and the overlap integrals were evaluated using INTE (*vide supra*). Other integrals of L_z were evaluated similarly.

Registry No. $Fe(CN)_6^{3-}$, 13408-62-3.

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Intensity Studies on the Raman-Active Fundamentals of Some Square-Planar (MX_4^{n-}) Ions and of the ICl_2^- Ion. Calculation of Parallel and Perpendicular Bond Polarizability Derivatives and Bond Anisotropies

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The Raman spectra of solid samples and aqueous acid solutions of the anions MX_4^{n-} (M = Pt, Pd, or Au; X = Cl or Br) and of acetonitrile solutions of the ICl_4^- and ICl_2^- ions have been recorded, and accurate values of the Raman-active fundamentals in each state are reported. The intensities in solution of all the Raman bands of each ion relative to that of the 935-cm^{-1} band of the perchlorate ion have been measured at four different exciting frequencies. On the basis of these measurements, bond polarizability derivatives, $\bar{\alpha}'_{MX}$, at zero exciting frequency have been calculated. A procedure for the calculation of both the parallel and the perpendicular components of $\bar{\alpha}'_{MX}$ for square–planar and linear ions is outlined, both for the case in which the MX bond is assumed to have cylindrical symmetry and for that in which it does not, and the magnitudes of these quantities are calculated for the ions in question and discussed. The quantity $\alpha_{\parallel}'$ is a measure of the degree of covalent character of a bond. Values for the bond anisotropy γ_{MX} have also been deduced for the square-planar ions from the intensity of the Raman-active bending mode of each ion.

Introduction

Previous studies of the intensities of Raman-active fundamentals of molecules and ions have primarily been concerned with octahedral,[1-4] tetrahedral,[5-8] linear,[9,10] and trigonal-planar[5,11] species. The present study, the first involving square-planar ions, has been carried out in order to establish values for the MX bond polarizability derivatives ($\bar{\alpha}'_{MX}$) for this interesting class of ions for comparison with the $\bar{\alpha}'_{MX}$ values of related ions of different stereochemistries. A procedure has been developed for the calculation of parallel and perpendicular bond polarizability derivatives in square-planar and linear ions, and the magnitudes of the quantities so calculated are discussed with reference to the degrees of covalent character of the MX bonds involved in the normal modes of vibration. Bond anisotropy derivatives as well as bond anisotropies have been deduced.

In all cases the intensities of the Raman-active fundamentals were measured relative to the 935-cm^{-1} band of the perchlorate ion as internal standard. All intensity measurements were carried out by use of the rotating-sample technique at four different exciting frequencies in order that suitable corrections for the preresonance Raman effect could be made. In the course of the work, accurate values for all the Raman-active fundamentals of each species have been determined.

Experimental Section

Samples. The compounds $KAuCl_4$, $KAuBr_4 \cdot 2H_2O$, K_2PdCl_4, K_2PdBr_4, and $(NH_4)_2PtCl_4$ were obtained from Johnson Matthey and Co. Ltd. K_2PtBr_4 was obtained from K & K Laboratories, Inc. $[(C_2H_5)_4N][AuCl_4]$ and $[(C_2H_5)_4N][AuBr_4]$ were prepared by standard procedures.[12] The compounds $[(C_2H_5)_4N][ICl_4]$ and $[(C_2H_5)_4N][ICl_2]$ were prepared according to the method of Popov and Buckles,[13] and their Raman spectra were recorded in dried acetonitrile, the 919-cm^{-1} band of the latter 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 hydrohalic acid to minimize hydrolysis and then sodium or potassium perchlorate was added in known amounts as internal standard.

Each solution was studied at two different relative concentrations of standard to solute. The approximate mole ratios (number of moles of solute/number of moles of perchlorate) used for each anion studied were as follows: $AuCl_4^-$, 0.4; $AuBr_4^-$, 0.1; $PdCl_4^{2-}$, 0.3; $PdBr_4^{2-}$, 0.2; $PtCl_4^{2-}$, 1.0; $PtBr_4^{2-}$, 1.0. The values for the polyhalide anions refer to the mole ratios relative to acetonitrile: ICl_4^-, 0.005; ICl_2^-, 0.008.

The relative intensities of each Raman-active fundamental of the ions ICl_4^- and ICl_2^- were checked by running an approximately equimolar solution of the two in acetonitrile. A curve analysis on the total band contour gave satisfactory agreement with the relative intensities obtained by running each ion separately *vs.* the 919-cm^{-1} band of acetonitrile.

In cases where the $\nu_2(b_{1g})$ band overlapped considerably with the $\nu_1(a_{1g})$ band, *e.g.*, for the $PtCl_4^{2-}$ ion, a contour analysis was carried out to determine the correct ratio of the intensities of ν_1 and ν_2.

Instrumental Work. The Raman spectra were recorded using a Spex 1401 spectrometer in conjunction with Coherent Radiation Ltd. Model 52 Ar^+ and Kr^+ lasers. The scattered radiation was collected at 90° and focused by an $f/0.95$ lens onto the entrance slit of the monochromator after having been passed through a polarization scrambler. The 0.75-m Czerny-Turner monochromator employed two 1200-line/mm Bausch and Lomb gratings blazed at 500 nm. The method of detection was photon counting in conjunction with a Grade I 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 the trace-and-weigh procedure and by use of a Kent Chromalog Two Signal integrator.

The relative spectral response of the instrument was determined by use of a tungsten strip lamp as described previously.[4]

Solutions were held in cylindrical cells (volume *ca.* 12 ml) which had flat bottoms and which could be rotated at speeds of *ca.* 1600 rpm.[14,15] 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_4^{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.*

$$\left(\frac{I_2}{I_1}\right)_{\text{true}} = \left(\frac{I_2}{I_1}\right)_{\text{apparent}} 10^{cd(\epsilon_2-\epsilon_1)} \qquad (1)$$

where c is the molar concentration of the MX_4^{n-} ion, and ϵ_2 and ϵ_1 are the extinction coefficients of 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 minimize self-absorption of the scattered radiation.

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

Results

Fundamental Frequencies. The frequencies found for the three Raman-active fundamentals of each square-planar ion are listed in Table I, together with previously reported values. The bands assigned to the $\nu_1(a_{1g})$ and $\nu_2(b_{1g})$ fundamentals are moderately strong and sharp and their frequencies can thus in most cases be determined with greater accuracy than that of the $\nu_4(b_{2g})$ band, which is usually very broad. For the $PdCl_4^{2-}$ and $PdBr_4^{2-}$ ions, no previous solution values for the fundamental frequencies could be found. High Rayleigh scattering obscured the ν_4 band in the solution Raman spectrum of the ICl_4^- ion, but it was clearly observable in the solid-state spectrum.

Only small frequency shifts on change of state occur for the $\nu_1(a_{1g})$ and $\nu_2(b_{1g})$ fundamentals of each ion, but the $\nu_4(b_{2g})$ bending fundamental behaves differently. The solution value of this fundamental is invariably less than the solid-state value, but whereas the shift is *ca.* 3 cm^{-1} for the AuX_4^- ions, it is 12 cm^{-1} for the ICl_4^- ion and 20–31 cm^{-1} for the PdX_4^{2-} and PtX_4^{2-} ions.

Raman Band Intensities and Bond Polarizability Derivatives. The relative molar intensities of the Raman-active fundamentals of each ion are listed in Table II, together with the corresponding frequency factor (see below). The frequency-corrected relative molar intensities and depolarization ratios are listed in Table III.

Table I. Frequencies of the Raman-Active Fundamentals of the MX_4^{n-} Ions in Aqueous Acid Solutions and as Crystalline Solids (cm^{-1})

Ion	State	Ref	$\nu_1(a_{1g})$	$\nu_2(b_{1g})$	$\nu_4(b_{2g})$
$AuCl_4^-$	Aq soln	*a*	347	324	171
	K^+ salt	*b*	349	324	183
	Aq soln	*b*	350	326	173
	Aq soln	*c*	349.0 ± 0.5	326.0 ± 0.5	170 ± 2
	Et_4N^+ salt	*c*	349.5 ± 0.5	325.8 ± 0.5	172.4 ± 1.0
$AuBr_4^-$	Aq soln	*a*	212	196	102
	K^+ salt	*b*	213	196	106
	Aq soln	*b*	215	197	104
	K^+ salt	*d*	214	196	102
	Aq soln	*c*	214.4 ± 0.5	196.5 ± 0.5	103.5 ± 2
	Et_4N^+ salt	*c*	213.9 ± 0.6	197.0 ± 0.7	106.9 ± 1.0
$PtCl_4^{2-}$	Aq soln	*a*	335	304	164
	K^+ salt	*b*	329	302	194
	Aq soln	*b*	332	314	170
	K^+ salt	*d*	333	306	196
	Aq soln	*c*	331.3 ± 0.6	311.0 ± 1.5	164.5 ± 4
	NH_4^+ salt	*c*	325.5 ± 0.5	301.6 ± 0.7	195.4 ± 0.5
$PtBr_4^{2-}$	Aq soln	*b*	208	194	
	K^+ salt	*b*	205	190	125
	K^+ salt	*d*	205	190	125
	Aq soln	*c*	206.4 ± 0.8	193.9 ± 0.8	105.5 ± 2
$PdCl_4^{2-}$	K^+ salt	*d*	310	275	198
	Aq soln	*c*	304.3 ± 0.7	278.3 ± 0.7	165.5 ± 4
	K^+ salt	*c*	303.6 ± 0.5	269.9 ± 1.0	195.8 ± 0.6
$PdBr_4^{2-}$	K^+ salt	*d*	192	165	125
	Aq soln	*c*	189.6 ± 0.7	174.1 ± 0.7	97 ± 4
	K^+ salt	*c*	187.4 ± 0.5	166.6 ± 0.7	125.4 ± 0.6
ICl_4^-	Aq soln	*a*	288	261	128
	Aq soln	*e*	288	261	128
	MeCN soln	*c*	282.9 ± 0.6	256.0 ± 0.6	
	Et_4N^+ salt	*c*	279.1 ± 0.5	255.5 ± 0.5	139.7 ± 0.7
ICl_2^-	Aq soln	*e*	272		
	$PhNO_2$ soln	*e*	262		
	Me_4N^+ salt	*e*	254.5		
	Rb^+ salt	*f*	278		
	Cs^+ salt	*f*	268		
	MeCN soln	*c*	263.4 ± 0.5		

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The intensities of the $\nu_1(a_{1g})$ fundamentals of the square-planar anions were used to calculate the appropriate mean molecular polarizability derivatives ($\bar{\alpha}'$) *via* the relationship[6,16]

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

where M is the molar concentration, ρ is the depolarization ratio for polarized incident radiation, and the subscript 2 refers to the square-planar anion and 1 to the perchlorate ion. The frequency factor f is defined as

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

where ν_0 is the exciting frequency, ν_2 is the Raman shift of the a_{1g} fundamental of the square-planar ion, and ν_1 is the Raman shift of the a_1 fundamental of the perchlorate ion (935 cm^{-1}).

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

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

where μ_2 and μ_1 are the reciprocals of the masses of the X and

Table II. 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]	Wavelength, nm	ν_i	I_2M_1/I_1M_2[a]	f[b]
		$KAuCl_4$				$(NH_4)_2PtCl_4$	
647.1	ν_1	8.0 ± 0.5	3.794	647.1	ν_1	1.5 ± 0.1	4.096
	ν_2	3.5 ± 0.4	4.197		ν_2	0.68 ± 0.07	4.505
	ν_4	2.9 ± 0.4	11.84		ν_4	0.81 ± 0.18	12.45
568.2	ν_1	9.5 ± 0.6	3.719	568.2	ν_1	1.7 ± 0.2	4.012
	ν_2	4.6 ± 0.2	4.111		ν_2	0.70 ± 0.08	4.410
	ν_4	3.3 ± 0.5	11.54		ν_4	0.80 ± 0.13	12.13
514.5	ν_1	12.7 ± 0.8	3.669	514.5	ν_1	1.3 ± 0.1	3.957
	ν_2	5.3 ± 0.2	4.054		ν_2	0.48 ± 0.03	4.347
	ν_4	4.7 ± 0.2	11.34		ν_4	0.51 ± 0.11	11.92
488.0	ν_1	14.5 ± 0.8	3.645	488.0	ν_1	1.5 ± 0.1	3.929
	ν_2	5.8 ± 0.4	4.026		ν_2	0.51 ± 0.05	4.316
	ν_4	4.9 ± 0.3	11.24		ν_4	0.50 ± 0.08	11.82
		$KAuBr_4$				K_2PtBr_4	
647.1	ν_1	25.4 ± 1.0	8.063	647.1	ν_1	3.1 ± 0.1	8.578
	ν_2	14.4 ± 1.6	9.259		ν_2	2.4 ± 0.2	9.497
	ν_4	7.0 ± 1.2	27.88		ν_4	0.94 ± 0.09	27.40
568.2	ν_1	32 ± 2	7.869	568.2	ν_1	3.2 ± 0.3	8.369
	ν_2	18.7 ± 1.0	9.031		ν_2	2.5 ± 0.3	9.261
	ν_4	7.6 ± 1.0	27.11		ν_4	1.1 ± 0.1	26.65
514.5	ν_1	50 ± 5	7.740	514.5	ν_1	3.3 ± 0.3	8.231
	ν_2	25.7 ± 2.0	8.879		ν_2	2.8 ± 0.2	9.106
	ν_4	13.6 ± 1.7	26.60		ν_4	1.1 ± 0.2	26.15
488.0	ν_1	66 ± 6	7.678	488.0	ν_1	3.9 ± 0.3	8.163
	ν_2	32 ± 4	8.806		ν_2	2.8 ± 0.2	9.030
	ν_4	33 ± 2	26.35		ν_4	1.1 ± 0.1	25.91
		K_2PdCl_4				$[Et_4N]ICl_4$	
647.1	ν_1	3.0 ± 0.2	4.655	647.1	ν_1	12.1 ± 1.2	5.203
	ν_2	0.63 ± 0.06	5.345		ν_2	8.9 ± 0.9	6.076
	ν_4	1.2 ± 0.2	12.33		ν_4[c]	0.63 ± 0.04	16.50
568.2	ν_1	3.6 ± 0.2	4.556	568.2	ν_1	13.9 ± 1.4	5.089
	ν_2	0.67 ± 0.05	5.227		ν_2	10.9 ± 1.1	5.938
	ν_4	1.4 ± 0.2	12.01		ν_4[c]	0.62 ± 0.02	16.06
514.5	ν_1	3.4 ± 0.2	4.491	514.5	ν_1	19.3 ± 1.9	5.013
	ν_2	0.66 ± 0.05	5.149		ν_2	15.4 ± 1.5	5.846
	ν_4	0.44 ± 0.05	11.80		ν_4		
488.0	ν_1	1.6 ± 0.1	4.459	488.0	ν_1	22.5 ± 2.2	4.976
	ν_2	0.88 ± 0.08	5.110		ν_2	17.8 ± 1.7	5.801
		K_2PdBr_4				$[Et_4N]ICl_2$	
647.1	ν_1	11.5 ± 0.9	9.864	647.1	ν_1	8.8 ± 0.7	5.811
	ν_2	4.3 ± 0.4	11.38	568.2	ν_1	10.8 ± 0.8	5.680
	ν_4	1.9 ± 0.6	31.60	514.5	ν_1	14.3 ± 1.1	5.593
568.2	ν_1	16.9 ± 1.1	9.618	488.0	ν_1	16.4 ± 1.3	5.551
	ν_2	3.9 ± 0.3	11.09				
	ν_4	3.0 ± 0.5	30.72				
514.5	ν_1	3.5 ± 0.2	9.455				
	ν_2	4.7 ± 0.5	10.90				
	ν_4	4.1 ± 0.8	30.14				
488.0	ν_1	13.1 ± 0.9	9.376				
	ν_2	5.6 ± 1.0	10.81				
	ν_4	4.2 ± 0.7	29.86				

[a] Corrected for spectral response; subscript 2 refers to the MX_4^{n-} anion and subscript 1 to the 935-cm^{-1} band of the perchlorate ion. [b] See eq 3. [c] ν_4 values refer to solid-state measurements.

O atoms, respectively. As $\rho_1 = 0$ for totally symmetric modes of cubic molecules and if we take the reference value[17] of $\bar{\alpha}'_{ClO}$ to be 1.73 Å^2, the last equation reduces to

$$\bar{\alpha}'_{MX} = 1.73\left[\frac{1}{f}\left(\frac{I_2M_1}{I_1M_2}\right)\left(\frac{\mu_1}{\mu_2}\right)\left(\frac{3-4\rho_2}{3(1+\rho_2)}\right)\right]^{1/2} \qquad (5)$$

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 preresonance conditions. The simplest frequency correction function is that of Shorygin,[18] *viz.*

$$I_A \propto \frac{(\nu_e^2 + \nu_0^2)^2}{(\nu_e^2 - \nu_0^2)^4} \qquad (6)$$

where ν_e is the frequency of the first allowed electronic transition of the molecule.

Since $\bar{\alpha}'_{MX}$ is a function of $\nu^2 I^{1/2}$, it is appropriate to plot $\bar{\alpha}'_{MX}$ *vs.* the function

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

Extrapolation of such a plot to the value $A = 1$ (*i.e.*, $\nu_0 = 0$) gives the $\bar{\alpha}'_{MX}$ value corrected for the preresonance Raman effect.

Discussion

General Introduction. The preresonance Raman effect (pre-RRE), *i.e.*, the effect by which certain Raman bands show a selective increase in their intensities when the frequency of

Table III. Depolarization Ratios[a] of the $\nu_1(a_{1g})$ Fundamental and Molar Intensities of Raman-Active Fundamentals of the Ions Studied Relative to That of the 935-cm^{-1} Band of the Perchlorate Ion, Corrected for Frequency Factors[b]

		Exciting wavelength, nm			
Anion	Fundamental	647.1	568.2	514.5	488.0
$AuCl_4^-$	ν_1	2.1 ± 0.2	2.6 ± 0.2	3.5 ± 0.2	4.0 ± 0.2
	ν_2	0.84 ± 0.09	1.11 ± 0.05	1.32 ± 0.04	1.4 ± 0.1
	ν_4	0.25 ± 0.03	0.28 ± 0.04	0.42 ± 0.02	0.43 ± 0.03
	$\rho(\nu_1)$	0.09	0.10	0.11	0.12
$AuBr_4^-$	ν_1	3.2 ± 0.1	4.1 ± 0.3	6.4 ± 0.7	8.6 ± 0.8
	ν_2	1.6 ± 0.2	2.1 ± 0.1	2.9 ± 0.2	3.6 ± 0.5
	ν_4	0.25 ± 0.04	0.28 ± 0.04	0.51 ± 0.07	1.3 ± 0.1
	$\rho(\nu_1)$	0.10	0.11	0.13	0.17
$PtCl_4^{2-}$	ν_1	0.36 ± 0.03	0.42 ± 0.04	0.34 ± 0.02	0.37 ± 0.03
	ν_2	0.15 ± 0.02	0.16 ± 0.02	0.11 ± 0.01	0.12 ± 0.01
	ν_4	0.07 ± 0.01	0.07 ± 0.01	0.04 ± 0.01	0.04 ± 0.01
	$\rho(\nu_1)$	0.11	0.10	0.09	0.10
$PtBr_4^{2-}$	ν_1	0.37 ± 0.01	0.39 ± 0.04	0.41 ± 0.04	0.48 ± 0.03
	ν_2	0.25 ± 0.02	0.27 ± 0.01	0.31 ± 0.01	0.31 ± 0.03
	ν_4	0.035 ± 0.003	0.039 ± 0.006	0.043 ± 0.009	0.044 ± 0.006
	$\rho(\nu_1)$	0.07	0.06	0.08	0.06
$PdCl_4^{2-}$	ν_1	0.65 ± 0.04	0.79 ± 0.05	0.76 ± 0.05	0.35 ± 0.03
	ν_2	0.12 ± 0.01	0.13 ± 0.01	0.13 ± 0.01	0.17 ± 0.02
	ν_4	0.10 ± 0.02	0.12 ± 0.01	0.040 ± 0.005	
	$\rho(\nu_1)$	0.07	0.07	0.07	0.07
$PdBr_4^{2-}$	ν_1	1.2 ± 0.1	1.8 ± 0.1	0.37 ± 0.02	1.4 ± 0.1
	ν_2	0.38 ± 0.03	0.35 ± 0.03	0.43 ± 0.04	0.52 ± 0.09
	ν_4	0.061 ± 0.017	0.099 ± 0.018	0.14 ± 0.02	0.14 ± 0.02
	$\rho(\nu_1)$	0.10	0.12	0.37	0.14
ICl_4^-	ν_1	2.3 ± 0.2	2.7 ± 0.3	3.9 ± 0.4	4.5 ± 0.5
	ν_2	1.5 ± 0.15	1.9 ± 0.19	2.6 ± 0.26	3.1 ± 0.3
	ν_4	0.038 ± 0.003	0.039 ± 0.001		
	$\rho(\nu_1)$	0.07	0.11	0.09	0.10
ICl_2^-	ν_1	1.5 ± 0.12	1.9 ± 0.15	2.6 ± 0.21	3.0 ± 0.24
	$\rho(\nu_1)$	0.27	0.27	0.27	0.27

[a] All ρ values are accurate to ±0.02. [b] 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.

Table IV. Energies of the Lowest Lying Charge-Transfer Absorption Bands for Relevant Square-Planar Anions and for the ICl_2^- Ion (Aqueous Solution)[a]

Anion	Color	Ref	ν_e, cm^{-1}	Assignment $b_{2u}(\pi), e_u(\pi^b) \rightarrow b_{1g}(\sigma^*)$	ν_s, cm^{-1}	Assignment $e_u(\sigma^b) \rightarrow b_{1g}(\sigma^*)$
$AuCl_4^-$	Yellow	*b*	31,800 (4570)	$^1A_{1g} \rightarrow {}^1A_{2u}, {}^1E_u$	44,200 (29,500)	$^1A_{1g} \rightarrow {}^1E_u$
$AuBr_4^-$	Red	*b*	26,300 (5010)	$^1A_{1g} \rightarrow {}^1A_{2u}, {}^1E_u$	39,400 (38,900)	$^1A_{1g} \rightarrow {}^1E_u$
$PtCl_4^{2-}$	Red	*c*	46,000 (9580)	$^1A_{1g} \rightarrow {}^1A_{2u}, {}^1E_u$		
$PtBr_4^{2-}$	Brown	*d*	37,300 (7000)	$^1A_{1g} \rightarrow {}^1A_{2u}, {}^1E_u$		
$PdCl_4^{2-}$	Red	*e, f*	36,000 (12,000)	$^1A_{1g} \rightarrow {}^1A_{2u}, {}^1E_u$	44,900 (30,000)	$^1A_{1g} \rightarrow {}^1E_u$
$PdBr_4^{2-}$	Brown	*e*	30,100 (10,400)	$^1A_{1g} \rightarrow {}^1A_{2u}, {}^1E_u$	40,500 (31,400)	$^1A_{1g} \rightarrow {}^1E_u$
ICl_4^-	Yellow	*g*	29,800 (~1100)[h]		43,800 (~51,000)	
ICl_2^-	Yellow	*i*	29,700 (319)[h]		44,050 (53,000)	

[a] Numbers in parentheses indicate molar extinction coefficients where available. The assignments are those of H. B. Gray, *Transition Metal Chem.*, 1, 240 (1965). It has been suggested (C. M. Harris and I. H. Reece, *Nature* (*London*), **182**, 1665 (1958), and footnote *e*) that the AuX_4^- (in nitrobenzene and nitromethane) and PdX_4^{2-} ions (in both aqueous and nonaqueous solution) form six-coordinate species in the presence of free halide ions. However, C. K. Jorgensen ("Inorganic Complexes," Academic Press, London, 1963, p 43; "Absorption Spectra and Chemical Bonding in Complexes," Pergamon Press, Oxford, 1962, p 259) investigated the electronic absorption spectra of the AuX_4^-, PdX_4^{2-}, and PtX_4^{2-} ions in aqueous solution and found no evidence for the formation of higher than tetracovalent complexes. We have investigated the electronic absorption and Raman spectra of the $AuBr_4^-$ ion in aqueous solutions containing different concentrations of bromide ion. No significant change was observed in the extinction coefficient of the lowest energy charge-transfer band, or in the frequencies and intensities (relative to the 935-cm^{-1} band of perchlorate) of the three Raman-active fundamentals on changing the mole ratio of $Br^-:AuBr_4^-$ from 0 to 50. [b] A. K. Gangopadhayay and A. Chakravorty, *J. Chem. Phys.*, 35, 2206 (1961). [c] J. Chatt, G. A. Gamlen, and L. E. Orgel, *J. Chem. Soc.*, 486 (1958). [d] H. B. Gray and C. J. Ballhausen, *J. Amer. Chem. Soc.*, 85, 260 (1963). [e] C. M. Harris, S. E. Livingstone, and I. H. Reece, *J. Chem. Soc.*, 1505 (1959). [f] C. K. Jorgensen, "Absorption Spectra of Complexes of Heavy Metals," Report to U. S. Army, Frankfurt am Main, Oct 1958. [g] This work; acetonitrile solution. [h] Evidently only partly allowed. [i] R. E. Buckles and J. F. Mills, *J. Amer. Chem. Soc.*, 76, 4845 (1954); acetonitrile solution.

the exciting radiation is made to approach that of an allowed electronic transition in the scattering molecule, requires special theoretical treatment. As previously discussed,[4] application of Albrecht's theory[19,20] to the case of octahedral scattering molecules leads to the prediction that all three Raman-active fundamentals should display the pre-RRE. Similar symmetry arguments[21] as applied to square-planar molecules lead similarly to the conclusion that all three Raman-active fundamentals, $\nu_1(a_{1g})$, $\nu_2(b_{1g})$, and $\nu_4(b_{2g})$, should show the pre-RRE. Accordingly, the intensity of each band for each ion has been measured relative to that of the 935-cm^{-1} band of the perchlorate ion at four different exciting frequencies. The results (Table III) clearly demonstrate that the pre-RRE is observed for each fundamental of each ion. In Table IV are listed the frequencies of the two lowest lying charge-transfer transitions of each ion, together with the band assignments, and in Table V the corresponding data are given for the ligand field transitions.

Intensity Functions. Under the preresonance conditions, the intensity of a given band no longer varies as ν_0^4. The deviation from ν_0^4 dependence may be described by various frequency functions, the simplest being that of Shorygin; *cf.* eq 6.

Table V. Energies (cm^{-1}) of the Spin-Allowed Ligand Field Bands for the MX_4^{2-} Ions (M = Pt, Pd; X = Cl, Br)[a]

Ion	Technique[b]	Band Maxima	Assignment	Ref
$PtCl_4^{2-}$	A	26,300 (28) *xy*	$^1A_{1g} \rightarrow {}^1A_{2g}$	*c, d*
	A	29,200 (37) *xy*, 29,800 (55) *z*	$^1A_{1g} \rightarrow {}^1E_g$	*c, d*
	B	36,500 (250)	$^1A_{1g} \rightarrow {}^1B_{1g}$	*d*
$PdCl_4^{2-}$	A	20,000 (67) *xy*	$^1A_{1g} \rightarrow {}^1A_{2g}$	*c, d*
	A	22,600 (128) *xy*, 23,000 (80) *z*	$^1A_{1g} \rightarrow {}^1E_g$	*c, d*
	A	29,500 (67) *xy*	$^1A_{1g} \rightarrow {}^1B_{1g}$	*c, d*
$PtBr_4^{2-}$	C	19,700 (15)	$^1A_{1g} \rightarrow {}^1A_{2g}$	*d, e*
	C	24,300 (100)	$^1A_{1g} \rightarrow {}^1E_g$	*d, e*
	C	28,200 (120)	$^1A_{1g} \rightarrow {}^1B_{1g}$	*d, e*
$PdBr_4^{2-}$	C	16,000	$^1A_{1g} \rightarrow {}^1A_{2g}$	*d, e*
	C	20,000 (330)	$^1A_{1g} \rightarrow {}^1E_g$	*d, e*
	C	26,000	$^1A_{1g} \rightarrow {}^1B_{1g}$	*d, e*

[a] Extinction coefficients are given in parentheses. The ligand field bands of the AuX_4^- ions are close to but very poorly resolved from the intense charge-transfer bands. They have been located in 2:1 2-methyltetrahydrofuran–methyl alcohol solution (300°K) and glass (77°K): W. R. Mason and H. B. Gray, *Inorg. Chem.*, 7, 55 (1968). [b] A = single-crystal absorption spectrum of potassium salt; B = reflectance spectrum (extinction coefficient from aqueous solution); C = aqueous solution spectrum. [c] D. S. Martin, M. A. Tucker, and A. J. Kassman, *Inorg. Chem.*, 4, 1682 (1965); *ibid.*, 5, 1298 (1966). [d] H. Basch and H. B. Gray, *Inorg. Chem.*, 6, 365 (1967). [e] H. B. Gray, *Transition Metal Chem.*, 1, 240 (1965).

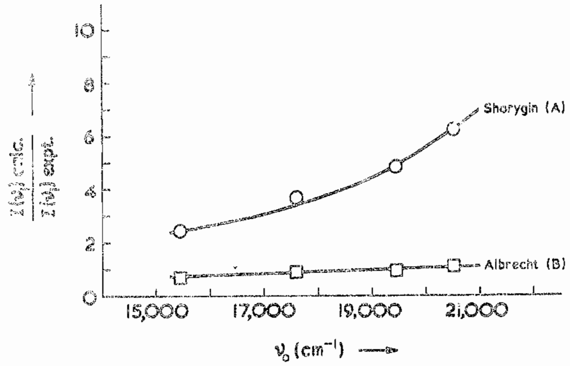

Figure 1. Plot of the Shorygin and Albrecht frequency functions divided at each exciting frequency by the values of $(1/f)(I_2/I_1)$ for the $\nu_1(a_{1g})$ fundamental of the complex $[(C_2H_5)_4N][ICl_4]$ *vs.* exciting frequency (*cf.* eq 2).

Another frequency function, I_B, has been derived by Albrecht,[19,20] *viz.*

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

where ν_e is the lowest and ν_s is the next lowest allowed electronic transition of the scattering molecule. A further expression derived by Peticolas[22,23] is, in the case of a square-planar anion, identical with that of Albrecht.

In order to test which frequency function best described the observed intensity enhancement of the $\nu_1(a_{1g})$ fundamental of each ion on change of exciting frequency, the ratio of the calculated to the experimental intensity of each band at each exciting frequency (ν_0) has been plotted *vs.* ν_0 for each frequency function. The results are given in Figure 1 for the ICl_4^- ion; it is clear that the plot is most nearly horizontal for the Albrecht function, and this was also the case for the other ions studied. Thus, in common with other work,[4] the Albrecht function best accounts for the pre-RRE in the ions studied. Accordingly, bond polarizability derivatives, obtained from band intensities at various ν_0, were extrapolated to zero exciting frequency by way of this function. The frequency-corrected relative molar intensities of each band of each ion, extrapolated to zero exciting frequency, are given in Table VI.

Table VI. Extrapolated Relative Molar Intensities for the $\nu_1(a_{1g})$, $\nu_2(b_{1g})$, and $\nu_4(b_{2g})$ Fundamentals and Bond Anisotropies for Some Square-Planar Anions MX_4^{n-}

	$(1/f)(I_2M_1/I_1M_2)_{\nu_0=0}$[a]				
Anion	$\nu_1(a_{1g})$	$\nu_2(b_{1g})$	$\nu_4(b_{2g})$	r_{MX}, Å	γ_{MX}, Å^3
$AuCl_4^-$	1.1	0.55	0.12	2.28[b]	3.0
$AuBr_4^-$	1.4	0.90	0.20[c]	2.42[d]	6.1
$PtCl_4^{2-}$	0.29	0.14	0.05_5	2.33[e]	2.0
$PtBr_4^{2-}$	0.30	0.20	0.03_0	2.47[d]	2.3
$PdCl_4^{2-}$	0.35[c]	0.08	0.06_5[c]	2.30[f]	2.2
$PdBr_4^{2-}$	0.38[c]	0.27	0.03_0	2.44[d]	2.5
ICl_4^-	1.3	0.72	0.04_0	2.34[g]	1.7

[a] Extrapolated by way of Albrecht's function. [b] M. Bonamico, G. Dessy, and A. Vaciago, *Atti. Accad. Naz. Lincei, Cl. Sci. Fis., Mat. Natur., Rend.*, 39, 504 (1965). [c] Extrapolated from 647.1- and 568.2-nm values only. [d] Based on an estimated difference of 0.14 Å between MCl and MBr bond distances; *cf.* halogen tetrahedral bond radii and average MX bond distances in MCl_6^{2-} and MBr_6^{2-} ions (M = Pt, Re).[4] The AuBr distances in the salt $KAuBr_4 \cdot 2H_2O$ (2.65 and 2.48 Å) appear to be in error: E. G. Cox and K. C. Webster, *J. Chem. Soc.*, 1635 (1936). [e] R. G. Dickinson, *J. Amer. Chem. Soc.*, 44, 2404 (1922). [f] W. Theilacker, *Z. Anorg. Allg. Chem.*, 234, 161 (1937). [g] R. C. L. Mooney, *Z. Kristallogr., Kristallgeometrie, Kristallphys., Kristallchem.*, 98, 377 (1938).

Table VII. Comparison of $\bar{\alpha}'_{MX}$ Values, Obtained by Extrapolation of Albrecht's and Shorygin's Plots to Zero Exciting Frequency, and the Fractional Covalent Character of the MX Bonds (χ)

	$\bar{\alpha}'_{MX}$,[a] Å^2		
Anion	Shorygin	Albrecht	χ (nqr results)[b]
$AuCl_4^-$	2.7	2.5_5	0.50[c]
$AuBr_4^-$	5.0_5	4.5	0.56[d]
$PtCl_4^{2-}$	1.3	1.3	0.33[c]
$PtBr_4^{2-}$	1.9_5	1.9	0.36[c]
$PdCl_4^{2-}$	1.4_5	1.4	
$PdBr_4^{2-}$	2.4	2.2_5	0.34[c]
ICl_4^-	2.7_5	2.6	0.41[e]
ICl_2^-	2.6	2.3_5	0.35[e]

[a] The extrapolations are based on $\bar{\alpha}'_{MX}$ values at four different exciting frequencies except in the case of the PdX_4^{2-} ions, for which they are based on 647.1- and 568.2-nm data only (see text). [b] Based on the assumption that the per cent s character and π character of the MX bond are each zero. [c] W. Van Bronswyk, *Struct. Bonding (Berlin)*, 7, 87 (1970), and references therein. [d] A. Sasane, T. Matuo, D. Nakamura, and M. Kubo, *Bull. Chem. Soc. Jap.*, 43, 1908 (1970). [e] C. D. Cornwall and R. S. Yamasaki, *J. Chem. Phys.*, 27, 1060 (1957).

Bond Polarizability Derivatives. The $\bar{\alpha}'_{MX}$ values extrapolated to zero exciting frequency are listed in Table VII. For all ions except $PdCl_4^{2-}$ and $PdBr_4^{2-}$, straight-line plots of $\bar{\alpha}'_{MX}$ *vs.* the frequency function were obtained and thus easy extrapolation to $\nu_0 = 0$ was possible. In Figure 2, plots of $\bar{\alpha}'_{AuBr}$ for the complex $KAuBr_4$ at each exciting frequency are given *vs.* the Shorygin (A) and Albrecht (B) functions ($\nu_e^2 I_A^{1/2}$ and $\nu_e^2 I_B^{1/2}$, respectively). However, for the PdX_4^{2-} ions, the intensity enhancement of the $\nu_1(a_{1g})$ fundamental on increase of ν_0 is unusual. From Table V it is apparent that these ions have several low-lying (~20,000 cm^{-1}) ligand field transitions of moderate intensity, and that these clearly influence the

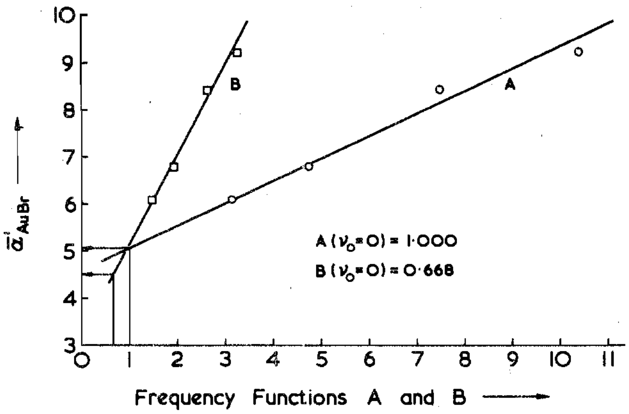

Figure 2. Plot of the $\bar{\alpha}'_{AuBr}$ values for the $AuBr_4^-$ ion against the Shorygin function A = $[1 + (\nu_0/\nu_e)^2]/[1 - (\nu_0/\nu_e)^2]^2$ and the Albrecht function B = $[(\nu_s/\nu_e) + (\nu_0/\nu_e)^2]/[(1 - (\nu_0/\nu_e)^2][(\nu_s/\nu_e)^2 - (\nu_0/\nu_e)^2]$ at four different exciting wavelengths (647.1, 568.2, 514.5, and 488.0 nm, reading from left to right on the plot).

intensity behavior of the $\nu_1(a_{1g})$ fundamental.[29] The corresponding transitions of the PtX_4^{2-} ions are less intense and occur at higher frequencies and therefore do not interfere in this respect. The $\bar{\alpha}'_{PdX}$ values at zero exciting frequency could accordingly only be very crudely estimated from the 647.1- and 568.2-nm results.

The $\bar{\alpha}'_{MX}(\nu_0 = 0)$ values obtained for all the ions studied are summarized in Table VII. The following conclusions may be drawn.

(a) Bond polarizability derivatives increase in the order $\bar{\alpha}'_{MCl} < \bar{\alpha}'_{MBr}$; *i.e*, they increase with increase in the polarizability of the halogen atom and with increase in the degree of covalent character of the MX bond. Independent support for the latter comes from the nqr results included in Table VII. The trend $\bar{\alpha}'_{MCl} < \bar{\alpha}'_{MBr}$ has also been observed for tetrahedral MX_4 molecules,[6,8] octahedral MX_6^{2-} ions,[4] linear MX_2 molecules,[10] and trigonal-planar MX_3 molecules.[11]

(b) For the isoelectronic ions Pt(II) and Au(III), the bond polarizability derivatives increase in the order $\bar{\alpha}'_{PtX} < \bar{\alpha}'_{AuX}$; *i.e.* they increase with increase in the oxidation state of the metal atom. This result is also in agreement with previous results on octahedral ions[4] and is to be expected on account of the increased degree of covalent character in the AuX bond over the PtX bond (*cf.* nqr results (Table VII) and general chemical considerations).

(c) The $\bar{\alpha}'_{MX}$ values for MX_4^{2-} ions are considerably less than those for the corresponding MX_6^{2-} ions, on account of the decreased degree of covalent character of the MX bond on lowering the oxidation state of the metal atom from 4 to 2, *viz.* (values in Å^2) $PtCl_4^{2-}$ (1.3) < $PtCl_6^{2-}$ (2.7), $PtBr_4^{2-}$ (1.9) < $PtBr_6^{2-}$ (3.6$_5$), and $PdCl_4^{2-}$ (1.4) < $PdCl_6^{2-}$ (1.9$_5$).

The intensities of the Raman-active bands of the AuX_4^- ions are much more sensitive to change of exciting frequency than those of the PtX_4^{2-} ions on account of smaller $\nu_e - \nu_0$ values for the former ions. This is a consequence of the lower ν_e values for the auric ions, which in turn is a consequence of easier ligand → metal charge transfer in complex ions in which the metal atom is in a relatively high oxidation state.

Derivation and Discussion of $\alpha_\parallel'$ and $\alpha_\perp'$. From the frequency-corrected relative intensities at zero exciting frequency (relative scattering activities)[9] of the $\nu_1(a_{1g})$ and $\nu_2(b_{1g})$ fundamentals of an MX_4^{n-} ion, it is possible to deduce a value for the ratio of the perpendicular ($\alpha_\perp'$) and parallel ($\alpha_\parallel'$) components of the MX bond polarizability derivative. If the excitation beam is plane polarized with its electric vector at right angles to the direction of scattering, the intensity of the scattered light for the *i*th normal mode of vibration of a molecule is given by the expression[16]

$$I_{\nu_i} = \left(\frac{KMI_0}{\mu}\right)\frac{(\nu_0 - \nu_i)^4}{\nu_i[1 - \exp(-hc\nu_i/kT)]}[45\bar{\alpha}'^2_i + 7\gamma'^2_i] \tag{9}$$

where *K* is a constant, depending on geometric and other factors, *M* is the molar concentration of the molecule, I_0 is the intensity of the incident light beam, μ is the reduced mass, ν_0 is, as before, the excitation frequency (in cm^{-1}), and ν_i is the Raman shift of normal mode Q_i (in cm^{-1}). On the basis of the Wolkenstein assumptions,[24,25] it may be shown that, for a square-planar MX_4^{n-} ion, the following relationships between the molecular polarizability derivatives ($\bar{\alpha}'_i$ and γ'_i), bond polarizability derivatives ($\bar{\alpha}'_{MX}$ and γ'_{MX}), and $\alpha_\parallel'$ and $\alpha_\perp'$ are valid. For the $\nu_1(a_{1g})$ fundamental

$$\bar{\alpha}'_1 = 2\sqrt{\mu_X}\bar{\alpha}'_{MX} = {}^2/_3\sqrt{\mu_X}(\alpha_\parallel' + 2\alpha_\perp') \tag{10}$$

$$\gamma'_1 = \sqrt{\mu_X}\gamma'_{MX} = \sqrt{\mu_X}(\alpha_\parallel' - \alpha_\perp') \tag{11}$$

for the $\nu_2(b_{1g})$ fundamental

$$\bar{\alpha}'_2 = 0 \tag{12}$$

$$\gamma'_2 = \sqrt{3\mu_X}\gamma'_{MX} = \sqrt{3\mu_X}(\alpha_\parallel' - \alpha_\perp') \tag{13}$$

and for the $\nu_4(b_{2g})$ fundamental

$$\bar{\alpha}'_4 = 0 \tag{14}$$

$$\gamma'_4 = 2\sqrt{3\mu_X}(\gamma_{MX}/r_{MX}) \tag{15}$$

In the above equations, μ_X is the reduced mass of the X atom, $\gamma'_{MX} = \alpha_\parallel' - \alpha_\perp'$ is the MX bond anisotropy derivative (Å^2), $\gamma_{MX} = \alpha_\parallel - \alpha_\perp$ is the MX bond anisotropy (Å^3), and r_{MX} is the MX bond length (Å).

Thus, on cancelation of common factors and incorporation of all frequency-dependent terms in the frequency factor *f*, *cf.* eq 3, it follows from eq 9 to eq 13 that

$$\frac{I_{\nu_1}}{I_{\nu_2}} = \left(\frac{f_{\nu_1}}{f_{\nu_2}}\right)\frac{27 + 66(\alpha_\perp'/\alpha_\parallel') + 87(\alpha_\perp'/\alpha_\parallel')^2}{21[1 - 2(\alpha_\perp'/\alpha_\parallel') + (\alpha_\perp'/\alpha_\parallel')^2]} \tag{16}$$

The MX bond polarizability derivatives at zero exciting frequencies (Table VII) are related to $\alpha_\parallel'$ and $\alpha_\perp'$ as follows

$$\bar{\alpha}'_{MX} = {}^1/_3(\alpha_\parallel' + 2\alpha_\perp') \tag{17}$$

Consequently, eq 16 and 17 provide two relationships on the basis of which values for both $\alpha_\parallel'$ and $\alpha_\perp'$ may be derived. Two solutions to the equations are found, but in common with previous practice[4,25] only that in which $\alpha_\parallel'$ is positive is taken to be acceptable. This conclusion has considerable theoretical backing.[26,27] The results of the calculations, based on the scattering activities given in Table VI, are shown in Table VIII. As a check on the validity of this analysis, separate plots of $\alpha_\parallel'$ and $\alpha_\perp'$ *vs.* the Albrecht frequency function were made. Extrapolation of each of these plots to zero exciting frequency led to values for $\alpha_\parallel'$ and $\alpha_\perp'$ not significantly different from those given in Table VIII.

In common with previous conclusions for octahedral ions,[4] it is apparent that (a) $\alpha_\perp'/\alpha_\parallel'$ decreases slightly in the order $MCl_x^{2-} > MBr_x^{2-}$, (b) $\alpha_\perp'$ is always small and in particular is in the range $0 < \alpha_\perp' < 0.75$ for the MX_6^{2-} and MX_4^{2-} ions under discussion, and (c) $\alpha_\parallel'$ is the quantity which principally determines the Raman band intensities of these ions. It increases in the order $\alpha_\parallel'$(MCl) < $\alpha_\parallel'$(MBr), and its value for an MX_4^{2-} ion is approximately half of that for an MX_6^{2-} ion. Both of these results strongly suggest that $\alpha_\parallel'$ may be regarded as a measure of the degree of covalent character of an MX bond.

Derivation and Discussion of $\alpha_\parallel'$, $\alpha_\perp'^a$ and $\alpha_\perp'^b$. The MX bond of a square-planar MX_4^{n-} ion is strictly not cylindrically symmetrical, as assumed to be the case in the treatment above.

Table VIII. Perpendicular ($\alpha_\perp'$) and Parallel ($\alpha_\|'$) Components of the Bond Polarizability Derivatives for Some Square-Planar and Related Octahedral Anions, Based on $\overline{\alpha}'_{MX}(\nu_0 = 0)^a$ Values and the Relative Intensities of the $\nu_1(a_{1g})^a$ and $\nu_2(b_{1g})^a$ Bands at zero exciting frequency, and Bond Anisotropy Derivatives

	Eq 16 and 17			Eq 18–22[b]				
Anion	$\alpha_\|'$	$\alpha_\perp'$	$\alpha_\perp'/\alpha_\|'$	$\alpha_\|'$	$\alpha_\perp'^a$	$\alpha_\perp'^b$	$\gamma'_{MX}{}^a$	$\gamma'_{MX}{}^b$
			Square-Planar Anions					
$AuCl_4^-$	6.5	0.59	0.09	5.9	0.36	1.4	5.5	4.5
				4.8	−0.82	3.7	5.6	1.1
$AuBr_4^-$	12.4	0.55	0.04	10.7	−0.06	2.9	10.8	7.8
				9.1	−1.7	6.1	10.8	3.0
$PtCl_4^{2-}$	3.1	0.34	0.11	3.1	0.33	0.36	2.8	2.7
				2.2	−0.59	2.2	2.8	0.0
$PtBr_4^{2-}$	5.4	0.15	0.03	5.2	0.10	0.45	5.1	4.7
				3.7	−1.4	3.4	5.1	0.3
$PdCl_4^{2-}$	2.8	0.74	0.26	2.9	0.80	0.57	2.1	2.3
				2.1	−0.05	2.3	2.1	−0.2
$PdBr_4^{2-}$	6.5	0.14	0.02	5.8	−0.02	0.92	5.8	4.9
				4.5	−1.3	3.6	5.8	0.9
ICl_4^-	6.9	0.48	0.07	6.9	0.50	0.39	6.4	6.5
				4.7	−1.7	4.8	6.4	−0.1
			Octahedral Anions[c]					
$PtCl_6^{2-}$	6.9	0.55	0.08					
$PtBr_6^{2-}$	10.6	0.20	0.02					
$PdCl_6^{2-}$	5.0_5	0.40	0.08					

[a] Extrapolated by way of Albrecht's function. [b] $\alpha_\perp'^a$ and $\alpha_\perp'^b$ refer to the in-plane and out-of-plane perpendicular bond polarizability derivatives, respectively. [c] Values based on $I(\nu_1)/I(\nu_2)$ ratios using 647.1-nm excitation and $\overline{\alpha}'_{MX}$ values extrapolated to zero exciting frequency by way of Albrecht's function.

It was therefore considered desirable to set up the appropriate intensity equations for the situation in which the two perpendicular bond polarizability derivatives ($\alpha_\perp'^a$, $\alpha_\perp'^b$) were taken to be *unequal* and to solve for all three bond parameters. The following relationships were derived. For the $\nu_1(a_{1g})$ fundamental

$$\overline{\alpha}'_1 = {}^2/_3\sqrt{\mu_X}(\alpha_\|' + \alpha_\perp'^a + \alpha_\perp'^b) \tag{18}$$

$$\gamma_1' = \sqrt{\mu_X}(\alpha_\|' + \alpha_\perp'^a - 2\alpha_\perp'^b) \tag{19}$$

and for the $\nu_2(b_{1g})$ fundamental

$$\overline{\alpha}_2' = 0 \tag{20}$$

$$\gamma_2' = \sqrt{3\mu_X}(\alpha_\|' - \alpha_\perp'^a) \tag{21}$$

In these equations, $\alpha_\perp'^a$ is the in-plane and $\alpha_\perp'^b$ is the out-of-plane perpendicular bond polarizability derivative. Further

$$\overline{\alpha}'_{MX} = {}^1/_3(\alpha_\|' + \lambda_\perp'^a + \alpha_\perp'^b) \tag{22}$$

thus, by use of eq 9 and eq 18–22, it is possible to derive $\alpha_\|'$, $\alpha_\perp'^a$, and $\alpha_\perp'^b$ for each bond. The eight solutions to these equations consist of two sets of mirror images.[28] Regarding, as before, only those solutions for which $\alpha_\|'$ is positive as acceptable, one is left with the two solutions listed in Table VIII as being the most probable. Of these two solutions, the first in each case is closely similar to that obtained by way of the previous analysis, in that $\alpha_\perp'^a$ is comparable with $\alpha_\perp'^b$ and each is similar to $\alpha_\perp'$; furthermore, the first solution in each case leads to a value for $\alpha_\|'$ which is likewise similar to that obtained by way of the previous analysis. The second solution in each case leads to extremely different values of $\alpha_\perp'^a$ and $\alpha_\perp'^b$ and to values for $\alpha_\|'$ which are very different from those obtained by way of the previous analysis. Thus the first solution in each case is regarded as being the more probable.

The present results lead unambiguously to the conclusion that *in square-planar MX_4^{n-} ions, the derived bond polarizability tensor is not cylindrically symmetric* (as it must be for MX_2 linear, MX_4 tetrahedral, and MX_6 octahedral species). The differences between $\alpha_\perp'^a$ and $\alpha_\perp'^b$ (*i.e.*, between the bond anisotropy derivatives $\gamma'_{MX}{}^a$ and $\gamma'_{MX}{}^b$) are not, however, very large, amounting at most to 1.0 Å^2 except for the $AuBr_4^-$ ion.

Table IX. Relative Molar Intensities and Depolarization Ratios of the ν_1 (Σ_g^+) Fundamental of the ICl_2^- Ion and the Mercury Dihalides HgX_2 (X = Cl, Br, or I), Including Perpendicular ($\alpha_\perp'$) and Parallel ($\alpha_\|'$) Components of the Bond Polarizability Derivatives

Compd	$(1/f)(I_2M_1/I_1M_2)$	ρ	$\alpha_\|'$	$\alpha_\perp'$
$[(C_2H_5)_4N]ICl_2$	0.84[a]	0.27	6.3	0.37
			1.6	−4.3
$HgCl_2$	0.22[b]	0.18	5.5	0.91
			0.63	−4.0
$HgBr_2$	0.23[b]	0.20	8.6	1.2
			1.3	−6.1
HgI_2	0.40[b]	0.29	14.8	0.60
			4.1	−10.1

[a] Based on $I(\nu_1)$ values at four different exciting frequencies extrapolated to zero exciting frequency using Albrecht's function. [b] Values are relative to the intensity of the 992-cm^{-1} band of benzene and were obtained using 488.0- or 514.5-nm excitation.[10]

Bond Anisotropies. From the scattering activity of the $\nu_4(b_{2g})$ fundamental of a square-planar ion, *cf.* eq 9, 14, and 15, it is evident that the nonderived bond quantity, γ_{MX}, can be determined (except for the sign). The resulting values (Table VI) are comparable with those determined previously for octahedral[4] and tetrahedral[8] ions. They increase in order $\gamma_{MCl} < \gamma_{MBr}$, *i.e.*, with increase in the polarizability of the ion, and in the order $\gamma_{PtX} < \gamma_{AuX}$, *i.e.*, with increase in the oxidation state of the metal atom.

The ICl_2^- Ion. The molar intensity of the $\nu_1(\Sigma_g^+)$ fundamental of the ICl_2^- ion relative to that of the $\nu_1(a_1)$ fundamental of the perchlorate ion is determined by eq 2 and 3. The relationship between the molecular and bond polarizability derivatives, on the basis of the Wolkenstein assumptions, is found to be

$$\overline{\alpha}_1' = \sqrt{2\mu_X}\,\overline{\alpha}'_{MX} = {}^1/_3\sqrt{2\mu_X}(\alpha_\|' + 2\alpha_\perp') \tag{23}$$

$$\gamma_1' = \sqrt{2\mu_X}\,\gamma'_{MX} = \sqrt{2\mu_X}(\alpha_\|' - \alpha_\perp') \tag{24}$$

Also, as

$$\rho = \frac{3(\alpha_\|' - \alpha_\perp')^2}{5(\alpha_\|' + 2\alpha_\perp')^2 + 4(\alpha_\|' - \alpha_\perp')^2} \tag{25}$$

it is possible from the scattering activity and the depolarization ratio of the ν_1 band to determine both $\alpha_\|'$ and $\alpha_\perp'$. The results are given in Table IX, together with the comparable results for the halides HgX_2 (X = Cl, Br, or I); the latter had not previously been calculated from the original intensity data.[10]

Two solutions for $\alpha_\|'$ and $\alpha_\perp'$ are obtained, but again, following earlier arguments,[26,27] only that for which $\alpha_\|'$ is positive is taken to be meaningful. Subsequent discussion is accordingly confined to this solution.

In common with the results for the square-planar ions, $\alpha_\|'$ for the linear species is found to vary in the order ICl ~ HgCl < HgBr < HgI, *i.e.*, to increase with increase in the expected degree of covalent character of the MX bond. By contrast to $\alpha_\|'$, $\alpha_\perp'$ is in all cases small (0.8 ± 0.4) and not dependent on the nature of the MX bond.

The value of $\overline{\alpha}'_{ICl}$ for the ICl_2^- ion (2.4 Å^2) is found to be less than that for the ICl_4^- ion (2.6 Å^2), suggesting a slightly higher degree of covalent character for the iodine–chlorine bonds of the latter. This conclusion is in agreement with the nqr results (Table VII).

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Registry No. $AuCl_4^-$, 14337-12-3; $AuBr_4^-$, 14337-14-5; $PtCl_4^{2-}$, 13965-91-8; $PtBr_4^{2-}$, 14493-01-7; $PdCl_4^{2-}$, 14349-67-8; $PdBr_4^{2-}$, 14127-70-9; ICl_4^-, 15392-46-8; ICl_2^-, 14522-79-3; $HgCl_2$, 7487-94-7; $HgBr_2$, 7789-47-1; HgI_2, 7774-29-0.

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Electronic Absorption Spectra of Tetragonal and Pseudotetragonal Cobalt(II). I. K_2CoF_4, Rb_2CoF_4, $K_2Mg(Co)F_4$, and $Rb_2Mg(Co)F_4$

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The electronic absorption spectra of K_2CoF_4, Rb_2CoF_4, $K_2Mg(Co)F_4$, and $Rb_2Mg(Co)F_4$ have been measured in polarized light and at low temperatures. Analyses of all of the main spectral features have been made using the complete d^7 tetragonal spin–orbit matrices in the weak-field formalism. These analyses provide, unambiguously, the signs of Dt in every case and the sign of Ds for all but $K_2Mg(Co)F_4$. It is concluded that K_2CoF_4 (Ds = 195 cm^{-1}, Dt = 10 cm^{-1}), $Rb_2Mg(Co)F_4$ (Ds = 230 cm^{-1}, Dt = 20 cm^{-1}), and Rb_2CoF_4 (Ds = 335 cm^{-1}, Dt = 30 cm^{-1}) have axially elongated fluoride octahedra with the magnitude of the distortion increasing from K_2CoF_4 to Rb_2CoF_4. The distortion in $K_2Mg(Co)F_4$ ($|Ds|$ = 60 cm^{-1}, Dt = −10 cm^{-1}) is an axial compression, in agreement with the known crystal structure of K_2MgF_4. The transitions to the components of $^4T_{2g}$ occur *via* magnetic and electric dipole mechanisms and it is probable that the detailed understanding of the spin–orbit structure of this state will require consideration of the dynamic Jahn–Teller effect.

Introduction

With the considerable increase in our understanding of the detailed properties of paramagnetic ions in exactly cubic environments, attention has turned in recent years to the optical and magnetic properties of compounds with symmetries lower than cubic. For a study of transition metal ions in sites of tetragonal symmetry, the series of fluorides crystallizing with the K_2NiF_4 structure represent highly attractive systems, since both the factor group symmetry and paramagnetic ion site symmetry are D_{4h}.

K_2CoF_4 and Rb_2CoF_4 have the K_2NiF_4 structure and both are two-dimensional antiferromagnets[2] whose magnetic properties have been studied extensively.[3-7] K_2MgF_4 and Rb_2MgF_4 also have the same structure and are ideal host crystals for Co^{2+} for use in spectroscopic studies.

There have been two reports of optical absorption measurements of K_2CoF_4. Tiwari, *et al.*,[8] reported the unpolarized room-temperature electronic absorption spectrum but failed to include in their analysis the tetragonal component of the crystal field. Maisch[9] extended this work by measuring the three possible polarized spectra at low temperatures. He was, however, unable to arrive at an unambiguous assignment, based on the tetragonal matrices of Jesson, although one of his alternatives gave closer agreement with the results of Folen, *et al.*[5]

The present paper presents the results of a spectroscopic study of the tetragonal fluorides K_2CoF_4, $K_2Mg(Co)F_4$, Rb_2CoF_4, and $Rb_2Mg(Co)F_4$. By collating spectral information from all four materials, an unambiguous assignment of the spin-allowed bands has been made, permitting a rational discussion of the significance of the appropriate crystal field parameters.

Theory for $d^{3,7}$ Ions in a Tetragonal Crystal Field. The matrices for the tetragonal field were published by Perumareddi[10] in the strong-field representation, without spin–orbit coupling, and Jesson[11] has made available the complete matrices in the weak-field scheme, both with and without spin–orbit coupling. With the inclusion of spin–orbit coupling, the crystal field matrix factors into two 30 × 30 matrices, transforming as the Γ_6 and Γ_7 representations of the D_{4h}' double group.

Two parameters are required to specify the tetragonal part of the field. Following their definition by Moffitt and Ballhausen,[12] the use of Ds and Dt has become established. In the limit of the point charge formalism, expressions for Dq and Dt may be combined to give the simple relation

$$Dt = {}^4/_7(Dq_{xy} - Dq_z)$$

where Dq_{xy} and Dq_z are the cubic crystal field parameters of the ligands in the xy plane and on the $\pm z$ axis of the octa-