

## 216. The Raman Spectra of Mercuric Cyanide and the Tetra-cyanomercurate Ion.

By L. A. WOODWARD and H. F. OWEN.

Using a solution of mercuric cyanide in methyl alcohol, we have observed the complete Raman spectrum of the  $\text{Hg}(\text{CN})_2$  molecule and have determined the states of polarisation of the lines. The results confirm recent fundamental assignments based upon combination frequencies observed in infrared absorption. An aqueous solution of mercuric cyanide containing excess of sodium cyanide shows a Raman spectrum attributable to the  $\text{Hg}(\text{CN})_4^{2-}$  ion. The effect of complex-ion formation upon the bond-stretching force constants is discussed.

THE object of this work was to investigate the changes of the stretching force constants of the Hg-C and C-N bonds produced by co-ordination of two cyanide ions with the  $\text{Hg}(\text{CN})_2$  molecule to form the  $\text{Hg}(\text{CN})_4^{2-}$  complex ion.

*Raman Spectrum of the  $\text{Hg}(\text{CN})_2$  Molecule.*—The linear symmetrical  $\text{Hg}(\text{CN})_2$  molecule (point group  $D_{\infty h}$ ) must have seven distinct fundamental frequencies, of which three ( $2\Sigma_g^+ + 1\Pi_g$ ) are permitted in the Raman effect but forbidden in infrared absorption and the remaining four ( $2\Sigma_u + 2\Pi_u$ ) are forbidden in the Raman effect but permitted in the infrared. Of the three Raman-permitted fundamentals, two (class  $\Sigma_g^+$ , frequencies  $\nu_1$  and  $\nu_2$ ) should appear as polarised lines and the other (class  $\Pi_g$ , frequency  $\nu_3$ ) as a depolarised line.

The Raman spectrum of  $\text{Hg}(\text{CN})_2$  has been previously investigated both in the solid state<sup>1</sup> and in solutions in water<sup>2</sup> and methyl alcohol,<sup>3,4</sup> where the degree of ionic dissociation is very low. All previous workers agree in finding a strong line at about  $\Delta\nu = 2200 \text{ cm.}^{-1}$ , which must obviously be assigned to the totally symmetrical mode involving principally C-N stretching, *i.e.*, to  $\nu_1$ . Some previous workers also report a second, weaker line at about  $270 \text{ cm.}^{-1}$ , which they attribute (not unnaturally) to the symmetrical mode involving principally Hg-C stretching, *i.e.*, to  $\nu_2$ . Only François,<sup>4</sup> using a solution of mercuric cyanide in methyl alcohol, reports all the three lines expected for the  $\text{Hg}(\text{CN})_2$  molecule on the basis of the selection rules. His frequencies are 2204, 404, and  $273 \text{ cm.}^{-1}$ . Since  $2204 \text{ cm.}^{-1}$  must certainly be assigned to  $\nu_1$ , only one of the two remaining frequencies should be polarised. The only work on polarisation of the lines appears to be that of François<sup>4</sup> and he reports the anomalous finding that 404 and  $273 \text{ cm.}^{-1}$  are both polarised.

Recently Jones<sup>5</sup> studied the infrared absorption of solid mercuric cyanide. Both  $\nu_2$  and  $\nu_3$  are forbidden in the infrared region as fundamentals, but Jones deduced from observed combinations that  $\nu_2$  must lie at  $415 \pm 5 \text{ cm.}^{-1}$  and  $\nu_3$  at  $276 \pm 5 \text{ cm.}^{-1}$ . That the observed Raman frequency near  $270 \text{ cm.}^{-1}$  should be  $\nu_3$  rather than  $\nu_2$  is contrary to all previous assignments, though admittedly these had been made without satisfactory evidence as to polarisation.

We have photographed the complete three-line Raman spectrum of the  $\text{Hg}(\text{CN})_2$  molecule in approximately 1.2M-mercuric cyanide in methyl alcohol. Aqueous solutions were also studied, but owing to the relatively low solubility (about 0.4M) and the spectra being impaired by a troublesome continuum, it was not possible to obtain all three Raman frequencies with certainty.

Table 1 gives the frequencies for the methyl alcoholic solution, the states of polarisation as determined with polarised incident light, and the estimated intensities. The polarisation evidence conclusively shows that  $274 \text{ cm.}^{-1}$  is to be assigned to  $\nu_3$  and  $412 \text{ cm.}^{-1}$  to  $\nu_2$ . This is in complete accord with Jones's conclusions.<sup>5</sup>

<sup>1</sup> Krishnamurti, *Indian J. Phys.*, 1930, **5**, 651.

<sup>2</sup> Woodward, *Physikal. Z.*, 1930, **17**, 792; Braun and Engelbrecht, *Z. phys. Chem.*, 1931, **11**, 409.

<sup>3</sup> Petrikain and Hochberg, *ibid.*, 1930, **8**, 440.

<sup>4</sup> François, *Compt. rend.*, 1939, **208**, 1002.

<sup>5</sup> Jones, *J. Chem. Phys.*, 1957, **27**, 665.

*Raman Spectrum of the  $\text{Hg}(\text{CN})_4^{2-}$  Ion.*—In aqueous solution and in the presence of excess of  $\text{CN}^-$  ions mercuric cyanide is almost completely converted into the tetracyanomercurate ion:  $\text{Hg}(\text{CN})_2 + 2\text{CN}^- = \text{Hg}(\text{CN})_4^{2-}$ . The Raman spectrum is expected to show (in addition to the single frequency, *ca.* 2080  $\text{cm}^{-1}$ , of the excess of cyanide ions) a number of lines due to the complex ion. Since the ion is tetrahedral (point group  $T_d$ ) only

TABLE 1. *Raman spectrum of  $\text{Hg}(\text{CN})_2$ .*

$\Delta\nu$ ( $\text{cm}^{-1}$ )	Polarisation	Intensity	Assignment
274	Depolarised	weak	$\nu_5$ ( $\Pi_g$ )
412	Polarised	weak	$\nu_2$ ( $\Sigma_g^+$ )
2189	Polarised	strong	$\nu_1$ ( $\Sigma_g^+$ )

two of these lines will be polarised, namely, those corresponding to the totally symmetric modes which involve mainly C–N stretching (frequency  $\nu_1$ ) and Hg–C stretching (frequency  $\nu_2$ ) respectively. Moreover owing to the spherical symmetry of the polarisability ellipsoid of the  $\text{Hg}(\text{CN})_4^{2-}$  ion these two lines will be completely polarised ( $\rho = 0$ ) and so will be clearly distinguishable from all the others (for which  $\rho = \frac{2}{3}$ ).

Again the aqueous solutions investigated were found to give Raman spectra with a troublesome continuum, which doubtless masked weaker lines. Nevertheless by suitable choice of concentration and exposure time it was found possible to observe three Raman frequencies: 2148 (strong), 342 (very weak), and 200  $\text{cm}^{-1}$  (very weak). In addition the spectrum showed the line due to  $\text{CN}^-$ , the measured frequency of which was 2082  $\text{cm}^{-1}$ .

The line at 2148 and the line at 342  $\text{cm}^{-1}$  are both polarised. This conclusively determines their assignments as  $\nu_1$  and  $\nu_2$  respectively.

*Stretching Force Constants.*—For  $\text{Hg}(\text{CN})_2$ , using a simple valency force field, we obtain from the frequencies  $\nu_1 = 2189$  and  $\nu_2 = 412$   $\text{cm}^{-1}$  (see Table 1) the values  $k_{\text{C-N}} = 17.3 \times 10^5$  and  $k_{\text{Hg-C}} = 2.74 \times 10^5$  dynes/cm. for the stretching force constants of the C–N and Hg–C bonds respectively. Using a potential including interaction terms, Jones<sup>5</sup> arrived at the values  $k_{\text{C-N}} = 17.6 \times 10^5$  and  $k_{\text{Hg-C}} = 2.61 \times 10^5$ . The simple valency force field is evidently quite a good approximation.

For  $\text{Hg}(\text{CN})_4^{2-}$ , likewise using a simple valency force field, we obtain from the frequencies  $\nu_1 = 2148$  and  $\nu_2 = 342$   $\text{cm}^{-1}$  the values  $k_{\text{C-N}} = 17.0 \times 10^5$  and  $k_{\text{Hg-C}} = 1.85 \times 10^5$ .

The  $\text{Hg}(\text{CN})_4^{2-}$  ion is formed from the  $\text{Hg}(\text{CN})_2$  molecule by the attachment of two  $\text{CN}^-$  ions, each of which forms a co-ordinate link with the mercury atom by the donation of a pair of electrons from its carbon atom. There is no reason to doubt that in the ion Hg is joined to the four C atoms by single bonds, for this completes the rare-gas valency octet of the mercury atom. In the  $\text{Hg}(\text{CN})_2$  molecule it is possible that the Hg–C bonds may have a small amount of double-bond character from  $\pi$ -bonding, as in  $\text{N}^+=\text{C}=\text{Hg}^--\text{C}\equiv\text{N}$ . Nevertheless in the formation of the ion from the molecule there is doubtless an increase in the number of electrons in the valency shell of the mercury atom, and this has two simultaneous and related consequences: (a) the screening of the Hg nucleus is increased and the effective value of its positive charge is diminished and (b) the linear arrangement of the two Hg–C bonds in the  $\text{Hg}(\text{CN})_2$  molecule gives place to the regular tetrahedral arrangement of the four bonds of the complex ion. Insofar as it is permissible to consider (a) and (b) separately, the effect of (a) will be to loosen the Hg–C bonds and so to lower the force constant  $k_{\text{Hg-C}}$ . The effect of (b) is difficult to assess, but is not likely to be large: in view of the marked stability of tetrahedral bond arrangements, (b) might possibly tend to cause some increase of  $k_{\text{Hg-C}}$ , but (as pointed out above) a small lowering of bond order may be involved. In fact, as we have seen, the observed overall effect is a very marked fall in  $k_{\text{Hg-C}}$ , so that probably the principal influence is the reduction of the effective positive charge of the Hg nucleus by the accession of electrons from the co-ordination of the  $\text{CN}^-$  ions.

A similar phenomenon is observed <sup>6</sup> in the formation of ions of the type  $\text{HgX}_4^{2-}$  from the corresponding mercuric halide molecules  $\text{HgX}_2$ , where X is Cl, Br, or I (see Table 2). The frequencies of the  $\text{HgX}_2$  molecules were all observed for solutions in non-dissociating solvents; those of the complex ions  $\text{HgX}_4^{2-}$  for aqueous solutions containing an excess of  $\text{X}^-$  ions. Table 2 includes also the present results. The ratio of  $k_{\text{Hg-O}}$  in the  $\text{Hg}(\text{CN})_2$

TABLE 2. *Stretching force constants of Hg-X bonds.*

Species	Symmetrical stretching frequencies (cm. <sup>-1</sup> )	$10^{-5}k_{\text{Hg-X}}$ (dynes/cm.)	$\frac{k_{\text{Hg-X}} \text{ in } \text{HgX}_2}{k_{\text{Hg-X}} \text{ in } \text{HgX}_4^{2-}}$
$\text{HgCl}_2$ .....	325	2.21	1.46
$\text{HgCl}_4^{2-}$ .....	269	1.51	
$\text{HgBr}_2$ .....	205	1.98	1.52
$\text{HgBr}_4^{2-}$ .....	166	1.30	
$\text{HgI}_2$ .....	150	1.68	1.51
$\text{HgI}_4^{2-}$ .....	122	1.11	
$\text{Hg}(\text{CN})_2$ .....	2189 & 412	2.74	1.48
$\text{Hg}(\text{CN})_4^{2-}$ .....	2148 & 342	1.85	

molecule to that in the  $\text{Hg}(\text{CN})_4^{2-}$  ion is remarkably close to the corresponding ratios for the halides.

The case of  $\text{HgCl}_2$  and  $\text{HgCl}_4^{2-}$  is specially interesting. We have supposed that the drop of  $k_{\text{Hg-Cl}}$  on passing from the molecule to the complex ion is due mainly to the reduction of the effective positive charge of the central nucleus. The effect of increasing the actual charge of the central nucleus (without altering the tetrahedral structure) can be seen by considering the isoelectronic molecule  $\text{PbCl}_4$ . In this the atomic number  $Z$  of the central atom has risen by two units without any alteration of the number of electrons present. The value of  $\nu_1$  for  $\text{PbCl}_4$  is <sup>7</sup> 327 cm.<sup>-1</sup>, from which we obtain the bond-stretching force constant  $2.23 \times 10^5$  dynes/cm. This is not only higher than in the  $\text{HgCl}_4^{2-}$  ion, but is also higher than in the  $\text{HgCl}_2$  molecule. Possible effects of change of bond orientation and bond order being ignored, it appears that (as expected) the reduction of the effective positive charge of the Hg nucleus caused by the donation of two pairs of electrons in the co-ordination of two  $\text{Cl}^-$  ions is considerably less than the increase caused by a rise of 2 in  $Z$ .

As regards the stretching force constant of the C-N bond, the calculated value for the  $\text{Hg}(\text{CN})_4^{2-}$  ion is slightly lower than that for the  $\text{Hg}(\text{CN})_2$  molecule. In view of the approximate force field used, however, it is doubtful whether the small difference (17.0 compared with 17.3) is significant. It is not unreasonable to expect that a small drop of  $k_{\text{C-N}}$  might accompany the drop of  $k_{\text{Hg-O}}$ ; for the latter has been explained above as due to a diminution of the attraction of the Hg nucleus for the bonding electrons, and this will cause a corresponding accession of electronic charge by the carbon atoms with consequent increased screening of the carbon nuclei and loosening of the C-N bonds.

The  $\text{Hg}(\text{CN})_2$  molecule itself can be thought of as formed by the co-ordination of two cyanide ions with a mercuric ion:  $\text{Hg}^{2+} + 2\text{CN}^- = \text{NC} \rightarrow \text{Hg} \leftarrow \text{CN}$ . The frequency  $\nu_1$  of the mainly C-N stretching vibration of the  $\text{Hg}(\text{CN})_2$  molecule is higher than the frequency of the  $\text{CN}^-$  ion, but this fact does not in itself mean that  $k_{\text{C-N}}$  is larger in the molecule than in the ion. Even if  $k_{\text{C-N}}$  were the same in both species, the mechanical coupling in the molecule must give rise to a frequency difference in the observed direction. In the case under consideration, however, calculation shows that  $k_{\text{C-N}}$  in the  $\text{CN}^-$  ion is  $16.5 \times 10^5$ , so that there is a small but definite increase associated with the formation of the  $\text{Hg}(\text{CN})_2$  molecule. This is as expected on the view (cf. above) that the donation of electron pairs to the  $\text{Hg}^{2+}$  ion by the C atoms of the  $\text{CN}^-$  ions must reduce the screening of the C nuclei, thus increasing their effective positive charge and tightening the C-N bonds.

*Experimental.*—Each solution was passed through a fine sintered glass filter into the Raman vessel. The spectra were excited by a Toronto-type mercury-arc lamp, the principal exciting

<sup>6</sup> Rolfe, Sheppard, and Woodward, *Trans. Faraday Soc.*, 1954, **50**, 1275.

<sup>7</sup> Neu and Gwinn, *J. Amer. Chem. Soc.*, 1948, **70**, 3463.

line being 4358 Å. Primary lines of lower wavelengths were effectively suppressed by the use of a filter of *m*-dinitrobenzene in benzene. The spectrograph was a Hilger E 612 instrument (two prisms and *f*/5.7 camera) giving a reciprocal dispersion of about 18 Å per mm. in the region studied. For each solution a wide range of exposure times was explored in order to find the best. The states of polarisation of the Raman lines were determined qualitatively by taking successive photographs with suitably oriented polaroid cylinders surrounding the Raman tube. Kodak special scientific plates, emulsion type Oa and sensitivity G, were used throughout. Frequencies were measured in the usual manner with an iron-arc spectrum as standard. For strong lines the limits of error of the measured  $\Delta\nu$  values are estimated at  $\pm 2$  cm.<sup>-1</sup>, but for very weak lines the errors may be larger.

We thank Dr. J. W. Linnett for helpful discussions.

INORGANIC CHEMISTRY LABORATORY,  
SOUTH PARKS ROAD, OXFORD.

[Received, November 17th, 1958.]

---