Picosecond Transient Infrared Spectrum of Electronically Excited *trans*-Stilbene in Acetonitrile and Excited Molecular Structure

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The picosecond transient infrared spectrum of the lowest excited singlet (S_1) state of *trans*-stilbene in an acetonitrile solution has been recorded in the fingerprint region. Several absorption bands (absorption coefficients $\varepsilon \lesssim 100$) attributable to in-plane vibrations of the S_1 species have been observed. A minor contribution of a polarized structure to the S_1 state is suggested.

Stilbene is an important compound as a prototype system of photoinduced *trans-cis* isomerization, and its photophysical and photochemical processes have been extensively studied from various aspects of ultrafast spectroscopy. It is of fundamental importance to reveal molecular structures of electronically excited states of *trans*-stilbene, for discussions of photoisomerization mechanisms. Various attempts have been made to obtain the structural information from vibrational analyses of transient Raman[1-4] and resonance Raman[5] spectra in solution and from those of electronic spectra in the gas phase.[6-8] In the gas phase, the equilibrium structure of the lowest allowed electronically excited (S_1) state is considered to possess a center of symmetry.[6,7] On the other hand, information on the excited molecular structure in solution is scant. We may get a much deeper insight into the molecular structure of *trans*-stilbene in the S_1 state, if we can observe the infrared spectrum of this species. Unfortunately, the experimental technique of ultrafast transient infrared spectroscopy is in general much more difficult than that of the transient Raman spectroscopy. So far there have been only very limited number of experimental reports on ultrafast infrared spectroscopy, especially in the fingerprint region.[9-12] The author has recently developed an experimental setup for picosecond transient infrared spectroscopy in the fingerprint region,[10,12] and presently has succeeded in recording a transient infrared spectrum of *trans*-stilbene in the S_1 state in solution. The results and preliminary discussion, including some implications about the molecular structure, are presented in this letter.

The experimental apparatus for the transient infrared spectroscopy was basically the same as that already reported elsewhere.[10,12] Only essential points are described here. Tunable picosecond infrared (probe) pulses in the fingerprint region were obtained by two-stage difference frequency mixing of outputs from an amplified picosecond dye laser (552 – 575 nm) and a Nd:YLF regenerative amplifier (1053 nm). The spectral width of the probe radiation was ≈8 cm^{-1}. The wavenumber of the infrared probe radiation was scanned by changing the wavelength of the dye-laser oscillation. The second harmonic of the amplified dye laser (ultraviolet) was used to pump the sample to the electronically excited state. This pump radiation was tuned to the $S_1 \leftarrow S_0$ transition of the sample. One amplified dye laser was used for generating the infrared probe light as well as the ultraviolet pump radiation. Consequently, the pump wavelength changes as the probe wavenumber is scanned. However, the scanning range of the pump wavelength (276 – 287 nm) is much narrower than the electronic absorption band-width of the sample solution. Effects of the pump-wavelength change may be hence no more than variation in the pumping efficiency caused by a change of the pump-pulse energy. The pump energy per pulse was 0.5 – 3 μJ, depending on the wavelength. The cross-correlation time between the pump and probe pulses was ≈4 ps, which determined the temporal resolution. The measurement was done at a delay time of 4 ps between the pump and probe pulses. The transient absorption signal was obtained by a method based on optically heterodyned detection of absorption anisotropy (OHDAA) which the author had developed recently.[12]

The sample solution was circulated through a BaF_2 flow cell (optical path length 0.015 mm) using a magnet gear pump. Acetonitrile was adopted as a solvent. The concentration of the sample solution was ≈3.4 × 10^{-2} mol dm^{-3}. Commercially available *trans*-stilbene (special reagent grade) and acetonitrile (liquid chromatography grade) were used without further purification. The infrared absorption spectrum of the sample in the ground electronic (S_0) state was measured for the same solution by a JASCO FT/IR-420 Fourier transform spectrophotometer.

In Figure 1, the observed picosecond transient infrared absorption spectrum of *trans*-stilbene in an acetonitrile solution is shown, together with the S_0-state spectrum. The transient infrared measurement was not successful around 1450 cm^{-1} and 1380 cm^{-1} because of strong absorption by an analyzing polarizer (polyethylene substrate) used for the OHDAA. Since the pump energy is dependent on the probe wavenumber, the ordinate scale

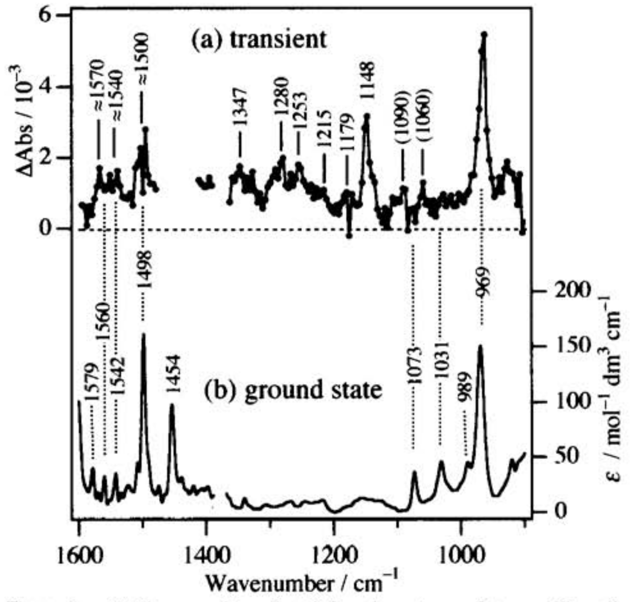

Figure 1. (a) Picosecond transient infrared spectrum of *trans*-stilbene in acetonitrile solution. Wavenumbers of bands attributed to the S_1 state is indicated above the trace. (b) FT-IR spectrum of *trans*-stilbene in the S_0 state in acetonitrile solution. The solvent bands are numerically removed.

of the transient spectrum should not be regarded as a quantitative measure.

Assignments of the infrared bands of *trans*-stilbene in the S_0 state have been well established.[13-15] The strongest band in the S_0 spectrum at 969 cm^{-1} is due to an out-of-plane vibration of the olefinic part. The molar absorption coefficient (ε) of this band is ≈ 150 mol^{-1} dm^3 cm^{-1} at the maximum. Principal features above 1000 cm^{-1} observed in the S_0 spectrum in Figure 1(b) have been assigned to in-plane vibrations of the phenyl groups. Several transient bands in Figure 1(a) are attributable to the bleached absorption by the S_0 species. The transient infrared absorption signal in the OHDAA depends on the angle (θ) between transition moments of the electronic and infrared transitions: a vibrational transition with $0 \leq \theta < 54.7°$ (parallel absorption band) gives a signal of an opposite sign to that with $54.7° < \theta \leq 90°$ (perpendicular absorption band).[12] In addition, the signal due to the bleached absorption by the ground state has an opposite sign to that due to the induced absorption by the excited state. In Figure 1(a), the parallel bands of the excited species or the perpendicular bands of the ground state give positive (upward) peaks. Since the $S_1 \leftarrow S_0$ electronic transition of *trans*-stilbene has an in-plane transition moment, the out-of-plane vibrations should give perpendicular bands. In the transient spectrum, a strong positive band is observed at ≈ 965 cm^{-1}, approximately the same position with the S_0-state absorption band in Figure 1(b). This band is reasonably explained as a bleached absorption due to the out-of-plane vibration of the S_0 state.

In addition to the bleached absorption bands, several reproducible bands are observed, which can be attributed to the induced absorption by the S_1 species. All the prominent induced absorption bands are positive, and are assigned to in-plane vibrational modes. At ≈ 1500 cm^{-1} a band with a sharp dip (negative peak) in the center (1498 cm^{-1}) is observed. The dip is explained as a bleached absorption due to an in-plane phenyl-group vibration of the S_0 species. The positive band with a little broader bandwidth may be attributed to a similar phenyl-group mode of the S_1 species, at nearly the same position with the S_0 band. The strong induced band at 1148 cm^{-1} may be assigned, from its frequency and intensity, to a hybrid mode of the C–Ph stretch and the olefinic CH in-plane bending of the S_1 species.

We should note weak positive absorption bands observed at ≈ 1570, ≈ 1250, and ≈ 1180 cm^{-1} (a sharp dip at 1175 cm^{-1} is not reproducible and may be due to a shot noise). These wavenumbers nearly coincide with those of strong Raman bands of the S_1 species.[1-4] It has been established that these strong Raman bands are attributed to the olefinic in-plane vibrations.[3,4,7] When the equilibrium molecular structure retains the center of symmetry, the mutual exclusion should hold among the infrared and Raman bands. If the weak infrared bands are due to the same vibrational modes as those giving the strong Raman bands, it means a breakdown of the mutual exclusion and suggests a molecular structure without a center of symmetry in acetonitrile solution. Recently, a polarized structure of the S_1 state of *trans*-stilbene (such as $C^{\delta+}{=}C^{\delta-}$ on the olefinic carbon atoms) has been discussed.[16,17] As a related phenomenon, it is well known that bianthryl, a hydrocarbon compound with a symmetric structure in the ground state, lowers the symmetry and becomes polarized in the excited electronic state in polar solvents.[18-20] If there is such a contribution of the polarized structure to the S_1 state of *trans*-stilbene, the mutual exclusion may break down. The present observation possibly indicates the contribution of the polarized structure. The three weak infrared bands have not been observed in an *n*-heptane solution. This result seems to be consistent with a general tendency that polarized structures are not stable in non-polar solvents. On the other hand, although the author presently considers that there definitely exists a positive absorption band at ≈ 1570 cm^{-1}, special care should be taken on treatment of this band, since spectral structures seen around the band, due probably to the bleached absorption (1560 and 1542 cm^{-1}), prevent straightforward determination of the peak position. To check further the reproducibility of the three bands may be also needed for more conclusive discussion.

Next we discuss the transient absorption intensity. Molar absorption coefficients of all the S_1 transient bands may be $\varepsilon \lesssim$ 100 mol^{-1} dm^3 cm^{-1}, considering that ε of the strongest bleached absorption band at 969 cm^{-1} is estimated to be ≈ 150 mol^{-1} dm^3 cm^{-1} from the ground-state spectrum. If the polarized structure significantly contributes to the S_1 state, the C=C stretch (≈ 1570 cm^{-1}) and C–Ph stretch (≈ 1180 cm^{-1}) should give very strong transient infrared bands.[21] However, their observed band intensities are rather weak (probably $\varepsilon < 50$ mol^{-1} dm^3 cm^{-1}). Therefore, contribution of the polarized structure to the S_1 state is considered to be, if there is, quite small.

In conclusion, the picosecond transient infrared spectrum of *trans*-stilbene in the S_1 state in solution has been successfully obtained in the fingerprint region. A minor contribution of a polarized structure, with no center of symmetry, to the S_1 state in acetonitrile solution has been suggested. Further investigation may be needed on this point. Assignments of other bands, comparison with the spectrum obtained in a non-polar solvent, and other details will be discussed elsewhere.

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