The Journal of Physical Chemistry A

© Copyright 1998 by the American Chemical Society VOLUME 102, NUMBER 31, JULY 30, 1998

LETTERS

Water Clusters: Fascinating Hydrogen-Bonding Networks, Solvation Shell Structures, and Proton Motion

Hai-Ping Cheng

Department of Physics and Quantum Theory Project, University of Florida, Gainesville, Florida 32611

Received: March 10, 1998; In Final Form: May 22, 1998

Structure, energetics, and dynamics of protonated water clusters $(H_2O)_nH^+$ ($n = 1,8$) are studied with first-principles Born−Oppenheimer molecular dynamics simulations. Two solvation shell structures, centered at H^+ and H_3O^+, respectively, are found to be nearly equivalent energetically. However, the dynamical and thermodynamical characteristics of these two competing structures are very different. Patterns of hydrogen-bonded networks as well as the mechanisms of proton transfer are revealed via systematic investigations.

The evolution patterns of physical properties as functions of cluster size for pure water clusters $(H_2O)_n$ and water hydrates $X_m(H_2O)_n$, in which X_m is a neutral species or ion, are among the most complex problems in molecular and cluster physics and have attracted intense attention.[1−13] Experiments and theory indicate that ionization,[5] charging,[6] and protonation[3,7] induce significant rearrangement in hydrogen-bonded networks. Understanding these patterns is of fundamental and practical importance in various scientific fields. Small water clusters are abundant in the earth's atmosphere[8] and in biological environments.[9] The energetics and dynamics of small water complexes govern many physical and chemical processes such as formation of aerosol particles,[8,10] proton pumping across protein membranes,[14,15] microsolvation[4,11] and proton-transfer dynamics.[12,13] Because of the unique role of these small water aggregates in nature, cluster studies serve a 2-fold purpose: understanding the physics of finite systems and understanding the implications for bulk matters. Current increasing experimental activities on water clusters have created the need and the opportunity for advanced theoretical modeling.

As perhaps the most ubiquitous ion in aqueous solution, the proton has been the focus of many research activities. The generally accepted model is an H_3O^+ surrounded by water molecules through hydrogen bonding. Lately, another model in which the proton is centered in a $H_5O_2^+$ complex was also proposed.[12] Since the reactivity of water clusters is closely related to the proton solvation state and dynamics, clusters of a selected size in a specific isomeric state provide unique conditions for chemical and physical processes. The protonated water dimer and larger clusters have thus become subjects of vast interest[3,6,7,11,12] since they are the key players in many chemical and biological processes. Nevertheless, the microscopic description of proton solvation and proton dynamics remains incomplete. Challenges to both accurate theoretical and experimental studies are mainly due to the relatively weak but complex intermolecular bonding, the high mobility of the proton, and the high polarizability of the water molecule. Even more challenging is including the effects of finite temperature since the topographic features of the energy landscape in aqueous clusters changes rapidly at thermal energies, where most important physical processes occur. Conventional approaches are often inadequate to describe and characterize these systems.

This letter reports results of a systematic, theoretical investigation of protonated water clusters $H^+(H_2O)_n$ ($n = 1, 8$). The investigation includes structures, electronic structures, energetics, and dynamics at finite temperature. From the evolution patterns of these properties, insights to the shell structures and stability of molecular clusters, isomerization, role of temperature in

S1089-5639(98)01433-9 CCC: $15.00 © 1998 American Chemical Society

proton transfer, formation of transient states, and solvation in water are revealed. Unlike metal clusters, the stability and magic numbers for these clusters are not determined by electronic shell structures based on a spherical jellium model but rather by the energetics of the hydrogen-bonded network. Thus, a different type of shell model is necessary to describe protonated water clusters. This study suggests that two parallel shell structures, or isomeric states, each requiring different sets of water molecules to form a complete shell, coexist in these clusters. The two shell structures create environments in which the proton displays completely different dynamical and thermodynamical characteristics. Temperature is found to be crucial for forming transient states and proton transfer. Our studies also indicate a strong size-dependent variation of physical properties such as the time scale of proton motion, height of the proton-transfer barrier, and rearrangment of hydrogen bonds. These properties and the observed dynamical switching between the two isomer states of proton solvation reveal the uniqueness of each cluster as well as clues about proton transfer in bulk water. Predictions and conclusions from this work are significant and timely for providing the basic elements to build a theoretical model as well as for stimulating further experiments in new directions.

The calculations and simulations are performed at the level of density functional theory (DFT) (Ceperly−Alder[16] exchange-correlation function with the Vosko and Wilks parametrization[17]) with generalized gradient approximations (GGA) (using the gradient exchange approximation of Becke and the gradient correlation approximation of Perdew[18]). Plane wave expansions in conjunction with nonconserving, nonlocal pseudopotentials (Troulier and Martin[19]) are used for the core electrons. An energy of 96 Ry is used throughout the calculations to ensure a numerical accuracy of 0.3 kcal/mol (or 13 meV). Careful checks are made on the validity of the results to probe energy differences of a fraction of kcal/mol. Results on $H_5O_2^+$ with this theoretical treatment confirm that it is in excellent agreement with extensive, high-level quantum chemistry calculations by Y. Xie et al.[12] Extensive comparisons are also made between theory and experiment regarding the characteristic vibrational frequencies. In general, the theory overestimates the frequencies by less than 3%.

The physical properties studied include the structures, energetics of ground states, isomers, proton-transfer barriers, dipole moments, and proton affinity (PA) which is defined as the energy of protonation, $PA = E(H^+(H_2O)_n) - E((H_2O)_n)$, where E is the total energy. We also analyze the hydration energy, $\Delta = E(H^+(H_2O)_n) - E(H^+(H_2O)_{n-1}) - E((H_2O))$, and vibrational spectra at finite temperatures.

Figure 1 depicts structures of $H^+(H_2O)_n$ ($n = 2, 4, 6, 7, 8$). For $n = 6$ and $n = 8$, two isomer states, centered on H_3O^+ and H^+, are obeserved. For $n = 6$, the energy difference between the two isomers is only about 0.3 kcal/mol, which is within the accuracy of the total energy evaluation. For $n = 8$, a 3.5 kcal/mol difference is observed between the two isomers. The destorted cubic structure (e) is slightly more stable than the twin-pentagon structure (f). Note that the number of water molecules required to form complete shells is 4 for the first shell (structure b) and 7 for the second shell (shtructure d) for the H_3O^+-centered structure, compared to 2 for the first shell (a), and 6 for the second shell (c) for the second structure. New features begin to develop at $n = 8$, in which molecules tend to form two-, and three-dimensional networks. A one-dimensional branch is another possible isomer state which has higher energy and is not included in Figure 1.

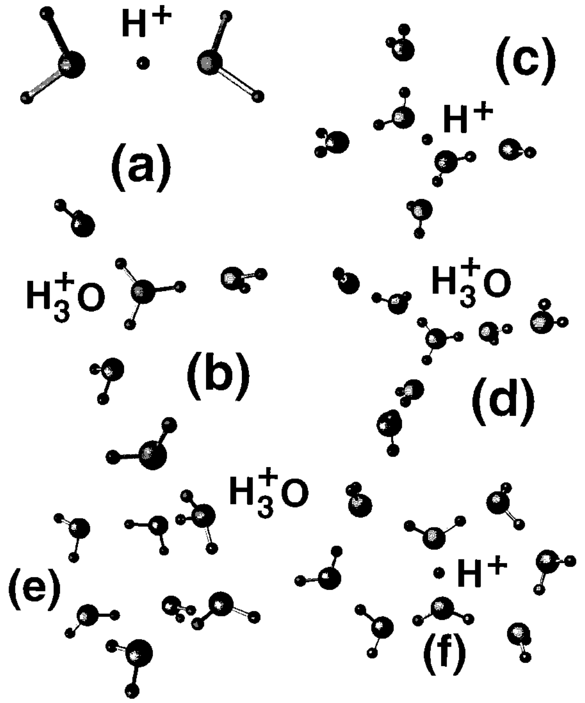

Figure 1. Structures of protonated water clusters, $H^+(H_2O)_n$ with (a) $n = 2$, (b) $n = 4$, (c) $n = 6$, (d) $n = 6$, (e) $n = 8$, and (f) $n = 8$. Structures (a) and (b) have complete first solvation shells for H^+ and H_3O^+ ions, respectively. Structures (c) and (d) have complete second solvation shells for the same ions. Structures (e) and (f) are isomers for the cluster with $n = 8$, H_3O^+-centered (e) and H^+-centered (f), respectively.

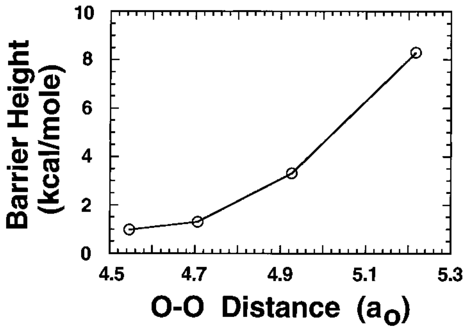

Figure 2. Energy barrier as a function of O−O distance for proton transfer in $H^+(H_2O)_6$. Note that the first point (~1 kcal/mol) corresponds to isomer e in Figure 1. The barrier does not exist in $H^+(H_2O)_2$, indicating the solvent effect due to the second-shell water molecules in the cluster.

In the H^+-centered state, the O−O distance in the first solvation shell is typically 4.51−4.56 a_0 compared to 4.90 a_0 for the O−O distance between the center oxygen and the first-shell oxygen atoms in the hydronium-centered state. The proton between the two water molecules causes the O−O distance to decrease such that the proton can move easily between the two molecules. For $n = 2$ and $n = 8$, the H^+ is centered between the two H_2O molecules with an O−H^+ distance of 2.26 a_0. For $n = 6$, an energy barrier of 1.0 kcal/mol is observed. The barrier height increases to 1.3, 3.3, and 8.3 kcal/mol when the O−O distance ($n = 6$) increases to 4.7, 4.9, and 5.22 a_0 (or 2.76 Å), respectively (Figure 2). The proton is located slightly toward one side of the system to form two asymmetrical hydrogen bonds with lengths of 2.11 and 2.45 a_0, respectively. This structure is different from the one proposed by D. Wei et al.,[7] in which the proton is located at an equal distance from the two oxygen atoms, with no barrier. The shorter O−H^+ distance

TABLE 1: Protonation Energy (eV), Hydration Energy (eV), and Dipole Moment (D) of Various Water Clusters

clusters $H^+(H_2O_n)$, n	proton affinity, $E_n - E[(H_2O)_n]$	hydration energy, $E_n - E_{n-1} - E[H_2O]$	dipole moment
1	7.52 (7.34−7.39)[a]		1.15
2	8.96 (8.68)	1.55 (1.370−1.561)[a]	0.76
3	9.26 (9.63)	0.98 (0.846−0.911)[a]	0.81
4	9.70 (10.41)	0.77 (0.776−0.694)[a]	0.97
5	10.0 (10.85)	0.47 (0.36−0.53)[a]	1.10
6		0.47 (0.32−0.48)[a]	0.56[b], 0.88[c]
7		0.43 (0.29−0.44)[a]	0.93
8		0.41[d], 0.29[e] (0.23−0.34)[a]	3.32[d], 0.91[e]

[a] Magnera et al. (ref 3) and references therein. [b] 1. H_3O^+-centered. [c] H^+-centered. [d] Cube. [e] Twin-pentagon.

is 2.11 a_0, about 13% longer than an O−H bond (1.87 a_0) in H_3O^+. At $n = 6$, an asymmetric H_3O^+ exists in a H^+-centered cluster. In this case, the H^+ center is a consequence of the thermodynamical considerations, in contrast to $H_5O_2^+$ in which the H^+ center is the zero-temperature structure. The energy barrier for proton-transfer motion is obtained by optimizing the structure with respect to a given O−O distance. The proton is constrained to have equal distance from the two oxygens but allowed to move in the direction perpendicular to the O−O direction.

Table 1 lists the proton affinity, hydration energy, and dipole moment for each cluster. A decrease of 0.3 eV in hydration energy is observed after the first solvation shell of the hydronium ion is complete. The hydration energy of the next shell is 0.47 eV, which is consistent with experimental results of Castleman et al.[3] The experiment found clusters with $n > 4$ only at lower temperatures. The second shell of the H^+-centered state is complete at $n = 6$, with a hydration energy of 0.46 eV. Note that both $n = 7$ and $n = 8$ support closed-shell structures, for H_3O^+-centered and H^+-centered states, respectively. The closed-shell structure and high hydration energy of the octamers support Castleman's conclusion that beyond $n = 8$ even lower temperatures are required for these clusters to be observed.

The analysis of structure and energetics and suggests that the two isomer states may have quite different physical properties, especially with respect to proton motion. To this end, Born−Oppenheimer molecular dynamics simulations (BOMD) with the above-mentioned theoretical treatment are performed to investigate the dynamical and thermodynamical properties of $H_5O_2^+$ and $H_9O_4^+$. These two systems represent the smallest units of H^+- and H_3O^+-centered solvation states. A detailed temperature-dependent study of $H_5O_2^+$ was presented previously by Cheng and Krause.[12] Here we shall focus on a comparison between the two solvation states. Figure 3 depicts the density of states (DOS) obtained by a Fourier transform of the momentum−velocity autocorrelation function $C(t)$. The function $C(t)$ is calculated by averaging 100 trajectories for a period of 2.0 ps, which gives a 10 cm^{-1} resolution in the DOS. It can be seen immediately that the feature near the water bending mode in $H_5O_2^+$ is more structured than that in $H_9O_4^+$. The extra band of peaks can be assigned to proton motion by calculating a partial DOS (Cheng et al.[12]) that is associated with H^+ only. In the $H_9O_4^+$ spectrum, no proton-transfer mode is observed. The peaks between 2500 and 3000 cm^{-1} are due to O−H stretching of the center hydronium ion.[3] In both systems, the temperature effects cause frequency shifts as well as broadening.

Analysis of the trajectories shows that in the $H_9O_4^+$ complex H_3O^+ is a rather stable subunit. No single event is recorded regarding proton transfer from the center to any of the terminal molecules. On the other hand, formation of H_3O^+ in $H_5O_2^+$ is a consequence only of finite temperature. At 360 K, the cluster spends 18% of its time in the form of a hydronium transient via proton rocking motion between the two molecules.

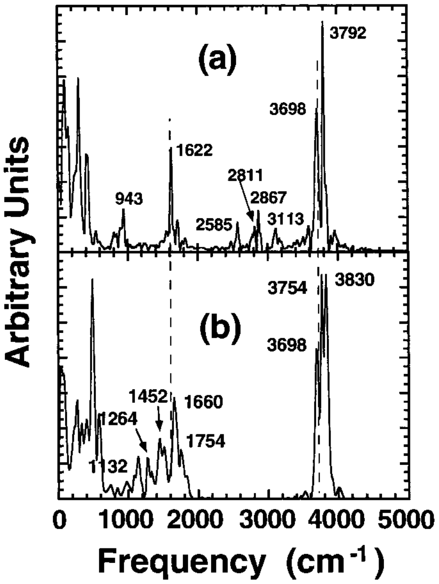

Figure 3. Density of vibrational states of $H^+(H_2O)_4$ (panel a), and $H^+(H_2O)_2$ (panel b). The spectra are obtained at 360 K. The proton-transfer modes are observed only in $H^+(H_2O)_2$, via a broad band between 1100 and 1450 cm^{-1} which is not observed in panel (a). The band between 2500 and 3150 cm^{-1} in panel (a) contains contributions from the H_3O^+ ion in the $H^+(H_2O)_4$ cluster.

BOMD simulations are currently underway for the $n = 6$ and $n = 8$ clusters, both H^+- and H_3O^+-centered. Preliminary indicates that for $n = 6$, the frequency of proton motion along O−O direction is approximately 20 ps^{-1} (or 650 cm^{-1}), which is 4 times faster than the estimated value in a bigger cluster (Tuckerman et al.[11]). Compared to the characteristic frequencies of H^+ in a $H_5O_2^+$ ion, 1200−1450 cm^{-1}, the proton-transfer frequency is red-shifted by about 400−600 cm^{-1}. This observation indicates a strong size dependence (solvent effects in this particular context) of the proton-transfer rate. For $n = 8$, the two isomers, H^+- and H_3O^+-centered, again display different dynamical characteristics. Unlike the $n = 4$ cluster, relatively slow proton transfer is observed in the H_3O^+-centered octamer. The detailed analysis of these clusters are underway.

The equivalence of the two solvation states implies that proton transfer in aqueous environments involves two basic steps: transformation from a H_3O^+-centered state to a H^+-centered one and then H^+ transfer from one H_2O to another. The first step involves cooperative molecular motion and hydrogen bond rearrangement, and the second step involves proton transfer over a smaller or zero barrier. In liquid water, at thermal energies, fulfilling the conditions for these two steps can occur easily, due to the mobility in liquid environments. The time scale for proton transfer is determined by the competition between the time for the O−O distance to decrease and the rate of proton transfer at that particular O−O distance, as well as by the time for reorientation of hydrogen bonds. The dynamical switching process actually traps the proton for a short period of time. Note that this dynamical trapping does not occur in ice because of the immobility of the oxygens. Consequently, the height of the barrier height will determine the proton-transfer rate.

Predictions from this study suggest that neutron scattering or infrared spectroscopy can be used to investigate the two solvation states of proton in water clusters because of the vastly different dynamical properties. Proton-transfer modes and energy barriers should be detected in H^+-centered clusters. At low temperature, proton tunneling splitting should also be observed for $n = 6$ and $n = 8$ via analysis of the vibration−rotation−tunneling states. Finally, it should be mentioned that for protonated water cations the quantum nature of the proton does not dominate the dynamics of transfer motion at room temperature. This fact has been discussed in detail by Cheng et al.[7] and Tuckerman et al.[7] using path integral in conjunction with DFT-GGA. Although rigorous methods that provide comparison between quantum and classical vibrational spectra in the first-principles simulations still remain to be developed, the results from this study reveal insights to the evolution patterns of proton motion and the underneath physical picture in the water clusters.

Acknowledgment. Acknowledgment is made by H.-P.C. to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research, to J. L. Krause for helpful discussions, and to the NIST and QTP supercomputer centers.

References and Notes

(1) See *Cluster of Atoms and Molecules*; Haberland, H.,Ed.; Springer Series in Chemical Physics; Springer: Berlin, 1994; p 56.

(2) Liu, K.; et al. *Nature* **1996**, *381*, 501. Liu, K.; et al. *Science* **1996**, *271*, 962 and 929. Gruenloh, C. J.; et al. *Science* **1997**, *276*, 5319.

(3) Okumura, M.; et al. *J. Phys. Chem.* **1990**, *94*, 3416. Yang, X., Jr.; et al. *Int. J. Mass Spectrom. Ion Processes* **1991**, *109*, 339. Magnera, T. F.; et al. *Chem. Phys. Lett.* **1991**, *182*, 363.

(4) Garvey, J. F.; et al. *J. Phys. Chem.* **1994**, *94*, 1999. Choi, J.-H.; et al. *J. Chem. Phys.* **1994**, *100*, 7153. Daly, G. M.; et al. *Chem. Phys. Lett.* **1993**, *206*, 500.

(5) Barnett, R. N.; Landman, U. *J. Phys. Chem. A* **1996**, *101*, 164. Haberland, H.; Bowen, K. H. In ref 1, p 134. Stace, A. J. *Phys. Rev. Lett.* **1988**, *61*, 306.

(6) Yang, X.; Castleman, A. W. Jr. *J. Phys. Chem.* **1990**, *94*, 8500. Castleman, A. W., Jr.; Brown, M. G. *J. Phys. Chem.* **1996**, *100*, 12911.

(7) Cheng, H.-P.; et al. *Chem. Phys. Lett.* **1995**, *237*, 161. Tuckerman, M.; et al. *Science* **1997**, *275*, 817. Wei, D.; et al. *J. Chem. Phys.* **1997**, *106*, 6086. Termath, V.; et al. *Mol. Phys.* **1997**, *91*, 963. Scheiner, S. *Annu. Rev. Phys. Chem.* **1994**, *45*, 23. Lee, E. P. F.; Dyke, J. M. *Mol. Phys.* **1991**, *73*, 375.

(8) (a) McEwan, M. J.; Phillips, L. F. *Chemistry of the Atmosphere*; Eward Arnold: London, 1975. (b) Wayne, R. P. *Chemistry of the Atmosphere*; Clarendon Press: Oxford, 1994.

(9) Teeter, M. M. *Proc. Natl. Acad. Sci. U.S.A.* **1984**, *81*, 6014. Neidle, S.; et al. *Nature* **1980**, *288*, 129. Lipscomb, L. A.; et al. *Biochemistry* **1994**, *33*, 3649.

(10) Kolb, C. E.; et al. *J. Am. Chem. Soc.* **1994**, *116*, 10314. Morokuma, K.; Muguruma, C. *J. Am. Chem. Soc.* **1994**, *116*, 10316.

(11) Barnett, R. N.; Landman, U. *Phys. Rev. Lett.* **1993**, *70*, 1775. Tuckerman, M.; et al. *J. Chem. Phys.* **1995**, *103*, 150. Watanabe, H.; Iwata, S. *J. Chem. Phys.* **1996**, *105*, 420. Tortonda, F. R.; et al. *Chem. Phys. Lett.* **1996**, *260*, 21.

(12) Cheng, H.-P. *J. Chem. Phys.* **1994**, *105*, 6844. Cheng, H.-P.; Krause, J. L. *J. Chem. Phys.* **1997**, *107*, 8461. Xie, Y.; et al. *J. Chem. Phys.* **1994**, *101*, 4878. Sobolewski, A. L.; Adamowicz, L. *J. Chem. Phys.* **1995**, *102*, 5708. Lobaugh, J.; Voth, G. A. *J. Chem. Phys.* **1996**, *104*, 2056.

(13) Honma, K.; Sunderling, L. S.; Armentrout, P. B. *Int. J. Mass Spectrom. Ion Processes* **1992**, *117*, 237; also *J. Chem. Phys.* **1993**, *99*, 1623.

(14) Nagle, J. F.; Tristram-Nagle, S. *J. Membrane Biol.* **1983**, *74*, 1. Akeson, M.; Deamer, D. W. *Biolphys. J.* **1991**, *60*, 101. Deamer, D. W.; Nichols, J. W. *J. Membrane Biol.* **1989**, *107*, 91.

(15) Sagnella, D. E.; et al. *Biolphys. J.* **1996**, *71*, 1172. Pomés, R.; Roux, B. *Chem. Phys. Lett.* **1995**, *234*, 416. Jeffrey, G. A. In Horizons in Hydrogen Bond Research, special issue of *J. Mol. Structure* **1994**, *322*, 21.

(16) Ceperley, D. M.; Alder, B. J. *Phys. Rev. Lett.* **1980**, *45*, 566.

(17) Vosko, S. H.; Wilks, L.; Nusair, M. *Can. J. Phys.* **1980**, *58*, 200. Vosko, S. H.; Wilks, L. *J. Phys.* **1982**, *C15*, 2139.

(18) Becke, A. D. *Phys. Rev.* **1988**, *A38*, 3098. Perdew, J. P. *Phys. Rev.* **1986**, *B33*, 8822.

(19) Troullier, N.; Martins, J. L. *Phys. Rev.* **1991**, *B43*, 1993 and 8861. Martins, J. L.; Cohen, M. L. *Phys. Rev.* **1988**, *B37*, 6134.