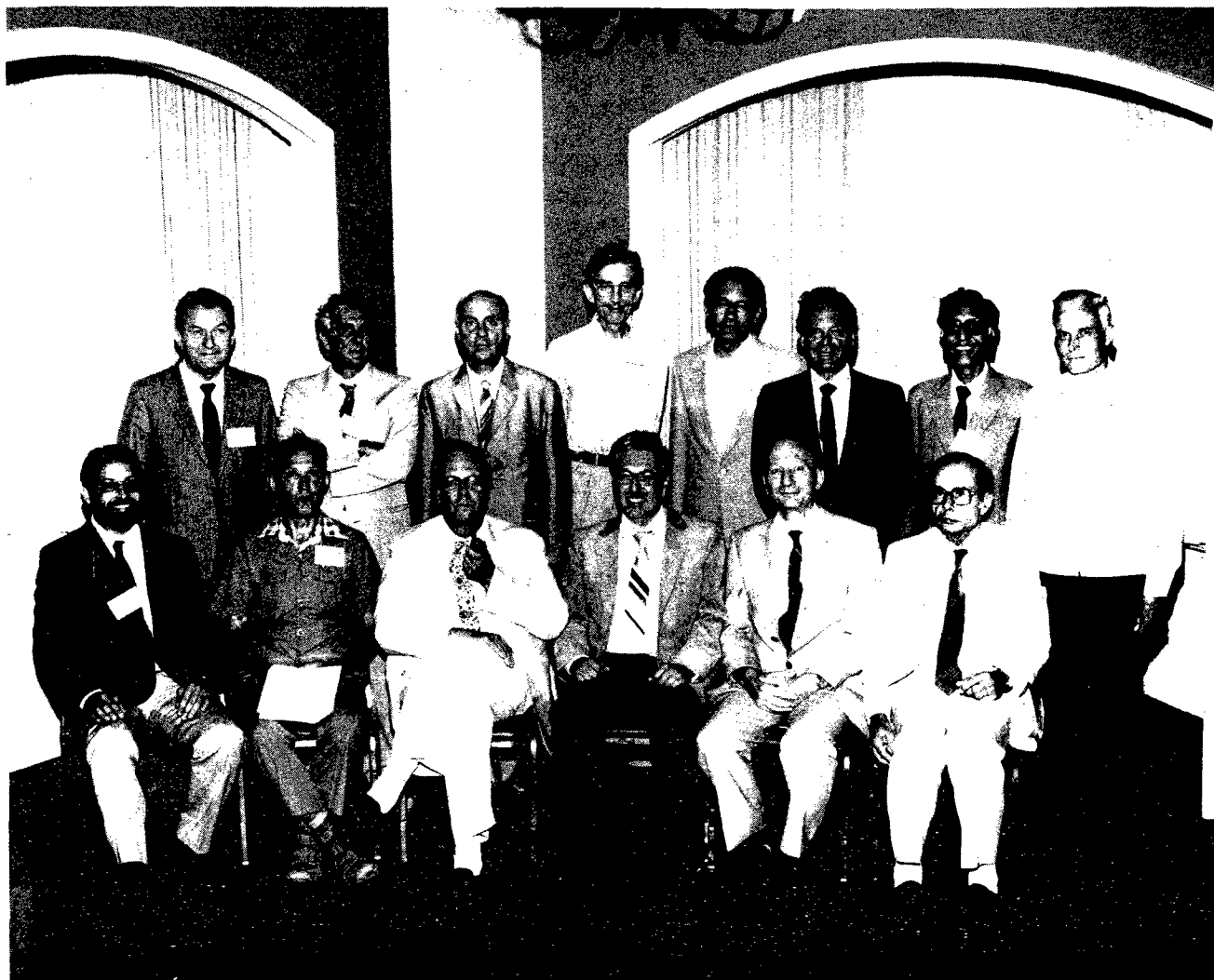
**Announcement of the ISMAR Award to
Professor Anatole Abragam,
College de France, Paris**

K. H. Hausser, Heidelberg, West Germany

Let me begin first by making an announcement concerning a previous ISMAR prize which was awarded to Professor Anatole Abragam from the College de France in Paris. Unfortunately it was not actually handed over to him because he could not come to the respective ISMAR meeting to receive the prize. It would have been a pleasure to present the prize to him here in Chi-

cago, but Professor Abragam could not be with us here today. In order to avoid further delay, the ISMAR Council has decided on the recommendation of the present ISMAR prize committee to forward the prize to Professor Abragam to Paris, and it is a great pleasure for me to announce that it was forwarded to him a few weeks ago.

Photograph of members of ISMAR Council taken at the site of the 8th ISMAR Meeting, Chicago, IL August 22-26, 1983.



standing: I. Ursu, F. Conti, R. Blinc, I. Solomon, R.R. Ernst, H.C. Wolf, P.T. Narasimhan, and E. Lippmaa
sitting: N.V. Vugman, J. Smidt, O. Jardetzky, D. Fiat, E.R. Andrew, and K.H. Hausser

**The Scientific Accomplishments of Professor B. Bleaney
(Introductory Award Address to the ISMAR Conference,
Chicago, 1983)**

**K.H. Hausser
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All but one of the ISMAR Prizes given so far have been awarded for work in the field of NMR. The only exception was the third ISMAR Prize which was awarded posthumously in Banff in 1977 to Professor Zavoisky for the discovery of a resonance phenomenon of electronic spins, in fact, the first successful experiment of any magnetic resonance at all. However, Professor Zavoisky did not continue to work in this field and left it to others to explore and to elaborate this discovery. In this pioneering period such a large number of original contributions to the development of the technique of electron spin resonance (ESR) and its application in various fields of physics is due to Professor B. Bleaney that it is fair to say that he has really developed ESR to what it is today. Hence the task for the Prize Committee for the 1983 ISMAR Prize was easy: it decided unanimously to award the 1983 ISMAR Prize to him. May I read the wording of the award to you: "The International Society of Magnetic Resonance hereby confers to Professor B. Bleaney of Oxford, Great Britain, the International Society of Magnetic Resonance Award for the year 1983 in recognition of his pioneering work in developing Electron Spin Resonance and his many important contributions to its application to solid state physics."

Bleaney was born in London and went to school there and then to Oxford University where he took his B.A. in physics in 1937 and D. Phil. in 1939. In 1940 Bleaney became the youngest member of a group working for the British Admiralty in the Clarendon Laboratory

on centimeter waves. In 1941-2, in collaboration with J. H. E. Griffiths, he built small klystrons which were used as local oscillators in experimental radar systems at 3 cm wavelength. After the war the microwave tubes developed for radar gave an important tool to physicists. An early application was the analysis of the rotational structure of the inversion band of ammonia. This was done in 1945-6 with R. P. Penrose. With the same co-author, Penrose, Bleaney investigated the temperature dependence of the ESR of transition metal compounds down to 14 K. After Penrose discovered the hyperfine structure during a visit to Leiden, Bleaney, with a number of collaborators, made detailed studies of this very important phenomenon of ESR in salts of the iron, the lanthanide, and the actinide groups. This was the time of a very fruitful collaboration in Clarendon Laboratory with a group of theorists, including A. Abragam, M. H. L. Pryce, K. W. H. Stevens, and others who studied the theory of magnetic resonance.

Other important work of Bleaney concerned the study of exchange interactions of pairs of ions in semi-dilute salts by measuring the spin-spin interactions from the resonance spectrum. The first successful experiment was carried out in 1951 based on his proposal to use the local anisotropy of a paramagnetic ion as the mechanism for producing orientation.

Although I have concentrated in this very brief and sketchy review on Bleaney's contributions to ESR in the pioneering time in the late forties and in the fifties, he is still as active in research in physics today as he has

been all his adult life. His main field of interest in recent years has been the enhancement of nuclear magnetism in rare earth compounds. These investigations were carried out using nuclear magnetic resonance in collaboration with F. N. H. Robinson and M. R. Wells, and with experiments involving enhanced nuclear cooling and nuclear orientation together with N. J. Stone and his group. He has just given in the week

prior to the ISMAR meeting an invited paper at a conference in Denver and he came to Chicago not only for the ISMAR meeting, but also in the course of his collaboration with Professor Clyde Hutchison at the University of Chicago.

So let me conclude by extending to Professor Bleaney our congratulations and our best wishes for many more years of fruitful, successful, and rewarding work in scientific research.



Professor B. Bleaney
The Clarendon Laboratory
Oxford, United Kingdom

Recipient of the 1983 ISMAR Award

Microwave Spectroscopy in Oxford: The Early Years
Remarks on the Occasion of Receiving the 1983 ISMAR Award

B. Bleaney

**The Clarendon Laboratory
Parks Road
Oxford OX1 3PU United Kingdom**

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I. INTRODUCTION

The first measurements of spectra at microwave frequencies using modern techniques were made before the end of World War II. The reason for this was that the frequency of 24 GHz (a wavelength of 12.5 mm; known as "K-band") had been picked by the Radiation Laboratory at M.I.T. for a precision radar system. Unfortunately, it turned out that this coincided with the region at which attenuation in the atmosphere becomes a serious problem. The attenuation arises mainly from water vapor (the H₂O molecule has an electric dipole moment), and to a lesser extent from oxygen (oxygen molecules have a magnetic dipole moment). The attenuation is small, amounting to about 0.2 decibel per km at the partial pressure of water vapor normally present in the

atmosphere. This is very small by laboratory standards, but in terms of a radar system aimed at detecting an echo from a distance of 50 km (a return path of 100 km), the return signal is reduced in power by a factor of 100, a very significant loss.

II. MICROWAVE ABSORPTION IN THE ATMOSPHERE

An absorption of order 0.2 db per km is extremely difficult to measure in the open atmosphere, though an ingenious radiometer was developed for this purpose at the Radiation Laboratory, M.I.T. by Dicke (1,2). It is almost equally difficult to measure in the laboratory, but a novel type of apparatus was developed by Becker and Autler (3) at Columbia University, New York, specifically for this purpose. The

absorption is small for a number of reasons. There is of course the well known fact that the quantum of energy involved is much smaller than the Boltzmann energy kT ($h\nu/kT$) being about 0.004 at room temperature for a frequency of 25 GHz; the stimulated emission and absorption are almost equal, and the net absorption is reduced by a factor $(h\nu/kT)$. Since the quantum absorption is $h\nu$, the power absorption coefficient falls as the square of the frequency, a problem that arises in nearly all radiofrequency spectroscopy (an exception is electron paramagnetic resonance, EPR, below a temperature of 1 K). In addition: (1) the water vapor absorption arises from a weak transition between two excited levels with a low Boltzmann factor of about 0.12 at room temperature; and (2) at atmospheric pressure the collision frequency is not much smaller than the resonant frequency, so the absorption line is broad, and correspondingly weak.

The results obtained by Becker and Autler are shown in Figure 1. The absorption has a maximum, arising from the water vapor line, very close to the K-band frequency of 0.8 cm^{-1} ; there is also a background absorption that rises steadily with increasing frequency. This is attributed to the low frequency tails of absorption lines centered at higher frequencies, and its value in the region shown in the figure depends on the widths and shapes of these lines. At atmospheric pressure, the linewidth is dominated completely by the effects of collisions with other molecules, and Van Vleck and Weisskopf (4) reconsidered the formulae of Lorentz for collision broadening when the collision frequency is comparable to the resonance frequency. In addition to the square of the frequency mentioned above, the line shape contains a "shape factor"

$$F(\nu_0, \nu) = (1/\pi) \left[\frac{\Delta\nu}{\Delta\nu^2 + (\nu_0 - \nu)^2} + \frac{\Delta\nu}{\Delta\nu^2 + (\nu_0 + \nu)^2} \right] \quad (1)$$

where the first term is similar to that of Lorentz, and the second term is important only for broad lines. The

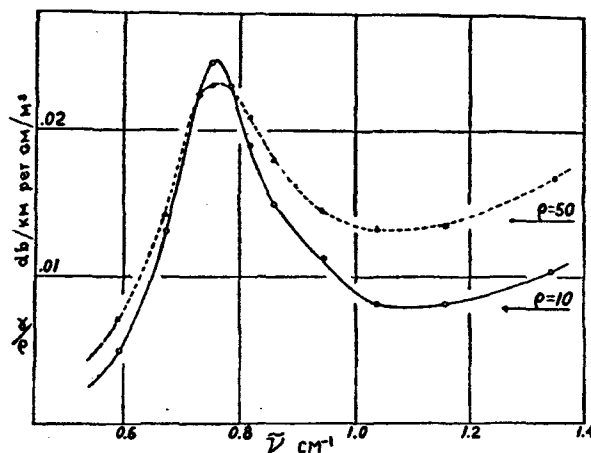


Figure 1. Absorption curve for water vapor in the atmosphere. The attenuation in db per km per g per m^3 of H_2O is plotted against wavenumber. The broken curve is for a density of 50 g/m^3 , the full curve for 10 g/m^3 . The increasing absorption at the higher wavenumbers arises from the tails of lines at higher frequencies. After Becker and Autler (3).

absorption coefficient at frequency ν is given by the relation

$$\alpha = n \frac{4\pi^3 \nu^2}{3ckT} |\mu_{ij}|^2 F \quad (2)$$

where n is the number of molecules per unit volume in the pair of levels between which transitions are induced at resonant frequency ν_0 , with transition matrix element μ_{ij} .

Because of the importance of this formula, I proposed at the beginning of 1945 that it should be checked using the microwave absorption spectrum of the ammonia molecule, NH_3 . This molecule gives an absorption stronger by a factor of 1000 than that of water vapor in the atmosphere, and since the vapor pressure of ammonia at room temperature is about 6 atm, it can be studied over a wide range of pressure. With the agreement of our employers, the British Board of Admiralty, R. P. Penrose and I began such experiments early in 1945.

III. THE INVERSION SPECTRUM OF AMMONIA

The origin of the NH_3 spectrum is quite different from that of H_2O or O_2 . The shape of the NH_3 molecule is a flat pyramid, with the nitrogen atom at the apex, on either side of an equilateral triangle of protons. Separating these two equilibrium configurations, there is only a rather low potential barrier, and the molecule tunnels through this barrier at a frequency of about 24 GHz. Since the direction of the electric dipole moment (1.45 Debye units) is reversed each time the barrier is traversed, there is a strong oscillating dipole moment that can interact with a microwave electric field. In 1934 Clee-

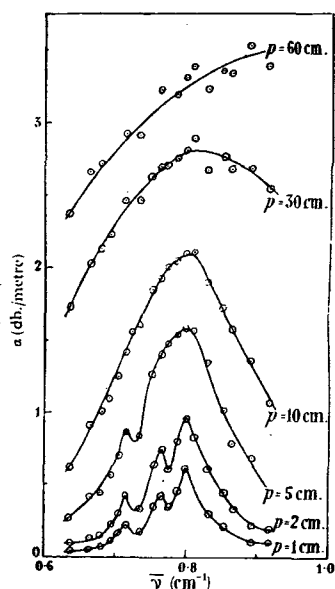


Figure 2. The inversion spectrum of ammonia gas at cm wavelengths, showing the absorption curves (in db/m) for ammonia gas at various pressures (in cm Hg). Structure becomes visible at the lower pressures. After Bleaney and Penrose (6).

ton and Williams (5) had observed the absorption using a cloth bag filled with ammonia gas; this was placed in the path of the radiation from some

split-anode magnetrons, whose wavelength was measured by an echelette grating rather like a Venetian blind. They had obtained an answer that proved to be not far from that given by our modern techniques; these included waveguides, tunable reflex klystrons (designed and constructed in the Clarendon Laboratory), and silicon-tungsten diodes as detectors. In our first experiments the ammonia was contained in a 1 m length of waveguide, closed by thin mica windows. The absorption was determined from the drop in power reaching the detector when ammonia gas was admitted to the guide, and the results (6) are shown in Figure 2. As the pressure is reduced, the absorption line becomes narrower and signs of structure become visible in the spectrum; to examine this more closely, it was necessary to go to lower pressures, and to improve the sensitivity a cavity resonator was used instead of the waveguide. This cavity, shown in Figure 3, had been designed for wavelength measurements, and it was adapted by incorporating thin mica windows. The damping of the cavity on admitting the ammonia gas was determined by tuning from one half-power point of the resonance curve to the other, the motion of the micrometer drive being amplified by a simple optical lever. The "Q" of the cavity approached 10,000, and it was equivalent to use of a guide of length $Q/2\pi$ wavelengths, so that the gain in sensitivity is considerable.

The spectrum of ammonia (7) obtained at a pressure of 1.2 mm Hg is shown in Figure 4. It displays a complex structure; this arises from centrifugal distortion of the molecule when rotating. This distortion modifies the potential barrier, with a consequent change in the tunnelling frequency, that becomes slightly different for each rotational state. "End-over-end" rotation increases the height of the barrier, and decreases the tunnelling frequency; the reverse happens when the molecule rotates about its symmetry axis, a line through the nitrogen atom, perpendicular to the plane containing the protons.

The splitting was expected to follow the formula of Sheng, Dennison, and Barker (8)

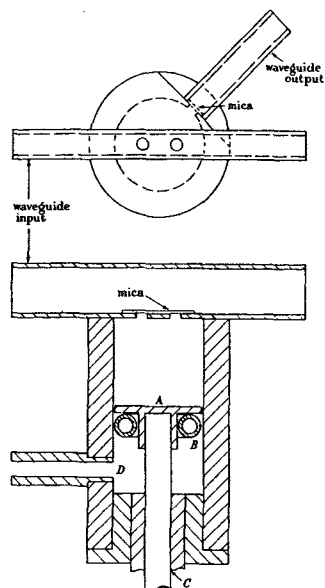


Figure 3. The cavity resonator used by Bleaney and Penrose (7) to measure the absorption of ammonia gas at lower pressures. The side view (above) shows the two-hole coupling used to select the $H_{0,1}$ ($TE_{0,1}$) mode that gives the highest quality factor Q . A similar resonator was used to measure the wavelength. A: plunger driven by micrometer; B: water in glass tube to eliminate unwanted modes; C: oil seal; D: to reservoir of ammonia gas.

$$\bar{\nu} = \bar{\nu}_0 - AJ(J+1) + BK^2 \quad (3)$$

and the formula used by us (7) was

$$\begin{aligned} \bar{\nu} = & 0.7935 - 0.00505 J(J+1) \\ & + 0.00704 K^2 \\ & + 0.63[-0.0050 J(J+1) \\ & + 0.0070 K^2]^2 \end{aligned} \quad (4)$$

in units of wavenumber (cm^{-1}). The higher order terms correspond simply to the expansion of an exponential for the tunnelling frequency.

The reason why such accurate

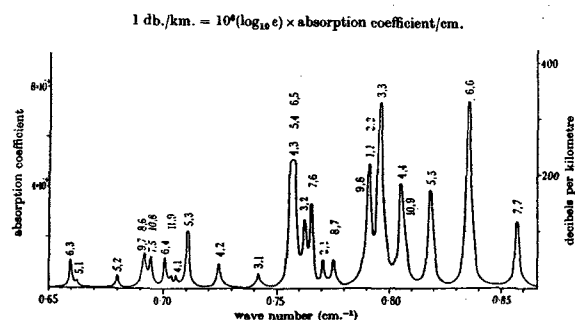


Figure 4. Absorption coefficient (per cm of path length) for the inversion spectrum of ammonia gas at a pressure of 1.2 mm Hg, measured by Bleaney and Penrose (7). The linewidth is about 10^{-3} cm^{-1} , and wholly due to collision broadening (the Doppler width is about 10^{-6} cm^{-1}). Each line arises from a different rotational level and is labelled by the rotational quantum numbers J, K . For $K = J$ the molecule is rotating about its symmetry axis, and centrifugal distortion lowers the potential barrier, increasing the inversion frequency. For $K \ll J$, the molecule is rotating "end over end", increasing the barrier height and reducing the inversion frequency. The frequencies of the lines are fitted to Eq. (4) in the text.

measurements of the ammonia spectrum were possible is readily seen from the intensity. The strongest lines in Figure 4 correspond to an attenuation approaching 400 db/km instead of 0.2 db/km for water vapor in the atmosphere. The integrated absorption at a pressure of 4.5 mm Hg between wavenumbers 0.67 and 0.87 cm^{-1} agreed with the calculated value within 1%, but the extensive rotational structure makes it difficult to verify the line shape of Van Vleck and Weisskopf in detail. The linewidths vary considerably from line to line and are noticeably larger than would be expected from kinetic theory values of the collision cross-section, being mainly determined by dipolar interactions between the molecules. A

further complication is that as the pressure increases towards 1 atm, multiple collisions become important, and the resonant frequency appears to shift downwards [see Bleaney and Loubser (9)], reaching zero at a pressure of about 2 atm.

The alternative to working at high pressures is to reduce the pressure to the point at which lines from different rotational states no longer overlap. This means working in a region where the second term in the shape factor is negligible; then, at the center of a line where $(\nu - \nu_0)$ is zero, the formula for the intensity reduces to

$$\alpha = \frac{4\pi^2\nu^2}{3ckT} |\mu_{ij}|^2 (n/\Delta\nu) \quad (5)$$

Since the linewidth parameter $\Delta\nu$ is proportional to the collision frequency, and hence to the pressure, and the number density of molecules n is also proportional to the pressure, this formula shows that the intensity at the center of the line should be independent of pressure, so long as no other contribution to the linewidth is significant. An experimental test (10) to this prediction is shown in Figure 5. As the pressure decreases, the intensity at the center of the line at first remains constant, as expected, but then starts to decrease at a pressure well above that at which other forms of broadening should begin to play a role. The figure shows that the effect is much worse at a higher power level in the cavity, confirming that it arises from "power saturation". This effect is much worse in a cavity than in a waveguide, because the radiation density is proportional to "Q". An unfortunate result is that we were defeated in our efforts to use Stark modulation in the cavity, because this needs such a low pressure that saturation effects greatly reduce the intensity.

The use of a cavity resonator has a second drawback: a sharply tuned device is tedious if not impossible to use in searching for a weak absorption line whose frequency is not precisely known. Apart from the ammonia spectrum, only the lowest rotational lines of molecules such as OCS occur at wavelengths longer than 1 cm, and investigations of

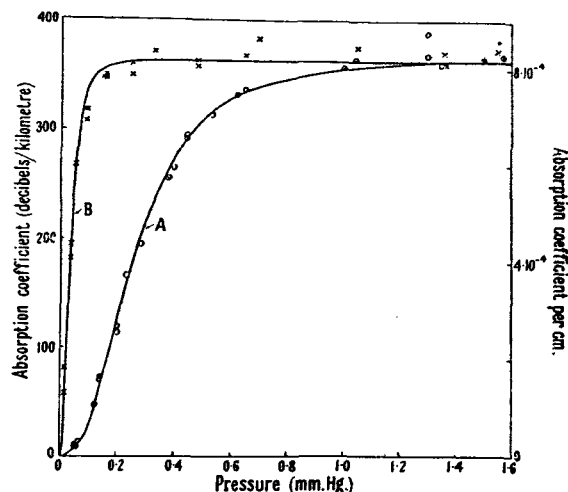


Figure 5. The absorption coefficient for ammonia gas at the center of the strongest line $J, K = 3, 3$, as a function of pressure. The fall in absorption at the lowest pressure arises from power saturation, and occurs at higher pressures when the radiation energy density is large (curve A, power entering cavity = 12 milliwatts) than for a lower density (curve B, power = 20 microwatts). After Bleaney and Penrose (10).

their spectra were being intensively pursued in the USA. [For an authoritative treatise, see Townes and Schawlow (11)]. In 1947 Penrose and I decided to turn our efforts to electron paramagnetic resonance, a subject much more closely linked with low temperature physics, the principal research activity in the Clarendon Laboratory at that time. Paramagnetic resonance experiments had just begun at room temperature, and we decided to extend these to lower temperatures (see below, section V).

IV. FERROMAGNETIC RESONANCE

In 1945 J. H. E. Griffiths decided to investigate the permeability of the ferromagnetic metals iron, cobalt and nickel at microwave frequencies. It was already known from reflectivity measurements that the oscillatory

permeability drops to unity at optical frequencies, but there was little sign of any decrease at radiofrequencies. To make measurements at centimeter wavelengths he used a resonant cavity in which one end wall was made of the ferromagnetic metal. The power loss depends on the product of the resistivity ρ and the magnetic permeability μ , because the skin depth depends on the permeability. The power loss is measured by the damping of the cavity resonance, and to separate the effect of the permeability from other losses, he measured the change in the damping as a function of external magnetic field. As magnetic saturation in the metal is approached, the permeability decreases to unity, while the resistivity should be independent of magnetic field. Unexpectedly, the cavity losses, instead of decreasing steadily, passed through a maximum, as shown in Fig. 6, where the quantity $(\mu\rho)$ is plotted as a function of magnetic field. The figure shows that at a shorter wavelength the maximum shifts to higher field. Griffiths (12) realized that this was a resonance phenomenon, and that it did not occur exactly at the electron spin resonance point

$$h\nu = g\mu_B B, \text{ with } g = 2$$

because of the presence of demagnetizing fields inside the metal sample. The problem of how to allow for such fields was solved using classical theory by Kittel (13), and using quantum theory by Van Vleck (14). Ferromagnetic resonance, and its later analogues antiferromagnetic and ferrimagnetic resonance, have been extensively used to investigate magnetically ordered materials.

V. ELECTRON PARAMAGNETIC RESONANCE

The discovery of ferromagnetic resonance, and of nuclear magnetic resonance by Bloch and Purcell, suggested at once that magnetic resonance could be observed in electronic paramagnetic crystals. In fact such an experiment had already been carried out by Zavoisky (15) at Kazan in the U.S.S.R., though this did not become known to us until later. His experiments,

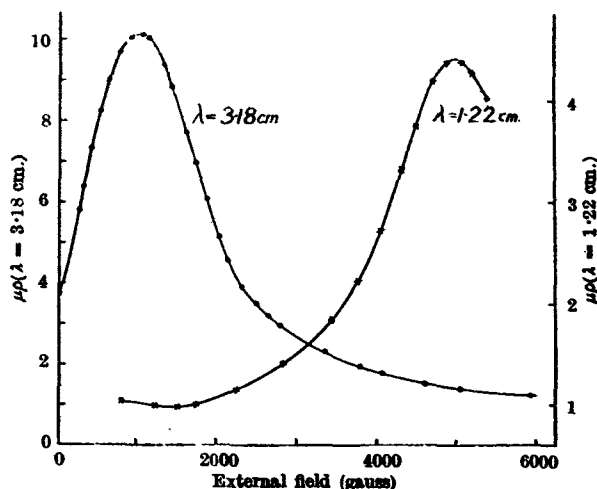


Figure 6. Ferromagnetic resonance curves of nickel metal at wavelengths of 3.18 and 1.22 cm, observed by Griffiths (12). The absorption is proportional to the product of the magnetic permeability μ and electric resistance ρ , and was determined by measuring the damping coefficient of the cavity as the applied magnetic field was increased. For higher frequencies the resonance is shifted to higher fields, but is displaced from the true resonance value by the internal field.

initially on solutions of manganese and copper salts at room temperature, were made at a frequency of 120 MHz. We were in the happy position of being able to work at frequencies 100 times greater, so that the resonance lines were much better resolved and much more intense. From pre-war use of paramagnetic salts for magnetic cooling we were aware that substances such as the alums of iron and chromium had ground states with splittings of a few GHz, and it was obvious that these could be measured by magnetic resonance with much greater precision than could be inferred from classical magneto-thermal experiments. Furthermore, large single crystals of such alums, and other substances such as copper sulphate, could readily be grown from aqueous solution.

The first electron paramagnetic

resonance experiments in Oxford were carried out by D. M. S. Bagguley in the autumn of 1946 at a wavelength of 3 cm. These quickly revealed the main features of ESR: anisotropic g -values, showing different spectra when the crystal unit cell contains ions on sites where the principal axes of the g -tensor are differently oriented; splittings in zero magnetic field, caused by higher order effects of the crystal field and spin-orbit coupling, when the ground state has a degeneracy greater than two-fold [see, for example, Bagguley and Griffiths (16)]; linewidths ranging from 0.01 to over 0.1 tesla, arising from spin-spin interactions between the magnetic ions; absence of resonance at room temperature for ions whose spin-lattice relaxation rates exceed 10 to 100 GHz.

The presence of exchange interactions between the magnetic ions in insulating crystals, in addition to magnetic dipolar interactions, was suspected but little quantitative information was available. In magnetic resonance, an effect known as "exchange narrowing" was predicted by Gorter and Van Vleck (17), and this was shown to occur in $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ by Bagguley and Griffiths (18). Such a narrow resonance line is shown in Figure 7; the linewidth is only 3mT, a factor ten-fold smaller than that calculated from the formulae of Van Vleck (19) for purely magnetic dipole interaction. In addition, the line shape is close to Lorentzian (exchange narrowing has similarities with motional narrowing) rather than Gaussian, the shape expected (in a good approximation) for dipolar interactions.

The resonance line in Figure 7 is observed when the applied magnetic field has a particular crystallographic direction such that the resonance lines from the two dissimilar ions in the unit cell are coincident. In other directions two resonance lines should appear because the g -value of each ion is anisotropic (g varies with angle from about 2.05 to 2.4 for the divalent cupric ion), and the principal axes of the g -tensor are different for the two ions. However, Bagguley and Griffiths (18) found that only one line appeared at a wavelength of 3.04 cm, but that at

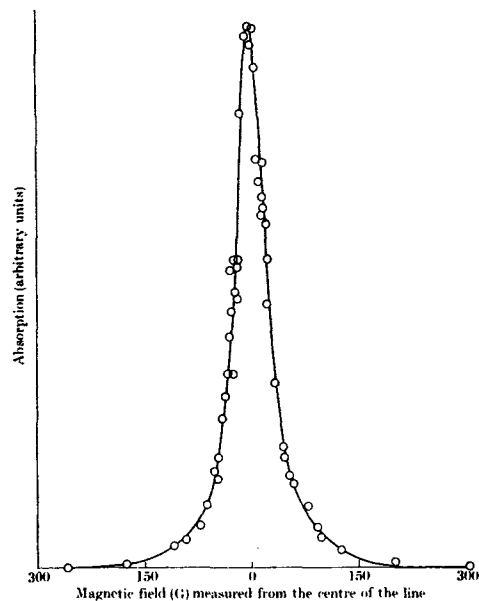


Figure 7. Electron paramagnetic resonance curve for $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ at a wavelength of 1.23 cm (frequency 24 GHz), in a direction where the line from the two copper ions in the unit cell have the same value of the spectroscopic splitting factor g . The linewidth is about one-tenth of that expected from magnetic dipole interaction between neighboring ions, showing the effect of "exchange narrowing". After Bagguley and Griffiths (18).

a shorter wavelength (0.85 cm) this was replaced by a pair of rather wide lines. This result is another effect of exchange interaction (Pryce 20). At the longer wavelength (lower field) the frequencies at which the two ions precess differ by an amount that is less than the exchange frequency; the ions are so strongly coupled that only one line is observed, at a frequency corresponding to the average of the two precession frequencies. As the applied field increases the difference between these two precession frequencies also increases, and when it approaches the exchange frequency, two lines become resolved. From these experiments an exchange frequency of about 0.15 cm^{-1}

was deduced for the Cu^{2+} ions in copper sulphate.

To overcome the problem of excessive broadening from rapid spin-lattice relaxation, measurements at lower temperatures were needed, and Penrose and I designed a simple resonant cavity, fed either by coaxial lines (for 3 cm wavelength) or waveguides (for 1.25 cm wavelength), that could be immersed in liquid oxygen or liquid hydrogen. It was then found that compounds of divalent cobalt ions $3d^7$ yielded spectra with exceedingly anisotropic g-values, and that for many compounds the small crystal field splittings were temperature dependent. For example, the divalent Ni^{2+} ion, $3d^8$, in nickel fluosilicate [see Penrose and Stevens (21)] has a zero-field splitting of trigonal symmetry that decreases from -0.5 cm^{-1} at room temperature to -0.12 cm^{-1} at temperatures below 20 K. A survey of results for the 3d group was published in two papers by Bagguley, Bleaney, Griffiths, Penrose, and Plumpton (22).

VI. HYPERFINE STRUCTURE IN EPR

At the invitation of Professor G. J. Gorter, Penrose spent about six months at the Kamerlingh Onnes Laboratorium, Leiden, in 1948-9. There he discovered hyperfine structure in a dilute double sulfate of copper, in which 99% of the copper ions were replaced by magnesium. The hyperfine structure consisted of $(2I + 1) = 4$ lines, corresponding to the known spins $I = 3/2$ of the stable copper isotopes. Tragically, Penrose contracted a brain tumor, and died in hospital in Leiden on 28 April 1949, at the age of 28. His discovery was reported in a short letter to Nature [Penrose (23)], composed by Gorter, and in a following letter, Abragam and Pryce (24) pointed out that the anisotropy observed by Penrose in the hyperfine structure was not consistent with that expected from theory. A similar but more dramatic difficulty presented itself in the same year, when an extensive hyperfine structure was observed in dilute compounds of manganese (see 25, 26). The Mn^{2+} ion has the configuration $3d^5$, 6S ; for such a half-filled shell there is no orbital momentum, and the distribution of electronic spin

magnetism, to a good approximation, has spherical symmetry. There should therefore be no hyperfine field at the nucleus, but in fact a large hyperfine structure is observed, of nearly the same size for a range of manganese compounds. It was shown by Abragam and Pryce (27) that this arose from a finite spin density at the nucleus, resulting from exchange interaction between the inner shells of electrons and the the polarized 3d shell. This interaction causes the inner sub-shells with parallel spins to be displaced by a small amount, opposite to that for the sub-shells with anti-parallel spins. The difference is minute, but an electron in an inner s-shell produces a very large hyperfine field at the nucleus; thus for the two electrons with opposite spin orientations in the same s-shell the cancellation of the fields at the nucleus is no longer exact when they are displaced radially. This phenomenon of "core polarization" has proved to be present for all paramagnetic ions, in varying degree (it is considerably smaller in the 4f group than in the 3d group). For ions such as Cu^{2+} it accounts for the discrepancy in the magnetic hyperfine interaction mentioned above.

The spectrum of the cupric ion provided several further points of interest:

(a) "Forbidden" transitions, corresponding to changes in the nuclear magnetic quantum number, were observed by Ingram (28). These arise from the presence of a nuclear electric quadrupole interaction that competes with the magnetic hyperfine interaction when the external magnetic field is in a direction such that the magnetic hyperfine field at the nucleus is not parallel to the electric field gradient. The presence of such weak transitions is shown in Figure 8 for a dilute double sulfate of copper (29) in which further reduction of the linewidth is obtained by replacing the protons in the water of crystallization by deuterons.

(b) In a cubic crystalline field with a distortion of trigonal symmetry the orbital ground state of the cupric ion is doubly degenerate, and allowing



Figure 8. Hyperfine structure of the two copper isotopes ^{63}Cu , ^{65}Cu in a heavily diluted double sulfate of copper, $\text{K}_2(\text{Zn,Cu})(\text{SO}_4)_2 \cdot 6\text{D}_2\text{O}$. The $(2I+1) = 4$ strongest lines arise from the $\delta m = 0$ transitions; each isotope has $I = 3/2$, and the less abundant isotope ^{65}Cu with the larger nuclear magnetic moment has the greater splitting. The arrows indicate "forbidden transitions," in which the nuclear magnetic quantum number changes; competition between the nuclear electric quadrupole interaction and the magnetic hyperfine interaction relaxes the selection rule $\delta m = 0$. [After Bleaney, Bowers, and Ingram (29).]

for the spin $S = 1/2$, the ground state has four-fold degeneracy. The orbital degeneracy is lifted by a change in the symmetry of the hydrated copper complex, through the Jahn-Teller effect. There is a continuous set of distortions that all give the same energy [Van Vleck (30)], and in copper fluosilicate at temperatures above about 100 K Bleaney and Ingram (31) observed a single line with an isotropic g -value, a result that was explained by Abragam and Pryce (32). Later, Bleaney and Bowers (33) found that as the temperature is lowered, the isotropic line is replaced by a spectrum corresponding to that of three ions, each in a field of tetragonal symmetry. These were the first direct observations of dynamic and static Jahn-Teller effects in the solid state.

(c) Copper acetate has an anomalous temperature variation of its susceptibility, and Bleaney and Bowers (34) found that its ESR spectrum was quite different from that of a single cupric ion. They suggested that the crystal contained pairs of copper ions with a strong exchange interaction, resulting in a singlet ground state with a triplet lying higher by about 300 cm^{-1} . The hyperfine structure of this triplet state contains 7 lines of unequal intensity, as expected for a "dimer" containing two copper ions and two nuclei, each of nuclear spin $I = 3/2$. This

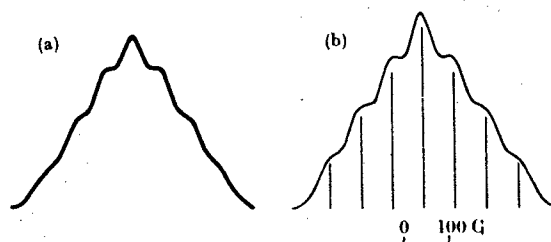


Figure 9. Measured (a) and calculated (b) hyperfine structure of copper in the triplet level of copper acetate [Bleaney and Bowers (34)]. The cupric ions occur in dimeric pairs, and the h.f.s. arises from the pair of copper nuclei, each with $I = 3/2$. The seven line h.f.s. should have intensity ratios 1:2:3:4:3:2:1.

structure is shown in Figure 9.

Measurements on neodymium ethylsulfate (35) represented the start of a comprehensive investigation of the lanthanide (4f) group, using two series of compounds, the ethylsulfates, and the double nitrates isomorphous with lanthanum magnesium nitrate. In the course of this work the nuclear spins of all the stable lanthanide isotopes were determined or confirmed, and the nature of the paramagnetism of these compounds was explained in detail. With the help of A.E.R.E., Harwell in growing radioactive single crystals of the 5f group, the spectra of neptunyl and plutonyl complexes in uranyl rubidium nitrate

were observed (36,37); the results were interpreted (38) in terms of covalent bonding involving the 5f electron, the first time that such bonding had been suggested. In addition, the nuclear spins of the isotopes ^{237}Np , ^{239}Pu , and ^{241}Pu were determined from the hyperfine structure. Measurements on trivalent uranium ions in single crystals of LaCl_3 , initiated by Clyde A. Hutchison, Jr. at Chicago, showed that in this compound the behavior of the uranium ion closely resembles its lanthanide analogue, Nd^{3+} , $4f^3$. The nuclear spins of the isotopes ^{233}U and ^{235}U were also determined (39,40).

Extensive work on ions of the other transition groups 4d,5d was carried out by Griffiths and Owen. This confirmed the presence of covalent bonding in these compounds, as in the complex cyanides of the 3d group. The wave functions of the magnetic electrons spread out onto the ligand ions, and result in a complex hyperfine structure if the ligand ions have nuclear spins and magnetic moments. An example of such a structure is shown in Figure 10 for a dilute chloroiridate compound

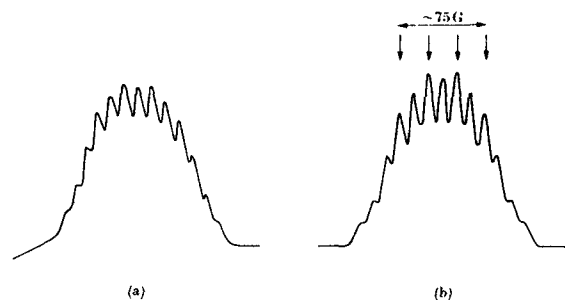


Figure 10. Complex hyperfine structure in the paramagnetic resonance spectrum of $\text{Na}_2(\text{Ir,PtCl}_6) \cdot 6\text{H}_2\text{O}$; (a) observed by Griffiths and Owen (41). In the reconstruction (b), the arrows indicate the position of the four hyperfine lines of the iridium nuclei ($I = 3/2$); the remaining structure arises from overlap of the magnetic electrons onto the ligand chlorine nuclei (for which also $I = 3/2$).

(41). In addition to the four hyperfine lines of the two iridium isotopes

191 and 193 (each with $I = 3/2$ and almost identical nuclear magnetic moments), there is a complex of lines from the ligand chlorine nuclei.

In another application of FPR, measurements of the spectra of pairs of ions in crystals of intermediate dilution were used to determine the size and nature of the interactions between the magnetic ions [see (42)].

VII. NUCLEAR ALIGNMENT

The electron paramagnetic resonance work in the Clarendon Laboratory was of direct interest to the large low temperature group in the same department under Professor Sir Francis Simon in suggesting the best substances for magnetic cooling and temperature measurements. Cerium magnesium nitrate was investigated by Cooke, Duffus, and Wolf (43); not only did it become the standard substance for thermometry below 1 K and for cooling to millikelvin temperatures by isentropic demagnetization [Daniels and Robinson (44)], but later it was the substance in which an Orbach relaxation process was first observed by Finn, Orbach, and Wolf (45). Another important contribution arose from the discovery that the hyperfine structure of divalent cobalt in many single crystals is highly anisotropic [Bleaney and Ingram (46)]. This led to the suggestion [Bleaney (47)] that in a cobalt salt an appreciable degree of alignment of the nuclear spins would be obtained on demagnetization to zero field, and that this would be a simpler and more efficient method than that proposed by Gorter (48) and by Rose (49). Such "alignment" does not result in any net nuclear polarization, but is sufficient to produce anisotropy in the spatial emission of gamma rays. The first successful experiment was carried out by Daniels, Grace, and Robinson (50) in the autumn of 1951, using a mixed crystal of a double sulphate containing 1% cobalt, 12% copper, 87% zinc, and a trace of the radioactive cobalt-60. A temperature of about 20 mK was obtained on demagnetization, and a ratio of 1.44:1 for the rates of emission of gamma rays in two mutually perpendicular directions was observed, decaying to 1:1 as the compound warmed up

towards 1 K. Nuclear orientation, combined with the use of nuclear resonance for precise measurement of the hyperfine frequencies of radioactive isotopes, has now become a far-ranging field in its own right.

VIII. CONCLUSION

This brief survey can give only an impression of the rapid progress made in electron paramagnetic resonance in those years. This was partly due to the simplicity of the apparatus used in most of the low temperature experiments, though that then required for liquid helium temperatures was more complicated than the systems commonly used now; fortunately only a few substances had such rapid spin-lattice relaxation rates that helium temperatures were required to obtain a resonance spectrum. On the theoretical side a very important part was played by Professor M. H. L. Pryce, who realized that the interpretation of the electron paramagnetic resonance results provided an excellent area for theoretical graduate students, together with A. Abragam, K. W. H. Stevens, R. J. Elliott, M. C. M. O'Brien, B. R. Judd, and Julius Eisenstein, who wrote their doctoral theses on various features of crystal field theory, hyperfine structure, and the detailed interpretation of other aspects of paramagnetism as revealed by electron spin resonance.

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Non-adiabatic Laser Induced Spin Coupling Phenomena

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A number of spin resonance properties can be measured in terms of rather novel if not always generally useful non-adiabatic effects. We consider the influence of spin hyperfine coupling upon laser excited optical transitions or upon electron paramagnetic resonance excited electron states.

1. NON-ADIABATIC OR ZEEMAN FIELD SWITCHING

As shown in Figure 1, suppose two coupled ground states, mixed by some internal spin-spin or spin-rotation interaction C , are expressed by the wave functions

$$\begin{aligned} |1'\rangle &= |a\rangle|1\rangle + |b\rangle|2\rangle \\ |2'\rangle &= -|b\rangle|1\rangle + |a\rangle|2\rangle \end{aligned} \quad (1)$$

with state

$$|3'\rangle = |3\rangle$$

remaining a pure state. Mixing coefficients are given by a and b with $a^2 + b^2 = 1$. When allowed external Zeeman or Stark interactions are switched on, which exceed the internal interaction energy C , then states $|1'\rangle$ and $|2'\rangle$ become pure basis states $|1\rangle$ and $|2\rangle$ respectively as $a \rightarrow 1$ and $b \rightarrow 0$. This problem is solved for four levels explicitly in ref. 1 for the case of spin-rotation interaction in $^{13}\text{CH}_3\text{F}$.

For any non-adiabatic jump in eigen-splitting between levels $|1'\rangle$ and $|2'\rangle$, the initial density matrix ρ of the three-level system is transformed to a

final matrix ρ' , given by

$$\rho' = U^{-1}\rho U. \quad (2)$$

Here

$$U = \begin{vmatrix} a' & -b' & 0 \\ b' & a' & 0 \\ 0 & 0 & 1 \end{vmatrix}. \quad (3)$$

If the final mixing coefficients are a_f and b_f and the initial mixing coefficients are a_i and b_i , therefore,

$$a' = a_f a_i + b_f b_i \quad \text{and}$$

$$b' = b_i a_f - b_f a_i.$$

Echo formation by the three-level system is shown in Figure 1. The first non-adiabatic Stark field pulse E_B brings the two level transition $|1\rangle \leftrightarrow |3\rangle$ into resonance with continuous laser or microwave radiation, and places the levels into a θ pulse coherent superposition state. The transition $|2\rangle \leftrightarrow |3\rangle$ is forbidden or is far off-resonance if the transition were allowed. Because of non-adiabatic switching at the end of the θ pulse, additional coherent superposition among $|1'\rangle$ and $|2'\rangle$ is provided as the pure states $|1\rangle$ and $|2\rangle$ switch back to states $|1'\rangle$ and $|2'\rangle$. During free precession the net coherence among all three states then operates for the time period $\tau_1 < t < \tau_1 + \tau_d$ where the applied continuous radiation is far off-resonance. This free precession behavior has been analyzed previously

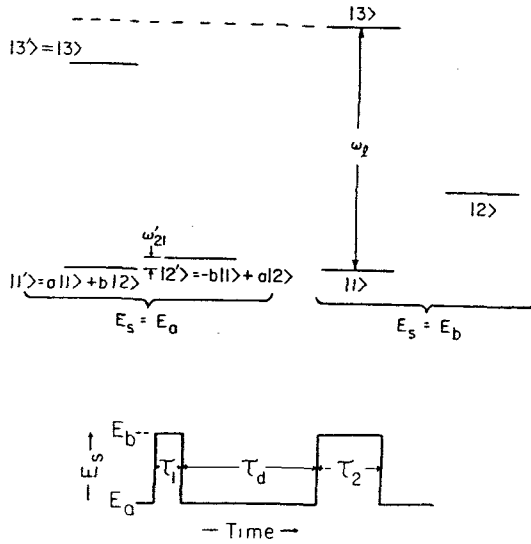


Figure 1. Level scheme (above) and Stark pulse scheme (below) for photon echo production. The laser radiation is constant at frequency ω_1 . The ground state levels $|1\rangle$ and $|2\rangle$, making up the ground states of a vibrational transition at ω_1 , exhibit a Stark splitting when E_s is applied.

(1). The second θ_2 non-adiabatic pulse imposes reorientation among states $|1\rangle$ and $|3\rangle$ and again does not affect state $|2\rangle$. Again the mixed set of three states couple freely after the θ_2 pulse is removed, and the maximum echo amplitude occurs at time $t_e = \tau_1 + 2\tau_d + \tau_2$.

The density matrix $\rho^i(t)$ which forms the echo in the mixed state representation is given by

$$\begin{aligned} \rho^i(t) &= P(t)^{-1} U^{-1} T(\theta_2)^{-1} \\ &\quad U P(\tau_d)^{-1} U^{-1} T(\theta_1)^{-1} \\ &\propto \rho_0 T(\theta_1) U P(\tau_d) U^{-1} T(\theta_2) U P(t). \quad (4) \end{aligned}$$

The initial density matrix at $t = 0$ is chosen as

$$\rho_0 = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 0 \end{pmatrix}, \quad (5)$$

and the θ pulse rotation matrix is

$$T(\theta) = \begin{pmatrix} \cos\theta/2 & 0 & \sin\theta/2 \\ 0 & 1 & 0 \\ -\sin\theta/2 & \theta & \cos\theta/2 \end{pmatrix}. \quad (6)$$

The free precession matrix in the frame rotating at ω is

$$\rho(t) = \begin{pmatrix} \exp(i\omega_1' t) & 0 & 0 \\ 0 & \exp(i\omega_2' t) & 0 \\ 0 & 0 & \exp[i(\omega_3' - \omega)t] \end{pmatrix} \quad (7)$$

where the eigenfrequencies are given by ω_i' ($i = 1, 2, 3$) and ω_1 is the applied radiation frequency. Any field inhomogeneity is contained in the $\omega_3' - \omega$ term. The echo intensity at time $t > \tau_1 + \tau_2 + \tau_d$ is proportional to

$$\begin{aligned} S &= \text{Tr}\{\rho^i \mu^i\} \\ &= a^* b^4 + 2a^2 b^2 \cos\omega_{21}' \tau_d, \end{aligned}$$

where the mixed state dipole operator is given by $\mu^i = U^{-1} \mu U$, with U defined by Eqn. (3) for $a_i = c_i = 1$, $b_i = 0$, and $a_f, b_f = a, b$. The pure state transition dipole matrix element is given by μ_{31} , and the mixed state matrix elements are $\mu_{31}' = a\mu_{31}$ and $\mu_{32}' = -b\mu_{31}$.

The envelope S displays a beat frequency $\omega_{21}' = C/h$ which corresponds to the splitting between levels $|1\rangle$ and $|2\rangle$ in the absence of applied external fields ($E_s = E_b = 0$ in Figure 1) which remove level degeneracy. Although ω_{21}' may exceed C/h if the fields are applied, the factor ab becomes too small to observe the cosine modulation, particularly if the damping time constant T_2 is very short. This was the case in a previous investigation (1). A slight reduction in echo amplitude, however, indicates a rough measure of C in the absence of B and E fields, compared to the condition when these fields are large and totally lift the degeneracy between levels $|1\rangle$ and $|2\rangle$. Thus a perceptible reduction in the echo can be observed although the cosine beat in S is overdamped by virtue of the condition $T_2 < 2\pi/\omega_{21}'$ as τ_d exceeds T_2 . The degeneracy lifting field $E_s = E_b$ acts as a bias field which controls the amount of state

mixing during the time τ_d between pulses θ_1 and θ_2 , and time τ_d after the θ_2 pulse.

The superposition created among the states $|1'\rangle$ and $|2'\rangle$ is, of course, brought about because the switching time t_s of the E or B field is short compared to the period $\omega_{2,1}'/2\pi$. If an appropriate resonance radiation pulse or step function source has Fourier components which exceed hyperfine level splittings, the various levels will be placed in coherent superposition by purely optical means. Hashi and co-workers (2) have reported an experiment in which the hyperfine coupled electron spin levels of $\text{Tm}^{2+}:\text{CaF}_2$ in the optical ground state are placed in coherent superposition by this principle. A short laser pulse of order nanoseconds in width creates excess spin populations among the Tm^{2+} hyperfine ground states in $\text{Tm}^{2+}:\text{SrF}_2$. The spin orientation is prepared non-adiabatically, perpendicular to a magnetic field (0-100 gauss) which in turn is normal to the laser beam k vector. By means of the magnetic circular dichroism effect, using cross polarizers to monitor optical Faraday rotation, a probe laser beam is modulated by the precessing spin population in the range of megahertz.

FREE NUCLEAR PRECESSION FOLLOWING NON-ADIABATIC SWITCHING IN SOLIDS

Analogies of non-adiabatic switching in NMR are well known. Eigenstates of coupled protons in solids may be investigated following non-adiabatic B field switching. An early experiment (3) showed that initial dipolar ordered states, produced by adiabatic demagnetization ($B \rightarrow 0$), result in free precession about new axes of quantization following the non-adiabatic switching of magnetic field $B = 0$ to $B = B$ where $\mu B \sim H_{\text{dipolar}}$.

Recently a related experiment, "zero-field NMR," by Weitekamp et al. (4), provides dipolar coupling spectra without the need for single crystals. Initial Zeeman spin ordered orientation among nuclei for $\mu B \gg H_{\text{dipolar}}$ is suddenly transformed to superposition among dipolar states by switching of B to zero. The resultant oscillations

from the initial Zeeman orientation about internal axes of quantization in zero field are Fourier analyzed to give a measure of local fields.

OPTICAL MEASUREMENTS OF ELECTRON SPIN HYPERFINE CROSS-RELAXATION IN CRYSTALS

The paramagnetic spin-spin interaction among neighboring optical ions, characterized as Kramer doublets in the optical ground state has been studied (5) by making use of the optical property of magnetic circular dichroism (MCD). A complete manifold of level crossings involving divalent thulium and divalent holmium ions contained in CaF_2 single crystal can be investigated

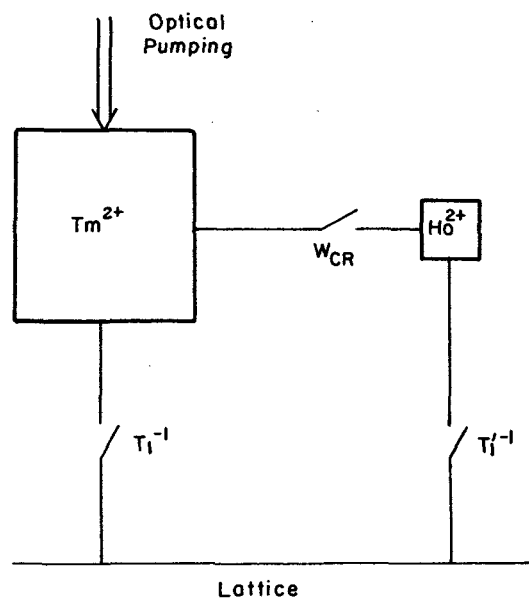


Figure 2. Schematic for hyperfine state cross-relaxation coupling among Tm^{2+} and Ho^{2+} ions in single crystal CaF_2 . Optical pumping creates non-equilibrium spin populations among Kramer doublet optical ground states of Tm^{2+} with $S = 1/2$ for the electron and $I_{\text{Tm}} = 1/2$ for the Tm nucleus. The cross-relaxation rate W_{CR} becomes finite at specific magnetic fields as the levels of Ho^{2+} ($S = 1/2$, $I_{\text{Ho}} = 7/2$) cross with the Tm^{2+} levels. Spin-lattice relaxation times T_1 and T_1' for each reservoir are indicated.

simply by adjustment of the external dc magnetic field without the need of microwave detection or excitation. Neighboring thulium-thulium or thulium-holmium hyperfine level crossing interactions may be adiabatically or non-adiabatically turned on by adjustment of the dc magnetic fields. The cross-relaxation signal appears as a change in population difference of the thulium optical transition by a dye laser (see Figure 2). Following the pumping a weak probe beam monitors the thulium spin population recovery towards equilibrium (or changes in population) by the effect of MCD. Direct and higher spin coupling processes are observed.

Evidence of a phonon bottleneck is indicated [6; first noted in ref. (7)] by the onset of Orbach transitions of holmium hyperfine levels that couple to a low lying holmium excited state. The phonons which allow the coupling appear to be created by radiationless phonon transitions in the thulium pumpband, where the phonons have a spectral width which is sufficient to overlap the ground hyperfine and a low lying excited state of holmium at 33 cm^{-1}

above the ground state. The inference of this effect, which requires further investigation, is as pointed out above, by observation of non-equilibrium cross-relaxation between matched thulium-holmium hyperfine spin levels, where the thulium spin populations are monitored by differential MCD transmission.

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Microwave Induced Nuclear Polarization

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The polarization of nuclear spin $I = 1/2$ is defined by

$$p_n = (N_+ - N_-) / (N_+ + N_-)$$

where the population of the Zeeman energy levels N_+ and N_- is determined by the Boltzmann factor

$$N_- = N_+ e^{-\Delta E/kT}.$$

A larger nuclear polarization p_n is desirable for several reasons:

- 1) In NMR the quantity to be measured is the absorbed radiofrequency energy. Since transitions from the higher to the lower level (induced emission) are induced with the same a priori probability as those from the lower to the higher level, the net absorption and hence the signal-to-noise ratio of an NMR experiment is linearly proportional to the polarization p_n .
- 2) Many experiments in nuclear physics require targets in which nuclei are polarized as much as possible.
- 3) The interesting phenomenon of nuclear ordering as studied by Abragam and his group requires a very high nuclear polarization p_n as well.

The classical method to increase the nuclear spin polarization is the "solid effect" mainly developed by Abragam and Jeffries, where the Boltzmann

polarization of unpaired electrons present in the sample is transferred to the nuclei by inducing forbidden transitions which flip one nucleus and one electron simultaneously (1,2).

A different method is the optical nuclear polarization (ONP) which we discovered in 1967. In this method the nuclear spins are polarized by their interaction with the unpaired electrons of an excited triplet state in a molecular crystal (3). It could be shown that the selection rules of spin-orbit coupling combined with the mixing of states in the triplet manifold by the hyperfine coupling results in different population (s_i) and decay rates (k_i) and hence in different equilibrium populations N_i of the electronic nuclear sublevels (4). This type of ONP produces an appreciable nuclear spin polarization p_n only in the level anti-crossing (LAC) region of the external magnetic field.

More recently we have combined the ONP with the solid effect, i.e., the induction of forbidden transitions between the electronic nuclear sublevels. The polarization of nuclei with this mechanism, which was termed Microwave Induced Optical Nuclear Polarization (MI-ONP), is the subject of this paper.

The energy levels and the relevant parameters of an excited triplet state are shown in Figure 1. The three sublevels T_x , T_y , and T_z are non-degenerate even in zero field due to the dipolar interaction between the two triplet electrons. This zero-field splitting

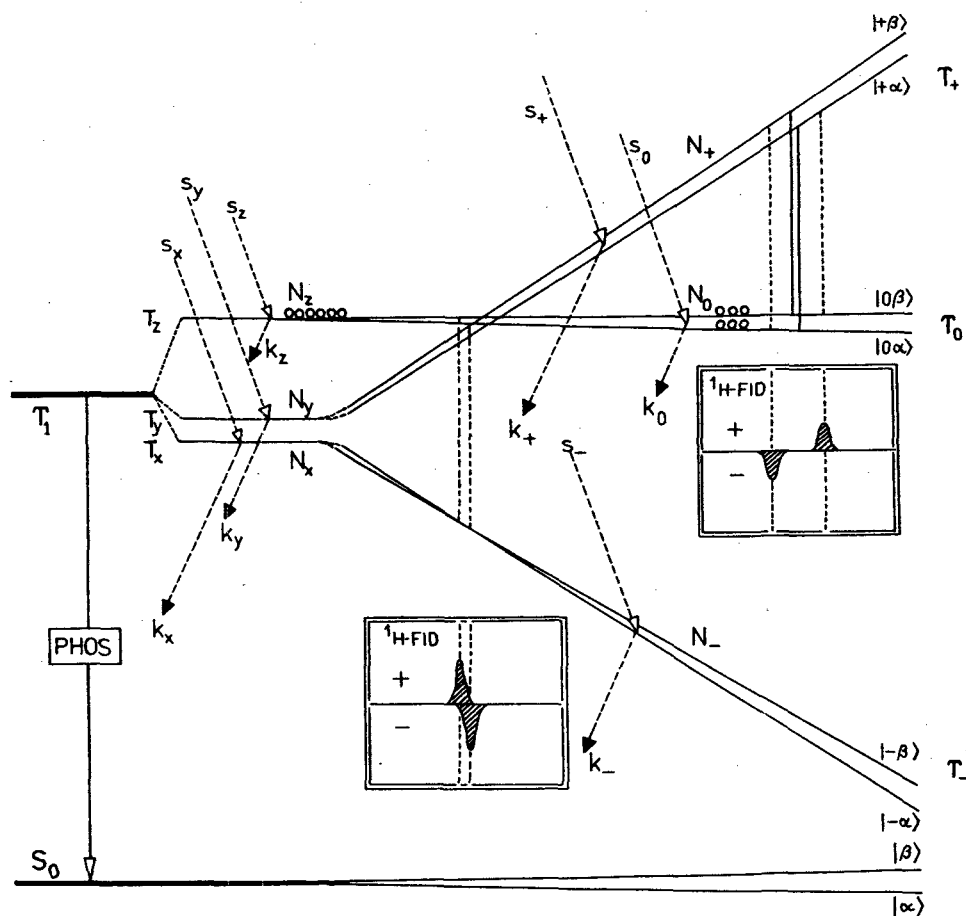


Figure 1. Energy levels of the first excited triplet state of an aromatic molecule in zero field and in an external magnetic field H_0 together with the population rate constants s_i , the depopulation rate constants k_i , and the steady-state population N_i . α, β = nuclear spin states, — allowed ODMR transitions, ---- forbidden transitions.

is not negligible even at magnetic fields of a few Tesla and results in different energy differences between T_+ and T_0 and between the T_0 and T_- electronic substates. The population rates s_i , the depopulation rates k_i , and the equilibrium population constants N_i of the electronic triplet sublevels are not equal but subject to the selection rules of spin-orbit interaction.

We have performed our experiments in host-guest single crystals with a guest concentration of the order of 100-1000 ppm. We assume for simplicity reasons

that the spin $S = 1$ is coupled with one proton with spin $I = 1/2$, and that the linewidth is smaller than the distance of the forbidden satellites from the allowed ESR transition so that they are completely separated, a situation which is termed "resolved solid state effect." We further assume that the highest level is exclusively populated in zero field, and hence in high field the T_0 level is populated, $N_0 = 100\%$, while the upper and the lower levels are empty, $N_+ = N_- = 0$. Under this condition the induction of the allowed

transitions $\Delta m_S = \pm 1$, $\Delta m_I = 0$, produce the ordinary ODMR signal by changing the population of the levels involved. Induction of the forbidden transitions $\Delta m_S = \pm 1$, $\Delta m_I = \pm 1$, on the other hand, for instance at the high field side of the high field line, $|0 \beta\rangle \rightarrow |1 \alpha\rangle$, depopulates the β spin state and results in a positive polarization in the ground state S_0 ; note that the decay into the ground state does not affect the nuclear spins and conserves their orientation. In analogy, the forbidden transition at the low field side of the high field line produces a negative polarization.

The main difference of MI-ONP with respect to the solid effect with doublet states is twofold:

- 1) The selective population of the three electronic triplet sublevels is a consequence of the selection rules of the spin-orbit coupling operator and is not proportional to the magnetic field in contrast to the Boltzmann factor.
- 2) The second and perhaps most important advantage of using excited triplet states instead of doublet ground states is their short lifetimes of the order of milliseconds to a few seconds. If the exciting light is switched off, the unpaired triplet electrons vanish and leave a diamagnetic crystal with polarized nuclei which preserve their polarization for many hours or days due to the, in most cases, very long nuclear spin-lattice relaxation times T_1^n of spins $I = 1/2$ in diamagnetic samples at very low temperatures.*

*Recently van Kesteren et al. (5) have reported a nuclear polarization experiment with excited triplet states with short electronic relaxation times T_1^e in which they have used the electronic Boltzmann equilibrium. From this point of view their experiment is identical with the traditional solid effect, but it also has the important advantage number 2, i.e., the disappearance of the unpaired electrons

In the next section I shall discuss the favorable conditions for obtaining a high nuclear spin polarization. In principle, there are two possibilities, i.e., a steady-state experiment in which both the light for exciting the triplet state and the microwaves are irradiated continuously (6) and a time-resolved experiment where both light and microwaves are irradiated in short pulses (7).

Let us consider the two upper levels since the third one is not in resonance with the irradiated microwaves at a given external magnetic field and can hence be neglected. We have discussed above an idealized case where the T_0 level is exclusively populated and the T_+ level is empty; in practical cases we must look for a molecule where the population difference in the steady state is as high as possible $N_+ \ll N_0$ or $N_+ \gg N_0$, since this limits the maximum obtainable nuclear spin polarization p_n .

However, in most cases the steady-state population difference is not very high, $N_+ \approx N_0$. This is due to the fact that the selection rules of spin-orbit interaction for the population rates s_i of the triplet sublevels which are based on the admixture of some singlet character to one particular triplet sublevel are usually valid for the depopulation rates k_i as well. Let us assume that $s_0 \gg s_+$ and $k_0 \gg k_+$ with the result that $N_+ \approx N_0$. In this situation it is obviously more promising to use a time-resolved MI-ONP, i.e., a short laser pulse, duration 10^{-8} s, and at the same time a microwave pulse of a time t_m which should be long enough to induce the forbidden transition, but short as compared to the lifetime τ^1 of the short-lived triplet sublevel (7), Figure 2. In this manner the effective population difference is proportional to the ratio of s_+/s_0 rather than of N_+/N_0 . However, if the decay constants are very different, for instance, $k_0 \gg k_+$, another version of time-resolved MI-ONP may be applied: if the microwave pulse is applied after a decay time of

after switching off the light.

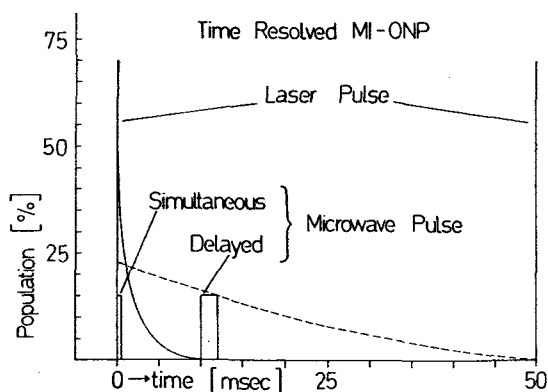


Figure 2. Time resolved MI-ONP with a laser pulse and simultaneous or delayed microwave pulse, schematic.

about five times τ^1 , the short-lived triplet sublevel N_0 will be empty and the nuclear spin polarization obtained in this manner could in principle be complete, $p_n = 1$. In both cases this procedure must, of course, be repeated many times.

However, there is an additional aspect which we have not considered so far. When irradiating into the triplet exciton band of the host, the mobile excitons do not contribute to the MI-ONP because they are out of resonance with the applied microwave frequency, but they contribute to the nuclear spin-lattice relaxation; as a matter of fact, the interaction of the nuclei with the triplet excitons is their predominant relaxation mechanism compared to which the nuclear relaxation in the dark is negligible. The maximum obtainable nuclear polarization depends, of course, on the equilibrium between the MI-ONP and the nuclear relaxation. Hence we expect the maximum nuclear polarization with a system in which the first excited singlet state of the guest possesses a lower energy than the triplet exciton band of the host. In this case it is possible to excite the triplet state of the guest without exciting the triplet excitons in the host.

The last point I would like to discuss before showing experimental

results is the time and light intensity required for MI-OPN. The size of our crystal was about 3X2X2 mm which corresponds with a specific weight of about 1.8 to 20 mg or to about 3×10^{20} protons. The intensity of the irradiation which we used with the mercury lamp was about 100 mW corresponding to about 2×10^{17} photons per second in the frequency range of 29000 cm^{-1} . When using a cw-laser the intensity was the same in order to avoid overheating the sample; in the case of the pulse laser the intensity was the same, i.e., 5 mJoule per pulse with a repetition rate of 20 s^{-1} . Assuming that 10% of the irradiated photons created an excited triplet state, the rest being lost due to incomplete absorption and a quantum yield below one, we calculate that in 2 min 1% of the protons could be polarized which corresponds to an enhancement with respect to the nuclear Boltzmann polarization of a factor of 100. The maximum nuclear polarization which can be obtained depends, of course, on the equilibrium between the polarization and the nuclear relaxation; we estimate that this equilibrium will be reached after a time of the order of a few hours.

Let us now look at the experimental results. With the first system investigated, p-dichlorobenzene in p-dibromobenzene, we obtained under steady-state conditions an enhancement of the nuclear spin polarization p of about a factor of 10. A much higher polarization was obtained with the system benzophenone (BPh) in dibromodiphenylether (DDE), concentration about 1000 ppm. The population and depopulation rates of this system were investigated by several authors (8,9). The absolute values as given by Hochstrasser et al. (8) for the lifetime of the short-lived triplet sublevels are $\tau_0^1 = 1.7 \text{ ms}$ and for the two long-lived triplet sublevels $\tau_+^1 \approx \tau_-^1 \approx 25 \text{ ms}$, which corresponds to decay rate constants $k_0 \approx 580 \text{ s}^{-1}$ and $k_+ \approx k_- \approx 40 \text{ s}^{-1}$ or, in terms of percentage of the total decay, $k_0 \approx 88\%$ and $k_+ \approx k_- \approx 6\%$. The relevant parameters are compiled in Table I. The numbers for the $S_0 \rightarrow S_1$ excitation in the guest BPh are taken from Hochstrasser et al. (8) who used a mercury arc for excitation, while those for $S_0 \rightarrow T_1$,

Table 1. Relevant Parameters of the Excited Triplet State of Benzophenone (BPh) in Dibromodiphenylether (DDE) for Different Excitation, in Percentage

Decay Rate Constants, $k_0 = 88\%$, k_+ , $k_- = 6\%$

Type of Excitation	Population Rate Constant		Steady-State Population		Elec. Pol. P_E (%)	First Msec Average Population		Elec. Pol. P_E (%)
	S_0	S_+, S_- (%)	N_0	N_+, N_- (%)		N_0	N_+, N_- (%)	
$S_0 - S_1$ (BPh)	85	7.5	28	36	12.5	50	7.5	74
$S_0 - T_1$ (DDE) (YAG-Laser)	54	23	7	46.5	74	40	22.5	28

excitation into the triplet exciton band of the host DDE were measured in our laboratory using a YAG-laser with 28200 cm^{-1} ; they differ slightly from those given in (8) with the same $S_0 \rightarrow T_1$ excitation but using a mercury lamp. Note that the equilibrium population N_0 of the triplet sublevel T_0 depends on the ratio s_0/k_0 ; hence due to the much larger decay constant k_0 the T_0 level is less populated in the steady state than the others in spite of its higher population rate constant s_0 . Using the equation given in the beginning for the polarization p_e for the two-level system N_0 and N_+ with the numbers for $S_0 \rightarrow T_1$ excitation into the triplet band of the host DDE $p_e \approx 74\%$ and for $S_0 \rightarrow S_1$ excitation in the guest BPh, $p_e \approx 12\%$.

Figure 3 shows in the upper part the low field ODMR line in a magnetic field B_0 parallel to the z-axis of BPh and in the lower part the corresponding nuclear polarization p_n . The maximum enhancement which we have obtained with this system is about a factor of 840 which corresponds to a spin temperature of about 1.4 mK at a lattice temperature of about 1.2 K or to an absolute nuclear polarization of $p_n = 11\%$ (10).

In the next section we shall discuss the time-resolved MI-ONP of Figure 2. As mentioned before, the experiment may be done in two ways: either the laser pulse and the microwave pulse are applied simultaneously, or the latter is applied after a certain time delay of the order of several τ_0^{-1} , the lifetime of the short-lived sublevel. For the first case of simultaneous laser

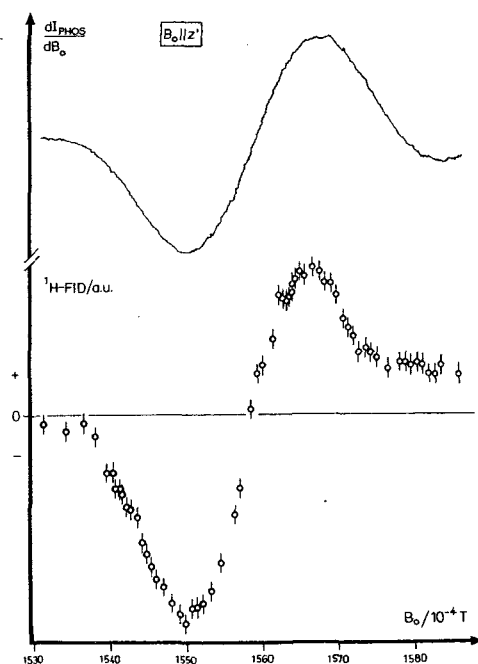


Figure 3. Low field ODMR line of benzophenone (BPh) in dibromodiphenylether (DDE) with the external magnetic field B_0 parallel to the C-O bond. Below the corresponding MI-ONP in arbitrary units.

and microwave irradiation the excitation of the triplet sublevel T_0 should

be as selective as possible, $s_0 \gg s_+ \approx s_-$. For our system BPh in DDE this condition is best fulfilled using a laser frequency of 26000 cm^{-1} which excites the $S_0 \rightarrow S_1$ transition of the guest BPh, Table I. Note that the s_i given in the table do not add up to 100% because the lifetime τ_0^{-1} of T_0 is not short as compared to the microwave pulse, and we have therefore averaged N_0 over the first ms. Nevertheless, we expect an electronic polarization of the order of 75% in this case. For the other type of MI-ONP where the microwave pulse is irradiated after a delay of several τ_0^{-1} , as much as possible of the excitation should go into the long-lived sub-level s_+, s_- . We learn from Table I that this occurs when using a laser frequency of about 29000 cm^{-1} which excites mainly $S_0 \rightarrow T_1$, the triplet state of the host, although the lower energy $S_0 \rightarrow S_1$ transition of the guest BPh is, of course, excited as well. However, this mixed excitation is already taken into account in the numbers given in the table.

We have carried out both experiments with a mixed crystal of BPh in DDE, concentration about 1000 ppm, a laser pulse of about 5 mJoule, duration 10^{-8} s, repetition rate 20 s^{-1} , and a microwave pulse of about 10 W and a pulse length of about .5 ms for the simultaneous irradiation and several ms for the irradiation with a delay of 10 ms. In both experiments we obtained a strong enhancement of the nuclear polarization, but this polarization remained hitherto below the 10% obtained with the steady-state experiment.

Let me conclude with the following remarks:

1. We have shown that it is possible to obtain a considerable nuclear polarization with the method of MI-ONP. Since the unpaired electrons vanish with the lifetime of the triplet state within seconds, the method provides a diamagnetic crystal with polarized nuclei for hours due to the very long spin-lattice relaxation time of nuclei with spin $I = 1/2$ at low temperature.

2. With the system of benzophenone in

dibromodiphenylether we have reached a nuclear polarization of about 10% under steady-state conditions. Since we have studied only a few systems so far, this is probably not the most favorable system.

3. Theoretical considerations led to the conclusion that time resolved MI-ONP with short laser and microwave pulses could produce still appreciably higher nuclear polarizations. We have shown experimentally that the method is feasible but in the early stage of our experiments we have not yet reached higher nuclear polarizations than the 10% obtained under steady-state conditions. However, I am convinced that in principle this is possible with time resolved MI-ONP

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BIOPHYSICAL APPLICATIONS OF ^{17}O NMR

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Oxygen plays a major role in many biophysical processes: in the determination of molecular structure and biological activity, in weak and in strong interactions, in being an important constituent of the peptide bond and nucleic acid bases, and in being a part of the carboxyl, hydroxyl and carboxamide groups of peptide side chains and end groups. It is important to emphasize the major role that weak interactions as van der Waals including hydrogen bonding have in physiological processes: in the binding of hormones (as peptide hormones to the receptor site) and in generating a stimulus that triggers a chain of intermediary steps leading to the final biological response; in determining the code of information transfer in the action of the hormone; and in the transfer of genetic information. Weak interactions play a major role in stabilizing the biologically active conformation of molecules and in the kinetics of biological processes.

The utilization of oxygen magnetic resonance as a probe in the investigation of biologically related processes encounters difficulties due to the low natural abundance of the ^{17}O isotope (.037%) that possesses a magnetic moment. Its utilization requires enrichment of biomolecules in the ^{17}O isotope. We have developed and utilized synthetic methods for ^{17}O enrichment of amino acids (1,2), peptides (2), and nucleic acid constituents (3) and studied the molecular conformation in solution, solute solvent interactions and metal ion complexation at the oxygen and nitrogen sites. We have found ^{17}O NMR to be an effective probe in studies of the intra- and intermolecular interactions and molecular dynamics of peptides and nucleic acid bases.

We have found that 1) hydrogen bonding has a marked effect on the ^{17}O chemical shift of the carbonyl group, by 2-3 orders of magnitude larger than its effect on ^1H (4,5) and 2) that bond character of the acyl group has a much larger effect on the ^{17}O chemical shift (6 - 8) than it has on the ^{13}C chemical shift. (See Table 1) Although the line widths of the ^{17}O resonance are broader than that of ^1H and ^{13}C , the much higher chemical shift variations more than compensate for the line widths, e.g., for a tripeptide the line width is a few hundred Hz at a field of 42 kG (2,7,9) and, therefore, the above variations in the chemical shift could easily be detected.

Recently, we have studied by means of ^{17}O and ^{14}N NMR the conformation, solute solvent interactions, pH effects, and determination of protonation sites of amino acids (8,10 - 12), carboxamides and methyl ester derivatives (13), amides (5,14), peptides (2,7 - 9), and nucleic acid constituents (3). We also studied metal ion binding to amino acids and peptides (15). Studies have been carried out as a function of pH, concentration, mixed solvent composition and temperature. Studies have also been carried out on model compounds of peptides in liquid crystals (16) yielding information on the ^{17}O nuclear quadrupole coupling constant of ^{17}O labeled compounds. A short description of our studies will be presented in this report.

I. pH EFFECTS ON THE ^{17}O CHEMICAL SHIFTS OF AMINO ACIDS, PEPTIDE CARBOXAMIDES AND METHYL ESTER DERIVATIVES

pH effects on the ^{17}O chemical shift of the carbonyl group in its several functional groups: ketones, aldehydes,

Table 1

^{17}O and ^{13}C Chemical Shifts of the Peptide Bond
(references for the chemical shifts: ^{17}O - H_2O ; ^{13}C - TMS)

Bond	Length A	C-13 ppm	O-17 ppm
C-O	1.43	40 - 80	-30 - +30
C=O (carbonyl)	1.22	170 - 220	520 - 590
C=O (amide)	1.23	162 - 173	300 - 360
C=O (peptide)	1.24	162 - 173	300 - 360
C-13 data, ref. (26)			
O-17 data, ref. (27)			

Table 2

^{17}O Nuclear Magnetic Resonance Parameters in Highly
Acidic Solvents (ref. 28)

Amino Acid	1 N HCl (ppm)	HFSO ₃ (ppm)
Val	256	239
Leu	252	234
Ile	256	238
Pro	249	234
His	257	243
Gly	253	233

peptides and its model compounds as amides, heterocyclic compounds as in nucleic acid bases and urea (Fig. 1) are most interesting in shedding light on the protonation sites and the electronic structure of these molecules.

A. Amino Acids

The pH dependence of the ^{17}O chemical shift shows a paramagnetic shift at around the pK value of amino acids of about 13 to 18 ppm for alanine, glycine, proline, leucine, histidine, valine, isoleucine, aspartic and glutamic acids. The paramagnetic shift at around the pK value for acetic acid

(17), formic acid (18), glycylglycine (19), the β COOH of aspartic acid (20) and the γ COOH of glutamic acid (10) results in a downfield shift greater than 22 ppm. This shift is most likely due to overriding effects of the bond order-charge density term in the paramagnetic contribution towards nuclear shielding (21). At highly acidic solvents a diamagnetic shift takes place.

In Table 2 the chemical shifts of several amino acids in HFSO₃ are shown to be shifted 14 to 20 ppm relative to their chemical shift in 1 N HCl. With further increase in acidity of the medium to magic acid (HFSO₃/SbF₅ 1:1 molar ratio), the glycine resonance

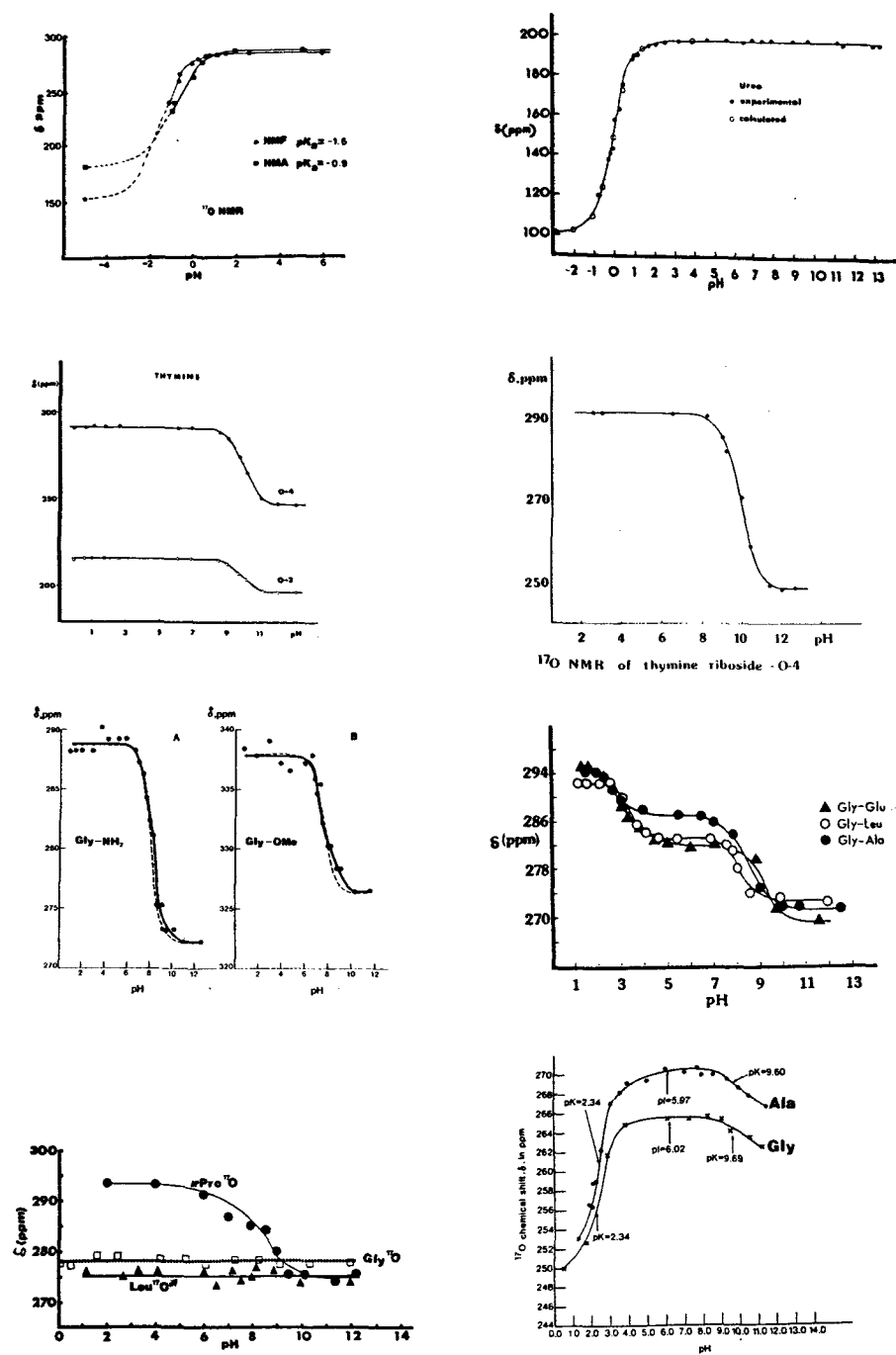


Figure 1. pH dependence of acyl oxygen-17 chemical shifts.

shifted to 209 ppm. We interpret 1) the chemical shift of 209 ppm of glycine in magic acid to represent the diprotonated form and 2) the chemical shifts in HFSO_3 to represent a contribution from a fraction of the molecules in the diprotonated form. Using a value of 45 ppm (the average value observed for glycine (44 ppm), acetic acid (46.5 ppm) and propionic acid (45 ppm) (22)) to represent the ^{17}O diamagnetic shift resulting from protonation of a carboxylic acid, the amino acids are estimated to be 30-40% diprotonated in HFSO_3 (assuming there is no significant amount of diprotonation at pH 0).

B. Peptide Carboxamides

The pH dependence of the chemical shift of Gly-NH_2 ^{17}O in aqueous solution showed a diamagnetic shift of 17 ppm at its pK value of 7.9 (23). This shift is due to deprotonation of the NH_3^+ group through a larger contribution of resonance structures in which the N donates its lone electron pair to the C-N bond.

C. Methyl Ester Derivatives

The pH dependence of $[\text{Gly-OMe}]^{17}\text{O}$ chemical shift showed a diamagnetic shift of 12 ppm at the pK value of 7.51 (24). This shift is due to deprotonation of the ester oxygen through an increase in the single bond character of the acyl oxygen.

The ^{17}O chemical-shift value of urea in the pH region 3 to 13 is about 195 ppm whereas that of ^{17}O in amides and peptides is between 275 and 295 ppm. The large diamagnetic shift of the ^{17}O of urea relative to that in amides and peptides is due to the increased single bond character of the carbonyl group in urea through resonance with two adjacent NH_2 groups.

^{17}O NMR studies of urea were practically pH independent in the region from pH 13 up to pH 3 and showed a large diamagnetic shift of 96 ppm at about pH 0 which we attributed to a

protonation reaction at the urea oxygen having a pK of 0.1. A paramagnetic shift of 36 ppm was observed in magic acid which is attributed to diprotonation of the urea where the second protonation takes place at the site of the nitrogen atom. These findings may be rationalized in terms of the acyl group bond character. The first protonation at the oxygen atom increases the single bond character of the carbonyl bond whereas the second protonation at the nitrogen atom eliminates one of the possible resonance structures of the urea resulting in an increase in the double bond character of the carbonyl bond and consequently ^{17}O resonance shift to a lower field.

Protonation of amides at about pH -1 is followed by a diamagnetic shift of about 40 ppm due to protonation at the site of the oxygen atom. pH dependence of nucleic acid bases as thymine shows a large region of pH independence between pH 0 and 9. The ^{17}O chemical shifts at position 4 of thymine are similar to that of amides and peptides, and that of oxygen in position 2 are similar to oxygen in urea as one could expect from the similarity in structure of the relevant molecular segments.

II. PEPTIDES

Previously reported studies primarily concerned with model compounds (5, 6, 8, 14) have been extended to oligopeptides and their derivatives, hexapeptides and nonapeptides (2, 7, 9). ^{17}O chemical shifts of peptides cover a region of approximately 70 ppm depending upon the solvent, pH and the neighboring amino acid residues and protecting groups. A correlation between the solvent proton donating ability and the ^{17}O chemical shift to high field exists e.g., upon addition of water to a solution of cationic Gly-Leu in DMSO an up-field shift of 30 ppm was observed.

Solvent dependence studies are most informative in providing means of discerning between the inter- and intramolecular H bonding (of utmost importance in understanding the molecular structure and biological activities of

peptides). One example will be given here. Pro-Leu-Gly-NH₂ (MIF) is biologically active in the CNS of rodents and is thought to inhibit MSH release in amphibians. It forms the C-terminal tripeptide in oxytocin and therefore studies of its conformation in solution constitutes an essential part of the investigation of the physiological activities of peptide hormones. Despite a substantial amount of experimental evidence, the conformation of MIF in solution remains ambiguous. ¹⁷O chemical shift of the tripeptide Pro-Leu-Gly-NH₂ (MIF) was measured as a function of the mole fraction of CH₃CN in a solution of mixed solvents of H₂O and CH₃CN (Fig. 2). These studies have answered an open question and have shown that intramolecular H bond is formed between the Gly NH₂ group and the proline peptide oxygen (9).

¹⁷O NMR Studies of Peptides and Model Compounds in Liquid Crystals (Fig. 3)

One example will be given of ¹⁷O labeled urea in lyotropic liquid crystalline phase of type II. ¹⁷O, ¹⁴N and ²H quadrupolar splitting of the Zeeman levels of urea were observed. Also, ¹⁷O and ²H quadrupolar splitting of H₂O molecules in type I and type II mesophases were used to determine the order parameters. The ¹⁷O nuclear quadrupole coupling constant was determined to be 10.2 MHz (16). The ternary lyotropic liquid crystalline mesophase formed by decyl ammonium chloride, sodium chloride and water was used as type II phase, and sodium decyl sulphate, sodium sulphate and water was used as type I phase in our investigation.

III. NUCLEIC ACID CONSTITUENTS

Only a short description of the pH dependencies of O-2 and O-4 for uracil and thymine will be given here. The pH dependencies are similar for both molecules; a large upfield shift for O-4 (46 and 44 ppm, respectively) and a small upfield shift for O-2 (18 and 19 ppm, respectively) have been determined. The diamagnetic shift is

due to the deprotonation of N-3 at a pH of 9.6 (3) in agreement with the literature value of pK 9.5 (25). The absolute value of the ¹⁷O chemical shift of O-4 is similar to the chemical shift of amides and peptides whereas the chemical shift of O-2 is similar to that of urea due to the similarity in structure.

In conclusion ¹⁷O was found to be an effective tool in studies of the electronic structure (e.g., conformation, cis-trans isomerism, H bonding sites) of amino acids, peptides, nucleic acid constituents and their derivatives. Synthetic methods have been developed to label the above materials with ¹⁷O. Several biologically active molecules as MIF and oxytocin have been examined. Sites of inter- and intramolecular H bonding have been determined and solute solvent interactions studied. Investigation of metal ion binding to amino acids and peptides have been found most illuminating. ¹⁷O resonance of complexes of proline bound to the cobaltous ion was observed (Fig. 4). Relative concentrations of the complexes have been determined and kinetics of metal ion bindings studied. ¹⁷O NMR of solutes in liquid crystalline media yielded information on the nuclear quadrupole coupling constants. In the future we hope to extend this work to biologically related studies of membranous materials.

ACKNOWLEDGMENTS

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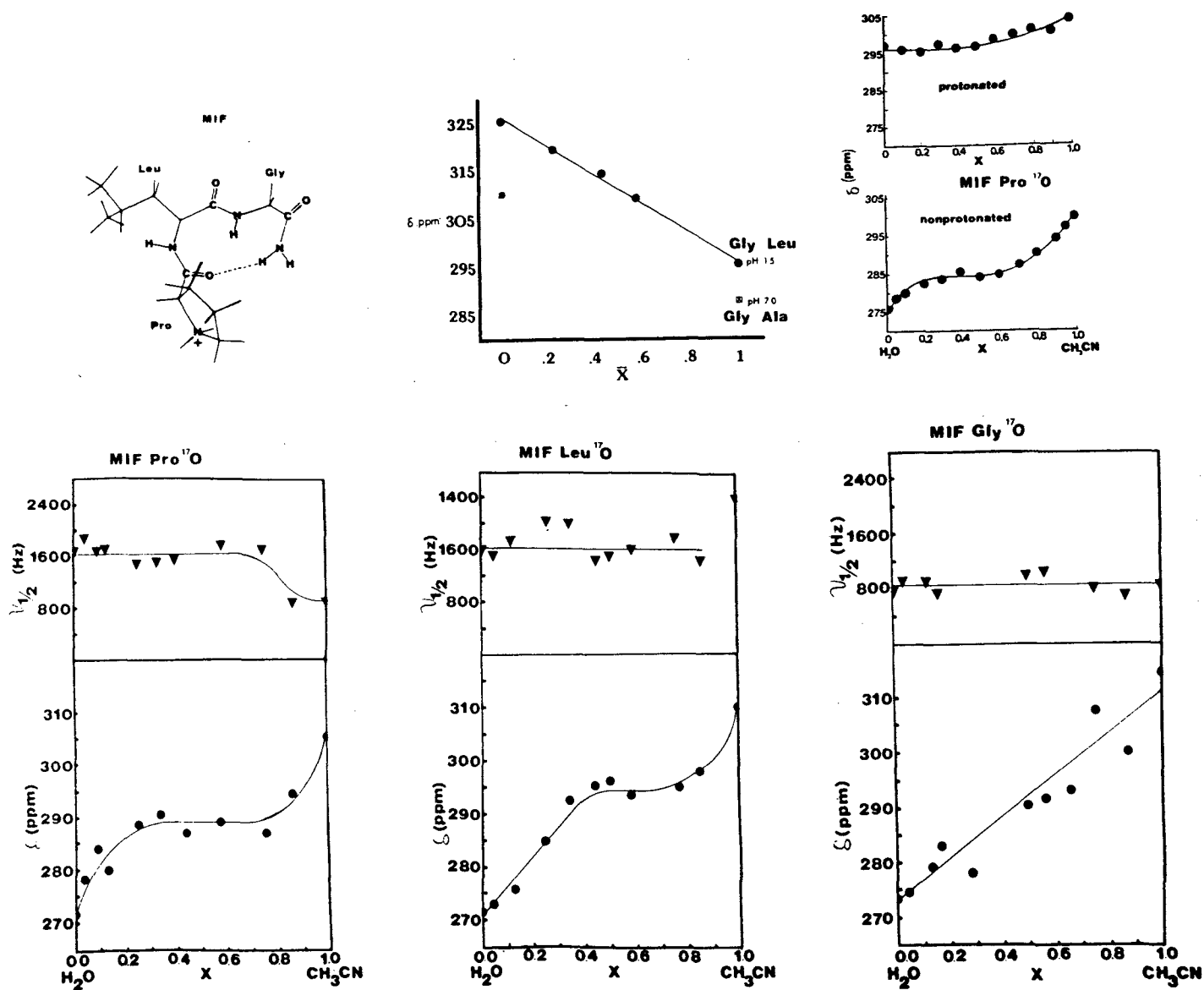


Figure 2. Solvent effects on peptide oxygen-17 chemical shifts.

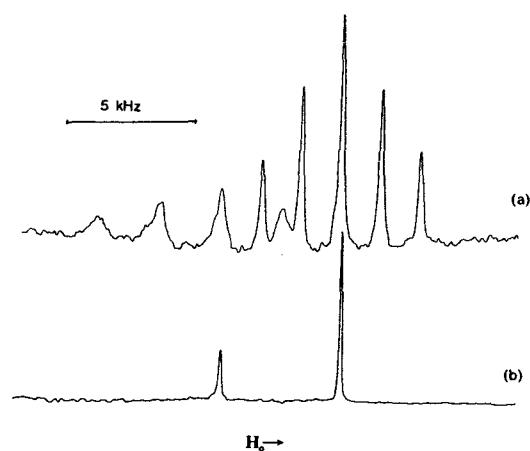


Figure 3. Oxygen-17 spectra of urea (a) in a lyotropic liquid crystalline medium of type II and (b) in the isotropic phase at 55°C.

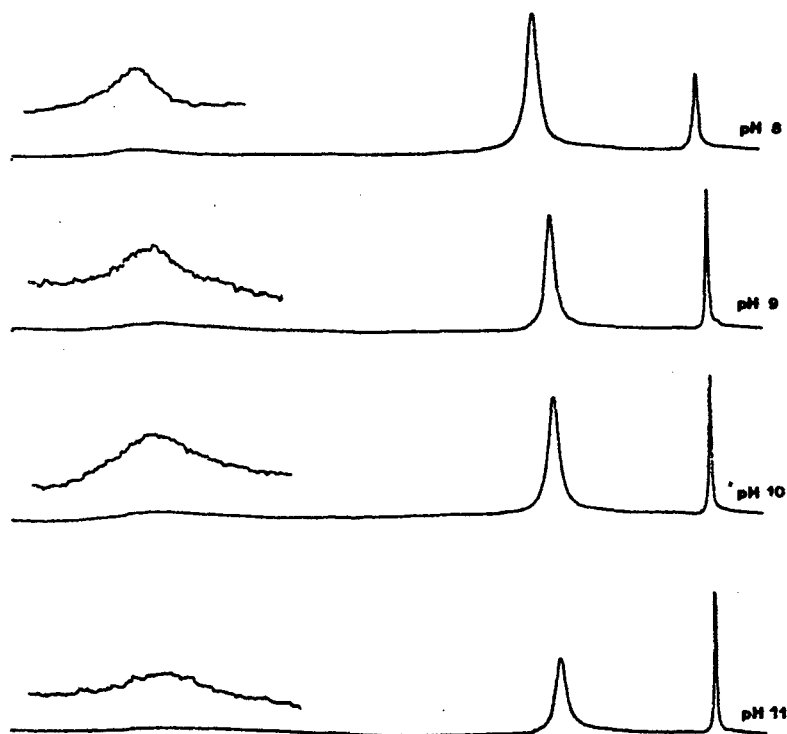


Figure 4. ^{17}O NMR spectra of 0.27 M ^{17}O labeled proline in 0.053 M cobaltous ion aqueous solution at 25°C at several pH values, (8;9;10;11).

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I. INTRODUCTION

Structural phase transitions may lead from a high temperature disordered phase with a space group G_0 and a unit cell edge a to:

- a) A *ferrodistortive* commensurate ordered state with a space group G_1 and an unchanged unit cell, $a' = a$.
- b) An *antiferrodistortive* commensurate ordered state with a space group G_2 and a unit cell size which is an integral multiple of the high temperature unit cell: $a' = m \cdot a$, $m = 2, 3, 4 \dots$
- c) An *incommensurately modulated* ordered phase where the wavelength λ of the modulation is irrational in units of the original lattice constant a : $\frac{\lambda}{a} \neq \frac{M}{N}$; $M, N = 1, 2, 3, 4 \dots$

Here the translational symmetry is lost and the crystal cannot be described by any of the 230 three-dimensional crystallographic space groups though the system exhibits perfect long range order.

- d) A *chaotic* state with no long range order which can in contrast to *amorphous* systems — transform itself at lower temperatures to a commensurate ordered state.

The transitions c) and d) take place when we have *deterministic* "competing interactions" and "frustration" (1); i.e. the competing structural units form a regular lattice. If the competing interactions are placed at *random* (such as in a mixed ferro—antiferroelectric crystal), a "spin glass" phase may be formed.

One of the most interesting aspects of *incommensurate* phases is the spontaneous appearance of *solitons* (2) which are arranged in a periodic lattice with a period which is ir-

rational in units of the original lattice. The *soliton lattice* may become *chaotic* thus leading to "chaos in space" as contrasted to "chaos in time" found in dynamical systems (3).

The problems of the

- i) possible existence of only a few universal routes from order to chaos in dynamical systems, and
- ii) the non—linearity of the underlying natural phenomena have been extensively investigated in the last few years and are among the most outstanding open problems of condensed matter physics.

The formation of solitons in spatial structures and the routes to spatial chaos have so far received considerably less attention.

Both in dynamic and in spatial structures the soliton formation and the routes to chaos can be simulated by the onedimensional sine—Gordon equation (3) which can be written in dimensionless units as:

$$\phi_{tt} - \phi_{xx} + \sin \phi = F(x,t) - \epsilon \phi_t \quad (1)$$

where $\phi_{tt} = \frac{\partial^2 \phi}{\partial t^2}$, $\phi_{xx} = \frac{\partial^2 \phi}{\partial x^2}$, $\phi_t = \frac{\partial \phi}{\partial t}$, ϵ is the damping parameter and $F(x,t)$ a driving force which is in dynamical systems usually written as $\Gamma \sin(\omega_d t)$. For small ϕ one finds the familiar harmonic solutions. For large ϕ "particle—like" solitons represent exact solutions. Though the equation is completely deterministic, "chaotic" temporal response is found at large Γ as a consequence of an interplay between an intrinsic periodic motion and an "incommensurate" external periodic perturbation. "Chaos in space" may

similarly be formed by an interplay between the period of the modulated structure and the original lattice constant which are incommensurate to each other. In the resulting "intermittent" chaotic phase the solitons are randomly pinned so that the situation in many ways corresponds to the one in "spin glasses".

Whereas magnetic resonance has been extensively used to study "ferrodistortive" and "anti-ferrodistortive" phase transitions little attention has been paid to "incommensurate" and "chaotic" type phase transitions until now. Here we shall review some recent results obtained by us in the study of:

- i) The "incommensurate" and "chaotic" states in Rb_2ZnCl_4 and Rb_2ZnBr_4 with particular emphasis on the detection of solitons and the transition to chaos.
- ii) Soliton-like "dynamics" in the pseudo-one dimensional antiferroelectric squaric acid, $\text{C}_4\text{H}_4\text{O}_2$.

II. INCOMMENSURATE STATES, CHAOTIC STATES AND SOLITONS IN Rb_2ZnCl_4 AND Rb_2ZnBr_4

Rb_2ZnCl_4 and Rb_2ZnBr_4 exhibit (4) on cooling a sequence of structural phase transitions

$$P \rightarrow I \rightarrow (\text{Ch}) \rightarrow C \rightarrow C'$$

from a high temperature disordered paraelectric (P) phase to an incommensurate (I) phase followed by a — probably metastable — chaotic (Ch) phase (5) and two commensurate (C and C') ferroelectric phases.

II.1. NMR Spectrum and Shape of the Frozen-out Modulation Wave

In translationally periodic systems the number of magnetic resonance lines in the spectrum equals to the number of physically non-equivalent nuclei per unit cell.

In incommensurate systems where the translational lattice periodicity is lost there is essentially an infinite number of nuclei which contribute to the NMR spectrum and which are equivalent to each other in the paraelectric phase. Instead of sharp lines one expects to find a frequency distribution $f(\nu)$ which reflects the spatial variation of the resonance frequencies, $\nu = \nu(x)$, which is in turn determined by the spatial variation of the frozen out modulation wave $u(x)$:

$$\nu = \nu[u(x)] \quad (2)$$

where

$$u(x) = A \cos[\phi(x) + \phi_0] \quad (3)$$

in the constant amplitude approximation.

Here ϕ_0 is an initial phase which depends on the crystal structure and is important only if $\phi(x)$ is not linear in x . The spatial variation of the phase of the modulation wave $\phi(x)$ is determined (6) in the present case by the time-independent sine-Gordon equation (1):

$$\frac{d^2 \phi}{dx^2} = -\frac{n\gamma}{2\kappa} A_0^{n-2} \cdot \sin(n\phi). \quad (4)$$

Here $n = 6$ for Rb_2ZnCl_4 and Rb_2ZnBr_4 representing the lowest power of the "lock-in" term describing the effect of the crystal lattice, κ is an elastic constant and the amplitude of the modulation wave varies with temperature as

$$A_0 \propto (T_I - T)^\beta \quad (5)$$

where T_I is P-I transition temperature. Close to T_I $\phi(x)$ is nearly linear in x (Fig. 1) and the modulation wave u can be described as a "plane wave". At lower temperature ϕ becomes non-linear in x . Nearly commensurate regions where $\phi(x) = \text{const}$ are separated by soliton-like "discommensurations" where the phase changes rapidly (Fig. 1). The phase

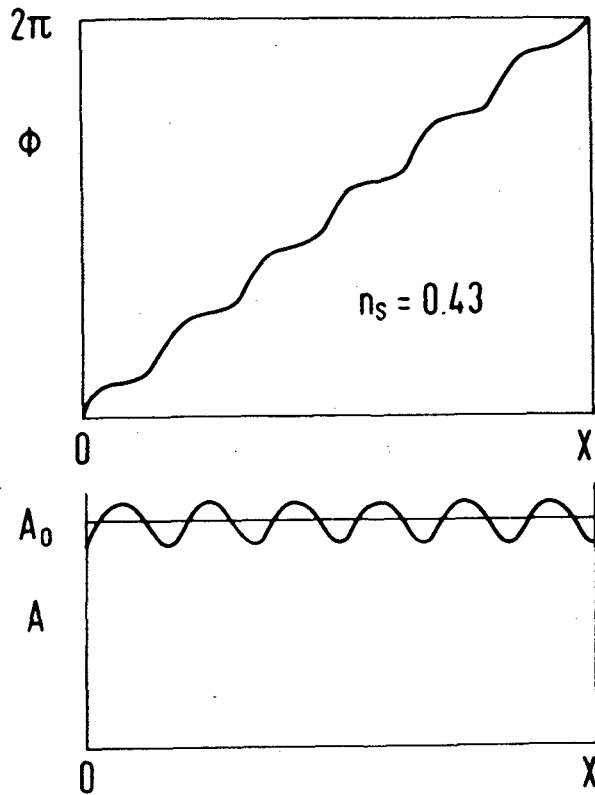


Fig. 1. Spatial variation of the phase and amplitude in an incommensurate system

solitons represent exact solutions of eq. 4 and form a regular lattice with a temperature dependent spacing x_0 which is generally irrational in units of the original lattice. The soliton density

$$n_s = \frac{d_0}{x_0} \quad (6)$$

is the ratio of soliton width d_0 to the inter-soliton distance x_0 and measures the volume fraction of the crystal occupied by the phase soliton domain walls. It is 1 in the plane wave limit just below T_1 and zero at the "lock-in" transition T_c where $x_0 \rightarrow \infty$.

For a space varying frequency $\nu(x)$ the spectral distribution function at ν_0 is given by

$$f(\nu_0) = \int \delta[\nu_0 - \nu(x)] dx \quad (7)$$

yielding

$$f(\nu) = \frac{\text{const}}{|d\nu/dx|} \quad (8)$$

or explicitly (4)

$$f(\nu) = \frac{\text{const}}{\left| \frac{d\nu}{du} \right| \left| \frac{du}{d\phi} \right| \left| \frac{d\phi}{dx} \right|} \quad (9)$$

The NMR line-shape thus represents an extremely sensitive local probe reflecting the spatial variations of the frozen out modulation wave.

The line-shape will be peaked whenever

$$\text{i) } d\nu/du \rightarrow 0 \quad (10a)$$

$$\text{ii) } du/d\phi \rightarrow 0 \quad (10b)$$

or

$$\text{iii) } d\phi/dx \rightarrow 0 \quad (10c)$$

It is this last point which allows for a direct determination of the soliton density (4).

To evaluate expression 9 let us expand the relation 2 in a power series and keep for simplicity only the leading linear term :

$$\nu = \nu_0 + a_1 u + \dots = \nu_0 + \nu_1 \cos[\phi(x) + \phi_0] + \dots \quad (11)$$

where

$$\nu_1 = a_1 A_0 \propto (T_1 - T)^\beta \quad (12)$$

In the above case $d\nu/du = a_1 = \text{const}$ and the singularities in $f(\nu)$ will come from the zeroes of $du/d\phi$ and $d\phi/dx$. We may now distinguish two different limits:

a) In the "plane wave" modulation limit

$$d\phi/dx = k_1 = \text{const} \neq 0 \quad (13)$$

and the lineshape is given by

$$f(\nu) = \frac{\text{const}}{|\sin \phi|} = \frac{\text{const}}{\sqrt{1-X^2}} \quad (14)$$

where $X = \frac{\nu - \nu_0}{\nu_1}$. The edge singularities corresponding to $X = \pm 1$ will occur at $\nu = \nu_0 - \nu_1$

and reflect the fact that the density of states has a maximum at the extreme displacements $u = \pm A_0$ of the modulation wave. The frequency separation between the edge singularities will be proportional to the amplitude of the modulation wave, i.e. to the order parameter:

$$\Delta\nu = \nu_+ - \nu_- = 2\nu_1 \propto (T_1 - T)^\beta \quad (15)$$

The above line-shape 14 has been observed below T_1 (Fig. 2) and the critical exponent β was determined (3) as $\beta = 0.34 \pm 0.03$.

b) In the "multi-soliton" lattice modulation limit $d\phi/dx \rightarrow 0$ in the "commensurate" regions giving rise to "commensurate" peaks in addition to the incommensurate edge singularities 14. The "commensurate" peaks are directly related to the volume fraction n_c of the "commensurate" regions in the crystal: $n_s + n_c = 1$.

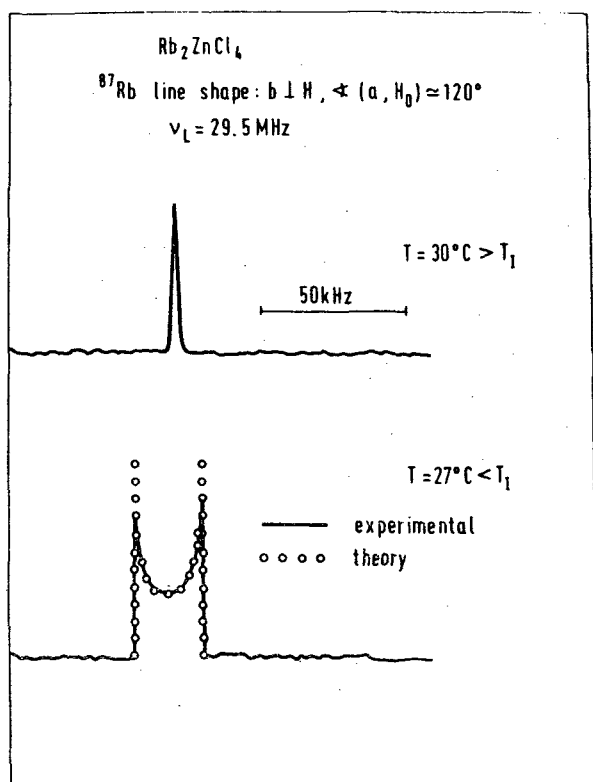


Fig. 2. ^{87}Rb $1/2 \rightarrow -1/2$ NMR lineshape in Rb_2ZnCl_4 close to T_1

By a straightforward integration of eq. 4 we find $d\phi/dx$ so that $f(\nu)$ becomes (4)

$$f(\nu) = \frac{\text{const}}{|\sin \phi(x)| \sqrt{\Delta^2 + \cos^2 [\frac{n}{2}(\phi(x) - \phi_0)]}} \quad (16)$$

The above expression is identical to eq. 4 for $\Delta \gg 1$ whereas up to n new "commensurate" lines appear for $\Delta \rightarrow 0$ (Fig. 3). The integration constant Δ is related to the soliton

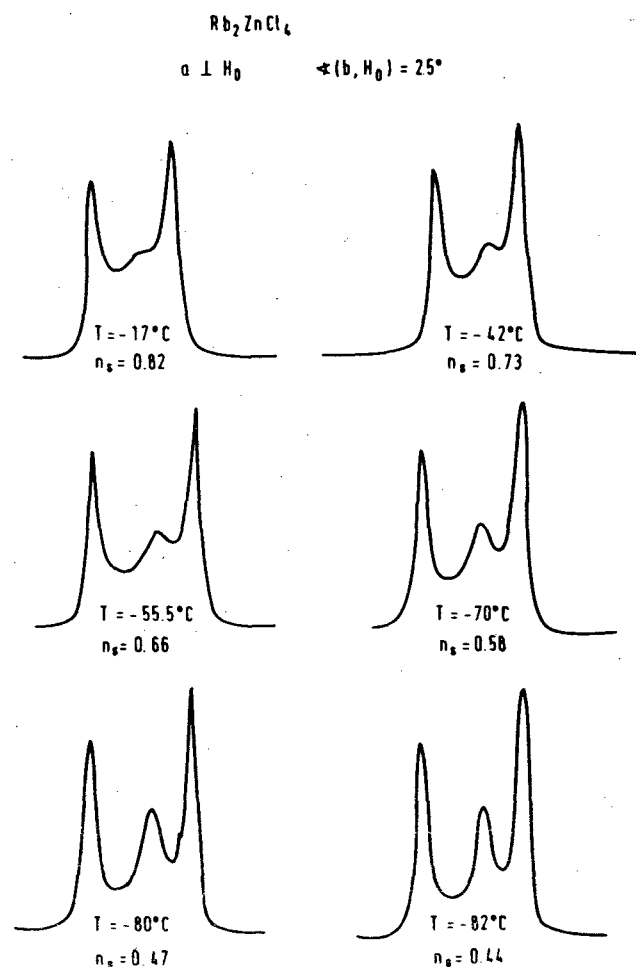


Fig. 3. ^{87}Rb $1/2 \rightarrow -1/2$ NMR lineshape in Rb_2ZnCl_4 showing the appearance of the "commensurate" line as the static multi-soliton lattice becomes more pronounced.

density n_s by (4):

$$n_s = \frac{\pi/2}{K(1/\sqrt{1+\Delta^2})} \quad (17)$$

where K is the complete elliptic integral of first kind. By comparing theoretical and experimental lineshapes Δ and n_s can be determined. This has been done for the ^{87}Rb $1/2 \rightarrow -1/2$ transition in both Rb_2ZnCl_4 and Rb_2ZnBr_4 .

The temperature dependence of n_s in Rb_2ZnCl_4 (5) is presented in Fig. 4. In evaluating n_s amplitude fluctuations (6) have been as well taken into account.

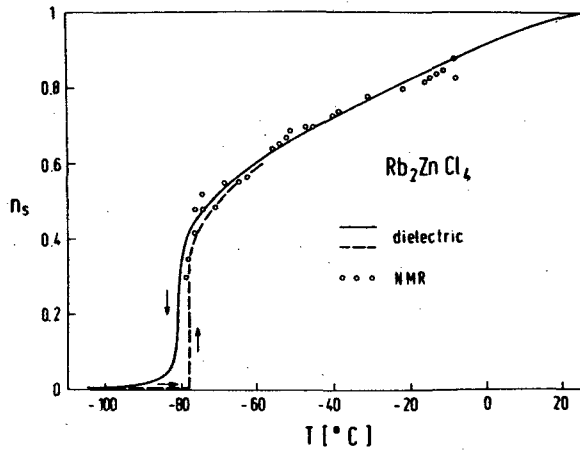


Fig. 4. Temperature dependence of the soliton density in Rb_2ZnCl_4

In contrast with the theoretical expectation n_s is finite at T_c . On cooling n_s is non-zero even in the C phase below T_c . This result can be explained by the existence of a (probably metastable) chaotic phase intermediate between the I and the C phases. In this phase the solitons are *randomly* pinned either by the coupling to the discrete lattice or by coupling to impurities and the long range order is destroyed. This result can be obtained from eq. 1 by identifying space with discrete "time" on the right hand side of this equation. The driving term $F(x)$ is thus given by the soliton-lattice or soliton-impurity coupling

which becomes the more important the closer we approach T_c and the weaker is the soliton-soliton interaction. The existence of the "chaotic" phase (7) is confirmed by the anomalous broadening of the incommensurate X-ray satellites. For $T > T_c$ the relative spread in the — uncorrelated — inter-soliton separations follows a Curie-Weiss law (8)

$$\frac{\delta x_0}{x_0} \propto \frac{1}{T - T_c}, \quad T > T_c \quad (18)$$

but saturates at T_c yielding a "chaotic" width of the X-ray incommensurate satellite peaks (8)

$$(\delta q)_T \leq T_c = \text{const. } n_s \quad (19)$$

which is proportional to the soliton density. The values of n_s obtained from eq. 19 or from the dielectric data (5)

$$\chi = \chi_0 + \text{const. } n_s, \quad T \leq T_c \quad (20)$$

agree rather well with those directly determined by NMR.

Analogous results were also obtained by EPR in K_2SeO_4 (9).

At low enough temperatures the chaotic state disappears and we have a commensurate (C) ferroelectric phase which is again translationally invariant.

It should be noted that in the narrow multi-soliton lattice limit — where the solitons do not overlap — the NMR line-shape for randomly spaced pinned solitons

$$\begin{aligned} \langle f(\nu_0) \rangle &= \left\langle \sum_i \frac{dx}{d\nu_i} \Big|_{\nu(x_i)=\nu_0} \right\rangle = \\ &= \int dx_1 D(x_1 - x_0) \dots \int dx_j D(x_j - x_0) \dots \\ &\dots \sum_i \frac{dx}{d\nu_i} \Big|_{\nu_i=\nu_0} \end{aligned} \quad (21)$$

equals to the one — $f(\nu) = \frac{dx}{d\nu}$ — for a periodic multi-soliton lattice. This is due to the fact that NMR measures just the local soliton density and is — if the solitons are

far apart — not affected by the destruction of long range order. In the above expression the position of the j -th soliton x_j is determined by the distribution function $D(x_j - jx_0)$.

11.2. Depinning of the Modulation Wave

The NMR lineshape studies in Rb_2ZnCl_4 and Rb_2ZnBr_4 have shown that the modulation wave is generally static due to lattice or impurity pinning. The dispersion of the phason induced spin-lattice relaxation rate showed (4) that the pinning gap is of the order of 100 MHz — 1 GHz. The dependence of the maximum value of the dielectric constant on the K-content in mixed $\text{Rb}_{2x}\text{K}_{2(1-x)}\text{ZnCl}_4$ crystals as well gave a soliton-impurity pinning energy (8) of

$$U_B = 1.4 \times 10^{-5} \text{ eV} . \quad (22)$$

In Nb Se_3 (10) the incommensurate charge density wave (CDW) has been depinned by an applied electric field E which was larger than a critical value E_0 . The resulting conductivity σ was of the form

$$\sigma = \sigma_0 + \sigma_a \exp(-E/E_0) \quad (23)$$

with the gap E_0 corresponding to about 0.1 K (10). For $E > E_0$ both periodic oscillations and a broad continuous noise appeared (10) signaling the approach to chaos.

In Rb_2ZnBr_4 thermal depinning has been observed (11) close to T_1 .

If the modulation wave is not static the resonance frequencies are not only space but also time dependent: $\omega = \omega(x, t)$. The NMR line-shape is now given by

$$I(\omega) = \frac{1}{2\pi} \int_{-\infty}^{+\infty} G(t) e^{i\omega t} dt \quad (24)$$

where

$$G(t) = \langle \exp[-i \int_0^t \omega(x, t') dt'] \rangle_x . \quad (25)$$

i) For the case of a *uniform sliding* of the

"plane wave" like modulation wave with a velocity v and a wave vector k_1 we have

$$\begin{aligned} u(x, t) &= A \cos k_1 [x + vt + \phi_0] = \\ &= A \cos [k_1 x + \Omega t + \phi_0] . \end{aligned} \quad (26)$$

Uniform sliding of the modulation wave thus corresponds to a harmonic oscillation of a given atom with a frequency $\Omega = k_1 \cdot v$.

Inserting eq.26 into eq.11 one can immediately obtain the autocorrelation function $G(t)$ as:

$$G(T) = J_0\left[\frac{2}{w} \sin(\pi T)\right] \quad (27)$$

where J_0 is the cylindrical Bessel function of order zero, $T = \frac{w}{2\pi} \cdot \omega_1 t$ and $w = vk_1/\omega_1 = \Omega/\omega_1$ with $\omega_1 = 2\pi \nu_1$. For small sliding velocities where $w \ll 1$ the static lineshape is recovered:

$$I(\omega) = \frac{\text{const}}{\sqrt{1 - \left(\frac{\omega - \omega_0}{\omega_1}\right)^2}}, \quad \Omega/\omega_1 \ll 1 . \quad (28)$$

For large sliding velocities the incommensurate line broadening is motionally averaged out:

$$I(\omega) \propto \delta(\omega - \omega_0), \quad \Omega/\omega_1 \gg 1 \quad (29)$$

and one finds just one sharp "paraelectric-like" line at ω_0 .

In the general case

$$I(\omega) = \sum_{n=-\infty}^{+\infty} J_n^2\left(\frac{1}{w}\right) \delta\left(\frac{\omega - \omega_0}{\omega_1} - nw\right) \quad (30)$$

a three component line-shape is expected with peaks around $\omega = 0$ and $\omega = \pm \omega_1$. The relative intensities of these lines and the positions of the outer peaks strongly vary with w (Fig. 5). This* result is significantly different from the one for "normal" motional narrowing due to a stochastic motion where $G(T)$ is not periodic.

ii) A similar lineshape is also found for a *thermally induced floating of a pinned modulation wave*:

$$u = A \cos [k_1 x + \psi(x, t) + \phi_0] \quad (31)$$

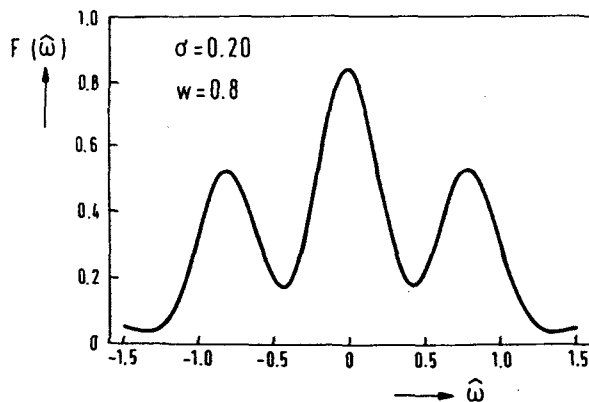


Fig. 5. NMR lineshape for a uniformly sliding modulation wave $\tilde{\omega} = (\omega - \omega_0)/\omega_1$. The line was convoluted with Gaussian of $\sigma = 0.2$.

where $\psi(x, t)$ describes the effect of pinning, e.g.:

$$\psi(x, t) = B \sin(kx) \sin(\omega t) \quad (32)$$

and ω is the thermally excited oscillation frequency of the pinned modulation wave. B is related to the average distance between the pinning centres and is thus T -dependent. For fast oscillations $\omega/\omega_1 \gg 1$ one finds

$$I(\tilde{\omega}) = \int_0^1 \delta\{\tilde{\omega} - \cos(\pi qu + \phi_0)\} J_0[B \sin(\pi u)] du \quad (33)$$

where $q = k_1/k$, $u = \frac{k}{\pi} \cdot x$ and $\tilde{\omega} = \omega/\omega_1$. Depending on the value of B , a static or a motionally averaged spectrum is obtained.

Between $T_1 - 12$ K and T_1 the ^{87}Rb $1/2 \rightarrow -1/2$ NMR spectrum in Rb_2ZnBr_4 shows (11) in addition to the two edge singularities also a motionally averaged "central" line as predicted by eqs. 30 and 33 (Fig. 6). This demonstrates the existence of thermal depinning and phase floating at least over a part of the Rb_2ZnBr_4 crystal (11).

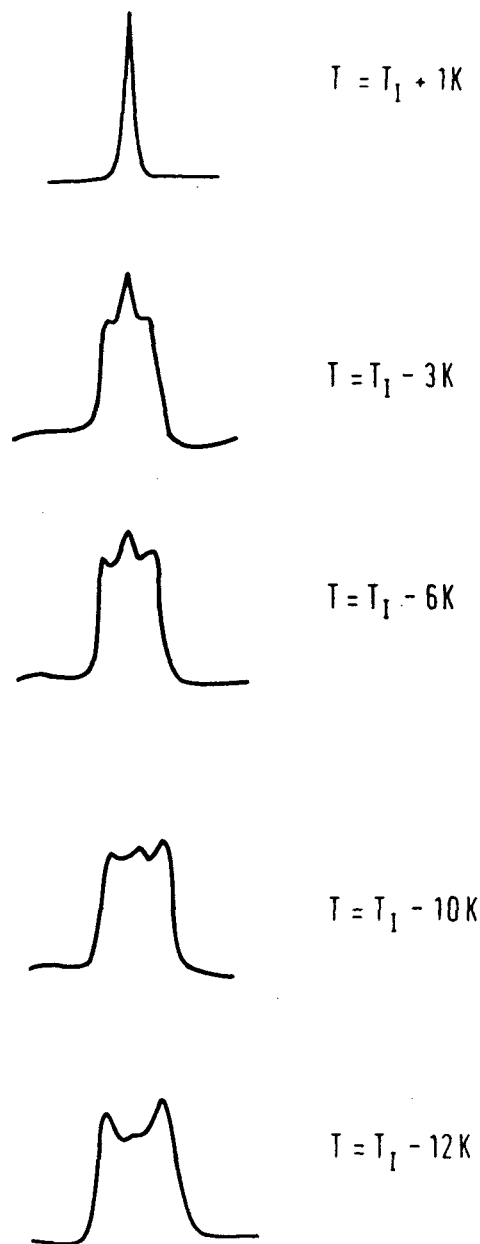
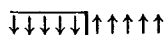


Fig. 6. ^{87}Rb $1/2 \rightarrow -1/2$ NMR lineshape in Rb_2ZnBr_4 close to T_1 showing motional narrowing effects due to thermal depinning and floating of the modulation wave $\nu_L = 88.3$ MHz, $\vec{a} \perp \vec{H}_0$, $\angle(\vec{c}, \vec{H}_0) = 60^\circ$.

III. SOLITON-LIKE EXCITATIONS AND THE PHASE TRANSITION IN PSEUDO-ONE DIMENSIONAL SQUARIC ACID

Whereas solitons are part of the ground state in incommensurate systems they are entropy favoured and part of the excitation spectrum in pseudo-one dimensional ferro-electrics.

The ordered state of squaric acid, $C_4H_4O_2$, consists (12) of layers of $O-H-O$ bonded ordered Ising chains where the Ising pseudo-spin variable $\uparrow, \downarrow$ refers to the two equivalent positions of the proton in the hydrogen bonds, i.e. $O-H-O$ and $O---H-O$. The $O-H-O$ bond length is 2.47 Å and the distance between the two proton equilibrium sites 0.44 Å as determined by the $^{17}O-H$ magnetic dipolar fine structure of the naturally abundant ^{17}O ($I = 5/2$) nuclear quadrupole resonance (NQR) spectra (12). For $T \leq T_c = 95^\circ C$ the chains are completely ordered: $\uparrow\uparrow\uparrow\uparrow\uparrow \dots$. As $T \rightarrow T_c$ soliton-like domain walls



start to move along the chains, resulting in a biased averaging of the ^{17}O electric field gradient tensor:

$$V = \frac{1}{2} [1 + S(t)] V(^{17}O-H-O) + \frac{1}{2} [1 - S(t)] V(^{17}O---H-O).$$

Here S is the local short range order parameter at a given ^{17}O site. At $T = T_c = 95^\circ C$ long range order between the chains disappears and only $S = S(t)$ remains. At $T = T_c + 15 K$ the time between two successive passages of a domain wall through a given ^{17}O site becomes of the order of the inverse splitting between the "close" and "far" — $^{17}O-H-O$ and $^{17}O---H-O$ NQR frequencies, i.e. $\sim 10^{-6}$ sec and the NQR line smears out (Fig. 7). At $T = T_c + 20 K$ $S \rightarrow 0$ and one finds just the paraelectric ^{17}O NQR frequencies though the

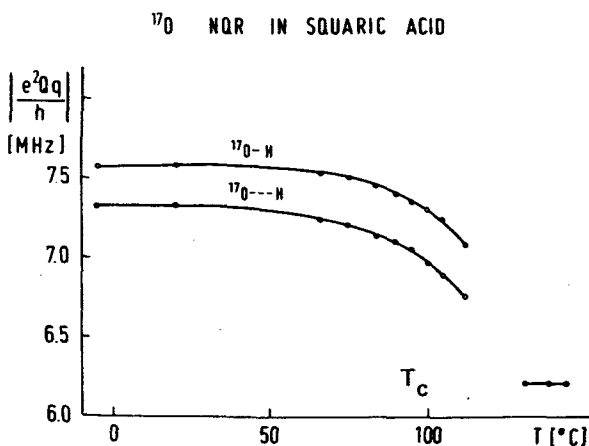


Fig. 7. Temperature dependence of the "close" ($^{17}O-H-O$) and "far" ($^{17}O---H-O$) ^{17}O quadrupole coupling constants in squaric acid.

neutron scattering data still show (12) a correlation length of about 50 unit cells along the $O-H-O$ bonded chains.

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NEW SOFTWARE METHODS IN NMR SPECTROSCOPY

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I. INTRODUCTION

Over the past twenty years, NMR spectroscopists and instrumentation have not kept pace with rapidly advancing computer technology. Even today, as instrumentation incorporates significant new computing power, advances in digital hardware and software are accelerating beyond their application to NMR.

In what ways can these increased capabilities affect the way a spectroscopist analyzes the results from an experiment? This paper will address that question with illustrations of several data analysis techniques for the optimal extraction of information from NMR experiments.

Of all the growing areas of computer technology, none is progressing with as much speed and momentum as the field of hardware. Von Neumann computer architecture has been successful for the past 40 years due to (at least in part) the nature of hardware technologies and the continuous growth of these technologies. In fact today, computer architectures radically different from the von Neumann design are being implemented. Rapid development of electronic hardware is also responsible for making computers accessible to the general population and to the laboratory. Computing capability that cost millions of dollars twenty years ago, is today available to the individual researcher.

Current computer systems are substantially different from those used on NMR spectrometers only 5 years ago. CPUs, disks, memory and terminals are much faster. The drop in memory and disk prices has been so precipitous that memory and disk storage can no longer be considered limiting factors when designing a system. Far less expensive

and new types of electronic components have resulted in new system designs. Modern NMR spectrometers routinely distribute computing functions among multiple processors; each performing a specific task. Array processors, for example, have been integrated into spectrometer systems for the explicit purpose of accelerating vector operations such as Fourier Transformations. Processors for data acquisition, data reduction, user I/O and spectrometer control can be found in most modern instrumentation. Performing data reduction on one or more computers independent of the data acquisition computer has advantages which will be discussed later.

Software developments are just as important as hardware developments, but the general consensus is that hardware advances have out-paced improvements in software. Nevertheless, substantial growth in software methods has been realized in the past few years. Until recently, operating systems were by necessity unique to each type of computer. UNIX is an operating system that has been designed to be machine independent and flexible enough to address the needs of a wide range of users. It is likely that some commercial NMR spectrometer systems will include UNIX in the near future. Standard high level computer languages were utilized long before standard operating systems; most NMR spectrometer systems are now programmed at least in part in PASCAL. This enables manufacturers to upgrade spectrometer performance with newer and more powerful computers without losing their investment in previously developed software. From the user's point of view, however, not much is gained with higher level languages unless the software can

be modified. Since the manufacturers are justifiably reluctant to release source code, they generally accomodate users by supporting user-written modules.

More powerful computer hardware is resulting in more powerful and sophisticated software. Faster computers have made practical new algorithms for spectroscopic data processing. These new algorithms tend to heavily utilize statistics and thus be more rigorous and complicated. Fast floating point performance and large memory address spaces are design assumptions for these algorithms. A natural extension of this programming methodology is the application of artificial intelligence techniques to the processing of spectroscopic data.

This paper discusses only data reduction software; it does not address problems in optimizing data acquisition. Examples of sophisticated software developed at our laboratory will be presented in the next few sections. This software has been developed to process NMR data, but the techniques in use are applicable to a wide range of spectroscopies and chromatography. The software is designed to run on 32-bit mini or micro-computers (DEC VAX series, Data General MV series, IBM instruments CS-9000) in single or multiuser configurations. This software is part of a new generation of laboratory data processing methods. While the individual techniques employed are more evolutionary than revolutionary, the software as a whole represents a significant advance in laboratory data processing.

II. AUTOMATION

One of the most rapidly advancing fields of analytical chemistry is laboratory automation. It is generally recognized that efficiency, quality and cost effectiveness of many laboratory tasks can be greatly increased through the successful application of automation. FT-NMR spectroscopy was one of the first experimental techniques to benefit from automation due to the requirement of an instrument computer. Modern spectrometers are capable of running a series of very complicated experiments without operator attention. Even automatic

sampling changing has been demonstrated at several laboratories. Fully automated data analysis is more difficult to accomplish, however, especially if that analysis is to include complicated tasks which the user would normally control based on the results of previous analysis steps.

The ease of automating a program is inversely proportional to the complexity and power of that program. Thus, in principle, it is relatively easy to automate simple software systems designed for the unsophisticated user. These automated and simplified systems are becoming increasingly popular. Of course, automating such a program does not afford the experienced spectroscopist much of the power or flexibility found in more sophisticated data analysis programs. Simple automated data processing, including data collecting, weighting or apodization, Fourier Transformation, and plotting) is much easier to realize than automated comprehensive data analysis (i.e. data processing, identification and characterization of all spectral peaks, quantification, evaluation, etc.).

Many of the steps taken in a typical processing sequence are linear and require only simple input. For example, an exponential weighting is generally performed in such a way that the user needs only to select a line broadening parameter. The success of processing is not extremely sensitive to the proper choice of this parameter. In fact, line broadening can be determined from one spectrum and then applied indiscriminately to all similar spectra. Phasing, on the other hand, is a linear process which is extremely sensitive to input parameters. Unless manually phased calibration spectra or phasing alternatives such as magnitude calculations are used, complicated algorithms are needed to reliably automate spectral phasing.

Automatic phase correction of Fourier transform NMR spectra was first demonstrated by Ernst (1). His iterative method arrives at optimum values for zero and first order corrections by taking linear combinations of the original spectrum and its Hilbert transform in various proportions until the ratio of the maximum positive signal excursion to maximum negative signal excursion is optimized. The applicability of the

procedure is limited by spectral signal-to-noise and the accuracy with which the baseline can be characterized. Another iterative technique (2) optimizes phase corrections by a modified simplex method, using maximization of the smallest spectral absorption mode intensity as the optimization criterion. Limited automatic phase correction has also been achieved by precalibration of the detector transfer function (3). An automatic phasing technique developed in our laboratory (4) is based on Dispersion vs. Absorption (DISPA) lineshape analysis and is summarized below.

A plot of "absorption" versus "dispersion" (normalized to the maximum apparent "absorption" peak height) for a misphased Lorentzian line gives a unit circle passing through the origin, but which has been rotated about the origin by a number of degrees equal to the applied phase misadjustment. Fortunately, phase misadjustment appears to be the only mechanism (of those examined to date (5-9)) that displays this type of DISPA behavior. To automate phasing using this method, a robust and non-interactive peak identification scheme must be used to locate each peak. We have found that locating peaks in the power spectrum gives the best results. The peak finding procedure, described elsewhere (10), tabulates peak location and peak phase information. A weighted linear least squares calculation is then performed to obtain the zero and first order phase corrections.

The DISPA phasing method has the advantage that it is non-interactive. Furthermore, a large number of peaks actually improves the quality of the spectral phase correction. Thus, best results are obtained on high resolution - narrow line spectra. A spectrum phased with this method is shown in figure 1.

Automatic phasing is the most difficult primary processing step to automate. Automated data analysis operations, however, are even more difficult to implement because of their non-linear nature. Furthermore, data analysis operations are characterized by extensive user interaction (and consequently user decision-making). To automate baseline calibration, spectral peak quantification (location, linewidth, intensity and integral) and final data presentation requires software

capable of making decisions normally made by the user.

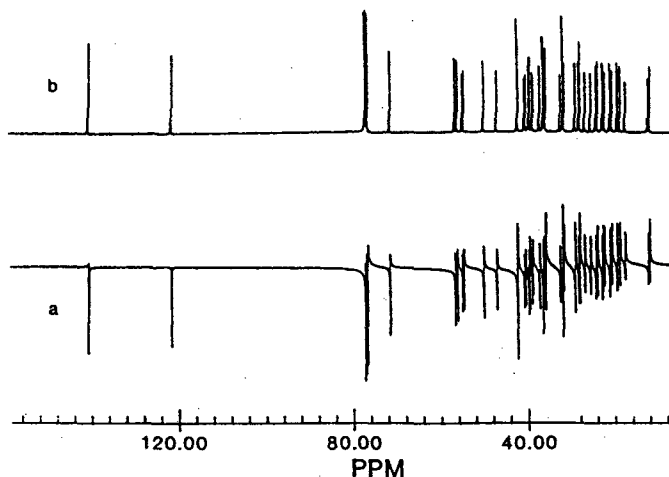


Figure 1. ^{13}C spectrum of a mixture of two steroids (a) before phasing and (b) after automatic phasing.

The peak quantification algorithms which we are using have multiple levels of operation - varying from total user control to fully automatic execution. The controlling software for automated data analysis has two manifestations. The first mechanism allows the user to string together processing commands which have only simple input (such as system parameters). The user can modify processing parameters during a "Dry Run" of the command execution if desired. Provisions exist to increment filenames or to internally loop within the command string.

A second mechanism is currently under development. It will allow a user familiar with the software system to train (or program) an automation sequence by processing, analyzing and generating output for a data file or a series of data files. During this training session, the trainer user can specify the required output, input and options that will be used for automated analysis. The end result of the training session will be a control file which a less sophisticated user can invoke to control processing and analysis for his own data sets. This automated

sequence can include command strings (via the first mechanism described) or other automated sequences. Customized messages within the sequence will make it easy for users with all levels of spectroscopy experience to perform repetitive analyses to the full extent of their ability. This level of automation is not restricted to simple operations and, in fact, can make full use of the sophisticated subroutines such as the peak quantitation and curve fitting routines described below.

III. QUANTITATIVE ANALYSIS

One of the most important features of NMR spectroscopy is its quantitative nature. Unfortunately, the inherent low sensitivity of the technique usually forces the spectroscopist to obtain data under non-linear conditions, particularly for nuclei other than proton. Recent advances in instrument sensitivity, however, are making quantitative experiments increasingly practical.

The requirements for quantitative data acquisition are well known (11-15). Instrument and experiment parameters such as filter settings, pulse width, pulse repetition rate and decoupling all play important roles in establishing a quantitative experiment. In addition, the chemical system itself can influence the linearity of the experiment if magnetization is transferred between nuclei after excitation. Quantitative experiments may not always be possible and usually they require conditions which reduce spectral signal-to-noise ratios.

Regardless of whether or not an experiment has been performed under analytical conditions, the highest accuracy possible for peak integrations is desirable. A wide variety of integration techniques exist and have been applied to NMR data. Continuous wave instruments use a capacitor to electrically integrate spectral resonances. FT NMR data systems, on the other hand, allow the user to plot an integral trace superimposed on the spectrum. Since most NMR spectral baselines are not perfect, the user must adjust the trace (generally with interactive knobs) to insure that the integral is constant in regions without signals. The integral trace is usually generated by determining

the running sum of all previous points. It is up to the user to measure the trace by hand to acquire the desired integrals. The user can introduce his bias at two points in the integral (baseline) determination - during the integral alignment phase and during the actual measurement. In particular, if proper procedures are not followed for high dynamic range spectra, very incorrect results can be obtained.

Clearly it is advantageous to remove the user from the integration mechanism altogether. However, it is not trivial to program a computer to automate this procedure. Numerical integration methods such as summing, trapezoidal rule and Simpson's rule are straightforward. Unfortunately, proper identification and correction of the baseline prior to integration is critical to the correct operation of all these techniques. In addition, the choice of integration limits can greatly affect the correctness of the results.

A number of mechanisms exist for the removal of distorted baselines. For example, the convolution difference method (16) removes broad features from a spectrum by subtraction after applying an appropriate weighting function in the data's Fourier co-domain. Successful baseline correction, however, is dependent on the proper choice of the ratio of narrow-to-broad component intensities. In practice, the convolution difference procedure is an iterative one in which the user performs the optimization.

A technique which we have found to be superior to all others can be performed automatically or interactively. The first step of the algorithm identifies baseline points by calculating the standard deviation for all points less than the previous estimate of the standard deviation. An n^{th} order polynomial ($n = 0$ to 9) is then fit to all the points identified as baseline. This polynomial function is subtracted from the data and the whole process is repeated until the coefficients of the polynomial approach zero.

The algorithm has provisions for user intervention if necessary. For example, the user can choose the order of the polynomial. The user can also delimit up to 20 regions within the data set which will be independently corrected. In another mode, regions which

contain many peaks and thus should not contribute to the calculation of the polynomial can be identified. In this case, the correction applied to these regions is determined only by baseline characteristics outside the selected regions.

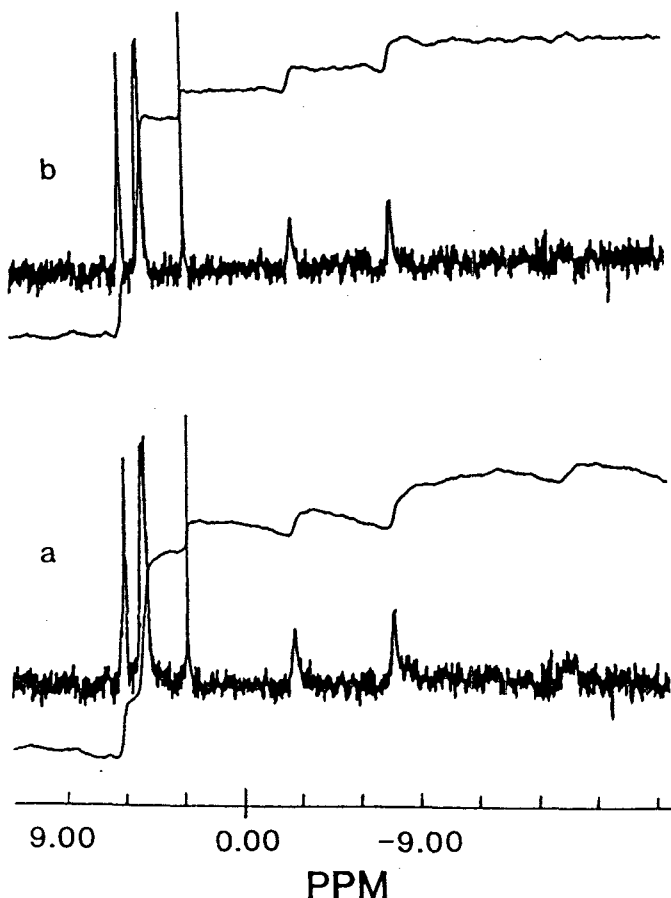


Figure 2. ^{31}P spectrum of human erythrocytes in Tris-ringer's buffer (a) before baseline flattening and (b) after a 4th order, 4 block baseline flattening.

This baseline flattening algorithm works well under most conditions. Figure 2 shows a low signal-to-noise ratio spectrum.

Simpson's rule integration is a powerful method for integrating well separated peaks. Peaks or interest often overlap, however, and alternative integration methods then become necessary.

IV. CURVE FITTING

The form of NMR spectral resonances can often be accurately described by one of several mathematical equations. The mathematical description for an entire spectrum is simply the sum of all the appropriate equations. For example, high resolution spectra of liquid samples (assuming no field homogeneity distortion) can be described as a sum of several Lorentzians, one for each resonance. Since each Lorentzian peak is defined by three parameters (linewidth, intensity and position), an entire spectrum of N peaks can be defined with $3N$ parameters. Other NMR spectral lineshapes exist which may require more than 3 parameters. Thus, the total number of parameters needed to completely describe a spectrum depends not only on the number of peaks but also on the assumed functional form.

In a general sense, the whole purpose of spectral data analysis is to learn the number of spectral peaks and calculate all the parameters for all the peaks. In the case of well resolved spectra, the numerical techniques previously described are perfectly adequate for spectral parameterization. These techniques make no assumption of spectral form and thus work well under most conditions. When these techniques are applied to partially resolved spectra, however, accurate determination of individual peak locations, linewidths, intensities and integrals becomes difficult, if not impossible. By assuming a spectral lineshape, non-linear regression analysis techniques can be used to parameterize a data set. We have developed and are using in our laboratory a non-linear least squares technique based on Brown's modification of the Levenberg-Marquardt algorithm to analyze spectral data.

Non-linear least square techniques can be complex and much work has been done in the development of these algorithms (17-19). If we assume that the i th data point of a spectrum is $\mathbf{X}_i = \mathbf{R}_i + \mathbf{e}_i$ where $\mathbf{R}_i$ is the true value for point i and $\mathbf{e}_i$ is a random error with a Gaussian distribution, then a function $f(\mathbf{A}, \mathbf{B}, \mathbf{C}, \dots)$ exists such that the error function

$$E = \sum_{i=1}^N \left[f(A, B, C, \dots) - X_i \right]^2$$

is minimized. Function f is simply the mathematical form of the spectral lines (Lorentzian, Gaussian, Voigt, their combinations, etc.). The independent variables $A, B, C, \dots$ represent the spectral quantities associated with the lineshapes of interest. At the global minimum of the error function, these variables provide the best approximation to the experimental data. The goal of a non-linear optimization algorithm is to efficiently find the global minimum of the error function while avoiding all other local minima.

The global minimum of the error function is a point in multi-dimensional space (where $A, B, C, \dots$ are the dimensions). Because the parameters are continuous, an exhaustive search is fundamentally impossible. Even if an exhaustive search could be performed it would be unacceptable in that calculations could take years on the fastest mainframe computers. Useful algorithms require that the error function be evaluated at only a relatively small number of points within the multidimensional space. From an examination of the local region surrounding a current point, an estimate is made for the optional direction and distance to travel to the next parameter point to be examined. The error function is reevaluated and the entire process is repeated until terminating criteria are satisfied. It is prudent to constrain the fit whenever possible so that the calculations are performed within a bounded region. thus, unreasonable values for some variables (for example, negative linewidths) can be prevented.

Determining which points to evaluate in multidimensional error space is the most difficult aspect of non-linear optimization. Good initial estimates of parameters are vital if the convergence is to be on the global minimum. Fortunately, the quantification algorithms described earlier usually provide reasonable initial estimates without user intervention. Many strategies for the location of maxima and minima of multi-dimensional functions have been shown

to be successful (17-20) although no single algorithm is always optimal. The Taylor series method extrapolates to the nearest minimum using a Taylor series expansion on points within a small region of the error function. The Newtonian method is a 1 dimensional Taylor expansion applied one axis at a time. A more efficient Taylor expansion can be performed in all dimensions using a matrix of second partial derivatives. The gradient method, on the other hand, calculates the multi-dimensional gradient and extrapolates to the nearest minimum. Both methods reevaluate the error function at the extrapolated point and iterate until convergence at the minimum is obtained.

When convergence occurs, the Taylor series and gradient methods will usually converge on the same region, but follow very different paths. The Levenberg-Marquart method combines the Taylor series and gradient methods to minimize the disadvantages of each. During optimization, this method selects new points through a suitable combination of the Taylor series and gradient method. The extent of combination is determined by the "Marquardt parameter" which is recalculated for each iteration.

Several terminating criteria can be used to stop the calculation. These include:

1. A preset number of iterations have been executed.
2. The proportional difference of successive error function evaluations falls below a preset value.
3. The proportional difference in successive approximations of all the parameters becomes less than some preset value.
4. The gradient defined by successive points in the multi-dimensional space becomes less than some preset value. (Requires normalized parameters).

We have found that criteria 3 has the best performance when the approximations are close to the global minimum. If criteria 1 is met (we use 100 iterations as the limit), the user is given the opportunity to continue the calculation.

Figure 3 shows a spectrum with overlapping resonances which cannot be quantified by ordinary numerical methods. Curve fitting was employed to resolve the data.

Integration of the Lorentzian equation is straightforward using integral calculus

techniques. Analytical integration of other lineshapes, however, can be non-trivial. We use standard integration algorithms to numerically integrate these functions.

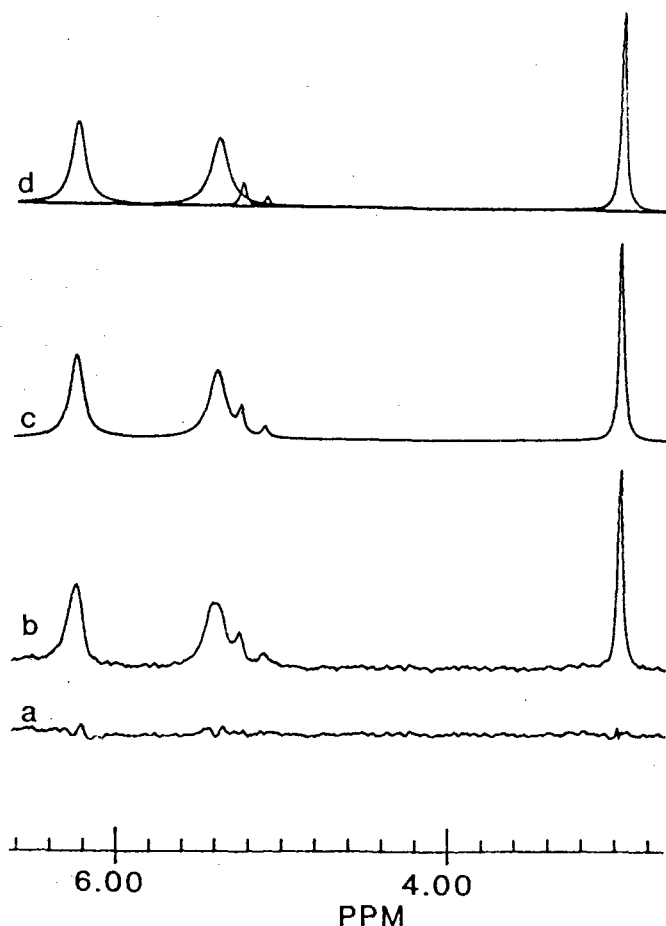


Figure 3. Downfield region of a ^{31}P spectrum of human erythrocytes after baseline flattening: (a) difference between the calculated and experimental spectra; (b) experimental spectrum; (c) calculated spectrum; (d) the individual components.

Even when the fit is very good, care should be taken when interpreting the results. Fitting more functions to the data than reasonably exist can lead to incorrect results despite good optimization and convergence. For example, a broad Gaussian peak can be approximated by two smaller overlapping Lorentzian peaks. This sort of over parameterization is one of the

most serious problems in automating a curve fitting processing sequence. The number of peaks and lineshape of each peak must be correctly determined to insure a meaningful fit.

V. CONCLUSION

Large software systems such as the one developed in our laboratory are the product of many man-years of work. Furthermore, any large software system requires maintenance, particularly if new capabilities and features are being continually added. Clearly, in-house development of large software systems is not in the best interest of most chemical laboratories. As the size and sophistication of large systems grow, fewer laboratories will be able to afford the necessary development effort. If software designed in a few laboratories is to be useful to the scientific community as a whole, then that software must be: (1) machine independent; (2) well documented; (3) rigorously correct; and (4) continually supported.

Careful attention has been paid to the constraints of large software system design in the development of our NMR Spectroscopy data analysis software system. Over 20 academic institutions are using the initial release NMR1 (previously named ORACLE - which is a registered trademark of the ORACLE Corporation). It has been implemented on three families of 32 bit computers and supports 10 different graphics devices. Other software systems under development in our laboratory include a 2 dimensional NMR data processing system and systems for processing data from other spectroscopies and chromatography.

Space does not permit us to list all of the people who have contributed to NMR1. Special acknowledgements, however, belong to the following people: Salar Abosaiedi, Dan Aquilino, John Begemann, Joel Diamond, Judy Harrington, Sener Ilgen, William Kahn, Anil Kumar, Alex Macur, S. Manogaran, Mark Newsham, Chris Paul, Chris Sotak, and Pierre Wellner. We would also like to acknowledge support from the NIH Division of Research Resources (Grant RR 01317) and the National Science Foundation (Grant CHE 81-05109).

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ELUCIDATION OF THE STRUCTURE OF METALLOTHIONEINS BY Cd-113 AND PROTON NMR

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I. INTRODUCTION

Metallothioneins (MTs) are a class of low molecular weight (~6100 dalton), cysteine-rich, heavy metal binding proteins. First isolated over 25 years ago from equine renal cortex (1), MTs have subsequently been found to be ubiquitously distributed in the animal and plant kingdoms and also in some procaryotes (2). Heavy metals have been shown to act as inducers at the transcriptional level *in vivo* (3) and mammalian MTs contain a maximum of 7 g-atoms of metal per mole of protein. MTs are known to bind several heavy metals, including zinc, copper, cadmium and mercury and the metal composition is found to reflect the tissue of origin, the stage of development and the exposure of the organism to heavy metals (4). These properties have lead to the postulate that MTs function in heavy metal detoxification by sequestering toxic metals (Cd and Hg) (5) in addition to playing an essential role in the metabolism and/or storage of essential metals such as Zn and Cu (6,7).

Mammalian MTs contain 61 amino acids, 20 of which are cysteines while another 18 are serines and lysines. All 20 cysteines are known to participate in metal ligation via mercaptide linkages and there is a total conservation of their positions in the amino acid sequences of all the mammalian MTs that have been sequenced (8). This suggests that specific metal-thiolate interactions are structurally important and have been conserved throughout evolution to preserve the functional viability of the protein. It is also perhaps noteworthy that while

MTs from lower organisms (i.e. *Scylla serrata* and *Neurospora crassa*) possess shorter amino acid chains with a smaller number of cysteines, they appear to utilize similar metal-thiolate interactions.

Additional structural characterization of this protein has been hampered for reasons related to the properties of MTs. There are no good chromophores for optical spectroscopy due to the absence of aromatic residues and histidine (9). The metal-thiolate charge transfer bands in UV and CD spectra (10,11) are indicative of metal-sulfur ligation, however, because these bands overlap severely, assertions of tetrahedral coordination, based on these data (11) must be viewed with caution. Finally, the d¹⁰ metal ions commonly found in MTs, Cu⁺, Zn²⁺ and Cd²⁺, are all ESR silent.

The application of NMR to the study of MTs has largely corrected this paucity of structural information. ¹¹³Cd NMR studies on isotopically enriched ¹¹³Cd-MTs have provided direct information on the structure of the cadmium binding sites and their spacial relationship (12), and 500 MHz ¹H NMR studies have extended our knowledge of the tertiary structure of this protein (13).

This article, which is intended to abstract our presentation at the 8th ISMAR meeting, will highlight the structural information on metallothioneins which we have obtained from ¹¹³Cd and ¹H NMR studies.

II. CADMIUM-113 NMR STUDIES

The suitability of Cd-113 NMR to the study of the solution structure and

dynamics of biological metal coordination sites has recently been reviewed (12). While the large Cd-113 chemical shift range (~ 850 ppm) observed for $^{113}\text{Cd}^{2+}$ -substituted metalloproteins reflects its sensitivity to the nature, number and coordination geometry of the ligands, deleterious effects from chemical exchange averaging may complicate spectral interpretations. That this latter phenomenon is not operative in the solution ^{113}Cd NMR studies of MT is indicated by the correspondence of the chemical shift in the solid (Fig. 1A & B) to that observed in solution (Fig. 1C). However, the large CSA, molecular motions on a timescale of $\leq 10^{-5}$ s, and

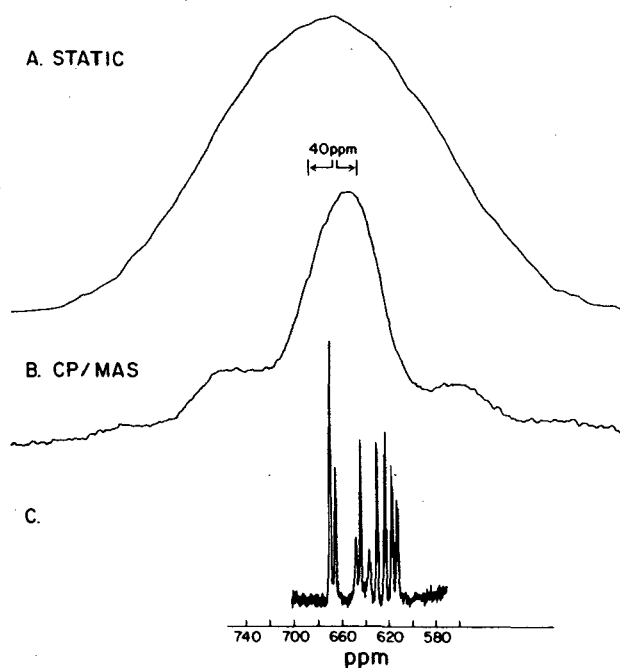


Figure 1. Comparison of the solution and solid state chemical shifts of the 44.4 MHz ^{113}Cd NMR spectra of rabbit liver ^{113}Cd -MT-1. (A) High power ^1H -decoupled CP spectrum, static. (B) High power ^1H -decoupled CP-MAS spectrum, spinning at $\sim 4\text{kHz}$. The ^1H pulse length was $7\mu\text{sec}$, the contact time 4.5 msec and the repetition time 2.5 sec. (C) The ^1H -decoupled solution spectrum at pH 8.6 ($\sim 8\text{mM}$) was accumulated using a pulse angle of 65° and a recycle time of 1.3 sec.

the multiple Cd^{2+} sites in MT precludes a further detailed structural analysis based on the solid state data. This was accomplished from the ^{113}Cd NMR spectral data in solution (Fig. 1C) where the resolution is such as to permit the observation of separate resonances for each of the metal binding sites in MT.

The proton-decoupled ^{113}Cd NMR spectra of aqueous solutions of ^{113}Cd -labeled MTs, isolated from rabbit, human, and calf livers, and from *Scylla serrata* hepatopancreas, are shown in Figure 2B-E. The chemical shifts of all the ^{113}Cd resonances (between 600-670 ppm) are consistent with tetrahedral coordination to cysteinyl sulfurs (12). Furthermore, the presence of ^{113}Cd - ^{113}Cd scalar coupling, which gives rise to the fine structure of each of the Cd resonances, provided the first definitive evidence that the metals were clustered together rather than bound as isolated mercaptide complexes. The magnitude of the observed spin couplings (19-50 Hz) is suggestive of a two bond interaction, indicating that adjacent metals are linked by bridging thiolate ligands (12).

A detailed analysis of the data from ^{113}Cd - ^{113}Cd homonuclear decoupling experiments indicated that the metals are located in two separate polynuclear clusters (12). In mammalian MTs, the 7 g-atoms of metal are located in a 3- and a 4-metal cluster. The 3-metal cluster corresponds to the cadmium resonances labeled 2,3 and 4, while the 4-metal cluster corresponds to the remaining resonances labeled 1,5,6 and 7 (Figure 2). A detailed discussion of these assignments and the origin of the duplication of the resonances from some of the sites has been presented elsewhere (13). In the invertebrate (*Scylla serrata*) the 6 g-atoms of metal are located in two 3-metal clusters.

The proposed cluster structures shown in Figure 2A are consistent with the ^{113}Cd NMR data and the participation of all 20 cysteines in mammalian MTs (18 Cys in crab MT) in metal

A. 3-METAL CLUSTER 4-METAL CLUSTER

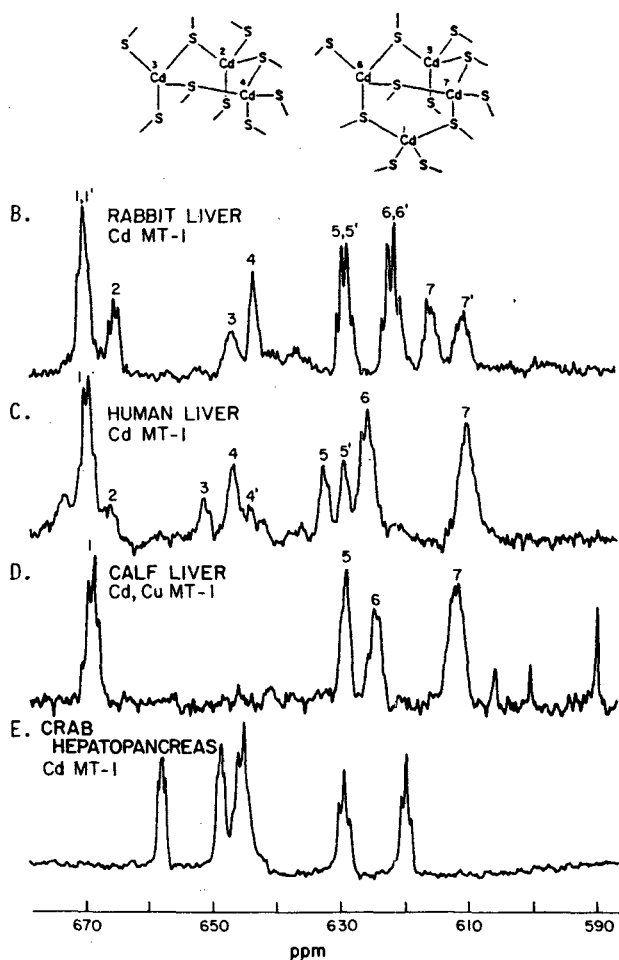


Figure 2. (A) The proposed structures of the 3-metal and 4-metal clusters of mammalian metallothioneins. (B-E) A comparison of proton-decoupled ^{113}Cd NMR spectra at 44.4 MHz of ^{113}Cd reconstituted mammalian metallothioneins and a ^{113}Cd induced invertebrate MT.

ligation. The 3-metal cluster forms a cyclohexane-like six-membered ring requiring 9 cysteine thiolate ligands, $\text{Cd}_3(\text{Cys})_9$; while the 4-metal cluster forms a bicyclo[3:1:3] structure requiring 11 cysteine thiolate ligands, $\text{Cd}_4(\text{Cys})_{11}$. These same ^{113}Cd NMR spectra have also provided considerable insight into the differential metal binding affini-

ties of the two clusters in mammalian MTs. For example, the lack of resonances from the 3-metal cluster in the spectrum of calf liver $^{113}\text{Cd}, \text{Cu-MT-I}$ (Fig. 2D) reflects the preference of Cu^+ for the 3-metal cluster. Further studies indicated that the 3-metal cluster preferentially binds $\text{Cu}^+ > \text{Zn}^{2+} > \text{Cd}^{2+}$, while the reverse order of affinities applies in the 4-metal cluster.

The disposition of the two metal clusters in two distinct structural domains in MTs was provided unequivocally by the ^{113}Cd NMR spectrum of a proteolytically cleaved fragment of rat liver MT-1. The 32-residue fragment had an amino acid composition which corresponded to residues 30-61 of the MT, contained 11 cysteines, bound 4 Cd^{2+} ions and displayed a ^{113}Cd NMR spectrum which corresponded to the resonances assigned to the 4-metal cluster of the intact protein (14). This clearly established the independence of the metal clusters in the protein. The carboxyl terminal portion forms the domain of the 4-metal cluster while the amino terminal portion forms the domain of the 3-metal cluster domain.

III. PROTON NMR STUDIES

Proton NMR studies of MTs from several sources (calf, human, rat, rabbit, crab and *Neurospora crassa*) have provided additional information on the disposition of the metal clusters in the tertiary structure of the protein (13, 15).

A representative one-dimensional 500 MHz ^1H NMR spectrum of crab MT-1 is shown in the top portion of Figure 3. Although several resonances could be assigned by one-dimensional techniques, overlapping resonances from the large number of repetitive residues have necessitated the application of two dimensional techniques [2D J-resolved, spin-echo correlated spectroscopy and 2D correlated spectroscopy (COSY)] to definitively assign a large number of ^1H resonances (15). As an example, a

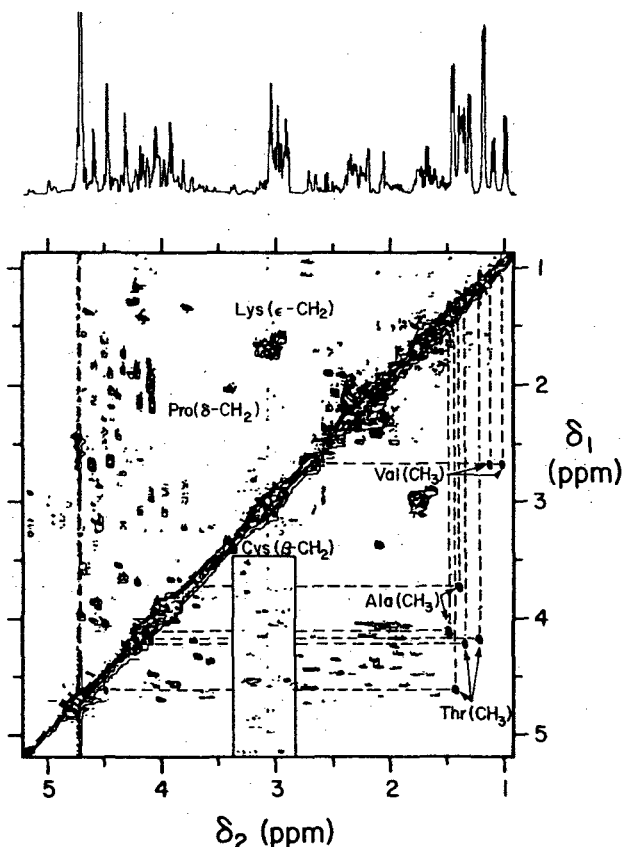


Figure 3. A contour plot of the 500 MHz 2D ^1H shift-correlated (COSY) data set of crab MT-1 (10mM) in $^2\text{H}_2\text{O}$ at 30°C .

contour plot of a 2D COSY data set on crab MT-1 is shown in the lower portion of Figure 3. The cross peaks in the contour plot correspond to the frequencies of the protons that are scalar coupled. The scalar connectivities between the methyl protons and the $\alpha\text{-CH(Ala)}$ and $\beta\text{-CH(Val,Thr)}$ protons are illustrated by a dashed line in the figure connecting the cross peaks to the two coupled proton frequencies located on the diagonal. A particularly striking illustration of the resolution obtained by spreading the data into two dimensions is the complete separation of the Cys($\beta\text{-CH}_2$) protons from the Lys($\epsilon\text{-CH}_2$) protons.

Additional three-dimensional structural information has been obtained from ^1H - ^1H nuclear Overhauser enhancement (NOE) difference spectra. Analysis of these spectra has enabled the spatial proximity of several residues to be established (13,15).

IV. CONCLUSION

Cadmium-113 and proton NMR have been key in the structural characterization of metallothioneins. Based on an analysis of these data, it has been possible to construct a model of the three-dimensional structure of the mammalian protein which is consistent with all the physicochemical data presently available. This model will almost certainly require a certain amount of refinement when the X-ray structure, currently in progress in the laboratory of C.D. Stout, becomes available. Nevertheless, we are confident that the structural refinement will be relatively modest and in no way negate our continued use of the solution derived model to elucidate the biological function(s) of MTs.

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APPLICATION OF NOE AND SELECTIVE T_1 FOR THE INVESTIGATION OF BINDING OF LIGANDS

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I. INTRODUCTION

One of the drawbacks of NMR is its low sensitivity relative to other spectroscopic methods. However, taking advantage of the averaging property of NMR of exchanging systems, one may obtain information concerning minute amounts of bound ligands from the signals of the excess free ligands. This was successfully used in systems of paramagnetically labelled enzymes (1). The present work deals with diamagnetic systems.

II. RESULTS AND DISCUSSION

Selective T_1 was shown to be a sensitive method for detecting binding of ligands to macromolecules (2). The dependence of selective T_1 on the concentration of the ligand which follows an equation analogous to that of T_1 and non selective T_1 (see e.g. ref.3) is a very convenient way to measure binding constants. In Fig.1, the determination of the binding constant of the activator carbobenzoxyglycine (Z-Gly) to Zn(II) carboxypeptidase A (CPA) is described.

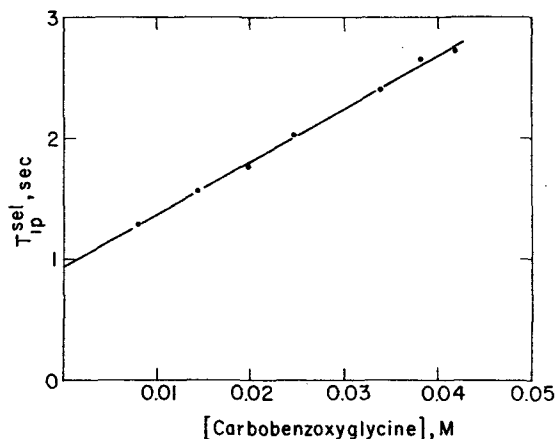


Fig. 1

The result $K_d=21.2$ mM at 28°C agrees with the dissociation constant found for the activation of the hydrolysis of dipeptides (3), inhibition of hydrolysis of esters (4) and tripeptides (5), and is similar also to K_d for Mn(II) CPA (3). The addition of substrates abolishes the relaxation effects of CPA on Z-Gly indicating competition for the same site, thus supporting the hypothesis of activation through productive and non productive binding sites (6).

Transferred NOE. Another sensitive method for detecting binding of ligands is the measurement of NOE which is transferred from bound to free ligand by chemical exchange (7-9). The expression for the overall NOE ($\eta_I(S)$) in the presence of exchange (7) may be written in the following simplified form:

$$\eta_I(S) = \frac{\langle I_z \rangle - I_o}{I_o} = \eta^b \frac{bT_{1f} + b f \tau_b}{f T_{1b} + f \tau_b + b T_{1f}} \quad (1)$$

where f and b are the fractions of free and bound ligand and τ_{1f} and T_{1b} are their selective T_1 . We can see that in the case $bT_{1f} \gg f\tau_b$, fT_{1b} one obtains $\eta_I(S) = \eta^b$. For ligands bound to macromolecules where $\omega\tau_c \gg 1$, η^b may reach the value of -1 . Therefore this is a very sensitive method for detecting minute amounts of binding to macromolecules or receptors.

In Fig. 2 the NOE of phenyl protons of Z-Gly bound to CPA was measured as a function of the bound fraction. The points are experimental results while the theoretical plot was not based on fitted parameters but was calculated using Eq.(1) with b , T_{1f} and T_{1b} independently measured as described in the first section.

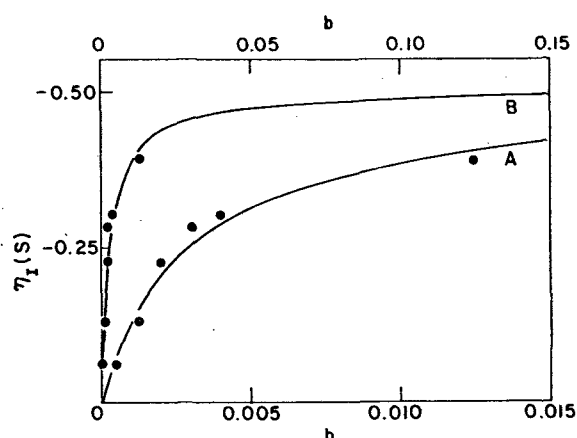


Fig. 2

The assignment of the functional groups on the receptor which interact with the ligand is hindered by spin diffusion. This can be demonstrated by the fact that a plot of the transferred NOE, $\eta_I(S)$, as a function of the irradiation frequency, is very similar to the spectrum of the enzyme itself. In Fig. 3, the "NOE spectrum" is given for the phenyl protons of two activators: cinnamic acid (71 mM) in the presence of CPA (0.33 mM) (A) and Z-Gly (57 mM) in the presence of CPA (0.3 mM) (B). The NMR spectrum of the enzyme itself (1mM) is given in the upper plot of the Figure. Note that in the "NOE spectrum" the region usually obscured by the water signal is also observable.

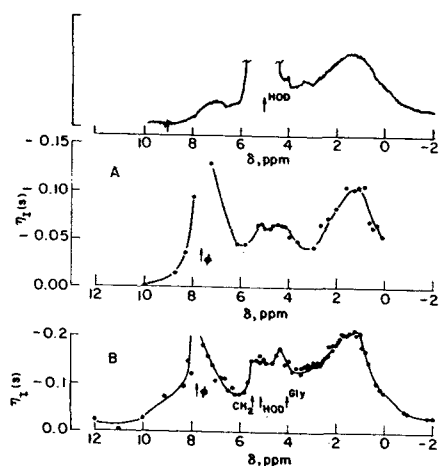


Fig. 3

Transient NOE. To avoid the effect of spin diffusion, the transient NOE methods were suggested by several authors (10-13). The equations of the time dependence of the transient NOE were developed for the case of a single species. Here we deal with exchanging ligands. There are two possible methods for measuring transient NOE (see Fig. 4).

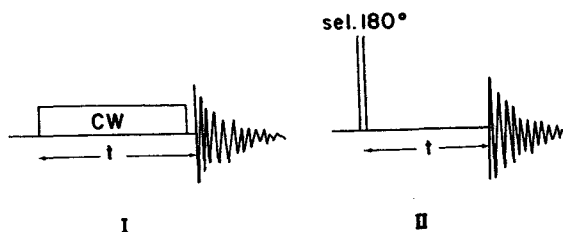


Fig. 4

I. Progressive saturation. In this method $\langle S_z \rangle$ does not reach a steady state level:

$$\langle S_z \rangle - S_0 = S_0 (e^{-Ct} - 1)$$

where C is the saturation rate of the irradiated spin. By introducing this expression into the general rate equations:

$$\frac{d\langle I_z \rangle^f}{dt} = -\rho^f (\langle I_z \rangle^f - I_0^f) - \frac{\langle I_z \rangle^f}{\tau_f} + \frac{\langle I_z \rangle^b}{\tau_b}$$

$$\frac{d\langle I_z \rangle^b}{dt} = -\rho^b (\langle I_z \rangle^b - I_0^b) \quad (2)$$

$$-\rho (\langle S_z \rangle - S_0) - \frac{\langle I_z \rangle^b}{\tau_b} + \frac{\langle I_z \rangle^f}{\tau_f}$$

where ρ^f and ρ^b are the relaxation rates of the free and bound ligand, respectively and τ_f , τ_b are their exchange lifetimes, we obtain for the case of fast exchange and $b \ll 1$:

$$\eta_T = \eta_I(S) \left[1 + \frac{1}{(C-\alpha)} (\alpha e^{-Ct} - C e^{-\alpha t}) \right]$$

where: $\alpha = \rho^f + b\rho^b$, and $\eta_I(S)$

is given by Eq.(1). Calculated values of observed NOE for several values of b are given in Fig. 5.

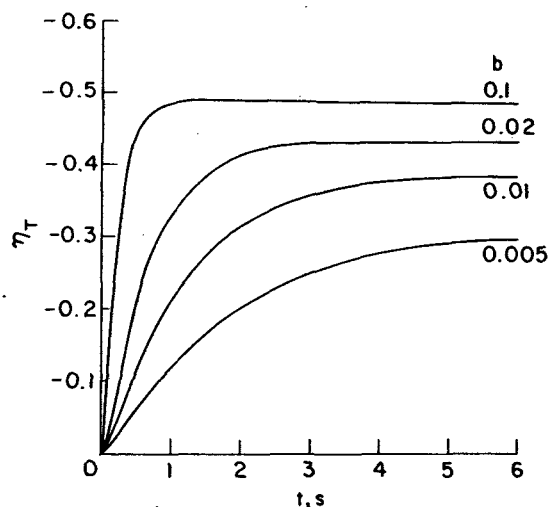


Fig. 5

II. Selective inversion. In this case the time dependence of the z component of the irradiated spins is given by the equation $\langle S_z \rangle - S_0 = -2S_0 e^{-Ct}$. Again, by introducing this expression into Eqs.(2) we obtain for the case of fast exchange:

$$\eta_p = 2\eta_b b \rho_b (e^{-\alpha t} - e^{-Ct}) / (C - \alpha)$$

In this case we get a maximum in the time dependence function, at a point $t_{(max)} = \ln(C/\alpha) / (C - \alpha)$, as can be seen in Fig. 6.

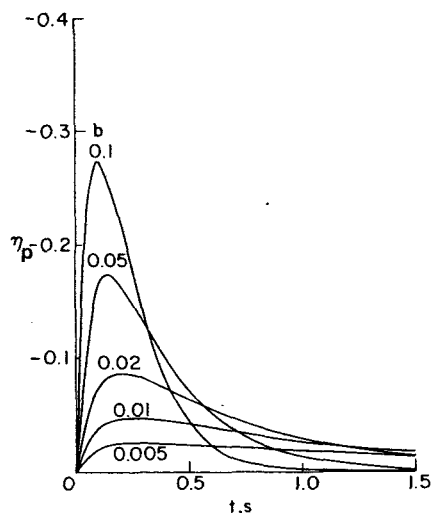


Fig. 6

By comparing the two methods for two values of b (Fig.7), it is seen that the second method is the more sensitive one for the NOE obtained within short time durations. However, the requirement of a selective inversion of magnetization is sometimes difficult to achieve in macromolecular systems, since the pulse has to be short enough to avoid relaxation during the pulse and long enough to be selective.

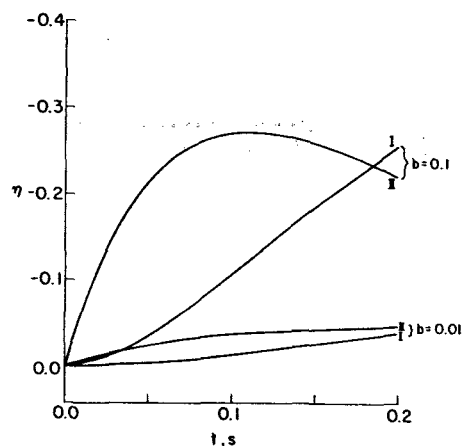


Fig. 7

In conclusion we see that selective T_1 and the transferred NOE are sensitive methods for the detection of binding of ligands to macromolecules. While selective T_1 is a convenient method for the determination of binding constants, the transferred NOE may give information concerning the mode of binding. However, in order to avoid effects of spin diffusion the transient methods of truncated or selective inversion should be used and may be analyzed according to the explicit expressions given above.

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PARAMAGNETIC RESONANCE AS A PROBE FOR CRITICAL PHENOMENA

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I. INTRODUCTION

Critical phenomena have been greatly in evidence in recent years, especially last year in view of the Nobel Prize being awarded to K. G. Wilson for his Renormalization-Group (R.G.) theory (1). With this theory, one can quantitatively calculate the response of cooperative systems undergoing phase transitions, be they of the continuous, second-order, or discontinuous, first-order, variety. Especially for the former, experimentalists had observed appreciable deviations from so-called mean-field theory. The properties observed in early experiments were, for example, specific heat c_p , compressibility κ , and the so-called order parameter η . The latter quantity measures the degree of order below a transition T_c in a ferromagnetic system, the magnetization m , in an antiferromagnet, the staggered magnetization m_s , etc. For the above-mentioned quantities, $c_p(T)$, $\kappa(T)$ or $\eta(T)$ power-law dependences were observed as

$$\eta = \eta_0 \left[\frac{(T_c - T)}{T_c} \right]^\beta, \quad (1)$$

in the range $t = (T_c - T)/T_c$ of 10^{-2} to 10^{-5} . In three dimensions, $\beta \approx 0.32$ as compared to the mean-field value $\beta = 1/2$. These power laws result from the divergent correlation length $\xi = \xi_0 t^{-\nu}$ towards T_c , where ξ measures the correlation between like spins, for example. They posed tremendous nonlinear problems which Wilson, Kadanoff, Fisher and others showed how to treat (1).

It is obvious that in systems where one of the above-mentioned properties has local character, which magnetic resonance measures, it can contribute to the field of critical phenomena, since

the resonance frequencies and magnetic fields are easily determined to the accuracies of 10^{-5} required, but this is also necessary for the relative temperature. Thus, if T_c is at 100 K, an accuracy of 1 millikelvin, or if T_c is at 800 K, 8 millikelvin stability is required. In the case of paramagnetic resonance, cavity systems were developed earlier in our laboratory applicable to T_c 's below room temperature, and most recently also above T_c going up to 1000 K (2), i.e. in a range where no other experiments of *any* kind have ever been performed.

In the present paper, examples of such investigations in the field of structural phase transitions will be given (3). A phase transition in a solid is called structural when a regular lattice is distorted by a small displacement or ordering in lattice positions of single atoms or molecules. In section II, early determinations of β will be summarized. These were of importance because previously, due to imprecision of the β measured by techniques other than magnetic resonance, $\beta = 1/2$ had been inferred. For the displacive variety of SPT's, an optical or acoustic mode ω_s vanishes if $\beta = 1/2$. It could subsequently be shown quantitatively by EPR that, if a system is critical and $\beta \approx 1/3$, a crossing over of displacive to order-disorder behavior will occur upon approaching T_c in quantitative agreement with nonvanishing ω_s . This we shall address in section III. The critical exponents are *universal*. They depend only on the lattice dimensionality d , the symmetry of the system and the order-parameter components n . One can break the symmetry by external fields; magnetic ones in case of magnetic order or electric fields in ferroelectrics. In the case of SPT's, uniaxial stresses can be applied. Several

second or first-order phase boundaries meet at such a multicritical point. EPR in SPT demonstrated such bi- and tetra-critical points as predicted by R.G. (4) and was first to show the existence of so-called Lifshitz (5) and Potts transitions (6) not observed before in other cooperative systems. Selected examples are discussed in section III.

II. CRITICAL BEHAVIOR IN SrTiO_3 AND LaAlO_3

Both crystals listed in the heading are cubic in their high-temperature phase, and crystallize in the perovskite lattice ABO_3 . In such a lattice, BO_6 octahedra are linked at the corners. The A ion is dodecahedrally coordinated. In each of the crystals upon cooling, one SPT occurs where TiO_6 or AlO_6 octahedra start to rotate, respectively. Adjacent octahedra rotate by $+\varphi(T)$ or $-\varphi(T)$ due to their common oxygen corner linkage. $\varphi(T)$ is the order parameter of the transition. It had been demonstrated previously by EPR that in SrTiO_3 this rotation occurs around $\langle 100 \rangle$, and in LaAlO_3 around $\langle 111 \rangle$ pseudocubic axes, i.e. SrTiO_3 becomes tetragonal with space group I4/mcm , and LaAlO_3 trigonal with group $\text{R}\bar{3}\text{c}$. The transition temperatures are 105 K and 796 K, respectively.

The temperature dependence of the octahedral rotation angle $\varphi(T)$ was monitored by EPR of Fe^{3+} replacing Al^{3+} and Ti^{4+} ions in LaAlO_3 and SrTiO_3 . The spin Hamiltonians are axial in both crystals below T_c with a cubic component

$$\mathcal{H} = g\beta\vec{S}\vec{H} + D\left[S_z^2 - \frac{S(S+1)}{3}\right] + a\left[S_x^4 + S_y^4 + S_z^4 - \text{const.}\right]. \quad (2)$$

For symmetry reasons, $D = c\varphi^2(T)$, which was monitored in LaAlO_3 with c known and $\zeta \parallel \langle 111 \rangle$. In eq. (2), the x, y and z axes in the Hamiltonian point towards the corners of the octahedra and rotate proportional to $\pm\varphi(T)$. The resulting magnetic resonance splitting ΔH , proportional to $2\varphi(T)$, was measured in SrTiO_3 . The two experiments thus exemplify that

one can use magnetic resonance to study properties proportional to φ or φ^2 .

In fig. 1, the measured order-parameter behavior is shown by plotting $\varphi(T)^2$ versus reduced temperature t for both crystals considered. This plot shows clearly a deviation of $\varphi(T)^2$ from mean-field behavior which, with $\beta = 1/2$, would yield a straight line, whereas a clear bending down is observed upon approaching T_c from below. In both cases, $\beta = 0.33 \pm 0.02$ was obtained. The crossing over from the straight mean-field line to critical behavior is closely the same in both LaAlO_3 and SrTiO_3 in reduced units despite the T_c 's differing by a factor eight.

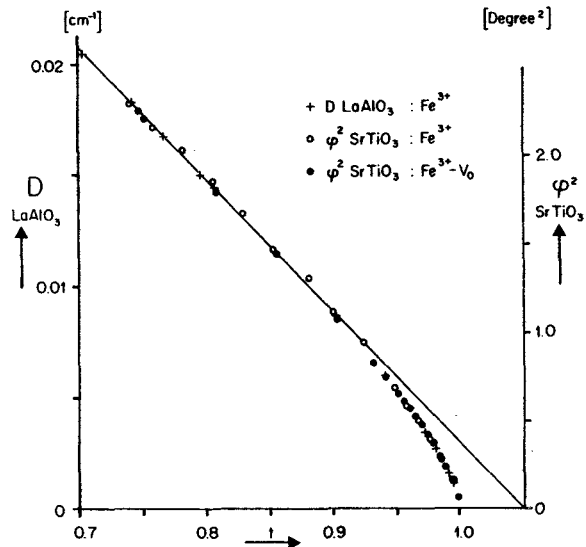


Fig. 1

φ^2 of SrTiO_3 and D of LaAlO_3 versus t between 0.7 and 1, showing the changeover from Landau to critical behavior. After K.A. Müller and W. Berlinger, Phys. Rev. Lett. 26, 13, 1971. © 1971 APS

III. DISPLACIVE TO ORDER-DISORDER CROSSOVER IN SrTiO_3

In dynamic lattice theory, it is in general assumed the atoms or molecular units move in a harmonic potential $V(r) = \alpha r^2 + \text{h.o.}$ In this theory, the probability distribution around the equilibrium position is a Gaussian $P(r) = P_0 \exp -(\alpha r)^2$. In displacive transitions, a soft mode freezes out at T_c , $\omega_s \rightarrow 0$.

However, for a transition to occur an anharmonicity in $V(r)$ has to be present. $V(r)$ is flatter than a parabola at least. Upon approaching T_c from above or below, computer simulations indicated this anharmonicity increases due to the correlated clusters of octahedral rotations. The soft mode ω_s did not freeze out at T_c but remained finite. Inelastic neutron and Raman scattering experiments gave $\omega_s(T_c) = 0.14$ THz. Because $\omega_s(T) = 0.69\phi(T)$ below T_c , one could estimate $\phi_{sr} = \pm 0.20^\circ$ where ϕ_{sr} is the nonvanishing short-range order parameter at T_c . The probability distribution would then be a superposition of two Gaussians $P(\phi)$ separated by $\pm 0.20^\circ$ of the octahedral units. X-ray and elastic neutron scattering had yielded 2.1° for the harmonic amplitude width of the Gaussian distribution. These scattering experiments were unable to resolve ϕ_{sr} of 0.20° because their intensities are measured in wave-vector space and need Fourier transformation, with much too low a precision due to background problems. EPR was able to resolve this problem because it acts as a low pass filter: The high-frequency ω_s amplitudes of 2.1° at 0.14 THz are so much faster than the inverse EPR linewidth and are thus motionally averaged out. On the other hand, the correlated clusters are pinned by impurities and move much slower than the inverse EPR linewidth. Thus, the anharmonic probability distribution can be probed by EPR.

The experiments were conducted with the $\text{Fe}^{3+}\text{-V}_0$ center in SrTiO_3 , an Fe^{3+} ion with a next-neighbor oxygen vacancy. Due to its large axality, $D \gg h\nu$, this center is more sensitive to $\phi(T)$ than the non-charge-compensated Fe^{3+} but exhibits the same linear dependence on ϕ as can be seen in fig. 1. In fig. 2, the EPR line shapes recorded at T_c are shown, both in the usual derivative as well as in the integrated form. The latter represents the probability distribution of $P(\phi)$ without the harmonic component. It is seen to be much better fitted by a superposition of two Gaussians separated by $0.44^\circ = 2\phi_{sr} = 2\sigma$ than a single Gaussian.

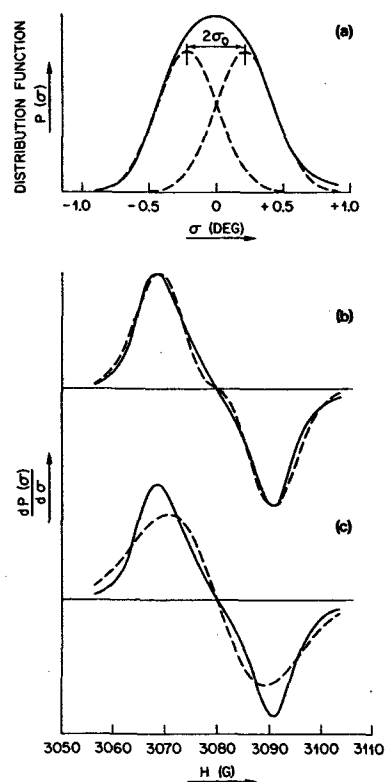


Fig. 2

(a) The experimental distribution function $P(\sigma) = P(\phi)$ at $T = 105.5$ K (solid line) together with two displaced Gaussians with whose superposition (not shown) we model the spectrum. (b) The derivative of the experimental $P(\sigma)$, solid line, and of its double-Gaussian representation defined in (a). (c) The derivative of the experimental $P(\sigma)$ and its single-Gaussian representation. After A.D. Bruce, K.A. Müller and W. Berlinger, Phys. Rev. Lett. 42, 185 (1979). © 1979 APS

This has been regarded as an important success of EPR in recent anharmonic investigations of SPT. The residual linewidth is caused by the strains in the crystal.

IV. MULTICRITICAL BEHAVIOR IN SrTiO_3 , LaAlO_3 AND RbCaF_3

In well-annealed crystals of SrTiO_3 or LaAlO_3 , three $\{100\}$ or four $\{111\}$ -type domains are equally possible. Applying uniaxial stress alters this. Pulling along a particular $[100]$ direction in

SrTiO_3 favors a $\{100\}$ domain above the other two $\{010\}$ or $\{001\}$ because the c/a ratio is larger than one. Pushing along a $[111]$ direction in trigonal LaAlO_3 favors this domain above the other three. T_c as a function of such Σ stress is increased. Mean field predicts a linear shift in T_c , R.G. theory $(T_c(\Sigma) - T_c(0))/T_c(0) \propto \Sigma^\psi$ with the shift exponent $\psi = 1.25$ for the particular boundary. Upon extrapolating EPR $D(T)$ parameters of Cr^{3+} , $S = 3/2$, substitutional in LaAlO_3 for given stresses Σ , to zero, $T_c(\Sigma)$ was determined (4). The resulting phase boundary is shown in fig. 3. It is the first boundary at such a high temperature of 800 K determined. $\psi = 1.31 \pm 0.7$ was measured, in agreement with R.G. predictions. The inset illustrates the phase diagram predicted for pushing and pulling. In the latter case, a second-order phase boundary separating the pseudocubic from the phase with three equivalent $\{111\}$ -type domains occurs. For $\Sigma = 0$, both second-order boundaries meet therefore the name bicritical point. Applying $[100]$ stress, four second-order boundaries separating four different phases meet a so-called tetracritical point. This has also been verified by EPR of Fe^{3+} for $\Sigma > 0$ (4).

The existence of more sophisticated multicritical points was also realized in structural phase transitions, again with EPR: a tricritical Lifshitz point in RbCaF_3 under near $[100]$ stress (5). Tricritical means here that the transition point changes from second to first-order character, and Lifshitz means highly anisotropic near two-dimensional correlations. For the order-parameter exponent, $\beta = 0.18$ was found intermediate between three-dimensional $\beta = 0.32$ and two-dimensional $\beta = 0.13$ (5). The existence of a so-called three-state Potts transition was first shown to occur in $[111]$ -stressed SrTiO_3 (6). The first-order character, i.e. the jump $\delta\phi$ of the order parameter, is strongly renormalized due to fluctuations. The jump is $\delta\phi \propto \phi^{\delta^*}$. The measured exponent is $\delta^* = 0.62 \pm 0.07$ as compared to $\delta^* = 0.56$ of R.G. and $\delta^* = 1$ from mean-field theory, respectively.

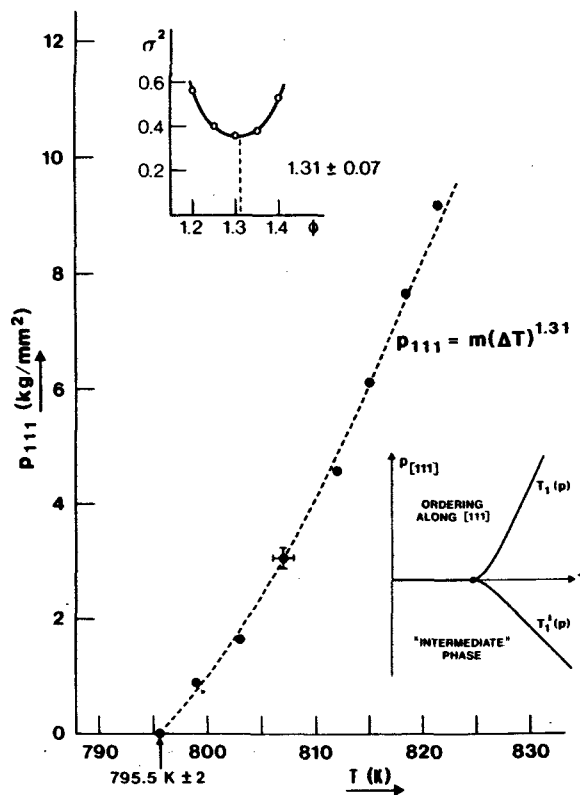


Fig. 3

Bicritical phase boundary T_1 of LaAlO_3 under $[111]$ stress. After ref. (4).

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g TENSOR ANISOTROPY AND ELECTRON-NUCLEUS DIPOLE-DIPOLE INTERACTION IN THE Cu (II) - (L-His)₂ COMPLEX IN SOLUTION

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1. INTRODUCTION

Cu(II) complexes with low molecular weight ligands have been suggested to play relevant roles in the biochemistry of copper. Among them the Cu(II)(L-His)₂ species has been recognized as the most abundant in biological fluids. However the binding features of the two L-His molecules have not been yet defined; histamine-like (one amino nitrogen plus one imidazole nitrogen) and/or glycine-like (one amino nitrogen plus one carboxyl oxygen) binding modes have been alternatively suggested. Different rapidly interchanging species can be present as well.

In this report we have combined NMR relaxation rate measurements and ESR lineshape analysis with the aim of delineating the structural and motional features of the title complex in solution.

II. RESULTS AND DISCUSSION

Nuclear relaxation rates measured in the presence of paramagnetic metal ions are usually accounted for by the Solomon Bloembergen-Morgan (SBM) theory which relates structural and motional parameters with the experimental paramagnetic nuclear relaxation rates T_{1p}^{-1} and T_{2p}^{-1} defined as

$$T_{ip}^{-1} = T_{imetal}^{-1} - T_{iblack}^{-1} \quad (i=1,2)$$

The experimental T_{ip}^{-1} values for the imidazole H₂ proton of L-His are

shown in figure 1 as a function of the Cu(II) concentration; since $T_{2p}^{-1} > T_{1p}^{-1}$ the following simplified equation can be used according to the SBM theory

$$T_{1p}^{-1} = \frac{1}{10} q f (\gamma_H^2 g^2 \beta^2 / r^6) (3 \tau_c / 1 + \omega_H^2 \tau_c^2)$$

where q is the number of coordinated nuclei, f the fraction of bound nuclei and all the other symbols have the usual meaning.

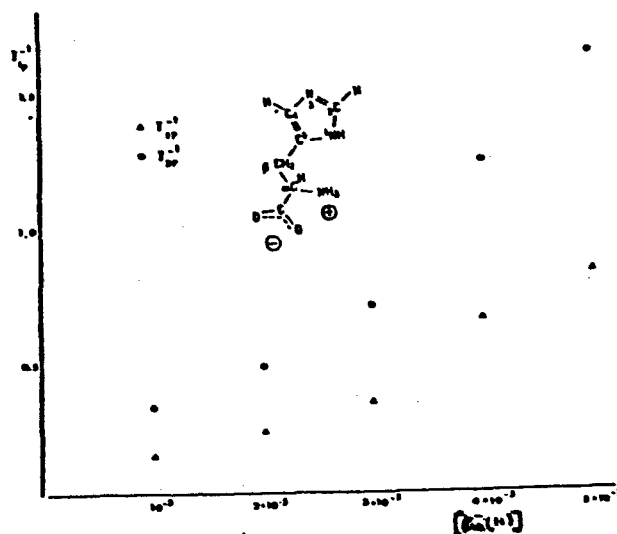


Fig.1 - T_{1p}^{-1} and T_{2p}^{-1} of H₂ of L-His 0.1 M in D₂O vs. the Cu(II) molar concentration; pH=7.0; T=298°K.

With the aim of calculating q for the imidazole moiety in the title complex, r was assumed from X-ray crystallographic data worked out for the Cu(II)(L-His)(D-His) complex¹ (r=3.27 Å)

and τ_c was approximated with that for the water molecules in the same complex ($\tau_c = 5.19 \times 10^{-10}$ s at 298 K) by measuring the $T_{1\rho}^{-1}$ values for the water protons and by assuming the crystallographic copper-water distance. The calculated q for H_2 was 0.05 ± 0.01 which is meaningless since $1 < q < 2$ was expected.

Since using τ_c of water molecules may be thought a rough approximation, computer fitting procedures of the ESR lineshape were utilized. The fit for the spectra at X band ($\omega = 5.97 \times 10^{10}$ rad/s) S band ($\omega = 2.14 \times 10^{10}$ rad/s) and L band ($\omega = 7.54 \times 10^9$ rad/s) is consistent with the following ESR parameters: $g_{iso} = 2.09$; $g_{\parallel} = 2.23$; $g_{\perp} = 2.02$; $A_{iso} = -65$ G; $A_{\parallel} = -179$ G; $A_{\perp} = -8$ G; two equivalent nitrogens with $a_N' = 13.5$ G plus two equivalent nitrogens with $a_N'' = 8.5$ G; residual line-width 4 G; $\tau_c = 8 \times 10^{-11}$ s at 298 K. The number of unknown variables could be suitably reduced in the following way: The values of $g_{\parallel}$ and $A_{\parallel}$ were measured from frozen solution ESR spectra. The distance between the $M_I = -\frac{1}{2}$ and the $M_I = +\frac{1}{2}$ lines gives reasonable estimate of A_{iso} from liquid phase ESR spectra at low frequency. The parameters obtained from the fitting procedure are quite reliable since only one set of values could be found to fit the ESR spectra at all three frequencies.

The correlation time is the reorientational time of the complex modulating the g and A anisotropies and it can be taken as the correlation time responsible for the modulation of the dipole-dipole interaction. It is worth emphasizing that the value of τ_c seems to be quite precise since the fit breaks down for deviations greater than 15%. It has been verified that the ESR lineshape at X band and 345

K is identical with that at S band and 290 K, to make sure that τ_c is a rotational tumbling time.

However even with this correlation time the NMR results are not self consistent since the q value is 0.3 ± 0.1 which is still about one order of magnitude smaller than expected. The simplified equation derived from the SBM theory breaks down for Cu(II) complexes in solution². As a matter of fact the SBM theory assumes an isotropic electron spin g tensor, while the large g tensor anisotropy of the title complex in solution ($\Delta g = 0.21$) gives rise, at high magnetic fields, to an electron g anisotropy Zeeman energy ($|\Delta g| \beta H_0 = 9.15 \times 10^{-17}$ erg) which cannot be averaged out completely by the rotational tumbling ($\hbar \tau_c^{-1} = 1.32 \times 10^{-17}$ erg). The incomplete averaging out of the electron spin anisotropy's energy brings about a decrease of the electron nucleus dipole-dipole interaction, which reflects in very small paramagnetic contributions. Therefore, the SBM theory results in overestimates of the dipolar interaction energy yielding meaningless values for structural and motional parameters.

It may be concluded that the quantitative analysis of nuclear relaxation rates in solution of Cu(II) ions is not a straightforward matter since ambiguities are arising about the evaluation of the dipole-dipole interaction energy. The ESR lineshape analysis is, on the other hand, to be preferred provided computer fitting at different frequencies can be carried out. The experimental results were fit using four nitrogen donor atoms including one pair of equivalent nitrogens with $a_N' = 13.5$ G and one pair of equivalent nitrogens with $a_N'' = 8.5$ G. These parameters gave the best fit between experimental and computer

simulated spectra at three frequencies. Despite the fact that the nitrogen hyperfine coupling is not resolved in the experimental data, the simulated results are consistent with the previously proposed interpretation. Then in the case of the Cu(II)(L-His)_2 complex the structure in which the two L-His ligands are both bound in the histamine-like way appears to be the predominant configuration in solution, although, in principle, minor contributions from other configurations cannot be ruled out, as it has been suggested elsewhere³.

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The Impact of the Symmetry Properties of Classical Reorienting and Tunnelling Methyl Groups on the Spin-lattice Relaxation in Solids

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I. INTRODUCTION

During the last two decades the random reorientations of methyl groups in solids have been the subject of many NMR studies. The purpose of such investigations can be the motional mechanism itself and/or the determination of the magnitude and shape of the hindering barrier governing the reorientations. This contributes to a better knowledge of the conformation of the molecule to which the methyl group is attached. To this end in a large majority of cases the Zeeman spin-lattice relaxation has been measured as a function of temperature. In the high temperature region, where the groups can be regarded as classical rotors, the experiments are usually interpreted with the results of the Bloembergen, Purcell and Pound theory, elaborated for the case of

methyl groups (1,2). At low temperatures the quantum character of the rotors becomes important, which induces new phenomena in the temperature dependence of the relaxation time (3-12).

In practice, discrepancies have been observed between the theoretical and experimental results, such as too small a value for the relaxation constant (13-22), a difference in slope of the curve $\ln T_1^{-1}$ versus T^{-1} on the high and low temperature side of the maximum in the temperature region where tunnelling can be neglected (3,17,19,23,24) and, last but not least, non-exponential relaxation, both for non-tunnelling (15,24-31) and tunnelling (32-34) groups. Especially the last discrepancy was in complete disagreement with the existing relaxation theories, where essentially an exponential relaxation is predicted. In some publications the

results were explained with the Hilt and Hubbard theory (35), where the spin-lattice relaxation is calculated for non-tunnelling, mutually isolated methyl groups. Indeed this theory results in a non-exponential relaxation, but the model used is rather unrealistic, because in most samples the methyl groups are close to each other and to other protons (if present) in the material. Under these circumstances it is well known that spin diffusion plays an important role. This process tends to establish a situation of internal equilibrium for the Zeeman and dipolar system on a time scale fast compared with the spin-lattice relaxation time (ref. (36) chap. 5, ref. (37) chap. 1). Incorporation of the spin diffusion leads to the exponential spin-lattice relaxation obtained in the other theories (1,2,5).

The problem of the above discrepancies has been solved by taking into account the symmetry properties of the methyl groups in the various parts of the hamiltonian necessary for the description of the spin-lattice relaxation. It was then found (38) that also in the presence of spin diffusion, a non-exponential relaxation is obtained.

In this paper a review of this theory is given, emphasizing the manner in which the symmetry should be included. This will be done both for classical reorienting and tunnelling methyl groups. The results will be illustrated with experimental examples.

II. THEORY

A. Introduction

A methyl group consists of three protons located at the corners of an equilateral triangle with side r , see Figure 1. A carbon atom is located somewhat below the center of the triangle. This atom is bonded to another one, often another carbon atom, of the molecule. In Figure 1 β denotes the angle between the symmetry axis of the methyl group and the external magnetic field H_0 . $V(\psi)$ is the potential barrier due to the steric hindrance of the methyl groups. As an example $V(\psi)$ is taken to have three-fold symmetry,

which means that the steric hindrance is invariant for a rotation of 120° of the methyl group.

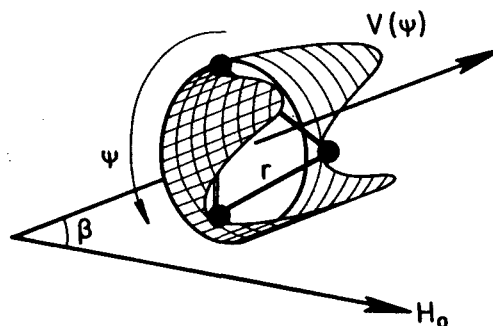


Figure 1. The methyl group in the presence of a three-fold hindering potential $V(\psi)$ and an external magnetic field H_0 .

In the presence of an external magnetic field with a strength H_0 the relevant hamiltonian is given by

$$\hat{H} = \hat{H}_Z + \hat{H}_R + \hat{H}_P + \hat{H}_{RP} + \hat{H}_D, \quad (1)$$

where $\hat{H}_Z$, $\hat{H}_R$ and $\hat{H}_P$ represent the zeroth-order operators of the Zeeman system, the rotor system and the phonon system, respectively. $\hat{H}_{RP}$ and $\hat{H}_D$ are perturbations describing the interactions between the rotor and phonon system and the dipolar interactions between the various protons, respectively.

The spin-lattice relaxation, observed with NMR, is caused by that part $\hat{H}_D(t)$ of $\hat{H}_D$ which is rendered time-dependent by random motions of the whole molecule or part of the molecule. Often in solids containing methyl groups the random reorientations of these groups are the dominant motional mechanism, as we shall assume in this paper. $\hat{H}_D(t)$ causes transition probabilities between the various spin eigenstates following from Eq. (1). These transition probabilities tend to restore, after some perturbation, the population differences between these

eigenstates towards the values corresponding to thermal equilibrium.

For a complete description of the spin-lattice relaxation, the different transition probabilities and the constants of the motion need to be determined. The latter quantities can be defined as the set of i populations N_i or a set of i combinations of populations $\sum_k c_{ki} N_{ki}$, which remain constant in time on a time scale short compared with the spin-lattice relaxation, and become time-dependent because of $\hat{H}_D(t)$. Consequently, if the hamiltonian consisted only of $\hat{H}_Z + \hat{H}_R + \hat{H}_D(t)$, the constants of the motion would be the individual populations of the eigenstates corresponding to $\hat{H}_Z + \hat{H}_R$; actually the number of constants of the motion is one less because of the constraint that the total population of all eigenstates is not influenced by $\hat{H}_D(t)$. However, it will be shown below that due to the terms $\hat{H}_{RP}$, $\hat{H}_P$ and the time-independent part of $\hat{H}_D$, extra transition probabilities exist between specific eigenstates with rates large compared with the relaxation rates, which reduce the number of constants of the motion.

In the next sections the unperturbed hamiltonian $\hat{H}_Z + \hat{H}_R$ will be considered first. Then the influence of $\hat{H}_{RP} + \hat{H}_P$ and the time-independent part of $\hat{H}_D$, and the resulting constants of the motion will be considered. Finally the spin-lattice relaxation due to $\hat{H}_D(t)$ will be investigated.

B. The Unperturbed Hamiltonian

$$\hat{H}_Z + \hat{H}_R$$

$\hat{H}_Z$ describes the interaction of the magnetic moments of the protons with H_0 and is, therefore, determined by the spin coordinates of the protons. $\hat{H}_R$ describes the rotations of the methyl group around its axis of symmetry in the presence of a hindering potential $V(\psi)$, and depends on the space coordinates of the three protons. ψ is a variable angle defined in the plane through the three protons, see Figure 1.

The first task is determining the eigenfunctions which diagonalize $\hat{H}_Z + \hat{H}_R$. Now it is well known that the search is simplified considerably if

the symmetry of the hamiltonian is taken into account (39). For a methyl group, bonded to a molecule, the feasible symmetry is given by the point group C_3 . This means that $\hat{H}_Z$ is invariant for a cyclic permutation of the spin coordinates and that $\hat{H}_R$ is invariant for a cyclic permutation of the space coordinates of the protons. Hence, if an operator $\hat{C}_3$, which might be $\hat{C}_3^S$ or $\hat{C}_3^R$, is defined as the cyclic permutation operator exchanging the spin (or respectively space) coordinates of the protons 1, 2, and 3 for those of 3, 1, and 2, $\hat{H}_Z$ commutes with $\hat{C}_3^S$ and $\hat{H}_R$ commutes with $\hat{C}_3^R$. Then the search for eigenfunctions of $\hat{H}_Z$ or $\hat{H}_R$ can be made separately within the classes of functions $\Psi(\lambda)$ having different eigenvalues λ of $\hat{C}_3$, following from $\hat{C}_3 \Psi(\lambda) = \lambda \Psi(\lambda)$. In our case $\lambda = 1, \epsilon, \text{ or } \epsilon^*$, with $\epsilon = \exp(2\pi i/3)$, which follows easily from the relation $\hat{C}_3 \hat{C}_3 \hat{C}_3 \Psi(\lambda) = \lambda^3 \Psi(\lambda) = \Psi(\lambda)$. Hence the eigenfunctions $\Psi_S(\lambda)$ of $\hat{H}_Z$ and $\Psi_R(\lambda_R)$ of $\hat{H}_R$ can be classified according to the A ($\lambda_R, \lambda_S = 1$), E^a ($\lambda_R, \lambda_S = \epsilon$) or E^b ($\lambda_R, \lambda_S = \epsilon^*$) irreducible representations of the point group C_3 . For explicit expressions of $\Psi_S(\lambda_S)$ and $\Psi_R(\lambda_R)$ see ref. (5).

Another advantage of the incorporation of the symmetry is that it also provides rules for the matrix elements due to perturbation operators. In our case an operator $\hat{O}$, which may depend on the spin and/or space coordinates, can be classified according to the A , E^a , or E^b symmetry, depending whether in the relation $\hat{C}_3 \hat{O}(\lambda) \hat{C}_3^{-1} = \lambda \hat{O}(\lambda)$, λ equals 1, ϵ , or ϵ^* . It can be shown that an operator with symmetry λ_j has possible non-zero matrix elements $\langle \Psi(\lambda_j) | \hat{O}(\lambda_j) | \Psi(\lambda_k) \rangle$ only if the condition

$$\lambda_i^* \lambda_j \lambda_k = 1, \quad (2)$$

is satisfied. This relation will prove to be very useful when the influence of $\hat{H}_{RP}$ and $\hat{H}_D$ is investigated.

We now return to the unperturbed hamiltonian $\hat{H}_Z + \hat{H}_R$. The eigenfunctions $\Psi_R(\lambda_R, R)$ of $\hat{H}_R$ correspond to eigenvalues $E_R(\lambda_R, R)$, where R ($R = 0, 1, \dots$) denotes the R -th rotor level. For a given value of R a difference in energy Δ_R is obtained for $\lambda_R = 1$ (A

symmetry) and $\lambda_R = \epsilon, \epsilon^*$ (E^a and E^b symmetry). The magnitude of Δ_R depends on the shape and height of the hindering barrier and is a measure of the probability that a methyl group tunnels through the barrier. Δ_R is called the tunnelling splitting of the R-th rotor state. The eigenfunctions of $\hat{H}_Z$ are characterized by $\Psi_S(\lambda_S, m)$, where m denotes the total magnetic quantum number of the three protons, with eigenvalues $E_S(m)$. For the total energy level scheme of $\hat{H}_Z + \hat{H}_R$ corresponding to the product eigenfunctions $\Psi_R \Psi_S$ the Pauli principle has to be taken into account, stating that an exchange of two protons changes $\Psi_R \Psi_S$ into $-\Psi_R \Psi_S$. Hence a rotation of the methyl group over 120° , characterized by the operation $\hat{C}_3 \hat{R}_3^S \Psi_R \Psi_S$ which gives the same result as two successive exchanges, would leave the eigenfunction invariant. As $\hat{C}_3 \hat{R}_3^S \Psi_R \Psi_S$ is also equal to $\lambda_R \lambda_S \Psi_R \Psi_S$, it follows that the symmetry parameters λ_R and λ_S of the rotor and spin system must obey the relation

$$\lambda_R \lambda_S = 1. \quad (3)$$

The energy level scheme of $\hat{H}_Z + \hat{H}_R$ is depicted in Figure 2. Here the energy gap E_{10} corresponds to the energy difference of the ground and first rotor level in case of an infinitely high barrier for which $\Delta_0 = \Delta_1 = 0$. The next step is the incorporation of $\hat{H}_{RP} + \hat{H}_P$ of Eq. (1).

C. The Terms $\hat{H}_{RP} + \hat{H}_P$

As has been stated above, $\hat{H}_{RP}$ is regarded as a perturbation of $\hat{H}_R$. It causes fluctuations of the hindering potential, both in amplitude and phase, which are rendered time dependent in a random way because of thermal excitations due to the phonon system. As a result non-magnetic transitions $W_{RR'}$ between the various rotor levels R and R' occur. Because $\hat{H}_{RP}$ operates only on the rotor system and because of Eq. (3) these transitions exist only between levels with a same spin eigenfunction $\Psi_S(\lambda_S, m)$ and between rotor states belonging to a same symmetry species A , E^a , or E^b and corresponding to a same value of m . The effect of these transitions is twofold:

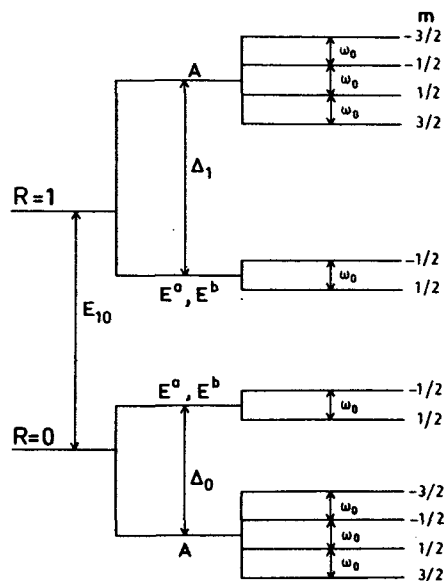


Figure 2. The energy level scheme of the lowest two torsional levels corresponding to $\hat{H}_Z + \hat{H}_R$.

(i) After some perturbation a state of internal equilibrium is restored within each symmetry species A , E^a , and E^b in a time of the order $W_{RR'}^{-1}$. Though $W_{RR'}^{-1}$ differs for different values of R and R' , this time, being of the order of the correlation time τ_c , see below, is much smaller than the relaxation time. Hence on the time scale of the relaxation the non-magnetic transitions maintain a Boltzmann distribution over the rotor levels within each symmetry species A , E^a , and E^b , corresponding to the same value of m . As a result the constants of the motion are no longer the individual populations corresponding to each value of R and m , the only populations which remain constant are the total populations of each symmetry species for a give magnetic quantum number m , $\sum_R \alpha(m)$, where α denotes A , E^a , or E^b . Using the assumption of ergodicity each methyl group belonging to the same symmetry species has the same average rotor energy. As a consequence the energy level scheme of Figure 2 is reduced to the effective eight-level scheme of Figure 3. Using

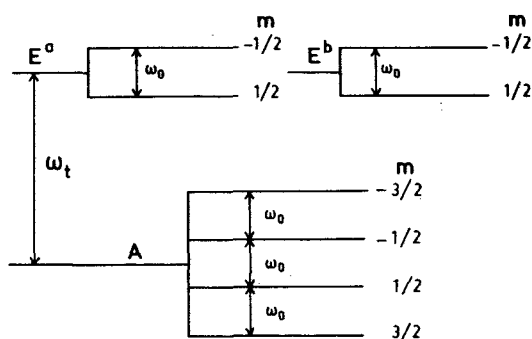


Figure 3. The effective energy level scheme corresponding to $\hat{H}_Z + \hat{H}_R + \hat{H}_{RP} + \hat{H}_P$.

again the constraint of conservation of the total population of all levels, it follows that the number of constants of the motion, which has to be regarded in spin-lattice relaxation, is reduced to seven. The energy difference between the A and E species is called the effective tunnelling splitting ω_t . The values of ω_t depends on the temperature. At very low temperatures (typically below 20 K), where the ground torsional levels are mainly occupied, ω_t equals Δ_0 . At higher temperatures the populations of the higher torsional levels increase and ω_t is found to decrease (10,40,41). Usually ω_t becomes negligibly small above ca. 50 K (moreover, for higher temperatures the meaning of ω_t becomes doubtful because then the broadening of the energy levels due to the non-magnetic transitions becomes comparable to or larger than ω_t). We note that at this moment different theories exist to explain the temperature dependence of ω_t (42-46). However, they all show the features described above.

(ii) Due to the non-magnetic transitions the methyl group may jump randomly from one well of the hindering potential into another. Though obviously this is a very complicated process and a result of many different transitions, in practice this random jumping can often be characterized by a single correlation time τ_c . Usually the temperature dependence of τ_c is

described by the Arrhenius law

$$\tau_c = \tau_0 \exp(E_a/kT) \quad (4)$$

where the activation energy E_a and the correlation constant τ_0 may depend on the temperature. At low temperatures (typically below 70 K) the lower torsional levels are mainly occupied. Then the random tunnelling of the methyl groups through the barrier is the dominant motional mechanism. At temperatures below ca. 30 K only the non-magnetic transition between the ground and first torsional levels is important, so that E_a is approximately given by $E_{1,0}$, see Figure 2. At temperatures above 70 K the classical random hopping of the methyl group over the hindering barrier becomes the dominant motion and E_a then is of the order of the barrier height (47,48).

D. The Term $\hat{H}_D$

The last term of Eq. (1) to be taken into account is $\hat{H}_D$, representing the dipolar interaction between the various protons. For the sake of simplicity we restrict ourselves to the case that all protons in the sample belong to methyl groups which experience the same hindering potential. The directions of their symmetry axes need not be the same. The results can easily be extended for the case that other protons are present as well (49).

It is well-known (ref. (36) chap. 4, ref (37) chap. 3) that the dipolar hamiltonian consists of several terms which can be classified according to the change Δm in the total magnetic quantum number caused by the spin operators

$$\hat{H}_D = \sum_{\mu} \hat{H}_D^{\mu} \quad \mu = \Delta m = 0, \pm 1, \pm 2. \quad (5)$$

Each term can be written as

$$\hat{H}_D^{\mu} = \sum_i (\hat{H}_i^{\mu} + \sum_{j < i} \hat{H}_{ij}^{\mu}) \quad (6)$$

where $\hat{H}_i^{\mu}$ represents the intra-methyl dipolar interaction within group i , and $\hat{H}_{ij}^{\mu}$ the inter-methyl dipolar interactions between the groups i and j . All terms in $\hat{H}_D$ consist of product functions of a spatial operator $\hat{V}$, depending on the angles β and ψ , depicted in

Figure 1, and a (bilinear) spin operator $\hat{S}$. Both operators can be classified with a symmetry parameter $\lambda_D = 1, \epsilon, \epsilon^*$ with the rule that the parameters of $\hat{V}$ and $\hat{S}$ are each others conjugate (5,49-52). Therefore Eq. (5) can be written as

$$\hat{H}_D = \sum_{\mu} \hat{H}_D^{\mu} = \sum_{\mu} [\hat{A}_i^{\mu}(\lambda_{Di}) + \sum_{j < i} \hat{A}_{ij}^{\mu}(\lambda_{Di}, \lambda_{Dj})], \quad (7)$$

where $\hat{H}_D$ contains both first-order and second-order perturbation terms. In a large magnetic field H_0 in first order, only the terms with $\mu = 0$ need to be taken into account. Moreover, if the random reorientations of the methyl groups are so fast that $|H_D|\tau_c \ll 1$, the first-order term is reduced to the time-averaged value of $\hat{H}_D^{\mu=0}$. In this respect it is important to note that, as the reorientations can be represented by rapid random rotations of the methyl groups over 120° , 240° , or 360° around their symmetry axes, the terms with A-symmetry, which are invariant for these rotations, are not influenced by the motion. Hence we reach the important conclusion that the terms in Eq. (7) with $\lambda_{Di} = \lambda_{Dj} = 1$ are time independent. The terms with $\lambda_{Di}, \lambda_{Dj} = \epsilon, \epsilon^*$ are time dependent, with an average value of zero. We shall consider these terms separately.

1. The Time-independent part of $\hat{H}_D$

The first-order term $\hat{H}_1$ of $\hat{H}_D$ is given by

$$\begin{aligned} \hat{H}_1 &= \overline{\hat{H}_D^{\mu=0}} = \sum_i [\hat{A}_i^{\mu=0}(\lambda_{Di} = 1) \\ &\quad + \sum_{j < i} \hat{A}_{ij}^{\mu=0}(\lambda_{Di} = \lambda_{Dj} = 1)] \\ &= \hat{H}_1^{\text{intra}} + \hat{H}_1^{\text{inter}} \end{aligned} \quad (8)$$

To illustrate the effect of $\hat{H}_1$ we consider an ensemble of methyl groups with a same orientation angle β between their symmetry axes and H_0 . It can be shown (53) that $\hat{H}_1^{\text{intra}}$ results in a shift d of the Zeeman levels corresponding to the A symmetry species, with

$$d = \frac{3\gamma^2\hbar}{4r^3}(1 - 3/2 \sin^2\beta),$$

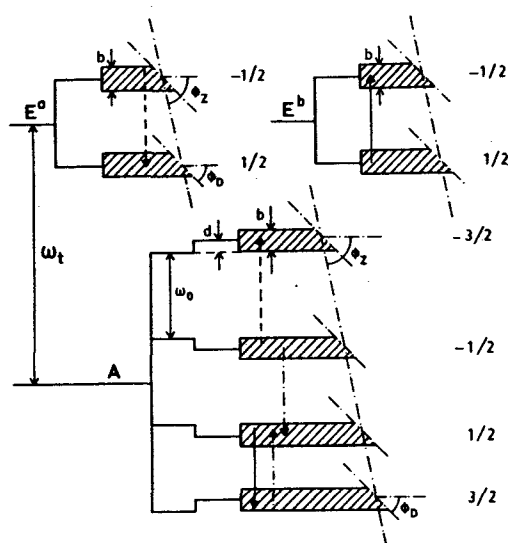


Figure 4. The effective energy level scheme corresponding to $\hat{H}_Z + \hat{H}_R + \hat{H}_{Rp} + \hat{H}_p + \hat{H}_1$. The different arrows are examples of pairs of simultaneous flip-flop transitions, which establish a single inverse Zeeman temperature α_Z and a single inverse dipolar temperature α_D . α_Z is proportional to $\text{tg}^{-1}\phi_Z$, and α_D is proportional to $\text{tg}^{-1}\phi_D$.

see Figure 4. The inter-methyl term $\hat{H}_1^{\text{inter}}$ consists of two parts, one proportional to the product spin operators $\hat{I}_{zi}\hat{I}_{zj}$, whereas the other one, the so-called flip-flop term, is proportional to $\hat{I}_{+i}\hat{I}_{-j} + \hat{I}_{-i}\hat{I}_{+j}$. Here for example $\hat{I}_{zi}$ is given by $\hat{I}_{zi} = \hat{I}_{zi}^1 + \hat{I}_{zi}^2 + \hat{I}_{zi}^3$, where 1, 2, and 3 label the three protons of methyl group i . Similar formulae can be given for the other spin operators. Both terms give rise to shifts of the Zeeman levels of all symmetry species, and as this shift usually is different for the different groups, the result is a broadening b , see Figure 4. In most non-diluted solids this broadening is of the same order of magnitude as the intra-methyl splitting d . Now the broadening due to the flip-flop is a result of the so-called flip-flop transitions, which are simultaneous jumps, occurring at a rate of the order b^{-1} , between pairs of adjacent Zeeman levels, in opposite

directions. For an extensive treatment of this phenomenon see refs. (36) chap. 5 and (37) chap. 1. The result of this so-called spin diffusion process is that, on a time scale of the order b^{-1} , the population distributions are given by a Boltzmann distribution, both over the energy levels split by the Zeeman and the dipolar interactions. As in most solids b^{-1} is much shorter than the spin-lattice relaxation time, the spin diffusion further reduces the number of constants of the motion. Until some years ago it was commonly assumed that only two constants of the motion remained, one proportional to the Zeeman energy and the other proportional to the dipolar energy. Both are characterized with single reciprocal spin temperatures α_Z and α_D , respectively, which after some perturbation were found to relax independently of each other, hence with single exponentials [(37) chap. 3].

For the case of reorienting methyl groups the situation is more complicated. It has already been stated above that both the spatial- and spin-operator of $\hat{H}_1$ are of A symmetry. This means that the flip-flop transitions occur only between pairs of Zeeman levels, where each pair corresponds to a same symmetry species. This process has been called Symmetry Restricted Spin Diffusion (38), and is illustrated in Figure 4. The important result is that the Zeeman and dipolar energies can still be characterized by α_Z and α_D respectively; the latter statement is only true if $b \approx d$, otherwise more reciprocal temperatures have to be defined (38,54). However, the total populations N_A , N_{Ea} , and N_{Eb} are unaffected by the spin diffusion. As a result two more constants of the motion have to be defined.

It is useful to consider the following constants of the motion:

- (i) the population difference between the E and A states, $(N_{Ea} + N_{Eb}) - N_A$. This has been called the tunnelling system, because in thermal equilibrium it equals the population difference due to the tunnelling splitting;
- (ii) the population difference between

the E^a and E^b states, $N_{Ea} - N_{Eb}$. This has been called the rotational polarization system (55).

In order to be consistent with the characterization of the Zeeman and dipolar systems by α_Z and α_D , we characterize the tunnelling system by the so-called reciprocal tunnelling temperature α_T proportional to $(N_{Ea} + N_{Eb}) - N_A$, and the rotational polarization system by α_R , proportional to $N_{Ea} - N_{Eb}$.

Summarizing we have found that due to the first type of perturbations $\hat{H}_{RP}$ and $\hat{H}_1$ in Eq. (1), the number of constants of the motion has been reduced to four, namely α_Z , α_D , α_R , and α_T . Each quantity can only vary in time due to the spin-lattice relaxation, which we shall now investigate. Before doing so, however, it must be remarked that the situation is more complicated in samples where the orientation angle β of the methyl groups can take more than one value.

It can be shown (49) that the Zeeman and dipolar systems can still be characterized by single inverse temperatures α_Z and α_D . This is not the case with the rotational polarization and tunnelling systems. These systems have to be divided into subsystems corresponding to methyl groups with orientation angles between β and $\beta + d\beta$. Each subsystem can be characterized by inverse temperatures $\alpha_R(\beta)$ and $\alpha_T(\beta)$. In thermal equilibrium all $\alpha_R(\beta)$ are equal to one another, but during relaxation they can become different. The same holds for $\alpha_T(\beta)$. Consequently, besides α_Z and α_D all $\alpha_R(\beta)$ and $\alpha_T(\beta)$ have to be taken as constants of the motion.

2. The Time-dependent Part of $\hat{H}_D$

The time-dependent part $\hat{H}_D(t)$ of $\hat{H}_D$ gives rise to spin-lattice relaxation. It follows from the previous section that $\hat{H}_D(t)$ is given by

$$\begin{aligned} \hat{H}_D(t) &= \sum_{\mu=-2}^2 [\hat{H}_i^{\mu}(\lambda_{Di} = \epsilon, \epsilon^*) \\ &\quad + \sum_{j < i} \hat{H}_{ij}^{\mu}(\lambda_{Di}, \lambda_{Dj} = \epsilon, \epsilon^*)] \\ &= \hat{H}_2^{\text{intra}}(t) + \hat{H}_2^{\text{inter}}(t). \quad (9) \end{aligned}$$

It follows from Eqs. (2) and (9) that the spin operators of $\hat{H}_D(t)$, being of either E^a or E^b symmetry, only result in possible non-zero transition probabilities W_{ij} between spin energy levels i and j belonging to different symmetry species, and with a difference in magnetic quantum number of zero, one or two. Hence only $A \leftrightarrow E^a$, $A \leftrightarrow E^b$, or $E^a \leftrightarrow E^b$ transitions are possible. Moreover, calculations show that for the intra-methyl relaxation due to $\hat{H}_2^{\text{intra}}(t)$ the $E^a \leftrightarrow E^b$ transitions are zero, so that only $A \leftrightarrow E^a$ and $A \leftrightarrow E^b$ transitions remain (5,35,43,49,54,56), where also explicit expressions for the different transition probabilities are given. Here we shall confine ourselves by remarking that generally W_{ij} is given by

$$W_{ij} = a_{ij} J(\Delta\omega_{ij}, \tau_c) \quad (10)$$

where a_{ij} is a constant depending on the orientation angle β of the methyl groups, and $\Delta\omega_{ij}$ the energy difference between the levels i and j . $J(\omega, \tau_c)$ is the spectral density function corresponding to the random reorientations of the methyl groups. It is usually assumed that $J(\omega, \tau_c)$ is of the Lorentzian type

$$J(\omega, \tau_c) = \tau_c / (1 + \omega^2 \tau_c^2). \quad (11)$$

It follows that:

- (i) the intra-methyl relaxation rates contain only the spectral density functions $J[(\omega_t \pm n\omega_0), \tau_c]$, $n = 0, 1, 2$;
- (ii) the inter-methyl relaxation rates contain the spectral density functions $J[\omega_t \pm n\omega_0, \tau_c]$ as well as $J(n\omega_0, \tau_c)$, $n = 0, 1, 2$ [the latter follows from the fact that non-zero inter-methyl relaxation transitions exist between the E^a and E^b species (5,49)].

The relaxation equations of the constants of the motion have to be calculated. It can be shown (43,49) that for equally oriented methyl groups these equations consist of a coupled set of four first-order differential equations, where, for example, $\dot{\alpha}_Z$ is given

by

$$\begin{aligned} \dot{\alpha}_Z = & S_{ZZ}\bar{\alpha}_Z + S_{ZR}\bar{\alpha}_R \\ & + S_{ZT}\bar{\alpha}_T + S_{ZD}\bar{\alpha}_D \end{aligned} \quad (12a)$$

$$\bar{\alpha} = \alpha^{\text{eq}} - \alpha \quad (12b)$$

α^{eq} denotes the thermal equilibrium value of α . Similar equations can be given for α_R , α_T , and α_D and the total set of equations can be summarized as

$$\dot{\vec{\alpha}} = \vec{S} \vec{\alpha} \quad (13)$$

where the vector $\vec{\alpha}$ has components α_Z , α_R , α_T , and α_D . Explicit expressions for $\vec{S}$ are given elsewhere (43,49), and also for the case of a distribution of the methyl orientation angles (in the latter case the number of differential equations has to be extended, because the number of constants of the motion is increased, see previous section).

To illustrate the effect of the various dynamical couplings we consider the case in which the sample consists of equally oriented methyl groups with an angle $\beta = 0$ between their symmetry axes and H_0 . For simplicity we assume that the inter-methyl interactions can be neglected, so that both the spin diffusion and the inter-methyl relaxation are zero. It can be shown (43) that in this case the only non-zero relaxation transitions W_1 and W_2 are between the $A_{-3/2}$ and $E_{+1/2}^b$ and the $A_{+3/2}$ and $E_{-1/2}^a$ levels respectively, with equal amplitudes but with different spectral densities if $\omega_t \neq 0$, see Figure 5a.

We consider the Zeeman relaxation, and we suppose that, starting from thermal equilibrium, the magnetization is destroyed by irradiating with a 90° rf pulse at exact resonance and with a duration short compared with the relaxation rates W_1 and W_2 . Then immediately after the pulse, which we shall call $t = 0$, the populations N_1 to N_8 of the eight levels are as depicted in Figure 5a. The Zeeman system, proportional to $(1/2)[(N_2 - N_1) + (N_4 - N_3) + (N_7 - N_6)] + (3/2)(N_8 - N_5)$, is zero, whereas the dipolar system, proportional to $N_5 + N_8 - (N_6 + N_7)$, the

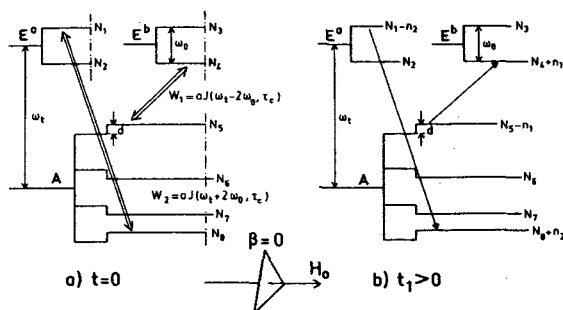


Figure 5. Intra-methyl relaxation for isolated methyl groups with $\beta = 0$. a) $t = 0$, immediately after a 90° rf pulse; b) $t_1 > 0$.

tunnelling system, proportional to $(N_1 + N_2 + N_3 + N_4) - (N_5 + N_6 + N_7 + N_8)$, and the rotational polarization system, proportional to $(N_1 + N_2) - (N_3 + N_4)$ remain in thermal equilibrium. The relaxation transitions will restore the population differences between the levels 1 and 8 and between 4 and 5 towards their thermal equilibrium values. It can easily be seen that immediately after the 90° pulse at $t = 0$ the population difference $N_8 - N_1$ is smaller than the value corresponding to thermal equilibrium, whereas $N_5 - N_4$ is larger than at thermal equilibrium. This means that if we observe the system at some instant $t_1 > 0$, the populations N_5 and N_1 have decreased by some amount n_1 and n_2 , whereas N_4 has increased by n_1 and n_8 by n_2 , see Figure 5b. It follows that now both the dipolar, the tunnelling and the rotational polarization systems are no longer in thermal equilibrium, provided that $n_1 \neq n_2$, thus proving the existence of non-zero coupling terms S_{ZD} , S_{ZT} , and S_{ZR} in Eq. (12). The reader can easily convince himself that the same result is found if the (symmetry restricted) spin diffusion and the inter-methyl relaxation are incorporated. It also follows from Figure 5b that if $n_1 = n_2$ the total ($E^a + E^b$) population, the total A population as well as $(N_5 + N_8)$ remain equal to the values for $t = 0$, so that then both the tunnelling system and the dipolar system remain in thermal equilibrium. However, the population difference between the E^a and E^b species

becomes different from that at $t = 0$, so that S_{ZR} still remains non-zero. Hence we can deduce the following rules for the different dynamic couplings.

- If $\omega_t = 0$, $(\omega_t \pm n\omega_0)^2 \tau_c^2 \ll 1$, or $\omega_t \gg n\omega_0$, $n = 0, 1, 2$, it follows from Eq. (11) that $W_1 = W_2$. Then $n_1 = n_2$ and the only dynamic couplings are between the Zeeman and rotational polarization system on the one hand and between the dipolar and tunnelling system on the other hand (the latter coupling can easily be seen from Figure 5 by choosing another initial condition where for example the tunnelling system is out of thermal equilibrium).
- If $\omega_t \neq 0$, if at least one of the terms $(\omega_t \pm n\omega_0)^2 \tau_c^2$ becomes comparable or larger than unity, and if ω_t is not much larger than $n\omega_0$, $W_1 \neq W_2$ and dynamic couplings exist between all four constants of the motion.

These rules appear to hold also for arbitrary orientations of the methyl groups and for polycrystalline samples.

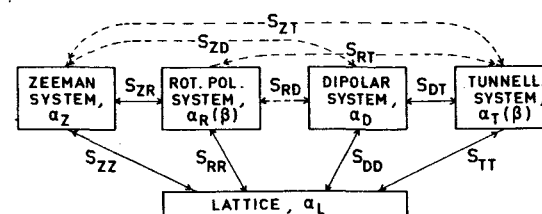


Figure 6. The constants of the motion and their dynamic couplings for reorienting or tunnelling methyl groups. Solid lines: non-zero couplings for $\omega_t = 0$, $\omega_t \gg n\omega_0$ or $(\omega_t \pm n\omega_0)^2 \tau_c^2 \ll 1$, $n = 0, 1, 2$. Solid lines + dashed lines: non-zero couplings for $\omega_t \neq 0$, ω_t comparable to $n\omega_0$ and at least one of the terms $(\omega_t \pm n\omega_0)^2 \tau_c^2$ comparable or larger than one; $n = 0, 1, 2$.

Figure 6 gives a summary of the different couplings, where the solid lines give the situation for condition (a) and the solid and dotted lines for

condition (b). As both ω_t and τ_c are temperature dependent, it follows that the validity of the conditions (a) and (b) depends on the temperature as well. This will be investigated in the next section.

III. EXPERIMENTS

In this section examples will be given of the effect of the various dynamic couplings on the observed spin-lattice relaxation. The emphasis will lay on the relaxation of the Zeeman system, because this is mostly investigated in practice. Most experiments have been performed with the help of a Bruker CXP 4-100 pulse spectrometer and a home-built cryostat (57). With this cryostat, operating in the frequency range 9 - 73 MHz, the temperature could be varied from 10 - 300 K. Moreover, in the whole temperature region the sample could be rotated around an axis perpendicular to H_0 with a frequency maximum of 100 Hz. The utility of the latter possibility will become clear later on.

As stated in section II.D.2, the number of non-zero dynamic couplings depends on the value of the effective tunnelling splitting ω_t . Therefore it is useful to discriminate between the case that ω_t is zero and non-zero.

A. The Limit of Non-tunnelling

$$\omega_t = 0$$

In this limit the only non-zero dynamic couplings are between α_z and $\alpha_R(\beta)$ and between α_D and $\alpha_T(\beta)$. Within the temperature range where $\omega_t = 0$ the value of $\omega_0\tau_c$ can be both smaller and larger than one. It is useful to investigate these limits separately as well.

1. $\omega_t = 0$, $\omega_0\tau_c \ll 1$

In this limit even for a polycrystalline sample the relaxation of α_z is described by a weighted sum of two exponentials (58). If for $t = 0$; $\alpha_z = 0$, the relaxation is given by

$$\begin{aligned} (\alpha_z^{\text{eq}} - \alpha_z) / \alpha_z^{\text{eq}} &= C \exp(-\lambda_1 t) \\ &+ (1 - C) \exp(-\lambda_2 t) \end{aligned} \quad (14)$$

The constant C and the relaxation rates λ_1 and λ_2 depend on the various elements of the relaxation matrix. Moreover, the value of C is determined by the initial values of α_z and α_R at $t = 0$. As a consequence the observed relaxation depends on the way the spin system has been prepared. This is illus-

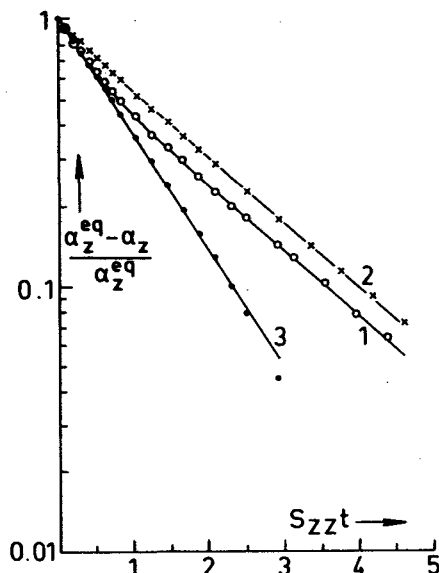


Figure 7. Zeeman relaxation of partially deuterated L-alanine, $\text{ND}_3^+\text{CHCH}_3\text{COO}^-$. $\omega_0/2\pi = 60.8$ MHz, $T = 296$ K, $\omega_0\tau_c = 0.48$. Curve 1: without sample rotation, after a single 90° rf pulse, duration $4 \mu\text{s}$; curve 2: without sample rotation, after saturation during 500 ms; curve 3: with sample rotation, $\omega_r/2\pi = 40$ Hz, after a single 90° pulse or saturation. $S_{zz}^{-1} = 48$ ms.

trated in Figure 7, curves 1 and 2. Curve 1 displays the Zeeman relaxation of a polycrystalline sample of partially deuterated L-alanine, $\text{ND}_3^+\text{CHCH}_3\text{COO}^-$, after a single 90° rf pulse with a duration much shorter than the inverse relaxation rates (49,57). Hence immediately after the pulse, which we define as $t = 0$, $\alpha_z = 0$ and $\alpha_R = \alpha_R^{\text{eq}} = 0$. The result is a rather obvious non-exponential relaxation, which can be described very accurately by a sum of two exponentials. The curve

2 of Figure 7 shows the relaxation obtained by saturating the system during a time long compared with the inverse relaxation rates. In this case at $t = 0$, defined as the time immediately after saturation, $\alpha_Z = 0$ but α_R is non-zero. This is due to the fact that during saturation the various relaxation transitions are able to establish a non-equilibrium population difference between the E^a and E^b species (in the example of Figure 5 the total E^a population would decrease, and the total E^b population would increase during saturation). It can be shown (58) that the coefficient corresponding to the smallest time constant in Eq. (14) decreases, in accordance with the experimental results.

Another relaxation behavior is observed if the sample is rotated around an axis perpendicular to H_0 and with an angular frequency ω_r much larger than the relaxation rates (59). In this case the relaxation becomes exponential and independent of the preparation of the system, see curve 3 in Figure 7. The explanation of this phenomenon is that due to the sample rotation, the Zeeman and rotational polarization system become decoupled, so that α_R remains at thermal equilibrium both during the preparation time as well as during the relaxation time. As a result α_Z relaxes with a single exponential with the rate S_{ZZ} . We note that the decoupling of α_Z and α_R by sample rotation also occurs for tunnelling methyl groups, where $\omega_t \neq 0$. A full explanation is given in ref. (60), here we shall confine ourselves by considering the example of Figure 5. For $\beta = 0^\circ$ the relaxation rates W_1 and W_2 operate between the levels 4 and 5 and between 1 and 8. Instead of sample rotation we consider an experiment where the sample is flipped through an angle of 180° around an axis perpendicular to H_0 with a fast repetition rate. This means that β jumps quickly between 0° and 180° . However, for $\beta = 180^\circ$, the non-zero relaxation rates are between the levels 2 and 5 with a strength W_1 , and between the levels 3 and 8 with a strength W_2 . Hence for $\beta = 0^\circ$ the total E^a population decreases whereas it increases for $\beta = 180^\circ$. As a consequence during the flipping on the

average the total E^a population, and also the total E^b population remain constant, so that α_R remains at thermal equilibrium.

For a polycrystalline sample S_{ZZ} is given by (58)

$$\begin{aligned} S_{ZZ} &= S_{ZZ}^{\text{intra}} + S_{ZZ}^{\text{inter}} \\ &= (9/20) K p d [J(\omega_0, \tau_c) \\ &\quad + 4J(2\omega_0, \tau_c)] \\ &\quad + S_{ZZ}^{\text{inter}} \end{aligned} \quad (15)$$

$K = \gamma^4 \hbar^2 / r^6$, d is the so-called efficiency factor (5,49) which usually is close to one and p takes into account that the total number of protons N_H need not be equal to the number of protons N_{Me} belonging to the methyl groups. This causes a reduction in S_{ZZ} by the factor p given by

$$p = N_{Me} / N_H. \quad (16)$$

We note that for $p = d = 1$, S_{ZZ}^{intra} represents the well-known BPP formula for T_{1Z}^{-1} , elaborated for reorienting methyl groups (1,2). It has been shown (58) that from the different experiment-dependent relaxation measurements all elements of the relaxation matrix governing the relaxation of α_Z and α_R as well as the magnitude of S_{ZZ}^{inter} can be determined. Moreover, other experiments can be performed by which the state of non-equilibrium of α_R during the relaxation can be demonstrated (61).

2. $\omega_t = 0$, $\omega_0 \tau_c$ arbitrary

In general the auto-relaxation rate S_{RR} of α_R contains a term proportional to $J(\omega = 0, \tau_c)$. (This is due to $A_{1/2}^+ \leftrightarrow E_{1/2}^a, E_{1/2}^b$ relaxation transitions.) It follows simply from Eqs. (11) and (17) that in the limit $\omega_0 \tau_c \gg 1$: $S_{RR} \gg S_{ZZ}$. Then α_R is driven towards thermal equilibrium in a time short compared with the other relaxation times, and as a result the observed relaxation of α_Z becomes almost a single exponential again with S_{ZZ} as a relaxation rate (62). This is illustrated in Figure 8a, where the Zeeman relaxation of $ND_3^+CHCH_3COO^-$ after a single 90° pulse

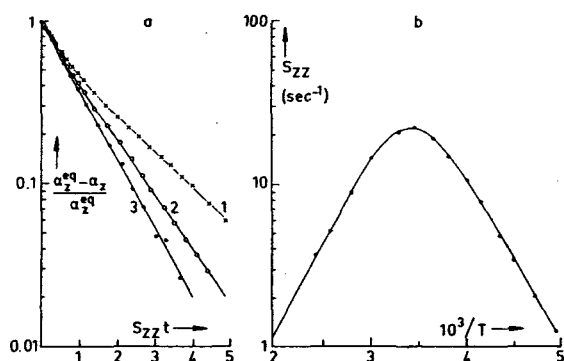


Figure 8. a) Zeeman relaxation of $\text{ND}_3\text{CHCH}_3\text{COO}^-$ for a non-rotating sample after a single 90° pulse. $\omega_0/2\pi = 60.8$ MHz. Curve 1: $T = 327$ K, $\omega_0\tau_c = 0.2$, $S_{ZZ}^{-1} = 70$ ms; Curve 2: $T = 258$ K, $\omega_0\tau_c = 1.6$, $S_{ZZ}^{-1} = 68$ ms; Curve 3: $T = 202$ K, $\omega_0\tau_c = 23$, $S_{ZZ}^{-1} = 830$ ms. b) S_{ZZ} of $\text{ND}_3\text{CHCH}_3\text{COO}^-$, determined with a rotating sample, as a function of temperature. Dots: experimental; solid curve: theoretical, using the data given in the text.

is given for three temperatures. In all cases the values of S_{ZZ} has been determined from the relaxation observed with a rotating sample (not shown here). Indeed for the lowest temperature the non-exponentiality has disappeared. As a consequence, if the relaxation rate S_{ZZ} , measured with a rotating sample, is compared with the apparent relaxation rate, observed in case of a non-rotating sample after long saturation, these rates will differ for $\omega_0\tau_c \ll 1$ and become equal for $\omega_0\tau_c \gg 1$.

We conclude that for $\omega_0\tau_c \ll 1$, experiment-dependent relaxation measurements are useful, for instance, for the determination of S_{ZZ}^{inter} , whereas especially the temperature dependence of S_{ZZ} , given by the Eqs. (4) and (17), can be used for determining the relaxation constant K , the activation energy E_a and the correlation constant τ_0 . The most accurate way to perform this is to use a rotating sample, because then problems like analyzing the non-exponentiality are avoided.

Figure 8b shows the temperature

dependence of S_{ZZ} for $\text{ND}_3\text{CHCH}_3\text{COO}^-$ as obtained in this manner. As is well-known, $\ln S_{ZZ}$ is proportional to T^{-1} for $\omega_0\tau_c \ll 1$ and $\omega_0\tau_c \gg 1$, from which the activation energy E_a can be determined. The maximum occurs at $\omega_0\tau_c = 0.616$ from which the correlation constant τ_0 can be calculated. Finally, the relaxation constant K can be obtained from the magnitude of the maximum.

For $\text{ND}_3\text{CHCH}_3\text{COO}^-$ the results are (44,53): (i) the strength of S_{ZZ}^{inter} is ca. 3% of that of S_{ZZ}^{intra} ; (ii) $E_a = (20.9 \pm 1.0)$ kJ/mol; (iii) $\tau_0 = (2.7 \pm 1) \times 10^{-13}$ s; and (iv) $K = (1.29 \pm 0.06) \times 10^{10} \text{ s}^{-2}$, corresponding to a value for the intra-methyl proton-proton distance r of 1.79 Å. The latter result is in accordance with neutron scattering measurements (63).

We note that the dynamic coupling between α_D and α_T , which, for example, results in a non-exponential, experiment-dependent relaxation of the dipolar system, has also been established experimentally (49,64). It is also shown in these references that the non-exponentiality is most pronounced when $\omega_0\tau_c \gg 1$.

B. The Limit of Tunnelling, $\omega_t \neq 0$

In this section the effect of tunnelling on the spin-lattice relaxation is investigated. The results are illustrated with measurements, performed on a polycrystalline sample of tetramethylgermanium, $\text{Ge}(\text{CH}_3)_4$, in the temperature region $170 \text{ K} > T > 33 \text{ K}$ (56,57). As stated in section II.C, for decreasing temperatures ω_t becomes non-zero and increases towards its final value Δ_0 , the ground torsional splitting. The values of $\omega_t(T)$ and Δ_0 strongly depend on the shape and magnitude of the hindering potential. For $\text{Ge}(\text{CH}_3)_4$, the hindering barrier was found to be a three-fold cosine shaped potential with a height of 5.8 kJ/mol (56,65) and Figure 9 shows the corresponding curve of ω_t as a function of T , calculated by a formula given in (43). In Figure 9 the temperature dependence of the correlation time τ_c of the methyl groups is given (56). It has been argued in section II.D.2 that the dynamic couplings between α_Z , $\alpha_R(\beta)$ and α_D , $\alpha_T(\beta)$ become

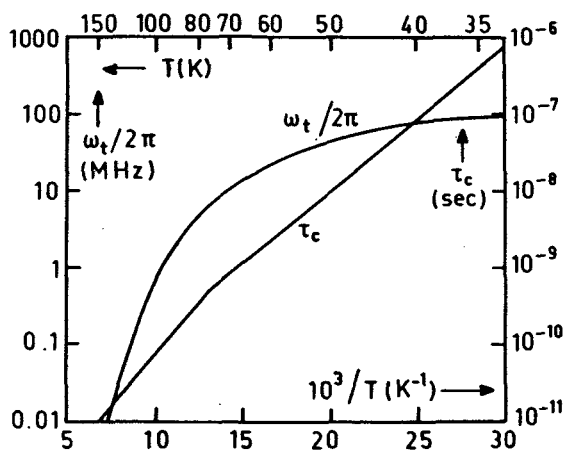


Figure 9. $\omega_t/2\pi$ and τ_c as a function of temperature for $\text{Ge}(\text{CH}_3)_4$.

non-zero when $J[(\omega_t + n\omega_0), \tau_c]$ differs from $J[(\omega_t - n\omega_0), \tau_c]$, $n = 1, 2$, which occurs when $\omega_t \neq 0$, $\omega_t \tau_c \geq 1$ and ω_t is comparable to ω_0 . Consequently we expect the non-exponentiality in the relaxation of α_z to increase for decreasing temperature. Moreover, the coupling terms between α_z and $\alpha_T(\beta)$, α_D appear to be independent of sample rotation. This can be understood from Figure 5. The population difference corresponding to the tunnelling and dipolar system, induced during the relaxation, is the same for $\beta = 0^\circ$ and 180° . Hence a rapid flipping of the methyl groups between 0° and 180° will not average out the deviation from non-equilibrium, as was the case for the rotational polarization system. Therefore we expect that sample rotation only partly removes the non-exponentiality. In practice sample rotation influences the effect of α_D on α_z as well. This rotation induces an extra time dependence in α_D such that α_D decays towards its thermal equilibrium value in a time which, depending on the spinning speed, can be short compared with the spin-lattice relaxation time (66). If this is the case the influence of α_D on the Zeeman relaxation can be neglected, for the same reason as that the influence of α_R could be neglected for $\omega_0 \tau_c \gg 1$, see section III.A.

In Figure 10 the Zeeman relaxation

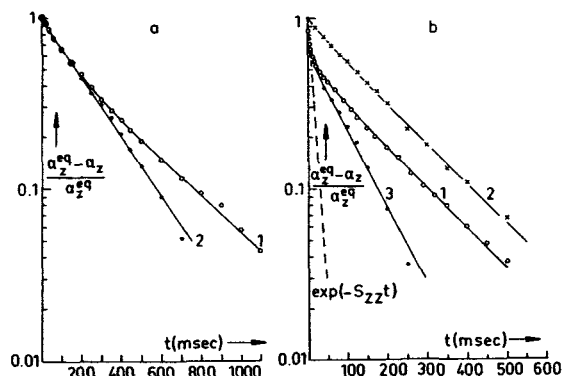


Figure 10. Zeeman relaxation of $\text{Ge}(\text{CH}_3)_4$, $\omega_0/2\pi = 38$ MHz. a) $T = 99$ K, $\omega_t \ll \omega_0$, $\omega_0 \tau_c = 0.02$. Curve 1: without sample rotation, after a single 90° rf pulse; curve 2: with sample rotation, $\omega_r/2\pi = 30$ Hz, after a single 90° pulse; $S_{ZZ}^{-1} = 250$ ms. b) $T = 44$ K, $\omega_t/2\pi = 66$ MHz, $\omega_0 \tau_c = 3.6$. Curve 1: without sample rotation, after a single 90° pulse; curve 2: without sample rotation, after saturation during 300 ms; curve 3: with sample rotation, $\omega_r/2\pi = 100$ Hz, after a single 90° rf pulse; $S_{ZZ}^{-1} = 12$ ms.

of $\text{Ge}(\text{CH}_3)_4$ is shown, observed after single 90° rf pulses, for two temperatures. In Figure 10a $T = 99$ K, which is high enough to neglect tunnelling effects. Moreover, $\omega_0 \tau_c \ll 1$ so that we encounter the same conditions as in section III.A.1; α_z is coupled only to $\alpha_R(\beta)$ and sample rotation results in an exponential Zeeman relaxation. In Figure 10b, where $T = 44$ K, $\omega_t/2\pi$ is of the order of magnitude as $\omega_0/2\pi = 38.2$ MHz, whereas $\omega_t \tau_c \approx 6.2$. Hence the coupling terms between all constants of the motion are non-zero and the relaxation remains non-exponential during sample rotation, mainly due to the coupling between α_z and α_T (67). In Figure 10b the relaxation after long saturation has also been given. Similarly to the case of non-tunnelling we observe that the fastest relaxation rates have disappeared almost completely.

The temperature dependence of the Zeeman relaxation for tunnelling methyl

groups is much more complicated than for non-tunnelling groups because of (i) the many dynamic couplings, (ii) the many different spectral density functions, and (iii) the temperature dependence of both τ_c and ω_t .

As a result $\alpha_Z(t)$ is governed by a weighted sum of many exponentials with corresponding rates which are complicated functions of the elements of the relaxation matrix $\tilde{S}$, so that analysis of the observed relaxation is very complex. However, there is one exception; when after preparation of the spin system only the Zeeman system has been brought out of thermal equilibrium (e.g., by a short rf pulse), then the short time behavior of α_Z is governed by its auto-relaxation rate S_{ZZ} . This follows readily from Eq. (12a): after a 90° pulse $\tilde{\alpha}_R$, $\tilde{\alpha}_D$, and $\tilde{\alpha}_T$ are still zero, so that on a time scale short compared with the relaxation times $\dot{\alpha}_Z \approx S_{ZZ}\tilde{\alpha}_Z$. Consequently, S_{ZZ} equals the initial rate constant of the Zeeman relaxation. In Figure 10 is shown the way in which S_{ZZ} is obtained. In Figure 10a, the initial rate of curve 1 equals the rate following from curve 2, because the latter one is governed solely by S_{ZZ} . Therefore we focus our attention on the temperature dependence of S_{ZZ} . For a polycrystalline sample S_{ZZ} is given by (56)

$$\begin{aligned} S_{ZZ} &= S_{ZZ}^{\text{intra}} + S_{ZZ}^{\text{inter}} \\ &= (9/40) \text{Kpd} [J\{(\omega_t + \omega_0), \tau_c\} \\ &\quad + J\{(\omega_t - \omega_0), \tau_c\} \\ &\quad + 4J\{(\omega_t + 2\omega_0), \tau_c\} \\ &\quad + 4J\{(\omega_t - 2\omega_0), \tau_c\}] \\ &\quad + S_{ZZ}^{\text{inter}} [J\{(\omega_t \pm n\omega_0), \tau_c\}, \\ &\quad J(n\omega_0, \tau_c)] \\ n &= 1, 2 \end{aligned} \quad (17)$$

Depending on the experimental circumstances and the material under investigation, S_{ZZ} as a function of temperature can show different features:

- (i) If $\omega_0\tau_c < 1$ for these temperatures where ω_t becomes non-zero, the

"classical" maximum in S_{ZZ} due to $\omega_0\tau_c \approx 1$ has not yet been reached. However, when $\omega_t \gg \omega_0$ a maximum can be expected for $\omega_t\tau_c \approx 1$.

- (ii) When $\omega_t \gg \omega_0$ and $\omega_t\tau_c \gg 1$ the inter-methyl relaxation, which at high temperature usually is of the order of 30% of the intra-methyl relaxation (68), can become dominant for the relaxation, because, unlike S_{ZZ}^{intra} , it contains the spectral density functions $J(n\omega_0, \tau_c)$, $n = 1, 2$, see Eq. (17). This can give rise to a classical maximum again occurring at those temperatures where $\omega_0\tau_c \approx 1$ (69,70).
- (iii) When at some temperature $\omega_t \approx \omega_0$ or $\omega_t \approx 2\omega_0$ and $\omega_t\tau_c \gg 1$, so-called tunnelling-assisted maxima in S_{ZZ} occur due to the terms $J[(\omega_t - \omega_0), \tau_c]$ and $J[(\omega_t - 2\omega_0), \tau_c]$ in Eq. (17).

To illustrate these features we con-

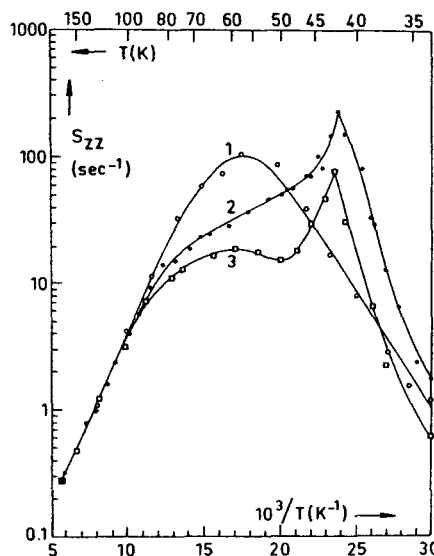


Figure 11. S_{ZZ}^{-1} of $\text{Ge}(\text{CH}_3)_4$ as a function of temperature. Curve 1: $\omega_0/2\pi = 9$ MHz; curve 2: $\omega_0/2\pi = 38$ MHz; curve 3: $\omega_0/2\pi = 73$ MHz.

sider Figure 11, where S_{ZZ} of $\text{Ge}(\text{CH}_3)_4$

has been given as a function of temperature for three rf frequencies. It follows:

1. $\omega_0/2\pi = 9$ MHz

For $T > 80$ K, ω_t can be neglected, and S_{zz} is given by Eq. (15) again, with $\omega_0\tau_c \ll 1$. The maximum at $T = 57$ K is determined mainly by the condition $\omega_t\tau_c \approx 1$, as here $\omega_t \approx 4.2\omega_0$. Though it has been found (56) that for $T < 40$ K the intermethyl relaxation is dominant, no separate maximum corresponding to $\omega_0\tau_c \approx 1$ is observed. This is because this maximum is expected at ca. 48 K, where the intra-methyl relaxation still dominates. Tunnelling assisted maxima, which would occur for $\omega_t/2\pi = 9$ MHz and 18 MHz, are not observed, because $\omega_t\tau_c \ll 1$ at the corresponding temperatures, see Figure 9.

2. $\omega_0/2\pi = 38$ MHz

The relaxation shows a pronounced maximum at 42 K. Inspection of Figure 9 shows that at this temperature $\omega_t/2\pi \approx 76$ MHz, so that this is a tunnelling-assisted maximum corresponding to $\omega_t = 2\omega_0$. The maximum corresponding to $\omega_t = \omega_0$ would occur at 55 K, but this is not observed because there the condition $\omega_t\tau_c \gg 1$ is not fulfilled.

3. $\omega_0/2\pi = 73$ MHz

The relaxation is maximal at 43 K, where $\omega_t \approx \omega_0$. Hence this is also a tunnelling-assisted maximum. The magnitude of this maximum is ca. 3 times smaller than that observed for 38 MHz, which would be expected because for $\omega_t = \omega_0$ the term $J[(\omega_t - \omega_0), \tau_c]$ in Eq. (17) is dominant, and for $\omega_t = 2\omega_0$ the term $4J[(\omega_t - 2\omega_0), \tau_c]$. Since according to Figure 9 the maximal value of ω_t is ca. 90 MHz, no tunnelling-assisted maximum can occur for $\omega_t = 2\omega_0$ and $\omega_0/2\pi = 73$ MHz.

At low temperatures the dipolar system can also be coupled to all other constants of the motion, resulting in a

non-exponential dipolar relaxation. This has been observed in $\text{Ge}(\text{CH}_3)_4$. However, as the dipolar relaxation has not been analyzed in great detail, the results will not be shown here.

A much more striking experiment, which clearly confirms the dynamic coupling between the dipolar and tunnelling system, has been performed by Haupt (71,72). He considered the dipolar signal of γ -picoline at low temperatures and found that after a sudden temperature jump the dipolar signal increased to a value much larger than the Zeeman signal and then decreased to its thermal equilibrium value ≈ 0 again, see Figure 12. The explanation

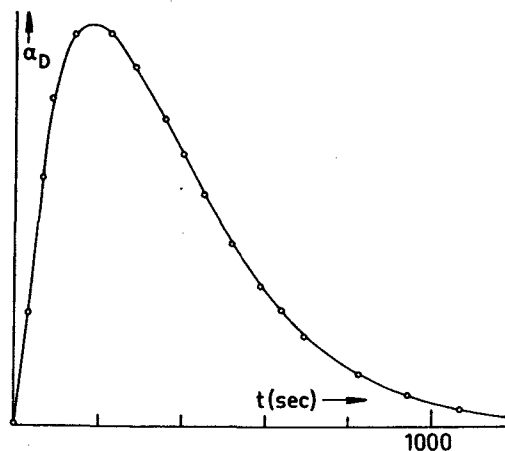


Figure 12. Dipolar polarization of γ -picoline after a temperature jump from 11 K to 26 K. After Haupt (72).

of this phenomenon is that in γ -picoline, which has a very low potential barrier, the tunnelling splitting is of the order of GHz, much larger than the rf frequency. Hence the tunnelling system is coupled only to the dipolar system. If starting from thermal equilibrium, a temperature jump is applied, then ω_t changes, but the population difference between the ($E^a + E^b$) and the A symmetry species still corresponds to the value of ω_t before the jump. Thus after the temperature change the tunnelling system is in a state of

non-equilibrium, and will relax towards the new thermal equilibrium value with rates determined by the elements of $\hat{S}$. Due to the dynamic coupling between α_T and α_D the dipolar polarization effect described above is induced.

IV. CONCLUSIONS

It has been shown that in solids the symmetry properties of the methyl groups lead to extra constants of the motion, the so-called rotational polarization and tunnelling system. At low temperatures, where the tunnelling splitting becomes non-zero, on the time scale of spin-lattice relaxation these systems are coupled dynamically to the Zeeman and dipolar systems. At high temperatures, where the tunnelling splitting can be neglected, non-zero couplings exist only between the Zeeman and rotational polarization and between the dipolar and tunnelling systems. The result is a Zeeman and dipolar relaxation which generally consist of weighted sums of many exponentials with rates determined by the various auto- and cross-relaxation rates. As a consequence the temperature dependence of the Zeeman relaxation is a complicated function of $\tau_c(T)$ and $\omega_t(T)$, which makes difficult the determination of these quantities from the measurements. However, there is one exception: the auto-relaxation rate of the Zeeman or dipolar system can be obtained rather easily, provided that the proper relaxation experiment has been chosen. From this quantity the values of $\tau_c(T)$ and $\omega_t(T)$, and so the height and shape of the hindering potential, can be determined rather accurately.

In the past the existence of the extra constants of the motion has not been recognized. This is due to the fact that it was assumed implicitly that the spin diffusion was not submitted to symmetry restrictions, leading to fast flip-flop transitions also between levels corresponding to different symmetry species. The result of this so-called complete spin diffusion (CSD) was that the rotational polarization and tunnelling systems are driven towards thermal equilibrium on a time scale fast compared with the spin-lattice relaxation, and the only remaining

constants of the motion are the Zeeman and dipolar systems each relaxing with a single exponential. Therefore in a lot of cases the apparent relaxation rate of e.g. the Zeeman relaxation has been interpreted with the CSD theory. Now it has been shown in this paper that in reality S_{ZZ} is equal to the initial rate value of the Zeeman relaxation, provided that only α_Z has been brought out of thermal equilibrium, or that S_{ZZ} is equal to the relaxation rate observed for a rotating sample (the latter is only true when $\omega_t = 0$). As S_{ZZ} can differ considerably from the apparent time constant, this can lead to erroneous results. For instance, if for the case of partially deuterated l-alanine the apparent time constant, observed after long saturation, has been interpreted with the CSD theory, the following results would have been obtained (62,73): (i) $\omega_0\tau_c \ll 1$: $E_a = 20.9$ kJ/mol; (ii) $\omega_0\tau_c \gg 1$: $E_a = 16.7$ kJ/mol; (iii) $\tau_0 = 1.9 \times 10^{-13}$ s and (iv) $K = 0.87 \times 10^{10}$ s⁻², corresponding to a value of r of 1.92 Å. These results differ considerably from those obtained with a rotating sample, see section III.A. Also, a misinterpretation of the measurements can also lead to a disregarding of the tunnelling-assisted maxima (56).

Finally it should be emphasized that the existence of constants of the motion as a result of symmetry properties is not restricted to methyl groups, but occur in any reorienting or tunnelling molecular group. Indeed, these constants of the motion have been found, both theoretically and experimentally, in flipping spin pairs (74) and have been predicted in reorienting groups with a 6-fold symmetry, like benzene rings (75,76). In the latter case, however, the relaxation couplings are small and the result is a relaxation close to that following from the CSD theory.

Note. We would like to mention that since submission of this paper an interesting and still ongoing discussion exists between Clough (77,78) and us (79). The discussion centers around the question of whether there are two distinguishable E species, as is the common view and also adopted by us, or

only one E species as is Clough's view.

In the first paper (77) Clough argued that the existence of two long-lived E symmetry species would be in conflict with the classical reorientation model. In a reply to this Emid (79) showed that the existence of two long-lived E symmetry species at high (as well as low) temperatures was in perfect harmony with the classical reorientation.

In the latest paper (78) Clough and McDonald argued that there could not be two distinguishable E species also at low temperatures, because the proper symmetry group is C_{3v} instead of C_3 , and because the wave functions should be fully antisymmetric for single pair exchange. In a paper to be published elsewhere we shall show that the use of C_{3v} instead of C_3 symmetry still allows two distinguishable E species (two partner states) to exist even when the full antisymmetric requirement is taken into account, see also Stevens (80). Finally, we note that our model has been fruitfully applied by others, see e.g. (81) and references therein.

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could be recorded in this column.

INSTRUCTIONS FOR AUTHORS

Because of the ever increasing difficulty of keeping up with the literature there is a growing need for critical, balanced reviews covering well-defined areas of magnetic resonance. To be useful these must be written at a level that can be comprehended by workers in related fields, although it is not the intention thereby to restrict the depth of the review. In order to reduce the amount of time authors must spend in writing we will encourage short, concise reviews, the main object of which is to inform nonexperts about recent developments in interesting aspects of magnetic resonance.

The editor and members of the editorial board invite reviews from authorities on subjects of current interest. Unsolicited reviews may also be accepted, but prospective authors are requested to contact the editor prior to writing in order to avoid duplication of effort. Reviews will be subject to critical scrutiny by experts in the field and must be submitted in English. Manuscripts should be sent to the editor, Dr. David G. Gorenstein, Chemistry Department, University of Illinois at Chicago, Box 4348, Chicago, Illinois, 60680, USA.

MANUSCRIPTS must be submitted in triplicate (one copy should be the original), on approximately 22 x 28 cm paper, typewritten on one side of the paper, and double spaced throughout. All pages are to be numbered consecutively, including references, tables, and captions to figures, which are to be placed at the end of the review.

ARRANGEMENT: Considerable thought should be given to a logical ordering of the subject matter and the review should be divided into appropriate

major sections, sections, and subsections, using Roman numerals, capital letters, and Arabic numerals respectively. A table of contents should be included.

TABLES: These are to be numbered consecutively in the text with Arabic numerals. Their place of insertion should be mentioned in the text, but they are to be placed in order at the end of the paper, each typed on a separate sheet. Each table should be supplied with a title. Footnotes to tables should be placed consecutively, using lower case letters as superscripts.

FIGURES are also to be numbered consecutively using Arabic numerals and the place of insertion mentioned in the manuscript. The figures are to be grouped in order at the end of the text and should be clearly marked along the edge or on the back with figure number and authors' names. Each figure should bear a caption, and these should be arranged in order and placed at the end of the text. Figures should be carefully prepared in black ink to draftsman's standards with proper care to lettering (typewritten or freehand lettering is not acceptable). Graphs should include numerical scales and units on both axes, and all figures and lettering should be large enough to be legible after reduction by 50-60%. Figures should be generally placed on sheets of the same size as the typescript and larger originals may be handled by supplying high-contrast photographic reductions. One set of original figures must be supplied; reproduction cannot be made from photocopies. Two additional copies of each figure are required. Complex molecular formula should be supplied as ink drawings.

REFERENCES to the literature should be cited in order of appearance in the text by numbers on the line, in parentheses. The reference list is to be placed on separate sheets in numerical order at the end of the paper. References to journals should follow the order: author's (or authors') initials, name, name of journal, volume number, page, and year of publication. The abbreviation of the journal follows that used in the Chemical Abstracts Service Source Index. Reference to books should include in order: author's (or authors') initials, name, title of book, volume, edition if other than the first, publisher, address, date of publication, and pages.

FOOTNOTES should be used sparingly and only in those cases in which the insertion of the information in the text would break the train of thought. Their position in the text should be marked with a superscript Arabic numeral and the footnote should be typed at the bottom of the relevant page in the text, separated from the latter by a line.

SYMBOLS AND ABBREVIATIONS: Mathematical symbols should be typewritten wherever possible. Greek letters should be identified in pencil in the margin. In reviews containing a number of mathematical equations and symbols, the author is urged to supply a list of these on a separate sheet for the assistance of the printer; this will not appear in print. Standard abbreviations will follow the American Chemical Society's HANDBOOK FOR AUTHORS names and symbols for units.

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REPRINTS: Thirty reprints of a review will be supplied free to its senior author and additional reprints may be purchased in lots of 100

REPORT OF THE ISMAR ELECTION COMMITTEE

1983

Dear ISMAR Member:

Thanks to each of you who participated in the recent election of our society. As such votes go, we feel that the submission of 185 valid ballots represents a very favorable return. Of these, there were only 14 negative votes on the proposed Constitution. Thus, the positive vote far surpassed the two-thirds majority of submitted ballots required for approval. A good fraction of these 14 negative votes were simply matters of omission. You will recall that in our cover letter with the ballot, it was mentioned that failure to vote would be considered a "no" vote. From the voting pattern we have reason to believe that there were some who did not take note of this point, thus leading to a larger than intended "no" vote.

In the only contested election, that for Secretary General, Professor Fiat received 114 votes to 49 for Professor Markley. The remaining 22 ballots had either no vote for either candidate or a vote for both candidates. These irregular ballots were, of course, not counted.

Less than 10 "no" votes were cast for any one of the candidates for President, Vice-President, or Treasurer. Thus, an overwhelmingly positive majority of votes were cast in favor of the nominated candidates.

The largest number of "no" votes for any Council candidate was 68. Thus, all candidates received more than the majority "yes" vote required for election.

In summary then, the results of the election are as following: (1) The Constitution was overwhelmingly approved; (2) The new officers are: E. R. Andrew (President), C. P. Slichter (Vice-President), D. Fiat (Secretary-General), and C. P. Poole (Treasurer); (3) The new Council is: E. R. Andrew (Gainesville), G. J. Bene (Geneve), R. Blinc (Ljubljana), M. Bloom (Vancouver), W. S. Brey, Jr. (Gainesville), V. Bystrov (Moscow), F. Conti (Rome), R. R. Ernst (Zurich), D. Fiat (Chicago), S. Forsen (Lund), S. Fujiwara (Urawa), M. Goldman (Gif sur Yvette), H. S. Gutowsky (Urbana), R. K. Harris (Norwich), K. H. Hausser (Heidelberg), J. Hennel (Krakow), O. Jardetzky (Stanford), J. Jeener (Brussels), V. J. Kowalewski (Buenos Aires), P. C. Lauterbur (Stony Brook), E. Lippmaa (Tallin), A. Losche (Leipzig), P. T. Narasimhan (Kanpur), D. Norberg (St. Louis), H. Pfeifer (Leipzig), A. Pines (Berkeley), L. W. Reeves (Waterloo), R. Richards (Oxford), J. D. Roberts (Altadena), J. Smidt (Delft), J. Stankowsky (Poznan), I. Ursu (Rome), N. V. Vugman (Rio de Janeiro), W. von Philipsborn (Zurich), and H. C. Wolf (Stuttgart).

Thank you again, each one who participated in this election so important to the forward thrust of ISMAR.

Sincerely,
The Elections Committee:
J. L. Bjorkstam (Chairman),
M. Bloom, and E. L. Hahn

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BULLETIN OF MAGNETIC RESONANCE

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Nuclear Quadrupole Resonance*

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A resonance phenomenon which is closely related to NMR is nuclear quadrupole resonance (NQR), which was discovered in 1950 by Dehmelt and Krüger. All nuclei with a spin ≥ 1 possess in addition to the magnetic moment, an electric quadrupole moment eQ , which measures the deviation of the distribution of the positive charge in the nucleus from spherical symmetry. While e is the elementary charge, $Q = \int r^2 (3\cos^2\theta - 1)\rho d\tau$ has the dimension cm^2 and is defined to be positive for a cigar-shaped nucleus and negative for a disc-shaped nucleus (ρ is the charge density per volume, r is the distance of the volume element $d\tau$ from the origin, and θ is the angle between the radius vector and the axis of quantization of the spins).

In non-cubic crystals and in almost all molecules the nuclei are situated in an inhomogeneous electric field q which is given by the second derivative of the electric potential in a given direction, for instance, the direction z of a chemical bond, $q_{ZZ} = \delta^2 V / z^2 = V_{ZZ}$. A nucleus with a quadrupole moment can orient itself only in certain discrete angles with respect to the field gradient, each of which corresponds to a discrete energy value. The quadrupole coupling constant $e^2 qQ$ is the quantity which is measured directly in an NQR experiment. If the electric field gradient is not axially symmetric with respect to the z -axis, the deviation is given by the asymmetry parameter $\eta = (V_{YY} - V_{XX}) / V_{ZZ}$.

In NQR magnetic dipole transitions are induced, in analogy to NMR, by a magnetic radiofrequency field which fulfills the resonance condition $h\nu = \Delta E_Q$ between energy levels E , the

energy of which is determined by electric interactions. If the nuclear quadrupole moment eQ is known, a measurement of NQR renders the value of the field gradient q , and hence information on quantities like ionic character and hybridization of a bond, which are correlated to q . The measurement of NQR is facilitated by the fact that it can be performed in a polycrystalline solid; on the other hand, it can be tedious to search for the absorption lines in a large frequency region since the frequency to be expected can be predicted only very approximately in many cases. When investigating nuclei with a small quadrupole moment such as deuterons where the quadrupole interaction is typically in the range between 100 and 200 kHz, the sensitivity becomes very low. In this case it is much more recommendable to measure the quadrupole splitting in an NMR experiment. If this measurement is performed with single crystals, it becomes possible to determine the complete quadrupole tensor and its orientation with respect to the molecular frame. Since the orientation of the quadrupole tensor is closely related to the bond direction in molecular crystals, measurements of the quadrupole interaction renders information on structural parameters which is frequently considerably more precise than X-ray data particularly for deuterons.

After this general introduction I would like to discuss two experiments which were recently performed in our Institute. The first one concerns the investigation of sodium nitroprusside SNP, $\text{Na}_2\text{Fe}(\text{CN})_5\text{NO} \cdot 2\text{H}_2\text{O}$. I shall restrict myself to the quadrupole interaction of the ^{14}N nucleus.

Why did we select SNP for our studies? The recent discovery by Mössbauer spectroscopy of a new state in this crystal has attracted a considerable amount of interest in this compound (1-5). The Mössbauer spectrum of Fe normal SNP consists of one pair of quadrupolar split lines. If

*Presented at the 6th Specialized Colloque Ampere on "Quadrupole Interactions and Spatially Resolved NMR in Solids," Crete, Greece, September 12-17, 1983.

a crystal of SNP is irradiated with intense laser light at a temperature, $T \leq 150$ K under appropriate polarization conditions (1), a new state develops which differs in two properties from the normal state. First, one observes a change of the optical absorption spectrum of SNP which can be seen with the bare eye as a bleaching of the crystal. Simultaneously with this bleaching two extra Mössbauer lines appear which correspond to a quadrupole interaction of the ^{57}Fe nucleus which is about 40% larger than in the normal state (Figure 1). This new state seems to persist indefinitely even after switching off the laser as

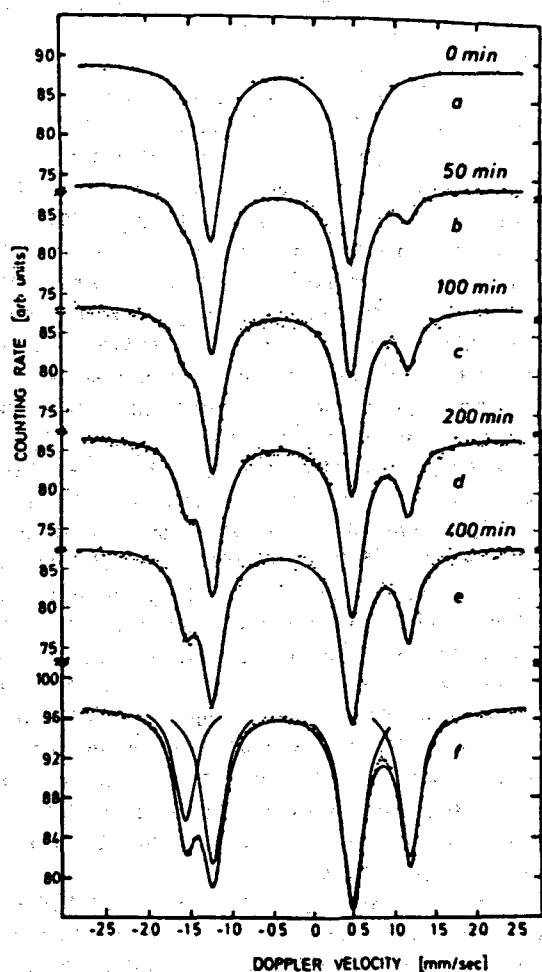


Figure 1. Mössbauer spectrum of sodium nitroprusside at 100 K with increasing irradiation time (U. Hauser et al.).

long as the temperature is kept below 150 K.

The nature of this new state in SNP in terms of its electronic and nuclear configuration is still unknown. However, it may safely be expected that one of the principal axes of the electric field gradient (EFG) is parallel to a good approximation to the CN or NO bond direction. Any rearrangement of the subgroups (CN, NO) of SNP are expected to affect the orientation of these subgroups and hence to manifest itself in the quadrupole interaction of the NMR spectrum. In addition, any change in the electronic configuration of these groups is expected to influence the quadrupole coupling constants QCC of the respective N nucleus.

In a first step we have measured the full quadrupole coupling tensors at all the nitrogen sites in the normal state of SNP (6). This is, of course, a necessary basis of the study of the new state by NMR, but it turned out that it is interesting by itself because it demonstrates a remarkable sensitivity of nitrogen NMR to orientations of molecular subgroups in crystals.

For a better understanding of the NMR results, let us first have a look at the structure of SNP as determined by Manoharan and Hamilton in 1963 (7) and refined by Bottemley and White in 1979 (8) (Figure 2). Crystals of SNP are orthorhombic, space group P_{nnm} , $a = 6.198$, $b = 11.897$, $c = 15.557$, with two pairs of SNP complexes $\text{Na}_2\text{Fe}(\text{CN})_5\text{NO} \cdot 2\text{H}_2\text{O}$ per unit cell (Figure 2). The total number of ^{14}N nuclei per unit cell is 24, but since the two complexes in each cell are related by inversion symmetry there are only 12 magnetically nonequivalent sites in an SNP crystal; hence the ^{14}N spectra of a single crystal of SNP consists in general of 12 pairs of resonance lines.

Furthermore, all of the complexes in SNP are related by twofold screw axes which leads to a further reduction of the resonance lines in certain planes. Hence it suffices when discussing the results to consider one single complex. Moreover, nitrogens N_2 and N_{2m} and N_3 and N_{3m} in each NP complex are related by a mirror plane which reduces the number of independent ^{14}N quadrupole coupling tensors e^2qQ/h to four. We designate them q_{N_0} , q_{N_1} , q_{N_2} , and q_{N_3} . Note that the NO-bond direction is not perpendicular to the plane spanned by the N_2 and N_3 nitrogens.

The single crystals of SNP were provided by Professor Haussuhl of Köln University, which we gratefully acknowledge. The NMR spectra were recorded by FT techniques using a superconducting magnet with a field $B = 8.4$ Tesla, corresponding to a Larmor frequency $\nu_L(^{14}\text{N}) = 25.7$ MHz. The full ^{14}N spectrum spans a range

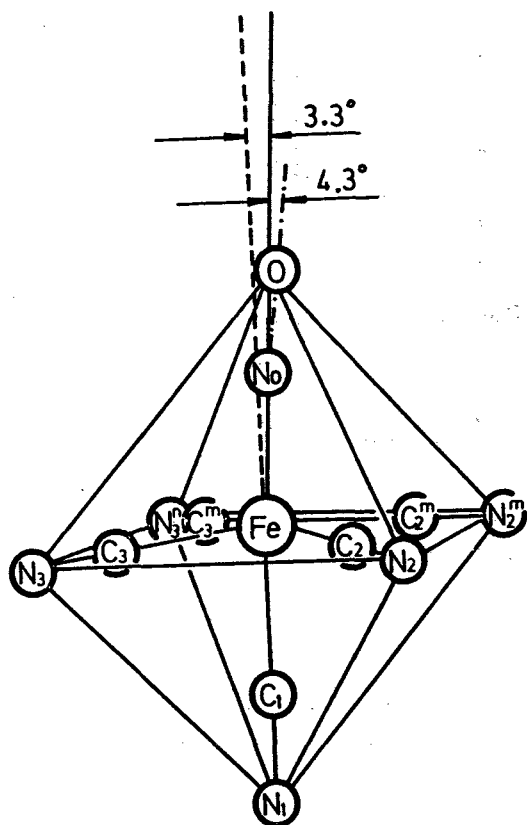


Figure 2. Structure of the nitroprusside ion $[\text{Fe}(\text{CN})_5\text{NO}]^{2-}$.

of up to 5 MHz. Since the spectral range of our $3 \mu\text{s}$ pulse as well as the bandwidths of the probe and receiver are far less than 5 MHz, the full ^{14}N spectrum had to be recorded in spectral slices. (Figure 3 shows how different slice spectra with ample overlap were combined to a full spectrum.)

The very marked sensitivity of the nitrogen NMR to orientations of molecular subgroups is illustrated in Figure 4. It shows a part of the ^{14}N spectra when B_0 is almost (a and b) and exactly (c) parallel to the c-axis of the crystal. We estimate on the basis of the width of the ^{14}N lines which is about 3 KHz, and on the slope of the quadrupole splittings versus rotation angle that B_0 must be parallel to c to better than 0.03 for the quadrupoles of lines to fully coalesce.

The rotation patterns of the line splittings of the ^{14}N NMR spectra are shown in Figure 5. We are now faced with the task of determining which of the traces in the "a", "b", and "c"

rotation patterns shown in the figure belongs to a certain ^{14}N site. This task is easy for N_0 and N_1 . Since their bond directions are perpendicular to the c-axis, the traces belonging to N_0 and N_1 should pass through an extremum at $B_0 \parallel c$. The "a"- and "b"-rotation patterns contain indeed two traces which possess these properties. Knowing their values for $B_0 \parallel a$ and $B_0 \parallel b$ enables us to identify the traces belonging to N_0 and N_1 in the "c"-rotation pattern as well. However, at this stage we do not know which belongs to N_0 and which to N_1 . By an analogous procedure we could attribute the rotation patterns which belong to the N_2 and N_3 sites and to work out the quadrupole coupling components and the asymmetry parameters; they are compiled in Table 1. A comparison of the components in the second row of Table 1 with the sets of principal components of N_2 and N_3 indicates that this set must belong to the quadrupole coupling tensor at the N_1 site.

The next step would be to record the ^{14}N NMR spectra of the new state and to evaluate the ^{14}N electric field gradients in this state. For doing this we are faced with the problem that we have to work with thin discs of single crystals, while the work in the normal state discussed so far was performed using rods of a diameter of $d = 10 \text{ mm}$ and a length l of about 15-20 mm. In the beginning we used discs of a thickness below 1 mm because with the light intensity which we considered tolerable for the crystal (200 mW/cm^2), it takes already at least a day to populate 90% of the maximum population of the new state (50% of the NP complexes). Such thin slices require, because of the low sensitivity of ^{14}N NMR, more than 1000 FIDs in order to achieve the same signal-to-noise ratio as obtained with the large sample with a single shot. After an irradiation time $\sim 3 \text{ h}$ at 120 K the ^{14}N NMR absorption spectrum vanished. After reheating the sample to rt the original spectrum of the normal state reappeared showing that the change of the ^{14}N NMR spectrum is a reversible process analogous to the changes in the optical transmission and in the ^{57}Fe Mössbauer spectrum. Although it is possible with relaxation times of the order of seconds to make measurements with more than a thousand FIDs, it is rather tedious. Hence we have tried to use thicker discs of about 5 mm length and increased the light intensity to about 700 mW. The result of this experiment was similar; after an irradiation time of about 24 h the intensity of the ^{14}N NMR spectrum was strongly reduced although it did not vanish completely with thicker samples.

Our working hypothesis for this behaviour is

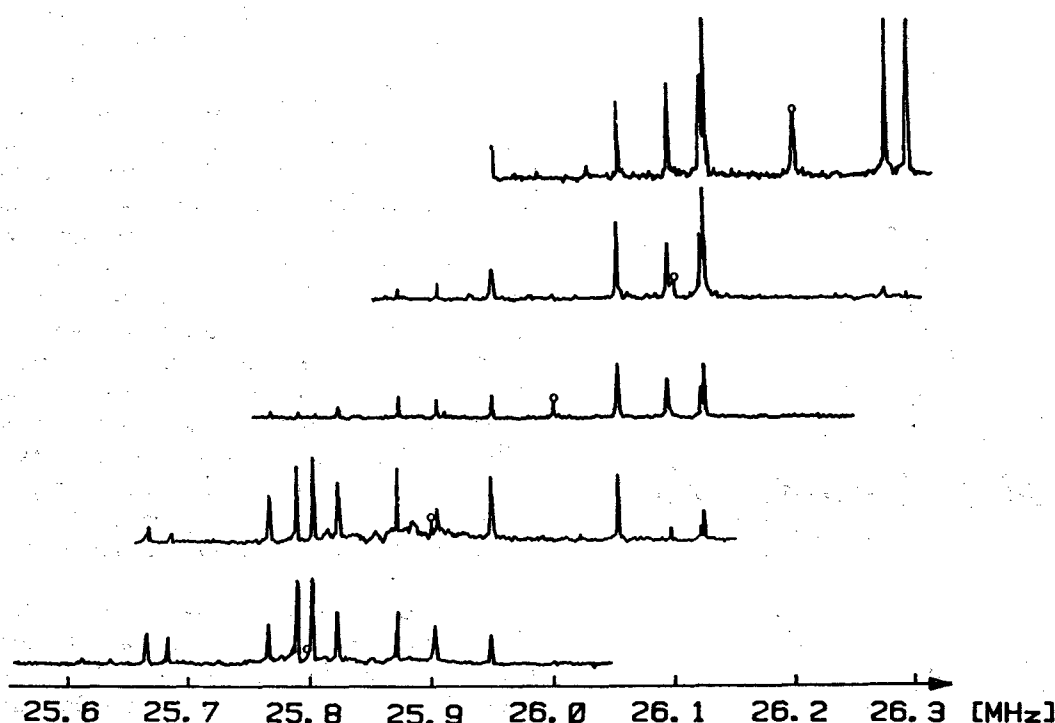


Figure 3. ^{14}N slices spectra of sodium nitroprusside (SNP) at 25.7 MHz ($B_0 = 8.4$ Tesla)..

Table 1.

^{14}N Quadrupole Coupling Tensor Components
of Sodium Nitroprusside (SNP).

Site	$e^2q_{11}Q/h$ (MHz)	$e^2q_{22}Q/h$ (MHz)	$e^2q_{33}Q/h$ (MHz)	$\eta = \frac{q_{22} - q_{11}}{q_{33}}$
N_0	1.155	1.084	2.239	0.032
N_1	1.791	1.773	3.560	0.005
N_2	1.867	1.651	3.489	0.062
N_3	1.897	1.756	3.635	0.038

at present that the "new state" is paramagnetic and that the ^{14}N NMR lines are broadened beyond detectability by their interaction with the

unpaired electrons. This hypothesis is, however, not in agreement with preliminary results obtained by ESR in Professor Elschner's



Figure 4. ^{14}N spectra of SNP when B_0 is near (a and b) and exactly (c) parallel to the c -axis of the crystal.

Institute in Darmstadt, which seem to indicate that the new state is not paramagnetic. Hence it is fair to say that the disappearance of the ^{14}N NMR spectrum, when generating the new state, is not understood.

The second example which I would like to discuss is the quadrupole coupling tensor of the ^{17}O nucleus in benzophenone (BPh), both in the ground state and in the excited state. In order to increase the sensitivity of our measurements we used BPh molecules in which the rare ^{17}O isotope was enriched from 0.037 to 50%.

In order to interpret our results we require two different coordinate systems as shown in Figure 6. The first (xyz) is a coordinate system defined by the planar $-\text{C}_1-\text{C}(\text{O})-\text{C}_1'-$ fragment of BPh with z parallel to the $\text{C}=\text{O}$ bond, in agreement with the C_2 symmetry of the molecule, y in the plane of this fragment perpendicular to the $\text{C}=\text{O}$ bond, and x normal to this plane. The second (q_{11}, q_{22}, q_{33}) is the principal axes system of the ^{17}O quadrupole coupling tensor. Further coordinate systems, such as the symmetry axes of the crystal and the principal axes of the fine structure tensor of BPh are not relevant for the discussions within the scope of this article.

The ground state of BPh was studied in our Institute by U. Haeberlen and W. Scheubel with a single crystal of BPh using NMR at high field (84.5 kG $\sim$ 48 MHz). The experimental procedure and the evaluation of the data have been separately presented as a poster at this

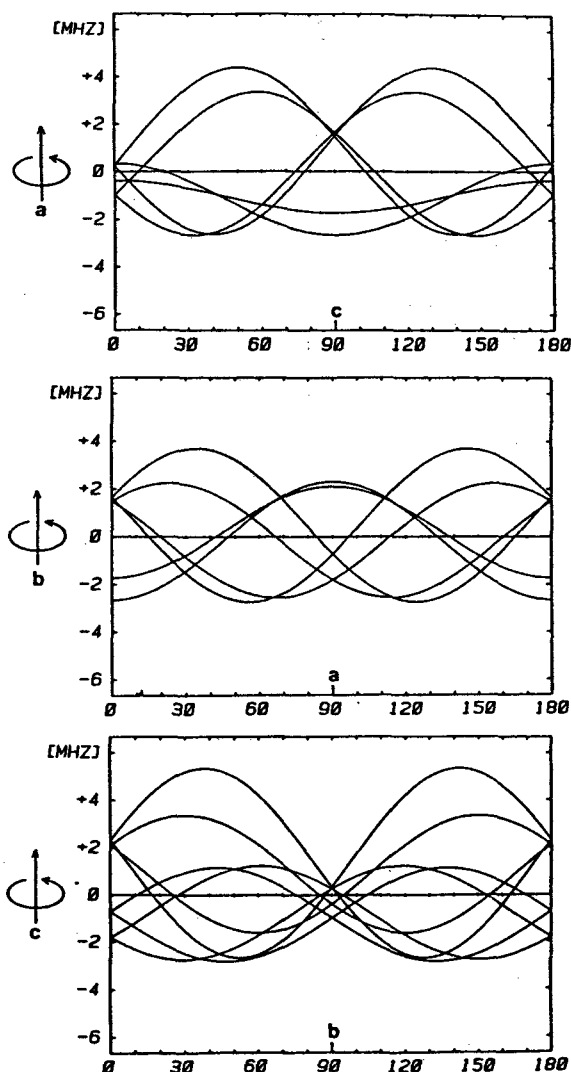


Figure 5. Orientational dependence of the quadrupole splittings e^2qQ of the ^{14}N resonances in SNP.

conference. The results are summarized in Figure 7. The value of $e^2qQ/h = 10.808$ MHz, $\eta = 0.369$. The deviation of the main axis of the quadrupole coupling tensor from the molecular symmetry axes are not more than one degree, in particular the q_{22} -axis is parallel to the $\text{C}=\text{O}$ bond direction within the experimental error of 0.4. Note that the tensor component $e^2q_{22}Q/h$ parallel to the $\text{C}-\text{O}$ bond direction is not the largest one as one might expect, but the smallest.

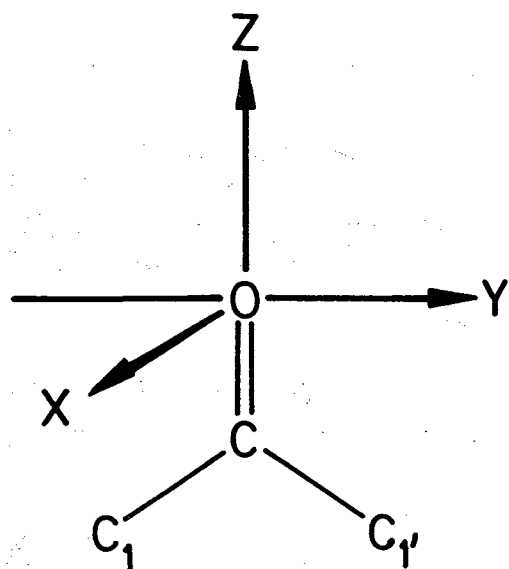


Figure 6. Fragment of benzophenone defining a local C_{2v} symmetry.

We shall later compare the ^{17}O quadrupole couple tensor and its orientation with respect to the molecular framework in the ground state and in the excited state of BPh.

These investigations were performed with a single crystal of BPh at rt. In distinction to these experimental conditions K. P. Dinse and G. Wackerle of our Institute have investigated a mixed crystal of BPh in dibromodiphenyl ether at 1.2 K using Optical Nuclear Double Resonance (ONDOR) (9). They used a stabilized single mode laser with a short-term stability of a few hundred KHz and a power incident on the sample of 30 mW in combination with a radiofrequency power of 1 W. This stability of the laser is sufficient since recently the same authors have succeeded in obtaining the first photon echo of a very similar mixed crystal, i.e. dibromo-BPh in DDE; with this method it was possible to determine T_2 to be $1\mu\text{s}$, corresponding to a linewidth of the order of 1 MHz in an inhomogeneous line of about 50 GHz. In other words the homogeneous linewidth is three or four times larger than the jitter of the laser. The ^{17}O enriched synthesis and the growing of the mixed crystals was done in our Institute by H. Zimmermann starting

Table 2.

Benzophenone- ^{17}O Quadrupole Coupling Tensor Components.

Molecular State	Experimental Method	$e^2q_{11}Q/h$ (MHz)	$e^2q_{22}Q/h$ (MHz)	$e^2q_{33}Q/h$ (MHz)	Asymmetry Parameter $\eta = \frac{q_{22} - q_{11}}{q_{33}}$
Ground State	NMR ^a	(-) 7.396	(-) 3.412	(+) 10.808	0.369
	Laser-RF Double Res. ^b	(-) 7.596	(-) 3.437	(+) 11.033	0.377
Excited State	ODENDOR ^{c,d}	+ 8.70	- 0.86	- 7.80	0.80

a) Scheubel et al., 6th Spec. Coll. Ampère. b) Reference (9). c) Wackerle et al., *J. Chem. Phys.* **76** 2275 (1982). d) Principal tensor axes rotated by 20° about the C=O bond direction.

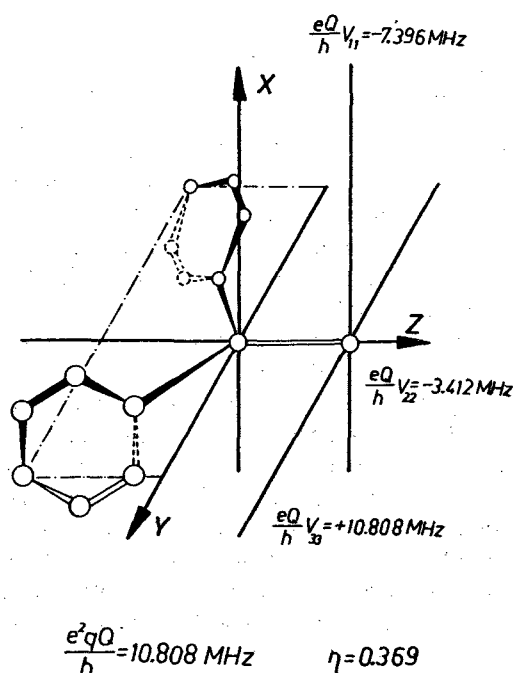


Figure 7. EFG tensor at the ^{17}O site of benzophenone.

with a guest concentration of BPh of 2000 ppm, although one should keep in mind that the final guest concentration is typically one order of magnitude lower as was verified by the GLC analysis.

The results obtained with the ONDOR method, i.e. by monitoring the phosphorescence when changing the population of the nuclear sublevels by irradiating the appropriate radiofrequency, are shown in Table 2, together with those obtained by NMR in a neat single crystal at rt. Since this is a zero-field experiment without an axis of preference, it is not possible to determine the orientation of the quadrupole tensor components with respect to the molecular framework. The difference of about 2% is mainly due to the temperature difference since the measurements by NMR of neat single crystals were performed at rt while the ONDOR measurements were performed at 1.2 K with mixed crystals, the latter difference probably being less important than the temperature. The ONDOR results are more suitable for comparison with the results in the photoexcited triplet state since they are obtained as well with mixed crystals at 1.2

K. Considering the small difference it can be safely assumed that the orientation of the quadrupole coupling tensor with respect to the molecular framework does not change with temperature.

The measurements of the quadrupole interaction in the excited triplet state were performed in our Institute by K. P. Dinse and G. Wackerle in collaboration with D. Pratt using Optical Detection of Magnetic Resonance (ODMR) and Optical Detection of Electron Nuclear Double Resonance (ODENDOR) both in zero field and in high magnetic field (10). The samples used were perdeuterated ^{17}O -enriched BPh in DDE in order to reduce the linewidth. Figure 8 shows the phosphorescence spectrum of this mixed crystal

BENZOPHENONE PHOSPHORESCENCE

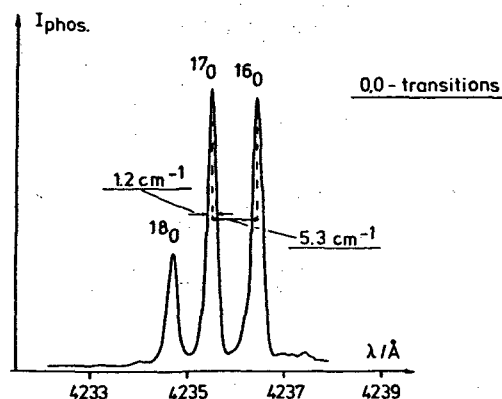


Figure 8. 500 ppm ^{17}O -benzophenone- d_{10} in a DDE single crystal. $[^{17}\text{O}] = 50\%$. Monochromator resolution $\Delta = 0.9 \text{ cm}^{-1}$, $T = 1.2 \text{ K}$.

in the vicinity of the (0,0) band at 1.2 K. The relative intensities of the three bands correspond to the isotopic enrichment factors.

Since the most important results, i.e. the quadrupole coupling tensor and its orientation with respect to the molecular framework including the signs, were obtained with the ODENDOR experiment, I shall restrict myself here to the discussion of this experiment. Dinse and Wackerle observed in zero field the change in the ODMR intensity when sweeping the radiofrequency in the range from 0-30 MHz. For the

high-field experiments they used a spectrometer which was developed in our Institute for measuring microwave induced optical nuclear polarization. The crystal was mounted on a cone wheel which could be turned by a full 2π angle around a vertical axis which could be oriented arbitrarily with respect to B_0 . It was placed into a cylindrical $TE_{1,12}$ X-band cavity into which an rf coil with 5 turns and a diameter of 13 mm was inserted.

The results of the ODENDOR experiments are given in Figure 9. The ODMR spectrum

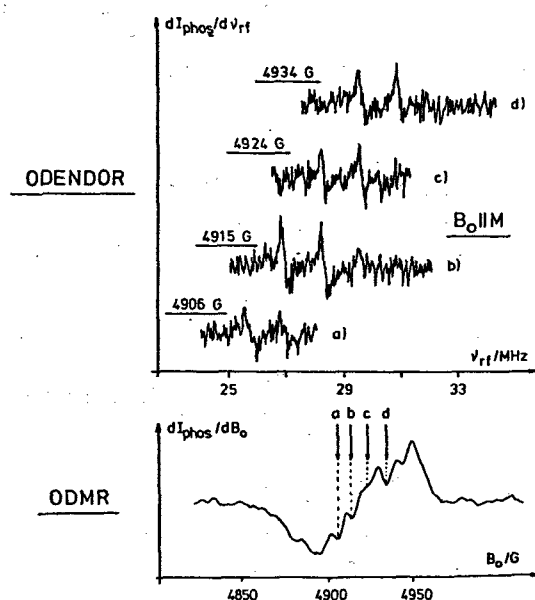


Figure 9. Magnetic resonance of ^{17}O -benzophenone- d_{10} .

consists of six hyperfine components with a separation of about 26 MHz which are not well resolved at high power. The field was then positioned at one of the resonance fields and the change in the ODMR intensity was monitored when the rf field was swept from 25 to 35 MHz. Five $\Delta m = \pm 1$ ENDOR transitions within the $m_S = +1$ sublevel were obtained in agreement with expectations for a $S = 1$, $I = 5/2$ system with differences between the first-order hyperfine coupling of 1.36 ± 0.01 MHz, which were found to be equal within experimental error.

The evaluation of these experimental data leads to the quadrupole coupling tensor components shown in Table 2, together with the

quadrupole coupling tensor components in the ground state of BPh discussed above. As mentioned before, the results for the quadrupole coupling tensor in the ground state obtained with NMR and with ONDOR differ by only 2%. This difference is due to the different temperatures—remember that the NMR measurements were performed at rt and the ONDOR measurements at 1.2 K. The signs of the quadrupole coupling tensor components are set in parenthesis since they are not determined experimentally but are the result of INDO calculations.

The most interesting result given in Table 2 is the striking difference of the quadrupole coupling tensor in the excited triplet state as compared to the ground state. The smallest component is still along the molecular z-axis, parallel to the C=O bond direction, but it is close to zero, leading, of course, to a very large asymmetry parameter $\eta = 0.80$. Note that the signs are not set in parenthesis because they could be determined experimentally. The largest component is in the excited triplet state along the $q_{1,1}$ axis of the quadrupole coupling tensor. However, it is not anymore in the plane of the fragment of the three carbon atoms and the oxygen atom, Figure 6, but the $q_{1,1}$ and $q_{3,3}$ axes are rotated around the C=O bond direction by 20° .

The quadrupole data show that the first excited triplet state is an π^* state in which one electron is transferred from the oxygen 2p-type lone pair orbital to a π^* orbital. The change in the direction of the largest component of the field gradient tensor is consistent with this description. However, a quantitative analysis shows that considerably less than one electron (about 2/3) is transferred out of the n orbital on excitation.

BPh is not a planar molecule. Due to steric hindrance the benzene rings are twisted in the ground state by 28° out of the plane of the fragment $-\text{C}_1-\text{C}(\text{O})-\text{C}_1'$. The orientation of the quadrupole tensor shows that this out-of-plane twisting of the benzene rings in a conrotatory fashion causes a rotation of the n- and π -type orbitals of the oxygen atom as well leading to a more favorable interaction of the n orbital with the π orbitals of the rings. This result was neither experimentally nor theoretically anticipated; it proves that triplet benzophenone is not a pure π^* state: since both the n and π orbitals of the carbonyl group are mixed with the aromatic π system, it has both π^* and $\pi\pi^*$ character in agreement with the so far unexplained fact that the transition to the excited state is much less forbidden than one would expect for a transition to a pure π^* state. However, this is more

theoretical chemistry than magnetic resonance and I shall not discuss it any further.

Let me finish by summarizing the main conclusion of this paper: quadrupole interactions in the ground state and in the excited state of molecules can be investigated in addition to pure NQR by NMR, ODMR, ONDOR, and ODENDOR. The results, either by themselves or in combination with other data, in particular the hyperfine interaction between the quadrupole nuclei and the unpaired electrons of the excited states, provide interesting information on the electronic structure of these molecules both in the ground state and in the excited state.

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Nuclear Quadrupole Resonance Studies of Schiff Bases*

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I. INTRODUCTION

Crystalline anils (Schiff bases, I) undergo photochromism or thermochromism by hydrogen transfer and present common features in their structures and reaction mechanisms:

- 1) The intramolecular hydrogen-transfer step occurs via a six-membered ring transition state.
- 2) The hydrogen-transfer produces quinoid structures.
- 3) The thermally stable forms are the *ortho*-OH substituted aromatic structures.
- 4) One or more processes occur to cause some stabilization of the photocolored species formed by the endothermic photolysis step.
- 5) The thermochromic compounds display planar structures while the photochromic ones, non-planar structures.
- 6) Both photochromic and thermochromic compounds show (in their transfer reaction) a high degree of reversibility.

Thus, if we prepare a thin polycrystalline film between two quartz plates, the photochromic phenomenon is illustrated in Figure 1A with the compound having X=H, Y=2-Cl, and thermochromism is illustrated in Figure 1B with the compound having X=5'-Cl, Y=H, i.e. reversible color change in the spectrum as a result of

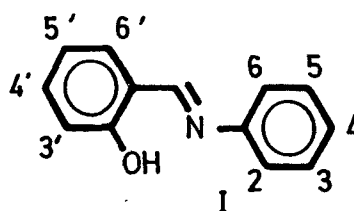


photo-irradiation or of variation in temperature

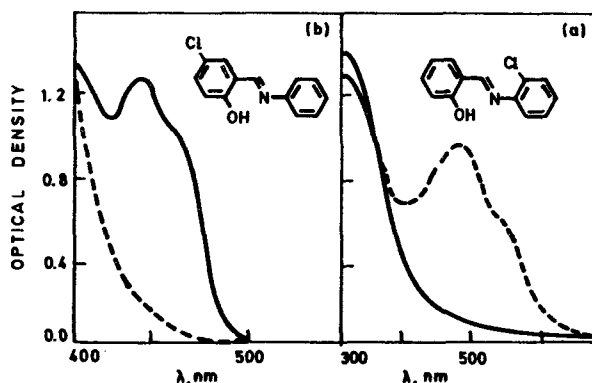


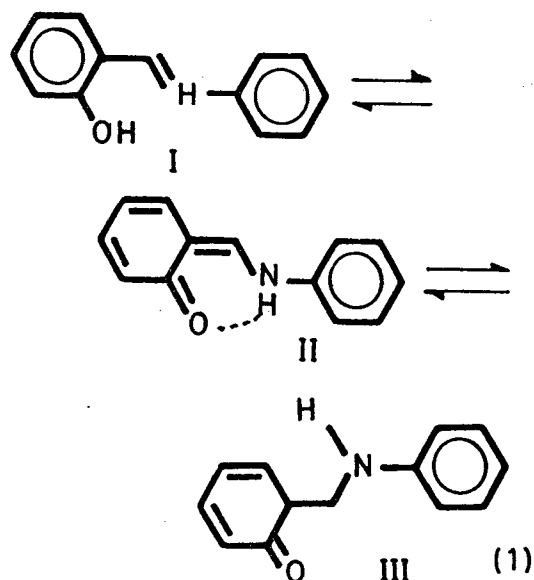
Figure 1(A). Photochromism of salicylidene-2-chloroaniline, before (-) and after (---) illumination, and (B) thermochromism of 5'-chlorosalicylideneaniline at rt (-) and liquid nitrogen temperature (---).

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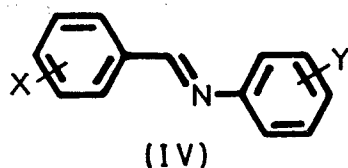
(1,2).

The interpretation of the color formation is as follows (3): there is a temperature sensitive

equilibrium in the crystal between two tautomers of the molecule, one with the chelating hydrogen covalently bonded to the oxygen, the "OH-form" (I), and the "NH-form" (II) with the hydrogen



bonded to the nitrogen (equation 1). The "NH-form" absorbs at longer wavelengths; raising the temperature increases the population of this form and thus causes a deepening of color. The intramolecular hydrogen transfer can occur in either the ground or excited electronic state. In contrast, a high energy is required for hydrogen transfer in the ground electronic state of molecules in photochromic crystals because of the non-planarity and, as a result, no absorption attributable to the NH-forms is observed. Hydrogen transfer can occur, however, in the excited state and the crystal is sufficiently open (non-planar molecules) to permit a subsequent geometric isomerization which leads to the colored photo-product, III. It was further claimed (1) that neither photochromism or thermochromism or the associated "chromo-isomerism" can be observed in the absence of the *ortho*-OH group and, therefore, benzylideneaniline and its derivatives IV should be inactive towards temperature



and light. Therefore, the active compounds have different solid phases with different dynamic states, and the inactive compounds have only one solid phase in which molecular motions are restricted to lattice or torsional oscillations. Thus, we expected that by examining a number of solid Schiff bases with the NQR technique, we could differentiate motions such as *enol-keto* tautomerization or *cis-trans* isomerization in addition to the temperature dependent shifts in the resonance frequency predicted by the Bayer (4) theory. It should be mentioned here that in spite of the continued efforts no clear direct evidence on the nature of the photo-induced colored species II or III have been obtained in the solid state. Thus, the color changes in thermochromic crystals ($X=5'-Cl$, $Y=H$) are not accompanied by an observable change in the crystal structure as determined by X-ray diffraction (5).

To achieve our goal we performed two kinds of measurements: we measured thermochromic compounds at various temperatures and photochromic compounds before and after irradiation. The nuclei measured were ^{35}Cl at various positions of the two rings and ^{14}N at the bridge of the molecules ($C=N$) and in the *ortho*-position of the aniline ring, that is in salicylidene-2-aminopyridines.

II. EXPERIMENTAL

The compounds used in this work were synthesized by direct condensation of the appropriate salicylaldehyde with the appropriate aniline or amino pyridine in ethanol, followed by repeated recrystallization from the same solvent. IR spectra, melting points, and elemental analysis were utilized to establish the purity of the compounds. Table 1 contains the compounds used for the NQR measurements together with their properties and the available structural information.

The ^{35}Cl NQR frequencies were measured by means of two spectrometers: one of the type described by Dean and Pollak (6) and another of the DECCA RADAR. These instruments gave a signal-to-noise ratio of about 20, which in most cases, decreased with a decrease in temperature. Thus, in many cases the temperature dependence could not be studied over the whole desired range because of loss of the signal.

The photochromic compounds were measured before and after irradiation with light of $\lambda = 365$ nm, that is in their yellow and red form at liquid nitrogen temperature; this was possible because when these compounds are irradiated at a temperature at which the yield of color is high (rt),

Table 1. Salicylideneanilines and Salicylideneaminopyridines

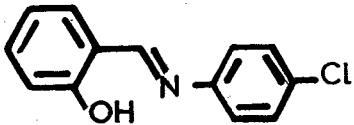
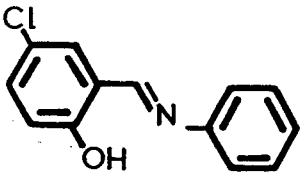
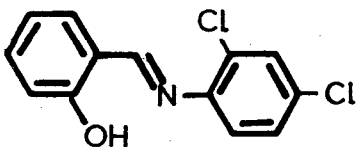
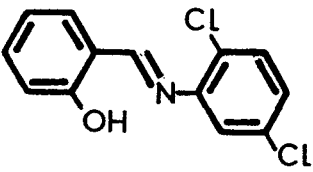
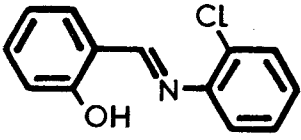
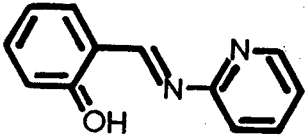
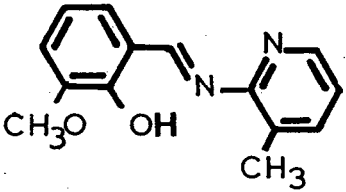
No.	Compound	mp (K)	Structure	Effect of Heat or Light
1		377	Planar ⁵	Thermochromic
2		383	Planar ⁵	Thermochromic
3		348	-	Thermochromic
4		367	-	Thermochromic
5		356	Non-planar ^{1 3}	Photochromic
6		330	Planar ^{1 3}	Thermochromic
7		400	Planar ^{1 3}	Thermochromic

Table 2. Pure Quadrupole Resonance (^{35}Cl and ^{14}N) of
Salicylidineanilines and Salicylideneaminopyridines

Compound	Observed Frequencies			
	^{35}Cl (MHz)	^{14}N (KHz)		
	290 K	77 K	298 K	170 K
1	34.024(296) ^a	34.520		
2	34.559(300)	34.900	$\nu_+ = 2890$ $\nu_- = 2590$ $\nu_+ = 3260$ $\nu_- = 2780$	$\nu_+ = 3740$ $\nu_- = 2960$
3	34.720(270)	35.132		
4	34.275	34.650		
5	34.410	35.040	$\nu_+ = 2715^b$ $\nu_- = 2625$	$\nu_+ = 2735^c$ $\nu_- = 2630$ $\nu_+ = 2915$ $\nu_- = 2830$
6			$\nu_+ = 2800$ $\nu_- = 2680$ $\nu_+ = 3535$ $\nu_- = 2968$	$\nu_+ = 3594(153)$ $\nu_- = 3000$
7			$\nu_+ = 2840$ $\nu_- = 2700$ $\nu_+ = 3600$ $\nu_- = 3000$	$\nu_+ = 3628(188)$ $\nu_- = 3024$

a) In parantheses is shown the temperature when different from 290 K and 170 K.

b) Before irradiation and c) after irradiation.

III. RESULTS AND DISCUSSION

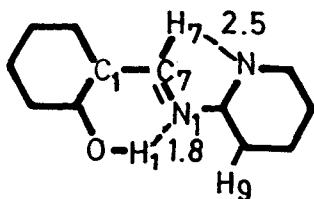


Figure 2. Bond angles (°) and distance (Å) for salicylidene-2-aminopyridine.

and are subsequently cooled to liquid nitrogen temperature, the photo-color is found to persist without loss of intensity.

The rather low ^{14}N NQR frequencies were measured with the help of a proton-nitrogen double resonance technique based on the solid effect (7). The method is based on rf-induced coupling between the dipolar frame of the protons and the rotating frame of the ^{14}N nuclei.

The NQR spectrum of ^{35}Cl in the chlorine substituted compounds listed in Table 1 has been studied over the temperature range 77 to 298 K (8). Although four of these compounds, 1-4, display thermochromic phenomena, i.e. a serious change of color with temperature, there was no evidence of a phase transition or discontinuity in the plot of NQR frequency vs temperature. We therefore give in Table 2 only the observed ^{35}Cl frequencies at 290 and 77 K. The inability to observe differences in the above measurements, which could be attributed to the proton transfer from the *ortho*-OH group to the nitrogen of the C=N bond (equation 1), is attributed to the fact that the charge distribution of the nitrogen atoms is outside the radius of the chlorine atom. Therefore, the contribution to the electric field gradient is less than 1% of that due to a typical p-valence electron in the case of the halogens (9). In order to gain information about the proton transfer we studied the changes in the ^{14}N spectra of photochromic salicylidene-2-chloroaniline induced by UV light to compare with the changes induced by temperature variations in the ^{14}N NQR spectra

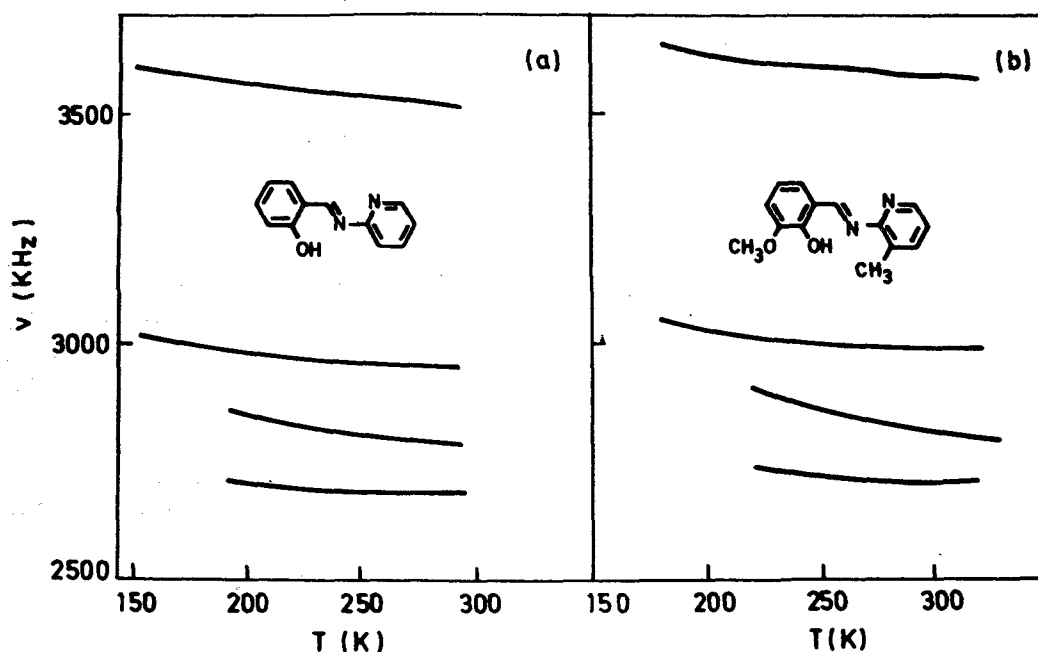
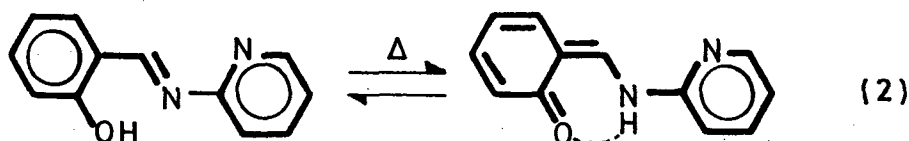


Figure 3. Frequency vs. temperature curves for (A) salicylidene-2-aminopyridine and (B) 3'-methoxysalicylidene-2-amino-3-methylpyridine.



of thermochromic 5'-chlorosalicylideneaniline (10). Table 2 shows the effect of temperature on the pure ^{14}N NQR spectra at 170 and 310 K. At low temperatures we observed two spectral lines in the NQR spectrum of ^{14}N (spin, 1) and therefore, one chemically non-equivalent ^{14}N sites per unit cell. The results obtained at high temperatures are evidently a superposition of the low and high temperature spectra, thus demonstrating the presence of a keto-enol equilibrium in solid 5'-chlorosalicylideneaniline (equation 1). Table 2 shows also the effect of irradiation on the pure ^{14}N NQR spectra of salicylidene-2-chloroaniline before and after irradiation. The results obtained in this case are also a superposition of the spectra before and after irradiation, demonstrating again the presence of the keto and enol forms (equation 1). It should be emphasized here that we succeeded in observing (11) in the case of 5'-chlorosalicylideneaniline at 295 all three resonances (V_+ , V_- , and V_0), and this allowed us an unambiguous pairing of the observed lines in the two distinct crystalline sites present.

The results with the salicylideneaminopyridines are not conclusive and are more complicated. These compounds contain one type of nitrogen atom (two-fold coordination) in their enol form and two types of nitrogen atoms (two-fold and three-fold coordination) in their keto form (equation 2). Therefore, one expects four frequency signals in the enol form and eight in the case of the equilibrium of equation 2. It should be pointed out that all the examined molecules of the salicylidene-2-aminopyridines are thermochromic in the solid state (12). This generality can be explained by examining the crystal and molecular structure of this class of compounds. Thus, salicylidene-2-aminopyridine, 5'-bromosalicylidene-2-aminopyridine, 5'-methoxysalicylidene-2-amino-5-chloropyridine and 3'-methoxysalicylidene-2-amino-methoxypyridine, investigated by X-ray diffraction, show that the molecules are essentially planar (13). In the planar molecular structure the lone pair of the imino nitrogen atom does not overlap with the electrons of the pyridine ring, and consequently the basicity of the bridge N atom and hence the strength of the hydrogen bond between the H atom of the OH group and the imino N atom should be higher. Therefore the proton transfer postulated in equation 2 (quinoid *cis* form) is favored in the planar as against a non-planar conformation. The molecular structures of all salicylidene-2-aminopyridines investigated so far show a strong intramolecular hydrogen bond

with a mean $\text{H}(1)\cdots\text{N}((1))$ distance of 1.8 Å, and and also show the appropriate geometry for the hydrogen atom to point towards the lone pair of the N(1) atom as it is shown in Figure 2 for the case of salicylidene-2-aminopyridine.

The molecular packing of the four compounds studied is characteristic of that of flat molecules arranged in stacks along the shortest crystal axis with mean interplanar distance of 3.54 Å. Based on their identical behavior it may well be justified to suppose that all the salicylidene-2-aminopyridine compounds will have a similar packing arrangement. We suggest that the planarity is achieved because of the hetero-nitrogen of the pyridine ring. In the case of salicylideneanilines there is steric hindrance due to the short distance of ~ 2 Å between the *ortho*-hydrogen H(9) and the exocyclic hydrogen H(7) when the molecule is planar (5). This repulsion is relieved in the case of salicylidene-2-aminopyridines because the hetero-nitrogen atom is always at the *cis*-position with respect to the H(7) hydrogen atom (Figure 2). The distance of about 2.5 Å between these atoms corresponds to normal van der Waals contact.

The NQR results (see Table 2) show that we observe at rt (where enol and quinoid forms are expected to coexist) four signals in each case and therefore two chemically non-equivalent ^{14}N sites per unit cell. Since, however, the low intensity of the NQR lines (low frequency) and the large spin lattice relaxation time (integer spin $I=1$) complicate the search for NQR signals (14), we decided to follow a number of them with temperature in order to differentiate if possible between enol and quinoid structures. Thus, Figure 3 shows the frequency vs. temperature curves for (a) salicylidene-2-aminopyridine and (b) 3'-methoxysalicylidene-2-amino-3-methylpyridine. The frequency vs. temperature results may be explained in at least two ways:

(a) The two sets of lines belong to the bridge nitrogen in two different configurations (enol and keto forms) and we do not observe the ring nitrogen. This is in agreement with the fact that at low temperatures we observe only two lines (the enol form).

(b) The observed signals, at least at rt, belong to both the bridge and ring nitrogen but not all are observable. The situation could be clarified by measuring the proton-nitrogen cross-relaxation time at different temperatures, since it depends on the population of states.

Such measurements are in progress.

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Nuclear Quadrupole Resonance Study of a One-dimensional XY System: a Review (1,2) of Chlorine NQR in PrCl_3 *

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I. INTRODUCTION

Crystals containing unpaired electron spins whose coupling is predominantly between nearest neighbors along chains provide physical systems for testing theoretical predictions for both the static and dynamic properties of idealized one-dimensional (1-D) chains. The Hamiltonian for a chain of spin 1/2 particles aligned along the z-axis is

$$H = J_{\parallel} \sum_i S_z^i S_z^{i+1} + J_{\perp} \sum_i (S_x^i S_x^{i+1} + S_y^i S_y^{i+1})$$

where $J_{\parallel}$ and $J_{\perp}$ are coupling constants parallel and perpendicular to the direction of the chain. The limiting case

$$H = J \sum_i (S_x^i S_x^{i+1} + S_y^i S_y^{i+1})$$

corresponds to what is called the XY chain. The hexagonal compound PrCl_3 provides a good approximation to the 1-D XY chain.

The structure of PrCl_3 is illustrated in Figure 1. Nearest neighbor Pr ions form chains along the hexagonal axis. Each Pr ion has nine close Cl neighbors which form three equilateral triangles; one triangle lies in the plane perpendicular to the hexagonal axis passing through the

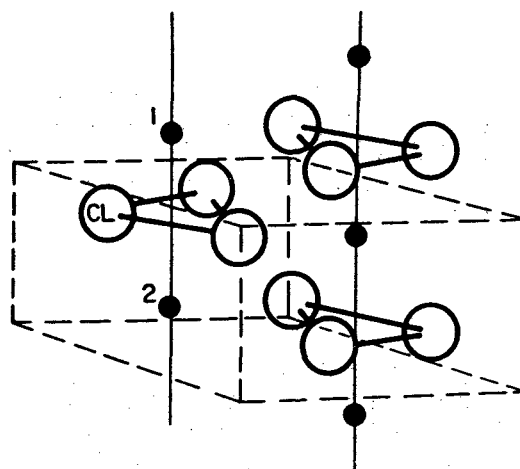


Figure 1. The crystal structure of PrCl_3 . The solid and open circles represent Pr and Cl ions, respectively. The dashed lines define a unit cell. The vertical lines indicate chains of nearest neighbor Pr ions parallel to the hexagonal axis.

Pr ion, and the other two triangles are located above and below the plane on mirror image sites. From EPR measurements (3) of Pr pairs in LaCl_3 it was concluded that the dominant Pr-Pr interaction was between nearest neighbors along the hexagonal chain and of the form

$$H \approx J \sum_i (S_x^i S_x^{i+1} + S_y^i S_y^{i+1}).$$

The low temperature ordering properties of

*Presented at the 6th Specialized Colloque Ampere on "Quadrupole Interactions and Spatially Resolved NMR in Solids," Crete, Greece, September 12-17, 1983.

PrCl_3 are therefore expected to show prominent 1-D XY character. Since the static properties of the XY chain can be calculated, the predicted 1-D character can be tested. This has been done for the specific heat (4) and susceptibility (5). The result for the susceptibility is shown in Fig-

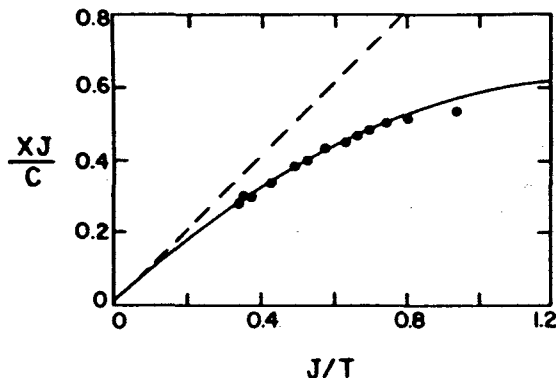


Figure 2. Comparison of experimental susceptibility data with the perpendicular susceptibility of the 1-D XY system (solid curve). The dashed line represents the Curie law for non-interacting dipoles.

ure 2; it shows that the XY model provides an excellent description of the data, at least above 3.6 K. The dynamic properties of the XY chain can also be calculated and the predictions tested using, for example, chlorine magnetic relaxation measurements. Experiments of this type (1) will be reviewed.

Long range ordering occurs in PrCl_3 at 0.4 K. Although no direct measurement of the low temperature structure has been performed, the splitting of the chlorine NQR spectrum (5) has been observed in the low temperature phase and this experimental observation has been interpreted (2) to yield a unique and unexpected structure. This work will be discussed.

It is the nature of the Pr ground electronic state in PrCl_3 that gives rise to the dominant XY interaction. The ground state electronic configuration of Pr^{3+} is $4f^2 \ ^3H_4$. The Pr^{3+} ion has point symmetry C_{3h} and the resultant crystal field splitting of the low lying manifold gives rise to a non-Kramers ground state doublet separated by 33 cm^{-1} from the first excited state. The ground doublet couples strongly to a Jahn-Teller

distortion and this leads to a large XY interaction between Pr sites in an effective spin 1/2 representation (7). This distortion transforms as (x,y) and therefore carries an electric dipole moment; it is represented by the operators S_x, S_y . In addition, the magnetic moment which is small and parallel to the hexagonal axis is responsible for a small $S_z^i S_z^{i+1}$ term.

II. HIGH TEMPERATURE PHASE: DYNAMIC RESPONSE OF A 1-D XY CHAIN (4)

In the high temperature phase all six chlorine sites in the unit cell are equivalent and a single NQR line is observed.

A. Spin-Lattice Relaxation Measurements

Earlier measurements (8) of the spin-lattice relaxation time T_1 were reported for the ^{35}Cl isotope at 4.2 K and below; they are shown in Figure 3. The objective of the more recent measurements (1) was to measure T_1 for both isotopes at a single temperature, 4.2 K, and with sufficient accuracy to identify unambiguously the relaxation mechanism. Figure 4 shows the data for the ^{35}Cl isotope; the straight line is a least squares fit to a single exponential decay function with time constant $T_1 = 4.11 \pm 0.04 \text{ ms}$. This new value, although more accurate, is consistent with the earlier results. The isotopic ratio of decay constants is $T_1(^{37}\text{Cl})/T_1(^{35}\text{Cl}) = 1.38 \pm 0.03$.

In an attempt to explain the spin-lattice relaxation measurements let us assume a magnetic hyperfine mechanism. In a simple model only the Pr ions labeled 1 and 2 in Figure 1 need be considered. Their contribution to T_1^{-1} is

$$T_1^{-1} = (A^2/\hbar)[\Phi_{ZZ}^{11}(\omega) + \Phi_{ZZ}^{12}(\omega)]$$

where A is the magnetic hyperfine interaction constant and it is proportional to the chlorine nuclear magnetogyric ratio, γ . The term $A^2/\hbar$ gives the dominant contribution to the isotopic ratio of T_1^{-1} values; with this term only, the predicted ratio is 1.44. The quantities $\Phi_{ZZ}^{mn}(\omega)$, where ω is the NQR frequency, are given by

$$\Phi_{ZZ}^{mn}(\omega) = \int_{-\infty}^{\infty} dt e^{i\omega t} \langle S_z^m(t) S_z^n(0) \rangle$$

where $\langle S_z^m(t) S_z^n(0) \rangle$ is the time-dependent, longitudinal correlation function for the electronic spins S^m and S^n . A general expression for this correlation function for the 1-D XY chain exists at all temperatures (9,10).

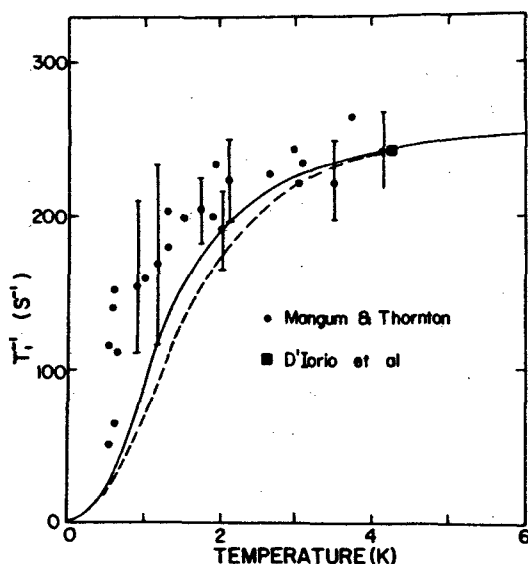


Figure 3. Temperature dependence of the relaxation rate T_1^{-1} . The uncertainty in the D'Iorio et al. data point is given by the size of the symbol. The solid curve represents the theoretical prediction for $J = 2.5$ K and with the single free parameter chosen to fit the data at 4.2 K; the dashed curve is for $J = 2.85$ K.

In the high temperature limit

$$\Phi_{ZZ}^{-1}(\omega)_{T=\infty} = (\hbar/2\pi J)K(1 - \tilde{\omega}^2/4)$$

where $\tilde{\omega} = \hbar\omega/J$ and $K(x)$ is the complete elliptic integral of the first kind. If only the autocorrelation term is considered

$$\begin{aligned} \frac{T_1(^{37}\text{Cl})}{T_1(^{35}\text{Cl})} &= \left[\frac{\gamma(^{35}\text{Cl})}{\gamma(^{37}\text{Cl})} \right]^2 \frac{K[1 - \tilde{\omega}^2(^{35}\text{Cl})]}{K[1 - \tilde{\omega}^2(^{37}\text{Cl})]} \\ &= (1.44)(0.98) \\ &= 1.41 \end{aligned}$$

In fact, the frequency dependence of the pair correlation function is virtually identical. This result is in good agreement with the measured ratio 1.38 ± 0.03 at 4.2 K.

Using the general expression for the correlation function for a 1-D chain, taking $J = 2.5$ K and accepting the present 4.2 K value as correct, the theoretical curve shown by the solid line in Figure 3 is deduced. The dashed line is for $J =$

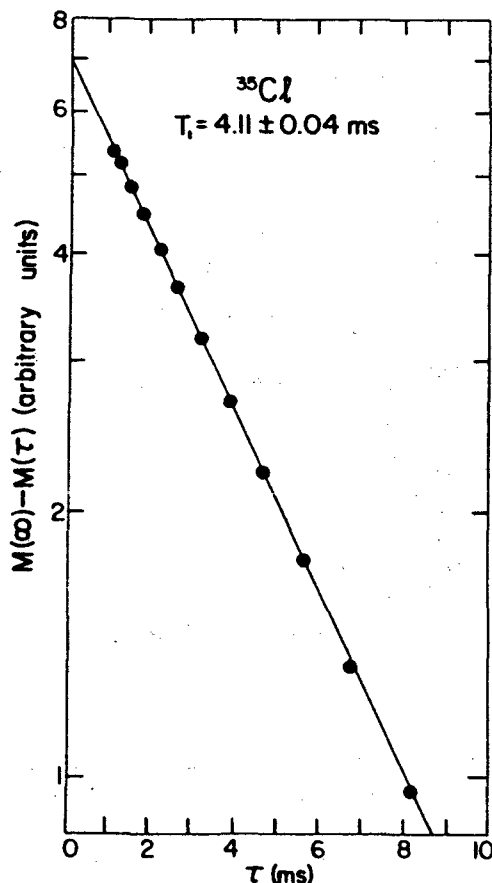


Figure 4. Typical spin-lattice relaxation data at 4.2 K showing exponential decay with time constant T_1 .

2.85 which until recently was assumed to be the best available value for this parameter.

The conclusion is that the spin-lattice relaxation is dominated by the magnetic hyperfine interaction and reflects the longitudinal fluctuations of a 1-D XY chain.

B. Spin-Spin Relaxation Measurements

Earlier measurements (8) of the effective spin-spin relaxation time $\hat{T}_2$ were reported for the ^{35}Cl isotope at 4.2 K and below; they are shown in Figure 5. One objective of the more recent measurements (1) was to measure $\hat{T}_2$ for both isotopes at a single temperature, 4.2 K, and with sufficient accuracy to identify unambiguously the relaxation mechanism. Figure 6 shows the data for the ^{35}Cl isotope. Note that the overall decay function is more rapid than exponential. The (dashed) straight line fit to the

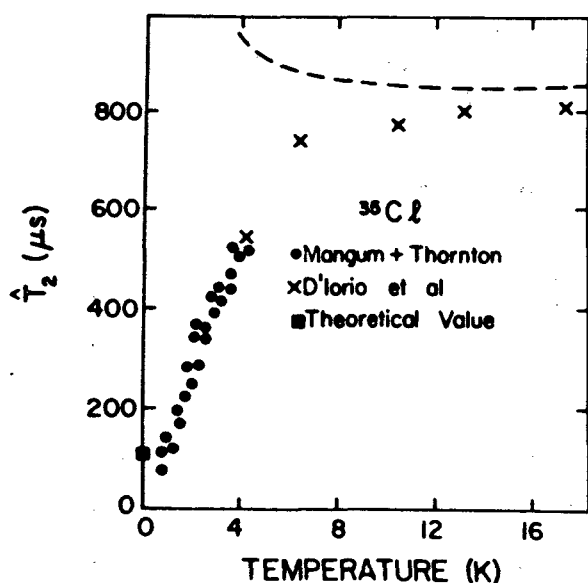


Figure 5. Temperature dependence of the effective spin-spin relaxation time $\hat{T}_2$. The dashed line is the estimated magnetic hyperfine contribution; the data point at $T=0$ represents the estimated electric hyperfine contribution.

initial part of the decay represents a single exponential decay function with time constant $\hat{T}_2 = 546 \pm 8 \mu s$. This value, although more accurate, is consistent with the earlier results. The isotopic ratio of decay constants is $\hat{T}_2(^{37}\text{Cl})/\hat{T}_2(^{35}\text{Cl}) = 1.59 \pm 0.04$. A second objective of the new measurements was to measure $\hat{T}_2$ at temperatures above 4.2 K. The results are shown in Figure 5; a plateau is reached quite abruptly at about 6 K.

As a first attempt to explain the spin-spin relaxation measurements, let us assume the same magnetic hyperfine mechanism responsible for spin-lattice relaxation. The relaxation rate, T_2^{-1} , is

$$T_2^{-1} = T_1^{-1}/2 +$$

$$(A^2/\hbar)[\Phi_{zz}^{-11}(0) + \Phi_{zz}^{-12}(0)]$$

where the $\omega=0$ terms represent dephasing due to variations in local precession frequencies. This approach fails because the quantity $\Phi_{zz}^{mn}(\omega)$ diverges as ω approaches zero. The conclusion is

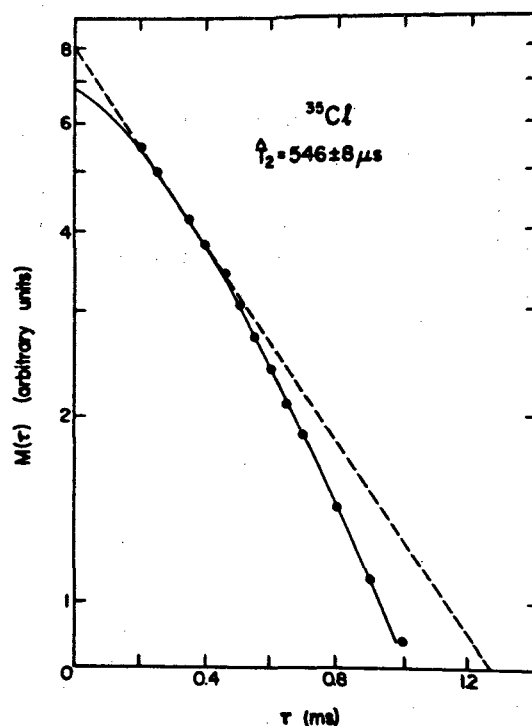


Figure 6. Typical spin-spin relaxation data at 4.2 K showing non-exponential decay. The solid line represents an $\exp(-at^3/2)$ decay the dashed line an exponential decay with time constant $\hat{T}_2$.

that the relaxation is non-exponential.

As a second attempt, let us assume the same relaxation mechanism but use a density matrix method (11) to calculate the two pulse echo decay function, $\phi(t)$. Using the value of A determined from the T_1 data, a unique prediction for the temperature dependence of $\hat{T}_2$ can be obtained. This is shown by the dashed line in Figure 5. Although the magnitude of $\hat{T}_2$ at high temperatures is in good agreement with the experimental values, the prediction is for $\hat{T}_2$ to increase at low temperatures whereas, in fact, $\hat{T}_2$ decreases dramatically below 6 K. This second attempt fails at low temperatures.

As a third attempt, an electric quadrupole mechanism is assumed. the transverse Pr moments S_x, S_y physically represent transverse distortions at Pr sites. these moments create electric field gradients at the chlorine sites proportional to S_x, S_y and lead to electric hyperfine interactions of the form $S_x T_m^2$ where T_m^2 is a

second-rank nuclear spin operator. In the simplest model

$$T_1^{-1} \simeq (B^2/\hbar)\Phi_{xx}^{-11}(\omega)$$

$$T_2^{-1} \simeq (B^2/\hbar)\Phi_{xx}^{-11}(0)$$

where

$$\Phi_{xx}^{-11}(\omega) = \int_{-\infty}^{\infty} dt e^{i\omega t} \langle S_x^{-1}(t) S_x^{-1}(0) \rangle.$$

At high temperatures (12)

$$\langle S_x^{-1}(t) S_x^{-1}(0) \rangle \sim \exp(-J^2 t^2 / 4\hbar^2)$$

and

$$T_1^{-1} \simeq T_2^{-1} \simeq \pi^{1/2} B^2 / 2J\hbar.$$

If B is roughly estimated using a point charge model and the transverse measured transverse electric dipole moment (4), it follows that

$$T_1^{-1} \simeq T_2^{-1} \simeq 1 \text{ s}^{-1}$$

which is more than two orders of magnitude slower than the magnetic hyperfine contribution. Electric quadrupole relaxation is ineffective in the high temperature regime both because B is smaller than A and also because the transverse spin correlation function decays more rapidly than the longitudinal correlation function.

At low temperatures, we have seen that the longitudinal correlations become less effective in producing relaxation. In contrast, the transverse correlation function develops a long time tail and in the $T = 0$ limit (13)

$$\langle S_x^{-1}(t) S_x^{-1}(0) \rangle \sim (\hbar/Jt)^{1/2}$$

Therefore, electric quadrupole relaxation is strongly enhanced at low temperatures. If it dominates at 4.2 K

$$\frac{\hat{T}_2(^{37}\text{Cl})}{\hat{T}_2(^{35}\text{Cl})} \simeq \left[\frac{Q(^{35}\text{Cl})}{Q(^{37}\text{Cl})} \right]^2$$

since the electric hyperfine interaction parameter B is proportional to the nuclear electric quadrupole moment Q . This theoretical ratio has the value 1.61; it is in excellent agreement with the measured ratio 1.59 ± 0.04 at 4.2 K.

Since $\Phi_{xx}^{-11}(\omega)$ diverges as ω approaches zero, it is necessary to calculate an echo decay function, $\phi(t)$, and from it deduce $\hat{T}_2$ values. In the low temperature limit

$$\phi(t) \sim \exp[-2B^2(\hbar/J)^{1/2} t^{3/2}].$$

This function is in excellent agreement with the observed decay function at 4.2 K (see solid line in Figure 6).

Lastly, an approximate value of $\hat{T}_2 = 100 \mu\text{s}$ is predicted at $T = 0$; this is the time for an e^{-1} decay of $\phi(t)$ for $T = 0$. The predicted value is consistent with the values measured at very low temperature as shown in Figure 5.

The conclusion is that at low temperature the spin-spin relaxation is electric quadrupolar in nature and reflects the transverse fluctuations of a 1-D XY chain.

III. LOW TEMPERATURE PHASE: WHAT IS THE ORDERED STRUCTURE?

The ^{35}Cl NQR spectrum as measured in the low temperature phase (6) is illustrated in Figure

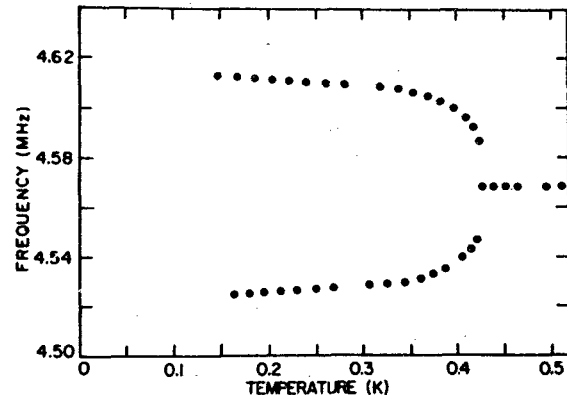


Figure 7. ^{35}Cl NQR spectrum of PrCl_3 as measured through the phase transition at 0.4 K.

7. The single line above T_c splits symmetrically into two lines below T_c . The two lines are of equal intensity so that the center of mass of the spectrum is conserved through the transition. Although it was at first assumed that the phase transition resulted from an antiferromagnetic ordering of Pr spins, it was subsequently concluded (14) from an NQR experiment performed in a small Zeeman field that the ordered state was not magnetic. It follows that the transition is structural in origin and presumably due to a cooperative Jahn-Teller distortion (15), but its precise nature is not known.

The observed change in the NQR spectrum places severe constraints on possible space groups of the low temperature structure (2).

Since the phase transition is due to a cooperative Jahn-Teller distortion, the space group of the high temperature phase must be a subgroup of the space group of the high temperature phase. The mathematical theory of symmetry as embodied in the principles of group theory, homotopy theory and representation theory may be used to advantage to discuss this example of a broken symmetry (16-18).

The space group of the high symmetry phase of PrCl_3 is C_{6h}^2 . The first Brillouin zone is depicted in Figure 8. Its points of symmetry are

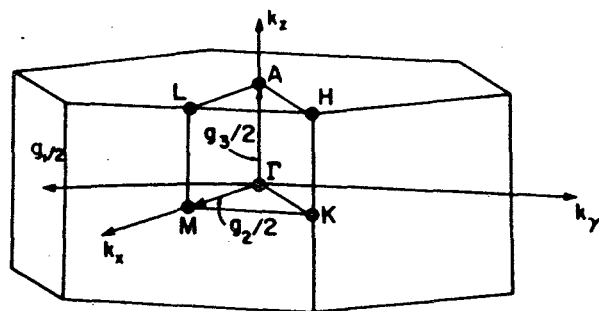


Figure 8. The Brillouin zone of the hexagonal lattice showing the points of symmetry.

Γ , M , A , L , K , and H . Starting from these, the theory of induction allows one to construct all of the commensurate group representations that may be responsible for a commensurate transition. Considering each irreducible representation in turn, representative order parameters and their little groups can be found. Finally, each little group may be identified as a possible space group for the low symmetry phase. Considerations of the site symmetry of the chlorine atoms leads to a classification scheme for the NQR spectra based on such characteristics of the predicted low symmetry phase spectra as the number of lines, their relative intensities, and the conservation or non-conservation of the spectral center of mass.

In fact, there are only two allowed low symmetry structures that are compatible with a two line chlorine NQR spectrum. These are C_{3i}^1 and C_{3h}^1 . The C_{3i}^1 structure has a unit cell which is doubled along the hexagonal axis of the C_{6h}^2 structure. The Pr ions no longer have special z coordinates, but since the C_{3i}^1 structure has an inversion center, the Pr ions form equivalent chains with alternating long and short Pr-Pr

separations. This structure describes a dimerized state. The C_{3h}^1 structure differs from the C_{6h}^2 structure (Figure 1) through the loss of the inversion center of the unit cell. This would occur if the two Cl triangles experience different expansions/contractions or rotations. The Pr point symmetry remains C_{3h} , but the two Pr ions in each unit cell, and therefore their respective chains, are nonequivalent.

A choice between the two low temperature structures identified by the group theoretical analysis can be made using physical arguments. The space group C_{3i}^1 is favored for several reasons. We mention only one. A transition to the C_{3h}^1 structure would not remove the electronic degeneracy. The individual chains would retain the symmetry of the high temperature phase, with the difference being that the two nonequivalent chains have slightly different values of the interaction parameter J . In contrast, a transition to the C_{3i}^1 structure *does* remove the electronic degeneracy. An interaction of the form

$$H = J \sum_i (S_x^i S_x^{i+1} + S_y^i S_y^{i+1})$$

implies that at the transition the unit cell will double along the hexagonal axis; the dimerized state is known to be the stable low temperature phase of an XY chain.

The question remains as to why Peierls dimerization occurs in PrCl_3 instead of conventional long-range ordering of individual Pr moments. In almost all known quasi 1-D spin systems, interchain interactions are sufficient to establish 3-D long-range order. Although the strength of the interchain interactions is not known in PrCl_3 , it is not expected to be remarkably small. It is, however, possible that the structure of this compound is such as to hinder the long-range ordering of the transverse moments. The separation between adjacent chains is not large, but interactions between them due to transverse displacements tend to cancel because each Pr ion on one chain is midway between two Pr ions on the adjacent chain. A high degree of cancellation between more distant chains is also expected because of the antiparallel ordering of moments within each chain, the hexagonal lattice structure and the dipolar nature of the long-range interactions.

It is concluded that PrCl_3 undergoes a novel type of Peierls dimerization, similar in some respects to the spin-Peierls transition, but different in that the spins involved are not real spins, but pseudospins associated with a Jahn-Teller coupling. Recall that the Peierls transition creates a singlet ground state by opening a gap

between filled and empty states in the electronic excitation spectrum, while in the spin-Peierls transition a similar gap appears in the spin excitation spectrum (19). Nonetheless, the analogy in the spin excitation with the electronic metal-insulator Peierls transition is direct since the dominant Pr-Pr interactions are well described by a 1-D XY coupling which has an exact mathematical transformation to a system of non-interacting fermions. Both the spin dynamics and the phase transition in PrCl_3 are almost unique, are of much physical interest, and merit further study at low temperature.

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*Applications of NMR Spin Imaging to the Study of Lungs**

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I. INTRODUCTION

Cardiopulmonary diseases are responsible for more than three million hospitalizations and 30,000 deaths yearly in the United States alone. Changes in lung water content or distribution are associated with virtually all pulmonary disorders. The development of noninvasive methods for measuring lung water and its distribution could have major impact upon evaluation of edematous states of the lung, such as adult respiratory distress syndrome (ARDS) and heart failure; states with altered lung density, such as pulmonary fibrosis and emphysema; and cardiac disorders associated with increased left atrial pressure (with increased pulmonary vascular volume but without lung edema). It is thus of obvious medical importance to develop methods for measuring the total water in the lung as well as its spatial distribution.

Existing non-NMR methods (1) for measuring lung water typically involve destructive or invasive techniques (double-indicator dilution, histologic, and gravimetric), depend on regional distribution of pulmonary vascular perfusion (blood flow in the arteries and veins of the lung; e.g., the double-indicator dilution technique) and regional distribution of ventilation (amount of air flow in the lung; e.g., the inert gas rebreathing technique), or involve harmful radiation (X-ray or isotopic double-indicator dilution). Most of these techniques measure only a *fraction* of the total water in the lungs rather than the total water. Furthermore, the distribution spaces of the various indicators differ and are poorly

defined.

NMR has obvious advantages in that it is noninvasive and nondestructive and clearly has the capability of *quantitative* determination of *total* lung water. NMR imaging has the further advantage of being able to determine regional abnormalities and, thus, the relationship between the appearance of these abnormalities and the occurrence of disease. NMR imaging is particularly well suited to time-course studies of the development of disease.

There are a number of difficulties in NMR imaging of lungs. First, the water density (and thus the signal-to-noise ratio) will be lower in lungs than in other tissue. A related problem is the effect of nearby water (either due to the chest wall or to pockets of water near the lung). It is a nontrivial problem just to define the boundaries of the lung in the edematous state. A second problem is that the lung image may be blurred by lung movement during breathing. This problem can be solved by breath holding or by gating the NMR signal from the respiratory cycle. If the chest motion can be constrained externally, the lung motion may be kept within acceptable bounds. A further problem, as we shall see later in this paper, arises from the fact that lung is a highly aerated organ with a large surface-to-volume ratio.

Our initial work has concerned validation of NMR methods for quantitative lung water measurement. By comparing the NMR results with results from standard gravimetric techniques, NMR can be shown to provide an absolute standard for the determination of total lung water content, changes in which can be used to study lung disease. Even though an NMR image may be well-defined, its validation is nontrivial. It is difficult to cut away sections of the lung for subsequent gravimetric measurements without causing irreversible changes in the tissue (due, for instance, to collapse of the lung and changes in fluid content). As a result, one does not know

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a priori which gravimetric sections correspond to which NMR pixels. Another source of error in performing *absolute* NMR measurements arises from the need to perform extrapolation of the spin-echo envelope to correct for the T_2 -decay of the magnetization. For selective NMR irradiation, pulses are needed whose widths may be several milliseconds. An incorrect determination of the time of the beginning of the magnetization decay may result in errors of 10 to 15% in the determination of the thermal equilibrium magnetization M_0 .

A second application of NMR imaging is to study the time course development of pulmonary edema (accumulation of fluid in the lungs). In particular, NMR imaging might detect spatial patterns of lung edema as well as changes in these patterns associated with exposure to different toxins and diseases.

A third purpose of our study is to use NMR imaging to determine the state of aeration of the lungs as well as to study possible effects of oxygen toxicity.

II. LINE-SCAN TECHNIQUES

The experiments described in this paper were performed in a 12" Varian electromagnet designed for broad-line solid-state physics. Because of the limited size of the homogeneous region in this magnet (approximately 20 cm³ sample volume for ± 0.1 Gauss), we use a line scan technique in which we observe only a narrow, pencil-shaped region located in the center (homogeneous region) of the magnet. We then sequentially step the specimen (in our case, a small rat) up or down and repeat the line scan. In this way a two-dimensional picture is obtained from a series of one-dimensional line scans, each of which arises only from nuclei in the homogeneous region.

A line scan (2) is obtained by selective excitation (i.e., using gradients and narrow frequency pulses) of two perpendicular planes, the first with a 90° pulse and the second with a 180° pulse. Thus, only their region of intersection (the shaded region of Figure 1) will have received *both* a 90° and a 180° pulse. A pulse sequence for achieving a line scan is shown in Figure 2. The z-gradient (applied only during the 90° pulse) guarantees that the 90° pulse excites only a planar region corresponding to a particular z-value whereas the y-gradient guarantees that only a particular y-plane sees the 180° pulse. Thus, only the "line" having a particular y- and z-coordinate will experience both pulses and will contribute to the spin-echo (shown in the

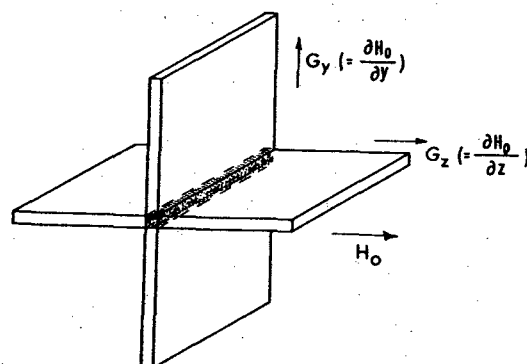


Figure 1. Intersecting planes used in the line-scan technique.

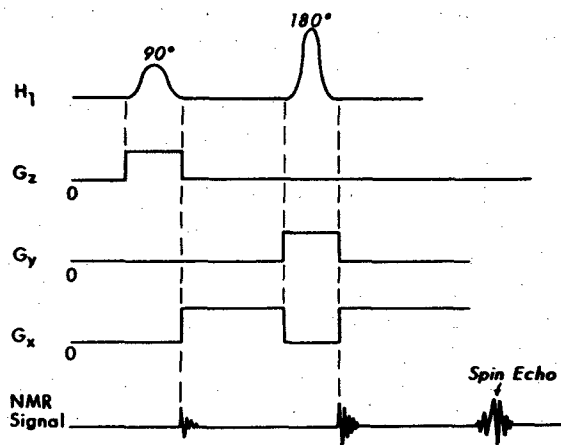


Figure 2. Pulse sequences used in the line-scan technique.

lowest trace of Figure 2). The application of an x-gradient (turned off during the 90° and 180° pulses to allow definition of the y- and z-planes) allows separation of data along the x-direction. (Several refinements of this simple sequence which are needed to correct for effects such as dephasing during the gradient pulses and dephasing due to field inhomogeneities will be discussed in a subsequent paper (3).)

III. VALIDATION OF NMR MEASUREMENTS IN LUNG

In order to obtain accurate quantitative determination of the water content in lung from the spin-echo amplitude, it is necessary to correct for the T_2 decay of the signal which occurred prior to the occurrence of the spin echo. A suitable back extrapolation can be obtained by varying the time interval between the 90° and 180° pulses. We obtained our data for two such intervals (11 ms and 19 ms) and formed an image after fitting this data to a single exponential which was then back-extrapolated to the center of the first pulse. (The justification for this procedure is discussed more fully in another paper(4).) We obtained the percentage water in each pixel of the image by dividing the lung magnetization pixel-for-pixel by the magnetization obtained for pure water which was previously placed in the same region.

In lung it is difficult to make a comparison between the water density of a small portion of the lung measured by NMR with that measured gravimetrically. The difficulty begins when one opens the chest cavity to obtain a lung fragment corresponding to an area in the NMR image. At this point the lung collapses, and one can no longer identify the specific lung tissue which generated any particular NMR signal in the image. Further, if one were to cut the lung, fluids that were imaged might leak out of the fragment and thus not be measured gravimetrically.

Our solution to this problem is to remove the lungs surgically: tying off the major blood vessels to retain close to normal physiological fluid content and then inserting a tube into the trachea so that the lungs could be kept in a steadily inflated state by an external air pressure supply. This preparation is then inflated snugly into a rectangular jig (see Figure 3) with small vials of water on either side for position reference. Then the entire jig is scanned until NMR images are collected from the entire volume. After imaging, the still inflated lung in the jig is removed from the magnet and rapidly frozen in liquid nitrogen to preserve the geometry and water content of all parts of the lung and jig. The frozen lung within the jig is then separated from the remainder of the lung and sectioned into 1.9 mm slices perpendicular to the long axis of the jig. The relation of each section to the reference vials of water is noted so that a correlation can be made between the frozen lung sections and the corresponding NMR image signals. The lung sections are then weighed and allowed to dry to

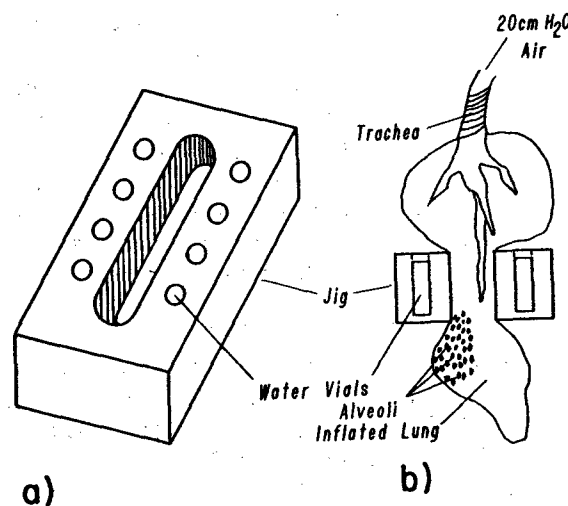


Figure 3. Jig used for validation studies. (a) Jig. (b) Cross-sectional view of jig with lung.

constant weight in an oven at 60° C, thereby providing an absolute gravimetric measure of the water in the region.

IV. INHOMOGENEOUS BROADENING CONTRAST TECHNIQUE (T_2')

A. Diamagnetic Line Broadening

In the process of performing the validation experiments described above, we discovered some surprising effects which led us to a new method for doing NMR imaging. In particular, we have observed that the NMR line of inflated lung is inhomogeneously broadened by an internal broadening mechanism (in contrast to external field inhomogeneities). Since this effect is not observed in most other tissues (other than fat), it has resulted in a new high-contrast technique for imaging lungs and fat.

Figure 4 show free induction decays (FID's) obtained from an inflated lobe of rat lung (Figure 4a) and from pure water (Figure 4b) in a relatively homogeneous field (i.e., no external gradients). Both samples had the same volume and were located in the same position in the magnet. As we can see from Figure 4b, T_2^* of the water is of order 18 ms in this magnetic field, thereby defining the broadening due to the external field inhomogeneity. Since T_2^* of the lung is only approximately 4 ms in the same field, the lung is

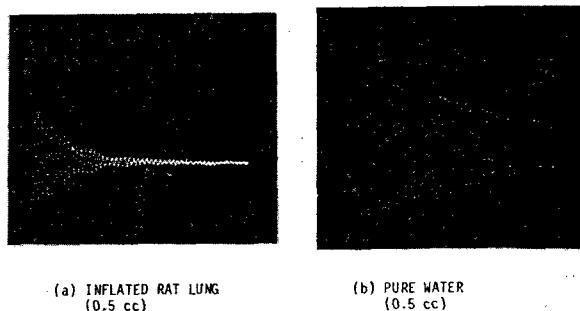


Figure 4. Free induction decays, (a) inflated rat lung (0.5 cc) and (b) pure water (0.5 cc). The time scale is 25 μ s/pt or 13.6 ms for the entire horizontal sweep.

experiencing an extra broadening mechanism which cannot be due to external field inhomogeneities. We found that, if the same lobe of lung is subjected to a Carr-Purcell sequence, T_2 (25-30 ms) will be much longer than T_2^* . Thus, the extra broadening mechanism experienced by the lung must be inhomogeneous broadening, but not due to inhomogeneities in the external field. Our evidence, as we shall see, is that the source of this internal magnetic field inhomogeneity in lung arises from different diamagnetic shifts experienced by water molecules at different distances from the lung surface (air-water interface).

Since water and most tissues are slightly diamagnetic (5), the proton resonance in liquid water is shifted by approximately 360 Hz in a 40 MHz NMR imaging apparatus. In a tissue specimen which is homogeneous across the resolution size, all protons in a pixel (though frequency shifted) will remain in phase with one another and the magnitude of the signal will not decrease. However, if the diamagnetism of the tissue is inhomogeneous, as in lung tissue which consists of a foam-like mixture of water and air, the protons within a pixel will precess with different frequencies (those near an air space being in a higher field than those deeper within the tissue).

If this interpretation is correct, it should be possible to simulate similar broadening and line shifts in other substances having boundary surfaces between regions of sharply different

diamagnetic susceptibility. Accordingly, we performed measurements of the NMR lines in foams (air-water interface) and in a dense slurry of alumina particles (alumina-water interface). The diamagnetic susceptibility of alumina is approximately twice that of water. Thus, the resonance of water molecules at an alumina-water interface should exhibit a shift of approximately the same order of magnitude as those at an air water interface but of opposite sign. *of opposite sign.* Figure 5a shows the narrow line of a sample of water containing the detergent JoyTM. This sample was then agitated to produce a foam, which has many air-liquid interfaces and exhibits line broadening (Figure 5b). We observed a similar line broadening in shaving cream (Figure 5c). Note that that the process of producing air-water interfaces causes a broadening and shift similar to that which is observed in lung. The results of a critical test as to whether this broadening and shift arises from surface diamagnetic susceptibility variations is shown (in Figure 5d) for a water-alumina slurry. This figure shows that the shift is indeed of opposite sign but comparable order of magnitude to that of the foam and shaving cream. We have thus shown that air-water interfaces can provide line broadening and shifts similar to that of lung and that this broadening and these line shifts may be varied by changing the diamagnetic susceptibility mismatch.

B. Technique for Observing Internal Inhomogeneity Effects on Spin Echo

As we stated earlier, our line-scan images involve refocusing of the magnetization into a spin echo. Since this spin echo involves a refocusing of the magnetization lost from all inhomogeneities (both internal and external), the question arises as to how we can see the effects of the internal broadening (described above) in an image formed from spin echoes. We now describe our technique for observing a new kind of spin echo: one in which only the signal lost from gradients (but not internal or external inhomogeneities) is refocused. The error due to loss of signal from external inhomogeneities can be corrected by use of a normalizing curve obtained from the signal intensity arising from a bucket of pure water placed in the same spatial region of the magnet.

First consider a 90° - 180° pulse sequence applied without field gradients. At 2τ we obtain a conventional spin echo, where τ is the time between the 90° and 180° pulses. the width of the echo defines an inhomogeneity window

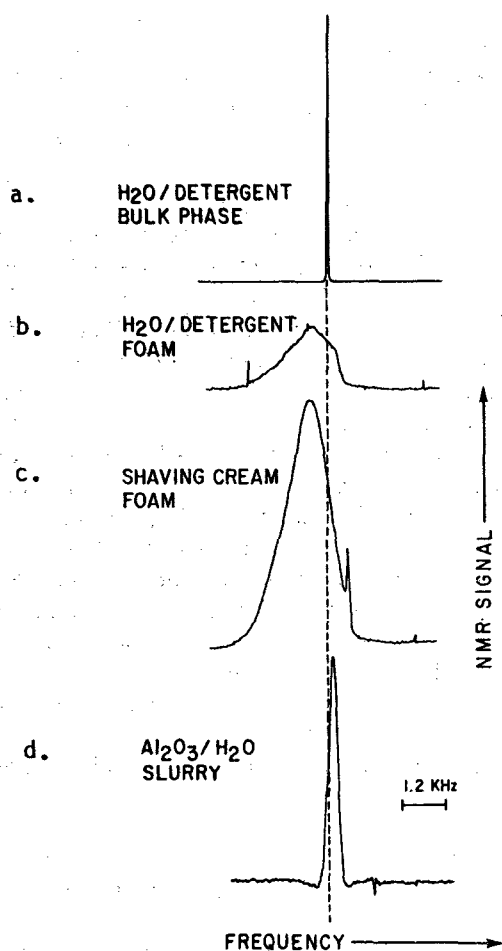


Figure 5. NMR lines for mixtures of substances having different diamagnetic susceptibilities.

(Figure 6a) in which it is possible to have a signal for a given value of τ . Similarly, if a gradient is applied following a 90° pulse, there will be rapid dephasing which will be reversed simply by reversing the direction of the gradients. An echo, whose width depends both on the sample and on the size of the gradients, will occur at $\tau' + \tau''$ when the total area under the gradient curve is zero (i.e., when the positive area equals the negative area in Figure 6b). If the positive and negative gradients are equal in magnitude,

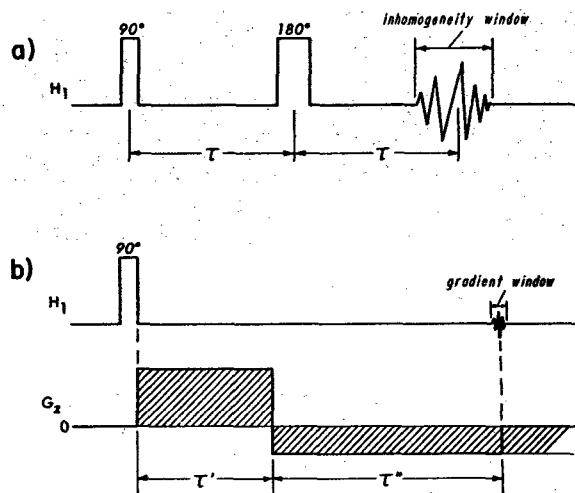


Figure 6. Two different kinds of spin echoes. (a) The conventional echo obtained from a 90° - 180° sequence; and (b) the echo obtained from reversing the dephasing in a gradient. The echo will occur when the area under the curve when G_z is negative equals the area when G_z is positive.

then $\tau'' = \tau'$, and the sequence is described as symmetric. However, if the gradients are unequal, $\tau'' \neq \tau'$, and the sequence is called asymmetric; thus the position of the gradient echo can be adjusted simply by varying the relative amplitudes of the two gradients. Furthermore, it should be noted that the width of the gradient echo of Figure 6b normally will be much less than that of the inhomogeneity echo of Figure 6a since it corresponds to a signal in a much more inhomogeneous field (that of the gradient). Now, if a 180° pulse is applied precisely at τ' (so that $\tau' = \tau$) and the second gradient is not reversed in sign, all the signal lost from inhomogeneities (both internal and external) is refocused and the maximum echo amplitude will have decayed from M_0 at a rate determined by T_2 . This sequence (i.e., when the gradient following the 180° pulse is equal in amplitude and sign to the gradient following the 90° pulse) is clearly symmetric in that $\tau' = \tau'' = \tau$. In this case the gradient and inhomogeneity windows are centered at the same point in time, $\tau' + \tau'' = 2\tau$

and the maximum possible spin echo will appear at the center of the inhomogeneity window (see Figure 7a). However, if the second gradient is

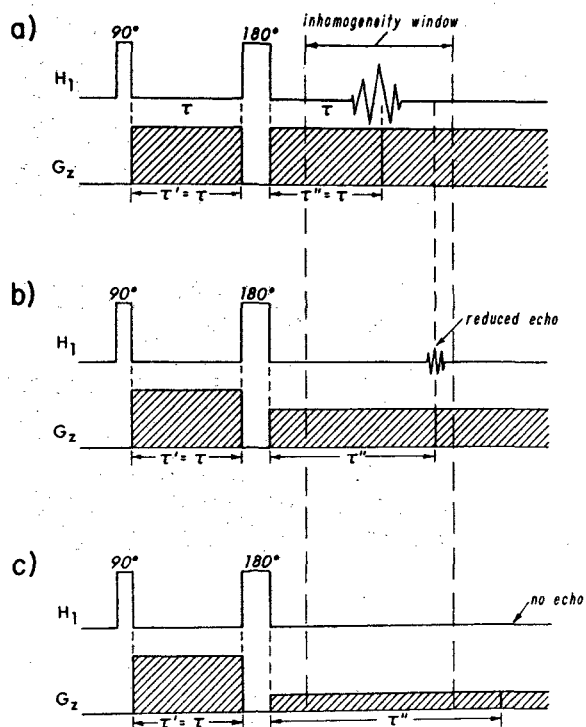


Figure 7. Effect of symmetric and asymmetric sequences. (a) Symmetric sequences. (b) Asymmetric sequences with partially overlapping windows and reduced echo. (c) Asymmetric sequences with no overlap of windows and zero echo.

reduced somewhat (so that $\tau'' \neq \tau'$ and the sequence is asymmetric), we will get a reduced echo if the τ'' interval ends within the inhomogeneity window (as in Figure 7b) or no echo if τ'' ends outside the inhomogeneity window (as in Figure 7c). This reduction in signal intensity can be understood by recognizing that, with unequal gradients, the signal loss due to external gradients is refocused at a different point in time than is the signal loss due to internal inhomogeneities. Thus, only part of the signal lost from internal inhomogeneities has been refocused at the point of optimal refocusing for the signal lost from external field gradients (i.e., center of gradient window). Figure 8 indicates a possible envelope of the inhomogeneity window generated by

asymmetric sequences having different sized

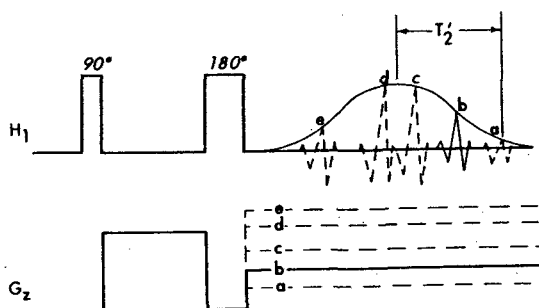


Figure 8. Shape of inhomogeneity window determined by echoes generated by a series of gradients of unequal amplitude.

gradients. The width of the inhomogeneity window in the absence of external gradients is approximately $2T_2^*$. However, for a perfectly homogeneous external field or for a sample (like lung) in which internal inhomogeneities determine the magnetization dephasing, the width of the window is $2T_2'$, where T_2' is defined as the FID decay time due to internal inhomogeneities (i.e., for a perfectly homogeneous external field assuming negligible contributions from T_2 , as described below).

We can understand in another way why the spin-echo amplitude is reduced for the asymmetric sequence when internal inhomogeneities are present. If we assume that different line-broadening mechanisms independently give rise to exponential decay of the FID, we can write the total FID decay rate, $1/T_2^*$, as a sum of contributions from different mechanisms,

$$\frac{1}{T_2^*} = \frac{1}{T_{2,g}} + \frac{1}{T_{2,m}} + \frac{1}{T_2'} + \frac{1}{T_2}, \quad (1)$$

where $1/T_{2,g}$, $1/T_{2,m}$, $1/T_2'$, and $1/T_2$ are, respectively, the contributions to the broadening from external field gradients, inhomogeneities in the static magnetic field H_0 , internal sources of field inhomogeneity, and irreversible sources. In a liquid, normally, $T_2 \gg T_{2,m}$, $T_{2,g}$. Since dephasing from irreversible sources is not refocused to a spin echo, the decay of the spin-echo magnetization from its peak value is given by

$M =$

$$M_p \exp[-t(1/T_{2,g} + 1/T_{2,m} + 1/T_2')], \quad (2)$$

where

$$M_p = M_0 \exp(-\tau''/T_2). \quad (3)$$

For the simple 90° - 180° pulse sequence of Figure 6a, the $1/T_{2,g}$ term is absent (since there are no external gradients). For aerated rat lung in our iron magnet, $T_{2,m} \gg T_2'$, since $T_2' \sim 4$ ms and $T_{2,m} \sim 18$ ms, as we have seen in Fig-

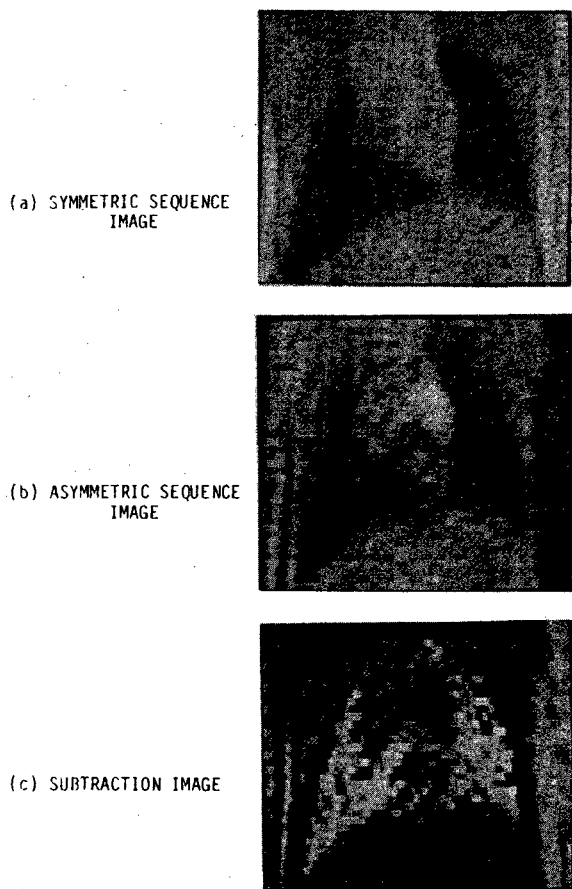


Figure 9. Thorax of dead intact rat. (a) Symmetric sequence image. (b) Asymmetric sequence image. (c) Subtraction image.

ure 4. Thus, the echo envelope in the absence of gradients (the inhomogeneity window) is determined primarily by T_2' and the magnetization decay of the echo is given by

$$M \approx M_p \exp(-t/T_2'). \quad (4)$$

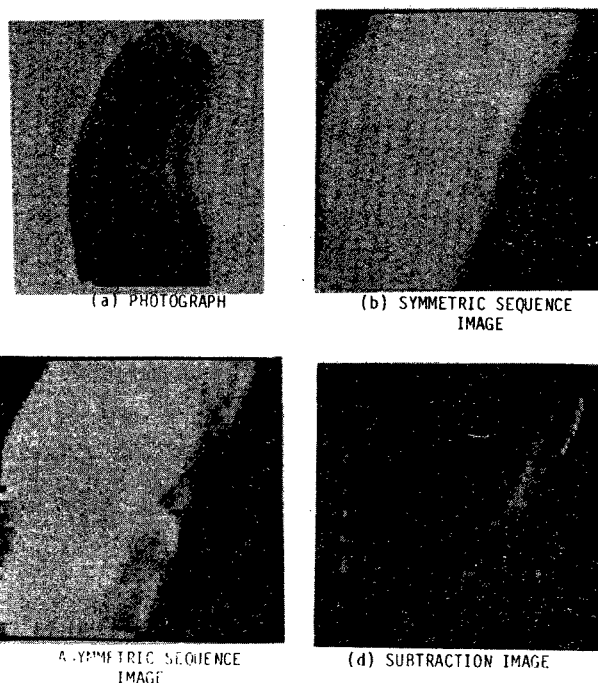


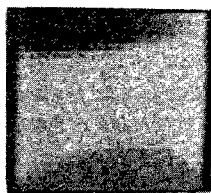
Figure 10. Human kidney. (a) Photograph. (b) Symmetric sequence image. (c) Asymmetric sequence image. (d) Subtraction image.

Now, in the presence of external gradients, we must include the $T_{2,g}$ term, in which case the echo width is determined by $T_{2,g}$, since $T_{2,g} \ll T_2$. The amplitude of the spin echo is determined by its position in the inhomogeneity window, as shown in Figure 8.

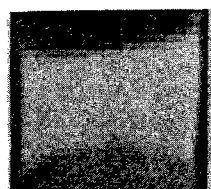
V. RESULTS

It is clear from the previous discussion that a T_2' image can be generated simply with an asymmetric imaging sequence (utilizing unequal gradients). If the gradient and inhomogeneity windows partially overlap, there will be a reduced signal due to internal inhomogeneity effects. If, on the other hand, a symmetric sequence is used so that the echo occurs in the center of the inhomogeneity window, there will be no loss in signal intensity, and we will get a conventional proton density image. If we subtract the asymmetric from the symmetric image pixel-by-pixel, we will obtain an image of *only those nuclei which experience internal broadening*

(a) SYMMETRIC SEQUENCE
IMAGE



(b) ASYMMETRIC SEQUENCE
IMAGE



(c) SUBTRACTION IMAGE



Figure 11. Salad oil floating on water. (a) Symmetric sequence image. (b) Asymmetric sequence image. (c) Subtraction image.

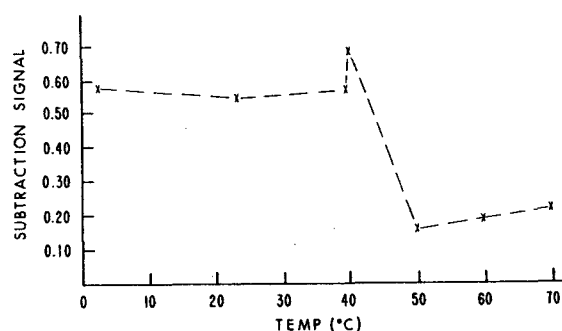
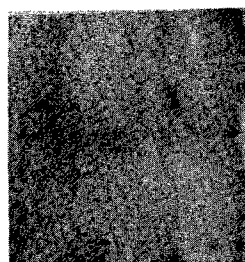
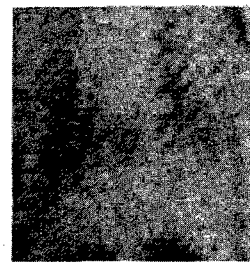


Figure 12. Temperature dependence of the relative intensity of the subtraction image in Crisco™. The subtraction signal intensity is expressed as a percentage of the normal signal intensity obtained with the symmetric sequence.

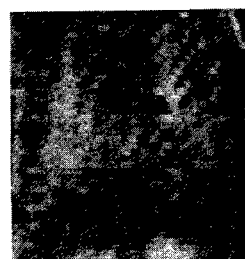
(like protons in lung). In such an image, regions containing protons but no internal broadening (like bulk water) will be dark as will regions containing no nuclei. Only those nuclei experiencing internal broadening will appear in the image. We now present a number of images which demon-



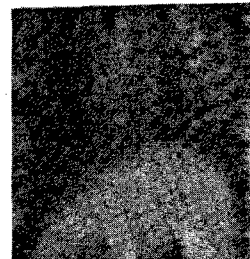
(a) SYMMETRIC SEQUENCE
IMAGE



(b) ASYMMETRIC SEQUENCE
IMAGE



(c) SUBTRACTION IMAGE



(d) T₁-ENHANCED IMAGE

Figure 13. Pulmonary edema in dead rat. (a) Symmetric sequence image. (b) Asymmetric sequence image. (c) Subtraction image. (d) T₁-enhanced image.

strate the effect.

Figure 9 shows the thorax of a dead intact rat. Figures 9a and 9b show the results with symmetric and asymmetric sequences, respectively. Note, in both cases the lungs are dark (due to their relatively low water content). In contrast, in the subtraction image, Figure 9c, the lungs appear bright whereas other regions appear dark (including the chest wall). However, it should be noted that some other regions also appear bright (e.g., the bright regions outside the lung on the right and on the left side of the pictures). We believe these regions to be fatty tissue, which also is intensified by our contrast technique.

Figure 10 shows a photograph of a piece of a human kidney (Figure 10a) as well as the three NMR images. Note that, in the subtraction

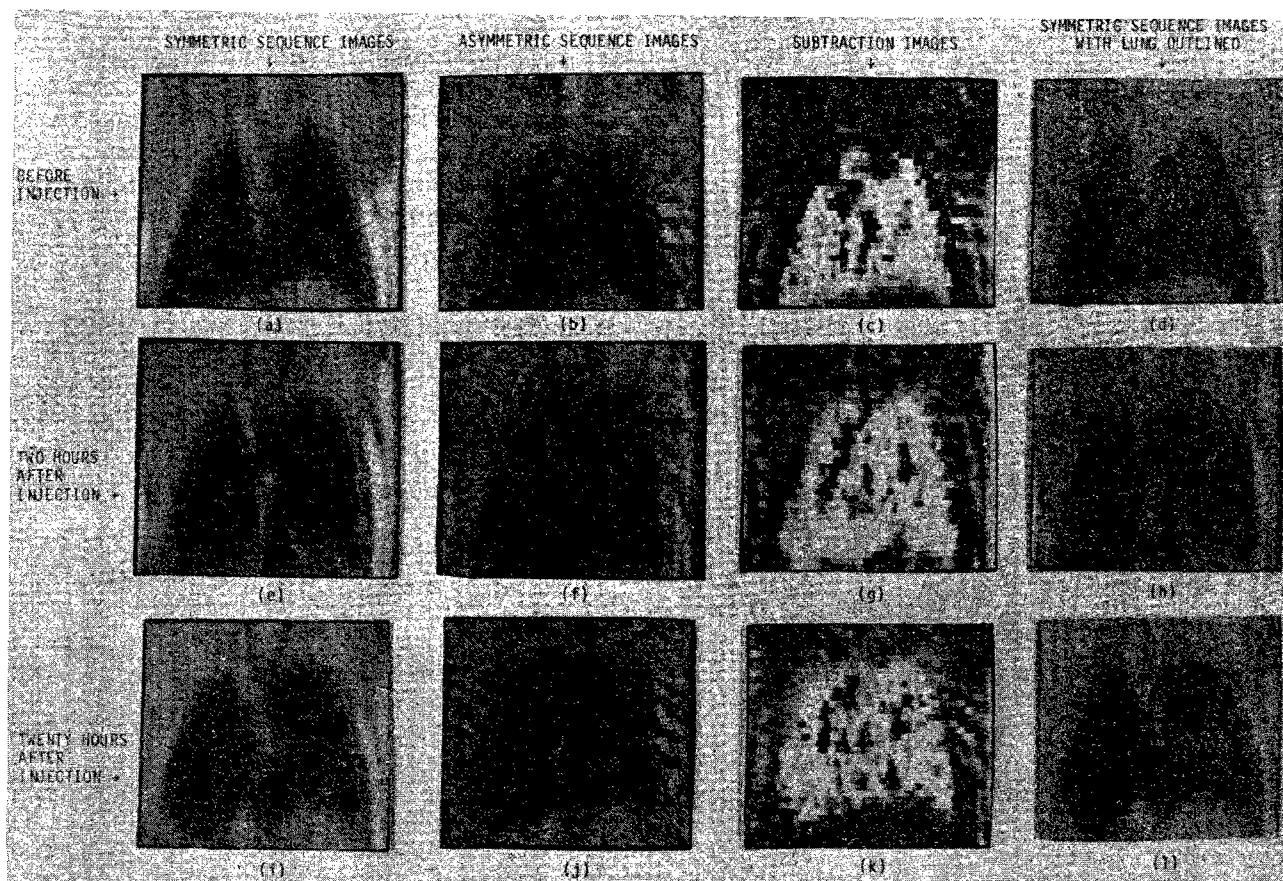


Figure 14. Oleic acid-induced lung edema in a live rat.

image (Figure 10d), the fatty region on the right (perihilar fat) as well as the surface regions are intensified.

In order to attempt to understand the mechanism for internal T_2 ' broadening in fat, we obtained images of liquid salad oil floating on water (Figure 11). Both liquids show up in our symmetric and asymmetric pictures (Figures 11a and 11b), but only the salad oil appeared in the difference image, thus demonstrating that even a fatty liquid will be contrasted by our technique. We also measured the temperature dependence of the relative intensity of the difference image in hydrogenated vegetable oil (CriscoTM) which is "solid" up to approximately 48 °C and then melts. As shown in Figure 12, there is a sharp reduction in the intensity and thus in the internal broadening in the liquid. Thus we conclude that the internal broadening mechanism in fat arises from at least two sources, one of which is motionally narrowed upon melting and possibly is due to dipolar interactions. The mechanism in

the liquid oil probably involves protons at different chemically shifted sites. This point will be discussed further in a subsequent paper (6). Since our contrast technique appears to work in *bulk* fat, it is clear that the mechanism for internal broadening here must be quite different from the diamagnetic susceptibility mismatch at the air-water interface in lung.

Figures 13 and 14 show the effects of edema (7) on the lungs of intact rats. In both cases, the lung edema was caused by 0.04 mL of oleic acid injected via the lateral tail vein. The rat in Figure 13 died, whereas the rat in Figure 14 survived. In the conventional proton density image (using a symmetric sequence) in Figure 13a the edema is so widespread that it is nearly impossible to distinguish the boundaries of the lung from the surrounding tissues. However, the difference image of Figure 13c shows the boundary of the lung quite clearly. The T_1 -enhanced image of Figure 13d offers some contrast for the lung, but much more for the liver (the bright region at the

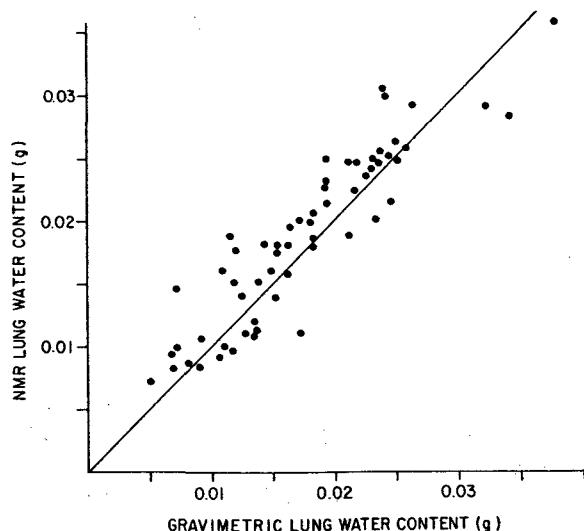


Figure 15. Validation study of NMR lung water measurements.

bottom of the photograph). This set of images shows an important application of our T_2' technique: that of determining the boundary of the lung in the presence of massive edema.

Figures 14a-l show three sets of images taken on a live spontaneously breathing rat, also subjected to oleic acid injection. The first set of four pictures (Figures 14a-d) was taken before the intravenous oleic acid injection, the second set (Figures 14e-h) was taken two hours after the oleic acid injection, and the third set (Figures 14i-l) was taken the next day, 20 hours after the injection. Figure 14e shows clearly the onset of edema in the right lower lobe and the difficulty in determining the lower boundary of the lobe (which is easily determined with an asymmetric sequence in Figure 14f and in the subtraction picture of Figure 14g). In Figure 14i-l taken the next day, there is partial resolution of lung edema but the appearance of a pleural effusion. Note that the difference between lung edema and pleura effusion is indicated in the subtraction image. It is also interesting to note in Figure 14g the persistence of bright regions even in areas of significant edema, indicating the maintenance of aeration of the edematous lung. Figures 14d,h,l are the images obtained with symmetric

sequences (Figures 14a,e,i) but with the lung boundaries *determined from* the subtraction pictures (Figures 14c,g,k) drawn in. These figures show the potential of NMR imaging for performing time-course studies and for obtaining significant physiologic and morphologic information in lungs.

Figure 15 shows the results of our validation experiments (8) in rat lung using the procedure described in Section IV. In order to avoid any errors due to T_2' decay, symmetrical gradients were used. Because of significant variations in water content in different parts of the lung, six different lungs were used, each being sectioned into ten slices. The NMR lung water content for each section of each specimen is plotted on the y-axis and the corresponding gravimetric lung water content on the x-axis. The scatter may also be due to inaccuracies in the gravimetric measurements for thin sections. Nevertheless, the best fit to the data is very close to a straight line of 45° slope through the origin.

ACKNOWLEDGMENT

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*NMR Imaging Methods Seen as Trajectories in the Reciprocal Space**

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During the last decade, several methods for proton NMR imaging of the human body were proposed and have been tested in various laboratories. The most efficient of these are the ones where the signals of a full slice, or even volume, are measured simultaneously. In this paper a rather general description of NMR imaging is presented. For reasons of simplicity, the description is limited to two dimensions only. A 2-dimensional case can be realized by selective excitation of a slice.

In many 2-dimensional methods, the excitation of the spins in the slice is followed by the application of constant or time-dependent homogeneous gradients in the main magnetic field. Such methods are, for instance, Projection Reconstruction, Fourier Zeugmatography in its various forms, and Echo Planar Imaging. They are all covered in the following description.

Let $f(x,y)$ be the function to be imaged, where x and y are the spatial coordinates of the slice. In simple cases this function is the spin density, but often it will also reflect the local relaxation times. In general, $f(x,y)$ represents the nuclear magnetization distribution at a certain instant.

For the description of the methods, we introduce $F(k_x, k_y)$ as the 2-dimensional Fourier transform of $f(x,y)$, i.e.

$$F(k_x, k_y) = \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} f(x,y) \exp[i(k_x x + k_y y)] dx dy.$$

The imaging methods mentioned above correspond to various ways of determining the

function $F(k_x, k_y)$. As soon as $F(k_x, k_y)$ is known to a certain extent, $f(x,y)$ will be known within corresponding limits.

In a simple form of NMR imaging, a constant gradient G is applied directly after the excitation, and the free induction decay signal is double-phase-sensitively detected, to give the complex low frequency signal $S(t)$. It is not difficult to show that this signal simply is the function $F(k_x, k_y)$ on a straight line k_u through the origin in the $k_x k_y$ -plane. (Here, effects of T_2 decay during detection are neglected.) This line k_u makes the same angle with k_x as G does with respect to x . The correspondence between k_u and t is given by $k_u = \gamma G t$, where γ is the gyromagnetic ratio. In other words, the detection of the signal $S(t)$ corresponds to probing $F(k_x, k_y)$ on a trajectory in k space that is determined by the equation of motion $dk/dt = \gamma G$.

This statement also holds if time-dependent gradients are applied. So in general we have $dk/dt = \gamma G(t)$. A change in the direction of G thus results in a corresponding modification of the direction in which the trajectory is followed, while a change in the magnitude of G affects the speed along it.

Descriptions of NMR imaging in terms of k -space trajectories have also been given by others (1,2) and might be a promising approach for finding new methods.

It is of special interest to find methods that have a considerably shorter measuring time than Fourier Zeugmatography and yet produce good-quality images. However, due to the dephasing effects of the unwanted inhomogeneities of the magnetic field, most trajectories cannot straightforwardly lead to an acceptable method.

As an example of a new practical method, we shall describe one particular trajectory in detail. Just as in Fourier Zeugmatography, the function $F(k_x, k_y)$ is measured on a rectangular grid, along lines parallel to k_x . In Fourier Zeugmatography, only one such line is measured after each

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excitation pulse. In the new method, several adjacent lines, e.g. 2, 3, or even more, are measured after an excitation pulse. This is achieved by means of a sinusoidal trajectory. In a limiting case, this method becomes equivalent to a version of the echo planar imaging method.

We finally note that the description can readily be extended to three dimensions.

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Dynamic NMR Spectroscopy on Rotation about the C=C Bond in Enamines Containing the N-H Bond

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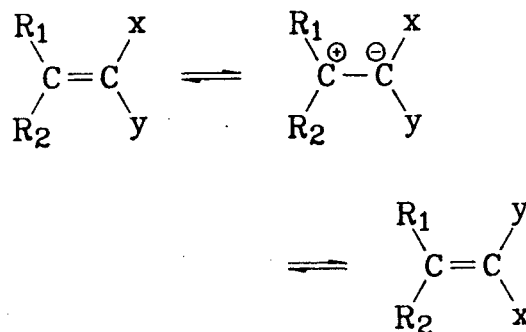
I. INTRODUCTION

Dynamic NMR spectroscopy provides a convenient means for studying the kinetics of chemical processes falling within the time scale of the method (1). Depending on the choice of indicator nuclei and on the technique applied, NMR spectroscopy allows one to measure the lifetimes of magnetically non-equivalent positions, ranging from 10^2 s [double resonance with transfer of saturation from one position to another (2)] to 10^{-6} s [pulse methods including $T_{1\rho}$ measurements (3)]. The rate constants of transitions affecting the lineshapes of NMR signals can be readily calculated, assuming two-center exchange, by the Gutowsky-Holm equation

$$k = 1/\tau = \pi\Delta\nu_0\sqrt{2} \quad (1)$$

at the coalescence temperature of the signals, where $\Delta\nu_0$ is the difference between the resonance frequencies of the signals in the absence of exchange (4). The complete analysis of NMR lineshapes with the use of a computer (1,5) yields the rate constants of the transitions at various temperatures and hence permits one to determine, from the Arrhenius and Eyring equations, activation parameters of the transitions. The dynamic NMR method has found wide use in

studying the simplest transformation of polar ethylenes - rotation about the double bond or their thermal Z,E-isomerization (the symbols Z and E correspond, respectively, to the cis and trans arrangement of the 'principal' substituents relative to the double bond). In NMR studies of mainly enamines containing a tertiary amino group, Sandström, Kessler, Shvo et al. (6-17) treated the Z,E-isomerization as a rotation through a dipolar transition state:



The magnitude of $\Delta G^\ddagger$ for rotation in such molecules is rather low (from 8 to 30 Kcal/mol) due to delocalization of the electron pair of the nitrogen atom. The principles of rotation about the C=C bond through the dipolar transition state

(the thermal mechanism of the Z,E-isomerization) have been discussed in previous reviews (15, 16) and may be summarized as follows:

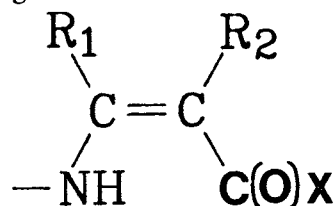
- 1) An increase in electron-donating power of R_1 , R_2 and in acceptor capacity of X, Y promotes polarization of the C=C bond in the molecular ground state and stabilizes the charges in the transition state, thereby decreasing the energy barrier to rotation.
- 2) An increase in size of the substituents at the double bond increases steric strain in the molecular ground state, which also decreases the rotation barrier.
- 3) An increase in dielectric constant of the medium favors polarization of the C=C bond in the ground state and separation of charges in the transition state, which decreases the barrier to rotation about the C=C bond.
- 4) The Z,E-isomerization is a unimolecular reaction. It is characterized by a 'normal' magnitude for the pre-exponential factor ($\log A = 12-13$) and a negative entropy change.

Thus, the rotation barrier is a very useful quantitative characteristic of the structure of tertiary enamines. Compared to enamines containing a tertiary amino group, those with an N-H bond are more complicated systems. Indeed, the latter can undergo tautomeric transformations (18-22) with tautomeric equilibrium fully shifted, as a rule, towards the enamine form. Such compounds are protonated and deprotonated to give cations and anions where the order of the C=C bond seems to be lower than that in the initial state (18). As a result, enamines containing the N-H bond may exhibit a variety of reaction pathways by which the geometrical isomerization can proceed. These pathways are analyzed in the present review on the basis of the available literature. It is to be noted that the data on enamine isomerization, discussed in this work, have all been obtained from NMR spectroscopy. This unique method permits a simultaneous investigation both of the isomerizations and of proton transfer reactions.

II. THE MECHANISM OF Z,E-ISOMERIZATION OF ENAMINES CONTAINING THE N-H BOND

The kinetics of isomerization of enamines containing a primary or secondary amino group were studied mainly by the proton resonance method with enamino ketones and enamino

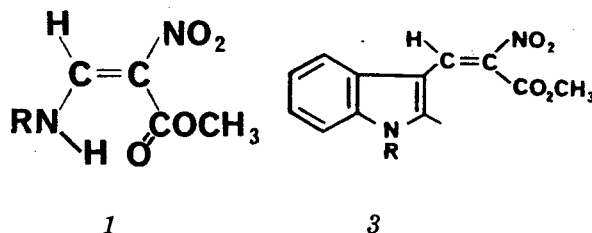
ethers of the general formula:



where X = Alk or OAlk. Determination of the spatial configuration of these compounds by 1H NMR is no problem when $R_1 = R_2 = H$, because the observed magnitude of the spin-spin coupling constant $J_{CH=CH}$ clearly reveals the spatial arrangement of the coupled protons (23). In the case of derivatives of tri-substituted ethylenes (for instance, $R_1 = H$, but $R_1 \neq R_2$) the configuration can be ascertained by comparing the observed value of the olefinic proton chemical shift with that calculated by the increment equation (24)

$$\delta_{CH} = 5.25 + Z_{gem} + Z_{cis} + Z_{trans} \quad (2)$$

It should be noted, however, that with unsaturated compounds containing bulky substituents, the difference between the experimental and calculated δ_{CH} is large and frequently equal to the difference between δ_{CH} of the isomers themselves. In such cases a need arises for additional experiments. Thus reference 25 dealt with unsaturated nitro-compounds such as 1, which are of interest from the viewpoint of synthesis of amino acids and other biologically important species. The resonance signals in the 1H NMR spectra of these compounds were assigned using the shift reagents $Eu(dpm)_3$ and $Eu(fod)_3$. In references 26 and 27 an alternative approach was suggested to establish the configuration of nitroalkenes such as 1 and 3; the approach is based on



the observation of the broadening of the olefinic proton signal on heating the sample. This broadening resulted from scalar relaxation of the second kind, which was more pronounced in the Z-configuration due to the trans relationship of the 1H and ^{14}N nuclei.

Table 1. The Kinetic Parameters of rotation about the C=C Bond of Enamines 1 in Nitrobenzene (30).*

R	E _{act} Kcal/mol		ΔH [‡] Kcal/mol		ΔS [‡] e.u.		ΔG [‡] ^{2,8} Kcal/mol	
	Z	E	Z	E	Z	E	Z	E
CH ₃	-	-	-	-	-	-	20.4 ^{3,4,7}	20.0 ^{3,4,7}
p-CH ₃ O-Ph	20.4	20.4	19.7	19.7	-14.2	-14.2	23.9	23.9
p-CH ₃ -Ph	22.0	22.0	21.6	21.6	-12.0	-12.0	25.2	25.2
Ph	24.7	24.7	24.0	24.0	-6.0	-6.0	26.0	26.0
p-Cl-Ph	25.0	25.0	24.2	24.2	-9.0	-9.0	27.0	27.0

*The estimated errors are 0.4 Kcal/mol for E_{act}, ΔH[‡], ΔG[‡] and 1.5 - 2.0 e.u. for ΔS[‡].

A. The Thermal Mechanism of Rotation about the C=C Bond

Recently, comprehensive ¹H NMR studies were carried out on the kinetics of isomeric transformations in a series of enamines 1 containing the N-H bond (28-32).

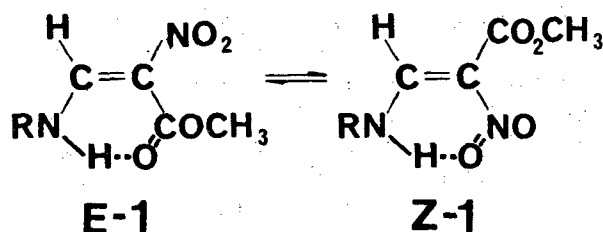
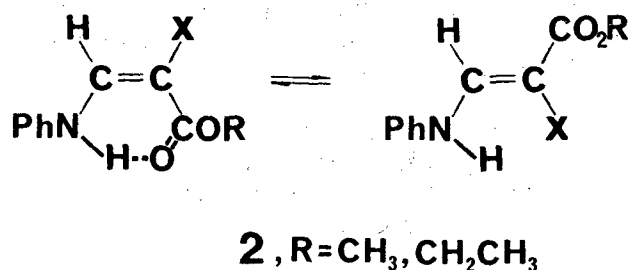


Table 1 lists the activation parameters for the Z,E-transitions, as calculated from the temperature dependence of the COOCH₃ signals through the full lineshape analysis (28-30). As seen from Table 1, the isomerization parameters ΔG[‡], ΔH[‡], and E_{act} of enamines 1 in nitrobenzene decreases with increasing electron-donating power of R. At the same time, in the series of N-aromatic enamines, a satisfactory correlation is observed between ln k_{Z,E} and σ_p of the substituent in the para position of the aromatic ring (30). These data, together with the fact that the kinetic order of the process is equal to unity, point to a thermal, unimolecular mechanism for the isomerizations. The same thermal

mechanism for rotation about the C=C bond, involving formation of a dipolar transition state, has been suggested by Knippel et al. (31) in studies on the temperature dependence of the ¹H NMR spectra of ethyl derivatives of enamines 1 in monitoring the CH= signals. As shown in Table 2, the rotation barrier in dimethylsulfoxide, as determined from the coalescence temperatures, diminishes with increasing electron-donating power of the para substituent of the aromatic ring. Thus, the Z,E-isomerization of enamines 1 containing an NH proton is similar in these cases to the isomerization of enamines containing a tertiary amino group. There are, however, a few differences. As seen from Table 3, an increase in electron-accepting capacity of substituent X results in simultaneously increasing, rather than decreasing, the energy barrier to rotation about the C=C bond in enamines 2:



Frank et al. (32) explain this phenomenon in terms of different effects exerted by substituent

Table 2. Barriers to rotation about the C=C bond of Enamines 1 in DMSO*.

R	$\Delta G^\ddagger$ t° C, Kcal/mol	
	Z	E
p-(CH ₃) ₂ N-Ph	15.6 ³²	15.1 ³²
p-CH ₃ O-Ph	17.2 ⁶⁵	16.9 ⁶⁵
p-CH ₃ -Ph	17.6 ⁷²	17.2 ⁷²
Ph	18.1 ⁸¹	17.7 ⁸¹
p-Cl-Ph	19.2 ⁹⁸	18.6 ⁹⁸
p-CH ₃ CO-Ph	19.8 ¹¹⁷	19.6 ¹¹⁷

*Reference 31 dealt with ethyl ethers of α -nitro- β -aminoacrylic acid.

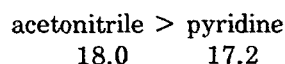
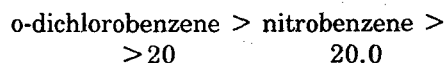
Table 3. Barriers to Rotation about the C=C Bond of Enamines 2 in Nitrobenzene for Various Substituents X.

X	$\Delta G^\ddagger$ t° C Kcal/mol	Reference
NO ₂	26.6 ¹⁶² , 26.2 ⁸⁸	30
C≡N	23.4 ¹⁶²	32
COOEt	19.8 ⁸⁸	32

X on the energy of the ground and transition states. In our opinion, the observed regularity can be attributed to the formation of an intramolecular hydrogen bond, whose strength rises as the acceptor power of substituent X is increased. The formation of intramolecular hydrogen bonds in enamines 1 and 2 and related compounds has been convincingly demonstrated by ¹H NMR studies of the chemical shifts of the amino proton in various solvents (29-36). Further evidence in favor of hydrogen-bond formation is provided by the magnitude of the spin-spin coupling constant in the =CH-NH fragment, which ranges from 13

to 16 Hz, depending on the nature of R, and is indicative of a trans orientation of the interacting nuclei. It should be noted that for enamine 1 with R = H, the constants $J_{\text{CH-NH}}^{\text{cis}}$ and $J_{\text{CH-NH}}^{\text{trans}}$ measured in pyridine are 8 and 16 Hz, respectively (37).

As mentioned above, an increase of the dielectric constant of the solvent reduces the rotation barrier about the C=C bond in tertiary enamines. It is not observed, however, with enamine 1 when R = CH₃. In this case $\Delta G_{Z,E}^{298}$ decreases, with varying nature of the solvent, in the following order (29):



which corresponds to increasing basic properties of the medium. This result also points to the influence of the intramolecular hydrogen bond on the rotation barrier height.

¹³C NMR studies (29) of enamines 1 have shown that an increase in electron-donating power of substituent R gives rise to a downfield shift of the resonance signal of the carbon atom bound to the amino group. According to reference 38, this results from molecular polarization of the following type:



which explains the decreasing energy barrier to rotation about the C=C bond. The strong interaction between the nitrogen electron pair and the π -system of the enamines is independently demonstrated by the magnitude of the amino group proton geminal constant for compound 1 with R = H, which is equal to ~2 Hz and typical of fragments such as H₂C=C, i.e., of fragments with an sp²-hybridized central atom (23). Further evidence for this interaction is furnished by ¹³C (39), ¹⁴N (40), and ¹⁵N (41) NMR spectra of related compounds.

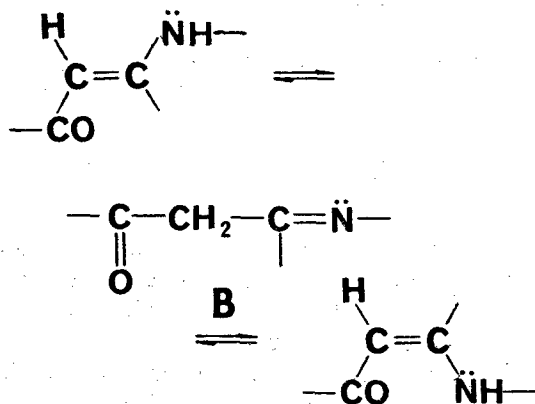
Thus the results reviewed in this section of the paper point toward the probability of the thermal mechanism for Z,E-isomerization of enamines containing the N-H bond. The amino proton is not involved in this isomerization. Indeed, in the ¹H NMR spectra of enamine 1

with $R = CH_3$ in nitrobenzene, the spin-spin coupling constant of the fragment $NH-CH_3$ remains unchanged after coalescence of the Z- and E-isomer signals (42).

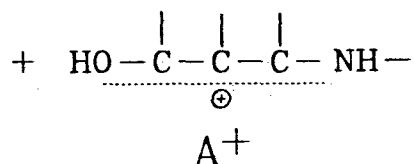
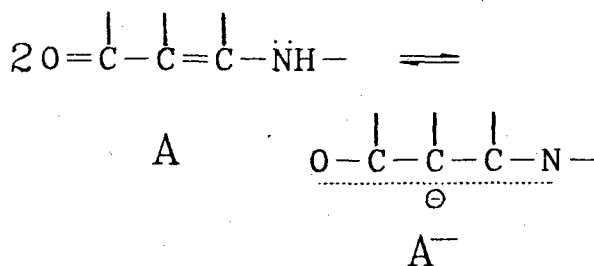
B. The Proton-transfer Induced *Z,E*-isomerization of Enamines

1. Associative Mechanism

When studying the ^1H NMR spectra of enamines of the general formula



Dabrowski et al. (43, 44) observed that in D_2O and ND_3 these compounds could undergo isomerization and, simultaneously, isotopic exchange of the olefinic proton, proceeding, as commonly accepted, via a tautomeric transition. Compounds containing a tertiary amino group exhibited no isomerization under the same conditions. This fact allowed the authors to conclude that the isomerization proceeded through a tautomeric transition to yield an unstable but 'freely rotating' imino form B. (The relation between isomeric transformations and isotopic exchange of the olefinic proton was also discussed in references 45, 46). The rate of the isomerization proved, however, to be well above the rate of isotopic exchange (qualitative estimates), which provided evidence for competing mechanisms for the process. Dabrowski and Terpinski (44) believe that one enamine molecule can act as a base on another molecule to eliminate a proton from the nitrogen atom. The double bonds of the resulting anion A^- and cation A^+



lose partly their double bond character, which facilitates rotation about the $C=C$ bond. The isomerization mechanism involving formation of the active (in the sense of rotation) forms due to interaction of two enamine molecules should be referred to as the 'associative' mechanism. This mechanism was supported kinetically by dynamic NMR spectroscopy in studies of isomerizations of enamine *1* with $R = H$ in pyridine (29). It should be noted that the structure of this compound has one amino proton not involved in formation of the intramolecular hydrogen bond. As seen from Figure 1, the lineshape of $COOCH_3$ signals depends on enamine concentra-

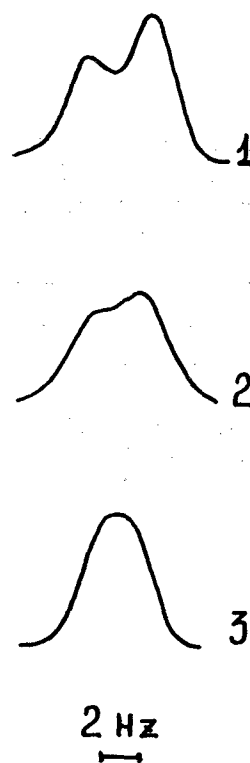


Figure 1. The lineshapes of COOCH_3 signals of enamine **1** with $\text{R} = \text{H}$ in pyridine at 70°C and various concentrations (1.0 - 0.1 M, 2.0 - 0.3 M, 3.0 - 0.4 M).

Table 4. Activation Parameters for Z,E-isomerization of Enamines 1 in Pyridine.

R	E_{act} Kcal/mol		$\Delta H^\ddagger$ Kcal/mol		$\Delta S^\ddagger$ e.u.		$\Delta G^\ddagger^{298}$ Kcal/mol	
	Z	E	Z	E	Z	E	Z	E
CH ₃	12.2	12.4	11.6	11.7	-20.2	-18.4	17.7	17.2
H	10.2	8.5	9.5	7.8	-26.4	-30.8	17.4	17.0

tion. The kinetic order of the Z,E-isomerization, n , determined from equation 3 (47)

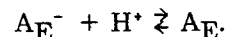
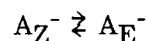
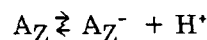
$$1/\tau_{Z(E)} = dZ(E)/dt[Z(E)] = k[Z(E)]^{n-1} \quad (3)$$

by calculating the lifetimes $\tau_{Z,E}$ at various concentrations of enamine 1 with R = H was found to be, at the indicated temperature, between 1.7 (100°C) and 2.0 (50°C). This corresponds to two enamine molecules being involved in the kinetically controlled stage of the process. It should be noted that the decrease in the isomerization parameters E_{act} , $\Delta H^\ddagger$, $\Delta S^\ddagger$ (Table 4) observed on going from the thermally isomerizing enamine 1 with R = CH₃ to enamine 1 with R = H is at variance with the effect of the substituent at the nitrogen atom. This could not be explained by the thermal rotation mechanism and also suggests that the isomerization mechanism has changed.

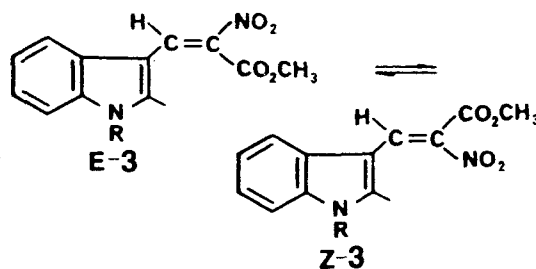
2. Dissociative Mechanism

The anion A^- in the above scheme can be generated by interaction of an enamine containing an N-H proton with a base whose role may be played by the solvent. Such a mechanism of Z,E-isomerization of enamines should be referred to as the 'dissociative' mechanism. The existence of the dissociative mechanism was confirmed by dynamic NMR studies of enamines 1 with N-aromatic substituents in dichloromethane-pyridine mixtures (30, 37). The lifetimes of the Z- and E-isomers were found by full analysis of the lineshapes of the COOCH₃-signals. The effect of substituent R on the Z,E-isomerization barrier

height in enamines 1 with R = Ar (Table 5), the partial first order kinetics of the reaction in enamine and pyridine (37), as well as the kinetic isotopic effect found from the lineshape of the COOCH₃ groups of enamine 1 with R = Ph, deuterated at the nitrogen atom, all pointed to a mechanism involving cleavage of the N-H bond, followed by rapid rotation in the anion



The dissociative mechanism was also supported by the kinetics of isomerization of enamine 3 with R = H (48).



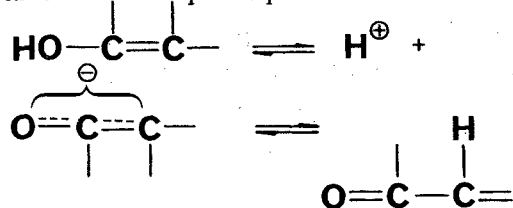
In acetonitrile and pyridine the compound showed isotopic effects (as established by analyzing the lineshapes of COOCH₃-signals, see Table 6 and Figure 2). Substitution of the radicals CH₃ and CH₃CO for the nitrogen proton resulted in a sharp increase of the rotation barrier ($\Delta G_{Z,E}^{298} = 17.5$ Kcal/mol for R = H in

Table 5. The Effect of Substituent R on Barriers of Z,E-isomerization of Enamines 1 in a CH₂Cl₂:Pyridine Solution (30).

R	p-NO ₂ -Ph	p-Cl-Ph	Ph	p-CH ₃ -Ph	p-OH-Ph
$\Delta G_Z^{\ddagger 298}$ Kcal/mol	14.2±0.2	15.6±0.2	15.9±0.2	16.5±0.2	16.8±0.2
$\Delta G_E^{\ddagger 298}$ Kcal/mol	14.3±0.2	15.4±0.2	15.7±0.2	16.3±0.2	16.5±0.2

acetonitrile and pyridine and $\Delta G_{Z,E}^{\ddagger 298} > 24$ Kcal/mol for R = CH₃, CH₃CO in dimethylsulfoxide). Finally, it is only the dissociative mechanism that can explain the inhibiting effects of an acid on the rate of isomerizations of enamine 3 with R = H in acetonitrile (Figure 3), where the acid reduces the lifetime of the anionic form (48).

The conformational lability of the anionic forms of enamines can be accounted for by the decreased order of the C=C bond. As demonstrated by MO LCAO calculations, the dissociation of the N-H bond in enamine 1 (R = CH₃) leads to CC double bond nonbonding interaction and to a threefold decrease of the rotation barrier about the C=C bond in the anionic form (49a). It should be noted that the decreased order of the C=C bond in the anionic form is not sufficient perhaps for the isomerization of the enolic systems. As demonstrated by the dynamic NMR spectroscopy in reference (49b,c) the fast isomerization of the enolic systems is achieved by the protonation-deprotonation reaction of the enolic anion with the participation of the keto form:



i.e., by the transformation from a double bond to a single bond.

Table 6. The Lifetimes of Z,E-isomers of Enamine 1 with R = Ph in a CH₂Cl₂:Pyridine Solution and of Enamine 3 with R = H in Pyridine and their N-deutero-derivatives under the Same Conditions.

Compound	$\tau_{\text{eff}}^{\text{t}^\circ\text{C}}(\text{H})^*$	$\tau_{\text{eff}}^{\text{t}^\circ\text{C}}(\text{D})$	Ref.
1 with R=Ph	0.014 ⁴⁰	0.028 ⁴⁰	30
3 with R=H	0.03 ⁴⁰	0.09 ⁴⁰	48

$$^* \tau_{\text{eff}} = \tau_Z \tau_E / (\tau_Z + \tau_E).$$

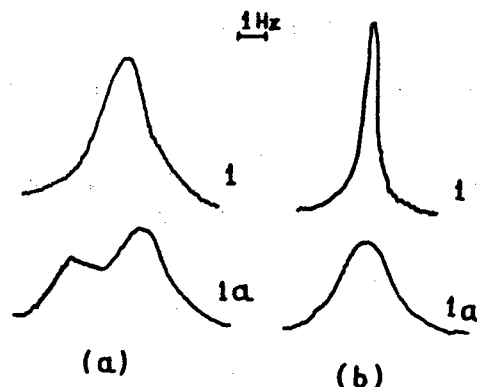
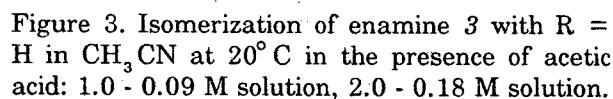
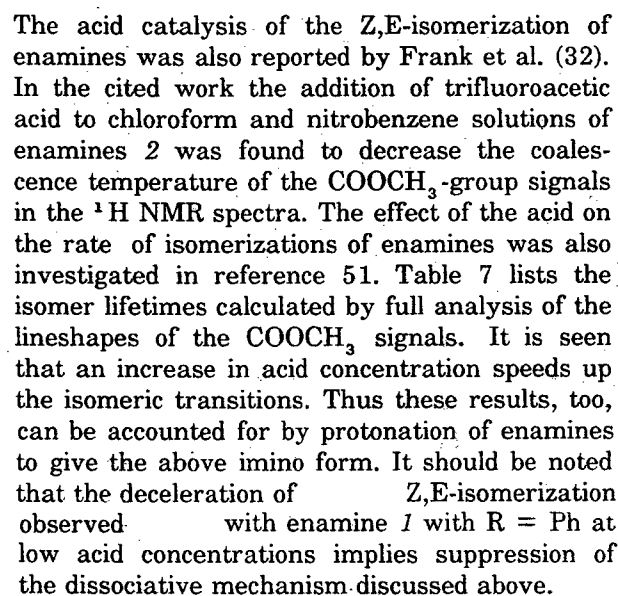
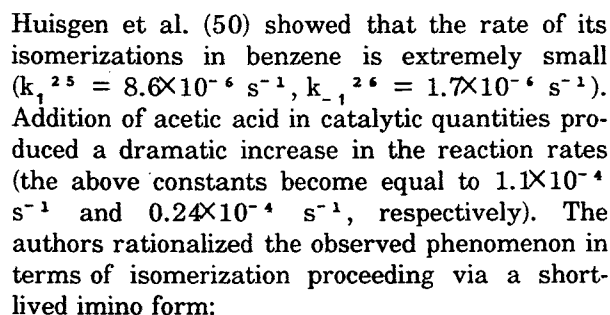


Figure 2. COOCH₃ signals of enamine 3 with R = H (1) and its deutero-analog (1a) in pyridine (a) and acetonitrile (b).



Inasmuch as enamines containing a primary or secondary amino group can undergo isomerization via migration of the N-H proton, a relationship should be expected to exist between the rate of Z,E-isomerization of these systems and acidic-basic properties of the solvent. In studies of enamine 4



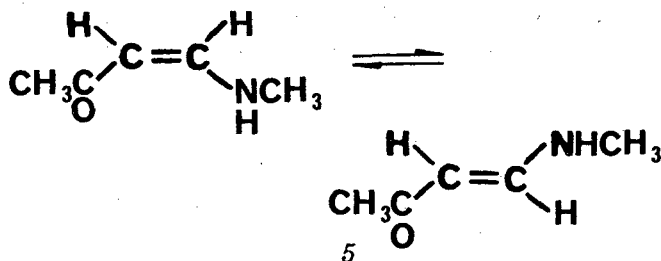
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Table 7. The Lifetimes of Z- and E-isomers of *1* with R = CH₃ and Ph in Acetonitrile at Various Concentrations of CF₃COOH (51).

[CF ₃ COOH] Mol/L	R = CH ₃		R = Ph	
	τ_E t°C	τ_Z t°C	τ_E t°C	τ_Z t°C
	s	s	s	s
0.0	0.16 ⁵³	0.30 ⁵³	0.82 ⁵³	1.0 ⁵³
0.027	0.17 ⁵³	0.32 ⁵³	-	-
0.135	0.14 ⁵³	0.27 ⁵³	>>0.82 ⁵³	>>1.0 ⁵³
0.27	0.073 ⁵³	0.13 ⁵³	-	-
2.7	0.127 ⁻²⁵	0.39 ⁻²⁵	0.035 ⁵³	0.053 ⁵³
5.4	0.037 ⁻²⁵	0.11 ⁻²⁵	0.095 ⁵³	0.019 ⁵³

III. Z,E-ISOMERIZATION AND PROTON EXCHANGE

As mentioned above, NMR spectroscopy offers an unique means for revealing the mechanisms of isomerizations in enamines containing the N-H bond. In particular, by using this method a relationship was found between the isomerizations and intermolecular proton exchange reactions. Kozerski et al. (52) studied the temperature behavior of the ¹H NMR spectra of enamines *5*



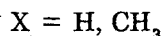
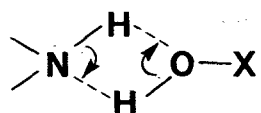
in the region of the CH₃CO signals, which are responsive to the isomerization, and the NCH₃ signals, which are indicators for intermolecular proton exchange due to the splitting on the NH proton. It was demonstrated that in aprotic solvents the activation energy parameters for both processes ($\Delta G^\ddagger$) were practically the same (Table 8). This coincidence allowed the authors to conclude that the isomerization occurs with participation of the NH proton, i.e., proceeds via formation of ionic forms. Similar results were reported in reference 42 for enamine *1* with R = Ar, where the full analysis of the lineshapes of the COOCH₃ and CH₃ group signals showed the rate of the isomerization in a dichloromethane-pyridine mixture to be very close to the rate of the N-H bond cleavage. The partial first order

Table 8. The values of $\Delta G^\ddagger$ for Rotation about the C=C Bond and for Proton Exchange in Enamine *5* in Various Solvents (52).

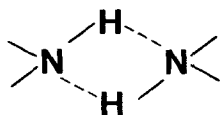
Solvent	Process	$\Delta G^\ddagger$ t°C Kcal/mol
in bulk	isomerization	19.6 ¹⁰²
	NH exchange in cis form	19.5 ⁹⁴
	NH exchange in trans form	19.6 ⁹⁸
C ₂ Cl ₆	isomerization	20.6 ¹¹⁶
	NH exchange in trans form	19.9 ¹⁰²
	NH exchange in cis form	18.9 ⁹⁴
C ₂ Cl ₆ : pyridine	isomerization	19.8 ⁹⁹
	NH exchange in trans form	19.0 ⁹⁵
	NH exchange in cis form	18.2 ⁷⁰
H ₂ O	isomerization	18.6 ⁹⁴
	NH exchange in both forms	14.7 ⁸

kinetics in enamine and pyridine, observed for both Z,E-isomerization and proton exchange, as well as the similar effect exerted by the substituent in the para position of the aromatic ring, suggested that the transfer of the NH proton between molecules of enamine *1* with R = Ar was catalyzed by pyridine and followed by the loss of conformational stability of the compounds. Thus, with aprotic solvents simultaneity may be

expected for the isomerizations and NH proton exchange in enamines *1* with $R = Ar$ and *5*. A very different situation is observed with proton-donating solvents. As seen from Table 8, in aqueous solution the isomerization of enamine *5* necessitates much greater energy than does the proton exchange reaction. Dynamic NMR studies of the isomerization and proton exchange kinetics for compounds *1* ($R = Ar$) and *3* ($R = H$) in CH_3OH (53), $CH_3OH-CHCl_3$ (54), and pyridine-water mixtures (55) demonstrated that enamines with N-H bonds are isomerized in the proton-donating solvents through a unimolecular transition state (thermal mechanism, Section II.A). On the other hand the proton transfer reactions go through a bimolecular transition state, containing one molecule of proton-donating solvent:



Perhaps the difference in the rates of the discussed processes can be accounted for by this fact. The relation between Z,E-isomerization and proton exchange in enamines containing the N-H proton depends not only on the nature of the solvent but also on the structure of the enamine. Thus in studies of the temperature behavior of the 1H NMR spectra of enamine *1* with $R = CH_3$ in pyridine (29), it turned out that the lineshape of the $COOCH_3$ signals - indicators for isomerizations - was independent of concentration of the isomerizing compound. However, for NCH_3 signals whose lineshape depends on the rate of proton exchange, such concentration dependence was clearly observed (Figure 4). Analysis of the spectra showed that Z,E-isomerization and proton exchange were characterized by first and second kinetic orders, respectively. In other words, the intermolecular NH exchange in enamine *1* with $R = CH_3$ seems to occur through a closed transition state



while the isomerizations proceed by the mechanism of thermal rotation about the $C=C$ bond, discussed in Section II. Thus kinetic studies of NH exchange in isomerizing enamines may provide a better insight into the mechanism of their

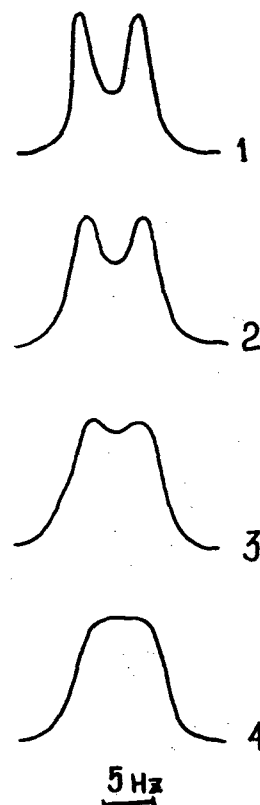


Figure 4. The lineshapes of CH_3N signals of enamine *1* with $R = CH_3$ in pyridine at $110^\circ C$ and various concentrations (1.0 - 0.1 M, 2.0 - 0.2 M, 3.0 - 0.5 M, 4.0 - 0.8 M).

Z,E-transitions.

IV. CONCLUSIONS

The data reviewed in this paper suggest that Z,E-isomerization of enamines containing a N-H bond do not follow a single mechanism. Depending on a number of factors, isomerizations of the enamines may proceed through the thermal mechanism and through the proton exchange reaction. Among the factors affecting the isomerization rate and pathway are the nature of N-substituents and those at the double bond as well as the properties of the solvent (first of all, its acidic-basic properties). It seems that in the general case, solutions of the enamines may exhibit several simultaneous pathways of

Z,E-isomerization. An increase in the ability of N-substituents and those at the double bond to be involved in delocalization of negative charge, as well as an increase in basic properties of the solvent, should raise the probability of the dissociative mechanism of the Z,E-isomerizations. An increase in enamine concentration should in turn favor the associative mechanism. The diversity of the mechanisms of 'rotation' about the C=C bond in enamines containing the N-H bond implies that the rotation barriers calculated from the temperature dependence of the NMR spectra cannot be used as a characteristic of the double bond if the 'rotation' mechanism is unknown. Thus in the case of enamines 1 with R = Ar these barriers characterize the cleavage of the N-H bond.

Considering enamines containing the N-H bond as model compounds, we believe that the data reviewed in this paper will aid in recognizing the nature of isomerization reactions of tautomeric molecules which are extensively investigated by NMR spectroscopy.

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**REPORT ON THE 10TH CONFERENCE ON
RADIO AND MICROWAVE
SPECTROSCOPY-RAMIS;
TWENTY-YEAR OLD TRADITION OF
APRIL MEETINGS AT POZNAN**

In April, 1964 Arkadiusz Piekara, Zdzisław Pająk, and Jan Stankowski organized the *Radiospectroscopy and Quantum Electronics* conference, abbreviated as REK. It was held from the 13th until the 15th of April, 1964 in the House of Technicians, Poznań. The conference was opened by the addresses of Janusz Groszkowski, President of the Polish Academy of Sciences, and Gerard Labuda, Rector of Poznań University. The opening of the conference was greeted with great interest, because of the recent development and application of masers and lasers throughout the world as well as in Poland, where they were being used for the first time. Quantum electronics united the basic research of physicists and chemists with engineers. Chemists participated because of the development of radiospectroscopy in magnetic resonance. The plenary lecture at this first REK by Arkadiusz Piekara was on *Coherence of Light*. Bohdan Paszkowski spoke on the *Technology of Lasers*, K. Antonowicz and J. Stankowski on *Electron Paramagnetic Resonance*, and J. Hennel and Z. Pająk on *Nuclear Magnetic Resonance*. It was a fine beginning.

The second conference of REK was held from the 25th until the 28th of April, 1966. Lectures on radiospectroscopy by K. Antonowicz, K. Leiber, J. Hennel, Z. Pająk, M. Surma, and J. Stankowski were presented at the plenary session of the conference. The presentation of papers was divided into three sections: Quantum Electronics, Nuclear Magnetic Resonance, and Electron Paramagnetic Resonance.

Because of the rapid development of non-linear optics, REK conferences after 1972 were divided into separate meetings: the *Conference on Quantum Electronics and Non-linear Optics (EKON)*, organized by Stanisław Kielich and Franciszek Kaczmarek, and the *Conference on Radio and Microwave Spectroscopy (RAMIS)*,

organized by the author of this report.

The first RAMIS Conference was held from the 22nd until the 24th of April, 1975 in the Institute of Molecular Physics of the Polish Academy of Sciences. Later meetings were organized every two years. The Proceedings of RAMIS-75 have 614 pages and were printed in Polish for the last time. RAMIS-77 was organized with Polish and international participation: R. Blinc (Ljubljana), A. R. Bates (Cardiff), M. Fujimoto (Guelph), I. P. Aleksandrova (Irkuck), A. J. Zviagyn (Kharkov), A. Pfeifer (Leipzig), A. Lösche (Leipzig), C. A. Bates (Nottingham), V. V. Eremienko (Kharkov), and V. A. Golenishchev-Kutuzov (Kazan).

The next RAMIS conferences included the participation of E. R. Andrew (Nottingham), D. Stehlik (West Berlin), D. Wemmer (Berkeley), F. Milia (Athens), D. E. Demko and L. Giurgiu (Bucuresti), W. S. Moore (Nottingham), K. A. Müller (Zürich), I. Svare (Trondheim), K. P. Dinse (Heidelberg), Semin (Moscow), V. Haeberlen (Heidelberg), F. Noack (Stuttgart), R. R. Ernst (Zürich), H. W. Spiess (Mainz), and others.

We have been trying to present other fields of knowledge besides radiospectroscopy which are concerned with molecular dynamics and phase transitions in solids. Because of this, we have invited spectroscopy specialists B. Jezowska-Trzebiatowska and E. Geissler, neutron scientist J. Janik, and adiabatic calorimetry scientists J. Janik and W. J. Huiskamp.

We are especially satisfied with the last RAMIS conference (RAMIS-83), which enjoyed the participation of 15 international scientists. RAMIS conferences are organized in close cooperation with the AMPERE Group and the ISMAR organizations, which provides a permanent connection with recent developments in radiospectroscopy.

I hope that the next RAMIS-85 conference, to be held from the 23rd until the 25th of April, 1985, will provide a fine continuation of this long tradition, now entering the third decade.

Jan Stankowski
Poznan

CALENDER OF FORTHCOMING CONFERENCES IN MAGNETIC RESONANCE

February 17-20, 1985

FIFTH NATIONAL NMR CONFERENCE will be held in Sydney, Australia. The conference will deal with all aspects of NMR spectroscopy and will include sessions on multiple quantum NMR spectroscopy, NMR imaging, NMR of solids and liquid crystals, biological applications of NMR spectroscopy and new methods in NMR spectroscopy. There will be invited and contributed papers as well as specialized discussion sessions and poster sessions. Further information may be obtained from the conference secretary:

Dr. R. S. Norton
School of
Biochemistry
University of New South
Wales
P.O. Box 1
Kensington 2033
N.S.W. Australia

March 22-26, 1985

THIRD ANNUAL MEETING of the SOCIETY for MAGNETIC IMAGING will be held at the Town and Country Hotel, San Diego, California. Organizing Committee:

Dr. Brian C. Lentle
Coordinator, Organizing
Dr. Gary Fullerton
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Education Program
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Contributions are

invited for these sessions and for any other topic related to the development of magnetic resonance imaging and its application. *The deadline for submission of abstracts is December 4, 1984.* For more information, please call or write:

Ronald J. Ross, MD
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Resonance
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Radiologic Medical
Imaging Associates
Fox Run
Gates Mills, OH 44040
(216) 461 5144

July 14-19, 1985 27th

ROCKY MOUNTAIN CONFERENCE will be held in Denver, Colorado and will include symposia on EPR and NMR. Contact

Jan Gurnsey
5531 Bitterbush Way
Loveland Colorado
80537

November 15-18, 1985

FIRST BEIJING CONFERENCE and EXHIBITION on INSTRUMENTAL ANALYSIS, will be held in Beijing, China. The exhibition will be held November 16-25, 1985. The conference and exhibition sponsored by five chinese academic societies including Spectroscopy at Radio and Microwave Frequencies will hold symposia on NMR, EPR, NQR, Double Resonance, and Multiple Quantum Resonance as well as other aspects of instrumentation. Abstracts should be submitted by

March 31, 1985. For further information please contact:

Secretariat of First
Beijing Conference and
Exhibition on
Instrumental Analysis
Room 912

Xi Yuan Hotel
Beijing, China
Tel. 890721 Ext. 912

The editor would be pleased to receive notices of future meetings in the field of magnetic resonance so that they could be recorded in this column.

INSTRUCTIONS FOR AUTHORS

Because of the ever increasing difficulty of keeping up with the literature there is a growing need for critical, balanced reviews covering well-defined areas of magnetic resonance. To be useful these must be written at a level that can be comprehended by workers in related fields, although it is not the intention thereby to restrict the depth of the review. In order to reduce the amount of time authors must spend in writing we will encourage short, concise reviews, the main object of which is to inform nonexperts about recent developments in interesting aspects of magnetic resonance.

The editor and members of the editorial board invite reviews from authorities on subjects of current interest. Unsolicited reviews may also be accepted, but prospective authors are requested to contact the editor prior to writing in order to avoid duplication of effort. Reviews will be subject to critical scrutiny by experts in the field and must be submitted in English. Manuscripts should be sent to the editor, Dr. David G. Gorenstein, Chemistry Department, University of Illinois at Chicago, Box 4348, Chicago, Illinois, 60680, USA.

MANUSCRIPTS must be submitted in triplicate (one copy should be the original), on approximately 22 x 28 cm paper, typewritten on one side of the paper, and double spaced throughout. All pages are to be numbered consecutively, including references, tables, and captions to figures, which are to be placed at the end of the review.

ARRANGEMENT: Considerable thought should be given to a logical ordering of the subject matter and the review should be divided into appropriate major sections, sections, and subsections, using Roman numerals, capital letters, and Arabic numerals respectively. A table of contents should be included.

TABLES: These are to be numbered consecutively in the text with Arabic numerals. Their place of insertion should be mentioned in the text, but they are to be placed in order at the end

of the paper, each typed on a separate sheet. Each table should be supplied with a title. Footnotes to tables should be placed consecutively, using lower case letters as superscripts.

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PAPERS TO APPEAR IN SUBSEQUENT ISSUES

Application of Lanthanide Shift Reagents in NMR-Spectroscopy for Studying Organophosphorus Compounds, B. I. Ionin, V. I. Zakharov, and G. A. Berkova, Leningrad Leningrad Institute of Technology, Leningrad, USSR.

Stochastic NMR Spectroscopy, B. Blümich, Universität Bayreuth, Bayreuth, West Germany.

2-Dimensional NMR Spectroscopy of Proteins, J. Markley, Purdue University, West Lafayette, Indiana, U.S.A.

Electron Spin Echo Method as Used to Analyze Spatial Distribution of Paramagnetic Centers, A. M. Raitsimring and K. M. Salikhov, Institute of

Chemical Kinetics and Combustion, USSR.

Analysis of Chain Microstructure by ^1H and ^{13}C NMR Spectroscopy, Yu. E. Shapiro, Yaroslavl Polytechnic Institute, USSR.

Felix Bloch Memorial Lectures, Contributions from V. S. Murty (Indian Institute of Technology), Yuanzhi Xu (Zhejiang University, China), P. Sohar (Budapest, Hungary), I. P. Gerothanassis (University de Lausanne, Switzerland), C. L. Khetrapal and G. Govil for the Ninth International Conference on Magnetic Resonance (India), R. Basosi (Istituto di Chimica Generale, Italy), I. Ursu (Bucharest, Romania), and A. Saika (Kyoto University, Japan).

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University of Illinois at Chicago

BULLETIN OF MAGNETIC RESONANCE

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EPR of Uranium Ions

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I. INTRODUCTION

Actinides, the last known group of the Periodic Table are the subject of a special interest, both practical and scientific. Though their use is mainly based on their unique nuclear properties, the electronic structure is of no little interest because it is of paramount importance in determining the physical and chemical properties of the actinides and their compounds. Despite the common tendency to consider the actinides group as a new rare-earth group, similar to the lanthanides, numerous data show that this group has a definite identity, evidenced mainly in the first half of the group. At the beginning of the actinides group, a contraction of the 5f electronic shell takes place (actinide contraction), but this is

not so sharply manifested as the contraction of the lanthanides 4f shell. In the actinide group the energy separation of the 5f, 6d, and 7s electronic levels is small, whereas for the lanthanides the 4f electrons are strongly localized. This leads to a strong competition between the 5f, 6d, and 7s electrons in determining the electronic properties of the actinides and their compounds. Another consequence of the weaker 5f contraction is that the ionic radius of the actinide ions is greater than that of the corresponding lanthanide ions. A determinant factor for actinides is the increased importance of the relativistic effects, mainly shown in the increase of the spin-orbit coupling (which is usually twice that of the lanthanides), which combined with a decrease in the Coulomb interelectronic repulsion, leads to a severe

breakdown of the Russell-Saunders coupling. These main factors together with other effects due to the complexity of the atomic systems under discussion lead to clear characteristics of the actinides, as follows:

(a) A great variety of valence states. Whereas with lanthanides the usual valence state in compounds +3 and sometimes also +2 and/or +4, with actinides the whole series of ions, from +2 to +6 (or even +7) is often found;

(b) The most stable valence state of the actinides is usually larger than for lanthanides, especially at the beginning of the group;

(c) The crystal field effects are about twice as strong as with the lanthanides;

(d) The extreme breakdown of the Russell-Saunders coupling makes it necessary to consider fully intermediate coupling in crystal field calculations.

These effects, shown especially with the lighter actinides, lead to the interesting situation that some of their properties are similar to those of the 3d elements rather than to the lanthanides. However, it would be incorrect to overemphasize this similarity, and the best way is to consider the actinides not only as f elements, but also to consider the whole electronic structure and the effective radii of the electronic shells. The stronger contraction of the 5f shell in the second half of the actinide group allows closer similarity with the lanthanides, but even here it is not perfect.

The great variety of valence states of the actinides makes it possible that the ions of a given element span a wide range of $5f^n$ configurations. For example, uranium ions span all the electronic configurations (from +6 to +2) at the beginning of the series, where the identity of the actinide group is chiefly manifested.

The very complex behavior of the actinides combined with, in many cases, a lack of spectroscopic data of free ions, makes it necessary to study their compounds by a multitude of physical methods. It is not the aim of this review to discuss fully the electronic properties of the actinides, but to show what results can be obtained by the use of electron paramagnetic resonance (EPR). This task is difficult since excellent reviews on the subject have been given by Abragam and Bleaney (1) and by Boatner and Abraham (2). However, some new results obtained since these reviews have been published, many of them by the present authors, makes it useful to present this review. A review of magnetic resonance studies on uranium compounds,

related mainly to their use in nuclear energetics has recently been published (3).

EPR has been very effective in the study of uranium ions in crystals; the main results being as follows:

(a) Determination of the nuclear spin, the nuclear magnetic moment and electric quadrupole moment for the isotopes 233 and 235;

(b) Identification of the valence state of uranium ions in crystals;

(c) Identification of the symmetry and structure of different uranium centers in crystals;

(d) Identification of the ground state of uranium ions in crystals and of the influence of other electronic states on this. These results show the importance of the intermediate coupling in the case of actinides;

(e) Crystal field studies, emphasizing the role of covalency.

We hope that this review clearly shows these results and also indicates that the EPR studies of uranium ions in crystals have further potential.

II. URANIUM IONS IN CRYSTALS

A. Electronic Structure of Uranium and its Ions

1. General Properties

Uranium was discovered in 1789 by M. H. Klaproth in pitchblende. In 1841 E. Peligot showed that the semimetallic substance separated by Klapworth was in fact the uranium dioxide. At the formulation of the periodic system of elements by D. Mendeleeff, uranium was the heaviest known element. In 1896 H. Becquerel discovered the radioactivity of uranium. This discovery gave a strong impetus to studies on uranium, and in 1939, when nuclear fission was discovered (Hahn and Strassman) uranium became one element of the greatest scientific and practical interest. This is because ^{235}U is the only natural nuclide which undergoes nuclear fission in a reaction with slow neutrons.

Uranium has fourteen isotopes, with mass numbers from 227 to 240. Only three of these, namely 234, 235, and 238 isotopes occur in nature with abundances of 0.006%, 0.71%, and 99.28% and with lifetimes for α -decay of 2.45×10^5 y, 7.1×10^8 y, and 4.51×10^9 y, respectively (4). For nuclear power, of great importance are the natural isotopes 235 and the synthetic isotope 233 (α -active, lifetime of 1.6×10^5

y) as fissile materials and the isotope 238 as a fertile material. The nuclei of the even isotopes have zero nuclear spin and magnetic moments, while the odd isotopes have half-integral values of the nuclear spin quantum number and non-zero nuclear magnetic moment.

The electronic structure of atomic uranium and its ions or compounds is still not completely clear. The optical spectra of neutral [U(I)], singly ionized [U⁺ or U(II)], four-fold ionized [U⁴⁺ or U(V)], and five-fold ionized [U⁵⁺ or U(VI)] uranium are known, and there is no reported analysis on the free-ion spectra of the other ions. On the other hand, in the condensed state only the ions U⁶⁺ to U²⁺ have been stabilized.

The ionic radii of the different uranium ions are not very large (1.03 Å for U³⁺, 0.93 Å for U⁴⁺, 0.88 Å for U⁵⁺, and 0.82 Å to 0.73 Å for U⁶⁺ (5), and they can easily substitute in crystals the alkali or alkaline-earth ions as well as other diamagnetic cations such as La³⁺, Y³⁺, or Th⁴⁺. Uranium ions can substitute for cations of a much lower valence in crystals; the electric charge difference being compensated by different means such as substitutional anions of higher valence, interstitial anions, cationic vacancies, substitutional cations of lower valency and so on. Thus a great variety of uranium centers in diamagnetic crystals can be obtained and detailed information on the electronic structure of the uranium ions can be inferred from these studies. However, much care must be exercised because the covalency in crystals may severely alter the properties of the ions in crystals as compared with the free ions.

The electronic structure of uranium has been the subject of a long debate. Though as early as 1923, Bohr (6) suggested that the filling of the 5f shell must begin around the element 91, early arguments in favor of uranium as a 6d element have been raised (7). This controversy lasted almost two decades until firm data on chemical properties of the uranium compounds, emission spectroscopy, optical absorption spectra in solutions and crystals, crystallographic, and magnetic studies have clearly established some of the main electronic properties of uranium and its compounds. The findings have subsequently been confirmed or completed by refined physical methods such as neutron diffraction, photoelectric emission spectroscopy, and EPR.

2. Brief Theoretical Account

A theoretical study of the atomic structure of uranium is a very difficult task due to the

inherent complications which arise in the study of large quantum systems (8-10). Many calculations have been performed in order to ascertain the electronic structure, spectroscopic parameters, and other parameters of interest such as the radial integrals for crystal field studies. Due to the complex interactions in such systems, the wave equation can be solved only approximately. We consider here a free atom without nuclear spin.

In a non-relativistic theory, the main terms in the Hamiltonian are the kinetic term $\sum_i p_i^2/2m$, the electron-nuclear electrostatic interaction $\sum_i -Ze^2/r_i$, the interelectronic repulsion $\sum_{i,j} e^2/r_{ij}$, and the spin-orbit coupling $\sum_i \zeta_i l_i \cdot s_i$. The main part of this Hamiltonian is composed of the first three which are of an order of magnitude of 10^6 cm⁻¹. Because of the lack of spherical symmetry of the interelectronic repulsion, the wave equation for these three terms cannot be solved exactly. For this reason the interelectronic repulsion is divided into two parts: the spherical symmetric part (the most important) is introduced together with the first two terms in the zeroth-order Hamiltonian H_1 , while the asymmetric part H_2 (of order 10^4 - 10^5 cm⁻¹) acts as a perturbation on the states of H_1 . The wave equation with the Hamiltonian H_1 is solved by Hartree or Hartree-Fock methods (12), which lead to the transformation of the multielectronic equation in a sum of unielectronic equations with central potential.

In the Hartree method the total wavefunction of the system is a product of unielectronic wavefunctions, with the only restriction given by the Pauli principle. The central potential represents in this case the spherical potential created at the site of a given electron by the nucleus and the other electrons. This potential does not include the exchange effects, and there is no correlation between the states of the different electrons. In the Hartree-Fock method, the multielectronic wavefunction is a totally antisymmetric determinantal product of unielectronic wavefunctions which leads to an additional exchange term in the central potential. Because the exact calculation of the exchange potential by the Hartree-Fock method is very difficult, different approximations such as the Slater potential (13), the Kohn-Sham potential (14), the parametrized Slater potential (15), the X α -potential (16) have been used. The unielectronic energies depend only on the quantum numbers n and l , while the unielectronic wavefunctions depend on n , l , m_l , and m_s . The energy state characterized by the quantum numbers (n_i , l_i) specifies a $2(2l_i + 1)$ degenerate electronic shell. The solution of the

multielectronic equation is a series of energy states specified by a sequence of quantum numbers

$$(n_1 l_1)^{i_1} (n_2 l_2)^{i_2} \dots (n_N l_N)^{i_N}$$

and called electronic configurations.

The nonspherical Hamiltonian potential H_2 acts usually as a perturbation on the central field wavefunctions within a given configuration. This approximation which neglects the configuration interaction may not be always correct, especially in case of the heavy atoms. When the interaction H_2 is much stronger than the spin-orbit coupling, it splits the electronic configurations in spectral terms characterized by the total orbital momentum L and total spin S quantum numbers (the so-called Russell-Saunders coupling). In the calculation of the effect of H_2 in a given electronic configuration (of equivalent or non-equivalent electrons) or in the calculation of the configuration mixing, two kinds of integrals (the electrostatic $F^{(k)}$ and exchange $G^{(k)}$) must be computed. For a configuration of equivalent electrons the effect of H_2 can be completely described by the electrostatic parameters $F^{(k)}$, with $k = 0, 2, 4$, and 6 .

The spin-orbit coupling of uranium is about $2 \times 10^3 \text{ cm}^{-1}$. This interaction couples the spin and the orbital angular momentum, and in the Russell-Saunders treatment L and S are coupled to give a total angular momentum J . This causes splitting of each spectral term into a number of energy levels characterized by the quantum number J which has values between $|L-S|$ and $L+S$. This splitting can be expressed with the spin-orbit radial integral ζ_{nl} . A level is $(2J+1)$ degenerate, each state being characterized by the quantum numbers $(n l L S J M_J)$. When the spin-orbit interaction is very strong, it can couple different spectral terms. This leads to a breakdown of the Russell-Saunders coupling, and the only "good" quantum number is the total angular momentum J . The wavefunction for each level contains admixtures from different L and S states but of the same J . This situation is called intermediate coupling and each level is labeled, besides the "good" quantum number J , by the L and S of the main component of the wavefunctions. The extreme situation when the spin-orbit coupling is stronger than the interaction H_2 , leads to a coupling of the individual spin and orbital momentum to give the total angular momentum j of each electron, then these are coupled to give the total momentum J of the atom. This coupling (j - j coupling) is a good approximation only for some particular levels in

heavy atoms and does not describe well a general situation even for the heaviest element known.

For heavy atoms, where the product $Z\alpha$ approaches unity (α being the fine structure constant), the relativistic effects become very important. These can be taken into account with different degrees of approximation. The simplest is to consider the intermediate coupling, due to strong spin-orbit interaction and a reduced H_2 interaction, both of these being relativistic effects. Another approximation is to use a non-relativistic theory and apply correction factors obtained by comparing the relativistic and non-relativistic calculations on simple systems.

However, many cases exist when a rigorous relativistic theory is necessary. In this case the unelectronic interactions are replaced by the Dirac Hamiltonian and the interelectronic term is corrected with the Breit interaction (17) which is treated as a first-order perturbation. The wave equation is solved in the same manner as in the non-relativistic case. Many variants exist, depending on how the exchange potential is taken into account. Thus almost all the variants found in the non-relativistic treatment have been adapted for relativistic calculations, and we have the relativistic Hartree (RH) method (18), the relativistic Hartree-Fock, or the Dirac-Fock method (DF) (19,20), the relativistic Hartree-Fock-Slater or Dirac-Slater method (D-S) (21) and so on (22). Since the Dirac Hamiltonian contains the spin-orbit coupling, the unelectronic wavefunctions are the eigenfunctions of the total angular momentum $j = l + s$. The unelectronic states are labeled by the quantum numbers nlj , the number l being retained in order to show the parity of states and the value of l to which a state of given j is reduced in the non-relativistic limit.

The atomic wavefunction is an antisymmetric product of unelectronic wavefunctions and is an eigenfunction of the total atomic angular momentum J . This leads to a j - j coupling. However, because this coupling is never achieved and usually it is necessary to use the intermediate coupling, the mixing of different configurations must be taken into account [mixed configuration Dirac-Fock-MDF-method (23)].

A comparison of the few existing methods, shows that the relativistic parameters rather than the non-relativistic ones approach more closely the experimental ones. The need for intermediate coupling is emphasized by the relativistic calculations (especially by the theories which include the exchange), which show a decrease in the electrostatic Slater parameters $F^{(k)}$, especially for the heavy ions. Atomic

Table 1. The Electronic Radial Parameters ζ_{5f} , $\langle r^2 \rangle$, $\langle r^4 \rangle$,
and $\langle r^6 \rangle$ for the Free Uranium Atom and Ions

Ion	Configuration	ζ, cm^{-1}		$\langle r^2 \rangle, \text{a.u.}$				$\langle r^4 \rangle, \text{a.u.}$				$\langle r^6 \rangle, \text{a.u.}$			
		DS ^b	DF ^c	HFS ^a	DS	DF	MDF ^d	HFS	DS	DF	MDF	HFS	DS	DF	MDF
U	5f ³ 6d 7s ²	1503	1503		3.091			28.43				773.8			
U ⁺	5f ³ 7s ²	1905			2.769			18.05				253.6			
U ²⁺	5f ⁴	1725	1391		3.278			27.19				472.6			
U ³⁺	5f ³	1977	1632	1.86	2.541	2.359	2.346	6.47	13.50	11.48	10.906	39.1	133.3	92.47	90.544
U ⁴⁺	5f ²	2212	1846	1.68	2.156	2.044	2.042	5.00	8.79	7.66	7.632	24.4	61.64	48.056	47.774
U ⁵⁺	5f ¹	2442	2051		1.905	1.833	1.833	6.45	5.84	5.838		35.64	29.81	29.793	

a) Parametrized Hartree-Fock-Slater values (24). b) Dirac-Slater values (25). c) Dirac-Fock values (25). d) Mixed configuration Dirac-Fock values (26).

parameters of neutral uranium and its ions, computed by non-relativistic parameterized Hartree-Fock-Slater (24), Dirac-Slater and Dirac-Fock (25), and mixed configuration Dirac-Fock (26) methods are given in Table 1.

The radial parameters $\langle r^i \rangle$ in the relativistic calculations are defined as

$$\langle r^i \rangle = \int_0^\infty [P^2(r) + Q^2(r)] r^i dr,$$

where $P(r)$ and $Q(r)$ are respectively, the large and small components of the one-electron radial wavefunctions (22). The relativistic values in Table 1 represent the weighted average of the values calculated for the relativistic $5f_{7/2}$ and $5f_{5/2}$ configurations: $\langle r^i \rangle = (6/14)\langle r^i \rangle_{5/2} + (8/14)\langle r^i \rangle_{7/2}$.

Free-ion spectroscopic data are available only on the neutral uranium, U^0 , and U^{5+} . For all the other uranium ions, the free-ion data have been deduced from studies on ions in crystals. However, the free-ion data deduced from the spectroscopic studies on uranium ions in crystals depend on the system under study. Two major effects are responsible for this. First, some atomic parameters are modified due to the fact that the ion is in a crystal. Thus the electron delocalization produces an orbital reduction which in turn modifies the spin-orbit coupling to a degree which differs for each particular system. Secondly, the interaction with the neighboring charges in a crystal produces considerable splitting and mixing of states and may even alter the relative energies of the levels. Due to these effects, systematic data obtained by a multitude of methods on a given ion in different crystals are necessary in order to deduce reliable "free-ion" values.

3. Spectroscopic Studies

3a. Neutral Uranium

The uranium atom has an extremely rich emission spectrum with about 100,000 identified lines (27,28). More than 1,000 energy levels have already been identified. New techniques such as multistep laser photoionization spectroscopy (29-31) and dye laser fluorescence spectroscopy (32, 33) allowed the identification of new high energy levels, including Rydberg states. In 1946 the ground state of uranium was identified as $(Rn)5f^3 6d^1 7s^2$ with the lowest level 5L_6 (34, 35). The uranium spectrum has been identified as an analogue of the element neodymium from the lanthanide group. We must note, however, that the ground configuration of neutral

neodymium is $(Xe)4f^3 6s^2$ with the lowest level 5I_4 (10, 36). This difference shows the effect of the competition between the 5f and 6d orbitals in determining the electronic properties of the actinides. Subsequent studies (37-39) have confirmed this identification for uranium. The theoretical treatment shows that the energy levels of a given configuration of uranium encompass a very broad energy spectrum and some levels of the ground configuration go beyond the ionization limit (6.1941 eV) (31). The labeling of the energy levels is very difficult because often none of the couplings (Russell-Saunders or j-j) allow for an intermediate coupling wavefunction with a dominant component, weighted at more than 30% (27). The lowest levels of the excited configurations are very close to the lowest level of the ground state, and a strong configuration mixing takes place. The theoretical parameters differ according to the method used, e.g. the spin-orbit parameter ζ_{5f} is 2480 cm^{-1} (H-F-S) (40), 1856 cm^{-1} (D-S) (25, 40), 1503 cm^{-1} (D-F) (25), or 1717 cm^{-1} (D-S with an exchange scaling factor $\alpha = 0.7$ (40)) as compared with the experimental values of 1773 cm^{-1} (41) or 1754 cm^{-1} (39). The theoretical value for ζ_{6d} is 1848 cm^{-1} (H-F-S), 1475 cm^{-1} (D-S), or 1363 cm^{-1} (α -D-S) (40).

3b. Single-ionized Uranium

The emission spectrum is again very complex (27,28). More than 3,000 lines have been identified so far. A very strong competition between the 5f, 6d, and 7s orbitals in determining the electronic properties of this ion is observed. The ground configuration is $5f^3 7s^2$ with the nearest excited configurations $5f^3 6d 7s$, $5f^3 6d^2$, and $5f^4 7s$. The theoretical (D-S) value for the ζ_{5f} constant is 1905 cm^{-1} for the ground configuration and 1682 cm^{-1} for the configuration $5f^4 7s$ (25).

3c. Divalent Uranium

No analysis of the free-ion spectra of this ion have been reported. Estimations of the theoretical structure are contradictory. The ground configuration for U^{2+} is given as $5f^3 6d$ with the ground state 5L_6 (27) while elsewhere (42) the $5f^3 7s$ configuration is the ground state, with $5f^3 6d$ and $5f^4$ at about 700 cm^{-1} . Considering the approximations used in these estimations (e.g. the estimated (42) ground state for U^+ is $5f^3 6d 7s$ with an error of 500 cm^{-1} , while the experimental data clearly show that it is $5f^3 7s^2$), it is not possible to reach a correct

conclusion without clear experimental evidence. In a systematic study of the optical spectra of uranium ions in fluorite, Hargreaves (43, 44) claims to have found a spectrum with an EPR signal from a non-Kramers ion, with $g_{\parallel} = 3.28$ and $g_{\perp} < 0.1$. Though initially the ground configuration was identified as $5f^3 6d$ with the lowest level 3L_6 (43), a subsequent analysis (44) replaced this with $5f^3 7s$ with the ground level 5I_4 . On the other hand the actinide Np^{3+} (45-47) and Pu^{3+} (48) in condensed media, and the lanthanide ion Nd^{2+} (49) and Pm^{3+} (50) have the ground configuration $5f^4$ and $4f^4$, respectively, with the lowest level 5I_4 . It is likely that for U^{2+} the ground configuration is $5f^4$. Situations in which the $5f$ shell becomes lower than $6d$ when passing from neutral atom to ions are known (for instance the ground configuration is $6d^2 7s^2$ for neutral thorium, $5f 6d$ for Th^{2+} and $5f$ for Th^{3+} (51-54).

The calculated spin-orbit parameter for the $5f^4$ configuration of U^{2+} is 1725 cm^{-1} (D-S) or 1391 cm^{-1} (D-F) (25).

3d. Trivalent Uranium

The only data on this ion come from optical spectra in crystals and solutions. The absorption study of U^{3+} in $LaCl_3$ has demonstrated that the ground state of this ion is $5f^3$ with a ground level $^4I_{9/2}$ (45) in agreement with an estimate (42). The optical spectra (45) allowed an estimation of the spectral parameters and of the spin-orbit coupling $\zeta_{5f} = 1666 \text{ cm}^{-1}$. However, this value is affected by the orbital reduction and is not a good estimate of the "free-ion" spin-orbit parameter. The calculations gave for this parameter the values of 1977 cm^{-1} (D-S) or 1632 cm^{-1} (D-F) (25). By comparing the values of the calculated spin-orbit parameters with the experimental values it was concluded (25) that the D-S values are closer to the experimental data and the agreement is quite good. With a numerical correction, the estimated value of the spin-orbit parameter for U^{3+} is 1787 cm^{-1} . The states of U^{3+} reflect the intermediate coupling. The ground level $^4I_{9/2}$ contains 83% 4I and 15% 2H . The first excited level at 4278.4 cm^{-1} has 95% $^4I_{11/2}$, then at 7377.7 cm^{-1} a $^4F_{3/2}$ level has 46% 4F and 25% 2D . The next levels are at 7948.8 cm^{-1} with 92% $^4I_{13/2}$, at 9490.9 cm^{-1} a level with $J=9/2$ and 38% 2H , 33% 2G , 12% 4I , 11% 4F and so on. The first excited configuration $5f^2 6d$ is not far from the ground configuration ($27.1 \times 10^3 \text{ cm}^{-1}$ (42)) and shows itself as a group of broad absorption bands in the visible part of the absorption spectra of U^{3+} in

crystals. The system $CaF_2:U^{3+}$ was the second crystal to lase (55-57, 44), although the structure of the active centers and the details of the spectra are still not completely elucidated.

3e. Tetravalent Uranium

The optical spectra of U^{4+} in crystals (43, 44, 58-60) established that the ground configuration is $5f^2$. The ground level is 3H_4 with 89% 3H and 10% 1G , the level at 3500 cm^{-1} has $J=2$ with 92% 3F and 7% 1D , the level 3H_5 at 5981 cm^{-1} and 3F_3 at 7033 cm^{-1} have pure LS composition, while the next level, at 7748.8 cm^{-1} with $J=4$ has 47% 3F and 44% 1G . The spectral parameters depend on the particular system under study. For instance ζ_{5f} is 1870 cm^{-1} for $CaF_2:U^{4+}$, 1780 cm^{-1} for $ZrSiO_4:U^{4+}$, and 1800 cm^{-1} for U^{4+} in Cs_2UCl_6 . The theoretical values for ζ_{5f} are 2212 cm^{-1} (D-S) and 1846 cm^{-1} (D-F) (25), from which the free-ion value of 1982 cm^{-1} is estimated.

The recently reported optical spectra of the free ion (61,62) are in good agreement with these results: the ground level has $J=4$ with 89.3% 3H and 9.8% 1G and the first excited level is at 4160.6 cm^{-1} and has $J=2$ with 86.3% 3F and 12.95% 1D ; the levels 5H_5 at 6136.9 cm^{-1} and 3F_3 at 8983.5 cm^{-1} have indeed pure Russell-Saunders composition. The measured spin-orbit coupling parameter for the free ion is $1968 \pm 2 \text{ cm}^{-1}$, sensibly larger than that measured from optical spectra of U^{4+} in crystals.

3f. Pentavalent Uranium

The optical spectra of the free ion U^{5+} (63) confirmed the ground configuration to be $5f^1$, determined previously from optical spectra in crystals. The two levels of this configuration, $^2F_{5/2}$ (ground level) and $^2F_{7/2}$ are separated by 7608.6 cm^{-1} , which gives the spin-orbit parameter $\zeta_{5f} = 2173.9 \text{ cm}^{-1}$. The calculated values for ζ_{5f} are 2442 cm^{-1} (D-S) or 2051 cm^{-1} (D-F) from which a value of 2172 cm^{-1} was estimated (25), in excellent agreement with the experimental data. The excited configurations lie very high (over $100,000 \text{ cm}^{-1}$) and have no noticeable influence on the ground configuration.

3g. Hexavalent Uranium

This ion has the closed electronic configuration of the inert gas radon. The ion U^{6+} is very stable in compounds and can form strong

covalent bonds with its neighbors in a crystal. Strong optical transitions have been found between the molecular orbitals of these bonds. Particularly strong are the bonds with oxygen with which uranium can form stable groups like the linear uranyl group UO_2^{2+} or the uranate (octahedral or tetrahedral) group, in which the uranium ion is equally or almost equally bonded to six or four oxygens.

The ground state of an octahedral U^{6+} complex is a singlet A_{1g} which characterizes a molecular electronic configuration composed of four γ_8 relativistic unielectronic orbitals with a majority 2p ligand character (64-69). The excited unielectronic molecular orbitals are non-bonding and have mainly uranium character: the first five states are γ_7' , γ_8' , γ_7'' , γ_8'' , and γ_6' (with over 95% uranium character), then states which originate mainly from 6d levels of uranium (over 87%), and after that levels with 7s uranium character (over 75%). The first excited molecular electronic configuration of the complex is $(\gamma_8)^3\gamma_7'$, which has three energy levels, E , T_1 , and T_2 . Thus, a charge transition of an electron from the ground $(\gamma_8)^4$ configuration to the first excited configuration $(\gamma_8)^3\gamma_7'$ under the action of an electromagnetic field (such as light) is accompanied by three optical absorption lines, from the ground level A_{1g} to these three levels. Usually these transitions are in the visible range of the spectrum and their intensity is governed by suitable selection rules.

An axial distortion of the octahedral complex splits the molecular states. Two major cases can be encountered:

(i) weak distortion (weaker than the interelectronic Coulombic interaction) which splits the excited levels (T_1 , $A_2 + E$, T_2 , $B_2 + E$, E , $A_1 + B_1$) but not the ground state;

(ii) strong distortion (stronger than the interelectronic interaction) which splits the unielectronic γ_8 levels in doublets $\gamma_6 = \gamma_7$. The ground configuration is now $(\gamma_7)^2$ and has a single electronic level A_{1g} , and the first electronic configuration is $\gamma_7\gamma_7'$ and has three levels, A_1 , A_2 , and E .

As can be seen, the picture of the electronic levels and of the corresponding optical transitions differ for the two cases. A careful analysis of the optical spectra, taking into account the additional information which can be obtained from such measurements as Zeeman effect or magnetic circular dichroism, could lead to an unambiguous assignment of the levels, and thus of the strength of distortion.

The U^{6+} complexes have a very large

electron affinity (6 to 8 eV). The electron is trapped on the lowest excited electronic level which originates from the γ_7' unielectronic state. Since this state is almost a pure uranium 5f state, the trapping of the electron practically transforms the U^{6+} ion into U^{5+} which is paramagnetic and can be studied by EPR. The electron charge is almost the same in both cases (67), and this situation is expected for uranates too. Thus the trapping of the electron in the antibonding γ_7' (5f) orbital does not modify the symmetry of the complex and does not alter significantly the unielectronic orbitals.

A similar situation holds for the uranyl complexes.

B. Uranium Ions in Crystals

1. General Account

If the ions are introduced in crystals (substitutionally or interstitially), an additional interaction with their neighbors takes place. The source of this interaction is the so-called crystal field which has a definite symmetry, closely connected to the symmetry of the crystalline environment around the ion in question, the electric charges of the neighbors, and their nature and the presence of some point defects. The magnitude of the crystal field interaction depends on the electric charges of the ion and of its neighbors, the nature of the ion and the symmetry of the crystal field, the dipole and quadrupole polarization of the ion, the modifications of the effect of the ligand charge due to its finite charge distribution (charge penetration and exchange penetration), overlap and exchange, covalence (charge transfer) effects, the ligand-ligand exchange charge, and triangular path contributions (70).

The crystal field interaction affects the electronic structure of the open-shell ions. The main effects of the crystal field are modification of the free-ion spectroscopic parameters (the Slater $F^{(k)}$ parameters (71), the spin-orbit parameter) and a splitting ($\sim 10^3 \text{ cm}^{-1}$ in case of the actinides) of the energy states of the free ion. An exact treatment of the crystal field interaction is very difficult. Usually, approximate methods are used that take into account the relative intensities of the crystal field interaction H_C , the nonspherical interelectronic interaction H_2 , and the spin-orbit coupling. Three main cases are observed:

(a) Weak crystal field, when the H_C is weaker than H_{S-O} . This implies calculation of matrix elements of H_C between functions of type $|n l s L J M_J\rangle$ (pure or as parts of the intermediate-coupling wavefunctions).

The crystal field interaction leads to a partial or even to a total removal of the degeneracies of the energy levels. For the ions with odd numbers of electrons a residual degeneracy of minimum two is always left (the Kramers theorem). The J quantum number is often used to label the levels, though the mixing of the J levels through the crystal field combined with the intermediate-coupling effects can lead to crystal field states containing considerable admixture from many energy levels. This situation is characteristic for U^{3+} and U^{4+} in crystals.

(b) Intermediate crystal field, when H_c is stronger than H_{s-0} , but weaker than H_2 . The matrix elements of H_c are calculated with the states $|n \mid S \mid L \mid M_S \mid M_L \rangle$ inside a given LS term. The crystal field leads to a partial removal of the M_L degeneracy. This situation is characteristic for U^{5+} in crystal fields of octahedral symmetry.

(c) Strong crystal field effects when H_c is of the same order of magnitude or stronger than H_2 .

2. Symmetry Considerations

The study of the crystal field effects can be substantially simplified by using group theory (72). In a free ion the $(2J+1)$ wavefunctions characterized by M_J form the basis for the irreducible representation D^J of the three-dimensional rotation group R_3 . The symmetry of the crystal field corresponds to one of the 32 crystallographic point groups which are subgroups of R_3 . As a consequence, under the action of a weak crystal field, the irreducible representation D^J of the rotation group is reduced according to the irreducible representations Γ_i of the crystal field point group. Physically, this corresponds to a splitting of the $(2J+1)$ degenerate J level into a number of components, each component being labeled by an irreducible representation of the point group and having a residual degeneracy equal to the dimension of the representation. In the intermediate field case, the same arguments are valid for the $(2L+1)$ -dimensional representation D^L of the rotation group.

When the angular momentum quantum number is integer, the groups involved are the simple point groups. For instance, in a cubic field, the representation D^L is reduced according to the irreducible representations $\Gamma_1, \Gamma_2, \Gamma_3, \Gamma_4$, and Γ_5 (of dimensions 1, 1, 2, 3, and 3) of the group O_h .

If J is half-integer, the reduction of D^J is

done according to the irreducible representations of the double point groups. The cubic double point group has eight representations, the first five being the same as for the simple group, and three new representations, Γ_6, Γ_7 , and Γ_8 of dimensions 2, 2, and 4, respectively.

Group theory shows only how a given spectral term or energy level is split in a crystal field of a known symmetry (the number of components and their degeneracy) but cannot give any information concerning the ordering of the levels and the splittings. This can be obtained only by an actual calculation of the crystal field effect on the free ion states.

3. The Fictitious Angular Momentum

In the reduction of D^J in a cubic field, for some values of J the representation D^J of the rotation group is reduced to only one representation Γ of the cubic group. This suggests the possibility of classifying the basis functions of these representations Γ as the eigenfunctions of a fictitious angular momentum J . Thus the reduction $D^1 \rightarrow \Gamma_4$ shows that the three basis functions of the representation Γ_4 (regardless of the value of J) can be identified as the eigenfunctions of a fictitious J with $J = 1$. The three functions $|\pm 1\rangle, |0\rangle$ of a fictitious J with $J = 1$, can be taken also as basis functions for the representation Γ_5 . The reduction $D^2 \rightarrow \Gamma_6$ shows that the basis functions of the Γ_6 doublet can be considered as the eigenfunctions of a fictitious angular momentum with $J = 1/2$, and this can also be demonstrated for Γ_7 . Finally, the reduction $D^{3/2} \rightarrow \Gamma_8$ shows that the states of the quartet correspond to the projections of a fictitious angular momentum $J = 3/2$ (even for J larger than $3/2$).

4. The Crystal Field Potential

To evaluate the crystal field splittings and the ordering of the levels, one must know the form of the Hamiltonian H_c . Since this interaction must reflect the symmetry of the crystal field, we can anticipate that the Hamiltonian H_c will be a combination of operators acting on the free-ion states and that the coefficients multiplying these operators and reflecting the strength of the interaction must be determined by experiment. However, it is important to have a theoretical model of the crystal field parameters. As shown above, many mechanisms can contribute to the crystal field interaction, and a theoretical consideration of all these interactions is a difficult task. Thus, simplified models are used which take into account only one or a few interactions

which are supposed to give an essential contribution to the crystal field potential.

In the electrostatic crystal field model, the crystal field interaction is determined only by the electrostatic interaction of the ion with its neighbors in a crystal (73). The electric charges of these neighbors are considered as point charges localized at the lattice sites. In the electrostatic approximation, the crystal field potential $V(r_i, \theta_i, \phi_i)$ acting on the electron (r_i, θ_i, ϕ_i) of the ion satisfies the Laplace equation $V(r_i, \theta_i, \phi_i) = 0$, i.e. there is no interpenetration of the electron charge and of its neighbors. As a first approximation, only the nearest neighbors of the ion in the crystal are taken into account. If we expand in spherical harmonics, the electrostatic potential of the crystal field interaction can be written as

$$H_c = \sum a_k^q r_i^k Y_k^q(\theta_i, \phi_i). \quad (1)$$

In tesseral harmonics, an expression in Cartesian coordinates can be obtained

$$H_c = \sum A_k^q P_k^q(x_i, y_i, z_i). \quad (2)$$

Some restrictions on the expressions of equations 1 and 2 must be imposed. Thus, the definition of the spherical harmonics $Y_k^q = (-1)^q Y_k^{-q}$ imposes that $a_k^{q*} = (-1)^q a_k^{-q}$. Also, the triangular rule $k \leq 2l$ for electrons in an (nl) shell must hold. When the crystal field has inversion, the odd k spherical harmonics have vanishing matrix elements inside a given (nl) state, so they can be omitted from H_c . Inside a given k , the number of components q is limited by the crystal field symmetry, provided a suitable choice of the reference frame is made. The term $k = 0$ is usually omitted since it gives an equal shift of all the lines in a given (nl) configuration.

The crystal field calculations for a multielectronic ion can be simplified by using the Wigner-Eckart theorem which allows the replacement of the unelectronic operators in equations 1 and 2 by operators acting directly on the eigenfunctions of the free ion. Thus, the Hamiltonian in equation 1 can be written as a combination of tensor operators U_k^q (53) having the same transformation properties as the spherical harmonics,

$$H_c = \sum B_k^q U_k^q. \quad (3)$$

If the Hamiltonian has the form of equation 2, the functions P_k^q can be replaced by the so-called equivalent operators O_k^q (74), with the same transformation properties and with matrix elements inside a given J proportional to those of

P_k^q :

$$\langle JM_J | \sum_i P_k^q(r_i) | JM_J \rangle = \Theta_k \langle r^k \rangle \langle JM_J | O_k^q(j) | JM_J \rangle$$

where Θ_k are the proportionality factors labeled usually $\Theta_2 = \alpha_J$, $\Theta_4 = \beta_J$, $\Theta_6 = \gamma_J$, their value depending on the particular J level and $\langle r^k \rangle$ are the radial integrals $\int R_{nl}^* r^k R_{nl} dr$. The equivalent operators can be obtained by replacing the Cartesian coordinates in P_k^q by the corresponding components of the angular momentum, by taking into account the commutation rules.

While the method of the equivalent operators is valid only inside a given J (or L), the tensorial operator method is more general. Tables with matrix elements of the tensorial operators are available (75).

5. Crystal Field Models

The coefficients A_k^q and B_k^q are estimated from a model of the crystal field. The electrostatic field models give the Hamiltonians of equations 1 or 2. However, a comparison of the theory with experiment shows that even if the parametrization in the Hamiltonians of equations 1 or 2 is correct, there is very poor agreement between the theoretical and experimental crystal field parameters. The equations 1 or 2 are far more general than their derivation in the nearest neighbor electrostatic approximation. Improvements to the calculated crystal field parameters were made by performing lattice sums, by introducing the overlap, exchange and covalency (charge transfer), and other effects. The configuration interaction effect is also included by calculating the shielding of the crystal field interaction of the inner electronic configuration, by the outer closed electronic shells (e.g. the shielding of the crystal field interaction of the 5f electrons by the closed 6s² 6p⁶ shells). This leads to a decrease of the crystal field parameters expressed in terms of a shielding factor σ_k such as

$$A_k^q \langle r^k \rangle_{sh} = (1 - \sigma_k) A_k^q \langle r^k \rangle_{\text{point charge}} \quad (4)$$

The calculated values of σ_2 , σ_4 , and σ_6 are 0.83, 0.026, and -0.039 for U^{3+} , and 0.88, 0.012, and -0.046 for U^{4+} , respectively (76).

An improvement in the crystal field potential has been introduced by the superposition model (70, 77). This model assumes that the total

crystal field can be considered as a superposition of individual contributions from each of the ions in the crystal. These individual crystal fields have cylindrical symmetry and, with the z-axis along this individual symmetry axis, the interaction potential can be described, for f-electrons, by only three "intrinsic" parameters, $\bar{A}_2^0$, $\bar{A}_4^0$, and $\bar{A}_6^0$, which depend on the distance R_i between the central ion and the ion which produces the individual field. The total crystal field parameters are then

$$A_k^q \langle r^k \rangle = n_{kq}(i) \bar{A}_k(R_i) \quad (5)$$

where $n_{kq}(i)$ are factors that depend on the angular position of the ions, which are the source of the crystal field. This method has considerable advantages over the traditional method in carrying out crystal field potential calculations.

6. An Example: The Cubic Field

As an example, we consider the case of an ion with an f electron in a crystal field of cubic symmetry. For a weak crystal field, when there is no J mixing, we can use equation 2 of the crystal field Hamiltonian, which in this particular symmetry becomes (if the reference frame is parallel to the cube edges)

$$\begin{aligned} H_c &= A_4(P_4^0 + 5P_4^4) + A_6(P_6^0 - 21P_6^4) \\ &= A_4 P_4 + A_6 P_6. \end{aligned} \quad (6)$$

If we introduce the equivalent operators defined above, this becomes

$$\begin{aligned} H_c &= A_4 \langle r^4 \rangle \beta_J O_4(J) + A_6 \langle r^6 \rangle \gamma_J O_6(J) \\ &= B_4 O_4(J) + B_6 O_6(J) \end{aligned} \quad (7)$$

where

$$O_4(J) = O_4^0(J) + 5O_4^4(J),$$

$$O_6(J) = O_6^0(J) - 21O_6^4(J).$$

In a nearest neighbor electrostatic crystal field approximation, the coefficients A_4 and A_6 are

(a) for eightfold cubic coordination

$$A_4 = -\frac{7 Ze^2}{18 R^5} \quad A_6 = \frac{1 Ze^2}{9 R^7}$$

(b) for octahedral coordination

$$A_4 = \frac{7 Ze^2}{16 R^5}; \quad A_6 = \frac{3 Ze^2}{64 R^7},$$

where Z_e is the charge of the ligand and R the distance from the central ion to the ligands.

For the splitting of the energy levels in a weak cubic crystal field (78), the crystal field Hamiltonian, equation 7, has been transformed into

$$H_c = B_4 F(4) O_4 / F(4) + B_6 F(6) O_6 / F(6) \quad (8)$$

where $F(4)$ and $F(6)$ are scaling factors given by

$$B_4 F(4) = Wx \text{ and}$$

$$B_6 F(6) = W(1 - |x|), \text{ with } -1 \leq x \leq 1 \quad (9)$$

This Hamiltonian becomes

$$H_c = W[x O_4(J)/F(4) + (1 - |x|) O_6(J)/F(6)] \quad (10)$$

The sign of W is determined by B_4 , while that of x is given by B_6 .

The diagonalization of the Hamiltonian of equation 10 for a given J multiplet for given values of x allows the determination of the energy eigenvalues of different crystal field levels as a function of the energy parameter W , which can be estimated from experiment. The eigenfunctions for each Γ_i state in terms of the magnetic quantum states $|M_J\rangle$ are also obtained. If a given representation enters in the reduction of D^J only, once its wavefunctions do not depend on the parameter x ; then the plot of the energy level versus x is a straight line. For the representations that enter more than once in the reduction of D^J , the wavefunctions depend on x , i.e. on the ratio of the sixth- to the fourth-order components of the crystal field potential, and the plot of the energy level versus x is a curved line.

7. The Ground State of Uranium Ions in Weak Cubic Crystal Field

The ground states for the uranium ions are $5f^3 {}^2F_{5/2}$ for U^{3+} , $5f^2 {}^3H_4$ for U^{4+} , $5f^3 {}^4I_{9/2}$ for U^{5+} , and either $5f^3 6d^1 L_6$, $5f^3 7s {}^5I_4$ or $5f^4 {}^5I_4$ for U^{6+} .

In the case of a weak cubic field, which does not produce J mixing, there are five cases as follows:

(a) The free ion ${}^2F_{5/2}$ level is split into $\Gamma_7 + \Gamma_8$. For octahedral symmetry, the ground state is the doublet Γ_7 , while in eightfold cubic or tetrahedral symmetry Γ_8 is lowest. The excited level ${}^2F_{7/2}$ is split

into $\Gamma_6 + \Gamma_7 + \Gamma_8$.

(b) The level 3H_4 reduces to $\Gamma_1 + \Gamma_3 + \Gamma_4 + \Gamma_5$. In octahedral symmetry, the ground state is the singlet Γ_1 , while in eightfold cubic or in tetrahedral symmetry, the ground state can be Γ_1 (for $x < 10/19$) or the triplet Γ_5 (for $x > 10/19$).

(c) The level $^4I_{9/2}$ is split by a cubic field into $\Gamma_6 + 2\Gamma_8$. In octahedral symmetry the ground state can be Γ_6 or one of the Γ_8 representations, while in eightfold cubic and in tetrahedral field, the ground state is Γ_8 .

(d) The level 5I_4 (as well as 3H_4) reduces to $\Gamma_1 + \Gamma_3 + \Gamma_4 + \Gamma_5$. The ground state in the octahedral field can be Γ_1 or Γ_5 (depending on x), while in eightfold cubic or tetrahedral symmetry, the ground state is the singlet Γ_1 .

(e) The level 5L_6 is split into $\Gamma_1 + \Gamma_2 + \Gamma_3 + \Gamma_4 + 2\Gamma_5$. In an octahedral field, the lowest state can be Γ_1 or Γ_2 , while in eightfold cubic or in tetrahedral symmetry the ground state can be the singlet Γ_2 or the doublet Γ_3 .

As can be seen, in the decomposition of some J levels in cubic crystal field, some representations show up more than once. The wavefunctions which form the basis for these representations depend in an intricate way on the composition parameter x of the crystal field potential. Usually this dependence is computed numerically and tables of wavefunctions calculated for a given increment of x are available (78). It is, however, a difficult and time consuming task to extract this parameter from experimental data which provide the matrix elements of some operators between such wavefunctions. In order to overcome these difficulties, an analytical method which gives explicit expressions for the wavefunctions appearing more than once in the cubic crystal field splitting of a given J level versus x has been recently reported (79, 80). This method is based on the complete use of the transformation properties of an electronic wavefunction in a cubic symmetry. For some values of J these analytical functions are particularly simple. For instance (79), in case of a $J = 9/2$ level, which in a cubic crystal field is split according to the rule $D^{(9/2)} \rightarrow 2\Gamma_8 + \Gamma_6$, the wavefunctions of one of the Γ_8 representations (which are isomorphous to a fictitious angular momentum $J = 3/2$) can be written as functions of the magnetic quantum components $|M_J\rangle$ according to:

$$|\Gamma_8', \pm 3/2\rangle = \pm(\sin\theta|\pm 5/2\rangle + \cos\theta|\pm 3/2\rangle,$$

$$|\Gamma_8', \pm 1/2\rangle = \pm[\sqrt{21}\cos\theta + 3\sin\theta]|\pm 9/2\rangle +$$

$$[\sqrt{6}\cos\theta + \sqrt{14}\sin\theta]|\pm 1/2\rangle +$$

$$[\sqrt{21}\cos\theta - 5\sin\theta]|\mp 7/2\rangle \quad (11a)$$

where the fictitious angle θ is connected to the composition parameter

$$x' = \frac{B_6}{B_4} = \frac{\gamma A_6 \langle r^6 \rangle}{\beta A_4 \langle r^4 \rangle} \\ = \frac{F(4)(1-x)}{F(6)x} \quad (11b)$$

with the relation

$$\tan 2\theta = \sqrt{\frac{3}{28}} \frac{5 + 336x'}{1 - 12x'} \quad (11c)$$

The wavefunctions of the other Γ_8'' representation have a similar form as for Γ_8' , but with the replacement

$$\theta(\Gamma_8'') = \theta(\Gamma_8') + \pi/2.$$

Suitable expressions for other J values can be written in a similar manner. The matrix elements calculated between such wavefunctions are explicit functions on the composition parameters; thus the experimental measurement of such matrix elements leads to an easy and direct determination of this parameter.

8. Lower Symmetries

For lower symmetries additional terms must be introduced in the crystal field Hamiltonian. Symmetry arguments can be used to deduce the form of the crystal field Hamiltonian.

The crystal field splits the J manifold into a number of states according to the reduction of D^J into the irreducible representations of the point group in question. If the crystal field potential is $\sum_{k,q} B_k^q O_k^q$, the wavefunctions of the states inside a given J are mixtures of states of different M_J 's which differ by multiples of q and can be written as $\sum_{\mathbf{M}} C_{J\mathbf{M}} |J, \mathbf{M}\rangle$ with $\sum_{\mathbf{M}} C_{J\mathbf{M}}^2 = 1$. Sometimes the crystal field can produce admixtures from states of different J's, and the wavefunctions are $\sum_{\mathbf{M}} C_{J\mathbf{M}} |J, \mathbf{M}\rangle + \sum_{\mathbf{M}'} C_{J'\mathbf{M}'} |J', \mathbf{M}'\rangle$.

9. Intermediate Coupling

The problem of the crystal field splitting in the intermediate coupling becomes very complex (10, 76, 81, 82). This case is frequently

encountered for the actinides where the non-spherical interelectronic interaction H_2 is of the order 5×10^4 to 10^5 cm^{-1} , and the spin-orbit coupling is of order 2×10^3 to $4 \times 10^3 \text{ cm}^{-1}$. A crystal field interaction of 10^3 cm^{-1} produces a considerable mixing of states of different J values. In fact, the crystal field interaction often approaches the spin-orbit coupling, and the only meaningful quantum numbers which can label the states are the irreducible representations of the crystal field symmetry group. This complex situation implies crystal field ground states strongly influenced by the mixing with the excited states, at least with those situated at several eV above it. Calculations for the electronic configurations $5f^2 - 5f^6$ [considering the mixing from all the levels up to about 2 eV from the ground state in octahedral fields (81) and for the $5f^2$ configuration in octahedral and eightfold symmetry (76)] have shown a strong influence of the excited states on the crystal field splitting of the ground level. Thus, the plots for the energies of different crystal field states Γ_i versus the fourth-order cubic crystal field parameter $A_4 \langle r^4 \rangle$ (drawn for different ratios of the sixth- to the fourth-order component) have shown that even the representations which enter once in the reduction of D^J become curved lines, and important modifications in the crossing points of the different crystal field levels occur. This can change substantially the order of the crystal field levels as compared to the case of no mixing. Thus, for large B_6/B_4 values and for reasonable $A_4 \langle r^4 \rangle$ parameters, the ground state of a $5f^2$ ion in eightfold cubic symmetry can be Γ_1 , instead of Γ_5 .

10. The Relativistic Crystal Field

The use of the relativistic Hartree-Fock wavefunctions leads to an additional complication since for each $(n l j)$ electron in a crystal field there are two radial integrals F and G (83). The relativistic crystal field radial integrals for the uranium ions have been calculated by various relativistic atomic methods (25, 26), and some of them are given in Table 1 together with the non-relativistic values (24). A fully relativistic crystal field calculation is rarely used. However, hybrid methods, using the classical formalism, but replacing the radial integrals by effective relativistic integrals are already in common use, as are, for instance, the integrals $\langle r^n \rangle$ for f -shells, obtained by a degeneracy-weighted average of the integrals calculated for the relativistic $f_{5/2}$ and $f_{7/2}$ shells.

11. The Intermediate Crystal Field

As mentioned earlier, the actinide contraction at the beginning of the series is smaller than in the case of the lanthanides. As a consequence, the radial charge distribution for the $5f$ electrons extends over those of the $6s$ and $6p$ electrons (at distances of 2 to 4 a.u. from the nucleus), unlike the lanthanides where the $4f$ electrons are well localized inside the $5s$ and $5p$ closed shells (84).

The larger extent of the $5f$ function at the beginning of the series implies an intermediate crystal field (85). Spectroscopic studies have shown that this is indeed the case for $5f^2$ in crystal fields of octahedral symmetry (1, 9, 85-95). The simultaneous diagonalization of the octahedral crystal field and spin-orbit interactions in the space spanned by the 14 functions $|lm_s m_s\rangle$ with $l = 3$ and $s = 1/2$ is difficult so that the symmetry properties are used to simplify the problem. To begin with, we suppose that the crystal field interaction is stronger than the spin-orbit coupling.

An octahedral crystal field splits the sevenfold orbit degeneracy of the $5f$ level, giving a singlet (Γ_2 or a_2) and two triplets Γ_4 or t_1 and Γ_5 or t_2) of energies

$$E_{\Gamma_2} = -12b_4 - 48b_6$$

$$E_{\Gamma_5} = -2b_4 + 36b_6$$

$$E_{\Gamma_4} = 6b_4 - 20b_6$$

where $b_4 = (3/33)A_4 \langle r^4 \rangle$ and $b_6 = -(80/42)A_6 \langle r^6 \rangle$.

The order of the levels depends on the ratio b_6/b_4 . For b_6/b_4 smaller than or equal to $5/42$, the ground level is Γ_2 . Over this limit Γ_5 becomes lowest. Usually the first case holds, and the order of the levels is $E_{\Gamma_2} < E_{\Gamma_4} < E_{\Gamma_5}$. The energy differences are usually labeled as $V = E_{\Gamma_5} - E_{\Gamma_2}$ and $V' = E_{\Gamma_4} - E_{\Gamma_2}$ (75) or as $\Theta = E_{\Gamma_4} - E_{\Gamma_5}$ and $\Delta = E_{\Gamma_5} - E_{\Gamma_2}$ (77). Since the two spin eigenfunctions are the basis of the irreducible representation Γ_6 of the octahedral group, the 14 spin-orbit wavefunctions can be classified according to the products of representations $\Gamma_2 \times \Gamma_6 \rightarrow \Gamma_7$, $\Gamma_5 \times \Gamma_6 \rightarrow \Gamma_7 + \Gamma_8$ and $\Gamma_4 \times \Gamma_6 \rightarrow \Gamma_8 + \Gamma_6$. Since the spin-orbit coupling is invariant under the octahedral group operators and commutes with J_z , it can be diagonalized inside each of the three representations Γ_6 , Γ_7 , and Γ_8 . The energy matrices are

$$\begin{aligned}
\Gamma_8 & \begin{vmatrix} V + k_{t_2 t_2} \zeta & 3\sqrt{5}k_{t_1 t_2} \zeta/4 \\ 3\sqrt{5}k_{t_2 t_2} \zeta/4 & V' - k_{t_1 t_2} \zeta \end{vmatrix} \\
\Gamma_7 & \begin{vmatrix} 0 & \sqrt{3}k_{a_2 t_2} \zeta \\ \sqrt{3}k_{a_2 t_2} \zeta & V' - k_{t_2 t_2} \zeta/2 \end{vmatrix} \\
\Gamma_6 & |V' + 3k_{t_1 t_2} \zeta/2|
\end{aligned} \quad (12)$$

where k_{ij} are the orbital reduction factors (95) defined as

$$k_{ij} = \frac{\langle f \Gamma_i | I | f \Gamma_j \rangle}{\langle f \Gamma_i | I | f \Gamma_j \rangle}$$

where the functions of the denominator are the purely ionic wavefunctions of the representation Γ_k , and the functions used in the numerator are the molecular orbitals for the same representations. The orbital reduction can be substantial, so while $k_{a_2 t_2}$ is of the order 0.9 to 1, $k_{t_2 t_2}$ can sometimes be as small as 0.5 (95).

The ordering of the five energy levels which are the basis of equations 12 depends on the relative magnitudes of the spin-orbit coupling and crystal field interaction. Figure 1 shows schematically the splitting of a $5f^1$ configuration in an octahedral crystal field. Diagrams showing the effect of the relative magnitude of the crystal field effect and of the spin-orbit coupling on the relative positions of the crystal field levels for particular ratios of b_6/b_4 can be constructed [e.g. Figure 2.3 of (9)]. In an octahedral crystal field, the ground state is always a doublet which contains admixtures from the Γ_7 level (originating from the orbital Γ_2 singlet) and from the Γ_7 level (from Γ_5).

The wavefunctions of this doublet are

$$\begin{aligned}
|+> &= \cos\Theta |\Gamma_7^+> - \sin\Theta |\Gamma_7'^+> \\
|-> &= \cos\Theta |\Gamma_7^-> - \sin\Theta |\Gamma_7'^->
\end{aligned} \quad (13)$$

where

$$\tan 2\Theta = 2\sqrt{3}k_{a_2 t_2} \zeta / (V - \frac{1}{2}k_{t_2 t_2} \zeta).$$

The first excited state can be Γ_7' or Γ_8 , the crossover occurring (90) when $\zeta(4\Delta\Theta + 15\Theta/4\Delta + 17/2) = \Theta + \Delta$.

If Θ is about twice the value of Δ , the crossover takes place at $\Delta \approx 6\zeta$, i.e. at quite strong crystal fields.

An axial distortion splits the Γ_8 quartets, giving rise to new levels. Thus a tetragonal

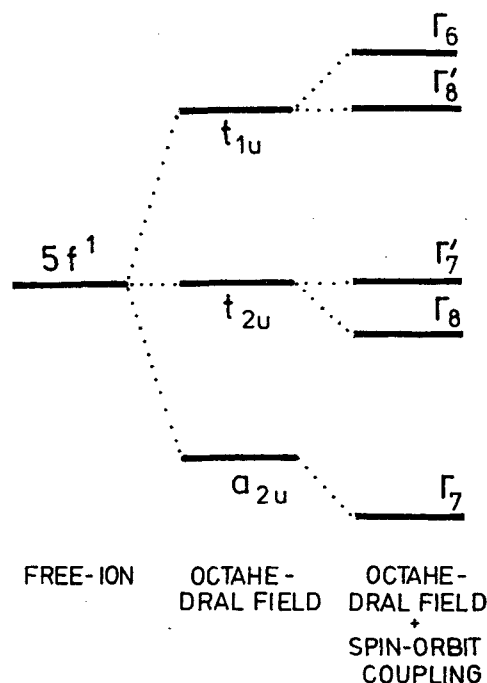


Figure 1. The splitting of the $5f^1$ configuration in a cubic octahedral crystal field (intermediate-field case).

distortion splits the Γ_8 quartet into two doublets, Γ_6^t and Γ_7^t , their order being determined by the sign of the distortion. At the same time, the axial distortion will produce a displacement of the original doublets. However, the splitting $\Gamma_7' - \Gamma_7$ is little affected by the distortion. If the tetragonal distortion is of moderate intensity, the ground state remains Γ_7^o but will contain admixture from all four Γ_7^t states. If the axial distortion is strong, it may happen that Γ_6^t crosses the original Γ_7^o and becomes the ground state for the system (91). For a trigonal distortion, the Γ_8 levels are split into a doublet Γ_6^T and a pair of singlets Γ_4^T and Γ_5^T , and the doublets Γ_7 are transformed into doublets Γ_6^T . Thus, five Γ_6^T doublets will be mixed in order to obtain the wavefunction of the ground doublet. If the distortion is very strong and its sign is suitable, the pair of singlets $\Gamma_4^T + \Gamma_5^T$ become lowest in energy. Instead of considering first the interaction with the crystal field, we could start by considering initially the effect of the spin-orbit coupling and then diagonalize the crystal field interaction.

A tetrahedral or an eightfold cubic crystal field has very little effect on the free-ion states of a $5f^1$ ion even in the case when the crystal field parameters are large (90). In this case, the

treatment for the weak crystal field can be applied, regardless of the value of the crystal field parameters. The lowest electronic level ${}^2F_{5/2}$ of the free ion is split in a cubic field into a doublet Γ_6 and a quartet Γ_8 . They are bunched together and the ratio between the crystal field strength and the spin-orbit parameters determines which of these two levels is lowest. In weak fields Γ_8 is lowest, but a crossing takes place in the intermediate field region when $\zeta(4\Delta\theta + 15\theta/4\Delta - 17/2) = \theta - \Delta$ where $\Delta = E_{a_1} - E_{t_1}$, $\theta = E_{t_2} - E_{t_1}$, and the order of the levels in the strong field limit is $E_{a_1} > E_{t_2} > E_{t_1}$. For $\Delta \approx 2\theta$, the crossing point is at $\theta = 11\zeta/8$. As in the case of the octahedral symmetry, a tetragonal distortion splits Γ_8 into the doublets Γ_6^t and Γ_7^t , while a trigonal distortion splits Γ_8 into the doublet Γ_6^T and a pair of singlets Γ_4^T and Γ_5^T .

12. Determination of the "Free-ion" Parameters from Data in Crystals

The optical adsorption spectra of the paramagnetic ions in crystals for the weak crystal field consists of groups of lines centered around the positions of the free-ion lines. These groups correspond to transitions between the crystal-split levels. In principle, a correct consideration of the crystal field effects should allow the estimation of the free-ion spectroscopic parameters from crystal data. However, often the free-ion parameters are determined by using an average energy (or center of gravity) of the group of crystal-field components. Sometimes additional parameters, not discussed above, are introduced to take into account other interactions in the free ion, as for instance, the interactions between states from different configurations.

Thus, the effect on the energy levels of a f^n configuration from the interaction with levels of a $f^{n-2}11'$ configuration can be expressed with the Tress parameters α , β , and γ (96), while the effect of the levels from a $f^{n-1}1'$ configuration is described with the Judd parameters T^2 , T^3 , T^4 , T^6 , T^7 , and T^8 (97). A complete analysis must also take into account weak interactions such as spin-spin or spin-other-orbit (98).

These "free-ion" values differ from the real free-ion parameters. One of the main reasons is that even these parameters are influenced by the crystalline environment (the orbit reduction and the reduction of the spectroscopic Slater parameters). For this reason, the calculated "free-ion" values differ from system to system, depending also on the method used and the levels chosen for the determination. However, it must be emphasized that the free-ion eigenstates determined

with these parameters are the best starting wavefunctions in the calculation of the crystal field effects for the given system.

The accuracy of this method is strongly affected by the intermediate coupling, hence those levels must be chosen for the estimation of the "free-ion" values which show the closest approach to the Russell-Saunders coupling (44). An example of "free-ion" parameters estimated from the spectra of ions in crystals is the case of the trigonal U^{4+} center in calcium fluorite (44): where $F_0 = 13175$, $F_2 = 200$, $F_4 = 40$, $F_6 = 8.05$, $\zeta = 1660$, $\alpha = 26$ (in cm^{-1}), as compared with the data reported earlier (58) on the same system: $F_2 = 204.56$, $F_4 = 29.1$, $F_6 = 3.24$, $\zeta = 1870$ as compared with the values $F_2 = 230.84$, $F_4 = 35.22$, $F_6 = 3.77$, $\zeta = 1968$, $\alpha = 35.5$, $\beta = -664$, $\gamma = 744$, $p^2 = 573$, $p^4 = 524$, $p^6 = 1173$ obtained from free-ion spectra (62).

13. The Dynamic Crystal Field

The previous discussion has been based on the static approximation of the crystal field, characterized by fixed positions for the paramagnetic ion and its neighbors. In fact, they undergo vibrations with known frequencies. The electronic states of the ion can couple with the vibrational movement of its neighbors, and its electrons will be characterized by the vibronic states (99, 100). The vibronic states of a paramagnetic ion in a crystal have definite symmetry properties.

One of the main consequences of the vibronic coupling is the Jahn-Teller effect. Given initially for molecules (101), the Jahn-Teller theorem has been extended for ions in crystals (102-104). This theorem states (104) that "an orbitally degenerate state of a nonlinear molecule or crystalline defect is unstable and removes some of the degeneracy." The driving force of the Jahn-Teller instability is the vibronic coupling (103). In the case of very strong coupling, the complex may exhibit a static Jahn-Teller distortion, while in the case of a weak coupling a dynamic Jahn-Teller effect shows up, manifested in the modification of some orbital interactions. A discussion of the application of the Jahn-Teller effect to actinides is given elsewhere (105).

C. Hyperfine Interactions

In the preceding sections, we have considered only the electrostatic interaction between nuclei and electrons, assuming the nucleus as a point charge. In fact, the nuclei are complex systems with odd power (i.e. dipole, octapole, etc.)

magnetic moments and even power (quadrupole, hexadecapole, etc.) electric moments which can interact with the magnetic or electric fields. These magnetic or electric fields can be created by the electrons of the atom, molecule or crystalline environment or by the nuclei of the neighboring atoms in molecules or crystals. These interactions lead to an additional splitting of the energy levels, which are very small (less than 1 cm^{-1}) and are known as hyperfine interactions. The hyperfine interactions are dominated by the interaction of the nuclear magnetic moment with the spin and orbital moments of the electrons (the magnetic hyperfine interaction) and by the interaction of the nuclear quadrupole moment with the gradient of the electric field (produced by electrons and/or the external charges) at the nucleus (the quadrupole interaction).

For an even Z element, as uranium, the ground nuclear state for even A isotopes has zero nuclear spin, while the odd isotopes have half-integer spin quantum numbers: $I = 5/2$ for ^{233}U and $I = 7/2$ for ^{235}U .

For the magnetic fields used in magnetic resonance, the magnetic dipole moment is $\mu_I = \gamma\beta_n I$, i.e. is proportional to the angular momentum I of the nuclear ground state, γ being the nuclear spectroscopic factor and β_n the nuclear magneton. The nuclei with spins greater than $1/2$ possess an electric quadrupole moment. An accurate knowledge of these moments is very helpful for the nuclear theories. Thus, while the spin and magnetic moments show the validity of the nuclear models, the nuclear electric quadrupole moment gives information concerning the departure from the spherical symmetry of the nuclear electric charge distribution. The study of the hyperfine interactions can supply information on the electronic structures of the system, the validity of the atomic structure calculations, the bonding in crystals, and the local structure of the crystals. Various nuclear (nuclear orientation, NMR, perturbed angular correlation, Mössbauer effect) or electric (optical spectroscopy of free ions and atoms, optical pumping, EPR of the ions in crystals, electron-nuclear double resonance, atom beam magnetic resonance, multistep laser photoionization spectroscopy, laser-radiofrequency double resonance) methods can be used in order to study these interactions. For uranium, the nuclear methods are not useful in the study of these interactions (106), and almost all data come from electronic measurements. For this reason we will treat the hyperfine interactions mainly with regard to their influence on the electronic structure of the uranium atoms and ions.

1. Magnetic Hyperfine Interaction in Free Atoms or Ions

Since the hyperfine interaction is very small compared to the other interactions in a free atom or ion, its effects can be treated as small perturbations on the fine-structure levels. Thus, the hyperfine structure calculations are a real test of the accuracy of the wavefunctions of electronic ground states.

The relativistic effects (107-110) are expected to be significant for uranium ions. However, for sake of simplicity, we will not consider here a full relativistic treatment but rather use some relativistic modifications of the classical hyperfine interactions. Inside a given (nl) configuration with l different from zero, the relativistic magnetic dipole hyperfine interaction can be written as:

$$H_{\text{hf}} = 2\gamma\beta_e\gamma_n \sum_i [l_i \langle R_i^{-3} \rangle - \sqrt{10}(sC^2)_i^{-1} \langle r_{sC}^{-3} \rangle + s \langle r_s^{-3} \rangle] I. \quad (14)$$

The first term in equation 14 is the interaction of the nuclear moment I with the orbital momentum of the electrons, the second represents the dipolar interaction between the nuclear and electronic spins where $\sqrt{10}(sC^2)_i^{-1}$ is the electronic spin dipole operator (111) identical to $[s_i \cdot 3r_0(r_0 s_i)]$, r_0 is a unit vector parallel to r , the electron position, and the last term has a similar form to the classical contact interaction (112) (which is zero except for the s electrons), but can be non-zero for any electron. The radial parameters in equation 14 are defined as combination of integrals $\langle r^{-3} \rangle_{jj}$, computed between electronic states of the two relativistic subshells. For $j = 7/2$ and $j = 5/2$, subshells of a nf shell:

$$\begin{aligned} \langle r_l^{-3} \rangle &= (1/49)[24\langle r^{-3} \rangle_{7/2, 7/2} + 24\langle r^{-3} \rangle_{5/2, 5/2} + \langle r^{-3} \rangle_{7/2, 5/2}] \\ \langle r_{sC}^{-3} \rangle &= (1/49)[-80\langle r^{-3} \rangle_{7/2, 5/2} + 144\langle r^{-3} \rangle_{5/2, 5/2} - 15\langle r^{-3} \rangle_{7/2, 5/2}] \\ \langle r_s^{-3} \rangle &= (1/49)[64\langle r^{-3} \rangle_{7/2, 7/2} - 48\langle r^{-3} \rangle_{5/2, 5/2} - 16\langle r^{-3} \rangle_{7/2, 5/2}] \end{aligned}$$

with

$$\langle r^{-3} \rangle_{jj} = \frac{-2}{\alpha a_0(K+K'+2)} \int_0^\infty (PQ' + QP') R^{-2} dr \quad (16)$$

where α is the fine structure constant, a_0 is the Bohr radius, $K = -4$ for $j = 7/2$ and $+3$ for $j = 5/2$, P and Q are the large and small radial components of the relativistic one-electron wavefunctions; K refers to j and K' refers to j' . In the non-relativistic limit $\langle r_l^{-3} \rangle = \langle r_{sc}^{-3} \rangle$ and $\langle r_s^{-3} \rangle = 0$.

The matrix elements of the hyperfine interactions within a given J manifold can be evaluated in two coupling schemes. In the absence of any external fields, the electronic angular momentum J and the nuclear spin moment I couple together to give the total angular momentum $F = I + J$. Each J level is split into levels characterized by the hyperfine quantum numbers F , which can take values $|I - J|$ and $I + J$. Each F level is $(2F + 1)$ -fold degenerate in the quantum number M_F . In this case, we must calculate matrix elements between states $|\sigma J I F M_F\rangle$, where σ denotes the other quantum numbers of the level J . Because the matrix elements between states of different J are very small, we will consider the diagonal matrix elements (which are also diagonal in M_F) and are equal to $(1/2)A[F(F+1) - J(J+1) - I(I+1)] \equiv (1/2)AK$. The parameter A is known as the magnetic hyperfine structure parameter. The non-relativistic calculation of this parameter (10) has been extended for the relativistic case in (25) where it is shown that for each Russell-Saunders component of an intermediate coupling wavefunction:

$$A = (2\gamma\beta_e\beta_n/I)\{[(2-g)\langle r_l^{-3} \rangle + (g-1)\langle r_s^{-3} \rangle + 2\{14(2J+1)/J(J+1)\}^{1/2} \times \langle \sigma SL | V^{(12)} | \sigma' S' L' \rangle \times \left\{ \begin{matrix} S & S' & 1 \\ L & L' & 2 \\ J & J' & 1 \end{matrix} \right\} \langle r_{sc}^{-3} \rangle\} \quad (17)$$

where

$$(2-g) = \langle \sigma SL || L || \sigma SL \rangle / [J(J+1)(2J+1)]^{1/2}$$

and

$$(g-1) = \langle \sigma SL || S || \sigma SL \rangle / [J(J+1)(2J+1)]^{1/2}$$

are diagonal in the SLJ representation, while the tensor operator $V^{(12)}$ may have non-diagonal matrix elements and makes A very sensitive to the use of the intermediate coupling (113).

In the presence of an external magnetic field, large compared to the interaction between I and J , each of these moments are quantized in the external field, and a more suitable coupling scheme is $(2J M_J I m_I)$. In this scheme, the matrix

elements, for which $M = M_J + m_I$ is conserved, have nonzero values. The diagonal matrix elements are equal to $AM_J m_I$ with A defined as above.

Various relativistic calculations have been performed in order to obtain the hyperfine radial parameters. Table 2 gives the $D - S$ (25), $D - F$ (25), and MDF (26) values together with the classical $\langle r^{-3} \rangle$ parameters (24) for the uranium atom and ions. In order to compare the relativistic and non-relativistic results, the weighted average relativistic values, as well as the "effective" values (106), are given.

The "effective" radial integrals have been estimated as follows. The hyperfine interaction can be considered as an interaction between the nuclear spin moment I and a hyperfine electronic magnetic field H_{hf}^{rel} , which is composed of three parts, H_l , H_{sC} , and H_s . In order to compare the relativistic and non-relativistic form as

$$H^{rel} = 2\beta \sum_i [l_i - \sqrt{10}(sC^2)_i] \langle r^{-3} \rangle_{eff} \quad (18)$$

where the effective radial parameter is

$$\langle r^{-3} \rangle_{eff} = \frac{H_l + H_{sC} + H_s}{H_l / \langle r_l^{-3} \rangle + H_{sC} / \langle r_{sC}^{-3} \rangle} \quad (19)$$

The $\langle r^{-3} \rangle_{eff}$ values for different uranium ions have been estimated by using the hyperfine fields calculated for the pure Hund's rule states of these ions (106).

The existence of different radial parameters for the various contributions to the hyperfine interaction has been clearly demonstrated by precise experimental measurements on different atoms or ions, which show differences up to about 10% between $\langle r_{sC}^{-3} \rangle$ and $\langle r_l^{-3} \rangle$. An examination of Table 2 shows also that the non-relativistic theories lead to serious overestimates (of about 30%) of $\langle r^{-3} \rangle$.

Another source of error in the calculation of the magnetic hyperfine parameter comes from the approximation used in the central-field theories. For this reason, effects such as the excited configuration mixing must be taken into account as well as the polarization of the closed-shell electrons by the electrons from incomplete shells, resulting in unpaired spin density at the nucleus. The last effect, known as "core polarization," can give large contributions to the hyperfine structure. An accurate calculation of the core polarization is extremely difficult for actinides. The very few data existing for core-polarization electronic hyperfine fields in actinides can be described by an empirical relation (106, 114).

Table 2. The Hyperfine Radial Parameter $\langle r^{-3} \rangle$ for Uranium Atom and Ions (in a.u.)

Ion	Configuration	HFS ^a	DS				MDFC			$\langle r^{-3} \rangle_{\text{eff}}^e$
			5/2, 5/2	7/2, 7/2	5/2, 7/2	DWA	5/2, 5/2	7/2, 7/2	DWA	
U	5f ³ 6d 7s ²		5.434	4.979	5.136	5.174				
U ⁺	5f ³ 7s ²		5.556	5.130	5.271	5.312				
U ²⁺	5f ⁴		5.044	4.604	4.758	4.793				
U ³⁺	5f ³	7.23	5.718	5.310	5.441	5.485	5.914	5.417	5.630	5.633
U ⁴⁺	5f ²	7.82	6.366	5.966	6.805	6.137	6.528	6.024	6.240	6.312
U ⁵⁺	5f ¹		6.999	6.600	6.711	6.771	7.130	6.612	6.834	6.999

a) Non-relativistic Hartree-Fock-Slater values (24). b) Dirac-Slater values (25). c) Mixed configuration Dirac-Fock values (26). d) Degeneracy-weighted average values $\langle r^{-3} \rangle = (6/14)\langle r^{-3} \rangle_{5/2} + (8/14)\langle r^{-3} \rangle_{7/2}$. e) "Effective" values (106).

$$H_{\text{core}} \approx (600 + 100)(g_J - 1)\langle J_z \rangle \quad (20)$$

where g_J is the Lande factor and H_{core} is expressed in kOe. This equation shows that the core-polarization effects are very strong in the case of actinides, about 6-7 times stronger than for the lanthanides. For the ground level of U³⁺, H_{core} is estimated to be 740 kOe from a total hyperfine magnetic field of 4900 kOe, for U⁴⁺, 480 kOe out of 4600 kOe, and for U⁵⁺, 210 kOe out of 3200 kOe (106).

2. Electric Quadrupole Interactions in Free Atoms and Ions

A relativistic treatment of the nuclear electric quadrupole interaction is very complex because additional terms in the interaction can appear. However, it can be shown (109) that the expectation values of the relativistic and non-relativistic quadrupole interactions are quite similar in value and exception to this can only be expected when all the diagonal matrix elements vanish, and the off-diagonal elements become dominant. This situation arises in the case of the half-filled shells. None of the uranium ions are in such a position, so we will restrict our discussion to the non-relativistic quadrupole interaction.

The Hamiltonian which describes the quadrupole interaction between a distribution of nuclear charges and a distribution of electronic charges can be written as a product of second rank tensor operators that act only in the nuclear space (A_2^q) or in the electronic space (B_2^q) respectively. This can be transformed to give

$$H_Q = \sum_{i,j} V_{ij} Q_{ij} \quad (21)$$

where

$$V_{ij} = \partial^2 V / \partial x_i \partial x_j |_{r=0}$$

and $V_{(x,y,z)}$ is the electrostatic potential created by electrons. The Q_{ij} in equation 21 are defined as

$$Q_{ij} = [eQ/6I(2I-1)][(3/2)(I_i I_j + I_j I_i) - \delta_{ij} I(I+1)]. \quad (22)$$

The parameter Q is the nuclear quadrupole moment (115).

The two second-order tensors V_{ij} and Q_{ij} can be brought to the principal axes (x,y,z). In this case, the electric field gradient can be completely described by two parameters: V_{zz} and the asymmetry parameter $\eta = (V_{xx} - V_{yy})/V_{zz}$.

For a given electronic level J , the electronic operators can be replaced by equivalent operators, and the quadrupole interaction can be written as:

$$H_Q = [B/2I(2I-1)J(J-1)][3(JI)^2 + 3(I - J(J+1))I(I+1)] \quad (23)$$

where

$$B = -J(2J-1)e^2 Q \langle r_q^{-3} \rangle \langle J || \alpha || J \rangle = e^2 q_J Q \quad (24)$$

The matrix elements $\langle J \| \alpha \| J \rangle$ are given in (74).

In the absence of an external field, the diagonal matrix elements of the quadrupole interaction for a given F state are equal to

$$[B/2I(2I-1)J(2J-1)][(3/4)K(K+1) - I(I+1)J(J+1)].$$

The radial integral $\langle r_q^{-3} \rangle$ can be calculated by relativistic and non-relativistic methods. In non-relativistic theories, this parameter is equal to that used in the magnetic dipolar interaction. In a relativistic treatment, the quadrupole radial integral is defined as

$$\langle r_q^{-3} \rangle_{jj'} = \int_0^\infty (FF' + GG')r^{-3} dr,$$

which is different from those used in the magnetic dipole interaction. A calculation has been made of the values $\langle r_q^{-3} \rangle_{jj'}$ by D-S and D-F methods for uranium atom and ions (25).

The V_{zz} component of the electric field gradient produced by the electrons of a given energy level J is:

$$V_{zz} = -e \langle r_q^{-3} \rangle \langle J \| \alpha \| J \rangle [3J_z^2 - J(J+1)]. \quad (25)$$

The distortion of the charge cloud of the inner closed shells produces a change in the electric field gradient at the nucleus. This influence is taken into account by introducing the inner-shell shielding Sternheimer factor R. In the case of uranium, this shielding has been estimated to be $R_{5f} \sim 0.15$ (116, 117), and thus the electric field gradient acting on the nucleus is $V_{zz}^{\text{eff}} \approx 0.85 V_{zz}$.

3. Measurement of the Magnetic Dipole and Nuclear Quadrupole Moments of Free Ions

Experimental measurements of the hyperfine interactions allow the determination of the nuclear magnetic dipole and electric quadrupole moments. For complex atomic systems with more than one open shell, additional difficulties are connected with the use of a proper coupling scheme. An example of this is uranium whose hyperfine structure for the 233 and 235 isotopes has been measured in free-atom optical spectra. Each of the levels involved in the optical transition shows hyperfine splitting, and the hyperfine structure of the optical lines is due to the difference in the splittings of these levels. After the hyperfine splitting of each level has been

separated, the A and B parameters defined above can be calculated from differences in the positions for different values of F. This requires a knowledge of the J and I quantum numbers. The accuracy in estimation of the nuclear magnetic dipole and electric quadrupole moments from values of A and B depends on the accuracy with which some atomic parameters, especially the wavefunctions and the radial parameters, are known. For the lowest 5L_6 level of the ground configuration $5f^3 6d 7s^2$ of uranium atoms, the experimental A and B parameters and the moments μ and Q are connected (118) by

$$A = (2\beta_e \beta_n \mu / I)(a \langle r^{-3} \rangle_{5f} + b \langle r^{-3} \rangle_{6d})$$

$$B = e^2 Q (c \langle r^{-3} \rangle_{5f} + d \langle r^{-3} \rangle_{6d}) \quad (26)$$

where a, b, c, and d depend on the intermediate coupling wavefunction. For the 5L_6 level, this is $0.875(^4I)^5L > - 0.356(^2H^2)^3K > + 0.234(^4I)^3K > + 0.129(^2H^1)^3K >$ (119) and $a = 1.002$, $b = 0.388$, $c = 0.180$, and $d = 0.477$, as compared to $a' = 0.992$, $b' = 0.380$, $c' = 0.239$, and $d' = 0.512$ for a pure Russell-Saunders ground level (118). The radial integral $\langle r^{-3} \rangle_{5f}$ from equation (26) has been estimated from the value of $\langle r^{-3} \rangle_{5f}$ for the neutral plutonium atom using the ratio for the spin-orbit parameters for the two atoms. Thus, a value of 5.9 a.u. was estimated for $\langle r^{-3} \rangle_{5f}$, and a value for $\langle r^{-3} \rangle_{6d}$ was taken as $0.6 \langle r^{-3} \rangle_{5f}$. With these quantities and the experimental values $A = -2.08 \times 10^{-3} \text{ cm}^{-1}$ and $B = 138.5 \times 10^{-3} \text{ cm}^{-1}$, the values $\mu = -0.31 \mu_n$ and $Q = 6.4 \text{ barn}$ for ^{235}U and $\mu = 0.487 \mu_n$ and $Q = 4.86 \text{ barn}$ for ^{233}U were calculated (118).

Recent measurements by multistep laser photoionization gave $A = -1.98 \times 10^{-3} \text{ cm}^{-1}$ and $B = 136.9 \times 10^{-3} \text{ cm}^{-1}$ (120), or $A = -2.03 \times 10^{-3} \text{ cm}^{-1}$ and $B = 138.73 \times 10^{-3} \text{ cm}^{-1}$ (121), while laser-radiofrequency double resonance gave the values $A = 2.02 \times 10^{-3} \text{ cm}^{-1}$ and $B = 136.9 \times 10^{-3} \text{ cm}^{-1}$ (122). These parameters have also been measured for some excited levels (120, 121, 123).

The values of μ and Q depend on the accuracy with which the experimental A and B parameters have been measured and on the radial integral involved. While the parameters A and B, measured by different methods, show only very slight differences, the differences between various estimates of the radial integrals are fairly large. Thus, the relativistic calculations (25) show a clear 15% overestimate for the radial integral $\langle r^{-3} \rangle_{5f}$ (118). Earlier estimates for ^{233}U have given $\mu = 0.73 \mu_n$ and $Q = 7.9$

barn (124).

4. Hyperfine Interactions in Solids

The electronic properties of the ions in crystals are influenced by their neighbors, and this is manifested in the hyperfine interactions. The main effects in the case of the actinide ions in crystals are as follows:

(a) J mixing through the crystal field modifies the hyperfine splitting.

(b) When the crystal field interaction is of the same order or stronger than the spin-orbit coupling, the intermediate or even strong crystal field scheme must be used.

(c) The overlap, exchange, and covalency (charge transfer) effects modify the radial $\langle r^{-3} \rangle$ integrals.

(d) When the neighboring nuclei possess magnetic or electric quadrupole moments, an additional interaction (known as super-hyperfine interaction) appears due to dipole interaction, overlap, or covalency.

(e) An additional quadrupole interaction due to the nonspherical electric charge distribution of the neighbors of the ion is produced. An additional polarization of the electronic shells of the ions takes place, and this can be expressed by an outer Sternheimer factor γ_∞ which is usually negative (antishielding) and has a very large value (for actinides about 100).

Due to the large line width compared to the hyperfine splitting, there are no data on hyperfine structure of the optical spectra for uranium ions in crystals. However, the above discussion is valid in the study of the hyperfine interaction of uranium ions in crystals by other methods, as for instance, EPR.

D. The Zeeman Effect

1. Zeeman Effect in a Free Atom without Nuclear Spin

In a free atom or ion whose nuclear spin is zero, each energy level is $(2J + 1)$ -fold degenerate. This degeneracy can be lifted by an external magnetic field which splits the level into $(2J + 1)$ components characterized by the magnetic quantum numbers M_J (Zeeman effect). When the energy levels are close to each other, and the external magnetic field is very strong, a mixing of the different levels through the Zeeman interaction also takes place.

The Zeeman effect is due to the interaction between the magnetic moment μ of the open

electronic shell of the ion and the external magnetic field H_0 , the energy of the interaction being:

$$W_Z = -\mu \cdot H_0.$$

In the case of a free atom or ion whose electrons in open-shells are characterized by the individual orbital l_i or spin s_i moments, the Hamiltonian of this interaction can be written as

$$H_Z = \beta H_0 \sum_{i=1} (l_i + g_s S_i) \quad (27)$$

where β is the Bohr magneton, and g_s is the spin magnetic factor ($\mu_s = -g_s \beta s$) and amounts to 2.0023 (in the relativistic approximation) or 2 (in the non-relativistic approximation).

The Hamiltonian of equation 27 commutes with the operator J_Z but not with J^2 , regardless of the coupling scheme, and its matrix elements are diagonal in M_J but not in J . For the Russell-Saunders coupling H_Z commutes also with L^2 and S^2 , and its matrix elements are diagonal in L and S . The non-vanishing matrix elements of the Zeeman interaction are then

$$\begin{aligned} \langle \sigma S L M_J | L + g_s S | \sigma S L J' M_J' \rangle = \\ (-1)^{J-M_J} \begin{pmatrix} J & 1 & J' \\ M_J & 0 & M_J' \end{pmatrix} \times \\ \langle \sigma S L J | L + g_s S | \sigma S L J' \rangle. \end{aligned} \quad (28a)$$

The diagonal matrix elements are given by

$$\langle \sigma S L M_J | L + g_s S | \sigma S L J M_J \rangle = g_J M_J \quad (28b)$$

where g_J is the Lande factor

$$g_J = [1 + (g_s - 1)J(J+1)] /$$

$$L(L+1) + S(S+1) / 2J(J+1).$$

The non-diagonal matrix elements are governed by the selection rule $|J - J'| = 1$.

According to equation 28b the Zeeman components of a level J are equidistant and form a symmetrical structure around the free-ion energy of the level. The Zeeman splitting is proportional to the Lande g -value. In real situations, when the intermediate coupling must be taken into account, the g -value can be sensibly different from the Lande factor.

2. Zeeman Effect and the Hyperfine Interaction in Free Atoms or Ions

When the nucleus of the atom or ion has

spin, in an external magnetic field, the hyperfine interaction will compete with the electronic Zeeman interaction (79) and with the nuclear Zeeman interaction $H_{zn} = \mu \bullet H_0 = g_I \beta_n H_0 \bullet I$.

For weak magnetic fields when the Zeeman interactions are small compared with the hyperfine interaction, the most appropriate coupling scheme for the hyperfine interaction is that of the coupling $J + I = F$. In this case the diagonal matrix elements in F are

$$\begin{aligned} \langle \sigma J I F_M | H_z + H_{zn} | \sigma J I F_M \rangle = \\ \frac{M_F H_0}{2F(F+1)} \{ [F(F+1) + J(J+1) - I(I+1)] g_J - \\ [F(F+1) + I(I+1) - J(J+1)] \beta_n g_I \} = \\ \beta g_F M_F H_0. \end{aligned} \quad (29)$$

In very weak (of order 10 Gauss) magnetic fields, only these diagonal matrix elements are taken into account, and within this approximation each hyperfine-structure level F is split into $(2F + 1)$ equally spaced components. In moderate magnetic fields the hyperfine structure is very complex and non-diagonal (in F) matrix elements must be considered.

For strong magnetic fields (10^3 - 10^4 Gauss) the coupling between the electronic angular momentum and the nuclear spin is broken, and the most appropriate scheme for characterization of the levels is $(J M_J I m_I)$. The diagonal matrix elements are now:

$$\begin{aligned} \langle \sigma J M_J I m_I | H_z + H_{zn} | \sigma J M_J I m_I \rangle = \\ H_0 (g_J M_J - g_I m_I \beta_n / \beta) \end{aligned} \quad (30)$$

If the non-diagonal matrix elements can be neglected, each Zeeman level is split into $(2I + 1)$ approximately equally spaced sublevels due to the hyperfine interaction $A M_J m_I$.

3. Zeeman Effect for Ions in Crystals

A crystal field can split the energy levels of the free ion and mix states characterized by different J values. As shown above for a weak crystal field, each level J is split in a crystal field according to the reduction of the irreducible representation D^J of the rotation group in the irreducible representations Γ_i of the symmetry point group of the crystal field. For the ions with even numbers of electrons, the resultant crystal field levels can be singlets, doublets, or triplets (the last ones only in cubic fields). For ions with odd

numbers of electrons, the crystal field levels will be at least doubly degenerate, regardless of the symmetry of the crystal field. This residual degeneracy, known as Kramers degeneracy, results from the condition that the Hamiltonian of the system commutes with the time-reversal operator O . The two wavefunctions of the doublet are Kramers conjugates, i.e. if one of them can be written as a combination of states $|J, M\rangle$:

$$|\zeta\rangle = \sum_{J, M} C_{JM} |J, M\rangle, \quad (31a)$$

the other is

$$|\bar{\zeta}\rangle = \sum_{J, M} C_{JM}^* (-1)^{J-M} |J, -M\rangle. \quad (31b)$$

For the intermediate crystal field, the eigenvalues of the crystal field plus spin-orbit coupling can be doublets Γ_6 or Γ_7 , or quartets Γ_8 (the latter only in cubic fields). In this case the Kramers doublets cannot be described by states of equations 31a and 31b since the angular momentum J is no longer a good quantum number, and the wavefunction of each doublet contain mixtures from the other doublets which have the same transformation properties.

The Zeeman interaction can split the levels left degenerate by the crystal field, but the equations given for the free-ion case are no longer valid. As shown before, the states inside the doublets Γ_6 and Γ_7 , the triplets Γ_4 and Γ_5 , and the quartet Γ_8 can be classified according to the eigenstates of a fictitious angular momentum $\mathcal{J}$ with $\mathcal{J}$ equal to $1/2$ (for the doublets), 1 (for the triplets), or $3/2$ (for the quartets). The calculation of the Zeeman effect $-\mu \bullet H_0$ implies a knowledge of the matrix elements of the magnetic moment μ between crystal field electronic states. This calculation can be simplified if some symmetry properties are used. The matrix elements of a given operator V (which transforms according to the representation Γ of a certain group G) between the two wavefunctions which transform according to the representations Γ' and Γ'' , respectively of the same group G is different from zero only if the decomposition of the product $\Gamma' \times \Gamma \times \Gamma''$ contains the unit representation of the group. If all of these representations have real characters (which is always the case with the representations encountered here), this condition is equivalent to the condition that the direct product $\Gamma' \times \Gamma$ contains Γ . In this case the interaction V can remove partially the degeneracy of the different eigenvalues of the Hamiltonian H_0 which is invariant to the transformations of the group G . If the operator V is a vector V , and the representation Γ enters in the

decomposition of the direct product $\Gamma \times \Gamma'$ only once, the Wigner-Eckart theorem states that, inside a given J manifold, the operator V can be replaced by the equivalent operator αJ , where α is a proportionality factor depending on the vector V. When the Hamiltonian H_0 is invariant on the time-reversal operation Θ , the condition to lift the degeneracy under a perturbation of a lower symmetry is more restrictive (1). The kinetic and the electrostatic interactions as well as the spin-orbit coupling are invariant with regard to time reversal. For a system with an odd number of electrons, the square of the time-reversal operator Θ is -1, while for systems with even number of electrons, it is +1.

The set of functions $\phi_i \chi_j$ which spans the product of representations $\Gamma \times \Gamma'$ can be divided into a symmetrical subset $\frac{1}{2}\{\phi_i \chi_j + \phi_j \chi_i\}$ and an antisymmetrical subset $\frac{1}{2}\{\phi_i \chi_j - \phi_j \chi_i\}$ which do not mix, and the representations resulting from the decomposition of the product can thus be referred as symmetric or antisymmetric. If a symbol ϵ_V is introduced so that for time-odd operators V, it is equal to -1 and for time even operators, it is +1, the condition that the operator V which transforms according to Γ has non-vanishing matrix elements between the states characterized by Γ' , is that, if $\Theta^2 \epsilon_V > 0$, Γ must be contained in the symmetric direct product $[\Gamma \times \Gamma']_s$. If $\Theta^2 \epsilon_V < 0$, it must be contained in the antisymmetric part of $\Gamma \times \Gamma'$.

The magnetic moment μ is an odd time operator which transforms according to the representation D^1 of the rotation group and to the representation Γ_4 of the cubic group. This implies that in the case of an ion with odd number of electrons, the Zeeman interaction can lift the degeneracy of a crystal field representation Γ' if Γ_4 appears at least once in the symmetric part of the decomposition of the direct product $\Gamma \times \Gamma'$. For the even-electron systems, this holds if Γ_4 belongs to the asymmetrical part of $\Gamma \times \Gamma'$.

As shown in Section II.B.3, the states of various representations of the cubic group can be classified as the states of a fictitious angular momentum. The Wigner-Eckart theorem shows that if the representation Γ_4 appears once (and in a proper way) in the decomposition $\Gamma \times \Gamma'$, the vector V can be replaced by $\alpha \tilde{J}$ where $\tilde{J}$ is the fictitious angular momentum of the representation Γ' . Thus, the magnetic moment can be replaced by the fictitious momentum $\alpha \tilde{J}$ for the doublets Γ_6 and Γ_7 , and the triplets Γ_4 and Γ_5 . The decomposition of $\Gamma_3 \times \Gamma_3$ does not contain Γ_4 , and thus the Zeeman interaction cannot lift the degeneracy of the doublet Γ_3 . On the other hand, Γ_4 appears twice in the decomposition $\Gamma_8 \times \Gamma_8$;

this case will be considered in more detail later.

3a. Zeeman Effect in a Kramers Doublet

Consider a Kramers doublet (the cubic Γ_6 or Γ_7 doublets for an ion with odd number of electrons or any doublet for such an ion in a crystal field of symmetry lower than cubic), well isolated from any other energy levels. The degeneracy of this doublet can be removed by the Zeeman effect. The time-odd operator μ has values opposite in sign in the two states of the doublet. As shown before, in this case the components of the vector μ can be considered proportional to the components of a fictitious angular momentum, or fictitious spin $\tilde{s}$ whose components are the Pauli matrices $\frac{1}{2}\sigma_1$, $\frac{1}{2}\sigma_2$, and $\frac{1}{2}\sigma_3$:

$$\mu_i = -\sum_j g_{ij} \tilde{S}_j. \quad (32)$$

The set of numbers q_{ij} represents the gyromagnetic factor (equivalent to the Landé factor introduced before), and the number of components g_{ij} depends on the symmetry of the crystal field. The set of numbers g_{ij} does not represent a tensor, and the common habit of calling the gyromagnetic factor a tensor comes from the confusion between the fictitious spin $\tilde{s}$ and a real electronic spin (1).

The numbers g_{ij} cannot be determined directly from experiment. In fact, for a given orientation of the external magnetic field with respect to the crystalline axes, the energy of the Zeeman levels is determined by an effective g-value

$$W = \pm \frac{1}{2} \beta g_{\text{eff}} H_0. \quad (33)$$

The effective g-value is connected to the gyromagnetic factors through the relation

$$g_{\text{eff}}^2 = l g \tilde{g} l, \quad (34)$$

where $\tilde{g}$ is the transposed matrix g , and l represents the vector (l_x, l_y, l_z) whose components are the direction cosines of the magnetic field in the laboratory system. The product $g^2 = g \tilde{g}$ represents a symmetrical tensor whose components can be determined by measuring the Zeeman energy transitions in three mutually perpendicular planes. It can be transformed in a diagonal form with a matrix L (125) so that

$$L g^2 L^* = d g^2. \quad (35)$$

The elements of the matrix L are the direction cosines which connect the principal (X, Y, Z)

axes of the tensors g^2 to the laboratory axes. After the principal components of g^2 are determined, the components g are determined by performing the square roots. As discussed before, in some situations the principal axes (X, Y, Z) can be connected with the geometrical axes of the system (for tetragonal, trigonal, and orthorhombic symmetry).

Once the elements of the d_{g^2} have been determined, the effective g_{eff} value can be written simply as

$$g_{\text{eff}}^2 = g_{XX}^2 l_X^2 + g_{YY}^2 l_Y^2 + g_{ZZ}^2 l_Z^2, \quad (36)$$

where l_X , l_Y , and l_Z are the direction cosines of the magnetic field in the reference frame (X, Y, Z) of the d_{g^2} tensor. For cubic symmetry $g_{XX}^2 = g_{YY}^2 = g_{ZZ}^2 = g^2$, and in case of axial symmetry, $g_{XX}^2 = g_{YY}^2 = g_{\perp}^2$ and $g_{ZZ}^2 = g_{\parallel}^2$ (if Z is along the distortion axis).

Inside a given J the principal g-values are given by $g_{\parallel} = 2g_J \langle \zeta | J_Z | \zeta \rangle$ and $g_{\perp} = g_J \langle \zeta | J^+ | \zeta \rangle$.

3b. Zeeman Effect in a Triplet

In the case of a Γ_4 or Γ_5 triplet, the magnetic momentum μ can be replaced by a fictitious angular momentum J , with $J = 1$. Since these triplet states appear only in cubic symmetry, the gyromagnetic factor has only one component: the triplet is split into three equidistant singlets, the splitting being proportional with the g-value and the intensity of the magnetic field, but independent of the orientation of the magnetic field with respect to the crystalline axes.

3c. Zeeman Effect in a Γ_8 Quadruplet

The representation Γ_4 appears twice in the decomposition of $\Gamma_8 \times \Gamma_8$. An adaptation of the Wigner-Eckart theorem shows (1, 126, 127) that the matrix elements of a time-odd vector within a manifold Γ_8 can be specified by two constants. The magnetic moment μ and the fictitious angular momentum $J = 3/2$ can be connected by the relations (126):

$$\begin{aligned} \mu_z &= aJ_z + bJ_z^3 \\ \mu_x &= aJ_x + bJ_x^3 \\ \mu_y &= aJ_y + bJ_y^3 \end{aligned} \quad (37)$$

such that

$$\pm \langle \pm 1/2 | \mu_z | \pm 1/2 \rangle = Q' = (4a + b)/8$$

$$\pm \langle \pm 3/2 | \mu_z | \pm 3/2 \rangle = P' = (12a + 27b)/8 \quad (38)$$

The electronic Zeeman interaction can thus be written as

$$\begin{aligned} H &= g\beta JH + u\beta [J_x^3 H_x + \\ &J_y^3 H_y + J_z^3 H_z - (J \cdot H) \times \\ &3J(J+1) - 1] / 5 \end{aligned} \quad (39)$$

where the last term in the square bracket has been added to give to the Hamiltonian definite transformation properties.

The eigenvalues of this Hamiltonian, expressed in units E/H are obtained by solving the secular equation

$$\begin{aligned} y^4 - (P^2 + Q^2)y^2 + P^2Q^2 + \\ (P-3Q)(P+Q)^2(3P-Q) \times \\ (n_1^2 n_2^2 + n_2^2 + n_3^2 + n_3^2 n_1^2) = 0 \end{aligned} \quad (40)$$

where n_i are the direction cosines of the external magnetic field relative to the cube edge, $P = g_{\parallel}P'$ and $Q = g_{\perp}Q'$. The energy levels are not equidistant, and they depend on the magnitude of the external magnetic field and its orientation relative to the cubic axes. When the last term in the left side of equation 40 vanishes, i.e. when either $P = 3Q$ or $P = -Q$ or $3P = Q$, the Zeeman levels do not depend on the orientation. When Γ_8 enters more than once in the decomposition of J in the crystal field, its wavefunctions depend on the composition parameter x of the cubic crystal field potential and so do the positions of the Zeeman levels. An exact analytical solution of equation 40 cannot be given except for special orientations of the magnetic field:

(a) For H parallel to $|100\rangle$, the four solutions of equation 40 are

$$Y_{1,2} = \pm P \text{ and } Y_{3,4} = \pm Q \quad (41)$$

(b) For H parallel to $|111\rangle$,

$$\begin{aligned} Y_{1,2} &= \pm \frac{1}{2} \sqrt{3(P^2 + Q^2) + 2PQ} \\ Y_{3,4} &= \pm \frac{1}{2} (P - Q) \end{aligned} \quad (42)$$

(c) For H parallel to $|110\rangle$,

$$Y_{1,2} =$$

$$\pm 1/\sqrt{2} \sqrt{P^2 + Q^2 + (P+Q)\sqrt{7(P^2 + Q^2) - 2PQ}}$$

$$Y_{3,4} =$$

$$\pm 1/\sqrt{2} \sqrt{P^2 + Q^2 - (P+Q)\sqrt{7(P^2 + Q^2) - 2PQ}} \quad (43)$$

An axial distortion of the crystal field will split the Γ_8 quartet. If the distortion is tetragonal, the quartet is split into two doublets, while a trigonal distortion splits Γ_8 into a doublet and a pair of singlets. However, according to the Kramers theorem, those two singlets must have the same energy. If the distortions are weak enough, they can leave the wavefunctions of the levels unchanged, and in the tetragonal field one of the doublets can be characterized by the wavefunctions $|\pm 1/2\rangle$ and the other by $|\pm 3/2\rangle$. The Zeeman effect inside each of these doublets will be characterized by two g-values, $g_{\parallel}$ and $g_{\perp}$ as follows:

(a) In the case of a weak tetragonal distortion:

$$\begin{aligned} &\text{-inside the } |\pm 1/2\rangle \text{ doublet,} \\ &g_{\parallel} = +2Q \\ &\text{and } g_{\perp} = \frac{1}{2}|3P - Q| \end{aligned} \quad (44a)$$

$$\begin{aligned} &\text{-inside the } |\pm 3/2\rangle \text{ doublet,} \\ &g_{\parallel} = -2P \\ &\text{and } g_{\perp} = \frac{1}{2}|P - 3Q| \end{aligned} \quad (44b)$$

(b) In the case of a weak trigonal distortion:

$$\begin{aligned} &\text{-inside the } |1/2\rangle \text{ doublet,} \\ &g_{\parallel} = |P - Q| \\ &\text{and } g_{\perp} = P + Q \end{aligned} \quad (45a)$$

-inside the $|3/2\rangle$ doublet, which in trigonal crystal fields is in fact composed of a pair of singlets Γ_4^T and Γ_5^T , the tensor g^2 has one non-vanishing component

$$g_{ZZ}^2 = 3(P^2 + Q^2) + 2PQ. \quad (45b)$$

3d. Zeeman Effect in the Case of a Cubic Γ_7 Doublet in Intermediate Crystal Field

The equations 13 for the two states of the cubic Γ_7 doublet lead to a g-value of

$$\begin{aligned} g_{\Gamma_7} &= 2\cos^2\theta - 8k_{a_2t_2} \sin\theta \cos\theta / \sqrt{3} + \\ &2(k_{t_2t_2} - 1)\sin^2\theta / 3. \end{aligned} \quad (46)$$

As shown by this relation, g_{Γ_7} depends on the ratio of the spin-orbit parameter ζ to the crystal field splitting V and on the two orbital reduction parameters. The g-value for the excited Γ_7' doublet is

$$\begin{aligned} g_{\Gamma_7'} &= 2\sin^2\theta - 8k_{a_2t_2} \sin\theta \cos\theta / \sqrt{3} + \\ &2(k_{t_2t_2} - 1)\cos^2\theta / 3. \end{aligned} \quad (47)$$

These two g-values together with the energy interval

$$E_{\Gamma_7'} - E_{\Gamma_7} = 2\sqrt{3}k_{a_2t_2}\zeta/\sin^2\theta \quad (48)$$

which can be measured by optical absorption, should make possible the estimation of the parameters $k_{a_2t_2}$, $k_{t_2t_2}$, and V (95). If the value of $g_{\Gamma_7'}$ cannot be measured, an approximate fitting procedure must be used.

4. Zeeman Effect and the Hyperfine Interaction in Crystals

For a given crystal field state characterized by a fictitious angular momentum J , the hyperfine interaction can be written as

$$H_{hf} = \mathcal{J}AI = \sum_{ij} J_i A_{ij} I_j \quad (49)$$

where the set of numbers A_{ij} represents the hyperfine interaction parameter and, like the gyromagnetic factor g_{ij} , it is not a tensor (1).

The treatment of the interaction for ions in crystals must take into account the relative strength of the hyperfine interaction as compared to the electronic and nuclear Zeeman interaction.

In the case of a Kramers doublet, the set A_{ij} can contain a large number of components and can be asymmetric. Usually the electronic Zeeman interaction is much stronger than the hyperfine interaction, and the electronic Zeeman interaction is much stronger than the hyperfine interaction, and the electronic and nuclear spins are quantized along different axes. When the nuclear quadrupole interaction can be neglected, the nuclear spin participates in the hyperfine and nuclear interaction. The nuclear Hamiltonian

$$H = \mathcal{J}AI - g_n \beta_n H I \quad (50)$$

may be written as an interaction between the nuclear spin and an effective magnetic field

$$H = -g_n \beta_n H^{\text{eff}} I. \quad (51)$$

This field is the sum of the external magnetic field and the hyperfine field H_{hf} created by the electrons at the site of the nucleus (128)

$$H^{eff} = H_{hf} + H = -(JA + H)/g_n \beta_n. \quad (52)$$

Such a hyperfine field H_{hf} is the orbital field defined by equation 18. It depends on the electronic state. Thus in the case of a Kramers doublet, the hyperfine fields for the two electronic states are collinear and equal, but of opposite sign. These hyperfine fields add to the external magnetic field and the resulting effective fields are noncollinear and of different modulus. The nuclear spin is quantized in the effective field for each electronic state and the nuclear wavefunctions corresponding to a given electronic state M_J are connected to those corresponding to another state M_J by the relation:

$$|m(M_J)\rangle = \sum_{\bar{m}} d_{\bar{m}m}^{(I)}(\omega) |m'(M'_J)\rangle \quad (53)$$

where $d_{\bar{m}m}^{(I)}(\omega)$ are the matrix elements of the irreducible representation of the rotation group, and ω is the rotation which carries the direction $H_{M_J}^{eff}$ over into $H_{M'_J}^{eff}$.

Three cases may be distinguished dependent on the relative magnitudes of H_{hf} and H in equation 52, viz.

(i) The hyperfine magnetic field is much stronger than the external magnetic field. This is the case for uranium ions, where an estimate of the orbital hyperfine magnetic field (106) gives values of the order 3.2×10^6 Oe for U^{3+} , 5.6×10^6 Oe for U^{4+} , and 4.9×10^6 Oe for U^{3+} as compared with the usual values 10^3 - 10^4 Oe for the external magnetic field. In this case the contribution of the external magnetic field to H^{eff} can safely be neglected, and the contribution of the nuclear Zeeman interaction is considered only as a perturbation.

(ii) The hyperfine and the external magnetic fields are of the same order of magnitude. This is of importance for the superhyperfine interaction and will be considered later.

(iii) The case when $|H| \gg |H_{hf}|$ is of no importance for our discussion.

In the case (i) the procedure for the determination of the components A_{ij} is similar to that of the gyromagnetic factor. As before, a symmetrical A^2 tensor can be defined which can be diagonalized by a suitable choice of axes. An important problem is that of the simultaneous diagonalization of the gyromagnetic g_{ij} and

hyperfine A_{ij} sets. This is possible if some restrictive assumptions on the spatial environment are made, and the wavefunctions of the Kramers doublet can be constructed from the wavefunctions of a single J level (1). The situation of simultaneous diagonalization of the gyromagnetic factor and hyperfine interaction is very common. The first-order contribution in the hyperfine energy can then be written as

$$H_{hf} = K M_J m_I \quad (54)$$

where K is given by the relation

$$g^2 K^2 = l_x^2 g_{xx}^2 A_{xx}^2 + l_y^2 g_{yy}^2 A_{yy}^2 + l_z^2 g_{zz}^2 A_{zz}^2 \quad (55)$$

for the case of rhombic symmetry and

$$g^2 K^2 = g_{\parallel}^2 A_{\parallel}^2 \cos^2 \Theta + g_{\perp}^2 A_{\perp}^2 \sin^2 \Theta \quad (56)$$

for the axial symmetry. In the case of cubic symmetry, the hyperfine energy does not depend on the orientation of the magnetic field and $K = A$.

For the systems where we can neglect any influence of other manifolds of different J , a general relation

$$A_x/g_x = A_y/g_y = A_z/g_z = A_J/g_J \quad (57)$$

holds. Any deviation from this relation shows that the J mixing must be taken into account.

For the triplets Γ_4 and Γ_5 , which arise only in cubic symmetry, the hyperfine Hamiltonian is characterized by a single parameter A and

$$H_{hf} = A \mathcal{J} I \quad (58)$$

with $\mathcal{J} = 1$.

In the case of a Γ_8 quartet, the same arguments as used in the deduction of the Zeeman interaction, lead to the following hyperfine Hamiltonian:

$$H_{hf} = A \mathcal{J} I + U \{ \mathcal{J}_x^3 I_x + \mathcal{J}_y^3 I_y - \mathcal{J}_y^3 I_z - [\mathcal{J} \bullet I] (3\mathcal{J}(\mathcal{J}+1)/5) \}. \quad (59)$$

When the nuclear spin $I \geq 1$, the nuclear quadrupole interaction must be taken into account. For a Kramers doublet, if the symmetry is rhombic, the quadrupole Hamiltonian is, as shown before

$$H_Q = P \{ [I_z^2 - I(I+1)/3] + \eta (I_x^2 - I_y^2)/3 \} \quad (60)$$

When the symmetry is axial, the "asymmetry parameter" η vanishes, and for cubic symmetry P is equal to zero.

In the case of the triplets Γ_4 and Γ_5 and the quadruplet Γ_8 , the quadrupole interaction depends, not only on the parameter P , but also on two constants m and n , and can generally be written as (1):

$$H_Q = P[(m/6)\sum_{q=1}^3 3I_q^2 - I(I+1)] + (3n/4)\sum_{p,q} (I_p I_q + I_q I_p)(J_p J_q + J_q J_p). \quad (61)$$

When the superhyperfine interaction with the ligand nuclei is also present, it leads to an additional splitting of the energy levels. The superhyperfine Hamiltonian is a sum of individual contributions. If the symmetry of the crystal field is cubic, such an individual is of the axial form:

$$H_L = A_{\parallel} L_z L_z + A_{\perp} (L_x L_x + L_y L_y) - g_n L \beta_n H \bullet I, \quad (62)$$

where the symmetry axis is along the ion-ligand bond. Sometimes, when $L \geq 1$, a ligand nuclear quadrupole interaction $P_{\parallel} [L_z^2 - L(L+1)/3]$ must be added to equation 62. When the symmetry of the crystal field is lower than cubic, more hyperfine parameters are necessary in equation 62. Thus, for a tetragonal distortion, the superhyperfine part is

$$H_L = \mathcal{J} \bullet A \bullet I$$

and depends (129) on five parameters:

$$A = \begin{vmatrix} A_1 & A_2 & A_4 \\ A_2 & A_1 & A_4 \\ A_5 & A_5 & A_3 \end{vmatrix}. \quad (63)$$

The superhyperfine interaction leads to a very complex splitting of the energy levels, depending on the number, nature, and the symmetry of the ligands around the central ion.

These considerations show that the Zeeman splitting in combination with (or without) the hyperfine interaction contains a large amount of information on the ion under study and on the host. However, the study of the Zeeman effect on the optical transitions of the ions in crystals is difficult since it amounts to much less than 1 cm^{-1} , and most information is lost because of the width of the optical transitions. A very useful

method, which circumvents many of the difficulties encountered in the study of the optical Zeeman effect is EPR.

III. SURVEY ON PARAMAGNETIC RESONANCE

Usually, only the lowest Zeeman components, which are populated at the temperature at which the experiment is carried out, are involved in the resonance phenomena. The ensemble of these states are characterized as the states of a fictitious (or "effective") spin S , $(2S+1)$ being the number of the levels involved in the resonance transitions. When the paramagnetic centers are ions in crystals, these levels are Zeeman components of the crystal field levels, and the effective spin S is usually different from the real spin S . In almost all cases only the states of a single crystal field level are involved in resonance, and the effective spin can be identical to the fictitious angular momentum J defined above. In this case, the electromagnetic field will induce transitions between states which are eigenfunctions of a so-called "spin Hamiltonian" which collects together all the interactions described in the Section II.D.4, written in the components of the effective spin: the electronic and nuclear Zeeman, the hyperfine, superhyperfine, and nuclear quadrupole interaction. In some situations the effective spin is larger than that determined from the number of levels involved in resonance. In this case, a zero-magnetic field splitting term (stronger than the electronic Zeeman interaction) must be added to the spin Hamiltonian in order to separate the levels which take part in the resonance phenomenon from the other levels which are not involved. A typical case is that of the resonance inside the doublet originating from a Γ_4 or Γ_5 triplet state due to an axial distortion. Though only two levels are involved in the resonance, the most suitable classification for them is as the states $|+1\rangle$ and $|-1\rangle$ of a fictitious spin $S=1$, and the state $|0\rangle$ is removed by adding a term $D[S_z - S(S+1)]$ to the spin Hamiltonian.

An electromagnetic field interacts with the electronic magnetic moments through its magnetic component $H_1 \cos \omega t$,

$$H = -\mu \bullet H_1 \cos \omega t. \quad (64)$$

If we consider a paramagnetic ion without nuclear spin, whose ground state is a Kramers doublet and whose gyromagnetic factor is characterized by three values (g_x , g_y , and g_z), and if $H_1 \ll H_0$, the interaction of equation 64 will

induce between its two states, transitions with the probability P per unit time which is proportional to

$$P \sim H_1^2 | \langle M_S | g_x S_x + g_y S_y + g_z S_z | M_S' \rangle |^2 g(\nu). \quad (65)$$

The function $g(\nu)$ is the line shape function and expresses the effect of the various interactions which can lead to a finite width of the resonance lines. The source of broadening can be inhomogeneities in the applied magnetic field, interactions between spins, and so on. For a Kramers ion the line shape is usually symmetric and $g(\nu)$ can be expressed by Gaussian or Lorentzian functions centered on the frequency ν_0 :

$$h\nu_0 = E_{M_S} - E_{M_S'}. \quad (66)$$

The matrix element in equation 65 shows that the transition is governed by the selection rule $|M_S - M_S'| = 1$, and the probability is maximum when the variable magnetic field is in the plane (x, y).

For a Kramers doublet equation 66 establishes a connection between the electromagnetic field frequency and the external magnetic field H_0 :

$$h\nu_0 = g_{\text{eff}} H_0. \quad (67)$$

For the usual magnetic fields of 10^3 - 10^4 Gauss, the frequency is of the order of 10^{10} Hz.

Spin-lattice relaxation can be accomplished through different processes based on the interaction of the paramagnetic ion with the lattice vibrations. This interaction leads to an exchange of energy between ion and lattice by absorption and/or emission of phonons (energy quanta of the lattice vibrations). The main processes of the spin-lattice relaxation are:

(a) The modulation of the interaction between spins due to the lattice vibrations. There are two such processes (130), a direct one by which the spin undergoes a resonance transition due to the absorption or emission of a resonant phonon ($\nu_p = \nu_0$), and biphononic (or Raman) process by which the spin interacts with a non-resonant phonon, undergoes a resonance transition and emits another phonon of frequency ($\nu_p \pm \nu_0$).

(b) the modulation of the crystal field due to the lattice vibrations (the Orbach process) (131, 132). This leads to a dynamic

orbit-lattice interaction which, through the spin-orbit interaction causes relaxation of the spin. As in the previous case, there are direct and bi-phononic Orbach processes.

The spin-lattice relaxation time T_1 has a characteristic temperature dependence for each of the processes described above. The relaxation phenomena have a strong influence on the EPR experiments. They can broaden the lines and in many instances EPR can be observed only at very low temperatures, when the relaxation processes are less effective.

When a hyperfine interaction is present and it is much weaker than the electronic Zeeman interaction (the usual case), the nuclear spin will be, as shown below, quantized along the effective electronic magnetic field. As a result the nuclear eigenfunctions depend parametrically on the electronic quantum number M_S for each electronic state, and the wave function of the system can be written as a product $|M_S m(M_S)\rangle = |M_S\rangle |m(M_S)\rangle$.

In this case the transition probability in unity time is proportional to

$$P \sim H_1^2 | \langle M_S | g_x S_x + g_y S_y + g_z S_z | M_S' \rangle |^2 g(\nu) |d_{mm'}^{(I)}(\omega)|^2 \quad (68)$$

where $d_{mm'}^{(I)}(\omega)$ has been defined in Section II.C. When the angle between the two electronic effective fields is equal to π , $d_{mm'}^{(I)}(\pi) = 0$, and the selection rule for the hyperfine transitions is $m - m' = 0$. Each electronic transition will then be split into $(2I + 1)$ hyperfine components of equal intensity. If the angle ω is different from π , transitions with $m - m'$ different from zero can appear (forbidden hyperfine transitions).

The superhyperfine interaction leads to an additional splitting of the resonance lines. In this case the effective electronic fields cannot be considered as collinear except for some orientations of the external magnetic field. For these special orientations only the allowed superhyperfine transitions with the selection rule $\Delta m^L = 0$ can occur, and each electronic transition is split into $(2I^L + 1)$ components. For all other orientations the spectra may contain forbidden superhyperfine transitions.

If the paramagnetic ion is surrounded by n equidistant ligands (ligands of the same isotopic species, at the same distance from the central ion), and the direction of the magnetic field makes the same angle with the central ion-ligand direction for all these ligands, the superhyperfine structure consists of $(2nI^L + 1)$ components whose intensity is symmetrically distributed

according to the binomial rule:

$$1 : n : n(n-1)/2 : \dots :$$

$$n!/k!(n-k)! : \dots :$$

$$n(n-1)/2 : n : 1.$$

In the case of an odd number of equivalent ligands, there will be an even number of superhyperfine components. When there are many groups of inequivalent nuclei, the superhyperfine structure from each group obeys the same rule, but the overall superhyperfine pattern is very complex. For arbitrary orientations of the magnetic field, this pattern is further complicated by the presence of the forbidden transitions. Usually the superhyperfine splitting is small and can be obscured by the linewidth. Also in many instances, it is impossible to make EPR superhyperfine measurements along the principal axes (which give directly the diagonal components of the interaction) because the structure due to the particular ligand is concealed by the unresolved structure due to the other ligands. In this case special techniques such as ENDOR (Electron Nuclear Double Resonance) must be used. This technique makes possible the measurement of the effect of a nuclear magnetic resonance-like transition ($\Delta m_I^L = 1$) on the electron paramagnetic resonance line by the simultaneous application of a strong microwave field and of a radiofrequency field of a frequency corresponding to the "nuclear" transition which is proportional to the superhyperfine splitting. This technique allows also the determination of some very fine effects as for instance the pseudonuclear g -value. This can arise when some low-lying excited states are admixed into the ground state, by the common action of the electronic Zeeman and hyperfine interaction or the pseudoquadrupole effect, which expresses the mixing of the excited states into the ground state through a second-order hyperfine interaction (133).

For a cubic triplet Γ_4 or Γ_5 , the spin Hamiltonian ($S = 1$) contains an electronic Zeeman term with an isotropic g -value and a sum of terms $D_{ij}S_i \bullet S_j$, which express the small zero-field splitting produced by the lattice strains. At the same time, these strains can mix the three states of the triplet, and the magnetic microwave field can induce transitions with $\Delta M = 1$ between the states $|-1\rangle \leftrightarrow |0\rangle$ and $|0\rangle \leftrightarrow |1\rangle$ and transitions $\Delta M = 2$ between the states $|-1\rangle$ and $|+1\rangle$. These latter transitions are known as "half-field" transitions because they show up at an apparent g -value, g^{app} , of $2g$. The transitions

$\Delta M = 2$ can also be induced by the electric component of the microwave field. At very high intensities, transitions of the type $\Delta M = 2$ can be induced by the simultaneous absorption of two microwave quanta at $g^{app} = g$ (134). The normal $\Delta M = 1$ transitions are very broad because the $M = 0$ Zeeman level is very sensitive to the lattice strains, especially to those of axial symmetry. The distribution of these lattice strains leads to a strong broadening of the $M = 0$ level and of all the resonance transitions in which this level is involved. The levels $M = +1$ are broadened only due to the lower symmetry strains through a second-order effect, so the "half-field" transitions are much narrower than the $M = 1$ transitions. The double-quantum transitions are still narrower because they are influenced by the broadening of only one of the levels $|\pm 1\rangle$. Thus the double quantum transitions show up as very sharp lines superimposed on the very broad lines with $\Delta M = 1$. In the case of an axial distortion, the triplets Γ_4 or Γ_5 are split into a doublet and a singlet. If the doublet is lowest, resonance transitions can be induced between its two levels. Though the resonance observed is inside of a doublet, which can be well isolated from any other levels, the best formalism to describe the resonance is an effective spin $S = 1$ formalism with two principal g -values ($g_{\parallel}$ and $g_{\perp}$) and with the axial zero-field splitting term $D[S_z^2 - S(S+1)]$ added as explained before. The apparent g -values at which the resonance is observed are $g_{\parallel}^{app} = 2g_{\parallel}$ and $g_{\perp}^{app} \sim 0$. The term corresponding to the lattice strains is also included. For a triplet (Γ_4 or Γ_5) or a non-Kramers doublet, the presence of strains has a strong effect on the line shape, which is no longer symmetrical as in the case of Kramers ions but is broad on the low magnetic field side and sharp on the high field side. The hyperfine interaction shows similar features to the g -value, i.e., for a non-Kramers doublet $A_{\parallel}^{app} = 2A_{\parallel}$, $A_{\perp}^{app} \sim 0$, and the quadrupole interaction has no effect upon the spectra.

The electron paramagnetic resonance for Γ_8 quartets is very unusual. The spin Hamiltonian when $I = 0$ is given by equation 3, and the energy eigenvalues can be obtained by solving the bi-quadratic secular equation 40. An accurate analytical solution for equation 40 cannot be obtained except for some special orientations of the external magnetic field with respect to the cubic axes. As expected from the form of equation 40, the Zeeman levels are anisotropic and are symmetric in pairs with respect to the zero energy. When the magnetic field is along the cube edge, three resonance transitions are

usually observed, the transition $|-1/2\rangle \leftrightarrow |1/2\rangle$ at an effective g-value of $2Q$ and with an intensity proportional to $(3P - Q)^2$, the line $|3/2\rangle \leftrightarrow |-3/2\rangle$ at $2P$ and with an intensity $(P - 3Q)^2$ and a line corresponding to the transitions $|\pm 1/2\rangle \leftrightarrow |\pm 3/2\rangle$ at $P - Q$, with an intensity $3(P + Q)^2$, the first two lines are sharp, but the third one is usually much broader, being very sensitive to any weak distortions of the cubic field. In many cases, because of its large line width and low intensity, this line is not seen in the spectra. The lines are usually very anisotropic. Thus the line at $2P$ with H along $|100\rangle$ goes in $\sqrt{3(P^2 + Q^2) + 2PQ}$ with H along $|111\rangle$ and in $\{2(P^2 + Q^2) - \frac{1}{2}(P + Q)\sqrt{7(P^2 + Q^2) - 2PQ}\}^{1/2}$ along $|110\rangle$, while the line at $2Q$ with H along $|100\rangle$ goes in $P - Q$ with H along $|111\rangle$ and $\{2(P^2 + Q^2) + \frac{1}{2}(P + Q)\sqrt{7(P^2 + Q^2) - 2PQ}\}^{1/2}$ with H parallel to $|110\rangle$ (135). The intensity of the lines also dependent on orientation. For instance, around $|111\rangle$ the lines $|1/2\rangle \leftrightarrow |-1/2\rangle$ and $|3/2\rangle \leftrightarrow |-3/2\rangle$ drop almost completely while the transitions $\pm 1/2\rangle \leftrightarrow |\pm 3/2\rangle$ become strong. The parameters $2P$ and $2Q$ which characterize EPR of an ion whose ground state in a cubic field is a Γ_8 quartet can be connected with the composition parameter of the crystal field potential using the analytical expression for the wavefunctions given in Section II.B.7. Thus in the case of a Γ_8 state originating from a $J = 9/2$ level, the EPR parameters can be calculated using the wavefunction of equation 11a. Finally we get (79, 80)

$$\begin{aligned} 2P &= (3\cos^2\Theta - 5\sin^2\Theta)K_J g_J \\ 2Q &= (3\cos^2\Theta - 5\sin^2\Theta + \\ &\quad 8\sqrt{2}\sin\Theta\cos\Theta)K_J g_J/3 \end{aligned} \quad (69)$$

where g_J is the Lande factor for the ground electronic state (in case of a pure $^4I_{9/2}$ state it is $8/11$), K_J is a reduction factor for g_J and the fictitious angle Θ is defined by equation 11c. The knowledge of the resonance parameters $2P$ and $2Q$ allows one the determination of both Θ and K_J .

For a weak distortion, the usual resonance is observed inside the lowest Kramers doublet with g-values given by equation 44a or b or by equation 45a, depending on the symmetry and sign of the distortion. When a trigonal distortion leaves the doublet $|\pm 3/2\rangle$ lowest, no resonance can be observed in this doublet.

We stress the fact that the strong g anisotropy given by equation 44a and b and 45a is connected only with the values of the cubic parameters P and Q and not with the intensity

of the axial distortion. If the axial distortion is strong, it can admix other states in the Kramers doublet and the g-values will be different from those given in equations 44a and b and 45a and b.

Transitions between the Zeeman components of the crystal field levels of the paramagnetic ions in crystals can be induced not only by an electromagnetic field, but also by the oscillations of the crystal field caused by an external acoustic field of suitable frequency. This kind of resonance is known as acoustic paramagnetic resonance (APR) or ultrasonic paramagnetic resonance (UPR) and has been used in the study of U^{4+} in fluorite.

This brief account of the EPR method shows that is of great value in determining the properties of the lowest Zeeman levels of the ground state. Because the Zeeman interaction and the other interactions described by the spin Hamiltonia are perturbations on the eigenstates of the other interactions, the parameters determined in an EPR experiment can be useful to understand some general properties of the ion under study.

IV. EPR STUDIES OF URANIUM IONS

A. Studies of Hexavalent Uranium

Hexavalent uranium is diamagnetic and cannot be studied by EPR. However, some EPR studies on paramagnetic centers connected with hexavalent uranium or on paramagnetic U^{5+} centers obtained by transforming U^{6+} by trapping an electron on the lowest excited level (as discussed in Section II.A.3g) proved to be useful in obtaining information on the U^{6+} centers. This electron can be supplied by irradiating the crystals which contain U^{6+} with gamma or X-rays at room temperature. As examples we discuss the case of U^{6+} in alkali- and alkaline-earth fluorites. The bright green or yellow luminescence of the U^{6+} complexes in alkali (Li, Na, K) or alkaline-earth (Ca, Sr) fluorite crystals grown in the presence of oxygen has been known for a long time.

1. Alkali Fluorides

Many studies of optical absorption, luminescence, piezospectroscopic effects, Stark effect or chronospectroscopy on hexavalent uranium in alkali fluorides (136-145) have established that there is a great variety of luminescent centers, all connected with the presence of oxygen and the symmetry of the prevailing centers is C_{4v} or C_{2v} . In all these cases the direction $|100\rangle$ plays a

particular role in the symmetry of the centers. For the main luminescent center in LiF and NaF, the symmetry has been established unambiguously as C_{4v} . The luminescence spectra from this center contain two series of lines, one of electric dipole nature (with zero-phonon lines at 5185 Å for LiF and 5528 Å for NaF) and one of magnetic dipole nature (5277 Å and 5636 Å). Because of its relatively small ionic radius, the hexavalent uranium (0.73 Å) can easily substitute for the alkali ions (Li^+ , 0.68 Å; Na^+ , 0.97 Å and K^+ , 1.33 Å) while O^{2-} (1.34 Å) substitutes easily for F^- (1.33 Å), thus assuring the charge compensation. Some other point defects can also contribute to the charge compensation. Despite the large amount of work devoted to these systems, the optical studies could not give the answer to some very important problems such as:

(i) The nature of the uranium centers. Basically the models proposed can be divided into two groups (146): those based on a uranyl (UO_2^{2+}) group, and those based on a uranate structure (U^{6+} equally bonded to more oxygens). In the first case it has been assumed that the uranyl group substitute for $F^- - M^+ - F^-$ (along a $[100]$ direction) (140, 143). A recent paper which disregards previously published data proposes a uranyl group directed along $[111]$ substituting for the alkali ion and a fluorine vacancy on the same axis (147). This model gives a trigonal symmetry for the center, though the previous measurements have shown clearly that none of the U^{6+} luminescent centers in LiF has trigonal symmetry. In the second group of models, Runciman (137) proposed that the main luminescent center was an octahedral uranate group UO_6^{6-} which substituted for the group MF_6^{5-} . Feofilov (139) proposed a model with U^{6+} substituting for M^+ and five O^{2-} substituting for F^- in the nearest neighborhood of uranium. A model based on a planar square uranate group has also been proposed (144).

(ii) The nature of the vicinity of the active uranium center. All the models presented above, except that of Feofilov (139), cannot assure the complete charge compensation of uranium. This model also gives C_{4v} symmetry for the center. However, it cannot explain the large variety of the luminescent centers, and thus other models must also be considered. In the case of the uranyl-based models, the charge compensation has been assumed to be by some

substitutional oxygen ions in the equatorial plane. The variety of the luminescent centers has been assumed to originate from the number of those substitutional O^{2-} ions. However, this model cannot explain the C_{4v} symmetry of the main luminescent center, except for the situation when a charge compensator is placed in the same direction as the uranyl axis.

For the octahedral uranate model proposed by Runciman, the extra negative charge has been assumed to be compensated either by a fluorine vacancy on the $[111]$ direction (this would give a trigonal symmetry for the centers, which has not been confirmed by experiment) or by some substitutional high valence cations. This later model can explain a large variety of centers as well as the C_4 or C_{4v} symmetry. Runciman was able to check this assumption by introducing calcium or silicon into uranium-doped NaF and by observing their effect on the uranium luminescence or absorption spectra.

A recent model, based on luminescence and electrical conductivity measurements, assumes that the main U^{6+} center in NaF is a UO_6^{6-} complex associated with a F^- vacancy on the $[100]$ axis (148-150).

EPR has proved to be very useful in giving information on the structure of these centers. Two main directions were investigated:

(a) In order to check the possibility of association of the octahedral uranate group with substitutional cations of valence higher than 1, paramagnetic ions of valence +2 (Cu^{2+} , Mn^{2+}), +3 (Fe^{3+} , Cr^{3+}) (151, 152), or +4 (Mn^{4+}) (153) have been introduced together with uranium in LiF and NaF.

The EPR spectra of these samples are very complex and show the presence of a large variety of paramagnetic centers involving either the paramagnetic dopant ion, or other ions accidentally present in the samples. Thus paramagnetic ions in valence states which generally cannot be obtained in the alkali fluorides could be stabilized this way. A typical example is the Cu^{2+} ion for which a large variety of centers have been obtained by co-doping LiF with uranium and copper oxides. Uranium is so effective in stabilizing Cu^{2+} in LiF that this ion shows up as an accidental impurity in almost all (even the purest) LiF:U crystals. The Cu^{2+} spectra show usually tetragonal or rhombic ($[100]$ or $[110]$) symmetry, and in most cases a superhyperfine structure with less than six fluorine nuclei (151, 152). The very large anisotropy of the g-value and of the hyperfine structure as well as the

strong quadrupole interaction, show that these ions are submitted to the action of a strong axial distortion of the crystal field. This means that the Cu^{2+} ions are not placed randomly in the lattice, but in such a position that the first coordinating sphere contains not only F^- ions but also O^{2-} . Together with the strong crystal field distortion, this suggests that the Cu^{2+} ions are placed in the near neighborhood of the U^{6+} ion surrounded by an oxygen octahedron and contribute to the charge compensation. No trigonal Cu^{2+} centers have been observed, but in case of the EPR spectra of higher valence paramagnetic co-dopants, this symmetry predominates. Thus for Mn^{4+} in uranium doped LiF crystals (135), only a trigonal EPR spectrum corresponding to a very strong axial crystal field (the fine structure term D is stronger than the electronic Zeeman interaction) has been observed. It is difficult to give an accurate model for this Mn^{4+} center, but obviously its presence is connected with the presence of the hexavalent uranium.

Thus the EPR studies have shown that Runčiman was correct in assuming that the hexavalent uranium can introduce in the alkali fluorite crystals more oxygen than necessary for its charge compensation and that the negative extra charge present can be compensated by introducing in the crystals cations with valence larger than +1. It was also shown that this aliovalent cation can occupy different substitutional positions around the uranium-oxygen complex, thus explaining, at least in part, the variety of the luminescent uranium centers in these crystals. The concentration of paramagnetic ions which could be introduced this way into the alkali fluorides was sensibly smaller than the total concentration of uranium centers.

(b) A more direct insight into the structure of luminescent U^{6+} centers in alkali fluorides is obtained if the U^{6+} ions can be converted into paramagnetic U^{5+} ions. From the characteristic features of the EPR spectra of these U^{5+} ions (symmetry, g-values, superhyperfine structure), the structure of the parent U^{6+} centers can sometimes be inferred. The irradiation at room temperature with X- or gamma rays has proven to be very effective in transforming U^{6+} into U^{5+} in LiF (154-156), NaF (155-157) and KF (158). A large variety of U^{5+} centers has been obtained whose study gives information about the parent U^{6+} centers too (146). It is concluded that even if a parent U^{6+} center can produce many U^{5+} centers by irradiation, the EPR studies show that there is a large variety of U^{6+} centers. The very small g-values of the EPR

spectra show that the paramagnetic centers are uranate (V) species and not uranyl (UO_2^{+}) structures for which values of $g_{\parallel} \sim 4$ and $g_{\perp} \sim 0$ should be expected (as for the case of the neptunyl groups (159)). This rules out completely the uranyl-based models for the luminescent centers in alkali fluorides.

The symmetry of the U^{5+} centers is either cubic, tetragonal, orthorhombic, or of lower symmetry. For almost all the EPR spectra, the crystal $[100]$ axis is one of the main symmetry axes. Rotations from this direction, observed for some low symmetry U^{5+} centers, can be connected with some defects associated with U^{5+} and are not connected with the original U^{6+} centers. No center of trigonal symmetry has been observed.

In LiF and NaF the prevailing U^{5+} center has tetragonal symmetry and shows superhyperfine structure due to a F^- ligand placed on the symmetry axis. Measurements on selected samples (which contain almost only one type of luminescent center) have shown that this U^{5+} center can be connected with the main luminescent center of C_{4v} symmetry (154, 155, 160). This shows that the main luminescent U^{6+} center in LiF and NaF has the structural model proposed by Feofilov (130). The likelihood of this model has been stressed in some recent studies on absorption and laser excitation and MCD or U^{6+} in LiF (161, 162), using as argument the EPR studies on U^{5+} (155). This rules out the model (148-150) based on a UO_6^{6-} complex associated with a fluorine vacancy on the 100 axis.

The prevailing U^{5+} center in KF has quasi-tetragonal symmetry with a superhyperfine structure due to two ligand nuclei with $I = 1/2$. Centers of tetragonal or lower symmetry with such structure have been observed also in NaF and LiF (146, 156, 158). The superhyperfine splitting for these centers is much smaller than for the center discussed above and can be due either to two protons (in two OH^- groups or a H_2O^- group) or to two fluorine nuclei in a F_2^- group placed on the symmetry axis. Most probably, this association, which involves two $I = 1/2$ nuclei, is formed during irradiation by trapping one of them by the other which is originally connected with the U^{6+} center.

Many U^{5+} centers without superhyperfine structure and with a slight anisotropy have been observed in LiF:U co-doped with silver, copper, or gold, which originate in the parent uranate UO_6^{6-} groups.

A very anisotropic tetragonal U^{5+} center without superhyperfine structure can be

explained by a model implying a fluorine vacancy on the distortion axis. Most probably this vacancy is formed during irradiation.

2. Alkaline-earth Fluorides

The green luminescence of uranium in fluorite prepared in the presence of oxygen has been known for a long time (136, 163, 164), but a definite structural model for this center has not been inferred from these studies. The first model for this luminescent center assumed that U^{6+} enters substitutionally for Ca^{2+} , and four of the eight F^- ions are substituted by O^{2-} ions in order to preserve the charge neutrality (165). Thus the U^{6+} ion would be surrounded by two tetrahedra, one of F^- ions, the other of O^{2-} ions, resulting in a crystal field of inversionless symmetry. Recent Zeeman studies on the main luminescent line at 5212.5 Å have shown that the center has trigonal symmetry with inversion (166). Three structural models were proposed without a definite preference for one of them, viz.

(a) a substitutional uranyl ion with the axis along a cubic $[111]$ direction;

(b) a substitutional U^{6+} ion surrounded by two fluorine vacancies on the same body diagonal of the cube, and with the other F^- ions substituted by O^{2-} ;

(c) an interstitial U^{6+} ion surrounded by six substitutional O^{2-} ions and two F^- ions on the same $[111]$ direction.

All these models assure a complete charge compensation within the first coordination sphere of uranium. In order to select the right model, an EPR study of the transformation of the hexavalent uranium into pentavalent uranium under gamma irradiation has been performed. The samples contained before irradiation, besides the hexavalent uranium, three U^{5+} centers (167-169): a trigonal center (Tr), without superhyperfine structure, which consisted of a substitutional U^{5+} ion surrounded by six substitutional O^{2-} ions and two fluorine vacancies on the same $[111]$ direction, a rhombic center (Rh_1) whose structure is similar to the Tr center except that there are only five substitutional O^{2-} ions and a F^- ligand in the first coordination sphere (these centers have also been identified in U^{4+} -doped fluorite (170-172)), and a low-symmetry U^{5+} center (Rh_3) without superhyperfine structure, which presumably has the same first coordination sphere as the Tr center plus a nearby additional charge compensating defect.

The gamma irradiation has a strong effect on the luminescent U^{6+} center, whose spectrum decreases with radiation dose while a similar

increase is noticed in the intensity of the trigonal U^{5+} EPR spectrum. The dependence on dose is not smooth, probably because of some competitive processes such as the decrease of the intensity of the Rh_1 and Rh_3 U^{5+} EPR spectra or a transformation of part of the Tr centers due to irradiation. The parallel behavior of the luminescent U^{6+} centers and of the Tr U^{5+} centers under irradiation shows that their structure is similar, and thus the luminescent U^{6+} ion is substitutional and has six O^{2-} and two fluorine vacancies in the first coordination sphere. The absence of any EPR spectrum with resonance parameters close to those of UO_2^{2+} in the irradiated samples shows that no uranyl centers are present in the non-irradiated crystals.

The trigonal U^{6+} center has a strongly emitting level at 5212.5 Å. This luminescence line can be used in order to measure ultratrace levels of uranium in aqueous solutions (173, 174). Uranium is co-precipitated from solutions with calcium fluoride, the precipitates are calcined in air so as to assure the formation of the uranate centers described above and the luminescence is excited with a suitable laser. By a careful choice of the experimental conditions, amounts as low as 4×10^{-14} M (10^{-5} parts per billion or 0.01 picograms per milliliter) could be detected by this method (173).

These few examples show that the EPR measurements can be very useful in obtaining information on the structure of luminescent U^{6+} centers. Connected with luminescence (154, 160, 161, 167-171) or thermoluminescence (175) studies, the EPR measurements can also be useful in the study of the conversion $U^{6+} \rightarrow U^{5+}$ during irradiation.

B. EPR of Pentavalent Uranium

As shown previously, because the actinide contraction is small at the beginning of the series, the 5f orbital is not so well localized as the 4f orbital in the lanthanide series. Thus, despite the large spin-orbit coupling in the actinides, the crystal field effects for the ions of $5f^1$ configuration can be for octahedral symmetry of the same order of magnitude or even stronger than the spin-orbit effects. For eightfold or tetrahedral symmetry, the crystal field effects are small, and a situation similar to the $4f^1$ ions is expected. The determination of the spectroscopic g-value by EPR is of great importance in obtaining information of the crystal field and bonding effects in crystals with U^{5+} . Some characteristics of the EPR of this ion are as follows:

(a) Because of the strong crystal field

effects with octahedrally-coordinated U^{5+} ions, the excited levels are high enough, so that the relaxation processes are slow, and the EPR spectra can be recorded at liquid nitrogen or even higher temperatures.

(b) For U^{5+} in extremely strong axial fields (e.g. the groups UO_2^{+}) some of the excited levels could be lowered near the ground state, leading to a strong spin-lattice relaxation. This in turn causes a pronounced broadening of the lines and the spectra can be recorded only at liquid helium temperature.

(c) For eightfold cubic coordination the Γ_8 and Γ_6 levels originating from the ground $^2F_{5/2}$ level of the free ion are bunched together, a strong relaxation takes place, and the spectra can be recorded only at very low temperatures. A strong distortion may spread the crystal field levels, the relaxation is weakened, and the resonance could be, in principle, observed at somewhat higher temperatures. For a trigonal distortion the ground state could be the non-magnetic doublet Γ_3 and in such a case no resonance takes place.

(d) The sign of the g-value is negative.

(e) The effective g-values are usually very small, and high magnetic fields must be employed in order to observe the resonance.

1. U^{5+} in Octahedral Crystalline Fields

The EPR data for U^{5+} in diluted and concentrated systems are given in Appendix I and Appendix IV.

For the concentrated systems the lines are broad and slightly asymmetric, but in diluted systems they are sharp and symmetric, characteristic for Kramers ions.

1a. U^{5+} in Concentrated Systems

EPR measurements have been performed on concentrated halides and oxides of U^{5+} . While in the case of halides, the measurements have been successful (88, 91, 95, 176-180), no clear evidence for U^{5+} resonance have been obtained for oxides.

For many U^{5+} concentrated systems, optical data are available, and thus some of the characteristics of the crystal split levels (the crystal field splitting and the orbital reduction factors) can be estimated.

The g-values for the U^{5+} ion in concentrated halides are very low. Some general trends can be

observed in case of the concentrated systems. The mean g-value (defined at $(2g_{\perp} + g_{\parallel})/3$ in the case of axial symmetry) is around 0.6 to 0.77 when the ligands are F^{-} ions, 1.09 to 1.21 when the ligands are Cl^{-} and 1.2 to 1.39 for compounds with Br^{-} , i.e. the g-values are larger in the more covalent compounds. The same trend is observed for the energy difference between the Kramers doublets Γ_7 and Γ_7' which is of the order of 7300 to 7400 cm^{-1} in the compounds with F^{-} , 6700 to 7000 in compounds with chlorine and 6700-6850 in compounds with bromine (91). An analysis of the crystal field splitting based on these experimental data shows that for cubic complexes of pentavalent uranium, while the orbital reduction factor $k_{a_2t_2}$ does not change much from compounds with F^{-} ($k_{a_2t_2} = 0.935$) to those with Br (0.906), the reduction factor $k_{t_2t_2}$ is very sensitive to the neighborhood of uranium (0.9 for UF_6^{-} , 0.75 for UCl_6^{-} , and 0.50 for UBr_6^{-}). The crystal field splitting decreases strongly along this series, being respectively 3369 cm^{-1} , 1119 cm^{-1} , and 835 cm^{-1} . Unfortunately, the data given by different authors are not easily comparable, because different approximations have been used. Thus, many papers use a purely electrostatic crystal field, neglecting completely the orbital reduction. Other authors use the approximation $k_{a_2t_2} = \sqrt{k_{t_2t_2}}$, which has been assumed in the study of neptunium hexafluoride (85) and which shows up to be incorrect (91, 95). This explains why sometimes contradictory results on the same system are reported, as is the case of $CsUF_6$ (181, 182). A connection between the data obtained from EPR and those obtained from magnetic susceptibility has been made (183).

A systematic search for U^{5+} EPR in some concentrated oxides of pentavalent uranium has been undertaken but none of the investigated compounds, namely $NaUO_3$, $LiUO_3$, KUO_3 and Ba_2ScUO_6 (perovskite structure), Li_3UO_4 and Na_3UO_4 (rock salt structure), and $BiUO_4$ (fluorite structure) has shown any detectable signal at temperatures as low as 7 K (184). More recent measurements on mixed oxides MUO_3 ($M = Li, Na, K, Rb$) have shown, even at room temperature, very broad signals with g-values between 2.4 and 4 (185). These resonances cannot be explained by simple crystal field models for U^{5+} .

1b. U^{5+} in Dilute Systems

If for concentrated compounds the problem of the structure of the paramagnetic center is not so difficult because crystallographic structural data can be used, with diluted systems the

problem is more complex. Two kinds of diluted systems have been studied, viz. systems for which the host cation has the same valence as the dopant and there is only one site of substitution, and systems where the valence of the host cation differs strongly from the dopant ion and the charge compensation mechanisms can give a large variety of paramagnetic centers.

1c. U^{5+} in Diluted Oxide Systems

The EPR studies on U^{5+} in $LiNbO_3$, $LiTaO_3$, and $BiNbO_3$ (184) refer to the first category. The U^{5+} ion gives a spectrum of g about 0.7, and the symmetry of the site appears to be almost perfectly octahedral. The energy difference between Γ_7 and Γ_7' is about 7050 cm^{-1} . From this transition and the lines corresponding to the $\Gamma_7 \leftrightarrow \Gamma_8$ and $\Gamma_7 \leftrightarrow \Gamma_6$ transitions, the reduction factors $k = 0.8$ and $k' = 0.34$ (in the assumption $k_{a_2t_2} = \sqrt{k_{t_2t_2}} = k$; $k_{t_1t_1} = k'$ and $k_{t_1t_2} = \sqrt{k_{t_1t_1}k_{t_2t_2}} = \sqrt{kk'}$) have been estimated. The search for EPR signals in some other U^{5+} -doped (1 to 5%) niobates or tantalates with octahedral coordination for the pentavalent cation has been unsuccessful (184).

1d. U^{5+} in Diluted Fluorides

There are two cases as follows:

(a) U^{5+} in alkali fluorides. As shown in Section IV.A, hexavalent uranium can be introduced substitutionally in alkali fluoride crystals grown in the presence of oxygen. The EPR and optical studies of the crystals show that they do not contain any paramagnetic uranium ion (U^{2+} to U^{5+}) and all the uranium is in the hexavalent form. These U^{6+} ions can be converted to U^{5+} by X- or gamma irradiation, and a great variety of paramagnetic centers can be formed this way, corresponding to the variety of initial U^{6+} centers. Moreover, a parent U^{6+} center can give rise to more types of U^{5+} centers. The structure and symmetry of these centers has been discussed in connection with the structure of the parent U^{6+} centers. As shown in Appendix I, taking into account the superhyperfine structure, these centers can be divided roughly into three groups: centers without superhyperfine structure, centers with a two-component and centers with a three-component superhyperfine structure (146). In Appendix I a cubic center C in LiF corresponds most probably to a U^{5+} ion surrounded by a regular octahedron of oxygens. The centers Tg4 and Rh5 for LiF: U^{5+} and the center Rh1 for NaF: U^{5+} most probably corre-

spond to the same structure (UO_6), but the cubic crystal field is perturbed by a defect in the next cationic coordination sphere (such as a substitutional M^{2+} or M^+ ion). The Tg3 center in LiF corresponds to a strong deformation of the crystal field due, probably, to an anionic vacancy in one of the corners of the octahedron. Two types of centers with two-line superhyperfine structure have been observed, which differ in the magnitude of splitting. The first type of such centers is characterized by superhyperfine splittings which can reach values up to $A_{\parallel}^L = 14.3 \times 10^{-4}\text{ cm}^{-1}$ in LiF and $A_{\parallel}^L = 9.8 \times 10^{-4}\text{ cm}^{-1}$ in NaF. These centers correspond to a substitutional U^{5+} ions surrounded by five substitutional O^{2-} ions and a F^- ion. In the case of the tetragonal centers Tg1 in LiF and NaF the negative extracharge of the complex is compensated far away. For the Rh1, Rh2, and Rh3 centers in LiF and for the center Rh2 in NaF, the extracharge compensation is done by a nearby point defect. Unfortunately, for such low-symmetry spectra, it is very difficult to make a clear connection between the symmetry axes of the g^2 tensor and the positions of the sources of the crystal field. For the second type of centers with two-line superhyperfine structure, the splitting is considerably smaller than in the first case, being of the order of 3 to $4 \times 10^{-4}\text{ cm}^{-1}$ (centers Tg3 and Rh3 in NaF). In this case the $I = 1/2$ ligand is obviously different from that in the previous group of centers. Tentative models for these centers imply complexes with U^{5+} surrounded by five O_2^- ions and a OH^- or $(FX)^-$ group (where X is a species without or with a small nuclear moment) for Tg3 and a similar structure perturbed by a nearby defect for Rh3. For the centers with three-component superhyperfine structure with an intensity ratio of 1:2:1, the splitting is sensibly smaller than the superhyperfine splitting in the case of the two-component structures due to a F^- ligand, but quite similar to the splitting observed for the second group of centers with two-line superhyperfine structure. This shows that the ligands which cause this structure are not isolated F^- ligands but either F_2^- groups, H_2O^- , or two OH^- ions (on the same cubic axis). A very slight rhombic distortion of the center Tg1 in KF and Tg2 in NaF as well as the presence of the Rh4 center in LiF seems to favor the first models, with a far away extracharge compensation in case of the Tg centers and a nearby one in case of the Rh4. Taking into account the similarity between the superhyperfine splitting in case of these three-component lines and in case of the second type of two-component centers, it is reasonable to assume that

the source of the splitting is the same for both cases. To check these models, ENDOR experiments in ^2D or ^{17}O -enriched samples would be necessary.

The low concentration as well as the great variety of centers prevents an accurate optical study of the U^{5+} centers. Using an ingenious combination of absorption, luminescence, and excitation measurements, Parrot et al. (186, 187) were able to measure all seven electronic transitions within the Tg1 center in $\text{LiF}:\text{U}^{5+}$ and within another unidentified center. Unfortunately in their analysis of the splitting of the $5f^1$ configuration in a strong tetragonal field, they did not make use of the reduction parameters for each orbital, but left the spin-orbit coupling and the crystal field parameters B_k^q as parameters to be obtained by fitting the energy levels and the g -values. More sets of spin-orbit coupling and crystal field parameters have been obtained (186, 187) without a definite preference for one of them. The neglect of the reduction factors for the orbitals makes these parameters unreliable. A calculation of the g -value anisotropy defined as

$$\delta g = 3|g_{\parallel} - g_{\perp}|/|g_{\parallel} + 2g_{\perp}|$$

for various tetragonal U^{5+} centers with superhyperfine structure, gives values of 0.55 to 1.15 for LiF and 0.38 to 0.96 for NaF . The same situation holds for center Tg3 in LiF ($\delta g = 0.1$), which is assumed to correspond to an O_2^- octahedron, but not for the center Tg4 in LiF ($\delta g = 0.1$), which is assumed to correspond to an O_2^- octahedron slightly distorted by a cation impurity. This shows that for the centers whose source of distortion of the pure octahedron symmetry is placed in the first coordination sphere of uranium, the distortion is strong. Taking into account the comparison (Section II.B.3g) between the U^{6+} and U^{5+} hexa-coordinated complexes, this result confirms the recent interpretation of the optical spectra of the main tetragonal U^{6+} centers in LiF and NaF based upon the assumption of an axial distortion stronger than the coulombic inter-electronic interaction (188). This shows that the weak distortion model (189) is not valid in this case. This stresses the need for extreme care when comparing the properties of the uranate centers in alkali fluorides with those of other hexa-coordinated U^{6+} compounds as, for instance, UF_6 .

(b) U^{5+} in alkaline-earth fluorides. Pentavalent uranium enters into calcium fluoride crystals during growth, accompanying U^{4+} (in green or yellow CaF-U crystals) or U^{6+} (in white cloudy

samples). The green or yellow crystals may contain a (prevailing) trigonal U^{5+} center Tr and a rhombic Rh1 center. The trigonal symmetry, absence of any superhyperfine structure, and the low g -values show that the Tr center consists of a substitutional U^{5+} ion surrounded by six O^{2-} ions and two fluorine vacancies on the same $[111]$ direction. Thus the vicinity of the uranium ion is a distorted octahedron rather than a distorted cube, and this explains the low g -values. The center Rh1 has a similar structure, but a F^- ion is left in the distorted octahedron. The heat treatment of the crystals or gamma irradiation at room temperature decreases the intensity of the Tr center, increases that of Rh1 and gives rise to a new center of rhombic symmetry. This new center shows superhyperfine structure of three components with the intensity ratio 1:2:1 for $[001]$ (indicating two equivalent F^- ligands) which transforms to a two-line structure for $[112]$ and $[110]$. It is difficult to give a precise model for this center, but it must include two F^- nearest neighbors. Since gamma irradiation and heat treatment up to 1000°C have similar effects in producing the Rh1 and Rh2 centers, it has been assumed (172) that their main sources are some low symmetry U^{4+} centers compensated by substitutional oxygens and fluorine vacancies. Fluorine interstitials stimulated by gamma irradiation or heating migrate through the crystals and could be trapped on fluorine vacancies in the neighborhood of uranium. A rearrangement of charge could transform U^{4+} into U^{5+} .

In the as-grown white cloudy samples containing U^{6+} , the most intense EPR spectrum of U^{5+} belongs to a center of very low symmetry (Rh3 in Appendix I). The very sharp lines without superhyperfine structure and the close resemblance of the g -values of this center to those of the Tr center, show that the first coordination sphere of uranium is the same in both cases, but while with the Tr center, the negative extracharge of the complex $(\text{U}^{\text{VO}_6})^{7-}$ as compared to CaF_8^{6-} is compensated far away, in case of the Rh3 center this is done in the neighborhood of the complex, possibly by a fluorine vacancy. No optical data on U^{5+} in fluorite have been measured.

The calculated mean g_0 value for the most symmetric U^{5+} centers in alkali and alkaline-earth fluorides are 0.33 to 0.4 for LiF , 0.49 to 0.58 for NaF , 0.55 for KF and 0.76 to 0.81 for CaF_2 . This shows that for oxygen octahedrally-coordinated U^{5+} ions, the g -values can be equal or slightly larger than for F^- coordinated complexes, when the distance U-O is large (as in the case of alkaline-earth fluorides and niobates) but

becomes smaller as this distance decreases (the alkali fluorides). At the same time the distance $\Gamma_7' - \Gamma_7$ increases with decreasing length of the U-O bond (7050 cm^{-1} in niobates and 7878 cm^{-1} in Tg1 in LiF). This shows (190) a close relation between the g_0 and $E_{\Gamma_7'} - E_{\Gamma_7}$ and the spectrochemical series (191).

2. EPR of U^{5+} in Nonoctahedral Crystalline Fields

As shown previously, for the eightfold or tetrahedral symmetry the crystal field has a very small effect on the free state of a $5f^1$ ion, and its behavior would be similar to that of a $4f^1$ ion, i.e. the ground state is mainly determined by the $^2F_{5/2}$ level of the free ion, with possible admixtures from the crystal-field states originated from the excited $^2F_{7/2}$ level. In cubic symmetry the ground level can be Γ_6 or Γ_8 . When Γ_6 is lowest, an isotropic resonance line with $g = 10/7$ is expected, while for Γ_8 some anisotropic transitions must be seen. An axial or lower symmetry distortion splits Γ_8 , as discussed in the previous section.

Very few experimental data on systems with U^{5+} in nonoctahedral symmetry have been reported. Thus a line with $g \sim 1.25$ in uranium-doped ThO_2 powder could correspond to such a center, because the host cation Th^{4+} occupies the center of a regular cube of O^{2-} ions (192). However, no EPR measurement on U^{5+} in single crystals of ThO_2 has been reported in order to confirm this identification. An attempt to observe EPR in cubic $UF_6 M_3$ ($M = Na, Cs, Rb, NH_4$) at liquid nitrogen temperature (193) was unsuccessful, but subsequent measurements (184) on polycrystalline $UF_6 Na_3$ gave a broad resonance signal at $g = 1.2$. A very interesting aspect of this situation is the Rh_4 center of U^{5+} in fluorite (194). This center is observed in the uranium-doped fluorite samples heat-treated at $1200^\circ C$ in quartz ampoules sealed in air. This center appears regardless of the initial valence state of uranium and the means of charge compensation. The hyperfine structure for ^{235}U -doped samples shows that the center contains a uranium ion, while the symmetrical lineshape and the temperature of observation show that the valence state of uranium is $+5$ (195). While for the other U^{5+} centers in fluorite, the lines are sharp (of several Gauss), the line corresponding to this center are broad, of about a hundred Gauss with the magnetic field along the $[100]$ direction. No superhyperfine structure was resolved for any orientation of the external magnetic field, but it is possible that the broad lines obscured an

unresolved structure determined by a large number of ligands in the next coordination sphere. The g -values for this center (0.540, 2.775, and 0.471) and $\delta = 1.8^\circ$ differ considerably from those observed for the other U^{5+} centers in fluorite and are very close to those reported for a rhombic $Ce^{3+} (4f^1)$ ion in cerium oxide-doped fluorite, for which the main g -values are 3.286, 0.22, and 0.844 and $\delta = 13.8^\circ$ (196).

The structure of this center as of other low-symmetry rare-earth centers in oxide-doped fluorite is not known. However, the g -values of the U^{5+} Rh_4 center cannot be explained if the vicinity of uranium is assumed to be octahedral, and models with distorted eightfold or tetrahedral symmetry must be employed. The lack of a resolved superhyperfine structure shows that no fluorine ligands are present in the nearest neighborhood of uranium, but rather that this is formed by oxygen ions. Thus a structural model for this center must be based on a tetrahedral vicinity with, perhaps, one or two additional O^{2-} ions (in order to compensate the charge) placed in the first coordination sphere or in a near interstitial, to give a low symmetry to the center. The arrangement of this center could be connected (195) with the transition of fluorite crystals to the disordered superionic state at $1150^\circ C$ (197) when the F^- ions can migrate from their normal positions in interstitials leaving vacancies which can then be occupied by oxygens. They can also originate from some low-symmetry oxygen-coordinated U^{4+} centers.

3. EPR Hyperfine Structure of U^{5+}

The EPR hyperfine structure corresponding to the isotope ^{235}U ($I = 7/2$) has been studied only in the case of U^{5+} in alkali fluorides and calcium fluorides, where the lines are sharp. Accurate measurements have been possible only for some axial centers (155, 156, 158, 171, 198, 199).

For the low-symmetry spectra the large number of lines belonging to the same center or to different centers present in the sample, the strong quadrupolar effects, and possible differences between the principal axes of the spectroscopic factor g and of the hyperfine interaction, make the analysis of the hyperfine structure extremely difficult. However, it was observed for all the U^{5+} spectra in alkali and alkaline-earth fluorides and has been used to prove that these centers belong to uranium.

Since the Tg1 center in $NaF:U^{5+}$ is the only center for which all the spectra could be recorded at 9 GHz with a magnetic field up to 20 kGauss,

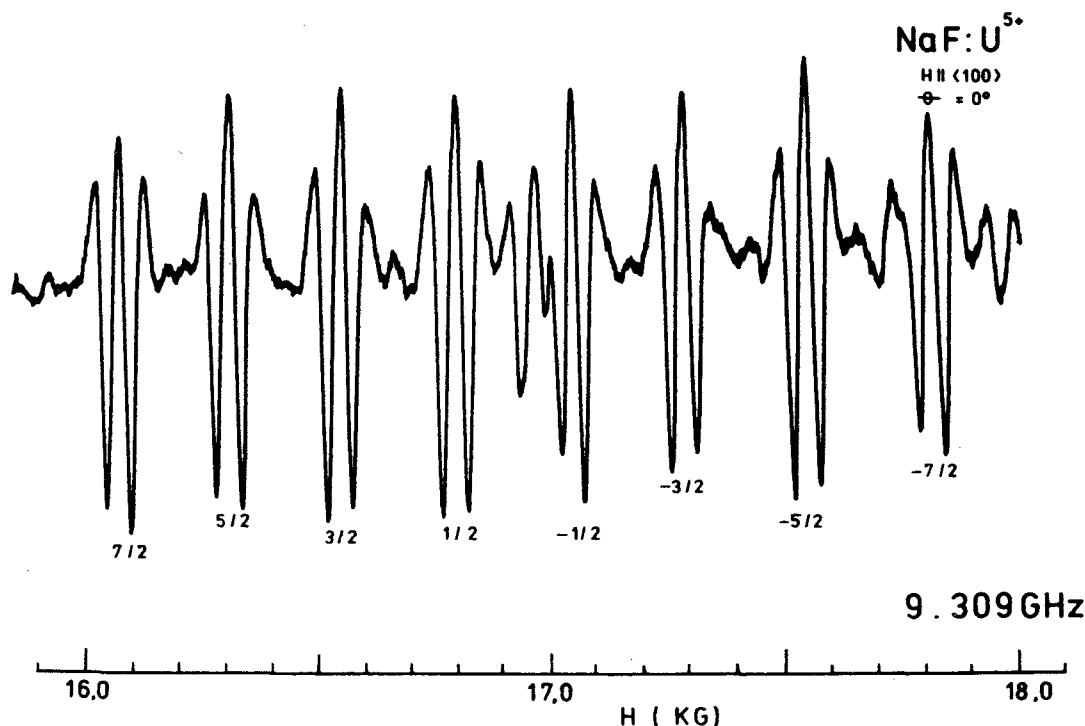


Figure 2. The parallel hyperfine structure for the Tg1 U⁵⁺ center in NaF.

we shall describe it as an illustrative example. For all the other axial centers, the EPR parameters for parallel orientation have been obtained from the angular dependence of the spectra. For the parallel orientation ($H \parallel [100]$), the hyperfine structure for the Tg1 (^{235}U)⁵⁺ center in NaF consists of eight equally intense and almost equally split components. As Figure 2 shows, each hyperfine component is split into two because of the superhyperfine interaction with the F⁻ ligand placed on the distortion axis.

Approximately in the center of the hyperfine pattern, a line corresponding to ^{238}U is observed. The ratio of the total intensity of the hyperfine spectrum due to the 235 isotope to the intensity of the 238 isotope line is in this case about 13:1, faithfully reflecting the isotopical composition of the uranium oxide used as dopant. This fact has been used as a method for measuring the isotopic abundance of minute amounts of non-volatile uranium salts which can easily be dissolved in molten sodium fluorite in the presence of oxygen (200, 201). When the magnetic field is turned away from $[100]$ in the (100) plane, the hyperfine pattern is drastically modified. If we denote the hyperfine components by m_I , when the angle between the external magnetic field and $[100]$ becomes 20°, the splitting of

the $\pm 1/2$ hyperfine lines is increased so that they overlap the $\pm 3/2$ components and for $\Theta = 45^\circ$, they overlap the doublet $\pm 7/2$. This splitting of the other hyperfine doublets decreases as Θ increases and vanishes at $\Theta = 90^\circ$ for the doublets $\pm 5/2$, $\pm 7/2$ (see Figure 3).

The lines 3 and 7 in Figure 3 correspond to the $\pm 1/2$ lines, the lines 4 and 6 to the $\pm 3/2$ doublet, and the line 5 to $\pm 5/2$ and $\pm 7/2$ components. The lines 1, 2, 8, and 9 are "forbidden" hyperfine transitions, which can be clearly observed at $\Theta > 60^\circ$.

In order to describe this unusual hyperfine structure, a new perturbation scheme has been used (155). The spin Hamiltonian contains the axial Zeeman interaction, the axial hyperfine interaction, and the nuclear quadrupole interaction. The unusual behavior of the $\pm 1/2$ hyperfine doublet suggests that the nuclear electric quadrupole interaction is of the same order or stronger than the hyperfine interaction. In this case the eigenvalue problem of the spin Hamiltonian must be solved numerically. In order to obtain the starting values for the parameters (which are then improved by a numerical diagonalization), a preliminary analytical treatment was used assuming that the magnitude of the interactions in the spin Hamiltonian are in the

order: Zeeman electronic, quadrupole interaction, and hyperfine interaction. In such a case the quadrupole interaction splits the nuclear spin degeneracy into four levels, degenerate after $\pm m_I$, and subsequently the hyperfine interaction is block diagonalized within each of these doublets. The resonance condition given by such a treatment is:

(a) for the doublet $\pm 1/2$,

$$h\nu = g\beta H \pm \frac{1}{2}K$$

with

$$g = (g_{\parallel}^2 \cos^2 \Theta + g_{\perp}^2 \sin^2 \Theta)^{1/2}$$

and

$$Kg = (A_{\parallel}^2 g_{\parallel}^2 \cos^2 \Theta + 16A_{\perp}^2 g_{\perp}^2 \sin^2 \Theta)^{1/2},$$

(b) for the doublets $\pm 3/2$, $\pm 5/2$, $\pm 7/2$,

$$h\nu = g\beta H + A_{\parallel} g_{\parallel} m_I \cos \Theta / g.$$

The doublet $\pm 3/2$ is split by second-order effects.

In the same way the angular dependence for the forbidden hyperfine lines has been obtained and was used to estimate the electric quadrupole parameter.

This analytical treatment predicts a maximum splitting for the hyperfine doublet $\pm 1/2$ at an angle Θ given by (168):

$$\cos^2 \Theta = 1 +$$

$$\frac{A_{\parallel}^2 g_{\parallel}^2 (2g_{\perp}^2 - g_{\parallel}^2) - 16A_{\perp}^2 g_{\perp}^2 g_{\parallel}^2}{A_{\parallel}^2 g_{\parallel}^2 (g_{\parallel}^2 - g_{\perp}^2) - 16A_{\perp}^2 g_{\perp}^2 (g_{\parallel}^2 - g_{\perp}^2)}$$

The spin Hamiltonian parameters obtained in this analytical treatment have been improved by numerical exact diagonalization of a 16×16 matrix. Similar hyperfine behavior has been observed for other U^{5+} centers (in alkali and alkaline-earth fluorides), and the determination of the parameters has been done in the same way. From an inspection of the hyperfine data given in Appendix I, the importance of the nuclear quadrupole effects is seen. For many centers (Tg1 in NaF, Tg1 in KF, Tr in CaF_2) the electric quadrupole parameter is larger than the magnetic hyperfine parameters, and in the case of Tg1 in LiF, they are of the same order of magnitude. A similar situation has been observed for the isoelectronic Np^{6+} ion (202). Thus, the hyperfine behaviour of the $5f^2$ ions in octahedral coordination parallel the electronic behaviour characterized by crystal field effects stronger than the spin-orbit coupling.

C. EPR of Tetravalent Uranium

As shown before, the ground level of the non-Kramers ion U^{4+} (f^2 ground configuration) in a crystal can be a singlet, doublet, or triplet depending on the symmetry of the crystal field, on the composition of the crystal field potential, and on the effect of the intermediate coupling and J mixing through the crystal field. Thus in the case of octahedral symmetry, the ground state is always a Γ_1 singlet. In the case of eightfold and tetrahedral cubic symmetry, the ground level can be a Γ_1 or a Γ_5 triplet, depending on the ratio of the fourth- to sixth-order terms in the crystal field potential. In lower symmetries the ground level can be either a singlet or a non-Kramers doublet. This explains why many systems of interest, for which the crystal field is octahedral or of lower symmetry, cannot be studied by EPR. The most suitable hosts for EPR studies on U^{4+} are those with eightfold cubic cationic positions. An EPR study of uranium-doped ThO_2 (192) shows at room temperature a line with $g \sim 2.7$, which has been attributed to U^{4+} . However, a calculation of the spin-lattice relaxation time for U^{4+} in cubic crystalline fields (203) shows that this becomes too short already at the liquid nitrogen temperature to allow an observable EPR signal from U^{4+} . Thus the nature of this center is uncertain. Unfortunately, no EPR study on single crystals of ThO_2 doped with uranium (preferably enriched in the 235 isotope) has been reported to check this identification (192).

More studies have been devoted to U^{4+} in alkaline-earth fluorides. In the case of calcium fluoride, the composition of the eightfold cubic crystal field potential favors Γ_5 as a ground level, and its states can be characterized as the eigenfunctions of a fictitious spin $S = 1$. Using the wavefunction of the Γ_5 triplet, single quantum transitions at $g = 2$ (governed by the selection rule $\Delta M_S = 1$) and at $g = 4$ (selection rule $\Delta M_S = 2$) and double-quantum transitions at $g = 2$ (selection rule $\Delta S = 2$) are expected, as in the case of the cubic Pr^{3+} ($4f^2$) center in fluorite (134). A single isotropic line of $g \sim 2$ has been observed for $CaF_2:U$, which has been attributed to U^{4+} in cubic sites (204). However, this line does not show any superhyperfine splitting, as expected for substitutional cationic sites. A further confirmation of this spectrum especially using ^{235}U -doped samples is necessary. The difficulties connected with the charge compensation for a cubic center of U^{4+} in CaF_2 must also be taken into account.

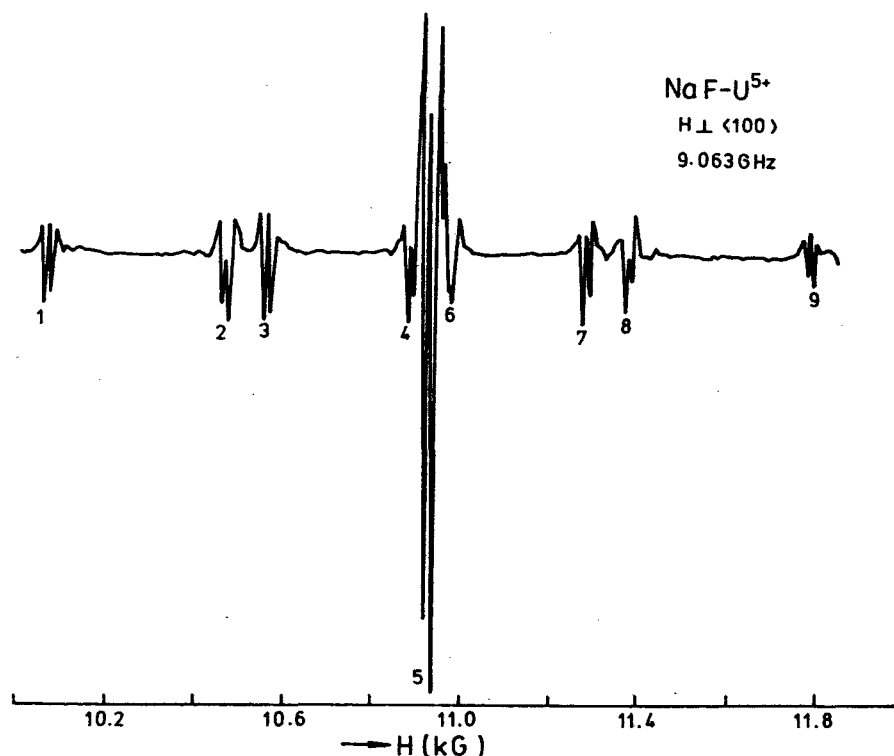


Figure 3. The perpendicular hyperfine structure for the Tg1 U^{5+} center in NaF.

An axial distortion (as caused, for instance, by charge compensating point defects) splits the Γ_5 triplet into a doublet and a singlet. The relative positions of the two components are given by the sign of the axial distortion. Thus a tetragonal distortion, due for instance to the presence of a charge-compensating interstitial anion (F^- or O^{2-}) in the empty cube next to uranium, leaves the singlet lowest, as occurs in the fluorine-compensated tetragonal Pr^{3+} ($4f^2$) centers in fluoride (205), and no EPR transition is expected. A trigonal distortion leaves the doublet lowest, and paramagnetic resonance transitions can be induced between its two states in the presence of an external magnetic field. As shown before, the most suitable spin Hamiltonian for such a non-Kramers doublet corresponds (206, 207) to a fictitious spin $S = 1$, and a strong additional zero-field splitting term must be added in order to remove the singlet. Three trigonal centers have been attributed to U^{4+} in CaF_2 . Various EPR and acoustic paramagnetic resonance studies on the center Tr1 (204, 208-217) have shown that the center is inversionless, and the resonance

transitions are induced mainly by the electric component of the microwave field. The superhyperfine structure shows that the U^{4+} ion occupies a substitutional lattice site and is surrounded by eight fluorine ligands. The interaction with two of them placed on the same body diagonal, is stronger than that corresponding to the other six. The distortion of the cube can be due to a static Jahn-Teller effect or, most probably, to the presence of a charge compensator which gives inversionless symmetry to the crystal field. The fact that the green or yellow crystals which contain this center can be grown if the dopant is UF_4 or if care is taken in order to eliminate the oxygen leads usually to the conclusion that the oxygen does not take part in this center. However, the presence of oxygen-coordinated U^{5+} centers (170-172) in some high quality green or yellow crystals containing the Tr1 U^{4+} center shows that the oxygen can be present in these crystals. Most probably, the charge compensation for this U^{4+} center is effected by a substitutional O^{2-} ion in the first empty cube along the $[111]$ direction. A compensation with

two interstitial F^- ions is improbable, because this would give a centrosymmetric complex.

The apparent g -value for this center is very close to that expected if a very slight distortion, which leaves the wavefunctions of the levels almost unaltered, is taken into account. An optical study of this system (43, 44) gave for the crystal field parameters values which lead to $g_{\parallel} \sim 4.8$. The disagreement between the EPR and optical data is due mainly to the fact that the crystal field parameters were determined to fit the splitting of a large number of levels and may not correspond to the best-fit values for the ground state.

In the case of the $Tr2$ U^{4+} center in fluorite, the superhyperfine structure due to the F^- ligands suggests a center with inversion symmetry (218). The fact that the superhyperfine structure is best resolved when the magnetic field is along the $[111]$ shows that all the $U^{4+}-F^-$ bonds are equivalent with respect to this direction, and this is possible only if no F^- is placed on the distortion axis. The odd number of components and the intensity ratios show that there are six F^- in the first coordination sphere. In such cases the charge compensation can be due to two substitutional O^{2-} ions on the distortion axis. This model gives a distortion of the right sign to assure the doublet as a ground level and a mixing of states which can explain the value of $g_{\parallel}$. The presence of the oxygens can explain why this center appears in the crystals doped with uranium oxide, or in samples obtained by heat treatment of U^{3+} -doped fluorite at $1200^\circ C$ in quartz ampoules sealed in vacuum (for which the quartz, evidently attacked during the treatment, can supply the necessary oxygen).

The nature of the $Tr3$ center in CaF_2 (and Tr centers in SrF_2 and BaF_2) is not established (219-222). From the crystal growth procedure it was concluded that a remnant contamination of the samples with oxygen is possible and, as a logical possible model, that given for the center $Tr2$ above has been proposed. However, the superhyperfine interaction with 24 ligands of $I = 1/2$ shows that this model cannot be correct for the $Tr3$ center. It is also impossible to explain the g -value by a trigonal distortion of the cube, since the dominant $A_2^0 \langle r^2 \rangle$ term of the distortion would give apparent g -values larger than 4 if its sign is taken as to leave the doublet lowest (223). The fluorite crystals which contain the $Tr3$ center show an optical absorption spectrum (43, 44) sensibly different from that observed for the crystals containing the $Tr1$ center. Hargreaves attributed this optical spectrum to a U^{2+} ion with $5f^3 7s$ ground configuration, which at

the same time has been considered as responsible for the EPR $Tr3$ center observed in the same crystal (224). The crystal growth conditions which were considered able to eliminate completely the oxygen, as well as the valence conversion of the uranium ions in fluorite under uv and X-irradiation were set forth in order to support this identification.

A chemical method of analysis of different uranium-doped fluorite samples, connected with optical absorption measurements (225), led to the conclusion that the samples studied by Hargreaves (43, 44) contain U^{4+} and not U^{2+} . The paper (225) connects the color of the $CaF_2:U$ crystals with the valence state of uranium and the means of charge compensation. We note, however, that in discussing this problem, the very complex situation of the $CaF_2:U$ system must be taken into account, in which many valence states and types of centers can be simultaneously present in a given sample. These centers make themselves conspicuous in different manner with respect to different measurements; thus the conclusions of (225) must be used with caution. As an example, in many good quality (low scattering, good cleavage) green $CaF_2:U$ crystals, we found besides the $Tr1$ U^{4+} center, various U^{5+} centers; the same situation may be observed in the yellow crystals.

The crystal growth conditions reported in different papers must be considered prudently. Both uranium and calcium have a strong tendency to oxidize, and sometimes strong reducing conditions may not be sufficient in order to eliminate all the oxygen from the system. There are cases when in a crystal containing a prevailing uranium center without oxygen, inclusions of calcium oxide or uranium dioxide are also present. The nature of a given center can be clarified only if a physical model which allows an estimate of a given parameter in agreement with the observed value is proposed.

Recently a new tentative model for the $Tr3$ center in $CaF_2:U$ has been proposed (226): a U^{4+} ion substitutes a Ca^{2+} ion, and the nearest cube of fluorines is replaced by five oxygens. Two of the oxygens are placed on the same body diagonal while the other three form a triangle which can replace one of the original F^- triangles (normal to the body diagonal in question) or may be displaced towards the equatorial site of the complex. This model can easily explain the g -values on the basis of a strong trigonal field acting on the 3H_4 ground level of the free ion. According to this model the observed superhyperfine structure is due to the 24 fluorine ions in the next-nearest positions.

The hyperfine structure of $(^{235}\text{U})^{4+}$ in fluorite has been studied in (218). The spectra show a hyperfine structure of eight allowed $\Delta m = 0$ components from which the apparent A parameter has been determined. The absence of the forbidden transitions in the spectra prevented the determination of the nuclear quadrupole parameter, although it is expected to be large. A peculiarity of this hyperfine structure must be noted. For the actinide ions the relation $A_J/g_J = A_x/g_x = A_y/g_y = A_z/g_z$, which is usually valid for the lanthanide ions, is expected to hold regardless of the host crystal. However, a marked difference in the ratio $A_{\parallel}/g_{\parallel}$ for the Tr1 and Tr2 U^{4+} centers in fluorite is observed. In the first case this ratio is 26.6, while in the second case it is 41.9 (in units of 10^{-4}). This prevents an estimate of the magnetic moment of the 235 isotope of uranium from the EPR hyperfine structure of the U^{4+} centers. The difference between the two cases can be accounted for only if we allow for crystal field effects which can produce a considerable mixing of the free-ion levels.

The EPR studies on U^{4+} in crystals can be explained under the assumption of weak to intermediate crystal effects on a given free-ion energy level, if the intermediate coupling and J mixing are taken into account. Thus a qualitative difference between U^{5+} and U^{4+} appears in that they are separated by the limit between the intermediate and weak crystal field effects.

D. EPR of Trivalent Uranium

The trivalent uranium ion has a $5f^3$ ground configuration with a $J = 9/2$ ground level composed of 83% ^4I and 15% ^2H intermediate coupling components. In a cubic field this level is split into a doublet Γ_6 and two Γ_8 quartets. In octahedral coordination the doublet is lowest, while in eightfold or tetrahedral cubic symmetry, the lowest is either Γ_6 or Γ_8 , depending on the composition parameter x of the cubic crystalline potential. A tetragonal distortion splits the quartet into two doublets, while a trigonal distortion splits it into a doublet and a degenerate pair of singlets. In a strong trigonal field, the lowest of the components can be either a singlet or a Kramers doublet.

The paramagnetic resonance studies on U^{3+} are concentrated on two types of hosts, the alkaline-earth fluorides and the lanthanum chloride. Most of those studies refer to calcium fluoride. The trivalent uranium ion can easily replace a Ca^{2+} ion, and the charge difference can be compensated in various ways (227) by (i) an

interstitial F^- ion, (ii) a substitutional M^+ cation, (iii) a substitutional O^{2-} ion, and (iv) substitution of three Ca^{2+} ions by two U^{3+} ions. The presence of the charge compensators in the vicinity of the uranium ion leads to a distortion of the cubic crystal field. If the charge compensator is far from the uranium ion, the distortion of the cubic field can be safely neglected in most cases.

If we express the position of the charge compensator in units of the lattice parameter taking U^{3+} as the origin, an interstitial F_i^- ion can occupy a (l, m, n) site characterized by $(l + m + n)$ equal to an odd number, at a distance of $(l^2 + m^2 + n^2)^{1/2}a_0$ from uranium, where a_0 is the lattice parameter (in case of CaF_2 , $a_0 = 2.726 \text{ \AA}$). The main sites of F_i^- in the vicinity of uranium are of the type $(1, 0, 0)$, $(1, 1, 1)$, $(2, 1, 0)$, and $(2, 2, 1)$. A substitutional M_s^+ ion can occupy sites with $(l + m + n)$ equal to an even number, and the main position in the vicinity of uranium are $(1, 1, 0)$, $(2, 0, 0)$ and $(2, 1, 1)$. The main nearest substitutional position of O^{2-} is $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$.

In the eightfold cubic substitutional sites of CaF_2 , a Γ_8 ground level is expected for U^{3+} . The first attempt (228) to observe EPR from cubic sites of U^{3+} in CaF_2 produced spectra which did not follow the predicted (126) angular dependence. These results have been criticized (221, 222) where a new center has been reported as cubic U^{3+} . This center can be approximately described by the Γ_8 theory only if the sixth-order parameter in the cubic potential is taken equal to zero. This is in contradiction with the observations on other actinide or rare earth ions in fluorite or in other cubic crystal field. Recent studies (79, 135, 229, 230) have unearthed a new center in fluorite (the center C in Appendix III), which is well described by the Γ_8 resonance theory and have shown that this is the substitutional cubic U^{3+} center. When the magnetic field is parallel to the cube edge, two strong resonance lines with a resolved superhyperfine structure of an odd number of components are observed. An analysis of this structure shows that it is due to an interaction with eight equivalent fluorine ligands. The superhyperfine components of the low magnetic field transitions have individual linewidths (between the points of maximum slope) of about 7 Gauss and are split apart at 10.2 Gauss. When the magnetic field is turned away from the $[100]$ direction in the (110) or (100) plane, the line positions and intensities change drastically (Figure 4).

Around the $[111]$ direction the intensity of the two transitions drops, and a very broad line appears between them. The two strong and sharp lines have been attributed to the

transitions $|1/2\rangle \leftrightarrow |-1/2\rangle$ (the line at high magnetic field with an effective g -value of $2Q$) and $|3/2\rangle \leftrightarrow |3/2\rangle$ (the line at low magnetic field with an effective g -value of $2P$). As shown in the previous sections since the Γ_8 representations enter twice in the decomposition of $D^{3/2}$, the wavefunctions of each Γ_8 quartet depend on the composition parameter x . This makes the resonance parameters P and Q dependent on x and can be used to determine it. An estimation of x from data on this center using equation 69 gives -0.4959 (from the value of Q) and -0.4582 (from the value of P), if we take for g_J the Landé factor of the ground state corrected for the intermediate coupling and $K_J = 1$. A unique x parameter of -0.4873 , which fits both P and Q parameters, can be obtained if a reduced value for $K_J g_J$ of 0.6794 (the reduction factor K_J being 0.918) is used. Three major sources for the reduction of g_J can be considered (135, 229, 230), but an accurate calculation of this effect is for the moment impossible because the positions of the excited states in the crystal field are not known:

(a) The J mixing through the cubic crystal field. As shown in Section 2.II.A.3d, there are many free-ion energy levels not very far from the ground state; thus at least six or seven Γ_8 quartets closer than $10,000 \text{ cm}^{-1}$ to the ground state can appear in a cubic field, and these can be admixed to the ground Γ_8 level. An estimation of the effect of the first excited level $J = 11/2$ shows that it lowers the g_J value of the ground state.

(b) The covalency effects. The presence of covalency is clearly shown by the superhyperfine structure. A previous estimation (231), shows that the covalency effects could be important in the case of cubic U^{3+} centers in fluorite.

(c) A dynamic Jahn-Teller effect (232).

The composition parameter x determined for this center is in very good agreement with the values obtained for the $4f^3$ ions Pr^{2+} (233, 234) and Nd^{3+} (230, 235) in cubic sites in fluorite or for the isoelectronic Np^{4+} in ThO_2 (236). Using this x value and the parameters β_J and γ_J for U^{3+} corrected for the intermediate coupling, a value of 0.177 for the ratio $A_6 \langle r^6 \rangle / A_4 \langle r^4 \rangle$ has been obtained, in very good agreement with the values obtained for the various rare-earth ions in fluorite and for the actinide ions in various eightfold or sixfold cubic lattices. We mention that a comparison between the data obtained for cubic U^{3+} ($5f^3$) and those on cubic $4f^3$ ions (Pr^{2+} and Nd^{3+}) in fluorite shows that U^{3+} is in many

respects (the value of x , the superhyperfine structure) more similar to Pr^{2+} than to Nd^{3+} (230). With these arguments in favor of this center, it is very difficult to explain the nature of the spectrum reported by Title (221, 222).

The g -values of the tetragonal Tg_2 center in CaF_2 doped with uranium and sodium (237) can be related to the P and Q parameters of the cubic center (135, 229, 230) by equation 44b, i.e. the tetragonal distortion in this case is characterized by a positive $A_2^0 \langle r^2 \rangle$ parameter and splits the quartet into two doublets, leaving the doublet $|\pm 3/2\rangle$ lowest with its wavefunction almost unchanged. The superhyperfine structure of an odd number of components observed for this center is best resolved with the external magnetic field along the distortion axis. A rough analysis shows that it consists of an interaction with eight almost equivalent F^- ligands and a weaker interaction with four other F^- ions which form a square normal to the distortion axis. This structure shows that no interstitial F^- ion is involved in the charge compensation. The most plausible model for this center is that of a substitutional Na_S^+ at a lattice site $(2, 0, 0)$ relative to uranium. Such type of centers have previously been reported in fluorite doped with neodymium and sodium, or with cerium and sodium (238). In this paper (238) the assignment Na_S^+ $(2, 0, 0)$ has been rejected on the argument that this ion is too remote from the rare-earth ion to induce such a large g -anisotropy. It can be shown (237) that the g -values for Nd^{3+} in such a center can be related to the values reported for cubic Nd^{3+} in fluorite (230, 235) in exactly the same way as in the case of uranium. In fact, as equation 44a shows, the g -anisotropy in such a case depends on the cubic parameters and not on the magnitude of the distortion and can be very large. Tetragonal centers have recently been observed in CaF_2 doped with uranium and either Li^+ , K^+ , or Ag^+ (239). This proves again that the center C (135, 229, 230) is the substitutional cubic U^{3+} center in fluorite.

When the charge compensation is done by an interstitial F_i $(1, 0, 0)$ (219, 227, 240), the g -values (center Tg_1 in Appendix III) cannot be related in a simple way to the cubic parameters, because a considerable mixing of states is induced by the strong tetragonal component. The same is also true for the rhombic Rh_2 center compensated by a substitutional M^+ ion ($M = Li, Na, K, Ag$) at a $(1, 1, 0)$ lattice site (239, 241). Thus, while the tetragonal M_S^+ $(2, 0, 0)$ centers have similar EPR spectra, the rhombic M_S^+ $(1, 1, 0)$ depends markedly on the compensating alkali ion (239).

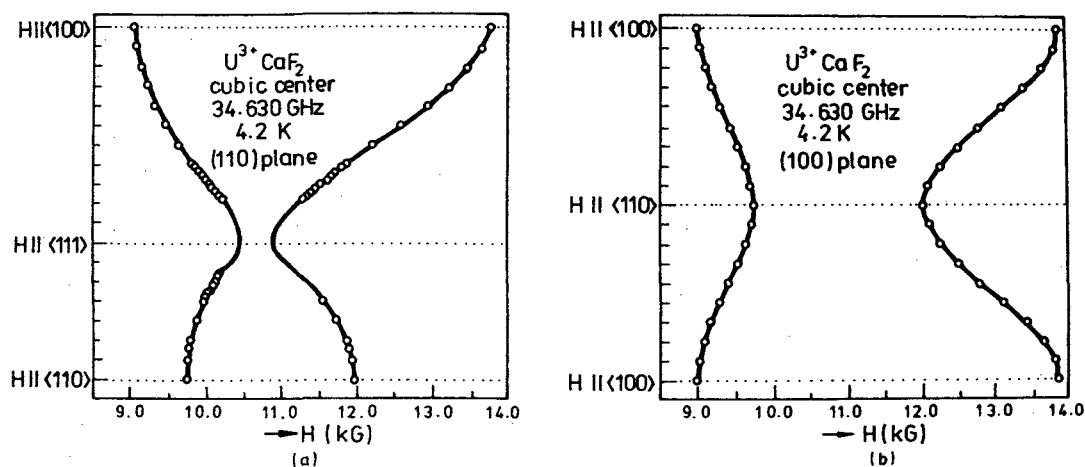


Figure 4. The angular variation of the two main transitions in the cubic U^{3+} center in CaF_2 .

The tetragonal center Tg1 in the fluorite lattice is the most studied uranium center. We also mention studies on linear electric field effects (242), electron spin-lattice relaxation (240, 243-247), ^{19}F NMR (248-250), the study of the superhyperfine structure by ENDOR (251, 252), discrete saturation (DS) (253, 254) and radiofrequency discrete saturation (RDS) (257) and optical detection of EPR (258). The EPR spectra of this center show a well resolved hyperfine structure with a large number of components due to an odd number of fluorine ligands. This shows that an interstitial fluorine ion is placed in the vicinity of uranium. Counting the superhyperfine components in an EPR spectrum with many ligands (which can be grouped in nonequivalent sets) is difficult, because the outer lines may be lost. Also a determination of the superhyperfine interaction parameters may prove impossible, because as many as five superhyperfine parameters are necessary to characterize the interaction with the nearest neighboring nuclei, when the symmetry of the crystal field is tetragonal. A fortunate situation is the case of cubic symmetry or for the ligand on the distortion axis, when only two superhyperfine parameters are necessary. The parameters of the superhyperfine interaction with the ligands from different coordination spheres can be determined with great accuracy by using ENDOR, DS, or RDS. These parameters can then be used in order to determine the dipolar and covalent contributions to

the superhyperfine interaction and the displacements of the various ligands and of the paramagnetic ion from their equilibrium positions in the unperturbed fluorite lattice. The measurements on the Tg1 U^{3+} center in CaF_2 have given a configuration of the charge-compensation model with an interstitial fluorine ion at a (1, 0, 0) lattice site and have produced a displacement $d = 0.09$ (252) (i.e. of the order of $0.12 \text{ \AA}$) of the U^{3+} ion towards the interstitial fluorine.

A low symmetry center Rh1 in fluorite doped with $NaUF_4$ has been assumed to originate from a substitutional U^{3+} center compensated by a fluorine ion at a (2, 2, 1) lattice site (259). Since the experimental angular dependence observed (259) does not show all the lines predicted by theory for such a center, this spectrum has been reinterpreted (260) as due to a F_i^- compensation at a (2, 1, 0) lattice site, and thermodynamical arguments were presented to show that such a center is more probable than that assumed (240). However, a recent record of the entire resonance spectrum (261) shows that the symmetry assignment (259) is correct. A structural model for this center is difficult, because for such low symmetry centers, the principal axes do not necessarily point toward the sources of the distortion. It seems, however, that the co-doping with alkali fluorides increases its probability because it appears frequently in the fluorite crystals doped with uranium and with NaF, KF, or LiF. It is possible that these fluorides supply

the F^- ions and help in its stabilization in such a position as to contradict the calculated thermodynamical distribution (260).

A remarkable fact is the absence of any trigonal U^{3+} EPR center in fluorite, in spite of the fact that a F^- ion can occupy easily the interstitial position (1, 1, 1). As shown (135) if the distortion potential $A_2 \langle r^2 \rangle$ created by such a F^- ion is positive, as in the case of some trigonal rare-earth centers in fluorite compensated this way, and if the condition of weak distortion is achieved, it will leave as the ground state the doublet $|\pm 3/2\rangle$, which is non-magnetic. Thus no EPR signal can be observed for the trigonal U^{3+} centers in fluorite even if they do exist. The same is true for the Nd^{3+} ion.

The tetragonal center Tg1 compensated by F_i^- (1, 0, 0) has also been observed in SrF_2 (227, 262). This center shows superhyperfine structure and an ENDOR study (252) shows that the displacement d of U^{3+} toward F_i^- is only 0.05. A low symmetry center Rh1 similar to Rh1 in CaF_2 has also been observed (262), but the direction x is no longer directed toward the direction (2, 2, 1), but makes an angle of only $15^\circ \pm 0.5$ with the direction $[110]$.

Neither the $SrF_2:U^{3+}$ crystals compensated with F_i^- or M_S^+ have shown cubic U^{3+} centers. Instead, the crystals compensated with M_S^+ (where $M = Na$ or K) show (263, 264) two new tetragonal centers with the g -values Tg2, $g_{||} = 2.824$ and $g_{\perp} = 1.97$ and for center Tg3, $g_{||} = 1.72$ and $g_{\perp} = 2.49$. These g -values can be deduced in a very good approximation from a unique set of EPR cubic crystal field parameters of a Γ_8 quartet if it is assumed that the two tetragonal distortions are weak and leave as the lowest doublet for center Tg3, the cubic pair of wavefunctions $|\pm 1/2\rangle$ and for center T2, the pair $|\pm 3/2\rangle$. The resonance parameters of this virtual cubic center are $2P = -2.824$ and $2Q = 1.72$, from which a value of -0.4928 for the composition parameter x and a value of 0.9473 for K_J can be reduced. These values are in a normal connection with the existing EPR data on the rare-earth ions in cubic sites in alkaline-earth fluorides. They show that in going from CaF_2 to SrF_2 , the value of the composition parameter x and that of K_J increase. Due to the similarity of the center Tg2 with the center M_S^+ (2, 0, 0) in CaF_2 , it has been assumed that they have the same structure. As concerns the center Tg3, whose EPR lines are broader, it was attributed to a far-compensated substitutional U^{3+} ion slightly displaced towards one of the cube faces (263, 264).

In barium fluoride only the TfF_i^- (1, 0, 0)

center has been studied (242, 265, 266). An analysis of the hyperfine structure by RDS (266) shows that the U^{3+} ion is displaced by 0.20 Å toward the interstitial compensator.

In a strong trigonal field the situation can be completely different from that in the weak distortion case, and a Kramers doublet can be left as a ground state. This is the case of U^{3+} in lanthanum chloride (268-270) for which a trigonal spectrum with sharp lines without superhyperfine structure has been observed. The spin-lattice relaxation for this center (271, 272), and the interaction of U^{3+} pairs in $LaCl_3$ (273) have also been studied.

These EPR studies show that the ground state of the U^{3+} ion can be interpreted as arising from the splitting of the lowest level $J = 9/2$ of the ground configuration $5f^3$ in a weak crystal field. The wavefunctions for the Kramers doublet in axial crystal fields, calculated from the resonance data can be expressed in terms of the $|M_J\rangle$ components of the $J = 9/2$ level as follows:

(a) for Tg1 (F_i^- (1, 0, 0)) in CaF_2 , SrF_2 , and BaF_2 , $\alpha|\pm 9/2\rangle + \beta|\pm 7/2\rangle + \gamma|\pm 1/2\rangle$ with α^2 equal, respectively, to 0.48, 0.47, and 0.43; $\beta^2 \sim 0$ in all three cases and γ^2 equal to 0.52, 0.45, and 0.57 (223).

(b) for Tg2 (M_S^+ (2, 0, 0)) in CaF_2 (237) and SrF_2 (263, 264), $a|\pm 3/2\rangle + b|\pm 5/2\rangle$ with a^2 equal respectively to 0.1209 and 0.1126, and b^2 equal to 0.8791 and 0.8874.

(c) for U^{3+} in $LaCl_3$ (271), $0.9578|\pm 7/2\rangle + 0.2873|\pm 5/2\rangle$.

There is only one report on EPR of U^{3+} in non-halide crystals, that referring to the tetragonal orthophosphates $ScPO_4$ and $LuPO_4$ (267). In these crystals U^{3+} enters substitutionally. As can be seen from the g -value anisotropy, the differences in the crystal field parameters for the two crystals are fairly large.

The hyperfine structure of the isotope 233 of uranium has been studied in the case of the Tr center in $LaCl_3$ (268, 270) and that of ^{235}U for the Tr center in $LaCl_3$ (269, 270), the centers C (135, 230), Tg1, Tg2, and Rh2 in CaF_2 and for Tg1 in SrF_2 (271). From the hyperfine structure of the spectra in $LaCl_3$, the magnetic dipole and electric quadrupole moments have been estimated (268-270) as follows: for ^{233}U , $\mu = 0.51\mu_n$ and $Q = 3.4$ barn and for ^{235}U , $\mu = 0.33\mu_n$ and $Q = 4.0$ barn.

The values of the nuclear moments estimated from the measured hyperfine parameters are very sensitive to the details of calculation, especially to the values used for the parameters

$\langle r^{-3} \rangle$. The value of $50 \text{ \AA}^{-3}$ used for $\langle r^{-3} \rangle$ has been estimated from the spin-orbit coupling, and no correction was made for the core polarization and J mixing. By using more precise ENDOR data on the same system from an unpublished work of Lerner and Hutchison in a calculation which takes into account the intermediate coupling, the relativistic radial parameters $\langle r^{-3} \rangle$ given by equation 15 and equation 17 for the free-ion hyperfine parameter A , Lewis et al. (25) obtained a value of $0.45 \mu_n$ for the nuclear magnetic moment of ^{235}U . However, they could not find the source of the discrepancy between this value and that reported in (245, 246). The ratios A_i/g_i along the main symmetry axes i for a large variety of $(^{235}\text{U})^{2+}$ centers in CaF_2 , SrF_2 , and LaCl_3 show a good grouping around an average value of $41 \times 10^{-4} \text{ cm}^{-1}$ (274). This value was used in equation 57 in order to determine the free-ion hyperfine parameter A_J and re-estimate the nuclear moment for ^{235}U using equation 17 with the relativistic radial parameters (25) or an effective relativistic expression for the hyperfine parameter

$$A_J = (2\beta_e \mu_I / 4\pi I) \langle r^{-3} \rangle_{\text{eff}} \langle J \| N \| J \rangle. \quad (70)$$

This is similar to the non-relativistic expression (275) with $\langle r^{-3} \rangle$ replaced by $\langle r^{-3} \rangle_{\text{eff}}$. The operator N , whose reduced matrix elements enter in equation 70, is given in the square bracket of equation 19. The effective radial integral $\langle r^{-3} \rangle_{\text{eff}}$ used to re-estimate the magnetic moment μ_I for ^{235}U has been estimated using three methods: (a) with equation 19 and the D-S parameters (25), $\langle r^{-3} \rangle_{\text{eff}}$ was equal to 5.633 a.u.; (b) the degeneracy-weighted value using the $\langle r^{-3} \rangle_{\text{jj}}$, MDF parameters (26) is equal to 5.630 a.u.; (c) the value estimated from the spin-orbit parameter using relativistic corrections is equal to 5.53 a.u. These three values agree very well and converge towards a value of 5.6 a.u. With this value and with A_J/g_J equal to $41 \times 10^{-4} \text{ cm}^{-1}$ and using the intermediate coupling wavefunctions for the ground state of U^{3+} , a value of $-(0.46 \pm 0.03) \mu_n$ has been estimated for μ_I^{235} (274). This estimate does not take into account explicitly the core polarization effects. It must be noted that this neglect is partly compensated by the neglect of reduction of the hyperfine parameter in crystals as compared to the free-ion value. This new value of μ_I for ^{235}U is about 30-40% larger than the values previously reported; this difference is, obviously, a relativistic effect.

E. Divalent Uranium

No firm EPR data on divalent uranium have been reported. As shown before, the assignment of the trigonal EPR spectrum Tr3 in $\text{CaF}_2:\text{U}$ described in Section IV.C to U^{2+} (43, 44) has been contested (225) on arguments based on a chemical analysis and optical absorption measurements. Even disregarding these arguments, it is difficult to explain how such a symmetry for the center and the g-values can originate from a U^{2+} ion. The ground configuration of U^{2+} is not firmly established, but as shown before, the possible configurations give either $^5\text{I}_4$ or $^5\text{L}_6$ as the lowest level. In an eightfold cubic crystal field, the ground level of $^5\text{I}_4$ is a singlet Γ_1 . This has been confirmed, for instance, in the case of Pu^{4+} (276, 277) in eightfold cubic coordination, and for Np^{3+} in trichlorides, tribromides, and triiodides (278) or for centers of tetragonal or trigonal symmetry in CaF_2 (279). On the other hand Pm^{3+} ($4f^4$, $^5\text{I}_4$) in lanthanum ethyl sulfate gives an EPR spectrum with $g_{\parallel} = 0.432$ and $g_{\perp} \sim 0$ (279). Both these situations are not compatible with the Tr3 center in CaF_2 . The same difficulties appear if a ground level $^5\text{L}_6$ is considered, because the ground state in crystals is either a singlet or the nonmagnetic doublet Γ_3 . If this doublet is split by a second-order Zeeman effect, very large g-values are expected. Thus, a definitive answer regarding the nature of the Tr3 center in $\text{CaF}_2:\text{U}$ cannot be given, but it is difficult to explain its g-values on the basis of a U^{2+} ion. We think, however, that there is enough evidence to assume that the U^{2+} ion in the eightfold coordination of the fluorite lattice does not have a magnetic ground state, and the center Tr3 corresponds better to the tentative model U^{4+} (226).

F. EPR in Concentrated Uranium Compounds

EPR on the concentrated compounds have given inconsistent results. Many concentrated systems of a given valence for uranium show strong EPR signals at temperatures much higher than the corresponding ions in diluted systems. Many times the g-values are far from those expected from a crystal field model.

The only cases where unambiguous EPR results have been obtained are the concentrated U(V) halide compounds discussed in Section IV.B.

Many concentrated compounds of trivalent or tetravalent uranium show strong and very broad EPR signals at room temperature. In some instances the spectrum was observed only for powdered samples and not in highly stoichiometric bulk samples.

Thus UF_3 powder shows (280, 281) at room temperature strong signals characterized by $g_{\parallel} = 2.8-2.9$ and $g_{\perp} = 2.1-2.2$. Even if combinations of free-ion $|\text{M}_J\rangle$ wavefunctions can be found which can explain these g -values, it is difficult to understand an EPR signal at room temperature.

Uranium tetrafluoride powder has shown at room temperature an EPR signal with $g = 2.15$ (281). However, the stoichiometric bulk samples did not show any signal either at room or at liquid nitrogen temperature (282).

Uranium dioxide powder shows at room temperature a signal of g equal to 2.33 (283, 284), but this is not observed in the stoichiometric bulk samples (282). Other uranium oxides show at room temperature EPR signals with g -values equal to 4.04 in U_2O_5 (284), 5.42 in U_3O_8 (284), 2.31 in U_4O_9 (285). The large g -values for U_2O_5 and U_3O_8 have been attributed to U^{4+} in trigonal sites. Signals arose with g -values 2.41 in Li_2UO_4 (285), 2.18 in BaUO_4 (285), 2.10 in MgUO_3 (286), 2.10 in $\text{MgU}_3\text{O}_{8.9}$ (286), 2.04 in CaUO_3 (286), 2.61 in $\text{CaU}_6\text{O}_{12}$ (286), 2.14 in SrUO_3 (286), 2.31 in $\text{SrU}_4\text{O}_{12}$ (286), 2.08 in $\text{BaUO}_{3.5}$ (286) and 2.08 in $\text{Ba}_2\text{U}_3\text{O}_{12}$ (285). Because many MUO_4 ($\text{M} = \text{Mg}, \text{Ca}, \text{Sr}, \text{Ba}$) compounds are deficient in oxygen (287) and $\text{SrU}_4\text{O}_{12.8}$ contains pentavalent uranium (288), the EPR signals reported for many of these systems could be due to U^{5+} , but it is difficult to explain the g -values on a simple crystal field model.

Recent EPR studies between 4.2 and 300 K on uranium trichalcogenides US_3 and UTe_3 show two lines with almost isotropic g -values of about 4 and 2 (289). The first of these lines was attributed to Fe^{3+} impurities in a strong crystal field, and the second line was assigned either to U^{5+} or to a localized electron arising from a broken bond. This last line shows a g -shift with temperature which was explained as due to the interaction of the paramagnetic center with a host U^{4+} ion.

V. CONCLUSION

Electron paramagnetic resonance is a very useful tool in obtaining information on uranium ions (1-3, 290-293). As shown in this review, some of the peculiarities of the actinide $5f$ configurations have a great impact on the EPR parameters. The uranium ions form a family which encompasses the first three $5f^n$ configurations, i.e. those where the identity of the actinides is best represented. The resonance data show clearly that a boundary line separates the

U^{5+} ($5f^1$) ion in octahedral symmetry from the other ions of uranium as concerns the crystal field effects. Strong effects of the intermediate coupling and J mixing and intermediate coupling must be considered. All these uranium ions show covalency effects, manifested in orbital reduction factors and in the superhyperfine structure of the spectra. Details of the crystal field interaction could be determined, as for instance the ratio $A_4 \langle r^4 \rangle / A_6 \langle r^6 \rangle$ for trivalent uranium in cubic symmetry and the reduction of the free-ion g_J -value in crystals. The valence state of the uranium ions could be in most cases unambiguously determined, except for peculiar situations such as the concentrated systems. Very useful information about the symmetry and structure of the uranium centers in diluted systems have been obtained. The hyperfine structure studies have been effective in determination of the nuclear spin, nuclear magnetic dipole moment and nuclear electric quadrupole moments. The need for using the relativistic radial parameters in these estimations is now evident.

Still more information can be obtained if these studies are extended to encompass systematically a whole family of crystals. Thus, the studies on a given crystal, for instance calcium fluoride, should be extended to the whole family of eightfold cubic fluorides in order to find a closer correlation between the resonance parameters and the structural details of the system. More advanced techniques such as ENDOR or RDS should be employed in order to study finer effects such as the pseudonuclear g -value or pseudoquadrupole effects. A closer correlation of the data obtained by EPR and other methods is also necessary.

Very useful information could be obtained from a study of isoelectronic actinide ions $\text{Pa}^{(n-1)+} - \text{U}^{n+} - \text{Np}^{(n+1)+} - \text{Pu}^{(n+2)+}$ or of the isovalent $\text{Pa}^{n+} - \text{U}^{n+} - \text{Np}^{n+} - \text{Pu}^{n+}$ ions in the same lattice.

Note Added in Proof. A recent observation of the ^{235}U NMR signal in UF_6 (294) leads to a nuclear magnetic moment of ^{235}U of $-0.35999\mu_n$. The discrepancy between this value and that determined from EPR of U^{3+} using a relativistic radial parameter could be accounted for only if large core polarization effects (of the order of 25%) in the hyperfine structure of $^{235}\text{U}^{3+}$ are supposed.

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Electron Paramagnetic Resonance data on U^{5+}

C denotes cubic, Tg tetragonal, Tr trigonal and Rh rhombic and centers at lower symmetry

Host	Center	T	g	Hyperfine structure ($^{235}U, I = 7/2$) (10^{-4} cm^{-1})	Superhyperfine structure (10^{-4} cm^{-1})	Ref.	Comments
LiF	C	77	0.333 ± 0.001		No	[146]	
LiF	Tg1	77	$g_{ } = 0.253 \pm 0.001$ $g_{\perp} = 0.4716 \pm 0.0005$	$A_{ } = 45 \pm 1$ $A_{\perp} = 45.5 \pm 0.5$ $P = 50.5 \pm 0.5$	$n_L = 1, I_L = 1/2$ $A_{ }^L = 14.3 \pm 0.2$ $A_{\perp}^L = 7.5 \pm 0.2$	[154], [156]	
LiF	Tg2	77	$g_{ } < 0.1$ $g_{\perp} = 0.587 \pm 0.001$		$n = 2, I = 1/2$ $A_{\perp}^L \sim 5.5$	[146]	
LiF	Tg3	77	$g_{ } = 0.13 \pm 0.05$ $g_{\perp} = 0.59 \pm 0.001$		No	[146]	
LiF	Tg4	77	$g_{ } = 0.326 \pm 0.01$ $g_{\perp} = 0.362 \pm 0.01$		No	[146]	
LiF	Rh1	77	$g_X = 0.517 \pm 0.001$ $g_Y = 0.387 \pm 0.001$ $g_Z = 0.20 \pm 0.05$		$n_L = 1, I_L = 1/2$	[146]	X [100], Y and Z in plane (110) at $\delta = 10.8^\circ$ from (110) and (001)

Appendix I. (2)

Host	Center	T	g	Hyperfine structure (^{235}U , $I = 7/2$) (10^{-4} cm^{-1})	Superhyperfine structure (10^{-4} cm^{-1})	Ref.	Comments
LiF	Rh2	77	$g_X = 0.562 \pm 0.001$ $g_Y = 0.563 \pm 0.001$ $g_Z = 0.337 \pm 0.005$		$n_L = 1$, $I_L = 1/2$	[146]	$Y \parallel 001 $, X and Z in plane (001) at $\delta = 5.7^\circ$ from $ 110 $ and $ 110 $
LiF	Rh3	77	$g_X = 1.110 \pm 0.001$ $g_Y = 0.537 \pm 0.001$ $g_Z = 0.20 \pm 0.05$		$n_L = 1$, $I_L = 1/2$	[146]	Transformation matrix from $ 110 $, $ 001 $, $ 110 $ to XYZ: $\mathcal{L} = \begin{vmatrix} 0.973 & 0.075 & 0.217 \\ 0.177 & 0.846 & 0.503 \\ -0.146 & -0.528 & -0.837 \end{vmatrix}$
LiF	Rh4	77	$g_X = 0.937 \pm 0.001$ $g_Y = 0.15 \pm 0.05$ $g_Z = 0.543 \pm 0.001$		$n_L = 2$, $I_L = 1/2$ $A_Z^L \sim 4.8$	[146]	Z $\parallel$ $ 001 $, X and Y in plane (110) at $\delta = 7.8^\circ$ from $ 110 $ and $ 010 $
LiF	Rh5	77	$g_X = 0.360 \pm 0.001$ $g_Y = 0.328 \pm 0.001$ $g_Z = 0.343 \pm 0.001$		No	[146]	X $\parallel$ $ 110 $, Y $\parallel$ $ 110 $, Z $\parallel$ $ 001 $
NaF	Tg1	77	$g_{\parallel} = 0.3935 \pm 0.0005$ $g_{\perp} = 0.5912 \pm 0.0005$	$A_{\parallel} = 46.0 \pm 0.2$ $A_{\perp} = 56.5 \pm 0.2$ P = 75.0 ± 0.5	$n_L = 1$, $I_L = 1/2$ $A_{\parallel}^L = 9.8$ $A_{\perp}^L = 4.5$	[155], [156] [157]	

Appendix I. (3)

Host	Center	T	g	Hyperfine structure (^{235}U , $I = 7/2$) (10^{-4} cm^{-1})	Superhyperfine structure (10^{-4} cm^{-1})	Ref.	Comments
NaF	Tg2	77	$g_{\parallel} = 0.109 \pm 0.001$ $g_{\perp} = 0.6813 \pm 0.0005$	$A_{\parallel} = 34 \pm 1$ $A_{\perp} = 58 \pm 0.5$ $P = 93 \pm 0.5$	$n_L = 2$, $I_L = 1/2$ $A_L = 3.2$	[155], [156]	
NaF	Tg3	77	$g_{\parallel} = 0.16 \pm 0.01$ $g_{\perp} = 0.677 \pm 0.001$		$n_L = 1$, $I_L = 1/2$ $A_L = 3.1$	[160]	
NaF	Rh1	77	$g_X = 0.5894 \pm 0.0001$ $g_Y = 0.5940 \pm 0.0001$ $g_Z = 0.5442 \pm 0.0001$		No	[157]	X $\parallel$ 110 , Y $\parallel$ 110 , Z $\parallel$ 001
NaF	Rh2	77	$g_X = 0.794 \pm 0.001$ $g_Y = 0.581 \pm 0.001$ $g_Z = 0.332 \pm 0.01$		$n_L = 1$, $I_L = 1/2$ $A_L = 4.6$ $A_X = 4.7$ $A_Y = 9.5$ $A_Z = 9.5$	[160]	Y $\parallel$ 001 , X and Z in plane (001) at $\delta = 15.5^\circ$ from 100 and 010
NaF	Rh3	77	$g_X = 0.766 \pm 0.001$ $g_Y = 0.659 \pm 0.001$ $g_Z = 0.15 \pm 0.01$		$n_L = 1$, $I_L = 1/2$ $A_X = 3.2$ $A_Y = 3.8$	[160]	Y $\parallel$ 001 , X and Z in plane (001) at $\delta = 1.8^\circ$ from 100 and 010

Host	Center	T	g	Hyperfine structure (^{235}U , $I = 7/2$) (10^{-4} cm^{-1})	Superhyperfine structure (10^{-4} cm^{-1})	Ref.	Comments
KF	Tgl	77	$g_{\parallel} = 0.169 \pm 0.001$ $g_{\perp} = 0.7258 \pm 0.0005$	$A_{\parallel} = 36 \pm 1$ $A_{\perp} = 59 \pm 0.5$ $P = 110.5 \pm 0.5$	$n_L = 2$, $I_L = 1/2$ $A_L^I = 2.7$	[158], [198]	
CaF_2	Tr	77	$g_{\parallel} = 0.190 \pm 0.005$ $g_{\perp} = 1.047 \pm 0.001$	$A_{\parallel} = 24.0 \pm 1$ $A_{\perp} = 66.0 \pm 0.5$ $P = 107.0 \pm 0.5$	No	[168], [170] [171], [199]	
CaF_2	Rh1	77	$g_X = 1.388 \pm 0.001$ $g_Y = 0.820 \pm 0.001$ $g_Z = 0.22 \pm 0.05$		$n_L = 1$, $I_L = 1/2$ $A_L^I = 9.2$ at 40° from 001	[168], [172]	X along $ 110\rangle$, Z and Y in plane (110) at $\delta = 0.7^\circ$ from $ 111\rangle$ and $ 112\rangle$
CaF_2	Rh2	77	$g_X = 0.880 \pm 0.001$ $g_Y = 1.614 \pm 0.001$ $g_Z = 0.17 \pm 0.05$		$n_L = 2$, $I_L = 1/2$	[168], [172]	X along $ 110\rangle$, Z and Y in plane (110) at $\delta \sim 4^\circ$ from $ 111\rangle$ and $ 112\rangle$
CaF_2	Rh3	77	$g_X = 1.019 \pm 0.001$ $g_Y = 1.054 \pm 0.001$ $g_Z = 0.20 \pm 0.05$		No	[167], [169]	Transformation matrix from $ 111\rangle$, $ 110\rangle$, $ 112\rangle$ to XYZ: $\begin{vmatrix} 0.9984 & -0.0553 & 0.005 \\ 0.0552 & 0.9983 & 0.005 \\ -0.005 & -0.012 & 0.9999 \end{vmatrix}$
CaF_2	Rh4	77	$g_X = 0.540 \pm 0.001$ $g_Y = 2.775 \pm 0.001$ $g_Z = 0.471 \pm 0.001$		No	[191], [195]	Z $\parallel$ $ 110\rangle$, X and Y in plane (110) at $\delta = 1.8^\circ$ from $ 001\rangle$ and $ 110\rangle$

Appendix II. (1)

Electron Paramagnetic Resonance data on $U^{4+}(5f^2)$

Host	Center	T	g^{app}	Hyperfine structure $A^{app} (10^{-4} \text{ cm}^{-1})$	Ref.	Comments
ThO ₂ Powder		290	~ 2.7		[192]	a)
CaF ₂	C	1.4	~ 2		[204]	a)
CaF ₂	Tr1	1.4; 4.2	$g_{ } = 4.02 \pm 0.01$ $g_{\perp} \leq 0.1$		[204]	Superhyperfine structure with eight fluorine ligands
		4.2	$g_{ } = 4.03 \pm 0.01$ $g_{\perp} \leq 0.1$	$A_{ } = 107 \pm 0.5$	[218]	
CaF ₂	Tr2	1.4	$g_{ } = 5.66 \pm 0.02$ $g_{\perp} \leq 0.1$		[204]	Superhyperfine structure with six fluorine ligands
		4.2	$g_{ } = 5.60 \pm 0.02$ $g_{\perp} \leq 0.1$	$A_{ } = 234.5 \pm 1$	[218]	
CaF ₂	Tr3	4.2	$g_{ } = 3.238 \pm 0.005$ $g_{\perp} = 0.00 \pm 0.15$		[219], [220]	Superhyperfine structure with 24 fluorine ligands
			$g_{ } = 3.27 \pm 0.05$ $g_{\perp} = 0.0 \pm 0.2$		[221], [222]	
SrF ₂	Tr	4.2	$g_{ } = 2.85 \pm 0.005$ $g_{\perp} = 0.0 \pm 0.15$		[219 - 222]	a)
BaF ₂	Tr	4.2	$g_{ } \sim 3$ $g_{\perp} \sim 0$		[219], [220]	a)

a) Nature of the center not firmly established.

Electron Paramagnetic Resonance data on $U^{3+} (5f^3)$

Host	Center	T	g	Hyperfine structure (10^{-4} cm^{-1})	Ref.	Comments
CaF ₂	C	4.2	2P = -2.740 ± 0.005 2Q = 1.793 ± 0.005	106.1 ± 1 82.8 ± 1	[135], [229] [230]	Superhyperfine structure
CaF ₂	Tg1	20	$g_{ } = 3.501 \pm 0.008$ $g_{\perp} = 1.866 \pm 0.002$		[227]	Superhyperfine structure
		4	$g_{ } = 3.528 \pm 0.005$ $g_{\perp} = 1.875 \pm 0.005$		[219]	
		4	$g_{ } = 3.531 \pm 0.004$ $g_{\perp} = 1.878 \pm 0.001$		[240]	
		4.2	$g_{ } = 3.533 \pm 0.002$ $g_{\perp} = 1.876 \pm 0.002$	$A_{ } = 164.1 \pm 0.5$ $A_{\perp} = 64.8 \pm 0.5$	[274]	
CaF ₂	Tg2(Na)	4.2	$g_{ } = 2.740 \pm 0.003$ $g_{\perp} = 2.029 \pm 0.005$	$A_{ } = 106 \pm 0.5$ $A_{\perp} = 92.5 \pm 1$	[237], [239], [274]	Co-doped with Na; Superhyperfine structure
CaF ₂	Tg2(Li)	4.2	$g_{ } = 2.746 \pm 0.005$ $g_{\perp} = 2.022 \pm 0.005$		[239]	Co-doped with Li
CaF ₂	Tg2(K)	4.2	$g_{ } = 2.747 \pm 0.005$ $g_{\perp} = 2.013 \pm 0.005$		[239]	Co-doped with K
CaF ₂	Tg2(Ag)	4.2	$g_{ } = 2.742 \pm 0.005$ $g_{\perp} = 2.017 \pm 0.005$		[239]	Co-doped with Ag

Host	Center	T	g	Hyperfine structure (10^{-4} cm^{-1})	Ref.	Comments
CaF_2	Rh1	20	$g_x = 1.38 \pm 0.001$ $g_y = 2.85 \pm 0.02$ $g_z = 2.94 \pm 0.01$		[259]	Z $ 110\rangle$, X $ 221\rangle$
		4.2	$g_x = 1.378 \pm 0.010$ $g_y = 2.838 \pm 0.008$ $g_z = 2.927 \pm 0.008$		[261]	
CaF_2	Rh2(Na)	4.2	$g_x = 2.308 \pm 0.002$ $g_y = 2.126 \pm 0.005$ $g_z = 1.090 \pm 0.005$	$A_x = 103 \pm 1$ $A_y = 82.6 \pm 1$ $A_z = 43.6 \pm 1$	[241], [274]	x $ 001\rangle$, y $ 110\rangle$, z $ 110\rangle$ Co-doped with Na
CaF_2	Rh2(Li)	4.2	$g_x = 2.438 \pm 0.005$ $g_y = 2.210 \pm 0.005$ $g_z = 2.119 \pm 0.005$		[239]	Co-doped with Li
CaF_2	Rh2(K)	4.2	$g_x = 2.298 \pm 0.005$ $g_y = 2.112 \pm 0.005$ $g_z = 1.147 \pm 0.005$		[239]	Co-doped with K
CaF_2	Rh2(Ag)	4.2	$g_x = 2.137 \pm 0.005$ $g_y = 2.359 \pm 0.005$ $g_z = 1.850 \pm 0.005$		[239]	Co-doped with Ag
SrF_2	Tg1	20	$g_{ } = 3.433 \pm 0.008$ $g_{\perp} = 1.971 \pm 0.002$		[227]	
		4.2	$g_{ } = 3.489 \pm 0.0005$ $g_{\perp} = 1.9831 \pm 0.0005$		[262]	
		4.2	$g_{ } = 3.4882 \pm 0.0008$ $g_{\perp} = 1.9830 \pm 0.0008$	$A_{ } = 158.3$	[274]	

Host	Center	T	g	Hyperfine structure (10^{-4} cm^{-1})	Ref.	Comments
SrF_2	Tg2	4.2	$g_{\parallel} = 2.824 \pm 0.005$ $g_{\perp} = 1.97 \pm 0.01$	$A_{\parallel} = 111.09$	[263], [264] [274]	Co-doped with Na or K
SrF_2	Tg3	4.2	$g_{\parallel} = 1.72 \pm 0.01$ $g_{\perp} = 2.49 \pm 0.01$		[263], [264]	Co-doped with Na or K
SrF_2	Rh1	4.2	$g_x = 1.3276 \pm 0.0005$ $g_y = 2.88 \pm 0.01$ $g_z = 3.183 \pm 0.002$		[262]	$z \parallel [110]$, x in plane (110) at (15+0.5) $^\circ$ from (110)
BaF_2	Tg1	10-20	$g_{\parallel} = 3.337 \pm 0.002$ $g_{\perp} = 2.115 \pm 0.001$		[265]	
		4.2	$g_{\parallel} = 3.233 \pm 0.008$ $g_{\perp} = 2.108 \pm 0.002$		[242]	
LaCl_3	Tr	4.2; 20	$g_{\parallel} = 4.153 \pm 0.005$ $g_{\perp} = 1.520 \pm 0.002$	$A_{\parallel}^{235} = 176 \pm 1$ $A_{\perp}^{235} = 58.5 \pm 0.5$ $P^{235} = 5.5 \pm 0.5$	[268], [269]	
			$g_{\parallel} = 4.149$ $g_{\perp} = 1.520$	$A_{\parallel}^{233} = 378.6 \pm 1.2$ $A_{\perp}^{233} = 123.6 \pm 1.0$ $P^{233} = 9.9$		
ScPO_4	Tg	4.2	$g_{\parallel} = 1.370$ $g_{\perp} = 1.736$		[267]	
LuPO_4	Tg	4.2	$g_{\parallel} = 3.13$ $g_{\perp} = 0.9$		[267]	

Electron Paramagnetic Resonance Data on Concentrated Uranium Compounds

Host	T	g	Ref.	Comments
ThO ₂ powder	77	1.25	[192]	
UF ₆ Li	77	$g_{ } = 0.801$ $g_{\perp} = 0.753$	[88], [176] [177]	U ⁵⁺ Trigonal Center
UF ₆ Na	77	$g_{ } = 0.817$ $g_{\perp} = 0.708$	[88], [176] [177]	U ⁵⁺ Trigonal Center
UF ₆ Cs	77	$g_{ } = 0.928$ $g_{\perp} = 0.681$	[88], [176] [177]	U ⁵⁺ Trigonal Center
UCl ₆ Rb powder	R.T.	~ 1.1	[178]	
UCl ₅	77	1.1882	[179]	Linewidth 734 G
UCl ₅ · SOCl ₂	R.T.	1.097	[178]	
UCl ₅ · PCl ₅	R.T.	1.11	[178]	
(n - C ₃ H ₇) ₄ NUCl ₆	R.T.	~ 1.1	[178]	
UCl ₅ · TCAC	R.T.	1.095	[178]	
NOUF ₆	77	0.748	[177]	
UOF ₅ ²⁻ complexes	R.T.	0.58	[180]	Linewidth 8000G
UCl ₆ ⁻ complexes	R.T.	1.12	[180]	Linewidth 1200G

Host	T	g	Ref.	Comments
UOCl_5^{2-} complexes	R. T.	1.09	[180]	Linewidth 1400G
UBr_6^- complexes	R. T.	1.21	[180]	Linewidth 850
$\text{UOB}_{\text{M}_5}^{2-}$ complexes	R. T.	1.24	[180]	Linewidth 1600G
Na_3UF_8	7	1.2	[184]	
LiNbO_3	R. T. 77	0.727	[184]	
LiTaO_3	R. T. 77	$g_{\parallel} = 0.773$ $g_{\perp} = 0.658$	[184]	
BiNbO_3	7	~ 0.7	[184]	
LiUO_3	R. T. 77	2.49 2.57	[185]	Linewidth 1658G at R. T. and 1660G at 77K
NaUO_3	R. T. 77	3.49 4	[185]	Linewidth 1296G at R. T. and 1726G at 77K
KUO_3	R. T. 77	2.42 2.61	[185]	Linewidth 1571 at R. T. and 1604G at 77K
RbUO_3	R. T. 77	2.43 2.48	[185]	Linewidth 1641 at R. T. and 1654G at 77K
US_3	R. T. 4.2	2; 4	[289]	
UTe_3	R. T. 4.2	2; 4	[289]	

Host	T	g	Ref.	Comments
UF ₃	R.T.	g = 2.8 - 2.9 g = 2.1 - 2.2	[280] [281]	Powder sample
UF ₄	R.T.	2.15	[281]	Powder sample
UC ₂	R.T.	2.33	[283, 284]	Powder sample

**CALENDER OF FORTHCOMING
CONFERENCES IN MAGNETIC
RESONANCE**

February 17-20, 1985 **FIFTH NATIONAL NMR CONFERENCE** will be held in Sydney, Australia. The conference will deal with all aspects of NMR spectroscopy and will include sessions on multiple quantum NMR spectroscopy, NMR imaging, NMR of solids and liquid crystals, biological applications of NMR spectroscopy and new methods in NMR spectroscopy. There will be invited and contributed papers as well as specialized discussion sessions and poster sessions. Further information may be obtained from the conference secretary:

Dr. R. S. Norton
School of
Biochemistry
University of New South
Wales
P.O. Box 1
Kensington 2033
N.S.W. Australia

March 22-26, 1985 **THIRD ANNUAL MEETING of the SOCIETY for MAGNETIC IMAGING** will be held at the Town and Country Hotel, San Diego, California. Organizing Committee:

Dr. Brian C. Lentle
Coordinator, Organizing
Dr. Gary Fullerton
Chairman
Scientific Program
Dr. John Gore
Chairman
Education Program
Dr. Ronald Ross
Chairman
Public Relations

Contributions are

invited for these sessions and for any other topic related to the development of magnetic resonance imaging and its application. *The deadline for submission of abstracts is December 4, 1984.* For more information, please call or write:

Ronald J. Ross, MD
Chairman
Public Relations
Committee
Society for Magnetic
Resonance
Imaging Annual Meeting
Radiologic Medical
Imaging Associates
Fox Run
Gates Mills, OH 44040
(216) 461 5144

July 14-19, 1985 **27th ROCKY MOUNTAIN CONFERENCE** will be held in Denver, Colorado and will include symposia on EPR and NMR. Contact

Jan Gurnsey
5531 Bitterbush Way
Loveland Colorado
80537

November 15-18, 1985 **FIRST BEIJING CONFERENCE and EXHIBITION on INSTRUMENTAL ANALYSIS**, will be held in Beijing, China. The exhibition will be held November 16-25, 1985. The conference and exhibition sponsored by five Chinese academic societies including Spectroscopy at Radio and Microwave Frequencies will hold symposia on NMR, EPR, NQR, Double Resonance, and Multiple Quantum Resonance as well as other aspects of instrumentation. Abstracts should be submitted by

March 31, 1985. For further information please contact:

Secretariat of First
Beijing Conference and
Exhibition on
Instrumental Analysis
Room 912

Xi Yuan Hotel
Beijing, China
Tel. 890721 Ext. 912

The editor would be pleased to receive notices of future meetings in the field of magnetic resonance so that they could be recorded in this column.

PAPERS TO APPEAR IN SUBSEQUENT ISSUES

Application of Lanthanide Shift Reagents in NMR-Spectroscopy for Studying Organophosphorus Compounds, B. I. Ionin, V. I. Zakharov, and G. A. Berkova, Leningrad Lensoviet Institute of Technology, Leningrad, USSR.

Stochastic NMR Spectroscopy, B. Blümich, Universität Bayreuth, Bayreuth, West Germany.

2-Dimensional NMR Spectroscopy of Proteins, J. Markley, Purdue University, West Lafayette, Indiana, U.S.A.

Electron Spin Echo Method as Used to Analyze Spatial Distribution of Paramagnetic Centers, A. M. Raitsimring and K. M. Salikhov, Institute of Chemical Kinetics and Combustion, USSR.

Analysis of Chain Microstructure by ^1H and ^{13}C NMR Spectroscopy, Yu. E. Shapiro, Yaroslavl Polytechnic Institute, USSR.

In Vivo Applications of ^{19}F NMR Spectroscopy and Imaging, Alice M. Wyrwicz, University of Illinois, Chicago, Illinois, USA.

Felix Bloch Memorial Lectures, Contributions from V. S. Murty (Indian Institute of Technology), Yuanzhi Xu (Zhejiang University, China), P. Sohar (Budapest, Hungary), I. P. Gerothanassis (University de Lausanne, Switzerland), C. L. Khetrpal and G. Govil for the Ninth International Conference on Magnetic Resonance (India), R. Basosi (Istituto di Chimica Generale, Italy), I. Ursu (Bucharest, Romania), and A. Saika (Kyoto University, Japan).