1367. *Spectroscopic Studies. Part VI.* The Infrared and Raman Spectra of* 1,1-*Dichloro-2-fluoroethylene,* 2-*Bromo*-1,1-*dichloroethylene, and Bromotrichloroethylene*

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The infrared and Raman spectra of the title compounds in the vapour, liquid, and solid phases are reported. Frequency assignments have been made and structural details deduced in each case.

ALTHOUGH the infrared and Raman spectra of halogenated ethylenes [1,2] have been studied fairly extensively over the last fifteen years, there exist several gaps in the work on these

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* Part V, R. G. Jones and W. J. Orville-Thomas, *J.*, 1965, 4632.

[1] D. E. Mann *et al.*, (*a*) *J. Chem. Phys.*, 1954, **22**, 1199; (*b*) *ibid.*, 1955, **23**, 2122; (*c*) *ibid.*, 1957, **26**, 773; (*d*) *ibid.*, 1955, **23**, 1989; (*e*) *ibid.*, 1957, **27**, 43, 51; (*f*) *ibid.*, 1953, **21**, 1949; (*g*) *ibid.*, 1954, **22**, 1586; (*h*) *ibid.*, 1956, **24**, 1018; (*i*) *J. Res. Nat. Bur. Stand.*, 1954, *A*, **53**, 67.

[2] J. R. Nielsen, (*a*) *J. Chem. Phys.*, 1950, **18**, 326; (*b*) *ibid.*, 1950, **18**, 485; (*c*) *ibid.*, 1950, **18**, 818; (*d*) *ibid.*, 1952, **20**, 1090; (*e*) *ibid.*, 1952, **20**, 1916; (*f*) *ibid.*, 1955, **23**, 1994; (*g*) *ibid.*, 1957, **26**, 1374; (*h*) *ibid.*, 1957, **27**, 264; (*i*) *ibid.*, 1959, **30**, 98; (*j*) *ibid.*, 1959, **30**, 103; (*k*) *ibid.*, 1952, **26**, 1566; (*m*) *J. Mol. Spectroscopy*, 1957, **1**, 158.

compounds. The spectra of the brominated compounds $CBrCl{=}CCl_2$ and $CHBr{=}CCl_2$ have, so far, not been reported, whilst the only work published [3] on $CHF{=}CCl_2$ is incomplete and contains inaccurate assignments. Furthermore, usually only vapour-phase infrared spectra have been reported, even though many interesting, and in some cases instructive, changes occur in the spectra on change of phase.[4-6]

This work was therefore undertaken in an attempt to obtain more complete spectra and a more reliable frequency assignment for $CHF{=}CCl_2$ and to obtain spectroscopic data for the corresponding bromo- and the bromochloro-derivatives.

EXPERIMENTAL

Preparation of Materials.—(*a*) 1,1-*Dichloro-2-fluoroethylene*, $CHF{=}CCl_2$. Dehydrochlorination of $CHClF{-}CHCl_2$ (Arcton 131, Imperial Chemical Industries Limited, Mond Division) using ethanolic potassium hydroxide would be expected to give a mixture of isomers, $CHF{=}CCl_2$ (b. p. 37°) and $CHCl{=}CFCl$ (b. p. 35°). The Arcton 131 was added dropwise with vigorous stirring and the product removed as it was formed. It was purified by fractional distillation, and its infrared spectrum showed it to be almost entirely $CHF{=}CCl_2$, n_D^{20} 1·4034 (lit.,[7] 1·40364). This is not unexpected since the hydrogen atom attached to the same carbon as the fluorine should be the most difficult to remove.

(*b*) *Bromotrichloroethylene*, $CClBr{=}CCl_2$. Trichloroethylene was brominated and the product ($CCl_2Br{-}CHClBr$, b. p. 204°) was dehydrobrominated using a lime sludge to give the required ethylene, b. p. 145°.

$$CHCl{=}CCl_2 + Br_2 \xrightarrow{\text{u.v.}} CCl_2Br{-}CHClBr$$

$$CCl_2Br{-}CHClBr - HBr \xrightarrow[\text{aq.}]{\text{lime}} CClBr{=}CCl_2$$

The bromination was carried out at 40—60° using liquid bromine under the influence of an ultraviolet (u.v.) lamp. Both the intermediate ethane and required ethylene were purified by fractional distillation under reduced pressure. Dehydrobromination was carried out at 100° in an atmosphere of nitrogen. Any unused trichloroethylene may give dichloroacetylene which explodes in the presence of oxygen. The required $CClBr{=}CCl_2$ boiled at 40°/16 mm. and it was stabilised against decomposition by using a trace of thymol. Vapour-phase chromatography (v.p.c.) showed a total of 1·5% impurity. The material was washed with 5% sodium carbonate solution and thoroughly dried before use, n_D^{20} 1·54154 (lit.,[8] 1·5434).

(*c*) 2-*Bromo*-1,1-*dichloroethylene*, $CHBr{=}CCl_2$. This compound (b. p. 107°) was prepared by dehydrobrominating the ethane (b. p. 176°) obtained by the bromination of vinylidene chloride,[9]

$$CH_2{=}CCl_2 + Br_2 \longrightarrow CH_2Br{-}CCl_2Br$$

$$CH_2Br{-}CCl_2Br - HBr \xrightarrow{\text{lime}} CHBr{=}CCl_2$$

No u.v. lamp was used during the bromination since this causes peroxide formation. The recommended dehydrobrominating agent is ethanolic potassium hydroxide,[9] but to avoid the formation of explosive bromochloroacetylene a lime sludge was used in an atmosphere of nitrogen. This compound was analysed using v.p.c. after being set aside for several weeks. The compound decomposes rapidly on standing and 6% impurity was found. The material was washed with 5% sodium carbonate solution and stabilised with a trace of thymol immediately prior to use. The compound boiled at 64—66°/20 mm., n_D^{20} 1·51882 (lit.,[9] n_D^{15} 1·52028).

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[3] C. J. Muelleman, K. Ramaswamy, F. F. Cleveland, and S. Sundaram, *J. Mol. Spectroscopy*, 1963, **11**, 262.

[4] R. E. Kagarise, *Spectrochim. Acta*, 1963, **19**, 1371.

[5] S. Krimm, " Infrared Spectroscopy and Molecular Structure," ed. M. M. Davies, Elsevier, London, 1963, ch. 8.

[6] N. Sheppard, " Molecular Spectroscopy," Institute of Petroleum, London, 1955, p. 136.

[7] A. L. Henne and E. C. Ladd, *J. Amer. Chem. Soc.*, 1936, **58**, 402; A. L. Henne and E. G. Wiest, *ibid.*, 1940, **62**, 2051.

[8] G. M. Mkryan, *Izvest. Akad. Nauk Armyan, S.S.R. khim. Nauki*, 1944, no. 5/6, 45.

[9] H. van de Walle, *Bull. Soc. chim. belges*, 1925, **34**, 10.

TABLE 1

The infrared and Raman spectra (bands in cm.$^{-1}$) of 1,1-dichloro-2-fluoroethylene

Gas (i.r.)	Type	Liquid (i.r.)	Solid (i.r.)	Liquid (Raman)	Assignment	Species	Type
4777 4752 vw	—	4748vw			3104 + 1649 = 4753	A'	*A–B*
4384vw	—	4374w	4374vw		3104 + 1289 = 4393	A'	*A–B*
					3104 + 796 + 470 = 4370	A''	*C*
4262 4251 vw	*A–B*	4233w			3104 + 1131 = 4235	A'	*A–B*
4084 4076 vw 4071	*A*	4061w	4077vw		3104 + 958 = 4062	A'	*A–B*
		3955w			2 × 1649 + 656 = 3954	A'	*A–B*
		3804w			3104 + 443 + 268 = 3815	A'	*A–B*
3766vw	—		3766vw		3104 + 656 = 3760	A'	*A–B*
3687 3676 vw 3662 3651	*A–B*	3649vw			2 × 282 + 3104 = 3668	A'	*A–B*
					3104 + 282 + 268 = 3654		
		3536w			3104 + 443 = 3547	A''	*C*
		3418w			1649 + 1289 + 470 = 3408	A'	*A–B*
3116 3112 ms 3104	*A*	3104ms	3107ms		ν(C–H)	A'	*A–B*
			2959w, sh		2 × 656 + 1649 = 2961	A'	*A–B*
2989 2973 w	*B*	2938w	2932w, sh		1649 + 1289 = 2938	A'	*A–B*
2902 2898 w 2882	*A*	2820w			3104 − 282 = 2822	A'	*A–B*
2803 2799 w 2793	*A*	2780w	2792w		1649 + 1131 = 2780	A'	*A–B*
2621vw	—	2608vw	2611vw		1649 + 958 = 2607	A'	*A–B*
2571vw	—	2571vw	2576vw		2 × 1289 = 2578	A'	*A–B*
2442 2429 vw	*A–B*				1289 + 1131 = 2420	A'	*A–B*
		2363vw			2 × 958 + 443 = 2359	A''	*C*
		2304vw			1649 + 656 = 2305	A'	*A–B*
					3104 − 796 = 2308	A''	*C*
2291 2286 w 2279	*A*	2257w			2 × 1131 = 2262	A'	*A–B*
			2238w		1289 + 958 = 2247	A'	*A–B*
			2138vw		2 × 958 + 211 = 2127	A'	*A–B*
2117vw	—	2091vw			1289 + 796 = 2085	A''	*C*
					1131 + 958 = 2089	A'	*A–B*
		1912w	1931vw		2 × 958 = 1916	A'	*A–B*
		1843w			2 × 443 + 958 = 1844	A'	*A–B*
					2 × 282 + 1289 = 1853	A'	*A–B*
		1702w, sh	1702vw		2 × 282 + 1131 = 1695	A'	*A–B*
1666 1661 vs 1654	*A*	1649ms	1654ms	1662s	ν(C=C)	A'	*A–B*
1600 1589 ms	*B*	1580s, sh	1597ms		2 × 796 = 1592	A'	*A–B*
					1289 + 282 = 1571	A'	*A–B*
			1415vw		1131 + 282 = 1413	A'	*A–B*
		1355w			2 × 282 + 796 = 1360	A''	*C*
					1649 − 282 = 1367	A'	*A–B*
			1314w, sh		*		
1300 1290 ms	*B*	1289ms	1288ms	1294ms	b(CHF)	A'	*A–B*
			1264w, sh		*		
		1202w			1649 − 443 = 1206	A''	*C*
					2 × 470 + 268 = 1208	A''	*C*
			1160w, sh		958 + 211 = 1169	A'	*A–B*
1157 1152 vs 1144	*A*	1131vs	1124vs	1144ms	ν_s(CHF)	A'	*A–B*

TABLE 1 (*Continued*)

Gas (i.r.)	Type	Liquid (i.r.)	Solid (i.r.)	Liquid (Raman)	Assignment	Species	Type
1067 1060 w 1053	*A*	1045w			2 × 282 + 470 = 1034	*A'*	*A–B*
977 971 vs	*A–B*	958vs	959vs		$\nu_a(CCl_2)$	*A'*	*A–B*
929 925 w 919	*C*	920w	922w		656 + 268 = 924	*A''*	*C*
			911w, sh		470 + 443 = 913	*A''*	*C*
		883w	889w		2 × 443 = 886	*A'*	*A–B*
		849w			1649 − 796 = 853	*A''*	*C*
808 798 vs 792	*C*	796ms	797vs	812w	w(CHF)	*A''*	*C*
			701w		2 × 211 + 282 = 704 443 + 268 = 711	*A'* *A'*	*A–B* *A–B*
668s	—	656vs	644ms	665ms	$\nu_s(CCl_2)$	*A'*	*A–B*
		529w			2 × 268 = 536	*A'*	*A–B*
				470ms	r(CHF)	*A'*	*A–B*
454 446 vs 440	*C*	443vs		455w, sh	$w(CCl_2)$	*A''*	*C*
284w, sh	—	282w, sh		285s	$r(CCl_2)$		
272 262 vs ?	*C*	268vs		274w, sh	Twisting mode	*A'* *A''*	*A–B* *C*
		245w			796 − 2 × 282 = 232	*A''*	*C*
204w	—			211w	$b(CCl_2)$	*A'*	*A–B*
				148w	958 − 796 = 162	*A''*	*C*

* Lattice mode combination.

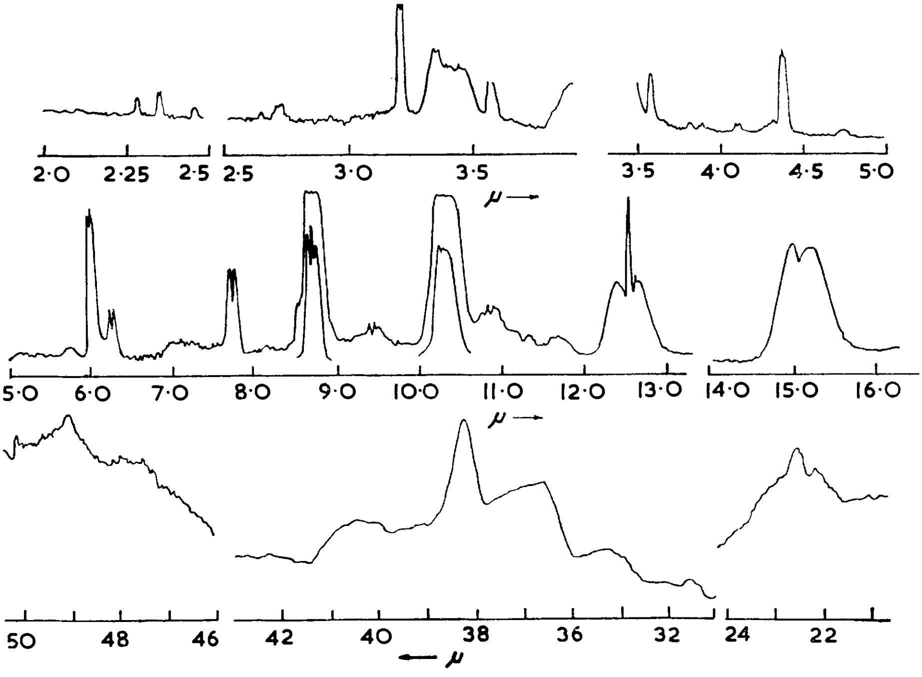

FIGURE 1(a). Infrared spectrum of 1,1-dichloro-2-fluoroethylene vapour at 30° (2—16 μ) and at 25° (20—50 μ)

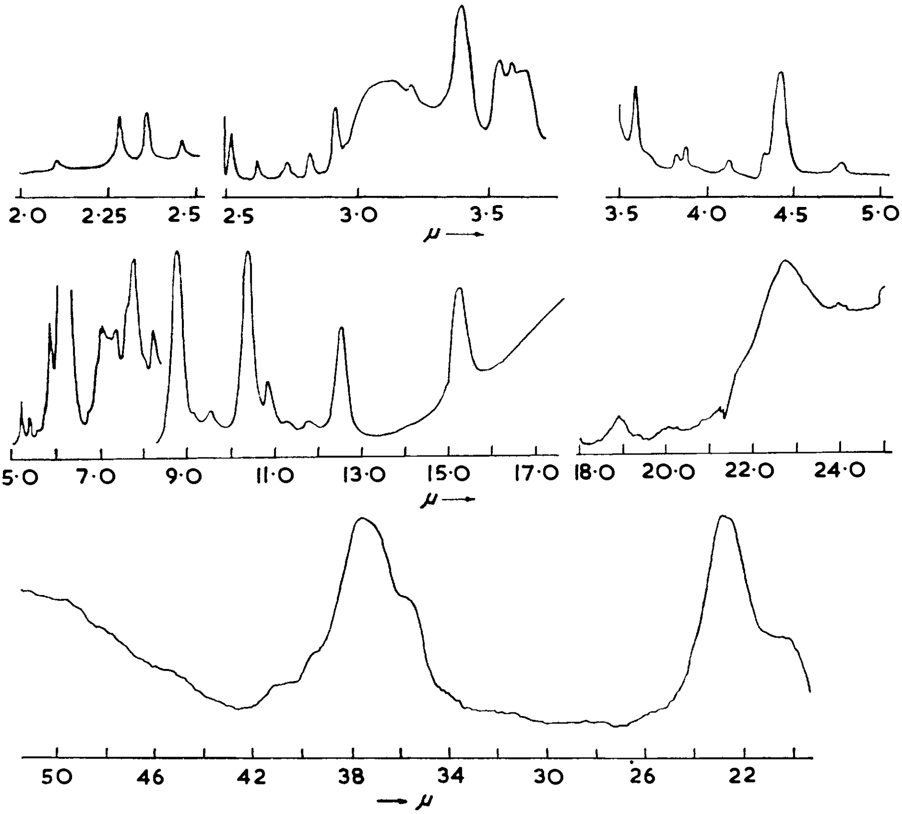

FIGURE 1(b). Infrared spectrum of 1,1-dichloro-2-fluoroethylene liquid at 25°

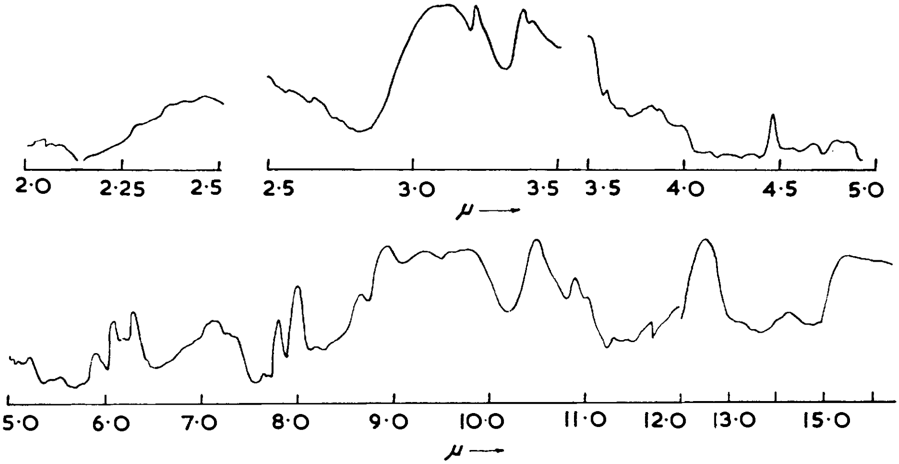

FIGURE 1(c). Infrared spectrum of 1,1-dichloro-2-fluoroethylene solid at −100°

TABLE 2

Infrared and Raman spectra (bands in cm.$^{-1}$) of 2-bromo-1,1-dichloroethylene

Gas (i.r.)	Type	Liquid (i.r.)	Liquid (Raman)	Assignment	Species	Type
		4714vw		3 × 1570 = 4710	A'	*A–B*
		4648vw		3094 + 1570 = 4664	A'	*A–B*
		4271vw		3094 + 742 + 445 = 4281	A''	*C*
		4260				
4295vw	—			3094 + 1203 = 4297	A'	*A–B*
		4034vw		2 × 1570 + 906 = 4046	A'	*A–B*
4014vw	—			3094 + 906 = 4000	A'	*A–B*
		3984vw		2 × 445 + 3094 = 3984	A'	*A–B*
		3828vw		3094 + 742 = 3836	A'	*A–B*
		3738vw		3094 + 445 + 192 = 3731	A''	*C*
		3690vw		1570 + 1203 + 906 = 3679	A'	*A–B*
		3599vw		2 × 245 + 3094 = 3584	A'	*A–B*
		3479vw		2 × 192 + 3094 = 3478 2 × 1570 + 342 = 3482	A' A'	*A–B* *A–B*
		3297vw		3094 + 192 = 3286	A'	*A–B*
3151w	—	3135w		2 × 157 = 3140	A'	*A–B*
3096ms	—	3094ms		$\sim\nu$(C–H)	A'	*A–B*
		2768vw		1570 + 1203 = 2773	A'	*A–B*
		2764vw				
		2670vw		2 × 1203 + 245 = 2651	A'	*A–B*
		2543vw		2 × 1203 + 140 = 2546	A''	*C*
		2475vw		1570 + 906 = 2476	A'	*A–B*
		2463vw		2 × 445 + 1570 = 2460	A'	*A–B*
		2398vw		2 × 1203 = 2406	A'	*A–B*
		2194vw		1570 + 614 = 2184	A'	*A–B*
		2113vw		1203 + 906 = 2109	A'	*A–B*
		2092vw		2 × 742 + 614 = 2098	A'	*A–B*
		1934vw		1203 + 742 = 1945	A'	*A–B*
1832	—			Impurity		
1815w	—	1799w		2 × 906 = 1812	A'	*A–B*
				1570 + 245 = 1815	A'	*A–B*
1778w	—	1757w		1570 + 192 = 1762	A'	*A–B*
		1730w		2 × 742 + 245 = 1729	A'	*A–B*
1587 1581 s	*A–B*	1570s	1597s	ν(C=C)	A'	*A–B*
		1556vw		1203 + 342 = 1545	A'	*A–B*
1535 1530 s	*A–B*	1517s		906 + 614 = 1520 2 × 765 = 1530	A' A'	*A–B* *A–B*
		1511vw		765 + 742 = 1507	A''	*C*
1405w	*A–B*	1403vw		1203 + 192 = 1395	A'	*A–B*
1346w	*A–B*	1344vw		1203 + 140 = 1343 906 + 445 = 1351	A'' A''	*C* *C*
		1328vw		1570 – 245 = 1325	A'	*A–B*
		1267vw		742 + 342 + 192 = 1276	A'	*A–B*
1235 1225 s	*A–B*	1223s		2 × 614 = 1228	A'	*A–B*
1217 1214 s 1208	*A*	1203ms	1209ms	b(CHBr)	A'	*A–B*
1154ms	—			906 + 245 = 1151	A'	*A–B*
1104ms	*A–B*			765 + 342 = 1107	A''	*C*
		1082vw		742 + 342 = 1084	A'	*A–B*
		1058vw		614 + 445 = 1059	A''	*C*
		1008vw		765 + 245 = 1010	A''	*C*
		995w		742 + 245 = 987	A'	*A–B*
		954w, sh		614 + 342 = 956 765 + 192 = 957	A' A''	*A–B* *C*
925 916 vs	*B*	906vs	913w	$\nu_a(CCl_2)$	A'	*A–B*
		872w, sh		742 + 140 = 882 614 + 245 = 859	A'' A'	*C* *A–B*
854 850 ms 846	*A*	838w		445 + 245 + 140 = 830	A'	*A–B*
774 770 s 766	*C*	765vs		w(CHBr)	A''	*C*

TABLE 2 (*Continued*)

Gas (i.r.)	Type	Liquid (i.r.)	Liquid (Raman)	Assignment	Species	Type
752vs	*A–B*	742vs		ν_s(CHBr)	*A′*	*A–B*
		706w		906 − 192 = 714	*A′*	*A–B*
		654vw		1570 − 906 = 664 906 − 245 = 661	*A′* *A′*	*A–B* *A–B*
624 620 s	*B*	614s	608ms	ν_s(CCl$_2$)	*A′*	*A–B*
454s	*C*?	445s		w(CCl$_2$)	*A″*	*C*
		421w, sh		765 − 342 = 423	*A″*	*C*
		398w		2 × 192 = 384 742 − 342 = 400	*A′* *A′*	*A–B* *A–B*
		342w	343ms	r(CHBr)	*A′*	*A–B*
		290w		2 × 140 = 280	*A′*	*A–B*
		345ms	241ms	r(CCl$_2$)	*A′*	*A–B*
			192w	b(CCl$_2$)	*A′*	*A–B*
			140w	Twisting mode	*A″*	*C*

TABLE 3

Infrared and Raman spectra (bands in cm.$^{-1}$) of bromotrichlorethylene

Gas (i.r.)	Type	Liquid (i.r.)	Solid (i.r.)	Liquid (Raman)	Assignment	Species	Type
		3605vw			2 × 1563 + 499 = 3625	*A′*	*A–B*
		2962vw	2959vw		1563 + 970 + 419 = 2952	*A″*	*C*
		2923vw, sh	2923vw		3 × 970 = 2910 1563 + 876 + 499 = 2938	 *A′*	 *A–B*
		2857vw			1563 + 970 + 316 = 2849 1563 + 876 + 419 = 2868	*A′* *A″*	*A–B* *C*
		2805vw			2 × 970 + 876 = 2816 1563 + 739 + 499 = 2801	*A′* *A′*	*A–B* *A–B*
2451vw	—	2439vw	2443vw		1563 + 876 = 2439	*A′*	*A–B*
1996vw	—				2 × 739 + 499 = 1977	*A′*	*A–B*
		1940vw	1937vw		2 × 970 = 1940	*A′*	*A–B*
		1876vw			1563 + 316 = 1879	*A″*	*A–B*
		1837w	1847vw		1563 + 278 = 1841	*A″*	*C*
		1747vw			2 × 876 = 1752	*A′*	*A–B*
		1708vw			970 + 739 = 1709 1563 + 148 = 1711	*A′* *A′*	*A–B* *A–B*
1572 1564 ms	*A–B*	1563ms	1564w	1566vs	ν(C=C)	*A′*	*A–B*
1406w	*A–B*				2 × 499 + 419 = 1417	*A″*	*C*
1295w	*A–B*	1292w	1292w		970 + 316 = 1286 876 + 419 = 1295	*A′* *A″*	*A–B* *C*
1193vw	*A–B*	1192vw	1190vw		970 + 213 = 1183 876 + 316 = 1192	*A′* *A′*	*A–B* *A–B*
1153vw	*A–B*	1148vw			876 + 268 = 1144 2 × 499 + 148 = 1146	*A′* *A′*	*A–B* *A–B*
		1127vw			970 + 148 = 1118	*A′*	*A–B*
1097w	*A–B*	1091w, sh	1092vw, sh		876 + 213 = 1089	*A′*	*A–B*
		1083vw, sh			1563 − 278 − 213 = 1072	*A″*	*C*
		1056w	1054w		739 + 316 = 1055	*A′*	*A–B*
1008w	*A–B*	1005w	1007w	1004vw	739 + 268 = 1007 2 × 499 = 998	*A′* *A′*	*A–B* *A–B*
981 974 ms	*B*	970s	970s	973vw	ν_a(CCl$_2$)	*A′*	*A–B*
			909w		*		
887 882 vs	*A–B*	876vs	878vs		ν_a(CClBr)	*A′*	*A–B*
			859w, sh		*		
			847w, sh		*		
		812w, sh			739 + 75 = 814 499 + 316 = 815	*A″* *A′*	*C* *A–B*
791 780 ms 776	*A–B*	777s	784s		499 + 278 = 777	*A″*	*C*
			763w		*		
743 vs 741	*A–B*	739vs	738vs	748w	ν_s(CClBr)	*A′*	*A–B*
			728w, sh		*		
		709w, sh	710vw		419 + 213 + 75 = 707	*A′*	*A–B*

TABLE 3 (*Continued*)

Gas (i.r)	Type	Liquid (i.r.)	Solid (i.r.)	Liquid (Raman)	Assignment	Species	Type
		679w	682vw		1563 − 876 = 687	*A'*	*A–B*
					419 + 268 = 687	*A'*	*A–B*
		600w			316 + 278 = 594	*A''*	*C*
		562w			419 + 148 = 567	*A''*	*C*
					2 × 278 = 556	*A'*	*A–B*
		499ms		504ms	$\nu_8(CCl_2)$	*A'*	*A–B*
		464vw			316 + 148 = 464	*A'*	*A–B*
		419w		417vs	w(CCl_2)	*A''*	*C*
				358w	499 − 148 = 351	*A'*	*A–B*
		316w		319s	r(CCl_2)	*A'*	*A–B*
		278vs			r(CClBr)	*A''*	*C*
		268w		270s	r(CClBr)	*A'*	*A–B*
		213w		218vs	b(CCl_2)	*A'*	*A–B*
				148ms	b(CClBr)	*A'*	*A–B*
				75vw	tw mode	*A'*	*C*

* Lattice mode combination.

Instruments and Cells Used.—The infrared spectra were obtained using Grubb–Parsons G.S.2, G.S.2A, and D.M.2 grating spectrometers. Between them these three models cover the region between 5000 and 220 cm.$^{-1}$ and the frequencies reported are accurate to within 1—2 cm.$^{-1}$. The Raman spectrometer used was a Hilger and Watts model fitted with direct photoelectric recording equipment. The mercury arc source was filtered with sodium nitrite solution and the 4358-Å line was used for excitation.

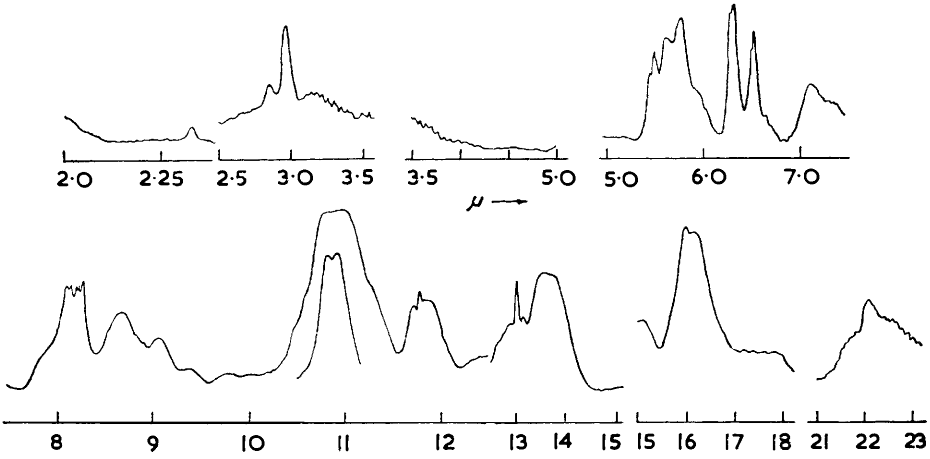

FIGURE 2(a). Infrared spectrum of 2-bromo-1,1-dichloroethylene vapour at 120°

Standard liquid and vapour absorption cells were used throughout, cæsium iodide or KRS-5 plates being used between 23 and 45 μ. Unfortunately the vapour cell used in the far-infrared region could not be heated and hence only the most volatile materials could be studied in the gas phase beyond 20 μ. The solid-state spectra were obtained using a liquid-air-cooled low-temperature cell. Up to three hours were required to cool the cell down to −100° and a similar period was employed when the cell was returned to room temperature.

The spectra obtained are shown in Figures 1—3, and the frequencies in Tables 1—3.

DESCRIPTION OF FUNDAMENTALS

All three molecules belong to the point groups C_s and therefore possess only one symmetry element, the plane of the molecule.[10] The twelve normal vibrations may therefore be divided up into two classes depending on whether they are symmetric, *A'*, or

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[10] G. Herzberg, " Infrared and Raman Spectra of Polyatomic Molecules " D. Van Nostrand Company, New York, 1945.

antisymmetric, A'', with respect to the plane of the molecule; $\Gamma = 9A' + 3A''$. The accompanying dipole-moment change is in-plane for type A' vibrations and perpendicular to it for type A'' vibrations.

All the vibrations are both Raman- and infrared-active and therefore all overtone and combinations of the fundamental modes are allowed in the infrared and Raman spectra. Vibrations of the class A'' should give rise to depolarised Raman lines while those arising from the class A' vibrations should be polarised.

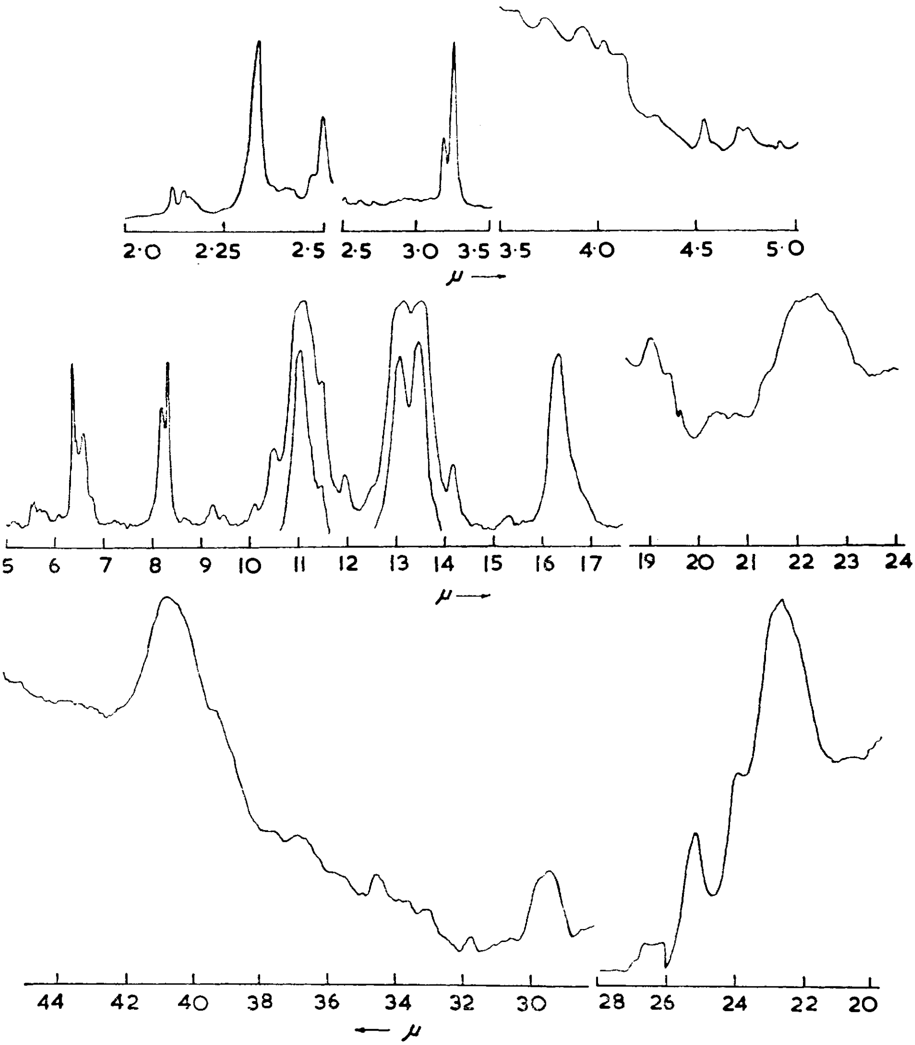

FIGURE 2(b). Infrared spectrum of 2-bromo-1,1-dichloroethylene liquid at 25°

The observed infrared band contours depend on the relative values of the principal moments of inertia I_A, I_B, and I_C (where $I_C > I_B > I_A$). The out-of-plane vibrations produce a dipole-moment change parallel to the axis, C, of greatest moment of inertia and should therefore give rise to infrared bands with C-type contours (ref. 10, p. 480). In the case of the A' vibrations, however, the dipole-moment change is in such a direction that it may be resolved into two components, one along each of the axes A and B. This results in the production of bands with A–B " hybrid " contours. If the moments of inertia are

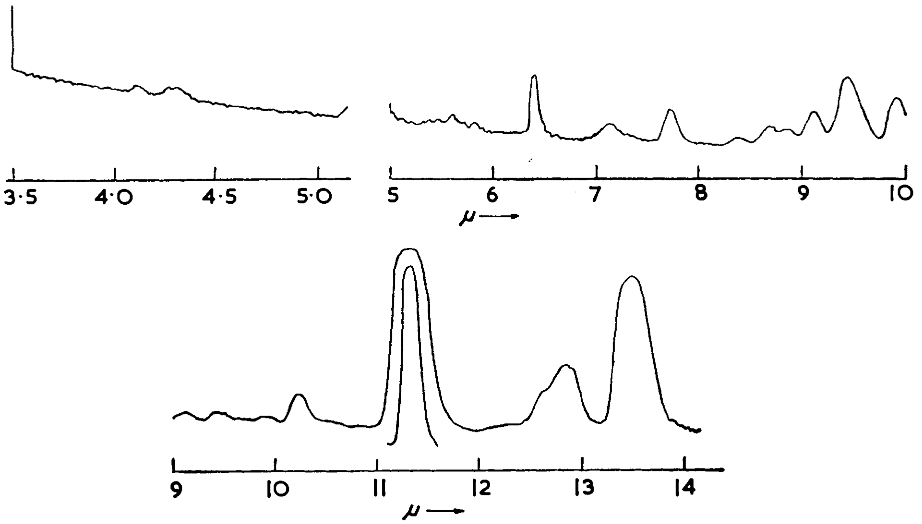

FIGURE 3(a). Infrared spectrum of bromotrichloroethylene vapour at 140°

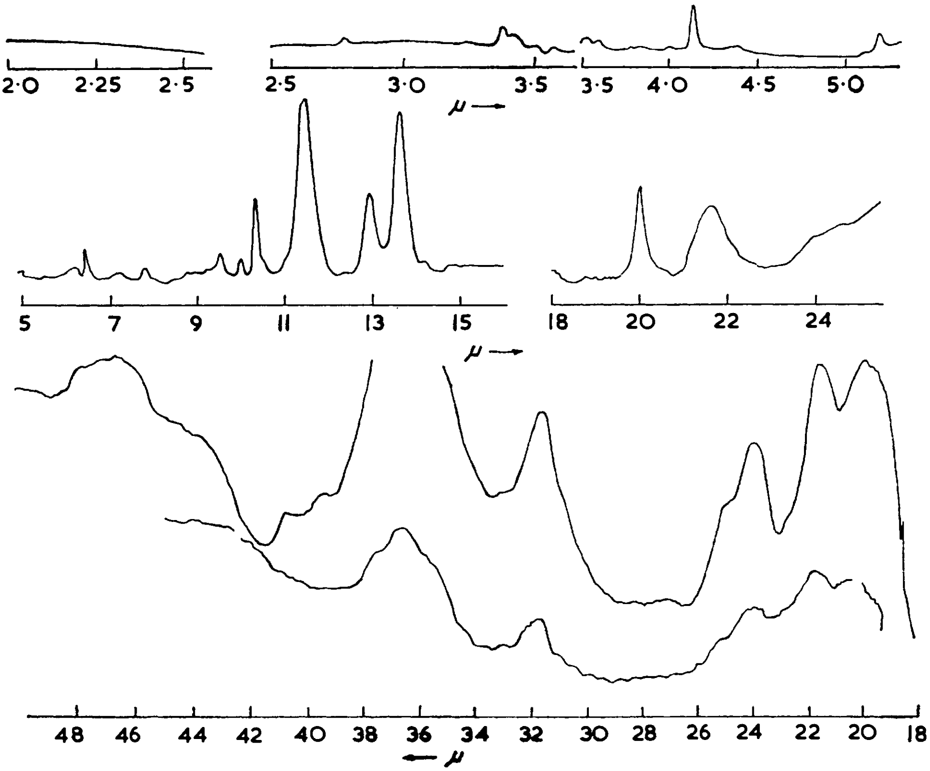

FIGURE 3(b). Infrared spectrum of bromotrichloroethylene liquid at 25°

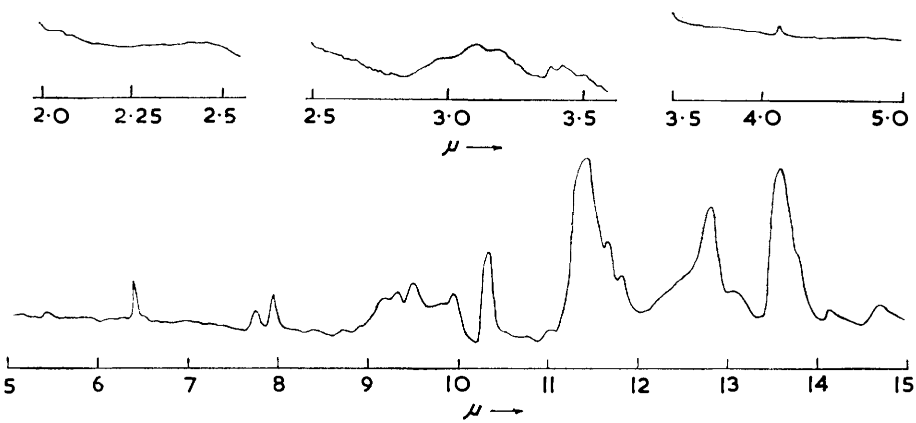

FIGURE 3(c). Infrared spectrum of bromotrichloroethylene solid at −100°

small enough for such rotational contours to be observed they will serve to distinguish class A'' vibrational bands from those arising from A' vibrations. Unfortunately, the molecular geometry has not been determined for these three molecules but, by assuming reasonable bond lengths and angles by comparison with related molecules of known structure, the moments of inertia were calculated[11] (Table 4). Also included are the parameters ρ and S of Badger and Zumwalt[12] and the predicted separation of the P and R branches of bands with C-type contours.

TABLE 4

Moments of inertia and P–R separations for C-type bands

Compound	Molecular geometry used	Ref.	Moments of inertia[a] I_A	I_B	I_C	S	ρ	$\Delta\nu$ (P, R) (cm.$^{-1}$)
$CHF{=}CCl_3$	r(C–H) = 1·084 Å r(C–F) = 1·337 Å r(C=C) = 1·326 Å r(C–Cl) = 1·691 Å $\mathrm{C\hat{C}Cl}$ = 126° $\mathrm{C\hat{C}H}$ = 122·5° $\mathrm{C\hat{C}F}$ = 123°	3	196·13	347·16	543·29	−0·35	1·12	14—16
$CHBr{=}CCl_2$	r(C–Cl) = 1·72 Å r(C–H) = 1·08 Å r(C–Br) = 1·91 Å r(C=C) = 1·36 Å $\mathrm{C\hat{C}Cl}$ = 121·5° $\mathrm{C\hat{C}H}$ = 120° $\mathrm{C\hat{C}Br}$ = 121°	13	213·08	914·92	1128·00	−0·89	3·48	10—12
$CClBr{=}CCl_2$	r(C–Cl) = 1·72 Å r(C–Br) = 1·91 Å r(C=C) = 1·36 Å $\mathrm{C\hat{C}Br}$ = 121° $\mathrm{C\hat{C}Cl}$ = 121·5°	13	549·56	915·91	1465·47	−0·28	1·05	8—10

[a] In units of 10^{-40} gm. cm.^{2}; m (Cl) = 35·457.

It can be seen that the moments of inertia calculated for $CHF{=}CCl_2$ are not in agreement with those published[13] although the same molecular dimensions have been used.

In order to describe each of the fundamental modes in these molecules it is convenient

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[11] J. O. Hirschfelder, *J. Chem. Phys.*, 1940, **8**, 431.

[12] R. M. Badger and L. R. Zumwalt, *J. Chem. Phys.*, 1938, **6**, 711.

[13] P. W. Allen and L. E. Sutton, *Acta Cryst.*, 1950, **3**, 46.

to classify them as having the general formula $CXY{=}CCl_2$. The vibrations may then be *approximately* described as those of the $=CXY$ or of the $=CCl_2$ group. Exactly how approximate this description is will depend on the nature of the individual vibrations involved and on the normal co-ordinates for each particular vibration since these describe accurately how well localised each vibration is within the group considered. In general, however, one may reasonably assume that the description will be a good one for the $=CXY$ group when X or Y = H and adequate when the stretching vibrations of groups are considered (including those of the $=CCl_2$ group). The description is probably somewhat inadequate when deformation vibrations of heavy groups are considered. Without actual normal co-ordinates it is impossible to tell which vibrations may be adequately described in this fashion and so the descriptions given here are to be regarded as qualitative only. The following symobls are used to give an approximate description of the fundamental vibrations,

	Class A'		Class A''
ν_a and $\nu_s(CCl_2)$	Symmetric and asymmetric stretch	$w(CCl_2)$, $w(CXY)$	Wagging
$\nu(CX)$, $\nu(CY)$, $\nu(CC)$	Stretch	$t(CCl_2)$ or $t(CXY)$	Twisting
$b(CCl_2)$, $b(CXY)$ ...	Bending		
$r(CCl_2)$, $r(CXY)$	Rocking		

Assignment of Observed Spectra

(i) *Out-of-plane Vibrations, Class* A″.—Since the bands which arise from these fundamental vibrations should have *C*-type contours of approximately known *P–R* separation (Table 4) they should be easily distinguished from bands arising from class A' vibrations. In $CHF{=}CCl_2$ and $CHBr{=}CCl_2$ the wagging ($=CXY$) vibrations involve a hydrogen atom and as such have high frequencies close to the $w(CH_2)$ frequency [14-16] at 869 cm.$^{-1}$ in $CH_2{=}CCl_2$.

In $CHCl'{=}CCl_2$ the $w(CHCl')$ mode has a frequency [16-19] of 783 cm.$^{-1}$ and thus the strong infrared, *C*-type bands at 798 and 770 cm.$^{-1}$ in $CHF{=}CCl_2$ and $CHBr{=}CCl_2$, respectively, may be assigned straightforwardly to the $w(CHX)$ modes. These bands have *P–R* separations of 16 and 8 cm.$^{-1}$, respectively, in good agreement with the predicted values. The $w(CCl_2)$ modes have, of course, much lower frequencies and it is fortunate that $CHF{=}CCl_2$ has small enough moments of inertia for the contour of an infrared band at 446 cm.$^{-1}$ to be easily distinguished as of the *C*-type. This band has a *P–R* separation of 14 cm.$^{-1}$ and fits in well with the corresponding vibrational bands [14-16] in $CH_2{=}CCl_2$ and $CHCl'{=}CCl_2$ which lie at 453 and 452 cm.$^{-1}$, respectively.[16-19] Confirmation of this assignment is afforded by the fact that the corresponding Raman line has been shown to be depolarised.[3] An infrared band at 454 cm.$^{-1}$ in $CHBr{=}CCl_2$ has a very prominent *Q* branch but unfortunately its *P* and *R* branches are ill-defined (see Figure 2). This band probably does belong to a vibration of the A'' class and is therefore assigned to the $w(CCl_2)$ mode in this molecule.

Because of its high boiling point and large moments of inertia $CClBr{=}CCl_2$ is not easy to study in the gas phase. Little help with the frequency assignment was therefore forthcoming from the band shapes since the structure was usually completely unresolved. The Raman spectrum of the liquid was, however, of considerable help in fixing the low frequencies of the deformation vibrations. A strong Raman line at 417 cm.$^{-1}$ (weak in the infrared spectrum) fits in as the $w(CCl_2)$ frequency especially in view of the fact that this vibrational frequency seems to change little in going from molecule to molecule (see Table 5). This assignment is supported by the assignment [1h] for C_2Cl_4 where the

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[14] H. W. Thompson and P. Torkington, *Proc. Roy. Soc.*, 1945, *A*, **184**, 21.
[15] P. Joyner and G. Glocker, *J. Chem. Phys.*, 1952, **20**, 302.
[16] J. Yarwood, Ph.D. Thesis, University of Wales, 1964.
[17] H. J. Bernstein, *Canad. J. Res.*, 1950, **28**, *B*, 132.
[18] G. Allen and H. J. Bernstein, *Canad. J. Chem.*, 1954, **32**, 1044.
[19] S. B. Sanyal, *Indian J. Phys.*, 1950, **24**, 151.

higher-frequency wagging mode is infrared-inactive. The w(CClBr) mode is expected to have a lower frequency than the w(CCl_2) mode by virtue of the higher mass of the bromine atom. Bands are observed in the infrared spectrum of the liquid at 268 and 278 cm.$^{-1}$. The former is very weak and corresponds to a very strong Raman line at 270 cm.$^{-1}$. The infrared band at 278 cm.$^{-1}$ is very intense. By analogy with C_2Cl_4 the w(CClBr) mode should be strongly active in the infrared and so this mode is assigned a frequency of 278 cm.$^{-1}$.

TABLE 5

Comparison of fundamental frequencies (in cm.$^{-1}$) in $CHX=CCl_2$ molecules

	$CHF=CCl_2$		$CHCl=CCl_2$		$CHBr=CCl_2$	
Approximate description	Gas	Liquid	Gas	Liquid	Gas	Liquid
ν(C–H)	3112	3104	3094	3086	3096	3094
ν(C=C)	1661	1649	1586	1582	1584	1570
b(CHX)	1295	1289	1250	1245	1214	1203
$\nu_a(CCl_2)$	974	958	940	930	921	906
$\nu_s(CCl_2)$	668	656	629	627	622	614
ν(CHX) or ν(C–X)	1152	1131	849	839	752	742
r(CHX)	—	470 [a]	—	396	—	342
r(CCl_2)	284	282	—	274	—	245
b(CCl_2)	204	211 [a]	—	172 [a]	—	192 [a]
w(CHX)	798	796	783	779	770	765
w(CCl_2)	446	450	452	443	454	445
tw mode	262	268	—	217 [a]	—	140 [a]

[a] Observed in Raman spectrum of liquid.

The twisting vibration [1h, 16-19] in substituted ethylenes such as C_2Cl_4 and $CHCl'=CCl_2$ has the lowest frequency of any fundamental and so the task of assigning a frequency to this mode, sometimes very difficult, is somewhat simplified. In $CHF=CCl_2$ a strong band at 262 cm.$^{-1}$ in the infrared clearly has a *C*-type contour (see Figure 1) and is assigned to the tw mode. The twisting mode in $CHCl=CCl_2$ has a frequency of 217 cm.$^{-1}$ (assigned on the basis of polarisation measurements) and it therefore follows that the twisting mode in $CHBr=CCl_2$ should be lower than this (since this frequency appears to decrease as the masses attached to the C=C bond are increased).[16-19] The line with lowest frequency in the Raman spectrum of this compound lies at 140 cm.$^{-1}$ and this line is therefore assigned to the twisting mode. In view of the weakness of this line, however, the assignment should be regarded as tentative. In $CClBr=CCl_2$ the large bulky atoms attached to the C=C skeleton make the expected twisting frequency about 100 cm.$^{-1}$ (the corresponding mode in C_2Cl_4 has a frequency [1h] of 110 cm.$^{-1}$). No Raman line was observed in this work near 100 cm.$^{-1}$ but a very weak one was observed at about 75 cm.$^{-1}$. In the absence of a suitable alternative this frequency is assigned to the twisting mode.

(ii) *Stretching Vibrations, Class A'*.—Each of the three molecules has a fundamental ν(C=C) vibration. This is expected to give rise to a band between 1550 and 1800 cm.$^{-1}$. The molecules $CHF=CCl_2$ and $CHBr=CCl_2$ show a very strong infrared and Raman band within this region and the bands have a "mixed" or "hybrid" *A–B* contour. The frequencies (gas phase) of these bands are 1661 and 1584 cm.$^{-1}$, respectively, for $CHF=CCl_2$ and $CHBr=CCl_2$. In trichloroethylene [16-19] this mode produces a band at about 1590 cm.$^{-1}$ and therefore these two bands fit into the pattern for $CHX=CCl_2$ molecules. In $CClBr=CCl_2$ a weaker band is observed in the gas phase at 1568 cm.$^{-1}$ and in the liquid phase at 1563 cm.$^{-1}$. In C_2Cl_4 the corresponding mode [1h] gives rise to a band at 1570 cm.$^{-1}$. Since this mode is infrared-inactive in C_2Cl_4 the corresponding band in $CClBr=CCl_2$ would be expected to be a good deal weaker than in $CHX=CCl_2$ type molecules.

By comparison with $CH_2=CCl_2$,[14-16] $CHCl'=CCl_2$,[16-19] and C_2Cl_4[1h], the $\nu_a(CCl_2)$ and $\nu_s(CCl_2)$ modes in the molecules $CXY=CCl_2$ would be expected to have frequencies lying between 600 and 1000 cm.$^{-1}$. In $CH_2=CCl_2$, where the band contours are easily distinguished and identified, it has been shown that the $\nu_a(CCl_2)$ mode has the higher frequency. Thus, in $CHCl'=CCl_2$ the $\nu_a(CCl_2)$ and $\nu_s(CCl_2)$ modes have been assigned frequencies of 940 and 629 cm.$^{-1}$, respectively. The corresponding modes in $CHF=CCl_2$ and $CHBr=CCl_2$ are expected to have similar frequencies and the strong infrared bands observed at 974 and 921 cm.$^{-1}$ are assigned to the $\nu_a(CCl_2)$ mode. Both bands are weak in the Raman spectrum, as is that at 940 cm.$^{-1}$ in the Raman spectrum of $CHCl'=CCl_2$. Raman lines at 665 and 622 cm.$^{-1}$ in the spectra of $CHF=CCl_2$ and $CHBr=CCl_2$, respectively, are assigned to the $\nu_s(CCl_2)$ modes. In the infrared spectrum of $CClBr=CCl_2$ a very strong band observed at 978 cm.$^{-1}$ is assigned to the $\nu_a(CCl_2)$ mode. No bands are observed in this compound in the 600—700-cm.$^{-1}$ region but a weak infrared line is produced in the liquid phase at 499 cm.$^{-1}$. This corresponds to a Raman line at 504 cm.$^{-1}$, whereas only an extremely weak Raman line is observed corresponding to the strong infrared band at 978 cm.$^{-1}$. Again this fits in with the data [1h] for C_2Cl_4 where the lowest-frequency CCl_2 stretching mode is Raman-active (at 447 cm.$^{-1}$) while a band assigned to one of the $\nu_a(CCl_2)$ modes, at 908 cm.$^{-1}$, is infrared-active.

It is highly probable that one of the $\nu(CXY)$ modes in the $CHX=CCl_2$ molecules, *viz.*, $\nu(CH)$, is well localised with the C–H bond. This mode is expected to have the normal frequency at about 3100 cm.$^{-1}$. Strong infrared and Raman bands found at 3096 and 3112 cm.$^{-1}$ in $CHBr=CCl_2$ and $CHF=CCl_2$, respectively, are therefore assigned to the $\nu(C–H)$ mode. The other $\nu(CXY)$ mode, described as the $\nu_a(CHX)$ or $\nu(CX)$ mode in these molecules, should have a frequency corresponding approximately to a C–X stretching frequency. In $CH_2=CFCl$ the $\nu(C–F)$ frequency [2k,16] is 1185 cm.$^{-1}$ while in $CF_2=CCl_2$ the $\nu_a(CF_2)$ and $\nu_s(CF_2)$ modes have frequencies of 1325 and 1032 cm.$^{-1}$, respectively.[1d,2b,16,20] A very strong band at 1152 cm.$^{-1}$ with an approximately *A*-type contour in $CHF=CCl_2$ may thus be assigned to the $\nu_a(CHF)$ mode. Few C–Br frequencies have been reported for substituted ethylenes, although examination of the assignments for $CClBr=CF_2$ and $CFBr=CCl_2$ show that the vibrations [1e,2i] which correspond most closely to a C–Br stretching mode have frequencies of 803 and 589 cm.$^{-1}$. A strong band at 752 cm.$^{-1}$ in $CHBr=CCl_2$ is therefore assigned to the $\nu_a(CHBr)$ mode.

The ν_s and $\nu_a(CClBr)$ modes in $CClB4=CCl_2$ are, of course, considerably less localised than in the compounds where a hydrogen atom is involved. In $CClBr=CF_2$ these vibrations have been allotted frequencies [2i] of 908 and 589 cm.$^{-1}$, and the only fundamental bands which lie within this region in $CClBr=CCl_2$ are the strong infrared bands at 885 and 742 cm.$^{-1}$ which are therefore assigned to the ν_a and $\nu_s(CClBr)$ modes, respectively.

(iii) *In-plane Deformation Vibrations, Class* A'.—The remaining four *A'* class vibrations involve the bending (scissors motion) and rocking motions of the $=CXY$ and $=CCl_2$ groups. In $CHF=CCl_2$ and $CHBr=CCl_2$ the b(CHX) mode is expected to have roughly the character of a normal C–H bending vibration. In $CH_2=CCl_2$ this bending motion [14–16] gives rise to a band at 1391 cm.$^{-1}$ while in $CHCl'=CCl_2$ the corresponding b(CHCl′) vibrational band [16–19] lies at 1250 cm.$^{-1}$. Strong infrared bands at 1295 and 1214 cm.$^{-1}$ in $CHF=CCl_2$ and $CHBr=CCl_2$, respectively, may therefore safely be assigned to these modes. The r(CHX) vibrations in these molecules are likely to have the highest frequencies of the remaining deformation modes since they involve movement of a hydrogen atom. In $CHCl'=CCl_2$ a Raman line at 383 cm.$^{-1}$ has been assigned to the in-plane C–Cl deformation mode [17–19] and this band (observed in the liquid-phase infrared spectrum at 395 cm.$^{-1}$) has been assigned [16] to the r(CHCl′) vibration on the basis mentioned above. The r(CHX) modes in $CHF=CCl_2$ and $CHBr=CCl_2$ are therefore expected to have frequencies which lie close to this value. The Raman spectra of liquid $CHF=CCl_2$ and $CHBr=CCl_2$ show lines at 470 and 343 cm.$^{-1}$, respectively, and these are assigned to the r(CHX) modes.

It now remains to assign frequencies to the in-plane deformation modes of the $=CCl_2$ and $=CClBr$ groups. In each of the three compounds studied the fundamental bands observed and not, so far, assigned to specific modes are $CHF=CCl_2$, 284 and 204 cm.$^{-1}$; $CHBr=CCl_2$, 241 and 192 cm.$^{-1}$; $CClBr=CCl_2$, 319, 270, 218, and 148 cm.$^{-1}$ (see Tables 1—3).

From the work on $CH_2=CCl_2$ where all the fundamental bands may be distinguished by

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[20] P. Torkington and H. W. Thompson, *Trans. Faraday Soc.*, 1945, **41**, 236.

their *PQR* structures [14-16,21] it has been shown that the order of the deformation frequencies of the $=CCl_2$ group are w > r > b. There seems no reason why this order should change on going to halogenated molecules of the type $CXY=CCl_2$ and, in fact, the wagging (CCl_2) vibrations in all three molecules studied agree very well with that found in $CH_2=CCl_2$. Furthermore, if one examines the frequency assignments for $CH_2=CCl_2$ and $CHCl'=CCl_2$ it is clear that the deformation modes of the $=CCl_2$ group lie in well-defined regions. These are as follows: w(CCl_2), 440—470 cm.$^{-1}$; r(CCl_2), 240—320 cm.$^{-1}$; b(CCl_2), 170—220 cm.$^{-1}$. With this basis it is therefore relatively easy to assign the bands at 284, 241, and 319 cm.$^{-1}$ in $CHF=CCl_2$, $CHBr=CCl_2$, and $CClBr=CCl_2$, respectively, to the r(CCl_2) mode and the bands at 204, 192, and 218, respectively, to the b(CCl_2) mode. The deformation modes of the $=CClBr$ group are expected to have lower frequencies than those of the $=CCl_2$ group because of the greater mass involved. Assuming that the order of the $=CClBr$ vibrational frequencies is the same as that of the $=CCl_2$ group the lines at 270 and 148 cm.$^{-1}$ may therefore be assigned to the r(CClBr) and b(CClBr) modes, respectively.

The complete frequency assignments for the three molecules studied are given in Tables 1—3, and fundamentals are summarised in Table 5.

DISCUSSION

From Tables 1—3 it can be seen that a reasonable interpretation of the vast majority of the observed bands has been found using the fundamental frequency assignments given in Table 5. In the infrared spectrum of $CHBr=CCl_2$ a rather prominent vapour-phase band, whose intensity increased with temperature, was observed at 1832 cm.$^{-1}$. This may be attributed to the $\nu(C=O)$ mode in the carbonyl halide impurities (probably $COCl_2$ and $COBr_2$) formed by thermal decomposition of $CHBr=CCl_2$. The C=O stretching frequency in these compounds has been reported [22] as 1828 cm.$^{-1}$.

The solid-state spectra of both $CHF=CCl_2$ and $CClBr=CCl_2$ are reported here in addition to the gas- and liquid-phase data. Both molecules show in their solid-state spectra evidence of " lattice " vibrations which combine with internal fundamental modes to give " lattice mode " combination bands.[5] Since the lattice vibrations [5] typically have frequencies less than 50 cm.$^{-1}$ this results in the observation of sharp side-bands accompanying the fundamental vibrational bands. Thus, the fundamental band at 1288 cm.$^{-1}$ in $CHF=CCl_2$ is accompanied in the solid phase by bands at 1314 and 1264 cm.$^{-1}$ (Figure 1). This particular lattice mode therefore has a frequency of 24 cm.$^{-1}$ and both the sum and difference bands have been observed. In $CClBr=CCl_2$ the fundamental band at 878 cm.$^{-1}$ is accompanied by combination bands at 909 and 847 cm.$^{-1}$ indicating a lattice mode of frequency 31 cm.$^{-1}$. Lattice-mode combination bands are also observed at 859, 763, and 728 cm.$^{-1}$ for the latter molecule, corresponding to lattice modes with frequencies of 19, 21, and 10 cm.$^{-1}$, respectively. Although in $CHCl'=CCl_2$ two examples of " correlation field " splitting [5] were observed in the solid state,[16] no evidence of such splitting was found in either $CHF=CCl_2$ or $CClBr=CCl_2$. Neither was there any evidence of the existence of more than one allotropic modification of these molecules within the temperature range −100° to −150°. $(CHF=CCl_2)$ or −50° to −100° $(CClBr=CCl_2)$. Owing to rapid decomposition, the quantity of $CHBr=CCl_2$ available was insufficient for its solid-state spectrum to be observed.

The spectra of $CHF=CCl_2$ reported here are more complete than those published previously [3] and it is believed that the frequency assignment is more in line with the assignments published for other halogenated ethylenes. The band at 966 cm.$^{-1}$, for example, seems too high to belong to a b(CCF) mode, while the band at 1291 cm.$^{-1}$ almost certainly belongs to the b(CHF) mode in the light of the results for $CHCl=CCl_2$ and $CHBr=CCl_2$. Muelleman *et al.*[3] assigned the Raman line at 284 cm.$^{-1}$ to the class A''

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[21] J. C. Evans, *J. Chem. Phys.*, 1959, **30**, 934.

[22] J. Overend and J. R. Sherer, *J. Chem. Phys.*, 1960, **32**, 1296.

fundamental twisting mode, but could only measure the polarisation ratio of the unresolved doublet formed by the lines at 278 and 284 cm.$^{-1}$. The gas-phase infrared spectrum, previously unreported, shows conclusively that, in fact, the band at 262 cm.$^{-1}$ (corresponding to the Raman line at 274 cm.$^{-1}$ in this work) really belongs to the class A'' fundamental (see Figure 1).

A good deal of interesting information regarding the normal vibrations of the $CHX{=}CCl_2$ molecules may be obtained by comparing the frequencies of the various modes in the three molecules. Table 5 and Figure 4 are included to make regular or irregular trends more apparent. Since the method of describing the fundamental modes of the $CHX{=}CCl_2$ differs from that published [17] for $CHCl'{=}CCl_2$ the data for this molecule are also included. The most interesting trend in going from $CHF{=}CCl_2$ to $CHBr{=}CCl_2$ is found in the frequencies of the $=CHX$ group.* In the bending, rocking, and wagging modes of this group there is a systematic fall in frequency as one goes from $CHF{=}CCl_2$ to $CHBr{=}CCl_2$. This is a clear indication that each of these normal modes involves the halogen atom to a considerable extent and cannot therefore be described accurately as b(CH) or r(C–H), etc. As the halogen atom gets heavier the frequency drops, as would be expected. It can be seen from Table 5 that the ν_s(CHX) frequency drops considerably in going from $CHF{=}CCl_2$ to $CHBr{=}CCl_2$. This would be expected since this mode may be quite accurately described as ν(C–X) (see Table 5) and therefore represents the stretching of a C–F, C–Cl, or C–Br bond. These have differing lengths and bond strengths and therefore very differing frequencies.

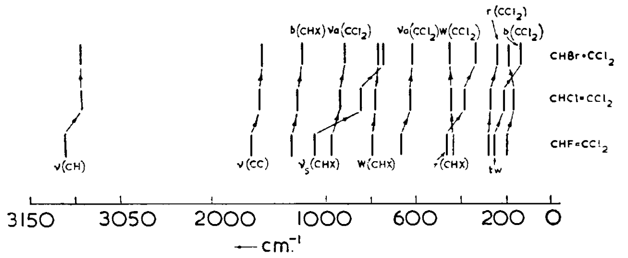

FIGURE 4. Variation of vibrational frequencies in the series $CHX{=}CCl_2$

The ν(C–H) mode mainly involves stretching of the C–H bond; it is expected to be relatively isolated and the changes which occur in this frequency should give a sensitive indication of how the bond character and bond strength of the C–H bond change in going from one molecule to another.

Using Kagarise's suggestion,[23] Jones *et al.*[24] have written the effective electronegativity of a =CXY group as:

$$\chi_{\text{eff}}\,(CXY) = \chi(C)/2 + [\chi(X) + \chi(Y)]/4$$

Using this relationship and the electronegativities of the atoms quoted by Gordy and Orville-Thomas [25] a plot was made of ν(C–H) in $CHX{=}CCl_2$ against $\chi_{\text{eff}}(=CHX)$. Figure 5 shows that such a plot is linear. It can be seen, however, that the ν(C–H) frequencies in $CHCl{=}CCl_2$ and $CHBr{=}CCl_2$ do not lie on the best straight line although they are within 2—3 cm.$^{-1}$ of it, *i.e.*, almost within experimental error. From the plot the ν(C–H) frequency in $CHI{=}CCl_2$ can be deduced. A value of 3089 cm.$^{-1}$ is obtained. The experimental data are not available for this molecule and so this prediction cannot be checked at the moment.

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* The r(CHX) and w(CHX) modes really involve the C=CHX group, otherwise they become rotations.

[23] R. E. Kagarise, *J. Amer. Chem. Soc.*, 1955, **77**, 1377.

[24] R. G. Jones, J. A. Ladd, and W. J. Orville-Thomas, *Spectrochim. Acta*, 1964, **20**, 1697.

[25] W. Gordy and W. J. Orville-Thomas, *J. Chem. Phys.*, 1956, **24**, 439.

The order of the deformation frequencies of the =CHX group is found to be the same for all three molecules and is b > w > r. This is different from the order of the corresponding frequencies of the $=CCl_2$ group which is w > r > b, and which is confirmed to a large extent by the assignments chosen for the $CHX=CCl_2$ molecules.

One might expect that the various modes which mainly involve vibrations of the $=CCl_2$ group might remain sensibly constant for the three related molecules. Table 5 shows that only the $w(CCl_2)$ frequencies do not change appreciably. The variation in the b and $r(CCl_2)$ frequencies is less than that for the =CHX group vibrations. The $w(CCl_2)$ mode is an out-of-plane mode which involves the wagging of the $=CCl_2$ group against the double bond. The constancy of the frequency associated with this mode is a good indication that it is well-localised. In general, however, the other deformation frequencies of the $C=CCl_2$ group are sensitive to changes in their molecular environment and this is a good indication that the vibrations are not entirely localised within the $=CCl_2$ group.

The Effect of Fluorine Substitution on the C=C *Bond Length and Bond Strength in Halogenated Ethylenes*.—It has been previously pointed out [26] that when ethylene hydrogen atoms are replaced by chlorine and/or bromine atoms there is a decrease in the ν(C=C) vibrational frequency but that when the molecule contains one or more fluorine atoms a sharp increase in the ν(C=C) frequency is observed. This is quite a general effect, as is amply demonstrated by the data given in Table 6, and has been attributed by Bellamy [26] to a shortening of the C=C bond length in fluorinated ethylenes. Such shortening has been demonstrated [27,28] but since ethylene itself has the longest measured bond length of the C_2X_4 molecules it follows from this argument that both C_2Cl_4 and C_2F_4 should have ν(C=C) frequencies higher than its value (1623 cm.$^{-1}$) in ethylene. Other effects must therefore be involved in determining the ν(C=C) frequency. Since the ν(C=C) vibration is unlikely to be localised within the C=C bond in such molecules it follows that the vibrational frequency changes from one molecule to another will depend to a considerable extent on how the normal co-ordinates for the ν(C=C) vibration differ from molecule to molecule. It has been suggested by Bauman [29] that in these molecules the influences of mechanical coupling and electrical perturbations are in competition. Considering the molecules to be " diatomic " joined by a double bond the ν(C=C) frequency should decrease as the masses attached to it increase and therefore this frequency should decrease in the order

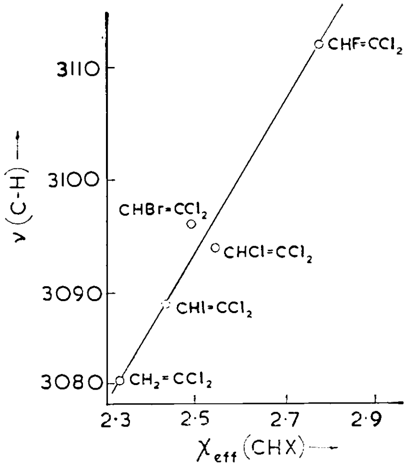

FIGURE 5. Plot of χ_{eff}(CHX) against ν(CH)

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[26] L. J. Bellamy, " The Infra-red Spectra of Complex Molecules," 2nd edn., Methuen and Co. Ltd., London, 1954.

[27] S. Castellano and J. S. Waugh, *J. Chem. Phys.*, 1961, **34**, 295.

[28] V. W. Laurie, *J. Chem. Phys.*, 1961, **34**, 291.

[29] R. P. Baumann, " Absorption Spectroscopy," J. Wiley and Sons Inc., London, 1962.

TABLE 6

Summary of bond lengths, angles, and ν(C=C) frequencies in halogenated ethylenes

Compound	ν(C=C) (cm.$^{-1}$)	r(C=C) (Å)	$\widehat{ClCCl}$	$\widehat{FCF}$	$\widehat{HCH}$	Method used to determine geometry
C_2F_4	1872	1·313	—	110°	—	Electron diffraction
CF_2=CCl_2 ...	1739	—	—	—	—	—
CH_2=CF_2	1728	1·315	—	109° 6′	121° 48′	Microwave spectroscopy
CHF=CCl_2 ...	1661	—	—	—	—	—
CFCl=CCl_2 ...	1650	—	—	—	—	—
CH_2=CHF ...	1650	1·337	—	—	—	Electron difraction
C_2H_4	1623	1·337	—	—	117° 22′	I.r. spectroscopy
C_2D_4............	1515	1·337	—	—	117° 22′	,,
CH_2=CCl_2 ...	1621	1·324	114° 30′		120° [a]	Electron diffraction
CH_2=CHCl ...	1608	1·38			122°	,,
CHCl=CCl_2 ...	1586	1·36	117°	—	—	,,
CHBr=CCl_2 ...	1584	—	—	—	—	—
CClBr=CCl_2 ...	1568	—	—	—	—	—
C_2Cl_4	1571	1·327	113°	—	—	Electron diffraction

[a] Assumed value.

H,D,F,Cl,Br, and I. Electrical interactions involving electron withdrawal from the C=C bond should result in an increase in this frequency and the effect should increase with increasing electronegativity of the halogen. This should give ν(C=C) frequencies increasing in the order H,I,Br,Cl, and F. The relative magnitude of these two effects therefore determines the value of the ν(C=C) frequency. What this, in fact, means is that if one takes the series CXY=CCl_2 and gradually increases the electronegativity of the CXY group then the frequency should first decrease in accordance with the mass factor (since when X or Y = Cl or Br the mass of the CXY group is increased) and then increase again (since if X or Y = F the electrical factor is likely to predominate). On plotting ν(C=C) against χ_{eff}(CXY) the result is as shown in Figure 6. This curve supports Bauman's theory that both electrical and mechanical influences affect the (C=C) frequency. The C=C bond shortening which occurs in the series, C_2H_4,C_2Cl_4,C_2F_4 can be accounted for at least qualitatively by the decrease in the XCX angle as one goes from C_2H_4 to C_2F_4 in the series. This means

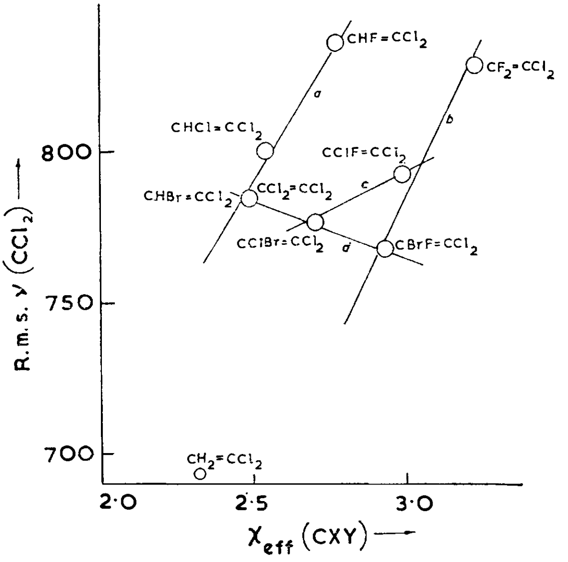

FIGURE 6. Plot of χ_{eff}(CXY) against root-mean-square ν(CCl_2)

that the C–C σ-bond has a greater percentage *S* character when a $=CF_2$ group is present and therefore that the resulting C=C bond is shorter. Whether or not this is true in other halogenated ethylenes is not certain since accurate determinations of the bond angles have not been made. There is a very good indication however, that this is not the only variable which determines the ν(C=C) frequency in these molecules.

Carbon–Halogen Vibrations in Halogenated Ethylenes.—A large number of molecules, including the ones reported here, contain a $=CCl_2$ group which is attached to a variable =CXY group. It should be possible to investigate the nature of the bonding in the $=CCl_2$ group by considering the effect on it of varying the =CXY groups.

The $=CCl_2$ group has two stretching vibrations. These two modes are almost certainly not completely localised within the CCl_2 group, but it can be seen from Table 7 that they give rise to bands at similar frequencies no matter what group =CXY is attached to the other end of the molecules. Nevertheless, there are changes in these frequencies and this means that the bonding in the $=CCl_2$ group is affected to some extent by changes in the atoms X and Y. The root-mean-square value of the $\nu_a(CX_2)$ and $\nu_s(CX_2)$ frequencies was plotted against χ_{eff}(CXY) (Figure 6). The resulting graph immediately shows four linear relationships corresponding to the series (*a*) $CHX=CCl_2$ where X = F, Cl, or Br; (*b*) $CFX=CCl_2$ where X = F, Cl, or Br; (*c*) $CClX=CCl_2$ where X = F, Cl, or Br; and (*d*) $CBrX=CCl_2$ where X = H, Cl, or F. It should be noticed, however, that the $CH_2=CCl_2$ molecule does not fit well on any of these lines. It is also interesting to note that the r.m.s. $\nu(CCl_2)$ frequency is, in three cases out of four, highest when the =CXY group contains a fluorine atom. Thus the two highest $\nu(CCl_2)$ frequencies belong to $CHF=CCl_2$ and $CF_2=CCl_2$. This means that the C–Cl bonds are in general strengthened by the presence of fluorine atoms, even attached to opposite ends of the molecule. The same effect can be seen by considering the ν_s(CXY) frequencies for $CClBr=CCl_2$, $CHBr=CCl_2$, and $CBrF=CCl_2$. This vibration involves mainly the stretching of the C–Br bond and the frequencies are 742, 752, and 803 cm.$^{-1}$, respectively. The C–Br bond is therefore also strengthened by the presence of the fluorine atom, the very strong inductive effect of which is well known. The electron-withdrawing power of this highly electronegative atom may be felt across the C=C double bond having the effect of drawing the C–Cl bonding electrons towards the double bond by induction. This results in stronger and possibly shorter C–Cl bonds with a higher average stretching frequency.

TABLE 7

Summary of frequencies (in cm.$^{-1}$) of $=CCl_2$ group variations in halogenated ethlenes

Compound	Ref.	χ_{eff} (CXY)	$\nu_a(CCl_2)$	$\nu_s(CCl_2)$	R.m.s. $\nu(CCl_2)$	$w(CCl_2)$	$r(CCl_2)$	$b(CCl_2)$
C_2Cl_4	1*h*	2·75	1000	777	895	512	347	310
			908	447	783	288	176	235
$CH_2=CCl_2$ ...	This work	2·33	793	600	693	453	370	297
$CF_2=CCl_2$ ...	,,	3·23	994	619	828	475	248	192
$CHF=CCl_2$ ...	,,	2·77	974	668	835	446	284	204
$CHCl=CCl_2$...	,,	2·54	940	629	800	452	274	172
$CHBr=CCl_2$	,,	2·49	921	622	785	454	245	192
$CClF=CCl_2$...	,,	2·99	990	522	792	403	316	177
$CClBr=CCl_2$	,,	2·70	978	499	776	419	316	213
$CBrF=CCl_2$...	1*e*	2·94	965	496	767			

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