Ultrafast Photoionization Dynamics of Indole in Water

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Indole in aqueous solution is photoionized near threshold following single photon absorption from a femtosecond laser pulse at 260 nm. Transient absorption measurements are performed using a white-light continuum probe pulse. Excited state absorption of neutral indole molecules is characterized accurately in 1-propanol where photoexcitation at 260 nm does not lead to photoionization. The presence of 0.75 M carbon tetrachloride in a solution of indole/1-propanol leads to the formation of indole radical cations on a picosecond time scale. While solvated electrons are formed in aqueous indole within our time resolution of 200 fs, measurements of the transient absorbance out to 100 ps are flat and indicate that geminate recombination is insignificant on this time scale. This result contrasts sharply with the geminate recombination dynamics observed following the photoionization of neat water. This indicates that the bimolecular reaction between indole radical cations and solvated electrons is considerably slower than the diffusion limit. We suggest that geminate recombination arising from solute photoionization in polar solvents may be slower than previously thought.

Introduction

The ionization of molecules in the condensed phase is a topic of fundamental importance in both radiation chemistry and photochemistry. Unlike the situation in the gas phase, ionization in liquids involves complex interactions between the photoexcited molecule and its environment. These interactions control both the ionization threshold and the geminate recombination dynamics in which some fraction of the ejected electrons recombine with their parent ions. The dynamics of geminate recombination between photoionized molecules in solution and their ejected electrons has been discussed most frequently by radiation chemists.[1] Following essentially instantaneous ionization, strong interactions with solvent molecules cause the departing electron to become trapped a distance away from its parent ion known as the thermalization distance. The time required for thermalization is estimated to be very short, much less than 1 ps in the case of polar solvents.[2] The thermalization distance or, more realistically, distribution of distances, has generally been assumed to be of the same order of magnitude as the Onsager radius in the liquid.[3] The relative proximity of the parent ion and its electron results in recombination of a significant fraction of geminate pairs. The ions have generally been assumed to diffuse as classical particles in their mutual Coulombic field, reacting at a diffusion-limited rate.

Although much effort has been made to characterize thermalization distances and the ensuing bimolecular reactions, the underlying dynamics in room-temperature liquids are too rapid to observe directly in the time domain by conventional pulse radiolysis techniques. In more recent years, photoionization experiments performed with increasingly shorter laser pulses have allowed direct observation of geminate dynamics.[4−7,13,20] Besides improved time resolution, the use of low-energy photons avoids the spur formation common in pulse radiolysis, which greatly complicates the kinetics of charge recombination. Scott and Braun were the first to use picosecond transient absorption spectroscopy to study geminate recombination in nonpolar liquids.[4,5] Their results and later ones from experiments by Eisenthal and co-workers on the femtosecond time scale[6,7] were interpreted in terms of the above model: fast (subpicosecond) thermalization, followed by slower geminate recombination at a diffusion-limited rate.

In this paper we present experiments on the geminate recombination dynamics following the photoionization of indole in water at excitation energies near threshold. Indole is of fundamental importance in photobiology as the chromophore of tryptophan.[8] Ionization is known to be a significant part of the photophysics of indole, and measurements of the ionization threshold for this molecule in a variety of polar solvents are available.[9] Recent femtosecond transient absorption measurements have shown that electron solvation in polar liquids is complete in 1−2 ps,[10−13] allowing the unfettered observation of geminate recombination at very short times.

Our aim is to test whether geminate recombination in this aqueous system actually proceeds at a diffusion-limited rate. In water, where the Onsager radius is just 7 Å, it seems likely that a dielectric continuum description of the solvent is an unrealistic starting point for discussing the kinetics of ion recombination, and significant departures from diffusion-limited behavior might be observable. By creating a solvated electron and a radical ion in close proximity to one another on a subpicosecond time scale, and then probing the ensuing recombination dynamics, time-resolved measurements such as the ones reported here can provide invaluable information about bimolecular reaction dynamics between ionic species in liquids.

Experimental Section

Transient absorption measurements were performed using femtosecond laser pulses from our chirped pulse amplified titanium sapphire laser system. In this laser system pulses from a mode-locked oscillator are stretched in a grating stretcher and regeneratively amplified at a 1 kHz repetition rate. Passage

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through a grating pulse compressor yields approximately 120 fs, 0.6 mJ pulses at a center wavelength of 780 nm.

Several microjoules were split off from the amplified pulse and used to generate a white-light continuum probe pulse in a 1 cm path length cell filled with water. Useable probe light was obtained from 400 to 1000 nm. The remainder of the fundamental pulse was used to generate a pump pulse at the laser third harmonic using two Type I BBO crystals. The final energy at the third harmonic wavelength of 260 nm was as high as 30 μJ corresponding to an energy conversion efficiency ($E_{3\omega}/E_{1\omega}$) of 6%. A prism compressor after the second BBO crystal was used to separate the third harmonic light and provide adjustable group velocity dispersion compensation. Due to the large dispersion in the ultraviolet, prechirping of the pump pulse is vital for attaining the highest time resolution at the sample position. Equilateral CaF_2 prisms were used in the compressor instead of the more customary fused silica optics. We have found fused silica to be a very efficient nonlinear absorber at 260 nm at the GW/cm^2 intensity levels that are common in femtosecond laser systems. This multiphoton absorption is accompanied by readily visible red luminescence due to color center formation.

The third harmonic pump pulse was variably delayed by a computer-controlled translation stage before passing through a half waveplate followed by a Glan Taylor calcite polarizer. The polarizer is set to magic angle with respect to the polarization of the probe light. By rotating the waveplate the pump energy dependence of the signals could be measured without introducing any displacement or pulse broadening of the pump beam. The latter feature is particularly important when multiphoton absorption is present.

Pump and probe beams were crossed in a free-flowing jet of the liquid sample under investigation. The use of jets was critical for avoiding artifacts. The fused silica commonly used in UV-grade optical flow cells is a significant nonlinear absorber at the high intensities produced by femtosecond laser pulses as mentioned earlier. This nonlinear absorption can significantly broaden and attenuate the pump pulse in the window before the sample, degrading the time resolution and prohibiting the accurate measurement of the dependence of the signal on the pump pulse energy. The jet also solves problems caused by the deposition of photoproducts on the inner walls of a flow cell where the flow velocity vanishes. At a 1 kHz pulse repetition rate, reexcitation of long-lived transient species and photochemical products is likely and femtosecond UV photoexcitation of indole in fused silica flow cells produced signals with dynamics vastly different from those of the jet signals reported here.

Careful attention to nozzle design is important for producing laminar jets, particularly when working with low-viscosity solvents such as water. Fortunately, interferometric flatness (the requirement for the jets used in dye lasers) is not essential for transient absorption spectroscopy. We obtained satisfactory jets from a home-built stainless steel and Teflon nozzle patterned after a design in the literature.[14] The thickness of the jet was determined photometrically to be 500 ± 50 μm. Two opposing requirements determine the optimal jet thickness. A thin jet is required to achieve the best time resolution by limiting group velocity walkoff between spectrally widely separated pump and probe pulses. On the other hand, extremely thin jets require higher solute concentrations to attain a given optical density for the pump light, which can lead to complexation problems for some solute/solvent systems. The pump beam was weakly focused to a spot size (1/e^2 beam radius) of 400 μm. The spot size of the probe pulse at the sample was approximately 100 μm.

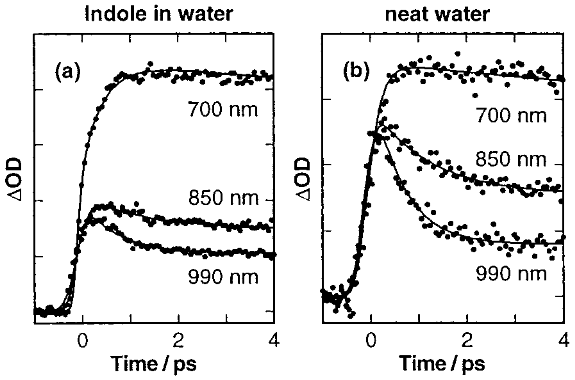

Figure 1. Short-time dynamics of the absorbance change (ΔOD) induced by a 260 nm femtosecond pump pulse in (a) 6.0 mM indole in water and (b) neat water. The probe wavelengths are indicated, and the curves have been vertically offset for clarity. Pump and probe polarizations are linear and offset with respect to each other by 54.7°.

Signals were acquired in one of two modes. In the first mode the continuum probe pulse was detected after the sample by an amplified Si photodiode. A 10 or 40 nm bandwidth (fwhm) interference filter positioned in front of the photodiode was used to spectrally select a desired portion of the continuum. The output of the photodiode was measured by a digital lock-in amplifier referenced to an optical chopper placed in the pump beam. In this manner the transient absorbance (ΔOD) of the sample could be recorded as a function of delay time between the pump and probe pulses. The instrument response is approximately 200 fs.

In the second mode, no interference filter was used and the entire continuum pulse was sent to a $f = {}^1/_4$ m imaging spectrometer and detected by a thermoelectrically cooled CCD camera. Simultaneously, a small fraction of the continuum pulse was split off before the sample and directed into the spectrometer and detected on a separate vertical region of the CCD chip. Ratioing of the two spectra permitted optical density changes as small as 10^{-3} to be readily detected. This mode allowed recording of transient spectra at fixed pump−probe delay times.

The highest purity indole available from Aldrich was used as received. Both UV/vis and fluorescence spectra confirmed the purity of the starting material. A Barnstead Nanopure system provided ultrapurified water for all solutions. Other solvents were obtained from Burdick & Jackson. Solutions were not deaerated since solvated electron scavenging by oxygen is slow enough to have no effect on dynamics on the sub-100 ps time scale considered here. Solutions were replaced frequently and no differences were observed between previously irradiated and fresh solutions. Diagnostic UV/vis spectra recorded on irradiated solutions confirmed the absence of photodegradation. All experiments were performed on room-temperature solutions.

Results

Past studies have demonstrated that aqueous solutions of indole can be photoionized on exposure to UV light.[9,15−18] Using quasi-monochromatic lamp excitation and N_2O scavenging detection of solvated electrons, Bernas and co-workers measured an ionization threshold of 4.35 eV for indole in water.[9] Photoexcitation at our pump wavelength of 260 nm (4.8 eV) is therefore expected to generate solvated electrons. Figure 1 compares the short time dynamics of the signals from a 6.0×10^{-3} M

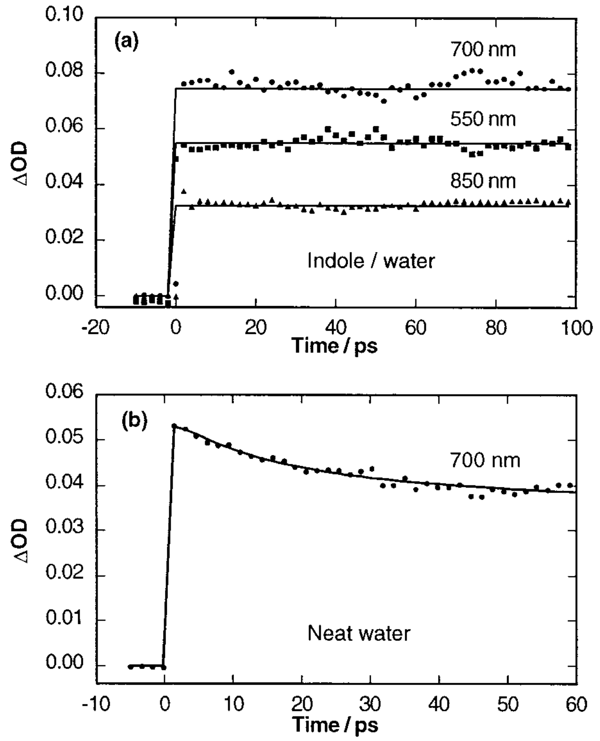

Figure 2. Longer time transient absorbance dynamics following photoionization of 6.0 mM indole in water (a) and neat water (b). In (a) no decay is evident in the first 100 ps and the solid lines are fits to a constant absorbance. In water geminate recombination causes a noticeable decay of the signal, and the solid line in (b) is a fit to the one-dimensional random walk model described in the text.

solution of indole in water (Figure 1a) with the signals recorded by photoionizing neat water (Figure 1b). Photoionization of water requires the simultaneous absorption of at least two photons for single-photon energies near 4.8 eV.[19−21] For our pump intensity of about 10 GW/cm^2 the absorbance at 700 nm from the aqueous indole solution is about a factor of 2 greater than the absorbance at the same wavelength from neat water. This indicates that the signal from the indole solution does not arise from the solvent. Further proof comes from the nonlinear dependence of the signal on pump intensity in the case of neat water. The signals from indole solution, on the other hand, vary linearly with pump intensity.

For both aqueous indole and neat water the transient absorbance at 700 nm is nearly flat at delay times greater than 500 fs. At longer wavelengths an overshoot and subpicosecond decay is observed in both cases. For neat water these signals are consistent with previous experimental[10,13,22,23] and theoretical[24] studies of the transient spectra of hydrated electrons on the femtosecond time scale. These changes reflect solvation and nonadiabatic electronic relaxation of presolvated electrons, which are known to have a red-shifted absorption spectrum relative to completely relaxed, solvated electrons. This transformation occurs in approximately 500 fs and has been interpreted as the nonadiabatic decay of an excited state of the solvated electron.[11,22,23] The similarity of the signals from indole in water to those in neat water strongly suggest that hydrated electrons are produced in both cases.

Figure 2 shows the transient absorbance for indole in water (Figure 2a) on a longer time scale. The signals recorded at several probe wavelengths show no decay from 2 to 100 ps within our experimental precision. The signal recorded in neat water is shown for comparison in Figure 2b. These results are analyzed in more detail in the discussion section below.

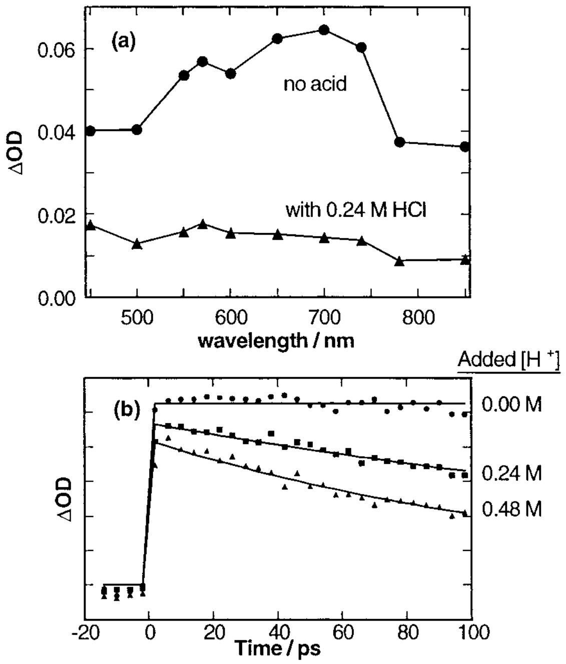

Figure 3. (a) Transient spectrum observed in 6.0 mM indole in water 500 ps after excitation by a 260 nm pump pulse before (circles) and after (triangles) the addition of hydrochloric acid. (b) Transient absorbance decays recorded at 700 nm for the same solution with varying amounts of added acid. The solid lines are fits to a single exponential. The 1/e decay times are no added H$^+$ (no decay observed), 0.24 M H$^+$ (280 ps), and 0.48 M H$^+$ (140 ps).

While the dynamics in Figure 1 are qualitatively similar, it is clear that the relative absorbance is different at different probe wavelengths. This indicates that one or more additional absorbing species are present in the indole solution besides solvated electrons. The quantum yield for photoionization of indole for excitation near 260 nm is considerably different from unity, although the exact value is controversial. Reported values range from 0.009[25] to 0.27.[18] Excitation at 260 nm thus prepares a time-dependent mixture of species that includes radical cations, neutral excited states, and solvated electrons. This possibility of spectral interference from other species is the principal difficulty of using transient absorption spectroscopy to measure the dynamics of excess electrons in liquids as pointed out by others.[4] We demonstrate next that careful characterization of the time-resolved absorption of all species on the ultrafast time scale provides a way around this apparent limitation. This extra effort is warranted in view of the unparalleled time resolution afforded by ultrafast pump−probe measurements.

The upper curve in Figure 3a shows the transient spectrum of indole recorded at 500 ps delay time from 10 separate measurements of the absorbance using interference filters. The broad maximum near 700 nm is consistent with the presence of solvated electrons, but a second peak near 580 nm indicates a second species that is shown below to be the indole radical cation. Addition of hydrochloric acid causes a strong decay of the absorbance at all wavelengths (Figure 3a, lower curve) with the greatest decay occurring on the red side of the spectrum. H$^+$ is a powerful scavenger of solvated electrons, reacting at a rate of 2.3×10^{10} M^{-1} s^{-1}.[26] Figure 3b compares the temporal evolution of the signal at 700 nm with and without added H$^+$. Without added acid the absorbance at 700 nm is essentially flat on the 100 ps time scale (Figure 3b, upper curve). Addition of acid leads to a decay in the signal due to scavenging of solvated electrons by H$^+$. Fitting single exponentials to the two lower curves of Figure 3b gives a scavenging rate of 1.5×10^{10}

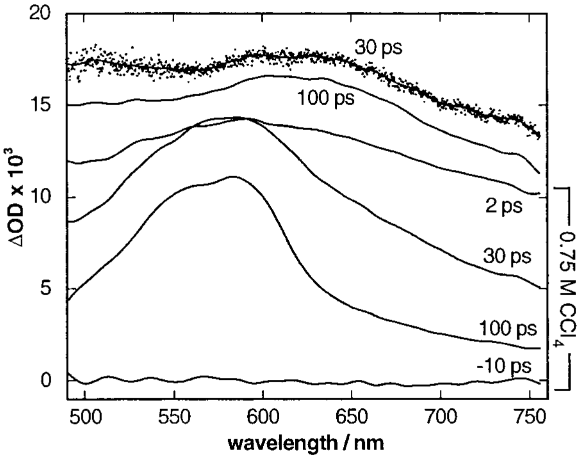

Figure 4. (Top two curves) transient spectra recorded with an imaging spectrometer and CCD detector following 260 nm photoexcitation of 6.0 mM indole in 1-propanol. (Bottom four spectra) transient spectra recorded on the same solution after addition of carbon tetrachloride (0.75 M). The spectrum recorded at −10 ps shows the instrument baseline. All spectra were minimally smoothed using a low-pass filter. The raw experimental data are shown as dots in the top spectrum.

M^{-1} s^{-1}. This value is lower than 2.3×10^{10} M^{-1} s^{-1} measured at low acid concentrations but is in good agreement with values measured at finite ionic strength.[27]

A further contribution to the ultrafast absorbance of indole is expected from neutral excited-state absorption ($S_1 \rightarrow S_N$). We are aware of only a single report in the literature of the $S_1 \rightarrow S_N$ spectrum of indole by Mataga and co-workers.[28] These investigators photoexcited indole in cyclohexane with picosecond pulses at 266 nm and attributed the resulting broad band to $S_1 \rightarrow S_N$ absorption, but the signal/noise ratio was rather low in this experiment. As the $S_1 \rightarrow S_N$ band in a nonpolar solvent such as cyclohexane might differ considerably from the band shape in a polar solvent like water, we chose to characterize this absorption by a pump−probe experiment in 1-propanol. Although the ionization threshold for indole has never been measured in this solvent, Bernas et al. predicted a value of 5.15 eV based on an extrapolation of their results for shorter alcohols.[9] These authors measured an ionization threshold of 4.85 eV for indole in ethanol, but this value is rather close to our photon energy. Thus, we selected 1-propanol where we are confident that photoionization by single photon absorption is not possible.

The transient spectrum of a 6.0×10^{-3} M solution of indole in 1-propanol at 30 ps delay is shown by the uppermost curve in Figure 4. The high S/N ratio permits a definitive characterization of this intermediate for the first time. The absorbance is rather flat across the visible spectrum with a weak peak at 600−650 nm. The absorbance falls gradually toward longer wavelengths. This spectrum differs considerably from the one measured in water solution (see Figure 3a) and is assigned to the $S_1 \rightarrow S_N$ spectrum of indole. The transient absorbance at 700 nm is constant out to 100 ps (upper curve of Figure 5). Measurement of transient spectra at different delay times up to 100 ps confirmed the absence of spectral changes, consistent with the 4.1 ns fluorescence lifetime of indole in water.[29] The addition of carbon tetrachloride to the indole in 1-propanol solution results in dramatic changes to the transient spectra (Figure 4) and to single wavelength scans of the transient absorbance as a function of delay (Figure 5). The concentration of CCl_4 in the indole solution in these two figures is 0.75 M. These changes are due to an ultrafast excited-state electron-transfer reaction from the S_1 state of indole to the good electron acceptor carbon tetrachloride. This is discussed in more detail in the next section.

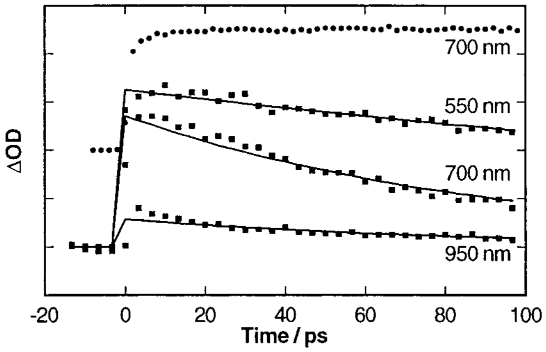

Figure 5. (Top, circles) transient absorbance at 700 nm following 260 nm photoexcitation of 6.0 mM indole in 1-propanol. The three transients at the bottom of the figure (squares) show decays at three different probe wavelengths after the addition of carbon tetrachloride (0.75 M).

Discussion

The goal of this investigation is a description of the ultrafast dynamics of charge pair formation and separation following the photoionization of indole in aqueous solution. The pump−probe signals are shown in Figures 1 and 2 for the short-time and long-time dynamics, respectively. To interpret these signals, efforts were taken to identify the spectral and temporal signatures of the different species produced by solute photoionization: solvated electrons, radical cations, and neutral excited states. Although the pK_a of the indole radical cation is 4.9 ± 0.1,[30] deprotonation to form neutral indolyl radicals occurs in microseconds,[17] and the neutral radicals can be safely neglected in our analysis. The excited-state absorption by neutral indole molecules was determined from the indole in 1-propanol data. The same solution in the presence of added carbon tetrachloride allows determination of the indole radical cation spectrum in the absence of interfering absorption from solvated electrons, as discussed next.

Photolysis of aromatic amines in the presence of halomethanes has been observed to produce the absorption spectra of the amine radical cations.[31] On the basis of microwave dielectric measurements it has been proposed that contact ion pairs are formed by an electron-transfer reaction.[32] Our data on indole in 1-propanol are consistent with such an excited-state electron-transfer reaction. Single-exponential fits to the transients in Figure 5 at 700 and 950 nm yield a time constant of 85 ± 10 ps. The time constant for reaction is likely controlled by diffusive encounters between S_1 indole molecules and CCl_4. The ensuing charge-transfer reaction leads to a loss of $S_1 \rightarrow S_N$ absorption, causing the red side of the transient spectra in Figure 4 to decay rapidly. Charge transfer forms indole radical cations, giving rise to a broad band with a maximum absorbance near 580 nm at 100 ps delay time (Figure 4). The observed spectrum at 100 ps delay time for the indole/1-propanol/CCl_4 solution is in excellent agreement with previous spectra of the indole radical cation obtained in aqueous solution by laser flash photolysis[16,17] and pulse radiolysis[30,33] experiments. A similar spectrum was observed at low temperature in polar matrix by Shida.[34] This demonstrates that addition of CCl_4 initiates an ultrafast electron-transfer reaction that quenches the indole S_1 state to form indole radical cations. The radical anion of carbon tetrachloride, CCl_4^-, formed in the electron transfer step is believed to dissociate promptly to form CCl_3 radical and chloride ion, neither of which absorb in the visible.

The relative contribution to the absorbance signals can now be estimated. The maximum extinction coefficient of the solvated electron in water is 19 000 M^{-1} cm^{-1} at 720 nm.[35] The extinction coefficient of the radical cation of indole was estimated by Jovanovic and Steenken to be 3000 M^{-1} cm^{-1} at 580 nm.[33] By comparing the indole/propanol spectrum at 30 ps, assumed to arise only from $S_1 \rightarrow S_N$ absorption, to the indole/propanol/CCl_4 spectrum at 100 ps, assumed due solely to indole radical cations, we estimate the extinction coefficient of $S_1 \rightarrow S_N$ at 700 nm to be 4000 M^{-1} cm^{-1}. This is a crude estimate that neglects the possibility of back electron transfer following radical ion pair formation and assumes that every S_1 excited state is quenched to a radical cation. The value is not likely to be grossly incorrect, however, in view of the fact that the transient spectrum recorded in water (Figure 3a) shows an obvious shoulder near 580 nm, which can only be due to indole radical ions. Given the low quantum yield of ionization at our pump wavelength, this shoulder would be much less pronounced in the presence of significant excited-state absorption by neutral indole.

Using the above values for the extinction coefficients and assuming a quantum yield for photoionization of 0.2, we estimate that at least 50% of the signal at 700 nm originates from solvated electrons with the remainder due to $S_1 \rightarrow S_N$ absorption. This has important consequences for the interpretation of the pump−probe data observed for indole in water. The flat signals in Figure 2a at multiple probe wavelengths indicate that *no significant geminate recombination occurs from 2 to 100 ps following the photoionization of indole in aqueous solution*. While a number of studies of the geminate recombination dynamics following solute photoionization in nonpolar solvents have been reported,[4,5,44−46] there have been almost no time-resolved studies in polar ones, making a comparison with earlier work difficult. One exception is a laser photolysis study using 27 ps pulses at 265 nm by Mialocq and co-workers who studied aqueous solutions of indole and tryptophan.[47] They concluded that no geminate recombination occurs following photoionization of indole from 50 ps to 2 ns after photoexcitation. Our results have now extended this conclusion down to the subpicosecond time scale.

The absence of geminate recombination in indole/water is in marked contrast to the dynamics in neat water. Several ultrafast studies have observed a substantial and wavelength-independent decay of the transient absorbance from solvated electrons produced by multiphoton ionization of water on the 100 ps time scale.[7,20,21,36−38] Our own measurement of the geminate recombination dynamics following the photoionization of neat water is shown in Figure 2b and is in excellent agreement with recent results obtained at the same pump wavelength by Vöhringer and co-workers.[21] The solid curve is a fit to the simple "random walk" model, which predicts the transient absorbance at time t, $\Delta OD(t)$, in terms of the initial value at $t = 0$, a characteristic time τ, and the fraction of geminate pairs, α, that ultimately recombine.[37] The best-fit parameters for our data are $\alpha = 0.45$ and $\tau = 7.7$ ps. This model is an overly simplistic description of geminate recombination,[20] but it does provide a simple and precise parametrization of the ultrafast data with just three fitting parameters.

Onsager was the first to treat geminate recombination in liquids.[39] In this model the radical ion and the solvated electron are treated as point charges separated at time equal zero by a fixed distance. The distance describes how far the electron traveled away from its parent ion before attaining thermal energy and becoming trapped. The point charges are assumed to move as Brownian particles subject to stochastic forces. In addition, the particles experience a nonrandom force due to their mutual Coulombic attraction. When the charges approach one another within a critical distance, reaction is assumed to occur irreversibly. The long-time probability of geminate recombination decays exponentially with distance with a characteristic length scale given by the Onsager radius. In neat water, the Onsager radius is just 7 Å and it is not clear that the assumption of classical diffusion in a dielectric continuum is justified.

For modeling the time-resolved experiments, a calculation of the time-dependent survival probability is needed. This problem has been treated both by Monte Carlo simulation[40,41] and by analytical theory.[42,43] The solutions show characteristic nonexponential decays and have been used to model geminate recombination kinetics from time-resolved experiments.[4,7,44−46] Assuming that recombination is limited only by the rate of transport of the separated ions, then the time scale of recombination is influenced most strongly by thermalization distance. A thermalization distance that is either very large or very small can give rise to negligible recombination on the time scale of 2−100 ps. In the former case, recombination occurs at a negligible rate during this time interval, while in the latter case, recombination is complete quasi-instantaneously. Both possibilities are considered next.

The dynamical consequences of a large thermalization distance between the electron and its parent ion are slower recombination and higher escape probability. Thus, measurements of the average recombination time have been used to estimate the most probable distance distribution function.[4,5,46] We believe that this explanation is unlikely for the following reason. It is generally assumed that the ejected electron carries away the energy in excess of the ionization threshold. Therefore, excitation at energies further above the ionization threshold is expected to produce larger radius geminate ion pairs. Given the ionization threshold measured by Bernas et al. of 4.35 eV,[9] photoionization at our photon energy corresponds to an excess energy of only 0.4 eV. It seems very unlikely that this amount of excess energy could produce geminate ion pairs much larger than those produced by two photon absorption of water with 4.8 eV photons. In the latter case, a final energy of 9.6 eV is reached, which is 0.7 eV above the estimated threshold required to excite electrons into the conduction band of water.[48] Since the geminate recombination is clearly observed in the case of neat water, we conclude that it is improbable that a smaller excess electron energy could produce an even greater initial separation between the geminate partners.

It seems equally improbable that the initial thermalization length is so small that recombination is complete in less than 2 ps. If this were the case, it would be difficult to explain how so many geminate pairs could ever escape to yield a substantial ionization quantum yield. We propose instead that the absence of geminate recombination in our data indicates that the reaction between solvated electrons and indole radical ions is considerably slower than diffusion-limited. This is perhaps surprising given the usual assumption that radical−radical recombination reactions proceed at the diffusion limit in liquids. It has, however, been observed that many bimolecular reactions involving solvated electrons are not diffusion-limited.[49] Given the high reactivity of organic radical ions, it is not surprising that measurements have not been previously performed.

A third possibility is that the thermalization distance following indole photoionization is similar to that in neat water, but the recombination reaction is considerably slower than the diffusion limit. It is interesting at this point to compare our results with those for geminate recombination in neat water, the system that has been examined and analyzed in greatest detail. In water, an ultrafast proton transfer reaction between the initially produced water cation with an adjacent water molecule,

$$H_2O^{\bullet+} + H_2O \rightarrow OH^{\bullet} + H_3O^{+}$$

is believed to be complete in <100 fs, leading to a three-body recombination problem. Goulet and Jay-Gerin have shown that the geminate recombination between solvated electrons and H_3O^+ is actually much less important than recombination with $OH^\bullet$, despite the Coulombic attraction with the former species. This is due to the fact that the reaction between solvated electrons and H_3O^+ is not diffusion limited.[50]

To our knowledge bimolecular reaction rates between solvated electrons and radical cations of organic molecules have never been measured. Our data suggest that indole radical cations and solvated electrons do not react on every encounter. Reaction rates below the diffusion limit can, in general, arise from the presence of an activation barrier or by special conformational or steric requirements of the reactants.[51] One possible barrier may arise if substantial reorganization of the solvent shells around the ions is required before reaction between a solvated electron and its bulky parent ion can take place. It is interesting to note that a free energy barrier to adiabatic electron recombination has recently been calculated for electrons detached from aqueous chloride ions.[52] Further investigations to determine the rate of recombination for this system and for other molecules in polar solution are currently underway.

An intriguing possibility is that the mechanism of charge separation itself can be understood through the recombination dynamics. Fascinating discussions in the literature in recent years have suggested that photoionization mechanisms exist in the condensed phase that have no counterpart in isolated molecules.[20,53-56] An important issue is whether photoejected electrons first travel through the conduction band of the liquid or whether they are directly promoted to preexisting trap sites by a mechanism resembling electron transfer or exciton decay. Such “liquid-only” mechanisms could reasonably be expected to dominate near the ionization threshold. Further studies of solute photoionization in polar solvents will help settle this issue.

Conclusions

We have applied femtosecond pump−probe techniques to study the photoionization of indole in aqueous solution at room temperature. Formation of solvated electrons is complete in less than 1 ps. The $S_1 \rightarrow S_N$ spectrum of indole in polar solvent has been tentatively characterized and an estimate made of the contribution of all species to the transient absorption measured. The use of a powerful electron acceptor for producing radical cations on an ultrafast time scale without interfering absorption from solvated electrons has been demonstrated. This technique provides a new tool for studying the ultrafast dynamics of radical cations in solution. The absence of geminate recombination for near-threshold photoionization strongly suggests that the rate of reaction between indole radical cations and solvated electrons is considerably below the diffusion limit, indicating that the geminate ion pairs are more stable than previously thought. Further time-resolved studies of solute photoionization in polar solvents will provide further insight into the molecular details of charge separation and recombination in liquids.

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