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Raman spectra from a low-symmetry form of mercury(I) fluoride

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Abstract. The Raman scattering of mercury(I) fluoride was investigated over the temperature range from 35 to 500 K. A low-lying peak was found at 23.5 cm^{-1} over the entire temperature range and is considered to be a tranverse acoustic mode frozen to the Γ point. The Raman spectrum accompanying the low-lying mode indicates the low symmetry reduced from the room-temperature phase ($I4/mmm$). The distance of the Hg–Hg bonding was evaluated to be 2.55 Å from the classical Badger rule.

1. Introduction

Mercury(I) halide crystals display a very high birefringence (Duffet 1898) and are useful as a polariser (Forman *et al* 1974). The elastic properties are also quite anomalous (Sil'vestrova *et al* 1975). The crystal is formed by straight parallel chains of $(\mathrm{X{-}Hg{-}Hg{-}X})_n$ molecules, where $\mathrm{X} \equiv$ halogen. The room-temperature phase belongs to the space group $I4/mmm$ (D_{4h}^{17}) with two molecules in the body-centred crystallographic unit cell (Wyckoff 1963). At low temperatures, Hg_2Cl_2 and Hg_2Br_2 undergo an improper ferroelastic phase transition to the space group $Bbmm$ (D_{2h}^{17}) (Barta *et al* 1975, Boiko and Vaipolin 1977). It is found that Hg_2I_2 also transforms its phase to the same space group as Hg_2Cl_2 and Hg_2Br_2 under hydrostatic pressure (Rehaber *et al* 1982).

Early work on the Raman scattering of mercury(I) halides investigated the metal–metal bonding distance of the crystal structure (Gager *et al* 1966, Stammreich and Teixeira 1967–8). Recent work is aimed at the phase transition at which a zone-boundary phonon of an acoustic branch becomes unstable and appears as a soft mode (Barta *et al* 1975, 1976, 1978, Boiko and Vaipolin 1977, Rosasco *et al* 1978). For Hg_2F_2, the Raman peak corresponding to the Hg–Hg stretching vibration (A_{1g} mode) is found to be 186 cm^{-1} at room temperature (Stammreich and Teixeira 1967–8). However, characteristics such as the phase transition are not well understood, and no detailed Raman spectrum has been observed. The room-temperature phase is found to be $I4/mmm$ for the same space group as the mercury(I) halides (Dorm 1971).

In the present paper, the Raman spectra of a new synthesised mercury(I) fluoride with a low-symmetry phase are measured over the temperature range from 35 to 500 K.

The phase and symmetry are discussed, while the Hg–Hg bonding distance is evaluated from the classical Badger rule.

2. Experimental procedure

The single crystal was grown from a vapour phase in a quartz ampoule which was first evacuated to 10^{-3} Torr, and then He gas was charged to about 100 Torr. The quartz ampoule filled with Hg_2F_2 powder at the end of the ampoule was laid in a furnace having a temperature gradient of about 100 °C from one end to the other. For a week, the quartz ampoule was set aside to crystallise. Different coloured crystals grew on opposite sides of the ampoule. Needle-shaped red–brown crystals grew copiously at the end and next yellow crystals and colourless crystals grew in the middle part of the quartz ampoule. The yellow crystals consist of many small single crystals of size 0.2–0.5 mm^3. We analysed the yellow compound by electron probe microanalysis and x-ray photoelectron spectroscopy and examined it chemically. This crystal showed the physical and chemical nature of mercury(I) fluoride. However, our yellow crystal presents a different Raman spectrum from that of the previous reports. The cell dimensions were determined from a precession photograph with Cu Kα radiation (1.5418 Å). A phase (monoclinic) different from that reported previously (Dorm 1971) was obtained.

The other products displayed a chemical nature different from mercury(I) fluoride. Space groups and cell dimensions were obtained as follows: for the red–brown substance, $A2/a$ or Aa ($a = 11.371$ Å, $b = 24.19$ Å, $c = 5.65$ Å and $\beta = 109°$); for the colourless substance, $Pmn2_1$ or $Pmmn$ ($a = 11.59$ Å, $b = 10.35$ Å and $c = 9.56$ Å). These substances show very complex Raman spectra corresponding to the large cell dimension. Further analysis will be required.

The Raman spectra were measured with a right-angled arrangement, using a 2 W Ar laser, a Jarrel–Ash double monochromater and single-photon-counting equipment. The light intensity from the Ar laser was adjusted with neutral density filters to obtain adequate excitation intensity, since the crystal is darkened by strong light. Low temperatures were achieved by Oxford refrigeration equipment.

3. Experimental results

Representative Raman spectra of Hg_2Br_2, Hg_2Cl_2 and our yellow crystals measured at room temperature are shown in figure 1. Three intensive peaks are observed for all crystals, the frequencies of those peaks decreasing from the lightest fluoride to the heaviest iodide (Barta *et al* 1974). However, the doublet structure of the peak at around 55–63 cm^{-1} and a few additional weak peaks at around 80–130 cm^{-1} can be observed in the spectrum of our mercury(I) fluoride. It should also be noticed that a low-lying peak is observed at 23.5 cm^{-1}.

Figure 2 shows the Raman spectra of the mercury(I) fluoride at various temperatures ranging from 41 to 374 K. No new peak appears at low temperatures down to 35 K while no peak disappears at high temperatures up to 500 K. With decreasing temperature, the higher-frequency peaks become more intensive and the weak peaks become clearer. The lowest-frequency peak becomes weaker with decreasing temperature but does not shift to lower energies. The doublet peak retains its frequencies over the entire

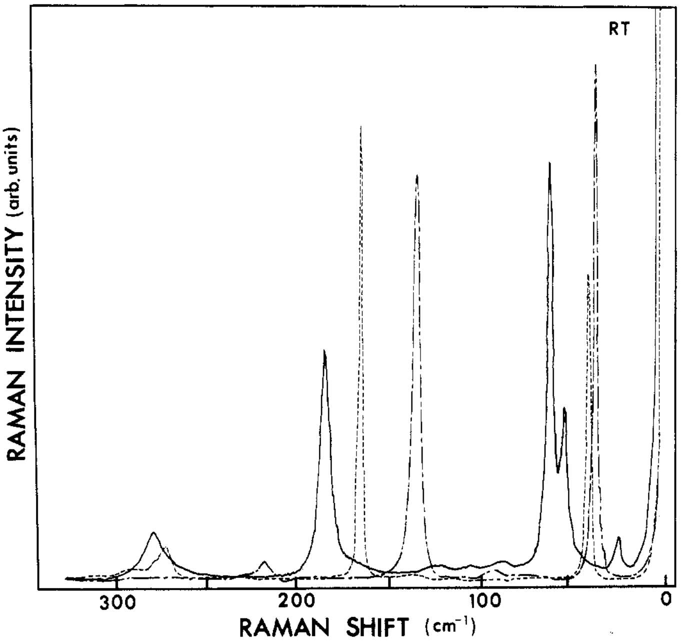

Figure 1. Raman spectra of three mercury(I) halides at room temperature: ——, this work (yellow crystals); -----, Hg_2Cl_2; —·—, Hg_2Br_2.

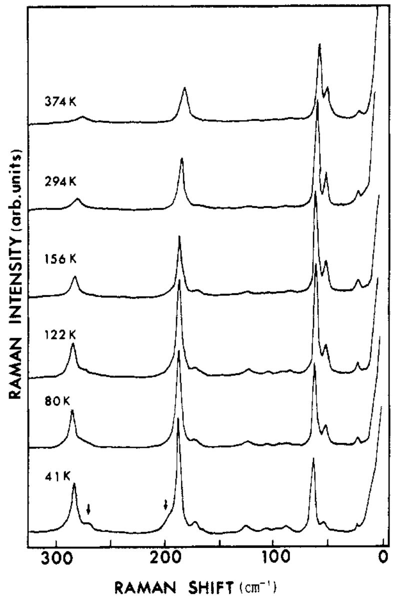

Figure 2. Raman spectra at various temperatures. The higher-frequency peak becomes more intensive with decreasing temperature. No other marked change is found.

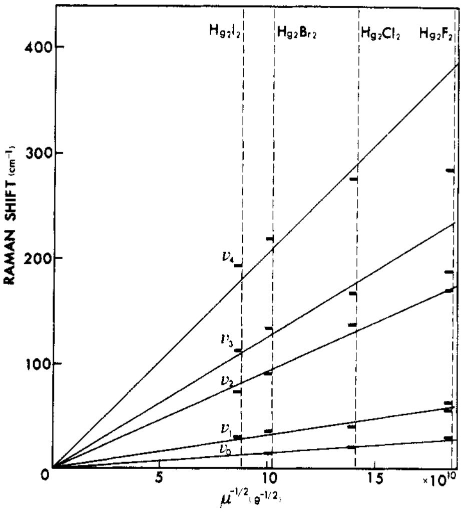

Figure 3. Relation of the Raman shifts to the reciprocal square root of reduced mass.

Table 1. Crystallographic parameters and the space groups.

	Hg_2F_2	This work	Hg_2Cl_2
	$I4/mmm$[a]		$I4/mmm$
a	3.68 Å		4.48 Å
c	10.90 Å		10.91 Å
		($P2_1/m$)	$Bbmm$[b]
a		5.47 Å	6.29 Å
b		6.64 Å	6.24 Å
c		11.41 Å	10.86 Å
β		98° 51′	—

[a] Dorm (1971).
[b] Wyckoff (1963).

Table 2. Fundamental frequencies at room temperature.

This work	$\left.\begin{matrix}55\\63\end{matrix}\right\}$ cm^{-1}	171 cm^{-1}	186 cm^{-1}	283 cm^{-1}
Hg_2Cl_2	41 cm^{-1}	138 cm^{-1}	168 cm^{-1}	276 cm^{-1}
Hg_2Br_2	36 cm^{-1}	91 cm^{-1}	135 cm^{-1}	220 cm^{-1}
Hg_2I_2	30 cm^{-1}	74 cm^{-1}	113 cm^{-1}	193 cm^{-1}

temperature range. Thus, the crystal phase does not alter in the temperature range from 35 to 500 K.

4. Discussion

Since the crystal is twinned, we cannot determine its unique crystal structure. However, the lattice type is considered to be monoclinic. The cell dimensions are given in table 1 with previously reported values and those of Hg_2Cl_2 in the low-temperature phase. The crystallographic unit cell of our mercury(I) fluoride is somewhat longer and more slender than that of Hg_2Cl_2.

To clarify the correspondence of each peak to each crystal, the relation between the frequency and the reciprocal square root $1/\sqrt{\mu}$ of the reduced mass is plotted for the five peaks in figure 3. The frequencies of the ν_1 and ν_2 modes in all the crystals are on straight lines, whereas those of the ν_3 and ν_4 modes are off the lines on the lower-frequency side for the lighter crystals. Nevertheless, the correspondences are fairly good. Here, the mode labelling follows that of Barta *et al* (1974). The soft mode ν_0, which appears in the Raman spectrum in the low-symmetry phase, is also linearly related. The frequencies of the major modes are summarised in table 2. The spectrum of the present crystal shows many features similar to that of the low-symmetry phase of the other mercury(I) halides. If it is assumed that the phase of the present crystal is slightly distorted to a monoclinic state from the low-symmetry phase of Hg_2Cl_2 or Hg_2Br_2, the crystal phase will be considered to belong to the same space group $P2_1/m$ as that indicated by Rosasco *et al* (1978) for the low-temperature phase of Hg_2Cl_2. The low-symmetry phase is constituted as a superstructure of the high-symmetry phase, resulting in zone folding of the phonon dispersion relation. Then, the low-lying mode is considered to be the transverse acoustic mode folded and frozen to the Γ point.

In our case, Raman spectroscopy plays an important role in evaluating the Hg–Hg distance, since a precise structure analysis of twinned crystal could not be made. Badger's (1934, 1935) rule for diatomic molecules will be applied to evaluate the structure, referring to the report by Stammreich and Teixeira (1967–8):

$$F_{\nu_3}^2(r-d)^3 = C \tag{1}$$

where F_{ν_3} is the mode frequency of the Hg–Hg stretching vibration, r is the Hg–Hg distance, and d and C are constants which should be determined from the known mercury(I) halides.

Substituting the r- and F_{ν_3}-values for Hg_2Cl_2 and Hg_2Br_2 into equation (1), we have

$$r(\mathrm{Cl}) = 2.53\ \text{Å} \qquad F_{\nu_3}(\mathrm{Cl}) = 168\ \mathrm{cm}^{-1} \qquad (\mathrm{Hg_2Cl_2})$$

$$r(\mathrm{Br}) = 2.49\ \text{Å} \qquad F_{\nu_3}(\mathrm{Br}) = 135\ \mathrm{cm}^{-1} \qquad (\mathrm{Hg_2Br_2})$$

where the Hg–Hg distances are adopted from the report by Dorm (1971). We can obtain two equations with two unknowns, d and C. These equations give $d = 2.785$ Å and $C = -468$ Å^3 s^{-2}. Substituting again the results into equation (1), we can obtain the Hg–Hg distance $r = 2.55$ Å for our mercury(I) fluoride.

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