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Treatment of Dilute Clusters of Methanol and Water by ab Initio Quantum Mechanical Calculations

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Large molecular clusters can be considered as intermediate states between gas and condensed phases, and information about them can help us understand condensed phases. In this paper, ab initio quantum mechanical methods have been used to examine clusters formed of methanol and water molecules. The main goal was to obtain information about the intermolecular interactions and the structure of methanol/water clusters at the molecular level. The large clusters ($CH_4O\cdots(H_2O)_{12}$ and $H_2O\cdots(CH_4O)_{10}$) containing one molecule of one component (methanol or water) and many (12, 10) molecules of the other component were considered. Møller−Plesset perturbation theory (MP2) was used in the calculations. Several representative cluster geometries were optimized, and nearest-neighbor interaction energies were calculated for the geometries obtained in the first step. The results of the calculations were compared to the available experimental information regarding the liquid methanol/water mixtures and to the molecular dynamics and Monte Carlo simulations, and good agreement was found. For the $CH_4O\cdots(H_2O)_{12}$ cluster, it was shown that the molecules of water can be subdivided into two classes: (i) H bonded to the central methanol molecule and (ii) not H bonded to the central methanol molecule. As expected, these two classes exhibited striking energy differences. Although they are located almost the same distance from the carbon atom of the central methanol molecule, they possess very different intermolecular interaction energies with the central molecule. The H bonding constitutes a dominant factor in the hydration of methanol in dilute aqueous solutions. For the $H_2O\cdots(CH_4O)_{10}$ cluster, it was shown that the central molecule of water has almost three H bonds with the methanol molecules; this result differs from those in the literature that concluded that the average number of H bonds between a central water molecule and methanol molecules in dilute solutions of water in methanol is about two, with the water molecules being incorporated into the chains of methanol. In contrast, the present predictions revealed that the central water molecule is not incorporated into a chain of methanol molecules, but it can be the center of several (2−3) chains of methanol molecules. The molecules of methanol, which are not H bonded to the central water molecule, have characteristics similar to those of the methane molecules around a central water molecule in the $H_2O\cdots(CH_4)_{10}$ cluster. The ab initio quantum mechanical methods employed in this paper have provided detailed information about the H bonds in the clusters investigated. In particular, they provided full information about two types of H bonds between water and methanol molecules (in which the water or the methanol molecule is the proton donor), including information about their energies and lengths. The average numbers of the two types of H bonds in the $CH_4O\cdots(H_2O)_{12}$ and $H_2O\cdots(CH_4O)_{10}$ clusters have been calculated. Such information could hardly be obtained with the simulation methods.

1. Introduction

Alcohol/water systems have attracted the attention of many scientists and technologists for a number of reasons: (i) The low cost of the lower members of the aliphatic alcohols and their miscibility with water make the alcohol/water mixtures useful as industrial solvents for a variety of chemical reactions and for small- and large-scale separation processes. In particular, the aqueous solutions of alcohols are often employed in the extraction and manipulation of labile materials such as proteins.[1] (ii) They have unusual thermodynamic properties that depend in a complex way on composition, pressure, and temperature.[1−8] (iii) They constitute a model for the investigation of the hydrophobic effect. Although the interaction of a nonpolar solute molecule such as methane (or other hydrocarbons, noble gases, etc.) with the surrounding water molecules represents the simplest manifestation of the hydrophobic hydration, the interactions with molecules of a dual nature, such as alcohols, involve not only the hydrophobic hydration of the nonpolar moiety of the molecule but also the hydrophilic interactions between the polar groups and the water molecules. (iv) Because alcohol molecules have a dual nature, details regarding the aqueous solvation of alcohols can be used to improve our understanding of aqueous solutions of much more complex amphiphilic molecules, such as proteins, drugs, and biomolecules. (v) Pure water and alcohol generate different H-bond networks in the liquid state; it is therefore natural to ask how these networks reorganize in water/alcohol mixtures and how

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the hydrophobic hydration of the nonpolar part and the H bonds formed between water and methanol cooperate.

The macroscopic properties of alcohol/water systems were carefully investigated, and excellent reviews[1−2,4−5] and books[6−8] are available. In contrast, the structural and energetic features on the nanometer level have not been as well investigated.

During the last two decades, the wide use of modern experimental tools, especially X-ray, neutron scattering, and modern spectroscopic methods,[9−17] allowed one to obtain valuable information about the nanostructure of aqueous mixtures containing alcohols or various hydrophobic solutes. The availability of powerful computers combined with refined methods of molecular simulations, such as molecular dynamics and Monte Carlo, were actively used to investigate the nanolevel scale of aqueous solutions.[18−25]

The present paper is devoted to the application of ab initio quantum mechanical investigation to dilute clusters of methanol and water. The ab initio quantum mechanical methods are based on the Born−Oppenheimer approximation to the Schrödinger equation and do not involve the traditional model interaction potentials that are employed in molecular dynamics and Monte Carlo simulations. The ab initio quantum mechanical methods have been used frequently to determine the geometry and energy of small molecular clusters such as dimers, and the obtained results were usually used to fit various intermolecular pair potentials. More recently, the ab initio quantum mechanical methods have been applied to large molecular clusters[26−30] formed of the same molecules or of molecules of two different kinds. Large molecular clusters can be considered as intermediate states between gas and condensed phases and can be helpful in the understanding of some properties of the latter phase, particularly the local organization of the molecules and the interactions between them.

The aim of the present paper is to use ab initio quantum mechanical methods, such as Møller−Plesset perturbation theory[31,32] (MP2 method), to examine large clusters formed of one molecule of methanol (or water) and up to 10−12 molecules of water (or methanol). Methanol was selected because it is one of the simplest amphiphile-like molecules. Furthermore, the results will be compared to those obtained for dilute clusters of methane and water.[33]

The paper is organized as follows: In the next section, the literature results regarding some features of the nanostructure of pure water or methanol and the water/methanol binary clusters will be summarized. Then, the quantum mechanical ab initio method that was employed will be described. This will be followed by the presentation of the results that were obtained for the dilute clusters of methanol and water. Furthermore, the results will be compared to the available information regarding the liquid methanol/water mixtures that were obtained experimentally and by simulations. Finally, they will be used to shed some light on the structure and other features of water molecules in the vicinity of an amphiphilic solute.

2. Nanometer Features of Water and Methanol and their Mixture

There is no single theory that can provide explanations for all of the properties of the most mysterious substance: water. However, much information is available about the properties of water and about the organization of molecules in liquid water at the molecular level. Cold liquid water (liquid water at 0° C) is a very structured liquid with many features resembling the nanostructure of ice. Indeed[34−38] (i) the number of nearest neighbors is 4.4 (4 in ice); (ii) the water molecules in cold water have tetrahedral coordination as in ice, with only a small deviation; (iii) the length of a H bond ($r_{oo} = 2.82$ Å) is only a little longer than that in ice ($r_{oo} = 2.76$ Å); and (iv) the average number of H bonds per molecule is 3.6 (in ice it is 4). However, there are many subtle characteristics in which liquid water is very different from ice. For instance, the fraction of four H-bonded molecules in water is about 55%, whereas in ice almost all of the molecules have four H bonds.

Methanol molecules form in the liquid-state chains of hydrogen-bonded molecules.[2,39−40] The average number of H bonds per methanol molecule in the liquid state is about 1.8, whereas a methanol molecule can form three H bonds: two as acceptors and one as a donor. The average distance between two H-bonded methanol molecules is 2.8 Å. As for water, there is a similarity with the methanol in the solid state, where the molecules form infinite chains with two H bonds per molecule.[41,42]

The nanostructure and energetic features of the liquid water/methanol mixture were investigated both experimentally and by molecular simulations. Neutron diffraction data[13] of a water-rich region (mole fraction of water 0.9) revealed that a hydration shell of water molecules is located at a distance of about 3.7 Å from the carbon atom of a methanol molecule. Although the water molecules in this shell generated a disordered cage, they retained roughly the tetrahedral local coordination of pure water. The water molecules in the above hydration shell were not greatly affected by the presence of methanol molecules.[13] This observation is in disagreement with the famous hypothesis of Frank and Evans[43] that an ordered structure (iceberg) is formed around a nonpolar solute in water. This iceberg structure was frequently[1−2,4−5] used to explain the large loss of entropy during the process of dissolution. A similar observation for the water-rich region was made by using the depolarized Rayleigh light-scattering technique[15] and by coupling neutron diffraction with hydrogen/deuterium isotope substitution.[17] Although no reorganization of the water surrounding the nonpolar groups was detected, a compression of the second-neighbor water−water contact distance was observed, which might constitute a structural feature of the hydrophobic hydration. The structure of methanol/water clusters and its dependence on the methanol mole fraction was investigated by mass spectrometry using clusters isolated from submicrometer droplets by adiabatic expansion in vacuum and by X-ray diffraction of bulk binary solutions.[44] It was found that in the water-rich range the water molecules had a tetrahedral orientation, the length of a H bond at a mole fraction of water of 0.9 being 2.82 Å, and the average distance between the carbon of a methanol molecule and the oxygen of the nearest touching water molecule (not H bonded to methanol) being 3.40 Å. However, in the methanol-rich region, chain clusters of methanol molecules became predominant, the length of a H bond at a mole fraction of methanol of 0.9 being 2.80 Å, and the average distance between the oxygen of a water molecule and the carbon of the nearest touching methanol molecule (not H bonded to methanol) being 3.38 Å.

The above experimental results provided many features regarding the local microscopic structure of methanol/water mixtures. However, for the time being, the experiment could not provide some subtleties regarding the local structure. For example, the hydration picture in the water-rich region was expected to be different around the hydrophobic moiety of methanol (methyl group) and around its hydrophilic hydroxyl group, but the experiment could not provide the details of the difference.

Meaningful results regarding the structural and energetic characteristics of methanol/water mixtures were obtained by

TABLE 1: Some Experimental and Computational Results Regarding the Local Structure of Water/Methanol Mixtures ($T = 298.15$ K)

	water-rich range	methanol-rich range	reference	comments
number of nearest neighbors that satisfy the condition ($r_{C_MO_W} \le 3.5$ Å)	3.1^{a}		47	experimental data
	3.4^{a}, 3.24^{a}	2.0^{b}, 1.9^{b}	44	
	3.4^{c}		18	molecular simulation
	$1.62^{d,e}$		22	
	2.9^{a}	2.6^{b}	46	
	2.6^{f}	3^{g}	48	
	2.5^{a}	2.51^{h}	49	
	3.4^{i}		23	
number of nearest neighbors that satisfy the condition (3.5Å $\le r_{C_M-O_W} \le 5.5$ Å)^{j}	10.7^{a}		47	experimental data
	10^{a}		13	
	17.6^{k}		17	
	20^{c}		18	molecular simulation
	11.3^{d}		22	
	16^{f}	8^{g}	48	
	12.4^{i}		23	
	$\sim 13^{l}$		45	
number of water/methanol H bonds with the central molecule that satisfy the condition ($r_{C_M-O_W} \le 3.5$ Å)	2.3^{c}		18	molecular simulation
	2.4^{l}		45	
average length of H bonds, $r_{O_M-O_W}$ (Å)	2.83^{a}		47	experimental data
	2.84^{a}, 2.82^{a}	2.76^{b}, 2.80^{b}	44	
	2.8^{c}		18	molecular simulation
	2.85^{a}	2.85^{b}	46	
average distance from a central molecule to the nearest neighbors, $r_{C_M-O_W}$(Å)	3.7^{a}		47	experimental data
	3.7^{a}		13	
	3.4^{a}	3.38^{b}	44	
	3.7^{i}		23	molecular simulation
	3.7^{l}		45	

[a] The mole fraction of methanol is 0.1. [b] The mole fraction of methanol is 0.9. [c] The mole fraction of methanol is 0.008. [d] The mole fraction of methanol is 0.002. [e] $r_{C_M - O_W} \le 3.3$ Å. [f] The mole fraction of methanol is 0.125. [g] The mole fraction of methanol is 0.875. [h] The mole fraction of methanol is 0.75. [i] The mole fraction of methanol is 0.003. [j] The nearest neighbors listed in the previous part of the Table ($r_{C_M-O_W} \le 3.5$ Å) are excluded. [k] The mole fraction of methanol is 0.05. [l] The mole fractions of methanol are 0.003 and 0.015.

molecular simulation. Two important papers[18,19] regarding the Monte Carlo simulations of dilute solutions of methanol in water were published about 20 years ago, and they provided some conflicting results. Okazaki et al.[19] concluded that by introducing one methanol molecule into water the potential energy and the structure of water had the tendency to be stabilized as a whole. This stabilization was attributed to the structural stabilization around the methyl group and to the strong H bonding in the hydrophilic region that acts cooperatively with the structural stabilization in the hydrophobic region. In contrast, according to Jorgensen and Madura,[18] the main feature of the hydration in the water-rich region is the favorable solute−solvent hydrogen bonding. They found that the first shell around the carbon of a methanol molecule (from 0 to 3.5 Å) contained 3.4 water molecules, which formed 2.3 hydrogen bonds with the methanol molecule, and an average of 2.9 water−water hydrogen bonds per water molecule. Consequently, they formed a total of 3.6 hydrogen bonds per water molecule, which was exactly the same as that for a water molecule in pure water. However, the water molecules from the second shell (from 3.5 to 4.5 Å) had a slightly lower average number of hydrogen bonds (3.39) than the bulk water (3.57). Although Okazaki et al.[19] found an iceberg-like structure of water molecules around a methanol molecule, Jorgensen and Madura[18] did not observe a large distortion of the water molecules around the methyl group. Results supporting the findings of Jorgensen and Madura[18] were recently obtained by Fidler and Rodger[24] via molecular dynamics simulations. They found[24] that the structure of water around the hydrophobic moiety of alcohol was essentially the same as that found in bulk water; in particular, there was no evidence of the presence of a clathrate-like cage around the hydrophobic moiety of the alcohol. Some change in the water structure was found in the vicinity of the hydroxyl group of the alcohol, with a hydrogen-bonding network closer to tetrahedral in the solvation shell than in bulk water. The Monte Carlo investigation of Hernandez-Cobos and Ortega-Blake[23] and the molecular dynamics results of Meng and Kollman[22] for dilute solutions of methanol in water also supported the results of Jorgensen and Madura.[18] The recently published density functional theory (DFT) based on molecular dynamics simulation[45] found that the “speculations that the normal water structure is significantly affected by the hydrophobic alkyl group are groundless”. However, much less information is available regarding the structural and energetic characteristics in the methanol-rich region. The molecular dynamics simulation of Palinkas, Hawlicka, and Heinzinger[46] for dilute solutions of water in methanol showed that when very little water was added to pure methanol (methanol-rich region) the water molecules associated with methanol were incorporated into the chains of the latter.

Some experimental and simulation results regarding the structural characteristics of methanol/water mixtures are listed in Table 1.

In contrast to the experimental methods, the molecular simulation techniques, such as molecular dynamics and Monte Carlo methods, allowed one to obtain some details about the molecular arrangements on the nanometer scale. However, the simulation techniques are very sensitive to the model potentials that are employed.

So far, ab initio quantum mechanical techniques were applied to the methanol/water dimer and the methanol/water/water trimer. It is well known that the methanol/water dimer can adopt two possible configurations depending on whether water (WdM) or methanol (MdW) acts as the hydrogen-bond donor. Because there is no large energetic difference between the two dimers, it was not easy to select the more stable dimer. Nevertheless, it was recently established that the dimer in which the water molecule is the proton donor (WdM) is more stable.[50,51] However, one should point out that a dimer or a trimer cannot represent a real patch of a dilute condensed phase because they cannot represent, for instance, the cooperative effect of many molecules. To achieve this goal, one must consider a much larger cluster.

3. Methodology of Calculations

Ab initio quantum mechanical methods were recently applied to the analysis of large clusters formed of one solute molecule and several molecules of solvent for water/methane mixtures.[33] It was shown[33] that they can provide information regarding the interaction energies and intermolecular distances between the molecules of methane and water. The obtained results were compared to the available experimental and molecular simulations regarding condensed mixtures, and agreement was found. A similar methodology of calculations will be used in the present paper as well.

Two types of clusters will be considered: (1) clusters with 1 methanol and 12 water molecules and (2) clusters with 1 water and 10 methanol molecules. Such clusters represent a computational compromise between the current capabilities of the modern ab initio methods and computer power on one hand and a feasible representation of dilute binary condensed mixtures on the other hand.

Second-order Møller−Plesset perturbation theory (MP2) is the quantum mechanical approach selected for the calculations because the sizes of the clusters that were employed were too large to use more accurate methods. In addition, MP2 provides accurate results regarding the calculation of the interaction energies for both H-bonded pairs[52] and van der Waals interacting pairs.[53]

The computational procedure presented below has the following objectives: (1) to find an optimal geometry for the clusters considered and (2) to determine the distances and the interaction energies between a central “solute” molecule and its nearest neighbors (“solvent” molecules).

The computational procedure consisted of three steps: (i) An initial cluster configuration was constructed using the Cerius^2 4.2 software. The solute molecule was placed in the center and was randomly surrounded by the molecules of the solvent. The configuration that was built was processed using the Cerius^2 CLEAN function, and the obtained structure was considered as the initial guess. (ii) The cluster geometry was obtained by optimizing the guess with respect to all coordinates using the MP2 method with a 6-31G basis set. This basis set makes the numerous geometry optimizations required tractable. For large clusters, it is difficult to reach the global minimum because the minimum reached can be a local one. To avoid the effect of the initially selected guess, we carried out the minimization procedure for a large number of initial guesses (12−16). In addition, vibrational frequencies were used to ensure that the optimized geometries were located at real minima. (iii) All of the pairwise intermolecular interaction energies were calculated for all of the optimized geometries. All of the interaction energies between molecules α and β ($E^{\mathrm{int}}_{\alpha\beta}$) were calculated using the supermolecular approach[26,27,54]

$$E^{\mathrm{int}}_{\alpha\beta} = E_{\alpha\beta}\{\alpha\beta\} - E_{\alpha}\{\alpha\beta\} - E_{\beta}\{\alpha\beta\} \qquad (1)$$

where $E_{\alpha\beta}\{\alpha\beta\}$ is the total energy of an $\alpha\beta$ pair obtained with an $\{\alpha\beta\}$ basis set and $E_{\alpha}\{\alpha\beta\}$ and $E_{\beta}\{\alpha\beta\}$ are the energies of the individual α and β molecules, respectively, also obtained with the $\{\alpha\beta\}$ basis set. The basis set superposition error (BSSE)[55] was partially accounted for by using the function counterpoise method (FCP).[56]

In contrast to the geometry optimization, which was carried out with the smaller 6-31G basis set, a larger 6-311++G (3d, 2p) basis set was employed to calculate the energies because, at least for small clusters,[57−59] the geometry is less sensitive, whereas the energies are very sensitive to the size of the basis set used.

We were tempted to use the same basis set for the cluster geometry optimization as that used for the calculations of the interaction energies between molecules (6-311++G (3d, 2p)). However, the present computer capabilities have not allowed us to perform such calculations in a reasonable amount of time.

4. Results of the ab Initio Computations

4.1. Dilute Mixture of Methanol in Water. Sixteen initial guesses, each containing 1 molecule of methanol and 12 molecules of water, were optimized in the present paper. The optimized clusters were treated as follows: (1) The geometries of the clusters were used to calculate the distances between the carbon and oxygen atoms of the central methanol molecule and the oxygen atoms of the water molecules. (2) The interaction energies between the central methanol molecule and the surrounding water molecules were calculated using eq 1.

Experimental data and simulation results for dilute solutions of methanol in water[13,23] indicated that the radial distribution function $g_{\mathrm{C_M O_W}}$ has the first maximum at a distance of about 3.7 Å and the first minimum at about 5.2−5.3 Å from the central methanol molecule. The water molecules located in the layer between 3.7 and 5.3 Å constitute the first solvation shell. According to recent data,[17] there are about 18 water molecules around a central methanol molecule in the first solvation shell. These molecules can be roughly subdivided into two groups:[33] (1) touching nearest neighbors and (2) nontouching nearest neighbors. The molecules of the first group are in contact with the central methanol molecule. In our paper regarding dilute clusters of methane in water,[33] we used (somewhat arbitrarily) a distance of 4.1 Å from the central methane molecule to separate these two groups of molecules from each other. These two groups of molecules have very different interaction energies with the central methane molecule. Besides, the molecules of the first group (touching nearest neighbors) are tangentially oriented toward the central methane molecule, and this sublayer is somewhat denser than the bulk water. We will use the same separation of water molecules around the central methanol molecule in the first solvation shell. A similar subdivision was used by Rossky and Karplus in a paper regarding dipeptide hydration.[60]

For each of the water molecules belonging to the first group, the distances between the O atom of water and the carbon atom of the methanol molecule and the intermolecular interaction energy were calculated. The results of these calculations are listed in Tables 2−4. These Tables contain the average distances and interaction energies as double arithmetic averages. First,

TABLE 2: Arithmetic Averages of the Distances and Interaction Energies[a] between a Central Solute Molecule and Touching Nearest-Neighbor Solvent Molecules[b] in the $CH_4O\cdots(H_2O)_{12}$ and $H_2O\cdots(CH_4O)_{10}$ Clusters

cluster	type of solvent molecules in the cluster	$r_{\mathrm{C_MO_W}}$, Å	$E^{\mathrm{int}}_{\mathrm{CH_4O-H_2O}}$, kJ/mol
$CH_4O\cdots(H_2O)_{12}$	not H bonded with the central methanol molecule	3.45	−2.7
	H bonded with the central methanol molecule	3.61	−15.79
$H_2O\cdots(CH_4O)_{10}$	not H bonded with the central water molecule	3.65	−1.8
	H bonded with the central water molecule	3.62	−17.29

[a] The interaction energies were calculated between a central solute molecule and all of the solvent molecules located not further than 4.1 Å from the central solute molecule. [b] The solvent molecules located not further than 4.1 Å from the central solute molecule were considered to be touching nearest neighbors of a central solute molecule.

TABLE 3: Average Orientation of Water Molecules[a] Not H Bonded with a Central Methanol Molecule toward the Central Methanol Molecule

	average distance between the carbon atom of methanol and the oxygen and hydrogen atoms of the water molecules in the $CH_4O\cdots(H_2O)_{12}$ cluster, Å		
layer	$r_{\mathrm{C_MO_W}}$	$r_{\mathrm{C_MH_{W(1)}}}$	$r_{\mathrm{C_MH_{W(2)}}}$
$r_{\mathrm{C_MO_W}} \leq 4.1$ Å	3.45	3.85	3.77

[a] The water molecules are not located further than 4.1 Å from the central methanol molecule.

calculations were made for all of the water molecules of a cluster belonging to one of the groups, and second, for all of the 16 clusters investigated. One of the typical minimized clusters ($CH_4O\cdots(H_2O)_{12}$) is presented in Figure 1a and b.The molecules of water in the vicinity of a central methanol molecule can be subdivided into two classes: (1) not H bonded with the central methanol molecule and (2) H bonded with it. (A hydrogen bond is defined here as suggested by Jorgensen and Madura.[18] Namely, any pair of molecules with an interaction energy of −9.5 (kJ/mole) or less is considered to be hydrogen bonded.) Although the average distances between the central methanol molecule and these two types of water molecules are almost the same, the interaction energies are enormously different (see Tables 2 and 4).

The arithmetic averages of the distances and of the interaction energies between a central methanol molecule and the water molecules belonging to each of the above two classes in the $CH_4O\cdots(H_2O)_{12}$ cluster are listed in Table 2. The orientation of the non-H-bonded water molecules with respect to the central methanol molecule is presented in Table 3.

Details regarding the second class of water molecules (H bonded with the central methanol molecule) in the $CH_4O\cdots(H_2O)_{12}$ cluster are listed in Table 4. A comparison with the literature data regarding the liquid methanol/water mixtures (Table 1) reveals that (1) the average number of water molecules having H bonds with a central methanol molecule is about 2.8, whereas molecular simulation[18,45] predicted 2.3−2.4 and (2) the obtained lengths of the H bonds are somewhat shorter than those obtained by molecular simulation[18,45] (see Discussion).

4.2. Dilute Mixture of Water in Methanol. Twelve initial guesses, each containing 1 molecule of water and 10 molecules of methanol, were optimized and then analyzed in the same way as the $CH_4O\cdots(H_2O)_{12}$ clusters in the preceding section. Namely, (1) the geometries of each cluster were determined, and the distances between the oxygen atom of water and the carbon and oxygen atoms of the methanols were calculated and (2) the interaction energies between a central water molecule and the surrounding methanol molecules were calculated using eq 1. The results of these calculations are presented in Tables 2 and 4. One of the typical minimized clusters ($H_2O\cdots(CH_4O)_{10}$) is presented in Figure 2a and b.As in the previous case ($CH_4O\cdots(H_2O)_{12}$ cluster), the molecules of methanol in the vicinity of a central water molecule can be subdivided into two different classes: (1) not H bonded with water and (2) H bonded with it.

The arithmetic averages of the distances and of the interaction energies between a central water molecule and the methanol molecules belonging to each of the above classes in the $H_2O\cdots(CH_4O)_{10}$ cluster are listed in Table 2. It is interesting to note that the methanol molecules not H bonded to a central water molecule have characteristics very similar to those of methane molecules around a central water molecule in the $H_2O\cdots(CH_4)_{10}$ cluster.[33] Indeed, in the latter cluster, the average distance and interaction energy between a central water molecule and the nearest touching methane molecules ($r_{\mathrm{C_{CH4}O_{H2O}}} = 3.69$ Å and $E^{\mathrm{int}}_{\mathrm{CH_4-H_2O}} = -1.83$ kJ/mol) are very close to the corresponding values in Table 2 ($r_{\mathrm{C_MO_W}} = 3.65$Å and $E^{\mathrm{int}}_{\mathrm{H_2O-CH_4O}} = -1.79$ kJ/mol). However, the average distance between a central water molecule and the nearest touching methanol molecules from Table 2 is somewhat different from the distance (3.38 Å, see Table 1) obtained experimentally[44] for a dilute solution of water in methanol.

Let us consider in more detail the second class of methanol molecules in the $H_2O\cdots(CH_4O)_{10}$ cluster, which are H bonded to a central water molecule (see Table 4). Comparing Tables 1 and 4, one can conclude that the lengths of H bonds in the $H_2O\cdots(CH_4O)_{10}$ clusters are in agreement with the experimental lengths;[44] the simulations [46] provided somewhat longer H bonds. Our results regarding the average number of H bonds between a central water molecule and methanol molecules in the $H_2O\cdots(CH_4O)_{10}$ cluster differ from those predicted in the literature.[46] According to the literature,[44,46] the average number of H bonds between a central water molecule and methanol molecules in a dilute solution of water in methanol is about 2, and the molecular dynamics simulation of Palinkas, Hawlicka, and Heinzinger[46] showed that the water molecules are associated with methanol, being incorporated into the chains of the latter. Our results (Table 4) provide for the average number of H bonds between a central water molecule and methanol molecules a value of about 3. This means that a central water molecule

TABLE 4: Methanol/Water Hydrogen Bonds in the $CH_4O\cdots(H_2O)_{12}$ and $H_2O\cdots(CH_4O)_{10}$ Clusters

	average number of H bonds between a central solute molecule and the solvent molecules		average length of the H bonds ($r_{\mathrm{O_M-O_W}}$), Å		average energy of the H bond, kJ/mol	
cluster	WdM[a]	MdW[b]	WdM[a]	MdW[b]	WdM[a]	MdW[b]
$CH_4O\cdots(H_2O)_{12}$	1.75	0.94	2.74	2.67	−18.34	−11.04
$H_2O\cdots(CH_4O)_{10}$	1.75	1.08	2.77	2.72	−18.50	−14.75

[a] The water molecule is the proton donor. [b] The methanol molecule is the proton donor.

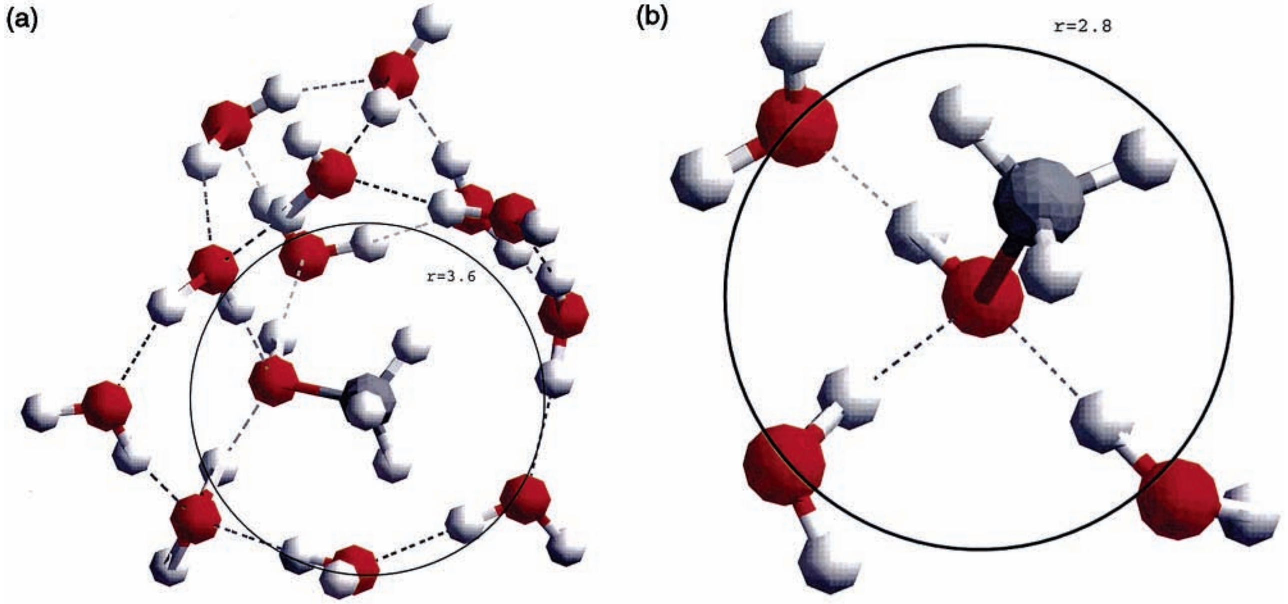

Figure 1. Optimized methanol (1)/water (12) cluster: (a) full cluster and (b) fragment containing only the central methanol molecule and the water molecules H bonded to the central one. (- - -) denotes H bonds. The circles (in a, $r = 3.6$ Å centered on a carbon atom of the methanol and in b, $r = 2.8$ Å centered on an oxygen atom of the methanol) are included for illustration.

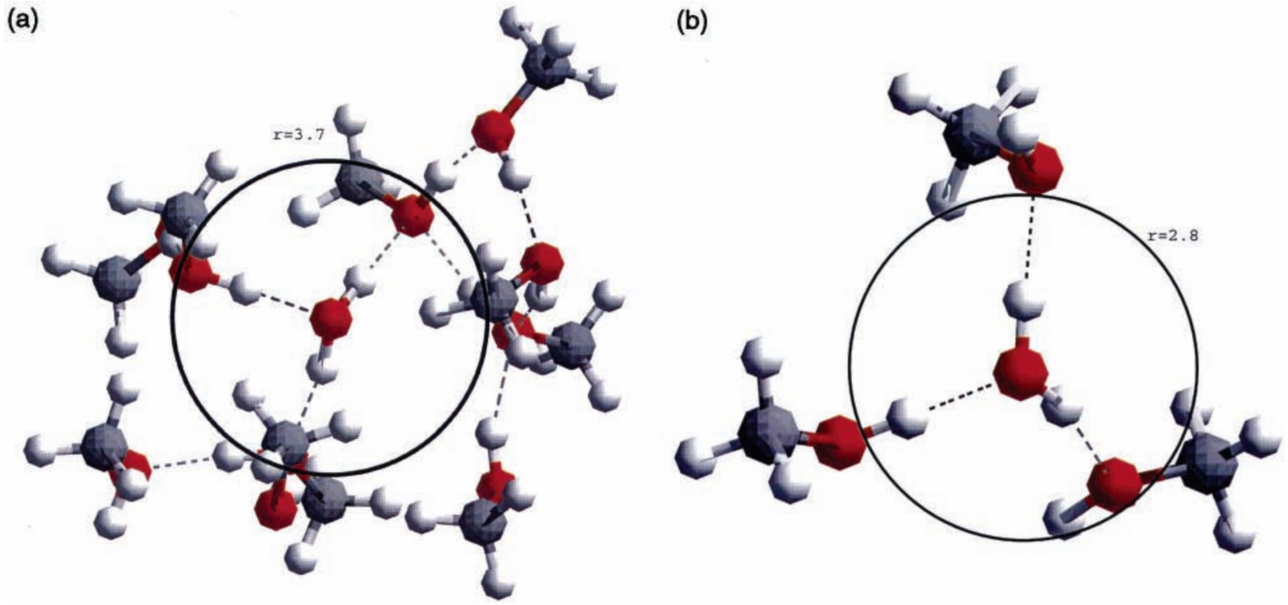

Figure 2. Optimized water (1)/methanol (10) cluster: (a) full cluster and (b) fragment containing only the central water molecule and the methanol molecules H bonded to the central one. (- - -) denotes H bonds. The circles (in a, $r = 3.7$ Å centered on an oxygen atom of the water, and in b, $r = 2.8$ Å centered on an oxygen atom of the water) are included for illustration.

cannot be incorporated into the middle of a chain of methanol molecules but can be, for instance, the center of several (2−3) chains of methanol molecules.

5. Discussion

Sixteen different $CH_4O\cdots(H_2O)_{12}$ clusters and twelve different $H_2O\cdots(CH_4O)_{10}$ clusters were optimized, and the results listed in Tables 2−4 represent double arithmetic averages per cluster and all of the clusters of the calculated properties. Table 5 provides the mean percentage deviation of the average H-bond lengths and energies (Table 2) from the values provided by the optimized clusters. Table 5 shows that the number of initial cluster configurations considered (16 and 12) is large enough to represent accurately the distances and the interaction energies between a central solute molecule and its nearest neighbors (solvent molecules).

The results listed in Tables 2−4 show that the interaction energies and the intermolecular distances between the molecules of water and methanol are quite different in the $CH_4O\cdots(H_2O)_{12}$ and $H_2O\cdots(CH_4O)_{10}$ clusters. This difference reflects the fact that the two kinds of clusters represent two different physical systems. Indeed, the two extreme cases at mole fractions of $x_1 \to 0$ and $x_2 \to 0$ are very different because the solute molecules have different solvent environments in the two clusters. This generates a difference between the water/methanol intermolecular interaction energies in the two cases and clearly indicates that the intermolecular interaction energy between the molecules of water and methanol depends on composition. This

TABLE 5: Mean Percentage Deviation of the Average H-Bond Length and Energy (Table 2) from the Values Obtained for All of the Optimized Clusters

cluster composition	number of optimized clusters	deviation (%)[a] length of the H bonds ($r_{O_M-O_W}$)	deviation (%)[a] energy of the H bonds
$CH_4O\cdots(H_2O)_{12}$	16	3.0	9.8
$H_2O\cdots(CH_4O)_{10}$	12	3.3	11.8

[a] Deviation (%) is the mean percentage deviation defined as

$$\frac{100\sum_{i=1}^{N}\left|\frac{x_i - x}{x}\right|}{N}$$

where x_i is either the length of the H bonds or the energy of the H bonds in the optimized cluster i, x is the arithmetic average value of these quantities (see Table 2), and N is the number of optimized clusters (here, 16 and 12).

TABLE 6: Average Intermolecular Distances between H-bonded Water Molecules in the Vicinity[a] of a Solute Molecule

cluster	r_{OO}, (Å) b	r_{OO}, (Å) c	data from the literature[35,37] regarding the length of H bonds in liquid water
$CH_4O\cdots(H_2O)_{12}$	2.74	2.74	$r_{OO} = 2.82$ (Å) in liquid water at 4 °C and
$CH_4\cdots(H_2O)_{10}$[d]	2.73		$r_{OO} = 2.84$ (Å) in liquid water at 20 °C

[a] The pairs of water molecules were selected such that at least one water molecule was located not further than 4.5 Å from the central solute molecule. [b] At least one water molecule is H bonded to the central solute molecule. [c] Neither water molecule is H bonded to the central solute molecule. [d] Data for the $CH_4\cdots(H_2O)_{10}$ cluster were calculated on the basis of previous results.[33]

fact should be taken into account when the intermolecular interaction energies are employed to calculate the thermodynamic properties at different compositions of a binary mixture.[61]

The molecules of solvent in both clusters ($CH_4O\cdots(H_2O)_{12}$ and $H_2O\cdots(CH_4O)_{10}$) can be subdivided into two very different classes: (1) H bonded with a central solute molecule and (2) not H bonded with a central solute molecule. As expected, these two classes possess striking energy differences. Indeed, although they are located at about the same distance from the central solute molecule ($r_{C_MO_W}$ in Table 2), their intermolecular interaction energies with the central molecule are extremely different. One can see from Table 2 that the H-bond energy between a central water molecule and a neighboring methanol molecule is almost 10 times larger (in magnitude) than when the water/methanol pair is not H bonded.

Let us examine the properties of the water molecules around a solute molecule by discussing how these molecules differ from those in pure water, how they are oriented toward the surface of the solute, and the properties of the H bonds between the water molecules (their lengths and energies). Such characteristics of the water molecules in the vicinity of a solute molecule are important not only for small molecules, such as alcohols and hydrocarbons, but also for "large" molecules such as biomolecules.

First, let us consider the lengths of the H bonds between the water molecules in the vicinity of a central methanol molecule in the $CH_4O\cdots(H_2O)_{12}$ clusters (Table 6). One can see from Table 6 that the lengths of the H bonds between the water molecules in the vicinity of a central methanol molecule are almost the same as those in the $CH_4\cdots(H_2O)_{10}$[33]cluster. However, the H bonds in the above clusters are shorter than those in pure water (see Table 6). This observation can be explained if one supposes that the layer of water molecules around a solute molecule (methane or methanol) is a little denser than that in pure water. This increase in density is probably caused by the so-called hydrophobic wall effect, which occurs when the water molecules have a hydrophobic surface on one side and cannot form four H bonds. Because the average number of H bonds per molecule of water in pure water is 3.6, the water molecules in the vicinity of a solute molecule should have a smaller number of H bonds, and therefore their characteristics should be different from those in pure water.

Second, the orientation of the water molecules (not H bonded with a central solute molecule) toward the hydrophobic surface of the solute plays a role in the understanding of the hydration of molecules of dual nature, such as methanol. Although for pure hydrophobic solutes, such as hydrocarbons and noble gases, the water molecules in the vicinity of a solute are tangentially oriented toward the surface of the solute (a fact also observed experimentally[62]), such an orientation is not obvious for the molecules of dual nature. Indeed, we found that the average orientation of the water molecules in the vicinity of a central methanol molecule is not fully tangential (Table 3). However, it is clear that not all of the water molecules in the vicinity of a central methanol molecule are under "the same conditions". The water molecules located on the C_M-O_M line beyond the CH_3 group can be tangentially oriented toward the surface of the CH_3 group; however, it is hardly possible for the water molecules located in the vicinity of the hydrophobic/hydrophilic interface of a methanol molecule to be tangentially oriented toward the methanol molecule.

As already noted, the methanol/water dimer can adopt two possible configurations (WdM or MdW), depending on whether the water or methanol molecule acts as the hydrogen-bond donor. It was recently established that the dimer in which the water molecule is the proton donor (WdM) is more stable.[50,51] However, in a condensed phase, which is represented here approximately by the $CH_4O\cdots(H_2O)_{12}$ and $H_2O\cdots(CH_4O)_{10}$ clusters, both types of H-bond configurations are present (see Table 4). Let us compare some of the characteristics of dimer WdM or MdW in the gas phase with the different H-bond configurations in the clusters investigated (Table 7). One can see from Table 7 that the lengths of the H bonds (O−O distances) in both kinds of H-bond configurations (WdM and MdW) in the $CH_4O\cdots(H_2O)_{12}$ and $H_2O\cdots(CH_4O)_{10}$ clusters are shorter and their interaction energies are smaller (in magnitude) than those of the gas-phase dimers. These results can be explained by the mutual steric hindrances between the solvent molecules that cannot be oriented in their optimal positions as they are for the gas-phase dimers. Table 7 also reveals that the average number of WdM configurations is twice as large as the average number of MdW configurations. For the $CH_4O\cdots(H_2O)_{12}$ clusters, this result can be explained by observing that the methanol molecule can donate only a single H bond but can accept two. However, for the $H_2O\cdots(CH_4O)_{10}$ clusters, the number of WdM and MdW configurations is determined by energetic and steric factors.

Although the average number of H bonds per molecule in cold water is 3.6 (in ice it is 4), in the $H_2O\cdots(CH_4O)_{10}$ clusters, the average number of H bonds per molecule of water is 2.7. Therefore, a molecule of water has lost about 1 H bond when compared to cold water. However, the average number of H bonds per molecule in liquid methanol is about 2, and we found that the average number of H bonds per molecule of methanol

TABLE 7: Comparison between the Two Types of Water/Methanol Hydrogen Bonds in the $CH_4O\cdots(H_2O)_{12}$ and $H_2O\cdots(CH_4O)_{10}$ Clusters

H-bond configuration	O−O distance, Å			H-bond energy, kJ/mole			average number of H bonds per solute molecule	
	a	b	c	a	b	c	a	b
WdM	2.74	2.77	2.85	−18.34	−18.50	−22.8	1.75	1.75
MdW	2.67	2.72	2.90	−11.04	−14.75	−19.2	0.94	1.08

[a] $CH_4O\cdots(H_2O)_{12}$. [b] $H_2O\cdots(CH_4O)_{10}$. [c] Water/methanol dimer.[50,51]

in the $CH_4O\cdots(H_2O)_{12}$ clusters is about 2.8; a molecule of methanol acquires about 0.8 additional H bond compared to pure liquid methanol, probably because the water molecules are smaller.

Two additional issues should be examined at least in passing: (1) the effect of cluster size and (2) the effect of temperature. (1) In our previous publication,[33] we considered clusters of 1 methane and several (1, 4, 6, 8, 10 and 12) water molecules, and the conclusion was that the clusters with 10−12 water molecules provided accurate results for the "average" distances and interaction energies between a methane molecule and the nearest water molecules in the $CH_4\cdots(H_2O)_n$ cluster. Of course, a full picture of the hydration phenomenon of small solutes can be obtained only if larger clusters (1 molecule of solute and 24 or 36 molecules of water) are considered. In particular, larger clusters are required to understand the structure and intermolecular interactions in the second and probably third hydration layers. The same conclusion is likely to be valid for the $CH_4O\cdots(H_2O)_{12}$ and $H_2O\cdots(CH_4O)_{10}$ clusters considered in the present paper. The clusters considered in the present paper are helpful in understanding the interactions between a central solute molecule and its nearest neighbors (solvent molecules). (2) The ab initio quantum mechanical methods provide results at 0 K and zero pressure. Although the interactions depend on temperature and pressure, this dependence is expected to be weak up to normal conditions.[63,64] Indeed, it was shown[63,64] for pure water that the length of the hydrogen bonds has changed by only 4 parts per 1000 at most when the temperature varied by 100 K. Furthermore, a comparison between the local structure of supercooled water and liquid water under ambient conditions indicated that the number of nearest neighbors and the position of the maximum on the radial distribution function $g_{oo} = g_{oo}(r_{oo})$ (where r_{oo} is the distance between the oxygen atoms of two water molecules) are only slightly different.[65−69] In addition, a simple procedure to account for the effect of temperature was suggested.[63,64] One should note that the results of the ab initio quantum mechanical method, such as those obtained in the present paper, cannot provide information about the temperature effect on the hydrophobic hydration. In contrast, the molecular simulation methods can provide such information but involve model interaction potentials.

6. Conclusions

In this paper, the Møller−Plesset perturbation theory was applied to clusters formed by 1 molecule of methanol and 12 molecules of water or 1 molecule of water and 10 molecules of methanol. The goal was to determine the intermolecular distances and interaction energies between water and methanol molecules in the $CH_4O\cdots(H_2O)_{12}$ and $H_2O\cdots(CH_4O)_{10}$ clusters to compare the obtained results with the available experimental data and to shed some light on the nanostructure and molecular interactions in dilute solutions of methanol and water.

It was found that the solvent molecules in both clusters ($CH_4O\cdots(H_2O)_{12}$ and $H_2O\cdots(CH_4O)_{10}$) can be subdivided into two classes: (1) not H bonded with a central solute molecule and (2) H bonded with a central solute molecule. Although they are located at almost the same distances ($r_{C_MO_W}$) from the central solute molecule, these two classes possess striking differences regarding the interaction energies with a solute.

The solvent molecules, which are not H bonded with a central solute molecule, do not exhibit any peculiar features different from those of pure solvents (water or methanol). However, the H bonds in the clusters investigated demonstrated the presence of salient features, which seem to be important in the understanding of the molecular interactions in dilute mixtures formed by water and methanol.

In general, the ab initio quantum mechanical method that was employed in the present paper provided useful information about the hydrogen bonds in the systems investigated. In particular, it gives full information about two types of H bonds (WdM and MdW) between water and methanol molecules, including information about their energies and lengths; it provided a relationship between the numbers of the two types of H bonds in the $CH_4O\cdots(H_2O)_{12}$ and $H_2O\cdots(CH_4O)_{10}$ clusters. Such unique information could hardly be obtained by other methods.

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References and Notes

(1) Franks, F.; Desnoyers, J. E. *Water Sci. Rev.* **1985**, *1*, 171.
(2) Franks, F.; Ives, D. *J. Rev. Chem. Soc.* **1966**, *20*, 1.
(3) Ott, J. B. *J. Chem. Thermodyn.* **1990**, *2*, 1129.
(4) Franks, F. In *Water: A Comprehensive Treatise;* Franks, F., Ed.; Plenum: New York, 1973; Vol. 2.
(5) Franks, F.; Reid, D. S. In *Water: A Comprehensive Treatise*; Franks, F., Ed.; Plenum: New York, 1973; Vol. 2.
(6) Tanford, C. *The Hydrophobic Effect: Formation of Micelles and Biological Membranes*, 2nd ed.; Wiley: New York, 1980.
(7) Ben-Naim, A. *Hydrophobic Interactions*; Plenum: New York, 1980.
(8) Belousov, V. P.; Panov, M. Y. *Thermodynamics of Aqueous Solutions of Non-Electrolytes* (in Russian); Khimiya: Leningrad, Russia, 1983.
(9) Nishikawa, K.; Kodera, Y.; Iijima, T. *J. Phys. Chem.* **1987**, *91*, 3694.
(10) Nishikawa, K.; Hayashi, H.; Iijima, T. *J. Phys. Chem.* **1989**, *93*, 6559.
(11) Hayashi, H.; Nishikawa, K.; Iijima, T. *J. Phys. Chem.* **1990**, *94*, 8334.
(12) Hayashi, H.; Udagawa, Y. *Bull. Chem. Soc. Jpn.* **1992**, *65*, 155.
(13) Soper, A. K.; Finney, J. L. *Phys. Rev. Lett.* **1993**, *71*, 4346.
(14) Turner, J.; Soper, A. K. *J. Chem. Phys.* **1994**, *101*, 6116.
(15) Micali, N.; Trusso, S.; Vasi, C.; Blaudez, D.; Mallamace, F. *Phys. Rev. E* **1996**, *54*, 1720.
(16) Dixit, S.; Poon, W. C. K.; Crain, J. *J. Phys.: Condens. Matter* **2000**, *12*, L323.
(17) Dixit, S.; Soper, A. K.; Finney, J. L.; Crain, J. *Europhys. Lett.* **2002**, *59*, 377.
(18) Jorgensen, W. L.; Madura, J. D. *J. Am. Chem. Soc.* **1983**, *105*, 1407.
(19) Okazaki, S.; Nakanishi, K.; Touhara, H. *J. Chem. Phys.* **1983**, *78*, 454.
(20) Nakanishi, K.; Ikari, S.; Okazaki, H.; Touhara, J. *Chem. Phys.* **1984**, *80*, 1656.

(21) Nakanishi, K. *Chem. Soc. Rev.* **1993**, *22*, 177.

(22) Meng, E. C.; Kollman, P. A. *J. Phys. Chem.* **1996**, *100*, 11460.

(23) Hernandez-Cobos, J.; Ortega-Blake, I. *J. Chem. Phys.* **1995**, *103*, 9261.

(24) Fidler, J.; Rodger, P. M. *J. Phys. Chem. B* **1999**, *103*, 7695.

(25) Kiselev, M.; Ivlev, D. *J. Mol. Liq.* **2004**, *110*, 193.

(26) Sum, A. K.; Sandler, S. I. *Ind. Eng. Chem. Res.* **1999**, *38*, 2849.

(27) Sum, A. K.; Sandler, S. I. *Fluid Phase Equilib.* **1999**, *160*, 375.

(28) Maheshwary, S.; Patel, N.; Sathyamurthy, N.; Kulkarni, A. D.; Gadre, S. R. *J. Phys. Chem. A* **2001**, *105*, 10525.

(29) Weinhold, F. *J. Chem. Phys.* **1998**, *109*, 367.

(30) Ludwig, R.; Weinhold, F. *Phys. Chem. Chem. Phys.* **2000**, *2*, 1613.

(31) Levine, I. N. *Quantum Chemistry*, 4th ed.; Prentice Hall: Englewood Cliffs, NJ,

(32) Szabo, A.; Ostlund, N. S. *Modern Quantum Chemistry: Introduction to Advanced Electronic Structure Theory*; Dover Publication: New York, 1996.

(33) Ruckenstein, E.; Shulgin, I. L.; Tilson, J. L. *J. Phys. Chem. A* **2003**, *107*, 2289.

(34) Eisenberg, D.; Kauzmann, W. *The Structure and Properties of Water*; Oxford University Press: Oxford, U.K., 1969.

(35) Narten, A. H.; Levy, H. A. *Science* **1969**, *165*, 447.

(36) Frank, H. S. *Science* **1970**, *169*, 635.

(37) Narten, A. H.; Levy, H. A. In *Water: A Comprehensive Treatise*; Franks, F., Ed.; Plenum: New York, 1972; Vol. 1.

(38) Stillinger, F. H. *Science* **1980**, *209*, 451.

(39) Narten, A. H.; Habenschuss, A. *J. Chem. Phys.* **1984**, *80*, 3387.

(40) Jorgensen, W. L. *J. Am. Chem. Soc.* **1980**, *102*, 543.

(41) Tauer, K.; Lipscomb, W. N. *Acta Crystallogr*. **1952**, *5*, 606.

(42) Nagayoshi, K.; Kitaura, K.; Koseki, S. et al. *Chem. Phys. Lett*. **2003**, *369*, 597.

(43) Frank, H. S.; Evans, M. W. *J. Chem. Phys.* **1945**, *13*, 507.

(44) Takamuku, T.; Yamaguchi, T.; Asato, M.; Matsumoto, M.; Nishi, N. *Z. Naturforsch., A: Phys. Sci.* **2000**, *55*, 513.

(45) van Erp, T. S.; Meijer, E. J. *Chem. Phys. Lett.* **2001**, *333*, 290.

(46) Palinkas, G.; Hawlicka, E.; Heinzinger, K. *Chem. Phys.* **1991**, *158*, 65.

(47) Bako, I.; Palinkas, G.; Heinzinger, K. *Z. Naturforsch., A: Phys. Sci.* **1994**, *49*, 967.

(48) Ferrario, M. Haughney, M.; McDonald, I. R.; Klein, M. L. *J. Chem. Phys.* **1990**, *93*, 5156.

(49) Freitas, L. C. G. *J. Mol. Struct.: THEOCHEM* **1993**, *101*, 151.

(50) González, L.; Mó, O.; Yáñez, M. *J. Chem. Phys.* **1998**, *109*, 139.

(51) Kirschner K. N.; Woods, R. J. *J. Phys. Chem. A* **2001**, *105*, 4150.

(52) Dunning, T. H. *J. Phys. Chem. A* **2000**, *104*, 9062.

(53) Woon, D. E. *Chem. Phys. Lett.* **1993**, *204*, 29.

(54) (a) Chalasinski, G.; Gutowski, M. *Chem. Rev.* **1988**, *88*, 943. (b) Jeziorski, B.; Szalewicz, K. In *Encyclopedia of Computational Chemistry*; Schleyer, P. v. R., Ed.; Wiley: New York, 1998; Vol. 2, p 1376.

(55) Liu, B.; McLean, A. D. *J. Chem. Phys.* **1973**, *59*, 4557.

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

(57) Tsuzuki, S.; Uchimaru, T.; Matsumura, K.; Mikami, M.; Tanabe, K. *J. Chem. Phys.* **1999**, *110*, 11906.

(58) Frisch, M. J.; Delbene, J. E.; Binkley, J. S.; Schaefer, H. F. *J. Chem. Phys.* **1986**, *84*, 2279.

(59) Gonzalez, L.; Mo, O.; Yanez, M. *J. Chem. Phys.* **1998**, *109*, 139.

(60) Rossky, P. J.; Karplus, M. *J. Am. Chem. Soc.* **1979**, *101*, 1913.

(61) Ruckenstein, E.; Shulgin, I. *Ind. Eng. Chem. Res.* **1999**, *38*, 4092.

(62) De Jong, P. H. K.; Wilson, J. E.; Neilson, G. W.; Buckingham, A. D. *Mol. Phys.* **1997**, *91*, 99.

(63) Dougherty, R. C. *J. Chem. Phys.* **1998**, *109*, 7372.

(64) Dougherty, R. C.; Howard, L. N. *J. Chem. Phys.* **1998**, *109*, 7379.

(65) Narten, A. H.; Thiessen, W. E.; Blum, L. *Science* **1982**, *217*, 1033.

(66) Kimura, N.; Yoneda, Y. *Phys. Lett. A* **1982**, *92*, 297.

(67) Bosio, L.; Chen, S. H.; Teixeira, J. *Phys. Rev. A* **1983**, *27*, 1468.

(68) Corban, R.; Zeidler, M. D. *Ber. Bunsen-Ges. Phys. Chem.* **1992**, *96*, 1463.

(69) Botti, A.; Bruni, F.; Isopo, A.; Ricci, M. A.; Soper, A. K. *J. Chem. Phys.* **2002**, *117*, 6196.