Multipole moments of water molecules in clusters and ice Ih from first principles calculations

Enrique R. Batista
Department of Physics, Box 351560, University of Washington, Seattle, Washington 98195-1560
and Department of Chemistry, Box 351700, University of Washington, Seattle, Washington 98195-1700

Sotiris S. Xantheas
Environmental Molecular Sciences Laboratory, Pacific Northwest National Laboratory,
906 Battelle Boulevard, PO Box 999, MS K8-91, Richland, Washington 99352

Hannes Jónsson
Department of Chemistry, Box 351700, University of Washington, Seattle, Washington 98195-1700

We have calculated *molecular* multipole moments for water molecules in clusters and in ice Ih by partitioning the charge density obtained from first principles calculations. Various schemes for dividing the electronic charge density among the water molecules were used. They include Bader's zero flux surfaces and Voronoi partitioning schemes. A comparison was also made with an induction model including dipole, dipole-quadrupole, quadrupole-quadrupole polarizability and first hyperpolarizability as well as fixed octopole and hexadecapole moments. We have found that the different density partitioning schemes lead to widely different values for the molecular multipoles, illustrating how poorly defined molecular multipoles are in clusters and condensed environments. For instance, the magnitude of the molecular dipole moment in ice Ih ranges between 2.3 D and 3.1 D depending on the partitioning scheme used. Within each scheme, though, the value for the molecular dipole moment in ice is larger than in the hexamer. The magnitude of the molecular dipole moment in the clusters shows a monotonic increase from the gas phase value to the one in ice Ih, with the molecular dipole moment in the water ring hexamer being smaller than the one in ice Ih for all the partitioning schemes used. © *1999 American Institute of Physics.*
[S0021-9606(99)51637-1]

I. INTRODUCTION

Molecular systems are often described in terms of properties of the individual molecules and their interactions.[1,2] These molecular properties are, in general, environment dependent and can, for example, be significantly different in a condensed than in a gas phase environment. It is interesting to investigate how such molecular properties evolve gradually in clusters of increasing size. Water is a particularly important example of such a system. Clusters of water molecules have been used to probe important properties of water and ice such as cooperative,[3,4] structural[5] and electrical trends.[6,7] These properties serve as important benchmarks in the development and parametrization of interaction potentials for water molecules. For instance, some of the most sophisticated potential functions for water include a molecular point dipole that is evaluated self-consistently via an induction scheme.[8–11] Therefore, the *molecular* dipole moment of water has received a great deal of attention and there have been many previous studies of the dipole moment of water molecules in various environments ranging from clusters to liquid water and ice (see, for example, Refs. 6,7,10,12–23). As a general rule the molecular dipole moment increases as a result of the interaction with other, neighboring water molecules.

The dipole moment of water molecules in ice Ih was studied a long time ago using a simple induction model.[12] In a recent study,[6] molecular dipole moments of water clusters up to the hexamer as well as a collection of 160 water molecules arranged into the lattice structure of ice Ih were obtained using a distributed multipole analysis (DMA) method.[24,25] The results indicated that the molecular dipole moment of the water hexamer is very similar to that of ice Ih and it was inferred that the dominant interactions that occur in condensed-phase environments, such as water and ice, are reasonably well represented in even this small (hexamer) cluster.[6] This is an unexpected result, because water molecules in ice and water have more nearest and distant neighbors than water molecules in a hexamer cluster. We have recently re-evaluated the molecular dipole moment in ice Ih using the induction model and obtained[21] 3.1 Debye, a value significantly larger than the previously[12] reported (2.6 Debye). We have attributed this difference to the use of less accurate values for the molecular quadrupole moment in the previous calculation, since experimental values for this quantity were not yet available at the time of that study. Our value for the molecular dipole moment in ice Ih is 0.4 Debye larger than the one previously obtained for the water hexamer with both the induction and DMA methods;[6] a fact that suggests that the dipole moment increase for the hexamer is not of similar magnitude with that for ice Ih. A recent study of the water molecular dipole in the liquid phase using ab initio molecular dynamics[22] produced an average value of 3.0 De-

bye, close to our result for ice Ih using the induction model. However, the distribution of the molecular dipole moments was quite broad spanning a range of almost 2.0 Debye and having a full width at half maximum of almost 1.0 Debye.

In order to compare the results for water clusters and condensed phases, such as ice Ih, it is essential to carry out the same type of analysis for the different environments. The individual molecular moments in a system containing two or more molecules cannot be measured directly from experiment. Only the total moment of the system is an observable. Attempts have, nevertheless, been made to estimate the molecular dipole moment from measured macroscopic quantities for both ice[14] and liquid water.[15] A common method for constructing molecular multipoles in a condensed phase environment is via the induction model, where a multipole expansion of the molecular charge density is carried out and the multipoles are then modified using polarizabilities of the isolated molecule. The success of this model is not guaranteed since the polarizability of a molecule in a cluster or condensed phase environment may be significantly different from that of an isolated molecule. An alternative way to estimate molecular multipoles is first principles calculations. Several previous studies have reported values for the molecular dipole moment of water in various environments.[6,16–20,22,23] One drawback of this approach is that there is no *a priori* criterion that dictates how to partition either the wave function or the electronic charge density among the individual molecules. Several partitioning schemes have been proposed[24–30] based on various different criteria on either the electron density or the wave function of the system.

In this study we report molecular dipole as well as higher order multipole moments of water molecules in clusters and in ice Ih. We compare various methods for extracting the molecular multipole moments and discuss their convergence with cluster size to the ice Ih values. In Sec. II we outline the technical details of the first principles calculations. The various schemes used to partition the charge density are given in Sec. III. Our results and additional discussion are presented in Sec. IV.

II. COMPUTATIONAL DETAILS

The electronic density for the water clusters up to and including the hexamer was calculated using the second order Møller–Plesset perturbation[31] theory (MP2) at the previously reported optimal cluster geometries[4,5,32,33] obtained with the aug-cc-pVDZ basis set.[34] A grid of about 3.4 million points evenly distributed on a rectangular grid was used to evaluate the MP2 density. This number of points resulted in an error in the integrated density that was smaller than 0.01 electrons for all clusters. For the trimer through pentamer clusters the global minima have quasi-planar ring homodromic arrangements. For the hexamer, the ring structure corresponds to a local minimum with the cage structure being slightly lower in energy.[35] There exist at least three isomers within 1 kcal/mol from the global minimum.[33,35]

We have also computed the electronic density in the water clusters and ice Ih using the plane wave based Density Functional Theory (DFT) method. The advantage of using this theoretical method is that it can be applied both to ice Ih as well as the clusters. The cluster results obtained with this method can be compared with the ones at the MP2 level. In the DFT calculations the wave functions were expanded in a plane wave basis set with an energy cutoff of 70 Ry. The pseudopotentials of Troullier and Martins[36] were used. A total of 16 molecules were included in the unit cell configuration for ice Ih. Only the Γ point was used in the Brillouin zone sampling. As shown previously by Lee *et al.*,[37] the Local Density Approximation (LDA) produces a nearest-neighbor O–O separation for ice Ih that is 10% smaller than the experimental value of 2.75 Å while the Becke–Perdew (BP) gradient-corrected functional[38] yields a value that is only 2% smaller than experiment. We used the Perdew–Wang (PW91) gradient-corrected functional[39] and obtained an O–O distance of 2.7 Å at 0 K which is 2% smaller than the experimental value. During the DFT calculations both the cluster and ice configurations were relaxed until the magnitude of the force on each of the ions dropped below 0.1 eV/Å.

The ice Ih configuration was constructed to satisfy the ''ice-rules'' [40] and the proton ordering was chosen to be anti-ferroelectric rather than random. This choice was made because of the small unit cell size.

We calculated traceless multipoles with respect to the center of mass of each molecule by partitioning the electronic density and assigning it to individual molecules using the four schemes outlined below. We used the notation in the Appendix of Ref. 21 for the definition of the multipoles.

III. PARTITIONING SCHEMES

We applied four different algorithms for partitioning the electronic charge density obtained from the first principles (MP2 and DFT) calculations. The first three of the methods are spatial decompositions, i.e., each point in space is assigned to only one molecule and there is no overlap of the electronic charge density assigned to two different molecules.

The four schemes used are as follows:

(i) The charge density is partitioned among the molecules according to Bader's Atoms In Molecules (AIM) method.[30] According to this method, the optimal partition into subsystems is achieved using a surface where the gradient of the charge density is parallel to the surface at all points, i.e., the charge density is stationary in the direction normal to the surface

$$\nabla \rho \cdot \hat{n} = 0, \tag{1}$$

where $\hat{n}$ is the normal to the surface and ρ is the charge density. The zero flux surfaces were calculated using an elastic sheet algorithm.[41] For the dimer, tetramer and pentamer, we repeated the same calculation with the Atoms In Molecules (AIM) module of the Gaussian-94 suite of programs[42] which is based on an algorithm of Stefanov and Cioslowski.[43] The two methods agreed to within 1%. For the trimer and ring hexamer the AIM calculation as implemented in Gaussian-94 did not converge while the elastic sheet method did. To test how sensitive the calculated molecular
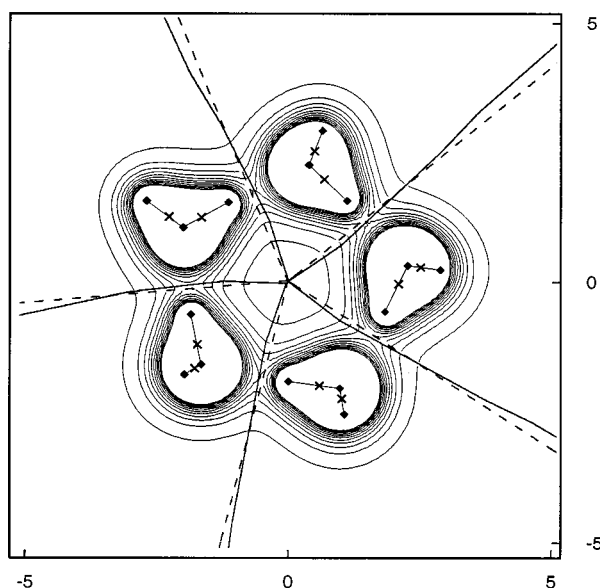
FIG. 1. Contour plot of the charge density of the water pentamer in the plane of the cluster. The figure displays the charge density partitioned according to the Voronoi I (dotted line) and Voronoi II (solid line) schemes (see text). In the Voronoi I scheme, the Voronoi cell is constructed around one center per molecule, placed at the center of nuclear charge. In Voronoi II, the Voronoi cells are around three ''atomic'' centers per molecule: one at the oxygen atom and the other two (shown with crosses) on the O–H bonds, at 40% of the displacement from the oxygen atom to the hydrogen nucleus. Although both surfaces are very similar, the latter passes closer through the minimum of the charge density between the molecules.

multipole moments are to slight changes in the partitioning of the charge density, we devised two other spatial partitioning schemes.

(ii) Voronoi I (V-I): The charge density is divided into Voronoi cells using the center of charge on each molecule as the center of the Voronoi cell. The charge closest to the center of ionic charge of a given molecule is assigned to that particular molecule. The molecule is then described by only one point, namely the center of charge. Therefore no information regarding the geometry and orientation of the molecule is used in this scheme.

(iii) Voronoi II (V-II): The charge density is divided into Voronoi cells taking the position of individual atoms into account. If the hydrogen atoms are treated on an equal footing as the oxygen atoms, then the Voronoi construction divides the space near a hydrogen bond midway between the hydrogen and oxygen atoms. The region associated with a hydrogen atom then cuts significantly into the charge density that is centered at oxygen atoms in neighboring molecules. We, therefore, have chosen to shift the Voronoi center associated with the hydrogen atoms along the O–H bonds toward the oxygen to make it lie closer to the minimum of the electron density. By inspection of contour plots of the charge density, we chose to displace the Voronoi centers for the hydrogen atoms by 60% from the hydrogen atom nucleus toward the oxygen nucleus in the molecule. The Voronoi cells in both schemes turn out to be very nearly charge neutral, to within 0.01 electronic charge.

Figure 1 shows a contour plot of the charge density of the pentamer in the plane of the cluster as well as Voronoi I

and Voronoi II dividing surfaces. In each of the three previously described spatial decomposition methods the volume associated with a water molecule is the volume corresponding to each of the two hydrogen atoms plus the volume corresponding to the oxygen atom. Similar contour plots are obtained for the other clusters.

(iv) Molecular Proportion Partitioning Method (MPP): The electronic charge density of the cluster at any point in space is partitioned among the individual molecules in proportion to the electronic charge density of the isolated molecules at that point.

The results for the multipoles obtained with the above four schemes are compared with the ones obtained from an induction model which is described in detail in Ref. 21. Briefly, every water molecule is represented in the induction model as a point dipole, quadrupole, octopole and hexadecapole moment tensor placed at the center of mass of the molecule.[44] The electric field at a molecule due to its neighbors induces both a dipole and a quadrupole moment. We used the experimentally measured values for the dipole and quadrupole moments, the MP2/aug-cc-pVQZ values for the octopole and hexadecapole moments, the experimentally measured molecular dipole polarizability, α_{ij},[45] and the results of previous *ab initio* calculations for the dipole-quadrupole, $A_{i,jk}$, quadrupole-quadrupole polarizability, $C_{ij,kl}$,[46] and the first hyperpolarizability, β_{ijk}.[47] The values of the moments and polarizabilities used here are the ones shown in Tables I and II of Ref. 21.

IV. RESULTS AND DISCUSSION

The variation of the average dipole moment with cluster size is shown in Fig. 2. The different partition schemes of the charge density clearly lead to very different molecular dipole moments. The average dipole moment of a molecule in ice Ih ranges from 2.3 D for the Voronoi II scheme to 3.1 D for the Voronoi I scheme. The AIM scheme gives intermediate results. Due to proton disorder, the dipole moment varies slightly from one molecule to another in a given ice Ih configuration (the standard deviation is 0.04 Debye). The difference in the dipole moments deduced from the MP2 and DFT calculations differ by less than 0.1 D for all the clusters. The results of the MPP scheme were also intermediate between the two Voronoi schemes, 2.05 D for the average molecular dipole moment in the dimer and 2.19 D in the pentamer. The induction model gives larger dipole moments than any of the schemes used to partition the charge density obtained from first principles calculations for larger clusters and ice Ih.

The large sensitivity of the calculated molecular moments to details of the partitioning scheme can also be seen from a particularly simple scheme, namely the assignment of a spherical region to each water molecule. Choosing the radius of the sphere to give charge neutrality in each case, the molecular dipole moment calculated for a water molecule in ice differs by 0.5 D depending on whether the center of the sphere is placed at the center of mass or center of charge of the water molecule. The two centers are only 0.08 Å apart.

Despite the large range of values obtained for the molecular dipole moment depending on which scheme is used, it is, nevertheless, apparent that the dipole moment of a wa-
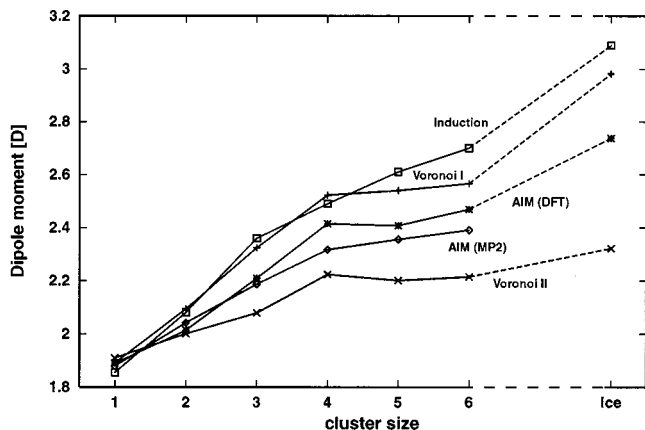
FIG. 2. Magnitude of the molecular dipole moment as a function of the size of the cluster and for ice Ih. The calculations are based on the charge density obtained from MP2 calculations for the clusters, and DFT calculations of ice Ih as well as of the clusters. The difference between dipole moments obtained from the DFT calculation and the MP2 calculation is less than 0.1 D. Different ways of partitioning the charge density are compared: In AIM the charge density is partitioned with zero flux surfaces as proposed by Bader (*). In the Voronoi I scheme the cells are constructed around the center of charge of each molecule ($+$). In Voronoi II the cells are constructed for each atom but the hydrogen atom centers are shifted by 60% of the distance towards the oxygen nucleus (see text and Fig. 1) ($\times$). The induction method includes polarizable dipole and quadrupole moments and fixed molecular octopoles, and hexadecapoles (open squares). Clearly, the vale of the molecular dipole moment depends very strongly on how the electron density of the cluster is partitioned among the molecules. But, for all schemes, the value of the molecular dipole moment in ice is larger than in the clusters.

ter molecule in a hexamer has not converged to the dipole moment of a water molecule in ice Ih. Irrespective of which scheme is used, the molecular dipole moment in ice Ih is larger, by up to 15%, than the corresponding one in the hexamer. This result is to be expected from the fact that a molecule in the ice lattice has twice as many nearest neighbors than in the ring hexamer cluster and many more next nearest and distant neighbors as well which contribute to the polarization.

The calculated molecular quadrupole moments are shown in Fig. 3. Here we have chosen to display the components of the tensor along the three principal axes. Clearly, there is not a smooth trend as the clusters increase in size. In ice Ih the variation of the quadrupole moment due to proton disorder amounts to 0.02 Debye Å. It turns out to be very important to include the quadrupole moment as well as octopole and hexadecapole moments in order to reproduce the electric field around water clusters at a distance where additional water molecules could attach to the cluster.

It is important to realize that the only well defined multipole moments are the multipole moments for the cluster as a whole. All the various schemes used here necessarily give the same total dipole moment, for example, even though the molecular dipole moments differ greatly. A larger molecular dipole moment can be accommodated by changing the orientation of the molecular dipole moment vectors in such a way that larger cancellation occurs. The various schemes for decomposing the charge density give, in fact, quite similar rate of convergence of the multipole expansion of the electric
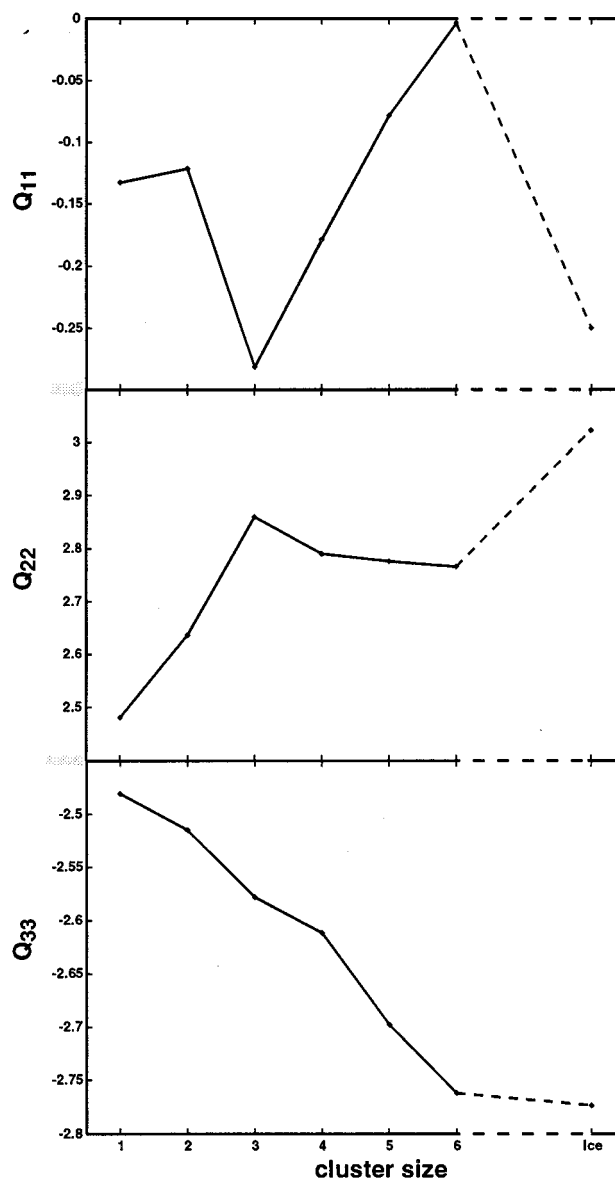

FIG. 3. Quadrupole moment as a function of the cluster size. The graphs trace the average of each eigenvalue of the quadrupole tensor over the values for each fragment in the cluster. The quadrupole moments were calculated dividing the MP2 charge density with zero flux surfaces and integrating over the regions of each molecule. In a free molecule axis 1 is along the bisector of the molecule, axis 2 is perpendicular to 1 and in the plane of the molecule and axis 3 is an axis perpendicular to 1 and 2.

field. This will be discussed in detail in a future publication.[48]

ACKNOWLEDGMENTS

[1] A. D. Buckingham, Adv. Chem. Phys. **12**, 107 (1967).

[2] C. E. Dykstra, Acc. Chem. Res. **21**, 355 (1988).

[3] S. S. Xantheas, J. Chem. Phys. **102**, 4505 (1995).

[4] S. S. Xantheas, Philos. Mag. B **73**, 107 (1996).

[5] S. S. Xantheas and T. H. Dunning, Jr., J. Chem. Phys. **99**, 8774 (1993).

[6] J. K. Gregory, D. C. Clary, K. Liu, M. G. Brown, and R. J. Saykally, Science **275**, 814 (1997).

[7] K. Liu, M. B. Brown, and R. J. Saykally, J. Phys. Chem. A **101**, 8995 (1997).

[8] P. Barnes, J. L. Finney, J. D. Nicholas, and J. E. Quinn, Nature (London) **282**, 459 (1979).

[9] J. Caldwell, L. X. Dang, and P. A. Kollman, J. Am. Chem. Soc. **112**, 9144 (1990).

[10] L. X. Dang and T-M. Chang, J. Chem. Phys. **106**, 8149 (1997).

[11] C. J. Burnham, J. Li, S. S. Xantheas, and M. Leslie, J. Chem. Phys. **110**, 4566 (1999).

[12] C. Coulson and D. Eisenberg, Proc. R. Soc. London, Ser. A **291**, 445 (1966).

[13] E. Whalley, J. Glaciol. **21**, 13 (1978).

[14] D. Adams, Nature (London) **293**, 447 (1981).

[15] M. Sprik, J. Chem. Phys. **95**, 6762 (1991).

[16] K. Laasonen, M. Sprik, M. Parrinello, and R. Car, J. Chem. Phys. **99**, 9080 (1993).

[17] D. Wei and D. R. Salahub, Chem. Phys. Lett. **224**, 291 (1994).

[18] E. S. Fois, M. Sprik, and M. Parrinello, Chem. Phys. Lett. **223**, 411 (1994).

[19] C. Gatti, B. Silvi, and F. Colonna, Chem. Phys. Lett. **247**, 135 (1995).

[20] M. I. Heggie, C. D. Latham, S. C. P. Maynard, and R. Jones, Chem. Phys. Lett. **249**, 485 (1996).

[21] E. R. Batista, S. S. Xantheas, and H. Jónsson, J. Chem. Phys. **109**, 4546 (1998).

[22] P. L. Silvestrelli and M. Parrinello, Phys. Rev. Lett. **82**, 3308 (1999).

[23] L. Delle Site, A. Alavi, and R. M. Lynden-Bell, *Molecular Physics* (in press, 1999).

[24] A. J. Stone, Chem. Phys. Lett. **83**, 233 (1981).

[25] A. J. Stone and M. Alderton, Mol. Phys. **56**, 1047 (1985).

[26] R. S. Mulliken, J. Chem. Phys. **23**, 1833 (1955).

[27] C. Edmiston and K. Ruedenberg, Rev. Mod. Phys. **35**, 457 (1963).

[28] J. E. Carpenter and F. Weinhold, J. Mol. Struct.: THEOCHEM **169**, 41 (1988), and references therein.

[29] J. Pipek and P. G. Mezey, J. Chem. Phys. **90**, 4916 (1989).

[30] R. Bader, *Atoms in Molecules. A Quantum Theory* (Oxford University Press, Oxford, 1990).

[31] B. Møller and M. S. Plesset, Phys. Rev. **46**, 618 (1934).

[32] S. S. Xantheas and T. H. Dunning, Jr., J. Chem. Phys. **98**, 8037 (1993).

[33] S. S. Xantheas and T. H. Dunning, Jr., in *Advances in Molecular Vibrations and Collision Dynamics*, edited by Z. Bacic and J. M. Bowman, Vol. 3 (JAI, Stamford, 1998), pp. 281–309.

[34] R. A. Kendall, T. H. Dunning, Jr., and R. J. Harrison, J. Chem. Phys. **96**, 6796 (1992).

[35] K. Liu, M. G. Brown, C. Carter, R. J. Saykally, J. K. Gregory, and D. C. Clary, Nature (London) **381**, 501 (1996).

[36] N. Troullier and J. Martins, Phys. Rev. B **43**, 1993 (1991).

[37] C. Lee, D. Vanderbilt, K. Laasonen, R. Car, and M. Parrinello, Phys. Rev. B **47**, 4863 (1993).

[38] A. Becke, Phys. Rev. A **38**, 3098 (1988); J. Perdew, Phys. Rev. B **33**, 8822 (1986).

[39] J. P. Perdew and Y. Wang, Phys. Rev. B **45**, 13244 (1992); J. P. Perdew, in *Electronic Structure of Solids '91*, edited by P. Ziesche and H. Eschrig (Akamemie Verlag, Berlin, 1991), p. 11.

[40] J. D. Bernal and R. H. Fowler, J. Phys. Chem. **1**, 515 (1933).

[41] B. P. Uberuaga, E. R. Batista, and H. Jónsson, J. Chem. Phys. (in press).

[42] Gaussian 94, Revision E.2, M. J. Frisch, G. W. Trucks, H. B. Schlegel, P. M. W. Gill, B. G. Johnson, M. A. Robb, J. R. Cheeseman, T. Keith, G. A. Petersson, J. A. Montgomery, K. Raghavachari, M. A. Al-Laham, V. G. Zakrzewski, J. V. Ortiz, J. B. Foresman, J. Cioslowski, B. B. Stefanov, A. Nanayakkara, M. Challacombe, C. Y. Peng, P. Y. Ayala, W. Chen, M. W. Wong, J. L. Andres, E. S. Replogle, R. Gomperts, R. L. Martin, D. J. Fox, J. S. Binkley, D. J. Defrees, J. Baker, J. P. Stewart, M. Head-Gordon, C. Gonzalez, and J. A. Pople (Gaussian, Inc., Pittsburgh, PA, 1995).

[43] C. Stefanov and J. Cioslowski, J. Comput. Chem. **16**, 1394 (1995).

[44] A. J. Stone, *The Theory of Intermolecular Forces* (Clarendon, Oxford, 1996).

[45] W. F. Murphy, J. Chem. Phys. **67**, 5877 (1977).

[46] C. Millot and A. J. Stone, Mol. Phys. **77**, 439 (1992).

[47] C. E. Dykstra, S. Y. Liu, and D. J. Malik, Adv. Chem. Phys. **75**, 37 (1989).

[48] E. R. Batista, S. S. Xantheas, and H. Jónsson (to be published).