RAMAN SPECTRUM OF MERCURIC CHLORIDE IN RELATION TO ITS STRUCTURE

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1. Introduction

The experimental determination of the relative positions in space of the atoms in a molecule, can now be effected by a variety of methods. Diffraction of X-rays by solids, diffraction of electrons by vapours, measurement of dipole moments, absorption spectra and Raman spectra in different states of aggregation are among the most important ones. A study of the structure of mercuric chloride, from some of the aspects stated above, has been undertaken by many earlier investigators.

Braekken and Scholten\(^1\) concluded, from studies on X-ray diffraction, that HgCl\(_2\) crystallises in the rhombic class with four molecules in the unit cell, the space group being \(V_h^6\). According to them, the structure is molecular and the atoms in each molecule are collinear. Braune and Knoke\(^2\) determined the nuclear distances of HgCl\(_2\) by the electron diffraction method. Greg\(^3\) also undertook a detailed study of the structure of mercury halides by the electron diffraction method and concluded that it is not possible to uniquely determine the configuration of the mercuric chloride and bromide owing to the relatively small scattering powers of the atoms attached to the mercury atom. These authors expressed the opinion that their results are, on the whole, in agreement with a linear structure for the molecule. The dipole moment of mercuric chloride, calculated by Bell\(^4\) from solubility data, is \(4 \times 10^{-18}\). Curran and Wenzke\(^5\) determined the same, using dioxane as solvent and found it to be \(1.29 \times 10^{-18}\). As the value is quite appreciable, the authors conclude that the configuration of mercuric chloride is not linear. On the contrary, Braune and Linke\(^6\) determined the dielectric constant of HgCl\(_2\) at temperatures between 320\(^\circ\) C. and 430\(^\circ\) C. and found the molecular polarisation to be independent of temperature. This shows that the molecule has no dipole moment and has therefore to be linear.

Krishnamurty\(^7\) studied the Raman spectrum of HgCl\(_2\) in the form of crystalline powder. He recorded two lines 312 (strong) and 381 (weak). As the spectrum resembles those of CO\(_2\) and CS\(_2\), he suggested a linear model for the HgCl\(_2\) molecule. The presence of the weak line is explained as due
to the oscillation of one of the chlorine atoms against the remaining group (HgCl). This explanation is, however, open to serious objections. He also examined a very concentrated solution of mercuric chloride in CH$_3$OH. The line is symmetrically broadened and slightly displaced (319). The broadening observed is explained as due to the increased rotational freedom of the molecules in the dissolved state. Braune and Engelbrecht$^8$ found that HgCl$_2$, dissolved in water, gives a strong line at 320 cm.$^{-1}$ and in acetic ester gives a line at 332 cm.$^{-1}$. They also studied the Raman spectrum in the molten and vapour states. Molten HgCl$_2$ gives a strong and broad line at 314 cm.$^{-1}$ and a very weak line at 376 cm.$^{-1}$. In the gaseous state the principal line, according to these authors, shifts to 355 cm.$^{-1}$. The variation of Raman frequencies, as we pass from the liquid or solid state to the gaseous state, is a characteristic of polar molecules. So the obvious conclusion to be drawn from the above result, is that HgCl$_2$ is polar and hence, a bent molecule.

The existence of strong Raman lines in HgCl$_2$ is an outstanding evidence that the link in the molecule is covalent. Sidgwick and Powell$^9$ collected the experimental evidence as to the stereochemistry of polyvalent atoms and tried to relate it to the simplest expression of electronic structure, the size of the valency groups and the number of shared electrons they contain. They generalised that the structure is always linear when the valency group is less than 8 with a covalency of 2. As HgCl$_2$ belongs to this category, it should be expected to be linear.

From what has been said in the foregoing paragraphs, it will be seen that evidence, available from different branches of investigation in the matter of the structure of HgCl$_2$, is conflicting. In some cases, different authors, working in the same branch, have arrived at different conclusions. It is very important that the structure of HgCl$_2$ should be definitely established and the discrepancies reconciled.

In the present paper, the author has made a detailed study of the different aspects of the Raman spectrum method. The results are presented and discussed with special reference to the structure of HgCl$_2$.

2. Experimental Technique

The following technique is adopted for obtaining a good specimen of the solid suitable for Raman spectrum studies. The substance is contained in a pyrex glass tube and is melted by means of cylindrical electric heater surrounding the tube. The substance is then slowly cooled down to the room temperature by reducing the current in the heater. In this way, a reasonably transparent solid lump is obtained in the glass tube. The tube is cautiously broken and a single transparent crystal of size 1 cm. $\times$ 1 cm. $\times$ 1.5 cm. is obtained from the lump. Two of its faces, one for illumination and the other for