Investigation of Single-Vibronic-Level Fluorescence Lifetimes of Jet-Cooled S_1 *trans*-Stilbene above the Isomerization Barrier

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The fluorescence lifetimes of jet-cooled trans-stilbene were measured for twenty eight S_1 vibronic levels in the 1300—1700 cm^{-1} region above the 0–0 transition. All fluorescence decay curves were well fitted to single exponential functions in the 0—3 ns time region. It was found that the fluorescence lifetime decreases monotonically with the increase of the excess vibrational energy. No anomalous lifetime dependence on the vibronic level was observed. The (time-integrated) dispersed fluorescence from the corresponding vibronic levels was also measured. The excitation of all twenty eight levels gave indistinguishable fluorescence spectra exhibiting only broad features, indicating that the IVR rate is much larger than the radiative decay rate regardless of the fundamental, overtone or combination levels. No direct evidence supporting the existence of a mode-selective isomerization channel was obtained.

Photochemistry of trans-stilbene has been studied extensively as a prototype of cis-trans photoisomerization.[1] This reaction starts with the photoexcitation of the ground (S_0) state molecules to the lowest excited singlet (S_1) state having a planar structure. The conformational change, i.e., twisting around the C=C bond, then takes place on the S_1 potential surface to form the perpendicular state. The relaxation from this perpendicular excited state to the ground state gives an 1 : 1 mixture of cis and trans S_0 stilbene.

The key process in this stilbene photochemistry is the twisting around the C=C double bond in the S_1 state. Picosecond fluorescence spectroscopy of isolated *trans*-stilbene in a supersonic jet afforded very informative data for this process. Syage et al. measured the fluorescence decays following the excitation of the S_1 vibronic levels. They found that the fluorescence lifetime is almost constant for excess energies less than 1200 cm^{-1} but that it starts to decrease rapidly for higher excess energies.[2] In the 1200—2700 cm^{-1} region, the lifetime decreases with increasing excess energy. The observed shortening of the fluorescence lifetime was explained in terms of the increase in the rate of the trans to perpendicular isomerization that competes with fluorescence emission. The threshold energy for this lifetime change (ca. 1200 cm^{-1}) has been regarded as the most reliable value of the energy barrier for the twisting motion in S_1 *trans*-stilbene. Several experimental supports have been given also by other groups.[3,4]

In a previous paper,[5] one of the present authors (HH) and co-workers measured the fluorescence excitation spectra of jet cooled *trans*-stilbene with three isotopic analogues, and established the vibrational assignments of several fundamental levels above the isomerization barrier. On the basis of these assignments, it was argued that the fluorescence excitation intensity of the C=C stretch band (ca. 1550 cm^{-1}) was significantly lower (ca. 1/5) than the corresponding absorption intensity which was estimated from a theoretical calculation, the Raman excitation profile, or the absorption spectrum of a low temperature crystal. The non-radiative decay rate calculated from this intensity difference suggested the possibility of an isomerization pathway specific to the C=C stretch mode. In order to further address this issue, we need to know the detailed excess energy dependence of the fluorescence lifetime. Unfortunately, the existing lifetime data above the isomerization barrier are limited, since the previous lifetime measurements[2,3] selected small number of vibronic levels that exhibit strong fluorescence. No lifetime data is available for the newly assigned C=C stretch band. Therefore, it is highly desirable to extend the fluorescence lifetime measurement to many other vibronic levels including those exhibiting relatively weak fluorescence.

In this paper, we examine the fluorescence lifetimes of isolated *trans*-stilbene with the excitation of twenty eight S_1 vibronic levels located in the 1300—1700 cm^{-1} region, with the use of a newly constructed apparatus equipped with a streak camera.

Experimental

1. Fluorescence Lifetime Measurements. The schematic diagram of the experimental setup for the fluorescence lifetime measurements is shown in Fig. 1. The picosecond laser system based on a cw mode locked Nd : YAG laser (Spectra Physics 3800S) has already been described elsewhere.[6] The output pulse from the mode locked Nd : YAG laser is compressed with a fiber-grating pulse compressor (Spectra Physics 3695-01), and the second harmonic of the compressed pulse is used as the excitation source of a

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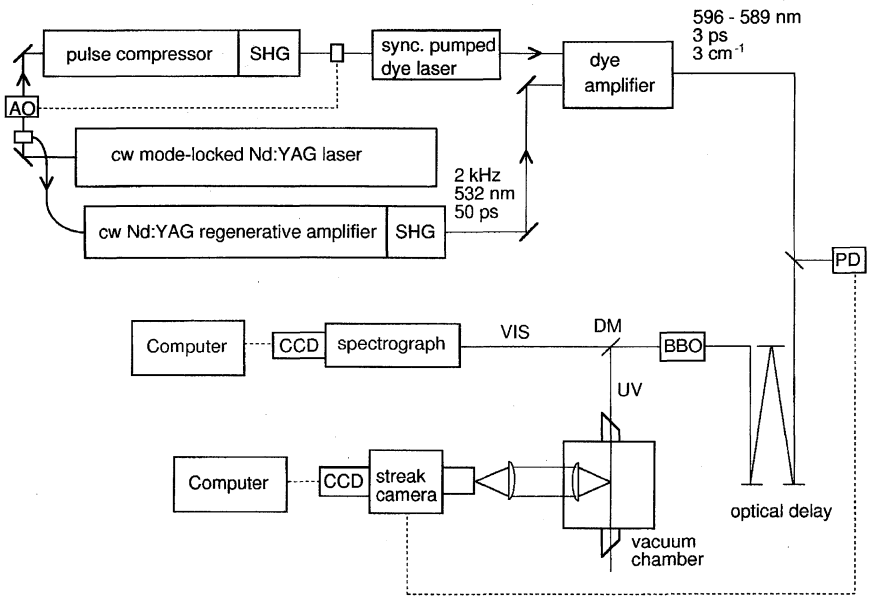


Fig. 1. Schematic diagram of an experimental setup for the measurement of the fluorescence decay from the jet-cooled molecules.

synchronously pumped dye laser (Spectra Physics 3520, rhodamine 6G). The dye laser output (82 MHz) was amplified in a two-stage dye amplifier (Spectra Physics PDA-L2), which is pumped by the second harmonic of the output from a cw Nd : YAG regenerative amplifier (Spectra Physics 3800RA). The obtained picosecond laser beam (589—596 nm, 2 kHz, 3.2 ps) is divided into two by a beam splitter. The minor portion of the laser beam is introduced to a photodiode (Hamamatsu C1083) to generate the triggering signal for the streak camera. The other major portion is introduced to a long optical delay line (ca. 14 m), which is required for compensating the time delay in the electronic circuit of the streak camera. After the delay line, the laser beam is collimated into a BBO crystal. The generated second harmonic UV light (ca. 0.1 μJ, 2 kHz, 2.2 ps) is separated from the fundamental by dichroic mirrors, and is introduced into a vacuum chamber for the excitation of molecules. The residual fundamental beam is introduced to a spectrograph (Jobin Yvon HR320) equipped with a CCD camera for the wavelength calibration.

The jet apparatus is equipped with two 10 inches diffusion pumps (Varian VHS-10 and Edwards Diffstak 2000) backed up by a mechanical booster pump (ULVAC PMB006C) and a rotary pump (ALCATEL 2063C). The *trans*-stilbene sample is heated to ca. 100 °C in a pyrex cw nozzle, and is expanded through a ca. 100 μm pinhole. The expansion of the jet is backed by 2 atm He, and an ambient pressure in the chamber is about 2×10^{-4} Torr (1 Torr = 133.322 Pa). The jet cooled molecules are excited at about 5 mm from the nozzle. Total fluorescence is collected and focused on the entrance slit of the streak camera (Hamamatsu C2909) by using a lens pair. The data accumulation and analysis are carried out with a personal computer (Apple Macintosh IIfx) using Program Photolumi (Hamamatsu). The fluorescence data were accumulated with the photon counting mode.[7] The time resolution of the system is primarily determined by the sweep rate of the streak camera. If we adopt the highest sweep rate of 0.3 ns/15 mm, the time-resolution of 10—15 ps (FWHM of the response function) is obtainable. In the present experiments, the slow sweep rate, 5 ns/15 mm, was chosen in order to cover the time range as wide as 3 ns. In this case, time-resolution of 50—60 ps (FWHM of the response function) was obtained.

2. Fluorescence Excitation Spectra and SVL Dispersed Fluorescence Spectra Measurements. A nanosecond laser system based on a pulsed Q-switch Nd:YAG laser is used as the excitation source. The output of a dye laser (Spectron SL4000G)pumped by the second harmonic of a pulsed Q-switch Nd : YAG laser (Spectron SL801, 10—50 Hz, 10-ns duration) is frequency-doubled with an auto-tracking unit (Spectron SL400EMX) equipped with a KD*P crystal. The generated UV pulses are separated from the fundamental by an optical filter (Hoya) and introduced into the vacuum chamber. A pulsed nozzle (General Valve, 400 or 800 μm orifice) is used to generate the supersonic jet beam. An ambient pressure in the chamber is about 8×10^{-6} Torr with the stagnation pressure of 5 atm He. In the case of fluorescence excitation measurement, the jet cooled molecules are excited at 10—15 mm downstream from the nozzle, and total fluorescence is collected with a single quartz lens and is detected by a photomultiplier (Hamamatsu R955) with a boxcar averager (Stanford Research Systems). A narrow slit is placed in front of the photomultiplier for rejecting the scattering of the excitation laser light. For the SVL dispersed fluorescence measurement, jet cooled molecules are excited at about 5 mm from the nozzle, and the fluorescence is collected and focused on the entrance slit of a spectrograph (Jobin Yvon HR320) equipped with an intensified photodiode array (Princeton Instruments IRY-700G/B/par). The wavelength resolution is about 0.7 nm. The wavelength calibration of the excitation laser is carried out by introducing the scattering of the fundamental to a spectrometer (Jobin Yvon T64000) equipped with an intensified photodiode array (Princeton Instruments IRY1024). In both cases, the data accumulation and the further analysis are carried out with a personal computer (NEC PC9801). The timing of the system was controlled by a delay generator (Stanford Research Systems DG535).

Results and Discussion

The fluorescence excitation spectrum of *trans*-stilbene in the 0—1700 cm^{-1} region from the 0–0 band is shown in Fig. 2. This spectrum was constructed from three spectra separately measured with three different dyes. The effect of the laser power change with scanning wavelength has been

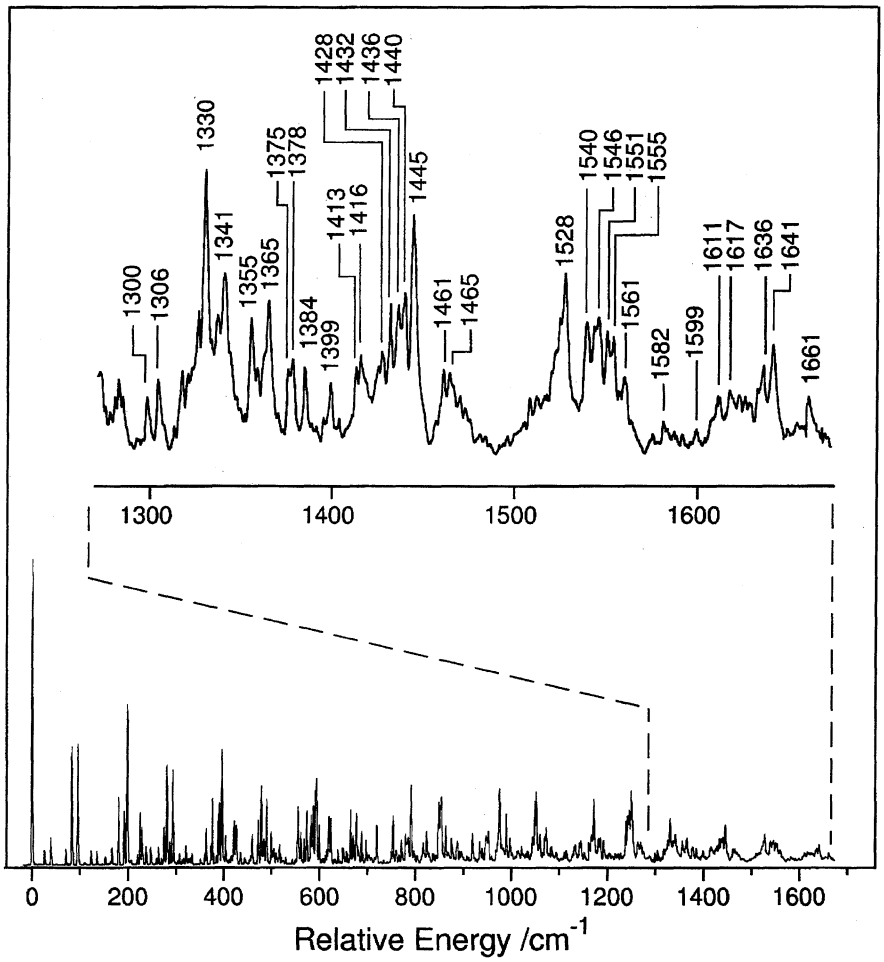


Fig. 2. The fluorescence excitation spectra of jet-cooled stilbene.

corrected. It is noteworthy that the band intensity starts to decrease significantly above the isomerization threshold of 1200 cm^{-1}.[2,5,8] The excitation spectrum in the region from 1300 to 1700 cm^{-1}, which we examine in detail in this work, is expanded in the upper trace. The vibrational energies of prominent vibronic bands are given in this figure. They are in good agreement with the reported values in the literature.[5,8]

Before the measurements of the fluorescence lifetime, we checked the band width of picosecond excitation laser. The spectrum of the UV excitation laser line was measured with a multichannel detection system which has been developed for picosecond Raman spectroscopy.[6] The slit function was also measured using the emission lines of a neon lamp, and the measured spectrum was deconvoluted with this slit function. The obtained band width (FWHM) of the excitation laser light was 5.2 cm^{-1}. This value is very close to the Fourier-transform limit of 5.6 cm^{-1} which is calculated for a pulse having the $sech^4$ temporal shape with 2.2 ps FWHM. The deconvoluted spectrum of an excitation line is compared with the fluorescence excitation spectrum of stilbene in Fig. 3. It is clearly seen that the band width of our excitation laser is narrow enough to excite each of the vibronic bands separately, except for some closely located bands such as 1375 and 1378 cm^{-1}.

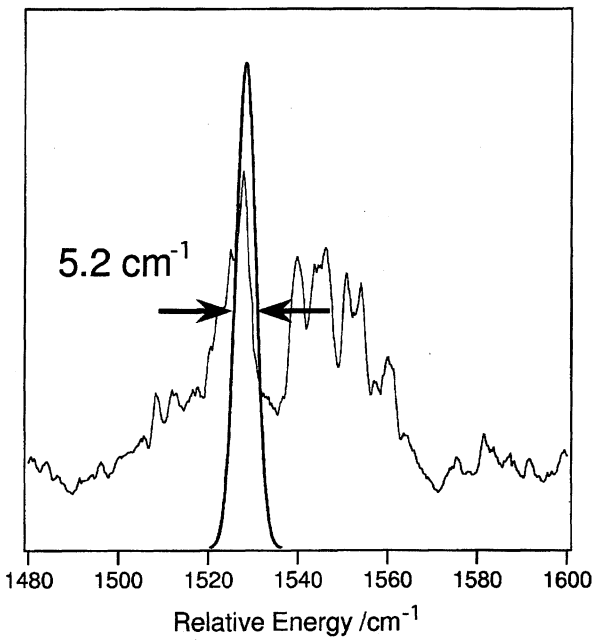


Fig. 3. A comparison between the line width of the picosecond excitation laser pulse and the fluorescence excitation spectrum of jet-cooled stilbene.

We measured fluorescence decays for twenty eight vibronic bands including the shoulder of the 1528 cm^{-1} band (1515 cm^{-1}). Eight representative decay curves are shown with semilogarithmic scales in Fig. 4 (the dotted curves). The fitting analysis for each decay curve was carried out with the use of a deconvolution method which takes into account the observed response function. All fluorescence decays were successfully fitted to single exponential functions in the observed 0—3 ns time region. We measured the fluorescence decay more than three times for each of the twenty eight vibronic levels, and averaged the obtained lifetimes. The determined fluorescence lifetimes are listed in Table 1, and also plotted in Fig. 5 with the fluorescence excitation spectrum. The fluorescence lifetime decreases monotonically with the increase of the excess energy in the region from 1300 to 1700 cm^{-1}. No anomalous lifetime dependence on the vibronic

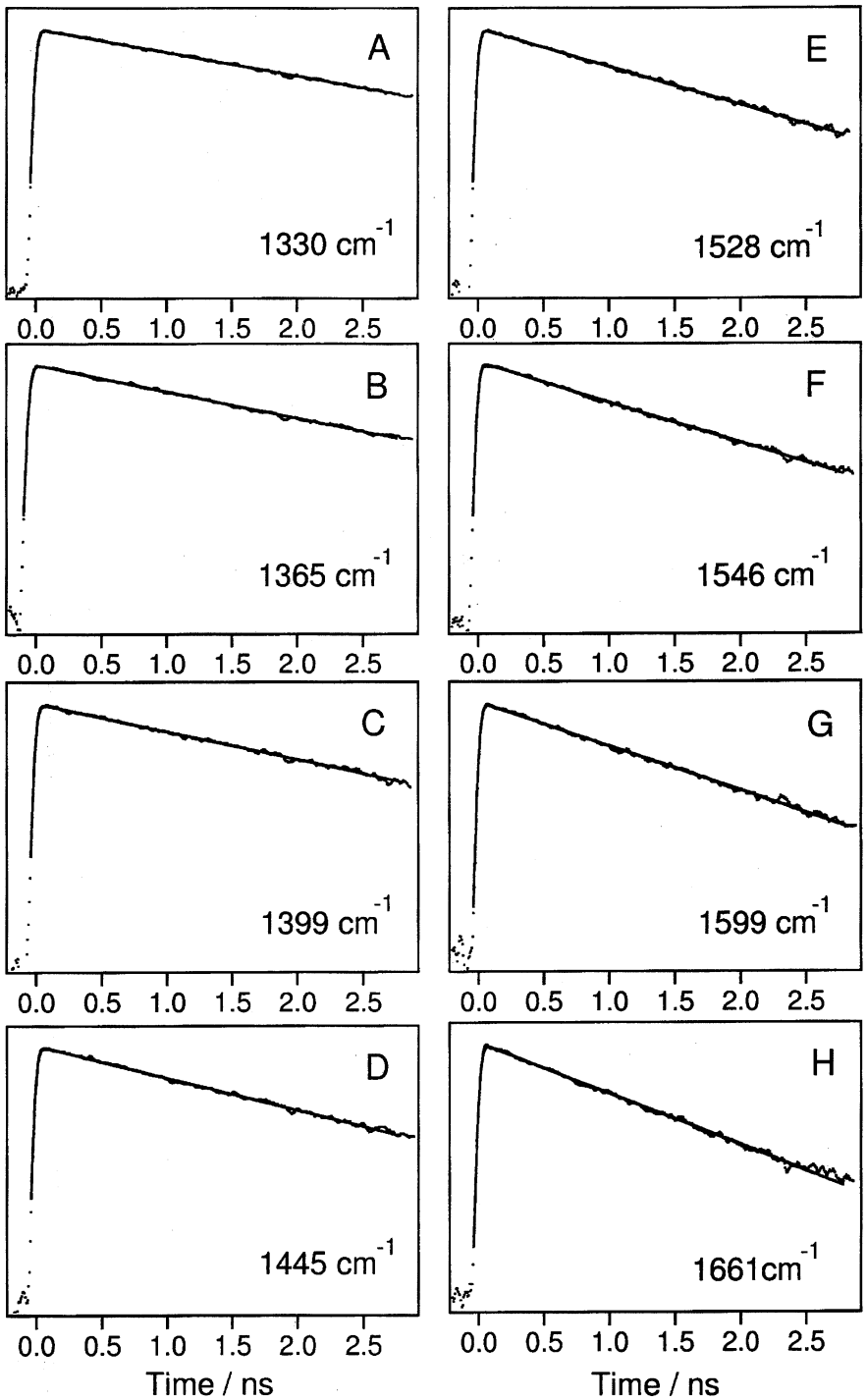


Fig. 4. Fluorescence decays following the excitation of the vibronic levels at 1330 cm^{-1} (A), 1365 cm^{-1} (B), 1399 cm^{-1} (C), 1445 cm^{-1} (D), 1528 cm^{-1} (E), 1546 cm^{-1} (F), 1599 cm^{-1} (G), and 1661 cm^{-1} (H). (The dotted curves, observed; the solid curves, fitted.)

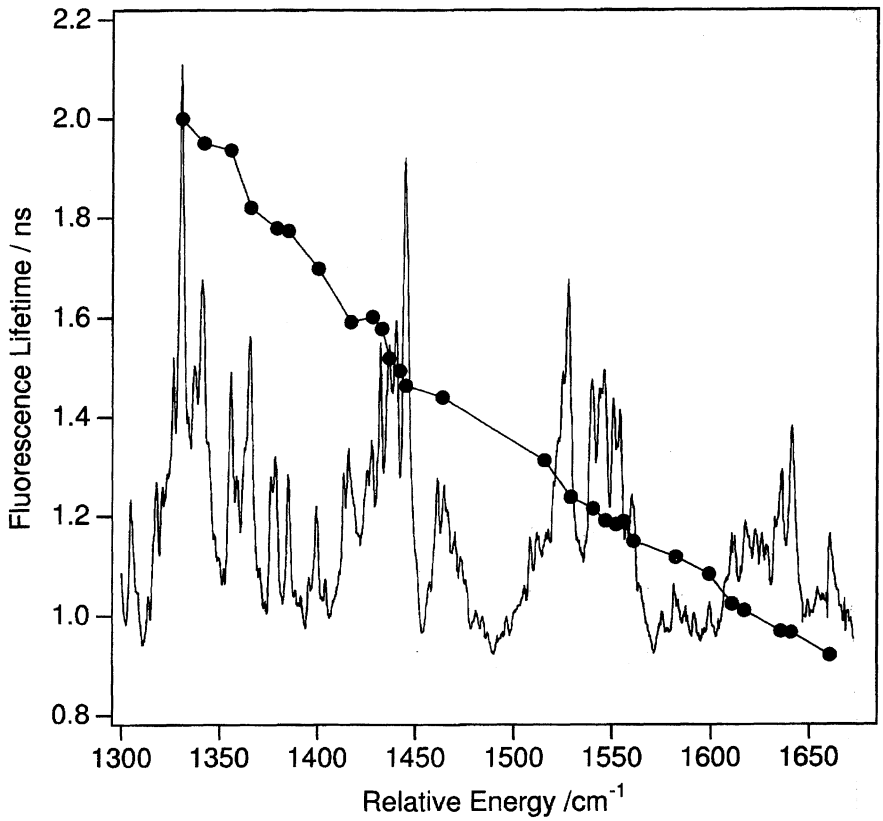


Fig. 5. The fluorescence lifetime of the vibronic bands located in the 1300—1700 cm^{-1} region.

level was found even for the C=C stretch around 1550 cm^{-1}.

We also measured dispersed fluorescence spectra with the excitation of the thirty two vibronic bands located in this region, including twenty eight levels whose fluorescence lifetimes were measured. Dispersed fluorescence spectra afford information about the IVR rate, which is important for the discussion of the possible mode-selective isomerization pathway. It is known that the fluorescence spectra from the state before IVR exhibit sharp features reflecting the initially photoexcited vibrational modes while those after IVR are broad and structureless. In fact, the IVR rate can be estimated from the intensity ratio between the sharp and the broad features in the dispersed fluorescence spectra.[2] Eight representative spectra of the dispersed fluorescence are shown in Fig. 6. It was found that the thirty two vibronic levels gave indistinguishable dispersed fluorescence spectra. They exhibit only broad features without any sharp structure. This fact implies that the IVR rate is much faster than the fluorescence decay rate regardless of the fundamentals, combinations or overtones in the energy region from 1300 to 1700 cm^{-1}.

Taking into account of the obtained decay and spectral data, we now address the possibility of a mode-selective isomerization pathway which was argued in a previous paper.[5] First, we consider the "complete IVR" scheme which Syage et al. adopted in the analysis of their fluorescence lifetime data.[2] The "complete IVR" scheme for S_1 stilbene can be described as follows,

$$|s\rangle \xrightarrow{k_{IVR}} \{|l\rangle\} \xrightarrow{k_{ISO}} |p\rangle \qquad \{|l\rangle\} \xrightarrow{k_{RAD}} |g\rangle , \tag{1}$$

where $|s>$, $\{|l>\}$, $|p>$, and $|g>$ represent the initially prepared state, the states after IVR, the perpendicular S_1 state, and the S_0 state, respectively. Here, the isomerization to the perpendicular S_1 state, $|p>$, is assumed to be the only non-radiative decay channel. In this case, the isomerization rate k_{ISO} can be expressed as follows, using the fluorescence decay rate k_{fl} and the radiative decay rate k_{RAD},

$$k_{ISO} = k_{fl} - k_{RAD} . \tag{2}$$

Thus, if we assume the k_{RAD} value to be the same as the fluorescence decay rate of the 0–0 level (k_{fl}^0=0.374 ns^{-1}), the isomerization rate is obtainable from the observed fluorescence lifetime.[2] The calculated isomerization rates for the twenty-eight levels located in the 1300—1700 cm^{-1} region are listed in Table 1. They increase monotonically with the increasing excess energy, reflecting the observed monotonic change of the fluorescence lifetime. The isomerization rate calculated for the C=C stretch level is 0.47 ns^{-1}, which is not anomalous value for this energy region. Consequently, if the "complete IVR scheme" holds, no mode-specific isomerization channel can exist in this energy region.

However, the isomerization rate thus calculated for the C=C stretch level does not agree with the value estimated

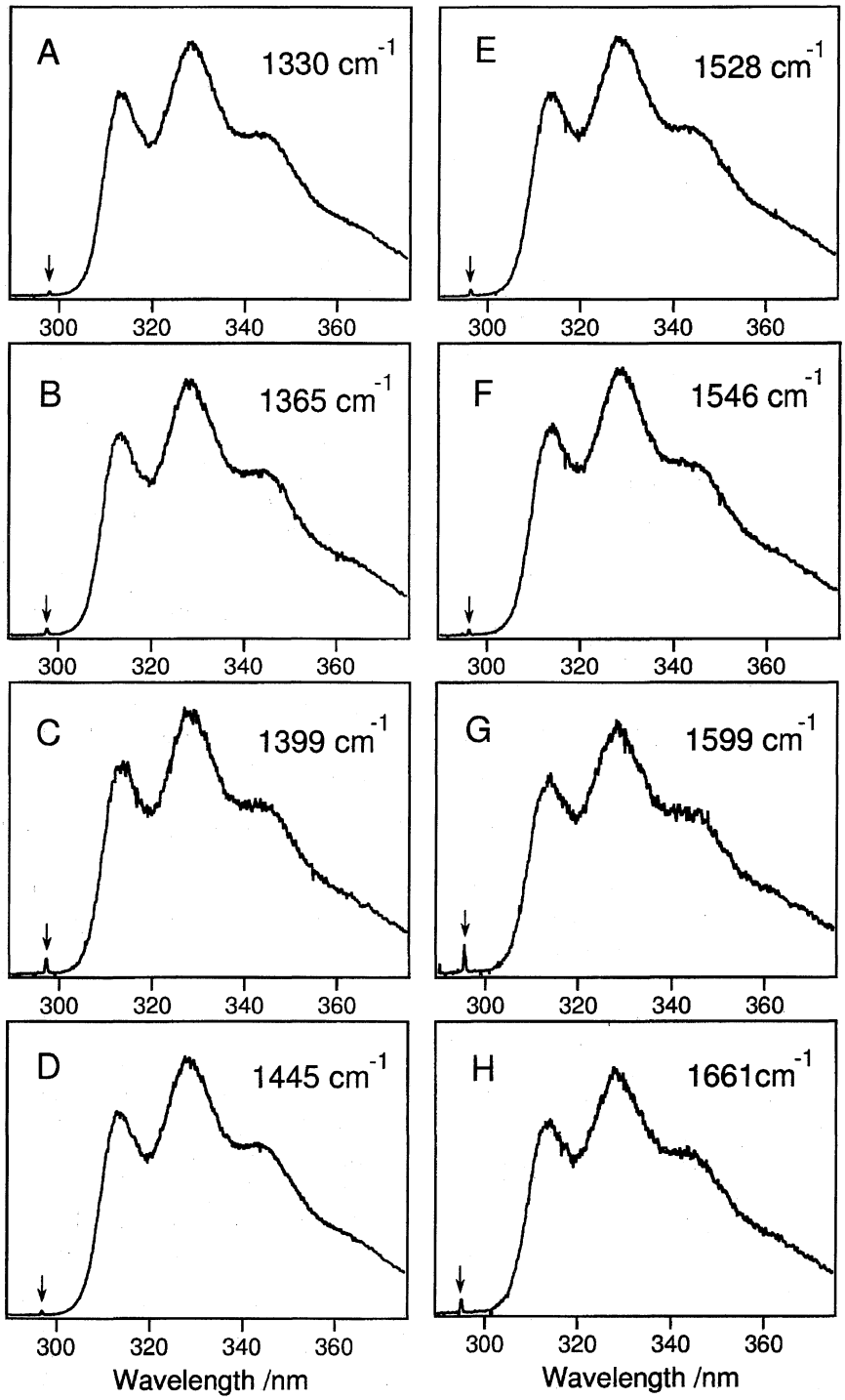


Fig. 6. Dispersed fluorescence spectra obtained with the excitation of the vibronic levels at 1330 cm^{-1} (A), 1365 cm^{-1} (B), 1399 cm^{-1} (C), 1445 cm^{-1} (D), 1528 cm^{-1} (E), 1546 cm^{-1} (F), 1599 cm^{-1} (G), and 1661 cm^{-1} (H). The scattering of the excitation light is marked by an arrow in each spectrum.

from the intensity difference between the fluorescence excitation and the absorption (1.5 ns^{-1}).[5] This discrepancy also manifests in the estimated fluorescence quantum yield. In the "complete IVR" scheme, the fluorescence quantum yield can be evaluated from the fluorescence decay rate as follows,

$$\frac{I_{fl}}{I_{abs}} = \Phi_{fl} = \frac{k_{RAD}}{k_{ISO} + k_{RAD}} \cong \frac{k_{fl}^0}{k_{fl}}. \quad (3)$$

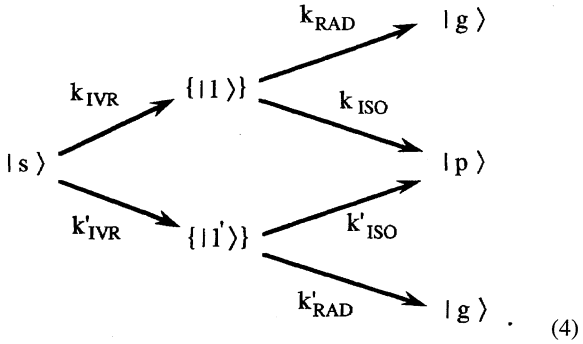
Using the k_{fl} value of 0.84 ns^{-1}, the fluorescence quantum yield is calculated as 0.45 for the C=C stretch band. On the other hand, the fluorescence quantum yield as low as 0.2 was obtained from the direct comparison between the fluorescence excitation intensity and the absorption intensity.[5] This disagreement might indicate that the "complete IVR" scheme does not hold, especially for the C=C stretch vibronic level.

Table 1. Measured Fluorescence Lifetime with Vibronic Excitation of *trans*-Stilbene

Vibrational energy	$\tau_f \pm 2.5\sigma$ [a]	k_{fl}	k_{nr}	τ_f [b]
cm^{-1}	ns	ns^{-1}	ns^{-1}	ns
1330	2.00±0.05	0.500	0.126	1.94±0.06
1341	1.95±0.02	0.513	0.139	
1355	1.94±0.02	0.515	0.141	
1365	1.82±0.03	0.549	0.175	
1378	1.78±0.01	0.562	0.188	
1384	1.77±0.01	0.565	0.191	
1399	1.70±0.01	0.588	0.214	
1416	1.59±0.01	0.629	0.255	
1428	1.60±0.02	0.625	0.251	
1432	1.58±0.01	0.633	0.259	
1436	1.52±0.03	0.658	0.284	
1440	1.49±0.02	0.671	0.297	
1445	1.46±0.03	0.685	0.311	1.50±0.08
1465	1.44±0.02	0.694	0.320	
(1515)	1.31±0.08	0.763	0.389	
1528	1.24±0.02	0.806	0.432	
1540	1.22±0.02	0.820	0.446	
1546	1.19±0.01	0.840	0.466	
1551	1.18±0.01	0.847	0.473	
1555	1.19±0.06	0.840	0.466	
1561	1.15±0.02	0.870	0.496	
1582	1.12±0.02	0.893	0.519	
1599	1.08±0.02	0.826	0.552	
1611	1.02±0.01	0.980	0.606	
1617	1.01±0.02	0.990	0.616	
1636	0.97±0.01	1.03	0.66	
1641	0.97±0.02	1.03	0.66	1.10±0.10
1661	0.92±0.01	1.09	0.71	

a) σ represents standard deviations; $\sigma = \sqrt{\frac{\sum(x_i-\bar{x})^2}{N(N-1)}}$. b) Ref. 2.

In a previous paper,[5] we discussed the "incomplete" IVR scheme, in which the initially prepared state $|s>$ is redistributed into two separate groups of states $\{|l>\}$ and $\{|l'>\}$:



With this scheme, fluorescence quantum yield Φ_{fl}^{total} is given by:

$$\Phi_{fl}^{total} = (1-\gamma)\Phi_{fl} + \gamma\Phi_{fl}' \quad (5)$$

where $\Phi_{fl}=k_{RAD}/(k_{RAD}+k_{ISO})$, $\Phi_{fl}'=k_{RAD}'/(k_{RAD}'+k_{ISO}')$, and $\gamma=k_{IVR}'/(k_{IVR}+k_{IVR}')$. If we assume that the emission originates from $\{|l>\}$ only, that is, Φ_{fl}' is negligibly small compared with Φ_{fl}, the very similar dispersed fluorescence spectra from all the vibronic levels are rationalized. In this case, the value obtained with Eq. 3 corresponds to Φ_{fl}, while that estimated from the intensity comparison is equivalent to Φ_{fl}^{total}. Thus, if we assume that k_{IVR}' is not negligible and that the ratio γ is mode dependent, the discrepancy in the calculated fluorescence quantum yield for the C=C stretch band can be explained. The assumed very low fluorescence quantum yield from $\{|l'>\}$ implies that $k_{RAD}' \ll k_{ISO}'$, which can hold for a large isomerization rate $k_{ISO}' > 10\ ns^{-1}$. To conclude, the present fluorescence decay data provide no evidence for the existence of a mode-selective isomerization channel in S_1 *trans*-stilbene within the framework of the "complete" IVR scheme. However, those data do not rule out the possibility of such mode selectivity in the more general scheme of "incomplete" IVR given in Eq. 4. The possibility of the "incomplete" IVR has already been suggested by other works.[3,9]

Finally, we note the potentiality of using a streak camera for the detection of fluorescence from jet cooled molecules. The high sensitivity of a streak camera allows us to measure fluorescence decay curves with high signal to noise ratios, even for the vibronic levels showing low fluorescence intensity. The unique feature of a streak camera lies in the fact that it provides the two-dimensional image of the time and frequency dispersed spectra.[10,11] Picosecond time-resolved dispersed fluorescence measurements would be the most promising experiments with the use of its two-dimensionality of a streak camera.

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