

292. *Infra-red Spectra of Fluorinated Hydrocarbons. Part III.*

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The infra-red absorption spectra of some fluorinated hydrocarbons have been measured between 2 and 20 μ . These include fully fluorinated *cyclohexane*, *methylcyclohexane*, *n-pentane*, and 2 : 3-dimethylpentane, *o*-, *m*-, and *p*-fluoro- and 2 : 4-difluoro-toluene; benzotrifluoride, *m*- and *p*-fluoro- and 2 : 5-difluoro-benzotrifluoride. The significance of some of the bands in terms of the molecular vibration frequencies has been discussed. The measurements provide useful data for analytical work on these compounds.

THIS paper summarises measurements on the infra-red absorption spectra of some fully fluorinated paraffins and naphthenes, and partly fluorinated toluenes. The original aim of the work was to explore the use of infra-red absorption for analysis of mixtures of these compounds, both in presence of each other and in the presence of contaminants. However, current interest in compounds containing fluorine, and fluorocarbons in particular, adds interest to the results although at present few vibrational assignments can be made.

EXPERIMENTAL.

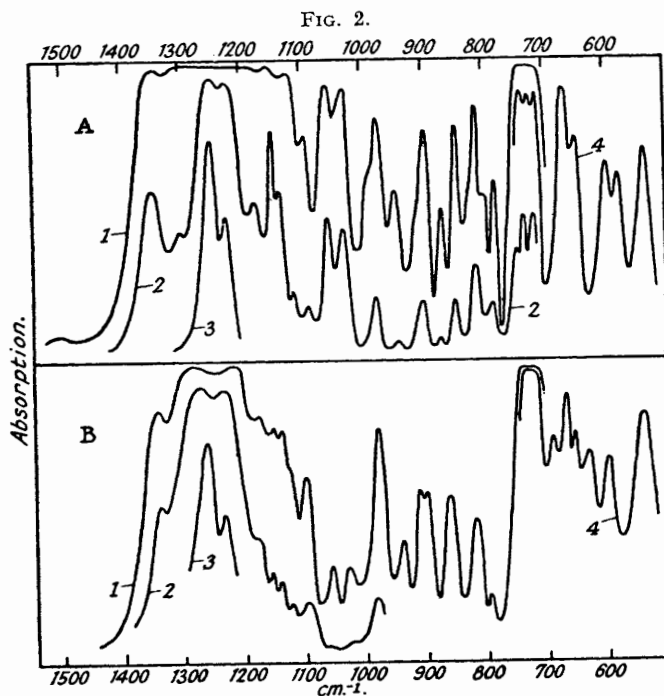
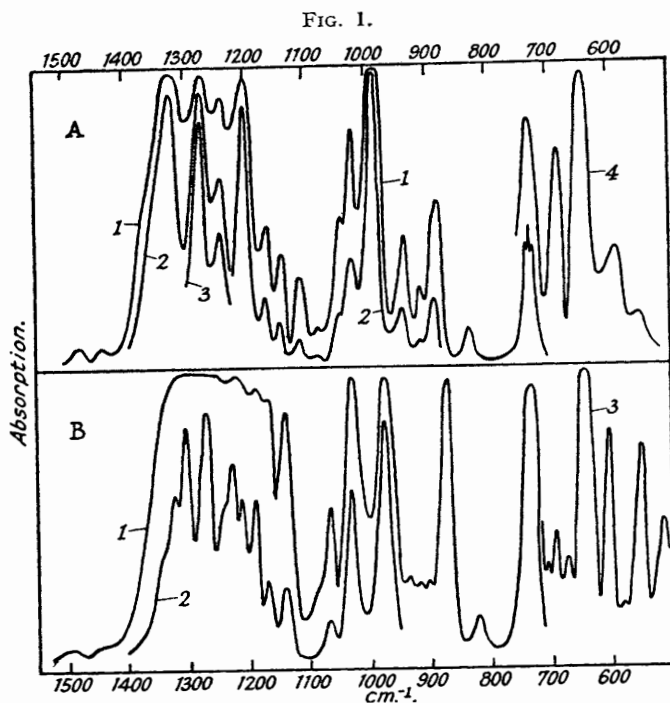
The spectrometers and other experimental arrangements were as described in the two preceding papers. Slit widths of 4–5 cm^{-1} were used over the important range 6–20 μ . The compounds were supplied by the research laboratory of I.C.I. (General Chemicals) Ltd., and had the following b. p.s: dodecafluorocyclohexane, 72° (m. p. 50°); tetradecafluoromethylcyclohexane, 77°; hexadecafluoro-*n*-heptane, 82°; hexadecafluoro-2 : 3-dimethylpentane, 82°; benzotrifluoride, 103°/757 mm.; *m*-fluoro-benzotrifluoride, 100°/757 mm.; *p*-fluorobenzotrifluoride, 102.5°/755 mm.; 2 : 5-difluorobenzotrifluoride, 109–109.5°; *m*-fluorotoluene, 116.5°/755 mm.; *p*-fluorotoluene, 116.5°/753 mm.; 2 : 4-difluorotoluene, 114.5°/757 mm. *o*-Fluorotoluene was a B.D.H. product, purified by redistillation.

Results and Discussion.—Figs. 1 and 2 show the spectra between 6 and 20 μ of the fully fluorinated paraffins and naphthenes, measured as vapours. With these compounds the absorption bands at shorter wave-lengths are feeble and cannot include any fundamental vibrations. The positions of the bands (cm^{-1}) are listed in Table I. An assignment of vibration frequencies to particular normal modes

TABLE I.

C_6F_{12} .		C_7F_{14} .		$\text{CF}_3[\text{CF}_2]_5\text{CF}_3$.		$\text{CF}_3[\text{CF}(\text{CF}_3)]_2\text{CF}_2\text{CF}_3$.	
555	1023	512	935	535	948	539	909
586	1041	546	975 s.	575	977	595	944
641 s.	1080	578?	1030 s.	596	990	635	982
680 s.	1161	601 m.	1062 m.	651	1030 s.	652	1028
730 s.	1200 v.s.	645 s.	1137 s.	669 s.	1058 s.	667	1058
831	1240 m.	671	1170 m.	714 s.	1095	690	1100
883	1270 v.s.	690	1185 m.	725 s.	1120	730 v.s.	1140
913	1323 v.s.	709	1212 m.	741 s.	1140	795	1150
940	1443	730 s.	1229 v.s.	782	1150 v.s.	815	1178
985 v.s.	1480	822	1270 v.s.	800	1183	860	1235 v.s.
		870 s.	1302 v.s.	812	1230 v.s.	900	1260 v.s.
		900	1322	846	1250 v.s.		
		916		870	1305		
				896	1348		

is at present impossible. Fully fluorinated *cyclohexane* shows four very intense bands at 985, 1200, 1270, and 1320 cm^{-1} . The last three of these may be connected with stretching vibrations of C-F bonds. The band at 985 might be connected with the ring of six carbon atoms, since *cyclohexane* and its derivatives usually have a strong band in this region, and the open-chain, fully fluorinated hydrocarbons do not appear to have a similar band. The band of fully fluorinated *cyclohexane* at 730 cm^{-1} shows a contour



with three sub-maxima. It may be connected with the deformation of CF_2 groups, since it is of about the correct magnitude for such a mode and a strong band of this value occurs with all the fluorocarbons studied.

Fully fluorinated methylcyclohexane also has a group of intense bands between 1200 and 1350 cm^{-1} , presumably connected with stretching vibrations of C-F bonds. It also shows the intense band at

FIG. 3.

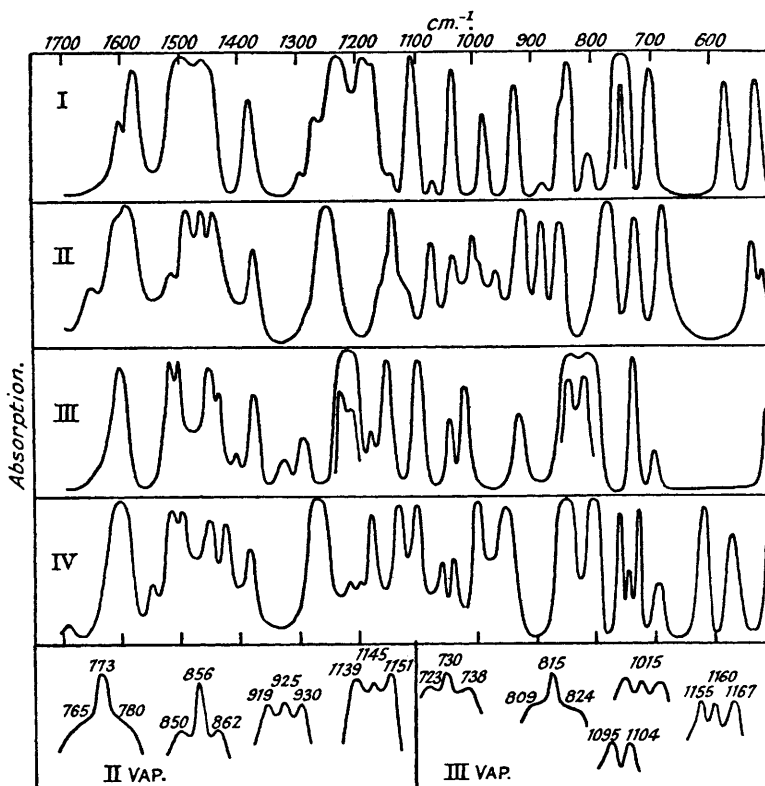


TABLE II.

<i>o</i> -Fluorotoluene.		<i>m</i> -Fluorotoluene.		<i>p</i> -Fluorotoluene.		2 : 4-Difluorotoluene.
Raman.	I.-Red.	Raman.	I.-Red.	Raman.	I.-Red.	I.-Red.
185	—	209	—	311	—	505
274	—	243	—	342	—	567
428	—	298	—	455	—	615
530	528	444	—	501	509	694
576	578	512	518	642	—	725
—	703	527	532	698	699	743
747	752	552	—	728	729	758
—	807	—	685	824	820	805
—	842	728	730	843	842	850
848	850	775	778	—	928	952
—	886	852	857	995	—	1000
—	934	—	888	—	1018	1040
986	985	—	922	—	1046	1060
1037	1037	—	968	—	1098	1098
1071	1072	—	995	1158	1151	1131
1110	1108	1003	1004	—	1179	1179
1149	1145	—	1039	1213	1210	1200
—	1172	1078	1075	—	1235	1215
—	1193	1153	1143	1294	1292	1270
1233	1233	1254	1255	—	1325	1380
1277	1275	1266	—	1380	1376	1425
—	1298	1379	1376	—	1408	1450
1381	1382	1445	1445	—	1435	1496
1441	1445	—	1465	1456	1450	1515
—	1465	—	1486	—	1505	1550
—	1500	—	1515	—	1518	1600
1583	1580	1590	1590	1605	1605	1695
—	1600	1618	1610	—	—	—
1618	—	—	1655	—	—	—

975 cm^{-1} , and the band at 730 cm^{-1} again shows contour. With the two fully fluorinated paraffins there are intense bands near 1250 and 730 cm^{-1} which again probably relate to stretching and deformational vibrations of C-F bonds. Again the spectra are too complex for detailed analysis at present.

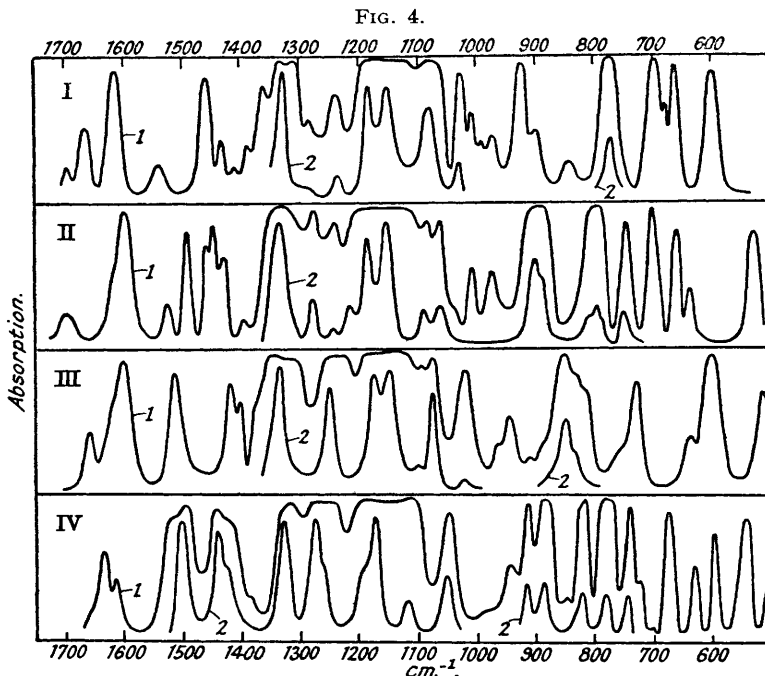


TABLE III.

Raman.	Benzotrifluoride.		I.-Red.	<i>m</i> -Fluoro-	<i>p</i> -Fluoro-	2 : 5-Difluoro-
	I.-Red.	Raman.		benzotri-	benzotri-	benzotri-
				fluoride.	fluoride.	fluoride.
				I.-Red.	I.-Red.	I.-Red.
139	—	—	1080 v.s.	526 s.	510	503
339	—	1116	—	637	600 s.	540 s.
396	—	1160	1150 v.s.	658 s.	638	598
—	599 s.	1189	1183 v.s.	699 s.	729	628
618	—	1222	—	747 s.	818	671 s.
656	664 s.	—	1238	792 v.s.	833	704
—	676	1254	—	895 v.s.	852 v.s.	728
—	699 s.	—	1290	974	888?	742 s.
771	771 s.	1324	1325 v.s.	1006	913	782 s.
839	844	—	1360	1062	947	822 s.
—	900	—	1390	1085	962	850
—	923 s.	—	1412	1152 v.s.	1020	887 s.
—	970	—	1430	1182 v.s.	1075 s.	912 s.
—	992	—	1455 s.	1215	1095	940
1005	1005	—	1540	1240	1105	1047 s.
1027	1027 s.	1585	—	1278	1150 v.s.	1115
1068	1065	1611	1615 s.	1335 v.s.	1175 v.s.	1172 s.
				1395	1250 v.s.	1193
				1429	1335 v.s.	1260
				1447	1403	1278 s.
				1458	1418	1333 s.
				1493	1515 s.	1430
				1524	1605 s.	1441 s.
				1600	1658	1495 s.
				1700		1511
						1616
						1631

Fig. 3 shows the spectra between 6 and 20 μ of *o*-, *m*-, and *p*-fluoro- and 2 : 4-difluoro-toluenes, measured as liquids in layers less than 0.1 mm. thick, and also depicts the contours of some of the bands found for the vapours of *m*- and *p*-fluorotoluenes. The spectra are again too complex for detailed analysis, but a few features may be noted. The bands appear in general more intense than with

unsubstituted toluene. Strong bands between 700 and 900 cm^{-1} characteristic of an out-of-plane bending mode of the C-H bonds of an aromatic nucleus have previously been correlated with substituted aromatics (Thompson and Torkington, *Trans. Faraday Soc.*, 1945, **41**, 285). The bands of *o*-fluorotoluene near 750 cm^{-1} , of *m*-fluorotoluene near 775 cm^{-1} , of *p*-fluorotoluene near 820 cm^{-1} , and of 2 : 4-difluorotoluene near 810 cm^{-1} are probably attributable to this mode. The positions of the bands (cm^{-1}) are listed in Table II, which also gives the Raman intervals for *o*-, *m*-, and *p*-fluorotoluene found by Kohlrausch (*Sitz. Akad. Wiss. Wien*, 1933, **142**, IIb, 650).

Fig. 4 shows the spectra between 6 and 20 μ of benzotrifluoride, and its *m*-fluoro-, *p*-fluoro-, and 2 : 5-difluoro-derivatives, measured as liquids and vapours. Table III lists the positions (cm^{-1}) of the bands, with Raman data for benzotrifluoride given by Pendl and Radinger (*ibid.*, 1939, **143**, IIb, 76). It is noteworthy that all these compounds show intense bands near 1330 and 1150 cm^{-1} which may be connected with vibrations of the CF_3 group. The band of benzotrifluoride at 771 cm^{-1} is probably associated with an out-of-plane bending mode of the monosubstituted benzene, but if so, it is noticeably higher than is usually found. This could arise as a result of electronic influences of the CF_3 group on the strengths of the neighbouring bonds. Similarly, the corresponding out-of-plane C-H bending mode of the *m*-substituted compound lies at 792 cm^{-1} , and that of the *p*-derivative probably at 850 cm^{-1} , in both cases higher than normal. Substitution by fluorine in the different ways also seems to affect the values and relative intensities of the two vibration bands near 1500 and 1600 cm^{-1} associated with the aromatic nucleus.

The above results may be useful in connexion with analyses of mixtures containing these compounds. Further, although the spectra of the fluorocarbons between 2 and 6 μ have not been shown, it may be noted that small quantities of residual C-H linkages should be detectable by their bands near 3.4 μ , where the fluorocarbons themselves have very weak absorption. As regards more detailed vibrational or structural analysis, however, further consideration must await the compilation of results with other substances of this type.

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