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The MgO(110) surface and CO adsorption thereon: II. CO adsorption

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Abstract. The adsorption of a monolayer of CO molecules on the MgO(110) surface was studied at an *ab initio* level. The equilibrium position of the CO molecules above the surface and their bond lengths are optimised and compared for two possible cases: when the molecule is bound to the surface via its C or its O atom. The adsorption energies are found to be relatively small and very close to each other in the two cases (about 6.5 kcal mol^{-1}). The modifications caused by CO adsorption in the electronic charge distribution at the surface and in the density of states are analysed. The relaxation of the CO-saturated surface is found to be almost the same as that of the clean one (about 6.7% of the interplanar distance). The results obtained are compared with those for the (100) surface.

1. Introduction

The CO molecule is widely used in studies of ionic surfaces, including alkali halides, magnesium oxide (MgO) and nickel oxide (Escalona Platero *et al* 1985). Changes in its infrared spectra enable us to learn more about the interaction of molecules with clean and defective solid surfaces and between molecules themselves (Zecchina and Scarano 1986).

In line with the preceding *ab initio* Hartree–Fock (HF) study of the clean MgO(110) surface (Causà *et al* 1987), we performed calculations of CO adsorption on this surface at the same level of accuracy using the CRYSTAL computer code (Dovesi *et al* 1983, 1984a, Causà *et al* 1986b). Despite the fact that no experimental data are available for the (110) surface, this crystal face is a convenient prototype of many real surfaces and can be considered as a set of (100) surfaces with a step in each lattice parameter. The qualitative conclusions drawn below are valid for both (100) and (110) surfaces and thus have a quite general character.

According to experimental studies (Gevirzman *et al* 1969), CO molecules are adsorbed on the surfaces of alkali halides and MgO in the form of a regular array of single molecules oriented perpendicular to the surface. An increase in the CO vibrational frequency at the MgO surface compared with free CO has been reported by Escalona Platero *et al* (1985) and attributed to the stretching of CO due to the interaction with the surface.

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We have considered the periodic 1:1 monolayer adsorption (i.e. to each surface Mg ion is attached one CO molecule) and have optimised the two main parameters determining the adsorption: z, the distance between CO and the surface and d, the CO interatomic separation (figure 1). Since in our opinion there is no clear experimental

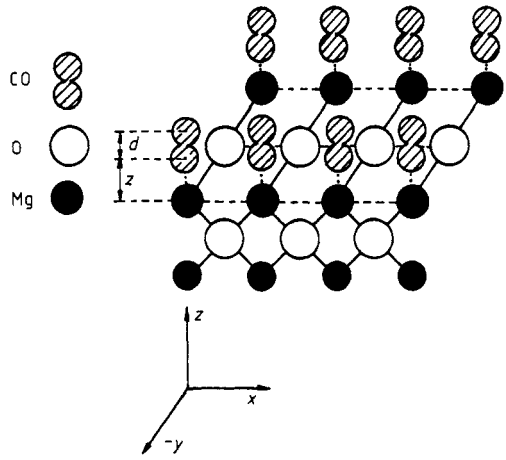

Figure 1. Schematic representation of CO monolayer adsorbed on the (110) surface in a 1:1 concentration and two basic parameters d and z determining adsorption.

discrimination between the two possible ways of binding (through C or O), both cases were considered. On the basis of the preceding study of the clean (110) surface (Causà *et al* 1987) and because of the weak adsorbent–adsorbate interaction, a slab containing two planes is a reasonably good model for the present study; the results have been checked with the three-plane slab. Note that, for the (100) surface, even a single plane has yielded very reasonable results (Dovesi et al 1987).

All the computational conditions referring to the MgO slab have been described previously by Causà *et al* (1986a, 1987). We should add only that for CO the 3-21 G basis set has been used, giving a reasonable compromise between accuracy of results and computational time (Binkley *et al* 1980).

In § 2, surface geometries, adsorption energies, atomic and bond populations are provided and discussed. Further information on the characteristics of the adsorption is also obtained from the difference density maps and density-of-state (DOS) data. General conclusions are drawn in § 3.

2. Results and discussion

2.1. Equilibrium geometry and adsorption energy

Table 1 summarises the main results for the CO adsorption on the two-plane unrelaxed slabs. The CO adsorption energy, which is about 6.5 kcal mol^{-1}, is larger by about 50% than that for the (100) surface. However, it is still considerably smaller than for ordinary chemical bonds. It should be noted that, at the coverage considered here, the shortest CO distance (2.97 Å) is smaller than twice the C atomic radius. The repulsive interaction

Table 1. Calculated geometries, energies and Mulliken populations for CO adsorption on the MgO two-plane slab. The bulk basis set and geometry are used for the latter. The parameters d and z are defined in figure 1. The three free CO bond populations refer to the distances d given in the second row. The indices s and i attached to Mg and O refer to atoms in the first layer (surface) and second layer (internal), respectively.

	Attached atom X		
	C	O	Separated systems
Equilibrium distances			
z (Å)	2.40	2.18	
d (Å)	1.120	1.125	1.129
Adsorption energy (kcal mol^{-1})	6.634	6.383	
Total atomic populations			
O (electrons)	8.422	8.477	8.438
C (electrons)	5.601	5.516	5.562
Mg^{s} (electrons)	10.074	10.079	10.073
O^{s} (electrons)	9.952	9.983	9.922
Mg^{i} (electrons)	10.071	10.071	10.073
O^{i} (electrons)	9.976	9.977	9.922
Net CO charge (electrons)	−0.023	0.007	0.0
Bond populations			
C–O (free CO) (electrons)	0.884	0.878	0.874
C–O (adsorbed CO) (electrons)	0.936	0.798	
Mg^{s}–X (electrons)	0.009	0.018	

between adsorbed molecules is therefore considerable and has been estimated to be about 3.57 kcal mol^{-1} by comparing the energy of the isolated CO monolayer with that of the free CO molecules. In the limit of low density, the adsorption energy at the (110) face should therefore be about 10 kcal mol^{-1}.

The adsorption energies for the bond via C or O are very similar, so that both CO orientations could occur with comparable probabilities even at low temperatures. For the (100) face the difference between the adsorption energies for binding via O or C was more appreciable; for 1:2 coverage, they were 4.13 kcal mol^{-1} and 3.29 kcal mol^{-1}, respectively.

The equilibrium bond length of the adsorbed CO molecule is slightly smaller than in the free molecule: the use of the frozen molecular geometry in this type of calculation can result in an underestimate of the adsorption energy sought for by about 10%. The distance of the molecule from the surface is fairly large, thus confirming the weakness of the chemisorption bond; the corresponding force constant is about 20 times smaller than the stretching one for CO. The frequency of vibration of the CO molecule with respect to the surface can be estimated to be at about 200 cm^{-1}. Unfortunately, no experimental information is available in this region.

The energy data do not change appreciably when a more realistic model is considered, namely CO-covered three-plane slabs and relaxed surface planes. In this case the adsorption energies are 6.82 kcal mol^{-1} and 6.32 kcal mol^{-1} for C and O bonds, respectively and the surface relaxation remains almost the same as in the clean crystal, i.e. 6.7% of the interplane distance.

2.2. Atomic and bond populations

Information on the nature of the adsorption can be obtained from the Mulliken population data reported in table 1. Atomic population data show that the atom of the CO molecule attached to the surface beomes more negatively charged, that atomic charges in the crystal are hardly affected and that electron transfer between the molecule and the surface is very small and of opposite sign in the two cases. The bond population between surface Mg and the attached atom is very small; however, there are appreciable changes in the bond populations between C and O, which reveals a relatively large redistribution of electrons in the adsorbed molecule.

Table 2. The bond populations in free and adsorbed CO molecules.

			Attached atom	
O	C	Free CO	C	O
2s	2s	−0.402	−0.324	−0.425
2s	$2p_z$	0.168	0.094	0.149
$2p_x$	$2p_x$	0.383	0.393	0.369
$2p_y$	$2p_y$	0.383	0.381	0.380
$2p_z$	2s	−0.032	0.024	−0.050
$2p_z$	$2p_z$	0.385	0.377	0.365

Table 2 represents the attempt to analyse the changes in the CO bond populations in terms of contributions from pairs of valence atomic orbitals belonging to these two atoms. There is no particular pair predominantly responsible for changes; when passing from the case of C binding to that of O binding, the populations of all p(C)–p(O) bonds are similarly reduced, together with an increase in antibonding 2s(C)–2s(O) and 2s(C)–$2p_z$(O) molecular orbitals.

2.3. Electron density maps

The effect of adsorption on the electron charge distribution is illustrated in more detail by the difference maps given in figure 2 for both types of bond. The main effect observed here is the polarisation of the CO charge distribution which is shifted downwards by the effect of the field created by the Mg^{2+} ion. As a result, there is a build-up of charge in the region between Mg^{2+} and the attached atom, which is not to be interpreted, however, in terms of covalent bonds. This electronic density concentration is more pronounced for C binding in agreement with the greater adsorption energy.

The present interpretation of the weak bond between CO and the MgO surface as essentially due to polarisation of the molecule in the crystal field is confirmed by the recent *ab initio* study of the CO–HCl system by Politzer *et al* (1981) (in our case the role of H is played by Mg). They also found that CO–HCl and OC–HCl complexes have close binding energies and the C-bonded form is energetically slightly more stable. In contrast, the present situation of similarly stable complexes formed when CO is bound to the surface via any of its end atoms differs greatly from CO chemisorption on transition-metal surfaces. In the latter case, there is a strong bonding between occupied metal d atomic orbitals and empty π^* CO molecular orbitals (see, e.g., Gumhalter 1985).

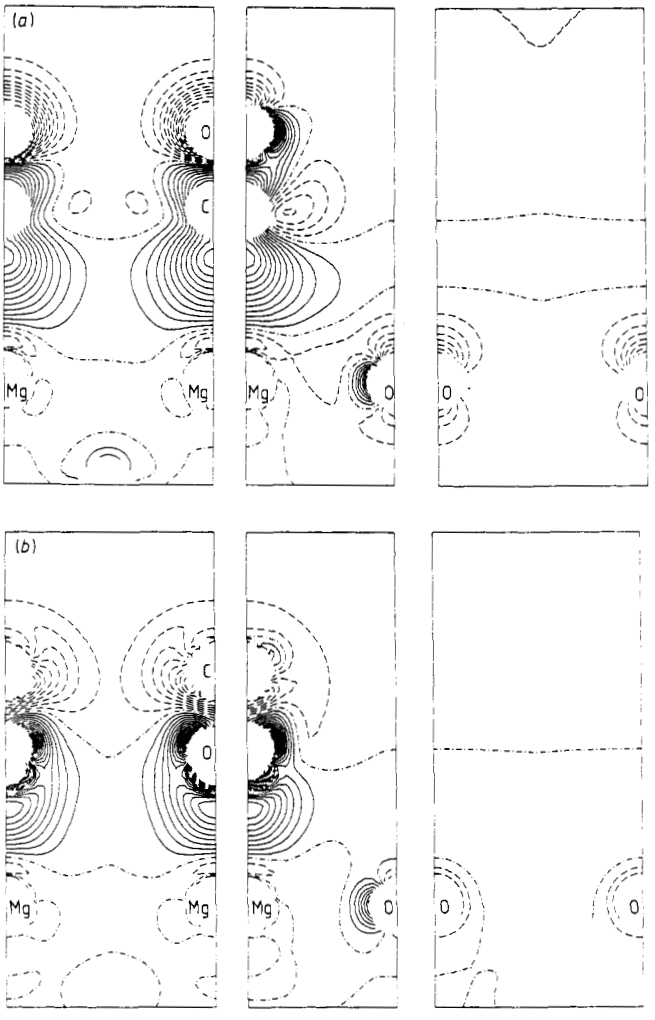

Figure 2. Difference density $\Delta\rho$ map for (*a*) C atom binding and (*b*) O atom binding :—, positive values; - - -, negative values; —·—, zero values. $\Delta\rho$ is the difference between the charge density obtained in the present self-consistent calculation and that for separated systems. The difference between contiguous lines is 0.0025e au^{-3}.

Note in conclusion that for CO adsorption on the (100) surface (Dovesi *et al* 1987) the electronic charge redistribution between CO and the surface is much smaller, as well as the adsorption energy.

2.4. Band-structure and density of states

An analysis of the band-structure of non-interacting CO monolayer and two-plane slab reveals that the energy spectra of the two are separated by a large gap, about 4 eV. It is therefore not surprising that no covalent chemisorption bonds are found since they would require the superposition of the energy spectra, which is the case, e.g., for H on Be (Angonoa *et al* 1984) and H on diamond (Dovesi *et al* 1984b). The repulsive interaction between CO molecules (3.57 kcal mol^{-1}) in the isolated monolayer leads to a shift of

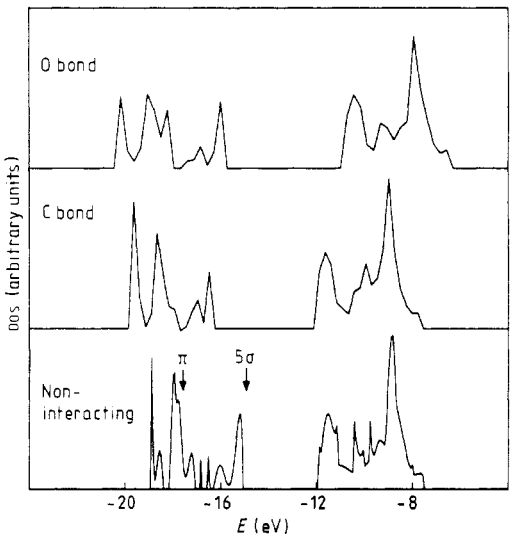

Figure 3. DOSS for CO adsorbed on a two-plane slab. The upper and middle plots refer to binding via O or C, respectively; in the lowest plot the spectra for the two non-interacting systems are superposed; the arrows indicate the position of the energy levels in the isolated molecule. In all cases the states with a lower energy are associated with CO, and those with a higher energy are associated with p orbitals of O^{2-} in the adsorbing crystal.

free CO energy levels and to a broadening into a continuous spectrum 4 eV wide, as shown in figure 3, lowest curve.

When the CO monolayer interacts with the surface, its energy spectrum is also shifted towards lower energies in both cases because of the stabilising field of the Mg ion. For binding via C the CO band-width becomes narrower, because the C lone-pair levels, which lie on the top of the band, are shifted downwards; the reverse happens for binding via O. Concerning the DOS of the valence band, almost rigid displacements are observed of opposite sign for C and O binding: −0.27 eV and 1.1 eV respectively. They seem to be due to the stabilising electric field produced on O p orbitals of MgO by the positively charged C and the destabilising field produced as a result of negatively charged O in the two cases, respectively. This analysis confirms that performed for the bare (110) surface in the preceding paper.

3. Conclusion

The main results emerging from the present *ab initio* study of CO adsorption on the MgO(110) surface can be summarised as follows.

(i) As a consequence of the lower coordination of the surface Mg^{2+} ions, the CO adsorption energy is larger by about 50% than that at the (100) face (Dovesi *et al* 1987); the difference could increase to 100% at lower coverages because of the absence of lateral repulsion between adsorbed molecules.

(ii) The adsorption energies calculated here should be very close to those occurring at ledges of (100) faces, which expose chains of four-coordinated atoms whose local

geometry reproduces that of chains on (110) surfaces. This contrasts with the results reported by Colbourn and Mackrodt (1984) who find CO adsorption energies at ledge cations to be quite similar to those at five-coordinated cations (9.4 and 9.0 kcal mol^{-1}, respectively, for the favoured case of binding through C). The difference can perhaps be attributed to the small size of the cluster employed by these researchers (only nearest neighbours of the cation at which adsorption takes place are treated explicitly). Such differences may be important in the analysis of experimental data of CO chemisorption on MgO, since the present results imply that all 'irregular' sites (corresponding to surface sites with coordination of less than five) are appreciably more populated than 'ordinary' sites.

(iii) In both the (100) and the (110) cases the interaction is essentially electrostatic in origin, as is proved by the small surface electronic charge redistribution and by the negligible DOS modification. This is confirmed by the small adsorption energies which are essentially associated with a charge–quadrupole interaction (the adsorbed molecule has a very small net charge and dipole moment).

(iv) The predicted shortening of the CO bond length (about 1%) must be accompanied by a change in its vibrational frequency. However, since the quantities in question are very small, of the order of 10 cm^{-1} (Escalona Platero *et al* 1985), it is beyond our present computational accuracy to predict the magnitude of the frequency shift.

(v) Since adsorption energies for the attachment of a CO molecule to the surface through C or O are very similar, both bonds should occur with close probabilities, even at liquid nitrogen temperature.

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