

Single-Crystal Raman Spectra of Mercurous Bromide, Mercurous Iodide, and Mercuric Iodide

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The Raman active factor-group fundamentals of Hg_2Br_2 , Hg_2I_2 , and HgI_2 are unambiguously assigned from the single-crystal observations.

The mercurous halides have been extensively investigated by means of both Raman and infrared spectroscopy,¹⁻⁹ and several complete vibrational assignments of the fundamentals have been proposed during the last 10 years.

In their study on Hg_2Cl_2 Mathieu *et al.*^{1,2} reported a vibrational assignment of the internal modes. Goldstein,³ however, observed a previously unreported absorption at *ca.* 260 cm^{-1} in a reinvestigation of the far infrared spectrum and a new assignment of the fundamentals was proposed. In more recent works by Durig *et al.*⁴ and by Conney *et al.*⁵ the vibrational spectra of mercurous bromide and iodide were analysed. The above-mentioned studies were based on a molecular model and insufficient attention was given to the external crystal modes. A single-crystal Raman study on Hg_2Cl_2 by Beattie and Gilson⁶ resulted in a revised assignment of the external and internal Raman active modes, and recently Ōsaka⁷ measured the infrared absorption spectra of Hg_2X_2 (X = Cl, Br, I) in detail and made an analysis in terms of crystalline solids. In the present work we have obtained single-crystal Raman polarisation data for Hg_2Br_2 and Hg_2I_2 and have attributed the Raman active fundamentals to their respective symmetry classes.

The two mercuric halides HgCl_2 and HgBr_2 have a linear configuration in all phases, and the crystal lattice is distinctly molecular.^{13,14} Mercuric iodide, however, has two modifications.^{15,16} The red form that is stable at room temperature undergoes a reversible phase transition to a yellow form at 126°C. The bonding in yellow HgI_2 [†] is apparently molecular, while the red form consists of layers of HgI_4 tetrahedra in the crystal.

A number of vibrational spectroscopic studies have been carried out already on these compounds. The ν_1 and ν_3 stretching frequencies are well

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established from gas and melt spectra.^{14,17-21} By comparing the ν_1 frequency in passing from vapour^{17,18} to melt^{19,20} it appears that the frequency shift decreases along the series HgCl_2 , HgBr_2 , HgI_2 . The bonding forces within HgI_2 are considered as being much less sensitive to environmental effects. The doubly degenerate bending frequency ν_2 is determined from infrared gas²² and matrix isolation studies.²¹ A considerable discrepancy from electronic spectral data²³ was found.

The solid state spectra of HgCl_2 ,^{2,24} HgBr_2 ,²⁴ and HgI_2 ,^{2,25,28} are interpreted on the basis of the symmetry properties of the crystals. Poulet and Mathieu² applied vibrational spectroscopy on an HgCl_2 single-crystal. While the present work was in progress Adams *et al.*²⁵ reported the single-crystal Raman spectrum of red mercuric iodide. However, the two translatory modes were unobserved. A crystal of good optical quality was grown and all the Raman active modes appeared. Raman spectra of HgBr_2 single-crystal were also obtained. However, the crystals were very imperfect and no meaningful interpretation in terms of crystal structure was possible.

EXPERIMENTAL

The single-crystals of Hg_2Br_2 and Hg_2I_2 were prepared by slow sublimation in a nitrogen atmosphere. The HgI_2 crystal was grown from the vapour phase in an evacuated glass-tube. The spectra were recorded with a Spex 1401 monochromator with a Spectra Physics He/Ne 6328 Å laser excitation of about 50 mW power. Since the mercurous iodide crystal quickly decomposed in the 50 mW laser beam, this crystal was excited with a He/Ne laser of about 0.5 mW power. No decomposition was observed under these conditions.

RESULTS AND DISCUSSION

Previous infrared and Raman data^{4,7} of the halides are consistent with the assumption that Hg_2X_2 ($\text{X} = \text{Cl}, \text{Br}, \text{I}$)¹¹ belong to the same space group as mercurous fluoride,¹² D_{4h} .¹⁷ The Hg_2X_2 molecules have a fourfold axis in common with the lattice and have consequently D_{4h} site symmetry. Factor group analysis gives four Raman active modes of symmetry type $2a_{1g} + 2e_g$, which should arise only in (xx) , (yy) , (zz) , and (xz) , (yz) observations, respectively.

The single-crystal observations are summarized in Tables 1 and 2 for Hg_2Br_2 and Hg_2I_2 , respectively.

The data enable an unambiguous assignment of the Raman active bands. Our results confirm the interpretation reported by Ōsaka.⁷ The weak Raman bands observed at 92 and 65 cm^{-1} for the bromide and iodide, respectively, by Durig *et al.*⁴ should clearly be associated with the non-totally symmetric $\text{Hg}-\text{Hg}-\text{X}$ bending mode ν_4 , whereas the strong band located at the lowest frequency in the spectra is attributed to the external mode of rotatory origin. Apparent from the (zz) , (zx) , (yx) , and (yz) measurements of the iodide the broad band at *ca.* 68 cm^{-1} consists of two partly overlapping bands, one associated with the ν_4 vibration, while the other might arise from a second-order process.

Table 1. Oriented single-crystal Raman polarisation data ^a for Hg₂Br₂.

ν (cm ⁻¹)	$I_{x(zz)y}$	$I_{x(zx)y}$	$I_{x(yx)y}$	$I_{x(yz)y}$	$I_{x(yx+zx)z}$ ^b	$I_{x(yy+yx)z}$ ^b	Assignment
221	1.17	0.33	0.06	0.08	0.18	0.07	$\nu_1(\alpha_{1g})$
135	17.04	4.72	0.70	1.25	2.78	0.45	$\nu_2(\alpha_{1g})$
92	0.13	0.42	0.08	0.19	0.18	0.08	$\nu_4(e_g)$
~72							$2\nu_L=72$
36	2.63	6.95	1.30	3.39	3.19	0.85	$\nu_L(e_g)$

^a Peak areas measured in arbitrary units.^b Recorded in a different intensity scale.Table 2. Oriented single-crystal Raman polarisation data ^a for Hg₂I₂.

ν (cm ⁻¹)	$I_{x(zz)y}$	$I_{x(zx)y}$	$I_{x(yx)y}$	$I_{x(yz)y}$	$I_{x(yz+zx)y}$ ^b	$I_{x(xx+yx)y}$ ^b	Assignment
~223							$2\nu_2=226$ or $\nu_L+\nu_1=224$
193	0.86	0.29	0.04	0.07	0.01	0.03	$\nu_1(\alpha_{1g})$
113	46.2	14.6	1.40	3.44	0.86	0.80	$\nu_2(\alpha_{1g})$
~73	0.06	0.14	0.12	0.29	0.09	0.05	$\nu_4(e_g)$
~64							$2\nu_L=62$
31	3.94	5.14	2.12	6.70	5.20	1.10	$\nu_L(e_g)$

^a Peak areas measured in arbitrary units.^b Recorded in a different intensity scale.

Table 3. Oriented single-crystal Raman polarisation data ^a for red HgI₂.

ν (cm ⁻¹)	$I_x(y'x')y'$	$I_x(y'z)y'$	$I_x(x'x')y'$	$I_x(x'z)y'$	$I_x(y'z)y',^b$	$I_x(y'x')y',^b$	$I_x(xz)y',^b$	$I_x'(xz)y',^b$	$I_x'(zx')y',^b$	Assignment
143.5	10.5	0.5	0	0	0.5	16	0	0	0	b_{1g}
114.0	24	20	336	68	68	68	219	70	70	a_{1g}
54.5	2.0	0	0.5	0	0.5	4.8	1.5	0.5	0.5	b_{1g}
49.0	0	2.5	0.8	3.0	4.5	0.5	1.5	5.5	5.5	e_g
28.5	204	730	114	584	402	201	228	476	476	e_g
17.5	200	1788	212	1112	745	276	430	88.5	88.5	e_g

^a Peak heights measured in arbitrary units.^b Recorded in a different intensity scale.

The crystal structure¹⁶ of red HgI_2 is built up from layers of HgI_4 tetrahedra. It has space symmetry $P4_2/nmc$ (D_{4h}^{15}) ($Z=2$) with I-atoms on sites of symmetry C_{2v} , and Hg-atoms on sites of D_{2d} symmetry. The factor group analysis leads to the irreducible representation.

$$\Gamma_{\text{cryst}} = a_{1g} + a_{2u} + 2b_{1g} + b_{2u} + 3e_g + 2e_u$$

The Raman tensor components are as follows: a_{1g} , $R_{xx} + R_{yy}$, R_{zz} ; b_{1g} , $R_{xx} - R_{yy}$; e_g , R_{xz} . To distinguish between a_{1g} and b_{1g} modes we recorded the polarisation measurements at 45° to x - and y -axis. By use of the experimental set of axes (x' , y' , z) the a_{1g} , b_{1g} , and e_g modes should arise only in ($x'x'$), ($y'y'$), (zz); ($x'y'$); ($x'z$) and ($y'z$) measurements, respectively. The results of the oriented single-crystal measurements are shown in Table 3. The data led to unambiguous assignments of the 6 Raman active modes. Weak bands were previously observed^{5,26} in the region $30-70 \text{ cm}^{-1}$ and attributed to combinations because of lack of single crystal observations. Two of these bands showed apparent orientation effects and are assigned to the two translational modes, ($b_{1g} + e_g$), unobserved by Adams *et al.*²⁵ In addition two weak bands were observed at 38 and 64 cm^{-1} , which may be due to second-order effects.

Acknowledgements. A British Council Fellowship is gratefully acknowledged. I thank professor I. R. Beattie for stimulating discussions and for all facilities placed at my disposal at the University of Southampton during the year 1970-71. I am also indebted to Dr. T. R. Gilson for many valuable discussions and help in obtaining the single-crystal Raman spectra.

REFERENCES

1. Hadni, A., Henry, C., Mathieu, J. P. and Polet, H. *Compt. Rend.* **252** (1961) 1585.
2. Poulet, H. and Mathieu, J. P. *J. Chim. Phys.* **60** (1963) 442.
3. Goldstein, M. *Spectrochim. Acta* **22** (1966) 1389.
4. Durig, J. R., Lau, K. K., Nagarajan, G., Walker, M. and Bragin, J. *J. Chem. Phys.* **50** (1969) 2130.
5. Conney, R. P. J., Hall, J. R. and Hooper, M. A. *Aust. J. Chem.* **21** (1968) 2145.
6. Beattie, I. R. and Gilson, T. R. *Proc. Roy. Soc. A* **307** (1968) 407.
7. Ōsaka, T. *J. Chem. Phys.* **54** (1971) 863.
8. Krishnamurti, P. *Indian J. Phys.* **5** (1930) 113.
9. Gager, H. M., Lewis, J. and Ware, M. J. *Chem. Commun.* **1966** 616.
10. Stammreich, H. and Sans, T. T. *J. Mol. Struct.* **1** (1967-68) 55.
11. Havighurst, R. J. *J. Am. Chem. Soc.* **48** (1926) 2113.
12. Ebert, F. and Weitinek, H. *Z. anorg. allgem. Chem.* **210** (1932) 269.
13. Wells, A. F. *Structural Inorganic Chemistry*, Oxford Univ. Press, London 1950.
14. Klemperer, W. and Lindeman, L. *J. Chem. Phys.* **25** (1956) 397.
15. Wyckoff, R. W. G. *Crystal Structures*, Vol. 1, Interscience, New York 1963.
16. Jeffrey, G. A. and Vlasse, M. *Inorg. Chem.* **6** (1967) 396.
17. Braune, H. and Engelbrecht, G. *Z. physik. Chem. (Leipzig)* **B 19** (1932) 303.
18. Beattie, I. R. and Horder, J. R. *J. Chem. Soc. A* **1970** 2433.
19. Janz, G. J. and James, D. W. *J. Chem. Phys.* **38** (1963) 902.
20. Clarke, J. H. R. and Solomons, C. *J. Chem. Phys.* **48** (1968) 528.
21. Loewenschuss, A., Ron, A. and Schnepp, O. *J. Chem. Phys.* **50** (1969) 2502.
22. Malt'sev, A. A., Selivanov, G. K., Yampolsky, V. I. and Zavalishin, N. I. *Nature Phys. Sci.* **231** (1971) 157.
23. Bell, S. *J. Mol. Spectry.* **23** (1967) 98, and references therein.
24. Mikawa, Y., Jakobsen, R. J. and Brasch, J. W. *J. Chem. Phys.* **45** (1966) 4528, and references therein.

25. Adams, D. M. and Hooper, M. A. *Aust. J. Chem.* **24** (1971) 885.
26. Melveger, A. J., Khanna, R. K., Guscott, B. R. and Lippincott, E. R. *Inorg. Chem.* **7** (1968) 1630.
27. Marqueton, Y., Abba, F., Decamps, E.-A. and Nusimovicic, M.-A. *Compt. Rend.* **B 272** (1971) 1014.
28. Krauzman, N., Krauzman, M. and Poulet, H. *Compt. Rend.* **B 273** (1971) 301.

Received June 9, 1972.