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Photoelectron spectroscopy of hydrated electrons

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ABSTRACT

We report a systematic study of the photoelectron spectroscopy of hydrated electrons in liquid water jets using multiple precursors and photodetachment wavelengths. Hydrated electrons were generated in and detached from liquid microjets using two photons from a single nanosecond laser pulse at 266 or 213 nm. Solutions of 50 to 250 mM potassium hexacyanoferrate(II) or potassium iodide were used to provide precursor anions. All of our experimental conditions yield similar results, giving a mean vertical binding energy of 3.6 ± 0.1 eV at a temperature of ~280 K, a slightly higher value than in recent reports.

1. Introduction

The hydrated electron e_{aq}^-, an electron in aqueous solution, was discovered as a product of water radiolysis by ionizing radiation [1] and has since become a species of central interest in the physical sciences. It plays a major role in radiation chemistry and biology, because hydrated electrons can be formed by ionizing radiation in living cells, and their high reactivity leads to free radical formation with significant potential for genetic damage. From a more fundamental perspective, e_{aq}^- represents the simplest quantum mechanical solute [2], thereby motivating many experimental and theoretical studies that have focused on understanding its spectroscopy, reactivity, and relaxation dynamics subsequent to electronic excitation [3–10]. A parallel experimental and theoretical effort has focused on gas phase water cluster anions, $(H_2O)_n^-$, in which an electron is bound to a known number of water molecules [11–16]. The cluster studies have provided valuable insights into the nature of e_{aq}^-, but have also raised the issue of how the properties of finite clusters can be extrapolated to bulk aqueous solutions [17,18]. For example, extrapolation of the vertical binding energies (VBE's) of water cluster anions to $n \to \infty$ yields an estimated value of 3.4 ± 0.2 eV for the VBE of the bulk hydrated electron, based on work with clusters up to $n = 69$ by Coe et al. [17]. Recent work by Siefermann et al. [19] on hydrated electrons in liquid water jets yielded the first actual measurement of this quantity, finding remarkable agreement (3.3 eV) with the cluster extrapolation. A similar value has been reported by Tang et al. [20].

In this Letter, the properties of hydrated electrons in liquid water jets are explored using a different experimental arrangement from that of Siefermann et al. The work described here is motivated in part by some unusual aspects of their results. In their experiment, photoelectrons were created within the jet by either ionization of pure water or charge-transfer-to-solvent (CTTS) excitation of the hexacyanoferrate(II) anion ($Fe(CN)_6^{4-}$) with a femtosecond laser pulse at 267 nm (4.64 eV). This was followed by photoemission using a femtosecond soft X-ray pulse at 32 nm (38.7 eV). The soft X-ray pulse results in photoelectrons with a kinetic energy around 35–37 eV, for which the electron attenuation length (EAL), the distance over which an electron signal is reduced by a factor of 1/e, is only ~2 nm [21,22]. As a result, these experiments were, in principle, much more sensitive to electrons at or very near the surface of the jet. Indeed, their experiments on pure water showed evidence for hydrated electrons with a relatively low VBE, 1.6 eV, and these were attributed to surface-bound electrons. This assignment appeared plausible since the VBE's of water cluster anions with surface-bound electrons extrapolated to a similar value [23]. Internally-bound electrons, for which the VBE was found to be 3.3 eV, could only be seen with difficulty, even at high concentrations (0.5 M) of $K_4Fe(CN)_6$.

Here, hydrated electrons are produced by CTTS excitation and ejected using two photons from a single 35 ns laser pulse at either 266 nm (4.66 eV) or 213 nm (5.82 eV). The EAL increases dramatically at low eKE [24], so this experiment should be considerably more sensitive to electrons in the jet interior, enabling us to observe this signal at lower salt concentrations and testing the possible of effect of concentration on the measured VBE. Moreover, by varying both the photoemission energy and the anion from which CTTS excitation occurs (hexacyanoferrate(II) and iodide), one obtains an important consistency check on the VBE. In fact, we find that under conditions of our experiment, the 'surface-bound' electrons are not seen, and that the VBE of the internally-bound electrons is 3.6 ± 0.1 eV, close but not identical to the previously reported value.

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2. Experiment

Experiments were conducted using dilute (50–250 mM) aqueous solutions of various salts introduced into a vacuum chamber using a liquid microjet similar to that pioneered by Faubel et al. [25,26]. A schematic drawing of our instrument is presented in Fig. 1. The apparatus consists of a liquid jet source chamber (I), a time-of-flight (TOF) chamber (II), and a negative ion source used for calibration (not pictured). The microjet enters the chamber by means of a three-axis translation stage mounted on a feedthrough flange (a). The nozzle assembly is of the type developed by Wilson et al. [27], consisting of a 9.5 ± 0.5 mm length of 30 μm I.D. fused silica capillary (b) clamped into $\sim$8 mm of PEEK tubing (c) by a Swagelok fitting (d). Constant flow through the nozzle is maintained by a syringe pump (Teledyne-Isco Model 500D) with a 2 μm in-line filter (e) to prevent clogging. Following construction, the nozzle assembly (b–e) is coated in carbon (Acheson, Aerodag G), to reduce charge buildup on the fused silica and improve signal stability.

The experiments presented in this report used deionized and filtered liquid water (18.2 MΩ resistivity Milli-Q, Millipore), with a measured total organic content of 3–4 ppb. All chemicals were used as supplied by the vendor (potassium hexacyanoferrate(II) trihydrate, Sigma Aldrich, $\geqslant$99%; sodium chloride, Fisher, ACS; potassium iodide, Fisher, USP/FCC). Flow rates of 1 mL/min were used throughout, resulting in a jet velocity of 24 m/s. The jets typically exhibited laminar flow for 6 to 10 mm from the tip before entering the turbulent flow regime and breaking into droplets.

A pulsed laser beam intercepted the liquid jet 1 to 2 mm downstream from the tip. The jet evaporatively cools in vacuum, achieving a surface temperature between 281 and 278 K based on the temperature gradient model of Smith *et al.* [28]. We used a nanosecond Nd:YAG laser, (Spectra-Physics Quanta-Ray Pro 290-30) operating at 266 or 213 nm. The interaction region is denoted with an asterisk $(*)$ in Fig. 1. For the data at 266 nm, we typically used 10–35 μJ/pulse, while the 213 nm data was taken with 3–20 μJ/pulse. The laser polarization was parallel to the axis of the TOF spectrometer at both wavelengths.

The principle underlying this experimental configuration is to use two photons from a single $\sim$35 ns laser pulse; the first creates a hydrated electron via CTTS excitation of the dissolved anions, and the second ejects the electron into vacuum. Hydrated electrons created by CTTS excitation equilibrate by 70 ps [29], which is considerably less than the laser pulse duration, so that the second photon will interact primarily with equilibrated electrons. Furthermore, the lifetime of the hydrated electron is several hundred microseconds [30,31], much longer than our laser pulse duration.

Once in vacuum, the photoelectrons were sampled by a 500 μm diameter skimmer (f), located 0.75 to 1.5 mm from the jet, and entered the TOF chamber. The electrons then traveled through a 63 cm, field-free drift tube (g), to a chevron mounted, dual microchannel plate detector (70 mm O.D., 9.7 msr acceptance angle, h in Fig. 1). Electron flight times were collected and averaged on an oscilloscope (Tektronix TDS3034B), passed to a computer and summed, typically for 30 000 laser shots.

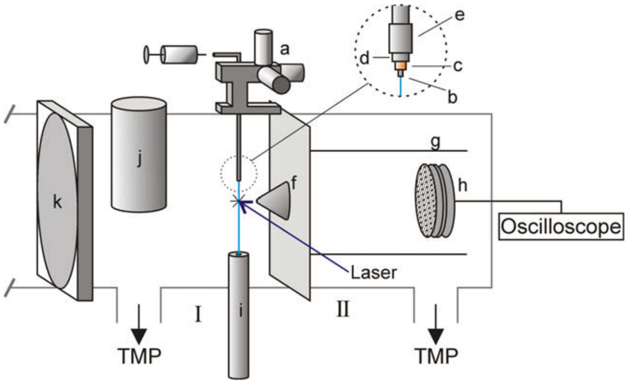

Fig. 1. Schematic drawing of the liquid microjet photoelectron spectrometer. See text for details.

Approximately 10 cm downstream of the nozzle, the jet entered a trap (i) consisting of a 3.8 × 60 cm stainless steel cylinder immersed in 30 cm of liquid nitrogen. The liquid source region was further pumped by a 150 L/s turbomolecular pump (Leybold Turbovac 151), and a condensation unit made of a 15 × 20 cm stainless steel cylinder filled with liquid nitrogen (j). The chamber typically reached 1×10^{-4} Torr during operation, and could run for 2.5 h before the traps needed to be removed and cleaned. The TOF chamber was pumped by three turbomolecular pumps with a combined speed of 1000 L/s (Seiko Seiki STP 400, Leybold Turbovac 151, Leybold Turbovac 150 CSV), and typically achieved pressures of 4×10^{-6} Torr.

The apparatus was calibrated using gas phase I^- and Br^-, introduced through a gate valve (k) from our previously described ion source and mass spectrometer [32]. Briefly, appropriate precursor gases were introduced to vacuum through a pulsed piezoelectric valve. Gas pulses from a supersonic expansion passed through a pair of high voltage discharge plates pulsed to ~ -900 V, and were intersected by a 1 keV electron beam for stabilization. Following collimation by a skimmer, the ions were injected into a linear reflectron mass spectrometer with a mass resolution $(m/\Delta m)$ of 2000. The photodetachment laser then detached the anions just in front of the 500 μm skimmer (f) shown in Fig. 1. A small fraction of the photoelectrons passed through the skimmer and was collected with the TOF system used in the liquid jet measurements. The known energies for photodetachment to the $^2P_{3/2}$ and $^2P_{1/2}$ states of I and Br [33] were used for calibration; these energies (3–4 eV) were in the range of the binding energies found in the liquid jet studies and hence were very suitable for calibration purposes.

3. Results

Photoelectron spectra were first recorded at several concentrations of $K_4Fe(CN)_6$ at 266 nm. The I^- CTTS band is not accessible at this wavelength [34], so we were unable to investigate precursor dependent effects here. Fig. 2 shows raw time-of-flight photoelectron spectra at 100 mM $Fe(CN)_6^{4-}$ and for pure water. The signal below 500 ns is from light scattered off the jet and into the flight tube. The broad feature peaking around 1000 ns in the spectrum from the salt solution is from ejected photoelectrons and is not seen in the pure water spectra. The TOF spectrum is converted into an electron kinetic energy (eKE) spectrum using the appropriate Jacobian transformation (t^{-3}). Pure water jets can undergo significant charge buildup, a process that is largely eliminated by even a low salt concentration in the jet [24]. In light of this, background data were taking using both pure water and sodium chloride solution since Cl^- does not have an accessible CTTS band at either photodetachment wavelength [35]. Pure water and Cl^- jets give very similar results, however the scattered light noise for chloride jets better matches the noise in $Fe(CN)_6^{4-}$ and I^- data. While this does not affect the 266 nm data, it becomes relevant under the lower signal-to-noise conditions of the 213 nm data.

Typical background subtracted photoelectron spectra are presented in Fig. 3, plotted versus electron binding energy (eBE) given by $\mathrm{eBE} = h\upsilon - \mathrm{eKE}$, where $h\upsilon$ is the photon energy. As shown, we find the most probable eBE, or vertical binding energy (VBE), to be 3.6 ± 0.1 eV at 50 mM, 3.5 ± 0.1 eV at 100 mM, and 3.6 ± 0.1 eV at 250 mM. We observe day-to-day variations of up to 0.1 eV with

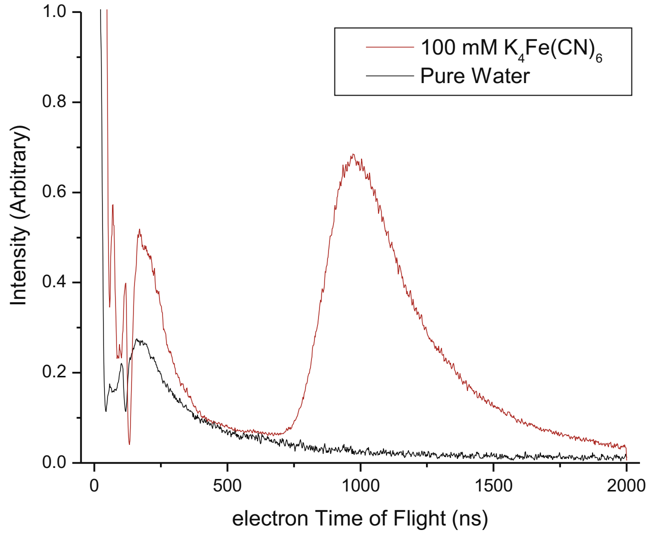

Fig. 2. Typical time-of-flight spectra for water and 100 mM potassium hexacyanoferrate(II) solution. The initial spike is from laser light scattered from the jet onto the detector. The broad feature around 1000 ns in the salt solution data, but absent in the pure water data, is from electrons ejected from the jet.

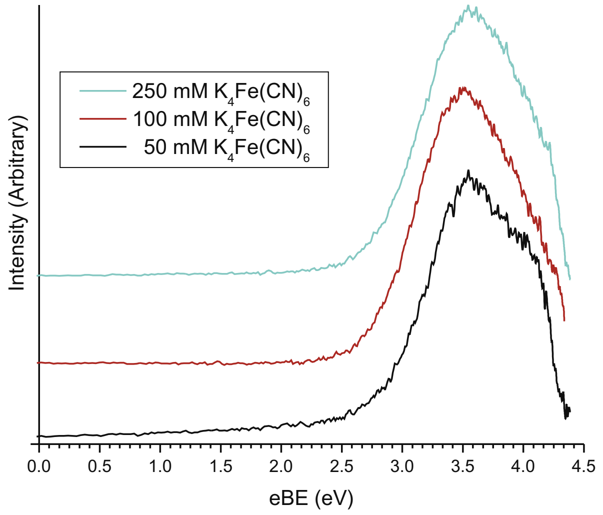

Fig. 3. Photoelectron spectra of aqueous solutions of $K_4Fe(CN)_6$ at concentrations of 250, 100, and 50 mM taken at 266 nm (4.66 eV). The spectra have been background subtracted using data from pure water jets and smoothed with a 10 meV Gaussian.

typical peak widths of 1.0 ± 0.2 eV full width at half maximum (FWHM). The three VBE's from Fig. 3 are within error bars of one another but are slightly higher than the value of 3.3 eV reported by Siefermann et al. [19] and Tang et al. [20]. We see no evidence for the previously reported peak with a VBE of 1.6 eV [19]. The 50 and 100 mM results are confirmed by repeated measurement over many days.

As a further check on these results, photoelectron spectra were recorded for several salt solutions at 213 nm, where the electron kinetic energy is higher for the same binding energy. Both $Fe(CN)_6^{4-}$ and I^- (from KI) were used as precursor anions to check against solute-specific effects. Typical background subtracted spectra are shown in Fig. 4. We find VBE's of 3.6 ± 0.1 eV using 50 mM $Fe(CN)_6^{4-}$, 3.6 ± 0.1 eV from 100 mM $Fe(CN)_6^{4-}$, and 3.7 ± 0.2 eV from 100 mM I^-. Again, we see day-to-day variations of 0.1 eV at this wavelength and each measurement was repeated in on multiple days with the majority of our effort focused on 100 mM $Fe(CN)_6^{4-}$.

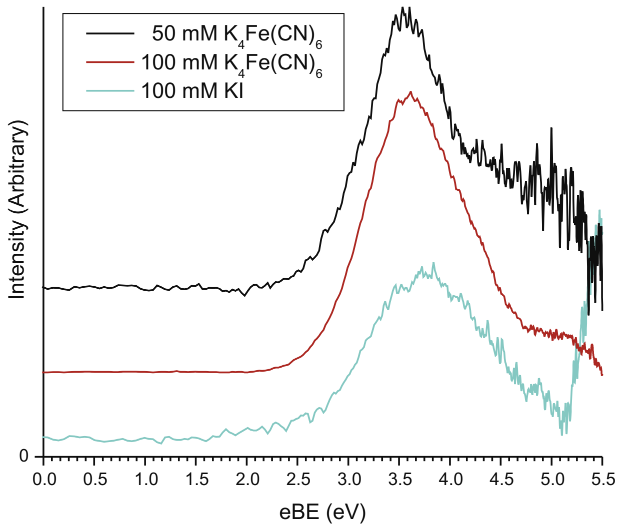

Fig. 4. Photoelectron spectra taken at 213 nm (5.82 eV) for aqueous solutions of $K_4Fe(CN)_6$ at concentrations of 50 and 100 mM and KI at 100 mM. The spectra have been background subtracted using data from pure water or sodium chloride solution jets, and smoothed with a 10 meV Gaussian.

4. Discussion

Averaged, our data give a VBE of 3.6 with a standard of deviation of 0.1 eV for the bulk hydrated electron, measured at ~280 K. This value appears to be independent of the precursor ion species or concentration, and it does not change over the range of laser intersection points or jet-to-skimmer distances used here. Moreover, the VBE does not vary with the mean electron kinetic energy at the two photodetachment wavelengths (1.1 eV at 266 nm, 2.2 eV at 213 nm). The EAL of an electron in water with 1–2 eV of kinetic energy is not precisely known, but is expected to be >10 nm based on recent theoretical and experimental work [22,36]. Hence, our experiment should probe bulk hydrated electrons. In contrast to our work, Siefermann *et al.* probed near the EAL minimum and were much more sensitive to electrons near the surface [19]. The absence of the feature at a VBE of 1.6 eV in our experiment is thus consistent with their assignment of this peak to a surface-bound electron.

The VBE obtained in our experiment is somewhat higher than the analogous feature observed at 3.3 eV by Siefermann et al., a discrepancy that could be attributed to the low signal-to-noise in their experiment associated with detection of internal electrons. However, our data also show a more tightly bound electron than recently reported by Tang et al. [20] in a femtosecond time-resolved pump probe experiment where I^- was detached at 240 nm and the electron ejected at 266 nm. We note that the peak in their photoelectron kinetic energy distribution shifted to lower energy, or higher VBE, as the delay between their pump and probe pulses was increased to 136 ps. Our long laser pulses imply a considerably longer delay between CTTS excitation and photoemission than in the fs pump-probe studies. Nonetheless, the 136 ps delay reported by Tang is already longer than the equilibration time for hydrated electrons (70 ps) formed via CTTS excitation [29], so it is not obvious that the longer delay time in our experiment can account for the differing VBE's. We also note that the reported jet surface temperatures in the previous measurements are very similar to ours (278 K in Ref. [19] and 280–290 K in Ref. [20]), so temperature variations among the experiments are unlikely to be an issue.

Since we are reporting a larger VBE than previous work, one obvious question to consider is whether our result reflects inelastic scattering after the electrons leave the jet. As shown by Faubel et al. [25], the effective vapor layer thickness provides a good estimate of the overall collision frequency and can be found by $Pd = P_0 r_0 \ln(r/r_0)$, where r_0 is the radius of the jet, r is the distance from the center of the jet to the skimmer entrance, and P_0 is the local equilibrium vapor pressure at the jet surface. Under our typical experimental conditions, with an estimate of 6.5–8.0 Torr for the equilibrium vapor pressure [37], we find our effective vapor thickness to be between 0.38 and 0.55 Torr mm. We find similar effective thicknesses that bracket our value for the conditions in previous reports (0.25 Torr mm for Siefermann et al. and at least 0.63 Torr mm for Tang et al.). While these numbers are all slightly higher than the desired value of $Pd \leqslant 0.1$ Torr mm for ultraviolet photoelectron spectroscopy [38], we cannot dismiss our VBE as an artifact from inelastic scattering in the local vapor sheath.

Another possible issue to consider is the streaming potential of the jet. As has been previously demonstrated [26,39,40], liquid microjets can generate significant streaming currents with radial surface potentials up to tens of volts. The resistance, and therefore the surface potential, of the jets decreases linearly with the concentration of salt [24], so we would expect a concentration dependent VBE if this were an issue with our work. As shown in Figs. 3 and 4, we see no such concentration dependence and conclude that surface potentials have not skewed our results.

Previous work on water cluster anions offers evidence in support of the larger VBE found in our liquid jet study. Specifically, if the VBE's for the largest 'isomer I' cluster anions measured in our laboratory ($n = 50$–200) are plotted vs. $n^{-1/3}$ and extrapolated to $n \to \infty$, one finds a bulk VBE of ~3.6 eV [18,41], in excellent agreement with the value reported here. A similar result was seen in recent work by Ma et al [42] on very cold cluster anions (10 K); in addition, they observed a new 'isomer I' cluster for which the extrapolated VBE was even higher, ~4 eV.

5. Conclusions

We have measured the vertical binding energy of the solvated electron in bulk water under a wide range of conditions using liquid microjets. In these experiments, two photons from a single ns laser pulse at either 266 or 213 nm were used to detach an electron from an anion is aqueous solution and then to eject the electron from the jet into vacuum. The low photon energies used here insure that we probe true bulk hydrated electrons. We find the vertical binding energy for these electrons to be 3.6 ± 0.1 eV at ~280 K. Our results are insensitive to the laser wavelength, the choice of parent anion (I^- or $Fe(CN)_6^{4-}$), and the anion concentration.

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