Intensity Studies on the Raman-active Fundamentals of Hexahalogeno-anions of Antimony(V) and Tellurium(IV); The Calculation of Parallel and Perpendicular Bond-polarisability Derivatives and Raman-band Excitation Profiles of the Hexabromotellurate(IV) Ion

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The Raman spectra of solutions (generally acetonitrile) of the ions $[SbCl_6]^-$, $[TeCl_6]^{2-}$, and $[TeBr_6]^{2-}$ have been recorded, and accurate values for the frequencies of the $\nu_1(a_{1g})$, $\nu_2(e_g)$, and (in some cases) $\nu_5(t_{2g})$ fundamentals are reported. The intensities of the fundamentals of each ion have been measured using the rotating-sample technique with 4–6 different exciting lines and they are reported by reference to the 935-cm^{-1} line of the perchlorate ion as internal standard. The intensity results, which are treated in terms of the pre-resonance Raman effect, have been extrapolated to zero exciting frequency to yield values for the polarisability derivatives $\bar{\alpha}_{MX}'$, $\alpha_{\|}'$, and $\alpha_{\perp}'$ for $[SbCl_6]^-$, $[TeCl_6]^{2-}$, and $[TeBr_6]^{2-}$. The $\alpha_{\|}'$ values for $Te^{IV}X$ are 40—50% higher than those for $Sn^{IV}X$, from which it is deduced that the a_{1g}^* molecular orbital which accommodates the lone pair of *s* electrons in the case of Te^{IV} is significantly involved in the Te–X bonding. Detailed excitation profiles of the $\nu_1(a_{1g})$ and $\nu_2(e_g)$ fundamentals of $[TeBr_6]^{2-}$ in acetonitrile have been obtained from dye- and ion-laser measurements with 10 different exciting lines, and the results are discussed with reference to the electronic spectrum of the ion in the 450—650 nm region.

ALTHOUGH the stereochemistries of d^{10} ions such as $[SbX_6]^-$ and $[SnX_6]^{2-}$ (X = Cl or Br) are well known to be octahedral, those of $d^{10}s^2$ ions have been the subject of much controversy.[1] However, on the basis of *X*-ray diffraction,[2-6] nuclear quadrupole resonance,[7] vibrational,[8-18] and Mössbauer [19] studies it is now established that $[TeCl_6]^{2-}$ and $[TeBr_6]^{2-}$ (although not necessarily other $d^{10}s^2$ species such as XeF_6) [20-23] also possess octahedral structures in their ground states. The nature of the bonding in these complex ions has been discussed by Urch [24] and, more recently, the electronic spectra of the $[TeX_6]^{2-}$ ions have been interpreted by Couch *et al.*[25] (in terms of distorted excited states) and of $[SeX_6]^{2-}$ and $[TeX_6]^{2-}$ by Stufkens [26] (in terms of a dynamic Jahn–Teller effect). Stufkens also suggested that the Raman intensities of the Jahn–Teller active fundamentals [$\nu_2(e_g)$ and $\nu_5(t_{2g})$] of these ions are unusually high relative to that of the $\nu_1(a_{1g})$ fundamental in each case. However, the observations made with respect to these ions are far from being unique since many species possessing the t_{2g}^6 electronic configuration, *viz.* $[PdX_6]^{2-}$, $[PtX_6]^{2-}$, and $[M(CO)_6]$ (M = Cr, Mo, or W),[27-29] display similar effects. Moreover Stufkens results pertain only to a single exciting wavelength (632.8 nm).

Recently the intensities of the Raman-active fundamentals of an extensive series of second- and third-row transition-metal ions and non-transition-metal ions of the type $[MX_6]^{n-}$ (X = Cl, Br, or I) have been recorded with a variety of different exciting lines.[27] These results have made it possible to extrapolate the intensities of the bands to zero exciting frequency so as to eliminate

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the pre-resonance Raman (pre-r.r.) enhancement to band intensities. This effect may occur when the exciting frequency (ν_0) approaches the frequency of the lowest-allowed electronic transition (ν_e) of the scattering species.[30-35] The present research is aimed at extending these results to further non-transition-metal ions, specifically to $[SbCl_6]^-$, $[TeCl_6]^{2-}$, and $[TeBr_6]^{2-}$. From the resulting data it was possible to calculate bond-polarisability derivatives ($\bar{\alpha}_{MX}'$), parallel and perpendicular bond-polarisability derivatives ($\alpha_{\parallel}'$ and $\alpha_{\perp}'$), and to relate these to the nature of the MX bond of each ion. Moreover, the wavelength dependences of the Raman-scattered radiation (excitation profiles) of the $\nu_1(a_{1g})$ and $\nu_2(e_g)$ fundamentals of $[TeBr_6]^{2-}$ have been studied in detail in order to assess the relation between excitation profiles and absorption spectra of the ion, a subject of much current interest.[36-40]

EXPERIMENTAL

Preparation of Solvents and Reagents.—Acetonitrile was distilled from P_4O_{10} and fractionated, the fraction boiling at 82.0 °C being collected. Methylene dichloride was dried over calcium hydride and subsequently distilled. The dried solvents were stored *in vacuo* in ampoules fitted with ' ROTAFLO ' stopcocks and vacuum distilled prior to use into the appropriate sample cells. Antimony pentachloride was outgassed and vacuum distilled. Pyridinium chloride was purified by vacuum sublimation.

Preparation of Compounds.—Pyridinium hexachloroantimonate(V) was isolated as colourless crystals on mixing solutions of anhydrous pyridinium chloride and antimony pentachloride in CH_2Cl_2. The crystals were washed with small volumes of solvent and kept in a desiccator over calcium chloride. The hexahalogenotellurate(IV) salts were prepared by standard methods [7,41] with a slight modification. The starting material was tellurium dioxide which was dissolved in the appropriate hot and concentrated acid HX (X = halide) and the solution was heated until complete reaction had taken place; addition of a saturated solution of the appropriate halide in the appropriate acid HX caused immediate precipitation of the required complex. The solution was then evaporated down to about one third of its original volume and cooled in ice. The crystals were collected on a sintered glass filter and washed with the appropriate acid HX.

Sample Preparation for Spectral Measurements.—In each case the Raman spectrum was observed using acetonitrile as solvent with the band at 918 cm^{-1} being used as internal standard. This band was subsequently calibrated against that of the perchlorate ion at 935 cm^{-1}.

Solutions were made directly in the cylindrical cells where they were held, the solvent being directly vacuum distilled into them. The weights of the hexahalides and of the solvent were determined by difference; the cells were sealed *in vacuo*. The quantity of solvent added was varied in accordance with the intensity of the Raman bands of the samples in order to have, wherever possible, the same order of magnitude for the intensities of the sample and reference peaks. Solutions of each anion were studied at at least two different concentrations in order to eliminate the possibility that intermolecular interactions might influence the molar intensities of each band. Good agreement between these values was found in each case.

Instrumental Techniques.—The Raman spectra were recorded using a Spex 1401 spectrometer in conjunction with Coherent Radiation Ar^+ and Kr^+ lasers and a model 490 tunable dye laser (rhodamine 6G). The scattered radiation was collected at 90° and focussed by a $f/0.95$ lens on to the entrance slit of the monochromator after having been passed through a polarisation scrambler. The 0.75-m Czerny–Turner monochromator employed two Bausch and Lomb gratings blazed at 500 nm. The method of detection was photon counting in conjunction with an RCA C31034 (Grade I) photo-tube (linear display). The power available with the five exciting lines 488.0, 514.5, 568.2, 647.1, and 676.4 nm was 1.0 W, 1.2 W, 100 mW, 500 mW, and 30 mW respectively; the power in the red region emitted by rhodamine 6G was in the 100—300 mW region. The spectra were calibrated by reference to the emission lines of neon.

Peak areas were determined by the trace-and-weigh procedure. The relative spectral response of the spectrometer was determined as described previously.[27] Solutions were held in cylindrical cells (volume *ca.* 12 cm^3) which had flat bottoms and which could be rotated at speeds of *ca.* 1 600 revolutions min^{-1}. In each case, the exciting beam was kept as close as possible to the cell edge in order to minimise self absorption of the scattered radiation.

The electronic spectra of the ions were recorded by use of a Cary 14 spectrometer.

RESULTS AND DISCUSSION

Fundamental Frequencies.—The wavenumbers found for the Raman-active fundamentals of the ions studied are listed in Table 1, together with previously reported values. The band assigned to the $\nu_5(t_{2g})$ fundamental was (except for $[SbCl_6]^-$) broad, close to the exciting line, and consequently difficult to locate especially in solution.

For $[TeX_6]^{2-}$ (X = Cl or Br) in non-aqueous solution, the wavenumbers of the observed Raman bands are generally in good agreement with those reported previously for the anions in crystalline solids and in aqueous solution. The Raman spectra of $[TeBr_6]^{2-}$ clearly showed a band at *ca.* 180 cm^{-1} due to the fundamental $\nu_3(t_{1u})$. This breakdown of the selection rules, which has been observed previously,[14] has been taken to be evidence of the existence of less symmetrical excited

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TABLE 1

Wavenumber (cm^{-1}) of the Raman-active fundamentals of the $[MX_6]^{n-}$ ions in solution and as crystalline solids

Ion	State	Ref.	$\nu_1(a_{1g})$	$\nu_2(e_g)$	$\nu_5(t_{2g})$
$[SbCl_6]^-$	$MeNO_2$ soln.	*a*	339	280	170
	MeCN soln.	*b*	330.3 ±0.5	281.2 ±0.5	170.6 ±1
$[TeCl_6]^{2-}$	MeCN soln.	*b*	287.4 ±0.5	249.4 ±0.5	
	K^+ salt	11	301	253	150
	Rb^+ salt	11	299	254	135
	Cs^+ salt	11	288	247	139
	$[NH_4]^+$ salt	11	300	250	142
	$[NMe_4]^+$ salt	11	281	243	136
	$[NEt_4]^+$ salt	11	282	243	127
	$[Hpy]^+$ salt	11	283		146
$[TeBr_6]^{2-}$	MeCN soln.	*b*	169 ±0.5	148 ±0.5	
	MeCN soln.	12	169	148	70
	K^+ salt	11	174	153	73
	Rb^+ salt	11	179	160	90
	Cs^+ salt	11	173	151	91
	$[NH_4]^+$ salt	11	180	155	83
	$[NMe_4]^+$ salt	11	170	148	96
	$[NEt_4]^+$ salt	11	168	144	
	$[NBu_4]^+$ salt	12	172	152	80
	$[Hpy]^+$ salt	11	173	157	
	Me_2CO soln.	13	166	151	73

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states. However, the Raman spectrum of $[TeCl_6]^{2-}$ showed no indication of the ν_3 band, despite the fact that this anion (according to the electronic-spectral work of Couch *et al.*)[25] is more distorted than the corresponding bromide in excited states derived from the $t_{1u}(\sigma^*)\leftarrow a_{1g}(\sigma^*)$ transition (see below) whether this is a consequence of the static[25] or dynamic Jahn–Teller effects.[26,42]

The ρ values of the $\nu_1(a_{1g})$ bands of each ion are zero within experimental error (*i.e.* $\leqslant 0.01$) in each case. This result confirms the evidence cited in the introduction that all of these ions are exactly octahedral in their ground states.

Intensities of Raman-active Fundamentals.—The intensities (I_2) of the bands arising from Raman-active fundamentals of the $[MX_6]^{n-}$ ions relative to that of the band at 918 cm^{-1} of acetonitrile (I_1) as intermediate internal standard are given in Table 2. The results are quoted in terms of relative molar intensities (I_2M_1/I_1M_2), corrected in each case for the spectral response of the instrument. By use of conversion factors, the molar intensities of the bands of the $[MX_6]^{n-}$ ions studied are also given relative to the band of the perchlorate ion at 935 cm^{-1}. The frequency-corrected relative molar intensities $(1/f)(I_2M_1/I_1M_2)$ (relative scattering activities) of the $\nu_1(a_{1g})$ and $\nu_2(e_g)$ fundamentals of each ion are given in the last column of Table 2 (see footnote *c* for the definition of *f*). The bond-polarisability derivatives, $\bar{\alpha}_{MX}'$, are then given by the expression (1)[27] where μ_1 is

$$\bar{\alpha}_{MX}' = \bar{\alpha}_{ClO}'\left[\frac{1}{f}\left(\frac{I_2M_1}{I_1M_2}\right)\left(\frac{4\mu_1}{6\mu_2}\right)\right]^{\frac{1}{2}} \qquad (1)$$

the reciprocal mass of the oxygen atom and μ_2 is the reciprocal mass of the X atom. The reference value $\bar{\alpha}_{ClO}'$ is taken to be 1.73 Å^2.[43]

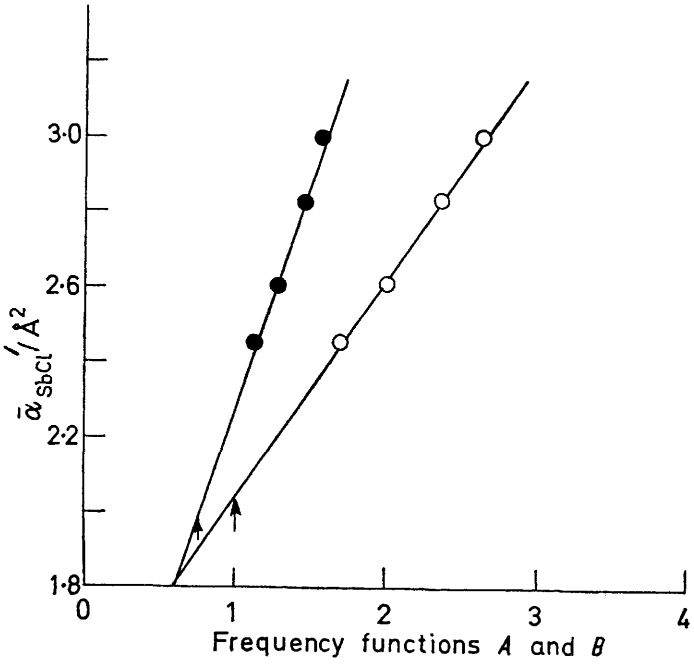

FIGURE 1 Plot of $\bar{\alpha}_{SbCl}'$ against the Shorygin function $A = [1 + (\nu_0/\nu_e)^2]/[1 - (\nu_0/\nu_e)^2]^2$ (○) and the Albrecht function $B = [(\nu_s/\nu_e) + (\nu_0/\nu_e)^2]/[1 - (\nu_0/\nu_e)^2][(\nu_s/\nu_e)^2 - (\nu_0/\nu_e)^2]$ (●) at four different exciting wavelengths (647.1, 568.2, 514.5, and 488.0 nm, reading from left to right on the plot). The values for ν_e and ν_s (Table 3) are taken to be 37 600 and 50 000 cm^{-1} respectively. $A(\nu_0 = 0) = 1.000$, $B(\nu_0 = 0) = 0.752$

In order to correct for the pre-r.r. effect, the $\bar{\alpha}_{MX}'$ values at each exciting frequency were plotted against frequency functions which describe the deviation of scattered intensity from the $\nu_0{}^4$ dependence. Two functions were taken for this purpose. That of Shorygin is thought to apply when only a single electronic state (the lowest allowed one) is responsible for the pre-r.r. effect, in which case $\bar{\alpha}_{MX}'$ depends on ν_0 and ν_e in the manner of the function *A* [equation (2)]. Extrapolation

$$A = \frac{1 + (\nu_0/\nu_e)^2}{[1 - (\nu_0/\nu_e)^2]^2} \qquad (2)$$

of such plots to $A = 1$ (*i.e.* $\nu_0 = 0$) yields $\bar{\alpha}_{MX}'$ values corrected for resonance enhancement. The Albrecht function (*B*) for the dependence of $\bar{\alpha}_{MX}'$ values on ν_0 emphasises the importance of vibronic coupling between the two lowest-lying electric-dipole-allowed states (frequencies ν_e and ν_s) of the scattering molecule, and it depends on ν_0, ν_e, and ν_s in the manner (3). The

$$B = \frac{(\nu_s/\nu_e) + (\nu_0/\nu_e)^2}{[1 - (\nu_0/\nu_e)^2][(\nu_s/\nu_e)^2 - (\nu_0/\nu_e)^2]} \qquad (3)$$

electronic-spectral data on the ions studied are listed in Table 3. The Shorygin and Albrecht plots for $[SbCl_6]^-$, $[TeCl_6]^{2-}$, and $[TeBr_6]^{2-}$ are shown in Figures 1—3, the ν_e and ν_s values assumed in the calculation being given in the captions in each case. Linear plots were obtained

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TABLE 2

Relative molar intensities of Raman-active fundamentals of the ions studied, the frequency factors, and the relative scattering activities of the $\nu_1(a_{1g})$ and $\nu_2(e_g)$ fundamentals of the ions [a]

Ion	λ/nm	ν_i	I_2M_1/I_1M_2 [a]	I_2M_1/I_1M_2 [b]	f [c]	$(1/f)(I_2M_1/I_1M_2)$ [b]	$\bar{\alpha}_{\mathrm{MX}}'/\text{Å}^2$
$[SbCl_6]^-$ (colourless)							
	647.1	ν_1	96.6 ± 3.8	$5.63 \pm 0.2_4$	4.13	1.36 ± 0.06	2.45
		ν_2	26.0 ± 1.5	$1.51 \pm 0.2_5$	5.27	0.28 ± 0.05	
		ν_5	23.8 ± 1.9	1.39 ± 0.1	11.83	$0.11_7 \pm 0.01$	
	568.2	ν_1	100.5 ± 2.3	6.24 ± 0.28	4.05	1.54 ± 0.07	2.61
		ν_2	27.7 ± 1.8	1.72 ± 0.32	5.16	0.33 ± 0.06	
		ν_5	21.8 ± 1.1	1.35 ± 0.07	11.53	$0.11_7 \pm 0.00_6$	
	514.5	ν_1	107.1 ± 3.3	7.22 ± 0.30	3.99	1.81 ± 0.07	2.83
		ν_2	28.3 ± 0.6	1.91 ± 0.30	5.08	0.37 ± 0.06	
		ν_5	20.55 ± 0.9	1.39 ± 0.006	11.33	$0.12_2 \pm 0.00_5$	
	488.0	ν_1	111.3 ± 3.5	$8.0_2 \pm 0.43$	3.96	2.02 ± 0.11	2.99
		ν_2	30.3 ± 1.5	2.18 ± 0.45	5.04	0.44 ± 0.09	
		ν_5	20.7 ± 2.8	1.49 ± 0.2	11.23	$0.13_3 \pm 0.02$	
$[TeCl_6]^{2-}$ (yellow)							
	620.0	ν_1	141 ± 7	8.2 ± 0.2	5.06	1.62 ± 0.04	2.68
		ν_2	116 ± 9.5	6.8 ± 0.3	6.31	1.08 ± 0.05	
	600.0	ν_1	142 ± 4.2	8.3 ± 0.2	5.03	1.65 ± 0.04	2.71
		ν_2	127 ± 16	7.4 ± 0.3	6.27	1.18 ± 0.05	
	568.2	ν_1	171 ± 9	10.6 ± 0.3	4.99	2.12 ± 0.06	3.07
		ν_2	153 ± 12	9.5 ± 0.3	6.21	1.53 ± 0.05	
	514.5	ν_1	187 ± 8	12.6 ± 0.3	4.91	2.57 ± 0.06	3.37
		ν_2	198 ± 13	13.4 ± 0.4	6.11	2.19 ± 0.07	
	488,0	ν_1	225 ± 15	16.2 ± 0.5			
		ν_2	253 ± 23	18.2 ± 0.5			
	457.9	ν_1	284 ± 4	20.5 ± 0.4			
		ν_2	241 ± 14	17.4 ± 0.5			
$[TeBr_6]^{2-}$ (orange)							
	676.4	ν_1	318 ± 9	18.6 ± 0.2	12.14	1.53 ± 0.02	3.91
		ν_2	275 ± 12	16.0 ± 0.2	15.22	1.05 ± 0.02	
	647.1	ν_1	326 ± 4	19.0 ± 0.2	12.02	1.58 ± 0.02	3.98
		ν_2	327 ± 26	19.0 ± 0.3	15.07	1.26 ± 0.02	
	620.0	ν_1	333 ± 3	19.4 ± 0.2	11.91	1.63 ± 0.02	4.04
		ν_2	339 ± 24	$19.7 \pm 0'3$	14.94	1.32 ± 0.02	
	600.0	ν_1	343 ± 32	20.0 ± 0.3	11.83	1.69 ± 0.03	4.11
		ν_2	313 ± 30	18.2 ± 0.3	14.84	1.23 ± 0.02	

[a] Molar intensities of the Raman-active fundamentals of the ions studied relative to that of the band of acetonitrile at 918 cm^{-1} and corrected for spectral response; subscript 2 refers to the ion and 1 refers to acetonitrile. The error limits refer to the scatter between the 10 different measurements of each datum (five of which were carried out at one concentration of the anion and five at a different one). [b] Molar intensities of the Raman-active fundamentals of the ions studied relative to that of the band of perchlorate ion at 935 cm^{-1} and corrected for spectral response; subscript 2 refers to the ion and 1 to the perchlorate ion. The I_2M_1/I_1M_2 values, where I_2 refers to the intensity of the band of acetonitrile at 918 cm^{-1} and I_1 to that of the band of perchlorate ion at 935 cm^{-1} are 0.058_3, 0.062_0, 0.067_4, and 0.072_1 at 647.1, 568.2, 514.5, and 488.0 nm respectively.

[c] $$f = \frac{f(\nu_2)}{f(\nu_1)} = \left(\frac{\nu_0 - \nu_2}{\nu_0 - \nu_1}\right)^4 \left(\frac{\nu_1}{\nu_2}\right) \left[\frac{1 - \exp(-hc\nu_1/kT)}{1 - \exp(-hc\nu_2/kT)}\right].$$

TABLE 3

Electronic absorption spectra of the $[TeX_6]^{2-}$ (X = Cl or Br) and the $[SbCl_6]^-$ ions

Complex	State	$\lambda_{\mathrm{max.}}$/nm	Band maxima (cm^{-1}) [a]	Assignment
$[NBu^n_4]_2[TeCl_6]$ [b]	CH_2Cl_2 soln.			t_{1u} $(\sigma^*) \leftarrow a$ $({}_{1g}\sigma^*)$ transition
	300 K			
		410	24 400 (sh) (1 350)	${}^3T_{1u}$ $({}^3P_1) \leftarrow {}^1A_{1g}$ [c]
		385	26 000 (3 700)	
		321	31 150 (6 000)	${}^3T_{1u}$ $({}^3P_2) \leftarrow {}^1A_{1g}$
		301	33 200 (sh) (15 500)	${}^1T_{1u} \leftarrow {}^1A_{1g}$ [c]
		288	34 700 (21 000)	
		276	36 200 (19 000)	
$[NBu^n_4]_2[TeBr_6]$	CH_2Cl_2 soln.			t_{1u} $(\sigma^*) \leftarrow a_{1g}$ (σ^*) transition
	300 K	467	21 400 (sh) (1 000)	${}^3T_{1u}$ $({}^3P_1) \leftarrow {}^1A_{1g}$
		446	22 400 (2 600)	
		381	26 250 (sh) (1 500)	${}^3T_{1u}$ $({}^3P_2) \leftarrow {}^1A_{1g}$
		323	31 000 (19 000)	${}^1T_{1u} \leftarrow {}^1A_{1g}$ [b]
		275	36 400 (sh) (28 000)	t_{1u} $(\sigma^*) \leftarrow t_{1g}$ (π^*)
$[NEt_4][SbCl_6]$ [d]	MeCN soln.	340.1	29 400 (*ca.* 100)	a_{1g} $(\sigma^*) \leftarrow t_{1g}$ (π)
	300 K	271.0	36 900 (9 500)	a_{1g} $(\sigma^*) \leftarrow t_{1u}$ $(\pi + \sigma)$
$[Hpy][SbCl_6]$ [e]	MeCN soln.	337.5	29 630	a_{1g} $(\sigma^*) \leftarrow t_{1g}$ (π)
	300 K	266.0	37 590	a_{1g} $(\sigma^*) \leftarrow t_{1g}$ $(\pi + \sigma)$

[a] Absorption coefficients (ε/dm^3 mol^{-1} cm^{-1}) are given in parentheses. [b] Ref. 25. [c] Band splitting is considered to be a consequence of the lowered symmetry of the excited states. [d] R. A. Walton, R. W. Matthews, and C. K. Jørgensen, *Inorg. Chim. Acta*, 1967, **1**, 355. [e] This work.

TABLE 4

Perpendicular ($\alpha_\perp'$) and parallel ($\alpha_\parallel'$) components of the bond-polarisability derivative for the octahedral anions studied, based on $\bar{\alpha}_{MX}'$ ($\nu_0 = 0$) and the relative intensities of the $\nu_1(a_{1g})$ and $\nu_2(e_g)$ bands at zero exciting frequency

Ion		$(1/f)(I_2M_1/I_1M_2)$ [a] for $\nu_0 = 0$	$\bar{\alpha}_{MX}'/\text{Å}^2$ ($\nu_0 = 0$) [b]	$[f(\nu_2)/f(\nu_1)] \times [I(\nu_1)/I(\nu_2)]$	$\alpha_\perp'/\alpha_\parallel'$	$\alpha_\perp'/\text{Å}^2$	$\alpha_\parallel'/\text{Å}^2$	$\alpha_\perp'/\alpha_\parallel'$	$\alpha_\perp'/\text{Å}^2$	$\alpha_\parallel'/\text{Å}^2$	γ_{MX}' [c]
$[SbCl_6]^-$	ν_1	0.83	2.00	5.35	0.37	1.2_5	3.4_5	5.0_5	2.7_5	0.5_5	2.2
	ν_2	0.15_5									
$[TeCl_6]^{2-}$	ν_1	0.92	2.19	2.79	0.24	1.1	4.4	−122	3.3	−0.03	3.3
	ν_2	0.33									
$[TeBr_6]^{2-}$	ν_1	1.34	3.68	1.44	0.12	1.1	8.9	−4.2	6.2_5	-1.5_0	7.8
	ν_2	0.92									

[a] Molar intensity relative to the band of the perchlorate ion at 935 cm^{-1}. [b] Extrapolated to $\nu_0 = 0$ by way of Albrecht's function (the corresponding values by a Shorygin-function extrapolation are 2.04, 2.32, and 3.73 Å^2 respectively). [c] $\gamma_{MX}' = \alpha_\parallel' - \alpha_\perp'$.

in each case; least-squares analyses of the results led to $\bar{\alpha}_{MX}'$ values corrected for the pre-r.r. effect (Table 4). Satisfactory as this procedure is, it is true that considerable difficulty is experienced in trying to make the correct choice of states, and therefore frequencies, to associate with ν_e and ν_s; nevertheless, the extrapolated values of $\bar{\alpha}_{MX}'$ are not very sensitive, for a given ν_e, to the ν_s value.

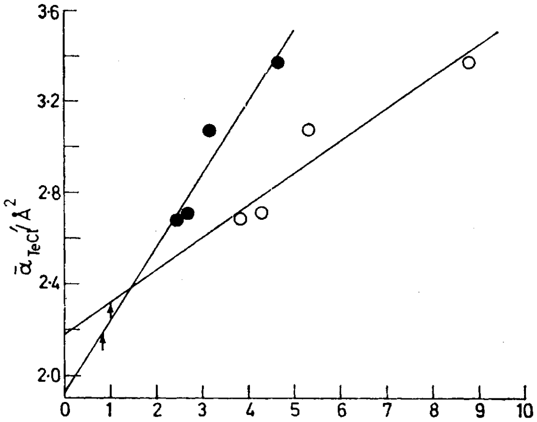

FIGURE 2 Plot of $\bar{\alpha}_{TeCl}'$ against the Shorygin A (○) and Albrecht B (●) functions at four different exciting wavelengths (620.0, 600.0, 568.2, and 514.5 nm, reading from left to right on the plot). The values for ν_e and ν_s (Table 3) are taken to be 25 000 and 31 150 cm^{-1} respectively. $A(\nu_0 = 0) = 1.000$, $B(\nu_0 = 0) = 0.822$

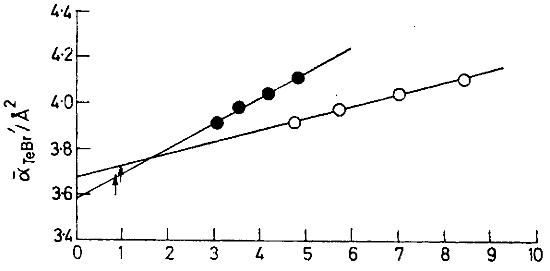

FIGURE 3 Plot of $\bar{\alpha}_{TeBr}'$ against the Shorygin A (○) and Albrecht B (●) functions at four different exciting wavelengths (676.4, 647.1, 620.0, and 600.0 nm, reading from left to right on the plot). Values for ν_e and ν_s (Table 3) are taken to be 22 100 and 26 250 cm^{-1} respectively. $A(\nu_0 = 0) = 1.000$, $B(\nu_0 = 0) = 0.842$

The parallel and perpendicular components of the bond-polarisability derivatives may be deduced from the scattering activities of the $\nu_1(a_{1g})$ and $\nu_2(e_g)$ fundamentals of the MX_6 species [equations (4)—(6)]. The

$$\bar{\alpha}_{MX}' = \tfrac{1}{3}(\alpha_\parallel' + 2\alpha_\perp') \tag{4}$$

$$\frac{I(\nu_1)}{I(\nu_2)} = \frac{f(\nu_1)}{f(\nu_2)}\left\{\frac{5[1 + (2\alpha_\perp'/\alpha_\parallel')^2]}{7[1 - (\alpha_\perp'/\alpha_\parallel')^2]}\right\} \tag{5}$$

$$f(\nu_j) = \frac{1}{\nu_j}\left[\frac{(\nu_0 - \nu_j)^4}{1 - \exp(-hc\nu_j/kT)}\right] \tag{6}$$

$I(\nu_1)/I(\nu_2)$ value used in each case was the value extrapolated to zero exciting frequency. Of the two roots to the quadratic equation for $\alpha_\parallel'$ and $\alpha_\perp'$ (Table 4) that for which $\alpha_\perp'/\alpha_\parallel'$ lay between −0.5 and 2.86 was accepted for reasons which have been argued previously.[27]

On the basis of a delta-function potential model, it has been deduced that there should be a linear relation between the $\alpha_\parallel'$ value of an MX bond and the fractional covalent character of the bond.[44] (The relation is stated in terms of $\bar{\alpha}_{MX}'$ values, but as $\alpha_\perp'$ is taken to be zero it strictly relates only to $\alpha_\parallel'$ values.) The present results for $\alpha_\parallel'$ for each ion, and for the closely related $[SnX_6]^{2-}$ ions [27] (whose values were confirmed independently) are as follows: $Sn^{IV}Cl$ (3.1) < $Sb^{V}Cl$ (3.4_5) < $Te^{IV}Cl$ (4.4); $Sn^{IV}Br$ (5.9) < $Te^{IV}Br$ (8.9 Å^2). The order of $\alpha_\parallel'$ values of MCl < MBr is in agreement with general chemical considerations, and also with the increase in the degree of σ-bond covalent character (σ) as deduced from n.q.r. measurements; *viz.* for $[SnCl_6]^{2-}$ and $[SnBr_6]^{2-}$ the σ values have been found to be 0.34 and 0.40 respectively,[45] and for $[TeCl_6]^{2-}$ and $[TeBr_6]^{2-}$ the values are 0.32 and 0.42 respectively.[7] Further, the $\alpha_\parallel'$ order $Sn^{IV}Cl$ < $Sb^{V}Cl$ is consistent with the expected increase in the degree of covalent character of the MX bond on increasing the oxidation state of the metal atom.

The most interesting result is that the $\alpha_\parallel'$ value for $Te^{IV}Cl$ is 40—50% higher than that for $Sn^{IV}Cl$. Although the electronegativity of tellurium is slightly higher than that of tin, this would lead (on the basis of the Long and Plane formula) [44] to an increase of only *ca.* 4% in the $\alpha_\parallel'$ value. Consequently our results strongly reinforce the conclusions of Couch *et al.*[25] that the a_{1g}* molecular orbital which accommodates the 'lone pair' of electrons in the valence shell of Te^{IV} is significantly involved in the bonding to the halogens. Accordingly, it makes a substantial contribution to the parallel component of the Te–X bond-polarisability

[44] T. V. Long and R. A. Plane, *J. Chem. Phys.*, 1965, **43**, 457.
[45] D. Nakamura, *Bull. Chem. Soc. Japan*, 1963, **36**, 1662.

change, a contribution which has no counterpart in the case of a Sn–X bond.

The only ion for which intensity measurements on the $\nu_5(t_{2g})$ fundamental were possible was $[SbCl_6]^-$. The scattering activity of such a fundamental is determined by $\gamma_5'^2$, as in equation (7) where r_{MX} is the MX bond

$$\gamma_5' = \left(\frac{2}{r_{MX}}\right)\left(\frac{3}{m_X}\right)^{\frac{1}{2}}\gamma_{MX} \qquad (7)$$

length in Å (assumed to be 2.40 Å for $[SbCl_6]^-$), m_X is the mass of the X atom, and γ_{MX} is the bond anisotropy $\alpha_{\parallel} - \alpha_{\perp}$ (in Å^3). On the basis of the $(1/f)(I_2M_1/I_1M_2)$ value for ν_5 of $[SbCl_6]^-$ with 647.1-nm excitation (0.117, Table 2, the value displaying no significant resonance enhancement), γ_5' is calculated to be 0.43 Å^2 and thus γ_{SbCl} is 1.8 Å^3 (*cf.* the corresponding value for γ_{SnCl} is 2.0 Å^3).[27]

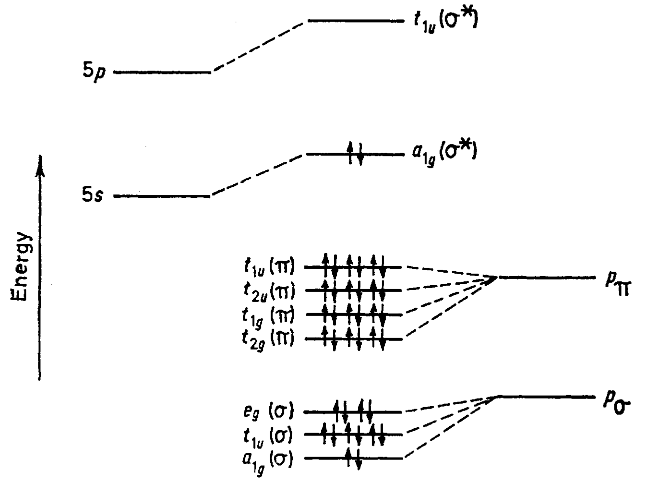

FIGURE 4 Relative orbital energies estimated (ref. 25) for the $[TeX_6]^{2-}$ ions

Excitation Profiles of the $\nu_1(a_{1g})$ *and* $\nu_2(e_g)$ *Bands of* $[TeBr_6{}^{2-}]$.—The excitation profiles of the $\nu_1(a_{1g})$ and $\nu_2(e_g)$ bands of $[TeBr_6]^{2-}$ have been studied in considerable detail because the relative intensities of these two bands are strongly affected by the proximity of the exciting frequency (ν_0) to that of the lowest electronic transition of the ion. The relative orbital energies estimated [25] for the $[TeX_6]^{2-}$ ions are given in Figure 4. The lowest electronic excited states ($^3T_{1u}$ and $^1T_{1u}$) are derived from the $sp \leftarrow s^2$ transition ($t_{1u}\,\sigma^* \leftarrow a_{1g}\,\sigma^*$).[46] The lowest transition ($^3T_{1u} \leftarrow {}^1A_{1g}$) is spin forbidden, but nevertheless has a substantial degree of allowed character ($\varepsilon_{max.}$ 2 600 dm^3 mol^{-1} cm^{-1}) owing to the large value of the spin–orbit coupling constant associated with the *p* orbitals of the tellurium ion.

The relative intensities of the ν_1 and ν_2 bands (Table 5) are affected by the exciting line in the following way. With 647.1-nm excitation the $\nu_2(e_g)$ band is 14% less intense than that of the $\nu_1(a_{1g})$ band, whereas with blue excitation this situation changes dramatically so that

TABLE 5

Molar intensities of $\nu_1(a_{1g})$ and $\nu_2(e_g)$ fundamentals of $[TeBr_6]^{2-}$ relative to that of the band of acetonitrile at 918 cm^{-1}

λ/nm	$\bar{\nu}_0$/cm^{-1}	$\bar{\nu}_i$	I_2M_1/I_1M_2 [a]	f [b]	$(1/f) \times (I_2M_1/I_1M_2)$
647.1	15 450	ν_1	326 ± 4	11.73	27.8
		ν_2	327 ± 26	14.72	22.2
568.2	17 595	ν_1	458 ± 36	11.44	40.0
		ν_2	483 ± 52	14.34	33.7
530.8	18.832	ν_1	631 ± 47	11.31	55.8
		ν_2	484 ± 37	14.16	34.2
520.8	19 195	ν_1	566 ± 33	11.27	50.3
		ν_2	411 ± 34	14.12	29.1
514.5	19 430	ν_1	726 ± 24	11.25	64.6
		ν_2	395 ± 27	14.09	28.0
501.7	19 926	ν_1	783 ± 57	11.20	69.9
		ν_2	602 ± 37	14.03	42.9
496.5	20 135	ν_1	726 ± 35	11.18	64.9
		ν_2	673 ± 40	14.01	48.1
488.0	20 487	ν_1	681 ± 57	11.15	61.1
		ν_2	1 970 ± 21	13.97	141
476.5	20 981	ν_1	641 ± 59	11.11	57.7
		ν_2	2 850 ± 220	13.92	204
457.9	21 831	ν_1	587 ± 79	11.05	53.1
		ν_2	3 490 ± 360	13.83	252

[a] The data are corrected for spectral response; subscript 2 refers to $[TeBr_6]^{2-}$ and subscript 1 to acetonitrile; the error limits refer to the scatter between five different measurements of each datum.

[b] $f = \dfrac{f(\nu_2)}{f(\nu_1)} = \left(\dfrac{\nu_0 - \nu_2}{\nu_0 - \nu_1}\right)^4 \dfrac{\nu_1}{\nu_2}\left[\dfrac{1 - \exp(-hc\nu_1/kT)}{1 - \exp(-hc\nu_2/kT)}\right]$ where 1 refers to acetonitrile and 2 refers to $[TeBr_6]^{2-}$.

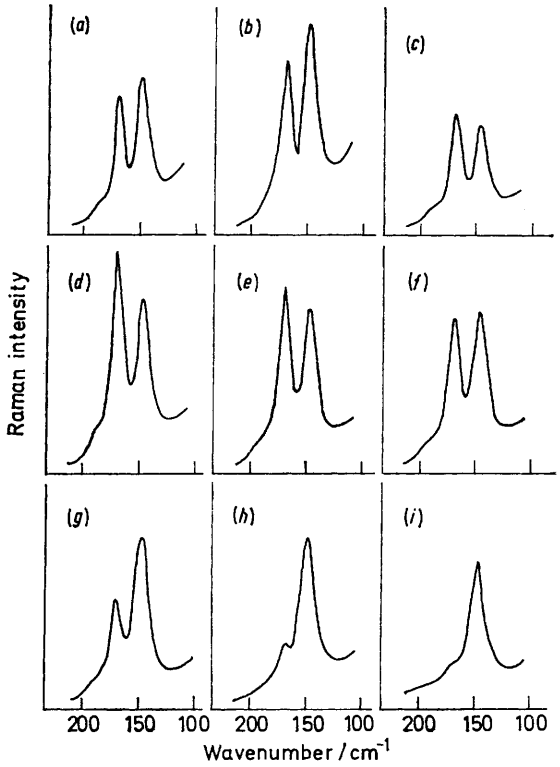

FIGURE 5 Raman spectrum of $[TeBr_6]^{2-}$ at exciting wavelengths of (*a*) 647.1, (*b*) 568.2, (*c*) 520.8, (*d*) 514.5, (*e*) 501.7, (*f*) 496.5, (*g*) 488.0, (*h*) 476.5, and (*i*) 468.0 nm, showing the dramatic change in the relative intensities of the bands arising from the $\nu_1(a_{1g})$ and $\nu_2(e_g)$ fundamentals

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[46] C. E. Moore, 'Atomic Energy Levels,' vol. 3, Nat. Bureau Stand. Circular 467, U.S. Government Printing Office, Washington D.C., 1958.

with 457.9-nm excitation the $\nu_2(e_g)$ band is now 5.95 times the more intense (Figure 5). This observation is strong evidence for Albrecht-type vibronic coupling (B-term enhancement)[30,31] between the T_{1u} excited states of $[TeBr_6]^{2-}$. (A-Term enhancement affects the intensities of totally symmetric modes only.)[47]

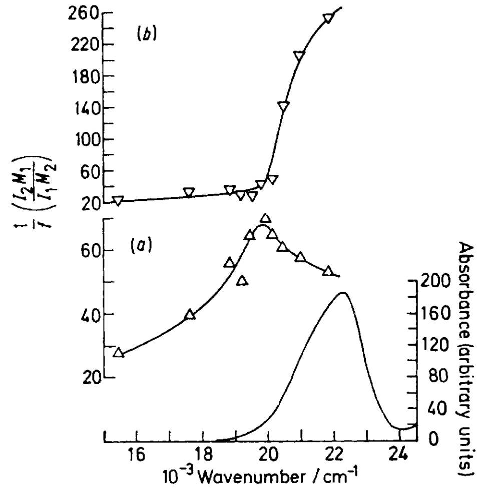

FIGURE 6 Excitation profiles of (a) the $\nu_1(a_{1g})$ and (b) the $\nu_2(e_g)$ fundamentals, together with the electronic-absorption spectrum of $[TeBr_6]^{2-}$

The excitation profiles of the $\nu_1(a_{1g})$ and $\nu_2(e_g)$ bands are given in Figure 6. That of the $\nu_1(a_{1g})$ band reaches a maximum *ca.* 2 500 cm^{-1} lower than the $^3T_{1u} \leftarrow {}^1A_{1g}$ electronic band maximum, and a minimum in the vicinity of this electronic band maximum. On the other hand, the excitation profile of the $\nu_2(e_g)$ band closely follows the absorption spectrum of the ion. These observations on the $\nu_1(a_{1g})$ band differ from those made on scattering species for which the resonant electronic transition is fully electric-dipole allowed[48,49] (as opposed to being spin forbidden). Indeed the observations resemble those made on totally symmetric modes of the ions $[PdCl_6]^{2-}$, $[PtCl_6]^{2-}$, $[RhCl_6]^{3-}$, $[IrCl_6]^{2-}$, $[PdX_4]^{2-}$ (X = Cl, Br, or I), and $[Co(en)_3]^{3+}$ (en = ethylenediamine) where ν_0 is in the vicinity of vibronically induced ligand-field bands.[27,35,40] The minima in the a_{1g} excitation profiles are thought[40,50] to arise from destructive interference in the dispersion equation between the pre-resonance intensity contributions of the spin-forbidden band and that of the higher frequency-allowed transition; this is possible since the Raman intensity is proportional to the square of the elements of the scattering tensor and contains (signed) cross terms.

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[6/669 *Received, 7th April,* 1976]

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[47] H. Hamaguchi, I. Harada, and T. Shimanouchi, *J. Raman Spectroscopy*, 1974, **2**, 517.

[48] R. J. H. Clark, in 'Advances in Infrared and Raman Spectroscopy,' eds. R. J. H. Clark and R. E. Hester, Heyden, London, 1975, p. 143.

[49] J. Behringer, in 'Molecular Spectroscopy,' *Specialist Period. Rep.*, The Chemical Society, London, vol. 3, p. 163.

[50] J. Friedman and R. M. Hochstrasser, *Chem. Phys. Letters*, 1975, **32**, 414.