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論文の内容の要旨

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論文題目 Local Structure Formation in an Ionic Liquid Studied

with Picosecond Time-resolved Raman Spectroscopy

（ピコ秒時間分解ラマン分光法を用いた

イオン液体中の局所構造形成の研究）

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【Introduction】

Ionic liquids attract much attention recently as a new class of liquids. They have many interesting properties that are not associated with usual molecular liquids. Recent intensive physicochemical studies have suggested that these properties originate from specific local structures formed in ionic liquids. However, there is no unified view on the nature of these local structures. In this study, I try to further elucidate the nature of local structures in ionic liquids with a focus placed on the lack of correlation between the macroscopic thermal property and the microscopic energy transfer that is observed with picosecond time-resolved Raman spectroscopy. The volume of the local structure formed in ionic liquids is estimated from the analysis based on the diffusion equation of heat.

Picosecond time-resolved Raman spectroscopy provides a direct means to monitor the microscopic energy transfer in solutions; the 1570 cm^{-1} Raman band of S_1 *trans*-stilbene can be used as a "picosecond Raman thermometer" because the peak position of this band changes linearly with temperature. With this "picosecond Raman thermometer," the cooling kinetics of *trans*-stilbene has been observed for a number of molecular liquids after it is photoexcited to the S_1 state with excess vibrational energy. The observed cooling rates correlate very well with the thermal diffusivities, indicating that they are controlled by the thermal diffusion in the solvents around the S_1 *trans*-

stilbene molecule.

  In the present thesis (partially in the Master thesis work), I extend the picosecond time-resolved Raman study of vibrational cooling of S_1 *trans*-stilbene to ionic liquids. The observed vibrational cooling rates and the thermal diffusivities are plotted for ionic liquids as well as for molecular liquids in Fig.1. There is no obvious correlation between the two quantities for the seven ionic liquids, while a good correlation is observed for the molecular liquids. The vibrational cooling rates in the ionic liquids are similar to those of normal alkanes, although their thermal diffusivities are considerably smaller. The presence of local structures in ionic liquids may well disturb a continuous heat transfer from the heat source S_1 *trans*-stilbene to outer solvent molecules. If heat transfer is slow at the boundary between the neighboring local structures, macroscopic thermal diffusion is not determined by the microscopic energy transfer represented by the cooling rate observed by the Raman thermometer.

Fig 1. Relationship between the observed vibrational cooling rates and thermal diffusivity

【Experimental】

  I constructed a picosecond time-resolved Raman spectrometer with two independently tunable light sources for the pump and probe pulses (Fig. 2). The output from a femtosecond mode-locked Ti:sapphire oscillator was amplified by a Ti:sapphire regenerative-multipass amplifier. A half of the amplified pulse was separated and delivered to a BBO crystal. The frequency-doubled output from the BBO crystal was used to pump an optical parametric amplifier (OPA) to generate the Raman probe pulses at 592 nm. The residual of the 800 nm amplified pulse pumped another OPA, which generated the pump pulse of 297 nm or 325 nm. For determining the precise peak position of the Raman band in the excess energy dependence measurement, I constructed a 4-f band pass filter which improved the spectral resolution to 8 cm^{-1}. The time resolution estimated from pump/

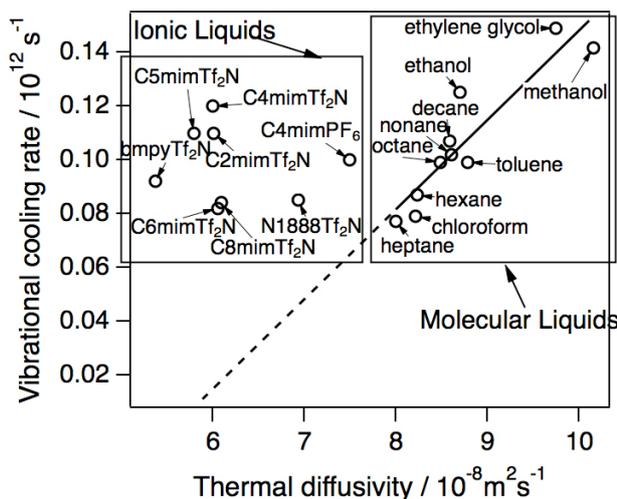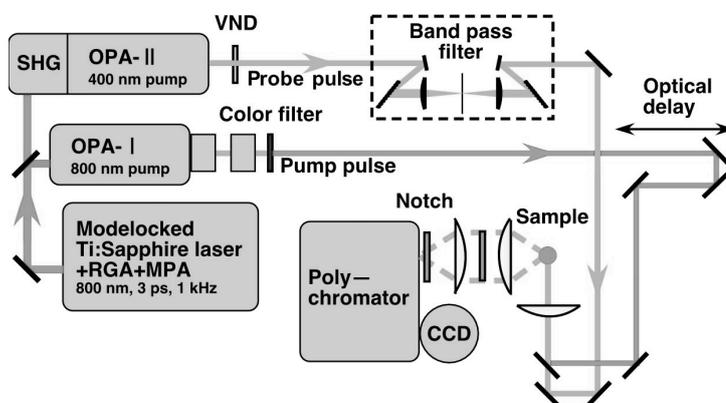Fig. 2 Layout of the constructed picosecond time-resolved Raman spectrometer

probe cross correlation was 4.0 ps. Wavelength of the pump pulse was set to 297 and 325 nm, corresponding to the excess energy of 2500 and 0 cm^{-1}, respectively. The pump and probe pulses, traveling the common light path after being combined with a dichroic mirror, were focused onto the sample solution, which was circulated through a dye laser jet nozzle. Rayleigh scattering and fluorescence in the ultraviolet region were eliminated before the spectrograph by an optical narrow band-rejection filter and an optical color filter. The scattered light was dispersed by a single imaging spectrograph and detected by a liquid-nitrogen cooled CCD detector. The sample concentration of *trans*-stilbene was 5.0×10^{-3} mol dm^{-3}. The ionic liquid used in the experiment was C_2mimTf_2N (1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)amide).

【**Results and Discussion**】

Vibrational Cooling Process with and without Excess Energy

I have measured the vibrational cooling kinetics of S_1 *trans*-stilbene with and without the vibrational excess energy, in order to examine whether or not the excess energy reaches the boundary of the local structure by diffusion. The observed time-resolved Raman spectra, with and without the excess energy, are shown in Fig.3. Two sets of cooling kinetics obtained from the two sets of time-resolved Raman spectra are shown in Fig. 4. The result for the 297 nm excitation, with an excess energy of 2500 cm^{-1}, shows a large temperature change reflecting the vibrational cooling process. No large 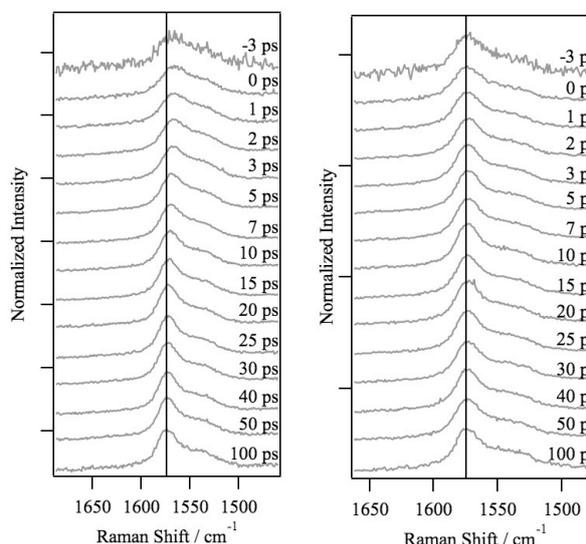change is observed for the excitation with the 325 nm light, which carries only very small excess energy. Peak positions after 50 ps with and without the excess

Fig. 3 Time-resolved Raman spectra of S_1 *trans*-stilbene in C_2mimTf_2N after photoexcitation (a) excitation: 297 nm, (b) excitation: 325 nm

energy agree with each other within the experimental uncertainties. This fact indicates that the temperature increased at the photoexcitation recovers to the room temperature in 50 ps. We thus conclude that the excess energy is fully dissipated within a local structure without reaching the boundary. The volume of the local structure in ionic liquids is large enough to keep the temperature increase at 50 ps below the detection limit.

Numerical Simulation of Thermal Diffusion in the Local Structure in C_2mimTf_2N

I have analyzed the observed vibrational cooling kinetics with a numerical model based on the

diffusion equation of heat, in order to estimate the size of the local structure in C_2mimTf_2N. Thermal diffusion within a local structure is modeled with the heat dissipation from a heat source in a finite volume. The heat source is regarded as a homogeneous distribution of temperature rise in a rectangular solid. This heat source represents S_1 *trans*-stilbene and the nearest solvent ions that share the excess energy immediately after the photoexcitation. The finite volume of the local structure in ionic liquids is modeled by a cube with a length L that corresponds to the diameter of the local structure. At the boundary of this
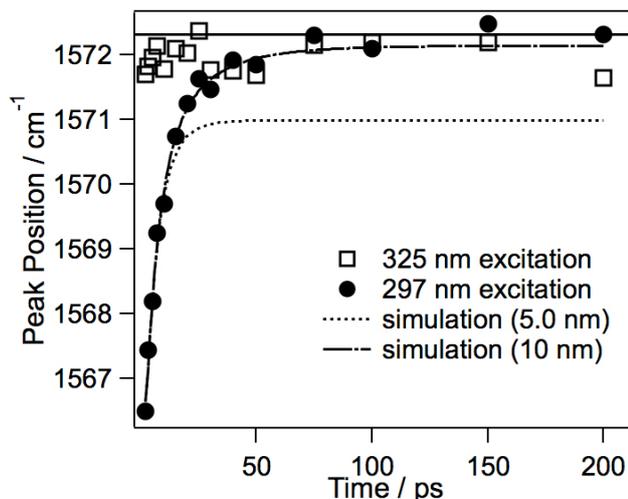

Fig. 4 Cooling kinetics with (filled circle) and without (open square) the excess energy and simulated with two diameters of the local structure, L, 5.0 (dotted curve) and 10 nm (dotted line), and the room temperature (solid line)

cube, heat flow is reflected to the opposite direction from the incident. Under these conditions, I simulated the thermal diffusion in the local structure and compared the resultant temperature change with the observed cooling kinetics (Fig. 4). It is obvious that the simulated cooling kinetics with L =10 nm reproduces the observed cooling kinetics very well, showing a complete recovery to the room temperature at time delays larger than 50 ps. However, the simulated curve stops cooling before reaching the room temperature if the L value is 5.0 nm. Simulations with smaller L values indicate that the temperature does not cool down to the room temperature because the heat remains within the local structure. This comparison between the observed and the simulated cooling kinetics shows that the diameter of the local structure is expected to be 10 nm or larger. I have thus estimated the minimum size of the local structure in C_2mimTf_2N, 10 nm, with picosecond time-resolved Raman spectroscopy and a numerical simulation based on the diffusion equation of heat.