

Mechanisms for Photodetachment in Water

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Abstract. The effect of excitation energy and solvent deuterium substitution is explored for photodetachment of aqueous iodide. The results are explained in part by a new *ab initio* characterization of the vertically excited state.

Threshold electron ejection processes, such as photodetachment via optical charge-transfer-to-solvent (CTTS) excitation, provide very simple models for understanding solvent-controlled electron transfer (ET). In previous work, we have demonstrated that ejection from the prototypical CTTS system, the aqueous iodide anion, is to short range into a caged pair [1]. The electron subsequently either diffuses out of the cage, an activated process due to the attractive interaction between the nascent electron and the polarizable iodine neutral, or undergoes reverse electron transfer from the cage to reform I^- [2]. In the current experiments, our goal was to gain additional insight into the molecular mechanism of ejection by exploring the effect of a large increase in the excitation energy and by isotopic substitution of the solvent. The results are rather unexpected and an *ab initio* characterization of the vertically excited bulk CTTS wavefunction turns out to be particularly useful in rationalizing the dynamics of the electron.

Aqueous iodide ions are excited at the red-most edge (250 nm) or at the band center (225 nm) of their CTTS absorption. 250 nm pulses of ~ 50 fs are generated by doubling the signal output of a 390 nm pumped OPA and 225 nm pulses (~ 150 fs) are produced by sum frequency mixing of the OPA signal with residual 390 nm. The ejected electrons once trapped are detectable by their absorption across the visible and near IR. Mapping the spectral evolution of this absorption at several probe wavelengths reports on the subsequent solvent response to the trapped electron [3]. Results are shown here for a 700 and 1000 nm probe selected by an interference filter from a variably delayed white light continuum. Fig. 1 shows the delayed appearance of the electron at earliest times (longer than instrument response) and a tens-of-picoseconds population decay due to geminate recombination at two different excitation energies. The fraction remaining has escaped iodine and any slow population decay after ~200 ps is due to secondary recombination [2]. The temporal signature of the geminate recombination directly relates the location of the newly formed electron with respect to its geminate partner (and parent) [1]. It is observed that there is no significant difference in the traces at any phase of the ejection and recombination dynamics. This suggests that ejection proceeds essentially unaltered despite the large increase in available energy that one might have predicted would be available for longer range, one would see a slower population decay phase and a higher escape fraction, as is

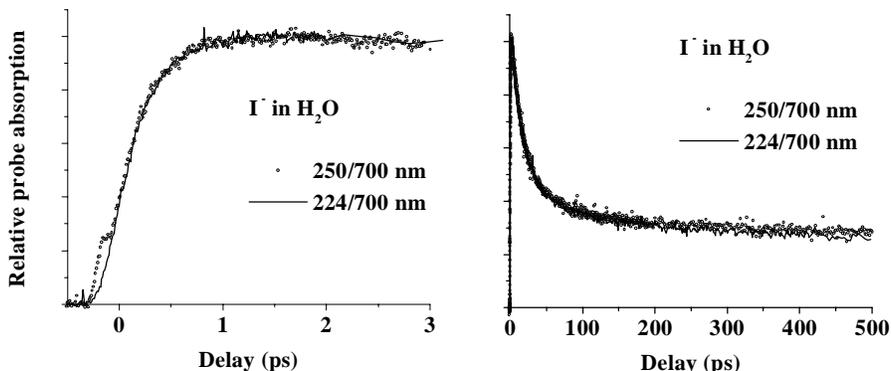


Fig. 1. Femtosecond transient absorption of aqueous I^- at 250 and 224 nm (5.0 and 5.5 eV).

observed in the detachment of Na^- [4] and in the multiphoton ionization of liquid water above 9 eV [5].

Figure 2 demonstrates the effect on the ejection mechanism on changing the solvent from H_2O to D_2O . It is observed that neither the appearance, as judged by the rising edge of the 1000 nm data, or the spectral evolution is significantly altered on isotopic substitution. One might expect that the dominant response of the water molecules in the first shell would be inertial libration of the adjacent solvent (giving a large deuterium effect) in response to the change in local charge density as observed for dye solvation dynamics in water. It appears that *translation* of the immediate solvent (which gives a small deuterium effect due only to the change in overall mass) dominates [6] and facilitates the budding of the electron into an adjacent solvent cavity. Interestingly, there is a large effect on the geminate recombination on solvent deuteration. This cannot be explained simply by the higher viscosity of D_2O . The fits shown in Fig. 2 are numerical diffusion simulations [2] for the encounter pair which include a reaction probability for non-adiabatic electron transfer if the electron and iodine are in contact. It is found that the effective rate constant for return ET must be a factor of 0.55 slower in D_2O to fit the data.

To consider these results it is useful to compare with benchmark mixed quantum classical molecular dynamics simulations for halide CTTS detachment [7]. These suggest that electron separation is solvent driven, but that the CTTS band is made up of both $p \rightarrow s$ and $p \rightarrow d$ electron promotions with the detachment timescale controlled by transitions between different angular momentum waves. Thus, tuning the pump over the absorption band should vary the angular momentum composition of the initially prepared state again predicting different ejection dynamics [7]. We have performed our own *ab initio* calculations in an attempt to get an improved description for the vertically-prepared wavefunction [8]. These calculations provide an explanation for the results in Fig. 1. Inclusion of all iodine valence electrons reveals that promotions into d character orbitals are at much higher energy and do not contribute to the CTTS band. Instead, exciting at varying photon energies selects from different non-degenerate occupied iodide

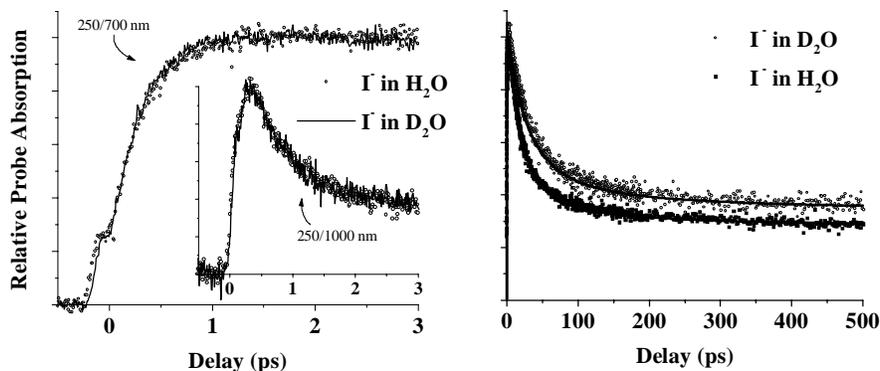


Fig. 2. The effect of isotopic substitution on the detachment dynamics. (Right panel) Lines represent numerical diffusion simulations for geminate recombination/escape, in the presence of a charge-polarizable atom potential, and include non-adiabatic reverse ET.

p-orbitals and more or less solvated ground state configurations for promotion to a single acceptor orbital which is primarily of *s* symmetry. Therefore, changing the excitation wavelength has rather little effect on the character of the optically prepared state in terms of its shape or kinetic energy. The pronounced difference in the excitation energy dependence in the geminate recombination in I⁻ versus Na⁺ [4] can be explained in terms of the reversal of the occupied and unoccupied orbital symmetries between the two systems. The calculation also shows that there is a large expansion in electron density and the CTTS electron occupies void space primarily within the first solvent shell. The pre-existing asymmetry of the local water network defines an initial direction for charge translation and this budding is presumably continued by displacement of the adjacent solvent.

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