Bonding between CO and the MgO(001) surface: A modified picture

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The interaction energy and equilibrium distance for adsorption of CO on a perfect MgO(001) surface has been calculated, using a cluster approach for representing the surface. The cluster size has been varied from one single Mg^{2+} ion up to $Mg_{14}O_5$. *Ab initio* model potentials (AIMP) were used to embed the explicitly described cluster while the rest of the crystal was taken to be point charges. The AIMP model potentials are shown to be a necessary and reliable improvement, compared with using only point charges as a model for the surrounding crystal. It is found that the electrostatic attraction and Pauli repulsion almost cancel each other and the small binding energy obtained is ascribed to dispersive forces. The interaction energy is calculated to be 0.07–0.09 eV (depending on which approach to basis set superposition errors corrections is taken); this is rather low in comparison with the experimental value of 0.3–0.4 eV.

I. INTRODUCTION

The interaction of a CO molecule with the MgO(001) surface has been studied in great detail both experimentally[1-5] and theoretically.[6-14] From IR studies[1] it has been found that it adsorbs mostly above an Mg^{2+} cation site and in a vertical position. The heat of adsorption was initially reported to be very low, only 0.15–0.17 eV,[2,3] indicative of a physisorbed system. However, these measurements were performed at rather high coverage and due to the repulsive adsorbate–adsorbate interactions,[7] the zero-coverage value should be higher. In fact, a value of 0.25 eV for the difference between the zero-coverage adsorption energy and the diffusion barrier for CO/MgO(001) has been deduced from a kinetic model describing experimental results for CO chemisorption on palladium clusters supported on MgO.[4] This would be indicative of a zero-coverage binding energy of 0.3–0.4 eV,[4] substantially higher than the originally reported 0.15–0.17 eV. The value of 0.43 eV obtained by He *et al.*[5] lends support to a higher value of the binding energy, but was obtained at rather high coverage of CO adsorbed on thin films of MgO and could possibly be due to adsorption on steps or rough spots in the film.

The CO/MgO(001) system provides a good benchmark for theoretical models of metal oxide surfaces since quantum chemical calculations can be performed at a very high accuracy for reasonable size models. The interaction between CO and the oxide surface can also be analyzed in detail and can provide information about the expected character of the bonding to other, more complicated metal oxides. In addition, the shift in the CO-stretch frequency upon adsorption is also used as a measure of the ionicity of the adsorption site and it has thus been of interest to obtain a theoretical understanding of the origin of these shifts.

The origin of the bonding between CO and the perfect MgO(001) surface has been described as arising mainly from electrostatic interactions between the multipoles of the CO molecule and the ionic surface. Charge transfer between adsorbate and substrate is negligible. Dovesi *et al.*[8] showed, using periodic Hartree–Fock calculations, that CO may bind to the surface in both the CO and OC configurations with a slight preference for the C–Mg^{2+} interaction. They also considered lateral interactions between the adsorbed CO molecules at different coverages and found a slight repulsion among the adsorbates, but still leading to binding up to monolayer coverage.[7,8] Rumpling of the surface, which has been shown by Pope *et al.*[11] to amount to less than 2% of the lattice parameters, was also considered but was found to have a negligible effect on the adsorption energy and geometry. Rather small basis sets were used and no correction for basis set superposition errors was performed, however.

Pacchioni and co-workers[9,10] have further presented a series of papers on this system and the similar NiO(100) surface with particular emphasis on a characterization of the bonding and origin of the shift in the CO vibrational energy. Their conclusions concerning the origin of the bonding are in agreement with those of Dovesi *et al.* with a balance between the repulsion against the O^{2-} ions at the surface and the electrostatic interactions resulting in a net binding of 0.2 eV in reasonable agreement with experiment. In this case the calculations were performed on a MgO_5 cluster model of the oxide surface using both self-consistent field (SCF) and multiconfiguration self-consistent field (MCSCF) wave functions. Effects of dynamical correlation were considered for the case of the interaction with an isolated Mg^{2+} ion. The size of these effects was computed by Pöhlchen *et al.*[12] for chemisorption of CO on the similar NiO(100) surface using NiO_5 and $Ni(H_2O)_3(OH)_2$ cluster models. In addition, for this system the electrostatics were found to dominate the interaction and dynamical correlation only affected the adsorption energy to a minor extent.

The picture emerging from local density functional calculations by Neyman and Rösch[13] is somewhat different. Charge transfer from the CO to the Mg^{2+} cation is found

to be more important with of the order of 0.1 electron transferred. Very high binding energies, around 1 eV, were obtained from cluster models as large as Mg_9O_9.

Finally, Lakhlifi and Girardet[14] have constructed the interaction surfaces for the interaction of a number of small molecules, among them CO, with the MgO(001) perfect crystal surface. They use a semiempirical potential expression to find the optimum distances and orientations at different points above the oxide surface. Interestingly they find the CO molecule preferentially lying down at the surface except above a Mg^{2+} site where an upright CO position is preferred. The energy differences are very small going from 0.107 eV above an O^{2-} ion to 0.152 eV above a Mg^{2+}. The lowest energy found was actually for a flat position between two Mg^{2+} sites where the binding energy was obtained as 0.164 eV. The computed binding energy is thus rather far from the 0.3–0.4 eV that would be the best experimental estimate.

The aim of the present work was initially to use this well-studied system to investigate the possibility to use the recently developed *ab initio* model potential[15] (AIMP) method to describe the surrounding ions completely without basis functions, which would enable important extensions of the size of cluster that can be studied. However, when embedding the standard MgO_5 cluster in a shell of AIMP's and studying the adsorption of CO on this embedded cluster, the effects of the AIMP embedding were surprisingly large and a more careful study of the process of CO adsorption became necessary.

In spite of the large amount of theoretical effort that has been spent on studying this system the present work gives a somewhat different picture of the interaction. For the small MgO_5 cluster we obtain the same results as in previous work, i.e., a binding energy around 0.15 eV and a bond distance of $4.87a_0$. However, when this cluster is further extended with either an approximate model potential description of the next-nearest neighbors or by including a second shell of thirteen all-electron Mg^{2+} ions, the interaction becomes only weakly attractive with a very shallow minimum of 0.02 eV at $6.2a_0$. The smaller model, where the cluster is embedded in a point-charge array with +2 charges as nearest neighbors to the O^{2-} ions, leads to a reduction of the electron density in the center of the cluster compared to when the cluster is further embedded in a more realistic surrounding. This then leads to a quite different picture of the bonding where the electrostatic attraction is balanced by the repulsion against the O^{2-} ionic charge distributions giving no net binding at the SCF level. In order to regain the attraction, dispersion has been considered and correlated calculations have thus been performed. However, the dispersive interactions only lead to a very weakly physisorbed CO molecule within this model and the origin of the relatively high binding energy deduced experimentally is still uncertain.

II. METHODS

The calculations have been performed for a number of different cluster models ranging from a single Mg^{2+} ion up to a $Mg_{14}O_5$ cluster representing the undistorted

MgO(001) surface. The experimental bulk Mg–O distance of 2.105 Å was used throughout.[16] The remainder of the crystal was included either simply through a point-charge surrounding of the Madelung potential or, in addition, a more careful consideration of the next shell of neighbors to the cluster through the use of model potentials (AIMP). Basis set superposition errors (BSSE) were found to be large and were always corrected for using the full counterpoise method[17] or a method where only the virtual orbitals of the CO are included in the BSSE estimate.[18] In particular, the BSSE associated with the O^{2-} ions in the standard MgO_5 cluster was found to be large enough that a reoptimization of the diffuse functions for the O^{2-} ion was judged to be necessary. The calculations were, for the most part, performed at the SCF level, but additional correlated calculations using the modified coupled pair functional (MCPF) method[19] were performed with up to 50 electrons correlated on a MgO_5+CO cluster model. The different models used will be described in some detail later.

The central Mg^{2+} ion and the CO molecule were always treated at the all-electron level, while the embedding was performed using different approximate descriptions. The standard treatment, $O_5(AE)$, consisted of including an all-electron description of the five nearest-neighbor oxygen anions described using a $[4s4p1d]$ contracted basis set.[20] Three different approximations to this closest environment were studied: $O_5(AIMP)$, $O_5(AIMP)0.65$, and $O_5(AIMP)(8/6)$. In $O_5(AIMP)$ an AIMP description without basis functions was used to replace the five oxygen anions. This was obtained in an iterative self-consistent embedded-ions calculation on an O^{2-} ion embedded in the bulk ionic crystal.[21] To generate the total ion AIMP only the wave function of the ion is required; the Coulomb potential is then obtained from the charge density, the exchange and Pauli repulsion are described using the atomic orbitals. Calculations on Mg^{2+} and O^{2-} embedded in the MgO lattice, for which an initial model potential representation is assumed, provide $\Phi^{Mg^{2+}}$ and $\Phi^{O^{2-}}$; the wave functions for the ions are then used to generate a new AIMP representation of the lattice ions. New calculations on Mg^{2+} and O^{2-} embedded in the new model potential representation of the MgO lattice are performed, and the process is repeated to self-consistency in the $\Phi^{Mg^{2+}}$ and $\Phi^{O^{2-}}$ wave functions. In these self-consistent embedded-ion calculations the perfect host crystal structure is used.[16] The basis sets used for the embedded-ion calculations are the Mg(433/4) and O(53/5) basis sets from the compilation by Huzinaga and co-workers[22] split as (43111/211) and (5111/3111), respectively, with a diffuse p function added to the anion. Once the wave functions, $\Phi^{Mg^{2+}}$ and $\Phi^{O^{2-}}$, for the embedded ions have been obtained the corresponding total ion *ab initio* embedding model potentials may be simply and automatically constructed.[15,21]

The formalism includes the usual long- and short-range Coulomb, exchange, and projector components,[15]

$$V_{\text{lr-Coul}}^{I,\text{MP}}(i) + V_{\text{sr-Coul}}^{I,\text{MP}}(i) + V_{\text{exch}}^{I,\text{MP}}(i) + P_{\text{roj}}^{I}(i), \qquad (3)$$

where $I = Mg^{2+}$, O^{2-}, and which take the following forms:[15]

$$V_{\text{lr-Coul}}^{I,MP}(i) = -\frac{Z_I - N_I}{r_{Ii}},$$

where Z_I and N_I are the nuclear charge and number of electrons of ion I; $V_{\text{lr-Coul}}^{I,MP}(i)$ is thus the point-charge potential. The short-range term is

$$V_{\text{sr-Coul}}^{I,MP}(i) = \frac{\Sigma_j A_j^I \exp(-\alpha_j^I r_{Ii}^2)}{r_{Ii}},$$

where the set of parameters $\{A_j^I, \alpha_j^I\}$ are straightforwardly obtained by fitting to the local short-range Coulomb potential, $-(N_I/r_{Ii}) + \hat{J}^I$, created by Φ^I. The nonlocal exchange operator $\hat{V}_{\text{exch}}^I$ is spectrally represented:

$$V_{\text{exch}}^{I,MP}(i) = \hat{P}_I \hat{V}_{\text{exch}}^I \hat{P}_I,$$

where $\hat{P}_I$ is the projection operator on the primitive basis set used for ion I (see the preceding), $\chi_I = (|\chi_{I_1}\rangle, |\chi_{I_2}\rangle, \dots)$,

$$\hat{P}_I = \chi_I S_I^{-1} \chi_I^\dagger$$

and S_I is the corresponding overlap matrix. Finally, the projection operator is defined as

$$P_{\text{roj}}^I(i) = \alpha \sum_{k \in I} (-2\epsilon_k^I) |\phi_{k,\text{occ}}^I\rangle \langle \phi_{k,\text{occ}}^I|,$$

where ϵ_k^I is the orbital energy of the occupied atomic (ion) orbital $\phi_{k,\text{occ}}^I$. α is an arbitrary constant, which is generally set to 1.0 in AIMP applications.

It should be noticed that the Mg^{2+} and O^{2-} AIMP's used here were generated in calculations where the Mg^{2+} and O^{2-} ions were embedded within the bulk MgO crystal.[21] However, exploratory calculations where both ions were located at their perfect surface site, that is, embedded-at-the-surface ion calculations lead to virtually unchanged $\Phi^{Mg^{2+}}$ and $\Phi^{O^{2-}}$ wave functions and corresponding AIMP's.

When the basis set is completely removed from the oxygen site, as in $O_5(\text{AIMP})$, the orthogonality between the cluster (Mg^{2+}) and the environment (O^{2-}) can no longer be strictly maintained which leads to a spurious energy increase due to the level-shift operator. In $O_5(\text{AIMP})0.65$ the level shift has been reduced by a (optimized) factor of 0.65, while in $O_5(\text{AIMP})(8/6)$ a totally contracted s and p function (corresponding to the $2s$ and $2p$ orbitals of the embedded O^{2-}) have been added to the oxygen site to improve the orthogonality.

The second shell of neighbors was described either using point charges as part of the representation of the Madelung potential, by a shell of $(\text{AIMP})0.65$ O^{2-} and Mg^{2+} ions or by an all-electron description of the nearest Mg^{2+} ions. In the latter case the same basis set was used as for the central Mg^{2+} and the calculations were performed using a modified and parallelized (Ref. 23) version of the direct SCF program DISCO (Ref. 24) running on between 4 and 8 processors of an Alliant FX/2800.

The basis set for Mg is the MIDI-3 basis of Tatewaki and Huzinaga[25] extended with two diffuse p functions ($\alpha_p = 0.2, 0.05$) which was previously used in studies of the hydrogen abstraction from methane over Li-doped MgO(001).[26] For both oxygen and carbon in CO, the $[4s3p]$ contraction of Dunning[20] was used extended to $[4s4p1d]$ by adding an even-tempered p function and a d function with exponent 1.33 and 1.0 for O and C, respectively. For oxygen this basis is the same as the original basis used for the oxygens in the MgO_5 cluster described earlier.

The MCPF calculations were performed in three different ways and always correcting for the CI superposition errors. The first calculation, MCPF(10), correlates the 10 valence electrons of the CO, the second adds 24 electrons on the cluster to the correlation treatment such that the six p electrons on the top four oxygens of the cluster were correlated together with the 10 valence electrons of the CO, MCPF(34), while the third calculation correlates all 50 valence electrons of the $MgO_5 + CO$ system, MCPF(50). The effect of correlating the Mg^{2+} central ion was obtained by adding a core-polarization potential[27,28] (CPP) to the Mg^{2+} site.

In order to have a well-defined orbital space for correlation at all points computed, we localized the remaining cluster orbitals using minimization of the expectation value of r^2 with respect to each center.[28] The binding energy was computed also using the CPF method in order to check that no error was introduced due to the orbital rotations; no deviation was found. The BSSE correction was obtained by performing the corresponding 24 electron MCPF calculation for the BSSE on the cluster due to either the complete (full) CO basis or due only to the virtual CO orbital space.[18] In the latter case the occupied CO orbitals were defined for CO at long distance from the cluster and then removed from the orbital space. The difference between the two approaches was insignificant and only the full BSSE correction was applied for the MCPF(50) calculations. The BSSE on the CO is small with the present basis sets and only the full correction was applied.

III. RESULTS AND DISCUSSION

The aim of the project when it started was to investigate to what extent it is possible to replace all-electron centers with AIMP model potentials in a theoretical description of adsorption on an ionic surface. When it turned out that an improvement in the description of the cluster surroundings removed the bond energy, computed with the standard cluster model, it became necessary to perform a more detailed analysis of the bonding including correlation effects between cluster and adsorbate. Furthermore, surprisingly large effects of BSSE were found which required a separate investigation. We will begin this section with a discussion of the treatment of BSSE.

A. Removal of basis set superposition errors

The existence of basis set superposition errors in quantum chemical calculations has been recognized for a long time and a number of methods to correct for this artificial

TABLE I. Total energies (in E_H) and energy decreases (in eV) of the MgO$_5$ cluster as function of basis set and type of embedding.

α_s	α_p	α_d	Total energy	Decrease
		Point-charge embedding		
0.284 60	0.059 667	1.33	−581.914 617	0.00
0.284 60	0.14	1.33	−581.993 028	−2.13
0.284 60	0.14	0.40	−582.008 746	−0.43
0.284 60 and 0.1175	0.14	0.40	−582.032 104	−0.64
		Total ion AIMP embedding		
0.284 60	0.059 667	1.33	−581.020 042	0.00
0.284 60	0.14	1.33	−581.020 254	−0.01
0.284 60	0.14	0.40	−581.031 693	−0.31
0.284 60 and 0.1175	0.14	0.40	−581.038 219	−0.18

lowering of the atomic energy have been proposed. The quality of basis sets normally employed in molecular quantum chemical calculations is such that the BSSE usually is not considered to be important and corrections are employed only when extreme accuracy is required. However, basis sets optimized for the atom and extended with diffuse functions for the molecule seem to perform rather poorly when used to describe an anion in a cluster representation of an ionic crystal. The effects are large and depend on the type of embedding performed and we will begin by discussing these basis set questions. It should be noted that we do not find any particular sensitivity to whether the full or only the unoccupied CO orbital space is used in the estimate and removal of the BSSE (see the MCPF results, Sec. D). The BSSE correction used as standard procedure includes the full CO orbital space.

The importance of considering the BSSE in relation to adsorption on oxide systems has previously been pointed out particularly by Pöhlchen and Staemmler in their work on CO and NO adsorption on NiO(100).[12,29] However, the effects are surprisingly large compared with the experience from molecular calculations and we have therefore undertaken to optimize the diffuse functions for an improved cluster description. The resulting total energies for the MgO$_5$ cluster in different embeddings are given in Table I.

The original basis contains as the most diffuse functions an s-exponent of 0.2846 and an added diffuse p exponent of 0.059 667. To this was added a d function with exponent 1.33. Optimizing the diffuse p function for O^{2-} in the bulk Madelung potential and with repulsive projection operators for the surrounding Mg^{2+} cores resulted in a substantially contracted p function with an exponent of 0.14. The energy decrease obtained for the MgO$_5$ cluster model in a point-charge surrounding was very large, 2.1 eV. Optimization of the d function (for a surface oxygen in an environment of five Mg^{2+} AIMP's) and an additional s function for O^{2-} also resulted in rather large decreases of the total energy of the cluster, 0.4 and 0.6 eV, respectively. When the cluster is embedded in a surrounding containing the next shell of Mg^{2+} and O^{2-} ions described by total ion AIMP's, the effects become very different. The effect of the diffuse p function now becomes negligible and also the energy decreases obtained from the d function and the additional s are much smaller, 0.3 and 0.2 eV. Thus the basis set requirements and effects of the optimization are very strongly dependent on the type of embedding performed. In addition, as we will show later, the counter-poise correction for the basis set superposition error turns out to be very reliable for these systems and after this correction the results are virtually independent of which basis set has been used. However, these results from the basis set optimization give a first indication of the importance of considering the embedding of the cluster in a proper surrounding for reliable results.

B. SCF results using minimum models of the surface

The simplest model considered for the interaction of CO with the MgO(001) surface is simply a Mg^{2+} ion embedded in the crystal Madelung potential. This very simple model gives results for both the Mg–C distance and the binding energy in very good agreement with both the periodic crystal calculations[8] and the results of Pacchioni et al.[9,10] The interaction is weak, with a corrected binding energy of 0.16 eV at a rather long distance above the surface, $4.66a_0$ (Table II, PC results); the BSSE correction is small. Embedding the Mg^{2+} ion in its first shell of all-electron oxygen neighbors using the original $[4s4p1d]$ basis

TABLE II. SCF results for CO adsorption on Mg^{2+} with different models of the MgO(001) surface. Binding energies (BE) in eV and Mg–C distance, R, in a_0.

Mg^{2+} embedding	Uncorrected		BSSE corrected	
	R	BE	R	BE
PC	4.64	0.20	4.66	0.16
O_5^{8-}(AE)+PC	4.53	0.46	4.87	0.17
O_5^{8-}(AIMP)+PC	4.94	0.17	4.96	0.12
O_5^{8-}(AIMP)(8/6)+PC	4.84	0.20	4.86	0.15
O_5^{8-}(AIMP)0.65+PC	4.68	0.21	4.70	0.17
O_5^{8-}(AE)+AIMP0.65+PC	5.39	0.15	6.15	0.01
O_5^{8-}(AEo)+AIMP0.65+PC	5.37	0.11	6.15	0.01
O_5^{8-}(AE)+Mg$_{13}$(AE)+PC	5.15	0.16	5.98	0.02
O_5^{8-}(AIMP)(8/6)+AIMP0.65+PC	4.82	0.21	4.85	0.16

has a rather small effect on the computed properties except that the BSSE is dramatically increased from 0.04 eV up to 0.29 eV. Correcting for this BSSE produces remarkably stable results, which has also been pointed out for the similar systems CO and NO on NiO in Refs. 12 and 29. The distance above the Mg^{2+} central ion increases by $0.2a_0$ due to the embedding, i.e., the increased repulsion against the charge density associated with the oxygen ions. This is all in good agreement with earlier results.

Replacing the five oxygen ions surrounding the Mg^{2+} by the corresponding O^{2-} AIMP description we find results in good agreement with those from the all-electron calculation. After the BSSE correction the binding energy is 0.12 eV compared with 0.17 in the all-electron calculation and the performance of the AIMP is further improved by also indicating a set of totally contracted functions on the oxygens, $O_5(AIMP)(8/6)$. This improves the orthogonality between the all-electron part of the wave function, i.e., $CO+Mg^{2+}$, and the part described by model potentials and leads to results in near-perfect agreement with the all-electron comparison. The resulting binding energy differs by 0.02 eV and the height above the Mg^{2+} by $0.01a_0$ from the all-electron comparison. The BSSE correction is of the same order of magnitude as for the simplest model where only a Mg^{2+} ion is used.

An even simpler computational model to reduce the artificial repulsion introduced by the reduction of the basis set and the resulting impossibility to maintain strict orthogonality between the central cluster and the embedding is obtained by simply scaling down the level-shift values in the projection operator. A scaling factor of 0.65 on the original level shifts of $-2\epsilon_k$ has been found empirically to reduce the repulsion sufficiently while maintaining an approximate orthogonality between the systems. The results for the CO adsorption on this $Mg^{2+}O_5(AIMP)0.65$ cluster are most similar to the adsorption on a single Mg^{2+} ion, but energetically this is also very similar to the $MgO_5(AE)$ cluster calculation. The results for the distance above the cluster show that the repulsion against the model potential oxygen ions is too small when the level shift has been reduced. This type of model should therefore be used as an embedding rather than as describing a directly interacting part of the system.

C. SCF results using enlarged models of the surface

The next set of calculations performed was then to embed the $MgO_5(AE)$ cluster in a surrounding of (AIMP)0.65 model potentials. This, however, resulted in an unexpectedly large effect on the binding energy and also on the distance above the cluster. The binding energy essentially becomes zero with only a very shallow minimum at $6.15a_0$. This effect was not expected and required additional investigations to ensure that it is not an artifact of the model potential formalism used.

The cluster was thus extended to include, at the all-electron level, also the nearest neighbors to the five O^{2-} ions surrounding the central Mg^{2+}. The cluster size then becomes $Mg_{14}O_5$, which at the all-electron level, requires direct techniques. The calculations were performed using a
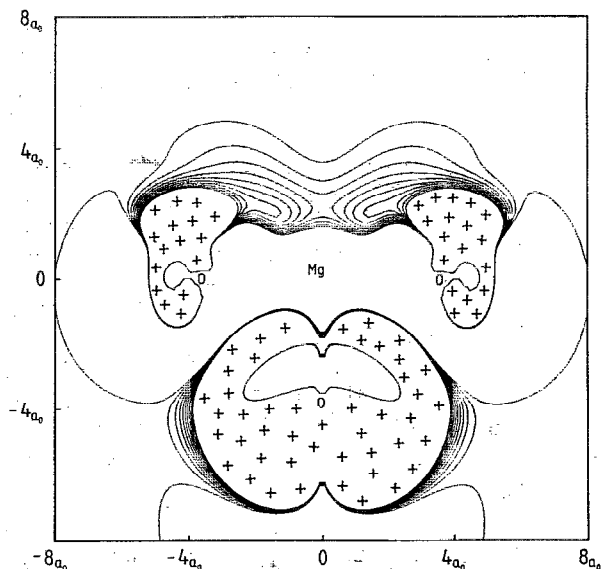

FIG. 1. Charge density difference plot taken as $MgO_5+AIMP-MgO_5+P.C.$ The plane shown contains two oxygens and the Mg^{2+} from the first layer and the second-layer oxygen. Only areas of increased charge density are shown.

parallel version of the DISCO program and were, in this approach, of quite manageable size. Each point of the potential curve for CO chemisorption on this cluster was furthermore corrected for the SCF-level superposition errors. The same all-electron oxygen and magnesium basis sets as for the central atoms in the embedded cluster above, were used for all atoms.

The results from this large all-electron cluster are in perfect agreement with those where the simple AIMP description is used. A very shallow minimum is found at $5.98a_0$ with a depth of only 0.02 eV. Thus, the repulsion from the embedding that was found at the AIMP level is a true effect. Pöhlchen and Staemmler have previously noted a similar effect[29] in the case of NO adsorption on a NiO_5 cluster model where the adsorption energy was strongly reduced when the cluster was embedded in a surrounding consisting of Mg^{2+} pseudopotentials. It thus seems to be of general importance to consider the embedding scheme at least when the cluster is terminated by anions.

When the MgO_5 cluster is embedded only in a set of point charges, the repulsion against the surrounding Mg^{2+} electronic charge distribution is not included and the O^{2-} ions are allowed to polarize towards the +2 point-charge neighbors. This reduces the charge in the center of the cluster and thus the repulsion felt by the incoming CO. Adding the surrounding neighbors pushes the charge density back towards the cluster and consequently increases the repulsion felt by the CO charge distribution. This is illustrated in Fig. 1, where the charge density difference taken as $MgO_5+AIMP-MgO_5+PC$ clearly shows the redistribution of charge towards the cluster. A secondary effect of the increased repulsion is that, as the distance increases, the attractive electrostatic interaction is strongly

reduced and the molecule becomes only very weakly bound.

Another aspect is the reduction of the BSSE when the MgO_5 cluster is embedded in this more realistic surrounding. From a BSSE of 0.29 eV using the MgO_5(AE) cluster embedded in a set of point charges, the BSSE is reduced to 0.14 eV when the repulsion against the surrounding neighbors is also included. Thus a large part of the BSSE is related to the exaggerated polarization of the O^{2-} ions towards the environment, which is not well described by the ion basis. As a final comment on the removal of the BSSE we note that the reoptimized basis (AEo) gives a reduction of the BSSE contribution to the D_e by 0.05 eV, but after correction the results are identical to those from the original basis. Attempting a complete removal of the BSSE through further basis set extensions and optimization thus seems neither fruitful nor necessary.

Attempting to replace the oxygen ions with AIMP descriptions we now use the AIMP(8/6) description that performed very well for the MgO_5 system in the comparison with the all-electron calculation. Surrounding this MgO_5(AIMP)(8/6) cluster with AIMP's with scaled down level shifts we find no effect from the embedding on the CO adsorption energy. This is not so surprising in light of the interpretation of the increased repulsion felt by the CO as due to charge moved back from the region between the oxygen ions and the +2 point charges; using AIMP's without electrons there is no charge that may move. Thus, the smallest computational model that takes all of these effects into account is the MgO_5(AE) cluster embedded in a shell of AIMP's and further embedded in the proper Madelung potential.

D. MCPF results

In order to try, within the present model, to obtain a significant contribution to the binding we will investigate the effects on the bonding of CO to MgO(001) from correlation, both the dispersion interaction between the CO and the surface (34 or 50 electrons correlated) and the effects of improving the electrical moments and polarizabilities of CO through correlation (10 electrons correlated). The calculations were performed for the MgO_5(AEo) cluster embedded in a shell of scaled AIMP's and the Madelung potential as represented by a large set of point charges. The optimized $[5s4p1d]$ basis set for O^{2-} was used for the cluster description, but in spite of this, care must be taken to remove the superposition errors in the calculation.

Two slightly different approaches to the cluster BSSE from the CO basis were used where either the full or only the unoccupied orbital space of the CO molecule were used in the evaluation of the BSSE. The results from both procedures are included in Table III, where the energies for each distance are given together with the corrected interaction energies. As is seen from Table III, the two different definitions of the correction lead to very similar results with a difference only of the order of 0.02 eV.

The CO bond distance was kept fixed at the experimental value of $2.13a_0$ in all calculations presented so far. This is also the optimized distance from the MCPF calcu-

lations on free CO, while the SCF value is $0.05a_0$ shorter (Table IV). The assumption of a fixed CO distance in the CO/MgO calculations was checked by optimizing the CO bond distance at the SCF level also for the CO above the embedded MgO_5 cluster for a fixed Mg–C distance of $5.50a_0$. The resulting bond distance was the same as for the free CO and this is true also of the computed vibrational frequency which was obtained as 2461 cm^{-1} for both free CO and CO above the cluster. The very weak interaction that is found at this point is not sufficient to affect the CO molecule.

Correlating only the CO molecule has a large effect on the CO dipole moment which changes sign to polarity C^-O^+ (Table IV), and is obtained in quite good agreement with experiment using the present basis sets. It should be noted that only when taken as an energy derivative with respect to the applied electric field (± 0.005 a.u.) does the MCPF dipole moment give a reasonable value. The expectation value over the MCPF wave function is as large as 0.247 D. The effects on the parallel component of the dipole polarizability and on the quadrupole moment are small. The repulsion between the CO and the cluster may also be somewhat reduced since correlation should allow the charge density on the CO to contract somewhat. However, these two effects are not sufficient to change the SCF level result of a binding energy that is essentially zero.

In order to obtain a binding energy different from zero and a height above the surface less than $6a_0$, we have to correlate both the CO and at least the $2p$ orbitals on the top four oxygens. This leads to a binding energy which, at 0.04–0.06 eV after BSSE correction, is still only $\approx 10\%$ of the experiment. This contribution will naturally increase somewhat by correlating additional electrons and by improvements of the basis sets, even if the present $[5s4p1d]O^{2-}$ optimized basis is already reasonably large. However, it is very unlikely that these improvements would give more than at most an additional 0.05 eV, which would still leave most of the binding energy unaccounted for. In fact, our best computed value from the MCPF(50) calculation and with an extended basis set on the CO is only 0.07 eV (see the following).

The contribution to the bonding from correlating the Mg^{2+} ion can be estimated using simplified techniques such as the core polarization potential method developed previously.[27,28] Including this attractive potential on the Mg in the cluster gives the effect of correlation between the Mg and the CO but increases the binding energy by only 0.004 eV, as found by adding the CPP at the computed equilibrium geometry.

The procedure to select a number of orbitals to correlate on the cluster (e.g., the $2p$ orbitals on the top four O^{2-} anions), to localize these and to include, in the correlation treatment, frozen cluster orbitals in the evaluation of the BSSE might lead to uncertainties in the computed binding energies. It might be of interest to attempt to reduce the BSSE by extending the basis sets, even though the previous effort to optimize the anion basis set turned out to give identical results after the counterpoise correction. We have

TABLE III. Interaction between CO and $MgO_5 + AIMP - 0.65$ model of the MgO(001) surface. SCF and MCPF results and computed BSSE corrections. Total energies in Hartree and interaction energies in eV. $R(C-O) = 2.13a_0$.

		SCF results			
		$MgO_5 + (g)$	$MgO_5 + (g)$	$CO + (g)$	
R	$OC-MgO_5$	Full	Unoccupied	Full	
∞		−581.044 935	−581.044 935	−112.750 588	
6.5	−693.798 579	−581.046 224		−112.751 501	
6.0	−693.799 094	−581.046 645	−581.046 293	−112.752 023	
5.5	−693.799 461	−581.047 101	−581.046 501	−112.752 103	
5.0	−693.799 180	−581.047 564	−581.046 631	−112.752 203	
4.5	−693.796 633	−581.048 076			

			MCPF results		
	$OC-MgO_5$	$OC-MgO_5$	$MgO_5 + (g)$	$MgO_5 + (g)$	$CO + (g)$
R	MCPF(34)	MCPF(10)	Full	Unoccupied	Full
∞			−581.615 002	−581.615 002	−113.061 752
6.0	−694.689 490	−694.110 881	−581.623 935	−581.623 470	−113.064 117
5.5	−694.690 359	−694.111 099	−581.624 510	−581.623 745	−113.064 390
5.0	−694.690 725	−694.110 534	−581.625 113	−581.623 938	−113.064 712
4.5	−694.689 034	−694.107 486	−581.625 796		−113.065 150

	Interaction energies (eV)					
	SCF		MCPF(10)		MCPF(34)	
R	ΔE_{int}	$+BSSE^a$	ΔE_{int}	$+BSSE^a$	ΔE_{int}	$+BSSE^a$
6.5	0.083	0.023				
6.0	0.097	0.012	0.114	0.002	0.346	0.038
5.5	0.107	0.007^b	0.120	-0.011^b	0.370	0.040^b
5.0	0.100	−0.016	0.105	−0.047	0.380	0.024
4.5	0.030		0.022	−0.156	0.334	−0.052

^{a}BSSE (full) corrected value.
^{b}BSSE corrected value without the CO occupied space in the BSSE estimate: SCF, 0.023 eV; MCPF(10), 0.005 eV; MCPF(34), 0.061 eV.

thus performed additional correlated calculations where we correlate all valence electrons in the $MgO_5 + CO$ system, MCPF(50), in which case only the $O(1s)$, $C(1s)$, and Mg^{2+} ion core are included in the localization procedure and excluded from the correlation treatment. The only practicable extension of the basis set concerns the CO description for which a $[5s5p2d1f]$ atomic natural orbital (ANO) contraction was used.[33,34] The results of these more extended calculations are collected in Table V.

The magnitude of the BSSE contribution on the CO entity is substantially reduced through the extension of the basis set; at the same time the BSSE contribution to the cluster energy is increased. After correction for these effects (using the full counterpoise correction) the results are very stable, however, and give an increased binding of only 0.025 eV at the MCPF(34) level. Addition of the $O(2s)$ electrons and the fifth oxygen to the correlation treatment only gives an exceedingly small contribution. The final result, including the effect of correlation of the Mg^{2+} core, is then 0.07 eV. Using the BSSE correction from only the unoccupied CO orbitals would only lead to a 0.02 eV increase of this value.

IV. CONCLUSIONS

We have investigated several different models for describing the adsorption of CO on the MgO(001) surface.

The standard model, where a small anion-terminated cluster is embedded in a point-charge representation of the Madelung potential, leads to an artificially reduced repulsion for the CO against the anions of the cluster and to an overestimated binding. Embedding the cluster in the next shell of Mg^{2+} ions leads to a more appropriate model where the O^{2-} species are not polarized towards the unscreened point charges. This embedding can be performed using a total ion AIMP description of the surrounding ions giving results for the CO adsorption in near-perfect agreement with those from the large all-electron $Mg_{14}O_5 + CO$ calculations.

At the SCF level the CO is bound very weakly at a

TABLE IV. Computed spectroscopic and electrostatic properties for CO using the $[4s4p1d]$ standard basis. Dipole moment (μ in Debye) and quadrupole moment relative to center of mass (Θ_{zz} in a.u.). The dipole polarizability along the molecular axis, $\alpha_{\parallel}$, is given in a_0^3.

Property	SCF	MCPF	Experiment
r_e	2.082	2.132	2.132^a
ω_e	2461	2225	2169.8^a
μ	−0.346	0.093^b	0.1222^a
Θ_{zz}	−1.821	−1.769	-1.44^c
$\alpha_{\parallel}$	13.8	14.6	15.72^d

^{a}Reference 30. ^{c}Reference 31.
^{b}Computed as energy derivative. ^{d}Reference 32.

TABLE V. Effects of extending basis set on CO and including all valence electrons in the correlation treatment [MCPF(50)]. CO at $5.5a_0$ above the surface. All energies are in eV.

Method	Basis	B.E. (eV)	BSSE[a] MgO$_5$	BSSE[a] CO
SCF	Small[b]	0.007	0.059	0.041
SCF	Large[c]	0.014	0.115	0.005
MCPF(10)	Small	−0.011	0.059	0.072
MCPF(10)	Large	−0.005	0.115	0.016
MCPF(34)	Small	0.040	0.259	0.072
MCPF(34)	Large	0.065	0.329	0.016
MCPF(50)	Large	0.066		0.016

[a]Computed basis set superposition errors.
[b]Standard [$4s4p1d$] basis on CO.
[c]Extended [$5s5p2d1f$] ANO basis on CO.

distance of more than $6a_0$ above the surface. Correlation of the CO species only, is not sufficient to regain any bonding and only when the p orbitals of the top four oxygens are included in the correlation treatment do we obtain a bound adsorbate. The contribution from correlation of the Mg^{2+} is small. Both at the SCF level and, in particular in the correlated calculations, it is essential to correct for the basis set superposition errors. Optimization of the basis set for the O^{2-} leads to large energy decreases for the case of embedding in a set of point charges, but has a much smaller effect when the environment is treated more correctly by inclusion of the next shell of ions either as all-electron ions or as total ion AIMP's.

We thus find the CO species physisorbed at the surface with no significant charge transfer in agreement with earlier results. The increased repulsion due to the proper embedding used in the present work leads to a reduced binding and an essentially unbound CO molecule at the SCF level. This is in contrast to earlier results where agreement with experiment has been obtained already at the SCF level. It is necessary to introduce dynamical correlation between adsorbate and substrate in order to obtain binding of CO to the perfect MgO crystal surface. Even so, the finally obtained binding energy is substantially lower than experiment. Additional extensions of the basis set and the correlation treatment are not expected to significantly alter the computed result.

It must be concluded that the present model of adsorption on the MgO surface must be modified. One promising approach at present would be to investigate the crystal potential at the surface. In fact, for NO adsorption on NiO(100) it has been shown that a reduced Madelung potential leads to a stronger interaction.[35] For CO adsorption on MgO(001), Neyman and Rösch[13] have demonstrated better agreement for the computed shift in the vibrational frequency of adsorbed CO when the embedding electrostatic potential was based on charges ± 1.5 instead of the normal ± 2. The effect on the adsorption energy for the CO/MgO(001) system of a reduction of the crystal potential should also be investigated and will be the subject of future work.

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