*Inorganica Chimica Acta*, 26 (1978) L43–L44

# Vibrational Spectroscopy at Very High Pressures. Part 19. The High Pressure and High Temperature Forms of Yellow Mercury(II) Iodide: Two Different Phases

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Received December 9, 1977

The phase diagram of $HgI_2$, described as “unnatural” by P. W. Bridgman [1] who was the first to investigate it, has long been regarded as anomalous. At ambient temperature and pressure the stable form of $HgI_2$ is the red layer-structure material ($P4_2/nmc$, Z = 2) in which mercury is tetrahedrally co-ordinated to four iodines. Above a transition temperature *ca.* 127 °C (quoted, variously, as 126 to 132 °C) at ambient pressure there is a transition to a yellow form consisting of nearly linear molecules in a lattice isostructural with that of $HgBr_2$ (ambient pressure form), $Cmc2_1$, Z = 4 [2]. The unexpected feature is that compression of the red form above *ca.* 10 kbar induces a change to a phase which is seen, under the microscope, also to be yellow and which was shown by Bridgman's compression measurements to be continuous with the yellow form obtained by thermal expansion of the red $HgI_2$ lattice. We refer to the two yellow preparations as $HgI_2$ II (h.t.) and II (h.p.) respectively (h.t. = high temperature, h.p. = high pressure).

## Experimental

The data were obtained using a diamond anvil high pressure cell and associated techniques, previously described [3]. $HgI_2$ samples were immersed in Nujol and subjected to known pressures, very close to hydrostatic, within molybdenum gaskets initially of thickness 0.2 mm and hole diameter 0.4 mm. The same cell and sample was transferred between the far-i.r. and Raman instruments.

## Results and Discussion

The far-i.r. and Raman spectra of $HgI_2$ II (h.t.) and of II (h.p.) are significantly different from each other (Figure 1) and suggest that the two yellow materials have different structures. The principal differences between the Rama spectra are: (i) there are no 15 and 11.5 $cm^{-1}$ bands, or any corresponding to them, in II (h.p.); (ii) the doublet below 100 $cm^{-1}$ has the relative intensities of its two components in the two forms; (iii) $\nu_1$ (*ca.* 145 $cm^{-1}$) has a pronounced shoulder on the low-frequency side in II (h.

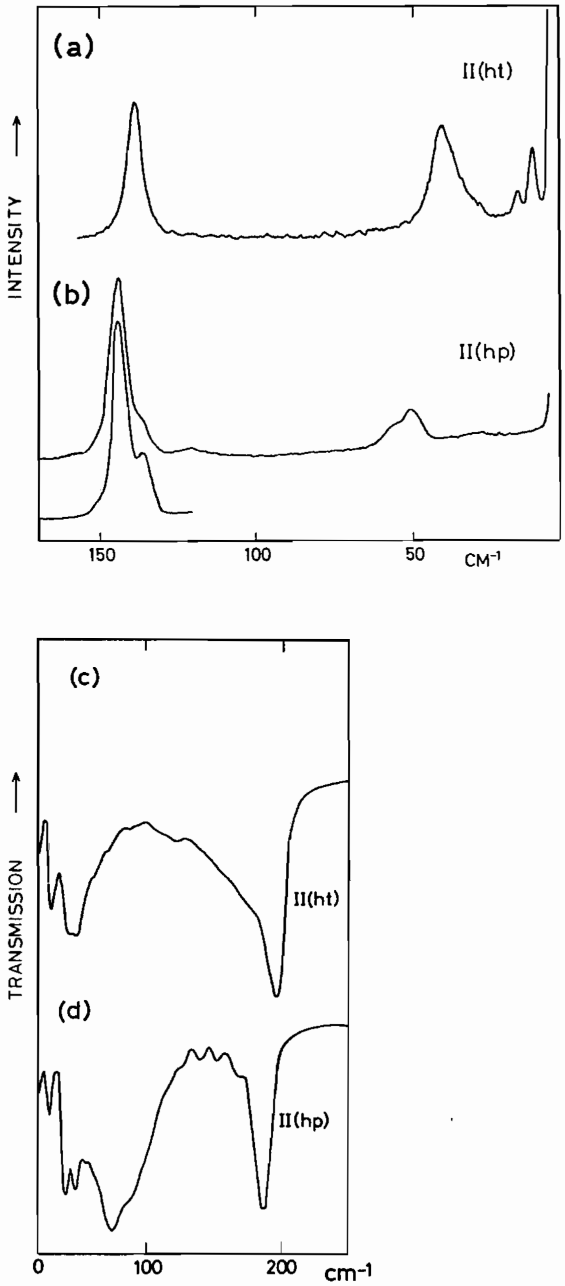

Figure 1. (a) Raman spectrum of $HgI_2$ II (h.t.) at 473 K and ambient pressure. Spectral slit width 0.6 $cm^{-1}$, 200 mW 647.1 nm radiation at the sample. (b) Raman spectrum of $HgI_2$ II (h.p.) at 295 K and 23.0 kbar in a diamond anvil cell. Spectral slit width 1 $cm^{-1}$, 150 mW 647.1 nm radiation at the sample. (c) Far-i.r. spectrum of $HgI_2$ II (h.t.) at 473 K and ambient pressure. (d) Far-i.r. spectrum of $HgI_2$ II (h.p.) at 295 K and 31.0 kbar in a diamond anvil cell.

p.) whereas the corresponding band in II (h.t.) is symmetrical. These differences are supported by observation of even more pronounced differences in the far-i.r. spectra: II (h.p.) has a more complex spectrum than II (h.t.) and, in particular, shows intense absorption *ca.* 80 $cm^{-1}$ which has no counterpart in the other form.

With the recognition that $HgI_2$ II (h.t.) and $HgI_2$ II (h.p.) are different phases, and the recent discovery that above 75 kbar there is a further transition [4] to a form with a structure believed [5] to be that of the 8H poly-type of $CdI_2$, the phase diagram of $HgI_2$ is now seen to be closely similar to that of $HgBr_2$ [5], apart from the presence of red $HgI_2$ in one corner. $HgBr_2$ shows a series of three phase transitions at successively increasing pressures, the highest phase (IV) having spectra [3] compatible with the $CdI_2$ structure type, and $HgBr_2$ III showing vibrational spectra [3] which are similar to those of $HgI_2$ II (h.p.). Thus, the behaviour of $HgI_2$ is seen to fit the general trend towards structures of higher coordination number with increase of pressure [5].

## Acknowledgement

We thank the S.R.C. for a grant to R.A., and for other support.

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