Remote substituent effects on methyl torsional barriers and Pi electron density in stilbenes
by Brian Scott Metzger

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:
Jet-cooled fluorescence excitation spectra and single vibronic level fluorescence spectra are presented for several substituted trans-stilbenes. Nearly complete assignments of the low-frequency skeletal modes and methyl torsional transitions are given. The methyl rotor barrier is used as a probe of the local μ electron density and is found to be very sensitive to the nature of the electronic state, along with substituents ten carbons away.

An extended conjugated system allows for the removal of possible steric interactions and the changes in the methyl barrier will be influenced by μ electronic effects. The trans-stilbenes examined are: p-hydroxy-trans-stilbene, p-methoxy-trans-stilbene, p-trifluoromethyl-trans-stilbene, p-dimethylamino-trans-stilbene, p’-hydroxy-p-methyl-trans-stilbene, p’-cyano-p-methyl-trans- stilbene, p’-trifluoromethyl-p-methyl-trans-stilbene, p’-dimethylamino-p-methyl-trans-stilbene, and p’-p-dimethyl-trans-stilbene. The molecules were chosen for the electron donating and withdrawing capabilities of the substituents. Jet expansion has been used to remove some of the spectral congestion arising from thermal population of low frequency vibrations. The methyl torsional barriers were measured and the substituent induced differences are discussed. The methyl barrier decreases with substitution of remote substituents.

Two electronic origins were found in the spectra of p-hydroxy-trans-stilbene and p-hydroxy-p'-methyl-trans-stilbene, and these origins are due to the two preferred conformers of the hydroxy group. The hydroxy functional group and the methoxy functional group act similarly in the excited state but differ as Van der Waals complexes with H2O.

A vibrational state mixing which accompanies methyl substitution is manifested as a Fermi resonance in the excitation spectrum and the positions and intensities of the coupled levels along with an approximate coupling matrix element are discussed.

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APPROVAL

of a thesis submitted by

Brian Scott Metzger

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.

Dr. Lee H. Spangler Lee H Spangler 4/24/96
Date

Approved for the Department of Chemistry

Dr. David M. Dooley David M Dooley 9/25/96
Date

Approved for the College of Graduate Studies

Dr. Robert H. Brown R L Brown 10/22/96
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ABSTRACT

Jet-cooled fluorescence excitation spectra and single vibronic level fluorescence spectra are presented for several substituted trans-stilbenes. Nearly complete assignments of the low-frequency skeletal modes and methyl torsional transitions are given. The methyl rotor barrier is used as a probe of the local π electron density and is found to be very sensitive to the nature of the electronic state, along with substituents ten carbons away.

An extended conjugated system allows for the removal of possible steric interactions and the changes in the methyl barrier will be influenced by π electronic effects. The trans-stilbenes examined are: p-hydroxy-trans-stilbene, p-methoxy-trans-stilbene, p-trifluoromethyl-trans-stilbene, p-dimethylamino-trans-stilbene, p'-hydroxy-p-methyl-trans-stilbene, p'-cyano-p-methyl-trans- stilbene, p'-trifluoromethyl-p-methyl-trans-stilbene, p'-dimethylamino-p-methyl-trans-stilbene, and p'-p-dimethyl-trans-stilbene. The molecules were chosen for the electron donating and withdrawing capabilities of the substituents. Jet expansion has been used to remove some of the spectral congestion arising from thermal population of low frequency vibrations. The methyl torsional barriers were measured and the substituent induced differences are discussed. The methyl barrier decreases with substitution of remote substituents.

Two electronic origins were found in the spectra of p-hydroxy-trans-stilbene and p-hydroxy-p'-methyl-trans-stilbene, and these origins are due to the two preferred conformers of the hydroxy group. The hydroxy functional group and the methoxy functional group act similarly in the excited state but differ as Van der Waals complexes with H_2O.

A vibrational state mixing which accompanies methyl substitution is manifested as a Fermi resonance in the excitation spectrum and the positions and intensities of the coupled levels along with an approximate coupling matrix element are discussed.

CHAPTER ONE

INTRODUCTION

The importance of molecular conformation to chemical activity can not be understated since there is a direct link between the physical properties of a molecule and its structure. From simple atomic structures to the complex folding of proteins, scientists have long sought to understand the source behind structural preference. A simple case long studied by scientists is the internal rotation about a single bond and the resulting conformational preference in ethane. The hindrance to free rotation about the C-C bond in ethane was discovered because of discrepancies between the experimental determined entropy and the calculated entropy from statistical mechanics[1]. The internal rotation of a methyl group has now become a classic subject and spectroscopic studies have made it possible to develop a well accepted explanation for the origin of barriers in the ground state[2].

Spectroscopy is the study of the interactions between matter and electromagnetic radiation[3]. Spectroscopic investigations give chemists detailed information about specific molecular processes, such as vibrations, rotations, and electronic transitions. Information concerning the barriers to internal rotation in the ground state can come from a number of sources including infrared, microwave, NMR, IR and Raman spectroscopy measurements[4-7].

Through comprehensive studies, the hindered internal rotation of the methyl group is well known for its extreme sensitivity to its local steric and electronic environment[8]. Any changes in molecular structure or the pi electronic density show up in the form of different barriers for the methyl group. Thus, when the methyl torsional transitions are observed in the spectrum, the methyl rotor can be used as a probe to study electronic features of the molecule.

Considering the methyl groups sensitivity to the local electron density, physical chemists anticipated a dramatic change in the potential for internal rotation by electronic excitation[9]. However, spectroscopy at room temperature is complicated by the inevitable hot band excitation originating from higher populated vibrational and torsional states. Consequently, there had been little information available for the internal rotation in electronically excited states[10]. With the advent of supersonic jet expansion, evidence of torsional motion in toluene, fluorotoluenes, and other substituted benzenes has been used to infer a relationship between changes in the torsional potential upon excitation and pi electron density within the molecule[11,12]. The supersonic expansion prepares isolated ultracold molecules with reduced spectral congestion and complex partners depending on expansion conditions[13].

The dramatic changes in the barrier heights for the methyl group upon electron excitation is generally discussed in terms of hyperconjugation and intramolecular hydrogen bonding[12]. Ab initio calculations confirm that hyperconjugation is the dominant interaction in determining the methyl behavior in aliphatic systems containing a methyl group adjacent to an sp^2 carbon[14]. Since hyperconjugation involves an overlap of the methyl group orbitals with those of the ring, the sensitivity to local π electron density and observed conformational changes can be rationalized.

Work on p-methyl-trans-stilbene (CH_3-Ph-CH=CH_2-Ph) suggests the effects due to hyperconjugation extend further than the intermediate π system, where substitution of remote functional groups affects motion at the other end of the molecule. Spangler presented spectral evidence in p-methyl-trans-stilbene of methyl rotor activity characteristic of a three-fold barrier, which indicates that the two meta positions are inequivalent[15]. P-methyl-styrene (CH_3-Ph-CH=CH_2), similar in structure to p-methyl-trans-stilbene, has a small six-fold barrier similar to toluene[16]. Given this, the three fold barrier to methyl internal rotation is probably due to the remote phenyl ring six carbons away. The large distance separating the remote ring from the methyl bearing ring in p-methyl-trans-stilbene rules out simple steric interaction and the threefold barrier is most likely an electronic effect interacting through the conjugated system.

The idea of remote interactions dictated by through-bond electron transfer is intriguing since the usefulness of this concept can easily be seen in the field of organic chemistry and molecular electronics. A slow decrease in the interaction as a function of distance is especially important in the field of electronics[17]. Current research in such diverse areas as molecular electronics, protein-folding kinetics, and applied regioselectivity is the driving force behind the desire to understand the nature of the excitation process on the π electron density in conjugated systems[18-21].

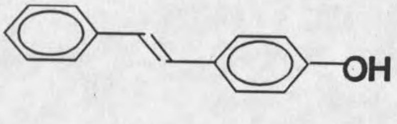
Statement of the problem

The aim of this research is to examine the effect of remote substituents on methyl torsional barriers in molecules where the substituted-phenyl ring is attached to a methyl bearing ring by means of a vinylene (-CH=CH-) linking group. Steric effects can be a strong factor in hindering the methyl torsion in single ring systems. Therefore, an extended conjugated system allows for the removal of possible steric interactions and the changes in the methyl barrier will be influenced by π electronic effects. The extended conjugated system of methyl substituted trans-stilbenes makes it ideal to measure these electronic effects.

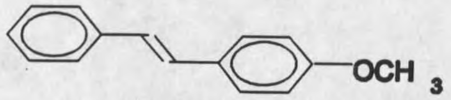
Previous research in this group has found that the strong donating character of remote functional groups, such as the amino and methoxy functional groups, reduce the barrier of the methyl group ten atoms away on the stilbene skeletal frame[22,23]. Moreover, there is a pattern in the reduction of the barrier suggesting that the stronger the electron-donating group, the lower the barrier. More evidence is desirable to solidify the difficult task of understanding the mechanism for the remote substituent effects on the methyl torsional barrier. Presently, there has been no unified viewpoint for the intramolecular interaction responsible for the rotational barrier in electronically excited states[11]. This thesis presents a study of the analysis of the barrier to internal rotation for the methyl group as a function of different remote substituents for several stilbenes.

A comprehensive data set should include at least two donors, two halogens, CH_3, H, and one acceptor to cover the wide range of substituent inductive properties. This study seeks to fulfill the above requirement by selecting previously uninvestigated functional groups shown in Figure 1 which are: p-hydroxy-trans-stilbene, p-methoxy-trans-stilbene, p-trifluoromethyl-trans-stilbene, p-dimethylamino-trans-stilbene, p'-hydroxy-p-methyl-trans-stilbene, p'-cyano-p-methyl-trans- stilbene, p'-trifluoromethyl-p-methyl-trans-stilbene, p'-dimethylamino-p-methyl-trans-stilbene, and p'-p-dimethyl-trans-stilbene. In these molecules, the perturbation to the methyl barrier is due to electronic effects and not steric effects from the remote substituent since the large distance between the methyl and remote ring and the rigidity of the stilbene frame prevent any through-space interaction. Comparison of the remote substituent effects on the methyl torsional barriers in the stilbenes mentioned here will allow for a sophisticated understanding to the origin of the methyl barrier in the stilbene system.

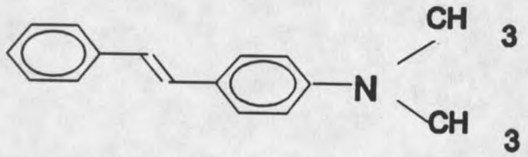
Also, the comparison of the slight differences in electronic effects of the remote substituent in these stilbenes furnishes an interesting look at a vibrational state mixing which accompanies methyl substitution. This coupling is manifested as a Fermi resonance in the excitation spectrum and the positions and intensities of the coupled levels along with an approximate coupling matrix element will be discussed.



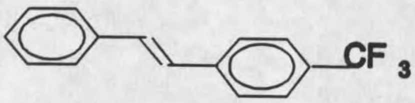
p-hydroxy-trans-stilbene



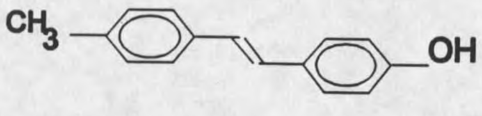
p-methoxy-trans-stilbene



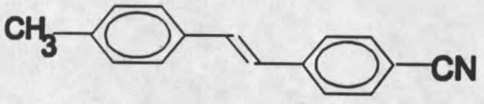
p-dimethylamino-trans-stilbene



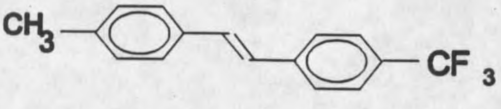
p-trifluoromethyl-trans-stilbene



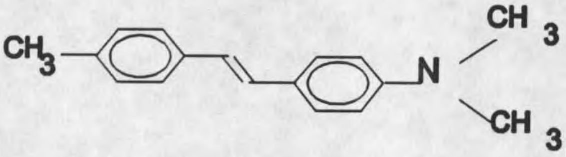
p'-hydroxy-p-methyl-trans-stilbene



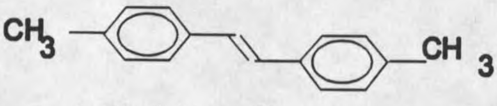
p'-cyano-p-methyl-trans-stilbene



p'-trifluoromethyl-p-methyl-trans-stilbene


CH3
CH 3
N
CH 3

p'-dimethylamino-p-methyl-trans-stilbene



p'-p-dimethyl-trans-stilbene

Figure 1. The stilbene analogues examined in this study.

Finally, It would be expected that the methyl group's tendency to couple with ring vibrations and the observed changes in the torsional barrier should perform an important role in the relaxation processes of the excited-state trans-stilbene. Experimental evidence and theoretical arguments suggest that the methyl rotor is an accelerating functional group for intramolecular vibrational redistribution (IVR) within an isolated molecule[24-26]. Recent studies concerning the photochemistry of trans-stilbene discuss possible isomerization mechanisms, including IVR, that occur in the excited state[27-30]. In light of our current research focus on methyl torsional barriers, it would be appropriate to comment on our observations of possible isomerization dynamics in the excited state of trans-stilbene in relation to different methyl rotor behavior caused by remote substitution.

CHAPTER TWO

METHYL ROTOR THEORY AND HISTORY

Information about molecular structure and bonding can be retrieved by considering the nature of the energy levels of the methyl group. In usual harmonic approximations, the vibrational modes of the molecules are assumed to be small amplitude and are uncoupled from each other. The low frequency and large amplitude motion of the methyl torsion make it unlike other normal modes of vibrations. The methyl rotor may be interpreted as a rigid body rotating in a plane or a mass point moving in a circle of radius r. In the case of a rigid, free internal rotation, the potential energy is taken to be zero. The appropriate wave function describing the motion would then be the orthonormal particle-in-a-ring functions shown here:

$$\Psi = \frac{1}{\sqrt{2}} e^{im\phi} \text{ , m = 0, ±1, ±2, ...}$$

The free rotor model above is incomplete for most molecules since a barrier generally hinders the internal rotation. This hindrance displays itself in the spectrum because the observed energy spacings are much larger than those predicted by the free rotor model. Due to the three equivalent C-H bonds, the potential well will possess three minima, or some integer multiple of three, and the appropriate form for the potential function for hindered internal rotation is:

$$V=\Sigma_n[\,(V_n/2)*(1-\cos(nf))]\qquad n=3, 6, 9 \ldots$$

where n is an integer > 0 and f is the torsional angle[31]. The dominant component in this summation is usually the lowest component possessing the correct symmetry. The relative signs of V_3 and V_6 are valuable in identifying the shape of the potential. With a small positive V_6 and larger positive V_3, the total potential well appears to be sharper at the base and broader at the top. The reverse is true for a small negative V_6 relative to a positive V_3.

As the barrier increases, the internal rotation becomes highly hindered and takes on pseudo vibrational motion in the states well below the top of the potential well. If the system is in a state below the barrier, it is classically locked in that configuration and does not have enough energy to move to another equivalent configuration on the other side of the barrier.

Quantum mechanically, the system can tunnel through the barrier from one conformer to another. Tunneling represents an exchange, or permutation of nuclei, a symmetry operation not adequately treated by point group symmetry. The molecular symmetry groups of Bunker and Longuet-Higgins are used allowing classification of the spin states, the states of nuclear motion, and electronic states of non-rigid molecules[32,33]. G_6 is the appropriate molecular symmetry group for single methylated trans-stilbenes since the frame to which the methyl group is attached has no symmetry about the torsional axis.

Table 1. The G_6 molecular symmetry table.

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

In the G_6 molecular symmetry group shown in table 1, E is the identity operation, (123) and (321) are permutations of the nuclei, and the * signifies inversion of the spatial coordinates of the entire molecule through its center of mass[34].

To determine the electronic spectrum emerging from these energy states shown in Table 2, the torsion-rotation wavefunctions must be classified according to the symmetry species of the molecular symmetry group. The total wave function must observe the Pauli exclusion principle for the exchange of fermions and can have either even or odd parity for inversion[32]. This restriction applies to the * column in the G_6 molecular symmetry group. The direct product

$$\Gamma_{tot} = \Gamma_e \otimes \Gamma_v \otimes \Gamma_{tor} \otimes \Gamma_{rot} \otimes \Gamma_{ns} \subset A_1, A_2$$

for the total symmetry of p-methyl-trans-stilbene must be either A_1 or A_2, as expressed in the above equation. The use of supersonic expansion, discussed in Chapter Three, should create molecules in their zero point (skeletal) vibrational state. Hence, the electronic and vibrational symmetries will be A_1, and the methyl torsional levels are A_1 and E symmetry. The rotational symmetries are either A_1 (ee, oe), or A_2 (eo, oo)^{35}. The symmetries of the torsional levels in p-methyl-trans-stilbene are resolved from how the torsional angles and basis functions transform under the operations of G_6 and are given in Table 2.

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

m	E $\tau_{\Theta=0}$ $2\cos m\Theta$	(123) $\tau+240$ $2\cos m\Theta$	(23)* τ	
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

In p-methyl-trans-stilbene, the nuclear spin wavefunctions are either A_1 or E symmetry. From Table 3, we find all the rotational levels within a particular torsional band have the same nuclear spin symmetry. In G_6, 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 E nuclear spin symmetry and a statistical weight of 4.

Table 3. The symmetry species for G_6 p-methyl-trans-stilbene.

Γ_{tor}	$\Gamma_e \otimes \Gamma_v$	Γ_{rot}	Γ_{ns}	Γ_{tot}
A_1	A_1	A_1	A_1	A_1
E	A_1	A_1	E	A_1
E	A_1	A_2	E	A_2
A_2	A_1	A_1	A_1	A_2
A_1	A_1	A_2	A_1	A_1

One of the effects of the different nuclear spin symmetries of the A and E torsional levels is the rigorous selection rule in electronic spectra. The A_1 and E spin isomers result in the observance of both A↔A and E↔E transitions in the excitation spectrum. On the other hand, transitions starting in E levels can only go to other E levels, and A_1 to A_1 levels. Consequently, the selection rules help with the identification of transitions by greatly simplifying the dispersed emission spectra. The statistical weight ratios of the torsional transitions affect their relative intensities directly and partly explains the electronic origin intensity ratio seen in the spectra for the methylated trans-stilbenes investigated in this thesis.

For the methyl substituted trans-stilbene compounds studied in this thesis, the energy levels of a methyl rotor are labeled $0a_1$, 1e, 2e, $3a_2$, $3a_1$, 4e, 5e, $6a_2$, $6a_1$... in order of increasing energy[15]. The dependence of the energy of each internal rotational transition as a function of a V_3 barrier height is illustrated in

Figure 2. By identifying some of the low torsional levels in the spectrum, higher transitions can often be located by a comparison with the calculated frequencies.

The geometric structure of an excited electronic state usually differs from that of the ground state[36]. The rotational fine structure of the vibrational bands is the basic way to yield information about the moments of inertia and hence the molecular structure. The experimental methods used in this thesis do not have the resolution necessary to observe rotational fine structure, thus the Franck-Condon principle offers the only other method of obtaining information about the geometrical structure of an electronic state.

A qualitative picture of The Franck-Condon principle has the sluggish nuclei retaining their position and momentum while the electrons quickly make a transition[37]. The nuclei experience new forces since they are usually displaced relative to the equilibrium geometry of the new potential surface. A change in the conformational preference, displacement of the potential energy surface, and barrier shape all contribute to the observed vibronic band intensities. The Franck-Condon principle does not influence the absolute intensity, but only affects its distribution among vibrational components[38].

The quantitative application of the Franck-Condon principle requires a brief quantum-mechanical discussion. The probability that an electronic transition between two states will occur is proportional to the square of the transition moment integral having the form: $M = \int \psi'^{*} \mu\, \psi\, d\tau$, where the prime

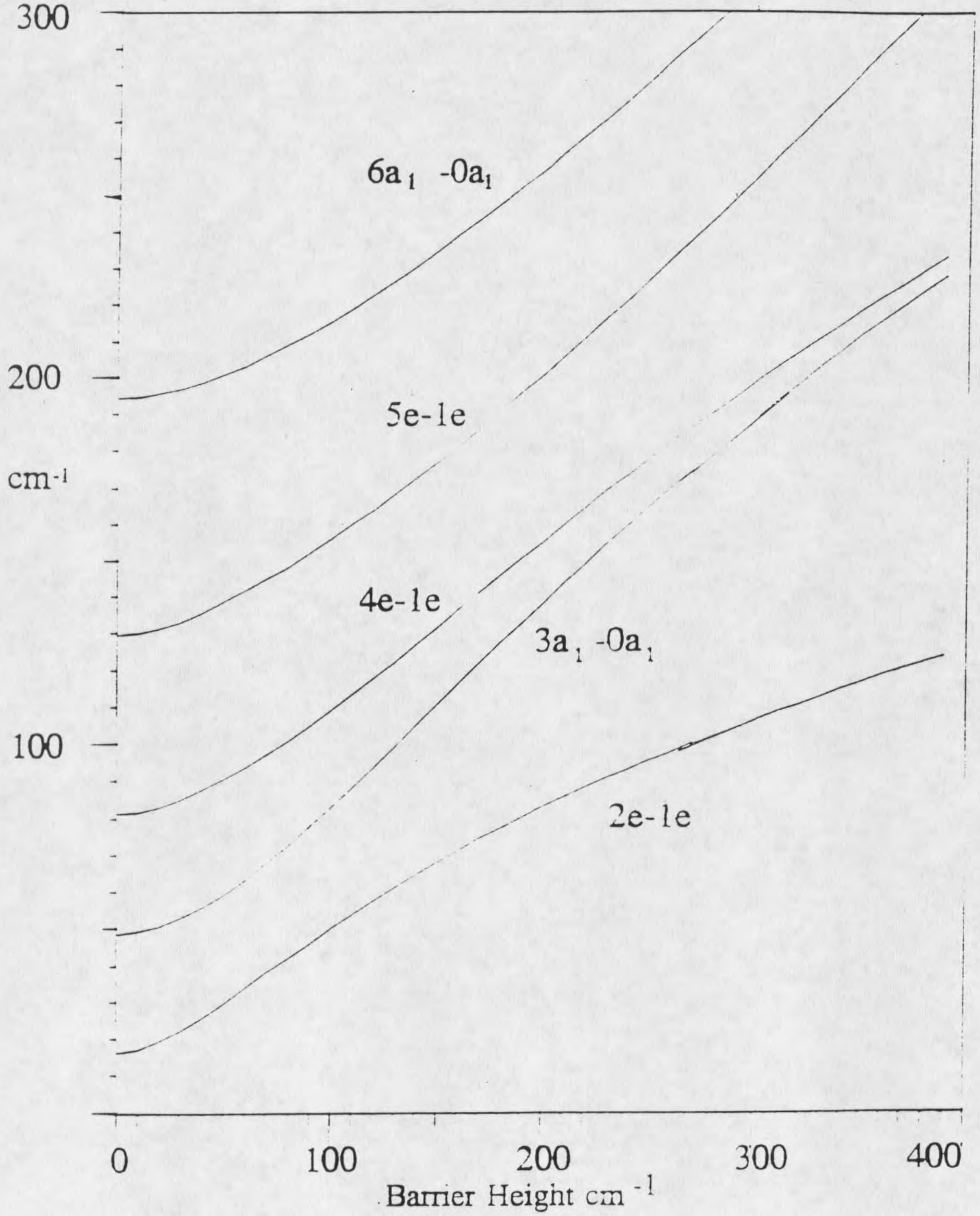


Figure 2. Methyl rotor splitting as a function of V_3 barrier height.

denotes an excited state and μ is the dipole moment operator. For most spectroscopic purposes the nuclei are assumed to be stationary and the dipole moment operator depends only on electronic motion. Since the nuclei move much more slowly than the electrons, the Born-Oppenheimer approximation states that it is reasonable to factor the total wave function for a molecule into a product of wave functions as follows:

$$\psi = \psi_e \psi_v$$

where ψ_e is the electronic wave function, and ψ_v is the vibrational wave function. In the Born-Oppenheimer approximation, transitions between torsional levels in two different electronic states can be described by an electronic transition moment integral times a vibrational overlap integral,

$$M = \int \psi^*_{e'} \, \mu_e \, \psi_e \, d_e \int \psi^*_{v'} \psi_v \, d_v \ .$$

The square of the vibrational integral on the right is commonly referred to as the Franck-Condon factor. This integral represents the overlap of the vibrational wave functions of the ground and excited states. The magnitude of this integral affects the relative intensities among vibrational components.

The first step in determining the potential barrier for a methyl group from experimental data is to use the fortran program, VNCOS, written by Laane and coworkers[39]. This program calculates the eigenvalues for a potential function of the type Σ_n $(V_n/2)(1\text{-}\cos nx)$. The V_3 and V_6 terms are optimized to reflect the barriers that generate the proper frequency differences of the rotor levels observed in the spectrum.

VNCOS was written to calculate vibrational levels for the potential energy surface of a single electronic state, but lacks the ability to calculate the band intensities in the excitation or dispersed emission spectra. A program written by Spangler, 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[40]. The intensities are calculated from the Franck-Condon factors. The values for the rotational barrier and conformational change of the methyl group can then be optimized to yield the observed intensities and frequencies.

As mentioned before, supersonic expansion cools the molecules down to its lowest a_1 and e levels. Thus transitions to the a_2 levels in the electronically excited state will be symmetry forbidden and only a_1 and e levels will be accessible. If the conformation of the methyl group was the same for both the ground and excited state, only the a_1-a_1 and e-e transitions would be observed, since only these transitions would have appreciable Franck-Condon overlaps. If many transitions in the methyl rotor progression have intensity in a spectrum, the conformation change is typically 30-60°.

Molecular Orbital Explanation for the Barrier to Internal Rotation

The conformational preferences in molecules can be traced to the nature of interactions between molecular orbitals. Barriers to internal rotation in molecules are among the most interesting properties that are amenable to qualitative molecular orbital theory. The acceptance of a simple qualitative molecular orbital explanation for the staggered preference and resulting barrier to internal rotation in ethane has led scientists to extend the model to more sophisticated molecules[2].

For example, the preferred eclipsed conformation for aliphatic systems in which one of the methyl hydrogens of a methyl group eclipses the double bond can be explained by the interaction between the occupied methyl group orbitals of π symmetry and the π and π^* orbitals of the unsaturated linkage[9]. The origin of the rotational barrier is similarly related to that of ethane[14]. The highest occupied and lowest unoccupied orbitals of the methyl rotor and the π system of a double bond are shown in Figure 3. The first of the four interactions are between filled valence shells. The overlap between the two fragments is greatest when the two methyl hydrogens are positioned directly over the double bond. The interaction between these filled orbitals (labeled A) is repulsive since they are both occupied, and the staggered conformation is more destabilized by closed-shell repulsion than the eclipsed one. This destabilization is most likely

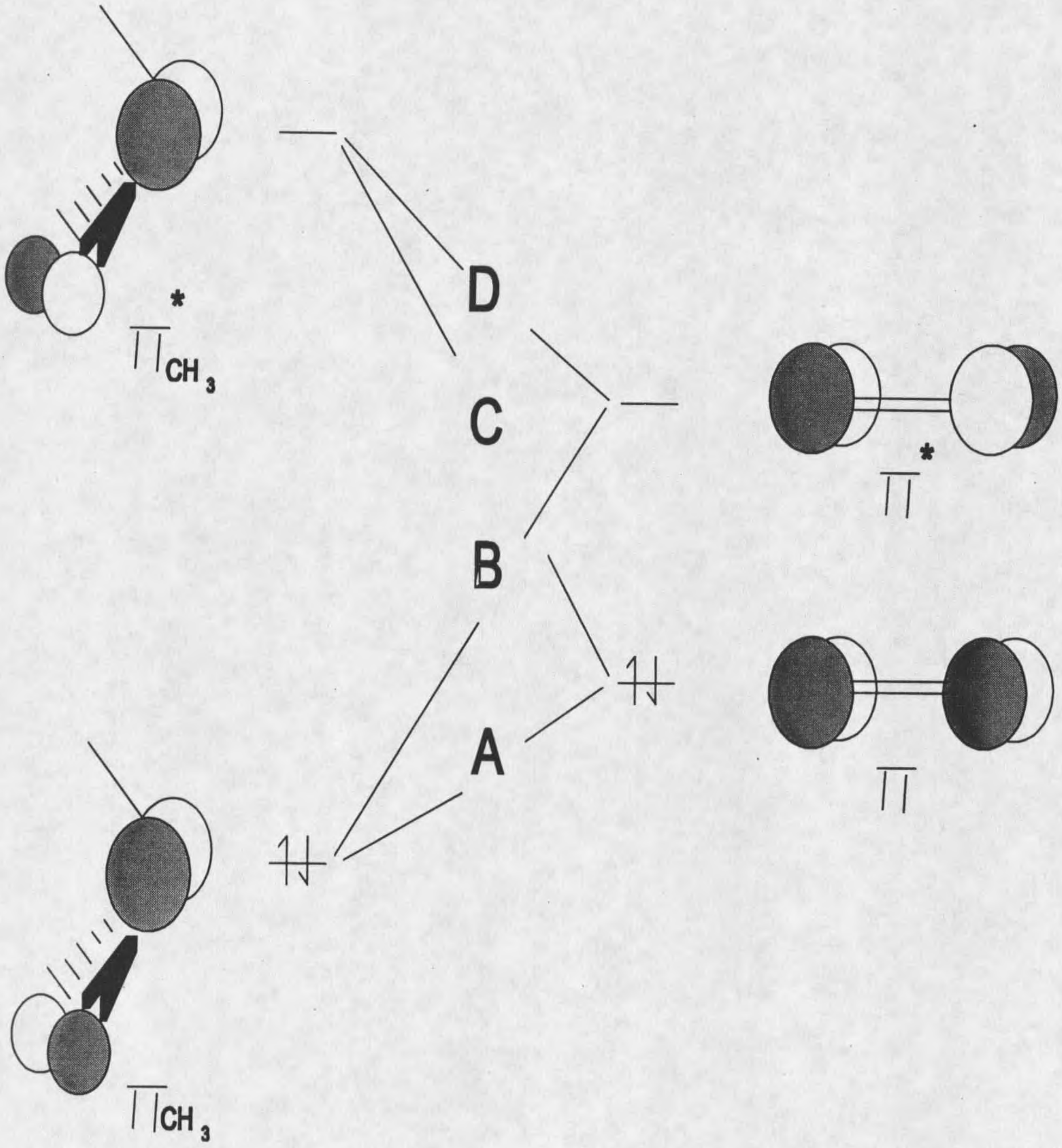

$\pi^*_{CH_3}$
D
C
B
A
π^*
π
π_{CH_3}

Figure 3. Interaction of the π system of a nonpolar double bond with the π and π* orbitals of a methyl group.

the main factor responsible for the preference for the eclipsed methyl group conformation. If the four electron interaction is eliminated by the promotion of an electron to a higher orbital; e.g., by $\pi\pi^*$ excitation, then other factors may dictate a different preferred conformation of the methyl group in an electronically excited state. For example, the methyl group has been found to prefer a staggered conformation of C-H bonds with respect to carbonyl functionality in the excited states of carbonyl compounds[14]. Thus the conformation having minimum π electron overlap is favored in the ground state and the conformation of maximum π overlap is favored in the excited state.

A particular carbonyl compound, acetaldehyde, has a considerably smaller barrier to rotation (1.16 kcal/mole) than does propene (2.0 kcal/mole)[41]. A qualitative description of a methyl group attached to a polar double bond has been proposed to explain this reduction in the barrier between propene and acetaldehyde[9]. The reduction in the barrier mainly involves a secondary overlap contribution involving the methyl hydrogens and the far end of the double bond. A general illustration of this secondary overlap contribution and brief discussion is presented here. Since the left atom in the polar double bond is more electronegative in Figure 4, the empty π^* double bond orbital will be heavily localized on the right atom. According to simple electronegativity perturbations, interaction B takes on added importance at the same time interaction C is diminished[9]. Figure 4 shows the dominating interaction between the π_{CH_3} and π^* fragment orbitals (labeled B in Figure 3). Thus the total positive overlap between

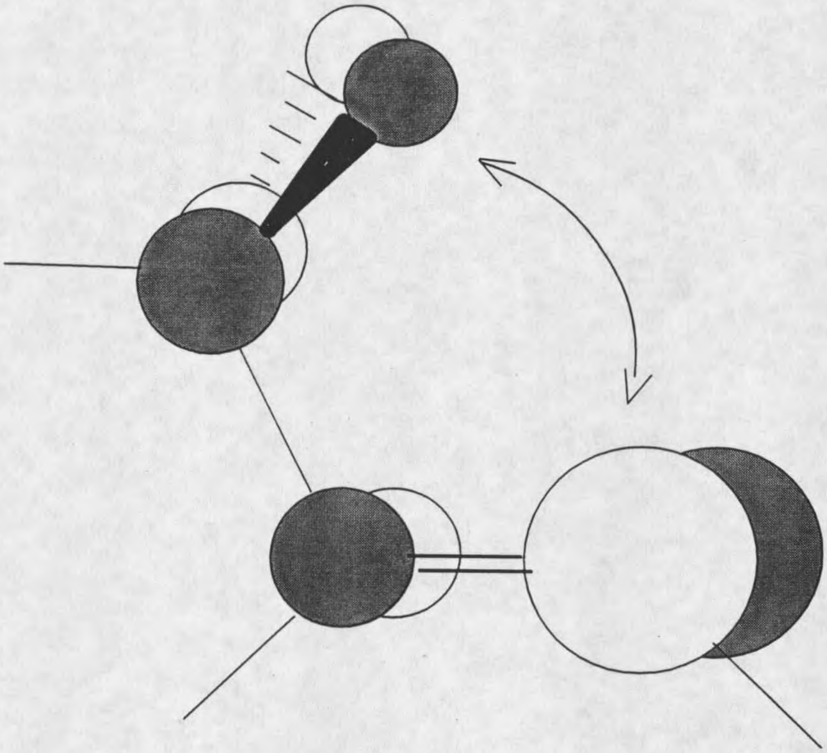


Figure 4. The secondary overlap contribution involving the out-of-plane methyl hydrogens (π_{CH3}) and the far end of the π^* system of a polar double bond.