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The mechanism of electron–cation geminate recombination in liquid isooctane

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Abstract

Electron–cation geminate recombination in isooctane has been reinvestigated by femtosecond spectroscopy. The observed recombination kinetics are well-fit by a single exponential decay ($\tau = 400 \pm 40$ fs) and exhibit a significant hydrogen/deuterium kinetic isotope effect. The kinetics are not affected by varying the incident intensity or by exciting the recombining electrons with a high power 800 nm pulse. These observations strongly suggest that the recombination rate is not limited by diffusive motion of the ions to form a contact ion pair, but rather by the electron transfer reaction rate between the ions in a contact ion pair.

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1. Introduction

Ultrafast experiments on the multiphoton ionization of neat alkanes have led to important insights on the structure and dynamics of excess charges in non-polar liquids [1–4]. There are two main charged species in the photoionization of liquids – the solvated electron (e_s^-) and the solvent hole or cation (M^+). In alkanes these ions have a Coulomb attraction energy of greater than k_BT for distances up to ~300 Å, i.e., the Onsager radius [5]. The ions undergo geminate recombination by a multistep mechanism (Eq. (1)) that involves the initial formation of a 'separated' electron–cation pair. This is followed by diffusive motion to form predominantly a 'contact' ion pair and a much smaller yield of 'free' ions

$$\begin{tikzcd} & & M^* & \\ M^+ + e_s^- \arrow[r, shift left, "k_d"] & {[M^+ + e_s^-]} \arrow[l, shift left, "k_{-d}"] \arrow[r, shift left, "k_c"] & {[M^+ \cdot e^-]} \arrow[l, shift left, "k_{-c}"] \arrow[u, "k'_{ea}"'] \arrow[r, "k_{ea}"] & M \\ \textit{free ions} & \textit{separated pair} & \textit{contact pair} & \end{tikzcd} \tag{1}$$

where k_c and k_{-c} are the rate coefficients for interconverting the separated and contact ion pairs, by translational diffusion. k_{ea} and k'_{ea} are the rate coefficients for the 'microscopic' electron attachment process to form the neutral ground state and excited state solvent molecules, M and M*, respectively. (k_d and k_{-d} are the rate coefficients for interconverting contact ion pairs and freely diffusing ions. The yield of free ions in the photoionization of alkanes, however, is relatively small due to the large Onsager radius.)

Many previous studies on the geminate recombination of liquid alkanes have modeled the kinetics as a diffusion-controlled process [4,6–8] in which the geminate recombination process is limited by the time for the ions to 'diffuse together' after the ions are initially separated by the photoionization event. This situation applies to the photoionization of water for which the hydrated

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electron and the solvent hole diffuse together over an initial separation of tens of Angstrom distances on the hundreds of picosecond timescale [9]. (For water the solvent hole actually fragments to form the hydronium and hydroxy radical with the latter species being predominantly responsible for geminate recombination.)

Cyclic and branched alkanes, such as isooctane, however, have extraordinarily large electron mobilities [5,8,10], and correspondingly, are expected to have very large solvated electron diffusion constants. Due to the large diffusion constants, the interconversion of separated and contact ion pairs is expected to occur on the subpicosecond timescale for 100 Å and less initial separations. Since electron transfer times for highly exothermic reactions are rarely shorter than hundreds of femtoseconds, the microscopic electron transfer processes might be expected to become rate-limiting for branched alkanes. In this Letter, we reexamine whether the geminate recombination mechanism of isooctane is actually diffusion controlled. The new experiments employ a faster time resolution method and a broader set of probe wavelengths than have previously been used [1,4,11,12] to study the photoionization of liquid isooctane.

2. Experimental

Isooctane (2,2,4-trimethylpentane, HPLC grade, Aldrich), deuterated isooctane (98% deuterated, Isotec), and trichloroethylene (99.9%, Fisher Scientific) were used as received. All experiments were done at 23 °C. The sample was flowed though a gravity guided nozzle [13–15] that produced a thin film liquid sample with a thickness of ~70 μm.

The femtosecond spectrometer used in these experiments has been described in detail elsewhere [16]. All pulses were derived from a multipass amplified Ti:sapphire system with 35–40 fs pulses centered at 800 nm at a 1 kHz repetition rate. For the photoionization/probe experiments 60 fs, 20 μJ ionization pulses (centered at 400 nm) were focused in the sample to a spot size of 80 μm producing a peak power of ~9 TW/cm^2. The 35 fs probe pulses (spot size = 40 μm, bandwidth = 30 nm FWHM, pulse energy <0.005 μJ) were derived from ultrafast continuum pulses that were wavelength selected and compressed in a prism pair configuration. For the photoionization/pump/probe experiments the pump beam (35–40 fs, 5 μJ) was focused to a spot size of 200 μm (peak power ~0.4 TW/cm^2). Reported pulse durations were determined by autocorrelation or cross-correlation of the appropriate pulses in thin NLO crystals. Based on the pulse duration measurements and calculations of time broadening due to group velocity dispersions and geometric factors in the sample, we estimate the IRF FWHM for the photoionization/probe experiment to be ~70 fs and for the photoionization/pump/probe experiments to be 60 fs.

3. Results and discussion

3.1. Transient absorption of solvated electrons and holes

Isooctane (IP ~ 8.4 eV [17]) was photoionized by the 400 nm ($h\nu$ = 3.1 eV) pulses via a 3-photon process and the induced optical density change was measured as a function of time delay at a specific probe wavelength. The observed pump/probe transient optical density at 950 nm (ΔOD_{950}) is well fit by a kinetic model with a single absorbing species that is formed within the experimental uncertainty of <30 fs (Fig. 1). Subsequent to the rapid appearance of the 950 nm absorption, ΔOD_{950} undergoes a single exponential decay with a time constant of 400 ± 40 fs (Fig. 1). Electron scavenging data demonstrate that ΔOD_{950} primarily probes the ground state to excited state absorption band of the solvated electron rather than absorption bands due to the cation and neutral excited states. In the presence of an electron scavenger (0.3 M C_2HCl_3, $k_{\mathrm{scavenging}} = 3.5 \times 10^{13}\ M^{-11}\ s^{-1}$ [18]), ΔOD_{950} has a much shorter lifetime due to scavenging, as shown in Fig. 2a. (A small absorption offset is observed at long times, however, due to absorption from the long-lived neutral excited state of the solvent and the surviving cation from the scavenging process.)

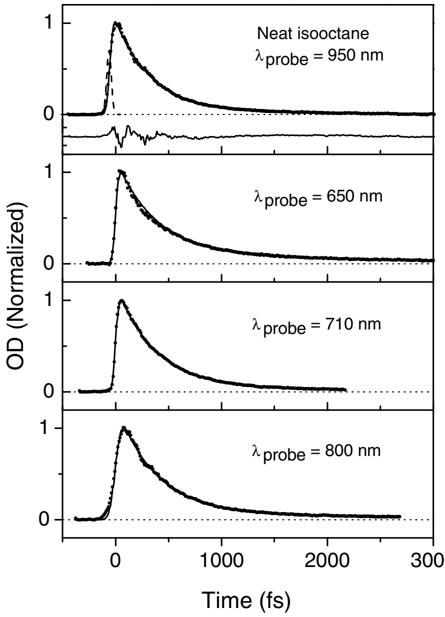

Fig. 1. Transient absorption data of the electron–hole pairs generated by 400 nm multiphoton ionization of isooctane probed at 950, 650, 710 and 800 nm (the filled points). The dashed line is the instrumental response function with a full-width half-maximum of 70 fs.

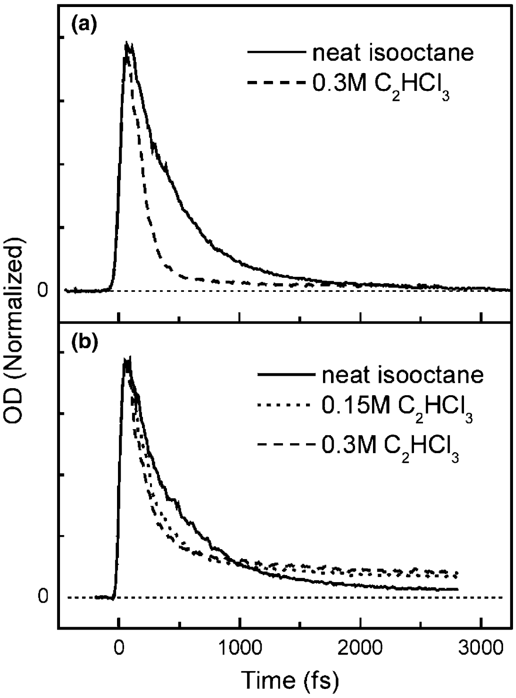

Fig. 2. The effect of electron scavenger (C_2HCl_3) on the pump/probe signal probed at 950 nm (a) and at 650 nm (b). The signal probed at 650 nm clearly shows increase of the long-lived component with increase of the scavenger concentration.

The situation is more complicated at 650 nm where the pump/probe data (Fig. 1b) exhibits a 390 ± 20 fs decay due to geminate recombination as well as a long-lived kinetic component with an amplitude of 6% assigned to an excited state of the solvent [19,20]. With an electron scavenger present (0.15 M C_2HCl_3) the transient absorption probed at 650 nm (Fig. 2b) exhibits a shorter decay time constant ($\tau = 210 \pm 20$ fs) than that of neat isooctane and an additional long-lived component due to absorption from surviving cations resulting from electron scavenging. The pump/probe data at 710 nm ($\tau = 380 \pm 20$ fs) and 800 nm ($\tau = 370 \pm 30$ fs) (Fig. 1) are intermediate in behavior between the 950 and the 650 nm ΔOD data. Increasing the concentration of C_2HCl_3 to 0.3 M causes a further decrease in the decay time ($\tau = 150 \pm 10$ fs) and a further increase in the amplitude (14.5 ± 0.5%) of the long-lived component. These results indicate that the fast decaying component at 650 nm should be assigned to absorption of solvated electrons, which can be scavenged by C_2HCl_3, and the long-lived component at high quencher concentration should be assigned to absorption of cations that survive the recombination process. At 0.3 M C_2HCl_3 the scavenging yield is estimated to be >60%. Based on the measured electron scavenging yield and the increased absorbance of the long-lived component of cations, the absorption coefficient of the electron is calculated to be ~6 times greater than that of the cation at 650 nm.

3.2. The mechanism of the geminate recombination process

The pump/probe ultrafast data indicate that an electron–hole pair is produced within 30 fs of the initial multiphoton ionization event and then undergoes geminate recombination with a ~400 fs single exponential decay. It is interesting to compare the observed kinetics to predictions from a diffusion-controlled model for the recombination kinetics, in which $k_c \ll (k_{ea} + k'_{ea})$. The Hong–Noolandi method [21] was used to calculate the electron survival probability as a function of time based on a diffusion coefficient calculated by the Einstein relation from the published thermalized electron mobility [8] and trial distribution functions for the initial electron–cation separation. Both Gaussian [3] and exponential [4] functions for the initial distribution were considered. For a broad range of trial distribution parameters the predicted survival curves were highly non-exponential and could not reproduce the data. A few typical examples with Gaussian functions are shown in Fig. 3. The large discrepancy between experiment and the simulated decay for a diffusion-controlled reaction strongly suggests that the geminate recombination of the ion pair in isooctane is not limited by diffusion, as previously assumed. The observed single exponential decay, therefore, is consistent with a non-diffusion-controlled simple first order electron attachment reaction within a contact ion pair, i.e., $k_{ea} = (400\ \text{fs})^{-1}$.

Another observation that argues against a diffusion-controlled mechanism for the geminate recombination is the absence of a photoionization pulse energy dependence of the geminate recombination kinetics in

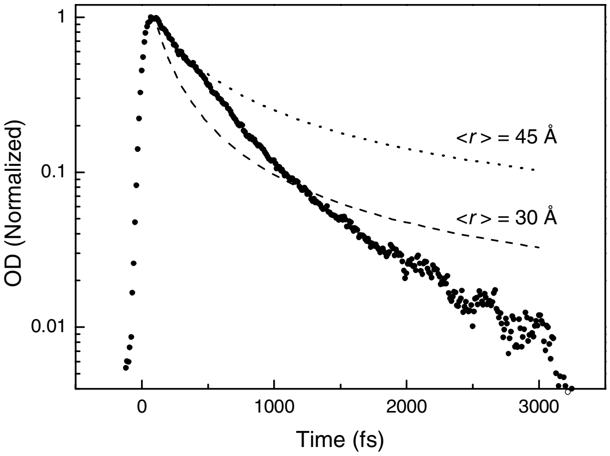

Fig. 3. The simulated results based on the diffusion-limited model are compared with the experimental data. For the simulation, the encounter complex radius is 13 Å, and the diffusion coefficient of the electron is 1.5×10^{-1} $cm^2\,s^{-1}$ calculated using Einstein relation with published electron mobility [5]. The initial distributions of the distance between the electron and hole are Gaussian functions with average distances of 30 and 45 Å.

isooctane. For comparison multipulse experiments on the hydrated electron geminate recombination, *which is diffusion controlled*, exhibit a significant slowing of the geminate recombination dynamics as the photoionization pulse energy is increased. This results from an increase of the electron–hole pair separation due to higher order photoionization channels and excitation of the rapidly formed solvated electron by the photoionization pulse. The latter effect for the hydrated electron has shown to be facilitated by accessing the conduction band. (In fact, for isooctane the latter effect might be expected to be particularly severe due to the rapid electron formation kinetics during the photoionization pulse duration.) The absence of a power dependence argues that geminate recombination for isooctane is not diffusion controlled.

In order to further test the limitation of the diffusion-controlled mechanism we have investigated the effect of deuteration on the geminate recombination kinetics (see Fig. 4). Isooctane-d_{18} exhibits a factor of 1.4 slower recombination rate than isooctane-h_{18}. In order for this to be consistent with a purely diffusion-controlled mechanism, the electron mobilities would also be expected to have an isotope effect of 1.4. However, this is unlikely since electron mobilities are typically a linear function of either the number density ratio [22] and/or the viscosity ratio [23] of a solvent, and both are close to unity for isooctane (i.e., the number density ratio is 1.00 [24] and the viscosity ratio 1.07 [24] for isooctane). In addition, previous studies have shown that electrons in liquid hydrocarbons are mainly scattered by C–C bond rather than C–H bond [25]. A more reasonable explanation is that the observed kinetic isotope effect is due to the rate constants (k_{ea} and k'_{ea}) for charge recombination in the contact ion pair for isooctane-h_{18} and isooctane-d_{18}. Hydrogen/deuterium kinetic isotope effects of this magnitude on electron transfer rates have indeed previously been observed due to accepting mode effects [26].

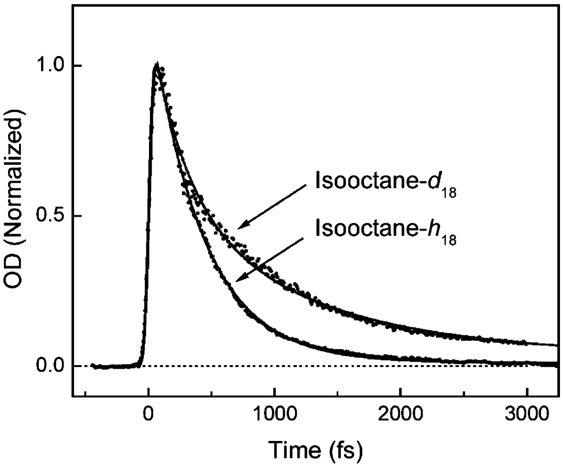

Fig. 4. The deuteration effect on the geminate recombination of electron cation pairs in isooctane probed at 950 nm. The decay time constant of isooctane-d_{18} is 1.4 times longer than that of isooctane-h_{18}.

3.3. 3-Pulse experiments on isooctane

We recently showed for the photoionization of water that a 3-pulse (photoionization, electron-pump and probe) sequence can be used to investigation the excited state physics and chemistry of the hydrated electron [16,27,28]. The experiments on water involve an electron-pump pulse that excites the hydrated electron to its quasi bound p-state or alternatively to its higher energy conduction band (depending on the wavelength of the electron-pump pulse). The electron-pump pulse for water induces a large bleach-recovery signals in the electron absorption (due to ground-state depletion/recovery) and efficient suppression of geminate recombination due to photodetrapping and photomigration of the hydrated electron to a distance far from its hole partner [16].

Fig. 5 shows data from an analogous 3-pulse sequence for isooctane. In contrast to the data in water, intense photo-excitation of isooctane solvated electrons produces an extremely small optical density change in the solvated electron absorbance with no evidence of

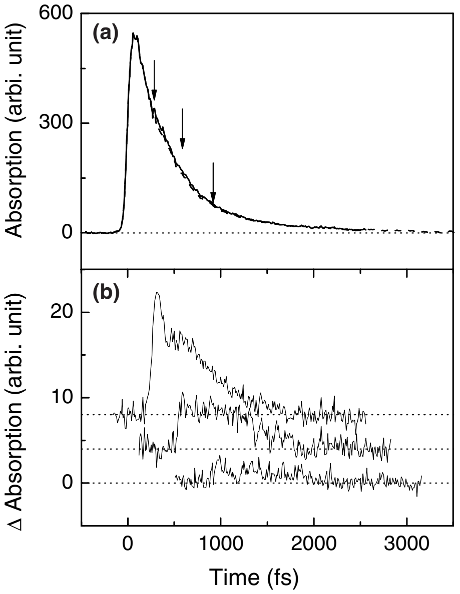

Fig. 5. (a) Comparison of the pump/probe data of the electron–hole pairs with (the solid line) and without (the dotted line) an electron-pump pulse at 800 nm (15 mJ/cm^2). The ionization pulse is 400 nm and the probe pulse is 950 nm. (b) The effect of the electron-pump pulse is shown in ΔOD varying the time delay between the ionization pulse and the electron-pump pulse. In sequence, the time delays are 270, 570 and 940 fs. The heights of the plateau are proportional to the OD signal (indicated as vertical arrows in (a)) when the electron-pump pulses arrive.

either bleach-recovery or geminate recombination suppression. The solvated electrons were excited by an 800-nm electron-pump pulse with a fluence of 15 mJ/cm^2. When the electron-pump pulse arrives, the OD at 800 nm is measured to be ~0.1. An electron-pump pulse with the fluence should be a sufficient energy to excite over 30 most of the existing solvated electrons, assuming that the absorption coefficient of isooctane solvated electrons is the same to the reported value of ~5000 $M^{-1}\,cm^{-1}$ at 800 nm for *n*-hexane solvated electrons [29]. Yet, the induced absorbance change (ΔOD_{950}) was positive (not a bleach) and has a magnitude that is only 3% of the initial optical density of the solvated electron. Similarly small effects were observed with two different electron-pump wavelengths (800 and 400 nm) and two different probe wavelengths (950 and 650 nm). The absence of a noticeable electron-pump effect on the recombination dynamics is consistent with the main result of this Letter that the recombination dynamics are not diffusion controlled.

The absence of a measurable bleach-recovery signal for the 3-pulse data is apparently due to an extremely short lifetime of the photo-excited state. The main effect of the electron-pump pulse is a small increase in the absorbance of the solvated electron which persists for ~1 ps in the form of an induction period or plateau in the recombination kinetics. As the arrival time of the electron-pump pulse is delayed, the 'height' of the plateau part decreases (Fig. 5), i.e., the height is linearly proportional to the solvated electron absorbance at the moment of the excitation. Furthermore, in the absence of the ionization pulse, no detectable absorption signal was observed only with the electron-pump pulse. These data indicate that while the electron-pump pulse does in fact excite the solvated electron, the main consequence on the ion pair is to simply delay the recombination process for a brief period while the electron is in its excited state (<30 fs).

4. Conclusion

Femtosecond time-resolved transient absorption spectroscopy has been used to investigate the geminate recombination process of electron–hole pairs in isooctane. The results strongly indicate that the gemination recombination is not limited by the diffusion of the electron, but by the recombination process itself in a contact ion pair.

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