Photo-dissociation dynamics of bis(p-dimethylaminophenyl) disulfide in ionic liquids studied by ultrafast transient absorption spectroscopy

Koji Osawa,[1]* Masahide Terazima,[1] and Yoshifumi Kimura[2*]


[1]Department of Chemistry, Graduate School of Science, Kyoto University, Kyoto 606-8502, Japan

[2] Department of Chemical Science and Technology, Faculty of Bioscience and Applied Chemistry, Hosei University, Koganei, Tokyo, 184-8584, Japan



Corresponding author

K. Osawa

Department of Chemistry, Graduate School of Science, Kyoto University, Kyoto 606-8502, Japan

Email: osawa@kuchem.kyoto-u.ac.jp

TEL: +81-75-753-4024

FAX: +81-75-753-4000

**Abstract**

Photo-dissociation reaction of bis(p-dimethylaminophenyl) disulfide in ionic liquids was studied by ultrafast transient absorption spectroscopy. Geminate recombination occurred more efficiently in the ionic liquids than in methanol due to the strong cage effect of the ionic liquids. An analysis based on the diffusion limited reaction model was performed to elucidate the recombination dynamics in ionic liquids. The very fast solvation dynamics less than 0.5 ps was observed in viscous solvents together with slow solvation dynamics on nanoseconds time scale. The relation between the solvation dynamics and geminate recombination was discussed.

## 1. Introduction

Various photochemical reactions in ionic liquids (ILs) such as electron transfer, proton transfer, energy transfer, photo-isomerization, and so on, have been studied to elucidate the unique solvent effect on the dynamics in ILs[ 1 , 2 ]. In particular, the photo-dissociation reaction is an interesting reaction to probe solvent effects such as cage effect, diffusional effect, solvation dynamics etc. Previously, our group has studied photo-dissociation of triiodide in ILs by sub-picosecond transient absorption spectroscopy[3,4]. By the UV excitation, triiodide dissociates into diiodide and iodine, and the photo-fragments geminately recombine partially in conventional solvents. In ILs, it was found that the photochemically dissociated diiodide and iodine exist as a caged contact pair and all the fractions geminately recombine due to the strong cage effect in ILs. It was also reported that the coherent vibration of the produced diiodide was not observed due to the formation of the caged contact pair. These strong cage effects were ascribed to the strong Coulomb interaction between solute and solvent. It is an interesting issue how this cage effect appears in the photo-dissociation dynamics of a larger organic molecule without charge.

In this work, we studied the photo-dissociation reaction of bis(p-dimethylaminophenyl) disulfide (BDMADS) into p-dimethylaminophenylthiyl (DMAPT) radicals (see Figure 1). While BDMADS is a non-dipolar molecule, the DMAPT radical is polar and its electronic state is sensitive to the environment[5]. Therefore it is expected that the geminate recombination dynamics is affected by the solvation dynamics around this polar radical. There are many preceding works on the photodissociation and recombination reaction of disulfide compounds in conventional liquids and supercritical fluids [ 6 - 13 ]. Bultmann et al. investigated the

photodissociation of bis(*p*-aminophenyl) disulfide into two p-aminophenylthiyl radicals by femtosecond transient absorption spectroscopy in various solvents[6]. They reported that geminate recombination of the p-aminophenylthiyl radicals in polar solvents occurs, only if the time scale for dielectric relaxation of the solvent is comparable to or slower than the time scale for recombination.  It is interesting how such competition between recombination and solvation affects the reaction dynamics in ILs, since these properties are expected to be strongly affected by the ionic environments in ILs.  It has been reported that the diffusion of a radical pair in a solvent cage is much faster than that predicted by the Stokes-Einstein relation from the study of the magnetic field effect on the caged radical pair[ 14 ].  Further the solvation dynamics in ILs show non-exponential dynamics in a wide time range[15].  Therefore, investigation of recombination dynamics of polar radicals in ILs is expected to give a new insight into the effect of characteristic structure of ILs on the reaction dynamics.  In this work, we have investigated the reaction dynamics of BDMADS in ILs by ultrafast transient absorption spectroscopy. In the following, after the presentation of the experimental procedure, the geminate recombination reaction dynamics will be analyzed by diffusion limited reaction model and its correlation with solvation dynamics will be discussed.

## 2. Experiment

The experimental setup for transient absorption spectroscopy was described elsewhere[3,16].  Briefly, an amplified Ti: sapphire laser system (Spectra Physics, Spitfire ProXP, 800nm, ca. 120fs FWHM) was employed for the measurement. The third harmonic pulse (266 nm) was produced by the fundamental pulse and the second harmonic pulse, which was used for the excitation. A white-light continuum was

generated by focusing the residual fundamental pulse into a 2 mm sapphire plate, and used for the probe pulse. The measurement was carried out by two different detection systems: transient absorption spectra measurement and time profile measurement. To obtain transient absorption spectra, the white-light continuum was separated into the sample and reference pulses, and the optical intensities of the sample pulse passing through a 0.5mm sample cell and of the reference pulse were detected by a CCD camera attached to a spectrometer (Princeton, Insight). The difference of optical densities with and without pump pulse ($\Delta$OD) was measured by using the optical shutter, and the intensity fluctuation of probe pulse was corrected by the reference pulse measured simultaneously. The FWHM of the response function was ca. 300fs. In the time profile measurement, a desirable wavelength of the probe and reference pulses was extracted by a band pass filter (FWHM 10nm) and detected by photo-diodes. $\Delta$OD at each delay time was evaluated by a toggle mode using an optical chopper, and the fluctuation of the probe pulse intensity was corrected by the reference pulse intensity. The FWHM of the response function was ca. 300 fs.

Bis(p-dimethylaminophenyl) disulfide (BDMADS) was prepared by the reaction of N,N-dimethylaniline with sulfur chloride[17] and purified by recrystallization from ethanol. Methanol and ethylene glycol were purchased from Nacalai Tesque and used as received. N-methyl-N-propylpyrrolidinium bis(trifluoromethanesulfonyl)imide ($[P_{1,3}][NTf_2]$) and N-methyl-N-propylpiperidinium bis(trifluoromethanesulfonyl)imide ($[Pp_{1,3}][NTf_2]$) were purchased from Kanto Kagaku. These ionic liquids were transparent at 266 nm. In the sample preparation, the absorbance of BDMADS in the solution was adjusted to be around 2.0 at 266 nm for the 1 mm optical path length. Before the measurement, the sample solution was evacuated

for more than 10 hour at 20°C in order to remove volatile impurities such as water. Typical water content of the sample solution before the measurement was 100 ppm. The transient absorption measurement was measured under the flow condition (1~2 cm$^3$ min$^{-1}$) at room temperature using the flow cell of 0.5 mm path length.

## 3. Results and Discussion

### 3.1. Transient absorption spectra

Transient absorption spectra of the DMAPT radical in methanol and in [P$_{1,3}$][NTf$_2$] from 0.5 to 15 ps after the excitation are shown in Figures 2(a) and (b). Both in methanol and [P$_{1,3}$][NTf$_2$], the absorption peak shifted to red with time. This is due to the stabilization of the DMAPT radical by the solvation. In [P$_{1,3}$][NTf$_2$], however, in addition to the red shift of the absorption spectrum, a fast decay of absorbance was observed. This corresponds to the disappearance of the DMAPT radicals by the geminate recombination process. A similar spectral dynamics to those in [P$_{1,3}$][NTf$_2$] were observed in [Pp$_{1,3}$][NTf$_2$] and ethylene glycol.

The time dependence of the absorption spectra on a fast time scale was measured with a good signal to noise ratio (S/N). However, the S/N in a longer time range was not enough to evaluate the spectral intensity, since the absorbance becomes very small due to the large yield of the geminate recombination. Therefore, we measured time profiles of ΔOD at eight wavelengths (530, 550, 570, 590, 610, 632, 650, and 700 nm) in better S/N and reconstruct the spectra by fitting the measured points at each delay time by a log-normal function (see supplementary material, Figure 1S). In the reconstruction of the transient absorption spectra in the longer time range, the spectra at a delay time of 1000 ps for the molecular solvents and 500 ps for the ionic

liquids were used as the reference. The time evolutions of the re-constructed spectra in methanol and [P$_{1,3}$][NTf$_2$] from 0.5 to 1000 ps after the excitation are shown in Figures 3(a) and(b). Here the background of the absorption spectrum (the broad weak absorption band covering the spectral region of the DMAPT radical) was subtracted, following the previous work by Bultmann et al.[6].

## 3.2 Population dynamics

Figure 4 (a) shows population decay of the DMAPT radical evaluated by the integral of the log-normal function used to fit the reconstructed spectra. No fast decay within a few picoseconds was observed in methanol, and the population was about 60 % of the initial intensity at 1ns. In viscous liquids, on the other hand, there was a very fast population decay within a few picoseconds, and the population of the radical decayed to ca. 30 % at 100 ps. These observations can be explained by the cage effect in the viscous solvents, which enhances geminate recombination process of the DMAPT radicals. The time profile of radical population was fitted by a tri-exponential decay function without any convolution with the system response function. The fitting curves are shown as dotted lines in Figure 4(a) and obtained parameters are summarized in Table 1.

Previously, initial fast decays of the p-aminophenylthiyl radical concentration in 1-butanol, ethylene glycol and propylene carbonate were analyzed using the diffusion model for geminate recombination by Bultmann et al.[6]. According to the model, the radical survival probability ($\Phi$(t)) was described as

$$\Phi(t) = 1 - \frac{R}{r_0}\left\{\frac{k_{rec}}{k_{rec} + 4\pi RDN_A}\right\}\left[erfc\left\{\frac{r_0 - R}{2\sqrt{Dt}}\right\} - \exp\left\{P^2 Dt + P(r_0 - R)\right\}erfc\left\{P\sqrt{Dt} + \frac{r_0 - R}{2\sqrt{Dt}}\right\}\right]$$

where

$$P = \frac{1}{R} \left\{ \frac{k_{rec} + 4\pi RDN_A}{4\pi RDN_A} \right\}$$

and

$$erfc(z) = \frac{2}{\sqrt{\pi}} \int_z^\infty \exp(-u^2) du$$

Here R denotes the contact distance, $r_0$ the initial distribution distance at t = 0, $k_{rec}$ the rate coefficient of the contact pair, D the diffusion coefficient, and $N_A$ Avogadro number, respectively. We used the same equation for the present system in order to evaluate the initial dynamics of the radical recombination. At first, we estimated the diffusion coefficient of the radical from the Stokes-Einstein (SE) equation

$$D = k_B T / 6\pi\eta a \qquad (2)$$

where η is the viscosity of the solvent, $k_B$ the Boltzmann constant, $a$ the hydrodynamic radius and T the absolute temperature. For the hydrodynamic radius $a$, the value of p-aminophenylthiyl radical (2.6 Å) was employed[6]. In the fitting, the contact distance R was fixed to 7.2 Å [5], and initial separation distance $r_0$ and the recombination rate $k_{rec}$ were assumed to be adjustable parameters. The result of the fitting is shown by the dotted line in Figure 4(b) and obtained parameters are summarized in Table 2. The simulation captured the initial dynamics of the population decay rather well, although in the longer time scale the model overestimate the decay as in the case of the previous study. Interestingly, the result shows that the values of $k_{rec}$ in ILs are about two times smaller than that in ethylene glycol. We consider that the origin of the slower geminate recombination rate in ILs may be due to errors in the estimated diffusion coefficient,

because $k_{rec}$ represents the reaction rate from the contact radical pair and the value may not strongly depend on the solvent. Instead, we consider that the estimation of the diffusion coefficient is not proper for the present case. It is well known that the diffusion coefficients of neutral molecule in ILs do not necessarily obey the SE equation[18,19]. As mentioned in the introduction, it was also reported that the diffusion of a radical pair is much faster than that predicted by the SE relation from the study of the magnetic field effect on the caged radical pair[14]. If we fix the value of $k_{rec}$ as 3.2 $\times 10^{13}$ cm$^3$ mol$^{-1}$ s$^{-1}$ (optimized value for ethylene glycol), the diffusion coefficients in $[P_{1,3}][NTf_2]$ and $[Pp_{1,3}][NTf_2]$ are estimated to be $5.4 \times 10^{-7}$ cm$^2$ s$^{-1}$ and $1.3 \times 10^{-7}$ cm$^2$ s$^{-1}$, respectively. This suggests that the translational dynamics of the radical pair is faster than is predicted from the SE relationship.

The small value of $a_\infty$ in Table 1 reflects the large cage effect on the population decay. From the conventional theory on the photo-dissociation recombination dynamics based on the diffusion limited kinetics, the photo-dissociation quantum yield depends on the viscosity ($\eta$) as $\eta^{-2}$[20]. However, the plot of the survival probability against the solvent viscosity does not follow the dependence of $\eta^{-2}$. This fact is consistent that in the longer time scale the prediction of Eq. (1) does not give the correct prediction of the experimental result. If we tried to fit the results by the power of viscosity, it was found that the exponent of -0.3 gives the best fit of the result (see supplementary material, Figure S2). Present experimental result indicates that the influence of viscosity on the cage effect is saturated at the higher viscosity, as shown in the case about photo-dissociation of triiodide[3].

### 3.3 Solvation dynamics

Figure 5 shows the absorption peak shift of the DMAPT radical against time. The absorption peak position generally moves by more than 600 cm$^{-1}$ within 1 ns. As shown in the figure, the solvation dynamics in viscous solvents is different from that in methanol. In viscous solvent, there is an initial fast solvation dynamics which is absent in methanol. The peak shift of the radical absorption spectrum was fitted by tri-exponential decay. The fitting curves are shown as dotted lines in Figure 5 and obtained parameters are summarized in Table S1 (supplementary materials).

Before the discussion on the relation with the recombination dynamics, it may be useful to compare our result of the solvation dynamics with the results obtained by the conventional fluorescence dynamics. Maroncelli et al. investigated complete solvation response of Coumarin 153 (C153) in RTILs which lasts to nano-second scale[21]. It is found that the solvation dynamics of the DMAPT radical in [P$_{1,3}$][NTf$_2$] is quite similar to that of C153 until 1 ns (supplementary material, Figure S3), although the solvation dynamics of C153 was observed longer than 1 ns. Comparing these data, we consider that the maximum time delay of 1 ns for the DMAPT radical is not enough to evaluate the complete solvation dynamics for ILs. Therefore, the values of $\nu_\infty$, $\nu_3$ and $\tau_3$ for ILs in table S1 are considered to be underestimated for the real values.

Nevertheless, it is notable the existence of the initial fast and large amount of solvation process (ca. 0.3 ps and 500 cm$^{-1}$) from the analysis for viscous solvent including ILs. Previous studies on the solvation dynamics in RTILs indicated that this component is associated with inertial motion of solvent ions[17][22-24]. Comparing the time constants of the solvation dynamics and the geminate recombination, we concluded that the fast solvation dynamics occurs in advance of the geminate

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recombination dynamics. It is speculated that the inertial motion at the initial solvation process reinforces cage effect and accelerate the following geminate recombination process. This result also supports that the translational dynamics of the radical pair is faster inside the cage.

**4. Conclusion**

The photo-dissociation reaction of BDMADS in ionic liquids has been investigated by ultrafast transient absorption spectroscopy. The very fast initial dynamics of the geminate recombination, which does not exist in the case of triiodide, was observed in ethylene glycol and ILs, and the values of its relaxation time were all around 1.4 ps. If we assume that $k_{rec}$ in ILs are the same as that in ethylene glycol, the diffusion coefficients in ILs estimated from the diffusion model are much larger than those predicted from the SE relation. The longer time dynamics was not well simulated by the diffusion model, and the photo-dissociation quantum yield did not follow the prediction of the diffusion model $\eta^{-2}$, as in the case of triiodide[3]. The initial fast and large solvation associated with the inertial motion of solvent molecules occurs in advance of geminate recombination. It is suggested that the fast solvation affects the cage effect and makes the translational dynamics of the radical pair faster inside the cage. More investigation in other viscous solvents with different polarity and RTILs with different size will confirm the relation between the fast solvation and the geminate recombination.

**Acknowledgement**

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Table 1   Parameters obtained by the fit of the time profile of the radical population (N(t)) to a tri-exponential function as follows. Only in methanol, the time profile was fitted to two exponential functions.

$$N(t) = a_\infty + \sum_{i=1}^{3} a_i \exp(-t/\tau_i)$$

| | $a_\infty$ | $a_1$ | $\tau_1$ / ps | $a_2$ | $\tau_2$ / ps | $a_3$ | $\tau_3$ / ps |
|---|---|---|---|---|---|---|---|
| Methanol | 0.56 | - | - | 0.27 | 46 | 0.17 | 300 |
| Ethylene glycol | 0.19 | 0.50 | 1.4 | 0.14 | 17 | 0.17 | 370 |
| [P$_{1,3}$][NTf$_2$] | 0.11 | 0.57 | 1.3 | 0.18 | 17 | 0.14 | 410 |
| [Pp$_{1,3}$][NTf$_2$] | 0.11 | 0.60 | 1.5 | 0.17 | 22 | 0.12 | 280 |

Table 2    Parameters obtained by the fit of the time profile of the radical absorption to

Eq. (1)

|  | $\eta$ / cP | $D_{SE}$ / $10^{-7}$cm$^2$s$^{-1}$ | $r_0$ / Å | $k_{rec}$ / $10^{13}$cm$^3$ mol$^{-1}$ s$^{-1}$ |
|---|---|---|---|---|
| Ethylene glycol | 17 | 4.49 | 7.27 | 3.2 |
| [P$_{1,3}$][NTf$_2$] | 57 | 1.41 | 7.23 | 1.6 |
| [Pp$_{1,3}$][NTf$_2$] | 150 | 0.55 | 7.23 | 2.1 |

# Figures for

# Photo-dissociation dynamics of

# bis(p-dimethylaminophenyl) disulfide in ionic liquids

# studied by ultrafast transient absorption spectroscopy

Koji Osawa*,[1] Masahide Terazima,[1] Yoshifumi Kimura*[2]

[1]Department of Chemistry, Graduate School of Science, Kyoto University, Kyoto 606-8502, Japan

[2]Department of Chemical Science and Technology, Faculty of Bioscience and Applied Chemistry, Hosei University, Koganei, Tokyo, 184-8584, Japan

E-mail: osawa@kuchem.kyoto-u.ac.jp

Figure 1.　Absorption spectra of BDMADS and the DMAPT radical in methanol.

Figures 2.　Transient absorption spectra of the DMAPT radical in (a) methanol and (b) $[P_{1,3}][NTf_2]$ from 0.5 to 15 ps after the excitation.

Figures 3.　Time evolutions of model spectra constructed by fitting time profiles of eight wavelengths to a log-normal function in (a) methanol and (b) $[P_{1,3}][NTf_2]$ from 0.5 to 1000 ps after the excitation.

Figures 4.　(a) Time profiles of the radical population and (b) their fitting to a diffusion model function in the earlier time. The dotted lines in (a) are the fitting curves by multiexponential functions and these in (b) are the fitting curves by diffusion limited model.

Figure 5.　Absorption peak of the DMAPT radical against time.
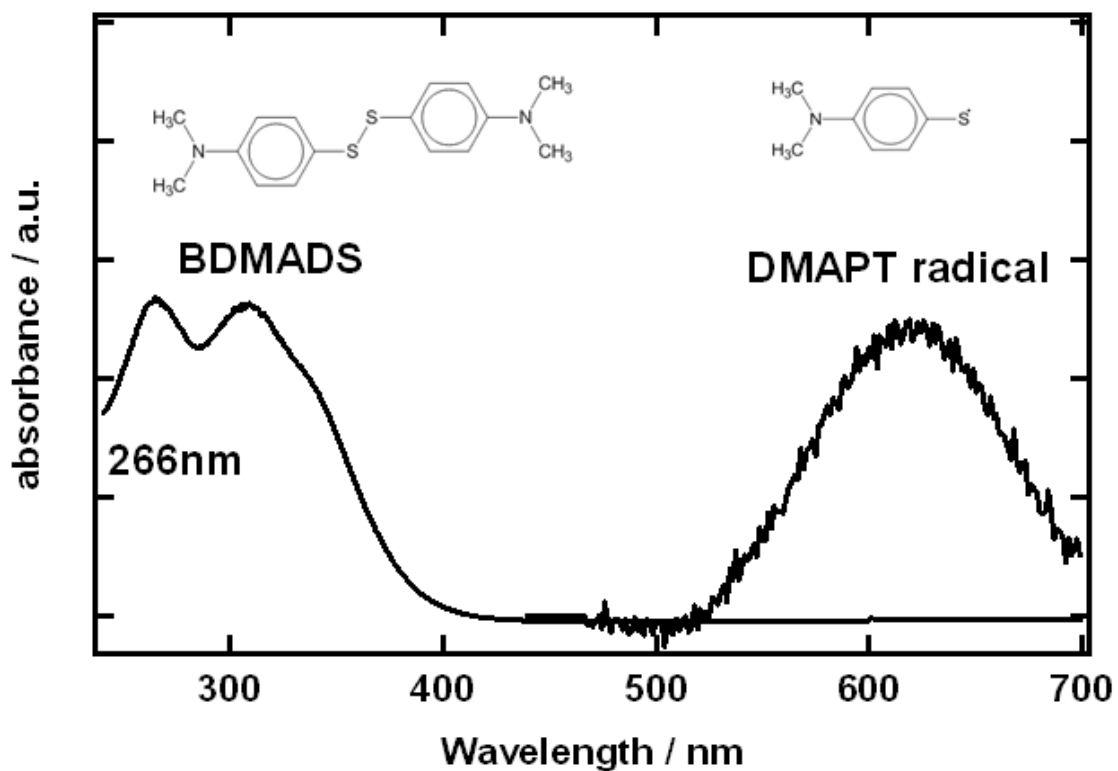
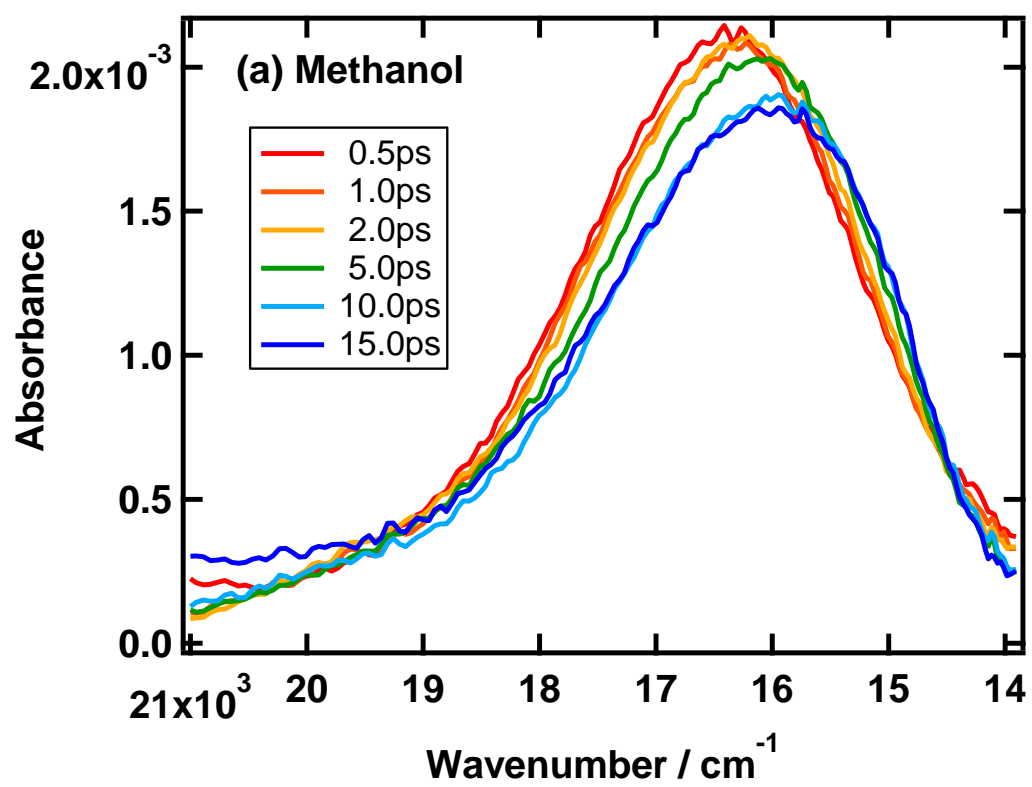Figure 1 K.Osawa et al.

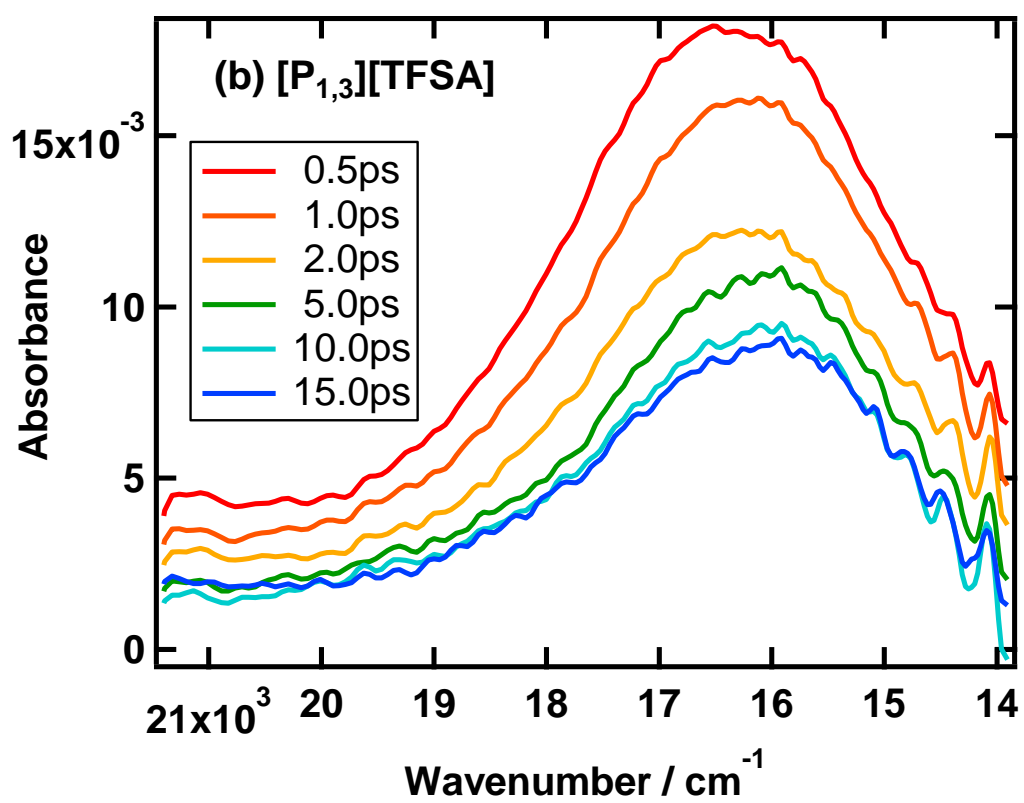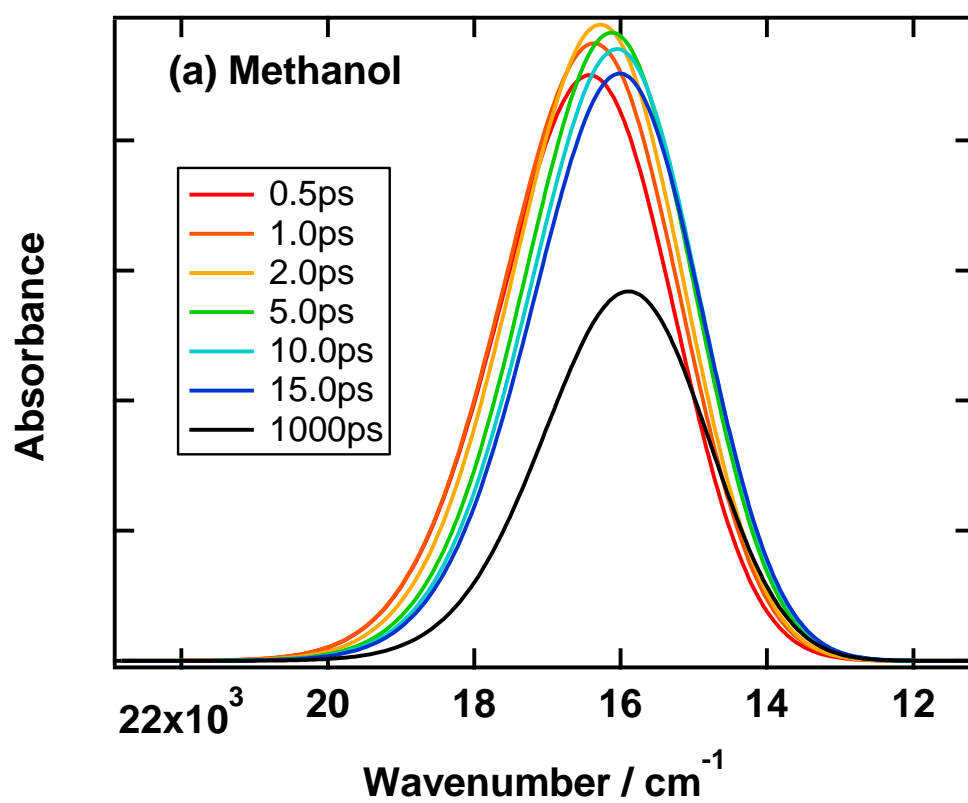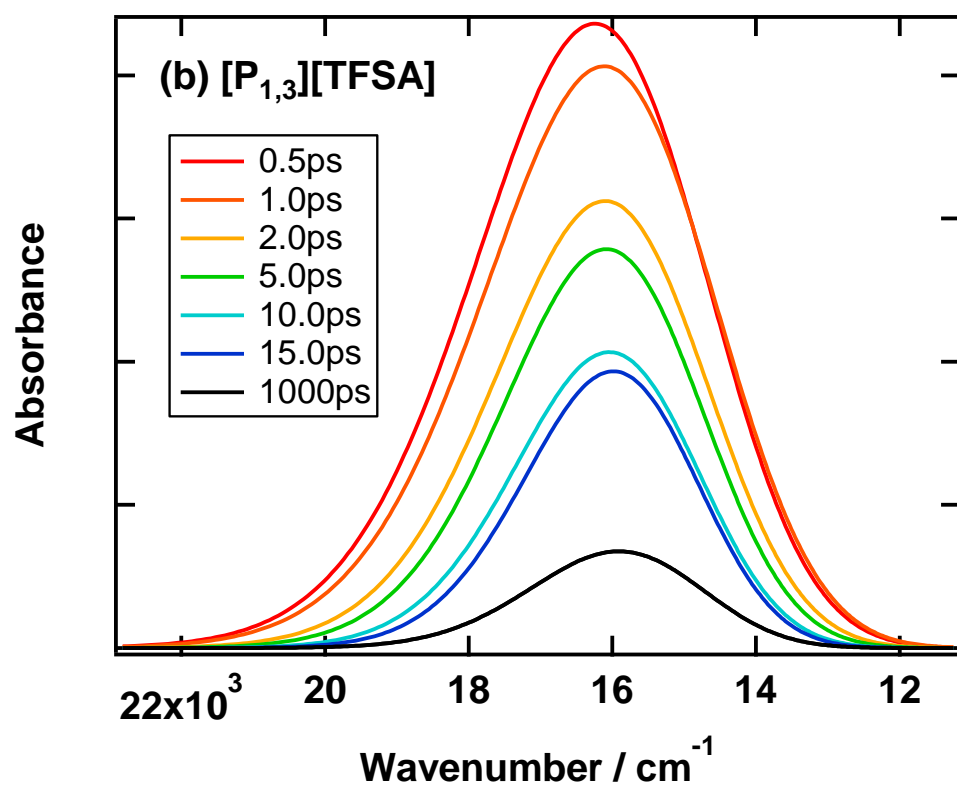Figure 2(a) K.Osawa et al.

Figure 2(b) K.Osawa et al.



(b) [P$_{1,3}$][TFSA]

Legend:
- 0.5ps
- 1.0ps
- 2.0ps
- 5.0ps
- 10.0ps
- 15.0ps

Y-axis: Absorbance ($15 \times 10^{-3}$, 10, 5, 0)

X-axis: Wavenumber / cm$^{-1}$ ($21 \times 10^3$, 20, 19, 18, 17, 16, 15, 14)

Figure 3(a) K.Osawa et al.



**(a) Methanol**

| | |
|---|---|
| —— | 0.5ps |
| —— | 1.0ps |
| —— | 2.0ps |
| —— | 5.0ps |
| —— | 10.0ps |
| —— | 15.0ps |
| —— | 1000ps |

Absorbance

Wavenumber / cm$^{-1}$

$22\times10^3$    20    18    16    14    12

Figure 3(b) K.Osawa et al.



**Absorbance**

**(b) [P$_{1,3}$][TFSA]**

- 0.5ps
- 1.0ps
- 2.0ps
- 5.0ps
- 10.0ps
- 15.0ps
- 1000ps

**22x10$^3$**    **20**    **18**    **16**    **14**    **12**
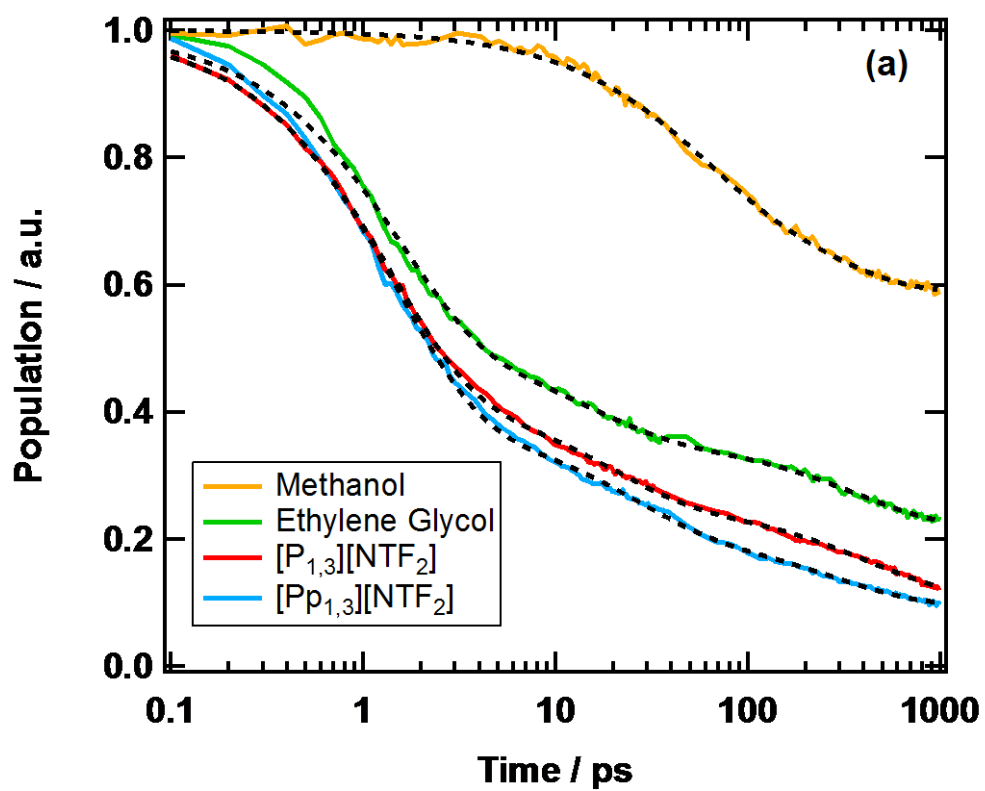
**Wavenumber / cm$^{-1}$**

Figure 4(a) K.Osawa et al.

Figure 4(b) K.Osawa et al.

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Figure 5 K.Osawa et al.