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Electron correlation contribution to the physisorption of CO on MgF₂(110)

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We have performed CCSD(T), MP2, and DF-LMP2 calculations of the interaction energy of CO on the MgF₂(110) surface by applying the method of increments and an embedded cluster model. In addition, we performed periodic HF, B3LYP, and DF-LMP2 calculations and compare them to the cluster results. The incremental CCSD(T) calculations predict an interaction energy of $E_{\text{int}} = -0.37$ eV with a C-down orientation of CO above a Mg²⁺ ion at the surface with a basis set of VTZ quality. We find that electron correlation constitutes about 50% of the binding energy and a detailed evaluation of the increments shows that the largest contribution to the correlation energy originates from the CO interaction with the closest F ions on the second layer. © 2012 American Institute of Physics. [<http://dx.doi.org/10.1063/1.3697867>]

I. INTRODUCTION

Adsorption processes are often initial steps in reaction pathways of heterogeneous catalysis and play an important role for surface characterization techniques. Their theoretical description is in particular difficult when dealing with physisorption. Physisorption is driven by two types of interactions: classical electrostatic interactions and/or dispersion interactions. Dispersion interaction is a type of long-range, non-local electron correlation, which is by definition not included in Hartree-Fock (HF) theory. In principle density functional theory (DFT) is feasible for large systems and could give the exact ground-state energy, but standard density functionals (LDA, GGA, hybrid functionals) often fail to describe non-local electron correlation correctly.¹⁻⁴ Recently, there have been a number of successful attempts to improve existing density functionals by including either classical force-fields,⁵⁻⁷ or correlation effects from second order perturbation-theory with Kohn-Sham orbitals.^{8,9} However, empirical corrections have the drawback of being dependent on parameters fitted to empirical data and may diversify in their reliability for certain systems, whereas non-empirical dispersion corrections often tend to become as complex as wavefunction based correlation methods.

Electron correlation is described more accurately and consistently in wave-function based post-Hartree-Fock methods, e.g., Møller-Plesset perturbation theory (MP2, MP4, ...) ¹⁰ or coupled-cluster theory (CC).¹¹ The use of these methods is very beneficial, but their computational demands, at least for standard implementations, scale unfavorably with the number of electrons which makes them only feasible for systems of modest size. However, significantly improved scaling is achieved when these methods are based on localized molecular orbitals.

Stollhoff and Fulde were one of the first to suggest the use of localized orbitals for the treatment of electron correlation in extended systems.¹²⁻¹⁴ They considered local excitations out of non-orthogonal orbitals, which later became known as the “local ansatz” (LA). Pulay and Saebø developed a local correlation scheme with an orthogonal

set of localized orbitals, where excitations into projected atomic orbital (PAO) domains are considered.¹⁵⁻¹⁸ This was implemented in the MOLPRO program for molecular systems by Werner and Schütz¹⁹⁻²¹ and recently extended to solids by Pisani *et al.*^{22,23} as implemented in the CRYSCOR program. In this paper we predominantly use another local correlation method invented by Stoll,²⁴⁻²⁶ which is called the “method of increments.” It relies on cluster schemes which mimic the infinitely extended system, and utilizes localized orbitals to treat the electron correlation energy as a many body expansion (for a review see Ref. 27). By modeling the extended system as a cluster it is possible to apply standard quantum chemical codes, which is one big advantage of this method. It is also possible to apply larger basis sets than in periodic calculations, where large basis sets can lead to linear dependencies. Due to the local character of the correlation hole, local correlation methods scale in principle with zeroth order of the system size, but often with a quite large prefactor.

The method of increments has been successfully applied to physisorbed systems and yields accurate interaction energies. Thus, for example, Müller *et al.* investigated the interaction energy of CO and N₂O adsorbed on ceria surfaces²⁸⁻³⁰ and recently Staemmler published his investigation on the CO/MgO system.³¹ In the present study, we performed both periodic slab and embedded cluster calculations to investigate interaction energies of CO—a common probe molecule—on MgF₂ at different levels of theory. Sol-gel prepared nanocrystalline MgF₂ exhibits promising properties as a catalyst,³² and a detailed characterization of MgF₂ surfaces facilitates the interpretation and prediction of these properties. For this purpose, ultra-high vacuum experiments often use CO as a probe molecule, and measurements of its vibrational spectrum aid the characterization of active sites in solid state materials.³³ Computational methods, on the other hand, can facilitate the interpretation of the results obtained in the characterization experiments. The weakly bound CO/MgF₂ system is an ideal case for applying sophisticated post-Hartree-Fock methods within incremental schemes. So in our cluster calculations,

we applied CCSD(T), MP2, and DF-LMP2 in an incremental fashion and compare to DF-LMP2 calculations with periodic slab models.

This paper is structured as following. In Sec. II we explain the applied methods and other computational details. In Sec. III we discuss our results for the CO/MgF₂(110) system. Conclusions follow in Sec. IV.

II. METHOD

A. Method of increments for interaction energies

In the method of increments the correlation energy is expanded in terms of electron correlation contributions (increments) from groups of localized orbitals.^{24–27} These groups are associated with an atom, a molecule or a bond between atoms. A *one-center increment*, ϵ_i , is defined as the electron correlation energy from the electrons in the orbitals of group i . Here, we consider one group of five orbitals for the CO molecule (M) and one group of four orbitals ($2s^2p^6$) for the Mg²⁺ and F⁻ ions in MgF₂. The two-center electron correlation energy increment, $\Delta\epsilon_{ij}$, of the correlation energy ϵ_{ij} from electrons in two groups of orbitals i and j is defined as

$$\Delta\epsilon_{ij} = \epsilon_{ij} - \epsilon_i - \epsilon_j. \quad (1)$$

Higher order increments are defined accordingly. Often a small number of one- and two-center increments is enough to obtain more than 97% of the total electron correlation energy, since the incremental contributions decay rapidly with the order of the increments and the distance between the orbitals from different groups. In principle, any size-extensive correlation method can be applied in an incremental fashion and due to the local character of the correlation, embedded cluster models may be used.

Adapting the method of increments to adsorption problems is straightforward.²⁸ The interaction energy between the molecule and the surface is defined as

$$\begin{aligned} E_{\text{int}} &= E_{\text{CO/MgF}_2} - E_{\text{MgF}_2}^{\text{CP}} - E_{\text{CO}}^{\text{CP}} \\ &= E_{\text{int}}^{\text{HF}} + E_{\text{int}}^{\text{corr}}, \end{aligned} \quad (2)$$

where $E_{\text{CO/MgF}_2}$ is the total energy of the CO/MgF₂ system, and $E_{\text{MgF}_2}^{\text{CP}}$ and $E_{\text{CO}}^{\text{CP}}$ are the energies of the fragments at the same coordinates as in the CO/MgF₂ system and corrected for the basis set superposition error (BSSE) according to the counterpoise scheme of Boys and Bernardi.³⁴ $E_{\text{int}}^{\text{corr}}$ is expanded in interaction energy increments η via the method of increments. There are two types of these increments. One type that involves orbitals from either the molecule or the surface and one type that involves orbitals from both. For example, the one-center interaction energy increment of the molecule is of the first type and calculated as

$$\eta_M = \epsilon_M^{\text{CO/MgF}_2} - \epsilon_M^{\text{CP}}. \quad (4)$$

Interaction energy increments of the second type, such as η_{Mi} are identical to the electron correlation energy increment $\Delta\epsilon_{Mi}$, since they only occur for the combined system of molecule and surface. Other interaction energy increments are defined accordingly and the total correlation contribution

to the interaction energy is

$$E_{\text{int}}^{\text{corr}} = \eta_M + \sum_i \eta_i + \sum_{\substack{ij \\ i \neq j}} \eta_{ij} + \sum_i \eta_{Mi} + \dots \quad (5)$$

Additionally, to the fast convergence of this series with the order of the increments and the distance between orbitals of different groups, this expansion is known to converge fast with the distance of the orbitals to the adsorption site,^{28–30} too.

Although we cannot compare our results to experimental data, which are not available, we would like to mention that the interaction energy is in principle not suitable for comparison with experimentally obtained adsorption energies. First of all, our definition of the interaction energy does not acknowledge different structures for an adsorbed CO molecule and the same molecule in vacuum. Relaxation of the surface due to the adsorption of CO is not considered neither. Both effects are considered of minor importance for physisorption and the latter is neglected in our calculation to make them more feasible. Second, we do not consider zero-point vibration energy, which is sizeable for weak interacting systems. However, the focus of this study is to estimate electron correlation effects in the CO/MgF₂ system, and before mentioned effects can be added later, when experimental results for comparison are available.

B. The surface model and computational details

1. Structure and embedding

In this paper we applied a surface model that originates from a periodic bulk calculation in which we optimized the cell and inner parameters of the rutile structure of MgF₂. For the optimization we applied DFT with the B3LYP functional and the basis set described later in this section. Based on the optimized bulk structures, we created a 15 layer slab with two (110) faces - the most low-index surface of MgF₂ - in which all ions were allowed to relax freely. For the construction of the clusters we used the embedding scheme described by Herschend *et al.*³⁵ and Müller and Hermansson.³⁶ This scheme works as following: Atoms surrounding a cluster of quantum mechanically (QM) treated atoms are replaced by formal point charges of +2 and -1 a.u. At a distance of 20 Å from the adsorption site the infinitely large array of formal point charges is truncated and point charges on the surface of a sphere with the same radius mimic the long-range interactions of the periodic slab. Finally, positive point charges, close to the borders of the QM-cluster, are replaced by Stuttgart effective-core potentials (ECPs) (Ref. 37) with an effective charge of +2 a.u.

In the following calculations the structure of the relaxed clean (110) surface was kept fixed. The CO molecule was placed atop an unsaturated Mg²⁺ surface-ion in the middle of the Mg₁₃F₂₆ cluster shown in Fig. 1. The same cluster was used for all cluster calculations in this study.

The positions of the C and O atom in CO with respect to the MgF₂ surface were optimized at the B3LYP level. Additionally, a single point MP2 calculation was carried out for the optimized structure. From this optimized structure increments were obtained in single point CCSD(T), MP2, and DF-LMP2

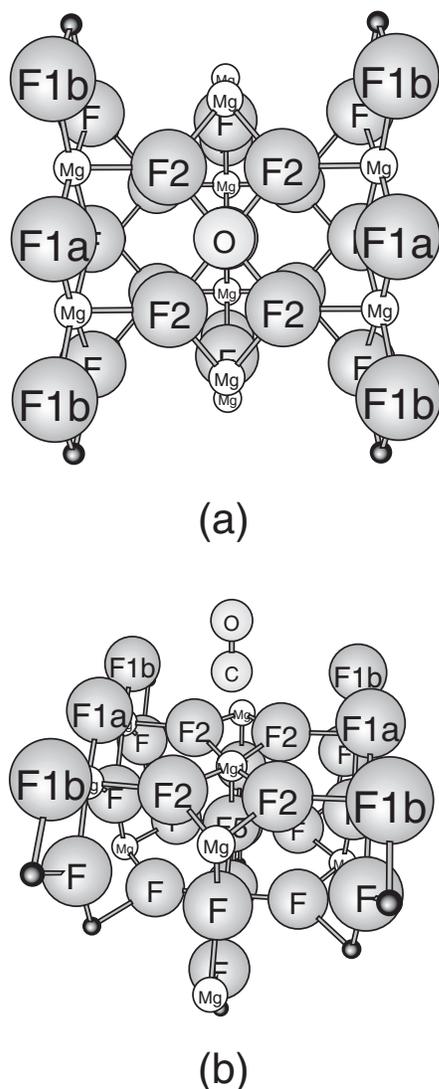


FIG. 1. Top (a) and side (b) view of the embedded $\text{MgF}_2(110)$ surface cluster with adsorbed CO atop the unsaturated $\text{Mg}1$ surface ion in the center of the cluster. White circles are Mg^{2+} , dark gray circles F^- , black circles are large-core ECPs and light gray circles represent the CO molecule. Point charges are not drawn for clarity.

calculations. Relaxation of surface atoms was neglected but is supposed to be small. Additionally, periodic single point calculations with two different coverages were performed at the B3LYP, HF, and DF-LMP2 levels using the optimized adsorption structure from the embedded cluster calculations. On top of the periodic B3LYP calculations we added the dispersion correction proposed by Grimme,³⁸ with a scaling factor of 1.05, a steepness of the damping function of 20, and a cutoff distance to truncate direct lattice summation of 25 Å, as suggested in the CRYSTAL09 manual.³⁹ C_6 coefficients and van der Waals radii were taken from Table I of Ref. 38.

2. Basis set

For the Mg^{2+} ions, a 8-511d1G basis set from Valenzano *et al.*⁴⁰ was used. For the F^- ions we used a 7-311G basis set from Nada *et al.*⁴¹ with an additional d-polarization function with an exponent of 0.7. In the cluster calculations we used

Dunning's uncontracted aug-cc-pVTZ and aug-cc-pVQZ basis sets^{42,43} for the CO molecule. The auxiliary basis sets in the density fitting routine were the aug-cc-pV5Z-mp2fit for F, C, and O atoms and the cc-pV5Z-mp2fit for the Mg ions, all of them optimized by Hättig⁴⁴ for RI-MP2 and RI-CC2 calculations.

Periodic calculations are often sensitive to linear dependencies due to diffuse basis functions. Fortunately, due to the compactness of solids, diffuse functions are not as much important as, for example, in molecules. Hence, in the periodic calculations, we choose Dunning's cc-pVTZ basis set for the atoms in CO and henceforth call this the periodic basis set for simplicity.

3. Technical details

In all periodic bulk and slab calculations we applied isotropic shrinking factors of 12 and 24 for the Monkhorst-Pack and Gilat k-point net, respectively. Values of 8, 8, 8, 16, and 32 were employed as truncation criteria for the bielectronic integrals (cf. CRYSTAL09 manual³⁹). An energy convergence criterion of 10^{-7} a.u. was used in the self-consistent field iteration.

For the cluster calculations with local MP2, default values as implemented in MOLPRO were applied for the distance criterion of strong, close, weak and distant pairs (0–1 Å, 1–3 Å, 3–8 Å, and 8–15 Å, respectively), as well as for the Boughton-Pulay parameter (0.98). In the periodic DF-LMP2 calculations the same shrinking factors as in the RHF and DFT calculations were employed for the Monkhorst-Pack and Gilat k-point net. The density fitting was performed purely in direct space using the “PG-AVTZ” fitting basis set.⁴⁵

All one-center interaction energy increments for atoms within a radius of 5 Å from the CO molecule (more precisely the C-atom) and a magnitude larger than 0.1 meV were included in the many-body expansion as well as pairs of increments constructed from these one-center increments with an inter-center distance (for the CO molecule this refers to the C-atom) smaller than 5 Å. Three-center increments were constructed to consist of the centers with the largest one- and two-center increments, namely, the CO molecule, the F2, and the F1a ions (cf. Figure 1).

There are several ways to define the domain sizes in the LMP2 method. By default the Boughton-Pulay procedure is applied. However, for the calculation of an adsorption energy, which is a difference of at least three energies, it is important to use the same domains in all calculations required. In CRYSCOR, there is not yet a procedure that takes care of this automatically. Hence, in this paper we explicitly specified the domains in all energy evaluations. For the fluorine ions we defined excitation domains that contain PAOs of fluorine itself and its nearest neighbours, i.e., three Mg^{2+} ions at the surface and four Mg^{2+} ions anywhere else. For CO we defined excitation domains that contain PAOs of the CO molecule itself, whereas PAOs from Mg were not considered.

For the cluster, the localization of the canonical Hartree-Fock solution was done using the Foster-Boys algorithm.⁴⁶ For treating the localized orbitals with perturbation methods

the “active orbitals” were re-canonized. In the periodic calculations, the Wannier orbitals were localized following the scheme in Refs. 47 and 48 as implemented in the CRYSTAL09 program^{39,49} with the same Pack-Monkhorst k-point mesh as for bulk and slab calculations.

Periodic optimizations and single point calculations were carried out with the CRYSTAL09 program.^{39,49} The structure optimization of CO on the cluster was performed with GAUSSIAN09, Revision A.02.⁵⁰ We employed the MOLPRO 2006.1 program^{51–54} for CCSD(T) and MP2 incremental calculations and the MOLPRO 2009.1 program package for the DF-LMP2 calculations of the cluster. For periodic DF-LMP2 calculations we employed the CRYSCOR09 program.^{55,56}

III. RESULTS

The cell constants and the free atomic coordinate of rutile-type MgF₂ were found to be $a = 4.665$ Å, $b = 3.083$ Å, and $x = 0.3041$ as obtained from periodic structure optimization at the B3LYP level. These values are in good agreement with experimental results determined by x-ray powder diffraction under ambient conditions.⁵⁷

In the periodic calculations we considered two coverages: full coverage, where each coordination site is occupied and a 50% coverage where in y-direction every second adsorption site is not occupied and which we will here refer to as half-covered. Periodic interaction energies are collected in Table I.

With the B3LYP functional we found binding of CO atop Mg²⁺ perpendicular to the normal plane of the MgF₂(110) surface, with the C atom pointing towards the surface. The equilibrium distances obtained with B3LYP were 1.120 Å and 2.538 Å for $r(\text{C}-\text{O})$ and $r(\text{C}-\text{Mg}_{\text{surface}})$, respectively. This means that the $r(\text{C}-\text{O})$ distance is shortened by about 0.006 Å compared to a CO molecule in vacuum.⁶²

Regarding the interaction energies, we find that HF underestimates the interaction energy compared to LMP2 by about 50% and B3LYP by about 30%. The dispersion corrected B3LYP overestimates the binding by about 30%. In fact similar trends were also observed for the CO/MgO (Ref. 58) and N₂O/MgO (Ref. 59) systems. In the former study, Civalleri *et al.* noticed that already the cell parameter of MgO is predicted too small, which they interpreted as an overbinding of the ions in MgO. Civalleri *et al.* concluded that the van der Waals radii provided by Grimme³⁸ are too small for condensed materials and demonstrated that when scaling these radii with a factor of 1.05, the B3LYP-D2 opti-

mized cell parameter agreed much better with experiment.⁵⁸ A similar effect was then observed for the dispersion corrected B3LYP binding energy of CO at the MgO(001) surface which improved from 122% with Grimmes original parameters to 110% with the re-scaled once, compared to experiment. The result seems convincing but for two reasons we prefer not to use re-scaled van der Waals radii as Civalleri *et al.* did. First of all, we believe that the effect of re-scaling Grimme’s parameters would be different for different interactions. Civalleri *et al.* choose their re-scaling parameter to describe correctly the ionic interactions in MgO and expect this re-scaling to have a similar effect for the van der Waals type interaction of CO physisorption. But there is no reason to expect that the electron dispersion contribution, provided by the Grimme scheme, would be the same for ionic and van der Waals type interactions. And second, there are no experimental interaction energies available for the CO/MgF₂(110) to justify a re-scaling of the van der Waals radii.

Indeed comparison of our results for CO/MgF₂(110) with results for CO/MgO(001) is interesting for another reason. There are certain similarities between MgF₂(110) and MgO(001). Both materials are highly ionic with the valence electrons of magnesium being strongly localized at the positions of the anions. The surface magnesium ions on the (001) surface of MgO are coordinatively unsaturated, which also applies to half of the magnesium ions on the (110) surface of MgF₂. From adsorption studies of the CO/MgO(001) system at the DFT, MP2, CI, and, recently, the incremental coupled electron pair approximation level, we know, that CO adsorption is weak and of van der Waals type.^{31,60,61} The CO adsorbs in a C-down orientation perpendicular to the surface plane atop a coordinatively unsaturated magnesium cation. Both HF and the B3LYP functional were found to underestimate the CO adsorption energy^{60,61} which agrees well with the results we obtained for the CO/MgF₂(110) system.

As pointed out in the introduction, with embedded clusters we can treat our system like a large molecule, and use any wavefunction based post-Hartree-Fock method that is available for molecules. However, embedded cluster calculations may suffer from embedding errors. We assessed the quality of our cluster model by comparing the interaction energies and electron densities obtained from both the embedded cluster and the periodic slab model at the HF and B3LYP level, respectively. To eliminate surface coverage effects from the comparison of embedded cluster and periodic slab calculations we first calculated BSSE corrected interaction energies at different levels of theory [HF, B3LYP, MP2, CCSD(T)] with the crystal basis set, for pairs of parallel oriented CO molecules at distances corresponding to those found in an adsorbed layer of CO at different coverages. We found that for a separation of 6 Å the interaction energy is less than 1 meV for all methods and conclude that calculations with a half covered slab are suitable for comparison with the cluster calculations with only one CO adsorbed at the surface.

Our results are summarized in Tables I and II. Depicted in Figure 2 is the difference electron density calculated from the embedded cluster and a corresponding periodic slab in a two-dimensional cut through Mg1, parallel to the line between F1a

TABLE I. MgF₂(110)/CO Interaction energies in meV for periodic single point calculations with full and half coverage. Structures, obtained at the B3LYP level, were kept fixed and the crystal basis set was used, as presented in II B.

Coverage	Interaction energy/meV			
	B3LYP	B3LYP-D2	HF	DF-LMP2
Full	−210	−409	−162	−302
Half	−219	−417	−155	−314

TABLE II. Interaction energy E_{int} in meV at a fixed cluster structure (periodic B3LYP optimization with the crystal basis set) in the cluster basis set.

Methods	$E_{\text{int}}/\text{meV}$
B3LYP	-272
RHF	-193
MP2 full	-384
MP2 incr	-385
CCSD(T) incr	-373
DF-LMP2 incr	-377

and F1b along the [110] direction. At the adsorption site, there is a good agreement in the electron densities, indicating a very good embedding quality. Significant differences are only observed at the borders of the cluster.

At the Hartree-Fock level, we obtained interaction energies of -183 meV with the embedded cluster and -162 meV with the periodic slab at full and -155 meV at half coverage. Hence, we estimate an embedding error of about 30 meV for the interaction energy. Assessing the quality of the embedding scheme, Müller *et al.* found an embedding error in the range of 20 meV for the interaction energy of the CO_2/CeO_2 system,³⁶ which compares well with our result.

With the cluster model we have the possibility to use the larger aug-cc-pVTZ basis set for CO (cluster basis set). In this case, the HF interaction energy increases by 10 meV to -193 meV. The influence of the larger basis set on the interaction energy is rather small. However, it is well known that the size of the basis set is much more important in calculations with post-HF electron-correlation methods. Indeed, MP2 calculations of our cluster with the cluster and crystal basis set yield values of -384 meV and -358 meV, respectively, which shows a considerably larger influence of the basis set.

If we consider again the CO molecules on the half-covered slab as quasi non-interacting and compare the periodic result with the crystal basis set to the cluster MP2 energy with the cluster basis set we obtain a difference of about

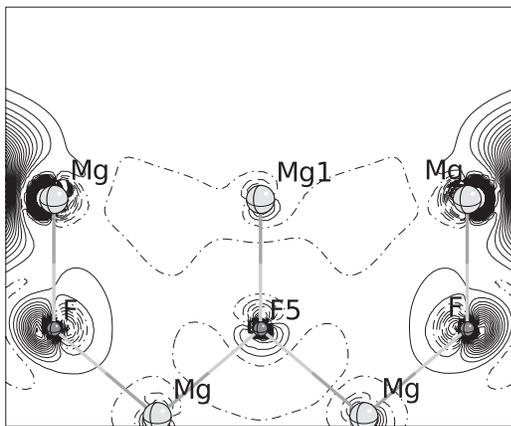


FIG. 2. Difference electron density calculated from the embedded cluster and a corresponding periodic slab in a two-dimensional cut through Mg1, parallel to the line between F1a and F1b along the [110] direction. The contour level interval is $0.001 e/\text{bohr}^3$ with solid lines for positive values, dashed lines for negative values and point-dash lines for the zero-contour. The cut-offs were set to $\pm 0.02 e/\text{bohr}^3$.

70 meV. Assuming an embedding error of about 30 meV, as discussed above, and an error of about 30 meV due to the smaller basis set, we conclude that the remaining 10 meV are due to the neglect of the semi $2s2p$ -core of Mg^{2+} excitations in the periodic LMP2 calculations. Indeed, as shown later in the incremental calculations the semi $2s2p$ -core of Mg^{2+} contributes about 10 meV to the interaction energy. As mentioned previously, this clearly shows the two big advantages of the cluster model. We can apply higher levels of theory like CCSD(T) and larger basis sets, which are important for post-HF electron correlation methods and since we can identify the sources of deviations between the two models we can confidently apply cluster schemes and the method of increments.

We performed interaction energy calculations at the CCSD(T) and the MP2 levels applying the method of increments for the B3LYP optimized structure. Results are shown in Table II. The incremental interaction energies are -385 meV and -373 meV at the MP2_{incr} and $\text{CCSD(T)}_{\text{incr}}$ levels, respectively.

To assess the quality of our incremental expansion, we also performed canonical MP2 for the embedded cluster. The difference to our incremental MP2 value is less than 1% which indicates that our incremental expansion is well converged. Interaction energy increments, η , are summarized in Table III. By comparison of the MP2_{incr} and $\text{CCSD(T)}_{\text{incr}}$ values to previous studies by Müller *et al.*^{28,29} we observe similar trends. In our calculations, the η_M is negative, which is different from previous studies of the CO/CeO_2 system^{28,29} or the CO/MgO system³¹ but has been observed previously for the $\text{N}_2\text{O}/\text{CeO}_2$ system.³⁰ The contribution to the electron correlation energy of η_M is large compared to η_i , consistent with previous incremental adsorption studies. One-body increments display the polarization of the molecule and the surface atoms, which appears to be rather small, hence the localized orbitals in the surface do not change very much due to physisorption. Only the orbitals, belonging to the four F^- that are closest to the CO molecule, are significantly polarized and the corresponding one-center interaction energy increment is relatively large. The same tendency was found in the previous studies mentioned above, as well as the fact that all one-center increments in the surface are positive.

We find that the two-center increments η_{Mi} yield in general the highest correlation contribution to the interaction energy, while two-center increments within the cluster, η_{ij} , are positive and rather small. Again, these observations are similar to previous investigations on CO/CeO_2 .^{28,29} The $\eta_{\text{CO}, \text{F}2}$ terms, originating from the four fluorine ions closest to the adsorbate (F2), are the largest of the interaction energy increments and contribute alone energies of -151 meV and -168 meV to E_{ads} at the MP2 and the CCSD(T) level, respectively. The $\eta_{\text{CO}, \text{F}1a}$ are already significantly smaller and add values of -26 meV and -28 meV for MP2 and CCSD(T), respectively. Surprisingly, the $\eta_{\text{CO}, \text{Mg}1}$ term is nearly one half of the $\eta_{\text{CO}, \text{F}1a}$, which means that the semi $2s2p$ -core of Mg^{2+} contributes significantly to the correlation energy. But since there arises only one $\eta_{\text{CO}, \text{Mg}1}$ term compared to, for example, four $\eta_{\text{CO}, \text{F}2}$ terms the contribution to the total correlation energy is small.

TABLE III. Incremental correlation energy contributions, η , (in meV) at the MP2, CCSD(T), and DF-LMP2 levels for CO physisorption on the MgF₂(110) surface. An atomic label indicates (the orbital groups on) all the atoms of the same type, e.g., 1-body F2 refers to the sum of the 1-body contributions from all F2 ions. All η terms are BSSE corrected, and a positive sign means repulsion. The values in parentheses indicate the closest interatomic distances, r , for the pairs considered. For the η_{Mi} interatomic distance refers to the distance between the C-atom and a center in the slab. According to their occurrence, increments are weighted by a factor ω .

	Orbital groups	ω	r	Weighted increments: $\omega \cdot \eta$ (in meV)		
				MP2	CCSD(T)	DF-LMP2
η_M	CO	1		-41	-15	-41
η_i	F2	4		33	31	31
	F1a	2		4	4	4
	F1b	4		1	1	1
	F5	1		0	0	0
	Mg1	1		2	2	2
$\sum \omega \cdot \eta_i$				40	38	38
η_{Mi}	CO-Mg1	1	(2.54 Å)	-16	-18	-16
	CO-F2	4	(3.04 Å)	-151	-168	-141
	CO-F1a	2	(3.49 Å)	-26	-28	-25
	CO-F1b	4	(4.65 Å)	-8	-8	-7
$\sum \omega \cdot \eta_{Mi}$				-201	-221	-189
η_{ij}	F2-Mg1	4	(1.99 Å)	3	4	3
	F5-Mg1	1	(1.93 Å)	0	0	0
	F1a-F2	4	(2.84 Å)	1	1	1
	F2-F2	2	(2.46 Å)	3	4	3
	F2-F2	2	(3.08 Å)	2	3	1
	F2-F2	2	(3.94 Å)	1	1	0
$\sum \omega \cdot \eta_{ij}$				10	13	8
η_{Mij}	CO-F2-F1a	4		0	2	
	CO-F2-F2	2		0	1	
	CO-F2-F2	2		0	3	
$\sum \omega \cdot \eta_{Mij}$				0	6	
$E_{\text{int}}^{\text{corr}}$				-192	-180	-184
$E_{\text{int}}^{\text{incr}} = E_{\text{int}}^{\text{RHF}} + E_{\text{int}}^{\text{corr}}$				-385	-373	-377
$E_{\text{int}}^{\text{full}}$				-384		
Error = $E_{\text{int}}^{\text{incr}} - E_{\text{int}}^{\text{full}}$				<0.5%		

We have tested a small selection of three-center increments including the CO molecule and found that they yield only a very small correlation contribution. At the MP2 level their contribution is always smaller than 1 meV. For this reason, we neglected the three-center increments in the DF-LMP2 calculation. However, MP2 has shown to be insufficient for describing three-body Axilrod-Teller dispersion, which can yield a significant contribution to dispersive interactions in weakly bond systems and are only accurately described by at least MP3 or CCSD(T).^{63,64} Indeed, with the CCSD(T) method, the correlation contribution of three-center increments is larger than with MP2, but in our case not significantly and none of the increments is larger than 3 meV, which is in agreement with previous studies on similar systems.^{28,29}

The periodic LMP2 energy can be understood as a sum of contributions from pairs of two Wannier-functions with their combined excitation domains. Provided that the correlation energy of each pair is converged with respect to the size of its excitation domain, each increment corresponds to a number of such pairs. As an example, we have summed up all pair contributions corresponding to the CO and F2 one-center

increments (-15 and +33 meV) and the CO-F2 two-center increment (-129 meV). Indeed these values agree very well with the corresponding increments as listed in Table III (-41, +31, and -141 meV), considering that the cluster calculations suffer from embedding errors, are compared to periodic calculations with full coverage, and the excitation domains in both calculations cannot be defined completely equivalently. The effect of the slightly different basis sets in the periodic and cluster calculations was found to be in the range of just a few meV.

At the DF-LMP2_{incr} level the interaction energy is -377 meV. The difference between the DF-LMP2_{incr} and the standard MP2_{incr} total correlation energy is 8 meV, which is bearable considering the speed up due to the use of density fitting and local excitation domains.

Since post-HF electron correlation methods are very basis set dependent, one would like to assure that the size of the basis set is sufficient. In principle, it is possible to increase the basis set in the cluster scheme. However, if done for all atoms in the cluster, this becomes unfeasible for large clusters. It is often more sensible to increase the basis set size at chemically relevant atoms when estimating the effect of basis

set size. When we increased the aug-cc-pVTZ basis set at the CO molecule to the aug-cc-pVQZ basis set, we observed only a small effect of 11 meV and we predict only small changes in the interaction energy when the basis set in the surface is further improved.

Based on the $\mathcal{O}(N^7)$ scaling of computer time for CCSD(T) with respect to the number of electrons, we estimate that a standard canonical CCSD(T) calculation for our system would require about 20 years on a single core Intel Xeon E5450@3.00 GHz node; provided that the amount of memory and disk space is unlimited. With the method of increments we obtain a result in about 28 days with an error of less than 1% (see the comparison of our incremental and canonical MP2 results). Conveniently, incremental calculations are embarrassingly parallel; in our case we have 19 increments that can be calculated independently.

IV. CONCLUSION

We have performed incremental embedded-cluster single point calculations at the MP2, CCSD(T), and DF-LMP2 levels and periodic calculations at the B3LYP, HF, and DF-LMP2 levels for the CO/MgF₂(110) system. With all methods applied, CO adsorbs with the C-end atop a Mg²⁺ ion with negative interaction energies in the range of 200–400 meV and small changes of the intra-molecular bond distance. The CCSD(T)_{incr} method reveals an interaction energy of –373 meV with an electron correlation contribution of about 50% and with the MP2_{incr} method we obtain an interaction energy of –384 meV. At the MP2 level, results for periodic slab and embedded cluster calculations agree very well and we can estimate the error of the cluster approximation to be small and acceptable considering that embedded clusters allow for the application of more sophisticated electron correlation methods and larger basis sets than in periodic calculations.

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