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Standardless Analysis of Multicomponent Mixtures of Substances by Time-Resolved Vibronic Spectroscopy

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Abstract—A new approach to the quantitative and qualitative standardless analysis of complex substances based on experimental time-dependent vibronic luminescence spectra (in the UV and visible regions) is proposed. The approach requires no preliminary calculation of absolute intensities for molecular models. It is shown that this analysis can be carried out for both individual substances and multicomponent mixtures, including unknown substances and mixtures of unknown composition. The concentration ranges of mixture components available for the analysis are evaluated, depending on the optical properties of mixtures.

Problems of the environmental monitoring of various media at a molecular level and tasks arising in the laboratory practice necessitate the development of experimental and theoretical methods for the quantitative analysis of chemical substances possessing a reasonable accuracy and predictive ability. The quantitative analysis methods employed for analytical purposes use, as a rule, various reference samples (standards). This fact considerably narrows the range of solvable tasks because of the problem of obtaining standard reference samples, which is complicated by the huge and ever-increasing number of known chemical compounds. Moreover, increasingly wider problems of the recognition and quantitative determination of unknown substances in mixtures of unknown composition have been emerging in recent years because of intricate, frequently unknown chemical transformations of toxic compounds in various media like air, soil, water, etc. In this connection, the development of quantitative analytical methods requiring no material standards (standard reference samples), that is, standardless methods becomes especially urgent. The possibility of the qualitative analysis of individual substances and their mixtures from the same experiment is also an essential requirement. The use of optical molecular spectrochemical analysis seems to be most promising for these purposes.

The breakthrough ideas in this field have been advanced recently [1], when it has been proposed to use computational methods of the theory of IR spectra that give estimations of the absolute absorption probabilities for solving purely analytical problems. Because the measured signal depends on the product of the concentration and the absolute intensity, the problems of quantitative analysis can be solved in this way. It has been not only demonstrated that such a standardless method is feasible, but also that its efficiency is rather high [2–4].

A similar approach has been developed for constructing methods of quantitative standardless analysis based on vibronic spectra in the UV and visible regions [5]. It has been shown that this analysis can be carried out using integral absolute intensities of the entire wide spectral band (structureless spectra) as well as several bands and individual lines of the vibrational structure (fine-structure spectra). Thus, substances with close spectral characteristics and their mixtures can be analyzed using this approach. The estimated expected errors in the concentration determined using this approach make up ≤ 30 rel % at very small amounts of a substance required for the analysis (≤ 1 mg) and low molecular concentrations of impurity substances to be analyzed ($\leq 10^{-4}\%$). Calculated spectral curves, especially in terms of integral absorbances [6], can also be used for quantitative analysis, which provides certain prerequisites not only for qualitative but also for quantitative analysis.

A drawback of this approach is that luminescence spectra cannot be used in this case. These spectra are very sensitive, and the desired signal can be enhanced by several orders of magnitude through increasing the illumination intensity. However, the measurement of absolute luminescence intensities involves severe difficulties. The second important drawback is in the necessity of invoking computational methods for determining absolute intensities, which significantly restricts the use of standardless methods for the diagnosis of unknown chemical compounds.

The experience accumulated in standardless analysis relates to conventional optical spectroscopy. The state of the art in the development of experimental spectral technique is characterized by the emergence of time-resolved methods of measuring vibronic spectra of complex molecules. Along with conventional methods of vibronic spectroscopy that produce highly infor-

mative fine-structure spectra with a line width of down to 1 cm^{-1}, these methods are intensively developed. This significantly extends the analytical potentialities of vibronic spectroscopy, because the time dependence of emission line intensities can be used for analysis in addition to the positions of absorption and emission bands, the contour shape, and its fine structure. Thus, the situation is changed qualitatively, because the experimental transition probabilities can be determined now directly from the spectra by measuring relaxation processes.

Hence, standardless quantitative analysis can be carried out based on experimental spectral data alone with the use of not only absorption spectra but also emission spectra. With the corresponding development of molecular simulation methods using specialized data banks, the quantitative and qualitative analysis of a substance can be carried out simultaneously based on a time-resolved spectral experiment of the same kind. Methods developed for modeling conventional absorption and fluorescence spectra of polyatomic molecules [7] can serve as a basis for such an approach.

This work is devoted to discussing the principal possibility of the standardless qualitative and quantitative analysis of mixtures of complex substances by time-resolved vibronic spectroscopy in the UV and visible regions.

STANDARDLESS ANALYSIS BASED ON TIME-RESOLVED VIBRONIC SPECTRA

The main idea of the approach proposed is outlined below. Let the test substance is excited by an optical radiation pulse of intensity I_0 with a relatively short duration τ, so that molecules do not luminesce during this time. After the completion of optical excitation ($t \geq 0$), the emission spectrum of substance molecules $I(\omega, t)$ is measured over sufficiently large frequency and time intervals. The luminescence intensity $I(\omega, t)$ depends on transition probabilities w_{ij} and the initial (at $t = 0$) population of levels n_0, which, in its turn, depends on the molecule concentration c, the pulse intensity I_0 (and duration τ) of the exciting radiation, and also on the transition probabilities. Therefore, both these probabilities w_{ij} (and transition frequencies ω_{ij}) and the desired concentration of molecules c can be determined by measuring the relative luminescence intensity $I(\omega, t)/I_0$ and, then, solving the inverse spectral problem.

The time dependence of the luminescence spectrum plays a very significant role in this method. It is directly determined by transition probabilities even for spectra in terms of relative intensities; therefore, their absolute values and, hence, the absolute value of concentration c can be found without calculating absolute intensities in advance, as well as in standardless methods proposed previously [1–5].

Consider this in more detail. The intensity of spontaneous emission in the $i \longrightarrow k$ transition equals

$$I_{ik}^{\text{em}}(\omega_{ik}, t) = \hbar \omega_{ik} w_{ik} n_i(t), \qquad (1)$$

where the time dependence of the population of the ith level $n_i(t)$ is determined by the initial population of levels due to light absorption $n_j(0) = n_{0j}$ and by transition probabilities. It can be found by solving the system of kinetic equations for populations [8] $n_i(t) = \sum_j [\Phi(t)]_{ij} n_{0j}$. Matrix elements $[\Phi(t)]$ in the general case take the form of sums of exponentials $\exp(-w_p t)$, where $w_p = \sum_{q < p} w_{pq}$ are the total probabilities of transitions from the pth state to all the underlying states. Preexponential factors are determined by probabilities w_{pq} and additionally in case of $w_{p'q'} = w_{pq}(p', q' \neq p, q)$ contain factors polynomial in t.

The initial population n_{0j} after absorption depends on the concentration of molecules c, their thermal distribution over levels N_l before absorption (Boltzmann distribution), absorption probabilities w_{lj}^{abs}, and exciting light intensities $I_0(\omega_{lj}, t)$ (pulse spectral composition and time dependence). It can be expressed by the equation

$$n_{0j} = \frac{1}{c^*} c \sum_l w_{lj}^{\text{abs}} N_l \int_0^\tau I_0(\omega_{lj}, t) dt, \qquad (2)$$

where c^* is the light velocity. We assume that the pulse duration is much shorter than the lifetime of excited states; therefore, the fluorescence during excitation can be neglected. Without the loss of generality, we may consider that the exciting light pulse is rectangular in shape $\int_0^\tau I_0(\omega_{lj}, t) dt = I_0(\omega_{lj}) \tau$ with a narrow spectral composition corresponding to the resonance excitation of molecules to the nth state with the frequency ω_{0n} ($I_0(\omega_{0j}) = I_0 \delta(\omega_{0j} - \omega_{0n})$) and that the temperature is sufficiently low ($T \approx 0$ K, which, for example, is typical for an experiment in a supersonic jet). Therefore, all molecules are in the ground (zero) state before light absorption, $N_l = \delta_{l0}$ (δ_{l0} is Kronecker delta symbol). Then, additionally taking into account the relationship between the emission and absorption probabilities ($w_{ik} = \frac{h}{\pi^2 c^{*3}} \omega_{ik}^3 w_{ki}^{\text{abs}}$), we transform Eq. (1) to the form

$$\frac{I_{ik}^{\text{em}}(\omega_{ik}, t)}{I_0} = \frac{\pi c^{*2}}{2} \tau c \omega_{ik} \omega_{0n}^{-3} w_{ik} w_{n0} [\Phi(t)]_{in}. \qquad (3)$$

The relative intensities of the observed luminescence spectrum $I^{\text{em}}(\omega, t)/I_0$ explicitly depend on the concentration of molecules c, which opens up possibil-

ities for its determination from such a spectrum. The structure of Eq. (3) allows one to solve the problem of quantitative and qualitative spectrochemical analysis in two stages, which considerably simplify setting up the experiment. Actually, one can measure the relative intensities (and transition frequencies) of lines of the time-dependent emission spectrum (Fig. 1a) $I_{ik}^{em}(\omega_{ik}, t) \sim \omega_{ik} w_{ik}[\Phi(t)]_{in}$ and to determine the frequencies and probabilities of vibronic transitions from these experimental data. Methods for solving such problems for time-independent vibrational and vibronic spectra (Figs. 1b, 1c) have been developed [6, 7] and can easily be generalized to the case of time-resolved spectra. The "experimental" values of transition frequencies and probabilities obtained in this way allow problems of the qualitative analysis of a substance to be posed and solved using the molecular simulation methods developed previously [7, 9] and also to refine the parameters of molecular models in ground and excited states (geometry, force constants, etc.).

In order to determine the concentration of molecules c and, hence, to carry out quantitative standardless analysis, it is now sufficient to measure the relative intensity $I^{em}(\omega_{ik}, t)/I_0$ Eq. (3) not in all (or many) spectral and time intervals, but only for one frequency ω_{ik}^* and instant of time t^* (Fig. 1d).

Thus, the approach proposed allows the qualitative and quantitative analysis of a substance without using standard reference samples and measuring the absolute integral absorption and luminescence intensities, which is difficult to accomplish.

The general idea of the approach is most readily illustrated using a three-level diagram as an example (Fig. 2). On initial excitation to state 3, the emission spectrum contains three lines corresponding to transitions $3 \longrightarrow 1$, $3 \longrightarrow 2$, and $2 \longrightarrow 1$ (Fig. 2b). Their intensities as functions of time differ in their behavior. In particular, the time dependence of the intensity for transition $2 \longrightarrow 1$ exhibits a two-exponential character (Figs. 2c–2e)

$$\frac{I_{31}^{em}(\omega_{31}, t)}{I_0} = \frac{\pi c^{*2}}{2} \tau c \omega_{31}^{-2} w_{31}^2 e^{-w_3 t}, \qquad (4)$$

$$\frac{I_{32}^{em}(\omega_{32}, t)}{I_0} = \frac{\pi c^{*2}}{2} \tau c \omega_{31}^{-3} \omega_{32} w_{31} w_{32} e^{-w_3 t}, \qquad (5)$$

$$\frac{I_{21}^{em}(\omega_{21}, t)}{I_0}$$
$$= \frac{\pi c^{*2}}{2} \tau c \omega_{31}^{-3} \omega_{21} \frac{w_{31} w_{21} w_{32}}{w_3 - w_2} (e^{-w_2 t} - e^{-w_3 t}), \qquad (6)$$

$$w_3 = w_{32} + w_{31}, \quad w_2 = w_{21}. \qquad (7)$$

The relative intensities of spectral lines at a given t_0 give a system of equations for determining the relative transition probabilities, for example, $\dfrac{w_{32}}{w_{31}} = \dfrac{\omega_{31} I_{32}^{em}(\omega_{32}, t_0)}{\omega_{32} I_{31}^{em}(\omega_{31}, t_0)}$. The additional information about the time dependence of the spectrum allows the total probabilities to be determined, for example, $w_3 = (t_2 - t_1)^{-1} \ln \dfrac{I_{31}^{em}(t_1)}{I_{31}^{em}(t_2)}$, which, with regard to Eq. (7), makes the problem of absolute values of transition probabilities w_{ij} fully determined and readily solvable either directly or by using methods for solving inverse problems. This always can be done with a sufficient amount of experimental data (relative intensities at different instants of time).

Therein lie the principal and qualitatively new possibilities that time-dependent spectra offer for the analysis of complex molecules and their mixtures as compared with the conventional methods.

With known transition probabilities w_{ij}, concentration c is readily determined from the relative fluorescence intensities given by Eqs. (4)–(6). In this case, measuring spectra not in the entire frequency range but only in its part that corresponds to transitions from one, initially excited state ($I_{31}^{em}(\omega_{31}, t)$ and $I_{32}^{em}(\omega_{32}, t)$, see Figs. 2c, 2e) is sufficient to carry out quantitative analysis, because the intensities of these lines do not depend on the characteristics of the $2 \longrightarrow 1$ transition. This fact significantly simplifies the solution of inverse problems and the analysis itself, because all these lines exhibit the same time dependence ($\exp(-w_3 t)$), which is determined by the total probability of the transitions from state 3. In its turn, this fact may also serve as a criterion for selecting experimental lines when inverse problems are posed (that is, excluding lines that correspond to another transition but fall within the given spectral range in frequency, see below). The other parts of the entire spectrum (in this case, $I_{21}^{em}(\omega_{21}, t)$, see Figs. 2b, 2d) can be useful in qualitative analysis, because they give more copious information on the molecular levels and transition probabilities (ω_{21}, w_{21}).

Real large molecules possess a complicated system of vibronic energy levels and, in this sense, significantly differ from the simplest three-level systems. Nevertheless, to a good approximation, the results obtained above are also applicable to large molecules if the experiment is carried out properly.

Actually, let a molecule is resonantly excited by a short light pulse to the second, purely electronic ($\nu_j' = 0$) state. The fluorescence spectrum of the $2 \longrightarrow 1$ tran-
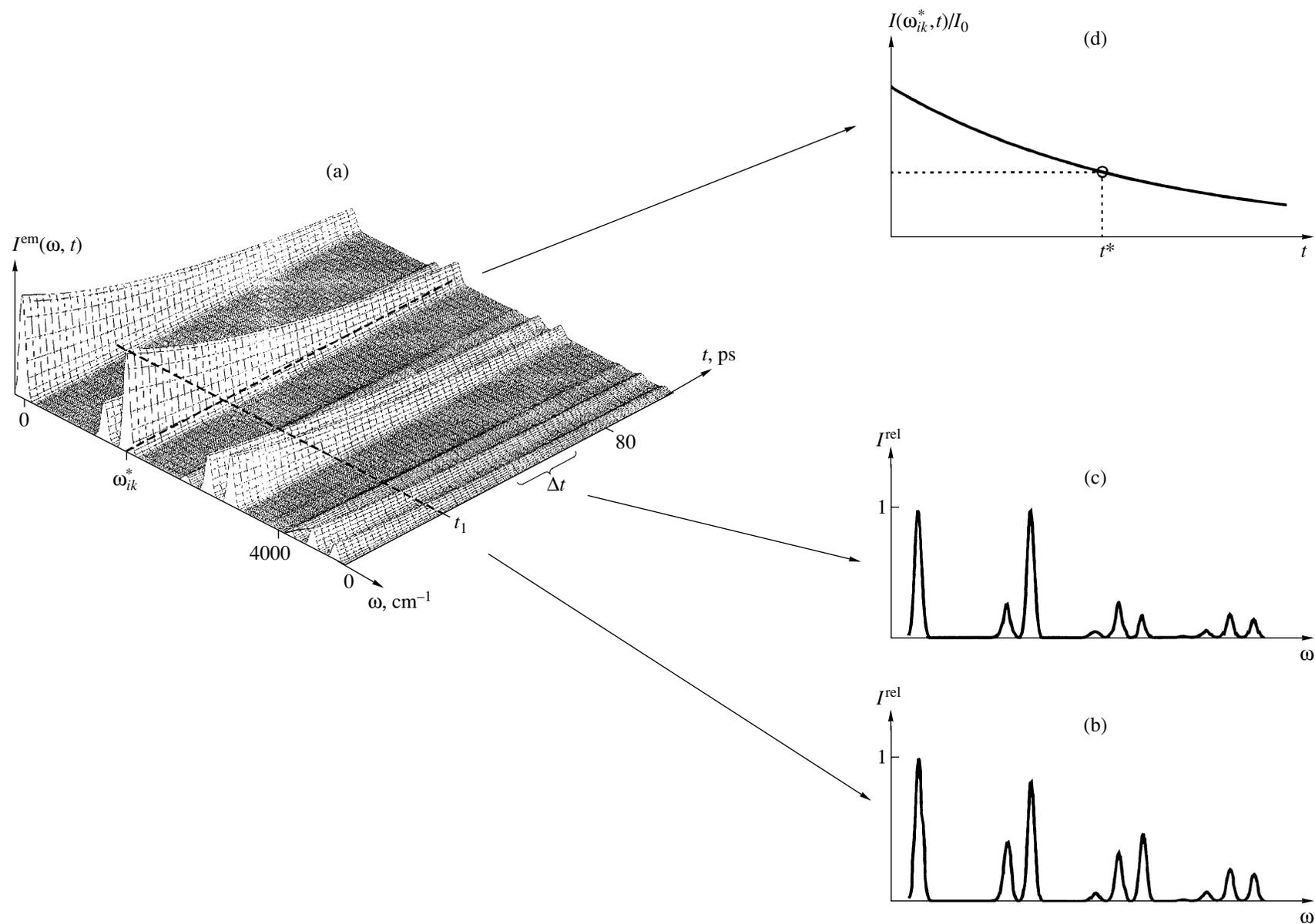
Fig. 1. (a) Multidimensional (time-dependent) luminescence spectrum of a model of the butadiene molecule, (b) a spectral curve for a fixed instance of time t_1, (c) an integral curve for the time Δt, and (d) a spectral curve for a fixed frequency ω_{ik}^* .
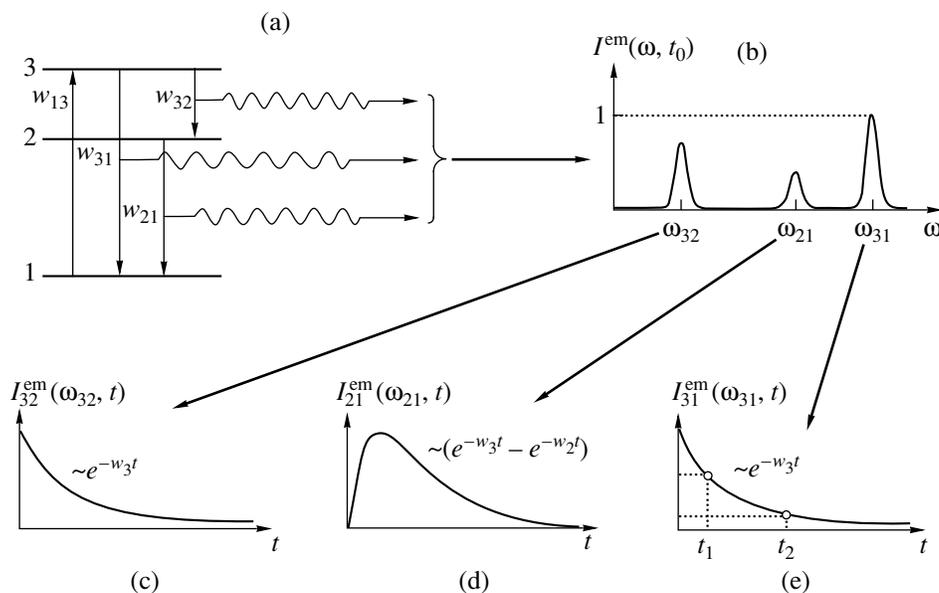
Fig. 2. Three-level diagram: (a) a system of levels; (b) an emission spectrum in the entire frequency range recorded at an instant of time t_0; and the time dependence of line intensities corresponding to transitions (c) $3 \longrightarrow 2$; (d) $2 \longrightarrow 1$; and (e) $3 \longrightarrow 1$.

sition will exhibit a vibrational structure ($0 \longrightarrow v$) with a large number of lines whose intensities equal

$$\frac{I_{21v}^{em}(\omega_{21v}, t)}{I_0} = \frac{\pi c^{*2}}{2} \tau c \omega_{21}^{-3} \omega_{21v} w_{20-10} w_{20-1v} e^{-w_{21}t}, \quad (8)$$

where $\omega_{21v} = \omega_{21} - \sum_i \omega_i v_i$, ω_i and v_i are the frequency and quantum number of the ith vibration, w_{21} is the probability of the purely electronic transition with a frequency of ω_{21}, $w_{20-1v} = w_{21}\langle 0|v\rangle^2$ are probabilities of vibronic 2, 0 $\longrightarrow$ 1, v transitions, and $\langle 0|v\rangle^2$ are Franck–Condon factors. We assume that $\omega_{20-1v} \approx \omega_{21}$, which is a good approximation (with an accuracy of $\leq$10 rel %), because the vibrational frequencies in large molecules are lower than the frequencies of electronic transitions by an order of magnitude. In addition, the changes of molecular structures due to electronic excitation are small. Therefore, the most significant $\langle v'|v\rangle$ integrals are those for which the changes of the quantum numbers do not exceed 1, and the total probability of the transition from state 2 equals the probability of the purely electronic transition w_{21} [8].

The line intensities of the vibrational structure of the spectrum have the same time dependence, and the problem is completely similar to the problem for a three-level system. In particular, it is thus clear that the vibrational $v_1 \longrightarrow v_2$ transitions in the electronic ground state (IR spectrum) are insignificant and can be neglected in quantitative analysis.

The same result is also obtained for rarefied gases (intermolecular interactions and radiationless transitions can be neglected) under broadband excitation of molecules.

MULTICOMPONENT MIXTURES

The given approach is easily generalized to the case of multicomponent mixtures of substances with concentrations $c_1, c_2, \ldots, c_N$

$$\frac{I_{ik}^{em}(\omega_{ik}, t)}{I_0} = \frac{\pi c^2}{2} \tau \sum_{q=1}^{N} c_q W_{ik}^q(\omega_{ik}^q, t), \quad (9)$$

where $W_{ik}^q = \omega_{ik}^q (\omega_{0n}^q)^{-3} w_{ik}^q w_{n0}^q [\Phi(t)]_{in}^q$. Actually, the intensities in fine-structure spectra are normalized to the line intensity of one of the mixture components (q_0)

$$\frac{I_{ik}^{em}(\omega_{ik}^q, t)}{I_0^{em}(\omega_0^{q_0}, t_0)} = \frac{1}{W_0^{q_0}(\omega_0, t_0)} \sum_{q=1}^{N} \frac{c_q}{c_{q_0}} W_{ik}^q(\omega_{ik}^q, t) \quad (10)$$

and depend on the relative concentrations c_q/c_{q_0}. The total probabilities w_i^q are determined from the time dependence of lines corresponding to the qth component of the mixture $\dfrac{I_{ik}^{em}(\omega_{ik}^q, t_1)}{I_{ik}^{em}(\omega_{ik}^q, t_2)} = \dfrac{W_{ik}^q(\omega_{ik}^q, t_1)}{W_{ik}^q(\omega_{ik}^q, t_2)}$, and

the relative transition probabilities $w_{ik}^q / w_{i_0 k_0}^q$ are determined from the relative line intensities of the vibrational structure of the spectrum corresponding to the qth component. Thus, the absolute values w_{ik}^q are determined as well, because the total w_i^q are known. Next, the ratio of line intensities of different components (Eq. (10)) gives the relative concentrations $c_q' = c_q/c_{q_0}$, and the relative intensities (Eq. (9)) give the

value of c_{q_0} and, hence, the absolute values of concentrations $c_q = c'_q c_{q_0}$.

In the case of structureless spectra with overlapping lines of various mixture components, the time dependence of their intensities will have a complex "multicomponent" character $I^{em}(t) \sim \sum_q A_q \exp(-w_q t)$. Nevertheless, all of the total probabilities w_q can be found given a sufficient amount of experimental values of spectral intensities $I^{em}(t_i)$ at various instants of time. The algorithm of solving the problem of the quantitative and qualitative analysis of a mixture is the same as for a fine-structure spectrum, except that a sum over all the mixture components should be taken in the line intensities.

Note that the spectra of mixture components whose excited states strongly differ in energy (the condition mentioned above is not fulfilled) will strongly differ in intensity at comparable concentrations $c_{q'} \approx c_{q''}$, because the probability of transitions to high overtone states ($\nu > 2$) is small. Therefore, varying the excitation frequency, one can obtain spectra that contain components of either the q' type or the q'' type and carry out analysis by these spectra separately for each group of mixture components.

The approach proposed reduces quantitative and qualitative analysis to the solution of inverse spectral problems by molecular simulation methods. These problems can be solved in the general form; however, the reliability of the answer obtained and the degree of its adequacy to the real system under study are considerably improved if additional information is used. In this case, the possibility of assigning lines of the vibrational structure of a spectrum to one or another component of the test mixture, determining the number of components that are revealed in the spectrum, etc. plays an important role. Measuring the variation of a spectrum with time provides this information. Actually, the time dependence of line intensities corresponding to different mixture components is different. As an example, Fig. 3 shows the results of model calculations of time-dependent spectra of a two-component mixture of molecules (hexatriene and octatetraene) close in their vibronic properties. This example demonstrates that the lines corresponding to different mixture components are easily identified even at close values of oscillator strengths of electronic transitions.

Let us dwell on this subject in more detail. We will obtain estimates for the regions of tolerable relative concentrations of mixture components with their optical properties given so that the spectral manifestation of each component in the measured spectrum of the mixture is "observable," and, hence, their quantitative and qualitative analysis is possible. For simplicity, without the loss of generality, we consider a mixture of substances containing two components each of which passes to the first excited state on absorbing incident

radiation (the results of analysis are readily generalized to multicomponent and multilevel cases). Let this mixture of two substances is characterized by the ratios of concentrations $r_c = c_1/c_2$, energies of the first excited states $r_\omega = \omega_1/\omega_2$, and oscillator strengths of the corresponding electronic transitions $r_f = f_1/f_2 < 1$ (we will designate the component with the lower oscillator strength by subscript 1). If the probability of vibrational relaxation is negligibly small (dilute gas), the fluorescence spectrum of the mixture on excitation to the first electronic states will consist of the lines of the two components with their decay rates determined by the corresponding lifetimes $\tau_1 \approx 0.12\,\omega_1^{-2} f_1^{-1}$ and $\tau_2 \approx 0.12\,\omega_2^{-2} f_2^{-1}$ (here, the electronic transition frequencies ω_1 and ω_2 are given in cm^{-1}). The ratio of intensities of slowly decaying lines of the first component in the spectrum $I_{1k}(t) \sim \exp(-t/\tau_1)$ to intensities of rapidly decaying lines of the second component $I_{2n}(t) \sim \exp(-t/\tau_2)$ will grow exponentially

$$R_{kn}(t) = \frac{I_{1k}(t)}{I_{2n}(t)} = R_{kn}(0)\exp\left[\frac{t}{\tau_1}\left(\frac{1}{r_\omega^2 r_f} - 1\right)\right]. \quad (11)$$

The function $R_{kn}(t)$ given by Eq. (11) depends on time in a similar way for any pair of lines k and n. It is the time dependence of $R_{kn}(t)$ that provides the possibility of identifying various mixture components by the spectrum and assigning the corresponding lines to various components.

It is natural to analyze this dependence for the kth and nth lines with the highest intensities in the spectra of the first and second components, which, in the case of polyatomic molecules, correspond as a rule to vibronic transitions without changing the vibrational quantum number

$$R(t) = R(0)\exp\left[\frac{t}{\tau_1}\left(\frac{1}{r_\omega^2 r_f} - 1\right)\right], \quad (12)$$

$$R(0) = r_c r_{FC}(r_\omega r_f)^2, \quad (13)$$

where $r_{FC} = \sum_{p=1}^{N_1} A_{1p} F_{1p} / \sum_{q=1}^{N_2} A_{2q} F_{2q}$, $A_{1p} = \langle 0|\nu'_{1p}\rangle^2$, and $A_{2q} = \langle 0|\nu'_{2q}\rangle^2$ are Franck–Condon factors for transitions from the ground state on the excitation of vibrational sublevels of the first electronic states of mixture molecules, and $F_{1p} = \langle \nu'_{1p}|\nu_{1p}\rangle^2$ and $F_{2q} = \langle \nu'_{2q}|\nu_{2q}\rangle^2$ are Franck–Condon factors for transitions without changing the vibrational quantum numbers on fluorescence from these sublevels ($\nu'_j - \nu_j = 0$). The number of sublevels populated upon absorption N_1 and N_2 for the first and second mixture components depends on the spectral composition of the exciting radiation and the transition energies of these molecules. These factors and also the extent to which the changes
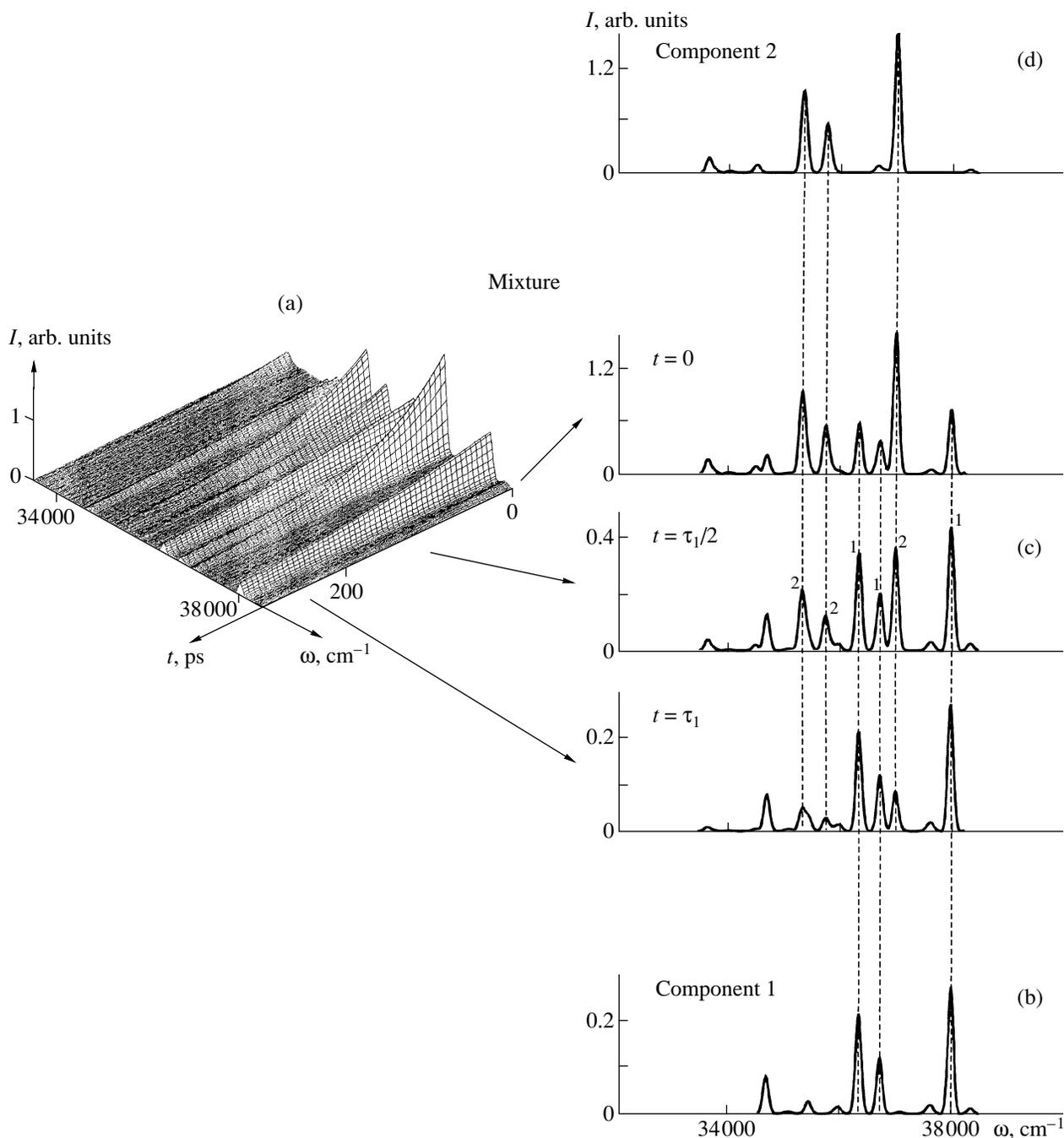
Fig. 3. (a) Time-dependent vibronic spectrum of a two-component mixture; (b) a spectrum of the first component; (c) cross-sections at different instants of time; (d) a spectrum of the second component; (parameters: $c_1/c_2 = 2$, $f_1/f_2 = 0.33$, $\omega_1/\omega_2 = 1.03$, $\tau_1 = 250$ ps, and $\tau_2 = 90$ ps).

in the potential energy surface due to excitation differ for different mixture components determine the magnitude of the r_{FC} parameter. Estimations of the Franck–Condon factors and calculations for models of particular molecules showed that typical values of the r_{FC} parameter fall in a rather wide range of the order of 0.01–100. If vibrational sublevels of the same type (with the same total quantum numbers) are excited in

mixture molecules, the range of possible values of r_{FC} is considerably reduced, $0.1 \le r_{FC} \le 10$. This can always be done if the electronic transition frequencies are close to each other (see below). Therefore, in the case of a pair of polyatomic molecules with a great number of vibrational sublevels, on the one side, the function $R(t)$ will significantly depend on the experimental conditions (spectral composition of exciting radiation), and,
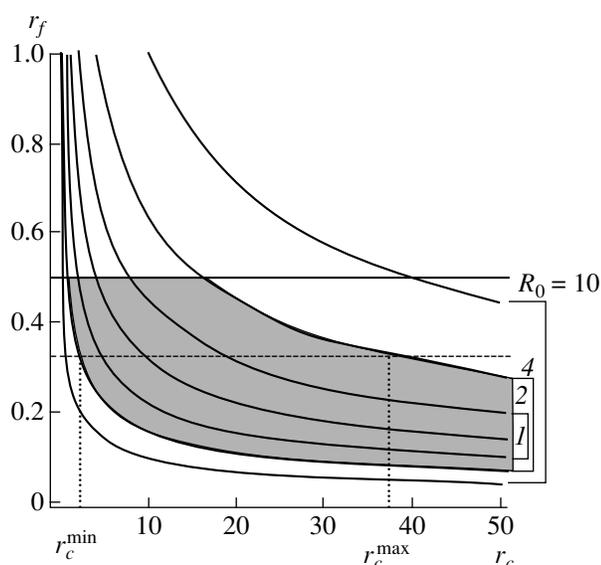
Fig. 4. Region of possible values of parameters r_f and r_c (Eq. (18)) for different initial ratios of intensities R_0 (designated in a gray color for $R_0 = 4$) at which mixture components are identified by the spectrum.

on the other side, the r_{FC} parameter can always be forced to be close to one by selecting proper excitation conditions. Hereafter, we will assume for simplicity that $r_{FC} = 1$. If $r_{FC} \neq 1$ for a specific mixture and particular excitation conditions, r_c in the estimates obtained below should be decreased by a factor of r_{FC}.

We will consider the most interesting case when molecules emit in the same frequency range so that their vibronic spectra overlap. This means that the electronic transition frequencies ω_1 and ω_2 can differ by no greater than a value of the order of the vibrational quantum frequency. Hence, the r_ω parameter is close to one ($0.9 \leq r_\omega \leq 1.1$), and we may assume that $r_\omega = 1$ to an accuracy of <20%.

The effect of the variation of the mixture spectrum with time due to the presence of various components will be notable if the value of $R(t)$ given by Eq. (12) significantly increases during the measurement time t_m, for example, by a factor of no less than e. Then, we obtain from Eq. (12) that $\frac{t_m}{\tau_1}\left(\frac{1}{r_\omega^2 r_f} - 1\right) \geq 1$. This gives the condition for the ratio of oscillator strengths $r_f \leq [r_\omega^2(1 + \tau_1/t_m)]^{-1}$, which takes the following form for the case of overlapping bands considered here ($r_\omega = 1$):

$$r_f \leq (1 + \tau_1/t_m)^{-1}. \tag{14}$$

The characteristic measurement time of the mixture spectrum t_m is determined by the decay rate of the slow component and equals τ_1 in the order of magnitude.

Therefore, the ratio of oscillator strengths of transitions (at $t_m = \tau_1$) must obey the condition

$$r_f \leq 0.5, \tag{15}$$

which means that the decay rates of line intensities of mixture components must differ by a factor of no less than 2. Equations (14) and (15) are the necessary conditions for the variation of the spectrum of a mixture of two given substances to be observable for the characteristic fluorescence decay time.

The initial ratio of intensities of mixture components $R(0)$ given by Eq. (13) depends on the concentration of substances and on the absorption and fluorescence probabilities. If $R(0)$ strongly differs from one, one of the components with a higher concentration or absorption will dominate in the spectrum regardless of the fulfillment of Eq. (15), and the second component will be virtually unobservable. This case is of no interest, because it corresponds to the single-component case (the second component gives only negligibly low "noise" in the spectral experiment). Therefore, it is natural to introduce the second general restriction on the possible values of mixture parameters at which both the components will be revealed in the spectrum in the form

$$R_0^{-1} \leq R(0) \leq R_0. \tag{16}$$

For example, we will consider that the spectral line intensity of one of the components makes up no less than 25% of the intensity of the other component at the initial instant of time ($t = 0$); that is, $R_0 = 4$, and, correspondingly,

$$0.25 \leq R(0) \leq 4. \tag{17}$$

Conditions given by Eqs. (14)–(17) functionally determine the region of mixture parameters r_f and r_c at which the required ($R(t_m)/R(0) \geq e$) change in the spectrum of substances with initially comparable (parameter R_0) fluorescence intensities will be attained in a restricted measurement time ($t_m \approx \tau_1$)

$$R_0^{-1} \leq r_c r_f^2 \leq R_0. \tag{18}$$

Figure 4 displays the region of values of r_f and r_c for a number of values of R_0 (for $R_0 = 4$, the region is shaded). It is clearly evident that, for two substance at a fixed parameter r_f, there is a concentration range $r_c^{min} \leq r_c \leq r_c^{max}$ ($r_c^{min} = (R_0 r_f^2)^{-1}$ and $r_c^{max} = R_0 r_f^{-2}$) in which the necessary effect of the spectral resolution of components is observed. This range of possible relative concentrations is rather wide. Its bounds differ by a factor of R_0^2 ($r_c^{max}/r_c^{min} = R_0^2$), that is, by a factor of 16 at $R_0 = 4$. For example, if the fluorescence decay rate of the second component is 3 times greater than that of the first one ($r_f = 0.33$), the presence of this component in the mixture can be identified by the spectrum at its rel-

ative (compared to the first component) concentration $3\% \leq c_2/c_1 \leq 44\%$. The closer the fluorescence decay rate of the second component to the decay rate of the first component (that is, the larger r_f), the larger the tolerable concentration range of the second component, $(c_2/c_1)^{max} - (c_2/c_1)^{min} = r_f^2 (R_0 - R_0^{-1})$, see Fig. 5. However, the conditions in Eqs. (14) and (15) bound the ratio of oscillator strengths from the above, because the variation of the spectrum during the measurement time will be insignificant in the case of close fluorescence decay rates of components.

The possibilities of the method with respect to tolerable concentrations and oscillator strengths can be extended through increasing the measurement time of the spectrum. Correspondingly, the condition given by Eq. (15) will be changed. Thus, for example, $r_f \leq 0.7$ at $t_m \approx 2\tau_1$, and $r_f \leq 0.8$ at $t_m \approx 5\tau_1$. The regions of possible concentrations corresponding to these conditions are shown in Fig. 5 by vertical lines (thus, $(c_2/c_1)^{max} = 256\%$ and $(c_2/c_1)^{min} = 16\%$ at $r_f = 0.8$). In its turn, the measurement time is restricted by the limiting relative sensitivity of the instrument that measures the intensity ($I_1(t_m)/I_1(0) \geq S$). Therefore, $t_m \leq -\tau_1 \ln S$, and $S = 0.01$, $t_m \leq 4.6\tau_1$ for a rather typical experimental situation.

The tolerable concentration range for the reliable interpretation of spectral lines can be considerably enlarged if the milder condition given by Eq. (17) is imposed on the ratio of initial intensities of mixture components, for example, $R_0 = 10$ ($0.1 \leq R(0) \leq 10$), which is quite typical in practice (see Fig. 6; the region bounded by thin lines). In this case, $r_c^{max}/r_c^{min} = 100$, and $1\% \leq c_2/c_1 \leq 111\%$ for $r_f = 0.33$. The selection of this condition is determined by the character of the experiment and the shape of the spectra (their structure and the degree of line overlapping). The optimal values of the R_0 parameters can be determined in a particular case by computer simulation methods for spectra of mixtures.

A small (within a vibrational quantum) difference in the frequencies of electronic transitions of molecules ($r_\omega \neq 1$) insignificantly affects the limits of tolerable values of mixture parameters (by no more than 20%, see regions in Fig. 6 bounded by dashed lines).

Thus, the difference in the time dependence of line intensities corresponding to different mixture components allows one to interpret the spectrum over a wide range of concentrations and optical properties of components, to reveal the presence of these components by the spectrum, and, hence, to solve problems of quantitative and qualitative analysis with a high degree of reliability. These estimates are also applicable in full measure to structureless spectra.

As distinct from the case of dilute gases considered above, intermolecular interactions can play a significant role in sufficiently dense media (dense gases, liquids, etc.). These interactions result in the transfer of
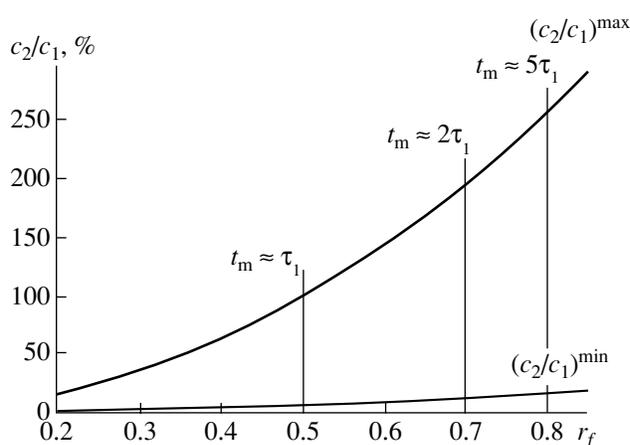

Fig. 5. Dependence of limiting relative concentrations of the second component $(c_2/c_1)^{max}$ and $(c_2/c_1)^{min}$ on r_f at $R_0 = 4$. The boundaries of the possible values of r_f at different measurement times t_m are shown by vertical lines.

the internal energy of a vibronically excited molecule to external (translational) degrees of freedom with the transition of the molecule to a lower vibronic state and an increase in the temperature of the medium. In this case, the information containing in the relative intensities of emission spectra is not sufficient to find all the necessary transition probabilities and to determine the concentration c. This is connected with the fact that the fraction of the absorbed energy transformed to the thermal motion of molecules as a result of radiationless transitions remains unknown when the experiment is set up in this way. It is necessary either to measure absolute intensities, which is rather difficult in practice, or to use an additional experiment to determine the fraction of energy transformed to heat. We will not dwell in detail on this problem, because it requires a special comprehensive consideration (a separate publication will be devoted to this problem). We only note here that a measurement of the change in the temperature of the medium due to light absorption and emission can serve as such an additional experiment. Hence, the approach proposed for the standardless spectrochemical analysis of substances can be applied not only to dilute gases but to sufficiently dense media as well. In this case, a possibility also arises of experimentally determining probabilities of radiationless transitions and constructing corresponding detailed molecular models [10].

Thus, the consideration presented here demonstrates the possibility of constructing a method for the standardless quantitative and qualitative analysis of complex substances and their mixtures based on time-resolved vibronic spectroscopy in the UV and visible radiation regions. Among the main advantages of this method as compared to the known methods [1–5], we will distinguish the following:
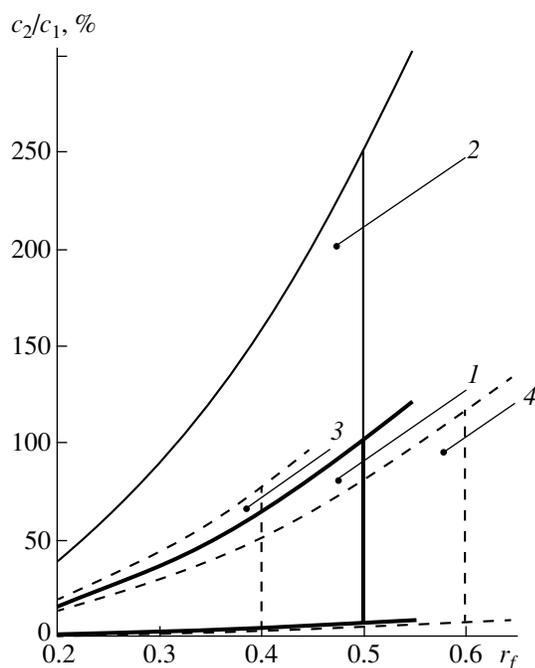
Fig. 6. Variation of ranges of possible concentrations c_2/c_1 and r_f at different values of parameters R_0 and r_ω: (*1*) $R_0 = 4$ and $r_\omega = 1$; (*2*) $R_0 = 10$ and $r_\omega = 1$; (*3*) $R_0 = 4$ and $r_\omega = 1.1$; (*4*) $R_0 = 4$ and $r_\omega = 0.9$.

Under certain conditions, qualitative analysis can be completely transferred to an experimental basis without a preliminary calculation of absolute intensities for molecular models corresponding to the substance under investigation. This opens the possibility of the simultaneous quantitative and qualitative analysis of unknown substances and their mixtures from the same experiment.

The use of luminescence spectra significantly enhances the sensitivity of standardless analysis and allows the probing of media under study to be performed remotely.

The method is most effective for dilute gases, which is easily accomplished in a great number of practically important cases (impurities in the air, in the upper air, analysis of samples under laboratory conditions, etc.).

With the use of an additional "temperature" experiment, one can also obtain information on radiationless transitions, which is extremely important in the direct analysis of dense gases and in the modeling of intermolecular interactions [10].

The problem of the metrological certification of new methods of qualitative and quantitative analysis using the approach proposed in this article is also important. A separate publication will be devoted to this problem.

REFERENCES

1. Gribov, L.A., *Zh. Anal. Khim.*, 1995, vol. 50, no. 6, p. 589.
2. Gribov, L.A., Elyashberg, M.E., and Karasev, Yu.Z., *Anal. Chim. Acta*, 1995, vol. 316, p. 217.
3. Elyashberg, M.E., Gribov, L.A., Karasev, Yu.Z., and Martirosian, E.R., *Anal. Chim. Acta*, 1997, vol. 353, p. 105.
4. Gribov, L.A., Sidelov, D.I., and Maslov, I.V., *Zh. Anal. Khim.,* 1998, vol. 53, no. 7, p. 706.
5. Baranov, V.I. and Gribov, L.A., *Zh. Anal. Khim.,* 1999, vol. 54, no. 4, p. 350.
6. Baranov, V.I. and Gribov, L.A., *Opt. Spektrosk.*, 1998, vol. 85, no. 1, p. 46.
7. Gribov, L.A., Baranov, V.I., and Zelentsov, D.Yu., *Elektronno-kolebatel'nye spektry mnogoatomnykh molekul. Teoriya i metody rascheta* (Vibronic Spectra of Polyatomic Molecules. Theory and Calculation), Moscow: Nauka, 1997.
8. Astakhov, S.A. and Baranov, V.I., *Opt. Spektrosk.*, 2000, vol. 90, no. 2, p. 237.
9. Elyashberg, M.E., Gribov, L.A., and Serov, V.V., *Molekulyarnyi spektral'nyi analiz i EVM* (Molecular Spectroscopic Analysis and Computers), Moscow: Nauka, 1980.
10. Baranov, V.I. and Gribov, L.A., *Zh. Prikl. Spektrosk.*, 2000, vol. 67, no. 3, p. 289.