*Journal of Organometallic Chemistry*, 246 (1983) 115–127
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

# FORCE FIELD STUDIES OF SOME TRIFLUOROMETHYL- AND TRICHLOROMETHYL-MERCURY(II) COMPOUNDS

J. MINK

*Institute of Isotopes of the Hungarian Academy of Sciences, 1525 Budapest (Hungary)*

and P.L. GOGGIN

*Department of Inorganic Chemistry, The University, Bristol BS8 1BS (Great Britain)*

(Received November 5th, 1982)

## Summary

Force constants of [Hg(CF$_3$)$_2$], [Hg(CCl$_3$)$_2$], [Hg(CF$_3$)X] (X = Cl, Br or I) and [Hg(CCl$_3$)X] (X = Cl or Br) have been calculated using a valence force field and wavenumber data from solutions. The potential energy distributions show substantial mixing between the symmetrical stretching and umbrella deformation coordinates of the trihalomethyl groups. The high degree of mixing of HgC and HgX stretching coordinates in [Hg(CF$_3$)Br] and [Hg(CF$_3$)I] accounts for the discontinuous frequency and intensity trends in the [Hg(CF$_3$)X] series.

The results are discussed in comparison with methylmercury and other trifluoromethyl systems.

## 1 Introduction

In the last 30 years there has been a substantial amount of work on the synthesis of trifluoromethyl organometallic compounds, but relatively little on corresponding trichloromethyls. For mercury(II) CF$_3$ and CCl$_3$ derivatives are well established, and for compounds [Hg(CY$_3$)$_2$] and [Hg(CY$_3$)X] (Y = H, F or Cl; X = Cl, Br or I) vibrational spectra have been studied in detail [e.g. references 1–3].

In the case of methylmercury compounds we have performed normal coordinate calculations [1,2] and to gain an insight into the effect of the electronegativity of substituents on the methyl group we report comparable force field studies for the trihalomethyl compounds.

Brauer et al. have also recently studied [Hg(CF$_3$)$_2$] [4] using a valence force field, as well as α-[Hg(CF$_3$)N$_3$] and [Hg(CF$_3$)NCO] [5], while Eugen has investigated the force field for [Hg(CH$_3$)(CF$_3$)] and its deuterated analogue [6]. Hase [7] used the data of ref. 3 in a Urey-Bradley approach but we do not understand the numerical

0022-328X/83/$03.00

values reported which bear no resemblence either to our own calculations or to published work on any other $CY_3$ systems.

## Force constant calculations

Tetrahedral angles about carbon and linear bonding about mercury have been assumed for $[Hg(CY_3)X]$ molecules. The CF and CCl bond lengths have been taken as 134 [5] and 177 [6] pm respectively. The CHg and HgX bond lengths have been assumed to be the same as used for calculations on corresponding methylmercury halides [2]. For $[Hg(CF_3)_2]$ we have used the exact gas phase parameters determined by Oberhammer [8]. The HgC bond length for $[Hg(CCl_3)_2]$ has been assumed to be 209 pm. Approximate descriptions and symmetry properties of the fundamental vibrational modes are given in Table 1. Wavenumbers from the study of solutions [3] were used as the goal for the force field refinements.

The internal and symmetry coordinates used follow those adopted for $[Hg(CH_3)_2]$ [1] and $[Hg(CH_3)X]$ [2]. The procedures used for calculating the $G$ matrices and refining the force constants have been outlined previously [9,10]. Initial force constants were taken from previous calculations for $[Hg(CF_3)_2]$ [4], $[Hg(CH_3)_2]$ [1], $[Hg(CH_3)X]$ [2] and $HCCl_3$ [11–13].

For the $CF_3$ derivatives, refinement gave satisfactory agreement with our experimental data. However, for the $CCl_3$ compounds the force field from $HCCl_3$ ($F_0'$) was not very successful in yielding an appropriate force constant matrix $F_0$ for further refinement, and the following procedure was adopted. First the $GF_0'$ matrix was diagonalised (eq. 1).

$$\tilde{L}_0 G F_0' L_0 = \Lambda \tag{1}$$

Using the inverse eigenvector matrix and the diagonal matrix of experimental values, $\Lambda_{\mathrm{exp}}$, the $F_0$ matrix can be obtained (eq. 2).

$$\tilde{L}_0^{-1} \Lambda_{\mathrm{exp}} L_0^{-1} = F_0 \tag{2}$$

For the $[Hg(CY_3)_2]$ molecules there are 13 experimental frequencies and we have attempted to refine 11 force constants with four others constrained. In his HOFF treatment of $CH_3$ derivatives, Mills [14] proposed criteria which, applied to the

TABLE 1

DISTRIBUTION OF FUNDAMENTAL VIBRATIONS FOR $[Hg(CY_3)_2]$ and $[Hg(CY_3)X]$

| Approximate vibrational description | $[Hg(CY_3)_2]$ | | | | $[Hg(CY_3)X]$ | |
|---|---|---|---|---|---|---|
| | $a_{1g}$ | $a_{2u}$ | $e_g$ | $e_u$ | $a_1$ | $e$ |
| $CY_3$ sym. str. | $\nu_1$ | $\nu_5$ | | | $\nu_1$ | |
| $CY_3$ asym. str. | | | $\nu_8$ | $\nu_{11}$ | | $\nu_5$ |
| $CY_3$ sym. def. | $\nu_2$ | $\nu_6$ | | | $\nu_2$ | |
| HgC str. | $\nu_3$ | $\nu_7$ | | | $\nu_4$ | |
| $CX_3$ asym. def. | | | $\nu_9$ | $\nu_{12}$ | | $\nu_6$ |
| $CY_3$ rock | | | $\nu_{10}$ | $\nu_{13}$ | | $\nu_7$ |
| $HgC_2$ bend | | | | $\nu_{14}$ | | |
| HgX str. | | | | | $\nu_3$ | |
| CHgX bend | | | | | | $\nu_8$ |

TABLE 2

FORCE CONSTANTS FOR [Hg(CF$_3$)$_2$] AND [Hg(CCl$_3$)$_2$] MOLECULES (UNITS 10$^2$ N m$^{-1}$).

| Force constant | Common atom(s) of internal coordinates | [Hg(CF$_3$)$_2$] | [Hg(CCl$_3$)$_2$] |
|---|---|---|---|
| $K$(CX) | – | 5.093 | 2.681 |
| $K$(CHg) | – | 2.217 | 2.173 |
| $F$(CX, CX) | C | 0.570 | 0.523 |
| $F$(CHg, CHg) | | 0.230 | 0.135 |
| $H$(XCX) | – | 0.865 | 0.388 |
| $H$(XCHg) | – | 0.407 | 0.291 |
| $H$(CHgC) | – | 0.129 | 0.088 |
| $h'$(CHg, XCHg)[a] | Hg | 0 | 0.037 |
| $h$(XCHg, XCHg) | C–X | 0.185 | 0.073 |
| $f'$(XCHg, HgCX)[a] | Hg | 0.022 | 0.042 |
| $f$(XCHg, CHgC) | C–Hg | 0.008 | −0.016 |
| constrained values | | | |
| $F$(CH, CHg) | C | 0.069 | 0.179 |
| $h$(CHg, XCHg) | C–Hg | 0.098 | 0.115 |
| $h$(CX, XCHg) | C–X | 0.426[b] | 0.208 |
| $f$(XCX, XCHg) | C–X | 0.056 | 0.032 |

[a] $f'$ and $h'$ interaction constants between two CX$_3$ groups.

[b] see text.

present problem, should lead to:

$$-F_{89} = F_{810} \tag{3}$$

$$F_{12} = \frac{1}{\sqrt{2}} F_{810} \tag{4}$$

These two interdependent constraints were satisfactory for [Hg(CCl$_3$)$_2$], but for [Hg(CF$_3$)$_2$] we could not find an acceptable set of force constants satisfying both eq. 3 and 4. For the latter we have used $-F_{89} = F_{810} = 0.575 \times 10^{-8}$ N rad$^{-1}$ and $F_{12} = 0.65 \times 10^{-8}$ N rad$^{-1}$; the value of $h$(CF, FCHg) $= 0.426 \times 10^2$ N m$^{-1}$, given in Table 2, is derived from $F_{810}$.

The final non-zero force constants in internal coordinates are listed in Table 2, and a comparison of experimental and calculated wavenumbers in Table 3 together with the potential energy distribution of internal symmetry coordinates between the normal modes. The symmetry coordinate force constants for [Hg(CF$_3$)$_2$] were virtually the same as those determined by Brauer et al. [4], the minor discrepencies being the result of slight differences for the Raman frequencies of $\nu_1$, $\nu_7$ and $\nu_8$ in ref. 3. The force constants for [Hg(CCl$_3$)$_2$] are the first values obtained for a trichloromethylmetal derivative; the CCl stretching force constant is lower than that for CCl$_4$ [15] or HCCl$_3$ [13] and must be the result of the presence of the metal atom.

For [Hg(CY$_3$)X] molecules there are eight experimental frequencies and so eight force constants could be refined, with six others constrained. The relations corresponding to eq. 3 and 4 are $-F_{56} = F_{57}$ and $F_{12} = \frac{1}{\sqrt{2}} F_{57}$ respectively. To obtain

(Continued on p. 121)

TABLE 3

EXPERIMENTAL AND CALCULATED WAVENUMBERS AND POTENTIAL ENERGY DISTRIBUTION (PED) FOR [Hg(CF$_3$)$_2$] AND [Hg(CCl$_3$)$_2$] (Point group $D_{3d}$).

| | | [Hg(CF$_3$)$_2$] | | | | | | [Hg(CCl$_3$)$_2$] | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | PED × 100 | | | | | | PED × 100 | | | |
| | | obs. | calc. | $s_1$ | $s_2$ | $s_3$ | | obs | calc. | $s_1$ | $s_2$ | $s_3$ | |
| $a_{1g}$ | $\nu_1$ | 1115 | 1115 | 37 | 70 | 23 | | 770 | 770 | 45 | 49 | 50 | |
| | $\nu_2$ | 712 | 713 | 69 | 60 | 2 | | 386 | 384 | 57 | 22 | 14 | |
| | $\nu_3$ | 225 | 227.6 | 2 | 15 | 77 | | 151 | 151 | 1 | 37 | 44 | |
| | | | | $s_5$ | $s_6$ | $s_7$ | | | | $s_5$ | $s_6$ | $s_7$ | |
| $a_{2u}$ | $\nu_5$ | 1138 | 1138 | 40 | 73 | 20 | | 796 | 796 | 40 | 46 | 45 | |
| | $\nu_6$ | 715 | 714 | 63 | 22 | 2 | | 393 | 394 | 63 | 14 | 13 | |
| | $\nu_7$ | 272 | 272 | 1 | 12 | 80 | | 200 | 201 | 0 | 43 | 45 | |
| | | | | $s_8$ | $s_9$ | $s_{10}$ | | | | $s_8$ | $s_9$ | $s_{10}$ | |
| $e_g$ | $\nu_8$ | 1044 | 1044 | 106 | 27 | 4 | | 724 | 724 | 102 | 29 | 11 | |
| | $\nu_9$ | 532 | 531.3 | 10 | 75 | 0 | | 280 | 276 | 13 | 65 | 2 | |
| | $\nu_{10}$ | 207 | 207 | 5 | 3 | 112 | | 131 | 135.6 | 0 | 12 | 99 | |
| | | | | $S_{11}$ | $s_{12}$ | $s_{13}$ | $s_{14}$ | | | $s_{11}$ | $s_{12}$ | $s_{13}$ | $s_{14}$ |
| $e_u$ | $\nu_{11}$ | 1083 | 1083 | 98 | 26 | 5 | 2 | 701 | 701 | 95 | 27 | 15 | 4 |
| | $\nu_{12}$ | 529 | 530 | 13 | 70 | 1 | 1 | 269 | 273 | 16 | 58 | 4 | 2 |
| | $\nu_{13}$ | 260 | 260 | 0 | 7 | 85 | 9 | 168 | 163 | 0 | 19 | 86 | 10 |
| | $\nu_{14}$ | 70 | 71.4 | 4 | 0 | 26 | 90 | – | 41.5 | 1 | 1 | 6 | 87 |

TABLE 4

FORCE CONSTANTS FOR [Hg(CF$_3$)X] (X = Cl, Br or I) AND [Hg(CCl$_3$)X] (X = Cl or Br) MOLECULES (UNITS $10^2$ N m$^{-1}$)

| Force constant | Common atom(s) internal coordinates | [Hg(CF$_3$)X] | | | [Hg(CCl$_3$)X] | |
|---|---|---|---|---|---|---|
| | | X = Cl | X = Br | X = I | X = Cl | X = Br |
| *K*(CF); *K*(CCl) | – | 5.450 | 5.345 | 5.464 | 2.764 | 2.792 |
| *K*(CHg) | – | 2.221 | 2.097 | 2.001 | 2.209 | 1.969 |
| *K*(HgX) | – | 2.556 | 2.170 | 1.789 | 2.038 | 2.119 |
| *F*(CF, CF); *F*(CCl, CCl) | C | 1.024 | 0.944 | 1.081 | 0.612 | 0.631 |
| *H*(FCF); *H*(ClCCl) | – | 0.839 | 0.835 | 0.833 | 0.396 | 0.386 |
| *H*(FCHg); *H*(ClCHg) | – | 0.427 | 0.436 | 0.425 | 0.197 | 0.183 |
| *H*(CHgX) | – | 0.156 | 0.145 | 0.133 | 0.136 | 0.151 |
| *f*(FCHg, FCHg); *f*(ClCHg, ClCHg) | C–F, C–Cl | 0.145 | 0.173 | 0.163 | 0.055 | 0.072 |
| *Constrained values* | | | | | | |
| *F*(CHg, HgX) | Hg | 0.160 | 0.100 | 0.060 | 0.220 | 0.210 |
| *F*(FC, CHg); *F*(ClC, CHg) | C | 0.271 | 0.271 | 0.271 | 0.150 | 0.150 |
| *h*(CHg, FCHg); *h*(CHg, ClCHg) | C–Hg | 0.146 | 0.146 | 0.146 | 0.111 | 0.171 |
| *h*(CF, FCHg); *F*(CCl, ClCHg) | C–F, C–Cl | 0.373 [a] | 0.373 [a] | 0.373 [a] | 0.208 | 0.208 |
| *f*(FCF, FCHg); *f*(ClCCl, ClCHg) | C–F, C–Cl | 0.056 | 0.056 | 0.056 | 0.032 | 0.032 |
| *f*(FCHg, CHgX); *f*(ClCHg, CHgX) | C–Hg | −0.005 | −0.005 | −0.005 | −0.016 | −0.024 |

[a] See text.

TABLE 5

EXPERIMENTAL AND CALCULATED FUNDAMENTAL WAVENUMBERS AND POTENTIAL ENERGY DISTRIBUTION FOR [Hg(CF$_3$)X] AND [Hg(CCl$_3$)X]

| | $a_1$ species | | | | | | | $e$ species | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | obs | calc. | PED × 100 | | | | | obs. | calc. | PED × 100 | | | |
| | | | | $s_1$ | $s_2$ | $s_3$ | $s_4$ | | | | $s_5$ | $s_6$ | $s_7$ | $s_8$ |
| [Hg(CF$_3$)Cl] | $\nu_1$ | 1130 | 1131 | 64 | 45 | 19 | 0 | $\nu_5$ | 1093 | 1093 | 100 | 25 | 5 | 2 |
| | $\nu_2$ | 723 | 723 | 39 | 41 | 11 | 0 | $\nu_6$ | 526 | 526 | 11 | 75 | 1 | 1 |
| | $\nu_3$ | 250 | 250 | 0 | 17 | 69 | 3 | $\nu_7$ | 240 | 240 | 1 | 3 | 115 | 2 |
| | $\nu_4$ | 355 | 355 | 0 | 0 | 4 | 97 | $\nu_8$ | 96 | 94 | 0 | 1 | 9 | 117 |
| [Hg(CF$_3$)Br] | $\nu_1$ | 1125 | 1125 | 60 | 30 | 19 | 0 | $\nu_5$ | 1088 | 1088 | 101 | 25 | 5 | 2 |
| | $\nu_2$ | 724 | 723.5 | 43 | 39 | 8 | 0 | $\nu_6$ | 525 | 525 | 11 | 75 | 1 | 0 |
| | $\nu_3$ | 277 | 275 | 0 | 7 | 41 | 51 | $\nu_7$ | 237 | 230 | 2 | 3 | 119 | 3 |
| | $\nu_4$ | 216 | 217.7 | 0 | 8 | 36 | 48 | $\nu_8$ | 73 | 70.4 | 0 | 1 | 9 | 118 |
| [Hg(CF$_3$)I] | $\nu_1$ | 1121 | 1121 | 68 | 46 | 14 | 0 | $\nu_5$ | 1085 | 1085 | 29 | 94 | 3 | 2 |
| | $\nu_2$ | 717 | 722 | 35 | 47 | 9 | 0 | $\nu_6$ | 524 | 524 | 89 | 9 | 2 | 3 |
| | $\nu_3$ | 256 | 257 | 0 | 8 | 50 | 34 | $\nu_7$ | 230 | 230 | 6 | 0 | 110 | 8 |
| | $\nu_4$ | 176 | 178 | 0 | 3 | 31 | 66 | $\nu_8$ | 60 | 71 | 4 | 0 | 9 | 89 |
| [Hg(CCl$_3$)Cl] | $\nu_1$ | 780.5 | 780.6 | 48 | 43 | 44 | 0 | $\nu_5$ | 717 | 717 | 36 | 91 | 10 | 4 |
| | $\nu_2$ | 396 | 394 | 54 | 20 | 16 | 0 | $\nu_6$ | 277 | 227 | 87 | 12 | 6 | 1 |
| | $\nu_3$ | 177 | 168 | 0 | 41 | 44 | 0 | $\nu_7$ | 156 | 156 | 0 | 2 | 99 | 10 |
| | $\nu_4$ | 350 | 351 | 0 | 0 | 1 | 100 | $\nu_8$ | 83 | 85 | 5 | 1 | 10 | 85 |
| [Hg(CCl$_3$)Br] | $\nu_1$ | 773 | 773 | 51 | 46 | 46 | 0 | $\nu_5$ | 714 | 714 | 36 | 91 | 10 | 4 |
| | $\nu_2$ | 391 | 393.5 | 51 | 24 | 18 | 0 | $\nu_6$ | 275 | 275 | 88 | 11 | 8 | 1 |
| | $\nu_3$ | 166 | 168.5 | 0 | 34 | 36 | 10 | $\nu_7$ | 152 | 153 | 1 | 2 | 103 | 10 |
| | $\nu_4$ | 244 | 247 | 0 | 4 | 9 | 91 | $\nu_8$ | 63 | 64 | 5 | 1 | 8 | 86 |

$F_{57}$ we used Torkington's method [16] of constructing ellipses relating diagonal and off-diagonal terms. Plots of $F_{55}$ and $F_{77}$ against $F_{57}$ gave minima for the diagonal terms and. indicated the value $-F_{56} = 0.37 \times 10^{8}$ N rad$^{-1}$ for [Hg($CCl_3$)-Cl]. For [Hg($CF_3$)Cl] this method gives $-F_{56} = 0.50 \times 10^{-8}$ N rad$^{-1}$, slightly lower than for the corresponding term ($F_{89}$) used for [Hg($CF_3$)$_2$]. The other related diagonal force constants, $F_{66}$ and $F_{88}$, did not display minima with $-F_{56}$ in the range 0–1 × $10^{-8}$ N rad$^{-1}$. In the same way as for [Hg($CF_3$)$_2$], we could not fix a set of force constants for the [Hg($CF_3$)X] molecules which satisfied the two relationships involving $F_{57}$. The value we quote, $h$(CF, FCHg) = 0.373 × $10^2$ N m$^{-1}$, arises from $F_{56}$, but for $F_{12}$ we have used 0.47 × $10^{-8}$ N rad$^{-1}$.

The force constants which gave the best fit for the [Hg($CY_3$)X] molecules are given in Table 4. Table 5 gives the comparison between experimental and calculated wavenumbers, together with the computed potential energy distributions.

## Discussion

For the trihalomethylmercury compounds, the potential energy distributions (Tables 3 and 5) show very strong coupling between $CY_3$ symmetric stretching and umbrella deformation contributions to the normal modes. Indeed this is so marked that simple qualitative descriptions of e.g. $\nu_1$ and $\nu_2$ are inapplicable. For the trichloromethyl compounds the mode that would conventionally be classified as the symmetric deformation showed well resolved chlorine isotope features in the low temperature Raman spectrum [3], a clear experimental manifestation of the strong CCl stretching contributions.

In the $CH_3$ and $CD_3$ mercury systems the contribution from metal–carbon stretching to $\nu_1$ is very small [1] but increases strongly in the order $CH_3 < CF_3 < CCl_3$. These two facets together demonstrate the extent to which the highest frequency totally symmetric modes are predominantly motions of the carbon atom.

The modes of the trifluoromethylmercury halides with predominantly Hg–C and Hg–X stretching character showed a specific behaviour. In [Hg($CF_3$)Cl] $\nu_3$ and $\nu_4$ are well separated in wavenumber and the Hg–Cl stretching mode is essentially individual. In contrast, for the bromide (and to a lesser extent for the iodide) the coupling between $\nu_3$ and $\nu_4$ is very strong. Indeed the contributions from $S_3$ and $S_4$ are practically equal to $\nu_3$ and $\nu_4$ and this manifested itself in discontinuous frequency and intensity trends in the [Hg($CF_3$)X] series [3]: with the similarity of $CF_3$ and Br masses, and of HgC and HgBr stretching force constants, $\nu_3$ and $\nu_4$ assume close correspondence to asymmetric and symmetric stretching modes of a linear YXY system. The features that might ordinarily be regarded as "HgC stretching" do not follow the usual trend Cl > Br > I for [Hg($CF_3$)X] but the $K$(CHg) force constants (Table 4) still do so.

For [Hg($CF_3$)X] the $K$(HgX) force constants follow the usual order but in [Hg($CCl_3$)X] $K$(HgBr) is marginally greater than $K$(HgCl), for which we can see no obvious explanation.

Strong coupling between $CH_3$ rocking and $CH_3$ asymmetric deformations was noted for [Hg($CH_3$)$_2$] [1], but similar coupling in the trihalomethyl systems is much less marked.

Table 6 compares skeletal wavenumbers and force constants for systems with two methyl or substituted methyl groups. For [Hg($CF_3$)($CH_3$)] and [Hg($CF_3$)($CD_3$)] [6,

TABLE 6

SKELETAL MODES AND FORCE CONSTANTS FOR DIMETHYL DERIVATIVES OF MERCURY

| | Wavenumbers ($cm^{-1}$) | | | | Force constants $10^2$ N $m^{-1}$ | | | |
|---|---|---|---|---|---|---|---|---|
| | $\nu_s$(CHgC) | $\nu_a$(CHgC) | $\delta$(CHgC) | | $K$(CHg) | $F$(CHg, CHg) | $H$(CHgC) | Ref. |
| $[Hg(CH_3)_2]$ | 520.4 [a] | 546.3 [a] | 153 [c] | gas | 2.38 | 0.031 | 0.104 | 1 |
| $[Hg(CD_3)_2]$ | 475.1 [b] | 496.7 [b] | 141 [e] | gas | | | | |
| $[Hg(CF_3)(CH_3)]$ | 551($CH_3$) | 241($CF_3$) | 115.3 [d] | gas | 2.23($CF_3$) [g] | 0.07 | 0.083 | 6,17 |
| $[Hg(CF_3)(CD_3)]$ | 502($CD_3$) | 241($CF_3$) | 105.4 [d] | gas | 2.68($CH_3$) [g] | | | 6,17 |
| $[Hg(CF_3)_2]$ | 225 | 272 | 70 | solution | 2.22 | 0.230 | 0.129 | this work |
| | 224 | 271 | 68 | solution | 2.18 | 0.200 | 0.111 | 4 |
| $[Hg(CCl_3)_2]$ | 151 | 200 | 41 [f] | solution | 2.17 | 0.135 | 0.088 | this work |

[a] High resolution IR measurement [18]. [b] Gas Raman measurement [19]. [c] Liquid phase [20]. [d] Raman liquid [7]. [e] Ref. [21]. [f] Calculated. [g] Force constant data communicated by Gunthard [17].

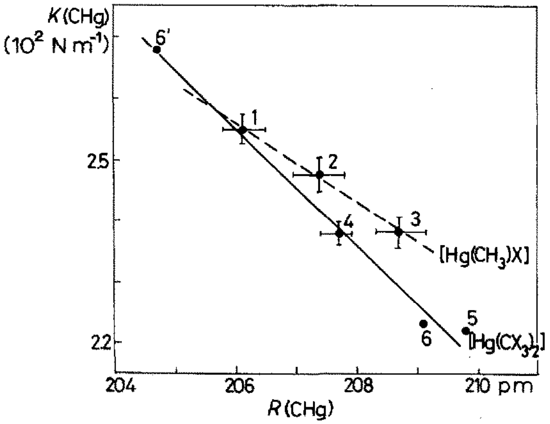

Fig. 1. Correlation between HgC bond lengths ($r_0$ or $r_e$) and stretching force constants. 1, $[Hg(CH_3)Cl]$ [2,22]; 2, $[Hg(CH_3)Br]$ [2,22]; 3, $[Hg(CH_3)I]$ [2,23]; 4, $[Hg(CH_3)_2]$ [1,24]; 5, $[Hg(CF_3)_2]$ [8]; 6 and 6′ $[Hg(CF_3)(CH_3)]$ [17].

17] the Hg–$CH_3$ or Hg–$CD_3$ stretches are slightly higher than the frequencies of the asymmetric stretches of the $[Hg(CH_3/D_3)_2]$ derivatives but the Hg–$CF_3$ stretch is nearer to the mean value of the two stretching modes in $[Hg(CF_3)_2]$. On the basis of this behaviour we could expect a molecule $[Hg(CCl_3)(CH_3)]$ to show its Hg–$CCl_3$ stretching vibration at about 170 $cm^{-1}$. As the masses of the methyl substituents in $[Hg(CY_3)_2]$ increases the separation of the symmetric and asymmetric stretching modes is proportionately greater. However, although for both the $CF_3$ and $CCl_3$ derivatives the $F$(CHg, CHg) interaction constants are much greater than for

TABLE 7

SKELETAL WAVENUMBERS FOR METHYL DERIVATIVES OF MERCURY(II), OBTAINED FROM SOLUTIONS

| Compound | $\nu$(CHg) | $\nu$(HgX) | $\delta$(CHgX) | Ref. |
|---|---|---|---|---|
| $[Hg(CH_3)Cl]$ | 553 | 335.5 | 135 | 2 |
| $[Hg(CD_3)Cl]$ | 506.8 | 334.8 | 125 | 2 |
| $[HgBr(CH_3)]$ | 545.3 | 228 | 121 | 2 |
| $[HgBr(CD_3)]$ | 499 | 227.8 | 110 | 2 |
| $[Hg(CH_3)I]$ | 533 | 181 | 122 | 2 |
| $[Hg(CD_3)I]$ | 498.5 | 181 | 104 | 2 |
| $[Hg(CH_3)CN]$ | 559 | 378 | 124 | 25 |
| $[Hg(CD_3)CN]$ | 510 | 384 | 115 | 25 |
| $[Hg(CF_3)Cl]$ | 250 | 355 | 96 | |
| $[HgBr(CF_3)]$ | 277 | 216 | 73 | |
| $[Hg(CF_3)I]$ | 256 | 176 | 60 | |
| $[Hg(CF_3)N_3]$ | 263 | 399 | 140 | 5 |
| $[Hg(CF_3)NCO]$ [a] | 264 | 404 | 140 | 5 |
| $[Hg(CCl_3)Cl]$ | 177 | 350 | 83 | |
| $[HgBr(CCl_3)]$ | 168.5 | 247 | 63 | |

[a] From Raman spectra of dimers in solid state.

TABLE 8

FORCE CONSTANTS FOR METHYL DERIVATIVES OF MERCURY(II) [$10^2$ N $m^{-1}$]

| Compound | *K*(CHg) | *K*(HgX) | *H*(CHgX) | *K*(CH)<br>*K*(CF)<br>*K*(CCl) | Ref. |
|---|---|---|---|---|---|
| [$Hg(CH_3)Cl$] | 2.55 | 2.08 | 0.097 | 4.87 | 2 |
| [$HgBr(CH_3)$] | 2.48 | 1.79 | 0.086 | 4.87 | 2 |
| [$Hg(CH_3)I$] | 2.38 | 1.55 | 0.076 | 4.86 | 2 |
| [$Hg(CH_3)CN$] | 2.45 | 2.38 | | 4.77 | 25 |
| [$Hg(CF_3)Cl$] | 2.22 | 2.57 | 0.156 | 5.45 | |
| [$HgBr(CF_3)$] | 2.10 | 2.17 | 0.145 | 5.34 | |
| [$Hg(CF_3)I$] | 2.00 | 1.79 | 0.133 | 5.46 | |
| [$Hg(CF_3)N_3$] | 2.37 | 2.00 | 0.155 | 5.06 | 5 |
| [$Hg(CF_3)NCO$] | 2.37 | 2.10 | 0.150 | 5.06 | 5 |
| [$Hg(CCl_3)Cl$] | 2.21 | 2.04 | 0.134 | 2.76 | |
| [$HgBr(CCl_3)$] | 1.97 | 2.12 | 0.151 | 2.79 | |

[$Hg(CH_3)_2$] it is by far the largest in [$Hg(CF_3)_2$]. The *K*(CHg) force constant decreases in the order $CH_3 > CF_3 > CCl_3$ but by less than 10% between the first and last.

Figure 1 shows a fair linear correlation between mercury–carbon bond lengths (gas phase values) and stretching force constants. The distances shown for [$Hg(CH_3)X$] are $r_0$ bond lengths from microwave measurements [22,23], for [$Hg(CH_3)_2$] [24] and [$Hg(CF_3)_2$] [8] are $r_e$ distances from electron diffraction, and those for [$Hg(CF_3)(CH_3)$] are the $r_0$ and $r_s$ values from microwave spectroscopy [17]. The approximate general correlation is much improved if it is viewed in terms of two series, [$Hg(CH_3)X$] and mercury dialkyls.

The skeletal frequencies of [$Hg(CY_3)X$] derivatives are summarised in Table 7,

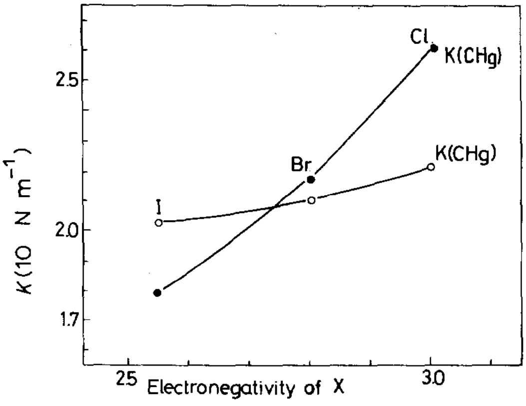

Fig. 2. Relationship of HgC and HgX stretching force constants to the electronegativity of X in [$Hg(CF_3)X$].

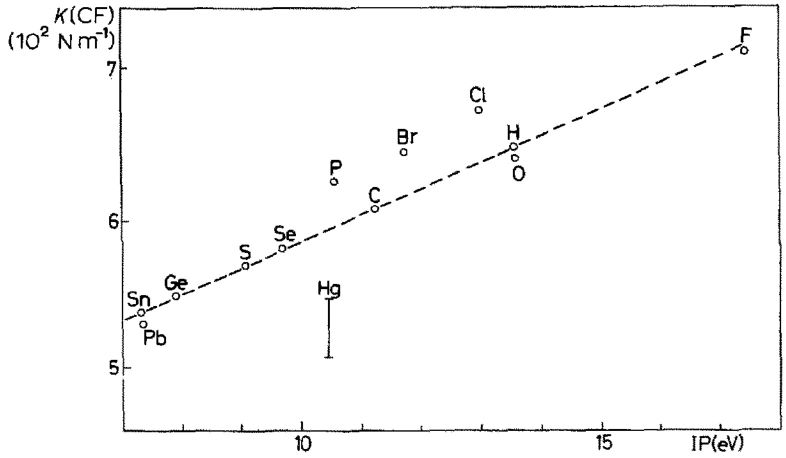

Fig. 3. Relationship of CF stretching force constants to the first ionisation potential of X in $CF_3X$. F, $CF_4$ [29,30]; H, $CF_3H$ [32,33]; O, $O(CF_3)_2$ [34]; C, $C(CF_3)_4$ [35]; Se, $CF_3SeX(Cl, Br)$ [37]; S, $N(SCF_3)_3$ [38]; Cl, $CF_3Cl$ [31]; Br, $CF_3Br$ [31]; P, $P(CF_3)_3$ [36]; Ge, $[Ge(CF_3)(CH_3)_3]$ [39]; Sn, $[Sn(CF_3)(CH_3)_3]$ [39]; Pb, $[Pb(CF_3)(CH_3)_3]$ [39].

and force constants of primary importance in Table 8. Between $CH_3$ and $CF_3$ series the Hg–C force constants fall by 13–16% whilst the Hg–X force constants rises by 24 (Cl), 21 (Br) and 15 (I) %. Figure 2 shows an almost linear correlation between the skeletal stretching force constants of $[Hg(CF_3)X]$ and the electronegativity of X, and similar relationships exist between these force constants and electron affinity or first ionisation potential of X as suggested previously for $[Hg(CH_3)X]$ [26].

An empirical relationship between HgX stretching force constants and bond

TABLE 9

CF STRETCHING FORCE CONSTANTS FOR $CF_3X$ TYPE DERIVATIVES

| Compound | X | K(CF) ($10^2$ N $m^{-1}$) | IP of X (eV) | Ref. |
|---|---|---|---|---|
| $CF_4$ | F | 6.97 | 17.4 | 29 |
| | | 7.16 | | 30 |
| $CF_3Cl$ | Cl | 6.75 | 1301 | 31 |
| $HCF_3$ | H | 6.48 | 13.6 | 32 |
| | | 6.45 | | 33 |
| $CF_3Br$ | Br | 6.46 | 11.84 | 30 |
| $O(CF_3)_2$ | O | 6.40 | 13.6 | 34 |
| $C(CF_3)_4$ | C | 6.09 | 11.3 | 35 |
| $P(CF_3)_3$ | P | 6.24 | 10.5 | 36 |
| $CF_3SeX$ (X = Cl, Br) | Se | 5.82 | 9.75 | 37 |
| $N(SCF_3)_3$ | S | 5.79 | 9.15 | 38 |
| $[Hg(CF_3)X]$ | Hg | 5.06–5.46 | 10.43 | this work |
| $[Ge(CF_3)(CH_3)_3]$ | Ge | 5.50 | 7.9 | 39 |
| $[Sn(CF_3)(CH_3)_3]$ | Sn | 5.38 | 7.34 | 39 |
| $[Pb(CF_3)(CH_3)_3]$ | Pb | 5.29 | 7.41 | 39 |

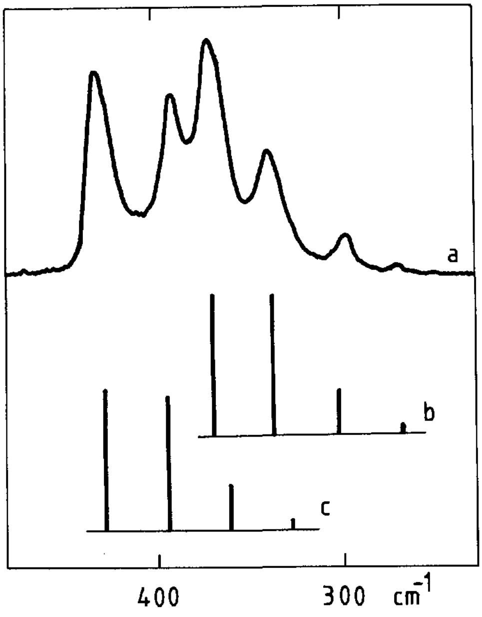

Fig. 4. Raman spectrum for solid [Hg(CCl$_3$)Cl] at 100 K in the range of $\nu_2$. (a) observed spectrum, (b) isotope effect of in-phase vibration, (c) isotope effect of out-of-phase vibration.

dissociation energies of HgX$_2$ molecules [27] is found, of the form

$$Q = 105\,K(\mathrm{HgX}) + 57.5 \qquad (5)$$

where $Q$ is in kJ mol$^{-1}$ and $K$(HgX) is in $10^2$ N m$^{-1}$. If this is used for organomercury halides the HgX bond dissociation energies are calculated to be:

| | [Hg(CH$_3$)X] | [Hg(C$_2$H$_5$)X] | [Hg(CF$_3$)X] | [Hg(CCl$_3$)X] |
|---|---|---|---|---|
| X = Cl | 276 | 254 | 327 | 272 |
| X = Br | 245 | 249 | 285 | 280 |
| X = I | 220 | 217 | 245 | |

The force constants for the ethyl derivatives are taken from reference [28].

For trifluoromethylmercury derivatives the CF stretching force constants are in the range 5.06–5.46 × $10^2$ N m$^{-1}$, which is much less than for many other CF$_3$ systems (Table 9) although similar to [M(CF$_3$)(CH$_3$)$_3$] compounds (M = Ge, Sn or Pb) [39]. Lower values have been reported for the anion [CF$_3$BF$_3$]$^-$ (4.85 × $10^2$ N m$^{-1}$) [40] and for CF$_3$CN (4.15 × $10^2$ N m$^{-1}$) [41]. The values reported in the literature correlate quite well with the first ionisation potential of the element to which the CF$_3$ group is attached (Fig. 3) but those of the mercury compounds are substantially lower than such a relationship implies. In the same way as $K$(CF) of [Hg(CF$_3$)$_2$] is lower than in CF$_4$, $K$(CCl) of [Hg(CCl$_3$)$_2$] is substantially lower than in CCl$_4$ [15,29].

For solid [Hg(CCl$_3$)Cl], the Raman spectrum recorded at 100 K showed a six band multiplet near 400 cm$^{-1}$ [3]. At natural abundance the CCl$_3$ group gives rise to four chlorine-isotopic species with relative abundances 100 (3$^{35}$Cl) 97 (1$^{37}$Cl, 2$^{35}$Cl) 31 (2$^{37}$Cl, 1$^{35}$Cl) 3 (3$^{37}$Cl). Using the force field given in Table 4 for [Hg(CCl$_3$)Cl] the wavenumber separation for the four isotopic species was calculated. With a 6.6 cm$^{-1}$ correlation splitting the eight bands expected partially overlap to give the six peak pattern observed as a result of the joint isotope and lattice effect as shown in Fig. 4.

## References

1 J. Mink and B. Gellai, J. Organometal. Chem., 66 (1974) 1.
2 P.L. Goggin, G. Kemény, and J. Mink, J. Chem. Soc., Faraday Trans. II, 72 (1976) 1025.
3 P.L. Goggin, R.J. Goodfellow, K. Kessler, and A.M. Prescott, J. Chem. Soc., Dalton Trans., (1978) 328.
4 D.J. Brauer, H. Bürger, and R. Eujen, J. Organometal. Chem., 135 (1977) 281.
5 D.J. Brauer, H. Bürger, G. Pawelke, K.H. Flegler, and A. Haas, J. Organometal. Chem., 160 (1978) 389.
6 R. Eujen, J. Mol. Struct., 53 (1975) 1.
7 Y. Hase, An. Acad. Bras. Cienc., 51 (1979) 623.
8 H. Oberhammer, J. Mol. Struct., 48 (1978) 389.
9 J. Mink. G. Kemény, and L.M. Mink. Hung. Acad. Sci., Central Res. Inst. Phys., KFKI-76-47 (1976).
10 J. Mink, L.M. Mink, and Yu.A. Pentin, Vestnik Mosk. Gos. Univ., 3 (1971) 286.
11 A. Ruoff and H. Bürger, Spectrochim. Acta, A, 26 (1970) 988.
12 K.H. Schmidt and A. Müller, J. Mol. Spectrosc., 50 (1974) 115.
13 R.J.H. Clark, O.H. Ellestad, and R. Escribano, Mol. Phys., 31 (1976) 65.
14 I.M. Mills, Spectrochim. Acta, 19 (1963) 1585.
15 I.W. Levin and W.C. Harris, J. Chem. Phys., 57 (1972) 2715.
16 P. Torkington, J. Chem. Phys., 17 (1949) 357.
17 H. Günther, Personal communication.
18 J. Mink, D. Chem. Sci. Thesis, Institute of Isotopes of the Hung. Acad. Sci., Budapest, 1980
19 G. Kemény, Ph.D. Thesis Institute of Isotopes of the Hung. Acad. Sci., Budapest, 1977.
20 J.R. Durig and S.C. Brown, J. Mol. Spectrosc., 45 (1973) 338.
21 L.A. Woodward, Spectrochim. Acta, 19 (1963) 1963.
22 W. Gordy and J. Sheridan, J. Chem. Phys., 22 (1954) 92.
23 G. Walls, D.G. Lister, and J. Sheridan, J. Chem. Soc., Faraday Trans. II, 71 (1975) 1091.
24 K. Kashiwabara, S. Konaka, T. Iijima, and M. Kimura, Bull. Chem. Soc. Jpn., 46 (1973) 407.
25 Y. Imai and K. Aida, J. Inorg. Nucl. Chem., 41 (1979) 963.
26 J. Mink and P.L. Goggin, J. Organometal. Chem., 156 (1978) 317.
27 T. Charnley and H.A. Skinner, J. Chem. Soc., (1951) 1921.
28 J. Mink and P.L. Goggin, J. Organometal. Chem., 185 (1980) 129.
29 W. Sawodny, Kémiai Közlemények, 46 (1976) 263.
30 A. Ruoff, Spectrochim. Acta, A, 23 (1967) 2421.
31 H. Bürger, K. Burzik, D. Bielefeldt, H. Willner, A. Ruoff, and K. Molt. Spectrochim. Acta, A, 35 (1979) 875.
32 R.W. Kirk and P.M. Wilt, J. Mol. Spectrosc., 58 (1975) 102.
33 A. Ruoff, H. Bürger, and S. Biedermann, Spectrochim. Acta, A, 27 (1971) 1377.
34 H. Bürger and G. Pavelke, Spectrochim. Acta. A, 31 (1975) 1965.
35 H. Bürger, R. Eujen, and R.J. Lagow, Spectrochim, Acta, A. 31 (1975) 777.
36 H. Bürger, J. Cichon, J. Grobe, and F. Höfler, Spectrochim. Acta, A, 28 (1972) 1275.
37 P.K. Wami and N.D. Patel, Can. J. Spectrosc., 20 (1975) 166.
38 H. Bürger, G. Pawelke, A. Haas, H. Willner, and A.J. Downs, Spectrochim. Acta, A, 34 (1978) 287.
39 R. Eujen and H. Bürger, Spectrochim, Acta, A, 35 (1979) 1135.
40 D.J. Brauer, H. Bürger, and G. Pawelke, Inorg. Chem., 16 (1977) 2305.
41 W.F. Edgell and R.M. Potter, J. Chem. Phys., 24 (1956) 80.