

# 論文内容の要旨

論文題目

Photoionization of *trans*-Stilbene in Solution  
Studied by Picosecond Time-Resolved Spectroscopy  
(ピコ秒時間分解分光法を用いた溶液中の  
トランス-スチルベンの光イオン化の研究)

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## **1. Introduction**

Photoionization dynamics in solution is affected by properties of solvents, such as polarity and viscosity, and is different from that in the gas phase. In order to understand the photoionization in solution, investigation on the dynamics immediately after photoexcitation, both in polar and non-polar environment, is indispensable. *Trans*-stilbene is a prototype organic molecule that shows many interesting photo-induced dynamics. It is known that photoionization of *trans*-stilbene occurs in solution to generate the *trans*-stilbene radical cation. However, the ionization mechanism still remains controversial.

In the present thesis, I have studied photoionization of *trans*-stilbene in non-polar and polar solvents by using picosecond time-resolved absorption and Raman spectroscopies. The structure and dynamics of a newly found transient species, which is found to exist just after the photoexcitation in acetonitrile and which I identify as a precursor of the *trans*-stilbene radical cation, are discussed. The same two-step photoionization via a precursor is also found to take place in an ionic liquid. I have found an unknown transient species in non-polar solvent, heptane, that shows similar behavior as the precursor in polar solvents. The lifetime of this unknown species is determined to be a nanosecond by transient Raman spectra. Photoionization mechanisms of *trans*-stilbene in polar and non-polar solvents are compared and possible implication of the newly found transient species in the non-polar

solvents is discussed.

## 2. Experimental (Chapter 2)

Sub-picosecond time-resolved visible absorption spectra were measured with a laboratory constructed pump-probe time-resolved ultraviolet-visible absorption spectroscopic system. The wavelength and the power of the pump light were 297 nm and  $\sim 1.2$  mW, respectively. The probe wavelength was 370 to 750 nm. The polarizations of the pump and probe beams were set to make the magic angle ( $54.7^\circ$ ). The instrumental response time was  $\sim 180$  fs. Picosecond time-resolved Raman spectra were measured with a laboratory constructed pump-probe Raman spectroscopic system. The wavelength and the power of pump beam were 300 nm and  $\sim 1$  mW, respectively. The temporal resolution of the instrument was 6 ps.

In order to avoid accumulation of photoproduct and interference from fluorescence from the cell wall, sample solution was circulated to form a flowing thin jet film at the sample position.

### 3. Photoionization of *trans*-stilbene in acetonitrile (Chapter 3)

Picosecond time-resolved visible absorption spectra of *trans*-stilbene in acetonitrile are shown in Figure 1. Strong transient absorption bands are observed at 580 nm and 470 nm. They are known to arise from the  $S_1$  state *trans*-stilbene and the *trans*-stilbene radical cation, respectively. In addition to these well-known bands, I find a new feature around 440 nm (the rectangle in Figure 1), whose decay time constant coincides with that of the rise of the radical cation.

Picosecond time-resolved Raman spectra of *trans*-stilbene in acetonitrile measured with 455nm excitation are shown in Figure 2. The 1 ps spectrum shows a small but significant deviation from the radical cation spectrum observed after 98 ps. The peak position of the  $1599\text{ cm}^{-1}$  band is  $10\text{ cm}^{-1}$

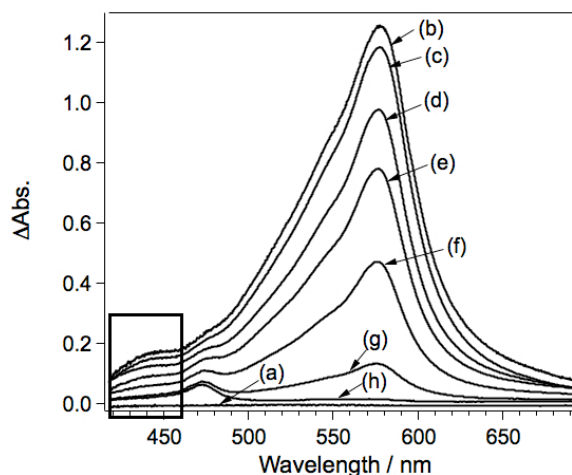


Figure 1. Picosecond time-resolved visible absorption spectra of *trans*-stilbene in acetonitrile measured at delay times (a) -1 ps, (b) 6 ps, (c) 10 ps, (d) 20 ps, (e) 30 ps, (f) 50 ps, (g) 100 ps and (h) 250 ps. Absorption bands surrounded by a rectangle is the new absorption band at 440 nm.

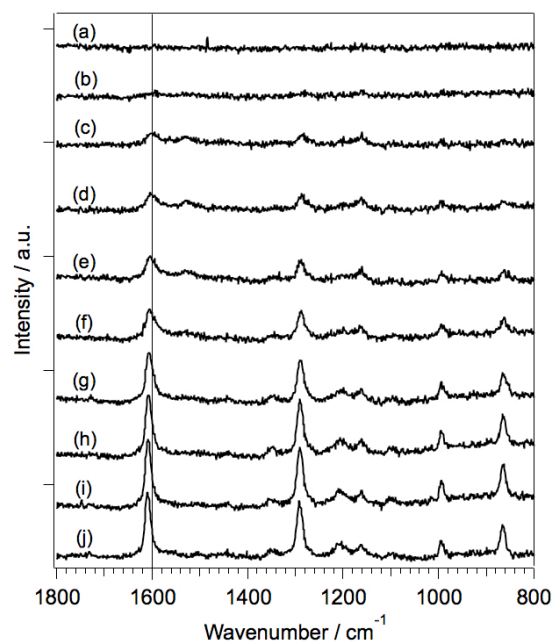


Figure 2. Picosecond time-resolved Raman spectra of *trans*-stilbene in acetonitrile measured at delay times of (a) -5 ps, (b) -2 ps, (c) 1 ps, (d) 3 ps, (e) 8 ps, (f) 18 ps, (g) 38 ps, (h) 58 ps, (i) 98 ps and (j) 1000 ps.

lower than the corresponding band ( $1609\text{ cm}^{-1}$ ) of the radical cation. This deviation indicates that the 1 ps Raman spectrum is contributed dominantly by a precursor of the radical cation. In order to confirm this assignment, the time dependence of the intensity of the  $1599/1609\text{ cm}^{-1}$  band is examined. Figure 3 shows the time dependence of the integrated intensity of the  $1599/1609\text{ cm}^{-1}$  band. This time dependence can not be fitted with a single exponential function; the intensities before 1 ps are too large to be fitted with a single exponential rise. Rather, fitting with a linear combination of two components, one with an instantaneous rise and a 24 ps exponential decay and the other with a 24 ps exponential

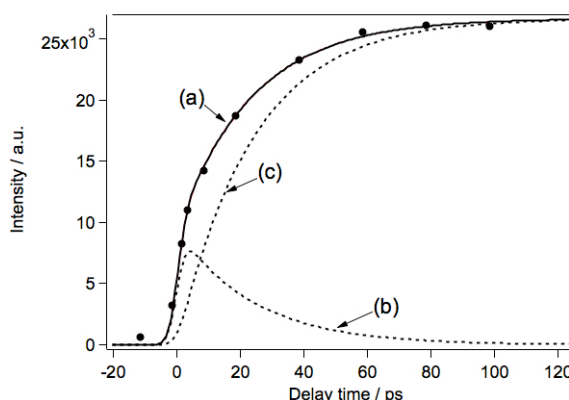


Figure 3. Time dependence of the integrated Raman intensity in the  $1560$  and  $1656\text{ cm}^{-1}$  region (filled circles). The full line (a) indicates the least-squares fitted exponential function,  $A_1 \exp(-t/\tau) + A_2\{1-\exp(-t/\tau)\}$  with  $A_1=27000$ ,  $A_2=9500$ ,  $\tau=24\text{ ps}$ . The dotted lines (b) and (c) show the two components  $A_1 \exp(-t/\tau)$  and  $A_2\{1-\exp(-t/\tau)\}$ , respectively, with  $A_1=27000$ ,  $A_2=9500$ ,  $\tau=24\text{ ps}$ . The two exponential functions are convoluted with the instrumental function represented by a Gaussian with full-width-half-maximum of  $5.5\text{ ps}$ .

rise, reproduce the observed curve very well (full line in Figure 3). This fitting analysis indicates that the 1 ps Raman spectrum is dominated by the bands due to the precursor of the radical cation. Extracted genuine Raman spectrum of the precursor is shown in Figure 4 in comparison with that of the radical cation observed at 1000 ps. Corresponding to the radical cation peaks at  $1609$ ,  $1349$ ,  $1291$ ,  $1207$ ,  $1162$ ,  $994$  and  $866\text{ cm}^{-1}$ , the precursor spectrum shows similar but appreciably broader peaks at  $1599$  and  $1285\text{ cm}^{-1}$ . The precursor may well be an ion pair that holds an ejected electron still around the cation.

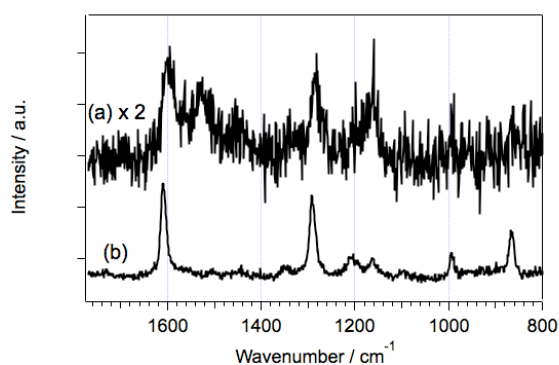


Figure 4. Raman spectra of (a) the ion-pair precursor plus the  $S_1$  state *trans*-stilbene and (b) the radical cation.

#### 4. Photoionization of *trans*-stilbene in a room-temperature ionic liquid (Chapter 4)

In order to investigate whether or not the two-step photoionization occurs in other polar-solvents, the picosecond time-resolved absorption and Raman spectra are measured in the solution of a room-temperature ionic liquid, 1-ethyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide (emimTFSI).

Picosecond time-resolved visible absorption spectra of *trans*-stilbene in emimTFSI are measured. The bands at  $440\text{ nm}$ , which I assign to the precursor of radical cation in acetonitrile, are also observed immediately after photoexcitation as well as the  $S_1$  state *trans*-stilbene. The rise of *trans*-stilbene radical cation band is also observed. Picosecond time-resolved Raman spectra of *trans*-stilbene in emimTFSI measured at  $-10$ ,  $3$ ,  $5$ ,  $10$  and  $100\text{ ps}$  with  $450\text{ nm}$  excitation are shown in Figure 5. The band at  $1595\text{ cm}^{-1}$  shifts to higher wavenumbers with increasing delay time and eventually reaches  $1607\text{ cm}^{-1}$  at  $100\text{ ps}$ , which is consistent with the observation in acetonitrile with

455 nm excitation. The similarity of dynamics in emimTFSI and acetonitrile implies that the photoionization of *trans*-stilbene in emimTFSI proceeds with the same two-step mechanism via precursor as in acetonitrile.

### 5. Photoionization of *trans*-stilbene in heptane (Chapter 5)

The photochemical reaction dynamics of *trans*-stilbene in a non-polar solvent, heptane is also studied by picosecond time-resolved absorption and Raman spectra. As expected, the  $S_1$  state *trans*-stilbene is observed while the band at 470 nm assigned to the *trans*-stilbene radical cation is not (Figure 6). However, the band at 440 nm, which I assign the precursor of radical cation in polar solvents, is also observed. The assignment of the band is made with reference to the picosecond time-resolved Raman spectra with 455 nm excitation (Figure 7). The transient Raman spectrum at early delay time, 3 ps, resembles the precursor spectrum observed in polar-solvents with a strong broad peak at  $1599\text{ cm}^{-1}$ . However, in contrast to the observation in acetonitrile, where spectra gradually transform into the radical spectrum, the precursor-like spectra remain even after 100 ps, with a peak shift smaller than  $4\text{ cm}^{-1}$ . This observation may indicate the formation of ion-pair like structure in non-polar solvents as an intermediate for geminate recombination.

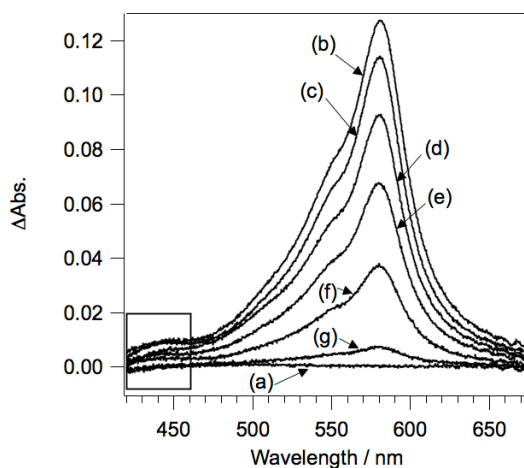


Figure 6. Picosecond time-resolved visible absorption spectra of *trans*-stilbene in heptane measured at delay times (a) -10 ps, (b) 10 ps, (c) 30 ps, (d) 50 ps, (e) 80 ps, (f) 130 ps and (g) 280 ps. Absorption bands surrounded by a rectangle is the new absorption band at 440 nm.

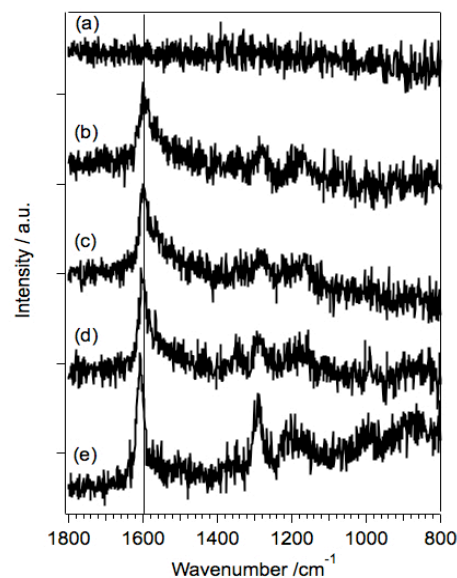


Figure 5. Picosecond time-resolved Raman spectra of *trans*-stilbene in emimTFSI measured at delay times of (a) -10 ps, (b) 3 ps, (c) 5 ps, (d) 10 ps and (e) 100 ps.

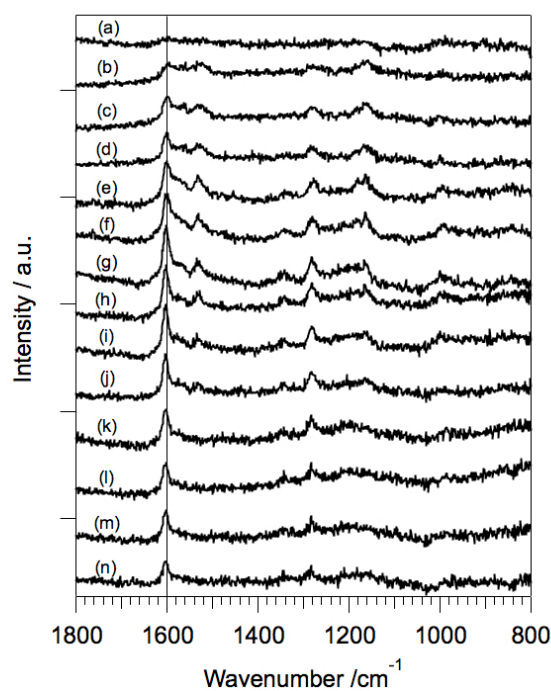


Figure 7. Picosecond time-resolved Raman spectra of *trans*-stilbene in heptane measured at delay times of (a) -3 ps, (b) 0 ps, (c) 3 ps, (d) 5 ps, (e) 10 ps, (f) 20 ps, (g) 40 ps, (h) 60 ps, (i) 80 ps, (j) 100 ps, (k) 300 ps, (l) 500 ps, (m) 700 ps and (n) 1000 ps.