

cluster—it reflects a peculiarity in the bonding of tetramers rather than unusual dynamics.

To check this notion, we have also made observations of the dissociation temperature T_{diss} (that is of the temperature for which the cluster dissociates during a heating interval of a quarter of a second). The values of T_{diss} plotted in Fig. 1 show the same general trends as the diffusion temperature—dissociation of the tetramer occurs at a substantially lower temperature than for the trimer or pentamer. The binding of cluster atoms in the tetramer is unusually weak, and it is this weakness that allows atomic displacement, and therefore diffusion, to occur so readily in the tetramer. For iridium clusters on Ir(111), which so far is the only two-dimensional system examined quantitatively, all the observations are consistent with cluster diffusion by the same mechanism, regardless of size—namely by displacements of the individual atoms making up the cluster.

This work was carried out with support from the Department of Energy under Grant No. DE-AC02-76ER01198.

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NOTES

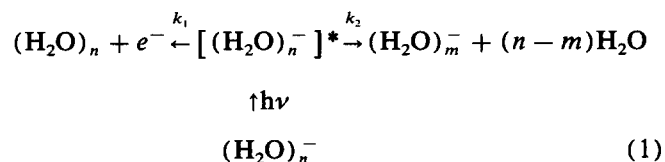
On the origin of the competition between photofragmentation and photodetachment in hydrated electron clusters, $(\text{H}_2\text{O})_n^-$

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(Received 9 June 1989; accepted 1 August 1989)

The interaction of excess electrons with water has been studied extensively in media ranging from the solid state to gas phase clusters. Such studies have included measurement of elastic and inelastic scattering cross sections for electrons in thin amorphous water films,^{1,2} ESR spectra of hydrated electrons (e_{aq}^-) frozen in glasses,^{3,4} optical spectra of e_{aq}^- in solution,⁵⁻⁷ and electron thermalization lengths in liquid water.⁸ The relaxation of electrons injected into liquid water has been investigated via the disappearance of a transient IR absorption⁹ and appearance of a relatively long-lived absorption peaking from 600 to 700 nm attributed to e_{aq}^- .^{5-7,10-12} Theoretical¹³⁻²¹ and experimental²²⁻³⁵ interest in hydrated electron clusters, $(\text{H}_2\text{O})_n^-$, has arisen because of the possible connection between cluster and condensed phase behavior. Experimental work has included mass spectrometry,²²⁻²⁶ photoelectron spectroscopy (PES),³⁰⁻³² low energy electron attachment,²⁷⁻²⁹ vibrational autodetachment,³⁵ as well as studies on the reactivity³⁴ of $(\text{H}_2\text{O})_n^-$. Previous work by Posey and Johnson³³ revealed that fragmentation competes with electron detachment:



when hydrated electron clusters $(\text{H}_2\text{O})_n^-$ ($15 \leq n \leq 40$) are excited at 1064 nm, near the photodetachment thresholds determined by PES.³⁰⁻³² The observed competition appears to be a general property of homogeneous anionic cluster systems.³⁶⁻⁴⁴

To quantify this connection between photodissociation and threshold photodetachment, we report the wavelength dependence of the photofragmentation quantum yield [Eq. (1)] and compare it to the electron binding energy (EBE) distribution measured by PES. We define the photofragmentation quantum yield as the integrated ionic photofragment intensity divided by the integrated parent depletion [$\phi = k_2/(k_2 + k_1)$]. Inherent in this definition is the assumption that all photons absorbed by the cluster lead to ion

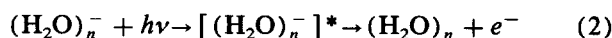
depletion, i.e., absorption leads either to photodetachment or photofragmentation.³³ Hence, $(1 - \phi)$ yields the photodetachment branching ratio. The details of $(\text{H}_2\text{O})_n^-$ cluster production as well as the experimental apparatus used in these photofragmentation studies at Yale have been described in previous work.³³ First and second Stokes orders of a Raman shifted (H_2) pulsed dye laser supplied the near IR wavelengths used for photofragmentation. Photoelectron data ($n = 2, 6, 7, 11-40$) was collected with the apparatus at Johns Hopkins^{31,45} which has also been described previously.

Since the present study focuses on the competition between photofragmentation and photodetachment, we restrict our attention to excitation energies above the electron photodetachment threshold ($h\nu \geq 0.8 \text{ eV}$), which also exceeds the energy required to eject a neutral water monomer ($D_0 \approx 0.48 \pm 0.05 \text{ eV}$, $n \geq 15$).^{46,47} Figure 1 displays the photofragmentation quantum yield (ϕ) measured on the Yale apparatus plotted as a function of photon energy for $(\text{H}_2\text{O})_{25}^-$ along with its EBE distribution measured using the continuous beam photoelectron spectrometer at Johns Hopkins. Remembering that the electron photodetachment quantum yield is $1 - \phi$, Fig. 1 reveals that only photodetachment is observed at excitation energies above 2 eV; however, as the photon energy decreases photofragmentation begins to compete with photodetachment with an onset in the range of EBE distribution. It should be noted that although the cluster ion sources used in the Yale³³ and Johns Hopkins experiments³⁰⁻³² are different, both groups have obtained nearly identical photoelectron spectra. The EBE distribution displayed in Fig. 1 was obtained at 488 nm (2.540 eV), a photon energy where photofragmentation no longer competes with photodetachment. Interestingly, the vertical detachment energy (VDE) of 1.4 eV for $(\text{H}_2\text{O})_{25}^-$ is in the range of that calculated for surface state electron localization.¹⁷

Thus, the photofragmentation channel drops rapidly with increasing photon energy over a range corresponding to the width of the EBE spectrum. The half-height of the photofragmentation onset ($\phi \approx 0.5$) is nearly the same as the

VDE (peak of the dashed spectrum), a correlation which holds for all clusters in the size range $20 \leq n \leq 40$.⁴⁸ Note that excitation below the EBE threshold ($\approx 0.8 \text{ eV}$) does not have sufficient energy to access the electron continuum; and therefore, ϕ must converge to unity for $h\nu \ll 0.8 \text{ eV}$.

The observation that photofragmentation only competes with photodetachment near the detachment threshold suggests that the energy of the photoexcited excess electron may control the fragmentation of $(\text{H}_2\text{O})_n^-$ clusters. In this picture, photoabsorption above the VDE appears to be channeled into excitation of the extra electron and hence increases its propensity to escape from the cluster (photodetach).^{33,48} In studying the reverse process, low energy electron attachment to neutral water clusters, Echt and co-workers^{27,28} observed that only near zero kinetic energy electrons ($\text{KE} \leq 0.5 \text{ eV}$, the limiting resolution of the apparatus) are efficiently attached to form negative ions. Kondow²⁹ has also prepared similar $(\text{H}_2\text{O})_n^-$ cluster ion distributions using collisional electron transfer from high-Rydberg rare gas atoms, a technique which provides a source of electrons with kinetic energies less than 10 meV. Furthermore, the detailed shape of the $(\text{H}_2\text{O})_n^-$ cluster ion distribution created by low energy electron attachment can be reconstructed considering only the photofragmentation pathways of $(\text{H}_2\text{O})_n^-$.^{33,48} The similarities between the electron attachment studies and this work suggest that cluster formation and photofragmentation proceed through a common intermediate.



perhaps with intracluster electron scattering mediating the decay dynamics. Thus, optically excited $(\text{H}_2\text{O})_n^-$ clusters appear to simulate the e^- -cluster complex at the "half-collision," where increasing photon energy above the detachment threshold corresponds to increasing the electron kinetic energy.

Acknowledgments. The research at Yale University was supported by NSF Grant No. CHE 8602195 and the Office of Naval Research. The research at Johns Hopkins was supported by NSF Grant No. CHE 8511320.

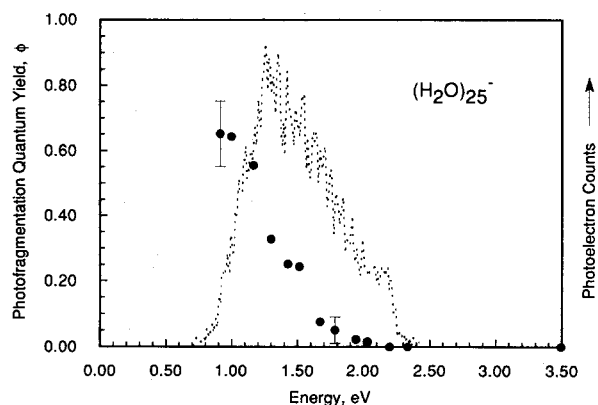


FIG. 1. Photon energy dependence of the photofragmentation quantum yield (\bullet) shown with representative error bars and the electron binding energy (EBE) distribution measured using photoelectron spectroscopy (dashed curve) for $(\text{H}_2\text{O})_{25}^-$. The displayed EBE distribution is artificially truncated above 2.3 eV due to limitations in low energy photoelectron collection.

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COMMENTS

Comment on predissociation of O₂ in the B state

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In their paper on the predissociation of O₂ in the B state, Wodtke *et al.*¹ attempt to match the observed excitation spectrum of some O₂ Schumann-Runge features with simulated spectra synthesized from triplet component line center spacings, obtained from the fine structure analysis of Bergeman and Wofsy,² and individual triplet component widths, based on the calculations of Julienne³ and Julienne and Krauss⁴ for curve crossings of the B ³Σ_u⁻ states of symmetries ³Π_u, ³Π_u, and ³Σ_u⁺ (or ¹Π_u), respectively. For example, the R(27) feature of the (11,2) band, which is partially resolved in the experimental excitation spectrum of Fig. 4 of Wodtke *et al.*, is compared with three simulated spectra of which only one, viz., that corresponding to the curve crossing by the repulsive ³Π_u state, is consistent, according to Wodtke *et al.*, with the experimental result. In their Fig. 4, the relative peak heights of the individual R₁, R₂, and R₃ components are given by the ratios of the reciprocals of the line widths of Julienne. These relative peak heights are used together with the component widths of Julienne and the component spacings calculated from the spin constants of

Bergeman and Wofsy² to generate three Lorentzians that are added to produce the resultant R(27) line profile, which is then convoluted with the (assumed Gaussian) laser profile for comparison with the experimental excitation spectrum.

We have verified that the relative peak heights of the components, shown in Fig. 4 of Wodtke *et al.* on the same ordinate as the resultant cross section, are not the relative peak cross sections of the component Lorentzians, but are instead the relative integrated cross sections. This significant distinction, nowhere stated in their paper, confirms that the simulated spectra in their Fig. 4 are excitation spectra and not absorption spectra.

Wodtke *et al.* used the spin-spin and spin-rotation constants of the v' = 11 level of Bergeman and Wofsy² to calculate the triplet spacings for the R(27) feature of the (11,2) band. Those spacings, estimated from Fig. 4 of Wodtke *et al.*, are R₂ - R₁ ≈ 0.9 and R₃ - R₂ ≈ 1.2 cm⁻¹. We have recently performed high resolution photographic absorption wavelength measurements of O₂ at ~520 K (unpublished), with the same spectrographic apparatus used in our earlier

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