Femtosecond Studies of the Presolvated Electron: An Excited State of the Solvated Electron?

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Femtosecond studies of the formation, decay, and absorption spectra of the wet or presolvated electron are presented. The discovery of an isosbestic wavelength shows for the first time that the wet-to-solvated electron transition involves only two states. The model of the wet electron as an excited state of the solvated electron and the wet-to-solvated electron transition, viewed as a radiationless transition, is discussed. An ultrafast component of the visible absorption signal is believed to be H_2O^+.

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The aqueous or hydrated electron is a problem of great interest in chemical physics. Beside being the simplest anion, it has a rich variety of physical and chemical properties that have made it an object of intensive experimental and theoretical investigation since its spectral identification in 1962.[1] The absorption spectra and other physical properties are well characterized experimentally.[2,3] Recently, we reported the first studies of aqueous-electron geminate recombination.[4-6] Theoretical work using computer-simulation methods has made important advances in the area of first-principles calculations of the equilibrium-solvated-electron absorption spectra.[7,8]

One of the most fundamental and least understood aspects of the aqueous electron is the dynamics of solvation. In the last few years, there has been a great deal of controversy about the mechanism of electron solvation. Recent theoretical and experimental efforts provide fundamentally incongruent points of view. Simulations,[9,10] the dielectric-continuum model[11] (DCM), and the mean-spherical approximation[12] (MSA) suggest that solvation involves a continuous change in the electron absorption spectra. Although picosecond time-resolved studies were able to measure electron solvation dynamics in alcohols,[13-15] until the development of subpicosecond lasers, solvation dynamics in water were largely unexplored.[4-6,16,17] The wet electron, i.e., the localized but not fully solvated electron, was found to absorb in the ir and the transition to the solvated electron corresponded approximately to the longitudinal dielectric relaxation time of water. Migus *et al.* claimed that their experimental measurements supported the proposed two-state model[13] for the solvation dynamics; however, this important point could not be established from their data since both the wet and the solvated electron absorb in the regions that were probed.[17] In order to clarify the situation, we have done experiments with improved time resolution and have found strong experimental evidence for the two-state model by demonstrating the existence of an isosbestic point. The dielectric-relaxation picture of solvation is fundamentally inconsistent with results of this study which support the two-state model for the wet-to-solvated electron transition. In this Letter it is proposed that the wet electron is an excited state of the solvated electron and that the rate-limiting step in the electron solvation dynamics involves an internal conversion process, consistent with the nonadiabatic process proposed by Rossky and Schnitker.[9]

The experiments described here were performed with an amplified colliding pulse mode-locked dye laser. The experiments were done with a uv pump and a tunable wavelength probe. The absorption from *n* octane was used as a system response.

The time evolution of the electron absorption at several different probe wavelengths was measured. In Fig. 1, a 625-nm probe was used; a fast and slow component in the rise is clearly observed. The fast rise is due to an ultrafast rise and decay which we attribute to H_2O^+ (Fig. 2). The slow component corresponds to the appearance of the wet or presolvated electron and its transition into the fully solvated electron. Our previous experiments have shown that the absorption spectra of this species is consistent with the equilibrium-solvated-electron absorption spectra.[4,5]

The two-state model means that a wet electron, identifiable by its characteristic absorption spectra, undergoes a transition to the solvated electron. In other words, there are only two electron species present in the kinetics rather than a series of wet-electron species, having their own spectra, that evolve into the equilibrium solvated electron. In the two-state model, if the absorp-

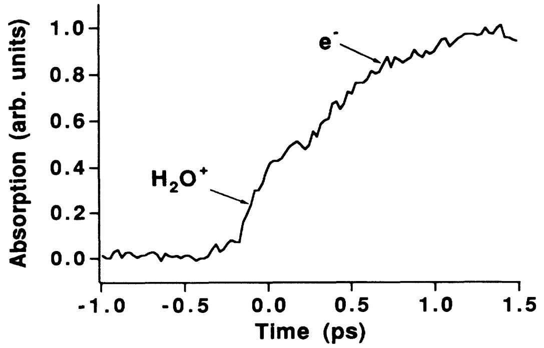

FIG. 1. The time evolution of the aqueous electron probed at 625 nm.

tions of the two species (states) overlap then there must be a wavelength where the two spectra intersect and therefore have the same absorption coefficient ϵ. A consequence of the presence of an isosbestic point can be seen by considering the absorption $A(t)$ at a time t and a wavelength λ,

$$A(t)=\epsilon_{\mathrm{wet}}N_{\mathrm{wet}}(t)+\epsilon_{\mathrm{sol}}N_{\mathrm{sol}}(t)\,,$$

where $N_{\mathrm{wet}}(t)$ and $N_{\mathrm{sol}}(t)$ are the concentrations of wet and solvated electrons. At the isosbestic wavelength, $\epsilon_{\mathrm{wet}}=\epsilon_{\mathrm{sol}}$ and the kinetics will therefore be appear to be characteristic of a single species, with one rise time and a long decay, since the total electron concentration, $N_{\mathrm{wet}}(t)+N_{\mathrm{sol}}(t)$, is conserved. To find the isosbestic point we scanned from the infrared to the visible. At 820 nm the isosbestic point was observed in the wet-to-solvated electron transition (Fig. 3). A small decay present due to the geminate recombination of the electron[4-6] has been corrected for using our previous results. This small amount of electrons ($<10\%$) which recombine in the first few picoseconds is due to the small fraction of electrons very close to the parent fragment. We conclude from the observation of the isosbestic point that the wet-to-solvated electron transition involves only two states.

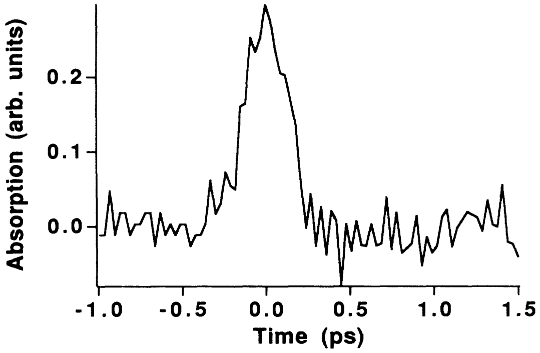

FIG. 2. The ultrafast component of the signal in Fig. 1. This may be due to H_2O^+ absorption at 625 nm.

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

$$e_{\mathrm{quasifree}}\xrightarrow{k_1}e_{\mathrm{wet}}\xrightarrow{k_2}e_{\mathrm{sol}}\,.$$

By solving the rate equations one obtains

$$N(t)=N_0\left[\frac{k_1}{k_1-k_2}(\epsilon_{\mathrm{wet}}-\epsilon_{\mathrm{sol}})e^{-k_2t}+\epsilon_{\mathrm{sol}}+\left(\frac{k_2\epsilon_{\mathrm{sol}}-k_1\epsilon_{\mathrm{wet}}}{k_1-k_2}\right)e^{-k_1t}\right].\qquad(1)$$

N_0 is the number of electrons made by the ionizing pump pulse. This model was used because it is physically reasonable and allows for an unambiguous fit to the data. By the discovery of the isosbestic point, the two-state model is verified. This suggests that the wet electron is really an excited state of the solvated electron. This would quite naturally lead to the two states observed in the dynamics. The excited state is likely to be the lowest excited state of the solvated electron corresponding to a p-like electron wave function.[7,8] It is unlikely that another long-lived species is present because it would probably absorb in the visible or the near ir. Our experimental results show that the wet-electron formation time, $1/k_1$, is 180 ± 40 fs. This time is interpreted as the total time needed for the electron to localize in a preexisting trap[18] followed by a further deepening of the well to a configuration appropriate to the wet electron. The lifetime of the wet electron, $1/k_2$, was found to be 540 ± 50 fs. We therefore see that the rate-limiting step in the solvation dynamics of the electron is really an energy relaxation process referred to as a radiationless transition in molecules. One anticipates that the internal conversion process can be described by the terms neglected in the Born-Oppenheimer approximation, as is the case with molecules. For the solvated electron, it is reasonable to say that the relevant motions might be water librations and translations.

The two-state picture, which in the present discussion assigns the wet electron as an excited state of the solvated electron, is fundamentally inconsistent with the DCM or any of its extensions. In contrast, molecular solvation in water and alcohols is characterized by continuously varying dynamic Stokes shifts.[19,20] However, it is interesting to note that the two times obtained in the electron solvation dynamics reported here are qualitatively consistent with the two times obtained from the MSA theory, if we regard the solvated electron as a classical ion with a radius of about 2 Å ($t_1=190$ fs, $t_2=600$ fs).[13,21] This result may be simply fortuitous or it may reflect that the rate of the nonradiative transition corresponds to molecular motions on this time scale.

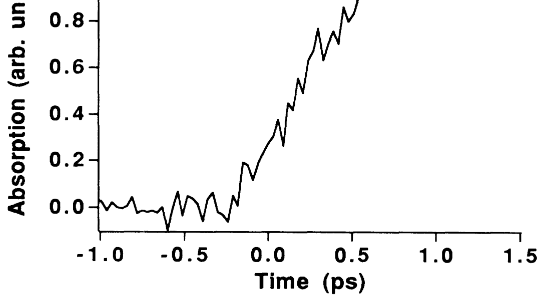

FIG. 3. The time evolution of the aqueous electron at 820 nm, the isosbestic wavelength.

Barnett, Landman, and Nitzan found that the solvated electron in either the ground or excited state of the solvated electron relaxed on the time scale of librations, 50–100 fs.[10] Similar conclusions were obtained in an analysis of the motion of a solvated electron[22] and in a nonadiabatic simulation.[23] These results are quite consistent with the known large energy fluctuations in neat water.[24] It is clear that these rapid relaxations do not correspond to the 540-fs process that we observe. However, it is worthwhile to note that the measured average lifetime of a hydrogen bond in water is 500 ± 100 fs.[25] It is therefore possible that the solvent motion that is important in the observed 540-fs wet-to-solvated electron transition involves the breaking of hydrogen bonds.

Using the known values for the solvated-electron absorption,[26] the wet-electron absorption spectrum is obtained (Fig. 4). This was done by comparing the signal at each wavelength to the absorption at long times which is due totally to the solvated electron. Both absorption spectra shown are normalized to the maximum of the solvated-electron absorption. The error bars correspond to the signal-to-noise ratio in the measured absorption of the solvated electron and the fraction of the signal at early times attributed to the wet electron. It can be seen that the wet-electron absorption has a blue tail extending out past 2.5 eV indicating that the potential well the electron sits in is already quite deep after 180 fs. The absorption has a broad maximum at around 900 nm or 1.4 eV and the overall absorption strength is similar to that of the solvated electron. It is of interest to note that Wallquist, Martyna, and Berne calculated the energy difference between the first excited state and the second excited state to be about 1.3 eV.[8] However, the transition we are observing most likely corresponds to a different solvent configuration.

Another result of interest is the very fast component (< 50 fs) seen in the rise-time kinetics at 625 nm (Figs. 1 and 2). We attribute this fast component to the formation and decay of H_2O^+. From gas-phase measurements, it is well established that H_2O^+ has a visible absorption band beginning at about 650 nm (Ref. 27) and is very reactive with neutral water molecules.[28] The very fast component (Fig. 2) only absorbs at wavelengths shorter than 625 nm, consistent with the gas-phase results.[27] If excited-state absorption by water were responsible for the very fast component then we would expect absorption at longer wavelengths as well, based on the known broad continuous spectra found in the gas phase.[29] More work is needed before a positive identification can be made.

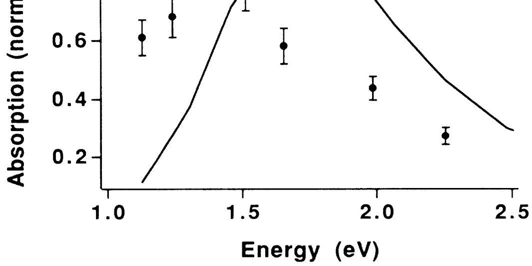

FIG. 4. The absorption spectra of the wet electron (solid circles) and the solvated electron (solid line).

In this Letter, we have shown that the wet-electron to solvated-electron transition involves only two states. We propose that the wet electron is really an excited state of the solvated electron, and that the rate-limiting step in the solvation dynamics is really an internal conversion process, consistent with nonadiabatic process noted by Rossky and co-workers.[9,23] This would quite naturally lead to the two states observed in the kinetics of electron solvation. In addition, an ultrafast component of the observed signal is attributed H_2O^+. This would be the first observation of these two short-lived species. The wet-electron formation time (180 ± 40 fs), lifetime (540 ± 50 fs), and the absorption spectra were measured. The wet-electron spectra are remarkably similar to the fully solvated-electron spectra. This result supports the physical picture that the wet electron is a highly localized state formed on the 180-fs time scale. In the description of the wet electron as an excited state of the solvated electron, the wet-to-solvated electron transition is viewed as a radiationless transition. However, further work is in progress to more clearly elucidate the physical mechanism involved.

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