PICOSECOND EXCITATION AND TRANS–CIS ISOMERIZATION OF STILBENE IN A SUPERSONIC JET: DYNAMICS AND SPECTRA*

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New details of the dynamics and spectroscopy of trans-stilbene are revealed by picosecond excitation of jet-cooled and collision-free molecules. The fluorescence spectra clearly show the low-frequency torsional modes of the ground state. The time-resolved fluorescence following S_1 excitation exhibit exponential decay times ranging from 2.7 ns to ≈190 ps for excitation wavelengths varying from 3102 Å (0 excess energy) to 2850 Å (2851 cm^{-1} excess energy). The results indicate that an energy threshold for isomerization occurs at ≈1200 cm^{-1}. The redistribution of vibrational energy from the optically excited modes to the ethylene bond torsional modes leading to isomerization is discussed.

1. Introduction

The problem of trans–cis photoisomerization of stilbene has been actively pursued for well over two decades, yet the mechanism is still not fully understood. Many fundamental questions remain regarding both the spectroscopy and photochemistry of this system. Neither the form of the excited-state surface near the trans configuration nor the shifts in equilibrium values of coordinates critical to the isomerization are known. The approaches that have been applied in the past range from the pioneering studies of fluorescence yields in solution by Lewis et al. [1] to the more elaborate picosecond time-resolved studies of vapor phase stilbene [2,3]. The latter studies showed that the lifetime, which relates to the isomerization rate, varies with excess energy in the excited singlet state of trans-stilbene. They measured time constants of 15 and 55 ps for excess energies of 8000 and 5200 cm^{-1}, respectively, and correlated these values with changes in the quantum yield of fluorescence from zero to 8000 cm^{-1} of excess energy. The predicted decay time for the 0,0 excitation was 1.6 ns and the barrier to isomerization was estimated to be between 1000 and 2000 cm^{-1}. The optical spectra in the bulb [3], however, show no vibrational structure of consequence; a fact which is attributed to spectral congestion arising from excitation of a thermal distribution involving low-frequency torsional modes. This congestion also prevents one from selectively exciting a single vibrational mode. Consequently the dynamical properties of levels below the barrier, the height of the barrier and the pathways of vibrational energy redistribution are not well known, being obscured in these bulb experiments by the thermal energy.

The ideal conditions in which to study the mechanism for the photoisomerization of ethylenes (and many other photochemical/photophysical processes) are those in which the molecules being studied are

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free from intermolecular interactions (i.e. collision free) and which may be excited into specific excited-state vibronic levels. To this end, we have undertaken the study of the photoisomerization of trans-stilbene in a supersonic jet expansion to produce collision-free and vibrationally cold molecules. We present for the first time vibrationally resolved spectra of isolated trans-stilbene molecules. Furthermore, we report direct time-resolved fluorescence measurements in the jet which allow us to focus on the state-selective rate of photoisomerization as a function of excess energy in the S_1 manifold.

2. Experimental

The use of scintillation grade (Eastman) and zone-refined (46 passes) trans-stilbene was found to give identical fluorescence spectra when exciting the 0,0 band. Hence, both grades were used throughout the experiments. The experimental arrangement (pico-second-jet setup) is very similar to the one published before by Lambert et al. [4]. In what follows we give a brief description and defer the details to a later publication.

The results in this paper were obtained by expanding *t*-stilbene at a nozzle temperature of ≈80°C through a 150 μm pinhole with a backing pressure of ≈35 psi of Ne. A variation of backing pressure and the use of He as the carrier gas resulted in identical fluorescence spectra indicating that no major clustering was occurring. The nozzle-to-laser distance was set at ≈5 mm. The molecular beam apparatus is equipped with a 12″ bore ring jet diffusion pump which maintains an ambient pressure in the expansion chamber of 10^{-4} Torr.

The laser pulses originated from a synchronously pumped dye laser employing a mode-locked (81.6 MHz) argon ion pump laser. The dye (rhodamine 6G) laser pulses were cavity-dumped to give a pulse repetition rate of 4.08 MHz. The frequency doubled ($LiIO_3$) UV pulses were determined to have temporal and frequency pulsewidths (fwhm) of ≈15 ps and ≈0.3 Å (3 cm^{-1}), respectively.

The fluorescence was dispersed with a microprocesser controlled Spex 0.5 m spectrometer. The resolution was 0.1 Å. The fluorescence, which was detected by a fast (photon-counting) photomultiplier, was collected in an MCA in both frequency and kinetic mode. Fluorescence decays were measured using time-correlated single-photon counting. The time response of the system was determined to be better than 300 ps. The ability to obtain the response function of the system (by measuring the time response of a laser pulse) allowed us to deconvolute observed decay curves to obtain time resolution of better than 100 ps when necessary.

3. Results and discussion

3.1. Jet-cooled fluorescence spectra

The fluorescence spectra of *t*-stilbene were recorded for excitation energies ranging from 3102 Å (0–0 band, $\bar{\nu}_0$ = 32237 cm^{-1}) to 2850 Å ($\delta\bar{\nu} = \bar{\nu} - \bar{\nu}_0$ = 2851 cm^{-1}). Representative spectra are presented in fig. 1.

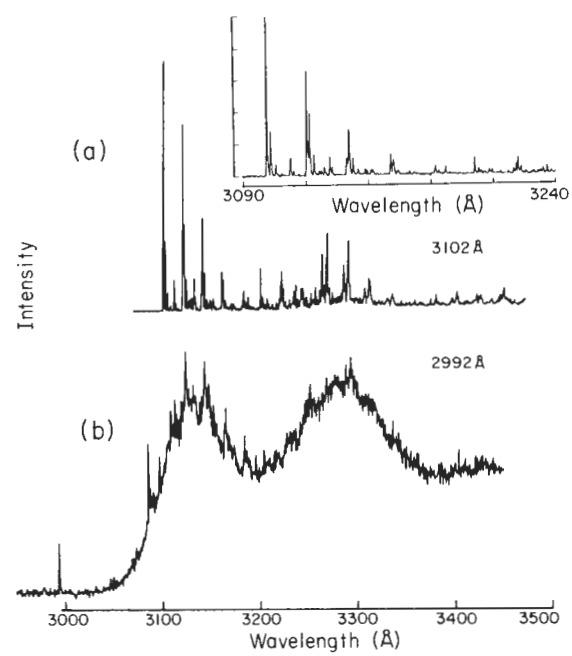

Fig. 1. Frequency-resolved fluorescence spectra for *t*-stilbene. (a) 0–0 excitation ($\delta\bar{\nu}$ = 0); an expanded view of the low-frequency intervals is provided in the insert which shows the prominent 205 cm^{-1} progression and the low-frequency intervals at 19, 44 and 116 cm^{-1}; (b) excitation at $\delta\bar{\nu}$ = 1185 cm^{-1} exhibiting predominantly broad fluorescence. The fluorescence was not corrected for the spectral response of the system.

The most prominent spectral features in the fluorescence spectrum following 0,0 excitation (fig. 1a) are the symmetric in-plane ethylene bending (205 cm^{-1}) and stretching (1654 cm^{-1}) modes. These and many lines in our jet-cooled spectrum correspond to vibrations that have been observed and assigned previously from the low-temperature spectra in mixed crystals [5] and from calculations [6]. One new feature in the present high-resolution spectra is the appearance of low-frequency intervals at 19, 44, and 116 cm^{-1}. The latter two can be correlated with torsional modes calculated by Warshel [6]. It is possible that the weak fluorescence lines at 449 and 485 cm^{-1} are the two modes corresponding to torsion about the double bond; each appearing within 2 cm^{-1} of the predicted frequencies.

An important phenomenon exhibited in the fluorescence spectra (fig. 1) is the emergence of a broad continuum fluorescence for increasing excitation energies. This characteristic is attributed to fluorescence from a "quasi-continuum" of modes into which the optically excited mode may redistribute. The rate for such an intramolecular vibrational redistribution (IVR) is dependent (among other things) on the density of states at the excitation energy. For *t*-stilbene, we have calculated the dependence of the density of vibrational states $\rho(\delta\bar{\nu})$ on the excess energy, $\delta\bar{\nu}$, within the S_1 manifold by assuming harmonic overtones and using Warshel's [6] calculated vibrational frequencies. This gives in the pertinent region,

$$\log_{10}\rho(\delta\bar{\nu}) \approx 0.0018\,\delta\bar{\nu} + 0.297. \qquad (1)$$

The fluorescence spectra at excess energies of $\delta\bar{\nu} \geqslant 1185$ cm^{-1} consist essentially of totally "redistributed" fluorescence suggesting that the dissipative modes behave as an effective bath, thus approaching the statistical limit. In fact, at 1200 cm^{-1}, we obtain $\rho(1200\ cm^{-1}) \approx 300$ states/cm^{-1}. This behavior is quite similar to that observed in anthracene [4,7] when differences in the density of states are accounted for.

3.2. Time-resolved spectra

Fig. 2 contains the fluorescence decay rates, τ_{fl}^{-1}, obtained from an exponential least-squares fit of the decay curves, as a function of excess energy, $\delta\bar{\nu}$. The following observations can be made:

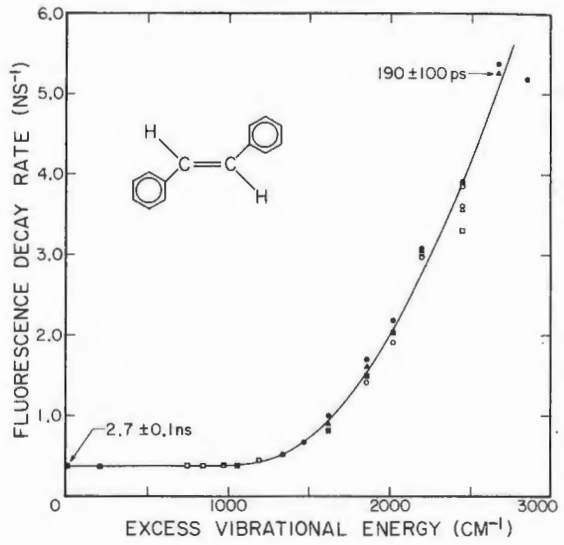

Fig. 2. Observed fluorescence decay rates as a function of excess energy, $\delta\bar{\nu}$. Data points represent different fluorescence wavelengths. The use of different symbols is to help resolve overlapping points.

(1) The fluorescence decay time for the 0,0 excitation was measured to be 2.7 ± 0.1 ns. This value should be compared with previously reported values in solution and with the estimated radiative lifetime (1.7 ns) [8,9].

(2) A sudden increase in τ_{fl}^{-1} at ≈1200 cm^{-1} excess energy was apparent.

(3) Quantum beats were observed for certain sharp fluorescence lines for excitations with excess energy $744 \leqslant \delta\bar{\nu} \leqslant 1185$ cm^{-1} [10]. At these energies the resonance fluorescence generally exhibited faster decay times than those for other components of the fluorescence spectra.

(4) For a given excitation energy, there was no discernible dependence of τ_{fl}^{-1} on the observed wavelength of fluorescence (with the exception of the beat region).

3.3. Mechanism for isomerization

The rapid increase in τ_{fl}^{-1} (fig. 2) very likely reflects the onset for the process of isomerization. Other non-radiative decay channels seem less likely to originate at these excess energies. The activation threshold of ≈1200 cm^{-1} (3.6 kcal/mol) compares

favorably with previous determinations of barriers for *t*-stilbene isomerization in solutions which range from 2–4 kcal/mol [5,9,11]. Our observation of a threshold implies that the barrier to isomerization cannot lie more than $\approx 1200\ cm^{-1}$ above the zero-point energy of S_1. It is conceivable that the isomerization is impeded by inefficient coupling between the optical and torsional modes in the region of relatively sparse level structure below $1200\ cm^{-1}$.

We present in fig. 3a an approximate potential energy diagram for the ethylene C_e–C_e torsional coordinate (θ). There is considerable uncertainty regarding the shapes of the potential surfaces important to isomerization and whether a second excited state S_2 participates in the isomerization process. In the view of Orlandi et al. [12] the barrier to isomerization arises from a crossing of the S_1 and S_2 surfaces since the latter surface is predicted to have a minimum at $\theta = 90°$ [12,13]. Here, we present a general picture of isomerization (fig. 3a) whereby the potential minimum at the perpendicular configuration ($\theta = 90°$) is denoted as S_p. The minimum may be ascribed to either the S_1 surface by an avoided crossing with S_2 (or other surfaces) or to the S_2 surface via an allowed crossing with S_1.

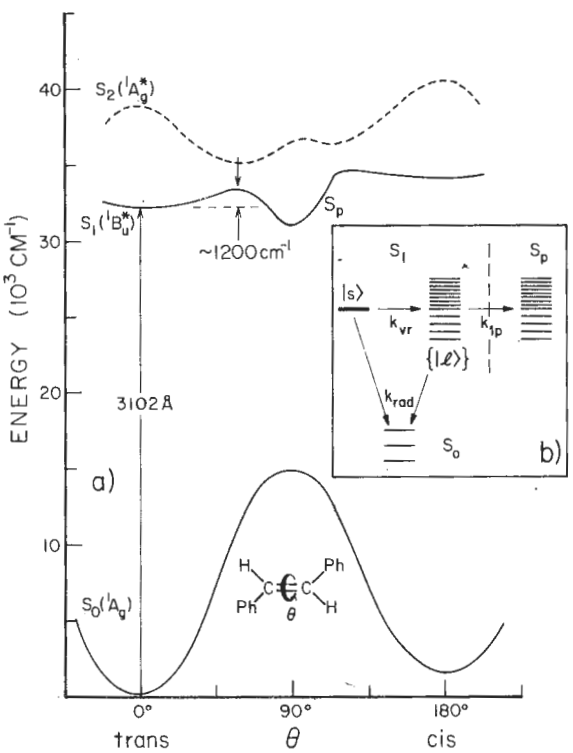

Fig. 3. (a) Approximate potential energy diagram for the ground state S_0 and the two lowest excited states S_1 and S_2 as a function of the C_e–C_e torsional rotation angle θ. (b) A schematic for the photoisomerization pathway discussed in the text: $|s\rangle$ represents the optically excited state and $\{|l\rangle\}$ the dissipative states. The rate constants are defined in the text.

The simple model in fig. 3b is adequate for interpreting our results in regard to the molecular steps responsible for isomerization. Implicit in this model are the reasonable assumptions that (i) the optically excited modes must redistribute into other modes including the torsional modes for ethylene bond rotation in order for isomerization to occur, (ii) the conversion from S_1 to S_p (k_{1p}) is irreversible, and (iii) the principal channel for non-radiative decay is isomerization. For $\delta\bar{\nu} < 1200\ cm^{-1}$, the non-radiative decay rate, ($k_{nr} = \tau_{fl}^{-1} - \tau_{rad}^{-1}$) is slow (fig. 2). Other non-radiative processes (e.g., $S_1 \rightarrow S_0$ internal conversion) are not expected to account for the rapid increase in τ_{fl}^{-1} for $\delta\bar{\nu} > 1200\ cm^{-1}$ [2].

For excitation energies where $\delta\bar{\nu} > 1200\ cm^{-1}$, essentially no sharp (unredistributed) fluorescence is observed ($\approx$1% or less) indicating that the observed fluorescence decay rates are proportional to the population of the S_1 $\{|l\rangle\}$ modes, and that $k_{vr} \geqslant 100 \times k_{rad}$ in this model. According to the kinetic scheme in fig. 3b, the time dependence of the S_1 $\{|l\rangle\}$ modes is given by

$$S_1^l(t) = [k_{vr} S_1^s(0)/(k_{vr} - k_{1p})] \times \{1 - \exp[-(k_{vr} - k_{1p})t]\} \exp[-(k_{1p} + k_{rad})t], \quad (2)$$

where $S_1^s(0)$ is the initial population of the optically excited mode $|s\rangle$. Under the realistic conditions $k_{vr} \gg k_{1p}, k_{rad}$, it is clear that the fluorescence decays by a single exponential with a decay constant given by $\tau_{fl}^{-1} = k_{1p} + k_{rad}$ as observed experimentally. Further evidence that $k_{vr} \gg k_{1p}$ is found in the smooth dependence of τ_{fl}^{-1} on $\delta\bar{\nu}$ (fig. 2) irrespective of the nature of the mode excited. From these observations it follows that the vibrational redistribution is a crucial step to the overall process of isomerization. Work is currently in progress towards unravelling and measuring the specific steps leading to isomerized stilbene products [14].

4. Conclusion

We present here the first report on the state-selective intramolecular isomerization pathways of trans-stilbene, achieved by employing the tandem arrangement of picosecond excitation and supersonic molecular expansion. The jet-cooled fluorescence spectra (fog 0–0 excitation) have resolved the very-low-frequency torsional modes of the isolated molecules. At higher excitation energies, a broad continuum fluorescence appears due to dissipation by vibrational energy redistribution of the optically excited modes to other modes. This broad fluorescence, which evolves completely within the response time of our system (i.e. <100 ps), accounts for virtually all fluorescence observed at excess excitation energies of $\delta\bar{\nu} > 1200$ cm^{-1} and compares with the emission of stilbene in a bulb [15]. Finally, time-resolved measurements of the fluorescence indicate that the decay times are independent of the fluorescence wavelength (except in the beat region) and range in value from 2.7 ns for $0 \leqslant \delta\bar{\nu} \leqslant 1062$ cm^{-1} to ≈190 ps at $\delta\bar{\nu} = 2667$ cm^{-1}. This dramatic change in the rate is attributed to isomerization, with the onset occurring at ≈1200 cm^{-1}.

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