Electrons in Water

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The Hydrated Electron: A Seemingly Familiar Chemical and Biological Transient

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Since the discovery of the hydrated electron in bulk water in 1962, the species has been the subject of intense research and speculation. For many decades even the basic features of the simplest of all chemical and biological transients and reactants—such as its structure, binding motifs, lifetimes, and binding energies—remained elusive. Recently, another milestone in the research of the hydrated electron was the determination of its vertical binding energy (VBE). Also a long-lived hydrated electron near the surface of liquid water has been discovered. The present Minireview discusses the implications and consequences of this and other new findings in addition to the emerging complex picture of a solvated electron in water.

1. Introduction

About 200 years ago, in 1808, Sir Humphry Davy made the first observation of the beautiful blue and bronze colors when dissolving alkali metals in ammonia.[1] Davy had never published his findings, and so the first publication on alkali–ammonia solutions was by W. Weyl in 1864.[2] Shortly afterwards, in 1897, the British physicist J. J. Thompson discovered "corpuscles" in cathode rays in the gas phase, being minuscule pieces of atoms, which were later termed electrons.[3] About 100 years ago, C. A. Kraus assigned the characteristic colors observed in alkali–ammonia solutions to be the signature of a new anionic species: a solvated electron in ammonia.[4] Speculations about a similar species in water ended in 1962 when the existence of solvated electrons in liquid water $e^-_{(aq)}$—which are also termed hydrated electrons—was demonstrated by E. Hart and J. W. Boag.[5] They irradiated a water sample and recorded a broad characteristic absorption band located at 720 nm, which they attributed to the absorption spectrum of the hydrated electron. This intense, broad, and characteristically asymmetric absorption spectrum has become the defining property of the hydrated electron.

The structure of this simple species was nevertheless not clear for a long time. The concept of an excess electron, which is trapped in a cavity or void in the hydrogen-bonded network of liquid water, was proposed more than 50 years ago.[6] In this picture, the 720 nm absorption band is attributed to a transition from the *s* ground state to a manifold of excited *p* states within the cavity. A comprehensive review of the early models of the hydrated electron was given by Feng and Kevan.[7] Since the 1980s, the cavity model of the hydrated electron has been elaborated in considerable detail by Rossky, Borgis, Schwartz and coworkers.[8] While the cavity model is the consensus picture of the hydrated electron since six decades, alternative proposals have been made.[9] Just recently, it has been proposed that the hydrated electron resides in a region of enhanced water density rather than in a void cavity.[9e,f] Earlier, it has been suggested that the hydrated hydronium radical (H_3O), consisting of a hydronium cation and a localized electron cloud, could be the carrier of the characteristic spectroscopic properties of the hydrated electron in liquid water.[9b–d] In particular, the ab initio calculated electronic and vibrational spectra of the hydrated H_3O exhibit striking similarities with the spectral signatures of the hydrated electron.[9c,d] Is this radical possibly the "solvated electron in water"?

In addition to pulse radiolysis with X-rays or electrons, the hydrated electron can be generated by single-photon or multiphoton excitation of water,[10] by photodetachment from anions in aqueous solution,[11] or by photoexcitation of organic chromophores with acidic groups, such as indole or phenol.[12] Despite decades of intensive research, the mechanisms involved in photoionization in aqueous solutions are not yet completely understood and thus still subject to experimental investigations. However, it seems obvious that

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electron ejection from neat water and photodetachment of anions in aqueous solution are quite distinct processes and subsequent relaxation mechanisms towards the fully equilibrated hydrated electron strongly depend on the excitation process.[10d,e,11b,d] In the case of anion photodetachment, it is assumed that excitation occurs into charge-transfer-to-solvent (CTTS) states and may involve the formation of donor-electron pairs that display a competition between recombination and separation.[11b,d] In the case of UV two-photon excitation of neat water, mechanisms strongly depend on the excitation energy,[10e] and an intermediate OH:e$^-$ complex has been postulated by Laenen et al.[10d] to interpret transient spectra. In the case of two-photon excitation of neat water, electron ejection competes with OH-bond dissociation whereas the ratio between these two channels depends on the excitation energy.[10f] Despite all this progress in understanding anion photodetachment in aqueous solution and UV two-photon excitation of water, the association of intermediate species with structural models remained a controversial issue.

The radiationless decay following s$\rightarrow$p excitation of the hydrated electron has been another vividly debated issue over several decades.[13]

In 2010, within a short period of time, four research groups reported the determination of the vertical binding energy (VBE) of the hydrated electron,[14] a quantity over which scientists have speculated since the discovery of the hydrated electron in 1962. The VBE is the energy required to remove the electron from its hydration cavity and to completely separate it from the water, while maintaining the initial geometry of the system. The first value of VBE($e^-_{(aq)}$) = 3.3 eV was measured and reported by Siefermann et al. (Figure 1 A).[14a] Later experiments by other groups yielded values of 3.27 eV (Tang et al.),[14b] 3.6 eV (Shreve et al.),[14c] and 3.4 eV (Lübcke et al.).[14d] Tang et al.[14b] and Lübcke et al.[14d] also reported the first femtosecond time-resolved photoelectron spectra of the hydrated electron. Siefermann et al.[14a] additionally generated a differently hydrated electron via 267 nm two-photon excitation of neat water. The existence of a long-lived (> 100 ps) electron solvated on the surface of liquid water with a VBE($e^-_{(surface)}$) of 1.6 eV has been established for the first time (Figure 1 B). The observed lifetime was surprising and explained by a dynamic barrier preventing the surface electrons from quickly penetrating into the bulk.[14a] The following Sections 2 and 3 describe the different experimental approaches for measuring VBEs of hydrated electrons and discuss respective results. Section 4 elaborates on the implications of these new results. It discusses how the VBE of $e^-_{(aq)}$ establishes an energy scale for hydrated electrons in water and sheds new light on the question of how hydrated electrons can very efficiently break strong covalent bonds of molecular systems in aqueous environments.

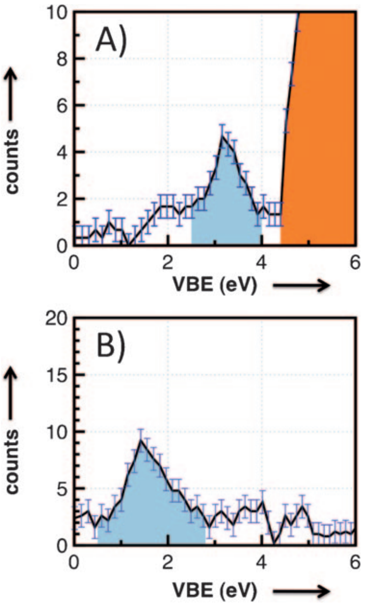

Figure 1. Photoemission spectra of hydrated electrons A) in bulk water ($e^-_{(aq)}$) and B) near the water-vacuum interface ($e^-_{(surface)}$).[14a] The emission lines of the bulk hydrated electron and surface hydrated electron are colored in blue. The brown emission arises from the $[Fe(CN)_6]^{4-}_{(aq)}$ precursor complex.

2. Experimental Characterization of Two Binding Motifs of Hydrated Electrons

Before the liquid jet experiment by Siefermann et al.[14a] directly measured the VBE of $e^-_{(aq)}$, research on anionic water clusters was performed with the goal to understand electron solvation in these confined systems and to extrap-

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olate bulk properties of $e^-_{(aq)}$ from cluster data. The experimentally determined vertical detachment energies VDE (equivalent to VBE) of the excess electron in $(H_2O)^-_n$ vary strongly with cluster size n and there is clear evidence for the existence of cluster isomers with distinctly different electron solvation motifs (Figure 2).[15] It was suggested by Neumark et al. that isomer I and isomer II in Figure 2 correspond to different isomers of clusters having the excess electron inside and clusters carrying it on the surface, respectively.[15b] This assignment was heavily debated in the light of theoretical studies which appeared at the same time.[16] Although more recent experimental[15e] and theoretical investigations,[17] contributed to our understanding of the different isomers, the accurate extrapolation of experimental cluster data to yield reliable values for bulk liquid water remained difficult (see shaded area in Figure 2). Only the recent liquid phase photoelectron spectroscopy experiments provided a reliable VBE for $e^-_{(aq)}$,[14] and the discovery of electrons solvated on the surface of liquid water with VBE($e^-_{(surface)}$) = 1.6 eV[14a] supports the initial assignments by Neumark and co-workers.[15b]

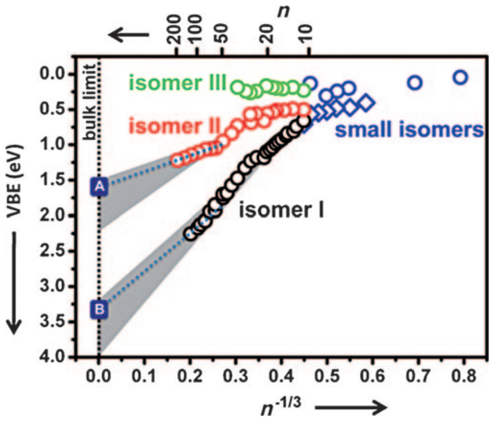

Figure 2. Experimental VBEs for anionic water clusters $(H_2O)_n^-$ of various sizes n. Blue open circles and diamonds are data for small clusters from Johnson's group.[15a] Black (isomers I), red (isomers II) and green (isomers III) open circles are cluster data from Neumark's group.[15b,c] The data from Bowen's group[15d] are close to those of isomer I. Results from v. Issendorff's group[15e] suggest that isomer I signals exhibit contributions of two species, isomers, Ia and Ib. The shaded area represents the uncertainty for an extrapolation of cluster values towards the bulk. The dotted lines interpolate between the largest clusters and our data.

Siefermann et al.[14a] directly measured VBEs of hydrated electrons using liquid micro jet technology in vacuum and a table top high harmonic light source driven by a femtosecond laser system (Figure 1).[18] The key feature to the experimental approach is generating solvated electrons by a short pump pulse of 267 nm light and recording photoelectron spectra using a time-delayed 38.7 eV (32 nm) high harmonic probe pulse. For different precursors ($K_4[Fe(CN)_6]$ and neat water) and experimental conditions, photoelectron spectra with prominent emission features at (3.3 ± 0.1) eV and (1.6 ± 0.1) eV were recorded, which were assigned to the VBEs of $e^-_{(aq)}$ and of electrons solvated on the water surface $e^-_{(surface)}$, respectively, in agreement with the cluster results above (Figure 3 A,B).[14a] The latter are also termed surface-bound or surface-solvated electrons (Figure 3 A) and their photoelectron spectrum is nearly unchanged at a time-delay of the pump and probe pulses of 100 ps. This implies that the lifetime of $e^-_{(surface)}$ significantly exceeds 100 ps.[14a] By comparing this lifetime with temperature dependent solvated electron diffusion in water, we estimate that the free energy barrier between $e^-_{(surface)}$ and $e^-_{(aq)}$ may exceed 0.2 eV and in turn the concerted breaking of more than 3 hydrogen bonds is necessary.[19] This result might be surprising in the light of recent theoretical work on water surfaces and large clusters which do not predict a stable surface species for liquid water.[17a,20] However, the energetics as well as the stability are consistent with experiments on water ice surfaces. Bovensiepen et al. performed 2-photon-photoemission (2PPE) experiments on water ice adsorbed on metal substrates.[21] They found that electrons on a crystalline water ice surface can exist up to minutes. Long living states even exist when the surface electron is only separated by 1.2 bilayers of water molecules from the metal substrate and thus from an apparent recombination channel.[21]

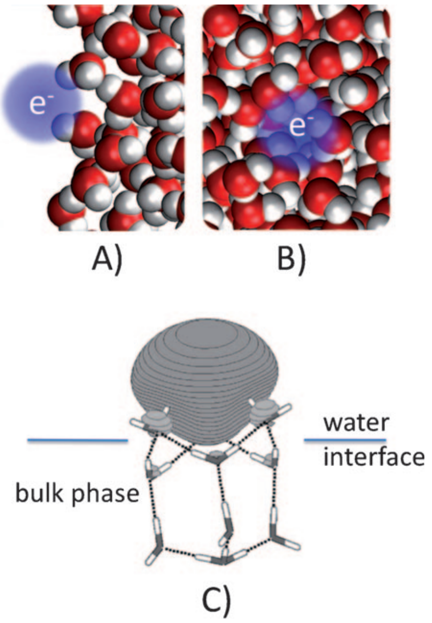

Figure 3. Upper panel: Cartoon of hydrated electrons A) near the water-vacuum interface ($e^-_{(surface)}$) and B) in bulk water ($e^-_{(aq)}$).[14a] Lower panel: The singly occupied molecular orbital of $H_3O(H_2O)_9$ clusters. Same structural motif may be present near the water-vacuum interface (Figure adapted from Ref. [9d]). See text for details.

The follow-up experiments by other groups used UV light (267–213 nm) to probe the binding energy of the hydrated electron and yielded values of 3.27 eV (Tang et al.),[14b] 3.6 eV (Shreve et al.),[14c] and 3.4 eV (Lübcke et al.)[14d] which are close to the value reported by Siefermann et al.[14a] Although there are deviations of the order of a few tenths of an electron volt in the measured binding energies of the bulk hydrated electron, there exists now a reference value (3.4 ± 0.2 eV) for the ionization potential of the hydrated electron in liquid water. A source for the variations might be that calibration procedures used in Refs. [14b–d] are based on gas phase measurements, and not on liquid phase measurements. Shreve et al.[14c] generated the hydrated electron from various precursors ($I^{-}_{(aq)}$ and $[Fe(CN)_6]^{4-}{}_{(aq)}$) and showed that the binding energy of $e^{-}_{(aq)}$ is insensitive to the choice of the precursor. The experiments by Tang et al.[14b] used I^{-} as the precursor and additionally revealed information on the solvation dynamics following charge transfer to solvent (CTTS) of I^{-} in aqueous solution. The work by Lübcke et al.[14d] provides a more detailed picture of the ultrafast ejection, solvation and recombination dynamics of this process.

The more weakly bound electron with a VBE of 1.6 eV, could only be detected in the experiment by Siefermann et al., in which it was prepared by two-photon excitation of neat water at 267 nm and probed with a 38.7 eV (32 nm) high harmonic probe pulse (Figure 1B and Figure 3A). Not surprisingly, this species is only accessible in an experimental approach which is particularly sensitive to the surface *and* to short lived species—such as the one by Siefermann et al.[14a] There, the photoelectrons possess kinetic energies of about 35 eV, which is near the minimum of the electron attenuation length (EAL) curve.[22] The EAL is defined as the distance over which an electron signal is reduced by a factor of 1/e. Because of these short EALs, the experiments by Siefermann et al.[14a] are particularly sensitive to surface species. For lower kinetic energies of about 1 eV such as in the experiments by Tang et al.[14b] and Lübcke et al.[14d] the EAL curve steeply increases. Although the EALs for such low kinetic energy electrons in water are not precisely known it can be assumed that they follow the trend of the universal EAL curve. In this case, the experiments in Refs. [14b,d] should be more sensitive to bulk hydrated electrons $e^{-}_{(aq)}$ by more than one order of magnitude, compared to the experiments by Siefermann et al.,[14a] which are particularly sensitive to the surface. Accordingly, a respective signal-to-noise ratio is necessary to be able to detect $e^{-}_{(surface)}$ besides $e^{-}_{(aq)}$. The fact that Lübcke et al.[14d] were not able to detect $e^{-}_{(surface)}$ despite the excellent dynamical range of their setup of $\geqslant 1000$, might also be due to the nature of their precursor $I^{-}_{(aq)}$ and its CTTS ejection mechanism. Further attempts to investigate $e^{-}_{(surface)}$ using the same precursor $I^{-}_{(aq)}$ in a time-resolved second harmonic generation (SHG) experiment were also not yet successful.[23] It is important to note that Siefermann et al.[14a] observed $e^{-}_{(surface)}$ following two-photon ionization of water molecules at 267 nm and that mechanisms for electron ejection from neat water and photodetachment of anions in aqueous solution are quite distinct processes.[10d,e,11b,d] The question is whether the nature of the precursor and its ejection and solvation mechanism play a decisive role for the formation of $e^{-}_{(surface)}$. Our preliminary conjecture is that water may be special because of its unique mechanisms to form solvated electrons. We will discuss this further in section 3.

3. Features of the Observed Transients

The observation of two significantly different ionization potentials of the solvated electron in liquid water is an important finding implying that the notion of a single equilibrated hydrated electron species in water seems to be an oversimplification of the phenomenon. We emphasize, however, that the two species with VBEs of 1.6 eV and 3.3 eV, were prepared from different precursors.[14a] The species with the lower VBE, was generated by two-photon excitation of water (2×267 nm $= 9.3$ eV). This is significantly below the ionization potential of liquid water (11.16 eV).[24] If excitation occurs near the surface, the electron can separate from the H_2O^{+} cation to form $e^{-}_{(surface)}$ (Figure 3A). Theory predicts that it is not possible to squeeze an excess electron into water without breaking hydrogen bonds, which is energetically unfavorable. This may be a reason for the stability and lifetime of $e^{-}_{(surface)}$.

In the case of photodetachment from a salt anion in an aqueous salt solution, the hydrated electron is accompanied by a (possibly nearby) positive counter-ion (Na^{+} or K^{+} in all the experiments discussed here). These counter-cations, which are known to be repelled from the surface, may—in principle—stabilize a hydrated electron in the interior of the solvent with a concomitantly higher binding energy. However, it has been shown by Shreve et al.[14c] that the binding energy of $e^{-}_{(aq)}$ is insensitive to the choice of the precursor salt and its concentration. We therefore anticipate that the measured VBE of 3.3 eV corresponds to an isolated hydrated electron, which is sufficiently far away from any precursor ions.

There is still another issue that deserves discussion in this context. The hydrated hydronium radical (H_3O) has been suggested to be alternative to the classical picture of the hydrated electron in a cavity.[9b–d] In particular, the calculated electronic absorption spectra of small $H_3O(H_2O)_n$ clusters cover roughly the energy range of the absorption spectrum of the hydrated electron. Respective theory suggests that the species formed upon UV excitation of a precursor—water molecule or anion—in aqueous environment can be viewed as a hypervalent H_3O radical or MH_2O radical (M = counter cation (M^{+}) + electron), respectively. In other words, there would be a positive counter ion involved, H^{+} or M^{+}, and the latter is essential for the existence of the hydrated electron. This counter ion picture could naturally explain the two different VBEs measured in the experiment by Siefermann et al., since the counter ions in the two experimental approaches are different: K^{+} in the case of VBE = 3.3 eV, and H^{+} in the case of VBE = 1.6 eV. However, it has been shown by Shreve et al.[14c] that the VBE of $e^{-}_{(aq)}$ is insensitive to the choice of the precursor salt. In addition, the measured VBE of $e^{-}_{(aq)}$ is consistent with the VBEs of anionic water clusters (Figure 2), in which no counter ion is present. From this our tentative conclusion is that the VBE of 3.3 eV corresponds to the classical hydrated electron in a cavity.

In the second experiment, water is excited with two 267 nm photons, that is at an energy of 9.30 eV. Excitation of a surface molecule may result in dissociation of this molecule into OH + H, whereas the H atom may be transferred to an adjacent water molecule to form a H_3O radical.[25] In small clusters, this radical is a H_3O^+ ion core surrounded by a 3s-type SOMO, which is solvated by dangling OH bonds of neighboring water molecules.[9c,d] The separation of ion core and electron cloud increases for increasing cluster size,[9c,d] so that at a water surface, the electron cloud would be literally squeezed out of the water, and could be solvated and stabilized as a surface-bound state (Figure 3 C). Since the measured VBE for $e^-_{(surface)}$[14a] is consistent with the VBEs of anionic water clusters (isomer II, Figure 2), in which no counter ion is present, one may be tempted to be biased against the H_3O radical species at the water interface. At the moment we do not have experimental evidence for this species. However, the concept that the surface and bulk solvated electrons are different chemical species may eliminate the problem of the explanation of the existence of a substantial barrier for incorporation of the surface electron into the bulk in case of an overall exothermic process.

4. Energetics of Dissociative Electron Attachment in Aqueous Solution

The results on the energetics and the nature of $e^-_{(aq)}$ and $e^-_{(surface)}$ may be crucial for understanding how electrons can attach to molecules in aqueous environments and efficiently break strong covalent bonds. In this context, it is illustrative to compare potential energy curves of neutral species and their corresponding anions, both in the gas phase and in aqueous environment (schematically displayed in Figure 4 A). For DNA, differences were first pointed out and explained by Barrios et al.[26] and Simons.[27] The three following points summarize their qualitative findings:

1) When an electron attaches to a neutral species in the gas phase, this electron attachment requires a certain amount of energy. The required energy corresponds to the difference in energy between the neutral and anionic potential energy curve at the equilibrium bond length of the neutral curve. Accordingly, the attaching electron has to possess a "matching" kinetic energy in order to successfully attach to the molecule and to form a so-called shape resonance anion.[27]
2) Breaking covalent bonds in a neutral species requires a significant amount of energy (ca. 4 eV in DNA), as indicated by the increase of the neutral potential energy curves with increasing internuclear distance in Figure 4 A. This situation is different after electron attachment to an antibonding orbital, that is for example, occupation of the lowest unoccupied molecular orbital (LUMO). For a bond break in such an anionic species, comparatively low energy barriers have to be surmounted (anionic curves in Figure 4 A).[27]
3) The situation in an aqueous environment is much different from the picture in the gas phase. Although the shape of the curves does not change explicitly with solvation,[26–27] the interactions with polar solvent molecules stabilize the anion. As a result, the potential energy curve of the anion lies below the corresponding neutral curve (see right part of Figure 4 A).[26–27]

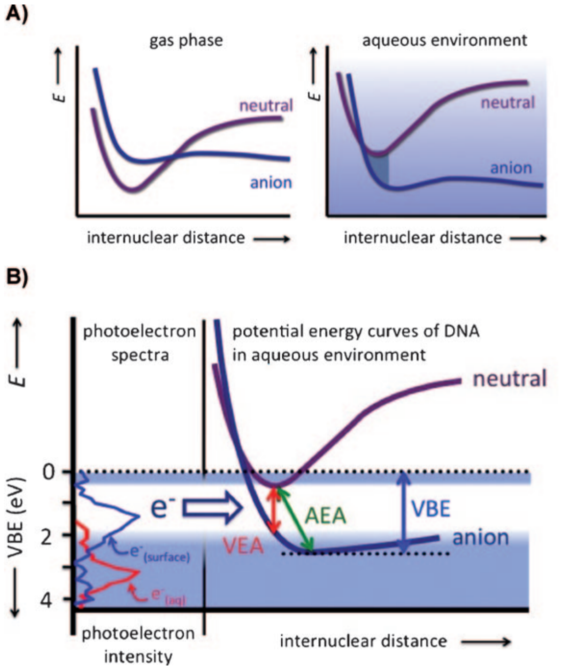

Figure 4. A) This qualitative sketch shows how the potential energy curves of neutral species and their corresponding anions in the gas phase (left) differ from their curves in an aqueous environment (right). Characteristics of the curves are adopted from Refs. [26,27]. See text for details. B) RDEA picture for electron attachment to the thymine base in 5′-dTMPH. Shown are the potential energy curves of the neutral and anionic species in aqueous solution (right part). The electron acceptance window is indicated by the white band and can be directly compared to the photoelectron spectra, or the VBEs, of $e^-_{(aq)}$ and $e^-_{(surface)}$ (left part). The energy axes for both, the potential energy curves and the photoelectron spectra is shown on the left. VEA = difference in energy between the neutral and anionic species, both with the optimized geometric structure and solvation structure of the neutral species. AEA = difference in energy between neutral and anionic species, whereas both are in their own optimized solvation environment and in their optimized geometric structure. VBE = difference in energy between the neutral and anionic species, both with the optimized geometric structure and solvation structure of the anionic species. Energies are relative to the reference energy level $E = 0$ (kinetic and binding energy = 0 at vacuum level). Note, for the sake of simplicity we have omitted zero point energies in (A) and (B).

These points nicely explain experimental findings on electron attachment to dry DNA.[26–29] However, they do not provide insight into electron attachment in aqueous environments which would be crucial for understanding for example DNA damage in any living system because there, DNA is solvated by water. The reason is the difficulty to reasonably relate the potential energy curves in aqueous solution (Figure 4 A, right) to an energy scale of hydrated electrons. This became possible only recently with the determination of VBEs of hydrated electrons.[14a] We suggest that electron attachment is only likely in the region of overlap of the neutral and anionic curves—indicated by the dark shaded area in Figure 4 A (left)—and term this overlap an *electron acceptance window.* Since this window represents the overlap of the wavefunctions of neutral and anionic species, it can also be considered as a Franck-Condon overlap. Employing the concept of Resonant Dissociative Electron Attachment (RDEA), we suggest a way to determine this electron acceptance window and relate it to the VBEs of $e^-_{(aq)}$ and $e^-_{(surface)}$, that is to an energy scale of the hydrated electron. The idea for RDEA is based on dissociative electron transfer and attachment experiments to molecules adsorbed on metal surfaces, polar ice surfaces and dissolved in polar liquids.[29] Although these experiments already suggested the existence of particular resonances for electron transfer and attachment, only now, knowledge of the VBE of $e^-_{(aq)}$ and $e^-_{(surface)}$ together with the RDEA concept allow for a better understanding of these processes.

5. Transient Electrons in Biosystems

The toxic effect of ionizing radiation on genetic material in cells is connected to cancer formation and therapy and it is therefore a vigorous field of research. Ionizing radiation formally induces two different DNA damaging processes in cells: Direct excitation or ionization of the DNA and the reactive attack by secondary species, which are products from the ionization of neighboring (water) molecules. The important secondary species in this context are OH radicals and more or less energetic electrons. Both are formed as products of the ionization of water:[10e]

$$H_2O_{(aq)} \;+\; \text{ionizing radiation} \;\rightarrow\; OH_{(aq)} + e^-_{\;(aq)} + H^+_{\;(aq)} \tag{1}$$

For a long time it was believed that OH radicals play the leading part, while damage induced by secondary electrons was not considered to be significant. Only in the last couple of years has the damaging potential of electrons been clearly revealed.[27–28,30] In the following we apply the RDEA concept to DNA in aqueous environments to shed light on how electrons can break covalent bonds in DNA.

In the following we only consider electron attachment to DNA bases within a DNA fragment, but we propose a general way to determine electron acceptance windows for any species in aqueous solution. We suggest that knowledge of three quantities is sufficient to roughly estimate the electron acceptance windows of a system under investigation: the vertical electron affinity (VEA), the adiabatic electron affinity (AEA) and the vertical binding energy (VBE) of the anion (see Figure 4B and caption).

These quantities define the upper and lower limit of the electron acceptance window (see Figure 4B).

$$\text{upper limit} = |\text{VBE}| - |\text{AEA}| \tag{2}$$

$$\text{lower limit} = |\text{VBE}| - |\text{AEA}| + |\text{VEA}| \tag{3}$$

Gu et al. theoretically determined the required quantities for the bases thymine and cytosine in various DNA fragments.[31] A complete set of data is available for 2′-deoxythymidine-5′-monophosphate (5′-dTMPH) and 2′-deoxycytidine-3′-mono-phosphate (3′-dCMPH) in Table 1.[31a,e]

Recently, Gu et al.[31a,e] found that in aqueous solution, deprotonation of the phosphate group resulting in 5′-dTMP⁻ and 3′-dCMP⁻, respectively, does not have a significant influence (≤ 0.1 eV) on the VEA, AEA and VBE values. This similarity suggests that the quantities are relatively independent of the counter ion in aqueous solution.[31a,e] For electron attachment to the thymine base in larger DNA fragments, such as dApdT, the AEA amounts 2.16 eV which is slightly larger compared to about 2.0 eV in 5′-dTMPH. This may indicate a slight increase in electron-capturing ability for larger DNA fragments.[31c]

Table 1: VEA, AEA, and VBE data for 2′-deoxythymidine-5′-monophosphate (5′-dTMPH) and 2′-deoxycytidine-3′-monophosphate (3′-dCMPH).

2′-Deoxythymidine-5′-monophosphate (5′-dTMPH)[31a]			
VEA	AEA	VBE	electron acceptance window
1.5 eV	2.0 eV	2.5 eV	0.5–2.0 eV
2′-Deoxycytidine-3′-monophosphate (3′-dCMPH)[31e]			
VEA	AEA	VBE	electron acceptance window
1.7 eV	2.2 eV	3.0 eV	0.8–2.5 eV

Figure 4B illustrates the RDEA concept for electron attachment to the thymine base in 5′-dTMPH. The right part of the Figure shows potential energy curves of the neutral and anionic species in aqueous solution. After electron attachment to the base, a glycosidic bond break between base and sugar unit, or a C–O bond break between sugar and phosphate unit can occur. The internuclear distance represents respective C–N and C–O bond distances. While the shape of the curves is qualitative, essential quantitative information for the relative and absolute position of the curves are obtained from the VEA, AEA and VBE values (Table 1). The electron acceptance window is indicated by the white band and can be directly compared to the photoelectron spectra, or the VBEs of $e^-_{(aq)}$ and $e^-_{(surface)}$[14a] shown in the left part of the figure. The ordinate on the left is the common energy scale for the potential energy curves, the photoelectron spectra and also possible kinetic energies of electrons.

The striking point is that surface-solvated electrons (blue spectrum) are in resonance with the electron acceptance windows of DNA bases. Bulk hydrated electrons (red spectrum), however, are almost out of the resonance and therefore a slowly reacting species in this context. The picture is consistent with the recent experimental finding by Wang et al. that "pre-hydrated electrons"—that is optically excited hydrated electrons—rapidly attach to DNA bases.[30]

Importantly, the RDEA picture requires that an electron has to possess a certain matching binding energy in order to successfully attach to a DNA base. This means that electrons with even smaller binding energies, that is with binding energies between 0 eV and the onset of the electron acceptance window and even free electrons with small kinetic energy (see Figure 4B) are less reactive in this context. In aqueous solution, initially free electrons with high kinetic energies are rapidly slowed down by collisions and stepwise hydrated by water molecules, finally resulting in $e^-_{(aq)}$. Importantly, Mucke et al.[32] recently recognized an extra source of particularly low energy electrons in water generated in an autoionization process called intermolecular coulombic decay (ICD). Since the hydration process of low energy electrons (≈ 0 eV) proceeds within a couple of picosecond (max. 5 ps),[10e] this does not leave the electron much time to resonantly attach. In other words, the time span in which the electron possesses a matching binding energy is very short ($<$ 1 ps). It is worthwhile to speculate whether electrons bound to interfaces between water and (hydrophobic) biomolecules have energetic properties similar to the surface-solvated electrons. Such interfaces may temporarily trap electrons at binding energies resonant with DNA bases, extend their lifetime and thus enhance their possibility to resonantly attach. However, not only electrons created by ionizing radiation should be considered in this context. Also electrons scattered in cellular red-ox processes might be a source of damage.

These new findings point the way for further experimental and theoretical studies with the goal to quantitatively understanding electron attachment to different DNA bases and the subsequent reaction paths. This might be also an interesting aspect for the improvement of cancer treatments. In experiments with the anticancer agent cisplatin, Zheng et al. showed that the capture of secondary low energy electrons in a cisplatin-DNA complex, and the following rupture of the DNA backbone, is increased compared to pure DNA.[33] An important point may be that the lowest energy state of the transient anions of cisplatin lies very close to the energy of hydrated electrons at water interfaces.[30a]

6. Role of Solvated Electrons in Atmospheric Chemistry?[34]

The RDEA concept may also be relevant for a recent discussion in the field of atmospheric chemistry. The well established and dominant mechanism for ozone depletion in the lower stratosphere involves radical species and heterogeneous photochemistry at the ice interfaces of polar stratospheric clouds (PSCs).[35] About 10 years ago, an additional mechanism for ozone depletion has been proposed on the basis of laboratory experiments.[29a,b,36] As depicted in Figure 5, the idea is that cosmic rays generate surface hydrated electrons ($e^-_{(surface)}$) at PSC interfaces via Equation (4).

$$H_2O + \text{cosmic rays} \rightarrow e^-_{(surface)} + H_3O^+ + OH \qquad (4)$$

These electrons may then attach to molecules adsorbed on the surface of the ice particles, such as organic molecules containing chlorine and fluorine atoms (CFCs), being abundant in the lower polar stratosphere and which adsorb on ice particles.[29b]

The RDEA results in bond breaking and release of Cl^- (Figure 5).

$$e^-_{surface} + RCl \rightarrow RCl^{*-} \rightarrow Cl^- + R \qquad (5)$$

From experimental data and estimates on the impact of a water ice surface on the electronic energies of adsorbed molecules, Lu et al. concluded that the electron resonance for CFCs ranges from about 1 to 1.5 eV binding energy.[29a,b] The left part of the Figure 5 B compares this acceptance window—represented by the white band—with the VBEs of $e^-_{(aq)}$ and $e^-_{(surface)}$. It may be reasonable to assume that the VBE of electrons on the surface of ice is close to the VBE of $e^-_{(surface)}$ measured in Ref. [14a]. This assumption is in agreement with cluster data for isomer II in Figure 2 and recent experimental and theoretical results on water ice surfaces.[21] The significant overlap of the white band with the photoelectron spectrum of $e^-_{(surface)}$ (blue spectrum on the left axis) indicates that $e^-_{(surface)}$ may be in resonance with the electron acceptance window of the target molecules. The lifetimes of electrons bound to the surface of ice range up to minutes,[21] which makes electron attachment to adsorbed molecules and subsequent reactions likely.

While such a step generating chloride anions and radicals seems to be very plausible with the above argumentation, it is not clear at all how this may affect any ozone balance. The question how the resulting Cl^- is subsequently converted into the harmful Cl species yet remained elusive.[37]

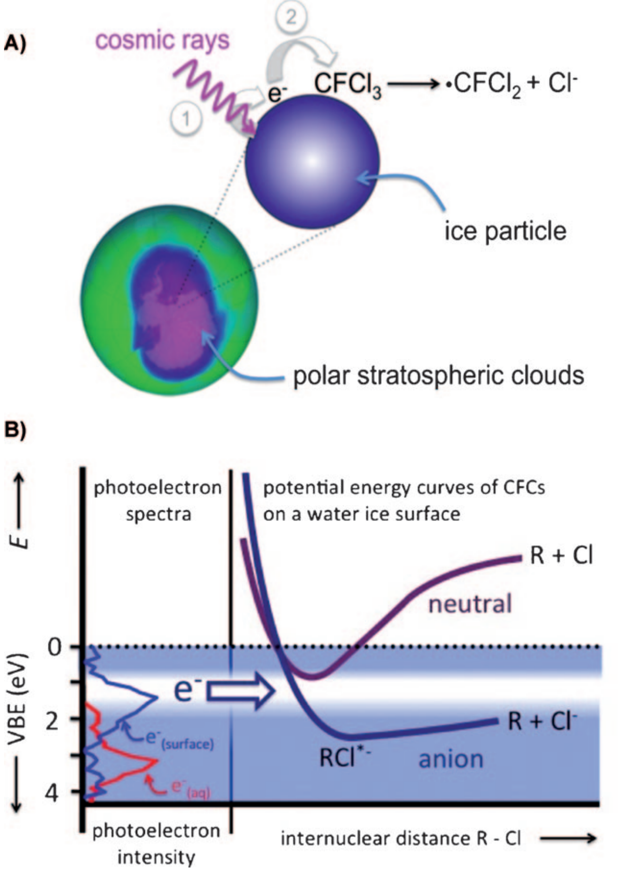

Figure 5. A) Cartoon of the initial steps of a reaction mechanism discussed in the context of the Antarctic ozone hole. 1) Ionizing cosmic rays generate surface-solvated electrons on the ice particles. 2) These electrons attach to chlorine-containing molecules (here: $CFCl_3$) adsorbed on the ice surface and thereby induce the splitting of a molecular bond. B) RDEA picture for electron attachment to chlorine-containing molecules on the surface of water ice. Shown is the situation for electron attachment to CFCs. Similar situations might be expected for many other Cl-, Br- and I-containing molecules.[29a,b]

We suggest that the Cl^- may subsequently react with the OH formed nearby in reaction (4).[38]

$$OH + Cl^- \rightarrow (OH\cdots Cl^-) \rightarrow OH^- + 1/2\,Cl_2 \qquad (6)$$

The simple reaction sequence (4)–(5) followed by reaction (6) discovered by Knipping et al.[38] is an efficient mechanism for a cosmic ray driven electron model for ozone depletion. It is important to note that the above reactions are temperature dependent and rely on sufficient OH concentrations at the ice surfaces. However, we want to emphasize, that this mechanism is heavily debated and may only contribute to a small extent to the ozone loss in the atmosphere.[39] However, if it plays a role in ozone hole formation, our new findings certainly show the direction for further investigations.

7. Conclusions and Outlook

The observation of two significantly different ionization potentials of the solvated electron in liquid water is an important milestone in the long and entangled history of the hydrated electron. The notion of a single equilibrated hydrated electron species in water, which pervades all previous experimental and theoretical research in the condensed phase, seems to be an oversimplification.

While the existence and features of the two species—the bulk hydrated electron and the surface hydrated electron—have been discussed and energetically characterized the molecular structure of both remains unclear. It is, for example, not clear at all how the recent theoretical results of Larsen et al., who suggest that excess electrons in bulk water reside in a region of enhanced water density rather than in a cavity,[9e] are related to the recent photoelectron emission studies and the measured binding energies. Judging the available experimental results, we also cannot support the picture of the hydrated hydronium (H_3O) radical as a charge-separated species in water. We anticipate, however, that the photoelectron spectra in our hands are fingerprints of the species' structure and electron density and they may indeed already be the key to unambiguously answer these questions soon. We will have to wait for theory to make a clear assignment via calculation of photoemission spectra of the systems under consideration in large hydrogen bound water networks with sufficient precision. The measured binding energies provide important reference values for electron transfer processes in aqueous solution, in particular for resonant dissociative electron attachment (RDEA). The binding energies of $e^-_{(aq)}$ and $e^-_{(surface)}$ together with the RDEA model allow us to understand under which conditions electrons in aqueous solution can break strong covalent bonds in systems like DNA or CFCs. In a similar way, the RDEA concept and the new data may enrich our understanding of many other processes involving "stray", excess or free electrons in aqueous environments.[40]

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