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Vibrational Spectroscopic Investigation of Molecular Crystals of Methylmercury(II) Halides*

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A nearly full assignment of the vibrational modes of methylmercury halide crystals has been proposed. Factor group analysis has been used to derive the vibrational selection rules for the lattice modes. It is concluded that the D_{4h}^{7} space group allows all the vibrations observed for the fluoride and chloride. CH_3HgI showed only five Raman and one infrared features below 50 cm^{-1}, *i.e.* much less than expected for the D_{2h}^{11} structure with four molecules in the unit cell. Lattice modes for CH_3HgI and CD_3HgI can be assigned on the basis of C_{2h}^{11} substructure with two molecules per unit cell. The bromide gave an ultra-low wavenumber band (7.0 cm^{-1}) which we were unable to assign. Force constants have been calculated on the basis of a primitive unit cell (containig two molecules). The internal HgX stretching force constants 2.112, 1.658, 1.507 and 1.347 N cm^{-1} and the transverse translatory force constants 0.719, 0.364, 0.266 and 0.218 N cm^{-1} obtained for fluoride, chloride, bromide, and iodide, respectively, show strong dependence on the kind of halide.

* Dedicated to Professor Dušan Hadži on the occasion of his seventieth birthday.

INTRODUCTION

The basic theory for the vibrational spectra of crystals was proposed by Bhagavantam and Venkatarayudu[1] in 1939, and further developed by Hornig[2] and Winston and Halford[3].

At the present stage, when the structure of a crystal is known, it is possible to predict the number of its infrared and Raman active bands, as well as their fine structure and polarization. The theory can also be useful in assigning a space group from the spectra.

Recent progress in laser Raman and Fourier transform mid- and far-infrared instrumentation has made it feasible to obtain complete vibrational spectra including the very low wavenumber characteristics of solids.

In this paper, we discuss the possible ways of interpreting the vibrational spectra of some molecular crystals. We describe the usefulness of the theoretical calculation of lattice force constants and summarize the present state of the art by reference to the results of our recent investigation on molecular crystals of organometallic samples.[4,5]

METHYLMERCURY CHLORIDE

There are significant changes between the vibrational spectra of the free molecule and the crystalline substance. These arise both from intermolecular interactions in the crystal lattice and the symmetry characteristics of the molecular environment.

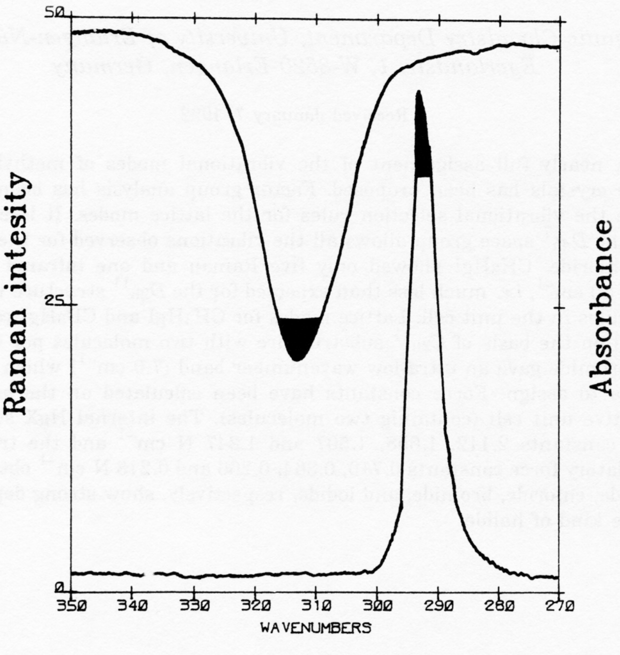

Figure 1. Hg–Cl stretching fundamentals observed in the infrared (upper trace) and Raman spectra (lower trace) of solid $CH_3Hg^{35}Cl$.

Publications by ourselves[6,7] and Z. Meić and M. Randić[8] have drawn attention to the great differences between the wavenumbers of the Hg-halide stretching vibration[5] observed in the infrared and those found in the Raman spectra of solid methylmercury halides. This correlation splitting due to the crystal field in CH_3HgCl, is shown in Figure 1.

We have previously determined the wavenumbers of fundamental vibrations of compounds CH_3HgX and CD_3HgX (X = Cl, Br, I) in solution and noted that they differed by 15–20 cm^{-1} from those of the solids.[4,9]

The X-ray diffraction study of Grdenić and Kitaigorodski[10] for CH_3HgCl showed a tetragonal symmetry with a unit cell belonging to the D_{4h}^7 ($P4/nmm$) space group (No. 129) with two molecules in it. Considering the CH_3HgCl molecule as a linear triatomic system (in which the methyl group is regarded as a point mass), in accordance with the C_2 site taken in the unit cell, all the atoms take the 2c position determined by the Wyckoff-site notation. Using the Adams-Newton tables[11] for the crystal space group No. 129, the factor-group analysis has been carried out, giving the fundamental vibrations of the unit cell as:

Internal vibrations: $\Gamma_{int} = 2a_g + e_g + 2a_{2u} + e_u$

Rotatory (librational) modes: $\Gamma_R = e_g + e_u$

Translatory vibrations: $\Gamma_T = a_{2u}$ (transverse) $+ e_u$ (longitudinal)

The result of the factor-group analysis provides an explanation of the difference between the solid phase infrared and Raman frequencies, and it is in good agreement with the appearance of four infrared and six Raman bands in the range below 600 cm^{-1}.[4]

The centrosymmetric relationship between neighbouring molecules immediately explains the lack of frequency correspondence between the infrared and Raman bands. It means that all fundamental vibrations of the free molecule are split into different infrared (a_{2u}, e_u) and Raman (a_{1g} and e_g) active modes. The assignments for the lattice vibrations are based on infrared and Raman studies of partially oriented crystals.[4] The Raman spectra of the iodides showed two additional bands in the very low wavenumber region, suggesting that it is not isomorphic with the chloride.

METHYLMERCURY FLUORIDE

Infrared and Raman spectra of crystalline CH_3HgF were published as a preliminary communication in 1971,[13] but only covered the internal modes above 170 cm^{-1}. We have measured the low frequency part of the spectra (below 170 cm^{-1}) and observed three Raman bands at 84, 72 and 41 cm^{-1} and one dominant IR band at 69 cm^{-1} (with a shoulder at 54 cm^{-1}). These lattice vibrations show a strong similarity to the spectral pattern of CH_3HgCl which suggests that the crystal structure of CH_3HgF is isomorphous with CH_3HgCl. Full assignments of the solid state spectra of CH_3HgF have been made by analogy with CH_3HgCl, based on D_{4h}^7 crystal structure. Assignments of the two isomorphous crystals are presented in Table II. Weak correlation splittings have been observed for internal vibrations above 500 cm^{-1}, but much bigger differences between infrared and Raman wavenumbers have been detected for HgF stretching and CHgF bending modes (see Table II).

TABLE I

Crystallographic data of methylmercury-chloride, -bromide and -iodide

	CH_3HgCl	CH_3HgBr	CH_3HgI
a/Å	4.735(2)	8.825(3)	8.678(2)
b/Å	= a	6.971(3)	7.399(3)
c/Å	9.206(2)	6.909(2)	7.214(2)
Space group	D_{4h}^7—$P4/nmm$	D_{2h}^{11}—$Pbcm$	D_{2h}^{11}—$Pbcm$
Z (formula units)	2	4	4
D_m/g cm^{-3}	3.83	–	–
D_x/g cm^{-3}	4.04	4.83	4.88

METHYLMERCURY BROMIDE AND IODIDE

We have previously attempted to account for the low wavenumber spectra of these two systems on the basis of a D_{4h}^7 structure.[4] This was not satisfactory because more very low wavenumber features were observed than such a structure predicts. Grdenić and his coworkers have now performed an X-ray crystallographic study on CH_3HgBr and CH_3HgI.[12] Their results (Table I) show structures with unit cells belonging to space group D_{2h}^{11} ($Pbcm$) containing 4 formula units.

For the skeletal atoms of the molecules, which take σ_{xy} sites in the unit cell, all heavy atoms are at the 4d positions based on the Wyckoff-site notation. Using the Adams-Newton tables for the factor-group analysis,[11] the lattice vibrations of the unit cell can be divided as:

Rotatory (librational) modes: $\Gamma_R = 2b_{2g} + 2b_{3g} + 2a_u + 2b_{1u}$

Acoustic translatory modes: $\Gamma_{Ac} = b_{1u} + b_{2u} + b_{3g}$

Translatory vibrations: $\Gamma_T = 2a_g + 2b_g + b_{2g} + b_{3g} + a_u + b_{2u} + b_{3u}$

Since a_u is inactive, ten Raman active and four infrared active modes are expected in the low frequency region of the spectra. Experimentally only five Raman bands and one infrared band can be detected, which is much less than what is predicted by factor-group analysis.

According to the unit cell geometry in CH_3HgI, there is a »short« distance (361 pm) and a »long« distance (370 pm) intermolecular interaction in the lattice. If one considers a primitive unit cell with the two closest molecules in it with a space group of C_{2h}^{11}, the factor group analysis gives the following distribution of lattice modes:

$$\Gamma_R = 2b_g + 2a_u \text{ (rotatory)}$$

$$\Gamma_T = 2a_g + b_g \text{ (translatory)}$$

which predicts five Raman bands and two infrared bands. This solution is very close to the experimental observations and should not be considered unrealistic.

Assignments of lattice modes in accordance with D_{2h}^{11} structure and four molecules per unit cell are presented in Table III. It is clear from this table that 6 experimental frequencies are distributed among 14 optically active lattice modes.

TABLE II

Infrared and Raman spectra of solid CH_3HgF, CH_3HgCl, $CH_3Hg^{35}Cl$ and CD_3HgCl

CH_3HgF		CH_3HgCl		$CH_3Hg^{35}Cl$		CD_3HgCl		Assignment (D_{4h}^{J})	
IR	Raman	IR	Raman	IR	Raman	IR	Raman		
2990w,b		3008w,m,b		3008w,m,b		2257w,b		e_u	CH_3, CD_3 asym. str.
	2985vw,b		3008vw,b		3011vw,b		2256vw,b	e_g	
2930w		2930m		2923.8w,m		2123.6m		a_{2u}	CH_3, CD_3 sym. str.
	2933w		2923.3w,m		2923.7w,m		2124.8m	a_{1g}	
		1410w,b				1030w,b		e_u	CH_3, CD_3 asym. def.
	1420w,b		1416vvw,b					e_g	
		1195w		1195.3w		925vw		a_{2u}	CH_3, CD_3 sym. def.
	1209w		1185.3m,s		1185.5m,s		918.1m,s	a_{1g}	
790vs		791vs		791vs,b		597vs		e_u	CH_3, CD_3 rock.
	785w		783vvw		793vvw,b			e_g	
564s		547m		547m		500.5m		a_{2u}	CHg str.
	570s		554.3vs		554.1vs		506.7vs	a_{1g}	
486s		313.2m,s		312.5m,s		312.5m,s		a_{2u}	HgX str.
	410m		292.7m		293.3m,s		292.0m	a_{1g}	
			288.4m				289.3m	(a_{1g})	
130vs		107m,s		106m,s		98m		e_u	CHgX
	170w		142vw		140vw		130vw	e_g	
	145vw,b							(e_g)	
69s		74m		74m		68m		e_u	rotatory
54sh								(e_u)	
	84sh		67.5vs		68vs		63.3vs	e_g	rotatory
	72vs		48.9m		48.8m		49.8m	a_{1g}	transl. (transv.)
	41s		37.1m,s		37.2m,s		36m,s	e_g	transl. (long.)

TABLE III

Suggested assignment of optically active lattice modes for CH_3HgI and CD_3HgI

MODE	SPECIES D_{2h}^{11}	CH_3HgI ν/cm^{-1}	CD_3HgI ν/cm^{-1}
Rotatory	b_{2g}	43.6	42.7
	b_{2g}	43.6	42.7
	b_{3g}	37.6	36.5
	b_{3g}	37.6	36.5
	b_{1u}	47	47
	b_{1u}	47	47
	b_{2u}	47	47
	b_{3u}	47	47
Translatory (transverse)	a_g	32.9	32.6
	a_g	32.9	32.6
Translatory (longitudinal)	b_{2g}	37.6	33.5
	b_{3g}	34.4	32.6
	b_{1g}	13.1	13.1
	b_{1g}	13.1	13.1

The alternative assignments for the simplified unit cell (C_{2h}^{11}, $Z = 2$) are presented in Table IV. Only one infrared band is missing from the perfect picture of factor group analysis, but all five Raman bands (in agreement with prediction) can be assigned on the basis of C_{2h}^{11} substructure.

TABLE IV

Lattice modes and suggested assignments for the simplified unit cell of CH_3HgI and CD_3HGI

MODE	SPECIES C_{2h}^{11}	CH_3HgI ν/cm^{-1}	CD_3HgI ν/cm^{-1}
Rotatory	a_u	47	47
	a_u	(47)	(47)
	b_g	43.6	42.7
	b_g	34.4	32.6
Translatory (transverse)	a_g	32.9	(32.6)
Translatory (longitudinal)	b_g	37.6	36.5
	a_g	13.1	13.1

The infrared and Raman spectra of solid CH_3HgI and CD_3HgI in the whole range of the internal and external vibrations are summarized in Table I. The doublets of the correlation splittings suggest that the vibrational coupling is detectable only between two neighbouring molecules. Nevertheless, the assignments in Table V are made in accordance with the D_{2h}^{11} structure.

TABLE V

Infrared and Raman spectra of solid CH_3HgBr, CD_3HgBr, CH_3HgI and CD_3HgI

CH_3HgBr		CD_3HgBr		CH_3HgI		CD_3HgI		Assignment[a] (D_{2h}^{11})	
IR	Raman	IR	Raman	IR	Raman	IR	Raman		
3012w,mb		2254w,b		2999w,b		2252w,b		»u« modes	CH_3, CD_3 asym. str.
	3015vw,b		2258vw,b		3008vw,b		2256vw	»g« modes	
2923.5m		2122.8m		2912.8m		2120.8m		b_{2u},b_{3u}	CH_3, CD_3 sym. str.
	2923.4m		2125.2m		2916m		2120.3m	a_g,b_{1g}	
1402w,b		1030w,b		1399w		1025w,b		»u« modes	CH_3, CD_3 asym. def.
	1415vvw,b							»g« modes	
1187.2w		915.4w		1173.5m		905.6w		b_{2u},b_{3u}	CH_3, CD_3 sym. def.
	1173.1m,s		909m,s		1161ms		898.1m,s	a_g,b_{1g}	
788vs,b		593vs		777vs		586vs		»u« modes	CH_3, CD_3 rock.
			595vvw,b		778vw,b		587vvw,b	»g« modes	
539.5m		493.4m,s		525.9m		482.1m,s		b_{2u},b_{3u}	CHg str.
	545.6vs		499.7vs		529.9vs		485.7vs	a_g,b_{1g}	
212.8m,s		213m,s		171m		170w		a_{2u},b_{3u}	HgX str.
	204m,s		203.6s		166.3m		166.2vs	a_g,b_{1g}	
94m,s		86m,s		94m		84m		b_{2u},b_{3u}	CHgX bend.
	119w		110w		115w		107m	a_g,b_{1g}	
56m,s		57m,s		47m,s		47s		b_{1u},b_{2u},b_{3u}	rotatory[b]
	53.1vs		50.5vs		43.6vs		42.7vs	b_{2g}	rotatory
					37.6sh		36.5sh	b_{3g} rot.,b_{2g}	transl. (long.)
					34.4s		32.6s	b_{3g} transl.	(longitudinal)
	39.7m		38.2m		32.9s		32.6s	a_g transl.	(transverse)
	7.0vs		7.0vs		13.1vs		13.1vs	b_{1g} transl.	(longitudinal)

[a] »u« modes = $b_{1u}+b_{2u}+b_{3u}$; »g« modes = $a_g+b_{1g}+b_{2g}+b_{3g}$.

[b] For the multiplicity of each lattice species see Table III.

TABLE VIa

Experimental and calculated wavenumbers of vibrations in methylmercury fluoride crystal

	Skeletal and lattice modes	CH_3HgF Obs.	CH_3HgF calc[a]
a_{1g}	CHg stretch	570	570.0
	HgF stretch	410	410.0
	Translatory (transverse)	72	71.9
a_{2u}	CHg stretch	564	564.0
	HgF stretch	486	486.0
e_g	CHgF bending	170	169.9
	Rotatory	84	84.2
	Translatory (longitudinal)	41	40.9
e_u	CHgF bending	130	130.0
	Rotatory	69	69.1

[a] Refinement was generally completed in 3–4 iteration steps.

TABLE VIb

Force constants for molecular crystals of CH_3HgF and CH_3HgCl

Force constant		Coordinate	CH_3HgF	CH_3HgCl		Units
Skeletal – internal	K (CHg)	Stretch	2.769	2.623	(17)[d]	a
	K (Hgx)	Stretch	2.112	1.658	(11)	a
	H (CHgx)	Bend	0.394	0.390	(6)	b
	F' (CHg, CHg)[c]	Str.–Str.	0.048	0.015	(17)	a
	F' (HgX, HgX)[c]	Str.–Str.	–0.369	–0.107	(11)	a
	F' (CHgX, CHgX)[c]	Bend–Bend	0.103	0.107	(6)	b
Lattice	f_t	Transl. transverse	0.719	0.364	(3)	a
	f_l	Transl. longitud.	0.233	0.201	(4)	a
	f_R	Rotatory	0.041	0.072	(1)	b
	f_{RR}[c]	Rotatory–rotatory	0.008	–0.005	(1)	b

[a] 10^2 N m^{-1}.
[b] 10^{-18} N m rad^{-2}.
[c] Intermolecular interaction force constants.
[d] In brackets: dispersion of force constants.

Although CH_3HgBr is isomorphous with CH_3HgI, the spectra are not so rich in lattice vibrations. The very strong band at 7 cm^{-1} is lower than anything observed for CH_3HgI and is out of keeping with any frequency trend expected. With the exception of this band, its spectra resemble those of CH_3HgCl of space group D_{4h}^7. It can be seen from Table I that the two intermolecular HgBr distances are very close, 349 and 345 pm, though not identical. Thus, deviation from a D_{4h}^7 arrangement is very small. The results are included in Table V, even though a satisfactory explanation is still awaited.

CALCULATION OF LATTICE FORCE CONSTANTS

The primitive unit cell chosen for the calculation of lattice force constants for CH_3HgF and CH_3HgCl is shown in Figure 2. The experimental and calculated skeletal and lattice modes for CH_3HgF are presented in Table VIa. The force constants give good agreement between the experimental and calculated wavenumbers (Table VIb).

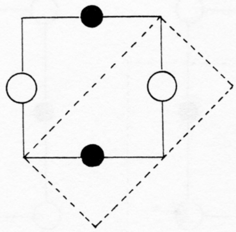

Figure 2. Unit cell (solid line) and primitive unit cell (dashed line) for CH_3HgCl. Point group D_{4h}^7, $Z = 2$, solid circles, Cl, empty circles, CH_3 group.

TABLE VII

Lattice force constants for CH_3HgI in symmetry coordinate representation

MODE	SPECIES D_{2h}^{11}	FORCE CONSTANT	UNITS
Rotatory	b_{1u}, b_{2u}, b_{3u}	0.068 (1)[c]	b
	b_{2g}	0.057 (0)	b
	b_{3g}	0.043 (1)	b
Translatory (transverse)	a_g	0.218 (1)	a
Translatory (longitudinal)	b_{1g}	0.035 (0)	a
	b_{2g}	0.279 (7)	a
	b_{3g}	0.228 (11)	a

[a] 10^2 N m^{-1}.
[b] 10^{-18} N m rad^{-2}.
[c] In brackets: dispersion of force constants.

TABLE VIII

Lattice force constants of CH_3HgI calculated for the simplified C_{2h}^{11} structure unit cell

Force constants	Coordinate	Force constant values	Units
f_t	Transl. transverse	0.218 (1)[d]	a
f_{11}	Transl. longitudinal	0.035 (0)	a
f_{12}	Transl. longitudinal	0.228 (11)	a
f_{R1}	Rotatory	0.063 (1)	b
f'_{RR}	Rotatory–rotatory[c]	0.005 (0)	b
f_{R2}	Rotatory	0.057 (0)	b
f'_{RR}	Rotatory–rotatory	–0.012 (0)	b

[a] 10^2 N m^{-1}.
[b] 10^{-18} N m rad^{-2}.
[c] Intermolecular interaction force constants.
[d] In brackets: dispersion of force constants.

Two different primitive unit cells were chosen for the calculation of lattice force constants for CH_3HgI, as shown in Figure 3. The unit cell with four molecules (Figure 3A) relates to lattice modes, as assigned in Table III. The calculated force constants using lattice modes of CH_3HgI and CD_3HgI are listed in Table VII.

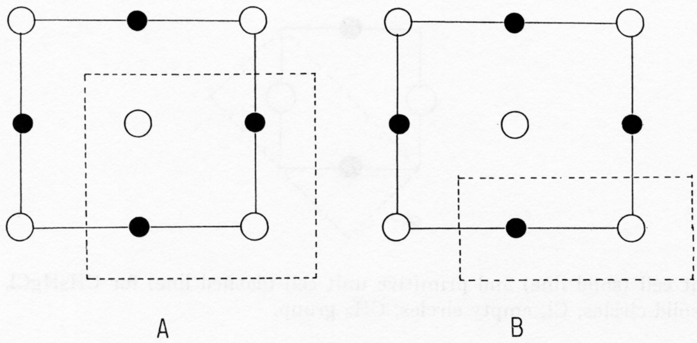

Figure 3. Unit cell (solid line) and different primitive unit cells (dashed lines) for CH_3HgI. A – four molecules/unit cell; point group D_{2h}^{11} $Z = 4$, B – two molecules/unit cell; point group C_{2h}^{11}, $Z = 2$. solid circles, I; empty circles, CH_3 group.

The same calculation has been performed for the simplified unit cell with two molecules per unit cell as shown in Figure 3B. The lattice force constants are given in Table VIII.

DISCUSSION

The external (or lattice) vibrations were taken into account using a dynamical matrix, as suggested by Shimanouchi and Harada[14] and Walmsley.[15]

According to our force constant calculation, it appears that rotatory modes show slightly stronger isotopic shifts with deuteration of methyl group than the translatory modes. This relationship is illustrated in Table IX for CH_3HgCl and CD_3HgCl. Thus, in addition to Raman observations of oriented crystals, the isotope shifts may also be used in assignment of the lattice modes.

TABLE IX

Isotope shift of lattice modes (cm^{-1})

MODES	SPECIES	CH_3HgCl ν/cm^{-1}	CD_3HgCl ν/cm^{-1}	$\Delta\nu_{obs}$	$\Delta\nu_{calc}$
Rotatory	e_u	74.0	68.0	6.0	2.4
Rotatory	e_g	68.0	63.3	4.3	2.2
Translatory long.	e_g	48.8	49.8	–1.0	0.3
Translatory transv.	a_g	37.2	36.0	1.2	0.2

The other argument that can be used in assignment of transverse and longitudinal translational modes can be illustrated by the following consideration. It is surprising that the e_g translatory mode for CH_3HgCl, which is closer to an asymmetric stretching mode of the HgX_4 fragment, occurs at a higher wavenumber than the a_g mode which resembles an HgX_4 out-of-plane deformation. These types of modes are shown in Figure 4.

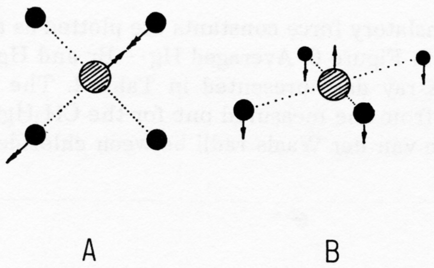

Figure 4. Raman active translatory modes. A – »In-plane« longitudinal mode (e_g) of HgX_4 fragment; B – »Out-of-plane« transverse mode (a_g) of HgX_4 fragment; solid circles, Cl; shaded circles, Hg.

The most substantial effect on the internal force constants on changing from benzene solution to the crystal state is the reduction in the HgX stretching force constant by 18, 16 and 14 %, respectively, for Cl, Br and I. The pairing of dipoles is doubtlessly a major contribution to the lattice forces, together with additional weak co-ordination of the strongly bound halide of each molecule to the neighbouring mercury atoms, which leads to distorted octahedral co-ordination about each mercury atom.

We have concluded, from the solution studies, that CH_3HgX molecules could add up to one additional halide in an equatorial site without any gross distortion of the strongly bound, linear Me–Hg–X fragment.[16] The Hg···X force constants of the weakly-bound halides have been calculated and they are remarkably close to the values for the longitudinal translatory force constants (f_{11}) in Table VI.

The translatory force constants of the lattices might be expected to show a relationship with other physical properties of the solids such as compressibilities, heats of sublimation and melting points. Unfortunately, the available data are confined to the last of these properties: 150 °C for I, 161 °C Br, 174 °C for Cl[17] and assumed to be about 220 °C for F (Figure 5).

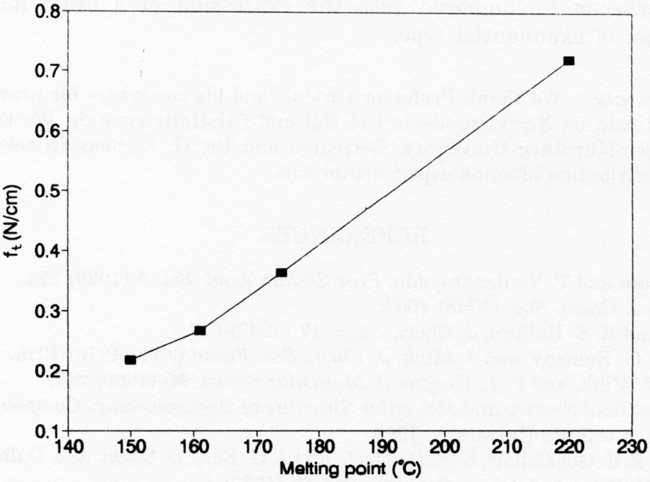

Figure 5. Correlation between melting points of methylmercury halides and their transverse translatory force constants.

The transverse translatory force constants are plotted as a function of Hg···X intermolecular distances in Figure 6. Averaged Hg···Br and Hg···I geometry has been used on the basis of X-ray data presented in Table I. The intermolecular distance Hg···F was calculated from the measured one for the CH_3HgCl crystal by reducing it by the difference of the van der Waals radii between chloride and fluoride.

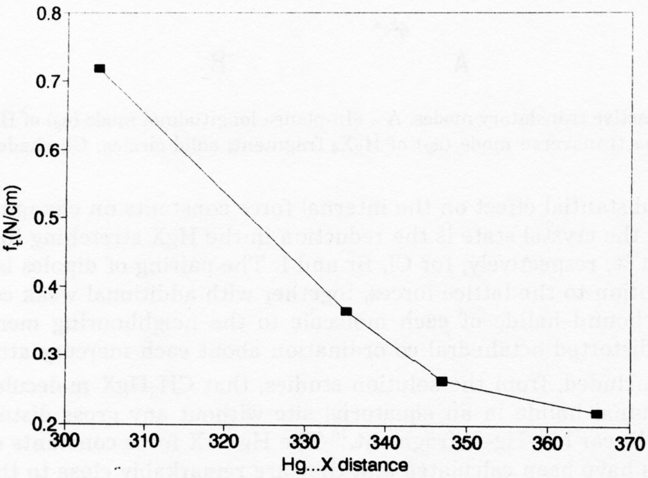

Figure 6. Correlation between intermolecular Hg···X distances and transverse translatory force constants. (Hg···F) – 304 pm; (Hg···Cl) = 335 pm; (Hg···Br) = 347 pm (averaged); (Hg···I) = 365 pm (averaged).

It can be concluded that the intermolecular interactions involving Hg and halide atoms show an exponential dependence on intermolecular distances, which is a reasonable correlation if compared with the expression of a usual intermolecular potential function of exponential type.

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SAŽETAK

Vibracijsko spektroskopsko istraživanje molekulskih kristala metal živa(II) halogenida

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Predlaže se gotovo potpuna asignacija vibracija kristala metal živa(II) halogenida. Za izvedbu vibracijskih izbornih pravila za kristalnu rešetku primijenjena je faktorska grupna analiza. Zaključeno je da prostorna grupa D_{4h}^{7} dozvoljava aktivnost svih vibracija fluorida i klorida. CH_3HgI pokazuje samo pet Ramanovih i jednu infracrvenu vrpcu ispod 50 cm^{-1}, tj. znatno manje nego se očekuje za strukturu D_{2h}^{11} sa četiri molekule u jediničnoj ćeliji. Vibracije rešetke za CH_3HgI i CD_3HgI mogu se asignirati na temelju podstrukture C_{2h}^{11} s divje molekule u jediničnoj ćeliji. Bromid pokazuje ultranisku vrpcu pri valnom broju od 7.0 cm^{-1}, koju nismo uspjeli asignirati. Konstante sile izračunane su na temelju primitivne jedinične ćelije, koja posjeduje dvije molekule. Unutarnje konstante sile istezanja su 2.112, 1.658, 1.507 i 1.347 Ncm^{-1}, a transverzalne translatorne konstante sile od 0.719, 0.364, 0.266 i 0.218 Ncm^{-1} m dobivene za fluorid, klorid, bromid i jodid, pokazuju jaku ovisnost o vrsti halogenida.