J. Phys. Chem. **1989,** *93,* 27–28

Femtosecond Studies of Electron–Cation Geminate Recombination in Water

Hong Lu, Frederick H. Long, Robert M. Bowman, and Kenneth B. Eisenthal*

Department of Chemistry, Columbia University, New York, New York 10027 (Received: November 18, 1988)

Femtosecond photoionization studies in neat water at room temperature have been performed. After the electron has solvated, we have seen for the first time geminate recombination of the electron–cation pair formed upon ionization. The recombination kinetics appears to level off after roughly 60 ps with 50–60% of the electrons having undergone geminate recombination.

Understanding the properties of water is one of the most fundamental and challenging problems in science. A very interesting example of this is the behavior of electrons in water. This has been a subject of great interest and controversy both experimentally and theoretically for many years. For example, attempts to predict the absorption spectrum of the solvated electron have only been partially successful.[1] With the development of femtosecond lasers, the dynamics of an electron solvating in neat water have been measured.[2] Another important phenomena common to all condensed media is geminate recombination of an electron–cation pair following ionization.[3] In a previous report, we discussed the first femtosecond time-resolved measurements of geminate recombination in a neat alkane at room temperature.[4] In this Letter, we will discuss what we believe is the first observation of geminate electron–cation recombination in any polar solvent, in this case neat water.

The measurements reported here were performed using an amplified colliding pulse mode-locked dye laser (CPM)[5] operating at 10 Hz, 625 nm, 300 μJ/pulse, 80–100 fs fwhm. The 312.5-nm (3.94-eV) pump beam was created by frequency doubling the CPM beam with a 1-mm KD*P crystal. Since the ionization potential for liquid water is 6.5 eV, the neat water can be two-photon ionized.[6] The probe beam was either a small fraction of the remaining fundamental beam or part of a continuum pulse. The signal recorded was the difference of the probe beam and a reference divided by the reference. The water used in these experiments was HPLC grade from Aldrich. Further details will be published at a later date.

There have been many experimental studies of electron solvation in water.[7] However, until recently, all attempts to measure the solvation dynamics were instrument limited. Wiesenfeld and Ippen obtained an upper limit of 0.3 ps for the electron solvation time in water.[8] Migus et al. were the first to directly measure the solvation dynamics of an electron in water by photoionizing the solvent. Their work supports the notion of a dry, wet, and solvated electron in water. This is characterized by the appearance of a delayed IR absorption which shifts to the visible with an absorption peak at 720 nm. This entire process occurs in approximately 350 fs. Our measurements at early times are in agreement with their results.

However, at longer times (5–100 ps) our data show dramatic and previously unreported events. There is a decay in the absorption signal which slows down after approximately 60 ps, and it appears that the curve levels off at approximately 50–60% of the original signal height. Typical data are shown in Figure 1a–c. Measurements at probe wavelengths of 550, 625, and 700 nm show the same behavior. The available evidence suggests that we are monitoring only the solvated electron. First, the signal occurs with a rise time consistent with the solvation time for an electron in water. If there was an excited-state absorption present, it would probably appear instantaneously. Second, the signals at all three probe wavelengths have an identical time dependence. This eliminates the possibility of having another species contributing to the signal unless it obeyed the same rise and decay kinetics as the electron. As the probe wavelength is varied from 550 to 700 nm, the known electron absorption increases by a factor of 2 (ϵ = 18 500 cm^{-1} M^{-1} at 720 nm).[7] This is the increase we observe. If there was any other species contributing to the absorption, then its absorption coefficient would have to change in exactly the same way as the solvated electron for the wavelengths we have studied. Furthermore, a second species would effect a change not only in the relative amplitudes at 550 and 700 nm but also in the kinetic curves; they would decay to different plateau values, contrary to what is observed. With respect to the possibility of the solvated electron undergoing a quenching reaction, it is well-known that on the picosecond time scale reactions with O_2 or other impurity quenchers are negligible.[7] The possibility of impurities was checked by using other water samples, and no change was seen in the early time behavior. We believe the most likely explanation is geminate recombination of the electron–cation pair formed upon photoionization.

This would imply that the remaining signal at times greater than 60 ps is due to the electrons that escape geminate recombination. On our time scale 50–60% of the solvated electrons undergo geminate recombination (Figure 1). In the contimuum limit, the probability that a thermalized electron, at a distance r away from the cation at $t = 0$, escapes geminate recombination is given by

$$\exp\left(-\frac{r_c}{r}\right) \tag{1}$$

where r_c is the Onsager length, $e^2/\epsilon kT$.[9] For water at 21 °C the Onsager length is 7 Å. The dielectric response on the time scale of the observed geminate recombination will havve reached its static value using the response given by the longitudinal relaxation time.[10] With respect to the electron–cation separation, it is more likely that there is a distribution of thermalization distances. To obtain the fraction that escape, we must integrate over this distribution

$$\int \mathrm{d}^3r \, g(r) \exp(-r_c/r) \tag{2}$$

---

* To whom correspondence should be addressed.

[1] For example: Wallqvist, A.; Martyna, G.; Berne, B. J. *J. Phys. Chem.* **1988**, *92*, 1721. Jonah, C. D.; Romero, C.; Rahman, A. *Chem. Phys. Lett.* **1986**, *123*, 209. Schnitker, J.; Rossky, P. J.; Kenney-Wallace, G. A. *J. Chem. Phys.* **1986**, *85*, 2986. Sprik, M.; Imprey, R. W.; Klein, M. L. *J. Stat. Phys.* **1986**, *43*, 967.

[2] Migus, A.; Gaudel, Y.; Martin, J. L.; Antonetti, A. *Phys. Rev. Lett.* **1987**, *58*, 15, 1559.

[3] Jonah, C. D. *Radiat. Phys. Chem.* **1983**, *21*, 53. Scott, T. W.; Braun, C. L. *Can. J. Chem.* **1985**, *63*, 228. Scott, T. W.; Braun, C. L. *Chem. Phys. Lett.* **1986**, *127*, 501. Braun, C. L.; Scott, T. W. *J. Phys. Chem.* **1987**, *91*, 4436, and the references therein.

[4] Bowman, R. M.; Lu, H.; Eisenthal, K. B. *J. Chem. Phys.* **1988**, *89*, 606.

[5] Fork, R. L.; Shank, C. V.; Yen, R. T. *Appl. Phys. Lett.* **1983**, *41*, 223.

[6] Nikogosyan, D. N.; Oraevsky, A. A.; Rupasov, V. I. *Chem. Phys.* **1983**, *77*, 131.

[7] Hart, E. J.; Boag, J. W. *J. Am. Chem. Soc.* **1962**, *84*, 4090. Boag, J. W.; Hart, E. J. *Nature* **1963**, *197*, 45. Chase, W. J.; Hunt, J. W. *J. Phys. Chem.* **1975**, *79*, 2835. Kenney-Wallace, G. A.; Jonah, C. D. *J. Phys. Chem.* **1982**, *86*, 2572.

[8] Wiesenfeld, J. M.; Ippen, E. P. *Chem. Phys. Lett.* **1980**, *73*, 47.

[9] Onsager, L. *Phys. Rev.* **1938**, *54*, 554.

[10] Fröhlich, H. *Theory of Dielectrics*; Oxford University Press: London, 1949.

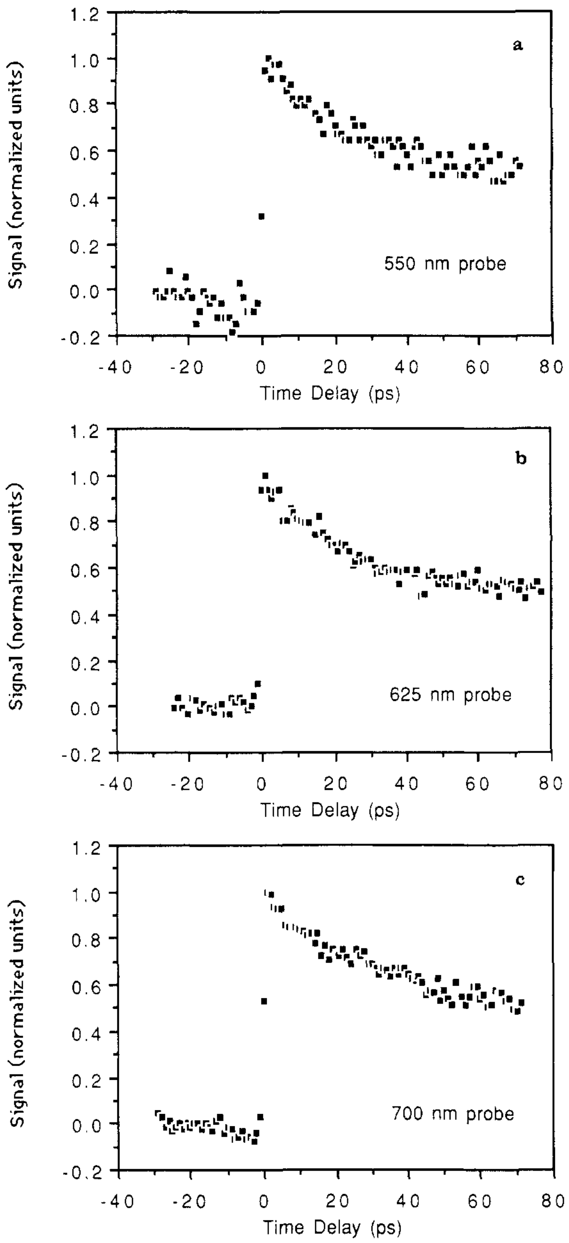

Figure 1. Transient solvated electron absorption signal in neat water, taken with 1-ps steps, at 21 °C. x axis is time delay in picoseconds, and y axis is $(I_0 - I)/I_0$ in normalized units where I is the transmitted beam signal and I_0 is the reference beam signal. (a) $\lambda_{\text{probe}} = 550$ nm; (b) $\lambda_{\text{probe}} = 625$ nm; (c) $\lambda_{\text{probe}} = 700$ nm.

where $g(r)$ is the probability density of the electron thermalization distances. If 50% of the electrons escape geminate recombination, and the distribution of thermalized electrons is Gaussian, we obtain a mean thermalization distance of 11 Å. In eq 2, $g(r)$ is given by $(1/\pi^{3/2}b^3)\exp(-r^2/b^2)$, where b is related to the mean thermalization distance $\langle r\rangle$, by $\langle r\rangle = 2b/\pi^{1/2}$. Similar thermalization distances are obtained for other distributions, for example exponential. It is important to note that any further decrease in the escape yield would only decrease the mean thermalization distance. We can crudely estimate the thermalization distance by assuming the motion of the electron is given by a random walk. By use of $r^2 = 6Dt$ and the experimentally known diffusion coefficient for a solvated electron (at 21 °C, $D = 4.75 \times 10^{-5}$ cm^2/s)[11] with a 60-ps recombination time, a thermalization length of 13 Å is obtained; once again we note that the thermalization distance is very small. Since the attractive Coulomb interaction is neglected, this distance is probably a lower bound on the thermalization distance. Also, due to the small size of this distance it is very possible that the simple continuum approach implicit in these calculations is only approximately valid. A more detailed discussion of these issues will be presented later.

Radiation chemists have measured the yield of solvated electrons in water after excitation with an electron beam. Several studies have shown that approximately 60% of the electrons escape geminate recombination.[12] Early attempts to obtain the time dependence of the electron escape were not successful due to the time width of the exciting electron beam.[13] Since the ejected electrons are expected to have more excess energy in the electron beam experiment, they will thermalize at a larger average separation, resulting in a greater fraction that escape. In our photoionization experiments, the electron has only 1.5-eV excess energy for a two-photon ionization process. Recent studies of photoejection of electrons from a metal electrode in water have shown that the thermalization distance is very energy dependent.[14] Thus, an escape yield of 60% can be viewed as an upper bound on our experiments.

In conclusion, we have performed femtosecond photoionization experiments on neat water. The early time results for the time evolution of the solvated electron spectrum are in agreement with the results of Migus et al.; however, dramatic previously unreported behavior at longer times has been observed. We have attributed the observed decays to geminate recombination of the electron–cation pair. Analysis of the kinetic data suggests that the thermalization distance is very short compared to the values obtained for alkanes ($\langle r\rangle$ = 50–100 Å for typical alkanes).[15,16] This result also has important implications for electron solvation since it suggests that more than half of the electrons are within 11 Å of the cation. The issue therefore arises as to whether the observed solvation dynamics and energetics are affected by the cation.

Acknowledgment. The authors thank the National Science Foundation, the Air Force Office of Scientific Research, and the donors of the Petroleum Research Fund, administered by the American Chemical Society, for their generous support.

---

(11) Schmidt, K. H.; Buck, W. L. *Science* **1966**, *151*, 70.

(12) Jou, F. Y.; Freeman, G. R. *J. Phys. Chem.* **1979**, *83*, 2383. Fielden, E. M.; Hart, E. *J. Radiat. Res.* **1967**, *32*, 564.

(13) Hunt, J. W.; Wolff, R. K.; Bronskill, M. J.; Jonah, C. D.; Hart, E. J.; Matheson, M. S. *J. Phys. Chem.* **1973**, *77*, 425.

(14) Konovalov, V. V.; Raitsimring, A. M.; Tsvetkov, Yu. D. *Radiat. Phys. Chem.* **1988**, *32*, 623.

(15) Schmidt, W. F.; Allen, A. O. *J. Chem. Phys.* **1970**, *52*, 2345.

(16) Bowman, R. M.; Lu, H.; Long, F. H.; Eisenthal, K. B., unpublished work.