242. *Raman Spectrum and Structure of the Hexabromostannate Ion in Aqueous Solution.*

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Raman spectra are photographed for a range of molar aqueous solutions of stannic bromide containing different concentrations of hydrobromic acid. The spectrum present at low concentrations of acid disappears progressively as the acid concentration is increased and is replaced by a new spectrum consisting of three lines: $\Delta\nu = 185$ cm.$^{-1}$, very strong, polarised; $\Delta\nu = 137$ cm.$^{-1}$, medium strong, depolarised; and $\Delta\nu = 95$ cm.$^{-1}$, medium strong, depolarised. The number of lines, states of polarisation, etc., are as expected for a regular octahedral species XY_6, and the spectrum is attributed to the $SnBr_6^{2-}$ ion. The conclusion of previous workers that this ion has a lower symmetry was evidently due to their assignment to it of all the Raman lines of a solution which must have contained other species.

The hexachlorostannate ($SnCl_6^{2-}$) and the hexabromostannate ($SnBr_6^{2-}$) ion have valency shells of twelve electrons like the hexafluorides of Group VI elements, and so should have the same regular octahedral structure and show the characteristic three-line Raman spectrum. This is true [1,2] for the hexachlorostannate ion, for example in aqueous solutions of stannic chloride containing hydrochloric acid. For a solution of stannic bromide containing hydrobromic acid, on the other hand, Redlich and co-workers [1,3] observed more than three Raman lines, and hence concluded that the hexabromostannate ion must have a shape less highly symmetrical than the regular octahedral: they suggested a configuration (point group D_{4h}) with two polar bromine atoms at a distance from the central tin atom different from that of the four equatorial bromine atoms.

The present investigation is concerned principally with the Raman spectra of a range of solutions of stannic bromide containing different concentrations of hydrobromic acid. The results show that the earlier conclusion about the shape of the hexabromostannate ion is wrong. The previously reported spectrum of the hexachlorostannate ion is confirmed.

RESULTS

Stannic bromide dissolves in aqueous hydrobromic acid with considerable evolution of heat. The temperature was prevented from rising unduly by water-cooling. The freshly prepared solutions varied from practically colourless to deep yellow, according to composition. For a series all containing the same concentration of stannic bromide, the strength of the yellow colour increased with increasing concentration of hydrobromic acid, *i.e.*, with increasing value of the fraction $R = [\text{total Br}]/[\text{Sn}]$. Also for solutions of the same value of R the colour was the stronger, the greater the actual concentration. For instance, with $R = 7$ the range was from nearly colourless for $[SnBr_4] = \frac{1}{2}$M to deep yellow for $[SnBr_4] = 3$M.

The series of solutions investigated by the Raman method were all molar with respect to stannic bromide and had R-values ranging from 4 to 13. For each solution the Raman spectrum was photographed with a series of exposure times. That with $R = 4$ was used immediately after being made up. It remained practically colourless long enough for its spectrum to be obtained both by excitation with the mercury blue line (4358 Å) and with the mercury green line (5461 Å). After a few hours this solution became noticeably yellow, darkening during several weeks until finally a turbidity appeared. The other solutions were all yellow from the start, so that only the green line could be used for excitation of their spectra.

For values of R from 4 to 6 the spectrum consisted of a single, somewhat diffuse line with $\Delta\nu = 220$ cm.$^{-1}$. For these solutions the primary line at 5461 Å also showed a distinct broadening, probably due to an unresolved diffuse Raman band centred at about $\Delta\nu = 80$ cm.$^{-1}$. For the solution with $R = 4$ this band could be more distinctly observed near the mercury blue

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[1] Redlich, Kurz, and Rosenfeld, *Z. phys. Chem.*, 1934, *B*, **19**, 231.

[2] Couture and Mathieu, *Compt. rend.*, 1947, **225**, 1140.

[3] Redlich, Kurz, and Stricks, *Monatsh.*, 1937, **71**, 1.

line, where the dispersion of the spectrograph is greater. At $R = 8$ the line characteristic of lower R-values was still present, though with diminished intensity and slightly shifted to lower $\Delta\nu$, while a new line had made its appearance with $\Delta\nu = 185$ cm.$^{-1}$. As R was further increased, the first line (as also the apparent broadening of the primary line) disappeared progressively, while at the same time the new line increased in intensity along with two other new and somewhat less intense companions ($\Delta\nu = 138$ and 95 cm.$^{-1}$). At values of R above about 11 these three new lines were the sole features of the Raman spectrum. The one of highest $\Delta\nu$ and greatest intensity was found to be highly polarised, the other two to be depolarised. The experimental results for the typical solutions with $R = 4$, 8, and 13 are given in Table 1. For strong sharp lines the estimated limits of error of the measured $\Delta\nu$-values are ± 3 cm.$^{-1}$; but for weaker or more diffuse lines the errors may be larger.

TABLE 1. *Raman spectra of molar aqueous solutions of stannic bromide containing different concentrations of hydrobromic acid.*

			$\Delta\nu$ (cm.$^{-1}$)		
R	Colour	Exciting line (Å)	Stokes	Anti-Stokes	Description
4	colourless	4358	218	221	strong, polarised
	(fresh)		~80	—	weak, broad
8	yellow	5461	209	209	medium, polarised
			184	187	medium, polarised
			140	139	weak, depolarised
			101	102	weak, depolarised
13	deep yellow	5461	185	185	very strong, polarised
			139	136	medium, depolarised
			96	94	medium, depolarised

For comparison, several 2M-solutions of stannic chloride in hydrochloric acid ($R = 4$—9) were similarly examined. Used immediately after preparation, all were clear and colourless, so that their spectra could be excited by the mercury blue line. All gave identical spectra consisting of three lines: $\Delta\nu = 311$ cm.$^{-1}$, strong, polarised; $\Delta\nu = 229$ cm.$^{-1}$, medium weak, depolarised; and $\Delta\nu = 158$ cm.$^{-1}$, medium strong, depolarised.

DISCUSSION

The colours of solutions of stannic bromide containing hydrobromic acid clearly indicate that at least two species are involved, one colourless and the other deep yellow. The equilibrium between them is shifted in favour of the latter by increase of bromide-ion concentration relative to that of tin or by increase of the concentration of the solution as a whole. These facts are consistent with the view that the colourless species might be $SnBr_4$ and that the yellow one is $SnBr_6^{2-}$, the equilibrium being $SnBr_4 + 2Br^- \rightleftharpoons SnBr_6^{2-}$. The possibility is not excluded, however, that other colourless species might be involved.

The Raman spectra (see Table 1) show that the line at $\Delta\nu = 220$ cm.$^{-1}$ characterises the colourless species at low R-values; and it is interesting to note that this frequency is identical with that of the most intense line of pure stannic bromide (Class A_1, polarised), as given by Herzberg.[4] The band centred at about $\Delta\nu = 80$ cm.$^{-1}$ is also near the positions of $\nu_2(E)$ and $\nu_4(F_2)$ of $SnBr_4$ (64 and 88 cm.$^{-1}$, respectively). The exact nature of the colourless species must remain uncertain; but there seems to be no doubt that the yellow species must be the hexabromostannate ion, $SnBr_6^{2-}$. Its three-line spectrum, alone present at sufficiently high values of [total Br]/[Sn], is precisely of the kind characteristic of a regular octahedral species (point group O_h) of type XY_6. We can confidently assign the observed frequencies as follows: $\nu_1\ (A_{1g}) = 185$ cm.$^{-1}$; $\nu_2\ (E_g) = 138$ cm.$^{-1}$; and $\nu_5\ (F_{2g}) = 95$ cm.$^{-1}$.

It is clear that the erroneous conclusion of previous workers[1, 3] that $SnBr_6^{2-}$ must have a lower symmetry (such as D_{4h}), was based upon their assignment to this ion of all the Raman lines of a solution which must have contained the colourless species as well. The composition of their solution was not specified exactly. Their observed frequencies (208, 183, 142, 102, and 72 cm.$^{-1}$) agree quite well with what we have observed for the

[4] Herzberg, "Infrared and Raman Spectra," Van Nostrand, New York, 1945, p. 167.

solution with $R = 8$, if we identify their $\Delta\nu = 72$ cm.$^{-1}$ with the band centred at approximately 80 cm.$^{-1}$ observed by us at $R = 4$ (see Table 1).

For the undoubtedly regular octahedral $SnCl_6^{2-}$ ion our observed frequencies agree satisfactorily with those of earlier workers,[1, 2, 5] and are clearly to be assigned as $\nu_1 = 311$, $\nu_2 = 229$, and $\nu_5 = 158$ cm.$^{-1}$. The difference of behaviour of solutions of stannic chloride, as compared with solutions of stannic bromide, is noteworthy. Even in absence of hydrochloric acid a freshly prepared solution of the chloride shows [5] the Raman lines of $SnCl_6^{2-}$ ions, due presumably to some reaction such as $3SnCl_4 = Sn^{4+} + 2SnCl_6^{2-}$. With stannic bromide, however, a considerable excess of bromide ions is necessary in order to obtain an appreciable proportion of $SnBr_6^{2-}$ ions.

Table 2 shows a comparison of the totally symmetric, purely bond-stretching vibrational frequencies of the $SnCl_6^{2-}$ and $SnBr_6^{2-}$ ions with those of the corresponding neutral tetrahalide molecules.[4] The stretching force constants, *k*, calculated by the simple valency force field, are also compared. The fact that the force-constant ratio is practically the same for the bromo- and the chloro-species provides evidence that we are correct in attributing to the $SnBr_6^{2-}$ ion the spectrum observed for the bromide solutions at high values of *R*.

TABLE 2. *Totally symmetric frequencies and force constants.*

Species	ν_1 (cm.$^{-1}$)	$10^{-5}k$ (dynes/cm.)	Force const. ratio	Species	ν_1 (cm.$^{-1}$)	$10^{-5}k$ (dynes/cm.)	Force const. ratio
$SnCl_4$	366	2·80	1·39	$SnBr_4$ ...	220	2·28	1·42
$SnCl_6^{2-}$ ...	311	2·02		$SnBr_6^{2-}$...	185	1·61	

EXPERIMENTAL

The Raman light source was a low-pressure mercury arc lamp with water-cooled electrodes (Toronto arc). The states of polarisation of the Raman lines were determined qualitatively by the method of polarised incident light, successive exposures being taken with cylinders of suitably oriented Polaroid surrounding the Raman vessel. The spectrograph was a 2-prism glass instrument with f/5·6 camera, giving dispersions of about 200 cm.$^{-1}$/mm. in the region of the mercury blue line (4358 Å) and about 300 cm.$^{-1}$/mm. in the region of the green line (5461 Å). The plates used were Kodak Special Scientific, emulsion type Oa, sensitivity G. Exposure times were of ½—3 hr., without Polaroid.

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[5] Guèron, *Ann. Chim.*, 1935, **3**, 305.