SOLUTE–SOLVENT ENERGY TRANSFER AND COOLING KINETICS OF PHOTOEXCITED S_1 *TRANS*-STILBENE PROBED WITH PICOSECOND RAMAN SPECTROSCOPY: COMPARISON BETWEEN CHLOROFORM AND CHLOROFORM-*d* SOLUTIONS

KOICHI IWATA^{a,*} and HIRO-O HAMAGUCHI^{a,b}

^a *Molecular Spectroscopy Laboratory, Kanagawa Academy of Science and Technology (KAST), KSP East 301, 3-2-1 Sakato, Kawasaki 213, Japan;*

^b *Department of Chemistry, School of Science, The University of Tokyo, 7-3-1 Hongo, Bunkyo-ku, Tokyo 113-0033, Japan*

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Cooling kinetics of *trans*-stilbene (*t*SB) photoexcited to a vibrationally excited state in the first excited singlet (S_1) manifold was studied with picosecond time-resolved Raman spectroscopy. The observed cooling curves of S_1 *t*SB in chloroform (CHCl_3) and in chloroform-*d* (CDCl_3) were identical within the experimental uncertainties. For S_1 *t*SB in chloroform, there was no experimental evidence for strong intermolecular vibration–vibration ($V-V$) resonance energy transfer in the picosecond to sub-picosecond time region.

Keywords: Solution; energy transfer; solvation; stilbene; chloroform; time-resolved Raman spectroscopy

INTRODUCTION

Intermolecular energy transfer is crucially important for chemical reactions in solution. The nature of the energy transfer in solution,

* Address for correspondence: Department of Chemistry, School of Science, The University of Tokyo, 7-3-1 Hongo, Bunkyo-ku, Tokyo 113-0033, Japan.

however, has not been well understood, mainly because the available experimental methods are limited. Little has been known, for example, on the contribution of the vibration–vibration (V–V) resonance intermolecular energy transfer in the whole energy transfer process.

When *trans*-stilbene (*t*SB) in solution is photoexcited to a vibrationally excited state of the first excited singlet (S_1) manifold, the generated S_1 *t*SB dissipates its excess energy to the surrounding solvent molecules. By monitoring this cooling kinetics of the photo-generated S_1 *t*SB, we can learn the nature of the solute–solvent energy transfer. We have been studying this cooling process of S_1 *t*SB by using picosecond time-resolved Raman spectroscopy.

After the photoexcitation, the 1570 cm^{-1} Raman band of S_1 *t*SB changes its position in a picosecond time scale [1–3]. We observed the same picosecond time-dependent change for the anti-Stokes/Stokes intensity ratio of the 285 cm^{-1} band [4]. We also observed that the 1570 cm^{-1} peak position changed linearly with the temperature of the bulk solution. This agreed with the result reported by Hester *et al.* [3] qualitatively. From these observations, we concluded that the 1570 cm^{-1} band position can be used as a “picosecond Raman thermometer”.

EXPERIMENTAL

The standard pump-probe technique was used to record the time-resolved Raman spectra of S_1 *t*SB. The chloroform solution of *t*SB was photoexcited at 294 nm and the resonance Raman spectra of S_1 *t*SB was recorded with the 588 nm excitation (repetition rate, 2 kHz; average probe power, 0.1 mW). The details of our picosecond time-resolved Raman spectrometer have been described elsewhere [5].

RESULTS AND DISCUSSION

By using the picosecond time-resolved Raman spectrometer, we measured the cooling kinetics of S_1 *t*SB after the photoexcitation. The results are shown in Figure 1. In the figure, the observed peak positions of the 1570 cm^{-1} Raman band (central C=C stretch) of

FIGURE 1 Observed cooling kinetics of photoexcited S_1 *trans*-stilbene in chloroform (filled square) and in chloroform-d (open circle). Plotted peak positions of the 1570 cm^{-1} band change linearly with the temperatures (see text for the details).

S_1 *t*SB are plotted against the time delays. Because the change in the peak position is proportional to the temperature change [4], the observed time evolution of the peak position is equivalent to the cooling kinetics of S_1 *t*SB. There is no difference observed between the cooling kinetics of S_1 *t*SB in chloroform and that in chloroform-d within the experimental uncertainties.

We reported that the observed cooling rate of S_1 *t*SB has a strong correlation with the thermal diffusivities of the solvents [4]. Thermal diffusivity κ is written as

$$\kappa = \lambda / (c\rho), \quad (1)$$

where λ is the thermal conductivity, c is the heat capacity and ρ is the density. From the known densities and the calculated heat capacities

of the two solvent molecules, the ratio $\kappa(\text{CDCl}_3)/\kappa(\text{CHCl}_3)$ is estimated to be $0.95 \lambda(\text{CDCl}_3)/\lambda(\text{CHCl}_3)$. Because chloroform and chloroform-d have almost the same molecular and electronic structures, the intermolecular interaction should be also very similar. The values $\lambda(\text{CDCl}_3)$ and $\lambda(\text{CHCl}_3)$ are likely to be quite similar. It is highly likely that $\kappa(\text{CDCl}_3)/\kappa(\text{CHCl}_3)$ is close to unity. Then the cooling kinetics of S_1 *t*SB in chloroform and chloroform-d are expected to be similar with each other, as actually observed in the present experiment.

As shown above, the observed cooling kinetics of S_1 *t*SB in chloroform and chloroform-d are well explained by the macroscopic thermal diffusivity κ . No experimental evidence has been obtained that suggests the existence of strong V–V resonance intermolecular energy transfer in the picosecond to sub-picosecond time region. Comparison among wider range of solvents will reveal the more general mechanism of the solute–solvent energy transfer.

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