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Ultrafast transient-absorption spectroscopy of the aqueous solvated electron

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We have performed the first direct pump-probe transient-absorption measurements on the near-infrared (IR) band of the equilibrated aqueous solvated electron. The pump pulse was centered at 780 nm. The absorption spectrum of the excited state is observed to be red-shifted relative to the ground-state absorption. The radiationless transition from the excited state to the ground state occurs with an average time constant of 550 ± 170 fs. In observing a subpicosecond lifetime and red-shifted absorption for the excited p-states, these experiments are in accord with a growing body of experimental and theoretical work, serving to provide a consistent picture of the photophysics of the solvated electron.

The behavior of electrons in liquids has been an area of interest since the first observation of electrons in liquid ammonia over 100 years ago.[1–4] A particularly important system is that of aqueous electrons, which play a prominent role in the radiation chemistry of water.[5,6] Recent ultrafast spectroscopic studies have observed the solvation and relaxation dynamics of electrons produced via multiphoton ionization of neat water.[7–10] These studies have revealed the existence of a precursor to the fully solvated electron, which relaxes to the solvated electron on a subpicosecond time scale. This precursor is characterized by a broad absorption band that is substantially red-shifted relative to the 720 nm band of the solvated electron. Both experimental[7–10] and theoretical[11–14] evidence support the model[9,11] that this precursor is an excited state of the electron, which is p-like in character; the ground state is spherically symmetric, or s-like.

In this Communication, we report the first near-infrared (IR) pump-probe transient absorption spectroscopy of the equilibrated solvated electron. We observe the existence of an excited state having an absorption band that is red-shifted from the ground-state solvated electron and that relaxes to the ground state with an average time constant of 550 ± 170 fs.

The ultrafast transient-absorption spectrometer used in these experiments has been detailed elsewhere.[15] Briefly, an argon-ion-pumped Ti:sapphire oscillator produced pulses of 90 fs duration, which were subsequently amplified using the technique of chirped-pulse amplification.[16] The oscillator pulses were temporally stretched to ~120 ps in a grating stretcher, amplified in a Nd:YLF-pumped (6 W, 2 kHz, 300 ns, 527 nm) Ti:sapphire regenerative amplifier, and recompressed in a grating compressor to yield pulses of 130 fs duration, centered at 780 nm, having a pulse energy of 200 μJ and a repetition rate of 2 kHz.

The experiment involved a pulse sequence consisting of a synthesis pulse, a pump pulse, and a probe pulse. About 45% of the amplified pulse was focused into a KD*P crystal to yield the synthesis pulse (30 μJ/pulse at 390 nm) used to generate solvated electrons via multiphoton ionization of water. After a delay of a few nanoseconds, a femtosecond pump pulse (25 μJ/pulse at 780 nm) was used to promote the solvated electron to an excited state. Finally, the temporal evolution of the system in the spectral range of 540–1060 nm was obtained using a variably delayed probe pulse produced via continuum generation in quartz. Water (HPLC-grade, EM Science) was circulated in a flow cell of 1 mm path length such that each pulse sequence encountered a fresh sample volume.

Representative pump-probe absorption transients are displayed in Figs. 1 and 2. The transients obtained probing at wavelengths of 680 nm or shorter (Fig. 1) show a fast, instrument-limited reduction in optical density (bleach), followed by a recovery having a time constant of 490 ± 180 fs. Conversely, transients probing at longer wavelengths ($\lambda \geqslant 900$ nm) show an instrument-limited *increase* in optical density, which decays with a time constant of 660 ± 60 fs (Fig. 2). Taking the average of all data sets collected at all wavelengths yields an average relaxation time of 550 ± 170 fs. Typical parameters extracted by fitting these pump-probe transients to a two-exponential functional form convoluted with the instrument response function are listed in Table I. Alternative fits with a single exponential functional form do not agree as well with the data as the fit with two exponentials.

The transients are interpreted as resulting from pump-probe spectroscopy of the solvated electron. The equilibrated solvated electron, produced in these experiments by the ultraviolet synthesis pulse, is known to have a broad, intense absorption in the visible and near-infrared spectral regions ($\lambda_{max} = 720$ nm, $\epsilon_{max} = 19\,000$ M^{-1} cm^{-1}).[17] The 780 nm pump pulse promotes the electron to an electronically excited state, which subsequently undergoes a radiationless decay back to the ground state with a time constant of 550 ± 170 fs.

To test this interpretation, the pure water sample was replaced with a solution of aqueous perchloric acid and the experiments were repeated. H$^+$ is known to be an efficient electron scavenger with a rate constant of 2.3×10^{10} dm^3 mol^{-1} s^{-1} for the reaction H$_3$O$^+$ + e^- → H$_2$O + H.[18] A solution of 0.14 M HClO$_4$ is calculated to scavenge electrons with a time constant of 300 ps. Thus, in this perchloric acid solution, any electrons produced by the synthesis pulse will be almost completely scavenged in the ~4 ns
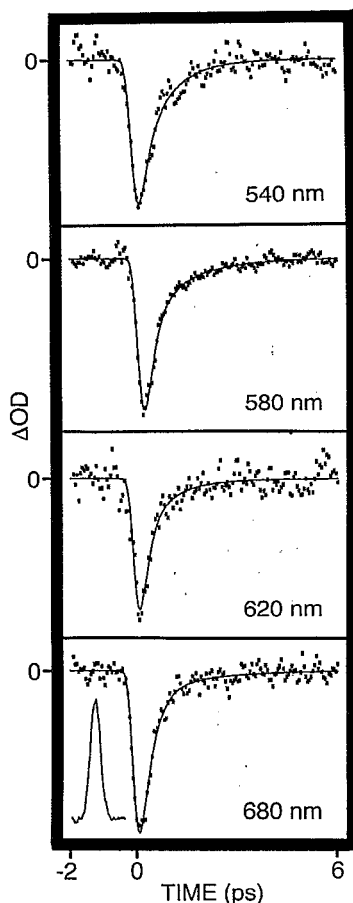
FIG. 1. Transient absorption spectra of solvated electrons in neat water. The data were fit to a biexponential function convoluted with the instrument response function (IRF) of the spectrometer. The IRF, shown in the bottom spectrum, was obtained utilizing the optical Kerr effect in water, and is 0.3 ps at full width half-maximum (FWHM). Maximum ΔOD values were 0.002, which correspond to changes in transmittance of 0.5%.

delay between the synthesis and pump pulses, and no transient absorption signals should be seen.

The experimental results are shown in Fig. 3. Upon switching from pure water to an aqueous solution of 0.14 M $HClO_4$ (Mallinckrodt), the transient absorption signals became unobservable within the experimental sensitivity, being reduced by a factor of > 10 (Fig. 3). Upon switching back to pure water, the signal reappeared. These experiments support the interpretation that the data in Figs. 1 and 2 originate from pump-probe transient absorption signals of the solvated electron.

The present experiments are closely related to a series of experiments on the thermalization and relaxation of electrons produced by photoionization of water.[7-10] The photoelectrons initially are delocalized, or "quasi-free," and subsequently become thermalized, localized, and solvated. The rate-limiting step in this process has been ascribed[9,11] to the radiationless transition of the excited p-states of the electron to the ground s-state, which has been found to occur with a time constant variously reported as 240 fs[7,8] and 540 ± 50 fs.[9-10] The excited p-states have an absorption red-shifted from the ground state.[9,13]
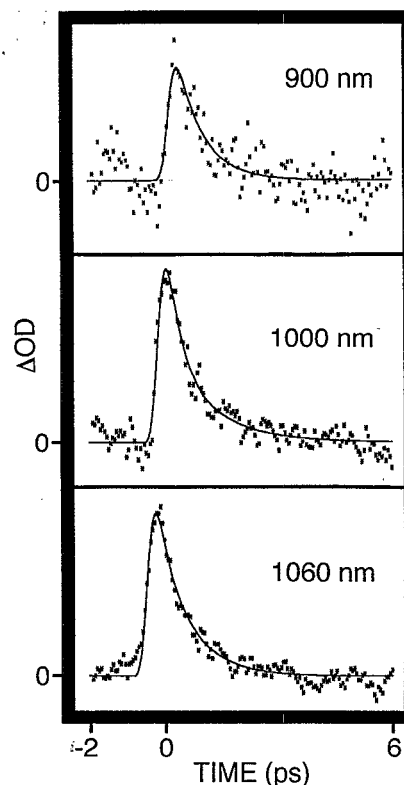

FIG. 2. Transient absorption spectra of solvated electrons in neat water taken at the red-edge of the ground-state absorption spectrum.

The ground and excited states exhibit an isosbestic point at 820 nm.[9] Our direct pump-probe measurements on the solvated electron are qualitatively consistent with the interpretation of the time-resolved experiments on photoionization of water. The spectral signature of the excited p-states observed here is consistent with that reported earlier, as we see a transient increase in absorption at wavelengths longer than 820 nm and a bleach at wavelengths shorter than 820 nm. Additionally, the average time constant of 550 ± 170 fs reported here for the radiationless decay of the excited state is consistent with the earlier measurements.

The solvated electron in water has recently been investigated by nonadiabatic molecular dynamics (MD) calculations.[13,14] Webster et al. employed a quantum treatment of the electron in a classical solvent and followed the dynamics of an electron initiated with 2 eV excess energy

TABLE I. Parameters obtained by fitting each transient in Figs. 1 and 2 to a biexponential function: $\Delta OD(t) = A_1 \exp(-t/\tau_1) + A_2 \exp(-t/\tau_2)$. Each amplitude is scaled so that $|A_1| + |A_2| = 1$. $\tau = |A_1|\tau_1 + |A_2|\tau_2$.

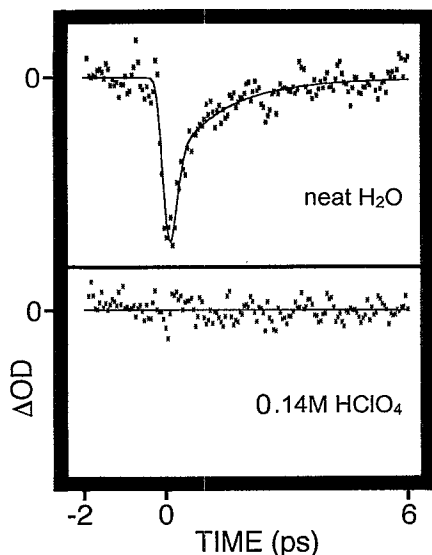| λ (nm)	τ_1 (ps)	τ_2 (ps)	A_1	A_2	τ (ps)
540	0.33	0.96	−0.59	−0.41	0.59
580	0.29	1.36	−0.77	−0.23	0.54
620	0.24	1.03	−0.81	−0.19	0.39
680	0.35	1.76	−0.91	−0.09	0.48
900	0.68		1	0	0.68
1000	0.38	1.27	0.67	0.33	0.67
1060	0.39	0.83	0.27	0.73	0.71

FIG. 3. Transient absorption spectra taken back-to-back at 580 nm. The top spectra show a typical signal in neat water. The sample was immediately switched to 0.14 M $HClO_4$, and the bottom spectrum was obtained. The signal was regained upon reintroduction of neat water.

above the vacuum level.[13] They observed a significant fraction of the electrons being trapped in a distorted p-type excited state. The excited-state lifetime was estimated to be ~1 ps. The excited state absorption spectrum was calculated to be broader and red-shifted by 0.2 eV from the ground-state absorption. Neria et $al.$ have also performed quantum nonadiabatic MD simulations, utilizing a semiclassical evaluation of the "golden-rule" expression for transitions between the excited p-states and the ground s-state.[14] They report excited state lifetimes of 120 and 220 fs for H_2O and D_2O, respectively, with error margins of 30%–40%. They note that these lifetimes may be lower bounds to the actual values, since only the lowest of the three excited p-states was explicitly treated. The absorption spectrum[13] and lifetime[13,14] of the excited p-states in these theoretical studies are in reasonable agreement with previous experiment[7-10] and with the data presented here.

In summary, we have performed direct pump-probe transient-absorption measurements on the near-IR band of the aqueous-solvated electron. The absorption spectrum of the excited p-states is observed to be red-shifted relative to the ground-state absorption. The radiationless transition from the excited state to the ground state occurs with an average time constant of 550 ± 170 fs. In observing a sub-picosecond lifetime and red-shifted absorption for the excited p-states, these experiments are in accord with a growing body of experimental and theoretical work. Future experiments will examine the dynamics of this system probing at additional wavelengths between 680 nm and 900 nm. Preliminary data in this spectral region have revealed complicated transient behavior which may be difficult to interpret with a strictly two-state model, indicating that other processes such as solvation and solvent cooling may play an important role in the observed spectral dynamics.

ACKNOWLEDGMENTS

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