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REVIEW

VIBRATIONAL SPECTRA OF POLYFLUOROAROMATIC COMPOUNDS

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SUMMARY

The review presents a survey of literature data on the IR and Raman spectra of polyfluorinated compounds of type C_6F_5X and Ar_FYAr_F (Y is an unsaturated bridge group). The results of normal coordinate calculations of frequencies and forms of vibrations for a number of fluorinated benzenes are given. The effect of the number and position of fluorine atoms in the benzene ring on frequencies and intensities of the stretching vibrations of the benzene ring and functional groups X and Y is considered. The assignments of bridge group Y vibrations are given, including those for ^{15}N labelled compounds. The possible reasons for the decreasing of the stretching vibrations of the benzene ring and multiple bonds in the Raman spectra under the fluorine effect are discussed.

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INTRODUCTION

Polyfluoroaromatic chemistry began to grow rapidly since the development of a convenient preparative synthesis of basic polyfluorinated arenes - hexafluorobenzene and octafluoronaphthalene [1] .Detailed studies on the chemical behaviour of these compounds and their applications called for the elaboration of simple and convenient methods of analytical control.

Vibrational spectroscopy is one of the basic methods of structure analysis of organic compounds. Investigation of the vibration spectra of polyfluoroaromatic compounds proceeded simultaneously with their reactivity studies. In this connection, it was of interest to study the spectral regularities brought about by introduction of fluorine in a molecule, and to reveal in the IR and Raman spectra the bands suitable for identification and analysis of polyfluoroaromatic compounds. In the case of pentafluorinated benzene derivatives C_6F_5X, it was interesting to examine the pentafluorophenyl effect on vibration frequencies and intensities of functional group X. At the same time, fluorinated benzenes may serve as models for the solution of some spectroscopic problems. Of special interest are the compounds where the accumulated fluorine atoms may bring about a qualitative change of their properties. A large amount of experimental material on the fluorine effect on stretching frequencies of aryl and functional groups has been amassed, but there is no general review of these data.The only review [2] is unavailable for general reader, and covers the data up to 1967. Since that time there have been a lot of specialist publications discussing vibrational spectra of polyfluoroaromatic compounds, which made attempts to review these data. Attention has been focused on recent works, with minor reference to earlier works.

1. ASSIGNMENT AND CALCULATIONS OF VIBRATIONAL SPECTRA OF FLUOROBENZENES

Extensive studies of vibrational spectra (IR and Raman) of aromatic compounds (see, e.g. [3-5]) have shown that the most important characteristics of the aromatic fragments in a molecule are the in-plane skeletal vibrations $\nu_{8a,b}$ (herein below the Wilson notation is used), $\nu_{19a,b}$, ν_1, and ν_{12} of the benzene ring. Vibrations ν_8 and ν_{19} show themselves in the spectra of benzene derivatives as doublets of different resolution at 1576-1625 and 1425-1525 cm^{-1} respectively. The vibration ν_{19} usually corresponds to a strong IR band, which is medium or weak in the Raman spectra. Vibrations ν_1 and ν_{12} give very strong polarised Raman bands. Position and intensities of ν_1, and ν_{12} very depending on the atomic weight and position of substituents in the ring [4].

Data on the origin position and peculiarities of similar bands in the spectra of polyfluoroaromatic compounds may be obtained by analysing the IR spectra in different physical states, the Raman spectra [2,6-14], and the results of fundamental mode calculations for a number of fluorinated benzenes [14-21]. The low-frequency spectra of some polyfluorinated benzenes are discussed in the work [22]. IR and Raman spectra of polyfluorinated compounds have been published in specialized atlases [2,23-28]. Attempts have been made to observe the effect of the accumulation of benzene fluorine atoms on the position, origin, and peculiarities of normal vibrations of fluorinated benzenes in some studies [15,19,29].

1.1. Peculiarities of vibrational spectra of fluorobenzenes

For the identification of a poly- (tetra- and penta-) fluoroaromatic fragment in a molecule, in-plane vibrations of the carbon ring (similar to ν_8, ν_{19}, ν_1, and ν_{12} of benzene) are most frequently used. Vibrations $\nu_{8a,b}$ corresponding to the doubly degenerate vibration (e_{2g}) of benzene remain practically the same in form upon introduction of fluorine into the molecule [29]. In the case of compounds with lower symmetry than that of C_6H_6 and C_6F_6, e.g. for compounds C_6F_5X, the vibrations ν_8 are active in both IR and Raman. As a result of degeneracy, the respective bands should be observed as a doublet, but the splitting, which depends on the nature of functional group X, is not always sufficient for resolution of its components [7,8,13,19].

With increased number of fluorine atoms in the benzene ring, the frequencies of ν_8 increase [15] and the intensities of the respective Raman bands decrease [29] (Table 1). In the spectra of tetra- and pentafluorosubstituted benzene derivatives, vibration ν_8 corresponds to the medium or weak band at 1640-1660 cm^{-1}. The authors of [29]

TABLE 1

Frequencies (ν, cm^{-1}) and Raman intensities (I, rel.un.)* of ν_8 in fluorobenzenes [29]

Compound	ν_8 calc.		ν_8 exp.	I	HOMO energy [30]
	ν_{8a}	ν_{8b}			
C_6H_6	1611	1611	1606	0.15	-9.24
C_6H_5F	1621	1607	1598 1605	0.11	
1,2-$C_6H_4F_2$	1603	1629	1604 1620	0.07	-9.30
1,4-$C_6H_4F_2$	1630	1596	1619 1620	0.09	-9.15
1,3,5-$C_6H_3F_3$	1614	1614	1619	0.05	-9.62
1,2,4,5-$C_6H_2F_4$	1648	1610	1614 1648	0.04	-9.36
C_6HF_5	1621	1647	1652	0.03	-9.64
C_6F_6	1642	1642	1658	0.03	-9.93

* The total integral intensities of ν_{8a} and ν_{8b} have been determined relative to the 1710 cm^{-1} band of acetone.

attribute the decreased intensities of these bands to the changed electronic structure of the molecule as a result of fluorine introduction and the changed energy of HOMO. In the IR spectrum, this band is generally much weaker than the absorption band at 1500 cm^{-1}, and in some cases it is observed only at high concentrations of the absorbent. The corresponding Raman band is depolarised and has varying intensity. The use of the IR absorption band at 1600-1660 cm^{-1} for identification of the polyfluorinated benzene ring is difficult due to its overlapping with the bands of such intensively absorbing groups as C=O, C=C, NH_2, etc., whereas in the Raman spectra the vibration is clear-cut and does not create difficulties in identification. The analysis of normal vibrations of fluorine-substituted benzenes based on the calculations has shown [5,31] that in the mono-, 1,4-di-, and tetrafluorobenzenes, the frequency of the ν_{8a} component is higher than of ν_{8b}, while in 1,3-, 1,2-, 1,2,3-, 1,2,4- and 1,2,3,4,5-substitution the position is reversed (for vibrations ν_{19a} and ν_{19b}, the same dependence has been observed). Vibrations $\nu_{19a,b}$ are also specific to benzene-type structures. These vibrations (e_{1u}) are observed in benzene at 1485 cm^{-1}. The mutual position of substituents in the benzene ring affects the frequencies of these vibrations in the same way as it affects $\nu_{8a,b}$. The detailed analysis of vibration pairs $\nu_{8a,b}$ and $\nu_{19a,b}$ in various fluorobenzenes based on calculations is given in ref. [19] which discusses the fluorine effect on the vibrations of benzene derivatives (Table 2).

It has been shown that in the series $C_6H_6 \longrightarrow C_6H_5F \longrightarrow$ o-$C_6H_4F_2 \longrightarrow$ p-$C_6H_4F_2$, the predominant contribution to the energy of vibrations ν_{19} is made by the C-C bonds and external angles of the ring (β), the contribution being the same for vibrations ν_{19a} and ν_{19b}. With increasing number of fluorine atoms, the vibration ν_{19} becomes more complex, with marked contributions from the CCF angle and internal angles of the benzene ring, while the major contribution to the potential energy of the molecule is made by the C-F bond [8,19 and references there in]. For the tetra-, penta-, and hexafluorobenzenes, these vibrations give rise to the absorption band at 1450-1540 cm^{-1}, which is one of the most intense in the IR spectrum and is generally used for identification of the pentafluorophenyl fragment in the molecule. In the case of tetrafluorobenzenes, the bands are of lower intensity, and, depending on the relative position of fluorine atoms in the benzene ring, one of the components of vibration ν_{19} may exceed the limits of the above interval [19]. The Raman band at 1485-1540 cm^{-1} of polyfluoroaromatic compounds has low intensity, which allows the vibrations of other functional groups, lying in this range [32-34] to be studied.

TABLE 2

Genetic relation of vibrations of fluorobenzenes $C_6H_{6-n}F_n$ (n = 1-6)

	Compound	C_6H_6	C_6H_5F	o-$C_6H_4F_2$	m-$C_6H_4F_2$	p-$C_6H_4F_2$
	Number of vibration according to Wilson	ν cm^{-1}**	ν cm^{-1} **	ν cm^{-1} **	ν cm^{-1} **	ν cm^{-1} **
ring vibrations	1	992 Q	806 γQ	762 γQ	734 γQ_F	859 $Q \gamma$
	4	690 $\rho \varkappa$	682 $\varkappa$	701 $\varkappa R$	674 $\varkappa R$	692 $\varkappa R$
	6a	606 γ	519 γ	568 R	522 γQ_F	451 $Q_F \gamma$
	6b	606 γ	615 γ	546 $\beta \gamma$	514 γ	635 $\gamma \beta_F$
	8a	1596 βQ	1592 $Q \gamma$	1610 $Q \gamma$	1605 QR	1605 $Q \beta$
	8b	1596 βQ	1594 $Q \gamma$	1619 $Q \gamma$	1613 γQ	1617 $Q \beta$
	12	1010 γ	1009 $Q \gamma$	856 γ	1007 γQ	736 γQ
	14	1310 βQ	1324 $Q \beta$	1313 $Q \beta$	1260 $Q \beta$	1285 Q
	19a	1485 βQ	1492 βQ	1472 $Q \beta$	1449 $Q Q_F$	1511 $Q \beta$
	19b	1485 βQ	1457 βQ	1511 $Q \beta$	1490 $Q \gamma$	1437 $Q \beta$
stretching vibrations of CH (CX)	2	3080 q	3049 q	1270 βR	3086 q	3085 q
	7a	3047 q	3036 q	3060 q	3086 q	1245 $Q_F Q$
	7b	3047 q	3049 q	3060 q	952 γQ	3084 q
	13	3080 q	1218 βQ_F	1206 βQ_F	1277 $\beta \gamma$	1212 $Q_F \beta$
	20a	3080 q	3065 q	3085 q	3095 q	3088 q
	20b	3080 q	3065 q	3085 q	3086 q	3088 q
in-plane deformation vibrations	3	1326 β	1282 βQ	1293 βQ_F	1327 βQ	1285 βQ
	9a	1178 βQ	1156 βQ	1152 $Q \beta$	329 β_F	1142 βQ
	9b	1178 βQ	1155 βQ	441 $\beta_F \gamma$	1157 βQ_F	434 $\beta_F \gamma$
	15	1146 βQ	407 β_F	196 $\gamma \beta_F$	478 β_F	350 β_F
	18a	1034 βQ	1020 Q	1101 $Q \beta$	1066 $Q \beta$	1012 $Q \gamma$
	18b	1037 βQ	1065 $\gamma \beta$	1025 γQ	1120 βQ	1085 βQ
out-of-plane deformation vibrations	5	984 $\rho \varkappa$	982 $\rho \varkappa$	982 ρ	850 $\rho \varkappa$	928 $\rho \varkappa$
	10a	850 ρ	831 $\rho \varkappa$	749 ρ	250 $\varkappa \rho$	800 ρ
	10b	850 ρ	752 $\varkappa \rho$	840 ρR	771 $\rho \varkappa$	375 R
	11	671 ρ	499 $\varkappa \rho$	451 $\varkappa R$	230 R	509 $\varkappa R$
	16a	405 $\rho \varkappa$	400 $\varkappa$	196 $\varkappa$	591 $R \varkappa$	405 $\varkappa$
	16b	405 $\rho \varkappa$	242 $\varkappa R$	298 $R \varkappa$	458 $\varkappa R$	165 $R \varkappa$
	17a	970 $\rho \varkappa$	957 ρ	588 $\varkappa R$	879 $\rho \varkappa$	943 ρ
	17b	970 $\rho \varkappa$	896 $\rho \varkappa$	930 $\rho \varkappa$	978 $\rho \varkappa$	833 $\rho \varkappa$

* Assignment, ** Normal vibration coordinates are indicated : Q, Q_F, variations of angles CCC, CCH and CCF, ρ, R, $\varkappa$ are deviations

to vibrations of benzene [19] *

1,3,5-$C_6H_3F_3$	1,2,3,4-$C_6H_2F_4$	1,2,4,6-$C_6H_2F_4$	2,3,5,6-$C_6H_2F_4$	C_6HF_5	C_6F_6
ν cm^{-1} **	ν cm^{-1} **	ν cm^{-1} **	ν cm^{-1} **	ν cm^{-1} **	ν cm^{-1} **
578 $Q\beta$	682 γQ_F	786 $Q\gamma$	748 γQ_F	718 γQ_F	559 Q_F
663 $\varkappa\rho$	713 $\varkappa R_F$	702 $\varkappa R$	687 $\varkappa R$	713 $\varkappa$	714 $R\varkappa$
500 γ	457 β_F	471 γ	480 γQ	470 γ	443 Q_F
500 γ	487 β_F	510 γ	635 β	435 γ	443 Q_F
1624 $Q\beta$	1632 γQ_F	1631 $Q\gamma$	1630 $Q\gamma$	1648 $Q\gamma$	1655 QQ_F
1624 $Q\beta$	1607 $Q\gamma$	1631 $Q\gamma$	1643 QQ_F	1639 $Q\gamma$	1655 QQ_F
1010 $Q\gamma$	310 γ	580 $Q_F\gamma$	667 $\gamma\beta_F$	578 $Q\gamma$	640 γQ_F
1310 βQ	1328 QQ_F	1240 βQ	1277 βQ	1268 $Q\beta$	1253 $Q\beta$
1475 QR	1515 Q_FQ	1523 QQ_F	1439 Q_FQ	1514 Q_FQ	1531 Q_FQ
1475 QR	1522 Q_FQ	1455 γQ	1534 Q_FQ	1525 γQ_F	1531 Q_FQ
3080 q	1165 $Q\beta$	1405 Q_FQ	3097 q	1410 Q_FQ	1490 QQ_F
1122 βQ_F	1050 $Q_F\beta$	997 QQ_F	1335 Q_FQ	1075 $Q\gamma$	1157 Q_FQ
1122 βQ_F	963 $Q\beta$	1058 γQ	1130 βQ_F	1138 βQ_F	1157 Q_FQ
1350 $Q_F\gamma$	1239 QQ_F	1286 QQ_F	1222 $Q\gamma$	1286 QQ_F	1323 $Q_F\gamma$
3109 q	3074 q	3090 q	3088 q	3105 q	1020 $Q_F\beta$
3109 q	3090 q	3030 q	852 Q_FQ	964 $Q_F\beta$	1020 $Q_F\beta$
1282 βQ	1402 β	641 $\beta\gamma$	1240 $Q\beta$	688 β_F	691 β_F
326 β_F	324 β_F	310 β_F	274 β_F	272 β_F	264 $\gamma\beta_F$
326 β_F	291 $\gamma\beta_F$	324 $\gamma\beta_F$	450 γ	304 $\gamma\beta_F$	264 $\gamma\beta_F$
279 β_F	268 γ	258 β_F	250 β_F	247 β_F	208 β_F
993 $Q\gamma$	747 $\gamma\beta_F$	1124 β	200 β_F	325 β_F	315 βQ
993 $Q\gamma$	1165 $Q\beta$	1176 QQ_F	1164 $Q\beta$	1182 QQ_F	315 βQ
843 $\rho\varkappa$	929 $\rho\varkappa$	840 ρ	871 $\rho\varkappa$	866 ρ	249 $R\varkappa$
253 $\varkappa$	597 $\varkappa R$	845 $\rho\varkappa$	417 R	391 R	370 R
253 $\varkappa$	157 $\varkappa$	368 $R\varkappa$	295 $R\varkappa$	327 R	370 R
214 R	170 $\varkappa$	217 $R\varkappa$	240 $R\varkappa$	217 R	215 R
595 $R\varkappa$	359 $R\varkappa$	645 $\varkappa R$	140 $\varkappa$	619 $\varkappa R$	595 R
595 $R\varkappa$	374 R	606 $\varkappa R$	461 $\varkappa R$	556 $R\varkappa$	595 R
847 ρ	568 $R\varkappa$	205 R	600 R	171 $\varkappa R$	175 $R\varkappa$
847 ρ	802 ρ	185 $\varkappa R$	882 $\rho\varkappa$	161 $\varkappa$	175 $R\varkappa$

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q are variations of CC, CF and CH bond lengths; γ, β, β_F are of the CH, CF and CC bonds from molecular plane.

The in-plane vibration of the benzene ring ν_1 (breathing vibration) shows itself as a very strong polarised Raman band and it is very weak in the IR spectrum. Position of the band largely depends on the number, position, and atomic weight of substituents in the benzene ring [4,5]. This must have led to some disagreement between authors in its assignment in the spectra of fluorobenzenes. Thus in [14] vibration ν_1 in the spectrum of 1,2-$C_6F_4I_2$ is assigned to 777 cm^{-1}. In [19], based on calculations of the frequencies and forms of vibrations the authors suggest the form of this vibration changes as a result of fluorine accumulation, and in different fluorinated benzenes it was assigned to different frequencies (Table 2). The latter statement is consistent with a conclusion [14] that vibration ν_1 involves significant interaction of the frame with C-Hal bonds, and, consequently, its frequency considerably depends on the nature and position of the halogen.

The Raman data for C_6F_5X (X = I, SH, $CH{=}CH_2$, NO_2, NH_2,CO_2^-) [13], $C_6F_5NH_2$ [10], $C_6F_4X_2$ (X = Cl, Br, I) [12], $C_6F_5CH_2X$ and $C_6F_5CHX_2$ (X = F, Cl, Br) [6], C_6F_5CN [7,35], $C_6F_5CH_3$ [8], $CH_3C_6F_4H$ [9], $C_6F_5CF_3$ [36], C_6F_6, C_6HF_5, 1,3,5-trichloro-, trifluorobenzene, C_6F_5CHO [37], $C_6H_2F_4$ [38], C_6F_5X (X = H, CH_3, Cl, Br) [39], $Sb(C_6F_5)_3$ [11], 1,3,5-$C_6H_3F_3$ [21] indicate that the in-plane vibration of the pentafluorinated benzene ring of a_1 symmetry is observed at 550-585 cm^{-1}, and the band is frequently the strongest one in the Raman spectrum. The Raman spectrum of 1,2-$C_6F_4I_2$ [14] also shows a strong band in the same range; this is not found in the IR spectrum and has been ascribed to the out-of-plane skeletal vibration ν_{16a} symmetry e_{2u}. For C_6HF_5, 2,3,5,6-$C_6H_2F_4$, 1,2,4,6-$C_6H_2F_4$ a similar band is assigned to vibration ν_{12}, and for 1,2,3,4-$C_6H_2F_4$ to vibration ν_{16a} [19]. Thus, notwithstanding the disagreement in the assignment of the 550-585 cm^{-1} band, it is characteristic for penta- and tetrafluorobenzenes and may be used for identification purposes.

The major contribution to vibrations ν_{13} and ν_{20a} for polyfluoroaromatic compounds is made by the C-F bonds, whereas vibrations ν_3 and ν_{9b} of benzene correspond to two CF in-plane bending vibrations. For vibrations ν_{13} and ν_{20} in the spectra of some pentafluorobenzenes, works [7,40-42] indicate the frequencies of 1295-1340 and 1000 cm^{-1}, in the spectrum of C_6HF_5 1286 and 964 cm^{-1} (ν_{20b}) [19], in that of 1,2-$C_6F_4I_2$ [14] 1310 and 1028 cm^{-1}. It should be noted that the band at 1000 cm^{-1} is one of the strongest in the IR spectra of all pentafluorosubstituted benzenes and for that reason is used, together with a very strong absorption band at 1485-1520 cm^{-1}, as a characteristic indication to the presence of pentafluorobenzene ring [2].

In [19], vibration ν_{13} is assigned to 1222-1286 cm^{-1} (tetrasubstituted) and 1320-1350 cm^{-1} (hexa- and 1,3,5-trifluorosubstituted benzene derivatives). As shown in [19], the C-F stretching vibration corresponds to vibration ν_{20b} which shows itself at 964 cm^{-1} for C_6HF_5 and at 1020 cm^{-1} for C_6F_6. For the tetrafluorosubstituted benzene derivatives, the authors of [19] consider vibrations $\nu_{20a,b}$ to be the CH vibrations which lie at 3080-3100 cm^{-1}.

A specific feature of the in-plane bending vibrations ν_3 and ν_9 is a wide frequency range resulting from different relative contributions of the C-F bonds to these vibrations, depending on the number of fluorine atoms in a molecule, though its character remains the same as in benzene (the in-plane bending vibration involving the CCC and CCHal angles and the CF bonds).

Korostelev and his co-workers [19] studied the effect of gradual introduction of fluorine atoms on these vibrations and reported that in the series of C_6H_5F- ortho-$C_6H_4F_2$- meta-$C_6H_4F_2$- para-$C_6H_4F_2$-1,3,5-$C_6H_3F_3$, ν_3 varies from 1254 to 1296 cm^{-1} and mainly corresponds, as in benzene, to the bending vibration of CCH angles. In C_6F_6, C_6HF_5, 2,3,5,6-$C_6H_2F_4$, and 1,2,4,6-$C_6H_2F_4$ this is a bending vibration of CCF whose frequency varies in the 635-691 cm^{-1} range. Other authors [6,14] for some substituted polyfluorobenzenes assign this vibration to other frequencies. The case is similar for vibration ν_{9b}. Because of this the bands corresponding to vibrations ν_3 and ν_9 are normally not used for identification of the polyfluoroaromatic fragment in a molecule.

The IR and Raman data for polyfluorinated benzene vapours (1,2- and 1,4-di; 1,2,4- and 1,3,5-tri; 1,2,4,5-, 1,2,3,5-tetra-, penta-, and hexafluorobenzenes) in a low-frequency (50-400 cm^{-1}) range were compared with the calculation data of [6-8] and analysed in terms of vibration symmetry in [22]. The assignments of some vibrations in that range for C_6F_6 on the basis of intensity measurements are given in [44]. The rotational Raman spectra of 1,3,5-trifluoro- and hexafluorobenzenes are discussed in [45]; the spectrum of decafluorobiphenyl in the 40-200 cm^{-1} range in [46].

1.2. Calculations of normal frequencies and forms of vibrations of polyfluorobenzenes

The vibration frequency calculations for various fluorinated benzenes have been reported in many works [14-20,29,31,36,37]. Force constants for 1,2,4,5-tetrafluorobenzene are given in [47]. In most works the calculation data are used for comparisons with experimental data in spectral interpretations, for frequency assignments of fluorinated benzene ring vibrations, vibration symmetry determination and for revealing the overtone and combination bands. The calculations have been carried out in various approximations : the Urey-Bradley [15-17], and the valence force field [14,18-20,29,31]. Different authors use different notation systems for vibrations, and some works lack experimental data (for example, Raman data). This seems to be the reason for certain disagreements between authors in assignment of vibrations exemplified in the previous section of this review. All this makes it difficult to use the data of different authors in assignments and calculations for other compounds. Nevertheless the use of calculation data provides a better understanding of spectral tendencies of polyfluoroaromatic compounds. The analysis of calculation data of [19] has shown the forms of vibrations in polyfluorinated benzenes to be similar to those of benzene, but the fluorine effect substantially changes the frequencies of some vibrations (e.g., of the breathing mode v_1) in polyfluorinated benzenes. As shown by D. Steele and his co-workers [15-17,22,48], who analysed the force field of fluorinated benzenes, introduction of fluorine atoms into the molecule brings about an essential change of force constants, which particularly affects the bending vibration frequencies below 1000 cm^{-1} both for the C-F and C-H bonds. The main reason for the changed force constants in polyfluoroaromatic compounds and, as a consequence, changed vibration frequencies as compared to other benzene derivatives is the effect of fluorine atoms, especially of those ortho to the substituents, on the electronic system of the whole molecule [15].

In [29], the frequencies and forms of normal vibrations have been calculated for a number of fluorosubstituted benzenes (see Table 3) in the valence force field approximation, and as zero approximation, the force field in [15] with a clear dependence of force constants on the number of ortho-fluorine atoms was used. The use of a common force

TABLE 3

Frequencies (ν, cm^{-1}) of functional group vibrations in compounds C_6F_5X *

X	IR	Raman (ϱ)	Symmetry type	Assignment	References
OH	3629 s.		a'	ν (OH)	37
	1313 s.	1313 v.s.	a'	δ(OH)	
	1225 s.	1232 v.w.	a'		
	977 v.s.		a'		
	782 m.		a'		
	345 m.		a''	r(OH)	
CH_3	2970		b_2	$\nu(CH_3)$	39
	2957		b_1	$\nu(CH_3)$	
	2951		a_1	$\nu(CH_3)$	
	1456		b_1 and b_2	$\delta(CH_3)$	
	1389		a_1	$\delta(CH_3)$	
	1082		b_2	$\varrho(CH_3)$	
	1034		b_1	$\varrho(CH_3)$	
	2978 w.sh.	2975 w.sh.	b_2	$\nu(CH_3)$	8
	2957 w.sh.		b_1	$\nu(CH_3)$	
	2947 s.	2940 s.	a_1	$\nu(CH_3)$	
	1455		b_1 and b_2	$\delta(CH_3)$	
	1375 m.	1083 m.	a_1	$\delta(CH_3)$	
	1079 v.s.		b_1	$\varrho(CH_3)$	
	1033 v.s.		b_1 and b_2	$\varrho(CH_3)$	
CH_2Cl	1269			$\nu(C-CH_2Cl)$	6
	703			$\nu(CCl)$	
CH_2Br	1233			$\nu(C-CH_2Br)$	
	620			$\nu(CBr)$	
CH_2F	1314			$\nu(C-CH_2F)$	6
	938			$\nu(CF)$	
	669			$\gamma(CH_2F)$	
$CHCl_2$	1219			$\nu(C-CHCl_2)$	6
	766			$\nu_{as}(CHCl_2)$	
	713			$\nu_s(CHCl_2)$	

(continued)

TABLE 3 (cont.)

CHF_2	1318					ν(C-CHF_2)	6
	1068					ν_{as}(CHF_2)	
	1012					ν_s(CHF_2)	
CF_3	1350	v.s.	1349	w.(0.1)	a_1	ν_s(CF_3)	36
	1177				b_2	ν(CF_3)	
	1160				b_1	ν(CF_3)	
	719	v.s.	718	s.(0.01)	a_1	β(CF_3)	
	549	m.	550	w.	b_2	β(CF_3)	
	440				b_1	β(CF_3)	
	338	m.	342	w.(0.75)	b_2	β(CF_3)	
	1217	($\Delta\nu$ ^{13}C=25)				ν_{as}(CF_3)	54
	1172	($\Delta\nu$ ^{13}C=28)				ν_s(CF_3)	
	1141	($\Delta\nu$ ^{13}C=35)				ν(C-CF_3)	
SH	2600	m.	2600	m.(0.1)	a_1	ν(SH)	13
	921	s.	922	w.(0.31)	b_2	δ(SH)	
NO_2	1565	v.s.	1567	m.(0.75)	b_2	ν(NO_2)	13
	1362	v.s.	1361	v.s.(0.14)	a_1	ν(NO_2)	
	938	s.	938	w.(0.05)	a_1	γ(NO_2)	
	766	v.s.			a_1	δ(NO_2)	
	750	m.			b_2	r (NO_2)	
NH_2	3500	s.			a'	ν_{as}(NH_2)	10
	3405	s.	3410	v.w.	a''	ν_s(NH_2)	
	1604	s.	1610	v.w.	a'	β(NH_2)	
	1097	v.w.			a''	δ(NH_2)	
	685	sh.			a'	δ(NH_2)	
CH=CH_2	1620	s.	1620	v.s.(0.21)	a'	ν(C=C)	13
	1410	s.	1409	w.(0.23)	a'		
	1306	s.	1306	w.(0.52)	a'	δ(CH)	
	1076	v.s.	1074	w.(0.53)	a'		
	978	v.s.			a''	γ(CH)	
	932	v.s.			a''		
	566	m.	567	sh.	a''	(CCX)	
	386	w.	386	s.(0.55)	a'	δ(CCX)	
	3039	m.	3040	m.(0.06)	a'		
	2951	w.			a'	ν(CH)	
	2928	w.	2934	v.w.	a'		

(continued)

TABLE 3 (cont.)

CHO	2875	m.	2894	w.(0.20)	a'	ν(CH)	37
	1730	v.s.	1730	v.s.(0.22)	a'	ν(CO)	
	1384				a'	β(CHO)	
	630				a''		
	1016	sh.	1023	s.		β(CHO)	
	58	s.	53	s.	a''	r(CHO)	
COF	1835					ν(C=O) dimer.	58
COOH	1723					ν(C=O) dimer.	58
	1764					ν(C=O) monomer.	
CONEt$_2$	1652					ν(C=O)	55
CONNH$_2$	1686					ν(C=O)	56
CH$_3$	3324					ν(NH)	
	3354					ν_{as}(NH)	
COO$^-$	1606	v.s.			b_2	ν_{as}(COO$^-$)	13
	1400	s.			a_1	ν_s(COO$^-$)	
	924	m.			a_1	γ(COO$^-$)	
	762	s.			a_1	δ(COO$^-$)	
	724	m.			b_2	r(COO$^-$)	
CN	2250	s.	2249	v.s.	a_1	ν(CN)	7
	468	m.	471	s.	b_2	β(CN)	
	130	m.	131	m.	b_1	γ(CN)	
	2248	v.s.	2251	(0.25)	a_1	ν(CN)	35
N=SCl$_2$	1346					ν(N=S)	57
	480-650					ν(SCl)	
N=S=O	1255					ν(N=S)	57
	1070					ν(S=O)	
	1270					ν(N=S)	53
	1180					ν(S=O)	

* The stretching frequencies of X = Hal groups (Hal = Cl, Br, I) were not included into the Table, as it is impossible (according to [13,20] to reveal a vibration with the predominant contribution of the C-Hal bond in the C_6F_5Hal molecule.

field for all fluorobenzenes gives a maximal 44 cm^{-1} deviation of the calculated frequencies from experimental ones. The calculation data show the 1600-1660 cm^{-1} frequency to be similar to vibrations ν_8 of benzene, the forms of these vibrations change insignificantly with introduction of fluorine atoms (the maximal difference between the shift ranges of atoms in various fluorobenzenes is 10% of the mean value). This suggests that variations in frequencies and intensities do not result from variations of the form of vibrations and that spectral band parameters of these vibrations may be used to study the fine structure of compounds such as, for example, the conjugation effect, in a similar way as for other benzene derivatives.

1.3. IR and Raman intensities of fluorobenzenes

The analysis of experimental values of IR intensities of hexafluorobenzene has been carried out in [49], and their theoretical investigation in [50]. The integrated band intensities in the IR spectrum of this molecule are determinated by both equilibrium charge distribution and charge fluxes accompanying the vibrational motion, the relative importance of the two effects depending on the type and symmetry of the vibrations. The intensity of C-F bands associated with stretching vibrations is largely related to rehybridization dipole contributions, while for the bending modes the equilibrium dipole terms make greater contributions to the band intensities. The intensity of the out-of-plane bending mode appears to be determined by both static and rehybridization contributions. The corresponding IR band intensities of benzene are entirely determined by classical dipole contributions, i. e., geometrical distortions of the equilibrium point charges.

It is stated in [51] that for the $C_6H_nF_{6-n}$ molecules, the calculated IR intensities do not agree well with the experimental ones if the polar tensor elements for their estimation are taken from the C_6H_6 and C_6F_6 molecules. The authors of [51] do not consider this result unexpected as the aromatic molecules are best described by the highly delocalized molecular orbitals.

As one of the reasons for the changed band intensities in the vibrational spectra of fluorobenzenes (Table 1) the authors of [29] consider the rearrangement in the electronic structure of the benzene ring under the fluorine effect. It is known [52] that the contribution of 2p orbitals to the highest occupied orbitals of π type is small, and the greatest contribution is made by the σ system and a deep π type level of a_{2u} symmetry. Due to this, fluorine atoms produce only a slight effect on the composition of HOMO in the benzene ring but markedly change the HOMO energy. Thus accumulation of fluorine atoms in the benzene ring leads to increase of the first ionization potentials from 9.24 for C_6H_6 to 9.93 eV for C_6F_6 [30] (Table 1). The observed tendency of changes in the Raman intensity of modes $\nu_{8a,b}$ in their dependence on the HOMO energy suggests that the latter does in fact produce a considerable effect on the intensity of this vibration.

2. IR AND RAMAN SPECTRA OF PENTAFLUOROBENZENE DERIVATIVES C_6F_5X

One of the features of the IR spectra of polyfluorinated aromatics is that the nature of the substituent X often causes severe perturbation of the aromatic ring modes [6]. As stated above, this especially refers to the deformation vibrations. At the same time, small changes upon the introduction of fluorine into the molecule have been observed [48] even for the CH vibration, where C are the atoms of the polyfluorinated benzene ring. An especially strong effect is produced by the ortho-fluorine atoms, which was taken into account in choosing a force field in the calculations of fluorinated compounds, as shown above.

For the CH stretching vibrations in fluoroaromatic compounds $C_6H_{6-n}F_n$, one can write a relationship

$$\nu = \nu_B + n_oX_o + n_mX_m + n_pX_p$$

where ν_B is the frequency of ν_{CH} in benzene, n_o, n_m, and n_p are the numbers of o-, m-, and p-fluorines; X_i is their contribution to force constant.

The differences between the CH stretching frequencies in the IR spectra fluorobenzenes in liquid and vapour states is substantially smaller than for the hydrocarbon analogues. The authors of [48] explain this by hydrogen bonding between hydrogen of the CH bond and the π-electron system of the benzene ring, which is weaker in the fluorinated compounds due to the decreased π-donor properties of polyfluorobenzene ring, under the influence of electronegative fluorine atoms. Nevertheless the highly characteristic absorption bands of in-plane skeletal vibrations of aromatic rings established for a variety of compounds [3] proved typical also for the polyfluorinated derivatives (see Section 1 of this review).

The effect of polyfluorinated ring on vibrations of other functional groups is diverse. Thus no stretching frequency changes have been found for CH and CY in the CH_3, CH_2Y, and CHY_2 groups, where Y = Cl, Br, I [6,8,39]; in the CN group [7,35], etc. At the same time, for some groups, such as, e. g., NSO [53], there are substantial changes. Table 3 gives the data on stretching frequencies of various functional groups.

Further sections review in detail the IR and Raman data for the aromatic compounds with functional groups, most fully studied in the literature.

2.1. Fluorine effect on the stretching frequencies of electron-donating substituents X in C_6F_5X

The stretching and deformation frequencies of the amino group bonded to the polyfluoroaromatic fragments are almost the same as in the non-fluorinated analogues. Thus replacement of the aromatic H by F atoms in aromatic amines leads only to a 10-20 cm^{-1} shift of the absorption bands corresponding to NH stretching vibrations to higher frequencies [2] (the IR and Raman spectra and assignments of fundamentals of pentafluoroaniline are given in [10], some reassignments in [13]) A higher NH_2 stretching frequency seems to be the result of conjugation of the non-bonded electron pair of nitrogen with the C_6F_5 group [13]. The authors of [13] also report the decreased intensities of NH_2 stretching vibrations in pentafluoroaniline as compared with aniline.

The IR and Raman studies and complete vibrational assignments for C_6F_5OH have been reported in [37]. The fluorine effect on ν_{OH} was not discussed in that work. Reference [2] reports the substantial effect of fluorine substitution for hydrogen in the aromatic ring on the stretching and bending vibrations of OH groups. Thus in the spectra of polyfluorophenol solutions, absorption bands of associated molecules are usually much weaker than in the spectra of non-fluorinated analogues. Evidently, for such compounds the equilibrium between the associated and monomeric molecules is slightly shifted towards the latter [3]. One of the reasons for this may be formation of the intramolecular hydrogen bond OH....F involving ortho-fluorine [59]. This is evident from the decreased frequency (by ~ 40 cm^{-1}) and the greater half-width of O-H stretching bands of polyfluorophenol monomer molecules as compared with non-fluorinated ones. In the cases where the hydroxyl group is separated from the polyfluoroaromatic ring by a group of atoms and formation of such intramolecular bond is impossible, the behaviour of the OH stretching band only slightly differs from its behaviour in the case of non-fluorinated analogues.

2.2. Stretching frequencies of electron-accepting groups X in pentafluorobenzenes

A shift to higher frequencies upon fluorine substitution for hydrogen in the aromatic ring is observed for the stretching bands of the nitro group. For the aromatic nitro-compounds, the symmetric stretching vibration of the NO_2 group lies at 1350 cm^{-1}, antisymmetric-at 1530 cm^{-1} [3]. For pentafluoronitrobenzene, strong absorption bands are observed, which correspond to the polarised and depolarised bands in the Raman spectra, assigned to the stretching vibrations $\nu_{s\ NO_2}$ = 1362 cm^{-1} and $\nu_{as\ NO_2}$ = 1565 cm^{-1} [2,13]. For the aromatic nitrocompounds, characteristic absorption bands are at 835-865, 700-750 cm^{-1} and around 530 cm^{-1}. The spectra of fluorine substituted nitrobenzenes [2] always show a band of varied intensity at 810-870 cm^{-1} (for pentafluoronitrobenzene 938 cm^{-1} [13]), a very strong band at 760-770 cm^{-1} (for $C_6F_5NO_2$ δ_{NO_2} = 766 cm^{-1} [13]), whereas a third absorption band is difficult to reveal in the spectra of this class of compounds.

Characteristic changes on passing from non-fluorinated to fluorinated aromatic compounds are observed for the C=O and C-O stretching vibrations of the carbonyl and ester groups [2]. Usually the carbonyl absorption band of the dimers of unsaturated aromatic carboxylic acids is located at 1680-1700 cm^{-1}, and that of their esters at 1715-1730 cm^{-1}. Upon introduction of fluorine atoms into the benzene ring the carbonyl absorption band of the dimers of tetra- and pentafluorobenzoic acids is shifted by ~ 40 cm^{-1}, and for the esters of these acids by 20-25 cm^{-1} towards higher frequencies. One of the reasons for this is the increased bond order of C=O, and, consequently, of its force constant with increasing electron-accepting ability of substituents in the benzene ring. Apart from the fluorine effect transmitted by the aromatic system, a pronounced contribution to the increased frequency of $\nu_{C=O}$ in the spectra of polyfluoroaromatic carboxylic acids and their derivatives may be made by the ortho-fluorine field effect. This effect shows itself in the presence of two carbonyl group absorption bands in the spectra of monomers of benzoic acids, in which only one ortho-position is occupied by fluorine. The presence of two bands associated with $\nu_{C=O}$ arises from the existence of compounds as two rotational isomers [58,60], the higher-frequency band ascribed to the isomer in which the carbonyl group and ortho-fluorine atom are in the cis-position.

Upon fluorine substitution for the hydrogen atoms in the benzene rings, the absorption bands corresponding to the CO-C stretching vibrations of an ester group also undergo substantial changes [2]. The C-O-C symmetric and antisymmetric stretching vibrations of polyfluoroaromatic carboxylates are shifted by 50-100 cm^{-1} to higher frequencies as compared with non-fluorinated analogues and are located in the regions 1200-1250 and 1300-1380 cm^{-1}. However it should be noted that these regions may also contain intense absorption bands of CF stretching vibrations. Therefore it is sometimes difficult to choose the bands corresponding to the C-O-C stretching vibrations of an ester group.

By analogy with carboxylic acids and esters, one could expect the carbonyl stretching band in the spectra of polyfluoroaromatic aldehydes and ketones to be also shifted to higher frequencies. Indeed, on passing from benzaldehyde to pentafluorobenzaldehyde the band is shifted from 1700 to 1720 cm^{-1} [2]. Reference [37] discusses assignment of torsional vibrations in pentafluorobenzaldehyde but does not consider the full spectrum and fluorine effect on the spectral data for the CHO group.

The fluorine effect in the benzene ring of hydrazides $C_6F_5CON(CH_3)NH_2$ on $\nu_{C=O}$ is examined in [56]. A 44 cm^{-1} shift of $\nu_{C=O}$ as compared to non-fluorinated analogue has been reported. This was explained by the inductive effect of the C_6F_5 fragment and decreased conjugation of the π-system of pentafluorobenzene ring with the C=O π-bond as a result of increased dihedral angle under the fluorine effect.

In the IR spectra of polyfluorobenzo-, naphtho-, and anthraquinones, the carbonyl stretching frequencies are also higher (a 20-40 cm^{-1} shift) than in the case of non-fluorinated quinones [2].

Fluorine substitution for hydrogen in N-sulphinylaniline affects the energy of NSO stretching vibrations. In the Raman spectrum of C_6H_5NSO [61], vibrations ν_{C-N}, $\nu_{N=S}$, and $\nu_{S=O}$ are assigned to strong bands at 1299, 1284, and 1158 cm^{-1} respectively. The use of ^{15}N and ^{18}O labels in [53] has led to the confident assignment of vibrations with the predominant contribution of S=O (in the spectrum of

C_6F_5NSO) to 1167 cm^{-1}, of S=N to 1255, and of C–N to 1328 cm^{-1}. It is noted [53] that assignments of vibrations involving nitrogen in this compound are difficult due to their coupling with vibrations of other fragments of the molecule. The band at 1065 cm^{-1} in the spectrum of C_6H_5NSO, as well as the bands at 1031, 1025, and 1088 cm^{-1} in the Raman spectra of $4\text{-}FC_6H_4NSO$, $2,4\text{-}C_6H_3F_2NSO$, and $4\text{-}CH_3OC_6F_4NSO$ were assigned [53] to the deformation vibration involving the NSO group but not to δ (CH) as in [61], as it is observed in the spectra of perfluorinated analogues C_6F_5NSO and is substantially shifted upon replacement of isotope ^{14}N by ^{15}N (Table 4).

On passing from C_6H_5NSO to C_6F_5NSO, the frequencies of ν_{C-N} and $\nu_{S=O}$ slightly increase, and the frequency of $\nu_{N=S}$ decreases (Table 4). The authors of [53] attribute these changes both to changed force constants (bond orders) in the NSO group, and to the changed conditions of interactions between the stretching vibrations of N-sulphinylamine group and other vibrations in the molecule. Comparison of the increased energy of ν_{C-N} with the ^{13}C and ^{15}N NMR data indicating the π-donor character of the NSO group in compound C_6F_5NSO and the increased effective negative charge on nitrogen on passing from C_6H_5NSO to C_6F_5NSO suggests that there occurs electron density redistribution between the aryl and N-sulphinylamine groups, decrease of electron density in the S=O fragment, and its increase in the ArN fragment, including increase of the CN bond order. According to [60], on passing from C_6H_5NSO to C_6F_5NSO the effective positive charge on sulphur changes very little. This suggests that for the main part electron density redistribution occurs between the ArN fragment and the oxygen atom.

In [53] it has been shown that in the series of $4\text{-}XC_6F_4NSO$ (X = F, OCH_3, CH_3, CF_3) substituents in the 4 position of the aromatic ring affect the stretching frequencies of ν_{C-N}, $\nu_{N=S}$, and $\nu_{S=O}$ (see Table 4). The presence of one or two fluorines in the molecule of N-sulphinylaniline also changes the frequencies of ν_{C-N}, $\nu_{S=N}$, and $\nu_{S=O}$, in some complex manner depending on the number of fluorine atoms in the ring and their position relative to the NSO group.

3. VIBRATIONAL SPECTRA OF FLUORINATED COMPOUNDS ArYAr' WITH UNSATURATED GROUPS Y

During recent years extensive studies have been carried out on the effect of the number and position of fluorine atoms in the

TABLE 4

Frequencies (ν, cm^{-1}) and Raman intensities (I, rel.un.)* of multiple bonds stretching vibrations of N-sulphinylanilines [53]

Compound	ν_8 Ar		$\nu_{N=S}$		$\nu_{S=O}$	
	ν	I	ν	I	ν	I
C_6H_5NSO	1594	1.10	1292	2.00	1164	3.00
4-FC_6H_4NSO	1602	1.25	1290	1.60	1156 1162	3.25
2,5-$C_6H_3F_2NSO$	1614	0.50	1228	0.50	1161	1.00
2,4-$C_6H_3F_2NSO$	1590 1607	0.70	1277	0.60	1146	1.40
2,3,5,6-C_6HF_4NSO	1644	0.40	1252	0.60	1168	1.35
C_6F_5NSO	1655	0.60	1270	0.45	1180	1.00
4-$CF_3C_6F_4NSO$	1660	0.40	1283	0.30	1139	0.50
4-$CH_3C_6F_4NSO$	1656	0.75	1253	0.40	1163	1.70
4-$CH_3OC_6F_4NSO$	1653	0.30	1256	0.25	1172	1.70

* Integral intensities have been determined relative to the 1710 cm^{-1} band of acetone.

benzene ring on the frequencies and intensities of the stretching vibrations of unsaturated bridge groups linking two benzene rings : -CH=N- [62] , -N=N- [33] , -N=N(O)- [34] , -CH=N(O)- [64] , and -N=S=N- [63] . For vibrational assignments the authors of these works used the ^{15}N and ^{18}O labelled compounds; for compounds with the azoxy group, the normal vibration calculations were used [34] (see Table 5).

The IR and Raman studies of azobenzene and its twelve fluoroderivatives, as well as a number of samples labelled with ^{15}N on both nitrogen atoms, carried out in [33] , allowed the confident assignment of the stretching bands of the azoxy group. Some difficulties in interpreting the spectra of azobenzenes and disagreement in assigning some bands arise from the existence of trans- and cis-isomers (according to [66] , the cis-isomer of azobenzene has a slightly higher -N=N-stretching frequency than trans-azobenzene). On passing from azobenzene to polyfluorinated azobenzenes, there is a small increase

TABLE 5

Stretching frequencies of Y groups in polyfluorinated compounds

Group	Vibration type	ν cm^{-1} ($\Delta\nu_{^{15}N}$ or $\Delta\nu_{^{18}O}$)			
		Fluoro-derivatives	Reference	Non-fluorinated compound	Reference
-CH=N-	C=N	1680-1640 ($\Delta\nu_{^{15}N}$ 12-20)	62,64	1605-1645	45
-CH=N(O)-	C=N	1510-1560	64	1500-1600	65
-N=N-	N=N	1440-1520 ($\Delta\nu_{^{15}N}$ 12-50) (sometimes 2 bonds)	33	1410-1440 trans 1510 cis	65
-N=N(O)-	N=N	1440-1495 ($\Delta\nu_{^{15}N}$ 12-31) (sometimes 2 bonds)	34	1450-1480	65
	$\mathrm{C\underset{\substack{\downarrow\\ O}}{N}{=}NC}$	1340-1370 ($\Delta\nu_{^{15}N}$ 11-22)		1315-1340	
-N=S=N-	asymm. N=S=N	1430-1450	63	1200-1300	61
	symm. N=S=N	1160-1205		960	

in the frequency of -N=N- vibrations. This difference possibly results from the absence of conjugation between the non-bonding electron pair of nitrogen of the -N=N- group in polyfluoroazobenzenes with the benzene ring π-system. Small differences in the frequencies of -N=N- vibrations arise from the inductive effect of the phenyl and polyfluorophenyl groups. Vibrations in the -N=N- stretching frequencies conform to the variations in Hammett σ-para-constants, *i. e.* to the nature of p-substituents to the -N=N- group in the benzene ring. At the same time, C-N stretching frequencies do not show linear dependence on substituent σ-para-constants.

In [62,64], the IR and Raman studies have been reported for compounds of type ArCH=NAr' and ArAr'C=NAr'', where Ar, Ar',

TABLE 6

Stretching frequencies (ν cm^{-1}) and intensities (I rel. un.)* in the IR

Compound			$\nu_{C=N}$	$\nu_{C_6F_5}$ (I in Raman)
Ar	Ar'	Ar''		
H	C_6H_5	C_6H_5	1633 (4.1)	
H	C_6H_5	C_6F_5	1633 (5.0)	1662 (0.6)
H	C_6F_5	C_6H_5	1629 (2.4)	1658 (1.5)
H	C_6F_5	$C_6H_4CH_3$-4	1629	1656
H	C_6F_5	C_6H_4F-4	1631 (2.1)	1665 (1.1)
H	C_6F_5	C_6H_4Cl-4	1625 (3.8)	1650 1660 (2.4)
H	C_6F_5	C_6H_4Br-4	1622 (3.8)	1660 (2.2)
H	C_6F_5	C_6H_4I-4	1618 (3.9)	1659 (2.3)
H	C_6F_5	$C_6H_4NO_2$-4	1628	1659
H	C_6F_5	C_6F_5	1635 (4.5)	1658 (2.4)
H	C_6F_5	$C_6H_4CH_3$-4	1631 (5.4)	1655 (3.2)
C_6H_5	C_6H_5	C_6H_5	1609	
C_6H_5	C_6H_5	C_6F_5	1631	1660** (0.8)
C_6H_5	C_6F_5	C_6H_5	1625	1656** (0.1)
C_6H_5	C_6F_5	C_6F_5	1627	1660** (0.9)
C_6F_5	C_6F_5	C_6H_5	1638	1659** (0.8)
C_6F_5	C_6F_5	C_6F_5	1623	1661

* The intensities have been measured relative to the 1710 cm^{-1} band

$\nu_{C_6H_5} \sim 1000$ cm^{-1}.

Ar'' are phenyl or polyfluorophenyl rings with various substituents for H or CH_3, and a series of ^{15}N labelled samples. The stretching frequencies in aromatic azomethines [62,67] depend in a complex way on the properties of adjacent bonds and are almost insensitive to the resonance effects of substituents in the benzene rings. With fluorine atoms introduced into the benzene rings, the C=N stretching frequency and Raman spectra of fluorinated azomethines ArAr'C=NAr'' [62,64]

$\nu_{C_6H_5}$ (I in Raman)	ν_{C-N}	λ_{max}, nm (lg ε)
1600	876	264 (4.30), 308 (4.02)
1584 (6.3)		
1605	893	264 (4.19), 310 (3.97)
1582 (3.7)		
1599 (4.0)	868	238 (4.17), 250 (4.18), 320 (3.81)
1599		242 (4.21), 254 (4.18), 326 (3.90)
1604 (4.3)	876	250 (4.23), 270 (4.03), 314 (3.80)
1592		242 (4.20), 258 (4.18), 324 (3.90)
1582 (5.0)		
1585 (4.3)		242 (4.24), 256 (4.21), 322 (3.96)
1583 (5.1)		248 (4.26), 328 (3.92)
1592		222 (4.12), 364 (4.28)
	996	
		253 (4.28), 320 (3.78)
1596		246 (4.28), 332 (3.44)
1583 (1.2)		
1599		258 (4.37), 320 (3.25)
1583 (1.8)		
1598** (1.7)		260 (4.30), 332 (3.40)
1605**		268 (4.28), 320 (3.50)
1584 (2.9)		
1598** (1.4)		220 (4.30), 238 (4.20), 334 (3.37)
	903	246 (4.15), 325 (3.44)

of acetone. ** The intensities have been measured relative to

changes very little, and does not show pronounced dependence on the σ-para-constants of substituents in para-position of the benzene ring (see Table 6). At the same time, the Raman spectra show a substantially decreased intensity of $\nu_{C=N}$ upon substitution of C_6H_5 by C_6F_5 at carbon (the ^{15}N NMR spectra show a decreased electron density at nitrogen), and increased intensity of this band upon substitution of C_6H_5 by C_6F_5 at nitrogen (according to the ^{15}N NMR data, here the introduction of fluorine leads to enhanced screening of nitrogen). The Raman intensity of $\nu_{C=N}$ varies depending on the electron-accepting abilities of substituents in the ring para-position. Thus, for the series of substituents $N(C_2H_5)_2$, OCH_3, CH_3, H, F, CF_3, along with the decreased intensity of $\nu_{C=N}$, one can observe the decreased intensity and the hypsochromic shift of a long-wave maximum in the UV spectra of the respective compounds. When the azomethine carbon atom bears a phenyl or pentafluorophenyl group, this group is essentially withdrawn out of conjugation, as indicated by the decreased intensity of the respective Raman band (see examples in [64] and Table 6).

In [34], the IR and Raman spectra of azoxybenzene and ten of its fluoroderivatives have been analysed, including the ^{15}N and ^{18}O labelled samples. The calculations of frequencies and forms of normal vibrations in the valence force field allowed more accurate assignment of stretching modes of azoxy group in azoxybenzene. Substitution of fluorine for hydrogen insignificantly changes the frequency range of N=N(O) stretching vibrations, but accumulation of fluorine atoms in the ring substantially decreases the Raman intensities of bands $\nu_{8a,b}$ and ν_{C-N}.

Band assignments in the IR and Raman spectra of nitrones ArAr'C=N(O)Ar'' were carried out [64] by their comparison with the spectra of the respective anils ArAr'C=NAr'', as well as of ^{15}N-labelled compounds. The lower values of $\nu_{C=N}$ of nitrones as compared with anils indicate the lower double bond character of C=N in nitrones (the π-order of azomethine bond determined from $\nu_{C=N}$ similarly to [68] is 0.90 for anils and 0.65 for nitrones). The UV spectra of nitrones, containing intense ($\lg \varepsilon > 4$) absorption π, π^* bands at 282-314 nm, indicate the conjugation effect involving the nitrone group. In the spectra of α,α-bis(pentafluorophenyl)-nitrones and the nitrones containing the C_6F_5 and C_6H_5 groups at the α-carbon atom these bands are shifted by ~ 20 nm to smaller wave-number relative to the respective absorption band in the spectra of α,α-diphenylnitrones, indicating a decreased conjugation effect for compounds with phenyl rings at α-carbon substituted by the polyfluorinated rings. The reduced Raman intensity of $\nu_{8a,b}$ of C_6F_5 also indicates rather a low degree of conjugation of the $\alpha(C_6F_5)$ group with the nitrone and azomethine groups.

The authors of [69] found a substantially altered structure of the thiodiimide group upon fluorine substitution for hydrogen in the aromatic ring. The fluorine effect brings about bond order changes in polyfluoroaromatic thiodiimides, as confirmed by the calculations of model compounds [69]. The IR and Raman studies of thiodiimides ArN=S=NAr' and a number of ^{15}N-labelled compounds have shown considerable difficulties in assigning the stretching vibrations of the N=S=N group, arising from coupling of S=N and N-C vibrations, and from the presence of various configurations, their distribution depending on the solvent [63]. Significant increase of S=N stretching frequencies in polyfluorinated diarylthiodiimides (see Table 7) (ν_s 1160 cm^{-1}, ν_{as} 1430-1450 cm^{-1}) as compared with non-fluorinated analogues (ν_s 960 cm^{-1}, ν_{as} 1264-1278 cm^{-1} [61] may not be explained by mechanical effects, indicating probably the increased force constants and order of these bonds in polyfluorinated compounds due to the electronic effects of the polyfluorinated benzene ring.

TABLE 7

Intensities (I, rel.un.)* of ν_8 in the Raman spectra of compounds C_6H_5X and C_6F_5X [29]

X	$I_{C_6H_5X}$	$I_{C_6F_5X}$	X	$I_{C_6H_5X}$	$I_{C_6F_5X}$
OH	0.11	0.04	CH_3	0.36	0.20
OCH_3	0.14	0.11	NO_2	0.55	0.23
CH_3	0.14	0.11	NH_2	0.24	0.20
Cl	0.16	0.10	$NHCH_3$	-	0.41
Br	0.21	0.14	$N(CH_3)_2$	0.37	0.25
I	-	0.15	$P(CH_3)_2$	-	0.32
H	0.15	0.03	CN	0.47	0.32
F	0.11	0.03	$Si(CH_3)_3$	-	0.13
CF_3	0.16	0.08	SO_2Cl	-	0.18

* Integral intensities were measured relative to the 1710 cm^{-1} band of acetone

The increased S=N bond order possibly results from weakening of the $p_p - p_\pi$ interaction between the non-bonding electron pair of nitrogen of the N=S=N fragment with the polyfluorinated ring as compared with the non-fluorinated one, which is consistent with the known low capability of the pentafluorophenyl group to undergo π-interaction.

As shown by the analysis of stretching vibrations of unsaturated group Y (see Table 5), introduction of fluorine into the benzene ring generally does not change them, though a tendency to increase of these frequencies is observed for compounds of the same type. The largest increase has been observed [63] in the case of Y = N=S=N.

4. EFFECT OF BENZENE FLUORINE ON THE FUNCTIONAL GROUPS STRETCHING INTENSITIES

For all pentafluorobenzene derivatives of type C_6F_5X, independently of the character of substituent X, the Raman spectra show the decreased intensity of multiple bond stretching vibrations as campared with compounds C_6H_5X [29] , Table 7. With heteroatom introduced into the functional group, several parameters change at a time : ionisation potentials related to mutual disposition of n- and π-levels, the share of the p-character of lone electron pair, which determines the p- π -conjugation degree and some others, showing different effects on spectral characteristics [70]. As shown by the X-ray fluorescence spectroscopy, the HOMO composition for polyfluorinated aromatic compounds is determined by the nature of heteroatoms in the functional group and depends on the efficiency of p- π -conjugation of non-bonding electron pair of an element with the benzene ring π-system and the energy level of HOMO [52]. In the series of C_6F_5X, the first ionisation potential is : NH_2 8.95, CH_3 9.20, OH 9.73, F 9.93 eV : the intensity of mode ν_8 changes respectively (0.20, 0.11, 0.04, 0.03). Thus the Raman intensity of ν_8 will be determined by several effects, among which an important role is possibly played by the energy and composition of HOMO [52,70] .

With substituent X containing a multiple bond, the Raman intensity of the ν_8 of both polyfluorinated and non-fluorinated compounds substantially increases [29] as a result of π- π -conjugation [71]. At the same time, as with perfluoroolefins [72] , substitution of hydrogen atoms in the ethylene fragment of polyfluorinated compounds by fluorine or chlorine leads to the decreased Raman intensities of ν_8 and $\nu_{C=C}$ (Table 8). Introduction of fluorine to the aromatic fragment decreases the efficiency of its conjugation with a multiple bond, which leads to the decreased intensity of the ν_8 in the Raman spectra of these compounds as compared with the non-fluorinated analogues [32,62] , and in some cases to changes in multiple bond frequencies [56] . This could be associated with the reduced efficiency of conjugation of the perfluorinated ethylene bond with the π-system of the benzene ring. It is important that the benzene ring has a fluorine atom in ortho-position to the multiple bond, which is evident in the case of N-arylsulphinylamine derivatives (see Table 4) [53] : the intensities of NSO bands are sensitive to the presence of ortho-fluorine atoms and change only slightly with accumulation of fluorine atoms in the molecule. Introduction of substituents to the para-position relative to the NSO group changes the intensity of the ν_8 band in the Raman spectra of polyfluorinated N-sulphinylanilines varies in accordance to σ-constants. In this case the introduction of a substituent to the para-position of the pentafluorophenyl ring raises the intensity of $\nu_{S=O}$ in the series CF_3, F, H, CH_3, OCH_3, $N(C_2H_5)_2$, whereas the intensity of $\nu_{N=S}$ is less sensitive to substituent.

TABLE 8

Frequencies (ν, cm^{-1}) and Raman intensities (I , rel.un.)* of multiple bond stretching vibrations of compounds ArX [29]

ArX	ν_8	I ν_8	$\nu_{C=C}$, C=N	I C=C,C=N
$C_6H_5CH=CH_2$	1602	0.81	1632	1.40
$C_6F_5CH=CH_2$	1640	0.86	1627	1.06
$C_6F_5CCl=CF_2$	1658	0.32	1750	0.32
$C_6F_5CF=CF_2$	1656	0.58	1785	0.42
$C_6F_5CF=CFCF_3$	1662	0.32	1730	0.65
$C_6F_5CF_2CF=CF_2$	1660	0.12	1800	0.12
$C_6H_5CH=NCH_3$	1590	0.46	1658	0.58
$C_6F_5CH=NCH_3$	1665	0.41	1641	0.28

* Integral intensities were measured relative to the 1710 cm^{-1} band of acetone

In the spectra of polyfluorinated azoxybenzenes [34] , a clear dependence on the nature of substituent in the 4- and 4'-positions of benzene rings is shown by the intensity of ν_{C-N} , increasing in the order $CF_3 < H < F < CH_3 < OCH_3$. The intensity and hypsochromic shift of long-wave maximum in the UV spectra increase in the same order. This is in qualitative agreement with the conclusion that the intensity of stretching vibrations of bridge group depends on the efficiency of conjugation of the non-bonding electron pair of nitrogen of this group with the benzene ring π-system.

CONCLUSION

As evident from the review, the literature contains much material on frequency assignments in the spectra of polyfluoroaromatic compounds, made both on the basis of experimental data and calculations. Literature analysis shows that generally introduction of fluorine atoms into the benzene ring very slightly affects the stretching frequencies of other substituents in the ring. At the same time, frequencies and intensities of skeletal modes also change. The analysis of vibration forms shows that many of them, e.g. stretching vibrations ν_8, are also preserved in polyfluorobenzenes. Therefore polyfluoroaromatic compounds show similar tendencies as their non-fluorinated analogues. For example, variations in the ν_8 intensities under the influence of substituents, involving those with multiple bonds, are similar to those observed for the non-fluorinated benzenes, being less pronounced. Accumulation of fluorine atoms in the benzene rings of compounds of type ArYAr' (Y is a bridge group) decreases the Raman intensities of stretching vibrations of the bridge and phenyl groups. The observed tendencies of variation in the vibration intensities of polyfluoroaromatic compounds have not been quite adequately explained as yet. Thus there have been no theoretical calculations of the intensities in the vibration spectra of polyfluoroaromatic compounds. It is in this direction, in our opinion, that interesting and unexpected results may lie.

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