

THE VIBRATIONAL SPECTRA OF PENTAFLUOROBENZOYLCHLORIDE

K. SINGH, S. R. SINGH AND I. S. SINGH

Spectroscopy Laboratory, Faculty of Science, Banaras Hindu University, Varanasi-5, India

ABSTRACT

The Raman spectrum of pentafluorobenzoylchloride (liquid) with polarization measurement has been recorded on a Spex-spectrophotometer using a He-Ne laser source. The infrared spectrum (liquid) of the sample has been recorded on a UR-10 as well as on a Perkin-Elmer 621 infrared spectrophotometer with slow scanning. Assignments have been proposed for the observed frequencies assuming C_s symmetry for the molecule.

INTRODUCTION

A LARGE number of highly fluorinated aromatic compounds are available in commercial quantities. These compounds are interesting due to the high electronegativity of fluorine. The fundamental vibrational frequencies of the parent compound hexafluorobenzene have been assigned by Steele and Whiffen¹. The infrared and Raman spectra of pentafluorobenzene and the infrared spectrum of pentafluorodeuterobenzene have also been recorded and assignments of the observed frequencies have been proposed². The in-plane vibrational frequencies of some model pentafluorobenzene derivatives of the type C_6F_5X (where X is taken as Cl, Br and I) have been reported by Long and Steele³. Recently, some more complicated pentafluorobenzene derivatives⁴⁻¹¹ have been studied. In this paper details of the Raman and infrared spectra and vibrational assignments for pentafluorobenzoylchloride are presented.

EXPERIMENTAL

Pentafluorobenzoylchloride (pure) for the present work was obtained from Pierce Chemical Co., U.S.A., and was used without further purification. The Raman spectrum, with polarization measurements, has been recorded in liquid phase on an assembled Raman apparatus which includes the following units¹²: Spex 1400 II double monochromator, spectra-Physics 125-He-Ne laser, Spex cryostat fitted with and ITT FW 130-S-20 photomultiplier detector, victoreen 1001 D.C. amplifier and a Texas Instruments strip chart recorder. The 6328 Å line of the He-Ne laser was used to excite the Raman spectrum. The accuracy of measurement is believed to be within 2 cm^{-1} .

The infrared spectrum (liquid phase) was recorded with slow scanning on a Perkin-Elmer grating spectrophotometer (Model 621) in the region $200\text{--}1700\text{ cm}^{-1}$. A NaCl cell of 0.05 mm pathlength was used in the region $600\text{--}1700\text{ cm}^{-1}$ and a KBr cell of 0.1 mm pathlength in the region $200\text{--}700\text{ cm}^{-1}$. The

accuracy of measurement is believed to be within 2 cm^{-1} . The infrared spectrum was also recorded on a Carl Zeiss UR-10 spectrophotometer in the region $700\text{--}4000\text{ cm}^{-1}$. The traces of the Raman and infrared spectra are shown in Figs. 1, 2, 3 and 4. The Raman and infrared frequencies along with their assignments are given in Table I.

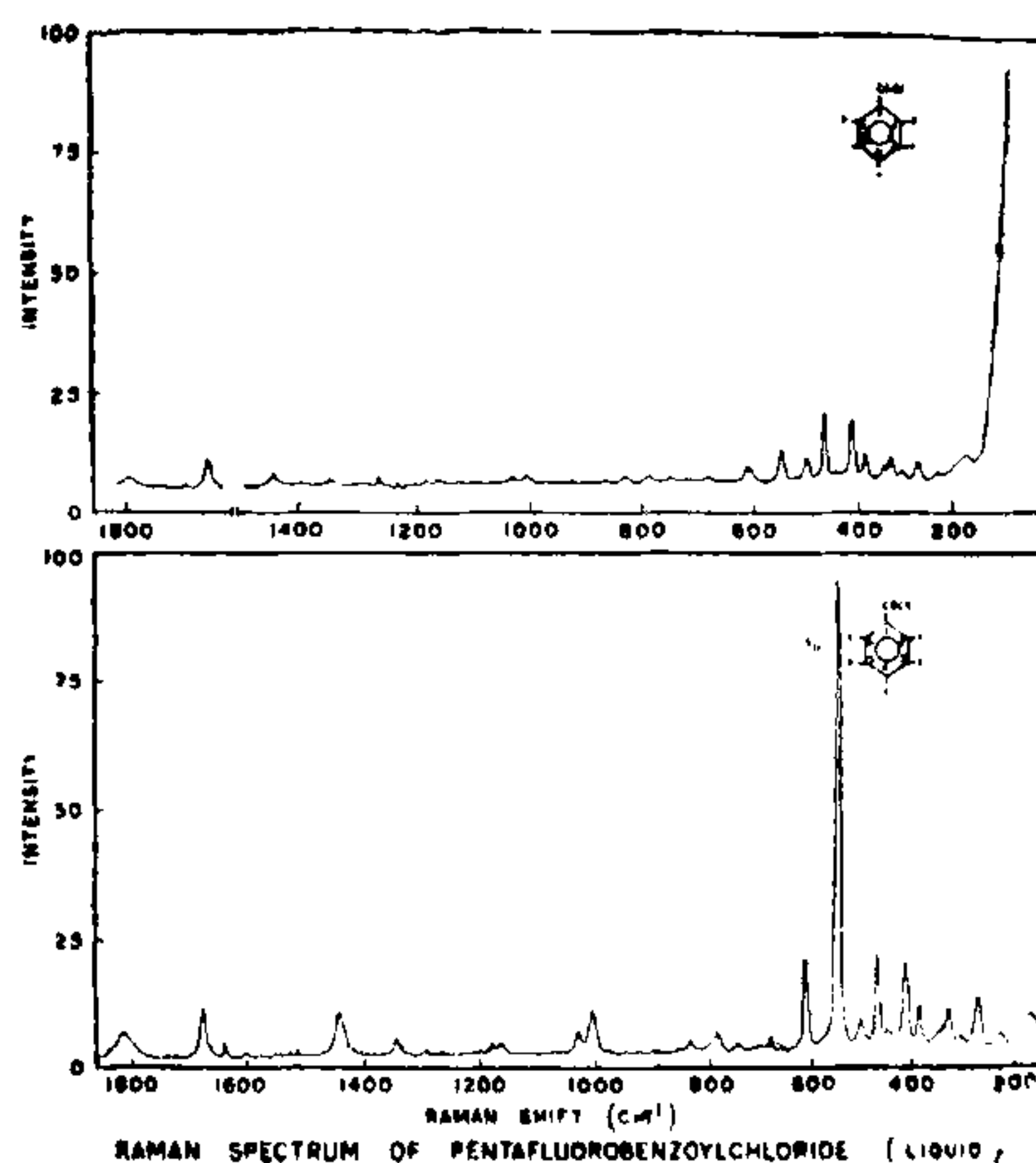


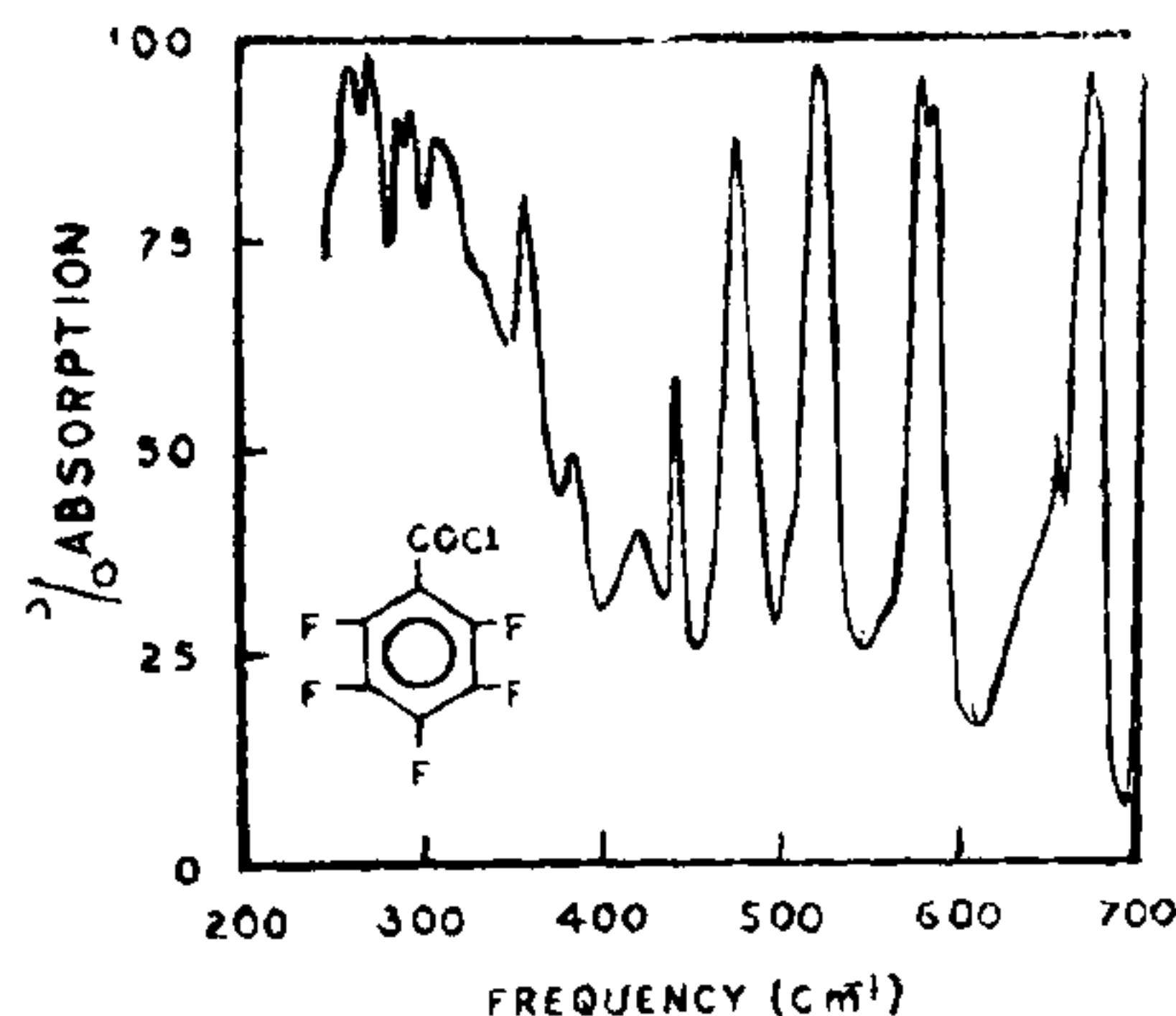
FIG. 1

RESULTS AND DISCUSSION

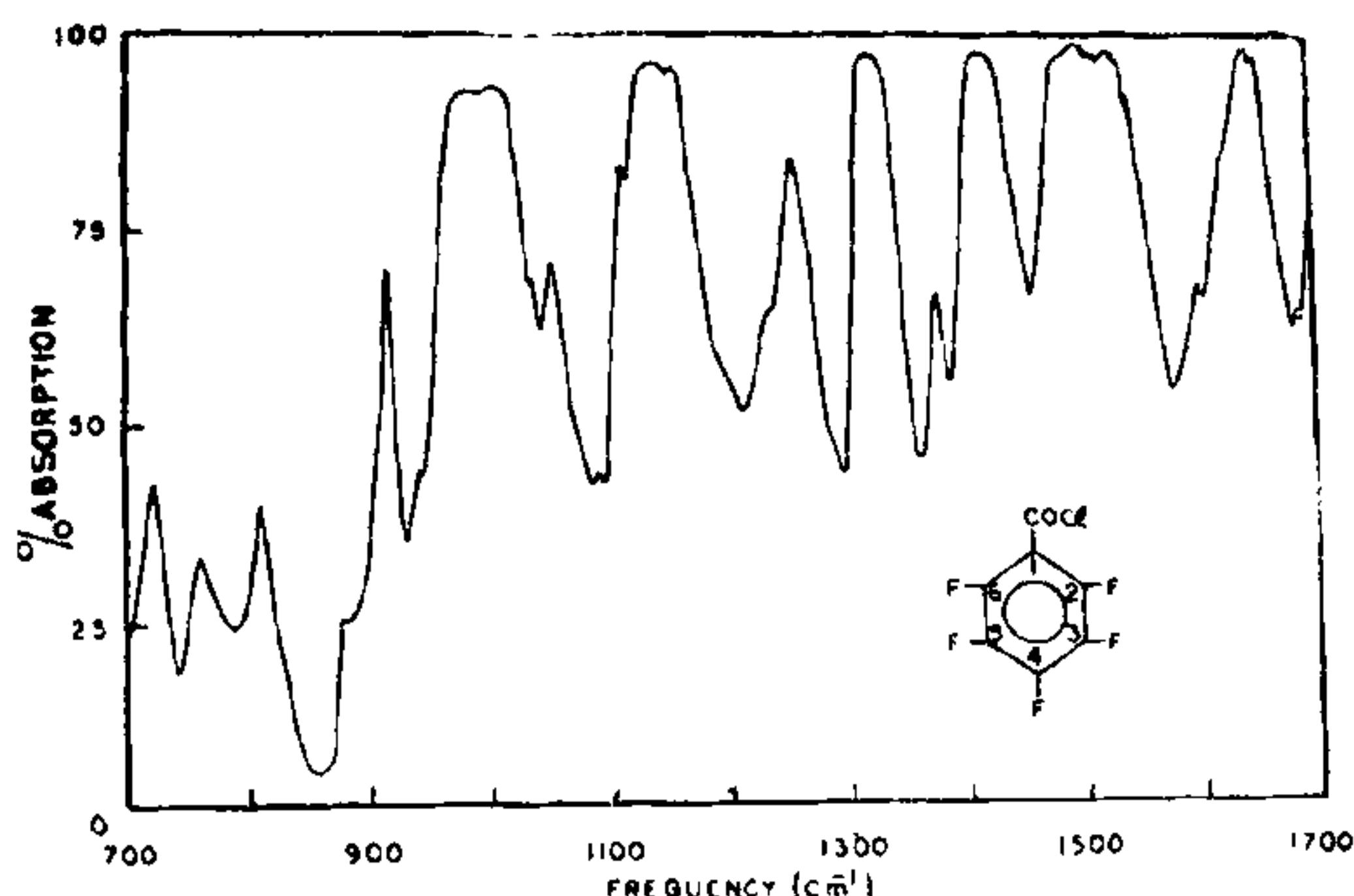
If the COCl group is taken to be in the plane of the ring, the pentafluorobenzoylchloride molecule will belong to C_s point group. This molecule having 14 atoms will give rise to 36 normal modes of vibrations. The 36 vibrations consist of 30 vibrations originating from phenyl part (ring vibrations) and 6 vibrations from C-COCl part. The 36 normal vibrations can be divided into 25 a' (planar) and 11 a'' (non-planar) vibrations. All of these are allowed in both the Raman and infrared spectra. The vibrations belonging to a' species are polarized and the vibrations belonging to a'' species are depolarized in the Raman spectrum.

Phenyl Ring Vibrations.—In hexafluorobenzene the frequencies 559 cm^{-1} (a_{1g}), 1253 cm^{-1} (b_{2g}), 1530 cm^{-1} (e_{1u}) and 1655 cm^{-1} (e_{2g}) have been assigned to $\text{C}=\text{C}$ stretching modes, the last two being doubly degenerate.

infrared spectrum may also be assigned to $\text{C}=\text{C}$ stretching mode. We are not very certain about the assignment of this frequency, since it could not be recorded in the Raman spectrum.

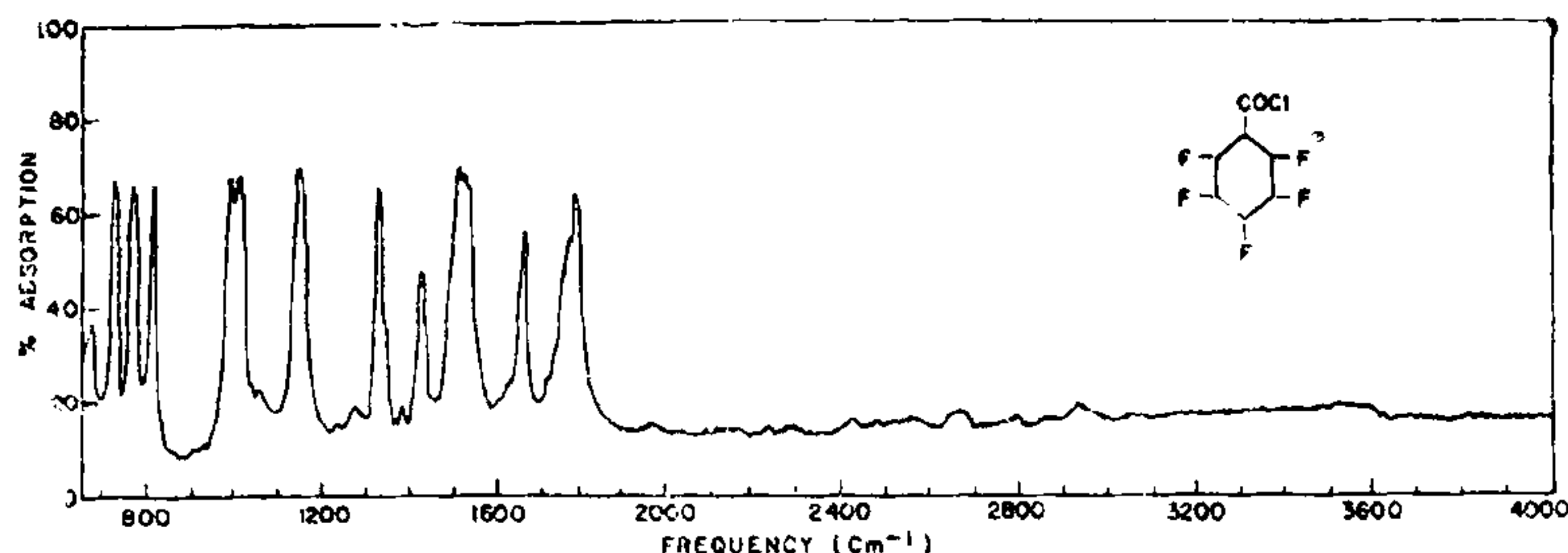


INFRARED SPECTRUM OF
PENTAFLUORO BENZOYLCHLORIDE
(LIQUID) 0.1 m.m.



INFRARED SPECTRUM OF PENTAFLUORO BENZOYLCHLORIDE
(LIQUID) 0.05 m.m.

FIGS. 2 & 3



INFRARED SPECTRUM OF PENTAFLUORO BENZOYL CHLORIDE
(THIN LIQUID FILM)

FIG. 4

In molecules having lower symmetry than D_6 , the doubly degenerate species e_{1u} and e_{2g} are expected to split up into two components each. Thus, in pentafluorobenzoylchloride, one would expect six $\text{C}=\text{C}$ stretching vibrations. The frequencies 522 cm^{-1} (vvs-R, vvs-IR), 1263 cm^{-1} (vbw-R, s-IR), 1513 cm^{-1} (vbw-R, vvs-IR), 1529 cm^{-1} (vbw-R, vvs-IR) and 1650 cm^{-1} (ms-R, s-IR) have been assigned to $\text{C}=\text{C}$ stretching modes. The frequencies 522 and 1650 cm^{-1} are polarized in the Raman spectrum. The depolarization ratios of the remaining frequencies could not be definitely determined as these are observed with very weak intensity in the Raman spectrum. The frequency 1658 cm^{-1} observed with strong intensity in the

$\text{C}-\text{F}$ stretching frequencies, in general, are exceptionally strong owing to the very high electronegativity of the fluorine atom. In hexafluorobenzene, the frequencies 1011 cm^{-1} (e_1), 1157 cm^{-1} (e_{2g}), 1323 cm^{-1} (b_{1u}), and 1490 cm^{-1} (a_{1g}) have been assigned to $\text{C}-\text{F}$ stretching modes. Of these the first two frequencies are doubly degenerate. In pentafluorobenzoylchloride five $\text{C}-\text{F}$ stretching vibrations are expected. The frequencies 984 cm^{-1} (ms-R, vvs-IR), 1006 cm^{-1} (w-R, vvs-IR), 1141 cm^{-1} (vbw-R, vvs-IR), 1322 cm^{-1} (vw-R, vs-IR) and 1421 cm^{-1} (ms-R, vvs-IR) have been assigned to $\text{C}-\text{F}$ stretching modes in the present investigation. The frequencies 984 and 1006 cm^{-1} arise due to the splitting

TABLE I
Vibrational frequencies and their assignments for pentafluorobenzoylchloride

Raman (liquid)			Infrared (liquid)		Assignment
cm ⁻¹	Int.	Dep.	cm ⁻¹	Int.	
142	m	0.86 D	a'' C-COCl twisting
198	vvw	0.90 D	a'' C-F o.p. bending
244	ms	0.34 P	a' C-F i.p. bending
278	vvw	0.80 P	272	ms	do.
301	m	0.64 P	297	ms	do.
316	vvw	0.83 P	312	ms	do.
355	m	0.88 D	358	m	a' C-F o.p. bending
384	s	0.86 D	386	mw	do.
421	vvw	P?	421	w	a' C-C-C i.p. bending
440	s	0.75 P	443	s	do.
473	m	1.0 D	478	s	a'' C-C-C o.p. bending
522	vvs	0.06 P	522	vvs	a' C-C stretching (ring breathing)
585	s	0.16 P	585	vs	a' C-C-C i.p. bending
654	vvw	..	656	mw	a'' C-C-C o.p. bending
670	vvw	0.87 D	672	ms	do.
721	vvw	0.75 P	724	vvs	a' C-F i.p. bending
761	vw	0.62 P	767	vs	a' C-Cl stretching
806	vvs	0.75 P	812	m	a' (C ₆ F ₅)-COCl stretching
984	ms	0.25 P	985	vvs	a' C-F stretching
1006	w	0.30 P	1007	vvs	do.
1141	vvw	0.27 P	1141	vvs	do.
1263	vvw	P?	1260	s	a' C=C stretching
1322	vw	0.37 P	1322	vs	a' C-F stretching
1421	ms	0.30 P	1420	vvs	do.
1513	vvw	P?	1507	vvs	a' C=C stretching
1529	vvw	P?	1522	vvs	do.
1650	ms	0.56 P	1650	s	do.
1774	w	0.36 P	1763	ms	Fermi-resonance between 1774 a' (C=O stretching) and 767+1007 A' (combination)
..	1785	s	

N.B.— Int. = Intensity, Dep. = Depolarization, D=depolarized, P=polarized, m=medium, w=weak, vw=very weak, mw=medium weak, s=strong, ms=medium strong, vs=very strong, vvs=very very strong, vwv=very very weak, R=Raman, I.R.=Infrared.

of 1011 cm⁻¹ (*e*_{1u}) frequency of C₆F₆. All these frequencies are polarized in the Raman spectrum. Our assignments are in good agreement with the assignments proposed for other pentafluorobenzene derivatives.

In pentafluorobenzoylchloride three C-C-C in-plane bending vibrations are expected, two arising from 443 cm⁻¹ (*e*_{2g}) and one from 640 cm⁻¹ (*b*_{1u}) frequencies of C₆F₆. The doubly degenerate vibration 443 cm⁻¹ (*e*_{2g}) splits up into two components in pentafluorobenzoylchloride due to reduction of symmetry from D_{6h} to C_s. From the earlier studies of pentafluorobenzene derivatives, it appears that one component of the *e*_{2g} vibration remains near 440 cm⁻¹ while the other component is slightly shifted towards lower frequency side. The frequencies 440 cm⁻¹ (s-R, s-IR) and 421 cm⁻¹ (vw-R, w-IR) have been assigned to these two modes. The third C-C-C in-plane bending vibration corresponding to 640 cm⁻¹ (*b*_{1u}) frequency of C₆F₆ practically stays near 585 cm⁻¹ in pentafluorobenzene

derivatives. We have assigned the frequency 585 cm⁻¹ (s-R, vs-IR) to this mode. The frequencies 440 and 585 cm⁻¹ are polarized in the Raman spectrum but the depolarization ratio of the frequency 421 cm⁻¹ is not known although the magnitude is in the expected region.

In C₆F₆, the frequencies 208 cm⁻¹ (*b*_{2u}), 264 cm⁻¹ (*e*_{2g}), 315 cm⁻¹ (*e*_{1u}) and 691 cm⁻¹ (*a*_{2g}) represent C-F in-plane bending modes. Each of the doubly degenerate vibrations 264 cm⁻¹ (*e*_{2g}) and 315 cm⁻¹ (*e*_{1u}) are expected to split up into two components in the case of pentafluorobenzoylchloride due to lowering of symmetry. Thus, in pentafluorobenzoylchloride five C-F in-plane bending vibrations are expected and all of these should be polarized in the Raman spectrum. The frequencies 244 cm⁻¹ (ms-R) and 278 cm⁻¹ (vw-R, ms-IR) correspond to the two components of 264 cm⁻¹ (*e*_{2g}) frequency of C₆F₆. The two components corresponding to 315 cm⁻¹ (*e*_{1u}) frequency of C₆F₆ have been observed to lie at 316 cm⁻¹ (vw-R, ms-IR) and 301 cm⁻¹ (m-R,

ms-IR). The 721 cm^{-1} (vw-R, vs-IR) frequency has been assigned as the fifth C-F in-plane bending vibration corresponding to 691 cm^{-1} (a_{2g}) frequency of C_6F_6 . This assignment is in agreement with the assignments proposed by Long and Steele³ for $\text{C}_6\text{F}_5\text{X}$ (where $\text{X} = \text{Cl}$, Br or I) molecules. All the frequencies assigned to C-F in-plane bending modes are polarized in the Raman spectrum.

In pentafluorobenzoylchloride, three C-C-C out-of-plane bending vibrations, corresponding to 714 cm^{-1} (b_{2g}) and 595 cm^{-1} (e_{2u}) frequencies of C_6F_6 , are expected. The frequencies 670 cm^{-1} (vw-R, ms-IR), 654 cm^{-1} (vw-R, mw-IR) and 473 cm^{-1} (m-R, s-IR) have been assigned to C-C-C out-of-plane bending modes in the present case. The frequencies 670 and 473 cm^{-1} are depolarized in the Raman spectrum but the depolarization ratio of the frequency 654 cm^{-1} could not be determined.

In hexafluorobenzene, the frequencies 125 cm^{-1} (e_{2u}), 215 cm^{-1} (a_{2u}), 249 cm^{-1} (b_{2g}) and 370 cm^{-1} (e_{1g}) are assigned to C-F out-of-plane bending modes. The frequencies 125 and 370 cm^{-1} are doubly degenerate and are expected to split up into two components in molecules having lower symmetry than D_{6h} . In pentafluorobenzoylchloride, of the expected five C-F out-of-plane bending frequencies, only three frequencies 198 cm^{-1} (vw-R), 355 cm^{-1} (m-R, m-IR) and 384 cm^{-1} (s-R, mw-IR) could be assigned. All these frequencies are depolarized in the Raman spectrum. The frequencies 384 and 355 cm^{-1} have been correlated with the two components of 370 cm^{-1} (e_{1g}) frequency of C_6F_6 . The frequency 198 cm^{-1} may be correlated with 215 cm^{-1} (a_{2u}) frequency of C_6F_6 .

Vibrations of the Substituent Group.—There are six vibrations associated with the substituent group. Out of these six vibrations, only four could be identified with certainty. The medium intense depolarized line at 142 cm^{-1} appearing in the Raman spectrum has been assigned to C-COCl twisting. The frequency 806 cm^{-1} (vw-R, m-IR) has been assigned to $(\text{C}_6\text{F}_5)\text{-COCl}$ stretching mode. This frequency is polarized in the Raman spectrum. In benzoylchloride, the frequency 873 cm^{-1} has been assigned to this mode. In the present investigation, the reduction in the magnitude of this frequency may be due to increase in the mass of the phenyl (C_6F_5 instead of C_6H_5) group. The C-Cl stretching frequency generally appears in the range $600\text{--}800\text{ cm}^{-1}$. In

the present case the frequency 767 cm^{-1} (vw-R, vs-IR) has been assigned to this mode. The two frequencies 1763 cm^{-1} and 1785 cm^{-1} observed with medium strong and strong intensity respectively in the infrared spectrum have been explained due to Fermi-resonance interaction between the $\text{C}=\text{O}$ stretching and a combination band. Two necessary requirements for such a resonance are that the two interacting frequencies must be quite close and should belong to the same species. In the present case, the two interacting frequencies are 1774 cm^{-1} ($\text{C}=\text{O}$ stretching, a') and 1773 cm^{-1} [combination of 1007 cm^{-1} (a') and 767 cm^{-1} (a')] such splittings have been observed in the infrared spectra of benzoylchloride¹³ and other substituted benzoylchlorides¹⁴. In the Raman spectrum a single polarized line has been observed at 1774 cm^{-1} .

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