kovian Langevin equation seems valid. The main complication in this approach for activated chemical reactions is the evaluation of the friction, which in the barrier region is expected to be quite different than the more familiar viscosity-based friction from the Stokes–Einstein formula.[4] In fact, the ab initio evaluation of this "excited-state" friction may be difficult, taking on aspects of and becoming mixed up with entropy concepts that depend on a full knowledge of the vibrational state distribution of the solvent/solute system in the barrier region.[26] Hidden somewhere in the evaluation of this friction is the connection between quantum and classical determinations of reaction rates.

The original empirical friction formula[16] of Lee et al., which has recently been put on a firmer theoretical footing,[3,9] indicated the need for "additional friction contributions from the molecular properties of the solute itself". This seems to be an unavoidable complication in the application of the generalized Langevin equation to activated condensed-phase chemical reactions.

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trans-Stilbene: A Rigid, Planar Asymmetric Top in the Zero-Point Vibrational Levels of Its S₀ and S₁ Electronic States

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Resolved rotational structure has been observed in the fluorescence excitation spectrum of the 0_0^0 band in the S₁ ← S₀ electronic transition of *trans*-stilbene (*t*S) in the collision-free environment of a molecular beam. Analysis of this structure yields rotational constants for the S₀ and S₁ states, their inertial defects, and the orientation of the optical transition moment in the molecular frame. The results demonstrate that *t*S is a rigid, planar asymmetric top in the zero-point vibrational levels of both electronic states.

trans-Stilbene (*t*S, 1) has played a pivotal role in previous studies of the photoisomerization of substituted ethylenes, both

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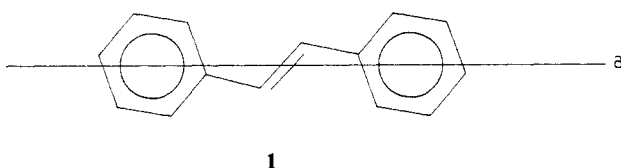
in the gas phase and in the condensed phase. The accepted model for the isomerization process[1] is that, following excitation and rapid equilibration to a planar minimum, the molecule passes over a barrier on the S₁ surface into a twisted, less-conjugated configuration which then decays rapidly into cis or trans ground-state structures. Both the barrier crossing and subsequent relaxation of the twisted form are strongly solvent dependent.

This picture has received support from several recent spectroscopic studies of the isolated molecule. Both frequency-[2] and time-resolved[3] experiments in supersonic jets give evidence for the existence of a barrier on the S₁ surface of order 1000 cm⁻¹. Additionally, careful analyses of vibrational structures in the S₁ ← S₀ jet spectra of *t*S[4] and its *p*-methyl and α-deuterio derivatives,[5]

and of rotational quantum beats in the time-resolved fluorescence decay of *t*S,[6] suggest that the molecule is a planar, centrosymmetric species low in the vibrational manifolds of its S₀ and S₁ states. Nonetheless, partly because the frequency-resolved spectra exhibit significant low-frequency mode activity, the image of *t*S as a large, nonrigid polyatomic molecule persists.

Molecular geometry considerations clearly are relevant to understanding *t*S and its dynamic behavior following the absorption of light. In this report, we describe the observation and analysis of resolved rotational structure in the 0_0^0 band of the S₁ ← S₀ fluorescence excitation spectrum (FES) of *t*S at ∼310 nm. The derived values of the rotational constants demonstrate, unambiguously, that *t*S is a rigid, planar asymmetric top in the zero-point vibrational levels of its S₀ and S₁ electronic states.

The experiments were performed with the high-resolution molecular beam laser spectrometers in Nijmegen[7] and Pittsburgh.[8] The beam was formed by expansion of a mixture of *t*S vapor (Merck, heated to 400 K) and Ar carrier gas (0.25–1 bar) through a heated 100-μm quartz nozzle, collimated with two skimmers, and crossed 30 cm (Nijmegen) or 100 cm (Pittsburgh) downstream by a tunable CW laser operating in the ultraviolet. Typically, ∼500 μW of UV power was employed; the laser frequency width is less than 1 MHz. Emission from the interaction zone was collected by spatially selective optics, imaged on a phototube, and detected by using photon-counting techniques. The FES, I₂ absorption spectrum, etalon markers, and laser power curve were recorded simultaneously with an on-line data acquisition system, providing calibrated and normalized data that are accurate to ±0.1

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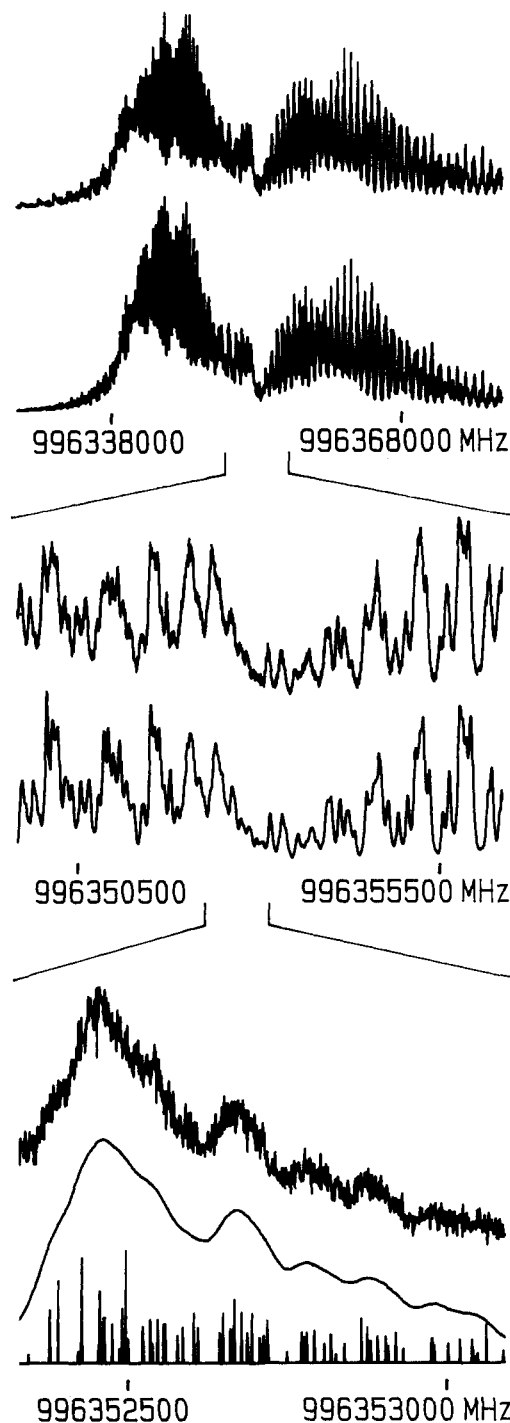
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MHz in relative frequency, and ±100 MHz in absolute frequency.

Representative results of these experiments are illustrated in Figure 1 in three successive horizontal scale expansions of the data. The markers in the top panel span 30 GHz (1 cm^{-1}), those in the middle panel span 5 GHz, and those in the bottom panel span 500 MHz. The entire 0_0^0 band (top panel) exhibits a rich rotational structure that consists of more than 500 identifiable transitions spread over ~2 cm^{-1}. Computer simulation (vide infra) of this band (lower spectrum in the top panel) satisfactorily reproduces the experimentally observed relative intensities and overall contour (upper spectrum). The middle panel shows the center portion of the 0_0^0 band that contains contributions from P-, Q-, and R-branch transitions ($\Delta J = -1$, 0, and +1, respectively). A comparison of the experimental trace (upper) with the calculated one (lower) demonstrates the high quality of the fit. Similarly excellent agreement between the calculated and experimental data was obtained throughout the entire band. The bottom panel shows a small segment of the Q branch at full experimental resolution (top trace). Also shown in this panel are two computer simulations of this segment, with assumed Lorentzian line widths (fwhm) of 70 MHz (middle trace) and 1 MHz (bottom trace). A comparison of the top two traces in this panel shows that an assumed fwhm of 70 ± 10 MHz reproduces accurately the experimentally observed line shape. The measured fluorescence lifetime of the zero-point vibrational level of S$_1$ tS is τ_f = 2.64 ± 0.03 ns.[3] Hence, the observed width in the frequency domain is homogeneous in nature since $[2\pi(70 \pm 10) \times 10^6 \text{ s}^{-1}]^{-1}$ = 2.3 ± 0.3 ns. (Typical Doppler widths observed in the two spectrometers are less than 10 MHz.) A comparison of the bottom two traces in this panel further shows that the underlying rotational structure which would be observed in the absence of lifetime broadening is, in fact, even more complex than that which is observed. More than 3000 calculated lines are included in the computer simulation of the entire band.

The calculations were performed using an expanded version of the program ASYROT[9] that employs Watson's distortable asymmetric rotor Hamiltonian.[10] Fits of the spectrum were made using the derivative approximation[11] and a standard least-squares statistical analysis.[12] Inputting the frequencies of 525 observed lines (with an assumed experimental error of 10 MHz) and including only rigid-rotor terms for both vibronic levels, we obtain a fit with a standard deviation of 8.7 MHz, significantly less than the experimental line width. Adding centrifugal distortion terms up to sixth order (within the A reduction)[10] improved the standard deviation, but only by 1 MHz. Moreover, the error bars for these constants were as large as the constants themselves so they were neglected in the final analysis. More than 95% of the experimentally observed intensity can be accounted for by assuming a-axis selection rules. There is little or no perpendicular character in the rotationally resolved spectrum of the 0_0^0 band. From this result we conclude that the S$_1$ ← S$_0$ optical transition moment is oriented parallel to the a inertial axis to within ±13°. The rotational temperature of the fit is 6 ± 0.5 K.

Several factors contributed to the success of the analysis. One is that the FES of tS is very similar to the corresponding spectrum of all-trans-1,4-diphenyl-1,3-butadiene (DPB).[13] Both exhibit well-developed K subbands, each with its own P, Q, and R branch. Additionally, both spectra are strongly influenced by relatively large changes in the A rotational constants (vide infra) which shift entire K subbands to the red by $\Delta\nu \sim \Delta A K^2$. These shifts are readily apparent in the spectrum of DPB since it is fully resolved, owing to its longer fluorescence lifetime (τ_f = 63 ns). But they also appear in the spectrum of tS despite its larger homogeneous

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Figure 1. The rotationally resolved fluorescence excitation spectrum of the 0_0^0 band in the S$_1$ ← S$_0$ transition of *trans*-stilbene, at ~310 nm. The top panel shows the overall experimental band contour (top trace), which spans ~2 cm^{-1}, and the corresponding computer simulation (bottom trace). The middle panel shows the center portion of the experimental spectrum at higher resolution (top trace) and the corresponding computer simulation (bottom trace). This portion of the spectrum contains contributions from (left) P-, (center) Q-, and (right) R-branch transitions. The bottom panel shows an expanded portion of the Q branch, at full experimental resolution (top trace), and two corresponding computer simulations, one with an assumed line width of 70 MHz (middle trace) and one with an assumed line width of 1 MHz (bottom trace). The two strongest lines in the experimental trace are the K subband Q-branch transitions with K' = 2 (left) and K' = 1 (right). The temperature of the computer simulations is 6 K. The weak progression of band structure that occurs on the red side of the P branch (top panel) is more prominent at higher temperatures and is caused by the formation of K subband heads at or near J' = 50.

TABLE I: Inertial Parameters of the Zero-Point Vibrational Levels of the Ground (^1A_g) and First Excited Singlet (^1B_u) States of *trans*-Stilbene

state	constant	experiment[a]	QCFF/PI[b]
^1A_g	A''	2611.3 ± 7.7 MHz	2659.1 MHz
	B''	262.86 ± 0.02 MHz	261.6 MHz
	C''	240.56 ± 0.02 MHz	238.2 MHz
	κ''	−0.9812	
	$\Delta I''^c$	−15.3 ± 0.6 amu Å^2	
^1B_u	ΔA	−71.14 ± 0.06 MHz	−61.0 MHz
	ΔB	5.928 ± 0.004 MHz	2.8 MHz
	ΔC	3.963 ± 0.005 MHz	1.8 MHz
	$\Delta \kappa$	+0.0023	
	$\Delta(\Delta I)^c$	2.9 ± 0.9 amu Å^2	
	band origin	32234.744 ± 0.002 cm^{-1}	

[a] Error bars for the rotational constants are the square roots of the variances obtained from the least-squares analysis. However, the B'' and C'' values may only be accurate to ±0.1 MHz owing to systematic errors in the experiment (ref 8), which also may affect the ΔA, ΔB, and ΔC values. [b] Reference 14. [c] Inertial defects, $\Delta I = I_c - I_b - I_a$.

widths. Note, for example (cf. Figure 1), how the Q-branch transitions in each successive K subband shift to the red in a K^2-dependent way. Less obvious in the *t*S spectrum is another consequence of the large ΔA, the mixing of J families. Not all K belonging to a particular J appear together. Instrumental in the analysis of these effects was newly developed software that made it possible to work with portions of the experimental spectrum, the simulated spectrum with an adjustable line width, and a deconvoluted "stick" spectrum simultaneously on a graphics monitor. With this software, we were able to separate out specific K subbands, manipulate their relative frequencies, and co-add them to produce simulated spectra of the desired line width and shape.

The parameters derived from the experimental spectrum are summarized in Table I. *t*S is a rigid, near-prolate asymmetric top in the zero-point vibrational levels of both electronic states, with $\kappa'' = -0.9812$ and $\kappa' = -0.9789$. This fact, together with the parallel-type nature of the 0_0^0 band, limits the accuracy of the derived A'' value to ±7.7 MHz. But B'' and C'' are known to within at least ±0.1 MHz, as are the changes in the rotational constants that occur on electronic excitation, ΔA, ΔB, and ΔC ($\Delta A = A' - A''$, etc.). The largest change in the rotational constants involves motion about the a axis: $\Delta A = -71.1$ MHz. Only very small (positive) changes in B and C occur ($\Delta B = 5.9$, $\Delta C = 4.0$ MHz). [The value of $B' + C' = 513.3 ± 0.1$ MHz, independently determined in this work, is the same within experimental error as that previously determined in the quantum beat studies of Zewail and co-workers,[6] $B' + C' = 513.2 ± 0.1$ MHz.] From these results we conclude that the absorption of a photon produces a slight expansion of the molecule in directions perpendicular to a. Additionally, the inertial defects (ΔI) of both vibronic levels are negative. From these results we conclude that *t*S is planar in the zero-point vibrational levels of both electronic states, in agreement with recent spectroscopic studies[4-6] and force-field (QCFF/PI) calculations.[14]

Also listed in Table I are the inertial parameters of S_0 and S_1 *t*S derived from the QCFF/PI calculations.[14] The agreement between theory and experiment is remarkably good, for both states. The calculated ΔA, ΔB, and ΔC values (−61.0, 2.8, and 1.8 MHz, respectively) are in close accord with the experimental ones. This agreement encourages speculation about geometry changes that might be responsible for the observed differences in the rotational constants of the two states. Negri et al.[14] found that two principal structural changes occur on electronic excitation, a lengthening

of the C_e–C_e bond (from 1.359 to 1.435 Å) and a shortening of the C_e–C_{ph} bonds (from 1.477 to 1.424 Å). If the theoretical S_0 geometry is modified by incorporating these changes, and these changes alone, ΔA, ΔB, and ΔC values of −10.7, 4.5, and 3.6 MHz result. Additionally, Negri et al.[14] found that the C–C bond lengths in the phenyl rings are only slightly affected by $S_1 \leftarrow S_0$ excitation, with the largest change being an increase in the C_{ph}–C_o bond lengths of ~0.03 Å. If the theoretical S_0 geometry is again modified by incorporating all calculated changes in the ring C–C bond lengths, and these changes alone, ΔA, ΔB, and ΔC values of −50.9, −1.2, and −1.8 MHz result. Comparing these two sets of calculated values with those observed experimentally (−71.1, 5.9, and 4.0 MHz, respectively), we conclude that both types of distortions are important but that changes in the ring C–C bond lengths (particularly those most perpendicular to a) are principally responsible for the change in A. These conclusions, although speculative, are consistent with the observed vibrational activity in the $S_1 \leftarrow S_0$ spectrum[4,5] and with recent electronic hyperpolarizability measurements in solution.[15] We note, also, that differences in the ring geometries of S_0 and S_1 DPB appear to make major contributions to the ΔA, ΔB, and ΔC values associated with the corresponding electronic transition in this molecule.[13]

The inertial defects of both vibronic levels in *t*S are relatively large in magnitude, $\Delta I'' = -15.3$ and $\Delta I' = -12.4$ amu Å^2. For comparison, the corresponding values derived from the rotationally resolved spectrum of the 0_0^0 band of naphthalene are $\Delta I'' = -1.4$ and $\Delta I' = -1.6$ amu Å^2.[7] No doubt the larger $|\Delta I|$'s in *t*S indicate some relatively large amplitude out-of-plane vibrational motion in the two connected levels, perhaps involving the C_e–C_{ph} a_g torsional mode. We calculate $\Delta I = -11.2$ amu Å^2 for a 10° twist along this coordinate, starting with the S_0 equilibrium geometry of Negri et al.[14] Significantly, the frequency of the a_g torsional mode increases on electronic excitation[4,5] which would account for the observation that $|\Delta I|$ is smaller in S_1. From this result we conclude, in agreement with the QCFF/PI calculations, that *t*S is more conjugated in the excited electronic state. Increased displacement along the a_g torsional coordinate at higher temperatures would explain the earlier conclusion from gas-phase electron diffraction data[16] that *t*S is nonplanar in the ground electronic state, a suggestion made by others as well.[5]

Summarizing, we have observed and assigned rotational structure that appears in the 0_0^0 band of the $S_1 \leftarrow S_0$ fluorescence excitation spectrum of *trans*-stilbene in the collision-free environment of a molecular beam. Individual lines show homogeneous widths of 70 MHz owing to the short fluorescence lifetime of the S_1 state. Despite this fact, our assignment of the spectrum yields highly accurate rotational constants for the zero-point vibrational levels of both electronic states. We also determined that the $S_1 \leftrightarrow S_0$ optical transition moment is parallel to the a inertial axis to within ±13°. The results show that electronic excitation produces small geometrical changes in both the ethylenic and phenylic portions of the molecule but that *trans*-stilbene is a rigid, planar asymmetric top low in the vibrational manifolds of both electronic states. Both zero-point vibrational levels appear to exhibit relatively large out-of-plane vibrational amplitudes. Further high-resolution studies promise to provide an increasingly accurate picture of the S_1 surface at higher energies.

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