COPY

2

SECURI

AD-A221 815

NTATION PAGE

Form Approved
OMB No 0704-0188

1a RE	1b. RESTRICTIVE MARKINGS
2a SECURITY CLASSIFICATION AUTHORITY	3 DISTRIBUTION/AVAILABILITY OF REPORT Approved for public release; distribution unlimited.
2b DECLASSIFICATION/DOWNGRADING SCHEDULE Unclassified	
4 PERFORMING ORGANIZATION REPORT NUMBER(S) N00014-79-C-0647	5. MONITORING ORGANIZATION REPORT NUMBER(S)
6a NAME OF PERFORMING ORGANIZATION Colorado State University 6b OFFICE SYMBOL *(If applicable)*	7a. NAME OF MONITORING ORGANIZATION
6c. ADDRESS *(City, State, and ZIP Code)* Department of Chemistry Fort Collins, CO 80523	7b ADDRESS *(City, State, and ZIP Code)*
8a. NAME OF FUNDING/SPONSORING ORGANIZATION Office of Naval Research 8b. OFFICE SYMBOL *(If applicable)*	9 PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER N00014-79-C-0647
8c. ADDRESS *(City, State, and ZIP Code)* 800 North Quincy Street Arlington, VA 22217-5000	10. SOURCE OF FUNDING NUMBERS PROGRAM ELEMENT NO PROJECT NO. TASK NO WORK UNIT ACCESSION NO

11 TITLE *(Include Security Classification)*
"Supersonic Jet Studies of Benzyl Alcohols: Minimum Energy Conformations and Torsional Motion"

12 PERSONAL AUTHOR(S)
Hoong-Sun Im, E. R. Bernstein, Jeffrey I. Seeman, and Henry V. Secor

13a. TYPE OF REPORT Technical Report	13b TIME COVERED FROM ______ TO ______	14. DATE OF REPORT *(Year, Month, Day)* 1990, May, 13	15 PAGE COUNT

16 SUPPLEMENTARY NOTATION

17 COSATI CODES		
FIELD	GROUP	SUB-GROUP

18. SUBJECT TERMS *(Continue on reverse if necessary and identify by block number)*
benzyl alcohol, torsional motion, supersonic jet mass resolved excitation, spectroscopy, aminobenzyl alcohols, TOFMS, minimum energy conformation, benzyl fluoride

19 ABSTRACT *(Continue on reverse if necessary and identify by block number)*

SEE ATTACHED ABSTRACT

3 1990
E D

20 DISTRIBUTION/AVAILABILITY OF ABSTRACT
☒ UNCLASSIFIED/UNLIMITED ☐ SAME AS RPT ☐ DTIC USERS

21 ABSTRACT SECURITY CLASSIFICATION
Unclassified

22a NAME OF RESPONSIBLE INDIVIDUAL
Elliot R. Bernstein

22b TELEPHONE *(Include Area Code)*
(303) 491-6347

22c OFFICE SYMBOL

DD Form 1473, JUN 86 Previous editions are obsolete SECURITY CLASSIFICATION OF THIS PAGE

S/N 0102-LF-014-6603

OFFICE OF NAVAL RESEARCH

Contract N00014-79-C-0647

TECHNICAL REPORT #69

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

by

Hoong-Sun Im, E. R. Bernstein, Jeffrey I Seeman, and Henry V. Secor

Submitted to the

Journal of the American Chemical Society

Department of Chemistry
Colorado State University
Fort Collins, Colorado 80523

May 13, 1990

Reproduction in whole or in part is permitted for any purpose of the United States Government.

This document has been approved for public release and sale; its distribution is unlimited

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

Hoong-Sun Im,[†] **E. R. Bernstein,**[*†] **Jeffrey I. Seeman,**[*‡] **and Henry V. Secor**[‡]

Contribution from the Department of Chemistry, Condensed Matter Sciences Laboratory, Colorado State University, Fort Collins, Colorado 80523, and the Philip Morris Research Center, P.O. Box 26583, Richmond, Virginia 23261

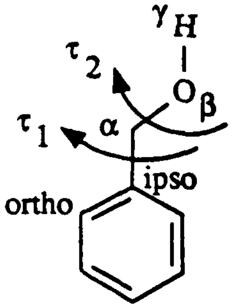
Abstract: Supersonic jet mass resolved excitation spectroscopy is employed to determine the minimum energy conformations of benzyl alcohol and a series of nine methyl-, ethyl-, fluoro-, and aminobenzyl alcohols. The interpretation of the time-of-flight mass spectra (TOFMS) of these molecules leads to 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 unemcumbered 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 the ground state and $V_2 = -330$ cm^{-1} and $V_4 = -3$ cm^{-1} for the excited state with a CH_2OH rotational constant of 0.52 cm^{-1} for both states.

[illegible]

Similar potential barriers are observed for methyl-substituted benzyl alcohols. The potential energy barrier 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 TOFMS of benzyl fluoride is very similar to that found for benzyl alcohol, suggesting that the conformations of the two compounds is similar, e.g., $\tau(C_{ortho}-C_{ipso}-C_{\alpha}-F) = 90^{\circ}$.

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-II).

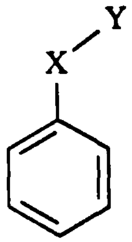


1

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

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[8b] calculations result in a planar minimum energy conformation. 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).

Recently, the geometry of the minimum energy conformations of various substituted aromatic compounds which share the same heavy atom substructure as benzyl alcohol (c.f. 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 conformational assignment of the ethyl, propyl, methoxy, vinyl, and allyl substitutents, as shown in Table I.[10-16]



5

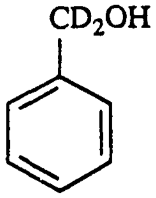
Supersonic jet laser spectroscopy has also been an important technique for the characterization of potential energy barriers and low frequency modes in various molecules (e.g., biphenyl[17], alkyl,[10-12,18] methoxy,[14,15] and fluoro[19] substituted toluenes). Studies of methyl torsional modes in aromatic 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 is almost the same as that of toluene itself, the potential barrier for 3-substituted toluenes increases significantly (especially for non-alkyl substituents), and the potential barrier for 2-substituted toluenes increases for alkyl substituents but decreases for non-alkyl 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.

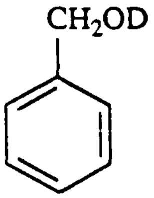
Spectroscopic studies of these systems are achieved through supersonic jet cooling and mass resolved excitation spectroscopy (time-of-flight mass spectroscopy - TOFMS).[21] Since each stable conformation of a molecule has a specific potential energy minimum in the ground state (S_0), the energy of the 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. Because the supersonic expansion process results in molecules at near 0 K, conformational interconversions which may occur rapidly at room temperature, or even at the lowest temperatures obtainable by DNMR, are stopped. Thus, the number of origins that are observed in the absorption (TOFMS) spectrum of a molecule corresponds to the number of stable conformations of that molecule.[22] 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. In order to determine the potential energy barrier for the CH_2OH group torsional mode, hindered rotor model calculations[23] 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 TOFMS 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. 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]



6



7

The TOFMS 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. Even though the isotope effect of the fourth peak is relatively small, it is unlikely to be an origin 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).

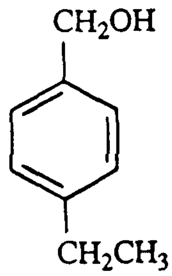
The TOFMS of **7** evidences no isotope shift when compared to that of benzyl alcohol, i.e., the positions of transitions A-D relative to the 0_0^0 transition are unchanged. Hence, the torsional motion must involve the entire CH_2OH moiety. Further, because of the symmetry of benzyl alcohol, this large amplitude, low frequency libration of the CH_2OH group should consist largely of oscillations 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_{ipso}, 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).[24] In this symmetry group, the above torsional mode does not belong to the same irreducible representation as any of the Cartesian coordinates, 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.[17,24]

Figure 2 presents the TOFMS of benzyl alcohol around the low energy side of the origin. 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 torsional bands in the excited state; features I and II are thus hot bands of the torsional mode.

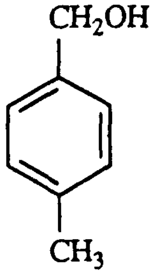
The potential for CH_2OH group rotation in **1** can be obtained by treating the system as a one-dimensional rigid rotor and diagonalizing the Hamiltonian in a basis set consisting of one-dimensional free rotor functions. Such an analysis has been carried out for the methyl groups of toluene,[10,12,18] 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 $B = 0.52\ cm^{-1}$, $V_2 = -330\ cm^{-1}$, $V_4 = -3.0\ cm^{-1}$ 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 TOFMS of **1** (transitions 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. This conclusion is consistent with the above potential surfaces for S_1 and S_0.

B. 4-Ethylbenzyl alcohol (8). The spectrum of 8 is shown in Figure 3. Two origins are identified, (36 992.0 and 36 999.5 cm^{-1}). The same vibronic features (B, C, and D) found in the spectrum of 1 are built upon both of these origins for 8. The data are collected in Table V. Since two 0_0^0 transitions are observed, 8 has two stable conformations in the ground state.

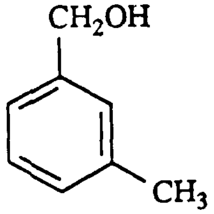


8

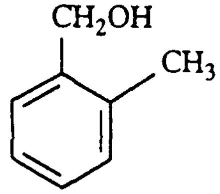
C. 4-, 3-, and 2-Methylbenzyl alcohols (9-11). The TOFMS of 9-11 are presented in Figures 4a, 4b, and 4c respectively. 4-Methylbenzyl alcohol (9) has the same symmetry group as 1 and thus only odd overtones of the CH_2OH torsional motion are observed. In the TOFMS of this system (Figure 4a), an intense torsional progression of the CH_2OH group is observed 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.



9



10

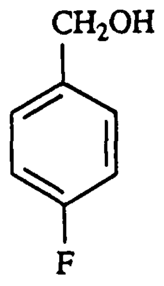


11

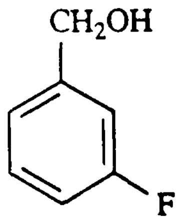
Figure 4b depicts the TOFMS of jet-cooled 3-methylbenzyl alcohol (**10**) around the origin of the $S_1 \leftarrow S_0$ transition. The symmetry group of this molecule is lower than the symmetry of **1** due to the substitution pattern, and thus the fundamental transition of the CH_2OH group torsional mode is allowed and is observed in the TOFMS of **10**. The origin band in this TOFMS possesses a doublet structure associated with methyl rotation, as is typically the case for meta 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 TOFMS 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 ortho 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 TOFMS of **11** indicates that τ_1 and τ_2 for this molecule are essentially the same in S_0 and S_1.

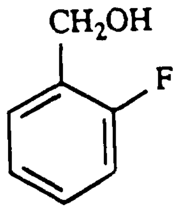
D. **4-, 3-, and 2-Fluorobenzyl alcohols (12-14)**. The TOFMS of **12-14** around the 0_0^0 transition region of the $S_1 \leftarrow S_0$ excitation are presented in Figures 5a, 5b, and 5c respectively. The long vibrational progression observed in the TOFMS of 4-fluorobenzyl alcohol (**12**) is due to 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 TOFMS of **12** and the relative intensity distribution of the torsional bands indicates that a geometry displacement occurs along the torsional angle coordinate $\tau(C_{ortho}\text{-}C_{ipso}\text{-}C_{\alpha}\text{-}O)$ between the ground and excited state.



12



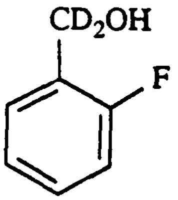
13



14

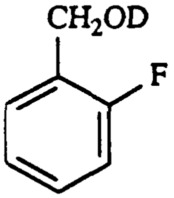
3-Fluorobenzyl alcohol (**13**) belongs to the same symmetry group as that of 3-methylbenzyl alcohol (**10**), and thus the CH_2OH torsional motion in **13** is also totally symmetric. The fundamental of this mode can be observed in the TOFMS of **13**. The fundamental frequency of this torsional motion is determined to be 49 cm^{-1}, almost twice that of **1** (see Table VII). The potential barrier increases due to the substitution of a fluorine atom at meta position.

As presented in Figure 5c, the TOFMS of 2-fluorobenzyl alcohol (**14**) is considerably different than the TOFMS 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 two 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, non-alkyl 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.



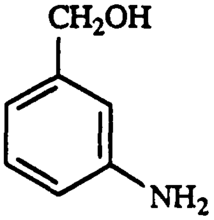
15

Secondly, 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 **12** is shown in Figure 6a and Figure 6c and Table VIII. 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 is probably associated with librational motion of the OH group coupled with H-atom oscillation in the O-H···F bond.[25-27] A hindered rotor model for OH rotation about 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 TOFMS of **14** suggests that a geometry displacement along the OH···F bond occurs during excitation from S_0 to S_1.

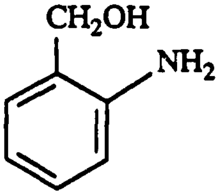


16

E. 3- and 2-Aminobenzyl alcohols (17-18). Figure 7a presents the TOFMS 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.



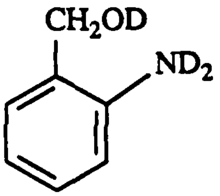
17



18

Figure 7b depicts the TOFMS 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 (c.f. Section IID above), based on the results of experiments on 2-aminobenzyl alcohol-d_3 (**19**). The TOFMS of **18** and **19** are nearly identical 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.



19

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 TOFMS 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 alcohol-α,α-d_2 (**6**), and benzyl alcohol-OD (**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).

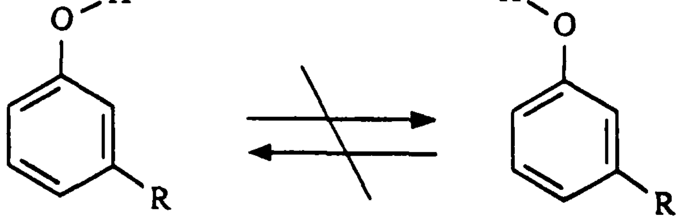
The TOFMS of 3-methyl-, 3-fluoro- and 3-aminobenzyl alcohols each display a single origin transition (see Figures 4b, 5b, 7a and Table II). Hence only one stable ground state conformation exists for these three compounds. These results, taken together, indicate that for ortho-unsubstituted benzyl alcohols, 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 $\tau(C_{ortho}-C_{ipso}-C_{\alpha}-Y_{\beta}) = 90^{\circ}$, while $\tau(C_{ortho}-C_{ipso}-O_{\alpha}-C_{\beta}) = 0^{\circ}$ for the methyl phenyl ether substructure.[14,15] Apparently, in these contrasting cases, the ground state energy minima for one substructure are the ground state energy maxima for the other, and visa 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. Due to possible steric and/or electronic effects, ortho substitution can drastically modify or control conformational preferences.[30-32] Three different 2-substituted benzyl alcohols were examined in this study: 2-methyl, 2-fluoro-, and 2-aminobenzyl alcohol. The TOFMS 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 TOFMS 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 the TOFMS of the deuteriated analogue **15** is identical to that of **14**. Importantly, the TOFMS 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,[29] 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 TOFMS of **12-14** reflect a displacement in the stable minimum energy conformations of these molecules in S_0 compared to S_1.

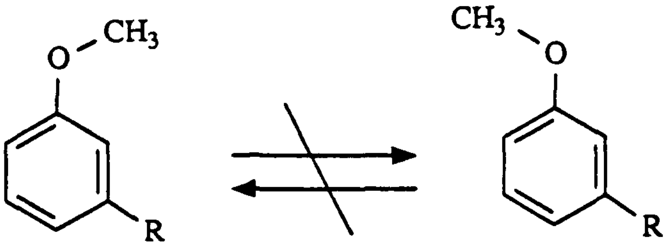
B. Determination of the O-H bond orientation. The doublet origin in 3-methylbenzyl alcohol could be interpreted as due to either the rotational isomers of the hydroxy group (Chart II) or methyl torsional transitions. In order to distinguish between these alternatives, 3-fluorobenzyl alcohol is examined by TOFMS. 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[33] (**20**) vs ~110 cm^{-1}



20, R = F

21, R = CH_3

for 3-methylphenol[34] (21); and ~157 cm^{-1} for 3-fluoroanisole[5] (22) vs ~60



22, R = F

23, R = CH_3

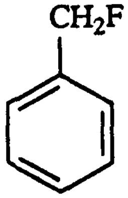
cm^{-1} for 3-methylanisole (**23**).[15] One can expect, therefore, that in 3-fluorobenzyl alcohol, the separation of two theoretically possible O-H rotamer origins would be much larger than that found for 3-methylbenzyl alcohol (~2 cm^{-1}, see Table VI) <u>if</u> the two origin features are due to OH rotational isomers. The observation of only one origin in the TOFMS 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]

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 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 conclusion 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).

The rotational barrier for the OH group in ethanol is known to be ~350 cm^{-1}.[36] 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 reasonably account for hydrogen bonding,[37,38] and have recently been used for various hydroxy- and and methoxy-substituted anisoles.[39] 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 two 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 fluroide (**24**), shown in Figure 8. Benzyl flouride has almost the same rotational constant as benzyl alcohol, but no hydrogen bonding. The TOFMS of benzyl fluoride is similar to that of benzyl 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 two 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.



24

Because the TOFMS 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., $\tau(C_{ortho}-C_{ipso}-C_{\alpha}-O) = \tau(C_{ortho}-C_{ipso}-C_{\alpha}-F) = 90^{\circ}$. 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 ($\tau = 0^{\circ}$ and $\tau = 90^{\circ}$, respectively).[40] 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.

More recently, Schaeffer et al. has concluded that **24** exists in a perpendicular conformation in solution phase, although his calculations suggested that the planar form was perferred in the gas phase.[41] Previously, Schaeffer, Sebastian and Penner reported that for benzyl chloride, $\tau(C_{ortho}-C_{ipso}-C_{\alpha}-Cl) = 90^{\circ}$ based on both NMR studies and STO-3G calculations.[42]

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 ortho 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 two 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 $O-H\cdots F$ hydrogen bond.

Due to 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.[43,44]

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.[45] 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 by the meta compounds with respect to those for unsubstituted benzyl alcohol. The ortho substituent effect is probably dominated by steric hindrance in 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 two 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 strong interaction of the amino group with the π-electron system of the ring and steric hindrance. The similar TOFMS 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.[46] 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.

TOFMS are obtained by monitoring the selected ion mass with a microchannel plate detector. 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 pumped by a Nd^{+3}/YAG laser with the residual 1.064 μm photons from the Nd^{+3}/YAG laser.

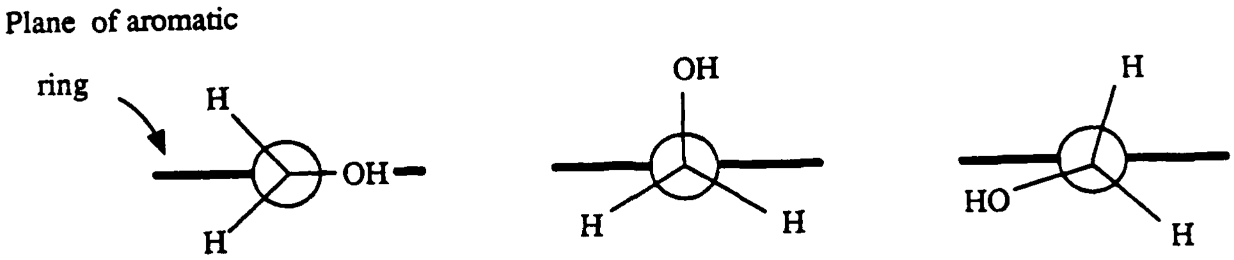
Benzyl alcohol, 2-, 3-, and 4-methylbenzyl alcohol, 2-, 3-, and 4-fluorobenzyl alcohol and 2- and 3-aminobenzyl alcohol are purchased from Aldrich. Benzyl fluoride was obtained from Pfaltz and Bauer. Partially deuteriated 2-fluorobenzyl alcohol and partially deuteriated 2-aminobenzyl alcohol are synthesized by H/D exchange with D_2O. All samples are used as obtained without additional purification.

Benzenemethan-d_2-ol (benzyl alcohol-d_2) (6). Preparation of this material was performed following the literature report[47] by reducing methyl benzoate with lithium aluminum deuteride in ether to give **6** in 55%: ^{1}H NMR ($CDCl_3$) δ 2.85 (br s, 1H), 7.2-7.4 (m, 5H); ^{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° (0.02 mmHg): ^{1}H NMR ($CDCl_3$) δ 4.15 (br s, 1H), 7.02 (t, 1H, *J* = 7.1 Hz), 7.17 (t, 1H, *J* = 7.6 Hz), 7.26-7.29 (m, 1H), 7.31-7.32 (m, 1H); ^{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.

Acknowledgment. We thank A. C. Lilly, B. LaRoy, and R. N. Ferguson for encouragement in and support of this effort and Professor T. Schaefer for helpful discussions and for sharing unpublished results. A portion of this work was supported in part by the ONR (to ERB).

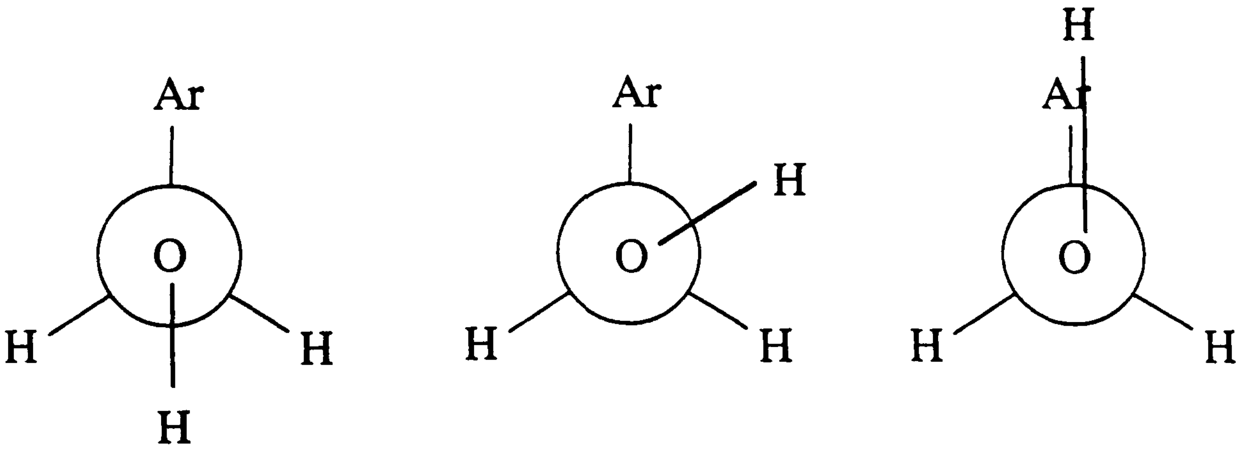
Chart I. Conformations of benzyl alcohols illustrated by rotation about $\tau_1 = \tau(C_{ortho}-C_{ipso}-C_{\alpha}-O)$.



planar perpendicular gauche

2 3 4

Chart II. Conformations of benzyl alcohols illustrated by rotation about $\tau_2 = \tau(C_{ipso}\text{-}C_{\alpha}\text{-O-H})$.



anti gauche eclipsed

References

[*] To whom correspondence should be addressed.

[†] Colorado State University.

[‡] Philip Morris Research Center.

(1) For the most recent publication on this subject and for a detailed list of references, see: Schaefer, T.; Sebastian, R.; Peeling, J.; Penner, G. H.; Koh, K. Can. J. Chem. **1989**, 67, 1015.

(2) For a preliminary report of some of these results, see: Seeman, J. I.; Secor, H. V.; Im, H.-S.; Bernstein, E. R. J. Chem. Soc., Chem. Commun. **1990**, 87.

(3) Schaefer, T.; Danchura, W.; Niemczura, W.; Parr, W. J. E. Can. J. Chem. **1978**, 56, 1721.

(4) Visser, T.; van der Maas, J. H. Spectrochim. Acta, Part A **1986**, 42A, 599.

(5) Traetteberg, M.; Østensen, H.; Seip, R. Acta Chem. Scand. **1980**, 34A, 449.

(6) Abraham, R. J.; Bakke, J. M. Tetrahedron **1978**, 2947.

(7) We thank Professor T. Schaefer for pointing out that for benzyl alcohol, ^6J has $\langle \sin^2\psi \rangle = 0.493$ in CS_2 at 300 K,[1] a value which is also consistent with essentially free rotation.

(8) (a) Hehre, W. J.; Radom, L.; Pople, J. A. J. Amer. Chem. Soc. **1972**, 94, 1496. (b) Ito, M.; Hirota, M. Bull. Chem. Soc., Jpn. **1981**, 54, 2093.

(9) Boul, A. D.; Meakins, G. D. J. Chem. Soc. **1974**, 1235.

(10) Breen, P. J.; Warren, J. A.; Bernstein, E. R.; Seeman, J. I. J. Am. Chem. Soc. **1987**, 109, 3453.

(11) Breen, P. J.; Bernstein, E. R.; Seeman, J. I. J. Chem. Phys. **1987**, 87, 3269.

(12) Breen, P. J.; Warren, J. A.; Bernstein, E. R.; Seeman, J. I. J. Chem. Phys. **1987**, 87, 1927.

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

(14) Seeman, J. I.; Secor, H. V.; Breen, P. J.; Bernstein, E. R. J. Chem. Soc., Chem. Commun. **1988**, 393.

(15) Breen, P. J.; Bernstein, E. R.; Secor, H. V.; Seeman, J. I. J. Am. Chem. Soc. **1989**, 111, 1958.

(16) Breen, P. J.; Bernstein, E. R.; Secor, H. V.; Seeman, J. I. J. Phys. Chem. **1989**, 93, 6731.

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

(18) Breen, P. J.; Warren, J. A.; Bernstein, E. R.; Seeman, J. I. J. Chem. Phys. **1987**, 87, 1917.

(19) Okyugama, K.; Mikami, N.; Ito, M. J. Phys. Chem. **1985**, 89, 5617.

(20) (a) Bakke, J. M.; Rønneberg, H.; Chadwick, D. J. Mag. Res. Chem. **1987**, 25, 251 and references cited therein. (b) For a recent excellent review on the related subject of $CH\cdots\pi$ interactions, see: Nishio, M.; Hirota, M. Tetrahedron **1989**, 45, 7201.

(21) The name "one (and two) color time of flight mass 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 ($S_0 \rightarrow S_1$). A second photon ν_2 subsequently ionizes those molecules in S_1 ($S_1 \rightarrow I^+$). 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 absorption spectrum of a mass selected species is obtained. This technique may also be called mass resolved excitation spectroscopy.

(22) Observation of a single origin transition in this work implies either (a) that only a single stable ground state conformation exists or (b) that one conformation is significantly more stable than the others, assuming there is no difference between the conformations' rate of cooling in the expansion gas.

(23) Lister, D. G.; MacDonald, J. N.; Owen, N. L. *Internal Rotation and Inversion*, Academic Press, New York: 1978.

(24) Buckner, P. R., *Molecular Symmetry and Spectroscopy*, Academic Press, New York: 1979.

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

(26) Grassian, V. H.; Bernstein, E. R.; Seeman, J. I.; Secor, H. V. *J. Phys. Chem*., submitted.

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

(28) Schaefer, T.; Parr, J. E. *Can. J. Chem*. **1976**, *65*, 1197.

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

(30) Berg, U.; Liljefors, T.; Roussel, C.; Sandström, J. *Acc. Chem. Res.* **1985**, *18*, 80.

(31) Berg, U.; Sandström, J. *Adv. Phys. Org. Chem.* **1989**, *25*, 1.

(32) (a) Seeman, J. I.; Schug, J. C.; Viers, J. W. *J. Am. Chem. Soc*. **1983**, *48*, 2399. (b) Seeman, J. I.; Viers, J. W.; Schug, J. C.; Stovall, M. D. *J. Am. Chem. Soc*. **1984**, *106*, 143. (c) Seeman, J. I. *Heterocycles* **1984**, *22*, 165.

(33) Oikawa, A; Abe, H.; Mikami, N.; Ito, M. J. Phys. Chem. 1984, 88, 5180.

(34) Mizuno, H.; Okuyama, K.; Ebata, T.; Ito, M. J. Phys. Chem. 1987, 91, 5589.

(35) Im, H.-S.; Bernstein, E. R. unpublished results.

(36) Dorigo, A. E.; Pratt, D. W.; Houk, K. N. J. Am. Chem. Soc. 1987, 109, 6591.

(37) Dewar, M. J. S.; Zoebisch, E. G.; Healy, E. F.; Stewart, J. J. P. J. Am. Chem. Soc. 1985, 107, 3902.

(38) See, however: Stewart, J. J. P. J. Comp. Chem. 1989, 13, 157.

(39) Suryan, M. M.; Kafafi, S. A.; Stein, S. E. J. Am. Chem. Soc. 1989, 111, 1423.

(40) Brownlee, R. T. C.; Craik, D. J. Tetrahedron Lett. 1980, 21, 1681.

(41) Schaeffer, T.; Beaulieu, C.; Sebastian, R.; Penner, G. H. Can. J. Chem. 1990, 68, in press.

(42) Schaeffer, T.; Sebastian, R.; Penner, G. H. Can. J. Chem. 1986, 64, 1372.

(43) Yadav, J.; Mishra, P.; Rai, D. Mol. Phys. 1973, 26, 193.

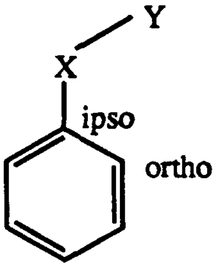
(44) Mishra, P.; Rai, D. Int. J. Quantum Chem. 1972, 6, 47.

(45) Hansch, C.; Leo, A. Substituent Constants for Correlation Analysis in Chemistry and Biology, John Wiley & Sons, New York: 1980.

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

(47) Hanzlik, R. P.; Schaefer, A. R.; Moon, J. B.; Judson, C. M. J. Am. Chem. Soc. 1987, 109, 4926.

Table I. Conformations of substituted benzenes as established by laser jet spectroscopy.

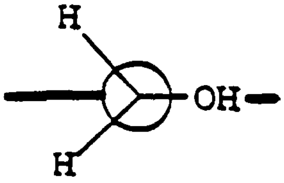


	$\tau(C_{ortho}\text{-}C_{ipso}\text{-}X\text{-}Y)$	reference
ethylbenzene	90°	[a]
propylbenzene	90°	[b]
methoxybenzene	0°	[c]
styrene	0°	[d]
allylbenzene	90°	[e]
benzyl alcohol	90°	This work.
benzyl fluoride	90°	This work.

[a] Ref. 10 and 11. [b] Ref. 10 and 12. [c] Ref. 14 and 15 [d] Ref. 13 [e] Ref. 16.

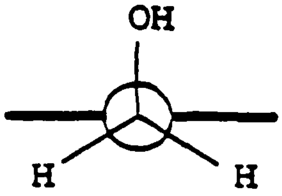
Table II. Number of conformations of 2-unsubstituted benzyl alcohols based on experiment and conformational analysis predictions.

Number of Conformations



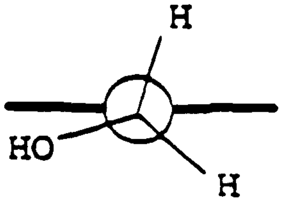
2

planar



3

perpendicular



4

gauche

compound	Number of Conformations			
	predicted			observed
	planar	perpendicular	gauche	
benzyl alcohol (1)	1	1	1	1
4-ethylbenzyl alcohol (8)	1	2	2	2
3-fluorobenzyl alcohol (3)	2	1	2	1
4-fluorobenzyl alcohol (2)	1	1	1	1
3-methylbenzyl alcohol (10)	2	1	2	1
4-methylbenzyl alcohol (9)	1	1	1	1
3-aminobenzyl alcohol (18)	2	1	2	1

Table III. Positions and assignments for benzyl alcohol and benzyl-d_2 alcohol features in the 0_0^0 region of the ($S_1 \leftarrow S_0$).

ν[a]	benzyl alcohol $\nu-\nu(0_0^0)$[b] (cm^{-1})	benzyl-d_2 alcohol. $\nu-\nu(0_0^0)$[c] (cm^{-1})	isotopeshift	Assignment
A	0	0	-	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 Fig. 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}.

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)	0 (36 999.5)	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 Figs. 1 and 2).

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.

v	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 parenthesis 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.

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.

v	benzyl alcohol	4-fluoro-benzyl alcohol	3-fluoro-benzyl alcohol	2-fluoro-benzyl 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 parenthesis are torsional energy levels not observed due to selection rules.

Table VIII. Positions of the features of 2-fluorobenzyl alcohol, 2-fluorobenzyl alcohol-α,α-d_2, and 2-fluorobenzyl alcohol-d_1.

$\underline{v}^a$	2-fluorobenzyl alcohol $\nu-\nu(0_0^0)$ (cm^{-1})	2-fluorobenzyl alcohol-α,α-d_2 $\nu-\nu(0_0^0)$ (cm^{-1})	2-fluorobenzyl alcohol-d_1 $\nu-\nu(0_0^0)$ (cm^{-1})
A	0(37 595.7)	0(37 597.9)	0(37 608.5)
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).

Table IX. Experimental torsional energy levels (in cm^{-1}) of the CH_2OH group in the S_1 state of benzyl alcohol and 2-aminobenzyl alcohol.

v	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 parenthesis are torsional energy levels not observed due to selection rules.

Figure Captions

Figure 1. TOFMS of jet-cooled (a) benzyl alcohol (**1**) and (b) benzyl alcohol-α, α-d_2 (**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.

Figure 2 TOFMS of the jet-cooled benzyl alcohol (**1**) to the low energy side of the 0^0_0 transition. 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.

Figure 3 TOFMS 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.

Figure 4 TOFMS 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.

Figure 5 TOFMS 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.

Figure 6 TOFMS of (a) 2-fluorobenzyl alcohol (**14**); (b) 2-fluorobenzyl-α,α-d_2 alcohol (**15**); and (3) 2-fluorobenzyl alcohol-d_1 (**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-d_1 alcohol. No isotope shift is observed for 2-fluorobenzyl-d_1 alcohol.

Figure 7 TOFMS of the 0_0^0 region of the $S_1 \leftarrow S_0$ transition of jet-cooled (a) 3-aminobenzyl alcohol (**17**); (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.

Figure 8 TOFMS 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 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).

Figure 1

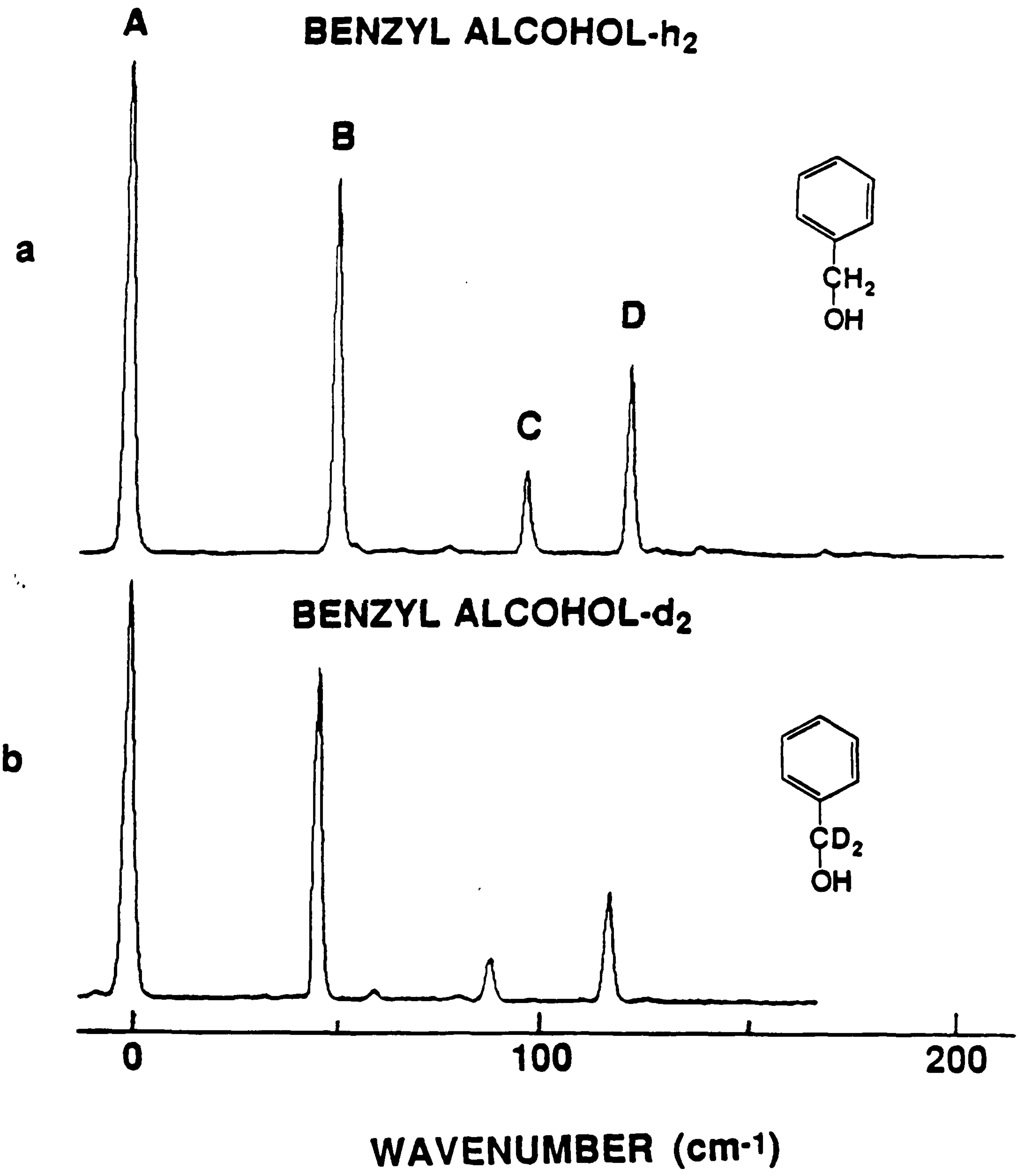

A
BENZYL ALCOHOL-h_2
B
a
CH_2
OH
D
C
BENZYL ALCOHOL-d_2
b
CD_2
OH
0
100
200
WAVENUMBER (cm^{-1})

Figure 2

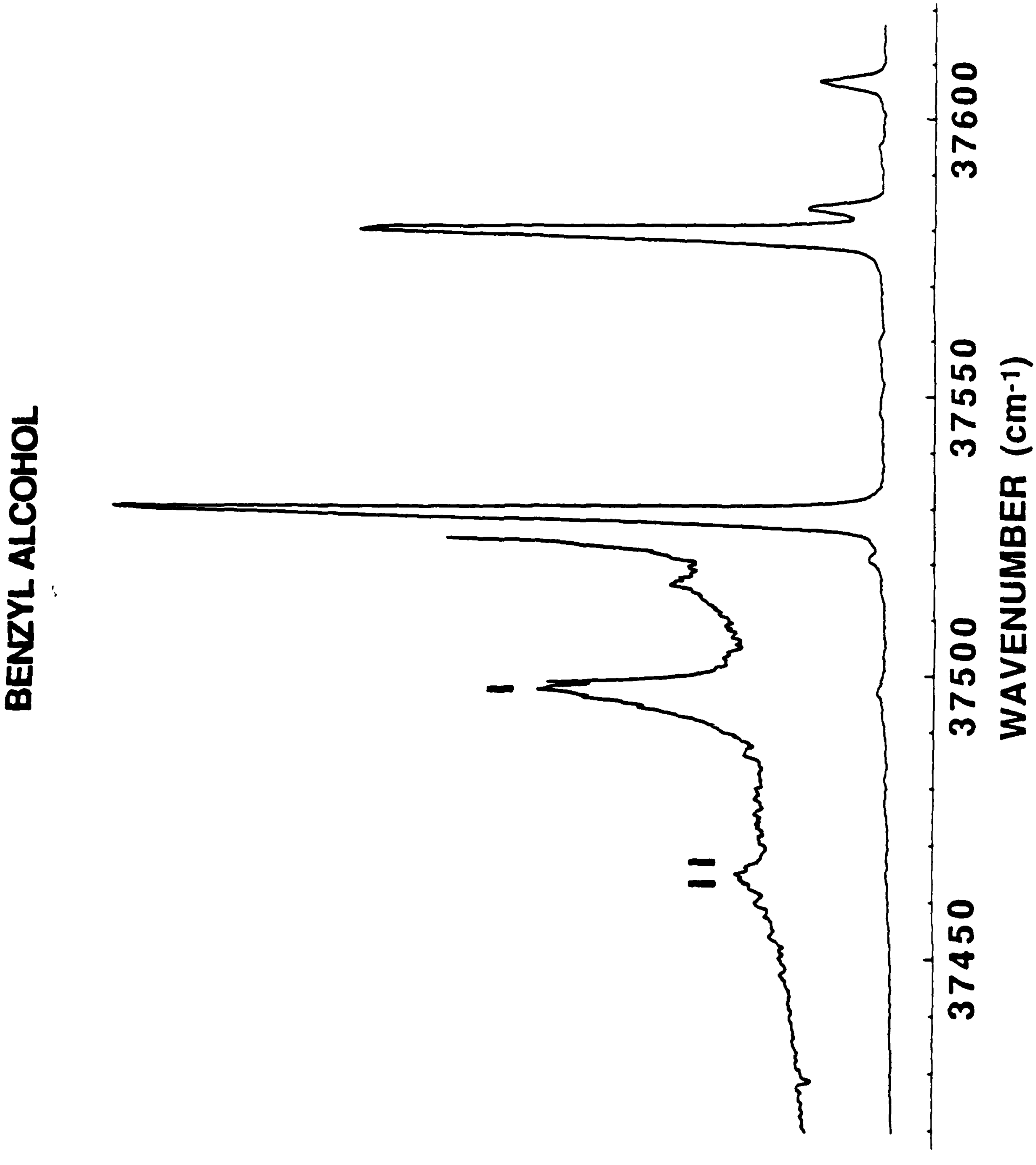


Figure 3

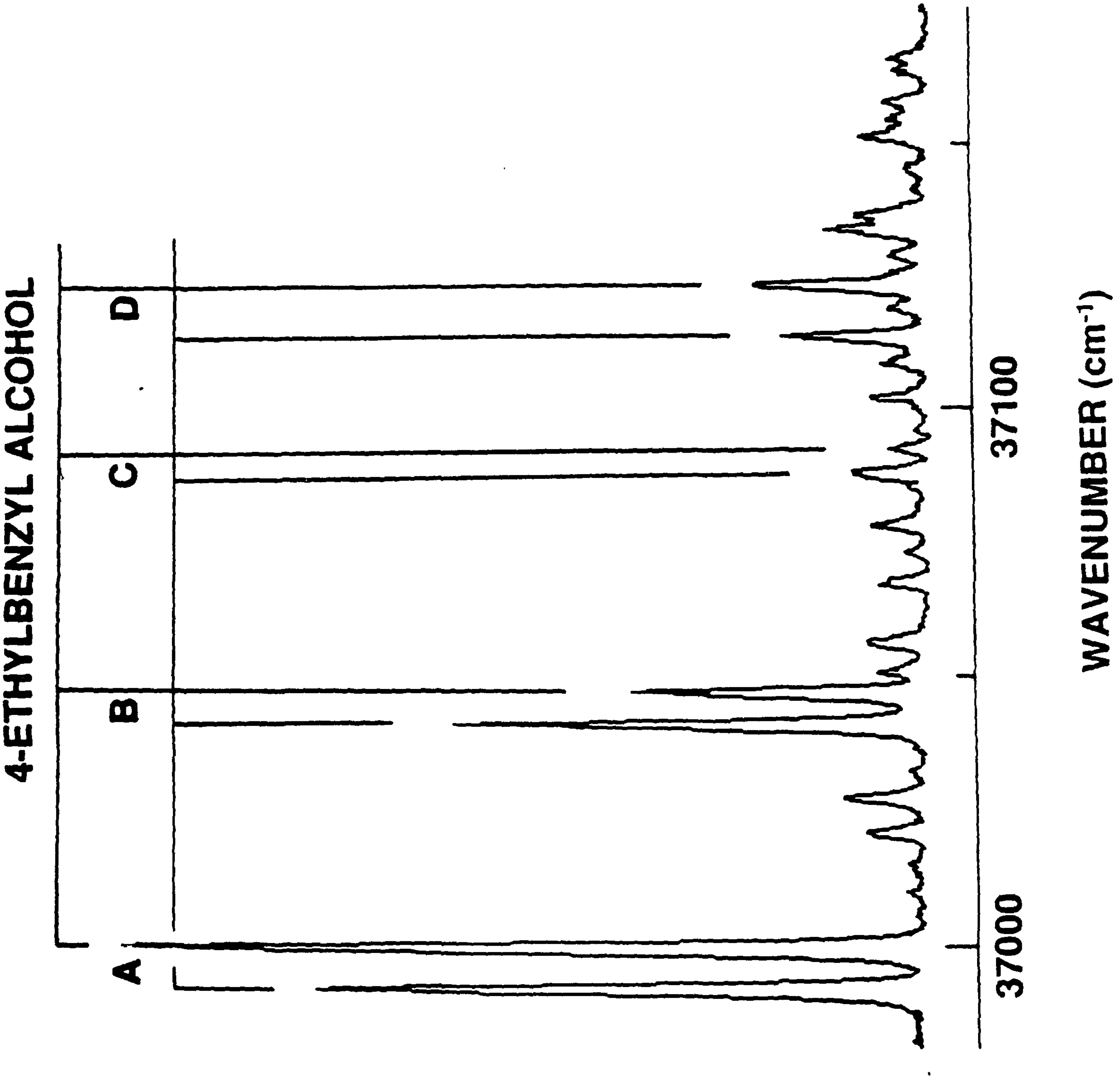


Figure 4

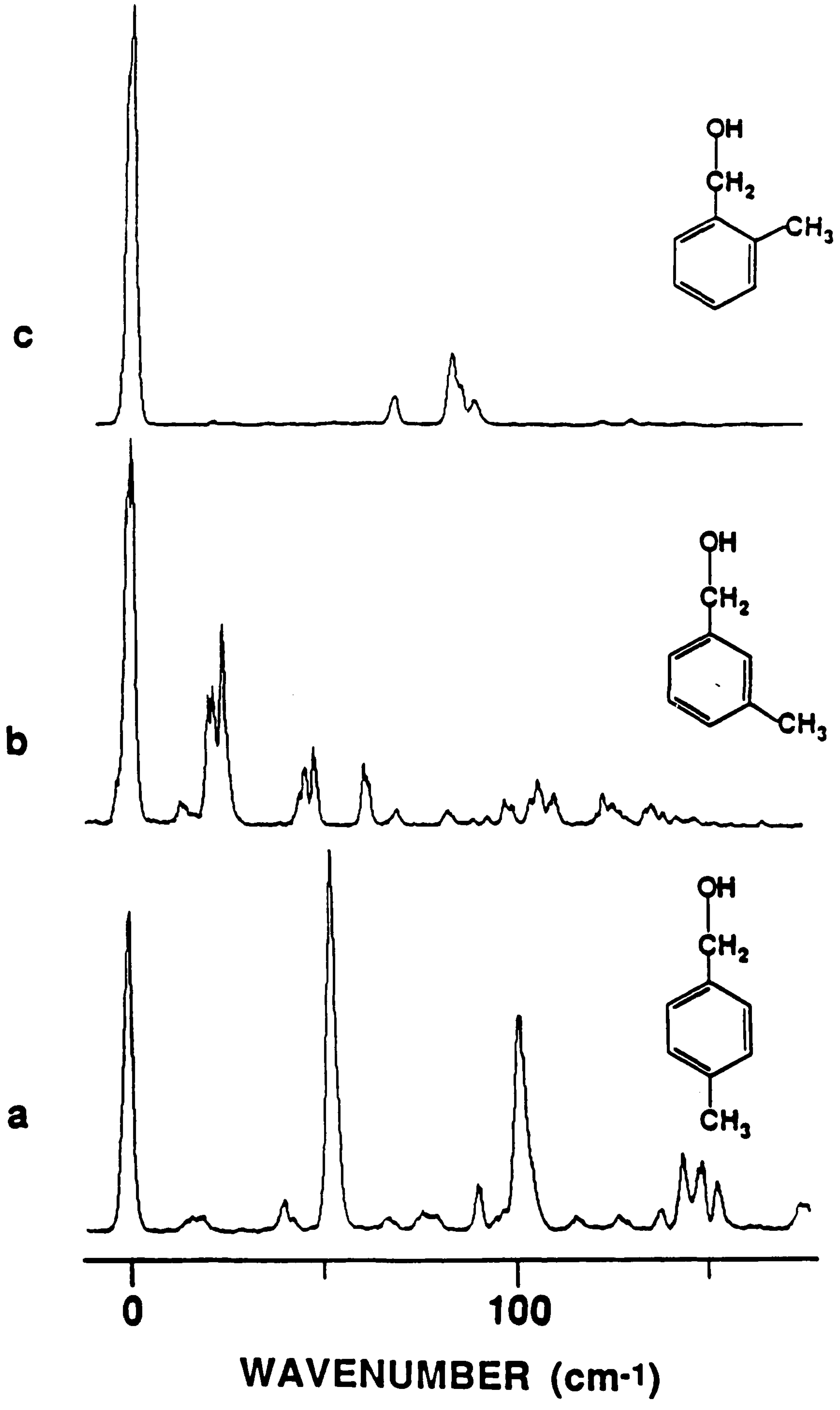


Figure 5

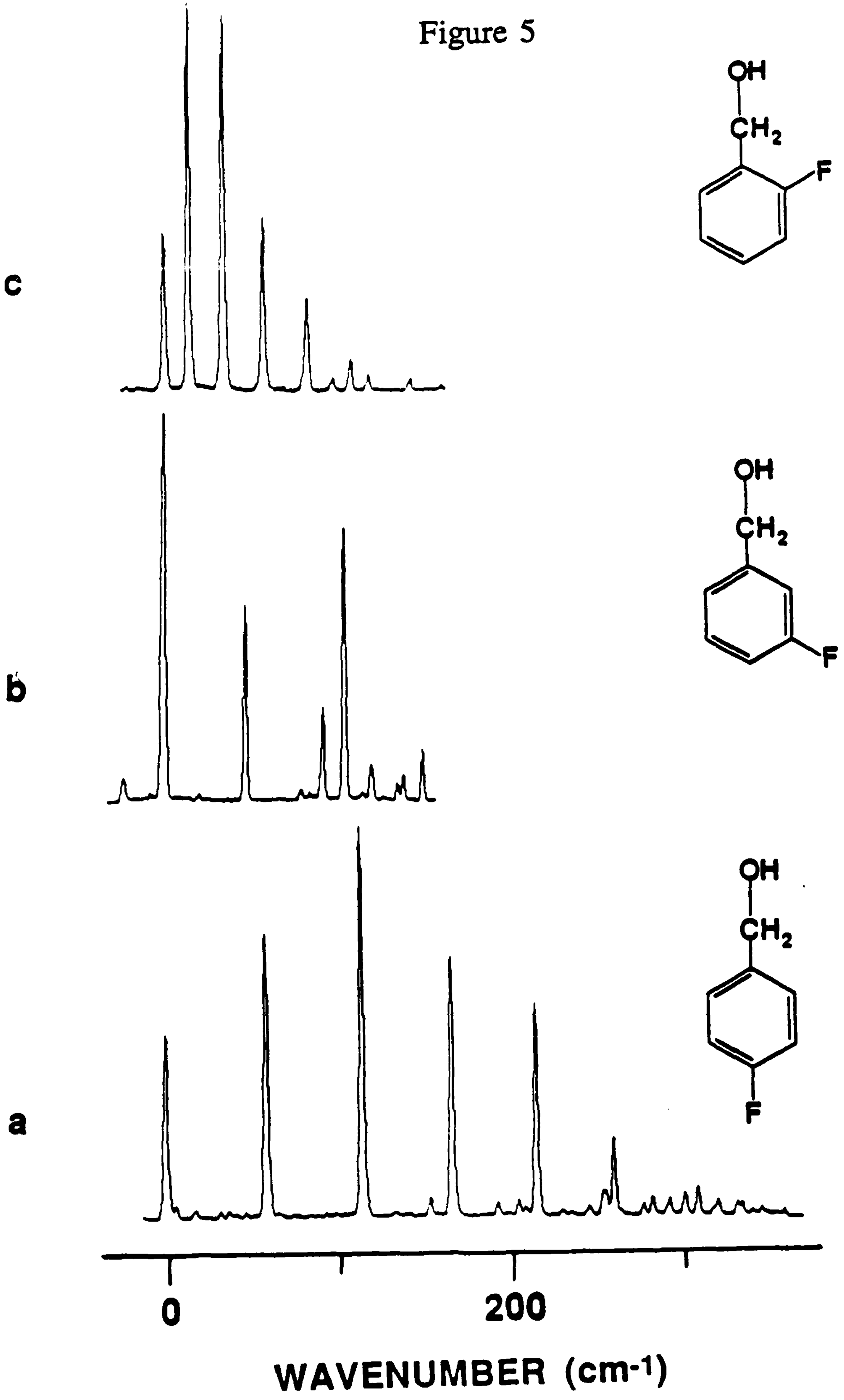


Figure 6

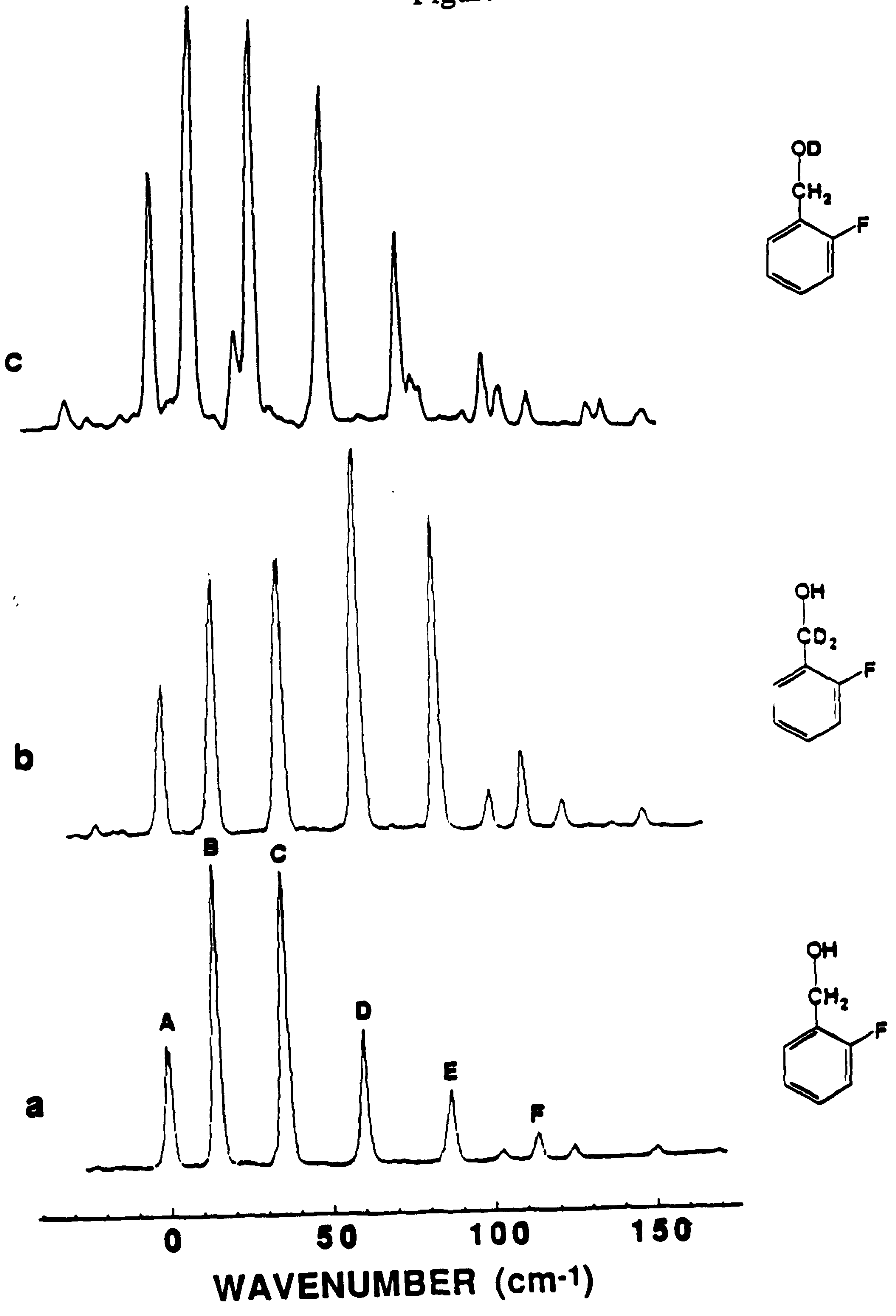


Figure 7

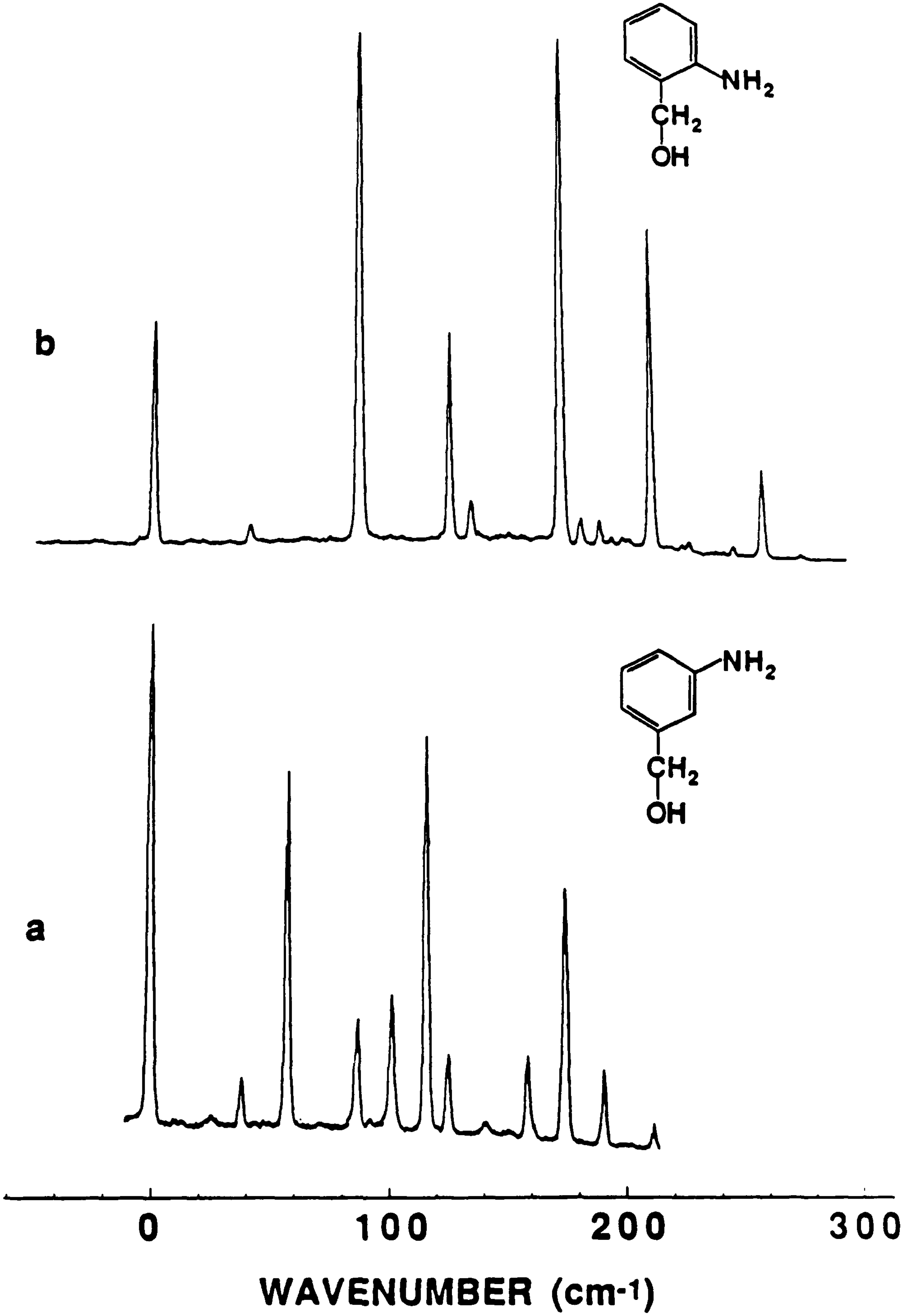
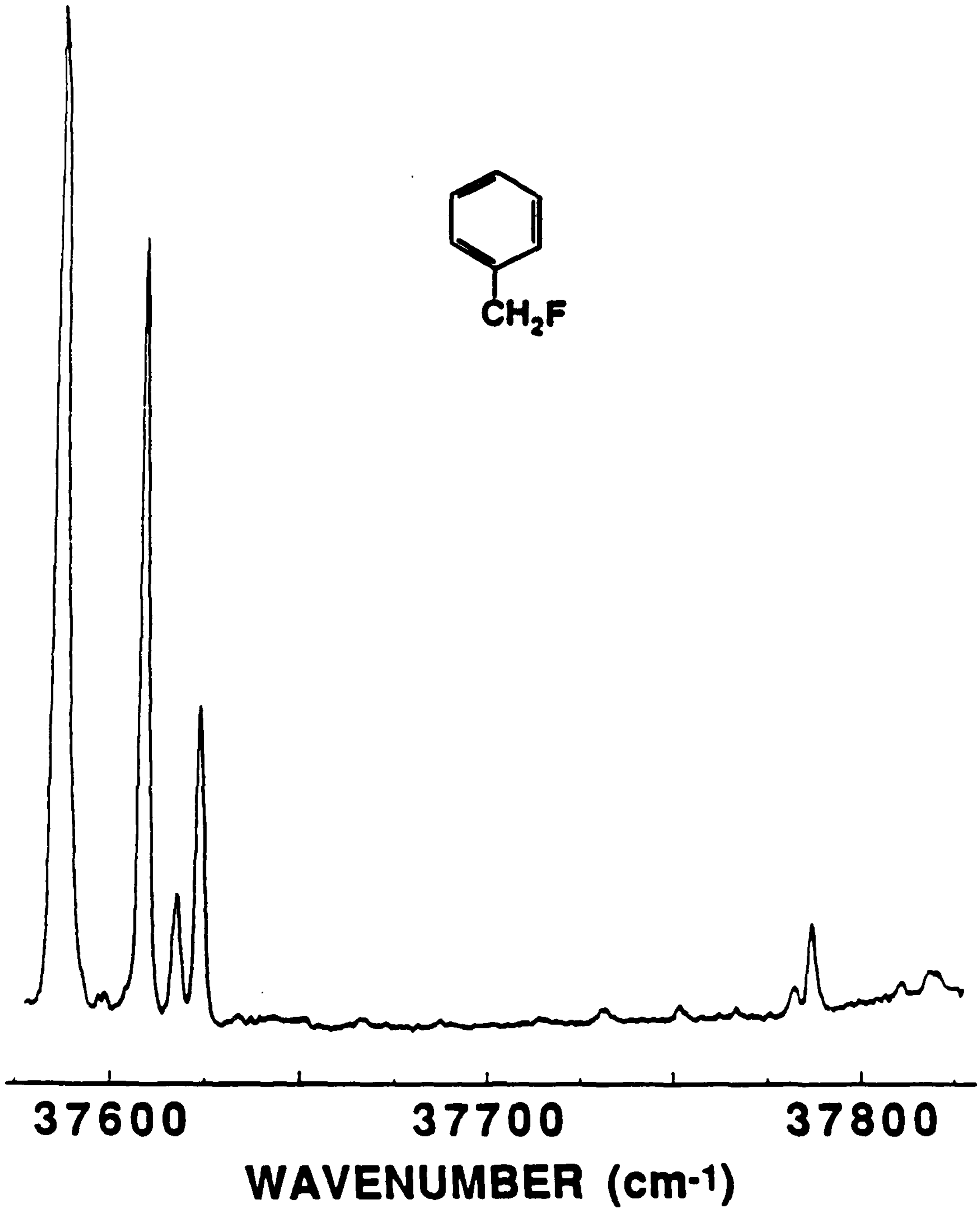


Figure 8



TECHNICAL REPORT DISTRIBUTION LIST - GENERAL

Office of Naval Research (2)
Chemistry Division, Code 1113
800 North Quincy Street
Arlington, Virginia 22217-5000

Commanding Officer (1)
Naval Weapons Support Center
Dr. Bernard E. Douda
Crane, Indiana 47522-5050

Dr. Richard W. Drisko (1)
Naval Civil Engineering Laboratory
Code L52
Port Hueneme, CA 93043

David Taylor Research Center (1)
Dr. Eugene C. Fischer
Annapolis, MD 21402-5067

Dr. James S. Murday (1)
Chemistry Division, Code 6100
Naval Research Laboratory
Washington, D.C. 20375-5000

Dr. Robert Green, Director (1)
Chemistry Division, Code 385
Naval Weapons Center
China Lake, CA 93555-6001

Chief of Naval Research (1)
Special Assistant for Marine Corps Matters
Code 00MC
800 North Quincy Street
Arlington, VA 22217-5000

Dr. Bernadette Eichinger (1)
Naval Ship Systems Engineering Station
Code 053
Philadelphia Naval Base
Philadelphia, PA 19112

Dr. Sachio Yamamoto (1)
Naval Ocean Systems Center
Code 52
San Diego, CA 92152-5000

Dr. Harold H. Singerman (1)
David Taylor Research Center
Code 283
Annapolis, MD 21402-5067