JET-COOLED STYRENE: SPECTRA AND ISOMERIZATION

J.A. SYAGE, F. AL ADEL and A.H. ZEWAIL *
Arthur Amos Noyes Laboratory of Chemical Physics, California Institute of Technology, Pasadena, California 91125, USA ‡

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The excitation and dispersed fluorescence spectra for the $\tilde{A}\,^1A' \leftarrow \tilde{X}\,^1A'$ transition of styrene, cooled in a supersonic jet, are reported. Assignment of the vibrational modes in the ground and excited electronic states are made and the excess energy dependence of the fluorescence spectra are analyzed in terms of their relevance to the dynamics of photoisomerization. We compare our results with those of stilbene and discuss the influence of IVR and mode mixing in the S_1 surface.

1. Introduction

In a previous paper [1], we presented the spectra and picosecond dynamics of photoisomerization in jet-cooled trans-stilbene. Being the first example of large molecule photochemistry in jet beams, we extended the studies to other similar systems in the hope of learning more about the origin of the threshold effect (barrier for isomerization) and the effect of IVR on the dynamics. Work on diphenylbutadiene [2] has been reported; here we present our findings on styrene (i.e. phenylethylene), which is lower in symmetry and has a lesser density of states than stilbene.

Although similar in structure to stilbene, styrene exhibits important differences which allow one to unravel critical interactions in the excited-state reactive surface of both molecules. For example, certain symmetry restrictions which bear on the "allowedness" of the proposed A_g, B_u excited-state crossing in *t*-stilbene [1,3] may be either reduced or absent in styrene, conceivably due to the overall reduction in symmetry. Moreover, the relative energies of these corresponding states in styrene are expected to be further apart in energy, making the avoided crossing less probable.

The role of the excited-state surface and vibrational "relaxation" in styrene isomerization has been the subject of previous investigations in the gas phase (bulb) [4,5]. In one of these studies, Hui and Rice [4] concluded that the lowest excited electronic state of styrene is stable for the twisted rather than the planar ethylenic configuration. Recent spectroscopic evidence, however, suggests a planar excited state similar to the ground state [6]. Hui and Rice [4] further concluded, based on their model of the excited state and using results from analogous systems, that the rate of isomerization is faster than intramolecular vibrational redistribution (IVR) and independent of the vibrational energy of the molecule, at least up to $\approx$2500 cm^{-1}. This result poses some interesting questions regarding intramolecular coupling in view of our recent observations of rapid IVR and strong vibrational energy dependent rates in photoreactive systems [1,7–9].

The elucidation of the intermode coupling interactions leading to IVR and reaction requires a detailed analysis of the vibrational modes and energy level structure of the molecule. Excellent spectroscopic studies of styrene have been reported recently for molecules in a bulb [6,10,11]. In this paper, we report the spectroscopy of jet-cooled styrene via single vibronic level (SVL) laser excitation and fluorescence. These studies reveal features of the mode structure and coupling for styrene in the absence of spectral congestion and sequence bands present in the bulb work. As a preliminary report, this work focuses on

* Camille and Henry Dreyfus Foundation Teacher–Scholar.
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the detailed assignments of the ground and first excited electronic state vibrations observed in excitation and fluorescence. In addition we include the resolved fluorescence spectra as a function of excess vibrational energy in order to assess the role of IVR and to probe the shape of the excited-state surface. Finally, we compare the styrene and stilbene results and comment on the nature of the S_1 reactive surface.

2. Experimental

The excitation and resolved fluorescence spectra were recorded using a pulsed supersonic jet system. A detailed description of the apparatus will be given elsewhere [9]. The pulsed nozzle relies on a low inductance solenoid modified to deliver pulse widths of typically 250 μs when driven by a pulsed amplifier (10 kW peak power). A digital temperature controller is used to maintain the nozzle temperature to better than 1°C. A YAG pumped dye laser (5 ns pulses) was operated at 15 Hz. UV pulses were generated with a KDP crystal whose angle was optimized via a computer-controlled feedback system, thus allowing continuous UV scans.

Styrene (Alfa, >99%) was heated to 70°C and expanded through a 300 μm aperture with a backing pressure of 50 psi He (unless otherwise stated). The nozzle-to-laser distance was 1.5–2.0 cm where cooling was determined to be complete as indicated by constant rotational bandwidths and hot band intensities at longer distances. Our compact beam is pumped by a 4″ diffusion pump which maintained an ambient pressure in the expansion chamber of less than 3×10^{-4} Torr.

The excitation spectra were recorded by collecting the fluorescence via *f*/1 optics and using a Schott WG320 cutoff filter to eliminate scattered laser light. Dispersed fluorescence spectra were recorded using a Jarrell–Ash 0.5 m monochromator with slit resolution of 1–2 Å. UV fluorescence was detected by an EMI6256B PMT. The fluorescence signal was normalized with respect to laser intensity using a 1P28 PMT, which detected a small portion of the UV laser output. The PMT outputs were fed into a dual channel boxcar integrator from which the normalized output was digitized by a voltage to frequency converter and stored on floppy disk.

The dye laser and monochromator wavelength scales were calibrated against known Ne lines observed in a Fe–Ne discharge lamp (see ref. [9] for further details). The vibrational modes observed in the excitation and resolved fluorescence spectra are reported to an accuracy of 0.5 and 5 cm^{-1}, respectively. Vacuum corrections have been made. The relative intensities in the resolved fluorescence spectra have not been corrected for the spectral response of the PMT.

3. Results and discussion

The frequency of the 0_0^0 transition to the first excited electronic state, $\tilde{A}^1A' \leftarrow \tilde{X}^1A'$, was detected at 34760 cm^{-1} (2876.9 Å). In C_s symmetry, the 42 normal vibrations in styrene fall into symmetries of a′ (ν_1 to ν_{29}) and a″ (ν_{30} to ν_{42}), where we adopt the mode numbering of Hollas et al. [6], based on Mulliken's convention [12]. When appropriate, the styrene modes are also associated with the corresponding benzene modes (which we express in brackets [ ]) using Wilson's numbering scheme [13]. The approximate motions of the styrene modes are designated in ref. [14].

3.1. Excitation spectra

The jet-cooled excitation spectrum of styrene is illustrated in fig. 1 and the frequencies and assignments of the excited electronic state vibrations tabulated in table 1. We obtain very good agreement (±0.5 cm^{-1}) with Hollas and co-workers [6] on essentially all frequencies and assignments. We shall therefore discuss only those features which are new in this work or which we find to be uncertain in previous bulb studies, because of thermal congestion.

Strong activity occurs in the 940–990 cm^{-1} region which makes assigning close lying transitions of comparable intensity very difficult. There are six fundamentals in this region (ν_{19} to ν_{24}), four of which are in-plane C–H bending vibrations (ν_{19}, ν_{20}, ν_{21} and ν_{23}). Consequently strong mixing (e.g. Duschinsky effects [6]) giving rise to frequency shifts and intensity anomalies can be expected. Nonetheless, we clearly resolve all the lines and hence propose the tentative assignments in table 1. We assign the $24_0^1[12_0^1]$ and $23_0^1[18a_0^1]$ modes to the strongest lines in the region

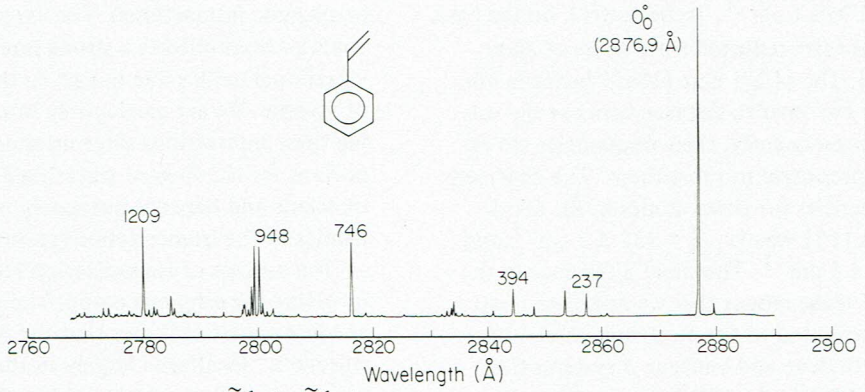

Fig. 1. Excitation spectrum of styrene for the $\tilde{A}\,^1A' \leftarrow \tilde{X}\,^1A'$ electronic transition. Expansion conditions were 50 psi Ar and 70°C sample temperature. Mode frequencies are expressed in wavenumbers. Spectra recorded under 50 psi He, which were used for the assignments in table 1, showed no noticeable differences.

Table 1
Assignment of the excitation spectrum of jet-cooled styrene [a]

Frequency [b] (cm^{-1})	Relative intensity	Assignment [c,d]	Frequency [b] (cm^{-1})	Relative intensity	Assignment [c,d]
0.0	100.0	0_0^0	972.4	1.7	$(537)_0^1 27_0^1$ (?)
59.5	0.6	$41_0^1 42_1^0$	980.7	3.1	$19_0^1[9a_0^1]$
193.2	0.9	41_0^2 [$10a_0^2$]	983.0	3.0	$21_0^1[18b_0^1]$ (?)
237.2	8.9	29_0^1	987.3	1.9	$25_0^1 29_0^1$ (?)
282.4	9.3	$41_0^1 42_0^1$	1029.2	1.7	$25_0^1 41_0^1 42_0^1$
349.1	4.0	$40_0^1 41_0^1$	1095.8	0.4	$25_0^1 40_0^1 41_0^1$
371.0	0.8	42_0^2	1117.9	0.3	
394.5	9.6	28_0^1 [$6a_0^1$]	1138.6	2.8	$25_0^1 28_0^1$
437.1	2.0	27_0^1	1145.8	6.3	17_0^1 [3_0^1]
505.5	0.6	40_0^2 [$16a_0^2$]	1153.0	0.2	28_0^3 (?)
517.5	0.6	$29_0^1 41_0^1 42_0^1$	1184.6	2.7	$29_0^1(948)_0^1$, $25_0^1 27_0^1$ (?)
523.2	4.6		1195.7	1.7	$29_0^1(959)_0^1$
528.2	2.9	26_0^1 [$6b_0^1$]	1209.0	25.6	18_0^1 [13_0^1]
537.3	2.0		1229.2	0.3	$41_0^1 42_0^1(948)_0^1$
548.7	0.8		1240.6	1.3	$41_0^1 42_0^1(959)_0^1$
563.6	0.2	$41_0^2 42_0^2$	1268.1	0.4	$25_0^1(523)_0^1$
630.0	0.3	$28_0^1 29_0^1$	1272.7	0.3	$25_0^1(528)_0^1$
678.7	0.3	$28_0^1 41_0^1 42_0^1$, $27_0^1 29_0^1$ (?)	1286.8	2.0	$25_0^1(537)_0^1$ (?)
745.8	23.6	25_0^1 [1_0^1]	1299.1	2.2	16_0^1
862.2	0.2	27_0^2, $28_0^1 29_0^2$ (?)	1308.3	0.3	$(349)_0^1(959)_0^1$
940.4	3.4	22_0^1	1341.7	1.1	$28_0^1(948)_0^1$
947.8	22.6	24_0^1 [12_0^1]	1353.3	0.9	$28_0^1(959)_0^1$
959.1	22.8	23_0^1 [$18a_0^1$]	1359.1	0.8	$28_0^1(966)_0^1$
965.4	8.3	20_0^1 [15_0^1]	1375.7	1.4	$22_0^1 27_0^1$ (?)

a) Assignments were based on spectra recorded under nozzle conditions of 50 psi He and 70°C sample temperature.
b) Frequencies are reported relative to the 0_0^0 at 34760 cm^{-1} to an accuracy of 0.5 cm^{-1}. The absolute cm^{-1} accuracy is ±2 cm^{-1}.
c) Notations in brackets [ ] designate benzene-like modes using Wilson's convention [13].
d) Combination bands involving fundamentals of uncertain assignment are designated by the frequency in parentheses ( ).

(i.e. 947.9 and 959.1 cm^{-1}, respectively), on the basis of jet-cooled spectra reported for a series of alkylbenzenes [15]. The $[12^1_0]$ and $[18a^1_0]$ benzene normal modes do not involve displacements at the substituent site, consequently, their frequencies are expected to be insensitive to substituent. The observed range of frequencies for these modes in the alkylbenzene series [15] was $[\nu_{12}] = 932 \pm 2$ cm^{-1} and $[\nu_{18a}] = 966 \pm 5$ cm^{-1}. The small difference in the frequencies of these modes that we associate to styrene may be attributed to the electronic interaction between the ethylene and benzene π systems (i.e. conjugation) [6,10,11,16,17]. Likewise, Fermi resonances or Duschinsky effects are not unexpected for this active region and could also account for the frequency differences. Although, the transition 23^1_0 $[18a^1_0]$ may be assigned to the less intense line at 965.4 cm^{-1}, we prefer to assign this line to 20^1_0 $[15^1_0]$ in agreement with a study that detected two-photon activity in the $\tilde{A}$ state of jet-cooled styrene [18].

We have identified possible combination bands at 972.4 and 983.0 cm^{-1} which may derive some intensity through Fermi resonances. The 22^1_0 fundamental at 940.4 cm^{-1} has previously been assigned [6], however the 19^1_0 $[9a^1_0]$ and 21^1_0 $[18b^1_0]$ remain uncertain.

The benzene $[\nu_{6b}]$ normal mode, corresponding to ν_{26} in styrene is also predicted to be insensitive to substitution (for example, it occurs at 526 ± 4 cm^{-1} in the alkylbenzenes [15]). Hollas [6] assigns this mode at 544.6 cm^{-1}, however, we observe no line near this frequency in our jet-cooled spectra. Hot bands are predicted at 547 cm^{-1} $(25^1_0 41^0_1)$ and 550 cm^{-1} $(25^1_0 42^0_4)$ which may account for this observation in the bulb spectra. We prefer to assign 26^1_0 $[6b^1_0]$ to either the 523.2 or the 528.2 cm^{-1} line, on the basis of the frequencies in the alkylbenzenes, although we cannot rule out the 537.3 cm^{-1} line. The appearance of three comparably intense lines where only one is expected is perhaps suggestive of Fermi resonance. Interestingly, both the 523 and 528 cm^{-1} lines form combination bands with 25^1_0 $[1^1_0]$.

The jet spectrum of styrene reveals many (albeit weak) combination bands. Nearly all lines of intensity greater than 0.2% of the 0^0_0 ($S/N \geqslant 1000$) can be identified by a fundamental or a combination band (the remaining few apparently due to Fermi resonance or vibronic interactions). The extensiveness of these combinations reflects a strong interaction between vibrational modes due in part to the low C_s symmetry of styrene. We are particularly interested in deciphering these interactions since intermode coupling is important for the flow of vibrational energy through a molecule and hence is intimately involved in the dynamics of the isomerization (section 3.3).

The process of isomerization relies on vibrations involving the ethylene group. The prevalence of benzene-like modes indicates that the $\tilde{A} \leftarrow \tilde{X}$ excitation in styrene is "localized" largely in the benzene ring. Vibronic excitations involving the ethylene group are mostly disallowed by symmetry (a″). An exception is the a′ mode, ν_{22}, which is attributed to the CH_2– rocking vibration [14]. The even overtones of the a″ modes, however, are allowed. Of these, only the 41^2_0 (C_1–C_α out-of-plane bend) and the 42^2_0 (C_1–C_α torsion) transitions are observable. These modes also form combinations (e.g. $41^1_0 42^1_0$, $41^2_0 42^2_0$) and hot bands involving cross sequences (e.g. $41^1_0 42^0_1$) indicating a strong coupling with each other. There is also evidence for a combination involving ν_{40} at 349.2 cm^{-1} $(40^1_0 41^1_0)$ in agreement with a previous study [6].

The ethylenic vibrations, particularly the torsional mode, ν_{42}, have been extensively studied in the past [6,10,11,19]; ν_{41} and ν_{42} were found to be strongly mixed in the excited state $\tilde{A}$, a result corroborated in this study. It has recently been established that the 282 cm^{-1} line is attributable to $41^1_0 42^1_0$ [10], thus correcting an earlier assignment [6]. Our analysis (table 1) further reveals that these vibrations form combination modes with benzene type vibrations. This has important consequences since it indicates that a vibrational coupling mechanism involving the ring and the ethylene group is available. We examine this point further (and its relevance to isomerization) in section 3.3.

3.2. Fluorescence spectra

The resolved fluorescence spectra of jet-cooled styrene following excitation at various energies (single vibronic level, SVL) is illustrated in fig. 2, and the frequencies and assignments from the 0^0_0 spectrum reported in table 2. A thorough high-resolution analysis of the resolved fluorescence spectra of styrene in

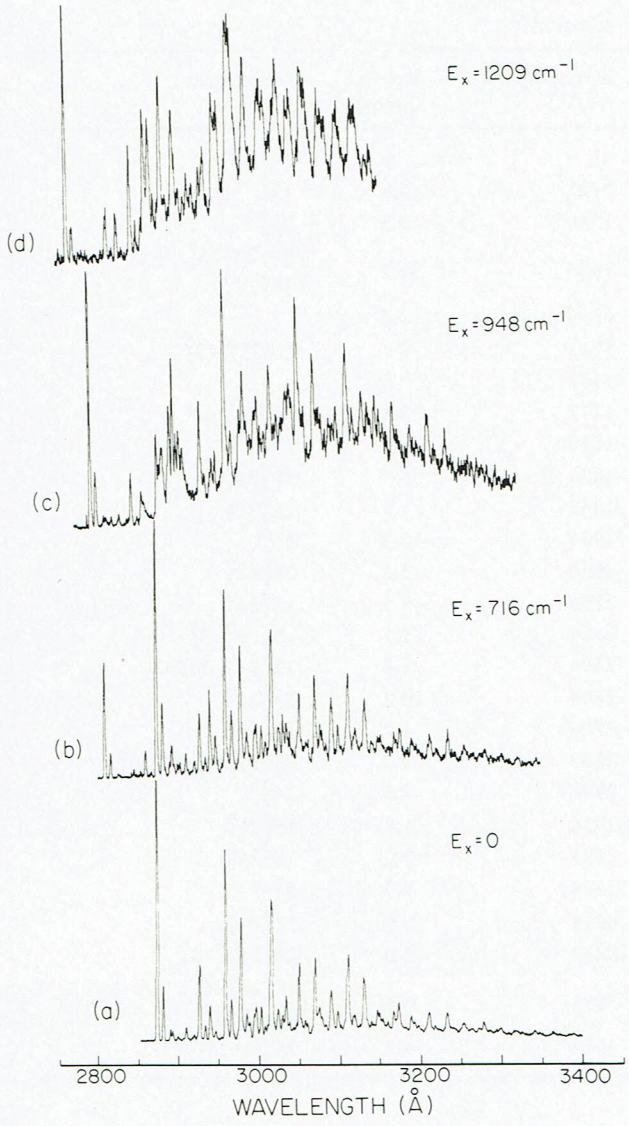

Fig. 2. Resolved fluorescence spectra of styrene for different energies of excitation; (a) E_x = 0 cm^{-1}, (0_0^0); (b) E_x = 746 cm^{-1}, (25_0^1); (c) E_x = 948 cm^{-1}, (24_0^1) and (d) E_x = 1209 cm^{-1}, (18_0^1). Expansion conditions were 50 psi He and 70°C sample temperature.

a bulb has been reported by Hollas et al. [10], hence, we defer the details of most of the assignments to that paper. However, we do note that, in spite of the fact that a large number of strong fundamentals is observed, a curious spacing of about 200 cm^{-1} between major lines extends throughout the fluorescence spectra. This effect becomes particularly apparent at higher excitation energies (see fig. 2).

The new features we report here primarily consist of combinations and overtones which indicate that there is extensive intermode coupling in the ground state $\tilde{X}$, as well as in the excited state $\tilde{A}$. The in-plane C–H bend modes (ν_{19}, ν_{20}, ν_{21} and ν_{23}) which are strongly coupled in the excited $\tilde{A}$ state are separated further from each other in the ground state.

An interesting observation in our 0_0^0 fluorescence spectrum is a weak line at 398 cm^{-1} which we tentatively assign to either the 42_8^0 or 41_2^0 transition. The former line has not previously been observed and if correct would allow a refinement in the calculation of the controversial ν_{42} torsional potential [19].

Changes in the properties of the ethylene group upon excitation are evident from our spectra. The absence of the ν_{41} C_1–C_α out-of-plane bend mode in the fluorescence spectra indicates that it does not couple strongly with the ν_{42} C_1–C_α torsion in the ground electronic state, a behavior in marked contrast to the strong coupling exhibited in the excited state. Other studies have shown that the ground-state frequencies (ν''_{41} = 199 cm^{-1}, ν''_{42} = 38 cm^{-1}), likewise, change dramatically in going to the excited state (ν'_{41} = 97 cm^{-1}, ν'_{42} = 186 cm^{-1}) [10]. This behavior is electronic in origin and is due to the fact that in the $\tilde{A}$ state, double bond character is gained by the C_1–C_α bond (thus increasing the frequency of the ν_{42} torsion) and lost by the ethylene bond. Hence, the $\tilde{A} \leftarrow \tilde{X}$ transition in styrene possesses some butadiene character. Unfortunately, the excited-state ethylene torsion (ν'_{38}) is not observable, thus a comparison with its ground-state value of ν''_{38} = 640 cm^{-1} [20] is not possible. Molecular orbital calculations [21,22] however, support a small butadienyl character for the ethylene group, one of the consequences of which is a lowering of the barrier to isomerization in the excited state compared to the ground state.

3.3. Excess energy and IVR – relevance to isomerization

The resolved fluorescence spectra in fig. 2 exhibit a build up of a broad fluorescence at increasing excess excitation energies (E_x). This effect has been observed before in jet-cooled stilbene [1,7]. In a qualitative sense, it reflects the degree of IVR from the optically

Table 2
Assignment of the fluorescence spectrum of jet-cooled styrene: 0_0^0 excitation [a]

Frequency [b] (cm^{-1})	Relative intensity	Assignment	Frequency [b] (cm^{-1})	Relative intensity	Assignment
0	100.0	0_0^0			
90	20.5	42_2^0	1492	6.8	12_1^0
199	2.5	42_4^0	1540	3.5	25_2^0
227	2.0	29_0^1	1625	46.1	$\{9_1^0, 24_1^0 26_1^0, 19_1^0 28_1^0$
310	1.3	42_6^0	1690	0.8	
330	0.6		1711	4	$(1625)_1^0 42_2^0$
398	0.8	42_8^0 (?), 41_2^0 (?)	1737	0.8	
433	4.4	28_1^0	1777	2.8	$24_1^0 25_1^0$
548	2.0	27_1^0	1810	0.9	
624	29.0	26_1^0	1824	5	$18_1^0 26_1^0$
673	0.5		1862	1.7	26_3^0 (?)
710	5	$26_1^0 42_2^0$	1993	10.2	24_2^0
779	14.5	25_1^0	2090	2.2	$24_2^0 42_2^0$
858	3.4	$25_1^0 42_2^0$ (?)	2195	8.5	$18_1^0 24_1^0$
932	0.8		2414	5.1	$18_2^0, 9_1^0 25_1^0$
996, 1011	75.1	$24_1^0, 23_1^0$	2494	3.4	$12_1^0 24_1^0, 18_2^0 42_2^0$
			2624	10.2	$24_2^0 26_1^0$
1084	14.8	$21_1^0, 24_1^0 42_2^0$	2704	1.7	$12_1^0 18_1^0$
1204	42.7	$18_1^0, 19_1^0$	2833	7.7	$9_1^0 18_1^0, 18_1^0 24_1^0 26_1^0$
1282, 1300	3, 3	$16_1^0, 17_1^0$	2997	1.6	24_3^0
		$18_1^0 42_2^0$	3018	1.8	$18_2^0 26_1^0$
1317	1.7	$26_2^0 42_1^0$ (?)	3191	2.0	$18_1^0 24_2^0$
1330	2.0	15_1^0	3264	2.3	9_2^0
1395	5	$25_1^0 26_1^0, 18_1^0 42_4^0$	3414	0.9	$18_2^0 24_1^0$
1416	5.5	14_1^0	3624	2.0	$24_3^0 26_1^0, 18_3^0$
1463	1		3825	1.6	$\{18_1^0 24_2^0 26_1^0, 9_1^0 18_1^0 24_1^0$
1477	1		4018	1.3	$25_1^0 (1625)_2^0$ (?)

[a] See table 1, footnote a).
[b] Frequencies are reported relative to the 0_0^0 to an accuracy of 5 cm^{-1}.

excited level to quasidegenerate rovibronic states that are not optically active from the ground state. Hui and Rice argue that IVR in styrene is very inefficient and in fact slower than the rate of isomerization [4]. However, they base this conclusion on the fact that their deduced rates for isomerization are constant (time ≈50 ns) with excess energy (up to 2500 cm^{-1}) and, therefore, independent of IVR. The rates which they deduced were determined by taking the differences in the non-radiative rates of styrene and ethylbenzene and attributing them to styrene isomerization.

If we assume a previous model for IVR and isomerization in *t*-stilbene (cf. ref. [1], fig. 3b) then we may associate the ratio of k_{ivr} to k_{fl} by the ratio of the so-called "relaxed" to "unrelaxed" fluorescence. (Some broadening may be the result of spectral congestion and the instrument, e.g. monochromator, resolution [23].) By using the measured fluorescence lifetime (τ_{fl}) for styrene of 20 ns at zero excess energy [‡], we

[‡] For footnote see next page.

estimate an approximate time for IVR (τ_{ivr}) on the order of 5 ns at $E_x \approx 900$ cm^{-1} and 1 ns at $E_x \approx 1200$ cm^{-1}. In *t*-stilbene, IVR is much faster than in styrene, occurring on the order of 100 ps at $E_x \approx 900$ cm^{-1} and 10 ps at $E_x \approx 1200$ cm^{-1} [1]. This situation is attributable to the larger density of states in stilbene. We have calculated the density of states of *t*-stilbene and styrene as a function of excess energy based on known or calculated vibrational frequencies for these molecules. Examples of these results, expressed as a ratio, are ≈35/1 (E_x = 900 cm^{-1}), 200/4 (1200 cm^{-1}) and 900/12 (1500 cm^{-1}). The scaling of the relative rates of IVR with the density of states for the two molecules implies that the coupling between modes is roughly similar in styrene and stilbene. It would appear, therefore, that the lower symmetry in styrene does not increase the *effective* density of states substantially.

Our data on the level structure, intermode coupling and relative rates of IVR in styrene allow us to speculate on the shape of the excited-state surface and the relevance to isomerization. Hui and Rice have proposed a surface whereby styrene is stable for a twisted ethylene bond ($\varphi = \pi/2$) with little or no barrier at the planar configuration. Our results, however, are in support of a stable planar ($\varphi = 0$) configuration with no evidence for a significant rate of isomerization at low excess energies. The excitation spectrum of styrene (fig. 1) exhibits sharp structure, indicative of a bound state, at energies up to 1200 cm^{-1} with no apparent onset of broadening similar to the one observed for *t*-stilbene in the region of isomerization. Furthermore, judging from our excitation spectrum and the published gas-phase (bulb) absorption spectrum [6], the fluorescence quantum yield does not decrease substantially, at least up to energies of about 1200 cm^{-1}. Significant reductions in quantum yield have been demonstrated for *t*-stilbene isomerization and other photoreactive systems above their threshold energy [1,7,9]. Even at high excess energies, the dispersed fluorescence spectra of styrene in fig. 2 exhibit *strong* and *sharp* resonance emission (i.e. emission at the excitation wavelength). Since IVR has been shown to be prevalent at these energies, the insignificant rate of isomerization indicates that the barrier is not small and may possibly be larger than in *t*-stilbene (≈1200 cm^{-1}).

A significant barrier to isomerization is not surprising. Since the $\tilde{A}$ state of styrene is largely benzene-like, the ethylene bond order is not markedly reduced from that in the ground state. For instance, the ν_{22} CH_2–rocking vibration, which is sensitive to the double bond strength, decreases by less than 10% (1032 [20] to 941 cm^{-1}) in going to the excited state. Calculations [21,22] are in agreement that a relatively large barrier to isomerization (≈15 kcal [21]) exists in the excited electronic state, $\tilde{A}$.

Finally, the observation by Hui and Rice of a Stokes shift in solution-phase styrene [4], on which they based their conclusion for a twisted ($\varphi = \pi/2$) ethylenic form, is not inconsistent with our above picture. Since styrene does not have the symmetric excited-state resonance forms of stilbene or ethylene, a polar excited state can result. A solvent stabilization energy of ≈500 cm^{-1} is not uncommon. Shifts between excitation and fluorescence wavelengths may arise from small geometry changes in the excited state followed by solvent reorganization. In fact, solvent–solute interactions with aromatics have resulted in shifts on the order of 200 cm^{-1} in jet-cooled beams [25]. Polarization of an excited state may also occur from the twisting of an olefinic bond, a case which has been extensively considered theoretically for systems relevant to isomerization [26].

We are currently engaged in picosecond studies, similar to those reported for *t*-stilbene [1] and diphenylbutadiene [2], on jet-cooled styrene and its isotopic derivatives. This will allow us to examine in more detail the involvement of IVR and the excited state surface in isomerization dynamics.

4. Conclusion

The principal conclusions in this work are as follows:

(1) The analysis and assignments of the ground and excited electronic state vibrations for jet-cooled styrene are reported. The spectroscopy reveals mode couplings and manifestations of IVR at high excess energy.

(2) Our results are consistent with a stable planar configuration in the excited state with a barrier height for isomerization that is comparable to or larger than

‡ The radiative lifetime for styrene at zero excess energy has been reported as 56 ns in ref. [4]. A radiative lifetime of 83 ns has also been measured for styrene in cyclohexane by Crosby and Salisbury [24].

that in trans-stilbene [1]. The density of states of styrene and *t*-stilbene are calculated and examined with regard to IVR and isomerization.

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