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Supersonic Jet Studies of Benzyl Alcohols: Minimum Energy Conformations and Torsional Motion

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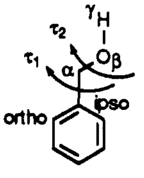
Abstract: Supersonic jet mass resolved excitation spectroscopy is employed to determine the minimum energy conformations of benzyl alcohol and a series of nine methyl-, ethyl-, fluoro-, and aminobenzyl alcohols. The interpretation of the mass resolved excitation spectra of these molecules leads to the assignment of specific molecular geometries for each system. The minimum energy conformation of the $-CH_2O$ moiety is determined to be perpendicular relative to the plane of the aromatic ring, i.e., $\tau(C_{ortho}-C_{ipso}-C_\alpha-O) = 90°$. The hydroxy proton in the sterically unencumbered benzyl alcohol points toward the benzene ring. The potential energy barrier for the low-frequency torsional motion of the hydroxymethyl group arises mainly from an internal hydrogen-bonding interaction between the OH group and π-system of the ring. Using hindered rotor model calculations, the potential barrier to this torsional mode is determined to be $V_2 = -140$ cm^{-1} for S_0 and $V_2 = -330$ cm^{-1} and $V_4 = -3$ cm^{-1} for S_1 with a CH_2OH rotational constant of 0.52 cm^{-1} for both states. Similar potential barriers are observed for methyl-substituted benzyl alcohols. The potential energy barrier in S_1 changes significantly, however, for fluoro- and amino-substituted benzyl alcohols, as these substituents interact strongly with the π-electron system of the aromatic ring. For 2-fluorobenzyl alcohol, the nature of the low-frequency torsional mode changes to a combination of (O—H···F) hydrogen motion and –OH motion. The spectrum of benzyl fluoride is very similar to that found for benzyl alcohol, suggesting that the conformations of the two compounds are similar, e.g., $\tau(C_{ortho}-C_{ipso}-C_\alpha-F) = 90°$.

I. Introduction

In spite of its structural simplicity, the conformational preference and torsional motion of benzyl alcohol (**1**) and its analogues have not been unambiguously defined.[1,2] This is particularly remarkable, given that benzyl alcohols are important in organic chemistry: they have significant synthetic utility, are frequently found in natural products, and play a central role in numerous mechanistic investigations. The conformational preference of the $-CH_2OH$ group relative to the aromatic ring can be described by two torsional angles, τ_1 and τ_2, as illustrated in **1** (cf. Charts I and II). Based on experimental results, the position of the oxygen atom relative to the aromatic ring (i.e., τ_1) has been variously assigned to be planar[3,4] (**2**), perpendicular[1,2] (**3**), gauche[1,4–6] (**4**), and freely rotating[6,7] (see Chart I). Moreover, theory has not led to a consensus for the molecular conformation of benzyl alcohol; ab initio calculations suggest both planar[8a] and gauche[1] conformations for τ_1, while molecular mechanics calculations predict a planar minimum energy conformation.[8b] NMR, IR, and electron diffraction studies indicate that the predominant conformation for τ_2 is gauche[1,4–6] (i.e., $\tau_2 = 60°$) though there is some indication that a minor component assigned as the anti conformation[1,6,9] (i.e., $\tau_2 = 180°$) is present in solution (see Chart II).



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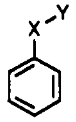
$\tau_1 = \tau(C_{ortho}-C_{ipso}-C_\alpha-O)$
$\tau_2 = \tau(C_{ipso}-C_\alpha-O-H)$

Recently, the geometry of the minimum energy conformations of various substituted aromatic compounds which share the same heavy atom substructure as benzyl alcohol (cf. **5**) have been determined in the gas phase using supersonic molecular jet laser spectroscopy. For example, spectroscopic data have been obtained for the stable conformations of 1,3-diethylbenzene,[10,11] 3-methylpropylbenzene,[10,12] 3-methylstyrene,[13] 3-methylanisole,[14,15] and 3-methylallylbenzene.[16] The results for these compounds and analogues thereof, in toto, have allowed the conformation assignment of the ethyl, propyl, methoxy, vinyl, and allyl substituents, as shown in Table I.[10–16]



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Supersonic jet laser spectroscopy has also been an important technique for the characterization of potential energy barriers and

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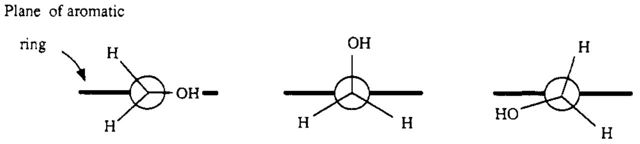
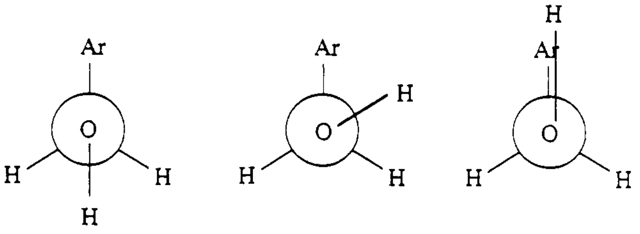
Chart I. Conformations of Benzyl Alcohols Illustrated by Rotation about $\tau_1 = \tau(C_{ortho}-C_{ipso}-C_\alpha-O)$



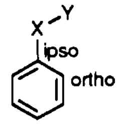
2 planar
3 perpendicular
4 gauche

Chart II. Conformations of Benzyl Alcohols Illustrated by Rotation about $\tau_2 = \tau(C_{ipso}-C_\alpha-O-H)$



anti gauche eclipsed

Table I. Conformations of Substituted Benzenes as Established by Laser Jet Spectroscopy



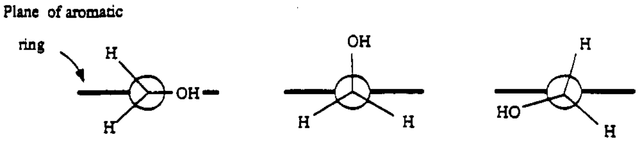
	$\tau(C_{ortho}-C_{ipso}-X-Y)$, deg	ref
ethylbenzene	90	*a*
propylbenzene	90	*b*
methoxybenzene	0	*c*
styrene	0	*d*
allylbenzene	90	*e*
benzyl alcohol	90	this work
benzyl fluoride	90	this work[f]

[a] References 10 and 11. [b] References 10 and 12. [c] References 14 and 15. [d] Reference 13. [e] Reference 16. [f] Based on a comparison of the MRES of benzyl alcohol and benzyl fluoride, as described in the text.

low-frequency modes in various molecules (e.g., biphenyl[17] and alkyl-,[10-12,18] methoxy-,[14,15] and fluoro-substituted[19] toluenes). Studies of methyl torsional modes in aromatic systems indicate that the barrier to internal methyl rotation in the excited state is strongly dependent upon both the position and nature of the various substituents. For example, the potential barrier for 4-substituted toluenes in S_1 is almost the same as that of toluene itself, the potential barrier for 3-substituted toluenes increases significantly (especially for nonalkyl substituents), and the potential barrier for 2-substituted toluenes increases for alkyl substituents but decreases for nonalkyl substituents.[5,10,18,19]

In this work, laser jet spectroscopy is employed to observe and identify the stable conformation(s) of various benzyl alcohols. In addition, this technique is used to examine the effect of substitution on the torsional motion of the hydroxymethyl group in the benzyl alcohol system: significant controversy is found in the recent literature[4,20] regarding the possibility of an attractive OH···π interaction and a repulsive oxygen lone pair···π electron interaction.

Table II. Number of Conformations of 2-Unsubstituted Benzyl Alcohols Based on Experiment and Conformational Analysis Predictions



planar perpendicular gauche

compound	number of conformations			
	predicted			
	planar	prependicular	gauche	obsd
benzyl alcohol (**1**)	1	1	1	1
4-ethylbenzyl alcohol (**8**)	1	2	2	2
3-fluorobenzyl alcohol (**13**)	2	1	2	1
4-fluorobenzyl alcohol (**12**)	1	1	1	1
3-methylbenzyl alcohol (**10**)	2	1	2	1
4-methylbenzyl alcohol (**9**)	1	1	1	1
3-aminobenzyl alcohol (**17**)	2	1	2	1

Spectroscopic studies of these systems are achieved through supersonic jet cooling and mass resolved excitation spectroscopy (MRES, sometimes referred to as time-of-flight mass spectroscopy).[21] These experiments are successful for three distinct reasons. First, the supersonic expansion process results in molecules at near 0 K (0.01 K translational temperature,[22] 3–5 K rotational temperature,[23] and ca. 10 K vibrational temperature[22]), and thus conformational interconversions which may occur rapidly at room temperature, or even at the lowest temperatures obtainable by DNMR, are stopped. Second, the low temperature also results in sharp, well-resolved spectral features. Third, the time scale of the optical absorption event is ca. 10^{-16} s, significantly shorter than the time scale of molecular motion.

Since each stable conformation of a molecule has a specific potential energy minimum in the ground state (S_0), the energy of the electronic origin for the $S_1 \leftarrow S_0$ (0_0^0) transition for each stable conformer is typically unique. In other words, each stable conformer generates its own origin transition; moreover, each origin transition can be assigned to a stable conformer. Thus, the number of origins that are observed in the $S_1 \leftarrow S_0$ MRES of a molecule corresponds to the number of stable conformations of that molecule.[24] By a comparison of the number of origins in the spectra of various substituted benzyl alcohols to those predicted by the symmetry of each molecule (Table II), the conformation of the benzyl alcohol side chain can be determined.

Origins can be identified in the mass resolved excitation spectra of a given species by three basic but qualitative techniques: method 1, spectroscopic analysis of the observed vibronic spectrum in the vicinity of the origin region;[22] method 2, isotopic substitution (H, D) which has a much greater intensity and (characteristic) energy effect on vibronic modes than on origins;[25a] and method 3, substitution (F, CH_3, C_2H_5, etc., for H) which changes the symmetry of the molecule and thus the number of potential conformers to

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(21) The name "one (and two) color mass resolved excitation spectroscopy" is generally employed to describe the following experiment. A sample is irradiated with a laser of energy ν_1, resulting in the generation of the first excited singlet state ($S_1 \leftarrow S_0$). A second photon ν_2 subsequently ionizes those molecules in S_1 ($I^+ \leftarrow S_1$). The ions are detected in given mass channels by time-of-flight mass spectroscopy, such that only ion current representing a chosen m/z is recorded. The energy of the ν_1 laser is changed, and an $S_1 \leftarrow S_0$ "absorption" or excitation spectrum of a mass selected species is obtained. This technique has also been referred to as time-of-flight mass spectroscopy.[10]

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(24) Observation of a single origin transition in this work implies that either (a) only a single stable ground-state conformation exists, (b) that one conformation is significantly more stable than the others, or (c) less likely, but possible, the transition energies for two origin transitions are unresolved. See ref 11 for a discussion of this point with regard to conformational studies.

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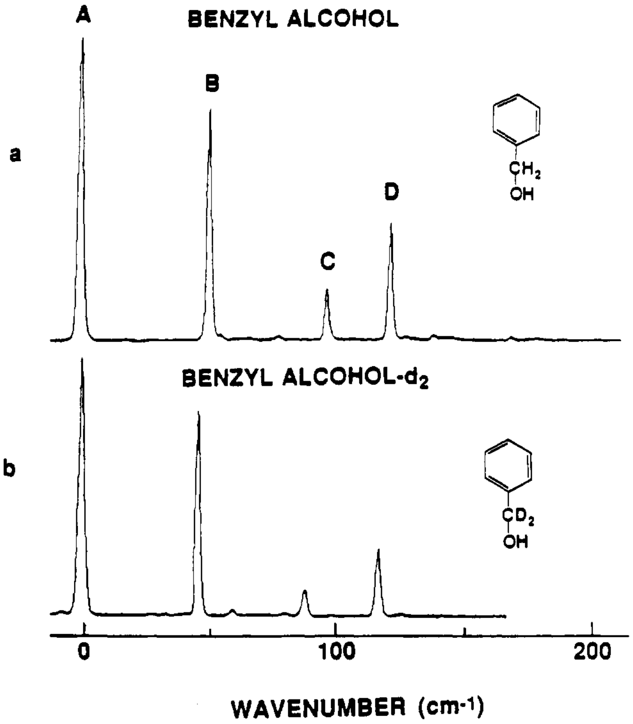
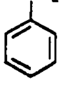


Figure 1. MRES of jet-cooled (a) benzyl alcohol (**1**) and (b) benzyl-α,α-d_2 alcohol (**6**) around their 0_0^0 regions. Both molecules show only one origin (indicated as A) at 37 526.6 and 37 543.8 cm^{-1} for benzyl alcohol and benzyl-α,α-d_2 alcohol, respectively. Peaks B and C are assigned as members of the CH_2OH group torsional progression.

be observed.[10-16] We have used and discussed these methods in a number of previous studies.[10-16] Other methods to identify origins based on pump-probe and saturation techniques have been reported.[25b,c,d] In some instances, one of these approaches is sufficient to identify the conformer origins in the spectrum of a given parent species and assign their geometries.[10-12] In other more complicated instances, all three approaches must be employed to locate origins.[13-16] As pointed out above, these methods have been previously used to determine conformations of other substituted aromatic species, and will thus only be mentioned below in conjunction with specific origin (conformer) assignments. In order to determine the potential energy barrier for the CH_2OH group torsional mode, hindered rotor model calculations[26] are also performed. Based on both spectra and calculations, the effect of ring substitution on this torsional motion can be determined.

II. Results

A. Benzyl Alcohol (1) and Benzyl-α,α-d_2 Alcohol (6). Figure 1a shows the MRES of jet-cooled benzyl alcohol around the origin region of the $S_1 \leftarrow S_0$ transition. In this spectrum, four distinct features are found [37 526.6 (A), 37 577.2 (B), 37 623.5 (C), and 37 649.1 (D) cm^{-1}]. The assignment of the four peaks in this spectrum cannot be made without further information. That is, Figure 1a does not allow the distinction between the two alternatives for **1**: (1) the spectrum consists of one origin and its vibronic additions; or (2) several origins are present, suggesting several stable conformations. In order to address this issue, the spectra of the deuteriated analogues **6** and **7** were obtained.



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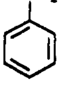

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Deuteriated derivatives of substituted aromatic compounds have previously been employed to great advantage to distinguish between 0_0^0 transitions and vibronic features.[13-15]

Table III. Positions and Assignments for Benzyl Alcohol and Benzyl-α,α-d_2 Alcohol Features in the 0_0^0 Region ($S_1 \leftarrow S_0$)

	$\nu - \nu(0_0^0)$ (cm^{-1})			
ν^a	benzyl alcohol	benzyl-α,α-d_2 alcohol	isotope shift, %	assignment
A	0^b	0^c		0_0^0
B	50.6	46.7	8	T_0^2
C	96.9	89.1	8	T_0^4
D	122.5	118.9	3	$16b_0^1$

[a] A through D are the notation for the observed vibronic features in each molecule (see Figure 1). [b] 0_0^0 occurs at 37 526.6 cm^{-1}. [c] 0_0^0 occurs at 37 543.8 cm^{-1}.

Table IV. Experimental and Calculated Hydroxymethyl Torsional Energy Levels of Benzyl Alcohol in S_0 and S_1

ground state			excited state		
	energy (cm^{-1})			energy (cm^{-1})	
level	$\Delta\nu_{exp}$	$\Delta\nu_{calc}{}^a$	level	$\Delta\nu_{exp}$	$\Delta\nu_{calc}{}^b$
T_2	31.18	32.49	T^2	50.60	50.00
T_4	63.57	62.60	T^4	96.90	97.90

[a] $B = 0.52$ cm^{-1}, $V_2 = -140.0$ cm^{-1}. [b] $B = 0.52$ cm^{-1}, $V_2 = -330.0$ cm^{-1}, $V_4 = -3.0$ cm^{-1}.

The MRES of **6** is shown in Figure 1b. Even though the total mass change is small (108 amu to 110 amu, 1.8%), the isotopic shift of each feature to the blue of the first peak is substantial, ranging from 3% to 8%. These isotope shifts, collected in Table III, suggest that the first peak in the spectrum of **1** and **6** is an origin transition (37 526.6 and 37 543.8 cm^{-1} for **1** and **6**, respectively), that the second and third peaks belong to a progression in one vibration, and that the fourth peak arises from another vibrational mode. Because of the relative change of frequency with isotopic substitution, the second and third peaks (B and C) are assigned to the progression in the torsional mode of the $-CH_2OH$ group. Peak D is not an origin because it has an associated isotope effect and because no associated subsequent vibronic progression can be identified to the blue of this feature. Consequently, peak D is assigned as the fundamental of a molecular vibration (see Table III).

The MRES of **7** evidences no isotope shift when compared to that of benzyl alcohol; i.e., the positions of transitions A–D relative to the 0_0^0 transition are unchanged. Hence, the torsional motion must involve the entire CH_2OH moiety. Further, because of the symmetry of benzyl alcohol, this large amplitude, low-frequency libration of the CH_2OH group should consist largely of motion in a plane containing the C_α–O bond which is nearly perpendicular to the axis passing through carbons C_α, C_{ipso}, and C_4 (the molecular *z* axis). As demonstrated below, the plane containing the C_4, C_{ipsp}, C_α, and O atoms is perpendicular to the plane of the aromatic ring.

The molecular symmetry group of **1** in its equilibrium geometry is C_{2v} (MS).[27] In this symmetry group, the above torsional mode is nontotally symmetric and so the fundamental transition is forbidden; therefore, only odd overtones of the torsional mode will be observed in the absorption spectrum of benzyl alcohol.[17,27]

Figure 2 presents the MRES of benzyl alcohol around the low-energy side of the origin. By controlling the expansion pressure and the backing temperature, the vibrational temperature of molecules in the supersonic beam can be increased. This technique can provide vibrational frequencies for low-lying vibrations of the ground state.[28] The inserted spectrum displayed in Figure 2 is obtained using this technique. This hot spectrum shows two features to the red of the origin at 31.2 (I) and 63.6 cm^{-1} (II). For **6**, these features have the same isotope effect (~8%) as the

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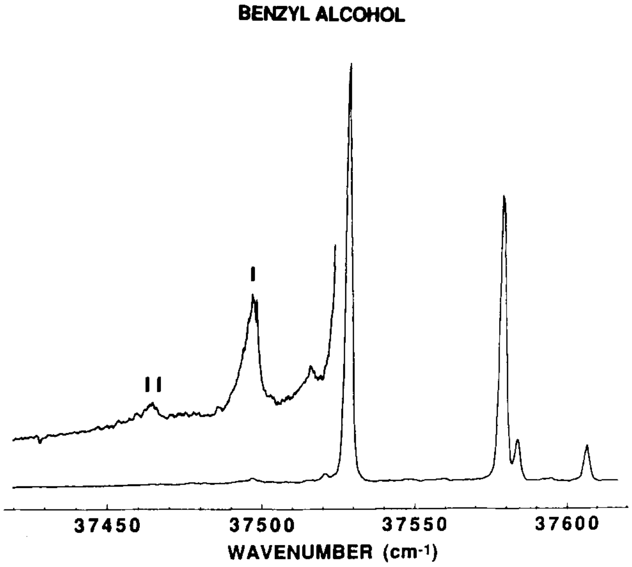
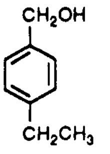


Figure 2. MRES of the jet-cooled benzyl alcohol (**1**) to the low-energy side of the 0_0^0 transition. The vibrational temperature of the sample associated with the main (lower) spectrum is estimated to be roughly 10 K. The inserted spectrum is obtained with an expansion pressure of 1 atm and a backing temperature of 60 °C. Peaks I and II are assigned as hot bands of the torsional mode.

torsional bands in the excited state; features I and II are thus hot bands of the torsional mode (see Tables III and IV).

The potential for CH_2OH group rotation in **1** can be obtained by treating the system as a one-dimensional rigid rotor and diagonalizing the Hamiltonian in a basis set consisting of one-dimensional free rotor functions. Such an analysis has been carried out for the methyl groups of toluene,[10,12,18] its derivatives,[10,12,19] and biphenyl.[17] A similar analysis is repeated herein for **1**. From this calculation, the torsional energy levels can be reproduced using model parameters $B = 0.52$ cm^{-1} and $V_2 = -140.0$ cm^{-1} for the ground state, and $B = 0.52$ cm^{-1}, $V_2 = -330$ cm^{-1}, and $V_4 = -3.0$ cm^{-1} for the excited state (see Table IV). The potential energy barrier in the ground state determined here is consistent with that determined by the NMR J method.[1] Since a short progression in the low-energy torsional mode is observed in the MRES of **1** (transition A, B, and C in Figure 1), the equilibrium position of (or the shape of) the S_1 potential surface must be different from that of the S_0 surface; however, since the 0_0^0 transition is the most intense, this difference must be small. Thus, both the relative intensities of peaks A–D and their spacings are consistent with the conclusion that the potential surfaces for S_1 and S_0 are similar.

To this point in the presentation, methods 1 and 2 (vibronic analysis and isotope effects; cf. section I) have been employed to determine that only one origin is present in the spectrum of **1** and thus only one conformation of **1** is present in the low-temperature population of the supersonic expansion. Below, the third experimental technique (chemical substitution) will be applied to determine detailed molecular symmetry and eventually the correct conformation of the benzyl alcohol species.



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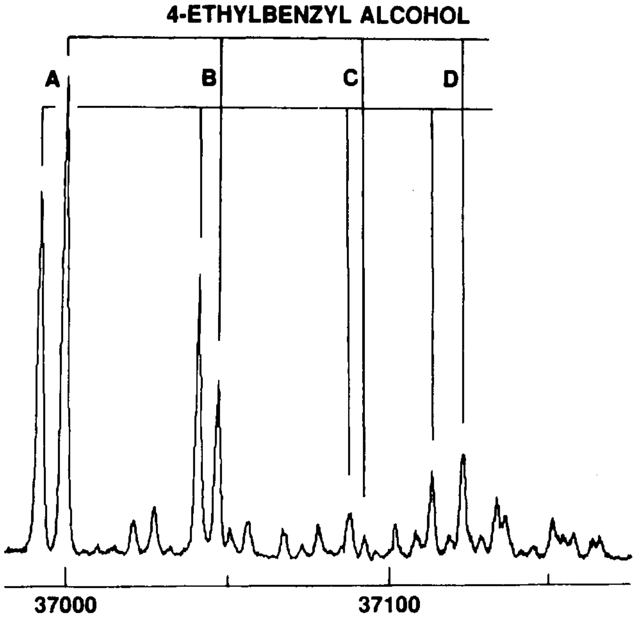


Figure 3. MRES of the 0_0^0 region of the $S_1 \leftarrow S_0$ transition of jet-cooled 4-ethylbenzyl alcohol (**8**). The spectrum contains two origins at 36 992.0 and 36 999.5 cm^{-1}. The vibronic features belonging to each origin are bracketed and labeled. See Table V for the assignment of the vibronic features indicated.

Table V. Positions and Assignments for Features of Each Conformer of 4-Ethylbenzyl Alcohol in the 0_0^0 Region ($S_1 \leftarrow S_0$)

ν^a	conformer I $\nu - \nu(0_0^0)$ (cm^{-1})	conformer II $\nu - \nu(0_0^0)$ (cm^{-1})	assignment
A	0 (36 992.0)^b	0 (36 999.5)^b	0_0^0
B	47.2	46.4	T_0^2
C	93.9	91.2	T_0^4
D	119.4	121.3	$16b_0^1$

[a] A through D are the notation for the observed vibronic features belonging to each conformer (see Figures 1 and 2). [b] Position of the origin transition.

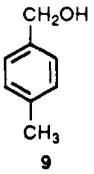
Table VI. Experimental Torsional Energy Levels (in cm^{-1}) of the CH_2OH Group in the S_1 State of Benzyl Alcohol, 4-Methylbenzyl Alcohol, and 3-Methylbenzyl Alcohol

ν	benzyl alcohol	4-methylbenzyl alcohol	3-methylbenzyl alcohol	
			(1e ← 1e)	(0a1 ← 0a1)^b
T^1	(25.3)^a	(26.5)	23.1	24.7
T^2	50.6	52.9	47.1	49.1
T^3	(73.8)	(77.6)	128.2	129.1
T^4	96.9	102.3		
T^5		(125.7)		
T^6		149.1		

[a] The values in parentheses are torsional energy levels not observed due to selection rules. [b] The assignment for the transitions is based on the experimental results of 3-substituted toluenes.

B. 4-Ethylbenzyl Alcohol (8). The MRES of **8** is shown in Figure 3. A comparison of Figures 1 and 3 indicates that each of the main peaks (A–D in Figure 1) for **1** (and for **2**) is doubled for **8** (Figure 3). Since **1** has a single origin, the doubling of the main vibronic features of **8** is direct evidence for two conformations (origins) for **8**. These two origins are at 36 992.0 and 36 999.5 cm^{-1}. The data are collected in Table V. Since two 0_0^0 transitions are observed, **8** has two stable conformations in the ground state. These results are nearly identical with those found for 1,4-diethylbenzene[11] (a ca. 5-cm^{-1} energy difference) and support the vibronic analysis given in section II.A.

C. 4-, 3-, and 2-Methylbenzyl Alcohols (9–11). The MRES of **9–11** are presented in Figure 4, a, b, and c, respectively. 4-



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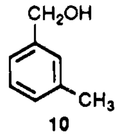

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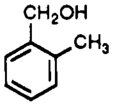

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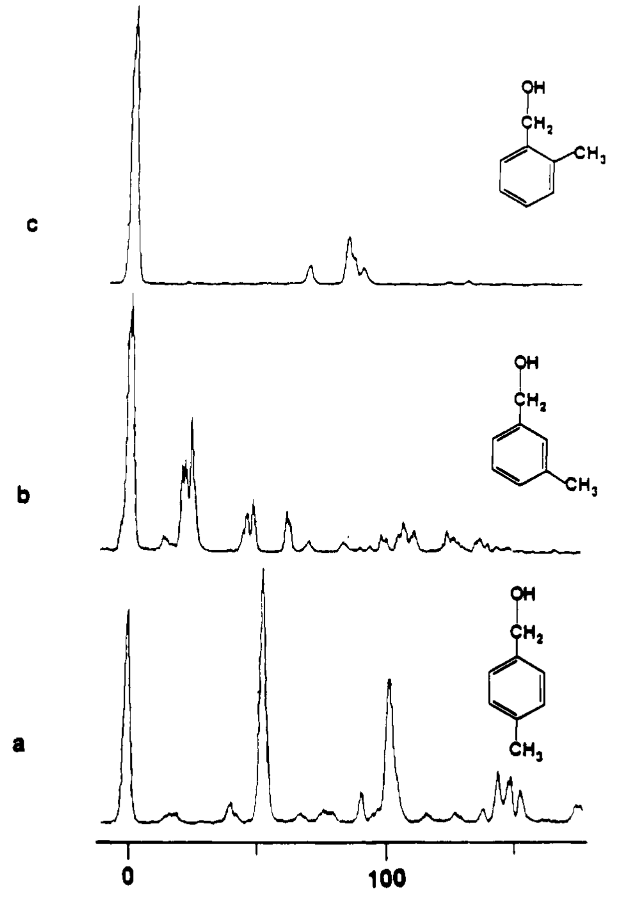


Figure 4. MRES of the 0_0^0 region of the $S_1 \leftarrow S_0$ transition of jet-cooled methyl-substituted benzyl alcohols: (a) 4-methylbenzyl alcohol (**9**), (b) 3-methylbenzyl alcohol (**10**), and (c) 2-methylbenzyl alcohol (**11**). The 0_0^0 transitions of these molecules occur at 36 882.7, 36 945.8 and 37 138.1 cm^{-1}, respectively.

Methylbenzyl alcohol (**9**) has the same symmetry group as **1**, and thus only odd overtones of the CH_2OH torsional motion are observed. In the MRES of this compound (Figure 4a), an intense torsional progression of the CH_2OH group is observed (Table VI) along with weak methyl rotation features built on (to the blue of) each CH_2OH torsional band. The torsional energy levels of the CH_2OH group in this molecule are almost the same as those found for **1**. This behavior is quite generally found for para-substituted aromatic systems.[10,12,18,19] The data for the CH_2OH torsional energy levels of **9** are collected and compared with those of **1** in Table VI.

Figure 4b depicts the MRES of jet-cooled 3-methylbenzyl alcohol (**10**) around the origin of the $S_1 \leftarrow S_0$ transition. The symmetry group of this molecule is lower than the symmetry of **1** due to the substitution pattern, and thus the fundamental transition of the CH_2OH group torsional mode is allowed and is observed in the MRES of **10**. The origin band in this MRES possesses a doublet structure associated with methyl rotation, as is typically the case for *m*-methyl-disubstituted benzenes.[10,12,18,19] The several doublets to the blue of the origin doublet at 36 944.7 and 36 945.8 cm^{-1} are assigned as CH_2OH torsional motion upon which is superimposed the methyl torsion. As presented in Table VI, the torsional energy levels in the excited state of this molecule show almost no change compared to those of **1**.

The CH_2OH torsional progression is not apparent in the MRES of 2-methylbenzyl alcohol (**11**) (see Figure 4c). Only one strong origin is present in the spectrum at 37 134.1 cm^{-1}. The weak features to higher energy of the origin are assigned as due to torsions of the methyl rotor.[10,12,18,19] For this system, a large steric interaction between CH_2OH and the *o*-methyl group is expected, and the potential barrier for the CH_2OH torsion should be larger than that of **1**. Because of this steric hindrance, no torsional progression of the hydroxymethyl group is observed. Again, this behavior is general for ortho alkyl-substituted hindered rotor systems.[10,12,18,19] The fact that no progression is observed in the MRES of **11** (due to the hindering potential) indicates that τ_1 and τ_2 for this molecule are essentially the same in S_0 and S_1.

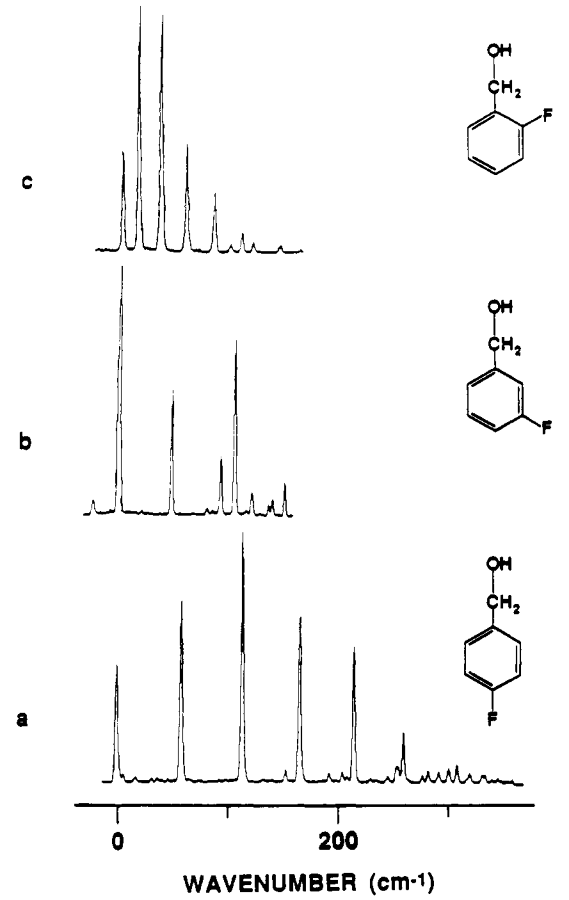
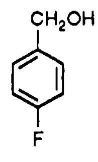


Figure 5. MRES of the 0_0^0 region of the $S_1 \leftarrow S_0$ transition of jet-cooled (a) 4-fluorobenzyl alcohol (**12**), (b) 3-fluorobenzyl alcohol (**13**), and (c) 2-fluorobenzyl alcohol (**14**). The 0_0^0 transitions are located at 37 076.5, 37 335.6, and 37 594.7 cm^{-1}, respectively. Note the change in the torsional mode spacings for different fluorine positions on the ring.

D. 4-, 3-, and 2-Fluorobenzyl Alcohols (12–14). The MRES of **12–14** around the 0_0^0 transition region of the $S_1 \leftarrow S_0$ excitation



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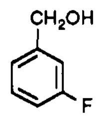

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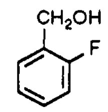


14

are presented in Figure 5, a, b, and c, respectively. The long vibrational progression observed in the MRES of 4-fluorobenzyl alcohol (**12**) is due to the torsional mode of the CH_2OH group built on the origin at 37 076.5 cm^{-1}. The symmetry group of this molecule is the same as that of **1**, and only odd overtones of the torsional mode(s) should be observed. The torsional energy spacings for **12** increase slightly (~10%; see Table VII) with respect to those of **1**. The progression seen in the MRES of **12** and the relative intensity distribution of the torsional bands indicate that a geometry displacement occurs along the torsional angle coordinate $\tau(C_{ortho}-C_{ipso}-C_\alpha-O)$ between the ground and excited state.

3-Fluorobenzyl alcohol (**13**) belongs to the same symmetry group as that of 3-methylbenzyl alcohol (**10**), and thus the CH_2OH torsional motion in **13** is also totally symmetric. The fundamental of this mode is observed in the MRES at 49 cm^{-1}, almost twice that of **1** (see Table VII). The potential barrier in S_1 increases

Table VII. Experimental Torsional Energy Levels (in cm^{-1}) of the CH_2OH Group in the S_1 State of Benzyl Alcohol, 4-Fluorobenzyl Alcohol, 3-Fluorobenzyl Alcohol, and 2-Fluorobenzyl Alcohol

ν	benzyl alcohol	4-fluorobenzyl alcohol	3-fluorobenzyl alcohol	2-fluorobenzyl alcohol
T^1	(25.3)[a]	(28.3)	48.8	15.3
T^2	50.6	56.5	94.9	37.5
T^3	(73.8)	(84.2)	139.4	60.2
T^4	96.9	111.9		86.9
T^5		(138.5)		114.8
T^6		165.1		
T^7		(189.8)		
T^8		214.5		
T^9		(237.8)		
T^{10}		261.0		
T^{11}		(281.4)		
T^{12}		301.8		

[a] The values in parentheses are torsional energy levels not observed due to selection rules.

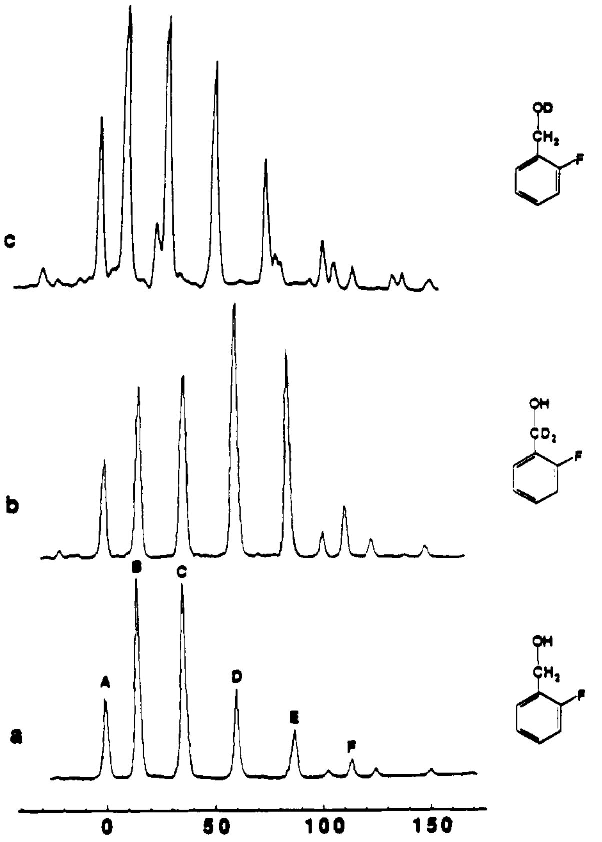


Figure 6. MRES of (a) 2-fluorobenzyl alcohol (**14**), (b) 2-fluorobenzyl-α,α-d_2 alcohol (**15**), and (3) 2-fluorobenzyl alcohol-*O*-*d* (**16**) around the 0_0^0 region. The origins occur at 37 595.7 cm^{-1} for 2-fluorobenzyl alcohol, 37 597.9 cm^{-1} for 2-fluorobenzyl-α,α-d_2 alcohol, and 37 608.5 cm^{-1} for 2-fluorobenzyl alcohol-*O*-*d*. No isotope shift is observed for 2-fluorobenzyl alcohol-*O*-*d*.

due to the substitution of a fluorine atom at meta position: electronic effects are probably the cause of the barrier increase upon fluorine meta substitution. This observation will be discussed in detail in the Discussion section.

Table VIII. Positions of the Features of 2-Fluorobenzyl Alcohol, 2-Fluorobenzyl-α,α-d_2 Alcohol, and 2-Fluorobenzyl Alcohol-*O*-*d*

	$\nu - \nu(0_0^0)$ (cm^{-1})		
ν[a]	2-fluorobenzyl alcohol	2-fluorobenzyl-α,α-d_2 alcohol	2-fluorobenzyl alcohol-*O*-*d*
A	0(37 595.7)[b]	0(37 597.9)[b]	0(37 608.5)[b]
B	15.3	15.8	12.2
C	37.5	37.3	31.5
D	60.2	61.3	54.2
E	86.9	86.2	77.7
F	114.8	113.2	104.3

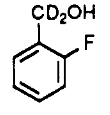
[a] A through F are the notation for the observed vibronic features in each molecule (see Figure 6). [b] Position of origin transition.

Table IX. Experimental Torsional Energy Levels (in cm^{-1}) of the CH_2OH Group in the S_1 State of Benzyl Alcohol and 2- and 3-Aminobenzyl Alcohol

ν	benzyl alcohol	3-aminobenzyl alcohol	2-aminobenzyl alcohol
T^1	(25.3)[a]	57.7	87.2
T^2	50.6	101.4	173.3
T^3	(73.8)	140.9	258.9

[a] The values in parentheses are torsional energy levels not observed due to selection rules.

As presented in Figure 5c, the MRES of 2-fluorobenzyl alcohol (**14**) is considerably different from the MRES of its isomers, **12** and **13**. As shown in Table VII, the energy of the torsional mode of **14** is reduced by about a factor of 2 with respect to that of **12**. Further, the torsional energy levels of **14** are not harmonic. Two possible explanations can be considered for this difference. First, substitution of a fluorine atom at the ortho position of benzyl alcohol could reduce the potential barrier for the torsional mode of the CH_2OH group. Generally, nonalkyl ortho-substituted rotor systems have relatively low potential barriers in the excited state.[10,12,18,19] The results for the deuteriated molecule **15**, however, exclude this explanation. Figure 6 (a and b) and Table VIII compare the low-frequency mode of **14** with that of **15**. The energy levels of this mode in both molecules are the same, confirming that the low-frequency mode of 2-fluorobenzyl alcohol observed in the spectrum is not due to the torsional motion of the entire CH_2OH group. The low-frequency mode in 2-fluorobenzyl alcohol is thus not of the same nature as that in the other fluoro-substituted benzyl alcohols.



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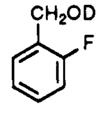
Second, a different motion, not related to the CH_2OH torsion appropriate for the other substituted benzyl alcohols, could be responsible for the observed spectrum of **15**. This could be a low-frequency mode related to the movement of the hydroxyl group alone. This possibility would predict the observation of an isotope effect if the hydrogen of the hydroxyl proton is exchanged by a deuteron (OH → OD). Comparison of the low-energy mode of **16** with that of **14** is shown in Figure 6 (a and c) and Table VIII.



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The isotope effect on this low-energy mode of 2-fluorobenzyl alcohol is ca. 10%, too large for the mode to be due to the motion of the entire CH_2OH group, but too small for the mode to be due entirely to motion of the hydroxyl hydrogen atom alone. Thus, the observed progression[29,30] is probably associated with librational motion of the OH group coupled with H-atom oscillation in the O—H···F bond.[31-33] A hindered rotor model for OH rotation about the C_α–O bond using parameters of $B = 17.0$ cm^{-1} and any V_1 term fails to reproduce the energy levels. The relative intensity distribution in the MRES of **14** suggests that a geometry dis-

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(29) Seeman, J. I.; Grassian, V. H.; Bernstein, E. R. *J. Am. Chem. Soc.* **1988**, *110*, 8542.

(30) Grassian, V. H.; Bernstein, E. R.; Secor, H. V.; Seeman, J. I. *J. Phys. Chem.* **1990**, *94*, 6691.

(31) Crowder, G. A. *J. Fluorine Chem.* **1979**, *13*, 77.

(32) Schaefer, T.; Parr, J. E. *J. Chem. Phys.* **1976**, *65*, 1197.

(33) Hansen, K.-V.; Pedersen, T. *J. Mol. Struct.* **1983**, *97*, 311.

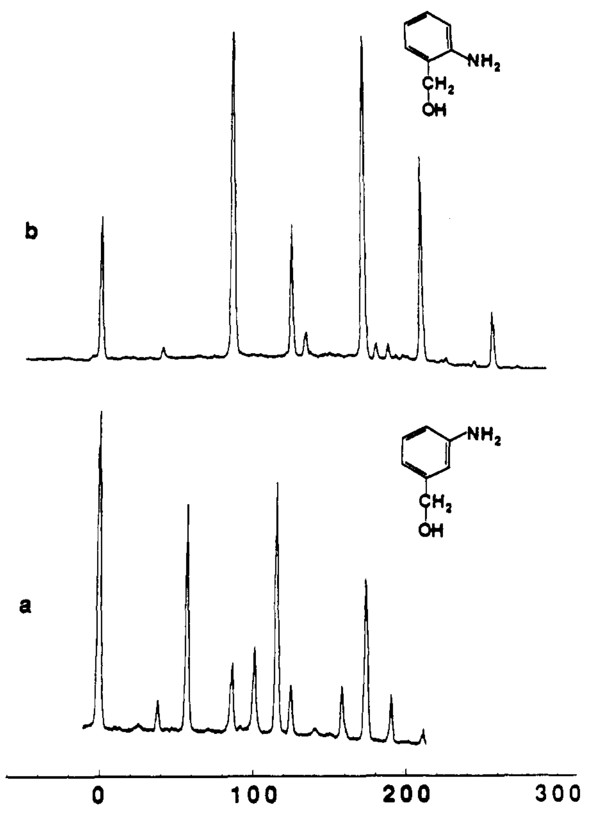
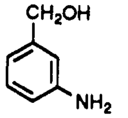


Figure 7. MRES of the 0_0^0 region of the $S_1 \leftarrow S_0$ transition of jet-cooled (a) 3-aminobenzyl alcohol (**17**) and (b) 2-aminobenzyl alcohol (**18**). The origins occur at 33 389.9 cm^{-1} for 3-aminobenzyl alcohol and 33 308.4 cm^{-1} for 2-aminobenzyl alcohol. The two molecules show different patterns for the torsional progression.

placement along the OH···F bond occurs during excitation from S_0 to S_1.

E. 3- and 2-Aminobenzyl Alcohols (17 and 18). Figure 7a presents the MRES of jet-cooled 3-aminobenzyl alcohol (**17**) about the 0_0^0 region of the $S_1 \leftarrow S_0$ transition. The spectrum contains an intense progression due to the CH_2OH torsional mode built on the origin at 33 389.9 cm^{-1}. The torsional mode of this molecule is totally symmetric and thus the fundamental is observed. The mode has a fundamental energy of 54 cm^{-1}, which is about two times larger than that of **1** (see Table IX). The potential barrier thus increases due to substitution of the amino group at the meta position.



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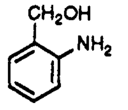

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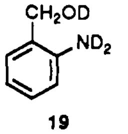
Figure 7b depicts the MRES of jet-cooled 2-aminobenzyl alcohol (**18**) around the 0_0^0 region of the $S_1 \leftarrow S_0$ transition. The origin occurs at 33 308.4 cm^{-1} with an accompanying vibrational progression. This progression is confirmed to be due to the torsional motion of the entire CH_2OH group, unlike the case of 2-fluorobenzyl alcohol (cf. section II.D above), based on the results of experiments on 2-amino-d_2-benzyl alcohol-*O-d* (**19**).[34] The MRES of **18** and **19** are nearly identical[34] and evidence only small isotopic shifts. The torsional energy spacings for **18** are larger by a factor of 3.5 than those of **1** (see Table IX). The relative intensity distribution of the torsional progression indicates that a geometry displacement occurs along the torsional angle coordinate $\tau(C_{ortho}–C_{ipso}–C_\alpha–O)$ between the ground and excited state.



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III. Discussion

A. The Benzyl Alcohol Conformation. The geometry of the minimum energy conformation(s) of these benzyl alcohols can, in principle, be established by comparing the number of 0_0^0 transitions observed in their MRES with the number of origin transitions predicted on the basis of "structural logic". As summarized in Table II for each substrate examined in this study, this structural logic involves both symmetry and potential energy considerations. For the asymmetrically substituted benzyl alcohols, these features are used to maximum advantage by creating (in principle) situations in which multiple conformations can have nearly equal stability and hence nearly equal population.

One origin is observed for benzyl alcohol (**1**), benzyl-α,α-d_2 alcohol (**6**), and benzyl alcohol-*O-d* (**7**), and thus only one stable conformation exists for these three compounds; in the stable conformer, $\tau_1 = \tau(C_{ortho}–C_{ipso}–C_\alpha–O)$ can be only one of those illustrated in Chart I: planar **2**, perpendicular **3**, or gauche **4**.

Since $\tau(C_{ortho}–C_{ipso}–C_\alpha–C_\beta)$ for the ethyl group of ethylbenzene is known to be 90° (i.e., perpendicular to the plane of the ring),[10,11] the presence of the ethyl substituent in 4-ethylbenzyl alcohol (**8**) will result in two stable conformations if $\tau(C_{ortho}–C_{ipso}–C_\alpha–O) \neq 0°$ and in one stable conformation if $\tau(C_{ortho}–C_{ipso}–C_\alpha–O) = 0°$. Since 4-ethylbenzyl alcohol displays two 0_0^0 transitions, the CH_2OH fragment must be out of the plane of the benzene ring. The perpendicular **3** and gauche **4** conformations can be distinguished by examining 3-substituted benzyl alcohols. The presence of a substituent (e.g., methyl, amino, fluoro) at the 3-position of benzyl alcohol will result in one stable ground-state conformation for the CH_2OH moiety if $\tau(C_{ortho}–C_{ipso}–C_\alpha–O) = 90°$ but in two conformations if $0° < \tau(C_{ortho}–C_{ipso}–C_\alpha–O) < 90°$ (i.e., gauche).

The MRES of 3-methyl-, 3-fluoro- and 3-aminobenzyl alcohols each display a single origin transition (see Figures 4b, 5b, 7a, and Table II). Hence only one stable ground-state conformation exists for these three compounds. These results, taken together, indicate that for ortho-unsubstituted benzyl alcohols, the heavy atoms in the $(C_{ipso}–C_\alpha–O)$ fragment are perpendicular to the plane of the benzene ring; i.e., $\tau(C_{ortho}–C_{ipso}–C_\alpha–O) = 90°$.

Comparison of the three systems which have the same heavy atom substructure **5**, namely, Ar–X–Y (ethylbenzene, benzyl alcohol, and methoxybenzene), proves to be quite interesting. (Note that these compounds have only two heavy atoms in the aromatic substituent.) Laser jet spectroscopy has now demonstrated that both the Ph–C–C[10,11] and Ph–C–O substructures have $\tau(C_{ortho}–C_{ipso}–C_\alpha–Y_\beta) = 90°$, while $\tau(C_{ortho}–C_{ipso}–O_\alpha–C_\beta) = 0°$ for the methyl phenyl ether substructure.[14,15] Apparently, in these contrasting cases, the ground-state energy minimum for one substructure is the ground-state energy maximum for the other, and vice versa. This structural change is associated with a balancing of steric and electronic factors. The planar conformation is destabilized by nonbonded interactions between $C_{ortho}–H_{ortho}$ atoms and Y_β, while these nonbonded interactions are minimized for the perpendicular conformation. On the other hand, the oxygen lone-pair electrons stabilize the planar conformation of methoxybenzenes due to overlap with the aromatic π-system. No such significant stabilization is found between the lone-pair electrons on the benzyl alcohol oxygen and the aromatic system.

The above "structural logic" applied to the determination of para and meta ring substituent conformation and geometry must be applied with great caution for cases having ortho substitution. Because of possible steric and/or electronic effects, ortho substitution can drastically modify or control conformational preferences.[35-36] Three different 2-substituted benzyl alcohols were

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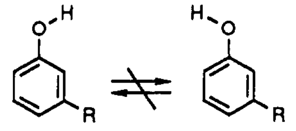
[34] Seeman, J. I.; Secor, H. V.; Im, H.-S.; Bernstein, E. R. *J. Am. Chem. Soc.* **1990**, *112*, 7073.

[35] (a) Berg, U.; Liljefors, T.; Roussel, C.; Sandström, J. *Acc. Chem. Res.* **1985**, *18*, 80. (b) Berg, U.; Sandström, J. *Adv. Phys. Org. Chem.* **1989**, *25*, 1.

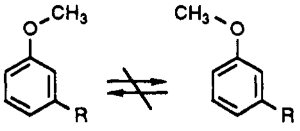
examined in this study: 2-methyl-, 2-fluoro-, and 2-aminobenzyl alcohol. The MRES of these three are quite different from each other (compare Figures 4c, 5c, and 7b). Because of the unique properties of each of these substituents, each one can interact differently with the CH_2OH functionality.

As described above, the progression in the MRES of 2-fluorobenzyl alcohol (**14**) (Figure 6a) is *not* due to rotation of the hydroxyl group about the C_{ipso}–C_{α} bond, since the MRES of the deuteriated analogue **15** is identical with that of **14**. Importantly, the MRES of the –OD analogue **16** shown in Figure 6c indicates significant isotope effects, strongly suggesting that these transitions are due to oscillatory motion of H(D) in the O—H···F (O—D···F) hydrogen bond. Unlike the suggestion that **14** exists in three conformations based on microwave spectroscopy,[33] our results are consistent with the existence of only a single stable ground-state conformation. Intramolecular CH_2—OH···F and π-electron hydrogen bonding in **12**–**14** differs significantly in the S_0 and S_1 electronic states. The observed spectroscopic transitions in the MRES of **12**–**14** reflect a displacement in the stable minimum energy conformations of these molecules in S_0 compared to S_1.

B. Determination of the O–H Bond Orientation. The doublet origin in 3-methylbenzyl alcohol could be interpreted as due to either the rotational isomers of the hydroxy group (Chart II) or methyl torsional transitions. In order to distinguish between these alternatives, 3-fluorobenzyl alcohol is examined by MRES. The energy difference for the two 0_0^0 transitions of 3-fluoro-substituted isomers is found to be quite large, in general. For example, this separation is ~210 cm^{-1} for 3-fluorophenol[37] (**20**) versus ~110 cm^{-1} for 3-methylphenol[38] (**21**), and ~157 cm^{-1} for 3-fluoroanisole[39] (**22**) versus ~60 cm^{-1} for 3-methylanisole (**23**).[15] One can expect, therefore, that for 3-fluorobenzyl alcohol, the separation of two theoretically possible O–H rotamer origins would be much larger than that found for 3-methylbenzyl alcohol (~2 cm^{-1}; see Table VI) *if* the two origin features are due to OH rotational isomers. The observation of only one origin in the MRES of 3-fluorobenzyl alcohol, however, excludes the possibility of the OH rotational isomer. This origin structure for 3-methylbenzyl alcohol must then be caused by methyl rotor torsional motion. This is consistent with other 3-methyl-1-substituted benzenes.[11,12,18]



20, R = F
21, R = CH_3



22, R = F
23, R = CH_3

The question still remains whether laser jet spectroscopy can determine the conformational preference of the hydroxy proton, i.e., unambiguously establish $\tau_2 = \tau(C_{ipso}–C_{\alpha}–O–H)$ as depicted in **1** and in Chart II. In all the cases examined and described above, we have not been able to assign multiple 0_0^0 transitions due to τ_2-conformational isomers. These results lead one to suggest that the hydroxyl hydrogen is symmetric (either anti or eclipsed) with respect to the aromatic ring. This is further supported by the investigation of 2-methylbenzyl alcohol (**11**). The mass resolved excitation spectrum of **11** shows only one origin (see Figure 4c).

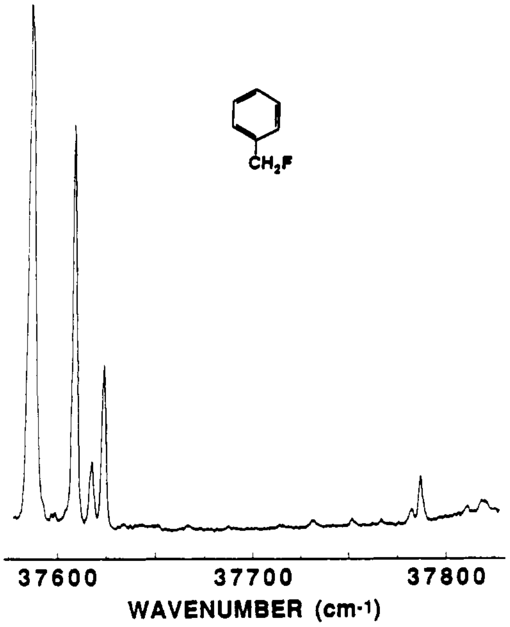
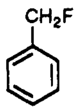


Figure 8. MRES around the 0_0^0 region of $S_1 \leftarrow S_0$ for jet-cooled benzyl fluoride (**24**). The torsional vibrational progression of the fluoromethyl group is observed built on the 0_0^0 transition at 37 387.1 cm^{-1}. Although the internal rotational constant is very similar to that for benzyl alcohol, the torsional energy spacings are half those of benzyl alcohol, suggesting a reduced substituent π-system interaction (see text).

The rotational barrier for the OH group in ethanol is known to be ~350 cm^{-1}.[40] This barrier in benzyl alcohol is almost certainly higher than 350 cm^{-1}, and thus the hydrogen atom appears to be in a relatively fixed position. The results of MOPAC calculations using an AM1 Hamiltonian agree with the above expectation, in that the calculated rotational barrier is ~500 cm^{-1}; a minimum is found at ca. $\tau_2 = 60°$. AM1 calculations have been reported to account for hydrogen bonding[41,42] and have recently been used for various hydroxy- and methoxy-substituted anisoles.[43] Since the experimental results which suggest that the OH hydrogen atom is in a symmetrical position (anti or eclipsed) is based on negative evidence, we tentatively conclude that the hydrogen atom is pointed toward the ring.

C. Potential Energy Barrier for CH_2OH Rotation. The potential energy barrier for the CH_2OH group rotation in benzyl alcohol can be thought of as arising from two main sources: a repulsive interaction of the CH_2OH group with the ortho ring hydrogens and an internal hydrogen-bonding interaction between the OH group and π-electron system. A 2-fold potential V_2 thus obtains. Based on the substituent effect on this torsional motion, one can suggest that OH/π hydrogen bonding should be the major contributor to the potential barrier.

This suggestion is further supported by the spectrum of benzyl fluoride (**24**), shown in Figure 8. Benzyl fluoride has almost the same rotational constant as benzyl alcohol, but no hydrogen bonding. The MRES of benzyl fluoride is similar to that of benzyl



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alcohol, with the major difference being the spacing of the observed torsional motion progression: the torsional energy level spacings in S_1 of benzyl fluoride are reduced by almost a factor of 2 with respect to those of benzyl alcohol. This observation thereby confirms that the internal hydrogen-bonding interaction in benzyl alcohol has a significant contribution to the potential barrier for the torsional motion.

Because the MRES of benzyl fluoride (**24**) is very similar to that found for benzyl alcohol (**1**), it is tempting to speculate that these two compounds have similar conformations, i.e., $\tau(C_{ortho}-C_{ipso}-C_\alpha-O) = \tau(C_{ortho}-C_{ipso}-C_\alpha-F) = 90°$. Brownlee and Craik reported significant temperature dependence of the ^{19}F NMR chemical shift of a series of 4-substituted benzyl fluorides and related those observations to a variable proportion of planar and perpendicular conformations ($\tau = 0°$ and $\tau = 90°$, respectively).[44] These investigators also performed STO-3G ab initio calculations on these systems and found very small differences in energy between these two conformations. They concluded that, for benzyl fluoride, the perpendicular conformation is preferred over the planar conformation by 0.7 kcal mol^{-1}; gauche conformations were not evaluated.[44]

More recently, Schaefer et al. have concluded that **24** exists in a perpendicular conformation in solution phase, although their calculations suggested that the planar form was preferred in the gase phase.[45] Previously, Schaefer, Sebastian, and Penner reported that for benzyl chloride, $\tau(C_{ortho}-C_{ipso}-C_\alpha-Cl) = 90°$ based on both NMR studies and STO-3G calculations.[46,47]

D. Substituent Effect on the Torsional Mode. 1. Methylbenzyl Alcohols. Results of the CH_2OH group torsional mode study for methyl-substituted benzyl alcohol systems show that the methyl substituent at either the 4- or 3-position has little effect on the potential barrier for this motion, and does not cause a large S_0/S_1 geometry displacement. Moreover, the methyl-free rotor does not couple to the CH_2OH group torsional mode for either substitution.

These observations imply that the 3- and 4-methyl substituent have only a small interaction with the ring π-electron system. 2-Methylbenzyl alcohol probably has a high potential barrier due to steric hindrance. The same trend is observed for the substituent effects on the methyl-free rotor in *o*-ethyl-substituted toluenes.[10]

2. Fluorobenzyl Alcohols. The potential barrier for the CH_2OH torsional motion of 4-fluorobenzyl alcohol is almost the same as that for benzyl alcohol. The relative intensity pattern of the torsional mode progression, however, indicates that a geometry displacement occurs for S_1 with respect to S_0. Spacings for the torsional motion of 3-fluorobenzyl alcohol are about twice as large as those for benzyl alcohol. The potential barrier, therefore, increases by at least a factor of 2 in 3-fluorobenzyl alcohol compared to 4-fluorobenzyl alcohol. The barrier is much greater for 2-fluorobenzyl alcohol: the CH_2OH torsional mode is not observed for 2-fluorobenzyl alcohol but instead has been replaced by oscillatory motion of the OH group coupled to H-atom motion in the O—H···F hydrogen bond.

Because of its high electronegativity, fluorine is known to have a large electron-withdrawing inductive effect on an aromatic ring. Consequently, the π-electron density at the meta carbon atom (with respect to the fluorine atom) is enhanced with respect to that at the ortho or para carbon atoms. Localization of π-electron density at the meta carbon atoms is further enhanced by π-electron excitation ($S_1 \leftarrow S_0$), as indicated by CNDO/s calculations for fluorobenzene.[48,49]

The observed geometry displacement in 4-fluorobenzyl alcohol and increase in potential barrier for the torsional motion of 3-fluorobenzyl alcohol must be due to the inductive interaction of the fluorine atom with the aromatic system. This interaction changes the direction and/or the strength of internal hydrogen bonding between the hydroxyl hydrogen of the CH_2OH group and the π-system of the ring. In 2-fluorobenzyl alcohol, fluorine provides the molecule with an additional hydrogen-bonding site for the hydroxyl hydrogen. This fluorine/hydrogen interaction is strong enough to change the nature of the observed motion from a CH_2OH torsional motion to OH/O—H···F coupled motion. The position of the fluorine substituent on the ring thus has a substantial effect on the torsional barrier for the CH_2OH motion.

3. Aminobenzyl Alcohols. The amino group, like fluorine, is known to have a strong interaction with the aromatic ring.[50] The experimental results suggest that the substituent effect for the amino group is similar to that for the fluorine atom: both substituents double the energy level spacings for the meta compounds with respect to those for unsubstituted benzyl alcohol. The ortho substituent effect is probably composed of both electronic and steric effects for the amino group.

IV. Conclusions

Supersonic jet mass resolved excitation spectroscopic techniques are capable of resolving the origins of individual stable conformations of a number of benzyl alcohols. A comparison of the number of origins observed in the excitation spectra to that predicted by "structural logic" (basically symmetry arguments) allows the experimental determination of the perpendicular conformation **3** as the most stable conformation of ortho-unsubstituted benzyl alcohols.

Potential energy barriers for the low-frequency torsional mode of the CH_2OH group in benzyl alcohol in both the ground and excited state are determined using supersonic jet laser spectroscopy and hindered rotor model calculations. Internal hydrogen bonding between the hydroxyl hydrogen and aromatic π-system in benzyl alcohol is an important source of the potential barrier for the CH_2OH group torsional mode. The CH_2OH torsion experiences an increased barrier by more than a factor of 2 upon $S_1 \leftarrow S_0$ electronic excitation.

A methyl substituent either meta or para to the CH_2OH moiety does not change the potential barrier (as expected) because the methyl substituent does not have a large effect on the π-electron system of the ring. On the other hand, changes in the torsional mode upon $S_1 \leftarrow S_0$ excitation are observed for fluorobenzyl alcohol systems: the equilibrium geometry changes, the potential barrier changes, and the character of the low-frequency mode changes as a function of the position of the fluorine on the ring. These differences are due to the strong interaction of fluorine with the π-electron system of the ring and the OH hydrogen atom. Similar behavior is found for the amino-substituted benzyl alcohols: the potential barrier increases due to interaction of the amino group with the π-electron system of the ring and steric hindrance. The similar MRES of benzyl alcohol and benzyl fluoride suggest that the most stable conformation of the latter is also the perpendicular conformation.

V. Experimental Procedures

The pulsed supersonic jet apparatus is described elsewhere.[51] Samples are heated to 60 °C in the head of an R.M. Jordan pulsed valve to obtain sufficient vapor pressure and are expanded with He or a He/10% Ar mixture. The gaseous mixture is expanded at ca. 50 psig into a vacuum chamber ($\sim 1 \times 10^{-6}$ Torr) through a 0.7-mm diameter orifice.

MRES are obtained by monitoring the selected ion mass with a microchannel plate detector. To establish that the major peaks were not saturated, the main vibronic features in each spectrum were checked for relative intensity by varying the laser power. The ion current is averaged by a boxcar averager (Stanford Research Systems) and stored in a computer. The exciting and ionizing photons are obtained by mixing the doubled output of an LDS 698 dye laser pumpsed by a Nd^{3+}/YAG laser with the residual 1.064-μm photons from the Nd^{3+}/YAG laser.

Benzyl alcohol, 2-, 3-, and 4-methylbenzyl alcohol, 2-, 3-, and 4-fluorobenzyl alcohol, and 2- and 3-aminobenzyl alcohol were purchased

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from Aldrich. Benzyl fluoride was obtained from Pfaltz and Bauer. Partially deuteriated 2-fluorobenzyl alcohol and partially deuteriated 2-aminobenzyl alcohol were synthesized by H/D exchange with D_2O. All samples were used as obtained without additional purification.

Benzenemethan-*d*$_2$-ol (Benzyl-α,α-*d*$_2$ Alcohol) (6). Preparation of this material was performed following the literature report[52] by reducing methyl benzoate with lithium aluminum deuteride in ether to give **6** in 55% yield: ^{1}H NMR ($CDCl_3$) δ 2.85 (br s, 1 H), 7.2–7.4 (m, 5 H); ^{13}C NMR ($CDCl_3$) δ 64.27 (quintet, $J = 21.76$ Hz), 127.08, 127.52, 128.40, 140.73.

2-Fluorobenzyl-α,α-*d*$_2$ Alcohol (15). The procedure used to prepare **6** was followed using ethyl 2-fluorobenzoate to give **15** (42%) as a colorless oil, bp 40 °C (0.02 mmHg): ^{1}H NMR ($CDCl_3$) δ 4.15 (br s, 1 H), 7.02 (t, 1 H, $J = 7.1$ Hz), 7.17 (t, 1 H, $J = 7.6$ Hz), 7.26–7.29 (m, 1 H), 7.31–7.32 (m, 1 H); ^{13}C NMR ($CDCl_3$) δ 57.83 (doublet of quintet, $J = 22.2$, 4.3 Hz), 114.89 (d, $J = 0.27$ Hz), 122.88, 129.00, 123.97, 160.25, 160.25 (d, $J = 3.26$ Hz). HRMS: calcd for $C_7H_5D_2FO$, *m/z* 128.0605; found, *m/z* 128.0606.

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Effect of Substituents on the Gas-Phase Acidity of Silanols

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Abstract: Eighteen siloxide ions have been prepared by the gas-phase reactions of various silanes with hydroxide. These siloxide ions have then been selected by using tandem flowing afterglow–selected ion flow tube (FA-SIFT) techniques and used to determine the gas-phase acidities (ΔG°_{acid}) of the corresponding silanols. Such determinations for the simple silanols studied herein are impossible in solution because of facile condensation reactions. A variety of substituents on silicon have been studied, including alkyl, hydrogen, phenyl, methoxy, fluoro, and chloro substituents. Alkyl groups decrease silanol acidity, in contrast to alkyl group effects in alcohols. Phenyl, methoxy, fluoro, and chloro substituents all lead to increased acidity for silanols. The gas-phase acidity of trichlorosilanol is comparable to that of HBr and HNO_3. Polarizabilities and inductive effects are used to explain the substituent effects in these silanols. In addition, the heat of formation of trifluorosilanol has been estimated.

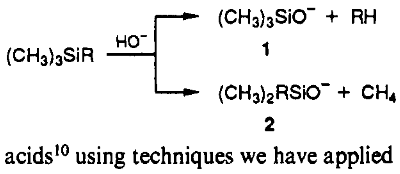
Introduction

The acidities of variously substituted silanols have been studied in solution in some detail, demonstrating (1) that silanols are considerably more acidic than their carbon analogues, (2) that they extensively hydrogen-bond, and (3) that aryl groups increase acidity, while steric hindrance has no effect.[1] Silicon substitution increases not only the acidity of an adjacent O–H but also that of the N–H, P–H, and S–H groups of amines, phosphines, and sulfides.[1] A major limitation of solution studies, however, is that simple substituent effects cannot be probed because unhindered silanols condense so rapidly to disiloxanes (eq 1).[2] Thus, despite their fundamental importance, simple substitution effects on silanol acidity have not been studied.

$$R_3SiOH + R_3SiOH \rightarrow R_3SiOSiR_3 + H_2O \qquad (1)$$

Pioneering work by Brauman and Blair has demonstrated that the order of gas-phase acidities can be quite different from that in solution.[3,4] The normal solution ordering for alcohols in protic solvents is $CH_3OH > CH_3CH_2OH > (CH_3)_2CHOH > (CH_3)_3COH$; in the gas phase, however, this order is reversed. Similarly, the acidity ordering for methyl-substituted amines in solution is different from that in the gas phase.[5] It has been suggested that in the gas phase negative charge is stabilized by dispersion (polarizability) effects to a greater extent than it is destabilized by inductive effects.[4] The reverse solution ordering then results from a combination of solvent effects. Polarizability effects are the most important determinant of the gas-phase acidities of amines[5] and alkanes[6] as well.

Because of our interests in gas-phase acidities[6–8] and in organosilicon chemistry,[9] questions about the gas-phase acidities of silanols naturally arise. Since unhindered silanols cannot be prepared in solution, gas-phase studies represent the only potential for acidity studies of silanols. The requirement of making a series of silanols is unnecessary in the gas phase, since we can easily prepare a series of siloxide ions (eq 2)[6] and study their protonation



$$(CH_3)_3SiR \xrightarrow{HO^-} \begin{cases} (CH_3)_3SiO^- + RH & \mathbf{1} \\ (CH_3)_2RSiO^- + CH_4 & \mathbf{2} \end{cases} \qquad (2)$$

by reference acids[10] using techniques we have applied widely.[9,11–13]

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