How strong is the bond between water and salt?

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A B S T R A C T

The interaction of water with salt is central to an almost endless list of scientific areas. However, one of the most fundamental and important questions of how strong the bond is between a water molecule and a salt surface is not yet well-established. Here, we examine water monomer adsorption on the (001) surface of NaCl with the purpose of obtaining a reliable theoretical estimate of the adsorption energy. The approach followed relies on established quantum chemistry methodologies and involves a separation of the total adsorption energy into contributions from Hartree–Fock and electron correlation, the use of embedded cluster models of the substrate, and extrapolations to the complete basis set limit. Application of this procedure, with electron correlation treated at the CCSD(T) level, yields an adsorption energy for a water monomer on a fixed NaCl(001) substrate of ~487 meV and ~517 meV when substrate relaxations are accounted for.

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“Chemical accuracy”– an accuracy of 1 kcal/mol or ~43 meV– is a much-discussed and highly sought after precision in the simulation of chemical processes and materials.1 It is the level of accuracy that must be achieved in order to make quantitative predictions of reaction rates. There are established techniques for obtaining this accuracy when dealing with the full range of interactions that govern molecular systems, as afforded through the application of correlated quantum chemistry methods (see, e.g., [1]). However, when it comes to moderately complex problems in condensed matter, such as the calculation of the adsorption energy of a molecule on a surface, achieving such accuracy is much more demanding. Given the central importance of the molecule–solid interaction to disciplines as diverse as catalysis, electrochemistry, and semiconductor processing, it remains a major challenge to theory to demonstrate that chemical accuracy in this area can be approached.

The state-of-the-art in computing adsorption at solid surfaces is the supercell approach, where the full arsenal of quantum chemistry can be employed. When quantum size effects are accounted for through an appropriate embedding scheme or by examining differences between clusters and periodic slab models of the substrate, such methods can be very powerful [9,13–23]. This general route has been followed with great success to the treatment of adsorbates on solids, and for certain systems shown to yield high accuracy below 0.3 eV (RPBE) to above 0.6 eV (LDA), with PBE (and PW91) in between (0.3–0.4 eV) [2–6]. The DFT “range” with just these three functionals is thus almost an order or magnitude larger than chemical accuracy. Water on salt is by no means an exceptional system. There are many others where the DFT range in absolute adsorption energies is unacceptably large: Cu on MgO and NO on NiO are two out of many other prominent examples [7,8].

There are, of course, remedies to account for certain deficiencies within the density-functional framework such as the missing dispersion interactions which may be relevant to some adsorption systems (like the one under consideration here) or the self interaction error which plagues others [9–11]. Van der Waals correction schemes [12] would be appropriate for the former and “hybrid” functionals for the latter. Such techniques offer great promise. However, given their partly ad hoc nature and the frequent absence of definitive experimental values, accurate theoretical reference data against which their reliability can at first be benchmarked is highly desirable.

The alternative to the DFT supercell scheme is the cluster approach, where the full arsenal of quantum chemistry can be employed. When quantum size effects are accounted for through an appropriate embedding scheme or by examining differences between clusters and periodic slab models of the substrate, such methods can be very powerful [9,13–23]. This general route has been followed with great success to the treatment of adsorbates on solids, and for certain systems shown to yield high accuracy (see, e.g., [7,8,16,24]). Here, we follow this general course and present a brief account of our work which is aimed at providing a high precision estimate of the adsorption energy of a water monomer on
sequent (cluster) calculations. The importance of substrate relax-
structure obtained on a fixed NaCl surface and use it for all sub-
0.3 Å for the LDA, PBE and RPBE xc functionals). Here, we adopt the
oxygen above the surface differs with the various functionals (within
truncated positions. This is also the most stable configuration pre-
the one shown in Fig. 1a. In this structure the molecule lies fairly flat
against the surface, the O atom is close to a Na site and the hydro-
the minority of the cluster calculations have been performed with NWChem [27].
For comparison with the periodic HF calculations performed with CRYSTAL a number
of CRYSTAL cluster calculations were also performed (the data for basis set 3 in Fig. 2).

The data for basis set 3 in Fig. 2. 4 A clear reduction in the cluster size dependence of
adsorption energy on the clusters shown in Fig. 1 for three (small) basis sets. Consis-
tently, a strong (>100 meV) dependence of $E_{\text{ads}}^{\text{HF}}$ on cluster size is observed and, moreover, $E_{\text{ads}}^{\text{HF}}$ does not appear to converge with respect to cluster size for the clusters tested. Thus it is unclear if any of the clusters serve as a suitable model for NaCl(001). It is well-
established, however, that such finite size effects can be mitigated with an appropriate embedding scheme, which for an ionic material such as NaCl would be point charges or a combination of point charges and effective core potentials (see, for example, [13,19,20,28–30]). Given the highly ionic nature (and associated large band gap) of NaCl one can, in fact, anticipate that embedding is likely to be very effective. Here, after testing a variety of schemes we followed one such recipe which leads to the results displayed in
Fig. 2b. 5 A clear reduction in the cluster size dependence of $E_{\text{ads}}^{\text{HF}}$ can be observed. For all basis sets $E_{\text{ads}}^{\text{HF}}$ becomes much less sensitive to cluster size and $E_{\text{ads}}^{\text{HF}}$ calculated with the Na$_5$Cl$_5$ cluster is within $\approx$35 meV of that obtained with the Na$_{25}$Cl$_{25}$ Cluster for all basis sets. This gives a strong indication that even the Na$_5$Cl$_5$ cluster, when suitably embedded, provides for water adsorption a good representation of NaCl(001). This is confirmed by periodic HF calculations on an NaCl slab: with an identical basis set the periodic HF adsorp-

2 Periodic DFT calculations have been carried out with the plane-wave pseudopotential approach as implemented in the CASTEP code [42]. Four layer NaCl slabs have been employed along with at least a 4 x 4 Monkhorst-Pack k-point mesh per 1 x 1 surface unit cell. A low water coverage of 1/8 monolayer was considered.

3 The majority of the cluster calculations have been performed with NWChem [27]. For comparison with the periodic HF calculations performed with CRYSTAL a number of CRYSTAL cluster calculations were also performed (the data for basis set 3 in Fig. 2).

4 For the embedding calculations each of the clusters displayed in Fig. 1 was surrounded with a set of Na effective core potentials at the nearest-neighbor Na sites and then outside this a ±1.0 e point charge array of dimension 21 x 21 x 6 placed on the NaCl lattice positions. In addition to the periodic HF data point reported in Fig. 2, extensive tests with other embedding procedures and larger point charge arrays established the reliability of the particular embedding procedure employed [41].

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**Fig. 1.** (a) Side and top view of the most stable structure of a water molecule adsorbed on NaCl(001) as obtained from DFT-PBE, displayed here on an Na$_5$Cl$_5$ cluster. Distances are given in Å. (b) The larger stoichiometric 2 layer clusters used (top view). Red, white, purple, and green spheres are oxygen, hydrogen, sodium, and chlorine atoms, respectively. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

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**Fig. 2.** Variation of the HF ($E_{\text{ads}}^{\text{HF}}$) and electron correlation ($E_{\text{ads}}^{\text{corr}}$) contribution to the adsorption energy with respect to cluster size for three basis sets without embedding (a,c) and with embedding (b,d). PHF: periodic HF calculations. Basis set 1: O,H,C = 6-311G*, Na = 6-31G; Basis set 2: all = cc-pVTZ; Basis set 3: O,H = 6-31+G*, C = 6-311G*, Cl = 6-31G, Na = 6-31G. The same adsorption geometry has been used throughout.
tion energy matches that on the Na$_2$Cl$_3$ cluster to within only \( \approx 20 \text{ meV} \). The weak dependence on cluster size and the near coincidence of the embedded cluster and periodic HF values gives us confidence that the long range electrostatic potential of the substrate is recovered with our embedding approach and that for water adsorption the Na$_2$Cl$_3$ cluster is a good model of the true periodic substrate.

Next, we explore the dependence on cluster size of \( E_{\text{ads}}^{\text{corr}} \), treated at this stage, at the MP2 level. The results obtained for non-embedded and embedded clusters are shown in Fig. 2c and d. It can be seen that even before embedding \( E_{\text{ads}}^{\text{corr}} \) is less sensitive to cluster size than \( E_{\text{ads}} \); the variation on all three clusters examined is \(< 36 \text{ meV} \). Nonetheless, embedding helps to reduce the dependence on cluster size; reducing the variation to 25 meV or less. As we saw for \( E_{\text{ads}} \), we see here for \( E_{\text{ads}}^{\text{corr}} \) that the embedded Na$_2$Cl$_3$ cluster is for water adsorption a good model for NaCl(001).

Having established that the embedded Na$_2$Cl$_3$ cluster faithfully represents the NaCl(001) surface we now use this cluster to do better quality (and thus much more computationally demanding) calculations. Specifically we address three important and related issues, namely: (i) basis set incompleteness; (ii) the question of how much better quality (and thus much more computationally demanding) representation of the embedded cluster and periodic HF values gives us confidence that the long range electrostatic potential of the substrate is recovered with our embedding approach and that for water adsorption the Na$_2$Cl$_3$ cluster is a good model of the true periodic substrate.

Finally, the value reported so far corresponds to adsorption on a fixed NaCl slab. As we have said the atoms at the surface do not remain at their bulk truncated positions, neither before [40] nor after adsorption. To estimate the importance of substrate relaxations on \( E_{\text{ads}} \), we performed DFT calculations on fixed and relaxed NaCl slabs with the PBE, RPBE, and LDA xc functionals. Here, DFT provides a consistent picture with each functional yielding a \( \approx 30 \text{ meV} \) larger \( E_{\text{ads}} \) on the relaxed NaCl(001) surface. Thus we can estimate that the adsorption energy on a relaxed NaCl(001) surface is likely to be \( \approx 517 \text{ meV} \).

In conclusion, we have followed a procedure to reach high accuracy in molecular adsorption energies at ionic surfaces. The route involves a separation of the adsorption energy into contributions from HF and electron correlation, embedded cluster models of the substrate, and extrapolations to the complete basis set limit. This leads to a value of \( E_{\text{ads}} \) for a monomer on a fixed NaCl(001) surface of \( \approx 487 \text{ meV} \) and \( \approx 517 \text{ meV} \) on a relaxed surface. These are likely the most reliable theoretical estimates of the adsorption energy of water on NaCl(001). However, we caution that we certainly do not expect that the preliminary estimate of the adsorption energy reported here is the “exact value”. Almost certainly there remains some error in our estimate, incurred as a result of the necessary approximations made (e.g., adoption of the PBE structure and extrapolations to obtain the CBS limit). In current work we are focussing on establishing precise “error bars” associated with each part of the adsorption energy estimate reported here and in making comparisons to available experimental data [41].

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For the periodic HF calculations the CRYSTAL code was used (R. Dovesi et al., CRYSTAL06 User’s Manual, Universita’d di Torino, 2006), with a water coverage of 1/8 monolayer. Examination of the coverage dependence of the water adsorption energy indicates that at this coverage the water-water interaction is negligible (about 1 meV).
References