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Anomalous Lifetime Shortening of S_1 trans-Stilbene in Carbon Tetrachloride as Revealed by Picosecond Time-resolved Raman, Absorption, and Fluorescence Spectroscopies

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The lifetime of the first excited singlet state of trans-stilbene (S_1 tSB) in carbon tetrachloride at room temperature is determined to be 3.1±0.2 ps with the use of time-resolved Raman, absorption, and fluorescence spectroscopies. The lifetime of 3.1 ps is shorter than the shortest value ever reported by an order of magnitude. The steady state photoirradiation of tSB in carbon tetrachloride shows that the decomposition of the tSB molecule is the primary cause of the lifetime shortening.

The dynamics of the first excited singlet state of trans-stilbene (S_1 tSB) has been well characterized by means of time-resolved UV-VIS absorption, fluorescence, and Raman spectroscopies. The tSB molecule is known to isomerize from the trans to the perpendicular configuration in the S_1 state and eventually relaxes either to the trans or cis isomer in the ground state.[1, 2] The rate of the isomerization in solution is much larger than the radiative decay rate (6 x 10^8 s^{-1})[3] and the S_1 lifetime is primarily determined by this isomerization rate, at least for all the solutions of tSB that have been studied so far. Thus, the lifetime of S_1 tSB is heavily dependent on the nature of the solvent which affects the rate of isomerization. Elaborate investigations have been performed so far to study the influence of the temperature, viscosity, or chemical characteristics of the solvent on the solute S_1 lifetime and hence to elucidate the role of the solvent in the isomerization reaction.[4-7] The pressure dependence of the S_1 lifetime in the ethane solution shows a broad minimum which is ascribed to Kramer's turnover.[8]

To the best of the authors' knowledge, all the S_1 lifetimes of trans-stilbene known thus far are longer than 30 ps (acetonitrile[9]) in room temperature solutions. In this paper, however, we report that the lifetime of S_1 tSB in carbon tetrachloride is 3.1 ps, shorter than the previously reported shortest lifetime by an order of magnitude. This has been confirmed with time-resolved Raman, absorption, and fluorescence spectroscopies.

Our transform-limited picosecond time-resolved Raman spectrometer has been described elsewhere in detail.[10, 11] In short, the output form a synchronously pumped dye laser (Spectra Physics 3520, R6G, 588 nm, 82 MHz) was amplified in a two stage dye amplifier with the use of the second harmonic of a cw Nd:YAG regenerative amplifier (Spectra Physics 3800RA, 532 nm, 2 kHz, 500 mW). The second harmonic (294 nm, 2 kHz, 2-5 mW) of the dye amplifier output (588 nm, 2 kHz, 10-20 mW) was used for pumping, while the residual visible light was used for probing. The timing between the pump and probe pulses was regulated with a computer controlled optical delay unit. The cross correlation time between the pump and probe pulses was 4.5 ps. The spectral width of the probe light was 3.5 cm^{-1}. The Raman scattered light was analyzed with a single

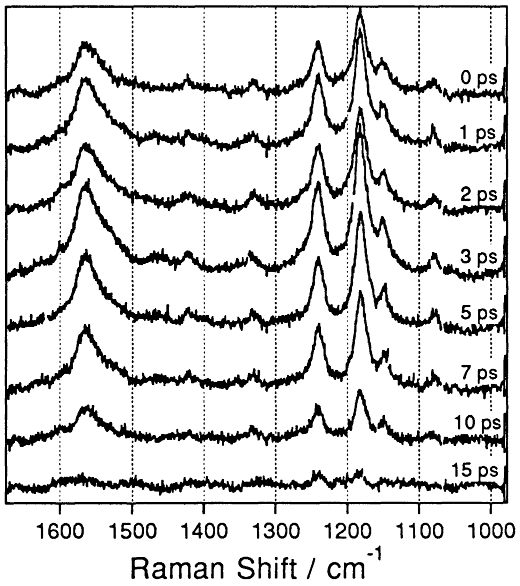

Fig. 1. Time-resolved Raman spectra of S_1 trans-stilbene in carbon tetrachloride (concentration, 3×10^{-3} mol dm^{-3}). The time delays between the pump (294 nm) and the probe (588 nm) pulses are shown in the right.

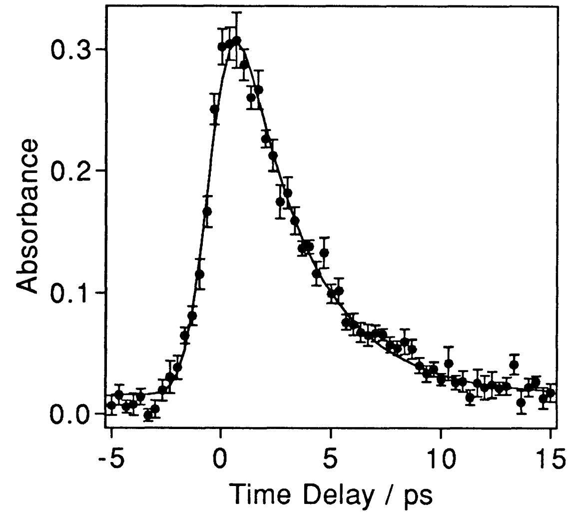

Fig. 2. Temporal profile of the S_n-S_1 absorption of trans-stilbene in carbon tetrachloride. The error bars were estimated from the standard deviations from ten independent measurements. See the text for details.

spectrograph (Instruments SA, HR 320) and detected with a CCD detector (Princeton Instruments LN/CCD-1024 TKB). Typical exposure time for the Raman measurement was 10 min.

For obtaining the time dependent S_n-S_1 absorption with a better time resolution, we modified the above mentioned picosecond apparatus. We compressed the dye laser pulses with a polarization preserving single mode optical fiber (New Port F-SPV, 10 m) and a grating pair (Spectrogon, type PC, 2400 gr/mm). The compressed pulses were amplified in the same way as mentioned above and the second harmonic of the amplified output (294 nm) and the residual visible light (588 nm) were used for pumping and probing, respectively. The angle between the polarizations of the two pulses was set to be 54.7° so that the effect of the rotational reorientation was eliminated. The cross correlation time between the pump and probe pulses was estimated to be 1.7 ps by the least squares fitting of the rise of the S_n-S_1 absorption signal of trans-stilbene and p-terphenyl, with a Gaussian function assumed for the cross correlation trace.

The time-resolved fluorescence spectra were obtained with a Hamamatsu streak camera (modified C2909)[12] with 10 to 12 ps instrumental response times. The excitation was at 294 nm (the same light source that was used for the pumping in the time-resolved Raman set up).

Carbon tetrachloride (Dotite, Spectrosol) and trans-stilbene (Wako Chemicals) were used as received.

The time-resolved Raman spectra of S_1 trans-stilbene in carbon tetrachloride (2×10^{-3}mol dm^{-3}) are shown in Fig. 1. The time t=0 was set to the moment of the maximum overlap between the pump and the probe pulses. All the observed features are identical with those established as the Raman bands of S_1 tSB.[13, 14] The signal intensities of the observed S_1 Raman bands are decreased at 10 ps and is almost diminished at 15 ps. Although the intensity changes as the time delay increases, the spectral feature keeps unaltered throughout the whole recorded time region. It is obvious from the figure that the S_1 state is actually formed and decays in several picoseconds in carbon tetrachloride.

In order to obtain more precise decay dynamics, the S_n-S_1 absorption profile was measured at 588 nm with the compressed pump and probe pulses. The results are shown in Fig. 2. In the figure, each circle represents an observed value, while the solid line is the best fitted curve. The model function for the fitting was a convolution of a single exponential decay function with a Gaussian cross correlation trace between the pump and probe pulses. The best fit was obtained when the decay time constant is 3.1±0.2 ps and the cross correlation time is 1.7±0.1 ps. It should be noted that there is no strong evidence which disfavors the single exponential decay of the S_1 trans-stilbene even if the lifetime is as short as 3.1 ps.

To further confirm the observation of the exceptionally short lifetime, time-resolved fluorescence spectra were measured with the streak camera. The fluorescence spectra from the photoexcited trans-stilbene in carbon tetrachloride agreed well with those from the heptane or chloroform solution. The deconvolution of the obtained decay curve with the instrumental response function gave the decay constant of 3.5 ps (Fig. 3a), which is in a good agreement with the lifetime determined by transient absorption spectroscopy.

As mentioned above, the S_1 lifetime of 3.1 ps is shorter than the reported shortest lifetime by an order of magnitude. A possible cause for the lifetime shortening is the acceleration of the intersystem crossing to a triplet state by the external heavy atom effect. However, the S_1 lifetime in chloroform, which has three chlorine atoms instead of four for carbon tetrachloride, is 49 ps (Fig. 3b) and is much longer than that in carbon tetrachloride. This means that the external heavy atom effect is not the primary cause for the S_1 lifetime shortening in carbon

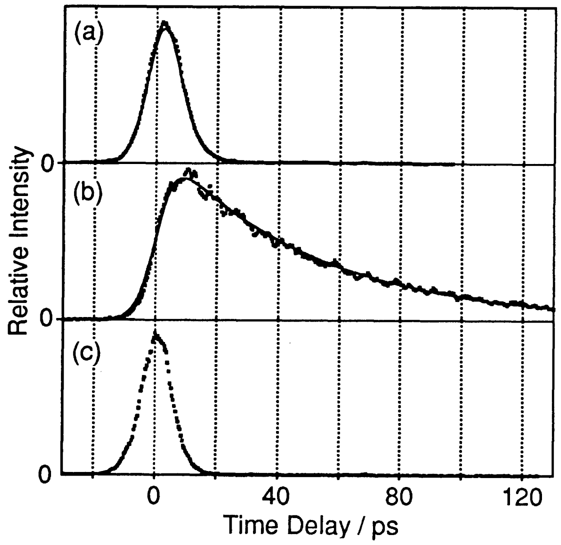

Fig. 3. Decay curves of the fluorescence at room temperature from trans-stilbene (a) in carbon tetrachloride probed at 355 nm and (b) in chloroform at 350 nm. The instrumental response function is also shown in (c). Excitation wavelength was 294 nm. Dotted curves represent the observed intensity changes while the solid traces show the best fitted convolutions of single exponential decay functions with the instrumental response function.

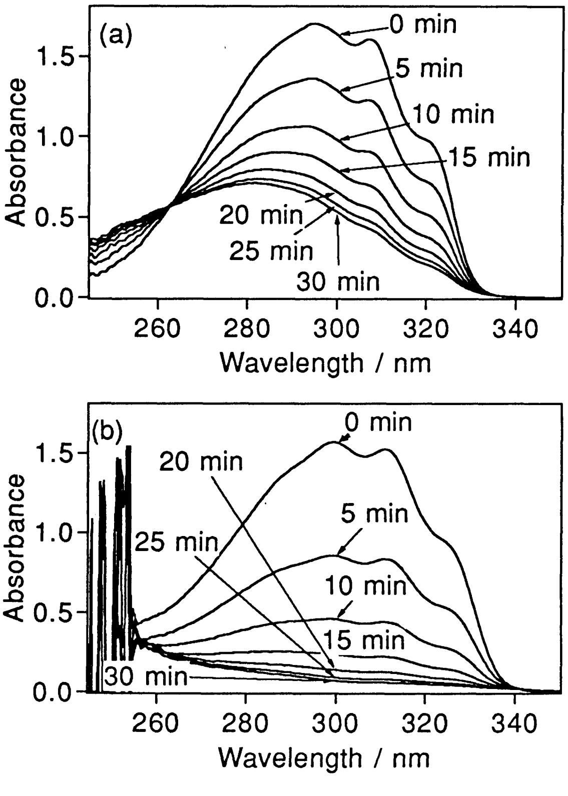

Fig. 4. Change of the UV-VIS spectra of trans-stilbene with the irradiation of the light of 300 nm or longer in a heptane solution (a), and in a carbon tetrachloride solution (b).

tetrachloride. It is also unlikely that the rate of isomerization increases by more than an order of magnitude on going from the other solvents to carbon tetrachloride.

To know the steady state photochemical properties, we irradiated the heptane and carbon tetrachloride solutions of tSB by using a Xe lamp with a filter which transmits the light of 300 nm or longer. The results are shown in Fig. 4. In the heptane solution, the absorption maximum due to the trans isomer at around 300 nm decreases as the irradiation continues, while the absorption from the cis isomer at around 250 nm increases (Fig. 4a). There is an isosbestic point observed in the figure, indicating that there are only two components in the spectrum, trans and cis. It was confirmed for the heptane solution that the trans isomer is converted to the cis isomer through photoisomerization. In the carbon tetrachloride solution, however, only the decrease of the trans isomer is observed (Fig. 4b); no cis isomer is formed with the irradiation. Because the photoproducts in the carbon tetrachloride solution show the absorption in the wavelength region shorter than the original stilbene absorption, it is probable that the products have shorter conjugated systems than stilbene. It has been known that some aromatic hydrocarbon molecules react with solvent carbon tetrachloride after the photoexcitation.15) We measured the ground state UV-VIS spectra and found no obvious feature suggesting the formation of stilbene-carbon tetrachloride complex in the ground state. It is most likely that S_1 tSB interacts strongly with carbon tetrachloride and decomposes with a time constant of about 3 ps. We conclude that the primary cause of the newly found anomalous lifetime shortening of S_1 tSB in carbon tetrachloride is a new type of photochemical reaction for S_1 tSB which involves the solvent carbon tetrachloride molecule (or molecules) and results in the decomposition of tSB.

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