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Picosecond Infrared Spectroscopy of Electronically Excited *trans*-Stilbene in Solution in the Fingerprint Region

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The picosecond transient infrared spectrum of the lowest excited singlet (S_1) state of *trans*-stilbene in solution has been recorded in the fingerprint region. Several absorption bands (molar absorption coefficients $\epsilon \lesssim 100$ mol^{-1} dm^3 cm^{-1}) attributable to in-plane vibrational modes of the S_1 species have been observed. The tentative assignments of the vibrational bands are described. Major spectral features are common between the infrared spectrum taken in *n*-heptane solution and that in acetonitrile solution. The mutual exclusion rule between infrared and Raman spectra of the S_1 species seems to hold in *n*-heptane solution, which suggests a molecular structure with a center of symmetry. On the other hand, additional weak infrared bands are found in acetonitrile, whose positions coincide with those of the strong Raman bands of the S_1 species. This result suggests that the S_1 species in acetonitrile is distorted slightly from the centrosymmetric structure. Polarized structures of excited species stabilized in polar solvents are discussed in relation to the distorted S_1 *trans*-stilbene in acetonitrile.

1. Introduction

Photophysical and photochemical processes of *trans*-stilbene (abbreviated as tS) have been extensively studied from various aspects of ultrafast spectroscopy, as a prototype system of photoinduced trans-cis isomerization.[1] It is of fundamental importance to reveal molecular structures of electronically excited states of this molecule, in order to discuss photoisomerization mechanisms. Various attempts have been made to obtain information on the structure of the lowest allowed electronically excited singlet (S_1) state, from vibrational analyses of electronic spectra in the gas phase[2−5] and from those of resonance Raman[6] and transient Raman[7−11] spectra in solution. In the gas phase, the equilibrium structure of the S_1 state is considered to possess a center of inversion symmetry, which is also the case in the ground electronic (S_0) state.[2,5] Since the first two reports in 1983,[7,8] the transient Raman spectrum of tS in the S_1 state in solution is very well studied,[7−16] and the vibrational assignments of the totally symmetric Raman bands are quite well established.[3,4,9,10,12,17,18] However, information on the excited molecular structure in solution is still scant. One of the reason for very limited structural information is that vibrational modes other than those belonging to the totally symmetric species are not observed.

Infrared absorption may be regarded as a complimentary method to Raman scattering in the field of vibrational spectroscopy. It is expected that knowledge about molecular structure of tS in the S_1 state is greatly improved if an infrared spectrum of this species is recorded. In addition, infrared spectroscopy is more advantageous than Raman spectroscopy in several points. For example, fluorescence from the sample and/or impurity does not interfere with the infrared measurements; polarization dependent (dichroism) measurements potentially provide direct information on molecular structures. In order to obtain the infrared spectrum of tS in the S_1 state we need a picosecond temporal resolution for the absorption measurement. However, development of ultrafast infrared spectroscopy[19−30] has been much behind in comparison with ultrafast Raman spectroscopy. Experimental reports on ultrafast infrared spectroscopy in the fingerprint region have been especially limited, which has become possible only in the past few years.[25−30] The author has recently developed an experimental setup for the picosecond transient infrared spectroscopy in the fingerprint region[26,29] and presently has succeeded in recording a transient infrared spectrum of tS in the S_1 state in solution. Some suggestion about the excited molecular structure has been obtained from the experimental results (the infrared spectrum in acetonitrile has been already briefly reported[30]). In this paper, detailed description of the spectra, including band assignments and comparison between spectrum in acetonitrile and that in *n*-heptane, is presented.

2. Experimental

The experimental apparatus for the transient infrared spectroscopy was basically the same as that already reported elsewhere.[26,29] Only essential points are described here. A synchronously pumped dye laser (gain medium rhodamine 560) was excited by the second harmonic output from a cw mode-locked Nd:YLF laser. The output from the dye laser was amplified by a dye amplifier (gain medium rhodamine 590) excited by the second harmonic output from a cw Nd:YLF

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regenerative amplifier at a repetition rate of 1 kHz. Tunable picosecond infrared (probe) pulses in the fingerprint region were obtained by two-stage difference frequency mixing of the output from the amplified dye laser and the fundamental output from the regenerative amplifier. The wavenumber of the infrared probe radiation was scanned by changing the wavelength of the dye laser oscillation (552−575 nm). The spectral width of the probe radiation was ∼8 cm^{-1}. The second harmonic of the amplified dye laser (ultraviolet) was used to pump the sample. This pump radiation was tuned to the $S_1 \leftarrow S_0$ transition of the sample.[31] 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 width of the electronic absorption band of the sample solution. Effects of the pump wavelength change may be hence no more than variation in the pumping efficiency caused principally by a change of the pump pulse energy. The pump energy per pulse was 0.5−3 μJ, depending on the wavelength. On the transient infrared measurements, the whole spectral wavenumber region was divided into several small regions (typically ca. 100 cm^{-1} per one small region), and the pieces of the spectrum recorded in small regions were rearranged to give a spectrum of the whole wavenumber region. The ordinate scale of each piece of spectrum was adjusted by multiplying a factor so as to connect smoothly to the next pieces at the borders. Other corrections of the intensity data, such as normalization against the pump pulse energy, were not made. The ordinate scale of the transient spectrum shown in the following should not be regarded as a quantitative measure, since the population of the transient species is dependent on the pump pulse energy as well as the pump wavelength, both of which change as the probe frequency is scanned.

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. From the picosecond anti-Stokes Raman spectroscopic study, it has been shown that the observed S_1 species is for the most part the vibrationally ground state about the Franck−Condon active modes, with a minor contribution from the lowest vibrationally excited state.[32,33]

The transient absorption signal was obtained by a method based on optically heterodyned detection of absorption anisotropy (OHDAA), which the author had developed recently.[29] By the OHDAA method we have in general much higher sensitivity in recording a transient infrared spectrum than by the conventional method. Both the infrared probe and the ultraviolet pump fields incident on the sample were linearly polarized. The angle between the probe and pump electric fields was ∼45°. The polarization direction of the analyzing polarizer in front of the infrared detector was set at ∼3° from perpendicular to the incident probe polarization. Since the OHDAA method is based on anisotropy of transient absorption and therefore effects of reorientational relaxation of the transient species contribute to the decay of the signal, kinetic traces do not directly reflect temporal changes of population of the transient species. Hence, in the present study, only wavenumber scans are performed and we do not discuss the temporal behavior of the transient.

Pulse-to-pulse fluctuation of the signal (after divided electronically by the reference signal[26]) was typically 2−10%, or sometimes even up to 20%. Accumulation of the signal in many hours was therefore essential to extract tiny absorption changes. One wavenumber scan was done by accumulating the infrared intensity data of typically 20 000 pulses for each spectral point. Such wavenumber scans were repeated for 5 to 10 times to check reproducibility, and the obtained spectra were averaged. The total measurement time required for obtaining one transient infrared spectrum shown in the following was about 15 h. Experimental errors of the transient absorption signals were typically $0.5 - 1 \times 10^{-3}$ Abs.

The sample solution was circulated through a BaF_2 flow cell using a magnet gear pump. *n*-Heptane and acetonitrile were adopted as solvents. Commercially available acetonitrile, *n*-heptane (liquid chromatography grade), and *trans*-stilbene (special reagent grade) were used without further purification. The concentration of the sample solution and the optical path length of the cell were $\sim 1.7 \times 10^{-2}$ mol dm^{-3} and 0.1 mm, respectively, for *n*-heptane solution and $\sim 3.4 \times 10^{-2}$ mol dm^{-3} and 0.015 mm, respectively, for acetonitrile solution. The infrared absorption spectra of the samples in the ground electronic (S_0) state were measured for the same solutions by a JASCO FT/IR-420 Fourier transform spectrophotometer.

3. Results and Discussion

3.1. Description of the Infrared Spectra and Assignments. In the OHDAA method, the transient absorption signal depends on the angle (θ) between transition moments of the electronic (for the pumping process) and the vibrational (for the probing process) transitions. A vibrational transition with $0° \le \theta < 54.7°$ (parallel absorption band) gives a signal of an opposite sign to that with $54.7° < \theta \le 90°$ (perpendicular absorption band).[29] The sign of the absorption signal also depends on the relation between the polarization directions of the pump and probe fields. 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 the figures shown in the following, the parallel bands of the excited species (or the perpendicular bands of the ground state) give positive (upward) peaks.

The $S_1 \leftarrow S_0$ electronic transition of tS is associated with an in-plane transition moment.[34] It has been reported that directions of the transition moments are slightly different among vibronic bands.[35,36] The transition moment of the 0−0 vibronic transition is considered to be nearly parallel to the single bonds between the phenyl groups and the olefinic carbons.[34] At around 280 nm, which corresponds to the present pump wavelength, the transition moment is inclined at 20−30° from that of the 0−0 transition, probably closer to the direction of the olefinic C═C double bond.[35,36] Because of the in-plane $S_1 \leftarrow S_0$ electronic transition moment, the out-of-plane vibrational modes should give perpendicular infrared absorption bands (unless an extraordinary structural distortion occurs). Equivalently, all of the parallel absorption bands should be attributed to in-plane vibrational modes. On the other hand, both parallel and perpendicular absorption bands are possible for the in-plane vibrations. From the direction of the electronic transition moment mentioned above, it is expected that, if we assume the C_{2v} local symmetry for the phenyl groups, in-plane phenyl group vibrational modes of the a_1 and b_2 symmetry species appear as parallel and perpendicular absorption bands, respectively.

Picosecond transient infrared absorption spectra of tS in *n*-heptane and in acetonitrile are shown in Figures 1B and 2B, respectively. Measurements are not successful around 1450 cm^{-1} and around 1380 cm^{-1} because of strong absorption by the polyethylene substrate of the analyzing polarizer needed for the OHDAA method. The static infrared spectra of the ground electronic state are also shown in Figures 1A and 2A. In each

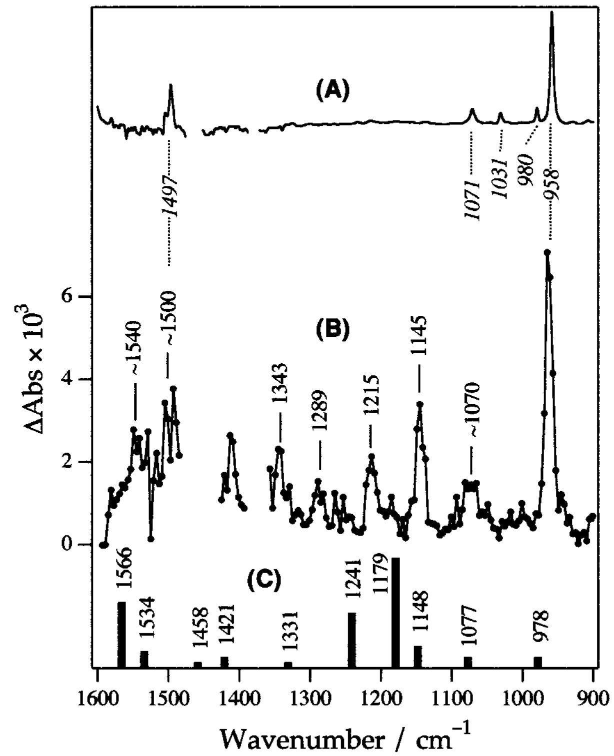

Figure 1. (A) Infrared spectrum of *trans*-stilbene in the S_0 state in *n*-heptane solution. The solvent bands are numerically removed. Wavenumbers of bands attributed to the S_0 species are indicated in italic. (B) Picosecond transient infrared spectrum of *trans*-stilbene in *n*-heptane solution. Wavenumbers of bands attributed to the S_1 species are indicated in the upright letters. (C) Representative Raman spectral pattern of *trans*-stilbene in the S_1 state in *n*-hexane solution.[9,13]

figure, the bands due to the solvent are numerically removed. Typical Raman spectral patterns of tS in the S_1 state are shown as bar graphs in Figures 1C and 2C.

3.1.1. Bleached Absorption Bands due to the Ground Electronic State. Static Spectra. Assignments of major infrared bands of ground-state tS are quite well established.[12,37−39] The strongest band in Figures 1A and 2A at ~960 cm^{-1} is attributed to the CH out-of-plane vibration of the olefinic moiety. The molar absorption coefficient of this band is $\epsilon \approx 250$ mol^{-1} dm^3 cm^{-1} at the maximum in *n*-heptane and $\epsilon \approx 150$ mol^{-1} dm^3 cm^{-1} in acetonitrile. The band at ~980 cm^{-1} is assigned to the out-of-plane vibrational mode of the phenyl ring (mode 4 in Wilson's numbering[40]). All of the principal features above 1000 cm^{-1} are attributed to phenyl group in-plane vibrations (~1600 cm^{-1}, mode 8*a*; ~1500 cm^{-1}, mode 19*a*; ~1450 cm^{-1}, mode 19*b*; ~1070 cm^{-1}, mode 18*b*; ~1030 cm^{-1}, mode 18*a*).

Bleached Absorption Bands in the Transient Spectra. A strong positive peak is observed around 960 cm^{-1}, whose position nearly coincides with that of the band in the static spectra. This band is reasonably explained as a bleached absorption band due to the out-of-plane vibration of the S_0 species. A band with a sharp dip (negative peak) in the center is found at ~1500 cm^{-1}. In the static spectra, a relatively strong band due to the phenyl group in-plane vibration (mode 19*a*) is observed at the corresponding position. If a parallel transition moment is associated with this mode, the dip in the transient spectra is reasonably explained as a bleached absorption due to this in-plane vibration. Since this vibrational mode is attributable to the a_1 local symmetry species of the phenyl group, it probably gives a parallel transition moment. Then the negative peak in the transient spectra may be assigned to a bleached absorption arising from the mode 19*a* of the S_0 species.

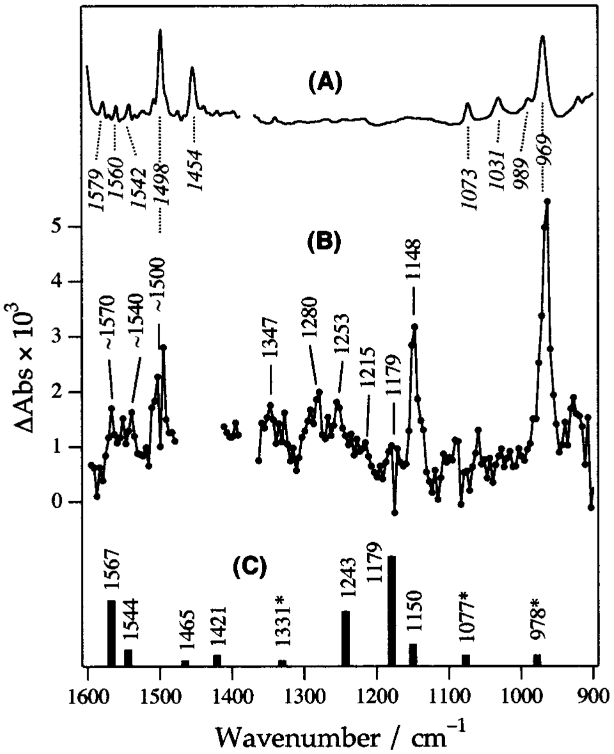

Figure 2. (A) Infrared spectrum of *trans*-stilbene in the S_0 state in acetonitrile solution. The solvent bands are numerically removed. Wavenumbers of bands attributed to the S_0 species are indicated in italic. (B) Picosecond transient infrared spectrum of *trans*-stilbene in acetonitrile solution. Wavenumbers of bands attributed to the S_1 species are indicated in the upright letters. (C) Representative Raman spectral pattern of *trans*-stilbene in the S_1 state in acetonitrile solution.[13] Wavenumbers marked with asterisks are those in *n*-hexane solution.[9,13]

3.1.2. Induced Absorption Bands due to the Electronically Excited State. In addition to the bleached absorption bands due to the S_0 species, several reproducible bands are observed in the transient spectra, which can be attributed to the S_1 species. All of the prominent induced bands have positive signs. This means that these bands are due to parallel transitions, or in other words, in-plane vibrational modes. The bands at ~1540, ~1500, ~1340, ~1280, and ~1150 cm^{-1} are common between the *n*-heptane and acetonitrile solutions. On the basis of well-established assignments of the infrared and Raman bands of the S_0 species[12,37−39] and those of Raman bands of the S_1 species,[3,4,9,10,12,17,18] we discuss here vibrational assignments of several observed infrared bands of the S_1 species. Bands due to electronic transitions possibly appear in the observed infrared region. However, since we have no strong evidence indicating electronic transitions, we assume here that all the observed infrared absorption bands are due to vibrational transitions.

Band at ~1540 cm^{-1}. Also in the Raman spectrum of the S_1 species, we can find a broad band at ~1540 cm^{-1} that is assigned to the in-phase (gerade) phenyl group vibrational mode (mode 8*a*).[9,10,17] The transient infrared band at ~1540 cm^{-1} presently observed may be attributed to the out-of-phase (ungerade) 8*a* mode of the two phenyl groups, whose vibrational frequency is nearly the same as that of the Raman active in-phase mode. For the S_0 species, the in-phase and out-of-phase 8*a* modes of the phenyl groups are observed at nearly the same position (1600−1590 cm^{-1}) in the Raman and infrared spectra, respectively.

Band at ~1500 cm^{-1}. As mentioned earlier, the band at ~1500 cm^{-1} is considered to be composed of a positive induced band (S_1 species) and a negative bleached band (mode 19*a* of the S_0 species). This induced band may be assigned to a mode with major contributions from the phenyl group vibrations (such as mode 19*a* and mode 8*a*).

Bands at ∼1340 and ∼1280 cm^{-1}. These bands seem to be reproducible in both *n*-heptane and acetonitrile solutions, although the signal-to-noise ratios are not excellent. Assignments of these bands are not clear. In this wavenumber region phenyl group modes such as mode 3 or mode 14 may appear. However, these modes belong to the b_2 symmetry species under the C_{2v} local symmetry, which might give perpendicular absorption bands. Contribution from other vibrational motion may be essential to explain the polarization characters of the bands.

Band at ∼1150 cm^{-1}. From its vibrational frequency, it is likely that the C_o−Ph stretching and the C_oH in-plane bending (and probably C_o=C_o stretching) coordinates (where C_o denotes the olefinic carbon atom) contribute to the vibrational mode giving rise to this strong induced band. In the infrared spectrum of the S_0 species, a weak band due to the C_o−Ph stretch is found at ∼1220 cm^{-1},[12,37] which is a higher frequency than that of the S_1 infrared band. This is seemingly not consistent with a simple idea, that the bond order of the conjugated single bond in the neighbor of the olefinic moiety increases on excitation to the S_1 state. However, in the Raman spectrum of the S_1 species, a strong band due to a gerade vibrational mode with major contributions from the C_o−Ph stretch, C_oH in-plane bend, and C_o=C_o stretch is observed at ∼1180 cm^{-1} (the mode 9*a* of phenyl groups may also have a certain contribution),[9,12,17] which is lower than the corresponding S_0 band at ∼1190 cm^{-1}.[12,37] This is again not consistent with the above-mentioned simple idea. Therefore, the simple prediction of the C_o−Ph stretching frequency based on bond-order considerations should be regarded as not valid for the present system. The reality may be that the force constant of the C_o−Ph stretch is not greatly changed on excitation from S_0 to S_1 state, and/or that hybridization of the internal coordinates is different between S_0 and S_1 states. In this case, to assign the induced band at ∼1150 cm^{-1} to a hybrid mode of the C_o−Ph stretch, C_oH in-plane bend and C_o=C_o stretch may be quite reasonable.

The band is possibly attributable to the out-of-phase 9*a* mode of the phenyl groups. In the infrared spectrum of the S_0 species, however, the band due to the 9*a* mode (∼1180 cm^{-1}) is very weak, in contrast to the present induced infrared band of the S_1 species. From its strong intensity, it is hard to consider that the vibrational amplitude of the mode giving rise to the induced band at ∼1150 cm^{-1} is concentrated on the mode 9*a* of the phenyl groups. Consequently, it may be most natural at present to consider that the induced band at ∼1150 cm^{-1} is due to an olefinic vibrational mode (C_o−Ph stretch, C_oH in-plane bend, and C_o=C_o stretch) with a contribution from the mode 9*a* of the phenyl groups, as is similar to the Raman band at ∼1180 cm^{-1} of the S_1 species.[9,12,17]

Other Transient Infrared Bands. In the *n*-heptane solution, reproducible bands are found at ∼1220 and ∼1070 cm^{-1} (reproducibility in these regions is poor in acetonitrile solution). The band at ∼1220 cm^{-1} may be assigned to the olefinic C_oH in-plane bending vibration. The band at ∼1070 cm^{-1} may be attributed to a mode with major contribution from the phenyl groups. These assignments should be reexamined when we can obtain the transient spectrum in much better signal-to-noise ratio. There seems to be a band at ∼1420 cm^{-1} in the *n*-heptane solution. However, the infrared polarizer and solvents (both *n*-heptane and acetonitrile) absorb the probe light in this region, and consequently reproducibility of the data is not sufficient because of low infrared intensity.

Bands Observed only in Acetonitrile. Weak bands at ∼1570 and ∼1180 cm^{-1} are observed only in the acetonitrile solution. The author considers that reproducibility of the band at ∼1570 cm^{-1} is sufficient. However, several weak absorption bands are found around 1550 cm^{-1} in the static spectrum of the S_0 species in acetonitrile. Spectral features in the region between 1580 and 1530 cm^{-1} of the transient spectrum (although not sufficiently reproducible) may be partly affected by the bleached absorption of these weak bands due to the S_0 species. It is consequently difficult to determine the exact peak position of the band in the present stage. The band at ∼1180 cm^{-1} seems to be reproducible, but further accumulation may be necessary. A sharp dip at 1175 cm^{-1} is not reproducible and is due to a shot noise. In addition, there seems to be a band at ∼1250 cm^{-1} only in the acetonitrile solution (reproducibility of this band is not sufficient at present). As shown in the bar graph of Figure 2C, the positions of these bands (∼1570, ∼1250, and ∼1180 cm^{-1}) nearly agree with those of the strong Raman bands arising from the olefinic in-plane vibrational modes.

On the other hand, the author considers that no transient absorption bands are found at these wavenumbers in the *n*-heptane solution within the experimental uncertainties (possibly a weak shoulder exists at ∼1570 cm^{-1}). We discuss the origin of these bands in the next subsection. The observed wavenumbers and their assignments of the infrared and Raman bands of the S_0 and S_1 species are summarized in Table 1.

3.2. Molecular structure in the S_1 State. In the gas phase, the equilibrium structure of the S_1 state of tS is considered to retain a center of symmetry.[2,5] If the molecule possesses a center of symmetry, the mutual exclusion should hold among the infrared and Raman bands. In *n*-heptane solution, the mutual exclusion seems to hold for the transient species except for a few bands attributable to vibrational modes of the phenyl groups. For the vibrational modes with the atomic amplitudes localized on the phenyl groups, it may be possible that an infrared active ungerade (out-of-phase) mode and a Raman active gerade (in-phase) mode oscillate in nearly the same frequency, even if the molecule possesses a center of symmetry. As mentioned in the last subsection, there is possibly a weak shoulder at ∼1570 cm^{-1}. If this band is arising from the olefinic C_o=C_o stretch which gives the strong Raman band, it should be said that the mutual exclusion breaks down to a small extent. Further examination may be necessary on this point. However, the structure of the tS molecule in the S_1 state in *n*-heptane may be treated to be nearly symmetric about the inversion operation.

In acetonitrile, on the other hand, weak bands are observed at ∼1570, (∼1250), and ∼1180 cm^{-1} which are absent in the transient spectrum in *n*-heptane. The positions of these bands are approximately the same as those of the strong Raman bands attributed to the olefinic in-plane vibrational modes of the S_1 state. We may consider that the mutual exclusion does not hold in the case of the S_1 species in acetonitrile, although further examination on reproducibility of these bands may be necessary. This suggests a molecular structure without a center of symmetry in the S_1 state of tS in acetonitrile.

Recently, a polarized structure of electronically excited tS has been discussed.[14,41] For example, the molecule may have a dipole moment when charge separation between the olefinic carbons ($\mathrm{Ph{-}C^{\delta+}{=}C^{\delta-}{-}Ph}$) or between two phenyl groups ($\mathrm{Ph^{\delta+}{-}C{=}C{-}Ph^{\delta-}}$) occurs. As a related phenomenon, it is believed that bianthryl, a hydrocarbon compound with a symmetric structure in the ground state, lowers its symmetry and becomes polarized in the excited electronic state in polar solvents.[42−44] It has been proposed that such polarized structures

TABLE 1: Summary of Vibrational Wavenumbers (in cm^{-1}) of the S_0 and S_1 States of *trans*-Stilbene

IR	Raman	sym. species[b]	assignment
S_0 state[a]			
	1639[c]	a_g	$C_o{=}C_o$ str[k,l]
1596[c]		b_u	8*a*[k,l]
	1594[c]	a_g	8*a*[k,l]
1498[g]		b_u	19*a*[k,l]
	1491[c]	a_g	19*a*[k,l]
1454[e]		b_u	19*b*[k,l]
	1445[c]	a_g	19*b*[k,l]
1218[c]		b_u	$C_o{-}Ph$ str[k]
	1193[c]	a_g	$C_o{-}Ph$ str[k]
	1187[c]	a_g	9*a*[k,l]
1181[c]		b_u	9*a*[k,l]
1072[g]		b_u	18*b*[k,l]
	1059[c]	a_g	18*b*[l]
1031[g]		b_u	18*a*[k,l]
	1027[c]	a_g	18*a*[k,l]
~985[g]		a_u	4[k]
~965[g]		a_u	C_oH op[k,l]
S_1 state			
~1570[ei]		a_g?	$C_o{=}C_o$ str?
	1567[h]	a_g	$C_o{=}C_o$ str[l]
~1540		b_u	8*a*[m]
	1539[h]	a_g	8*a*[k]
~1500		b_u	19*a* or 8*a*[m]
	1461[h]	a_g	19*a*[k]
	1421[h]	a_g	19*b*[k]
1345[g]		b_u	
	1331[f]	a_g	3[k]
1284[g]		b_u	
~1250[e,j]		a_g?	C_oH ip?
	1242[h]	a_g	C_oH ip[k]
1215[g]		b_u	
1179[e,j]		a_g?	$C_o{-}Ph$ str, C_oH ip?
	1179[h]	a_g	$C_o{-}Ph$ str, C_oH ip[k]
	1149[h]	a_g	9*a*, $C_o{-}Ph$ str[k]
1146[g]		b_u	$C_o{-}Ph$ str, C_oH ip, $C_o{=}C_o$ str, 9*a*[m]
	1077[f]	a_g	18*b*[k]
~1070[d]		b_u	
	978[f]	a_g	12[k]

[a] Only those bands concerned to the discussion in the text are shown. [b] Under C_{2h} symmetry. [c] Wavenumber in the solid state, from ref 37. [d] Wavenumber in *n*-heptane. [e] Wavenumber in acetonitrile. [f] Wavenumber in *n*-hexane. [g] Average of wavenumber in *n*-heptane and that in acetonitrile. [h] Average of wavenumber in *n*-hexane and that in acetonitrile. [i] Shoulder in *n*-heptane(?). [j] Further check of reproducibility may be needed. [k] References 12 and 17. [l] Reference 37. [m] Tentative assignment(s).

contribute to the S_1 state of tS,[14,41] but experimental support is scanty. Under such a polarized structure, the molecule loses the center of symmetry, and the mutual exclusion between the infrared and Raman spectra may be broken down. On the other hand, it is expected as a general tendency that a molecule with a polarized structure is stabilized in polar solvents. The present transient infrared measurements on the S_1 state of tS have shown that the mutual exclusion rule holds in *n*-heptane solution while it does not in acetonitrile. This result seems to be consistent with the idea that the S_1 state of tS is polarized in polar solvents to give a distorted molecular structure. From these considerations, it is suggested that the S_1 species has a polarized structure in acetonitrile (Figure 3).

We should note now the transient infrared intensities. In general, strongly polarized molecules tend to give strong infrared absorption bands,[26] since infrared transition moments are given by the differential coefficients of the dipole moment with respect to the vibrational coordinates. If the S_1 species of tS in acetonitrile is strongly polarized, the infrared bands at ~1570 ($C_o{=}C_o$ stretch) and/or ~1180 ($C_o{-}Ph$ stretch) of the transient should have very strong intensities. However, the intensities of the induced bands are rather weak (ϵ may be less than 100 mol^{-1} dm^3 cm^{-1}), if we judge from the bleached absorption intensity of the out-of-plane vibrational band of the S_0 species at ~960 cm^{-1} ($\epsilon \approx 150$ mol^{-1} dm^3 cm^{-1} estimated from Figure 2A). Although it is difficult to estimate transient bandwidths because of a relatively broad line width of the infrared probe light (~8 cm^{-1}) and/or band congestion in the region between 1600 and 1500 cm^{-1}, the widths (approximately 10 cm^{-1}) of the bands at ~1570 and ~1180 cm^{-1} appear to be similar to that of the band at ~960 cm^{-1}. Therefore, the oscillator strengths of the bands at ~1570 and ~1180 cm^{-1} may be much smaller than that of the S_0 band at ~960 cm^{-1}. In addition, while the $C_o{=}C_o$ stretching frequency is expected to be dependent on the solvent if the molecule is strongly polarized in polar solvents,[45] the observed Raman frequencies of the S_1 species in the literature[7-13] are almost solvent-independent. Therefore, the polarization of the S_1 state of tS (or contribution of the polarized molecules to the whole population of the S_1 species) in acetonitrile may be small.

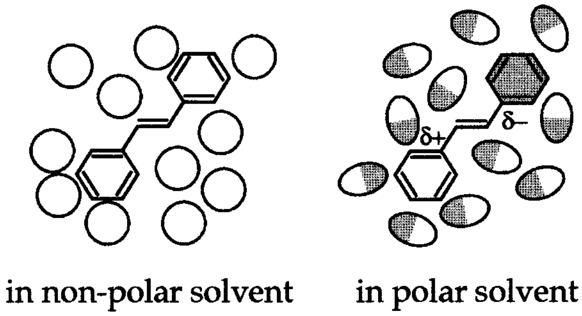

Figure 3. Schematic diagram of electronic structure of *trans*-stilbene in S_1 state in solution suggested from the present results. The S_1 species is not polarized and retains the center of symmetry in a nonpolar solvent (left), while it is slightly polarized and eventually loses the center of symmetry in a polar solvent (right).

In conclusion, the picosecond transient infrared spectrum of tS in the S_1 state in solution has been recorded in the fingerprint region. From the spectra obtained it has been suggested that the S_1 species has a center of symmetry in a nonpolar solvent (*n*-heptane), while it may have a polarized structure without a center of symmetry in a polar solvent (acetonitrile). More sensitive and accurate measurements and definitive vibrational assignments by measuring isotope-substituted species are desired in the future studies. If we can determine directions of vibrational transition moments from accurate polarization-dependence experiments, further detailed information on the excited molecular structure is expected.

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References and Notes

(1) Waldeck, D. H. *Chem. Rev.* **1991**, *91*, 415.

(2) Suzuki, T.; Mikami, N.; Ito, M. *J. Phys. Chem.* **1986**, *90*, 6431.

(3) Urano, T.; Hamaguchi, H.; Tasumi, M.; Yamanouchi, K.; Tsuchiya, S. *Chem. Phys. Lett.* **1987**, *137*, 559.

(4) Urano, T.; Hamaguchi, H.; Tasumi, M.; Yamanouchi, K.; Tsuchiya, S.; Gustafson, T. L. *J. Chem. Phys.* **1989**, *91*, 3884.

(5) Chiang W.-Y.; Laane, J. *J. Chem. Phys.* **1994**, *100*, 8755.

(6) Ci, X.; Myers, A. B. *Chem. Phys. Lett.* **1989**, *158*, 263.

(7) Gustafson, T. L.; Roberts, D. M.; Chernoff, D. A. *J. Chem. Phys.* **1983**, *79*, 1559.

(8) Hamaguchi, H.; Kato, C.; Tasumi, M. *Chem. Phys. Lett.* **1983**, *100*, 3.

(9) Hamaguchi, H.; Urano, T.; Tasumi, M. *Chem. Phys. Lett.* **1984**, *106*, 153.

(10) Hamaguchi, H. In *Vibrational Spectra and Structure*; Durig, J. R., Ed.; Elsevier: Amsterdam, 1987; Vol. 16, pp 227−309.

(11) Hamaguchi H.; Gustafson, T. L. *Annu. Rev. Phys. Chem.* **1994**, *45*, 593.

(12) Urano, T., Doctoral Thesis, The University of Tokyo, 1989.

(13) Weaver, W. L.; Huston, L. A.; Iwata, K.; Gustafson, T. L. *J. Phys. Chem.* **1992**, *96*, 8956.

(14) Hamaguchi H.; Iwata, K. *Chem. Phys. Lett.* **1993**, *208*, 465.

(15) Hester, R. E.; Matousek, P.; Moore, J. N.; Parker, A. W.; Toner, W. T.; Towrie, M. *Chem. Phys. Lett.* **1993**, *208*, 471.

(16) Leonard, J. D., Jr.; Gustafson, T. L. *J. Mol. Struct.* **1996**, *379*, 109.

(17) Tasumi, M.; Urano, T.; Hamaguchi, H. In *Time-Resolved Vibrational Spectroscopy*; Atkinson, G. H., Ed.; Gordon and Breach: New York, 1987; pp 252−264.

(18) Negri, F.; Orlandi, G.; Zerbetto, F. *J. Phys. Chem.* **1989**, *93*, 5124.

(19) Spanner, K.; Laubereau, A.; Kaiser, W. *Chem. Phys. Lett.* **1976**, *44*, 88.

(20) Moore, J. N.; Hansen, P. A.; Hochstrasser, R. M. *Chem. Phys. Lett.* **1987**, *138*, 110.

(21) Graener, H.; Ye, T.-Q.; Laubereau, A. *Chem. Phys. Lett.* **1989**, *164*, 12.

(22) Hübner, H.-J.; Wörner, M.; Kaiser, W.; Seilmeier, A *Chem. Phys. Lett.* **1991**, *182*, 315.

(23) Beckerle, J. D.; Cavanagh, R. R.; Casassa, M. P.; Heilweil, E. J.; Stephenson, J. C. *J. Chem. Phys.* **1991**, *95*, 5403.

(24) Stoutland, P. O.; Dyer, R. B.; Woodruff, W. H. *Science* **1992**, *257*, 1913.

(25) Hamm, P.; Zurek, M.; Mäntele, W.; Meyer, M.; Scheer H.; Zinth, W. *Proc. Natl. Acad. Sci. U.S.A.* **1995**, *92*, 1826.

(26) Okamoto, H.; Tasumi, M. *Chem. Phys. Lett.* **1996**, *256*, 502.

(27) Hamm, P.; Zurek, M.; Röschinger, T.; Platzelt, H.; Oesterhelt D.; Zinth, W. *Chem. Phys. Lett.* **1997**, *268*, 180.

(28) Hamm, P.; Ohline, S. M.; Zinth, W. *J. Chem. Phys.* **1997**, *106*, 519.

(29) Okamoto, H. *Chem. Phys. Lett.* **1998**, *283*, 33.

(30) Okamoto, H. *Chem. Lett.* **1998**, 1141.

(31) Dyck, R. H.; McClure, D. S. *J. Chem. Phys.* **1962**, *36*, 2326.

(32) Nakabayashi, T.; Okamoto, H.; Tasumi, M. *J. Phys. Chem.* **1998**, *102*, 9686.

(33) Nakabayashi, T.; Okamoto, H.; Tasumi, M. *J. Phys. Chem.* **1997**, *101*, 7189.

(34) Molina, V.; Merchán, M.; Roos, B. O. *J. Phys. Chem. A* **1997**, *101*, 3478.

(35) Uznanski, P.; Kryszewski, M.; Thulstrup, E. W. *Spectrochim. Acta* **1990**, *46A*, 23.

(36) Gudipati, M. S.; Johannes, M. M.; Daverkausen, J.; Hohlneicher, G. *Chem. Phys.* **1995**, *192*, 37.

(37) Meić, Z.; Güsten, H. *Spectrochim. Acta* **1978**, *34A*, 101.

(38) Arenas, J. F.; Tocón, I. L.; Otero, J. C.; Marcos, J. I. *J. Phys. Chem.* **1995**, *99*, 11392.

(39) Baranović, G.; Meić, Z.; Maulitz, A. H. *Spectrochim. Acta A* **1998**, *54*, 1017.

(40) Wilson, E. B., Jr. *Phys. Rev.* **1934**, *45*, 706.

(41) Hamaguchi, H. *Mol. Phys.* **1996**, *89*, 463.

(42) Kang, T. J.; Jarzeba, W.; Barbara, P. F.; Fonseca, T. *Chem. Phys.* **1990**, *149*, 81.

(43) Honma, K.; Arita, K.; Yamasaki, K.; Kajimoto, O. *J. Chem. Phys.* **1991**, *94*, 3496.

(44) Dobkowski, J.; Grabowski, Z. R.; Paeplow, B.; Rettig, W.; Koch, K. H.; Müllen, K.; Lapouyade, R. *New J. Chem.* **1994**, *18*, 525.

(45) Nakabayashi, T.; Okamoto, H.; Tasumi, M. *J. Raman Spectrosc.* **1995**, *26*, 841.