

Vibrational Cooling Process of S_1 *trans*-Stilbene in Ionic Liquids Observed with Picosecond Time-resolved Raman Spectroscopy

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Vibrational cooling rates in room temperature ionic liquids were measured with picosecond time-resolved Raman spectroscopy. The 1570-cm^{-1} Raman band of the first excited singlet (S_1) state of *trans*-stilbene was used as a "Raman thermometer." The recorded vibrational cooling rates in 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide (emimTf₂N) and 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide (bmimTf₂N) were close to those in ordinary molecular solvents despite a large difference in thermal diffusivity. The result is consistent with the assumption that local structures are formed in the ionic liquids.

Room temperature ionic liquids are composed of positive and negative ions.^{1,2} There are no neutral species in the ionic liquids. The presence of ionic species and the lack of neutral species should affect the chemical reactions proceeding in the ionic liquids. Although ionic liquids attract much attention as new reaction media, solute-solvent interaction and its fluctuation therein have not been well characterized yet. It is important to elucidate how the positive and negative charges affect the chemical reactions in the ionic liquids.

When a solute molecule is photoexcited to its vibrationally excited state, the vibrational excess energy is dissipated to the solvent molecules by intermolecular energy transfer. This fundamental process is an essential part of the chemical reaction in solutions. We can monitor the intermolecular energy transfer by measuring the vibrational cooling process of the excited solute molecule. When measuring the vibrational temperature, the first excited singlet (S_1) state of *trans*-stilbene serves as a good thermometer. With the use of picosecond time-resolved Raman spectroscopy, or "picosecond Raman thermometer," we can measure the vibrational cooling process with a picosecond time resolution.^{3,4}

We photoexcited *trans*-stilbene dissolved in two imidazolium-based ionic liquids, 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide (emimTf₂N) and 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide (bmimTf₂N). Picosecond time-resolved Raman spectra of S_1 *trans*-stilbene were measured in the ionic liquids for observing the vibrational cooling process.

Picosecond time-resolved Raman spectra were measured with the pump-probe method. The 592 nm output from an optical parametric amplifier (Quantronix, TOPAS) pumped by the second harmonic of a Ti:sapphire regenerative-multipass amplifier (Quantronix, Integra 2.5, wavelength 800 nm, repetition rate 1 kHz, pulse width 2 ps, pulse energy, 1.5 mJ) was used as the probe light. The 296-nm light generated by the frequency doubling of another 592-nm OPA output was used as the pump light. The energies of the probe and pump light were 0.25 and 1.0 μJ

at the sample point, respectively. The cross correlation time between the pump and probe pulses estimated from the rise of the S_n - S_1 absorption of *trans*-stilbene was 1.7 ps. The sample solution was held in a rotating quartz cell. The light scattered from the sample solution was analyzed by a single imaging spectrograph (Horiba Jobin Yvon, Triax-320) and detected by a liquid-nitrogen cooled CCD detector (Princeton Instruments, Spec 10:400B/LN). The Rayleigh scattering light was rejected before the spectrograph by an optical filter (Notch Filter, Kaiser Optical Systems). The spectral width of the probe light including the slit function of $150\ \mu\text{m}$ was $15.2\ \text{cm}^{-1}$. *trans*-Stilbene (special grade) was purchased from Wako Chemical and was recrystallized from ethanol before the measurement. BmimTf₂N was purchased from Kanto Chemical (lot number 609041). EmimTf₂N was synthesized from 1-methylimidazole with the reported method.⁵ Viscosity of the ionic liquids was measured with a viscometer (Brookfield DV-I+ Digital Viscometer).

Time-resolved Raman spectra of S_1 *trans*-stilbene were measured in the solutions of bmimTf₂N, emimTf₂N, heptane, and ethanol at time delays of -5, 0, 2, 5, 10, 15, 20, 30, 50, and 100 ps. The vibrational excess energy given to S_1 *trans*-stilbene on the photoexcitation was approximately $2500\ \text{cm}^{-1}$. The concentration was $3.0\text{--}5.0 \times 10^{-3}\ \text{mol}\cdot\text{dm}^{-3}$. The results for the emimTf₂N solution are shown in Figure 1. In Figure 1, Raman bands from the solvent (emimTf₂N) have been subtracted. All the bands shown in the figure are those from S_1 *trans*-stilbene. Positions and relative intensities of the recorded Raman bands agree with those of S_1 *trans*-stilbene measured in ordinary solvents.^{3,4,6-8}

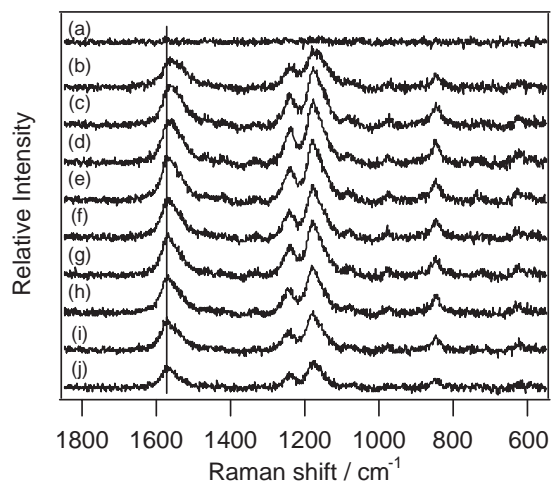


Figure 1. Time-resolved Raman spectra of S_1 *trans*-stilbene in emimTf₂N, measured at -5 ps (a), 0 ps (b), 2 ps (c), 5 ps (d), 10 ps (e), 15 ps (f), 20 ps (g), 30 ps (h), 50 ps (i), and 100 ps (j). The concentration was $5.0 \times 10^{-3}\ \text{mol}\cdot\text{dm}^{-3}$.

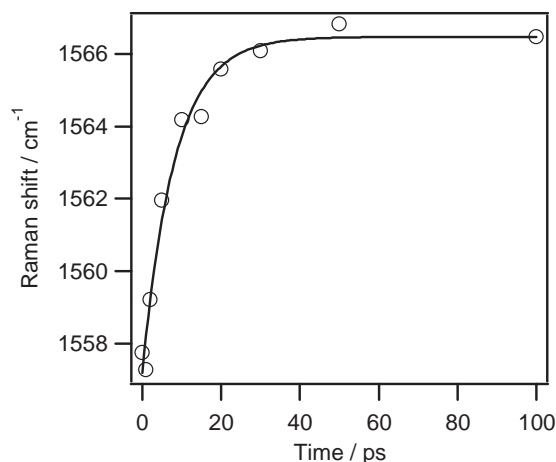


Figure 2. Position of the 1570 cm^{-1} Raman band of S_1 *trans*-stilbene in emimTf₂N (open circle) plotted against the time delay. The result of the fitting analysis by a single-exponential decay function is shown in a solid curve.

It is obvious from Figure 1 that the Raman band at 1570 cm^{-1} , the stretch vibration of the central C=C bond, changes its shape and position as the time delay changes. This change reflects the cooling process of S_1 *trans*-stilbene.^{6–8} As the stilbene molecule dissipates its vibrational excess energy in the S_1 state, its temperature decreases, which changes the shape and position of the 1570-cm^{-1} Raman band. Time dependence of the peak position obtained from the time-resolved spectra in emimTf₂N (Figure 1) is shown in Figure 2.

The position of the 1570-cm^{-1} band changes linearly with the temperature of S_1 *trans*-stilbene.^{7,8} The experimental data in Figure 2 thus represent the vibrational cooling kinetics of S_1 *trans*-stilbene. By fitting a single-exponential decay function to the observed cooling curve, we obtain the vibrational cooling rate. The cooling rates of S_1 *trans*-stilbene, k_{vib} , in the two ionic liquids, together with those in two ordinary molecular solvents, are summarized in Table 1. The vibrational cooling rates in the ionic liquids (0.11 and 0.12 ps^{-1}) are close to those in heptane (0.08 ps^{-1}) and in ethanol (0.13 ps^{-1}).

While the vibrational cooling is similar between the ionic liquids and the molecular solvents, their viscosity shows a marked difference. The viscosity of emimTf₂N and bmimTf₂N are 31 and $50\text{ mPa}\cdot\text{s}$, larger than the viscosity of heptane ($0.41\text{ mPa}\cdot\text{s}$) or ethanol ($1.1\text{ mPa}\cdot\text{s}$) by a factor of 120 at maximum (Table 1).

It has been shown that the vibrational cooling rate of S_1 *trans*-stilbene has a positive correlation with the thermal diffusivity of the solvent.^{3,4} We have explained this experimental result with a simple numerical model by assuming that the vibrational excess energy is shared with the solvent molecules in the first solvation shell within a few picoseconds and that slower solvent–solvent energy-transfer process follows. The entire cooling process was well described by the macroscopic diffusion equation of heat,

$$\frac{\partial U}{\partial t} = \kappa \Delta U, \quad (1)$$

Table 1. Vibrational cooling rate of S_1 *trans*-stilbene (k_{vib}) and viscosity (η) and thermal diffusivity (κ) of solvent

Solvent	$k_{\text{vib}}/\text{ps}^{-1}$	$\eta/\text{mPa}\cdot\text{s}$	$\kappa/10^{-8}\text{ m}^2\text{ s}^{-1}$
emimTf ₂ N	0.11 ± 0.02	31 ± 0.5	$6.01 \pm 0.04^{\text{d}}$
bmimTf ₂ N	0.12 ± 0.02	50 ± 0.5	$6.0 \pm 0.1^{\text{d}}$
Heptane	0.08^{a}	0.41^{b}	8.01^{a}
Ethanol	0.13^{a}	1.2^{c}	8.70^{a}

^aRef. 3. ^bRef. 9, p. II-42. ^cRef. 9, p. II-49. ^dRef. 10.

where U is the temperature, κ is the thermal diffusivity, and t is time.

Thermal diffusivities of emimTf₂N and bmimTf₂N, recently reported by Frez et al.,¹⁰ are listed in Table 1. The values, $6.01 \pm 0.04 \times 10^{-8}$ and $6.0 \pm 0.1 \times 10^{-8}\text{ m}^2\text{ s}^{-1}$, are smaller than those for heptane (8.01×10^{-8}) and ethanol (8.70×10^{-8}) by a factor of 1.3 or more. However, the cooling rates observed in the ionic liquids are similar with the ones in the molecular liquids.

The lack of correlation between the observed vibrational cooling rate and the thermal diffusivity of the ionic liquids suggests that the macroscopic thermal diffusivity does not represent the microscopic environments in the ionic liquids. This result is consistent with the assumption that there are local structures formed in the ionic liquids.² It is possible that the energy transfer within the local structure is as efficient as in the molecular liquids while the transfer in a larger volume beyond the local structure, which determines the macroscopic heat conduction, is less efficient. It should also be noted that the normal viscosity dependence of the photoisomerization rate of *trans*-stilbene, which is well established for ordinary molecular solvents, did not explain the photoisomerization rate in bmim[PF₆].¹¹

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