724. *Raman Spectrum and Constitution of Fused Gallium Dichloride.*

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The Raman spectrum of fused gallium dichloride at approx. 190° c is found to consist of four frequencies : 115 cm.$^{-1}$, strong, sharp, depolarised; 153 cm.$^{-1}$, weak, diffuse, depolarised; 346 cm.$^{-1}$, very strong, sharp, highly polarised; and 380 cm.$^{-1}$, very weak, diffuse, depolarised. This spectrum is in close agreement with that found for the $GaCl_4^-$ ion in aqueous solution. In the fused state, therefore, gallium dichloride is to be formulated as gallium(I) tetrachlorogallate(III), $[Ga^+][GaCl_4^-]$. The results do not support the hypothesis that Ga–Ga bonds are involved.

ALL the metals of Group IIIB show the expected valency of three : for thallium the more stable valency is one. " Gallium dichloride " has the empirical formula $GaCl_2$, which appears to indicate the intermediate valency two. First reported in 1881 by de Boisbaudran,[1] it has been comparatively little investigated and its structure has not so far been determined. If it involved bivalent gallium, the compound would be paramagnetic on account of the single unpaired electron of the gallium atom. In 1932, however, Klemm and Tilk [2] observed that solid gallium dichloride is diamagnetic, from which they concluded that the molecule must involve a covalent link between two gallium atoms, *viz.*, $Cl_2Ga–GaCl_2$.

An alternative formulation is possible, however. The compound can be written as gallium(I) tetrachlorogallate(III), $[Ga^+][GaCl_4^-]$, in which the apparent valency of two is due to univalency of one and tervalency of the other gallium atom.

The Raman effect offers a powerful method of deciding between alternative proposed molecular models of different symmetries, since these must have different rules of selection and polarisation. The position is especially favourable when, as here, one of the formulations involves only an ion for which the Raman spectrum has already been observed in other circumstances. The preceding paper [3] has described the spectrum of the tetrachlorogallate ion $GaCl_4^-$ in an aqueous solution of gallium trichloride (1·5M) containing excess of hydrochloric acid (6·3M).

Results and Discussion.—We have obtained the Raman spectrum of gallium dichloride in the fused state at approx. 190° c, *i.e.*, about 25° above its melting point. The annexed Table shows the observed Raman frequencies, estimated intensities, appearances of lines, and states of polarisation. The agreement with Table 1 of the preceding paper for the

Raman spectrum of fused gallium dichloride.

Δν (cm.$^{-1}$)	115	153	346	380
Intensity	Strong	Weak	Very strong	Very weak
Appearance	Sharp	Diffuse	Sharp	Diffuse
Polarisation	Depolarised	Depolarised	Highly polarised	Depolarised

tetrachlorogallate ion is very close, and there can be little doubt that the spectrum observed for fused gallium dichloride is due to the presence of $GaCl_4^-$ ions. All the differences between corresponding Δν values are probably within the limits of experimental error. In the present work these were about ±3 cm.$^{-1}$ for strong sharp lines : weaker and more diffuse lines, like those with Raman frequencies 153 and 380 cm.$^{-1}$, were subject to larger errors.

It is remarkable that the most intense and sharpest line, corresponding to the totally symmetrical " breathing " mode of the regular tetrahedral ion, should give exactly the same frequency (v_1) in the molten gallium dichloride as in the aqueous 1·5M-gallium trichloride containing excess of hydrochloric acid (6·3M), for in view of the markedly different

[1] de Boisbaudran, *Compt. rend.*, 1881, **93**, 294.
[2] Klemm and Tilk, *Z. anorg. Chem.*, 1932, **207**, 175.
[3] Woodward and Nord, preceding paper.

environments in the two cases some frequency displacement might have been expected. In this connexion the results for the isoelectronic ion $ZnCl_4^{2-}$ are of interest. The value of v_1 in aqueous solution, as observed by Delwaulle,[4] is 282 cm.$^{-1}$, while for a fused mixture of zinc chloride and potassium chloride Bues [5] found practically the same value (280 cm.$^{-1}$). For these ions, therefore, it appears that the frequency of the totally symmetrical mode is insensitive to changes of molecular environment. The lowest frequency (v_2) is also very little different in the two Tables.

On the other hand the two modes of class F_2 (triply degenerate) appear more weakly and more diffusely for the fused dichloride than for the $GaCl_4^-$ ion in aqueous solution. It is probable that ionic interactions in the fused state relieve the degeneracy and so affect the appearance and apparent relative intensity of these lines.

Our finding that the fused dichloride contains $GaCl_4^-$ ions is in harmony with Hampe's observation [6] that the fused salt is a conductor of electricity. If the compound involved Ga–Ga links, as suggested by Klemm and Tilk,[2] its electrical conductivity would imply that the Cl_2Ga–$GaCl_2$ molecules are at least partially dissociated into ions. The following considerations show that none of the species so formed would give a Raman spectrum consistent with the one observed.

On account of chlorine–chlorine repulsions the neutral Cl_2Ga–$GaCl_2$ molecule would probably have the staggered configuration (as in the allene molecule) with the planes of the two $GaCl_2$ groups mutually perpendicular. The point group would be D_{2v}, the number of Raman lines (*i.e.*, Raman-active fundamentals) would be nine, and the number polarised would be three. For the less likely planar configuration (as in the ethylene molecule, point group D_{2h}) the corresponding numbers would be six and three. The first stage of ionisation would give the ion $(Cl_2Ga$–$GaCl)^+$, which would doubtless be planar and Y-shaped (point group C_{2v}). For this the number of Raman lines would be nine, and the number polarised would be four. The second stage of ionisation could occur in two ways, giving either $(ClGa$–$GaCl)^{2+}$ or $(Cl_2Ga$–$Ga)^{2+}$. The former would be linear (point group $D_{\infty h}$) with three Raman lines, two of them polarised : the latter would be planar Y-shaped (point group C_{2v}) with six lines, three of them polarised. Further ionisation would produce the linear $(ClGa$–$Ga)^{3+}$, which would give three Raman lines, two polarised ; and finally $(Ga$–$Ga)^{4+}$, which would give only one.

The observed spectrum (Table) is not consistent with the theoretical prediction either for the Cl_2Ga–$GaCl_2$ molecules or for any of the ions derivable from it. Since weak lines may sometimes escape observation, however, the argument from numbers is not always convincing. It is therefore important to note (i) that all the species here under consideration (with the obvious exception of Ga_2^{4+}) must have at least one totally symmetrical mode of vibration involving principally Ga–Cl stretching, and in addition one totally symmetrical mode involving principally Ga–Ga stretching; and (ii) that both of these will be expected, like all totally symmetrical stretching modes, to appear strongly in the observed Raman spectrum. It is true that the postulated Ga–Ga bond is an unusual one; but a close parallel is found in the mercurous ion $(Hg$–$Hg)^{2+}$ for which a strong Raman line has been observed.[7] It follows that the Raman spectrum of all the species being considered would show at least two lines that would be strong and polarised. In fact (see Table) only one polarised line is observed. The evidence therefore gives no support to the hypothesis of the Ga–Ga bond.

No sign was found of any dissociation of the tetrachlorogallate ion according to the equation $GaCl_4^- = GaCl_3 + Cl^-$, despite the absence of an excess of chlorine ions. Such a dissociation would have been followed by the formation of Ga_2Cl_6 molecules, and had it occurred to any appreciable extent the melt would have given the Raman frequencies characteristic of fused gallium trichloride, the most intense of which have been found [8] to be 96 and 410 cm.$^{-1}$. Extended exposures with fused gallium dichloride failed to

[4] Delwaulle, *Compt. rend.*, 1955, **240**, 2132.
[5] Bues, *Z. anorg. Chem.*, 1955, **279**, 104.
[6] Hampe, *Jahresber.*, 1888, Part 1, p. 388.
[7] Woodward, *Phil. Mag.*, 1934, **18**, 823.
[8] Gerding, Haring, and Renes, *Rec. Trav. chim.*, 1953, **72**, 78.

show either of these frequencies, though they were at once confirmed with fused gallium trichloride.

From the results we conclude that $GaCl_4-$ is the preponderant polyatomic species in fused gallium dichloride at 190°, and that under these conditions the compound is to be formulated as gallium(I) tetrachlorogallate (III).

EXPERIMENTAL

Preparation of Gallium Dichloride (cf. Laubengayer and Schirmer [9]).—A weighed amount of pure gallium (supplied by Messrs. Johnson, Matthey & Co.) was converted into the trichloride by passing a stream of pure dry chlorine over the gently heated metal. The trichloride was condensed into a bulb *A* containing a further quantity of gallium, slightly in excess of the calculated weight for the complete reduction of the trichloride to dichloride. To this was connected another bulb, *B*, which was in turn connected to the Raman tube. Bulb *B* was constructed with a long neck. The whole system was evacuated, sealed off, and kept at 180° for 24 hr. with occasional shaking. The product was distilled into the bulb *B*, and bulb *A* was drawn off. The remaining apparatus was placed overnight at 200°, except for a short portion of the long neck of bulb *B*, which was left projecting and was kept cool with an air blast. In this way any excess of gallium trichloride was distilled off from the less volatile dichloride. Finally the pure dichloride was poured *in vacuo* into the Raman tube, which was then sealed off.

As thus prepared, gallium dichloride was an opaque, somewhat waxy, white solid, melting at 165° to a colourless liquid (Found: Ga, 48·9; Cl, 50·7. Calc. for $GaCl_2$: Ga, 49·6; Cl, 50·4%). Similar preparations (Brewer, Garton, *et al.*, unpublished work) consistently yielded specimens containing not more than 3% of $GaCl_3$ as impurity.

Raman Spectra.—The technique was that described in the preceding paper.[3] A sodium nitrite filter was used to diminish the intensity of the primary lines of shorter wavelength than 4358 Å.

The sample of gallium dichloride was melted and kept `at approx. 190° by a stream of electrically preheated air passing through the annular space between the Raman tube and the surrounding Dewar sleeve. The Raman scattering was intense : with natural incident light the complete Raman spectrum could be photographed on Ilford Zenith plates with an exposure time of only 2 min. Longer times were used in unsuccessful attempts to find additional weaker lines. During the work the sample was allowed to solidify and was remelted several times. No consequent change in the spectrum was observed. In all, the compound was irradiated in the fused state for several hours. No signs of chemical decomposition (such as deposition of gallium metal) were noticeable : the melt was always clear and colourless.

[9] Laubengayer and Schirmer, *J. Amer. Chem. Soc.*, 1940, **62**, 1578.