

ULTRAFAST SPECTROSCOPY

Ejecting electrons from water

The interactions of electrons and water molecules are not just of great fundamental interest but are also studied to understand the role electrons have in damaging biomolecules. Now using ultrafast photoelectron spectroscopy, key details about the energy and lifetime of the hydrated electron in bulk and at an interface have been determined.

Daniel M. Neumark

The hydrated electron, an electron in aqueous solution, has captured the attention of scientists since it was discovered in 1962 as a product of water radiolysis¹. Many properties of the hydrated electron are consistent with the 'cavity' model, in which it resides in a non-spherical solvent cavity with an average radius of ~ 2.4 Å and is stabilized by hydrogen-bonding interactions with, on average, six water molecules². This species plays a major part in radiation chemistry and biology: hydrated electrons can be formed by ionizing radiation in living cells, and their high reactivity leads to free-radical formation with significant potential for genetic damage. Moreover, hydrated electrons may be able to attack DNA directly, resulting in single- and double-strand breaks.

On a more fundamental level, the hydrated electron represents the simplest quantum mechanical solute, motivating many studies of its spectroscopy, reactivity and relaxation dynamics. This research in aqueous solution has been complemented by parallel efforts in the gas phase on water cluster anions, $(\text{H}_2\text{O})_n^-$, in which an electron is bound to a known number (n) of water molecules³. Experimental and theoretical work on these clusters has provided valuable insights into the nature of the hydrated electron, but has also raised the important conceptual issue of how the properties of finite clusters can be extrapolated to bulk aqueous solutions.

Writing in *Nature Chemistry*, Bernd Abel and colleagues report⁴ the first measurements of the energy needed to eject a hydrated electron from bulk liquid water into the vacuum without a change in solvent configuration, that is, its vertical binding energy (VBE). This experiment represents a breakthrough in our understanding of hydrated electrons on several fronts. First, the VBE itself, found to be 3.3 eV, is a key property that has been estimated but never directly determined before. It represents a sensitive probe of the electron-solvent interactions that govern

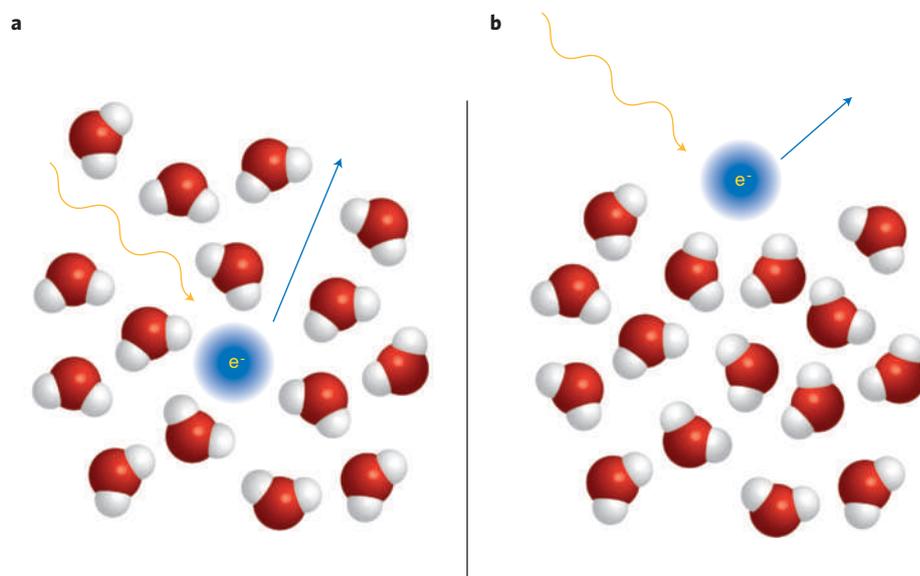


Figure 1 | Schematic showing the ejection of a hydrated electron (e^-) from the bulk of a water solution and at an interface. **a,b**, Hydrated electrons were ejected (blue arrow) using a delayed femtosecond EUV pulse (orange arrow) formed by high-harmonic generation. The VBEs in bulk (**a**) and at the interface (**b**) were found to be 3.3 eV and 1.6 eV, respectively.

many of the attributes of the hydrated electron and places it and its excited states on an absolute scale relative to the vacuum. Second, the experiment shows evidence for an alternative type of hydrated electron with a VBE of 1.6 eV, which is attributed to an electron bound at the surface of liquid water. Third, the results represent a 'missing link' between the hydrated electron and $(\text{H}_2\text{O})_n^-$ clusters. VBEs of water cluster anions were first reported by Bowen *et al.*⁵ and extrapolated to the infinite size limit to estimate the VBE of bulk hydrated electrons, but the validity of such an extrapolation had not been confirmed until now.

Abel and colleagues measure electron binding energies with photoelectron spectroscopy (PES), in which a sample is irradiated with light of a known frequency and the kinetic energy of the ejected photoelectrons is measured. The binding energy of the electron to the sample is then given by subtracting the measured

photoelectron kinetic energy from the incident photon energy.

Nearly all PES experiments have been performed on gas-phase systems or on solid surfaces. PES of liquids is complicated by the fact that photoelectron energy analysers, regardless of design, work best under high- or ultrahigh-vacuum conditions, seemingly incompatible with the many interesting liquids that have substantial vapour pressures, such as water. PES of water and ions in aqueous solution was only made possible through the development of liquid water microjets by Faubel⁶. These jets are formed by forcing water at high pressure through an orifice into a vacuum chamber, resulting in a collimated liquid jet with a diameter of 30 μm or less that undergoes laminar flow for 5–10 mm before breaking up into droplets. The surface area of the jet is small enough to ensure that low vacuum chamber pressures in the ionization region are attainable with reasonably sized pumps.

The experiments of Abel and co-workers would not have been possible without vacuum-compatible water microjets.

Abel and colleagues, in their experiments, generate hydrated electrons within a water microjet and then eject them using two individual femtosecond laser pulses separated by a known time delay. Two schemes were used to generate hydrated electrons: two-photon ionization of a pure-water microjet by an ultraviolet laser pulse or one-photon ionization of ferrocyanide anions ($\text{Fe}(\text{CN})_4^{2-}$) from $\text{K}_2\text{Fe}(\text{CN})_4$ dissolved in the jet. Photoelectrons were ejected using a delayed femtosecond extreme-ultraviolet (EUV) pulse formed by high-harmonic generation. These two generation methods yielded markedly different results: the VBE of hydrated electrons from the pure-water jet was 1.6 eV, whereas it was 3.3 eV from the $\text{K}_2\text{Fe}(\text{CN})_4$ solution.

Abel and colleagues explain the two measured binding energies in terms of a key factor in liquid-jet photoelectron spectroscopy: the inelastic mean free path (IMFP) of the photoelectron. Photoelectrons formed in any condensed-phase media can lose kinetic energy to the environment through inelastic scattering; the IMFP is a measure of how far the photoelectrons can travel before this effect becomes appreciable. The IMFP is strongly dependent on the nascent kinetic energy of the electron. Under the conditions of these experiments, where the nascent kinetic energy is about 36 eV, the IMFP is less than 5 Å (it is considerably longer for much slower or much faster electrons)⁶. Hence, the experiments were much more sensitive to photoelectrons generated at or very near the surface of the jet than to interior electrons.

As a result, the photoelectron spectrum — and thus the VBE of 1.6 eV — measured in the pure-water experiments is attributed to electrons bound to the surface of the liquid jet. In contrast, because $\text{Fe}(\text{CN})_4^{2-}$ anions are believed to be repelled from the liquid/vapour interface, photoelectrons from ionization of this species should originate from the interior rather than the surface of the liquid jet, and the resulting photoelectrons with 3.3 eV binding energy are assigned to bulk hydrated electrons. This value agrees well with the earlier estimate⁵ based on photoconductivity measurements in liquid water.

The comparison of these results to the VBEs of water cluster anions is illuminating. As shown in Fig. 3 of the Article from Abel and co-workers, several classes of $(\text{H}_2\text{O})_n^-$ clusters have been observed previously, and extrapolation of the VBEs for the two observed isomers — simply named isomers I and II — to $n \rightarrow \infty$ yields binding energies of ~3.5 and 1.6 eV, respectively. Isomer II clusters were previously attributed to clusters with surface-bound electrons⁷, and this assignment is strongly supported by the new liquid-jet experiments. The liquid-jet binding energy of 3.3 eV under conditions favouring detection of interior hydrated electrons is more intriguing. There has been considerable discussion in the literature as to whether the excess electron in isomer I clusters is internally or surface-solvated^{3,8,9}, and the agreement of the VBEs extrapolated from isomer I with the results of the liquid jet is consistent with internal solvation, at least for the largest isomer I clusters with $n \geq 50$. However, one must still exercise caution given that cluster VBEs are not a definitive structural probe.

The experiments of Abel and colleagues leave several questions open for future investigation. It is not clear, for example, what the relative concentrations of bulk and surface-bound electrons are in the liquid jet after solvent (or solute) ionization. Photoelectron ejection with an EUV laser pulse is, as mentioned above, very sensitive to electrons at or near the jet surface, so the extent of surface binding is likely to be over emphasized in this experiment. Indeed, preliminary experiments in our laboratory using a much lower energy to eject photoelectrons, where the IMFP is longer by at least an order of magnitude, show no evidence for the lower-binding electrons at the jet surface. It is therefore difficult to evaluate the authors' suggestion these surface-bound electrons will affect important processes in nature such as electron attachment to DNA and other molecules. □

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References

- Hart, E. J. & Boag, J. W. *J. Am. Chem. Soc.* **84**, 4090–4095 (1962).
- Rosicky, P. J. & Schnitker, J. *J. Phys. Chem.* **92**, 4277–4285 (1988).
- Neumark, D. M. *Mol. Phys.* **106**, 2183–2197 (2008).
- Siefermann, K. R. *et al. Nature Chem.* **2**, 274–279 (2010).
- Coe, J. V. *et al. J. Chem. Phys.* **92**, 3980–3982 (1990).
- Winter, B. & Faubel, M. *Chem. Rev.* **106**, 1176–1211 (2006).
- Verlet, J. R. R., Bragg, A. E., Kammrath, A., Cheshnovsky, O. & Neumark, D. M. *Science* **307**, 93–96 (2005).
- Turi, L., Sheu, W.-S. & Rosicky, P. J. *Science* **309**, 914–917 (2005).
- Roscioli, J. R., Hammer, N. I. & Johnson, M. A. *J. Phys. Chem. A* **110**, 7517–7520 (2006).

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SUPRAMOLECULAR CAPSULES

Under control

Macrocyclic compounds can serve as hosts for smaller organic molecules, but precise control over the uptake and release of the guests remains challenging. Now, a host–guest system has been built that responds to the addition of metal ions, showing promise for drug-delivery applications.

Werner M. Nau

In the science fiction movie *Fantastic Voyage*, a whole submarine transporting a medical team is shrunk to microscopic size and injected into the brain of a scientist to remove a blood clot. Chemists take a different approach to delivering drugs, but the ultimate idea — to use tiny vehicles to carry drugs to their targets and release them in a controlled manner — is the same. Now,

writing in *Journal of the American Chemical Society*, Achikanath Bhasikuttan and colleagues demonstrate that guest molecules can be taken up by, or released from, simple synthetic organic hosts at will through the addition of metal cations to the solution¹. These hosts therefore show promise as submarine-like carriers that could deliver encapsulated drugs.

The pumpkin-shaped organic hosts used by Bhasikuttan and colleagues are known as cucurbiturils. These molecules were first prepared by the German chemist Behrend more than 100 years ago²; they were re-discovered in the 1980s, structurally identified as macrocyclic molecules³, and subsequently isolated in different sizes^{4–6}. The homologue investigated in this study