A free electron can be trapped by solvent reori-
entation in polar solvents such as ammonia (I) or water (2). These “solvated” electrons play an
important role in condensed phase chemistry,
including radiation chemistry, electron transfer,
and charge-induced reactivity. A microscopic
understanding of the electron-solvent and sol-
vent-solvent interactions that govern electron
solvation is therefore a fundamental and chal-
lenging problem. These considerations have
motivated femtosecond time-resolved studies
that have demonstrated rich and complex dy-
namics after electronic excitation of electrons in
water (3, 4).

To gain a complementary perspective on
this problem, we studied solvated electron
dynamics in finite clusters and compared
these results with our understanding of bulk
solvation phenomena. We used two-photon
anion femtosecond (10−15 s) photoelectron
spectroscopy (FPES) (5, 6) to study electron
solvation dynamics in the mass-selected anion
clusters I−(D2O)n and I−(H2O)n in order to
address the following questions: (i) What
is a minimum solvent cluster size needed
to solvate an electron? (ii) What is a typical
time scale for solvent reorientation in a cluster?
(iii) What type of solvent motion is involved
in electron solvation dynamics?

Aqueous solutions of I− exhibit broad
external electronic bands in the ultraviolet (UV)
corresponding to electron ejection from I− into
the solvent (7), known as “charge-transfer-
solvated” (CTTS) states. Excitation of these
states is an elegant means of generating sol-
vated electrons, as was first demonstrated by
Jortner (8). The dynamics of these states have
been investigated by Eisenthal (9), Gaudeul
(10), Bradforth (11), and their co-workers, all
of whom excited the CTTS states to inject an
electron into the water and then followed the
subsequent electron solvation dynamics by
femtosecond absorption spectroscopy. These
experimental studies along with simulations
by Sheu and Rossky (12) and Staib and Bor-
gis (13) show that excitation of the lowest
energy CTTS band results in the generation of
fully solvated electrons on a 200-fs time scale
(11). Once generated, these electrons
thermalize with the solvent molecules, and
some are then lost through geminate recom-
bination with the neutral halogen atom over a
time scale of tens of picoseconds.

The issue of how the CTTS bands mani-
fest themselves in finite clusters was first
addressed in experiments by Johnson and
co-workers (14), in which a diffuse absorp-
tion band was seen just above the detachment

**Reports**

Electron Solvation in Finite Systems: Femtosecond Dynamics of Iodide (Water) Anion Clusters

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Electron solvation dynamics in photoexcited anion clusters of I−(D2O)n and I−(H2O)n were probed by using femtosecond photoelectron spectroscopy (FPES). An ultrafast pump pulse excited the anion to the cluster analog of the charge-transfer-to-solvent state seen for I− in aqueous solution. Evolution of this state was monitored by time-resolved photoelectron spectroscopy using an ultrafast probe pulse. The excited n = 4 clusters showed simple population decay, but in the n = 5 and 6 clusters the solvent molecules rearranged to stabilize and localize the excess electron, showing characteristics associated with electron solvation dynamics in bulk water. Comparison of the FPES of I−(D2O)n with I−(H2O)n indicates more rapid solvation in the H2O clusters.

**References**


6. Femur and humerus length were virtually complete in A.L. 288-1 [D. C. Johanson et al., Am. J. Phys. Anthropol. 87, 403 (1982)]. In BOU-VP-12/1, the humerus is preserved from the intersection of the medial terminus of the neck with the (missing) femoral head (proximal) to a point on the medial supracondylar line. Humerus length is measured from the surface just superior to the gastrocnemius impression (distally). This distance was measured in a sex- and species-balanced sample of chimpanzees and bonobos (de Gruyter, New York, 1988); A. C. Walker, R. E. Leakey, J. M. Harris, F. H. Brown, Nature 322, 517 (1986); H. M. McHenry, in Contemporary Issues in Human Evolution, W. E. Meikle, F. C. Howell, N. G. Jablonski, Eds. (California Academy of Sciences, San Francisco, 1996), pp. 77-92.

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threshold for $\Gamma^{-}(\text{H}_2\text{O})_n$ clusters ($n = 1$ to 4). As the number of water molecules increases, this band shifts to the blue and appears to converge toward the lower energy CTTS band in aqueous solution. These cluster analogs to the CTTS band most likely correspond to excitation of the electron from an orbital localized on the $\Gamma^{-}$ into a more delocalized state supported by the network of water molecules in the cluster.

The work reported here builds on these spectroscopic measurements in that we use FPES to perform time-resolved measurements of the microscopic electron solvation dynamics subsequent to excitation of the CTTS cluster analog bands. In these experiments, mass-selected clusters of $\Gamma^{-}(\text{H}_2\text{O})_n$ are electronically excited with a UV pump laser pulse (263 nm and 4.71 eV) of $\sim 100$ fs duration. The upper state evolves for a fixed time interval and is then photodetached by a probe laser pulse (790 nm and 1.57 eV) of similar duration. The resulting photoelectron (PE) spectrum provides a “snapshot” of the upper state. Measurement of the PE spectrum at a series of pump-probe delay times thus provides a detailed probe of the electron and solvent dynamics in the electronically excited state. The overall experiment is described in detail elsewhere (5, 15, 16).

Results are presented here for $\Gamma^{-}(\text{D}_2\text{O})_n$ and $\Gamma^{-}(\text{H}_2\text{O})_n$ ($n = 4$ to 6). Our results suggest that for all the clusters, the electron is photoexcited into a dipole-bound state supported by the network of water molecules. In the $n = 4$ cluster, this state decays rapidly by vibrational autodetachment. However, the $n = 5$ and $n = 6$ clusters undergo solvent rearrangement that stabilizes the excess electron. These systems are therefore the simplest in which the cluster analog of electron solvation occurs.

FPE spectra for $\Gamma^{-}(\text{D}_2\text{O})_4$–6 are shown in Fig. 1, A through C; those for $\Gamma^{-}(\text{H}_2\text{O})_n$ are shown in Fig. 1D. Each plot shows a two-dimensional contour plot of PE intensity versus electron kinetic energy (eKE) and pump-probe delay. Figure 2 shows the average eKE as a function of time for these four clusters as well as for $\Gamma^{-}(\text{H}_2\text{O})_4$ and $\Gamma^{-}(\text{H}_2\text{O})_6$.

In the FPE spectra of $\Gamma^{-}(\text{D}_2\text{O})_4$ (Fig. 1A), the intensity rises to a maximum during the first 200 fs, and during this time the average eKE decreases by about 0.07 eV. By 200 fs, the contour plot in Fig. 1 shows a slight dip in maximum intensity around 500 fs before rising at longer times. The shift in eKE is accompanied by an increase in the overall width of the spectrum, from 0.27 eV at 180 fs to 0.34 eV at 800 fs. Similar trends are seen for $\Gamma^{-}(\text{D}_2\text{O})_6$. The main differences are that the shift toward lower eKE (from 1.33 to 1.05 eV) is slower, with a time constant of 560 fs. The contour plot in Fig. 1 shows a slight dip in maximum intensity around 500 fs before rising at longer times. The signal ultimately decays with a time constant of about 37 ± 1 ps. The shift in eKE is accompanied by an increase in the overall width of the spectrum, from 0.27 eV at 180 fs to 0.34 eV at 800 fs. Similar trends are seen for $\Gamma^{-}(\text{D}_2\text{O})_6$. The main differences are that the shift toward lower eKE (from 1.33 to 1.05 eV) is slower, with a time constant of 560 fs. The contour plot in Fig. 1 shows a slight dip in maximum intensity around 500 fs before rising at longer times. The signal ultimately decays with a time constant of about 37 ± 1 ps.

Comparison of $\Gamma^{-}(\text{D}_2\text{O})_4$ and $\Gamma^{-}(\text{H}_2\text{O})_n$ results in Figs. 1 and 2 reveals the effects of isotopic substitution. The $\Gamma^{-}(\text{H}_2\text{O})_n$ clusters are all shifted by 20 meV toward higher eKE, a shift attributed to zero-point energy effects. We find virtually no difference in the time evolution of the $n = 4$ clusters. For $n = 5$ and $n = 6$, the shift toward lower electron energy begins about 100 fs earlier in the $\text{H}_2\text{O}$ clusters. The time constant for this shift is the same for the $n = 5$ clusters but is about 17% lower for $\Gamma^{-}(\text{H}_2\text{O})_4$ (470 fs) than for $\Gamma^{-}(\text{D}_2\text{O})_4$.

The most important feature of these results is the marked change in the time evolution of the spectra in going from the $n = 4$ to $n = 5$ clusters. The results suggest that simple population decay of an excited state occurs for $n = 4$, whereas for $n \geq 4$ a severe reorganization within the cluster must take place. The initial excitation and subsequent dynamics responsible for these effects are considered below.

Ground state structures for $X^{-}(\text{H}_2\text{O})_{n=4}$ clusters have been calculated by Jortner and co-workers (17), Perera and Berkowitz (18), and Xantheas (19). These structures all show the halide bound to a water cluster, with the water molecules oriented so as to maximize their interaction with each other and with the halide anion. For example, in the solvent network for $X^{-}(\text{H}_2\text{O})_4$, each water molecule binds to another with one hydrogen bond and simultaneously offers the other dangling hydrogen to the anion, to form a ring of water molecules, each with an H atom pointing toward the halide. As more waters are added, the $X^-$ is predicted to remain on the “surface” of the water cluster, although this point is somewhat controversial [based on comparison with PE spectra of $\Gamma^{-}(\text{H}_2\text{O})_n$ clusters obtained by Cheshnovsky and co-workers (17, 20)].

Johnson and co-workers have pointed out that the orientation of the water molecules induced by the halide results in a high dipole moment, estimated at $\mu = 4.4$ debye (D) for the water network in $\Gamma^{-}(\text{H}_2\text{O})_4$ for example (14). Neutral molecules with a dipole moment larger than $\sim 2$ D can bind an electron in a “dipole-bound” state (27)—the negative ion analog of a Rydberg state, in which the orbital for the excess electron is exceptionally diffuse. It is therefore reasonable to assign the upper state initially generated by the pump pulse to a short-lived state of the form $\text{I}(\pi_2)^{2}\pi^{-}\Gamma^{-}(\text{H}_2\text{O})_n$, in which the...
electron is transferred from the halide to a dipole-bound state of the solvent network.

The FPE spectra for $I^-(D_2O)_4$ and $I^-(H_2O)_4$ indicate that the initially excited electronic state undergoes population decay, with no other dynamics occurring. The pump photon energy, 4.71 eV, lies well above the adiabatic detachment energy of $I^-(D_2O)_4$, 4.36 eV (22), so decay of the excited state by electron emission is certainly energetically accessible. Moreover, the PE spectrum is centered at 1.38 eV, whereas the probe photon energy is 1.57 eV, so the vertical detachment energy for the excited state is 0.19 eV. Excitation at the pump wavelength thus results in an excited electronic state with $\sim 0.45$ eV of vibrational energy. We attribute the decay of this state to vibrational autodetachment to form $I^-(F_{25/2})(D_2O)_4 + e^-$. The time evolution of the FPE spectra for $n = 5$ and $n = 6$ clusters shows that complex dynamics occur after initial photoexcitation into the dipole-bound state. The lowering of the mean electron energy by $\sim 0.3$ eV during the first picosecond implies that the excess electron is stabilized by solvent motion on this time scale. Moreover, the nonmonotonict variation of integrated electron intensity suggests that the nature of the orbital in which the excess electron resides changes significantly over the time scale of this intensity variation. Overall, we attribute these trends to solvent isomerization from the initial dipole-bound state to a second more stable conformer with the character of a partially solvated electron.

Figure 3 presents a qualitative potential energy surface diagram consistent with our results for the $n = 5$ and $n = 6$ clusters. The dipole-bound state discussed above is resonantly excited by the pump pulse at 263 nm, and subsequent dynamics are probed by photodetachment with the time-delayed probe pulse at 790 nm. As shown by Bowen and co-workers (23), photodetachment of a dipole-bound state results in minimal Franck-Condon activity, which is consistent with the narrow width of the PE spectrum at short delay times. If isomerization into a lower energy cluster conformer then occurs, electronic energy is converted into vibrational energy. For a cluster of this size, this vibrational energy should be dispersed over many vibrational modes. The relatively small broadening accompanying the electron energy shift indicates only slightly more Franck-Condon activity in the partially solvated state than in the initially excited state. Thus, the excess vibrational energy of this state largely remains as vibrational energy upon photodetachment, so the 0.3-eV shift of the eKE is approximately equal to the difference in the vertical detachment energies of the conformers.

The time-dependent intensities for the $n = 5$ and $n = 6$ clusters (Fig. 1) cannot be attributed to the population of excited-state anions, as this must decline monotonically once the pump pulse terminates. Instead, it appears that the dynamics associated with stabilization of the excess electron also result in an increased photodetachment cross-section. This result is consistent with isomerization from a dipole-bound state, in which the electron cloud is exceedingly diffuse, to a conformer in which the excess electron is more solvated and hence more localized. Two isomers are known to exist for $(H_2O)_6^-$, and the photodetachment cross-section for the more weakly bound isomer (with respect to electron detachment) is considerably less than for the more strongly bound isomer (24). The vertical detachment energies for these isomers (0.2 and 0.5 eV) are quite close to those for the two excited $I^-(H_2O)_6$ species in our experiment.

We next consider isotopic effects. The earlier onset (by 100 fs) of the shift in electron energy for $I^-(H_2O)_4$ and $I^-(H_2O)_6$ as compared to that of the analogous $D_2O$ clusters indicates that isomerization begins earlier in the $H_2O$ clusters, and suggests that librational-rotational motion of the solvent molecules plays an important role in stabilizing the excess electron. A large isotope effect attributed to librational solvent motion has also been seen at very early times (30 to 80 fs) in bulk hydrated electron studies (4).

Figure 4 presents a qualitative picture of the isomerization and electronic localization dynamics that is consistent with our experimental results. At short delay times, the geometry of the initially excited state (Fig. 4B) should resemble that of the ground state (Fig. 4A) (17), and the excess electron in Fig. 4B is bound by the dipole moment of the solvent network. However, Kim and co-workers (25) calculate that the lowest energy structure for $(H_2O)_6^-$ is quite different from the solvent network in Fig. 4B; they find instead a "half-cage" structure in which the excess electron is considerably more localized. Their calculation is the basis for the structure in Fig. 4C, which has a different hydrogen bonding network than that in Fig. 4B.

One must realize the approximate nature of Fig. 4. First, because of the finite (and unknown) cluster temperature, it is possible that fluctuational as well as rigid structures play a role in the dynamics. For example, recent infrared (IR) spectroscopy experiments on $I^-(H_2O)_4$ (48) suggest that the interwater hydrogen bond is disrupted at finite temperatures (26). In addition, many low-lying isomers are expected for $(H_2O)_6^-$ (25), including a linear structure that appears to be consistent with its IR spectrum (27). Finally, perturbations and
We close by comparing our results to Bradforth’s experiments (11) on CTTS excitation of 1− in liquid water, because these are the liquid-phase experiments most analogous to ours. In his experiments, transient absorption at 800 nm was monitored after excitation at 255 nm. Bradforth observed a short-lived (~50 fs) transient assigned to the initially excited CTTS state, followed by an increasing absorption with a rise time of 200 fs associated with formation of the solvated electron; this then decayed biexponentially with time constants of 9 and 60 ps. This interpretation suggests several parallels with the n = 5 and n = 6 FPES results presented here; namely that the CTTS state in the bulk is analogous to the short-lived dipole-bound state seen in our experiments, and that the bulk solvation on a 200-fs time scale corresponds to the isomerization and solvation dynamics in our experiments. There are, however, important differences. Simulations of CTTS excitation show that solvation is accompanied by the electron moving away from the halogen species (12, 13), which is a reasonable result for an infinite number of water molecules but may not occur in a small cluster. Also, in liquid water, the longer time decay of the solvated electron signal occurs by recombination with neutral I atoms. Although this may be responsible for the long time decay in the clusters, a likelier mechanism is thermionic emission, which generally does not occur in liquids.

Requirements for Tec Kinases

RLK and ITK in T Cell Receptor Signaling and Immunity

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T cell receptor (TCR) signaling requires activation of Zap-70 and Src family tyrosine kinases, but requirements for other tyrosine kinases are less clear. Combined deletion in mice of two Tec kinases, RLK and ITK, caused marked defects in TCR responses including proliferation, cytokine production, and apoptosis. The cytokine and apoptosis defects in vitro and adaptive immune responses to Toxoplasma gondii in vivo. Molecular events immediately downstream of the TCR were intact in rlk−/−itk−/− cells, but intermediate events including inositol trisphosphate production, calcium mobilization, and mitogen-activated protein kinase activation were impaired, establishing Tec kinases as critical regulators of TCR signaling required for phospholipase C-γ activation.

RLK and TEC (3). Ikl-deficient mice have only mildly impaired responses to infection (5), suggesting functional redundancy between these kinases.

RLK (also called TSK) is a Tec kinase expressed in developing and mature T lymphocytes (6). RLK resembles other Tec kinases in that it lacks the COOH-terminal regulatory tyrosine and myristoylation sequences of Src kinases, has a proline-rich region that binds SH3 domains, and is activated by phosphorylation by Src kinases. However, RLK lacks the phosphotyrosinylphosphate-binding pleckstrin homology domain common to other Tec kinases and is activated independently of phosphotyrosine 3-kinase (PI3K) activity. Instead, RLK has a palmitoylated cysteine-string motif, required for subcellular localization (7). To better understand the contribution of Tec kinases to T cell signaling, we analyzed mice mutated in RlK, Itk, or both kinases.

Because alternate translation initiation generates at least two RlK isoforms, a full-length protein and a shorter species lacking the cysteine string (7), we introduced a targeted mutation downstream of the second