Vibrational Spectra of Some Trichloromethyl- and Trifluoromethyl-mercury(II) Compounds

By **Peter L. Goggin,* Robin J. Goodfellow, Katerina Kessler,** and **Aileen M. Prescott,** Department of Inorganic Chemistry, The University, Bristol BS8 1TS

Complete assignments of vibrational fundamentals of [Hg(CF$_3$)X] (X = Cl, Br, I, or CF$_3$) and [Hg(CCl$_3$)X] (X = Cl, Br, or CCl$_3$) are presented on the basis of i.r. and Raman spectra of solutions, in which the molecules appear to be monomeric. The spectra of the solids, including Raman measurements at 100 K, are also discussed in relation to crystal structures where known. The intensity of the Hg–CF$_3$ stretching mode, relative to other CF$_3$ modes, shows marked dependence on the *trans* halide in [Hg(CF$_3$)X].

TRICHLORO- and trifluoro-methyl compounds of mercury(II) have long been known.[1,2] However, there is conflicting evidence as to whether [Hg(CY$_3$)$_2$] or [Hg(CY$_3$)X] (Y = F or Cl; X = Cl, Br, or I) form complex anions with additional halide.[3,4] Vibrational spectra were of particular significance in our investigation [5] of the formation of anions from [HgMeX] but it is essential to have a thorough understanding of the spectra of the parent compounds. Previously, only for [Hg(CF$_3$)$_2$] have the vibrational spectra been fully considered [4] although there are assignments for the HgX stretching wavenumbers of [Hg(CF$_3$)X] and [Hg(CCl$_3$)X] (X = Cl or Br) and for the Hg–CF$_3$ vibration in [Hg(CF$_3$)X] (X = Cl, Br, or I).[6]

In this paper we report and discuss the i.r. and Raman spectra of [Hg(CCl$_3$)X] (X = Cl, Br, or CCl$_3$) and [Hg(CF$_3$)X] (X = Cl, Br, I, or CF$_3$) measured in solution and as solids.

RESULTS

Spectra in Solution.—The results for the compounds [Hg(CY$_3$)X] are given in Table 1. We assume that in the

---

[1] A. N. Nesmeyanov, R. Kh. Friedlina, and F. K. Velichko, *Doklady Akad. Nauk. S.S.S.R.*, 1957, **114**, 557.

[2] A. A. Banks, H. J. Emeleus, R. N. Haszeldine, and J. Kerrigan, *J. Chem. Soc.*, 1948, 2188.

[3] H. J. Emeleus and J. J. Lagowski, *J. Chem. Soc.*, 1959, 1497.

[4] A. J. Downs, *J. Chem. Soc.*, 1963, 5273.

[5] P. L. Goggin, R. J. Goodfellow, and N. W. Hurst, *J.C.S. Dalton*, 1978, in the press.

[6] G. E. Coates and D. Ridley, *J. Chem. Soc.*, 1964, 166.

solvents used these complexes will be of C_{3v} symmetry with eight vibrational fundamentals, $4A_1 + 4E$, all i.r. and Raman active.

Since the CF$_3$ stretching and deformation wavenumbers in CF$_3$X (X = Cl, Br, or I) [7,8] are relatively insensitive to X, they should provide a good guide for these assignments in [Hg(CF$_3$)X]. There are two very intense i.r. bands near 1 100 cm^{-1} (CF$_3$ stretching) but we only clearly see the higher in our Raman spectra; this band is found to be polarised, albeit slightly, identifying it as the A_1 mode. We note that the lower-wavenumber i.r. feature is more than twice as wide as the upper. Thus, the wavenumber order of these two modes is reversed relative to CF$_3$X, but similar to that proposed for some trifluoromethyl transition-metal compounds.[9] The CF$_3$ deformation modes are unambiguously assigned from the Raman spectra at positions *ca.* 20 cm^{-1} lower than their counterparts in CF$_3$I.[8]

TABLE 1

Solution i.r. and Raman spectra of [Hg(CF$_3$)X] (X = Cl, Br, or I) below 1 200 cm^{-1} and [Hg(CCl$_3$)X] (X = Cl or Br) below 800 cm^{-1}

Assignment	[Hg(CF$_3$)Cl]		[HgBr(CF$_3$)]		[Hg(CF$_3$)I]		[Hg(CCl$_3$)Cl] [a]		[HgBr(CCl$_3$)] [b]	
A_1	I.r.	Raman [c,d]	I.r.	Raman	I.r.	Raman	I.r.	Raman	I.r. [e]	Raman [e]
ν_1 CY$_3$ sym. str.	1 130vvs [f]	1 128w (0.65)	1 125vvs [f]	1 128wm (0.45) [g]	1 121vvs [f]	1 121m (0.2) [g]	780wm [e]	781wm (0.55) [e]	771w	775wm (0.45)
ν_2 CY$_3$ sym. def.	722s [c]	723wm (0.1)	720s [c]	724wm (*ca.* 0) [g]	717s [c]	717m (*ca.* 0) [g]	397m [f]	396s (0.0) [f]	391w	391s (0.0)
ν_3 HgX str.	353vs [c]	357m (0.15)	216w [c]	216vs (0.25) [g]	176w [h]	175vs (0.2) [g]	356s [f]	350vs (0.15)	244s	244s (0.15)
	345(sh) [c]	348(sh)								
ν_4 Hg–CY$_3$ str.	250m [c]	250s (0.25)	277s [c]	277vw (*ca.* 0) [c]	255vs [h]	256wm (0.2) [c]	177w [g]	177vs (0.25) [f]		166vs (0.25)
E										
ν_5 CY$_3$ asym. str.	1 093vvs		1 090vvs [f]		1 085vvs [f]		717vs [e]	718w (dp) [e]	714s	715w(dp)
ν_6 CY$_3$ asym. def.		*ca.* 526vvw		524vw (dp) [g]		524vw (dp) [g]		277wm (dp) [g]		275wm (dp) [e]
ν_7 CY$_3$ rock	241m [c]		237w [c]		230w [h]	230vw (dp) [g]	157w [g]	156wm (dp) [f]	151w	153w (dp)
ν_8 CHgX bend	96s [c]	*i*	73s [g]	*i*	60m [h]	*i*	83m [e]	*i*	63m	*i*
Other bands			261vw [c]							

[a] [Hg(CCl$_3$)Cl] in thf has at ν_2 at 393, ν_3 at 347, and ν_4 at 177 cm^{-1}. [b] [HgBr(CCl$_3$)] in CH$_2$Cl$_2$ has ν_2 at 394 and ν_3 at 251 cm^{-1}. [c] In CH$_2$Br$_2$. [d] ρ values for polarised bands are given in parentheses; depolarised bands ($\rho \simeq 0.75$) are marked dp. [e] In thf. [f] In CH$_2$Cl$_2$. [g] In CDCl$_3$. [h] In C$_6$H$_6$. [i] Masked by solvent.

Further to low wavenumbers, the Raman spectrum of [Hg(CF$_3$)Cl] has two polarised bands. That to higher wavenumber has the shoulder expected on the HgCl stretching feature as a result of chlorine isotopes, leaving the lower, shoulderless, band as the Hg–CF$_3$ stretch. The i.r. band at 241 cm^{-1} is assigned as CF$_3$ rocking, but no counterpart was observed in the Raman spectrum. Intense Raman scattering by the solvent precluded observation of the CHgCl bending mode but it was easily located in the i.r. spectrum. Thus, by use of the two methods of vibrational spectroscopy, a complete assignment of fundamentals can be obtained.

Below 400 cm^{-1} in the Raman spectrum of [HgBr(CF$_3$)] the higher of the two polarised bands (277 cm^{-1}) is much weaker than the lower (216 cm^{-1}); the trend in relative intensities is reversed for their i.r. counterparts. The HgCl stretch of [Hg(CF$_3$)Cl] was 6% higher in wavenumbers than that of [HgMeCl] in benzene,[10] and thus HgBr stretching in [HgBr(CF$_3$)] might be expected between 228 and 240 cm^{-1}; 277 cm^{-1} certainly seems unreasonably high for this mode and we regard 216 cm^{-1} as most representative of this motion. The elevation of Hg–CF$_3$ stretching by 27 cm^{-1} from the chloro- to the bromo-compound would be unusual for an essentially isolated vibration [10–12] and will be discussed later, together with the intensity characteristics of bands described in Table 1 as Hg–CY$_3$ and HgX stretching.

TABLE 2

Solution i.r. and Raman spectra of [Hg(CF$_3$)$_2$] below 1 200 cm^{-1} and [Hg(CCl$_3$)$_2$] below 800 cm^{-1} (point group D_{3d})

Assignment			[Hg(CF$_3$)$_2$] Raman	[Hg(CCl$_3$)$_2$] Raman [a]
A_{1g}	ν_1	CX$_3$ sym. str.	1 159w(dp) [a]	770ms(0.55)
	ν_2	CX$_3$ sym. def.	712m(0.05) [a]	386vs(0.0)
	ν_3	Hg(CY$_3$)$_2$ str.	225vs(0.3) [a]	151vs(0.25)
E_g	ν_8	CX$_3$ asym. str.	1 044w,br(dp) [b]	$\left.\begin{matrix}724\\706\end{matrix}\right\}$ vw(dp)
	ν_9	CX$_3$ asym. def.	532vw(dp) [a]	280m(dp)
	ν_{10}	CX$_3$ rock	207vw(dp) [a]	131m(dp)
Other bands			253vw [a]	345vw(0.1) [c] 172vw(dp)
			I.r.	I.r.
A_{2u}	ν_5	CX$_3$ sym. str.	1 138vvs [d]	796w [a]
	ν_6	CX$_3$ sym. def.	715s [e]	393s [e]
	ν_7	Hg(CY$_3$)$_2$ str.	272vs [e]	200s [f]
E_u	ν_{11}	CX$_3$ asym. str.	1 083vvs [d]	701vs [a]
	ν_{12}	CX$_3$ asym. def.	529wm [d]	269m [e]
	ν_{13}	CX$_3$ rock	260m [e]	168m [f]
	ν_{14}	HgC$_2$ bend	*ca.* 70w [g]	
Other bands				350vw [c,e]

[a] In thf. [b] In water. [c] [Hg(CCl$_3$)Cl] impurity. [d] In CH$_2$Cl$_2$. [e] In CH$_2$Br$_2$. [f] In CDCl$_3$. [g] In C$_6$H$_6$.

Our observed wavenumbers for solutions of [Hg(CF$_3$)$_2$] (Table 2) agree quite well with those of Downs.[4] Assignments are based on the centrosymmetric D_{3d} point group, in

---

[7] H. W. Thompson and R. B. Temple, *J. Chem. Soc.*, 1948, 1422.

[8] W. F. Edgell and C. E. May, *J. Chem. Phys.*, 1954, **22**, 1808.

[9] M. P. Johnson, *Inorg. Chim. Acta*, 1969, **3**, 232.

[10] P. L. Goggin, G. Kemeny, and J. Mink, *J.C.S. Faraday II*, 1976, 1025.

[11] P. L. Goggin, R. J. Goodfellow, S. R. Haddock, and J. G. Eary, *J.C.S. Dalton*, 1972, 647.

[12] D. A. Duddell, P. L. Goggin, R. J. Goodfellow, M. G. Norton, and J. G. Smith, *J. Chem. Soc. (A)*, 1970, 545.

agreement with the lack of wavenumber coincidence between the i.r. and Raman spectra for most types of vibration. The major difference in interpretation concerns the CF_3 stretching assignments. Although neither of the Raman bands above 1 000 cm^{-1} is detectably polarised, the higher one is much the sharper. This similarly to the spectra of $[Hg(CF_3)X]$ is a strong indication that the symmetric mode is at higher wavenumbers than the asymmetric in this case too. Downs assigned a questionable band at 261 cm^{-1} to the Raman-active CF_3 rocking mode. We also observed a very weak band in this region, but it appears to be polarised and we do not know its origin. However, we found an additional depolarised band at 207 cm^{-1} and tentatively assign it as the rocking mode.

For $[Hg(CCl_3)Cl]$ the higher of the two bands between 700 and 800 cm^{-1} is slightly polarised in the Raman spectrum, showing the order of the CCl_3 stretches to be the same as the CF_3 stretches on mercury, and the opposite of that in CCl_3I.[13] The Raman band at 396 cm^{-1} is attributed to the CCl_3 symmetric deformation although, as discussed below, such a description may not be entirely appropriate.

The very intense, polarised, Raman band at 177 cm^{-1} must reflect the $Hg-CCl_3$ stretch. The CCl_3 asymmetric deformation and rocking modes must correspond to the depolarised Raman bands between 300 and 100 cm^{-1} and are assigned according to the usual order.

Assignments for $[Hg(CCl_3)_2]$ (Table 2) are straightforward except that we cannot account for there being two Raman features just above 700 cm^{-1}, when only one appropriate mode (E_g) is predicted. There are no overtones or binary combinations to account for the extra band although there are ternary possibilities. The assignment of CCl_3 rocking modes is clear and lends support to the tentative assignment of the E_g rocking mode of $[Hg(CF_3)_2]$ at substantially lower wavenumbers than the E_u mode. We note that the i.r. active CX_3 stretching modes straddle the related Raman-active modes, whereas the reverse is true for $[Hg(CF_3)_2]$.

It has been suggested that perfluoromethylmercury(II) halides are dimeric in solution.[14] We tried to check this by molecular-weight measurements with a vapour-pressure osmometer but could not get reliable or consistent results, apparently because of decomposition of the compounds on the thermistor probe. Any dimerisation is likely to arise from some form of HgX bridging, so that in the vibrational spectra the Hg–X stretches should be the most sensitive to the presence of a centrosymmetric dimer {*cf.* the wide separation of Hg–X frequencies between i.r. and Raman spectra of solid $[Hg(CH_3)X]$ [10] which has a simple bimolecular centrosymmetric unit cell}. Although Hg–X stretching wavenumbers differ somewhat with solvent, where both i.r. and Raman spectra have been recorded for the same solvent the bands are coincident within experimental error, and there are no additional bands which the greater aggregation would require. There is thus no vibrational evidence to suggest dimerisation.

Spectra of Solids.—The spectra of the solids are much more complicated than those of solutions, although there is a general correspondence between them. The Raman spectra at 100 K are much richer in detail than those at room temperature and we will largely confine comment to them.

The spectra of $[Hg(CY_3)X]$ seem to divide into two categories, those of $[Hg(CF_3)X]$ (X = Br or I) being relatively simple especially when compared to the very complex spectra of the other three compounds. Those of $[Hg(CF_3)Cl]$, $[HgBr(CF_3)]$, and $[Hg(CCl_3)Cl]$ are listed in Table **3**, whilst the details for $[Hg(CF_3)I]$ and $[HgBr(CCl_3)]$ are available in Supplementary Publication No. SUP 22199 (6 pp.).* The compound $[Hg(CCl_3)Cl]$ is isomorphous (space group D_{2h}^{16}) with $[HgBr(CCl_3)]$ which has been studied in detail.[15] The centrosymmetric unit cell contains eight molecules which are of two crystallographically independent types with seemingly different bond lengths.

Below 130 cm^{-1}, $[Hg(CCl_3)Cl]$ shows 15 distinct features but even this falls far short of the 24 lattice and eight CHgCl bending modes which factor-group analysis [16] predicts to be Raman active, and there must be band overlap. There should be four ($2A_g + 2B_{2g}$) $Hg-CCl_3$ and Hg–X Raman-active stretching modes, and three bands assignable to each set are observed for each in the case of $[Hg(CCl_3)Cl]$. We expected to observe isotope effects on the HgCl feature but these are evidently masked by the factor-group effects since the lowest component seems too intense to be so attributed (Figure 1). Three features are also found in the Hg–Br stretching region of $[HgBr(CCl_3)]$ (239, 233, and 227 cm^{-1} at 293 K) but the lowest is much the weakest and may not relate to a fundamental.

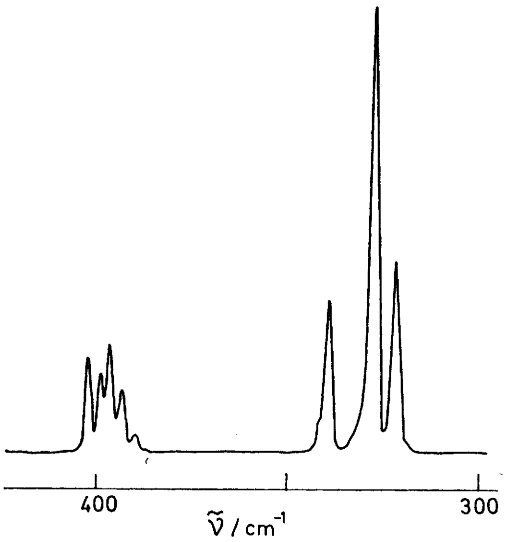

FIGURE 1 Raman spectrum (300—420 cm^{-1}) of solid $[Hg(CCl_3)Cl]$ at 100 K

The bands above 785 cm^{-1} for both the compounds $[Hg(CCl_3)X]$ are much weaker than those just below and are of appropriate wavenumber to arise from overtones. The remaining six bands above 700 cm^{-1} can be accounted for in terms of the two differently sited types of CCl_3 groups with splitting of the degeneracy of the *E* modes of the free molecules in the crystal environment. The far greater complexity predicted by the factor-group approach is not observed.

A CCl_3 mode showing chlorine-isotope effects should be a

---

* For details see Notices to Authors No. 7, *J.C.S. Dalton*, 1977, Index issue.

[13] R. H. Mann and P. H. Manis, *J. Mol. Spectroscopy*, 1973, **45**, 65.

[14] V. S. Petrosyan, V. I. Bakhmutov, and O. A. Reutov, *J. Organometallic Chem.*, 1974, **72**, 87.

[15] T. A. Babushkina, E. V. Bryukhova, F. K. Velichko, V. I. Pakhomov, and G. K. Semin, *J. Struct. Chem.*, 1968, **9**, 153.

[16] D. M. Adams and D. C. Newton, *J. Chem. Soc.* (*A*), 1970, 2822.

quartet with, from low wavenumber, relative intensity 3 : 32 : 98 : 100. The detail observed near 400 cm^{-1} is quite well accounted for in terms of overlapping of two such quartets, *e.g.* for $[Hg(CCl_3)Cl]$ at 387, 390, 394, and 397, and 394, 397, 399, and 403 cm^{-1} (Figure 1).

TABLE 3

Infrared and Raman spectra of solid $[Hg(CF_3)X]$ (X = Cl or Br) below 1 250 cm^{-1} and $[Hg(CCl_3)Cl]$ below 850 cm^{-1} [a]

	$[Hg(CF_3)Cl]$			$[HgBt(CF_3)]$		
Assignment	I.r.	Raman 293 K [b]	Raman 100 K [c]	I.r.	Raman 293 K [b]	Raman 100 K [c]
CF_3 str.		1 168(3)	1 166(20)	1 145w(sh)	1 140(4)	1 144(8)
	1 150	1 113(2)	1 135(13)	1 120vs	1 128(sh)	1 132(1)
	1 125 vvs, br	1 103(2)	1 104(7)	1 102vs		1 118(3)
	1 095	1 084(3)	1 087(20)	1 047w(sh)		
	1 060		1 075(7)			
			1 073(6)			
CF_3 sym. def.	725s	728(32)	727(80)	729s	731(17)	730(23)
			724(28)			
CF_3 asym. def.	524w	526(3)	525(4)		529vvw	
			521(3)			
HgX str.		353(8)	353(20)	204m	197(100)	197(100)
	343(sh)	340(sh)	340(24)			
	337 s		335(30)			
	329(sh)	330(29)	330(68)			
HgC str.			259(53)	279(sh)	274(14)	276(22)
		255(sh)	253(38)	267s		
	250m	251(100)	251(100)			
CF_3 rock			246(2)	232m	239(4)	243(4)
			243(4)			238(4)
	241m	240(19)	238(20)			
CHgX bending, lattice modes, low-wavenumber overtones, *etc.*			128(4)		85(10)	86(7)
		113(5)	111(15)	67s		51(sh)
	92vs	96(18)	99(25)		42(70)	46(24)
		87(17)	84(33)			30(16)
			79(sh)			26(sh)
			55br(27)		15(100)	21(30)
		49(40)	48(sh)			
		41(47)	40(42)			
			38(sh)			
		34(sh)	33(sh)			
			20(14)			
		15(7)	14(15)			

	$[Hg(CCl_3)Cl]$		
Assignment	I.r.	Raman 293 K [b]	Raman 100 K [c]
CCl_3 sym. str.			804(2) [d]
			799(4) [d]
			792(4) [d]
	779wm	777(32)	784(68)
	772wm	772(sh)	774(27)
CCl_3 asym. str.			733 (9)
	729s	725br(4)	727(5)
	717s	713(4)	714(4)
			709(5)
CCl_3 sym. def.			403(22)
	401w(sh)	400(sh)	399(18)
	396wm	397(24)	397(25)
		395(sh)	394(14)
			390(4)
			387(1)
CCl_3 asym. def.		283(sh)	285(12)
		278(17)	279br(12)
	274w		273br(5)
HgX str.	334s	336(15)	340(33)
	324w(sh)	326(57)	328(100)
		324(sh)	323(42)
$Hg(CCl_3)$ str.			185(14)
		181(sh)	183(4)
	177w	174(100)	176(83)
CCl_3 rock		164(14)	166(26)
			163(2)
	157w	156(18)	157(20)
CHgX bending, lattice modes, low-wavenumber overtones, *etc.*			128(sh)
		125(27)	125(61)
	117m	109(11)	116(21)
	89(sh)	88(11)	93(14)
	81m	51(sh)	56br(11)
			49(11)
		44(29)	46(12)
			43(2)
			38(18)
		35(30)	36(18)
			33(13)
		30(34)	30(5)
			26(2)
			23(4)
		16(14)	19(2)

Numbers in parentheses are peak heights relative to the largest feature (=100); br = broad, sh = shoulder without distinct peak top.

[a] For the spectra of $[Hg(CF_3)I]$ and $[HgBr(CCl_3)]$ see SUP 22199. [b] 2 cm^{-1} resolution. [c] 1 cm^{-1} resolution. [d] Probably overtones.

We do not know the crystal structure of $[Hg(CF_3)Cl]$ but one possibility is that it is isomorphous with the trichloromethyl analogue. The four Hg–Cl bands would be consistent with D_{2h}^{16} and three Hg–CF_3 features are resolved (Figure 2). The two CF_3 symmetric deformations and six CF_3 stretches also agree with our interpretation above for the CCl_3 systems. In contrast, the Raman spectra of $[HgBr(CF_3)]$ and $[Hg(CF_3)I]$ have only single Hg–CF_3, HgX stretching, and CF_3 symmetric deformation modes and only two CF_3 stretching modes. The Hg–X stretches are lower in the Raman spectra than in the i.r. and the reverse is found for the Hg–CF_3 modes, closely paralleling observations on the corresponding $[Hg(CH_3)X]$.[10] {For $[Hg(CF_3)I]$ the bands are at 163 and 261 cm^{-1} in the Raman spectra, and 166 and 255 cm^{-1} in the i.r.}.

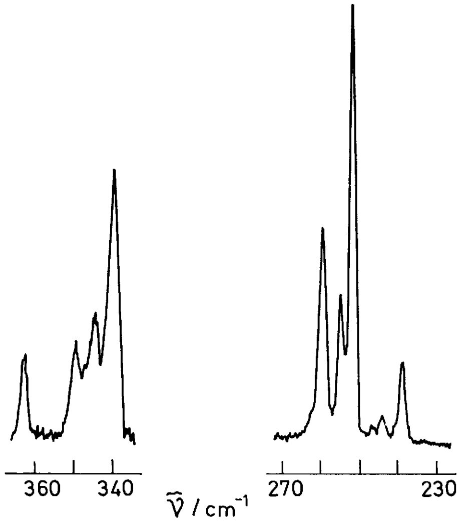

FIGURE 2 Raman features (200—400 cm^{-1}) of solid $[Hg(CF_3)Cl]$ at 100 K

For $[Hg(CY_3)_2]$ the only crystal information is that $[Hg(CCl_3)_2]$ has a centrosymmetric monoclinic unit cell containing four molecules.[15] Presumably the space group is of type C_{2h}^{n} and there are two crystallographically different types of molecule. The complexity of the spectra is quite compatible with such an interpretation, but there are insufficient details to justify fuller discussion. The observed wavenumbers and classification of vibrational types are in SUP 22199.

DISCUSSION

In the Tables we have used the conventional descriptions ' CY_3 stretch ' and ' CY_3 deformation ', applying the latter to the lower set of bands. For the trichloromethyl complexes the band thus assigned as the CY_3 symmetric deformation is not greatly lower in energy than the symmetric breathing mode of CCl_4 (459 cm^{-1}) and resembles the latter in being very highly polarised and in being the only C–Cl vibration to show well resolved chlorine-isotope features. From their frequencies, both the highest A_1 vibration and the E CY_3 stretch relate to the T_2 mode of CCl_4 which probably explains the almost depolarised nature of the highest A_1 mode. Where the outer atoms in a tetrahedral AX_4 molecule are heavier than the central atom the T_2 stretch is largely the three-dimensionally degenerate motion of the light atom within a nearly static X_4 cage, whereas the symmetric breathing mode is the motion of the heavy X atoms and appears at much lower wavenumbers. The spectral similarity of the $Hg(CCl_3)$ systems to CCl_4 suggests that the highest A_1 and E modes might alternatively be regarded as the motion of the carbon atom within a $HgCl_3$ cage whilst the lower A_1 mode is a breathing mode of the Cl_3 group. A consequence of this description is that the $Hg-CCl_3$ stretch must be regarded as a motion of the whole CCl_3 group, rather than just of the carbon atom, as befits its low energy. (It may be formally related to the A_1 component which would be obtained from the T_2 deformation of CCl_4 on lowering the symmetry to C_{3v}.) Similar characteristics apply to the CF_3 compounds, except that the wavenumbers are substantially lower than ν_1 and ν_3 of CF_4.

The most striking feature of the spectra of $[Hg(CF_3)X]$ is the intensity behaviour of the band which seems to be predominantly $Hg-CF_3$ stretching. If it is considered in conjunction with the Hg-X stretch, whichever is the higher wavenumber gives a strong i.r. band and a relatively weak Raman band, whereas the reverse is true for the lower mode. This is most marked in $[HgBr(CF_3)]$ where the Raman feature at 277 cm^{-1} is extremely weak. If, as we suggest above, this vibration should be regarded as being of the whole CF_3 group, then the effective mass (69) is quite close to that of Br whilst the two stretching vibrations are respectively within 14 cm^{-1} of the two stretching modes of $[Hg(CF_3)_2]$ and $HgBr_2$ (263 and 203 cm^{-1} in solution [17]). We suggest that the motions about the mercury atom have become approximately those of a symmetrical [YXY] molecule with the lower the symmetric mode and the higher the asymmetric. In the chloro- and iodo-species, where there is a greater disparity in the masses of the groups attached to mercury, there is still something of the same effect with the lower- and higher-wavenumber modes reflecting the intensity characteristics expected for the symmetric and asymmetric stretches of a [YXY] system respectively. An important conclusion is that, when comparing spectra of related complexes (*e.g.* a chloride with a bromide), the usual expectation that there will be approximate correlation of intensities as well as of frequencies for the stretching vibrations of common groups may not pertain.

In the series $[Hg(CF_3)X]$ the order of $Hg-CF_3$ stretching wavenumbers is $Br > I > Cl$ instead of the usual regular decrease with increasing mass of the *trans* halide. This may be expected from the mixing patterns discussed above since the effect of the separation between the pseudo-symmetric and -antisymmetric modes, and of the *trans* interaction constant, will operate in the contrary sense for the chloride compared with the other halides.

Despite these complications of the motions about the metal, it is interesting to note that the trends in frequency with halide for the two highest A_1 modes seems quite normal, and their absorption coefficients and bandwidths in the i.r. do not vary with halide within experimental error.

Further comment on the relation between the bond properties of corresponding CH_3, CF_3, and CCl_3 compounds of Hg^{II} must await the results of detailed normal-co-ordinate analysis.

EXPERIMENTAL

The general procedures for the spectroscopic measurements were as described in ref. 10 except that all the Raman results were from the Coderg T-800 spectrometer with 514.5-nm argon-ion laser excitation. For far-i.r. spectra in tetrahydrofuran (thf), freshly distilled dry solvent was used in 0.2-mm cells with polyethylene windows.

Although the preparation of $[Hg(CF_3)_2]$ was carried out as described by Knunyants *et al.*,[18] poor yields of the product were obtained which still contained undecarboxylated trifluoroacetate. The material was purified by repeated vacuum sublimation until there was no trace of $[CF_3CO_2]^-$ in the i.r. or ^{19}F n.m.r. spectrum. The compounds $[Hg(CF_3)Cl]$ and $[HgBr(CF_3)]$ were prepared as described by Seyferth *et al.*[19] from $[Hg(O_2CCF_3)_2]$ *via* $[Hg(CF_3)(O_2CCF_3)]$. Because the iodide we obtained in this way was contaminated with HgI_2 which was difficult to remove, we used the alternative method [20] of the reaction of mercury with CF_3I at 220 °C. Only the lower part of the reaction vessel was heated and, probably as a consequence, the yields were only 10—15% (based on CF_3I used). The compounds $[Hg(CCl_3)X]$ were prepared, in good yields, as described by Logan.[21] The melting points of all the compounds were within 2 °C of the literature values.

We thank the S.R.C. for funds to provide the Raman facilities, the University of Bristol for the award of a Research Scholarship (to K. K.), and Mr. Robert Eason for technical assistance.

[7/1390 *Received, 1st August*, 1977]

---

[17] N. W. Hurst, Ph.D. Thesis, University of Bristol, 1975.

[18] I. L. Knunyants, Ya. F. Komissarov, B. L. Daytkin, and L. T. Lantseva, *Izvest. Akad. Nauk S.S.S.R., Ser. khim.*, 1973, **4**, 943.

[19] D. Seyferth, S. P. Hopper, and G. J. Murphy, *J. Organometallic Chem.*, 1972, **46**, 201.

[20] K.-H Flegler and A. Haas, *Z. anorg. Chem.*, 1976, **426**, 288.

[21] T. J. Logan, *J. Org. Chem.*, 1963, **28**, 1129.