Resonance Raman Spectroscopic Studies on the Group 6B Polyatomic Cations S_4^{2+}, Se_4^{2+}, and Te_4^{2+} †

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The Raman and resonance Raman (r.R.) spectra of S_4^{2+} and Se_4^{2+} in oleum at room temperature, of Te_4^{2+} in H_2SO_4, and of $Te_4[Al_2Cl_7]_2$ at *ca.* 80 K, have been recorded with a variety of excitation lines. The r.R. spectra display long progressions, v_1v_1, in the v_1 (a_{1g}) mode in each case, together with shorter progressions of the sort $v_1v_1 + v_2$ (b_{1g}). Analysis of the results leads to harmonic wavenumbers (ω_1) of 584.7, 321.8, and 219.5 cm⁻¹ for S_4^{2+}, Se_4^{2+}, and Te_4^{2+}, respectively, in solution, and anharmonicity constants (x_{11}) of -0.35, -0.55, and -0.30 cm⁻¹, respectively. Stretching force constants (valence force field) for S_4^{2+}, Se_4^{2+}, and Te_4^{2+} in solution are calculated to be 2.78, 2.10, and 1.45 mdyn Å⁻¹, respectively, the *trans*-bond stretch–stretch interaction constants being more than an order of magnitude greater than the *cis*-bond ones. The v_1 band excitation profile of each ion maximises within the band contour of the lowest allowed electronic transition of each ion, *i.e.* that at 330 nm for S_4^{2+}, 410 nm for Se_4^{2+}, and 510 nm for Te_4^{2+}. These data, coupled with detailed measurements on the Raman band polarizations at resonance, indicate that the assignment of the lowest allowed transition of each ion is $\pi^*(b_{2u}) \longleftarrow \pi(e_g)$, $^1E_u \longleftarrow ^1A_{1g}$.

The chemistry of sulphur, selenium, and tellurium in highly acidic media has been studied extensively,[1–5] and it has been shown that these elements are oxidized to form intensely coloured polyatomic cationic species. Using a combination of physicochemical techniques, involving cryoscopic, conducto-metric, and spectroscopic measurements, Gillespie and co-workers [5–15] have established the presence of S_{19}^{2+}, S_8^{2+}, S_4^{2+}, Se_{10}^{2+}, Se_8^{2+}, Se_4^{2+}, Te_6^{4+}, and Te_4^{2+} in acidic solutions. X-Ray crystallographic measurements on $Se_4[HS_2O_7]_2$, and on compounds obtained from melts containing M, MCl_4, and $AlCl_3$ (M = Se or Te), have established a square-planar (D_{4h}) geometry for the M_4^{2+} species [10,16,17] and a bicyclic structure for Se_8^{2+}.[8] The square-planar geometry for the M_4^{2+} ions gives rise to the following molecular vibrations: v_1 (a_{1g}), v_2 (b_{2g}), and v_3 (b_{1g}) (all Raman active), v_4 (b_{2u}) (inactive), and v_5 (e_u) (i.r. active); v_4 is an out-of-plane motion, but the other modes are all in-plane. I.r. and Raman spectroscopic measurements have confirmed the D_{4h} structure for the ions in solution although a lowering of symmetry, resulting in site- and factor-group effects, has been deduced from solid-state spectra.

Molecular orbital calculations on the M_4^{2+} species have been carried out;[15,18–21] the π-orbital levels are shown in Figure 1. The ions are examples of 6π-electron systems, and they are thus examples of inorganic aromatic compounds. Their π-bond order is 0.25 (0.50 according to the Hückel molecular-orbital definition of π-electron bond order, this strictly relating to the electron occupancy number of the π orbitals [20]), and so the overall M–M (valence bond) bond order is 1.25. The ions can be regarded as examples of ' class III ' mixed-valence species, owing to the equivalence of each atom both structurally and with respect to charge ($+0.5$). The lowest allowed electronic transition for these ions assuming D_{4h} symmetry is $\pi^* \leftarrow \pi$ ($^1E_u \leftarrow ^1A_{1g}$), *i.e.* that corresponding to the transition of an electron from the non-bonding e_g orbital to the antibonding b_{2u} orbital. These transitions are thought to give rise to the bands at 330, 410, and 510 nm for S_4^{2+}, Se_4^{2+}, and Te_4^{2+}, respectively. Booth *et al.*[22] have obtained resonance Raman (r.R.) spectra on the Te_4^{2+} ion in H_2SO_4 solution by excitation with the 514.5 nm line of an argon-ion laser, the most prominent
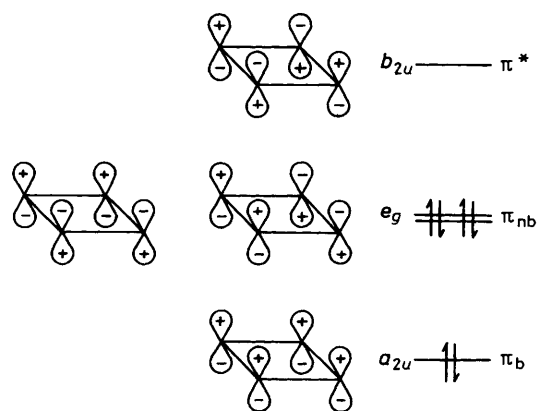

Figure 1. π Molecular orbital scheme for the M_4^{2+} species; b = bonding, nb = non-bonding

feature being an overtone progression v_1v_1, extending to $v_1 = 4$. No r.R. studies of Se_4^{2+} and S_4^{2+} have yet been reported, presumably because their lowest energy absorption bands lie to shorter wavelengths than those of laser lines commonly available. However, by the use of violet and u.v. exciting lines from a high power krypton-ion laser, we have successfully measured the r.R. spectra of Se_4^{2+} and S_4^{2+}. These results are reported in the present study, together with some improved r.R. data on the Te_4^{2+} ion. Raman band polarization data lead to confirmation of the assignment of the resonant transitions.

Experimental

(*a*) *Sample Preparation.*—Te_4^{2+} was generated by dissolving elemental tellurium in concentrated H_2SO_4, and studied within 24 h owing to the slow precipitation of TeO_2. $Te_4[Al_2Cl_7]_2$ was prepared by heating elemental tellurium with $TeCl_4$ and $AlCl_3$ in an evacuated sealed tube at 260 °C for *ca.* 1 week.[16] Se_4^{2+} was generated by dissolving elemental selenium in 25% oleum to produce Se_8^{2+}, which was then oxidized to Se_4^{2+} with $[NH_4]_2[S_2O_8]$.[4] S_4^{2+} was prepared by dissolving elemental sulphur in 65% oleum.[3] This solution contains S_4^{2+}, S_8^{2+}, and S_{16}^{2+}; it is deep blue due to the 590
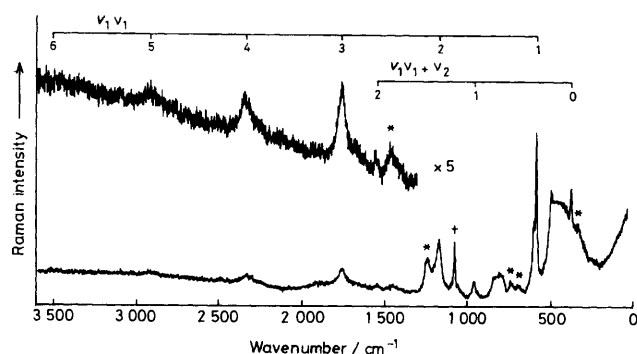
Figure 2. Resonance Raman spectrum of a solution of S_4^{2+} in 65% oleum recorded with 350.7 nm excitation. Power at the sample = 100 mW, scan speed = 1 cm⁻¹ s⁻¹, time constant = 1 s, and spectral slitwidth = 5 cm⁻¹ at 350.7 nm. The bands marked (*) are due to oleum, the one at 1 071 cm⁻¹ marked (†) is due to SO_3 present in the oleum, and the broad features centred on *ca.* 450 cm⁻¹ and *ca.* 800 cm⁻¹ are due to Raman scattering from the silica cell

Table 1. Details of the r.R. spectrum ^{a} of S_4^{2+} in 65% oleum

Assignment	$\tilde{v}$/cm⁻¹	f.w.h.m./cm⁻¹	Relative intensity	$\rho(\pi/2)$
v_2 (b_{1g})	371.2 ± 0.5	12 ± 1	0.30	0.65 ^{b}
v_1 (a_{1g})	583.6 ± 0.5		1.00	0.17 ^{c}
v_3 (b_{2g})	598.1 ± 0.5		0.37	0.50 ^{b}
$v_1 + v_2$ (B_{2g})	953.7 ± 0.5		0.15	
$2v_1$ (A_{1g}) ^{d}	1 168.1 ± 0.5	32 ± 2	0.68	
$2v_1 + v_2$ (B_{1g})	1 539 ± 2		0.05	
$3v_1$ (A_{1g})	1 750 ± 2	45 ± 5	0.24	
$4v_1$ (A_{1g})	2 332 ± 5		0.19	
$5v_1$ (A_{1g})	2 912 ± 5		0.11	
$6v_1$ (A_{1g})	3 480 ± 10		0.05	

^{a} λ_0 = 350.7 nm. ^{b} ±0.05. ^{c} ±0.02. ^{d} Possibly overlapped by $v_1 + v_3$.

nm absorption band of the S_8^{2+} species. For Raman measurements the solutions were sealed in either Pyrex or silica cells, which were spun at >1 000 r.p.m. to minimize thermal and photochemical decomposition. The spectra of solid Te₄-[Al₂Cl₇]₂ were recorded at 80 K using a cell cooled with liquid nitrogen.

(*b*) *Raman Spectroscopy.*—Raman spectra were recorded using Spex 1401 and 14018 (Ramalog 6) spectrometers in conjunction with Coherent Radiation model CR15UV argon-ion and CR3000K krypton-ion lasers, and a Coherent Radiation model CR490 dye laser employing stilbene-3 as the lasing medium (some of the measurements on Se_4^{2+} were obtained using a Jobin-Yvon Ramanor spectrometer with a Spectra Physics 170 krypton-ion laser, by courtesy of Dr. R. E. Hester, University of York). Band wavenumber measurements were calibrated using the emission spectrum of neon, and band intensities, determined as the product of peak height and full width at half-maximum (f.w.h.m.) were corrected for the spectral response of the appropriate spectrometer. Measurements of depolarization ratios in the u.v. region were obtained using a Polaroid HNP′B linear polarizer. Resolution of overlapping bands was performed using a Nicolet 1180 computer interfaced to the Spex Ramalog 6 spectrometer.

(*c*) *Electronic Absorption Spectroscopy.*—Electronic absorption spectra were obtained from solutions in silica cuvettes using a Cary 14 spectrophotometer.
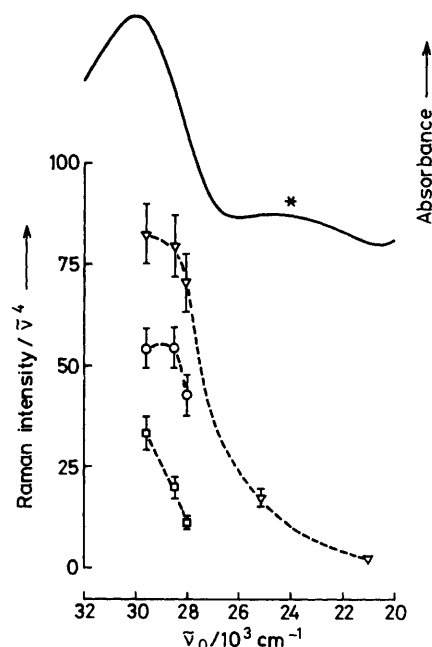
Figure 3. Excitation profiles of the v_1 ($\triangledown$), $2v_1$ ($\bigcirc$), and $3v_1$ ($\square$) bands of S_4^{2+}, together with the absorption spectrum of the ion. The band marked (*) in the absorption spectrum is due to the S_{16}^{2+} species which is also present in the solution
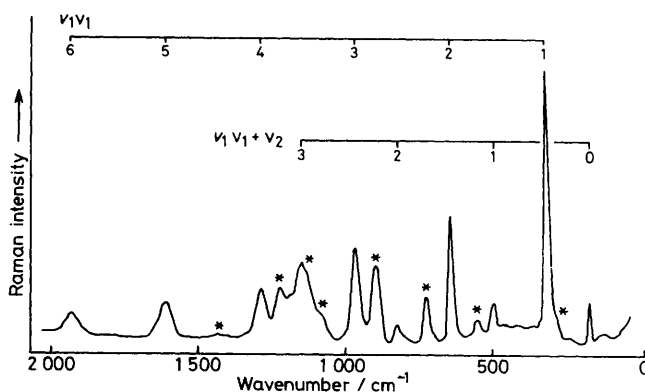
Figure 4. Resonance Raman spectrum of a solution of Se_4^{2+} in 25% oleum recorded with 406.7 nm excitation. Power at the sample = 100 mW, scan speed = 1 cm⁻¹ s⁻¹, time constant = 1 s, and spectral slitwidth = 5 cm⁻¹ at 406.7 nm. The bands marked (*) are due to oleum

Results

(*a*) S_4^{2+}.—The Raman spectrum of a solution of sulphur in 65% oleum was recorded for laser excitation in the range 337.5—476.2 nm. Excitation at longer wavelengths results in strong luminescence, believed to be due to the presence of the S_8^{2+} species ($\lambda_{max.}$ = 590 nm). No Raman bands attributable to either S_8^{2+} or S_{16}^{2+} were observed with any exciting lines, probably because these species are present in lower concentrations than is S_4^{2+}, and decrease in concentration with time. However, it was found that excitation with u.v. laser lines caused a regeneration of S_8^{2+}, as evidenced by a deepening of the blue colour of the solution, most markedly at the laser focus.

Excitation with lines which fall within the contour of the 330 nm band ($\varepsilon_{max.}$ = 2 200 dm³ mol⁻¹ cm⁻¹) ^{9} produced r.R.
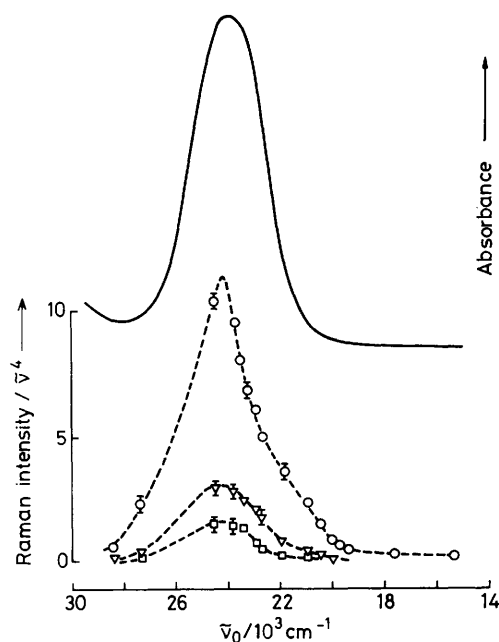
Figure 5. Excitation profiles of the v_1 ($\bigcirc$), $2v_1$ (∇), and $3v_1$ ($\square$) bands of Se_4^{2+}, together with the absorption spectrum of the ion

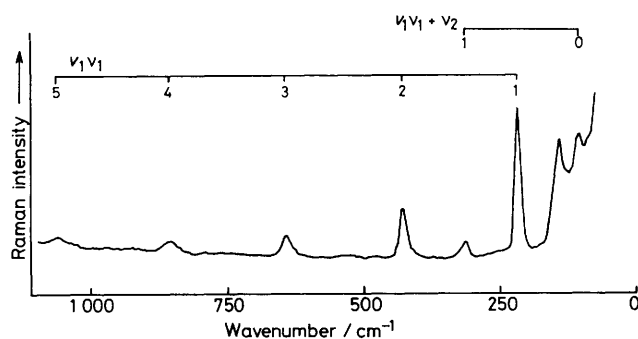**Figure 6.** Resonance Raman spectrum of $Te_4[Al_2Cl_7]_2$ at 80 K recorded with 514.5 nm excitation. Power at the sample = 100 mW, scan speed = 1 cm^{-1} s^{-1}, time constant = 1 s, and spectral slitwidth = 5 cm^{-1} at 514.5 nm

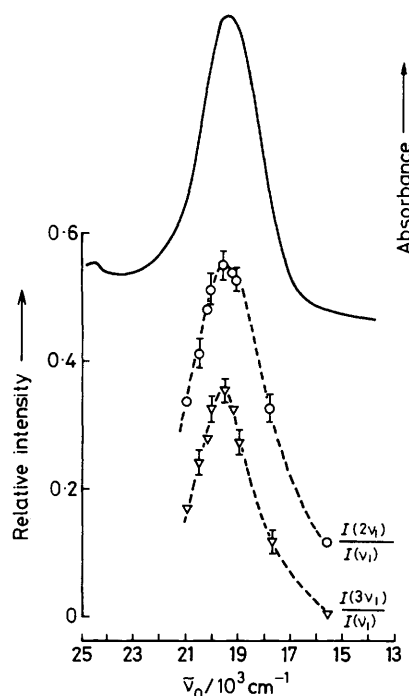**Table 2.** Details of the r.R. spectrum ^{a} of Se_4^{2+} in 25% oleum

Assignment	$\tilde{v}/cm^{-1}$	f.w.h.m./ cm^{-1}	$\rho(\pi/2)$
v_2 (b_{1g})	182.3 ± 0.5	16	0.70
v_1 (a_{1g}) $\}$ v_3 (b_{2g})	321.3 ± 0.5	10	0.33
$v_1 + v_2$ (B_{1g})	501 ± 1	25	
$2v_1$ (A_{1g}) ^{b}	639.6 ± 0.5	15	0.36
$2v_1 + v_2$ (B_{1g})	819 ± 1	32	
$3v_1$ (A_{1g})	957.4 ± 0.5	24	
$3v_1 + v_2$ (B_{1g})	$1\,136 \pm 2$		
$4v_1$ (A_{1g})	$1\,275 \pm 1$	40	
$5v_1$ (A_{1g})	$1\,592 \pm 1$	48	
$6v_1$ (A_{1g})	$1\,910 \pm 2$	60	

^{a} $\lambda_0 = 406.7$ nm. ^{b} Possibly overlapped by $v_1 + v_3$.

spectra of S_4^{2+} (colourless), characterized by an overtone progression in $v_1 v_1$, extending to $v_1 = 6$, and a combination band progression $v_1 v_1 + v_2$, extending to $v_1 = 2$. The third Raman-active fundamental, v_3 (b_{2g}), is observed as a shoulder on the high-wavenumber side of v_1, and it is possible that a progression of the type $v_1 v_1 + v_3$ overlaps that of $v_1 v_1$. The r.R. spectrum of S_4^{2+} is shown in Figure 2 and the band wavenumber measurements, assignments, depolarization ratios, and bandwidths (f.w.h.m.) are given in Table 1. The assignments of the S_4^{2+} bands were confirmed by recording r.R. spectra of solutions containing different concentrations of S_4^{2+}. Although the concentration of S_4^{2+} in the solutions decreases with time, we were able to obtain approximate excitation profiles for v_1, $2v_1$, and $3v_1$ using the $1\,071$ cm^{-1} band of the SO_3 present in the oleum as internal standard. These profiles are shown, together with the absorption spectrum, in Figure 3.

(*b*) Se_4^{2+}.—The lowest allowed electronic band of Se_4^{2+} (yellow-orange) maximizes at 410 nm, with $\varepsilon_{max.} = 8\,000$ dm^3 mol^{-1} cm^{-1}.[7] The r.R. spectrum of Se_4^{2+} in 25% oleum, obtained with 406.7 nm excitation, is shown in Figure 4; it is

Figure 7. Plots of $I(2v_1)/I(v_1)$ ($\bigcirc$) and $I(3v_1)/I(v_1)$ (∇) for Te_4-$[Al_2Cl_7]_2$, together with the absorption spectrum of Te_4^{2+} in H_2SO_4 solution

characterized by an overtone progression $v_1 v_1$ extending to $v_1 = 6$ and a combination tone progression $v_1 v_1 + v_2$, extending to $v_1 = 3$. No band attributable to the third Raman-active fundamental, v_3 (b_{2g}), is observed, apparently because its wavenumber coincides with that of v_1 (see below). Band wavenumber measurements, assignments, bandwidths (f.w.h.m.), and depolarization ratios are given in Table 2. Excitation profiles were measured for v_1, $2v_1$, and $3v_1$ using the 730 cm^{-1} band of oleum as an internal standard; these are shown in Figure 5, together with the absorption spectrum of the ion.

(*c*) Te_4^{2+}.—The lowest allowed electronic band of Te_4^{2+} (red) maximizes at 510 nm, with $\varepsilon_{max.} > 6\,000$ dm^3 mol^{-1} cm^{-1}.[4] Resonance Raman spectra of Te_4^{2+} in H_2SO_4 solution at room temperature and of $Te_4[Al_2Cl_7]_2$ solid at 80 K were obtained using 514.5 nm excitation. The spectrum of Te_4-

Table 3. Details of the r.R. spectrum [a] of Te_4^{2+} in H_2SO_4 and $Te_4[Al_2Cl_7]_2$

| Assignment | Te_4^{2+} in H_2SO_4 solution | | | $Te_4[Al_2Cl_7]_2$ [b] | |
	$\tilde{v}/cm^{-1}$	f.w.h.m./cm^{-1}	$\rho(\pi/2)$	$\tilde{v}/cm^{-1}$	f.w.h.m./cm^{-1}
$v_2 (b_{1g})$	109.0 ± 0.5	8	0.75	95.0 ± 0.5	8
$v_1 (a_{1g})$	219.0 ± 0.5	10	0.33	213.8 ± 0.5	10
$v_1 (b_{2g})$					
$v_1 + v_2 (B_{1g})$				308 ± 1	15
$2v_1 (A_{1g})$ [c]	437.0 ± 0.5	15		427.0 ± 0.5	15
$3v_1 (A_{1g})$	655 ± 1	25		640.3 ± 0.5	24
$4v_1 (A_{1g})$				852.7 ± 1	40
$5v_1 (A_{1g})$				$1\,065.4 \pm 1$	48
$6v_1 (A_{1g})$				$1\,278 \pm 2$	60

[a] $\lambda_0 = 514.5$ nm. [b] At 80 K. $[Al_2Cl_7]^-$ ion bands occur at 194, 342, 364, and 386 cm^{-1}. [c] Possibly overlapped by $v_1 + v_3$.

Table 4. Wavenumbers of the fundamental modes of vibration for S_4^{2+}, Se_4^{2+}, and Te_4^{2+}

Mode [a]	Form	S_4^{2+}	Se_4^{2+}	Te_4^{2+}
$v_1 (a_{1g})$		583.6	321.3	219
$v_2 (b_{1g})$		371.2	182.3	109
$v_3 (b_{2g})$		598.1	321.3	219
$v_5 (e_u)$ [b]		542	302	187

[a] D_{4h} nomenclature, with the x and y axes passing through opposite atoms, and the z axis perpendicular to the square plane. The v_4 (b_{2u}) mode , which is analogous to the v_6 (t_{2u}) mode of an MX_6 octahedral species, is inactive. [b] Ref. 15.

$[Al_2Cl_7]_2$, shown in Figure 6, is characterized by an overtone progression v_1v_1, extending to $v_1 = 5$, and a combination band $v_1v_1 + v_2$. As for Se_4^{2+}, the wavenumber of v_3 (b_{2g}) apparently coincides with that of v_1. Band wavenumber measurements, assignments, bandwidths (f.w.h.m.), and depolarization ratios are given in Table 3. It was not possible to obtain an excitation profile for $Te_4[Al_2Cl_7]_2$, due to the decomposition of this species when mixed with another compound as an internal intensity standard. Instead, we have plotted $I(2v_1)/I(v_1)$ and $I(3v_1)/I(v_1)$ for excitation within the range 476.5—647.1 nm; the results are shown in Figure 7, together with the absorption spectrum of the complex.

Discussion

(a) *Vibrational Analysis.*—The wavenumbers of the fundamental modes of vibration of S_4^{2+}, Se_4^{2+}, and Te_4^{2+}, including the i.r.-active v_5 (e_u) modes, are presented in Table 4. The band assignments for Se_4^{2+} and Te_4^{2+} are in agreement with those of Gillespie and co-workers [6,22] and therefore merit no further discussion, except for the assertion that v_3 (b_{2g}) apparently coincides with v_1 (a_{1g}) for each ion. The justification for this statement is based on two arguments.

(1) The v_3 (b_{2g}) mode is Jahn–Teller active in the ^1E_u excited state (see below) and ought therefore to give rise to a band of sufficient intensity to be observed in the r.R. spectrum of each ion.

(2) The $\rho(\pi/2)$ value measured for the band assigned to v_1 (a_{1g}) is 0.33 for both Se_4^{2+} and Te_4^{2+}, whereas at resonance with a $\pi^* \leftarrow \pi$ transition, it should have the value 0.125 (see below). The v_3 band must be depolarized, *i.e.* $\rho(\pi/2) = 0.75$, and the unexpected ρ value for v_1 is due to v_1/v_3 band overlap. From the measured depolarization ratio of the v_1/v_3 band and those expected for v_1 and v_3 alone, we calculated that an

intensity ratio $I(v_1)/I(v_3) = 1.3$ would lead to the observed $\rho(\pi/2)$ value.

In the case of S_4^{2+}, bands attributable to all three fundamentals are observed, v_3 appearing as a shoulder 14.5 cm^{-1} above v_1. Although the wavenumber of v_1 is in agreement with the value obtained by Gillespie *et al.*[9] (584 cm^{-1}), those obtained for v_2 and v_3 are not; the earlier values [12] of v_2 (330 cm^{-1}) and v_3 (530 cm^{-1}) probably arose from confusion of S_4^{2+} and counter-ion bands. Our results agree closely with recently revised values of Burns and Gillespie.[15]

Using the wavenumber data in Table 4 we have performed a force constant calculation, employing a valence force field (VFF). The symmetry co-ordinates and F and G matrix elements for a square-planar X_4 type molecule have been determined by Cyvin;[23] these are summarized, for the in-plane vibrations, in Table 5. A generalized valence force field treatment requires eight force constants to describe the in-plane motion, but we have only four band wavenumbers; hence it is necessary to assume zero values for four of the force constants. As a first approximation we put $f_{rr'} = f_{\theta\theta'} = f_{r\theta} = f_{r\theta'} = 0$ and retained f_r, f_{rr}, f_θ, and $f_{\theta\theta}$. However, the calculation produced negative values for all of the f_θ and $f_{\theta\theta}$ force constants and, furthermore, produced $f_{\theta\theta}$ values that were of the same order as those for f_θ, whereas it would normally be expected that $f_{\theta\theta} < f_\theta$. This prompted us to test a second approximation, in which $f_{\theta\theta} = f_{\theta\theta'} = f_{r\theta} = f_{r\theta'} = 0$ and f_r, f_{rr}, $f_{rr'}$, and f_θ are retained. The results of this calculation are shown in Table 6. The VFF stretching force constant, f_r, decreases with increasing atomic number, *i.e.* in the order S_4^{2+} (2.78 mdyn $Å^{-1}$) > Se_4^{2+} (2.10) > Te_4^{2+} (1.45). The f_r value for S_4^{2+}, with its formal (valence bond) bond order of 1.25, is almost identical with that for S_3^- (2.77 mdyn $Å^{-1}$)[24] which also has a formal bond order of 1.25, is less than that for S_2^- (3.33 mdyn $Å^{-1}$)[24] which has a formal bond order of 1.5, and is greater than that for the single-bonded species S_6 (2.23 mdyn $Å^{-1}$),[25] S_2^{2-} (2.11),[24] and S_3^{2-} (2.00).[24] Thus the f_r value for S_4^{2+} fits naturally into the expected relationship between stretching force constant and bond order.

It is interesting to note that, for each ion, the interaction force constant associated with adjacent bonds, f_{rr}, is very much smaller than that associated with opposite bonds, $f_{rr'}$ (this is why the first approximation, in which $f_{rr'} = 0$, produces unacceptable results). Indeed, it is because of this that the v_1 and v_3 band wavenumbers lie so close together; moreover, f_{rr} for S_4^{2+} is negative, since $v_3 > v_1$. The values obtained for f_θ are only approximate since these will include contributions from $f_{\theta\theta}$ and $f_{\theta\theta'}$ which, although small, may nevertheless be non-zero. No further information can be obtained that would enable $f_{\theta\theta}$ and $f_{\theta\theta'}$ to be calculated. The remaining fundamental, v_4 (b_{2u}), which involves out-of-plane deformation motions only, will be independent of the eight in-

Table 5. Symmetry co-ordinates and G and F matrix elements for square-planar X_4 type molecules

Symmetry species	Symmetry co-ordinate	G Matrix element	F Matrix element *
A_{1g}	$\frac{1}{2}(\Delta r_1 + \Delta r_2 + \Delta r_3 + \Delta r_4)$	$2\mu_x$	$f_r + 2f_{rr} + f_{rr'}$
B_{1g}	$\frac{r}{2}(\Delta\theta_{12} - \Delta\theta_{23} + \Delta\theta_{34} - \Delta\theta_{14})$	$8\mu_x$	$f_\theta - 2f_{\theta\theta} + f_{\theta\theta'}$
B_{2g}	$\frac{1}{2}(\Delta r_1 - \Delta r_2 + \Delta r_3 - \Delta r_4)$	$2\mu_x$	$f_r - 2f_{rr} + f_{rr'}$
E_u	$\frac{1}{\sqrt{12}}(\Delta r_1 - \Delta r_2 - \Delta r_3 + \Delta r_4) - \sqrt{\frac{r}{3}}(\Delta\theta_{14} - \Delta\theta_{23})$	$6\mu_x$	$\frac{1}{2}(f_r - f_{rr'}) - \frac{1}{2}(f_{r\theta} - f_{r\theta'}) + \frac{1}{2}(f_\theta - f_{\theta\theta'})$
	and $\frac{1}{\sqrt{12}}(\Delta r_1 + \Delta r_2 - \Delta r_3 - \Delta r_4) - \sqrt{\frac{r}{3}}(\Delta\theta_{12} - \Delta\theta_{34})$		

* f_{rr} and $f_{rr'}$ refer to a pair of adjacent and opposite bonds, respectively, and $f_{\theta\theta}$ and $f_{\theta\theta'}$ are similarly defined. For $f_{r\theta}$ and $f_{r\theta'}$, the numbers of common atoms are two and one respectively; μ_x is the reciprocal mass of the X atom.

Table 6. Force constants for S_4^{2+}, Se_4^{2+}, and Te_4^{2+}

	S_4^{2+}	Se_4^{2+}	Te_4^{2+}
f_r/mdyn Å^{-1}	2.78	2.10	1.45
f_{rr}/mdyn Å^{-1}	−0.04	0	0
$f_{rr'}$/mdyn Å^{-1}	0.51	0.30	0.36
f_θ/mdyn Å^{-1}	0.33	0.19	0.11

Table 7. Harmonic wavenumbers and anharmonicity constants

	S_4^{2+}	Se_4^{2+}	Te_4^{2+}	$Te_4[Al_2Cl_7]_2$
ω_1/cm^{-1}	584.7	321.8	219.5	214.1
	±0.5	±0.5	±0.5	±0.5
x_{11}/cm^{-1}	−0.35	−0.55	−0.30	−0.16
	±0.05	±0.05	±0.05	±0.05
x_{12}/cm^{-1}	−0.5	−1.3		−0.8
	±1	±1.0		±0.5

Figure 8. $^\perp I_\perp$ and $^\perp I_{||}$ spectra of S_4^{2+} in the region 550—630 cm^{-1} for spectral slitwidths of (a) 5 cm^{-1} and (b) 20 cm^{-1}. (c) The result of a curve analysis of the I_{total} spectrum in the region 550—630 cm^{-1}: (i) experimental spectrum, (ii) calculated spectrum, (iii) resolved bands

plane force constants. This fundamental is neither Raman nor i.r. active and has not therefore been located for the M_4^{2+} species. Its first overtone would be Raman active, but a search for this was unsuccessful. The only spectroscopic technique available for its location may be hyper-Raman spectroscopy, but as yet very few applications of this technique have been reported.[26]

From the wavenumber measurements of the observed overtone and combination tone progressions we have calculated a number of harmonic wavenumbers and anharmonicity constants, which are summarized in Table 7. It is noted that, in each case, the anharmonicity constant x_{11} is very small; thus the v_1 modes in the ground state behave very nearly as harmonic oscillators, a situation which seems to prevail for most simple inorganic molecules.[27]

(b) *Depolarization Ratios.*—The electronic transitions of the M_4^{2+} ions around which the present r.R. studies are centred are thought [20] to be of the $\pi^* \leftarrow \pi$ ($^1E_u \leftarrow {}^1A_{1g}$) type, *i.e.* they are transitions which would be polarized in the xy plane. In this situation, $\alpha_{xx} = \alpha_{yy}$ and $\alpha_{zz} = 0$, leading to an expected value of 0.125 for the depolarization ratios of a_{1g} modes at resonance, the b_{1g} and b_{2g} modes being depolarized. The results for S_4^{2+} are consistent with this assignment. The v_2 (b_{2g}) band is 14.5 cm^{-1} above v_1 (a_{1g}) and these two bands are partially, but not totally, resolved. The measured depolarization ratios are 0.17 for v_1 and 0.50 for v_3, the deviation from the expected values of 0.125 and 0.75, respectively, being ascribed to the partial overlap of the bands.

The situation for Se_4^{2+} and Te_4^{2+} is more complicated in that, for each ion, the wavenumbers of v_1 (a_{1g}) and v_3 (b_{2g}) coincide, producing a single band for which the depolarization

ratio at resonance is measured to be 0.33. Although this value would be consistent with expectation for resonance with a z-polarized transition, we believe that it in fact arises from the superposition of the v_1 and v_3 bands, with relative intensities $I(v_1)/I(v_3) = 1.3$, and the expected depolarization ratios of 0.125 and 0.75. There is no polarization dispersion for the v_1/v_3 bands, the depolarization ratios being the same for each ion, both on and off resonance.

Resolution of the v_1 and v_3 bands of S_4^{2+}, assuming Lorentzian bandshapes, enabled us to calculate the intensity ratio $I(v_1)/I(v_3) = 2.7$. In order to demonstrate that our calculation of $I(v_1)/I(v_3)$ for Se_4^{2+} and Te_4^{2+} is valid, we obtained the spectrum of S_4^{2+} in the v_1/v_3 region using a spectral slitwidth of 20 cm^{-1}, such that a single band of symmetrical shape was observed. The measured depolarization ratio of this band is 0.24 from which it is calculated that $I(v_1)/I(v_3) = 2.9$, in excellent agreement with the value obtained from the resolution of the partially resolved bands in the absence of an analyser. The $^\perp I_\perp$ and $^\perp I_{||}$ spectra for both 5 cm^{-1} and 20 cm^{-1} spectral slitwidths are shown in Figure 8, together with the resolution of the I_{total} spectrum. The polarization data thus confirm the assignments for the resonant electronic transitions of these ions.

(c) *Excited State Geometry.*—The observation of overtone progressions involving the totally symmetric modes in the r.R. spectra of S_4^{2+}, Se_4^{2+}, and Te_4^{2+} is a consequence of the displacement of the excited-state potential minimum, with respect to that of the ground state, along the normal co-ordinate Q_1 (a_{1g}). That is, on excitation to the resonant state,

the M–M bond distances increase, due to transfer of an electron from an orbital which may formally be regarded as non-bonding (e_g) to one which is antibonding (b_{2u}).

The appearance of subsidiary progressions of the type $v_1v_1 + v_x$ in r.R. spectra, where v_x is a non-totally symmetric fundamental, is evidence for a Jahn-Teller distortion in a degenerate excited state along the normal co-ordinate Q_x. For the M_4^{2+} species the excited state is of ^1E_u type, the Jahn-Teller-active normal co-ordinates being Q_2 (b_{1g}) and Q_3 (b_{2g}). A progression of the type $v_1v_1 + v_2$ is observed for all three of the ions and it is expected that $v_1v_1 + v_3$ progressions are also present but overlapped by the v_1v_1 progressions. The combination of distortions along the Q_2 and Q_3 coordinates suggests that the excited state geometry is likely to C_{2h}.

Acknowledgements

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