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"Observation and Geometry Assignment of the Conformation of Benzyl Alcohol in the Gas Phase"

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Jeffrey I. Seeman, Henry V. Secor,
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Observation and Geometry Assignment of the Conformation of Benzyl Alcohol in the Gas Phase

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

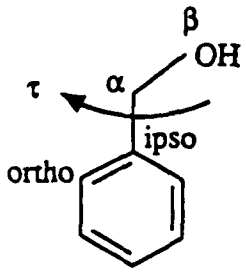
[a]Philip Morris Research Center, P.O. Box 26583, Richmond, Virginia 23261, U.S.A.

[b]Department of Chemistry, Condensed Matter Sciences Laboratory, Colorado State University, Fort Collins, Colorado 80523, U.S.A.

Supersonic molecular jet laser spectroscopy is used to establish the perpendicular conformation of benzyl alcohol and a number of sterically unencumbered derivatives in the gas phase.

Benzyl alcohol (1) and its derivatives have vast synthetic utility, are frequently found in natural products, and play a central role in numerous mechanistic investigations. In spite of this chemical importance, the conformational preference of the $-CH_2OH$ group relative to the aromatic ring has not been unambiguously established: various experimental and theoretical studies have failed to lead to a unified and consistent picture. Planar[1,2]

(2) and gauche[3,4] (4) conformations as well as a freely rotating model[4] have been proposed for benzyl alcohols (see Scheme 1).



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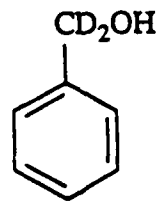


(5)

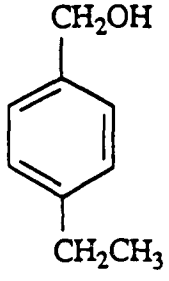
$\tau = \tau(C_{ortho}\text{-}C_{ipso}\text{-}C_{\alpha}\text{-}C_{\beta})$

The geometry of the minimum energy conformations of a variety of aromatic ring substituents has recently been established using molecular jet laser spectroscopy.[5-7] The supersonic expansion process results in molecules at near 0 K: intramolecular conformational interconversions are thereby stopped, and electronic transitions become very sharp and well resolved.[5-7] Since each stable conformation of a molecule has a specific potential energy minimum in S_0 and S_1, the energy of the electronic origin (0_0^0 transition) for the $S_1 \leftarrow S_0$ transition for each stable conformer is generally unique. Hence, each stable conformation is associated with its own spectroscopic 0_0^0 transition; the converse is also true. Mass resolved excitation spectra (time of flight mass spectra - TOFMS) can thus be readily obtained for each conformer of the system under study. Structural assignments can then be made by an 'origin counting' procedure.* Herein, we report the conformation of benzyl alcohol in the gas phase.

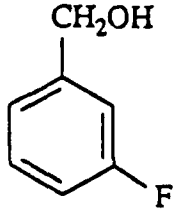
*see ‡ page

The TOFMS of (1) and benzyl alcohol-d_2 (5) each exhibit four distinct features, as shown in Figures 1(A) and (B). The isotope shifts for the second, third, and fourth transitions of (5) relative to those of (1) are substantial, ranging from 3% to 8% for these features. These data

indicate that only a single 0_0^0 transition is found for benzyl alcohol. (Similiar origin assignments have been made using deuterated anisoles[5] and styrenes[7].) Hence, only a single stable conformation [(2) or (3) or (4)] exists for benzyl alcohol in the gas phase. 'Structural logic' involving symmetry and potential energy considerations permits a distinction amongst these three conformations to be made. The strategy involves examination of the TOFMS of suitably substituted benzyl alcohols, in particularly 4-ethylbenzyl alcohol (6), 3-fluorobenzyl alcohol (7) and 3-methylbenzyl alcohol (8).



(6)



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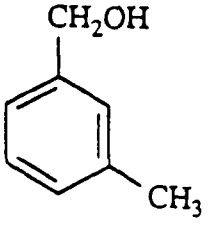
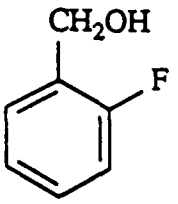


(8)

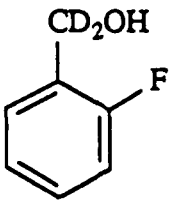
The torsional angle $\tau(C_{ortho}\text{-}C_{ipso}\text{-}C_{\alpha}\text{-}C_{\beta})$ is ca. 90° for a sterically unhindered aromatic ethyl group. The TOFMS of (6), shown in Figure 1(C), exhibits a doubling of all the transitions for benzyl alcohol, indicating that the oxygen atom of these benzyl alcohols must be out of the plane of the aromatic ring, i.e., conformation (2) is excluded from consideration as outlined in Scheme 1. Conformations (3) and (4) can be distinguished by examination of the TOFMS of (7), which is shown in Figure 1(D). The spectra of (1) and (7) are nearly identical, indicating that the C-O bond must lie in the plane perpendicular to the phenyl ring plane and passing through the $C_{ipso}\text{-}C_4$ axis. Hence, only conformer (3) is found for these benzyl alcohols. This conclusion is confirmed by the observation of a single

origin for 3-methylbenzyl alcohol (8): a closely spaced doublet with components at 36,944.7 and 36,945.8 cm^{-1} is observed due to the torsional motion of the methyl group.[6]

Meta and para substituents on the benzyl alcohol ring system have apparently little or no essential influence on the $-CH_2OH$ conformation. In contrast, ortho fluoro substitution does alter the benzyl alcohol geometrical and electronic properties. The TOFMS of 2-fluorobenzyl alcohol (9) [Figure 2(A)] is considerably different than the TOFMS of benzyl alcohol and the 3- and 4-substituted benzyl alcohols shown in Figure 1. The progression shown in Figure 2(A) is <u>not</u> due to rotation of the hydroxyl group about the C_{ipso}-C_α bond, since the TOFMS of the deuterated analogue (10) is identical to that of (9). Importantly, the TOFMS of the -OD analogue (11) shown in Figure 2(B) indicates significant isotope effects, strongly suggesting that the transitions depicted in Figure 2 are due to oscillatory motion of H(D) in the O-H$\cdots$F (O-D$\cdots$F) hydrogen bond. Unlike the suggestion that (9) exists in three conformations based on microwave spectroscopy,[8] our results are consistent with the existence of only a single stable ground state conformation. Intramolecular CH_2-OH$\cdots$F hydrogen bonding in (9)-(11) differs significantly in the S_0 and S_1 electronic states. The observed spectroscopic transitions in the TOFMS of (9)-(11) reflect a displacement in the stable minimum energy conformations of these molecules in S_0 compared to S_1.



(9)



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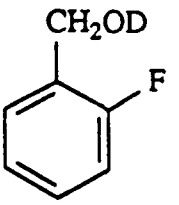
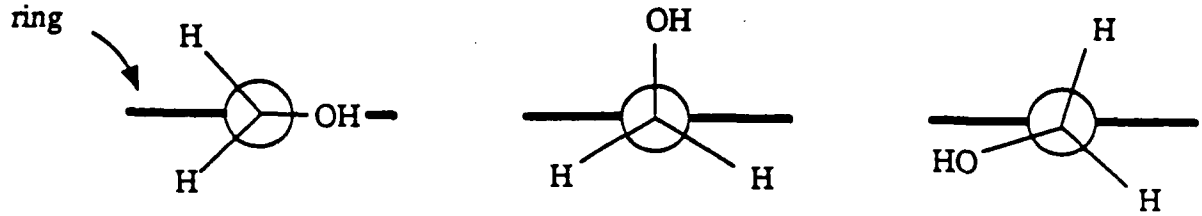


(11)

We draw two major conclusions from this work: sterically unencumbered benzyl alcohols exist in the perpendicular conformation (3) in the gas phase; and the $-CH_2OH$ conformation in 2-fluorobenzyl alcohol is altered, relative to (1) by intramolecular hydrogen bonding, which causes different equilibrium positions for the -OH proton in S_1 as compared to S_0. A full paper on this work will deal with internal motion of additional heteroatom-substituted benzyl alcohols.

Plane of aromatic ring



2 planar

3 perpendicular

4 gauche

Compound	No. of conformations Predicted (2)	Predicted (3)	Predicted (4)	Observed
Benzyl alcohol (1)	1	1	1	1
4-Ethylbenzyl alcohol (5)	1	2	2	2
3-Fluorobenzyl alcohol (6)	2	1	2	1
3-Methylbenzyl alcohol (8)	2	1	2	1

Scheme 1

Footnote

≠ 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.

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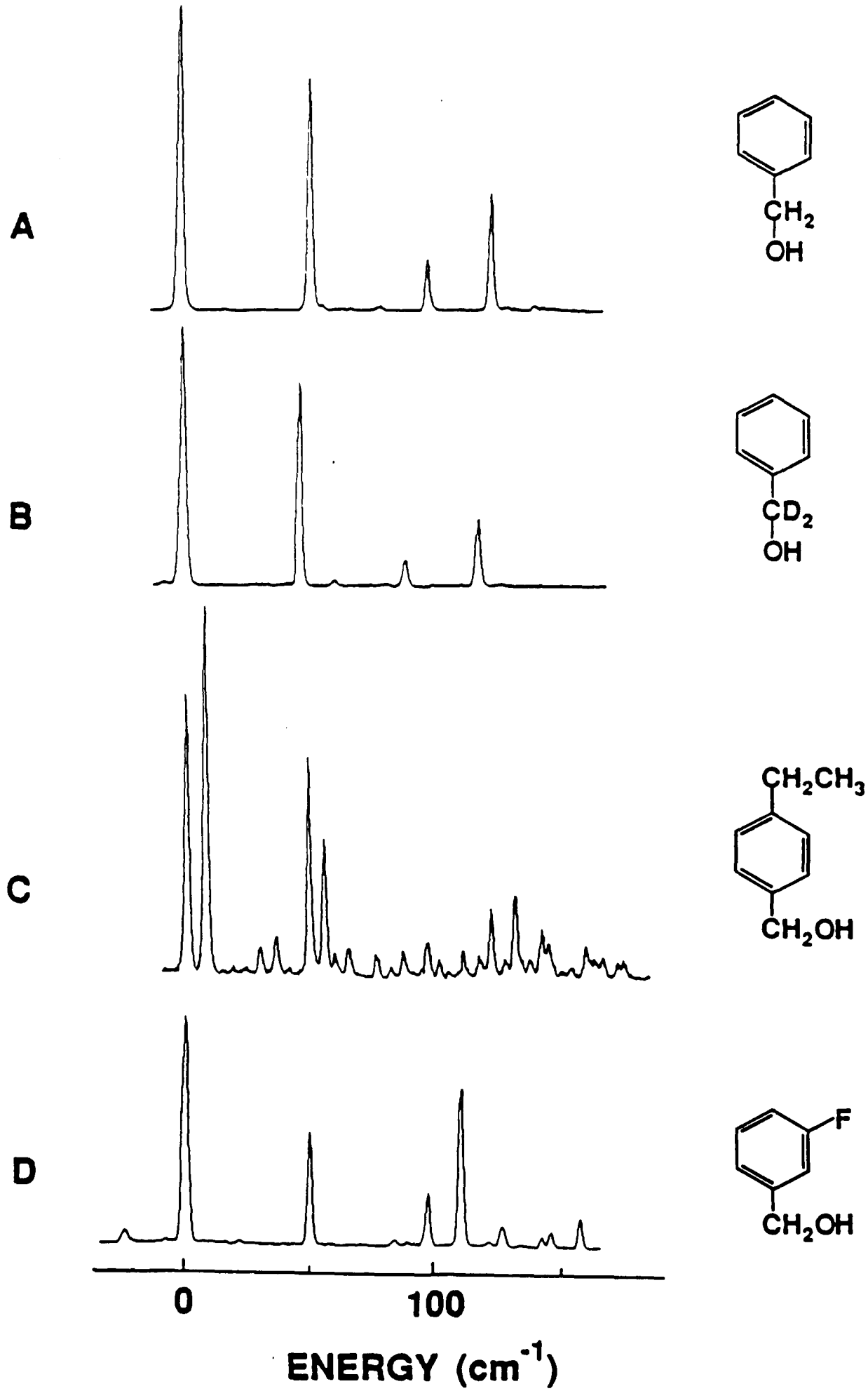
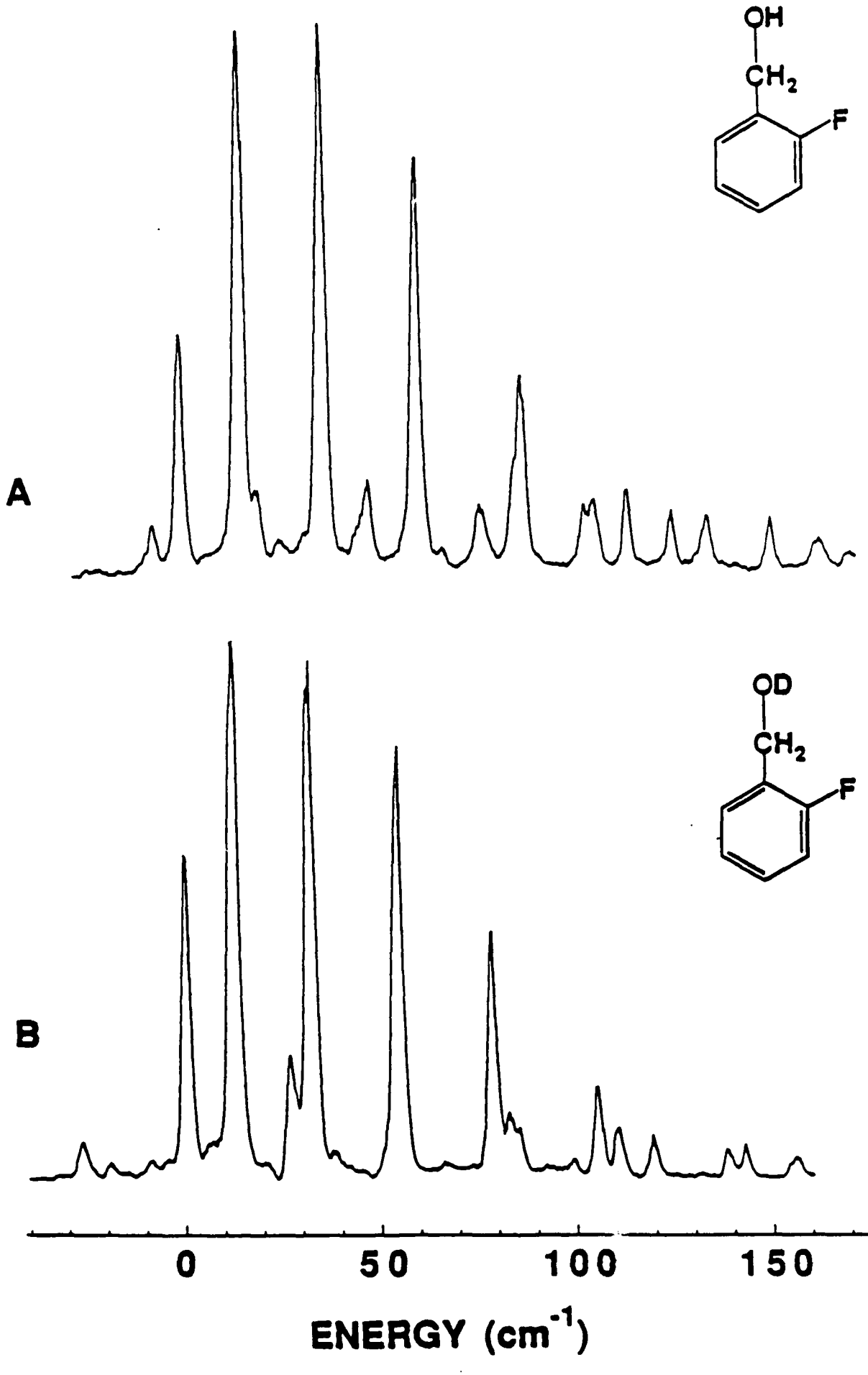
Figure Captions

Figure 1. TOFMS of the 0_0^0 region of (A) benzyl alcohol (1), (B) benzyl alcohol-d_2 (5), 4-ethylbenzyl alcohol (6), and 3-fluorobenzyl alcohol (7). Comparison of the four transitions in (A) and (B) indicates that benzyl alcohol exists in a single conformation, since the transition energy of the second, third, and fourth transitions are all shifted slightly to the red due to the known isotope effect on vibrational motion. These four transitions are each doubled in (C) due to the presence of <u>two</u> conformations for (6). The near identical spectrum of (7) in (D) compared to (A) and (B) indicates that 3-fluorobenzyl alcohol exists in a single conformation.

Figure 2. TOFMS of the 0_0^0 region of (A) 2-fluorobenzyl alcohol (9) and (B) 2-fluorobenzyl alcohol-OD (11). The TOFMS of the 0_0^0 region of (10) is essentially identical to that found for (9). The dissimilarity between these spectra and the spectra shown in Figure 1 indicates that the geometry of the ground and excited states of 2-fluorobenzyl alcohol are different from each other. The isotope shifts seen in the comparison of (A) and (B) indicate that the observed spectrum is due to an oscillatory motion of the hydrogen atom in the H$\cdots$F intramolecular hydrogen bond.


A
B
C
D
CH2
OH
CD2
OH
CH2CH3
CH2OH
F
CH2OH
0
100
ENERGY (cm-1)


OH
CH2
F
A
OD
CH2
F
B
0
50
100
150
ENERGY (cm-1)

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