

# Observation of resonant two-photon photodetachment of water cluster anions via femtosecond photoelectron spectroscopy

J.M. Weber <sup>a</sup>, J. Kim <sup>a</sup>, E.A. Woronowicz <sup>a</sup>, G.H. Weddle <sup>c</sup>, I. Becker <sup>b</sup>,  
O. Cheshnovsky <sup>b,1</sup>, M.A. Johnson <sup>a,\*</sup>

<sup>a</sup> Sterling Chemistry Laboratory, Department of Chemistry, Yale University, P.O. Box 208107, 225 Prospect Street, New Haven, CT 06520-8107, USA

<sup>b</sup> School of Chemistry, Raymond and Beverly Sackler Faculty of Exact Sciences, Tel Aviv University, Tel Aviv 69978, Israel

<sup>c</sup> Department of Chemistry, Fairfield University, Fairfield, CT 06430, USA

Received 29 January 2001; in final form 14 February 2001

## Abstract

Photoexcitation of the  $(\text{H}_2\text{O})_n^-$  ( $n = 20\text{--}100$ ) clusters with 100 fs pulses at 800 nm results in an increasing propensity for two-photon electron photoejection with increasing cluster size. This increase correlates with the size range ( $n \approx 30$ ) where the first excited electronic state drops below the electron continuum, and the electronic absorption band approaches the energy of the 800 nm pump photon. No above-threshold, two-photon detachment is observed for  $n = 20$ . Differences in the shape of the resonant two-photon photoelectron spectrum compared to that arising from direct (high energy) photodetachment are interpreted in terms of the vibrational state selection created in the resonant step. © 2001 Elsevier Science B.V. All rights reserved.

## 1. Introduction

The hydrated electron continues to capture the attention of photophysicists as it has proven surprisingly difficult to pin down even the qualitative mechanism describing the order of events by which the optically pumped species relaxes back to the ground state. Important dynamics occur on the tens of fs time scale [1–6], presenting a profound experimental challenge, while the interaction of a self-trapped electron with a medium as

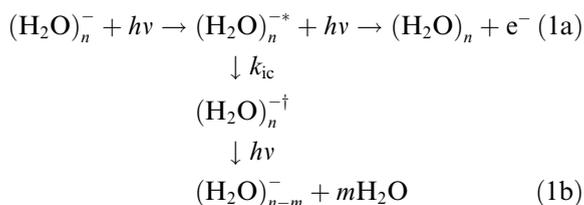
complex as water has made simulation of the process an equally daunting task [6–12]. One of the experimental difficulties arising in the study of the bulk species via time-resolved photobleaching is that it has not been possible to establish whether the transients are due to sequential absorption into the conduction band or relaxation back to ground state, effectively recycling the original absorption chromophore [1,5]. In this Letter, we report the first results of a different class of ultrafast experiments involving the (size-selected) cluster analogues of the hydrated electron,  $(\text{H}_2\text{O})_n^-$ . In our approach, we propose to separate the sequential absorption pathway from ground state recovery since, in clusters, excitation of the excited state species with a second photon can

\* Corresponding author. Fax: +1-203-432-6144.

E-mail address: mark.johnson@yale.edu (M.A. Johnson).

<sup>1</sup> Also corresponding author.

directly access the photodetachment continuum, while absorption from a repopulated ground state is known [13,14] to result in monomer evaporation. This scheme is described in Eqs. (1a) and (1b):



where  $(\text{H}_2\text{O})_n^{-*}$  denotes the electronically excited state,  $k_{\text{ic}}$  denotes the internal conversion relaxation rate, and  $(\text{H}_2\text{O})_n^{-\dagger}$  indicates the (hot) ground state species. With nanosecond laser pulses, multiple photon absorption occurs exclusively through the sequential photoevaporation pathway (Eq. (1b) with up to at least 5 photons [14]), indicating that  $1/k_{\text{ic}} \ll 10$  ns [13]. Here, we establish that two-photon electron ejection (Eq. (1a)) can be observed upon photoexcitation with  $\sim 100$  fs pulses and carry out a size dependence study of the resulting two-photon photoelectron spectra. The observation of a clear signature for the two-photon detachment pathway enables us to directly monitor the electronically excited state population of the hydrated electron in the larger clusters. We discuss the size and wavelength dependence of the photoelectron spectra and the possible use of clusters to resolve the difficulties in understanding the relaxation dynamics of the excited hydrated electron in the bulk.

## 2. Experimental

Water cluster anions  $(\text{H}_2\text{O})_n^-$  were prepared by electron attachment in the high-density region of a pulsed supersonic expansion containing water vapor in 3 bar Ar [15]. The slow electrons necessary for this process were generated by 1 keV electron impact ionization at the throat of the expansion, creating an overall electrically neutral plasma. Size selection was achieved by timing the fs pulse to intercept a particular ion packet at the transient focus of a Wiley–McLaren time-of-flight (TOF) mass spectrometer [16].

Femtosecond pulses from a commercial mode-locked Ti:Sapphire oscillator (Spectra Physics Tsunami, pumped by a Spectra Physics Millennia V solid state laser) were stretched, amplified, and recompressed in a regenerative amplifier (Spectra Physics Spitfire) pumped by a Nd:YLF laser (Spectra Physics Merlin) at a repetition rate of 1 kHz. The amplified output was interfaced to the ion beam apparatus at a repetition rate of 40 Hz. Maximum pulse energies were typically 780  $\mu\text{J}$ , with a pulse duration of 110 fs (determined by measuring the autocorrelation function of the fs laser pulse using frequency doubling in a 1 mm long BBO crystal).

The photoelectrons were energy-analyzed in a magnetic bottle TOF spectrometer described previously [17]. Electron TOF traces were sampled using a 100 MHz transient recorder. Photoelectron spectra shown in this work typically result from an accumulation of about  $10^5$  pulses.

## 3. Results and discussion

### 3.1. Emergence of resonant two-photon photodetachment with increasing cluster size

Fig. 1 shows the size dependence of the photoelectron spectra of water cluster anions  $(\text{H}_2\text{O})_n^-$  for cluster sizes in the range  $20 \leq n \leq 100$  upon irradiation with 800 nm pulses ( $20 \mu\text{J}/\text{mm}^2$ ). The character of the spectra changes with growing cluster size, where small clusters display a broad dominant band at low electron kinetic energies, but develop a peak at high electron kinetic energies that increases in relative intensity and finally dominates the spectra for large clusters. We interpret these peaks to be the signatures of electron detachment after the absorption of one and two photons by the parent cluster, and we will label them in the following discussion with I and II, respectively. The low-energy peak (I) represents the ‘normal’ photoelectron spectrum of  $(\text{H}_2\text{O})_n^-$  clusters, and the arrow on the lowest ( $n = 20$ ) trace in Fig. 1 corresponds to the vertical detachment energy of  $(\text{H}_2\text{O})_{20}^-$  determined by Bowen and co-workers [18] using cw photodetachment at 488 nm.

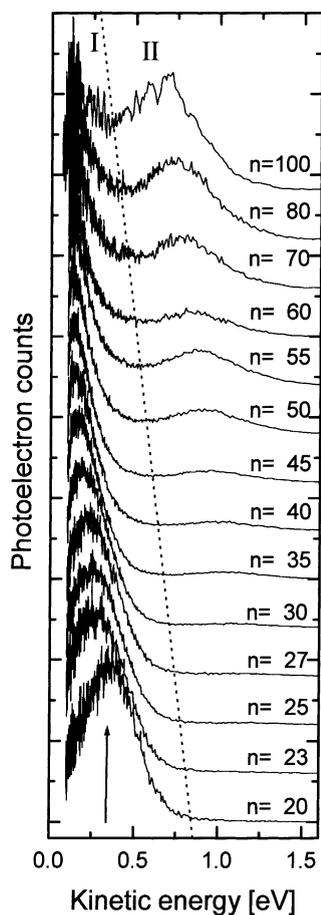


Fig. 1. Photoelectron spectra from photodetachment of  $(\text{H}_2\text{O})_n^-$  ( $n = 20\text{--}100$ ) clusters with  $\sim 100$  fs laser pulses at 800 nm. The electron kinetic energy ranges associated with the absorption of one and two photons are labeled I and II, respectively. The arrow in the bottom trace corresponds to the vertical detachment energy of  $(\text{H}_2\text{O})_{20}^-$  as determined by Bowen and co-workers [18].

The assignment of peak II to a two-photon process is supported by the fluence dependence of the peak II photoelectron yield relative to that of peak I presented in Fig. 2. The peak identified as a two-photon feature increases linearly with increasing fluence below  $10 \mu\text{J}/\text{mm}^2$ , with a saturation plateau in the  $50 \mu\text{J}/\text{mm}^2$  range. In addition, peak II could not be observed in a photodetachment experiment using nanosecond pulses from a Nd:YAG laser (1064 nm), even if the fluence of these pulses ( $>200 \text{ J}/\text{mm}^2$ ) was much higher than that of the fs pulses ( $\sim 0.1 \text{ mJ}/\text{mm}^2$ ).

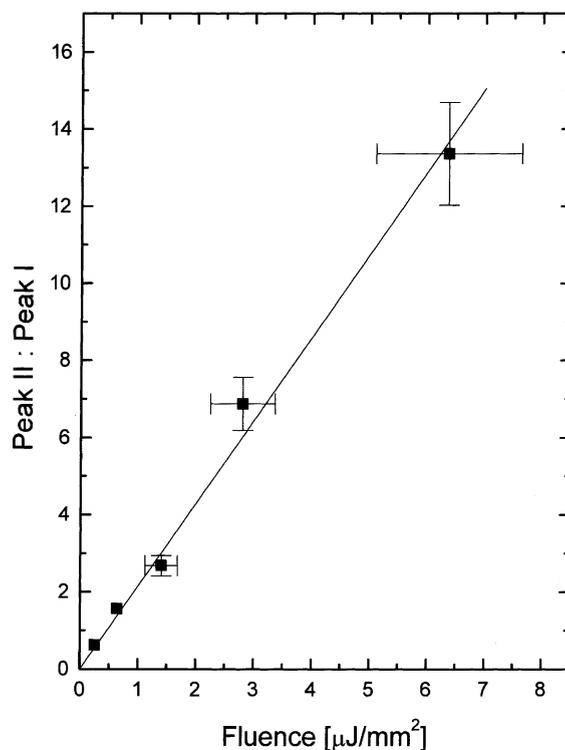


Fig. 2. Fluence dependence of the two-photon photoelectron band (peak II) relative to the one-photon feature (peak I) for  $n = 40$ . The full line is a linear fit.

The emergence of the two-photon absorption peak can be qualitatively understood in terms of the known size dependence of the  $(\text{H}_2\text{O})_n^-$  ground and excited state energetics. These trends were determined by photoelectron [18] and absorption spectroscopies, [19] respectively, and the vertical energetics are summarized in Fig. 3. These trends were determined by photoelectron [18] and absorption spectroscopies [19], respectively, and the vertical energetics are summarized in Fig. 3. The transition to the excited state effectively “tunes” into resonance with the fixed 1.55 eV excitation energy with increasing cluster size, while at the same time, this excited state becomes more stable with respect to autodetachment as it falls further below the continuum. On the other hand, two photon absorption can access the continuum for very large  $n$ .

At very small clusters, therefore, the 1.55 eV photon provides direct access to the detachment

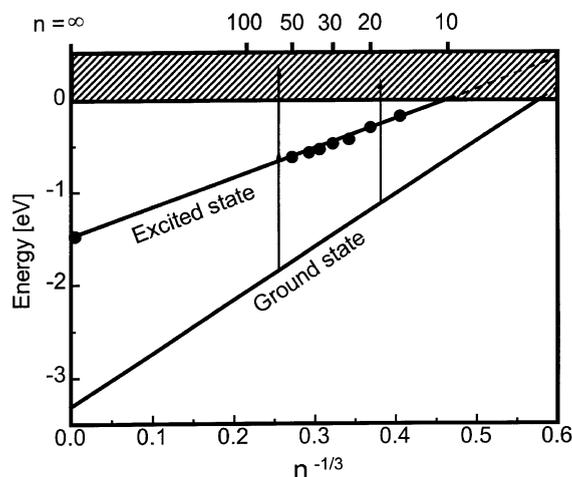


Fig. 3. Energetics of water cluster anions after [19]. The circles denote the electronically excited states experimentally determined in [19]. The straight line corresponding to the ground state energies represents the analytical form for the size dependence of the vertical detachment energy established by Bowen and co-workers [18].

continuum, and electronically excited states embedded in this continuum can undergo rapid autodetachment in competition with direct detachment. This suppresses the two-photon peak II (no above-threshold detachment was observed for small clusters) and explains the origin of the large direct detachment peak (I). One observes a shift of both photoelectron peaks toward lower kinetic energies with increasing cluster size, reflecting the net increase in electron binding energy depicted in Fig. 3. Summarizing, the resonant two-photon detachment (R2PD) [20] peak emerges with increasing cluster size as the direct (one photon) detachment peak diminishes, reflecting the size-dependences of absorption spectra and electron binding energies.

### 3.2. Size-dependent differences in the R2PD vs direct photoelectron spectra

Fig. 4 presents a comparison between the envelopes of the two-photon bands (II in Fig. 1) and the direct detachment photoelectron spectra obtained with 400 nm radiation (generated by frequency doubling the (100 fs) 800 nm radiation in a 1 mm long BBO crystal) at  $n = 40$  and 80. Note

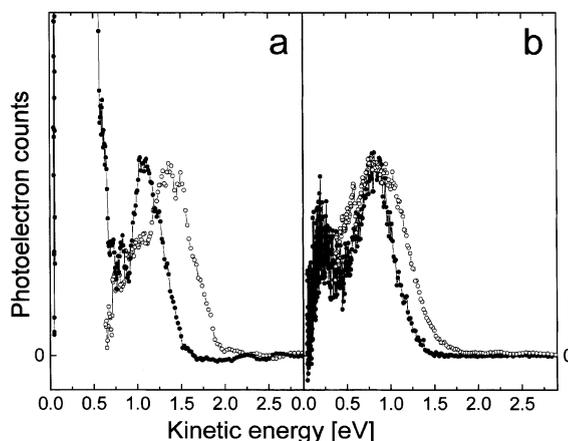


Fig. 4. Comparison of the photoelectron spectra of (a) small ( $n = 40$ ) and (b) large ( $n = 80$ )  $(\text{H}_2\text{O})_n^-$  clusters at 800 nm (full circles) and 400 nm (open circles). The direct one-photon (400 nm) detachment spectra are normalized to the height of the two-photon peak in the 800 nm spectra.

that the survey spectra (Fig. 1) were taken with the parent ion beam kinetic energy at 2 keV, which degrades the resolution of the magnetic bottle spectrometer to  $\Delta E \sim 300$  meV for 1 eV photoelectrons. To investigate the details of the bands, we have therefore re-acquired spectra after impulsively decelerating the beam prior to detachment, resulting in a resolution of 150 meV for 1 eV electrons. At both cluster sizes, peak II is narrower than the direct detachment envelope (e.g., 390 vs. 720 meV for the two-photon and direct one-photon detachment bands, respectively, in  $n = 40$ ). The large breadth of both the absorption and photoelectron bands presumably arises from a shift in equilibrium geometry in the ground state relative to that of the electronically excited state (as well as that of the neutral, leading to the so-called reorganization energy). In the case where the excited state and the neutral have similar geometries, one would expect the first step in the resonant two-photon detachment process would select a small range of vibrational levels, which are more-or-less preserved upon photodetachment [21]. Such a mechanism would explain the size-dependent displacement of the peak in band II relative to that in the direct photoelectron spectrum (Fig. 4). This displacement is large for  $n = 40$ , where 1.55 eV excitation occurs at the

upper end of the absorption profile, leading to selective population of high vibrational levels. This population would be preserved upon vertical photodetachment to a similarly configured neutral state, leading to the observed depletion of the high kinetic energy side of the photoelectron band in the  $n = 40$  spectrum as this region corresponds to population of lower vibrational levels. At larger cluster size, the first photon selects lower vibrational levels, leading to the smaller observed shift in the relative position of peak II in the  $n = 80$  spectra (Fig. 4b).

#### 4. Remarks on the prospects for cluster analogues of bulk relaxation dynamics

We noted in the introduction that recent work has led to two conflicting pictures of the relaxation pathway followed by the optically pumped, hydrated electron [5]. The relevant states are sketched in Fig. 5a to facilitate the discussion. The basic point of disagreement is whether the observed absorption (bleach) transients are due to ground state recovery (fast  $\tau_{ic}$ ) or sequential absorption from the excited state to the conduction band (slow  $\tau_{ic}$ ). The situation in clusters is depicted in Fig. 5b, where, for moderately large clusters, the excited state is sufficiently close to the detachment continuum that excitation of the ‘conduction band’ now corresponds to two-photon photodetachment. On the other hand, if the system relaxes back to the ground state, absorption of a second photon (or more, resulting in the net absorption of  $n$  photons) by this pathway can be detected via the number,  $m$ , of water molecules photoejected on a much longer time scale, where  $m \approx n h\nu / (\Delta H_{vap})$ . About 3 water molecules are evaporated upon absorption of a 1.55 eV photon [22] so that fragments arising from sequential absorption events are well separated. Thus, the branching between the two-photon photodetachment and photofragmentation channels should unambiguously identify not only how many photons were absorbed by the system, but the state of the system at the time of the absorption.

Time-resolved measurements of these two pathways are presently underway in our labora-

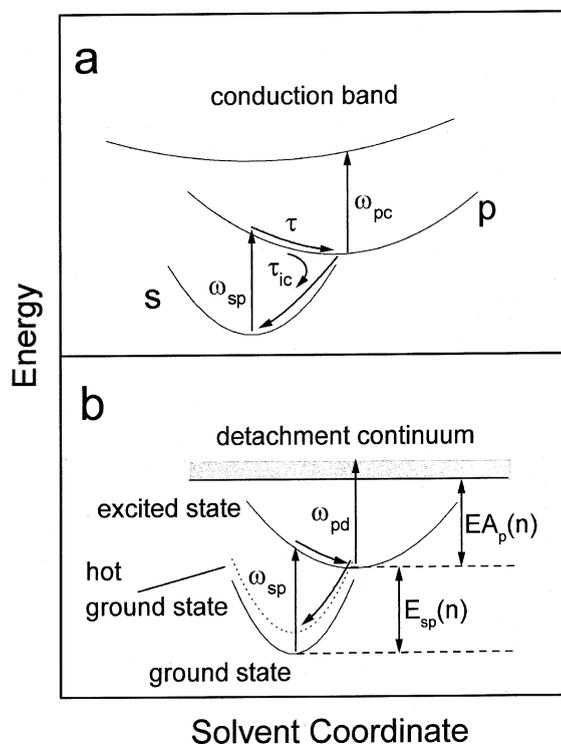


Fig. 5. Comparison of the photochemical pathways for the hydrated electron in the bulk (a) and in clusters (b).  $\omega_{sp}$  denotes the optical  $s \rightarrow p$  transition, while  $\omega_{pc}$  and  $\omega_{pd}$  are the transitions into the conduction band and the detachment continuum, respectively.  $1/\tau_{ic}$  denotes the radiationless transition rate from the p state to the s state.  $E_{Ap}(n)$  and  $E_{sp}(n)$  are the size-dependent vertical detachment and  $s \rightarrow p$  transition energies, respectively.

tory. In preliminary, one-color pump–probe experiments performed at 800 nm, we observe an enhancement in the intensity of peak II as the pump laser pulse coincides with the probe (with either parallel or perpendicular relative polarizations of the two beams). While we are not yet able to measure a response outside of the instrument autocorrelation time of about 150 fs, this observation appears to place an upper bound for the excited state lifetime on the order of the pulse width.

Of course, it is important to emphasize that the cluster system may bring different processes into the relaxation dynamics arising from the proximity of the surface, and indeed raises the important question of exactly where the excess electron

resides in a cluster [23]. Nonetheless, we propose that an exploration of the relaxation processes and time scales in these finite systems will contribute to our overall understanding of the hydrated electron, especially since the clusters targeted for this study are rather large ( $n \approx 100$ ).

## 5. Conclusion

Two-photon electron photodetachment has been observed upon  $\sim 100$  fs excitation of size selected, negatively charged water clusters at 800 nm. The two-photon detachment cross-section is found to be strongly size-dependent, increasing dramatically in the size range  $n = 30$ – $60$ . This is correlated with the size-dependent blue shift in the absorption spectra with increasing cluster size, which effectively tunes the absorption band into resonance with the fixed 1.55 eV excitation energy. The kinetic energy distribution of the photoelectrons ejected with the second photon are found to be significantly narrower (about  $2\times$ ) than those arising from direct detachment, indicating that some of the vibrational selection achieved in the resonant step is preserved upon photodetachment.

## Acknowledgements

We are grateful to Department of Energy for support of this work, as well as the National Science Foundation, which provided funds for the ultrafast laser system under the University Research Instrumentation program. This research was partly supported by the US–Israel Binational Science Foundation. We also thank Prof. K.D. Jordan for valuable discussions pertaining to the interpretation of this data.

## References

- [1] C. Silva, P.K. Walhout, K. Yokoyama, P.F. Barbara, *Phys. Rev. Lett.* 80 (1998) 1086.
- [2] M. Assel, R. Laenen, A. Laubereau, *J. Phys. Chem. A* 102 (1998) 2256.
- [3] M.F. Emde, A. Baltuska, A. Kummrow, M.S. Pshenichnikov, D.A. Wiersma, *Phys. Rev. Lett.* 80 (1998) 4645.
- [4] A. Kummrow, M.F. Emde, A. Baltuska, M.S. Pshenichnikov, D.A. Wiersma, *J. Phys. Chem. A* 102 (1998) 4172.
- [5] K. Yokoyama, C. Silva, D.H. Son, P.K. Walhout, P.F. Barbara, *J. Phys. Chem. A* 102 (1998) 6957.
- [6] A. Baltuska, M.F. Emde, M.S. Pshenichnikov, D.A. Wiersma, *J. Phys. Chem. A* 103 (1999) 10065.
- [7] B.J. Schwartz, P.J. Rossky, *J. Chem. Phys.* 101 (1994) 6902.
- [8] B.J. Schwartz, P.J. Rossky, *J. Chem. Phys.* 101 (1994) 6917.
- [9] A. Staib, D. Borgis, *J. Chem. Phys.* 103 (1995) 2642.
- [10] B.J. Schwartz, E.R. Bittner, O.V. Prezhdo, P.J. Rossky, *J. Chem. Phys.* 104 (1996) 5942.
- [11] B.J. Schwartz, P.J. Rossky, *J. Chem. Phys.* 105 (1996) 6997.
- [12] M.A. Berg, *J. Chem. Phys.* 110 (1999) 8577.
- [13] D.J. Lavrich, P.J. Campagnola, M.A. Johnson, *NATO ASI Ser. B* 326 (1994) 183.
- [14] L.A. Posey, Ph.D. Thesis, Yale University, New Haven, CT, 1989.
- [15] M.A. Johnson, W.C. Lineberger, in: J.M. Farrar, W. Saunders (Eds.), *Techniques for the Study of Gas-Phase Ion Molecule Reactions*, Wiley, New York, 1988, p. 591.
- [16] W.C. Wiley, I.H. McLaren, *Rev. Sci. Instrum.* 26 (1955) 1150.
- [17] O. Cheshnovsky, S.H. Yang, C.L. Pettiette, M.J. Craycraft, R.E. Smalley, *Rev. Sci. Instrum.* 58 (1987) 2131.
- [18] J.V. Coe, G.H. Lee, J.G. Eaton, S.T. Arnold, H.W. Sarkas, K.H. Bowen, C. Ludewigt, H. Haberland, D.R. Worsnop, *J. Chem. Phys.* 92 (1990) 3980.
- [19] P. Ayotte, M.A. Johnson, *J. Chem. Phys.* 106 (1997) 811.
- [20] W.C. Lineberger, T.A. Patterson, *Chem. Phys. Lett.* 13 (1972) 40.
- [21] S.L. Anderson, D.M. Rider, R.N. Zare, *Chem. Phys. Lett.* 93 (1982) 11.
- [22] P.J. Campagnola, L.A. Posey, M.A. Johnson, *J. Chem. Phys.* 95 (1991) 7998.
- [23] R.N. Barnett, U. Landman, C.L. Cleveland, J. Jortner, *Phys. Rev. Lett.* 59 (1987) 811.