139. *Raman Spectra of the Tetraiodogallate* (GaI_4^-) *and Tetraiodoindate* (InI_4^-) *Ions in Aqueous Solution.*

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An aqueous solution of gallium(III) iodide containing hydriodic acid gives four Raman frequencies, which are attributed to the GaI_4^- ion of regular tetrahedral shape: $\nu_2(E) = 52$, $\nu_4(F_2) = 73$, $\nu_1(A_1) = 145$, and $\nu_3(F_2) = 222$ cm.$^{-1}$. A corresponding solution of indium(III) iodide containing hydriodic acid shows an analogous spectrum, attributed to the tetrahedral InI_4^- ion: $\nu_2 = 42$, $\nu_4 = 58$, $\nu_1 = 139$, and $\nu_3 = 185$ cm.$^{-1}$. Comparisons are made with the frequencies of isoelectronic species.

Previous work[1,2] on the Raman spectra of the tetrachlorogallate ($GaCl_4^-$) and tetrabromogallate ($GaBr_4^-$) ions in aqueous solutions of the gallium(III) halide in presence of excess of the corresponding hydrogen halide has been extended to gallium(III) iodide (1·4 moles of GaI_3 per l.) containing excess of hydriodic acid (2·8M). An intense Raman spectrum, analogous in all respects to those of $GaCl_4^-$ and $GaBr_4^-$, was observed, whose characteristics are in Table 1. The spectrum is attributed to the GaI_4^- ion.

Table 1. *Raman spectrum of the* GaI_4^- *ion in aqueous solution.*

$\Delta\nu$ (cm.$^{-1}$)	52	73	145	222
Intensity	Medium	Medium	Very strong	Weak
Appearance	Sharp	Sharp	Sharp	Diffuse
Polarization	Depolarized	Depolarized	Highly polarized	Depolarized
Assignment	$\nu_2(E)$	$\nu_4(F_2)$	$\nu_1(A_1)$	$\nu_3(F_2)$

The regular decrease of frequencies in the series $GaCl_4^-$, $GaBr_4^-$, GaI_4^- (Table 2), together with the number of the observed frequencies and the states of polarization, provide very strong evidence that all three species are of the same regular tetrahedral XY_4 shape (point group T_d).

Table 2. *Vibrational frequencies of tetrahalogenogallate ions.*

	$\nu_2(E)$	$\nu_4(F_2)$	$\nu_1(A_1)$	$\nu_3(F_2)$	Ref.
$GaCl_4^-$	114	149	346	386	1
$GaBr_4^-$	71	102	210	278	2
GaI_4^-	52	73	145	222	Present work

As the Raman spectra of aqueous solutions of indium(III) bromide (1 mole of $InBr_3$ per l.) containing excess of hydrobromic acid (up to 6M) provide no evidence[3] for the presence of the $InBr_4^-$ ion, the tendency in aqueous solution to complex formation with bromide ions is less for In^{3+} than for Ga^{3+}: only by extraction into an organic solvent could the four-line Raman spectrum characteristic of the $InBr_4^-$ ion be obtained. With iodide ions the tendency to complex formation is expected to be stronger; we have now found that an aqueous solution of indium(III) iodide (1·0 mole of InI_3 per l.) containing

Table 3. *Raman spectrum of the* InI_4^- *ion in aqueous solution.*

$\Delta\nu$ (cm.$^{-1}$)	42	58	139	185
Intensity	Medium	Medium	Very strong	Medium
Appearance	Sharp	Sharp	Sharp	Diffuse
Polarization	Depolarized	Depolarized	Highly polarized	Depolarized
Assignment	$\nu_2(E)$	$\nu_4(F_2)$	$\nu_1(A_1)$	$\nu_3(F_2)$

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[1] Woodward and Nord, *J.*, 1956, 3721.

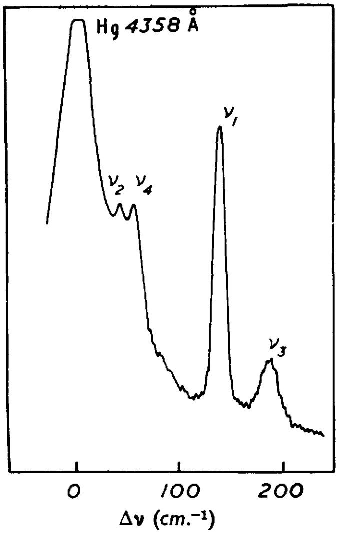
[2] *Idem*, *J.*, 1955, 2655.

[3] Woodward and Bill, *ibid.*, p. 1699.

excess of hydriodic acid (4M) gives an intense Raman spectrum (Table 3) entirely analogous to that reported above for GaI_4^- and clearly attributable to the ion InI_4^-, which must be the predominant complex present in the solution.

The value of ν_2 (42 cm.$^{-1}$) is amongst the lowest vibrational frequencies so far measured for any tetrahedral XY_4 species. The microphotometer trace of the spectrum reproduced in the Figure shows that, despite their close proximity to the relatively very intense primary line (Hg 4358 Å), both ν_2 and ν_4 are well resolved. As is generally found, they appear even more distinct when the original photograph is examined visually.

As In^{3+} shows less tendency to form halide complexes than does Ga^{3+}, it has not so far been possible to obtain the Raman spectrum of the $InCl_4^-$ ion, so a full comparison of the kind made for gallium in Table 2 cannot be presented; but the frequencies ascribed to InI_4^- in Table 3 clearly bear the same kind of relation to those[3] of $InBr_4^-$ ($\nu_2 = 55$; $\nu_4 = 79$; $\nu_1 = 197$; $\nu_3 = 239$ cm.$^{-1}$) as do the frequencies of GaI_4^- to those of $GaBr_4^-$ (Table 2).



Raman spectrum of the InI_4^- *ion in aqueous solution, excited by* Hg 4358 Å *radiation.*

The GaI_4^- ion is isoelectronic with the doubly-negative ZnI_4^{2-} ion and with the neutral GeI_4 molecule. The InI_4^- ion likewise forms the middle member of an isoelectronic triad with CdI_4^{2-} and SnI_4. The observed Raman frequencies (cm.$^{-1}$) are compared in Table 4.

TABLE 4. *Vibrational frequencies of Isoelectronic Triads.*

	ν_2	ν_4	ν_1	ν_3	$10^{-5}k$	Ref.
ZnI_4^{2-}	44	62	122	170	1·11	4
GaI_4^-	52	73	145	222	1·57	Present work
GeI_4	60	80	159	264	1·80	5
CdI_4^{2-}	36	44	117	145	1·02	6
InI_4^-	42	58	139	185	1·44	Present work
SnI_4	47	63	149	216	1·66	5

In both triads there is a progressive increase of all four fundamental frequencies as the atomic number of the central metal atom increases. As regards the totally symmetrical " breathing " frequencies ν_1, this means that the stretching force constant k of the metal–iodine bond increases in the same order. The values of $10^{-5}k$ (dynes per cm.), calculated

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[4] Delwaulle, *Compt. rend.*, 1955, **240**, 2132.

[5] Stammreich, Forneris, and Tavares, *J. Chem. Phys.*, 1956, **25**, 1275.

[6] Delwaulle, François, and Wiemann, *Compt. rend.*, 1939, **208**, 184; Rolfe, Sheppard, and Woodward, *Trans. Faraday Soc.*, 1954, **50**, 1275.

on the basis of a simple valency-force field, are included in Table 4. For both triads the value of k (or of ν_1, from which k is derived) for the singly-negative ion is not midway between the corresponding values for the other two isoelectronic species. In fact the increase in passing from the doubly to the singly charged ion is greater than that in passing from the latter to the neutral molecule. This non-linear variation of k with the atomic number of the central atom, which is qualitatively the same as for other sets [1,7,8] of isoelectronic species of the regular tetrahedral XY_4 type, will be discussed subsequently.

EXPERIMENTAL

Preparation of Solutions.—The solution of gallium iodide was prepared by dissolving the appropriate weight of gallium metal, previously reduced to small particles by adding warm water and shaking vigorously until resolidification occurred, in a known quantity of constant-boiling hydriodic acid in a flask fitted with a Bunsen valve. The acid had been redistilled in a current of nitrogen and contained some hypophosphorous acid to keep it colourless. The resulting gallium iodide solution was quite clear and showed no colour due to free iodine. It had been anticipated that the principal experimental difficulty in obtaining the Raman spectra would be absorption of the light due to liberation of iodine by the oxidation of the excess of hydriodic acid—a reaction which occurs readily, especially under intense illumination. Care was taken to exclude air as far as possible from the Raman vessel containing the solution. The trace of hypophosphorous acid minimized the amount of free iodine formed, and only a slight iodine colour, insufficient to interfere, developed at the free surface of the solution during the Raman exposures.

The indium iodide solution, prepared similarly, had to be filtered to remove a small quantity of suspended solid particles, apparently due to reaction with the trace of hypophosphorous acid. As first prepared the solution was pale yellow. Before each Raman exposure it was decolorised by adding a very small fragment of indium metal (which evolved hydrogen) and waiting until it was completely dissolved. The solution coloured during illumination in the Raman source, and even on lengthy standing in the dark; good Raman spectra (see Figure) were nevertheless obtained easily.

Raman Spectra.—The excitation was by means of a " Toronto arc," the blue mercury line (4358 Å) being used. Primary lines of lower wavelength were reduced in intensity by a sodium nitrite filter. Qualitative determinations of the states of polarization of the Raman lines were made by the method of polarized incident light, successive exposures being taken with suitable Polaroid cylinders surrounding the Raman tube. The volume of solution was in each case about 19 ml. In view of the low $\Delta\nu$ values a Hilger type E.612 two-prism spectrograph with *f*/5·6 camera was used; a higher dispersion and resolving power was thus obtained than in the work on the chloro- and bromo-complex ions. The frequency shifts were measured in the usual way with an iron-arc spectrum as standard. The values given are correct to within ±2 cm.$^{-1}$; for the sharper lines the accuracy is probably better. The photographic plates used were Kodak Special Scientific, emulsion type Oa, sensitivity G. The four-line spectra were obtained with exposure times of only 5 min. The intensity of Raman scattering by the ions GaI_4^- and InI_4^- is evidently very great. Longer times showed no further features.

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[7] Woodward and Roberts, *J.*, 1956, 1170.

[8] *Idem, Trans. Faraday Soc.*, 1956, **52**, 1458.