



The methyl rotor as a probe of electronic character via fluorescence excitation of para-substituted toluenes

by Steven Gregory Mayer

A thesis submitted in partial fulfillment of the requirements for the degree of Master of Science in Chemistry

Montana State University

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Abstract:

The laser induced fluorescence excitation spectra of p-toluidine and p-methylstyrene, were obtained by the method of supersonic jet molecular spectroscopy. In this work, the methyl rotor was used as a probe of electronic character. The spectrum of p-toluidine revealed the effect of time dependent coupling of the methyl rotor and NH₂ motion through the benzene ring. The spectral manifestation of this interaction is a splitting of the peaks involving amine motion at 709 cm⁻¹ (assigned as T₀²) and 736 cm⁻¹ (assigned as I₀²) which was absent in the aniline spectrum. The p-methylstyrene spectrum revealed a paradox when compared to previous work done on styrene. The p-methylstyrene spectrum showed significantly more Franck-Condon activity in several modes than did styrene which would indicate that the methyl group in the para position had a significant effect on ring-double bond conjugation. This is exactly opposite to the effects seen in trans-stilbene and p-methyl-trans-stilbene which have relative intensities that are very similar to each other. However, when the p-methylstyrene and p-methyl-trans-stilbene spectra are compared, the methyl rotor structure is markedly different. Therefore, it is concluded that the remote ring in stilbene had a significant effect on π electron interaction in the para position on the main ring.

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A thesis submitted in partial fulfillment
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of
Master of Science
in
Chemistry

MONTANA STATE UNIVERSITY
Bozeman, Montana

May 1990

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APPROVAL

of the thesis submitted by

Steven Gregory Mayer

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5/9/90
Date

Lee K. Sangler
Chairperson, Graduate Committee

Approved for the Major Department

5/10/90
Date

Edwin H. Abbott
Head, Major Department

Approved for the College of Graduate Studies

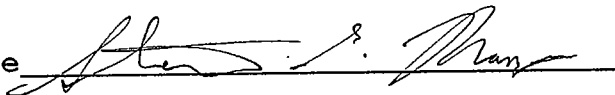
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ACKNOWLEDGEMENTS

The completion of a thesis is the final culmination of a series of events in one's academic career. Mine has not been without its hardships or its private victories and I would like to express my deepest appreciation and love to those who were most vital in seeing me to my destination, my family. It has been their unending love and support that allowed me to successfully complete my academic pursuits. To them I dedicate this thesis.

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ABSTRACT

The laser induced fluorescence excitation spectra of p-toluidine and p-methylstyrene, were obtained by the method of supersonic jet molecular spectroscopy. In this work, the methyl rotor was used as a probe of electronic character. The spectrum of p-toluidine revealed the effect of time dependent coupling of the methyl rotor and NH_2 motion through the benzene ring. The spectral manifestation of this interaction is a splitting of the peaks involving amine motion at 709 cm^{-1} (assigned as T_0^2) and 736 cm^{-1} (assigned as I_0^2) which was absent in the aniline spectrum. The p-methylstyrene spectrum revealed a paradox when compared to previous work done on styrene. The p-methylstyrene spectrum showed significantly more Franck-Condon activity in several modes than did styrene which would indicate that the methyl group in the para position had a significant effect on ring-double bond conjugation. This is exactly opposite to the effects seen in trans-stilbene and p-methyl-trans-stilbene which have relative intensities that are very similar to each other. However, when the p-methylstyrene and p-methyl-trans-stilbene spectra are compared, the methyl rotor structure is markedly different. Therefore, it is concluded that the remote ring in stilbene had a significant effect on π electron interaction in the para position on the main ring.

INTRODUCTION

Laser induced fluorescence excitation spectroscopy is an extremely useful method for determining conformations and barriers to internal rotation for molecules which contain a methyl rotor. The results of such experiments are of interest not only to physical chemists but also to synthetic chemists who are in search of exact mechanistic pathways and depend upon the accurate knowledge of electron densities in the molecule of interest.

A multitude of spectroscopic methods exist for ground state conformational studies such as Raman, FTIR, NMR, and microwave spectroscopies. However, excited state spectra of molecules were found inaccessible by these means due to the large spectral congestion caused by hot bands (transitions originating from vibrationally populated ground state levels). Recently, the excited state has been accessed via the method known as supersonic jet molecular spectroscopy.

Supersonic Jet Expansion Theory

When a gas is expanded through a small orifice at supersonic speeds, the temperature of the molecule is decreased. According to the Boltzmann distribution $N_2/N_1 =$

$e^{-E/kT}$, the vibrational states above $v=0$ in the ground electronic state are not appreciably populated.¹ There are many binary collisions at the orifice and the thermal energy produced is converted into directed flow as the gas passes through the orifice into the vacuum chamber. Since the velocity distribution is narrow, the translational temperature of the gas is lowered.²

According to statistical mechanics theory, molecules can be cooled by collisionally imparting energy to the carrier gas atoms inside the vacuum chamber. This has the effect of accelerating the molecule to the same speed as the carrier gas. By not populating the energy levels corresponding to the internal degrees of freedom of the molecule, the rotational transitions are "cooled out" which simplifies the spectrum due to line narrowing in the vibrational bands.²

Laser System

The frequency range necessary to excite the transition $S_1 \leftarrow S_0$ in para-substituted toluenes is on the order of 32000 - 36000 cm^{-1} . In order to resolve rotational structure of molecules, a high resolution excitation source is required. The use of tuneable dye lasers as the pump source for the molecular transitions offers the high resolution and power needed for this method. The system of choice for the present application is a Nd:YAG pumped dye laser. The Nd:YAG can operate at either 1064nm, 532nm, or 355nm depending upon the

dye pumping requirements.

Since the molecular signal is relatively weak compared to the laser light, scattered light inside the detection system presents a major problem. Therefore, great care must be taken to ensure that scattered light is reduced to a minimum. The two main factors which cause this problem are beam quality and poor alignment along the vacuum chamber axis. Beam quality is a problem that arises in the amplifier cell in the dye laser. Theoretically, the beam from the oscillator cell should have near $TEM_{0,0}$ mode structure if the pump beam is uniform. If this is the case, then beam quality is strictly a function of amplifier alignment and pumping scheme. Careful optimization of the dye laser will yield a comet shaped beam. The comet shape is due to the configuration of the amplifier cell and the side pumping of the Nd:YAG beam. Further discussion of this problem will be addressed in the EXPERIMENTAL section.

The Methyl Rotor

The methyl rotor is a CH_3 group attached to the molecule of interest. The quantum mechanical treatment of this system uses the particle in a ring wavefunction ($\exp(\pm im\Theta)$) perturbed by a $(1/2)V_n[1-\cos(n\Theta)]$ potential^{4,5} which has the form

$$\int [\exp(-\pm im\Theta)] (1/2)V_n(1-\cos n\Theta) [\exp(\pm im\Theta)] d\Theta \quad (1)$$

Since the methyl rotor has three equivalent positions for the hydrogens, the potential must go in multiples of three.

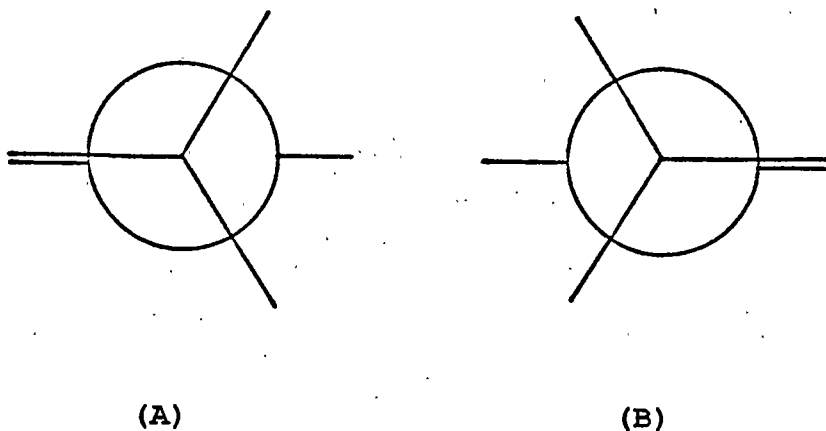
$$\begin{aligned} & (1/2)V_3[1-\cos(3\Theta)] + (1/2)V_6[1-\cos(6\Theta)] \\ & + (1/2)V_9[1-\cos(9\Theta)] + \dots \end{aligned} \quad (2)$$

The source of the hindering potential is used to describe the interaction of molecular orbitals between the methyl group and the ring. This phenomenon is known as hyperconjugation. Several groups, both experimental²¹ and computational²² in nature, have identified hyperconjugation as the dominant influence on the preferred conformation and the barrier to internal rotation for methyl groups attached to π electron containing systems. Since hyperconjugation is the interaction between π -like orbitals on the methyl group and the π electron density in the vicinity of the attached CH_3 , spectroscopic determination of the methyl behavior (conformational changes upon excitation and barriers to internal rotation) can be used as a probe of local π electron density. This information can be extracted from excitation and dispersed fluorescence spectra by fitting the experimental frequencies for the methyl rotor to those calculated from the matrix elements of equation 1.²³

The exponentials are the unperturbed particle in a ring wavefunctions and the cosine term represents the barrier to internal rotation. Intensities can be fit via Franck-Condon

factors determined using eigenvectors obtained from diagonalization of the aforementioned matrix. The conformational change between the ground and excited states is obtained by phase shifting the excited state wavefunctions until a best fit for relative intensities in the rotor spectrum is obtained. The FORTRAN program ROTIN running on a MicroVAX was used for this purpose.¹⁷

Figure 1a and 1b are the Neuman projections which physically illustrate the concept of interchange of hydrogen nuclei. The point at the center represents the carbon and the lines are the C-H bonds. Two equivalent positions are shown, and there are a total of six equivalent positions which are obtained by rotating the methyl group by $\pm 120^\circ$.



Neuman projections of the methyl rotor showing 3 and 6 fold potentials

FIGURE 1

There is no point group symmetry operation which correctly describes the permutation of nuclei caused by tunneling of the Me-hydrogens through the small barrier to internal rotation. The correct treatment is the molecular symmetry group approach used by Longuet-Higgins⁶ and Bunker.⁷ The molecular symmetry groups allow one to classify the spin states, states of nuclear motion, and electronic states of a non-rigid molecule. Since the molecules of interest can pass from one conformation to another, it is necessary to define a set of all permutations of the positions and spins of identical nuclei which appear reasonable along with the corresponding inversions. As mentioned above, the dominant influence on the methyl behavior (conformational preference and barrier height) is hyperconjugation, and since these properties of the rotor can be measured spectroscopically, the CH_3 group can be developed as a sensitive probe of local π electron density. Furthermore, extracting this information from the spectrum is often straightforward since the methyl torsion is typically the lowest frequency vibration in the molecule.

The energy levels for the methyl rotor go as $0a_1, 1e, 2e, 3a_1, 3a_2, 4e, 5e, 6a_1, 6a_2, \dots$ where a and e are the first two torsional energy levels of the methyl rotor and the $0, 1, 2, 3, \dots$ are the quantum numbers of the torsional levels. The selection rules for the methyl rotor transitions are $a_1 \leftrightarrow a_1, a_2 \leftrightarrow a_2, e \leftrightarrow e$. The nuclear spin statistical

weights are 2 and 1 for the a and o levels respectively. This means that there are twice as many molecules with a symmetry as there are with o symmetry.

The contour of the methyl rotor structure in the spectrum reveals the degree of conformational change in the molecule upon excitation.

The molecular conformation is dependent upon the change in the equilibrium internuclear distance in going from the ground to the excited state. If the change is small then the only vibrational band with appreciable intensity will be the origin. If the change is large then there will be a long progression in the intensities of the bands with respect to frequency. This phenomenon is known as the Franck-Condon principle. The relative intensities of the vibrational bands are directly proportional to the square of the vibrational overlap integral.⁸

$$|\int \psi_{\text{vib}}^* \psi_{\text{vib}} dR|^2 = |\langle v' | v \rangle|^2 \quad (3)$$

The square of the overlap integral between the vibrational wave functions of the upper and lower states of the electronic transition is called the Franck-Condon factor, $q_{v',v''}$. The Franck-Condon factor is a quantitative assessment of the degree of vibrational overlap between two electronic states. If we sum over all the vibrational states, equation 3 becomes

$$\begin{aligned}
\sum_{v''} q_{v', v''} &= \sum_{v''} |\langle v' | v'' \rangle|^2 \\
&= \sum_{v''} \langle v' | v'' \rangle \langle v'' | v' \rangle \\
&= \langle v' | v' \rangle = 1
\end{aligned}
\tag{4}$$

Figure 2 is a physical illustration of the Franck-Condon principle.

If the Born-Oppenheimer approximation is assumed, the integral containing both electronic and vibrational wavefunctions can be written in terms of the nuclear coordinates, Q and the electronic coordinates, r .

$$\langle \psi_{e''}(r, Q) \psi_{v''}(Q) | \mu_x | \psi_{e'}(r, Q) \psi_{v'}(Q) \rangle
\tag{5}$$

The standard approach to evaluating this integral in order to find the relative vibronic intensities is to use the Condon approximation.⁹ The Condon approximation implies that the integral over the electronic coordinates is independent of nuclear position. Equation 5 can then be written as follows.

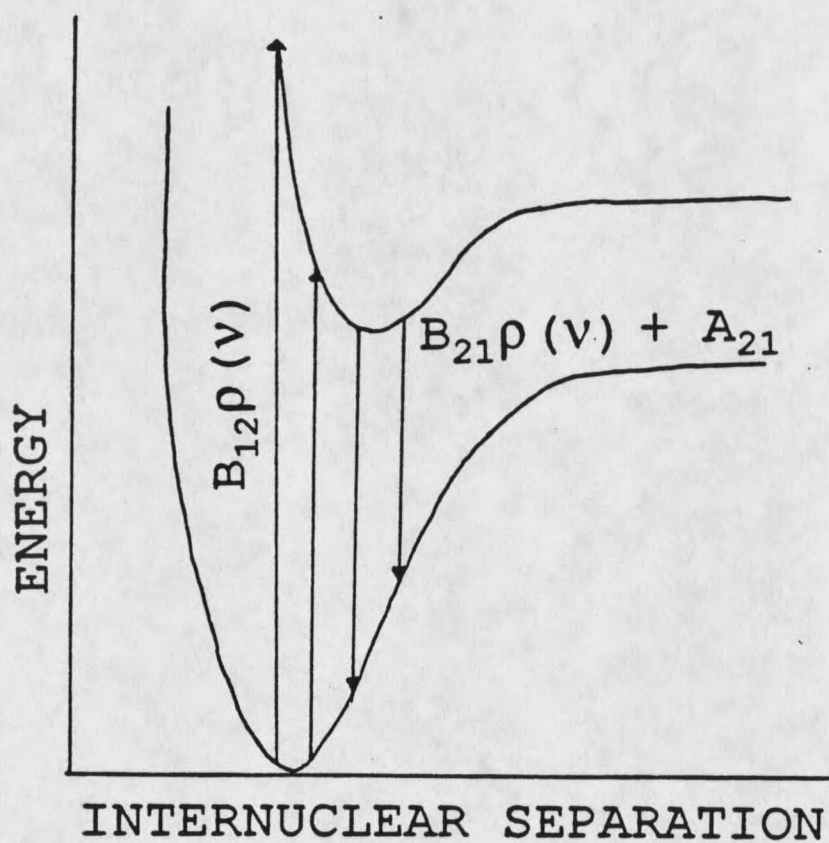
$$\begin{aligned}
&\langle \psi_{v''}(Q) | \langle \psi_{e''} | \mu_x | \psi_{e'} \rangle | \psi_{v'}(Q) \rangle \\
&= \langle \psi_{v''} | \mu_{e''e'}(Q) | \psi_{v'} \rangle
\end{aligned}
\tag{6}$$

If $\mu_{e''e'}(Q)$ is assumed to be a constant then equation 6 can be written as follows.

$$\langle \psi_{e''} | \mu_{xyz} | \psi_{e'} \rangle \langle \psi_{v''} | \psi_{v'} \rangle \quad (7)$$

The second integral of equation 7 is the Franck-Condon overlap integral. The result of this overlap is illustrated in Figure 2 where the electron undergoes a vertical transition to a higher electronic state on the potential curves with the same internuclear separation as it had in the ground state. In order for the transition to be allowed there must be a finite amplitude in the excited state for the ground state vibrational wavefunction. The degree of overlap between the ground and excited state vibrational wavefunctions determines the conformational change in the excited state of the molecule.

According to the Boltzmann distribution, when the temperature is approximately 20 K or lower, only the $v=0$ level in the ground state has appreciable population. This temperature range can be achieved for a molecule when it is jet cooled. Therefore, unless vibronic coupling is occurring in the molecule, only the totally symmetric vibrations will appear in a jet cooled spectrum. If the Condon approximation integral (equation 7) is evaluated, the following symmetry conditions are implied.



Electronic transition on Morse potential curves illustrating the Franck-Condon principle.

FIGURE 2

$$\Gamma_{e''} \otimes \Gamma_{xyz} \otimes \Gamma_{e'} \subset A_1$$

(8)

$$\Gamma_{v''} \otimes \Gamma_{v'} \subset A_1$$

However, since each vibration corresponds to a different dimension in the S_1 state, the $v=0$ vibration in the S_0 state can populate two quanta of an asymmetric vibration which gives a totally symmetric band. This can be shown mathematically by

$$\Gamma_{v1'} \otimes \Gamma_{v1'} \subset A_1$$

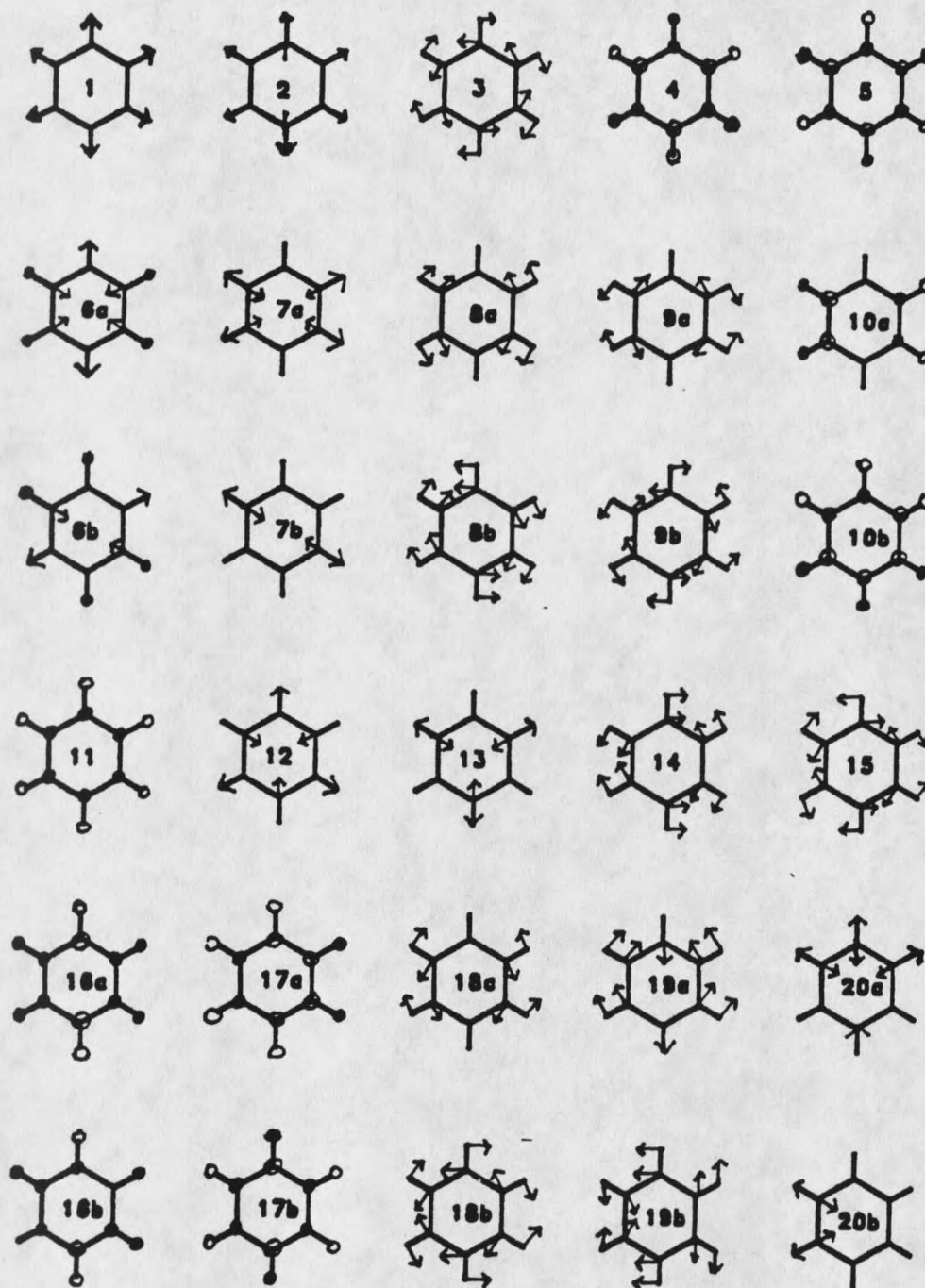
(9)

It follows then that the vibrations can go as multiples of two quanta in each dimension and appear in the spectrum.

In the case where the methyl rotor structure is of importance, it is necessary to use the molecular symmetry group. However, standard point group theory is sufficient to describe the molecule for symmetry assignments of the normal modes of vibration. Figure 3 lists the 30 benzene-like modes of vibration for any six membered ring system.¹⁰

Time Dependent Coupling Between Para Substituents

Analogous to the methyl rotor are the interactions of the functional group para to the methyl group. In the case of an amine group (p-toluidine) the hydrogens can invert or the entire group can have a torsion much like the methyl torsion.



The thirty benzene-like modes of vibration for any six membered ring system

FIGURE 3

Previous work done on aniline has shown that the amine group is non-planar in the ground state and that the NH_2 -inversion has a two-fold potential barrier.¹¹

The interesting possibility is that a time dependent wavefunction can couple the two para-substituents through the π system on the ring. The results of a series of studies on para-substituted toluenes promises to reveal information about electron densities on aromatic rings and ultimately lead to quantitative results regarding regio-specificity. This paper deals with the initial investigations involving p-toluidine and p-methylstyrene.

EXPERIMENTAL

The method of Supersonic Jet Molecular Spectroscopy was used to investigate the electronic character and methyl rotor structure of p-toluidine and p-methylstyrene. The jet apparatus consisted of a General Valve series 9 pulsed jet nozzle mounted on one axis of a six inch nominal, six-way cross purchased from MDC. The pumping system was a Varian VHS-6, six inch diffusion pump with a Varian SD 450 mechanical backing pump. The capability of the system was on the order of 10^{-7} torr without the pulsed jet nozzle operating and 10^{-5} torr with the nozzle operating.

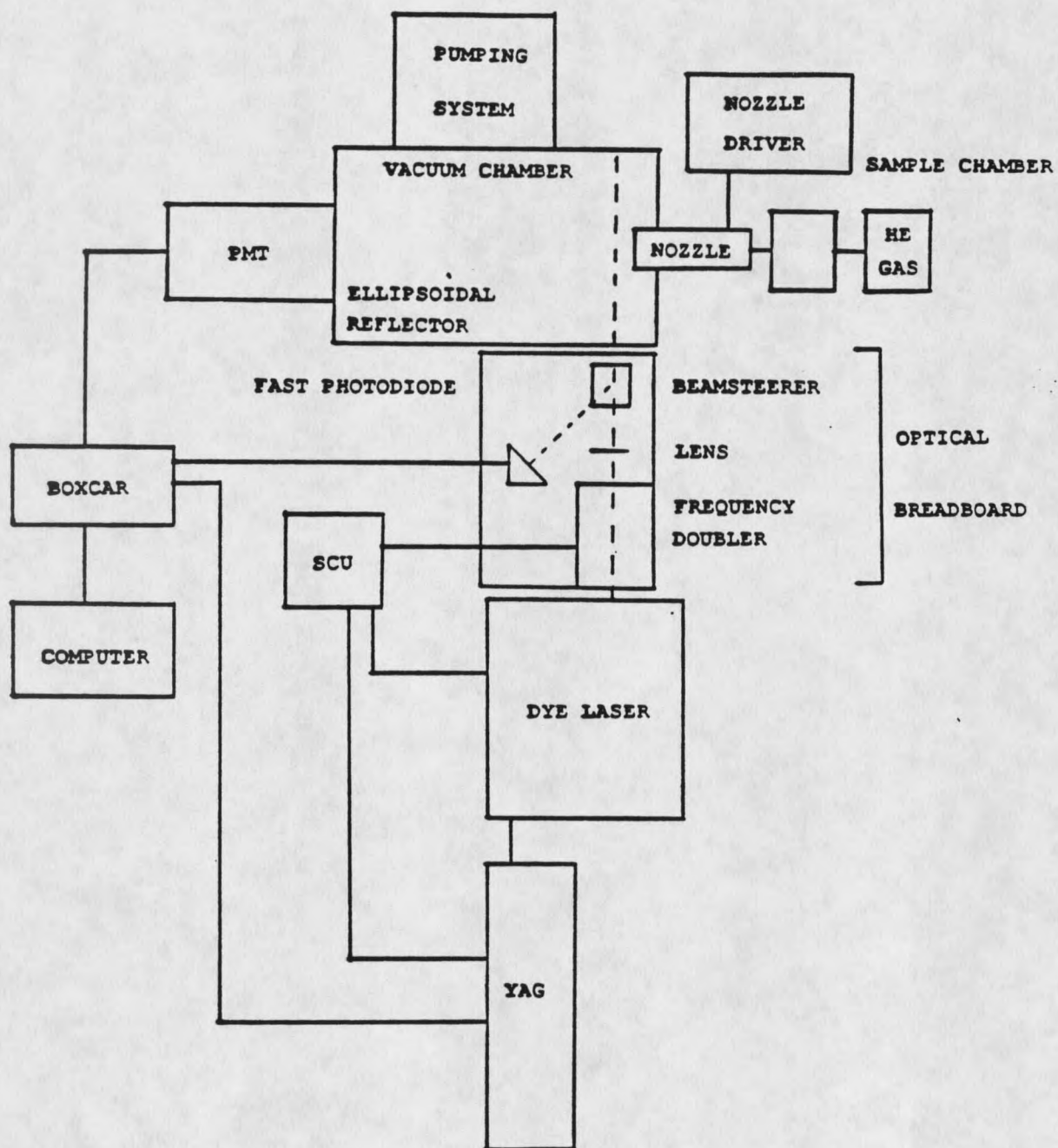
The molecular excitation source was a Lumonics HY 750 Nd:YAG pumped dye laser model HD 300 with a Hypertrack 1000 autotracker for frequency doubling. The linewidth of the laser after frequency doubling was 0.14cm^{-1} . The Nd:YAG was frequency doubled to obtain the green beam at 532nm. This afforded efficient pumping of the dyes in the frequency doubled region 33000 cm^{-1} to 35000 cm^{-1} . The dyes used for the p-toluidine and p-toluidine (ND_2) experiments were Kiton Red 620, Rhodamine 590/Rhodamine 610, and Rhodamine 590. The dyes used for the p-methylstyrene experiment were Rhodamine 590 and Coumarin 540A. All dyes were obtained from Exciton.

Beam quality of the laser was greatly improved with the use of a Bethune cell in place of the amplifier cell in the dye laser cavity. The pumping scheme provided a nearly perfect cylindrical beam at the laser output. This gave a uniform near Gaussian far-field energy distribution. Ultimately, the scattered light inside the detection system was reduced and the signal-to-noise ratio was increased.

The detection system was on the axis of jet expansion normal to the laser excitation axis (see Figure 7). The system consisted of a Melles Griot REM 014 ellipsoidal reflector, an EMI 9813 QB photomultiplier tube, and supporting electronics. An iris and appropriate cutoff filters were placed in front of the photomultiplier tube to reduce scattered light from the fundamental excitation wavelength.

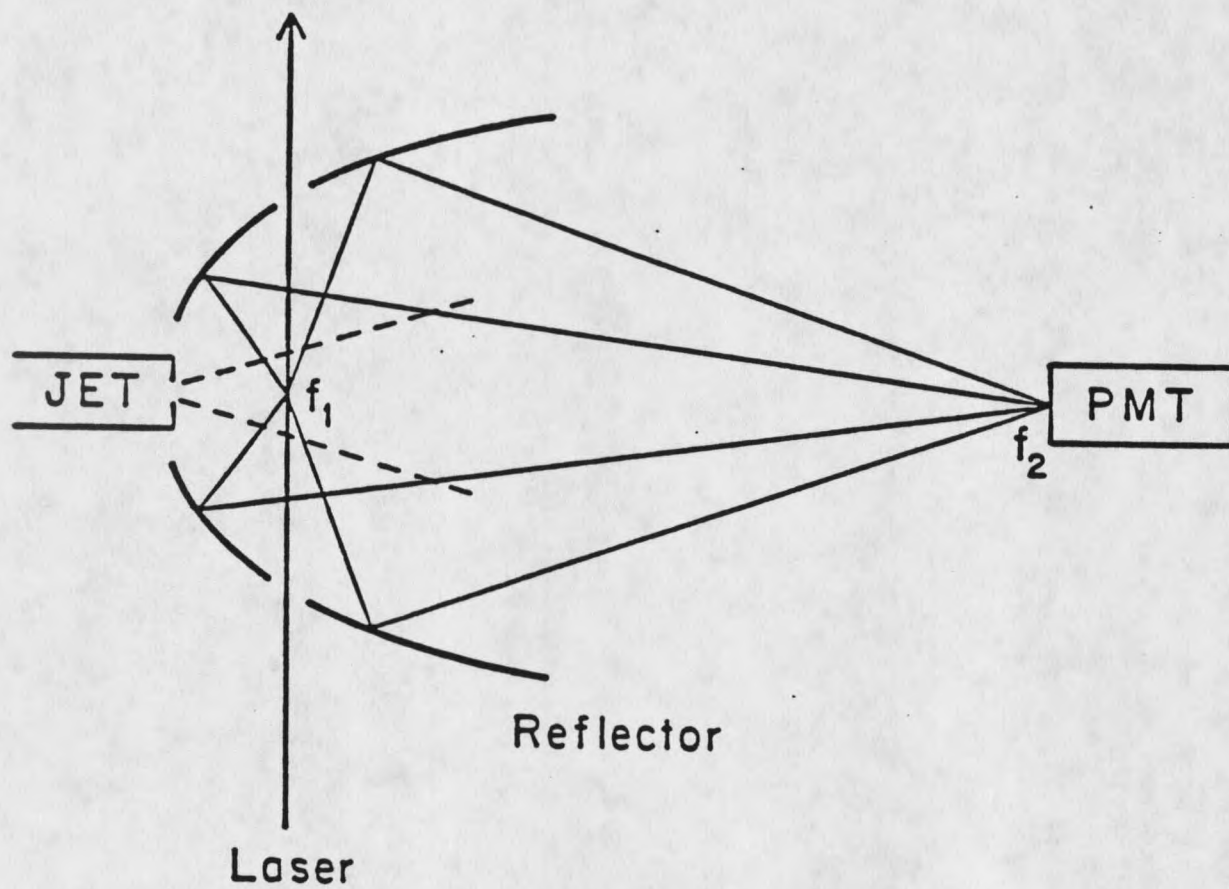
Data acquisition was by a Zenith ZF 248 microcomputer with supporting software by Stanford Research Systems which accompanied the SRS modular boxcar averager. Synchronization was provided by a homebuilt signal delay generator.

The p-toluidine and p-methylstyrene were obtained from Aldrich (99.9%). The deuterated p-toluidine was synthesized in the lab by our group. The molecule of interest was placed in a stainless steel pressure sealed tube. The tube was connected to the backside of the nozzle and pressurized with 4 atmospheres high purity grade He. Both p-toluidine samples were heated to 60° C and the p-methylstyrene was run at room temperature.



Block Diagram of the Apparatus

FIGURE 6



Ellipsoidal reflector light collection system

FIGURE 7

THE ELECTRONIC CHARACTER OF PARA-TOLUIDINE
EVIDENCE FOR TIME DEPENDENT COUPLING BETWEEN PARA SUBSTITUENTS

Results and Interpretation

The jet-cooled fluorescence excitation spectrum of p-toluidine is shown in Figure 8 with the vibrational assignments in Table 3. A qualitative assessment can be made regarding the methyl rotor structure, conformational changes and the normal modes of vibration. The methyl rotor structure at the 0_0^0 , $6a_0^1$, and 1_0^1 band regions exhibit 0° conformational changes (see Figures 10, 11, 12). The evidence to support this lack of change is that nearly all the intensity is contained in the first band of the methyl rotor structure.

An interesting feature of the p-toluidine spectrum is the two quartet structures centered at 709 cm^{-1} and 736 cm^{-1} . These two structures are proposed to be the two quanta inversion and the two quanta torsion of the amine group. The peak at 297 cm^{-1} is a hot band determined to be I_1^1 by comparison with the high temperature spectrum of p-toluidine (see Figure 13). The band at 376 cm^{-1} is unassigned but does form combination bands. It is labeled ? in the spectrum.

If the CH_3 and NH_2 groups are assumed to be point masses, p-toluidine has C_{2v} symmetry. This is a reasonable assumption

since the normal mode vibrations are not expected to be strongly coupled to the rotation of the methyl group or the tunneling of the NH_2 protons. Table 1 is the character table for the C_{2v} point group. This symmetry condition was found to be reasonable for assignment of the normal modes of vibration. However, in order to properly describe the molecule while taking into account the methyl rotor, it was necessary to define the appropriate molecular symmetry group (see Figure 9, Table 2¹²). Table 3¹³ lists the normal mode assignments made according to previous ground state work.^{14,15,16}

Table 1. The C_{2v} point group

C_{2v}	E	C_2	σ_{xz}	σ_{yz}	
A_1	1	1	1	1	z
A_2	1	1	-1	-1	
B_1	1	-1	1	-1	x
B_2	1	-1	-1	1	y

Table 2. The G_6 molecular symmetry group

G_6	E	(123)	(23)*
A_1	1	1	1
A_2	1	1	- 1
E	2	-1	0

E is the identity operation, (123) is permutation of three identical nuclei (hydrogens of the methyl rotor), and (23)* is permutation of hydrogens 2 and 3 followed by inversion of all coordinates.

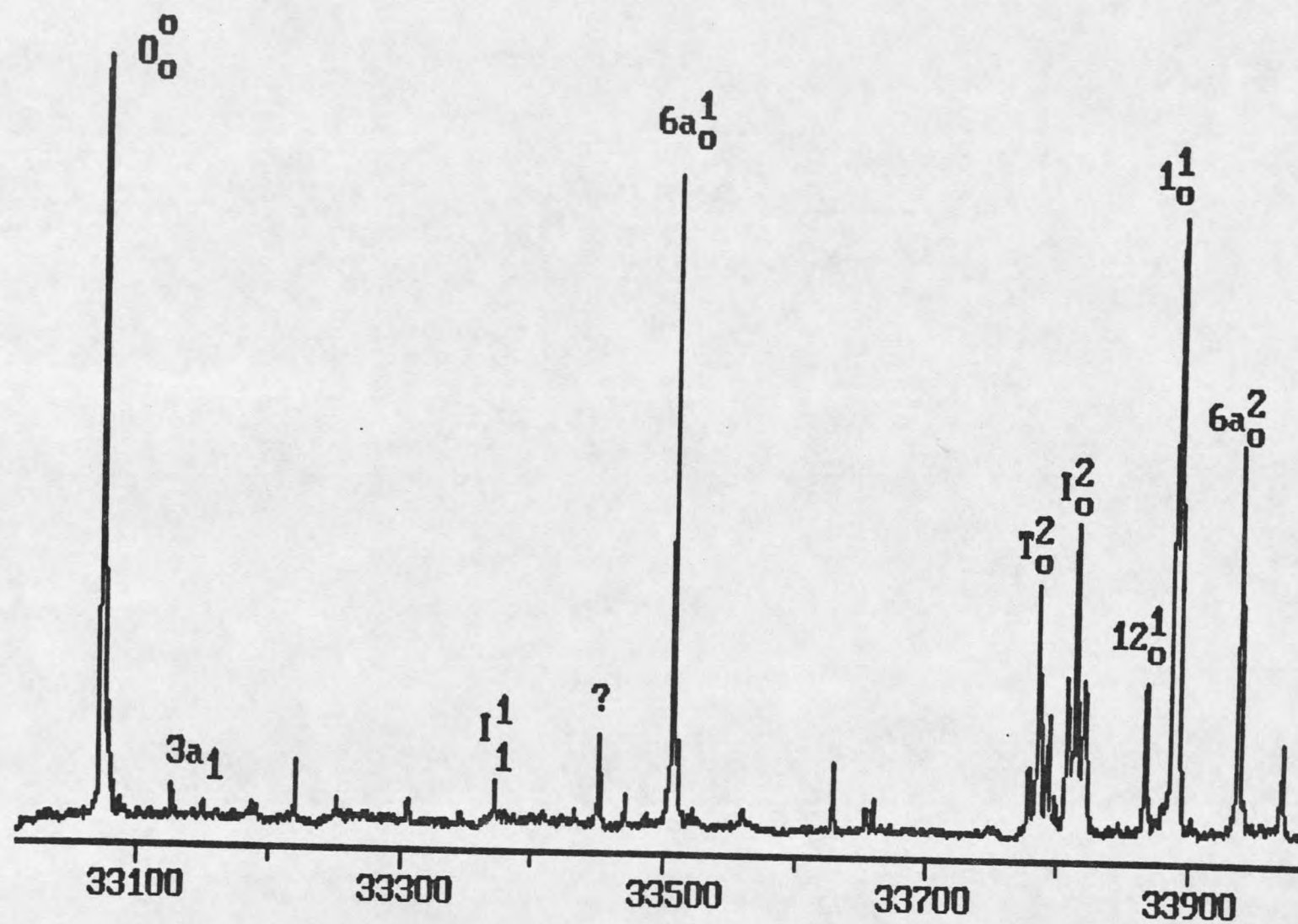


FIGURE 8 The Jet Cooled Vibronic Spectrum of p-Toluidine

Table 3. Vibrational band assignments of p-toluidine

BAND	FREQUENCY*	BAND	FREQUENCY
0_0^0	0 cm ⁻¹	$1_0^1 T_0^2$	1176
+ $2e$	18	$7a_0^1$	1195
+ $3a_1$	51	$6a_0^1 12_0^1$	1222
I_1^1	297	$6a_0^1 1_0^1$	1248
?	376	$6a_0^3$	1296
$6a_0^1$	432	$6a_0^1 16b_0^2$	1329
+ $2e$	450	T_0^4	1418
+ $3a_1$	481	$12_0^1 T_0^2$	1501
T_0^2	709	$1_0^1 T_0^2$	1532
$6a_0^1 I_1^1$	731	-	1548
I_0^2	736	$6a_0^2 T_0^2$	1574
12_0^1	792	12_0^2	1588
1_0^1	820	$6a_0^2 I_0^2$	1600
+ $2e$	838	$12_0^1 1_0^1$	1610
$6a_0^2$	864	$6a_0^1 7a_0^1$	1627
$16b_0^2$	898	$16b_0^2 I_0^2$	1633
$12_0^1 I_1^1$	1089	$7a_0^1 T_0^2$	1902
$6a_0^1 T_0^2$	1142	$7a_0^1 I_0^2$	1930
$6a_0^1 I_0^2$	1168	$1_0^1 7a_0^1$	2011
$? 12_0^1$	1168		

* All frequencies are given as displacements from the origin.

Totally Symmetric Bands

It was stated earlier in this paper that with the exception of combination bands, only the totally symmetric bands appear in the jet-cooled spectrum. Therefore, only the normal modes and combination bands of A_1 symmetry were assigned to the spectrum. The symmetry condition for the combination bands to appear in the spectrum is given by

$$\Gamma_{vx}^n \otimes \Gamma_{vz}^n \subset A_1 \quad (11)$$

The normal modes of vibration for any benzene-like molecule are given in Figure 3. The correct symmetries for the C_{2v} point group are given in Table 4.

Methyl Rotor Structure

The barriers to internal rotation for all regions in the p-toluidine spectrum were fit using a FORTRAN program on the MSU VAX 8550 cluster.¹⁷ The barrier heights for the 0_0^0 and $6a_0^1$ regions were determined to be 3-fold potentials with no 6-fold character exhibited by the methyl rotor. A 3-fold potential is indicative of an inequivalence of π electron densities in the two positions meta to the CH_3 which is caused by the asymmetry of the para substituents (in this case, NH_2 and CH_3).

Amine Inversion and Torsion Modes

Vibrational modes due to motion of the amine group have been assigned to three peaks in the spectrum. These also form various combination bands with other normal mode vibrations. The peak at 297 cm^{-1} is currently assigned I_1^1 . This was concluded by comparison with the high temperature spectrum where the intensity of the peak was much larger than in the jet-cooled spectrum (see Figure 13). The two sets of quartets with maximum peak heights at 709 cm^{-1} and 736 cm^{-1} were concluded to be motions of the amine group by comparison with the spectrum of the deuterated molecule (see Figure 14). The two quartets were observed to undergo a large red shift relative to the origin and also a shift with respect to each other. Only modes which involve nearly exclusive motion of the amine protons should show this large a deuterium shift. Two such motions proposed in this region are inversion of the amino hydrogens and torsion of the entire group with respect to the ring. Previous work by Brand et al. on aniline revealed that these modes do exist, although, it has not been determined which peak belongs to which motion. Tentatively, the peaks are labeled as $709\text{ cm}^{-1} = T_0^2$ and $736\text{ cm}^{-1} = I_0^2$.

Table 4. Normal modes of vibration for a C_{2v} molecule.

MODE	SYMMETRY	MODE	SYMMETRY
1	A_1	11	B_1
2	A_1	12	A_1
3	B_2	13	A_1
4	B_1	14	B_2
5	B_1	15	B_2
6a	A_1	16a	A_2
6b	B_2	16b	B_1
7a	A_1	17a	A_2
7b	B_2	17b	B_1
8a	A_1	18a	A_1
8b	B_2	18b	B_2
9a	A_1	19a	A_1
9b	B_2	19b	B_2
10a	A_2	20a	A_1
10b	B_1	20b	B_2

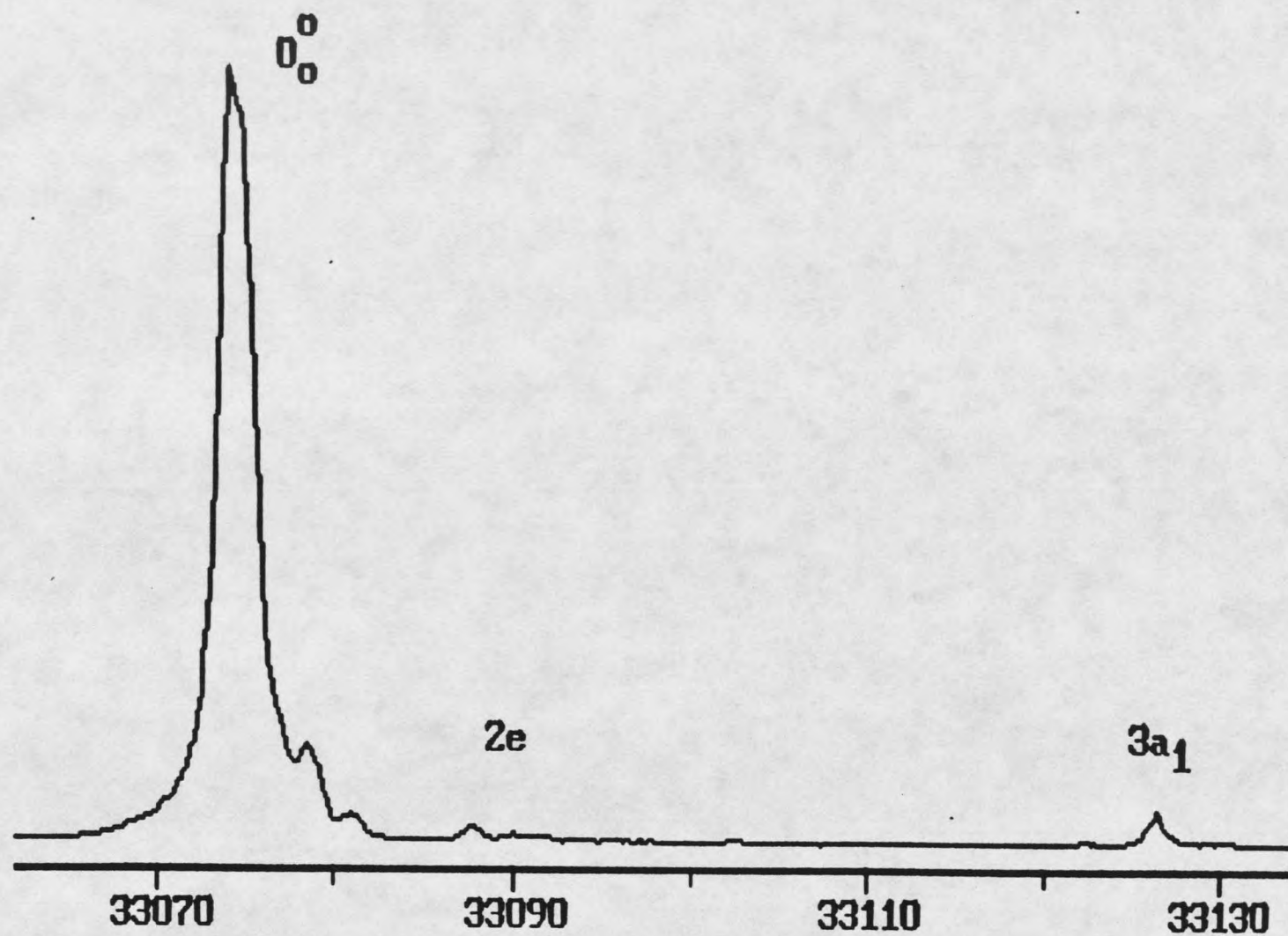


FIGURE 9 Expanded View of the Spectrum at the Origin

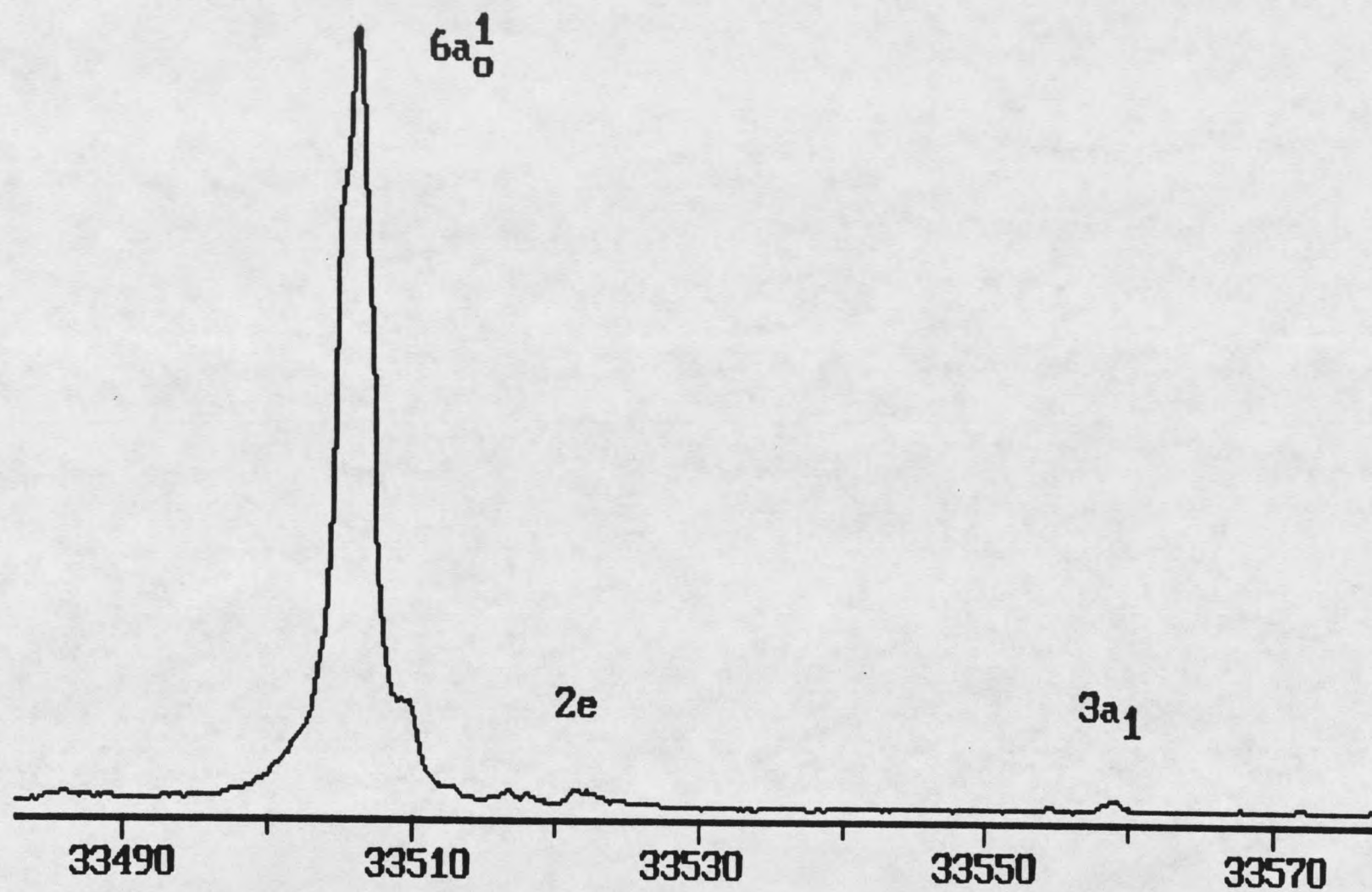


FIGURE 10 Expanded View of the Spectrum at the $6a_0^1$ Band

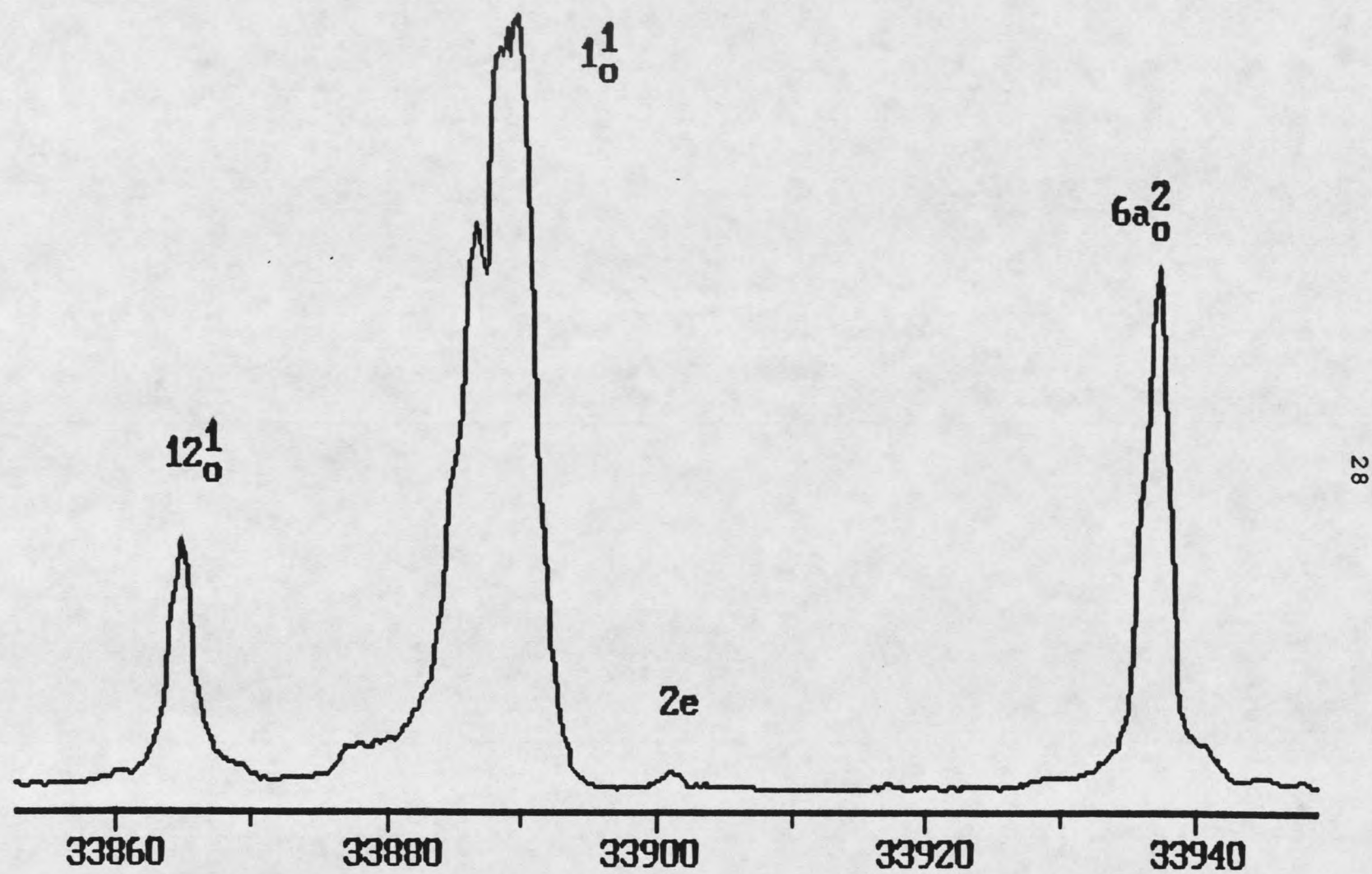


FIGURE 11 Expanded View of the Spectrum at the 1_0^1 Band

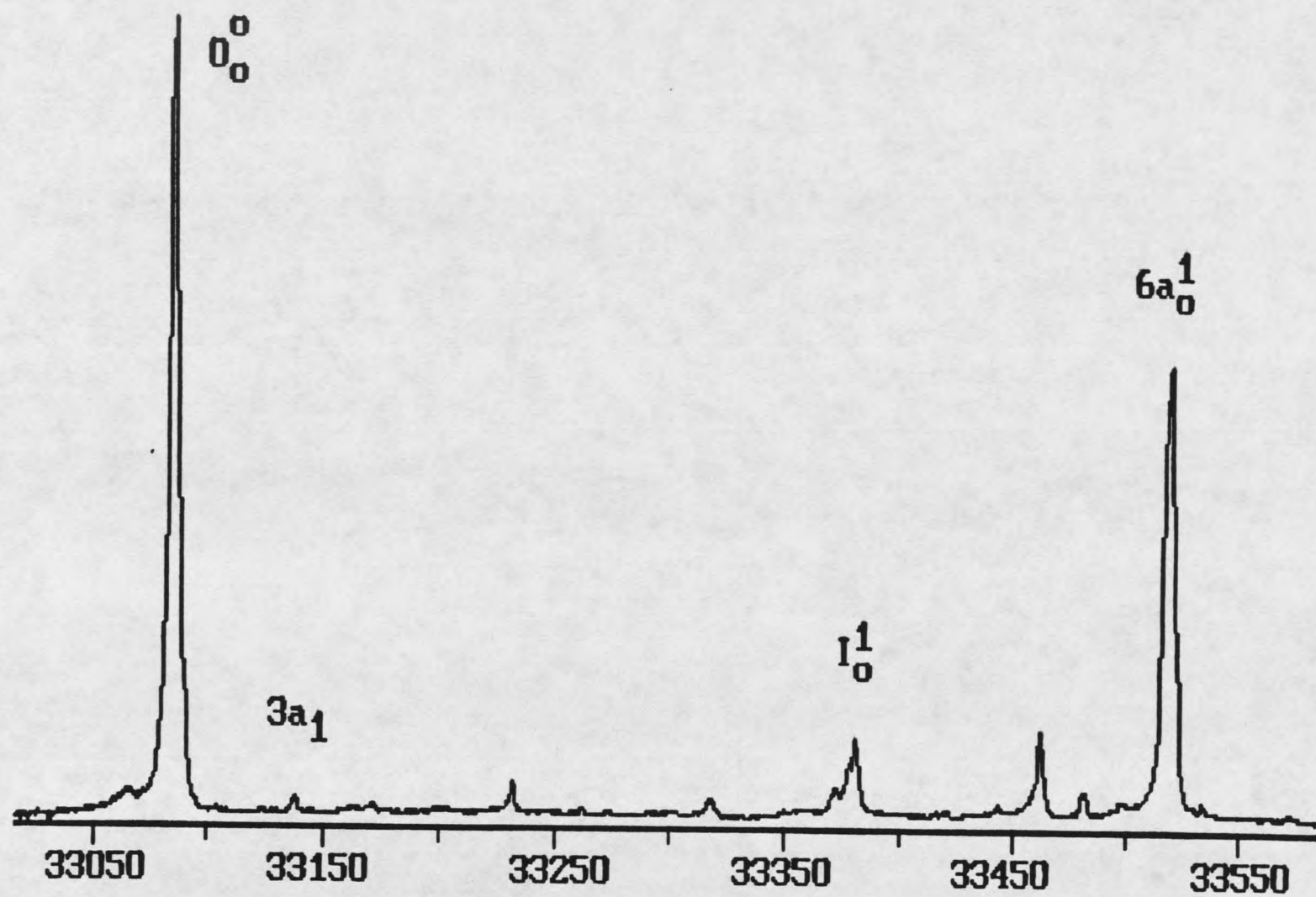


FIGURE 12 The "Hot" Vibronic Spectrum of p-Toluidine

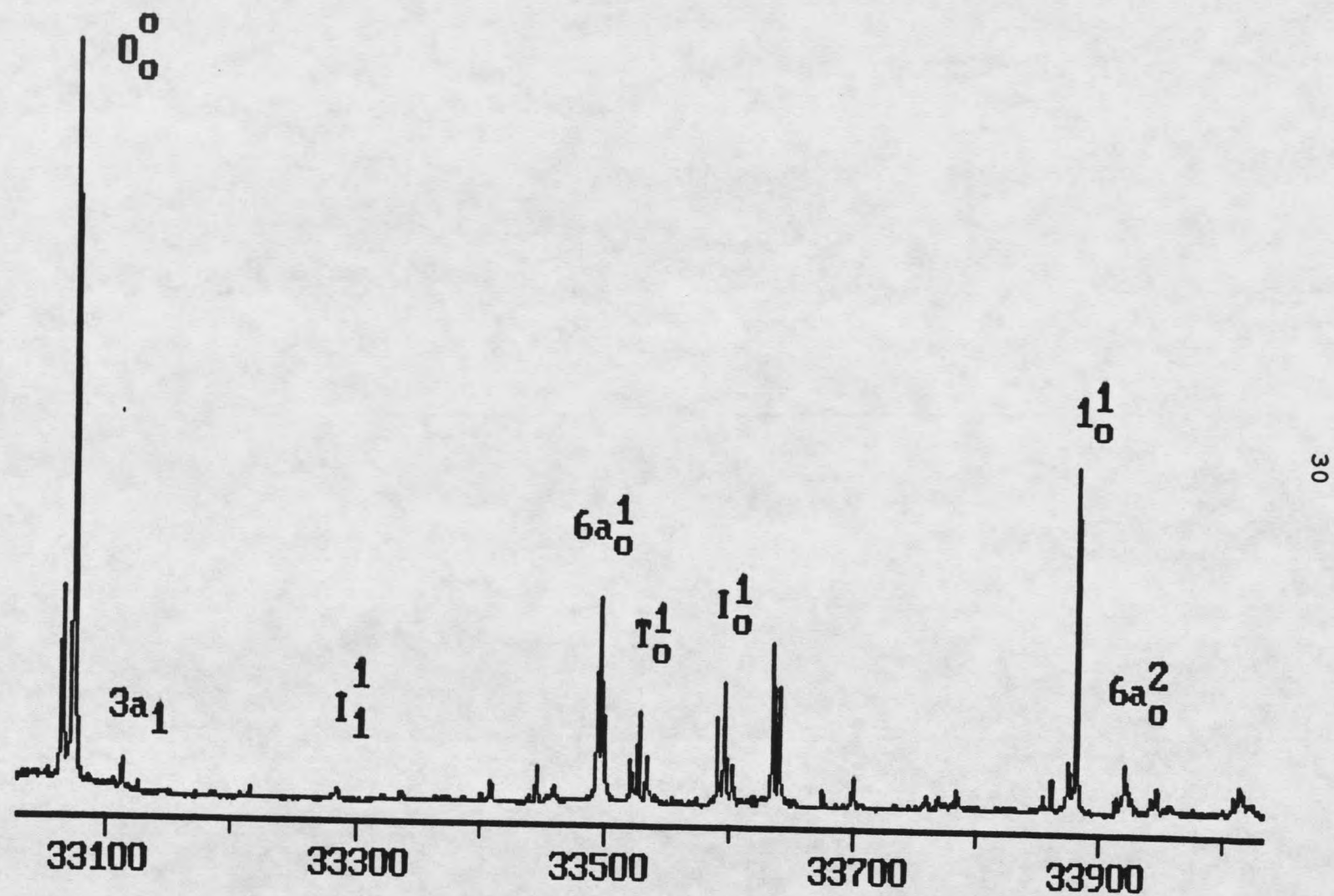


FIGURE 13 The Spectrum of p-Toluidine (ND₂)

Table 5. Methyl rotor structure of the p-toluidine spectrum

Tho 0_0^0 band (origin)

barrier heights: ground state = 25 cm^{-1}
 excited state = 20.8 cm^{-1}
 conformational change: 0°

Transition	<u>calculated</u>		<u>observed</u>	
	v	Int	v	Int
$2e \leftarrow 1e$	19	0.75	18	0.5
$3a_1 \leftarrow 0a_1$	51	0.21	51	0.5
$4e \leftarrow 1e$	83	0.04	--	0

Tho $6a_0^1$ band

barrier heights: ground state = 25 cm^{-1}
 excited state = 20.8 cm^{-1}
 conformational change: 0°

Transition	<u>calculated</u>		<u>observed</u>	
	v	Int	v	Int
$2e \leftarrow 1e$	451	0.75	450	0.5
$3a_1 \leftarrow 0a_1$	481	0.21	481	0.5
$4e \leftarrow 1e$	515	0.04	--	0

Tho 1_0^1 band

barrier heights: ground state = 25 cm^{-1}
 excited state = 20.8 cm^{-1}
 conformational change: 0°

Transition	<u>calculated</u>		<u>observed</u>	
	v	Int	v	Int
$2e \leftarrow 1e$	839	0.75	838	0.5
$3a_0^1 \leftarrow 0a_1$	871	0.21	871	*
$4e \leftarrow 1e$	903	0.04	--	*

* The absolute intensities were impossible to determine due to the congestion in the spectrum.

Discussion

The general trends pertaining to intermolecular motion in the excited state observed by Tembreull et al. in para-disubstituted benzenes supports the assignments and theories contained herein.¹⁸ The only minor discrepancies are the peaks in the region from 690 - 850 cm^{-1} which they assumed to all be due to ring bending modes. In the case of p-toluidine, it is true that the most prominent peaks from 790 - 900 cm^{-1} are due to ring modes. However, the intense quartet groups centered at 709 cm^{-1} and 736 cm^{-1} are definitely not ring modes, rather, they are due to amine group modes. This was concluded by examining the deuterated amine group spectrum relative to the protonated spectrum. Tembreulle et al. assigned the peak at 707 cm^{-1} (709 cm^{-1} in this work) as 12_0^1 . This was determined to be incorrect from the information afforded by the spectrum of the deuterated amine group. The spectrum of the deuterated amine group revealed a significant red shift of the two quartets relative to the origin. The peak assigned as I_1^1 was also significantly red shifted as were all the combination bands of amine group fundamentals. The peaks at 792 cm^{-1} and 820 cm^{-1} did not move upon deuteration and were determined to definitely be ring modes. By comparison with several aniline spectra, it was concluded that the lower frequency peak must be 12_0^1 and the higher frequency 1_0^1 . In general, the ring modes were all relatively unaffected

upon deuteration of the amine group.

It is certain that the peaks at 709 cm^{-1} and 736 cm^{-1} are amine group modes, however, it has not been determined which motion belongs to which peak although tentative assignments have been made where $709\text{ cm}^{-1} = T_0^2$ and $736\text{ cm}^{-1} = I_0^2$. The two motions are described as a torsion (T_0^2) of the NH_2 group and an inversion (I_0^2) of the amino hydrogens.

Calculations first carried out by Brand et al. and later by Ito et al.¹⁹ both revealed that the amine group lies in the plane of the benzene ring or the quasi-planar structure in the excited state. However, it was determined by Christoffersen et al.²⁰ from the rotational constants that the amine group has an out of plane angle of $30^\circ \pm 10^\circ$. This discrepancy is puzzling and has not been resolved. Thus, a good picture of aniline or p-toluidine is not yet available.

The work by Brand et al.¹¹ revealed that aniline exhibits an inversion and a torsion of the amine group. However, only the inversion was assigned (I^1 at 325 cm^{-1} and $I^2\text{ cm}^{-1}$) and it was unclear what peak was being referred to as the torsion. The amine group modes in p-toluidine appear to be vastly different than in aniline. The quartet structure and peak splittings indicate that some other effect must be taking place.

Vibronic coupling may be suspected as the cause from the two quartet splittings and subsequent combination bands but it is not likely since this structure is not seen in aniline.

This leads to a very important assumption, that is the two quartet splittings are due solely to the addition of the methyl group. A reasonable explanation is that a time dependent coupling between the methyl group and amine group is taking place through the ring via hyperconjugation. Hyperconjugation has been observed in toluene where the methyl hydrogens interact with the π system on the ring to create a potential barrier to internal rotation. This effect may occur in aniline but should be more pronounced in p-toluidine where the π density is affected by one group which, in turn, affects the group on the opposite end of the ring. Thus, vibronic interactions between the methyl rotor potential and the amine group potential would be expected to exhibit a complex splitting of peaks.

The methyl rotor structure at the origin, $6a_0^1$, and 1_0^1 bands exhibit no change in conformation of the molecule. However, due to the effects of hyperconjugation with the NH_2 group, a definite change in the methyl rotor structure is expected in the T_0^2 and I_0^2 regions. While it is apparent that the methyl rotor structure is different in this region, it is not clear which peaks are affected. Further investigations on the $\text{CD}_3\text{C}_6\text{H}_4\text{NH}_2$ molecule may reveal the methyl rotor structure when it is affected by hyperconjugation with the NH_2 group.

Conclusion

Time dependent coupling between the methyl rotor and NH_2 group on p-toluidine is readily apparent in the fluorescence excitation spectrum. This phenomenon was revealed by the quartet splittings at 709 cm^{-1} and 736 cm^{-1} which were assigned as T_0^2 (NH_2 torsion) and I_0^2 (NH_2 inversion). It is certain then that these peaks are due to NH_2 group interactions.

The major evidence for this proposed mechanism is the fact that aniline does exhibit a torsion and inversion of the NH_2 group. However, the peaks attributed to the NH_2 motions in aniline look nothing like those in p-toluidine. Therefore, the quartet splittings in the p-toluidine spectrum are proposed to be mostly a function of hyperconjugation through the ring between the methyl rotor and NH_2 group.

There is clearly a difference in the methyl rotor structure at the T_0^2 and I_0^2 peaks although it has not been determined which peaks are methyl rotor structure and more importantly what the physical significance of this difference reveals. Further experiments with the deuterated molecules $\text{CD}_3\text{C}_6\text{H}_4\text{NH}_2$ and $\text{CD}_3\text{C}_6\text{H}_4\text{ND}_2$ may lead to a conclusion.

The major point of this paper was to expose the newfound information regarding hyperconjugation between the methyl rotor and para substituents through the π system on benzene rings. Ultimately, the hope is to predict the electron densities on the benzene ring by examining the methyl rotor

structure. This work, together with several other recent discoveries has afforded a greater understanding of the final goal.

THE PARA-METHYLSTYRENE SPECTRUM

Introduction

Styrene and stilbene have both attracted the interest of chemists for a variety of reasons. They are model systems for studying photoisomerization and for consideration of aromaticity in conjugated systems. In spite of the significant interest in these molecules, structural questions remained until very recent studies which have shown that both molecules are planar in both the S_0 and S_1 states.^{21,22} In order to probe the issue of resonance interactions and aromaticity, we have obtained the jet-cooled fluorescence excitation spectrum of p-methylstyrene.

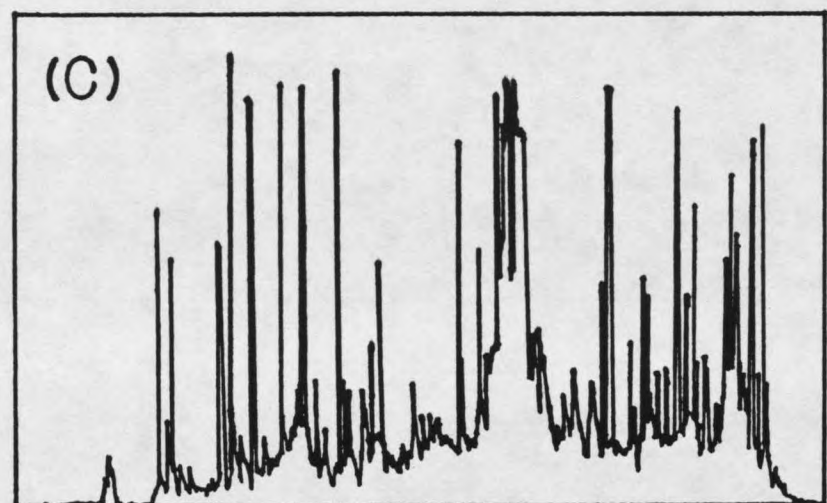
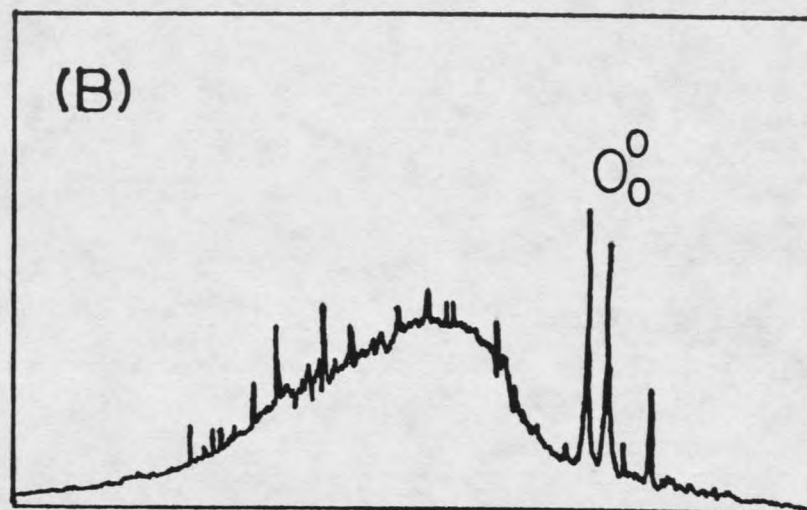
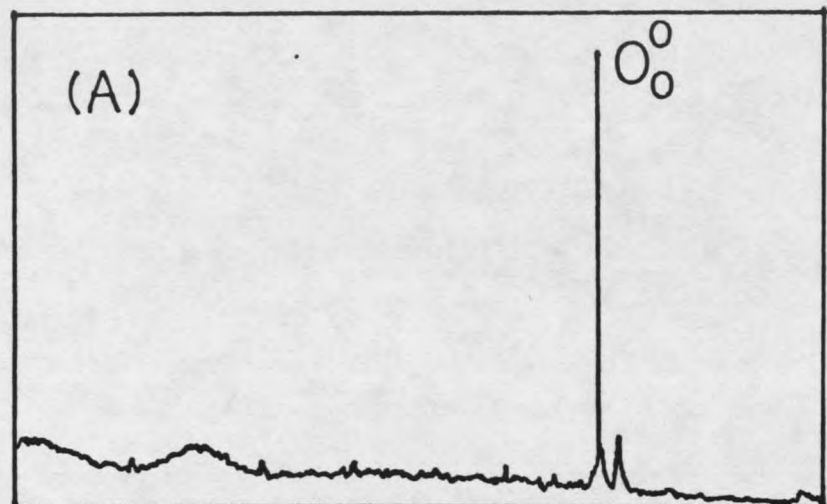
Recent work on p-methyl-trans-stilbene²⁶ indicated that the difference in the two ring positions adjacent to the methyl substituted position is significantly increased upon excitation to S_1 as determined by the CH_3 barrier height, $V_3'' = 28 \text{ cm}^{-1}$, $V_3' = 150 \text{ cm}^{-1}$. Furthermore, a conformational change of $\sim 30^\circ$ was observed which could not be explained. In an attempt to further understand the interactions which could influence the methyl behavior in such systems, investigations into the similarities and differences between p-methyl-trans-stilbene and p-methylstyrene are in progress.

Experimental

The procedure for obtaining the p-methylstyrene spectrum was given in the general experimental section of this paper. The purpose of this addendum is to cover the experimental difficulties peculiar to p-methylstyrene.

When the p-methylstyrene was heated to $\sim 60^{\circ}\text{C}$, polymerization began to occur in the sample chamber and a mixture of monomer, dimer, and possibly trimer were released from the jet nozzle and excited by the laser. The effect of exciting three different species caused a great deal of spectral congestion. In fact, as the concentration of the polymer species increased relative to monomer, the spectrum changed shape with respect to peak intensities and exhibited some broad background fluorescence. Figures 14a and 14b are spectra of the region surrounding the origin at ~ 5 minutes (14a) and ~ 2 hours (14b) after the sample came to the equilibrium temperature of 60°C . Figure 14c is a spectrum under the same conditions as 14b at the region to the blue where most of the combination bands occur.

The problem of polymerization was nearly eliminated by keeping the sample at room temperature and lining the stainless steel sample chamber with a Nalgene[®] plastic tube to prevent catalysis by the nickel present in the steel. The spectrum in Figure 15 is the result of operating under these conditions.



The p-methylstyrene spectrum (a) at 60°C for ~5 minutes and (b) at 60°C for ~2 hrs

FIGURE 14

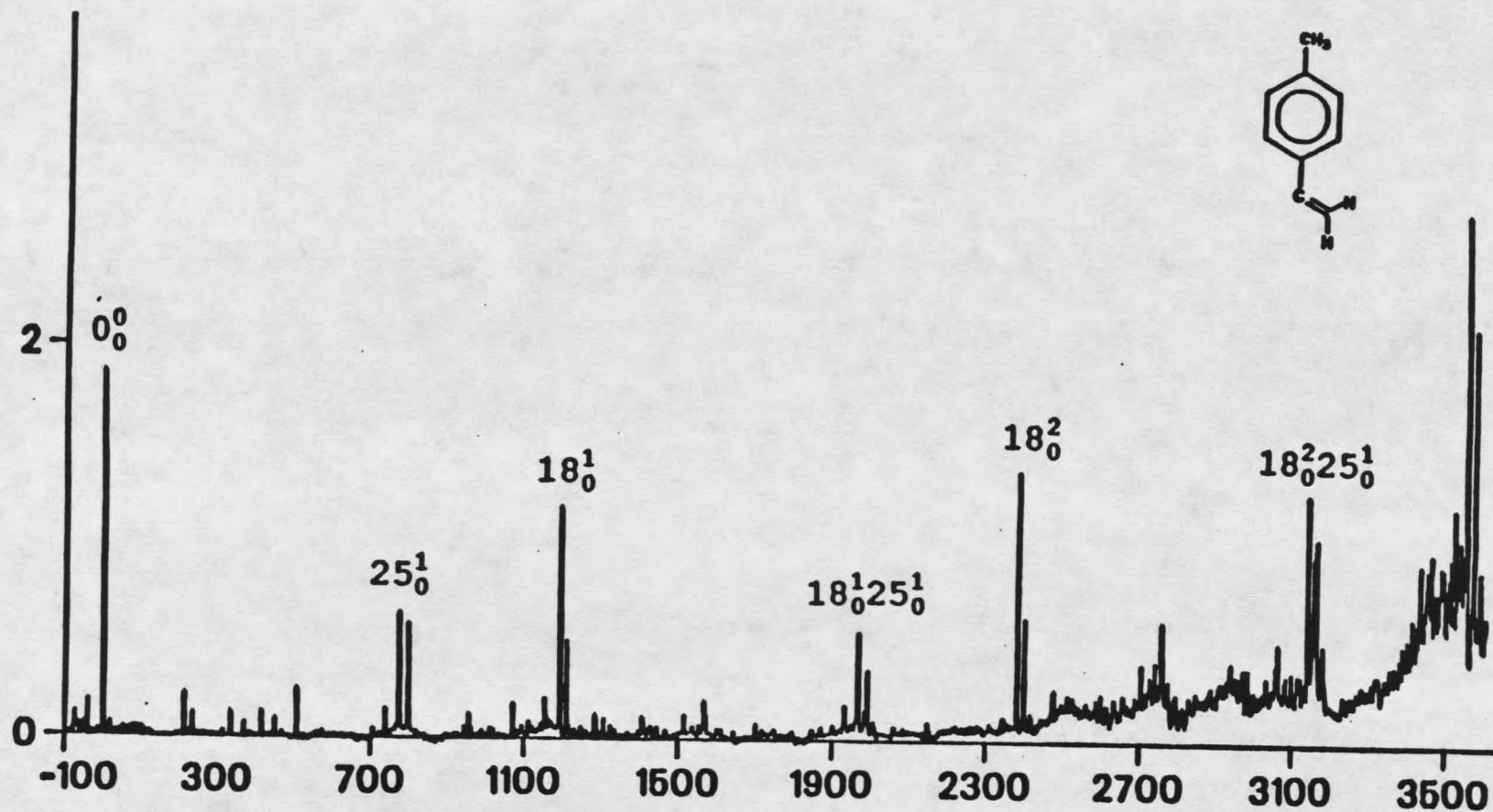


FIGURE 15 The jet-cooled p-methylstyrene spectrum with sample at room temperature

Results and Discussion

The low frequency region of the jet cooled fluorescence excitation spectrum of p-methylstyrene is shown in Figure 13. The raised baseline in the vicinity of the origin is due to presence of the dimer which formed in the liquid phase in the sample container via Ni catalyzed polymerization as discussed in the experimental section. The spectrum shows no sign of methyl rotor activity indicating that the conformation of the methyl group is identical in both states. Because there are no observable methyl rotor peaks, we cannot determine the barrier to internal rotation. Considering that the dominant influence on the methyl behavior in this molecule is expected to be hyperconjugation, it would appear that the influence of the vinylic π electrons on the local π electron density in the vicinity of the methyl group is comparable in the two electronic states. This result is most interesting when compared to previously published results on the related molecule p-methyl-trans-stilbene for which a significant change in barrier height ($V_3''=28\text{cm}^{-1}$, $V_3'=150\text{ cm}^{-1}$) and an $\sim 30^\circ$ change in conformation were observed upon excitation. This dramatic change in CH_3 behavior is indicative of a significant change in the π electron density near the methyl group and is, in part, due to the asymmetry with respect to the para axis of the π electron containing substituents. p-methylstyrene exhibits a similar asymmetry but displays

significantly different methyl rotor behavior. Thus, it can be concluded that the dramatic behavior observed in stilbene is predominately due to the second phenyl group which is 6 carbons away from the methyl probe!

Additional insight to the differences in these two conjugated π electron systems may be gained by considering the vibronic nature of the fluorescence excitation spectra. *trans*-stilbene and *p*-methyl-*trans*-stilbene show very similar relative intensities for all vibrations which appear in both spectra (once intensity distribution over all of the methyl rotor peaks is taken into account).^{21,26} However, the spectrum of *p*-methylstyrene shown in Figure 13 is markedly different than published spectra for styrene.²⁷ The most intense band of the styrene spectrum is the origin and the 18_0^1 is second with 25% of the 0_0^0 intensity. The *p*-methylstyrene spectrum is dominated by the modes appearing at 775, 799, 1194, and 1211 cm^{-1} and their combinations and overtones. The 775 cm^{-1} peak is assigned as 25_0^1 and the 1194 cm^{-1} peak as 18_0^1 by analogy with styrene. Relative intensities of 0_0^0 , 18_0^1 , and 18_0^2 for *p*-methylstyrene are 100, 110, and 50, respectively. Karplus and coworkers²⁸ have performed an extended PPP-CI vibrational analysis of styrene which describes ν_{18} as a fairly democratic mix of the $\text{C}=\text{CH}_2$ bond angle, ring bending, ring-ethylene stretching and a ring stretch. This moiety will clearly be affected by the resonance between the phenyl and ethylenic groups and the relative intensities in the styrene

and p-methylstyrene spectra indicate that the methyl group has a strong influence on that resonance interaction. The torsional mode between the ring and substituent will give the most direct measure of the bond order and resonance between the phenyl and ethyl groups. The ring torsion mode in *trans*-stilbene is very low frequency and anharmonic in the ground state but is higher frequency and harmonic in the excited state. p-methyl-*trans*-stilbene shows nearly identical frequencies and similar relative intensities for bands containing this moiety (only even quanta transitions are observed for symmetry reasons). Similar but less dramatic behavior is seen in styrene for the ring-ethyl torsion (38 cm^{-1} and anharmonic in S_0 , 97 cm^{-1} in S_1)²⁹ but we are unable to assign this mode in the p-methylstyrene spectrum.

Conclusion

An apparent paradox has resulted from the study of p-methylstyrene when the results are compared to those for styrene, *trans*-stilbene, and p-methyl-*trans*-stilbene. The p-methylstyrene and p-methyl-*trans*-stilbene spectra show extremely different methyl rotor signatures indicating a conformational change in the methylated stilbene on excitation which does not occur in p-methylstyrene. The methyl rotor behavior is determined, to a large degree, by the local π electron density which would indicate that the striking changes in the p-methyl-*trans*-stilbene spectrum are due mainly

to resonance effects caused by the remote ring which is not present in the styrene molecule. The paradox arises when comparing p-methylstyrene to its parent molecule, styrene. The p-methylstyrene spectrum shows significantly more Franck-Condon activity in several modes, one of which should be heavily affected by resonance between the ethylenic group and the ring. Thus, the presence of the methyl in the para position seems to have a significant effect on the π electron interactions at the opposite end of the ring in the substituted styrene but showed no such effect in the substituted stilbene. While this casts some doubt on use of the methyl rotor as a probe of π electron density in such molecules, it also confirms that the remote ring in stilbene has a significant effect on π electron interaction in the para position by showing that para substitution in these two molecules has a measurable effect on the opposite end of the ring.

A more detailed picture can be obtained via studies of the deuterated molecule and dispersed fluorescence experiments which will allow for identification of the ring-vinyl torsion, the mode which should be most sensitive to bond order and therefore, resonance between the phenyl and ethylene groups. These studies are currently underway in our laboratory.

REFERENCES

1. Steinfeld, J.I. Molecules and Radiation, 2nd ed., MIT Press, Cambridge, MA: 1986.
2. L.H. Spangler, D.W. Pratt, J. Chem. Phys. **84** (9), (1986).
3. D.S. Bethune, Appl. Optics **20**, 1987 (1981).
4. R.M. Kilb, C.C. Lin and E.B. Wilson, J. Chem. Phys. **26**, 1965 (1957).
5. D.R. Herschbach, J. Chem. Phys. **31**, 91 (1959).
6. H.C. Longuet-Higgins, Mol. Phys. **6**, 445 (1963).
7. Bunker, P.R. Molecular Symmetry and Spectroscopy, Academic Press, New York: 1979.
8. Steinfeld, pp. 145-150.
9. Steinfeld, pp. 77-79.
10. Stephenson, Radloff, and Rice, J. Chem. Phys. **81**, 1060-1072 (1984).
11. J.C.D. Brand, D.R. Williams, and T.J. Cook, Journal of Molecular Spectroscopy, **20**, 359-380 (1966).
12. Lowe, J.P. Quantum Chemistry, Academic Press, New York: 1978.
13. L.H. Spangler, D.W. Pratt, J. Chem. Phys. **84** (9), (1986).
14. J. Jha, S. Chattopadhyay, Indian J. Phys. **44**, 9-18 (1970).
15. J.H.S. Green, D.J. Harrison, and W. Kynaston, Spectrochimica Acta **27A**, 2199-2217 (1971).
16. R.J. Jakobsen, Spectrochimica Acta **21**, 433-442 (1965).

17. FORTRAN PROGRAM ROTIN, L.H. Spangler.
18. R. Tembreulle, T.M. Dunn, and D.M. Lubman, Spectrochimica Acta, 42A, 899-906, (1986).
19. N. Mikami, A. Hiraya, I. Fujiwara, and M. Ito, Chemical Physics Letters, 74, 531-535, (1980).
20. J. Christoffersen, J.M. Hollas, and G.H. Kirby, Molecular Physics, 16, 441-452, (1969).
21. L.H. Spangler, T.S. Zwier, R.D. vanZee, S.C. Blenkespoor, J. Phys. Chem. 91 (24), 6077-6079 (1987).
22. V.H. Grassian, E.R. Bernstein, H.V. Secor, J.I. Seeman, J. Phys. Chem. 93, 3470-3474 (1989).
23. M. Ito, J. Phys. Chem. 91, 517 (1987).
24. A.E. Dorrgo, D.W. Pratt and K.N. Houk, J. Am. Chem. Soc. 109, 6591 (1987).
25. M. Baba, I. Hanazaki and N. Nagashima, J. Chem. Phys. 82, 3938 (1988).
26. L.H. Spangler, W.B. Bosma, R.D. vanZee, T.S. Zwier J. Chem. Phys. 88 (11), 6768-6777 (1988).
27. J.A. Syange, F. AL Adel and A.H. Zewail, C. P. Lett. 103 (1), 15-21 (1983).
28. R.J. Hemeley, L.V. Varda, M. Karplus, J. Chem. Phys. 82 (12), 5379-5397 (1985).
29. J.M. Hollas, T. Ridley, C. P. Lett. 75, 94 (1980).

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