Femtosecond Electron Solvation Kinetics in Water

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Recent experimental and theoretical studies of electron solvation in liquid water have led to a detailed kinetic picture of this process. The electron solvation dynamics can be viewed as an excited state relaxation process between different electronic energy levels of the solvated electron. Simulations have suggested the importance of direct relaxation from upper excited electronic states as well as from the lowest excited electronic state (the wet electron state) to the ground electronic state. Using this as a model to analyze the experimental data, it is found that the quantum yield of wet electron formation cannot be less than 0.5 and that the peak of the wet electron absorption spectrum shifts to the IR with a decrease of wet electron formation quantum yield, with limiting values for the peak of 1.1−1.5 eV.

I. Introduction

The problem of the solvated electron or equilibrated electron in water has been of great experimental[1−8] and theoretical interest.[9−18] Although the absorption spectra of the solvated electron in water are understood,[10,14] it is only recently that the details of the dynamics of electron solvation have begun to emerge from ultrafast absorption spectroscopy. Multiphoton ionization of neat water at room temperature using femtosecond lasers as the pump source to generate excess electrons followed by femtosecond transient absorption measurements of the evolving electrons in water indicates that there are only two species involved in the solvation dynamics: the wet electron and the solvated electron. The wet electron is proposed to be the lowest excited state of the solvated electron and the equilibrium solvated electron is the ground state of the electron. Recent experimental results using I^- in H_2O to generate the electron in aqueous solution further supports the hypothesis that the wet electron is an excited state of the solvated electron.[19]

Stimulated by the experimental results, a considerable amount of theoretical work has been done on electron solvation using molecular dynamics simulations methods.[14−18] The results of early simulations of electron solvation based on adiabatic relaxation of the electron in water did not agree with experimental observations.[14] The disagreement between the adiabatic simulations and experimental results suggested the importance of nonadiabatic transitions between different electronic states during electron solvation. The recently developed molecular dynamics methods involving nonadiabatic transitions have made the simulations of electronic relaxation of the excess electron possible.[20] Simulations have theoretically demonstrated the role of nonadiabatic relaxation in the electron solvation dynamics.[16,17] Similar results have been obtained for electron solvation in liquid water using slightly different simulation methods.[18] The results from nonadiabatic simulations with flexible water solvent molecules are consistent with experimental observations.[16b]

Based on recent nonadiabatic simulations, a modified kinetic model describing the electron solvation process in water has been proposed.[21,22] In addition to the relaxation path considered in the standard two-state model, in which the ground electronic state (hydrated electron) is populated solely from the lowest excited electronic state (wet electron), the modified kinetic model included a new relaxation path of the electron directly from quasi-free electronic state to the ground electronic state (s-like state) without going through the intermediate wet electron. The inclusion of this new relaxation path in the kinetic model will impact the kinetic parameters and wet electron absorption spectrum obtained using the standard two-state model.[5] In this paper, the effects of the new relaxation path on the kinetic parameters and the wet electron absorption spectrum will be examined.

II. Experimental Section

The experiments discussed in this paper were done by femtosecond absorption spectroscopy. The sample cells used were 200 μm in thickness, and the water was prepared using a homebuilt distillation apparatus. The cross-correlation function of the pump and the continuum probe was determined to be 230 fs fwhm from difference frequency generation measurements. Convolution procedure was used in data analysis because the electron solvation times are comparable to the system response time. Further details can be found in our previous papers.[3−6]

III. Results and Discussion

A. Electron Solvation Dynamics and the Standard Two-State Model. Theoretically, if there are only two species present in the kinetics, one is the precursor of the other and both are identifiable by their characteristic absorption spectra, then one would expect to observe an isosbestic wavelength where the absorption coefficients of the wet electron and the solvated electron are equal, provided that the adiabatic relaxation of the electron is much faster than nonadiabatic transitions as suggested in the adiabatic simulations.[14] The existence of an isosbestic wavelength in the electron solvation dynamics has also been suggested in the nonadiabatic simulations.[16a]

Clearly, experimental examinations on whether there exists such an isosbestic wavelength in the dynamics are important to prove or disprove the two-state model of electron solvation in water. To find such an isosbestic point we have scanned the probe wavelength from the infrared to the visible. Typical data

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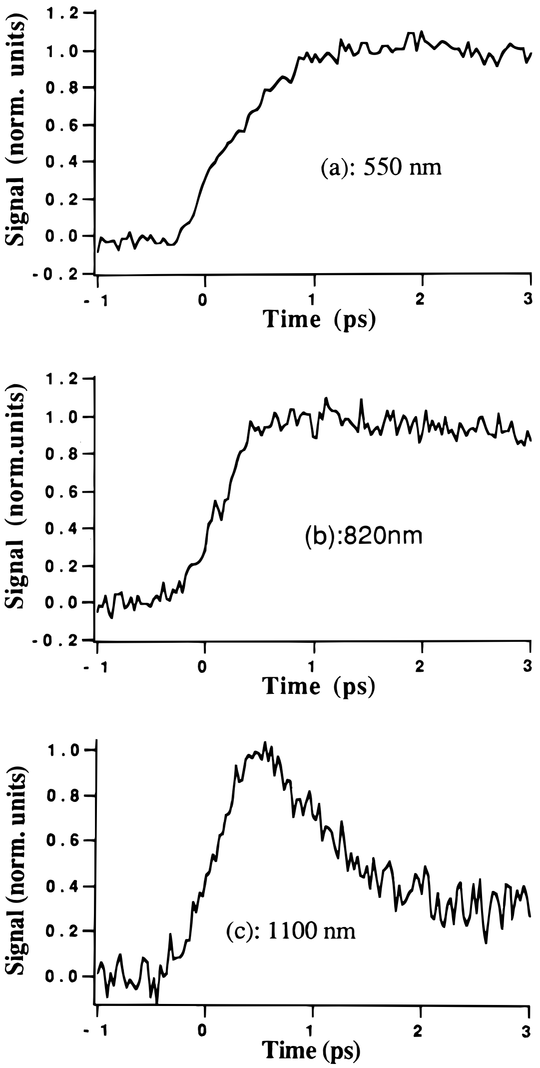

Figure 1. Electron solvation dynamics in neat water: (a) 550, (b) 820, and (c) 1000 nm.

at 550, 820, and 1100 nm are shown in Figure 1. At short probewavelengths, a slow increase in the signal is observed due to the formation of the solvated electron, while the signal decreases at longer probe wavelengths after its initial rise due to the decay of the wet electron population. This behavior is a consequence of the fact that the wet electron absorbs more strongly than the solvated electron in the IR region. At 820 nm, the signal remains constant after its fast rise, which is an indication of an isosbestic wavelength. In other words, the absorption coefficients of the wet and the solvated electron are equal at this particular wavelength so that for an optical experiment the two species are indistinguishable and the transition of the wet electron into the solvated electron becomes irrelevant. The existence of such an isosbestic point is strong evidence that the wet to solvated electron transition involves only two states, which is in agreement with the experiments and interpretation of other researchers: A small decay (with a rate of about 1/15 ps^{-1}) present at times greater than several picoseconds is due to the much slower geminate recombination of the solvated electron.[6]

Accordingly, we used a simple kinetic model to fit the data.

$$e_{\text{quasi-free}} \xrightarrow{k_1} e_{\text{wet}} \xrightarrow{k_2} e_{\text{solvated}} \qquad (1)$$

where $1/K_1$ and $1/K_2$ are the formation times of the wet and the solvated electrons respectively. For the purposes of this paper, this will be called the standard two-state model. By solving the rate equations one obtains an expression for ABS(t), the time-dependent absorption signal.

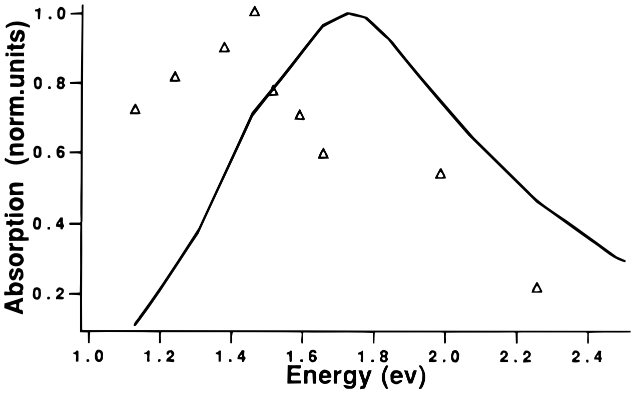

Figure 2. Wet and solvated electron absorption spectra wet (triangles) and solvated electron (line).

$$\mathrm{ABS}(t) = N_0\epsilon_{\text{wet}}\left\{\frac{\epsilon_{\text{sol}}}{\epsilon_{\text{wet}}}(1 - e^{-k_1 t}) + \frac{k_1}{k_2 - k_1}\left(1 - \frac{\epsilon_{\text{sol}}}{\epsilon_{\text{wet}}}\right) \times (e^{-k_1 t} - e^{-k_2 t})\right\} \qquad (2)$$

where N_0 is the number of electrons made by the ionizing pump pulse and ϵ_{wet} and ϵ_{sol} are the absorption coefficients of the wet electrons and the solvated electrons at wavelength λ. From the data analysis using the standard two-state model, it has been found that the wet electron formation time, $1/k_1$, was 300 ± 40 fs, and the lifetime of the wet electron, $1/k_2$, was 540 ± 50 fs.

Using the known values for the solvated electron absorption at different wavelengths,[23,24] the wet electron absorption spectrum can also be inferred from data analysis without relying on absolute absorption measurements, as shown in Figure 2. UV power fluctuations and the difficulty in reproducing the spatial overlap of the pump and probe pulses as the probe wavelength is varied make the absolute absorption measurements difficult. It can be seen that the wet electron absorption has a blue tail extending out past 2.5 eV. The absorption has a broad maximum around 850 nm or 1.46 eV and the overall absorption strength is similar to that of the solvated electron. It is important to note that the absorption spectra of the wet and the solvated electron overlap sufficiently that the absorption of both species must be considered in the data analysis at all the wavelengths studied (550−1100 nm). The wet electron absorption spectrum obtained from our data analysis is similar to the absorption spectrum of the intermediate excited state from simulations results.[16a]

B. Two-Channel Model of Electron Solvation. In addition to demonstrating the importance of nonadiabatic transitions in the dynamics, the recent nonadiabatic simulations revealed another important feature of electron solvation. The simulations showed that about 50% of the electrons go directly to the electronic ground state from the quasi-free electronic state without going through the intermediate state, while other quasi-free electrons relax following the path as described in the standard two-state model, going to an excited intermediate state before they reach the electronic ground state.

Stimulated by these results, an interesting comparison can be made with an extension of the standard two-state kinetic model by including direct decay from quasi-free electronic state to the ground electronic state of the electron, without passing through the lowest excited state, i.e., the wet electron.

$$\begin{tikzcd} e_{\text{quasi-free}} \arrow[r, "K_1'"] \arrow[rr, bend right, "K_3'"'] & e_{\text{wet}} \arrow[r, "K_2'"] & e_{\text{sol}} \end{tikzcd} \qquad (3)$$

One obtains the following by solving the rate equations for eq 3,where $k_{\mathrm{T}} = k'_1 + k'_3$. For the purpose of this paper we

$$\mathrm{ABS}(t) = N_0\epsilon'_{\text{wet}}\left\{\frac{\epsilon'_{\text{sol}}}{\epsilon'_{\text{wet}}}(1 - \mathrm{e}^{-k_{\mathrm{T}}t}) + \frac{k'_1}{k'_2 - k_{\mathrm{T}}}\left(1 - \frac{\epsilon'_{\text{sol}}}{\epsilon'_{\text{wet}}}\right) \times (\mathrm{e}^{-k_{\mathrm{T}}t} - \mathrm{e}^{-k'_2t})\right\} \quad (4)$$

will call this the two-channel model.

The two-channel model implies the existence of a finite "quantum yield" of wet electrons, i.e., not all quasi-free electrons become wet electrons. In terms of the constants in eq 3 we obtain the wet electron quantum yield $\phi_{\text{wet}} = k'_1/k_{\mathrm{T}}$. If $k'_3 \ll k'_1$, then almost all the quasi-free electrons pass through the intermediate wet electron state and the corresponding wet electron quantum yield is high. In contrast, if $k'_3 \gg k'_1$ then relatively few wet electrons are formed and thereby wet electrons would hardly be observed.

In the standard two-state kinetic model, at the isobestic wavelength, only the formation of the wet electron appears in the dynamics and that rate is given by k_1. In the two-channel model, there is still an isosbestic wavelength observable; however, the rate of appearance of the wet electron is now given by k_{T}. The rates of wet electron decay are given by k_2 and k'_2 in the standard and the channel models, respectively. Since both models can be fit to our experimental results, the parameters in the two models must be consistent with each other. In other words, eqs 2 and 4 require $k_{\mathrm{T}} = {}_{k1}$ and $k_2 = k'_2$. Furthermore, agreement between the two models is obtained if the time-independent preexponential terms in eqs 2 and 4 are equal, which leads to the following relation,

$$\frac{(\epsilon_{\text{wet}} - \epsilon_{\text{sol}})k_1}{k_1 - k_2} = \frac{k'_1(\epsilon'_{\text{wet}} - \epsilon'_{\text{sol}})}{k_{\mathrm{T}} - k'_2} \quad (5)$$

where the primes indicate the absorption coefficients in the case of the channel model. Using $k_1 = k_{\mathrm{T}}$, $k_2 = k'_2$ and noting that $\epsilon_{\text{sol}} = \epsilon'_{\text{sol}}$ since the solvated electron absorption must be the same for both cases, it is found that

$$\epsilon'_{\text{wet}} = \epsilon_{\text{sol}}\left[1 + \frac{\left(\frac{\epsilon_{\text{wet}}}{\epsilon_{\text{sol}}} - 1\right)}{\phi_{\text{wet}}}\right] \quad (6)$$

This result has a simple physical interpretation. As the quantum yield of wet electrons changes, the absorption of the wet electron also must change to compensate for the decreased number of wet electrons. In the IR where the wet electron absorbs more than the solvated electron, the wet electron absorption must be larger in the two-channel model than in the standard two-state model, as seen from eq 6 and shown in Figure 3. The reverse will happen in the visible where the solvated electron absorbs more than the wet electron. This also means that the absorption maxima of the wet electron will shift to the IR as the quantum yield of wet electron decreases. We note that for quantum yields less than approximately 50%, the experimental wet electron absorption will become negative at short wavelengths, which is physically unrealistic. This indicates that at least 50% of the quasi-free electrons pass through the wet electron intermediate state, which is in agreement with computer simulations.[16a]

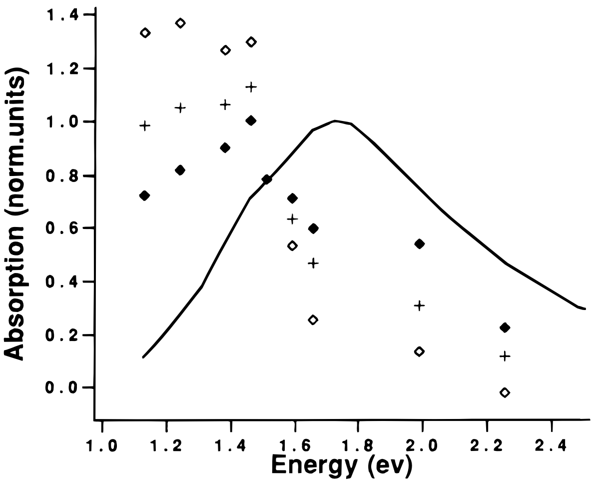

Figure 3. Channel model effect of the wet electron yield on the wet electron absorption spectra: (solid diamond) $\phi_{\text{wet}} = 100\%$; (cross) $\phi_{\text{wet}} = 70\%$; (open diamond) $\phi_{\text{wet}} = 50\%$.

IV. Summary

Recent experimental and theoretical work have led to the development of a detailed picture of the dynamics of electron solvation in liquid water. Experimentally, the two electron species observed are the solvated electron and the wet electron, an IR absorbing precursor. The existence of only two states was verified by the confirmation of an isosbestic wavelength in the solvation dynamics. The formation rate, decay rate, and the absorption spectrum of the wet electron were measured. Data analysis based on a two-channel model, which is derived from theoretical simulations, shows that the kinetic parameters and the wet electron absorption spectrum will depend on the quantum yield of the wet electron. An important result of the two-channel model is the finding that the quantum yield for wet electron formation must be greater than or equal to 0.5. This puts limits on the peak of the wet electron absorption from roughly 1.1 to 1.5 eV. Because the absorption peak of the wet electrons shifts toward IR with the decrease of wet electron quantum yield limits on the wet electron absorption peak can be set between roughly 1.2 and 1.5 eV. These observations are qualitatively consistent with recent simulation results.

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