FEMTOSECOND STUDIES OF ELECTRON-CATION DYNAMICS IN NEAT WATER: THE EFFECTS OF ISOTOPE SUBSTITUTION

Frederick H. LONG, Hong LU, Kenneth B. EISENTHAL [1]
Department of Chemistry, Columbia University, New York, NY 10027, USA

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Femtosecond photoionization studies in neat protio and deuterio water at room temperature have been performed. The rate of appearance of the solvated electron is slower in D_2O than in H_2O, consistent with the predictions of continuum theories. The observed geminate recombination dynamics of the cation-electron pair is also isotope dependent. The recombination time is slower in D_2O and the fraction of solvated electrons that escape recombination is greater in D_2O than in H_2O. After 165 ps, $54 \pm 1\%$ ($\pm$ one standard deviation) of the solvated electrons escape geminate recombination in H_2O and $62 \pm 1\%$ escape in D_2O. The increased electron escape yield is attributed to an energy transfer effect on the electron thermalization distance.

1. Introduction

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, the physical origin of the blue tail in the absorption spectrum of a solvated electron in water is still unknown [1]. With the development of femtosecond lasers, the dynamics of an electron solvating in neat water have been measured [2]. The observed solvation time was found to be qualitatively consistent with the continuum model of electron solvation; however, there is some conflict with the continuum model since the electron spectrum does not evolve continuously as the model predicts [3]. Another important phenomenum common to all condensed media is geminate recombination of an electron and cation following ionization [4]. In previous reports, we discussed the first observation of geminate electron-cation recombination in water as well as the first femtosecond time-resolved measurements of geminate recombination in a neat alkane at room temperature [5,6]. In this paper, we will discuss how the electron solvation dynamics and geminate recombination kinetics are affected, by isotopic substitution in neat water.

2. Materials and methods

The measurements reported here were performed using an amplified colliding pulse mode-locked dye laser (CPM) [7] operating at 10 Hz, 625 nm, 500 μJ/pulse, 100–120 fs fwhm. The 312.5 nm (3.94 eV) pump beam was generated by frequency doubling the CPM beam with a 1 mm KD*P crystal. Since the two-photon ionization potential (IP) of liquid water is 6.5 eV [#1], neat water can be ionized by a high peak power UV pulse [9]. The IP of D_2O will be higher due to the decrease in zero-point energy; however, this effect is small (i.e. about 0.15 eV). The probe beam was either a small fraction of the remaining fundamental beam or part of a continuum pulse generated in a 2 cm pathlength cell of D_2O. The signal recorded was the difference of the probe beam and a reference divided by the reference. The water used was HPLC grade and the D_2O was the highest grade

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[1] To whom correspondence should be addressed.

[#1] Other work by Delahay and von Burg [8], suggests that the ionization potential is much higher, 10.0 eV; in either case it does not alter the results reported here.

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purity from Aldrich. Further details will be published at a later date.

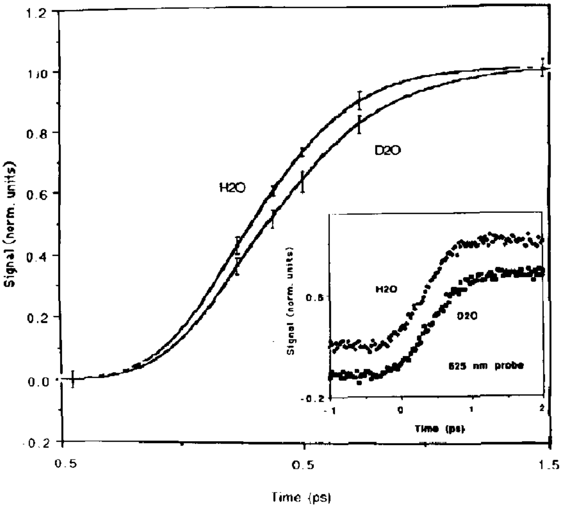

Fig. 1. The solvated electron absorption signal displayed in two ways to aid the viewer. In the larger figure the signals are normalized with error bars of ± 1 standard deviation shown. The inset shows all of the data points with the H_2O signal displaced by 0.3 units. Data taken with $\lambda_{\text{probe}} = 625$ nm at 21 °C; x-axis is time delay in ps; y-axis is $(I_0 - I)/I_0$ in normalized units where I is the transmitted beam signal, I_0 is the reference beam signal.

3. Results and discussion

There have been many experimental studies of electron solvation in water [10]. However, until recently, all attempts to measure the solvation dynamics were all instrument limited. Wiesenfeld and Ippen obtained a value of 0.3 ps for the electron solvation time in water [11]. Migus et al. were the first to directly measure the solvation dynamics of an electron in water by directly 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 that shifts to the visible with an absorption peak at 720 nm. This entire process occurred in approximately 350 fs. Our measurements at early times are in agreement with their results.

Since the dielectric properties of D_2O and H_2O are similar, an important test of continuum theories governing electron solvation is to learn whether the solvation dynamics of the liquids are consistent with these theories. According to the continuum model, the electron solvation time is given by the longitudinal dielectric relaxation time [3],

$$\tau_L = \tau_D(\epsilon_\infty/\epsilon_0) , \qquad (1)$$

where ϵ_∞ is the high frequency dielectric constant, ϵ_0 the static dielectric constant and τ_D the Debye dielectric relaxation time. One can normally set ϵ_∞ equal to n^2, where n is the index of refraction. The static dielectric constant and the index of refraction for the two water isotopes are approximately the same; however, the Debye relaxation time, τ_D is 30% longer in D_2O [12]. Therefore, the ratio of the electron solvation times is predicted to be 1.3 at 20°C. Using the n-octane as an instantaneous response function we extract a 1/e rise time for the appearance of the solvated electron following photoionization to be 340 fs for H_2O and 460 fs for D_2O, as shown in fig. 1. This corresponds to a 35% increase in the appearance time of the solvated electron. The value for H_2O is in agreement with the rise time of the solvated electron from the data of Migus et al. The agreement of our data with the continuum prediction could be partially fortuitous due to a change in the thermalization time in the deuterated solvent due to a change in the rate of energy loss for the ejected electron, as will be discussed shortly. Although it is generally assumed that the thermalization time is much faster than the solvation time, we note that this assumption may not be true for water.

After the electron is fully solvated, approximately 1 ps, the D_2O and H_2O signals are observed to decay. Although the general shapes of the two decay curves (fig. 2) are similar we see in fig. 3 that there are significant differences. The amplitude of the signal from D_2O at the longest times measured is higher by 15 ± 2% than the H_2O signal and we note that the decay is also slower in D_2O. The available evidence suggests that we are monitoring only the solvated electron. It has been established that the solvated electron in deuterated water has an absorption spectrum very similar to normal water [13]. In addition, 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. Secondly, the signals at

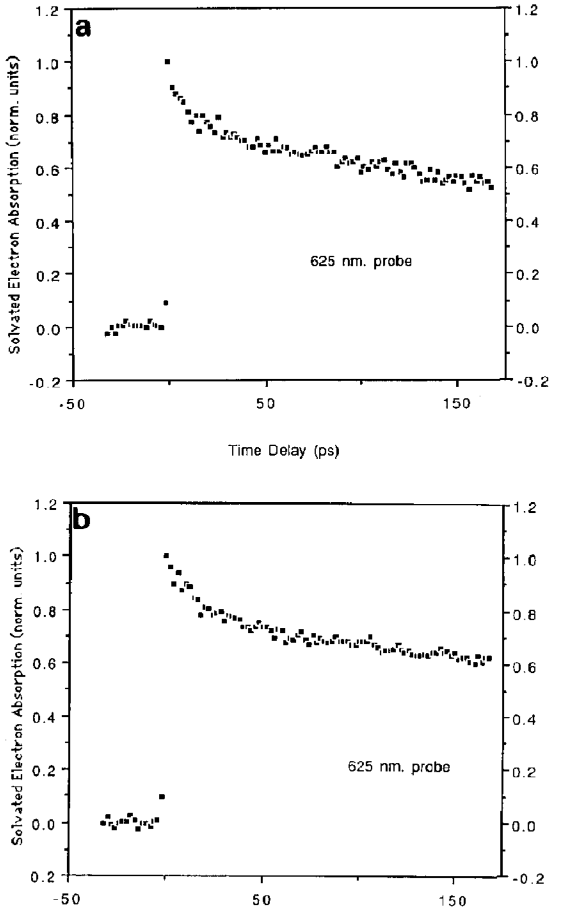

Fig. 2. (a) Solvated electron absorption signal in neat H_2O. Data taken with 2 ps time steps, other conditions same as fig. 1. (b) Solvated electron absorption signal in neat D_2O. Data taken with 2 ps time steps, other conditions same as fig. 1.

three different probe wavelengths have an identical time dependence [6]. This is inconsistent with the possibility of having another species contributing to the signal unless it obeyed the same kinetics as the solvated electron. Also, as the probe wavelength is varied from 550 to 700 nm the electron absorption is known [10] to increase by about a factor of two ($\epsilon = 18500$ cm^{-1} M^{-1} at 720 nm), which is consistent with our observations. If another species were contributing to the absorption it would be unlikely that its absorption would vary with wavelength by the same amount as that of the solvated electron. With respect to the possibility of the solvated electron undergoing a quenching reaction, it is well known that reactions with O_2 or other quenchers in small concentrations are negligible on the picosecond time scale [10]. The possibility of impurities was checked by using the highest grade purity available as well as other samples kept under different conditions; no change was seen in the observed behavior of the solvated electron. We therefore believe that the most likely explanation for the observed decay is geminate recombination of the electron–cation pair formed upon photoionization. The geminate nature of the kinetics was verified by decreasing the pump intensity and observing no change in the decay rate or the ratio of the peak to its longer time value. With respect to the electron–cation recombination it is possible that we are seeing recombination of the solvated electron with the daughter ion of H_2O^+, i.e. H_3O^+. It is thought that the water cation quickly decays yielding H_3O^+ plus an OH radical; however, this process has not yet been observed.

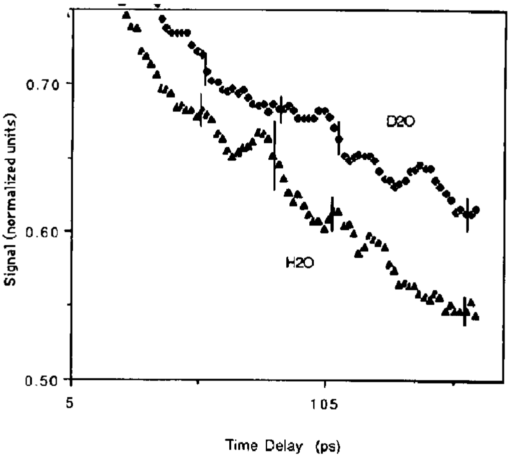

Fig. 3. Figs. 2a and 2b superimposed on an expanded scale. Data smoothed as a visual aid for the reader; error bars are ± 1 standard deviation calculated from the original data.

In the last twenty years numerous radiation chemists have measured solvated electron yields in water by pulse radiolysis [13,14]. Measurements in water have shown that the escape yield is between 10–25% higher in D_2O than in H_2O. It was therefore concluded that the spur, generated by the electron beam, produced in D_2O was larger than the one produced in H_2O. Recent electron pulse radiolysis and electrode photoejection studies done on the nanosecond time scale have supported this observation [15,16]. These studies, as well as some theoretical work have also shown that the thermalization distance in water is also energy dependent [17]. A simple explanation of this isotope effect has been suggested by several groups [14–16]. Following photoionization the electron is thermalized by collisions with solvent molecules. Since thermalization is dependent on the transfer of the electron's kinetic energy to vibrations and rotations of the solvent molecules we can anticipate a difference in the cross sections based on the larger vibrational frequency of H_2O. Thus the electron would have more collisions with the D_2O molecules than with H_2O molecules in the thermalization process and thereby would achieve a larger initial separation. A consequence of this is the increased yield of solvated electrons that escape geminate recombination in D_2O versus H_2O.

From our measurements of the fraction of solvated electrons that escape geminate recombination we can obtain the thermalization distance using a continuum model. In this model, developed by Onsager, the probability, P, that a thermalized electron, a distance r away from the cation at $t=0$, escapes geminate recombination is given by

$$P=\exp(-r_c/r)\ , \tag{2}$$

where r_c, the Onsager length, is given by $e^2/\epsilon kT$ [18]. For water at 21°C the Onsager length is 7 Å. Since the longitudinal relaxation time is much shorter than the observed geminate recombination time, the static dielectric constant is used. It is assumed that the continuum model is applicable at relatively small electron–cation separations and thus our use of the bulk dielectric constant. With respect to the electron–cation separation, it is likely that there is a distribution of thermalization distances. To obtain the fraction that escapes, Ω, we integrate over a distribution of thermalization distances,

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

where $g(r)$ is the probability density of the electron thermalization distances. We obtain a mean thermalization distance of 13 ± 0.5 Å for H_2O. This was done using eq. (3) and our measured value of $54\pm1\%$ for Ω and assuming that the distribution of thermalized electrons is Gaussian [#2]. For deuterated water, a mean thermalization length of 17 ± 0.5 Å is obtained. Similar thermalization distances are obtained for other distributions, for example an exponential distribution. We note that this is an upper estimate of the electron thermalization distance since the recombination is almost but not quite over; however, other factors such as finite size effects will act in the other direction.

To obtain a ballpark estimate of the average thermalization distance another approach is now taken. Since the electron mobility for an aqueous electron and hydronium ion is known (at 22°C, $D_{e^-}=4.75\times10^{-5}\ \mathrm{cm^2/s}$, $D_{H_3O^+}=9.0\times10^{-5}\ \mathrm{cm^2/s}$) [19] the thermalization distance can be crudely estimated by assuming that the motion of the electron is given by a random walk. However, the diffusion we are considering is anisotropic in nature. The electron will drift toward the cation and can diffuse freely perpendicular to the field. Thus the appropriate dimensionality for the motion is not clear. For one-dimensional motion, using $r^2=2Dt$ (i.e. neglecting the electron–cation Coulomb interaction) with the 60 ps recombination time we obtained for H_2O with D given by $D_{e^-}+D_{H_3O^+}$, a 13 Å thermalization length is obtained. Similarly using $r^2=6Dt$, the three-dimensional case, we obtain 22 Å for the thermalization length. Since the role of the electric field is neglected, these distances represent lower bounds on the thermalization distance. From fig. 3 we note that the electron–cation geminate recombination kinetics are slower in the D_2O. This could be due to the larger electron thermalization distance in D_2O discussed earlier or a decrease in the diffusion coefficients for the electron and the cation in D_2O. A more detailed discussion of the recombination kinetics will be presented later.

4. Conclusion

We have performed femtosecond photoionization

[#2] In eq. (3), $g(r)$ 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 $\langle r\rangle=2b/\pi^{1/2}$.

experiments on neat H_2O and D_2O. An isotope dependence is seen in both the recombination dynamics and the electron solvation dynamics. The early time electron solvation dynamics are found to be slower in D_2O than H_2O, consistent with the predictions of the continuum model of dielectric relaxation. However, the observed difference may also be partially due to an increase in the electron thermalization time in D_2O. We have attributed the observed picosecond decay kinetics to geminate recombination of the electron–cation pair, where the cation is probably H_3O^+, i.e. the ion produced when H_2O^+ reacts with H_2O. The recombination kinetics are slower in D_2O and approximately 15% more solvated electrons escape in D_2O than H_2O, in our experiments. The increase in escape yield can be explained by the difference in the electron's translational to vibrational energy transfer rates between the two water isotopes. Analysis of the data suggests that the thermalization distance is very short, 13 ± 0.5 Å for H_2O and 17 ± 0.5 Å for D_2O.

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