

*Research Paper*

## **An *ab initio* Molecular Dynamics Study of Electron Hydration Dynamics in Water Hexamer Cluster at a Finite Temperature**

SUBHA PRATI HAR<sup>1</sup> and AMALENDU CHANDRA

Department of Chemistry, Indian Institute of Technology, Kanpur 208 016, India

(Received on 18 November 2013; Revised on 22 May 2014; Accepted on 29 May 2014)

Electron hydration dynamics in water hexamer cluster is studied through *ab initio* molecular dynamics simulations at a finite temperature within density functional theory. Second-order perturbative MP2 calculations with appropriate basis set containing extra diffuse functions are also performed on simulated structures to obtain more accurate results of the energetics. It is found that the structure of the neutral cluster significantly changes upon insertion of the excess electron. Both, surface bound and partially interior states are found for the excess electron in the present simulations. After the electron capture, the relative energy of the system first decreases very fast because of the structural relaxation and then changes slowly towards the long-time value due to slower evolution of the systems through different configurations. The changes of the average population of water molecules in different hydrogen bonding environments during electron hydration process are also investigated.

**Key Words:** Electron Hydration; Water Cluster; Quantum Calculations; Ab Initio; Molecular Dynamics

### **Introduction**

When an excess electron is injected into polar solvents, e.g., water or ammonia, either by photoionization or electron beam methods, a solvated electron is formed. This occurs through a complex sequence of events involving thermalization, electronic relaxation, trapping and solvation dynamics (Keszal *et al.*, 1995). Since the discovery of 'hydrated electron' in 1962 (Hart and Boag, 1962), this species has been studied immensely from both experimental and theoretical points of view. Haberland and co-workers (Haberland *et al.*, 1984) experimentally showed that the smallest water cluster anion that could be formed is  $(\text{H}_2\text{O})_{2n}^-$ . It has been found that for smaller anionic clusters,  $(\text{H}_2\text{O})_n^-$  with  $n=2, 6, 7$  and  $11$  are preferentially formed while those with  $n=3, 4, 5$  and  $8$  are weakly stable and show very weak peaks in mass spectra (Kim *et al.*, 1997a; Kim *et al.*, 1997b, Lee *et al.*, 2005). Recent experiments

(Paik *et al.*, 2004; Paik *et al.*, 2003; Verlet *et al.*, 2005; Bragg *et al.*, 2004, Lehr *et al.*, 1999; Hammer *et al.*, 2005; Ayotte and Johnson, 1997; Hammer *et al.*, 2004; Jordan, 2004) have investigated negatively charged water clusters containing 4 to 50 water molecules to elucidate their arrangement in the vicinity of a hydrated electron and to study its dynamics. Vibrational predissociation spectroscopy has been applied to obtain knowledge about the motifs of electron binding in smaller clusters with four to six water molecules with an excess electron (Hammer *et al.*, 2005). These studies have shown that electron is closely associated with a single water molecule attached to the supporting network through a double hydrogen bond acceptor motif. Depending on the nature of electron binding, the presence of three groups of electron-water  $(\text{H}_2\text{O})_n^-$  clusters, e.g. dipole bound states, intermediate states and bulk embryons, have been shown (Coe *et al.*, 1990; Coe *et al.*, 2006).

\*Author for Correspondence: E-mail: amalen@iitk.ac.in

<sup>1</sup>Present address: Department of Chemistry and Biochemistry, Texas Tech University, Lubbock, TX 79409-1061, USA

The surface bound states are considered to be more stable than the internal bound states for small anionic water clusters. The issue of surface versus interior states of water cluster anions has been recently addressed in more details by means of finite-temperature molecular simulations applying quantum-classical simulation protocol (Turi *et al.*, 2005). This study has shown that, apart from cluster size, temperature can also play an important role in deciding the surface versus internal states of the solvated electron. For example, at  $T=200$  and  $300$  K, only surface states were found for  $n=20-104$ , whereas at  $T=100$  K, interior states were found only for  $n \geq 45$  although it has been debated by others (Verlet *et al.*, 2005; Turi *et al.*, 2005). Thus, it is very clear that the hydrated electron is far more complex because of the fast dynamics of structural changes and solvation.

Finite temperature behaviour of  $(\text{H}_2\text{O})_6^-$  using parallel tempering Monte Carlo method together with a quantum Drude model predicted presence of many isomers of this small cluster with different electron binding energies (Wang and Jordan, 2003; Sommerfeld *et al.*, 2006). Various isomeric structures of anionic water clusters of different sizes have also been calculated through high-level quantum chemical and polarization potential based model based calculations (Vysotskiy *et al.*, 2012; Voora *et al.*, 2013). Recently, a hybrid *ab initio* molecular dynamics scheme was introduced for simulating supra molecular anions and simulated vibrational and photoelectron spectra of  $(\text{H}_2\text{O})_n^-$  ( $n=4$ ) treating all electrons quantum mechanically (Herbert and Gordon, 2006). We also note that recent simulations (Boero *et al.*, 2003) have also studied the finite temperature behaviour of hydrated electrons in normal and supercritical water from first principles. Very recently, *ab initio* molecular dynamics simulations of water (Frigato *et al.*, 2008) and water-ammonia (Pratihari *et al.*, 2011) clusters with an excess electron have been carried out with an aim to address the issue of interior versus exterior solvation of the unbound electron. These studies primarily focused on the cluster structures, electron binding motifs and equilibrium photoelectron spectra of the anionic aqueous clusters at finite temperature (Frigato

*et al.*, 2008; Pratihari *et al.*, 2011). The dynamics of the solvation process of an excess electron in water or other polar clusters is also an important and very interesting issue to be addressed.

Although the structures and energetics of the water cluster anions have been studied extensively, the dynamics of electron hydration process have not been explored much through theoretical investigations. On the experimental side, picosecond and femtosecond spectroscopic techniques (Rentzepis, 1968; Shank *et al.*, 1982) have provided a means whereby ultrafast dynamics of chemically interesting systems can be directly studied. The rapid hydration dynamics of elementary ions like electrons and protons have thus become accessible to experimental investigations. Lee *et al.* (1985) investigated electron hydration dynamics from the charge transfer state of 2-anilinonaphthalene in water/alcohol mixtures using picosecond spectroscopy. Early femtosecond transient absorption studies (Migus *et al.*, 1987; Long *et al.*, 1990) have resolved electron hydration dynamics in bulk water. These works have addressed the problem of resolving in time the absorptions by electron in liquid water starting from injection up to its full solvation. A prehydrated state of the excess electron has been proposed. A recent experimental study (Paik *et al.*, 2003; Paik *et al.*, 2004) have captured the ultrafast dynamics of the electron in the presolvated and hydrated states in water clusters and obtained, as a function of cluster size, the subsequent relaxation times by resolving the binding energy of the excess electron in real-time with femtosecond resolution. Electron solvation dynamics in various nonaqueous systems have also been looked at by different groups (Bragg *et al.*, 2010; Bragg *et al.*, 2008; Cavanagh *et al.*, 2007; Larsen and Schwartz, 2009; Lindner *et al.*, 2006; Frischkorn *et al.*, 2000; Lee *et al.*, 2008) in recent years. In the context of clusters, we note the work of Frischkorn *et al.* (2000), where femtosecond photoelectron spectroscopy was employed to monitor the dynamics associated with the excitation of the charge-transfer-to-solvent (CTTS) precursor states in  $\Gamma(\text{NH}_3)_{n=4-15}$  clusters. The experimental results implied that the weakly bound excess electron in the excited state undergoes partial solvation via solvent

rearrangement on a time scale of 0.5-2 ps, and this partially solvated state decays by electron emission on a 10-15 ps time scale. The extent of solvation and lifetimes increase gradually with cluster size. The solvation dynamics of electrons in ammonia clusters of varying size have been studied by applying both steady-state and time-resolved photoelectron spectroscopic methods (Lee *et al.*, 2008). It was found that  $(\text{NH}_3)_n^-$  exists with lowest value of  $n$  being 13. The real-time dynamics of  $(\text{NH}_3)_n^-$  with  $n=20$  to 60 have been investigated and compared with dynamics in  $(\text{H}_2\text{O})_n^-$ . For both the cases, the p-state of excess electron converts to the ground state in 150 fs, but the relaxation process of the solvent molecules is found to be different from each other. Very recently, the dynamics of electron solvation in molecular clusters like  $(\text{H}_2\text{O})_n^-$  and  $(\text{MeOH})_n^-$  and halide ion doped  $\text{I}^-(\text{H}_2\text{O})_n$  and  $\text{I}^-(\text{CH}_3\text{CN})_n$  have been investigated by applying time resolved photoelectron spectroscopy (Ehrler and Neumark, 2009). The internal conversion lifetimes for  $p \rightarrow s$  state were reported to be 50 and 157 fs for bulk water and methanol, respectively.

Regarding theoretical studies done till now, short-time solvation dynamics of the hydrated electron in liquid water have been studied by quantum-classical molecular dynamics simulations (Yang *et al.*, 2001; Nicolas *et al.*, 2003) and by using direct *ab initio* trajectory method (Tachikawa, 2003; Tachikawa, 2010). In the present work, we examine the electron hydration dynamics in the cluster of water hexamer  $(\text{H}_2\text{O})_6$  by means of *ab initio* molecular dynamics simulations. Such studies of size-selected clusters help in understanding the nature of solute-solvent interactions and also bridge the gap between isolated gas-phase and condensed-phase dynamics.

### Simulation Details

Two simulations have been carried out starting from two different structures 1(a) and 2(a) (Figs. 1 and 2) which were reported earlier as the stable cage and prism structures of the neutral water hexamer  $(\text{H}_2\text{O})_6$  (Maheshwary *et al.*, 2001). The *ab initio* molecular dynamics simulations are performed by using the Car-Parrinello method (Car and Parrinello, 1985; Marx and Hutter, 2000) and the CPMD code (Hutter *et al.*).

In these simulations, the interatomic forces are calculated ‘on the fly’ at each time step from an electronic structure calculation based on density functional theory (DFT) (Kohn and Sham, 1965). We have employed the so-called BLYP functional (Becke, 1988; Lee *et al.*, 1988) which was also employed in many earlier studies of Fig. 1.

Water, ammonia and alcohols in bulk and confined phases are well described by BLYP functional (Laasonen *et al.*, 1993; Sprik *et al.*, 1996; Mallik *et al.*, 2008; Diraison *et al.*, 1999; Silvestrelli and Parrinello, 1999; Liu and Tuckerman, 2001; Boese *et al.*, 2003). The clusters have been kept in the central region of a cubic box (box length = 15.0 Å) with enough empty space around the cluster in all directions. Plane wave basis within local spin density (LSD) functional theory with an energy cut-off of 80 Ry is used. The core electrons are treated via the Troullier-Martins norm conserving pseudopotentials (Troullier and Martins, 1993). A fictitious electron mass of 400 a.u. is assigned to orbitals and the coupled equations of motion describing the system dynamics are integrated by using a time step of 3 a.u. (0.0725 fs). In these systems, one free electron is introduced to the initial configuration and then simulations are carried out for 5 ps at 150 K in NVT ensemble for

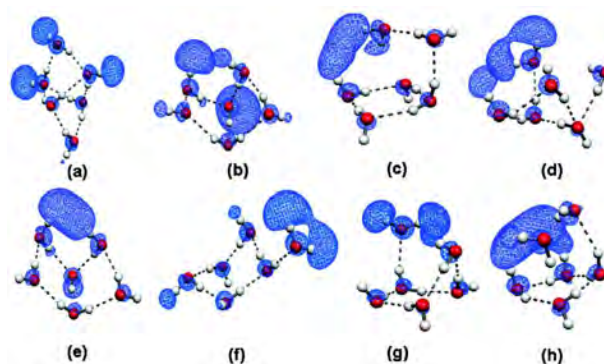


Fig. 1: Snapshots of different structures of  $(\text{H}_2\text{O})_6$  cluster during the electron hydration process as generated by *ab initio* molecular dynamics simulations. The density distribution of the excess electron is illustrated in blue mesh while the red and grey spheres represent the oxygen and hydrogen atoms, respectively. The simulations were started from optimized geometry of the cage conformer of  $(\text{H}_2\text{O})_6$ , shown in (a). The snapshots of (b)-(f) were taken at different time instants between 0-3000 fs along the simulation trajectory

evaluation of different structural properties and energetics as functions of time. We note that the temperature fluctuations upon addition of the excess electron were absorbed through Nose-Hoover thermostating (Nose, 1984; Hoover, 1985) of the cluster at 150 K during the simulations. The density distribution of the excess electron held by the singly occupied molecular orbital (SOMO) is calculated from the Wannier functions. The electron density of the SOMO is shown with an isosurface cutoff of 0.004-0.006  $e \text{ \AA}^{-3}$ .

After the atomic configurations are generated along the simulated trajectories, we have performed additional all-electron quantum chemical calculations of these clusters at regular time intervals using MP2 method to determine more accurate energies of different configurations that appeared during the real-time dynamics of the systems. These all-electron quantum chemical calculations at MP2 level are carried out using the 6-31(1+3+)g\* basis set (Pratihari and Chandra, 2007; Pratihari and Chandra, 2008) which contains one diffuse *sp* function on each heavier atom like O and three diffuse *s* functions on each H atom (Pratihari and Chandra, 2007; Pratihari and Chandra, 2008). We note in this context that functionals like BLYP have been reported to overestimate the true binding energies of anionic water clusters when compared with more accurate quantum chemical and experimental results (Pratihari and Chandra, 2007; Herbert and Gordon, 2005; Herbert and Gordon, 2006). This overestimation of the binding energies arises from the lack of a long range exchange repulsion that is not captured by the BLYP functional (Yagi *et al.*, 2008). However, the structures obtained through these DFT calculations were found to be very close to those produced by more involved calculations such as MP2 (Pratihari and Chandra, 2007; Herbert and Gordon, 2005; Herbert and Gordon, 2006). In the present work, the all-electron MP2 calculations were performed using the Gaussian03 program (Frisch *et al.*, 2003).

## Results and Discussion

From the finite temperature simulation trajectories, we could see the real-time evolution of the water cluster ( $\text{H}_2\text{O}$ )<sub>6</sub> when an electron is injected into it.

The structure as well as hydrogen bond network of the neutral water cluster changed with time. Mainly the water molecules rearrange among themselves to give a high dipole moment structure with time so as to hold the excess electron more effectively. Snapshots of representative structures and excess electron densities of the cluster along the simulation trajectories after the electron capture are shown in Figs. 1 and 2 for two different initial configurations. For the analysis of hydrogen bonding environments of water molecules, we have employed a geometric definition (Chandra, 2000; Balasubramanian *et al.*, 2002; Xu and Berne, 2001; Xu *et al.*, 2002; Paul and Patey, 2007; Pattanayak and Chowdhuri, 2011; Marti *et al.*, 2010; Jana and Bandyopadhyay, 2011) of hydrogen bonds. Specifically, the existence of a hydrogen bond between two water molecules is determined by using the simple geometric criterion that the HO distance should be less than 2.35 Å. For a given water, a donor hydrogen bond through one of its hydrogens is denoted by D and an acceptor hydrogen bond through its oxygen is denoted by A. For example, the hydrogen bonding coordination state of a water having one acceptor and one donor hydrogen bonds is represented by AD. Other hydrogen bonding states are also represented in a similar manner.

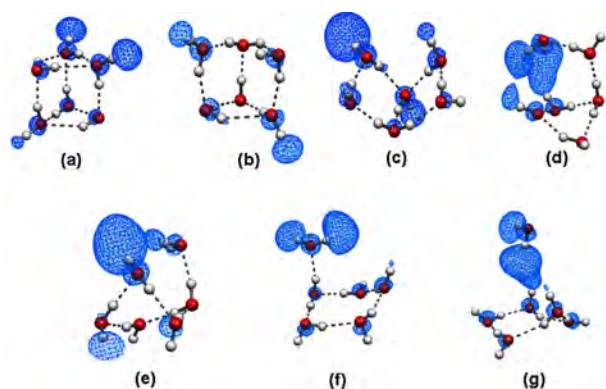
For the first case where electron was inserted into the cage structure of water hexamer, initially the electron was mostly distributed on the dangling H's of two AAD-type and AD-type water molecules (Fig. 1(a)). As defined above, here AAD means a hydrogen bonding state where a water is engaged in two acceptor and one donor hydrogen bonds. Since the local H-bonding environments of these two types of water molecules are different, the electron density on these water molecules differs from each other. With time, the number of dangling hydrogens increases quite fast and the excess electron gets captured in a more localized state. Different representative configurations taken from the simulation trajectory of the cluster are illustrated in Fig. 1(a-h) where the bound-electron charge distributions of the singly occupied molecular orbitals (SOMO) can be clearly visualized. The density of the excess electron is mainly found to be in the

vicinity of the dangling hydrogens of water molecules. The structure of 1(b) is quite similar to the open book like structure reported earlier as a stable structure of the anionic water hexamer. It has four water molecules in single acceptor-single donor (AD) sites, one in double acceptor-single donor (AAD) site and one in single acceptor-double donor (ADD) site. The excess electron density is mainly distributed over the free hydrogen atoms of two AD and one AAD-type water molecules. The structure of 1(c) has a four-membered ring consisting of three AD and one ADD-type water molecule which is connected to a two-membered water chain by one AD-type water molecule. One single acceptor (A) type water molecule is found to be present at the end of the chain. The excess electron density is mainly localized on the dangling hydrogens of the A-type water molecule. The structure of 1(d) has two AD, one ADD and one AAD-type water molecule in a four-membered ring, with ADD and AAD-type water monomers being hydrogen-bonded to A and D-type water molecules, respectively. The free electron is being held by free hydrogens of one A and one AD-type water monomers. The structure of 1(e) is very much similar to 1(b). It is also an open book like structure, but it contains four AD-type, one double donor (DD) type and one double acceptor (AA) type water molecules, and here the excess electron density is more localized over the free hydrogens of AD-type and AA-type water molecules. 1(f) has a puckered five-membered ring structure consisting of four water monomers in AD sites and one in ADD site which is hydrogen bonded to the A-type water molecule on its top. Here the excess electron density is mainly localized on the dangling hydrogens of the A-type water molecule. 1(g) has all the six water monomers in the same H-bonding sites as in 1(f). Here the five-membered ring becomes more twisted towards the A-type water molecule to better bind the free electron. In the structure of 1(h), the four-membered ring contains three AD and one ADD-type water monomers, one A-type water molecule being H-bonded to the ADD-type water monomer and one free (NIL, which means having neither an acceptor nor a donor hydrogen bond) water molecule. The excess electron is mainly captured by the dangling hydrogens of A, NIL and

AD-type water molecules.

Like this, in the second case where the excess electron has been inserted into the prism like structure of water hexamer (2a), structural changes have occurred and the free electron became more localized with the progress of time. Different representative configurations taken from this simulation trajectory of the cluster are illustrated in Fig. 2(a-g). The initial prism like configuration of 2(a) has three AAD and three ADD-type water molecules.

Initially the excess electron is in a very diffuse state and mostly distributed on the dangling hydrogens of AAD-type water molecules. Here also, with progress of time, the excess electron disrupts the hydrogen bonded structure of the neutral cluster and the water molecules reorient themselves to bind the free electron in a more effective way. The structure of 2(b) consists of two AAD, two ADD and two AD-type water molecules. The free electron is still in a diffuse state and distributed on the free hydrogens of AAD and AD-type water molecules. 2(c) is the open book like structure. It has four AD-type, one AAD and one ADD-type water molecules. The free hydrogens of AD and AAD-type water molecules hold the excess electron in this structure. 2(d) has one four-membered ring of three AD and one ADD water molecule which is bound to the two-membered chain of one AD and one A-type water molecules on top of it. The excess electron is primarily captured by the dangling hydrogens of A and one AD-type water molecules. The structure of 2(e) consists of a non-planer five-membered ring of four AD and one ADD-type water molecules with one A-type molecule H-bonded to the ADD-type water molecule. The excess electron is captured by the free hydrogens of A and AD-type water molecules. 2(f) is structurally very similar to 2(e), although in 2(f) the five-membered ring has become almost planer and the free electron is mostly bound to the free hydrogens of A-type water molecule. The structure of 2(g) consists of a five-membered ring of five AD type water molecules with a free (NIL) water molecule on top of it. The excess electron density is mainly captured by the free hydrogens of the NIL-type and one AD-type water molecule.

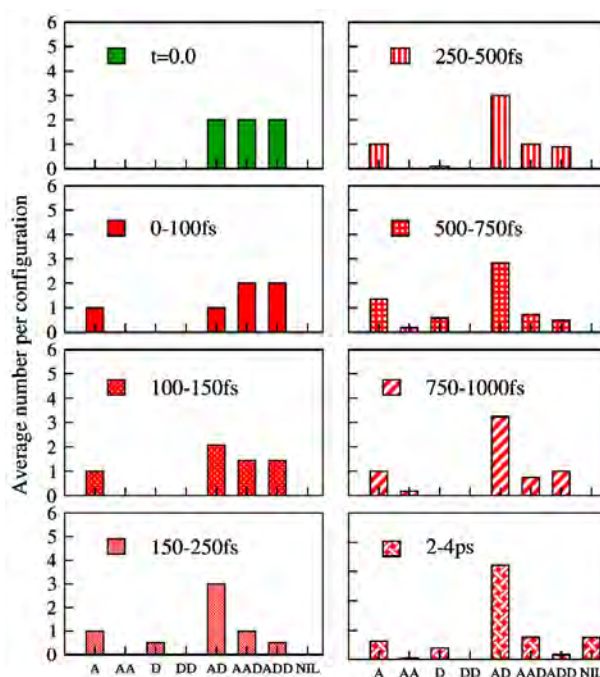


**Fig. 2:** Snapshots of different structures of  $(\text{H}_2\text{O})_6$  cluster during the electron hydration process as generated by *ab initio* molecular dynamics simulations starting from optimized geometry of the prism conformer (a). As in Fig.1, the density distribution of the excess electron is illustrated in blue while the red and grey spheres represent the oxygen and hydrogen atoms, respectively. The snapshots of (b)-(f) were taken at different time instants between 0-3000 fs along the simulation trajectory

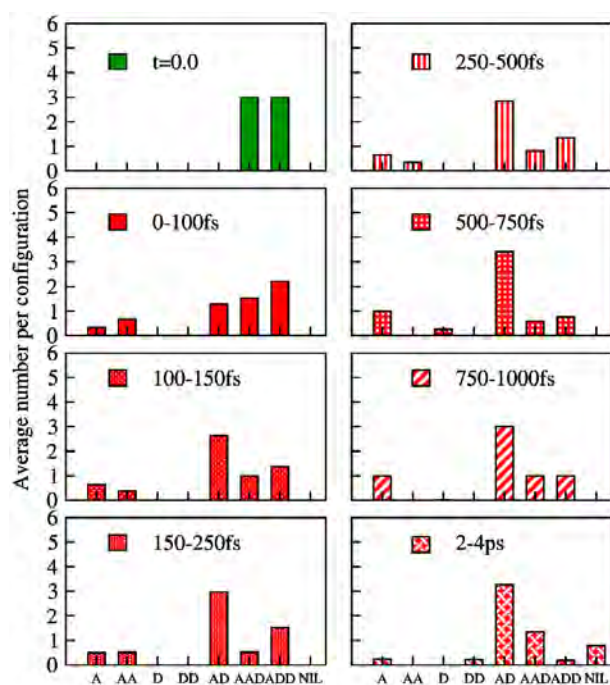
Comparing both the cases, we can say that the attachment of an excess electron to water hexamer provides sufficient interaction effects to alter the H-bonded structures of the neutral clusters. Although the simulations were started from two different initial configurations, evolution with time leads to many structurally similar conformers. At the initial stage, the injected electron is found to be very diffuse but with time it becomes more and more localized. Addition of the excess electron to the neutral structures of water hexamer leads to an increase in the number of free dangling hydrogens that are mainly engaged in capturing the excess electron density. In some conformers, the excess electron is bound to the cluster surface and in few others the electron is in partially interior like states with  $\text{OH}\{\text{e}\}\text{HO}$  type interactions.

The evolutions of the hydrogen-bonding environment of the water molecules with time are illustrated in Figs. 3 and 4 for the two simulations mentioned above. The results are presented in terms of distributions averaged over time windows of finite width as described in these figures. From Fig. 3, it is seen that although initially the cage structure contained 33% AD, 33% AAD and 33% ADD-type water molecules, once the trapping of the excess

electron occurs in the system, the population of A-type water molecules starts building up to an extent of 16.6% and remains the same up to 1000 fs. Towards the end of the simulation trajectory it decreases to 10%. Population of AD-type water molecules diminishes initially to 16.6% till 100 fs, but again increases and goes up to 50% and remains the same for the rest of the trajectory. After 100 fs, the population of both AAD and ADD-type water molecules decreases to 25% till 150 fs. After that, the population of AAD-type water molecules further decreases to 16.6% till 500 fs and then finally stays at 13.3% for the rest of the simulation run. The population of ADD-type water molecules shows a fluctuating behaviour. It decreases to 8.3% till 750 fs with a jump to 15% for a short period only. Again at 1000 fs, the population of ADD-type water molecules rises to 16.6%, but finally at the end of the simulation trajectory it remains only at 3.3%. Some D-type water molecules appear from 150 fs onward, initially with a population of 8.3%, but vary with time and at the



**Fig. 3:** The average population of water molecules in different hydrogen bonding environments during electron hydration process along the simulation trajectory. The time intervals over which averages are performed are shown in each figure. The meanings of A, AA etc are described in the text. The simulations were started from the optimized geometry of cage conformer of  $(\text{H}_2\text{O})_6$  shown in 1(a)



**Fig. 4:** The average population of water molecules in different hydrogen bonding environments during electron hydration process along the simulation trajectory. The time intervals over which averages are performed are shown in each figure. The simulations were started from the optimized geometry of prism conformer of  $(\text{H}_2\text{O})_6$  shown in 2(a)

end of the simulation trajectory it remains only at 6.6%. Small amounts of AA-type water molecules also appear from time to time with a population variation from 3.3% to 0.1%. NIL type water molecules appear towards the end (2-4 ps) of the simulation trajectory with a population of about 13%.

In the second case where the simulations started from a prism structure (Fig. 2(a)), initially both AAD and ADD-type water molecules had 50% populations. On capturing the excess electron, the H-bonded structure of the cluster changes and it is clearly reflected on the time averaged population of water molecules with different H-bonding environments shown in Fig. 4. Similar to the previous case, here also the populations of A and AA-type water molecules start building up and vary to different extents at different time intervals. At first, the population of A-type water molecules is found to be 5% till 100 fs, then it jumps up to 10% by 150 fs,

decreases to 8.16% for next 100 fs, but again increases to 11% at 500 fs and to 16.6% at 1000 fs. Towards the end of the simulations, it again diminishes to only 3.3%. Although 11.6% population of AA-type water molecules appears in the first 100 fs of simulation trajectory, it decreases gradually to 8.5% by 250 fs, 5.8% by 500 fs, and after that it becomes essentially zero for the rest of the simulation trajectory. Population of AD-type water molecules also starts building up to an extent of 16.6% initially, but keeps on increasing until it reaches 50% after 100 fs, and remains almost the same for the rest of the trajectory. From the very beginning, the populations of both AAD and ADD-type water molecules show monotonous decrease along the simulation trajectory. After 100 fs, the population of AAD-type water molecules becomes 25%, it then diminishes to 8.3% for the next 100 fs, again increases to 16.6% after 750 fs and remains almost the same for the rest of the simulation trajectory. On the other hand, the population of ADD-type water molecules decreases to 23.2% after 100 fs of simulation run, again jumps up to 25% by 250 fs, but starts diminishing gradually after that. Towards the end (2-4 ps) of the simulation trajectory, only 3.3% population of ADD-type water molecules exists. Small amounts of D and DD-type water molecules appeared from time to time for very short time spans. NIL-type water molecules appear towards the end (2-4 ps) of the simulation trajectory, with a population of 13.2%. We note that the distributions of water molecules in different hydrogen bonding environments as found from the later parts of the simulation trajectories are very similar for the two cases even though their starting configurations were very different.

In addition to the time evolution of the structure, we have also looked at the energies and the results are shown in Figs. 5(a) and 5(b) as functions of time for the two cases studied here. As described earlier, these energies are obtained through all-electron MP2 calculations and the results shown in these figures are the deviations from initial energies. After the capture of excess electron to water hexamer, the energy of the system goes down to  $-4.5$  and  $-5.23$  kcal/mol from the initial values for the two different starting configurations of the neutral water hexamer,

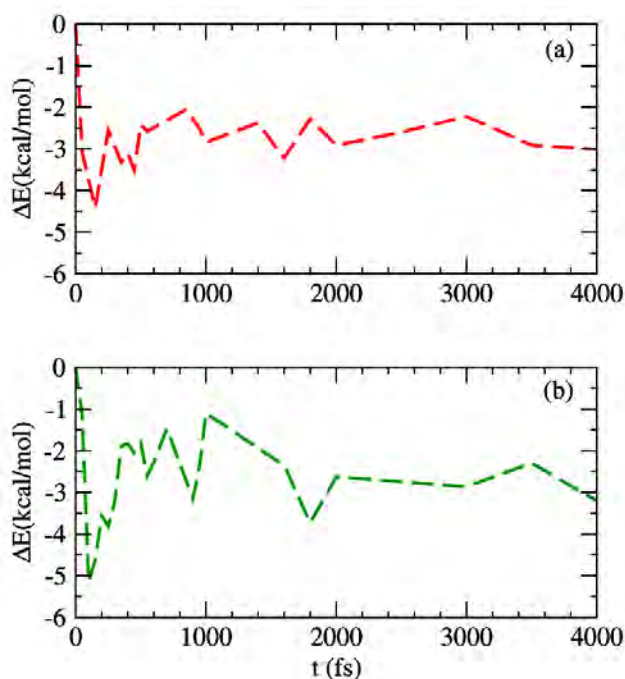


Fig. 5: The time evolution of the relative energies ( $E$ ) of  $(\text{H}_2\text{O})_6$  cluster during the electron hydration process. The energies are calculated through all-electron MP2 calculations on structures produced by *ab initio* molecular dynamics simulations at regular time intervals. Also, the energies are expressed relative to the initial energies. The results of (a) and (b) correspond to cases where the excess electron was injected to the optimized cage (1a) and prism (2a) structures of the neutral cluster, respectively

e.g. cage and prism structures, respectively. This is due to fast structural relaxation of water molecules at short times on capture of the excess electron. These early changes in the energy profile occur within 100-200 fs for both the cases. After that, the energies of the systems change slowly towards the respective long-time values due to slower evolution of the systems through different conformational structures.

## Conclusions

In the present work, we have investigated the hydration dynamics of an excess electron in water hexamer cluster at a finite temperature by means of *ab initio* molecular dynamics simulations. The energies and forces during the simulations are calculated within density functional theory. In

addition, the second-order perturbative MP2 calculations with appropriate basis set containing extra diffuse functions are also performed on simulated structures along the trajectory in order to obtain more accurate results of the energetics. The primary focus has been to study the structural and energetics changes that occur during the process of electron localization and also the role of hydrogen bonds in localization of the unbound electron. The present calculations are done with two different initial configurations of the hexamer cluster.

It is found that the hydrogen bonded structures of neutral water hexamer cluster change drastically upon the insertion of the excess electron. The cluster evolves with time through many different structures of different electron binding motifs and hydrogen bonding configurations during the finite temperature simulations. The spatial distribution of the excess electron density shows where and how the excess electron is primarily localized during the hydration process. Both surface bound states and partially interior states have been found for the excess electron in the course of both the simulations. After the electron capture, the relative energy of the system first goes down very fast because of the fast structural relaxation and then the energies of the systems are found to change slowly towards the respective long-time values due to slower evolution of the systems through different conformational structures. The changes of the average population of water molecules in different hydrogen bonding environments during electron hydration process are also investigated. Substantial changes in the hydrogen bonding distributions are noticed during the hydration process. Generally, the hydrogen bonding changes are found to be driven towards formation of more water molecules with dangling hydrogens, which lead to more effective binding of the excess electron. Finally, we note that in the present study we have dealt with electron hydration dynamics in a pure water cluster of six water molecules. It would be interesting to look at similar dynamical processes in clusters of larger sizes and also in other polar clusters.



## Acknowledgment

We gratefully acknowledge the financial support from Department of Science and Technology (DST), Government of India.

## References

- Ayotte P and Johnson MA (1997) Electronic absorption spectra of size-selected hydrated electron clusters:  $(\text{H}_2\text{O})_n^-$ ,  $n=6-50$  *J Chem Phys* **106** 811
- Balasubramanian S, Pal S and Bagchi B (2002) Hydrogen-bond dynamics near a Micellar surface: origin of the universal slow relaxation at complex aqueous interfaces *Phys Rev Lett* **89** 115505
- Becke A D (1988) Density-functional exchange-energy approximation with correct asymptotic behavior *Phys Rev A* **38** 3098
- Boero M, Parrinello M, Erakura K, Ikeshoji T and Liew C C (2003) First-principles molecular-dynamics simulations of a hydrated electron in normal and supercritical water *Phys Rev Lett* **90** 226403
- Boese A D, Chandra A, Martin J M L and Marx D (2003) From ab initio quantum chemistry to molecular dynamics: The delicate case of hydrogen bonding in ammonia *J Chem Phys* **119** 5965
- Bragg A E, Cavanagh M C and Schwartz B J (2008) Linear response breakdown in solvation dynamics induced by atomic electron-transfer reactions *Science* **321** 1817
- Bragg A E, Glover W J and Schwartz B J (2010) Watching the solvation of atoms in liquids one solvent molecule at a time *Phys Rev Lett* **104** 233005
- Bragg A E, Verlet J R R, Kamrath A, Cheshnovsky O and Neumark D M (2004) Hydrated electron dynamics: From clusters to bulk *Science* **306** 669
- Car R and Parrinello M (1985) Unified approach for molecular dynamics and density-functional theory *Phys Rev Lett* **55** 2471
- Cavanagh M C, Larsen R E and Schwartz B J (2007) Watching Na atoms solvate into  $(\text{Na}^+, \text{e}^-)$  contact pairs: untangling the ultrafast charge-transfer-to-solvent dynamics of  $\text{Na}^-$  in tetrahydrofuran (THF) *J Phys Chem A* **111** 5144
- Chandra A (2000) Effects of ion atmosphere on hydrogen-bond dynamics in aqueous electrolyte solutions *Phys Rev Lett* **85** 768
- Coe J V, Arnold S T, Eaton J E, Lee G H and Bowen K H (2006) Photoelectron spectra of hydrated electron clusters: Fitting line shapes and grouping isomers *J Chem Phys* **125** 014315
- Coe J V, Lee G H, Eatson J G, Arnold S T, Sarkas W H, Bowen K H, Ludewigt C, Heberland H and Wornshop D R (1990) Photoelectron spectroscopy of hydrated electron cluster anions,  $(\text{H}_2\text{O})_n^-$ ,  $n=269$  *J Chem Phys* **92** 3980
- Diraison M, Martyna G J and Tuckerman M E (1999) Simulation studies of liquid ammonia by classical ab initio, classical, and path-integral molecular dynamics *J Chem Phys* **111** 1096
- Ehrler O T and Neumark D M (2009) Dynamics of Electron Solvation in Molecular Clusters *Acc Chem Res* **42** 769
- Frigato T, Vondele J V, Schmidt B, Schütte C and Jungwirth P (2008) Ab Initio molecular dynamics simulation of a medium-sized water cluster anion: From an Interior to a Surface-Located Excess Electron via a Delocalized State *J Phys Chem A* **112** 6125
- Frisch M J, Trucks G W, Schlegel H B *et al.* (2003) GAUSSIAN **03** (Gaussian Inc. Pittsburgh, PA)
- Frischkorn C, Zanni M T, Davis A V and Neumark D M (2000) Electron solvation dynamics in  $\text{I}(\text{NH}_3)_n$  clusters *Faraday Discuss* **115** 49
- Haberland H, Ludewigt C, Schindler H G and Worsnop D R (1984) Experimental observation of the negatively charged water dimer and other small  $(\text{H}_2\text{O})_n$  clusters *J Chem Phys* **81** 3742
- Hammer N I, Roscioli J R and Johnson MA (2005) Identification of two distinct electron binding motifs in the anionic water clusters: A vibrational spectroscopic study of the  $(\text{H}_2\text{O})_6^-$  isomers *J Phys Chem A* **109** 7896
- Hammer N I, Shin J W, Headrick J M, Diken E G, Roscioli J R, Weddle G H and Johnson MA (2004) How do small water clusters bind an excess electron? *Science* **306** 675
- Hart E J and Boag J W (1962) Absorption spectrum of the hydrated electron in water and in aqueous solutions *J Am Chem Soc* **84** 4090
- Herbert J M and Head-Gordon M (2005) Calculation of electron detachment energies for water cluster anions: An appraisal of electronic structure methods, with application to  $(\text{H}_2\text{O})_{20}^-$  and  $(\text{H}_2\text{O})_{24}^-$  *J Phys Chem A* **109** 5217
- Herbert J M and Head-Gordon M (2006) Accuracy and limitations of second-order many-body perturbation theory for predicting vertical detachment energies of solvated-electron clusters *Phys Chem Chem Phys* **8** 68
- Herbert J M and Head-Gordon M (2006) First-principles, quantum-mechanical simulations of electron solvation by a water cluster *PNAS* **103** 14282
- Hoover W G (1985) Canonical dynamics: Equilibrium phase-space distributions *Phys Rev A* **31** 1695
- CPMD Program, Hutter J, Alavi A, Deutsch T, Bernasconi M, Goedecker St, Marx D, Tuckerman M and Parrinello M

- MPI für Festkörperforschung and IBM Zurich Research Laboratory
- Jana M and Bandyopadhyay S (2011) Kinetics of hydrogen bonds in aqueous solutions of cyclodextrin and its methyl-substituted forms *J Chem Phys* **134** 025103
- Jordan K D (2004) A fresh look at electron hydration *Science* **306** 618
- Keszler E, Murphrey H T and Rosky P J (1995) Electron hydration dynamics: simulation results compared to pump and probe experiments *J Phys Chem* **99** 22
- Kim J, Park J M, Oh K, Lee J Y, Lee S and Kim K S (1997) Structure, vertical electron-detachment energy, and OH stretching frequencies of  $e^-(H_2O)_n$  *J Chem Phys* **106** 10207
- Kohn W and Sham L J (1965) Self-consistent equations including exchange and correlation effects *Phys Rev* **140** A1133
- Laasonen K, Sprik M, Parrinello M and Car R (1993) Ab initio liquid water *J Chem Phys* **99** 9080
- Larsen M C and Schwartz B J, Searching for solvent cavities via electron photodetachment: The ultrafast charge-transfer-to-solvent dynamics of sodide in a series of ether solvents
- Lee S, Kim J, Lee S L and Kim K S (1997) Novel structures for the excess electron state of the water hexamer and the interaction forces governing the structures *Phys Rev Lett* **79** 2038
- Lee I-R, Lee W and Zewail A H (2008) Dynamics of electrons in ammonia cages: The discovery system of solvation *Chem Phys Chem* **9** 83
- Lee J and Robinson G W (1985) Electron hydration dynamics using the 2-anilino-naphthalene precursor *J Am Chem Soc* **107** 6153
- Lee H M, Suh S B, Tarakeshwar P and Kim K S (2005) Origin of the magic numbers of water clusters with an excess electron *J Chem Phys* **122** 044309
- Lee C, Yang W and Parr R G (1988) Development of the Colle-Salvetti correlation-energy formula into a functional of the electron density *Phys Rev B* **37** 785
- Lehr L, Zanni M T, Frischkorn C, Weinkauff R and Neumark D M (1999) Electron solvation in finite systems: Femtosecond dynamics of Iodide-(Water) $_n$  anion clusters *Science* **284** 635
- Lindner J, Unterreiner A N and Vöhringer P (2006) Femtosecond relaxation dynamics of solvated electrons in liquid ammonia *Chem Phys Chem* **7** 363
- Liu Y and Tuckerman M E (2001) Protonic defects in hydrogen bonded liquids: structure and dynamics in ammonia and comparison with water *J Phys Chem B* **105** 6598
- Long F H, Lu H and Eisenthal K B (1990) Femtosecond studies of the presolvated electron: An excited state of the solvated electron? *Phys Rev Lett* **64** 1469
- Maheshwary S, Patel N, Sathyamurthy N, Kulkarni A D and Gadre S R (2001) Structure and stability of water clusters ( $H_2O$ ),  $n=8-20$ : An ab initio investigation *J Phys Chem A* **105** 10525
- Mallik B S, Semparathi A and Chandra A (2008) Vibrational spectral diffusion and hydrogen bond dynamics in heavy water from first principles *J Phys Chem A* **112** 5104
- Marti J, Sala J and Guardia E (2010) Molecular dynamics simulations of water confined in graphene nanochannels: From ambient to supercritical environments *J Mol Liq* **153** 72
- Marx D and Hutter J (2000) Ab Initio molecular dynamics: Theory and implementation in modern methods and algorithms of quantum chemistry, edited by J Grotendorst, NIC, FZ Jülich
- Migus A, Gauduel Y, Martin J L and Antonetti (1987) Excess electrons in liquid water: First evidence of a prehydrated state with femtosecond lifetime *Phys Rev Lett* **58** 1559
- Nicolas C, Boutin A, Levy B and Borgis D (2003) Molecular simulation of a hydrated electron at different thermodynamic state points *J Chem Phys* **118** 9689
- Nose S (1984) A unified formulation of the constant temperature molecular dynamics methods *J Chem Phys* **81** 511
- Paik D H, Lee I R D, Yang S, Baskin J S and Zewail A H (2004) Electrons in Finite-Sized Water Cavities: Hydration Dynamics Observed in Real Time *Science* **306** 672
- Paik D H, Kim N J and Zewail A H (2003) Femtosecond dynamics of solvated oxygen anions. I. Bifurcated electron transfer dynamics probed by photoelectron spectroscopy *J Chem Phys* **118** 6923
- Pattanayak S K and Chowdhuri S (2011) Effect of water on solvation structure and dynamics of ions in the peptide bond environment: Importance of Hydrogen bonding and dynamics of the solvents *J Phys Chem B* **115** 13241
- Paul S and Patey G N (2007) Structure and interaction in aqueous urea Trimethylamine-N-oxide solutions *J Am Chem Soc* **129** 4476
- Pratihari S and Chandra A (2007) Electron solvation in water-ammonia mixed clusters: Structure, energetics and the nature of localization states of the excess electron *J Chem Phys* **126** 234510
- Pratihari S and Chandra A (2008) Microscopic solvation of a lithium atom in water-ammonia mixed cluster: Solvent coordination and electron localization in presence of counterion *J Chem Phys* **129** 024511

- Pratihari S and Chandra A (2010) Excess electron and lithium atom solvation *J Phys Chem A* **114** 11869
- Pratihari S and Chandra A (2011) A first principles molecular dynamics study of excess *J Chem Phys* **134** 034302
- Rentzepis P M (1968) Lasers in Chemistry Photochem *Photobiol* **8** 579
- Senapati S (2007) How strongly can calcium ion influence the hydrogen-bond dynamics at complex aqueous interfaces? *J Chem Phys* **126** 204710
- Shank C V, Fork R L and Yen R T (1982) Moving from the Picosecond to the Femtosecond Time Regime, Picosecond Phenomena, III, edited by K B Eisenthal, R M Hochstrasser, W Kaiser and A Laubereau, Springer-Verlag, Berlin, p2, 1982.
- Silvestrelli P L and Parrinello M (1999) Water molecule dipole in the gas and in the liquid phase *Phys Rev Lett* **82** 3308
- Sommerfeld T, Gardner S D, Fusco A D and Jordan K D (2006) Low-lying isomers and finite temperature behavior of  $(\text{H}_2\text{O})_6$  *J Chem Phys* **125** 174301
- Sprink M, Hutter J and Parrinello M (1996) Ab initio molecular dynamics simulation of liquid water: Comparison of three gradient-corrected density functionals *J Chem Phys* **105** 1142
- Tachikawa H (2003) Electron capture dynamics of the water dimer: a direct ab initio dynamics study *Chem Phys Lett* **370** 188
- Tachikawa H (2006) Electron hydration dynamics in water clusters: A direct ab initio molecular dynamics approach *J Chem Phys* **125** 144307
- Tachikawa H (2010) Electron capture dynamics of a water molecule connected to a cyclic water trimer: A direct ab initio MD approach *J Phys Chem A* **114** 10309
- Turi L, Sheu W S and Rossky P J (2005) Characterization of excess electrons in water-cluster anions by quantum simulations *Science* **309** 914
- Turi L, Sheu W S and Rossky P J (2005) Response to comment on "Characterization of excess electrons in water-cluster anions by quantum simulations *Science* **310** 1769
- Troullier N and Martins J L (1991) Efficient pseudopotentials for plane-wave calculations *Phys Rev B* **43** 1993
- Verlet J R R, Bragg A E, Kammrath A, Cheshnovsky O and Neumark D M (2005) Observation of large water-cluster anions with surface-bound excess electrons *Science* **307** 93
- Verlet J R R, Bragg A E, Kammrath A, Cheshnovsky O and Neumark D M (2005) Comment on Characterization of excess electrons in water-cluster anions by quantum simulations *Science* **310** 1769
- Vysotskiy V P, Cederbaum L S, Sommerfeld T, Voora V K and Jordan K D (2012) Benchmark calculations of the energies of binding for binding excess electrons to water clusters, *J Chem Theo Comput* **8** 893
- Voora V K, Ding J, Sommerfeld T and Jordan K D (2013) A self-consistent polarization potential model for describing excess electrons interacting with water clusters, *J Phys chem B* **117** 4365
- Wang F and Jordan K D (2003) Parallel-tempering Monte Carlo simulations of the finite temperature behavior of  $(\text{H}_2\text{O})_6$  *J Chem Phys* **119** 11645
- Xu H and Berne B J (2001) Hydrogen-bond kinetics in the solvation shell of a polypeptide *J Phys Chem B* **105** 11929
- Xu H, Stern H A and Berne B J (2002) Can water polarizability be ignored in hydrogen bond kinetics? *J Phys Chem B* **106** 2054
- Yagi K, Okano Y, Sato T, Kawashima Y, Tsuneda T and Hirao K (2008) Water cluster anions studied by the long-range corrected density functional theory *J Phys Chem A* **112** 9845
- Yang C Y, Wong K F, Staff M S and Rossky P J (2001) Instantaneous normal mode analysis of hydrated electron solvation dynamics *J Chem Phys* **114** 3598.

