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Dynamics of Electron Solvation in Molecular Clusters

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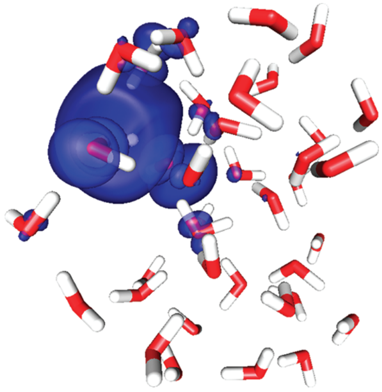

Solvated electrons, and hydrated electrons in particular, are important species in condensed phase chemistry, physics, and biology. Many studies have examined the formation mechanism, reactivity, spectroscopy, and dynamics of electrons in aqueous solution and other solvents, leading to a fundamental understanding of the electron–solvent interaction. However, key aspects of solvated electrons remain controversial, and the interaction between hydrated electrons and water is of central interest. For example, although researchers generally accept that hydrated electrons, e^-_{aq}, occupy solvent cavities, another picture suggests that the electron resides in a diffuse orbital localized on a H_3O radical. In addition, researchers have proposed two physically distinct models for the relaxation mechanism when the electron is excited. These models, formulated to interpret condensed phase experiments, have markedly different time scales for the internal conversion from the excited p state to the ground s state.

Studies of negatively charged clusters, such as $(H_2O)_n^-$ and $I^-(H_2O)_n$, offer a complementary perspective for studying aqueous electron solvation. In this Account, we use time-resolved photoelectron spectroscopy (TRPES), a femtosecond pump–probe technique in which mass-selected anions are electronically excited and then photodetached at a series of delay times, to focus on time-resolved dynamics in these and similar species. In $(H_2O)_n^-$, TRPES gives evidence for ultrafast internal conversion in clusters up to $n = 100$. Extrapolation of these results yields a p-state lifetime of 50 fs in the bulk limit. This is in good agreement with the nonadiabatic solvation model, one of the models proposed for relaxation of e^-_{aq}. Similarly, experiments on $(MeOH)_n^-$ up to $n = 450$ give an extrapolated p-state lifetime of 150 fs.

TRPES investigations of $I^-(H_2O)_n$ and $I^-(CH_3CN)_n$ probe a different aspect of electron solvation dynamics. In these experiments, an ultraviolet pump pulse excites the cluster analog of the charge-transfer-to-solvent (CTTS) band, ejecting an electron from the iodide into the solvent network. The probe pulse then monitors the solvent response to this excess electron, specifically its stabilization via solvent rearrangement. In $I^-(H_2O)_n$, the iodide sits outside the solvent network, as does the excess electron initially formed by CTTS excitation. However, the iodide in $I^-(CH_3CN)_n$ is internally solvated, and both experimental and theoretical evidence indicate that electrons in $(CH_3CN)_n^-$ are internally solvated. Hence, these experiments reflect the complex dynamics that ensue when the electron is photodetached within a highly confined solvent cavity.

Introduction

Solvated electrons have received considerable attention since Weyl's report,[1] almost 150 years ago, describing the bluish color of sodium dissolved in liquid ammonia. While electrons can be found in many solvents, the *hydrated* electron (e^-_{aq}) is of particular interest owing to the paramount importance of water as the most abundant solvent in nature. The observation of the absorption spectrum of e^-_{aq} in 1962,[2] a broad band peaking at 720 nm, has triggered many experimental and theoretical studies. Hydrated electrons are most commonly generated by photoemission with ionizing radiation.[3] The high reactivity and reduction potential of e^-_{aq} make it an important transient spe-

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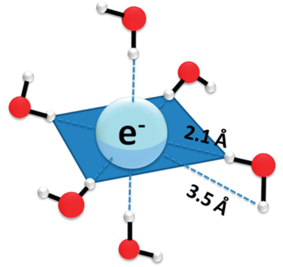

FIGURE 1. Structure of the first solvation shell surrounding the hydrated electron in bulk water (adapted from ref 6).

cies in condensed phase radiation chemistry,[3] particularly the radiative damage of DNA.[4] Electron hydration is an intrinsically bulk phenomenon, but much insight into the electron–solvent interaction can be gained from studying the appropriate negatively charged clusters.[5] Studies of the time-resolved dynamics of such clusters are the primary focus of this Account.

Isolated water molecules do not possess unoccupied bound orbitals and therefore cannot form stable molecular anions. Consequently, the existence of e^-_{aq} must result from cooperative interactions of the excess charge and the solvent network. Its electronic structure is largely determined by the geometry and fluctuations of its environment, leading to strong vibronic coupling. Electron spin resonance experiments on glassy ice identify a spherical s-type excess electron distribution within an octahedral cavity[6] and OH groups pointing toward the center, as illustrated in Figure 1. The broad asymmetric absorption spectrum peaking around 720 nm is then attributed to the excitation to a manifold of p-type excited states whose degeneracy is removed owing to the non-spherical solvent cavity.[7] An alternate picture, the so-called chemical model, has also been proposed suggesting that the electron resides in a diffuse orbital on a neutral H_3O radical.[8]

Formation of e^-_{aq} in the bulk generally proceeds either by ionization of the solvent or by detachment from a solute.[9] Both processes can produce highly excited electrons that relax through a combination of solvent dynamics and nonadiabatic transitions, and unraveling the overall relaxation mechanism has proved challenging. As part of this effort, the electronic dynamics associated with the s → p excitation have been studied extensively in the condensed phase.[10] The general dynamical scheme is given by eq 1. Since equilibrated solvent cavities surrounding ground and excited state e^-_{aq} have substantially different geometries, rearrangement of the solvent network is expected to precede and follow internal conversion (IC) from the p-state to the s-state with time constants τ_p and τ_s, respectively:

$$|p^*\rangle \xrightarrow{\tau_p} |p\rangle \xrightarrow{\tau_{IC}} |s^*\rangle \xrightarrow{\tau_s} |s\rangle \qquad (1)$$

Time-resolved experiments based primarily on transient absorption spectroscopy have found a transient infrared signal that eventually evolves into the equilibrium spectrum of e^-_{aq}.[10−13] Three time scales associated with this spectral evolution have been identified, $\tau_1 \approx 30-80$ fs, $\tau_2 \approx 200-300$ fs, and $\tau_3 \approx 1$ ps,[10−12] with reported isotopic shifts of the first time scale between 1.4 and 2.0 in perdeuterated water. These experiments, in conjunction with simulations,[13] have led to the formulation of two nearly orthogonal mechanisms to explain the observed dynamics. In the "adiabatic solvation model", the fastest time constant, τ_1, is associated with excited-state solvation dynamics, while τ_{IC} is on the order of 200 fs to 1 ps.[13] In contrast, the "nonadiabatic" model associates τ_1 with internal conversion, with the remaining time constants attributed to subsequent solvent relaxation.[12,14,15] These seemingly incommensurate models are both consistent with the aqueous phase data; the discrepancies arise from how these data are interpreted and, specifically, which measured time constant is associated with IC. The cluster dynamics experiments described below are aimed at resolving this issue.

Gas Phase Experiments

Negatively charged water clusters can serve as a model system for the bulk hydrated electron.[16] Measurements on finite-sized clusters probe the evolution of electronic and geometrical properties as the solvent network is built around the excess charge and, in principle, converge to the bulk values at the infinite size limit. A particularly valuable tool is photoelectron spectroscopy (PES),[17] in which the excess electron is photodetached from a mass-selected cluster with a fixed-frequency laser and its kinetic energy is measured to obtain binding energies.

$$(H_2O)_n^- \xrightarrow{h\nu} (H_2O)_n + e^- \qquad (2)$$

Complementary information comes from infrared (IR) predissociation spectroscopy, in which clusters are irradiated with a tunable IR laser. Excitation of cluster vibrations with one or more photons results in the loss of either a neutral water molecule or weakly bound Ar messenger atoms, and parent depletion or ion daughter production is detected.[18]

$$\begin{aligned} (H_2O)_n^- &\xrightarrow{i\,h\nu_{IR}} (H_2O)_n^- + H_2O \\ (H_2O)_n^- \cdot Ar_m &\xrightarrow{i\,h\nu_{IR}} (H_2O)_n^- \cdot Ar_{m-k} + k\ Ar \end{aligned} \tag{3}$$

These experiments yield vibrational spectra of the clusters, which can then be compared with results from *ab initio* theory to obtain structural information.

Beyond ground-state properties, time-resolved photoelectron spectroscopy (TRPES) allows one to monitor the evolution of electronic excitations under well-defined conditions.[19] For example, water cluster anions can be excited with a femtosecond pump laser pulse and subsequently photodetached with a probe femtosecond pulse after delay time Δt:

$$(H_2O)_n^- \xrightarrow{h\nu_{pump}} ((H_2O)_n^-)^* \xrightarrow{\Delta t} \cdot\ \cdot\ \cdot \xrightarrow{h\nu_{probe}} (H_2O)_n + e^- \tag{4}$$

Analysis of time-dependent electron kinetic energies yields two-dimensional time and energy information and allows the direct measurement of both relaxation time scales and pathways of the excitation induced by the pump laser.

The focus of this Account is on TRPES. Two classes of experiments are performed, one of which focuses on electronic relaxation dynamics of excess charges in molecular solvent clusters, and the other on dynamics of the photoinduced formation and subsequent stabilization of solvated excess electrons within the solvent network. For example, one can excite bare water cluster anions $(H_2O)_n^-$ with a near-infrared pump pulse and subsequently follow the ensuing dynamics back to the ground state (Figure 2a). Alternatively, upon UV photoexcitation of halide−solvent clusters such as $I^-(H_2O)_n$, the excess charge is ejected from the halide into the solvent network and one can probe the subsequent localization and equilibration of this electron (Figure 2b). These experiments are the cluster analog of transient absorption and charge-transfer-to-solvent experiments[9] performed to characterize electron hydration dynamics in aqueous solution.

Experimental Setup

Figure 3 shows the photoelectron imaging instrument used for investigation of dynamics in solvent cluster ions.[20] Negatively charged clusters are created in the pulsed source in region (a) and separated with the linear time-of-flight mass spectrometer (b). To form water cluster anions, water vapor is coexpanded with several atmospheres of argon through a pulsed valve, while iodide-doped clusters are formed by seeding the gas mixture with methyl iodide.

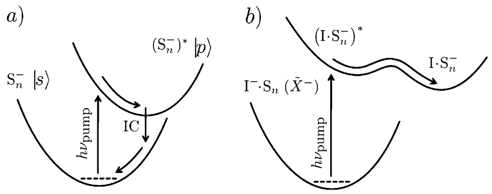

FIGURE 2. Photoinduced dynamics in bare and halide-doped water cluster anions.

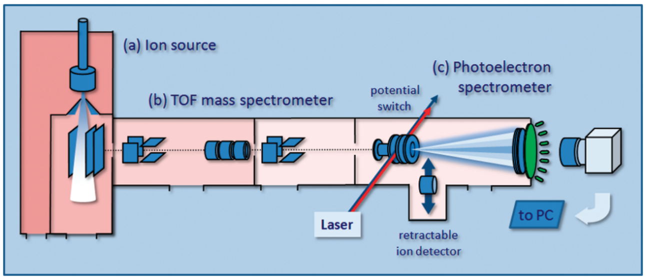

FIGURE 3. Photoelectron imaging apparatus: (a) ion source; (b) time-of-flight mass spectrometer; (c) photoelectron spectrometer with velocity map imaging lens and the photoelectron imaging system.

Mass-selected clusters then undergo excitation and detachment in the center of the velocity-map-imaging lens (c).[21] The ejected electrons are accelerated toward a microchannel plate detector/phosphor screen; the projected electron emission distribution is captured with a charge-coupled device (CCD) camera and integrated on a personal computer. Femtosecond laser pulses are produced by a commercial Ti:sapphire laser system (Clark-MXR NJA-5 and CPA-1000) with typical durations between 80 and 100 fs. The output can be converted through parametric amplification (TOPAS, Light Conversion Ltd.) or other nonlinear conversion schemes to yield wavelengths covering the spectral range from the near IR to the UV, suitable for the different types of experiments described below. Pump and probe laser pulses are delayed with respect to each other by a computer-controlled retroreflector setup before they are collinearly recombined and focused into the detachment region.

Integrated photoelectron images are symmetrized to account for detector inhomogeneities and converted into three-dimensional momentum distributions by standard methods.[22] From these, photoelectron kinetic energy (eKE) and angular distributions are readily obtained. In many of the spectra shown here, one observes broad features with maximum intensity at kinetic energy eKE_{max}; these features are characterized by their vertical detachment energy, VDE, defined by VDE $= h\nu_{probe} - eKE_{max}$. The VDE is the energy needed to detach an electron to form a particular neutral state with no geometric relaxation of the neutral.

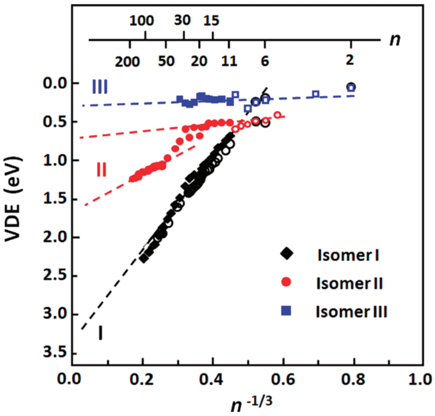

FIGURE 4. Vertical detachment energies of the different isomers of water cluster anions $(H_2O)_n^-$ as a function of cluster size *n*. Black open circles are taken from Coe et al.[17] and red open circles and blue open squares are taken from Kim et al.,[25] respectively.

Water Cluster Anions

Haberland and co-workers were the first to report mass spectra of negatively charged water clusters $(H_2O)_n^-$ after injection of low-energy electrons into the expansion of water vapor seeded in various rare gases.[23] They observed water dimer anions, clusters comprising $n = 6$ and 7 molecules, and a continuous cluster distribution from $n = 11$ to 25. The first photoelectron spectra of water cluster anions were reported by Bowen[17] in the size range $n = 2-69$. Spectra were broad and structureless and generally showed VDEs that increased with cluster size (see Figure 4). The excess electron in the dimer was bound by only ∼50 meV and attributed to a dipole-bound state, but VDEs for clusters with $n \geq 11$ were larger and increased proportionally to the inverse cluster radius (or $\propto n^{-1/3}$). Extrapolation of detachment energies to the infinite cluster size limit yielded $\mathrm{VDE}_\infty = 3.3$ eV, in coincidence with the estimated photoelectric threshold of 3.2 eV for emission of a hydrated electron from bulk water.[16]

The experiments by Bowen coincided with theoretical work by Landman and co-workers[24] on excess electrons in finite sized clusters of polar molecules. In these papers, quantum path integral molecular dynamics (QUPID) indicated surface localization of the extra charge to be thermodynamically favored for clusters with up to 32 water molecules, while larger systems ($n = 64$, 128) preferred internal states. The experimental $n^{-1/3}$ dependence of VDEs was reproduced for *internalized* excess charges, but the calculated values were too small. Instead, VDEs of the calculated *surface states* showed overall better agreement with the experimental values, leaving the question about the binding motif unanswered.

These findings motivated further photoelectron experiments in other laboratories that extended the range of experimental VDEs and revealed two additional isomers (II and III, see Figure 4) with lower electron binding energies than seen previously.[25−27] Formation of these weakly bound clusters under colder source conditions suggested that they were metastable surface states, while isomer I clusters with higher VDEs should then be the internalized structures, as implied from theory.[24] However, IR depletion spectroscopy by Johnson and co-workers[18,28] on clusters with $n = 3-24$ revealed red-shifted HOH bending modes for isomer I, attributed to double hydrogen bond acceptor (AA) water molecules on the cluster surface with both protons pointing toward a largely external excess electron. The set of vibrational spectra has been recently extended with the infrared free electron laser FELIX to clusters as large as $n = 50$.[29] While IR spectra up to $n = 24$ reproduced the previous findings, larger clusters showed continuous broadening of the AA feature until it merged with the main bending mode at 1640 cm^{-1} around $n = 50$, raising the question about a potential structural transition in this size range. The nature of the electron binding motif in larger water cluster anions has also been the focus of several recent theoretical investigations.[30−32]

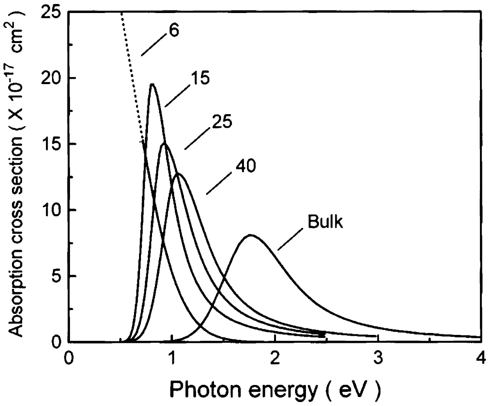

FIGURE 5. Electronic absorption spectra of size-selected water cluster anions. Reprinted with permission from ref 33. Copyright 1997, American Institute of Physics.

Electronic Relaxation Dynamics in $(H_2O)_n^-$

Water cluster anions $(H_2O)_n^-$ possess an electronic resonance in the near IR. Absorption spectra in the 0.7−1.6 eV range measured by photodestruction of clusters with $n = 6-50$ have been reported by the Johnson group (Figure 5).[33] The observed asymmetric band shows a systematic blue shift from 0.8 eV ($n = 15$) to 1.2 eV ($n = 50$), apparently converging to the spectrum of the hydrated electron.[34] An upper limit of $\tau_{max} = 150$ fs for the lifetime of the excitation in clusters with $n = 20-100$ was inferred from the resonant two-photon detachment cross sections measured with a short 800 nm laser pulse.[35]

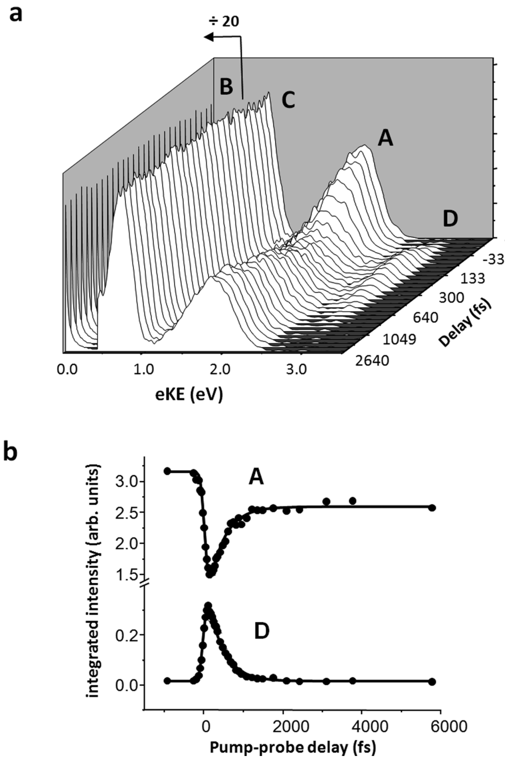

FIGURE 6. (a) Time-resolved photoelectron spectra of water cluster anions $(\mathrm{D2O})_{25}^-$ at pump and probe photon energies of 1.0 and 3.1 eV, respectively. (b) Integrated photoelectron intensities of ground- and excited-state detachment features A and D.

A systematic examination of the nonadiabatic relaxation and complementary structural dynamics associated with this electronic transition has been performed with two-color, time-resolved photoelectron spectroscopy.[20,36,37] Clusters as large as $n = 100$ were excited close to their absorption maximum, using pump photon energies ranging from 0.75 to 1.5 eV, and the response was probed with a delayed 3.1 eV femtosecond laser pulse. Figure 6a shows time-dependent photoelectron spectra of $(\mathrm{D_2O})_{25}^-$ (isomer I) measured at a pump wavelength of 1250 nm.[20] After excitation, the ground-state feature (A) is partially depleted and a transient detachment signal (D) appears, directly reflecting the time-dependent populations of both the s-type ground and excited p-state. Integrated electron intensities from both features as a function of pump−probe delay are shown in Figure 6b. Recovery of the ground-state depletion and the concomitant decay of the excited state occur with a lifetime of ~400 fs, indicating a direct nonadiabatic transition between them. The similarity in time scales and the lack of dynamics in any other feature indicate that the p-state decays solely by internal conversion (IC).

Extracted p-state lifetimes of $(\mathrm{H_2O})_n^-$ and $(\mathrm{D_2O})_n^-$ for isomer I and II clusters with $13 \leq n \leq 100$ are shown in Figure 7. Values for the larger isomer I clusters are proportional to $1/n$ and show a significant isotope effect ($\tau_{\mathrm{D_2O}}/\tau_{\mathrm{H_2O}} \approx 2$). Extrapolation to $n \rightarrow \infty$ yields lifetimes of 50 and 70 fs for $(\mathrm{H_2O})_n^-$ and $(\mathrm{D_2O})_n^-$, respectively. The linear relation implies size effects far beyond the first hydration shell, effects that have been attributed to long-range dipolar couplings in theoretical work by Fischer and Dietz.[38] Clusters with $n \leq 25$ appear to deviate from this mechanism and show a faster decay than expected from the linear regression. This trend results from excited-state autodetachment in the smaller systems, $(\mathrm{H_2O})_n^{-*} \rightarrow (\mathrm{H_2O})_n + e^-$, a competing excited-state decay path parallel to IC.[20]

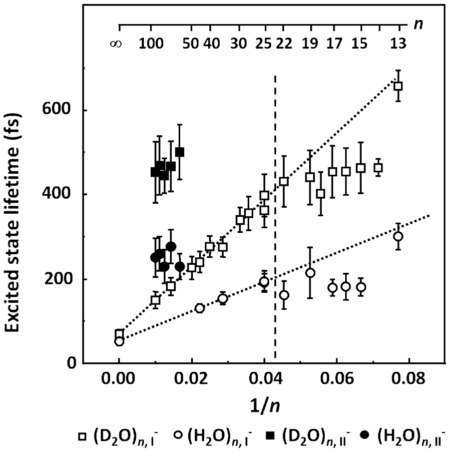

FIGURE 7. Internal conversion lifetimes of the p → s relaxation for isomer I and II water clusters as a function of cluster size.

The observed fast relaxation, dynamical isotope effects, absence of solvent dynamics upon photoexcitation, and extrapolation to ultrafast IC rate of 50 fs are consistent with the "nonadiabatic" relaxation mechanism of the bulk hydrated electron.[11,12] According to this mechanism, IC occurs on an ultrafast 50 fs time scale, followed by a two-step solvent relaxation on the longer ~300 fs and ~1 ps time scales. Further support for the assignment of the latter lifetimes to solvent dynamics comes from measurements by Paik et al.,[37] who found biexponential ground-state relaxation with lifetimes of ~380 fs and 2−10 ps following IC in clusters with $15 \leq n \leq 35$.

In order to test whether multiple isomers and ultrafast internal conversion are unique to water cluster anions, one-photon and time-resolved photoelectron spectra were measured for methanol cluster anions, $(\mathrm{MeOH})_n^-$.[5] These experiments were also motivated by the many parallels between e_{aq}^- and electrons dissolved in methanol.[39] Photoelectron spectra of $(\mathrm{MeOH})_n^-$ clusters in the size range $n \approx 145-535$ indeed showed evidence for two isomers under similar conditions as isomers I and II in $(\mathrm{H_2O})_n^-$ clusters.[40] TRPES of the more strongly bound isomer I of $(\mathrm{MeOH})_n^-$ clusters yielded internal conversion lifetimes subsequent to s → p excitation at

1.55 eV that scaled as $1/n$ and that extrapolated to $\tau_\infty = 157$ fs for $n \rightarrow \infty$.[41] This value is similar to the shortest time scale observed for solvated electrons in bulk methanol,[42] thus implying that the fastest time constant in the condensed phase results from a nonadiabatic transition rather than excited-state relaxation. Our extrapolated lifetimes for water and methanol cluster anions agree well with recent theoretical work by Fischer[43] that predicted IC lifetimes of 50 and 150 fs for the two solvents. Comparison of the electron relaxation dynamics in water and methanol cluster anions and the corresponding bulk solvents lead to the same conclusions for both solvents, namely, extremely fast internal conversion consistent with the nonadiabatic relaxation model for the bulk solvated electron.

Photoinduced Charge Transfer in $I^-(H_2O)_n$

Aqueous halides exhibit broad absorption bands in the deep UV, associated with the detachment of the strongly bound excess charge into the solvent network and, ultimately, formation of a hydrated electron.[44] Excitation of these charge-transfer-to-solvent (CTTS) bands is an efficient way to prepare e^-_{aq} and has been exploited in several time-resolved experiments to examine the underlying dynamics.[45,46] The analog of CTTS bands also exists in halide–solvent clusters, with $I^-(H_2O)_n$ clusters as small as $n = 2$ exhibiting broad, CTTS-like electronic absorptions.[47]

In our laboratory, we have excited these bands in TRPES experiments to study photoinduced charge transfer in halide–solvent clusters.[48–50] Smaller water cluster complexes with $n \leq 10$ were pumped at 4.65 eV, and the ensuing dynamics were probed by detachment with a delayed 1.55 eV probe pulse. Exemplary pump–probe spectra of $I^-(H_2O)_7$ are shown in Figure 8. Upon excitation of the CTTS band, the transient feature B appears, and its eKE subsequently drops by around 0.3 eV on a time scale of ~1 ps, reflecting an increase in the VDE. Over the following tens of picoseconds, the VDE drops by ~50 meV, and the transient signal fades out within 60 ps to 3 ns, being slower for larger clusters. These trends were attributed to solvent dynamics, in which the water molecules rearrange to stabilize the detached electron, and to the neutral iodine atom leaving the cluster. The final decay of the transient is commensurate with the recovery of a very slow electron signal and is ascribed to excited-state autodetachment (ESAD). In experiments on larger species with $n \leq 28$, the pump photon energy was increased to 5.12 eV as the CTTS band shifts toward higher energies.[49] The time scale for the VDE increase remains around ~1 ps, but the extent of the shift is progressively larger, reaching 700 meV for $n = 25$. No ESAD is seen in the larger clusters, since the electron affinity exceeds the pump photon energy.[51]

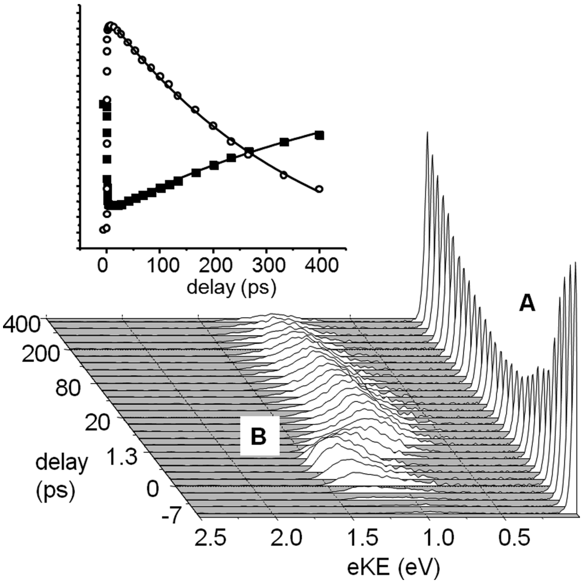

FIGURE 8. Time-resolved photoelectron spectrum of I^-(H2O)$_7$ taken with pump and probe photon energies of 4.65 and 1.55 eV, respectively.[50] The inset illustrates the varying intensities of the transient feature (B) and the autodetachment signal (A).

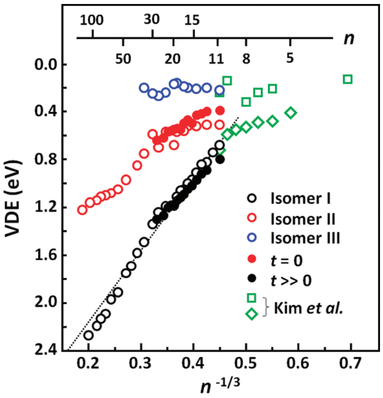

FIGURE 9. Size dependence of early ($t = 0$, filled red circles) and late ($t \gg 0$, filled black circles) VDEs of $I^-(H_2O)_n$ following absorption in the CTTS band, along with VDEs of bare isomer I, II, and III water cluster anions.

Size-dependent VDEs at early and late times are shown in Figure 9. These values reveal fundamental aspects of the dynamics and are shown along with VDEs of the different isomers of bare water cluster anions.[49] Early time VDEs ($t = 0$) are similar to those of isomer II water clusters. As halide ions preferentially bind to the surface of the water cluster,[52,53] this supports the idea of a diffuse external electron cloud being formed upon excitation of the CTTS band. In the ensuing relaxation, the excess electron becomes more strongly bound and detachment energies shift toward bare isomer I values. The extent of stabilization strongly indicates solvent rearrange-

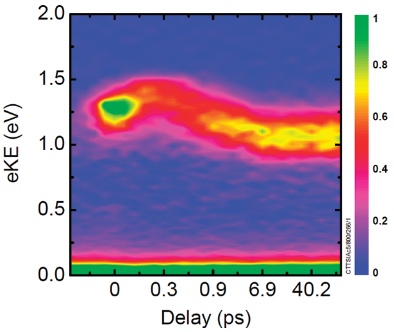

FIGURE 10. False color map of time-resolved photoelectron spectra of $I^-(CH_3CN)_5$ taken with $h\nu_{pump} = 4.68$ eV and $h\nu_{probe} = 1.56$ eV.[57]

ment to be its cause and implies that the iodine atom mainly plays the role of a spectator. One may speculate as whether the observed dynamics reflect the isomerization of an external excess electron to a more internalized one, at least for the larger clusters.

CTTS Dynamics in $I^-(CH_3CN)_n$

In iodide–water clusters, the iodide resides on the surface of the solvent network,[53] as does the electron produced by CTTS excitation, at least at the earliest times. In order to gain additional insight into the cluster analog of CTTS excitation and electron solvation, experiments on clusters with internally solvated charge carriers are desirable. This is readily achieved by substituting CH_3CN for water as the solvent. Photoelectron spectra and simulations of $I^-(CH_3CN)_n$ clusters indicate internal solvation of the halide,[54] while there is evidence that $(CH_3CN)_n^-$ clusters exist in two distinct forms with internally solvated electrons: a strongly bound valence anion with VDEs of ~2.5 eV (isomer II) and a cavity state with lower binding energies of 0.3–0.5 eV (isomer I).[55,56]

We have studied CTTS dynamics in $I^-(CH_3CN)_n$ with $5 \leq n \leq 10$ using TRPES.[57] The pump energies were 4.6 ($n = 5-8$) and 5.1 eV ($n = 9$, 10), and the probe photon energy was 1.56 eV. Spectra for $n = 5$ are shown in Figure 10. Both the VDE and electron yield from the excited-state show modulations within the experimental time window and are plotted in Figure 11. Around $t = 0$, the excited-state feature appears at eKE ≈ 1.3 eV. Its intensity drops within the cross-correlation, while the VDE shows a delayed decrease to reach its minimum after ~300 fs. Detachment energies biexponentially increase again by ~200 meV over several picoseconds, to finally drop by ~50 meV with a time constant of ~100 ps. Larger clusters show generally similar trends with slower early dynamics and no long-time drop in the VDE for $n \geq 7$.

Based on experimental VDEs of bare acetonitrile cluster anions,[55] the final state is identified as an internally solvated

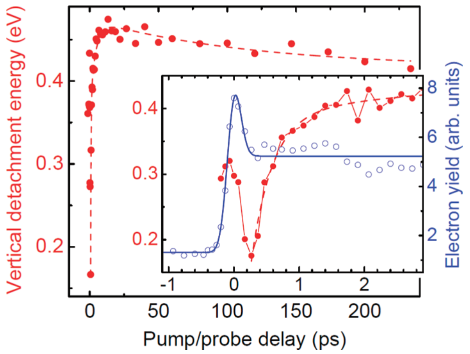

FIGURE 11. Extracted VDE (red circles) and excited-state detachment yield (blue circles) from time-dependent spectra of $I^-(CH_3CN)_5$ in Figure 10.[57]

electron. The intermediate dynamics are assigned with the aid of MD simulations by Takayanagi.[58] Upon excitation of the CTTS band, the excess electron is detached from the halide into a confined solvent cavity, defined by the prevailing orientation of the dipolar acetonitrile molecules. Repulsion from the surrounding solvent molecules and the neutral iodine atom lead to destabilization of this geminate iodine:e⁻ pair. As the solvent cage enlarges, the extra charge localizes on one or two acetonitrile molecules, giving rise to the minimum in VDE. Over the next few picoseconds, the halogen is repelled from the solvent cage, which undergoes final structural relaxation and now solely hosts the excess electron. The remaining internal energy leads to unimolecular dissociation of solvent molecules or the halogen atom, reflected by the small final decrease in VDE for clusters with $n = 5$ and 6.

Concluding Remarks

This Account summarizes time-resolved photoelectron spectroscopy experiments on anion clusters aimed at gaining new insights into the dynamics of electron solvation. Two types of clusters were investigated: $(H_2O)_n^-$ and $(MeOH)_n^-$ clusters, comprising an excess electron bound to a known number of solvent molecules, and $I^-(H_2O)_n$ and $I^-(CH_3CN)_n$ clusters, in which the solvent molecules are doped with a halide ion. In the experiments on bare solvent cluster anions, the excess electron is excited from its ground s-state to its excited p-state, and its relaxation dynamics are monitored. The time-resolved PE spectra directly yield p → s internal conversion times as a function of cluster size. Extrapolation of these values to $n \to \infty$ yields IC lifetimes of 50 and 157 fs for water and methanol, respectively. These lifetimes are close to the fastest relaxation time constants measured in the transient absorption of bulk solvated electrons and support the "nonadiabatic" solvation model for electrons in solution. In the experiments on halide-doped clusters, the cluster analog of the UV charge-transfer-to-solvent transition is pumped, ejecting an electron from the halide into the solvent network, and the ensuing electron solvation dynamics are monitored. The experiments on $I^-(H_2O)_n$ and $I^-(CH_3CN)_n$ show how these dynamics differ depending on whether the halide anion is initially at the cluster surface (H_2O) or internally solvated (CH_3CN).

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BIOGRAPHICAL INFORMATION

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Daniel M. Neumark is Professor of Chemistry at the University of California, Berkeley, and Director of the Chemical Sciences Division at Lawrence Berkeley National Laboratory. His research interests focus on using photoelectron spectroscopy to probe reaction and cluster dynamics. His awards include Alfred P. Sloan Fellow (1989), Camille and Henry Dreyfus Teacher-Scholar (1991), Fellow, American Physical Society (1993), Fellow, American Association for the Advancement of Science (1994), Fellow of the American Academy of Arts and Sciences (2000), American Chemical Society Nobel Laureate Signature Award (with Martin Zanni) (2000), Bomem-Michelson Award (2001), William F. Meggers Award (2005), and Irving Langmuir Award (2008).

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