Raman, Resonance-Raman, and Electronic Spectra of Tetraethylammonium Hexabromoantimonate(v) and of Tetra-n-butylammonium Hexabromoantimonate(v) [1]

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The resonance-Raman (r.r.) spectrum of the $[SbBr_6]^-$ ion, as the tetraethylammonium salt, is dominated by a high-intensity overtone progression in the $\nu_1(a_{1g})$ fundamental (191.5 cm^{-1}) extending as far as $9\nu_1$. Three other progressions have also been observed, in each of which ν_1 is the progression-forming mode, *viz.* $\nu_2(e_g) + v_1\nu_1$ (to $v_1 = 5$), $\nu_5(t_{2g}) + v_1\nu_1$ (to $v_1 = 1$), and $\nu_L + v_1\nu_1$ (to $v_1 = 3$, ν_L being a lattice mode at 49 cm^{-1}). The fifth observed progression in the r.r. spectrum of this ion involves the $\nu_2(e_g)$ fundamental (169 cm^{-1}) as the progression-forming mode, to $v_2 = 4$. Calculated harmonic frequencies ω_1 and ω_2 are 191.6 and 169.5 cm^{-1} respectively, and anharmonicity constants x_{11}, x_{22}, and x_{12} are −0.05, −0.14, and 0.15 cm^{-1} respectively. The resonant electronic transition (maximum at 21 500 cm^{-1}) is concluded to be the electric-dipole allowed transition $a_{1g}(\sigma^*) \leftarrow t_{1u}(\pi)$, $^1T_{1u} \leftarrow {}^1A_{1g}$, in O_h nomenclature.

MANY inorganic molecules and ions have been shown in the last few years to display resonance Raman (r.r.) spectra when irradiated with exciting lines which fall within the contours of allowed electronic transitions of the irradiated species.[2] Tetraethylammonium hexabromoantimonate(v) is a dark red-brown complex,[3-5] which, in contrast to earlier opinions as to its structure, has now been shown by single-crystal *X*-ray analysis to contain discrete $[SbBr_6]^-$ ions, slightly distorted from octahedral symmetry.[5] The stability of this ion in the solid state (it is not stable in solution) is thought [5] to be due to efficient packing of the large, rather diffuse, and similarly sized $[SbBr_6]^-$ and $[NEt_4]^+$ ions. In acetonitrile it is reported [4] to decompose into the species $SbBr_3$ and $[Br_3]^-$. The colour of the ion renders it very suitable for r.r. studies with currently available exciting lines, and in consequence its Raman spectra were studied in detail. The ion was indeed found to display a very rich r.r. spectrum, five different progressions being identified; these data have not only rendered possible the calculation of several harmonic frequencies and anharmonicity constants, but also allowed certain deductions concerning the nature of the resonant electronic state of the ion to be made.

EXPERIMENTAL

Preparation of the Samples.—The tetraethylammonium hexabromoantimonate(v) was prepared and recrystallized by the method of Lawton and Jacobson [3] (Found: C, 13.05; H, 2.75; Br, 65.3; N, 1.90. Calc. for $[NEt_4][SbBr_6]$: C, 13.15; H, 2.75; Br, 65.55; N, 1.90%). The tetra-n-butylammonium salt has been prepared for the first time. The procedure used was analogous (Found: C, 23.4; H, 4.45; Br, 56.2; N, 1.82. Calc. for $[NBu^n_4][SbBr_6]$: C, 22.8; H, 4.30; Br, 56.85; N, 1.65%). Attempts to prepare tetraphenylarsonium and caesium salts of the $[SbBr_6]^-$ ion were not successful. In the second case a black hygroscopic mass resulted, possibly containing mixed-valence compounds. Both salts obtained are deep red-brown in colour, and were shown to be reasonably stable in air and to resist hydrolysis. However, a solution study was not possible because of their immediate decomposition in the organic solvents in which they were soluble (acetonitrile and acetone) and their lack of solubility in others, including HBr.

Instrumental Details.—The Raman spectra were recorded by use of a Spex 1401 double spectrometer in conjunction with Coherent Radiation model CR 12 Ar^+ and model 52 Kr^+ ion lasers. The powers of all the lines were arranged to be in the range 30 mW—1 W. The method of detection was photon counting in conjunction with a cooled, grade I RCA C31034, phototube with a linear response. The system is described in detail elsewhere.[2] Spectra were calibrated by reference to the emission lines of neon which were superimposed directly on the recording. Band areas were determined by the trace cut-and-weigh procedure and then corrected for the spectral response of the instrument. Samples were rotated at *ca.* 1 400 revolutions min^{-1} in order to minimize thermal decomposition of the sample at the beam focus.[1]

Relative band areas were measured with respect to the $\nu_1(a_{1g})$ band of the ion as internal standard, since there was evidence for decomposition of the sample in the beam when it was diluted in the solid state with potassium sulphate [the $\nu_1(a_1)$ band of which was the intended internal standard]. Even so, in order to minimize the decomposition of the sample the procedure was adopted of (*a*) using low laser power and a defocused beam and (*b*) using fast recording times and the highest available speed of rotation of the sample. A large number of different samples of the $[SbBr_6]^-$ ion were required in order to obtain all the required intensity data.

Diffuse-reflectance spectra were recorded using a Cary 14 spectrometer, the sample being held in a liquid-nitrogen attachment such that the sample temperature was *ca.* 100 K. Infrared spectra were recorded on a Perkin-Elmer 225 instrument. The far-i.r. spectra were recorded as Nujol mulls between Polythene plates on an evacuated Fourier-transform FS 720 spectrometer with an effective resolution of 2.4 cm^{-1} (courtesy of Dr. R. Ferri).

RESULTS AND DISCUSSION

Vibrational Assignments.—The vibrational spectra of the $[SbBr_6]^-$ ion are given in Table 1 in terms of O_h

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[1] Presented in part at the Fifth Internat. Conf. Raman Spectroscopy, Freiburg, 2—8 September 1976.

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[3] S. L. Lawton and R. A. Jacobson, *Inorg. Chem.*, 1968, **7**, 2124.

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nomenclature, on the basis of which three Raman-active bands [$\nu_1(a_{1g})$, $\nu_2(e_g)$, and $\nu_5(t_{2g})$] and two i.r. active bands [$\nu_3(t_{1u})$ and $\nu_4(t_{1u})$] are expected to be observable. Raman (647.1- and 676.4-nm excitation, Figure 1) and i.r. spectra of the tetraethylammonium and tetra-n-butylammonium salts of the $[SbBr_6]^-$ ion contained bands which can, by comparison with results on other similar compounds (*e.g.* $[SnBr_6]^{2-}$, $[ZrBr_6]^{2-}$, $[HfBr_6]^{2-}$, $[NbBr_6]^-$, and $[TaBr_6]^-$),[6-11] be readily assigned to the various fundamentals. The only previous information relating to the vibrational spectrum of this ion was the report[12] that a strong Raman band of the complex $[NEt_4][SbBr_6]$ occurred at 194 cm^{-1}; the values obtained for this band (obviously ν_1) in the present study are slightly (2—2.5 cm^{-1}) lower. The triple degeneracies of the ν_3 and ν_5 fundamentals are evidently resolved in each lattice. {The $[SbBr_6]^-$ ion is reported to have crystallographic C_{2v} symmetry and to be slightly (*ca.* 3°) distorted from O_h symmetry in the case of the tetraethylammonium salt.[5]} Substantial splittings of the ν_3 bands of octahedral $[MX_6]^{n-}$ ions, as tetraethylammonium salts, have been observed several times previously,[13-15] as also is the case for the ν_5 band (*e.g* for $K_2[SnBr_6]$ and $K_2[TeBr_6]$ the splitting of ν_5 is reported to be 24 and 25 cm^{-1} respectively).[14,15] However, in the case of ν_5 the possibility that the band at *ca.* 78 cm^{-1} arises from a lattice mode cannot be entirely excluded, despite the virtually zero shift in its value on changing from the lighter to the heavier cation in the complex. More extensive studies of this matter were precluded by the fact that we could not isolate any other salts of the $[SbBr_6]^-$ ion with cations of different mass.

TABLE 1

Fundamental frequencies of the $[SbBr_6]^-$ ion [a]

Salt	$\nu_1(a_{1g})$	$\nu_2(e_g)$	$\nu_3(t_{1u})$	$\nu_4(t_{1u})$	$\nu_5(t_{2g})$
$[NEt_4]^+$	191.5vs	169.0m	238.5s 223.5	118.5m	103.3w 77.8w [b]
$[NBu^n{}_4]^+$	192.0vs	167.3m			104.3w 77.3w [b]

[a] Values listed in cm^{-1}. vs = Very strong, s = strong, m = medium, and w = weak. Raman data relate to 647.1- or 676.4-nm excitation. [b] The possibility that the lowest observed band of each salt arises from a lattice mode cannot be excluded.

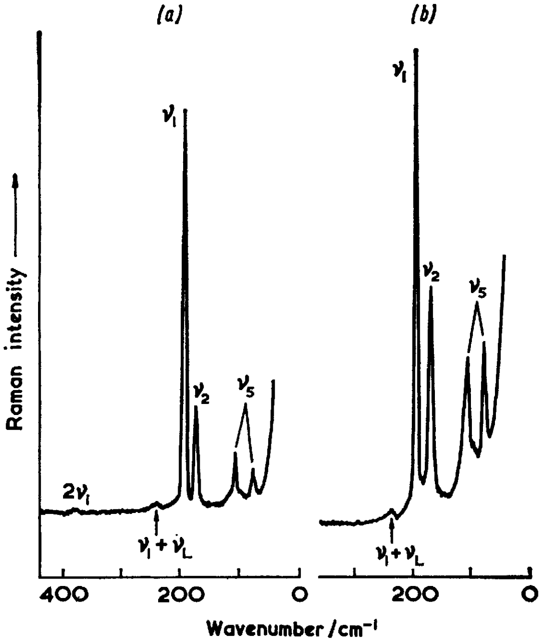

FIGURE 1 Raman spectra of the complexes (*a*) $[NEt_4][SbBr_6]$ and (*b*) $[NBu^n{}_4][SbBr_6]$ with the 676.4-nm excitation line of the Kr^+ ion laser (slit widths 180/300/180 and 150/300/150 µm respectively, *ca.* 2.5 cm^{-1})

Resonance-Raman Spectra.—The resonance-Raman (r.r.) spectra of both salts of the $[SbBr_6]^-$ ion were measured with several different exciting lines, and were found to depend markedly on the exciting frequencies (ν_0). However, the spectra obtained for the tetraethylammonium salt were better than those obtained for the tetra-n-butylammonium salt; moreover, the latter salt was less stable than the former in the laser beam. Accordingly, detailed measurements of r.r. band frequencies and intensities were confined to the tetraethylammonium salt.

The r.r. spectrum of the complex $[NEt_4][SbBr_6]$ was characterized by an enormous enhancement in the intensity of the $\nu_1(a_{1g})$ fundamental of the anion as ν_0 was made to approach the frequency (ν_e) of the maximum of the broad charge-transfer band of the ion at 21 500 cm^{-1}. At the same time, an intense progression (in which ν_1 is the progression-forming mode) was observed to reach at most $2\nu_1$, $2\nu_1$, $3\nu_1$, $4\nu_1$, $5\nu_1$, $7\nu_1$, $7\nu_1$, $8\nu_1$, and $9\nu_1$ with the 676.4-, 647.1-, 568.2-, 520.8-, 514.5-, 488.0-, 476.5-, 465.8-, and 457.9-nm exciting lines respectively; the effectiveness of the resonance is thus clearly a function of $\nu_e - \nu_0$. The r.r. spectrum of this salt is shown in Figure 2.

In addition to the main progression [progression (*i*)], four other progressions were observed in the r.r. spectrum of the $[SbBr_6]^-$ion, for three of which ν_1 is the progression-forming mode. They are: (*ii*) $\nu_2 + v_1\nu_1$ to $v_1 = 5$; (*iii*) $\nu_5 + v_1\nu_1$ to $v_1 = 1$ (only the band at 77.8 cm^{-1} appears to act as the enabling mode, possibly because it may be totally symmetric in the C_{2v} site symmetry of the Sb

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atom); (*iv*) $\nu_L + v_1\nu_1$ to $v_1 = 3$, ν_L being a lattice mode, which could not be observed directly owing to its proximity to the exciting line (its value is deduced to be 49 cm^{-1}); and (*v*) $v_2\nu_2$ *to* $v_2 = 4$. The r.r. spectrum of the $[SbBr_6]^-$ ion is thus very rich in detail. It is unusual to find a lattice mode acting as the enabling mode for a progression in a totally symmetric mode. Nevertheless a precedent for such a situation occurs for $Cs_2[SbCl_6]$,[16] for which $\nu_L = 60$ cm^{-1}; the anion is lighter in this case, consistent with the higher value deduced for the frequency of the lattice mode.

The most distinctive feature of the r.r. spectrum is the fifth progression, which is the longest progression yet observed by this technique involving a non-totally symmetric fundamental. The longest such progression previously observed was for the $[PtBr_6]^{2-}$ and $[PtI_6]^{2-}$ ions, for which the $v_2\nu_2$ progression was found to reach only as far as $v_2 = 2$ in each case.[17] Unfortunately, owing to the fact that the $[SbBr_6]^-$ ion appears not to be stable in solution, no band-depolarization ratios could be measured. However, by analogy with results for the $[PtX_6]^{2-}$ ion,[17] it seems probable that it is the A_{1g} component of the overtone which is being resonantly enhanced in each case ($E_g^2 = A_{1g} + E_g$; $E_g^3 = A_{1g} + A_{2g} + E_g$; $E_g^4 = A_{1g} + 2E_g$).

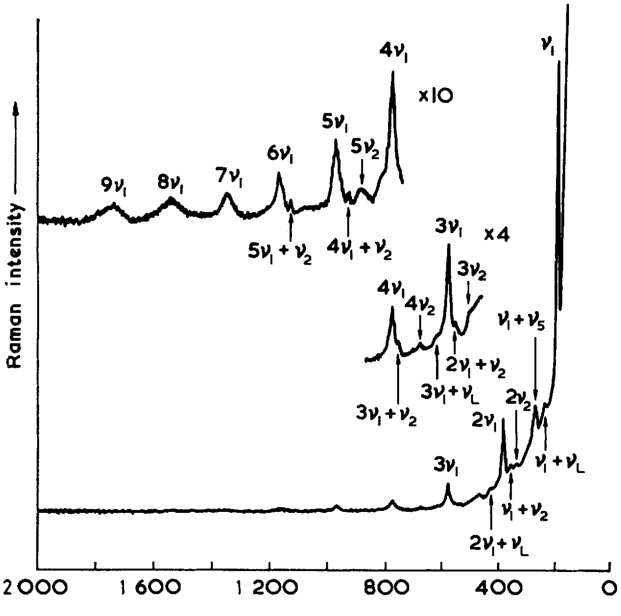

FIGURE 2 Resonance-Raman spectrum of the complex $[NEt_4]$-$[SbBr_6]$ obtained with the 457.9-nm exciting line of the Ar^+ ion laser (slit widths 120/300/120 μm, *ca.* 3 cm^{-1})

As in all previously observed r.r. spectra,[1] the members of each progression both decreased in intensity and increased in half-bandwidth with increase in the vibrational quantum number. The long overtone progressions of the totally symmetric modes are characteristic of resonance enhancement due to the *A* term of Albrecht's theory (*i.e.* enhancement associated with a single excited electronic state), whereas the *B* term (*i.e.* enhancement associated with vibronic coupling of two excited electronic states) is primarily required for the enhancement of non-totally symmetric modes.[17,18]

The frequencies and half-bandwidths of each member of each series are listed in Table 2.

TABLE 2

Wavenumbers and half-bandwidths (cm^{-1}) of the bands observed in the resonance-Raman spectrum of the complex $[NEt_4][SbBr_6]$ with 457.9-nm excitation

Band	$\tilde{\nu}$	$\Delta\tilde{\nu}_{\frac{1}{2}}$	Band	$\tilde{\nu}$	$\Delta\tilde{\nu}_{\frac{1}{2}}$
(*a*) Progression (*i*)					
ν_1	191.5	5	$6\nu_1$	1 147.5	38
$2\nu_1$	382.8	9	$7\nu_1$	1 338.5	48
$3\nu_1$	574.2	14	$8\nu_1$	(1 531 ± 4)	55
$4\nu_1$	765.3	21	$9\nu_1$	(1 720 ± 5)	*ca.* 65
$5\nu_1$	956.5	27			
(*b*) Progression (*ii*)					
$\nu_2 + \nu_1$	360.3	12	$\nu_2 + 4\nu_1$	933.3	
$\nu_2 + 2\nu_1$	551.4	20	$\nu_2 + 5\nu_1$	(1 121)	
$\nu_2 + 3\nu_1$	742.6	*ca.* 21			
(*c*) Progression (*iii*)					
ν_5	77.8	6	$\nu_5 + \nu_1$	272.5	32
(*d*) Progression (*iv*)					
$\nu_L + \nu_1$	240.3 *	25	$\nu_L + 3\nu_1$	622.1	*ca.* 28
$\nu_L + 2\nu_1$	429.6	*ca.* 26			
(*e*) Progression (*v*)					
ν_2	169.0	8	$3\nu_2$	506.2	20
$2\nu_2$	337.9	15	$4\nu_2$	674.4	30

* $\nu_L + \nu_1$ occurs at 234 cm^{-1} for $[NBu^n{}_4][SbBr_6]$, which implies that $\nu_L = 42$ cm^{-1} for this salt as compared with 49 cm^{-1} for the $[NEt_4]^+$ salt.

Harmonic Frequencies and Anharmonicity Constants.—The presence of a large number of overtones of vibrational fundamentals in the r.r. spectra allows the accurate determination of certain harmonic frequencies ω_i and anharmonicity constants x_{ii} and x_{ij}. The observed wavenumber $\nu(v_i)$ of the overtone of a polyatomic oscillator is given by the expression (1) where v_i and d_i are

$$\nu(v_i) = \omega_i v_i + x_{ii}\,(v_i^2 + v_i d_i) + v_i\left[x_{ij}\left(v_j + \frac{d_j}{2}\right) + \ldots .\, x_{in}\left(v_n + \frac{d_n}{2}\right)\right];\quad n \neq i \qquad (1)$$

the vibrational quantum number and degeneracy respectively of the *i*th fundamental. To a first approximation the sum involving the cross terms x_{ij} is commonly taken to be zero. On this basis a plot of $\nu(v_i)/v_i$ against v_i should be a straight line with a gradient of x_{ii} and an intercept of $\omega_i + x_{ii}d_i$; accordingly both ω_i and x_{ii} may be deduced (for the $v_1\nu_1$ and $v_2\nu_2$ progression, $d_i =$ 1 and 2 respectively). The results (based on a least-squares fitting procedure) are given in Table 3. In common with other fundamentals found to display the r.r. effect, the ν_1 fundamental (harmonic frequency at 191.6 cm^{-1}) is almost exactly a harmonic oscillator (x_{11} -0.05 cm^{-1}). The present r.r. results on ν_2 [progression (*v*)] are the first on a non-totally symmetric fundamental

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to be sufficiently detailed to permit the calculation of the harmonic frequency (found to be at 169.5 cm^{-1}); the anharmonicity constant x_{22} (−0.14 cm^{-1}) was also found to be very small. The results for the ν_2 progression are not as accurate as those for the ν_1 progression owing to the fewer observed members and their lower intensities and larger half-bandwidths.

TABLE 3

Harmonic frequencies and anharmonicity constants of the $[SbBr_6]^-$ ion (in cm^{-1})

$v_1\nu_1$ Progression		$\nu_2 + v_1\nu_1$ Progression	
ω_1	x_{11}	$\omega_1 - x_{12}$	x_{11}
191.6 ± 0.2	-0.05 ± 0.01	$191.4_5 \pm 0.2$	-0.07 ± 0.01
$v_2\nu_2$ Progression		$x_{12} \approx 0.15$	
ω_2	x_{22}		
169.5 ± 0.2	-0.14 ± 0.03		

The other progressions [(*ii*)—(*iv*)] in the ν_1 fundamental are based on one quantum of a non-totally symmetric fundamental (ν_i). For such a progression a plot of $\{[\nu_i + \nu(v_1)] - \nu_i\}/v_1$ against v_1 leads to a straight line [19-21] with a gradient of x_{11} in each case, and an intercept of $\omega_1 + x_{11} - x_{1i}$; consequently the difference between the intercepts of the plots of $\nu(v_1)/v_1$ against v_1 and $\{[\nu_i + \nu(v_1)] - \nu_i\}/v_1$ against v_1 is a direct measure, albeit imprecise, of the cross term x_{1i}. The value found in this way for the cross term x_{12} was 0.15 cm^{-1}, which should be regarded as an order-of-magnitude result only.

Diffuse-reflectance Spectra and Excitation Profiles of the $[SbBr_6]^-$ *Ion.*—The diffuse-reflectance spectrum of the complex $[NEt_4][SbBr_6]$, as a finely ground-up powder diluted with magnesium carbonate (*ca.* 1 : 5 v/v), is shown in Figure 3. The spectrum was also recorded at *ca.* 100 K using a liquid-nitrogen attachment, but without significant improvement in the resolution. The principal spectral feature is a broad intense band at 21 500 cm^{-1}, together with poorly defined shoulders at *ca.* 18 000 and 27 000 cm^{-1}. In seeking an assignment for the band at 21 500 cm^{-1}, which, from its intensity, seems to be electric-dipole allowed, it is natural to seek guidance from previous spectral assignments for other d^{10} ions. In this respect, the spectra of the $[SbCl_6]^-$ and $[SnCl_6]^{2-}$ ions seem particularly relevant.

For the $[SbCl_6]^-$ and $[SnCl_6]^{2-}$ ions, magnetic circular dichroism studies [22] have shown (from the positive signs for the ratio of the Faraday parameter A to the dipole strength D) that the lowest electric-dipole allowed transition (37 000 and 45 000 cm^{-1} respectively, both being solution values; 31 600 and 39 200 cm^{-1} respectively as tetra-alkylammonium salts by diffuse reflectance) is $a_{1g}(\sigma^*) \leftarrow t_{1u}(\pi)$, ${}^1T_{1u} \leftarrow {}^1A_{1g}$, rather than $t_{1u}(\sigma^*) \leftarrow e_g(\sigma^*)$, ${}^1T_{1u} \leftarrow {}^1A_{1g}$, for each ion. The lowest electric-dipole allowed transition of the $[SbBr_6]^-$ and $[SnBr_6]^{2-}$ ions (21 500 and 30 600 cm^{-1}) respectively, both being measured as tetra-alkylammonium salts by diffuse reflectance, [7,23] almost certainly have the same assignment, *viz.* $a_{1g}(\sigma^*) \leftarrow t_{1u}(\pi)$, ${}^1T_{1u} \leftarrow {}^1A_{1g}$. The shoulder at *ca.* 18 000 cm^{-1} in the diffuse-reflectance spectrum of the $[SbBr_6]^-$ ion may be due to either or both of the 'forbidden' transitions $a_{1g}(\sigma^*) \leftarrow t_{1g}(\pi)$, $t_{2g}(\pi)$, or to splitting of the ${}^1T_{1u}$ excited state (by site-symmetry or spin-orbit coupling effects).

Resonance-Raman spectra have only been observed,[2] and are only expected to be observed,[24] in cases where the exciting frequency is made to fall within the contour of an electric-dipole allowed transition. The excitation profiles of the $2\nu_1$ and $3\nu_1$ bands of the ion, plotted as values of $I(2\nu_1)/I(\nu_1)$ and $I(3\nu_1)/I(\nu_1)$ against wavenumber (Figure 3) parallel closely the diffuse-reflectance spectrum of the ion, and this result confirms that the resonant electronic transition must be electric-dipole allowed, and thus (in O_h nomenclature) that it has the assignment ${}^1T_{1u} \leftarrow {}^1A_{1g}$.

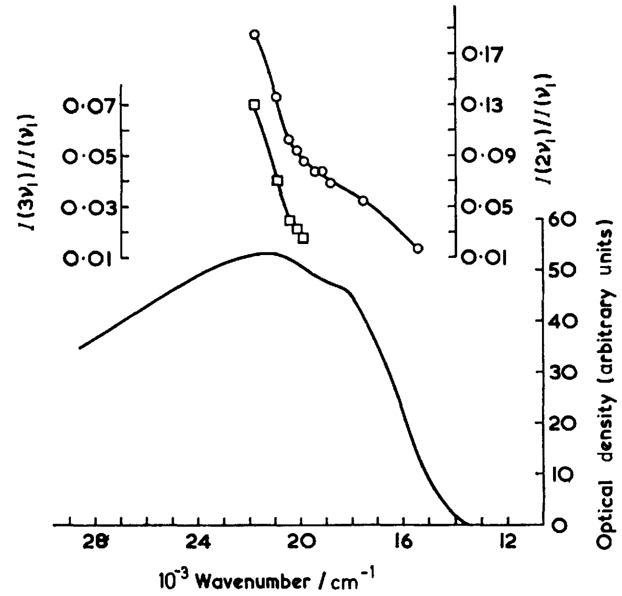

FIGURE 3 Excitation profiles of the first and second overtones of the $\nu_1(a_{1g})$ band of the $[SbBr_6]^-$ ion, derived from $I(2\nu_1)/I(\nu_1)$ (○) and $I(3\nu_1)/I(\nu_1)$ values (□), together with the diffuse-reflectance spectrum (lower curve) of the ion

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