Conformational Study of Jet-Cooled Styrene Derivatives. Demonstration of the Planarity of Nonsterically Hindered Styrenes

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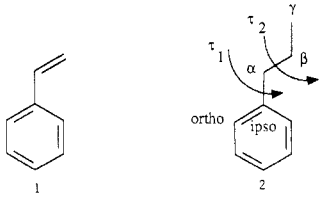
One-color time-of-flight mass spectroscopy (mass-resolved excitation spectroscopy) is used to determine ground- and excited-state geometries and molecular parameters for styrene and a number of its derivatives cooled in a supersonic jet expansion. In this paper we present results for styrene and a series of sterically unhindered substituted derivatives: *trans*-β-methylstyrene, 3-methylstyrene, 4-ethylstyrene, and 4-methoxy-*trans*-β-methylstyrene (anethole). Styrene, *trans*-β-methylstyrene, and 4-ethylstyrene all exhibit one spectroscopic origin corresponding to a single conformation, whereas 3-methylstyrene and anethole exhibit two origins corresponding to syn and anti ground-state conformations. The vinyl group is concluded to be planar with respect to the aromatic ring for all of these molecules in both S_0 and S_1. A one-dimensional methyl rotor analysis for the two conformers of 3-methylstyrene in the first excited singlet state S_1 yields the parameters for methyl rotation in the anti conformer, B = 5.20 cm^{-1}, V_3 = 80.0 cm^{-1}, and V_6 = −15.0 cm^{-1} and in the more hindered syn conformer, B = 5.95 cm^{-1}, V_3 = 185.0 cm^{-1}, and V_6 = −27.5 cm^{-1}.

I. Introduction

Styrene (**1**) and its derivatives play an important role in many aspects of organic chemistry: in the understanding of conjugation and aromaticity; as synthetic intermediates, notably in polymer chemistry; and as substructures in many natural products. Planarity of styrene in the ground state is widely assumed but not proven, although the planar conformation does indeed appear to be the best explanation for the currently available data.[1-3] To illustrate this point, consider the correlation between $S_1 \leftarrow S_0$ transition energy and the degree of conjugation between the two π-systems.[4] The 0_0^0 transition of ethylbenzene is at 37 587.8 cm^{-1} whereas the 0_0^0 transition for styrene is at 34 778.7 cm^{-1}, a decrease in energy of over 2800 cm^{-1} presumably facilitated through the interaction (conjugation) of the two π-systems. Thus some degree of conjugation or delocalization between the vinyl and aromatic π-systems does occur in styrene demonstrating that τ_1 in **2** is less than 90°. Nonetheless, whether τ_1 = 0° or not is still an open question because one does not know if the decrease in the transition energy of styrene with respect to that of ethylbenzene (2810 cm^{-1}) is at its maximum value as would be required for a planar (τ_1 = 0°) conformation of styrene.



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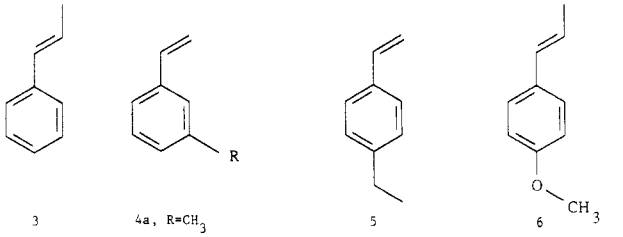
Spectroscopic studies have revealed a great deal of information concerning the electronic potential energy surfaces of styrene.[1-5] The major difficulty in establishing the geometry of the ground-state energy minimum of styrene and its analogues is related to the very low rotational barriers involved, typically <5 kcal/mol for the sterically unhindered molecules.[6] A wide range of theoretical treatments has also been applied to study the ground and excited states of styrene.[7-9] The excited-state conformation of styrene and its derivatives will greatly influence both their photochemical and photophysical properties,[10] and our detailed understanding of such properties would be enhanced if such structural information were available.

Supersonic molecular jet spectroscopy has been demonstrated to be an effective technique for determining various stable conformtions of alkyl-substituted benzenes.[11] Employing asymmetrically substituted substrates and considering the various possible conformations of these molecules, we were able to establish the torsional angles, τ_1 and τ_2 as defined in **2** for a variety of aromatic molecules.[11,12] In the present work, we observe the time of flight mass spectra (TOFMS) (mass-resolved excitation spectra) for a set of substituted styrenes [*trans*-β-methylstyrene (**3**), 3-methylstyrene (**4a**), 4-ethylstyrene (**5**), and 4-methoxy-*trans*-β-methylstyrene (anethole) (**6**)], establish a planar conformation



3 4a, R=CH3 4b, R=CD3 5 6

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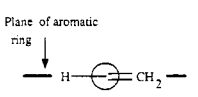
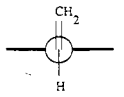
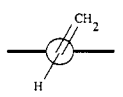
TABLE I: Number of Conformations for Styrene and Styrene Derivatives Based on Experiment and Conformational Analysis Predictions

	number of conformations			
	predicted[a]			
				
	7	**8**	**9**	
compound	planar	perpendicular	gauche	obsd[b]
styrene (**1**)	1	1	1	1
trans-β-methylstyrene (**3**)	1	1	1	1
3-methylstyrene (**4a**)	2	1	2	2
4-ethylstyrene (**5**)	1	2	2	1
anethole (**6**)	2	1	2	2

[a] Based on counting all possible molecular conformations having the specific substituent conformation depicted but counting degenerate conformations only once. [b] Number of origin transitions observed by TOFMS. See text for additional discussion.

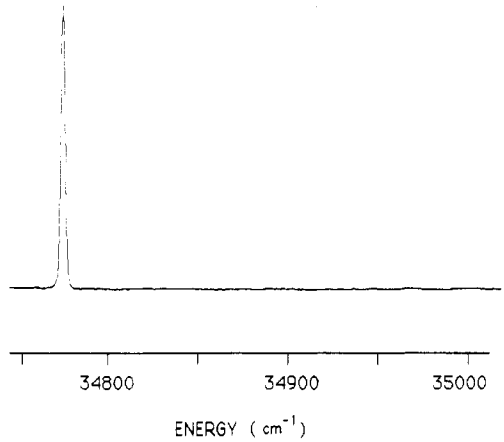


Figure 1. One-color TOFMS of jet-cooled styrene (**1**). The He expansion pressure was 100 psig. The 0_0^0 transition is at 34 778.7 cm^{-1}.

for styrene and these sterically unhindered derivatives, and determine the methyl rotor potentials in the first excited state for the two stable conformations of 3-methylstyrene (**4**).

II. Results and Discussion

A. Conformational Analysis. The $\pi^* \leftarrow \pi$ electronic transition ($S_1 \leftarrow S_0$) for each stable conformation of an aromatic molecule will, in principle, generate its own spectroscopic 0_0^0 transition (i.e., an origin transition). The converse is also true; i.e., each origin transition is associated with a specific ground-state conformational energy minimum. Thus, the TOFMS of a jet-coled substituted aromatic compound will, in principle, contain an origin transition peak for each of its existing stable conformations.

As shown in Table I, styrene and its analogues can exist in one (or more) of three possible conformations: planar, perpendicular, and gauche (**7**–**9**). The one-color TOFMS of styrene seeded in a He supersonic jet expansion is shown in Figure 1. This spectrum is identical with that of the jet-cooled fluorescence excitation first reported by Syage et al.[2] The 0_0^0 transition occurs at 34 778.7 cm^{-1}. The spectrum within 200 cm^{-1} of the spectroscopic origin consists solely of this single intense peak. As only a single 0_0^0 transition is observed for styrene in the TOFMS, then only one of the three conformations **7**–**9** can exist in the expansion.

The one-color TOFMS for *trans*-β-methylstyrene (**3**) is shown in Figure 2. Similar to that of the styrene spectrum, the intense feature at 34 585.0 cm^{-1} is the only origin observed in the spectrum. By the argument presented above, and as shown in Table I, *trans*-β-methylstyrene exists in a single ground-state energy minimum. The intensity at the origin and the absence of a progression[11e] of vibrational features for both styrene and *trans*-β-methylstyrene suggest that the excited-state conformation of these molecules is similar to the ground-state conformation.

An experimental distinction can be made between the three conformations **7**–**9** (see Table I) by examining suitably substituted

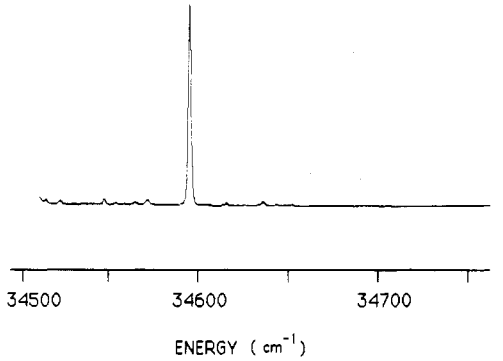


Figure 2. TOFMS of *trans*-β-methylstyrene (**3**). The 0_0^0 transition is at 34 585.0 cm^{-1}.

molecules. To do so, one can utilize various molecular substructures: a substructure which is asymmetric about the C_1–C_4 axis (e.g., as in 3-methylstyrene and anethole); and a substructure which is asymmetric above and below the plane of the aromatic ring (e.g., as in 4-ethylstyrene). As shown in Table I, the substrates chosen following these structural considerations are contained in **3**–**6**.

The one-color TOFMS of 3-methylstyrene (**4a**) is shown in Figure 3a. The spectrum in the origin region for **4a** is much richer than that for styrene and *trans*-β-methylstyrene. The spectrum may consist of 0_0^0 transitions for different conformers, as well as transitions associated with the internal rotational states of the methyl rotor. The distinction between 0_0^0 transitions and methyl rotor transitions for 3-methylstyrene can be made with the aid of the TOFMS of the partially deuteriated compound 3-methyl-d_3-styrene (**4b**), shown in Figure 3b.

The assignment of one origin, due to one of the conformers, is straightforward; the origin is taken to be the lowest frequency intense peak in the spectrum. This feature is a doublet in the 3-methylstyrene (**4a**) spectrum (at 34 082.7 and 34 086.3 cm^{-1}; the doublet nature of the peak is described in more detail later) and a single intense peak at (34 116.5 cm^{-1}) in the TOFMS of **4b**. The assignment of any other origin due to the other possible conformers (cf. Table I) is more difficult because of the number and intensity of the methyl rotor transitions in the spectrum.

The separation between the two origins for **4a** and **4b** is expected to change at most a few cm^{-1} upon deuteriation, whereas other peaks in the spectrum, which are due to methyl rotor transitions, should shift considerably more. In addition, the second origin should also be a fairly intense peak in the spectrum. From these considerations, the second origin is assigned as the intense peak at 34 215.0 cm^{-1} for **4a** and at 34 242.5 cm^{-1} for **4b**. The second origin is higher in energy by 132.3 and 126 cm^{-1} with respect to the first origin for **4a** and **4b**, respectively.

Although the two origins have been identified in the TOFMS of 3-methylstyrene, two questions remain: (1) is the vinyl group planar (**7**) or gauche (**9**) (see Table I) relative to the plane of the aromatic ring; and (2) for either **7** or **9**, is the vinyl group syn

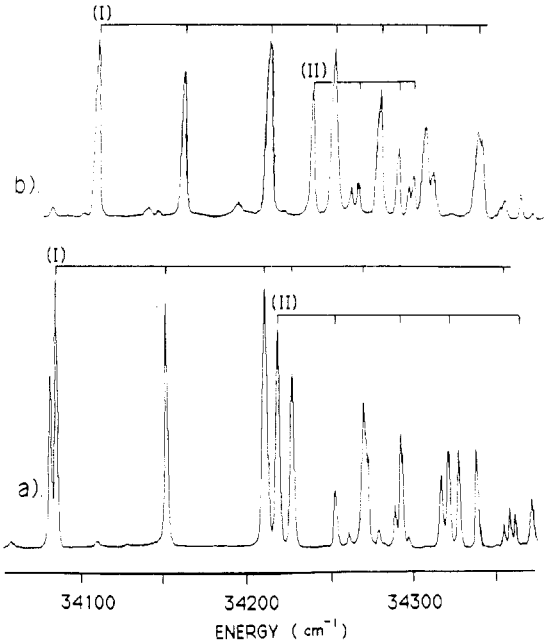


Figure 3. One-color TOFMS of 3-methylstyrene (**4a**) and 3-methyl-d_3-styrene (**4b**), (a) and (b), respectively. The spectrum for each molecule consists of two origins, due to the syn (**10**) and anti (**11**) conformers, and internal rotational transitions of the methyl group (see text). The origins for **4a** are at 34086.3 and 34215.0 cm^{-1} and **4b** origins are at 34116.5 and 34242.5 cm^{-1}.

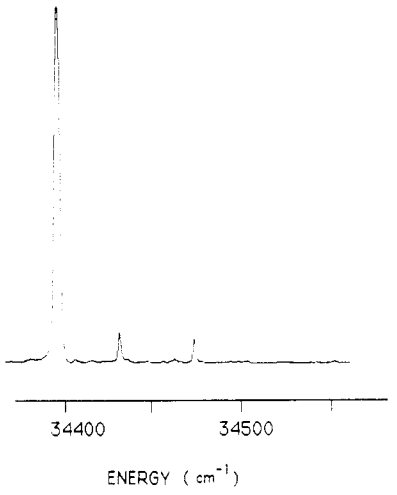


Figure 4. One-color TOFMS of jet-cooled 4-ethylstyrene (**5**). Only one origin, at 34388.0 cm^{-1}, is presented in the spectrum consistent with a planar conformation of the vinyl group in both S_0 and S_1 (see text).

or anti relative to the methyl group, as depicted in **10** and **11**, respectively. The assignment of the syn and anti conformers can

10 11

be made by the analysis of the methyl rotor transitions for this compound as will be discussed in the next section.

The question of a planar or gauche conformation of the vinyl group can be answered by examination of the TOFMS of 4-ethylstyrene. The TOFMS of 4-ethylstyrene is shown in Figure 4. The spectrum consists of an intense peak at 34388.0 cm^{-1} identified as the origin and two weaker peaks which are 27.7 and 67 cm^{-1} higher in energy than the origin. From an earlier study,[11c] the conformation of the ethyl group in a series of substituted benzenes is known to be perpendicular to the plane of the aromatic ring, i.e., $\tau_1 = 90°$ (cf. **2**). The orientation of the vinyl group in styrene can thus be determined from the number of origins in the

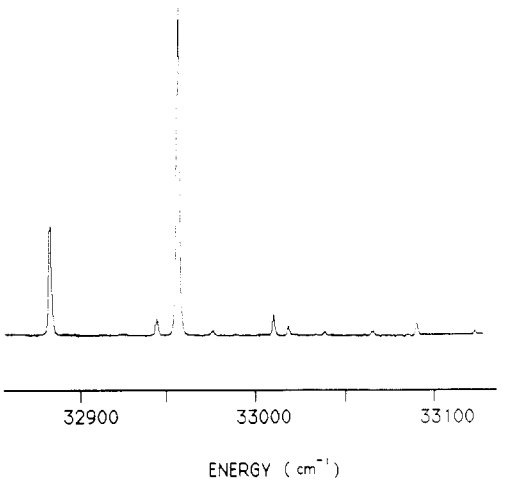
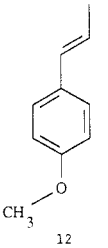


Figure 5. TOFMS of jet-cooled anethole, 4-methoxy-*trans*-β-methylstyrene (**6**). Two origins corresponding to the syn (**6**) and anti (**12**) conformers are seen at 32889 and 32958 cm^{-1}.

4-ethylstyrene spectrum. If the vinyl group were planar with respect to the aromatic ring, only one origin would be observed; if, however, $0 < \tau_1 < 180$, two origins would be observed in the 4-ethylstyrene TOFMS (see Table I). One of these latter origins would correspond to a conformation with the ethyl and vinyl groups on the same side of the aromatic ring, and the other origin would correspond to a conformation with the ethyl and vinyl groups on opposite sides of the ring. These two origins should be separate by approximately 2–5 cm^{-1} in energy, in analogy with the splitting observed for 1,4-diethylbenzene[11c] and 4-ethyl-1-propylbenzene.[11d] The spectrum shown in Figure 4 reveals only a single intense peak and not the doublet that would be expected for a nonplanar vinyl group. The other peaks in the spectrum must be associated with the low-frequency motions of the ethyl group. We thereby conclude that, for 4-ethylstyrene, the vinyl group is planar with respect to the aromatic ring. By analogy, the planar conformation of the vinyl group occurs for styrene and other sterically unhindered styrene derivatives.

To confirm these structural assignments and to determine if these spectroscopic studies could be successfully extended to more complex molecules, the one-color TOFMS of anethole (**6**) was obtained and is presented in Figure 5. The spectrum shows two origins at 32889 and 32958 cm^{-1}. The origins are tentatively assigned to the syn and anti conformations of anethole, **6** and **12**, respectively, on the basis of their intensities.



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Since the methoxy group has been previously determined to have a planar orientation with respect to the ring plane,[12] the orientation of the vinyl group an then be either syn or anti with respect to the methoxy group. The origins corresponding to the two orientations are separated by 69 cm^{-1}. In analogy to 3-methylstyrene (discussed in the next section) and *m*-cresol,[13] the lower energy origin is assigned to the syn conformer and the high-energy origin to the anti conformer. The lower energy for the 0_0^0 transitions of **6** with respect to that of *trans*-β-methylstyrene (**2**) reflects the increased conjugation of the π-system due to the presence of the methoxy group.

B. Methyl Rotor Analysis of 3-Methylstyrene. The theoretical analysis of methyl rotor transitions for toluene and alkyl-sub-

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TABLE II: Rotational Assignment for the Methyl Rotor Transitions in 3-Methylstyrene (4a) and 3-Methyl-d_3-styrene (4b); Origin I (Syn Conformer)[a]

transition[a]	calcd,[a] cm^{-1}	obsd,[b] cm^{-1}
	3-Methylstyrene	
$0a_1$–$0a_1$	0	0
1e–1e	−3.8	−3.6
1e–2e	68.1	69.9
$0a_1$–$3a_2$	77.7	
$0a_1$–$3a_1$	129.9	122.7
1e–4e	145.7	139.9
1e–5e	198.4	196.4
$0a_1$–$6a_2$	260.9	
$0a_1$–$6a_1$	265.4	259.9
	3-Methyl-d_3-styrene	
$0a_1$–$0a_1$	0	0
1e–1e	−1.3	0
1e–2e	51.4	51.0
$0a_1$–$3a_2$	53.2	51.0
$0a_1$–$3a_1$	104.0	100.4
1e–4e	106.7	100.4
1e–5e	147.2	138.7
$0a_1$–$6a_2$	165.0	165.6
$0a_1$–$6a_1$	181.4	192.7

[a] For a full discussion of the states of a methyl rotor, see ref 11a. [b] Ground-state potential parameters: V_3 = 25.0 cm^{-1} and V_6 = 0.0 cm^{-1}. The rotational constant, B, is 5.2 cm^{-1} for CH_3 (in **4a**) and 2.6 cm^{-1} for CD_3 (in **4b**). Excited-state potential parameters: V_3 = 185.0 cm^{-1} and V_6 = −27.5 cm^{-1}. The rotational constant, B, is 5.95 cm^{-1} for CH_3 (in **4a**) and 3.0 cm^{-1} for CD_3 (in **4b**).

stituted toluenes has been described in detail preivously.[11a] The parameters used to fit the data include the rotational constant B and the potential barriers V_3 and V_6. The potential for a hindered methyl rotor has the form

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

The eigenvalues are calculated with the equation

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

For a free rotor, $V(\phi) = 0$ and $E_m = m^2B$. The parameters V_3 and V_6 are varied to obtain to the best fit of the data for the first and second origins and are given in Table II and Table III, respectively. The tables compare observed and calculated frequencies for metyl rotor transitions associated with both origins. The ground-state potential barrier for both syn and anti conformers are assumed to be the same. The value of the potential parameters used for the ground-state potential functions in these calculations is taken to be similar to that for 1-methoxy-3-methylbenzene (V_3 = +25.0 cm^{-1} and V_6 = 0.0 cm^{-1}).[12]

Excited-state potential barriers for the methyl rotor transitions,[11a] as determined from these calculations, are higher for one conformer than the other. For the lower energy origin (I) of 3-methylstyrene (**4a**), the excited-state potential corresponds to V_3 = 185.0 cm^{-1} and V_6 = −27.5 cm^{-1} with a rotational constant of B = 5.95 cm^{-1}. The best fit to the same potential function for 3-methyl-d_3-styrene yields a rotational constant of B = 3.0 cm^{-1}. The doublet character of the origin for **4a** is caused by a large difference in the potential barrier for the rotation of the methyl group in S_0 as compared to S_1. The higher barrier for methyl rotation in S_1 causes the $0a_1$–1e separation to be smaller in S_1 than in S_0. the lower energy peak for the 0_0^0 transition corresponds to the 1e–1e rotational transition, and the higher energy peak corresponds to the true 0_0^0 transition, the $0a_1$–$0a_1$ transition. Such doublet structure is not observed for the deuteriated methyl compound because its rotational constant is smaller. The reduced B value has the effect of making the $0a_1$–1e splitting less in both the ground and excited states, thereby reducing the energy difference between the $0a_1$–$0a_1$ and 1e–1e rotational transitions for CD_3.

TABLE III: Rotational Assignment for the Methyl Rotor Transitions in 3-Methylstyrene (4a) and 3-Methyl-d_3-styrene (4b); Origin II (Anti Conformer)[a]

transition[a]	calcd,[a] cm^{-1}	obsd,[b] cm^{-1}
	3-Methylstyrene	
$0a_1$–$0a_1$	0	0
1e–1e	−2.7	0
1e–2e	36.0	33.9
$0a_1$–$3a_2$	53.0	
$0a_1$–$3a_1$	72.7	72.2
1e–4e	95.0	96.0
1e–5e	140.4	137.6
	3-Methyl-d_3-styrene	
$0a_1$–$0a_1$	0	0
1e–1e	−1.1	0
1e–2e	29.1	29.0
$0a_1$–$3a_2$	32.7	
$0a_1$–$3a_1$	56.1	51.1
1e–4e	63.4	60.0

[a] See footnote *a* in Table II. [b] Ground-state potential parameters: V_3 = 25.0 cm^{-1} and V_6 = 0.0 cm^{-1}. The rotational constant, B, is 5.2 cm^{-1} for CH_3 (in **4a**) and 2.6 cm^{-1} for CD_3 (in **4b**). Excited-state potential parameters: V_3 = 80.0 cm^{-1} and V_6 = −15.0 cm^{-1}. The rotational constant, B, is 5.2 cm^{-1} for CH_3 (in **4a**) and 2.6 cm^{-1} for CD_3 (in **4b**).

The second origin (origin II) arises from a conformer of 3-methylstyrene with a methyl rotor which is more freely rotating in the excited state. The potential barrier to methyl rotation in this conformer is given by V_3 = 80.0 cm^{-1}, V_6 = −15.0 cm^{-1}, and the methyl rotation constant B = 5.2 cm^{-1}. The rotational constant for deuteriated **4b** that best fits the data and keeps the same potential parameters is B = 2.6 cm^{-1}.

The assignment of each origin to a specific conformer is made as follows. The conformer with the small barrier to methyl rotation is assigned to the less sterically hindered anti conformer, origin II, and the syn conformer is assigned to origin I with the significantly higher barrier to methyl rotation.

These assignments are in agreement with jet studies of Mizuno et al. for *m*-cresol.[13] Two conformations are observed in the jet expansion for this molecule, syn and anti (referred to as cis and trans in their paper). The anti conformer is characterized by a methyl group with a lower barrier to rotation than the syn conformer in S_1. The 0_0^0 transitions corresponding to the two conformers for *m*-cresol are separated by 109.8 cm^{-1}. Similar to our findings on 3-methylstyrene, the syn form is found to have the lower transition energy for *m*-cresol.

III. Conclusions

In this paper we have presented one-color TOFMS of styrene and several of its derivatives. The following conclusions can be made based on the analysis of the data presented:

1. In the ground state, the vinyl group is planar with respect to the ring for styrenes without steric hindrance. The intense 0_0^0 transition and absence of a torsional mode progression suggests this is also true for the excited state.

2. Two stable conformations have been observed spectroscopically for 3-methylstyrene and for 4-methoxy-*trans*-β-methylstyrene (anethole): the vinyl group can be syn and anti to the asymmetrically substituted aromatic ring. The syn conformation is tentatively assigned to have the lower transition energy in each case.

3. A one-dimensional rotor analysis for the two conformations of 3-methylstyrene yields excited-state potential parameters of V_3 = 80.0 cm^{-1} and V_6 = −15.0 cm^{-1} for the anti conformer and V_3 = 185.0 cm^{-1} and V_6 = −27.5 cm^{-1} for the syn conformer.

IV. Experimental Procedure

The supersonic jet expansion as well as the time-of-flight mass spectrometer have been described in detail elsewhere.[14] Briefly, the supersonic expansion is generated by a R. M. Jordan pulsed

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valve. A tunable pulsed dye laser, pumped by the doubled output of a pulsed Nd:YAG laser, is frequency doubled and focused into the interaction region of the chamber. The same laser beam, in these one-color TOFMS (mass-resolved excitation) experiments, is used to excite the molecules to S_1 and to photoionize them. Ions are accelerated into a flight tube and detected by a microchannel plate. The laser line width is measured to be 0.2 cm^{-1}: transitions can be measured to 0.1 cm^{-1}.

Styrene, *trans*-β-methylstyrene, 3-methylstyrene, and anethole were all purchased from Aldrich, and 4-ethylstyrene was purchased from Karl Industries; all were used without further purification. The specificaly labeled compound, 3-methyl-d_3-styrene, was synthesized as described below. All of the chemicals used were inhibited with a trace of 4-*tert*-butylcatechol and stored in the dark at 4 °C. The neat samples of these molecules were clear and viscous prior to use (except for anethole, which is a solid at 25 °C).

Synthesis of 3-Methyl-d_3-styrene (**4b**).[15] To a solution of 3-bromostyrene (5.0 g, 27.3 mmol) and [bis(diphenylphosphino)propane]nickel(II) chloride (90 mg, 0.175 mmol) in ether (85 mL) was added dropwise methyl-d_3-magnesium iodide in ether (33 mL of a 1.0 M solution, 33 mmol). The mixture was heated under reflux overnight and was quenched with half-saturated NH_4Cl. Extraction with ether and removal of solvent afforded the crude product which was taken up in methylene chloride, treated with 4-*tert*-butylcatechol (trace), filtered, concentrated, and distilled into a receiver containing trace amounts of 4-*tert*-butylcatechol, giving 3-methyl-d_3-styrene (2.7 g, 81.7% yield) as a colorless liquid. bp < rt (0.05 mm); ^1H NMR ($CDCl_3$) δ 5.18 (d, 1 H, J = 10.9 Hz), 5.70 (d, 1 H, J = 17.5 Hz), 6.66 (dd, 1 H, J = 10.9, 17.5 Hz), 7.01–7.08 (m, 1 H), 7.15–7.19 (m, 3 H); ^{13}C NMR ($CDCl_3$) δ 20.52 (septet, J = 19.3 Hz), 113.51, 123.35, 126.95, 128.40, 128.58, 136.97, 137.50, and 137.89.

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Ab Initio Calculations of the Electronic Structure and Vibrational Frequencies of the Dichloromethyl Radical and Cation

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Ab initio molecular orbital calculations on the $\tilde{X}\ ^1A_1$ (C_{2v}) state of the $CHCl_2$ cation and on the $\tilde{X}\ ^2B_1$ (C_{2v}), $\tilde{X}\ ^2A'$ (C_s), $\tilde{A}\ ^2A_1$ (C_{2v}), and $\tilde{C}\ ^2B_2$ (C_{2v}) valence states of the $CHCl_2$ radical are reported. The qualitative features of the molecular orbital interactions are presented. Using the 6-31G* basis set, we computed optimized structures with the Hartree–Fock and second-order Møller–Plesset levels of theory. The optimized structure of the $CHCl_2$ cation is a C_{2v} structure. The optimized structure of the ground-state radical predicts that the C–H bond lies 15.5° out of the Cl–C–Cl plane. Frozen core single-point calculations using fourth-order Møller–Plesset theory and the 6-31G* basis set predict that the barrier to inversion in the $\tilde{X}\ ^2A'$ (C_s) state of the $CHCl_2$ radical is 220 cm^{-1}. Vibrational frequencies for each $CHCl_2$ species were computed from the HF/6-31G* optimized structures. These calculated frequencies compare favorably with previously reported experimental frequencies.

Introduction

In recent years multiphoton ionization, photoelectron, and infrared spectroscopies have furnished an extensive list of vibrational frequencies for dichloromethyl ($CHCl_2$) cations and radicals.[1-8] In contrast, there are no published theoretical calculations of the $CHCl_2$ cation and few calculations of the $CHCl_2$ radical.[9-11] The objective of this work is to provide the theoretical framework that can support discussions of vibrational spectroscopy of the dichloromethyl cation and radical. We construct this framework by presenting qualitative molecular orbital theory (QMOT) arguments[12-14] and ab initio calculations of dichloromethyl cations and radicals. The QMOT arguments outline the principal interactions that cause differences of geometry and normal-mode frequencies among $CHCl_2$ species. The ab initio calculations predict vibrational frequencies for the ground states of $CHCl_2^+$ and $CHCl_2$ radical. In addition, we present calculations for the two lowest excited doublet valence states of planar $CHCl_2$ radical. Calculations were performed at several levels of theory and basis set size.

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