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VIBRATIONAL SPECTRA AND CONFORMATIONAL BEHAVIOR OF BENZYL FLUORIDE

G.A. CROWDER and MARY JANE TOWNSEND

Department of Chemistry
West Texas State University
Canyon, Texas 79016 (USA)

SUMMARY

Infrared and Raman spectra have been obtained for benzyl fluoride and a vibrational assignment has been made. The spectra indicate the presence of a large number of conformers that differ only in the orientation of the C-F bond, as a result of free or nearly free internal rotation.

INTRODUCTION

Infrared and Raman spectra have been published for benzyl chloride (1,2) and benzyl bromide (1-3), and these references include some band assignments. From Raman polarization data, Verdonck and van der Kelen (2) concluded that benzyl chloride, bromide, and iodide molecules belong to the C_1 point group and therefore, the C-C-X plane neither lies in nor is perpendicular to the plane through the phenyl group. However, Schaefer, et al (4) concluded from coupling constants that the C-C-X plane is perpendicular to the phenyl plane for benzyl bromide and chloride, and that the C-C-F plane lies in the phenyl plane for benzyl fluoride (5).

Vibrational spectra have not been published for benzyl fluoride, so infrared and Raman spectra have been determined for this compound in order to make a vibrational assignment and to draw conclusions about the molecular symmetry.

EXPERIMENTAL

Infrared spectra were obtained with a Beckman IR12 spectrophotometer. Raman spectra were obtained with a Beckman Model 700 spectrometer equipped with a Coherent Radiation Labs model 54 Argon ion laser. The sample was obtained from K & K Labs and was used without further purification. No impurities were detected by gas chromatography.

RESULTS AND DISCUSSION

The infrared spectrum of benzyl fluoride is shown in Fig. 1 and the Raman spectrum is shown in Fig. 2. The observed wavenumbers are listed in Table 1, along with the band assignments. The assignments of the phenyl group are given simply as in-plane and out-of-plane modes.

Vibrational assignments and molecular symmetry

A molecule of benzyl fluoride will have C_s symmetry if the C-C-F plane lies in the plane that passes through the phenyl ring or is perpendicular to the phenyl plane. The molecule would have C_1 symmetry for all other orientations of the C-F bond. However, most of the vibrational frequencies of the phenyl group will be relatively independent of the CH_2F group. Likewise, the CH_2F group frequencies will not be affected very much by the presence of the phenyl group. Vibrational frequencies of monosubstituted benzenes have been discussed by various authors, and the cartesian displacement coordinates are illustrated by Dollish, Fateley, and Bentley (6).

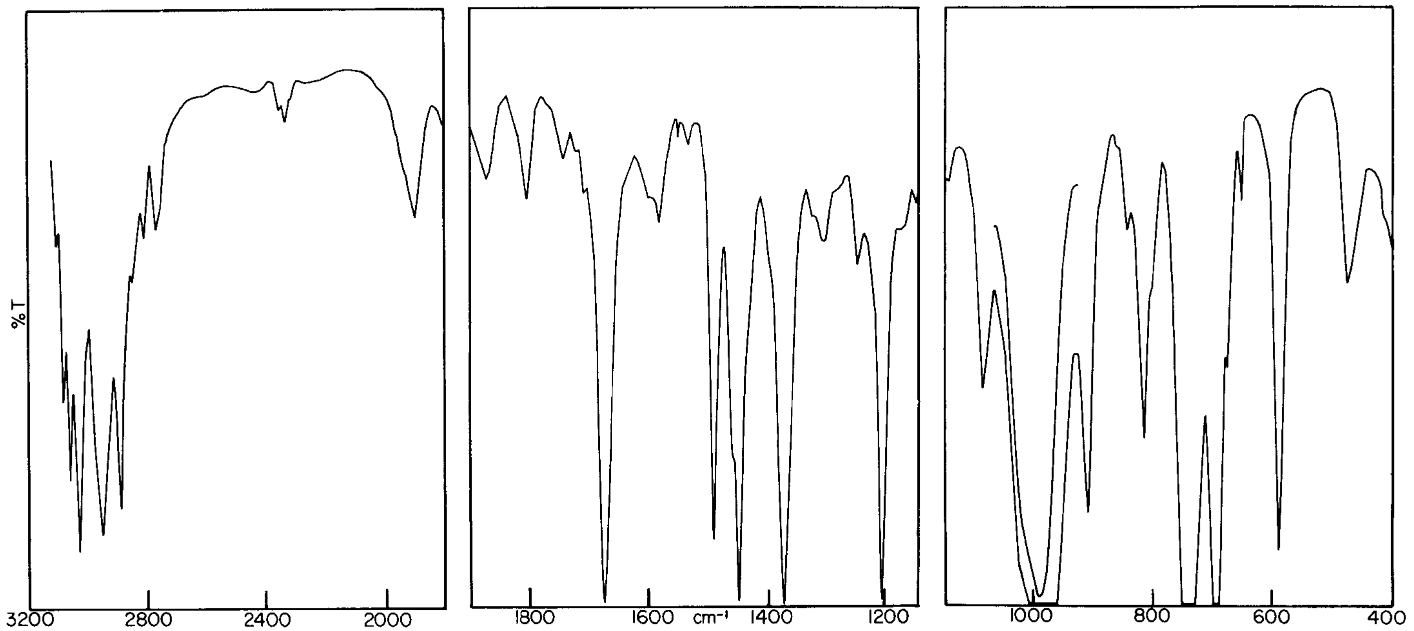

Fig. 1. Infrared spectrum of benzyl fluoride (neat).

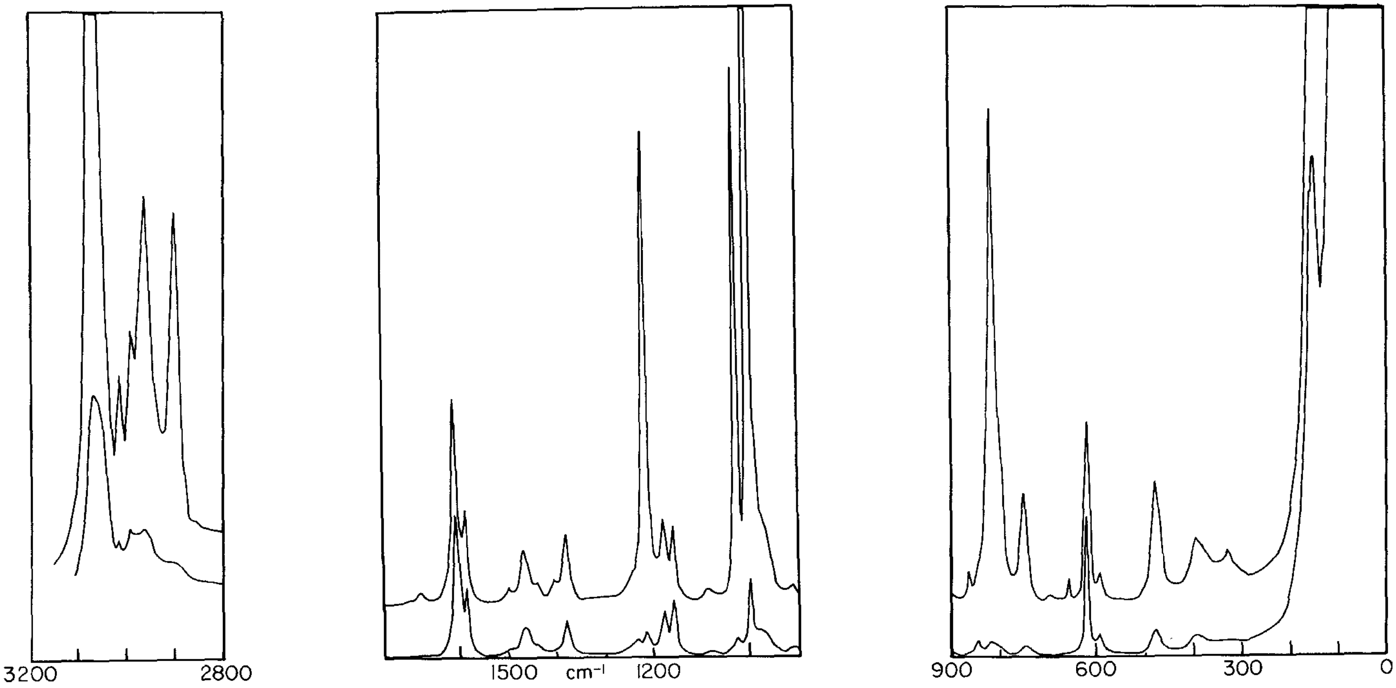

Fig. 2. Raman spectra of benzyl fluoride, showing polarization of the bands.

TABLE 1

Infrared and Raman wavenumbers and band assignments for benzyl fluoride

Infrared cm^{-1}	Raman cm^{-1}	Assignment	Wilson Number
	158 vvs d	ring-C o-p bend	
	338 w p	i-p fundamental	
	404 w p	C-C-F bend	
476 m	480 mw p	i-p fundamental	
	542 vvw p	o-p fundamental	16b
595 ms	597 vw d	ring-C i-p bend	6a
	624 m d	i-p fundamental	6b
662 w	663 vw p	823 - 158 = 665	
682 w		2 x 338 = 676	
701 vs	704 vvw p	o-p fundamental	4
748 vs	750 mw p	o-p fundamental	11
ca. 808 sh	ca. 810 sh	CH_2 rock	
824 m	823 s p	ϕ-C stretch	
849 w	850 vw d	o-p fundamental	10a
	870 vw p	404 + 480 = 884	
915 ms	919 vvw d	o-p fundamental	17b
	ca. 980 sh	158 + 823 = 981; o-p fundamental	17a
ca. 990 vvs		C-F stretch	
	ca. 995 sh	o-p fundamental	5
	1006 vs p	i-p fundamental	12
ca. 1030 sh	1032 s p	i-p fundamental	18a
1091 m	1096 vvw	i-p fundamental	18b
ca. 1150 vvw		158 + 990 = 1148	
ca. 1160 vw	1163 w p	i-p fundamental	15
ca. 1180 vw	1182 w p	i-p fundamental	9a
1217 s	1220 s p	i-p fundamental	
	ca. 1238 sh d?	2 x 624 = 1248	
1260 w		CH_2 twist	
ca. 1290 sh		i-p fundamental	3

TABLE 1. Continued.

Infrared cm^{-1}	Raman cm^{-1}	Assignment	Wilson Number
1313 w		i-p fundamental	14
1330 vw		595 + 748 = 1343	
1381 s	1383 w p	CH_2 wag	
ca. 1400 sh	1409 vvw p	404 + 1006 = 1410	
	1444 vvw d?	624 + 823 = 1447	
1458 s		i-p fundamental	19b
ca. 1470 sh	1473 w p	CH_2 bend	
1449 ms	1506 vvw p	i-p fundamental	19a
1561 vvw		748 + 824 = 1572	
1590 w	1592 w d	i-p fundamental	8b
1610 vw	1613 m d?	i-p fundamental	8a
1682 s	1687 vw p	701 + 990 = 1691	
1717 vw		701 + 1030 = 1731	
1751 vw		748 + 990 = 1738	
1844 w		849 + 990 = 1839	
1881 w		915 + 990 = 1905	
1957 w		748 + 1217 = 1965	
1975 vw		2 x 990 = 1980	
2316 vw		824 + 1499 = 2323	
2340 vw		748 + 1590 = 2338	
	2620 vw	1220 + 1383 = 2603	
	2752 vw	2 x 1383 = 2766	
2780 w	2790 vw	1182 + 1610 = 2792	
2822 w	2830 vvw	1381 + 1458 = 2839	
2865 w		1381 + 1499 = 2880	
2903 ms	2903 m p	2 x 1458	F.R.
2964 ms	2965 ms p	CH_2 symmetric stretch	
	2990 w p		
	3016 w p	i-p fundamental	
3038 ms		CH_2 antisymmetric stretch	
	ca. 3060 sh d?	i-p fundamental	
3071 m	3068 vs p	i-p fundamental	
3093 mw		i-p fundamental	

Several of the CH_2F group vibrations can be assigned without difficulty. The C-F stretch can undoubtedly be assigned to the very strong infrared band observed at about 990 cm^{-1}. The CH_2 deformation is assigned to the Raman band at 1473 cm^{-1}, which shows up as a shoulder on band 19b in the infrared. The CH_2 bend in ethyl fluoride was observed at 1479 cm^{-1} (7). The CH_2 wag at 1381 cm^{-1} is characteristic of the CH_2F group. The value for the wag in ethyl fluoride is 1365 cm^{-1} (7). This band is analogous to the 1266 cm^{-1} band of benzyl chloride discussed by Mannion and Wang (8). The assignments of the CH_2 rock and twist are less certain than other modes. The assigned values of ca. 810 and 1260 cm^{-1}, respectively, are near the values in ethyl fluoride. The C-C stretching mode involving the carbon of the CH_2F group and the ring carbon to which it is bonded can be assigned to the strong Raman band at 823 cm^{-1}.

The C-C-F bend can be assigned to the very broad band whose peak is observed at 404 cm^{-1}. This mode is lowered to 274 cm^{-1} in benzyl chloride (3). Verdonck and van der Kelen have assigned the 334 cm^{-1} band of benzyl chloride to the C-C-Cl bend (2). Our spectra show a band at 338 cm^{-1} for both the fluoride and chloride and both show a band in the 550-600 cm^{-1} region. The 404 (F) and 274 (Cl) cm^{-1} bands represent the only difference in the lower region of the spectra of these two compounds.

The spectra of benzyl fluoride show a medium intensity band at 2903 cm^{-1}. The lowest-frequency C-H stretch will be the symmetric CH_2 stretch, but 2903 cm^{-1} seems to be too low for this vibration. The CH_2 symmetric stretch was observed at 2941 cm^{-1} in ethyl fluoride (7), and it seems more likely that the bands at 2903 and 2965 cm^{-1} result from the overtone of the CH_2 bend being in Fermi resonance with the CH_2 symmetric stretch. There is a relatively strong band present in the infrared spectrum at 3038 cm^{-1} that is absent in the Raman spectrum, as might be expected for the antisymmetric CH_2 stretch, which is therefore assigned to this band. This band was observed at 3005 cm^{-1} in ethyl fluoride (7).

If the C-F bond lies in the plane formed by the phenyl ring, thirteen of the fifteen atoms will lie in the plane of symmetry and the thirty-nine fundamental vibrations would be distributed as 26a' + 13a". If the C-C-F plane were perpendicular to the phenyl plane, only five atoms would lie in the symmetry plane and the vibrational distribution would be 22a' + 17a". Therefore, it may be possible to make conclusions about the molecular symmetry from the Raman polarization data.

Table 1 shows eight depolarized Raman bands assigned as fundamentals, ten bands assigned as fundamentals that are either unobserved in the Raman spectrum or do not have depolarization ratios determined because of low intensity or overlapping bands. There are two fundamentals that were unobserved in both infrared and Raman spectra, namely the torsion and one of the ring C-H stretches.

If the molecule has C_1 symmetry, all Raman bands would be polarized to some extent, although some bands could be polarized so slightly as to be indistinguishable from depolarized bands. It is not possible to distinguish between the two C_s structures and one of C_1 symmetry just from the number of polarized and depolarized Raman bands. However, the Raman bands observed at 705 and 750 cm^{-1} seem to rule out the conformation with the C-F bond lying in the plane passing through the phenyl group. Both of these bands are highly characteristic of a monosubstituted benzene, both involve out-of-plane atomic displacements, and both bands would be depolarized for this conformer. They are both clearly polarized, with $\rho = 0.15$ for the 750 cm^{-1} band.

If the C-C-F plane were perpendicular to the phenyl plane, the following Raman bands would be expected to be depolarized, based on the assignments given in Table 1: 338, 597, 624, 810, 850, 980, 1096, 1163, 1592, and two ring C-H stretches. One ring C-H stretch appears to be depolarized and one is unobserved Several other fundamentals whose Raman bands would be depolarized are unobserved in the Raman spectrum. Of the bands just listed, only one band is definitely polarized, namely that at 338 cm^{-1}, although assignment of this band is not certain.

It seems that the most logical answer concerning the orientation of the C-F bond is provided by the 404 cm^{-1} band. We believe the tail on the low-frequency side of the 338 cm^{-1} band is actually part of the 404 cm^{-1} band, which is therefore more than 100 cm^{-1} broad. From the change in slope, it appears that the 338 cm^{-1} band is simply superimposed on the side of the very broad band whose peak is 404 cm^{-1}. The observation of this broad asymmetric band indicates nearly free internal rotation about the C-C bond connecting the two groups. This conclusion agrees with the low barrier to rotation of 260 ± 50 cal/mole obtained by Schaefer, et al (5). This barrier is considerably less than the thermal energy available at room temperature, and it is expected that all orientations of the C-F bond will be present in a sample of this compound. The C-C-F bending frequency will be dependent on the conformation, so the broad band results from the overlapping of a large number of bands of slightly different frequencies. Most of the frequencies of all conformers are independent of conformation and therefore show up as sharp bands. This behavior was shown to exist in 1,4-dichloro-2-butyne (9). Since all the conformers except four will have C_1 symmetry, the resultant Raman bands will essentially be those of C_1 symmetry. The observation of several apparently depolarized bands must simply indicate very little polarization of these bands.

The conclusions presented in the preceding paragraph are supported by the C-C-Cl bending band observed at 274 cm^{-1} in the Raman spectrum of benzyl chloride. Unlike the C-C-F bending band of benzyl fluoride, this band is relatively sharp. The barrier to internal rotation in benzyl chloride has been determined to be 2.1 ± 0.4 kcal/mole (4), which is considerably greater than the thermal energy available at room termperature. Therefore, only the most stable conformers of this compound will be present in appreciable amounts.

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REFERENCES

1 S. Chattopadhyay, Indian J. Phys., 41 (1967) 759.
2 L. Verdonck and G.P. van der Kelen, Spectrochim. Acta, 28A (1972) 51.
3 A.K. Ray, Indian J. Phys., 26 (1952) 226.
4 T. Schaefer, L.J. Kruczynski, and W.J.E. Parr, Can. J. Chem., 54 (1976) 3210.
5 T. Schaefer, J.B. Rowbotham, W.J.E. Parr, K. Marat, and A.F. Janzen, Can. J. Chem., 54 (1976) 1322.
6 F.R. Dollish, W.G. Fateley, and F.F. Bentley, "Characteristic Raman Frequencies of Organic Compounds," John Wiley & Sons, New York (1974), p. 173.
7 T. Shimanouchi, "Tables of Molecular Vibrational Frequencies Consolidated Volume I." Nat. Stand. Ref. Data Ser., Nat. Bur. Stand., 39 (1972) (NSRDS-NBS 39).
8 J.J. Mannion and T.S. Wang, Spectrochim. Acta, 20 (1964) 45.
9 G.A. Crowder, J. Mol. Struct., 12 (1972) 302.