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VIBRATIONAL SPECTRA AND TORSIONAL BARRIER OF PENTAFLUOROPHENOL

JOSHUA A. FANIRAN

Department of Chemistry, University of Ibadan, Ibadan, Nigeria

SUMMARY

The vibrational spectra of pentafluorophenol (PFP) have been investigated in the gaseous and solid states and as solutions in non-polar solvents. An assignment of the thirty-three fundamental modes is proposed using the band contours and Raman depolarization ratios. Thermodynamic properties, calculated for a rigid-rotor harmonic oscillator approximation, are also reported. The potential barrier restricting the internal rotation about the phenyl-O bond was evaluated to be 1273 cm^{-1}.

INTRODUCTION

Although the vibrational spectra of phenol has been widely studied[1-3], little is known about that of pentafluorophenol. Birchall and Haszeldine reported a partial assignment of the observed infrared frequencies during the preparation of PFP[4] and showed that substitution of fluorine caused a marked increase in the pKa thus rendering PFP more acidic than phenol[5]. It was also observed that there is less intermolecular hydrogen bonding in PFP than to the intermolecular association found in phenol [5] although intermolecular association to the ortho-F is possible.

To further understand the effect of fluorine substitution in phenol, it was therefore of interest to make a complete vibrational assignment of pentafluorophenol. The assignments are discussed in terms of vibrations of pentafluoro substituted benzene (C_6F_5X) and the -COH group.

EXPERIMENTAL

The experimental procedure is similar to that described for pentafluoroaniline[6]. A Perkin-Elmer model 577 was employed for the infrared measurements while a Spex model 1401 double monochromator with argon ion excitation was used to record the Raman spectrum. The infrared vapour spectrum was measured with a 10cm variable temperature gas cell[7].

RESULTS AND DISCUSSION

Pentafluorophenol is assumed to be planar and belongs to point group Cs. The thirty-three fundamental modes thus divide as: 23a' + 10a". The in-plane infrared band envelopes will have mostly hybrid characters since, because of low symmetry, only a few of the a' vibrations will give rise to dipole moment changes parallel to any of the principal axes. The a" modes can, however, be identified with the C-type band contours. In the Raman, the a' will be polarized while the a" are depolarized.

Although coupling of modes will modify the description somewhat the normal vibrations can be divided into two groups viz:

(a) three vibrations originating from the -COH group and

(b) the thirty vibrational modes generated by the aromatic nucleus.

The assignments of the observed frequencies are listed in Table 1. The classification into various normal vibrations was aided by the spectra of phenol[1-3] and perfluorinated aromatics[6]. The infrared and Raman spectra are shown in Fig. 1-3.

-COH group vibrations

The three vibrations arising from the -COH group comprise one OH stretch, OH bend and a torsional oscillation about the C-O bond.

With minor frequency differences, the observed spectrum in the OH stretching region agrees with the partial report of Birchall and Haszeldine

TABLE 1

Observed frequencies[a] of the fundamentals of pentafluorophenol

INFRARED			RAMAN	ASSIGNMENT
Vapour[b]	Solid	Solution	Solution[c]	
3640wB	3580s	3580s	3580mw P	ν(O-H) monomer
-	3200vbs	3260vb, m	-	ν(O-H) H-bonded
-	1660 sh	1662vw	1660w P	ν(C-C)
1540vsH	1534 vs	1532vs	-	ν(C-C)
1475w B	1480 mw	1482mw	1480w P	ν(C-C)
1352w H	1350 s	1348 m	-	ν(C-C)
-	1310 s	1310 ms	-	ν(C-C)
1248w H	1250 ms	1245m	-	ν(C-O)
1230s H	1230 ms	1229 s	-	β(O-H)
1156w	1151 w	1151 w	1155w P	X-sens
1143w H	1135 w	1139 m	1135vw P	ν(C-F)
1024vs H	1016vs	1016 vs	-	ν(C-F)
1002vs H	994 vs	995 vs	-	ring breathing
987 s H	978 vs	974 vs	-	ν(C-F)
780w H	780w	780w	787w P	X-sens
-	706 vw	706 vw	-	X-sens
-	650 vw	648 vw	642 vw	α(C-C-C)
-	605w	-	605 w P	ring mode
-	562 w	564w	560vs P	β(C-F)
-	448 w	447w	443 s P	β(C-F)
-	378 w	378w	375 s dp	γ(C-F)
-	-	-	360s dp	X-sens
-	378 sh	340 sh	-	β(C-F)
320s C	319 s	318s	320 vw	torsion

Table 1 contd.

INFRARED			RAMAN	ASSIGNMENT
Vapour[b]	Solid	Solution	Solution[c]	
-	300 w	300 sh	-	β(C-F)
-	285 w	285 w	287 vw	γ(C-F)
-	273 w	272 w	270w dp	β(C-F)
-	218 m	218m	217w dp	X-sens
-	-	-	195w dp	γ(C-F)
-	-	-	145w dp	γ(C-F)
-	-	-	140w dp	X-sens
-	-	-	(109)[d]	γ(C-F)

(a) : The small letters after the frequencies denote relative intensities:: v = very, s = strong, m = medium sh = shoulder and w = weak.

(b) : B, C and H denote band shape in the gas phase.

(c) : P and dp denote polarized and depolarized respectively.

(d) : Deduced from the combination band.

[4]. However, we differ in frequency assignments. The band at 3580 cm^{-1} (solid and solution) shifting to 3640 cm^{-1} in the gas phase is assigned to the free OH stretch rather than the end group OH polymer suggested by Birchall and Haszeldine. Furthermore, the weak absorption appearing at ca 3680 cm^{-1} (infrared solid and solution only) previously assigned to ν(O-H) monomer[4] is now attributed to an overtone probably in resonance with the OH fundamental.

The OH bend, β(O-H), and torsion about the C-O bond usually occur around 1300 and 200 cm^{-1} respectively in the spectra of phenolic compunds. The former, observed in the spectrum of phenol at 1340 cm^{-1} [1,2], has been assigned to 1230 cm^{-1} with a characteristic broadness of associated OH.

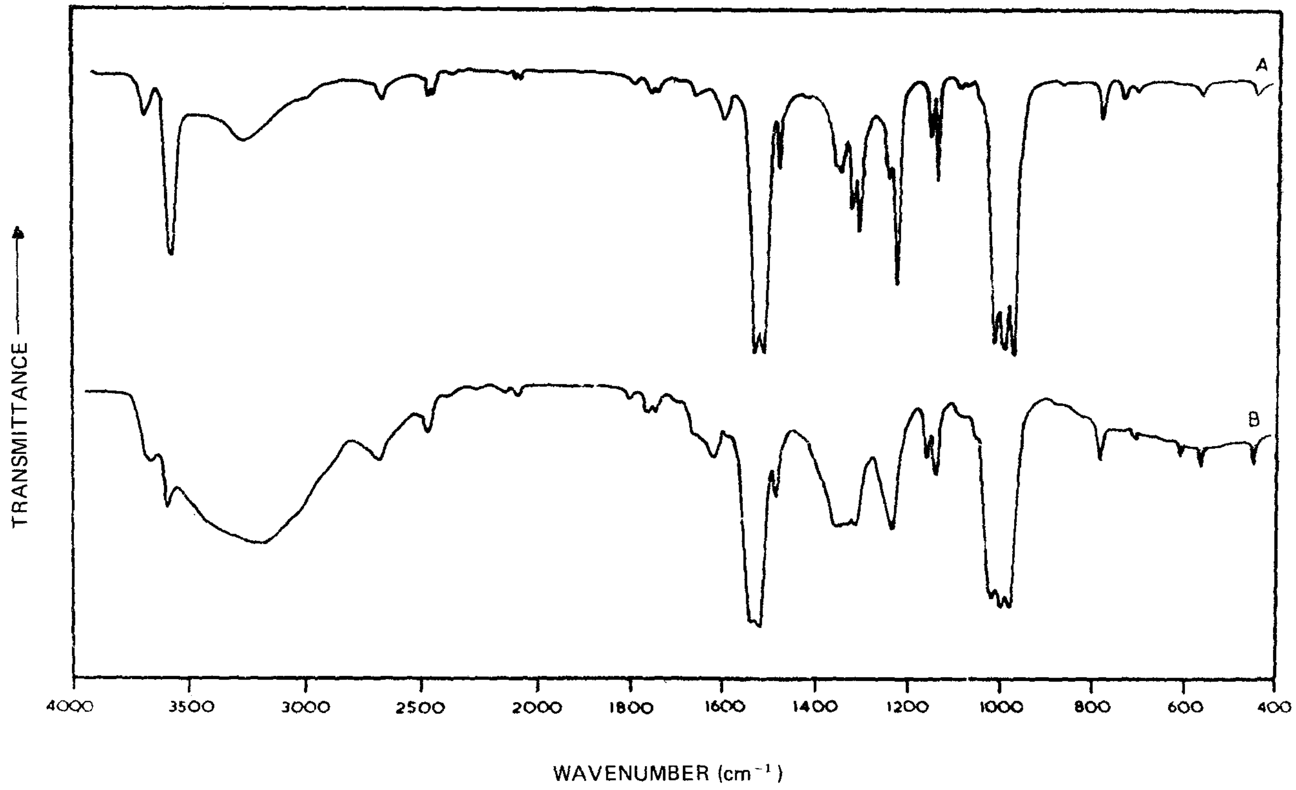


Fig. 1. The infrared spectrum of pentafluorophenol (A) in CCl_4 solution and (B) as a thin solid film.

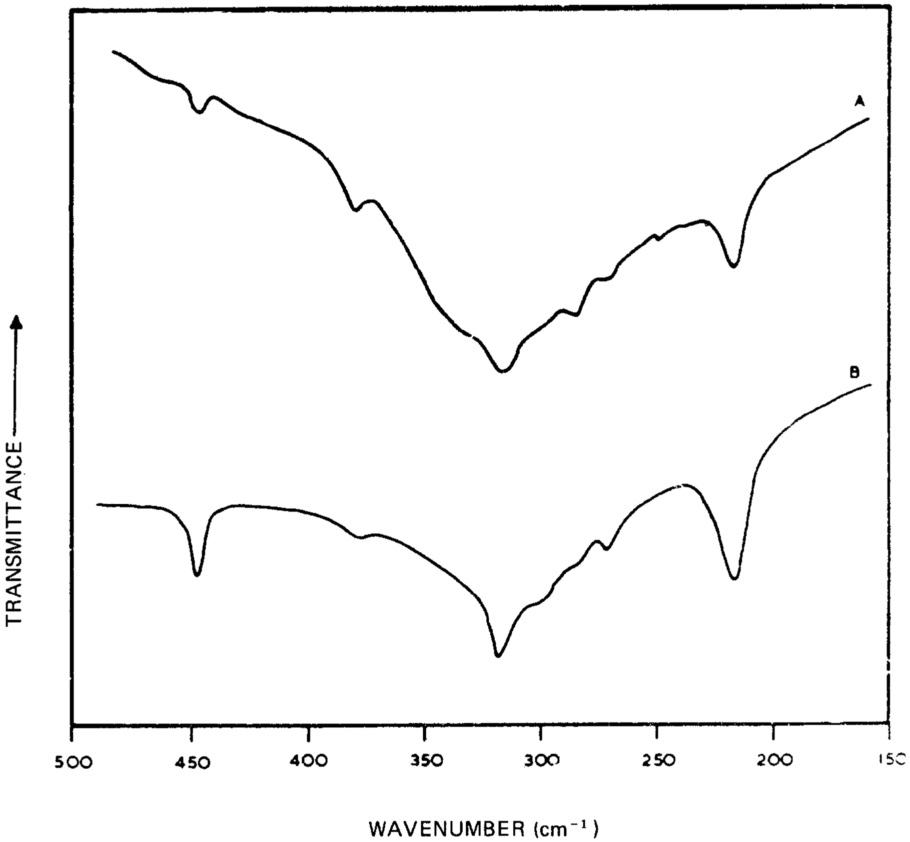


Fig. 2. The far infrared spectrum of pentafluorophenol (A) in CCl_4 solution and (B) as a thin film.

Another strong candidate for the assignment in this region is the band at ca 1250 cm^{-1}. This was however ruled out because it is very sharp and rather weaker than the 1230 cm^{-1} peak. The β(O-H) is known to shift to higher frequency the stronger the association of the OH group. Thus, the lower energy of this mode in PFP as compared to phenol is no doubt attributable to the very weak nature of the intermolecular H-bonding occuring in PFP[5,6]. It is expected that β(O-H) will couple with the ring and ν(C-F) vibrations as was observed in phenol[1-3].

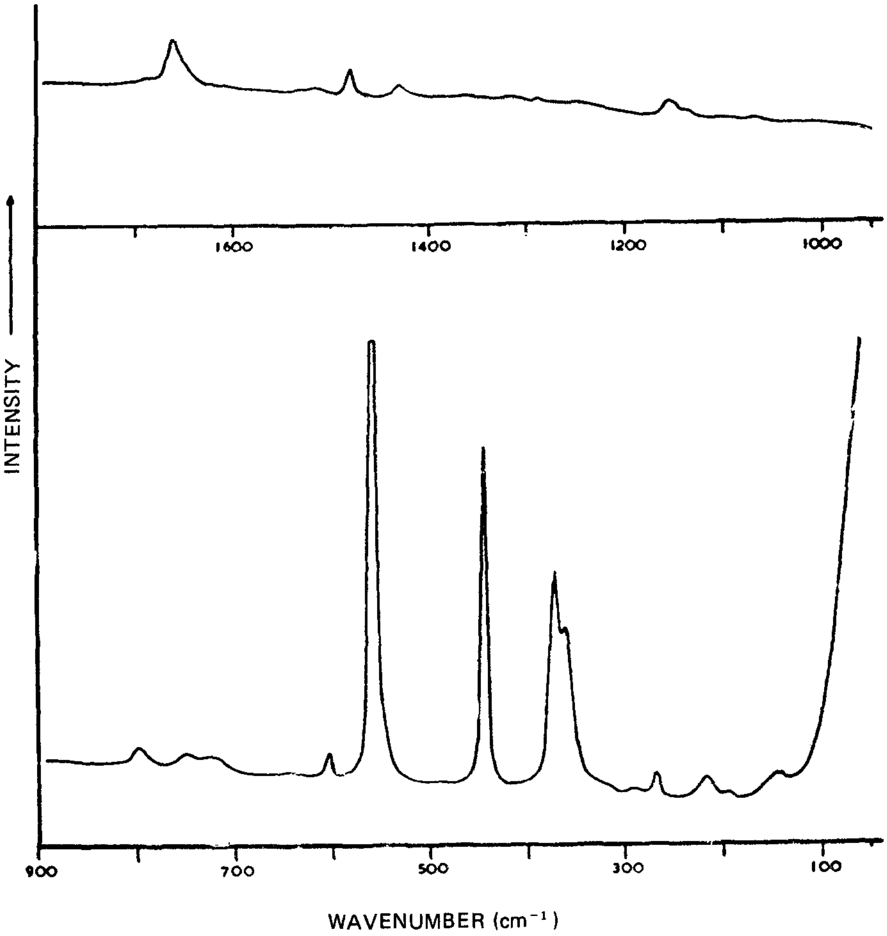


Fig. 3. The Raman spectrum of pentafluorophenol in solution.

By comparison with other phenols, the torsional frequency has been tentatively assigned to the band with a C-type contour in the gas phase at 320 cm^{-1}. Another possible assignment at 300 cm^{-1} was rejected on intensity grounds and more so that this absorption was observed in the solid and solution infrared spectra only.

C_6F_5X vibrations

The spectra of C_6F_5X molecules appear to have received much attention[6, 9-11] and hence only a few interesting features will now be discussed.

Two of the expected five C-F stretching vibrations ν(C-F) are readily assigned to the infrared doublet at 1016 and 987 cm^{-1}. These are in strong Fermi resonance with the ring breathing mode at ca 1000 cm^{-1}. The remaining ν(C-F) frequencies located at 1530, 1520 and 1140 cm^{-1} (Table 1) followed from the previous work on pentafluoroaniline[6]. Preliminary assignment by Birchall and Haszeldine had put the bands at 1530 and 1520 cm^{-1} as the ring modes while 1000 cm^{-1} was assigned to ν(C-F)[4]. Recent works on pentafluorinated benzenes[6,9-11] however show that the present assignment should be preferred. Although the ν(C-F) are very strong in the infrared, they were not observed in the Raman. This probably indicates that the C-F bonds are poor Raman scatterers in C_6F_5X molecules.

The assignment of the polarized Raman lines at 1660 and 1480 cm^{-1} and the infrared features at 1615, 1350 and 1310 cm^{-1} to ring stretch is consistent with pentafluoro aromatic ring vibrations[6,9,-11].

In the low frequency region, not only are the absorptions weak, but also considerable band mixing and overlapping occurs. To identify the CF deformations, β(C-F) and γ(C-F), the correlation diagram of Jakobsen [10] on polyfluorinated aromatics was very useful. This author had demonstrated that the CF deformations and, in particular, γ(C-F) modes are characteristic of polyfluorobenzenes and indeed could be used for their identifications. Using the chart and the spectra of pentafluoroaniline the proposed assignment to β(C-F) and γ(C-F) given in Table 1 was arrived at. It must be emphasized that the lowest energy γ(C-F) near 110 cm^{-1} has not been observed in this study but was derived from the combination band.

The potential energy $V(\alpha)$ opposing internal rotation about single bonds can be expressed as:

$$V(\alpha) = \tfrac{1}{2}V_1\ (1-\cos\ \alpha) + \tfrac{1}{2}V_2(1-\cos\ 2\alpha) + \tfrac{1}{2}V_3(1-\cos\ 3\alpha) \qquad (1)$$

where α is the torsional angle and V_1, V_2, V_3 are the potential constants which are contributions to the barrier heights from 1, 2, 3-fold energy terms respectively. For a harmonic torsional potential barrier, $V(\alpha)$ is composed of the individual Fourier series

$$V_{(\alpha)} = (\tfrac{1}{2}V_1 + V_2 + 9/4\ V_3 + - - -)\alpha^2 \qquad (2)$$

which, in terms of the torsional frequency ν_t, becomes

$$V_{(\alpha)} = (2\pi^2c^2\nu_t^{\,2}I_R)\alpha^2 \qquad (3)$$

where I_R is the reduced moment of inertia of the rotating group. Assuming a planar configuration for pentafluorophenol the internal rotation about the phenyl-O bond will be largely two-fold symmetric with the energy term V_2 given by

$$V_{2(erg)} = 2\pi^2c^2\nu_t^{\,2}I_R \qquad (4)$$

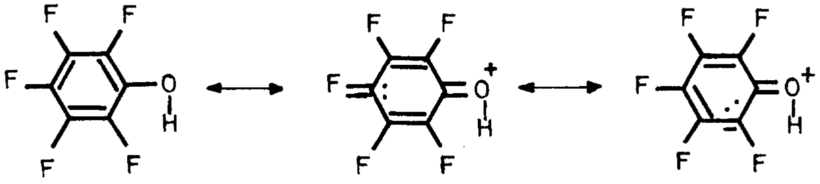
As no structural data are available, the following parameters were adopted [12,13,14]: C-C = 1.39 A°; C-F = 1.34A°; C-O = 1.364A°; O-H = 0.956A°; $\angle$COH = 118°; $\angle$CCC = 120° and $\Phi = 5°$ where Φ is the displacement of the C-O bond from the torsional axis. The reduced moment of inertia I_R computed from these data using Pitzer's equation[15,16] is 0.838 a.m.u. A^{o^2}. This gave a potential barrier to internal rotation about the C-O bond of 1273 cm^{-1} (3.64 Kcals). Comparison with available data for phenol and p-fluorophenol (Table 2) shows that, within the experimental approximation, pentafluorination of phenol significantly increases the barrier height hindering rotation about the C-O bond while p-fluorination leads to a decrease in barrier height.

This could be explained in terms of an inductive effect and mesomeric interaction produced by the fluoro substituents. Halogens as aromatic sub-

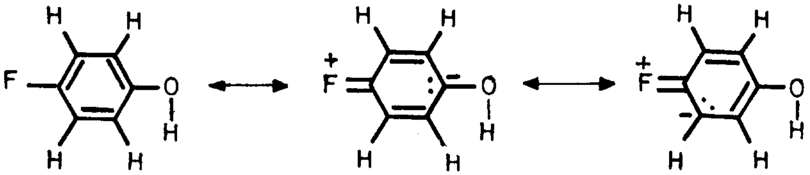
TABLE 2

Torsional frequencies (ν_t) and barrier heights (V_2) in phenol, p-fluorophenol (p-FP) and pentafluorophenol (PFP)

Compound	V_2		ν_t	Method	Ref.
	cm^{-1}	Kcal/mole	cm^{-1}		
Phenol	1180	3.37	307	Infrared	1
	1103	3.15	309	Microwave	17
	1215	3.47	309.6	Infrared	3
	1063	3.04	309.6	Inversion	12
p-fluorophenol	940	2.69	280	Infrared	18
P F P	1273	3.64	320	Infrared	This work



(a) INDUCTIVE EFFECT



(b) MESOMERIC INTERACTION

Fig. 4 Possible canonical forms for pentafluorophenol and p-fluorophenol.

stituents are known to be unusual in producing a strong inductive effect as well as mesomeric interactions. If the inductive effect is operative then the oxygen lone pair electrons will be attracted towards the aromatic ring and thereby strengthen the C-O bond as shown in Fig. 4a. Mesomeric interaction, on the other hand, would create resonance structures whereby the location of the negative charge within the aromatic nucleus prevents any effective contribution from the oxygen lone pair electrons (Fig. 4b). It is believed that, in PFP, the inductive effect outweighs mesomeric interaction. Hence, there is greater conjugation between the ring and oxygen lone pair electrons leading to increased torsional barrier. For p-fluorophenol however, mesomeric interation seems to predominate and this would favour the observed lowering of the barrier height.

THERMODYNAMIC FUNCTIONS

The thermodynamic properties were calculated from the thirty-three fundamental frequencies using the assumed molecular parameters by the usual statistical methods[19]. The evaluation was carried out for an ideal gaseous state at one atmosphere pressure using the rigid rotator harmonic oscillator approximation. The results are given in Table 3. Unlike phenol [20] however, there are no calorimetric data with which to compare these values.

CONCLUSION

The thirty-three fundamental frequencies of pentafluorophenol have been assigned on the basis of a structure with C_s symmetry. The results are in good agreement with our earlier conclusion[6] that the strong infrared absorptions at ca 1660, 1520, and 980 cm^{-1} together with the Fermi doublet at ca 1000 cm^{-1} are characteristic of C_6F_5X molecules and could be used for diagnostic identification of pentafluoro aromatic nucleus.

TABLE 3

Thermodynamic functions of pentafluorophenol in cal/deg/mole

T(K)	$(H^o-E_o^o)/T$	$-(F^o-E_o^o)/T$	S^o	C_p^o
200	17.58	66.86	84.44	29.15
300	22.86	75.02	97.87	37.36
400	27.36	82.22	109.59	44.18
500	31.31	88.76	120.07	49.74
600	34.76	94.78	129.54	54.10
700	37.77	100.37	138.15	57.45
800	40.40	105.59	146.00	60.03
900	42.71	110.49	153.19	62.04
1000	44.73	115.10	159.82	63.64
1100	46.51	119.45	165.96	64.92
1200	48.10	123.57	171.66	65.97
1300	49.51	127.48	176.99	66.84
1400	50.78	131.20	181.98	67.57
1500	51.93	134.74	186.67	68.19

As a result of the inductive effect of the fluorine substituents there is a considerable electron delocalisation from the oxygen lone pair electrons to the aromatic ring leading to the strengthening of the C-O bond. This will explain the observed higher potential barrier across the phenyl-O bond in PFP as compared to phenol.

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