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Femtosecond studies of electron photodetachment of simple ions in liquid water: Solvation and geminate recombination dynamics

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Aqueous solutions of simple ions such as OH⁻ and Cl⁻ have fascinated many scientists. In this communication we present the first femtosecond time-resolved studies of electron photodetachment in aqueous solution. The solvation of the ejected electron in the aqueous media and the subsequent recombination dynamics of the neutral atom with the electron have been measured. Relevant to this are several recent experimental studies of electrons in neat liquids using femtosecond lasers.¹⁻⁴

The experiments discussed here were performed with a Nd:YAG amplified CPM laser; the operational details can be found elsewhere.^{2,3}

Work done over 30 years ago showed that solvated electrons were produced when UV light irradiated simple ions in solution.⁵ These transitions are called CTTS, charge transfer to solvent spectra.⁶ The production of electrons in this case is not due to photoionization, in the normal sense, since an intermediate excited state of the parent species is involved. The existence of an excited state from which the electron originates was inferred from several studies in which the effect of quenchers and temperature on the quantum yield of solvated electrons was measured.^{7,8}

Reflecting the widespread interest in the dynamics of electron solvation in water, are the many theoretical⁹⁻²⁸ and experimental studies^{1,3,4,29,30} of electron and ion solvation. Using femtosecond pump/probe spectroscopy at 312.5 nm/625 nm, we find that the solvation dynamics of the electron ejected from a chloride ion Cl⁻, in aqueous solution are slower than that for an electron originating from a water molecule, Fig. 1(a). Using the signal from *n*-octane as an instrumental response, a rise time of 500 fs is found for the Cl⁻, compared with 350 fs for water. The solvation time for the electron originating from the OH⁻ was also found to differ from neat water. These results are inconsistent with continuum theories of electron solvation, which predict that there be almost no change in the observed solvation dynamics.^{31,32} We thus conclude that molecular effects are playing a large role in the electron solvation dynamics. It should be noted that the rise time in the infrared, i.e., the region where the presolvated electron absorbs, is as fast as the *n*-octane

signal. We therefore conclude that the lifetime of the CTTS state is much shorter than the solvation times that we are observing, but it is our view that improved time resolution is needed to confirm fully this point. If the electron ejected from the CTTS state thermalizes very near the atom, then the solvent structure around the previously solvated species can greatly influence the solvation dynamics. In our previous multiphoton ionization experiments we estimated the electron thermalization distance to be about 13 Å.^{3,4} At these larger electron-atom separations, much smaller local solvent effects would be expected.

At longer times, decays are seen in the solvated electron absorption signal, Fig. 1(b). The decays seen in NaCl, NaOH and neat water are all different from each other.^{3,4} It is known that solvated electrons do not react with Na⁺, Cl⁻, OH⁻ ions on the time scale of these experiments.³³ With the additional fact that there was no concentration dependence seen in the decay, the possibility of the solvated electron reaction with the Na⁺ or the Cl⁻ ions is discounted; concentrations of up to 1M were studied. Therefore we conclude that the observed decays are due to geminate recombination of the electron with the chlorine atom or OH radical formed upon photodetachment of the electron by the UV pulse. The marked differences we have observed between the neat water and the ionic solution experiments are thus expected, since in the former the electron recombines with an ion, whereas in the latter the electron recombines with a neutral.

In this initial report we have compared our data to a continuum diffusion model.³⁴ Using a survival probability for the geminate recombination of hard spheres, i.e., the solvated electron and the chlorine atom, we see from Fig. 1(b) that the best fit we can obtain is poor. The fit was not significantly improved by using a distribution. Although we have not completed a quantitative comparison, we find that the molecular theory of Northrup and Hynes yields a trend consistent with our results.³⁵

In conclusion, we have performed femtosecond electron photodetachment studies of simple ions in aqueous solutions. On the femtosecond time scale, the solvation dynamics of the electron originating from Cl⁻ and OH⁻ are slower

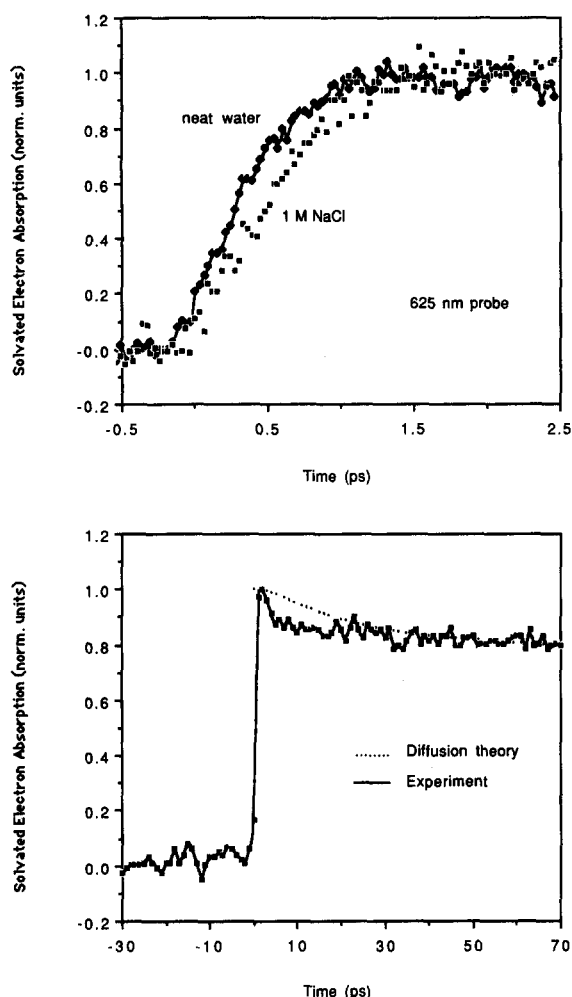


FIG. 1. (a) The appearance of the solvated electron in water following ejection from a chloride ion (squares) and from a neutral water molecule (diamonds). The line connecting the neat water data was drawn to aid the viewer. The signals occur with rise times of 350 and 500 fs, respectively. Both experiments done at room temperature, with a 625 nm probe. A 1 M concentration of NaCl was used. (b) Decay of the solvated electron originating from a chloride ion. Superimposed is a plot (dotted line) of the diffusive recombination of hard spheres with the following parameters: the mutual diffusion coefficient $D = 0.7 \times 10^{-4} \text{ cm}^2/\text{s}$, the initial separation of the two species, with respect to their centers, $R = 8.5 \text{ \AA}$, the reaction radius $r_a = 3 \text{ \AA}$. (Refs. 39 and 40).

than that of neat water, with OH^- being closer to water. These results are contrary to the predictions of continuum theory. On the picosecond time scale, decay rates and escape yields are distinctly different from neat water, which we attribute to geminate recombination of the solvated electron and its neutral partner. The solvation and the geminate recombination dynamics that we have observed in aqueous electrolyte solutions strongly suggests that short range molecular effects are important.³⁵⁻³⁸

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