Vibrational Spectroscopy at Very High Pressures. Part 16.[1] A Raman and Infrared Study of Mercury(II) Bromide †

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All the four solid phases I, II, III, and IV of $HgBr_2$ have been characterised by i.r. and Raman spectroscopy under hydrostatic or near-hydrostatic conditions in a diamond anvil cell. The structures of the three high-pressure phases are discussed on the basis of the spectral evidence with the conclusions: IV probably has the CdI_2 structure, or a polytype thereof; III appears to have a (probably unique) monoclinic molecular structure with factor group C_{2h}; the structure of II is closely related to I but cannot be deduced from present evidence. The natures of the transitions I—IV in $HgCl_2$ and I—II in $HgBr_2$ are contrasted.

MERCURY(II) bromide exists in four polymorphic modifications [2,3] (Figure 1). The structure of the ambient-pressure phase, $HgBr_2$ (I), is known but no information is available on the other three. We report a Raman and i.r. study of all the four phases which was undertaken with the objectives of characterising each phase, and of identifying its structure insofar as that is possible by vibrational spectroscopy. A longer term objective is to uncover the principles operative in causing these phases to adopt the structures they exhibit. This study complements a recent one [1] dealing with $HgCl_2$, which has an entirely different set of structures from $HgBr_2$. The principal results from our work with $HgCl_2$, $HgBr_2$, and HgI_2 have been communicated.[4]

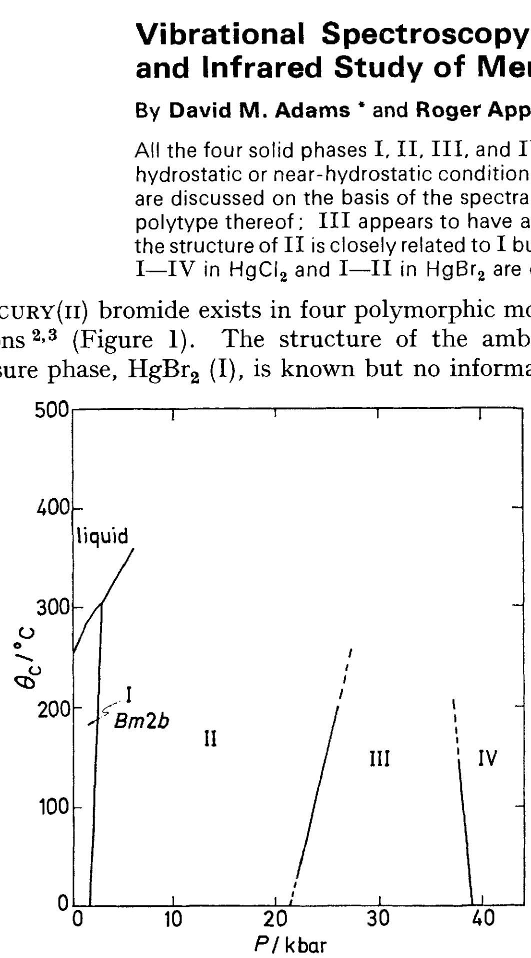

FIGURE 1 Phase diagram of $HgBr_2$[3]

EXPERIMENTAL

Commercial $HgBr_2$ was recrystallised twice from diethyl ether before use. Details of the equipment and experimental procedure have been given elsewhere.[1] It should be emphasised, however, that i.r. and Raman spectra are obtained on the same sample in the same cell under identical conditions. Usually we obtained the Raman spectrum first under the desired pressure and temperature combination, and determined the pressure by reference to the fluorescence bands of a chip of ruby powder loaded with the sample, both being under hydrostatic pressure within a suitable liquid [1] (until pressure-induced freezing occurs). The cell was then carried, under pressure, to the i.r. spectrometer and the measurements were carried out at once. The cell was left for at least 2 h after each change of pressure before spectra were recorded. Since $HgBr_2$ reacts with inconel, molybdenum gaskets were used. Throughout our

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† No reprints available.

[1] Part 15, D. M. Adams and R. Appleby, *J.C.S. Dalton*, preceding paper.

[2] P. W. Bridgman, *Proc. Amer. Acad. Arts Sci.*, 1937, **72**, 45.

[3] C. W. F. T. Pistorius, *Progr. Solid-State Chem.*, 1976, **11**, 1.

[4] D. M. Adams and R. Appleby, *J.C.S. Chem. Comm.*, 1976, 975.

experiments the widths of the ruby lines remained almost constant, indicating that no significant shear stresses were developed.

RESULTS AND DISCUSSION

The Raman and i.r. spectra of the four phases are shown in Figures 2—4, and wavenumbers are listed in Tables 1 and 2.

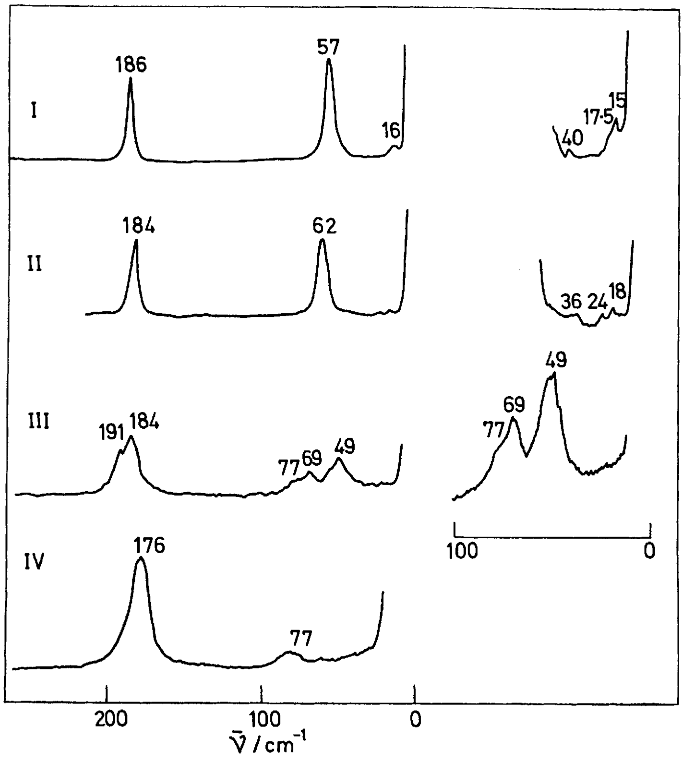

FIGURE 2 Raman spectra of polymorphs of $HgBr_2$ at 295 K. Spectral slit width 1.5 cm^{-1}, 60 mW 514.5-nm radiation at the sample. Pressure = 0 (I), 13.5 (II), 31.5 (III), and 49.5 kbar (IV)

$HgBr_2$ (I).—Although many reports [5-7] have been made of its i.r. and Raman spectra no satisfactory assignment exists for $HgBr_2$ (I), chiefly because no single-crystal study has been made of it. It has a layer structure [8] which is related to that of the cadmium dihalides but differs from it in that two collinear Hg–Br bonds are much shorter than the other four which complete a tetragonally distorted octahedron. In fact, the structure of $CuCl_2$ can be obtained by the opposite kind of tetragonal distortion of the $CdCl_2$ type, *viz.* the creation of four short and two long Cu–Cl bonds.[9] The two very different Hg–Br bond lengths (2.49 and 3.25 Å) indicate that, to a good approximation, it may be regarded as a molecular crystal in which internal and external modes can be treated separately. Nevertheless, the structure is profoundly different from that of $HgCl_2$ (I), indicating that the intermolecular interactions are of a specific nature.

The structure of $HgBr_2$ (I) is orthorhombic, $C_{2v}^{12} = Cmc2_1$, with a bimolecular primitive cell.[8] The factor-group analysis (f.g.a.) is shown in Table 3. This clearly predicts that all the i.r. modes will also be Raman active but, in practice, the molecular symmetry, $D_{\infty h}$, exerts the major influence in determining the relative intensities in the two effects.

In the region where ν_1, $\nu_{sym}(HgBr_2)$, lies the Raman spectrum shows a single band (186 cm^{-1} at 295 K) which can be resolved into a doublet at low temperature,[9] in accord with f.g.a. predictions which require two componnets, $A_1 + B_2$. However, these bands do not appear in the i.r. spectra under the conditions we have used in this work, although it is possible that they might be seen given a large single crystal. Similarly, the intense i.r.-active ν_3, $\nu_{asym}(HgBr_2)$ (247 cm^{-1} at 295 K), was not seen in the Raman spectra.

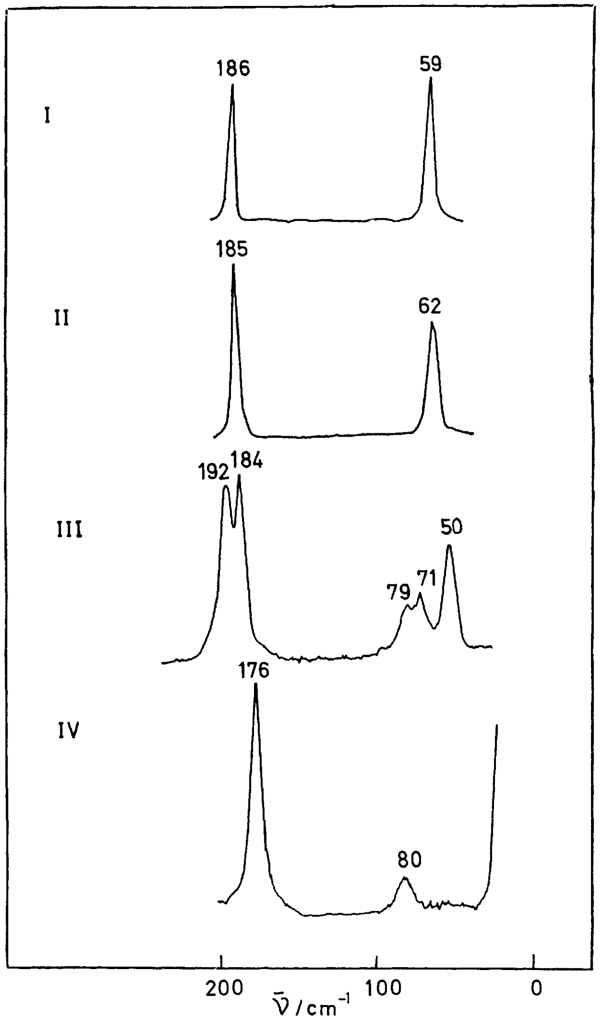

FIGURE 3 Raman spectra of polymorphs of $HgBr_2$ at 150 K. Conditions as for Figure 2. Pressure = 0 (I), 15 (II), 31.0 (III), and 50 kbar (IV)

Below 100 cm^{-1} both i.r. and Raman spectra show

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[5] Y. Mikawa, R. J. Jakobsen, and J. W. Brasch, *J. Chem. Phys.*, 1966, **45**, 4528.

[6] E. A. Decamps and A. Hadni, *J. Chim. Phys.*, 1968, **65**, 1030.

[7] E. A. Decamps, Y. Marqueton, M. Durand, and F. Abba, *J. Mol. Structure*, 1973, **19**, 505.

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

[9] D. Breitinger, personal communication.

several bands: these may originate from factor-group components of ν_2, $\delta(HgBr_2)$, and from rotatory and translatory lattice modes. We have no *a priori* means of identifying individual contributions, and it is probable that they will, in any case, be significantly mixed. However, on the basis of the behaviour found for ν_1 and ν_3, we consider that ν_2 will be intense in the i.r. spectra (it should yield three bands, $A_1 + B_1 + B_2$) but either weak or absent from Raman spectra. An analogous argument suggests that the rotatory modes ($A_1 + A_2 + B_1 + B_2$) will be present in Raman but not in i.r. spectra, as is the case for $HgCl_2$ (I).[1]

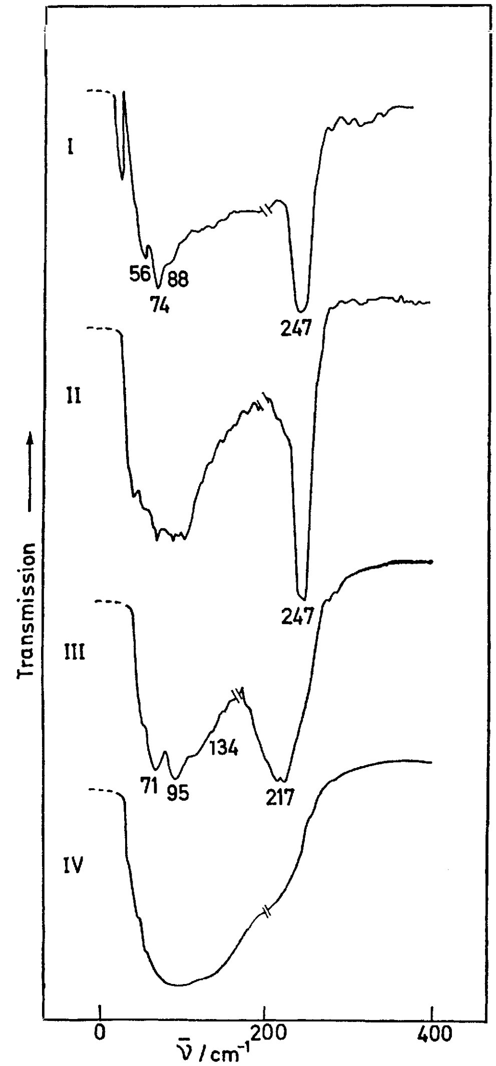


FIGURE 4 Infrared transmission spectra of polymorphs of $HgBr_2$ at 295 K. Pressure = 0 (I), 13 (II), 31 (III), and 50 kbar (IV)

TABLE 1

Raman wavenumbers (cm^{-1}) for $HgBr_2$ at various pressures at ambient temperature

Pressure/kbar	0	6.3	18.8	23.3	31.6	35.8	49.5
Phase	I	II	II	III	III	IV	IV
				191	191		
	186	185	184	184	184	179	176
				74	77	78.5	77
	57	61	60	60	69		
				50	49		
	40	38					
	17.5	22	24				
	15	17	18				

TABLE 2

I.r. wavenumbers (cm^{-1}) for $HgBr_2$ at various pressures at ambient temperature

Pressure/ kbar	0	10	20	30	40
Phase	I	II	II	III	IV
ν_3	247.5	247	238	*ca.* 217br [a]	*ca.* 210 (sh) [b]
				134 (sh)	
	88 (sh)			95	
	74	*ca.* 86br	82br	71	*ca.* 100 [b]
	56			56 (sh)	
	31				

[a] Unresolved components on low-frequency side. [b] See Figure 4.

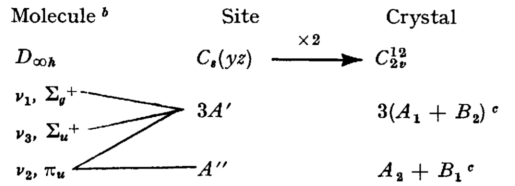
TABLE 3

Factor-group analysis (*a*) and correlation scheme (*b*) for $HgBr_2$

(*a*)

C_{2v}^{12}	N_T [a]	T_A	T	$R(x,y)$	ν_i	Activity I.r.	Activity Raman
A_1	6	1	1	1	3	z	x^2, y^2, z^2
A_2	3		1	1	1		xy
B_1	3	1		1	1	x	zx
B_2	6	1	1	1	3	y	yz

(*b*)



[a] N_T = Total number of unit cell modes, T_A = acoustic branch modes, T = optic-branch translatory lattice modes, $R(x,y)$ = rotatory lattice modes (two axes only), and ν_i = molecular internal modes. [b] Approximate geometry (see text). [c] These sum to give column ν_i in (*a*).

At room temperature the Raman spectrum is dominated by an intense band at 57 cm^{-1} which we accordingly attribute to librational motion of the molecules. The i.r. spectrum is more complex in this region exhibiting three intense bands which could well be the expected ν_2 components (56, 74, and 88 cm^{-1}), together with weak features at <50 cm^{-1} which correspond to some weak, sharp bands in the Raman spectra which are probably due to translatory modes.

$HgBr_2$ (II).—According to Bridgman[2] the I–II transition takes place at room temperature at *ca.* 3 kbar, after which phase II is stable up to *ca.* 23 kbar.* The transition is known to be sluggish at this temperature: we therefore prepared $HgBr_2$ (II) by heating I to 348 K before applying pressure, as well as by direct application of pressure at 295 and 150 K. Spectra obtained at these three temperatures were consistent with each other and differed from those of $HgBr_2$ (I) only in rather minor respects.

The most significant spectroscopic change associated with the transition was that ν_1 *decreased* in frequency

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* Throughout this paper: 1 kbar = 10^8 Pa.

slightly with increase of pressure, whereas the band at 57 cm^{-1} (probably due to rotatory motion) showed a normal increase and lost intensity slightly in comparison *with* ν_1. *In* the i.r. spectra the complex region <100 cm^{-1} became broadened to the extent that most of the components could not be seen clearly. The weak Raman bands at <50 cm^{-1} also suffered positive shifts with increase of pressure.

Because the pressure range in which $HgBr_2$ (II) is stable is considerable we believe that we have obtained this phase, and characterised it by i.r. and Raman spectroscopy. Nevertheless, it is doubtful whether the above differences would have been associated with a phase change in the absence of knowledge of the phase diagram. In contrast, the major spectral changes accompanying the transformations to phases III and IV are self-evident.

$HgBr_2$ (III) *and* (IV).—Further increase of pressure on phase II eventually resulted in development of new features which first showed in the Raman spectra as wings on either side of the band at *ca.* 60 cm^{-1}, and as broadening of the ν_1 region. These features rapidly developed with pressure yielding the spectrum of pure $HgBr_2$ (III) shown in Figure 2. Equally marked changes occurred in the i.r. spectra (Figure 4). Above *ca.* 40 kbar the rather complex Raman spectrum of phase III was dramatically simplified leaving a spectrum (phase IV) consisting of two rather broad bands at 80 and 176 cm^{-1}; cooling to 150 K produced some sharpening but did not reveal any new features. The i.r. spectrum also showed major changes. These observations independently confirm Bridgman's reports of these phase transitions.

Structures of $HgBr_2$ (II), (III), *and* (IV).—As there are no structural data for these phases we are restricted to making such deductions as are possible on the basis of the spectra. The most striking feature of our results is the trend of the ν(Hg–Br) frequencies to lower values as the pressure is increased. This is contrary to normal behaviour, since a symmetric mode might reasonably be expected to shift to higher frequency by at least 0.5 cm^{-1} $kbar^{-1}$. The only exception to this unusual trend is seen in the Raman spectrum of phase III in which it appears that correlation coupling has raised one component. We consider that the basic structural reason for this frequency decrease is a trend to higher co-ordination number at mercury as is now explained.

The structures of the n.t.p. phases (I) of $HgCl_2$ and $HgBr_2$ are profoundly different.[8] Whereas $HgCl_2$ (I) has the type of structure expected for a molecular crystal composed of linear units, $HgBr_2$ (I) is closely related to the kind of layer found in $CdCl_2$ and CdI_2. It has been suggested that mesomeric π bonding is important in $HgBr_2$ (I) and accounts for the longer Hg–Br bonds which are shorter than Br–Br van der Waals contact distances.[10] The implication of our suggestion is that, with increase of pressure, the intermolecular bonding becomes more favoured relative to the intramolecular bonding. Since $HgBr_2$ (I) is reasonably regarded as a distorted variant of the CdX_2 layer-structure types, it is not unlikely that at some high pressure $HgBr_2$ will eventually assume the CdI_2 structure or a polytype of it. One feature of mercury(II) chemistry that has become clear only recently is that Hg^{II} can adopt a considerable variety of environments in solid structures; some approximate to tetrahedral, trigonal, linear, or octahedral co-ordination, whilst others are not readily described. Our suggestion, that the structures of the four solid phases of $HgBr_2$ represent four different solutions to the problem of semicovalent intermolecular bonding each of which has a region of stability in P–T space associated with the particular values of the valence-electron-level energies in those P–T regions, is therefore compatible with what is known of the structural chemistry of Hg^{II}.

On the present evidence a transition from this general understanding to the particular structures of phases II, III, and IV is almost impossible. Our results characterise these phases by means of their vibrational spectra but raise intriguing problems which must eventually be settled by single-crystal *X*-ray crystallography at equivalent pressures. Undoubtedly the most puzzling result is that the spectra of phases I and II are almost identical. No bands were lost or gained in the transition, with the reservation that the breadth of the i.r. absorption below 100 cm^{-1} may obscure some more significant difference. By 18.8 kbar the two Raman bands have moved together by only 5 cm^{-1}. A similar situation was found[1] for $HgCl_2$ in that the ambient phase I and the first high-pressure phase IV showed only the most minor spectral differences, although these were more pronounced than those shown by the $HgBr_2$ (I, II) comparison. What is more significant is that the I–IV transition in $HgCl_2$ is second order and was not detected by Bridgman[2] who used a compression-curve method, whereas the I–II transition in $HgBr_2$ is first order and *was* detected by him; it has an accompanying volume change comparable with those for the II–III and III–IV transitions. We suggested that the I–II transition in $HgCl_2$ involves reorientation of the $HgCl_2$ molecules within the mirror planes upon which they lie, thereby retaining the space group of phase I. It may be that such an explanation should be attached to the I–II transition in $HgBr_2$ as well as to, or instead of, the I–IV in $HgCl_2$: we feel intuitively that an essentially different explanation is required for each case.

The spectra of $HgBr_2$ (IV) are strongly reminiscent of those yielded by materials with the CdI_2 structure.[11,12] A high-symmetry environment is implied by the profound simplification of the Raman spectra on leaving phase III, whilst the i.r. spectra similarly show pronounced differences (Figure 4). Significantly, there is a further decrease in ν(Hg–Br) in the Raman spectra, reaching 176 cm^{-1} at 49.5 kbar, making a shift of -10 cm^{-1} from ambient pressure. The difficulty is that there is no basis for deciding whether this decrease is large

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[10] D. M. Adams, 'Inorganic Solids,' Wiley, Chichester, 1974.
[11] D. J. Lockwood, *J. Opt. Soc. Amer.*, 1973, **63**, 374.
[12] D. M. Adams and R. Appleby, unpublished work.

enough to imply a change from a structure in which some of the Hg–Br bonds differ in length from others, to one in which they are all equal (as they must be in a CdI_2-type layer). We therefore content ourselves with noting that both i.r. and Raman spectra are consistent with selection rules for both the $CdCl_2$ and CdI_2 structures; thus we obtain $A_{1g} + E_g + A_{2u} + E_u$ where the g modes are Raman-active and the u modes i.r.-active. However, comparison of the structures of $HgBr_2$ (I), $CdCl_2$, and CdI_2 implies that a transition to the CdI_2 type would be less disruptive.

Phase III appears still to be composed of molecules in that the ν(Hg–Br) frequencies are close to or higher than those of phase I. The presence of a ν(Hg–Br) doublet clearly implies a primitive cell that is at least bi- and, probably, tetra-molecular. Increased complexity below 150 cm^{-1} in both the i.r. and Raman spectra implies a low-symmetry structure, and is compatible with one of monoclinic symmetry. The spectra also imply retention of the inversion centre since there appear to be i.r.–Raman exclusions, although this evidence is possibly equivocal in view of the analysis of $HgBr_2$ (I) above. Structurally, it appears that the layers of $HgBr_2$ (I) must have been buckled because removal of the mirror planes present in it is the only major change possible. A transition to a monoclinic cell with factor group C_{2h} would accommodate our observations. We are not aware of any linear AB_2 molecule that crystallises in a monoclinic structure. A transition to the monoclinic $CuCl_2$ structure, though feasible, is ruled out by the selection rules, and the positions of ν(Hg–Br).

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