J. Phys. Chem. **1990,** *94,* 6691-6695

distinct spectroscopic signatures.

Conclusions

The data presented here for the Ln(TPP)$_2$ and Ln(TPnP)$_2$ complexes in conjunction with our earlier results for the Ln(OEP)$_2$ sandwiches indicate that the energy of the intradimer charge-transfer transition and the frequencies of the intradimer vibrational mode are sensitive indicators of the extent of $\pi\pi$ overlap and of the strength of the metal–porphyrin interactions in these types of systems. These interactions can be modulated by the size of the central metal ion, by the electron donating/withdrawing character of the substituents, and by the steric bulk of the substituents on the porphyrin ligand. In the complexes we have investigated, the energy of the intradimer charge-transfer transition varies over $\sim$0.4 eV whereas the frequency of the Q_{AB} mode varies over $\sim$200 cm^{-1}. It is conceivable that these ranges can be expanded further by a judicious combination of metal ions and other porphyrin ligands. The ability to tune the energy of the intradimer charge-transfer band of these types of complexes could have application in areas where tunable near-IR absorbers are important. We are currently investigating such possibilities.

Acknowledgment. This work was supported by grant GM-36243 (D.F.B.) from the National Institute of General Medical Sciences. We thank Professor J. S. Lindsey and Dr. R. W. Wagner for the gift of H$_2$TPnP.

Spectroscopy and Structure of Jet-Cooled α-Methylstyrene

V. H. Grassian, E. R. Bernstein,*

Department of Chemistry, Colorado State University, Fort Collins, Colorado 80523

Henry V. Secor, and Jeffrey I. Seeman*

Philip Morris Research Center, P.O. Box 26583, Richmond, Virginia 23261 *(Received: November 29, 1989; In Final Form: February 14, 1990)*

The ground (S_0) and excited (S_1) state geometries of α-methylstyrene (2-phenylpropene, **2**) are investigated by mass-resolved excitation spectroscopy. In contrast to styrene, which has an intense spectral $S_1 \leftarrow S_0$ origin transition, α-methylstyrene exhibits a weak origin transition and a long progression in a low-frequency torsional mode, with an energy level spacing of $\sim$69 cm^{-1}. The intensity maximum of this progression occurs at the eighth peak position, indicating that the minimum-energy geometries of the ground and excited state are considerably displaced from one another. The torsional progression is assigned to the hindered rotation of the propenyl group with respect to the aromatic ring. Based on hot band transitions in the region of the origin, this torsional mode is assigned an energy level spacing of $\sim$32 cm^{-1} in the ground state. Potential parameters derived from an analysis of the spectra are $V_2 \sim 0$ cm^{-1} and $V_4 \sim -150$ cm^{-1} for S_0 and $V_2 = 4867$ cm^{-1}, $V_4 = -500$ cm^{-1}, and $V_6 = -80$ cm^{-1} for S_1. These two derived potential surfaces suggest that α-methylstyrene is nearly planar in its first excited singlet state and that the propene group is ca. 45° out of the aromatic plane in its ground state. An additional estimate of the S_0 geometry is made based on electronic transition energy for analogous systems, and this approach also yields a nonplanar ground-state geometry (ca. 30°) for α-methylstyrene. Analysis of the Franck–Condon intensity profile yields a displacement in the excited state for the angle between the aromatic and ethylenic groups of ca. 30° relative to the ground state. α-Methylstyrene is thereby suggested to be nearly planar in its first excited π–π^* state.

I. Introduction

Styrene (**1**) has been the subject of numerous experimental and theoretical studies, in part because it is the prototypic molecule containing an aromatic ring–sp^2 bond.[1-20] Styrene is planar in its ground and first excited singlet states and has a low barrier to rotation about its sp^2–sp^2 bond in S_0 (<4 kcal/mol).[2,15-20] Recently, using supersonic molecular jet spectroscopy, we have shown that sterically unhindered styrene derivatives also have planar conformations in both S_0 and S_1.[18,19] In addition to styrene

---

(1) Lewis, P. L.; Hagopian, C.; Kuch, P. *Kirk-Othmer Encyclopedia of Chemical Technology*, 3rd ed.; Wiley: New York, 1983; pp 770–801.

(2) (a) Hollas, J. M.; Ridley, T. *Chem. Phys. Lett.* **1980**, *75*, 94. (b) Hollas, J. M.; Ridley, T. *J. Mol. Spectrosc.* **1981**, *89*, 232. (c) Hollas, J. M.; Musa, H.; Ridley, T.; Turner, P. H.; Weisenberger, K. H.; Fawcett, V. *J. Mol. Spectrosc.* **1982**, *94*, 437. (d) Hollas, J. M.; Taday, P. F. *J. Chem. Soc., Faraday Trans.* **1990**, *86*, 217. (e) Hollas, J. M.; Bin Hussein, M. Z. *Chem. Phys. Lett.* **1989**, *154*, 228.

(3) Syage, J. A.; Al Adel, F.; Zewail, A. H. *Chem. Phys. Lett.* **1983**, *103*, 15.

(4) Leopold, D. G.; Hemley, R. J.; Vaida, V.; Roebber, J. L. *J. Chem. Phys.* **1981**, *75*, 4758.

(5) (a) Suzuki, H. *Electronic Absorption Spectra and Geometry of Organic Molecules*; Academic Press: New York, 1976; Chapter 13. (b) Suzuki, H. *Bull. Chem. Soc. Jpn.* **1960**, *33*, 619.

(6) Braude, E. A.; Sondheimer, F. *J. Chem. Soc.* **1955**, 3773.

(7) Talati, A. M.; Shah, B. V. *Indian J. Chem.* **1973**, *11*, 1328.

(8) Maier, J. P.; Turner, D. W. *J. Chem. Soc., Faraday Trans. 2* **1973**, *69*, 196.

(9) Kobayashi, T.; Arai, T.; Sakuragi, H.; Tokumaru, K.; Utsunomiya, C. *Bull. Chem. Soc. Jpn.* **1981**, *54*, 1658.

(10) Schmid, E. D.; Topsom, R. D. *J. Raman Spectrosc.* **1983**, *14*, 191.

(11) See, for example: Greenberg, A.; Liebman, J. F. *J. Org. Chem.* **1982**, *47*, 2084.

(12) Lyons, A. L., Jr.; Turro, N. J. *J. Am. Chem. Soc.* **1978**, *100*, 3177.

(13) Hemley, R. J.; Dinur, U.; Vaida, V.; Karplus, M. *J. Am. Chem. Soc.* **1985**, *107*, 836.

(14) Bruni, M. C.; Momicchioli, F.; Baraldi, I.; Langlet, J. *Chem. Phys. Lett.* **1975**, *36*, 484.

(15) Fabian, W. M. F. *J. Comput. Chem.* **1988**, *9*, 369.

(16) Leister, D.; Kao, J. *J. Mol. Struct.* (*THEOCHEM*) **1988**, *168*, 105.

(17) Anderson, J. E.; Barkel, D. J. D.; Parkin, J. E. *J. Chem. Soc., Perkin Trans. 2* **1987**, 955. See also: Facchine, K. L.; Staley, S. W.; van Zijl, P. C. M.; Mishra, P. K.; Bothner-By, A. A. *J. Am. Chem. Soc.* **1988**, *110*, 4900.

(18) Grassian, V. H.; Bernstein, E. R.; Secor, H. V.; Seeman, J. I. *J. Phys. Chem.* **1989**, *93*, 3470.

(19) For a preliminary report of some of these results, see: Seeman, J. I.; Grassian, V. H.; Bernstein, E. R. *J. Am. Chem. Soc.* **1988**, *110*, 8542.

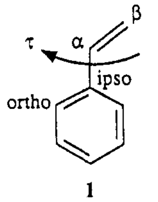
(20) (a) Ōki, M. *Applications of Dynamic NMR Spectroscopy to Organic Chemistry*; VCH Publishers: Deerfield Beach, FL, 1985; Chapter 4. (b) Jackman, L. M.; Cotton, F. A. *Dynamic NMR Spectroscopy*; Wiley: New York, 1975. (c) Anderson, J. E. *Tetrahedron* **1987**, *43*, 3041, and references therein.

0022-3654/90/2094-6691$02.50/0 © 1990 American Chemical Society

TABLE I: α-Methylstyrene Torsional Structure about the Origin Transition (35 063.7 cm^{-1})

	vib energy, cm^{-1}	spacing, cm^{-1}		vib energy, cm^{-1}	spacing, cm^{-1}
T^0	0.0		T^6	401.6	71.6
T^1	63.6	63.6	T^7	472.1	70.5
T^2	127.6	64.0	T^8	543.2	71.1
T^3	194.0	66.4	T^9	614.6	71.4
T^4	262.0	68.0	T^{10}	687.7	73.1
T^5	330.0	68.0	T^{11}	760.0	72.3

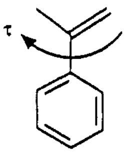
itself, the molecules examined by this technique included *trans*-β-methylstyrene, 3-methylstyrene, 4-ethylstyrene, and 4-methoxy-*trans*-β-methylstyrene (anethole).



1

$$\tau = \tau(C_{ortho}\text{-}C_{ipso}\text{-}C_\alpha\text{-}C_\beta)$$

Of the vast literature regarding conformational preferences and rotational barriers for molecules containing an sp^2–sp^2 bond,[20] most studies have been performed (out of experimental necessity[21]) on highly substituted molecules. The stabilization energy gained from π conjugation in an extended planar geometry is countered by that lost from steric interactions which are typically maximized in the planar conformation. Consequently, bulky substituents on or near the sp^2–sp^2 bond not only raise the barrier to rotation about this bond but also modify the conformational profile: the stable planar conformer for styrene becomes an energy maximum for sterically hindered styrenes.[14,17,20] The present work extends our laser jet studies and focuses attention on α-methylstyrene (**2**) which contains a small stepwise jump in steric hindrance (H → CH$_3$) on the styrene molecular framework.



2

The nonplanarity of **2** in the ground state has been postulated from the decrease in λ_{max} relative to that of styrene for the π–π^* ($S_1 \leftarrow S_0$) transition of **2** in solution.[4] The deviation from planarity (as defined by the angle τ) for **2** has been estimated to be 28–35° in S_0 based on solution-phase absorption data,[4-7] 22–46° by photoelectron spectroscopy,[8,9] and 24–30° by Raman spectroscopy[10] although the coplanarity of the exocyclic group with the phenyl ring has also been assumed.[11] Recent molecular mechanics–molecular orbital (MOMM) calculations have suggested that τ for α-methylstyrene is 36° in S_0.[16] The conformation of this molecule in the excited state has, until the present, not been reported.

Supersonic molecular jet spectroscopy is ideally suited for the conformational studies of sterically hindered styrenes. The rotationally and vibrationally cooled molecules produced in the expansion exhibit uncongested spectra relative to room-temperature gas-phase spectra.[22] If a displacement of the energy minimum occurs in the excited state relative to the ground state, a progression in the spectral features associated with the torsional motion will be observed in the excitation spectrum.[23-25] The extent of such changes upon excitation can be calculated from a Franck–Condon intensity analysis. This type of torsional progression for nonrigid systems cooled in a supersonic jet expansion has been observed for biphenyl,[23] 9-phenylanthracene,[24] and 9-(2-naphthyl)anthracene,[25] and torsional analysis has been successfully applied to the spectra thereby obtained.

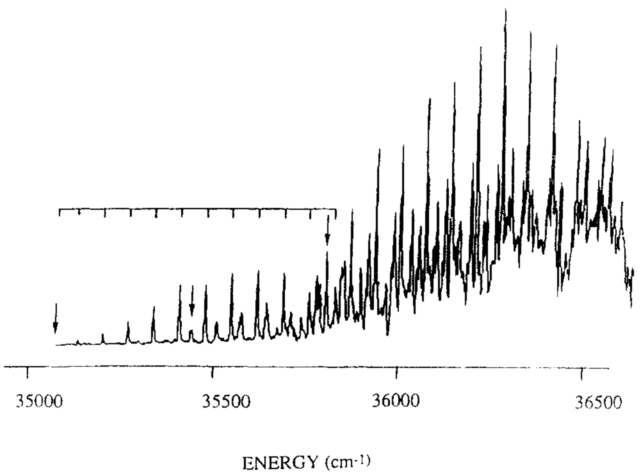
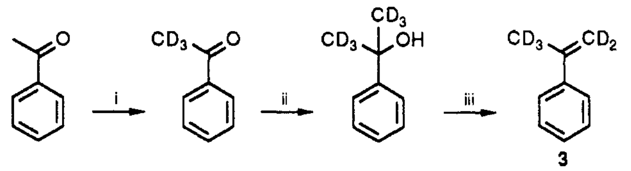


Figure 1. TOFMS of α-methylstyrene (**2**) from ~35 000 to ~36 500 cm^{-1}. The origin is very weak in intensity and marked by an arrow. Two other higher vibrational features are also marked by an arrow in the spectrum. A low-frequency motion which is built on the origin, and higher vibrations, is seen in the spectrum with an energy level spacing of 69 cm^{-1}.

SCHEME I[a]



[a] i, NaOD/D$_2$O/reflux; ii, CD$_3$MgI/Et$_2$O; iii, KHSO$_4$/220 °C

II. Experimental Section

The supersonic jet expansion as well as the time-of-flight mass spectrometer has been described previously.[26] Briefly, the supersonic expansion is generated by a pulsed R.M. Jordon valve. Helium is used as the carrier gas at a pressure of 3–4 atm. Argon is used for the carrier gas in determining the spectroscopic origin so as to eliminate any hot bands in that region. A tunable pulsed dye laser, which is pumped by the second harmonic (532 nm) of a Nd:YAG laser, is frequency-doubled and focused with a 1-m quartz lens into the vacuum chamber. Fluorescein dye is used as the laser gain medium in all of these experiments. The ions are produced by sequential photon absorption and are accelerated into the flight tube where they are detected by a microchannel plate.

α-Methylstyrene was purchased from Aldrich and used without further purification. All compounds are stored in the dark at 4 °C to prevent polymerization. α-Methyl-d_3-styrene-β,β-d_2 (**3**) was prepared as shown in Scheme I. Full experimental details are described in the Appendix.

---

(21) In the absence of severe steric hindrance, the activation energy for rotation about an sp^2–sp^2 bond is only a few kcal/mol: too low to be detected by dynamic NMR spectroscopy.[20] For systems which are not coplanar about the sp^2–sp^2 bond, rotation corresponds to racemization of the molecule and suitable substituents on or near the sp^2–sp^2 bond can then serve as experimental monitors of the rotational processes.[20a]

(22) Levy, D. H.; Wharton, L.; Smalley, R. In *Chemical and Biochemical Applications of Lasers*; Moore, C. B., Ed.; Academic Press: New York, 1977; Vol. II.

(23) Im, H.-S.; Bernstein, E. R. *J. Chem. Phys.* **1988**, *88*, 7337.

(24) Werst, D. W.; Gentry, W. R.; Barbara, P. F. *J. Phys. Chem.* **1985**, *89*, 729.

(25) Werst, D. W.; Gentry, W. R.; Barbara, P. F. *J. Am. Chem. Soc.* **1985**, *109*, 32.

(26) Bernstein, E. R.; Law, K.; Schauer, M. J. *J. Chem. Phys.* **1984**, *80*, 207.

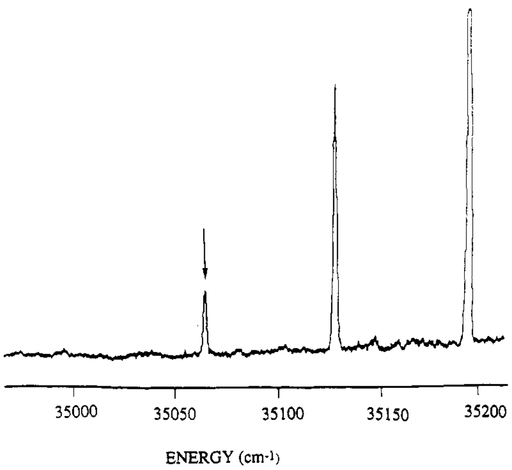


Figure 2. An expanded view of the origin transition region of **2** (see Figure 1). The 0_0^0 transition is identified at 35 063.7 cm^{-1}.

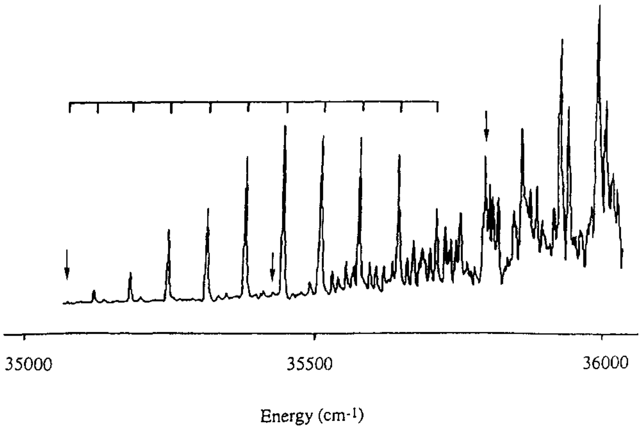


Figure 3. TOFMS of α-methyl-d_3-styrene-β,β-d_2 (**3**) scanned from 35 000 to 36 000 cm^{-1}. The origin and two higher vibrational features are marked by arrows. A low-frequency mode is seen in the spectrum which has a spacing of ~64 cm^{-1}.

III. Results

The time-of-flight mass spectrum (TOFMS, mass-resolved excitation spectrum) of **2** is shown in Figure 1. The spectrum extends from the origin, 0_0^0 transition, to 1500 cm^{-1} higher in energy. A low-frequency vibronic progression built on the above origin is clearly visible in the spectrum. Table I lists the energies of the progression as well as the spacings between each energy level. The spacings between the energy levels become larger at higher levels. The negative anharmonicity suggests that the potential energy surface for this motion in the excited state is flat near the equilibrium position but has steeply rising walls.[27] This low-energy motion is also built on other, higher energy vibrational modes.

The origin region is shown in an expanded scale in Figure 2. Both argon and helium are each used as the carrier gases in determining the position of the spectral origin so as to eliminate any hot bands in the spectrum. The lowest energy peak at 35 063.7 cm^{-1} is assigned to the spectral origin, i.e., the 0_0^0 transition.

The TOFMS of **3** is shown in Figure 3, recorded from 35 000 to 36 000 cm^{-1}: the 0_0^0 transition is determined to be at 35 083.6 cm^{-1}. Listed in Table II are the energies of the low-frequency vibration and the energy level spacings for its progression for the partially deuteriated compound. The energy of this mode is reduced ca. 5 cm^{-1} upon deuteriation of the propenyl group. The most intense feature in the progression occurs at the seventh peak position.

TABLE II: α-Methyl-d_3-styrene-β,β-d_2 Torsional Structure about the Origin Transition (35 083.6 cm^{-1})

	vib energy, cm^{-1}	spacing, cm^{-1}		vib energy, cm^{-1}	spacing, cm^{-1}
T^0	0.0		T^6	373.3	65.1
T^1	58.4	58.4	T^7	438.3	65.0
T^2	119.0	60.6	T^8	504.3	66.0
T^3	181.4	62.4	T^9	570.8	66.5
T^4	245.0	63.6	T^{10}	639.3	68.5
T^5	308.2	63.6			

TABLE III: Vibrational Mode Assignments for S_1

	vibrational energy, cm^{-1}		
assignt	α-methylstyrene	α-methyl-d_3-styrene-β,β-d_2	styrene[a]
1^1	738.7	722.1	745.8
$6a^1$	369.5	341.1	394.5

[a] The vibrational energies for jet-cooled styrene are taken from ref 3.

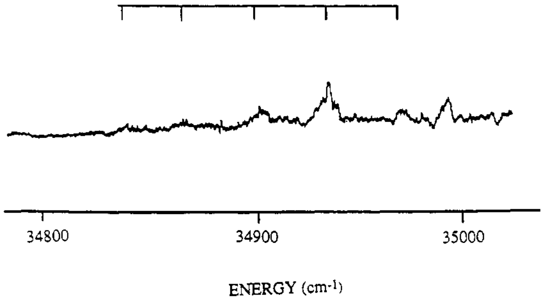


Figure 4. TOFMS of α-methylstyrene at low He expansion pressures. Hot band transitions are observed for the torsional motion of the propenyl group. $P_{He} < 40$ psig.

Although the spectra of **2** and **3** are quite congested, the other higher energy vibrational modes of α-methylstyrene in the excited state can be determined. One mode is observed at an energy of 369.5 cm^{-1} for **2** which shifts to 341.1 cm^{-1} for **3** (compare Figures 1 and 3).

The other peak identified as a vibrational mode occurs at 738.7 cm^{-1} for **2** and 722.1 cm^{-1} for **3**. The energies of these vibrations are listed in Table III and compared with those of styrene. The low-energy mode progression is built on both of these vibrations, with an energy level spacing of approximately 69 cm^{-1} for **2** in the excited state. The progression built on these two vibronic features is similar in intensity to that observed for the origin; the maximum peak intensity for the progression occurs at the ninth member.

Information on this 69-cm^{-1} mode can be obtained for the ground state as well. At low backing pressures for the expansion (<40 psig of He), hot bands appear around the origin. Figure 4 shows such spectra from which the torsional mode energy in the ground state can be determined to be ca. 32 cm^{-1}. Clearly, however, the value of this mode in the ground state cannot be as well determined as the value of this mode in the excited state.

IV. Analysis and Discussion

A. Assignment of the Low-Energy Mode. Assignment of the low-energy mode in S_1 and S_0 of α-methylstyrene (**2**) can be made based on the following two considerations. First, in contrast to the spectrum of **2** (Figure 1), the 0_0^0 transition of styrene (**1**) (Figure 5) is intense and the origin region is devoid of any spectral features up to 0_0^0 + 200 cm^{-1}. Second, this mode undergoes a substantial shift (ca. 5 cm^{-1}) upon deuteriation of the propenyl group. We conclude therefore, that this low-energy mode can be assigned to the torsional motion whose displacement is described by $\tau(C_{ortho}-C_{ipso}-C_{\alpha}-C_{\beta})$ in **2**.

The repulsive steric interactions between the α-methyl group, the syn β-vinyl hydrogen, and the ortho hydrogens destabilize the planar conformation of **2**. The potential energy surface for **2** has

---

[27] See, for example: Herzberg, G. *Electronic Spectra of Polyatomic Molecules*; van Nostrand: Princeton, NJ, 1966. Steinfeld, J. I. *Molecules and Radiation*, 2nd ed.; MIT: Cambridge, MA, 1985.

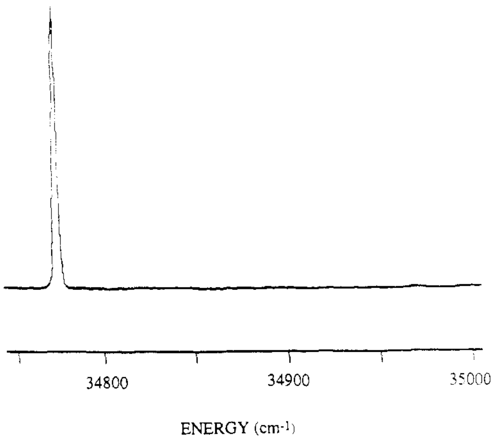


Figure 5. One-color TOFMS of styrene (**1**). The origin region consists solely of an intense peak with no other spectral features up to 200 cm^{-1}. The 0_0^0 transition is at 34778.7 cm^{-1}. From ref 18.

a minimum at some angle τ not equal to zero; i.e., the planar conformation is unfavorable for this sterically hindered styrene derivative in one or both of the electronic states S_0 and S_1. The potential energy surface for styrene and its derivatives reflects the stabilizing effects of conjugation and the destabilizing effects of steric repulsive interactions.

A displacement along the coordinate τ occurs in the excited state (with respect to the ground state) as is evidenced by the presence of the Franck–Condon intensity envelope for this motion in the jet-cooled excitation spectrum. The change in the torsional angle τ can be determined from a Franck–Condon intensity analysis of the spectrum. Such an analysis depends on accurate torsional eigenvectors for both the ground and excited states, and thus the form of the potential surface must be determined for the molecule. These are discussed in section IV.C.

B. Assignment of Higher Frequency Vibrational Modes. Vibrational assignments for two of the higher energy modes of **2** in S_1 can be made from a comparison of the present results with those for jet-cooled styrene[3] (see Table III). The 6a^1 vibration at 394.5 cm^{-1} in styrene shifts to lower energy for both **2** and **3**, 369.5 and 341.1 cm^{-1}, respectively. The 1^1 vibration of **2** is assigned to the peak at 738.7 cm^{-1}, shifted to 722.1 cm^{-1} for **3**. These energies can be compared to the energy of the 1^1 vibrational mode for styrene which is at 745.8 cm^{-1}.

C. Calculations of the Torsional Energy Levels and Franck–Condon Factors. A one-dimensional rotor analysis is used to fit the energies of the torsional mode.[27,28] The general form of the potential function can be expressed as a cosine Fourier series

$$V(\tau) = \tfrac{1}{2}\sum_n V_n(1 - \cos n\tau) \qquad (1)$$

The Hamiltonian of the free rotor is then modified by inclusion of this potential term. The Schrödinger equation for the hindered rotor can be written as

$$\left[-B\frac{\partial^2}{\partial\tau^2} + V(\tau)\right]\psi_m(\tau) = E_m\psi_m(\tau) \qquad (2)$$

in which B is the reduced rotational constant[23-25] for the internal torsional mode. Free rotor wave functions are used as a basis set in the diagonalization of the Hamiltonian in eq 2: a total of 109 basis functions are needed to ensure convergence of all the energy levels. The best fit to the excited-state data for **2** and **3** using eq 2 is obtained with the following parameters: V_2 = 4867 cm^{-1}, V_4 = −500 cm^{-1}, V_6 = −80 cm^{-1}, and B = 0.444 cm^{-1} for **2** and B = 0.387 cm^{-1} for **3**. The inclusion of a V_6 term is necessary to reproduce the large negative anharmonicity in the energy level spacings (see Tables I and II). Table IV lists the observed and calculated energy level values; the two are in good agreement for both **2** and **3**. The value of B is calculated for the reduced internal rotational constant of the torsional mode based on the bond lengths and angles of an α-methylvinyl group and a benzene ring and then varied (±10%) to achieve a best fit to the data.

TABLE IV: Calculated and Observed Energies (cm^{-1}) of the Torsional Motion of α-Methylstyrene and α-Methyl-d_3-styrene-β,β-d_2 in S_1

	α-methylstyrene		α-methyl-d_3-styrene-β,β-d_2	
	obsd	calcd[a]	obsd	calcd[b]
T^0	0.0	0.0	0.0	0.0
T^1	63.6	63.5	58.4	59.2
T^2	127.6	128.6	119.0	119.8
T^3	194.0	195.0	181.4	181.6
T^4	262.0	262.7	245.0	244.5
T^5	330.0	331.5	308.2	308.3
T^6	401.6	401.1	373.3	373.1
T^7	472.1	471.6	438.3	438.5
T^8	543.2	542.9	504.3	504.7
T^9	614.6	614.8	570.8	571.4
T^{10}	687.7	687.2	639.3	638.8
T^{11}	760.0	750.2		

[a] Potential parameters: V_2 = 4867 cm^{-1}, V_4 = −500 cm^{-1}; V_6 = −80 cm^{-1}, and B = 0.444 cm^{-1}. [b] Potential parameters: V_2 = 4867 cm^{-1}, V_4 = −500 cm^{-1}, V_6 = −80 cm^{-1}, and B = 0.387 cm^{-1}.

The form of the ground-state potential should differ somewhat from that of the excited state. We assume that the ground-state potential should have maxima at τ = 0° and τ = 90°. The reason for the potential being a maximum at τ = 0° has been discussed above and is attributed to the steric interaction between the propenyl substituent and the ortho hydrogens. The complete loss of resonance stabilization between the aromatic and ethylenic π systems at τ = 90° causes the potential to be a maximum at this angle also. The dominant term in the potential function will then be a V_4 term with maxima at 0°, 90°, 180°, and 270°. Employing a potential for the ground-state torsional motion with a dominant V_4 term and a small V_2 term, we find $V_2 \sim 0$ cm^{-1} and $V_4 \sim -150$ cm^{-1} (B = 0.444 cm^{-1}) for the best fit to the ca. 32 cm^{-1} observed ground-state torsional mode. Considering the hot band spectrum of Figure 4, this form must be taken as quite approximate.

The displacement in the coordinate in the excited state with respect to its ground-state equilibrium position can be determined by a Franck–Condon intensity analysis of the torsional progression. The eigenvectors for the torsional motion can be written as $\psi_g(\tau)$ and $\psi_e(\tau+\Delta\tau)$ for the ground and excited states, respectively. The Franck–Condon factors for transitions from the lowest level in the ground-state potential well (zero-point energy level) to the torsional levels of the excited-state potential surface can be written as

$$\langle\psi_e(\tau+\Delta\tau)|\psi_g(\tau)\rangle = \langle\sum_m c_m^e\phi_m(\tau+\Delta\tau)|\sum c_m^g\phi_m(\tau)\rangle \qquad (3)$$

$$= \sum_m c_m^e c_m^g\langle\phi_m(\tau+\Delta\tau)|\phi_m(\tau)\rangle \qquad (4)$$

$$= \sum_m c_m^e c_m^g \cos m(\Delta\tau) \qquad (5)$$

$$m = 0, \pm1, \pm2, \pm3, ...$$

These Franck–Condon calculations give a displacement angle in τ of 30 ± 5° for an intensity pattern in which the eighth peak position is a maximum. The uncertainty in the displacement angle is caused by two factors: the approximate form of the ground-state potential and the uncertainty in the maximum intensity peak position (8 ± 1).

D. Determination of the Equilibrium Value of τ in the Ground and Excited States. The analysis presented thus far demonstrates three points for the ground and excited states of **2** and **3**: (1) the ground-state geometry is nonplanar by ca. 45° ($V_2 \sim 0$ cm^{-1}, $V_4 \sim -150$ cm^{-1}), (2) the excited-state geometry is approximately planar (V_2 = 4867 cm^{-1}, V_4 = −500 cm^{-1}, V_6 = −80 cm^{-1}), and

---

[28] Breen, P. J.; Warren, J. A.; Bernstein, E. R.; Seeman, J. I. *J. Chem. Phys.* **1987**, *87*, 1917, and references therein.

(3) the difference between the ground- and excited-state torsion angle $\Delta\tau$ is ca. 30° (Franck–Condon analysis). The S_0 potential, and thus the equilibrium geometry for the torsional propene motion, are not very well determined based on the spectra displayed in Figure 4. We have thereby sought an additional estimate for the equilibrium geometry of **2** and **3**. The relationship between the geometry of molecules and their electronic absorption spectra has been discussed by Suzuki.[5] We follow the method developed by Suzuki, which employs orbital theory to determine the ground-state geometry of **2** in solution, and apply it to the supersonic jet data of **2**.[5-9]

The resonance energy associated with the interaction between the aromatic and ethylenic π systems of styrene is at a maximum at $\tau = 0°$ and a minimum at $\tau = 90°$. The energy of the electronic transition increases as τ increases from 0° to 90°. In the limit of $\tau = 90°$, the two π systems are orthogonal to each other, and the electronic absorption spectrum, in particular the 0_0^0 transition energy, should be similar to that of an alkylbenzene. In the limit of maximum resonance energy ($\tau = 0°$), the electronic transition energy will be similar to that found for sterically unhindered substituted styrenes, such as *trans*-β-methylstyrene which is known to be planar.[18]

These transition energies have been calculated[5] by using Hückel theory[29] for the planar and perpendicular limits. The analysis considers only a one-electron transition and neglects relaxation effects. The calculated and the experimentally determined transition energy are assumed to be linearly related in this treatment. The transition energy for $0° < \tau < 90°$ can be calculated from

$$\Delta E = \Delta E_{\tau=90} - \frac{(\Delta E_{\tau=90} - \Delta E_{\tau=0})(\nu_{\tau=90} - \nu)}{\nu_{\tau=90} - \nu_{\tau=0}} \qquad (6)$$

$\Delta E_{\tau=90}$ and $\Delta E_{\tau=0}$ are taken from the calculations of Suzuki and are equal to 1.4744 and 2.0000, in units of $-\beta$, respectively. The reference values of the experimentally determined energies $\nu_{\tau=90}$ and $\nu_{\tau=0}$ are taken as the 0_0^0 transition energies of isopropylbenzene and *trans*-β-methylstyrene (37 668.5 and 34 585.0 cm^{-1}, respectively). Using these values, we calculated $\Delta E(-\beta)$ to be 1.5556. Figure 6 shows the angle τ plotted as a function of ΔE (taken from the tabulated values given by Suzuki): the value $\tau = 31°$ correlates with the calculated value of ΔE. The value of τ calculated here for S_0 is almost identical with that calculated for **2** in solution.[4] Both values of τ for the ground state are close to that obtained by semiempirical methods.[16]

The two estimates of the ground-state torsional angle for **2** and **3** are thus qualitatively similar: $\tau \sim 45°$ based on an S_0 potential of $V_4 \sim -150\ \text{cm}^{-1}$ and $\tau \sim 30°$ based on the above electronic origin energy shift calculation (e.g., eq 6 and Figure 6). An estimate of $35° \leq \tau(S_0) \leq 40°$ is probably most reasonable. Since the S_1 potential minimum is close to $\tau \sim 0°$ and $\Delta\tau \sim 30°$ based on the Franck–Condon calculation of the last section, we suggest that the first excited state of **2** and **3** is nearly planar.

V. Conclusions

The mass-resolved $S_1 \leftarrow S_0$ excitation spectrum of α-methylstyrene is presented and analyzed. The main results of this analysis are as follows: (1) the ground-state torsional angle is between 35° and 40°, (2) the excited-state torsional angle is near 0°, and (3) the displacement of the torsional angle between the ground and excited state is ~30°. α-Methylstyrene is thus nonplanar in its ground state but approximately planar in its first excited singlet. The potential parameters determined from a hindered rotor analysis of the internal torsional motion of **2** yields ground-state parameters $V_2 \sim 0\ \text{cm}^{-1}$ and $V_4 \sim -150\ \text{cm}^{-1}$ and excited-state parameters of $V_2 = 4867\ \text{cm}^{-1}$, $V_4 = -500\ \text{cm}^{-1}$, and $V_6 = -80\ \text{cm}^{-1}$ with a reduced rotational constant of $B = 0.444\ \text{cm}^{-1}$.

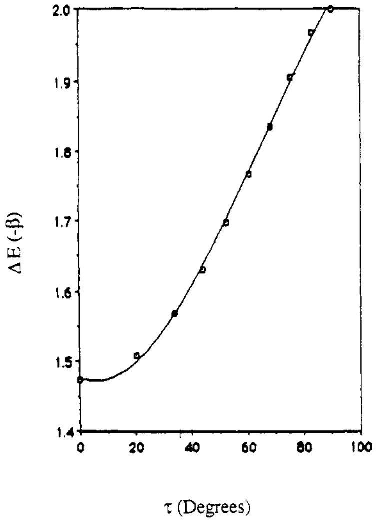


Figure 6. Electronic transition energy plotted as a function of the torsional angle τ for styrene and its derivatives, as calculated by Suzuki (see ref 5a).

Acknowledgment. This work was supported in part by the ONR to E. R. Bernstein. We thank A. C. Lilly, B. LaRoy, and R. Ferguson for their encouragement and support of this work and J. Paine for helpful discussions.

Appendix

Synthesis of α,α-Dimethyl-d_3-benzenemethanol.[30] A stirred solution of CD_3MgI (80 mL of 1 M solution in ether) at 0 °C under N_2 was slowly treated over a 1-h period with a solution of acetophenone-*2,2,2-d_3*[31] (9.0 g, 73.1 nmol) in 50 mL of ether. After being allowed to stir for an additional 0.5 h and stand overnight, the reaction was quenched by the addition of water and 5% hydrochloric acid. The separated ether phase was washed (50% KOH), dried (Na_2SO_4), and concentrated under vacuum. The residue was distilled bulb-to-bulb (45 °C/0.05 mmHg using an ice-cooled receiver) to give 9.25 g of the title compound (97%) as a colorless oil which crystallized as a low melting solid.

Synthesis of [1-(Methyl-d_3)-ethenyl-2,2,-d_2]benzene[32] (***3***). This material was prepared from α,α-dimethyl-d_3-benzenemethanol following the general procedure previously described[33] and gave **3** as a clear colorless oil which was stabilized by the addition of a trace of *p*-*tert*-butylcatechol.

---

(29) Imamura, A.; Hoffmann, R. *J. Chem. Soc.* **1968**, *90*, 5379.

(30) Protiva, M.; Jilek, J.; Rajsner, M.; Sindelar, K.; Bartl, V.; Ryska, M.; Korvna, I.; Holvbek, J.; Svatek, E. *Collect. Czech. Chem. Commun.* **1987**, *52*, 1811.

(31) Arrowsmith, C. H.; Kresge, A. J. *J. Am. Chem. Soc.* **1986**, *108*, 7918.

(32) Ryabov, A. D.; Eliseer, A. V.; Yatsimirskii, A. K. *Appl. Organomet. Chem.* **1988**, *2*, 101.

(33) Overburger, C. G.; Saunders, J. H. *Organic Syntheses*; Wiley: New York, 1955; Collect. Vol. No. 3, p 204.