

ers used a large data set involving 56 New Guinea tree species (4) to estimate the number of herbivorous canopy beetle species, and their degree of effective specialization (5).

For most of the links in Erwin's chain, Hamilton *et al.*'s probability distributions do not differ much from Erwin's single values. Erwin estimates 40% of canopy arthropods to be beetles (mirroring the global fraction for all arthropods), while Hamilton *et al.* estimate an equal probability that the percentage is between 25 and 66%. Likewise, the estimated total number of tropical tree species differs only slightly: Erwin takes the total to be 50,000, whereas Hamilton *et al.* estimate from 43,000 to 50,000 tropical tree species.

The big difference, however, lies in the use of the much larger data set for the 56 New Guinea tree species. This leads, in effect, to the conclusion that the average beetle is less specialized—feeds on more different tree species—than suggested by Erwin, and thus to overall estimates for the total number of tropical arthropod species that are far lower than Erwin's 30 to 100 million.

In model A, for instance, the probability distribution suggests that the total is around 3.7 million, with a 90% probability that the number is between 2.0 and 7.4 million. Model B—essentially a refinement of model A that puts greater weight on the New Guinea tree data (6)—suggests 2.5 million tropical arthropod species, with a 90% probability that the number is between 1.1 and 5.4 million. Both models assign a very low probability (on the order of  $10^{-3}$ ) to Erwin's higher estimates.

Overall, these conclusions imply that around two-thirds of all arthropod species still await discovery and description. In part, this sorry state of affairs reflects inefficient distribution of taxonomic attention, which is disproportionately directed to the more appealing furry and feathery vertebrates. It also often reflects a tendency for funding agencies, in the United Kingdom and elsewhere, to view research on basic systematics and taxonomy as insufficiently sexy, or not conforming to simplistic Popperesque notions of falsifiable hypotheses (7). My guess is that the hypothetical aliens would take a dim view of all this.

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4. Effective specialization,  $f_k$ , is calculated as  $f_k = \sum_i (1/i) p_k(i)$ , where  $p_k(i)$  is the proportion of species, such as herbivorous beetles, using tree species  $k$ , out of a total of  $i$  different tree species used; see (3).
5. V. Y. Novotny *et al.*, *Nature* **416**, 841 (2002).
6. Model B acknowledges that some New Guinea tree genera are much more speciose than others. In three cases among the 56-tree data set (4), Hamilton *et al.* had more than one tree species per genus; they used a representative host and its associated beetle species (with separate randomization for each species).
7. See paragraph 5.4 from the UK House of Lords' Science and Technology Select Committee, 5th Report (2007–2008), *Systematics and Taxonomy: Follow-up* (HL Paper 162), which found that "The evidence we received about the willingness of the Research Councils to fund taxonomy was confused." The government's response said that "Research proposals including classical taxonomic approaches may have the best chance of success if they take account of (a) the hypothesis testing science that typifies responsive mode grants, ..." (chapter 5, paragraph 7.19, item 6). For further discussion see [www.publications.parliament.uk/pa/ld200708/ldselect/stech/162/162.pdf](http://www.publications.parliament.uk/pa/ld200708/ldselect/stech/162/162.pdf).

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## CHEMISTRY

# Downsizing the Hydrated Electron's Lair

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The hydrated electron is a key reactive intermediate in many chemical reactions, including those responsible for the biological effects of radiation. When water molecules (or molecules dissolved in it) encounter radiation, they ionize and emit electrons that can react with biomolecules, often in deleterious ways. Despite being so reactive, these electrons can have appreciable lifetimes because they are stabilized by surrounding water molecules. The hydrated electron,  $e_{aq}^-$ , has been understood for more than 50 years in terms of a cavity model in which the electron is excluded from regions where the water molecules have appreciable electron density, and the void or cavity it occupies is stabilized by the interaction of the charge with the dielectric medium outside the void (1–3). On page 65 of this issue, Larsen *et al.* (4) challenge both of these tra-

ditional views with a new model in which the  $e_{aq}^-$  not only penetrates the charge distribution of the water molecules but also is associated with a region of enhanced water density rather than a cavity. The electron wave function is distributed like tentacles that wrap around and between the water molecules.

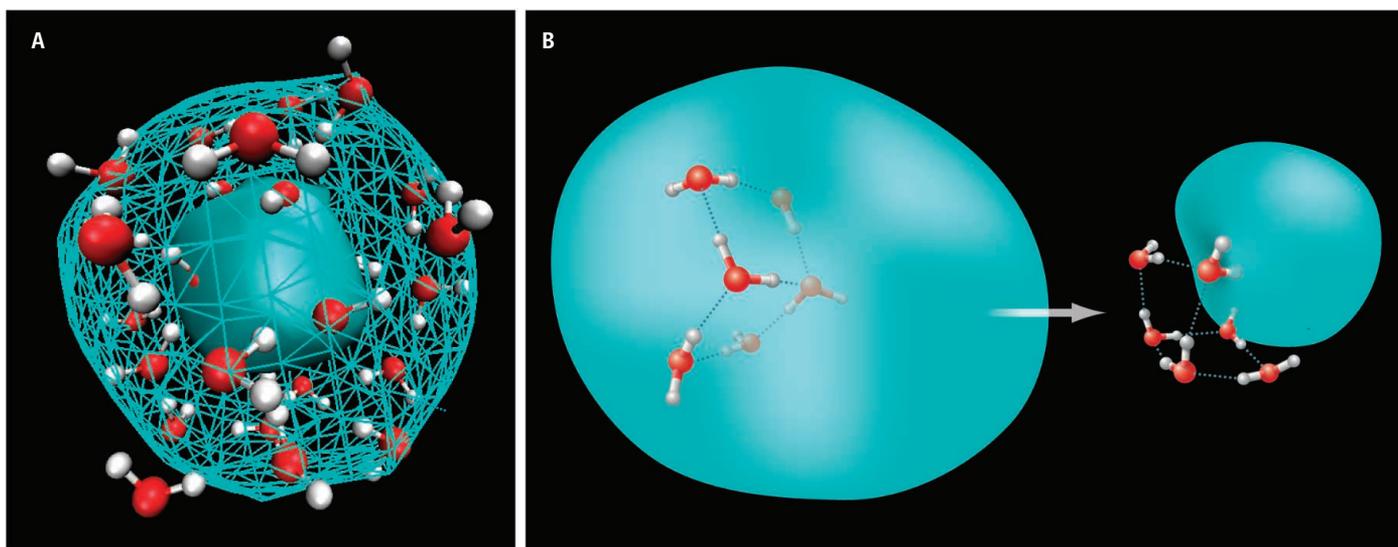
One challenge in definitively establishing the structure of  $e_{aq}^-$  is that it is observed experimentally in indirect ways. The characteristic signature of  $e_{aq}^-$  is its broad asymmetric absorption band peaking at 1.7 eV (in the red region of the visible spectrum) that is the result of  $e_{aq}^-$  forming an excited state. Analysis of this band yields a "radius of gyration" for  $e_{aq}^-$  of about 2.5 Å (5), which is generally taken to be the radius of the cavity (the volume is equivalent to about two water molecules). The first hydration shell of  $e_{aq}^-$  is most often viewed as having multiple water molecules (typically six) pointing OH groups, which bear H atoms with partial positive charge, toward the center of the cavity.

A new model for free electrons in water suggests that they are localized in regions of enhanced rather than depleted water density.

This geometry creates a sizable attractive potential that stabilizes the excess electron. Previous molecular dynamics simulations of  $e_{aq}^-$  have basically supported the cavity model. However, one persistent and troubling aspect of the cavity model is its inability to account for the incredibly fast electronic relaxation kinetics of the excited state of the excess electron. These studies use ultrafast laser pulses to create and study the excited state and have been done in liquid water as well as in model studies based on anionic water clusters (6).

The model of Larsen *et al.* can account for a wide range of properties of the hydrated electron, including the location of the absorption maximum and the excited-state dynamics, in a scenario that does not accommodate the electron in a cavity (see the figure, panel A). These new simulations use a recently developed model for the potential between an electron and a water molecule that has stronger attractive forces near the O atom relative to the potentials used in ear-

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**Wet electrons.** (A) The simulations by Larsen *et al.* find that the hydrated electron is in intimate contact with water molecules within the radius of gyration of the electron. Here, a representative configuration shows all water molecules within 6 Å of the center of mass of the electron. (B) Model studies on water clusters

provide additional insights into the hydrated electron in solution. Depicted here is the rearrangement of a cluster of six water molecules before and after it captures an electron. The surfaces depicting the distribution of the excess electron enclose 50% of the charge.

lier simulations of  $e_{aq}^-$ . Stronger attractions might appear to be counterintuitive because the O atom of a water molecule carries a partial negative charge, which would create a repulsive interaction for an electron at short distances. However, at very short distances (1.5 Å), where the excess electron penetrates the charge distribution of the O atom, it begins to feel an attraction from the oxygen atom nucleus.

Only a small amount of the excess electron density is calculated to fall within 1.5 Å of the O atom nucleus, but it appears to be fundamental in explaining the absence of the cavity in the simulations of Larsen *et al.* An important aspect of their contribution is that it highlights how our qualitative picture of the hydrated electron profoundly depends on subtle refinements in the electronic potentials used to describe interactions. This new model is most intriguing, but we caution that it is probably not the final word for this challenging and fascinating problem. In particular, it does not account for the states responsible for the high-energy tail observed in the electronic absorption spectrum. Such details may seem like loose ends, but an accurate description of the hydrated electron is important in other contexts. For example,  $e_{aq}^-$  serves as a paradigm for mapping complex many-body problems, where electron correlation effects are important, into simpler one-electron models.

One example of the challenges involved in accurately describing  $e_{aq}^-$  under ambient conditions is the ongoing controversy concerning the related problem of surface ver-

sus interior binding of an excess electron trapped on a cold cluster of neutral water molecules in the gas phase. At the smallest cluster sizes (two to six water molecules), the molecules form network structures that have been unambiguously established through a combination of vibrational spectroscopy and electronic structure calculations (7, 8). Even though the excess electron is generally viewed as being bound to the surfaces of these small clusters, it causes dramatic rearrangements of the supporting water networks. The rearrangement of a neutral  $(\text{H}_2\text{O})_6$  cluster after electron attachment (9) is shown in panel B of the figure.

Several research groups have extended the cluster studies to much larger sizes (up to 200 or so) (10, 11). In principle, molecular features of  $e_{aq}^-$  might be uncovered by extrapolating the cluster behavior to bulk asymptotes, but there are complications. For such an extrapolation to be meaningful, the cluster anions would have to have the excess electron localized in the interior rather than on the surface of the cluster. Although both the Neumark (10) and Issendorff (11) groups assigned the high electron binding species observed in their experiments to interior states (for clusters with 20 or more molecules), simulations from two theory groups (12, 13) have concluded otherwise. A major issue, which has been noted by these and other researchers, is that under the experimental conditions (temperatures below 150 K), the clusters are almost certainly solidlike. As such, the anions formed under typical experimental conditions are likely meta-

stable, adopting structures quite different from the hydrated electron in bulk water.

The study of Larsen *et al.* dramatically illustrates how small changes in the model potentials, at distances thought to be irrelevant, can drastically alter the structure of  $e_{aq}^-$ . Outstanding issues still remain, and a wide range of theoretical and experimental studies will be needed as we inch closer to unveiling a robust, consensus molecular description of the hydrated electron.

#### References and Notes

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