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Estimating the Strength of the Water/Single-Layer Graphite Interaction

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Second-order Møller−Plesset perturbation theory has been used to calculate the interaction energy between a water molecule and acenes as large as $C_{96}H_{24}$. The results of these calculations lead to an estimated value of −5.8 ± 0.4 kcal/mol for the electronic binding energy of a water molecule with single-layer graphite. This value is comparable to the −5.0 ± 0.1 kcal/mol binding energy of the hydrogen bonded water dimer, suggesting that the water/graphite interactions will play an important role in determining the structure of water on graphite, as well as of water inside carbon nanotubes. The present estimate of the binding energy of a water molecule to a graphite sheet is appreciably larger than those previously reported in the literature.

I. Introduction

Carbon nanotubes are elongated analogues of the spherical carbon molecules known as fullerenes or “buckyballs”. Alternatively, they can be considered to be formed from a single layer of graphite that has been rolled into a cylinder.[1−3] There has been growing interest in the properties of nanotubes[4] and in their abilities to function as very small chemical reaction chambers, or “nanoreactors”.[5,6] Because water is likely to be the preferred solvent for many applications, it is important from a theoretical point of view to develop a reliable computational model of the behavior of water in such an environment.

Carbon nanotubes are particularly intriguing because they can be created with a wide range of diameters, with the narrowest being on the order of 5 Å.[7] For the purpose of comparison, the diameter of the C_{60} fullerene is ∼7 Å. Inside narrow nanotubes, water may assemble into pseudo-one dimensional structures that exhibit significantly different behavior than bulk water. A proper description of both water−water and water−nanotube interactions will be critical for describing the behavior of such systems. Several good water−water and solute−water potentials are available in the literature.[8−15] However, reliable water−nanotube potentials do not yet exist and will need to be developed before molecular dynamics simulations of various solute/water mixtures inside a nanotube can be performed.

A natural starting point for this endeavor is the development of a model potential for water on single-layer graphite. Although there already exist model potentials for the water/graphite system, the reliability of these model potentials has not been tested, as there are no high quality ab initio data and surprisingly little experimental data. The existing water/graphite model potentials give binding energies for a single water monomer interacting with the surface ranging from −1.65 to −4.3 kcal/mol.[16,17] There also exists an experimental value of −3.6 kcal/mol for the binding energy.[18] However, these values seem somewhat low in light of the most recent high-level ab initio results for the water-benzene system, for which the electronic binding energy has been estimated to be −3.9 ± 0.2 kcal/mol.[19]

In this study, second-order Møller−Plesset perturbation theory (MP2) has been used to determine the binding energies of water to a sequence of centro-symmetric, fused-benzene ring structures, denoted $H_2O-(fbz)_n$, $n = 1-37$. This information, along with the results of future studies of water interacting with models of carbon nanotube walls, will be useful for parametrizing the classical force field previously discussed.

II. Procedure

In this work, a sequence of increasing size carbon clusters was employed to model the graphite surface. These clusters range from an isolated benzene molecule to a system with 37 fused benzene rings, denoted $(fbz)_{37}$. Intermediate-sized models with 4, 7, and 19 fused benzene rings are also considered. The estimate of the interaction energy between a water molecule and a single sheet of a graphite surface was obtained by extrapolating the results of our calculations to the infinitely repeating structure limit.

Past studies of hydrogen-bonded complexes involving water as the ligand found the MP2 method to be adequate for predicting binding energies to an accuracy of a few tenths of a kcal/mol.[20−23] In fact, for the water-benzene system, it has been estimated that in the complete-basis set (CBS) limit, the MP2-level binding energy for this system is within 0.1 kcal/mol of the value predicted by coupled cluster theory with a perturbative estimate of connected triples, CCSD(T).[24−26] For this reason, the MP2 method will be employed to estimate the interaction energy between a water molecule and a graphite sheet, which will be modeled as a system of fused benzene rings. The MP2 calculations will be carried out within the frozen-core approximation, i.e., the molecular orbitals dominated by C and O 1s atomic orbitals are eliminated from the correlation treatment. For the water−benzene system, core/valence corrections obtained by relaxing the frozen-core restriction were found to contribute only −0.03 kcal/mol to the binding energy,[19] and their importance is not expected to grow to the point where they become significant for the water−graphite system.

Despite the encouraging results for the water-benzene system, a potential problem exists in applying low-order perturbation theory to the interaction between a water molecule and large cluster models of a single layer of graphite. Namely, for the infinite graphite sheet, a perturbative treatment would fail due to the vanishingly small HOMO−LUMO gap as the system approaches conductor-like behavior. However, for the largest cluster model employed, consisting of 37 fused benzene rings,

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the HOMO−LUMO gap, as measured by small basis set restricted Hartree−Fock (RHF) calculations, is about 6 eV. This indicates that for our model systems perturbation theory should still be applicable.

We now turn to the choice of atomic basis sets. It is well established that in order to reliably describe a wide range of interactions between water and other molecular species, it is necessary to use large, flexible basis sets. This requirement can be considered as arising from two sources: (1) the need to accurately describe the "true" physical interactions, and (2) the need to minimize undesirable basis set superposition error (BSSE). For purposes of this discussion, BSSE is defined as the energy difference between the raw (i.e., uncorrected) binding energy and the value adjusted by the full counterpoise correction (CP) of Boys and Bernardi[27] using the relaxed fragment geometries.

All calculations in the present study were performed with the correlation consistent basis sets, cc-pVxZ, where x = D (double ζ), T (triple ζ) and Q (quadruple ζ)[28,29] or the diffuse function augmented correlation consistent basis sets (aug-cc-pVxZ). For the sake of brevity, we will denote the aug-cc-pVxZ basis sets as aVxZ. Although the inclusion of diffuse functions typically does not result in large changes in the net binding energy, their presence does markedly reduce BSSE. The relative lack of change in the binding energy is a consequence of the opposing effects of the reduction in the BSSE and improved description of the true physical interactions upon the inclusion of such functions. For example, at the triple ζ basis set level, the difference in water-benzene binding energies between calculations done with and without diffuse functions is 0.4 kcal/mol, whereas the corresponding BSSE is reduced from 1.7 to 0.9 kcal/mol.

For the largest of the fused-ring systems to be studied, MP2 calculations with the aVQZ basis set were not computationally feasible. As a result, both the raw and the CP-corrected binding energies will be far from the complete basis set limit. Experience has shown that in some hydrogen-bonded chemical systems, the CBS limit is closer to the raw binding energies than the CP-corrected values.[22,30,31] However, in the case of water−benzene the apparent CBS limit falls roughly midway between the raw and the CP-corrected binding energies obtained from aVDZ through V5Z basis sets. On the basis of this finding, we will adopt the average of the raw and CP-corrected binding energies as our best estimate of the basis set limit in the present work.

Given the computational demands of MP2 calculations on large clusters, a natural question is whether density functional theory (DFT), which is comparatively inexpensive, might be applicable to this problem. DFT calculations using standard functionals such as BLYP[32,33] are unable to describe long-range dispersion interactions. In fact, they produce purely repulsive potentials for inert gas dimers.[34] Moreover, for the water−benzene system DFT calculations using the Becke3LYP functional and large basis sets underestimate the binding energy by about a factor of 2.[35] Because dispersion forces are expected to comprise a major portion of the interaction energy between a water molecule and the larger cluster models of the graphite surface, we anticipate that DFT calculations would also prove inadequate for these systems. The success of Becke3LYP calculations in explaining the trends in the OH stretch spectra of benzene−$(H_2O)_n$ clusters, is a consequence of the small perturbations induced by the benzene molecule on the OH stretch vibrational spectra and the use of basis sets for which BSSE was sizable.[35] The "overbinding" due to the BSSE roughly compensated for the inadequate treatment of dispersion interactions.

Most of the MP2 calculations were performed with NWChem[36] on the 512-node IBM SP2 in the Molecular Science Computing Facility at the Pacific Northwest National Laboratory. Preliminary calculations on the water−$(\text{fbz})_n$ clusters were carried out at the Becke3LYP level using the Gaussian 98 program.[37]

Calculations with large, diffuse function augmented basis sets on multiple atomic centers are prone to linear dependency problems, which can lead to convergence failure in the Hartree−Fock step and loss of accuracy in the perturbation theory energy. This problem is addressed by the NWChem code, which was used for the majority of our calculations, by removing all eigenvectors of the overlap matrix with eigenvalues smaller than 10^{-5}. The number of overlap eigenvectors eliminated from the basis set ranged from 23 for the smallest fused-ring clusters to 51 for the largest.

It should be noted that there is no completely satisfactory solution to the problem of linear dependency in basis sets. Although the elimination of eigenvectors with small overlap eigenvalues, as is done in NWChem and Gaussian 98, improves the chances of converging the Hartree−Fock equations, this procedure does not solve the problem associated with the potential loss of accuracy in post Hartree−Fock steps. It is hoped that the consistent use of a fixed elimination threshold for all of the MP2 calculations will avoid introducing a significant amount of numerical noise in the computed binding energies reported here.

As will be seen, the problem of achieving a satisfactory level of completeness in the basis set while simultaneously avoiding excessive linear dependency is nontrivial. The origin of this problem is the use of large atom-centered basis sets, which perform very well in small to medium-size chemical systems but lead to the linear dependency problems just discussed in spatially compact systems, such as the graphite fragments under study. Although alternative approaches, such as plane-wave-based DFT can avoid the linear dependency problem, as noted above, DFT is poorly suited for describing interactions where dispersion plays a major role. A hybrid approach, wherein a single-center expansion of Gaussians is combined with small atom-centered basis sets, might prove a more effective approach but was considered beyond the scope of the present work because of the cost of such calculations.

MP2 geometry optimizations, which proved possible for the smaller clusters, were performed using a convergence criterion of 10^{-4} E_h/a_o. This should be sufficient to yield C−C bond lengths to a precision of approximately ±0.002 Å.

III. Results and Discussion

In the lowest energy water−benzene conformation, the water molecule rests atop the π-electron cloud, with one of the hydrogen atoms in water pointed toward a carbon atom in the ring.[38−40,35,41,19] Large basis set MP2 calculations show a slow convergence of the raw and CP-corrected binding energies as a function of the basis set size.[19] The difference between the raw and CP-corrected binding energies is 2 kcal/mol with the aVDZ basis set, falling to 0.9 kcal/mol with the aVTZ basis set, 0.6 kcal/mol with the aVQZ basis and 0.3 kcal/mol with the aV5Z basis set. An analysis of the convergence of the behavior of the water−benzene binding as a function of the basis set size has led to a best estimate of -3.9 ± 0.2 kcal/mol for the electronic binding (ΔE_{el}). The corresponding binding energy, corrected for vibrational zero-point energy, is $\Delta E_0 = -2.9 \pm 0.2$ kcal/mol, in reasonably good agreement with the -2.4 ± 0.1 kcal/mol determined from threshold photoionization measurements.[42]

The smallest graphite model examined in the present work consists of four fused rings (triphenylene, $C_{18}H_{12}$) and is shown

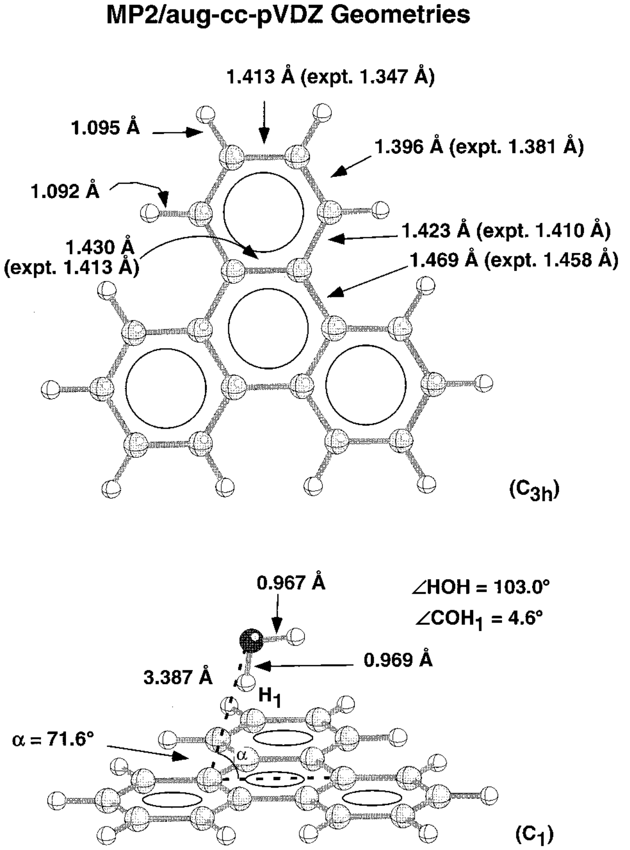

Figure 1. The MP2/aug-cc-pVDZ geometries of $(fbz)_4$ and $H_2O-(fbz)_4$.

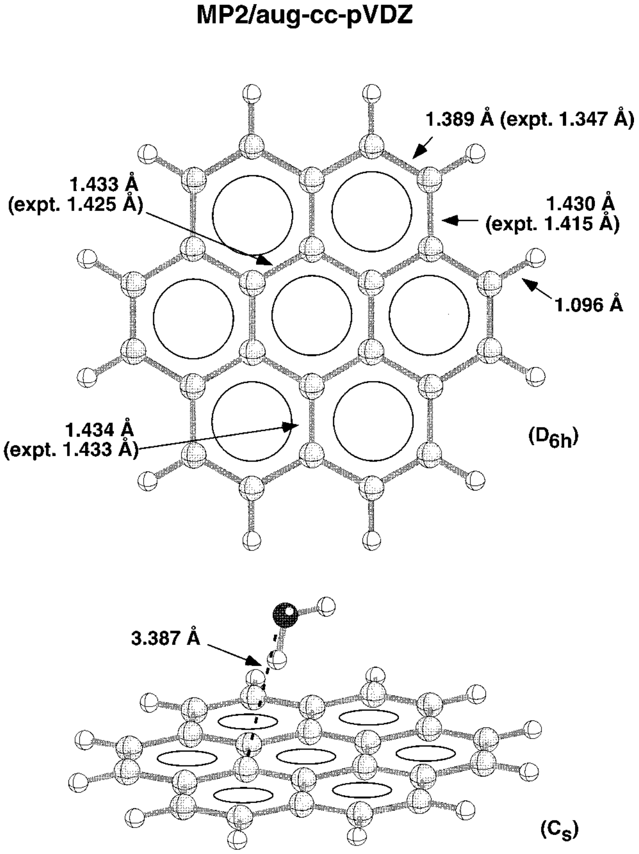

Figure 2. The MP2/aug-cc-pVDZ geometries of $(fbz)_7$ and $H_2O-(fbz)_7$.

in Figure 1, along with the experimental bond lengths reported by Herdon.[43] The experimental values are averages of X-ray and neutron diffraction data.[44,45] The MP2/aVDZ optimizations predict the central ring to have CC bond lengths of 1.430 and 1.469 Å. This large bond length alternation is a result of the steric repulsion of the H atoms around the perimeter of the fused-ring system. At the MP2/aVDZ level of theory, the distance between the oxygen atom in water and the nearest carbon atom is 0.05 Å smaller than the corresponding distance in the water−benzene complex. Nearly the same geometry is obtained at the MP2/aVTZ level of theory.

The BSSE in the MP2 calculations with the aVDZ and aVTZ basis sets is 60−80% larger for the interaction of water with $(fbz)_4$ than with benzene. This is due both to the closer approach of the water molecule to the ring system and the increased number of electrons to be correlated in the larger fused-ring fragment. The average of the raw and CP-corrected MP2/aVTZ binding energies, which represents our best estimate of the binding energy of water−$(fbz)_4$, is −4.2 kcal/mol, or 17% larger in magnitude than the corresponding estimate of the binding energy of the water−benzene complex. The use of aVTZ-optimized rather than aVDZ-optimized geometries has little effect on the calculated binding energy.

The next larger model of the graphite sheet is $(fbz)_7$ (coronene, $C_{24}H_{12}$), shown in Figure 2, along with the available experimental data.[46] In coronene, the central ring is surrounded by six secondary rings in a system with D_{6h} symmetry. At the MP2/aVDZ level of theory, the C−C bonds of the interior ring of $(fbz)_7$ are predicted to be 0.025 Å longer than those of benzene. MP2-level geometry optimizations of the water interacting with $(fbz)_7$ and larger graphite models would have been prohibitively expensive. Instead, for these systems, the position of the water molecule was simply adopted from the water−$(fbz)_4$ complex, optimized at the MP2/aVDZ level. The centro-symmetric nature of $(fbz)_7$ creates a binding site that more closely resembles the environment found in the infinitely repeating structure than the smaller, less symmetric $(fbz)_4$ cluster.

To minimize linear dependency problems, and to keep the MP2/calculations on $H_2O-(fbz)_7$ with the larger (i.e., aVTZ and aVQZ basis sets) tractable, the diffuse functions were retained on only the six central carbon atoms. The validity of this approach was checked by also performing on the $H_2O-(fbz)_7$ complex MP2 calculations with the aVDZ basis set modified so that the diffuse functions are retained on only the central ring and the water molecule. After correcting for BSSE, MP2 calculations with the mixed aVDZ/VDZ basis set gave a binding energy only 0.2 kcal/mol larger in magnitude than that with VDZ result. The average of the raw and CP-corrected binding energies obtained with the mixed aVDZ/VDZ basis set, was also only 0.2 kcal/mol larger than the corresponding aVDZ result. We expect the difference in binding energies calculated with the mixed and full basis sets to decrease in approximately the same manner as the BSSE, namely, it should be roughly halved for each step up in basis set size (i.e., VDZ, to VTZ, to VQZ).

The average of the raw and CP-corrected MP2 binding energies for the $H_2O-(fbz)_7$ system is −4.68, −4.47 and −4.46 kcal/mol with the aVDZ, aVTZ/VTZ and aVQZ/VQZ basis sets, respectively. These values represent a 25% increase in binding energy relative to water with a single benzene and a 10% increase relative to the binding energy of the water-$(fbz)_4$ complex. A plot of the binding energy versus basis set size (see Figure 4) reveals a significantly larger BSSE contribution to ΔE, even at the aVQZ level, than was observed in water-

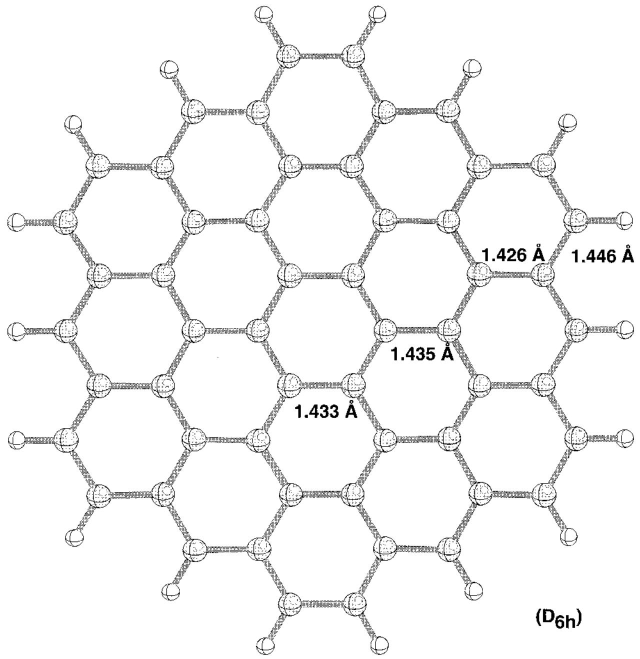

Figure 3. The MP2/aug-cc-pVDZ geometry of $(fbz)_{19}$.

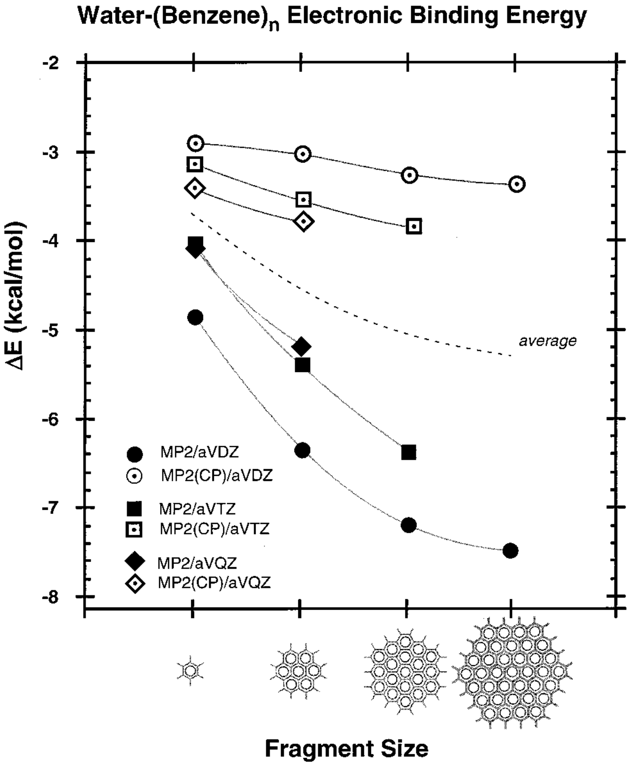

Figure 4. The variation in the $H_2O-(fbz)_n$ electronic binding energy as a function of the fused ring fragment size.

benzene. It is unclear how much of this increase is due to the use of the mixed aV*x*Z/V*x*Z style basis sets, as opposed to a growth in BSSE due to the growth in the size of the cluster. However, at nearly 1400 basis functions, the mixed basis set calculations were already near the limits of our hardware capabilities. At the raw and CP-corrected RHF/aVQZ levels of theory, the $H_2O-(fbz)_7$ complex is *unbound* by 0.30 and 0.35 kcal/mol, respectively. This result indicates that dispersion interactions play a major role in the binding of the water molecule to coronene (and the other annulene models of graphite).

The next larger fused-ring cluster, $(fbz)_{19}$ (dodecabenzocoronen, $C_{54}H_{18}$), was too large for geometry optimization even at the MP2/aVDZ level of theory. Instead, we adopted the optimized MP2/aVDZ geometry of $(fbz)_7$ for the inner seven rings and constructed the outermost rings with the approximate bond lengths shown in Figure 3. The water molecule was positioned as described above for water$-(fbz)_7$. For the water$-(fbz)_{19}$ system, the smallest basis set consisted of a mixture of aVDZ for the central 24 carbon atoms and the water molecule and VDZ for the remainder of the cluster. Next, in terms of increasing size, was a basis set composed of aVTZ for the central ring and water, VTZ for the remainder of the carbons and VDZ on the peripheral hydrogens. The average of the raw and CP-corrected MP2/aVTZ binding energies is -5.2 kcal/mol, about 17% larger than the corresponding binding energy for the smaller $H_2O-(fbz)_7$ cluster. As can be seen in Figure 4, where ΔE_{el} is plotted as a function of the size of the fused-ring system, the counterpoise correction for BSSE is slightly less than 3 kcal/mol at the MP2/aVTZ level of theory. Most of the BSSE originates with the fused-ring portion of the complex, making it difficult to reduce without simultaneously exacerbating the linear dependency problem.

The largest graphite-like cluster examined in this study, $(fbz)_{37}$, has a chemical formula of $C_{96}H_{24}$. As for the $(fbz)_{19}$ carbon structure, the geometry was "synthesized" using the MP2/aVDZ geometry of $(fbz)_7$ for the inner seven rings and approximate bond lengths for the outermost rings. The water molecule was positioned as for the water-$(fbz)_7$ and water-$(fbz)_{19}$ complexes. In this case, only the mixed aVDZ/DZ basis set, which included diffuse functions on only the C_{24} innermost seven fused rings and the water molecule, could be afforded. Even with this truncated basis set, the single-point MP2 energy calculations on the complex took over 7400 total CPU hours (29 h × 256 nodes of the EMSL IBM SP with 120 MHz processors), making this the largest MP2 calculation attempted during this project. In light of the low symmetry (C_s for water-$(fbz)_{37}$) and large number of electrons (610), this calculation is likely to be one of the largest MP2 calculations performed to date with a high quality basis set. Averaging the raw and CP-corrected binding energies of water-$(fbz)_{37}$ results in a value of $\Delta E_{el} = -5.4$ kcal/mol. For purposes of estimating the large system limit, this value was adjusted upward to -5.3 kcal/mol on the basis of the difference between aVDZ and aVTZ results for water-$(fbz)_{19}$.

An exponential fit of the average of the raw and CP-corrected MP2/VTZ binding energies for the water$-$benzene, water$-(fbz)_7$ and water$-(fbz)_{19}$ clusters (see Figure 4) leads to a prediction of -5.4 kcal/mol for the electronic binding energy of a water molecule with a single sheet of graphite. If we also incorporate our results for the water$-(fbz)_{37}$ cluster, this estimate is increased slightly to -5.8 kcal/mol. We adopt the latter value as our best estimate and take the difference between the two extrapolated limits as a crude measure of the uncertainty in our result, i.e., -5.8 ± 0.4 kcal/mol. It is currently not possible to accurately estimate the contribution of higher-order electron correlation effects to ΔE_{el}, but the data available for water$-$benzene suggests that it is not large.

IV. Conclusions

Large basis set MP2 calculations on a series of fragment models up to $C_{96}H_{24}$ in size have been used to estimate the electronic binding energy of an individual water molecule to single-layer graphite. The resulting D_e value is -5.8 kcal/mol, with conservative error bars of $\pm$ 0.4 kcal/mol, assuming no subtle breakdown in perturbation theory for the larger systems examined here. This value is appreciably larger than the −3.7 and −4.3 kcal/mol binding energies reported previously in the literature. The former is an experimental estimate and the latter is based on model-potential calculations. We note, however, that it is not clear whether the former value has separated out the effects of vibrational zero point energy. The largest source of uncertainty in our estimated binding energy arises from a combination of basis set superposition and basis set incompleteness errors. At the same time it must be acknowledged that there is little experience with extrapolating binding energies along a sequence of clusters and this contributes some indeterminate uncertainty to the our best estimate of D_e. These calculations highlight the difficulty of approaching the complete basis set limit in extended systems, such as graphite, using traditional atom-centered basis sets. A secondary source of error is the use of estimated geometries in the larger cluster models

Our estimate of the water−graphite binding energy is slightly larger than that for the interaction between two water molecules (−5.0 ± 0.1 kcal/mol).[20,23] At the same time, this interaction is significantly smaller than the average electronic binding energy of water monomers in bulk water, where the hydrogen bonding network involves each water molecule in (up to) four hydrogen bonds. Nonetheless, our estimate of the water-graphite interaction is sufficiently large to lead us to expect that in carbon nanotubes, the interaction of water with the nanotube walls will play a significant role in determining the structure of the confined water.

In the water−benzene complex, the important attractive interactions are the dipole−quadrupole, dipole−induced dipole (induction), and dispersion contributions. All three of these are expected to be important in the binding of a water monomer to a graphite sheet, although, we have not attempted to decompose the net interaction energy into constituent parts. However, as our counterpoise-corrected Hartree−Fock interaction energies are repulsive, it is clear that the dispersion interaction is critical, contributing on the order of −6 kcal/mol to the binding energy.

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References and Notes

(1) Iijima, S. *Nature* **1991**, *354*, 56.

(2) Iijima, S. *Nature* **1993**, *363*, 603.

(3) Bethune, D. S.; Kiang, C. H.; Vries, d., M. S.; Gorman, G.; Savoy, R.; Vazquez, J.; Beyers, R. *Nature* **1993**, *363*, 605.

(4) Dekker, C. *Phys. Today* **1999**, *May*, 22.

(5) Fisher, E. R. *Langmuir* **1999**, *15*, 750.

(6) Kong, J.; Franklin, N. R.; Zhou, C.; Chapline, M. G.; Peng, S.; Cho, K.; Dai, H. *Science* **2000**, *287*, 622.

(7) Sun, L. F.; Xie, S. S.; Liu, W.; Zhou, W. Y.; Liu, Z. Q.; Tang, D. S.; Wang, G.; Qian, L. X. *Nature* **2000**, *403*, 384.

(8) Rahman, A.; Stillinger, H. F. *J. Chem. Phys.* **1971**, *55*, 3336.

(9) Stillinger, F. H.; David, C. W. *J. Chem. Phys.* **1978**, *69*, 1473.

(10) Niesar, U.; Corongiu, G.; Clementi, E.; Kneller, G. R.; Bhattachrya, D. K. *J. Phys. Chem.* **1990**, *98*, 7949.

(11) Corongiu, G.; Clementi, E. *J. Chem. Phys.* **1992**, *64*, 97.

(12) Sprik, M.; Klein, M. L. *J. Chem. Phys.* **1988**, *89*, 7556.

(13) Rick, S. W.; Stuart, S. J.; Berne, B. J. *J. Chem. Phys.* **1994**, *101*, 6141.

(14) Dang, L. X.; Chang, T.-M. *J. Chem. Phys.* **1997**, *106*, 8149.

(15) Burnham, C. J.; Li, J.; Xantheas, S. S.; Leslie, M. *J. Chem. Phys.* **1999**, *110*, 4566.

(16) Vernov, A.; Steele, W. A. *Langmuir* **1992**, *8*, 155.

(17) Gale, R. L.; Beebe, R. A. *J. Phys. Chem.* **1964**, *68*, 555.

(18) Avgul, N. N., Kieslev, A. V. In *Chemistry and Physics of Carbon*; Walker, P. L., Ed.; Dekker: New York, 1970; Vol. 6.

(19) Feller, D. *J. Phys. Chem. A* **1999**, *103*, 7558.

(20) Feller, D. *J. Chem. Phys.* **1992**, *96*, 6104.

(21) Feller, D.; Glendening, E. D.; Kendall, R. A.; Peterson, K. A. *J. Chem. Phys.* **1994**, *100*, 4981.

(22) Feller, D.; Glendening, E. D.; Woon, D. E.; Feyereisen, M. W. *J. Chem. Phys.* **1995**, *103*, 3526.

(23) Feyereisen, M. W.; Feller, D.; Dixon, D. A. *J. Phys. Chem.* **1996**, *100*, 2993.

(24) Purvis, G. D., III.; Bartlett, R. J. *J. Chem. Phys.* **1982**, *76*, 1910.

(25) Raghavachari, K.; Trucks, G. W.; Pople, J. A.; Head-Gordon, M. *Chem. Phys. Lett.* **1989**, *157*, 479.

(26) Watts, J. D.; Gauss, J.; Bartlett, R. J. *J. Chem. Phys.* **1993**, *98*, 8718.

(27) Boys, S. F.; Bernardi, F. *Mol. Phys.* **1970**, *19*, 553.

(28) Dunning, T. H., Jr. *J. Chem. Phys.* **1989**, *90*, 1007.

(29) Kendall, R. A.; Dunning, T. H., Jr.; Harrison, R. J. *J. Chem. Phys.* **1992**, *96*, 6796.

(30) Feller, D.; Aprà, E.; Nichols, J. A.; Bernholdt, D. E. *J. Chem. Phys.* **1996**, *105*, 1940.

(31) Feller, D. *Chem. Phys. Lett.* in press.

(32) Becke, A. D. *Phys. Rev. A* **1988**, *38*, 3098.

(33) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785.

(34) Kristyan, S.; Pulay, P. *Chem. Phys. Lett.* **1994**, *229*, 175.

(35) Fredericks, S. Y.; Jordan, K. D.; Zwier, T. S. *J. Phys. Chem.* **1996**, *100*, 7810.

(36) *NWChem Version 3.3*, Anchell, J.; Apra, E.; Bernholdt, D.; Borowski, P.; Bylaska, E.; Clark, T.; Clerc, D.; Dachsel, H.; de Jong, B.; Deegan, M.; Dupuis, M.; Dyall, K.; Elwood, D.; Fann, G.; Fruchtl, H.; Glendening, E. D.; Gutowski, M.; Harrison, R.; Hess, A.; Jaffe, J.; Johnson, B.; Ju, J.; Kendall, R.; Kobayashi, R.; Kutteh, R.; Lin, Z.; Littlefield, R.; Long, X.; Meng, B.; Nichols, J.; Nieplocha, J.; Rendall, A.; Rosing, M.; Sandrone, G.; Stave, M.; Straatsma, T.; Taylor, H.; Thomas, G.; van Lenthe, J.; Windus, T.; Wolinski, K.; Wong, A.; Zhang, Z. NWChem; as developed and distributed by Pacific Northwest National Laboratory, Richland, P.O. Box 999, WA 99352 (USA) and funded by the U.S. Department of Energy, was used to obtain some of these results, 1999.

(37) *Gaussian 98, A.4*, Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Petersson, G. A.; Montgomery, J. A., Jr.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaroni, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T. A.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B. G.; Chen, W.; Wong, M. W.; Andreas, J. L.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. Gaussian, Inc. Pittsburgh PA, 1998.

(38) Brédas, J. L.; Street, G. B. *J. Chem. Phys.* **1989**, *90*, 7291.

(39) Cheny, B. V.; Schulz, M. W. *J. Phys. Chem.* **1990**, *94*, 6268.

(40) Suzuki, S.; Green, P. G.; Bumgarner, R. E.; Dasgupta, S.; Goddard, W. A., III.; Blake, G. A. *Science* **1992**, *275*, 942.

(41) Gregory, J. K.; Clary, D. C. *Mol. Phys.* **1996**, *88*, 33.

(42) Courty, A.; Mons, M.; Dimicoli, I.; Piuzzi, F.; Gaigeot, M.-P.; Brenner, V.; Pujo, P. d.; Millié, P. *J. Phys. Chem. A* **1998**, *106*, 6590.

(43) Herndon, W. C. *J. Am. Chem. Soc.* **1974**, *96*, 7605.

(44) Ahmed, F. R.; Trotter, J. *Acta Crystallogr.* **1963**, *16*, 503.

(45) Ferraris, G.; Jones, D. W.; Yerkess, J. *Z. Kristallogr.* **1973**, *138*, 113.

(46) Fawcett, J. K.; Trotter, J. *Proc. R. Soc. Ser. A* **1966**, *279*, 366.