

### 723. Raman Spectrum of the Tetrachlorogallate Ion ( $\text{GaCl}_4^-$ ) in Aqueous Solution.

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An approximately 1.5M-aqueous solution of gallium trichloride containing 6.3M-hydrochloric acid gives four Raman frequencies, which are attributed to the  $\text{GaCl}_4^-$  ion of regular tetrahedral shape:  $\nu_2 (E) = 114 \text{ cm.}^{-1}$ , strong, sharp, depolarised;  $\nu_4 (F_2) = 149 \text{ cm.}^{-1}$ , strong, sharp, depolarised;  $\nu_1 (A_1) = 346 \text{ cm.}^{-1}$ , very strong, sharp, highly polarised; and  $\nu_3 (F_2) = 386 \text{ cm.}^{-1}$ , weak, diffuse, depolarised.

In a previous paper<sup>1</sup> we described the Raman spectrum of the tetrabromogallate ion,  $\text{GaBr}_4^-$ , in an aqueous solution of gallium tribromide containing excess of hydrobromic acid. We have now investigated a solution of gallium trichloride (1.5M) containing an excess of hydrochloric acid (6.3M) and have observed an entirely analogous Raman spectrum. The observed frequency shifts, estimated intensities, appearances of lines, states of polarisation, and assignments are given in Table I.

TABLE I. Raman spectrum of the  $\text{GaCl}_4^-$  ion in aqueous solution.

$\Delta\nu$ (cm. <sup>-1</sup> )	114	149	346	386
Intensity	Strong	Strong	Very strong	Weak
Appearance	Sharp	Sharp	Sharp	Diffuse
Polarisation	Depolarised	Depolarised	Highly polarised	Depolarised
Assignment	$\nu_2 (E)$	$\nu_4 (F_2)$	$\nu_1 (A_1)$	$\nu_3 (F_2)$

As with the tetrabromogallate ion<sup>1</sup> the observation of four Raman frequencies, one highly polarised and the other three depolarised, provides evidence that the scattering species is of the regular tetrahedral  $\text{XY}_4$  type (point group  $T_d$ ); and the spectrum can be attributed with confidence to the tetrachlorogallate ion  $\text{GaCl}_4^-$ . This must be the predominant complex in the solution investigated.

This ion is isoelectronic with both  $\text{GeCl}_4$  and  $\text{ZnCl}_4^{2-}$ . The observed vibrational frequencies are compared in Table 2, where the values for  $\text{GeCl}_4$  are as given by Herzberg<sup>2</sup> and the values for  $\text{ZnCl}_4^{2-}$  are those of Delwaille.<sup>3</sup> For the latter species, only  $\nu_1$  could be determined satisfactorily:  $\nu_3$  was not observed, no doubt owing to its weakness, its probable diffuseness, and its proximity to the much stronger  $\nu_1$ , while at lower frequencies the spectrum showed only a rather wide unresolved band which doubtless includes both  $\nu_2$  and  $\nu_4$ .

<sup>1</sup> Woodward and Nord, *J.*, 1955, 2655.

<sup>2</sup> Herzberg, "Molecular Spectra and Molecular Structure," van Nostrand Co., New York, 1945, Vol. II, p. 167.

<sup>3</sup> Delwaille, *Compt. rend.*, 1955, 240, 2132.

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From Table 2 it is seen that there is a decrease of all four fundamental frequencies as we pass from the neutral  $\text{GeCl}_4$  molecule to the singly negatively charged  $\text{GaCl}_4^-$  ion, and that the decrease continues for  $\nu_1$  (and probably also for the other fundamentals) as we pass from  $\text{GaCl}_4^-$  to the doubly-negatively charged ion  $\text{ZnCl}_4^{2-}$ . This behaviour is quite similar to that observed for other corresponding isoelectronic sets, such as  $^4\text{SnBr}_4$ ,  $\text{InBr}_4^-$ , and  $\text{CdBr}_4^{2-}$ , and further supports the view that the spectrum of Table 1 is to be attributed

TABLE 2. *Fundamental vibrational frequencies ( $\text{cm}^{-1}$ ) of isoelectronic species.*

	$\nu_3$	$\nu_4$	$\nu_1$	$\nu_2$
$\text{GeCl}_4$ .....	134	172	396	453
$\text{GaCl}_4^-$ .....	114	149	346	386
$\text{ZnCl}_4^{2-}$ .....		61—82	282	?

to the tetrachlorogallate ion. As far as the totally symmetrical "breathing" frequencies  $\nu_1$  are concerned, the progressive decrease indicates that the stretching force  $k$  of the metal-chlorine bond likewise decreases in the order given. The values of  $10^{-5}k$  calculated on the basis of a simple valency force field are:  $\text{GeCl}_4$ , 3.28;  $\text{GaCl}_4^-$ , 2.50; and  $\text{ZnCl}_4^{2-}$ , 1.64 dynes per cm. The value of  $k$  (or of  $\nu_1$ ) for the singly charged species  $\text{GaCl}_4^-$  is not midway between the corresponding values for the isoelectronic neutral and doubly charged species,  $\text{GeCl}_4$  and  $\text{ZnCl}_4^{2-}$ . In fact the decrease in passing from  $\text{GaCl}_4^-$  to  $\text{ZnCl}_4^{2-}$  is greater than that in passing from  $\text{GeCl}_4$  to  $\text{GaCl}_4^-$ . This kind of non-linear variation of  $k$  with the atomic number of the central atom has been noted<sup>5</sup> for other sets of isoelectronic species of the regular tetrahedral  $\text{XY}_4$  type.

### EXPERIMENTAL

A weighed quantity of pure gallium, supplied by Messrs. Johnson, Matthey and Co., was dissolved in sufficient concentrated hydrochloric acid to give a 1.5M-solution of gallium trichloride containing approximately 6.3M-excess of acid. The metal dissolved slowly but completely, to a clear colourless solution which, however, continued to evolve hydrogen (apparently from irregularities on the surface of the glass vessel) and was strongly reducing. At this stage the solution no doubt contained gallium in a lower than trivalent state. Before use it was kept in a warm water-bath until hydrogen evolution had ceased, by which time the reducing properties had disappeared.

The Raman spectra were photographed with the apparatus previously described,<sup>1,6</sup> excitation was by means of a "Toronto arc," and the principal primary line was Hg 4358 Å. Qualitative information on the states of polarisation of the Raman lines was obtained by the method of polarised incident light, suitable Polaroid cylinders surrounding the Raman tube. The  $\Delta\nu$  values were measured in the usual way with a copper-arc spectrum as standard. The estimated limits of error are about  $\pm 2 \text{ cm}^{-1}$  for strong sharp lines. The value for  $\nu_3$  given in Table 1 may be less precise, as its Raman line is weak and diffuse and lies rather near the very intense line of  $\nu_1$ . With natural light the Raman spectrum of  $\text{GaCl}_4^-$  excited by the mercury line 4358 Å could be photographed with an exposure time of  $1\frac{1}{2}$  hr.

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[Received, May 25th, 1956.]

<sup>4</sup> Woodward and Bill, *J.*, 1955, 1699.

<sup>5</sup> Woodward and Roberts, *J.*, 1956, 1170.

<sup>6</sup> George, Rolfe, and Woodward, *Trans. Faraday Soc.*, 1953, 49, 375.