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Comparing van der Waals DFT methods for water on NaCl(001) and MgO(001)

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In this work, a range of van der Waals type density functionals are applied to the H₂O/NaCl(001) and H₂O/MgO(001) interface systems to explore the effect of an explicit dispersion treatment. The functionals we use are the self-consistent vdW functionals vdW-DF, vdW-DF2, optPBE-vdW, optB88-vdW, optB86b-vdW, and vdW-DF-cx, as well as the dispersion-corrected PBE-TS and PBE-D2 methods; they are all compared with the standard PBE functional. For both NaCl(001) and MgO(001), we find that the dispersion-flavoured functionals stabilize the water-surface interface by approximately 20%-40% compared to the PBE results. For NaCl(001), where the water molecules remain intact for all overlayers, the dominant contribution to the adsorption energy from “density functional theory dispersion” stems from the water-surface interactions rather than the water-water interactions. The optPBE-vdW and vdW-DF-cx functionals yield adsorption energies in good agreement with available experimental values for both NaCl and MgO. To probe the strengths of the perturbations of the adsorbed water molecules, we also calculated water dipole moments and found an increase up to 85% for water at the MgO(001) surface and 70% at the NaCl(001) surface, compared to the gas-phase dipole moment. *Published by AIP Publishing.* [<http://dx.doi.org/10.1063/1.4971790>]

I. INTRODUCTION

The crucial role of water in mineralogy, atmospheric chemistry, biology, electrochemistry, and material chemistry is to a large extent governed by water/solid interface interactions. Many metal oxide surfaces are hydroxylated under normal conditions. The degree and nature of the hydroxylation, i.e., the presence of the surface water or OH groups, influence the surface's stability, its reactivity, and its interactions with other molecules. Given the complexity of such interfaces, theoretical calculations can be of immense help in discovering valuable structural detail, disentangling the water-water and water-surface contributions to the interface stability, and providing insight about the nature of the interactions. Simultaneously such systems, involving both ionic solid-state components and hydrogen-bonded molecular components, as they do, place high demands on the capability of the theoretical model chosen.

It has been shown in the literature that the adsorption of non-polar, or weakly polar, molecules on ionic surfaces requires a treatment beyond standard density functional theory.¹ Thus in Ref. 1, for example, the incorporation of dispersion interactions (of the Grimme D3 type) for CO on MgO(001) and C₂H₂ on NaCl(001) led to significantly improved agreement with experimental results.¹ The interaction between water and an ionic surface, on the other hand, is mainly electrostatic in nature, and here the effect of dispersion interactions is less obvious. Nevertheless, studies in the literature suggest that dispersion interactions play more than a minor

role for the interfacial structure and energetics of such systems. For example, the adsorption energy for the water monolayer on NaCl(001) was calculated at the DFT-GGA level by Park *et al.*² and later by others,^{3–5} and was found to be considerably smaller than the experimental value.^{6,7} Similarly, for a water monolayer on MgO(001), the adsorption energies reported in previous DFT calculations (see, for example, Refs. 8–11) are much smaller than the experimental values.¹² With the aid of standard GGA-based *ab initio* MD simulations, it was found that a more accurate description of the adsorption energy is required to predict the frequency prefactors for the thermal desorption of water on MgO(001) in agreement with TPD experiment.¹³

Li *et al.*¹⁴ studied the adsorption of a water monomer on NaCl(001) with high-level quantum-chemistry calculations (at the coupled-cluster CCSD(T)/cc-pCVTZ level) and revealed that the GGA value is much smaller than the CCSD(T) value. When dispersion interactions were included in the GGA treatment of the water monomer on NaCl(001) (using their optB88-vdW functional),¹⁵ an encouraging agreement with the CCSD(T) value was achieved.

Apart from these studies, we are not aware of any systematic exploration of the performance of van der Waals (vdW) type density functionals for interfaces between water and ionic surfaces in the literature although these systems are of high fundamental and applied interest. In the present study we report such an effort, using eight DFT-based dispersion methods for two prototypic water/ionic surface interfaces, namely, H₂O/NaCl(001) and H₂O/MgO(001), at a range of coverages, and we will show that the vdW DFT methods typically increase the adsorption energies by 20%-40% compared to the PBE values.

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Recent advances in the DFT community have resulted in a range of methods which incorporate dispersion interactions beyond the DFT-GGA level. One strategy consists of treating the dispersion term as part of the exchange-correlation energy and searching for an appropriate exchange functional to be paired with the correlation,^{15–19} and here we explore six such vdW functionals (sometimes collectively referred to as “self-consistent vdW functionals” in the following). They are the original *vdW-DF* functional [Dion *et al.*],¹⁶ *vdW-DF2* [Lee *et al.*],¹⁷ *optPBE-vdW*, *optB88-vdW*, *optB86b-vdW* [Klimeš *et al.*],^{15,18} and the *vdW-DF-cx* functional [Berland and Hyldgaard].¹⁹ Other strategies add a post correction dispersion term (a C_6 correction) to the total DFT energy,^{20–22} and we explore two such “*a posteriori methods*,” namely, the dispersion-corrected *PBE-TS* [Tkatchenko and Scheffler]²² and *PBE-D2* [Grimme]²⁰ methods. A comprehensive overview of many DFT-vdW methods has been presented by Klimeš and Michaelides,²³ who introduced the term “stairway to heaven” based on the level of approximation set to account for dispersion interactions. In this work, we climb this ladder and test the applicability of the different dispersion treatments to the description of the $\text{H}_2\text{O}/\text{NaCl}(001)$ and $\text{H}_2\text{O}/\text{MgO}(001)$ water interface systems.

Section II of this paper presents the computational methods and the interface systems. Section III is a Results section and focuses on the water/NaCl systems, starting with a brief review of the most relevant experimental and theoretical studies in the literature, followed by the analysis of our own results using the eight dispersion-corrected functionals. Section IV is arranged in a similar way, but for the water/MgO systems. In both cases, we also make use of the calculations to help disentangle the water-water and water-surface contributions to the interface stability. Also in Section V, we make use of calculations to extract information that is difficult to derive

from experiment, namely, the induced dipole moment of each adsorbed water molecule; this polarisation probes the perturbation generated by the molecule’s surroundings at the interface. Section VI gives a brief overview of how the eight functionals listed above (and PBE) perform for the clean systems, and finally, in Section VII, we summarise our conclusions and loosely rank the performance of the functionals for our water/surface interface systems.

II. COMPUTATIONAL DETAILS

A. System

The $\text{H}_2\text{O}/\text{NaCl}(001)$ and $\text{H}_2\text{O}/\text{MgO}(001)$ interfaces, and the corresponding bare (001) surfaces, were modelled as slabs, using the 3D periodicity inherent in the Vienna Ab Initio Simulation Package (VASP).^{24–28} The experimental lattice constants (5.640 Å for NaCl²⁹ and 4.212 Å for MgO³⁰) were used to build the slabs. In all cases, the supercell contained 4 substrate layers and a 15 Å vacuum gap perpendicular to the surface normal.

Different water coverages were explored. For NaCl(001), the tested interface systems were an “isolated” adsorbed water molecule in a $p(2\sqrt{2} \times 2\sqrt{2})$ surface cell, an “isolated” water dimer in a $p(2\sqrt{2} \times 2\sqrt{2})$ surface cell, and three overlayer structures from the literature, namely, the 1.0 ML $p(1 \times 1)$ overlayer, the 1.5 ML $c(4 \times 2)$, and the 2.0 ML $p(1 \times 1)$ structure, all shown in Fig. 1. Here monolayer (1.0 ML) coverage means that there is one adsorbed water molecule (intact or dissociated) per surface formula unit.

For MgO(001), calculations were performed for the following systems: the water monomer and dimer in $p(2\sqrt{2} \times 2\sqrt{2})$ supercells and two water overlayer structures that have been amply discussed in the literature, namely, the 1.0 ML $p(3 \times 2)$ structure and the 1.25 ML $c(4 \times 2)$ structure, see Fig. 2.

FIG. 1. Top and side views of the PBE-optimized adsorbed water structures on NaCl(001) studied in this work. A monolayer (ML) is defined as the number of adsorbed water molecules per surface formula unit. There are one, six, and two structurally unique water molecules in the 1, 1.5, and 2 ML supercells; each unique water molecule has been labelled. The optimized structures resulting from the nine functionals used in this study are overall very similar. The sodium ions, chloride ions, water oxygen atoms, and hydrogen atoms are represented by violet, green, red, and white spheres, respectively.

FIG. 2. Top and side views of the PBE-optimized adsorbed water structures on MgO(001) studied in this work. There are three structurally unique water molecules (intact or dissociated) in both the 1 ML and 1.25 ML supercells. The optimized structures resulting from the nine functionals used in this study are overall very similar. The magnesium ions are yellow, surface oxide ions are magenta, water oxygen atoms are red, hydroxide oxygen atoms are orange, and hydrogen atoms are white.

The supercells used for these nine interface systems were chosen as required by the overlayer structures, except that, as mentioned, for the 1.0 ML and 2.0 ML structures of NaCl(001) we used a $p(2\sqrt{2} \times 2\sqrt{2})$ supercell, although a $p(1 \times 1)$ cell would of course have been sufficient. In all interface calculations, the water molecules were adsorbed on one side of the slab. To find the minimum energy structures for the various interface systems, in each case we first performed a search at the PBE level of theory starting from the previously reported structures (see the references in Sec. V) and then used the PBE minimum energy structure as the starting geometry for the optimizations with the other functionals.

Bulk NaCl(s) and MgO(s), the bare (001) surfaces, and isolated gas-phase molecules or clusters were included as reference systems (e.g., in the calculation of the adsorption energy) but also in their own right, as part of our exploration of the performance of the vdW functionals. The cluster optimizations were performed with 3D periodic boundary conditions in a $29 \text{ \AA} \times 30 \text{ \AA} \times 31 \text{ \AA}$ simulation box.

B. Electronic structure calculations

We performed plane-wave 3D periodic DFT calculations with eight vdW functionals as we climb the “stairway to heaven,” namely, vdW-DF,¹⁶ vdW-DF2,¹⁷ optPBE-vdW,¹⁵ optB88-vdW,¹⁵ optB86b-vdW,¹⁸ vdW-DF-cx,¹⁹ and the dispersion-corrected PBE-TS²² and PBE-D2²⁰ functionals; they are all compared with the standard PBE functional.³¹

The valence-core electron interaction was represented by the PAW scheme.^{28,32} For H, O, Na, Mg, and Cl, the $1s^1$, $2s^2 2p^4$, $2p^6 3s^1$, $2p^6 3s^2$, and $3s^2 3p^5$ electrons, respectively, were treated as valence electrons. All calculations were performed with a plane-wave kinetic energy cutoff (E_{cut}) of 400 eV. A $4 \times 4 \times 1$ Monkhorst-Pack k -point mesh was used for

the slab systems and $4 \times 4 \times 4$ for the bulk systems, and only the Γ point for the gas-phase systems. A Gaussian smearing with a broadening of 0.1 eV was applied.

Full geometry optimizations were performed for all systems, except for the interface systems where the atoms residing in the two “bottom” layers of the ionic slabs were kept fixed. The conjugate-gradient algorithm was used for the structure optimizations with a convergence criterion of 10^{-6} eV for the total energy threshold.

Using the optPBE-vdW functional, test calculations for the water monomer adsorption on MgO(001) were performed to find out how sensitive the adsorption energy (E_{ads}) was to the choices of k -point mesh, energy cut-off, and slab-thickness. We found that with our final settings quoted above, E_{ads} converged to within 0.01 eV of those obtained using a $6 \times 6 \times 1$ k -point mesh, $E_{\text{cut}} = 500$ eV, and a six-layered ionic slab.

C. Interface properties: Adsorption energy and its partitioning

The adsorption energy per water molecule adsorbed on the MgO(001) and NaCl(001) surfaces was calculated using the standard expression

$$E_{\text{ads}} = -\{E_{\text{tot}}[(\text{H}_2\text{O})_n/\text{NaCl}(001)] - E_{\text{tot}}[\text{NaCl}(001)] - n \cdot E_{\text{tot}}[\text{H}_2\text{O}(\text{g})]\}/n, \quad (1)$$

where $E_{\text{tot}}[(\text{H}_2\text{O})_n/\text{NaCl}(001)]$ is the total energy of the interface supercell, $E_{\text{tot}}[\text{NaCl}(001)]$ is the total energy of the clean slab supercell, $E[\text{H}_2\text{O}(\text{g})]$ is the total energy of the gas-phase water monomer, and n is the number of water molecules per supercell, be it a water overlayer or a water cluster. All the energies refer to geometry-optimized systems.

For NaCl(100) we find that water adsorbs molecularly using all functionals, and therefore it is also meaningful to

analyze the adsorption energy in terms of its contributions from the adsorbate-substrate and adsorbate-adsorbate interactions, respectively. Following several papers in the literature,^{2–5,33} we define

$$E_{\text{WW}} = -\{E_{\text{tot}}[(\text{H}_2\text{O})_n \text{ at opt. interface geometry}] - n \cdot E_{\text{tot}}[\text{H}_2\text{O}(\text{g})]\} / n, \quad (2)$$

$$E_{\text{SW}} = -\{E_{\text{tot}}[(\text{H}_2\text{O})_n / \text{NaCl}(001)] - E_{\text{tot}}[\text{NaCl}(001)] - E_{\text{tot}}[(\text{H}_2\text{O})_n \text{ at opt. interface geometry}]\}. \quad (3)$$

Here $E_{\text{tot}}[(\text{H}_2\text{O})_n \text{ at opt. interface geometry}]$ is the energy of a (formerly) interface system where the ionic support has been removed and only the water part is left, frozen at the optimized structure of the interface system. All the other terms in expressions (2) and (3) refer to fully optimized systems.

D. Interface properties: Polarization of the water molecules

For three of the functionals (PBE, optPBE-vdW, and PBE-D2) we have also calculated the dipole moment for each intact water molecule. We will use the water dipole moment as a probe of the strength of the perturbation from the surroundings (i.e., from the ionic slab and any other water molecule/OH group) on the targeted water molecule. Thus Wannier orbitals and their centers³⁴ were calculated from the final electronic wave function using the WANNIER90 program,³⁵ and the dipole moment of each water molecule was calculated using the positions of its four Wannier centers and its three atomic nuclei.

E. Properties of the bulk oxides and bare surfaces

The “atoms(g) $\Rightarrow$ crystal” cohesive energies (E_{coh}) of bulk NaCl and MgO were calculated from the standard expressions, i.e., using NaCl as an example,

$$E_{\text{coh}} = -\{E_{\text{tot}}[\text{NaCl}(\text{s})] - E_{\text{tot}}[\text{Na}(\text{g})] - E_{\text{tot}}[\text{Cl}(\text{g})]\}. \quad (4)$$

The $E_{\text{tot}}[\text{Na}(\text{g})]$ and $E_{\text{tot}}[\text{Cl}(\text{g})]$ energies were calculated in $20 \text{ \AA} \times 19 \text{ \AA} \times 18 \text{ \AA}$ simulation boxes.

The surface energy for the clean NaCl(001) surface was calculated from our optimized slab (with the bottom layers fixed) using an expression from Ref. 36, namely,

$$E_{\text{surf}} = -\{2 \cdot E_{\text{tot}}[\text{NaCl}(001)] - E_{\text{tot}}^{\text{unrelaxed}}[\text{NaCl}(001)] - n \cdot E_{\text{bulk}}[\text{NaCl}(\text{s})]\} / 2A, \quad (5)$$

where $E_{\text{tot}}^{\text{unrelaxed}}[\text{NaCl}(001)]$ is the total energy of the NaCl slab supercell kept at the optimized bulk structure, n is the number of NaCl formula units in the slab supercell, E_{bulk} is the total energy per formula unit for the optimized bulk structure, and A is the surface area of the slab supercell.

III. RESULTS—H₂O ON NaCl(001)

A. Adsorption energies from calculations and comparisons to experiments

We start with the *isolated water monomer* on NaCl(001) [Fig. 1(a)] and use the CCSD(T) level calculations of Ref. 14 as

FIG. 3. Calculated (a) adsorption energies (E_{ads}), (b) water-water interactions (E_{ww}), and (c) water-substrate interactions (E_{sw}) for adsorption of the water monomer, dimer, and different water overlayers on NaCl(001) with the nine functionals used in this study. The experimental values are from Refs. 6 and 7 and the CCSD(T) value is from Ref. 13.

a possible reference value for the adsorption energy, 0.517 eV. This is the bottommost horizontal reference line in Fig. 3(a). The CCSD(T) calculation was performed using a cc-pCVTZ basis set and an embedded cluster model. Going from left to right in the figure, we first note that our PBE value, 0.360 eV, clearly underestimates E_{ads} , which agrees with earlier DFT-PW91 studies where E_{ads} values in the range 0.32–0.39 eV

TABLE I. Calculated adsorption energies (E_{ads}) for adsorption of the water monomer, dimer, and different water overlayer structures on NaCl(001). The water-water (E_{ww}) and water-substrate (E_{sw}) interactions are defined in Section II. Unless otherwise mentioned, here and in the following tables, the results are given for the nine functionals used in this study, namely, PBE, six self-consistent vdW functionals, and the two vdW post-correction methods. In this table also the PBE-TS+SCS method, discussed in Section VII, is included. All values are in units of eV.

		Monomer	Dimer	1 ML	1.5 ML	2 ML
PBE	E_{ads}	0.360	0.405	0.395	0.556	0.532
	E_{ww}		0.085	0.094	0.375	0.363
	E_{sw}		0.310	0.300	0.181	0.170
vdW-DF	E_{ads}	0.410	0.443	0.482	0.579	0.545
	E_{ww}		0.065	0.134	0.318	0.312
	E_{sw}		0.377	0.348	0.261	0.232
vdW-DF-cx	E_{ads}	0.430	0.487	0.513	0.652	0.639
	E_{ww}		0.077	0.121	0.373	0.377
	E_{sw}		0.410	0.392	0.279	0.262
vdW-DF2	E_{ads}	0.446	0.485	0.505	0.636	0.614
	E_{ww}		0.083	0.113	0.361	0.369
	E_{sw}		0.403	0.390	0.275	0.244
optPBE-vdW	E_{ads}	0.480	0.522	0.555	0.682	0.664
	E_{ww}		0.085	0.135	0.378	0.390
	E_{sw}		0.437	0.420	0.304	0.274
optB88-vdW	E_{ads}	0.483	0.528	0.550	0.696	0.689
	E_{ww}		0.080	0.103	0.380	0.395
	E_{sw}		0.448	0.448	0.316	0.290
optB86b-vdW	E_{ads}	0.480	0.526	0.549	0.695	0.685
	E_{ww}		0.082	0.114	0.385	0.399
	E_{sw}		0.444	0.434	0.309	0.286
PBE-D2	E_{ads}	0.510	0.547	0.550	0.711	0.702
	E_{ww}		0.095	0.106	0.423	0.447
	E_{sw}		0.452	0.444	0.288	0.255
PBE-TS	E_{ads}	0.565	0.619	0.653	0.788	0.793
	E_{ww}		0.089	0.113	0.403	0.412
	E_{sw}		0.530	0.540	0.385	0.380
PBE-TS+SCS	E_{ads}	0.554	0.593	0.631	...	...
	E_{ww}		0.094	0.205	...	...
	E_{sw}		0.500	0.425	...	...

have been reported.^{2,4,5} Next we turn to the vdW exchange-correlation functionals, namely, vdW-DF, vdW-DF2, and vdW-DF-cx, and the three “opt” functionals. As seen in Table I, they all give larger E_{ads} values than PBE, with upshifts of 0.05–0.12 eV from the PBE value, approaching the CCSD(T) value. Finally, among the *a posteriori* methods, PBE-D2 gives a very good adsorption energy compared to the CCSD(T) value, while PBE-TS deviates more. We find the same method trend regarding the adsorbed water dimer and other small water clusters on the NaCl(001) surface (not presented here).

For completeness, we mention that Klimeš *et al.* also calculated the adsorption energy for a single water molecule on the NaCl(001) surface using their own optB88-vdW-DF functional.¹⁵ The difference between our value (0.483 eV) and theirs (0.424 eV) is most likely due to differences in the description of the substrate and the mode of self-consistency in the calculation of the vdW-DF energy.

Next we discuss three H₂O/NaCl(001) overlayer structures: the 1 ML $p(1 \times 1)$ structure [Fig. 1(c)], the 1.5 ML $c(4 \times 2)$ [Fig. 1(d)], and the 2 ML $p(1 \times 1)$ [Fig. 1(e)]. All of

them have been studied extensively in the literature.^{2–5} It is our PBE-optimized structures that are displayed in the figure, but the *overall* structures are very similar with all nine methods which are used here; only the details differ.

Bruch *et al.*⁷ performed helium atom scattering (HAS) measurements for water overlayer(s) on single-crystal NaCl(001), in the temperature range 80–120 K, and found a $p(1 \times 1)$ diffraction pattern. They proposed a monolayer structure similar to Fig. 1(c) and reported an (isosteric) heat of adsorption value of 58 ± 3 kJ/mol (0.60 eV) per H₂O molecule. This value is indicated as the middlemost horizontal reference line in Fig. 3(a). Neither of the previous DFT-GGA calculations in the literature^{2,4,5} nor our own PBE value (0.39 eV; Table I) reproduces their experimental value. However, we find that the vdW functionals tested here give values in quite good agreement with experiment, 0.50–0.65 eV, for all but the vdW-DF functional. Incidentally, DFT-LDA calculations in Ref. 3 reported an E_{ads} value of 0.56 eV (together with the usual underestimation of the NaCl lattice constant).

Earlier low-energy electron diffraction (LEED) studies by Fölsch *et al.*⁶ reported a $c(4 \times 2)$ water arrangement on NaCl(001) with an isosteric heat of adsorption value of 65 kJ/mol (0.67 eV) in the temperature range 135–155 K. The uppermost horizontal reference line in Fig. 3(a) refers to this energy value. Our PBE calculations for the 1.5 ML $c(4 \times 2)$ structure give an E_{ads} value (0.56 eV), which is considerably lower than the experimental E_{ads} value of 0.67 eV.⁶ The vdW functionals (except PBE-TS and now also vdW-DF), on the other hand, give E_{ads} values that are about 0.10–0.15 eV larger than the PBE value, in good agreement with the experimental value of Fölsch *et al.*

As for the 2 ML system included in our study, this is essentially the (1×1) “bilayer” that was suggested by Yang *et al.*⁴ and Cabrera-Sanfeliix *et al.*⁵ Based on DFT-PW91 calculations, these two groups independently found the (1×1) bilayer structure to constitute a stable low-energy structure on NaCl(001). In fact it was suggested by both these author groups that the published (1×1) structure from the helium atom scattering (HAS) measurements of Ref. 7 might actually have corresponded to this bilayer structure. For all nine methods (except PBE-TS), we find the $c(4 \times 2)$ and $p(1 \times 1)$ bilayer structures to yield very similar adsorption energies, differing only by a few hundredths of an eV (i.e., a few kJ/mol) per water molecule.

In summary, using the CCSD(T) monomer adsorption energy and the two experimental values quoted above for 1 and 1.5 ML as our reference data for E_{ads} , we conclude that the “opt” functionals and the vdW-cx functional perform the best in describing the water/NaCl(001) interfaces. The PBE-D2 functional performs well for the water monomer but overestimates the adsorption energy at higher coverages. The E_{ads} variation with coverage follows the same trend for all functionals, where the two higher coverages give similar values, much larger than the 1.0 ML value.

B. Water-surface vs. water-water interactions

Above we found that the E_{ads} value is rather much affected by the choice of functional. For the 1 ML case, for example, the values cover a range from 0.40 to 0.56 eV/water

molecule (excluding PBE-TS). Is this spread in E_{ads} values mostly due to systematic differences (errors) in the description of the water-surface interactions or in the water-water interactions? We have calculated the E_{WW} and E_{SW} contributions to E_{ads} to understand this issue. The definitions were given in expressions (2) and (3), and expressed in words, E_{WW} is the energy gained by forming a free-standing overlayer (with the atomic positions taken from the structure of the optimized interface system) from isolated water molecules while E_{SW} is the energy gained by rigidly placing this overlayer on the surface. As with any energy partitioning scheme, there are advantages and disadvantages. With the partitioning scheme used here any changes in the water-water interaction arising as a consequence of the surface-water interaction will be included in the E_{SW} part. However, the benefits of the partitioning scheme are that it will give us some insight regarding the relative importance of the two types of energy contributions, and the scheme is consistent for all the coverages and functionals used here.

Fig. 3(b) and the hard numbers in Table I show that E_{WW} varies only little with the choice of functional. For the 1 ML case, for example, all E_{WW} values lie within 0.12 ± 0.02 eV per water molecule, while as we saw the E_{ads} values themselves vary from 0.40 to 0.65 eV per water molecule, depending on the functional. Thus, at this coverage, E_{SW} makes the main contribution to E_{ads} , both in terms of magnitude and functional dependence; E_{SW} varies from 0.30 to 0.54 eV per water molecule, calculated over all functionals.

The impact of the water-water interactions of course increases with water coverage. For the two larger coverages (1.5 ML and 2.0 ML), E_{WW} is roughly of a similar order of magnitude as E_{SW} and even constitutes the main contributor to E_{ads} . However, E_{SW} still appears to be more sensitive to the choice of functional than E_{WW} . Inspection of Table I shows that for 1.5 ML coverage,

- E_{ads} for PBE is 0.56 eV and for the vdW functionals lie within 0.64 ± 0.06 eV,
- E_{WW} for PBE is 0.38 eV and for the vdW functionals lie within 0.35 ± 0.04 eV,
- E_{SW} for PBE is 0.18 eV and for the vdW functionals lie within 0.29 ± 0.03 eV.

In fact we find that for all three of the 1.0, 1.5, and 2.0 ML overlayers, the six self-consistent vdW functionals give rise to an E_{SW} upshift of about 0.10 ± 0.05 eV with respect to PBE, and this shift is transferred to E_{ads} . We therefore conclude that the functional dependence of E_{ads} largely originates from how the different functionals manage

to describe the E_{SW} energies, and for water on NaCl(001), selecting a functional that manages to describe E_{SW} appears to be of particular importance as this is where PBE performs less well. This result is consistent with the observations of Carrasco *et al.* for the adsorption of water on metal surfaces.³³

C. Rationale behind the water-surface and water-water interactions

Above we noted that increasing the coverage from 1.0 ML to 1.5 ML, E_{WW} (per water molecule), increases drastically with all functionals, while E_{SW} decreases equally drastically. On the other hand, going from 1.5 ML to 2.0 ML, neither E_{WW} nor E_{SW} hardly change at all; again this is true for all methods. *Can we understand this from a simple picture of the water structures on the surface?*

The surroundings of the water molecule in the 1 ML structure [Fig. 1(c)] are similar to that of the “isolated” water molecule [Fig. 1(a)]. The 1 ML structure just contains one unique type of water molecule, schematically depicted in Scheme 1.

The right-hand picture pinpoints the nearest-neighbour coordination around the water molecule and the dashed line on the right-hand side indicates the H-bond donated by the water molecule (we will use the same convention in the schematic figures below). The water molecule remains intact, which is true for all water molecules at all coverages on NaCl(001). At 1 ML coverage, the water molecule is involved in one stronger and one weaker contact with neighbouring Cl^- ions. With the PBE method, for example, the $R(\text{O}_{\text{w}} \cdots \text{Cl}^-)$ distances are 3.23 and 3.36 Å for the isolated monomer and 3.13 and 3.47 Å for the monolayer. The longer one represents a weakly stabilizing dipole-ion interaction but is too long to be called a hydrogen bond.³⁵

As all the nearest neighbours of the water molecule are surface ions at 1 ML coverage, the water-surface interaction dominates, which it does with all methods; E_{SW} constitutes about 75% of E_{ads} (Table I). The remaining 25% constitutes the dipole-dipole interaction between the rather well separated water molecules in the overlayer (approximately 4.0 Å apart).

Now going to the 1.5 ML structure [Fig. 1(d)], the surroundings of the water molecules are quite different from the 1.0 ML case. The surface cell here contains six unique water molecules, i.e., with different surroundings (Scheme 2). There are two of each of these molecular types (W_1 - W_6) in the $c(4 \times 2)$ cell. In each schematic figure, the dashed lines indicate hydrogen bonds *accepted by* (left side) and *donated by* (right side) the central water molecule. All water molecules at this coverage are seen to have two or three H-bonded water neighbours and in fact there are infinite water $\cdots$ water

SCHEME 1.

SCHEME 2.

hydrogen-bond chains running in two directions in this structure, and the entailing cooperative effects strengthen the H-bonds further. The water-water H-bond distances span the range $2.7 \text{ \AA} < R(\text{O} \cdots \text{O}) < 3.0 \text{ \AA}$ for PBE, i.e., they are of average length and strength. Clearly, E_{WW} (per water molecule) should increase compared to the 1.0 ML case, as is seen to occur in Table I. On the other hand, compared to the 1.0 ML coverage, the E_{SW} value at 1.5 ML coverage should be expected to decrease, as all water molecules (except W1) now have just one water-surface bond compared to two at the lower coverage. And indeed that is what we find; see Fig. 3(c). The $R(\text{O}_{\text{W}} \cdots \text{Cl}^-)$ distances lie in the range 3.1–3.3 Å for the 1.5 ML coverage.

In the 2.0 ML structure [Fig. 1(e)], infinite zigzag water $\cdots$ water hydrogen-bond chains run through the overlayer structure, consisting of two unique types of water molecules, equally many of each (Scheme 3). Both types of water molecules have two H-bonded water neighbours, i.e., fewer than in the 1.5 ML case. On the other hand, the $R(\text{O} \cdots \text{O})$ hydrogen-bond distances are considerably shorter for the 2.0 ML structure (2.65 Å with PBE). The E_{WW} values turn out to be almost identical for the two coverages. This is also true for the E_{SW} values, consistent with the schematic figures above, which show that for 2.0 ML each water molecule has only one contact with the surface, and for 1.5 ML the same is true except for water W1.

We will carry this simplistic nearest-neighbour exercise a little bit further and use it to predict the relative magnitudes of E_{SW} and E_{WW} for the two highest coverages. We compare the average *number* of water-water vs. water-surface nearest-neighbour contacts for the 1.5 and 2.0 ML structures, using the illustrations shown above. This gives the prediction that E_{SW} makes up 47% of the total adsorption energy for 1.5 ML and 50% for 2.0 ML, which are close to the actual DFT calculated $E_{\text{SW}}/E_{\text{ads}}$ ratios, which lie in the range 40–45% for all six self-consistent vdW functionals for both structures (based on values in Table I). Thus this nearest-neighbour counting exercise gives a rough estimate of the

SCHEME 3.

relative magnitudes of E_{SW} and E_{WW} for these two overlayers. However, for the 1.0 ML coverage, with no water-water hydrogen bonds, one clearly has to go beyond nearest neighbours to account for the modest but significant magnitude of E_{WW} .

IV. RESULTS—H₂O ON MgO(001)

A. Adsorption energies from calculations and comparisons to experiments

Next we will discuss the four water/MgO(001) interfaces treated in this work. Our PBE-optimized structures are displayed in Fig. 2, and again, the *overall* structures are very similar with all nine methods used here; only the details differ.

Let us start with two overlayer structures which have been much debated in the literature, although some consensus now appears to have been reached concerning their existence and hydroxylation. In 1995, using LEED measurements at 150 K, Heidberg *et al.*³⁷ found a $c(4 \times 2)$ diffraction pattern and, aided by FTIR experiments, suggested molecular adsorption of water on MgO(001). Since then, the degree of dissociation for this structure has been the topic of many experimental^{12,38} and theoretical studies.^{8–10,39} A recent combined experimental-computational study by Włodarczyk *et al.*⁴⁰ suggested the partially dissociated structure shown in Fig. 2(d) for the $c(4 \times 2)$ structure. The water coverage is 1.25 ML, one fifth of them dissociated.

One year after the Heidberg paper appeared, LEED and HAS studies by Ferry *et al.*¹² revealed that the $c(4 \times 2)$ structure is only stable up to 180 K, where further heating led to a transformation to a $p(3 \times 2)$ structure, stable up to 220 K. The authors measured an isosteric heat of adsorption value of $85.3 \pm 2.1 \text{ kJ/mol}$ ($0.884 \pm 0.022 \text{ eV}$) for the $p(3 \times 2)$ structure; this value is the horizontal line drawn in our Fig. 4 and is here used by us to help benchmark the performance of the nine functionals. The atomic positions of the $p(3 \times 2)$ structure and the degree of water dissociation were first reported in the theoretical study by Giordano.⁸ The water coverage is 1.0 ML, one third of them dissociated.

The experimental adsorption energy measured by Ferry *et al.* (0.88 eV per water molecule) is larger than the PBE-calculated value (0.72 eV; Table II and Fig. 4). Fortunately, the vdW functionals (except vdW-DF and vdW-DF2) give rise to a significant increase to the E_{ads} value, resulting in almost perfect agreement between optPBE-vdW, vdW-DF-cx, and the

FIG. 4. Calculated adsorption energies (E_{ads}) for the adsorption of the water monomer and dimer, and of two different water overlayer structures on MgO(001) using the nine functionals. The experimental value is from Ref. 12.

E_{ads} value of Ferry *et al.* The last four methods in the figure tend to overestimate E_{ads} by up to 0.1 eV. As for the vdW-DF and vdW-DF2 methods, the latter brings only a very small improvement over PBE while the former leads to a smaller E_{ads} value than even PBE.

Karalitis *et al.* reported a benchmark energy value of 0.48 eV for water monomer adsorption on MgO(001) based on diffusion Monte Carlo (DMC) calculations for a 2-layer slab.⁴¹ Our vdW-DF-cx and optPBE-vdW values for the monomer/MgO(001) system agree quite well with their value. We note, however, that the two benchmark values for monomer adsorption that we refer to in our paper, namely, the CCSD(T) value for NaCl¹⁴ and the DMC value for MgO,⁴¹ are very similar in magnitude, which we find slightly disturbing, as the molecule on MgO should be expected to be more strongly bound.

In summary, we find that the vdW functionals describe the water/surface interaction better than PBE for all the H₂O/NaCl and H₂O/MgO interfaces. The adsorption energy increases by 0.1–0.25 eV compared to PBE. The same functionals, namely, optPBE-vdW and vdW-DF-cx, perform the best for both NaCl and MgO.

B. Water-surface vs. water-water interactions

Since many of the adsorbed water molecules dissociate on the MgO surface, we cannot calculate E_{SW} and E_{WW} as we did for NaCl(001). However, in a similar way to NaCl(001), we will use the schematic illustrations to calculate the average

TABLE II. Calculated adsorption energies (E_{ads}) for adsorption of the water monomer, dimer, and two water overlayer structures on MgO(001). All values are in units of eV.

	Monomer	Dimer	1 ML	1.25 ML
PBE	0.422	0.504	0.723	0.758
vdW-DF	0.435	0.521	0.674	0.742
vdW-DF-cx	0.574	0.565	0.919	0.937
vdW-DF2	0.476	0.662	0.745	0.827
optPBE-vdW	0.551	0.642	0.911	0.915
optB88-vdW	0.589	0.679	0.960	0.981
optB86b-vdW	0.667	0.688	0.970	0.984
PBE-D2	0.617	0.686	0.975	0.995
PBE-TS	0.662	0.748	1.002	1.027
PBE-TS+SCS	0.630	0.712	0.923	0.998

number of water-water and water-surface nearest-neighbour contacts to make a qualitative estimate of the relative importance of the water-water and water-surface interactions for the water molecules that remain intact.

First, let us compare the cases of a 1 ML water layer on NaCl(001) and MgO(001). With PBE (for example), the corresponding E_{ads} values are 0.40 eV and 0.72 eV per H₂O. The 1 ML $p(3 \times 2)$ MgO(001) structure [Fig. 2(c)] contains six water molecules per surface unit cell, three of which are unique, namely, one dissociated and two intact ones with the surroundings as seen in Scheme 4. There are two water molecules of each type in the surface cell. Given that the charges of MgO are twice as large as in NaCl and that the water molecules in the 1 ML overlayer on MgO form H-bonded chains with stabilizing cooperative effects, which is not the case for 1 ML NaCl(001), it is no wonder that the E_{ads} values are wildly different in the two cases. In fact, structurally, it may be more adequate to compare the 1.0 ML water/MgO overlayer with 1.5 ML water/NaCl, where there are also infinite water chains running in two directions. Counting nearest-neighbour interactions and averaging over the water molecules in the surface cells gives us 1.0 water-surface interactions and 1.33 water-water interactions per adsorbed water molecule for the 1 ML water/MgO interface, and a rather similar result for the 1.5 ML water/NaCl structure, namely, 1.2 water-surface + 1.33 water-water interactions. Largely because of the charges, E_{ads} is of course still considerably larger for the water/MgO interface.

Going from 1 ML to 1.25 ML H₂O/MgO, E_{ads} changes very little. Here the water molecules represent three different surroundings (Scheme 5), with four water molecules of the first type, four of the second, and two of the third. Altogether there are thus 10 water molecules in the surface cell, two of which are dissociated and the rest remain intact.

SCHEME 4.

SCHEME 5.

In the 1.25 ML structure, there are on average 0.8 water-surface interactions and 1.6 water-water interactions per adsorbed water molecule, i.e., in total 2.4 interactions, using our simplistic nearest-neighbour counting procedure. This sum is very similar to the sum 2.3 interactions per water molecule that we also had for the 1.0 ML coverage, which provides a rationale for the similarity between the two E_{ads} values.

V. RESULTS—HOW MUCH ARE THE WATER MOLECULES PERTURBED?

Here we will use the polarization, i.e., the induced dipole moment, of the water molecules (see Section II D) as a probe of the perturbation of the surroundings on the water molecule. We report the results for PBE, optPBE-vdW, and PBE-D2 (Table III).

Our reference system is the optimized $\text{H}_2\text{O}(\text{g})$ molecule whose calculated dipole moment lies in the range 1.80–1.85 D with all three methods, and as shown in Table III, with all three methods the dipole moment increases to 2.2 D for the isolated water monomer residing on NaCl(001) and to 2.3 D for the monomer on MgO(001). Thus, the water molecule is polarized by about 20% by the NaCl surface, and this value does not change much for the 1 ML overlayer where the water molecules are still quite far apart. For the 1.5 ML overlayer on NaCl, on the other hand, surface–water···water cooperative effects lead to a significant dipole moment enhancement for some of the water molecules, such as W3, which is polarised by

~70% compared to the gas-phase permanent dipole moment. Altogether, for this coverage the water dipole moments span the range 2.6–3.2 D, and for the 2.0 ML case, the situation is similar.

For the MgO(001) surface, the average *induced* dipole moment of the undissociated surface water molecules varies from approximately 25% $\Rightarrow$ 80% $\Rightarrow$ 85% of the permanent dipole moment as the coverage increases from the isolated monomer $\Rightarrow$ 1 ML $\Rightarrow$ 1.25 ML. Again, the large induced dipole moment is a consequence of polarisation effects from both the surface and water neighbours. We note that the three DFT methods examined here all give rather similar results (cf. Table III), a result which we find somewhat intriguing as the corresponding E_{ads} values are so different. We have no explanation for this.

Fig. 5 relates the adsorption energy and the dipole moment for the nine interface systems and the three selected methods. As E_{ads} reflects the strength of adsorption of *all* the water molecules in an overlayer, the dipole moment plotted in the figure was calculated as *the average* over the water dipole moments for each overlayer. We notice that (i) the points for the two substrates follow the same curves and (ii) we obtain qualitatively similar results for the three selected methods. We suggest that the “ μ_{average} vs. E_{ads} ” relations in Fig. 5 could possibly be used to provide a qualitative estimate of the average water dipole moment from the (experimental) knowledge of the adsorption energy.

TABLE III. Calculated dipole moments of water on NaCl(001) and MgO(001) from Wannier centers using the PBE, optPBE-vdW, and PBE-D2 functionals. The calculated dipole moment of the optimized isolated water molecule is (in the same method order) 1.845, 1.809, and 1.839 D, respectively. The superscripts w1, w2, etc. are deciphered in Schemes 2–5. The angle bracket means that the average was taken over all water molecules in the cell. All values are in units of Debye.

	PBE	optPBE-vdW	PBE-D2
H₂O/NaCl(001)			
Monomer	2.18	2.17	2.15
Dimer	2.48, 2.44	2.46, 2.39	2.48, 2.46
1 ML	2.30	2.27	2.30
1.5 ML	2.82 ^{w1} , 2.78 ^{w2} , 3.20 ^{w3} , 3.05 ^{w4} , 2.86 ^{w5} , 2.74 ^{w6} $\langle \rangle = 2.91$ D	2.77, 2.64, 3.08, 2.98, 2.77, 2.70 $\langle \rangle = 2.82$ D	2.85, 2.79, 3.19, 3.03, 2.85, 2.72 $\langle \rangle = 2.91$ D
2 ML	3.01 ^{w1} , 3.00 ^{w2}	2.88, 2.78	3.04, 2.91
H₂O/MgO(001)			
Monomer	2.34	2.30	2.32
Dimer	2.70, 2.65	2.627, 2.59	3.05, 2.64
1 ML	3.29 ^{w1} , 3.38 ^{w2}	3.14, 3.26	3.32, 3.20
1.25 ML	3.50 ^{w1} , 3.40 ^{w2}	3.46, 3.33	3.50, 3.30

FIG. 5. Calculated Wannier-type water dipole moment vs. adsorption energy for all intact water molecules in Figs. 1 and 3 with three selected functionals. For each functional, a second-order polynomial was fitted to the data points. Each curve was constrained to pass through the pertinent gas-phase dipole moment for $E_{\text{ads}} = 0$.

VI. RESULTS—FROM THE CLEAN SYSTEMS TO THE INTERFACES

Above we concluded that the vdW functionals tend to reproduce the experimental (and CCSD(T)) adsorption energies better than PBE for all the $\text{H}_2\text{O}/\text{NaCl}$ and $\text{H}_2\text{O}/\text{MgO}$ interfaces and that the optPBE-vdW and vdW-DF-cx functionals performed the best. In this section, based on data from the literature and from some new calculations performed here, we will summarise the performance of the nine functionals for some key properties of the pure NaCl and MgO systems (bulk and surface) and of gas-phase water clusters, and we will find out if an accurate description of the bare systems is a prerequisite for a good description of the interface systems.

A. Gas-phase water clusters

The effect of dispersion interactions on the stability trends of gas-phase water clusters and the water hexamers in particular has been amply studied in the literature.^{42–44} Here, using PBE and the eight vdW models, we optimized six $(\text{H}_2\text{O})_n$ ($n = 2–7$) gas-phase water clusters (Fig. 6(a)) with starting

(a)

FIG. 6. Comparison of interaction energies and distances for gas-phase clusters $(\text{H}_2\text{O})_n$, $n = 2–7$, calculated with the nine functionals. (a) PBE-optimized structures. (b) Water interaction energy per water molecule. (c) Selected $R(\text{H}\cdots\text{O})$ distances from the clusters. The CCSD(T) values are from Ref. 45.

(b)

(c)

structures taken from the RI-MP2/aVDZ results of Ref. 42. Fig. 6(b) displays the interaction energy, $\Delta E = -E_{\text{tot}}[(\text{H}_2\text{O})_n] + n \cdot E_{\text{tot}}[\text{H}_2\text{O}(\text{g})]/n$, and selected $R(\text{H} \cdots \text{O})$ distances of the fully relaxed gas-phase clusters. Literature values for ΔE obtained at the RI-CCSD(T)/CBS//MP2/CBS level by Temelso *et al.*⁴⁵ are included as reference.

Figs. 6(b) and 6(c) show that all models, PBE as well as the vdW models, display the same trends and most of them tend to overestimate ΔE compared to the CCSD(T)/CBS results. Some vdW models perform better than PBE, others worse. For ΔE , the best agreement with CCSD(T) is achieved by vdW-DF-cx, optPBE-vdW, and vdW-DF2.

B. NaCl and MgO properties

Klimeš *et al.*,¹⁸ Zhang *et al.*,⁴⁶ and Bučko *et al.*,⁴⁷ among others, have demonstrated that the contribution of dispersion interactions to the bulk properties of ionic crystals [lattice constant (a_o), bulk modulus (B_o), and cohesive energies (E_{coh})] is crucial and cannot be neglected. Also we have computed these properties for bulk NaCl(s) and MgO(s) using our set of methods, where only the vdW-DF-cx¹⁹ results are not already present in the literature. For the eight remaining methods, our a_o values agree with those in the literature¹⁸ within 0.01 Å, B_o within 1 GPa, and E_{coh} within 0.04 eV.

Thus, as we are not aware of any published results for bulk NaCl(s) or MgO(s) with the vdW-DF-cx functional, we present such data here, namely, $a_o = 5.65$ Å (experiment 5.64 Å²⁹), $B_o = 26.7$ GPa (experiment 26.6 GPa⁴⁸), and $E_{\text{coh}} = 6.57$ eV (experiment 6.68 eV⁴⁸) and for MgO(s) $a_o = 4.22$ Å (experiment 4.21 Å³⁰), $B_o = 155.6$ GPa (experiment 165 GPa⁴⁸), and $E_{\text{coh}} = 10.53$ eV (experiment 10.54 eV⁴⁸).

From earlier reports in the literature,^{18,46,47} and from our own calculations, we conclude that most of the vdW methods (the self-consistent vdW functionals as well as the *a posteriori* methods) manage to reproduce the experimental a_o and B_o of both NaCl(s) and MgO(s) reasonably well, where the vdW-DF functional overestimates the cell parameter by the largest amount (~ 0.1 Å) compared to experiment and the PBE-TS method significantly underestimates a_o of NaCl (by ~ 0.25 Å in our calculations) and overestimates B_o (by ~ 50 GPa). As for the cohesive energies, PBE and vdW-DF2 tend to underestimate E_{coh} for both crystals, while PBE-TS overestimates it. The best overall performance for the bulk systems is demonstrated by vdW-DF-cx, optB86-vdW-DF, and optPBE-vdW-DF.

Finally, we turn to the bare NaCl(001) and MgO(001) surfaces, which have not been studied with the vdW functionals in the literature, as far as we are aware. We explore how sensitive (or not) the surface energy is to the inclusion of dispersion interactions. The experimental E_{surf} value for NaCl(001) is very small,⁴⁹ only ~ 0.30 J/m² and close to four times as large for MgO(001).^{49,50} We find that, indeed, E_{surf} is quite sensitive to the inclusion of vdW effects, which typically increase E_{surf} by several tenths of J/m² compared to the PBE values (cf. Table IV); this is consistent with the fact that the vdW methods increase E_{coh} compared to the PBE value. It is interesting to note that the vdW methods (except PBE-TS)

TABLE IV. The surface energy (E_{surf}) calculated for the geometry-optimized NaCl(001) and MgO(001) slabs using the nine DFT methods and compared with experimental values. All Values are in J/m².

	Bare NaCl(001)	Bare MgO(001)
Experiment	0.28-0.32 ^a	1.04-1.12 ^{a,b}
PBE	0.15	0.84
vdW-DF	0.26	0.90
vdW-DF-cx	0.34	1.07
vdW-DF2	0.28	0.85
optPBE-vdW	0.30	1.05
optB88-vdW	0.18	1.14
optB86b-vdW	0.30	1.17
PBE-D2	0.28	1.28
PBE-TS	0.81	1.74

^aReference 49.

^bReference 50.

provide better agreement with the experimental E_{surf} than PBE does.

C. The interfaces

We noted above that *optPBE-vdW* and *vdW-DF-cx* deliver E_{ads} values in very good agreement with experiment for both water/NaCl and water/MgO and they also give good descriptions of the substrate's bulk properties as well as E_{surf} values. The *vdW-DF2* functional also performs very well for the water/NaCl interfaces but it slightly underestimates E_{ads} for MgO, which is consistent with the low E_{surf} of MgO(001) at the PBE level (Table IV).

As for the *optB88-vdW*, *optB86-vdW*, and *PBE-D2* methods, they are able to describe the substrate properties properly but overestimate E_{ads} moderately for water on MgO, probably to a large extent a consequence of an overestimation of the strength of the water-water interactions, which is evident already from the gas-phase water clusters [Fig. 6(b)].

PBE-TS overestimates E_{ads} , possibly due to the rather poor description of the ionic substrates (underestimates a_o and overestimates B_o), which is also consistent with the large E_{SW} values for PBE-TS for the water overlayers on NaCl in Fig. 3(c).

The *vdW-DF* functional underestimates E_{ads} for both NaCl and MgO, which appears to largely be due to the underestimation of the strength of the water-water interactions which is seen both from the gas-phase water clusters [Fig. 6(b)] and for NaCl(001) in Fig. 3. The clean ionic systems, on the other hand, are adequately described.

Finally, the *PBE* functional significantly underestimates E_{ads} compared to the available experimental adsorption energies. This appears to be a consequence of limitations in the description of the clean surface system (E_{surf} , Table IV) and the surface-water interaction contribution [Fig. 3(c)].

Relating back to the question posed at the beginning of this section, we find that whenever the calculated adsorption energy greatly deviates from the experimental value we can also find deficiencies in the chosen functional's description of either the bare ionic systems or the pure water systems, or both (Table V).

TABLE V. Overview of the performance of the functionals used in this study. The methods that perform the best are given a tick-mark (see text).

	H ₂ O/NaCl(001)	H ₂ O/MgO(001)	(H ₂ O) _n clusters	Bulk NaCl(s) and MgO(s)	Clean NaCl(001) and MgO(001)
PBE				✓	
vdW-DF					✓
vdW-DF-cx	✓	✓	✓	✓	✓
vdW-DF2	✓		✓	✓	✓
optPBE-vdW	✓	✓	✓	✓	✓
optB88-vdW	✓			✓	✓
optB86b-vdW	✓			✓	✓
PBE-D2				✓	✓
PBE-TS					

VII. LONG-RANGE SCREENING AND MANY BODY DISPERSION EFFECTS FOR PBE-TS

The poor performance found for the PBE-TS functional regarding the description of the NaCl bulk structure has in the literature been suggested to originate from lack of long-range screening.⁴⁷ Such contribution could of course also be important in the description of the adsorbed water molecules studied in this paper. To test this, we have here used the PBE-TS+SCS⁵¹ functional for the bulk NaCl structure and for the adsorption of water (monomer molecule, the dimer, and the 1ML coverage) on both NaCl(001) and MgO(001). In these calculations, we used the standard implementation and parameters provided in the VASP package.

For the NaCl bulk structure, inclusion of long-range screening clearly improves the description, yielding lattice parameter and bulk modulus values ($a_0 = 5.53$ Å, $B_0 = 32$ GPa) in better agreement with experiment ($a_0 = 5.64$ Å,²⁹ $B_0 = 27$ GPa⁴⁸). This was already observed by Bučko *et al.* in previous work.⁴⁷

FIG. 7. Comparison of adsorption energies calculated with PBE-TS and PBE-TS+SCS for the adsorption of the water monomer, dimer, and 1 ML overlayer on NaCl(001) and MgO(001). The numbers written across the red and green bars were obtained by subtracting the PBE-TS+SCS values from the PBE-TS and are thus an estimate of long-range screening effect (eV).

For the water adsorptions, the calculated adsorption energies for PBE-TS with and without long-range screening effects are reported in Fig. 7. As can be seen in the figure, inclusion of long-range screening amends the over-binding nature of PBE-TS, and the resulting E_{ads} values are in better agreement with the experimental values quoted in Sections III A and IV A.

As for explicit many-body dispersion contributions, Tkatchenko *et al.* have formulated a many-body dispersion-corrected version of PBE-TS,^{51,52} which was recently implemented in VASP.⁵³ However, this functional sometimes suffers from numerical instabilities, especially for highly polarizable atoms, and this is indeed what we have experienced for our water/NaCl and water/MgO interfaces as well, and which made it impossible to include it as a test case in the present study, and is therefore left for future investigations.

VIII. CONCLUSIONS

In this work, a range of van der Waals type density functionals are applied in the study of adsorbed water structures on NaCl(001) and MgO(001): the monomer, dimer, and different overlayer structures. Our main conclusions are as follows:

- All nine functionals (including PBE) yield very similar structures, with respect to hydroxylation and hydrogen-bond patterns.
- For both NaCl(001) and MgO(001), we find that the dispersion-flavoured functionals stabilize the water-surface interface by approximately 20%-40% compared to the PBE results. This is so, despite their rather different characters. For NaCl(001), where the water molecules remain intact for all overlayers, the dominant contribution to the adsorption energy from “DFT dispersion” stems from the water-surface interactions rather than from the water-water interactions.
- The *optPBE-vdW* and *vdW-DF-cx* functionals yield adsorption energies in good agreement with available experimental values for both NaCl and MgO, but many of the others also perform quite satisfactorily. For the PBE-TS functional, we note that the inclusion of long-range screening is needed to get a similar accuracy as for the self-consistent vdW functionals.

- (iv) We found that in cases when the calculated adsorption energy greatly deviated from the experimental value we could also find deficiencies in the chosen functional's description of either the bare ionic systems or the pure water systems, or both. This suggests that a functional needs to perform well for both the bare substrate and bare adsorbate in order to achieve accurate results for the interface between them (Table V).
- (v) We found that just the consideration of the nearest-neighbour coordination of the adsorbed (intact or dissociated) water molecules gives a rough estimate of, and some insight concerning, the relative contributions of water-surface and water-water interactions to the adsorption energy.
- (vi) The perturbation of each adsorbed water molecule was probed by calculating its dipole moment (using Wannier centers and nuclear positions) for all overlayers using PBE, optPBE-vdW, and PBE-D2. For NaCl(001) the resulting dipole moments lie in the range 2.3-3.0 D and for MgO(001) in the range 3.1-3.5 D. The water molecule can thus be highly polarised at the surface (more polarised than water in liquid water which is 3.1 D at the PBE-level). The isolated gas-phase water dipole moment is around 1.8 D with all three methods, and the dipole moments are also very method-insensitive for the surface structures. Moreover, we find a correlation between the average polarisation of the intact water molecules on the surface and the adsorption energy of the overlayer.

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