Hydration and translocation of an excess proton in water clusters: An *ab initio* molecular dynamics study

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Abstract. The hydration structure and translocation of an excess proton in hydrogen bonded water clusters of two different sizes are investigated by means of finite temperature quantum simulations. The simulations are performed by employing the method of Car–Parrinello molecular dynamics where the forces on the nuclei are obtained directly from 'on the fly' quantum electronic structure calculations. Since no predefined interaction potentials are used in this scheme, it is ideally suited to study proton translocation processes which proceed through breaking and formation of chemical bonds. The coordination number of the hydrated proton and the index of oxygen to which the excess proton is attached are calculated along the simulation trajectories for both the clusters.

1. Introduction

The present work is concerned with the behaviour of an excess proton in water clusters of varying sizes. Proton hydration and its translocation in hydrogen bonded systems is a process of fundamental importance in chemistry and biology. In many hydrogen bonded liquids, such as water and methanol, the proton translocation has been shown to proceed through oriented chains of solvent molecules [1,2]. Such structures are often described as 'proton wires' [3,4]. Recently, the development of high-resolution nanoscale experiments has provided opportunities for studying hydration and translocation of protons in hydrogen bonded molecular clusters [5–8]. Experimental investigations of excess protonic systems have been carried out on clusters that are small but still can exhibit features such as breaking and reformation of hydrogen bonds that are associated with proton transfers. The proton transfer in some of the small water clusters and mixed water–ammonia clusters has also been investigated by means of quantum chemical calculations and *ab initio* molecular dynamics simulations which have revealed many interesting results [9–12]. Since there have been only a few theoretical studies on excess protons in

clusters, and that too for rather small clusters, much more work is needed in this area to have a better understanding of the hydration and translocation of protons in hydrogen bonded clusters of nanodimensions. Nanoscale clusters have properties which differ from both small aggregates composed of 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. Thus, a detailed study of the structural and dynamical aspects of an excess proton in water clusters of varying sizes, from few molecules to few tens of molecules, would provide us important information on the kinetics of translocation process in finite-sized systems. The present study is a contribution towards this end.

In this work, we have carried out finite temperature *ab initio* molecular dynamics studies of protonated water clusters of two different sizes: one cluster consisting of a hydronium ion and four water molecules and the other consisting of a hydronium ion and sixteen water molecules. For both systems, the coordination number of the hydrated proton and the index of the oxygen to which the excess proton is attached are calculated along the simulation trajectory. The frequency of the change of hydronium oxygen index provides information on how fast the proton is translocated in a given cluster. The average values of the coordination numbers of the hydrated proton are also calculated.

The rest of the paper is organized as follows. In §2, we describe the methodology and details of *ab initio* molecular dynamics simulations that are employed here. In §3, we discuss our results of hydration structure and translocation of the excess proton and §4 includes a brief conclusion.

2. *Ab initio* molecular dynamics simulations

The *ab initio* molecular dynamics simulations were performed by means of the Car–Parrinello method [13,14] and the CPMD code [15]. A simple cubic box of length L containing one H_3O^+ ion immersed in a cluster of N water molecules was taken in isolation for carrying out the simulations. We considered two different cluster sizes: $N = 4$ and 16 with box length $L = 15.0$ and 18.0 Å, respectively. In each case the cluster was kept in the central region of the box and the box length is sufficiently large to provide enough empty space around the cluster in all directions. The electronic structure of the system was represented by the Kohn–Sham (KS) formulation [16] of DFT within a plane-wave basis. The core electrons were treated via the Troullier–Martins norm-conserving pseudopotentials [17] and the plane-wave expansion of the KS orbitals was truncated at a kinetic energy of 70 Ry. A fictitious mass of $\mu = 800$ a.u. was assigned to the electronic degrees of freedom and the coupled equation of motion describing the system dynamics was integrated by using a time step of 5 a.u. The hydrogen atoms were given the mass of deuterium in order to reduce the influence of quantum effects on the dynamical properties. The *ab initio* MD simulations have been performed using the BLYP [18] functionals. We used the BLYP functional because it has been shown to provide a good description of hydrogen bonded systems such as water [19–21], methanol [22] and also ammonia [23–25]. We equilibrated the systems for about 10 ps at 300 K

in NVT ensemble using Nose–Hoover chain method and, thereafter, we continued the simulations in NVE ensemble for another 10 ps for the calculation of various structural and dynamical quantities.

3. Results and discussion

In order to identify the oxygen of the hydronium ion, i.e. the oxygen to which the excess proton is attached for a given configuration, we first assign to each oxygen its two nearest hydrogen atoms. Then the hydrogen that is left out is the excess proton and it is then assigned to its nearest oxygen and this particular oxygen is identified as the hydronium oxygen O^*. The hydration structure of this hydronium ion is investigated by calculating the number of water molecules in its first hydration shell and also by counting the number of hydrogen bonds that this species donates through its three hydrogens. We call the first number as coordination number and denote it as N_{O^*} while the second number is called the hydrogen bond number which is denoted as N_{HB}. The hydrogen bonds are calculated by using a cut-off of 2.5 Å for the hydrogen–oxygen distance of two neighbouring molecules. In figures 1 and 2, we have shown the instantaneous values of the coordination and hydrogen bond numbers of the hydronium ion for both the clusters. It is found that the
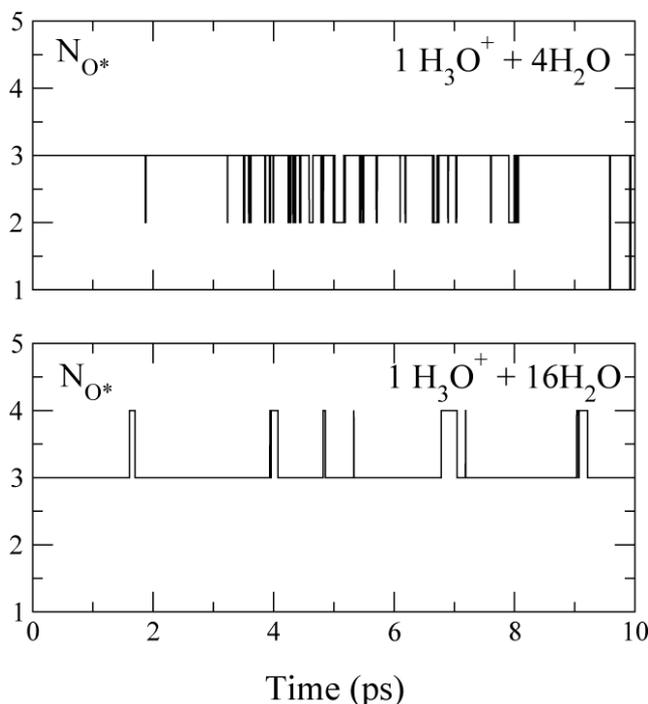

Figure 1. The instantaneous number of water molecules present in the hydration shell of O^* of the hydronium ion.
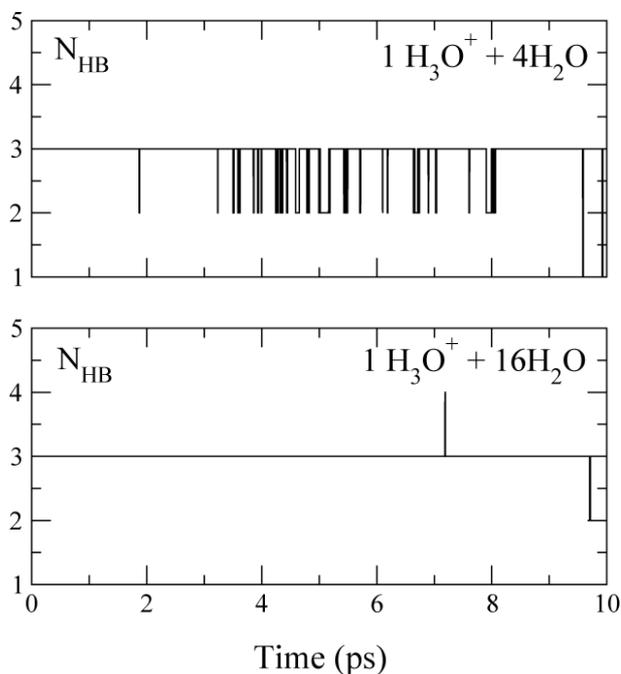
Figure 2. The instantaneous number of hydrogen bonds donated by the hydrogen atoms of the hydronium ion.

hydronium ion almost always donates three hydrogen bonds, one through each of its hydrogen atoms. However, for the bigger cluster, the coordination number is found to be larger than three in some of the configurations. The average values of these hydration numbers are: $N_{O^*} = 2.92$, 3.1 and $N_{HB} = 2.92$, 3.0 for the smaller and the larger clusters, respectively.

The kinetics of proton translocation is determined by the rate at which the index of the hydronium oxygen changes. The index of the hydronium oxygen changes due to proton transfer and the identity of the hydronium oxygen is found out by the method described above. In figure 3, we have shown the index of the hydronium oxygen along the simulation trajectory. It is seen that, for the smallest cluster, the excess proton always stays essentially with the same oxygen. There are few transfer events due to proton rattling effects. For the larger cluster, however, the excess proton is found to move between some of the oxygen atoms. Hence, this bigger cluster provides a more favourable environment for translocation of the excess proton than the smaller cluster. Since majority of water molecules are exposed to the surface, both of their hydrogens are not hydrogen bonded. However, all three hydrogens of the hydronium ion are hydrogen bonded in essentially all the configurations as can be seen from figure 2. Thus, a water molecule can act as an effective proton acceptor only when its oxygen atom is hydrogen bonded to one of the hydrogens of the hydronium ion and, at the same time, both of its hydrogens are hydrogen bonded to neighbouring water molecules. For a finite-sized cluster with a large fraction of surface molecules with dangling hydrogens, the above two criteria
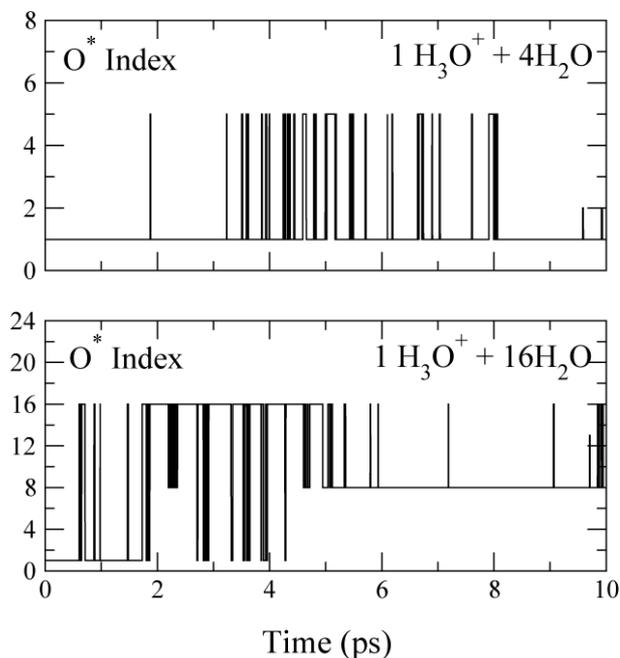
Figure 3. The index of the hydronium oxygen O^* along the simulation trajectories of the two systems studied in the present work.

are not satisfied very frequently and we observe effectively two proton transfer events for the larger cluster, excluding proton rattling effects, with the index of the hydronium ion changing from 1 to 16 and then to 8 during the 10 ps production run of the present study.

4. Conclusions

We have carried out *ab initio* molecular dynamics simulations to investigate the hydration and translocation of an excess proton in water clusters of two different sizes. For both the clusters, the hydronium ion is found to donate three hydrogen bonds through each of its hydrogen in almost all configurations. However, in some of the configurations for the larger cluster, an additional water molecule is also found in the hydration shell of the hydronium ion which is not hydrogen bonded to any of its hydrogen atoms. The larger cluster is found to provide a more favourable environment for proton translocation.

The results presented here are of preliminary nature. Further work is in progress which deals with excess protons in even larger clusters. There are many questions which are still to be addressed such as the surface versus interior states of the excess proton in nanosized clusters, kinetics of proton translocation and its dependence on cluster size etc. We hope to address these issues in a future publication.

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