Raman and Infrared Spectra of the High Pressure Phases of the Mercury(II)†

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Summary The high pressure phases of HgX_2, (X = Cl, Br, or I), have been characterised by i.r. and Raman spectroscopy under hydrostatic conditions; their structures are discussed.

Within the past three years significant developments have taken place in the design and method of calibration of the diamond anvil cell (DAC).[1,2] This is an opposed-anvil high-pressure device particularly suitable for spectroscopic applications. Hitherto, its principal disadvantage has been the highly non-hydrostatic pressure distribution across the anvils; this can be taken care of if a metal gasket is placed between the anvils but at the expense of a significant reduction in the amount of light which can be transmitted.

We report here far-i.r. and Raman spectra obtained from samples contained in molybdenum gaskets 0·05 mm thick with a hole of 0·4 mm diameter (initial dimensions). Within the gasket hole the sample is contained within a pressure transmitting fluid to ensure hydrostatic conditions, and is accompanied by a chip of ruby powder which acts as internal pressure calibrant. Full details of this microsampling technique are given elsewhere.[2,3] Using this technique we have obtained far-i.r. and Raman spectra in the same cell under identical conditions and at known pressure and temperature; the cell is used in the two spectrometers alternately. In demonstration of the power of this method we report the vibrational spectra of the solid phases of the halides HgX_2, (X = Cl, Br, or I); most of the Raman spectra have been obtained at both 295 and 150 K.

The new data, which will be discussed in detail elsewhere, are illustrated by Figures 1 and 2. For $HgCl_2$ and $HgBr_2$ only the structures of their phases I are known.[4] Both show transitions at fairly low pressures to new phases [$HgCl_2$ (phase IV) and $HgBr_2$ (phase II)] which are very similar in spectrum, and hence structure, to the initial phases. We suggest that these are examples of a recently discovered type of second-order transition characterised by molecular reorientation with retention of space group.

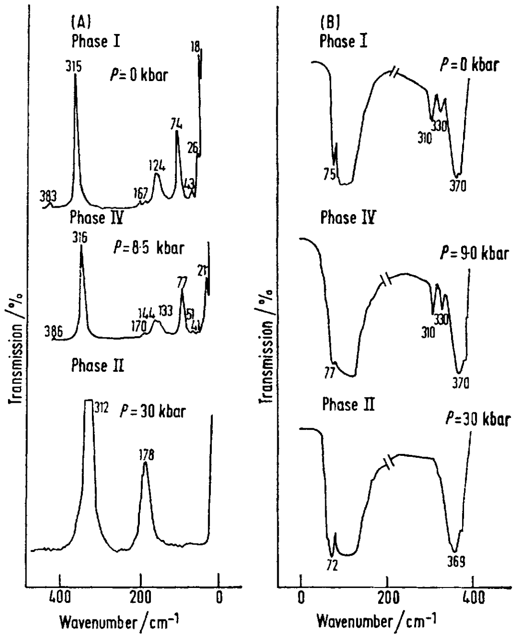

Figure 1. (A) Raman spectra of polymorphs of $HgCl_2$ at 295 K. Spectral slit width 1·5 cm^{-1}, 60 mW 5145 nm radiation at the sample. (B) I.r. transmission spectra of the polymorphs of $HgCl_2$ at 295 K.

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† No reprints available.

Phase II of $HgCl_2$ has very simple spectra indicative of high symmetry. The corresponding i.r. spectra are characterised by the prompt disappearance of two factor-group components of $\nu(Hg\text{–}Cl)_s$ at 310 and 330 cm^{-1} from the spectra consequent upon the phase transition IV → II. These data are consistent with phase II having a structure isomorphous with that[4] of solid CO_2, T_h^6 with $Z = 4$. This transition appears to be driven chiefly by molecular rotary modes.

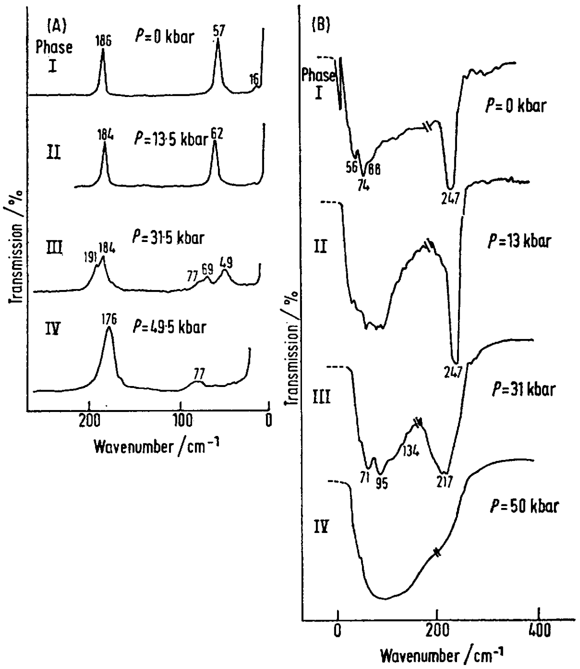

FIGURE 2. (A) Raman spectra of polymorphs of $HgBr_2$ at 295 K. Spectral slit width 1·5 cm^{-1}, 60 mW 5145 nm radiation at the sample. (B) I.r. transmission spectra of the polymorphs of $HgBr_2$ at 295 K.

Phase I of $HgBr_2$ has a very different structure from phase I of $HgCl_2$ and, with the exception of the I → II phase transition (which compares with the $HgCl_2$ I → IV transition), behaves quite differently at high pressures. Both Raman and i.r. spectra of $HgBr_2$ are characterised by a significant decrease in $\nu(Hg\text{–}Br)$ with increase of pressure. We account for this most unusual result by postulating that this series of structures allows a steady increase in the effective co-ordination number at Hg. Consistent with this suggestion, the very simple i.r. and Raman spectra of phase IV of $HgBr_2$ exactly fit the selection rule requirements for the CdI_2 structure. The structurally complex phase III of $HgBr_2$ has spectra consistent with space group *Cmcm* with $Z = 4$; on this basis reasonable mechanisms can be found which inter-relate phases I, II, and III.

Finally, we have reinvestigated the phase behaviour of HgI_2 in some detail, studying the familiar red (layer structure) and yellow forms (isostructural with phase I of $HgBr_2$) over considerable ranges of temperature and pressure In addition we have characterised the recently discovered phase IV of HgI_2 by both i.r. and Raman spectra. Its structure is unknown but the spectra are very similar to those of the tetragonal red phase III of HgI_2. The transition III → IV can be detected as a break in the slope of a plot of the mode frequencies with pressure.

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[1] J. D. Barnett, S. Block, and G. J. Piermarini, *Rev. Sci. Instr.*, 1973, **44**, 1; G. J. Piermarini, S. Block, J. D. Barnett, and R. A. Forman, *J. Appl. Phys.*, 1975, **46**, 2774; D. M. Adams, K. Martin, and S. J. Payne, *Appl. Spectroscopy*, 1973, **27**, 377.

[2] D. M. Adams, R. Appleby, and S. K. Sharma, *J. Phys. E.*, in the press.

[3] D. M. Adams and R. Appleby, unpublished work.

[4] R. W. G. Wyckoff, 'Crystal Structures,' Vol. 1, Wiley, New York, 1964.