



Methyl rotor analysis as a function of electronic state, conformation and functionality in indoles and stilbenes

by Sonja Sue Siewert

A thesis submitted in partial fulfillment of the requirements for the degree of Doctor of Philosophy in Chemistry

Montana State University

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Abstract:

A normal mode and methyl torsional analysis as a function of electronic state, substituent effects and extent of conjugation has been performed using one and two-photon fluorescence excitation and dispersed fluorescence techniques. The methyl rotor barrier is used as a probe of the local π electron density and is found to be very sensitive to substituents ten carbons away, along with the nature of the electronic state.

3-methylindole, 3-trideuterio-methylindole, and 5-methylindole were examined for their methyl rotor structure. The indoles have two close-lying electronic states, 1La and 1Lb. The 5MI 1Lb methyl barrier is $V_3 = 80 \text{ cm}^{-1}$ with a V_6 contribution of -21 cm^{-1} . Methyl barriers were also found for complexes of 5MI with water and helium, which aid in identifying the site of complexation. The barrier for 3MI for 1Lb is $V_3 = 306.6 \text{ cm}^{-1}$, $V_6 = -10.9 \text{ cm}^{-1}$, with a ground state barrier of 443.2 cm^{-1} .

Substituted trans-stilbenes were examined because the extent of conjugation allows the study of electronic effects rather than steric interferences for the methyl group. The trans-stilbenes examined, are: p-methyl-trans-stilbene, p-methoxy-trans-stilbene, p'-methoxy-p-methyl-trans-stilbene, p'-chloro-p-methyl-trans-stilbene, p'-fluoro-p-methyl-trans-stilbene and p'-chloro-m-methyl-trans-stilbene. The molecules were chosen for the electron donating and withdrawing capabilities of the substituents. The low-frequency skeletal modes, torsional transitions, and the methyl barriers for the S0 and S1 states are assigned. The spectra for the methoxy-stilbenes displays two electronic origins, indicating the presence of two preferred conformers for the methoxy group. The methyl barriers for the two p'-methoxy-p-methyl-trans-stilbene conformers differ by 12 cm^{-1} , showing extreme sensitivity to the conformation of the methoxy group ten carbons away, different by 12 cm^{-1} . The excited state torsional barrier for p-methyl-trans-stilbene is 150 cm^{-1} , and the barrier decreases for every substituted trans-stilbene examined, indicating that the methyl hyperconjugation is extremely sensitive to π electronic effects through the extended conjugated system.

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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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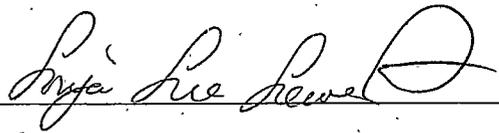
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TABLE OF CONTENTS

	Page
1. INTRODUCTION	1
Statement of the Problem	3
2. METHYL ROTOR THEORY AND HISTORY	6
3. EXPERIMENTAL PROCEDURES	18
Compounds	18
Sample Preparation	20
1hv and 2hv Theory	23
Experimental Apparatus	25
4. EXPERIMENTAL RESULTS: INDOLES	35
5-methylindole Experimental Results	36
3-methylindole and 3-CD ₃ -indole	39
5. DISCUSSION: METHYLINDOLES	42
5-methylindole	42
3-methylindole	51
6. EXPERIMENTAL RESULTS: STILBENES	58
Experimental Results	61
p-methyl-trans-stilbene	61
p-methoxy-trans-stilbene	67
p'-methoxy-p-methyl-trans-stilbene	75
p'-chloro-p-methyl-trans-stilbene	84
p'-fluoro-p-methyl-trans-stilbene	90
p'-chloro-m-methyl-trans-stilbene	95

TABLE OF CONTENTS-Continued

	Page
7. DISCUSSION: STILBENES	103
p-methyl-trans-stilbene	104
The Methoxy Conformation in para-methoxy-stilbenes	106
Comparison of Vibrations	113
Methyl Rotor Analysis	119
8. CONCLUSION	123
REFERENCES CITED	126

LIST OF TABLES

Table	Page
1. The G_6 molecular symmetry table	8
2. The internal rotation angular momentum quantum number relating to the symmetry of the torsional state with G_6 symmetry	10
3. The melting points and temperature in $^{\circ}\text{C}$ needed to obtain sufficient vapor pressure.	22
4. Calculated barriers and experimental and calculated transition frequencies for 5-methylindole and complexes.	46
5. Calculated frequencies and intensities for the 1L_b of 3-methylindole using two different ground-state barriers. ($V_3 = 307.6 \text{ cm}^{-1}$, $V_6 = -10.9 \text{ cm}^{-1}$ and $B = 5.30 \text{ cm}^{-1}$)	55
6. The symmetry correlation between C_{2h} and C_s	61
7. Torsional frequencies for p-methyl-trans-stilbene.	63
8. The major vibrational frequencies for the S_1 states of p-methoxy-trans-stilbene.	71
9. The torsional and vibrational frequencies for S_0 and S_1 of the A and B conformers of p'-methoxy-p-methyl-trans-stilbene. The ground state frequencies are expressed as combination differences.	83
10. The experimental and calculated frequencies and intensities for the A and B conformers in S_1 for p'-methoxy-p-methyl-trans-stilbene.	84

LIST OF TABLES: continued

Table	Page
11. The experimental and calculated frequencies/intensities for p'-chloro-p-methyl-trans-stilbene. ($V'_3 = 104.3 \text{ cm}^{-1}$, $V'_6 = 4.9 \text{ cm}^{-1}$, 60° conformation change.)	88
12. The calculated and experimental torsional frequencies for p'-fluoro-p-methyl-trans-stilbene. ($V'_3 = 100.5 \text{ cm}^{-1}$, $V'_6 = 12 \text{ cm}^{-1}$)	91
13. The experimental and calculated frequencies and intensities for the A isomer of p'-chloro-m-methyl-trans-stilbene.	98
14. The experimental and calculated frequencies and intensities for the B isomer of p'-chloro-m-methyl-trans-stilbene.	99
15. Experimental and calculated frequencies and intensities for the S_1 state of p-methyl-trans-stilbene. The 60° and 30° refer to the conformation change of the methyl group upon excitation.	106
16. Heats of formation calculated for p-methoxy-trans-stilbene from AMPAC AM1.	108
17. Relative intensities for the torsional progressions in p'-methoxy-p-methyl-trans-stilbene. (each progression lists relative intensities to each origin progression.)	113
18. The ground state low-frequency vibrational assignments for trans-stilbenes. Expressed as cm^{-1} above the vibrationless level.	114
19. The excited state low-frequency vibrational assignments for trans-stilbenes. Expressed as cm^{-1} above 0_0^0	117
20. Dimensionless displacements for ν_{25} in the stilbene analogues.	118
21. Methyl rotor barriers and conformation changes upon excitation for stilbene analogues.	121

LIST OF FIGURES

Figure		Page
1.	The indole and stilbene analogues examined in this study.	4
2.	Methyl rotor splitting as a function of V_3 barrier height.	11
3.	The potential barrier for S_0 and S_1 for the hindered methyl rotor in p-methyl-trans-stilbene.	14
4.	The supersonic jet expansions	22
5.	The process of fluorescence for isolated molecules.	23
6.	The process of dispersed fluorescence.	25
7.	The apparatus for 1hv fluorescence excitation experiments	27
8.	The apparatus for dispersed fluorescence experiments utilizing the CCD detection system.	30
9.	Comparison of the scanning 0.25 meter monochromator dispersed fluorescence apparatus versus the CCD/0.5 meter monochromator system from exciting the B origin of p-methoxy-trans-stilbene.	32
10.	The experimental apparatus for 2hv fluorescence spectroscopy.	33
11.	The 1hv fluorescence excitation spectrum of 5-methylindole.	38
12.	The 1hv fluorescence excitation spectrum of 3-methylindole.	40
13.	The 1hv fluorescence excitation spectrum of 3-trideuterio-methylindole.	41

LIST OF FIGURES: continued

Figure		Page
14.	The low frequency region of the 5-methylindole spectrum (top). Two-photon contours of the first four transitions using both linearly and circularly polarized light are shown at the bottom. These contours span 9 cm^{-1} with tic marks appearing every 0.5 cm^{-1} .	43
15.	Torsional progression for 5-methylindole helium complexes, with a water complex progression on the bottom trace. The torsional levels show a measurable change in their relative frequencies.	48
16.	Comparison of the weak peaks in the low frequency region of the 3MI and 3MI-CD ₃ spectra. The transitions correlate as indicated by the tie lines.	52
17.	Plots of excited-state combination differences (same as relative frequencies) vs. a V_3 barrier height. The corresponding 3MI spectra are shown plotted to the same frequency scale indicating the assignment of the torsional transitions and the approximate barrier height.	54
18.	Low frequency modes of trans-stilbene.	60
19.	The $1h\nu$ fluorescence excitation spectrum of p-methyl-trans-stilbene.	62
20.	$1h\nu$ fluorescence excitation spectra of p-methyl-trans-stilbene under different expansion conditions.	64
21.	The linearly polarized $2h\nu$ contour of the origin of p-methyl-trans-stilbene on the top trace with the fluorescence excitation contour below.	66
22.	The $1h\nu$ fluorescence excitation spectrum of p-methoxy-trans-stilbene.	68
23.	A vs. B conformer spectra for p-methoxy-trans-stilbene.	69
24.	The dispersed fluorescence from the origins of the A and B conformers of p-methoxy-trans-stilbene.	72
25.	The dispersed fluorescence spectra of the low-frequency vibrations for the A and B conformers of p-methoxy-trans-stilbene.	74

LIST OF FIGURES: continued

Figure		Page
26.	The 1hv FE spectrum of p'-methoxy-p-methyl-trans-stilbene. The conformer origins are identified with labels A and B.	77
27.	The first 300 cm ⁻¹ of the 1hv FE spectrum for each conformer. Note that the B conformer origin has been placed directly under the A origin for comparison purposes.	78
28.	The DE from the A conformer torsional features of p'-methoxy-p-methyl-trans-stilbene.	80
29.	The DE from the 0a ₁ , 1e, 2e and 3a ₁ transitions for the B conformer of p'-methoxy-p-methyl-trans-stilbene.	82
30.	The 1hv FE spectrum of p'-chloro-p-methyl-trans-stilbene.	86
31.	The DE of the 0 ₀ ⁰ methyl rotor structure for p'-chloro-p-methyl-trans-stilbene.	89
32.	The 1hv FE spectrum of p'-fluoro-p-methyl-trans-stilbene.	92
33.	The DF of the rotor levels for p'-fluoro-p-methyl-trans-stilbene.	93
34.	The DF from 24 ¹ and 25 ¹ for p'-fluoro-p-methyl-trans-stilbene.	94
35.	The 1hv FE spectrum of p'-chloro-m-methyl-trans-stilbene. The first isomer is labeled A and the second isomer is labeled B. Tie lines indicate torsional structure.	96
36.	The DE for the A isomer of p'-chloro-m-methyl-trans-stilbene.	100
37.	The DE for the B origin of p'-chloro-m-methyl-trans-stilbene.	101
38.	Dispersed fluorescence from the "X" transitions of p-methoxy-trans-stilbene.	110
39.	The B-25 ¹ ₀ 37 ² ₀ Fermi resonance of p-methoxy-trans-stilbene. The 1hv trace is on the top, the dispersed fluorescence from both transitions below.	112

ABSTRACT

A normal mode and methyl torsional analysis as a function of electronic state, substituent effects and extent of conjugation has been performed using one and two-photon fluorescence excitation and dispersed fluorescence techniques. The methyl rotor barrier is used as a probe of the local π electron density and is found to be very sensitive to substituents ten carbons away, along with the nature of the electronic state.

3-methylindole, 3-trideuterio-methylindole, and 5-methylindole were examined for their methyl rotor structure. The indoles have two close-lying electronic states, 1L_a and 1L_b . The 5MI 1L_b methyl barrier is $V_3 = 80 \text{ cm}^{-1}$ with a V_6 contribution of -21 cm^{-1} . Methyl barriers were also found for complexes of 5MI with water and helium, which aid in identifying the site of complexation. The barrier for 3MI for 1L_b is $V_3 = 306.6 \text{ cm}^{-1}$, $V_6 = -10.9 \text{ cm}^{-1}$, with a ground state barrier of 443.2 cm^{-1} .

Substituted trans-stilbenes were examined because the extent of conjugation allows the study of electronic effects rather than steric interferences for the methyl group. The trans-stilbenes examined are: p-methyl-trans-stilbene, p-methoxy-trans-stilbene, p'-methoxy-p-methyl-trans-stilbene, p'-chloro-p-methyl-trans-stilbene, p'-fluoro-p-methyl-trans-stilbene and p'-chloro-m-methyl-trans-stilbene. The molecules were chosen for the electron donating and withdrawing capabilities of the substituents. The low-frequency skeletal modes, torsional transitions, and the methyl barriers for the S_0 and S_1 states are assigned. The spectra for the methoxy-stilbenes displays two electronic origins, indicating the presence of two preferred conformers for the methoxy group. The methyl barriers for the two p'-methoxy-p-methyl-trans-stilbene conformers differ by 12 cm^{-1} , showing extreme sensitivity to the conformation of the methoxy group ten carbons away, different by 12 cm^{-1} . The excited state torsional barrier for p-methyl-trans-stilbene is 150 cm^{-1} , and the barrier decreases for every substituted trans-stilbene examined, indicating that the methyl hyperconjugation is extremely sensitive to π electronic effects through the extended conjugated system.

CHAPTER ONE

INTRODUCTION

Spectroscopy is the study of the interaction of electromagnetic radiation with matter.¹ The broad range of energies in the electromagnetic spectrum allows scientists to examine the fundamental chemistry and physics of matter. The work in this thesis utilizes the visible and ultraviolet region. In this wavelength region, the interaction of light with matter is known as electronic spectroscopy, where the higher energy light promotes the redistribution of electrons in the molecule. Molecules and atoms absorb the ultraviolet and visible light at a resonant energy, and then the energy is lost through fluorescence or phosphorescence. Fluorescence is detected in the research presented here, and from the resulting spectra, the molecular structure and chemical reactivity can be examined. With the advent of moderate resolution tunable dye lasers and supersonic expansions, several issues that previously could not be examined can now be addressed.

One area which can now be examined is the internal rotation of methyl groups. The torsion of a methyl group is interesting since it is intrinsically different in its behavior than other normal modes of vibration, and often is the driving force of many of the dynamics for molecules.²⁻⁴ Vibrations, such as the stretching and bending motions of functional groups common in organic chemistry, are commonly examined using infrared spectroscopy. The

methyl group is unique in that it is an internal rotation of low frequency and large amplitude. The internal modes are typically anharmonic in behavior, making spectral analysis more challenging. Before the advent of supersonic expansions to introduce the sample to the exciting radiation, these low frequency torsional transitions were often unresolvable in the electronic spectrum due to spectral congestion. The expansion forces the vibrational and rotational temperatures to be dramatically reduced, thus only the lowest levels of the ground state molecule are populated prior to excitation, making the excitation spectrum much less congested.

The potential energy surface that describes the torsional coordinates often changes upon electronic excitation. The methyl group will frequently have a conformational (or phase) change upon excitation, typically 30° or 60° due to the the three equivalent hydrogens and the resulting symmetry. The light hydrogens and low barriers of the methyl group result in torsional tunneling, and because of this rigid molecular point group symmetry cannot be used to describe this internal motion, and instead non-rigid group theoretical methods are utilized.

The methyl group typically does not rotate freely, the motion is usually hindered. This barrier to internal motion was originally examined using microwave spectroscopy⁵ (which obtains ground state information), and with the improved technology available for electronic spectroscopy, the examination of the methyl barrier in excited states is possible. The contributing factors to these barriers have been under examination for several years and is the topic of this thesis. The interactions of the methyl group with the π molecular orbitals is one contribution to the barrier, and is strongly influenced by the local π electron density.

Statement of the Problem

The goal of this research is to examine the sensitivity of the methyl group to the local π electron density in molecules with more than a single aromatic ring. The sensitivity of the methyl group to the local π electron density has been studied in several single ring systems,^{2, 6-11} however it has not been examined in extended conjugated systems. In single ring systems, steric effects can be a strong factor in hindering the methyl torsion. By expanding the studies to extended conjugated systems, the methyl group should be more strongly influenced by electronic effects than steric effects. This thesis presents a study of the analysis of the barrier to internal rotation for the methyl group as a function of electronic state and conformational changes, site of the methyl rotor, substituent effects and van der Waals complexes for several indole and stilbene analogues. The barrier to internal rotation is obtained by analyzing the fluorescence spectra for all of these molecules, and conclusions will be made regarding the above effects on the barrier to internal rotation. With further understanding of the methyl group and the effects of the local π electron density upon its rotation, it is hoped that the methyl group can be used as a probe of the local π electron density in aromatic compounds.

Figure one shows the indole and stilbene derivatives that will be examined in this study. The specific reasons why these molecules were chosen will be discussed in their respective chapters. Briefly, indole is the chromophore of the amino acid tryptophan, and has two-close lying electronic states. Information regarding these electronic states is important because tryptophan is responsible for the majority of the fluorescence in proteins.¹² The indole analogues examined in this thesis are 5-methylindole, 3-methylindole, and 3-trideuterio-

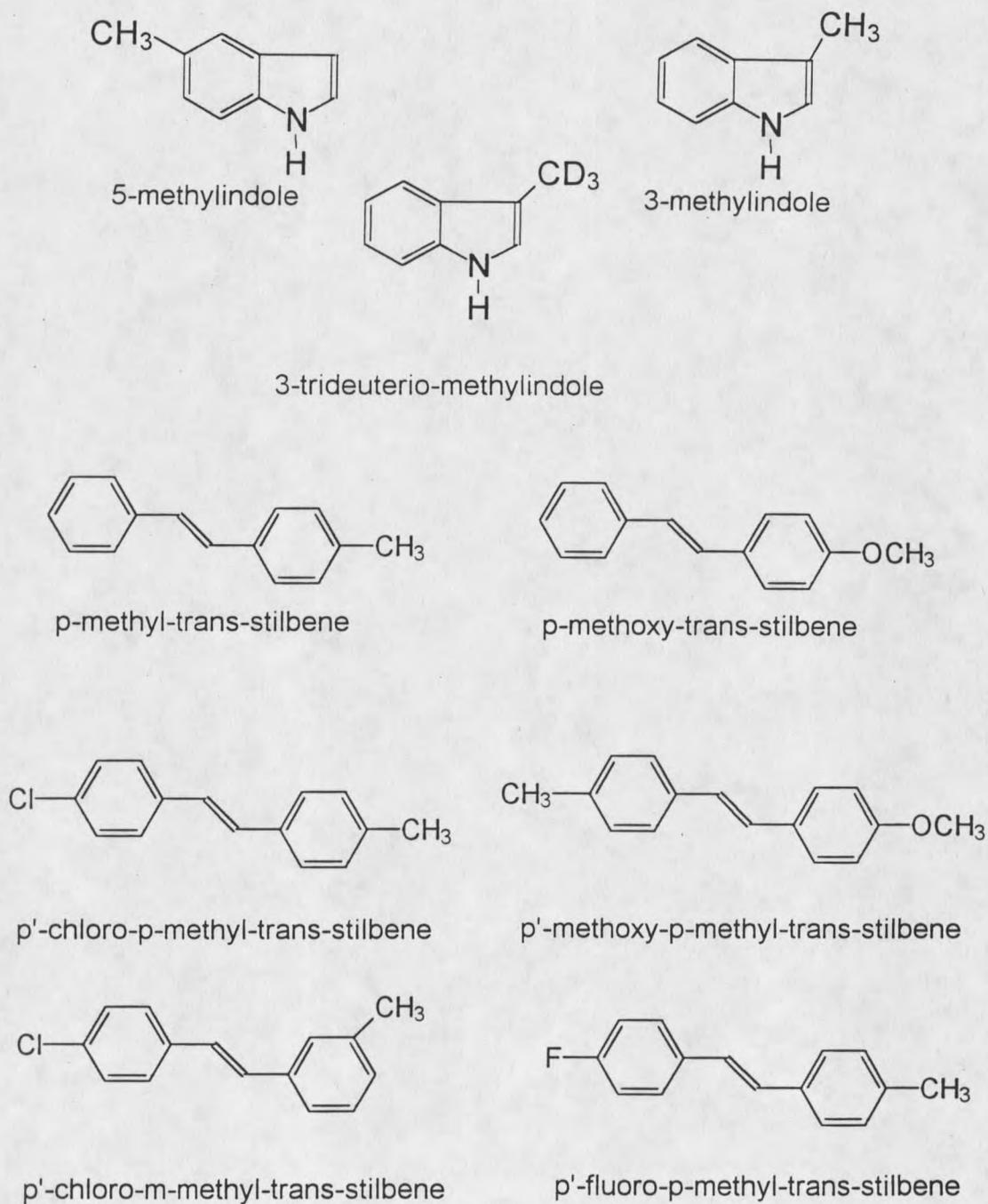


Figure 1: The indole and stilbene analogues examined in this study.

methylindole. The spectra of these methylated indoles exhibit characteristics due to hindered internal rotation of the methyl group along with dynamics driven by the methyl group.

The second group of molecules examined are the stilbenes. Stilbene is the prototypical model for the study of reaction dynamic in the gas phase, and undergoes cis/trans photoisomerization.¹³ Stilbene has an extended π conjugated system which makes it an ideal system to examine electronic effects since the π system is delocalized, even more so in the excited state, and it should allow substituents on one phenyl ring to affect the π electron density on the other phenyl ring. These effects can then be measured by the methyl barrier. Spectral analysis in stilbenes is made more difficult by several low-frequency vibrations, and these vibrational assignments will be made for the stilbene analogues. The stilbenes examined in this study are also shown in Figure one and are: p-methyl-trans-stilbene, p-methoxy-trans-stilbene, p'-methoxy-p-methyl-trans-stilbene, p'-chloro-p-methyl-trans-stilbene, p'-chloro-m-methyl-trans-stilbene and p'-fluoro-p-methyl-trans-stilbene.

CHAPTER TWO

METHYL ROTOR THEORY AND HISTORY

Methyl groups are attached to their parent molecule by a single bond resulting in a possibility for internal rotation. This rotation is not necessarily free and several factors can contribute to the barrier including steric and π electronic effects. Microwave spectroscopy⁵ results were used for many years to determine the barrier in the ground state, however, the advent of supersonic jet molecular laser spectroscopy has allowed the investigation of the methyl group in other electronic states by reducing the spectral congestion. The barriers obtained for ground and excited electronic states and in different molecules can then be compared to examine how functionality, conformation, the extent of conjugation, and other factors effect the barrier. The barrier therefore can be utilized as a probe of the local electron density in the molecule.¹⁴

If the methyl group is treated as a rigid body, able to rotate freely with fixed bond angles and distances, the Hamiltonian is that of a particle-in-a-ring, where ϕ is the internal rotation angle.

$$H = -B \frac{d^2}{d\phi^2}$$

The eigenvalues for this Hamiltonian are m^2B , where $m = 0, \pm 1, \pm 2, \dots$, and B is the internal rotation constant $B = \hbar^2/2I_\phi$, where I_ϕ is the reduced moment of inertia $I_\phi = [(I_{\text{CH}_3}I_{\text{frame}})/(I_{\text{CH}_3} + I_{\text{frame}})]$.^{4,5} In most of the molecules with methyl rotors, there is at least a small barrier to internal rotation. The barrier can be describe using a Fourier series of $\cos(n3\phi)$ terms where $n = 1, 2, \dots$, ϕ is the internal rotation angle, and the 3 comes from the threefold rotational symmetry of the methyl group. The Schrödinger equation for torsional motion is

$$-B \frac{d^2 \Psi}{d\phi^2} + V\phi = E \Psi$$

The appropriate basis set is the free rotor representation:

$$\Psi = \frac{1}{\sqrt{2\pi}} e^{im\phi}, \quad m = 0, \pm 1, \pm 2, \dots$$

The potential energy of the torsional motion can be described using the following expression.

$$H_1 = V(\phi) = \frac{V_3}{2}(1 - \cos 3\phi) + \frac{V_6}{2}(1 - \cos 6\phi) + \dots$$

The first non-zero term in this series will depend on the number of equivalent conformations. For example, in toluene¹⁵ the methyl has threefold symmetry about the rotor axis (phenyl-methyl bond) and the ring has twofold symmetry about the same axis giving rise to six equivalent conformations. Therefore, V_6 will be the first non-zero term. In the molecules studied here, V_3 will typically be the dominant term. V_3 will determine the height

of the potential, while V_6 will determine the shape of the wells. Contributions from V_9 are minimal.

Owing to the multiple minima along the CH_3 torsional coordinate, the relatively low barriers, and the low mass of the hydrogen atoms involved, tunneling can occur between the wells, which makes point-group theory inadequate in treating the symmetry of these non-rigid molecules.^{16,17} The tunneling represents an exchange or permutation of nuclei, and the molecular symmetry groups developed by Longuet-Higgins and Bunker must be used. If all possible nuclear permutations and inversions are used, the group used is the complete nuclear permutation and inversion (CNPI) group. Many of the CNPI operations are physically unlikely and can be discarded, resulting in the molecular symmetry group. In every molecule examined in this study, the CH_3 groups can best be described using G_6 symmetry, which is isomorphic with the C_{2v} group. See Table 1 for the G_6 symmetry table.

Table 1: The G_6 molecular symmetry table.

G_6	E	(123)	(23)*
		(321)	(12)*
			(31)*
	[1]	[2]	[3]
A_1	1	1	1
A_2	1	1	-1
E	2	-1	0

In the case of low-medium barriers ($1-300\text{ cm}^{-1}$), the tunneling interaction of the rotor wave functions splits the triply degenerate levels from the harmonic oscillator basis set (which describes an infinitely high barrier with triply degenerate levels compared to the free rotor where the torsional levels are as $E = m^2B$) into singly and doubly degenerate levels (a_1 or a_2 and e). The energy levels of the methyl rotor will be labeled by the above internal rotation angular momentum quantum number m and the symmetry of the level. See Table 2 for a description of how the internal rotation angular momentum quantum number relates to the symmetry of the torsional state. In terms increasing energy the torsional levels for the methyl rotor are: $0a_1, 1e, 2e, 3a_2, 3a_1, 4e, 5e, \dots$ ¹⁴ These labels will be used throughout as identification of the methyl rotor levels. To identify the torsional levels, the basis set used is the free rotor representation shown above, and it can be solved where:

$$e^{+im\theta} + e^{-im\theta} = \cos(m\theta) + i \sin(m\theta) + \cos(m\theta) - i \sin(m\theta) = 2 \cos(m\theta)$$

The use of a supersonic jet expansion, discussed in chapter three, to introduce the sample ensures that we will be populating only the lowest levels for the methyl rotor, these being the $0a_1$ and $1e$ levels. Torsional selection rules for electronic transitions state that in transitions for the methyl rotor, like must go to like. Therefore, transitions starting in the $1e$ level can only go to other E levels, A_1 to A_1 levels. The A_1 and E species are different nuclear spin isomers of the same molecule, and the differences in their selection rules are useful in interpreting a spectrum.⁵ Another difference is that A levels are nondegenerate and the E levels are doubly degenerate. In G_6 , the A_1 and A_2 torsions have A_1 nuclear spin symmetry and have a statistical weight of 8. Torsions with E symmetry must have a nuclear spin symmetry

statistical weight of 4. Hence, the A_1 and E levels cannot cool into one another in the expansion resulting in two spin isomers and simplifying the identification of spectra through fluorescence excitation and dispersed fluorescence work.⁴

Table 2: The internal rotation angular momentum quantum number relating to the symmetry of the torsional state with G_6 symmetry.

	E	(123)	(23)*	
	$\tau_{\Theta=0}$	$\tau+240$	τ	
m	$2\cos m\Theta$	$2\cos m\Theta$		
0	1	1	1	A_1
± 1	2	-1	0	E
± 2	2	-1	0	E
± 3	2	2	0	$A_1 + A_2$
± 4	2	-1	0	E
± 5	2	-1	0	E
± 6	2	2	0	$A_1 + A_2$

For levels with A symmetry, the internal motion resembles a vibration, a torsional oscillation localized in the potential wells. The internal motion of the E states has more of the character of free rotation passing from one potential well to another by tunneling. The degeneracy of the free rotor remains for the E states which is related to the two possible directions of internal rotation. Overall rotation of the molecule slightly splits the E degeneracy via angular momentum coupling, and if the perturbation is strong enough, the E contours will appear to be broader than the A_1 contours. In the spectra obtained in this study, for both the methyl indoles and stilbenes, the E levels in fact are broader, aiding in their

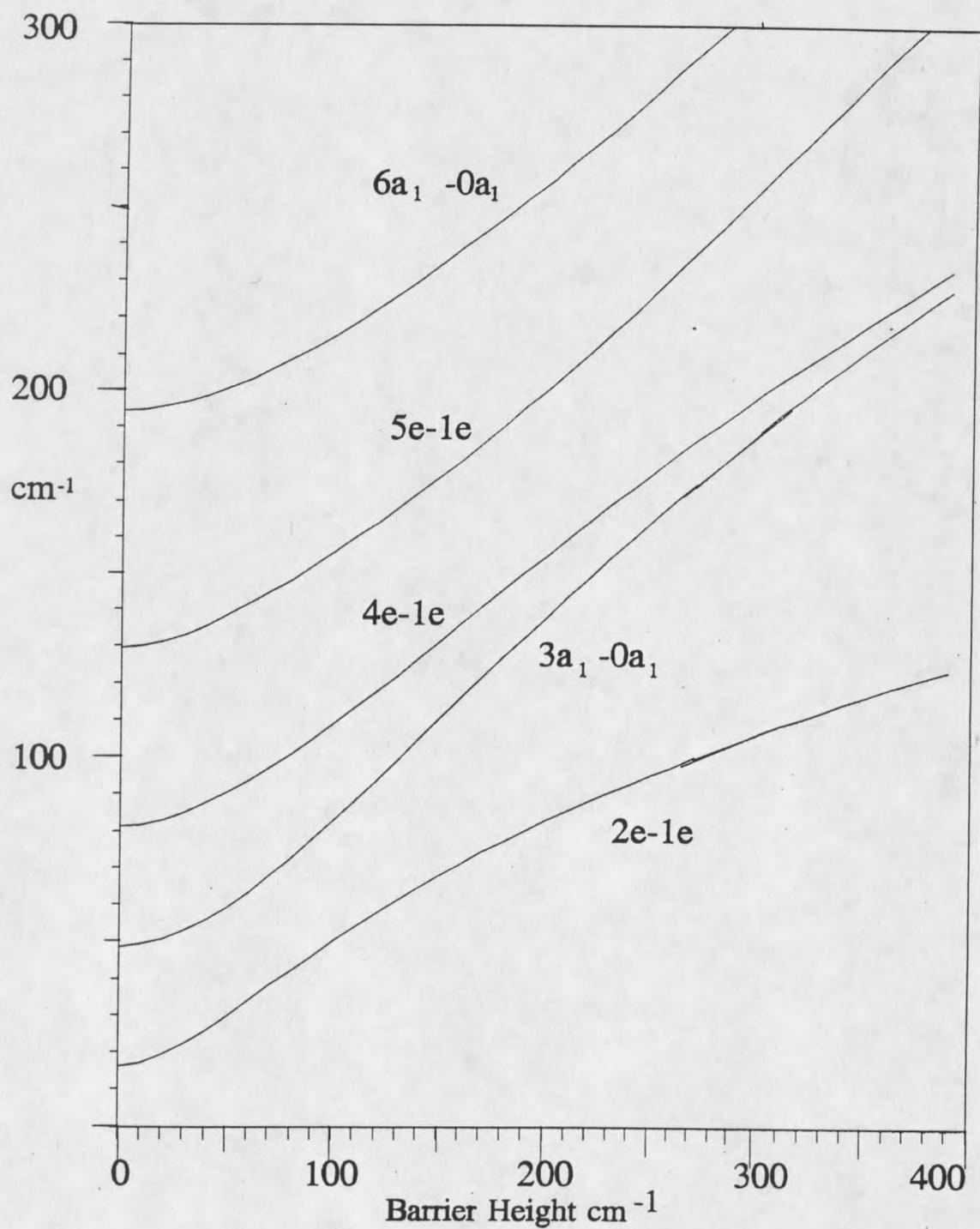


Figure 2: Methyl rotor splitting as a function of V_3 barrier height.

identification. Once these E and A_1 levels have been identified in a spectrum, their frequencies and intensities are used to determine a value for a potential barrier. (See Figure 2)¹⁸ By identifying the first few members of the torsional progression in a spectrum, the higher transitions can often be located by comparison with the calculated frequencies.

The first step in determining the potential barrier for the methyl group from experimental data is to use a FORTRAN program, VNCOS, written by Laane and coworkers.¹⁹ This program calculates the eigenvalues for a potential function of the type $\sum_n (V_n/2)(1-\cos nx)$. Based on the frequency differences of the rotor levels, the V_3 and V_6 terms are optimized to reflect the barriers. There is one other factor in the calculation which is optimized, B , the internal rotation constant. For CH_3 , this value typically ranges from 5.2-5.4 cm^{-1} . Using the VNCOS program, we can then obtain the potential terms for the ground and excited state barriers if we have experimental data available. Transitions higher than $3a_1$ are typically above the barrier and are not as well fit by VNCOS.

VNCOS was written to calculate IR transitions for a single electronic state. While it can be used to determine barriers for both the ground and excited states, it cannot calculate intensities in excitation or dispersed emission spectra. A program written by Spangler²⁰ known as INROT calculates the frequency of a transition and its intensity based on the barriers previously calculated from VNCOS for the ground and excited states. These values can then be optimized to find barriers that would yield the observed intensities and frequencies. The intensities are calculated from the Franck-Condon factors. The Franck-

$$S_{v'v''} = \int \psi_{v'}^* \psi_{v''} d\tau_N$$

Condon factors are determined by an integral^{1,21} which is the overlap of vibrational wave functions of the ground and excited electronic state, occasionally expressed as the integral squared to reflect the probability. A change in conformational preference, displacement of the potential energy surface, barrier shape and height all contribute to the observed intensities. If many transitions in the methyl rotor progression have intensity in a spectrum, the conformation change is typically 30°-60°, while if only the origin has significant intensity (98%), there is no conformation change between the two states.

An example of the hindered internal rotation potential barriers for the methyl group are the potentials for p-methyl-trans-stilbene. These barriers were assigned previously by Zwier and Spangler.¹⁴ The barriers for the ground and excited states, reflecting the conformation change for the methyl group, are shown in Figure 3, with $V_3'' = 28 \text{ cm}^{-1}$ and $V_3' = 150 \text{ cm}^{-1}$, and the internal rotation constant is $B = 5.35 \text{ cm}^{-1}$ for both states. This molecule was previously assigned with a 35° conformation change. The conformation change was modified to 60° upon reassignment of the $3a_2$ level as discussed in chapter seven. The barrier for rotation increased 5-times upon excitation, indicating that the methyl group in this molecule is very sensitive to changes in the electronic structure.

There are many possible causes for the barrier that hinders the internal rotation of the methyl group. An early example of internal rotation in the excited state was work by Ito, in the mid-1980's. He examined this in fluorotoluene as a function of *ortho*, *meta* and *para* substitution.² For *o*-fluorotoluene the ground state barrier is 228 cm^{-1} and reduces to 21.8 cm^{-1} upon excitation. The *ortho* position can make steric factors the dominant factor hindering the rotation. In the ground state for both *meta* and *para* fluorotoluene the barrier

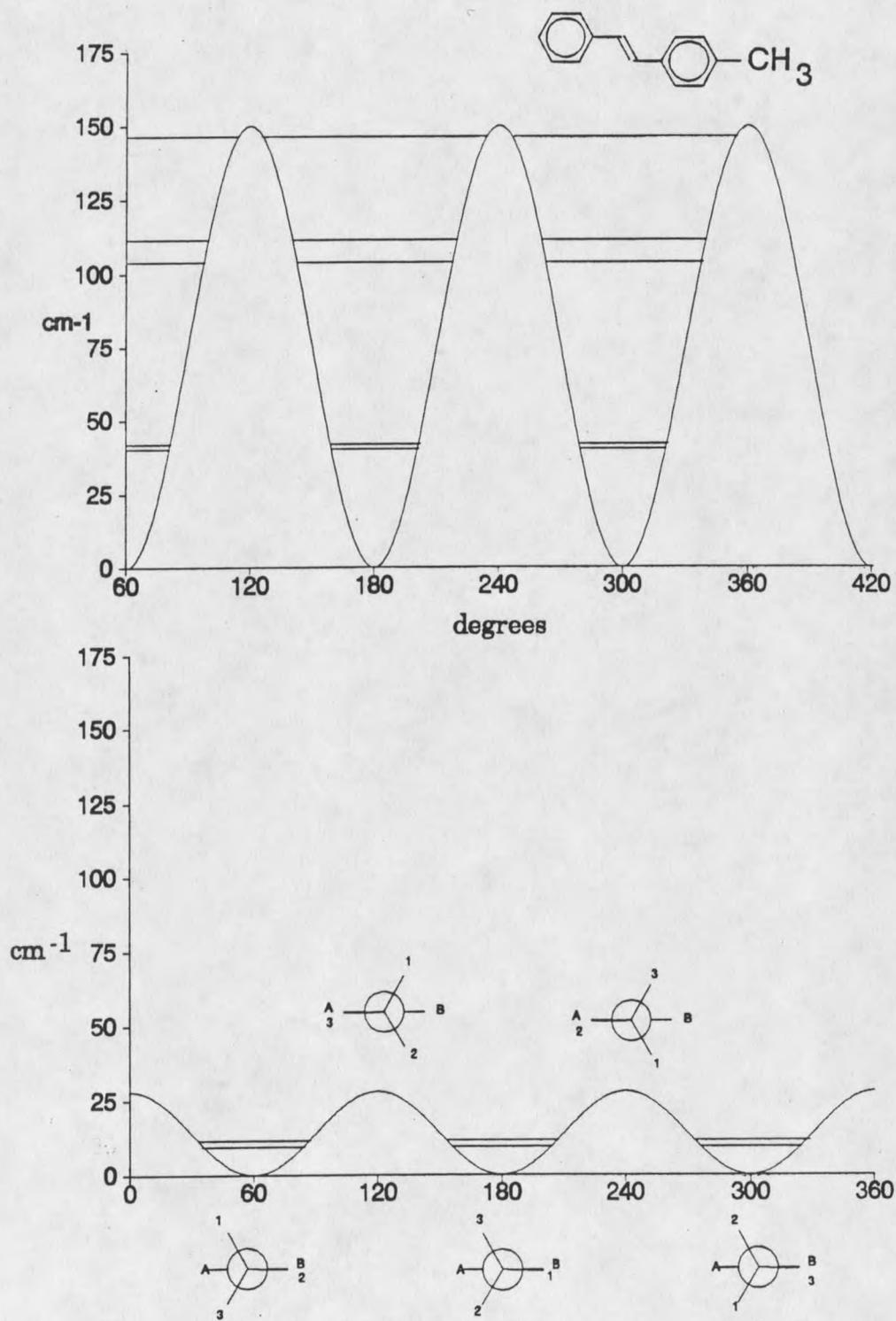


Figure 3: The potential barriers for S_0 and S_1 for the hindered methyl rotor in p-methyl-trans-stilbene.

is very low, but for *m*-fluorotoluene it increases dramatically upon excitation. This group of molecules is one of the best starting points for looking at π electronic effects in phenyl ring systems since it systematically looks at the different positions around the phenyl ring. There have been many other comprehensive examinations of methylated single ring systems such as pyrimidines^{10,11}, toluenes^{2,9}, cresols^{22,23}, anilines²⁴ and styrenes¹⁰⁻¹². As discussed in later chapters, the study of methylated stilbenes will show that π electronic effects are a contributing factor to the barrier to internal rotation, as steric effects are ruled out by the large separation of the substituents.

The role of hyperconjugation in relation to the barrier has been a point of contention for many years. Hyperconjugation is a resonance stabilization due to delocalization of a σ bond with the adjacent π orbitals.²⁵ Over the past several decades, several different models of hyperconjugation have been developed. Hehre states that the interactions between a methyl group and the π electron system of the molecule to which the methyl group is attached to can be explained by considering the π and π^* orbitals of a double bond and the π -like orbitals of the CH_3 group.²⁶ There are four different interactions that can contribute to hyperconjugation, and the preferred staggered or eclipsed conformation depends upon the orbital interactions. If an electronic excitation takes place, the staggered conformer would be favored over the eclipsed for two of the interactions (propene is an example) but the contributions from the other two interactions must be taken into consideration. For small molecules this theory does explain the experimental evidence, however, in larger molecules many more interactions must be taken into consideration.

A theoretical approach to hyperconjugation involves looking at the methyl group such as in propylene ($C_1=C_2-C_3-H_{1,2,3}$), where $H_{1,2,3}$ are the three methyl hydrogens.²⁷ The wavefunction is a set of 3 C-H bond functions, each being a linear combination of a hydrogen 1s orbital and a C sp^3 orbital. These are used to form group orbitals as a linear combination of the three H orbitals. These are mutually orthogonal if overlap integrals are neglected.

$$\phi_1 = \frac{1}{\sqrt{3}}(\phi_{H_1} + \phi_{H_2} + \phi_{H_3})$$

$$\phi_2 = \frac{1}{\sqrt{6}}(2\phi_{H_1} - \phi_{H_2} - \phi_{H_3})$$

$$\phi_3 = \frac{1}{\sqrt{2}}(\phi_{H_2} - \phi_{H_3})$$

The function ϕ_1 has no node and can overlap with whatever 2s and $2p_x$ orbital of C_3 that is "left over" from the σ bond to carbon 2. The function ϕ_2 has a nodal plane roughly approximate to the nodal plane of $2p_z$, and ϕ_3 has a nodal plane in the xz plane, with orbital overlap occurring with the carbon p_y orbital. Therefore, the C_3-2p_z orbitals and the ϕ_2 group orbital can by symmetry join the π -lattice, which is the 2 electrons in the C_3-H_3 π -type bond, and are now treated as part of the π system. There are two other models of hyperconjugation in the literature. One is the Pauling model, which is described in terms of an inductive model and in which conjugation is neglected. The other is the Matsen and Stevenson Heteroatom Model, in which the electrons in a methyl group behave as a single electron pair contribution to the π system.

The model that we feel best represents hyperconjugation is the first model which contributes π electron density from the C-H bonds to the π system. There are many influences which affect the hyperconjugation when the methyl group is attached to aromatic systems along with other functional groups. The methyl group is shown to be sensitive to π electronic effects from the functionality of substituent effects, as will be shown in this thesis for the substituted stilbenes.

CHAPTER THREE

EXPERIMENTAL PROCEDURES

The details of the experimental procedures developed and used in this thesis work are presented in this chapter. The main experimental technique, supersonic jet laser spectroscopy, has been developed extensively over the past decades.^{2-4,6-15,22-24,28} When the need has arisen, new procedures were developed in the laboratory to obtain more information, including the application of a charged coupled device (CCD) to take exposures of the dispersed fluorescence. The origination and/or synthesis of the molecules used in this study will be presented first. The experimental setups for 1hv, 2hv, and dispersed fluorescence will then be presented, along with discussions pertaining to the theory and use of these methods.

Compounds

The indole compounds used for the methyl rotor studies came from a variety of sources. 5-methylindole was obtained from Aldrich Chemical, while the 3-methyl-indole was obtained from Sigma Chemical. Both were used without further purification with a stated purity of >98%. 3-trideutero-methyl-indole was synthesized by Dr. C.J. Lee as discussed in the thesis of David Sammeth.²⁹

The stilbene analogues were obtained from several different sources. The p-methyl-trans-stilbene was synthesized for the earlier studies performed at Calvin College and was obtained from T.S. Zwier now at Purdue University. The p-methoxy-trans-stilbene was obtained from the Sigma Chemical Company and was used without further purification. P'-methoxy-p-methyl-trans-stilbene was synthesized in our research group by reacting 0.03 moles of the Arbusov product, $\text{CH}_3\text{-C}_6\text{H}_4\text{-CH}_2\text{-P=O(Et)}$ dissolved in 0.06 moles NaH in 1,2-dimethoxyethane (DME), into which was added 0.03 moles p-anisaldehyde. This solution was refluxed at 70°C for 0.5 hours during which time H_2 gas was produced by the reaction, indicative of formation of the stilbene. The reaction was quenched with water, and the resulting stilbene crystals were collected and recrystallized twice in ethanol and then dried. The yield was approximately 75%, and the melting point is 158° Celsius. The compound was examined with $^1\text{H-NMR}$ and FTIR, and compared to the commercially available p-methoxy-trans-stilbene.

The three halogenated methylstilbenes were prepared in a similar manner. They are p'-chloro-p-methyl-trans-stilbene, p'-chloro-m-methyl-trans-stilbene and p'-fluoro-p-methyl-trans-stilbene. The Arbusov product used above was replaced with the appropriate phosphinate obtained from Lancaster Chemical, along with the proper halogenated aldehyde compound. The p'-chloro-p-methyl-trans-stilbene and the p'-chloro-m-methyl-trans-stilbene were synthesized originally as a project in Dr. Arnold Craig's organic 206 laboratory, and further work was done by our research group, Brian Pagenkopf, and Susan Sheehan. A version of the Wittig reaction is utilized, involving the transfer of an alkylidene-phosphorane, derived from an alkyl triphenylphosphonium salt, to a carbonyl compound with displacement

of the carbonyl oxygen.³⁰ This synthesis results in the majority of the compound to be of trans stereochemistry. The formation of cis isomers does not affect the experiments performed in this project as cis-stilbene in jets has a fluorescence spectrum that is broad and featureless, and absorbs in a different wavelength region than trans-stilbenes.¹³ One equivalent of n-BuLi was used as a base, then it was reacted with 3-(or 4)-methylbenzyltriphenyl-phosphonium chloride in THF as a solvent. One equivalent of 4-chloro-benzaldehyde was added and the solution was refluxed. The product was filtered, recrystallized in ethanol, and dried on a high-vacuum line. ¹H-NMR, FTIR and gas chromatography were used to test for purity and identification.

The p'-fluoro-p-methyl-trans-stilbene was prepared in a similar manner by Brian Pagenkopf. One equivalent of 4-methylbenzyl-triphenylphosphonium bromide was dissolved in THF and one equivalent n-BuLi. 4-fluoro-benzaldehyde was added and the solution was refluxed. The product was recrystallized in ethanol and the solvent removed. Once again the sample was examined for purity with gas chromatography, and analyzed with ¹H-NMR and FTIR.

Sample Preparation

The vapor pressure of these compounds is very low at room temperature, therefore the samples are heated to get adequate concentration in the expansion. The indoles were heated to approximately 100° Celsius, while the stilbene had to be heated to 125° Celsius, near the temperature limit of the sample system. See Table 3 for specific sample temperatures. The stilbenes were placed into a Pyrex beaker inside of a stainless steel sample

chamber to help inhibit polymerization. This also made for easier sample recovery. Glass wool was occasionally used inside of the sample chamber to raise the sample closer to the outtake tube.

As mentioned above, the samples were introduced via a supersonic jet expansion. Without cooling the sample via the expansion, the spectrum would be very congested due to hot bands, which are transitions that begin from higher vibrational levels of the ground state, and the low-frequency modes that are examined in this work would be difficult to observe. A seeded jet is used, in which vaporized sample is entrained in helium and the gas mixture is flowed through a pulsed nozzle. The cooling occurs when gas from a high pressure reservoir is discharged into a low pressure region through a small nozzle. The seeded molecule is embedded in a translationally cold environment which cools the internal degrees of freedom through collisional energy transfer. At the point where the gas density becomes too low to support collisions, the final temperature becomes fixed. During the expansion the gas acquires a net flow velocity which exceeds the local speed of sound.³¹ With our system, optimal cooling was achieved with a He backing pressure of 5-7 bars. This allows a sufficient quantity of sample made available for excitation. With this pressure, the molecules rotational temperature is near 5K while the vibrational temperatures are typically less than 50K. In order to increase the thermal population of higher vibrational levels of the electronic ground state to identify hot bands, the helium backing pressure can be reduced to 0.4 barr He. See Figure 4 for a diagram showing the expansion conditions necessary to obtain supersonic jet-cooling. In the figure, P_0 refers to the helium backing pressure at temperature T_0 , which goes through a nozzle with a diameter D , where it expands into a low pressure (P_1) chamber

