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Hydrogen Bonding in Protonated Water Clusters: An Atoms-in-Molecules Perspective

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This article highlights the results of a detailed study of hydrogen bonding in the first and the second solvation shells of Eigen (H_3O^+) and Zundel ($H_5O_2^+$) cations solvated by water in a stepwise manner. It is evident from the results that an electron density analysis clearly distinguishes the first and the second solvation shell and helps in quantifying the strength of hydrogen bonding in these clusters.

Introduction

The ability of water to solvate positive, negative, and neutral species gives it a prominent place among solvents. Among the hydrated species, the hydrated proton has received special attention.[1−3] There is a lot of interest in the structure and stability of water and protonated water clusters under different conditions as they hold the key to the understanding of cloud/ice formation, structure of liquid water, and solvation of various ionic and molecular species.[4]

Two main structural models have emerged for the hydrated proton. When a proton interacts with a single water molecule, it forms a strong covalent bond with the oxygen atom to form the hydronium ion H_3O^+, of C_{3v} symmetry, known as the Eigen cation.[1] Eigen proposed a protonated water cluster with a core structure of H_3O^+. Zundel, however, suggested an $H_5O_2^+$ complex in which a proton is shared between two water molecules. The interaction of a water molecule with the hydronium ion leads to the Zundel ion,[5] $H_5O_2^+$, with a stabilization energy of 34.4 kcal/mol.[6] From accurate ab initio calculations on $H_5O_2^+$, it was found that the equilibrium geometry has C_2 symmetry with an O−O bond length of 2.38 Å. Larger clusters involving Eigen and Zundel cations as well as a hydroxyl ion with H_2O have been investigated in detail.[7−14] Quantum chemistry calculations, molecular dynamics, and Monte Carlo simulations as well as various spectroscopic techniques have led to the conclusion that the hydrated proton forms a fluxional defect in the hydrogen-bonded (H-bonded) network, with both Eigen and Zundel ions occurring in the sense of “limiting” or “ideal” structures.

For $H^+(H_2O)_n$, $n = 3$, the possible structures considered by different groups in their calculations and spectral interpretations are a trihydrated proton in which three water molecules surround the proton and a dihydrated hydronium ion in which two equivalent water molecules are connected symmetrically to two different H atoms of a hydronium ion. $H^+(H_2O)_4$ is an interesting species among hydrated protons. In this case, the first solvation shell around the H_3O^+ core is filled.[15,16] The size-selected clusters of protonated water, $H^+(H_2O)_n$, $n = 4−7$, have been studied in the gas phase.[7] An extensive analysis of their spectra has shown that for $n = 4−7$ the clusters are chainlike. As the number of water molecules increases, water molecules with terminal free hydrogens are involved in H-bonding, and a networklike structure is formed. When $n \approx 19$, a two-dimensional (2D) network structure changes to a cage type involving H bonds by the free hydrogen atoms of the water molecules. These types of H-bonded network structures are quite different from those of the neutral water clusters, which form 3D cage structures at $n = 6$.[17] Various theoretical studies on $H^+(H_2O)_n$ provide the equilibrium geometry in the electronic ground state, stabilization energy (SE), and vibrational spectra. Different model structures were used by various groups in understanding the spectral information on protonated water. Only very few experimental studies on the structure of protonated water clusters with $n > 8$ existed until the end of the past decade, with the exception of $n = 21$, the magic number cluster.[7,9] Most of the experimental studies on larger protonated water clusters were limited to mass spectrometric studies. Infrared studies become complicated as the cluster size increases. However, recent advances in IR spectroscopy have enabled researchers to study size-selected protonated water clusters.[7] Recent reports on protonated water clusters using this technique along with higher-level theoretical calculations provide valuable information on the hydrated proton vibrations in water clusters.[10,12,18]

To establish the role of H_3O^+ and $H_5O_2^+$ ion cores in larger clusters, Headrick et al. studied extensively the spectral signature of hydrated proton vibrations in water clusters.[10] To interpret their spectra, optimization of the geometries of the clusters was carried out by them, followed by the computation of harmonic frequencies at the MP2/aug-cc-pVDZ level of theory.

The main focus of the earlier studies on water clusters of Eigen and Zundel ions has been on the (i) proton-transfer mechanism, (ii) structure of the first solvation shell, and (iii)

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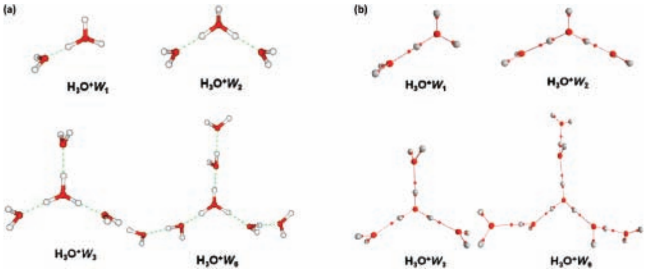


Figure 1. (a) Molecular structure and (b) electron density topology of (H_3O^+)−water clusters.

TABLE 1: Calculated Stabilization Energies (MP2/6-311++G Level) for Various (H_3O^+)−Water Clusters**

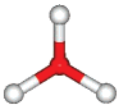
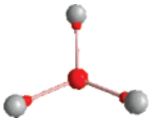
 cluster	number of H-bonds (distances in Å)	SE (kcal/mol)	SE(kcal/mol)/ H-bond
$H_3O^+W_1$	1 (1.2)	50.0	50.0
$H_3O^+W_2$	2 (1.5)	58.3	29.1
$H_3O^+W_3$	3 (1.5)	75.2	25.1
$H_3O^+W_6$	6 (1.5−1.7)	111.1	18.5

TABLE 2: Electron Density ($\rho(r_c)$) and the Laplacian of Electron Density ($\nabla^2\rho(r_c)$) Values at HBCPs for Various (H_3O^+)−Water Clusters in the First and the Second Solvation Shells (MP2/6-311++G Level)**

 cluster	solvation shell	$\rho(r_c)$ (e/a_o^3)	$\nabla^2\rho(r_c)$ (e/a_o^5)
$H_3O^+W_1$	first	0.16	−0.11
$H_3O^+W_2$	first	0.07	0.05
		0.07	0.05
$H_3O^+W_3$	first	0.06	0.05
		0.06	0.05
		0.06	0.05
$H_3O^+W_6$	first	0.06	0.05
		0.06	0.05
		0.06	0.05
	second	0.03	0.04
		0.03	0.04
		0.03	0.04

computation of a high-quality interaction potential to describe the clusters. These studies revealed the stepwise development of solvation, which involved 4−6 solvent molecules. Because the H-bonding sites in the clusters are not blocked, protonated water clusters exhibit an infinite network. The presence of a cyclic and branched H-bonded network can also be observed in these clusters.

From these studies, several interesting results on the structure and stability of $H_3O^+(H_2O)_n$ clusters have been obtained. Further, these clusters act as an effective probe of H-bonding, allowing the OH···O bond strengths to vary from very strong to very weak. Because the cause for the anomalously high rate of proton transfer in bulk water was identified as the difference between the first and the second solvation shells, characterization and quantification of the strength of individual interactions in them are extremely important.[19] The usefulness of AIM theory to understand and characterize H-bonding is well documented.[20−22] Therefore, we have undertaken an ab initio electronic structure investigation of protonated water clusters to quantify H-bonded interaction in the first and the second solvation shells using electron density.

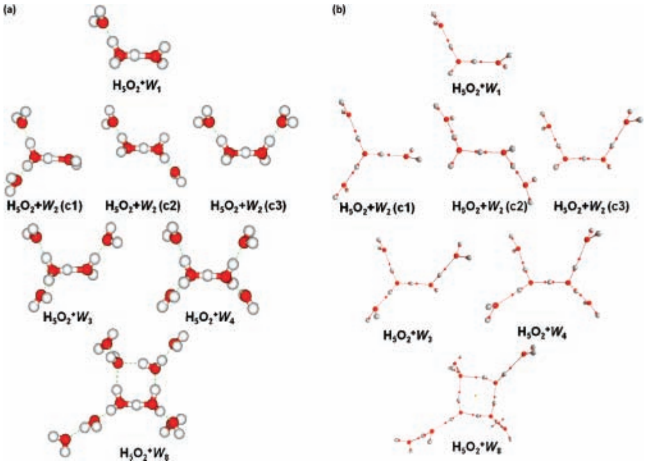


Figure 2. (a) Molecular structure of $(H_5O_2^+)$−water clusters. (b) Molecular electron density topology of $(H_5O_2^+)$−water clusters.

Computational Details

The geometries of $H_3O^+(H_2O)_n$ (n = 1−3, 6) (henceforth referred to as $H_3O^+W_n$) and $H_5O_2^+W_n$ (n = 1−4, 8) clusters of chainlike, including branched chain, clusters that include first and second solvation shells were selected and optimized using the MP2/6-311++G** level of theory, with the help of the Gaussian 98W suite of programs.[23] Frequency calculations were carried out to check the true minimum energy structures. Stabilization energies of all of the clusters have been calculated using the supermolecule approach and corrected for basis set superposition error (BSSE) using the counterpoise (CP) procedure suggested by Boys and Bernardi[24]

$$\mathrm{SE} = |E_{\mathrm{cluster}} - \{E_{\mathrm{W+}} + E_{\mathrm{W}_n}\}| \qquad (1)$$

where E_{cluster} is the total energy of a cluster and $E_{\mathrm{W^+}}$ ($= E_{\mathrm{H_3O^+}}$ or $E_{\mathrm{H_5O_2^+}}$) and E_{W_n} are the total energies of the hydronium ion or Zundel ion and water molecules/clusters, respectively, calculated using the CP method with the same basis set. AIM calculations were carried out using the wave functions generated from the MP2/6-311++G** level calculations using the AIM2000 package.[25]

Results and Discussion

H-Bonding in Hydration of the Eigen Cation. In this section, an analysis of the strength of the H-bonded interaction when water molecules interact with the Eigen cation in a stepwise manner is presented. Figure 1a depicts the structure of a solvated Eigen cation, the ground-state geometries of $H_3O^+W_n$ (n = 1−3, 6) obtained using the MP2/6-311++G** method. The electron density topological features of protonated water clusters are shown in Figure 1b. In the first shell, the hydronium ion donates all three hydrogen atoms to bond with the neighboring water molecules and is hence at the center of the bonding network.

The calculated SEs for various protonated water clusters are listed in Table 1 along with the number of H-bonds and H-bond distances from MP2/6-311++G** level of calculations. The SE per H-bond is considerably higher for $H_3O^+W_1$. Further stepwise addition of water molecules to $H_3O^+W_1$ drastically decreases the SE per H-bond. Variation in the H-bonding distances reveals that the first shell H-bonds are shorter than those in the second shell. The same trend has been observed for all other clusters in accordance with the earlier findings on dipole moment and hydration energy.[15]

The arrangement of the first and the second shell water molecules around a metal ion has been investigated recently.[26] This study highlights the influence of the cation size and charge on the local structure of hydrated ions, the high-charge cations causing chemical changes and the low-charge cations being less efficient in maintaining the local order of water molecules.[26] In addition, it is found that the first coordination sphere M···O distances are linearly related to the charge/radius ratio. However, the second coordination sphere distances are not as well-correlated, suggesting an enhanced influence of competing H-bonding interactions. Such a hydrogen bonding interaction is difficult to quantify. An easy and reliable differentiation of the first and the second coordination spheres has been demonstrated with the help of AIM theory.

The electron density and its Laplacian values at the hydrogen bond critical point (HBCP) in the first and the second solvation shells are listed in Table 2. The value of $\rho(r_c)$ for $H_3O^+W_1$ is 0.16 a.u. The addition of the second water molecule results in a sudden decrease in the electron density values at the HBCP. Marginal changes in $\rho(r_c)$ can be seen from the values shown in Table 2 for the addition of the third water molecule to the hydronium ion. As was found in the earlier studies, three water molecules are sufficient to form the first solvation shell around H_3O^+.[15,16] To quantify the strength of the H-bond formed in the second solvation shell, three more water molecules are added to form the structure $H_3O^+W_6$ as depicted in Figure 1. The calculated $\rho(r_c)$ values for the second solvation shell H-bonds are all the same and on the order of 0.03 a.u., which is approximately half of what was found for the first hydration shell. It is interesting to note that the Laplacian of electron density at the HBCP is negative for the $H_3O^+W_1$ cluster,[22e] indicating the covalent character of the bond. For other H-bonds, the Laplacian is positive, implying a classical H-bonded interaction.

The strength of the first H-bond formed in $H_3O^+W_1$ is 50.0 kcal/mol, which is in accordance with its covalent character. The SE per H-bond in $H_3O^+W_2$ is ~29 kcal/mol, in agreement with the decrease in the corresponding $\rho(r_c)$ values. For the completed first solvation shell structure $H_3O^+W_3$, SE per H-bond is ~25 kcal/mol, and this is reflected in the corresponding drop in the $\rho(r_c)$ values. SE per H-bond in the second solvation shell is ~19 kcal/mol in accordance with the decrease in the $\rho(r_c)$ value at various HBCPs. The $\rho(r_c)$ values at the HBCP clearly distinguish the first shell and second shell H-bonding in the hydration of Eigen cation and quantify the strength of the interaction of H_2O with H_3O^+.

H-Bonding in Hydration of the Zundel Cation. Minimum energy structures of the first and the second shell solvation of the Zundel cation by water molecules are depicted in Figure 2a. The molecular electron density graphs obtained from AIM analysis for various hydrated Zundel cation clusters are shown in Figure 2b. The calculated SEs for these clusters are presented in Table 3. Electron density and the Laplacian of electron density for the solvated Zundel ions are given in Table 4. It is interesting to note that for the completion of the first solvation shell of the Zundel cation four water molecules are sufficient. This arrangement is one of the favorable geometries for capturing the symmetrical Zundel cation within a complete first hydration shell. This cluster has also been observed in earlier experimental and theoretical investigations.[6,12,13,19]

TABLE 3: Calculated Stabilization Energies (MP2/6-311++G Level) for Various ($H_5O_2^+$)−Water Clusters**

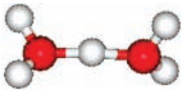
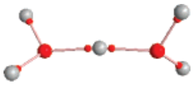
 cluster	number of H-bonds (distances in Å)	SE (kcal/mol)	SE(kcal/mol)/H-bond
$H_5O_2^+W_1$	1 (1.45)	25.6	25.6
$H_5O_2^+W_2$ (c1)	2 (1.54)	45.0	22.5
$H_5O_2^+W_2$ (c2)	2 (1.6)	38.5	19.2
$H_5O_2^+W_2$ (c3)	2 (1.6)	38.3	19.1
$H_5O_2^+W_3$	3 (1.6−1.7)	55.8	18.6
$H_5O_2^+W_4$	4 (1.6−1.7)	65.6	16.4
$H_5O_2^+W_8$	9 (1.6−1.9)	110.4	12.4

TABLE 4: Electron Density ($\rho(r_c)$) and the Laplacian of Electron Density ($\nabla^2\rho(r_c)$) Values at the HBCPs for Various ($H_5O_2^+$)−Water Clusters in the First and the Second Solvation Shells

 cluster	solvation shell	$\rho(r_c)$ (e/a_o^3)	$\nabla^2\rho(r_c)$ (e/a_o^5)
$H_5O_2^+W_1$	first	0.07	0.05
$H_5O_2^+W_2$ (c1)	first	0.06	0.05
		0.06	0.05
$H_5O_2^+W_2$ (c2)	first	0.05	0.05
		0.06	0.04
$H_5O_2^+W_2$ (c3)	first	0.05	0.04
		0.05	0.04
$H_5O_2^+W_3$	first	0.04	0.04
		0.05	0.04
		0.05	0.04
$H_5O_2^+W_4$	first	0.04	0.04
		0.04	0.04
		0.04	0.04
		0.04	0.04
$H_5O_2^+W_8$	first	0.06	0.05
		0.07	0.05
		0.02	0.03
		0.04	0.04
	second	0.03	0.03
		0.03	0.03
		0.03	0.03
		0.03	0.03
		0.02	0.03

It can be seen from Table 3 that the calculated SE per H-bond is the highest for the $H_5O_2^+W_1$ cluster. For other clusters, the SE per H-bond decreases due to changes in the electrostatic interactions, akin to the solvation of the Eigen cation by water. Further stepwise addition of water molecules to the $H_5O_2^+W_1$ cluster drastically decreases the SE. The strength of the first H-bond formed in $H_5O_2^+W_1$ is 25.6 kcal/mol, which is in accordance with a strong H-bond.[21] An examination of three different conformations of $H_5O_2^+W_2$ shows that $H_5O_2^+W_2$ (C1) is the most stable. The SE of $H_5O_2^+W_3$ is 18.6 kcal/mol per H-bond. For the completed first solvation shell structure ($H_5O_2^+W_4$), SE per H-bond is ~16.4 kcal/mol and is reflected in the corresponding fall in the $\rho(r_c)$ values. The energy per H-bond in the second solvation shell is ~12 kcal/mol, in accordance with a further decrease in the $\rho(r_c)$ value at various HBCPs.

Close scrutiny of the electron density values at the HBCPs of these clusters reveals a similar pattern as that of solvation of the Eigen cation by water. There is a decrease in the electron density value at the HBCPs in the second solvation shell when compared to the first shell, implying that the H-bonded interaction between water molecules and the Zundel ion is the strongest in the first solvation shell. It is important to point out that solvation by more than three water molecules reduces the

SE for each H-bond as well as the electron density value, which implies the opening of the second solvation shell in the protonated water cluster.

Conclusion

Ab initio calculations along with an AIM analysis have clearly provided answers to the fascinating questions related to the solvation of the Eigen and Zundel cations by water. The calculated SE for various clusters and the AIM results have clearly brought out the nature of the interaction in the first and the second solvation shells and the presence of other secondary interactions. It is possible to quantify the H-bond interaction with the AIM-derived parameters. It is interesting to note that the interaction of the first water molecule with the Eigen ion is covalent in nature, with a maximum SE when compared to the other H-bonds in the first and second solvation shells. Successive formation of H-bonds in protonated H-bonded clusters shows that the first two bonds are stronger than the subsequent, revealing the presence of strong and medium interactions in these clusters.

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