Good performance of the M06 family of hybrid meta generalized gradient approximation density functionals on a difficult case: CO adsorption on MgO(001)

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The adsorption of CO on Mg(001) constitutes a challenge for current density functional approximations because of its weak interaction character. In the present work we show that the M06-2X and M06-HF exchange-correlation functionals are the first ones to provide a simultaneously satisfactory description of adsorbate geometry, vibrational frequency shift, and adsorption energy of CO on MgO(001). For a sufficiently large embedded cluster model, the three functionals of the M06 family—which contain a nonzero percentage of Hartree–Fock exchange (M06, M06-2X, and M06-HF)—all predict positive C–O vibrational shifts, in agreement with the experimental findings, while the local M06-L functional gives large negative shifts. Moreover, the shifts computed with the M06-2X and M06-HF potentials are in good agreement with the experimental shift of +14 cm^{-1}. The interaction energy (D_e) calculated with M06-2X and M06-HF is ~6.0 kcal/mol, which agrees well with the D_e value (~4 kcal/mol) deduced from the D_0 obtained in thermal desorption measurements on single-crystal surfaces. © 2008 American Institute of Physics. [DOI: 10.1063/1.2982923]

I. INTRODUCTION

Magnesium oxide has generally been considered to be representative of ionic oxides and ionic crystals, and the size, simplicity, and catalytic importance of the CO molecule have turned this species into a widely used probe in surface science and heterogeneous catalysis. Combining these considerations has resulted in a wide range of studies of the interaction of CO with the MgO(001) surface by both experimentalists and theorists, and controversies have arisen regarding the strength and type of the adsorbate-substrate interaction. Debate on this subject started in the early 1990s as a result of the differences between the experimentally derived values of the interaction energy,[1–4] between the experimental and calculated values,[5–8] and between the results coming from the application of different theoretical approaches, surface models, and computational strategies.[5–31]

Early experimental works reported an interaction energy of about 3.5–4.0 kcal/mol for the adsorption of CO on MgO.[1,2] A decade later, Henry *et al.*[3] and He *et al.*[4] reported somewhat higher values of 9–10 kcal/mol. However, these works used different MgO substrates (polycrystalline material, large particles, and thin films). As discussed in a comprehensive review,[32] the higher values[3,4] are now understood to result from binding of three-coordinated or four-coordinated defect sites. Modern experimental studies on regular (001) surfaces with binding at the five-coordinated

sites are now in good agreement with three separate experiments yielding 3.0,[32] 3.0,[33] and 2.6 kcal/mol (Ref. 34). These values correspond to desorption of CO from the ground vibrational state or a thermal mix of low-lying vibrational states and are considered to be an approximation to what Herzberg calls D_0 (dissociation energy from the ground state). We must add the net loss of zero-point vibrational energy (ZPVE) for the vibrational modes corresponding to CO desorption to obtain D_e (equilibrium dissociation energy from the ground state). In Sec. III we estimate the net loss of ZPVE to be 0.9 kcal/mol, yielding a best estimate of 3.9 kcal/mol for D_e.

In parallel to these experimental works, several theoretical studies appeared in literature, at first using Hartree–Fock (HF) theory[9–16] and the local density approximation (LDA) (Refs. 5 and 6) and making use of either periodic boundary conditions[12,13] or cluster models.[5,6,15] HF calculations with periodic boundary conditions but without a counterpoise correction (CPC) for basis set superposition error (BSSE) yielded[11,13] interaction energies of 7–9 kcal/mol. However, HF cluster model calculations corrected for BSSE yielded[7,8] a smaller value of ~4 kcal/mol. Employing also a similar cluster model with the LDA exchange-correlation potential, Neyman and Rösch[5,6] obtained much larger binding energy estimates,[9–13] even after BSSE corrections. Furthermore, the LDA calculations by Neyman and Rösch[5,6] showed significant charge transfer from CO to the surface, whereas other works[15,35] indicated that the interaction is a purely electrostatic interaction of the ionic surface with the multipoles of

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the CO molecule. Despite all these differences, both experimental and theoretical works agreed in that the preferred adsorption configuration for CO on the regular MgO(001) surface is perpendicular to the substrate, in a C-down bonding mode and above the fivefold coordinated Mg sites.[36]

In the mid-1990s, several theoretical attempts were made to solve the puzzle of the CO interaction with the MgO(001) surface. First, Nygren *et al.*[7] showed that the previous cluster models suffered from a severe deficiency caused by surrounding the model clusters only by unscreened point charges (PCs) and that the spurious polarization of the outer atoms, which drastically changed the Madelung potential felt at the center of the cluster, was responsible for the too large calculated value and for an exceedingly large BSSE. These authors overcame the problem by embedding the cluster with *ab initio* model potentials.[7,20] The BSSE-corrected binding energies for a CO molecule interacting with a Mg^{2+} cation calculated using different embedding schemes and explicitly correlated wave functions were only about 2 kcal/mol.[7] Nygren *et al.*[7] concluded also that the electrostatic attraction and Pauli repulsion almost cancel each other and that the small binding energy obtained is due to dispersion forces.[7] The BSSE of the calculated interaction energies was found to be rather large, especially for the correlated wave-function methods. A subsequent paper by Mejías *et al.*[8] compared the interaction energies calculated with large or embedded (in compact model potentials) clusters to those calculated with periodic boundary conditions. The calculations based on HF gave BSSE-corrected interaction energies of only 0.2 kcal/mol, and the resulting binding energies were independent of the surface model when a minimum embedded cluster was used.[8] The constrained space orbital variation (CSOV) method[37,38] applied to the HF cluster model wave function showed that chemical contributions to the interaction between CO and the MgO(001) surface were insignificant and that the electrostatic contribution was clearly affected by cluster model termination;[8] this influences the electric fields at the carbon and oxygen atoms of CO as already observed by Nygren *et al.*[7]

Exchange-correlation density functionals based on the generalized gradient approximation (GGA) were also applied to this problem. Neyman *et al.*[18] studied the interaction of CO on MgO(001) using two GGA functionals, namely, BLYP[39,40] and BP86,[39,41] and found, in agreement with known trends for other systems,[42] that the simpler LDA density functionals give a systematic overbinding, as reported in their previous works.[5,6] However, they still concluded that the interaction of CO with the MgO(001) surface has a significant σ charge transfer component, and their CSOV analysis applied to the Kohn–Sham density (or orbitals) indicated that the magnitude of the charge transfer is similar to that of the electrostatic contribution. Here, a new element entered into the discussion, namely, the vibrational frequency of the adsorbed CO molecule. The CO molecule is a common probe in surface science, and the difference of the vibrational frequency of the adsorbed molecule from that of gaseous CO is used to infer the nature and extent of charge transfer by comparing to the vibrational frequency of gas-phase CO^+ and CO^-, although this has proven to be less straightforward

than generally assumed.[43–46] The calculations of Neyman *et al.*[18] predicted a C–O stretching frequency shift significantly larger than the experimentally observed one. Calculated shifts with the $X\alpha$ method (which involves LDA-type exchange and no dynamical correlation) and BLYP were 54 and 59 cm^{-1}, respectively, while the reported experimental results were between 14 and 35 cm^{-1}.[4,47] They attributed this large shift to the PCs surrounding the cluster; these had a magnitude of ± 2.0 a.u. Although MgO is almost a fully ionic compound,[35,48] calculations using PCs equal to ± 1.8 a.u., which quantitatively reproduce the Madelung field outside the MgO(001) surface, yielded smaller frequency shifts similar to the 31 cm^{-1} shift previously reported by Pacchioni *et al.*[16] However, a further complication is that the reported experimental values of 14 and 35 cm^{-1} for the vibrational shift correspond, in the former case, to MgO thin films grown on a metallic support and, in the latter case, to MgO polycrystalline samples.[4,47] The adsorption on thin films and some polycrystalline samples is now believed to occur at surface sites.[32] The modern value[32,47] for low-coverage adsorption at the carbon end on five-coordinated sites is 14 cm^{-1}, that is, 2157 cm^{-1} versus a gas-phase value of 2143 cm^{-1}. (Note that this is the experimental fundamental frequency, whereas the harmonic frequency (ω_e) is[49] 2169 cm^{-1}. Experimental shifts are shift of the fundamental, whereas theoretical frequencies and shifts in this article are harmonic).

Nygren and Pettersson[20] used an embedded cluster model and the correlated coupled-pair functional (CPF) method (which, despite its name, is a wave function calculation as opposed to a density functional calculation) to calculate the binding energy and frequency shift for CO adsorbed directly above terrace and low-coordinated (steps and edge) Mg^{2+} sites of the MgO(001) surface. They obtained an interaction energy of 1.8 kcal/mol and a frequency shift of 9 cm^{-1} on the regular (five-coordinated) site.[20] For the step (four-coordinated site) and corner (three-coordinated site), the adsorption energies were 4.2 and 11 kcal/mol, respectively, and the CO vibrational shifts were 27 and 56 cm^{-1}, respectively.[20] The vibrational frequency blueshifts found were in good agreement with the experimental data and assignment reported by Scarano *et al.*[47] on regular (+14 cm^{-1}), step (+25 cm^{-1}), and corner (+58 cm^{-1}) sites. At this point, it became clear that correlated wave-function methods and embedded cluster models were able to provide an accurate description of this simple system whereas density functional approximations were much less successful.

Further important background for the present study involves subsequent applications of DFT to the computation of the binding energy for CO on MgO(001). Yudanov *et al.*[22] further improved the embedding and boundary conditions of the MgO clusters already used in previous works[5,6,18] and found that now the BLYP functional predicted a negative interaction energy while the value predicted by the BP86 functional together with the new embedding scheme, 1.2 kcal/mol, was even smaller than that reported previously, 2.1 kcal/mol.[18] However, the result reported by Wesolowski *et al.*,[27] within the constrained electron density formalism,

the BP86 potential and a cluster model approach, was significantly larger (10 kcal/mol), further illustrating the dependence on the computational scheme.

Hybrid density functionals, which mix HF exchange with density-dependent exchange, might be expected to be more accurate than local functionals (such as LDA and GGA functionals) because HF exchange removes self-interaction errors, which can be important in systems with large charge separation, such as ionic crystals. The most popular hybrid functional is B3LYP,[40,50,51] which has 20% HF exchange and therefore removes 20% of the self-interaction error. Soave and Pacchioni[52] used the hybrid B3LYP and an embedded cluster model; the BSSE-corrected calculated binding energy was 4.4 kcal/mol before BSSE correction and 0.2 kcal/mol after, and the frequency shift is negative (-7 cm^{-1}).[52] Importantly, the same hybrid functional and Mg_9O_9 cluster model was used by Xu et al.,[33] and their calculated interaction energy and frequency shift were 5.5 kcal/mol and +41 cm^{-1}, respectively. These results show the crucial effects of the basis sets and of the number and positions of the PCs on the calculated data. Periodic boundary condition calculations using the Perdew–Burke–Ernzerhof (PBE) (Ref. 53) density functional (a GGA) and a full potential linearized augmented plane-wave (FLAPW) method were performed by Wu and Zhang[26] and corrected previous exceedingly large binding energy values obtained with the LDA approximation[24] by the same group; the new calculations yielded 2.8 kcal/mol and 6 cm^{-1} for the interaction energy and vibrational shift, respectively,[26] whereas the LDA functional results were 6.5 kcal/mol and 33 cm^{-1}, respectively.[24] Similar results were obtained by Snyder et al.[28] in a comparative study of LDA and various GGA functionals using localized basis functions. The BSSE-corrected energies were 7.0, 1.8, -0.3, and 0.3 kcal/mol with the LDA, PBE, BLYP, and BP86 functionals, respectively. The periodic B3LYP calculations of Damin et al.[29] yielded a binding energy at low coverage of 0.9 kcal/mol and a frequency shift from +1 to +3 cm^{-1} depending on the basis set. The same authors corrected the interaction energy calculated at the B3LYP level of theory by incorporating a complete basis set extrapolated MP2 energy.[30] The corrected interaction energy was 3.0 kcal/mol,[30] in excellent agreement with experiment (see above).[32,34,54] Thus, the PBE/periodic model,[26,28] BP86/cluster model,[22] MCPF/cluster model,[20] and B3LYP+MP2/periodic model[30] are in reasonable agreement with the modern experimental results. Very recently, Qin[55] considered also the Mg_9O_9 cluster model surrounded by an array of ionic core potentials and the configuration interaction (CI) method and the reported data (2.5 kcal/mol and +19 cm^{-1}) give further support to the later experimental and computational results summarized above. One key element that emerged from the B3LYP +MP2 study of Ugliengo and Damin[30] is an estimate of the importance of dispersion interactions for the binding energy of CO on MgO(001). They estimated that their calculated binding energy of 3.0 kcal/mol arises as 1.4 kcal/mol from electrostatics and 1.6 kcal/mol from dispersive forces.[30] Since none of the density functionals mentioned so far provides an accurate account of weak interactions dominated by dispersion-like interactions, it is not surprising that they pro-

vide unreliable estimates of the binding energy. Recently, a suite of new functionals, generically called the M06 family,[56–59] has been developed and has been found to be able to describe weak interactions at the geometries of van der Waals minima. Note that the interaction energies at such minima are dominated by medium-range correlation energy not by the long-range dipole terms. The M06 family consists of hybrid meta functionals that mix a fraction of the HF exchange, as in the well known B3LYP potential, but here it may vary from 0% to 100%. The adjective "meta" denotes that they also depend on the kinetic energy density. The main aim of the present work is to test the performance of the M06 family of functionals[56–59] for the prototype interaction of CO with the regular sites of the MgO(001) surface. It has previously been anticipated[56,59] that for systems like this, which do not involve transition metals but which do involve significant charge separation, the functionals with the higher percentage of HF exchange, called M06-2X and M06-HF, would be most accurate. To test their accuracy, all four M06-class functionals have been applied to two different sizes of embedded cluster models (Mg_9O_9 and $Mg_{25}O_{25}$) as described in Sec. II.

II. COMPUTATIONAL DETAILS

The interaction of CO with a cationic regular (five-fold coordinated) site on the MgO(001) surface was modeled with two different stoichiometric cluster models embedded in an environment that accounts for short- and long-range interactions with the remainder of the crystal,[22,52,60–65] and in particular that accounts for the long-range Madelung potential. The two clusters used in the present study are Mg_9O_9 and $Mg_{25}O_{25}$ and hence have 9 Mg and 9 O atoms or 25 Mg and 25 O atoms with all electrons treated explicitly with each of the density functionals considered. In both clusters, the Mg^{2+} cations external to the Mg_9O_9 and $Mg_{25}O_{25}$ clusters and directly coordinated to the oxygen anions at the cluster edge were modeled as total ion potentials (TIPs), which are pseudopotentials that prevent the spurious polarization of the oxygen anions. The TIPs consisted only on a pseudopotential simulating the Mg^{2+} cations. A sufficiently large array of PCs with ± 2.0 a.u. values has been used as usual. The two cluster models plus TIPs are shown in Fig. 1. In particular, the Mg_9O_9 cluster is surrounded by 17 TIPs, 312 positive PCs, and 329 negative PCs, and for the $Mg_{25}O_{25}$ cluster these numbers are 33, 280, and 313, respectively.

In this work, four different combinations of basis sets were employed for the description of the CO molecule and of the cluster models. In a combination that from now on will be named basis A, the electrons of the central Mg^{2+} cation in the cluster model were described by the [13s, 8p/6s, 3p] Huzinaga's basis set as in Ref. 16, while for the rest of the Mg^{2+} cations the [12s, 7p/5s, 2p] basis set is used. The O^{2-} anions electrons were described by the [8s, 4p/4s, 2p] basis set,[66] and for those surrounding the central Mg^{2+} cation (four in the upper layer and one in the second layer) the basis set was augmented with a d polarization shell. A second combination, named basis B, uses the [13s, 8p/6s, 3p] basis for the central Mg^{2+} cation and the [8s, 3p,
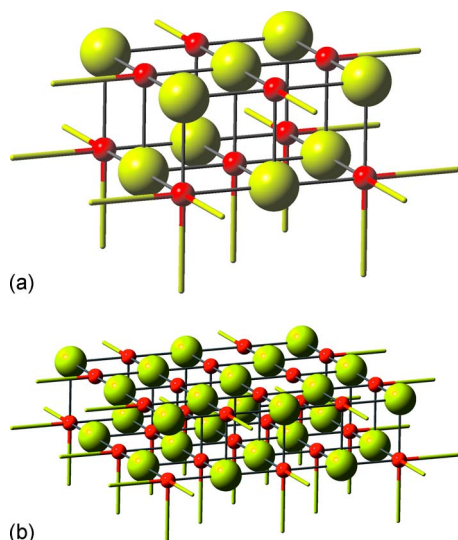
FIG. 1. (Color online) (a) Mg_9O_9 and (b) $Mg_{25}O_{25}$ cluster models (ball and stick) and TIPs (sticks) used to simulate the MgO(001) surface. Large balls (yellow) and small balls (red) denote Mg^{2+} and O^{2-} ions, respectively. The array of PCs is not shown.

$1d/4s, 2p, 1d$] basis for the O^{2-} anions surrounding the central cation. The remaining Mg^{2+} and O^{2-} ions are described in basis B by the CRENBL basis set and the CRENBL–effective core potential (ECP) for $1s$ core electrons only.[67] Basis C is identical to basis A but the central Mg^{2+} cation basis is Pople's $6-311++G(3df,2p)$ basis instead of the $[13s, 8p/6s, 3p]$ one. In all cases, the Ahlrichs' VTZ basis set was used for the CO molecule. Finally, basis set D is identical to basis set A for the cluster atoms but the CO molecule is described with Ahlrichs' TZVP basis set.

The four hybrid meta functionals of the M06 family, M06-L,[57] M06,[56] M06-2X,[56] and M06-HF, were employed to optimize the C–O internuclear distance and its distance and orientation with respect to the surface, which was maintained frozen at the bulk geometry. The direction of the Mg–C axis was also frozen (normal to the surface). Geometries were optimized without a CPC for BSSE, and then the CPC was applied at this geometry. Vibrational frequencies were calculated with the PCs fixed but all atoms and TIPs allowed to move; thus, the Hessian is 111×111 for CO/Mg_9O_9 and 255×255 for CO/$Mg_{25}O_{25}$.

The functionals considered differ in the percentage of

HF exchange as well as in the strategy followed in their optimization.[56] The percentages are 0%, 27%, 54%, and 100% for M06-L, M06, M06-2X, and M06-HF, respectively.[56–58] The results obtained with the M06 family of functionals were also compared with those obtained from the popular B3LYP hybrid exchange-correlation functional.

All the calculations were performed with a locally modified version of GAUSSIAN 03 Revision D.01,[68] employing the MN-GFM module.[69]

III. RESULTS AND DISCUSSION

First we discuss results for the two surface cluster models obtained with the M06 family of functionals and also with the B3LYP method and considering only basis set A. A summary of relevant calculated data is reported in Table I. Note that, as discussed in Sec. I, the best experimental estimate, 3.0 kcal/mol, of the binding energy includes the change in ZPVE upon binding whereas the electronic structure calculations do not include this. Thus, we estimated the change in ZPVE in the harmonic approximation for the $Mg_{25}O_{25}$ model with the M06-2X functional and basis set A. In particular, four contributions are considered: three soft modes with frequencies of 234, 234, and 145 cm^{-1}, which combined with a 15 cm^{-1} increase in the CO stretch, leads to a zero-point increase of 0.9 kcal/mol (the contributions of the other two newly created modes and the changes in the frequencies of the surface phonon modes are neglected here) and a best estimate of 3.9 kcal/mol for D_e, and this value is used in the following discussion.

In the case of the isolated CO molecule, the comparison between the computed C–O bond length and stretching CO frequency with the corresponding experimental results, $d(C-O)_{gas}=1.128$ Å and $\omega(C-O)_{gas}=2169$ cm^{-1},[49] shows that there is a clear improvement in going from the M06-L to the M06-HF functional, that is, with the increase in the percentage of the HF exchange. Notice that the results computed with the B3LYP method (20% HF exchange) are clearly between those obtained with the M06-L (0% HF exchange) and M06 (27% HF exchange) and that the M06-HF calculated stretching frequency is larger than the experimental result. Note, however, that the B3LYP harmonic vibrational frequency obtained using either $6-31G^*$ or Alrichs VTZP basis sets is somewhat larger ($\sim$2220 cm^{-1}) than the

TABLE I. Calculated results (basis set A) for gas-phase CO (two first rows) and for CO adsorbed on a regular Mg site on the embedded Mg_9O_9 and $Mg_{25}O_{25}$ surface cluster model representations of the MgO(001) surface. Distances are given in Å, interaction energies are in kcal/mol, and vibrational frequencies and shifts are in cm^{-1}.

	B3LYP		M06-L		M06		M06-2X		M06-HF	
$d(C-O)_{gas}$	1.146		1.151		1.144		1.140		1.129	
$\omega(CO)_{gas}$	2059		2045		2088		2128		2204	
Cluster model	Mg_9O_9	$Mg_{25}O_{25}$	Mg_9O_9	$Mg_{25}O_{25}$	Mg_9O_9	$Mg_{25}O_{25}$	Mg_9O_9	$Mg_{25}O_{25}$	Mg_9O_9	$Mg_{25}O_{25}$
$d(C-O)_{ads}$	1.148	1.146	1.154	1.152	1.143	1.143	1.139	1.138	1.127	1.127
$d(Mg\cdots CO)$	2.378	2.423	2.286	2.317	2.390	2.427	2.343	2.374	2.346	2.369
D_e (without CPC)	6.5	5.2	13.5	12.3	9.7	12.7	11.5	10.1	11.8	11.5
D_e (with CPC)	0.5	1.4	7.2	7.7	4.4	9.1	5.6	6.6	5.1	8.0
$\omega(C-O)_{ads}$	2041	2053	2019	2031	2087	2092	2134	2143	2217	2226
$\Delta\omega$	−17.8	−6.0	−26	−14	−1	+4	+6	+15	+13	+22

TABLE II. Calculated results (basis sets A, B, C, and D) for gas-phase CO (two first rows) and for CO adsorbed on a regular Mg site of the embedded $Mg_{25}O_{25}$ surface cluster model representation of the MgO(001) surface using the M06-2X and M06-HF functionals. Distances are given in Å and interaction energies are in kcal/mol.

Basis set	M06-2X				M06-HF		
	A	**B**	**C**	**D**	**A**	**C**	**D**
$d(C-O)_{gas}$	1.140	1.140	1.140	1.122	1.129	1.129	1.112
$d(C-O)$	1.138	1.140	1.138	1.120	1.127	1.126	1.110
$d(Mg \cdots CO)$	2.374	2.382	2.308	2.396	2.369	2.304	2.382
D_e (without CPC)	10.1	11.2	13.3	10.5	11.5	13.2	11.0
D_e (with CPC)	6.6	7.4	6.4	6.5	8.0	5.9	6.9

present value and becomes comparable to experiment once calculated by means of a proper fit of calculated points to a third order polynomial.[70,71] Thus, a validation of the predictions for absolute frequencies requires detailed consideration of the CO basis set quality and anharmonic effects, but the focus here is not on reproducing the experimental CO vibrational frequency but rather on the vibrational shift between the gas phase and the adsorbed molecule, which is much less sensitive to these issues.

Upon adsorption, the internal geometry of CO is almost unchanged, which indicates a rather weak interaction between CO and the oxide surface. Interestingly, in the case of the two functionals with lowest percentage of HF exchange (M06-L and B3LYP), there is a slight elongation of the CO bond length while the functionals with larger amounts of HF exchange predict a shortening of the C–O bond. Contrary to the situation for the internal C–O bond length, the distance between the CO molecule and the Mg site on the oxide surface [$d(Mg \cdots CO)$ in Table I] has no obvious variation with the amount of HF exchange in the potential. The values calculated with the Mg_9O_9 cluster vary in the range of 2.286–2.390 Å, i.e., 0.07 Å or more shorter than the BLYP and BP86 distances reported by Yudanov et al.[22] using also a Mg_9O_9 cluster model. In the case of the larger $Mg_{25}O_{25}$ model, the calculated Mg$\cdots$CO distances vary in the interval of 2.317–2.423 Å. An increase in the Mg$\cdots$CO distance with the size of the cluster model was also reported previously by Neyman et al.[18] In that work, the Mg$\cdots$CO distance calculated with the BLYP functional using a $Mg_{21}O_{21}$ model was 0.04 Å larger than that computed for a Mg_9O_9 cluster.

Next consider the calculated interaction energies and vibrational shifts which are also reported in Table I. The B3LYP method yields too small of a BSSE-corrected D_e when compared with the estimated experimental D_e of 3.9 kcal/mol. The bonding energy calculated with the Mg_9O_9 cluster is 0.5 kcal/mol, which is only 0.3 kcal/mol higher than the result computed previously by Soave and Pacchioni[52] also with the B3LYP and a Mg_9O_9 cluster model but different basis sets. The B3LYP BSSE-corrected interaction energy calculated with the larger $Mg_{25}O_{25}$ cluster is 1.4 kcal/mol. This value is in better agreement with experiment and with the B3LYP+MP2 result of Ugliengo and Damin.[30] The interaction energy calculated with the larger $Mg_{25}O_{25}$ model is 2.5 kcal/mol lower than the D_e value deduced from the experimental D_0. Besides, the B3LYP method always

predicts negative shifts for the C–O stretching frequency; −18 and −6 cm^{-1} for the embedded Mg_9O_9 and $Mg_{25}O_{25}$ clusters, respectively.

A negative C–O shift is also found when the M06-L functional is used either with the smaller or the larger cluster models. The values are even more redshifted than those calculated with the B3LYP computational approach. The BSSE-corrected interaction energy is 7.2 kcal/mol, 85% larger than the experimental binding energy. The comparison of the results calculated with the other three M06 functionals shows that the shifts become more positive, and the largest blueshifts are obtained with the M06-HF functional. In agreement with the B3LYP and M06-L results, the vibrational shifts for these three functionals are more positive in the case of the larger cluster model than in the smaller one. The calculated interaction energies for the M06-family functionals containing HF exchange are in the interval of 4.4–5.6 kcal/mol in the case of the smaller cluster and in the range of 6.6–9.1 kcal/mol in the case of the larger model. Again, there is no any apparent linear variation in the interaction energies with the increase of the HF exchange in the M06-class of functionals. The BSSE-corrected interaction energies calculated with any of the M06-functionals are always slightly larger than the estimated experimental value of 3.9 kcal/mol. Nevertheless, the calculated vibrational shifts obtained with the M06-2X (larger model) and M06-HF (smaller and larger models) functionals are not far from the 14 cm^{-1} experimental shift due to Zecchina and co-workers.[47,54] The values obtained with M06-2X and M06-HF are larger than the, in principle, best computational results reported in the past[20,26,29] but in nice agreement with the very recent CI value calculated by Qin.[55]

The influence of the basis set on the calculated interaction energies and geometries has been analyzed for the M06-2X and M06-HF functionals with data reported in Table II. As can be seen, the use of a larger basis set on the central Mg^{2+} cation that is directly interacting with the CO molecule, has a noticeable effect on the calculated Mg–CO distances. In fact, the Mg–CO distances calculated with basis A or C differ by more than 0.06 Å; the augmented basis set yields a smaller Mg–CO distance. Interestingly, the C–O bond length remains almost unchanged. The calculated BSSE-uncorrected energies using basis set C are larger than the corresponding ones obtained with basis set A. An opposite variation is found for the BSSE-corrected binding energies, although the energy differences are within 1−2 kcal/

TABLE III. Summary of theoretical and experimental results for CO adsorbed on a regular Mg site on the MgO(001) surface. Interaction energies are given in kcal/mol and vibrational frequency shifts in cm^{-1}.

Method	Ref.	Model	D_e	$\Delta\omega$
MCPF	7	Cluster	1.6−2.1	⋯
HF	8	Cluster	0.2	⋯
HF	15	Cluster	5.5	+31
$X\alpha$, BLYP	18	Cluster	12.9, 6.2	+54, +59
MCPF	20	Cluster	1.8	+9
LDA/FLAPW	24	Periodic slab	6.5	+33
PBE96/FLAPW	26	Periodic slab	2.8	+6
PBE96	28	Periodic slab	1.9	+4
B3LYP	29	Periodic slab	0.9	+1, +3
B3LYP+MP2	30	Periodic slab	3.1	⋯
B3LYP	52	Cluster	0.2	−0.7
B3LYP	33	Cluster	5.5	+41
CI	55	Cluster	2.5	+19
M06-2X	Present work	Cluster	6.4[a]	+15 [b]
M06-HF	Present work	Cluster	5.9[a]	+22 [b]
Expt.[c]	32,34,54	⋯	3.9	+14

[a]Results for $Mg_{25}O_{25}$ cluster and basis set C.
[b]Results for $Mg_{25}O_{25}$ cluster and basis set A.
[c]See text.

mol only. The M06-2X and M06-HF binding energies calculated with the larger cluster model and with the largest basis set C are ∼5.9∼6.4 kcal/mol, which are about 50%–65% larger than our estimate of the experimental D_e. In the case of the M06-2X functional, we tested the effect of the use of an ECP together with a small basis set for the ions surrounding the central Mg^{2+} cation and five O^{2-} anions, i.e., basis set B. The results reported in Table II show that there is a small increase in the Mg–CO distance and a large increase in the BSSE-corrected interaction energy. The geometric and energetic variations in the results calculated with basis set B when compared with those obtained with basis set A go in the opposite direction to those calculated with basis set C. This seems to suggest that the use of a more complete basis set for the cluster will move the calculated interaction energy in the direction of the experimental value. On the other hand, the quality of the CO basis set has been tested by comparing the results of using basis sets A and D, where the CO molecule is described with Ahlrichs' VTZ or with Ahlrichs' TZVP basis sets, respectively. The results indicate that there is a significant dependence of the equilibrium distance and vibrational frequency of gas-phase CO on the basis set. For example, for the M06-2X functional the calculated vibrational frequency is 2128 and 2290 cm^{-1} for basis sets A and D, respectively. Despite these differences, as can be seen in Table II, the interaction energy with the $Mg_{25}O_{25}$ cluster changes by at most 1 kcal/mol when going from basis set A to basis set D. Furthermore, when basis set D is employed, the vibrational shifts (not shown) increase by only 3 and 4 cm^{-1} for M06-2X and M06-HF, respectively, with respect to the values reported in Table I. In conclusion, the VTZ basis is good enough to describe the CO molecule and its interaction with the Mg(001) surface.

Finally, Table III presents a summary of the theoretical results obtained from previous works and the best results obtained from the present work including experimental results. Table III clearly shows that the M06-2X and M06-HF represent a substantial improvement over the previous DFT results and are able to provide a consistent simultaneous description of the interaction energy and vibrational frequency shift.

IV. CONCLUSIONS

In the present work, the adsorption of CO on the Mg(001) surface, which in the past has proven to be a difficult case for DFT, has been considered as a case study for benchmarking the recently introduced M06 family of hybrid meta GGA functionals. It was found that the increase in the percentage of HF exchange in the M06-class of functionals yields better agreement with available C–O distance and C–O stretching frequency for gas-phase CO. Using the same molecular cluster for the modeling of the regular Mg(001) surface, it is found that the vibrational stretching frequency in adsorbed CO is shifted to more positive values with the increase in the HF exchange. The blueshift in the case of the larger $Mg_{25}O_{25}$ cluster model is more dramatic than on the Mg_9O_9 cluster with differences of about 10 cm^{-1}.

The functionals that yield calculated vibrational frequency shifts in best agreement with experimental data are M06-2X and M06-HF. Although we tested all four functionals of the M06 family as a theoretical exercise, we might have tested only these two because previous work[56] shows that M06-L and M06 are usually preferred only when transition metals are involved. The binding energies calculated with the M06-2X and M06-HF functionals are ∼6 kcal/mol, a value which qualitatively agrees with the latest experimental number, although from a quantitative point of view the result is less satisfactory, with an overestimate of 50%−65% compared to our best estimate of the experimental result. Interestingly, in the case of CO adsorbed on the MgO(001) surface, the results obtained with the four functionals are sensitive to the percentage of HF exchange, which contrasts with a recent finding for the prediction of magnetic coupling in organic and inorganic molecules.[72] The PBE functional also gives reasonable results for the binding energy (1.9–2.8 kcal/mol), and the predicted vibrational frequency (4−6 cm^{-1}) is comparable in accuracy to that predicted by M06-HF, whereas the results obtained with HF, LDA, $X\alpha$, BLYP, and B3LYP are less satisfactory. (In comparison, for adsorption of CO on transition metal surfaces, a very recent study by Stroppa and Kresse[73] found that BLYP and B3LYP yield more accurate adsorption energies than PBE.) We conclude that PBE, M06-2X, and M06-HF methods are good candidates for further studies of CO adsorption on main-group metal oxides. If the ultimate goal is to study catalysis, the M06-2X and M06-HF methods are more satisfactory because these functionals have been found to give much more accurate predictions for barrier heights, molecular bond energies for main-group molecules, proton affinities, noncovalent interactions, and electronically excited states than does the PBE functional (see Table 18 of Ref. 56). The present results demonstrate the predictive capability of these new exchange-correlation functionals for main-group

surface science and also illustrate some residual difficulties and uncertainties that need to be overcome in future developments.

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