Raman Effect and Solvent Extraction. Spectrum of the $InBr_4^-$ *Ion.*

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Molar aqueous solutions of indium bromide containing hydrobromic acid at concentrations up to 6N are extracted with ether or *iso*butyl methyl ketone. The extracts all show the following Raman frequencies (cm.$^{-1}$) due to solute: 55, strong, sharp, depolarised; 79, strong, sharp, depolarised; 197, very strong, sharp, polarized; and 239, medium, slightly diffuse, depolarized. Reasons are given for ascribing this spectrum to the regular tetrahedral $InBr_4^-$ ion. The Raman spectra of the aqueous solutions before extraction show a band whose position varies with hydrobromic acid concentration, but no lines characteristic of $InBr_4^-$.

THE extraction of indium by organic solvents from aqueous solutions of indium bromide containing hydrobromic acid has been studied recently by Irving and Rossotti (*J.*, in the press), with initial indium concentrations from tracer values up to nearly 0·1M. Their results provide evidence that the acido-complex $HInBr_4$ predominates in the organic phase, and they suggest that this complex may be present as a solvated ion pair $(H^+)(InBr_4^-)$.

The Raman effect provides a very direct method for the detection of covalently linked species and, in favourable cases, for the determination of their structure. The present paper gives an account of the application of this method to systems of the kind referred to above.

Raman Spectra of Organic Extracts.—Owing to the small intensity of Raman scattering, the concentration of indium in the aqueous phase before extraction was made molar in all the experiments. This is higher than was investigated by Irving and Rossotti (*loc. cit.*). The principal solvent used for extraction was ethyl ether, but some experiments were also made with *iso*butyl methyl ketone. All extractions were carried out at room temperature. It was found that the amount of extraction of indium by ether from M-aqueous indium bromide solution containing no added hydrobromic acid was negligible. Table 1 shows the Raman frequencies ($\Delta\nu$) observed for the solute in organic extracts from aqueous solutions containing different concentrations of hydrobromic acid. The Raman lines due to the solute were easily distinguishable from the solvent lines, all of which have considerably higher frequencies. The spectra of the pure solvents were photographed for comparison.

TABLE 1. *Raman spectra of solute in organic extracts.*

Normality of HBr before extraction	2	4	4	6
Solvent	ether	ether	ketone	ether
Observed Raman frequencies (cm.$^{-1}$)	56 79 197 238	54 77 196 239	55 79 197 240	56 80 198 239

Within the accuracy of the measurements the spectra of all the extracts are identical. The two lines of lowest frequency lie close to the exciting line, but with suitably chosen exposure times they could be clearly discerned and accurately measured. They were observable not only as Stokes lines excited by Hg 4358 Å, but also as both Stokes and anti-Stokes lines excited by Hg 4046 Å.

The states of polarization of the lines were investigated by the method of polarized incident light (Rank and Kagarise, *J. Opt. Soc. Amer.*, 1950, **40**, 89), a photoelectric recording instrument being used and with cylinders of Polaroid surrounding the Raman tube. It was found that the line with $\Delta\nu = 197$ cm.$^{-1}$ is very strongly polarized, whereas the other three are all strongly depolarized. The mean frequencies, estimated relative intensities, appearances of lines, and states of polarization are shown in Table 2. The number of observed lines and their states of polarization provide strong evidence that the spectrum is to be ascribed to a regular tetrahedral species of type XY_4. There can be little doubt that the species in question is the $InBr_4^-$ ion. This view is in agreement with Irving and Rossotti's conclusion (*loc. cit.*) that the predominant species in the organic phase is the acido-complex $HInBr_4$, and our observations show that this complex must be regarded as an ion-pair of the type $(H^+)(InBr_4^-)$. The purely electrostatic binding between the two ions will not be expected to show a Raman effect (George, Rolfe, and Woodward, *Trans. Faraday Soc.*, 1953, **49**, 375). Further support was obtained by chemical analysis of the organic extracts. In all cases it was found that $[Br]/[In] = 4{\cdot}0 \pm 0{\cdot}1$.

TABLE 2. *Raman spectrum of* $InBr_4^-$.

cm.$^{-1}$	Intensity	Appearance	Polarization	cm.$^{-1}$	Intensity	Appearance	Polarization
55	strong	sharp	depolarized	197	very strong	sharp	polarized
79	strong	sharp	depolarized	239	medium	slightly diffuse	depolarized

It is noteworthy that the singly charged $InBr_4^-$ ion is isoelectronic with the uncharged molecule $SnBr_4$ and the doubly charged ion $CdBr_4^{=}$, and it is of interest to compare the fundamental vibrational frequencies of these three species (see Table 3). The values for $SnBr_4$ are those quoted by Herzberg (" Molecular Spectra and Molecular Structure," van Nostrand Co., New York, 1945, Vol. II, p. 167); those for $CdBr_4^{=}$ are from the observations of Delwaulle, François, and Wiemann (*Compt. rend.*, 1939, **208**, 1818) and Rolfe, Sheppard, and Woodward (*Trans. Faraday Soc.*, 1954, **50**, 1275). It is seen that the frequencies observed in the present work all lie between the corresponding ones for $SnBr_4$ and $CdBr_4^{=}$, and this may be taken as further support for the view that the species with which we are concerned is $InBr_4^-$. The assignment of the observed frequencies to the vibrational modes follows the assignment for $SnBr_4$ (Herzberg, *op. cit.*) and is included in Table 3. In particular we may remark that the assignment of 197 cm.$^{-1}$ to the totally symmetrical (A_1) " breathing " mode (frequency ν_1) is in harmony with the observation that the corresponding Raman line is polarized.

TABLE 3. *Fundamental vibrational frequencies* (*cm.*$^{-1}$) *of isoelectronic species* XBr_4.

	ν_2 (E)	ν_4 (F_2)	ν_1 (A_1)	ν_3 (F_2)
$SnBr_4$	64	88	220	279
$InBr_4^-$	55	79	197	239
$CdBr_4^{=}$	53	62	166	183

From Table 3 it is seen that all the fundamental frequencies become progressively smaller as we pass from $SnBr_4$ to $InBr_4^-$ and then to $CdBr_4^{=}$. As far as the " breathing " frequencies ν_1 are concerned this indicates that the stretching force constant k of the metal–bromine bond decreases in the same order. The values of $10^{-5}k$ calculated on the basis of a simple valency force field are: $SnBr_4$, 2·28; $InBr_4^-$, 2·16; and $CdBr_4^{=}$, 1·98 dynes per cm. Force constants of these isoelectronic species derived from more general force fields will be discussed in a later publication.

Raman Spectra of Aqueous Solutions before Extraction.—The Raman spectrum of molar aqueous indium bromide solution without added hydrobromic acid was found to consist of a single band of medium intensity. Its width is approximately 30 cm.$^{-1}$ and its centre is at about $\Delta\nu = 205$ cm.$^{-1}$. With increasing concentration of added acid the position of the band centre moves progressively to lower $\Delta\nu$ values until in the strongest acid used (6N) it is at approximately 185 cm.$^{-1}$. The exact position of the centre of the band is difficult to judge precisely, but the gradual displacement with increasing acid concentration is quite certain. The band width and intensity remain approximately constant over the range of acid concentrations investigated. In some of the spectrograms there was an indication of a very feeble line at about $\Delta\nu$ 140 cm.$^{-1}$ excited by Hg 4358 Å; but its existence must be regarded as doubtful.

The broadness of the band may well be due to the simultaneous presence of several different species (such as $InBr^{++}$, $InBr_2^+$, $InBr_3$) in equilibrium. The stretching-mode frequencies of all such species will be expected to lie in the same region as ν_1 of $InBr_4^-$

and, since Raman lines in aqueous solutions are often somewhat diffuse, the observed band may be due to unresolved overlapping. Its apparent gradual displacement with increasing addition of hydrobromic acid would then be explicable as due to a progressive displacement of the equilibria between the various species involved, with corresponding alteration of the intensities of their contributions to the band. From the evidence of the Raman spectra it is not possible to say what species are present in the aqueous solutions. Comparison with the intense " regular tetrahedral XY_4 " pattern of the spectra of the organic extracts shows, however, that the species ($InBr_4^-$) which predominates in the organic layer after extraction cannot have been present in appreciable concentration in the aqueous solution before extraction.

EXPERIMENTAL

Preparation of Aqueous Solutions.—Weighed quantities of finely sliced indium (99·7% pure, supplied by Messrs. Johnson Matthey and Co.) were dissolved in the appropriate calculated quantities of hydrobromic acid, free from bromine. All solutions were carefully filtered to remove suspended dust particles before their Raman spectra were measured.

Solvents and Extractions.—Diethyl ether was purified and freed from peroxides as described by Weissberger and Proskauer (" Organic Solvents," Oxford, **1935**). The *iso*butyl methyl ketone used was kindly supplied by Dr. Rossotti and had been purified as described by Irving and Rossotti (*loc. cit.*). Each aqueous solution was extracted by shaking it with an approximately equal volume of organic solvent at room temperature.

Chemical Analyses.—For the analysis of the ethereal extracts, the sample was first added to excess of water and the ether removed by warming. Because of its lower volatility, *iso*butyl methyl ketone could not be removed in this way, and so ketonic extracts were exhaustively extracted with successive quantities of water. In the aqueous solutions so obtained bromine and indium were determined gravimetrically, the former as silver salt and the latter as oxide (Moser and Siegmann, *Sitzungsber. Akad. Wiss. Wien*, **1929**, **139**, **612**). A check on these analyses was obtained by titration of measured samples with 0·1N-sodium hydroxide solution (phenol-red as indicator). The value of [H] + 3[In] thus obtained was found to be satisfactorily in agreement with [Br].

Raman Spectra.—The Raman apparatus was that previously used by George, Rolfe, and Woodward (*loc. cit.*). The spectra were excited by a mercury-arc lamp with water-cooled electrodes (" Toronto " arc). The volume of the Raman tube was about **16** ml. For each solution a number of spectra were photographed with different exposure times up to **5** hr. on Kodak Special Scientific plates (emulsion type Oa, sensitivity G). The dispersion of the instrument is about **30** Å per mm. in the region of the lines excited by Hg **4358** Å. Frequencies were determined in the usual manner, a copper arc spectrum being used as standard. The limits of error of the $\Delta\nu$ values are $\pm$ 2 cm.$^{-1}$. The determinations of states of polarization were made with a photoelectric recording Raman spectrograph. This instrument is a much improved version of that described by Miller, Long, Woodward, and Thompson (*Proc. Roy. Soc.*, **1949**, **62**, *A*, **401**); a full account of it is to be published in the near future.

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