The structure of water on the (0001) surface of graphite

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Abstract

The structure of water layers on the close-packed surface of graphite has been studied using electronic structure total energy computations. At all coverages, the water molecules are found to be only physisorbed, lying at least 3.5 Å above the graphite and showing no bonding interactions evidenced in electronic orbitals or total electron density. At low coverages, the water shows little preference for orientation or surface site. Increasing coverage by reducing the size of the unit cell leads to a preference for orientation of molecules such that the dipole is parallel to the surface. This is shown to arise from the electrostatic interaction of molecules with their own periodic images. The structures of small water clusters are found to agree with those determined for free, gas-phase clusters. Further increases of coverage lead to the formation of extended ice-like layers.

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1. Introduction

The adsorption of water on the surfaces of metals has been much studied due to its importance in electrochemistry, corrosion and catalysis. It is generally accepted [1] that the initial layers form an ice-like bilayer of puckered hexagonal rings with each O atom hydrogen bonded to three neighbours, as in the (0001) surface of hexagonal ice Ih [2]. It has also been suggested on the basis of density functional theory (DFT) total energy calculations that the water can be partially dissociated [3], supported by further DFT calculations showing H2O stably coadsorbed with OH [4]. The structure of water itself is of greater importance in atmospheric chemistry. Ice is present in clouds and may be involved as a catalyst in reactions involved in ozone depletion. Ice is also important in the astrophysical environment, present in comets and in protoplanetary clouds [5,6]. In these environments, the ice is often not pure water. Dust grains in interstellar space are believed to be largely carbonaceous and silicate particles coated with ices [7]. Chemistry, in particular photochemistry, that occurs on these ice-covered particles is believed to play an important role in the formation of molecules in outer space [8–10]. Similarly ice in the atmosphere often forms on soot particles from industrial pollution.

Graphite is a good surface science model for the structure of dust grains. Chakarov and Kasemo [11,12] have shown that ice will grow in an amorphous, clustered fashion on graphite when
deposited at \(T_s < 100\) K. Irradiation with UV photons causes the ice film to crystallize by an indirect mechanism; the decrease of crystallization with film thickness indicates a substrate mediated mechanism involving tunnelling of hot electrons from the graphite to the \(\text{H}_2\text{O}\) molecules. The water is presumed not to interact chemically with the graphite, and the clusters should then have the same structures as those found for isolated water clusters. However, recent photochemical experiments [13] have observed an intriguing and counter-intuitive coverage dependence of the product yields of \(\text{D}^+\) and \(\text{D}_3\text{O}^+\): at low coverages, \(\text{D}_3\text{O}^+\) desorption dominates at high photon energies, while the fraction of \(\text{D}^+\) desorbed increases with the coverage. The \(\text{D}^+\) presumably desorbs from dangling bonds, however, both the orientation and the relative number of dangling bonds should change with coverage and this will affect the yield of \(\text{D}^+\). To interpret these, it is essential that we better understand the structure and binding of the adsorbed water layers. In this paper, we address this issue by computing the optimised geometries formed by water molecules adsorbed at various coverages on the (0001) surface of graphite.

2. Computational details

All computations of electronic total energies have been done using the CASTEP programs [14,15]. These use a plane-wave basis set with ultra-soft pseudo-potentials. DFT is used to describe the exchange correlation potential, specifically, we used the PW91 [16] version of generalized gradient approximation (GGA), as has been done for water adsorption on metal surfaces. Our comparison with gas-phase water cluster calculations may suffer somewhat from the use of this functional rather than another, as in gas-phase work [17] it is more common to use the B3LYP GGA. However, we are primarily interested in the gross features of the bonding, rather than in precise descriptions of the many, nearly degenerate isomers of water clusters, and so this difference is not significant.

The graphite substrate was represented by a single layer. This was found to be sufficient because of the very large interplanar spacing in graphite and because, as we shall discuss below, the water molecules are adsorbed more than 3.5 Å from the surface at all coverages. CASTEP uses a supercell/slab geometry to represent the surface, with the vacuum approximated by a large gap between periodic repeats of the substrate slab. We have used a vacuum gap of 10.6 Å. This was found to be large enough for all calculations. Graphite is metallic, and although the valence band only crosses the Fermi energy at one point in the Brillouin zone [18], we should in principal use the standard methods for treating a metal, namely smeared, partial occupancy of levels, and a larger set of \(k\)-points on which the wave function is calculated. Again, because of the very large separation between the water and graphite, we find that it makes no difference whether we use a metallic or insulator treatment. Although the total energies differ, the relative energies of different structures are the same, as are the optimised structures themselves. This was confirmed explicitly for the adsorption of a single molecule in a \(2 \times 2\) unit cell, for which optimised geometries were essentially identical using a metallic treatment with 25 \(k\)-points and energy cutoffs of 450–1200 eV or using an insulator treatment with only 1 or 2 \(k\)-points and an energy cutoff of 380 eV. In the following, therefore, we have used the less expensive insulator treatment with a plane wave cutoff energy of 400 eV, unless otherwise stated.

3. Results and discussion

3.1. Singly adsorbed molecules

The adsorption of a single molecule on a semi-infinite surface cannot be treated with the methods employed here, rather the molecule is adsorbed within a unit cell (usually larger than that of the underlying substrate), which repeats periodically. The size of the unit cell can be varied to change the surface coverage, but this leads to problems when the molecule interacts with itself (actually with its periodic images), as we shall discuss below. We have initiated optimised geometry searches with the molecule placed both close to and far from the
surface, in different high symmetry and low symmetry configurations in various sized unit cells. When the molecule is close to the surface, we find a very strong preference for it to bind hydrogens down rather than through the lone pair electrons on the oxygen. Indeed, during optimisation, the molecule will flip over to this orientation if it is initially O down. The interaction between the hydrogens and the carbons disturbs the sp$^2$ bonding in the graphite layer, causing it to buckle substantially. However, proceeding with optimisation, we find that this structure is much higher in energy than the ground state. For all initial configurations, we find that the molecule moves away from the surface by at least 3.5 Å, leaving behind a perfectly flat graphite layer. At this distance, the water is clearly physisorbed to the graphite. DFT does not accurately represent the physisorption interaction, and so we have not attempted to compute absolute adsorption energies for the water molecule, rather we concentrate on comparing the energies of similar geometries.

Optimized geometries can be obtained with molecules oriented hydrogens up or down by initially placing the molecule far enough from the surface to overcome any chemical bonding to the carbons. We find no significant dependence of the total energy on the adsorption site of the molecule, however, for small unit cell sizes, we find a strong preference for the water to be oriented with the molecular dipole in the plane of the surface. This is illustrated in Fig. 1, which shows the energy difference between a molecule with dipole oriented perpendicular to the surface and one with dipole oriented parallel to the surface as a function of the distance between the O atom and its neighbouring periodic image (i.e. the length of the unit cell). For the shortest O–O distance of 2.426 Å (one molecule per unit cell), the molecular geometries are not relaxed, because the optimised geometries are the same for both initial configurations. For the $2 \times 2$ adsorption geometry with an O–O distance of 4.832 Å, we have explicitly checked the convergence of the total energies with the number of $k$-points and the kinetic energy cutoff, treating the system as both metallic and insulating. We find that in all cases the molecules with parallel oriented dipoles are $\sim$0.1 eV lower in energy than the vertically oriented molecules, independent of the surface site and the actual orientation of the molecule itself (i.e. whether it is hydrogens up or down or whether the molecules with parallel dipoles lie in the plane of the surface or are tilted).

Fig. 1. Difference in total energy between water molecules adsorbed on graphite (0001) with dipole perpendicular to the surface plane, and water molecules adsorbed with dipole parallel to the surface as a function of the separation of the oxygens on adjacent water molecules. Only one molecule is adsorbed per computational unit cell, so the O–O distance is actually the size of this unit cell, and the molecules are identical.

Since it is a function of the unit cell size, the energy difference between the vertical and parallel orientations is clearly an ‘artefact’ of the supercell geometry. If we examine the structure of the complete overlayer, we find not only a preference for the orientation of the molecular dipole with respect to the surface plane, but also a particular orientation of the water molecules with respect to their (identical) neighbours, shown in Fig. 2a for a flat-lying molecule. This preferred orientation is due to the electrostatic interaction between the neighbouring molecules. If we simply sum the electrostatic potentials for each of the three atoms of a molecule interacting with the atoms of its six neighbours (using atomic charges obtained from CASTEP using Mulliken population analysis), then we get the result shown in Fig. 2b, as a function of the angle orientation of the molecule with respect to its neighbours. $0^\circ$ corresponds to the geometry of Fig. 2a, and in this configuration we can see that the hydrogens point almost exactly to the oxygens of the neighbouring molecules giving a favourable interaction. This pattern repeats after $60^\circ$ due to the rotational symmetry of the surface. At an angle of $30^\circ$, the hydrogens are
less favourably oriented with respect to neighbouring oxygens because these subtend an angle of only 60° at the central molecule and the H–O–H bond angle is ~104.5°. The attractive hydrogen-oxygen interaction is therefore not as great and overall there is an increase in potential. This simple electrostatic model also explains the lower total energy of molecules oriented with dipoles parallel to the surface compared to the perpendicular orientation. For the perpendicular orientation, the molecules are all oriented hydrogens up or down and so there can be no favourable electrostatic interaction of O and H on neighbouring molecules to lower the energy. The reduction in the electrostatic interaction with distance is mirrored in the reduction of the energy difference of perpendicular and parallel orientations with increasing molecular separation.

In the 4 × 4 geometry, the molecules are separated by ~9.7 Å. This represents an almost isolated molecule, as evidenced by the smaller difference of ~44 meV between the parallel and vertical orientations of the molecule. For the former, the O–H bond length is 0.97 Å and the bond angle is 104.7° compared to gas-phase values of 0.96 Å and 104.5°. For the latter orientation, the molecular bond length is similar, 0.973 Å, but the bond angle is increased to 105.3°. There is no obvious reason for this increase in the bond angle; however, we have found this to be a general feature of the vertical orientation irrespective of whether the hydrogens are up or down and independent of adsorption site. For both orientations, the charge transfer from hydrogen to oxygen is similar ~0.55 electrons per H atom, as determined by Mulliken population analysis. The total energy and structure of the water molecule is essentially independent of the adsorption site, except that when adsorbed on the atop site, there is a weak preference for the molecule to tilt so that one hydrogen points down to the centre of a carbon hexagon where there is a slight depression in the electron density.

3.2. Adsorption of clusters

Adding a second molecule to the 2 × 2 unit cell, we can approximate an adsorbed water dimer. The starting point for geometry optimisation of this structure was an up-pointing molecule adsorbed next to a down-pointing molecule. Two minimum energy structures can be found after optimisation, differing in energy by an insignificant amount of ~14 meV. The structures are shown in Fig. 3. Both are composed of one molecule lying flat on the surface, indicated on the right, and one molecule oriented with a hydrogen pointing towards or away from the surface. These structures are very similar to those found for isolated water dimers using a wide range of electronic structure methods.
O–O separations of 2.9–2.99 Å compare favourably with our value of 3.02 and 3.08 Å. The overall appearance is not quite correct, however. For an isolated dimer, the left-hand molecule should be rotated so that both hydrogens point downwards/upwards to the left and the right-hand molecule should be rotated until the non-bonded hydrogen points upwards/downwards. Also, the bond lengths and angles should be similar to those of isolated molecules, whereas we have elongated bonds and one bond angle noticeably smaller and the other considerably larger. These differences arise from the finite unit cell size. Examination of the structure on a larger scale shows that there is again considerable bonding across the unit cell boundaries. The two ‘edge’ hydrogens in the plane bond to oxygens in the neighbouring unit cells. Overall the structure is an open hexagonal hydrogen-bonded network, as shown in Fig. 4a.

Increasing the coverage to examine the water trimer, we find similar hydrogen bonding across the unit cells. The extended structure now breaks into a recognizable bilayer, although with only three molecules in a 2 × 2 unit cell, the structure is more open than a complete bilayer. For isolated trimers, the structure is a triangular ring [17]. We find that in the same (rather small) unit cell this structure is only 14 meV higher in energy than the extended bilayer. This small difference results from compensation by the more favourable bonding within the cluster for the less favourable hydrogen bonding to molecules in adjacent unit cells.

Hexamers represent an important breakpoint in the structures of water clusters [17]. For smaller clusters, the optimum structures are planar rings. This is also true of the hexamer, but there are a great many almost degenerate isomers having three-dimensional structures. We have examined two planar hexagonal structures and the three-dimensional prism cluster in a 4 × 4 unit cell. The higher energy ring structure was formed by truncating the two-dimensional layer in Fig. 4a to a single hexagon. This turns out to have considerably higher energy than a cluster with the same structure as the gas-phase buckled hexagonal ring shown in Fig. 4b. On close examination, this can be seen to result from the truncation of the extended structure. One water molecule is left bonding to two neighbours in the ring, while another has both hydrogens directed away from the ring. In the extended structure, one of these seemingly non-bonding hydrogens is actually connected to the neighbouring ring, thus reducing the overall energy.

Fig. 3. Two essentially degenerate optimum geometries determined for a water dimer adsorbed on a graphite (0001) surface. In (a) the non-bonding hydrogen points down to the graphite plane, while in (b) it is directed away. There is essentially no difference between these geometries because of the large distance between the molecules and the surface, indicative of a physisorption interaction. The H–O–H bond angles are substantially different from those of a free molecule (for which it is 104.5°) because of hydrogen bonding of molecules with their neighbours in the next computational unit cell, as shown in Fig. 4a.

[17,19,20]. O–O separations of 2.9–2.99 Å compare favourably with our value of 3.02 and 3.08 Å. The overall appearance is not quite correct, however. For an isolated dimer, the left-hand molecule should be rotated so that both hydrogens point downwards/upwards to the left and the right-hand molecule should be rotated until the non-bonded hydrogen points upwards/downwards. Also, the bond lengths and angles should be similar to those of isolated molecules, whereas we have elongated bonds and one bond angle noticeably smaller and the other considerably larger. These differences arise from the finite unit cell size. Examination of the structure on a larger scale shows that there is again considerable bonding across the unit cell boundaries. The two ‘edge’ hydrogens in the plane bond to oxygens in the neighbouring unit cells. Overall the structure is an open hexagonal hydrogen-bonded network, as shown in Fig. 4a.
The structure of the minimum energy ring is in good agreement with the structure obtained for an isolated ring [17]. The average O–O distance is 2.63 Å compared to 2.71 Å, while the minimum angle in the ring is 109° compared to 119°. This discrepancy in the angle is most likely due to an incompletely optimised structure; the maximum bond angle has the somewhat large value of 128°. The structure of the prism shaped cluster formed from two triangles bonded one above the other is also close to that of the isolated cluster [17]. The average O–O bond distance is 2.85 Å compared to 2.84 Å in the literature, and the minimum triangular bond angle is 58.7° compared to 57°. We find the energy of the prism structure to lie ~0.25 eV above that of the ring structure. This is somewhat higher than that found for isolated structures (~60 meV), however this is most likely due to an incompletely optimised geometry for the prism.

4. Conclusions

We have studied the structure of water layers on the close-packed surface of graphite using electronic structure total energy computations, employing pseudo-potentials, a plane wave expansion of the wave functions and the PW91 GGA to electronic exchange and correlation. Molecules forced close to the surface show a strong preference to bind hydrogens down, causing substantial buckling of the graphite layer. Such structures are, however, far from optimal, in all cases, for all surface sites and molecular orientations investigated, the minimum energy configuration has the water at least 3.5 Å above the surface, indicative of physisorption, and the graphite plane is flat. At low coverages (large unit cell sizes) there is no adsorption site or molecular orientation preference, but for compressed structures (small unit cell sizes) the electrostatic interaction between molecules and their periodic images in adjacent unit cells causes them to adopt configurations with molecular dipoles parallel to the surface plane. Clusters of water molecules on the graphite are found to be largely the same as those in the gas-phase, although again bonding across unit cell boundaries results in some distortion of the cluster shape. The graphite does not influence the structure of the water cluster in any way, the
molecule-surface distance remains at least 3.5 Å, even when extended ice-like structures are formed.

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References