

Dynamics of Electron Localization in Warm vs. Cold Water Clusters

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The process of electron localization on a cluster of 32 water molecules at 20, 50, and 300 K is unraveled using ab initio molecular dynamics simulations. In warm, liquid clusters, the excess electron relaxes from an initial diffuse and weakly bound structure to an equilibrated, strongly bound species within 1.5 ps. In contrast, on cold, glassy clusters the relaxation processes is not completed and the electron becomes trapped in a metastable surface state with an intermediate binding energy. These results question the validity of extrapolations of the properties of solvated electrons from cold clusters of increasing size to the liquid bulk.

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Interaction of ionizing radiation with water leads to formation of a quasi-free electron and a partially delocalized cationic hole. Both of these species undergo ultrafast reactive dynamics. H_2O^+ reacts on a 100 fs timescale with a neighboring water molecule forming H_3O^+ and OH [1, 2]. The latter is a key radical involved in indirect radiation damage of DNA. In this process, the quasi-free electron also plays a role [1, 3], however, the aqueous environment causes its localization and formation of a solvated electron on a picosecond timescale [4, 5]. Depending on water purity, solvated electrons survive for up to microseconds or milliseconds before reacting with salt ions, dissolved oxygen molecules, OH radicals, protons, or water molecules themselves [1, 6–10]. These are fundamental reactions in radiation chemistry, which are important, among others, in nuclear waste treatment [1].

A very detailed molecular insight into the structure of an electron in aqueous environment has been gained from cluster studies. Both experiments and calculations show that the character of this species changes from a weakly (dipole) bound electron in small water clusters to a more bulk-like solvated electron in larger clusters [11–19]. This behavior has been utilized for extrapolating the binding energy and other properties of the electron from clusters of increasing size into the aqueous bulk [12, 20]. These extrapolations are, however, not free of contradictions, which concern the occurrence of several isomers and electron binding motifs, as well as surface vs interior location of the electron in water clusters of different sizes [12, 14, 19]. A crucial issue, which has gained more attention recently [15, 21] and will be addressed in this study, is the fact that extrapolations to liquid water are done using clusters at very low (typically below 100 K) temperatures. Under these conditions, clusters with tens to hundreds of water molecules are unlikely to be liquid, but rather resemble amorphous solids [22]. In such a glassy state, translational motion is dramatically slowed

down. Therefore, kinetically trapped electron-cluster geometries which depend on preparation conditions, rather than fully relaxed structures, can prevail in the experiment [12, 15]. Measurements and simulations show that the observed state sensitively depends on the history of the cluster both before and after electron attachment [15, 21].

Here, we address the question of electron localization on medium-size water clusters at warm vs cold conditions using ab initio molecular dynamics (AIMD) simulations. Initially, an electron is vertically (i.e., without any geometry change) attached to a neutral cluster comprising 32 water molecules and its subsequent dynamics is followed at cluster temperatures ranging from 20 to 300 K. We show below that the resulting localization process dramatically depends on temperature, which puts a question mark over extrapolations from cold clusters to the liquid bulk.

The computational methodology has been described in detail in our recent paper on electron-proton recombination in water [9]. Briefly, we perform AIMD using the BLYP density functional [23, 24] with a dispersion correction [25]. Pseudopotentials [26] replace the oxygen core electrons and the hybrid GPW scheme is used for efficient evaluation of the energies and forces [27]. The self-interaction correction is employed for the singly-occupied orbital in a restricted open-shell Kohn-Sham framework [28]. The Kohn-Sham orbitals are represented using a TZV2P basis set [29] augmented with diffuse Gaussian functions placed on a regular grid spanning the whole simulation box. Open boundary conditions together with a suitable electrostatic solver [30] are used, as is appropriate for a cluster system. The vertical detachment energy (VDE) is calculated directly from the energy difference between the anionic and the neutral system at the same geometry. The excess electron is plotted as the unpaired spin density of the system [31]. Comparison to RIMP2

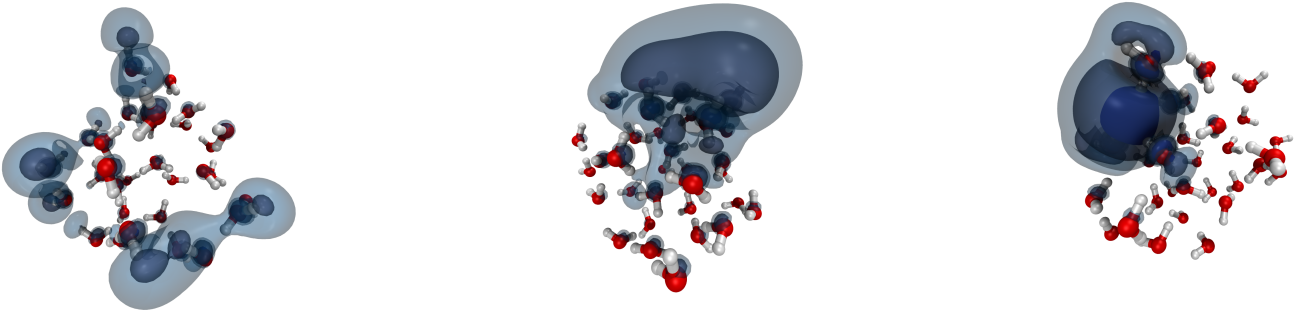


FIG. 1: Snapshots from a representative trajectory at times (a) 0 fs, (b) 950 fs, and (c) 4250 fs after the vertical attachment of the excess electron to a cluster of 32 water molecules at 300 K.

84 calculations suggests that the present DFT calculations₁₂₅
 85 only slightly overestimate the VDE of the excess electron₁₂₆
 86 [31].₁₂₇

87 All the localization trajectories were started from the₁₂₈
 88 geometry of a neutral water cluster. For comparison,₁₂₉
 89 equilibrium trajectories were also performed, started₁₃₀
 90 with a pre-existing polarized cavity [31]. Initial geome-₁₃₁
 91 tries for localization at low temperatures were obtained₁₃₂
 92 by energy minimization, while the 300 K simulations used₁₃₃
 93 snapshots from dynamics at 300 K as their initial condi-₁₃₄
 94 tion. All production simulations are performed at con-₁₃₅
 95 stant total energy using the CP2K package [32].₁₃₆

96 We simulated six localization trajectories with an elec-₁₃₇
 97 tron added to a cluster of 32 water molecules equilibrated₁₃₈
 98 at 300 K. Figure 1 shows three snapshots from a repre-₁₃₉
 99 sentative trajectory, taken at 0, 950, and 4250 fs. Upon₁₄₀
 100 attachment to the neutral cluster, the excess electron is₁₄₁
 101 initially delocalized over the outer surface of the water₁₄₂
 102 cluster (Fig. 1(a)), with a radius of gyration of about₁₄₃
 103 6 Å. However, the excess electron immediately starts₁₄₄
 104 to shrink, polarizing neighboring water molecules. This₁₄₅
 105 localization process can be roughly separated into two₁₄₆
 106 steps. First, water molecules locally reorient forming the₁₄₇
 107 initial solvation structure within less than a picosecond₁₄₈
 108 (Fig. 1(b)). The structure then becomes even more fa-₁₄₉
 109 vorable for electron binding by translational and further₁₅₀
 110 rotational motion of water molecules. This process cre-₁₅₁
 111 ates a polarized cavity and moves the electron deeper₁₅₂
 112 into the cluster. Nevertheless, for most of the simulation₁₅₃
 113 time the electron remains solvated asymmetrically with₁₅₄
 114 respect to the center of the cluster, i.e., close to the sur-₁₅₅
 115 face (Fig. 1(c)). In less than 1.5 ps the electron thus₁₅₆
 116 acquires its final size of about 2.75 Å and becomes in-₁₅₇
 117 distinguishable from an equilibrated solvated electron in₁₅₈
 118 a 32 water cluster, as investigated in our previous study₁₅₉
 119 [31].₁₆₀

120 The main physical characteristics, i.e., radius of gyra-₁₆₁
 121 tion, VDE, and average distance from the cluster center₁₆₂
 122 of mass (COM) [31] of the excess electron along the tra-₁₆₃
 123 jectory depicted in Fig. 1 are plotted in Fig. 2. The top₁₆₄
 124 panel shows the process of shrinking of the excess electron₁₆₅

from its initial size of 6 Å to about 5 Å in less than 1 ps,
 and then to the final value of ~ 2.75 Å in another 0.5 ps.
 The middle panel depicts the VDE, the negative value of
 which strongly correlates with the radius of gyration of
 the excess electron, as observed also for the equilibrated
 solvated electron [31]. The initial delocalized electron is
 bound to the neutral water cluster by less than 1 eV,
 however, within 1.5 ps its vertical binding energy triples,
 fluctuating around its final value of about 3 eV. The last
 panel of Fig. 2 shows the time evolution of the average
 distance of the excess electron from the COM of the water
 cluster [31]. This distance decreases from its initial
 value of 6 Å to about 5 Å. The excess electron is thus
 brought closer to the COM of the cluster by the localiza-
 tion process. Nevertheless, it remains to be situated pre-
 dominantly in the interfacial region, in agreement with
 previous studies of an equilibrium solvated electron in
 a cluster of the same size [19, 31]. Finally, note that
 there is little correlation between the position of the ex-
 cess electron within the cluster and its vertical binding
 energy [31].

Time evolution of the radius of gyration of the excess
 electron [9] for the six simulated trajectories at 300 K is
 depicted in Fig. 3. Due to different geometries of the neu-
 tral clusters at the moment of electron attachment, the
 localization process is unique for each trajectory. Nev-
 ertheless, the feature common to all of them is that the
 excess electron shrinks from ~ 6 Å to roughly 2.75 Å
 in less than 1.5 ps. For comparison, the red plot at the
 left hand side of Fig. 3 shows the distribution of radii of
 gyration of electrons attached to neutral water clusters
 at 200 different geometries, while the green plot at the
 right hand side corresponds to radii of gyration obtained
 from 40 ps of simulation time of an equilibrium solvated
 electron. Note that the initial and final distributions of
 radii of gyration of the localization trajectories match the
 former and the latter plot, despite the fact that the final
 distribution is taken from entirely independent simula-
 tions.

Let us now move from clusters at ambient temperature
 to very cold ones. Figure 4 shows the time evolution of

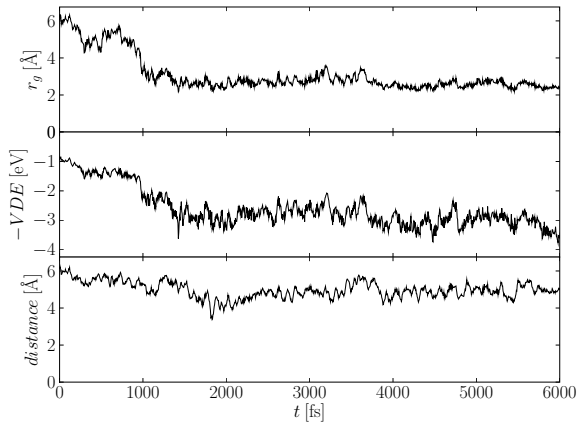


FIG. 2: Time evolution of the radius of gyration (top panel), vertical detachment energy (middle panel), and average distance of the excess electron from the cluster center of mass (bottom panel) for a representative localization trajectory at 300 K.

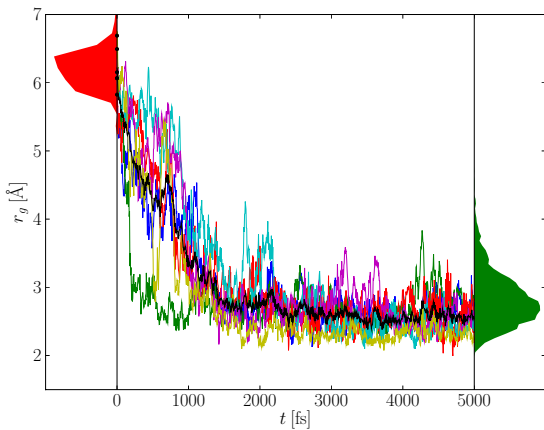


FIG. 3: Time evolution of the radius of gyration of the excess electron in the six localization trajectories at 300 K. Black curve shows the average of these trajectories. Black dots mark the values at $t=0$ fs. Left, red: distribution of radii of gyration of electrons attached to neutral water clusters. Right, green: distribution of radii of gyration of the solvated electron in equilibrium trajectories.

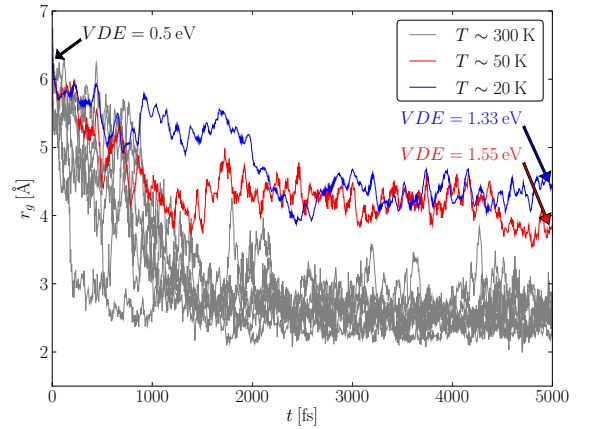


FIG. 4: Time evolution of the radius of gyration of the excess electron in localization trajectories at 20 and 50 K. Arrows with labels show the VDE for both trajectories at the beginning (same geometry for both) and at $t = 5$ ps. Data for 300 K are shown for comparison (gray).

166 the radius of gyration of the excess electron for clusters
 167 with mean temperature of 20 or 50 K, compared to those
 168 at 300 K. We see that upon moving from warm liquid
 169 to cold solid clusters the situation changes dramatically.
 170 The initial (sub-picosecond) electron localization phase
 171 is similar for all temperatures, except that the vertical
 172 electron affinity at $t = 0$ is slightly lower in cold clus-
 173 ters. However, at later stages the electron on cold clus-
 174 ters does not localize further, but rather gets trapped
 175 in geometries with a radius of gyration between 4 and
 176 5 Å and VDE of 1.3 - 1.5 eV. Clearly, the initial (par-
 177 tial) reorientation of water molecules is feasible also in
 178 the cold glassy clusters, but further stabilization of the

179 electron solvation structure by translational motion of
 180 water molecules is hindered at low temperatures. The
 181 cold clusters thus get trapped in a metastable situation
 182 about half way between the initial geometry and the equi-
 183 librated solvated electron. This trapping will persist on
 184 longer timescales than those of the present simulations
 185 (up to 15 ps). This is due to the extremely small diffu-
 186 sion rate in amorphous solid water, which is at least six
 187 orders of magnitude below that in liquid water [33, 34].
 188 Therefore, the excess electron in cold clusters is likely to
 189 be kinetically trapped in metastable geometries for the
 190 micro to milisecond timescales pertinent to the experi-
 191 ment [12, 15].

192 The trapping and non-ergodic behavior in cold water
 193 clusters is further demonstrated in Fig. 5, which shows
 194 the correlation between the radius of gyration of the ex-
 195 cess electron and its average distance from the COM of
 196 the cluster at different temperatures. Comparison to sim-
 197 ulations of an equilibrated solvated electron at 300 K
 198 shows again the pronounced difference between localiza-
 199 tion in warm vs cold clusters. During electron localiza-
 200 tion at 300 K the system explores the same phase space
 201 region as the equilibrated electron (actually an even
 202 broader one thanks to the initially strongly delocalized
 203 geometries). In cold clusters, however, the excess elec-
 204 tron remains localized in a narrow phase space region
 205 corresponding to large distances from the cluster center
 206 and large to medium values of the radius of gyration.
 207 Most notably, at 20 or 50 K the system never visits the
 208 region of small radii of gyration, which are characteris-
 209 tic for equilibrium solvated electrons, nor does it leave
 210 the outer surface of the cluster.

The present results have far-reaching consequences for
 attempts to extrapolate electron binding energies from
 cold water clusters to the liquid bulk. Experiments show

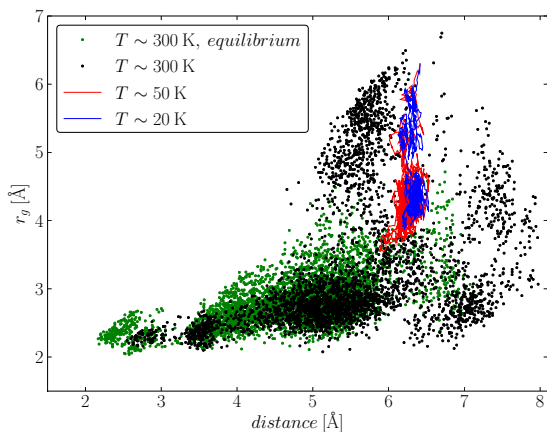


FIG. 5: Correlation between the average distance of the electron from the cluster center of mass and the radius of gyration of the electron. Green: data from equilibrium trajectories at 300 K. Black: data from the first 3 ps of the six localization trajectories at 300 K. Red, blue: data from localization trajectories at 20 and 50 K.

that in such cold clusters several isomers of the excess electron with distinct binding energies can be found [12]. Our simulations support previous suggestions [12, 15, 19] that most, if not all, of these isomers can be metastable structures kinetically trapped in the glassy clusters. The present calculations show that in liquid clusters at ambient conditions, which are, however, not readily accessible to experiment due to evaporative cooling, no such distinct isomers exist. The electron, initially attached to a neutral system at 300 K, always relaxes within 1.5 ps into its equilibrated state. Only for this situation, extrapolation with increasing cluster size to the aqueous bulk would be fully justified and should provide an accurate value of the VDE of a solvated electron in liquid water.

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