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Interaction Energy of a Water Molecule with a Single-Layer Graphitic Surface Modeled by Hydrogen- and Fluorine-Terminated Clusters

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In ab initio calculations a finite graphitic cluster model is often used to approximate the interaction energy of a water molecule with an infinite single-layer graphitic surface (graphene). In previous studies, the graphitic cluster model is a collection of fused benzene rings terminated by hydrogen atoms. In this study, the effect of using fluorine instead of hydrogen atoms for terminating the cluster model is examined to clarify the role of the boundary. The interaction energy of a water molecule with the graphitic cluster was computed using ab initio methods at the MP2 level of theory and with the 6-31G(d=0.25) basis set. The interaction energy of a water molecule with graphene is estimated by extrapolation of two series of increasing size graphitic cluster models ($C_{6n^2}H_{6n}$ and $C_{6n^2}F_{6n}$, $n = 1-3$). Two fixed orientations of water molecule are considered: (a) both hydrogen atoms of water pointing toward the cluster (mode A) and (b) both hydrogen atoms of water pointing away from the cluster (mode B). The interaction energies for water mode A are found to be −2.39 and −2.49 kcal/mol for $C_{6n^2}H_{6n}$ and $C_{6n^2}F_{6n}$ cluster models, respectively. For water mode B, the interaction energies are −2.32 and −2.44 kcal/mol for $C_{6n^2}H_{6n}$ and $C_{6n^2}F_{6n}$ cluster models, respectively.

1. Introduction

The interaction energy of a water molecule with a graphitic surface, whether single-layer (graphene) or multilayer, is important for many applications ranging from biochemistry and nanotechnology to atmospheric science. This interaction energy is important for parametrizing force field parameters of the water−carbon atom of graphite. These parameters are then used in molecular dynamics (MD) simulations to study, for example, properties of nanotubes and fullerenes in water and to study water adsorption on an atmospheric soot aerosol.

It is believed that freshly formed soot is usually hydrophobic whereas aged soot can become hydrophilic and a condensation nucleus for cloud droplets.[1] This has important consequences on the lifetime of soot aerosols and water vapor in the atmosphere and on the absorption of solar radiation. To determine the properties of freshly formed soot and also the time scale for its hydrophobic to hydrophilic conversion, investigation by molecular dynamics simulation is needed. To perform simulations accurately, we need to use accurate force field parameters of water−carbon atom interactions.

There are two methods that can be used to estimate the force field parameters. The first method is by comparing molecular simulations with a measurement of the contact angle of water on a graphite surface. There is a range of experimental values for the contact angle of water on a graphite surface. Fowkes and Harkins[2] reported a contact angle of $\Theta = 86°$ and Schrader[3] has reported $\Theta = 42 \pm 7°$. Werder et al.[4] have carried out a series of molecular dynamics numerical simulations based on Lennard-Jones potentials for the water−carbon interaction. The contact angle Θ of a water droplet on a graphite surface was determined as a function of the binding energy of a single water molecule on the surface. Large values of this binding energy relative to the water−water interaction favor a small contact angle. From their numerical simulations Werder et al.[4] determined the values of the interaction energy corresponding to the above experimental contact angles to be −1.51 and −2.24 kcal/mol, respectively.

The second method to estimate the force field parameters is by performing ab initio computations. In previous studies, the electronic interaction energy (zero point energy excluded) was found to be[5,6] −5.8 ± 0.1 and −2.9 kcal/mol. In a recent as yet unpublished work Geldart et al.[7] estimated the electronic interaction energy to be −4.0 kcal/mol with the correction due to zero point energy being 0.3 kcal/mol. In all three of these studies, the interaction energy of a water with graphene is estimated by using a series of hydrogen-terminated cluster models where graphene is approximated by a series of fused benzene rings terminated by hydrogen atoms in the form of symmetric polycyclic aromatic hydrocarbons ($C_{6n^2}H_{6n}$ where n is an integer). Once the interaction energies are computed for different cluster sizes, the interaction energy of water and graphene is then estimated by extrapolating the interaction energies to the large size cluster limit. Discussion of these results will be given later. It is clear that there is considerable variation in the ab initio results (just as in the experimental contact angles).

In this paper, we determine the interaction energy of a water molecule and a graphite surface by performing ab initio computations using hydrogen-terminated and fluorine-terminated cluster models with the second-order Møller−Plesset perturbation theory (MP2) with medium basis set 6-31(d=0.25). The 6-31G(d=0.25) basis set was used previously by Raimondi et al.[8] in a study of the water−benzene−hexafluorobenzene complex and by Lee et al.[9,10] for benzene−naphthalene complex and the naphthalene dimer. We use medium basis sets because

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TABLE 1: Partial Charges C_6H_6 and C_6F_6 Computed Using the Merz−Kollman−Singh (MKS) Method[24,25] with the MP2/6-31G(d=0.25) Electron Density

molecule	C	H or F
C_6H_6	−0.123	0.123
C_6F_6	0.115	−0.115

[a] These partial charges are the average of six partial charges of the corresponding atoms. The C−C bond length used here is 1.421 Å, the C−H bond length is 1.084 Å, and the C−F bond length is 1.339 Å.

we consider large molecular structures. The use of fluorine atoms as terminating atoms for the cluster model of graphene, to our knowledge, has not been reported previously. It is expected that by increasing the size of the cluster, interaction energies computed by using hydrogen- and fluorine-terminated clusters should approach the same value as for the single-layer graphitic surface. Using a fluorine-terminated cluster, we have an additional test to confirm the value of interaction energies.

The extrapolation of the interaction energy to the large size cluster limit can be improved by removing contributions to the interaction energy, which are caused by the boundary of the clusters. This boundary effect is mainly due to electrostatic energy between charge distribution at the boundary of the clusters and water dipole moment. To see how the boundary charge distribution affects the interaction energy, we first look at the partial charges model of the clusters. As a first approximation in modeling a molecular system, one can compute the partial charges at the atomic centers in such a way that these partial charges reproduce the electric potentials surrounding the molecules. It is known from the ab initio calculation of benzene (C_6H_6) that the partial charges of the hydrogen atoms at the perimeter boundary are positive and the partial charges of the carbon atoms are negative[11] (see also Table 1). This produces dipole moments pointing outward from the center of the isolated benzene molecule. For larger clusters the terminating boundary causes a corresponding permanent multipole moment distribution on the cluster. Because the water molecule has a permanent dipole moment this indicates that the interaction energy of water−graphitic clusters is affected by the perimeter of the cluster. The electrostatic interaction is a long-range interaction; therefore the extrapolation procedure for obtaining the interaction energy of the water−graphene system can be greatly affected by the boundary. Because this long-range boundary effect varies with cluster size and is also totally extraneous to the water−graphene limit, it should be removed before the extrapolation procedure is performed.

We emphasize that this boundary effect is due to the termination of the cluster model. This also suggests that changing the terminating atoms, such as to fluorine atoms, may affect the extrapolation of the series of clusters. This is the reason for including the fluorine-terminated clusters in the determination of interaction energy of water−graphene. When the hydrogen atoms of C_6H_6 are replaced by fluorine atoms, giving hexafluorobenzene (C_6F_6), the sign of the partial charges changes because of the large electronegativity of fluorine. It is shown in Table 1 that the effect of fluorine is to produce positive partial charges on the carbons and negative partial charges on the fluorines. Therefore the sign of the partial charges on C_6F_6 is opposite to the partial charges on C_6H_6. This indicates that changing the terminating hydrogen atoms with the fluorine atoms produces a different series for modeling graphene and therefore an additional series to estimate the interaction energy. Opposite signs of the partial charges are also found for all larger clusters.

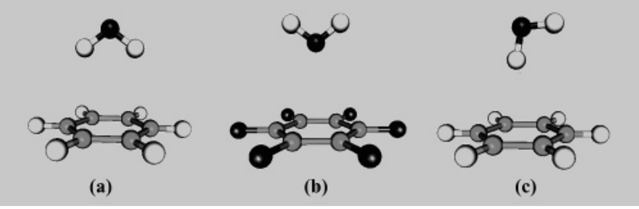

Figure 1. Orientations of a water molecule above benzene and hexafluorobenzene: (a) vibrational averaging structure of the water−benzene complex (two hydrogen atoms of water pointing toward the benzene ring (called mode A)); (b) optimized structure of the water−hexafluorobenzene complex (called mode B); (c) optimized structure of the water−benzene complex (one hydrogen atom of water pointing toward the benzene ring). The gOpenMol program is used for creating these illustrations.[31,32]

The effect of the boundary of clusters is also seen in the optimized configuration of water and graphite clusters. In previous studies of the water−C_6H_6 complex, water was found to have one hydrogen atom pointing toward the benzene ring, as shown in Figure 1c.[8,12] Although the structure in Figure 1c is the minimum electronic energy, the vibrational averaging structure of the water−C_6H_6 complex was found to have both hydrogen atoms pointing toward the benzene ring (Figure 1a).[13] For the water−C_6F_6 complex, the stable structure of water is with the oxygen atom pointing toward the C_6F_6 ring (Figure 1b).[8,14] This is the opposite direction found in the case of water interacting with benzene (Figure 1a). This indicates that the effect of changing the boundary atoms in the cluster model can change the orientation of water. The electrostatic interaction between the dipole moments of the cluster boundary and the dipole moment of water is important in determining the orientation of the water above the cluster surface. Besides the electrostatic interaction, the dispersion interaction of water and the cluster boundary is also important but its magnitude is found to be smaller than that of the electrostatic interaction.

In ab initio computations of binding energy, energy optimization should be first performed. Full energy optimization with the MP2 level theory or any other correlated methods is computationally demanding, and therefore it can only be performed for small molecules. In the case of the water−graphitic cluster complex, the water molecular structure is optimized only for a small graphitic cluster. The optimized water structure obtained with the small graphitic cluster is then used to compute interaction energy of water with larger graphitic clusters. This implies that there is a bias in the structure of water on a single-layer graphite due to the optimization of water−small graphite cluster system. As a consequence, the resulting orientation of water might not be the true orientation of water above a graphene. If one uses hydrogen-terminated clusters ($C_{6n^2}H_{6n}$) as a model for the graphite layer, one starts with the water−C_6H_6 complex and finds the optimized water orientation is with a single hydrogen pointing to the cluster (as in Figure 1c). In a different case, if one uses fluorine-terminated clusters ($C_{6n^2}F_{6n}$), one starts with water−C_6F_6 complex and then the optimized water orientation is with both hydrogen atoms pointing away from the cluster (as in Figure 1b). Depending on the starting orientation and the performed optimization, one might find different final orientations for the water molecule interacting with the single-layer graphitic surface.

In this study, because the true optimized water structure on the graphite surface is a priori unknown, two orientations of water as in Figure 1a,b are investigated. The water orientation as in Figure 1c is not considered because it is known that the

TABLE 2: Interaction Energies (kcal/mol) with CP Correction and without CP Correction (in Parentheses) Computed Using the MP2 Method

	water in mode A		water in mode B	
cluster	X = H	X = F	X = H	X = F
C_6X_6	−2.55 (−4.68)	no minimum	no minimum	−2.32 (−5.38)
$C_{24}X_{12}$	−2.81 (−5.20)	−0.86 (−3.17)	−0.93 (−4.58)	−3.15 (−6.78)
$C_{54}X_{18}$	−2.80 (−5.28)	not available	−1.66 (−5.41)	not available

vibrational averaged structure for the water−benzene complex is as in Figure 1a.[13] Moreover, it is found by Lin et al.[6] that for the water−$C_{24}H_{12}$ complex, the orientation of water is as in Figure 1a.

The purpose of this paper is to investigate the effect of the cluster boundary and the orientation of water on the interaction energy of water and a graphene surface. The remainder of this paper is divided into three sections. The next section gives the method used in this investigation. The results of computations and discussions are shown in section 3. The last section summarizes the conclusions.

2. Methodology

In this study all of the ab initio calculations are done by using the Gaussian98 and Gaussian03 packages.[15,16] The correlation energy is included by employing a second-order Moller−Plesset perturbation theory (MP2) calculation with frozen core approximation. In this study, the 6-31G(d=0.25) basis set is used. The 6-31G(d=0.25) basis set is the same as 6-31G(d) but with an exception that the exponent of the *d* functions in the 6-31G-(d) basis set (equal to 0.8) is replaced by 0.25, thereby making it more diffuse.[17] Larger basis sets such as correlated consistent basis sets with diffuse functions (e.g., aug-cc-pVDZ or aug-cc-pVTZ) lead to linear dependency problems for clusters larger than C_6H_6 and C_6F_6 and so are not included in this study. The basis set superposition errors (BSSE) are corrected by the counterpoise (CP) method of Boys and Bernardi.[18] The CP correction is included in computation of interaction energies and in geometry optimizations by using a method described in ref 19.

For the graphite−cluster model, fixed carbon−carbon (C−C), fixed carbon−hydrogen (C−H) and fixed carbon−fluorine (C−F) bond lengths are used. The C−C bond length[20,21] is 1.421 Å, and the C−H bond length[22] is 1.084 Å. The C−F bond length of 1.339 Å found in 1,3,5-trifluorobenzene[23] is used. The use of a fixed C−C bond length of bulk graphite is justified, because our main interest is the interaction of water and an infinite graphene.

In this paper we consider two orientations of water above a cluster surface: (a) the two hydrogen atoms of water pointing toward the cluster surface as in Figure 1a (here it is called mode A) and (b) the two hydrogen atoms of water pointing away from the cluster surface as in Figure 1b (it is called mode B).

It is known from previous studies that the axis of C_{2v} symmetry of water coincides with the center of the cluster and the plane of C_{2v} symmetry coincides with the D_{6h} symmetry plane of the cluster.[14] To reduce the computational burden, the water−graphite cluster system is constrained to have C_{2v} symmetry. In this paper only three variables are used for energy optimization: the distance of water above the center of the surface of the cluster, the oxygen−hydrogen bond lengths and the hydrogen−oxygen−hydrogen bond angle of water. The minimum interaction energy is searched by optimizing all these variables.

TABLE 3: Optimized Distances (Å) of Water Molecule and the Surface of Graphitic Clusters Obtained Using the MP2/6-31G(d=0.25) Method

	water in mode A		water in mode B	
cluster	X = H	X = F	X = H	X = F
C_6X_6	3.45	no minimum	no minimum	3.18
$C_{24}X_{12}$	3.39	3.41	3.12	3.07
$C_{54}X_{18}$	3.41	not available	3.09	not available

3. Results and Discussion

The interaction energies with and without CP correction for different configurations of water above the graphite cluster and as a function of cluster size are given in Table 2. The optimized distances of oxygen of water and surface of graphitic cluster are shown in Table 3. It was found that C_6H_6 with water in mode B does not have a minimum configuration. The results for C54F18 using 6-31G(d=0.25) could not be determined due to limitation of computational resources.

It can be noted from these results that there are no pronounced trends in the interaction energies as a function of cluster size. However, the effect of boundary is clearly shown in these results. It can be seen clearly that changing terminating atoms from hydrogen atom to fluorine atom decreases the magnitude of interaction energies for water in mode A. This is in contrast to water in mode B where changing the terminating atom from hydrogen to fluorine produces an increase in magnitude of interaction energies. The interaction energy of the water−graphitic cluster system is lowered or raised by the presence of the terminating atoms depending on the electrostatic interaction between the multipole moments of clusters and the dipole moment of water.

Using a series of CP corrected interaction energies, an interaction energy of water−graphene is then estimated by extrapolating to large cluster size limit. To improve convergence of the series, the effect of boundary of the clusters must be removed before the extrapolation. To understand various contributions to the boundary effect, the interaction energies are partitioned into the electrostatic energies (ΔE_{ES}), induced energies (ΔE_{I}), exchange−repulsion energies (ΔE_{ER}) and correlation energies (ΔE_{CORR}):

$$\Delta E = \Delta E_{\mathrm{ES}} + \Delta E_{\mathrm{I}} + \Delta E_{\mathrm{ER}} + \Delta E_{\mathrm{CORR}} \tag{1}$$

Charge-transfer energy is not included in eq 1 because its contribution to the total interaction energy is negligible. The electrostatic energy includes the contribution due to the boundary of cluster. The exchange−repulsion energy is short-range energy; therefore there is a small variation with respect to the size of the cluster and it can be considered as a constant for all clusters. The induced energy is in the form of $C_{6,\mathrm{I}}/R^6$. Similarly, correlation energy at long-range distances varies as $C_{6,\mathrm{CORR}}/R^6$. Both induced energy and correlation energy also include the boundary contributions. The induced energy is generally much smaller compared to the correlation energy. Therefore the electrostatic energy and correlation energy of the water and cluster boundary are two main contributions of the boundary to the interaction energy.

To remove the electrostatic energy of the water and cluster boundary, the electrostatic energy of water and the cluster are first removed from the total interaction energy. The large cluster limit of the electrostatic interaction energy is then estimated separately by computing the total electrostatic energy of all carbons (having a permanent quadrupole moment) in a graphene with the dipole moment of water. In this study, the electrostatic energy of water and the graphitic cluster is computed by using the partial charge of water and the electrostatic potential due to the graphitic cluster at the positions of water atoms and using the expression

$$\Delta E_{\mathrm{ES}} = \sum_{i=1}^{3} q_i V_i \qquad (2)$$

where q_i is the partial charge of water computed using the MP2 electron density and the Merz−Kollman−Singh (MKS) method[24,25] and V_i is the potential at the position of the ith atom of water computed using the MP2 electron density of the isolated graphite cluster.

The electrostatic energies of the water−graphite cluster are shown in Table 4. It can be noted that the electrostatic energies are attractive for hydrogen-terminated clusters with water mode A and for fluorine-terminated clusters with water mode B. However, the electrostatic energies become repulsive when the orientations of water are reversed. It can also be noted that the magnitude of electrostatic energies decreases slowly as the size of the cluster increases.

After the electrostatic energy is removed, the correlation energy due to the boundary of the cluster also needs to be removed. This correlation energy is the interaction of perimeter hydrogen or fluorine atoms with water and is estimated by using a dispersion formula given by

$$\Delta E_{\mathrm{Corr\ perimeter}} = -C_6^{\mathrm{W-H,F}} \sum_{j=\mathrm{perimeter}} \frac{1}{R_{j\mathrm{O}}^{\ 6}} \qquad (3)$$

where $R_{j\mathrm{O}}$ is the distance from the oxygen atom of the water molecule to the jth atom of the cluster and $C_6^{\mathrm{W-H,F}}$ is a constant. This boundary correction is estimated by using a mixing formula and dispersion constants $C_6^{\mathrm{W-H,F}}$ given by Grimme.[26] The dispersion constants are computed to be 321.94 kcal/mol Å^6 for water−fluorine and 138.53 kcal/mol Å^6 for water−hydrogen.

After the electrostatic energy and the correlation energy of the water and cluster boundary are removed, the data are then fitted to the expression

$$\Delta E^{\mathrm{W-C}}(n) = \Delta E_{\mathrm{ER}}^{\mathrm{W-C}} - \sum_{j=\mathrm{all\ carbons}} \frac{C_6^{\mathrm{W-C}}}{R_{j\mathrm{O}}^{\ 6}} \qquad (4)$$

where $E^{\mathrm{W-C}}(n)$ is the computed interaction energy of the cluster of index n without the electrostatic energy and boundary dispersion contribution. $\Delta E_{\mathrm{ER}}^{\mathrm{W-C}}$ is the repulsion energy of water and the cluster, which is assumed to be constant for all clusters. The last term on the right-hand side is the induced and the dispersion interaction of water with the carbon atom of the clusters. $C_6^{\mathrm{W-C}}$ is a fitting constant. After obtaining the fitting parameters, eq 4 is then used to extrapolate to the large cluster limit of the interaction energy $\Delta E^{\mathrm{W-C}}(\infty)$.

TABLE 4: Electrostatic Energies (kcal/mol) of Water and Graphitic Clusters Computed Using Eq 2[a]

	water in mode A		water in mode B	
cluster	X = H	X = F	X = H	X = F
C_6X_6	−1.85			−1.53
$C_{24}X_{12}$	−0.89	1.22	0.87	−1.30
$C_{54}X_{18}$	−0.53		0.49	

[a] The partial charge of water is computed using the MKS method using the MP2 electron density. The electrostatic potentials at the atomic centers of water atoms are computed using MP2 electron density.

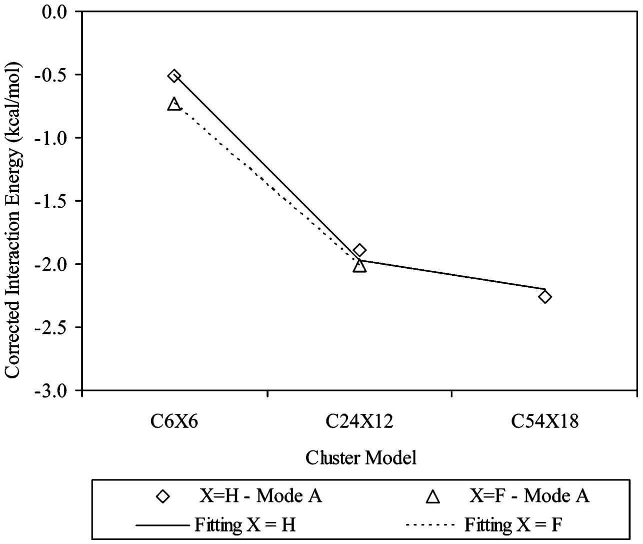

Figure 2. Fitting the corrected interaction energies of water mode A for hydrogen-terminated and fluorine-terminated clusters after electrostatic and boundary correlation energies are removed with the 6-31G-(d=0.25) basis set.

As seen in Table 3, the optimized distances of the oxygen of water above hydrogen-terminated or fluorine-terminated clusters are about 3.4 and 3.1 Å for water in mode A and water in mode B, respectively. To ensure that the repulsion energy of water and the cluster are the same for all clusters, we need to use the same water−cluster distance for all clusters. Therefore the interaction energies and electrostatic energies for water−C_6H_6 (mode B) and water−C_6F_6 (mode A) are recomputed for distances of 3.4 and 3.1 Å for water in mode A and water in mode B, respectively. The results of interaction energies with and without CP correction are given in Table 5.

The results of the corrected interaction energy and the fitting procedure are shown in Figures 2 and 3. It is noted that eq 4 can fit closely all the interaction energies. The interaction energies of water and the graphene limit are given in Table 6. It is noted that the interaction energies for a hydrogen-terminated cluster are in excellent agreement with the interaction energies for the fluorine-terminated cluster. This proves that the fluorine-terminated cluster can be used as an additional test for modeling graphene. The agreement between the results of hydrogen- and fluorine-terminated cluster models shows that the boundary effect has been accounted for accurately.

In the results of interaction energies without ES in Table 6, all the electrostatic energies are removed before the extrapolation procedure. This is done so that the electrostatic energies due to the perimeter are removed. As a consequence, the true electrostatic interaction of the water−graphite cluster has also been removed. To recover the electrostatic contribution to the total interaction energy, we compute the total electrostatic energy of

TABLE 5: Recalculation of Interaction Energies (kcal/mol) with and without (in Parentheses) CP Correction and Electrostatic Energies for Water−C_6H_6 and Water−C_6F_6 Computed with the 6-31G(d=0.25) Basis Set for Water in Modes A and B Using Water−Cluster Distances of 3.4 and 3.09 Å for Water in Mode A and Water in Mode B, Respectively

	water−C_6X_6 (mode A)		water−C_6X_6 (mode B)	
terminating atom	interaction energy	electrostatic energy	interaction energy	electrostatic energy
X = H	−2.54 (−4.81)	−1.93	1.62 (−1.66)	2.15
X = F	0.49 (−2.84)	1.50	−2.28 (−5.90)	−1.58

TABLE 6: Resulting Interaction Energies for Single-Layer Graphene Limit with and without Electrostatic Energy (ES) and the Resulting Fitting Constants for Two Orientations of Water and for 6-31G(d=0.25) Basis Set

				interaction energy (kcal/mol)	
orientation	terminating atom	ΔE_{ER}^{W-C} (kcal/mol)	C_6^{W-C} [kcal/(mol Å^6)]	without ES	with ES
water mode A	hydrogen	1.40	849	−2.39	−2.39
	fluorine	1.30	848	−2.49	−2.49
water mode B	hydrogen	2.46	735	−2.27	−2.32
	fluorine	2.68	788	−2.39	−2.44

all carbon atoms in a graphene with the dipole moment of water. It is found experimentally that carbon in graphite has a quadrupole moment[27] of -3.03×10^{-40} C m^2. Similar to previous calculations, the electrostatic interaction is computed by using the partial charges of water (obtained using MKS method with MP2 electron density) and eq 2, but now the potential V_i is given by[28]

$$V_i(x_i,y_i,z_i) = \frac{1}{8\pi\epsilon_0}\Theta_C\sum_j\left[\frac{3z_i^{\,2}}{R_{ij}^{\,5}} - \frac{1}{R_{ij}^{\,3}}\right] \tag{5}$$

where (x_i, y_i, z_i) is the position of the ith atom of water above the graphite surface, Θ_C is the quadrupole moment of carbon atom in graphite, and ϵ_0 is the permittivity of free space. R_{ij} is the distance of the ith atom of water and the jth carbon of graphite. By direct numerical summation, it is found that for water mode A, the electrostatic energy of water−graphene is −0.01 kcal/mol and can be neglected. For water mode B, the electrostatic energy is −0.05 kcal/mol. These values are comparable to the values given by Vernov and Steele.[29]

Adding the electrostatic energy to the results in Table 6, it is found that the interaction energies of water in mode A and a single layer graphite with the 6-31G(d=0.25) basis set are −2.39 and −2.49 kcal/mol for hydrogen- and fluorine-terminated clusters, respectively. For water in mode B, the interaction energies are −2.32 and −2.44 kcal/mol. We conclude that water in mode B has energy similar to that for water in mode A. This is not apparent from the small cluster interaction energies prior to correcting for the boundary. However, the preferred orientation of a water molecule on a graphene surface is still unknown. Taking an average of interaction energies for the two cluster models, the interaction energy of water and graphene is −2.44 and −2.38 kcal/mol for mode A and B, respectively. In comparison, Geldart et al.[7] computed the interaction energy using the MP2 method with large basis sets and with only hydrogen-terminated clusters, taking account of the boundary correction, and found an interaction energy of −4.0 kcal/mol. Using similar ab initio methods and clusters, but without boundary corrections, Feller and Jordan[5] found an interaction energy of −5.8 ± 0.1 kcal/mol. However, as indicated by Karapetian and Jordan,[30] the result of Feller and Jordan[5] has a large BSSE so that the error in the interaction energy is difficult to determine. In another study, Lin et al.[6] computed the interaction energy using a density functional theory (DFT) tight binding method with an empirical correction for dispersion, but also without the boundary correction, to be −2.9 kcal/mol. Our interaction energy about −2.4 kcal/mol is much closer to −2.9 kcal/mol of Lin et al.[7] and −4.0 kcal/mol of Geldart et al. and much less in magnitude than −5.8 kcal/mol of Feller and Jordan.[5] This verifies that correcting the boundary of the cluster model is necessary to get an accurate interaction energy of a water molecule and graphene and that consistent results are obtained using two different methods for terminating the cluster boundary. Our interaction energies are smaller than those of Geldart et al. because we used smaller basis set.

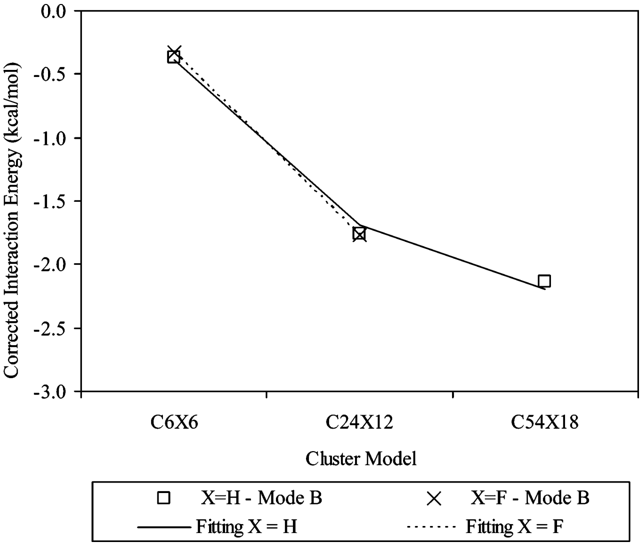

Figure 3. Same as in Figure 2 except that this is water mode B.

4. Conclusions

A graphitic cluster model with fluorine atoms instead of hydrogen as the terminating boundary has been successfully used for modeling the interaction of a water molecule with graphene. The terminating atoms for the cluster model affect strongly the interaction energy of the water molecule with a finite cluster. Removal of this boundary effect before any extrapolation to the large cluster limit sharply improves the accuracy of estimated interaction energies. With the removal of the boundary effect, it is found that the interaction energies using hydrogen-terminated clusters and fluorine-terminated clusters are in excellent agreement, which confirms that the effect of the boundary has been correctly removed and that interpretation is indeed correct. The interaction energies for water mode A using the 6-31G(d=0.25) basis set are found to be −2.39 and −2.49 kcal/mol for the hydrogen-terminated cluster and fluorine-terminated cluster, respectively. The interaction energies for water mode B are −2.32 and −2.44 kcal/mol for the hydrogen-terminated cluster and fluorine-terminated cluster respectively, which implies that mode B has the same energy as water mode A. It is concluded that the treatment of the boundary energy is correct and is necessary for the extrapolation to the graphene limit. The uncertainty in the water orientation on a graphitic surface will be resolved by future study using a larger size of basis sets and a higher level of theory to improve the interaction energies.

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