

Photo-detrapping of solvated electrons in an ionic liquid

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Photo-degradation of Imidazolium Ionic Liquids

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Abstract

Degradation of imidazolium ionic liquid, [bmim⁺][TFSA⁻] and iodide solution of [bmim⁺][TFSA⁻] by UV-laser irradiation has been studied through ground state absorption and transient absorption spectroscopy. We found that excited state [bmim⁺]^{*} undergoes degradation efficiently.

Introduction

Room-temperature ionic liquids are receiving considerable attention because of their remarkable properties, such as extremely low vapor pressure [Welton, 1999; Earle and Seddon, 2000]. As a result, ionic liquids are now used in various fields as solvents in chemical processes, such as organic synthesis, separation processes, and electrochemical processes. Recently, the application of ionic liquids as next generation diluents for extraction in nuclear cycle separation has been proposed [Earle and Seddon, 2000]. For the application of ionic liquids as a solvent for various chemical processes, chemical stability of ionic liquids is an important issue that must be addressed. For example, the thermal stability [Dupont and Suarez, 2006] and radiation damage [Allen et al., 2002; Berthon et al., 2006] has been studied.

Here we study the photochemical degradation of ionic liquids under pulsed laser irradiation to clarify the mechanism of degradation processes. We studied the degradation of 1-methyl-3-butylimidazolium bis(trifluoromethanesulfonyl) amide [bmim⁺][TFSA⁻] by direct excitation of [bmim⁺] using 220-nm light pulse excitation. We also examined the charge transfer complex between [bmim⁺] and iodide by 280-nm excitation. We found

that the excited state of [bmim]⁺ efficiently undergoes degradation and the neutral radical [bmim][·] is relatively stable.

Experimental

[bmim⁺]I (Merck), and [bmim⁺][TFSA⁻] (Kanto Chemical Co.) were used without further purification. Irradiation of laser pulses (220 nm or 280 nm) was carried out with the second harmonic of an optical parametric oscillator (Spectra Physics, MOPO-SL) excited by a Nd³⁺:YAG laser (Spectra Physics, Pro-230-10). Absorption spectra were measured with an absorption spectrophotometer (Shimadzu, UV-3101PC).

For the transient absorption spectra measurements, excitation light pulses (280 nm) were generated by the same laser used for the irradiation. The pulse duration of the laser was about 8 ns. A Xe flash lamp (Hamamatsu, L4642, 2 μs pulse duration) was used as a probe light source. The probe light transmitted through the sample was detected with a Si-photodiode (Hamamatsu, S-1722) after being dispersed with a monochromator (Ritsu, MC-10N). Signals from the photodetector were processed with a digital oscilloscope (Tektronix, TDS680C) and were analyzed with a computer.

For transient absorption decay measurements, the fourth harmonic (266 nm) of a Nd³⁺:YAG laser after pulse compression (Ekspla, SL311) was employed for excitation. The repetition rate of the laser was 10 Hz and the pulse duration was about 150 ps. A Xe flash lamp (Hamamatsu, L4642, 2-μs pulse duration) was used as a probe light source. The probe light was introduced into a Si photodiode (New Focus, 1601). The signal from the detector was introduced into a digital oscilloscope (LeCroy, 6200A). The rise time of the overall system was about 400 ps. The intensity of the laser pulse was measured with a pyroelectric energy meter (OPHIR, PE25-SH-V2). All measurements were carried out at 295 K.

Results and Discussion

Figure 1 shows the absorption spectra of ionic liquids; [bmim⁺][TFSA⁻] [Katoh, 2007], [bmim⁺]I⁻ [Katoh et al. 2008] and 30 mM solution of [bmim⁺]I⁻ in [bmim⁺][TFSA⁻]. For neat ionic liquids, absorption spectrum measurements are technically difficult because of the high concentration. For typical ionic liquids, the concentration of ions is c.a. 5 mol dcm⁻³, which necessitates the use of extremely thin optical cells (< 500 nm) for transmission measurements. A recent

report proposes an easy method for measuring absorption spectra of neat ionic liquid using a clamp cell [Katoh, 2007]. For [bmim⁺][TFSA⁻], strong absorption at 211 nm can be assigned to a $\pi-\pi^*$ transition that originates from the C=C bond of the imidazolium cation, based on the similarity with imidazole (Fig. 1A). For [bmim⁺]I⁻, very broad absorption indicates formation of charge transfer complex between [bmim⁺] and iodide (Fig. 1B) [Katoh et al.]. In the solution of [bmim⁺]I⁻, absorption tail at the longer wavelength range can be seen. This clearly shows that the charge transfer complexes are also formed in the solution (Fig. 1C).

Figure 2 shows the absorption spectral change of [bmim⁺][TFSA⁻] in a 1-cm quartz cell containing a 3 ml sample after irradiation by 220-nm laser pulses. The intensity of the laser pulses was 6 mJcm⁻². Under this condition, nonlinear effects can be ruled out [Katoh et al., 1998]. Absorbance at longer wavelengths increased after laser irradiations. Subsequently, the intensity of blue fluorescence increased. We tentatively assign this absorption tail to polymerized species based on its similarity to the absorption spectra after gamma-ray irradiation [Allen et al., 2002; Berthon et al., 2006]. Assuming that the absorption coefficient of the degraded compounds is 10⁴ mol⁻¹ dm³ cm⁻¹ at 300 nm, the quantum efficiency of the conversion is estimated to be 0.1. This clearly shows degradation is one of the main channels of excited [bmim⁺].



Figure 3 shows absorption spectral change of [bmim⁺]I⁻ in [bmim⁺][TFSA⁻] (30 mM) in a 0.2-cm quartz cell containing 0.6 ml sample liquid during irradiation of 1000 shots of 280-nm laser pulses. Intensity of the laser pulse was 1.4 mJcm⁻². At this wavelength, the charge transfer complex [bmim⁺]I⁻ can be excited. As shown in the figure, degradation did not efficiently occur under this condition.

To study primary excited species upon laser irradiation, transient absorption measurements were examined. Figure 4 shows the transient absorption spectrum of [bmim⁺]I⁻ in [bmim⁺][TFSA⁻] (30 mM) excited by 280-nm light. Figure 5 shows transient decay probed at 330 nm and 850 nm. Decay time was about 4 ns and did not depend on the wavelength of the probe light. The reaction between excited species and iodide in [bmim⁺][TFSA⁻] is possible and the rate constant can be estimated to be 1.3 x 10⁸ M⁻¹s⁻¹ using the value of viscosity of [bmim⁺][TFSA⁻] (52 mPa·s). Based on this, it should take at least 250 ns to meet

together. Therefore, the secondary reaction with iodide can be ruled out in the time range of transient absorption measurements (< 10 ns).

Upon photoexcitation of the complex by 280-nm light pulse a charge shift occurs. As shown in Fig. 4, at 320 nm, the sharp peak was observed, which can be assigned to a neutral radical [bmim][•] [Marcinek et al., 1999]. This suggests that dissociation of the excited complex occurs. In addition to the 320 nm peak, the broad absorption in visible wavelength range can be seen, which is not observed by pulse radiolysis measurements [Marcinek et al., 1999]. This suggests that iodine forms complex with [bmim⁺] and gives the absorption in visible wavelength region. Finally, these species recombine within several nanoseconds. During the lifetime of these species, degradation did not occur efficiently, suggesting that [bmim][•] is stable for several nanoseconds.



Conclusion

We studied degradation of imidazolium ionic liquid, [bmim⁺][TFSA⁻] and iodide solution of [bmim⁺][TFSA⁻] by UV-laser irradiation. We found that excited state [bmim⁺]^{*} undergoes degradation efficiently and neutral radical [bmim][•] is relatively stable.

Acknowledgement

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Figure captions

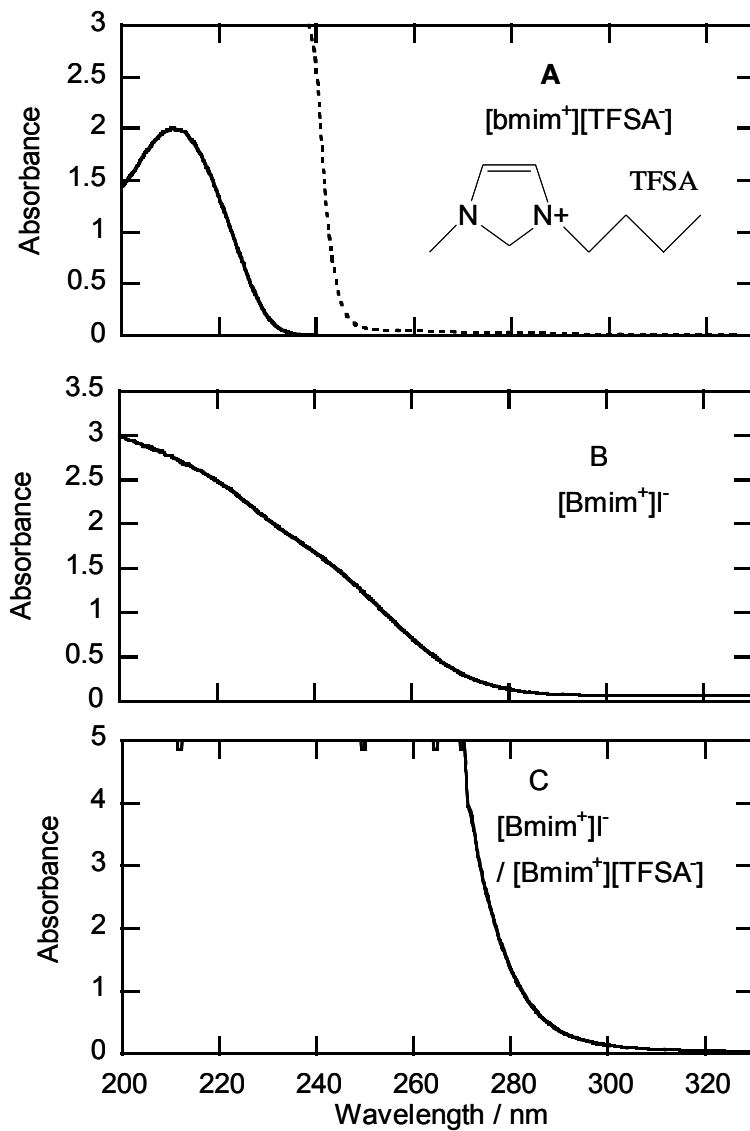


Figure 1

Absorption spectra of ionic liquids. (a) $[\text{bmim}^+][\text{TFSA}^-]$, in a clamp cell (solid line) and in an 1-cm cell (dotted line), (b) $[\text{bmim}^+]\text{I}^-$ a clamp cell and (c) 30 mM $[\text{bmim}^+]\text{I}^-$ in $[\text{bmim}^+][\text{TFSA}^-]$ in an 1-cm cell.

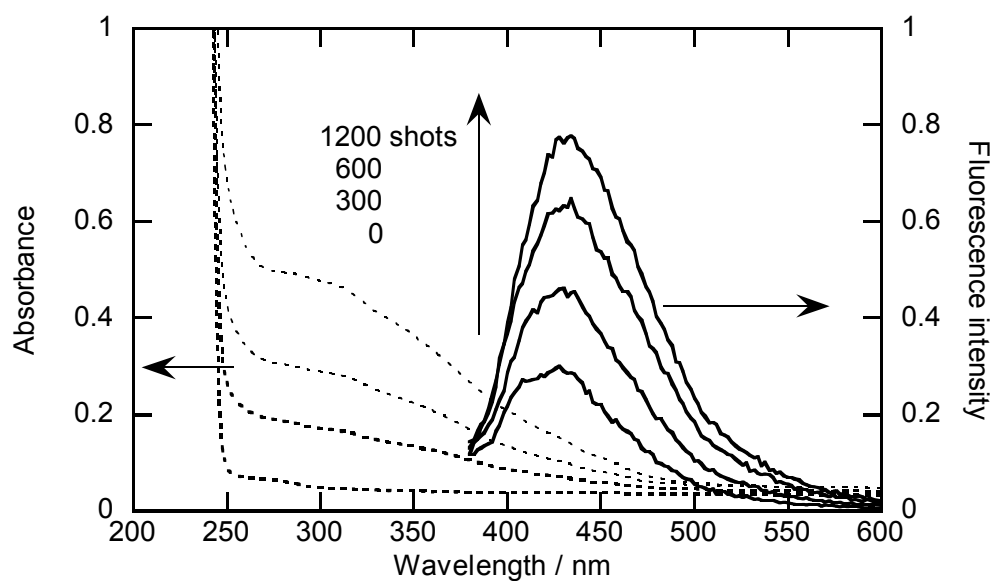


Figure 2

Spectral change of absorption and fluorescence of [bmim⁺][TFSA⁻] during 220-nm laser irradiation.

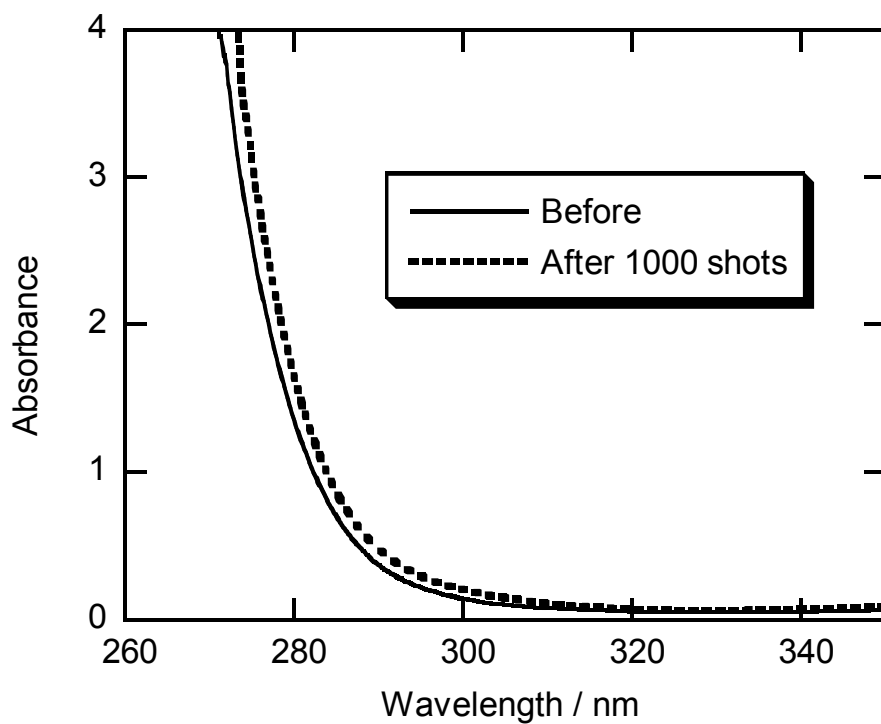


Figure 3

Absorption spectra of 30 mM [bmim⁺]⁻ in [bmim⁺][TFSA⁻] in an 0.2-cm cell before and after 1000 shots irradiation of 280-nm laser pulse.

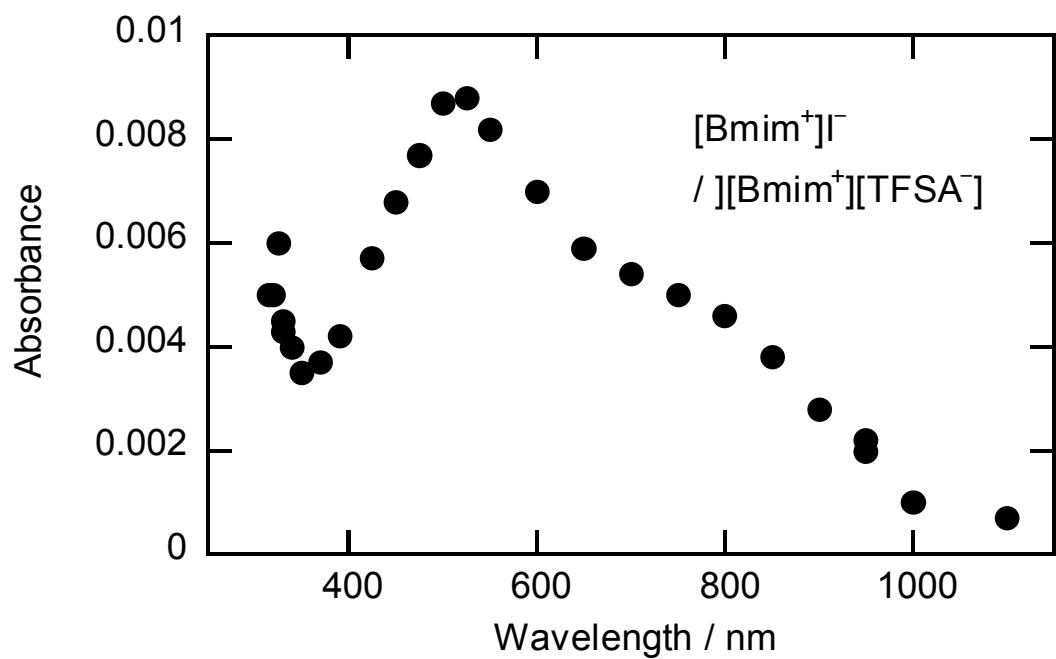


Figure 4

Transient absorption spectrum of 30 mM $[\text{bmim}^+]\text{I}^-$ in $[\text{bmim}^+][\text{TFSA}^-]$ excited by 280 nm light.

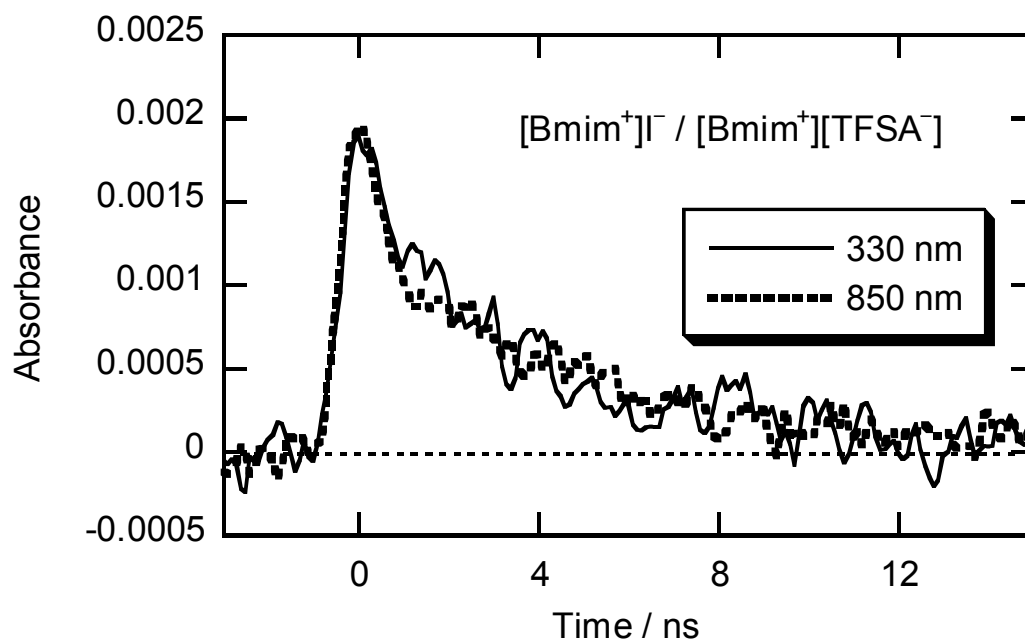


Figure 5

Decay profile of transient absorption of 30 mM $[bmim^+]I^-$ in $[bmim^+][TFSA^-]$ excited by 266 nm light.