Density Functional Investigations of Adsorption at Metal Oxide Surfaces

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Abstract. Density functional investigations of molecular adsorption at ionic metal oxide surfaces are reviewed. As a typical example, we have considered the adsorption of CO at a perfect and at a Ni-doped MgO(001) plane as well as at edge and corner sites of MgO. The geometry of the complexes, the binding mechanism and the spectroscopic manifestation of the surface species are analyzed. Special attention is paid to vibrational frequencies and intensities. A reduction of the Mg-O bond ionicity below the value of complete charge separation (±2 au) and its possible effect on values of computed parameters are also discussed.

1. Introduction

In the past decade a growing number of investigators have turned their attention to the surface chemistry and physics of ionic solids. These studies have demonstrated that the chemical bonds and the structure of adsorption complexes at insulating surfaces may differ significantly from those found at metals and semiconductors [1,2 and other articles in this volume]. Theoricians responded quite strongly to these experimental activities. Their efforts to rationalize the adsorption and reaction phenomena on ionic materials using various quantum chemical models have been reviewed elsewhere [3,4 and other articles in this volume]. However, one of the most powerful tools of quantum chemistry, the first-principles density functional approach, has not been used until recently for the elucidation of this type of surface problems. Here, we will review the applications of the linear combination of Gaussian-type orbitals local density functional (LCGTO-LDF) cluster method [5-7] to adsorption complexes at ionic metal oxide surfaces. This method combines a rather accurate description of structural and vibrational spectroscopy parameters with computational efficiency which permits one to consider realistic cluster models, also containing heavy many-electron atoms [5,7]. In spite of some deficiencies of the LDF approach, e.g. the underestimation of band gaps and the insufficient localization of the valence electrons in narrow-gap oxides of 3d metals [8], one may hope for a

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successful modelling of ground-state features of wide-gap insulators. Moreover, where necessary, the LDF results can be systematically improved with the help of self-interaction corrections [8]. As will be demonstrated, the LCGTO-LDF method is a very useful instrument for investigations of molecular interactions and processes at ionic surfaces.

Alkali-metal halides and oxides of the alkaline-earth metals of the rock salt structure exhibit a rather similar adsorption affinity to CO molecules which are commonly used as a probe for detecting Lewis acid sites with the help of infrared (IR) spectroscopy [9]. On the (001) plane, CO is found to adsorb only at low temperatures, on top of the cations and with its molecular axis normal to the surface [10-12]. (A different structure of the NaCl(001)/CO monolayer has been reported below 35 K [13].) For the adsorption on cations in this coordination, a blue shift $\Delta \omega$(C-O) of the C-O frequency by 10 - 20 cm$^{-1}$ (relative to its value in the gas phase) is observed in the zero-coverage limit. The frequency gradually moves to smaller values when the coverage increases. The adsorption of CO on low-coordinated cations of sintered polycrystallites [9,11] or smoke [12] is usually accompanied by larger values of $\Delta \omega$(C-O). The vibrational polarizability of adsorbed CO, which is proportional to the IR intensity of the C-O mode, was determined on the surface of MgO and of alkali-metal halides to be half that of the free molecule [10]. The polarizability increases noticeably for the carbonyl complex with Ni$^{2+}$ impurity at MgO(001) [11]. However, no direct measurement of the C-O molar absorption coefficient has been reported so far.

Here, the adsorption system MgO/CO is discussed as a representative for weakly bonded carbonyl complexes at ionic surfaces. We will review the results of the first attempts [14-17] to rationalize a large body of structural, binding and vibrational spectroscopy parameters (including IR intensities) of various MgO/CO adsorption species within the framework of LCGTO-LDF model cluster approach. The results are supplemented by LCGTO-LDF calculations of MgO slabs [18] based on the FILMS program package [19,20] to examine in detail the charge distribution and the Madelung field at the adsorption sites of a clean surface.

2. Computational Details

The LCGTO-LDF method [5-7] is employed in the X$\alpha$ approximation ($\alpha = 0.7$). Spin-polarization has been taken into account for the open-shell models of the Ni impurity centers ($3B_1$ state). A five-fold coordinated site, Mg$_{5c}$, on a perfect MgO(001) surface is represented by the clusters Mg$_3$O$_6$(9,9) and Mg$_{13}$O$_{13}$(21,5) of $D_{4h}$ symmetry [14,15]. The designation $(n, m, ...)$ indicates a cluster with $n$ substrate atoms in the first layer, $m$ atoms in the second layer etc. The cluster Mg$_{13}$O$_{13}$(21,5) offers five cationic adsorption sites for CO. A Ni$^{2+}$ impurity is modeled by the cluster NiMg$_3$O$_6$(9,9). The clusters Mg$_3$O$_6$(3,6,3) ($C_{2v}$) and Mg$_4$O$_4$(1,3,3,1) ($C_{3v}$) are chosen to describe low-coordinated cations at edges (Mg$_{ak}$) and corners (Mg$_{3c}$) of microcrystallites, respectively [17]. The central
position of these clusters is occupied by either a Mg or a Ni cation. All cluster models exhibit a stoichiometric constitution. They are embedded in electroneutral matrices of point charges (PC) to reproduce the Madelung field at the adsorption site. The PC arrays contain up to about 1700 charges of ±2 au. In some cases, the charge was reduced from its nominal value to ±1.5 au for comparison. Simplified substrate clusters consisting only of the PC arrays were used to evaluate electrostatic effects. The results are reported for unrelaxed substrate models based on a lattice parameter of 4.21 Å (for a validation of this approach see refs. [16,17]).

Two of the four conceivable MgO/CO vertical adsorption situations at on-top sites, namely the -CO and -OC binding to anions, are ruled out because of the repulsive character of the corresponding interactions [14,21]. The distances M-CO (M = Mg, Ni) and C-O were computed for the complexes where the CO molecule was assumed to be oriented upright along the main (z) axis of a corresponding point group C₅ᵥ, either C- or O-end down. First, the M-C (M-O) distance was optimized for a fixed C-O bond length and then the C-O distance was varied, keeping the CO center of mass fixed as calculated in the previous step. The normal modes of MgO/CO have been approximated by the MgO-CO and C-O internal modes. Absolute IR intensities have been calculated in the double-harmonic approach [22] according to which an IR intensity is proportional to the square of the dynamical dipole moment of the i-th normal mode, \( \partial \mu / \partial r_i \). Basis sets for the LCGTO-LDF cluster models have been described elsewhere [6,7,14]. The same orbital basis sets were employed in the cluster and in the slab calculations [18] in order to minimize discrepancies between both methods.

3. Adsorption of CO Molecules at the Ideal and Ni-Doped MgO(001) Surface

3.1 Isolated CO at Perfect MgO(001)

We start our discussion with the case of an isolated CO on a perfect MgO(001) surface (Table 1, models I, II, V and VI). The following questions are relevant to this topic:
1. What is the structure of the surface complexes manifested in the IR spectra?
2. Is the adsorption bond purely electrostatic or does a charge transfer contribute as well?
3. Which interactions determine the adsorption-induced shift of the C-O frequency?
4. How and why does the IR intensity change of the C-O mode take place?
5. How rigorous is to embed the cluster into an array of point charges of ±2.0 au? Both the adsorption energies and the frequencies \( \omega (M-CO) \) indicate a rather weak interaction which is somewhat overestimated in the LDF cluster approach [14]. The computed results, low frequency < 200 cm⁻¹ and small intensity of \( \approx 0.5 \) km/mol, are in line with the fact that no detection of the corresponding
vibrational peak has been reported. The classical C-down orientation of the carbonyl (model I) is favoured energetically. However, model VI with CO coordinated via oxygen also exhibits an energy minimum along the Mg-CO coordinate, possibly corresponding to a stable complex. In the case of C-end adsorption, a calculated blue frequency shift +54 cm⁻¹ of the C-O mode with respect to the value for free CO is consistent with the experimental value of +14 cm⁻¹ [11], but far too large. Model V for the O-end CO adsorption yields a red shift (Table 1). Thus, the alternative orientation of CO with the oxygen "downward" may be ruled out by this comparison. Nevertheless, it would be interesting to define experimental conditions under which such an unusual "isocarbonyl" moiety may be detectable and to predict its properties (models VI-X). The Mg-CO distance has not yet been measured and the LDF data can only be compared to Hartree-Fock (HF) results [23] which are noticeably longer (by 0.1 to 0.3 Å) than those for the models I and V. This difference seems to reflect a general tendency of the HF level of theory to underestimate the weak M-CO bonding for oxide surfaces compared to the LDF method [14,17].

The Mg₅₋₆-CO bonding, being mostly electrostatic [23], was shown to be accompanied by a small σ charge redistribution directed to the substrate [14,15]. The transferred charge is about 0.1 au. Interpreting the dynamical dipole moment $\partial \mu / \partial z$ as an effective charge, one can see from Table 1 that the Mg₅₋₆-CO bond stretching causes a displacement of 0.12 au of the electronic density from CO to the surface. It is not easy to isolate the charge transfer contribution to the adsorption energy, but it can be illustrated by the effect on the overall C-O frequency shift. The value due to charge transfer alone, 17 cm⁻¹ [14], is comparable both to the experimental shift of 14 cm⁻¹ [11] and to that of Pauli repulsion component calculated by HF method [23]. The direct interaction of a CO molecule with the Madelung field of the surface (model II) generates a small red shift. One may therefore conclude that a substantial part of the overall shift $\Delta \omega (C-O) = 54 \text{ cm}^{-1}$ computed for the model I is associated with the charge transfer and thus is "chemically" induced.

The discrepancy between the LDF and the experimental value of $\Delta \omega (C-O)$ warrants a further remark. While the direct influence of the surrounding point charges on the C-O frequency shift is small, their indirect effect through a modification of the substrate cluster may be quite important. This follows from a study where the environment of the cluster Mg₉O₇-CO was constructed from charges of ±1.5 au. In this model, the shift $\Delta \omega (C-O)$ is reduced to 16 cm⁻¹ (Table 1) which (fortuitously) agrees with the experimental value. A similar tendency to "improve" the computed shift for the models IV and V (Mg₅₋₆-CO and Mg₅₋₆-CO) with point charges of ±1.5 should also be mentioned (Section 4 and ref. [17]). This finding supports the assumption that field effects are overestimated in embedded cluster models which are based on the nominal ionicity Mg²⁺-O²⁻. Further arguments along the same line will be given in the next section and can be also found elsewhere [14,17].

The computed IR intensity of the C-O mode for adsorption on MgO(001) does not reveal a decrease relative to the value for the gas phase CO, as might be
Table 1: LCGTO-LDF results for cluster models of MgO/CO adsorption complexes and for the free CO molecule: equilibrium height $z_e$ of the nearest adsorbate atom above the surface cationic center, C-O distance $r_e$, energy $\omega_{(M-CO)}$ of the substrate-adsorbate stretching fundamental vibrational transition, shift $\Delta \omega_{(C-O)}$ of the C-O vibrational frequency (with respect to the value calculated for the CO molecule) and the corresponding absolute IR intensity $I_{(C-O)}$, adsorption energy $D_e$, induced dipole moment $\Delta \mu = \mu(N_2H_5-CO) - \mu(N_2H_5) - \mu(CO)$, derivatives of the dipole moment $\partial \mu / \partial z$ and $\partial \mu / \partial r$ along with the $\sigma$ and $\pi$ components $\partial \mu / \partial r_{\sigma}$ and $\partial \mu / \partial r_{\pi}$.

<table>
<thead>
<tr>
<th>Cluster</th>
<th>$z_e$ (Å)</th>
<th>$\omega_{(M-CO)}$ (cm$^{-1}$)</th>
<th>$\partial \mu / \partial z$ (au)</th>
<th>$r_e$ (Å)</th>
<th>$\Delta \omega_{(C-O)}$ (cm$^{-1}$)</th>
<th>$I_{(C-O)}$ (km/mol)</th>
<th>$\partial \mu / \partial r_{\sigma}$ (au)</th>
<th>$\partial \mu / \partial r_{\pi}$ (au)</th>
<th>$D_e$ (eV)</th>
<th>$\Delta \mu$ (D)</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>MgO$_2$-CO</td>
<td>2.22</td>
<td>183 (158)</td>
<td>0.12</td>
<td>1.124</td>
<td>54 (16)</td>
<td>124</td>
<td>-0.93</td>
<td>0.50</td>
<td>-1.42</td>
</tr>
<tr>
<td>II</td>
<td>PC(001)-CO</td>
<td>2.22$^{(c)}$</td>
<td>-</td>
<td>-1.132</td>
<td>-8 (0)</td>
<td>40</td>
<td>-0.53</td>
<td>0.54</td>
<td>-1.07</td>
<td>0.62</td>
</tr>
<tr>
<td>III</td>
<td>NiMg$_2$O$_5$-CO</td>
<td>1.88</td>
<td>327</td>
<td>0.41</td>
<td>1.126</td>
<td>45</td>
<td>283</td>
<td>-1.41</td>
<td>0.72</td>
<td>-2.15</td>
</tr>
<tr>
<td>IV</td>
<td>Mg$_5$O$_3$-CO</td>
<td>2.18</td>
<td>198 (185)</td>
<td>0.08</td>
<td>1.124</td>
<td>56 (33)</td>
<td>125</td>
<td>-0.94</td>
<td>0.46</td>
<td>-1.39</td>
</tr>
<tr>
<td>V</td>
<td>Mg$_4$O$_3$-CO</td>
<td>2.23</td>
<td>197 (184)</td>
<td>0.01</td>
<td>1.121</td>
<td>85 (59)</td>
<td>88</td>
<td>-0.79</td>
<td>0.48</td>
<td>-1.27</td>
</tr>
<tr>
<td>CO</td>
<td>-</td>
<td>-</td>
<td>-1.130</td>
<td>2 $169^{(d)}$</td>
<td>66</td>
<td>-0.68</td>
<td>0.37</td>
<td>-1.05</td>
<td>-</td>
<td>0.26$^{(e)}$</td>
</tr>
<tr>
<td>VI</td>
<td>MgO$_2$-OC</td>
<td>2.19</td>
<td>122</td>
<td>-0.17</td>
<td>1.137</td>
<td>-60</td>
<td>201</td>
<td>1.18</td>
<td>-0.17</td>
<td>1.34</td>
</tr>
<tr>
<td>VII</td>
<td>PC(001)-OC</td>
<td>2.19$^{(c)}$</td>
<td>-</td>
<td>-1.132</td>
<td>-18</td>
<td>99</td>
<td>0.83</td>
<td>-0.26</td>
<td>1.09</td>
<td>0.24</td>
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<tr>
<td>VIII</td>
<td>NiMg$_2$O$_5$-OC</td>
<td>2.06</td>
<td>202</td>
<td>-0.19</td>
<td>1.136</td>
<td>-42</td>
<td>206</td>
<td>1.20</td>
<td>0.09</td>
<td>1.10</td>
</tr>
<tr>
<td>IX</td>
<td>Mg$_5$O$_3$-OC</td>
<td>2.07</td>
<td>176</td>
<td>-0.21</td>
<td>1.139</td>
<td>-76</td>
<td>196</td>
<td>1.17</td>
<td>-0.18</td>
<td>1.35</td>
</tr>
<tr>
<td>X</td>
<td>Mg$_4$O$_3$-OC</td>
<td>2.05</td>
<td>197</td>
<td>-0.29</td>
<td>1.143</td>
<td>-98</td>
<td>269</td>
<td>1.37</td>
<td>-0.12</td>
<td>1.49</td>
</tr>
<tr>
<td>OC</td>
<td>-</td>
<td>-</td>
<td>-1.130</td>
<td>2 $169^{(d)}$</td>
<td>66</td>
<td>0.68</td>
<td>-0.37</td>
<td>1.05</td>
<td>-</td>
<td>-0.26$^{(e)}$</td>
</tr>
</tbody>
</table>

$^{(a)}$ Results obtained with surrounding point charges of $\pm 1.5$ au are shown in parentheses.  
$^{(b)}$ For $\partial \mu / \partial r$: 1 au = 4.80 D/Å  
$^{(c)}$ Not varied.  
$^{(d)}$ Reference value for the determination of $\Delta \omega_{(C-O)}$.  
$^{(e)}$ Computed dipole moment for free CO or OC.
expected from the analysis of the dynamic contribution to the C-O frequency shift with increasing coverage [10]. A detailed discussion of the reasons why this indirectly determined intensity is believed to be underestimated has been presented previously [14]. The calculated intensity enhancement can be rationalized in terms of $\sigma$ and $\pi$ components of the dynamical dipole moment $\partial \mu / \partial r$(C-O) which coincides here with the electronic dynamical dipole moment (the center of nuclear charges remains fixed when the C-O bond stretches). In this approach $\partial \mu_{\sigma} / \partial r$ and $\partial \mu_{\pi} / \partial r$ should be identified with the "oscillating" charge density of $\sigma$ and $\pi$ orbitals. An increase of $\partial \mu / \partial r$ concomitant with the C-O bond elongation corresponds to a displacement of the electronic density down to the surface, a decrease indicates an upward displacement. The effects may be caused by field, Pauli repulsion, charge transfer and polarization.

The dynamical dipole moment of CO is the sum of a small (by the absolute value) $\sigma$ component and a large $\pi$ component of opposite signs. Inspection of Table 1 reveals that the electrostatic field (model II) causes a decrease of I(C-O) due to a polarization of the CO $\sigma$ charge directed to the (001) plane. The $1\pi$ orbital of CO is only slightly affected by the field and the $\sigma$ channel is responsible for the reduction of the absolute value of $\partial \mu / \partial r$ and thus for the smaller intensity. A similar analysis may be carried out for the field-induced intensity enhancement in model VII with the O-end coordinated CO. The attraction of the $\sigma$ charge by the field increases the negative $\partial \mu_{\sigma} / \partial r$ component and therefore also the intensity since the $\pi$ contribution is negligible. In the presence of the substrate atoms (model I) which allow additional interaction mechanisms to occur the prevailing effect is a decrease of the negative $\partial \mu_{\sigma} / \partial r$ component. This is mainly due to the interaction of the CO $1\pi$ orbital with the nearest-neighbour oxygen anions [14]. For the O-down CO (model VI), both the $\sigma$ and the $\pi$ interactions with the substrate contribute to the overall increase of the intensity. It is interesting to note that in this case the $\sigma$ charge transfer, as measured by a Mulliken population analysis, takes place predominantly via the CO $4\sigma$ orbital. The $\pi$ charge displacement, also in the direction toward the substrate, is essentially due to changes in the CO $1\pi$ orbital.

### 3.2 On the Ionicity of the Mg-O Bond

The results of the cluster models for isolated CO at a perfect MgO(001) surface provide some evidence for a reduced metal-oxygen charge separation [14]. On the other hand, HF calculations for bulk MgO [24] and MgO(001) slabs [25] find the Mg-O bond to be perfectly ionic. To investigate the question of possible covalent contributions, we have carried out LCGTO-LDF calculations of 2D-periodic MgO(001) slabs of up to three layers [18]. The analysis of the charge separation is based exclusively on the charge density and its ultimate goal is to define effective point charges to be used in the PC arrays surrounding the adsorption cluster models. Two procedures were employed: one following the topological
Fig. 1: Valence one-electron wave functions of the MgO(001) monolayer: O 2s dominated wave function (at $\Gamma$ point, left); O 2p dominated wave function (at $\bar{M}$ point, right). The plots display the plane of the nuclei, oxygen at the center surrounded by four magnesium neighbours. Positive and negative values are indicated as solid and dashed lines, the nodes are shown as dotted lines. The values of the contours are 0.56, 0.32, 0.18, 0.10, and 0.056 au.

Atom approach suggested by Bader [26] and a direct analysis of the Madelung field near the surface.

The first method relies on a division of space into disjoint, space-filling atomic regions of reasonable shape and thus avoids the ambiguities associated with a Mulliken population analysis. Atomic boundaries are defined as zero-flux surfaces in the gradient field of the total charge density [26].

The valence electronic structure of MgO is dominated by the 2s and 2p electrons of the $O^{2-}$ anion. Two typical examples for O 2s and 2p dominated one-electron wave functions are shown in Fig. 1. The atomic orbital contributions around the oxygen atom are clearly discernible. A significant overlap between neighbouring O 2p orbitals can also be seen. However, in the present context, the most important features are the non-vanishing s- or p-type contributions at the Mg sites. From their nodal pattern, they obviously have to be attributed to admixtures of Mg 3s and 3p orbitals. For the derivation of an effective point charge model it is irrelevant whether these contributions represent a covalent contribution to the Mg-O bond or whether they are regarded as a consequence of the orthogonalization of the rather extended oxygen orbitals with respect to the magnesium core orbitals.

To quantify the charge separation in MgO, effective atomic charges were calculated for the topologically defined atomic regions (Table 2). Their size and shape are illustrated in Fig. 2 for a triple layer (3L). The two types of ions are clearly discernible and the Mg cations are, as expected, smaller than the oxygen anions. In agreement with the view that O 2p electrons are "pushed" into the unoccupied states of the neighbouring magnesium ions, the effective charges are found to decrease with increasing coordination of the atomic regions.
Table 2: Atomic charges of the Mg cation (in au) derived from the LDF charge distribution in MgO slab models of one to three layers (L).

<table>
<thead>
<tr>
<th></th>
<th>1L</th>
<th>2L</th>
<th>3L</th>
</tr>
</thead>
<tbody>
<tr>
<td>topological atoms</td>
<td>1.70</td>
<td>1.66</td>
<td>1.66 (outer)</td>
</tr>
<tr>
<td>Madelung field</td>
<td>1.60</td>
<td>1.77</td>
<td>1.81</td>
</tr>
</tbody>
</table>

Alternatively, one may directly analyze the Madelung field around the adsorption site. If this analysis were based on an extended surface with the finite cluster removed, significant contributions to the electric field would be due to the boundary region and the results would depend crucially on the choice of the boundary. Therefore, the well-defined Madelung field of a complete substrate slab was analyzed. From a 2D-periodic version of the classical multipole expansion one finds [18] that the electrostatic potential above a slab which does not exhibit a total dipole moment, like MgO(001), can be expressed as

\[
\varphi(r, z) = \frac{2\pi}{A_{UC}} \sum_K \frac{M_K}{|K|} e^{iKr} e^{-|K|z}, \quad \text{with} \quad M_K = \int \rho(r, z) e^{-iKx} e^{iKy} d^2r dz .
\]

The main contribution to the Madelung field is connected to the reciprocal lattice vectors \(K = (2\pi/a, 0), (0, 2\pi/a)\) and, due to the alternating phase factor \(\exp(-iKr)\), provides a suitable measure for the charge separation in a MgO(001) layer. This field is essentially determined by the charge distribution in the top substrate layer.

Almost no interlayer charge redistribution occurs as can be seen from the

Fig. 2: Valence electron density of a MgO(001) triple layer shown in the [100] plane perpendicular to the surface. Large circles enclose the oxygen, small circles the magnesium sites. The values of the contours (solid lines) are 0.32, 0.10, 0.032, and 0.010 au, the dotted lines indicate the zero-flux boundaries of the atomic regions.
small difference between the atomic charges determined for the double and the triple layer (Table 2). The Madelung charges for a monolayer are smaller, reflecting the unique geometrical fact that the O 2p electrons can be delocalized into the vacuum at both sides of the layer.

It is important to note that both procedures yield effective charges which are significantly reduced from the nominal value ±2 au. They may be even used to construct embedding models with spatially varying point charges.

3.3 CO at a Ni Impurity Site

Characteristics of carbonyl complexes on pure MgO [11,12] have been compared to those on NiO and on Ni impurities of doped MgO [10,11]. The experimental data for the latter systems exhibit notable differences: the shift Δν(C-O) is smaller, the C-O vibrational polarizability is larger and the bonding to the substrate stronger. However, minimal cluster HF models [23] do not reveal any significant differences between the CO adsorption on MgO(001) and on NiO(001). In particular, no contribution of the Ni 3d orbitals to the adsorption bonding has been found which is usually assumed to cause the observed diversity of the adsorption parameters in oxides of alkaline-earth and of transition metals [10,11].

The experimental data were obtained in an IR spectroscopic study of CO adsorbed on polycrystallites of MgO as well as on a NiO/MgO solid solution (10% NiO) [11]. The latter case was aimed at creating an environment of the Ni^{2+} sites which is close to that experienced by the cations in pure MgO. These experiments were interpreted to indicate a Ni(3d)-CO(π) overlap bonding contribution besides a strong electrostatic interaction. Results of the LDF investigation [17] are given in Table 1 (models I, III, VI and VIII). A shorter Ni-CO distance and a larger adsorption energy as well as the frequency ν(Ni-CO), in particular for the C-down models I and III, clearly indicate a noticeably stronger adsorption interaction at a Ni_{3c} site compared to that at Mg_{3c}. The charge exchange between CO and a Ni_{3c} site is more intense than that in model I, as can be seen from the increase of the dynamical dipole moment ∂ν/∂z. It seems to be a classical charge transfer of σ and π type where the σ channel dominates. Mulliken populations indicate that the partial occupation of the antibonding CO 2π* orbital is accompanied by a notable depletion of the CO 1π orbital [17]. The π interaction is mainly responsible for the reduction of the C-O frequency in the cluster NiMg_{0.9}O_{0.9}-CO (III) related to that for Mg_{0.9}O_{0.9}-CO (I) by 9 cm⁻¹, in line with the measured value of 13 cm⁻¹ [11]. In the IR spectra of CO on the NiO/MgO solid solution [11] one finds several characteristic peaks around 2094-2060 cm⁻¹, some of which may well be a manifestation of CO adsorbed O-down at Ni_{3c} or other Ni-sites. These complexes (model VIII) should exhibit C-O vibrations red-shifted relative to that of free CO. A decisive argument for the presence of marked π contribution in the Ni_{3c}-CO bond, an intrinsic feature of d-metal complexes, can be drawn from the enhanced intensity I(C-O) in the model.
III compared to I, which is in qualitative agreement with experiment [11]. A σ
donation to the substrate increases ∂μσ/∂r, but the back-donation in the π channel
has obviously a stronger effect on the intensity, decreasing the ∂μπ/∂r component
for NiMg5O-CO by a third compared to that in the Mg5O-CO model. The
present results are at variance with those of HF calculations [23] where no
difference was found for CO adsorption at Ni3c and Mg3c centers in oxides.
However, important experimental evidence [11] of specific interactions with the
d-metal sites is qualitatively reproduced and rationalized at the LCGTO-LDF
level of theory. Further studies are necessary to explain why the HF and LDF
cluster results for CO adsorption on alkaline-earth and d-metal oxides exhibit
such large differences.

3.4 Lateral Interaction between the Adsorbed CO Molecules and
Propagation of the Electronic Effects through the Substrate

We will address two questions:
1. What are the reasons for coverage dependence of the static C-O frequency shift
and which role does the substrate play in this phenomenon?
2. Does the lateral interaction between adsorbed molecules affect the absolute IR
intensity of the C-O vibrational mode in a noticeable way?
The coverage dependence of the stretching frequency of adsorbed CO is a
characteristic feature of ionic surfaces [10]. CO adsorbed on the (001) plane of
sintered powder MgO samples exhibits an IR peak at 2157 cm⁻¹ which shifts to
2148 cm⁻¹ when the CO coverage increases to saturation [11] (where the
monolayer, 1CO:2Mg₅O₃, exhibits a c(2×2) surface structure). It is possible to
discriminate dynamic (due to the mutual perturbation of vibrating CO molecules)
and static contributions to the adsorbate-adsorbate interaction. An isotopic
dilution technique yields a positive dynamic shift Δω(C-O) = 3.5 cm⁻¹ when the
MgO(001)/CO coverage increases from zero to the maximum value. Combining
the observed difference of the C-O frequency shift for isolated CO on MgO and
that at saturation, 9 cm⁻¹, one derives a shift of -12.5 cm⁻¹ which is attributed
exclusively to the static CO-CO interaction in the MgO/CO monolayer [11].

A "solvent" and a "chemical" mechanism have been suggested to rationalize
this shift. The solvent effect is a through-space interaction caused by changes in
the local environment at a given site, brought about by filling the nearby sites.
The chemical effect is due to a through-bond perturbation among molecules
adsorbed in adjacent positions. It can occur only through the substrate because
the shortest CO-CO separation, even in the monolayer (4.21 Å), is larger than the
van der Waals distance. If the next molecule coming to the surface finds its
adsorption site in a state of lower acceptor ability because some of the charge
donated by the first CO has been transmitted through the solid, then the
corresponding C-O frequency would be decreased compared to that of an isolated
CO on MgO(001).
The computed frequency for the central CO moiety in a model of monolayer coverage based on the cluster Mg\textsubscript{13}O\textsubscript{13}-(CO)\textsubscript{5}, 2188 cm\textsuperscript{-1}, is red-shifted relative to the value 2199 cm\textsuperscript{-1} for the cluster Mg\textsubscript{13}O\textsubscript{13}-CO (2192 cm\textsuperscript{-1} when corrected for the basis set superposition error) [15]. The agreement with the experimentally derived static shift of -12.5 cm\textsuperscript{-1} [11] may be considered reasonable since the long-range effect of a large number of the surrounding adsorbates is only partly taken into account by the cluster model.

For those models where the substrate is either absent or described as a PC array the calculated static C-O frequency shift is positive [15]. This implies that the through-space perturbation among the adsorbates without a charge exchange involving the substrate can not explain the observed coverage dependence of the C-O frequency. Although the CO adsorption is accompanied by some \( \sigma \) charge transfer to the nearest Mg\textsubscript{5c} ion [14], no delocalization of this charge beyond its oxygen neighbours was found [15]. Thus, the propagation of an electronic effect through a MgO substrate may be ruled out as the dominating mechanism responsible for the coverage dependent static red shift of the C-O frequency. Rather, a change of the electrostatic field in the vicinity of a vibrating CO due to the charge transfer occurring at the adjacent sites may be invoked as a rationalization consistent with the overall picture. To test this hypothesis, each CO molecule has been replaced by point charges: 0.1 au at the CO center of mass and a change of -0.1 au in the Mg\textsubscript{5c} position. The following two models were considered: (i) only the four nearest neighbours of the central CO above a PC(001) array are simulated by these dipoles; (ii) all 80 suitable cationic positions on the upper plane of this array are modified as described. The frequency shift -12 cm\textsuperscript{-1} (with respect to the unmodified PC(001)-CO) in model (ii) is more than twice as large as that of model (i), -5 cm\textsuperscript{-1}. This clearly illustrates the importance of long-range field contributions and supports the explanation of the coverage-induced static frequency shift as an electrostatic solvent effect [15].

Finally, a rather small effect of the MgO/CO coverage on the C-O vibrational intensity should be pointed out. The calculated vibrational intensities for the singleton (165 km/mol) and the monolayer models (148 km/mol) are rather similar and more than twice as large as that calculated for free CO, 66 km/mol. Therefore, the adsorption-induced intensity change may be rationalized in the same way as in section 3.1, leaving aside a coverage dependence.

4. Adsorption of CO Molecules at the Structural Defects of MgO

The calculated C-O frequencies (Table 1, models IV and V) agree qualitatively with the HF data [27] and support the assignment of the high-energy features in the carbonyl region of the IR spectra of CO on polycrystalline MgO: these features are associated with complexes of coordinatively unsaturated cations located at edge and corner positions [10,11]. As discussed in the previous sections, the models based on the surrounding point charges of \( \pm 2.0 \) au
overestimate the Madelung field on MgO(001). The MgO/C-O frequencies for the clusters embedded in PC arrays of smaller charges ±1.5 au are in significantly better agreement with experiment (Δω(C-O) = 27 cm⁻¹ for Mg₄C-CO and Δω(C-O) = 60 cm⁻¹ for Mg₃C-CO complexes [11]), thus also supporting a sub-nominal value of the ionicity of MgO. The strengthened field at the more open Mg₄C and Mg₃C sites is obviously responsible for the main difference in their properties compared to the regular Mg₅C coordination [17]. This effect forces the adsorbate to come closer to the surface and increases the induced dipole moment as well as the adsorption energies. At the same time, a field-induced shift of the C-O frequency becomes noticeable for Mg₃C-CO (25 cm⁻¹ versus -8 cm⁻¹ in the model II). The chemical contribution to the bonding is not very different from that at Mg₅C centers and may be rationalized in a similar way. A partial decrease of the absolute intensity I(C-O) calculated for model V is mainly connected to the missing π interaction with the nearest-neighbour oxygen anions which results in a reduction of the ∂μ/∂r component.

5. Conclusion

The present study demonstrates that the LCGTO-LDF cluster models are adequate to describe very sensitive parameters of weakly bonded adsorption complexes at ionic surfaces. For MgO, a typical representative of such systems, the calculations confirm the assignment of the IR spectra of various MgO/CO species and clarify the origin of the C-O frequency shift. The adsorption-induced enhancement of the absolute IR intensity of the C-O mode is predicted and rationalized in terms of the σ and π components of the CO dynamical dipole moment.

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