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INFRARED, RAMAN AND FORCE FIELD STUDIES OF ETHYLMERCURY(II) HALIDES

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Summary. Vibrational assignments for $Hg(C_2H_5)X$ (X = Cl, Br or I) and $HgBr(C_2D_5)$ are proposed, on the basis of solution studies as far as possible. For the bromides, 21 force constants are refined in the presence of 12 constrained values from C_2H_5Cl and 12 of these are used as additional constraints in refining 9 force constants for the chloride and iodide. The nature of the normal modes of $Hg(C_2H_5)Cl$ is discussed. The Hg-C stretching force constants of the ethyl compounds is marginally higher than in corresponding methyl derivatives.

There have been several investigations of the vibrational spectra of diethylmercury [1-9] but those of the ethylmercury halides have received comparatively little attention [3,5,6,10]. Infrared and Raman spectra of liquid ethylmercury cyclopentadienyl [11] and of solid bis-ethylmercury-cyanamide [11] and ethylmercury azide [12] have been studied. The measurements reported for the ethylmercury halides have

for the most part been from infrared spectra of solids; only limited Raman data are available [11,12]. In no case has there been any report of spectra of deuteriated ethylmercury halides, although those of $Hg(CH_2CD_3)_2$ [7] and $Hg(C_2D_5)_2$ [8] have been documented. Normal coordinate calculations have only been performed for $Hg(C_2H_5)_2$ [5,12,13].

The incompleteness of vibrational data and force field studies for ethyl derivatives of metals has recently been noted in books by both Maslowsky [14] and Nakamoto [15]. It seemed important, therefore, to make a careful re-examination of the vibrational spectra of the ethylmercury halides in solution and in the solid state. Here we present our attempt at interpretation of the infrared and Raman spectra of $Hg(C_2H_5)X$ (X = Cl, Br, and I) and $HgBr(C_2D_5)$, together with the calculation of their force constants.

Results

Vibrational assignments: Molecules $Hg(C_2H_5)X$ with the gauche ethyl group configuration are of point group C_s. They have 21 vibrational fundamentals, 13 symmetrical with respect to the plane of symmetry (A' modes) and 8 unsymmetrical (A" modes). The A' modes may be unambiguously identified in Raman spectra of solutions if they give rise to detectably polarised bands. In addition to our own measurements, results of previous assignments for these [6,10,13] and the related molecules diethylmercury [5,6,7,10], ethyl halides [16-21] and ethyl cyanide [22] have been used.

Most of the fundamentals have been determined from solution spectra and are summarised in Table 1; values from solid state measurements are only included where solubility limitations or solvent interference prevented their observation in solution.

Overlap of CH_3 and CH_2 modes gives rise to some difficulty in assigning CH stretching vibrations. Four intense i.r. bands are observed and Raman measurements confirm that two of them contain A' components. It is probably valid that the highest includes the CH_2 symmetric stretch and that the lowest is the CH_3 symmetric stretch [21],

and that the depolarised feature observed for the bromide and iodide is A" CH_3 asymmetric stretch. The assignment of ν_{14} as coincident with ν_1 is somewhat arbitrary; in ethyl iodide the asymmetric CH_2 stretch is assigned to a weak band above 3000 cm^{-1} [16] and it is possible that we are not observing it for the ethylmercury compounds.

Asymmetric deformations of methyl groups and methylene bending modes invariably occur in the same range, 1400-1500 cm^{-1}. The highest band in this region showed two components in the i.r. spectra of the solids. For solutions the i.r. spectrum of the chloride showed a high wavenumber shoulder on the band just above 1450 as did the Raman spectrum of the iodide. We assign the two methyl group modes above the methylene mode. The CH_3 symmetric deformation is assigned around 1380 cm^{-1}.

The intense, coincident i.r. and polarised Raman bands just below 1200 cm^{-1} are the most halide-sensitive of the ethyl group modes and can be readily assigned to CH_2 wagging (they are akin to the symmetric CH_3 deformation of $Hg(CH_3)X$ which shows similar X-sensitivity [23]). This differs from earlier assignments of this mode in ethylmercury systems which were studied by i.r. alone and/or without the aid of a deuteriated analogue [6,10-13]; it is in keeping with the behaviour observed in other heavy-atom ethyls [7,24].

The observation that the Raman band around 960 cm^{-1} for the bromide and iodide is polarised suggests its origin as C-C stretching. We note that in the i.r. spectra of the solids there are always two bands in this region separated by 11, 14 and 16 cm^{-1} respectively for increasing X mass, but there is only one band observed for the solutions. The CH_3 rocking mode in $Hg(CH_3)X$ was observed as a very strong i.r. band near 760 cm^{-1}, with at best a very weak Raman counterpart [23]. The band just below 700 cm^{-1} for the ethyl analogues has the same intensity characteristics and is thus assigned as CH_2 rocking (ν_{19}).

The strong, polarised Raman band just above 500 cm^{-1} is clearly due to Hg-C stretching (ν_{10}) and shows the same halide sensitivity

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TABLE 1

OBSERVED VIBRATIONAL WAVENUMBERS[a], AND ASSIGNMENTS PROPOSED, FOR ETHYLMERCURY HALIDES

	$Hg(C_2H_5)Cl$		$HgBr(C_2H_5)$		$HgBr(C_2D_5)$		$Hg(C_2H_5)I$		
	I.r. ($CDCl_3$)	R (C_6H_6)	I.r. ($CDCl_3$)	R ($CDCl_3$)	I.r. (CCl_4 or CS_2)	R (dioxane)	I.r. ($CDCl_3$)	R ($CDCl_3$)	
A'	2 978ms[b]		2 979s[b]			2 155m,p	2 977s[b]		ν_1 $CH_2(CD_2)$ sym str
	2 925ms	2 930w	2 932s	2 931w,p	2 208ms[b]	2 220w,p	2 929s	2 930m,p	ν_2 $CH_3(CD_3)$ asym str
	2 873s	2 864w	2 872vs	2 871w,p	2 071s	2 083m,p	2 869s	2 871wm,p	ν_3 $CH_3(CD_3)$ sym str
	1 455ms	1 455w	1 453m[b]	1 450vw[b]	1 059m	1 061vw	1 453w,br	1 453w,br,p	ν_4 $CH_3(CD_3)$ asym def
	1 431w	1 430vvw	1 430w	1 424vvw	1 055m,sh[b]		1 429vw,sh	1 424vw	ν_5 $CH_2(CD_2)$ bend
	1 379m	1 373vw	1 379w	1 372vw	1 128w		1 377w	1 383vw,dp	ν_6 $CH_3(CD_3)$ sym def
	1 193vs	1 197s,p	1 186s	1 189s,p	976vs	987m,p	1 178vs	1 178s,p	ν_7 $CH_2(CD_2)$ wag
	1 024wm[b]	1 026vw	1 021w	1 037vvw	885vw[b]		1 027vw[b]	1 034w	ν_8 $CH_3(CD_3)$ rock
	967m	967vvw	965m	959vw,p		735vw[b]	963w	963vw,p	ν_9 CC str
	530s	527s,p	520s	521s,p	466m	475s,p		508vs,p	ν_{10} HgC str
	251m	254m,p	260w	255w,br	258w	244w,p		247wm,p[c]	ν_{11} CCHg bend
	330s	326s,p	218s[c]	221s,p	206m	217m,p	174s[c]	176vs,p	ν_{12} HgX str
	84s,br[c]		65m,br[c]		72m,br[c]		60m,br[c]		ν_{13} CHgX bend (in plane)

A"	2 978ms[b]		2 979s[b]		2 230ms		2 977s[b]		ν_{14} $CH_2(CD_2)$ asym str
	2 958ms	2 954w	2 957s	2 956vw,dp	2 208ms[b]		2 956s	2 953s,dp	ν_{15} $CH_3(CD_3)$ asym str
	1 470vw,sh		1 453m[b]	1 450vw[b]	1 055m,sh[b]			1 468sh,dp	ν_{16} $CH_3(CD_3)$ asym def
	1 122w	1 122w	1 122vw,br	1 122vvw	885vw[b]		1 120vvw		$\nu_{17}CH_3(CD_3)$ rock
	1 024wm[b]	1 025wm	1 021w	1 018vvw		735vw[b]	1 027vw[b]	1 034w	ν_{18} $CH_2(CD_2)$ twist
	694vs[d]		692s[d]		517m		692vs[d]		ν_{19} $CH_2(CD_2)$ rock
	173vw[c]		177w[c]						ν_{20} $CH_3(CD_3)$ torsion
	120w,sh[c]		120w,sh[c]	118vw,br				98w,br	ν_{21} CHgX def (out of plane)
	Other bands								
	2 932w,sh	2 915w,sh	2 921sh	2 914w,sh	2 146w	2 140sh			
	2 902w		2 900vw		2 124vw		2 901vw,sh	2 906vw,sh	$2\nu_4$
	2 832w,sh		2 833vw		2 160vw		2 835vw,sh		$\nu_4 + \nu_6$
	2 739w	2 730vvw	2 738w				2 736vw		$2\nu_6$
					2 098vw				$2\nu_5$
					2 036vw	2 033vw			$\nu_5 + \nu_7$
						1 970w,p			$2\nu_7$
	1 222w,sh		1 233w,sh	953vvw	698w		1 212vw,sh		$\nu_{10} + \nu_{19}$
	76m,sh		80sh	78w,sh			1 230vw		

[a]Solution values given where possible. Wavenumbers of features found only in solid state spectra are in italics.

[b]Wavenumber assigned to two fundamentals

[c]C_6H_6 solution.

[d]$(CH_3)_2CO$ solution.

as the corresponding mode of $Hg(CH_3)X$. The solid Raman spectrum of $Hg(C_2H_5)Cl$ showed an additional weak feature 17 cm^{-1} to low wavenumber which may be the corresponding Hg-^{13}C mode.

In addition to the HgX stretching modes which are obvious and the CHgX bending modes to be expected below 130 cm^{-1} [23] there are two more low wavenumber fundamentals to be assigned, CCHg bending (ν_{11}) and the internal ethyl-group torsion (ν_{20}). The former is readily distinguished by its polarised character in the Raman spectra.

The ethyl group modes so far not discussed are A' and A" CH_3 rocking, and A" CH_2 twisting, with i.r. bands about 1 120 cm^{-1} and, i.r. and Raman bands about 1 020 cm^{-1} in all cases to consider. The assignments are somewhat arbitrary but previous assignments for ethyl halides have always placed the two CH_3 rocking modes well separated, although not by as much as 100 cm^{-1}.

For $HgBr(C_2D_5)$, there are three polarised Raman features in the CD stretching region identifying the A' modes. The medium, polarised band at 967 cm^{-1} is presumably the CD_2 wagging mode. Between 900 and 700 cm^{-1}, where C-C stretching CD_2 twisting and two CD_3 rocking modes would be expected on the basis of assignments for C_2D_5Br, we only observe one i.r. band (885 cm^{-1}) and one Raman band (735 cm^{-1}); we tentatively associate the two rocking modes with the higher wavenumber feature and the other two vibrations with the lower.

Force Constant Calculations: For the normal coordinate calculations tetrahedral angles about C and linear geometry about Hg have been assumed. Bond lengths have been taken from similar molecules [25,26]: r_{CH} = 109 pm; r_{CC} = 156 pm; r_{HgC} = 206, 207, 209 and r_{HgX} = 228, 241, 253 pm for X = Cl, Br and I respectively.

The internal coordinates are shown in Fig. 1. The procedures used for calculating the G matrix and refining the force constants have been outlined previously [27,28]. Initial trial force constants were taken from the ethyl halides [17,20,21,29] and the methylmercury halides [23]. The force field applied by Dempster and Zerbi [20] gave the best

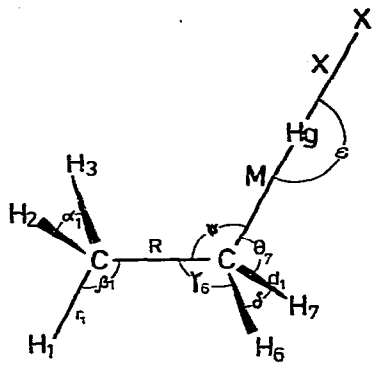

Figure 1. Internal co-ordinates for C_2H_5HgX
Additional co-ordinates: ε' out-of-plane CHgX deformation, τ methyl torsional mode.

agreement between observed and calculated wavenumbers for the ethyl and is the basis of the results presented here.

There are 42 possible fundamentals for $HgBr(C_2H_5)$ and $HgBr(C_2D_5)$ together. For the latter only one feature is observed below 200 cm^{-1}. We are reasonably confident of 33 of our assignments. Whilst the remaining ones are debatable those proposed are in roughly the right wavenumber region. We have attempted to refine 21 force constants which include all 13 diagonal force constants, 4 stretch-stretch interaction constants, 3 angle-angle cross terms (one about the CH_3 group and two about the CH_2 group), and the torsional force constant. The stretch-bend and other bend-bend interaction constants have been constrained to the values of Dempster and Zerbi for C_2H_5Cl [20].

The refined force constants for the bromides were transferred to $Hg(C_2H_5)Cl$ and $Hg(C_2H_5)I$, and the stretch and stretch-stretch interaction force constants for the CH_2HgX (X = Cl and I) groups further refined together with C-C stretching and CHgX bending force constants.

The final force constants, expressed in terms of internal coordinates are given in Table 2. Comparisons between assigned experimental and calculated wavenumbers are presented in Table 3.

TABLE 2.

FORCE CONSTANTS FOR $Hg(C_2H_5)X$ (X = Cl, Br or I) MOLECULES

Force constant	Group	Coordinates involved	Common atom(s)	X = Cl	X = Br	X = I	
Stretch							
K_r	CH_3	CH	-		4.642		a
K_d	CH_2	CH	-	4.844	4.845	4.841	a
K_R	CC	CC	-	4.202	3.99	4.187	a
K_M	CHg	CHg	-	2.643	2.517	2.469	a
K_X	HgX	HgX	-	1.876	1.792	1.518	a
Stretch-stretch							
F_r	CH_3	CH,CH	C		0.106		a
F_d	CH_2	CH,CH	C	0.121	0.120	0.121	a
F_{RM}	C,CHg	CC,CHg	C	0.581	0.563	0.541	a
F_{MX}	CHg,HgX	CHg,HgX	Hg	0.025	0.024	0.004	a
Bend							
H_α	CH_3	HCH	-		0.536		c
H_β	CH_3	HCC	-		0.621		c
H_δ	CH_2	HCH	-		0.361		c
H_γ	CH_2	HCC	-		0.586		c
H_ψ	CCHg	CCHg	-		0.939		c
H_θ	HCHg	HCHg	-		0.811		c
H_ϵ	CHgX	in-plane	-	0.545	0.356	0.256	c
$H_{\epsilon'}$	CHgX	out-of-plane	-	0.456	0.456	0.456	c
Stretch-bend							
$F_{R\beta}$	CH_3-C	CC,HCC	C-C		(0.173)		b
$F_{R\gamma}$	C-CH_2	CC,CCH	C-C		(0.215)		b
$F_{R\psi}$	CCHg	CC,CCHg	C-C		(-0.114)		b
$F_{R\theta}$	C-CH_2-Hg	CC,HCHg	C		(-0.139)		
$F_{M\psi}$	CCHg	CHg,CCHg	C-Hg		(0.293)		
$F_{M\theta}$	C-CH_2-Hg	CHg,HCHg	C-Hg		(0.550)		

Bend-bend					
F_{β}	CH_3-C	HCC,HCC	C-C	-0.019	c
F_{γ}	C-CH_2	HCC,HCC	C-C	-0.002	c
F_{θ}	CH_2Hg	HCHg,HCHg	C-Hg	0.313	c
$f^{t}_{\beta\psi}$	CH-C-Hg	$\{^{HCC,CCHg}_{trans}$	C-C	(0.037)	c
$f^{g}_{\beta\psi}$	CH-C-Hg	$\{^{HCC,CCHg}_{gauche}$	C-C	(-0.037)	c
$f^{t}_{\beta\gamma}$	-CH_2-CH_2-	$\{^{HCC,CCH}_{trans}$	C-C	(0.075)	c
$f^{g}_{\beta\gamma}$	-CH_2-CH_2-	$\{^{HCC,CCH}_{gauche}$	C-C	(-0.068)	c
$f_{\gamma\theta}$	C-CH_2-Hg	H_6CC,H_6CHg	H-C	(0.091)	c
$f_{\gamma\theta'}$	C-CH_2-Hg	H_6CC,H_7CHg	C	(0.029)	c
Torsion					
H_{τ}	HC-CHg	C-C	-	0.056	c

a)/10^{2} N m^{-1}; b)/10^{-8} N rad^{-1}; c)/10^{-18} N m rad^{-2}

Remarks: bracketed values were constrained; values omitted for Hg(C_2H_5)Cl and Hg(C_2H_5)I were set equal to those of HgBr(C_2H_5).

Discussion

For the two isotopic variants of ethylmercury bromide agreement between proposed experimental assignments and calculated wavenumbers is quite good, but the CH_3 rocking modes ν_8 and ν_{17} which depend to a great extent on constrained force constants, and for which assignments were the more speculative, proved the most difficult to accommodate. These modes proved the most difficult to fit in the detailed studies on the ethyl halides; indeed the highly mixed nature of the modes in this frequency region could well lead to a number of equally acceptable solutions even with a completely general force field.

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TABLE 3

EXPERIMENTAL AND CALCULATED FUNDAMENTAL WAVENUMBERS FOR $Hg(C_2H_5)X$

ASSIGNMENT AND APPROXIMATE DESCRIPTION OF MODE		$Hg(C_2H_5)Cl$		$HgBr(C_2H_5)$		$HgBr(C_2D_5)$[a]		$Hg(C_2H_5)I$	
		Obs.	Calc.	Obs.	Calc.	Obs.	Calc.	Obs.	Calc.
A'	ν_1 CH_2 sym str	2978[b]	2978	2979[b]	2975.1	2155	2170.7	2977[b]	2977
	ν_2 CH_3 asym str	2925	2923.1	2931	2943.4	2208[b]	2196.5	2930	2922.5
	ν_3 CH_3 sym str	2873	2903.9	2871	2870.5	2071	2071.7	2871	2903.7
	ν_4 CH_3 asym def	1455	1463.5	1453	1464.4	1059[b]	1051.0	1453	1463.5
	ν_5 CH_2 bend	1431	1443.2	1430	1441.4	1055	1036.0	1429	1442.8
	ν_6 CH_3 sym def	1379	1367.6	1379	1368	1128	1128.2	1383	1367.4
	ν_7 CH_2 wag	1193	1199.8	1189	1196.7	976	945.8	1178	1198.8
	ν_8 CH_3 rock	1024[b]	1069.5	1021[b]	1067.3	885[b,c]	850.5	1027[b]	1067.5
	ν_9 CC str	967	966.3	959	950.8	735	769.8	963	964.1
	ν_{10} CHg str	527	526.7	521	513.0	475	475.5	508	507.7
	ν_{11} CCHg bend	254	264.5	255	268.6	244	247.4	247	263.6
	ν_{12} HgX str	326	326	221	222.7	217	215.9	176	176
	ν_{13} CHgX def (in plane)	84[d]	101.8	65[d]	75.9	72[d]	71.7	60	56

A" ν_{14} CH_2 asym str	2978[b]	2979.9	2979[b]	2980.6	2230	2223.6	2977[b]	2980
ν_{15} CH_3 asym str	2958	2921.9	2956	2921.8	2208[b]	2179.3	2953	2920.6
ν_{16} CH_3 asym def	1470	1480.1	1450	1480.0	1059[b]	1065.9	1468	1480.1
ν_{17} CH_3 rock	1122	1086.4	1122	1086.3	885[b,c]	854.4	1120	1085.8
ν_{18} CH_2 twist	1024[b]	1019.5	1021[b]	1019.6	735	732	1027[b]	1019.7
ν_{19} CH_2 rock	694	689.3	692	689.2	517	511.7	692	688.7
ν_{20} CH_3 torsion	174	181.3	177	180		135.1		180.2
ν_{21} CHgX def (out of plane)	120	122.9	120	112.3		96.9		107.9

[a] The ν_1, ν_9-ν_{12} modes taken from Raman spectra of dioxane solution

[b] Wavenumber used twice

[c] From i.r. spectrum of solid

[d] Broad band the maximum position is not certain

TABLE 4

POTENTIAL ENERGY DISTRIBUTION FOR $Hg(C_2H_5)Cl$

		P.E.D. x 100	Approximate descriptions
A'	ν_1	99(d)	CH_2 sym str
	ν_2	68(r_1) 34(r_{23})	CH_3 asym str
	ν_3	31(r_1) 65(r_{23})	CH_3 sym str
	ν_4	96(α) 12(β_1)	CH_3 asym def
	ν_5	100(θ)	CH_2 bend
	ν_6	90(α) 31(β_1) 88(β_{23}) 12(γ)	CH_3 sym def
	ν_7	140(γ) 35(θ)	CH_2 wag
	ν_8	11(α) 69(β_1) 72(β_{23})	CH_3 rock
	ν_9	74(R) 27(β_1)	CC str
	ν_{10}	117(M) 23(γ) 21(ψ) 20(θ)	CHg str
	ν_{11}	12(M) 81(ψ)	CCHg bend
	ν_{12}	95(X)	HgCl str
	ν_{13}	92(ε)	CHgCl def (in plane)
A"	ν_{14}	99(d)	CH_2 asym str
	ν_{15}	99(r)	CH_3 asym str
	ν_{16}	90(α) 6(β)	CH_3 asym def
	ν_{17}	57(β) 19(θ)	CH_3 rock
	ν_{18}	8(β) 87(γ) 21(θ)	CH_2 twist
	ν_{19}	34(β) 13(γ) 68(θ)	CH_2 rock
	ν_{20}	90(τ) 9(ε')	CH_3 torsion
	ν_{21}	9(τ) 37(ε')	CHgCl def (out of plane)

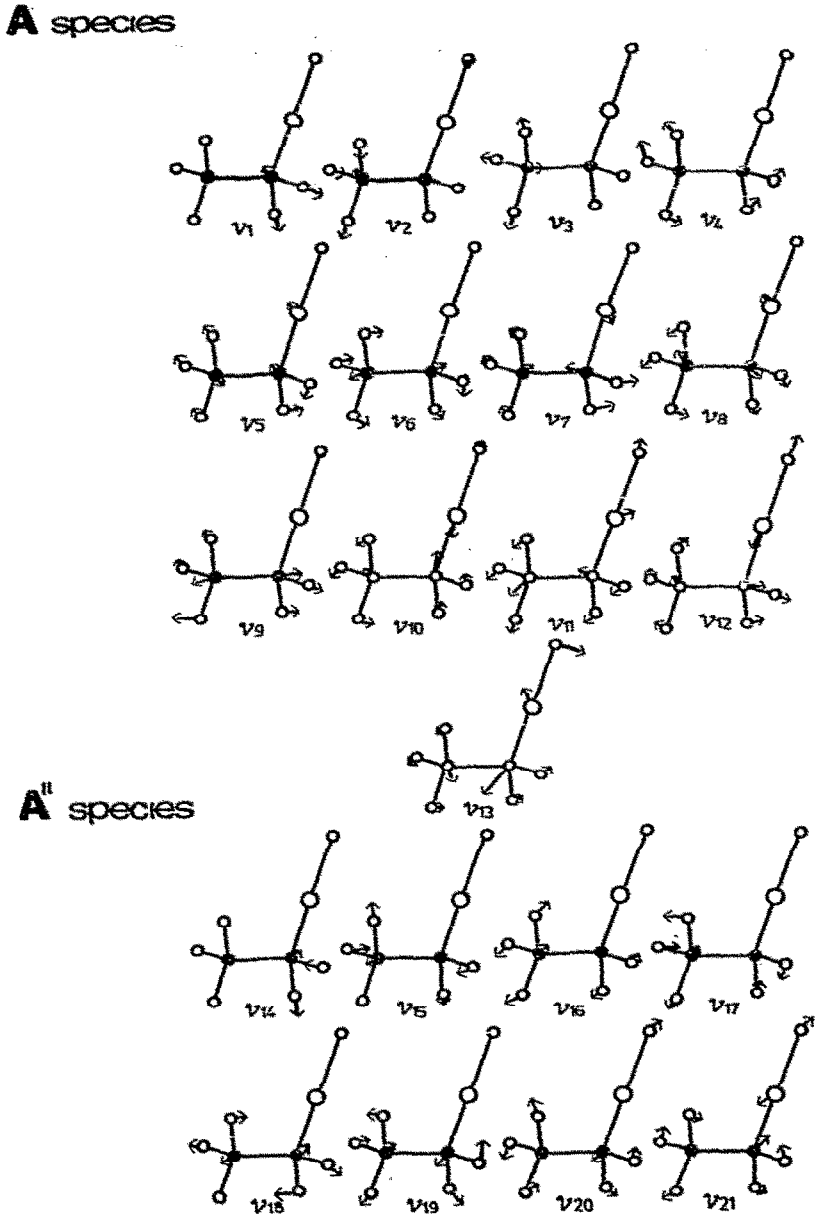

Figure 2. Mass-weighted Cartesian displacement in the normal modes of $Hg(C_2H_5)Cl$.

TABLE 5

METAL-CARBON-HALIDE SKELETAL MODES (cm^{-1}) FOR METHYL- AND ETHYL-MERCURY HALIDES (in solutions)

	ν(HgC)	δ(CCHg)	ν(HgX)	δ(CHgX)	Refs.
$Hg(CH_3)Cl$	553.8	-	335.5	135	[23]
$Hg(CH_3)^{35}Cl$	553.8	-	336.6	135	
$Hg(CH_3)^{37}Cl$	553.8	-	325.9	135	
$Hg(CD_3)Cl$	506.8	-	334.8	125	
$HgBr(CH_3)$	545.3	-	228.0	121	
$HgBr(CD_3)$	499.0	-	227.8	110	
$Hg(CH_3)I$	533.2	-	181.0	112	
$Hg(CD_3)I$	489.5	-	181.0	104	
$Hg(C_2H_5)Cl$	527	254	326	$120^{\dagger}$, 84^{*}	this work
$HgBr(C_2H_5)$	521	255	221	$120^{\dagger}$, 65^{*}	
$HgBr(C_2D_5)$	475	244	217	$97^{\dagger\S}$, 72^{*}	
$Hg(C_2H_5)I$	508	247	176	$108^{\dagger\S}$, 60^{*}	

†out-of-plane deformation

*in-plane deformation

§calculated values

The potential energy distribution of internal coordinates in the normal modes of $Hg(C_2H_5)Cl$ are given in Table 4. This shows that some of them are much more complicated than the approximate descriptions suggest (e.g. ν_6).

The presence of considerable vibrational interaction can be seen from mass-weighted Cartesian displacements shown in Fig. 2 for $Hg(C_2H_5)Cl$. Whilst the strengthening modes of CH_3 and CH_2 are perfectly localised within their respective groups many of the other motions show

TABLE 6

METAL-CARBON SKELETAL FORCE CONSTANTS FOR METHYL- AND ETHYL DERIVATIVES OF MERCURY ($/10^2$ N m^{-1})

	K(CHg)	K(HgX)	F(CHg,CHg) F(CHg,HgX)	H(CHgX) H(CHgC)	Refs.
$Hg(CH_3)Cl$	2.55	2.01	0.025	0.097	[23]
$HgBr(CH_3)$	2.48	1.79	0.024	0.086	[23]
$Hg(CH_3)I$	2.38	1.55	0.004	0.076	[23]
$Hg(CH_3)_2$	2.38	-	0.031	0.104	[30]
$Hg(C_2H_5)Cl$	2.64	1.88	(0.025)	$0.116^{\dagger}$, 0.097^{*}	this work
$HgBr(C_2H_5)$	2.52	1.79	(0.024)	$0.071^{\dagger}$, 0.091^{*}	this work
$Hg(C_2H_5)I$	2.47	1.52	(0.004)	$0.048^{\dagger}$, 0.086^{*}	this work

( ) constrained to the corresponding $Hg(CH_3)X$

†for in-plane deformation

*for out-of-plane deformation

involvement throughout the molecule. The C-Hg stretching mode (ν_{10}) displays considerable involvement from CCHg bending and CH_2 wagging motions.

In all the skeletal modes about mercury (ν_{10}-ν_{13} and ν_{21}) both the metal and halide atoms are moving with considerable amplitude. All these modes show halogen sensitivity in their wavenumbers. The CCHg bending modes (ν_{11}) show stronger halide dependence than the calculations reproduce. The CH_2 wagging mode (ν_7) also shows halide dependence experimentally; because the stretch-bend interaction $F_{X\theta}$ has been set to zero and the bending force constant H_θ has been constrained to its value from $HgBr(C_2H_5)$ and $HgBr(C_2D_5)$ for the chloride and iodide this trend is not reflected in the calculations.

The skeletal vibrational frequencies and the force constants about

mercury are compared for methyl- and ethy-mercury systems in Tables 5 and 6, respectively. The Hg-C stretching force constants for the latter are slightly the larger for each halide, and the Hg-X force constants trans to ethyl tend to be slightly the lower. This suggests that ethyl has a maginally enhanced trans influence compared to methyl. The sum of K(HgC) and K(HgX) is virtually constant for a given X.

Preliminary studies indicate that this force field gives a good account of the experimental wavenumbers of $Hg(C_2H_5)_2$, and the $-CH_2HgX$ part of it can be applied to $Hg(n\text{-}C_3H_7)X$ and $Hg(n\text{-}C_4H_9)X$.

Experimental

For the C_2H_5- compounds, infrared spectra in the range 4000-200 cm^{-1} were measured with a Perkin-Elmer model 225 double-beam grating spectrophotometer, and in the range 400-10 cm^{-1} with a Grubb-Parsons I.R.I.S. interferometer using 0.01 and 0.04 mm beam splitters. The i.r. spectra of $HgBr(C_2D_5)$ were recorded with a Digilab FTS-14 interferometer in the range 4000-40 cm^{-1}. Some of the far i.r. measurements were repeated with a Beckman-RIIC FS-720 interferometer.

Raman spectra were recorded with Coderg PHO double- and/or T800 triple- monochromators with excitation from Coherent Radiation Laboratories Model 52 krypton- or argon-ion lasers.

The ethylmercury halides were prepared by equilibriating equivalent quantities of diethylmercury and the appropriate mercury(II) dihalide in acetone or ethanol. The crude products were recrystallised from methanol and characterised by elemental analysis and melting points.

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References

1. N.G. Pai, Proc.Roy.Soc., A149 (1935) 29.
2. H.D. Kaesz and F.G.A. Stone, Spectrochim.Acta, 15 (1959) 360.
3. G.E. Coates and D. Ridley, J.Chem.Soc., (1964) 166.
4. D.K. Huggins and H.D. Kaesz, Progress in Solid State Chemistry, 1 (1964) 417.
5. J. Mink and Yu. A. Pentin, Acta Chim.Acad.Sci.Hung., 65 (1970) 273
6. J. Mink and Yu. A. Pentin, J.Organometal.Chem., 23 (1970) 293.
7. J.L. Bribes and R. Gaufrès, Spectrochim.Acta, 27A (1971) 2133.
8. J. Mink, L. Bursics and G. Végh, J.Organometal.Chem., 34 (1972) C4.
9. G. Kemény, Ph.D. Thesis, Institute of Isotopes of the Hungarian Academy of Sciences (Budapest) 1977.
10. J. Mink and Yu. A. Pentin, Progress in Physical Chemistry - Ed. Moscow State Univ., 7 (1973) 244.
11. J. Lorberth and F. Weller, J.Organometal.Chem., 32 (1971) 145.
12. K. Dehnicke and D. Seybold, J.Organometal.Chem., 11 (1968) 227.
13. J.H.S. Green, Spectrochim.Acta, 24A (1968) 863.
14. E. Maslowsky Jr., Vibrational Spectra of Organometallic Compounds, John Wiley, New York (1977).
15. K. Nakamoto, Infrared and Raman Spectra of Inorganic and Coordination Compounds, 3rd Edn., John Wiley, New York (1978).
16. N. Sheppard, J.Chem.Phys., 17 (1949) 79.
17. R.G. Snyder and J.H. Schachtsneider, J.Mol.Spectroscopy, 30 (1969) 290.
18. F.A. Miller and F.E. Kiviat, Spectrochim.Acta, 25A (1969) 1363.
19. R. Gaufrès and M. Béjaud-Bianchi, Spectrochim.Acta, 27A (1971) 2249.
20. A.B. Dempster and G. Zerbi, J.Mol.Spectroscopy, 39 (1971) 1.
21. S. Suzuki, J.L. Bribes and R. Gaufrès, J.Mol.Spectroscopy, 47 (1973) 119.
22. C.J. Wurrey, W.E. Bucy and J.R. Durig, J.Phys.Chem., 80 (1976) 1129.
23. P.L. Goggin, G. Kemény and J. Mink, J.Chem.Soc.Faraday II, 72 (1976) 1025.
24. H. Kriegsmann, C. Peuker, R. Heess and H. Geissler, Z.Naturforsch., A24, (1969) 773.

25. Interatomic Distances, The Chemical Society, London (1958).

26. C. Walls, D.G. Lister and J. Sheridan, J.Chem.Soc.Faraday II, 71 (1975) 1091.

27. J. Mink, G. Kemény and L.M. Mink, Hungarian Acad.Sci., Central Res.Inst.Phys., KFKI- 76-47 (1976).

28. J. Mink, L.M. Mink and Yu. A. Pentin, Vestnik Mosk.Gos. Univ., 3 (1971) 286.

29. G.A. Crowder, J.Mol.Spectroscopy, 48 (1973) 467.

30. J. Mink and B. Gellai, J.Organometal.Chem., 66 (1974) 1.