Photo-degradation of imidazolium ionic liquids

Photo-detrapping of solvated electrons in an ionic liquid

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Abstract

We studied the dynamics of photo-detrapped solvated electrons in the ionic liquid trimethyl-N-propylammonium bis (trifluoromethanesulfonyl)imide (TMPA-TFSI) using laser flash photolysis. The solvated electrons were produced by the electron photodetachment from iodide via a 248 nm KrF excimer laser. The solvated electron decayed by first-order kinetics with a lifetime of about 240 ns. The spectrum of the solvated electron in the ionic liquid TMPA-TFSI is very broad with a peak around 1100 nm. After the 248 nm pulse, a 532 nm pulse was used to subsequently detrap the solvated electrons. After the detrapping pulse, quasi-permanent bleaching was observed. The relative magnitude of the bleaching in the solvated electron absorbance was measured from 500 nm to 1000 nm. The amount of bleaching depends on the probe wavelength. The fraction of bleached absorbance was larger at 500nm than that at 1000nm, suggesting that there are at least two species that absorb 532 nm light. We discuss the present results from viewpoint of the heterogeneity of ionic liquids.

Keyword: Solvated electron; Dry electron; Heterogeneous environment;

Introduction

Experimental and theoretical studies on the solvated electron have been extensively studied and its reaction dynamics in a number of molecular solvents has been characterized. The excess electron may be produced either by pulse radiolysis or by photoionization. While the solvated electron has been extensively studied in normal molecular solvents, there are only a few experimental studies on solvated electrons in ionic liquids (ILs). Ionic liquids can have very unique properties, such as negligible vapor pressure, excellent solvation ability and high thermal stability (Welton, 1999; Wasserscheid and Welton, 2003; Rogers and Seddon, 2003; Ranke et al., 2007). One important application of ionic liquids is as a medium for the processing of spent nuclear fuel (Allen et al., 2002; Harmon et al., 2001; Shkrob et al., 2007). Successful use of ionic liquids in radiation environments requires an understanding of the radiation chemistry of ionic liquids (Grodkowski and Neta, 2002a; Grodkowski and Neta, 2002b; Grodkowski and Neta, 2002c). Wishart and Neta have for the first time observed absorption spectrum and reaction kinetics of solvated electrons in an ionic liquid methyltributylammonium bis (trifluoromethylsulfonyl) imide (R_4N-TFSI) using pulse radiolysis (Wishart and Neta, 2003). Solvated electrons in ionic liquids have been also studied using photodetachment of iodide through charge-transfer-to-solvent (CTTS) band excitation for the first time by one of us (Katoh et al., 2007).

A number of recent studies of ILs have mentioned the dispersive nature of their dynamics and kinetics. For example, Maroncelli's group observed that the time-dependent response to a solute electronic perturbation in ILs extends over 3 or more decades in time (Arzhantsev et al., 2007; Jin et al., 2007). In the case of conventional supercooled liquids, it is generally agreed that dispersive kinetics are the results of heterogeneity (Ediger, 2000). In such situations, molecules in different local environments relax at significantly different rates. The presence of such heterogeneity in ILs has been clearly demonstrated both experimentally and in computational studies (Hu and Margulis, 2006; Jin et al., 2007; Lopes and Padua, 2006; Mandal et al. 2004). Such inhomogeneous environments may have significant effects on formation and reactions of solvated electron in ILs. In the present work we study such a possibility for inhomogeneous environments in ILs through excitation of the solvated electron in ground state. The excitation of the solvated electron is performed by irradiation by a 532 nm laser pulse, and we follow the changes in the dynamics of transient absorption.

Experimental Section

The solvated electrons were produced by electron photodetachment from iodide in ionic liquid solution by a KrF excimer laser (Lambda Physik, Lextra 100, 248 nm, pulse duration: 15 ns). For the measurements of the transient absorption signal, a 300 W xenon arc lamp (Ushio, UXL-300D) was used as the probing light source. The excitation pulse irradiated the sample in a cuvette through a 10 × 6 mm rectangular mask, while the analyzing light passed through 2-mm pinholes. After the 248 nm pulse, a 532nm pulse from a Nd-YAG laser (Spectra Physics Indi 50, pulse duration: 5 ns) irradiated the sample. The timing between the laser pulses was adjusted using a delay generator (Stanford Research Systems DG535A). A wide band-pass filter (FWHM = 40 nm, Opto-line) was used to select the analyzing wavelength. Transient signals were detected with a fast silicon photodiode (NewFocus 1801 or Thorlabs PDA10A) with a 300MHz oscilloscope (Tektronix, TDS350).

The ionic liquid *N*,*N*,*N*-trimethyl-*N*-propylammonium bis(trifluoromethylsulfonyl)imide (TMPA-TFSI) was purchased from Kanto Chemical Co., Inc (Tokyo, Japan). The ionic liquid solutions of KI were prepared in a bottle and dried under vacuum for 8 hr. The samples filled in the cuvettes were dried again under vacuum before use. The concentrations of KI were between 0.4 and 3 mM for the photodetachment experiments.

Results and Discussion

We have previously reported the solvated electron absorption spectrum in the ionic liquid TMPA-TFSI (Katoh et al., 2007). The absorption maximum is located around 1100nm. The decay kinetics of the solvated electron in TMPA-TFSI was first-order and the lifetime was about 250 ns. The observation of first-order decay in this case implies the presence of unknown electron scavenging impurities, but at a level low enough that they do not impede kinetics studies.

Figure 1(a) shows a transient absorption signal observed at 1000nm. When a 532nm laser pulse was used to irradiate the sample during the lifetime of the solvated electron, the transient absorption signal displayed an instrument-limited decrease, and the decrease of

absorption did not recover within the lifetime of the solvated electron. Therefore, a fraction of the solvated electron population was permanently removed by 532 nm excitation. In Figures 1(b) to 1(d), transient absorption signals monitored at several different wavelengths are shown. We observed similar permanent bleaching at all of the monitored wavelengths.

The above results suggest that a portion of the solvated electrons react and disappear during the 532 nm laser pulse. One possible explanation maybe the reaction of the dry electron with its parent iodine atom via the following reaction scheme;

$$I^- + h\nu(248nm) \longrightarrow I + e_d^- \quad (1)$$

$$e_d^- \longrightarrow e_s^- \quad (2)$$

$$e_s^- + h\nu(532nm) \longrightarrow \left(e_s^-\right)^* \quad (3)$$

$$\left(e_s^-\right)^* + I \longrightarrow I^- \quad (4)$$

$$I^- + I \longrightarrow I_2^- \quad (5)$$

$$I_2^- + I_2^- \longrightarrow I_3^- + I^- \quad (6)$$

where e_d^- is the so-called dry electron, e_s^- is solvated electron, $\left(e_s^-\right)^*$ indicates the electron after excitation with 532nm light. If the permanent bleaching of the solvated electron is due to the above reactions, it may be possible to observe a decrease in I_2^- concentration. Therefore we measured the transient absorption of I_2^- with a wide time window. We have already reported the absorption spectrum of I_2^- in TMPA-TFSI (Takahashi et al., 2007). The absorption spectrum in TMPA-TFSI is similar to that in water, with absorption maxima located at 400nm and 740nm. We monitored the evolution of the absorption signal from I_2^- at 830nm. At this wavelength we observe not only the I_2^- species, but also the reactivity of solvated electrons. The results are shown in Figure 2. In the early time regime (t < 500 ns) the absorption signal is mostly due to the solvated electron. After the decay of solvated electron, a slow build-up of I_2^- was observed. As shown in Figure 2, when the sample was irradiated by a 532 nm laser pulse approximately 200 ns after production of the solvated electron a permanent bleaching was observed, however in the microsecond regime, where the absorption is mainly due to I_2^-, there is no significant change in the absorption. We conclude that the iodine atom is not a reaction partner with the photo-detrapped electrons since the yield of I_2^- at longer times remains unchanged.

Although at the present time we cannot identify the reaction mechanism(s) for the photo-induced bleaching of the solvated electrons with 532 nm light, we can gain some insight from previous work done on water and alcohols (Silva et al., 1998; Yokoyama et al., 1998; Kambhampati et al., 2001). In their studies, pump-probe spectroscopy of the solvated electron in water, methanol and ethanol was studied with 300 fs time resolution. At low pump power the observed dynamics were assigned to $s \rightarrow p$ excitation and subsequent relaxation of the localized solvated electron. In contrast, at high pump power, two-photon absorption produces mobile conduction band electrons, which are subsequently trapped and relax at a resonant site far away from the initial equilibrated electron site. Interestingly, in the two-photon excitation, they observed an ultrafast proton-transfer reaction from the alcohol molecules resulting in a permanent bleach. Although we cannot conclusively say we are observing the same process, we tentatively conclude that excitation of the solvated electron results in the generation of a reactive dry electron. A new experiment using different excitation wavelengths is now proceeding to clarify the bleaching mechanism.

We next examined the spectral dependence of the proportion of solvated electron bleaching (Figure 3). As can be seen in the figure, the fraction of bleached signal depends on the observed wavelength. This variation suggests that there exist at least two species with different absorption profiles having different responses to being pumped with 532 nm light. The results comport with accumulating literature evidence of structural and dynamical heterogeneity in ILs as mentioned in the Introduction. Once the photodetached electrons are trapped in such heterogeneous environments, it is very likely that the solvated electrons might have various different kinds of characteristics depending on the localized state. Therefore it is quite reasonable to expect that excitation at a single wavelength (532 nm), would affect different subpopulations of the heterogeneous solvated electron distribution to different degrees.

Conclusion

We observe a permanent bleach of the solvated electron after excitation of this species at 532 nm in the ionic liquid TMPA-TFSI. The fraction of the bleached absorption varies over the probed spectral region (500 to 1000nm). Although currently the mechanism for bleaching is not clear, we interpret the present results from the viewpoint of heterogeneity in ionic liquids. To understand nature of solvated electron in ILs further, ultrafast dynamic studies and high-level computer simulations will be required.

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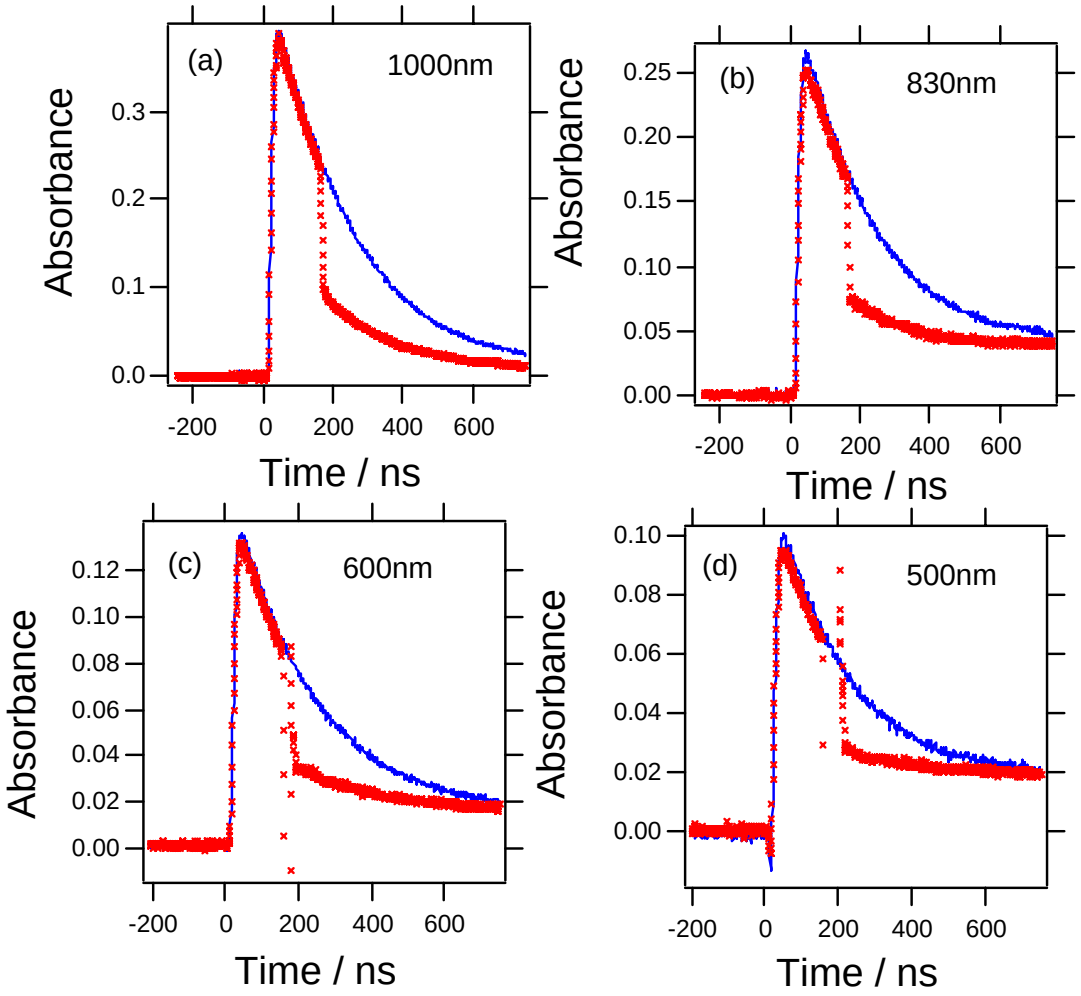
Figure Captions

Figure 1. Transient absorption signal for the solvated electron after a 248 nm laser pulse in ionic liquids TMPA-TFSI with (red cross symbols) and without (blue lines) a subsequent 532 nm laser pulse.

Figure 2. Time course of the transient absorbance at 830 nm after 248 nm excitation of KI in TMPA-TFSI with (red cross symbols) and without (blue dots) a subsequent 532 nm pulse. The 532 nm pulse was delayed 200 ns after the 248 nm pulse.

Figure 3. Wavelength dependence of the fraction of the absorption signal bleached by the 532 nm laser pulse.



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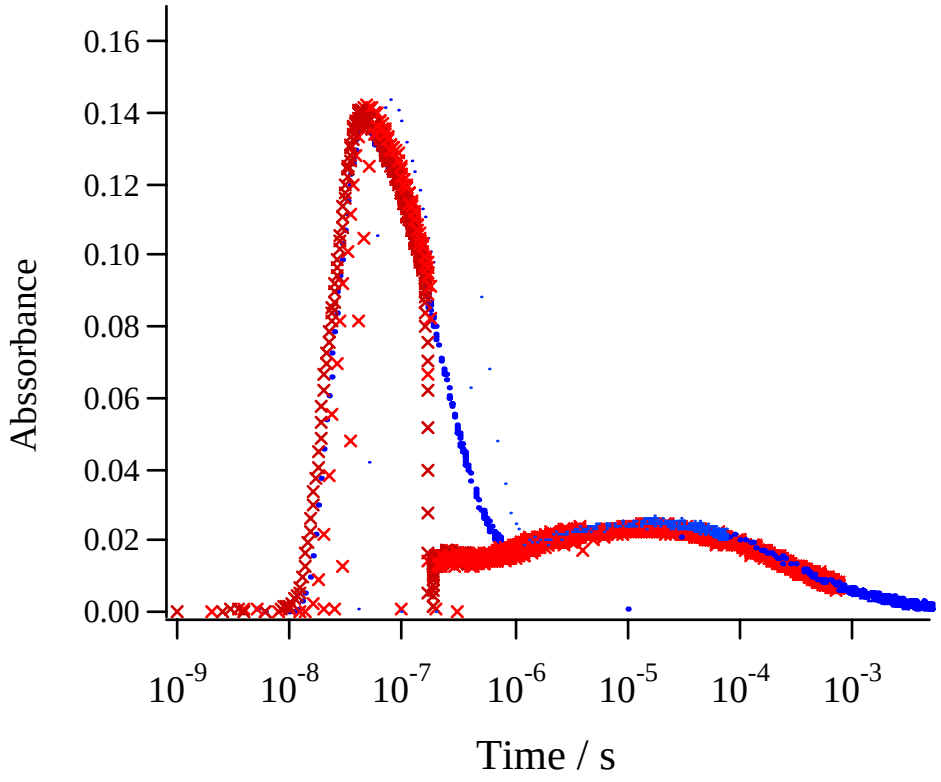

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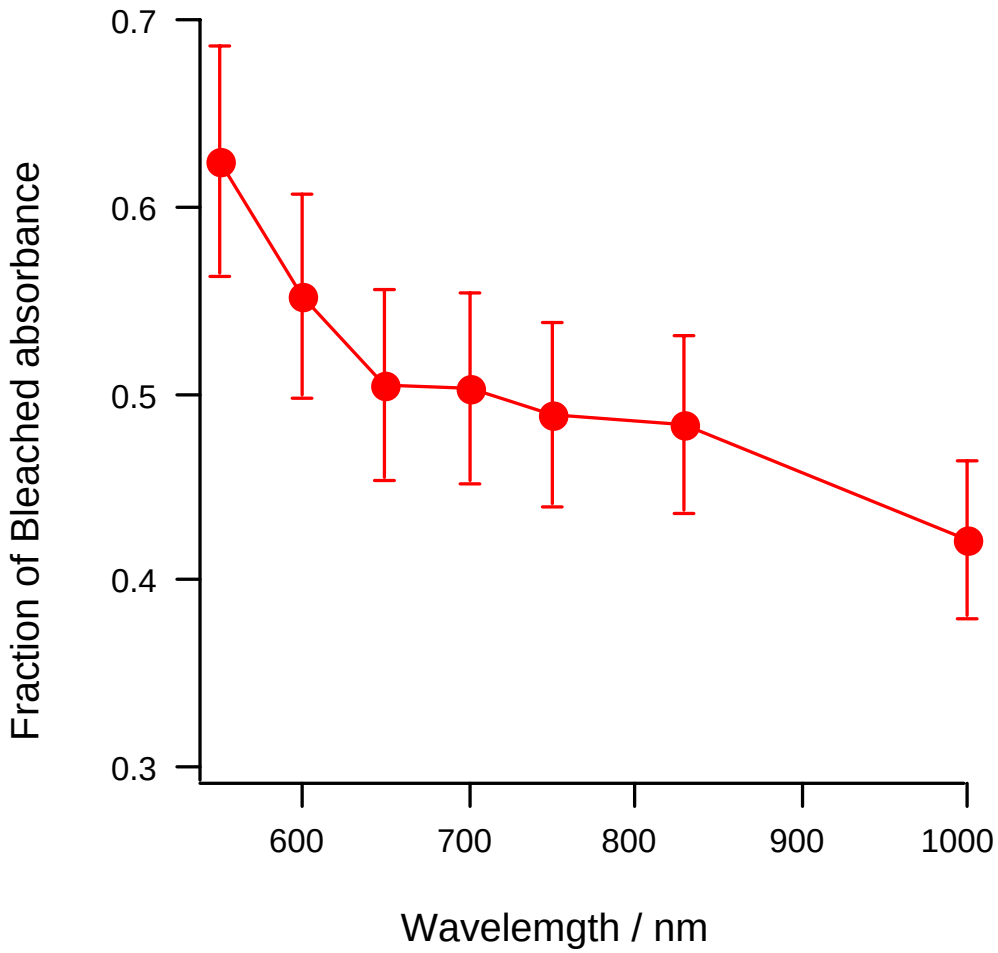

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