

Electron at the Surface of Water: Dehydrated or Not?

Frank Uhlig, Ondrej Marsalek, and Pavel Jungwirth*

*Institute of Organic Chemistry and Biochemistry, Academy of Sciences of the Czech Republic and
Flemingovo nám. 2, CZ-16610 Prague 6, Czech Republic*

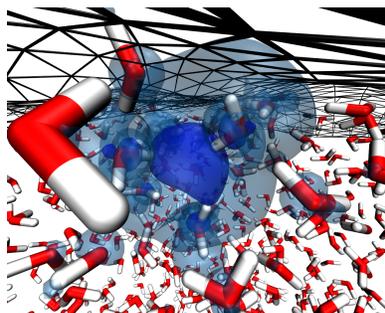
E-mail: pavel.jungwirth@uochb.cas.cz

*To whom correspondence should be addressed

Abstract

Hydrated electron is a crucial species in radiative processes and it has been speculated that its behavior at the water surface could lead to specific interfacial chemical properties. Here, we address fundamental questions concerning structure and energetics of an electron at the surface of water. We use the method of ab initio molecular dynamics, which was shown to provide a faithful description of solvated electrons in large water clusters and in bulk water. The present results clearly demonstrate that the surface electron is mostly buried in the interfacial water layer, with only about ten percent of its density protruding into the vapor phase. Consequently, it has structure which is very similar to that of an electron solvated in the aqueous bulk. This points to a general feature of charges at the surface of water, namely that they do not behave as half dehydrated but rather as almost fully hydrated species.

TOC graphics



Keywords: DFT, QM/MM, hydrated electron, water, photoionization, ionization potentials, air/water interface

The bulk dynamics and chemistry of an excess electron in water, a key intermediate in aqueous radiolysis and photolysis, are relatively well understood.¹⁻⁴ From the structural point of view, there has recently been a lively debate about the validity of the traditional cavity picture of the hydrated electron.⁵⁻¹⁰ The most recent view which may be emerging from this debate is that the electron in bulk water has a complex structure with the cavity as a leading motif.^{9,11} However, there are also additional important contributions. Namely, these comprise a diffuse tail and the overlap with valence electrons of the neighboring water molecules, which together account for more than 50 % of the excess electron density.¹¹ In this context, it is fortunate that a many-electron dynamical description of the solvated electron in water based on density functional theory (DFT) has become computationally feasible.¹¹⁻¹⁵ When properly benchmarked, such a description can faithfully describe the interactions of the excess electron with the electronic structure of the solvent.¹⁶

Compared to the aqueous bulk, the behavior of the solvated electron at the surface of water is poorly established. Traditionally, charged particles (such as inorganic ions) are expected to always remain well hydrated, thus leaving the surface layer effectively charge-free.¹⁷ This view, however, does not hold in the light of modern molecular simulations and spectroscopic experiments, which show that large and polarizable ions (iodide, thiocyanate, and others) exhibit an affinity for the surface of water (for representative reviews on the subject see Refs.¹⁸⁻²⁰). These ions can then get involved in surface-specific chemistry with implications, e.g., for heterogeneous atmospheric processes.^{21,22} Does a solvated electron, as a prominent example of a polarizable charged species,²³ also show a propensity for the surface of water? If yes, how does its structure, energetics, and chemical reactivity differ from that in the aqueous bulk?

Until recently, the above questions have been addressed by performing extrapolations from clusters to extended systems. Several isomers of negatively charged water clusters of increasing size have been found by photoelectron spectroscopy (PES),²⁴⁻²⁶ as well as by IR spectroscopy.^{27,28} Based on PES, isomers with strongly bound electrons, extrapolating to vertical detachment energy (VDE) above 3 eV, were assigned to interior states, while those with weakly bound electrons, extrapolating to VDE of about 1.6 eV, were attributed to surface structures.^{24,29} Based on these

assignments, the results of the first microjet PES study of electrons in an extended aqueous system were interpreted in terms of the existence of bulk and surface hydrated electrons as two distinct species with VDEs coinciding with values extrapolated from clusters.^{30,31} There are, however, several problems with this interpretation. First, the interpretation of the strongly bound isomer in terms of an interior structure has been questioned.³² Both pseudopotential calculations³³ and all (valence) electron ab initio molecular dynamics (MD) simulations¹⁴ showed that while weakly bound isomers indeed reside on the cluster surface, strongly bound electrons can be found both in the interior and at the surface. Calculations thus indicate that VDE is a measure of the size rather than the location of the solvated electron.^{16,34} Second, cluster experiments are typically performed at cold temperatures at which the clusters end up being solid.^{25,26} Therefore, any extrapolations should be made towards ice or amorphous solid, rather than to liquid water. Ab initio MD simulations demonstrated that this indeed makes a difference — while distinct isomers exist for solid clusters at cryogenic conditions, they disappear when the cluster becomes liquid.¹⁴ Third, later experiments in liquid microjets,^{35–37} albeit with a different ionization setup, did not find any signature of the weakly bound surface structure deduced from the first measurement.³⁰

In this paper, we elucidate the structure and energetics of an electron solvated at the surface of water by means of molecular dynamics simulations using a combined quantum mechanics/molecular mechanics (QM/MM) approach. Details of the calculations are described in the methods section; here it suffices to say that we have evaluated the equilibrium structure of an electron at an extended aqueous slab at 300 K using a benchmarked DFT description¹¹ that takes into account explicitly the electronic structure of both the solvated electron and the surrounding water molecules. Such an approach allows us to faithfully characterize the surface solvated electron, including its many-electron aspects, and to compare it quantitatively to an electron solvated in the aqueous bulk.

Let us now discuss the structure of the solvated electron equilibrated at the surface of water, as obtained from the present simulations. Figure 1 shows a representative snapshot (a) together with the averaged spin density (b) representing the surface solvated electron and its decomposition into

individual spatial contributions. As in our previous study of an electron solvated in the aqueous bulk,¹¹ the electron spin density is divided into contributions from the inner cavity, overlap with surrounding water molecules, and a diffuse tail. Additionally, at the surface there is a fourth contribution originating from the part of the density protruding into the vapor phase. 1 compares the present results with those for the aqueous bulk.¹¹ The key finding of our study is that the character of the surface solvated electron is strikingly similar to that in the bulk. The cavity contribution is the largest one, amounting to about 37 %, which is only 4 % less than the bulk value. As in the bulk, the contributions from the overlap with water molecules and from the diffuse tail are also important, amounting together to roughly 50 % of the surface electron density. Compared to the bulk situation, each of these two contributions is slightly smaller, which stems from the intrinsic anisotropy of the surface geometry. Indeed, while the electron close to the water surface mostly maintains its first solvent shell (*vide infra*) it is not completely surrounded by water molecules of the second solvent shell as it is in the bulk. This mostly affects the diffuse tail of the electron density, the contribution of which is reduced by 4 % compared to the bulk value. The final contribution, which has no analogue in the aqueous bulk, is the part of the electron density protruding into the vapor phase. It, however, amounts only to 11 % of the total density of the solvated electron, implying that the electron is mostly buried within the surface water layer (it is, therefore, more a sub-surface than surface electron). This observation is in agreement with a second harmonic generation spectroscopic study, which showed that the surface solvated electron is not affected by surfactants residing *on* water but only by surface active species penetrating *into* the surface layer⁵¹ and in accord with structures observed in recent pseudopotential calculations.³⁴

Table 1: Decomposition of the spin density of the hydrated electron: Comparison of individual contributions at the water surface vs. bulk.

contribution	surface	bulk
inner cavity	37	41
overlap with water	21	24
diffuse tail	31	35
in vapor	11	-

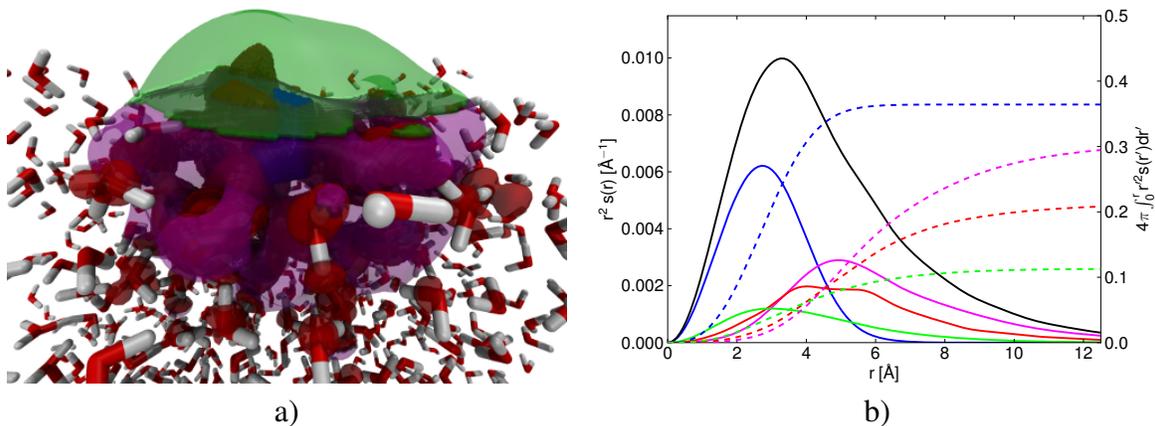


Figure 1: a) A representative snapshot of the hydrated electron using the same color coding for the individual contributions as isosurfaces of the spin density (at 10^{-6} Bohr $^{-3}$). b) Radial profiles of the dissected total spin density of the surface hydrated electron (black) into contributions (full lines, with integrals as dashed lines) from the inner cavity (blue), overlap with water molecules (red), diffuse tail in the water phase (magenta) and the part protruding into the vapor (green). The origin is set to the center of the total spin distribution r_c .

Water structure around the hydrated electron can be characterized by radial distribution functions (RDFs) of oxygen and hydrogen atoms around the center of the hydrated electron spin density (Figure 2), with the caveat that at each instant it deviates from a perfectly spherical geometry.^{11,52} Both RDFs for oxygen (in red) and hydrogen atoms (in green) around the center of the hydrated electron show a clear peak due to first solvent shell water molecules. The structuring is present, albeit less pronounced, also in the second solvent shell of water molecules around the hydrated electron. The first solvation shell of the hydrated electron comprises on average four water molecules (see inset of Figure 2) and it looks very similar to that of a bulk hydrated electron,¹¹ with appreciable differences in hydration numbers appearing only in the second shell and beyond due to the anisotropy of the water surface. For most of the simulation time, one of the first four solvating water molecules is located directly at surface. For short instances, when the electron penetrates closer to the interface, it becomes solvated by only three water molecules in the first shell, with part of its cavity being directly exposed to the surface.

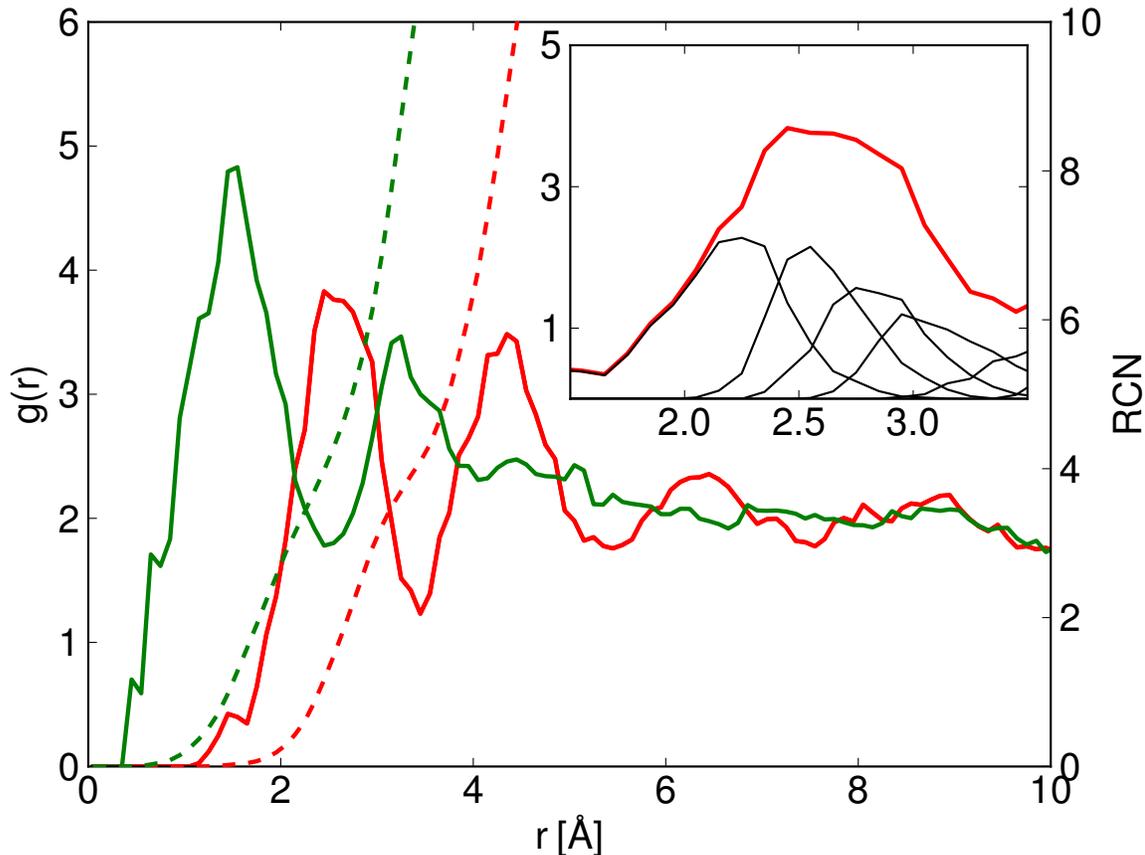


Figure 2: Radial distribution functions (full lines) of water oxygen (red) and water hydrogen (green) atoms around the center of the electron. Integrals of the radial distribution functions, i.e., running coordination numbers are shown as dashed lines. The depletion of water molecules around the center of the surface solvated electron clearly points to the existence of an inner cavity. The inset depicts individual contributions to the first peak of the oxygen radial distribution function which is formed on average by four water molecules.

The closer the electron comes to the surface, the larger the part of its density that protrudes out of water. This is demonstrated in Figure 3 which shows the anticorrelation between the distance of the center of the electron from the water surface and the amount of the electron density in the vapor phase. For most of the simulation, the center of the electron is between 1–2.5 Å from the instantaneous surface (see inset of Figure 3) and, consequently the amount of the electron density in the vapor is below 10 %. Only on the rare occasions when the electron drifts closer to the surface the amount of its density leaking out of water increases to up to 30 %. However,

the inset of Figure 4 shows that such fluctuations of the position of the electron with respect to the water surface do not have a systematic effect on its energetics, in other words there is no correlation between the distance from the surface and the VDE. The signal measured by PES thus does not correlate with the position of the electron but rather with its size, as shown in Figure 4. Similarly as in the aqueous bulk,^{11,34,53} this figure demonstrates the anticorrelation between these two quantities. The size distribution peaks at 2.7 Å and the VDE at 3.3 eV which are values very similar to those we calculated for the bulk solvated electron.¹¹

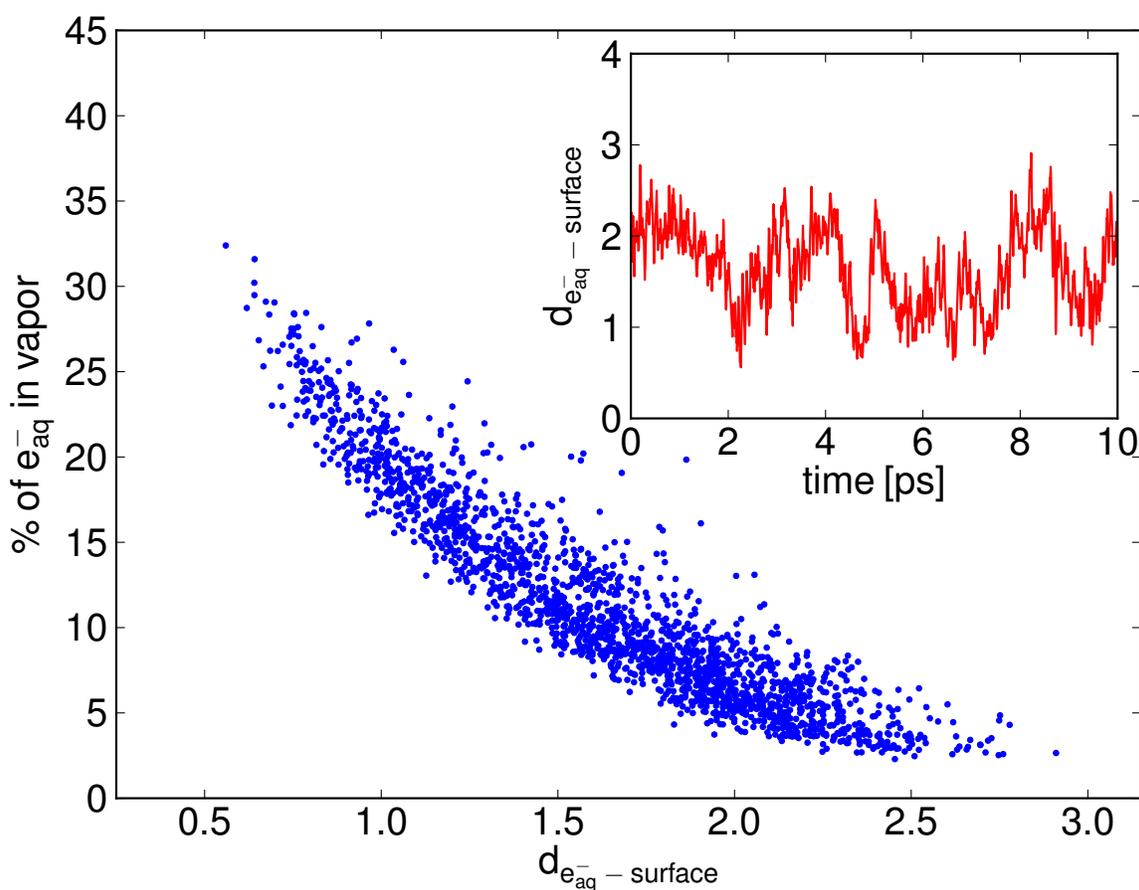


Figure 3: Correlated distributions of the distance of the center of the hydrated electron to the water surface $d_{e_{aq}^- - \text{surface}}$ and the percentage of the hydrated electron density protruding into the vapor phase. The inset shows the time evolution of $d_{e_{aq}^- - \text{surface}}$ for a representative trajectory.

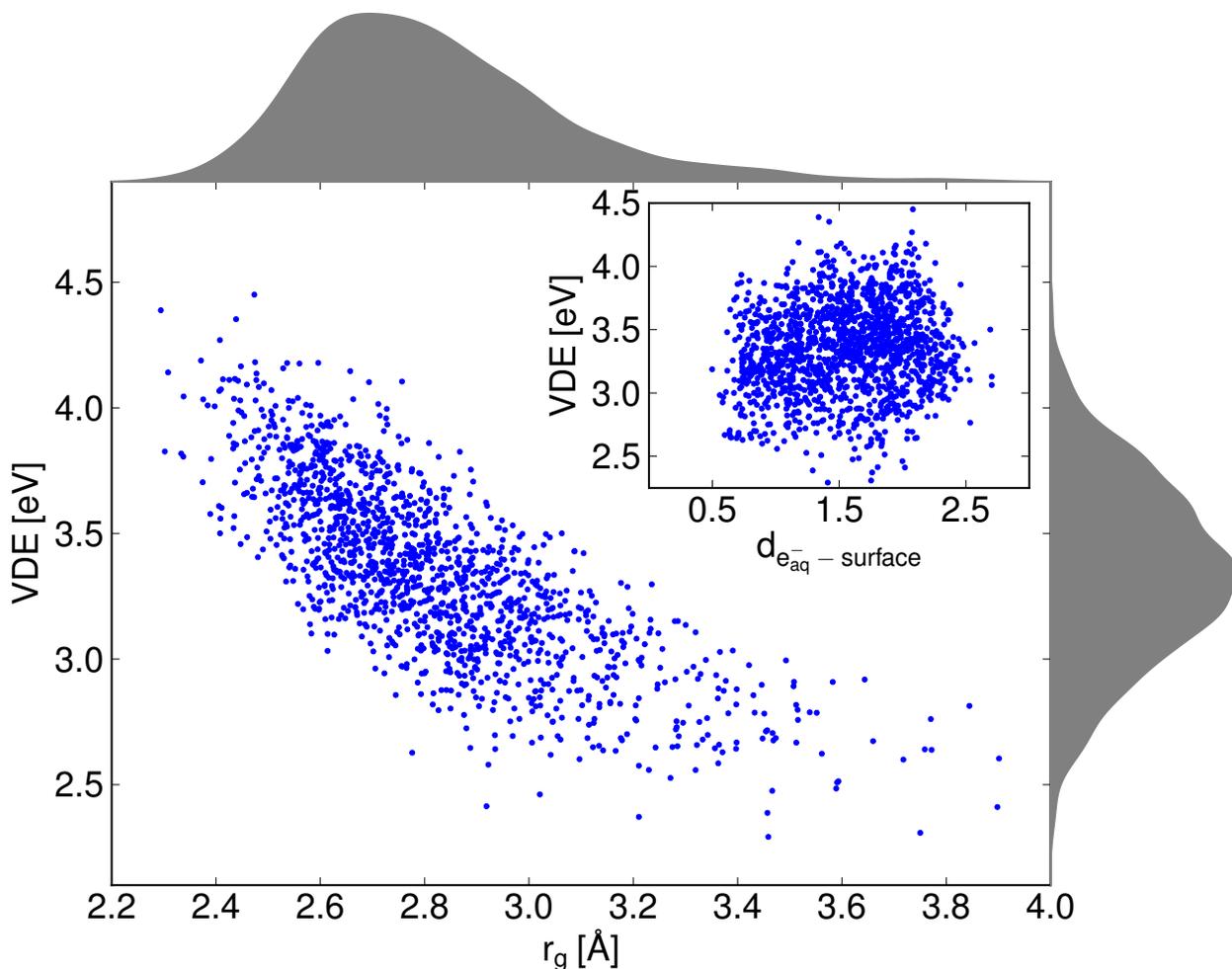


Figure 4: Correlated distributions of VDEs and radii of gyration r_g of the surface hydrated electron. The gray histograms represent projections of each of the distributions onto the respective axis. The inset demonstrates that there is no correlation between VDE and the distance of the hydrated electron from the water surface $d_{e_{aq}^- - \text{surface}}$.

Conclusions

By means of many-electron dynamical calculations, results of which compare quantitatively with experiments in clusters¹⁴ and in the aqueous bulk,¹¹ we have established the structure of the electron solvated at the surface of water. The present results clearly show that the surface and bulk electrons are very similar to each other both in structure and in binding energies. During the equilibrium simulation the electron resides preferentially just below the surface with only a small part of its density penetrating into the gas phase. Its mostly buried location at the interface, which exhibits relatively large fluctuations of the distance from the surface, and its similarity to the bulk

solvated electron indicate that the electron is about equally well solvated at the water surface as it is in the aqueous bulk. There is no signature of a stable, chemically distinct, weakly bound electron at the surface of water as suggested previously;^{30,31} an electron initially added to a neutral water surface spontaneously forms a fully hydrated species at the interface (see also Methods). In this respect, the solvated electron behaves rather like a large polarizable anion, such as iodide, which can reside at the water/vapor interface but maintains similar electronic properties as in the bulk.⁵⁴ This demonstrates that, analogously to ions,⁵⁵ an electron at the surface of water does not behave as a half-dehydrated species, but maintains practically all of its bulk hydration features. Extrapolating to biological aqueous interfaces, the present picture can be used as a guidance for assessing the interactions between the solvated electron and DNA or proteins.

Computational Details

Molecular dynamics simulations of an electron in an aqueous slab were performed using a combined QM/MM approach. The computational methodology is similar to our previous calculations of a hydrated electron in bulk water.¹¹ The system consisted of 1024 water molecules in total and was replicated periodically in all three dimensions. Initial structures were generated by, first, sampling the canonical (NpT) ensemble at 300 K and 1 bar of a bulk water system of 1024 water molecules described by an extended simple point charge (SPC/E) model for about 100 ns. The density after equilibration was about 992 kg/m³. Next, to obtain slab structures, the z-dimension was increased to 100 Å and the canonical (NVT) ensemble was sampled for about 100 ns. Structures from the resulting trajectory were used as input for QM/MM simulations. The QM system was taken as 32 water molecules hemispherically surrounding a given point on the water surface. Equilibration of the neutral system for several picoseconds was performed. The excess electron was then introduced by increasing the charge of the QM system by one. On further dynamics the excess electron in the system localized within 1–2 ps, forming a fully hydrated electron. The final geometry was then taken as input for the production run. The size of the QM system was increased to comprise 64 water molecules surrounding the center of the solvated electron. Short equilibration followed and production simulation was then run for 10 ps. This time scale proved to be sufficient

to observe migration of the electron from the air/water interface to the interior of a slab geometry in pseudopotential calculations.³⁸ In all simulations temperature was kept constant at 300 K by the canonical sampling through velocity rescaling thermostat with a time constant of 16.68 fs.³⁹

All QM/MM calculations were carried out using the CP2K program suite.⁴⁰ The nuclei were propagated according to Newton’s equations of motion with forces obtained from density functional theory (DFT) calculations. The Becke-Lee-Yang-Parr^{41,42} (BLYP) exchange-correlation functional was used throughout the simulations with an additional, pairwise-additive term effectively accounting for dispersion interactions.⁴³ All calculations use the restricted open-shell formulation of DFT and we identify the hydrated electron as the density of the singly occupied molecular orbital. The BLYP functional was furthermore augmented by a spin-density dependent term correcting the spurious self-interaction present in the density functional.⁴⁴ Parameters for the latter were $a = 0.3$ and $b = 0.2$. All core electrons were replaced by Goedecker-Hutter-Teter norm-conserving pseudopotentials.⁴⁵ The valence-electron wavefunction of the system was expanded into an atom-centered basis set of triple- ζ quality⁴⁶ (molopt-TZV2P) and an auxiliary basis set of plane waves with a kinetic-energy cutoff of 280 Ry was used for the electron density. The atom-centered basis set was further augmented by a set of spatially fixed Gaussian functions ($\zeta = 0.1$ Bohr) spherically surrounding the center of the spin density in the first MD step (81 additional functions with a distance of 2 Å). In all initial configurations the hydrated electron is located right underneath the water surface and the auxiliary basis functions spread sufficiently out into vacuum in order to avoid spurious bias towards bulk solvation. The QM system was centered in a cubic box with a side length of 25 Å and Poisson’s equation for the QM system in the field of the surrounding MM charge distributions was solved using the density-derived atomic charges.⁴⁷ A harmonic potential located at the box edge prevented diffusion of water in the QM subsystem out of the QM box, but did not affect the motion of the water molecules in the MM subsystem.

The MM part of the system was treated by an empirical, extended simple point charge model (SPC/E)⁴⁸ with flexible bonds. In order to avoid so-called “spill-out” effects the point-charges were treated as Gaussian functions centered at the corresponding nuclei. For the coupling between

the QM and MM system we used the multigrid approach proposed by Laino et al.⁴⁹ This way, we can account for the periodicity of both the MM and the QM subsystem. The electrostatic potential of the MM subsystem was evaluated with the smooth particle-mesh Ewald method. The VDE was evaluated as the energy difference between the system with and without the hydrated electron at the geometry of the former system.¹¹

The analysis of the spin density was performed on gridded data which was obtained in Gaussian cube file format from the simulations with a stride of 5 fs along all trajectories. The center of the normalized spin density is defined as:

$$\mathbf{r}_c = \int s(\mathbf{r})\mathbf{r}d\mathbf{r}. \quad (1)$$

The radius of gyration of the spin density is obtained from the eigenvalues λ_1^2 , λ_2^2 , λ_3^2 of the gyration tensor $\mathbf{S} = \int (\mathbf{r} - \mathbf{r}_c)(\mathbf{r} - \mathbf{r}_c)s(\mathbf{r})d\mathbf{r}$:

$$r_g = \sqrt{\lambda_1^2 + \lambda_2^2 + \lambda_3^2}. \quad (2)$$

The partitioning of the spin density into spatially non-overlapping parts (inner cavity, overlap with water, diffuse tail) is described in detail in Ref. 11. For the slab simulations we define an additional contribution, namely the spin density protruding into the vapor phase. The water surface is defined according to Ref.⁵⁰. The distance of the electron to the water/vapor interface $d_{e_{aq}-surface}$ is obtained as the distance of \mathbf{r}_c to the closest voxel of the surface representation. The surface is calculated first on the original grid of data points and a refinement step is added once the closest part of the surface to \mathbf{r}_c is identified.

Acknowledgement

We acknowledge the Czech Science Foundation (Grant P208/12/G016) for support. PJ thanks the Academy of Sciences for the Praemium Academie award. FU and OM acknowledge support from the IMPRS Dresden.

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