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Adsorption of a water molecule on the MgO(100) surface as described by cluster and slab models

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The interaction of a water molecule with the (100) surface of MgO as described by cluster models is studied using MP2, coupled MP2 (MP2C) and symmetry–adapted perturbation theory (SAPT) methods. In addition, diffusion Monte Carlo (DMC) results are presented for several slab models as well as for the smallest, 2X2 cluster model. For the 2X2 model it is found that the MP2C, DMC, and CCSD(T) methods give nearly the same potential energy curve for the water–cluster interaction, whereas the potential energy curve from the SAPT calculations differs slightly from those of the other methods. The interaction of the water molecule with the cluster models of the MgO(100) surface is weakened upon expanding the number of layers from one to two and also upon expanding the description of the layers from 2X2 to 4X4 to 6X6. The SAPT calculations reveal that both these expansions of the cluster model are accompanied by reductions in the magnitudes of the induction and dispersion constributions. The best estimate of the energy for binding an isolated water molecule to the surface obtained from the cluster model calculations is in good agreement with that obtained from the DMC calculations using a 2–layer slab model with periodic boundary conditions.

1 Introduction

The adsorption of atoms and molecules on surfaces is of fundamental importance in a wide range of processes. MgO is an important component of the Earth's subsurface and is used as a constituent in some superconductors and glasses as well as a catalyst. The nature of water adsorption on the MgO(100) surface has attracted considerable attention, being the subject of several experimental and theoretical studies.^{1–9} It appears that even at low coverages, molecularly adsorbed water is H–bonded to surface OH groups resulting from water dissociation and, as a result, an experimental value for the interaction energy of an isolated water molecule with the surface is not available. On the computational side, the water/MgO system has been investigated using semi–empirical methods,⁸ density functional theory (DFT),¹ and a mixed Hartree-Fock/coupled–cluster procedure combined with an

embedded cluster model.⁴ There has also been a study of the quantum nuclear effects on the adsorption energy.²

In the present work, we calculate the interaction energy between a water monomer and various cluster models of the MgO(100) surface. The methods used include density-fitted Møller-Plesset second-order perturbation theory (DF-MP2),^{10,11} density-fitted coupled MP2 (DF-MP2C),^{12,13} and explicitly (DF-MP2-F12),¹⁴ DF-MP2 DF-MP2C correlated (DF-MP2C-F12), and CCSD(T) (CCSD(T)-F12).14,15 In addition, calculations using the wavefunction-based^{16,17} and density-fitted density functional theory-based¹⁸ symmetryadapted perturbation theory (SAPT) are carried out. These are referred to as WF-SAPT and DFT-SAPT, respectively. The SAPT calculations are particularly useful for elucidating the factors at play in the adsorption of the water monomer as they provide physical dissections of the net interaction into electrostatics, exchange-repulsion, induction, and dispersion contributions. This information should prove especially valuable in designing force fields for simulating water on the MgO(100) surface. Due to the computational cost, the coupled cluster and WF-SAPT methods were applied only to the smallest cluster model.

In addition to the methods discussed above, the interaction energy between water and the MgO(100) surface was calculated using the diffusion Monte Carlo (DMC) method together with slab models and periodic boundary conditions. For comparative purposes the DMC method was also applied to a water monomer interacting with the smallest cluster model of the surface.

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2 Computational details

The MgO cluster models considered are single–layer 2X2, 4X4, and 6X6, and double–layer 4X4 (the *n*X*n* nomenclature indicates that the cluster contains *n* rows of *n* atoms in the layer). The lattice constant used in the geometries of the (MgO)_n clusters were taken from a slab–model optimized with DFT-PBE using the VASP code.¹⁹ The single–layer cluster models of the bare surface have D_{2h} symmetry and the doublelayer cluster model have D_{2d} symmetry. All nearest neighbor MgO bond lengths are 2.115 Å. With one exception, described below, the geometry of the water monomer (OH bond lengths of 0.989 Å and HOH bond angle of 103.2°) as well its orientation with respect to the surface were taken from a DFT-PBE optimized geometry, without allowing the Mg and O atoms of the slab model to move (see Fig. 1).

Due to the computational cost, WF-SAPT calculations were carried out only for the 2X2 cluster model, and the main approach for analyzing the interaction energies for the sequence of cluster models is the DFT-SAPT method. This method and the closely related SAPT(DFT) method of Szalewicz and co-workers²⁰ determine the electrostatic and exchange-repulsion contributions to the interaction energy from integrals over the Coulomb operator evaluated using Kohn-Sham orbitals. Thus these approaches are free of the problems inherent in evaluating exchange-repulsion using common density functional methods. The induction and dispersion contributions were calculated using response functions from time-dependent DFT. The DFT-SAPT calculations made use of the LPBE0AC functional,¹⁸ which replaces the 25% Hartree-Fock exchange of the PBE0 functional²¹ with the 25% localized Hartree–Fock exchange of Sala and Görling²² and includes an asymptotic correction.²³ The correction scheme requires ionization potentials of the fragments. For water the experimental IP reported in the NIST Chemistry Web Book²⁴ was used, and for the $(MgO)_n$ clusters, Koopmans' theorem IPs from Hartree-Fock calculations with the same basis set as employed in the DFT-SAPT calculations were used.

For the single–layer 2X2 and 4X4 cluster models, the DFT–SAPT calculations were performed using the aug–cc–pVQZ



Fig. 1 Geometry used in the current study, illustrated in the case of a water molecule on a single-layer 6X6 (MgO)₁₈ cluster. The Xs denote surface atoms employing the aug-cc-pVQZ basis set in the larger cluster models.

basis set²⁵ on all atoms. For the larger clusters, a mixed aug-cc-pVQZ/aug-cc-pVDZ²⁶ basis set was used. This was generated by employing the aug-cc-pVQZ basis set for the water molecule and the two closest magnesium and two closest oxygen atoms in the top layer (the atoms marked by Xs in Fig. 1), with the aug-cc-pVDZ basis set being used for the remaining atoms. For the monomer SCF calculations and for the evaluation of the first-order electrostatics $(E_{Flst}^{(1)})$ and exhange $(E_{Exch}^{(1)})$ interactions, and the second-order induction $(E_{Ind}^{(2)})$ and exchange-induction $(E_{Exch-Ind}^{(2)})$ terms the cc-pVQZ JK-fitting set of Weigend²⁷ was used for the oxygen and hydrogen atoms, and the MP2-fitting set of Weigend and co-workers²⁸ was used for the magnesium atoms. For the second-order dispersion and exchange-dispersion terms, the aug-cc-pVQZ MP2-fitting set of Weigend and co-workers²⁸ was used for all atoms. In the case of the mixed basis set calculations double-zeta versions of the fitting sets were used on the atoms employing the aug-cc-pVDZ basis sets.

The DF-MP2 and DF-MP2C calculations were carried out using the same basis sets and auxiliary fitting sets as used in the DFT-SAPT calculations. These two approaches and the CCSD(T) method were also used in combination with F12a corrections.²⁹ The F12a calculations used the cc-pVQZ-F12 (VQZ-F12) basis sets of Peterson and co-workers³⁰ for the single-layer 2X2 and 4X4 cluster models and a combination of the cc-pVDZ-F12 (VDZ-F12) and VOZ-F12 basis sets for the larger clusters following the same strategy described above for the DFT-SAPT calculations. For the oxygen and hydrogen atoms, the auxiliary basis sets implemented in MOLPRO2010.1 were used.²⁷ For the magnesium atoms, the cc-pVDZ and cc-pVQZ MP2-fitting sets of Weigend and co-workers were used as the auxiliary basis sets for the calculations using the VDZ-F12 and VOZ-F12 basis sets, respectively. The various MP2 and CCSD(T) calculations were carried out with the non-valence core orbitals frozen. All calculations other than the quantum Monte Carlo calculations were performed with the MOLPRO2010.1 package.³¹

In reporting the results of the SAPT calculations the dispersion and exchange–dispersion contributions were combined as were the induction, exchange–induction and δ (HF) contributions.¹⁸ In the SAPT procedure the induction and exchange–induction contributions are calculated to second–order in the intermolecular interaction. The higher order induction and exchange–induction interactions are accounted for by the so–called δ (HF) term.¹⁸

The quantum Monte Carlo calculations were performed with the CASINO code,³² using the diffusion Monte Carlo (DMC) method, together with trial wavefunctions that enforce fixed nodal surfaces.³³ The trial wavefunctions employed were of the Slater–Jastrow type:

$$\Psi_T(\mathbf{R}) = D^{\uparrow} D^{\downarrow} e^J, \qquad (1)$$

where D^{\uparrow} and D^{\downarrow} are Slater determinants of up- and down-spin single-electron orbitals, and e' is a Jastrow factor, which is the exponential of a sum of one-body (electron-nucleus), two-body (electron-electron), and three body (electron-electronnucleus) terms, that are parametrized functions of electronnucleus, electron-electron and electron-nucleus separations, and were designed to satisfy the cusp conditions. The parameters in the Jastrow factor are varied to minimize the variance of the local energy.^{34,35} Imaginary time evolution of the Schrödinger equation has been performed with the usual short time approximation with a time step of 0.005 a.u. and the locality approximation.³⁶ Dirac-Fock pseudo-potentials (PP) of Trail and Needs were used for O and H,³⁷ and a density functional theory (DFT) PP generated with the local density approximation (LDA) was employed for Mg.³⁸ The O and Mg PPs replace the 1s² cores. The single particle orbitals were obtained from DFT plane-wave (PW) calculations using the LDA and a PW cutoff of 300 Ry (4082 eV), and re-expanded in terms of B-splines,³⁹ using the natural B-spline grid spacing given by $a = \pi/G_{\text{max}}$, where G_{max} is the length of the largest vector employed in the PW calculations. The plane-wave calculations were performed using the PWscf package.40

For the slab model LDA and DMC calculations, periodicity was used only in the two directions parallel to the MgO surface. For these calculations long-range electrostatics were treated using the Ewald method.⁴¹ The MgO distances in the slab models were taken from an optimization of bulk MgO carried out using DFT calculations with the PBE functional.⁴² The geometry of the water on the MgO slab also obtained from a PBE–DFT optimization in which only the water degrees of freedom are allowed to relax. The other geometries on the binding energy curve were obtained by rigidly displacing the water molecule. Computed in this way, the binding energy curve does not account for contributions due to relaxation of the slab which are expected to be quite small.

The slab model calculations employed a supercell with two 4X4 MgO layers. Exploratory calculations with larger slab models showed that the 2–layer 4X4 model was adequate for achieving nearly converged results of the water–surface interaction energies.

3 Results

2X2 cluster model calculations were carried out for all theoretical methods described above, while for the larger clusters, calculations were performed only for the DFT–SAPT, MP2–F12, and MP2C–F12 methods. Potential energy curves for approach of a water molecule to the (100) MgO surface were calculated for each of the cluster models of the surface.

3.1 2X2 cluster model

The calculated potential energy curves for water adsorption on the 2X2 cluster model are shown in Fig. 2(a). The DMC results are not included in this figure, but will be considered below. Of the methods reported, the CCSD(T)–F12 method is expected to most accurately describe the interaction potential and will be used as the reference for assessing the performance of the other theoretical methods. At this level of theory, the potential energy minimum has the water O atom located 2.14 Å from the closest Mg atom of the surface, with the binding energy being -25.0 kcal mol⁻¹. For the MP2 and MP2C methods, the potential energy curves calculated using the aug-cc-pVQZ basis set are as much as 1 kcal mol⁻¹ above the corresponding curves obtained with the VQZ–F12 method, and, for this reason, we focus on the VQZ–F12 results in the following discussion.



Fig. 2 Potential energy curves for approach of a water molecule to the MgO surface as described by the 2*X*2 cluster model. (a) O_w -Mg distances from 1.9 to 6.5 Å; (b) expanded scale results for distances of 1.9 to 2.6 Å.

The potential energy curve from the MP2C-F12 calculations is very close to that obtained from the CCSD(T)-F12 calculations over the range of distances considered (1.98-6.50 Å). Here and elsewhere in this study distances are measured between the O atom of water and the closest Mg atom of the surface. However, at short distances the MP2-F12 potential lies as much as 2 kcal mol^{-1} above the CCSD(T)-F12 potential. Thus the MP2C-F12 procedure is more reliable than the MP2-F12 procedure for describing the interaction of the water molecule with the surface. For $R \ge 2.3$ Å the DFT-SAPT potential energy curve is very close to the MP2/aug-cc-pVOZ potential, but at shorter distances the DFT-SAPT potential energy curve is more attractive and has a different shape from the MP2C-F12 and CCSD(T)-F12 potentials. This problem is exacerbated in the WF-SAPT approach for which the potential is about 5 kcal mol⁻¹ too attractive at R = 2 Å. This is a consequence of the strong overlap of the electron distributions of H_2O and $(MgO)_2$ near the potential energy minimum which leads to a breakdown in the perturbative expansion in the WF-SAPT procedure. In the case of the DFT-SAPT method, it is not clear whether the error in the interaction energy at short distance reflects a problem with the procedure used to calculate the induction and dispersion contributions or whether it reflects an inadequacy of using DFT orbitals to calculate the electrostatic and exchange interactions.

The individual components of the DFT-SAPT interaction energies for the single–layer $2X^2$ model are reported in Fig. 3. Near the minimum energy structure the exchange–repulsion and the electrostatic interaction contributions are about 85 and -73 kcal mol⁻¹, respectively. As a result, the electrostatics plus exchange–repulsion contribution is repulsive and the induction (-22 kcal mol⁻¹) and dispersion (-14 kcal mol⁻¹) contributions are crucial for the binding of the water molecule to the cluster.

In Fig. 4 we compare the CCSD(T)-F12, MP2C-F12, DFT-SAPT, and DMC potential energy curves of a water monomer interacting with the single-layer 2X2 model of the MgO surface. (These calculations were carried out with a slightly different geometry of the water monomer than used in the rest of this study.) Interestingly the MP2C-F12, CCSD(T)-F12, and DMC potentials are nearly identical whereas the DFT-SAPT potential differs noticeably from the others even when calculated using the aug-cc-pV5Z basis set.²⁵ Specifically, the DFT-SAPT potential lies appreciably above other potentials for distances about 2–2.5 Å, but drops below the other potentials for $R \leq 1.8$ Å. CCSD(T)–F12 calculations were also carried out accounting for correlation of the 2s and 2p orbitals of the Mg atoms (not shown in the figure). Near the minimum of the potential energy curve inclusion of correlation effects involving the Mg 2s and 2p orbitals results in a 0.7 kcal mol⁻¹ increase in the magnitude of the interaction energy.

3.2 4X4 cluster models

The MP2–F12, MP2C–F12, and DFT–SAPT potential energy curves for a water molecule interacting with the 4X4 cluster model of the surface are shown in Fig. 5. For each method the binding energy at the potential energy minimum is about half that obtained for the 2X2 model. At the potential energy minimum the binding energy obtained with the DFT–SAPT and MP2–F12 methods are about 1.5 and 0.5 kcal mol⁻¹ smaller in magnitude, respectively, than obtained in the MP2C–F12 calculations. The weaker binding with the DFT–SAPT than with the MP2–F12 method is primarily a reflection of the limitation of the aug-cc-pVQZ basis set used for the DFT–SAPT calculations. The individual contributions



Fig. 3 Components of the interaction energy from DFT-SAPT calculations for approach of a water molecule to the MgO surface described by the 2*X*2 cluster model.



Fig. 4 Potential energy curves of a water molecule to the MgO surface described by the 2X2 cluster model. These potentials were generated using a slightly different water structure than we used in the other calculations reported in this study.



Fig. 5 Potential energy curves for approach of a water molecule to the MgO surface described by the single-layer 4*X*4 cluster model.

to the interaction energy determined from the DFT-SAPT calculations are tabulated in Table 1. At R = 2.14 Å, which corresponds to the equilibrium separation of the H₂O–(MgO)₂ system, both the electrostatics and exchange–repulsion of H₂O–(MgO)₈ are reduced in magnitude compared to the H₂O–(MgO)₂ system, with the net electrostatics plus exchange–repulsion contributions being 6 kcal mol⁻¹ more positive for the 4*X*4 case. As a result, at the equilibrium structure the water molecule is displaced further from the 'surface' in the 4*X*4 than

Table 1 DFT-SAPT interaction energies (kcal mol^{-1}) for water-MgO (single-layer 4X4)

Total	Ind	Disp	Exch-Rep	Elst	R (Angs)
-5.2	-20.4	-17.8	108.1	-75.6	1.98
-9.8	-13.5	-14.2	70.6	-52.7	2.14
-10.9	-8.9	-11.3	46.1	-36.7	2.31
-10.4	-5.8	-9.0	30.0	-25.5	2.47
-9.4	-3.8	-7.2	19.4	-17.8	2.63
-7.0	-1.7	-4.6	8.1	-8.9	2.97
-4.0	-0.5	-2.2	1.9	-3.2	3.49
-2.0	-0.2	-1.2	0.5	-1.7	3.97
-1.0	-0.1	-0.6	0.1	-1.0	4.49
-0.8	0.0	-0.2	0.0	-0.6	5.49
-0.3	0.0	-0.1	0.0	-0.4	6.49
	$ \begin{array}{r} -8.9 \\ -5.8 \\ -3.8 \\ -1.7 \\ -0.5 \\ -0.2 \\ -0.1 \\ 0.0 \\ 0.0 \\ \end{array} $	$-11.3 \\ -9.0 \\ -7.2 \\ -4.6 \\ -2.2 \\ -1.2 \\ -0.6 \\ -0.2 \\ -0.1$	46.1 30.0 19.4 8.1 1.9 0.5 0.1 0.0 0.0	$-36.7 \\ -25.5 \\ -17.8 \\ -8.9 \\ -3.2 \\ -1.7 \\ -1.0 \\ -0.6 \\ -0.4$	2.31 2.47 2.63 2.97 3.49 3.97 4.49 5.49 6.49

2X2 cluster model (2.31 vs. 2.14 Å) which further weakens the interaction, primarily due to a reduction in the magnitude of the induction and dispersion interactions, with the change in the induction energy being more important. It should be noted that the breakdown in the DFT–SAPT procedure found for the 2X2 model is not seen for the 4X4 model, presumably due to the reduction of the magnitude of the electrostatics and exchange interactions in the larger cluster model.

Fig. 6 and Table 2 report the interaction energies of a water monomer with the double–layer 4X4 cluster model. Compared to the single–layer 4X4 model, the net interaction energy at the potential minimum is about 1 kcal mol⁻¹ smaller in magnitude in the two–layer model, but the equilibrium distance remains nearly the same. In going from the single–layer to the double– layer 4X4 model, the electrostatic and exchange–repulsion interactions of the water molecule with the surface change by 1.7 and -1.7 kcal mol⁻¹ respectively at the equilibrium distance of 2.31 Å. Hence there is no net change in the electrostatics plus exchange–repulsion. On the other hand, the induction and dispersion contributions change by 0.8 and 0.2 kcal mol⁻¹, leading to about a 10% weaker interaction in the double–layer model.

3.3 6X6 cluster model

The DFT-SAPT, MP2-F12 and MP2C-F12 interaction potentials for a water molecule interacting with the 6X6 cluster model of the surface are reported in Fig. 7, and the decomposition of the DFT-SAPT interaction energies is reported in Table 3. The distance of the minimum of the resulting potential energy curves is close to those obtained with the one- and two-layer 4X4 cluster models. The MP2C-F12 binding energies of a water molecule interacting with the MgO(100) surface as described by the various cluster models are reported in Table 4. Examination of the DFT-SAPT results reveals that in going from the single-layer 4X4 to single–layer 6X6 model the electrostatic plus exchange contribution to the interaction energy changes by only -0.3 kcal mol⁻¹, whereas the induction plus dispersion contribution decreases by 1.0 kcal mol⁻¹ in magnitude. Table 4 also includes MP2C-F12 results for the double-layer and triple-layer 2X2 models of the surface. From these results it is seen that adsorption energy is essentially converged at two layers. The convergence of the



Fig. 6 Potential energy curves for approach of a water molecule to the MgO surface described by the double-layer 4X4 cluster model.

Table 2 DFT-SAPT interaction energies (kcal mol⁻¹) for water-MgO (double-layer 4X4)

R (Angs)	Elst	Exch-Rep	Disp	Ind	Total
1.98	-73.3	105.6	-17.0	-19.0	-3.7
2.14	-50.8	68.6	-13.6	-12.5	-8.3
2.31	-35.0	44.4	-10.9	-8.1	-9.6
2.47	-24.0	28.7	-8.7	-5.3	-9.3
2.63	-16.5	18.5	-6.9	-3.4	-8.4
2.97	-7.9	7.6	-4.4	-1.5	-6.3
3.49	-2.5	1.7	-2.1	-0.4	-3.4
3.97	-1.2	0.5	-1.2	-0.2	-2.1
4.49	-0.6	0.1	-0.6	-0.1	-1.2
5.49	-0.3	0.0	-0.2	0.0	-0.5
6.49	-0.2	0.0	-0.1	0.0	-0.3



Fig. 7 Potential energy curves for approach of a water molecule to the MgO surface described by the single-layer 6*X*6 cluster model.

Table 3 DFT-SAPT interaction energies (kcal mol⁻¹) for water-MgO (single-layer 6X6)

R (Angs)	Elst	Exch-Rep	Disp	Ind	Total
1.98	-75.3	107.0	-16.3	-19.9	-4.4
2.14	-52.3	69.8	-13.1	-13.2	-8.9
2.25	-40.4	51.6	-11.2	-9.9	-9.9
2.28	-38.6	49.0	-10.9	-9.4	-10.0
2.31	-36.2	45.3	-10.5	-8.7	-10.0
2.47	-25.0	29.4	-8.4	-5.7	-9.7
2.63	-17.3	19.0	-6.7	-3.7	-8.7
2.97	-8.4	7.9	-4.3	-1.6	-6.4
3.49	-2.8	1.8	-2.1	-0.4	-3.5
3.97	-1.3	0.5	-1.2	-0.2	-2.2
4.49	-0.7	0.1	-0.6	-0.1	-1.3
5.49	-0.4	0.0	-0.2	0.0	-0.7
6.49	-0.3	0.0	-0.1	0.0	-0.4

adsorption energy along the 2X2, 4X4, and 6X6 sequence of single–layer cluster models is shown in Fig. 8. Combining the results (at the minima of the potential energy scans) of the single–layer, and double–layer 4X4 models and the single–layer 6X6 model, we estimate the binding energy of a water molecule for a double–layer 6X6 cluster model to be about -10.6 kcal mol⁻¹, which is in reasonable agreement with the -11.1 kcal mol⁻¹ DMC result for a water molecule interacting with a 2–layer model of the MgO(100) surface. A comparison of the potential energy curves estimated for the double–layer 6X6 model using MP2C–F12 energies and from the DMC calculations for the 2–layer slab with periodic boundary

Geometry	E _{MP2C-F12}
2X2 1-Layer (VQZ-F12)	-25.1
2X2 2-Layer (VQZ-F12)	-24.7
2X2 3-Layer (VQZ-F12)	-24.5
4X4 1-Layer (VQZ-F12)	-12.5
4X4 2-Layer (VQZ-F12/VDZ-F12)	-11.1
6X6 1-Layer (VQZ-F12/VDZ-F12)	-11.8
6X6 2-Layer (VQZ-F12)	$(-10.6)^{b}$
DMC 2-Layer slab model	-11.1

^a For a water O–Mg separation of 2.31 Å, which is close to the minima of the scanned potentials for the one-layer and two-layer 4X4 models. A water O–Mg separation of 2.14 Å is used for 2X2 cluster models.
^b Estimated as described in the text.



Fig. 8 Change in the binding energy of a water molecule to the MgO(100) surface as described by single-layer cluster models.

conditions is presented in Fig. 9. Overall the agreement between the two potential energy curves is good, with the small discrepency near the potential energy minimum reflecting a limitation of the strategy used to estimate the 2–layer 6X6 cluster model results and not including the core correlation effects for the Mg atoms.

We note that the temperature programmed desorption measurements of ref. 5, which gave a value of 15 kcal mol⁻¹ energy for desorbing from the Mg (100) surface at low coverages, probably detected water molecules that were H–bonded to OH groups on the surface, thereby, enhancing their binding energies.⁹



Fig. 9 Potential energy curves of a water molecule interacting with the MgO(100) surface as described by MP2C-F12 calculations with a double-layer 6*X*6 cluster model (see text) and by DMC calculations with a double-layer slab model.

3.4 GDMA calculations

The electrostatic interaction energy from the DFT-SAPT calculations includes the effects of charge-penetration. In order to estimate the charge-penetration contribution to the electrostatic energy, we calculated atomic charges, dipoles, and quadrupoles using Stone's generalized distributed moment analysis (GDMA)⁴³ of the MP2/cc-pVDZ²⁶ densities for the (MgO), cluster models. (The MP2 calculations were performed using Gaussian 03.44) The resulting moments are summarized in Table 5. This analysis shows that the charge on the interior Mg and O atoms is relatively independent of the cluster model. The magnitude of the dipole moment on the central atoms decreases along the sequence of single-layer models and it becomes zero for the single-layer 6X6 cluster model. The corresponding dipoles on the central O atoms in the 4X4 double layer model are 0.26 au. (The absolute values of the dipoles are reported.) The changes in the quadrupole moments with cluster model are more striking. For example, for the central Mg atoms, the value of the Q_{20} component of the quadrupole is -0.39, -0.07, -0.02, and -0.05 au for the single-layer 2X2, single-layer 4X4, double-layer 4X4, and single-layer 6X6 cluster models, respectively. The corresponding results for the central O atoms are -0.89, -1.48, -0.74, and -1.40 au. Using the moments from the GDMA analyses of H_2O and the $(MgO)_n$ cluster models we calculated the electrostatic interaction energies, with the results being tabulated in Table 6. The resulting interaction energies are 32.3, 22.1, 22.3 and 22.5 kcal mol^{-1} smaller in magnitude than the DFT-SAPT electrostatic interaction energies for the single-layer 2X2, single-layer 4X4, double-layer 4X4, and single-layer 6X6 cluster models, respectively. These differences can be taken as estimates of the charge-penetration contributions to the electrostatic interaction energies. The greater charge-penetration contribution in the 2X2 model arises in part from the shorter separation of the water molecule from the surface in this case. Calculations using a 2X2 cluster model with GDMA moments from the interior 2X2 sub-cluster in the 4X4 cluster model actually gives even stronger binding of the water molecule to the cluster than obtained with the original 2X2 model. Thus the main factor causing the weakening of the electrostatic interaction between the water molecule and the surface as one goes from the 2X2 to the 4X4 cluster model is the unfavorable electrostatic interaction with the non-central Mg and O atoms rather than changes of the charge distribution of the atoms in the central 2X2 region caused by the presence of surrounding ions.

4 Conclusions

In this study, we have used the MP2, MP2C, and DFT–SAPT methods to calculate the interaction energy of a water molecule with a sequence of cluster models of the MgO(100) surface as well as DMC calculations of a water monomer interacting with a 2–layer model of the surface. Our calculations show that even a basis set as large as aug-cc-pVQZ does not give well converged interaction energies of a water molecule with cluster models of the surface, and the F12 approach was adopted to circumvent this problem. Based on the comparison

 Table 5
 Multipole moments (in atomic units) for the magnesium and oxygen atoms in the cluster models^a

Atom	q				$ \mu $			$ Q_2 $				
Туре	2X2 1L	4X4 1L	4X4 2L	6X6 1L	2X2 1L	4X4 1L	4X4 2L	6X6 1L	2X2 1L	4X4 1L	4X4 2L	6X6 1L
Mgl	0.99	0.98	0.97	1.03	0.32	0.05	0.06	0.00	0.59	0.09	0.04	0.05
01	-0.99	-1.07	-1.03	-1.04	0.05	0.03	0.26	0.00	0.95	1.48	0.75	1.40
Mg2		1.02	1.03	1.00		0.17	0.11	0.07		0.32	0.20	0.10
02		-1.04	-1.04	-1.04		0.29	0.39	0.04		1.19	0.74	1.38
Mg3		1.13	1.11	0.98		0.31	0.27	0.05		0.68	0.62	0.05
O3		-1.01	-1.03	-1.07		0.14	0.38	0.02		0.93	0.01	1.50
Mg4				1.09				0.09				0.19
O4				-1.05				0.26				1.26
Mg5				1.15				0.33				0.68
05				-1.02				0.16				0.91
^a The atom numbering scheme is defined in Fig. 1.												

Table 6 Electrostatic interaction energies (kcal mol^{-1}) between a water molecule and cluster models of the MgO(100) surface at the minimum energy structures of the potential scans

Cluster size	SAPT-Elst	GDMA-Elst	Charge-penetration
2 <i>X</i> 2 1 Layer	-52.6	-20.4	-32.3
4 <i>X</i> 4 1 Layer	-36.7	-14.6	-22.1
4 <i>X</i> 4 2 Layers	-35.0	-12.7	-22.3
6 <i>X</i> 6 1 Layer	-36.2	-13.7	-22.5

with the results of CCSD(T)-F12 and DMC calculations using the small 2X2 cluster model, it is concluded that the MP2C-F12 approach accurately describes the interaction of a water molecule with the cluster models of the surface. Compared to MP2C-F12, the MP2-F12 method underbinds by about 1 kcal mol⁻¹ and the DFT-SAPT method underbinds by about 2.5 kcal mol^{-1} with about half the error in this latter case being due to limitations in the basis set employed. Going from a single–layer 4X4 model to a double–layer 4X4model, leads to about a 10% reduction of the magnitude of the binding energy. This can be understood in terms of the unfavorable electrostatic interaction of the water molecule with the second layer Mg and O atoms. Our best estimate of binding energy of a water molecule to the MgO(100) surface obtained from the cluster model calculations is -10.6 kcal mol⁻¹ which is in good agreement with the DMC slab model result of -11.1 kcal mol⁻¹. At the equilibrium structure of a water molecule on the (100) MgO surface charge-penetration contributes about -22 kcal mol⁻¹ to the interaction energy. As a result, the development of an accurate force field for describing the adsorption of a water on metal oxide surfaces will require inclusion of explicit charge-penetration terms.

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