

Electronic absorption spectra of size-selected hydrated electron clusters: $(\text{H}_2\text{O})_n$, $n=6-50$

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COMMUNICATIONS

Electronic absorption spectra of size-selected hydrated electron clusters: $(\text{H}_2\text{O})_n^-$, $n=6-50$

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We report photodestruction spectra for the $(\text{H}_2\text{O})_n^-$ clusters ($n=6, 11, 15, 20, 25, 30, 35, 40$, and 50) in the range $0.7-1.6$ eV. The spectra are observed to strongly redshift and narrow with decreasing cluster size, with a concomitant increase in peak intensity. The maxima occur well below the vertical detachment energies for $n>20$ and almost exclusively result from excitation of a bound-bound transition. © 1997 American Institute of Physics. [S0021-9606(97)02602-0]

I. INTRODUCTION

The hydrated electron clusters,¹ $(\text{H}_2\text{O})_n^-$, allow us to study the evolution of the excess electron state in a dipolar medium from a diffuse, dipole bound system in the dimer^{2,3} to a cavity species⁴ in the bulk. One of the most prominent characteristics of the bulk hydrated electron (e_{aq}^-) is, of course, its near infrared electronic absorption spectrum peaking at about 1.7 eV.^{5,6} Some time ago, we reported⁷ preliminary “spectra” consisting of a few wavelengths for two clusters, ($n=18$ and 30) indicating that their electronic absorption bands are red-shifted in a fashion that roughly follows their vertical electron binding energies.⁸ Recent advances in tunable solid state laser technology now enable the entire spectrum to be acquired in a single scan, resulting in substantially improved spectra. In this paper, we present much more complete spectra of the $(\text{H}_2\text{O})_n^-$ clusters to define the band shapes and exact locations of the maxima to quantify the evolution of the cluster spectra toward that of e_{aq}^- .

II. EXPERIMENT

The ion source and mass spectrometer have been described in detail previously⁹ and only a brief account will be given here. A high energy cw electron beam (1 keV) ionizes a pulsed supersonic expansion of argon saturated with water vapor at 20 °C (20 torr). Negatively charged water clusters are formed by attachment of slow secondary electrons to existing neutral water clusters and are stabilized either by collisions or monomer evaporation. After drifting for approximately 15 cm, the charged clusters are injected into a tandem time-of-flight (TOF) photofragmentation spectrometer. The laser beam strikes the ion packet at the transient spatial focus, and the daughter ions are separated from the parent beam by a secondary “reflectron-type” mass spectrometer.

The laser beam was generated by a commercial optical parametric oscillator (Spectra Physics MOPO 710) pumped

by the third harmonic of a Nd:YAG (Spectra-Ray GCR-4). The present experiments utilized the idler beam which was scanned continuously from 730 nm to $1.8\text{ }\mu\text{m}$, the range containing most of the oscillator strength in the intermediate sized clusters ($n\approx 25$). Because the idler beam fluence drops by an order of magnitude with strong oscillatory modulation over that range, it was kept constant over the scan using a servo-controlled, four-plate attenuator. The destruction of the parent ions is determined by laser on-laser off cycles averaging 600 laser shots at each photon energy to correct for fluctuations in parent ion intensity. The depletion spectrum therefore appears as a square wave modulation in parent intensity as the laser is scanned over the electronic absorption band.

When acquiring spectra using action (in this case photodestruction) spectroscopy, it is essential to correct for the “kinetic shift” which occurs when an excited species does not decompose in the time window ($\approx 10\text{ }\mu\text{s}$) of the experiment. Since we observe a falling destruction cross section on the low energy side of the spectra [for $n\geq 15$ (Fig. 1)] where we expect such an effect, we now consider in detail the possibility that decay kinetics are affecting the spectra. Basically, we can avoid a kinetic shift if we can be sure that the entire excited parent cluster ensemble has sufficient energy to decompose prior to detection. This, in turn, requires that the clusters possess some initial internal energy and that the width of its distribution is small compared to the excitation energy. These requirements can be met if the cluster source is governed by the evaporative ensemble,¹⁰ which we have recently shown to give a reasonable account of the internal energy content of the $(\text{H}_2\text{O})_n^-$ clusters produced in our source.¹¹ In the present experiment, we observe about 5% spontaneous decay of the parent, indicating significant initial internal excitation. In addition, the fragment distribution is very narrow (typically displaying one dominant fragment at a given energy), indicating a narrow internal energy distribution. We have previously shown¹² how to use the photon energy dependence of the fragment distribution to quantify

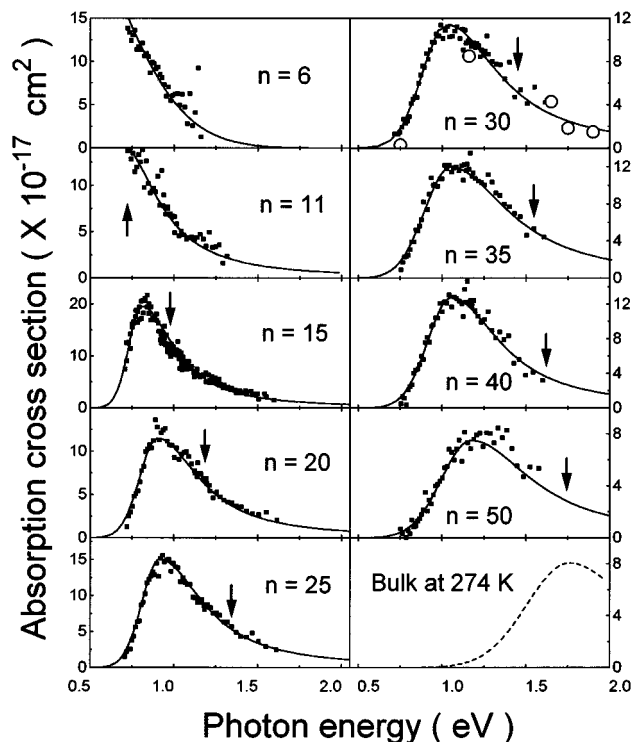


FIG. 1. Absorption of $(\text{H}_2\text{O})_n^-$ in the photon energy range 0.7–1.6 eV for $n=6, 11, 15, 20, 25, 30, 35, 40$, and 50. The curves through the data result from fitting Gaussian and Lorentzian curves to the red and blue side of the maxima, respectively. The arrows are the VDEs from Coe *et al.* (Ref. 8). The bulk spectrum (at 274 K) is from Jou and Freeman (Ref. 16). Open circles overlaid on the $(\text{H}_2\text{O})_{30}^-$ spectrum show results from a previous measurement (Ref. 7).

the kinetic shift by constructing the photofragmentation breakdown curves.¹³ These curves display the evolution of the fragmentation branching ratio as a function of photoexcitation energy. In the case of $(\text{H}_2\text{O})_{25}^-$, the width of an individual channel (e.g., loss of two monomers) breakdown curve is about ≈ 0.4 eV, close to the monomer binding energy ($\Delta E=0.37$ eV).¹⁴ The kinetic shift is therefore minimized so long as there is a significant contribution from loss of two monomers. The $(\text{H}_2\text{O})_{50}^-$ parent is observed to lose an average of 1.3 monomers (i.e., loss of 2 is about half as intense as loss of 1) at 1.00 eV, so we are confident that the drop in absorption cross section below 1 eV is due to a decrease in absorption cross section rather than a kinetic artifact. We also note that the integrated oscillator strength is the same for $n=15$ –40, confirming that most of the absorption is accounted for in the spectrum.¹⁵ The current apparatus is limited to clusters $n \leq 50$ by the resolution of the fragmentation spectrometer since the loss of one monomer fragment peak begins to partially overlap the broadening parent peak for large n .

The absorbance spectra were generated by taking the log of the fractional parent depletion at each photon energy. The absolute cross sections were determined by scaling the relative spectra from each cluster to their carefully measured cross sections at 1064 nm. These values were determined

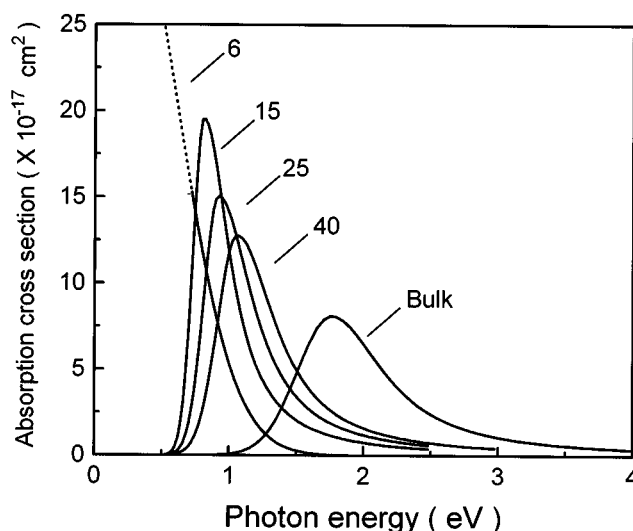


FIG. 2. Fits of the $(\text{H}_2\text{O})_n^-$ absorption cross sections in the photon energy range 0.7–1.6 eV for $n=6, 15, 25, 40$, and the bulk.

using the spatially filtered core from the far field expansion of the (doughnut) Nd:YAG (Spectra Physics DCR-11) beam. Proper overlap of the laser with the ion beam was ensured by quasicomplete depletion of the parent beam ($>97\%$) with full laser power.

III. RESULTS

The absorption spectra for $(\text{H}_2\text{O})_n^-$ $n=6$ –50 are displayed in Fig. 1. The squares are experimental data points and the smooth lines through the data result from a fit to a Gaussian function on the red side of the maximum and to a Lorentzian function on the blue side, an empirical form observed to recover the shape of the bulk spectrum.¹⁶ With the exception of $n=6$ and 11, the absorption maxima are clearly observed in the higher cluster sizes, whose band shapes agree remarkably well with the functional form that characterizes the bulk spectrum. The general trend is that the band maxima shift to higher photon energies and that the bandwidths increase, both monotonically, with increasing cluster size. In our previous report,⁷ the largest cross sections were found at 1.165 eV for both $n=18$ and 30, followed by a gap in spectral coverage before smaller values were obtained at 0.75 eV. The previous data are included for $n=30$ (open circles) to illustrate the point. From the data in Fig. 1, it is clear that the peaks occur between the widely separated points (0.75 and 1.165 eV) in the earlier spectra.

To compare the evolution of the absolute cross sections, we plot the fitted curves (without the data) on the same axes in Fig. 2. This display is useful in that it captures the fact that the spectra narrow and increase in intensity with decreasing size. Qualitatively, we regard this increase as a reflection of the increasing size of the ground state electronic wave function which results in large amplitude motion upon resonant electronic excitation and hence large values of the transition moment $\mu^2 \propto \langle \Psi_g | r | \Psi_{\text{ex}} \rangle^2$. This is, of course, another way of acknowledging that the ground state radius is governed by

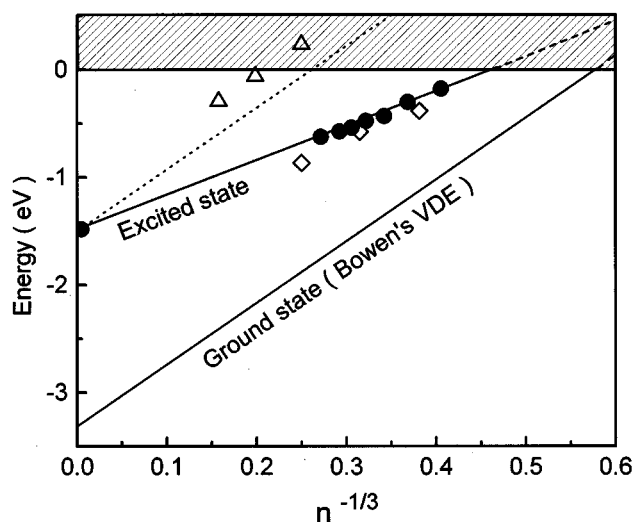


FIG. 3. Location of the $(\text{H}_2\text{O})_n^-$ ground and first excited (filled circles) states relative to the electron continuum (hashed region) at the geometry of the anion vs $n^{-1/3}$. The former were obtained from the VDE [Coe *et al.* (Ref. 8)], while the latter were generated by adding E_{max} from the absorption spectra to their VDE. Open diamonds and triangles are calculated spectra for surface and interior states from Barnett *et al.* (Ref. 28).

the -1st moment of the absorption spectrum.^{17–19} The spectra display conservation of area with size-independent integrated cross sections corresponding to oscillator strengths (f) of 0.78, 0.77, and 0.78 for $n=15$, 25, and 40, respectively.¹⁵ Perhaps coincidentally, these oscillator strengths are remarkably close to the value in the bulk ($f=0.75$),¹⁶ which is nonunity due to the presence of the dielectric (i.e., $nf \approx 1$; where n =index of refraction of water).²⁰ While we caution that absolute cross sections are notoriously difficult to measure to better than 20%, the present data indicate that the f values for the clusters are similar to the bulk value. In other words, the oscillator strength does not appear to increase as the medium is removed.

One of the most important outstanding issues regarding the photophysics of $(\text{H}_2\text{O})_n^-$ is the location of the excited electronic states relative to the detachment continua. The vertical detachment energies (VDEs) have already been determined by Coe *et al.*⁸ using photoelectron spectroscopy for clusters in this size range and are included as arrows in Fig. 1. While the maximum of the $n=15$ spectrum occurs quite close to the VDE, the absorption maxima quickly drop well below the VDEs such that by $n=50$, the excited state lies about 0.5 eV below the (vertical) continuum. This indicates that most of the band intensity occurs in the region corresponding to a bound excited state, which decays by fragmentation rather than electron detachment.²¹

In analyzing the size-dependence of charge stabilization in clusters, it is useful to remove the “excluded” polarization energy to isolate nontrivial solvation effects.²² This scaling is conveniently displayed by plotting experimental quantities as a function of the inverse cluster radius, or equivalently, $n^{-1/3}$. To explore the size dependence of the absorption spectra, we have chosen to plot the energies of the

ground and excited states relative to the electron continuum vs $n^{-1/3}$ in Fig. 3. The ground state energies correspond to the VDE values obtained by photoelectron spectroscopy, which were observed by Coe *et al.*⁸ to follow a linear dependence on the $n^{-1/3}$ plot. When the solute ion is well contained within the cluster, Barnett *et al.*²² pointed out that the slope of the binding energy vs cluster radius depends only on the polarization of the dielectric

$$\text{VDE}(n) = \text{VDE}(\infty) - e^2/2R_s \{1 + \epsilon_\infty^{-1} - 2\epsilon_s^{-1}\} n^{-1/3}. \quad (1)$$

While this assumption need not apply to diffuse, self-trapped particles like hydrated electrons [as opposed to size-invariant species such as small inorganic anions (e.g., I^-)], Coe *et al.*⁸ recovered the VDE vs $n^{-1/3}$ slope (5.73 eV) using only bulk water parameters. They interpreted the fact that the VDE values fall on the “universal” curve (i.e., defined by the bulk solvent) to indicate that the clusters should be considered as species which smoothly converge toward e_{aq}^- (i.e., where the electron is contained within the cluster). Interestingly, a similar slope (5.76 eV) was recently found to recover the cluster size dependence of the stabilization energy of the I^- ion by water clusters,²³ while several molecular dynamics calculations on the $\text{I}^-(\text{H}_2\text{O})_n$ system agree that the halide anion resides *on the surface of the cluster*.^{24–26} Apparently, both the continuum (Barnett *et al.*²²) and the surface (Makov and Nitzan²⁷) solvation models yield about the same slope! Therefore, it may not be possible to establish ground state configuration based solely on how the energetics scale with cluster radius.

In the very large size range, where the excited state orbital is much smaller than the cluster radius, the cluster spectra should converge to that of the bulk species since both ground and excited states will eventually be shifted by the same missing polarization energy.^{22,28} The binding energies of the excited states were obtained from the difference between the absorption maxima and the VDE value for each cluster and are shown as filled circles in Fig. 3. The intercept is estimated by adding the peak of the bulk spectrum to the ground state VDE asymptote. Coe *et al.*⁸ estimated the ground state asymptote by summing the photoconduction threshold of e_{aq}^- with the edge of the conduction band, V_0 . Universal scaling of the excited state is indicated by the dotted line. Clearly, the observed excited state also displays a linear dependence vs $n^{-1/3}$, but with a *different slope* (3.2 eV), much smaller than the universal slope [$e^2/2R_s \{1 + \epsilon_\infty^{-1} - 2\epsilon_s^{-1}\} \approx 5.73$ eV] followed by the ground state. The size dependence of the cluster spectra therefore reveals a nontrivial change (e.g., beyond energetics) in the clusters relative to the bulk.

This intrinsic cluster effect might involve the fact that the weakly bound excited state is larger than the ground state. For example, moment analysis of the e_{aq}^- absorption spectrum¹² indicates that the bulk radius is about 2.5 Å, similar to the size of the small clusters ($R_{n=15} \approx 3.5$ Å).¹⁵ Thus an excited state significantly larger than the ground state cannot be described by excluded polarization alone even in moder-

ately large clusters ($n=40$) since a significant portion of the excited state wave function extends beyond the cluster boundaries.

While the different slope can be rationalized by in the context of the spatial extent of the excited state, it is puzzling that these spectra, apparently unique to the clusters, extrapolate in the $n^{-1/3}$ plot very accurately to the energy of the bulk excited state $[(1.71 \pm 0.06) \text{ eV vs } 1.793 \text{ eV and } 1.725 \text{ eV at } 274 \text{ and } 298 \text{ K, respectively}]^{16}$, indicating a smooth evolution to e_{aq}^- . As the bulk surely corresponds to internal solvation, this paradox calls into question the procedure used to estimate the bulk VDE asymptote, the only datum in Fig. 3 which is not directly measured. The fact that the excited state energies do not fall on the universal curve also raises the unresolved issue of exactly where the electron resides in the ground states of the clusters. Barnett *et al.*²⁸ calculated the bound-bound contributions to the absorption spectra for both surface and internal states in the size range of interest in the present work. Their results are included in Fig. 3: the open diamonds represent surface states while the open triangles correspond to the interior states. The surface states are obviously in much better agreement with the experimental data than the interior states. Note that some calculated interior states appear in the continuum (at the geometry of the anion) and indeed fall close to the universal solvation line. Barnett *et al.*²⁸ suggested that the cluster spectra should shift dramatically from the surface curve to the universal curve (lying about 1 eV higher in energy) when the internal ground state form is adopted. They calculated that this transition should occur between $32 < n < 64$, but our $(\text{H}_2\text{O})_n^-$ spectra indicate that this shift has not occurred by $n=50$. We remark that while the calculated spectra indeed agree with the observed spectra, the calculated VDEs²⁸ did not reproduce the experimental values.⁸ This was attributed to artifacts in the calculation (i.e., boundary conditions, etc.) which were expected to cancel out in the difference between ground and excited states required to estimate the absorption spectra. Thus, the deceptively complicated $(\text{H}_2\text{O})_n^-$ system has not yet yielded to self-consistent explanation of the experimental observations.

Summarizing, we report strong, size dependent absorption in $(\text{H}_2\text{O})_n^-$ clusters which sharpen and increase in peak intensity with decreasing cluster size. The excited state energies extracted from the absorption maxima scale linearly with $n^{-1/3}$, but with a smaller slope than the universal value (i.e., defined only by the parameters of bulk water), which describes the ground state energies of $(\text{H}_2\text{O})_n^-$ clusters as well as the hydrated halide anions, $\text{X}^-(\text{H}_2\text{O})_n$. The absorption maxima agree well with that calculated for the $(\text{H}_2\text{O})_n^-$ "surface" states, while the size-dependence indicates a smooth evolution toward the bulk value.

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