



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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MONTANA STATE UNIVERSITY
Bozeman, Montana

May 1990

11378
11449

APPROVAL

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This thesis has been read by each member of the thesis committee and has been found to be satisfactory regarding content, English usage, format, citations, bibliographic style, and consistency, and is ready for submission to the College of Graduate Studies.

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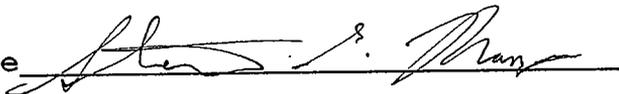
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ACKNOWLEDGEMENTS

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.

TABLE OF CONTENTS

	Page
ACKNOWLEDGEMENTS.....	iv
TABLE OF CONTENTS.....	v
LIST OF TABLES.....	vii
LIST OF FIGURES.....	viii
ABSTRACT.....	ix
INTRODUCTION.....	1
Supersonic Jet Expansion Theory.....	1
Laser System.....	2
The Methyl Rotor.....	3
Time Dependent Coupling Between Para Substituents.....	13
EXPERIMENTAL.....	14
THE ELECTRONIC CHARACTER OF PARA-TOLUIDINE EVIDENCE FOR TIME DEPENDENT COUPLING BETWEEN PARA SUBSTITUENTS.....	18
Results and Interpretation.....	18
Totally Symmetric Bands.....	23
Methyl Rotor Structure.....	23
Amine Inversion and Torsion Modes.....	24
Discussion.....	32
Conclusion.....	35

TABLE OF CONTENTS - Continued

	Page
THE PARA-METHYLSTYRENE SPECTRUM.....	37
Introduction.....	37
Experimental.....	38
Results and Discussion.....	41
Conclusion.....	43
REFERENCES.....	45

LIST OF TABLES

Table	Page
1. The C_{2v} point group character table.....	20
2. The G_6 molecular symmetry group character table.....	20
3. The vibrational and methyl rotor band assignments of p-toluidine.....	22
4. The normal modes of vibration for a molecule with C_{2v} symmetry.....	25
5. The methyl rotor structure interpretation and analysis of the p-toluidine spectrum.....	31

LIST OF FIGURES

Figure	Page
1. Neuman projections of the methyl rotor showing 3 and 6 fold potentials.....	5
2. Electronic transition on Morse potential curves illustrating the Franck-Condon principle.....	10
3. The thirty benzene-like modes of vibration for any six membered ring system.....	12
6. Block diagram of the apparatus.....	16
7. Ellipsoidal reflector light collection system.....	17
8. The jet-cooled vibronic spectrum of p-toluidine...	21
9. Expanded view of the spectrum at the origin.....	26
10. Expanded view of the spectrum at the $6a_0^1$ band.....	27
11. Expanded view of the spectrum at the 1_0^1 band.....	28
12. The "Hot" vibronic spectrum of p-toluidine.....	29
13. The spectrum of p-toluidine (ND_2).....	30
14. The p-methylstyrene spectrum (a) at 60°C after ~5 minutes and (b) at 60°C for ~2hrs.....	39
15. The jet-cooled p-methylstyrene spectrum with sample at room temperature.....	40

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 CH₃ 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.

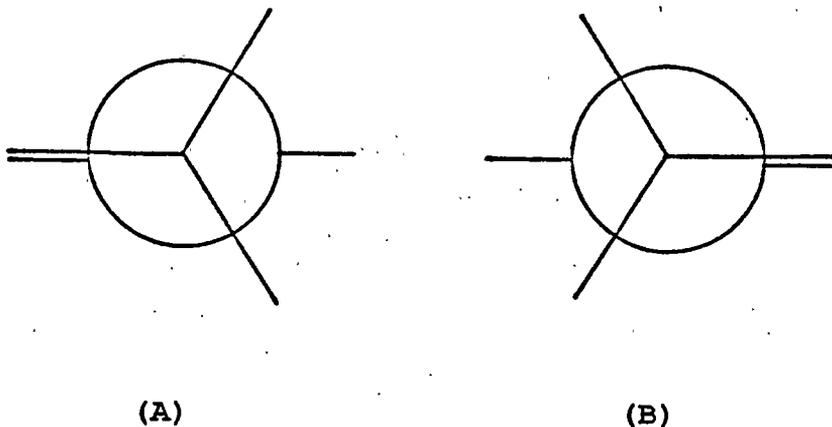
$$\begin{aligned} & (1/2)V_3[1-\cos(3\Theta)] + (1/2)V_6[1-\cos(6\Theta)] \\ & + (1/2)V_9[1-\cos(9\Theta)] + \dots \end{aligned} \quad (2)$$

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 CH₃ 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

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

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.

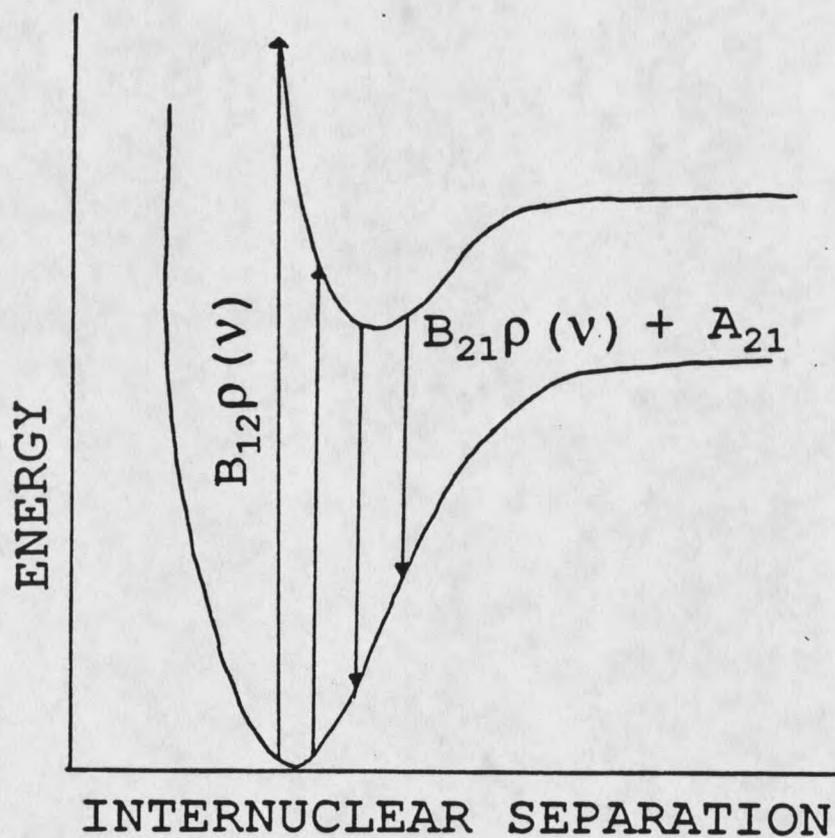
$$\begin{aligned}
 &\langle \Psi_{v''}(Q) | \langle \Psi_{e''} | \mu_x | \Psi_{e'} \rangle | \Psi_{v'}(Q) \rangle \\
 &= \langle \Psi_{v''} | \mu_{e''e'}(Q) | \Psi_{v'} \rangle
 \end{aligned}
 \tag{6}$$

If $\mu_{e''e'}(\mathcal{Q})$ 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

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

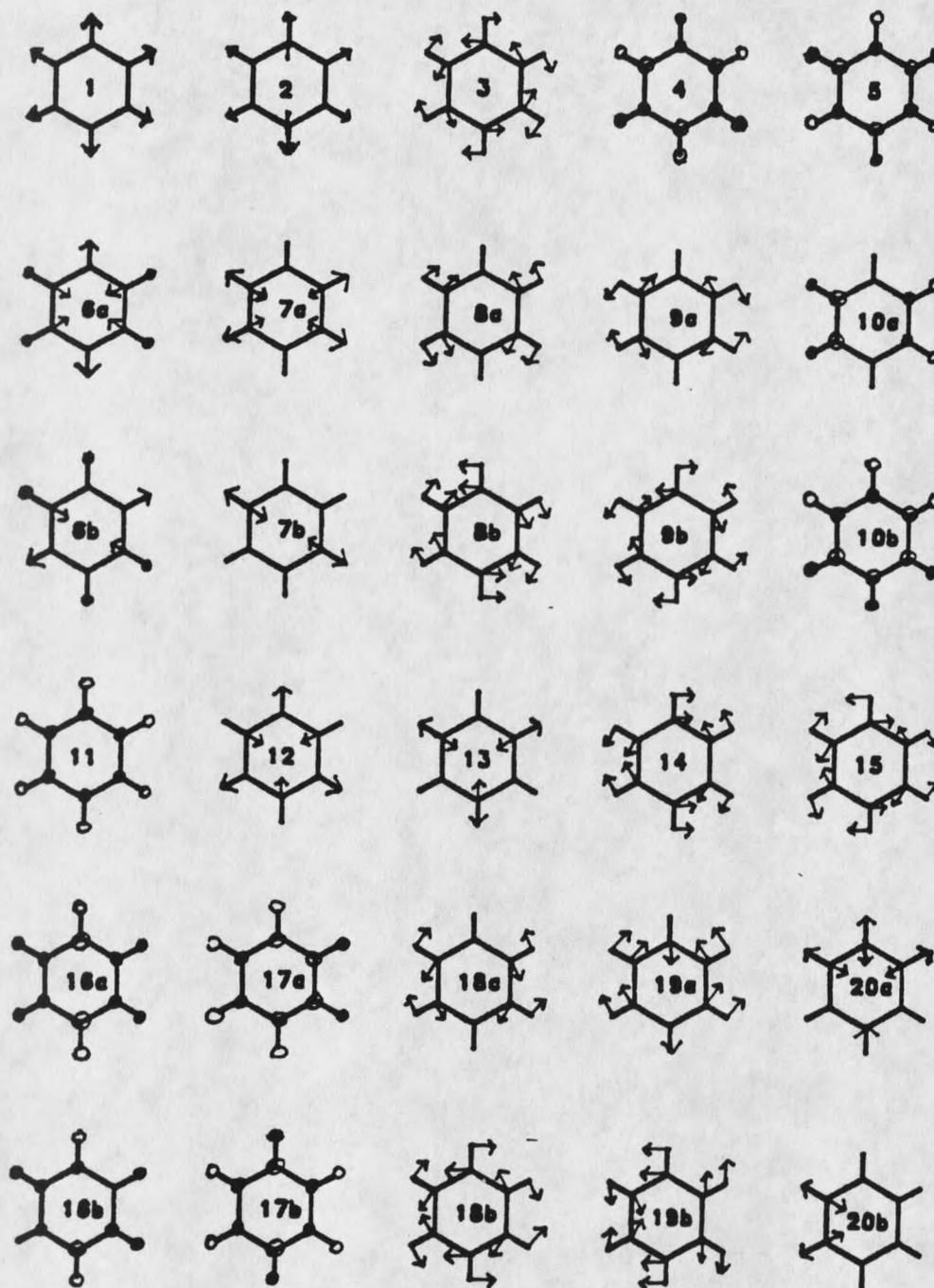
(9)

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.

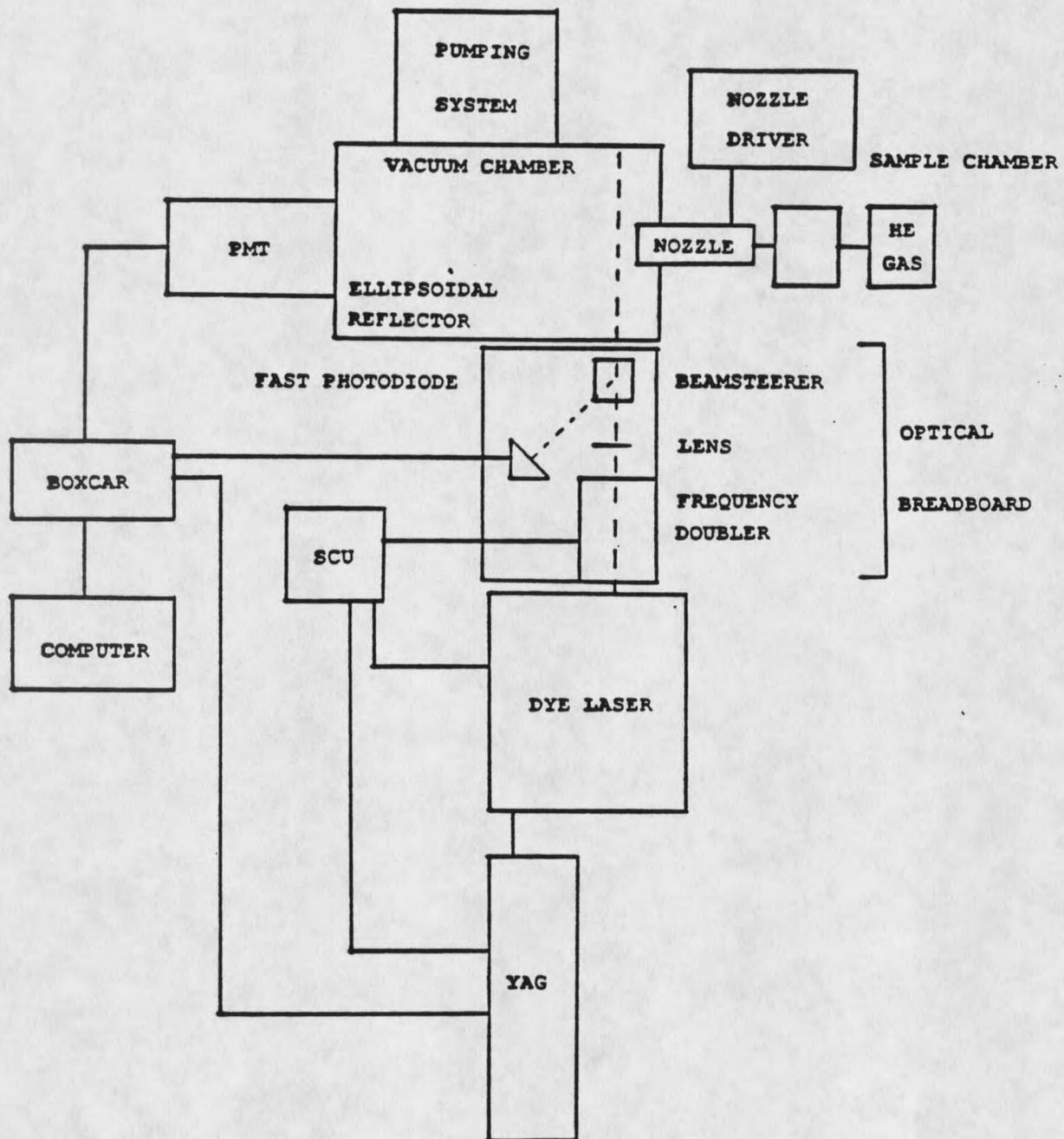
The molecular excitation source was a Lumonics HY 750 Nd:YAG pumped dye laser model HD 300 with a Hypertrack 1000 autotracker for frequency doubling. The linewidth of the laser after frequency doubling was 0.14cm^{-1} . The Nd:YAG was frequency doubled to obtain the green beam at 532nm. This afforded 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

