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Theory of CO adsorption on MgO(100): the influence of intermolecular interactions on the CO orientation

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Abstract

From periodic Hartree-Fock calculations, the mode of CO chemisorption on MgO(100) is found to vary with the coverage. At low coverage, the best adsorption mode is predicted to be perpendicular to the surface. At higher coverages, the interaction between the adsorbed molecules influences the ordering of the surface. At coverage $\theta = 1/2$ monolayer, lateral effects dominate and CO is adsorbed parallel to the surface, bridging pairs of nearest-neighbor Mg atoms. At $\theta = 3/4$, for the (4×2) unit cell, the COs are adsorbed differently: whereas one third of the COs remains perpendicular to the surface, the two other thirds are bent on the surface. In this case, we find two geometrical arrangements that are equally favorable from an energetic standpoint. In a first arrangement, the non-perpendicular COs differ: one of them is tilted off-normal while the other one is parallel to the surface and bridges Mg atoms as at $\theta = 1/2$. This arrangement therefore distinguishes three kinds of COs. It is very close to results obtained by potential energy calculations. In another model, the two non-perpendicular COs are symmetrically positioned relative to the perpendicular one. This model distinguishes only two kinds of COs in a 2:1 ratio and is very close to results derived from spectroscopies at low temperature.

Keywords: Ab initio quantum chemical methods and calculations; Carbon monoxide; Low index single crystal surfaces; Magnesium oxides

1. Introduction

The adsorption of CO on ionic surfaces leads to ordered phases. According to infrared spectroscopy analysis, CO molecules form a regular array [1] of molecules oriented perpendicular to the surface, the CO vibrational frequency being shifted with respect to that of the free molecule [1,2]. The shift is observed both on MgO(100) [3] and on alkali halides

with the rocksalt structure [4]. At low temperature, the adsorption mode is different. From recent LEED studies [5] at low temperature (below 40 K), the cell is (4×2) with a $\theta = 3/4$ monolayer coverage (where one monolayer corresponds to one CO molecule for each surface Mg atom). The cell is shown in Fig. 1; it contains 8 MgO units and for this coverage, 6 CO molecules. The COs are assumed to stand close to perpendicular to the MgO surface along the Mg rows. It is also suggested that the interaction between CO molecules imposes that neighboring molecules are tilted in opposite directions. At higher tempera-

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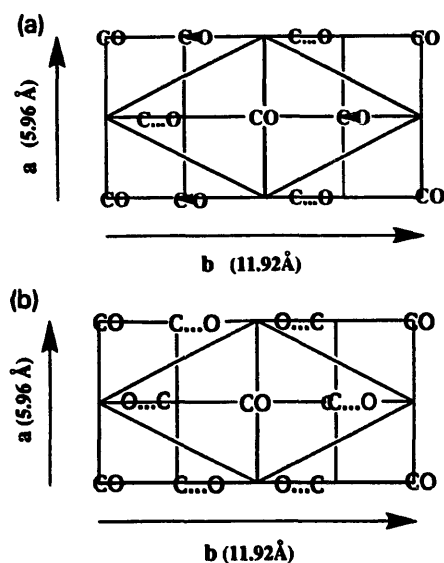


Fig. 1. Top view of CO adsorption with $c(4 \times 2)$ unit mesh and $c1m1$ symmetry on $MgO(100)$. $c1m1$ implies a centered cell with one-fold rotation and symmetry and only one mirror plane. The outermost magnesium atoms are at the vertices of the squares and the outermost oxygen atoms are at the centers of the squares. The largest rectangle represents a (4×2) unit cell while the rhombus shows a $c(4 \times 2)$ unit cell. The primitive cell for the MgO surface layer corresponds to a small square. The CO molecule at the four corners and center of the (4×2) cell are perpendicular to the surface.

ture (above 50 K), there is a uniaxial expansion along Mg rows that leads to another structure.

From potential energy calculations, the CO orientation is everywhere parallel to the surface except at the Mg site where it is upright; the heat of adsorption for a single CO is found to be 3.3 kcal/mol [6]; CO molecules are shown to move along the rows with a small activation barrier. The most stable phase at $\theta = 3/4$ is the (4×2) phase containing 6 molecules per (4×2) mesh when both adsorbate–substrate and molecule–molecule contributions are taken into account [7]. The heat of adsorption is then 5 kcal/mol. Two molecules are perpendicular to the surface nearly above an Mg site, two are displaced relative to the Mg sites and tilted by 20° and the last two lie flat and link two adjacent Mg atoms. The adsorption mode is interpreted on the basis of a competition between the molecule/surface and the molecule/molecule interactions. Fig. 1a sketches this structure and indicates a (4×2) and a $c(4 \times 2)$ unit mesh: pairwise translational equivalence of the CO molecules [7] results in the $c(4 \times 2)$ mesh.

By helium atom scattering studies at low temperature [8] and by polarization infrared spectroscopy [9], the structure is also shown to be different at temperatures below and above 45 K. At temperatures below 45 K, the spectroscopy indicates an ordered monolayer with two energetically different sites per unit cell. The $c(4 \times 2)$ symmetry is assumed. There are two bridging COs, energetically equivalent, but tilted in opposite directions, for one perpendicular atop CO. This is shown in Fig. 1b. We will refer to this model as the Hannover–Göttingen model. At temperatures above 45 K, the spectrum indicates a CO dipole perpendicular to the surface. The main difference between the model of Girardet and Hoang [7] and the Hannover–Göttingen model concerns the non-perpendicular COs: in the former model, the two non-perpendicular COs are inequivalent, whereas they are related by symmetry in the latter model.

An adsorption heat value of 3.6 kcal/mol has first been derived from IR measurements [10]. Values in the range 7.2–9.2 kcal/mol have been found for the adsorption on a $MgO(100)$ surface supporting Pd particles [11] (the saddle energy for surface diffusion is also determined as 5.8 kcal/mol). A value of 9.9 kcal/mol [12] (He et al.) has been determined for MgO thin films grown on $Mo(100)$ surfaces. On MgO powder, the heat of adsorption has been measured to be 3.9 kcal/mol; this low value must probably be associated with a high coverage [12].

First theoretical studies on the adsorption of CO on $MgO(100)$ favor a perpendicular mode. For the adsorption at a $\theta = 1/2$ coverage, CRYSTAL calculations [13], using a 321G basis set for CO and a full basis set accounting for all the electrons for MgO favor the perpendicular approach [14,15], the Mg–CO orientation being slightly favored over the Mg–OC orientation. The adsorption energy is 4.13 kcal/mol (4.48 for $\theta = 1/4$) for the (100) face [14] and 6.63 kcal/mol for the (110) face [15]. Improved calculations [16] show a decrease with the coverage from 7.6 kcal/mol for infinite dilution to 6.7, 6.0 and 2.0 kcal/mol for $\theta = 1/4$, $1/2$ and 1, respectively. A recent calculation with the CRYSTAL program on a 3-layer slab [17] (instead of a monolayer) and with a larger basis set leads to 7.2 kcal/mol at a $\theta = 1/4$ coverage.

Cluster calculations find the same orientation with often a larger adsorption energy (4.6 kcal/mol [18],

8.6 kcal/mol [19], 9 kcal/mol [20]); as they model the adsorption of a single adsorbate, they should be compared with experimental results at low coverage. Adsorption energies at the Hartree–Fock level are in the range of 4–12 kcal/mol [17]. They increase with the cluster size (from 5 to 12 kcal for Mg_nO_n , $n = 9 \rightarrow 21$ when a single zeta basis set is used [17]) and decrease when the basis set is improved (from 9 to 4 kcal/mol for $\text{Mg}_{13}\text{O}_{13}$) or when basis set superposition errors (BSSE) are corrected (to 1.6–1.9 kcal/mol, then they do not vary with the cluster size) [17]. Ab initio calculations on clusters embedded in a distribution of point charges [20] give nearly no binding energy (a shallow minimum at 3.25 Å corresponding to an extremely weak physisorption); a correction for correlation effects and one for the basis set superposition error lead to 2.1 kcal/mol [21].

By contrast, the LDF [22,23] results give much larger adsorption energies. They slowly decrease with the cluster size from 26 to 11 kcal/mol for $n = 5 \rightarrow 13$. These adsorption energies are weaker than those for more acidic oxide surfaces [3,24]. For instance, the adsorption energies on bare TiO_2 surfaces (an amphoteric oxide; CO is perpendicular to the surface on a titanium center) are 11.6 kcal/mol [25]. The CO–substrate interaction is mostly electrostatic. However, some overlap is present: both the σ -donation and the local field effect explain the IR shift to higher frequencies [25]; this transfer is more visible with LDF results [17,22] than with HF calculations. The π -backdonation is also present [24,26].

In all the calculations except Ref. [19] the C-down orientation is favored over the O-down orientation. The O-down orientation, however, also shows a noticeable attraction. It is found at the SCF level on metal ions [25] devoid of valence electrons or on very ionic species [27]; in this case, the contradiction with experiment is attributed to correlation errors. The O-down orientation is also not the best orientation on TiO_2 surfaces [25]. It is easily distinguishable by IR spectroscopy [23].

In this paper we present calculations of ordered structures for CO adsorbed on a monolayer of MgO at various coverages. At low coverage, the CO molecules are far from each other (5.96 Å at $\theta = 1/4$) and do not interact; thus only interaction with the substrate imposes the geometry. The σ -donation

and π -backdonation orient the CO above the magnesium cation perpendicular to the surface (with the carbon atom oriented toward the surface) [28–30]. At high coverage, the adjacent COs are close to each other and lateral CO–CO interactions can modify the adsorption mode: to force some CO molecules to orient differently, to bend along a Mg–Mg bond and eventually to become parallel to the surface. Our goal in this paper is to study the adsorption mode at various coverages and to explain why some CO can be adsorbed without being perpendicular to the surface. We have started by an evaluation of the CO–CO interactions in the Girardet and Hoang model (at $\theta = 3/4$) in the absence of a substrate. This first study confirms that the lateral interactions are important. Next we compare different models after adsorption on the substrate: the Girardet and Hoang model, a model with all the COs perpendicular to the surface and variations of these models. We show that the ordering of the adsorbates at this coverage results from a compromise between the interactions of the adsorbate with the substrate and with the adjacent adsorbates. This conclusion is also valid for the recently proposed Hannover–Göttingen model. Finally we have performed calculations of the CO adsorption at low coverage to show that, with the same method and the same basis set, the perpendicular orientation was the best when the interaction with the substrate dominates; this is the case at $\theta = 1/4$.

2. Calculations

We performed Hartree–Fock periodic calculations [13] (CRYSTAL program) at the SCF level with a Restricted Hartree–Fock Hamiltonian (RHF). We chose to use pseudopotentials in order to improve the description of the valence orbitals of the magnesium. The pseudopotentials are those from Durand–Barthelat [31]. The basis set for the O^{2-} ions is a PS-31G basis derived from Ref. [29]; it has been used for titanium oxides [25,35,36]. For the magnesium atoms, we have used the PS-21G basis set given in Table 1. With these basis sets, the bulk energy per MgO ($\text{Mg–Mg} = 2.98 \text{ \AA}$) is -16.667 a.u. (One Hartree, the atomic unit of energy, corresponds to 627.5 kcal/mol for a molar energy.) This represents an ionic crystal lattice energy of 1030 kcal/mol (the experimental value for the bulk is 940

Table 1
Basis sets for the magnesium and oxygen

Orbital	Exponent	s coefficient	p coefficient
Mg(3s)	2.115163	0.040482	
	0.46535	0.185526	
Mg(3sp)	0.11	1	1
O(2sp)	19.591534	0.003424	0.036496
	4.432919	-0.189923	0.204118
	1.12974	0.593574	0.522515
	0.281139	0.58122	0.479467
O(2sp')	0.165	1	1

For oxygen, the PS31G basis set is obtained from Ref. [29] by contracting only the first three primitive functions and isolating that with the exponent of 0.281139. The PS41G basis set is shown in the table; it is also derived from Ref. [29] by the addition of the O(2sp') diffuse function. The pseudopotentials are those from Barthelat et al. [31].

kcal/mol [33]). For the bulk, MgO is polarized $\text{Mg}^{+1.43}\text{-O}^{-1.43}$ and the overlap population between Mg and O is 0.078. These basis sets allow more valence electrons to reside on the magnesium than the basis set used in Ref. [34], where the valence orbital is represented by a single 3sp Gaussian orbital ($\zeta = 0.25$). The monolayer is more covalent, is polarized $\text{Mg}^{+1.33}\text{-O}^{-1.33}$ and the overlap population between Mg and O is 0.110. Such basis sets seem to overestimate the covalent character. The electronic density on the magnesium ions could therefore be too large, leading to an underestimation of the adsorption energies. We have therefore recalculated the optimized adsorption modes with an improved description of the O^{2-} ions adding diffuse orbitals (a PS-41G basis set, see Table 1). Then, the bulk is mostly ionic with an overlap population (OP) of 0.028 (the large Mulliken charge, 2.04, has no meaning since the large overlap between the atomic orbitals produces a counter-intuitive effect [37]); the ionic crystal lattice energy is 947 kcal/mol (Mg–Mg = 3.03 Å) with a fortunate agreement with experiment. The MgO(100) monolayer is polarized $\text{Mg}^{+1.63}\text{-O}^{-1.63}$ with an overlap population between Mg and O of 0.074.

We have used two different basis sets for the carbon and the oxygen of the CO molecule: the PS-31G for most of the calculations and the 6-31G* basis sets [38] to recalculate the best adsorption mode at each coverage. Then, the RHF energies for the CO molecule are respectively -21.149 a.u. (valence electrons) and -112.738 a.u. (all electrons);

the C–O distances are $d = 1.129$ Å and $d = 1.114$ Å, respectively.

We have represented the MgO substrate by a single rigid atomic layer. The adsorption energies are defined to be positive when the adsorption is exothermic: $E_{\text{ads}} = E_{\text{adsorbate}} + E_{\text{MgO}} - E_{(\text{adsorbate} + \text{MgO})}$. The value E_{MgO} is recalculated when a large cell is used instead of the primitive cell (this eliminates small variations by 0.5 kcal/mol or less that are artifacts). The adsorption energies are overestimated by the calculations with small basis sets since improving the basis set improves $E_{\text{adsorbate}}$ (a molecular calculation) more than the other terms (periodic calculations). The improvement of the quality of the basis set for the valence orbitals of MgO decreases its intrinsic reactivity. As a result, the calculated adsorption energies are small relative to previous results [17,31]. For cluster calculations, it was similarly noticed that an improvement of the basis set decreased the heat of adsorption [17]. The use of PS-41G basis sets instead of PS-31G for the oxygen ions induces another reduction of the heats of adsorption (as will be shown later – see Table 6). We have not taken into account the basis set superposition error; according to Ref. [17], this would also contribute to reduce the calculated values. The use of a slab would also contribute to a reduction of the adsorption energies. On the other hand, corrections to include the correlation effects would probably increase the adsorption energies since the adsorbate is more ionic than the gas-phase molecule. The correlation effects indeed are much larger for the ions than for the atoms (the difference is 93.5 kcal/mol for the couple $\text{O}^{2-}\text{-O}$). They should be larger for E_{ads} , where the adsorbed CO is polarized, than for $E_{\text{adsorbate}}$, where the isolated CO is nearly apolar.

Our calculations of the intermolecular interactions ($\theta = 3/4$) without substrate will assume the (4×2) unit mesh; however since it will be concluded (Section 3) that allowing the independence of 6 molecules instead of 3 does not improve the energy, we use the $c(4 \times 2)$ unit mesh to study adsorption.

3. Intermolecular interactions

As the interaction between the CO and the MgO surface is rather small, lateral effects must be impor-

tant at high coverage. We therefore start our calculations by estimating the intermolecular interactions using the PS-31G basis set. First, we place 6 CO molecules along the Mg rows in a (4×2) unit cell as proposed by Girardet and Hoang (see Fig. 1) and we compare the intermolecular energies for different orientations.

Let us compare the first four lines in Table 2. They show that the geometry proposed by Girardet and Hoang (Fig. 2) is much more favorable than that with all the COs perpendicular to the surface (6T). Having two adjacent bridging CO molecules (4B + 2T) is not favorable either when the bridging geometry is strictly that proposed by Girardet and Hoang; the intermolecular distance is too short. Increasing this distance to separate the bridging COs decreases the repulsion: two opposite shifts of 0.045 fractional units ($b = 11.92 \text{ \AA}$) represent a noticeable increase of the distance separating the molecules (from 1.85 to 2.80 \AA) and lead to an intermolecular repulsion close to that for the Girardet and Hoang model.

In the last lines of Table 2, we reconstruct the Girardet and Hoang model by successive steps. We start with a very simplified model and unfreeze

Table 2

The intermolecular energy (in kcal/mol, minus sign associated with repulsion) and the adsorption energies relative to $6N$ CO molecules (N is the Avogadro number)

Geometry	Intermolecular energy	Adsorption energy
6T	-36	-26.6
4B + 2T	-137.4	
4B + 2T (Separated)	-7.45	-10.3
Girardet and Hoang	-6.9	
(B + 2T) ₂	-15.7	-7.6
(B + T _{shift} + T) ₂	-12.2	-4.4
(B + T _{shift} + T _{shift}) ₂	-7.85	+1.0
(B + T _{shift} + T _{shift} ^{tilt}) ₂	-6.75	+1.8
(B _{opt} + T _{shift} + T _{shift} ^{tilt}) ₂	-5.76	+6.0

Symbols T and B refer to atop CO perpendicular to the surface and to flat-lying CO respectively; the label "shift" refers to a small translation along the b -direction (Fig. 1) and the label "tilt" to a bending of the Mg–C–O angle. Note that for the intermolecular energies, the geometrical parameters are taken from Girardet and Hoang (the unit mesh is either (4×2) or $c(4 \times 2)$) while for the adsorption energies they are optimized ($c(4 \times 2)$ unit mesh). For the 4B + 2T (Separated) the pairs of bridging COs are moved apart from each other by two opposite translations of 0.536 \AA . For B_{opt}, the geometry of the bridging COs is optimized (see text in Section 4.1).

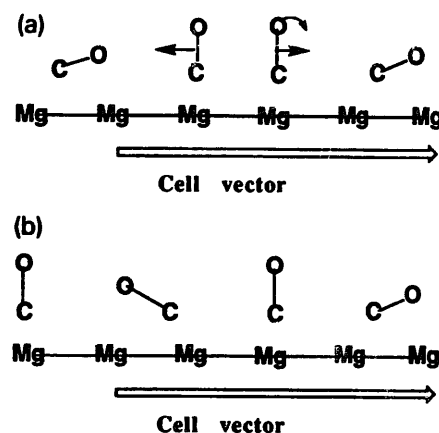


Fig. 2. Side view of CO adsorption for the two models. (a) The Girardet and Hoang model [13]. The COs perpendicular to the surface are shifted away from each other. A CO is tilted towards the adjacent carbon atom of the bridging CO. (b) The Hannover–Göttingen model [6,7]. One CO is perpendicular, whereas the two others are symmetrically bent.

degrees of freedom one by one. The positions of the COs always refer to the surface even if the surface atoms are not present for the calculation of the intermolecular repulsion. In every case, $c1m1$ symmetry is assumed (see Fig. 1). Pairs of CO molecules are thus strictly equivalent. The index 2 in the labels used in Table 2 and below, as in $(3 \text{ CO})_2$, refers to this pairing. For comparison with the results for the (4×2) unit mesh, the adsorption energies in Table 2 again refer to 6 molecules.

In the $(B + 2T)_2$ structure, the geometry of the bridges is taken from Girardet and Hoang while the other COs are made perpendicular to the surface and located strictly above the surface magnesium atoms (no lateral shift). The repulsion is twice that for the Girardet and Hoang model, 15.7 kcal/mol. In the $(B + T_{\text{shift}} + T)_2$ geometry, two perpendicular molecules are shifted by 0.0125 fractional units (0.15 \AA); then, the repulsion decreases by 3.6 kcal/mol. Next, the remaining set of perpendicular COs is tilted by 9° (the system is stabilized by 1.1 kcal/mol) and shifted by 0.028 fractional units (0.337 \AA) (a stabilization by 4.3 kcal/mol). The final system with the $c1m1$ symmetry is found to be slightly better than that proposed by Girardet and Hoang. The inequivalence of the pairs of CO and the deviation from the direction along the b -axis assumed by Girardet and Hoang do not bring significant extra stabilization.

In all the calculated geometries, the interaction

between the COs is repulsive. Whereas the CO–CO interaction in the dimer is weakly attractive (by 0.3 kcal/mol) that in pairs of COs with a geometry extracted from the model by Girardet and Hoang are always repulsive: the repulsion between a perpendicular CO and a bridging CO is 0.6 kcal/mol, that between a tilted CO and a bridging CO is 0.9 kcal/mol and that between a perpendicular CO and a tilted CO is 1 kcal/mol. The sum of these values gives a repulsion of 5 kcal/mol for 6 molecules, close to the value 6.9 kcal/mol calculated for the corresponding CO layer. The repulsion between two parallel molecules at 2.98 Å is much larger, 3.5 kcal/mol, and thus the geometry proposed by Girardet and Hoang is much better than that with all the CO in atop positions. In our calculations, the energy optimization results from a minimum of repulsion; this contrasts with the description by Girardet and Hoang where the CO–CO interaction is always attractive and where the structure of the adsorbate layer results from the optimization of attractive terms. To reach a high coverage in our calculations, the substrate–adsorbate interaction must be strong enough to overcome the repulsion between the adsorbates. The adsorbate–adsorbate interaction however can control the topology of the adsorbate distribution since this term varies rapidly with the CO orientation.

The intermolecular energies obtained from these calculations are sufficiently large relative to the heat of adsorption to conclude that the relative position of the adsorbates must be an important factor. Lateral interactions should predominate as also found for other surroundings [24,39]. IR studies on oxide powders [40] show that the band positions depend on the surface coverage (a shift downward on increasing the CO concentration). The two bands are attributed to different adsorption sites, both above the metal cations for different faces. Cluster calculations are inadequate to easily take this phenomenon into account.

4. Adsorption at high coverage, $\theta = 3/4$

4.1. The Girardet and Hoang model

In the last column of Table 2 are given the adsorption energies calculated with the PS-31G basis

set for CO for the structures presented in Section 3. The topologies remain the same but the parameters for the structures differ; they are now optimized whereas in Section 3 they were transferred from Girardet and Hoang. Calculations have been performed using the *c1m1* symmetry; for comparison with the results for the (4×2) unit mesh, the adsorption energies in Table 2 again refer to 6 molecules. The trend for the stability is similar; this demonstrates the importance of the intermolecular interactions.

The distances of the CO molecules to the surface have been optimized and are generally longer than assumed by Girardet and Hoang. For the perpendicular CO, our calculated Mg–C distance is 2.70 Å versus 2.46 Å. In a first approach, we have used the geometry proposed by Girardet and Hoang when the COs are parallel to the Mg–Mg pairs. The $(B + T_{\text{shift}} + T_{\text{shift}}^{\text{tilt}})_2$ system is the closest to the Girardet and Hoang model; the 6 COs are made pairwise equivalent by the choice of the *c1m1* symmetry; this gives a positive heat of adsorption (exothermic adsorption). This value per CO, 0.3 kcal/mol, remains smaller than experimental results (from 3 to 10 kcal/mol) [10–12]. The adsorption energies for the other systems are mostly negative and do not lead to a favorable adsorption. This is the case when all the COs are assumed to be perpendicular. This is also the case for the “4B + 2T (separated)” system, which was nearly equivalent to the Girardet and Hoang model in the absence of the substrate. The adsorbate–substrate interactions are responsible for the difference between this model and that of Girardet and Hoang.

Starting again with the simplified $(B + 2T)_2$ model, we can analyze the different motions that lead to the best structure: the shift of the atop COs by 0.0125 fractional unit (0.149 Å) leads to a stabilization by 3.2 kcal/mol (see $(B + T_{\text{shift}} + T)_2$); the bending of the Mg–C–O angle to 15° stabilizes by 0.8 kcal/mol and the shift by 0.035 fractional unit (0.417 Å) of these two COs stabilizes by 5.4 kcal/mol. Shifts are thus the main factor stabilizing the system. They separate the perpendicular COs as shown in Fig. 2. The tilt takes place for the CO, which is adjacent to the carbon atom of the bridging CO (exchanging T and T^{tilt} decreases the adsorption energy by 2.8 kcal/mol). The energies associated

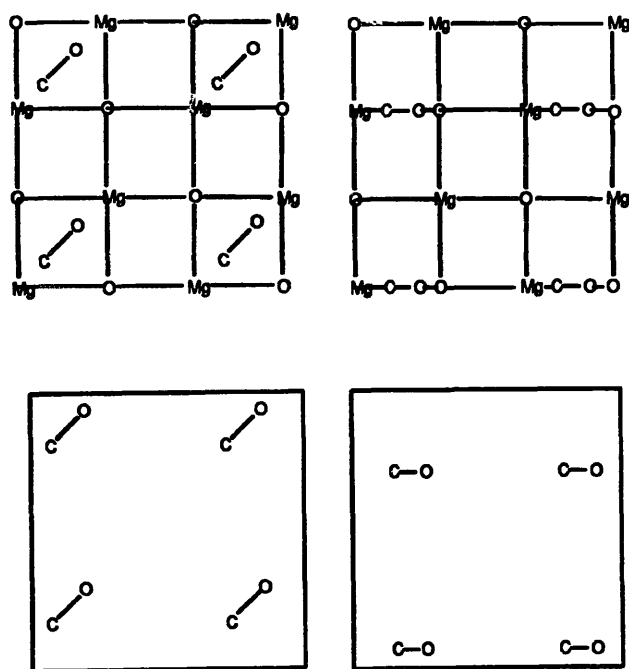


Fig. 3. CO/MgO at $\theta = 1/2$. The adsorbate–adsorbate interactions are favorable when the molecules are oriented along the Mg–Mg directions. At the bottom of the figure, we have represented the adsorbate without the substrate. Only, the orientation at the right-hand side leads for the CO layer to a stabilization.

with the different motions are very close to those from Section 3.

Next, we have optimized the geometry for the bridging COs. The h distance from the middle of the CO bond to the surface becomes 2.954 Å, larger than

that calculated by Girardet and Hoang (2.68 Å); this is similar to the difference found for the perpendicular COs. The shift of the middle of the CO bond, 0.0208 fractional unit (0.25 Å from the middle of the Mg–Mg bond), and the bending angle of 6°5 are much closer to the values given by Girardet and Hoang. As shown in Fig. 3, a positive angle means that the carbon atom is closer to the surface than the oxygen atom; however, the Mg–C distance is very close to the Mg–O distance, 3.12 Å versus 3.18 Å, because of the shift.

Finally, we had to take into account that the optimization of each parameter is not independent from those of the other parameters. This requires an iteration of the optimizations. The CO bond length is also allowed to vary. The CO bond length is longer when CO is bridging than when it is perpendicular. For the perpendicular orientation, the σ -donation to the magnesium ion decreases the population of the HOMO of the carbonyl. This orbital, mainly the σ pair of the carbon atom, has an antibonding CO character; thus its depopulation is accompanied by an increase of the CO bond strength. For the bridging orientation, the interactions of the substrate with the π_{CO} orbitals contribute to weaken the CO bonding.

Thus, we obtained the parameters reported in Table 3 and the total adsorption energy of 1.0 kcal/mol per CO reported in Table 2 for 6 molecules.

Table 3

The optimized parameters for the $(B_{opt} + T_{shift} + T_{shift}^{tilt})_2$ model derived from Girardet and Hoang [7] and those for the $(T + 2B_{opt})_2$ model derived from Toennies [8] and Heidberg [9]

Basis set for CO	$(B_{opt} + T_{shift} + T_{shift}^{tilt})_2$			$(T + 2B_{opt})_2$	
	PS31G	6-31G *	Ref. [13]	PS31G	6-31G *
Adsorption energy (kcal)	6.16	5.91	29	5.38	7.96
T_{shift}	h_C (Å)	2.696	2.716	2.93	2.716
	Shift (f.u.)	0.020	0.027	0.000	0.000
T_{shift}^{tilt}	h_C (Å)	2.83	2.76	2.46	
	Tilt	28°	20°		
	Shift (f.u.)	0.033	0.033	0.062	
B_{opt}	h (Å)	2.954	2.954	2.986	3.10
	x (f.u.)	0.0208	0.0208	0.0324	0.036
	x (Å)	0.25	0.25	0.43	0.45
	θ	83°50	83°50	46°5	43°5

h_C (Å) is the distance from the carbon atom to the surface. The shifts are in fractional units (the corresponding cell vector is 11.92 Å long) measured from the closest Mg atom. Parameters for the bridging COs are indicated in Fig. 3.

Table 4
Charges (Q) and overlap populations (OP) of the CO in the isolated molecule and under adsorption, for the $(B + T_{\text{shift}} + T_{\text{shift}}^{\text{tilt}})_2$ system with the PS-31G basis set

Molecule	$Q(O)$	$Q(C)$	OP(CO)
CO alone	-0.366	0.366	0.442
CO adsorbed T_{shift}	-0.372	0.380	0.450
CO adsorbed $T_{\text{shift}}^{\text{tilt}}$	-0.383	0.382	0.468
CO adsorbed B	-0.389	0.398	0.430

At the SCF level, the dipole moment for the CO molecule is $C^{\delta+}..O^{\delta-}$ contrary to experiment. The σ -donation slightly dominates the backdonation (except for the tilted CO). The bridged CO is the most polarized one and the most weakened.

This is significantly smaller than the published values, 3.3 kcal/mol [6] or 4–12 kcal/mol [17]. As emphasized in Section 2, the improvement of the basis set for the valence electrons of MgO reduces the adsorption energies.

After adsorption, the three COs are polarized as $C^{\delta+}..O^{\delta-}$, cf. Table 4. The overlap populations (OPs) for the perpendicular and tilted COs are larger than the OP for the isolated molecule; this is associated with the σ -donation from the carbon to the surface, which removes the antibonding character of the 5σ orbital even if the total charge transfer is dominated by the π -backdonation.

4.2. The Hannover–Göttingen model

The model derived by helium atom scattering studies [8] and polarization infrared spectroscopy [9], here called the Hannover–Göttingen model, corresponds to the coverage $\theta = 3/4$ and the $c(4 \times 2)$ unit cell used in Section 4.1. One CO remains perpendicular on a top position with no shift, the two others are equivalent and tilted in opposite directions. We have optimized the location for these molecules: Mg–C distances are respectively 2.95 and 2.68 Å. The shift for the two bridging COs are 0.032 fractional unit; this represents 0.43 Å; the tilts are $43^\circ 5'$. The adsorption energy per CO is 0.90 kcal/mol. This is very close to that obtained with the model derived from Girardet and Hoang (see Table 3). The intermolecular energy (per 6 COs) is slightly more repulsive, -9.4 kcal/mol, than that from Girardet and Hoang, -5.76 kcal/mol; this explains the difference between the two models. This mode however

also corresponds to a decrease of the adsorbate–adsorbate interactions relative to the perpendicular orientation.

4.3. Calculations with the 6-31G* basis set

We have concluded from the calculations at the PS-31G level that, at high coverage, the COs are not all oriented perpendicular to the surface in order to maximize the interaction with the Mg^+ cations of the surface but are partly relocated and reoriented to also optimize their relation with surrounding molecules. The adsorbate–adsorbate interactions should be better described with polarization functions on the CO. In this prospect, we performed calculations with the standard 6-31G* basis set [34] for CO. Another reason to improve the basis set is the comparison of the adsorption energies at different coverages. We have emphasized that the adsorption energies at $\theta = 3/4$ were weak; they can be improved by the introduction of polarization functions if those are necessary for the interactions between COs. On the other hand, we expect the value at low coverage to decrease (see Section 2). The relative adsorption energy at $\theta = 3/4$ should then increase.

With the geometrical parameters obtained in the previous section, the Hannover–Göttingen model becomes slightly better than that of Girardet and Hoang (by 0.36 kcal/mol for 6 COs). The two models remain very close in energy and difficult to compare unless a full optimization is done on each one. Such accuracy is difficult to obtain because of the large number of parameters. As the Hannover–Göttingen model has fewer parameters and as it is a better starting point (the most stable), we have optimized its parameters, mainly to determine accurately the adsorption energy and to compare it with those at low coverages. Results are given in Table 3.

5. Adsorption at $\theta = 1/2$ coverage and at $\theta = 1/4$ coverage

5.1. Calculations with the PS-31G basis set

If one discards the $\theta = 1$ coverage that is too dense, the simplest system in which all the COs are

Table 5
Adsorption energies at low coverage

Adsorption mode	$\theta = 1/2$	$\theta = 1/4$
Perpendicular	+1.7	+2.4
Mg–Mg bridging	+2.1	+1.4
<i>Mg–O bridging</i>		
(Mg–OC–O)	–0.3	+1.2
(Mg–CO–O)	–2.2	–0.7

equivalent is obtained for a $\theta = 1/2$ coverage with the $c(2 \times 2)$ and $p1m1$ symmetry. The bridging mode along the Mg–Mg and Mg–O pairs are represented in Fig. 3. The heats of adsorption for the different modes are given in Table 5.

A side view is shown in Fig. 4 where the optimization parameters (h , the distance to the surface, θ , the CO tilt angle, and x the shift) are defined. For the Mg–Mg orientation, these parameters are given in Table 6. Except for the distance to the surface, these values are close to those given by Girardet and Hoang. For the Mg–O orientation, the CO can be oriented in two opposite directions. For the Mg–OC–O orientation, we give in Table 6 the result for the optimum h value, 3.284 Å. For the Mg–CO–O orientation, the system is unstable with respect to desorption. In Table 6, we also give the result for $h = 3.284$ Å.

It is a priori surprising that the bridging CO lies above a non-polar MgMg bond rather than over a polarized MgO bond. Purely electrostatic terms are very weak since the dipole moment of CO is small (it does not necessarily determine the CO orientation on the surface [25]) and since the charge transfer between the surface and the adsorbate is negligible.

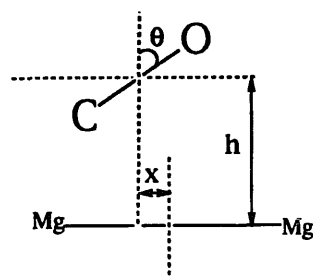


Fig. 4. Side view of CO bridging Mg–Mg. h represents the distance from the middle of the CO bond to the surface; x the shift along the b -direction and θ the tilting of the CO (90° when parallel to the surface and 0° when normal to the surface).

Table 6
The adsorption energies and the optimized parameters for calculations with the 6-31G* basis set

	Adsorption energy		
	1.76–1.64	1.70–0.94	1.16–0.80
	$\theta = 1/4$	$\theta = 1/2$	$\theta = 3/4$
<i>CO perpendicular</i>			
CO (Å)	1.112	–	1.111
Mg–C (Å)	2.78	–	2.716
<i>CO bridging</i>			
h (Å)	–	3.284	3.10
CO (Å)	–	1.115	1.114
Mg–C (Å)	–	3.295	2.689
Mg–O (Å)	–	3.240	Not bounded
Shift (f.u.)	–	0.0695	0.036
Angle θ	–	80°	43°

The two values for the adsorption energies correspond to different basis sets for the O^{2-} ions in MgO (PS-31G and PS-41G). For $\theta = 1/4$, the COs are perpendicular; for $\theta = 1/2$, they are bridging a Mg–Mg bond and $\theta = 3/4$ corresponds to the model derived from Toennies [8] and Heidberg [9].

The Mg–OC–O orientation is favored relative to Mg–CO–O; this corresponds to the best orientation of the dipole (after adsorption the CO is polarized as $C^{\delta+}..O^{\delta-}$) and to the best interaction with the π_{CO} orbitals. The large adsorption energy for the Mg–Mg bridging is a consequence of adsorbate–adsorbate interactions. In the absence of the substrate, the structure associated with this bridging mode corresponds to an intermolecular attraction (0.6 kcal/mol) while that associated with the MgO bridging corresponds to a repulsion (–1.4 kcal/mol).

The adsorption energy for the perpendicular adsorption (Mg–C = 2.696 Å) is very close to that for the bridging CO. At lower coverage, the intermolecular interactions are less important and the adsorption mode results from the substrate–adsorbate interaction. CO is a weak base that interacts with the acidic centers of the surface, the magnesium cations. The most basic center for the CO is the carbon atom. The interaction that involves the 5σ orbital [25,32] leads to the perpendicular mode of adsorption.

5.2. Calculations with improved basis set

The most stable systems for each coverage have been recalculated using the 6-31G* basis set for CO.

Results are displayed in Table 6. The isolated CO molecule is better represented when polarization functions are included; this stabilizes the reference used to define the adsorption energies and smaller values are found. The successive adsorption steps leading to $\theta = 3/4$ are exothermic: $\theta = 1/4 \rightarrow \theta = 1/2$ by 1.64 kcal/mol and $\theta = 1/2 \rightarrow \theta = 3/4$ by 0.08 kcal/mol. As $\theta = 3/4$ represents the saturation, no exothermic adsorption occurs beyond this limit.

Finally we used a PS-41G instead of a PS-31G basis set for the O^{2-} ions in MgO. Despite the more acidic charge on the magnesium, the adsorption energies again decrease. The substrate is stabilized and is less reactive. This decrease is more pronounced for the coverage $\theta = 1/2$ and the adsorption energy for step $\theta = 1/2 \rightarrow \theta = 3/4$ becomes exothermic by 0.52 kcal/mol. Moreover, this coverage would not be stable with respect to phase separation into two equal surfaces with coverages $\theta = 1/4$ and $\theta = 3/4$ (the calculated adsorption energies per 4 adsorbates are 3.76 and 4.04 kcal/mol for the uniform and segregated distributions, respectively). This comparison is however uncertain because the energies themselves are uncertain. Enlarging the basis set for the oxygen ions allowed MgO to become more ionic and consequently the magnesium ions to become more acidic. This is indeed the effect on the charges and on the overlap population of MgO (see Section 2). However, the interaction between the Mg ions and the CO is reduced as seen with the heats of adsorption. Another criterion is the Mg–C distance. We emphasized that this distance was small, less than obtained by other techniques [7,8]. We have calculated the optimized distance for $\theta = 1/4$. The stabilization in energy is negligible (0.04 kcal/mol) but the optimal distance varies; it increases from 2.78 to 2.83 Å. From this point of view, the CO adsorption is also weaker. Improving the basis set for the substrate or for the adsorbate corresponds to a stabilization of each partner and to a decrease of their mutual interaction.

6. Conclusion

At low coverage, the adsorption of CO on MgO is above the metal cation in upright position as on

TiO₂, but weaker so that it is more sensitive to lateral effects. At $\theta = 1/4$, CO is perpendicular above the surface. The intermolecular distance is 5.96 Å and the repulsion between the adsorbates is weak, 0.17 kcal/mol. At higher coverage, this repulsion is large and the best adsorption mode changes. At $\theta = 1/2$, the best adsorption mode is obtained when the CO molecules are bridging a Mg–Mg bond. When the CO molecules are aligned along the Mg–Mg directions, they stabilize each other and the adsorption energy is the largest; when they are oriented along the MgO directions, they repel and the adsorption is not favorable. Lateral effects dominate at high coverage, at $\theta = 3/4$. Then, three molecules are differently adsorbed; one is bridging a Mg–Mg pair, another is perpendicular and the last one is bent. This is much better than having all the CO perpendicular. Hartree–Fock periodic results match the experimental results except for the absolute values of the adsorption energies that are too weak; the $c(4 \times 2)$ phase at $\theta = 3/4$ is the most stable ordered phase obtained at saturation provided that the COs orient with respect to each other to improve their mutual interaction (this is the case for both the Girardet and Hoang model and of the Hannover–Göttingen model). The general agreement is also remarkably good with potential calculations, the main difference being a longer distance from the adsorbate to the surface.

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