The origin of disorder in CH₃HgX (X = Cl, Br and I) crystals investigated by temperature dependent Raman spectroscopy

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Abstract. Methyl-mercury(II) halides CH_3HgX (X = Cl, Br and I) were studied by means of temperature dependent Raman spectroscopy from 10 K to 410 K. In addition to the previously reported soft phonons, new changes in the low frequency spectra were observed at $T \approx 70$ K in CH_3HgBr and at $T \approx 100$ K in CH_3HgI. The bandwidths of the two internal modes in CH_3HgBr, the CH_3 symmetric stretching band and the C-Hg-Br bending band, rise towards a local maximum at $T \approx 50$ K as the temperature is raised from 10 K to 300 K. On the other hand the bandwidths of the two corresponding modes in CH_3HgI crystals monotonously increase with temperature, obeying an Arrhenius law. Besides the three phonon modes present in the Raman spectra of CH_3HgCl at room temperature, the fourth phonon band that has been observed at temperatures below 245 K might correspond to the freezing of methyl librations. The huge bandwidth of the C-Hg-Br bending mode could suggest the presence of additional weak bonding of a mercury atom with bromine atoms from other molecules, thus inducing positional disorder.

PACS. 78.30.-j Infrared and Raman spectra – 63.50.+x Vibrational states in disordered systems

1 Introduction

Mercuric Hg(II) compounds like mercury(II) halides have a range of properties amenable to various applications: they can be used as solid state nuclear radiation detectors [1], and polarizer elements or acousto-optical filters [2]. Whereas much is known in the literature about Hg_2Cl_2, Hg_2Br_2 and Hg_2I_2 where they are cited as examples of improper ferroelectrics [2–4] and also about $HgCl_2$ [5,6], $HgBr_2$ [5,7], and HgI_2 [5,8], there is less data on CH_3HgX (X = Cl, Br and I) compounds.

The crystal chemistry of mercury differs in many respects from the chemistry of other group IIb elements, as already pointed out in [9]. Its basic characteristics originate from its $5d^{10}6s^2$ orbitals. Most of the Hg(II) structures have covalent Hg-X bonds which can contain sp, sp^2 or sp^3 hybrid bond orbitals of the Hg atom (here X = Cl, Br or I). The Hg-X bond roughly corresponds to the sum of covalent radii $r(Hg) + r(X)$. Additional bonds between a Hg and other X atoms could appear, however, if next nearest neighbour distances are smaller than the sum of the van der Waals radii of mercury and X atom [9].

Although CH_3HgX compounds form molecular crystals [10,11] and their vibrational spectra can be assigned *via* internal (intramolecular) and external (intermolecular or lattice) vibrations [12–18], there is evidence of a strong crystal field both from the NQR study of CH_3HgCl, as from the unusually large difference in the infrared

(312 cm⁻¹, [13]) and Raman (293 cm⁻¹) values of the observed Hg-Cl stretching band. We undertook a temperature dependent Raman study in order to collect more information on the nature of bonding in the CH_3HgX crystals.

Crystal structures

The crystal structure of CH_3HgCl at room temperature is tetragonal, P4/nmm, (D_{4h}^7), with $Z = 2$ molecules per unit cell with $a = b = 4.62$ Å and $c = 9.39$ Å (see Fig. 1) [10]. The relative orientation of methyl groups remained undetermined, since the authors stated that there was an almost free rotation of methyl groups. The disorder of methyl groups at room temperature is apparent from the mismatch of molecular (C_{3v}) and site symmetry (C_{4v}).

Both CH_3HgBr and CH_3HgI crystallize at room temperature in the orthorhombic space group Pbcm, (D_{2h}^{11}), with $Z = 4$ (see Fig. 2) [11]. For CH_3HgBr the cell parameters are $a = 8.825$ Å, $b = 6.971$ Å, $c = 6.909$ Å, and for CH_3HgI $a = 8.678$ Å, $b = 7.399$ Å, $c = 7.214$ Å. The bond lengths in the molecules are: $r(Hg-Br) = 2.50$ Å, $r(Hg-I) = 2.60$ Å. The next nearest bromine atoms are more than 3.58 Å away from the central mercury atom. In CH_3HgI the distance from a Hg atom to the next nearest iodine atom is 3.69 Å. Here, as for CH_3HgCl, we assumed the C-H bond length to be 1.098 Å and the H-C-H bond angle to be 107.3°, based on the data from nitromethane [20].
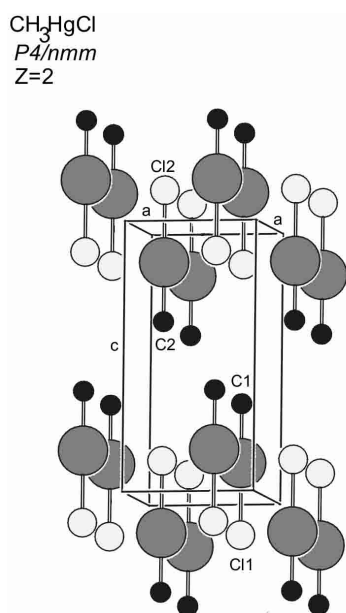
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Fig. 1. Crystal structure P4/nmm of CH_3HgCl at room temperature with $Z = 2$. Methyl protons are not shown.

Fig. 2. Crystal structure Pbcm of CH_3HgBr and CH_3HgI at room temperature with $Z = 4$.

The site symmetry of each molecule is C_s, that is, each molecule lies in a symmetry plane. On the other hand Adams and Pogson [12] cite an unpublished result of Russell who determined the crystal structure of CH_3HgBr as tetragonal $P\bar{4}2_1m$, D^3_{2d}, with $Z = 4$. They did not report any data on the crystal structure of CH_3HgI. There is an important difference in the molecular structure of CH_3HgBr as reported by these two groups: while Kotur *et al.* claim C-Hg-Br atoms to be collinear, Figure 13 in the work of Adams and Pogson [12] shows them curved.

Phase transitions

All compounds exhibit a structural phase transition accompanied by a well pronounced Raman active soft phonon [18]: CH_3HgCl at the $T_d = 156$ K, CH_3HgBr at 315 K and CH_3HgI at $T_d > 400$ K. Therefore, the crystal structures that are known are at temperatures both above T_d (CH_3HgCl), and below T_d (for CH_3HgBr and CH_3HgI). The phase transition is described as ferroelastic, and driven by the softening of the phonon at the Brillouin zone boundary in the high temperature phase, as described in [18]. For CH_3HgCl, Pirnat *et al.* [19] state that only the ^{35}Cl nuclear quadrupolar resonance line shows a discontinuity at 159 K, whereas proton spin-lattice relaxation time T_1 as well as ^{35}Cl longitudinal and transverse relaxation times vary continuously across T_d. They attribute the mechanism of the phase change to the small rearrangements in the neighboring Hg-Cl layers, to which the motion of the CH_3 groups is not very sensitive. Their value of activation energy for the proton relaxation is 161 cm^{-1} [19].

We undertook a temperature dependent Raman study of CH_3HgX (X = Cl, Br and I) compounds from 10 K to
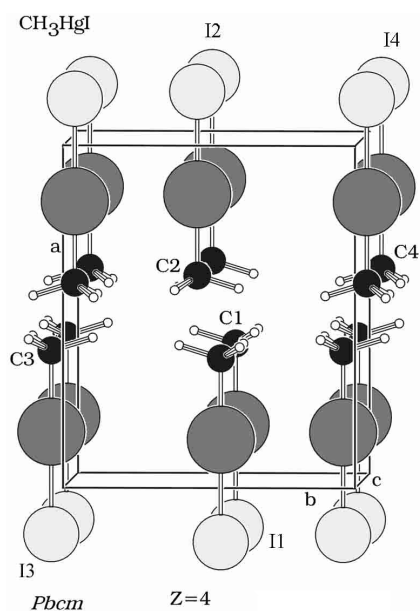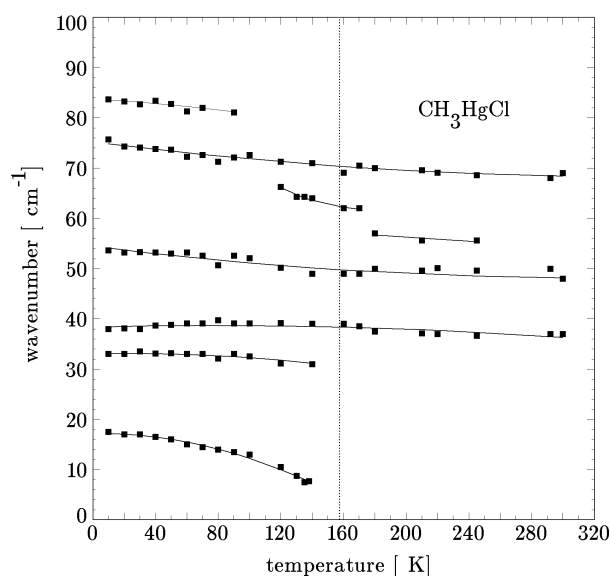

Fig. 3. Temperature dependence of the observed Raman phonon positions in CH_3HgCl. Solid lines serve as guides for the eye. The vertical dotted line indicates the temperature T_d.

410 K. In addition to the low frequency spectra (Figs. 3, 4 and 5), positions of internal modes were also reccorded (Tabs. 1, 2 and 3). Some of the observed bands corresponding to internal modes appeared particularly temperature sensitive: they are attributed to the C-Hg-Br and the C-Hg-I bending and the CH_3 symmetric stretching bands. The temperature dependence of their full-width at half-maximum (FWHM) bandwidths is shown in Figures 6 and 7.

Fig. 4. Temperature dependence of the observed Raman phonon positions in CH₃HgBr. Solid lines serve as guides for the eye. Vertical dotted lines correspond to temperatures of expected phase transitions.
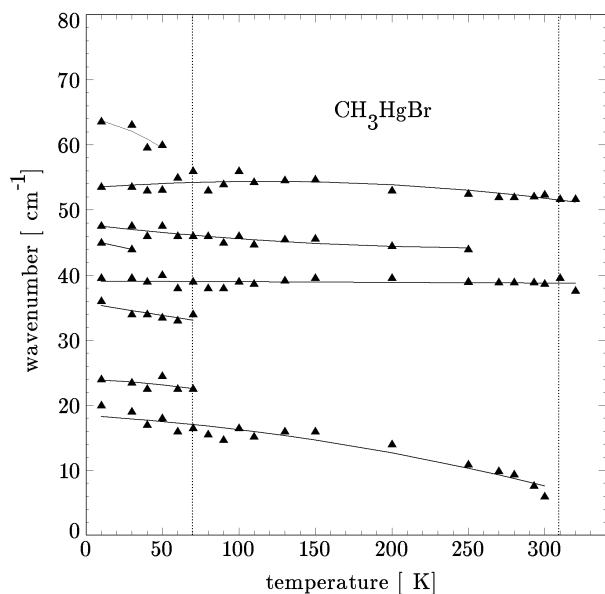

Fig. 5. Temperature dependence of the observed Raman phonon positions in CH₃HgI. Solid lines serve as guides for the eye. Vertical dotted lines correspond to temperatures of expected phase transitions.

2 Experimental

CH₃HgBr was obtained by courtesy of Prof. J. Mink, while CH₃HgCl and CH₃HgI were purchased from Strem Chemicals, with a purity better than 98 %. All samples which are highly toxic were sealed in a capillary, wrapped into an indium foil and mounted on a brass holder attached to the cooling head of CTI Cryogenics Model 21 cryostat [21].

Raman spectra were recorded with a DILOR Z 24 Raman spectrometer with a triple monochromator. An argon ion laser COHERENT Innova 100 operating at 514.5 nm was used. The power at the sample was kept at 40 mW or below, therefore multiscanning and long time constants had to be used. The spectral slitwidths were 2 cm⁻¹ and 3 cm⁻¹, respectively.

At a laser power > 60 mW sample degradation occurs, particularly in the case of CH₃HgBr which decomposes into Hg₂Br₂ (two strong bands at 37 cm⁻¹ and 135 cm⁻¹ appear). In CH₃HgI we always found traces of yellow HgI₂ (indicated by presence of the 140 cm⁻¹ band).

3 Results

Temperature dependent Raman spectra of CH₃HgCl, CH₃HgBr and CH₃HgI were recorded between 10 K and 410 K, and the variation of phonon positions are shown in Figures 3, 4 and 5.

It is virtually impossible to derive the number of expected phonons for CH₃HgCl at room temperature owing to the mismatch of the molecular and site symmetry. If the methyl group is replaced by a sphere (resembling the situation with freely rotating methyl groups), the number
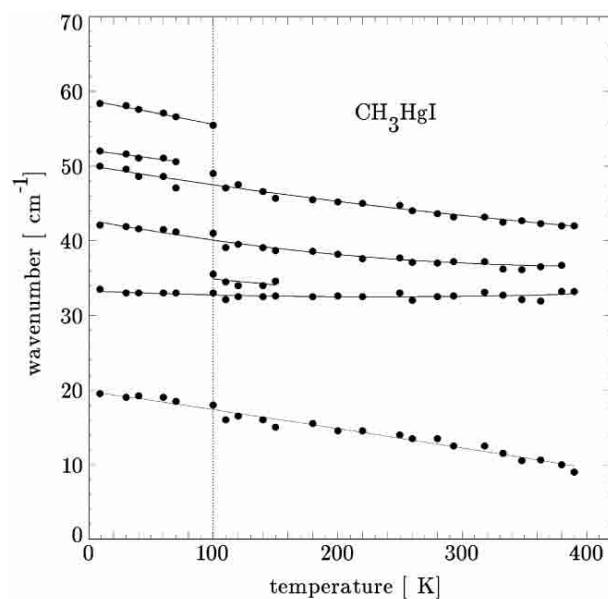
of external vibrations expected is

$$\Gamma_{\text{ext}} = A_{1g} \oplus 2E_g \oplus A_{2u} \oplus 2E_u. \tag{1}$$

On the other hand if there is a non-negligible methyl rotation potential, methyl group librations could be observed as very weak transitions in addition to the aforementioned bands. Three phonon bands observed in the Raman spectra at room temperature at 37 cm⁻¹, 49 cm⁻¹ and 68 cm⁻¹ are in agreement with this prediction. On lowering the temperature, at 245 K a fourth phonon band at 57.5 cm⁻¹ appears. The positions of the observed bands (Tab. 1) do not correspond to the values from any of the high pressure phases (see Fig. 2 in [12]).

For space group Pbcm with $Z = 4$ (which includes both CH₃HgBr and CH₃HgI), factor-group analysis predicts twelve Raman active and six infrared active modes (A_u modes are both Raman and infrared inactive):

$$\Gamma_{\text{ext}}^{\text{Pbcm}} = 3A_g \oplus 3B_{1g} \oplus 3B_{2g} \oplus 3B_{3g} \oplus 3A_u$$
$$\oplus 2B_{1u} \oplus 2B_{2u} \oplus 2B_{3u}. \tag{2}$$

If the P$\bar{4}$2₁m space group with $Z = 4$ is assumed [12], one would expect

$$\Gamma_{\text{ext}}^{\text{P}\bar{4}2_1\text{m}} = 3A_1 \oplus 3A_2 \oplus 3B_1 \oplus 2B_2 \oplus 5E. \tag{3}$$

Here all but A_2 modes are Raman active, whereas B_2 and E are infrared active modes. E modes would appear both in Raman and infrared spectra, but no coincidences were observed [13,17]. The band positions observed (Tabs. 2 and 3) are in agreement with the data from [13,17], but in disagreement with the results of Adams and Pogson in the case of CH₃HgBr [12]. At room temperature with ambient

Table 1. Observed Raman bands for CH_3HgCl at 10 K, 180 K and 300 K in cm^{-1}.

10 K	180 K	300 K	assignment
3012 m			
	3007 vvw	3008 vw	asym. CH_3 stretching
2924.5 s	2923.5 m	2926 m	sym. CH_3 stretching
1185 s	1185 s	1185 m	sym. CH_3 bending
557 vs	555 vs	554 vs	C-Hg stretching
293 s	292 s	293 s	Hg-Cl stretching
287.5 ms	287 ms	289 s	
146 sh,w			
140.5 w	140 vw	140 vw	C-Hg-Cl bending
84 sh			
74.5 s	70 vs	68 s	$R_x, R_y^\dagger$
	57.5 m		
52.5 m	50 m	49 m	T_z
36.5 mw	37.5 ms	37 ms	T_x, T_y
32 mw			
17.5 m			

s - strong, m - medium, w - weak, v - very, sh - shoulder.
[†]The phonon assignment refers to the room temperature structure.

Table 2. Observed Raman bands for CH_3HgBr at 10 K, 45 K and 297 K in cm^{-1}.

10 K	45 K	297 K	assignment
3024 m	3023 w,sh		
3019 m	3018 w	3015 vvw	asym. CH_3 stretching
2932 s	2929 m	2925 m	sym. CH_3 stretching
1173 s	1174 s	1174 m	sym. CH_3 bending
549 s	550 s	547 s	C-Hg stretching
208 s	207 s	204 s	Hg-Br stretching
199 w	198 w	196 w	
151 w,br	141 w,br	118 w,br	C-Hg-Br bending
64 m	60 s,br		
54 m	54 sh	53 s,br	$R_y, R_z^\dagger$
48 w			
45 w	47 mw,sh		
39 w,sh	40 mw	39 m	T_y, T_z
36 w			
24 w,sh	22,5 w,sh		
20 m	17 s	6 s	T_y

s - strong, m - medium, w - weak, v - very, sh - shoulder, br - broad.
[†]The phonon assignment refers to the room temperature structure.

pressure Adams and Pogson observed four phonon bands: at 40 cm^{-1}, 46 cm^{-1}, 52 cm^{-1} and 70.2 cm^{-1}. Different origin of the sample and possible polymorphism of the methylmercury(II) bromide may be the reason why we do not observe the 70.2 cm^{-1} band. On further cooling of CH_3HgBr, new bands appear at $T \approx 70$ K (Fig. 4), and the bandwidth of the symmetric CH_3 stretching band, δ_{Br,CH_3}, has a maximum at $T \approx 50$ K (Fig. 6).

CH_3HgI δ_{I,CH_3} does not show any abrupt changes. Moreover it obeys the Arrhenius law

$$\delta_{I,CH_3} = \delta_{I,CH_3}^o + C'e^{-\frac{E_{I,CH_3}^a}{kT}} \qquad (4)$$

quite well (see Fig. 6, solid line), with $E_{I,CH_3}^a = 116 \pm 7$ cm^{-1}. This value was obtained by fitting the points using the MINUIT minimization program [22]. In the low temperature limit the bandwidth approaches the vibrational relaxation value δ_{I,CH_3}^o, whereas the temperature dependent part is described as orientational relaxation [39,40]. The change in the number of phonons occurs at $T \approx 100$ K: two weak bands at 52 cm^{-1} and 58 cm^{-1} at 10 K merge into one band at 56 cm^{-1} at 100 K (Fig. 5). Since a high pressure study reported phonon bands at 52 cm^{-1} and 58 cm^{-1} when the applied pressure was between 5 kbar and 12 kbar [12], it is possible that a phase change around 100 K is taking place.

Additional information on the temperature dependence of vibrational dynamics of CH_3HgX compounds is obtained from the variation of the C-Hg-X bending mode bandwidth δ_{C-Hg-X}. In CH_3HgCl the weak and narrow band at 140 cm^{-1} at room temperature splits into two

Table 3. Observed Raman bands for CH_3HgI at 10 K, 100 K and 294 K in cm^{-1}.

10 K	100 K	294 K	assignment
3012 m			
3009 m	3009 w	3015 w	asym. CH_3 stretching
3005 m			
2917 s	2917 s	2917 m	sym. CH_3 stretching
1163 s	1162 s	1161 s	sym. CH_3 bending
532.5 vs	533 vs	531 s	C-Hg stretching
		524 w,sh	
170 s	169 s	167 s	Hg-I stretching
149	148	146	HgI_2 sym. stretch.
140 w,br	134 w, br	118 w,br	C-Hg-I bending
58 w	56 w		methyl libration?
52 ms			
49 m,sh	49 m	44.5 ms	$R_y, R_z^\dagger$
42 mw	41 mw	38 m	T_x
	35.5 sh	34 m	T_y, T_z
33 mw	33 mw		
19.5 s	18 s	14 s	T_y

s - strong, m - medium, w - weak, v - very, sh - shoulder, br - broad.
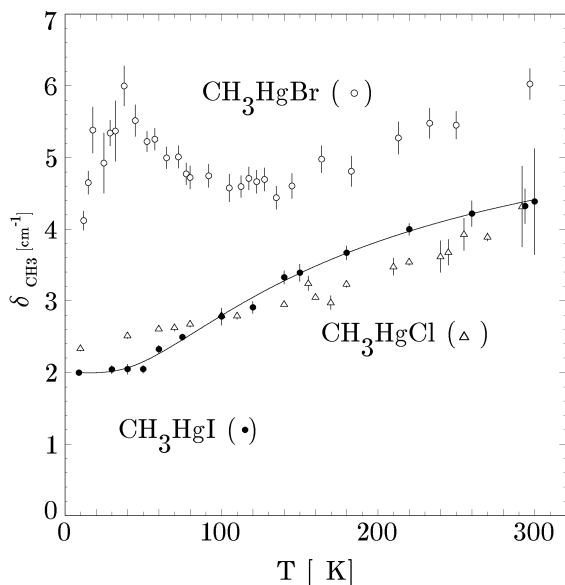[†]The phonon assignment refers to the room temperature structure.

Fig. 6. Temperature dependence of the FWHM δ of the symmetric CH$_3$ stretching band in CH$_3$HgBr (○), CH$_3$HgCl (△) and CH$_3$HgI (●). The solid line is a fit by an Arrhenius law (4). Vertical lines through the points correspond to error bars.

Fig. 7. Temperature dependence of the FWHM of the C-Hg-X bending band (X = Br and I) in CH$_3$HgBr (○) and CH$_3$HgI (■). Vertical lines through the points correspond to error bars.

bands below T_d. For CH$_3$HgBr and CH$_3$HgI the variation of the $\delta_{\text{C-Hg-X}}$ with temperature is shown in Figure 7. For the space group Pbcm group theory predicts two Raman active modes corresponding to C-Hg-Br or C-Hg-I bending. However there is only one of considerable bandwidth in both compounds. Again there is a remarkable difference in the temperature behaviour of $\delta_{\text{C-Hg-Br}}$ and $\delta_{\text{C-Hg-I}}$. The solid line in Figure 7 is a fit to equation (4) with $\mathrm{E}^a_{\mathrm{bend}} = 43 \pm 3$ cm^{-1}.

4 Discussion

There is a longstanding interest in the subject of large amplitude motion of molecular ions in crystals, and especially puzzling is the internal rotation of the methyl group [24,25]. Recently, particular attention has been paid to systems of interacting methyl groups [26–31]. In aspirin, acetic acid, and many other systems the methyl rotation potential was calculated as a sum of intramolecular and intermolecular contributions [32–34]. Among two-dimensional systems of coupled rotors that have been studied experimentally are monolayers of homonuclear diatomic molecules adsorbed on graphite or some other substrate [35], while quantum anisotropic planar rotor model simulated by path integral Monte Carlo method [36], or uniformly frustrated *XY* model of planar Brownian rotors studied by molecular dynamics [37] are only some of the theoretical models used. In all CH$_3$HgX crystals, methyl groups are confined to planes (see Figs. 1 and 2). While in CH$_3$HgCl the smallest methyl-methyl distance is estimated to be 2.40 Å for two groups from the *opposite* planes (between molecules 1 and 2 in Fig. 1), in CH$_3$HgBr and CH$_3$HgI it is 2.36 Å and 2.59 Å for the groups from
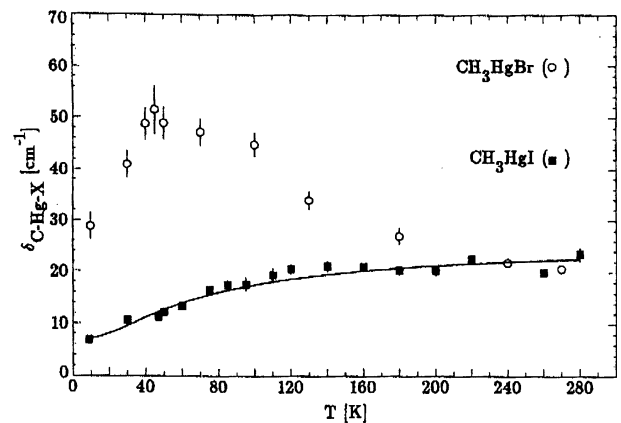
the *same* plane (between molecules 1 and the molecule 3 translated by the vector **b**).

There are no data on crystal structure of CH$_3$HgCl below 300 K, but at room temperature methyl groups are freely rotating [10] and three Raman active phonons are observed. The appearance of the fourth phonon at 245 K could correspond to orientational freezing of methyl groups, while at $T_\mathrm{d} = 156$ K the rearrangement of Hg and Cl atoms dominates [19].

A smooth variation of the linewidth $\delta_{\mathrm{I,CH3}}$ in CH$_3$HgI according to an Arrhenius law (4) can provide an estimate of the hindering barrier for the methyl libration [42]. Assuming the simple form of the potential $V(\phi) = \frac{1}{2}V_3(1 - \cos(3\phi))$ for the librations, V_3 would be of the order $\mathrm{E}^a_{\mathrm{I,CH3}} = 116$ cm^{-1}. For such a $V(\phi)$ the 0A→1A Raman transition would be at 67 cm^{-1} (calculated by VIBAR [43]). The weak band at 58 cm^{-1} at 10 K could be a methyl libration band which disappears at ≈ 100 K, the temperature tentatively suggested as the phase transition temperature.

The temperature anomaly present in $\delta_{\mathrm{Br,CH3}}$ and in $\delta_{\text{C-Hg-Br}}$, with the maximum at $T \approx 50$ K, as well as the appearance of new phonon bands below $T \approx 70$ K (see Fig. 4) support the hypothesis of a new phase transition in CH$_3$HgBr below T_d. Such temperature behaviour of a band attributed to the internal mode was reported for ND$_4$TeBr$_6$ [44] and K$_3$D$_x$H$_{1-x}$(SO$_4$)$_2$ [45]. In both cases a phase transition was simultaneously taking place. The two modes in CH$_3$HgBr that exhibit such an anomaly include displacements of the methyl group and/or mercury and bromine atoms, indicating a multidimensional order parameter of the transition. In 4-methyl-pyridine the bandwidth of the 66 cm^{-1} band also shows similar behaviour [29], but the model of one-dimensional chains of coupled methyl groups that was provided as explanation for the dynamics was questioned after different methyl tunneling transitions were observed in additional neutron scattering experiments [30].

Although the magnitude of the C-Hg-Br and C-Hg-I bending bands are similar at 300 K (20 and 24 cm^{-1}) their

temperature behaviour differs (Fig. 7). Since the bandwidth of the C-Hg-Br bending band is 28 cm^{-1} at 10 K, we propose the existence of the static disorder of mercury and/or bromine atoms. The disorder could originate from the chemical bonding of one mercury atom with bromine atoms from other molecules. Although at room temperature the distance between one Hg atom and four next nearest Br atoms is 3.69 Å, on lowering the temperature these atoms may approach, and form new chemical bonds.

5 Conclusion

In addition to changes in the number of Raman phonon bands previously observed [18] new ones appear at $T \approx$ 70 K in CH$_3$HgBr, and at $T \approx$ 100 K in CH$_3$HgI. The band at 57.5 cm^{-1} in CH$_3$HgCl that is present in the temperature range between T_d and 245 K could be related to the ordering of methyl groups. The disappearance of the weak band observed at 56 cm^{-1}, followed by the appearance of the shoulder at 36 cm^{-1} in CH$_3$HgI at $T \approx$ 100 K, might correspond to a change in crystal structure, while a new, yet unidentified crystal phase, exists below $T \approx$ 70 K in CH$_3$HgBr. Here the huge bandwidth of the bending mode observed at all temperatures (10 K–300 K) strongly indicates static disorder of mercury and/or bromine atoms. These hypotheses need to be verified by further elucidation of the low temperature structures, since at present only room temperature data are available.

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