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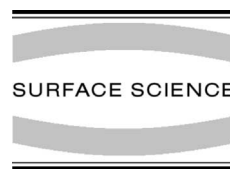Piero Ugliengo
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SURFACE SCIENCE

CO/MgO(0 0 1) at different CO coverages: a periodic ab initio Hartree–Fock and B3-LYP study

A. Damin, R. Dovesi, A. Zecchina, P. Ugliengo [*]

Dipartimento di Chimica IFM, Universitá di Torino, Via P. Giuria 7, 10125 Torino, Italy

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Abstract

The adsorption of CO at various coverages on the regular MgO(0 0 1) surface has been studied using a rigorous ab initio approach based on the solution of the periodic Schrödinger equation at both Hartree–Fock and DFT levels. The crystal orbitals are expanded in Gaussian atomic orbitals and the Coulomb and exchange series are treated rigorously as implemented in the CRYSTAL-98 computer code, ensuring the correct behavior of electric field outside the crystalline surfaces. For DFT calculations, the B3-LYP functional coupled with Gaussian basis sets of high quality for periodic calculations have been adopted. Three different CO coverages (namely $1 \times 2(CO \times Mg)$, 1×4 and 1×8) have been considered. Because of the very small binding energies (BEs), a careful analysis of the effects of the basis set superposition error as well as the computation of the harmonic CO frequency shift with numerical procedures of better quality than in the past have been carried out. Comparison with the results obtained for the CO/Na^+ and CO/CO_2 complexes has also been made in order to clarify the bonding at ionic surfaces. Neither charge transfer nor polarization play a significant role, and the weak BE results from a large cancellation between electrostatic and exchange repulsion components as formerly suggested by accurate cluster calculations embedded in total-ion ab initio model potential. Our best binding energy and CO frequency shift are still underestimated with respect to the most updated experimental data and in good agreement with the best data from embedded cluster calculations. The disagreement with experiment seems to suggest that the dispersive contribution to the BE, unfortunately not accounted for by the Hamiltonians encoded in the available computer periodic codes, may play an important role to reconcile the data of computer simulation with those from experiment. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Magnesium oxides; Carbon monoxide; Physical adsorption; Ab initio quantum chemical methods and calculations; Computer simulations

1. Introduction

The quest of structurally well defined surfaces of ionic materials is an important target for the accurate study of the adsorption processes. The detailed structural knowledge of the surface on which adsorption is taking place, is an absolute need for experimentalists, because the experimental outcome can be interpreted by means of feasible models for the interaction. This is, however, even more true for computational chemists, for two simple reasons; the first one rely on being able to design a model, either a cluster or a periodic representation of the surface itself, which can only

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[*] Corresponding author. Fax: +39-011-670-7855.
E-mail address: piero.ugliengo@unito.it (P. Ugliengo).

be accounted for if the structure of the material is well known and defined. The second reason is, perhaps, even more relevant than the previous one: if the structure of the material is well known, one hopes to have a strict correspondence between the computed quantities of interest and the one coming from the experiment, a fact far from being trivial on the vast majority of poorly defined materials.

The (0 0 1) surface of MgO is certainly one of these "ideal surfaces", for which a vast collection of both experimental and computational modeling results has been gathered since long ago.

The MgO bulk sports a simple salt-like structure and its (0 0 1) surface is known to be regular, with almost negligible relaxation of the positions of the surface ions with respect to their idealized geometrical location. Despite its structural simplicity, a great deal of both experimental and computer modeling work has been done on such a surface, either free or in interaction with simple molecules, the most often used being the CO molecule. The main targets have been the value of the binding energy (BE) and the perturbation of the stretching frequency of the CO caused by the adsorption process. The interested reader may refer to a number of review papers on this topic for more details see Refs. [1,2]. In this section, only a brief recap, of the results we feel more relevant for the present context is carried out by making reference to data in Table 1.

From the experimental side, a number of difficulties arise in order to prepare a MgO(0 0 1) surface free from both structural defects and metal impurities. Indeed, their presence may dramatically change the picture of the interaction between MgO(0 0 1) and CO and the value of 42 kJ/mol for the CO BE, considered as the reference value until recently [3], has now been critically reexamined. After a long series of carefully designed experiment on an MgO(0 0 1) surface free from the above mentioned defects, a much lower value of 14 kJ/mol for the BE of CO has been reported [4,5].

The same kind of problems plagued the accurate determination of the adsorbed CO stretching frequency, because of its extreme sensitivity to the presence of defects, metals impurities and loading of the CO itself. For instance, the same group of Goodman that measured a too high value of the binding also reported a CO frequency shift as high as $+35$ cm^{-1} [3] (see Table 1).

On the other hand, a much lower value of $+14$ cm^{-1} for the CO shift has been measured by some of us [6], by recording and analyzing the IR spectra of CO adsorbed, at very low loading, on smoked MgO microcrystals carefully synthesized. The synthesized material exhibits a well defined set of (0 0 1) facets which are defect free, so that this value is assumed as our reference in the present paper.

From the computational side, which is here only very briefly summarized, the first serious attempt to model the infinite MgO(0 0 1) clean surface has been done by Causà et al. [7] almost 15 years ago with the CRYSTAL periodic code. A year later, a paper from the same group [8] dealt with the interaction of CO with the regular MgO(0 0 1) surface. The same system was the focus of a perturbed-cluster treatment carried out with the EMBED code by Pisani and coworkers [9]. All these

Table 1
Selected computed BEs (kJ/mol) of CO adsorbed on models of the MgO(0 0 1) surface and the corresponding harmonic $\Delta\omega$ frequency shift (cm^{-1})

Approach	Method	BE	$\Delta\omega(CO)$	Reference
Cluster	B3-LYP	1.0[a]	-7	[23]
Embedded cluster	MCPF-AE	7.7[a]	$+7$	[17]
Embedded cluster	CI-AE	30.9	$+43$	[16]
Periodic	LDA-FLAPW	27.0	$+33$	[10]
Periodic	LDA-AE	30.9[a]	-5	[11]
Periodic	PBE96-AE	8.0[a]	$+4$	[11]
Experiment		41.5	$+35$	[3]
Experiment		13.5	$+14$	[6]

[a] BE corrected for the BSSE.

attempts, because of the modest computational resource available at that time, were run at HF only and using a rather poor basis set, particular for the description of the CO molecule. Even if the results cannot be trusted for quantitative predictions, the main conclusions were: (i) the BE is in the range between 18 and 33 kJ/mol; (ii) CO can be adsorbed both ended on top of the Mg^{2+} ion, with that via the carbon atom being slightly preferred; (iii) no charge transfer occurs between CO and the MgO surface; (iv) CO polarization is sizeable.

Two papers, both dealing with a periodic approach to the CO/MgO(0 0 1) system have recently appeared in the literature [10,11]. The one from Chen et al. [10] is based on a plane waves basis and use an LDA Hamiltonian in the context of the full potential linearized augmented plane wave (FLAPW) method. The results, reported in Table 1, show again very large values of both the BE and CO frequency shift, in agreement with the experiment from the Goodman group [3]. This fortuitous agreement is the result of the well known inadequacy of LDA to compute the BEs for intermolecular complexes, which are usually grossly overestimated, and the experimental overestimation resulting from the presence of defects at the MgO surface, as already discussed (see also Ref. [2] for a full account). The paper from Snyder and coworkers [11], is a periodic density functional LDA and GGA study performed with a Gaussian basis set, using the NWCHEM computer code [12]. The computed BEs were 30 and 8 kJ/mol at LDA and GGA, respectively with corresponding values of the CO shift of -5 and $+4$ cm^{-1} (see Table 1). A significant charge transfer was also detected, at variance with previous findings.

Pacchioni and coworkers [13–16], long ago have proposed to treat ionic systems, like the MgO(0 0 1) surface, by a cluster approach, in which the quantum zone, treated with standard basis sets and Hamiltonian, is embedded in a large array of bare charges. The value of the charges and the number of the included ions have been chosen in such a way that the Madelung potential at the Mg^{2+} cation, is reproduced within "reasonable accuracy" [14–16]. Constrained space orbital variation (CSOV) scheme was adopted as a technique for partitioning both the BE and the CO

frequency shift. The analysis revealed that electrostatic and Pauli exchange repulsion were the main driving forces, whereas charge transfer was negligible. The obtained BE range between 23 and 32 kJ/mol, at HF and CI level, respectively. The CO shift was as large as $+31$ cm^{-1}, a value which appears clearly overestimated when compared to experiment ($+14$ cm^{-1}).

From these data, it is clear that the modeling of ionic surfaces is less straightforward than it was thought, and the MgO quantum cluster, either free or embedded in a bare ions, may not be the proper solution. That this was the case has been proved only recently by a seminal paper from the Pettersson group [17]. They shown that in order to obtain meaningful results, the quantum mechanical MgO cluster should be embedded in a total-ion ab initio model potential (AIMP) representation of the surrounding ions. The proposed procedure avoids the huge polarization of the atoms at the border of the quantum zone due to the unscreened charges. With the AIMP method they computed a CO BE of only 9 kJ/mol and a blue shifted vibrational frequency of $+7$ cm^{-1}, both obtained at correlated level and in general good agreement with the revised experimental results from the Freund laboratory (see Table 1).

This result stimulated Pacchioni and coworkers [18,19], Meijas et al. [20] and Pascual and Pettersson [21] to fully exploit the deformation of the electrostatic potential in the binding region, as a function of the cluster size and the embedding technique (AIMP or bare charges). For the first time, a comparison between the electrostatic potential resulting from CRYSTAL calculation with that computed for the embedded cluster was also addressed [18]. The Rösch group [22] also reported a DFT-GGA cluster calculation following the AIMP recipe, obtaining a very small BE of 7–10 kJ/mol at Becke–Perdew and B-LYP level of Hamiltonians, respectively.

The results confirmed the large deformation of the potential due to the unscreened charges at the quantum frontier which, in turn, deeply affect the adsorption properties of the surface. This means that, the role played by the electrostatic and exchange repulsion terms, computed with the former cluster calculations, should be revised accordingly.

That the CO/MgO(0 0 1) system is still an open case, is confirmed by a very recent paper by Soave and Pacchioni [23]. A B3-LYP/6-31G(d) level of calculus was adopted on a Mg_9O_9 cluster, either bare or embedded in point charges in which the positive ones have been represented by ECP to avoid the spurious polarization at the cluster borders. The use of a bare cluster follows a suggestion by Pelmenschikov and coworkers [24], that embedding the quantum cluster in net charges may worsen the results as it is now clear from the above discussion. The data reported in Table 1 show almost no binding and a CO frequency red shifted of -7 and -5 cm^{-1} for the bare and the embedded clusters, respectively.

The purpose of this paper is then to address again the adsorption of CO on MgO(0 0 1), with the least number of computational compromises, by using the following strategy: (i) a periodic approach as implemented in the CRYSTAL-98 computer code; (ii) the electron correlation at DFT with the state of art B3-LYP functional, available at present only in CRYSTAL-98 among the periodic codes; (iii) a re-examination of the electrostatic model for the adsorption, in terms of the physically sound multipolar expansion of the interaction energy, rather than using some arbitrary partition of the HF wave function; (iv) a comparison with molecular cases, to gauge the relevance between the various components of the BE for the CO/MgO(0 0 1) system; (v) the interpretation of the CO shift in term of a multipolar expansion inclusive of higher terms than the simpler Bagus–Pacchioni relationship [13]; (vi) the role of lateral interactions on the above observables.

2. Models

The MgO(0 0 1) surface has been modeled by a three-layers slab cut from a perfect MgO bulk crystal unit cell whose has been optimized within the Fm3m space group. The adopted slab was thick enough to ensure good convergence of the surface energy when compared to that computed for a five-layers slab. As a further check of the slab thickness, we computed the electrostatic potential outside the surface and found it to be almost in-

distinguishable from that computed with a five-layers slab. Three different CO coverages have been considered, namely the (1×2), (1×4) and (1×8) (one CO molecule per two, four and eight Mg^{2+} ions, respectively), in order to study the effect of the lateral interactions (vide infra) on the computed quantities. The carbon monoxide has been adsorbed perpendicularly to the surface Mg^{2+} through its carbon atom. Previous studies [25] have already shown that, when appropriate correlated methods are adopted, the adsorption through the oxygen atom is disfavored in comparison to that via the carbon atom, so that the latter has not been considered here. The resulting 2D unit cells are shown in Fig. 1. To keep as much as symmetry as possible, the CO has been adsorbed on both sides of the MgO(0 0 1) slab, after checking for the negligible intraslab CO/CO interaction. The number of symmetry operators is 16 for all the considered CO coverages. In order to discuss in some details the results of the CO/MgO(0 0 1) system, two different molecular systems have also been considered for comparison: the CO/Na$^+$ adduct and the CO/CO$_2$ van der Waals complex, respectively. The latter has a T-shaped structure with the CO monomer along the C_2 symmetry axis of the CO_2 molecule and the two C atoms facing each other. The CO_2 molecule, in virtue of its large quadrupole moment, sports a molecular electrostatic potential along the line perpendicular to the C atom which is topologically similar to that of the region above the Mg^{2+} ion of the MgO(0 0 1) surface.
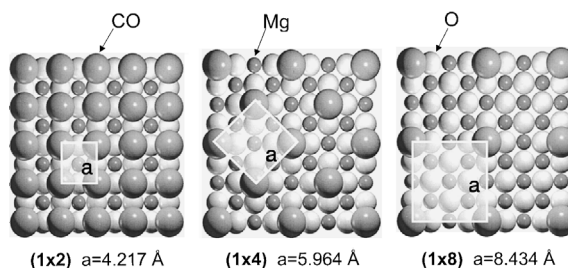

Fig. 1. Pictorial view of the CO/Mg(0 0 1) system at different CO coverages. Ionic radii have been used for the spheres representing Mg^{2+} and O^{2-} ions, and van der Waals radii for CO. The unit cell length a is based on the experimental Mg–O distance of 2.109 Å.

The CO/Na$^+$ adduct has been recently fully characterized computationally by some of us [26], whereas the CO/CO$_2$ complex has been studied in a pulsed molecular beam by Legon and Suckley [27] using diode laser spectroscopy combined with Fourier transform microwave spectroscopy as well as with high resolution infrared spectroscopy by Randall et al. [28]. Very recently, accurate molecular mechanics calculations have also been reported [29].

3. Computational methods

All calculations have been carried out at Hartree–Fock (HF) and DFT level. For the latter, the majority of the calculations use the B3-LYP functional with the Becke's hybrid exchange B3 [30] and the Lee, Yang and Parr [31] correlation functionals. For the CO (1×2) coverage only, some calculations have been done using a local density functional (S-VWN) and two gradient corrected ones (B-LYP and B3-PW). For S-VWN, the local exchange derives from the Dirac proposal [32], supplemented by the local correlation VWN [33] functional; the B-LYP uses the Becke's exchange [34] functional combined with the LYP [31] correlation functional, whereas the B3-PW combines the Becke's hybrid exchange B3 [30] with the Perdew–Wang's correlation functional [35–37]. All periodic calculations have been carried out by using the CRYSTAL-98 [38,39] computer code. In the DFT calculations [40], the exchange-correlation potential is expanded in an auxiliary basis set of Gaussian-type functions, with even tempered exponents. At each SCF iteration the auxiliary basis set is fitted to the actual analytic form of the exchange-correlation potential, which changes with the evolving charge density. In the present case, we have redefined the auxiliary basis set in order to further improve the quality of the fit (the new auxiliary basis set has been deposited [41]). For the numerical integration, the atomic partition method proposed by Becke [42] has been adopted, combined with the Gauss–Legendre (radial) and Lebedev (angular) quadratures. The grid of sample points suggested in the CRYSTAL-98 user's manual [39] has been adopted. The numerical values of the

parameters controlling the evaluation of the infinite Coulomb (both for HF and DFT) and exchange (for HF) series have been fixed to 6, 6, 6, 12, respectively, to ensure the high numerical accuracy required to evaluate the small CO BE and for the numerical evaluation of the CO vibrational frequency. The number of reciprocal lattice points ("k-points") at which the Hamiltonian matrix has been diagonalized is 6, corresponding to a shrinking factor $S = 4$. Calculations performed for the isolated CO molecule have been done with the GAUSSIAN 98 [43] computer code.

The BEs of CO on the MgO(0 0 1) surface were corrected for the basis set superposition error (BSSE) by using the full counterpoise method [44] as implemented in CRYSTAL-98.

About 10 different Gaussian basis sets have been checked as a preliminary tests, in order to achieve the best compromise between accuracy and speed of the calculation. For the production stage, two basis sets have been selected, named A and B, respectively. Basis set A, results from a previous study [45], and uses an 8-511G contraction for Mg (outermost $\zeta_{sp}(Mg) = 0.28$ Bohr^{-2}) and an 8-411G one (outermost $\zeta_{sp}(O) = 0.179$ Bohr^{-2}) for the oxygen atoms belonging to the MgO slab. For the CO molecule the standard 6-311G(d) [46] basis set $(\zeta_d(O) = 1.29$ Bohr^{-2}; $\zeta_d(C) = 0.626$ Bohr^{-2}) has been adopted. Basis set B is the TZV developed by Ahlrichs and coworkers [47] which has been adopted for Mg and O atom of the MgO slab, with the original 73211-51G and 62111-411G contraction schemes, respectively; for C and O atoms of the CO molecule, the VTZ 511111-411G contraction from the Ahlrichs collection [48] has been adopted. This basis set, when supplemented by polarization functions as described below, has been successfully used to model the interaction between CO molecule and the complete series of alkaline cations, using well correlated computational techniques [26]. Because of the linear dependence problems which may arise in CRYSTAL-98 with too diffuse Gaussian basis functions, the outermost s shell of the Mg basis set $(\zeta_s(Mg)$ 0.036 Bohr^{-2}) has been deleted, whereas the outermost p shell of the O atom has been kept unchanged $(\zeta_p(O)$ 0.175 Bohr^{-2}). The Mg and O atoms of the MgO slab were also supplemented

with one set of polarization functions, with standard exponents [48] ($\zeta_p(Mg) = 0.189$ Bohr^{-2}, $\zeta_d(O) = 1.2$ Bohr^{-2}), whereas for both the oxygen and the carbon atoms of the CO molecule two sets of polarization functions have been added with exponents derived from the standard ones [48] following an even tempered recipe ($\zeta_d(O) = 2.4/0.6$ Bohr^{-2}; $\zeta_d(C) = 1.6/0.4$ Bohr^{-2}). Five components only for the polarization functions have been used for both basis set A and B.

For computing the properties of CO/Na$^+$ and CO/CO$_2$ complexes, the same basis set B has been used for both CO and CO$_2$ molecules, whereas a TZV 73211-51G [47] with two set of diffuse p functions ($\zeta_p = 0.0196/0.131$) has been adopted for the Na$^+$ cation. For the MgO(0 0 1)/CO system, geometry optimization, as discussed in details in the specific subsections, has been carried out by a series of three-points energy evaluations, followed by a parabolic search of the minimum configuration for each degree of freedom. The procedure is then iterated, until the global minimum was reached. This procedure, even if inefficient for complex molecules, is particularly convenient here, because of the symmetry constraints and the few degrees of freedom to be considered.

The CO vibrational frequency has been computed numerically by exploring a range of displacements, x, around the CO equilibrium bond length of ± 0.06 Å in steps of 0.0075 Å each and adding two extra points at the opposite extremes at ± 0.08 for a total of 19 energy points. The energy points have been fitted with a function containing two independent Morse curves, $E(x) = \sum_{i=1}^{2} \alpha_i[1 - \exp(-\beta_i(x - \gamma_i))]$ and the force constant was computed by the analytical second derivative of $E(x)$, evaluated at $x = 0$. To check for the accuracy, the harmonic stretching frequency was then compared to that from a full analytical calculation performed with GAUSSIAN 98 and an agreement within 1 cm^{-1} has been found. A careful check showed that this function ensures both a better numerical stability than a polynomial fit, usually adopted in the literature and the higher accuracy needed to compute the CO frequency. The same procedure was then followed for the calculation of the adsorbed CO harmonic fre-

quency. In that case, the CO centre of masses (CO$_{com}$) was kept fixed at the value resulting from the optimized geometry of the adsorbed CO, while stretching the CO bond length of the same amount used to compute the CO stretching frequency for the free molecule.

4. Results and discussion

4.1. Features of the isolated CO and the MgO(0 0 1) slab

The main features of the isolated CO molecule computed in the present work have been summarized in Table 2. The bond length, the numerical harmonic stretching frequency and the electric multipoles and polarizability are in very good agreement with the available experimental data, when the highest B3-LYP/B level of theory is considered. The B3-LYP/A gives already satisfactory results, whereas basis set B is needed to improve the agreement, particularly for the molecular polarizability. As already discussed in full details [26], HF level of theory, irrespective of the adopted basis set, gives a wrong description of the CO molecular electrostatic potential. This fact is shown from the data in Table 2, in which the di-

Table 2
Comparison between calculated and experimental features of the isolated CO molecule

Method	HF/A	B3-LYP/A	B3-LYP/B	Experiment
R	1.105	1.127	1.125	1.128 [69]
ω_h	2443	2219	2203	2170 [70]
μ_z	−0.060	0.048	0.038	0.043 [71]
Θ_{zz}	−1.68	−1.58	−1.53	−1.5 [72]
Ω_{zzz}	4.00	3.26	3.52	
Φ_{zzzz}	−9.44	−8.28	−9.01	
α_{zz}	12.45	13.17	14.49	15.51 [73]
Q_C	0.1863	0.0790	0.1913	

R, bond distance in Å; ω_h, harmonic stretching vibrational frequency in cm^{-1}; z components of: the dipole moment μ_z, quadrupole moment Θ_{zz}, octupole moment Ω_{zzz}, hexadecupole moment Φ_{zzzz} (all in a.u. and referred to the molecular center of mass) and of the dipole polarizability α_{zz} (a.u.). Q_C is the Mulliken net atomic charge of the carbon atom (electron). Data computed with GAUSSIAN 98 code.

pole moment has the wrong sign along with a general overestimation of the values of the higher multipoles, whereas the value of the molecular polarizability is too low.

The geometry of MgO bulk was optimized by minimizing the total energy as a function of the unit cell parameter, within the Fd3m space group. The optimized values were 4.210, 4.250, and 4.242 Å at HF/A B3-LYP/A and B3-LYP/B, respectively, in very good agreement with experimental [49,50] and previous computations results [51,52]. The optimized bulk structures have then been manipulated by CRYSTAL-98 code, to define the three-layers slab. The surface Mg^{2+} and O^{2-} ions have been allowed to relax in a direction normal to the surface, by keeping the ions of the central layer fixed at their original positions. The resulting rumpling is minute (the Mg^{2+} ions move inwards by less than 0.001 Å whereas the O^{2-} ions move outwards by the same amount), in agreement with previous computational findings for the related cases of the NaCl(0 0 1) [53], LiH(0 0 1) [54] and LiF(0 0 1) [55] surfaces, respectively. To avoid any bias, all the subsequent calculations have been carried out on the rumpled surface.

4.2. Features of the interacting MgO(0 0 1)/CO system

4.2.1. Geometries

For the adsorption of carbon monoxide, the MgO(0 0 1) surface geometry was kept fixed at that optimized for the free surface. Any attempt to reconstruct the MgO(0 0 1) surface as a results of the CO interaction, changed the BE by less than 0.1 kJ/mol, so that only the CO bond length and the Mg^{2+}/CO_{com} distance were then optimized.

The results are reported in Table 3: the (1×8) coverage was not treated at the highest B3-LYP/B level, because too demanding for our computational resources. The comparison between the optimized CO bond length in the MgO(0 0 1)/CO system with that for the free molecule, (see Table 2) shows almost no changes. This is a first indication of the very small perturbation induced in the CO molecule by the electric field generated by the MgO(0 0 1) slab.

The optimized $Mg^{2+}\cdots C$ distance shows some dependence to the method and basis set adopted, whereas almost no dependence is shown as a function of the CO coverage. The largest effects is, however, due to the introduction of electron correlation, by which the optimized HF $Mg^{2+}\cdots C$ distance of about 3 Å reduces to ≈ 2.6 Å at B3-LYP level. This effect is expected, considering the general shrinking of the HF electron density caused when dynamic electron correlation is taken into account; this, in turn, reduces both the van der Waals radius of the carbon atom and the ionic radii of the surface Mg^{2+} and O^{2-} ions, allowing the CO molecule to get closer to the MgO(0 0 1) surface.

In this way, the CO molecule experiences a higher electric field from the MgO(0 0 1) surface at B3-LYP level than at the HF one.

4.2.2. Binding energies and basis set superposition error

In a periodic treatment of surface adsorption phenomena, the BE per unit cell per adsorbate molecule is defined as:

$$\text{BE} = E(\text{slab}) + E(\text{ads}) - E(\text{slab/ads})$$

where, $E(\text{slab/ads})$ is the total energy of the slab in interaction with the periodic array of adsorbed molecules; $E(\text{slab})$ is the energy of the slab alone, and $E(\text{ads})$ is the energy of the periodic array of adsorbed molecules without the underneath solid surface. All these quantities are defined per unit cell and are negative.

However, the observed BE, BE_{exp}, corresponds to the process in which the molecules move from an ideal gas state onto the surface, and is defined as:

$$\text{BE}_{exp} = E(\text{slab}) + NE(\text{mol}) - E(\text{slab/ads})$$

where, $E(\text{mol})$ is the energy of one isolated adsorbate molecule and N is the number of adsorbed molecules per unit cell. The difference between the computed BE and the experimental BE_{exp} is due to the interaction energy, per unit cell, between the adsorbate molecules themselves, i.e., without the underneath surface:

$$\text{BE}_{exp} - \text{BE} = E_L = E(\text{ads}) - NE(\text{mol})$$

Table 3
Geometrical features (Å) of the CO/MgO(1 0 0) system as a function of CO coverage, Hamiltonian and basis set

Method:	HF/A			B3-LYP/A			B3-LYP/B	
Coverage:	(1×2)	(1×4)	(1×8)	(1×2)	(1×4)	(1×8)	(1×2)	(1×4)
CO	1.105	1.105	1.105	1.127	1.127	1.127	1.125	1.125
CO$\cdots$CO	4.21	5.95	8.42	4.25	6.01	8.49	4.24	6.00
Mg$\cdots$C	3.01	2.99	2.99	2.61	2.61	2.61	2.64	2.63
Mg$\cdots$CO$_{com}$	3.64	3.62	3.62	3.25	3.25	3.25	3.28	3.27

E_L is also known as the lateral interaction energy and can be either positive (repulsion) or negative (attraction) depending on the nature of the admolecules and on their separations. In the limit of very low coverages, i.e., large distances between the adsorbate molecules, E_L will obviously tend to zero, so that $BE_{exp} \approx BE$. When dealing with intermolecular interactions, the computed BE should always be corrected for the BSSE following the counterpoise method proposed for molecular complexes. Therefore, the BSSE corrected BE^C becomes:

$$BE^C = E(\text{slab}/[\text{ads}]) + E([\text{slab}]/\text{ads})$$
$$- E(\text{slab}/\text{ads})$$

in which $E(\text{slab}/[\text{ads}])$ and $E([\text{slab}]/\text{ads})$ are respectively the energy of the slab with the basis functions only of the adsorbate and vice versa.

Table 4 shows the HF and B3-LYP computed quantities, calculated with the same basis set adopted for the geometry optimization. The BEs are all very small, within 10 kJ/mol at the best B3-LYP/B level: the HF/A BE are also grossly underestimated with respect to the corresponding B3-LYP/A data.

The striking feature here, is the size of the BSSE at all levels of calculus: the BE^C practically vanishes at HF/A level, is around 2.5 kJ/mol at B3-LYP/A level and 3.7 kJ/mol at B3-LYP/B for the CO (1×4) coverage.

Some further test calculations were also carried out at S-VWN/A and B-LYP/A levels, but no new insights emerged: as expected, the local density BE was largely overestimated, whereas the B-LYP value was very close to the corresponding B3-LYP one.

The lateral interaction energy E_L is only significative at the (1×2) coverage, so that the final BE_N at B3-LYP/B level for the (1×4) case is 3.3 kJ/mol, very close to BE^C reported above.

It is worthnoting that the BSSE is evaluated in a coherent way within the CRYSTAL-98 code, at variance with the estimate reported by Gutowsky and coworkers [11] using the NWCHEM package [12] and a similar periodic approach, in which the BSSE was estimated by means of a finite cluster calculation. In that case, it was assumed that the BSSE will be the same of that resulting from the periodic calculation, an assumption hard to support, in light of the differences of both the electronic structure of the cluster and the outside

Table 4
BE (kJ/mol) of CO adsorbed on the MgO(0 0 1) surface as a function of CO coverage, Hamiltonian and basis set. BE^C is corrected for BSSE

Method:	HF/A			B3-LYP/A			B3-LYP/B	
Coverage:	(1×2)	(1×4)	(1×8)	(1×2)	(1×4)	(1×8)	(1×2)	(1×4)
BE	6.2	6.4	6.4	13.6	14.0	14.0	9.1	10.3
BE^C	0.9	0.8	0.7	2.8	3.0	2.0	3.0	3.7
E^L	2.4	0.6	0.1	1.6	0.4	0.1	2.6	0.4
BE_N	−1.5	0.2	0.6	1.2	2.6	1.9	0.4	3.3

E_L is the lateral interaction; $BE_N = BE^C - E_L$ is the net binding energy.

electric field when compared to that of a periodic slab.

From the accumulated experience in the calculation of intermolecular complexes, such a large BSSE associated to a weakly bound adsorbate at the ionic MgO surface is surprising. To better understand this point, we have computed the BSSE correction for 10 different configurations, in which the Mg^{2+}/CO_{com} distance spans the 2.7/3.8 Å range. Fig. 4(a) shows, for the case of CO at (1×2) coverage, the B3-LYP/B curves of BE and BE^C, respectively: clearly, the BSSE is very large (on the relative scale) and decreases only slowly with the separation between CO_{com} and the MgO(0 0 1) surface. It is worthnoting, that no significant change in the Mg^{2+}/CO_{com} equilibrium distance results, when comparing the BE^C and the BE curves.

The analysis of the BSSE origin, revealed that the largest fraction comes from the MgO(0 0 1) surface, showing some deficiency in the basis set used to describe the MgO slab. At the present stage of the CRYSTAL-98 technology, it is very difficult to further improve the MgO basis set, because of technical problems when dealing with too diffuse basis sets. In that respect, it is worthnoting the large decrease of the BSSE when passing from A to B basis sets (see Table 4).

Comparison with the related molecular complexes is addressed in Fig. 4, in which similar curves for the CO/Na^+ and CO/CO_2 complexes are reported. The BSSE for the CO/Na^+ is so small (less than 1 kJ/mol at the equilibrium separation on a total BE of about 42 kJ/mol), that only the uncorrected curve has been reported; for the CO/CO_2 complex, the BSSE is about 0.5 kJ/mol with respect to the uncorrected BE of about 1.5 kJ/mol. This value of the BE is in fair agreement with the value of 1.3 kJ/mol computed by Randall and coworkers [28] using an accurate empirical potential derived from ab initio properties of the separated molecules. The CO_{com}/Na^+ in the CO/Na^+ complex is about the same (3.2 Å) of that optimized for the CO/MgO(0 0 1) system, whereas a much larger separation (4.1 Å) is computed for the CO/CO_2 complex.

These facts have a simple explanation based on the ionic and van der Waals radii of the atoms in

direct contact. By assuming standard values of the ionic radii of 1.13, 0.80 and 1.25 Å for Na^+, Mg^{2+} and O^{2-} ions, respectively and the van der Waals radii of 1.70 and 1.52 Å for the carbon and oxygen atoms of the CO and CO_2 molecules, the minimum approach distances of 3.2, 3.5 and 4.1 Å are computed between CO_{com} and MgO(0 0 1), Na^+ and the carbon of CO_2, respectively. These values are extremely close to that resulting from the full B3-LYP/B ab initio calculations (see Table 4). In turn, these values modulate the final value of both BEs and BSSE.

For instance, even if the CO_{com} distance is similar for the MgO(0 0 1) and Na^+ complexes, the Mg^{2+} cation is surrounded by four bulky oxygen ions: these anions are responsible of the large BSSE coming from the MgO(0 0 1) surface, because the negative charge of the surface O^{2-}, not completely screened by the Madelung potential, penetrates the wave function of the adsorbed CO molecule. This effect is obviously absent for CO/Na^+ case and much smaller in the CO_2/CO complex where both the larger separation between its constituents and the presence of only two covalent oxygen atoms bound to the central carbon atom reduces the BSSE.

The increased penetration of the CO molecule for the MgO(0 0 1)/CO case has also a profound effect on the electric field felt by the CO itself, and particularly in the region nearby the carbon atom, as already pointed out by Pelmenschikov and coworkers [24]. Fig. 2 shows the electric field computed ab initio: (i) along the line from Mg^{2+} and normal to the surface; (ii) along the line from the carbon atom and normal to the molecular axis of the CO_2 molecule; (iii) away from the Na^+ cation.

For the MgO(0 0 1) case, the electric field is obtained by analytical differentiation of the electrostatic potential computed with CRYSTAL-98 at the B3-LYP/B level, along the line starting from the Mg^{2+} ion and normal to the MgO(0 0 1) plane. The electrostatic potential points have been best fitted with the function:

$$V(d) = \frac{a}{e^{bd} - 1} \tag{1}$$

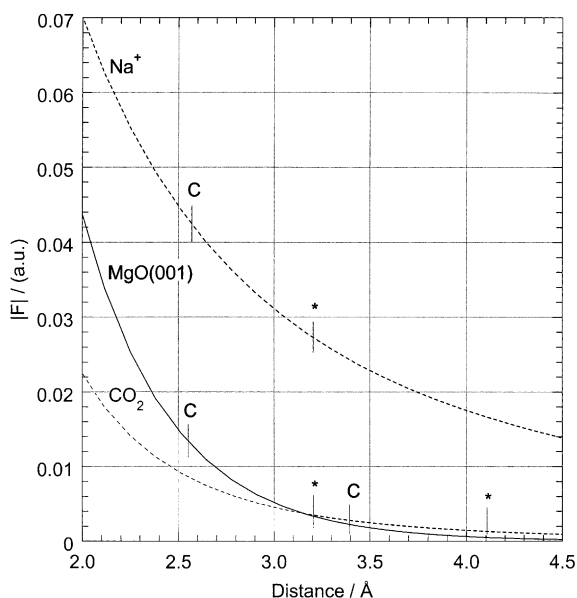in which $a = 2.583$ Hartree and $b = 1.118$ Bohr^{-1}, respectively, where d is the distance from the

Fig. 2. Modulus of the electric field (atomic unit) as a function of the distance (Å) from: the Mg^{2+} ion of the MgO(0 0 1) (continuous line), the Na^+ ion and the C atom of the CO_2 molecule (dotted lines). Also reported are the positions of the C atom and $CO_{com}(*)$ of the adsorbed CO molecule in the corresponding complexes. For the CO/MgO(0 0 1) system the (1×2) case is considered. Results at B3-LYP/B level.

Mg^{2+} ion. It is worthnoting that the electric field computed at the HF/A level (not shown) is indistinguishable from that at the B3-LYP/B level, showing that the electric field outside the surface of an ionic solid (of which the MgO is a good prototype) is not influenced by electron correlation and follows the expected exponentially decay [56,57].

For the Na^+ cation, the potential is simply $V(d) = 1/d$, whereas for the CO_2 molecule the B3-LYP/B electrostatic potential has been best fitted with the expression: $V(d) = 1.4414/d^{2.943}$.

Also reported in Fig. 2, is the optimized position of both the carbon atom and the CO_{com} in the corresponding complexes.

For the CO/MgO(0 0 1) case, the field is more than three times larger than that experienced by the CO carbon atom in the CO/CO_2 complex: indeed, a much steeper field is also experienced by the carbon σ lone pair (region from 2 to 2.6 Å) for the CO/MgO(0 0 1) system with respect to the al-

most uniform field felt by CO in the CO/CO_2 adduct (region from 2.8 to 3.4 Å). The larger variation of the electric field throughout the CO molecule for the MgO(0 0 1) case, becomes almost negligible (uniform field) in the region where CO becomes bound to the CO_2 molecule. The variation of the electric field for the MgO(0 0 1) case is close to that resulting from the bare Na^+ cation, even if smaller on an absolute scale, so that one may expect that also the CO polarization is of some relevance for the surface/adsorbate case. This fact brings some doubts, at least from a formal viewpoint, about treatments in which the CO response to such perturbations is interpreted in terms of a uniform electric field [13,26].

An important contribution to the binding is the charge transfer term, which is of pure quantum mechanical nature. It is in general difficult to evaluate this term without making use of some arbitrary partition of the wave function, avoiding the bias introduced by the BSSE. For the CO/MgO(0 0 1) case, the Mulliken analysis of the B3-LYP/B wave function, gives a minute charge transfer of 0.001 electrons (from MgO to the CO) at (1×2) coverage. The same evidence comes from the graph of the density of states (DOS) of the CO/MgO(0 0 1) system, in comparison with the DOS for the noninteracting CO slab (see Fig. 3): here, only the 5σ level (i.e., the carbon atom lone pair) is shifted to lower energies by 0.024 Hartree as a consequence of the stabilizing effect due to the positive electric field felt by the 5σ in that region (see Fig. 2 for details).

These data are in disagreement with the same set of results computed by Gutowsky and coworkers [11] with a similar periodic approach. They reported a much larger charge transfer from the MgO to the CO molecule of 0.087 and 0.085 electrons at LDA and PBE96 levels, respectively. Furthermore, their published DOSs show large shifts of all CO levels, with the 5σ of the carbon atom being shifted up in energy (i.e., the CO lone pair is destabilized by the surface field) by 0.021 Hartree. These authors explained these puzzling results as a consequence of the large charge transfer, whereas the present results do not support such a view, which seems unlikely in light of the very small BEs.
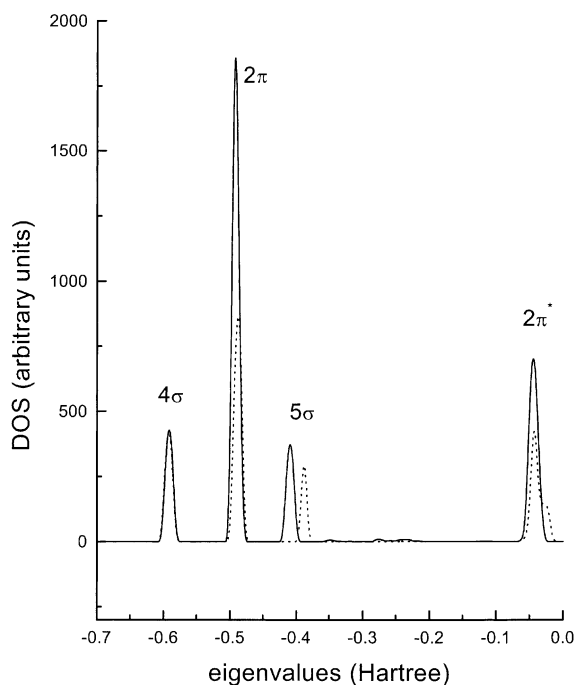
Fig. 3. Density of states (DOS) (arbitrary units) for the CO/MgO(0 0 1) system at (1×2) CO coverage. Continuous line is for the CO/MgO(0 0 1) system; dotted line is for the free CO(1×2) slab. Energies in Hartree.

4.3. Origin of the binding energy of MgO(0 0 1)/CO

From basic electrostatic, the BE of the CO molecule adsorbed on top of the Mg^{2+} ion belonging to the MgO(0 0 1) surface, can be described in terms of the well known expansion, involving the central electric multipole moments and the polarization of the CO molecule and the derivatives of the electrostatic potential outside the surface Mg^{2+} ion evaluated at the distance d where

the CO_{com} is located in the MgO(0 0 1)/CO complex [58]:

$$U_E = \mu_z F + \tfrac{1}{2}\Theta_{zz}\nabla F + \tfrac{1}{6}\Omega_{zzz}\nabla^2 F + \tfrac{1}{24}\Phi_{zzzz}\nabla^3 F$$
$$+ \cdots + \tfrac{1}{2}\alpha_{zz}F^2 + \cdots \tag{2}$$

in which μ_z, Θ_{zz}, Ω_{zzz}, Φ_{zzzz} are the z-components of the dipole, quadrupole, octupole, hexadecupole electric moments and α_{zz} is the static dipole polarizability of the free CO molecule, respectively, evaluated at the CO_{com}. F is the electric field defined as $F(d) = -\nabla V(d)$. The same procedure is followed for the CO/Na^+ and CO/CO_2 adducts. Results of such electrostatic analysis, evaluated at the equilibrium separations, are shown in Table 5, whereas values for a larger range of separations are shown in Fig. 4.

We have also checked for the convergence of the multipolar expansion, using the atom centered distributed multipoles for CO, computed with the CRYSTAL-98 program and found no significant difference with the adopted central multipolar expansion.

These data show a striking difference between the CO/MgO(0 0 1) case and the molecular cases: the electrostatic model predicts a U_E value of -16.1 kJ/mol, almost six times bigger than the BSSE corrected ab initio BE. The U_E value can be reconciled with the ab initio BE^C value by considering a value of 14 kJ/mol of exchange repulsion (not accounted for in the electrostatic analysis) caused by the oxygen anions surrounding the Mg^{2+} cation. The exchange repulsion term decreases slowly in the range of distances of interest (see Fig. 4), so that only around 4 Å the U_E becomes close to the $-BE^C$. The delicate interplay between exchange repulsion and electrostatic attraction has already put in evidence by means of

Table 5
Electrostatic contributions to the interaction energies (kJ/mol) for the CO/MgO(0 0 1), CO/Na$^+$ and CO/CO$_2$ systems

System	U_μ	U_θ	U_ω	U_ϕ	U_α	U_E	$-BE^C$
CO/MgO(0 0 1)	−0.28	−6.4	−5.4	−3.9	−0.15	−16.1	−3.0
CO/Na$^+$	−2.7	−17.5	−6.6	−2.7	−13.5	−43.0	−41.8
CO/CO$_2$	−0.13	−1.35	−0.67	−0.33	−0.03	−2.5	−1.28

U_μ, U_θ, U_ω, U_ϕ, U_α are the contribution from the dipole, quadrupole, octupole, hexadecupole and polarizability to the total U_E electrostatic energy. BE^C is the BSSE corrected ab initio BE. Data are at B3-LYP with basis set described in the text. For CO/MgO(0 0 1), BE^C at (1×2) coverage has been considered.
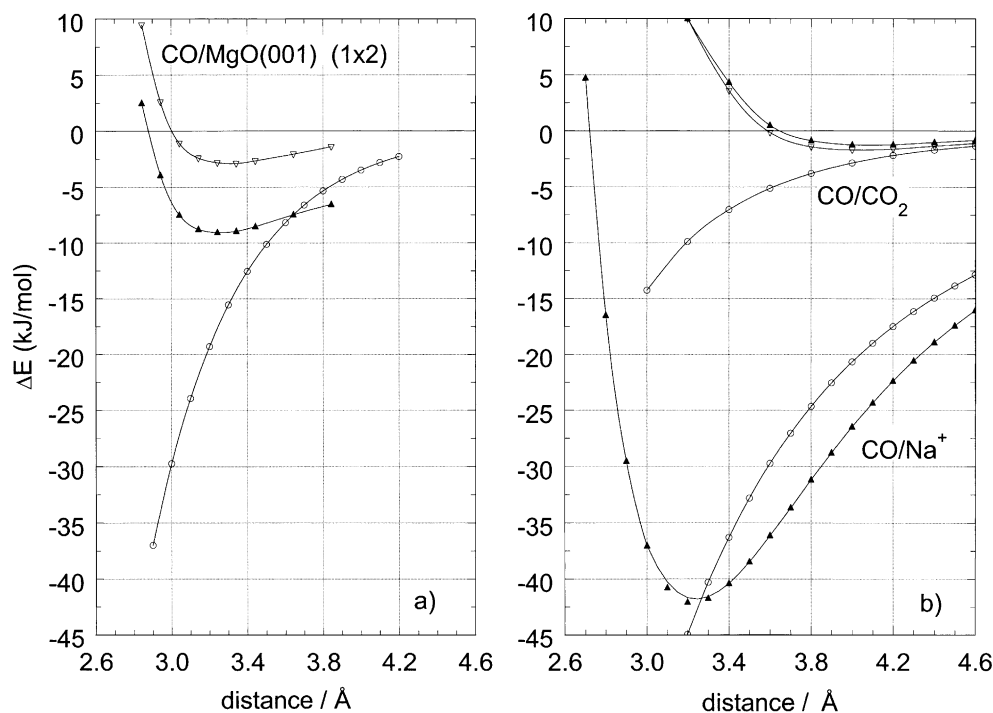
Fig. 4. B3-LYP/B energy of interaction, ΔE (kJ/mol) as a function of the distance (Å) between the CO center of masses and the Mg^{2+} ion of the MgO(0 0 1) surface (a); the C atom of the CO_2 molecule in the CO/CO_2 complex and the Na^+ cation in the CO/Na^+ adduct (b). Filled triangles represent $-BE$ (see Table 4), unfilled triangles $-BE^C$ and empty circles the energy of interaction computed with the classical electrostatic expression (see text for details).

the CSOV analysis applied to the CO adsorption modeled by embedded MgO clusters [14–16] and it is reassuring that a very similar result has obtained here using a completely different approach.

The story is completely different for the CO/Na^+ case: here U_L is already very close to the ab initio results, showing that exchange repulsion is almost absent in this case, because of the bare nature of the isolated Na^+ cation. Inspection of both data on a larger range of distances reveals that the ab initio values are always larger than the electrostatic ones because of the stabilizing charge transfer contribution (about 0.055 electrons at the equilibrium CO/Na^+ distance, from the Mulliken analysis) not accounted for by the electrostatic expansion.

As already anticipated when discussing the geometrical features of the considered systems, the case of the CO/CO_2 complex is different from the other two cases: the large exchange repulsion value

due to the large van der Waals radius of the C atoms, prevents CO to approach more closely the CO_2 molecule. This means that the U_E contribution is already close to the ab initio $-BE^C$.

As a further point, the electric field and its derivatives are smaller than those computed for the MgO(0 0 1) surface, resulting in a smaller U_E.

A more strict comparison between the three systems can be addressed by analyzing the U_E curves at the fixed distance of 3.2 Å between the CO_{com} and the Mg^{2+}, Na^+ and C atoms, respectively. As already discussed, the exchange repulsion is about 14 kJ/mol for CO/MgO(0 0 1), almost negligible for CO/Na^+ and more than 20 kJ/mol for the CO/CO_2 complex. The fact that the CO is bound at that distance at the MgO(0 0 1) surface and unbound in the CO/CO_2 complex is because of the lower value of the U_E (less than 10 kJ/mol) for the latter when compared to the value of about 16 kJ/mol for the former.

A careful analysis of the components of the U_E reported in Table 5 reveals some interesting features: the leading contributions for the CO/MgO(0 0 1) case come from the U_θ, U_ω and U_ϕ terms, whereas the U_μ term is negligible. This means that, at least for adsorbates with small dipole and large quadrupole moments like CO and CO_2, the BE is sensitive to higher derivatives of the electric field outside the surface, rather than on the electrostatic potential or the field itself. The higher order derivatives of F are indeed large in virtue of the exponential nature of the electrostatic potential outside an infinite surface of a ionic material, at variance with the inverse power of the distance for the molecular cases. The relevance of the higher derivatives of F for the case of CO/MgO(0 0 1) system is clearly shown in Table 5 in which the U_ω and U_ϕ values are even larger than the corresponding values computed for the much stronger bound CO/Na^+ complex.

This fact has not been previously recognized when modeling the surface properties by means of the cluster approach, in which the exponentially decaying shape of the surface potential is difficult to be accurately modeled by the finite cluster. Usually only the electrostatic potential and, in some cases the electric field outside the clusters were compared to those resulting from the periodic calculation [18–20].

4.3.1. Vibrational features

Table 6 shows the computed harmonic ω stretching frequency of CO as an isolated molecule, as a periodic slab in the (1×2), (1×4) and (1×8) arrangements and when adsorbed on the MgO(0 0 1) surface at the same coverages. The way in which these values have been computed is described in the computational methods section. As a further check of the goodness of the adopted numerical procedure, a comparison was carried out between $\Delta\omega$ for the CO/CO_2 complex computed at B3-LYP/B, using the analytical harmonic frequency from the GAUSSIAN 98 program with that computed with our numerical recipe. The analytical result gives a CO blue shift of 6 cm^{-1}, in very good agreement with the measured value of 5 cm^{-1} [28] and with our numerical estimate of 6 cm^{-1}. This indicates that: (i) the best method here adopted, namely, B3-LYP/B, is able to cope with both the BE and the CO frequency shift for a very weakly bound complex, giving credits to the results obtained for the CO/MgO(0 0 1) system; (ii) the numerical method adopted for computing the CO stretching frequency is robust and accurate enough, even for very small shifts.

As a first step, we consider the effect of the CO coverage on the $\omega(CO)$ frequency. δ_{sf} values show that $\omega(CO)$ is indeed sensitive to the CO loading and that the static shift is decreasing with the CO dilution, becoming negligible for the (1×8) case. This trend is followed by both HF and B3-LYP schemes, even if with some significant dependence on the adopted method and basis set, particularly for the (1×2) loading. The computed trend of the static shift is, unfortunately, opposite to that found by a number of experiments [6]: we do not

Table 6
Numerical harmonic CO stretching frequency (cm^{-1}) for: free CO molecule (ω_f); slab of CO at various coverages without the underneath MgO(0 0 1) surface (ω_s); CO adsorbed on the MgO(0 0 1) surface at different coverages (ω_a)

Method	ω_f	Coverage	ω_s	ω_a	$\delta_{sf} = (\omega_s - \omega_f)$	$\delta_{af} = (\omega_a - \omega_f)$	$\delta_{as} = (\omega_a - \omega_s)$
HF/A	2443	(1×2)	2454	2456	+11	+13	+2
		(1×4)	2448	2448	+5	+5	+0
		(1×8)	2444	2445	+1	+2	+1
B3-LYP/A	2219	(1×2)	2224	2225	+5	+6	+1
		(1×4)	2221	2219	+2	+0	−2
		(1×8)	2220	2218	+1	−1	−2
B3-LYP/B	2203	(1×2)	2208	2211	+5	+8	+3
		(1×4)	2206	2208	+3	+5	+2

have a clever explanation to propose. As a further check of our procedure, the analytical frequencies of $(CO)_2$, $(CO)_4$ and $(CO)_8$ have been computed at B3-LYP/B with GAUSSIAN 98. The computed trend matches the one from the periodic cases, even if absolute values are different because of the finite nature of the adopted clusters.

The data that are directly comparable with the experimental $\Delta\omega(CO)$ shift is δ_{af}, the difference between the $\omega(CO)$ frequency of the adsorbed CO and that for the free molecule. Our best value is $+5$ cm^{-1} at B3-LYP/B and (1×4) coverage. Our computer facility does not allow the calculation for the (1×8) coverage, but no dramatic changes are expected.

Because these values are very small, the influence of the coupling between the CO high frequency mode and the soft $Mg^{2+} \cdots C$ mode has also been considered. The latter frequency falls around 100 cm^{-1}, so that the solution of a two mechanical coupled oscillators problem introduces a negligible blue shift of 0.5 cm^{-1} to $\omega(CO)$.

The last entry in Table 6, δ_{as}, shows the net effect of the MgO(0 0 1) surface on the $\omega(CO)$ frequency, separated by the static contribution. It turns out that the interaction with the MgO(0 0 1) surface has a smaller effect on the $\omega(CO)$ than that resulting from the lateral interactions among the adsorbed CO, and the best B3-LYP/B method, for the (1×4) coverage gives a value close to zero. As a further precaution, one should also consider that all data in Table 6 have been computed without taking BSSE into account.

4.4. Origin of the CO frequency shift

The analysis based on the classical electrostatic expansion of the interaction energy can be extended to cover also the harmonic frequency shift of the CO stretching mode.

The mathematical treatment usually based on the assumption of uniform electric field has already been proposed in the past [13,59] and used recently by some of us for the case of CO interacting with bare alkaline cations [26]. From the previous discussion on the BE, it is however clear that the assumption of a uniform electric field is, at least, questionable.

In order to evaluate the effect that higher derivatives of the electric field may have on the CO frequency shift, we have generalized the formulae reported in Ref. [26], to include terms in the interaction energy as high as the CO hexadecapole, interacting with the third derivative of the electric field exerted by the substrate (formulae not reported here). The value of the electric field and its derivatives have been computed at the position where the CO center of masses is located in the CO/Na^+ and CO/CO_2 complexes as well as in the $CO/MgO(0\,0\,1)$ system, by means of the analytical formulae previously discussed.

Table 7 shows the contribution to $\Delta\omega(CO)$ from the terms depending on higher order derivatives of the electric field, which are compared with the full ab initio value. For all considered systems, the constant field assumption is generally poor: for the $CO/MgO(0\,0\,1)$ case, the correction due to the field gradient $(+6$ cm$^{-1})$ which depends on the CO quadrupole moment, is as large as the contribution coming from the classical Bagus–Pacchioni constant field term $(+7$ cm$^{-1})$. Higher order terms, albeit smaller in absolute value, are of the opposite sign. A similar trend is shown by the CO/CO_2 case, and even for the extreme case of the CO/Na^+ system, the field gradient correction is sizeable, and brings the final shift very close to the full ab initio value (78 vs 77 cm^{-1}, respectively). Such an agreement also holds for the CO/CO_2 system (4 vs 6 cm^{-1}, respectively), whereas a value of 10 cm^{-1} is computed for $CO/MgO(0\,0\,1)$, definitely overestimated with respect to the full B3-LYP/B ab initio δ_{sf} datum of only 2 cm^{-1} (see Table 6). The last point shows that, in contrast with previous interpretation [15], the sole electrostatic contribution to the shift will overestimate the value of the shift itself, when compared to the full ab initio datum. This means that the exchange repulsion term, fully accounted for by the ab initio calculation, will decrease the pure electrostatic CO shift, a fact just opposite to the "wall-effect" invoked by Pacchioni and coworkers [15] on the base of the CSOV decomposition of $\Delta\omega$ for the case of CO adsorbed on model clusters. To further clarify this point we have also computed the contribution to the CO $\Delta\omega$ resulting from the polarization term, which has not included in the above discussion.

Table 7

Harmonic CO stretching frequency shift contributions $\Delta\omega$ (cm^{-1}) for CO/MgO(001), CO/Na$^+$ and CO/CO$_2$ systems resulting from multipolar expansion of the interaction energy

System	Multipolar expansion					Ab initio
	$\Delta\omega(\mu)$	$\Delta\omega(\theta)$	$\Delta\omega(\omega)$	$\Delta\omega(\phi)$	$\Delta\omega(E)$	$\Delta\omega$
CO/MgO (001)	7	6	−1	−2	10	2
CO/Na$^+$	65	16	−1	−2	78	77
CO/CO$_2$	3	2	−0.5	−0.5	4	6

$\Delta\omega(E) = \Delta\omega(\mu) + \Delta\omega(\theta) + \Delta\omega(\omega) + \Delta\omega(\phi)$; $\Delta\omega$ is the full ab initio result in the harmonic approximation. See Table 6 for further details about the adopted notation.

Because of the F^2 dependence this term is, however, completely negligible and the purely electrostatic shift is changed by 0.1 cm^{-1} only.

5. Summary and conclusions

In the present work the long studied CO/MgO(001) system, has been tackled again using a state of the art technique, i.e. ab initio periodic quantum mechanical treatment performed with the CRYSTAL-98 code [38]. A set of well balanced Gaussian basis sets has been adopted, coupled to the B3-LYP functional which is so successful for molecular [60] and crystalline materials [61,62]. The following variables have been carefully checked in order to gauge their relevance on both the computed BE and the CO harmonic frequency shift $\Delta\omega$: surface ions rumpling, behavior of both surface energy and electric field at the MgO(001) surface as a function of the thickness of the MgO(001) slab, basis set dependence, basis set superposition error, Hamiltonian, coupling between the ω(CO) and the Mg⋯C intermolecular modes, accuracy of the numerical procedure used to compute the CO stretching frequency, lateral interactions between adsorbed CO. A complete analysis based on the classical multipolar expansion inclusive of the third derivative of the electric field exerted by the MgO(001) surface for both the interaction energy and the CO frequency shift has also been carried out.

The analysis of the present results allows to conclude that:

1. Surface ions rumpling is negligible.

2. The electric field in the CO bonding region is almost insensitive to the thickness of the MgO(001) slab as it is the resulting surface energy.

3. The electric field outside the MgO surface computed at HF level is indistinguishable from that at B3-LYP level.

4. The BE is very small and for its correct evaluation, the BSSE should be properly accounted for, being almost half of the uncorrected BE value. This is at variance with the much smaller BSSE for the molecular cases taken as reference systems, namely the CO/Na$^+$ and CO/CO$_2$ and it is due to the larger exchange repulsion suffered by the CO molecule with the oxygen anion close to the absorption Mg^{2+} site.

5. Electron correlation is important for reducing the exchange repulsion which, in turn, allows a tighter contact between the surface and the adsorbate.

6. The BSSE corrected HF BE are almost zero and even negative for the (1 × 2) loading of CO, whereas the corresponding B3-LYP data give higher values of the BE for all considered loading.

7. The best B3-LYP/B value of 3.3 kJ/mol for the CO BE at the (1 × 4) loading is still much smaller than the best experimental measurement of 13.5 kJ/mol. In that respect, we do not expect that better quality basis sets than those here adopted will drastically change the present picture. Unfortunately, better Hamiltonians than those derived from DFT theory are, at present, out of reach for periodic calculations, and it does not appear feasible to have MP2-like theory available in a periodic code in the foreseeable future. This is a serious drawback for the study of weak interactions, because dispersive interactions can be accounted for if at least MP2 level of theory is adopted [63], at variance with the present DFT

functionals which are unable to handle dispersive forces properly [64–67]. Significant dispersive contribution to the BE has been invoked by Pettersson and coworkers [17], using a cluster embedded in point charges screened by a suitable total-ion model potential for which traditional correlated calculations were feasible.

Similar conclusions have been reached by Stone and Meredith [53], for the CO/NaCl(0 0 1) system. They compute a very small BE at HF level and compute significative contribution from dispersive forces, obtained by means of a perturbation expansion of the electron density.

In the absence of a more accurate level of theory for our own case, one can resort to the interesting results, recently published by Jordan and Feller [68], on a single water molecule interacting with the surface of graphite, the latter being modeled by aromatic acenes as large as $C_{96}H_{24}$. They found that at HF level, the complex is unbound, whereas at MP2 level the BE becomes as large as 24 kJ/mol, i.e. close to the BE of the water dimer! In that case, they concluded that dispersive forces are the dominant component of the interaction energy. The same line of reasoning can be proposed for the CO/MgO(0 0 1) case, in consideration of the larger polarizability of CO compared to that of the H_2O molecule. On the other hand, the polarizability of the graphite layer is obviously much larger than that of the MgO(0 0 1) surface, in view of the strong ionic nature of the latter, so that no quantitative conclusion is reachable along this line of thought. It is, however, reasonable to believe that dispersive forces may increase the computed B3-LYP/B BE by an amount large enough to reduce the discrepancy with the experiment.

8. The calculated BE is the result of a large cancellation between the electrostatic interaction of CO with the surface field and the exchange repulsion with the oxygen anions nearby the adsorption Mg^{2+} cation. The exchange repulsion felt by CO is higher for the CO/MgO(0 0 1) case when compared to molecular complex as CO/CO_2, because of the small ionic radius of the Mg^{2+} ion which allows the CO to get quite close to the surface atoms. Because of the exponential behavior of the electric field outside the MgO(0 0 1) surface, the classical electrostatic model for the

interaction should include higher multipoles of the CO molecule as well as higher derivatives of the surface electric field. Both polarization and charge transfer components play a negligible role in the binding process of CO to the MgO(0 0 1) surface.

9. Lateral interactions are always repulsive and smaller than the BE^C of CO with the MgO(0 0 1) surface, at least at the B3-LYP/B level. They become smaller already at the (1×4) coverage and negligible at the lowest (1×8) coverage. Dispersive forces may, also in this case, decrease the repulsion component of the lateral interaction and then favor the adsorption at the MgO(0 0 1) surface.

10. The CO frequency is perturbed by the electric field outside the MgO(0 0 1) surface and the value of the harmonic frequency is blue shifted with respect to the unperturbed value. The B3-LYP/B shift is, however, around 5 cm^{-1} at variance with the experimental measurement of 14 cm^{-1}. From a qualitative viewpoint, it is reasonable to believe that dispersion forces will bring the CO molecule closer to the MgO(0 0 1) surface, so that a higher electric field will be felt by CO which, in turn, will increase the computed CO frequency, improving the agreement with experiment; the classical multipolar expansion of the CO frequency shift shows that the pure electrostatic contribution will push the shift up, whereas the "wall effect" deriving from the exchange repulsion, contrary to previous suggestions, will decrease its value considerably.

11. The interpretation of the $\Delta\omega(CO)$ frequency shift in term of constant electric field is inaccurate, and at least the contribution from the field gradient term should be included for molecules possessing large quadrupole moment.

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