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How strong is the bond between water and salt?

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ABSTRACT

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 that provided by density-functional theory (DFT). If combined with the supercell approach, one can ensure that the treatment of the exchange-correlation (xc) functional remains the only relevant approximation. The fact that DFT with the supercell approach is still far from achieving chemical accuracy in adsorption energies is illustrated by the example of water on salt. For the "simple" case of a water monomer on the perfect (001) surface, the predicted values, obtained with three widely used xc functionals, range from 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

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[1] Sometimes chemical accuracy is referred to as a precision of 1–2 kcal/mol or 2 kcal/mol. Here, we adopt the stricter and more common definition of 1 kcal/mol.

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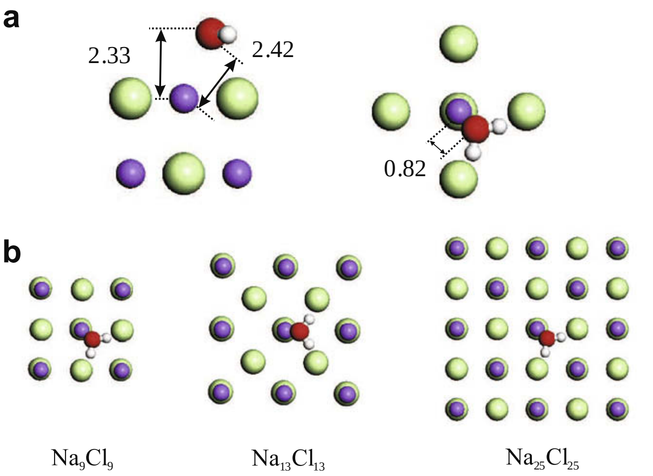

Fig. 1. (a) Side and top view of the most stable structure of a water molecule adsorbed on NaCl(001) as obtained from DFT-PBE, displayed here on an Na_5Cl_5 cluster. Distances are given in Å. (b) The larger stoichiometric 2 layer clusters used (top view). Red, white, purple, and green spheres are oxygen, 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.)

on NaCl(001). The route adopted involves a separation of the adsorption energy (E_{ads}) into contributions from Hartree–Fock (HF) (E_{ads}^{HF}) and electron correlation (E_{ads}^{corr}), the use of embedded cluster models of the substrate, and extrapolations to the complete basis set (CBS) limit. For the treatment of electron correlation we employ second order Møller–Plesset perturbation theory (MP2) and coupled cluster with single and double excitations plus a perturbative correction for connected triples (CCSD(T)). Upon following the above "roadmap" we arrive at a value of E_{ads} for a monomer on a fixed NaCl(001) surface of ≈487 meV and ≈517 meV on a relaxed surface. These values should serve well to benchmark future experimental and theoretical studies of water on NaCl.

At the outset we determine the most stable adsorption site and adsorption structure for a water molecule on the surface. To this end we performed a series of periodic DFT calculations for water adsorption at low coverage.[2] In agreement with previous DFT studies [2–5], the most stable structure for a monomer on NaCl(001) is 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 hydrogens are directed at neighboring Cls. The Na and Cl atoms of the substrate undergo on the order of 0.05 Å displacements from their bulk truncated positions. This is also the most stable configuration predicted when MP2 is used to examine adsorption on NaCl clusters and it matches the 1 ML water/NaCl(001) structure characterized by helium atom scattering [25]. Of course the precise height of the oxygen above the surface differs with the various functionals (within 0.3 Å for the LDA, PBE and RPBE xc functionals). Here, we adopt the PBE structure obtained on a fixed NaCl surface and use it for all subsequent (cluster) calculations. The importance of substrate relaxations will be discussed at the end.

Now we explore water adsorption on NaCl clusters[3] [26,27]. The first aim is to identify a suitable cluster set-up that will for water adsorption faithfully mimic the NaCl(001) surface but is still small enough that explicitly correlated calculations with very large basis sets on it remain within reach. To this end we systematically explore the dependence of the water adsorption energy on cluster size, using the following series of two layer NaCl clusters: Na_5Cl_5, Na_9Cl_9, $Na_{13}Cl_{13}$, and $Na_{25}Cl_{25}$. We find that E_{ads}^{HF} and E_{ads}^{corr} exhibit distinct behavior with cluster size (see below) and so for the discussion that follows we split E_{ads} into these two contributions, i.e., $E_{ads} = E_{ads}^{HF} + E_{ads}^{corr}$.

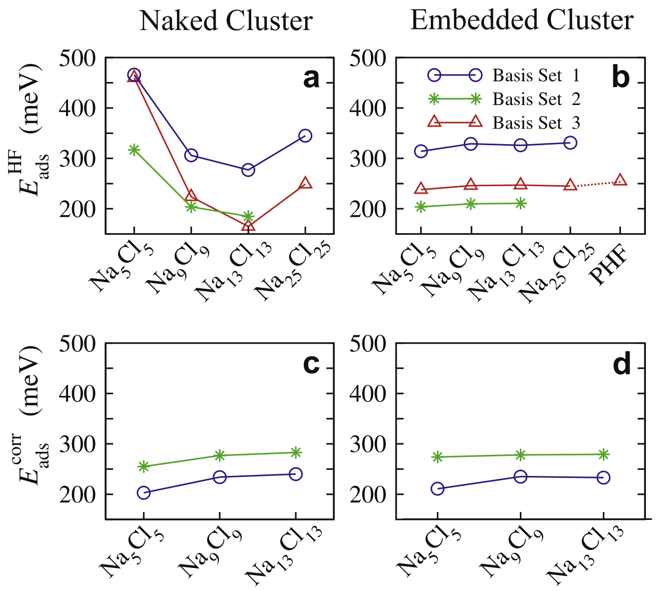

Fig. 2. Variation of the HF (E_{ads}^{HF}) and electron correlation (E_{ads}^{corr}) contribution to the adsorption energy with respect to cluster size for three basis sets without embedding (a,c) and with embedding (b,d). PHF: periodic HF calculations. Basis set 1: O,H,Cl = 6-311G*, Na = 6-31G; Basis set 2: all = cc-pVTZ; Basis set 3: O,H = 6-311G*, Cl = 86-311G, Na = 8-511G. The same adsorption geometry has been used throughout.

First, we deal with E_{ads}^{HF}. Fig. 2(a) displays the dependence of E_{ads}^{HF} on the clusters shown in Fig. 1 for three (small) basis sets. Consistently, a strong (>100 meV) dependence of E_{ads}^{HF} on cluster size is observed and, moreover, E_{ads}^{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.[4] A clear reduction in the cluster size dependence of E_{ads}^{HF} can be observed. For all basis sets E_{ads}^{HF} becomes much less sensitive to cluster size and E_{ads}^{HF} calculated with the Na_5Cl_5 cluster is within ≈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_5Cl_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 adsorption energy matches that on the Na_5Cl_5 cluster to within only $\approx$20 meV.[5] 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_5Cl_5 cluster is a good model of the true periodic substrate.

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[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 × 4 Monkhorst–Pack *k*-point mesh per 1 × 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 comparision 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 × 21 × 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].

Next, we explore the dependence on cluster size of $E^{\rm corr}_{\rm ads}$, 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 $E^{\rm corr}_{\rm ads}$ is less sensitive to cluster size than $E^{\rm HF}_{\rm ads}$ is: the variation on all three clusters examined is <36 meV. Nonetheless, embedding helps to reduce the dependence on cluster size; reducing the variation to 25 meV or less. As we saw for $E^{\rm HF}_{\rm ads}$, we see here for $E^{\rm corr}_{\rm ads}$ that the embedded Na_5Cl_5 cluster is for water adsorption a good model for NaCl(001).

Having established that the embedded Na_5Cl_5 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 which electrons need to be correlated; and (iii) an improvement upon the MP2 treatment of electron correlation.

First, the basis sets. So far we have employed rather small Gaussian-type basis sets which will lead to basis set incompleteness errors in $E_{\rm ads}$. To eliminate these errors we employ Dunning's correlation consistent basis sets, cc-pV*X*Z, aug-cc-pV*X* Z, and aug-cc-pCV*X* Z (X = 3, 4 and 5) [31,32], counterpoise corrections for basis set superposition error (BSSE), and standard heuristic schemes for extrapolating to the CBS limit (for more details see e.g. [1,33,34]). For extrapolation of the HF energies we employ an exponential fit:

$$E_X = E^{\rm HF}_{\rm CBS} + Ae^{-BX} \tag{1}$$

and for extrapolation of the correlation energies we use

$$E^{corr}_{CBS} = \frac{X^3}{X^3-(X-1)^3}E_{(X)} - \frac{(X-1)^3}{X^3-(X-1)^3}E_{(X-1)} \tag{2}$$

where E_X is the energy computed with the corresponding basis set (X =3, 4, 5), $E_{\rm CBS}$ is the energy at the CBS limit, and A and B are fitting parameters. As input to the HF extrapolation we use BSSE corrected 3-, 4-, and 5-ζ data and for extrapolation of the correlation energy BSSE corrected 3- and 4-ζ data. Using the above scheme we obtain CBS HF and MP2 correlation contributions to the adsorption energy of 191 and 244 meV, respectively. This leads to a preliminary estimate of $E_{\rm ads}$ at 435 meV, which we strive to further improve.

Second, we address the question of which electrons need to be correlated in this system in order to achieve very high accuracy. So far in the calculations of $E^{\rm corr}_{\rm ads}$ only the valence electrons (see Table 1 for a classification) have been correlated. This is the so-called "frozen core" approach, which is common practice since sub-valence electrons are generally known not to participate in chemical bonding. However, occasionally, correlating only the valence electrons can introduce non-negligible errors, particularly for alkali metals [35–38]. Indeed, we find here that inclusion of sub-valence correlations is important to this system with the frozen core and all-electron calculations differing by 62 meV (Table 1). A careful series of calculations in which the contributions to $E^{\rm corr}_{\rm ads}$ for each of the elements in this system is explored, reveals that the crucial difference between the frozen core and all-electron correlation calculations is the Na 2*s* and 2*p* electrons. Indeed, as can be seen from Table 1, using the frozen core approximation for H, O, and Cl and correlating the 2*s* and 2*p* electrons of Na yields an $E^{\rm corr}_{\rm ads}$ within 3 meV of the all electron correlation calculations.

Table 1
Variation of $E^{\rm corr}_{\rm ads}$ (at the MP2 level) on the electrons correlated and frozen for the adsorption of a water molecule on an embedded Na_5Cl_5 cluster.

Elements	Frozen	Correlated	$E^{\rm corr}_{\rm ads}$ (CBS) (meV)
O	1*s*	2*s*, 2*p*	
Cl	1*s*, 2*s*, 2*p*	3*s*, 3*p*	244
Na	1*s*, 2*s*, 2*p*	3*s*	
O	1*s*	2*s*, 2*p*	
Cl	1*s*, 2*s*, 2*p*	3*s*, 3*p*	303
Na	1*s*	2*s*, 2*p*, 3*s*	
O	None	1*s*, 2*s*, 2*p*	
Cl	"	1*s*, 2*s*, 2*p*, 3*s*, 3*p*	306
Na	"	1*s*, 2*s*, 2*p*, 3*s*	

Third, we go beyond MP2 and in so-doing evaluate its performance. We do this here by employing the quantum chemistry "gold standard" CCSD(T). Specifically, we determine the difference between MP2 and CCSD(T) at the triple-ζ level, i.e., the so-called ΔCCSD(T) approach [39]. The Na 2*s* and 2*p* electrons are included in the CCSD(T) calculations and a cc-pCVTZ basis set employed. Given the $\approx N^7$ scaling, where N is the number of basis functions, these CCSD(T) calculations required an enormous computational effort. With this set-up the difference between $E^{\rm corr}_{\rm ads}$ at the MP2 and CCSD(T) levels is just 10 meV. Specifically, $E^{\rm corr}_{\rm ads}$ is 10 meV less with CCSD(T), thus reducing our estimate of $E_{\rm ads}$ to 487 meV.

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 $E_{\rm ads}$ 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 meV larger $E_{\rm ads}$ 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 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 $E_{\rm ads}$ for a monomer on a fixed NaCl(001) surface of $\approx$487 meV and $\approx$517 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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[5] For the periodic HF calculations the CRYSTAL code was used (R. Dovesi et al., CRYSTAL06 User's Manual, Universit'a 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

[1] T.H. Dunning, J. Phys. Chem. A 104 (2000) 9062.
[2] H. Meyer, P. Entel, J. Hafner, Surf. Sci. 177 (2001) 488.
[3] J.M. Park, J.H. Cho, K.S. Kim, Phys. Rev. B. 69 (2004) 233403.
[4] Y. Yang, S. Meng, E.G. Wang, Phys. Rev. B. 74 (2006) 245409.
[5] P. Cabrera-Sanfelix, A. Arnau, G.R. Darling, D. Sanchez-Portal, J. Phys. Chem. B 110 (2006) 24559.
[6] L. Liu, M. Krack, A. Michaelides, J. Am. Chem. Soc. 130 (2008) 8572.
[7] N. Lopez et al., J. Chem. Phys. 110 (1999) 4873.
[8] C. di Valentin et al., J. Chem. Phys. 117 (2002) 2299.
[9] Q.M. Hu, K. Reuter, M. Scheffler, Phys. Rev. Lett. 98 (2007) 176103;
Q.M. Hu, K. Reuter, M. Scheffler, Phys. Rev. Lett. 99 (2007) 169903. E.
[10] A. Stroppa et al., Phys. Rev. B 76 (2007) 195440.
[11] A. Michaelides, Faraday Disc. 136 (2007) 287;
A. Michaelides, K. Morgenstern, Nature Mater. 6 (2007) 597.
[12] See, for example: M. Dion et al., Phys. Rev. Lett. 92 (2004) 246401;
O.A. von Lilienfeld et al., Phys. Rev. B 71 (2005) 195119;
T. Schwabe, S. Grimme, Phys. Chem. Chem. Phys. 9 (2007) 3397.
[13] J. Sauer, Chem. Rev. 89 (1989) 199.
[14] G. Pacchioni, J. Ricart, F. Illas, J. Am. Chem. Soc. 116 (1994) 10152.
[15] J.L. Whitten, H. Yang, Surf. Sci. Rep. 24 (1996) 55.
[16] M.A. Nygrena, L.G.M. Pettersson, J. Chem. Phys. 105 (1996) 9339.
[17] S. Humbel, S. Sieber, K. Morokuma, J. Chem. Phys. 105 (1996) 1959.
[18] U. Gutdeutsch, U. Birkenheuer, S. Krüger, N. Rösch, J. Chem. Phys. 106 (1997) 6020. and references therein.
[19] P. Sushko, A.L. Shluger, C.R.A. Catlow, Surf. Sci. 450 (2000) 153.
[20] M. Seth, P.M. Margl, T. Ziegler, Macromolecules 35 (2002) 7815.
[21] P. Huang, E.A. Carter, J. Chem. Phys. 125 (2006) 084102.
[22] C. Tuma, J. Sauer, Phys. Chem. Chem. Phys. 8 (2006) 3955.
[23] B. Li, A. Michaelides, M. Scheffler, Phys. Rev. Lett. 97 (2006) 046802.
[24] T. Klüner, N. Govind, Y.A. Wang, E.A. Carter, J. Chem. Phys. 116 (2002) 42.
[25] L.W. Bruch et al., J. Chem. Phys. 103 (1995) 5109.
[26] M.J. Frisch et al., Gaussian 03, Revision C.02, Gaussian, Inc., Wallingford CT, 2004.
[27] E.J. Bylaska et al., NWChem, A Computational Chemistry Package for Parallel Computers, Version 4.7, 2005, Pacific Northwest National Laboratory, Richland, Washington 99352-0999, USA.
[28] E.A. Colbourn, W.C. Mackrodt, Surf. Sci. 143 (1984) 391.
[29] M.A. Nygren, L.G.M. Pettersson, Z. Barandiarhn, L. Seijo, J. Chem. Phys. 100 (1994) 2010.
[30] J.A. Mejías et al., Surf. Sci. 327 (1995) 59.
[31] T.H. Dunning, J. Chem. Phys. 90 (1989) 1007.
[32] D.E. Woon, T.H. Dunning, J. Chem. Phys. 103 (1995) 4572.
[33] A.K. Wilson, T.H. Dunning Jr., J. Chem. Phys. 106 (1997) 8718.
[34] B. Santra, A. Michaelides, M. Scheffler, J. Chem. Phys. 127 (2007) 184104.
[35] C.W.J. Bauschlicher, S.R. Langhoff, H. Partridge, J.E. Rice, J. Chem. Phys. 95 (1991) 5142.
[36] D. Feller, E.D. Glendening, D.E. Woon, M.W. Feyereisen, J. Chem. Phys. 103 (1995) 3526.
[37] A. Schulz, B.J. Smith, L. Radom, J. Phys. Chem. A 103 (1999) 7522.
[38] M.A. Iron, M. Oren, J.M.L. Martin, Mol. Phys. 101 (2003) 1345.
[39] P. Jurečka, P. Hobza, Chem. Phys. Lett. 365 (2002) 89.
[40] B. Li, A. Michaelides, M. Scheffler, Phys. Rev. B 76 (2007) 075401.
[41] B. Li, A. Michaelides, M. Scheffler, in preparation.
[42] S.J. Clark et al., Zeitschrift fur Krystallographie 220 (2005) 567.