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CO Adsorption at 77 K on CoO/MgO and NiO/MgO Solid Solutions: A Fourier-transform Infrared Study

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The infrared spectra of CO adsorbed at 77 K on sintered polycrystalline MgO and Ni/MgO, Co/MgO solid solutions, containing 10% nickel and cobalt in atoms are reported. These solids are properly designed for the estimation of the role played by d–π overlap in the bonding between the isolated transition-metal cations and the CO molecules adsorbed on them. In fact, since the Ni^{2+} or Co^{2+} ions emerging on the (100) faces are diluted in a common MgO matrix, they experience an environment and an ionicity similar to that of the Mg^{2+} ions. Consequently any difference in the CO stretching frequency can principally be ascribed to overlap contributions. Moreover, the nature of the lateral interactions between Ni^{2+}—CO and Co^{2+}—CO complexes and the surrounding (predominant) Mg^{2+}—CO species can be investigated and compared with those observed on the pure oxides. The examination of the experimental results on such model solids confirms that, although the interaction of CO with Ni^{2+} and Co^{2+} ions is mainly electrostatic, some d–π overlap contribution is present.

The molecular adsorption of diatomic molecules, such as CO, at the surface of metal oxides (MgO, NiO, ZnO, TiO_2 *etc.*) or alkali-metal halides, is associated with adsorption enthalpies in the 15–50 kJ mol^{-1} range[1–4] and can consequently be classified as a weak interaction, almost of the physisorptive type. Although very weak, the adsorption is localized, as it occurs preferentially on the cations, as extensively shown by many authors.[5–8]

Owing to the adsorption process, the six degrees of freedom of the gaseous molecule (three translations of the centre of mass, two rotations and one stretching vibration) change into a C—O stretching mode, an M—C stretching mode (from translation), two modes of hindered translations and two modes of hindered rotations. The C—O stretching mode is found at high wavenumbers ($2100 \leqslant \bar{\nu}/cm^{-1} \leqslant 2200$) while the remaining five fall at much lower wavenumbers ($\bar{\nu} \leqslant 200$ cm^{-1}) and consequently can be hardly detected by IR spectroscopy (because they are overshadowed by the manifestations of the adsorbent solid). Owing to this limitation, direct information concerning the low-frequency modes is generally missing. However, indirect information can be gained from the high-frequency combination bands involving the CO stretching and one or more of the low-frequency bands. Finally, the role of the hindered translational modes in determining the band halfwidth has been analysed in great detail by Ewing and co-workers.[9]

The interaction of the CO molecule with the surface cations is generally considered to be essentially electrostatic in nature[10–12] as it results from the interaction of the electric field at the surface cation positions with the CO charge distribution. This interaction causes the vibrational frequency of isolated CO species adsorbed on oxides or halides to be higher than that of CO gas.[1–12] In connection with this problem, note that a correlation has been proposed between the local field strength and the frequency shift,[8,11–13] as well as between the frequency shift and the heat of adsorption.[14] On the basis of spectroscopic results, Escalona Platero *et al.*[1,2] and Scarano *et al.*[15] ascribe some role also to back-donation from the transition-metal cations. Although a clear distinction between the two views cannot be made, for purely electrostatic interactions charge transfer from the surface to the molecule or *vice versa* cannot occur, while if σ and/or π bonding is present some charge transfer can be hypothesized. In our opinion, the presence or absence of a weak 'overlap contribution' can still be considered as an open question, in particular in the case of transition-metal oxides.

Independently of the relative importance of the electrostatic and 'overlap' (chemical) contributions, the adsorption of the CO molecule necessarily involves a change of the dipole, quadrupole *etc.* moments as well as of the transition moments (or, classically, the first derivative of μ, $\delta\mu/\delta Q$). Since the square of the μ derivative (transition moment) is the dynamic polarizability α_v (which in turn is proportional to the absorption coefficient),[7] it is plain that information about $\delta\mu/\delta Q$ and hence, indirectly, on the nature of the CO—surface bond comes out of the evaluation of the specific intensity of the peak when the coverage θ approaches 0 (as will be shown).

When the coverage increases from 0 to 1, the CO molecule experiences a gradual change in its environment and, consequently, lateral interactions build up. As already discussed by some authors,[16–18] the interactions among various oscillators can be classified into two main groups: (i) through space and (ii) through the solid. The interactions through space are either dynamic or static in nature and involve dipole–dipole, quadrupole–quadrupole, dipole–quadrupole *etc.* interactions; moreover, dipole–induced dipole, induced dipole–induced dipole and static dispersion effects have to be included. The interactions through the solid are essentially chemical in nature and can be ascribed to the influence at a given site of the charge transfer (either from the molecule to the surface or from the surface to the molecule) occurring at another site.

According to the previous considerations, the interaction of CO with the surface of the oxide is essentially electrostatic in nature, with a minor (or even vanishing) contribution from d–π overlap. Consequently, the interaction through the solid should play a limited role. Therefore, in the following we shall deal with direct interactions through the space only.

In agreement with Ewing and co-workers,[10] these interactions can be analysed by considering first the dimer and then the infinite monolayer. Following this treatment, if we denote by μ_{00}, θ_{00}, Ω_{00} *etc.* and by μ_{11}, θ_{11}, Ω_{11} and so on the permanent moments averaged over the vibrational states $v = 0$ and $v = 1$ and by μ_{01}, θ_{01}, Ω_{01} *etc.* the transition moments between the $v = 0$ and $v = 1$ states (which correspond to $\delta\mu/\delta r$, $\delta\theta/\delta r$ *etc.* according to classical theories), the various interactions can be described with static and dynamic terms as follows

Static interactions:	$(\mu_{11} - \mu_{00})\mu_{00}$	dipole–dipole
	$(\theta_{11} - \theta_{00})\theta_{00}$	quadrupole–quadrupole
	etc.	
Dynamic interactions:	$\mu_{01}\mu_{01}$	dipole–dipole
	$\theta_{01}\theta_{01}$	quadrupole–quadrupole
	etc.	

In order to evaluate the whole interaction within the entire monolayer, the dimer results have to be multiplied by the infinite lattice square sums $S_n = \sum_{j=1}^{\infty}(r_{ij})^{-n}$, where $n = 3$, $n = 5$ or $n = 7$ for dipole–dipole, quadrupole–quadrupole or octapole–octapole couplings, respectively.

Although Ewing and co-workers[10] stressed the relevance of the quadrupole–quadrupole and octapole–octapole terms in determining the monolayer frequency of CO adsorbed on NaCl, it is normally accepted that, owing to their slow decay with distance, the dipole–dipole interactions play the major role. In fact, as the decay of the dipole–dipole interaction by r^{-3} is compensated by the growth of the number of adsorbed molecules, which goes as r^2, it turns out that the dipole–dipole term depends on r^{-1} and so involves the contribution of many neighbours. Quadrupole–quadrupole interactions *etc.* can become relevant at the shortest CO—CO distances (in densely packed monolayers). However, this is not so in our case, because the minimum CO—CO distance is 4.10 Å only.[1] On the basis of this approximation, the frequency shift with coverage on passing from $\theta = 0$ to $\theta = \theta_{max}$ is primarily due to dipole–dipole (either static or dynamic) and dispersion (purely static) interactions.

Hammaker *et al.*[16] have calculated the effect on the vibrational frequency of the dynamic contribution in the dipole–dipole approximation:

$$(\omega/\omega_0)^2 = 1 + \alpha_v T_0 \quad \text{or} \quad \Delta\omega \approx \tfrac{1}{2}\omega_0(\alpha_v T_0) \qquad (1)$$

where ω is the monolayer frequency, ω_0 is the singleton frequency, α_v is the dynamical polarizability, which is proportional to $(\delta\mu/\delta r)^2$ and hence to $\mu_{01}{}^2$ and T_0 is the direct dipolar sum. They suggested an experimental method of detecting the frequency shift. This equation has been modified by Mahan and Lucas in order to take into account the dielectric screening in the adsorbed monolayer.[17] For a complete monolayer, the modified equation becomes:

$$(\omega/\omega_0)^2 = 1 + \alpha_v T_0(1 + \alpha_e T_0)^{-1}$$

or

$$\Delta\omega \approx \tfrac{1}{2}\omega_0(\mu_{01}^2 T_0)(1 + \alpha_e T_0)^{-1} \qquad (2)$$

where α_e is the electronic polarizability. These authors included the factor $(1 + \alpha_e T_0)^{-1}$, which arises from the electronic polarizability of the CO molecules that form a monolayer on the surface. Similar equations hold for the static dipole–dipole shifts, whereby the μ_{01}^2 term is substituted by $(\mu_{11} - \mu_{00})\mu_{00}$. Owing to the similar dependence upon r the static shift should depend upon θ in the same way.

Following the method of the $^{12}CO/^{13}CO$ isotopic mixtures suggested by Hammaker *et al.*,[16] the relative weights of the static and dynamic effects have been estimated on various oxides and halides.[1,2,15–19] These experimental data show that the two effects do depend upon the coverage in a very similar way: this suggests that the pre-eminent static interaction is of the dipole–dipole type, whereas dispersion plays a minor role.

Coming back to the presence or absence of overlap interactions and to the role played by the back-donation in transition-metal oxides,[2,15] we reconsider now the frequencies of the CO molecule adsorbed on the (100) surface of MgO and NiO. On such oxides we detected a slight difference in the frequencies of the peaks at $\theta \approx 0$ (2157 cm^{-1} on MgO and 2152 cm^{-1} on NiO) which has been explained in terms of back-donation from the d orbitals of Ni^{2+} into the $2\pi^*$ antibonding orbitals of CO. This explanation does not agree with the electrostatic model, unless a smaller ionicity is ascribed to NiO. In this case, the NiO, by having a more covalent character, should show a lower polarizing effect on CO and hence a reduced interaction energy (and reduced frequency shift with respect to CO gas as well).

In order to investigate this discrepancy, we performed the following experiment. Ni^{2+} and Co^{2+} ions were doped into an MgO matrix (which has the same rock salt structure and exposes the same crystallographic faces of NiO and CoO). In this way, the Ni^{2+} and Co^{2+} ions in the framework experience an environment and an ionicity as similar as possible to those of the Mg^{2+} ions in MgO. On such properly designed structures different values of the frequency of CO adsorbed on Mg^{2+}, Ni^{2+} and Co^{2+} cations emerging on (100) faces and terraces could not be ascribed to ionicity differences, but only to overlap contributions. Furthermore, as the CO oscillators adsorbed on the Ni^{2+} and Co^{2+} ions were completely surrounded by those adsorbed on Mg^{2+}, the system should provide (by comparison with the results of the NiO–CO, CoO–CO systems) further data on the nature of the lateral interactions.

Experimental

The samples used in this study were obtained by overnight sintering (at 1073 K in 200 Torr CO_2) of high surface MgO and MO/MgO (M = Ni or Co) solid solutions, at a ratio M/Mg = 0.1, prepared following the procedures described in references.[20–24] After this sintering procedure the specific surface area is in the 20–30 $m^2\ g^{-1}$ range. The surface composition of the solid solutions prepared in this way is not appreciably different with respect to the bulk as already shown in ref. 25.

Before CO adsorption the sintered samples were outgassed *in vacuo* at 1073 K in order to remove all the adsorbed impurities.

The IR spectra were recorded in transmission mode at 1 cm^{-1} resolution on a Bruker IFS 88 FTIR spectrophotometer equipped with an MCT cryogenic detector. All the spectra of CO adsorbed at liquid-nitrogen temperature are given in absorbance units after subtraction of the gas-phase spectrum (recorded at the same temperature). Owing to the combined effect of the IR radiation and low thermal conductivity, the temperature of the sample during the IR experiments would be higher than 77 K (*ca.* 100 K).

The high-resolution micrographs were obtained on a JEOL JEM 2000EX transmission electron microscope equipped with a top-entry stage.

Results and Discussion

Electron Micrographs

After they have been sintered the MgO, NiO/MgO and CoO/MgO samples show very similar crystalline habits. In particular, they are formed of large aggregates, with linear dimensions in the 50–100 nm range (in broad agreement with the surface area data), which cannot be further broken down either by mechanical grinding or by prolonged treatment in an ultrasonic bath. As an example, a representative image of a CoO/MgO solid solution is reported in Fig. 1. The presence of different regions can be distinguished: (i) extended, almost flat and scarcely defective zones (A) covering areas of (15–20) × 10^3 $Å^2$; (ii) zones mainly located on the borders of the aggregates where single, nearly cubic microcrystals are bound

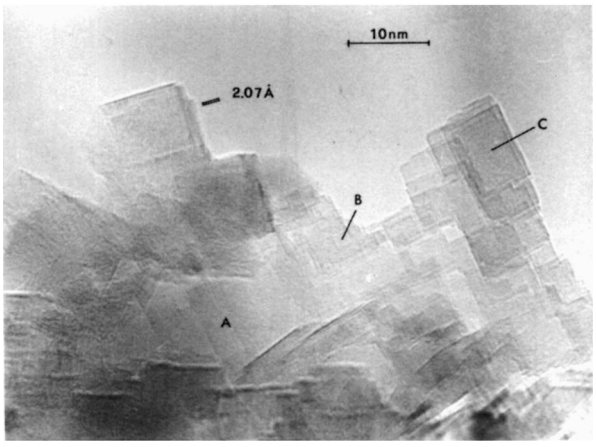


Fig. 1 High-resolution transmission electron micrographs of a sintered CoO/MgO solid solution. A, B, C, see text

and interpenetrate to form stepped terraces whose dimensions range from 350 Å^2 (B) to 7500 Å^2 (C).

In some cases interference fringes *ca.* 2.07 Å apart, and hence originating from the (400) crystallographic planes of MgO, are clearly visible. Their orientation with respect to the traces of the borders of the microcrystals allows the conclusion to be drawn that the {100} planes are preferentially exposed. Different kinds of coordinatively unsaturated (cus) M^{2+} (M = Mg^{2+}, Co^{2+}, Ni^{2+}) and O^{2-} ions emerge on the surface: (i) pentacoordinated M^{2+}_{5cus} and O^{2-}_{5cus} located on the {100} faces: (ii) tetracoordinated M^{2+}_{4cus} and O^{2-}_{4cus} on the edges and (iii) tricoordinated M^{2+}_{3cus} and O^{2-}_{3cus} on the corners. The relative concentrations of these unsaturated moieties, and hence their contribution to the spectrum of adsorbed CO, depends on the extension of the flat areas. If a distance of *ca.* 2.9 Å (calculated on the basis of the 8.12 Å lattice parameter of MgO) is assumed for M^{2+}–M^{2+} nearest neighbours, the total number of cations emerging on flat surfaces with dimensions of 20000, 7500 and 350 Å^2 is *ca.* 2400, *ca.* 900 and *ca.* 40 respectively, while the percentage of ions on the edges are *ca.* 3%, *ca.* 5% and *ca.* 22%, respectively. On the basis of these figures and the evidence that terraces with dimensions in the range 20000–7500 Å^2 predominate (as shown by the electron micrographs), it follows that the spectral features described in the next section of the paper are mainly due to CO adsorbed on the M^{2+}_{5cus} ions that emerge from the extended {100} faces and terraces. The number of parallel oscillators adsorbed on these flat regions is high enough to allow a preliminary study of the adsorbate–adsorbate interactions (either dynamic or static). As the dipolar sums are not infinite, the measured IR frequency shifts will never reach the upper limiting value corresponding to the infinite crystal.

CO Adsorption on Sintered MgO

The absorption of CO at liquid-nitrogen temperature on MgO sintered at 1073 K in a CO_2 atmosphere has already been reported in a previous paper.[1] Owing to the fact that the first measurements were carried out on a dispersive spectrometer under low-resolution conditions, in this paper this system is reinvestigated. The results are illustrated in Fig. 2, where the IR spectra of adsorbed CO in the 2250–2050 cm^{-1} interval for θ ranging from $\theta \rightarrow \theta_{max}$ to $\theta \rightarrow 0$ are shown. On MgO, as well as in the solid solutions, the maximum coverage (θ_{max}) corresponds to the 1CO : 2Me^{x+} stoichiometry because the nearest-neighbour cation–cation distance (*ca.* 2.9 Å) is lower than the van der Waals distance of CO (*ca.* 3.3 Å).

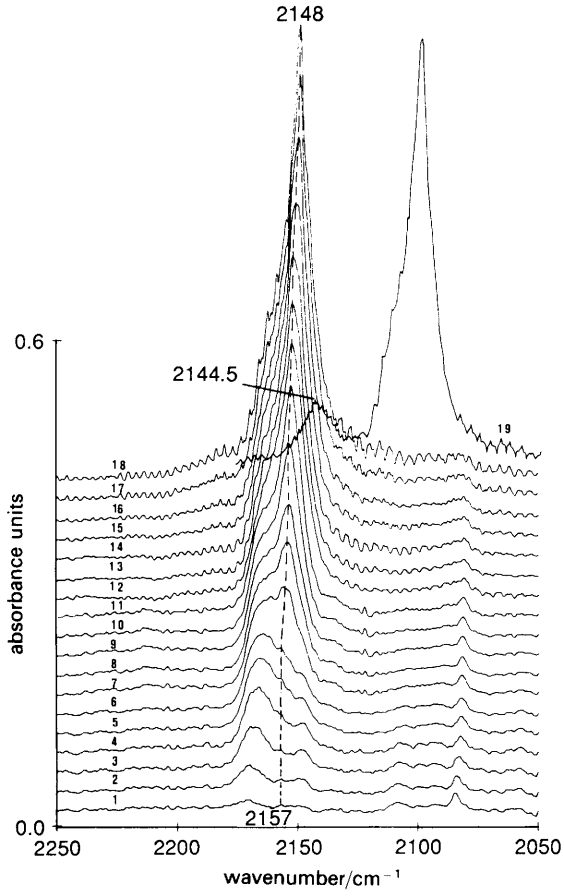


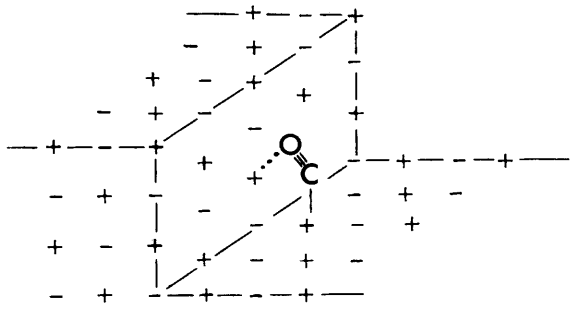
Fig. 2 IR spectra of CO adsorbed at 77 K on sintered MgO. 1–18, ^{12}CO at increasing coverages (final pressure 40 Torr); 19, ^{12}CO/^{13}CO (*ca.* 15 : 85) at maximum coverage

The complex spectrum of Fig. 2 can be explained by the superposition of several absorptions as follows: (i) absorption at 2170–2164 cm^{-1}; this appears as a shoulder at high coverages and becomes a well shaped peak at $\theta \rightarrow 0$; (ii) absorption at 2157–2148 cm^{-1}; this is the main band and is associated with the predominant surface sites; (iii) weak absorption at 2150–2146 cm^{-1}; this is distinctly observable only at the lowest coverages and is associated with a species more strongly adsorbed with respect to the previous one; (iv) weak absorptions in the 2120–2070 cm^{-1} interval: these weak bands are the first to appear upon dosing with CO and, unlike the previous ones, are not destroyed upon desorption of CO even at room temperature.

The bands in the 2170–2164, 2150–2146 and 2120–2070 cm^{-1} intervals are particularly strong on high surface area (unsintered) samples and hence must be associated with defective sites. The assignment of the 2157–2148 cm^{-1} peak to CO adsorbed on Mg^{2+}_{5cus} ions emerging on the (100) faces is confirmed by CO adsorption experiments on MgO smoke (*i.e.* MgO constituted by nearly perfect cubic microcrystals with predominant (100) faces.[26,27]

As the aim of our paper does not concern the assignment of CO bands associated with defects, we briefly recall that: (i) the 2170–2164 cm^{-1} absorption is due to CO on tetracoordinated ions located on edges or steps;[26,28] (ii) the 2150–2146 cm^{-1} peak is probably due to CO bonded on both the C and O sides at step sites as found on unsintered alkali-metal halides[29] as shown in Scheme 1; (iii) the low-frequency features at 2120–2070 cm^{-1} correspond to the stretching vibrations of ketenic C=C=O groups in $C_nO^{2-}_{n+1}$ species formed by interaction of CO with unsaturated

O^{2-}_{3cus} ions located on corners.[28] Note also that on unsintered samples a weak band at *ca.* 2203 cm^{-1} is also observed, and has been assigned to CO adsorbed on Mg^{2+}_{3cus} sites.[28]



Scheme 1

Returning to CO adsorbed on the (100) faces, the stretching band involved gradually shifts from 2157 ($\theta \rightarrow 0$) to 2148 cm^{-1} ($\theta = 1$) as a consequence of the build-up of lateral interactions. According to the considerations already included in the Introduction, these interactions are essentially of the through-space type and, in the dipole–dipole approximation, the frequency shift results from either static and dynamic effects. The relative weights of the two contributions can be estimated by using the limit dilution method as proposed by Hammaker *et al.*[16] The difference (Fig. 2) between the stretching frequency of pure ^{12}CO (2148 cm^{-1}) and the frequency of ^{12}CO diluted by ^{13}CO in the ^{12}CO–^{13}CO mixture (2144.5 cm^{-1}), both measured at $\theta = 1$, gives an estimate of the dynamic dipole–dipole interaction (positive shift $\Delta\tilde{\nu}_{dyn} = +3.5 \pm 0.5$ cm^{-1}). According to the usual methods the effect of the static interactions on the stretching frequency can then be evaluated as $\Delta\tilde{\nu}_{stat} = -12.5 \pm 0.5$ cm^{-1}). Note that the frequency of adsorbed CO and the total shift, as well as the $\Delta\tilde{\nu}_{dyn}$ and $\Delta\tilde{\nu}_{stat}$ shifts, are similar to those observed on NaCl.[10]

On the basis of the previous literature,[1–13] it is evident that all these phenomena can be explained by assuming that the adsorbed CO is in an end-on configuration, with the carbon pointing towards the Mg^{2+} ions and that this interaction is mainly due to the electrostatic fields at the surface cations.

As shown by Escalona Platero *et al.*[1] and further confirmed by specific intensity data,[14] the CO adsorption on cationic sites does not change the dynamic polarizability α_v of CO very much, in agreement with the view that the orbital overlap contributions to the adsorption energy on non-transition-metal ions is small or negligible.

CO Adsorption on Sintered NiO/MgO Solid Solutions

The CO adsorption at low temperature on NiO/MgO (*ca.* 10%) solid solutions gives rise to a complex spectrum in the 2250–2050 cm^{-1} range (Fig. 3). Besides the already discussed bands, typical of CO adsorbed on the Ni^{2+}-free regions of the MgO matrix, the following new features are observed: (i) an additional band in the 2130 cm^{-1} ($\theta = 1$)–2144 cm^{-1} ($\theta \rightarrow 0$) range; (ii) an extra triplet at 2094, 2068, 2060 cm^{-1}. As already reported[20,21] these bands are due to surface carbonylic species formed by interaction of CO with Ni^{2+} ions in particularly exposed positions and hence highly coordinatively unsaturated (typically defective). Since these species rise from defective sites, they shall not be discussed in detail (for more detailed investigation see ref. 21).

As discussed, the main band in the 2144–2130 cm^{-1} (by far the most intense) is associated with CO adsorbed on penta-

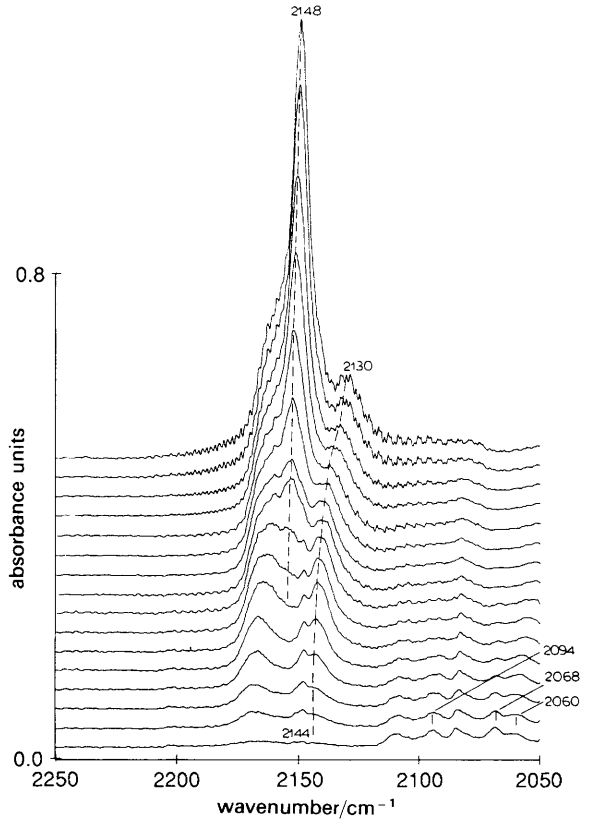
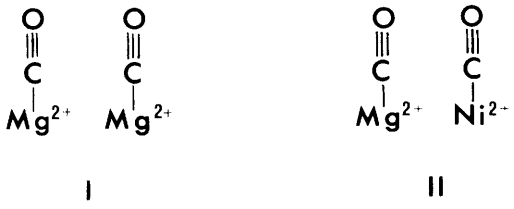


Fig. 3 IR spectra of CO adsorbed at 77 K on sintered NiO/MgO solid solution (increasing coverages, final pressure 40 Torr)

coordinated Ni^{2+} ions located on (100) faces and terraces. The interaction energy of CO on Ni^{2+} is very similar to that of CO on Mg^{2+} ions on the same terrace; in fact both adsorptions are fully reversible at the temperature of the IR experiment.

According to the preliminary considerations made in the introduction, the Ni^{2+} ions that emerge from the (100) face of the solid solution not only experience the same coordination state of Mg^{2+} ions, but also the nearest possible ionicity (*i.e.* that typical of MgO). Therefore the frequencies of CO adsorbed on Ni^{2+} and Mg^{2+} can be suitably compared (either at low or high coverages) in order to estimate the possible presence of orbital overlap on Ni^{2+} (with the subsequent effects on the permanent dipoles, on the transition dipole moments, and ultimately on the dynamic and static shifts). By first comparing the position of the band of CO adsorbed at low coverage ($\theta \rightarrow 0$) on MgO (2157 cm^{-1}), on NiO (2152 cm^{-1}) and on NiO/MgO solid solutions (2144 cm^{-1}), it can be inferred that the stretching frequency of CO on the solid solution does not tend to the value observed on MgO, as on the contrary expected on the basis of a fully electrostatic model (because Mg^{2+} and Ni^{2+} are surrounded by a medium of very similar ionicity). We are thus forced to admit that a small contribution of d–π orbitals overlap must be involved. It appears that the explanation is really the classic one: an increased ionicity on Ni^{2+} ions induced by the matrix, increases not only the local electrostatic field, but promotes d-orbital overlap with subsequent π-back-bonding. As found for other homogeneous analogues such as $[(NH_3)RuCO]^{2+}$,[30] the effect is weak and the increase of charge density on the CO $2\pi^*$ antibonding orbitals is consequently very small. Nevertheless, this is sufficient to cause an increase of μ_{00}, μ_{11} and μ_{01} in the adsorbed state with subsequent influence on the frequency of CO on Ni^{2+} and on the lateral interactions. This explains why as the CO cover-

age on the Mg^{2+} ions surrounding Ni^{2+} progressively increases (Fig. 3), the band associated with the Ni^{2+}_{5cus}—CO moieties progressively moves from 2144 ($\theta \rightarrow 0$) to 2130 ($\theta = 1$) cm^{-1} ($\Delta\bar{\nu} = -14 \pm 1$ cm^{-1}). As the frequency of CO on Ni^{2+} (2144 cm^{-1}) differs sufficiently from that of CO on Mg^{2+} (2157 cm^{-1}) to prevent relevant dynamic interactions (which means that the observed shift is completely static in nature), it is possible to quantify the variation of μ_{00}. As usual, we shall consider first the two dimers (scheme 2). In **I** the dipole–dipole static shift is proportional to $[\mu_{11}(Mg) - \mu_{00}(Mg)]\mu_{00}(Mg)$, whereas that concerning **II** is proportional to $[\mu_{11}(Mg) - \mu_{00}(Mg)]\ \mu_{00}(Ni)$. The monolayer



I II

Scheme 2

shifts are obtained by multiplying the two terms by the same dipolar sum. On this basis, the shift ratio is:

$$\frac{\Delta\bar{\nu}_{MgO}}{\Delta\bar{\nu}_{(Ni/MgO)}} = \frac{\mu_{00}(Mg)}{\mu_{00}(Ni/MgO)}$$

Since $\Delta\bar{\nu}_{MgO} = -12.5 \pm 0.5$ cm^{-1} and $\Delta\bar{\nu}_{(Ni/MgO)} = -14 \pm 1$ cm^{-1}, the CO adsorption on Ni^{2+} ions in solid solution gives rise to an increment of *ca.* 1.2 times. If we consider that, as shown by Bauschlicher *et al.*,[31,32] the CO interactions on Fe^0, Co^0 and Ni^0 induces a dipole moment increase equivalent to 6 or 7, it is concluded that in our case a very small, but not negligible, π back-bonding is present.

As already shown in the Introduction, the intensity of the absorption peak can give information about the transition dipole moments (in fact the intensity is proportional to μ_{01}^2). In fact, if there were no difference between the μ_{01} transition moments of CO on Mg^{2+} and Ni^{2+} (as expected on the basis of the electrostatic model) the intensity of the Ni^{2+}—CO peak should be *ca.* 10% of the total intensity (Ni^{2+}—CO plus Mg^{2+}—CO). The measured value is *ca.* 20% and is associated with an increase of μ_{01} by a factor of 1.4–1.5. This can also be explained by hypothesizing that some overlap is involved.

CO Adsorption on Sintered CoO/MgO Solid Solutions

We must state beforehand that the stretching frequency of CO on CoO (100) faces at $\theta \approx 0$ falls at 2136 cm^{-1},[33] *i.e.* at a lower frequency than that observed on NiO (2152 cm^{-1}) and on MgO (2157 cm^{-1}). Also in this case the adsorption is weak and reversible at the temperature of the IR experiment.

In general terms, the IR spectrum (Fig. 4) is similar to that observed on NiO/MgO solid solutions, with the following differences: (i) the band associated with Co^{2+} ions is shifted to lower frequency (2118–2100 cm^{-1}); (ii) the ketenic species on the defective sites of the matrix shows a weak intensity; (iii) a new peak at 2083 cm^{-1}, due to CO on highly coordinatively unsaturated Co^{2+} ions on defective sites,[22–24] is present; (iv) a gradual shift ($\Delta\bar{\nu} = -18 \pm 1$ cm^{-1}) of the Co^{2+}_{5cus}—CO peak towards lower frequencies is observed by increasing the coverage on the Mg^{2+} ions. From these data it is evident that the dilution of Co^{2+} ions inside the ionic MgO lattice affects the frequency of adsorbed CO in a manner similar to that observed for Ni^{2+} ions in solid solution. As a consequence of the dilution, a decrease from 2136 (CoO) to 2118 cm^{-1} (Co^{2+}/MgO) and from 2152 (NiO) to 2144 cm^{-1} (Ni^{2+}/MgO) is observed. It is noticeable that the frequency difference between CO on Co^{2+} in MgO and CO on Mg^{2+} in MgO is quite consistent (40–50 cm^{-1}): this seems to imply a stronger back-donation from the Co^{2+} d-orbitals. In this respect, the CO^{2+}_{5cus}—CO complexes are slightly more stable to outgassing.

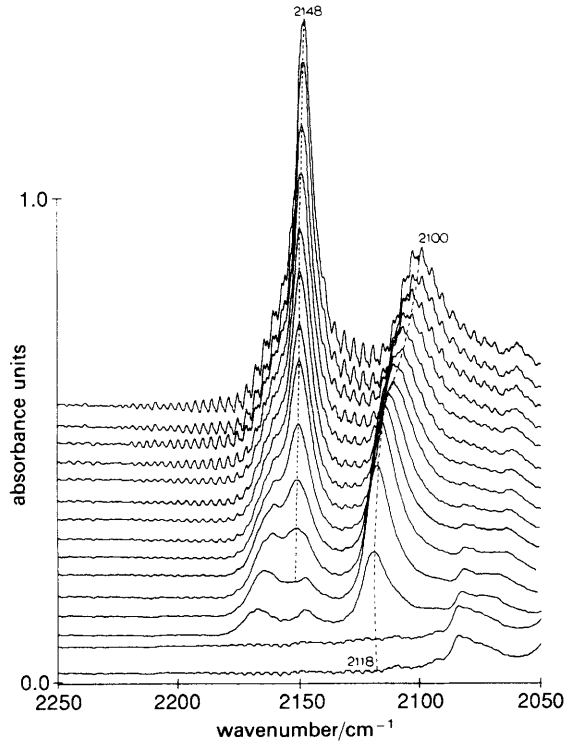


Fig. 4 IR spectra of CO adsorbed at 77 K on sintered CoO/MgO solid solution (increasing coverages, final pressure 40 Torr)

For the same reasons as discussed before, the $\Delta\bar{\nu} = -18 \pm 1$ cm^{-1} shift is totally static in nature and must be compared with the $\Delta\bar{\nu} = -14 \pm 1$ cm^{-1} shift observed on NiO/MgO. Following the considerations developed for the NiO/MgO system, the larger shift is a consequence of the increase of μ_{00} for CO on Co^{2+} (an increment of *ca.* 1.4 is inferred with respect to Mg^{2+}) and is in agreement with the stronger d–π overlap hypothesized before.

Some additional information about the perturbation caused by the adsorption on Co^{2+} sites on the electronic structure of the CO molecule, comes also from the intensity evaluation of the Co^{2+}_{5cus}—CO peak. The intensity of the 2100 cm^{-1} band is *ca.* 40% of the total (instead of 10% as expected on the basis of a purely electrostatic model). This means that μ_{01} has increased (with respect to Mg^{2+}—CO) by a factor of 2 (while for the Ni^{2+}—CO case an increment of 1.4–1.5 was observed). This observation further supports the hypothesized presence of a modest d–π overlap contribution.

Conclusions

In a simple experiment, the dilution of Ni^{2+} and Co^{2+} ions inside an MgO ionic lattice is obtained through formation of solid solutions. Mg^{2+}, Ni^{2+} and Co^{2+} emerging on the surface experience the same coordination state and very similar ionicity (typical of the MgO matrix). By comparing the frequencies of CO adsorbed on Ni^{2+} (or Co^{2+}) and Mg^{2+} ions, it is also possible to verify the validity of the fully electrostatic model of CO bonding and to investigate the possible contribution of d–π overlap.

We conclude that on Ni^{2+} and Co^{2+} d–π overlap contributes, with subsequent effect on the permanent and on the transition dipole moments and, ultimately, on dynamic and static frequency shifts (observed when the coverage is increased from 0 to 1). As the frequency of CO on Ni^{2+} and Co^{2+} differs sufficiently from that of CO on Mg^{2+} to prevent relevant dynamic interactions, the observed shift, completely static in nature, allows estimation of the variation of μ_{00}. With respect to CO on MgO the increment of μ_{00} is *ca.* 1.2 times for Ni^{2+} and *ca.* 1.4 for Co^{2+}. Also the transition dipole moments are modified by a factor of *ca.* 1.4 (Ni^{2+}) and *ca.* 2 (Co^{2+}).

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