

Raman Spectrum of the Tetrabromogallate(III) (GaBr₄⁻) Ion.

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An approximately 1.5M-aqueous solution of gallium tribromide containing 6M-hydrobromic acid gives four Raman frequencies: 71 cm.⁻¹, strong, sharp, depolarized; 102 cm.⁻¹, strong, sharp, depolarized; 210 cm.⁻¹, very strong, sharp, polarized; and 278 cm.⁻¹, rather weak, diffuse, depolarized. This spectrum is attributed to the ion GaBr₄⁻, of regular tetrahedral shape.

CONTINUING previous work, in which the Raman spectrum of the InBr₄⁻ ion was observed (Woodward and Bill, *J.*, 1955, 1699), we have observed a spectrum attributable to the corresponding ion GaBr₄⁻. The aqueous solution contained both gallium tribromide (*ca.* 1.5M) and hydrobromic acid (6M). The observed Raman frequencies, estimated intensities, appearances of lines, states of polarization, and assignments are given in Table 1.

Table 1. *Raman spectrum of the GaBr₄⁻ ion.*

$\Delta\nu$ (cm. ⁻¹)	71	102	210	278
Intensity	strong	strong	very strong	rather weak
Appearance	sharp	sharp	sharp	diffuse
Polarization	depolarized	depolarized	strongly polarized	depolarized
Assignment	$\nu_3 (E)$	$\nu_4 (F_2)$	$\nu_1 (A_1)$	$\nu_3 (F_2)$

The number of observed frequencies and the states of polarization provide strong evidence of a species XY₄ of regular tetrahedral shape, and the spectrum may be confidently attributed to the ion GaBr₄⁻. This must be the predominant species in the solution investigated.

Table 2 gives a comparison of the frequencies of the ions GaBr₄⁻, InBr₄⁻ (Woodward and Bill, *loc. cit.*), and TlBr₄⁻ (Delwaille, *Compt. rend.*, 1954, 238, 2522). It is seen that each of the frequencies shows a gradual decrease in the order: gallium, indium, thallium.

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As far as the totally symmetrical "breathing" frequencies ν_1 are concerned, this indicates that the stretching force constant k of the metal-bromine bond decreases in the order given. The values of $10^{-5}k$ calculated on the basis of a simple valency force field are: GaBr₄⁻, 2.08; InBr₄⁻, 1.83; and TlBr₄⁻, 1.70 dynes per cm.

TABLE 2. *Vibrational frequencies of complex ions MBr₄⁻ of Group IIIB elements.*

	ν_2	ν_4	ν_1	ν_3
GaBr ₄ ⁻	71	102	210	278
InBr ₄ ⁻	55	79	197	239
TlBr ₄ ⁻	51	64	190	209

The GaBr₄⁻ ion is isoelectronic with the neutral germanium tetrabromide molecule. The observed Raman frequencies are compared in Table 3, where the values for germanium tetrabromide are those given by Herzberg ("Molecular Spectra and Molecular Structure," van Nostrand Co., New York, 1945, Vol. 2, p. 167). A corresponding comparison for the related isoelectronic pair, stannic bromide (Herzberg, *op. cit.*) and InBr₄⁻ (Woodward and Bill, *loc. cit.*), is also given.

TABLE 3. *Vibrational frequencies of isoelectronic species.*

	ν_2	ν_4	ν_1	ν_3		ν_2	ν_4	ν_1	ν_3
GeBr ₄	78	111	234	328	SnBr ₄	64	88	220	279
GaBr ₄ ⁻	71	102	210	278	InBr ₄ ⁻	55	79	197	239
$\nu_{\text{GeBr}_4}/\nu_{\text{GaBr}_4^-}$	1.10	1.09	1.11	1.18	$\nu_{\text{SnBr}_4}/\nu_{\text{InBr}_4^-}$	1.16	1.11	1.12	1.17

From Table 3 it is seen that the frequencies attributed to GaBr₄⁻ in the present work bear to the frequencies of the isoelectronic germanium tetrabromide molecule a relationship which is very similar to that borne by the frequencies of InBr₄⁻ to the isoelectronic stannic bromide.

The spectrum of GaBr₄⁻, like that of TlBr₄⁻ as reported by Delwaille (*loc. cit.*), is shown by an aqueous solution of the tribromide in presence of hydrobromic acid, but corresponding aqueous solutions of indium tribromide in presence of hydrobromic acid (up to 6M) do not show the spectrum of InBr₄⁻. The latter spectrum is only observed for extracts from the aqueous phase into organic solvents. Thus, although indium occupies a position in Group IIIB intermediate between gallium and thallium, the tendency to form the ion MBr₄⁻ in aqueous solution is less for indium than for either gallium or thallium.

These investigations are being extended.

EXPERIMENTAL

A known weight of pure gallium, supplied by Messrs. Johnson, Matthey and Co., was dissolved in the appropriate amount of bromine-free hydrobromic acid (approx. 11M) to give a nearly 1.5M-solution of gallium tribromide containing 6M excess of acid.

The Raman spectra were photographed with "Toronto arc" excitation with the apparatus previously described (George, Rolfe, and Woodward, *Trans. Faraday Soc.*, 1953, **49**, 375), slightly modified to allow of the insertion of Polaroid cylinders around the Raman tube. The states of polarization of the Raman lines were investigated by Rank and Kagarise's method (*J. Opt. Soc. Amer.*, 1950, **40**, 89), successive spectra being photographed with cylinders having their directions of polarization respectively parallel and perpendicular to the tube axis. Frequencies were determined in the usual way with an interpolation formula based upon a copper-arc spectrum as standard. The estimated limits of error in the measured values of $\Delta\nu$ are ± 2 cm.⁻¹. The principal exciting line was that of mercury at 4358 Å. A sodium nitrite filter was used to diminish the intensity of primary lines of lower wavelength. The Raman spectrum of GaBr₄⁻ could be observed clearly with an exposure time of 1 hr. without Polaroid cylinders.