

# VIBRATIONAL SPECTRA OF THE THREE ISOMERIC FLUOROBENZOYLCHLORIDES

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## ABSTRACT

The infrared absorption spectra of *o*-, *m*- and *p*-fluorobenzoylchlorides have been recorded in the region 350–4000  $\text{cm}^{-1}$  on a Perkin-Elmer 621 grating spectrophotometer. The observed fundamental frequencies have been assigned to different modes of vibration on the basis of magnitude and relative intensities of the observed bands. The doublet nature of the carbonyl band has been interpreted in terms of Fermi-resonance.

## INTRODUCTION

THE electronic absorption spectra of *o*-, *m*- and *p*-fluorobenzoylchlorides in liquid phase have been studied by Forbes and Myron<sup>1</sup> and the mesomeric effect in each case has been discussed. In studying the spectral changes of the infrared carbonyl bands in mono-substituted benzoylchlorides in carbon tetrachloride solution, they also observed the doublet carbonyl bands in *m*- and *p*-fluorobenzoylchlorides. The Raman spectrum of *p*-fluorobenzoylchloride along with the Raman spectra of several other substituted benzenes has been recorded by Pendl and Radinger<sup>2</sup>. By reviewing the earlier literature on the vibrational spectra of isomeric fluorobenzoylchlorides, it appears that none of the earlier workers has given complete assignment of their fundamental frequencies and, therefore, it was considered desirable to record the infrared spectra of the isomeric fluorobenzoylchlorides and present a complete assignment of the observed fundamental frequencies.

## EXPERIMENTAL

The infrared absorption spectrum of *o*-fluorobenzoylchloride was recorded in the region 650–4000  $\text{cm}^{-1}$  by making paste of the compound with nujol and pressing a small quantity of the paste between two NaCl windows. In the region 350–650  $\text{cm}^{-1}$ , the absorption spectrum of the ortho-isomer was recorded by KBr pellet technique. The spectra of *m*- and *p*-fluorobenzoylchlorides were recorded in the region 650–4000  $\text{cm}^{-1}$  in liquid phase by enclosing a thin film of liquid between two NaCl windows. In the region 350–650  $\text{cm}^{-1}$ , the spectra of the pure liquids of meta- and para-isomers were recorded using a KBr cell of 0.05 mm thickness. All these spectra were recorded on a Perkin-Elmer 621 grating spectrophotometer. The specific infrared traces of the isomeric fluorobenzoylchlorides are reproduced in Figs. 1, 2 and 3.

The chemicals used in these investigations were manufactured by Koch-Light Laboratories Ltd. (England) and were of pure quality.

## RESULTS AND DISCUSSION

The molecule fluorobenzoylchloride contains 14 atoms and therefore we expect a total of 36 normal vibrations which include the internal vibrations of the substituent group. For convenient spectral interpretation, we may assume the COCl group to lie in the plane of the phenyl ring. Then all the three fluorobenzoylchloride isomers would belong to the  $C_s$  point group with the molecular plane as the only element of symmetry. The 36 normal modes of vibrations can be divided into 25  $a'$  type and 11  $a''$  type. Vibrations of both these types are allowed in Raman as well as in infrared spectra.

The analysis of the observed bands and the assignments of the fundamental frequencies have been made essentially on the basis of the magnitude and relative intensities of the observed infrared bands. In addition, help has been taken from comparative assignments in related molecules like benzoylchloride<sup>3</sup>, substituted benzoylchlorides<sup>1,4-6</sup>, disubstituted benzenes<sup>7-14</sup>, etc. The frequencies arising from C–F group could be easily identified with the help of similar studies in fluorinated aromatic compounds<sup>15-22</sup>. A correlation of all the observed fundamental frequencies in the infrared spectra of *o*-, *m*- and *p*-fluorobenzoylchlorides along with their relative intensities and proposed assignments has been given in Table I. The vibrational frequencies can be conveniently divided among three distinct groups: (a) phenyl ring, (b) C–COCl group, and (c) C–F group.

### (A) Phenyl Ring Vibrations

The frequencies of magnitudes 1085, 977 and 1102  $\text{cm}^{-1}$  in *o*-, *m*- and *p*-fluorobenzoylchlorides respectively are observed with medium intensities and we have assigned these to the 'ring breathing' mode, corresponding to 992  $\text{cm}^{-1}$  ( $a_{1g}$ ) vibration of benzene. This assignment is in good agreement with the assignments made by Randle and Whiffen<sup>7</sup> and by Venkateswarlu and Radhakrishnan<sup>23</sup> in case of several disubstituted benzene derivatives,

We expect five more frequencies to arise from the C=C stretching vibrations of the ring. Four of these correspond to the two doubly degenerate vibrations  $e_{2g}$  ( $1585\text{ cm}^{-1}$ ) and  $e_{1u}$  ( $1485\text{ cm}^{-1}$ ) of benzene. The fifth is the analogue of the  $b_{2u}$  ( $1310\text{ cm}^{-1}$ ) frequency of benzene. These two  $e_{2g}$  and  $e_{1u}$  vibrations of benzene give rise to four frequencies of  $a'$  type. It is usually observed that one of the components of these two frequencies is lowered but the other component retains the magnitude of the degenerate vibration in benzene. All the four components of these two frequencies are

the two components of  $e_{2g}$  ( $1585\text{ cm}^{-1}$ ) vibration of benzene. Similarly, the pairs of frequencies  $1485, 1463$ ;  $1482, 1436$  and  $1501, 1412\text{ cm}^{-1}$  have been assigned as the two components of  $e_{1u}$  ( $1485\text{ cm}^{-1}$ ) frequency of benzene, in *o*-, *m*- and *p*-fluorobenzoylchlorides, respectively. The frequencies  $1308, 1310$  and  $1295\text{ cm}^{-1}$  in *o*-, *m*- and *p*-isomers respectively have been assigned to the C=C stretching mode corresponding to  $b_{2u}$  ( $1310\text{ cm}^{-1}$ ) vibration of benzene. These assignments are in good agreement with those proposed for other disubstituted benzenes<sup>7,10-12</sup>.

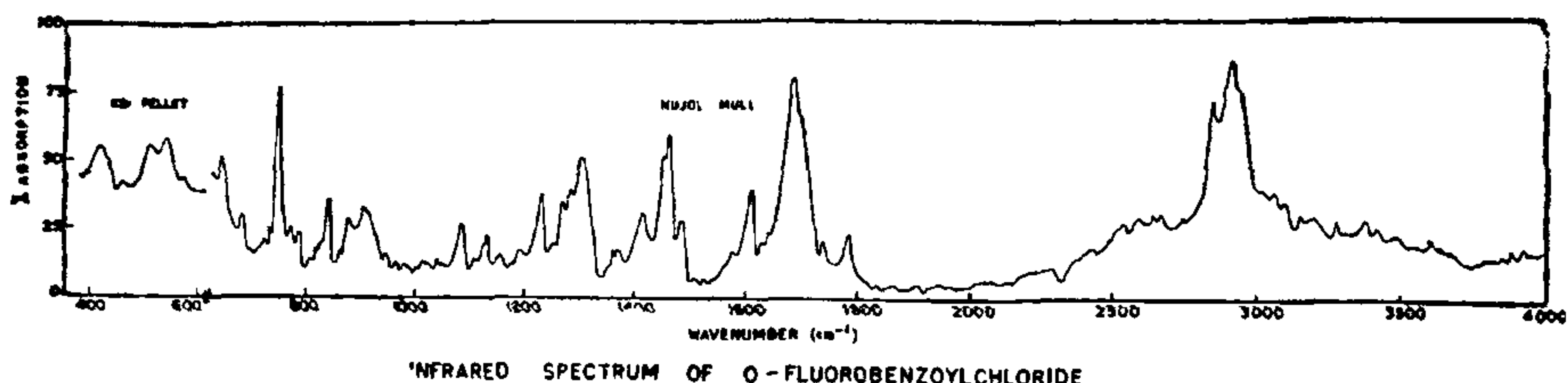


FIG. 1

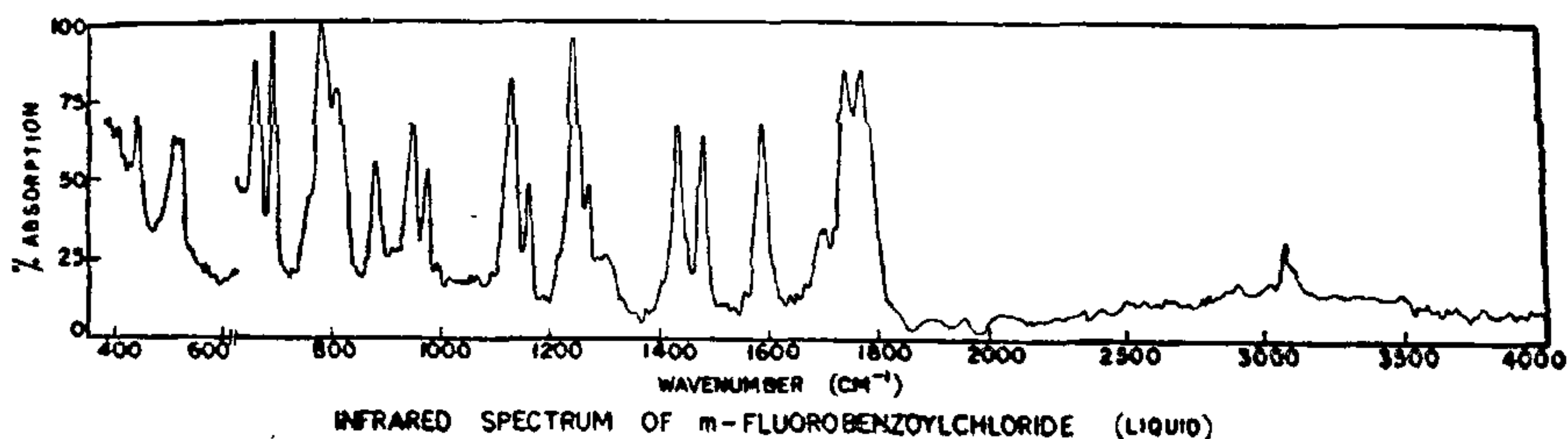


FIG. 2

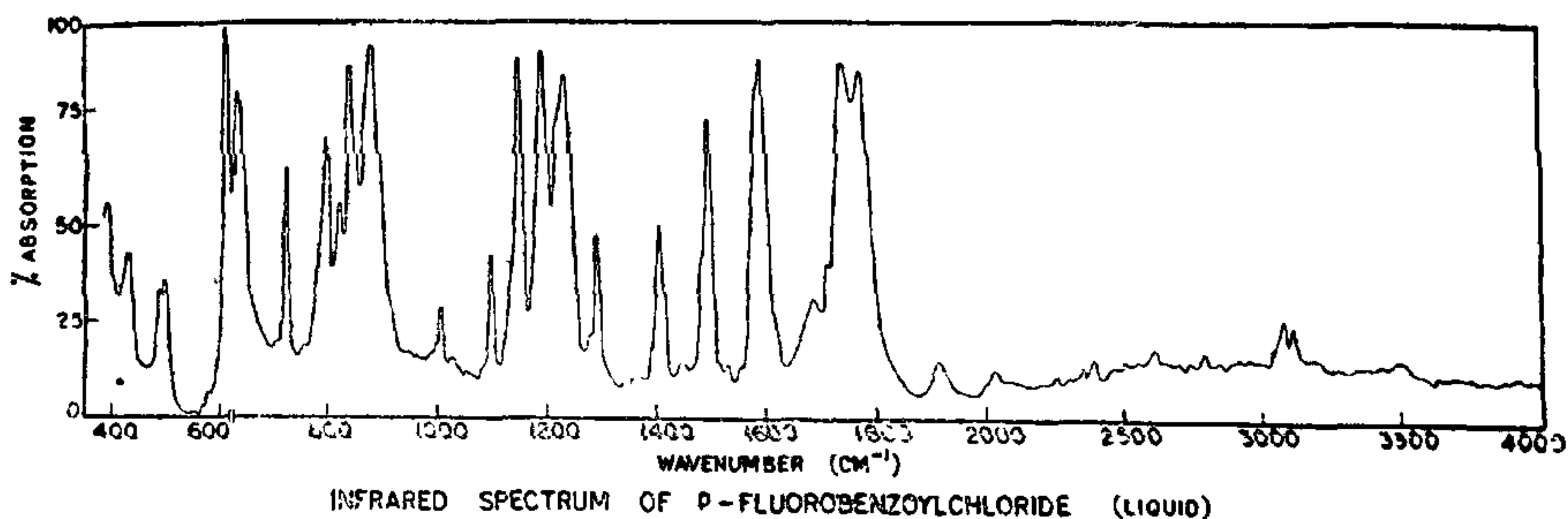


FIG. 3

expected to be intense. On the basis of the above criteria we have assigned the frequencies  $1610$  and  $1579\text{ cm}^{-1}$  in *ortho*-,  $1590$  and  $1558\text{ cm}^{-1}$  in *meta*- and  $1600$  and  $1536\text{ cm}^{-1}$  in *para*-fluorobenzoylchloride to

In all the three fluorobenzoylchlorides four C-H stretching and two C-substituent stretching vibrations are expected. The C-H stretching modes in benzene derivatives are derived



TABLE I  
 Correlation of the Vibrational Frequencies of o-, m- and p-fluorobenzoylchlorides

<i>p</i> -fluorobenzoyl- chloride		<i>m</i> -fluorobenzoyl- chloride		<i>p</i> -fluorobenzoyl- chloride		Assigned mode of vibration
cm <sup>-1</sup>	Int.	cm <sup>-1</sup>	Int.	cm <sup>-1</sup>	Int.	
3100	(42)	3108	(19)	3106	Sh	C-H Stretching
		3085	(29)	3086	(21)	do.
3064	(48)	3062	(18)	3060	Sh	do.
3015	(48)	3035	(16)			do.
1786	(25)	1775	(85)	1778	(90)	Fermi-Resonance between C=O stretching & the second quantum of C-COCl stretching
1738	(20)	1745	(85)	1746	(95)	
1610	(50)	1590	(66)	1600	(97)	C=C stretching
1579	(18)	1558	(11)	1536	(8)	do.
1485	(34)	1482	(63)	1501	(78)	do.
1463	(75)	1436	(66)	1412	(47)	do.
1308	(42)	1310	(22)	1295	(44)	do.
1288	(48)	1274	(46)	1284	Sh	C-H i.p. bending
1230	(47)	1248	(96)	1240	(91)	C-F stretching
1192	(18)	1164	(46)	1198	(98)	C-H i.p. bending
1133	(26)	1134	(82)	1155	(95)	do.
1085	(32)	977	(52)	1102	(38)	C-C stretching (ring breathing)
1028	(14)	1057	(15)	1030	(9)	C-H i.p. bending
1018	(14)	1018	(14)	1009	(21)	C-C-C i.p. bending
985	(11)	998	(19)	994	Sh	C-H o.p. bending
946	(17)	950	(67)	950	(13)	do.
909	(40)	915	(25)	844	(94)	do.
881	(34)	880	(53)	881	(100)	C-COCl stretching
820	(19)	812	(79)	823	(53)	C-F i.p. bending
749	(100)	783	(100)	800	(73)	C-Cl stretching
695	(18)	694	(97)	724	(63)	C-C-C o.p. bending
680	(35)	730	(17)	710	Sh	C-H o.p. bending
645	(65)	663	(88)	635	(85)	C-C-C i.p. bending
511	(59)	513	(50)	500	(32)	C-F o.p. bending
455	(46)	442	(43)	492	(29)	C-C-C i.p. bending
417	(62)	405	(37)	433	(26)	C-C-C o.p. bending
392	(48)	390	(40)	394	(50)	do.

N.B.—Sh = shoulder, i.p. = in-plane, and o.p. = out-of-plane.

from  $a_{1g}$  ( $3062\text{ cm}^{-1}$ ),  $e_{2g}$  ( $3047\text{ cm}^{-1}$ ),  $b_{1g}$  ( $3060\text{ cm}^{-1}$ ) and  $e_{1u}$  ( $3099\text{ cm}^{-1}$ ) vibrations of benzene. From the study of a large number of benzene derivatives it is found that the magnitude of these C-H stretching vibrations change very slightly. These vibrations remain confined to the region  $3,000\text{--}3,100\text{ cm}^{-1}$ . In the present study, the frequencies  $3015$ ,  $3064$  and  $3100\text{ cm}^{-1}$  in the case of ortho;  $3035$ ,  $3062$ ,  $3085$  and  $3108\text{ cm}^{-1}$  in the case of meta- and  $3060$ ,  $3086$  and  $3106\text{ cm}^{-1}$  in the case of para-isomer have been assigned to C-H stretching mode.

The C-H in-plane bending vibrations in benzene are observed in the region  $1,000\text{--}1,350\text{ cm}^{-1}$ . In the present case, the frequencies  $1028$ ,  $1133$ ,  $1192$  and  $1288\text{ cm}^{-1}$  in ortho-,  $1057$ ,  $1134$ ,  $1164$  and  $1274\text{ cm}^{-1}$  in meta- and  $1030$ ,  $1155$ ,  $1198$  and  $1284\text{ cm}^{-1}$  in para-compound have been assigned to C-H in-plane bending mode.

Similarly, C-H out-of-plane bending vibrations are observed in the range  $700\text{--}1,000\text{ cm}^{-1}$  and arise from the  $b_{2u}$  ( $995\text{ cm}^{-1}$ ),  $e_{2u}$  ( $975\text{ cm}^{-1}$ ),  $e_{2g}$  ( $850\text{ cm}^{-1}$ ) and  $a_{2u}$  ( $673\text{ cm}^{-1}$ ) modes of benzene. In the present case, the frequencies  $680$ ,  $909$ ,  $946$  and  $985\text{ cm}^{-1}$  in ortho-,  $730$ ,  $915$ ,  $950$  and  $998\text{ cm}^{-1}$  in meta-, and  $710$ ,  $844$ ,  $950$  and  $994\text{ cm}^{-1}$  in para-fluorobenzoylchlorides are assigned to C-H out-of-plane bending modes.

According to Randle and Whiffen<sup>24</sup>, the C-C-C in-plane bending vibration of benzene,  $606\text{ cm}^{-1}$  ( $e_{2g}$ ) splits up into two components on substitution, the magnitude of one component remains almost unchanged while that of the other component is reduced considerably. The pair of frequencies  $455$ ,  $645\text{ cm}^{-1}$ ;  $442$ ,  $663\text{ cm}^{-1}$ ; and  $492$ ,  $635\text{ cm}^{-1}$  in ortho-, meta- and para-derivatives have been correlated with these two components. Also, the frequencies  $1018$ ,  $1018$  and  $1009\text{ cm}^{-1}$  in *o*-, *m*- and *p*-fluorobenzoylchlorides respectively have been assigned to the C-C-C in-plane bending mode corresponding to  $1010\text{ cm}^{-1}$  ( $b_{1u}$ ) frequency of benzene.

The  $e_{2u}$  ( $404\text{ cm}^{-1}$ ) and  $b_{2u}$  ( $703\text{ cm}^{-1}$ ) modes of benzene give rise to three C-C-C out-of-plane bending vibrations in disubstituted benzenes. The pair of frequencies  $392$ ,  $417\text{ cm}^{-1}$ ;  $390$ ,  $405\text{ cm}^{-1}$ ; and  $394$ ,  $433\text{ cm}^{-1}$  in ortho-, meta- and para-compounds respectively have been assigned to the two components of the  $404\text{ cm}^{-1}$  ( $e_{2u}$ ) vibration of benzene. The frequencies  $695$ ,  $694$  and  $724\text{ cm}^{-1}$  in the three isomeric fluorobenzoylchlorides respectively have been assigned to the C-C-C out-of-plane bending mode and are correlated to  $703\text{ cm}^{-1}$  ( $b_{2g}$ ) vibration of benzene.

#### (B) C-COCl Group Vibrations

The magnitude of the C-COCl stretching frequency in aromatic compounds is expected to be observed with appreciable intensity in the range  $800\text{--}900\text{ cm}^{-1}$ . The frequencies  $881$ ,  $880$  and  $881\text{ cm}^{-1}$  observed in *o*-, *m*- and *p*-fluorobenzoylchlorides, respectively with good intensity have been assigned as the C-COCl stretching mode. The magnitude of C-COCl stretching frequency in benzoylchloride<sup>3</sup> is  $873\text{ cm}^{-1}$  which is in good agreement with this assignment.

The assignment of C-Cl stretching frequencies in aromatic molecules is very ambiguous. It has been observed that several workers<sup>8,9,18,25-27</sup> have assigned the C-Cl stretching frequencies in rather a wide range from  $1150$  to  $300\text{ cm}^{-1}$ , and the earlier studies show a lack of consistency in the assignment of C-Cl group vibrations. Recently, Singh<sup>28</sup> has studied the polarized infrared and Raman spectra of *p*-dichlorobenzene single crystals and he has assigned the frequencies  $742$  and  $814\text{ cm}^{-1}$  to C-Cl stretching mode. In conformity with this assignment, we have assigned the frequencies  $749$ ,  $783$  and  $800\text{ cm}^{-1}$  to C-Cl stretching mode in *o*-, *m*- and *p*-fluorobenzoylchlorides, respectively.

The doublet nature of the carbonyl band in benzoylchlorides has been interpreted in terms of Fermi-resonance by several workers<sup>1,3-6</sup>. Although there does not seem to be any dispute about this interpretation, the choice of the interacting frequencies is not yet settled. The necessary requirements for Fermi-resonance are that the two frequencies must be very close in magnitude and nearly equal in intensity and both must belong to the same symmetry species. If it is accepted that the doublet nature of the carbonyl band results due to Fermi-resonance, the magnitude of the C=O stretching mode (of the COCl group), which is one of the two interacting frequencies, must be the mean of the two observed doublet components. The symmetry of the C=O stretching mode is of  $a'$  type. The other component of the Fermi-resonance (probably an overtone or a combination band), therefore, should also belong to  $a'$  symmetry species and should have nearly the same magnitude and intensity. In the case of *p*-fluorobenzoylchloride, two bands of equal intensities appear with magnitudes  $1746$  and  $1778\text{ cm}^{-1}$ . The mean of these two frequencies is  $1762\text{ cm}^{-1}$  which may be assigned to C=O stretching mode of the COCl group. A very strong band appears at  $881\text{ cm}^{-1}$  which is assigned to C-COCl stretching mode ( $a'$  class). The first overtone of this frequency will have a magnitude of  $\sim 1762\text{ cm}^{-1}$  and would belong to  $a'$  species. Thus the  $1762\text{ cm}^{-1}$



C=O stretching frequency of the COCl group and the above-mentioned overtone band  $1762\text{ cm}^{-1}$  satisfy the requirements for Fermi-resonance, due to which these two frequencies may be equally shifted from their original positions. In the case of ortho- and meta-fluorobenzoylchlorides also, the doublet nature of the carbonyl band has been explained due to Fermi-resonance and the nature of the interacting frequencies is the same as in the case of the para-isomer.

### (C) C-F Group Vibrations

In fluorinated aromatics, the C-F stretching frequencies<sup>15-16</sup> are generally observed in the region  $1200\text{--}1300\text{ cm}^{-1}$ . Smith *et al.*<sup>17</sup> have assigned the frequency  $1220\text{ cm}^{-1}$  in fluorobenzene, the frequencies  $1183$  and  $1245\text{ cm}^{-1}$  in *p*-difluorobenzene and the frequencies  $1204$ ,  $1250$  and  $1308\text{ cm}^{-1}$  in 1, 2, 4-trifluorobenzene to C-F stretching modes. Accordingly, we have assigned the frequencies  $1230$ ,  $1248$  and  $1240\text{ cm}^{-1}$  in *o*-, *m*- and *p*-fluorobenzoylchlorides, respectively, to C-F stretching mode.

The C-F in-plane bending vibrations have been observed in the region  $700\text{--}850\text{ cm}^{-1}$  for several compounds. The frequency  $754\text{ cm}^{-1}$  in fluorobenzene,  $753\text{ cm}^{-1}$  in *p*-fluorochlorobenzene and  $753\text{ cm}^{-1}$  in *p*-fluorobromobenzene has been assigned by Narasimhan *et al.*<sup>18</sup> to C-F in-plane bending mode. Lal *et al.*<sup>12,19</sup> have assigned the frequencies  $770$  and  $842\text{ cm}^{-1}$  to C-F in-plane bending mode in the case of 2, 3-difluoroaniline. Therefore, in conformity with these assignments we have assigned the frequencies  $820$ ,  $812$  and  $823\text{ cm}^{-1}$  in *o*-, *m*- and *p*-fluorobenzoylchlorides, respectively, to C-F in-plane bending mode.

In the present case, the bands at  $511$ ,  $513$  and  $500\text{ cm}^{-1}$  observed in ortho-, meta- and para-compounds, respectively, have been assigned to C-F out-of-plane bending mode. The  $527\text{ cm}^{-1}$  frequency in *o*-fluorotoluene<sup>21</sup>,  $534\text{ cm}^{-1}$  frequency in *o*-fluoroanisole<sup>22</sup> and  $498$  and  $566\text{ cm}^{-1}$  frequencies in 2,3-difluoroaniline<sup>12</sup> have been assigned to C-F out-of-plane bending modes. Thus the assignments proposed in the present case are in agreement with those proposed by earlier workers.

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