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PROTONIC DEFECTS IN LARGE WATER CLUSTERS AT FINITE TEMPERATURE

ARINDAM BANKURA AND AMALENDU CHANDRA*

Department of Chemistry, Indian Institute of Technology, Kanpur 208016 (India)

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We present a brief overview of recent experimental and theoretical studies of the hydration shell structure and translocation of protonic defects in large water clusters. The primary focus of the present article is on finite temperature behaviour of large water clusters with one proton less so that the cluster is overall negatively charged. We present some results of our own work on $(H_2O)_{20}OH^-$ which we have taken up as a case study and have looked at the structure and dynamics of the cluster by means of quantum chemical calculations and finite temperature *ab initio* molecular dynamics simulations. In the latter method, the forces on the nuclei are obtained directly from 'on the fly' quantum electronic structure calculations and it is ideally suited to study proton translocation processes which proceed through breaking and formation of chemical bonds. Results are discussed for the structure of hydration shell of the protonic defect at zero and room temperatures and also the frequency of proton translocation events at room temperature.

Key Words: Protonic defects; *ab initio* Molecular dynamics; Water clusters; Proton rattling and translocation

1 Introduction

Studies of hydration and translocation of protonic defects created by the addition or removal of a proton in water clusters are of fundamental importance in chemistry, biology and atmospheric science. It is, therefore, not surprising that these cluster ions have been the subject of extensive studies, both experimentally and theoretically. Earlier experiments[1-5] on larger clusters with protonic defects identified some of the magic numbers such as $(H_2O)_nH^+$ with n=21, 28, 30, 34 and $(H_2O)_mOH^-$ with m=20, 28, 29, 30 etc. for n,m $\geq$ 20. Recent developments of high resolution nanoscale experiments have provided opportunities for studying molecular details of the hydration structure of protonic defects in these clusters[6,7]. Nanoscale clusters have properties which differ from both small aggregates composed of a few molecules and bulk phases. They are sufficiently large to exhibit some of the bulk-like properties, yet the surface forces play an important role in determining their structural and dynamical behaviour. One important issue regarding the structure of these nano-sized cluster ions is the hydration state of the protonic defect - whether it is solvated inside the cluster or at the surface. A related issue is the presence or absence of dangling hydrogens of the core ion containing the protonic defect. The core ion can be a hydronium ion (H_3O^+) or a Zundel cation ($H_5O_2^+$) when there is an excess proton and it is the hydroxyl ion (OH^-) when the defect is due to the shortage of a proton. Another important issue is how the protonic defect is translocated in such finite-sized clusters and to what extent the mechanism of translocation in these clusters differs from that in bulk liquids[8].

Recent experimental studies[6,7] on nano-sized protonated water clusters have used infrared spectroscopy to probe vibrational transitions of the OH stretch modes of the clusters. These modes show high sensitivity on the hydrogen bonded environment of the OH bonds. The frequency of a hydrogen bonded OH group is lower than that of a non-hydrogen bonded or dangling OH and the presence of these dangling hydrogens contains important information about the structure of the clusters. Although these studies showed transitions from multiple ring to cage like structures with increase of cluster size, no definite conclusion was made regarding the internal or the surface state of the hydrated proton in a given cluster[9]. A very recent theoretical study[10] on these protonated clusters based on finite temperature simulations have shown that the observed structures can vary depending on the

**Email:* amalen@iitk.ac.in

temperature of the clusters. Recent experiments[11,12] have also investigated proton transfer in protonated hydrogen bonded systems which are smaller in size but can exhibit features such as breaking and reformation of hydrogen bonds that are associated with proton transfers. The proton transfer in some of the smaller water and mixed water-ammonia clusters has also been investigated theoretically by means of quantum chemical calculations and *ab initio* molecular dynamics simulations and have revealed many interesting results[13-17].

Contrary to the rather large number of studies that have been carried out on hydrogen bonded clusters with an excess proton, not many studies have been reported on water clusters with one proton less, i.e. water clusters containing a hydroxyl ion. Robertson *et al.*[18] reported high-resolution infrared studies on $(H_2O)_nOH^-$ with n = 1 - 5 and there have been a few quantum chemical[19,20] and finite temperature Monte Carlo[21] studies on these systems. These studies have primarily focused on the hydrogen bonded structure of the OH^- ion and the relative binding energies for different isomers of different cluster sizes. Since there have been only a few theoretical studies on water clusters with one proton less, and that too primarily for smaller clusters, much more work is needed in this area to have a better understanding of the hydration and translocation of protonic defects in nano-sized hydrogen bonded clusters. In the present article, we report some of our work in this area based on quantum chemical calculations and finite temperature *ab initio* molecular dynamics simulations. In particular, we present results of a cluster made of 20 water molecules and an OH^- ion. We look at the hydration structure of the core ion and also find out the index of the oxygen to which the protonic defect is attached as we move along the simulation trajectory. The frequency of the change of this oxygen index provides information on how fast the proton is translocated in the cluster.

2 OH^- in $(H_2O)_{20}$: A Case Study using Quantum Chemical Calculations and Quantum Simulations

We have carried out all-electron quantum chemical calculations of the $(H_2O)_{20}OH^-$ cluster to find the location of the protonic defect in some of its optimized geometries. The calculations are done at Hartree-Fock level with the 6-31G* basis set

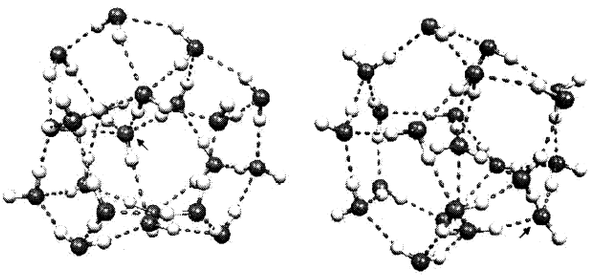

Fig.1 The optimized structures of $(H_2O)_{20}OH^-$ with hydroxyl ion at the centre (left) and at the surface (right) of the dodecahedral cage. The arrow points to the hydroxyl ion

using the Gaussian 03 package[22]. In Fig.1, we have shown two optimized geometries with different locations and hydration structures of the OH^- ion. In the first configuration (left), OH^- is located in an inner state whereas it is located at a surface state in the second configuration (right). In the inner state, the oxygen of OH^- is having four hydrogen bonds with surrounding water molecules and its hydrogen is also forming a weak hydrogen bond. For the surface state, the hydrogen of OH^- is dangling and its oxygen is participating in three hydrogen bonds. In both cases, the hydrogen bonds are defined by using a distance criterion of $R_{O\cdots H} \leq 2.5$ Å. Between these two structures, the configuration with the inner state of OH^- is found to be more stable than the one with the surface state by about 0.17 eV.

Next, we have carried out finite temperature *ab initio* molecular dynamics simulations of the cluster starting from the inner state of the hydroxyl ion. The simulations are performed by means of the Car-Parrinello method[23,24] and the CPMD code[25]. The cluster is kept in the central region of a simple cubic box of length 18.5 Å. The length of the box is sufficiently large so that there is enough empty space around the cluster in all directions. The electronic structure of the system is represented by the Kohn-Sham (KS) formulation[26] of DFT within a plane wave basis and BLYP functional. We have used the BLYP functional[27] because it has been shown to provide a good description of hydrogen bonded systems such as water[28-30], methanol[31] and also ammonia[32,33]. The core electrons are treated via the Troullier–Martins normconserving pseudopotentials[34] and the plane wave expansion of the KS orbitals is truncated at a kinetic energy of 70 Ry. A fictitious mass of μ = 800 a.u. has been assigned to the electronic degrees of freedom and

the coupled equations of motion describing the system dynamics are integrated by using a time step of 5 a.u. or 0.12094 fs. The hydrogen atoms are given the mass of deuterium in order to reduce the influence of quantum effects on the structural and dynamical properties. We note that the above values of the fictitious electronic mass, time step and hydrogen mass ensured adiabatic separation of electronic and nuclear motion and energy conservation during the simulation run as required by the Car-Parrinello algorithm[23,24]. We have equilibrated the systems for about 10 ps in the canonical ensemble at 300K using Nose-Hoover chain method and, thereafter, the simulations are continued in microcanonical ensemble for another 9.1 ps for calculation of the various structural and dynamical quantities.

We note that in our finite temperature simulations, the protonic defect is not attached to a given oxygen for the entire trajectory due to the presence of proton translocation process. In order to identify the oxygen to which the defect is attached, i.e. of the hydroxyl ion, we first assign to each oxygen its two nearest hydrogen atoms. Then the hydrogen that has been assigned to two oxygens is found out and it is assigned to its nearest oxygen. The other oxygen, having only one hydrogen assigned to it, is identified as the hydroxyl oxygen O*. The hydration structure of this hydroxyl ion is investigated by calculating the number of hydrogen bonds that the oxygen and hydrogen atoms of the hydroxyl ion make with surrounding water molecules in its first hydration shell. The first number we call the accepted hydrogen bond number and denote it as N_{O^*} while the second number is called the donated hydrogen bond number which is denoted as N_{H^*}. In Fig. 2, we have shown the instantaneous values of the hydrogen bond numbers of the hydroxyl ion over the simulation run period. It is found that the hydroxyl ion prefers to accept four hydrogen bonds through its oxygen atom and it does not donate any hydrogen bond through its hydrogen atom. The hydrogen atom of the OH^- is dangling almost all the time and thus it prefers a surface state. The average values of the hydrogen bond numbers are: N_{O^*}=3.73 and N_{H^*}=0.02. In Fig.3, we have shown a representative configuration taken from the simulation trajectory where the presence of dangling hydrogen of the hydroxyl ion is clearly seen.

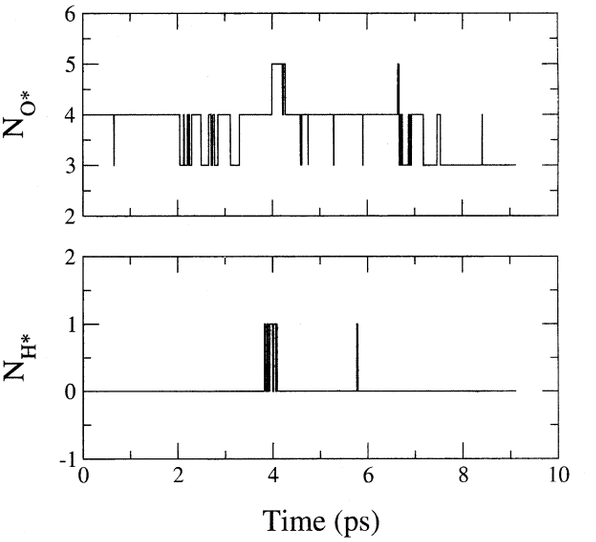

Fig. 2 The instantaneous numbers of hydrogen bonds accepted by the oxygen (N_{O^*}) and donated by the hydrogen atoms (N_{H^*}) of the hydroxyl ion in $(H_2O)_{20}OH^-$ at room temperature

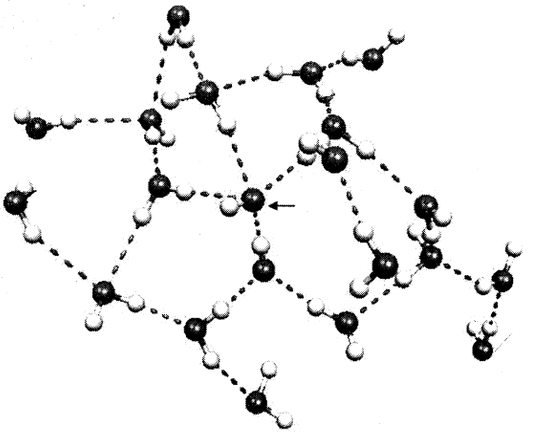

Fig. 3 A representative configuration taken from the simulation trajectory of the $(H_2O)_{20}OH^-$ cluster at room temperature. The arrow points to the hydroxyl ion

As discussed earlier, the protonic defect is not located at the same oxygen all the time. It moves within the cluster due to proton translocation which is aided by interconversion of covalent and hydrogen bonds. In the present cluster, there are 21 oxygen atoms which are identified by numbers from 1 to 21 and the number assigned to a given oxygen atom is called its index. The kinetics of proton translocation can be determined by the rate at which the index of the hydroxyl oxygen changes due to proton transfer. In Fig.4, we have shown the index of the hydroxyl oxygen along the simulation trajectory. Firstly, we note that there are few transfer events

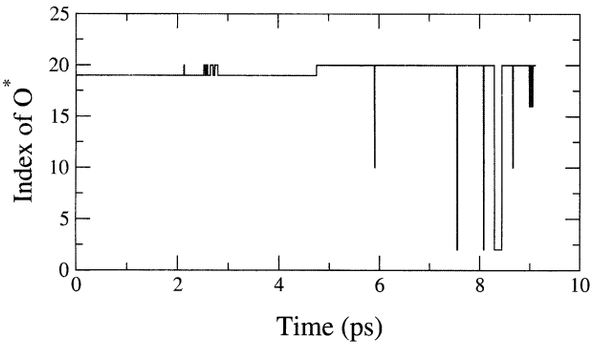

Fig. 4 The index of the hydroxyl oxygen O* along the simulation trajectory of $(H_2O)_{20}OH^-$

due to rattling effects caused by intermolecular vibrations. These are not 'real' proton transfers and will not contribute to the average mobility of the charge defect. When these rattling events are filtered out, it is seen that, for first 4.75 ps, the protonic defect stays essentially all the time with the same oxygen and then it switches to a different oxygen atom. Another change with a shorter lifetime is found at around 8.25 ps. Thus, this cluster of OH- in 20 H_2O is found to be large enough to provide a favourable environment for proton translocation.

3 Conclusions

We have discussed the hydration and translocation of protonic defects in large water clusters at finite temperatures. The defects can be created by the addition or removal of a proton. In the present article, we have primarily focused on large water clusters with one proton less so that the overall cluster is negatively charged and contains a hydroxyl ion. We considered $(H_2O)_{20}OH^-$ as a case study and investigated its structure and dynamics by means of quantum chemical calculations and *ab initio* molecular dynamics simulations. Two lower-energy isomers are found from quantum chemical calculations, one with an inner state and the other with a surface state of the hydroxyl ion. Energetically, the isomer with the inner state of the hydroxyl ion is found to be slightly more stable than the one with the surface state. In the inner state, the oxygen and hydrogen atoms of the hydroxyl ion are found to form four and one hydrogen bonds, respectively. When the hydroxyl ion is at the surface, its oxygen forms three hydrogen bonds and its hydrogen remains dangling outward without forming any hydrogen bond. At finite temperature, the hydroxyl ion is seen to prefer a surface-like state with no hydrogen bond through its hydrogen and its oxygen atom forms 3.7 hydrogen bonds when averaged over the entire trajectory. The index of the oxygen of the hydroxyl ion is found to change due to proton rattling aided by intermolecular vibrations and 'real' proton translocations aided by interconversion of covalent and hydrogen bonds.

In the present article, we have discussed hydration and translocation of protonic defects in water clusters which are free from any external confining potential. A recent study[35] has employed *ab initio* molecular dynamics and an empirical valance bond model to investigate the transport of an excess proton through a one dimensional hydrogen bonded water chain confined in a narrow carbon nanotube. The mechanism of proton transport in this confined environment was found to be quite different from that in bulk liquid water. Theoretical studies[36] have also been carried out on solvation and transport of an excess proton in complex biological channels by using a combination of classical and quantum methods. Recent quantum chemical calculations have shown that the nature of hydrogen bonds and the overall structure of a water cluster in a confined environment can be very different from that of the corresponding free cluster[37,38]. The effects of confinement on the hydration structure and translocation of protonic defects in hydrogen bonded systems are still open problems which are important not only in chemistry but also in biology and nanomaterials science.

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References

1 S S Lin *Rev Sci Instrum* **44** (1973) 516

2 J Q Searcy and J B Fenn *J Chem Phys* **77** (1974) 2549

3 J L Kassner, Jr and D E Hagen *J Chem Phys* **64** (1976) 1860

4 X Yang and A W Castleman Jr *J Am Chem Soc* **111** (1989) 6845

5 X Yang and A W Castleman Jr *J Phys Chem* **94** (1990) 8500

6 M Miyazaki, A Fujii, T Ebata and N Mikami *Science* **304** (2004) 1134

7 J-W Shin, N I Hammer, E G Diken, M A Johnson, R S Walters, T D Jaeger, M A Duncun, R A Christie and K D Jordan *Science* **304** (2004) 1137

8 D Marx, M Tuckerman, J Hutter and M Parrinello *Nature* **397** (1999) 601; M E Tuckerman, D Marx and M Parrinello *Nature* **417** (2002) 926

9 T S Zwier *Science* **304** (2004) 1119

10 J-L Kuo and M L Klein *J Chem Phys* **122** (2005) 24516; C-C Wu, C-K Lin, H-C Chang, J-C Jiang, J-L Kuo and M L Klein *J Chem Phys* **122** (2005) 74315

11 A Bach and S Leutwyler *J Chem Phys* **112** (2000) 560

12 M Meuwly, A Bach and S Leutwyler *J Am Chem Soc* **123** (2001) 11446

13 H-P Chang *J Chem Phys* **105** (1996) 6844

14 M Meuwly and M Karplus *J Chem Phys* **116** (2002) 2572

15 P L Geissler, C Dellago, D Chandler, J Hutter and M Parrinello *Chem Phys Lett* **321** (2000) 225

16 H-P Cheng, R N Bernett and U Landman Chem Phys Lett **237** (1995) 161

17 A Bankura and A Chandra *Pramana - J Phys* **65** (2005) 763

18 W H Robertson, E G Diken, E A Price, J-W Shin and M A Johnson *Science* **299** (2003) 1367

19 J J Novoa, F Mota, C P del Valle and M Planas *J Phys Chem A* **101** (1997) 7842

20 H M Lee, P Tarakeshwar and K S Kım *J Chem Phys* **121** (2004) 4657

21 A Vegiri and S V Shevkunov *J Chem Phys* **113** (2000) 8521

22 M J Frisch, G W Trucks, H B Schlegel *et al GAUSSIAN 03* gaussian Inc. Pittsburgh P A (2003)

23 R Car and M Parrinello *Phys Rev Lett* **55** (1985) 2471

24 D Marx and J Hutter *Ab Initio Molecular Dynamics: Theory and Implementation in Modern Methods and Algorithms of Quantum Chemistry*, Ed. J. Grotendorst (NIC, FZ Jülich, 2000).

25 CPMD Program, J Hutter, A Alavi, T Deutsch, M Bernasconi, St Goedecker, D Marx, M Tuckerman and M Parrinello, MPI für Festkörperforschung and IBM Zurich Research Laboratory.

26 W Kohn and L J Sham *Phys Rev A* **140** (1965) 1133

27 D Becke *Phys Rev A* **38** (1988) 3098; C Lee, W Yang, R G Parr *Phys Rev B* **37** (1988) 785

28 K Laasonen, M Sprik, M Parrinello and R Car *J Chem Phys* **99** (1993) 9080

29 M Sprik, J Hutter and M Parrinello *J Chem Phys* **105** (1995) 1142

30 P L Silvestrelli and M Parrinello *Phys Rev Lett* **82** (1999) 3308; *J Chem Phys* **111** (1999) 3572

31 E Tsuchida, Y Kanada and M Tsukada *Chem Phys Lett* **311** (1999) 236

32 M Diraison, G J Martyna and M E Tuckerman *J Chem Phys* **111** (1999) 1096 Y Liu and M E Tuckerman *J Phys Chem B* **105** (2001) 6598

33 D Boese, A Chandra, J M Martin and D Marx *J Chem Phys* **119** (2003) 5965

34 N Troullier and J M Martins *Phys Rev B* **43** (1991) 1993

35 C Dellago, M M Naor and G Hummer *Phys Rev Lett* **90** (2003) 105902

36 M L Brewer, U Schmitt and G A Voth *Biophys J* **80** (2001) 1691; Y Wu and G A Voth *Biophys J* **85** (2003) 864

37 M Elango, R Parthasarathi, V Subramanian, C N Ramachandran and N Sathyamurthy *Proc Ind Nat Sci Acad* **71A** (2005) 405

38 C N Ramachandran and N Sathyamurthy *Chem Phys Lett* **410** (2005) 348; S Maheshwary, N Patel, N Sathyamurthy, A D Kulkarni and S R Gadre *J Phys Chem A* **105** (2001) 10525