

INVITED TOPICAL REVIEW

Spectroscopy and dynamics of excess electrons in clusters

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Anionic clusters comprising solvent molecules and excess electrons can provide new insights into electron solvation in liquids, an intrinsically bulk phenomenon. This paper reviews experimental and theoretical studies of this class of clusters, focusing primarily on water cluster anions, $(H_2O)_n^-$, but also on iodide-water clusters, $I^-(H_2O)_n$, and methanol cluster anions $(CH_3OH)_n^-$. Issues of particular interest include the relationship of time-resolved dynamics in these clusters to those of bulk solvated electrons, and the nature of the electron binding motifs supported by these clusters.

Keywords: clusters; hydrated electrons; photodetachment

1. Introduction

One of the primary goals in the field of cluster science is to gain a fundamental understanding of how the properties of matter evolve from the molecular to macroscopic regimes [1,2]. Experimental and theoretical advances in recent years have led to significant advances into some aspects of this evolution, such as how the discrete vibrational and electronic levels of a metal or semiconductor cluster evolve into the continuous phonon and electronic bands characteristic of the corresponding bulk material [3–5]. On the other hand, there are attributes of matter that are intrinsically associated with the macroscopic limit, and the question then arises regarding how these attributes map onto finite-sized systems [6]. In this article, we consider one of these phenomena, electron hydration, and discuss how spectroscopic and dynamical studies of clusters comprising a known number of solvent molecules and an excess electron can provide new insights into this fundamentally important process.

The hydrated electron (e_{aq}) represents a particularly important example of electron solvation, a phenomenon of considerable interest since electrons dissolved in ammonia were reported almost 150 years ago [7]. Hydrated electrons, i.e. electrons in aqueous solution, have captured the attention of physical scientists since their more recent discovery in 1962 [8,9]. The hydrated electron plays a major role in radiation chemistry [10], and is an important reagent in charge-induced reactivity, molecular biological processes, and condensed-phase chemistry. It was discovered as a product of the radiolysis of water and detected through its broad absorption spectrum peaking around 720 nm [8]. This band, and many other properties, are consistent with the 'cavity' model of the hydrated electron, 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 six water molecules, on average [11,12] The 720 nm band is then attributed to excitation from an occupied s state to a broadened manifold of p states within this nonspherical cavity [13,14]. A competing picture has also been proposed, the so-called chemical model in which the electron is not free but resides in a diffuse orbital on a neutral H₃O radical [15,16].

The relaxation dynamics associated with $s \rightarrow p$ excitation of e_{aq}^- are of considerable interest. Timeresolved experiments based primarily on transient absorption show that subsequent to electronic excitation, the transient absorption spectrum of e_{aq}^- is shifted much further to the infrared, with recovery of the equilibrium absorption occurring within 1–2 ps [17–22]. The dynamics of e_{aq}^- subsequent to electronic excitation can be modeled as follows [23–25]:

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

Here, p^* refers to the electron/solvent configuration just after excitation, τ_p is the time constant for solvent

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relaxation around the electronically excited electron, τ_{IC} is the internal conversion lifetime, and τ_s refers to solvent relaxation subsequent to IC.

Experimentally, relaxation takes place on three timescales, $\tau_1 \sim 30-80$ fs (60-120 fs in D₂O) $\tau_2 \sim 200-$ 300 fs, and $\tau_3 \sim 1 \text{ ps.}$ These timescales have been variously attributed to the three time constants in (1). The interpretations put forth generally follow one of two nearly orthogonal models: the 'adiabatic solvation' mechanism, [24] in which τ_{IC} is on the order of 1 ps, and the 'non-adiabatic solvation' mechanism in which the IC lifetime is 50 fs [22,25,26]. In the adiabatic solvation mechanism, the fastest time constant τ_1 is associated with τ_p in Equation (1) [19], whereas the non-adiabatic mechanism implies that either excited state relaxation does not occur prior to IC or $\tau_{\rm p}$ is too fast to resolve [25]. These seemingly irreconcilable mechanisms do not reflect issues with the experimental data themselves, but the interpretation of the rather complicated transient absorption signals seen in aqueous solution.

The controversies associated with the nature of e_{aq}^{-} and its relaxation dynamics have motivated many experimental and theoretical groups to study finitesized, negatively-charged clusters that might serve as model systems for the bulk hydrated electron and provide new insights into the electron-water interactions that govern its properties. Much of this work has centered on water cluster anions $(H_2O)_n^-$, and these clusters are indeed the main focus of this review. An impressive array of frequency- and time-domain experiments has been carried out water cluster anions. These experiments include photoelectron spectroscopy (PES) [27], in which mass-selected anions are photodetached with a fixed-frequency laser and the resulting electron kinetic energy distribution is measured,

$$(\mathrm{H}_{2}\mathrm{O})_{n}^{-} \xrightarrow{hv} (\mathrm{H}_{2}\mathrm{O})_{n} + e^{-}$$
(2)

and time-resolved photoelectron spectroscopy [28], a femtosecond pump-probe experiment in which the pump laser excites the anion cluster, the probe laser detaches it at various delay times τ , and the resulting photoelectron spectrum is measured

$$(\mathrm{H}_{2}\mathrm{O})_{n}^{-} \xrightarrow{h\nu_{pu}} \left[(\mathrm{H}_{2}\mathrm{O})_{n}^{-} \right]^{*} \xrightarrow{\tau, h\nu_{pr}} (\mathrm{H}_{2}\mathrm{O})_{n} + e^{-}.$$
(3)

While PES yields the electron binding energy of the cluster in question, time-resolved PES probes the lifetime and relaxation dynamics of the excited state created by the pump pulse.

Another important experiment is infrared (IR) action spectroscopy, in which absorption of one or more infrared photons is detected through dissociation

of either a pure water cluster anion or a cluster complexed to Ar atoms [29,30].

$$(\mathrm{H}_{2}\mathrm{O})_{n}^{-} \xrightarrow{hv_{IR}} (\mathrm{H}_{2}\mathrm{O})_{n-m}^{-} + m\mathrm{H}_{2}\mathrm{O}$$
(4)

$$\mathrm{H}_{2}\mathrm{O})_{n}^{-}\cdot\mathrm{Ar}_{m}\xrightarrow{h\nu_{IR}}(\mathrm{H}_{2}\mathrm{O})_{n}^{-}\cdot\mathrm{Ar}_{m-k}+k\mathrm{Ar}\quad(5)$$

The IR experiments yield vibrational frequencies of the clusters which can then be compared to results from electronic structure calculations, providing a detailed structural probe of these species.

This set of experiments and the accompanying theoretical treatments are the main focus of this review. They have explored the nature of the binding between the electron and the water molecules in these clusters as well as the relaxation dynamics subsequent to their electronic excitation. These studies have addressed some of the issues regarding bulk hydrated electrons but have also raised new controversies. Other classes of negatively charged clusters provide additional and complementary insights into electron solvation, and two of those are also considered here: iodide-water clusters, $I^-(H_2O)_n$, and methanol cluster anions, $(CH_3OH)_n^-$.

2. Water cluster anions

2.1. Early experimental and theoretical results (prior to 2004)

Water cluster anions, $(H_2O)_n^-$, were first detected in mass spectroscopy experiments by Haberland et al. [31,32] in which low energy electrons were injected into a free jet expansion of water vapour seeded in various rare gases. The smallest cluster, observed, n=2, was attributed to a dipole-bound state, an assignment confirmed by subsequent experimental and theoretical work [33,34]. Clusters as large as n = 16 were seen by Haberland; larger clusters were reported in a subsequent paper by Knapp et al. [35], Johnson, Viggiano, and others [36-40] carried out a series of mass spectroscopy experiments that investigated the formation, reactivity and photochemistry of these species, including the competition between electron detachment and solvent evaporation in response to either photoabsorption or thermal excitation.

One of the most important early experiments to be performed on water cluster anions was the work by Bowen and co-workers [41,42], published in 1990/1991, in which they measured photoelectron (PE) spectra of $(H_2O)_n^-$ clusters in the size range n=2-69, and PE spectra of ammonia cluster anions up to n=1100. The spectra generally comprised broad, unstructured peaks, from which one could obtain vertical detachment energies (VDE's), representing the energy required to remove an electron with no change in nuclear geometry. Remarkably, a plot of the VDE's for water cluster ions with $n \ge 11$ vs. $n^{-1/3}$ yielded a straight line, with the VDE increasing for larger clusters. The extrapolated limit as $n \to \infty$ was 3.3 eV, in agreement with the estimated photoelectric threshold of 3.2 eV for ejection of hydrated electrons from bulk water. Hence, these experiments implied that the properties of water cluster anions smoothly extrapolate to those of e_{aq}^{-} .

This experimental work approximately coincided with a series of theoretical papers by Landman, Jortner, and co-workers [43-46], who explored the interaction of excess electrons with water clusters using quantum path integral molecular dynamics (QUPID) simulations. These calculations found two binding motifs for the excess electron: a diffuse surface state. and an internally solvated state. The surface state was more stable for clusters with up to 32 water molecules, while the internal state was more stable for clusters with n = 64 and 128 [43,47]. These papers pointed out that surface and internal states could be distinguished, in principle, through measurement of their VDEs, since the calculated VDE's for internal states were considerably larger than for surface states. The VDEs for internal states showed a linear dependence vs. $n^{-1/3}$, similar to the trend seen in Bowen's PE spectra [41], but the calculated VDE's for the surface states were in better overall agreement with the experimental values. This somewhat inconclusive comparison initiated a long-standing (and ongoing) controversy about whether the $(H_2O)_n^-$ clusters seen by Bowen have internally-solvated or surface-bound electrons.

During the 14 years following publication of Bowen's paper (up to mid-2004), several experimental and theoretical investigations led to a significantly refined view of water cluster anions. On the experimental side, additional cluster anion PE spectra were reported by the Bowen [33] and Johnson [48,49] groups; the latter work showed evidence for the existence of two structural isomers for several clusters with 11 or fewer water molecules. Photodetachment of small clusters $(n \le 11)$ in the near infrared and visible was investigated by Mikami and co-workers [50]. A more extensive study by the Johnson group [51] yielded the electronic absorption cross section for anion clusters up to n = 50. This work showed that clusters starting at n = 15 exhibited a distinct maximum (around 1 eV for n=25) that shifted toward higher energy with increasing cluster size. The size-dependence of the peak shifts scales as $n^{-1/3}$ and extrapolates to the bulk absorption maximum, consistent with internal electrons, but the actual values are in better

agreement with those calculated for surface states. These trends are similar to the situation with the VDE's, as discussed in several subsequent papers and reviews [52–54]. The dynamics of the excited electronic state in these clusters were investigated by Johnson and Cheshnovsky in a femtosecond two-photon experiment, providing indirect evidence for a very short (150 fs) upper state lifetime [55].

Johnson and co-workers [56,57] also reported infrared spectra in the OH stretching region (3000- $4000 \,\mathrm{cm}^{-1}$) of water cluster anions up to n = 11, by performing infrared action spectroscopy on massselected, Ar-complexed clusters (Equation (5)). These experiments represented the first experimental structural characterization of water cluster anions. They coincided with a flurry of theoretical activity in which electronic structure calculations were carried out to elucidate the nature of the hydrogen bonding network and the excess electron binding motif in these clusters [34,58-65]. Calculations by Kim and co-workers [58,59,66–71] considering clusters with up to 12 water molecules were particularly valuable. They discovered many low-lying isomers for the anion clusters, and, in particular, found that the most stable structures often comprised hydrogen-bonding networks that would be quite unfavourable for neutral water clusters, including geometries in which one or more water molecules had both hydrogen atoms directed toward the excess electron.

2.2. More recent results

Starting in 2004, a series of experimental and theoretical papers was published that addressed, for the first time, several key issues in water cluster anions and their relationship with bulk hydrated electrons. Photoelectron imaging experiments by the Neumark group, in collaboration with Cheshnovsky, revealed the existence of multiple isomers of water cluster anions with as many as 200 water molecules [72,73]. The Johnson group measured infrared spectra in the water bending region ($\sim 1500 \,\mathrm{cm}^{-1}$), revealing how electrons were bound to small water clusters [74]. Time-resolved photoelectron spectroscopy experiments were carried out by the Neumark [75,76] and Zewail [77] groups; these experiments probed excited state lifetimes as a function of cluster size and the ground state dynamics subsequent to electronic relaxation. On the theoretical front, Rossky and coworkers [78] carried out simulations of the electronic spectrum and vertical detachment energies on water cluster anions as large as n = 200 with both internally solvated and surface-bound electrons. The remainder of this section considers these papers and other work stimulated by them.

Figure 1 shows the photoelectron imaging instrument used in the Neumark group for investigating water cluster anions [76,79]. Water cluster anions were generated with a pulsed source in region (a), massseparated by time-of-flight in region (b), and photodetached by one or more laser pulses. The resulting photoelectrons were collected and analyzed with a collinear velocity-map imaging system [80] comprising electron optics (c) and a detector/camera (d), yielding the electron kinetic energy (eKE) and photoelectron angular distributions (PADs). Water cluster anions were generated in region (a) by passing 30-70 psig of Ar over H₂O/D₂O prior to supersonic expansion into vacuum through an Even-Lavie pulsed valve operating at a repetition rate of 100 Hz. The neutral beam produced subsequently intersected a pulsed which formed anion clusters through ionization of the carrier gas followed by secondary electron attachment, which generated cations and anions through collisional detachment and secondary electron attachment, respectively.

The photoelectron images and corresponding photoelectron spectra exhibit a remarkable dependence upon ion source conditions [72]. Figure 2 shows images for $(D_2O)_{50}^-$ at two different backing pressures of Ar gas. The image is considerably larger at higher backing pressure, and the corresponding photoelectron

spectra, also shown in Figure 2, show markedly different VDEs of 1.8 eV at 30 psig and 1.0 eV at 70 psig. Moreover, by varying the backing pressure between those values, one sees that there are two contributions to the PE spectra whose weightings change with pressure, indicative of distinct isomers whose populations can be continuously varied.

Figure 3 shows experimental VDE's obtained from the photoelectron images for cluster anions as large as $n\sim200$, along with other experimental and theoretical results [81]. Three distinct isomer classes can be discerned in the spectra. The VDEs for the class of isomers with the most tightly bound electrons,



Figure 1. Photoelectron imaging apparatus: (a) ion source region; (b) time-of-flight (TOF) mass spectrometer; (c) laser interaction region and ion-beam collinear velocity map imaging (VMI) lens; (d) photoelectron imaging system. DP = diffusion pump, TMP = turbomolecular pump. Reprinted from Ref. [76] with permission of AIP.



Figure 2. Left panels: Photoelectron images of $(D_2O)_{50}^-$ at $h\nu = 3.1 \text{ eV}$. Raw (top) and transformed (bottom) images were obtained at Ar backing pressures of 30 and 70 psi. Right panel: Photoelectron spectrum of $(D_2O)_{50}^-$ as function of Ar backing gas, showing dominance of isomer I at 30 psi and isomer II at 70 psi.

Isomer I, agree with the values found by Bowen [41]. Two additional general classes of cluster isomers, Isomer II and the less prevalent Isomer III, had not been observed prior to our work and have considerably lower VDE's. Isomers I and II could be observed over a wide range of cluster sizes, up to n = 200, whereas isomer III, the most weakly bound isomer, was seen only for $(D_2O)_n^-$ and the size range over which it was observed was considerably smaller.

Based on expectations from theory that internally solvated electrons should be bound more strongly than those on the surface [43]. Isomer I was assigned to water clusters with internally solvated electrons, in agreement with the original assignment by Bowen and co-workers [41], while Isomers II and III were assigned as surface-bound species. By scaling the VDEs calculated by Barnett et al. [43] by 60%, excellent agreement was achieved between experimental and calculated VDEs taking isomer I to be internal states and isomer II to be surface states [72]. Moreover, as shown in Figure 3 [81], the experimental VDEs for isomer I and II agree quite well with more recent calculations of VDEs for internal and surface states calculated by Rossky [78] in mixed quantum-classical simulations. While these results appear at first glance to resolve the internal-surface controversy in water cluster anions, the assignment of isomer I to internal

states has been questioned in the work by Rossky and elsewhere as discussed below.

In parallel with the experiments just described, Johnson and co-workers [74] were making major strides in extending the infrared spectral range over which water cluster anions could be studied through the use of tabletop pulsed infrared lasers based on nonlinear mixing in an AgGaSe₂ crystal. Figure 4 shows their results for $(H_2O)_n^-$, n = 4-6, in the region where bending transitions of H_2O are expected. These spectra all show a strong peak around $1540 \,\mathrm{cm}^{-1}$ that is significantly red-shifted from the H₂O bend fundamental at $1590 \,\mathrm{cm}^{-1}$ (see arrow). Comparison with electronic structure calculations indicates that this feature is from a unique double-acceptor (AA) water molecule with both H atoms pointing into the diffuse orbital of the excess electron, as shown in Figure 5 for $(H_2O)_4^-$, similar to the structures predicted theoretically by Kim and co-workers [67]. Subsequent experiments in Johnson's laboratory showed that this AA binding motif is not restricted to very small clusters but is quite robust, appearing in the bending regions of the IR spectrum for clusters as large as n = 24 [82], and in the OH stretching region for clusters up to n = 21 [83]. Moreover, the ion source conditions used to generate these clusters were analogous to those



Figure 3. Experimental and calculated vertical detachment energies (VDEs) for water cluster anions. Black, red, and blue solid symbols are experimental values for isomers I, II, and III, respectively. Red and blue open symbols are experimental values for smaller clusters from Ref. [49]. Green solid and open circles are calculated VDEs from Ref. [78] for surface and interior states, respectively (from Ref. [81]).



Figure 4. Infrared action spectra of $(H_2O)_n^-$ (n=4-6) in water bend region. The peak around 1550 cm^{-1} is assigned to the double acceptor (AA) water molecule. Reprinted from Ref. [74] with permission of AAAS.



Figure 5. Contour of calculated orbital showing excess electron bound to $(H_2O)_4^-$. Reprinted from Ref. [74] with permission of AAAS.

favoring isomer I. In contrast, the signature of the unique AA water is absent in IR spectra of isomer II for $(H_2O)_6^-$ and $(H_2O)_8^-$; for these species, a broadened shoulder on the low-frequency side of the main bending peak is seen, rather than a well-separated narrow peak, suggesting a more delocalized electron binding motif [84,85].

The tabletop IR laser spectroscopy of water cluster anions has been recently complemented by experiments using an infrared free electron laser (IRFEL) [86], in which IR spectra of trapped and cooled ions are measured through resonant multiple-photon dissociation (Equation (4)) in the regions of the IR spectrum where bending and librational transitions occur. Clusters as large as n = 50 were investigated. The IRFEL spectra, shown in Figure 6, agree well in the water bending region with the tabletop spectra up to n = 24 but show the AA feature becoming considerably less distinct for the larger clusters; by n = 50 it has evolved into a broad shoulder to the red of the main bending peak around 1640 cm^{-1} .

The third set of experiments comprise a series of time-resolved photoelectron imaging/spectroscopy experiments (Equation (3)). In these experiments, the $s \rightarrow p$ electronic transition in size-selected water cluster anions as large as n = 200 was excited with a femtosecond pump pulse with photon energies ranging from 0.75–1.5 eV [75–77]. The resulting dynamics were monitored by photodetachment with a time-delayed femtosecond probe pulse and measurement of the resulting PE spectrum. Figure 7 shows results for $(D_2O)_{25}^{-25}$. The $s \rightarrow p$ transition was excited at 1.0 eV and the upper state dynamics probed at 3.1 eV.



Figure 6. Infrared multiple photon dissociation spectra of $(H_2O)_n^-$ clusters ranging from n=15-50 taken using a free electron laser. Spectra are shown in the region of water libration $(560-1000 \text{ cm}^{-1})$ and the water bend modes $(1450-1755 \text{ cm}^{-1})$. Peak B is from the AA water molecule. Reprinted from Ref. [86] with permission of AIP.

The resulting pump-probe signal yields photoelectrons at electron kinetic energy D. In addition, the probe laser can directly photodetach ground state ions, yielding photoelectrons at the lower energy A. Hence, signal at energies D and A measures the *p*-state and s-state populations, respectively. In Figure 7, the signal at D rises according to the cross-correlation of the pump and probe pulses and falls with a time constant of ~ 400 fs. Feature A evolves oppositely; it is first depleted then rises with a time constant equal to the fall time of D. No other dynamics (such as autodetachment) occur on this time scale, as evidenced by the fact that the lower energy features B and C are constant [76]. These measurements thus provide an unambiguous value for the lifetime of the cluster *p*-state and show that it decays solely by internal conversion to the s-state. The ultrafast lifetimes in our experiments are consistent with results by Zewail [77]. which focused more on the dynamics of the cluster ground states subsequent to internal conversion.



Figure 7. Left: Pump (red, 1.55 eV) and probe (blue, 3.1 eV) excitation scheme used in time-resolved photoelectron spectroscopy of water cluster anions. Pump laser excites $s \rightarrow p$ transition, and probe laser detaches excited state at delay time $\Delta \tau$. Photoelectron signal with eKE = D represent *p*-state population at time $\Delta \tau$, whereas electrons with eKE = A represent *s*-state population. Right: Time-resolved photoelectron spectra of $(D_2O)_{50}^-$ (isomer I). Note that fall of D and rise of A mirror one another, indicating *p*-state decays by internal conversion to *s*-state. Data are from Ref. [76].



Figure 8. Excited-state lifetimes for isomer I and II water cluster anions plotted *vs.* 1/n. Data are from Ref. [76].

Measured excited state lifetimes τ for a range of cluster sizes up to $n\sim200$ are plotted vs. 1/n in Figure 8. Results are shown for Isomers I and II of $(H_2O)_n^-$ and $(D_2O)_n^-$. The key finding in is that isomer I lifetimes for $n \ge 25$ lie on a straight line and that extrapolation to the infinite size limit leads to internal conversion lifetimes of 50 and 70 fs for H₂O and D₂O, respectively. These values match the fastest time constants reported by Barbara [19] for the relaxation of e_{aq}^- in H₂O and D₂O, as well as the IC lifetimes for the bulk hydrated electrons extracted by Wiersma [22] within the context of the non-adiabatic solvation model of the hydrated electron. The dependence of these lifetimes on 1/n has

been discussed by Fischer [87] and rationalized based on a long-range vibronic coupling model. The strong isotope effect in the isomer I lifetimes was not considered in this model, but it is consistent with other gas and condensed phase results in which higher frequency vibrational modes promote electronically non-adiabatic transitions driven by vibronic coupling [88].

Isomer I clusters with $n \le 25$ show shorter relaxation times than expected based on the linear fit in Figure 8. Detailed analysis of the features B and C for these smaller clusters shows that the excited state undergoes autodetachment in addition to internal conversion, thereby providing a parallel pathway for upper state decay [76]. Finally, lifetimes for isomer II clusters show no detectable dependence on cluster size, consistent with their assignment as surface states in which the excess electron is only weakly coupled to the solvent network.

Extrapolation of isomer I lifetimes to $n \to \infty$ implies that the relaxation time constants of 50 fs and 70 fs reported for e_{aq}^- by both Barbara [19] and Wiersma [22] correspond to $p \to s$ internal conversion lifetimes rather than solvent response on the excited state. Hence, the measurements on finite clusters support the nonadiabatic solvation model of e_{aq}^- , in which the *p*-state lifetime is very fast, as opposed to the adiabatic solvation model for which the *p*-state lifetime is several hundred femtoseconds. These cluster experiments have therefore apparently resolved a long-standing controversy in condensed phase chemical physics. In a recent theoretical paper, Borgis *et al.* [89] found the internal conversion lifetime for an *equilibrated* hydrated electron in its *p*-state to be very short, on the order of tens of femtoseconds, depending on the details of the calculations, as opposed to much longer lifetimes in their earlier work. This would seem, at first glance, to narrow the gap between the adiabatic and non-adiabatic solvation models. However, this paper did not address the lifetime of the *nascent* electronic created by $s \rightarrow p$ excitation, and a more recent paper [90] in which solvent relaxation on the excited state is included predicts an overall lifetime of 300 fs.

The other issue raised by this new set of results is the nature of the electron binding motif in water cluster anions. There have been several recent developments that suggest the classification of the observed isomers to be more complex than in the initial interpretation of Figure 3 [72]. For example, calculations by Rossky and co-workers [78,91] yielded VDEs and electronic absorption spectra for internal and surface-bound cluster anions. While their calculated VDEs are in reasonable agreement with those in Figure 3 and seem consistent with the original assignment, the experimental electronic spectra measured by Johnson [51] are in better agreement with Rossky's calculated spectra for surface states than for internal states, and on this basis it was proposed that the isomer I clusters are also surface states. In addition, as discussed above, IR spectroscopy shows the AA electron binding motif to be important in isomer I clusters with at least 24 water molecules [82], while the electron binding in small isomer II clusters (n = 6, 8) is more delocalized [84,85]. These results suggest that up to n = 24, isomers I and II are not internal and surface states but instead represent localized and delocalized surface binding motifs, respectively.

Further information on the structure of water cluster anions comes from recent electronic structure calculations by Jordan [92-94], Head-Gordon [95-98], and Khan [65,99,100] in which relative stabilities and vertical detachment energies have been calculated for numerous isomeric structures with up to 24 water molecules. These calculations have shown that vertical detachment energies for cluster anions with AA binding and more delocalized surface binding motifs can be comparable to calculated VDE's for internally solvated structures. The calculations have also indicated that higher VDEs do not necessarily signify more stable anions, since, since vertical detachment from an internally solvated structure or an AA isomer can result in an energetically unfavorable hydrogen-bonding geometry for the neutral cluster. The calculations have also hinted at complex potential energy landscapes for water cluster anions with multiple potential energy minima separated by significant barriers [94,97] raising the possibility that if multiple isomers are formed in a free jet, their populations may be far out of thermal equilibrium.

Nonetheless, in the face of this complexity, it does appear from the infrared spectra that isomer I clusters as larger as n = 24 exhibit AA binding, and that this type of binding is associated with a surface state. Moreover, as shown in the IRFEL spectra of trapped and cooled ions [86], this binding motif survives multiple collisions with buffer gas in the ion trap. suggesting that it represents, at the very least, a deep local minimum rather than a fragile, metastable structure formed under non-equilibrium conditions in the ion source. On the other hand, the cluster VDE's appear to extrapolate smoothly to a reasonable value of the photoelectric threshold for the bulk hydrated electron, and, as discussed in a recent review by Coe et al. [54], the cluster electronic absorption spectra can also be correlated to those of e_{aq}^- . In addition, the cluster excited state lifetimes extrapolate to time constants obtained in two separate experiments on e_{aa}^{-} . These considerations raise the general question of how water cluster anions evolve structurally toward e_{aa}^{-} , and, specifically, how many waters are needed to achieve an unequivocally internally solved electron.

While these questions are being considered in numerous experimental and theoretical laboratories, it is worth noting that three separate measurements point to significant structural evolution of isomer I clusters starting around n = 25. First, as discussed with reference to Figure 8, excited state autodetachment occurs for clusters up to n = 25, but not for larger clusters, which decay only by internal conversion [76]. Although this trend does not represent an explicit structural probe, autodetachment should generally more facile for a pure surface state than for one with partial internal character. Secondly, the IR spectra for isomer I clusters from n = 25-50 show a shifting and broadening of the AA bending feature [86], as shown in Figure 6, suggesting a trend in which the interaction of the excess electron with a single water is becoming progressively less important, with a more delocalized bonding motif starting to dominate. Such an interpretation is consistent with recent *ab initio* molecular dynamics simulations by Jungwirth [101]. Finally, upon closer inspection, the VDEs themselves show a change in slope in the size of n = 25-35, as shown in Figure 9. Whether these three observations signify the onset of gradual internalization of the excess electron remains to be seen, but they are consistent with such an effect.

3. Related clusters

One can obtain additional insights into electron solvation in clusters by examining other classes of cluster anions. For example, both one-photon and



Figure 9. Detailed view of VDEs for isomer I water cluster anions plotted vs. $n^{-1/3}$, showing change in slope around n = 25-35. Data are from Ref. [72].

time-resolved photoelectron spectra have been reported for $(NH_3)_n^-$ clusters [42,102]. Photoelectron spectra have been measured for several clusters of the type $(S_n)^-$, where S is an organic solvent [103–106].

Neumark and co-workers have performed onephoton and time-resolved photoelectron spectroscopy on $I^{-}(H_2O)_n$ clusters [107–109] and $(CH_3OH)_n^{-}$ clusters [110,111] to gain a better understanding of some of the spectroscopic and dynamical issues raised in the work described above on water cluster anions. The experiments on $I^{-}(H_2O)_n$ clusters are highly complementary to those on $(H_2O)_n^-$ clusters as they probe the dynamics of electron hydration subsequent to transfer of the excess electron from the iodide anion into the solvent network. $(CH_3OH)_n^-$ clusters offer the opportunity to test whether the key results seen for $(H_2O)_n^-$ cluster anions, namely multiple isomers and ultrafast excited state lifetimes, are also observed for a nominally similar system. Photoelectron and infrared spectra of $I^{-}(H_2O)_n$ clusters have been measured [30,112–116], while ground state geometries and electron binding energies have been investigated in electronic structure calculations [117,118] and molecular dynamics simulations [119-123]. In contrast, aside from the results from our laboratory, there has been almost no experimental or theoretical characterization of methanol cluster anions, the exception being a theoretical study of small anion clusters by Turi [124].

3.1. $I^-(H_2O)_n$ clusters

In time-resolved photoelectron imaging experiments on $I^-(H_2O)_n$ clusters [108,109], the dynamics are launched not by electronic excitation of a solvated electron, but rather by excitation of the cluster analog to the charge-transfer-to-solvent (CTTS) band in which the strongly

bound excess electron in the iodide is ejected into the surrounding solvent network, ultimately resulting in a solvated electron [125,126]. CTTS transitions have been studied for many years in the condensed phase, and their cluster analog was first observed in small $I^{-}(H_2O)_n$ clusters by Johnson [127]. In the initial time-resolved photoelectron spectroscopy experiments [107], the CTTS transition in $I^{-}(H_2O)_n$ ($n \le 6$) clusters was excited with a femtosecond pump pulse at 267 nm, and the ensuing dynamics were probed by photodetachment at 1.57 eV. The time-resolved spectra showed that the VDE of the excited cluster increased by 0.1-0.2 eV in less than 1 ps. Similar results were seen for clusters of I⁻ with methanol and ammonia [128,129]. These results were interpreted in terms of stabilization of the ejected electron through solvent dynamics. Subsequent theoretical work by Sheu [130] proposed that the increase in VDE was due to the I atom leaving the cluster, owing to a repulsive interaction between the I atom and diffuse electron cloud created by the pump pulse. Calculations by Jordan [131] and Peslherbe [132] suggested that both solvent stabilization and I atom ejection contributed to the overall dynamics.

In order to gain a more complete understanding of these issues, TRPEI experiments were carried out on $I^-(H_2O)_n$ clusters as large as n = 28, and over a much larger time range than in our initial studies [108,109]. Figure 10(a) shows a typical set of time-resolved photoelectron spectra for $I^-(D_2O)_{17}$, using pump and probe wavelengths of 242 nm and 800 nm, respectively. The results show that the peak of the electron kinetic energy, eKE_{max} , distribution shifts to markedly lower values over the time scale of the experiment, corresponding to an increase in the VDE, since $VDE = hv_{pr} - eKE_{max}$.

This trend is illustrated further in Figure 10(b) over the entire range of cluster sizes. The short-time ($\sim 1 \text{ ps}$) increase in VDE seen for the smaller clusters grows with cluster size, reaching 0.7 eV for $I^{-}(H_2O)_{25}$. The strong dependence of the magnitude of this shift with cluster size implies that it originates primarily from solvent dynamics, an interpretation supported by recent ab initio direct dynamics simulations on the excited state by Kim [133] and Takayanagi [134,135]. In addition, the photoelectron images show signal at very low electron kinetic energies (< 0.1 eV) that grows in on the same time scale as the CTTS excited state decays. This low energy signal was assigned to excited state autodetachment, which our new results confirm to be the primary decay mechanism for the CTTS state. Values measured for the lifetime with respect to autodetachment ranged from 60 ps to > 3 ns, depending on the cluster size.



Figure 10. (a) Time-resolved photoelectron spectra of $I^-(D_2O)_{17}$ taken using pump and probe wavelengths of 242 and 800 nm, respectively. (b) Time-dependent shifts in eKE_{max} for $I^-(D_2O)_n$ clusters, n = 11-25, subsequent to excitation at 242 nm, showing stabilization of excess electron upon injection into the solvent network. Data are from Ref. [109].

Figure 11 compares the time-dependent VDEs of $I^{-}(H_2O)_n$ clusters with VDEs obtained for bare water cluster anions. The VDEs for $I^{-}(H_2O)_n$ clusters at early times are very similar to those for isomer II water cluster anions, whereas after $1-2\,\mathrm{ps}$, the time-dependent VDEs are similar to those for isomer I. It is now generally accepted that the iodide anion resides at the surface of an $I^{-}(H_2O)_n$ cluster in the size regime probed here [119,122], so the agreement with isomer II at early time is consistent with creation of a diffuse electron cloud at the surface of the cluster. The results then imply spontaneous conversion, on a time scale of $\sim 1 \text{ ps}$, from species resembling isomer II to those resembling isomer I, i.e. from water cluster anions with surface-bound electrons to structures in which the excess electron is more strongly bound and possibly more internalized within the solvent network.

In our earlier work on pure water cluster anions [72], we proposed that the isomer II clusters formed under 'cold' ion source conditions were higher energy, metastable species trapped in a local potential energy minimum. Our energy ordering of isomer II vs. isomer I was based on the VDEs for the two isomers. However, as discussed above, electronic structure calculations on water cluster anions have shown that VDEs are a crude measure, at best, of the energy ordering of anionic isomers since they are also sensitive to the energy of the neutral structure formed by photodetachment. The results found here, in which spontaneous ionization from isomer II to I is observed, do in fact support our proposed energy ordering. A representative energy diagram illustrating the dynamics observed here is presented in Figure 12.



Figure 11. Early (t = 0, solid red) and late ($t \gg 0$, solid black) VDE's measured for I⁻(H₂O)_n clusters compared with VDE's for isomers I, II, and III of (H₂O)_n⁻ clusters. The early-time VDEs match the isomer II VDE's, while the late-time VDE's match those of isomer I. Data are from Ref. [109].

3.2. $(CH_3OH)_n^-$ clusters

Experiments on $(CH_3OH)_n^-$ clusters were motivated by our interest in determining whether the multiple isomers and ultrafast relaxation dynamics seen in water cluster anions would also be observed in methanol cluster anions, and also by the similarities between electron solvation in liquid methanol and aqueous solution. Simulations indicate that an electron in bulk methanol resides in a roughly circular cavity of a few angstroms surrounded by ~6 OH groups [136], while its ground and first excited states are approximated as an 's-state' and three 'p-states,' respectively, resulting in a single broad, visible absorption feature [137]. The relaxation dynamics of electrons in methanol have been studied theoretically [138] and in time-resolved transient absorption experiments by several groups [139-144]. The experiments show substantial variations in the reported time constants but raise similar issues regarding assignment of the time constants as were found for the hydrated electron, although there is general agreement that the dynamics are slower in methanol than in water. For example, Barbara [141,142] found two or three time constants for relaxation, depending on the probe wavelength, with the first time scale observed being the fastest, on the order of 200 fs. Thaller et al. [144] reported relaxation on three distinct timescales with $\tau_1 = 105 \pm 25$ fs, $\tau_2 = 670 \pm 100$ fs, and $\tau_3 = 5.3 \pm 0.5$ ps which they assigned to solvent relaxation on the excited *p*-state, followed by internal conversion to excited ground state and, finally, solvent relaxation on the ground state.

One-photon photoelectron spectra [110] of $(MeOH)_n^-$ clusters are shown in Figure 13. Figure 13(a) shows the PE spectrum of $(MeOH)_{190}^{-}$ under varying source conditions. The other panels show photoelectron spectra of $(MeOH)_n^-$ with backing pressures of (b) 20 psig ($n \sim 143-458$) and (c) 30 psig $(n \sim 73-458)$. There are clear analogies with the water cluster anion spectra. In particular, there is evidence for two isomers over a wide cluster size range and one can vary the populations of the two isomers by adjusting the backing pressure, just as for water cluster anions. The source conditions under which each isomer is favored are similar to those for water cluster anions, with nominally colder source conditions (i.e. higher backing pressure) favoring the more weakly-bound isomers. Methanol I, with VDEs ranging from 2-2.5 eV high binding energy, is favored at lower backing pressure, whereas methanol II, with much lower VDEs between 0.2 and 0.5 eV, dominates at higher backing pressure. Key differences are that (i) the minimum and maximum cluster sizes observed (n=73 and 458,respectively) are considerably larger than for water cluster anions, and (ii) the differences in VDEs between methanol I and II are greater than for the analogous $(H_2O)_n^-$ isomers. The size-dependent VDEs for both species are summarized in Figure 14.

We have proposed that the excess electron is internally solvated in methanol I clusters, whereas in methanol II it resides in a dipole-bound surface-state. Several factors are expected to simplify the issues of surface vs. internal states of methanol cluster anions compared to water cluster anions. First of all, the AA electron binding motif in small water cluster anions, in



Figure 12. Representative energy diagram illustrating the dynamics observed upon CTTS excitation of $I^-(H_2O)_n$ clusters. Initially, the cluster resembles isomer II of the bare water cluster anion, then undergoes spontaneous isomerization to form a cluster similar to isomer I. Reprinted from Ref. [109] with permission of AIP.



Figure 13. (a) PE spectrum of $(MeOH)_{190}^{-}$ taken at 3.1 eV at Ar backing pressures ranging from 20–35 psia. (b) PE spectra of $(MeOH)_{n}^{-}$, $n \sim 140-460$, at 3.1 eV with 20 psia backing pressure compared to (c) $n \sim 70-460$ with 30 psia backing pressure. Reprinted from Ref. [110] with permission of AIP.

which both hydrogen atoms of a single water molecule can bind the excess electron to the surface with high VDE [74,92], is clearly not accessible in a methanol cluster anion. Moreover, the CH_3 groups tend to lie at the surface of a neutral methanol cluster (and, for that matter, of liquid methanol [145]) in order to maximize internal hydrogen bonding among OH groups [146], so even single OH groups are not available on the surface to bind the electron without structural rearrangement of the cluster. Overall, there appears to be no obvious surface-binding motif of electrons to a methanol cluster that would result in the high VDE's observed for methanol I, supporting our assignment of methanol I to an internally solvated electron.

Time-resolved photoelectron imaging experiments [111] were carried out on methanol I cluster anions in order to probe excited state lifetimes as a function of size. Results for (CH₃OD)₂₆₅ are shown in Figure 15(a). The feature at highest electron kinetic energy, feature B, represents the excited state population created by the pump pulse at 1.55 eV; it decays exponentially with a time constant of around 270 fs. Figure 15(b) shows size-dependent excited state lifetimes for $(CH_3OH)_n^-$, $(CH_3OD)_n^-$, and $(CD_3OD)_n^-$ and compares them to isomer I of $(H_2O)_n^-$ and $(D_2O)_n^-$. Compared with water clusters, the methanol lifetimes are longer and show a much weaker isotope dependence. They do, however, vary with 1/n, just like in water cluster anions. However, the most interesting result in Figure 15(b) is the extrapolation to the infinite size limit, yielding a lifetime of 157 fs for the excited state of an electron solvated in bulk methanol. This value is in the range of the fastest time constants reported for electrons in methanol [142,144], implying, as with water, that these time constants represent an upper state lifetime rather than solvent relaxation dynamics on the excited. Our value of 157 fs is in good agreement with the theoretical value of 150 fs obtained by Zharikov and Fischer [147] for electrons in methanol using a continuum solvated electron model,

which also recovers the 50 fs value for the lifetime of the p-state in water.

4. Summary and outlook

Our time-resolved experiments on water and methanol cluster anions, taken together, provide strong support for ultrafast *p*-state relaxation in the corresponding bulk solvents on time scales most consistent with the non-adiabatic solvation model for electrons in solution. The question of electron binding motif for large



Figure 14. VBE plotted vs. inverse cluster radius $(n^{-1/3})$ for both methanol isomers and the three isomers of water, as shown in legend. The dotted lines are linear fits of the experimental data from Ref. [110], and the dashed line is taken from Ref. [41]. Reprinted from Ref. [110] with permission of AIP.



Figure 15. Left: Time resolved photoelectron spectra of $(CH_3OD)_{265}^-$ with pump and probe energies of 1.55 and 3.1 eV, respectively. Right: Internal conversion lifetimes for $(methanol)_n^-$ isotopologs compared to $(water)_n^-$ as indicated in the legend, plotted as a function of inverse cluster size, 1/n.

clusters is more unsettled. As discussed in Section 2, results from three separate experiments imply a structural evolution in water cluster anions in the size range of n=25-35. Moreover, isomer I clusters for water and methanol cluster anions appear to be closely related. Their formation is favoured under similar ion source conditions, their VDEs are similar for comparably-sized clusters, and their excited state relaxation dynamics exhibit similar trends. Hence, it would be surprising if the electron binding motifs were totally different for the two solvents. While we have argued that electrons are likely to be internally solvated in large methanol I clusters, this supposition requires additional experimental and theoretical investigation to provide structural probes of these species.

We close by considering future experiments that should further explore the relationship between the spectroscopy and dynamics of excess electrons in clusters and bulk solvated electrons. It is of particular interest to test the extrapolations of the VDEs in Figure 3 and the $p \rightarrow s$ internal conversion lifetimes in Figure 8 by performing the analogue of one-photon and time-resolved photoelectron spectroscopy experiments on electrons in aqueous solution. These experiments may in fact be feasible using liquid water microjets. In such a jet, electrons can be generated using the same methods that have been used in bulk water [19], and one would certainly expect these electrons to be true 'hydrated electrons'. In addition, liquid jets are, with some effort, compatible with the high vacuum instrumentation needed to perform PES experiments, as has been demonstrated in several laboratories [148-151]. Hence, PES experiments on hydrated electrons in liquid jets could provide the 'missing link' between the cluster and condensed phase experiments and thus provide fundamental new insights into the nature of electron solvation dynamics in both media.

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References

- [1] J. Jortner, Z. Phys. D 24, 247 (1992).
- [2] A.W. Castleman Jr and K.H. Bowen Jr, J. Phys. Chem. 100, 12911 (1996).
- [3] D.G. Leopold, J. Ho, and W.C. Lineberger, J. Chem. Phys. 86, 1715 (1987).

- [4] O. Cheshnovsky, K.J. Taylor, J. Conceicao, *et al.*, Phys. Rev. Lett. **64**, 1785 (1990).
- [5] M.G. Bawendi, M.L. Steigerwald, and L.E. Brus, Annu. Rev. Phys. Chem. 41, 477 (1990).
- [6] J.R.R. Verlet, Chem. Soc. Rev. 37, 505 (2008).
- [7] W. Weyl, Pogg. Ann. 123, 350 (1864).
- [8] E.J. Hart and J.W. Boag, J. Am. Chem. Soc. 84, 4090 (1962).
- [9] E.J. Hart and M. Anbar, *The Hydrated Electron* (Wiley-Interscience, New York, 1970).
- [10] C. Von Sonntag, The Chemical Basis of Radiation Biology (London, Taylor and Francis, 1987).
- [11] S. Golden and T.R. Tuttle, J. Chem. Soc. Faraday Trans. II 75, 474 (1979).
- [12] L. Kevan, Accts. Chem. Res. 14, 138 (1981).
- [13] P.J. Rossky and J. Schnitker, J. Phys. Chem. 92, 4277 (1988).
- [14] M. Boero, M. Parrinello, K. Terakura, *et al.*, Phys. Rev. Lett. **90**, 226403 (2003).
- [15] H.F. Hameka, G.W. Robinson, and C.J. Marsden, J. Phys. Chem. 91, 3150 (1987).
- [16] A.L. Sobolewski and W. Domcke, Phys. Chem. Chem. Phys. 9, 3818 (2007).
- [17] A. Migus, Y. Gauduel, J.L. Martin, *et al.*, Phys. Rev. Lett. **58**, 1559 (1987).
- [18] Y. Kimura, J.C. Alfano, P.K. Walhout, *et al.*, J. Phys. Chem. **98**, 3450 (1994).
- [19] K. Yokoyama, C. Silva, D.H. Son, *et al.*, J. Phys. Chem. A **102**, 6957 (1998).
- [20] M. Assel, R. Laenen, and A. Laubereau, J. Phys. Chem. A 102, 2256 (1998).
- [21] X. Shi, F.H. Long, H. Lu et al., J. Phys. Chem. 100, 11903 (1996).
- [22] M.S. Pshenichnikov, A. Baltuska, and D.A. Wiersma, Chem. Phys. Lett. 389, 171 (2004).
- [23] R.B. Barnett, U. Landman, and A. Nitzan, J. Chem. Phys. 90, 4413 (1989).
- [24] B.J. Schwartz and P.J. Rossky, J. Chem. Phys. 101, 6917 (1994).
- [25] P.O.J. Scherer and S.F. Fischer, Chem. Phys. Lett. 421, 427 (2006).
- [26] A. Hertwig, H. Hippler, A.N. Unterreiner, *et al.*, Ber. Bunsen-Ges. Phys. Chem. **102**, 805 (1998).
- [27] H. Hotop and W.C. Lineberger, J. Phys. Chem. Ref. Data 14, 731 (1985).
- [28] A. Stolow, A.E. Bragg, and D.M. Neumark, Chem. Rev. 104, 1719 (2004).
- [29] S.A. Corcelli, J.A. Kelley, J.C. Tully, *et al.*, J. Phys. Chem. A **106**, 4872 (2002).
- [30] W.H. Robertson and M.A. Johnson, Annu. Rev. Phys. Chem. 54, 173 (2003).
- [31] H. Haberland, C. Ludewigt, H.-G. Schindler, *et al.*, J. Chem. Phys. **81**, 3742 (1984).
- [32] H. Haberland, H.-G. Schindler, and D.R. Worsnop, Ber. Bunsen-Ges. Phys. Chem. 88, 270 (1984).
- [33] G.H. Lee, S.T. Arnold, J.G. Eaton, *et al.*, Chem. Phys. Lett. **321**, 333 (2000).
- [34] D.C. Clary and D.M. Benoit, J. Chem. Phys. 111, 10559 (1999).

- [35] M. Knapp, O. Echt, D. Kreisle, et al., J. Chem. Phys. 85, 636 (1986).
- [36] L.A. Posey and M.A. Johnson, J. Chem. Phys. 89, 4807 (1988).
- [37] L.A. Posey, P.J. Campagnola, M.A. Johnson, *et al.*, J. Chem. Phys. **91**, 6536 (1989).
- [38] S.T. Arnold, R.A. Morris, and A.A. Viggiano, J. Chem. Phys. 103, 9242 (1995).
- [39] S.T. Arnold, R.A. Morris, A.A. Viggiano, *et al.*, J. Phys. Chem. **100**, 2900 (1996).
- [40] J.M. Weber, E. Leber, M.W. Ruf, et al., Eur. Phys. J. D 7, 587 (1999).
- [41] J.V. Coe, G.H. Lee, J.G. Eaton, *et al.*, J. Chem. Phys. 92, 3980 (1990).
- [42] G.H. Lee, S.T. Arnold, J.G. Eaton, *et al.*, Z. Phys. D 20, 9 (1991).
- [43] R.N. Barnett, U. Landman, C.L. Cleveland, *et al.*, J. Chem. Phys. 88, 4429 (1988).
- [44] R.N. Barnett, U. Landman, C.L. Cleveland, et al., J. Chem. Phys. 88, 4421 (1988).
- [45] R.N. Barnett, U. Landman, C.L. Cleveland, *et al.*, Phys. Rev. Lett. **59**, 811 (1987).
- [46] R.N. Barnett, U. Landman, G. Makov, *et al.*, J. Chem. Phys. **93**, 6226 (1990).
- [47] R.N. Barnett, U. Landman, D. Scharf, *et al.*, Accts. Chem. Res. **22**, 350 (1989).
- [48] C.G. Bailey and M.A. Johnson, Chem. Phys. Lett. 265, 185 (1997).
- [49] J. Kim, I. Becker, O. Cheshnovsky, *et al.*, Chem. Phys. Lett. **297**, 90 (1998).
- [50] T. Maeyama, T. Tsumura, A. Fujii, *et al.*, Chem. Phys. Lett. **264**, 292 (1997).
- [51] P. Ayotte and M.A. Johnson, J. Chem. Phys. 106, 811 (1997).
- [52] D.M. Bartels, J. Chem. Phys. 115, 4404 (2001).
- [53] J.V. Coe, Int. Rev. Phys. Chem. 20, 33 (2001).
- [54] J.V. Coe, S.M. Williams, and K.H. Bowen, Int. Rev. Phys. Chem. 27, 27 (2008).
- [55] J.M. Weber, J. Kim, E.A. Woronowicz, *et al.*, Chem. Phys. Lett. **339**, 337 (2001).
- [56] P. Ayotte, C.G. Bailey, J. Kim, et al., J. Chem. Phys. 108, 444 (1998).
- [57] P. Ayotte, G.H. Weddle, C.G. Bailey, *et al.*, J. Chem. Phys. **110**, 6268 (1999).
- [58] S. Lee, J. Kim, S.J. Lee, *et al.*, Phys. Rev. Lett. **79**, 2038 (1997).
- [59] J. Kim, J.M. Park, K.S. Oh, et al., J. Chem. Phys. 106, 10207 (1997).
- [60] D.M.A. Smith, J. Smets, Y. Elkadi, et al., J. Chem. Phys. 107, 5788 (1997).
- [61] D.M.A. Smith, J. Smets, Y. Elkadi, et al., J. Chem. Phys. 109, 1238 (1998).
- [62] Y.V. Novakovskaya and N.F. Stepanov, J. Phys. Chem. A 103, 10975 (1999).
- [63] H.Y. Chen and W.S. Sheu, J. Chem. Phys. 115, 10678 (2001).
- [64] F. Wang and K.D. Jordan, J. Chem. Phys. 116, 6973 (2002).
- [65] A. Khan, J. Chem. Phys. 121, 280 (2004).

- [66] J. Kim, J.Y. Lee, K.S. Oh, et al., Phys. Rev. A 59, 930 (1999).
- [67] J. Kim, S.B. Suh, and K.S. Kim, J. Chem. Phys. 111, 10077 (1999).
- [68] S.B. Suh, H.M. Lee, J. Kim, et al., J. Chem. Phys. 113, 5273 (2000).
- [69] H.M. Lee and K.S. Kim, J. Chem. Phys. 117, 706 (2002).
- [70] H.M. Lee, S. Lee, and K.S. Kim, J. Chem. Phys. 119, 187 (2003).
- [71] H.M. Lee, S.B. Suh, and K.S. Kim, J. Chem. Phys. 118, 9981 (2003).
- [72] J.R.R. Verlet, A.E. Bragg, A. Kammrath, *et al.*, Science 307, 93 (2005).
- [73] A. Kammrath, J.R.R. Verlet, G.B. Griffin, *et al.*, J. Chem. Phys. **125**, 171102 (2006).
- [74] N.I. Hammer, J.W. Shin, J.M. Headrick, *et al.*, Science 306, 675 (2004).
- [75] A.E. Bragg, J.R.R. Verlet, A. Kammrath, *et al.*, Science 306, 669 (2004).
- [76] A.E. Bragg, J.R.R. Verlet, A. Kammrath, *et al.*, J. Am. Chem. Soc. **127**, 15283 (2005).
- [77] D.H. Paik, I. Lee, D. Yang, et al., Science 306, 672 (2004).
- [78] L. Turi, W.-S. Sheu, and P.J. Rossky, Science 309, 914 (2005).
- [79] A.V. Davis, R. Wester, A.E. Bragg, *et al.*, J. Chem. Phys. **118**, 999 (2003).
- [80] A.T.J.B. Eppink and D.H. Parker, Rev. Sci. Instrum. 68, 3477 (1997).
- [81] J.R.R. Verlet, A.E. Bragg, A. Kammrath, *et al.*, Science 310, 1769b (2005).
- [82] J.R. Roscioli, N.I. Hammer, and M.A. Johnson, J. Phys. Chem. A 110, 7517 (2006).
- [83] N.I. Hammer, J.R. Roscioli, J.C. Bopp, *et al.*, J. Chem. Phys. **123**, 244311 (2005).
- [84] N.I. Hammer, J.R. Roscioli, and M.A. Johnson, J. Phys. Chem. A 109, 7896 (2005).
- [85] J.R. Roscioli and M.A. Johnson, J. Chem. Phys. 126, 024307 (2007).
- [86] K.R. Asmis, G. Santambrogio, J. Zhou, et al., J. Chem. Phys. 126, 191105 (2007).
- [87] S.F. Fischer and W. Dietz, Z. Phys. Chem. 221, 585 (2007).
- [88] R. Englman and J. Jortner, Mol. Phys. 18, 145 (1970).
- [89] D. Borgis, P.J. Rossky, and L. Turi, J. Chem. Phys. 125, 064501 (2006).
- [90] D. Borgis, P.J. Rossky, and L. Turi, J. Chem. Phys. 127, 174508 (2007).
- [91] L. Turi, A. Madarasz, and P.J. Rossky, J. Chem. Phys. 125, 014308 (2006).
- [92] T. Sommerfeld and K.D. Jordan, J. Phys. Chem. A 109, 11531 (2005).
- [93] T. Sommerfeld and K.D. Jordan, J. Am. Chem. Soc. 128, 5828 (2006).
- [94] T. Sommerfeld, S.D. Gardner, A. DeFusco, *et al.*, J. Chem. Phys. **125**, 174301 (2006).
- [95] J.M. Herbert and M. Head-Gordon, J. Phys. Chem. A 109, 5217 (2005).
- [96] J.M. Herbert and M. Head-Gordon, J. Am. Chem. Soc. 128, 13932 (2006).

- [97] J.M. Herbert and M. Head-Gordon, PNAS 103, 14282 (2006).
- [98] J.M. Herbert and M. Head-Gordon, Phys. Chem. Chem. Phys. 8, 68 (2006).
- [99] A. Khan, J. Chem. Phys. 125, 024307 (2006).
- [100] A. Khan, Journal of Molecular Structure-Theochem 850, 144 (2008).
- [101] T. Frigato, J. VandeVondele, B. Schmidt, et al., J. Phys. Chem. A 112, 6125 (2008).
- [102] I.R. Lee, W. Lee, and A.H. Zewail, Chemphyschem 9, 83 (2008).
- [103] S.Y. Han, J.K. Song, J.H. Kim, *et al.*, J. Chem. Phys. 111, 4041 (1999).
- [104] M. Mitsui, A. Nakajima, and K. Kaya, J. Chem. Phys. 117, 9740 (2002).
- [105] M. Mitsui, N. Ando, S. Kokubo, *et al.*, Phys. Rev. Lett. **91**, 153002 (2003).
- [106] T. Maeyama, Y. Negishi, T. Tsukuda, *et al.*, Phys. Chem. Chem. Phys. 8, 827 (2006).
- [107] L. Lehr, M.T. Zanni, C. Frischkorn, *et al.*, Science 284, 635 (1999).
- [108] A. Kammrath, J.R.R. Verlet, A.E. Bragg, et al., J. Phys. Chem. A 109, 11475 (2005).
- [109] J.R.R. Verlet, A. Kammrath, G.B. Griffin, *et al.*, J. Chem. Phys. **123**, 231102 (2005).
- [110] A. Kammrath, J.R.R. Verlet, G.B. Griffin, *et al.*, J. Chem. Phys. **125**, 171102 (2006).
- [111] A. Kammrath, G.B. Griffin, J.R.R. Verlet, *et al.*, J. Chem. Phys. **126**, 244306 (2007).
- [112] G. Markovich, R. Giniger, M. Levin, et al., J. Chem. Phys. 95, 9416 (1991).
- [113] G. Markovich, S. Pollack, R. Giniger, *et al.*, J. Chem. Phys. **101**, 9344 (1994).
- [114] M.S. Johnson, K.T. Kuwata, C.K. Wong, et al., Chem. Phys. Lett. 260, 551 (1996).
- [115] C.G. Bailey, J. Kim, C.E.H. Dessent, *et al.*, Chem. Phys. Lett. **269**, 122 (1997).
- [116] P. Ayotte, G.H. Weddle, J. Kim, *et al.*, J. Phys. Chem. A **103**, 443 (1999).
- [117] H.M. Lee and K.S. Kim, J. Chem. Phys. 114, 4461 (2001).
- [118] H.M. Lee, D. Kim, and K.S. Kim, J. Chem. Phys. 116, 5509 (2002).
- [119] L. Perera and M.L. Berkowitz, J. Chem. Phys. 99, 4222 (1993).
- [120] L.X. Dang and B.C. Garrett, J. Chem. Phys. 99, 2972 (1993).
- [121] L.X. Dang, J. Chem. Phys. 110, 1526 (1999).
- [122] D.M. Koch and G.H. Peslherbe, Chem. Phys. Lett. 359, 381 (2002).
- [123] M.D. Elola and D. Laria, J. Chem. Phys. 117, 2238 (2002).
- [124] L. Turi, J. Chem. Phys. 110, 10364 (1999).

- [125] M.J. Blandamer and M.F. Fox, Chem. Rev. 70, 59 (1970).
- [126] J. Jortner, M. Ottolenghi, and G. Stein, J. Phys. Chem. 68, 247 (1964).
- [127] D. Serxner, C.E.H. Dessent, and M.A. Johnson, J. Chem. Phys. 105, 7231 (1996).
- [128] A.V. Davis, M.T. Zanni, C. Frischkorn, *et al.*, J. Electron Spectrosc. and Rel. Phenom. **108**, 203 (2000).
- [129] C. Frischkorn, M.T. Zanni, A.V. Davis, *et al.*, Faraday Disc. **115**, 49 (2000).
- [130] H.Y. Chen and W.S. Sheu, Chem. Phys. Lett. 335, 475 (2001).
- [131] F.D. Vila and K.D. Jordan, J. Phys. Chem. 106, 1391 (2002).
- [132] Q.K. Timerghazin and G.H. Peslherbe, J. Am. Chem. Soc. 125, 9904 (2003).
- [133] M. Kolaski, H.M. Lee, C. Pak, *et al.*, J. Am. Chem. Soc. **130**, 103 (2008).
- [134] T. Takayanagi and K. Takahashi, Chem. Phys. Lett. 431, 28 (2006).
- [135] K. Takahashi and T. Takayanagi, Chem. Phys. 342, 95 (2007).
- [136] L. Turi, A.A. Mosyak, and P.J. Rossky, J. Chem. Phys. 107, 1970 (1997).
- [137] V. Herrmann and P. Krebs, J. Phys. Chem. 99, 6794 (1995).
- [138] P. Minary, L. Turi, and P.J. Rossky, J. Chem. Phys. 110, 10953 (1999).
- [139] C. Pepin, T. Goulet, D. Houde, *et al.*, J. Phys. Chem. 98, 7009 (1994).
- [140] X. Shi, F.H. Long, H. Lu, et al., J. Phys. Chem. 99, 6917 (1995).
- [141] P.K. Walhout, J.C. Alfano, Y. Kimura, *et al.*, Chem. Phys. Lett. **232**, 135 (1995).
- [142] C. Silva, P.K. Walhout, P.J. Reid, *et al.*, J. Phys. Chem. A **102**, 5701 (1998).
- [143] T. Scheidt and R. Laenen, Chem. Phys. Lett. 371, 445 (2003).
- [144] A. Thaller, R. Laenen, and A. Laubereau, J. Chem. Phys. 124, 024515 (2006).
- [145] C.D. Stanners, Q. Du, R.P. Chin, *et al.*, Chem. Phys. Lett. **232**, 407 (1995).
- [146] U. Buck and F. Huisken, Chem. Rev. 100, 3863 (2000).
- [147] A.A. Zharikov and S.F. Fischer, J. Chem. Phys. 124, 054506 (2006).
- [148] M. Faubel, B. Steiner, and J.P. Toennies, J. Chem. Phys. 106, 9013 (1997).
- [149] K.R. Wilson, M. Cavalleri, B.S. Rude, *et al.*, J. Phys. Chem. B **109**, 10194 (2005).
- [150] F. Mafune and T. Kondow, Aust. J. Chem. 57, 1165 (2004).
- [151] B. Winter and M. Faubel, Chem. Rev. 106, 1176 (2006).