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Theoretical investigation of hydrogen bonding interaction in $H_3O^+(H_2O)_9$ complex

Gul Afroz Meraj · Ajay Chaudhari

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Abstract Hydrogen bonding interaction of hydronium ion with water molecules in its first and second solvation shell is studied using density functional theory with B3LYP functional and aug-cc-pvtz basis set. The nature of interaction and contribution from various interaction energies to the binding energy of a complex is studied using many-body analysis approach. The hydrogen bonds between hydronium and water molecules in its first solvation shell are stronger than those between water molecules in its second solvation shell. Many-body analysis shows that not only two-body but higher many-body energies up to seven-body interactions are also not negligible whereas eight-, nine-, and ten-body interaction energies are negligible for this complex. The terms containing hydronium ion as one of the many-body components have higher contribution to the respective total many-body interaction energy than those from the terms containing only water molecules. Additive as well as non-additive interactions are attractive and contribute about 58.6 and 44.3 % respectively to the binding energy of a complex.

Keywords Hydrated hydronium · Hydrogen bonding · Many-body analysis

Introduction

Hydrogen bonding, one of the most important non-covalent interactions encountered in natural science, is of great importance in many fields of biology, chemistry, and physics [1–3]. In aqueous environment, hydrogen bonding interactions play a crucial role in the process of proton transfer. The intermolecular forces through hydrogen bonding also play an important role in protein folding, solute-solvent interaction, and molecular solvation [4–15]. In the last two decades, there has been considerable interest in the structure and dynamics of hydrogen bonded molecular clusters due to the importance of these types of interaction force in many physical, chemical, and biological phenomena. Numerous theoretical and experimental studies have been carried out to understand the importance of hydrogen bonding through small molecular clusters [9–13].

In bulk water, water molecules are held together by strong hydrogen bonds by cooperative behavior. Water clusters play an important role in understanding the cloud and ice formation, solution chemistry, and many biological processes. Water clusters have been the subject of a number of experimental and theoretical investigations. Understanding the structural and binding properties of small water clusters also helps to understand the properties of bulk water. Hydrated water clusters and water clusters have been extensively studied [16–36].

Protonated water clusters are formed by neutral water molecules with an excess proton, H^+. This highly reactive excess proton immediately associates with the oxygen atom of one of the neighboring water molecules in water cluster thereby forming the hydronium ion, H_3O^+. Protonated water clusters are thought to be present in a wide range of natural environments. They are also found to be an influential element in the chemistry of the upper atmosphere. Protonated water clusters have attracted lots of attention in recent years. Unprotonated as well as protonated water clusters have been the subject of rich experimental [29, 37–45] and theoretical investigations [46–73].

Understanding properties of protonated water clusters helps us to gain insight into the solvation structures and dynamics of protons in aqueous environment. Understanding the nature of an extra proton in bulk water is also essential for explaining the proton transport phenomenon in membrane, mobility of the proton in water and the acid–base chemistry in solution [49, 74, 75]. Protonated water clusters are the key elements in dissociation and transport phenomena in aqueous chemistry and biological systems. The hydronium ion and zündel ion are the two

G. A. Meraj
School of Physical Sciences, Swami Ramanand Teerth Marathwada University, Nanded 431 606, India

A. Chaudhari (✉)
Department of Physics, The Institute of Science, FORT, Mumbai 400032, India
e-mail: ajaychau5@yahoo.com

important structures formed when an extra proton is introduced in the hydrogen bonded network of water. Although protonated water clusters are important from upper atmospheric, solution chemistry, and biological processes point of view, thorough molecular-level understanding of these clusters remains unclear. These clusters are quite different from those of neutral water clusters and water clusters containing anion and cation. Also, for the protonated water clusters, a reliable potential is not available. In order to develop the reliable potential for protonated water clusters a thorough understanding of these clusters in terms of structure and energetics is necessary.

The aim of this work is to study the hydrogen bonding interaction in hydrated hydronium ion complex using the density functional theory method. We have considered hydronium ion with its first and second solvation shell ($H_3O^+(H_2O)_9$) for the study. The interaction between hydronium ion and water molecules in its first and second solvation shell as well as that between water molecules is studied using the many-body analysis technique [53, 76–86]. This article is structured as follows: The next section gives computational details along with many-body analysis technique. Result and discussion comprises the third section followed by the conclusions.

Computational details

Geometries of hydrated hydronium ion, i.e., $H_3O^+(H_2O)_9$ hydrogen bonded complex are optimized using density functional theory with B3LYP functional and aug-cc-pVTZ basis set. Table 1 gives Cartesian coordinates for atoms in a $H_3O^+(H_2O)_9$ complex optimized at B3LYP/aug-cc-pvtz level. Various interaction energies are obtained for $H_3O^+(H_2O)_9$ complex using the many-body analysis approach. All the calculations are carried out using the Gaussian suit of programs [87].

Table 1 Cartesian coordinates for atoms in a $H_3O^+(H_2O)_9$ complex optimized at B3LYP/aug-cc-pvtz level

Molecule	Atom no.	X	Y	Z
W1	4 O	−1.4	1.3	−1.6
	5 H	−2.3	1.0	−1.6
	6 H	−1.3	1.8	−0.7
W2	7 H	−0.2	−2.3	0.8
	8 O	−0.8	−2.4	0.0
	9 H	−1.7	−2.1	0.4
W3	1 O	2.3	−0.0	−0.1
	2 H	3.2	−0.2	−0.4
	3 H	2.2	0.9	0.3
HDN	10 H	−0.5	0.2	−1.6
	11 O	0.2	−0.6	−1.5
	12 H	−0.3	−1.4	−0.9
	13 H	1.0	−0.4	−1.0
W4	26 O	−0.9	2.4	1.0
	28 H	−1.1	1.6	1.6
	29 H	−1.4	3.1	1.3
W5	27 O	−3.9	0.3	−1.2
	30 H	−4.4	−0.3	−1.8
	31 H	−3.8	−0.2	−0.4
W6	15 O	−3.1	−1.1	1.1
	18 H	−3.7	−1.5	1.8
	19 H	−2.6	−0.4	1.6
W7	14 O	1.0	−1.7	1.9
	16 H	0.5	−1.1	2.5
	17 H	1.6	−1.1	1.4
W8	21 O	4.8	−0.6	−1.0
	24 H	5.0	−0.5	−2.0
	25 H	5.2	−1.4	−0.8
W9	20 O	1.9	2.4	0.9
	22 H	0.9	2.5	1.0
	23 H	2.3	2.6	1.8

Many body energies for $H_3O^+(H_2O)_9$ complex

Many-body energies (two-, three-, four-, and ten-body interaction energies) are calculated as: follows: The decomposition of total energy of a complex can be written as

$$\begin{aligned}\Delta E &= E(ijk\ldots.n)-\{E_H+9E_W\}\\ &= \sum_{i=1}^{n} E(i)-\{E_H+9E_W\} \qquad (relaxation\ energy)\\ &+\sum_{i=1}^{n-1}\sum_{j>i}^{n} \Delta^2E(ij) \qquad (Two-body)\\ &+\sum_{i=1}^{n-2}\sum_{j>i}^{n-1}\sum_{k>j}^{n} \Delta^3E(ijk) \qquad (Three-body)\\ &+\ldots\ldots..+\Delta^nE(ijk\ldots.n) \qquad (n-body) \qquad (1)\end{aligned}$$

where $E(i)$, $E(ij)$, $E(ijk)$, $E(ijkl)$, are the energies of the various monomers, dimers, trimers, tetramer, in a complex and E_H, E_W are the energies of isolated hydronium ion and water molecule, respectively. The pairwise two-body interaction energies and many-body interaction energies are defined as:

$$\Delta^2E(ij) = E(ij)-\{E(i)+E(j)\} \qquad (2)$$

$$\begin{aligned}\Delta^3E(ijk) &= E(ijk)-\{E(i)+E(j)+E(k)\}\\ &-\{\Delta^2E(ij)+\Delta^2E(ik)+\Delta^2E(jk)\}\end{aligned} \qquad (3)$$

$$\Delta^4E(ijkl) = E(ijkl) - \{E(i) + E(j) + E(k) + E(l)\} - \Big\{\Delta^2E(ij) + \Delta^2E(ik) + \Delta^2E(il) + \Delta^2E(jk) + \Delta^2E(jl) + \Delta^2E(kl)\Big\} - \{\Delta^3E(ijk) + \Delta^3E(ijl) + \Delta^3E(ikl) + \Delta^3E(jkl)\} \quad (4)$$

and so on.

The basis set superposition error (BSSE) corrected energy of a subsystem (e.g., *ijkl*) is evaluated in the full basis of a larger system (*ijk….n*), and denoted by the term *E*(*ijk*|*ijk….n*). Accordingly, the *n*-body terms are substituted with the BSSE corrected ones:

$$\Delta^2E_C(ij) = E\left(ij\middle|ijk\ldots.n\right) - \left\{E\left(i\middle|ijk\ldots.n\right) + E\left(j\middle|ijk\ldots.n\right)\right\} \quad (5)$$

$$\Delta^3E_C(ijk) = E\left(ijk\middle|ijk\ldots.n\right) - \left\{E\left(i\middle|ijk\ldots.n\right) + E\left(j\middle|ijk\ldots.n\right) + E\left(k\middle|ijk\ldots.n\right)\right\} - \left\{\Delta^2E\left(ij\middle|ijk\ldots.n\right) + \Delta^2E\left(ik\middle|ijk\ldots.n\right) + \Delta^2E\left(jk\middle|ijk\ldots.n\right)\right\} \quad (6)$$

$$\Delta^4E_C(ijkl) = E(ijkl) - \left\{E\left(i\middle|ijk\ldots.n\right) + E\left(j\middle|ijk\ldots.n\right) + E\left(k\middle|ijk\ldots.n\right) + E\left(l\middle|ijk\ldots.n\right)\right\} - \left\{\Delta^2E\left(ij\middle|ijk\ldots.n\right) + \Delta^2E\left(ik\middle|ijk\ldots.n\right) + \Delta^2E\left(il\middle|ijk\ldots.n\right) + \Delta^2E\left(jk\middle|ijk\ldots.n\right) + \Delta^2E\left(jl\middle|ijk\ldots.n\right) + \Delta^2E\left(kl\middle|ijk\ldots.n\right)\right\} - \left\{\Delta^3E\left(ijk\middle|ijk\ldots.n\right) + \Delta^3E\left(ijl\middle|ijk\ldots.n\right) + \Delta^3E\left(ikl\middle|ijk\ldots.n\right) + \Delta^3E\left(jkl\middle|ijk\ldots.n\right)\right\} \quad (7)$$

and so on.

The sum of relaxation energy, two-body energy, three-body energy, four-body, … and ten-body energy gives the binding energy of a complex. All energies reported here are BSSE corrected.

Result and discussion

Figure 1 shows the optimized structure of hydronium ion with its first and second solvation shell. In its first and second solvation shell, there are three and six water molecules respectively. There are a total of 12 hydrogen bonds in a complex, three in the first solvation shell and nine in the second. The hydrogen bonds, O-H bond lengths, oxygen-oxygen distances, and the bond angles are represented in Table 2. Out of nine water molecules, six water molecules act as hydrogen bond donors as well as acceptors. The remaining three water molecules act as hydrogen bond acceptors only. The hydrogen bonds formed by the hydronium ion with water molecules in its first solvation shell are stronger than those formed between the water molecules in the second solvation shell. The three hydrogen bonds formed by the hydronium ion are not equal whereas those are equal when only the first solvation shell was considered [65]. The hydrogen bonds formed between different water molecules in a second solvation shell are also not equal. The strongest and weakest hydrogen bond is formed between W_3-W_9 and W_3-W_7 pairs of water molecules respectively.

The three O-H bonds for the hydronium ion in a complex are also not equal. Similarly, the O-H bonds of solvating water molecules are not equal except for the molecule W_8. All the O-H bonds in the water molecules as well as hydronium ion get elongated in a complex as compared to those for the isolated water molecule and hydronium ion. On comparing the O-H bonds in the three water molecules W_4, W_6, and W_8, which are acting as hydrogen bond acceptors only, it can be said that the two O-H bonds in W_4 as well as W_6 molecules are not

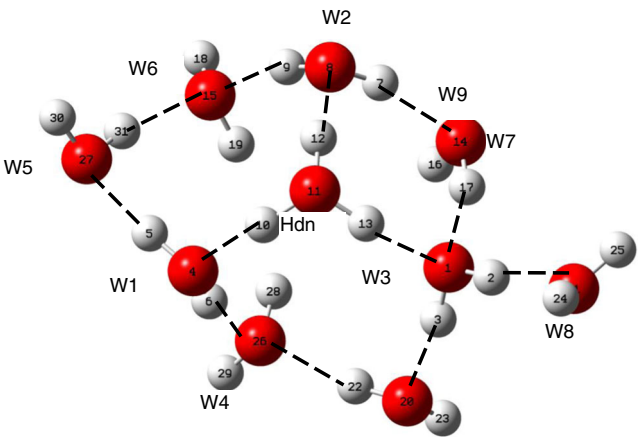

Fig. 1 Optimized structure of H_3O^+-$(H_2O)_9$ hydrogen bonded complex at B3LYP/aug-cc- pvtz level

Table 2 Structural parameters of H_3O^+–$(H_2O)_9$ complex using B3LYP/aug-cc-pvtz level of theory. Hdn and Wi represent hydronium and ith water molecule in a complex, respectively

	O-H bond length (Å)		Bond angle (degrees)
Hydronium	1.054, 1.046, 1.009		108.9, 106.6, 108.5
W1	0.985, 0.978		105.51
W2	0.977, 0.986		104.522
W3	0.975, 0.99		108.129
W4	0.971, 0.993		104.612
W5	0.962, 0.978		106.645
W6	0.970, 0.991		104.77
W7	0.970, 0.974		104.913
W8	0.962, 0.962		106.005
W9	0.981, 0.963		105.699
Hydrogen bonds		O-O distances	
Hdn-W1	1.456	Hdn-W1	2.510
Hdn-W2	1.485	Hdn-W2	2.528
Hdn-W3	1.612	Hdn-W3	2.615
W1-W4	1.887	W1-W4	2.848
W1-W5	1.765	W1-W5	2.736
W2-W6	1.899	W2-W6	2.856
W2-W7	1.798	W2-W7	2.756
W3-W8	1.839	W3-W8	2.813
W3-W9	1.713	W3-W9	2.696
W3-W7	1.974	W3-W7	2.920
W4-W9	1.825	W4-W9	2.794
W5-W6	1.871	W5-W6	2.827

Table 3 Two body interaction energy (kcal mol^{-1}) for H_3O^+–$(H_2O)_9$ hydrogen bonded complex using B3LYP/aug-cc-pvtz level

Two-body term		Int. energy
Hdn	W1	−8.52
Hdn	W2	−8.24
Hdn	W3	−7.62
Hdn	W4	−0.50
Hdn	W5	−0.49
Hdn	W6	−0.40
Hdn	W7	−0.39
Hdn	W8	−0.45
Hdn	W9	−0.67
W1	W2	1.01
W1	W3	0.81
W1	W4	−3.56
W1	W5	−3.39
W1	W6	−0.12
W1	W7	0.14
W1	W8	0.08
W1	W9	1.23
W2	W3	0.14
W2	W4	0.54
W2	W5	0.99
W2	W6	−3.32
W2	W7	−3.04
W2	W8	−0.02
W2	W9	0.17
W3	W4	−0.62
W3	W5	−0.01
W3	W6	0.25
W3	W7	−3.25
W3	W8	−4.34
W3	W9	−3.82
W4	W5	0.72
W4	W6	1.67
W4	W7	0.16
W4	W8	0.21
W4	W9	−3.68
W5	W6	−4.08
W5	W7	−0.14
W5	W8	0.05
W5	W9	−0.05
W6	W7	0.91
W6	W8	−0.01
W6	W9	0.28
W7	W8	−0.66
W7	W9	−0.48
W8	W9	0.73

All energies are BSSE corrected. Hdn is hydronium ion and Wi denotes ith water molecule in the complex

Table 4 Three body interaction energy (kcal mol^{-1}) for H_3O^+–$(H_2O)_9$ hydrogen bonded complex using B3LYP/aug-cc-pvtz level

Three-body term			Int. energy
Hdn	W1	W2	−2.66
Hdn	W1	W3	−1.68
Hdn	W1	W4	−3.17
Hdn	W1	W5	−4.16
Hdn	W1	W6	−0.43
Hdn	W1	W7	−0.48
Hdn	W1	W8	0.07
Hdn	W1	W9	−0.68
Hdn	W2	W3	−0.94
Hdn	W2	W4	−0.19
Hdn	W2	W5	−0.26
Hdn	W2	W6	−2.88
Hdn	W2	W7	−4.57

Table 4 (continued)

Three-body term			Int. energy
Hdn	W2	W8	0.29
Hdn	W2	W9	−0.11
Hdn	W3	W4	0.00
Hdn	W3	W5	0.14
Hdn	W3	W6	−0.02
Hdn	W3	W7	2.13
Hdn	W3	W8	−2.21
Hdn	W3	W9	−3.33
Hdn	W4	W5	−0.40
Hdn	W4	W6	0.04
Hdn	W4	W7	0.27
Hdn	W4	W8	−0.05
Hdn	W4	W9	−0.06
Hdn	W5	W6	0.10
Hdn	W5	W7	0.15
Hdn	W5	W8	0.04
Hdn	W5	W9	0.09
Hdn	W6	W7	−0.52
Hdn	W6	W8	0.15
Hdn	W6	W9	0.08
Hdn	W7	W8	0.41
Hdn	W7	W9	0.43
Hdn	W8	W9	−0.22
W1	W2	W3	−0.09
W1	W2	W4	0.13
W1	W2	W5	0.16
W1	W2	W6	0.23
W1	W2	W7	0.04
W1	W2	W8	−0.01
W1	W2	W9	−0.04
W1	W3	W4	0.15
W1	W3	W5	0.07
W1	W3	W6	−0.03
W1	W3	W7	−0.14
W1	W3	W8	0.04
W1	W3	W9	0.26
W1	W4	W5	1.27
W1	W4	W6	0.36
W1	W4	W7	0.13
W1	W4	W8	−0.03
W1	W4	W9	0.95
W1	W5	W6	−1.15
W1	W5	W7	−0.12
W1	W5	W8	0.07
W1	W5	W9	−0.02
W1	W6	W7	−0.04
W1	W6	W8	0.00
W1	W6	W9	−0.03
W1	W7	W8	0.00

Table 4 (continued)

Three-body term			Int. energy
W1	W7	W9	−0.01
W1	W8	W9	−0.02
W2	W3	W4	−0.02
W2	W3	W5	−0.04
W2	W3	W6	0.26
W2	W3	W7	−0.91
W2	W3	W8	−0.06
W2	W3	W9	0.04
W2	W4	W5	−0.04
W2	W4	W6	0.12
W2	W4	W7	−0.01
W2	W4	W8	0.00
W2	W4	W9	0.03
W2	W5	W6	0.82
W2	W5	W7	−0.13
W2	W5	W8	−0.01
W2	W5	W9	−0.01
W2	W6	W7	1.26
W2	W6	W8	0.04
W2	W6	W9	0.10
W2	W7	W8	−0.12
W2	W7	W9	−0.12
W2	W8	W9	−0.01
W3	W4	W5	−0.02
W3	W4	W6	0.02
W3	W4	W7	−0.24
W3	W4	W8	0.18
W3	W4	W9	−1.38
W3	W5	W6	−0.05
W3	W5	W7	−0.07
W3	W5	W8	0.03
W3	W5	W9	−0.04
W3	W6	W7	−0.07
W3	W6	W8	−0.01
W3	W6	W9	0.11
W3	W7	W8	−0.97
W3	W7	W9	−0.88
W3	W8	W9	1.16
W4	W5	W6	0.19
W4	W5	W7	−0.02
W4	W5	W8	0.00
W4	W5	W9	−0.09
W4	W6	W7	−0.07
W4	W6	W8	0.00
W4	W6	W9	0.13
W4	W7	W8	−0.01
W4	W7	W9	−0.14
W4	W8	W9	0.15
W5	W6	W7	0.00

Table 4 (continued)

Three-body term			Int. energy
W5	W6	W8	−0.02
W5	W6	W9	0.03
W5	W7	W8	0.00
W5	W7	W9	−0.01
W5	W8	W9	0.00
W6	W7	W8	0.00
W6	W7	W9	−0.02
W6	W8	W9	0.00
W7	W8	W9	0.01

All energies are BSSE corrected. Hdn is hydronium ion and Wi denotes ith water molecule in the complex

Table 5 Four-body interaction energy (kcal mol^{-1}) for H_3O^+–$(H_2O)_9$ hydrogen bonded complex using B3LYP/aug-cc-pvtz level

Four-body term				Int. energy
Hdn	W1	W2	W3	−0.78
Hdn	W1	W2	W4	−1.26
Hdn	W1	W2	W5	−1.21
Hdn	W1	W2	W6	−0.63
Hdn	W1	W2	W7	0.51
Hdn	W1	W2	W8	−0.44
Hdn	W1	W2	W9	−0.93
Hdn	W1	W3	W4	0.19
Hdn	W1	W3	W5	0.25
Hdn	W1	W3	W6	−0.82
Hdn	W1	W3	W7	−0.52
Hdn	W1	W3	W8	0.18
Hdn	W1	W3	W9	−1.52
Hdn	W1	W4	W5	−1.07
Hdn	W1	W4	W6	−1.10
Hdn	W1	W4	W7	−0.17
Hdn	W1	W4	W8	−0.04
Hdn	W1	W4	W9	0.41
Hdn	W1	W5	W6	−0.14
Hdn	W1	W5	W7	0.31
Hdn	W1	W5	W8	−0.12
Hdn	W1	W5	W9	0.16
Hdn	W1	W6	W7	−0.40
Hdn	W1	W6	W8	0.00
Hdn	W1	W6	W9	−0.42
Hdn	W1	W7	W8	0.13
Hdn	W1	W7	W9	−0.01
Hdn	W1	W8	W9	−0.12
Hdn	W2	W3	W4	−0.57
Hdn	W2	W3	W5	−0.64
Hdn	W2	W3	W6	−0.81
Hdn	W2	W3	W7	0.34
Hdn	W2	W3	W8	0.24
Hdn	W2	W3	W9	−0.33
Hdn	W2	W4	W5	−0.48
Hdn	W2	W4	W6	−0.74
Hdn	W2	W4	W7	0.06
Hdn	W2	W4	W8	−0.11
Hdn	W2	W4	W9	−0.26
Hdn	W2	W5	W6	0.53
Hdn	W2	W5	W7	0.28
Hdn	W2	W5	W8	−0.12
Hdn	W2	W5	W9	−0.11
Hdn	W2	W6	W7	−0.89
Hdn	W2	W6	W8	−0.03
Hdn	W2	W6	W9	−0.32
Hdn	W2	W7	W8	0.41
Hdn	W2	W7	W9	0.39
Hdn	W2	W8	W9	−0.11
Hdn	W3	W4	W5	−0.22
Hdn	W3	W4	W6	−0.28
Hdn	W3	W4	W7	0.24
Hdn	W3	W4	W8	−0.19
Hdn	W3	W4	W9	−0.44
Hdn	W3	W5	W6	0.08
Hdn	W3	W5	W7	0.12
Hdn	W3	W5	W8	−0.03
Hdn	W3	W5	W9	0.10
Hdn	W3	W6	W7	−0.11
Hdn	W3	W6	W8	0.13
Hdn	W3	W6	W9	−0.25
Hdn	W3	W7	W8	0.38
Hdn	W3	W7	W9	0.08
Hdn	W3	W8	W9	−0.35
Hdn	W4	W5	W6	−0.11
Hdn	W4	W5	W7	0.03
Hdn	W4	W5	W8	−0.04
Hdn	W4	W5	W9	−0.05
Hdn	W4	W6	W7	−0.12
Hdn	W4	W6	W8	−0.03
Hdn	W4	W6	W9	−0.10
Hdn	W4	W7	W8	0.02
Hdn	W4	W7	W9	0.11
Hdn	W4	W8	W9	−0.04
Hdn	W5	W6	W7	−0.09
Hdn	W5	W6	W8	0.03
Hdn	W5	W6	W9	0.02
Hdn	W5	W7	W8	0.05
Hdn	W5	W7	W9	0.05
Hdn	W5	W8	W9	−0.01
Hdn	W6	W7	W8	0.01

Table 5 (continued)

Four-body term				Int. energy
Hdn	W6	W7	W9	0.00
Hdn	W6	W8	W9	−0.03
Hdn	W7	W8	W9	−0.10
W1	W2	W3	W4	0.00
W1	W2	W3	W5	−0.02
W1	W2	W3	W6	−0.01
W1	W2	W3	W7	0.00
W1	W2	W3	W8	−0.01
W1	W2	W3	W9	−0.01
W1	W2	W4	W5	−0.02
W1	W2	W4	W6	0.02
W1	W2	W4	W7	0.08
W1	W2	W4	W8	0.00
W1	W2	W4	W9	−0.01
W1	W2	W5	W6	0.09
W1	W2	W5	W7	−0.05
W1	W2	W5	W8	0.00
W1	W2	W5	W9	0.00
W1	W2	W6	W7	−0.01
W1	W2	W6	W8	0.00
W1	W2	W6	W9	−0.01
W1	W2	W7	W8	0.00
W1	W2	W7	W9	0.00
W1	W2	W8	W9	0.00
W1	W3	W4	W5	−0.01
W1	W3	W4	W6	−0.01
W1	W3	W4	W7	−0.02
W1	W3	W4	W8	−0.02
W1	W3	W4	W9	0.14
W1	W3	W5	W6	0.00
W1	W3	W5	W7	−0.04
W1	W3	W5	W8	0.06
W1	W3	W5	W9	−0.02
W1	W3	W6	W7	0.00
W1	W3	W6	W8	0.00
W1	W3	W6	W9	−0.01
W1	W3	W7	W8	0.00
W1	W3	W7	W9	0.00
W1	W3	W8	W9	0.00
W1	W4	W5	W6	0.14
W1	W4	W5	W7	0.00
W1	W4	W5	W8	0.00
W1	W4	W5	W9	−0.04
W1	W4	W6	W7	−0.01
W1	W4	W6	W8	0.00
W1	W4	W6	W9	−0.03
W1	W4	W7	W8	0.00
W1	W4	W7	W9	0.00
W1	W4	W8	W9	−0.01

Table 5 (continued)

Four-body term				Int. energy
W1	W5	W6	W7	0.00
W1	W5	W6	W8	0.00
W1	W5	W6	W9	−0.01
W1	W5	W7	W8	0.00
W1	W5	W7	W9	0.00
W1	W5	W8	W9	0.00
W1	W6	W7	W8	0.00
W1	W6	W7	W9	0.00
W1	W6	W8	W9	0.00
W1	W7	W8	W9	0.00
W2	W3	W4	W5	0.00
W2	W3	W4	W6	0.01
W2	W3	W4	W7	0.00
W2	W3	W4	W8	0.00
W2	W3	W4	W9	0.00
W2	W3	W5	W6	−0.01
W2	W3	W5	W7	0.00
W2	W3	W5	W8	0.00
W2	W3	W5	W9	−0.01
W2	W3	W6	W7	0.02
W2	W3	W6	W8	0.03
W2	W3	W6	W9	0.08
W2	W3	W7	W8	−0.09
W2	W3	W7	W9	−0.05
W2	W3	W8	W9	−0.01
W2	W4	W5	W6	−0.03
W2	W4	W5	W7	0.00
W2	W4	W5	W8	0.00
W2	W4	W5	W9	0.00
W2	W4	W6	W7	−0.01
W2	W4	W6	W8	0.00
W2	W4	W6	W9	0.06
W2	W4	W7	W8	0.00
W2	W4	W7	W9	−0.05
W2	W4	W8	W9	0.00
W2	W5	W6	W7	−0.02
W2	W5	W6	W8	0.00
W2	W5	W6	W9	−0.01
W2	W5	W7	W8	0.00
W2	W5	W7	W9	0.00
W2	W5	W8	W9	0.00
W2	W6	W7	W8	0.00
W2	W6	W7	W9	0.00
W2	W6	W8	W9	0.00
W2	W7	W8	W9	0.01
W3	W4	W5	W6	0.01
W3	W4	W5	W7	0.00
W3	W4	W5	W8	0.00
W3	W4	W5	W9	−0.01

Table 5 (continued)

Four-body term				Int. energy
W3	W4	W6	W7	0.01
W3	W4	W6	W8	0.00
W3	W4	W6	W9	0.02
W3	W4	W7	W8	0.00
W3	W4	W7	W9	−0.09
W3	W4	W8	W9	0.04
W3	W5	W6	W7	−0.04
W3	W5	W6	W8	−0.01
W3	W5	W6	W9	0.00
W3	W5	W7	W8	0.00
W3	W5	W7	W9	0.00
W3	W5	W8	W9	0.00
W3	W6	W7	W8	0.00
W3	W6	W7	W9	−0.01
W3	W6	W8	W9	0.00
W3	W7	W8	W9	0.02
W4	W5	W6	W7	0.00
W4	W5	W6	W8	0.00
W4	W5	W6	W9	0.03
W4	W5	W7	W8	0.00
W4	W5	W7	W9	0.00
W4	W5	W8	W9	0.00
W4	W6	W7	W8	0.00
W4	W6	W7	W9	0.00
W4	W6	W8	W9	0.00
W4	W7	W8	W9	0.00
W5	W6	W7	W8	0.00
W5	W6	W7	W9	−0.01
W5	W6	W8	W9	0.00
W5	W7	W8	W9	0.00
W6	W7	W8	W9	0.00

All energies are BSSE corrected. Hdn is hydronium ion and Wi denotes ith water molecule in the complex

equal but differ by about 0.021 Å whereas the two O-H bonds in water molecule W_8 are equal. This is due to the fact that though all three water molecules W_4, W_6, and W_8 are acting as hydrogen bond acceptors, W_4 and W_6 water molecules are accepting two hydrogen bonds whereas W_8 is accepting only one hydrogen bond as can be seen from Fig. 1. The difference between the two O-H bond distances of the same water molecule is the largest for the water molecule W_3 which forms four hydrogen bonds. For the two hydrogen bonds, it acts as a hydrogen bond donor and for the remaining two as an acceptor. The difference between the two O-H bonds of the same water molecule is almost equal for W_4 and W_6 water molecules since both are acting as hydrogen bond acceptors for the two hydrogen bonds they formed. The angle ∠H-O-H for these two water molecules is also equal. The water molecule

Table 6 Five-body interaction energy (kcal mol^{-1}) for H_3O^+–$(H_2O)_9$ hydrogen bonded complex using B3LYP/aug-cc-pvtz level

Five-body term					Int. energy
Hdn	W1	W2	W3	W4	0.31
Hdn	W1	W2	W3	W5	0.42
Hdn	W1	W2	W3	W6	0.38
Hdn	W1	W2	W3	W7	0.03
Hdn	W1	W2	W3	W8	−0.02
Hdn	W1	W2	W3	W9	0.51
Hdn	W1	W2	W4	W5	−0.12
Hdn	W1	W2	W4	W6	−0.62
Hdn	W1	W2	W4	W7	−0.11
Hdn	W1	W2	W4	W8	−0.04
Hdn	W1	W2	W4	W9	−0.12
Hdn	W1	W2	W5	W6	0.62
Hdn	W1	W2	W5	W7	0.62
Hdn	W1	W2	W5	W8	−0.11
Hdn	W1	W2	W5	W9	0.13
Hdn	W1	W2	W6	W7	−0.22
Hdn	W1	W2	W6	W8	−0.09
Hdn	W1	W2	W6	W9	−0.29
Hdn	W1	W2	W7	W8	−0.06
Hdn	W1	W2	W7	W9	−0.19
Hdn	W1	W2	W8	W9	0.12
Hdn	W1	W3	W4	W5	−0.43
Hdn	W1	W3	W4	W6	−0.43
Hdn	W1	W3	W4	W7	0.00
Hdn	W1	W3	W4	W8	−0.10
Hdn	W1	W3	W4	W9	0.40
Hdn	W1	W3	W5	W6	−0.05
Hdn	W1	W3	W5	W7	0.02
Hdn	W1	W3	W5	W8	−0.07
Hdn	W1	W3	W5	W9	0.33
Hdn	W1	W3	W6	W7	0.10
Hdn	W1	W3	W6	W8	−0.02
Hdn	W1	W3	W6	W9	−0.34
Hdn	W1	W3	W7	W8	0.07
Hdn	W1	W3	W7	W9	−0.15
Hdn	W1	W3	W8	W9	−0.17
Hdn	W1	W4	W5	W6	−0.46
Hdn	W1	W4	W5	W7	−0.04
Hdn	W1	W4	W5	W8	−0.08
Hdn	W1	W4	W5	W9	−0.37
Hdn	W1	W4	W6	W7	−0.18
Hdn	W1	W4	W6	W8	−0.12
Hdn	W1	W4	W6	W9	−0.35
Hdn	W1	W4	W7	W8	−0.01
Hdn	W1	W4	W7	W9	0.00
Hdn	W1	W4	W8	W9	−0.03
Hdn	W1	W5	W6	W7	−0.24
Hdn	W1	W5	W6	W8	0.02

Table 6 (continued)

Five-body term					Int. energy
Hdn	W1	W5	W6	W9	−0.05
Hdn	W1	W5	W7	W8	0.03
Hdn	W1	W5	W7	W9	0.00
Hdn	W1	W5	W8	W9	0.03
Hdn	W1	W6	W7	W8	−0.03
Hdn	W1	W6	W7	W9	−0.02
Hdn	W1	W6	W8	W9	−0.02
Hdn	W1	W7	W8	W9	−0.08
Hdn	W2	W3	W4	W5	−0.10
Hdn	W2	W3	W4	W6	−0.45
Hdn	W2	W3	W4	W7	0.16
Hdn	W2	W3	W4	W8	−0.21
Hdn	W2	W3	W4	W9	−0.37
Hdn	W2	W3	W5	W6	−0.02
Hdn	W2	W3	W5	W7	0.21
Hdn	W2	W3	W5	W8	−0.16
Hdn	W2	W3	W5	W9	−0.09
Hdn	W2	W3	W6	W7	−0.11
Hdn	W2	W3	W6	W8	−0.01
Hdn	W2	W3	W6	W9	−0.43
Hdn	W2	W3	W7	W8	0.32
Hdn	W2	W3	W7	W9	−0.01
Hdn	W2	W3	W8	W9	−0.21
Hdn	W2	W4	W5	W6	−0.23
Hdn	W2	W4	W5	W7	0.10
Hdn	W2	W4	W5	W8	−0.04
Hdn	W2	W4	W5	W9	−0.12
Hdn	W2	W4	W6	W7	−0.35
Hdn	W2	W4	W6	W8	−0.09
Hdn	W2	W4	W6	W9	−0.45
Hdn	W2	W4	W7	W8	−0.02
Hdn	W2	W4	W7	W9	0.00
Hdn	W2	W4	W8	W9	−0.02
Hdn	W2	W5	W6	W7	−0.44
Hdn	W2	W5	W6	W8	0.02
Hdn	W2	W5	W6	W9	−0.02
Hdn	W2	W5	W7	W8	0.04
Hdn	W2	W5	W7	W9	0.03
Hdn	W2	W5	W8	W9	0.00
Hdn	W2	W6	W7	W8	−0.13
Hdn	W2	W6	W7	W9	−0.15
Hdn	W2	W6	W8	W9	−0.02
Hdn	W2	W7	W8	W9	−0.11
Hdn	W3	W4	W5	W6	−0.15
Hdn	W3	W4	W5	W7	0.01
Hdn	W3	W4	W5	W8	−0.05
Hdn	W3	W4	W5	W9	−0.15
Hdn	W3	W4	W6	W7	−0.06
Hdn	W3	W4	W6	W8	−0.12

Table 6 (continued)

Five-body term					Int. energy
Hdn	W3	W4	W6	W9	−0.39
Hdn	W3	W4	W7	W8	−0.06
Hdn	W3	W4	W7	W9	0.00
Hdn	W3	W4	W8	W9	−0.01
Hdn	W3	W5	W6	W7	−0.03
Hdn	W3	W5	W6	W8	0.04
Hdn	W3	W5	W6	W9	−0.05
Hdn	W3	W5	W7	W8	0.05
Hdn	W3	W5	W7	W9	0.02
Hdn	W3	W5	W8	W9	−0.04
Hdn	W3	W6	W7	W8	0.01
Hdn	W3	W6	W7	W9	−0.02
Hdn	W3	W6	W8	W9	−0.11
Hdn	W3	W7	W8	W9	−0.27
Hdn	W4	W5	W6	W7	−0.02
Hdn	W4	W5	W6	W8	−0.02
Hdn	W4	W5	W6	W9	−0.08
Hdn	W4	W5	W7	W8	−0.01
Hdn	W4	W5	W7	W9	0.00
Hdn	W4	W5	W8	W9	0.00
Hdn	W4	W6	W7	W8	−0.01
Hdn	W4	W6	W7	W9	−0.05
Hdn	W4	W6	W8	W9	−0.02
Hdn	W4	W7	W8	W9	−0.02
Hdn	W5	W6	W7	W8	0.00
Hdn	W5	W6	W7	W9	0.00
Hdn	W5	W6	W8	W9	0.00
Hdn	W5	W7	W8	W9	−0.01
Hdn	W6	W7	W8	W9	−0.01
W1	W2	W3	W4	W5	0.00
W1	W2	W3	W4	W6	0.00
W1	W2	W3	W4	W7	0.00
W1	W2	W3	W4	W8	0.00
W1	W2	W3	W4	W9	0.00
W1	W2	W3	W5	W6	0.00
W1	W2	W3	W5	W7	0.00
W1	W2	W3	W5	W8	0.00
W1	W2	W3	W5	W9	0.00
W1	W2	W3	W6	W7	0.00
W1	W2	W3	W6	W8	0.00
W1	W2	W3	W6	W9	0.00
W1	W2	W3	W7	W8	0.00
W1	W2	W3	W7	W9	0.00
W1	W2	W3	W8	W9	0.00
W1	W2	W4	W5	W6	−0.02
W1	W2	W4	W5	W7	0.00
W1	W2	W4	W5	W8	0.00
W1	W2	W4	W5	W9	0.00
W1	W2	W4	W6	W7	−0.01

Table 6 (continued)

Five-body term					Int. energy
W1	W2	W4	W6	W8	0.00
W1	W2	W4	W6	W9	−0.01
W1	W2	W4	W7	W8	0.00
W1	W2	W4	W7	W9	0.00
W1	W2	W4	W8	W9	0.00
W1	W2	W5	W6	W7	0.00
W1	W2	W5	W6	W8	0.00
W1	W2	W5	W6	W9	0.00
W1	W2	W5	W7	W8	0.00
W1	W2	W5	W7	W9	0.00
W1	W2	W5	W8	W9	0.00
W1	W2	W6	W7	W8	0.00
W1	W2	W6	W7	W9	0.00
W1	W2	W6	W8	W9	0.00
W1	W2	W7	W8	W9	0.00
W1	W3	W4	W5	W6	0.00
W1	W3	W4	W5	W7	0.00
W1	W3	W4	W5	W8	−0.01
W1	W3	W4	W5	W9	0.00
W1	W3	W4	W6	W7	0.00
W1	W3	W4	W6	W8	0.00
W1	W3	W4	W6	W9	0.00
W1	W3	W4	W7	W8	0.00
W1	W3	W4	W7	W9	0.00
W1	W3	W4	W8	W9	0.00
W1	W3	W5	W6	W7	−0.01
W1	W3	W5	W6	W8	0.00
W1	W3	W5	W6	W9	0.00
W1	W3	W5	W7	W8	0.00
W1	W3	W5	W7	W9	0.00
W1	W3	W5	W8	W9	0.00
W1	W3	W6	W7	W8	0.00
W1	W3	W6	W7	W9	0.00
W1	W3	W6	W8	W9	0.00
W1	W3	W7	W8	W9	0.00
W1	W4	W5	W6	W7	0.00
W1	W4	W5	W6	W8	0.00
W1	W4	W5	W6	W9	0.00
W1	W4	W5	W7	W8	0.00
W1	W4	W5	W7	W9	0.00
W1	W4	W5	W8	W9	0.00
W1	W4	W6	W7	W8	0.00
W1	W4	W6	W7	W9	0.00
W1	W4	W6	W8	W9	0.00
W1	W4	W7	W8	W9	0.00
W1	W5	W6	W7	W8	0.00
W1	W5	W6	W7	W9	0.00
W1	W5	W6	W8	W9	0.00
W1	W5	W7	W8	W9	0.00

Table 6 (continued)

Five-body term					Int. energy
W1	W6	W7	W8	W9	0.00
W2	W3	W4	W5	W6	0.00
W2	W3	W4	W5	W7	0.00
W2	W3	W4	W5	W8	0.00
W2	W3	W4	W5	W9	0.00
W2	W3	W4	W6	W7	0.00
W2	W3	W4	W6	W8	0.00
W2	W3	W4	W6	W9	0.01
W2	W3	W4	W7	W8	0.00
W2	W3	W4	W7	W9	0.00
W2	W3	W4	W8	W9	0.00
W2	W3	W5	W6	W7	0.00
W2	W3	W5	W6	W8	0.00
W2	W3	W5	W6	W9	0.00
W2	W3	W5	W7	W8	0.00
W2	W3	W5	W7	W9	0.00
W2	W3	W5	W8	W9	0.00
W2	W3	W6	W7	W8	0.00
W2	W3	W6	W7	W9	−0.01
W2	W3	W6	W8	W9	0.00
W2	W3	W7	W8	W9	0.01
W2	W4	W5	W6	W7	0.00
W2	W4	W5	W6	W8	0.00
W2	W4	W5	W6	W9	0.00
W2	W4	W5	W7	W8	0.00
W2	W4	W5	W7	W9	0.00
W2	W4	W5	W8	W9	0.00
W2	W4	W6	W7	W8	0.00
W2	W4	W6	W7	W9	0.00
W2	W4	W6	W8	W9	0.00
W2	W4	W7	W8	W9	0.00
W2	W5	W6	W7	W8	0.00
W2	W5	W6	W7	W9	0.00
W2	W5	W6	W8	W9	0.00
W2	W5	W7	W8	W9	0.00
W2	W6	W7	W8	W9	0.00
W3	W4	W5	W6	W7	0.00
W3	W4	W5	W6	W8	0.00
W3	W4	W5	W6	W9	0.00
W3	W4	W5	W7	W8	0.00
W3	W4	W5	W7	W9	0.00
W3	W4	W5	W8	W9	0.00
W3	W4	W6	W7	W8	0.00
W3	W4	W6	W7	W9	0.00
W3	W4	W6	W8	W9	0.00
W3	W4	W7	W8	W9	0.00
W3	W5	W6	W7	W8	0.00
W3	W5	W6	W7	W9	0.00
W3	W5	W6	W8	W9	0.00

Table 6 (continued)

Five-body term					Int. energy
W3	W5	W7	W8	W9	0.00
W3	W6	W7	W8	W9	0.00
W4	W5	W6	W7	W8	0.00
W4	W5	W6	W7	W9	0.00
W4	W5	W6	W8	W9	0.00
W4	W5	W7	W8	W9	0.00
W4	W6	W7	W8	W9	0.00
W5	W6	W7	W8	W9	0.00

All energies are BSSE corrected. Hdn is hydronium ion and Wi denotes ith water molecule in the complex

Table 7 Six-body interaction energy (kcal mol^{-1}) for H_3O^+–$(H_2O)_9$ hydrogen bonded complex using B3LYP/aug-cc-pvtz level

Six-body term						Int. energy
Hdn	W1	W2	W3	W4	W5	0.53
Hdn	W1	W2	W3	W4	W6	0.73
Hdn	W1	W2	W3	W4	W7	−0.03
Hdn	W1	W2	W3	W4	W8	0.14
Hdn	W1	W2	W3	W4	W9	0.32
Hdn	W1	W2	W3	W5	W6	0.06
Hdn	W1	W2	W3	W5	W7	−0.13
Hdn	W1	W2	W3	W5	W8	0.04
Hdn	W1	W2	W3	W5	W9	0.14
Hdn	W1	W2	W3	W6	W7	0.45
Hdn	W1	W2	W3	W6	W8	−0.01
Hdn	W1	W2	W3	W6	W9	0.55
Hdn	W1	W2	W3	W7	W8	−0.19
Hdn	W1	W2	W3	W7	W9	−0.04
Hdn	W1	W2	W3	W8	W9	0.29
Hdn	W1	W2	W4	W5	W6	0.19
Hdn	W1	W2	W4	W5	W7	−0.04
Hdn	W1	W2	W4	W5	W8	0.10
Hdn	W1	W2	W4	W5	W9	0.11
Hdn	W1	W2	W4	W6	W7	0.23
Hdn	W1	W2	W4	W6	W8	0.07
Hdn	W1	W2	W4	W6	W9	0.37
Hdn	W1	W2	W4	W7	W8	−0.08
Hdn	W1	W2	W4	W7	W9	−0.10
Hdn	W1	W2	W4	W8	W9	0.07
Hdn	W1	W2	W5	W6	W7	−0.35
Hdn	W1	W2	W5	W6	W8	0.04
Hdn	W1	W2	W5	W6	W9	0.04
Hdn	W1	W2	W5	W7	W8	−0.06
Hdn	W1	W2	W5	W7	W9	−0.10
Hdn	W1	W2	W5	W8	W9	0.05
Hdn	W1	W2	W6	W7	W8	−0.05

Table 7 (continued)

Six-body term						Int. energy
Hdn	W1	W2	W6	W7	W9	0.13
Hdn	W1	W2	W6	W8	W9	0.06
Hdn	W1	W2	W7	W8	W9	−0.03
Hdn	W1	W3	W4	W5	W6	0.05
Hdn	W1	W3	W4	W5	W7	−0.04
Hdn	W1	W3	W4	W5	W8	−0.01
Hdn	W1	W3	W4	W5	W9	−0.17
Hdn	W1	W3	W4	W6	W7	0.07
Hdn	W1	W3	W4	W6	W8	−0.05
Hdn	W1	W3	W4	W6	W9	0.22
Hdn	W1	W3	W4	W7	W8	−0.01
Hdn	W1	W3	W4	W7	W9	0.08
Hdn	W1	W3	W4	W8	W9	−0.01
Hdn	W1	W3	W5	W6	W7	−0.06
Hdn	W1	W3	W5	W6	W8	0.02
Hdn	W1	W3	W5	W6	W9	−0.08
Hdn	W1	W3	W5	W7	W8	0.03
Hdn	W1	W3	W5	W7	W9	−0.06
Hdn	W1	W3	W5	W8	W9	0.05
Hdn	W1	W3	W6	W7	W8	−0.04
Hdn	W1	W3	W6	W7	W9	0.13
Hdn	W1	W3	W6	W8	W9	0.00
Hdn	W1	W3	W7	W8	W9	−0.10
Hdn	W1	W4	W5	W6	W7	0.00
Hdn	W1	W4	W5	W6	W8	−0.02
Hdn	W1	W4	W5	W6	W9	−0.08
Hdn	W1	W4	W5	W7	W8	−0.05
Hdn	W1	W4	W5	W7	W9	−0.08
Hdn	W1	W4	W5	W8	W9	0.03
Hdn	W1	W4	W6	W7	W8	−0.04
Hdn	W1	W4	W6	W7	W9	−0.04
Hdn	W1	W4	W6	W8	W9	0.03
Hdn	W1	W4	W7	W8	W9	−0.01
Hdn	W1	W5	W6	W7	W8	−0.01
Hdn	W1	W5	W6	W7	W9	−0.04
Hdn	W1	W5	W6	W8	W9	0.00
Hdn	W1	W5	W7	W8	W9	−0.01
Hdn	W1	W6	W7	W8	W9	0.00
Hdn	W2	W3	W4	W5	W6	0.11
Hdn	W2	W3	W4	W5	W7	−0.05
Hdn	W2	W3	W4	W5	W8	0.03
Hdn	W2	W3	W4	W5	W9	0.00
Hdn	W2	W3	W4	W6	W7	−0.04
Hdn	W2	W3	W4	W6	W8	−0.04
Hdn	W2	W3	W4	W6	W9	0.06
Hdn	W2	W3	W4	W7	W8	−0.09
Hdn	W2	W3	W4	W7	W9	−0.04
Hdn	W2	W3	W4	W8	W9	0.09
Hdn	W2	W3	W5	W6	W7	−0.08

Table 7 (continued)

Six-body term						Int. energy
Hdn	W2	W3	W5	W6	W8	0.01
Hdn	W2	W3	W5	W6	W9	−0.02
Hdn	W2	W3	W5	W7	W8	0.01
Hdn	W2	W3	W5	W7	W9	−0.02
Hdn	W2	W3	W5	W8	W9	0.05
Hdn	W2	W3	W6	W7	W8	−0.14
Hdn	W2	W3	W6	W7	W9	−0.01
Hdn	W2	W3	W6	W8	W9	0.01
Hdn	W2	W3	W7	W8	W9	−0.29
Hdn	W2	W4	W5	W6	W7	−0.01
Hdn	W2	W4	W5	W6	W8	0.00
Hdn	W2	W4	W5	W6	W9	−0.02
Hdn	W2	W4	W5	W7	W8	−0.03
Hdn	W2	W4	W5	W7	W9	−0.04
Hdn	W2	W4	W5	W8	W9	0.01
Hdn	W2	W4	W6	W7	W8	−0.06
Hdn	W2	W4	W6	W7	W9	−0.09
Hdn	W2	W4	W6	W8	W9	0.01
Hdn	W2	W4	W7	W8	W9	−0.04
Hdn	W2	W5	W6	W7	W8	−0.04
Hdn	W2	W5	W6	W7	W9	−0.06
Hdn	W2	W5	W6	W8	W9	0.00
Hdn	W2	W5	W7	W8	W9	−0.01
Hdn	W2	W6	W7	W8	W9	0.01
Hdn	W3	W4	W5	W6	W7	−0.02
Hdn	W3	W4	W5	W6	W8	−0.04
Hdn	W3	W4	W5	W6	W9	−0.13
Hdn	W3	W4	W5	W7	W8	−0.02
Hdn	W3	W4	W5	W7	W9	−0.01
Hdn	W3	W4	W5	W8	W9	0.02
Hdn	W3	W4	W6	W7	W8	−0.03
Hdn	W3	W4	W6	W7	W9	−0.04
Hdn	W3	W4	W6	W8	W9	0.00
Hdn	W3	W4	W7	W8	W9	−0.01
Hdn	W3	W5	W6	W7	W8	0.00
Hdn	W3	W5	W6	W7	W9	−0.03
Hdn	W3	W5	W6	W8	W9	−0.02
Hdn	W3	W5	W7	W8	W9	−0.03
Hdn	W3	W6	W7	W8	W9	−0.02
Hdn	W4	W5	W6	W7	W8	−0.01
Hdn	W4	W5	W6	W7	W9	−0.03
Hdn	W4	W5	W6	W8	W9	0.00
Hdn	W4	W5	W7	W8	W9	0.00
Hdn	W4	W6	W7	W8	W9	−0.01
Hdn	W5	W6	W7	W8	W9	0.00
W1	W2	W3	W4	W5	W6	0.00
W1	W2	W3	W4	W5	W7	0.00
W1	W2	W3	W4	W5	W8	0.00
W1	W2	W3	W4	W5	W9	0.00

Table 7 (continued)

Six-body term						Int. energy
W1	W2	W3	W4	W6	W7	0.00
W1	W2	W3	W4	W6	W8	0.00
W1	W2	W3	W4	W6	W9	0.00
W1	W2	W3	W4	W7	W8	0.00
W1	W2	W3	W4	W7	W9	0.00
W1	W2	W3	W4	W8	W9	0.00
W1	W2	W3	W5	W6	W7	0.00
W1	W2	W3	W5	W6	W8	0.00
W1	W2	W3	W5	W6	W9	0.00
W1	W2	W3	W5	W7	W8	0.00
W1	W2	W3	W5	W7	W9	0.00
W1	W2	W3	W5	W8	W9	0.00
W1	W2	W3	W6	W7	W8	0.00
W1	W2	W3	W6	W7	W9	0.00
W1	W2	W3	W6	W8	W9	0.00
W1	W2	W3	W7	W8	W9	0.00
W1	W2	W4	W5	W6	W7	0.00
W1	W2	W4	W5	W6	W8	0.00
W1	W2	W4	W5	W6	W9	0.00
W1	W2	W4	W5	W7	W8	0.00
W1	W2	W4	W5	W7	W9	0.00
W1	W2	W4	W5	W8	W9	0.00
W1	W2	W4	W6	W7	W8	0.00
W1	W2	W4	W6	W7	W9	0.00
W1	W2	W4	W6	W8	W9	0.00
W1	W2	W4	W7	W8	W9	0.00
W1	W2	W5	W6	W7	W8	0.00
W1	W2	W5	W6	W7	W9	0.00
W1	W2	W5	W6	W8	W9	0.00
W1	W2	W5	W7	W8	W9	0.00
W1	W2	W6	W7	W8	W9	0.00
W1	W3	W4	W5	W6	W7	0.00
W1	W3	W4	W5	W6	W8	0.00
W1	W3	W4	W5	W6	W9	0.00
W1	W3	W4	W5	W7	W8	0.00
W1	W3	W4	W5	W7	W9	0.00
W1	W3	W4	W5	W8	W9	0.00
W1	W3	W4	W6	W7	W8	0.00
W1	W3	W4	W6	W7	W9	0.00
W1	W3	W4	W6	W8	W9	0.00
W1	W3	W4	W7	W8	W9	0.00
W1	W3	W5	W6	W7	W8	0.00
W1	W3	W5	W6	W7	W9	0.00
W1	W3	W5	W6	W8	W9	0.00
W1	W3	W5	W7	W8	W9	0.00
W1	W3	W6	W7	W8	W9	0.00
W1	W4	W5	W6	W7	W8	0.00
W1	W4	W5	W6	W7	W9	0.00
W1	W4	W5	W6	W8	W9	0.00

Table 7 (continued)

Six-body term						Int. energy
W1	W4	W5	W7	W8	W9	0.00
W1	W4	W6	W7	W8	W9	0.00
W1	W5	W6	W7	W8	W9	0.00
W2	W3	W4	W5	W6	W7	0.00
W2	W3	W4	W5	W6	W8	0.00
W2	W3	W4	W5	W6	W9	0.00
W2	W3	W4	W5	W7	W8	0.00
W2	W3	W4	W5	W7	W9	0.00
W2	W3	W4	W5	W8	W9	0.00
W2	W3	W4	W6	W7	W8	0.00
W2	W3	W4	W6	W7	W9	0.00
W2	W3	W4	W6	W8	W9	0.00
W2	W3	W4	W7	W8	W9	0.00
W2	W3	W5	W6	W7	W8	0.00
W2	W3	W5	W6	W7	W9	0.00
W2	W3	W5	W6	W8	W9	0.00
W2	W3	W5	W7	W8	W9	0.00
W2	W3	W6	W7	W8	W9	0.00
W2	W4	W5	W6	W7	W8	0.00
W2	W4	W5	W6	W7	W9	0.00
W2	W4	W5	W6	W8	W9	0.00
W2	W4	W5	W7	W8	W9	0.00
W2	W4	W6	W7	W8	W9	0.00
W2	W5	W6	W7	W8	W9	0.00
W3	W4	W5	W6	W7	W8	0.00
W3	W4	W5	W6	W7	W9	0.00
W3	W4	W5	W6	W8	W9	0.00
W3	W4	W5	W7	W8	W9	0.00
W3	W4	W6	W7	W8	W9	0.00
W3	W5	W6	W7	W8	W9	0.00
W4	W5	W6	W7	W8	W9	0.00

All energies are BSSE corrected. Hdn is hydronium ion and Wi denotes ith water molecule in the complex

W_3, which is the only water molecule in a complex forming four hydrogen bonds, has the largest angle ∠H-O-H of 108.1°. The oxygen-oxygen distance between the hydronium ion and water molecule is shorter as compared to that between water molecules in the second solvation shell. This is due to the fact that the hydrogen bonds for the former are stronger than those for the latter. The strongest hydrogen bond in the second solvation shell between W_3 and W_9 water molecules gives shortest O-O distance among different O-O distances in the second solvation shell. For the weakest hydrogen bond between W_3 and W_7 water molecules, the opposite is true.

The many body analysis technique is used to study the nature of various interactions in a complex. For this complex there are 45 two-body, 120 three-body, 210 four-body, 252 five-body, 210 six-body, 120 seven-body, 45 eight-body, 10

Table 8 Seven-body interaction energy (kcal mol^{-1}) for H_3O^+–$(H_2O)_9$ hydrogen bonded complex using B3LYP/aug-cc-pvtz level

Seven-body term							Int. energy
Hdn	W1	W2	W3	W4	W5	W6	0.10
Hdn	W1	W2	W3	W4	W5	W7	0.00
Hdn	W1	W2	W3	W4	W5	W8	0.08
Hdn	W1	W2	W3	W4	W5	W9	0.11
Hdn	W1	W2	W3	W4	W6	W7	0.11
Hdn	W1	W2	W3	W4	W6	W8	0.10
Hdn	W1	W2	W3	W4	W6	W9	0.09
Hdn	W1	W2	W3	W4	W7	W8	0.03
Hdn	W1	W2	W3	W4	W7	W9	0.06
Hdn	W1	W2	W3	W4	W8	W9	0.02
Hdn	W1	W2	W3	W5	W6	W7	0.14
Hdn	W1	W2	W3	W5	W6	W8	0.01
Hdn	W1	W2	W3	W5	W6	W9	−0.01
Hdn	W1	W2	W3	W5	W7	W8	−0.03
Hdn	W1	W2	W3	W5	W7	W9	−0.02
Hdn	W1	W2	W3	W5	W8	W9	0.04
Hdn	W1	W2	W3	W6	W7	W8	0.06
Hdn	W1	W2	W3	W6	W7	W9	0.11
Hdn	W1	W2	W3	W6	W8	W9	0.07
Hdn	W1	W2	W3	W7	W8	W9	0.17
Hdn	W1	W2	W4	W5	W6	W7	0.23
Hdn	W1	W2	W4	W5	W6	W8	0.03
Hdn	W1	W2	W4	W5	W6	W9	0.14
Hdn	W1	W2	W4	W5	W7	W8	−0.02
Hdn	W1	W2	W4	W5	W7	W9	0.00
Hdn	W1	W2	W4	W5	W8	W9	0.01
Hdn	W1	W2	W4	W6	W7	W8	0.06
Hdn	W1	W2	W4	W6	W7	W9	0.12
Hdn	W1	W2	W4	W6	W8	W9	0.02
Hdn	W1	W2	W4	W7	W8	W9	0.05
Hdn	W1	W2	W5	W6	W7	W8	0.04
Hdn	W1	W2	W5	W6	W7	W9	0.07
Hdn	W1	W2	W5	W6	W8	W9	−0.01
Hdn	W1	W2	W5	W7	W8	W9	0.01
Hdn	W1	W2	W6	W7	W8	W9	0.05
Hdn	W1	W3	W4	W5	W6	W7	0.07
Hdn	W1	W3	W4	W5	W6	W8	0.03
Hdn	W1	W3	W4	W5	W6	W9	0.17
Hdn	W1	W3	W4	W5	W7	W8	−0.05
Hdn	W1	W3	W4	W5	W7	W9	0.01
Hdn	W1	W3	W4	W5	W8	W9	0.07
Hdn	W1	W3	W4	W6	W7	W8	0.03
Hdn	W1	W3	W4	W6	W7	W9	0.04
Hdn	W1	W3	W4	W6	W8	W9	0.11
Hdn	W1	W3	W4	W7	W8	W9	0.03
Hdn	W1	W3	W5	W6	W7	W8	−0.02
Hdn	W1	W3	W5	W6	W7	W9	0.02
Hdn	W1	W3	W5	W6	W8	W9	0.00

Table 8 (continued)

Seven-body term							Int. energy
Hdn	W1	W3	W5	W7	W8	W9	−0.02
Hdn	W1	W3	W6	W7	W8	W9	0.06
Hdn	W1	W4	W5	W6	W7	W8	0.00
Hdn	W1	W4	W5	W6	W7	W9	0.04
Hdn	W1	W4	W5	W6	W8	W9	0.02
Hdn	W1	W4	W5	W7	W8	W9	0.01
Hdn	W1	W4	W6	W7	W8	W9	0.03
Hdn	W1	W5	W6	W7	W8	W9	0.00
Hdn	W2	W3	W4	W5	W6	W7	0.05
Hdn	W2	W3	W4	W5	W6	W8	0.04
Hdn	W2	W3	W4	W5	W6	W9	0.15
Hdn	W2	W3	W4	W5	W7	W8	−0.03
Hdn	W2	W3	W4	W5	W7	W9	−0.01
Hdn	W2	W3	W4	W5	W8	W9	0.03
Hdn	W2	W3	W4	W6	W7	W8	0.04
Hdn	W2	W3	W4	W6	W7	W9	0.15
Hdn	W2	W3	W4	W6	W8	W9	0.10
Hdn	W2	W3	W4	W7	W8	W9	0.05
Hdn	W2	W3	W5	W6	W7	W8	−0.01
Hdn	W2	W3	W5	W6	W7	W9	0.01
Hdn	W2	W3	W5	W6	W8	W9	0.01
Hdn	W2	W3	W5	W7	W8	W9	0.00
Hdn	W2	W3	W6	W7	W8	W9	0.12
Hdn	W2	W4	W5	W6	W7	W8	0.01
Hdn	W2	W4	W5	W6	W7	W9	0.02
Hdn	W2	W4	W5	W6	W8	W9	0.01
Hdn	W2	W4	W5	W7	W8	W9	0.00
Hdn	W2	W4	W6	W7	W8	W9	0.04
Hdn	W2	W5	W6	W7	W8	W9	0.01
Hdn	W3	W4	W5	W6	W7	W8	−0.01
Hdn	W3	W4	W5	W6	W7	W9	−0.01
Hdn	W3	W4	W5	W6	W8	W9	0.02
Hdn	W3	W4	W5	W7	W8	W9	0.01
Hdn	W3	W4	W6	W7	W8	W9	0.03
Hdn	W3	W5	W6	W7	W8	W9	−0.01
Hdn	W4	W5	W6	W7	W8	W9	0.00
W1	W2	W3	W4	W5	W6	W7	0.00
W1	W2	W3	W4	W5	W6	W8	0.00
W1	W2	W3	W4	W5	W6	W9	0.00
W1	W2	W3	W4	W5	W7	W8	0.00
W1	W2	W3	W4	W5	W7	W9	0.00
W1	W2	W3	W4	W5	W8	W9	0.00
W1	W2	W3	W4	W6	W7	W8	0.00
W1	W2	W3	W4	W6	W7	W9	0.00
W1	W2	W3	W4	W6	W8	W9	0.00
W1	W2	W3	W4	W7	W8	W9	0.00
W1	W2	W3	W5	W6	W7	W8	0.00
W1	W2	W3	W5	W6	W7	W9	0.00
W1	W2	W3	W5	W6	W8	W9	0.00

Table 8 (continued)

Seven-body term							Int. energy
W1	W2	W3	W5	W7	W8	W9	0.00
W1	W2	W3	W6	W7	W8	W9	0.00
W1	W2	W4	W5	W6	W7	W8	0.00
W1	W2	W4	W5	W6	W7	W9	0.00
W1	W2	W4	W5	W6	W8	W9	0.00
W1	W2	W4	W5	W7	W8	W9	0.00
W1	W2	W4	W6	W7	W8	W9	0.00
W1	W2	W5	W6	W7	W8	W9	0.00
W1	W3	W4	W5	W6	W7	W8	0.00
W1	W3	W4	W5	W6	W7	W9	0.00
W1	W3	W4	W5	W6	W8	W9	0.00
W1	W3	W4	W5	W7	W8	W9	0.00
W1	W3	W4	W6	W7	W8	W9	0.00
W1	W3	W5	W6	W7	W8	W9	0.00
W1	W4	W5	W6	W7	W8	W9	0.00
W2	W3	W4	W5	W6	W7	W8	0.00
W2	W3	W4	W5	W6	W7	W9	0.00
W2	W3	W4	W5	W6	W8	W9	0.00
W2	W3	W4	W5	W7	W8	W9	0.00
W2	W3	W4	W6	W7	W8	W9	0.00
W2	W3	W5	W6	W7	W8	W9	0.00
W2	W4	W5	W6	W7	W8	W9	0.00
W3	W4	W5	W6	W7	W8	W9	0.00

All energies are BSSE corrected. Hdn is hydronium ion and Wi denotes ith water molecule in the complex

Table 9 Eight-body interaction energy (kcal mol^{-1}) for H_3O^+–$(H_2O)_9$ hydrogen bonded complex using B3LYP/aug-cc-pvtz level

Eight-body term								Int. energy
Hdn	W1	W2	W3	W4	W5	W6	W7	−0.08
Hdn	W1	W2	W3	W4	W5	W6	W8	−0.04
Hdn	W1	W2	W3	W4	W5	W6	W9	−0.11
Hdn	W1	W2	W3	W4	W5	W7	W8	0.03
Hdn	W1	W2	W3	W4	W5	W7	W9	0.03
Hdn	W1	W2	W3	W4	W5	W8	W9	−0.08
Hdn	W1	W2	W3	W4	W6	W7	W8	−0.01
Hdn	W1	W2	W3	W4	W6	W7	W9	−0.12
Hdn	W1	W2	W3	W4	W6	W8	W9	−0.10
Hdn	W1	W2	W3	W4	W7	W8	W9	0.03
Hdn	W1	W2	W3	W5	W6	W7	W8	0.03
Hdn	W1	W2	W3	W5	W6	W7	W9	0.03
Hdn	W1	W2	W3	W5	W6	W8	W9	−0.02
Hdn	W1	W2	W3	W5	W7	W8	W9	0.04
Hdn	W1	W2	W3	W6	W7	W8	W9	−0.01
Hdn	W1	W2	W4	W5	W6	W7	W8	0.03
Hdn	W1	W2	W4	W5	W6	W7	W9	0.03
Hdn	W1	W2	W4	W5	W6	W8	W9	−0.02

Table 9 (continued)

Eight-body term								Int. energy
Hdn	W1	W2	W4	W5	W7	W8	W9	0.03
Hdn	W1	W2	W4	W6	W7	W8	W9	0.00
Hdn	W1	W2	W5	W6	W7	W8	W9	0.00
Hdn	W1	W3	W4	W5	W6	W7	W8	0.02
Hdn	W1	W3	W4	W5	W6	W7	W9	0.03
Hdn	W1	W3	W4	W5	W6	W8	W9	0.00
Hdn	W1	W3	W4	W5	W7	W8	W9	0.05
Hdn	W1	W3	W4	W6	W7	W8	W9	0.01
Hdn	W1	W3	W5	W6	W7	W8	W9	0.02
Hdn	W1	W4	W5	W6	W7	W8	W9	0.01
Hdn	W2	W3	W4	W5	W6	W7	W8	0.03
Hdn	W2	W3	W4	W5	W6	W7	W9	0.03
Hdn	W2	W3	W4	W5	W6	W8	W9	−0.01
Hdn	W2	W3	W4	W5	W7	W8	W9	0.03
Hdn	W2	W3	W4	W6	W7	W8	W9	0.03
Hdn	W2	W3	W5	W6	W7	W8	W9	0.02
Hdn	W2	W4	W5	W6	W7	W8	W9	0.01
Hdn	W3	W4	W5	W6	W7	W8	W9	0.02
W1	W2	W3	W4	W5	W6	W7	W8	0.00
W1	W2	W3	W4	W5	W6	W7	W9	0.00
W1	W2	W3	W4	W5	W6	W8	W9	0.00
W1	W2	W3	W4	W5	W7	W8	W9	0.00
W1	W2	W3	W4	W6	W7	W8	W9	0.00
W1	W2	W3	W5	W6	W7	W8	W9	0.00
W1	W2	W4	W5	W6	W7	W8	W9	0.00
W1	W3	W4	W5	W6	W7	W8	W9	0.00
W2	W3	W4	W5	W6	W7	W8	W9	0.00

All energies are BSSE corrected. Hdn is hydronium ion and Wi denotes ith water molecule in the complex

Table 10 Nine-body interaction energy (kcal mol^{-1}) for H_3O^+–$(H_2O)_9$ hydrogen bonded complex using B3LYP/aug-cc-pvtz level

Nine-body term									Int. energy
Hdn	W1	W2	W3	W4	W5	W6	W7	W8	−0.03
Hdn	W1	W2	W3	W4	W5	W6	W7	W9	−0.07
Hdn	W1	W2	W3	W4	W5	W6	W8	W9	−0.01
Hdn	W1	W2	W3	W4	W5	W7	W8	W9	−0.02
Hdn	W1	W2	W3	W4	W6	W7	W8	W9	−0.06
Hdn	W1	W2	W3	W5	W6	W7	W8	W9	−0.03
Hdn	W1	W2	W4	W5	W6	W7	W8	W9	−0.02
Hdn	W1	W3	W4	W5	W6	W7	W8	W9	−0.02
Hdn	W2	W3	W4	W5	W6	W7	W8	W9	−0.03
W1	W2	W3	W4	W5	W6	W7	W8	W9	0.00

All energies are BSSE corrected. Hdn is hydronium ion and Wi denotes ith water molecule in a complex

Table 11 Ten-body interaction energy (kcal mol^{-1}) for H_3O^+–$(H_2O)_9$ hydrogen bonded complex using B3LYP/aug-cc-pvtz level

Ten-body term										Int. energy
Hdn	W1	W2	W3	W4	W5	W6	W7	W8	W9	0.00

All energies are BSSE corrected. Hdn is hydronium ion and Wi denotes ith water molecule in the complex

nine-body and one ten-body term. Many body interaction energies are represented in Tables 3, 4, 5, 6, 7, 8, 9, 10, and 11. Total two-body to total ten-body interaction energies, relaxation energy, additive energy, non-additive energy, binding energy, and B.S.S.E corrected total energy of a complex are represented in Table 12. Table 13 gives contribution from various total many-body energies to the binding energy of a complex and their nature of interaction. In Table 14, percentage contributions from the terms containing hydronium ion as one of the many-body components and from terms containing only water molecules to the respective total many-body energy are represented along with the nature of interaction of these contributions.

From Table 3, the two-body interaction energies between hydrogen bonded pair of molecules are attractive and higher as compared to the other two-body interaction energies. The nature of interaction of hydronium ion with all nine water molecules in its first and second solvation shell is attractive

Table 12 Total n-body energies in kcal mol^{-1} alongwith interaction energies from terms containing hydronium ion as one of the many-body components and interaction energies from the many-body terms containing only water molecules for H_3O^+–$(H_2O)_9$ hydrogen bonded complex at B3LYP/aug-cc-pvtz level

	Total n-body int. energy	Int. energy from terms ontaining Hdn ion	Int. energy from terms containing only water molecules
Total two-body	−51.80	−27.28	−24.52
Total three-body	−23.40	−24.62	1.21
Total four-body	−13.98	−14.00	0.03
Total five-body	−6.93	−6.81	−0.12
Total six-body	1.95	1.93	0.02
Total seven-body	3.51	3.51	0.00
Total eight-body	−0.04	−0.04	0.00
Total nine-body	−0.28	−0.28	0.00
Total Ten-body	0.00	0.00	————
Relaxation Energy	2.60		
Additive Energy	−51.8		
Non-additive Energy	−39.2		
Binding Energy	−88.4		
BSSE corrected total energy (Hartree)		−765.28845	

Table 13 % contribution of many body energies to the binding energy for H_3O^+–$(H_2O)_9$ hydrogen bonded complex at B3LYP/aug-cc-pvtz level

Many-body term	% contribution	Nature of interaction
Total two-body	58.7	Attractive
Total three-body	26.5	Attractive
Total four-body	15.8	Attractive
Total five-body	7.8	Attractive
Total six-body	2.2	Repulsive
Total seven-body	3.9	Repulsive
Total eight-body	0.04	Attractive
Total nine-body	0.3	Attractive
Total ten-body	0.0	Repulsive
Relaxation energy	2.9	Repulsive

irregardless of whether it is hydrogen-bonded or not. However, the interaction energies of hydronium with the water molecules in its first solvation shell are much higher than those between the hydronium with water molecules in a second solvation shell. The interaction energy between 12 hydrogen-bonded pair of molecules is also not equal. There are two kinds of hydrogen-bonded pairs in a complex viz. hydronium-water and water-water. The interaction energies for the former pairs are much higher than those for the latter. The highest two-body interaction energy is obtained for the hydronium and W_1 molecule whereas the W-W interaction energy is highest for the W_3-W_8 pair. Their attractive contribution is about 16.4 and 8.37 % respectively to the total two-body interaction energy.

The contribution from the total two-body energy to the binding energy of a complex is about 58.6 % and is attractive in nature. The hydronium-water and water-water interaction terms contribute about 52.7 and 47.3 % respectively to the total two-body interaction energy. Total energy from hydronium-water interaction terms is −27.3 kcal mol^{-1} and that from the water-water interaction terms is −24.5 kcal mol^{-1}. The relaxation energy contributes about 2.9 % to the binding energy of a complex and is of a repulsive nature. The relaxation energy is found to be 2.6 kcal mol^{-1} for this complex.

Table 14 Percentage contribution from terms containing hydronium ion as one of the many-body components and from terms containing only water molecules to the respective total many-body energy for H_3O^+-$(H_2O)_9$ hydrogen bonded complex at B3LYP/aug-cc-pvtz level

Many-body term	Int. energy from terms containing Hdn ion	Int. energy from terms containing only water molecules
Total two-body	52.7 (A)	47.3 (A)
Total three-body	105.2 (A)	5.2 (R)
Total four-body	100.2 (A)	0.2 (R)
Total five-body	98.3 (A)	1.7 (A)
Total six-body	98.8 (A)	1.2 (A)
Total seven-body	100.1 (A)	0.1 (R)
Total eight-body	102.4 (A)	2.4 (R)
Total nine-body	99.9 (A)	0.1 (A)
Total ten-body	100 (A)	———

The letters A and R in parenthesis represents attractive and repulsive nature respectively

Table 4 represents the three-body interaction energies for a complex. The highest attractive three-body interaction energy is shown by the hydronium-W_2-W_7 three-body term and contributes about 19.5 % to the total three-body interaction energy. The three-body terms for which at least two hydrogen bonds are formed by the molecules involved for that term show higher interaction energies than the terms with one or no hydrogen bonds formed. The W_3- W_4- W_9 interaction energy is highest among the attractive water-water-water interaction energies and has about 5.9 % contribution to the total three-body interaction energy, whereas the W_1- W_4- W_5 interaction energy is the highest three-body repulsive energy. The contribution from the three-body terms involving hydronium as one of the three-body component and that from the water-water-water interaction energy terms to the total three-body energy is about 105.2 % (attractive) and 5.2 % (repulsive) respectively. The contribution from the total three-body energy to the binding energy of a complex is about 26.5 % and is of an attractive nature.

Total four-body and total five-body energies are of attractive nature and contribute about 15.8 and 7.8 % respectively to the binding energy of a complex. Interaction energies from W-W-W-W and W-W-W-W-W four and five body terms are close to zero and are negligible as compared to the four and five body interaction energy terms involving hydronium as one of the many-body components. The percentage contribution from the four-body terms involving hydronium as one of the four-body components and that from water-water-water-water interactions to the total four-body interaction energy is 100.2 % (attractive) and 0.2 % (repulsive) respectively. The interaction energies from the five-body terms containing hydronium and without hydronium contribute about 98.26 and 1.74 % respectively to the total five-body interaction energy and both contributions are attractive in nature. The highest contribution to the total four-body energy is from the hydronium-W_1- W_3- W_9 term which is about 10.9 % and is of an attractive nature.

Total six- and seven-body energies are also not negligible but contribute about 2.2 and 3.9 % respectively to the binding energy of a complex and both of them are repulsive in nature. The six-body terms involving hydronium and those without hydronium contribute (attractive) about 98.8 and 1.2 % respectively to the total six-body interaction energy. For the seven-body case, the seven- body terms containing hydronium has 100.1 % attractive contribution and that from terms

containing only water molecules is about 0.1 % (repulsive) to the total seven-body energy.

As compared to the total two-body to seven-body interaction energies, the total eight-body, total nine-body, and ten-body interaction energies are negligible. The additive and non-additive energies are attractive and contribute about 58.6 and 44.3 % to the binding energy of a complex.

Conclusions

Hydrogen bonding interaction of hydronium with water molecules in its first and second solvation shell is studied using density functional method with B3LYP functional and aug-cc-pvtz basis set. Many-body analysis is used to study the nature of various many-body interactions in a complex. Many-body energies up to seven-body are not negligible whereas eight-, nine- and ten-body energies are negligible. The percentage contribution from various many-body energies to the binding energy of a complex is reported. From four-body onward, the interaction among water molecules is negligible as compared to the many-body terms involving hydronium ion as one of the many-body components. This study should provide useful guidelines for developing the potential for protonated water systems.

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