

FORCE CONSTANTS OF METHYLMERCURY(II) COMPOUNDS

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Summary

The results of force constant calculations of systems $\text{Hg}(\text{CH}_3)\text{X}$ ($\text{X} = \text{CH}_3, \text{Cl}, \text{Br}, \text{I}, \text{CN}, \text{SCH}_3$ and $\{\text{As}(\text{CH}_3)_3\}^+$) are briefly reviewed and the importance of data compatibility in comparative studies is stressed. Aspects of relationships between the force constants and other physical properties are discussed, but outside the limited series $\text{X} = \text{Cl}, \text{Br}$ or I do not appear to be of fundamental significance.

Methylmercury compounds have been attractive for spectroscopic studies, partly on account of their molecular simplicity and partly because of their significance in the natural environment. Recently, Iwasaki [1] has studied force constants of a wide range of such systems to establish a *trans*-influence order of groups X in $\text{Hg}(\text{CH}_3)\text{X}$ from their effect on $\text{Hg}-\text{C}$ stretching force constants, as well as comparing these parameters with other properties such as the ionisation potential of X . He has drawn attention to the need for a uniform approach in calculations if meaningful comparisons between results for different molecules are to be made. Whilst not disagreeing with this view, we wish to point out that true comparability between vibrational data used for such calculations is of even greater importance for these systems.

Results

Table 1 summarises results for $\text{Hg}(\text{CH}_3)_2$ from studies employing different force fields and different wavenumbers in the calculations, and includes results for the simple triatomic treatment (mass of $\text{CH}_3 = 15$) of Iwasaki for the various data sets.

We have shown that in $\text{Hg}(\text{CH}_3)\text{X}$ ($\text{X} = \text{Cl}, \text{Br}$ and I) [4] HgC and HgX stretching wavenumbers have a marked dependence on the phase measured,

TABLE 1
SKELETAL VIBRATIONS (cm^{-1}) AND FORCE CONSTANTS (10^2 N m^{-1}) FOR DIMETHYLMERCURY

Force constants	[1]	[2] ^a	<i>b</i>	[3] ^a	<i>b</i>
$f(\text{HgC})$	2.33	2.311	2.301	2.379	2.356
$f(\text{HgC}, \text{HgC})$	0.10	0.068	0.069	0.031	0.038
$f(\text{CHgC})$	0.093	0.110	0.098	0.104	0.093
<i>Calculated (cm^{-1}) ^c</i>					
HgC_2 asym. str.	550	539	549.2		
HgC_2 sym. str.	515	518	520.6		
CHgC bend	156	160	155.5		

^a Using modified valence force field (MVFF) for best least squares fit for $\text{Hg}(\text{CH}_3)_2$ and $\text{Hg}(\text{CD}_3)_2$. ^b Force constants for simple triatomic model with methyl mass 15. ^c Wavenumbers observed for gas phase are 546.3, 520.4 and 153.

that for solids there is a big difference between the infrared and Raman active modes, and that for solutions they are solvent dependent [5] (Table 2). Our calculations were based primarily on benzene solution values, with as complete a valence force field (VFF) as data permitted and with least squares refinement for corresponding $\text{Hg}(\text{CH}_3)\text{X}$ and $\text{Hg}(\text{CD}_3)\text{X}$ molecules. The relevant results are given in Table 3, together with those from application of Iwasaki's treatment applied to the same data. For purposes of comparison we can include Iwasaki's values for $\text{Hg}(\text{CH}_3)\text{CN}$ (data from aqueous solution), $\text{Hg}(\text{CH}_3)\text{SCH}_3$ (data from liquid) and $[\text{Hg}(\text{CH}_3)\{\text{As}(\text{CH}_3)_3\}]^+$ (data for solid which differ very little from those for aqueous solution for vibrations involving Hg). We have not included the other examples discussed by Iwasaki ($\text{X} = \text{F}, \text{SCN}, \text{SHg}(\text{CH}_3)$ or $\text{S}\{\text{Hg}(\text{CH}_3)\}_2^+$) where solid state wavenumbers are known to, or are likely to, differ significantly from those of solutions. Consideration of all systems as solids does not constitute a criterion for data compatibility because intermolecular interactions in the crystals are not uniform throughout the series.

The first important result here is that the trend in HgC stretching force con-

TABLE 2
WAVENUMBERS OF SKELETAL MODES OF METHYLMERCURY HALIDES [4]

		$\text{Hg}(\text{CH}_3)^{35}\text{Cl}$		$\text{HgBr}(\text{CH}_3)$		$\text{Hg}(\text{CH}_3)\text{I}$	
		Solid	Solution ^a	Solid	Solution	Solid	Solution
$\nu(\text{HgC})$ {	Raman	554.1		545.6		529.5	
	IR		553.8		545.3		533.2
$\nu(\text{HgX})$ {	Raman	293.3		204.0		166.3	
	IR		335.5		228.0		181
$\delta(\text{CHgX})$ {	Raman	140	135	119	121	115	112
	IR			94		94	

^a Lowest frequency determined for CDCl_3 solutions, others for C_6H_6 solutions.

TABLE 3
 SKELETAL FORCE CONSTANTS (10^2 N m^{-1}) OF METHYLMERCURY COMPOUNDS AND COMPARISON WITH OTHER PHYSICAL PARAMETERS

	Wave- number source	$f(\text{HgC})$	$f(\text{HgX})$	$f(\text{CHgX})$	Calcu- lation	IP of X (eV) [6]	EA of X (eV) [6]	$D(\text{HgC})$ (kJ mol ⁻¹) [7]	$^1J(\text{HgC})$ (Hz)
Hg(CH ₃)Cl	Solution ^a	2.55 2.51	2.01 2.01	0.097 0.090	[4] ^b _d	13.01	3.61	266 ± 12	1431 [8] ^c
HgBr(CH ₃)	Solution ^a	2.48 2.43	1.79 1.79	0.086 0.080	[4] ^b _d	11.84	3.361	256 ± 12	1394 [8] ^c
Hg(CH ₃)I	Solution ^a	2.38 2.33	1.55 1.55	0.076 0.069	[4] ^b _d	10.45	3.06	245 ± 13	1301 [8] ^c
Hg(CH ₃)CN	Aqueous solution [9]	2.80 2.61	2.10 2.13	0.035 0.033	[9] ^e [1]	14.1	3.17		1450 ^f
Hg(CH ₃) ₂	^g	2.38 2.36	—	0.104 0.093	[3] _d	9.95	1.08	215 ± 8	689 [8] ^c
Hg(CH ₃)(SCH ₃)	Liquid [1]	2.33	1.52	0.078	[1]	(9.84) ^h	1.32		—
[Hg(CH ₃)(As(CH ₃) ₃)] ⁺	Solid [10]	2.37	1.53	0.084	[1]	ⁱ			1343 ^f

^a Table 2. ^b From best least squares fit for CH₃ and CD₃ systems using MVFF. ^c CDCl₃ solution. ^d From tritatomic treatment with mass of CH₃ = 15 (as ref. 1). ^e From SVFF. ^f 0.6 M solution in 1/1 D₂O/CH₃OH measured with JEOL PFT 100 spectrometer. ^g Table 1. ^h Ionisation potential of CH₃SH. ⁱ As(CH₃)₃ has IP 8.3 eV.

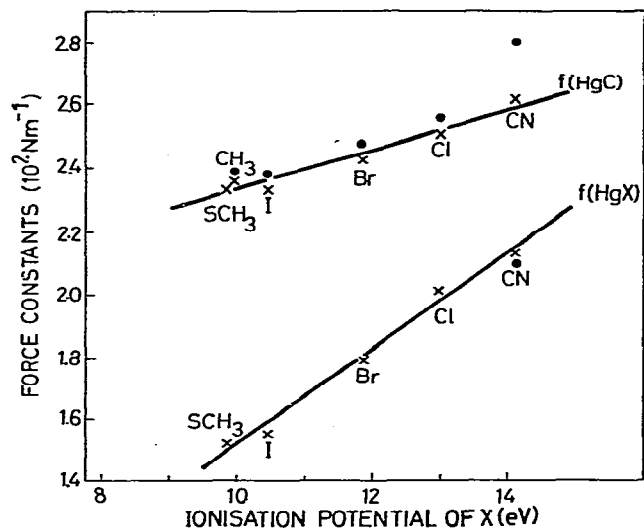


Fig. 1. Relationship of HgC and HgX stretching force constants to the ionisation potential of X in $\text{Hg}(\text{CH}_3)\text{X}$. Values marked X are from calculation treating CH_3 as a point mass, those marked • are from fuller treatments.

stant for the series Cl, Br, I is now even (cf. ref. 1). If these higher values are considered the correlation of $f(\text{HgC})$ with ionisation potential (IP) of X, pointed out by Iwasaki, is considerably improved (see Fig. 1). It should be noted that for $\text{S}(\text{CH}_3)$ the IP for $\text{HS}(\text{CH}_3)$ is used, which is not entirely appropriate, and that for $[\text{Hg}(\text{CH}_3)\{\text{As}(\text{CH}_3)_3\}]^+$ the second IP which would be the truly comparable figure, would be much higher and probably destroy the whole correlation. A similar objection also applies to an apparent correlation between $f(\text{HgX})$ and IP of X, which in addition fails to hold for $\text{X} = \text{CH}_3$. These relationships may in any case be quite fortuitous since electron affinity of X [or $\{\text{As}(\text{CH}_3)_3\}^+$] would be a more relevant property and certainly shows no general agreement with force constant trends. For the halides there is a linear relationship between $f(\text{HgC})$ and the Hg—C bond dissociation energy but this does not encompass $\text{Hg}(\text{CH}_3)_2$.

As with the other properties examined, the NMR coupling constant $^1J(\text{HgC})$ follows the trend in $f(\text{HgC})$ for the halides, but is drastically reduced in $\text{Hg}(\text{CH}_3)_2$. This may be the clue to the problem since there is evidently only about half the mercury 6s orbital character in a Hg—C bond when two methyl groups are present as when there is only one. Any direct relationship between HgC stretching force constant and bond strength relies on the form of the potential energy function for the bond being the same throughout the series and this is unlikely to hold if there is a marked discontinuity in orbital make-up of the HgC bond between examples within the series. If this is the explanation of failures in the correlations it also means that *trans* influences ranking from $f(\text{HgC})$ will also be invalid.

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