Ultrafast thermalization dynamics of hot photoelectrons injected into water

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Abstract. We present results on the mechanism of solvated electron production by photoionization of water and photodetachment of iodide with 50fs deep-UV pulses. The relaxation of photoejected electrons from the two systems differs markedly, consistent with the suggestion that iodide detachment leads to an electron:iodine caged pair.

1. Introduction

Recent advances in ultrashort UV pulse sources has allowed for the investigation of the early time dynamics of photoejected electrons in the condensed phase. This in turn allows detailed comparisons with, and calibration of, molecular dynamics simulations for quantum solutes in water. Because of the simplicity of the electron transfer system, comparisons may also be made with experiments in gas-phase water clusters.

In this paper, we present broadband studies of the nascent electron following photoexcitation of dilute aqueous I^- and H_2O itself. Electrons are produced either by photoionizing water via two-photon absorption (9.7 eV) or, subsequent to excitation into the iodide ion charge-transfer-to-solvent (CTTS) state with a single 4.9 eV photon, by break up of the short-lived CTTS state. It has been suggested that electrons produced by two-photon excitation of liquid water into its conduction band have enough energy to populate the excited *p*-state of the trapped hydrated electron.[1] However, electrons produced through the solvent induced destruction of the CTTS state should have insufficient energy to reach the excited electron state.[2] Furthermore, the electrons generated from water ionization, having greater kinetic energy, are ejected several solvent shells away from the parent molecule.[3] For excitation into the iodide CTTS state, quantum simulations suggest that adiabatic detachment leads to a ground *s*-state electron and an iodine radical arranged as a contact pair.[2,4] Evidence based on picosecond geminate recombination dynamics from our lab suggests these contrasting ejection scenarios are indeed occurring.[5] In this paper, we present our early-time, multicolor probe data for both photoejection systems. Global fitting of both datasets with a spectral evolution model as suggested by Jay-Gerin [1] allows for quantitative comparison. We suggest that the caged pair formed slows the relaxation dynamics of the photodetached electron.

2.   Experimental Methods

The pump-probe experiments are performed using a 200 kHz Ti:Sapphire regeneratively amplified system and OPA. The UV pump pulses were obtained by frequency doubling 510 nm from the OPA output using a Type-I BBO crystal. A deliberate positive chirp on the 510 nm pulse is optimized, using a pair of fused silica prisms in the beam path prior to the doubling crystal, to yield maximum UV bandwidth and conversion efficiency. The resulting beam passes through a pair of calcium fluoride prisms for dispersion compensation of the deep-UV pulses. This process results in 255 nm pump pulses of ~50 fs.[5] The probe pulse is obtained by using a white light continuum and selecting the color of interest with either an interference filter or by using a monochromator after the entire continuum has been transmitted through the sample. Data is recorded for probes wavelengths every 50 nm from 400 – 1000 nm. The sample is a free flowing jet of either an aqueous 60 mM KI solution or neat deionized water at room temperature. The instrument response is measured for each probe wavelength by DFG cross-correlation; it is ~80 fs over the entire probe continuum.

3.   Results and Discussion

Iodide ions are resonantly pumped into the CTTS state by a 255 nm laser pulse. The experiment monitors the appearance of the detached electron produced upon break up of this initial state. Fig. 2(a) shows the results obtained by detecting the ejected electrons at different probe wavelengths. Absorption appears first at the red edge; an electron appearance time of ~200 fs is observed. To gain further insight
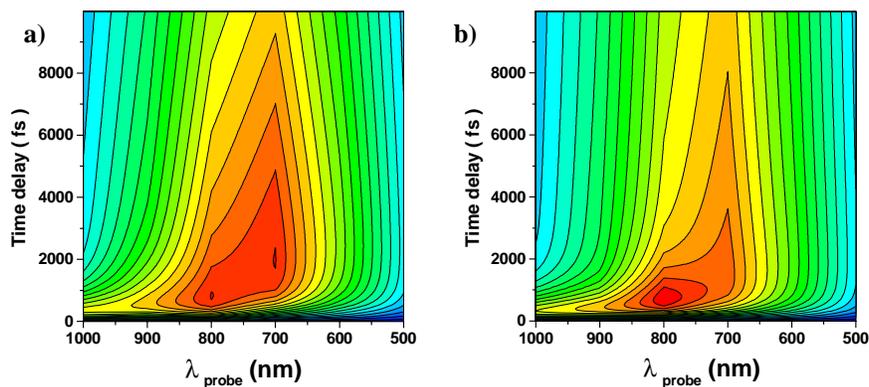

Fig. 1. (a) Transient absorption data for photodetached electrons generated by resonantly exciting iodide ions into the lowest CTTS-state. (b) Transient absorption data for ejected electrons produced by 2-photon ionization of neat deionized water. Each contour plot is generated by fitting high S/N experimental data for each probe wavelength to an unbiased functional form and then normalizing each absorption signal at 10 ps to the literature equilibrium solvated electron spectrum.[6]

into the results for anion photodetachment, we performed complementary experiments and analysis on a previously investigated system, the photoionization of water. Fig. 2(b) shows our results for pure water at higher pump intensity. The appearance time of the solvent ionized electron at the reddest wavelength measured is ~170 fs. The principal observation is that photoelectrons produced by both processes undergo substantial spectral shifting, but the iodide-detached electrons manifest appreciably slower relaxation. This spectral shifting is primarily due to solvation of the electron due to rearrangement of its hydration shell. The electron relaxation phase is followed by geminate recombination which takes place over ~20 ps. The recombination kinetics are qualitatively different for the two systems.[5] Recombination after two-photon water ionization can best be described by a diffusion-limited random walk of the electron from a 15 Å ejection radius. In the case of anion CTTS detachment, recombination is better modeled by competitive kinetics of recombination or escape of the geminate partners from a rapidly-formed caged pair.[4]

First, we have compared the electron relaxation results for pure water to the comprehensive photoionization study by Jay-Gerin and co-workers. A spectral evolution model was proposed for the early time dynamics of the nascent electron.[1] The model takes into account population relaxation and solvation dynamics of both excited p- and ground s-state electrons. In contrast, we are able to globally fit all of our data with a simple one state (ground state) spectral evolution model with only four adjustable parameters. We note that the p-state transient absorption is centered at 1250 nm, slightly beyond the range of our current experiments. The extent of ground state shifting is 0.46 eV, and a similar spectral correlation time is found (450 fs) to that of Jay Gerin. We then applied the same model to the relaxation of photodetached electrons. Global fitting of Figure 2(a) yields a longer spectral correlation timescale of 850 fs and a smaller overall band shift of 0.35 eV.

If the electron is adiabatically detached from the CTTS state to form a contact pair, as suggested by quantum simulations [2,4] and supported by the recombination kinetics, one might expect the electron spectrum and its evolution due to solvent rearrangement to be distorted by the presence of the iodine within the same solvent shell. The current results indicating a factor-of-two slower solvation for photodetached electrons attest to a rather different ejection mechanism in operation. This work is supported by NSF, the Donors of the Petroleum Research Fund and the Research Corporation.

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