Intensity Studies on the Raman-active Fundamentals of Hexahalogeno-anions of Second- and Third-row Transition and Non-transition Metals. The Calculation of Parallel and Perpendicular Bond Polarisability Derivatives

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The Raman spectra of solutions (generally aqueous acid) of the ions MF_6^{2-} (M = Pt or Sn), MCl_6^{2-} (M = Re, Os, Ir, Pd, Pt, Sn, or Pb), MCl_6^{3-} (M = Rh or Ir), MBr_6^{2-} (M = Os, Ir, Pt, or Sn) and MI_6^{2-} (M = Pt or Sn) have been recorded, and accurate values for the frequencies of the $\nu_1(a_{1g})$, $\nu_2(e_g)$, and $\nu_5(t_{2g})$ fundamentals are reported, some for the first time. The intensities of these three fundamentals of each ion were measured using the rotating sample technique at four different exciting lines and they are reported by reference to the 935 cm^{-1} band of the perchlorate ion as internal standard. The results are discussed in terms of the pre-resonance Raman effect. The intensities of $\nu_1(a_{1g})$ fundamentals have been used to determine values for the metal–halogen bond polarisability derivatives ($\bar{\alpha}_{MX}'$) at zero exciting frequency. These $\bar{\alpha}_{MX}'$ values, coupled with the relative molar intensities of the $\nu_1(a_{1g})$ and $\nu_2(e_g)$ fundamentals in each case, lead to values for the parallel and perpendicular MX bond polarisability derivatives. Factors affecting the magnitudes of these quantities are discussed.

In earlier studies of the intensities of the Raman-active fundamentals of the PtX_6^{2-} ions (X = Cl or Br) and of the $PdCl_6^{2-}$ ion, it was found[1,2a] that the relative intensities of the $\nu_1(a_{1g})$ and $\nu_2(e_g)$ fundamentals (as estimated by eye) were in each case less than one and less than for the PtF_6^{2-} ion and other MX_6^{n-} ions then studied. It was suggested that the key difference between these groups of ions was the presence of $d_\pi(M) \longrightarrow d_\pi(X)$ π-back-bonding in the former group, a possibility which is denied to hexafluoro-complex ions and unlikely for SnX_6^{2-} ions. However, it seemed improbable to us that such π-bonding from a metal atom in the quadrivalent state could be of any significance. Moreover, by use of modern laser/photon counting techniques, many Raman-active fundamentals have been found[3,4] which display the pre-resonance Raman effect (pre-r.r.e.) by which the Raman intensities of certain fundamentals increase as the exciting frequency (ν_0) is made to approach the first allowed electronic transition (ν_e) of the molecule. The possibility of a selective enhancement to the $\nu_1(a_{1g})$ or $\nu_2(e_g)$ fundamentals of the PtX_6^{2-} ions has been considered previously, but dismissed on the basis of an admittedly very qualitative measurement on the $PtCl_6^{2-}$ ion alone.

However, the MX_6^{n-} (X = Cl, Br, or I) ions of the second- and third-row transition series are all strongly coloured, and the Raman intensities of their fundamentals are likely to depend on the exciting frequency used to obtain the spectrum. Thus we considered it desirable to carry out a systematic study of the intensities of the Raman-active fundamentals of the ions referred to above, as well as other transition metal complex ions, as a function of the exciting frequency, and by use of modern counting techniques. Analogous studies of the corresponding non-transition metal ions SnF_6^{2-}, $SnCl_6^{2-}$, $SnBr_6^{2-}$, SnI_6^{2-}, and $PbCl_6^{2-}$, have been carried out for comparative purposes. Particularly advantageous for such studies has been the development of the rotating sample technique, whereby the sample may be rotated at speeds of *ca.* 1600 r.p.m.[5,6] In this manner, higher frequency exciting lines may be employed without fear of thermal decomposition of the sample.

In the course of the work, some hitherto unknown solution values for certain fundamentals have been established. Where possible, from the intensity measurements on the $\nu_1(a_{1g})$ fundamentals, bond polarisability derivatives ($\bar{\alpha}_{MX}'$) extrapolated to zero exciting frequency have been calculated. These $\bar{\alpha}_{MX}'$ values have then been coupled with relative intensity measurements on the $\nu_1(a_{1g})$ and $\nu_2(e_g)$ fundamentals to give parallel and perpendicular bond polarisability derivatives ($\alpha_{\parallel}'$ and $\alpha_{\perp}'$ respectively). The interpretation of $\alpha_{\perp}'/\alpha_{\parallel}'$ and of the nature of the π-bonding in MX_6^{2-} ions is discussed.

EXPERIMENTAL

Samples.—The compounds $Na_2OsCl_6,\frac{1}{2}H_2O$, $(NH_4)_2OsBr_6$, $Na_2IrCl_6,6H_2O$, K_2IrBr_6, Na_2PdCl_6, $Na_2PtCl_6,6H_2O$, $Na_2PtBr_6,6H_2O$, K_2PtI_6, $Na_3RhCl_6,12H_2O$, and $Na_3IrCl_6,12H_2O$ were obtained from Johnson Matthey and Co. Ltd. The compound $(NH_4)_2ReCl_6$ was obtained from ROC/RIC Inc. The compound $(NH_4)_2SnF_6$ was prepared from SnI_4 and NH_4F. The compound Na_2PtF_6 was kindly supplied by Mr. K. Turner of Imperial College, London. The $SnCl_6^{2-}$ and $SnBr_6^{2-}$ ions were prepared from the corresponding tetrahalides by the method of Woodward and Anderson.[7] Pyridinium hexachloroplumbate(IV) was prepared by the method of Gutbier and Wissmuller,[8] while tetraethylammonium hexaiodostannate(IV) was prepared according

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[1] L. A. Woodward and J. A. Creighton, *Spectrochim. Acta*, 1961, **17**, 594.

[2] (*a*) L. A. Woodward and M. J. Ware, *Spectrochim. Acta*, 1963, **19**, 775; (*b*) *ibid.*, 1964, **20**, 711.

[3] R. J. H. Clark and C. J. Willis, *Inorg. Chem.*, 1971, **10**, 1118.

[4] R. J. H. Clark and P. D. Mitchell, *J.C.S. Faraday II*, 1972, 476, and unpublished work.

[5] W. Kiefer and H. J. Bernstein, *Appl. Spectroscopy*, 1971, **25**, 501.

[6] R. J. H. Clark, *Spex Speaker*, 1973, **18**, 1.

[7] L. A. Woodward and L. E. Anderson, *J. Chem. Soc.*, 1957, 1284.

[8] K. Gutbier and H. Wissmuller, *J. prakt. Chem.*, 1914, **90**, 491.

TABLE 1

Frequencies of the Raman-active fundamentals of the MX_6^{n-} ions in aqueous acid solution and as crystalline solids (cm^{-1})

Ion	Configuration	State	Ref.	$\nu_1(a_{1g})$	$\nu_2(e_g)$	$\nu_5(t_{2g})$
SnF_6^{2-}	d^{10}	Aqueous soln.	*a*	585	470	241
		Cs^+ Salt	*b*	572	460	247
		NH_4^+ Salt	*c*	581·9 ± 0·5	465·2 ± 0·7	248·6 ± 0·6
		Aqueous soln.	*c*	584·8 ± 0·6		
$SnCl_6^{2-}$	d^{10}	Aqueous soln.	*d*	311	229	158
		Et_4N^+ Salt	*e*	309	232	159
		K^+ Salt	*f*	311 ± 2	235 ± 2	165 ± 2
		Aqueous soln.	*c*	313·1 ± 0·5	228·7 ± 0·5	156·7 ± 1·0
$SnBr_6^{2-}$	d^{10}	Aqueous soln.	*d*	185	138	96
		Et_4N^+ Salt	*e*	182	135	101
		K^+ Salt	*f*	190 ± 2	144 ± 2	109 ± 2
		Aqueous soln.	*c*	185·1 ± 0·7	138·3 ± 1·0	93·9 ± 1·0
SnI_6^{2-}	d^{10}	Et_4N Salt	*g*	122	93	78
		MeCN Soln.	*c*	135·6 ± 0·6	112·8 ± 0·6	
$PbCl_6^{2-}$	d^{10}	Aqueous soln.	*h*	285 ± 2	215 ± 5	137 ± 5
		K^+ Salt	*f*	292 ± 2	222 ± 2	153 ± 2
		Aqueous soln.	*c*	285·2 ± 0·6		
$PdCl_6^{2-}$	t_{2g}^6	Aqueous soln.	*i*	317	292	164
		K^+ Salt	*j*	317	292	164
		Aqueous soln.	*c*	317·0 ± 0·7	293·4 ± 0·5	154·3 ± 0·7
PtF_6^{2-}	t_{2g}^6	Aqueous soln.	*k*	600	576	210
		Aqueous soln.	*c*	600·0 ± 0·8	575·6 ± 1·3	
$PtCl_6^{2-}$	t_{2g}^6	Aqueous soln.	*i*	344	320	162
		K^+ Salt	*j*	344	320	162
		Na^+ Salt (hydrate)	*l*	343	319	163
		Aqueous soln.	*l*	345	324	161
		K^+ Salt	*f*	348 ± 2	318 ± 2	171 ± 2
		K^+ Salt	*m*	350	320	171
		Aqueous soln.	*c*	342·8 ± 0·5	319·3 ± 0·7	159·8 ± 1·0
$PtBr_6^{2-}$	t_{2g}^6	Aqueous soln.	*i*	207	190	97
		K^+ Salt	*f*	215 ± 2	191 ± 2	111 ± 2
		K^+ Salt	*m*	217	195	115
		Aqueous soln.	*c*	209·6 ± 0·5	192·0 ± 0·5	95·0 ± 1·0
PtI_6^{2-}	t_{2g}^6	Aqueous soln.	*c*	150·3 ± 0·5	131·0 ± 1·0	69·5 ± 1·0
$RhCl_6^{3-}$	t_{2g}^6	Aqueous soln.	*n*	336	298	
		Aqueous soln.	*c*	302·1 ± 0·5	280·4 ± 0·5	
$IrCl_6^{3-}$	t_{2g}^6	Aqueous soln.	*n*	316		175
		K^+ Salt	*o*	323	303	161
		Aqueous soln.	*c*	314·6 ± 0·5	296·3 ± 1·0	
$IrCl_6^{2-}$	t_{2g}^5	K^+ Salt	*o*	352	(295) [p]	188
		K^+ Salt	*j*	352	(225) [q]	190
		Aqueous soln.	*c*	345·7 ± 0·5	293·3 ± 0·7	160 ± 1·5
$IrBr_6^{2-}$	t_{2g}^5	K^+ Salt	*o*	216	178	
		Aqueous soln.	*o*	212	178	
		Aqueous soln.	*c*	209·6 ± 0·5	174·1 ± 0·5	97 ± 1·2
$OsCl_6^{2-}$	t_{2g}^4	Aqueous soln.	*r*	346	(274) [q]	165
		K^+ Salt	*o*	352		177
		K^+ Salt	*j*	345	(274) [q]	165
		Aqueous soln.	*c*	345·3 ± 0·7	245·2 ± 0·5	160 ± 2
$OsBr_6^{2-}$	t_{2g}^4	K^+ Salt	*o*	218	162	
		Aqueous soln.	*c*	210·6 ± 0·5	169·2 ± 0·8	100 ± 2
$ReCl_6^{2-}$	t_{2g}^3	Aqueous soln.	*r*	346	(275) [q]	159
		Aqueous soln.	*c*	346·1 ± 0·5		155·6 ± 1·0

[a] P. A. W. Dean and D. F. Evans, *J. Chem. Soc. (A)*, 1967, 698. [b] W. Klemm, J. Krause, K. Wahl, E. Huss, R. Hoppe, E. Weise, and W. Brandt, *Forschungsber. Wirtschafts u. Verkehrsministerium Nordrhein–Westfalen*, 1955, **160**, 38. [c] This work. [d] L. A. Woodward and L. E. Anderson, *J. Chem. Soc. (A)*, 1957, 1284. [e] R. J. H. Clark, L. Maresca, and R. J. Puddephatt, *Inorg. Chem.*, 1968, **7**, 1603. [f] M. Debeau and M. Krauzman, *Compt. rend.*, 1967, **264B**, 1724. [g] I. Wharf and D. F. Shriver, *Inorg. Chem.*, 1969, **8**, 914. [h] J. A. Creighton and L. A. Woodward, *Trans. Faraday Soc.*, 1962, **58**, 1077. [i] L. A. Woodward and J. A. Creighton, *Spectrochim. Acta*, 1961, **17**, 594. [j] P. J. Hendra and P. J. D. Park, *Spectrochim. Acta*, 1967, **23A**, 1635. [k] L. A. Woodward and M. J. Ware, *Spectrochim. Acta*, 1963, **19**, 775. [l] D. W. James and M. J. Nolan, *Inorg. Nuclear Chem. Letters*, 1968, **4**, 97. [m] D. M. Adams and D. M. Morris, *J. Chem. Soc. (A)*, 1967, 1666. [n] M. Debeau and M. Krauzman, *Compt. rend.*, 1966, **262B**, 765. [o] G. L. Bottger and A. E. Salwin, *Spectrochim. Acta*, 1972, **28A**, 925, 1631. [p] Calculated from force constants. [q] Derived from i.r.-active combination bands. [r] L. A. Woodward and M. J. Ware, *Spectrochim. Acta*, 1964, **20**, 711.

to the method of Wharf and Shriver.[9] Its Raman spectrum was observed using dried acetonitrile as solvent with the 377 cm^{-1} band being used as internal standard. This band was subsequently calibrated against the 935 cm^{-1} band of the perchlorate ion. In all other cases the samples were dissolved in aqueous solutions of the appropriate hydrohalogenic acid and then 60% perchloric acid was added as internal standard. The molarities of the solutions ranged from 0·004 to 0·35M.

The possibility that intermolecular interactions might bring about changes in molar intensities of the Raman bands was eliminated by studying solutions at two different mole ratios for each ion and finding good agreement between the relative molar intensities in each case.

Instrumental Techniques.—The Raman spectra were recorded using a Spex 1401 spectrometer in conjunction with Coherent Radiation Ltd. Ar$^+$ and Kr$^+$ lasers. The scattered radiation was collected at 90° and focussed by a $f/0{\cdot}95$ lens onto the entrance slit of the monochromator after having been passed through a polarisation scrambler. The 0·75 m Czerny–Turner monochromator employed two 1200 lines mm^{-1} Bausch and Lomb gratings blazed at 500 nm. The method of detection was photon counting in conjunction with an RCA C31034 phototube (linear display). The power available with the four exciting lines 488·0, 514·5, 568·2, and 647·1 nm used to gather the data was 1·6 W, 1·9 W, 100 mW, and 500 mW respectively. The spectra were calibrated by reference to the emission lines of neon.

Peak areas were determined by feeding the signal from the photomultiplier to the chart recorder and simultaneously to a Kent Chromalog Two integrator. In cases where the base line was changing rapidly, it was found to be preferable to use the trace-and-weigh procedure. The two methods were cross-checked against each other with satisfactory internal consistency.

The relative spectral response of the instrument was determined by use of a tungsten strip lamp. The relative spectral radiance of this lamp was determined at a brightness temperature of 2073 °C by comparison with a black body lamp.[10] This comparison was carried out at the National Physical Laboratory, Teddington.

Solutions were held in cylindrical cells (volume *ca.* 12 ml) which had flat bottoms, and which could be rotated at speeds of *ca.* 1600 r.p.m.[5,6] This procedure eliminated thermal decomposition of the sample at the beam focus. For cases in which ν_0 (the exciting frequency) approached ν_e (the first allowed electronic transition of the MX_6^{n-} ion), the apparent intensity of a fundamental (I_2) relative to that of a standard (I_1) can be affected by the path length (d) through which the scattered light travels, *viz.*

$$\left(\frac{I_2}{I_1}\right)_{\text{true}} = \left(\frac{I_2}{I_1}\right)_{\text{apparent}} 10^{cd(\varepsilon_2 - \varepsilon_1)} \qquad (1)$$

where c is the concentration (mol l^{-1}) of the MX_6^{n-} ion, and ε_2 and ε_1 are the extinction coefficients of the MX_6^{n-} solutions at the two scattered frequencies, $\nu_0 - \nu_2$ and $\nu_0 - \nu_1$, under comparison. Thus in all cases the exciting beam was kept as close as possible to the cell edge in order to minimise self-absorption of the scattered radiation, this being particularly important where $\varepsilon_2 - \varepsilon_1$ is significant. For the most highly absorbing solutions (*e.g.* those of the ions $IrCl_6^{2-}$, $IrBr_6^{2-}$, $OsBr_6^{2-}$, PtI_6^{2-}, and SnI_6^{2-}), grazing internal incidence was preferred. Difficulties associated with obtaining zero-path-length conditions are reflected in the higher errors in the relative molar intensities of the above deeply coloured ions.

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

RESULTS

Fundamental Frequencies.—The frequencies found for the Raman-active fundamentals of the ions studied are listed in Table 1, together with values previously reported. In each case, the band assigned to the $\nu_5(t_{2g})$ fundamental is broad and thus its frequency cannot be determined with the same accuracy as that of the $\nu_1(a_{1g})$ or $\nu_2(e_g)$ fundamentals.

For the $IrCl_6^{2-}$ and $OsCl_6^{2-}$ ions, a band attributable to the $\nu_2(e_g)$ fundamental has not previously been observed in a Raman spectrum. Values have previously been deduced for the frequency of this fundamental of each ion from the analysis of i.r.-active combination bands, but the values so obtained are not in agreement with our directly located Raman values. Accordingly, we have investigated the i.r. spectra of salts of these ions. In the case of the $OsCl_6^{2-}$ ion, for neither the potassium nor the caesium salt are there any bands at 478w and 588mw cm^{-1} as reported [2b] and assigned to the $\nu_3 + \nu_5$ and $\nu_2 + \nu_3$ combination bands respectively. The assignments for the combination bands actually seen in the i.r. spectrum of this ion are given in Table 2. These assignments allow the deduction of i.r.-based values for $\nu_2(e_g)$ and $\nu_5(t_{2g})$ which are completely consistent with the Raman-based values. A similar situation prevails for the $IrCl_6^{2-}$ ion as reinvestigation of the i.r. spectrum of the caesium salt failed to yield any evidence for a band within 40 cm^{-1} of that reported to be at 560 cm^{-1}, and assigned [11] to $\nu_2 + \nu_3$. The deduction [11] of an i.r.-based value of 225 cm^{-1} for $\nu_2(e_g)$ is thus erroneous, and there is no inconsistency with the Raman results.

TABLE 2

Frequencies and assignments of i.r.-active bands of the complexes K_2OsCl_6 and Cs_2OsCl_6 (700—200 cm^{-1})

Assignment	K_2OsCl_6	Cs_2OsCl_6
$\nu_1 + \nu_3$	668vw	667vw
$\nu_2 + \nu_3$	568vvw	
$\nu_2 + \nu_4$	417w	418w
$\nu_2 + \nu_6$	396w	396w
ν_3	325vs	313vs

The Raman spectrum of the PtI_6^{2-} ion is reported herein for the first time. The band assigned to $\nu_5(t_{2g})$ could not be observed by use of the 488·0 nm exciting line as it was obscured by Rayleigh scattering. In the case of the $IrBr_6^{2-}$ and $OsBr_6^{2-}$ ions, the $\nu_5(t_{2g})$ fundamental is reported for the first time. For $OsBr_6^{2-}$, $\nu_2(e_g)$ and $\nu_5(t_{2g})$ were observable only with the 514·5 and 488·0 nm exciting lines.

Intensities of Raman-active Fundamentals.—The intensities (I_2) of the Raman-active fundamentals of the MX_6^{n-} ions relative to that of the $\nu_1(a_1)$ fundamental of the pechlorate ion (I_1) as internal standard are given in Table 3. In each case it was necessary to correct the apparent relative intensities of the bands for the spectral response of the instrument and for the relative molarities of the

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[9] I. Wharf and D. F. Shriver, *Inorg. Chem.*, 1969, **8**, 914.

[10] T. J. Quinn and C. R. Barker, *Internat. J. Sci. Metrology*, 1967, **3**, 19.

[11] P. J. Hendra and P. J. D. Park, *Spectrochim. Acta*, 1967, **23A**, 1635.

sample and the standard; this procedure leads to the I_2M_1/I_1M_2 values listed in Table 3.

It should be noted that these values cannot be compared directly with those obtained in some cases previously, owing to the fact that any previous results were (*a*) confined only to the relative intensities of the Raman-active fundamentals, (*b*) obtained with exciting lines of different frequencies, and (*c*) obtained by use of unpolarised as against

TABLE 3

Relative molar intensities (I_2M_1/I_1M_2) of Raman-active fundamentals of the ions studied and the frequency factors

Wavelength/ nm	ν_i	(I_2M_1/I_1M_2) [a]	f [b]
		$(NH_4)_2SnF_6$ [c]	
647·1	ν_1	0·52 ± 0·06	1·845
	ν_2	0·05 ± 0·01	2·519
	ν_5	0·22 ± 0·04	6·347
568·2	ν_1	0·46 ± 0·03	1·824
	ν_2	0·04 ± 0·01	2·479
	ν_5	0·21 ± 0·04	6·201
514·5	ν_1	0·53 ± 0·04	1·809
	ν_2	0·06 ± 0·01	2·452
	ν_5	0·26 ± 0·05	6·104
488·0	ν_1	0·53 ± 0·05	1·802
	ν_2	0·05 ± 0·01	2·439
	ν_5	0·24 ± 0·04	6·057
		HCl–$SnCl_4$	
647·1	ν_1	6·1 ± 0·3	4·459
	ν_2	0·43 ± 0·04	7·251
	ν_5	1·9 ± 0·2	13·55
568·2	ν_1	6·2 ± 0·4	4·366
	ν_2	0·46 ± 0·03	7·080
	ν_5	1·7 ± 0·1	13·20
514·5	ν_1	6·5 ± 0·3	4·304
	ν_2	0·41 ± 0·04	6·966
	ν_5	1·7 ± 0·1	12·96
488·0	ν_1	6·7 ± 0·6	4·273
	ν_2	0·51 ± 0·06	6·911
	ν_5	1·7 ± 0·1	12·85
		HBr–$SnBr_4$	
647·1	ν_1	21·4 ± 1·2	10·27
	ν_2	3·4 ± 0·2	16·92
	ν_5	2·5 ± 0·1	33·45
568·2	ν_1	24·2 ± 0·9	10·01
	ν_2	4·4 ± 0·3	16·47
	ν_5	2·4 ± 0·2	32·52
514·5	ν_1	28·6 ± 1·2	9·838
	ν_2	4·6 ± 0·4	16·17
	ν_5	2·2 ± 0·2	31·90
488·0	ν_1	31·7 ± 1·5	9·755
	ν_2	5·2 ± 0·3	16·03
	ν_5	2·1 ± 0·5	31·60
		$(Et_4N)_2SnI$	
647·1	ν_1	21 ± 9	17·44
568·2	ν_1	89 ± 27	16·97
514·5	ν_1	233 ± 70	16·67
	ν_2	54 ± 12	22·94
488·0	ν_1	272 ± 110	16·52
	ν_2	104 ± 50	22·74
		$(PyH)_2PbCl_6$	
647·1	ν_1	7·4 ± 0·6	5·139
568·2	ν_1	9·0 ± 1·0	5·026
514·5	ν_1	11·3 ± 1·0	4·952
488·0	ν_1	13·0 ± 1·0	4·916
		Na_2PdCl_6	
647·1	ν_1	22·0 ± 2·0	4·377
	ν_2	21·7 ± 1·0	4·931
	ν_5	10·7 ± 1·2	14·00
568·2	ν_1	35·6 ± 2·2	4·286
	ν_2	33·0 ± 3·0	4·824
	ν_5	13·1 ± 1·8	13·64
514·5	ν_1	30·0 ± 1·8	4·225
	ν_2	32·3 ± 4·2	4·754
	ν_5	12·2 ± 1·0	13·39
488·0	ν_1	23·5 ± 1·2	4·196
	ν_2	31·8 ± 2·0	4·719
	ν_5	9·4 ± 1·2	13·28
		Na_2PtF_6	
647·1	ν_1	1·8 ± 0·2	1·784
	ν_2	0·96 ± 0·20	1·884
568·2	ν_1	1·8 ± 0·2	1·764
	ν_2	0·95 ± 0·15	1·861
514·5	ν_1	1·6 ± 0·2	1·750
	ν_2	0·73 ± 0·28	1·845
488·0	ν_1	1·6 ± 0·3	1·743
	ν_2	0·66 ± 0·32	1·838
		Na_2PtCl_6	
647·1	ν_1	10·1 ± 1·0	3·896
	ν_2	9·8 ± 0·8	4·336
	ν_5	7·2 ± 1·0	13·12
568·2	ν_1	11·5 ± 1·0	3·818
	ν_2	11·0 ± 0·9	4·246
	ν_5	8·3 ± 0·6	12·78
514·5	ν_1	12·5 ± 1·2	3·766
	ν_2	11·8 ± 1·0	4·186
	ν_5	7·7 ± 0·7	12·55
488·0	ν_1	14·3 ± 0·2	3·741
	ν_2	12·6 ± 0·5	4·157
	ν_5	5·8 ± 0·6	12·45
		Na_2PtBr_6	
647·1	ν_1	25·3 ± 3·7	8·366
	ν_2	36·8 ± 3·2	9·660
	ν_5	14·7 ± 1·1	32·82
568·2	ν_1	34·2 ± 2·7	8·163
	ν_2	45 ± 3	9·421
	ν_5	15·7 ± 1·6	31·90
514·5	ν_1	31·0 ± 2·1	8·028
	ν_2	45 ± 2	9·262
	ν_5	11·7 ± 1·1	31·30
488·0	ν_1	52 ± 5	7·963
	ν_2	64 ± 4	9·185
	ν_5	14·3 ± 2·1	31·00
		K_2PtI_6	
647·1	ν_1	104 ± 12	14·60
	ν_2	209 ± 9	18·52
	ν_5	32·2 ± 3·0	57·46
568·2	ν_1	232 ± 36	14·21
	ν_2	483 ± 60	18·02
	ν_5	47 ± 5	55·81
514·5	ν_1	406 ± 40	13·96
	ν_2	343 ± 48	17·70
	ν_5	30·4 ± 6·0	54·73
488·0	ν_1	635 ± 100	13·84
	ν_2	381 ± 120	17·54
		Na_3RhCl_6	
647·1	ν_1	7·1 ± 0·3	4·707
	ν_2	3·0 ± 0·2	5·286
568·2	ν_1	6·4 ± 0·2	4·606
	ν_2	3·1 ± 0·1	5·170
514·5	ν_1	4·7 ± 0·5	4·540
	ν_2	1·9 ± 0·4	5·092
488·0	ν_1	9·1 ± 0·8	4·507
	ν_2	4·0 ± 0·2	5·055

TABLE 3 (*Continued*)

Wavelength/ nm	ν_i	(I_2M_1/I_1M_2) [a]	f [b]
		Na_3IrCl_6	
647·1	ν_1	2·1 ± 0·3	4·427
	ν_2	1·1 ± 0·1	4·855
568·2	ν_1	2·0 ± 0·2	4·334
	ν_2	0·85 ± 0·1	4·750
514·5	ν_1	2·1 ± 0·3	4·273
	ν_2	1·3 ± 0·1	4·681
488·0	ν_1	2·1 ± 0·2	4·243
	ν_2	1·4 ± 0·2	4·647
		Na_2IrCl_6	
647·1	ν_1	9·1 ± 1·2	3·861
568·2	ν_1	10·7 ± 1·8	3·784
514·5	ν_1	96 ± 9	3·733
	ν_2	28·1 ± 3·6	4·803
	ν_5	52 ± 9	12·55
488·0	ν_1	122 ± 12	3·708
	ν_2	58 ± 6	4·768
	ν_5	116 ± 6	12·45
		K_2IrBr_6	
647·1	ν_1	106 ± 12	8·366
	ν_2	70 ± 10	11·38
	ν_5	51 ± 11	31·60
568·2	ν_1	302 ± 16	8·163
	ν_2	71 ± 6	11·09
	ν_5	121 ± 15	30·72
514·5	ν_1	8·1 ± 0·4	8·004
	ν_2	27 ± 2	10·90
	ν_5	54 ± 4	30·14
488·0	ν_1	56 ± 9	7·963
	ν_2	84 ± 8	10·81
	ν_5	31 ± 2	29·86
		Na_2OsCl_6	
647·1	ν_1	3·9 ± 0·3	3·854
	ν_2	0·58 ± 0·14	6·512
	ν_5	3·1 ± 0·2	13·12
568·2	ν_1	3·7 ± 0·3	3·777
	ν_2	0·55 ± 0·15	6·361
	ν_5	2·9 ± 0·3	12·78
514·5	ν_1	5·1 ± 0·4	3·726
	ν_2	1·4 ± 0·2	6·261
	ν_5	4·7 ± 0·2	12·55
488·0	ν_1	6·4 ± 0·5	3·701
	ν_2	2·6 ± 0·5	6·213
	ν_5	4·3 ± 0·3	12·45
		$(NH_4)_2OsBr_6$	
647·1	ν_1	11·3 ± 1·0	8·301
568·2	ν_1	10·3 ± 1·7	8·099
514·5	ν_1	36 ± 2	7·967
	ν_2	20·8 ± 3·6	11·45
	ν_5	51 ± 6	28·54
488·0	ν_1	104 ± 7	7·902
	ν_2	14·5 ± 3·0	11·35
	ν_5	56 ± 6	28·27
		$(NH_4)_2ReCl_6$	
647·1	ν_1	2·2 ± 0·3	3·841
	ν_5	4·1 ± 0·8	13·69
568·2	ν_1	2·3 ± 0·5	3·764
	ν_5	4·1 ± 1·0	13·34
514·5	ν_1	2·7 ± 0·4	3·714
	ν_5	4·1 ± 1·2	13·10
488·0	ν_1	2·9 ± 0·2	3·689
	ν_5	4·2 ± 1·0	12·99

[a] Corrected for spectral response; subscript 2 refers to the hexahalogenide, whereas 1 refers to perchlorate. [b] $f = \left(\frac{\nu_0 - \nu_2}{\nu_0 - \nu_1}\right)^4 \left(\frac{\nu_1}{\nu_2}\right) \left[\frac{1 - \exp(-hc\nu_1/kT)}{1 - \exp(-hc\nu_2/kT)}\right]$. [c] Intensity values for the $\nu_2(e_g)$ and $\nu_5(t_{2g})$ fundamentals are obtained from measurements on the solid.

polarised exciting lines. Thus even after allowing for points (*a*) and (*b*), any previous Raman intensities of non-totally symmetric fundamentals of MX_6^{n-} ions should be multiplied by the factor 7/13 to allow for the different anisotropic contributions to the Raman scattering implicit in the different situations described under point (*c*).

The frequency-corrected relative molar intensities (relative scattering activities) of the various bands at four exciting frequencies are listed in Table 4.

Bond Polarisability Derivatives.—The intensities of the $\nu_1(a_{1g})$ fundamentals of the hexahalogenide ions were used to calculate the appropriate mean molecular polarisability derivatives ($\bar{\alpha}'$) *via* the relationships [3]

$$\frac{I_2M_1}{I_1M_2} = f\left(\frac{\bar{\alpha}_2'}{\bar{\alpha}_1'}\right)^2 \left(\frac{1+\rho_2}{1+\rho_1}\right)\left(\frac{3-4\rho_1}{3-4\rho_2}\right) \tag{2}$$

where M is the molar concentration, ρ is the depolarisation ratio, and the subscript 2 refers to the hexahalogenide and 1 to perchlorate. The frequency factor f is defined as:

$$f = \left(\frac{\nu_0 - \nu_2}{\nu_0 - \nu_1}\right)^4 \left(\frac{\nu_1}{\nu_2}\right) \left[\frac{1 - \exp(-hc\nu_1/kT)}{1 - \exp(-hc\nu_2/kT)}\right] \tag{3}$$

where ν_0 is the exciting frequency, ν_2 is the Raman shift of the a_{1g} fundamental of the hexahalogenide ion, and ν_1 is the Raman shift of the a_1 fundamental of the perchlorate ion (in cm^{-1}).

The corresponding bond polarisability derivatives $\bar{\alpha}_{MX}'$ are then determined *via* the relationship

$$\left(\frac{\bar{\alpha}_2'}{\bar{\alpha}_1'}\right) = \left(\frac{6\mu_2}{4\mu_1}\right)^{\frac{1}{2}} \frac{\bar{\alpha}_{MX}'}{\bar{\alpha}_{ClO}'} \tag{4}$$

where μ is the reciprocal of the mass of the X atom. As $\rho_1 = \rho_2 = 0$ for totally symmetric modes of cubic molecules and by taking the reference value [12] $\bar{\alpha}_{ClO}'$ to be 1·73 Å^2, the last equation reduces to

$$\bar{\alpha}_{MX}' = 1{\cdot}73\left[\frac{1}{f}\left(\frac{I_2M_1}{I_1M_2}\right)\left(\frac{4\mu_1}{6\mu_2}\right)\right]^{\frac{1}{2}} \tag{5}$$

In order to obtain $\bar{\alpha}_{MX}'$ values in the absence of resonance enhancement, it is necessary to plot the $\bar{\alpha}_{MX}'$ values at each exciting frequency (ν_0) against a frequency function which describes the deviation from ν_0^4 dependence of intensity under pre-resonance conditions. The simplest frequency-correction function is that of Shorygin,[13] *viz.*

$$I_A \propto \frac{(\nu_e^2 + \nu_0^2)^2}{(\nu_e^2 - \nu_0^2)^2} \tag{6}$$

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[12] G. W. Chantry and R. A. Plane, *J. Chem. Phys.*, 1960, **32**, 319.

[13] J. Behringer, in 'Raman Spectroscopy,' ed. H. A. Szymanski, Plenum, New York, 1967, p. 168.

Dividing numerator and denominator by ν_e^8 and taking the square root of the function (since $\bar{\alpha}_{MX}'$ is a function of $I^{\frac{1}{2}}$), we plot $\bar{\alpha}_{MX}'$ *versus* the function

$$A = \frac{1 + (\nu_0/\nu_e)^2}{[1 - (\nu_0/\nu_e)^2]^2} \qquad (7)$$

where, as before, ν_e is the frequency of the first allowed electronic transition of the molecule. (The $1/\nu_e^2$ term which would appear in A is ignored as it is independent of ν_0.) Extrapolation of such a plot to the value $A = 1$ (*i.e.* $\nu_0 = 0$) gives the $\bar{\alpha}_{MX}'$ value corrected for resonance enhancement.

TABLE 4

Molar intensities of Raman-active fundamentals of MX_6^{n-} ions relative to that of the 935 cm^{-1} band of the perchlorate ion, corrected for frequency factors [a]

		Exciting wavelength/nm			
Anion	Fundamental	647·1	568·2	514·5	488·0
SnF_6^{2-}	ν_1	0·28 ± 0·03	0·25 ± 0·02	0·29 ± 0·02	0·29 ± 0·03
	ν_2	0·020 ± 0·004	0·018 ± 0·003	0·024 ± 0·004	0·022 ± 0·004
	ν_5	0·035 ± 0·006	0·035 ± 0·006	0·04 ± 0·01	0·04 ± 0·01
$SnCl_6^{2-}$	ν_1	1·37 ± 0·07	1·43 ± 0·09	1·52 ± 0·07	1·57 ± 0·14
	ν_2	0·06 ± 0·006	0·06 ± 0·005	0·06 ± 0·006	0·07 ± 0·01
	ν_5	0·14 ± 0·01	0·13 ± 0·01	0·13 ± 0·01	0·13 ± 0·01
$SnBr_6^{2-}$	ν_1	2·1 ± 0·1	2·4 ± 0·1	2·9 ± 0·1	3·2 ± 0·1
	ν_2	0·20 ± 0·01	0·27 ± 0·02	0·28 ± 0·02	0·32 ± 0·02
	ν_5	0·07 ± 0·003	0·07 ± 0·005	0·07 ± 0·005	0·07 ± 0·01
SnI_6^{2-} [b]	ν_1	1·2 ± 0·5	5·2 ± 1·6	14 ± 4	17 ± 7
	ν_2			2·3 ± 0·5	4·6 ± 2·2
$PbCl_6^{2-}$	ν_1	1·44 ± 0·11	1·79 ± 0·20	2·29 ± 0·20	2·65 ± 0·20
$PdCl_6^{2-}$	ν_1	5·0 ± 0·5	8·4 ± 0·5	7·1 ± 0·4	5·6 ± 0·3
	ν_2	4·4 ± 0·2	6·9 ± 0·6	6·8 ± 0·9	6·7 ± 0·4
	ν_5	0·76 ± 0·08	0·96 ± 0·13	0·91 ± 0·07	0·71 ± 0·08
PtF_6^{2-}	ν_1	1·03 ± 0·03	1·03 ± 0·13	0·93 ± 0·12	0·93 ± 0·18
	ν_2	0·51 ± 0·08	0·51 ± 0·08	0·40 ± 0·15	0·36 ± 0·17
$PtCl_6^{2-}$	ν_1	2·6 ± 0·3	3·0 ± 0·3	3·3 ± 0·3	3·8 ± 0·1
	ν_2	2·3 ± 0·2	2·6 ± 0·2	2·8 ± 0·3	3·0 ± 0·1
	ν_5	0·55 ± 0·08	0·65 ± 0·04	0·61 ± 0·05	0·47 ± 0·05
$PtBr_6^{2-}$	ν_1	3·0 ± 0·4	4·2 ± 0·3	3·9 ± 0·3	6·5 ± 0·7
	ν_2	3·8 ± 0·3	4·8 ± 0·3	4·8 ± 0·2	7·0 ± 0·5
	ν_5	0·46 ± 0·02	0·49 ± 0·05	0·37 ± 0·03	0·46 ± 0·07
PtI_6^{2-}	ν_1	7·1 ± 0·8	16·3 ± 2·5	29·1 ± 3·0	46 ± 7
	ν_2	11·3 ± 0·5	26·8 ± 3·0	19·4 ± 2·5	21·7 ± 6·5
	ν_5	0·56 ± 0·05	0·84 ± 0·08	0·56 ± 0·11	
$RhCl_6^{3-}$	ν_1	1·5 ± 0·1	1·4 ± 0·1	1·0 ± 0·1	2·0 ± 0·2
	ν_2	0·56 ± 0·03	0·61 ± 0·05	0·37 ± 0·08	0·78 ± 0·05
$IrCl_6^{3-}$	ν_1	0·48 ± 0·06	0·47 ± 0·04	0·50 ± 0·07	0·50 ± 0·05
	ν_2	0·23 ± 0·01	0·18 ± 0·03	0·29 ± 0·02	0·30 ± 0·04
$IrCl_6^{2-}$	ν_1	2·4 ± 0·3	2·8 ± 0·4	25·8 ± 2·4	33 ± 3
	ν_2			5·9 ± 0·8	12·1 ± 1·3
	ν_5			4·1 ± 0·7	9·3 ± 0·5
$IrBr_6^{2-}$	ν_1	12·7 ± 1·5	37 ± 2·0	1·00 ± 0·06	7·0 ± 1·1
	ν_2	6·2 ± 0·9	6·4 ± 0·5	2·48 ± 0·20	7·8 ± 0·7
	ν_5	1·62 ± 0·35	3·9 ± 0·5	1·79 ± 0·12	1·02 ± 0·08
$OsCl_6^{2-}$	ν_1	1·01 ± 0·07	0·97 ± 0·08	1·37 ± 0·10	1·74 ± 0·13
	ν_2	0·089 ± 0·020	0·085 ± 0·020	0·22 ± 0·03	0·42 ± 0·08
	ν_5	0·24 ± 0·02	0·23 ± 0·02	0·37 ± 0·02	0·35 ± 0·02
$OsBr_6^{2-}$	ν_1	1·36 ± 0·12	1·27 ± 0·21	4·55 ± 0·25	13·2 ± 0·9
	ν_2			1·82 ± 0·30	1·27 ± 0·26
	ν_5			1·80 ± 0·20	1·97 ± 0·20
$ReCl_6^{2-}$	ν_1	0·56 ± 0·08	0·61 ± 0·13	0·73 ± 0·11	0·79 ± 0·05
	ν_5	0·30 ± 0·06	0·30 ± 0·08	0·31 ± 0·09	0·33 ± 0·07

[a] The error limits refer to the scatter between the ten different measurements of each datum (five of which were carried out at one concentration of the anion, and five at a different one). Standard deviations on the data are considerably smaller than the quoted error limits. [b] Very approximate data, owing to partial solvolysis of the ion in the only suitable solvent, namely acetonitrile, and to the fact that the intensity measurements necessarily involved an intermediate standard, *viz.* the 377 cm^{-1} band of acetonitrile.

DISCUSSION

A. *General Introduction, Discussion of Intensity Changes, and the Rigorous Resonance Raman Effect.*— When the frequency of the incident light is well removed from the region of electronic absorption, it was shown by Placzek[14] that the intensity of molecular Raman scattering arises from the dependence of the ground state polarisability on nuclear vibrations. The so-called polarisability theory of Placzek has led to the bond polarisability theory commonly used to analyse vibrational Raman spectra in terms of ground-state properties of molecules. No reference to virtual states is necessary, and thus the role of excited electronic states in contributing to the polarisability is not clear. Recently, interest has developed in the resonance

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[14] G. Placzek, 'Handbuch der Radiologie,' ed. E. Marx, Akademische Verlagsgesellschaft, Leipzig, 1934, vol. VI, Part 2, p. 205.

Raman effect (r.r.e.) in which the incident frequency is made to approach that of a virtual transition and thus the role of low-lying electronic (virtual) states is much more important. Since Placzek's theory requires that the exciting frequency is far removed from the first allowed electronic transition of the molecule, the r.r.e. requires special theoretical treatment. As developed by Albrecht,[15,16] this approach takes as its starting point the Kramers–Heisenberg dispersion equation and van Vleck's expansion of this equation. Albrecht has derived a relationship between the Raman intensities of the ground state vibrations and the vibronic intensities of allowed transitions of a molecule. He found that it is the 'forbidden' character (*i.e.* vibrationally induced character) of allowed transitions which is responsible for Raman intensities. In particular, the normal mode most responsible for the 'forbidden' intensity in the lowest electronic transition of the molecule should show the greatest enhancement of its intensity as the exciting frequency approaches that of the lowest electronic transition. In molecules of O_h symmetry, all three Raman-active fundamentals could (by symmetry arguments) [17] be responsible for the mixing of the two lowest allowed electronic states and thus show resonance enhancement of their intensities as ν_0 approaches ν_e. The intensity changes with change of ν_0 for the $\nu_1(a_{1g})$, $\nu_2(e_g)$, and $\nu_5(t_{2g})$ fundamentals of the ions studied are given in Table 4, while the frequencies and extinction coefficients of the first two allowed electronic transitions of each ion are given in Table 5. (As many of the electronic spectra are very complicated the decision as to which are the first two allowed transitions is not necessarily unambiguous.)

TABLE 5

The energies of the lowest-lying charge transfer absorption bands for the hexahalogenide anions studied (aqueous soln) [a]

Anion	Colour	Ref.	Wavenumber/cm^{-1} ν_e	ν_s
SnF_6^{2-}	Colourless	*b*	$>$50,000	
$SnCl_6^{2-}$	Colourless	*c*	44,900 (*ca.* 10,000)	
$SnBr_6^{2-}$ [d]	Colourless	*e*	31,900 (*ca.* 9000)	34,900 (*ca.* 10,400)
SnI_6^{2-} [d]	Maroon	*b*	27,650	34,350
$PbCl_6^{2-}$	Yellow	*f*	32,600 (9700)	48,100 (*ca.* 24,000)
$PdCl_6^{2-}$	Deep red	*c*	29,400 (14,000)	41,700 (55,000)
PtF_6^{2-}	Yellow	*b*	$>$50,000	
$PtCl_6^{2-}$	Orange	*g*	38,200 (24,800)	49,800 (51,900)
$PtBr_6^{2-}$	Red	*c*	31,800 (18,000)	44,200 (70,000)
PtI_6^{2-}	Deep red	*c*	20,250 (12,800)	29,150 (17,000)
$RhCl_6^{3-}$	Red	*c*	39,200 (29,000)	
$IrCl_6^{3-}$	Yellow	*c*	48,500 (28,000)	
$IrCl_6^{2-}$	Brown	*c*	20,450 (3280)	23,050 (2560)
$IrBr_6^{2-}$	Purple	*c*	17,150 (3220)	18,350 (1780)
$OsCl_6^{2-}$	Red	*c*	27,000 (7300)	30,000 (7900)
$OsBr_6^{2-}$	Deep red	*c*	20,450 (5600)	22,600 (7500)
$ReCl_6^{2-}$	Green	*c, h*	35,600 (12,500)	48,000

[a] Values in parentheses indicate molar extinction coefficients where available. [b] This work; in cases where the value of ν_s is unknown, it is taken to be 50,000 cm^{-1} in the calculations of intensity functions. [c] C. K. Jørgensen, *Mol. Phys.*, 1959, **2**, 309. [d] Measurements taken in acetonitrile solution. [e] R. A. Walton, R. W. Matthews, and C. K. Jørgensen, *Inorg. Chim. Acta*, 1967, **1**, 355. [f] H. G. Heal and J. May, *J. Amer. Chem. Soc.*, 1958, **80**, 2374. [g] C. K. Jørgensen and J. S. Brinen, *Mol. Phys.*, 1962, **5**, 535. [h] J. C. Eisenstein, *J. Chem. Phys.*, 1961, **34**, 1628.

In general, it is apparent from the data in Table 4 that the fundamentals $\nu_1(a_{1g})$ and $\nu_2(e_g)$ show the greatest pre-r.r.e., and that the extent of the enhancement increases with decrease in $\nu_e - \nu_0$. Thus for the PtX_6^{2-} ions, the $(1/f)(I_2M_1/I_1M_2)$ values for ν_1 change by the factors *ca.* 0, 1·5, 2·2, and 6·5 from 647·1 to 488·0 nm excitation as X changes from F to Cl to Br to I. The effect in the case of the PtI_6^{2-} ion is illustrated in Figure 1. The relationship between the frequencies of

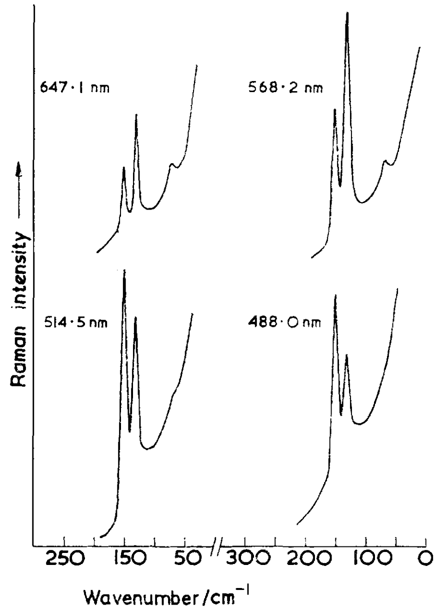

FIGURE 1 Raman spectra of the PtI_6^{2-} ion at the four exciting wavelengths 647·1, 568·2, 514·5, and 488·0 nm, showing the pronounced pre-r.r.e. on the $\nu_1(a_{1g})$ fundamental of this ion

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[15] A. C. Albrecht, *J. Chem. Phys.*, 1960, **33**, 156.

[16] A. C. Albrecht, *J. Chem. Phys.*, 1961, **34**, 1476.

[17] The symmetry species to which the electronic states *e* and *s* belong is T_{1u} for molecules and ions of the symmetry point group O_h. (*E.g.* ions with the electronic configuration t_{2g}^0, t_{2g}^3, t_{2g}^6, or $t_{2g}^6e_g^4$.)

the exciting lines and the electronic spectra of those complex ions which possess very detailed spectra in the visible region, *viz.* $IrCl_6^{2-}$, $IrBr_6^{2-}$, $OsBr_6^{2-}$, and PtI_6^{2-}, are shown in Figure 2. For the d^6 and d^{10} ions (with the exception of the two iodides) there is no systematic variation in the ratio of the scattering activities of the $\nu_1(a_{1g})$ and $\nu_2(e_g)$ fundamentals on change of ν_0 from 647·1 to 488·0, but for the ions of the t_{2g}^4 and t_{2g}^5 configurations ($OsCl_6^{2-}$, $OsBr_6^{2-}$, $IrCl_6^{2-}$, and $IrBr_6^{2-}$), the $\nu_2(e_g)$ fundamental shows selective enhancement. Thus although the ratios of the $(1/f)(I_{2M_1}/I_{1M_2})$ values for the $\nu_1(a_{1g})$ and $\nu_2(e_g)$ fundamentals of the $IrCl_6^{2-}$ and $IrCl_6^{3-}$ ions are comparable using 488·0 nm excitation, that of the $IrCl_6^{2-}$ ion is immeasurably bigger than that of the $IrCl_6^{3-}$ ion using 647·1 nm excitation.

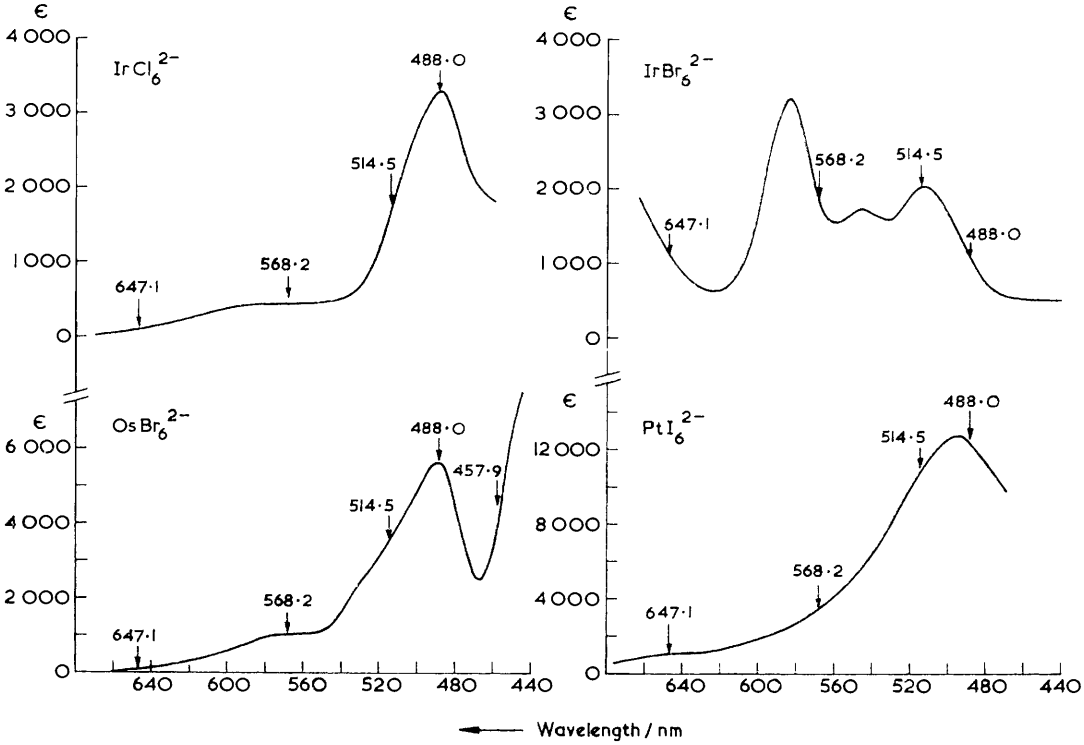

FIGURE 2 Electronic spectra of the $IrCl_6^{2-}$, $IrBr_6^{2-}$, $OsBr_6^{2-}$, and PtI_6^{2-} ions showing the positions of the Raman exciting lines relative to the absorption bands of each complex ion

Rigorous resonance Raman spectra may be observed in those cases in which the exciting frequency lies within the electronic band. The effect is characterised by a pronounced increase in the intensity of overtones of the totally symmetric fundamental.[18,19] The observation of resonance Raman spectra thus seemed likely in the cases of those ions for which available exciting frequencies coincided or nearly coincided with the frequency of an allowed electronic transition in the ion. Hence (Table 5) for the $IrCl_6^{2-}$ ion ($\nu_e = 20\,450$ cm^{-1}, ε 3280) resonance seems probable with 488·0 nm excitation. Similarly for the $OsBr_6^{2-}$ ion ($\nu_e = 20\,450$, ε 5600), the $IrBr_6^{2-}$ ion ($\nu_e = 17\,150$, ε 3220) and the PtI_6^{2-} ion ($\nu_e = 20\,250$ cm^{-1}, ε 12 800) resonance seems likely with 488·0 nm, 568·2 nm, and either 514·5 or 488·0 nm excitation respectively.

Careful study of the above ions under the stated conditions has led, as expected, to the observation of overtones with all the ions mentioned but in no case was the progression observed to exceed $3\nu_1$ (Table 6).

TABLE 6

Overtones of the $\nu_1(a_{1g})$ fundamental observed for complex ions under r.r.e. conditions (cm^{-1})

Ion	ν_1	$2\nu_1$	$3\nu_1$	λ_0/nm
$IrCl_6^{2-}$	345·7 ± 0·5	690·9 ± 1·3		488·0
$OsBr_6^{2-}$	210·6 ± 0·5	421·2 ± 1·0		457·9
$IrBr_6^{2-}$	209·6 ± 0·5	420·5 ± 1·0	630 ± 2	568·2
PtI_6^{2-}	150·3 ± 0·5	299·2 ± 1·0		514·5 and 488·0

In the light of earlier observations of progressions in the $\nu_1(a_1)$ fundamental of titanium [20] and tin tetraiodides [21] under resonance conditions to $13\nu_1$ and $11\nu_1$ respectively, these results were disappointing. The $\nu_1(a_{1g})$ fundamental vibration was harmonic within experimental error in each case.

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[18] W. Holzer, W. F. Murphy, and H. J. Bernstein, *J. Chem. Phys.*, 1970, **52**, 399.

[19] L. A. Nafie, P. Stein, and W. L. Peticolas, *Chem. Phys. Letters*, 1971, **12**, 131.

[20] R. J. H. Clark and P. D. Mitchell, *J. Amer. Chem. Soc.*, 1973, **95**, 8300.

[21] R. J. H. Clark and P. D. Mitchell, *J.C.S. Chem. Comm.*, 1973, 762.

In the case of the PtI_6^{2-} ion, the first overtone of $\nu_2(e_g)$ is apparent in the Raman spectrum when the latter is obtained using 568·2, 514·5, or 488·0 nm excitation. It occurs at 261·9 ± 0·5 cm^{-1} (*cf.* $\nu_2 = 131{\cdot}0 \pm 0{\cdot}9$ cm^{-1}).

B. *Choice of Pre-resonance Raman Effect Functions.*—It was stated earlier that in order to derive a value for the bond-polarisability derivative in the absence of resonance enhancement it is necessary to plot the $\bar{\alpha}_{MX}'$ values obtained for each exciting frequency against an appropriate frequency function and to extrapolate to zero exciting frequency. The simplest frequency function, due to Shorygin, is given above (equation 7). Albrecht has derived a different expression for the dependence of the intensity of Raman bands on ν_0 and ν_e, an expression which emphasises the importance of vibronic coupling of the two lowest-lying dipole-allowed electronic states ν_e and ν_s. The frequency correction expression is [15,16]

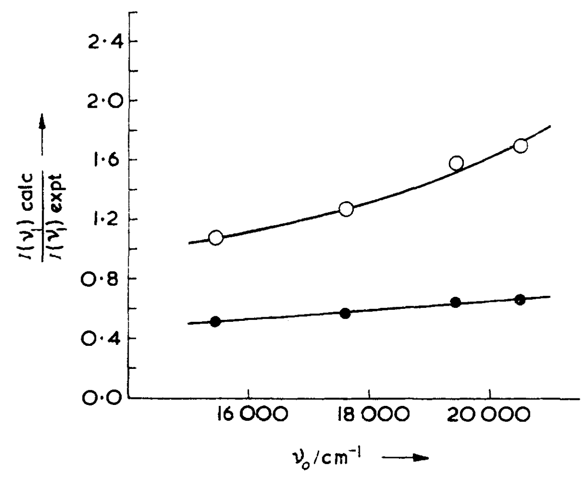

FIGURE 3 Plot of the value of the Shorygin (I_A) and Albrecht (I_B) frequency functions [$I(\nu_1)$ calc] divided at each exciting frequency (ν_0) by the value of $(1/f)(I_2M_1/I_1M_2)$ for the $\nu_1(a_{1g})$ fundamental of Na_2PtCl_6 [$I(\nu_1)$ expt] against ν_0 (○, ● respectively)

$$I_B \propto \frac{(\nu_e\nu_s + \nu_0^2)^2}{(\nu_e^2 - \nu_0^2)^2(\nu_s^2 - \nu_0^2)^2} \qquad (8)$$

A further expression, due to Peticolas *et al.*,[22] simplifies in the case of an O_h molecule to give:

$$I_C \propto \left[\frac{1}{(\nu_e - \nu_0)(\nu_s - \nu_0)} + \frac{1}{(\nu_e + \nu_0)(\nu_s + \nu_0)}\right]^2 \qquad (9)$$

which is identical to that of Albrecht.

In order to test which expression best describes the observed intensity enhancement of the $\nu_1(a_{1g})$ mode for each ion with changing exciting frequency, the ratio of the calculated to the experimental intensity has been plotted *versus* ν_0 for each of the four exciting lines. The results are shown in Figure 3 for the $PtCl_6^{2-}$ ion. It is seen that the plot is more nearly ' horizontal ' in the case of Albrecht's function than of Shorygin's function. This result was found to apply to all the hexahalogenide ions studied and therefore Albrecht's function has been preferred to Shorygin's to determine bond polarisability derivatives at zero exciting frequency. This conclusion is in agreement with that of Innes *et al.*[23] on pyrazine, and it demonstrates the importance of two, rather than one, electronic states in determining Raman intensities.

C. *Discussion of $\bar{\alpha}_{MX}'$ Values, and Derivation of γ_n' Values.*—The resulting values of $\bar{\alpha}_{MX}'$ at $\nu_0 = 0$ for each ion are listed in Table 7. In the case of the d^{10} ions SnF_6^{2-}, $SnCl_6^{2-}$, $SnBr_6^{2-}$, $PbCl_6^{2-}$, the d^3 ion $ReCl_6^{2-}$, the d^4 ion $OsCl_6^{2-}$ and the d^6 ions $IrCl_6^{3-}$, PtF_6^{2-}, and $PtCl_6^{2-}$, plots of $\bar{\alpha}_{MX}'$ *versus* the Albrecht function give straight lines which allow easy extrapolation of $\bar{\alpha}_{MX}'$ to $\nu_0 = 0$ (see Figures 4 and 5). Thus $\bar{\alpha}_{MX}'$ values corrected for the pre-r.r.e. can readily be obtained. The pre-resonance behaviour of the $\nu_1(a_{1g})$ fundamentals and of the derived $\bar{\alpha}_{MX}'$ values for these ions thus closely parallel that reported [3] for the $\nu_1(a_1)$ fundamentals and the $\bar{\alpha}_{MX}'$ values respectively of tetrahedral molecules MX_4.

The pre-r.r.e. behaviour of $\bar{\alpha}_{MX}'$ is similar for several of the other d^6 ions studied, *viz.* $PtBr_6^{2-}$, $PdCl_6^{2-}$, and $RhCl_6^{3-}$, except that deviations from the straight line plot are evident in each case with 488·0 nm excitation. It seems possible that these deviations are brought about

TABLE 7

Comparison of $\bar{\alpha}_{MX}'$ values obtained by extrapolation of Albrecht's and Shorygin's plots to zero exciting frequency

Anion	$\bar{\alpha}_{MX}'$ (Shorygin) /Å^2	$\bar{\alpha}_{MX}'$ (Albrecht) /Å^2	Points [a]	γ_{MX} [b] /Å^3
SnF_6^{2-}	0·81	0·81	4	0·6 [c]
$SnCl_6^{2-}$	2·3	2·3	4	2·0
$SnBr_6^{2-}$	3·9	3·9	4	2·4
SnI_6^{2-} [d]	*ca.* 5	*ca.* 5		
$PbCl_6^{2-}$	2·0	1·8$_5$	4	
$PdCl_6^{2-}$	2·2	1·9$_5$	2	4·4
PtF_6^{2-}	1·5	1·5	4	
$PtCl_6^{2-}$	2·8	2·7	4	3·8
$PtBr_6^{2-}$	4·0	3·6$_5$	4	5·5
PtI_6^{2-}	8·4	6·6	2	8·3
$RhCl_6^{3-}$	2·0$_5$	2·0	4	
$IrCl_6^{3-}$	1·4	1·4	4	
$IrCl_6^{2-}$	3·1	3·0$_5$	2	
$OsCl_6^{2-}$	1·7	1·7	4	2·5
$OsBr_6^{2-}$	3·6	3·6	2	
$ReCl_6^{2-}$	1·3$_5$	1·3$_5$	4	2·8

[a] Number of points used in extrapolation; two points refer to 647·1 and 568·2 nm data only, three points to 647·1, 568·2, and 514·5 nm data and four points to the use of all four exciting lines. [b] The r_{MX} values were taken to be 2·00, 2·43, and 2·64 Å for the SnF_6^{2-}, $SnCl_6^{2-}$, and $SnBr_6^{2-}$ ions respectively, and 2·35, 2·49, and 2·68 Å for the other chlorides, bromides, and iodides respectively (except for $r_{PdCl} = 2{\cdot}32$ Å). [c] Value based on solid state intensity measurements. [d] Very approximate, see footnote to Table 4.

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[22] W. L. Peticolas, L. Nafie, P. Stein, and B. Fanconi, *J. Chem. Phys.*, 1970, **52**, 1576.

[23] A. H. Kalantar, E. S. Franzosa, and K. K. Innes, *Chem. Phys. Letters*, 1972, **17**, 335.

by the influence of low-lying, intense ligand field bands which may be stealing intensity from allowed transitions.

For the t_{2g}^4 and t_{2g}^5 ions $IrCl_6^{2-}$, $IrBr_6^{2-}$, and $OsBr_6^{2-}$ as well as for PtI_6^{2-} the Albrecht plots were not satisfactory. These ions have very complicated electronic spectra with many low-lying charge-transfer bands and many relatively intense ligand field bands throughout the visible region (Figure 2). No satisfactory method for extrapolating $\bar{\alpha}_{MX}'$ values to zero exciting frequency could be found in these cases, and the values could only be estimated (albeit very crudely) from the 647·1 and 568·2 nm values.

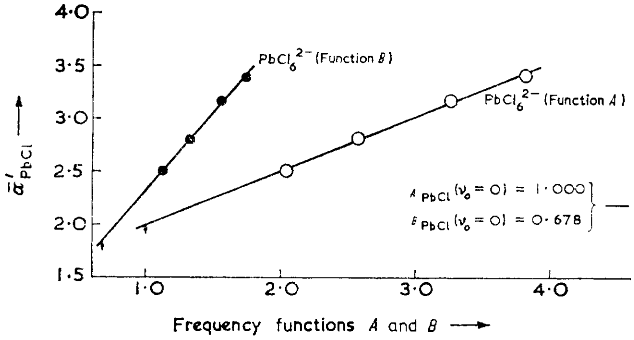

FIGURE 4 Plot of $\bar{\alpha}_{PbCl}'$ against the Shorygin function $A = [1 + (\nu_0/\nu_e)^2]/[1 - (\nu_0/\nu_e)^2]^2$ and the Albrecht function $B = [(\nu_s/\nu_e) + (\nu_0/\nu_e)^2]/[1 - (\nu_0/\nu_e)^2][(\nu_s/\nu_e)^2 - (\nu_0/\nu_e)^2]$ at four different exciting wavelengths (647·1, 568·2, 514·5, and 488·0 nm, reading from left to right on the plot) (○, ● respectively). Values for ν_e and ν_s are taken from Table 5

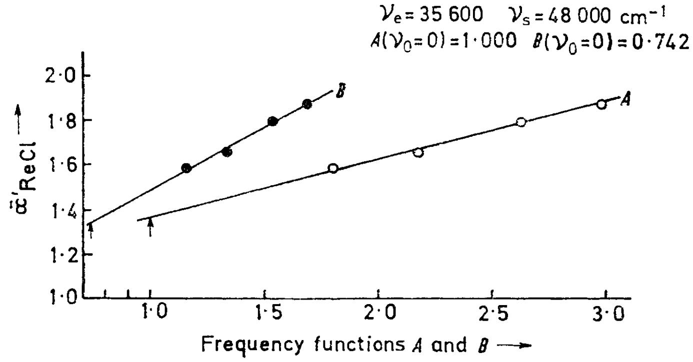

FIGURE 5 Plot of $\bar{\alpha}_{ReCl}'$ of the $ReCl_6^{2-}$ ion against the Shorygin (A) and Albrecht (B) frequency functions at 647·1, 568·2, 514·5, and 488·0 nm. The ν_e and ν_s values are taken from Table 5

The results shown in Table 7 allow the following conclusions to be drawn: (a) bond polarisability derivatives increase in the order $\bar{\alpha}_{MF}' < \bar{\alpha}_{MCl}' < \bar{\alpha}_{MBr}' < \bar{\alpha}_{MI}'$, in agreement with all previous results of this sort. This result is considered to arise on account of the increased polarisability of the heavier halogen atoms and of the increase in the degree of covalent character of the MX bond in the order MF < MCl < MBr < MI; this behaviour is in line with the delta function description of the $\bar{\alpha}_{MX}'$ values.[24] Independent evidence that the degree of covalent character of MX bonds increases in this order is provided by the n.q.r. results listed in Table 8, in which it is also evident that the degree of covalent character of SnX bonds is less than that for PtX bonds, in line with the same behaviour of $\bar{\alpha}_{MX}'$ values. The reason for this difference is believed to be associated with the use of outer rather than inner d-orbitals in the hybridisation scheme.

TABLE 8

Comparison of the degree of covalent character of MX bonds (n.q.r. results) and $\bar{\alpha}_{MX}'$ values (Å^2)

	N.q.r. data [a]				α_{MX}'
Compound	Config.	π	σ	Ref.	(This work)
K_2SnCl_6	d^{10}	0	0·34	b	2·3
K_2SnBr_6	d^{10}	0	0·40	c	3·9
Rb_2SnI_6	d^{10}	0	0·45	b	*ca.* 5
$(NH_4)_2PbCl_6$	d^{10}	0	0·37	b	$1·8_5$
K_2PdCl_6	t_{2g}^6	0	0·57	d	$1·9_5$
K_2PtCl_6	t_{2g}^6	0	0·56	e	2·7
K_2IrCl_6	t_{2g}^5	0·054	0·48	f	$3·0_5$
K_2OsCl_6	t_{2g}^4	0·108	0·43	f	1·7
K_2ReCl_6	t_{2g}^3	0·16	0·39	g	$1·3_5$
K_2PtBr_6	t_{2g}^6	0	0·62	e	$3·6_5$
K_2ReBr_6	t_{2g}^3	0·16	0·45	g	
K_2PtI_6	t_{2g}^6	0	0·70	e	6·6
K_2ReI_6	t_{2g}^3	0·16	0·52	g	

[a] The σ-values (degrees of σ-bond covalent character) are obtained from the nuclear quadrupole coupling constant of the halogen atom on the assumption of the stated amount (π) of π-bond covalent character; the latter are based on the e.s.r. measurements on the $IrCl_6^{2-}$ ion. [b] D. Nakamura, *Bull. Chem. Soc. Japan*, 1963, **36**, 1662. [c] D. Nakamura, K. Ito, and M. Kubo, *Inorg. Chem.*, 1962, **1**, 592. [d] K. Ito, D. Nakamura, Y. Kurita, K. Ito, and M. Kubo, *J. Amer. Chem. Soc.*, 1961, **83**, 4526. [e] D. Nakamura, Y. Kurita, K. Ito, and M. Kubo, *J. Amer. Chem. Soc.*, 1960, **82**, 5783. [f] K. Ito, D. Nakamura, K. Ito, and M. Kubo, *Inorg. Chem.*, 1963, **2**, 690. [g] R. Ikeda, D. Nakamura, and M. Kubo, *J. Phys. Chem.*, 1965, **69**, 2101.

(b) Bond polarisability derivatives increase with t_{2g} orbital occupancy (with the apparent exception of the t_{2g}^5 configuration) along a series of complex ions in which the metal atom belongs to the same row of the transition series, *viz.* ($\bar{\alpha}_{MCl}'$ values in parentheses)

$$Re^{IV}, t_{2g}^3, (1·3_5) < Os^{IV}, t_{2g}^4, (1·7) < Ir^{IV}, t_{2g}^5, (3·0_5) \sim Pt^{IV}, t_{2g}^6, (2·7)\ \text{Å}^2$$

This result implies an increase in the degree of σ-bond covalent character along the series from rhenium(IV) to platinum(IV) (the π-bond order decreases along this series, see later discussion). This conclusion is in agreement with both the results of n.q.r. measurements (coupled with e.s.r. measurements on the $IrCl_6^{2-}$ ion),[25] and with molecular orbital calculations [26] on these ions.

(c) Bond polarisability derivatives increase with increase in the oxidation state of the metal atom, *viz.*:

$$\bar{\alpha}_{Ir^{III}Cl}', 1·4\ \text{Å}^2 < \bar{\alpha}_{Ir^{IV}Cl}', 3·0\ \text{Å}^2$$

This result suggests that the degree of covalent character of MX bonds increases with increase in the oxidation state of the metal atom, a conclusion already discussed

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[24] T. V. Long and R. A. Plane, *J. Chem. Phys.*, 1965, **43**, 457.

[25] M. Kubo and D. Nakamura, *Adv. Inorg. Chem. Radiochem.*, 1966, **8**, 257.

[26] F. A. Cotton and C. B. Harris, *Inorg. Chem.*, 1967, **6**, 376.

on the basis of changes in MX stretching frequencies[27] and on the basis of the observed reductions in the inter-electronic repulsion Racah parameter B on increase in the oxidation states of the metal atoms.[28,29]

The scattering activities of the $\nu_2(e_g)$ fundamental of the MX_6^{n-} ions are determined by the quantities

$$\bar{\alpha}_2' = 0,\ \gamma_2' = (3/m_X)^{\frac{1}{2}}\gamma_{MX}' \qquad (10)$$

where $\gamma_{MX}' = \alpha_{\parallel}' - \alpha_{\perp}'$, the difference between the parallel and perpendicular MX bond polarisability derivatives; these last two quantities are evaluated and discussed in the next section.

The scattering activities of the $\nu_5(t_{2g})$ fundamentals of the ions are determined by the quantities

$$\bar{\alpha}_5' = 0,\ \gamma_5' = (2/r_{MX})(3/m_X)^{\frac{1}{2}}\gamma_{MX} \qquad (11)$$

where r_{MX} is the MX bond length (in Å), and γ is the MX bond anisotropy $(\alpha_{\parallel} - \alpha_{\perp})$ (in Å^3). The scattering activities of the $\nu_5(t_{2g})$ fundamentals are always low (in most cases the lowest of the three Raman-active fundamentals). The values calculated for γ_{MX} in each case are based on the 647·1 nm results and are included in Table 7; they evidently range from 0·6 to 8·3 Å^3, and increase in the order $\gamma_{MCl} < \gamma_{MBr} < \gamma_{MI}$.

TABLE 9

Perpendicular ($\alpha_{\perp}'$) and parallel ($\alpha_{\parallel}'$) components of the bond-polarisability derivative for some octahedral anions, based on $\bar{\alpha}_{MX}'$ ($\nu_0 = 0$)[a] values and the relative intensities of the $\nu_1(a_{1g})$ and $\nu_2(e_g)$ bands on 647·1 nm excitation

Anion	$\bar{\alpha}_{MX}'$/ Å^2	$f(\nu_2)/f(\nu_1) \times I(\nu_1)/I(\nu_2)$	$\alpha_{\perp}'/\alpha_{\parallel}'$	$\alpha_{\perp}'$/Å^2	$\alpha_{\parallel}'$/Å^2	$\alpha_{\perp}'/\alpha_{\parallel}'$	$\alpha_{\perp}'$/Å^2	$\alpha_{\parallel}'$/Å^2
SnF_6^{2-}	0·81	>50	*ca.* 1·00[b]	*ca.* 0·81	*ca.* 0·81	*ca.* 1·0	*ca.* 0·81	*ca.* 0·81
$SnCl_6^{2-}$	2·3	23·2	0·61[c]	1·9	3·1	1·8	2·7	1·5
$SnBr_6^{2-}$	3·9	10·4	0·48	$2{\cdot}8_5$	5·9	$2{\cdot}6_5$	4·9	1·8
$PbCl_6^{2-}$	$1{\cdot}8_5$		*ca.* 1·00[b]	*ca* $1{\cdot}8_5$	*ca.* $1{\cdot}8_5$	*ca.* 1·0	*ca.* $1{\cdot}8_5$	$-1{\cdot}8_5$
$PdCl_6^{2-}$	$1{\cdot}9_5$	1·14	0·08	0·41	5·0	−3·1	3·5	$-1{\cdot}1_5$
PtF_6^{2-}	1·5	2·02	0·19[d]	0·62	$3{\cdot}3_5$	−8·4	2·4	−0·29
$PtCl_6^{2-}$	2·7	1·15	0·08[e]	0·56	6·9	−3·1	4·8	−1·6
$PtBr_6^{2-}$	$3{\cdot}6_5$	0·80	0·02	0·19	10·6	−2·2	7·1	−3·3
PtI_6^{2-}	6·6	0·63	−0·02	−0·43	20·7	−1·8	13·6	−7·5
$RhCl_6^{3-}$	2·0	2·70	0·24	0·98	4·1	−51·6	3·0	−0·06
$IrCl_6^{3-}$	1·4	2·12	0·19	0·58	3·0	−9·7	2·2	−0·22
$IrCl_6^{2-}$	$3{\cdot}0_5$		*ca.* 1·0[b]	*ca.* 3·0	*ca.* 3·0	*ca.* 1·0	*ca.* 3·0	*ca.* 3·0
$OsCl_6^{2-}$	1·7	11·3	0·50	1·3	$2{\cdot}5_5$	2·5	2·1	0·85
$OsBr_6^{2-}$	3·6		*ca.* 1·0[b]	*ca.* 3·6	*ca.* 3·6	*ca.* 1·0	*ca.* 3·6	*ca.* 3·6
$ReCl_6^{2-}$	$1{\cdot}3_5$		*ca.* 1·0[b]	*ca.* $1{\cdot}3_5$	*ca.* $1{\cdot}3_5$	*ca.* 1·0	*ca.* $1{\cdot}3_5$	*ca.* $1{\cdot}3_5$

[a] Extrapolated to $\nu_0 = 0$ by way of Albrecht's function (Table 7). [b] $I(\nu_2)$ was too weak to be measured using 647·1 nm excitation. [c] The value 0·55 was obtained in ref. 1. [d] The value 0·39 obtained in ref. 2 is evidently incorrect. [e] The value 0·12 was obtained in ref. 1.

Derivation and Discussion of $\alpha_{\parallel}'$ *and* $\alpha_{\perp}'$.—From the relative scattering activities of the $\nu_1(a_{1g})$ and $\nu_2(e_g)$ fundamentals of MX_6 species, it is possible to deduce values for the ratio of the perpendicular ($\alpha_{\perp}'$) and parallel ($\alpha_{\parallel}'$) components of the MX bond polarisability derivatives. The relationship,[1,2a] which is based on the Wolkenstein assumptions,[30,31] is as follows:

$$\frac{I(\nu_1)}{I(\nu_2)} = \frac{f(\nu_1)}{f(\nu_2)} \cdot \left[\frac{5(1 + 2\alpha_{\perp}'/\alpha_{\parallel}')^2}{7(1 - \alpha_{\perp}'/\alpha_{\parallel}')^2}\right] \qquad (12)$$

In this equation, $I(\nu_1)$ and $I(\nu_2)$ are the intensities of the $\nu_1(a_{1g})$ and $\nu_2(e_g)$ fundamentals respectively, f is the frequency factor defined previously [equation (3)], and the numerical factor 5/7 on the right hand side of the equation differs from that given originally (5/13),[1,2a] because the present analysis is based on polarised incident light whereas the previous one was based on unpolarised incident light.

The MX bond polarisability derivatives at zero exciting frequency (Table 7) are related to $\alpha_{\perp}'$ and $\alpha_{\parallel}'$ as follows:

$$\bar{\alpha}_{MX}' = \tfrac{1}{3}(\alpha_{\parallel}' + 2\alpha_{\perp}') \qquad (13)$$

Consequently equations (12) and (13) provide two relationships, on the basis of which values for both $\alpha_{\parallel}'$ and $\alpha_{\perp}'$ for an MX bond of any MX_6 species may be deduced. Two solutions to $\alpha_{\perp}'/\alpha_{\parallel}'$ are obtained from equation (12) (Table 9) and these are shown graphically in Figure 6 for the $PtCl_6^{2-}$ ion, for which $f(\nu_1)/f(\nu_2) = 0{\cdot}899$. (The latter lies between 0·592 and 0·947 for the ions studied.) One root for $\alpha_{\perp}'/\alpha_{\parallel}'$, the one which we have accepted, lies between −0·5 and +2·86 for $I(\nu_1)/I(\nu_2)$ ranging from 0 to ∞; this root increases monotonically with increase in $I(\nu_1)/I(\nu_2)$ and it corresponds to the root previously accepted in the belief[1,2,32] that $\alpha_{\perp}'/\alpha_{\parallel}'$ should lie between 0 and +1. It is now apparent that the choice of this root can be substantiated as follows. The alternative root corresponds to the two branches for which $\alpha_{\perp}'/\alpha_{\parallel}'$ lies between $-\infty$ and −0·5 and +2·86 and $+\infty$. The transition from the value $-\infty$ to $+\infty$ for $\alpha_{\perp}'/\alpha_{\parallel}'$ occurs either side of the $I(\nu_1)/I(\nu_2)$

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[27] R. J. H. Clark, *Spectrochim. Acta*, 1965, **21**, 955.

[28] T. M. Dunn, *J. Chem. Soc.*, 1959, 623.

[29] C. K. Jørgensen, 'Absorption Spectra and Chemical Bonding in Complexes,' Pergamon, Oxford, 1962, p. 134.

[30] M. Eliashevich and M. Wolkenstein, *J. Phys. U.S.S.R.*, 1945, **9**, 101, 326.

[31] G. W. Chantry, in 'The Raman Effect,' ed. A. Anderson, Dekker, New York, 1971, p. 49.

[32] G. W. Chantry and R. A. Plane, *J. Chem. Phys.*, 1960, **33**, 634.

ratio of 2·86, a situation which, although being mathematically feasible, is physically unacceptable. Accordingly the first solution is the only one which is considered further. The relative scattering activities obtained with 647·1 nm excitation were used in each case, as the results were then least likely to be affected by a selective pre-r.r.e. on either of the two bands (*cf.* section A).

Although the $f(\nu_2)/f(\nu_1) : I(\nu_1)/I(\nu_2)$ ratio does depend on the exciting wavelength for some ions (*e.g.* the t_{2g}^4 and t_{2g}^5 ions), this is not the case for the $PtCl_6^{2-}$ ion (in agreement with the qualitative result of Woodward and Creighton)[1] or for the $PdCl_6^{2-}$ ion ($\lambda_0 \geqslant 514{\cdot}5$ nm), the $PtBr_6^{2-}$ ion, or for many other ions. Thus the small value for this ratio (0·6—2·7) for all t_{2g}^6 ions cannot be ascribed to a selective pre-r.r.e. on the $\nu_2(e_g)$ fundamental, and an alternative explanation of this result must be sought in terms of the $\alpha_{\parallel}'$ and $\alpha_{\perp}'$ values. Note that the variation of $f(\nu_2)/f(\nu_1) : I(\nu_1)/I(\nu_2)$ ratios for the $OsCl_6^{2-}$ and $OsBr_6^{2-}$ ions with ν_0 is directly contrary to the report by Bottger and Damsgard,[33] who used solid materials and who may have made no corrections for spectrometer response.

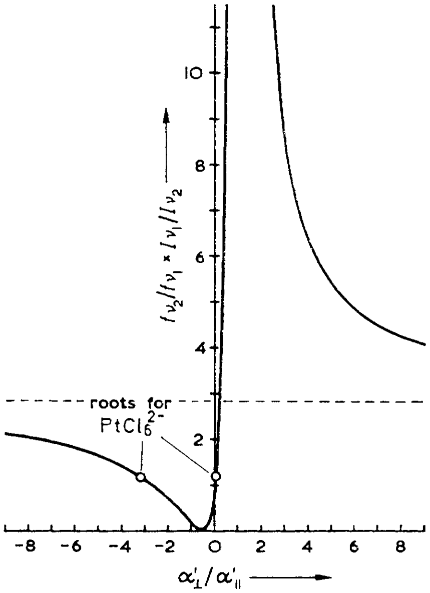

FIGURE 6 Plot of $\alpha_{\perp}'/\alpha_{\parallel}'$ *versus* $f(\nu_2)/f(\nu_1) \times I(\nu_1)/I(\nu_2)$ showing the two possible roots for the $PtCl_6^{2-}$ ion

The results indicate that $\alpha_{\parallel}'$ varies in the following manner:

(*a*) $MF_6^{2-} < MCl_6^{2-} < MBr_6^{2-} < MI_6^{2-}$ *viz.* for the platinum(IV) series, the values of $\alpha_{\parallel}'$ are 3·3, 6·9, 10·6, and *ca.* 20 Å^2 respectively. The increase along this series parallels that expected on the basis of the delta-function potential model[24] (see earlier discussion of $\bar{\alpha}_{MX}'$ values), while the fact that the platinum(IV) series has considerably higher values for $\alpha_{\parallel}'$ than the tin(IV) series is consistent with the higher degree of covalent character of the PtX than the SnX bonds (Table 8).

(*b*) $\alpha_{\parallel}'$ increases with increase in t_{2g} orbital occupancy *viz.*

$$\mathrm{Re^{IV}},\ t_{2g}^3,\ 1{\cdot}35 < \mathrm{Os^{IV}},\ t_{2g}^4,\ 2{\cdot}5_5 < \mathrm{Ir^{IV}},\ t_{2g}^5,\ 3{\cdot}0 < \mathrm{Pt^{IV}},\ t_{2g}^6,\ 6{\cdot}9\ \text{Å}^2.$$

This result suggests that the change in the parallel component of the polarisability of the MX bond on stretching the bond increases with increase in the degree of σ-bond covalent character of the MX bond and/or with decrease in π-bond order [$p_\pi(X) \longrightarrow d_\pi(M)$ type].[25] The molecular orbital calculations of Cotton and Harris[26] suggest that the former is the dominant factor.

(*c*) $\alpha_{\parallel}'$ values for the SnX bonds of the SnX_6^{2-} ions are about half of those for the tin tetrahalogenides (which range from 7·1 to 15·0 Å^2).[34] This result also strongly suggests that $\alpha_{\parallel}'$ is directly related to the degree of covalent character of the MX bond, because there can be little doubt that the SnX bond of SnX_4 is much more covalent than that of the corresponding SnX_6^{2-} ion.

The $\alpha_{\perp}'$ values are in all cases small and much less sensitive to change of halogen atom, being 0·3 ± 0·7 for all the t_{2g}^6 ions but 2·2 ± 1·4 for all the remaining ions. Their interpretation in terms of bonding patterns in the complex ions seems obscure. In this context it is worth noting that the $\alpha_{\perp}'$ values for the SnX bonds of the $SnCl_6^{2-}$ and $SnBr_6^{2-}$ ions (Table 9) are similar to those of the tetrahalogenides $SnCl_4$, $SnBr_4$, and SnI_4 (2·0, 3·0, and 3·0 Å^2 respectively).[34]

It has previously been argued[1,2a] that the ratio $\alpha_{\perp}'/\alpha_{\parallel}'$ for the PtF_6^{2-} ion is greater than that for the $PtCl_6^{2-}$ ion on account of significant $d_\pi(M) \longrightarrow d_\pi(X)$ π-bonding in the case of X = Cl but not in the case of X = F. However, it is difficult to believe that this kind of π-back bonding could be of any significance for any metal complex in which the metal atom is in an oxidation state as high as four. Indeed, in the interpretation of the n.q.r. results on these ions[25,35] (Table 8), and in molecular orbital calculations,[26] this possibility has been discounted, and the important π-bonding in MX_6^{2-} ions is considered to be in the reverse direction *i.e.* $p_\pi(X) \longrightarrow d_\pi(M)$. On this basis, the amount of π-bonding in MX_6^{2-} ions increases progressively from zero for t_{2g}^6 ions in the order $t_{2g}^6 < t_{2g}^5 < t_{2g}^4 < t_{2g}^3$, *i.e.* it increases progressively with increase in the valence shell *d*-electron deficiency. Our results (Table 9) indicate that the ratio $\alpha_{\perp}'/\alpha_{\parallel}'$ also increases (with the exception of t_{2g}^5 case) with increase in the number of holes in the t_{2g} sub-shell, *i.e.* with increase in π-bond order of the MX bonds. Such a conclusion would be the opposite to that drawn by Woodward and Ware[2a] from studies of these ions, but would be in agreement with that of Chantry and Plane on other systems.[32] However, we believe that this apparent relationship between $\alpha_{\perp}'/\alpha_{\parallel}'$

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[33] G. L. Bottger and C. V. Damsgard, *Spectrochim. Acta*, 1972, **28A**, 1631.

[34] R. J. H. Clark and P. D. Mitchell *J. Mol. Spectroscopy*, in the press.

[35] E. A. C. Lucken, ' Nuclear Quadrupole Coupling Constants,' Academic Press, London, 1969.

and π-bond order is without foundation for MX_6^{2-} ions, and that the principal factor controlling the value of $\alpha_\perp'/\alpha_\parallel'$ is the degree of σ-bond covalent character (*cf.* earlier discussion of $\alpha_\parallel'$).

Two other series of complex ions have very large $f(\nu_2)/f(\nu_1) : I(\nu_1)/I(\nu_2)$ values and thus large $\alpha_\perp'/\alpha_\parallel'$ values (0·5—1·0). The first of these is a series of d^0 complexes, MX_6^{2-} (M = Ti, Zr, or Hf; X = Cl or Br), MX_6^- (M = Nb or Ta; X = Cl or Br) and WCl_6, for which the $\nu_2(e_g)$ fundamental is frequently unobservably weak.[36,37] For d^0 species, $p_\pi(X) \longrightarrow d_\pi(M)$ would be at a maximum, and this expectation receives support from both ^{19}F n.m.r. data [38] and from molecular orbital calculations.[39] The second series of ions displaying the same behaviour is the d^{10} species SnX_6^{2-} and $PbCl_6^{2-}$; for this series, however, π-bonding of the sort $p_\pi(X) \longrightarrow 5d_\pi(M)$ is very unlikely on account of poor energy match of the relevant orbitals. Hence, as these two series of ions have very different π-bonding capabilities, but display the same intensity patterns, it seems improbable that π-bonding effects are responsible for these patterns.

Examination of the results in Table 9 indicates that the larger value for $\alpha_\perp'/\alpha_\parallel'$ for the tin than for the platinum series is brought about partly because of larger values for $\alpha_\perp'$ (for which we have offered no explanation) and partly because of smaller values for $\alpha_\parallel'$ (which is clearly to be associated with a smaller degree of σ-bond covalent character in SnX than in PtX bonds, *cf.* Table 8). We have been unable to establish whether the second-order Jahn–Teller effect plays any significant role in determining the small $f(\nu_1/f(\nu_2) : I(\nu_1)/I(\nu_2)$ ratios for t_{2g}^6 ions, a possibility which has been suggested by Stufkens [40] both for these ions as well as for the MX_6^{2-} ions (M = Se or Te; X = Cl or Br) which likewise display small $f(\nu_1)/f(\nu_2) : I(\nu_1)/I(\nu_2)$ values. The suggestion [41] that for t_{2g}^6 ions only non-totally symmetric fundamentals should display the pre-r.r.e. is not borne out by the facts.

It is also worth pointing out that the ratio $\alpha_\perp'/\alpha_\parallel'$ changes systematically in the order $MF_6^{2-} > MCl_6^{2-} > MBr_6^{2-} > MI_6^{2-}$. Thus (*a*) the platinum series is not unique in this respect and (*b*) the change in $\alpha_\perp'/\alpha_\parallel'$ from MF_6^{2-} to MCl_6^{2-} is continued for the remaining hexahalogeno-ions. This suggests that the observed trend on changing the halogen atom may simply be related to the electronegativity difference between M and X, and *not* to any fundamental difference between MF and MCl bonds, as suggested previously.[2a] However, $\alpha_\perp'/\alpha_\parallel'$ is clearly a complicated function, the trends in which are necessarily difficult to interpret. We consider it preferable in all cases to obtain and to concentrate discussion (as we have done earlier in this paper, and elsewhere for tetrahedral molecules [34]) on the separate quantities $\alpha_\parallel'$ and $\alpha_\perp'$ themselves.

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