SINGLE-CRYSTAL RAMAN SPECTRUM OF RED MERCURY(II) IODIDE

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Although the Raman spectrum of red mercury(II) iodide is well known,[1-3] and is frequently used to demonstrate the low frequency performance of Raman instruments, the symmetry species of the modes observed have not been reported. We have determined their symmetries using a single crystal.

Experimental

Relatively large tetragonal crystals (*c.* 5 by 3 by 2 mm^3) were readily grown from acetone solution. Unfortunately their optical quality was poor, resulting in partial depolarization of light within the crystals. The 110, $1\bar{1}0$, and 001 faces were well developed. The crystals were oriented by X-ray diffraction methods. Raman spectra were recorded on a Coderg PH1 spectrometer using 632·8 nm excitation. Measured frequencies are accurate to better than ± 1 cm^{-1}.

Results and Discussion

The derived Raman polarizability tensor axes are coincident with the crystal axes, but the face development of the crystals forces the use of an axis set which is related to the crystal *a* and *b* axes by a 45° rotation about *z*. The tensor components are related as follows:

	Experimental Axes (x, y, z)	Crystal Axes (x', y', z)
A_{1g}	x^2+y^2, z^2	$x'^2+y'^2$, z^2
B_{1g}	xy	$x'^2-y'^2$
B_{2g}	x^2-y^2	$x'y'$
E_g	xz, yz	$x'z$, $y'z$

Factor group analysis predicts four Raman-active internal modes, ($A_{1g}+B_{1g}+2E_g$), and two Raman-active translational lattice modes, ($B_{1g}+E_g$). Although the poor optical quality of the crystal prevents complete extinctions, the orientation effects are sufficiently pronounced to allow assignment (see Table 1).

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[1] Cooney, R. P. J., Hall, J. R., and Hooper, M. A., *Aust. J. Chem.*, 1968, **21**, 2145.

[2] Mon, J. P., *C. r. hebd. Séanc. Acad. Sci. Paris* (*B*), 1966, **262**, 493.

[3] Melveger, A. J., Khanna, R. K., Guscott, B. R., and Lippincott, E. R., *Inorg. Chem.*, 1968, **7**, 1630.

There can be no doubt that the B_{1g} line at 142 cm^{-1} is associated with an internal mode and that the B_{1g} translatory mode is unobserved, even to 2·5 cm^{-1} (Fig. 1). There is no evidence to show whether one of the E_g modes is the required lattice mode. By analogy with the B_{1g} species, we consider that neither lattice mode has been observed.

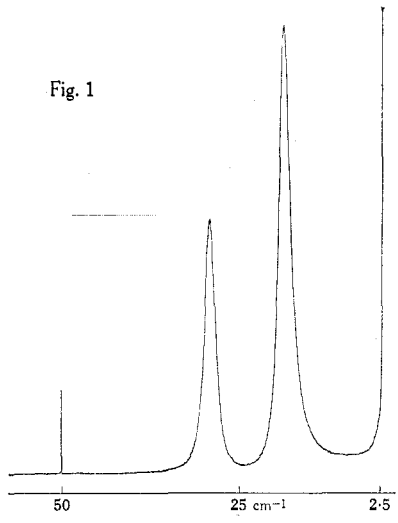
TABLE 1

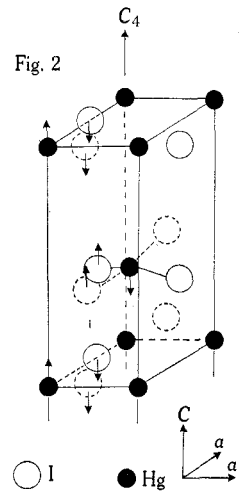
RAMAN LINES (cm^{-1}) AND RELATIVE INTENSITIES FOR RED MERCURY(II) IODIDE SINGLE CRYSTALS

Line (cm^{-1})		$y(zz)x$	$y(xy)x$	$y(zy)x$	$y(xz)x$	$y(xx)z$	$y(zx)z$
17	E_g	55[a]	84[a]	148	75	75[a]	151
29	E_g	29[a]	50[a]	79	40	40[a]	77
114	A_{1g}	28	32[a]	25[a]	15[a]	50	48[a]
142	B_{1g}	0	4	0	0	0	0

[a] Ideally extinction should occur.

Fig. 1.—Raman spectrum of red mercury(II) iodide powder. Spectral slit width 0·25 cm^{-1}, 632·8 nm excitation.
Fig. 2.—B_{1g} internal mode of red mercury(II) iodide.





These results confirm the proposed assignment of Cooney, Hall, and Hooper. (Note: the subscripts 1 and 2 on the b-modes in ref.[1] should be interchanged to conform with standard notation for the C_2' and C_2'' axes.) Figure 2 shows the form of the B_{1g} mode in relation to the unit cell axes.