

# RAMAN SPECTRUM OF THIOMERCURATE(II) ION\*

By R. P. J. COONEY† and J. R. HALL†

Mercury(II) sulphide dissolves to an appreciable extent in aqueous sodium sulphide solution, and the solubility is enhanced by the addition of alkali.<sup>1</sup> It has been concluded<sup>2</sup> that the species present vary with pH, and that  $\text{HgS}_2^{2-}$  predominates at pH greater than 9. Statements<sup>3,4</sup> referring to the existence of the ion  $\text{HgS}_2^{2-}$  would appear to be justified, particularly in the light of evidence from Raman spectra reported here.

TABLE I  
SELECTION RULES FOR POSSIBLE MODELS FOR  $\text{HgS}_2^{2-}$

Model	Point Group	Symmetry Species and Activity
$[\text{S}-\text{Hg}-\text{S}]^{2-}$	$D_{\infty h}$	$\sigma_g^+(\text{Raman, pol.}) + \sigma_u^+(\text{i.r.}) + \pi_u(\text{i.r.})$
$\left[ \begin{array}{c} \text{Hg} \\ / \quad \backslash \\ \text{S} \quad \text{S} \end{array} \right]^{2-}$	$C_{2v}$	$2a_1(\text{Raman, pol.; i.r.}) + b_2(\text{Raman, depol.; i.r.})$

## Experimental

The  $\text{Na}_2\text{S}\cdot 9\text{H}_2\text{O}$  and KOH used were B.D.H. analytical reagents. HgS was prepared by precipitation from Judactan analytical reagent  $\text{HgCl}_2$ , and was washed with  $\text{CS}_2$  to remove traces of sulphur.

The solutions for Raman study were prepared by addition of weighed quantities of HgS to 2M  $\text{Na}_2\text{S}$  solution (pH > 10). Without additional hydroxide HgS dissolved to the extent of 0.6M and with the  $\text{Na}_2\text{S}$  solution 4M in KOH the HgS concentration reached approximately 1M. Spectra were taken of solutions where the ratio  $[\text{Na}_2\text{S}]/[\text{HgS}]$  ranged from 2 to 10. Potassium hydroxide was present only in those solutions for which the ratio was less than 3.

Spectra were obtained with a Hilger E612 Spectrograph with F/5.7 camera and recorded on Ilford Zenith plates. The exciting line was Hg 4358 Å of the Toronto arc. Qualitative polarization measurements were made by surrounding the Raman tube with cylinders of polaroid film with their planes of polarization parallel and perpendicular to the tube axis. The Fe arc spectrum was used as standard for frequency measurement.

\* Manuscript received April 4, 1966.

† Department of Chemistry, University of Queensland, St. Lucia, Brisbane.

<sup>1</sup> Dubey, K. P., and Ghosh, S., *Proc. natn. Acad. Sci. India A*, 1959, **28**, 301 (*Chem. Abstr.* **55**, 12133).

<sup>2</sup> Schwarzenbach, G., and Widmer, M., *Helv. chim. Acta*, 1963, **46**, 2613.

<sup>3</sup> Remy, H., "Treatise on Inorganic Chemistry." Vol. 2, p. 465. (Elsevier: Amsterdam 1956.)

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*Results and Discussion*

Raman spectra of the sulphide or sulphide-hydroxide solutions showed only a single line at  $2575\text{ cm}^{-1}$  ascribable to the sulphur-hydrogen stretch.<sup>5</sup> In solutions containing HgS the sole new feature was a strong, sharp, polarized line at  $352\text{ cm}^{-1}$ . The line appeared clearly on a 15 min exposure of a 1M HgS solution and no more lines were observed after exposures up to 3 hr. This spectrum compares with the infrared spectrum of cinnabar ( $-\text{S}-\text{Hg}-\text{S}-\text{Hg}-$  infinite chains<sup>6</sup>) which consists<sup>7</sup> of a very strong, sharp line at  $349\text{ cm}^{-1}$ .

The simplicity of the Raman spectrum suggests the occurrence of a simple and highly symmetrical species in solution and Table 1 lists the selection rules for the possible models for  $\text{HgS}_2^{2-}$ . The observed spectrum (one sharp, polarized line) clearly favours the linear model and supports the conclusion that  $\text{HgS}_2^{2-}$  predominates in solution. The  $352\text{ cm}^{-1}$  line is therefore assigned to the  $\sigma_g^+$  mode, Hg-S stretching. The force constant  $k(\text{Hg}-\text{S})$  derived<sup>8</sup> from  $\nu_1(\sigma_g^+)$  is  $2.34 \times 10^5\text{ dyn/cm}$  and is comparable with the value  $2.29 \times 10^5\text{ dyn/cm}$  found<sup>9</sup> for  $k(\text{Hg}-\text{Cl})$  from  $\text{HgCl}_2$ .

Species  $(\text{HgS})_x\text{S}^{2-}$  ( $x > 1$ ) which have been postulated<sup>2</sup> would, like a non-linear  $\text{HgS}_2^{2-}$ , be expected to show more than one Raman line. Also, a mixture of ions in comparable population would probably result in the observation of a *diffuse* Raman band for Hg-S stretching.

The conclusion that  $\text{HgS}_2^{2-}$  is linear is supported by X-ray crystal studies<sup>10</sup> of the oxomercurates( $\text{II}$ ),  $\text{M}_2\text{HgO}_2$  ( $\text{M} = \text{Li}, \text{Na}$ ), which contain linear  $[\text{O}-\text{Hg}-\text{O}]^{2-}$  units in the lattice. Solid compounds having the empirical composition  $\text{K}_2\text{S}_x\text{HgS}_y\text{H}_2\text{O}$  have been isolated<sup>11</sup> from the system  $\text{K}_2\text{S}-\text{HgS}-\text{H}_2\text{O}$ , but no X-ray studies have been reported.

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<sup>6</sup> Aurivillius, K. L., *Acta chem. scand.*, 1950, **4**, 1413.

<sup>7</sup> Miller, F. A., Carlson, G. L., Bentley, F. F., and Jones, W. H., *Spectrochim. Acta*, 1960, **16**, 135.

<sup>8</sup> Herzberg, G., "Infrared and Raman Spectra." p. 172. (Van Nostrand: New York 1945.)

<sup>9</sup> Braune, H., and Engelbrecht, G., *Z. phys. Chem. B*, 1932, **19**, 303.

<sup>10</sup> Hoppe, R., and Rohrborn, H. J., *Z. anorg. Chem.*, 1964, **329**, 110.

<sup>11</sup> Pascal, P., "Nouveau Traité de Chimie Minérale." Vol. 5, p. 786. (Masson: Paris 1962.)