Single-crystal Infrared Study and Assignment for Mercury(II) Chloride and Bromide

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A study of $HgCl_2$ and $HgBr_2$ has been made using single-crystal i.r. reflectance (115 and 295 K) and absorption (295 K) methods. All the fundamentals predicted by factor-group analysis have been observed and assigned to their symmetry species for both materials. Existing single-crystal Raman data have been accounted for in detail in the case of $HgCl_2$. Infrared bands at 32 and 40 cm^{-1} in $HgCl_2$ are attributed to translatory modes, and it is probable that the ν_2 components are at higher frequencies than the libratory lattice modes. The lack of single-crystal Raman data for $HgBr_2$ requires the deferment of the assignment of all the details of the Raman spectra from polycrystalline samples, and is desirable for confirmation of weaker features in the i.r. spectra.

MERCURY(II) chloride and bromide have been studied often using Raman[1-20] and i.r.[14,17,20-33] spectroscopy. The positions of the two stretching modes allowed to these linear ($D_{\infty h}$) molecules [ν_1, Σ_g^+, ν_{sym}(Hg–X); ν_3, Σ_u^+, ν_{asym}(Hg–X)] have been assigned beyond doubt for gaseous, molten, and dissolved samples on the basis of the Raman polarisation property of ν_1, ν_3 being assigned by elimination and force-constant relations. The first information on the positions of ν_2, [π_u, $\delta(HgX_2)$] came from analyses of fine structure in the electronic spectra of the vapours,[34,35] revealing surprisingly low values: $HgCl_2$, 70; $HgBr_2$, 41 cm^{-1}. These were corrected after direct observation of ν_2 in gas-phase spectra in the far-i.r. ($HgCl_2$, 100; $HgBr_2$, 68 cm^{-1}),[32] and similar values have been obtained for matrix-isolated molecules[30] [107 ($HgCl_2$) and 73 cm^{-1} ($HgBr_2$) respectively].

Rao,[6] the first to report low-shift Raman data for solid $HgCl_2$, found bands at 73, 95, and 124 cm^{-1}, noting that the lowest one might be ν_2 and the others lattice modes. The most complete Raman data for $HgCl_2$ are in two single-crystal studies,[13,14] both at ambient temperature, and shifts have been listed for a polycrystalline sample at liquid-nitrogen temperature.[17] No single-crystal Raman study of $HgBr_2$ has appeared, but there is a recent report of the Raman shifts shown by the solid at liquid-nitrogen temperature.[17] Both solids have recently been studied by Raman and i.r. methods at very high pressures.[36,37]

Although there are many reports of i.r. absorption by solid $HgCl_2$ (refs. 14, 17, 22–24, 26, 27, and 36) and $HgBr_2$ (refs. 17, 22—27, 31, and 37) few give information on the regions below those of the stretching modes ($HgCl_2$, refs. 26, 27, and 36; $HgBr_2$, refs. 17, 26, 27, 31, and 37) and none has involved the use of polarised light. Accordingly there is no information on which to base an assignment of these data, and it is doubtful whether the spectra themselves have been established adequately. We report the results of a study of the i.r. spectra of these solids using orientated single crystals in polarised light. Most of the data were collected using reflectance spectroscopy, which is particularly convenient for use with highly absorbing materials, but weaker features have been investigated also using transmission of polarised light through thin, orientated, crystal flakes.

EXPERIMENTAL

Commercial $HgCl_2$ and $HgBr_2$ were purified by vacuum sublimation. Crystals were grown from the sublimates by vapour-phase transport in an evacuated tube which was passed through a thermal gradient, moving *ca.* 8 cm during

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1 week. For $HgCl_2$ the peak temperature was set at 130 °C, and at 110 °C for $HgBr_2$. Each crystal boule was cut into sections and polished to expose faces which showed extinction directions under the polarising microscope. Axes, which corresponded with the optical extinction directions, were located by *X*-ray methods. For both crystals the standard axis set was chosen: for $HgCl_2$, $a = 12.735$, $b = 5.963$, and $c = 4.325$ Å; for $HgBr_2$, $a = 4.624$, $b = 6.798$, and $c = 12.445$ Å.

For $HgCl_2$, i.r. reflectance spectra were obtained from a crystal *ca.* 5 (*x*) × 3 (*z*) × 2 (*y*) mm. Transmission spectra were investigated using thin cleavage fragments *ca.* 1.5 mm² (*xz* face); only the bands at 32, 40, 312, and 330 cm⁻¹ were weak enough to be seen in transmission since all the others showed complete extinction. A crystal of $HgBr_2$ *ca.* 15 (*z*) × 6 (*x*) × 3 (*y*) mm was used for reflectance work; the axes are shown in parentheses. A small flake *ca.* 1.5 mm² (*xy* face) was used for transmission work.

Far-i.r. data were collected using a Beckman-RIIC FS-720 Fourier spectrometer and an RS-7F reflectance module which allows collection of reflected radiation at *ca.* 15° from the normal from a crystal mounted at the beam focus. Perkin-Elmer wire-grid polarisers were used. Crystals were mounted on copper blocks with ' 5-minute ' epoxy resin and cooled in a home-made cryostat using liquid nitrogen. The temperature at the crystals was estimated to be 115 K.

RESULTS

The observed i.r. reflectance spectra were analysed by the Kramers–Krönig procedure [38] to yield the refractive index (*n*), extinction coefficient (*k*), and the real (ε′) and imaginary (ε″) parts of the complex dielectric function, ε*. These quantities are related by $\varepsilon^* = \varepsilon' + i\varepsilon''$, $\varepsilon^* = (n^*)^2$, and $n^* = n + ik$. For our purpose, their significance is that the *n,k* crossover points yield values of the transverse optical (t.o.) and longitudinal optical (l.o.) modes of the lattice. However, often cases arise in which *n* and *k* do not show crossover points for all the oscillators in the spectrum [for example in Figure 1(*a*)]; an additional source of this information is available in that the maxima of $\varepsilon'' = 2nk$ correspond to t.o. mode frequencies and nodes of ε′ to those of the l.o. modes. At any frequency the reflectance, *R*, is given by $[(n - 1)^2 + k^2]/[(n + 1)^2 + k^2]$. At frequencies well above the highest i.r.-active mode (*i.e.* at optical frequencies) $k \approx 0$ and *R* may therefore be calculated to a good approximation from a knowledge of the refractive index of the material and compared with the observed percent reflectance. Figures 1 and 2 show the observed reflectance and the derived parameters, whilst the data are summarised in Tables 1 and 2. The t.o. maxima quoted are believed to be accurate to ±1.5 cm⁻¹.

TABLE 1

Transverse and longitudinal optic modes (cm⁻¹) for $HgCl_2$ derived from Kramers–Krönig analysis of observed i.r. reflectance spectra

295 K		115 K		
t.o.	l.o.	t.o.	l.o.	Assignment [a]
B_{1u} modes (*z* polarised)				
ca. 39 [b]	*ca.* 44	39	44	ν_T
74	83	76	85	ν_2, $\delta(HgCl_2)$; (or ν_R)
108 [c]	133 [c]	113 [c]	137 [c]	ν_R (or ν_2)
310 [f]	316	310	316	ν_1, $\nu_{sym}(HgCl_2)$
379	388	384	392	ν_3, $\nu_{asym}(HgCl_2)$
B_{2u} modes (*y* polarised)				
94	*ca.* 107 [d]	96	*ca.* 112 [d]	ν_2, $\delta(HgCl_2)$; (or ν_R)
115	132	120	134	ν_R (or ν_2)
B_{3u} modes (*x*-polarised)				
30 [e]	35	32	37	ν_T
96	112	99	116	ν_2, $\delta(HgCl_2)$; (or ν_R)
123	130	127	136	ν_R (or ν_2)
n.o. [f]	n.o.	330	334	ν_1, $\nu_{sym}(HgCl_2)$
372	386	380	390	ν_3, $\nu_{asym}(HgCl_2)$

[a] ν_T = Translatory lattice mode, ν_R = librational lattice mode. [b] At 40 cm⁻¹ in single-crystal transmission spectra. Only seen clearly in reflectance at 115 K. [c] Obtained by treating the band as due to one fundamental, with a second-order feature appearing at 127 cm⁻¹ at 115 K (Figure 1). [d] Estimated visually. [e] At 32 cm⁻¹ in single-crystal transmission spectra. [f] At 330 (B_{3u}) and 312 cm⁻¹ (B_{1u}) respectively in single-crystal transmission spectra; n.o. = not observed.

TABLE 2

Transverse and longitudinal optic modes (cm⁻¹) for $HgBr_2$ derived from Kramers–Krönig analysis of observed i.r. reflectance spectra

295 K		115 K		
t.o.	l.o.	t.o.	l.o.	Assignment
A_1 modes (*z* polarised) [a]				
15 [b]		n.o.		
30 [c]	33 [d]	31	33 [d]	
70	100	73	104	
252	258	253	260	ν_3, $\nu_{asym}(HgBr_2)$
B_1 modes (*x* polarised)				
33	93	35	96	
ca. 50		*ca.* 50		
B_2 modes (*y* polarised)				
n.o.	n.o.	42	*ca.* 44 [d]	
53	*ca.* 70 [d]	53	*ca.* 70 [d]	
76	92	79	96	
ca. 220		222	234 [d]	ν_3, $\nu_{asym}(HgBr_2)$

[a] An additional band at 185vw cm⁻¹ was found in single crystal transmission. [b] Single-crystal transmission result. [c] At 29 cm⁻¹ in single-crystal transmission spectra. [d] Estimated visually from the reflectance spectrum. All the other values are ε″ maxima (t.o. modes) or ε′ nodes (t.o. modes) (see text).

DISCUSSION

Mercury(II) *Chloride*.—This solid has the symmetry *Pnma* (D_{2h}^{16}) with $Z = 4$.[39] All the atoms are on sites 4*c*, the molecules being in planar sheets stacked along *b*. Crystallographically the two Hg–Cl bonds are not required to be either equal in length or collinear, but the actual distortions are sufficiently small that $D_{\infty h}$ forms a good basis for understanding the spectra. A factor-group analysis (f.g.a.) has been published.[36] We note the correlation of Table 3 for the internal modes. In

$$\Gamma(\text{libratory}) = A_g + B_{1g} + B_{2g} + B_{3g} + (A_u) + B_{1u} + B_{2u} + B_{3u} \quad (1)$$

$$\Gamma(\text{translatory}) = 2A_g + B_{1g} + 2B_{2g} + B_{3g} + (A_u) + B_{1u} + B_{3u} \quad (2)$$

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[38] G. R. Wilkinson, in ' Laboratory Methods in Infrared Spectroscopy,' ed. R. G. J. Miller, Heyden London, 1965, ch. 10.

[39] R. W. G. Wyckoff, ' Crystal Structures,' vol. 1, 2nd edn., Wiley–Interscience, New York, 1964.

addition there are lattice modes which span the representations (1) and (2), where the g modes are Raman active and the B_{nu} modes are i.r. active. Acoustic branch modes have been deducted from (2), and the standard axis set[40] is used, not Wyckoff's.[39] The decomposition into internal modes and two types of lattice mode (ν_R and ν_T) is for accounting purposes and does not necessarily imply that an actual distinction exists.

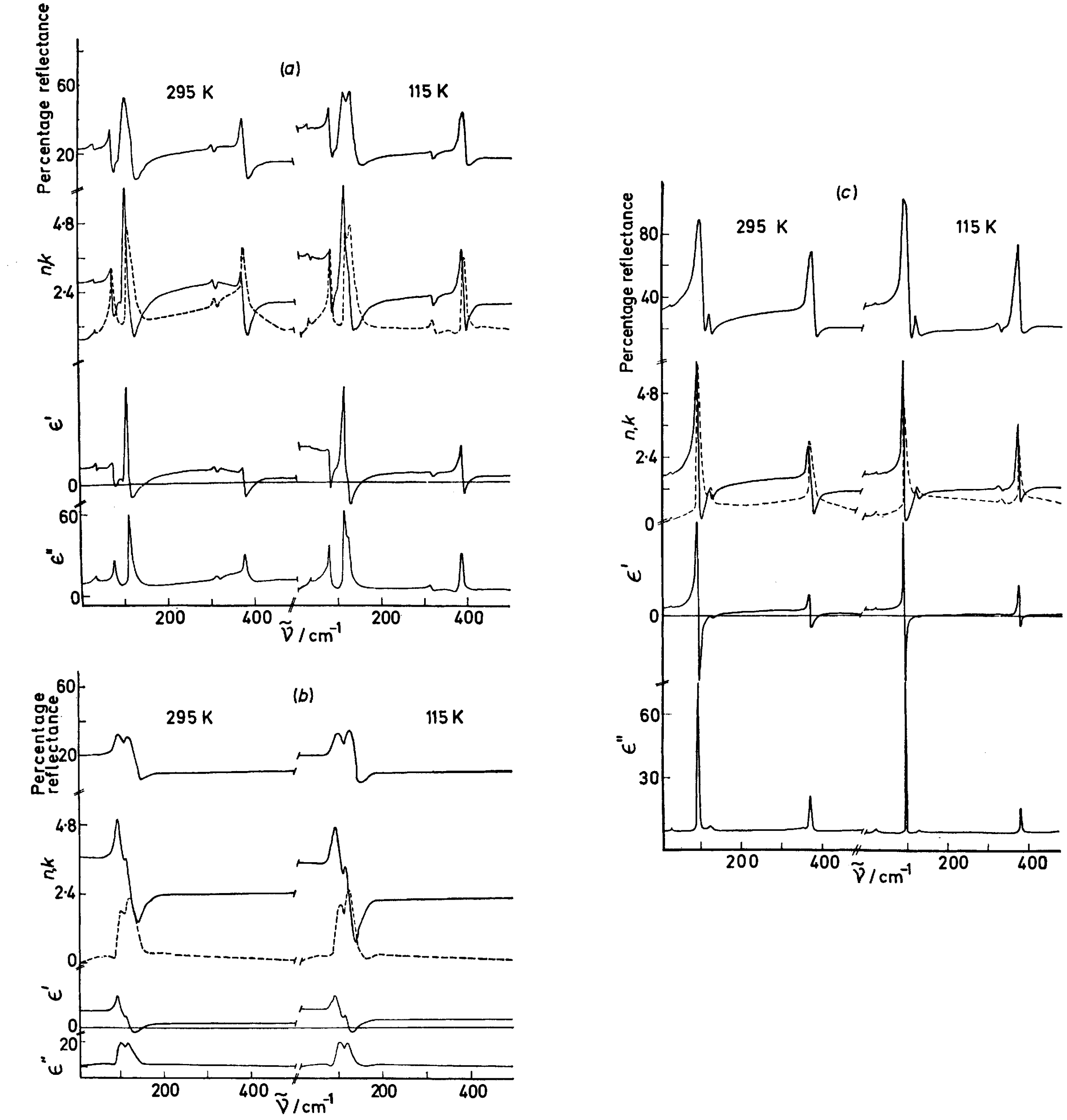

FIGURE 1 Infrared reflectance spectra for $HgCl_2$ at 295 and 115 K: (a) $E||c$ (B_{1u} modes), z polarised; (b) $E||b$ (B_{2u} modes), y polarised; and (c) $E||a$ (B_{3u} modes), x polarised. Each frame shows the observed reflectance spectrum, together with the computed n(——), k(– – – –), ε′, and ε″ functions

With the exception of the B_{1u} component of ν_1 which was only seen in reflectance at low temperature, all the expected Davydov components of ν_1 and ν_3 were seen clearly in reflectance at ambient temperature. The symmetry species of the weaker ν_1 components, which are a distinctive feature of the spectra of polycrystalline

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[40] 'International Tables for X-Ray Crystallography,' eds. N. F. M. Henry and K. Lonsdale, Kynoch Press, Birmingham, 1952.

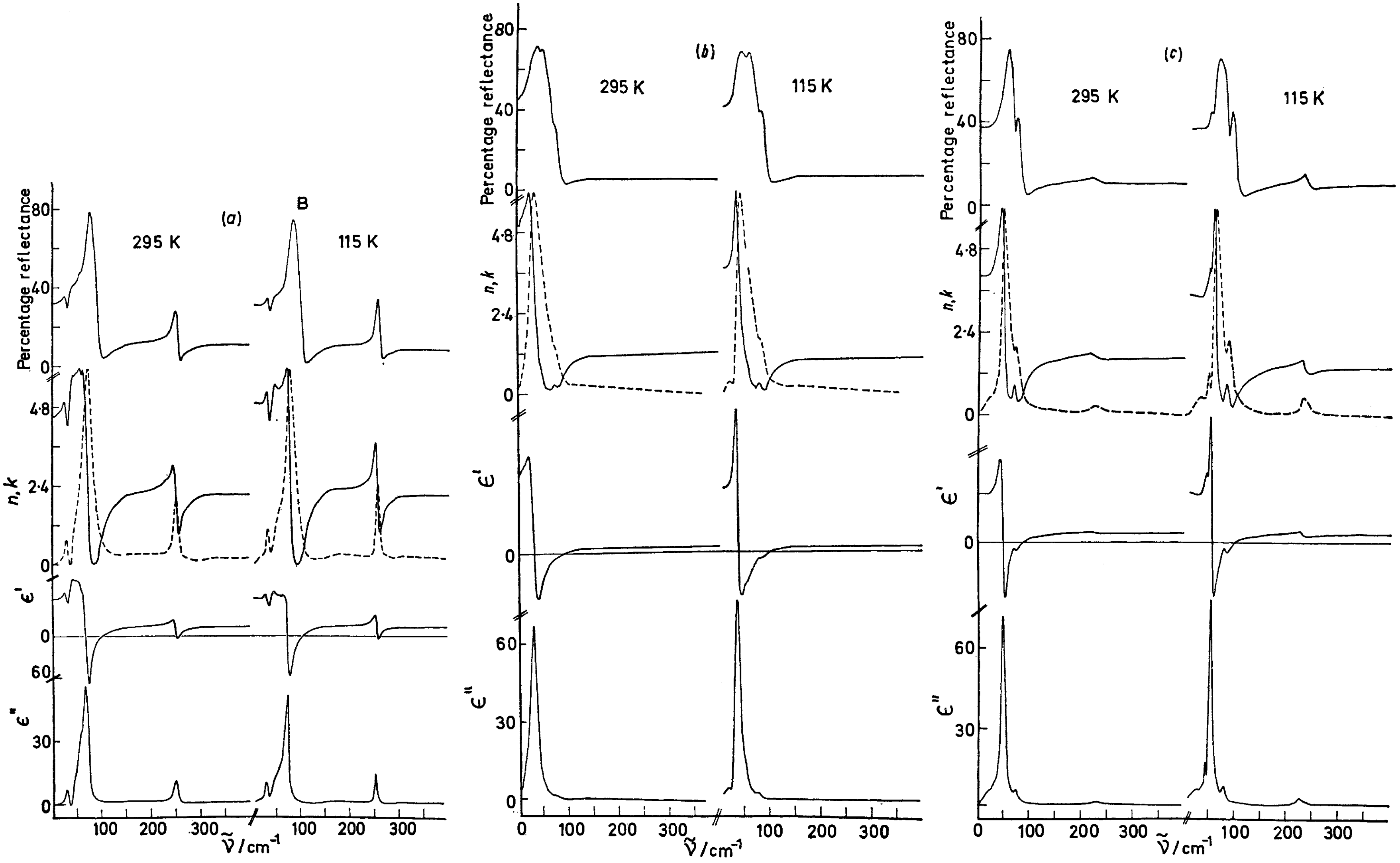
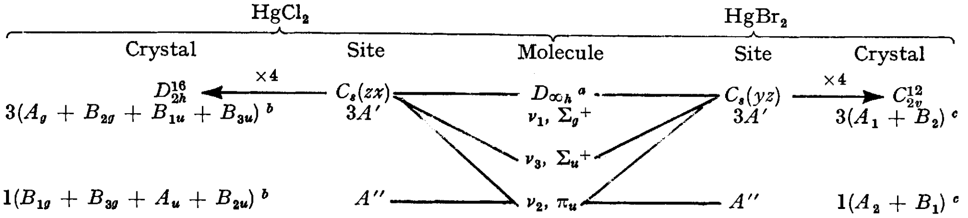


FIGURE 2 Infrared reflectance spectra for $HgBr_2$ at 295 and 115 K: (*a*) $E||c$ (A_1 modes), z polarised; (*b*) $E||a$ (B_1 modes), x polarised; and (*c*) $E||b$ (B_2 modes), y polarised. Other details as in Figure 1

samples,[36] were confirmed by single-crystal transmission experiments. Incorporating the Raman data of Brahms and Mathieu [13] we have the assignment of all the ν_1 and ν_3 components (wavenumbers/cm^{-1}); n.o. = not observed):

TABLE 3

Correlation schemes for $HgCl_2$ and $HgBr_2$



[a] Approximate geometry: neither molecule has strict $D_{\infty h}$ symmetry in the solid state. [b] All the g modes are Raman active. B_{nu} modes are i.r. active. [c] All the modes are Raman active; only A_2 modes are *not* i.r. active.

	A_g	B_{2g}	B_{1u}	B_{2u}	average	vapour [28]	$\Delta\nu$
ν_1	310	316	312	330	317	360	−43
ν_3	n.o.	375	379	372	365	413	−38

Here $\Delta\nu$ is the static field shift and represents the effect of taking a molecule from the vapour phase into the crystal. We have interchanged the subscripts 2 and 3 on Brahms and Mathieu's symmetry species [13] to conform with the standard setting which we have used. The forms of these Davydov components are illustrated in Figure 3(*a*).

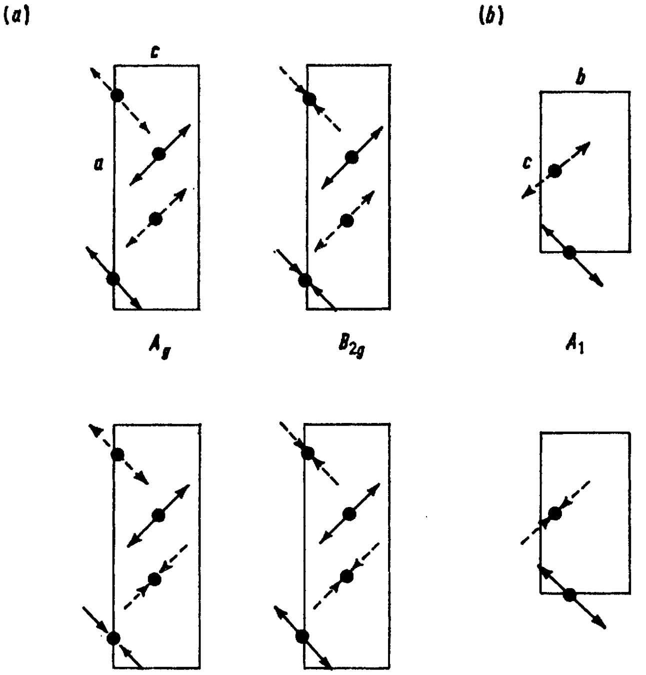


FIGURE 3 Forms of the ν_1 mode coupling schemes for (*a*) $HgCl_2$ and (*b*) $HgBr_2$. Broken lines indicate molecules in layers below those shown in full lines

The only adequate report of the far-i.r. spectrum of solid $HgCl_2$ is that of Décamps and Hadni [27] who found a weak doublet at 32, 39 cm^{-1}, followed by bands at 75.5 (sharp) and *ca.* 97 (broad) cm^{-1}, in unpolarised single-crystal transmission. Other workers [26,36] have reported the band at 75 cm^{-1} and have given various estimates (106, 110 cm^{-1}) of the position of the broad feature above it. Our reflectance spectra (Figure 1) show that this broad feature is a composite of five bands with t.o. frequencies at 94, 96, 108, 115, and 123 cm^{-1}. For polycrystalline samples the appearance of this broad adsorption will be distorted by overlain reflectance effects. In transmission through a thin crystal flake the weak bands at 32 and 40 cm^{-1} were observed and their polarisation behaviour shown to conform with that seen in the reflectance experiments: under these conditions the bands at >70 cm^{-1} were too strong to be seen as other than regions of total absorption.

Raman spectra of solid $HgCl_2$ at shifts less than 180 cm^{-1} show scatter in regions similar to the i.r. spectra, as is to be expected from the f.g.a. We consider the single-crystal Raman results [13,14] in conjunction with our own i.r. data.

The B_{2u} reflectance spectrum should show only two bands due to fundamentals, both at <200 cm^{-1} since neither ν_1 nor ν_3 can have components of this species (Table 3). Bands were found at 94 and 115 cm^{-1} and correspond to the expected libratory mode [vector (1)] and the ν_2 component, although which is which cannot yet be ascertained.

The B_{1u} and B_{3u} spectra in the region below ν_1 and ν_3 should each exhibit three bands due to a ν_2 component (Table 3), a libratory mode (1), and a translatory mode (2). At ambient temperature we found: B_{1u} at 39, 74, and 108 cm^{-1}; B_{3u} at 30, 96, and 123 cm^{-1}. However, at 115 K the B_{1u} band initially at 108 cm^{-1} splits into a doublet (113, 127 cm^{-1}), thus providing one more than the theoretical number of modes. Two alternative assignments might be advanced to account for these data. (*i*) The three B_{1u} bands found at 115 K (76, 113, and 127 cm^{-1}) are the three fundamentals, and the B_{3u} spectrum is accidentally short of one band in this region. The absorptions at 32 and 40 cm^{-1} must then be regarded as other than fundamentals. (*ii*) The B_{1u} band at 127 cm^{-1} is a second-order feature but all the other bands are fundamentals. We consider that the second view more naturally accounts for the Raman and i.r. data taken together. The Raman spectra show bands at 16, 25, and 45 cm^{-1}, as well as at higher shifts, and it seems unlikely that all of them should not be fundamentals.

Since no translatory lattice mode is allowed in B_{2u} and since no band of this species is found at <90 cm^{-1}, we regard the bands at 40 and 32 cm^{-1} in B_{1u} and B_{3u} as translatory in origin, with their Raman counterparts at 16 (B_{2g} and B_{3g}), 25 (A_g), and 45 cm^{-1} (B_{2g}). There is no *a priori* evidence on which a distinction can be drawn between bands due to ν_2 and to libratory motion (ν_R). It is probable that they will couple strongly since the mode displacements involved are similar, but this is by no means certain.[41] Since the gas-phase[32] and matrix-isolation data[30] show ν_2 to be of *ca.* 100 cm^{-1}, it is probable that the bands at 120 (A_g), 126 (B_{1g}), 108 (B_{1u}), 115 (B_{2u}), and 123 cm^{-1} (B_{3u}) should be considered as having a major contribution from ν_2, whereas those at 72 ($B_{1g} + B_{3g}$), 75 ($A_g + B_{2g}$), 74 (B_{1u}), 94 (B_{2u}), and 96 cm^{-1} (B_{3u}) would be principally libratory in type. On the other hand, there is some evidence from the behaviour of these spectra at very high pressures to suggest that the description of these two regions should be reversed.[36]

With this, the assignment of the vibrational spectra of $HgCl_2$ is essentially complete, although a single-crystal Raman study at low temperature is desirable to complement the i.r. data, and an analysis of the crystal dynamics would be valuable.

Mercury(II) *Bromide*.—This compound crystallises with the symmetry of the orthorhombic space group $Cmc2_1$ (C_{2v}^{12}) with a bimolecular primitive cell.[39] In addition to the internal modes shown in the correlation scheme of Table 3 there are optic branch external modes which span the representations (3) and (4).[37] All

$$\Gamma(\text{libratory}) = A_1 + A_2 + B_1 + B_2 \qquad (3)$$

$$\Gamma(\text{translatory}) = A_1 + A_2 + B_2 \qquad (4)$$

the modes are Raman active and all except the A_2 modes are also i.r. active. Since all these lattice modes and all the Davydov components of ν_2 appear in a narrow energy range <80 cm^{-1}, and since the crystal structure of $HgBr_2$ (which is very different from that of $HgCl_2$, a typically molecular crystal) is suggestive of much stronger intermolecular interactions than in $HgCl_2$, there may not be a meaningful distinction between modes labelled as above. Nevertheless, we retain the nomenclature for accounting purposes during the discussion.

Despite the crystal selection rules, which require coincident i.r. and Raman spectra (apart from the A_2 species), the Raman spectra are of extreme simplicity, showing intense bands at 187 [ν_1, ν_{sym}(Hg–Br)] and 57 cm^{-1}, and very little else. The lower band splits (58, 59 cm^{-1}) at low temperature.[17] There are two very weak, sharp, bands at 15 and 18 cm^{-1} (ref. 37) (the band at 18 cm^{-1} has been reported earlier[17]) and some less well defined scatter at *ca.* 40 cm^{-1}.[37] No single-crystal Raman data have been reported for this compound, and our attempts to obtain them were frustrated by the microdomain structure of our crystals. We note that because the factor group is non-centric the Raman spectra may show l.o. modes in addition to those predicted by f.g.a., although such bands should be identifiable by the coincidences they are required to show with the l.o. mode frequencies determined from Kramers–Krönig analysis of the i.r. reflectance data (Table 2).

The far-i.r. data for $HgBr_2$ of Décamps and Hadni,[27] obtained by transmission through a single-crystal using unpolarised light, show ν_3 as a single band at 250 cm^{-1}, with a very weak ν_1 at 185 cm^{-1}. The latter band is not seen in mull spectra,[31] except at low temperature (185 cm^{-1}), when ν_3 is resolved into a doublet (230, 248 cm^{-1}).[17] We were unable to locate either Davydov component of ν_1 in our reflectance spectra, even at 115 K, but the A_1 component was identified at 187 cm^{-1} in transmission through a thin crystal slice (*xz* face): this is coincident with the Raman value for ν_1.

The ν(Hg–Br) mode prominent in i.r. spectra of mulls at 252 cm^{-1} is the A_1 Davydov component of ν_3, the much weaker B_2 component being at 220 cm^{-1}. The average of these, 236 cm^{-1}, may be compared with the ν_3 vapour-phase value[28] of 293 cm^{-1}, yielding a static field shift, $\Delta\nu$, of −57 cm^{-1}. Similarly, $\Delta\nu$ is −38 cm^{-1} for ν_1, for which the gas-phase value is 225 cm^{-1}. These shifts are comparable with those found for $HgCl_2$. All the other modes should be well below ν_1 and ν_3 in energy. Décamps and Hadni's i.r. transmission spectra show[27] bands at 35(sh), 53s, and 71s, br cm^{-1}, whilst at liquid-nitrogen temperature there is some resolution:[17] 32, 55, 65, 86, and 113 cm^{-1} (no intensities recorded). A room-temperature mull spectrum broadly supports these findings.[31]

The B_1 (*x* polarised) i.r. reflectance spectrum should show only two modes, deriving from ν_2 (Table 3) and ν_R (3) respectively. At both ambient temperature and 115 K this spectrum [Figure 2(*b*)] shows intense reflectance at <100 cm^{-1} which appears to be a doublet with t.o. frequencies at 33 and 50 cm^{-1}. In single-crystal transmission this polarisation shows strong absorption from *ca.* 15 to 90 cm^{-1} which could not be resolved into components but which is consistent with the presence of two intense absorption bands. We conclude that these are the two bands predicted by f.g.a.

Both the *z*- and *y*-polarised spectra should exhibit three very-low-frequency bands originating, in each case, from a ν_2 component plus a translatory and a libratory mode. The *z*-polarised spectrum (A_1 modes) shows reflectance bands with t.o. values of 30 and 70 cm^{-1}. Single-crystal transmission confirmed the weaker of these bands (29 cm^{-1}) and revealed in addition another weak and sharp band at 15 cm^{-1}, coincident with a weak Raman band which is accordingly identified as of A_1 symmetry. Finally, the B_2 spectrum showed three reflectance bands (42, 53, and 79 cm^{-1}), although one (42 cm^{-1}) was seen clearly only at 115 K.

These i.r. experiments have therefore yielded exactly

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[41] P. Gans, ' Vibrating Molecules,' Chapman and Hall, London, 1971, p. 160.

the number of bands predicted for each symmetry species (apart from A_2) by f.g.a. When superimposed they account well for the observed mull spectra of $HgBr_2$. It remains to assign the Raman features not found to be coincident with i.r. bands. The band at 18 cm^{-1} is assigned as of A_2 symmetry [unique to the Raman spectrum (f.g.a.)] and may well be the expected translatory mode. The weak scatter at *ca.* 40 cm^{-1} is taken to be the counterpart of the B_2 band found in the i.r. spectrum at 42 cm^{-1}, although its breadth may imply an l.o. component in addition. The intense Raman band at 57 cm^{-1} is nearly coincident with the B_2 i.r. band at 53 cm^{-1}. However, the appearance of a second component on this Raman band at low temperature raises a problem which cannot be resolved without recourse to single-crystal Raman data at this temperature. There are three possible explanations. (*i*) The new Raman feature is the A_1 (l.o.) component: as such it should be coincident with an l.o. frequency determined from the *z*-polarised i.r. reflectance spectrum; it is not, and therefore this possibility is rejected. (*ii*) It is one of the two A_2 modes yet to be identified. We regard this as probable. (*iii*) It represents another genuine A_1 fundamental: if this is so then the band found in i.r. transmission at 15 cm^{-1} must be rejected and treated as an artefact. In view of the considerable difficulties of obtaining i.r. spectra at such very low frequencies, it is desirable that this band (15 cm^{-1}) be confirmed using a lamellar grating instrument. It is unlikely that ν_2 will decrease substantially in the crystal from the value found for it in a krypton matrix [30] (*i.e.* 73 cm^{-1}). Therefore it seems probable that we should identify it with the intense i.r. bands at *ca.* 75 cm^{-1} in the crystal. This automatically forces us to describe the i.r. band at 53 cm^{-1} and, in particular, the intense Raman band at 57 cm^{-1} as principally libratory in type, which accords with the origin of these modes in the Raman-active π_g species of $D_{\infty h}$ which would be expected to show strong Raman activity in the crystal. If we are correct in this view the implication is that the coupling between ν_2 and ν_R is relatively slight.

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