A Further Investigation of the Polarized Single-crystal Electronic Absorption Spectrum of $[AsPh_4][CrOCl_4]$

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Polarized single-crystal electronic absorption spectra have been recorded for $[AsPh_4][CrOCl_4]$ at 77 and 4.2 K in the energy range 4 000—40 000 cm^{-1}. Three band systems have been identified and have been assigned to the three possible *d–d* transitions in C_{4v} symmetry. The previously unreported band system originating at *ca.* 20 000 cm^{-1} has been assigned to the one-electron promotion $d_{xy}\rightarrow d_{z^2}$.

Although it has been possible to give a self-consistent assignment of the electronic absorption spectra of a wide variety of complexes containing the VO^{2+} chromophore,[1] no such common assignment is currently available[2] for the electronic absorption spectra of the MO^{3+} (M = Cr, Mo, or W) chromophores. Similarities between these oxy cations had been suggested in the original molecular orbital (m.o.) calculations of Gray and co-workers.[3,4] The observed transitions were identified for a *d*-orbital ordering $d_{xy} < d_{xz}, d_{yz} < d_{x^2-y^2} < d_{z^2}$ for complexes of the type $[MOCl_4]^{n-}$ (n = 1 or 2). There have been many subsequent studies (see ref. 1 and refs. therein) and for the VO^{2+} systems a general agreement in the spectral interpretation has been reached. Recent work[1] divided the vanadyl spectra into bands I, II, and III on the following basis: band I varied in position depending on the nature of the ligands *cis* to the oxo groups, $d_{xy}\rightarrow d_{x^2-y^2}$; band II was essentially invariant to ligand substitution, $d_{xy}\rightarrow d_{xz},d_{yz}$; band III shifted, presumably to higher energy, on six-co-ordination, $d_{xy}\rightarrow d_{z^2}$. These assignments were consistent with the observed vibrational fine structure and polarization characteristics of the absorption bands.

The CrO^{3+} unit has not been studied in detail apart from $[CrOCl_4]^-$,[5] where differences with the VO^{2+} assignment and that of Gray and Hare[4] were proposed. Two absorption bands were identified originating at *ca.* 13 000 and 18 000 cm^{-1}. The former was assigned as a $^2B_2\rightarrow{}^2E$ transition, arising from the one-electron promotion $d_{xy}\rightarrow d_{xz},d_{yz}$, since the band had greater absorbance in *xy versus z* polarization and carried a vibrational progression, the frequency of which was consistent with a Cr–O stretching mode in the electronic excited state. The absorption at *ca.* 18 000 cm^{-1} was assigned Cr–O(π)→Cr–O(σ*): an oxygen to metal charge-transfer (c.t.) process. Both this band and the 'first' band were assigned with reference to the results[5] of *ab initio* configuration interaction (CI) calculations, together with the following arguments. The *xy* polarized nature of the band suggested a $^2B_2\rightarrow{}^2E$ state transition. The calculated and experimental (in solution) oscillator strengths of the band *versus* the first transition were judged to be comparable. The observed vibrational fine structure (average separation *ca.* 300 cm^{-1}) was assumed to be an A_1(Cr–Cl) vibrational mode and a B_1 or B_2 Cr–Cl mode was used to relax the appropriate selection rules. This assignment was at variance with the assumption[3] that the second band in the electronic spectrum of $[CrOCl_4]^-$ was due to the $d_{xy}\rightarrow d_{x^2-y^2}$ transition but further evidence was taken from the temperature dependence[6] of the electronic spectrum of the $[PtCl_4]^{2-}$ chromophore. Here the transition at *ca.* 20 000 cm^{-1} assigned $d_{xy}\rightarrow d_{x^2-y^2}$ was markedly reduced in intensity at low temperature where vibrational fine structure was observed. Thus, in $[CrOCl_4]^-$ since, (*a*) the apparent intensity of the 'second' (*ca.* 18 000 cm^{-1}) band is greater than that of the $d_{xy}\rightarrow d_{xz},d_{yz}$ transition; (*b*) the intensity of the 'second' band is only slightly reduced on cooling; (*c*) the 'second' band was thought to be invariant to change of ligand within each of the series VO^{2+}, CrO^{3+}, MoO^{3+}; and (*d*) from the results of the theoretical calculation,[5] the oxygen to metal c.t. nature of the transition was inferred.

In an attempt to examine the possibility of self consistency in the assignment of the electronic absorption spectra of the MO^{3+} (M = Cr, Mo, or W) complexes, the electronic spectrum[1] of $[CrOCl_4]^-$ has been re-investigated. This seemed justifiable in view of the good understanding of the electronic spectrum of $[VOCl_4]^{2-}$, the theoretical calculations accomplished[5,7] for $[CrOCl_4]^-$, and the suitability of the $[AsPh_4]^+$ salt for the recording of polarized electronic spectra.[5] This re-investigation has identified a previously unreported *xy* polarized band system, originating at *ca.* 20 000 cm^{-1}, which greatly improves the understanding of the electronic structure of the CrO^{3+} chromophore and relates this to that of the VO^{2+} moiety. It will be shown that this band may be assigned to the one-electron promotion $d_{xy}\rightarrow d_{z^2}$, from its polarization characteristics and observed vibrational fine structure.

Experimental

Preparation of $[AsPh_4][CrOCl_4]$.—This compound was prepared by the method of Ziebarth and Selbin[8] using standard Schlenk tube techniques. Chromium trioxide (0.25 g, 2.5 mmol) was treated with hydrogen chloride dissolved in acetic acid–acetic anhydride (25 cm^3, 10:1 v/v), followed by the addition of $[AsPh_4]Cl$ (1.0 g, 2.5 mmol). The orange product was removed by filtration and dried *in vacuo*. Crystals were grown overnight by permitting the evaporation of a solution of the compound in dry CH_2Cl_2, in a dry-box, yielding deep red single crystals suitable for polarized spectral measurements.

Electronic Spectral Studies.—The compound $[AsPh_4][CrOCl_4]$ has been shown[9] to crystallize in the *P*4/*n* space group and previous work[5] has shown that the Cr–O(terminal) axes lie parallel to the elongated direction of the tetragonal block. Spectra which were recorded with the electric vector of the incident radiation aligned parallel or perpendicular to this direction are designated *z* or *xy*, respectively. The results obtained are shown in the Figure. Spectra were obtained by mounting the crystals on a silica substrate and after suitable thinning, cooling them in a bath cryostat.* These measurements on the silica substrate give improved resolution of band III (see below), probably because the glass substrate used previously[5] may not be transparent above 22 000 cm^{-1}.

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* Spectra were obtained using an Oxford Instruments MD404 Immersion Dewar. The details of operation will be described elsewhere.

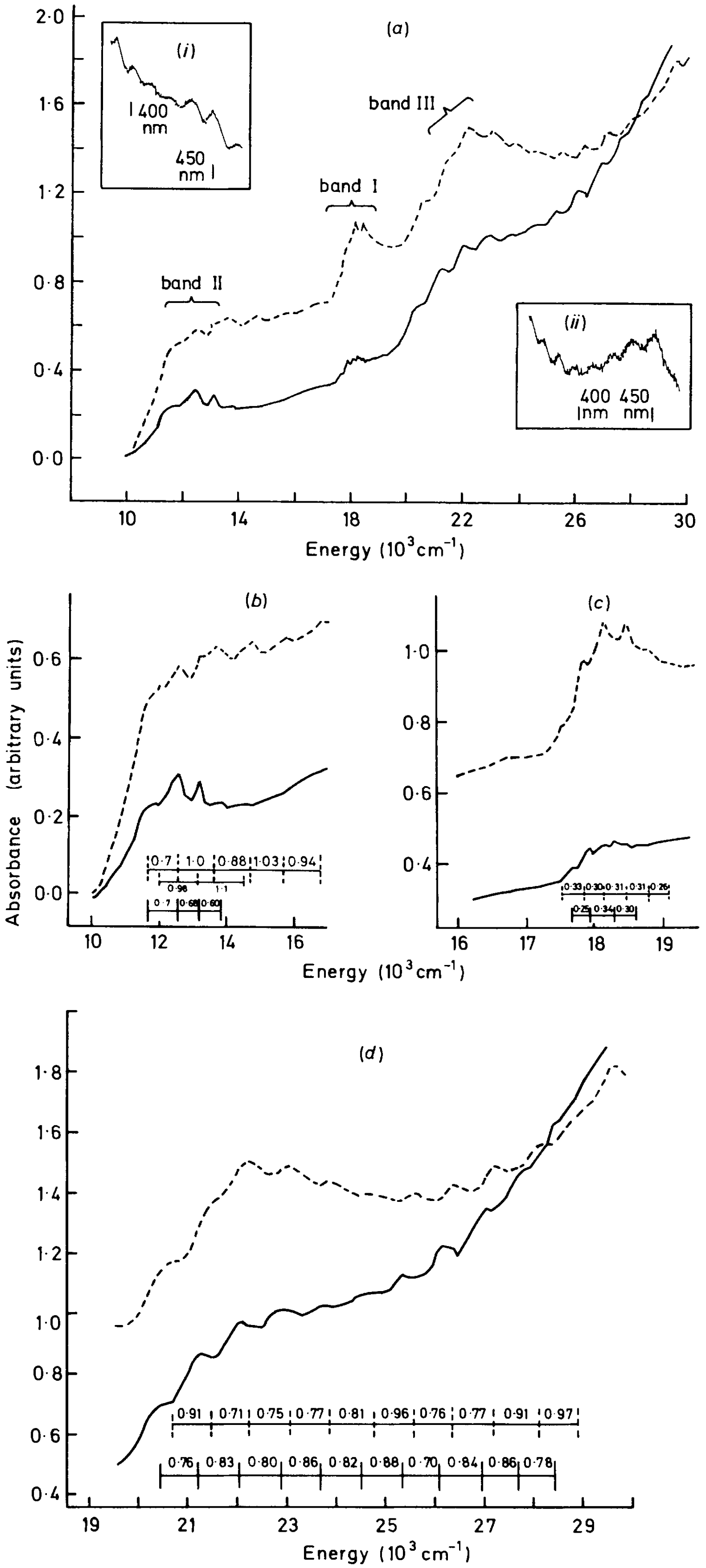

Figure. Polarized single-crystal electronic absorption spectrum of [AsPh$_4$][CrOCl$_4$]: (——) *z* polarization, (– – –) *xy* polarization, (*a*) Full spectrum with insets [(*i*) *z* polarization, (*ii*) *xy* polarization] showing the spectrometer trace in the band III region. (*b*) Enlargement of 10 000—17 000 cm^{-1} region. (*c*) Enlargement of 16 500—19 500 cm^{-1} region. (*d*) Enlargement of 19 500—30 000 cm^{-1} region

Table. Selection rules for electric dipole transitions of a d^1 complex in C_{4v} point symmetry (F = forbidden, A = allowed). The symmetry of the vibration which will make an electronically forbidden band allowed is given in parentheses

	C_{4v}	Polarization		$C_{4v'}$	Polarization	
Promotion	Transition	z	xy	Transition	z	xy
$d_{xy}\rightarrow d_{z^2}$	$b_2\rightarrow a_1$	$F(B_2)$	$F(E)$	$\Gamma_7\rightarrow\Gamma_6$	$F(E,B_1,A_2)$	A
$d_{xy}\rightarrow d_{x^2-y^2}$	$b_2\rightarrow a_1$	$F(A_2)$	$F(E)$	$\Gamma_7\rightarrow\Gamma_7$	A	A
$d_{xy}\rightarrow d_{xz},d_{yz}$	$b_2\rightarrow e$	$F(E)$	A	$\Gamma_7\rightarrow\Gamma_6$	$F(E,B_1,B_2)$	A
				$\Gamma_7\rightarrow\Gamma_7$	A	A

The spectrum appears to comprise three distinct band envelopes and these are designated as bands I, II, and III, in a manner analogous to that for the VO^{2+} spectra described previously.[1] All three absorptions show greater apparent absorbance in xy than in z polarization. The general background of absorption tailing from the u.v. region means that it is difficult to obtain accurate values for the relative intensities in xy and z polarization for the three band systems.

Considering first the newly identified band III, it is noted that, in order to see the individual components of this band, it was necessary to obtain spectra on a very thin crystal which was then unsuitable for the examination of the first two band envelopes. Thus, Figure (*a*) is a composite of the 4.2 K spectrum of a thick crystal (*ca.* 0.075 mm), for bands I and II, and a 77 K measurement on a thinner crystal (*ca.* 0.025 mm) for band III. The two measurements were combined by consideration of the relative intensities of the envelope of band I. The existence of features in the band III region was suggested in the previous study[5] but, even at 4.2 K, a crystal which is too thick produces strangely distorted spectral traces, probably caused by the low level of light incident on the detector. The apparent absorbance is greater in xy than in z polarization and both progressions carry a splitting of *ca.* 800 cm^{-1}.

The low-energy band system (band II) has an overlapping progression in xy polarization, comprising irregular spacings beginning with a shoulder at *ca.* 11 800 cm^{-1} in common with the z polarized spectrum. Similarly, the first band envelope in the visible region of the spectrum (band I) is more intense and better resolved in xy than in z polarization. A six-membered vibrational progression of average splitting 300 cm^{-1}, originating as a shoulder at 17 550 cm^{-1}, is evident in perpendicular polarization and compares with a broad, five-component band profile with average spacing 280 cm^{-1} and beginning 220 cm^{-1} to higher energy in z polarization.

Discussion

Using the same model as the previous interpretation[5] and, in common with that of VO^{2+}, an electronic ground state with a single unpaired electron in the $3d_{xy}$ in-plane antibonding molecular orbital, which is predominantly metal in character, has been established. The appropriate selection rules for electric dipole transitions derived for this model are given in the Table.

Band III.—From the basis formed by the assignments of VO^{2+} complexes[1] a description of a self-consistent assignment for the band envelope designated III will be attempted. In the following discussion the comparison between the spectra of $[CrOCl_4]^-$ and $[VOCl_4]^{2-}$ will be drawn upon[1] to develop the assignment. As for VO^{2+}, it is the visible band envelope above 20 000 cm^{-1} which has produced the most marked vibrational fine structure at low temperature. Here for CrO^{3+}, in both polarizations, the position of each individual feature can be determined with reasonable accuracy, and hence the difference in the band origins, 20 460 and 20 630 cm^{-1} in z and xy polarizations, respectively, is unambiguous. Unfortunately, again due to the general background absorption it is not possible (as in the case[1] of $[VOCl_4]^{2-}$) accurately to compare the relative intensity of an absorption band recorded in xy and z polarizations. From the selection rules for C_{4v} symmetry (see Table) the $3d_{xy} \rightarrow 3d_{z^2}$ transition, although orbitally forbidden, is allowed in xy polarization by coupling with an E vibrational mode and by coupling with a B_2 mode in z polarization. It is, therefore, necessary to determine reasonable values for E and B_2 vibrational modes, taking account of the earlier estimates[5] as *ca.* 400 and *ca.* 300 cm^{-1}, respectively. Comparing the vibrational data for $[CrOCl_5]^{2-}$ [10] with those of $[AsPh_4][MoOCl_4]$ obtained by Collin *et al.*,[11] a value for the B_2 vibrational mode of $[CrOCl_4]^-$ may be estimated at *ca.* 170 cm^{-1}. Whilst being aware that ground-state frequencies are being used to explain excited-state observations, generally accepted trends[12] in vibronic coupling may be anticipated. Assuming coupling with an E vibrational mode of *ca.* 360 cm^{-1} in xy polarization and a B_2 vibrational mode of 170 cm^{-1} in z polarization, an observed separation of *ca.* 190 cm^{-1} between the first elements of each polarized progression would be anticipated. The observed difference in band origin between each polarization is 170 cm^{-1}, with the first xy polarized feature at higher energy than the z false origin. This gives a $3d_{xy}$–$3d_{z^2}$ separation of *ca.* 20 270 cm^{-1} for $[CrOCl_4]^-$. The difference in position of the false origins suggests that vibronic coupling and not spin–orbit coupling[13] is the major effect responsible for relaxation of the selection rules. Hence, there is an obvious comparison between the nature of band III in $[CrOCl_4]^-$ and $[VOCl_4]^{2-}$.

Since band III manifests a progression of *ca.* 800 cm^{-1} (in both polarizations), indicative of coupling with the ν[Cr–O(terminal)] stretching mode in the electronic excited state, the characteristics of this transition are consistent with a $3d_{xy}\rightarrow 3d_{z^2}$ one-electron promotion. This conclusion may be drawn by comparison with the five-co-ordinate complexes containing VO^{2+}, where a reduction of ν[V–O(terminal)] from 1 000 cm^{-1} in ground electronic state to a mean separation of *ca.* 750 cm^{-1} in the electronic excited state is observed.[1,4] This reduction is a consequence of the removal of an electron from an in-plane antibonding π molecular orbital into an axial antibonding σ molecular orbital.

The foregoing discussion provides strong evidence for a close analogy between the CrO^{3+} and VO^{2+} chromophores. Previously, good spectroscopic evidence for this comparison was unavailable and it did not seem possible to relate electronic structural arguments between the d^1 systems VO^{2+} and MoO^{3+} *via* CrO^{3+} complexes.

Band II.—The lowest energy feature (labelled band II by analogy with the VO^{2+} assignment[1]) is assigned to the one-electron promotion $3d_{xy}\rightarrow 3d_{xz},3d_{yz}$, from its polarization characteristics, energy, and comparison of spectral details with those of VO^{2+} complexes.[1] The greater intensity in xy *versus* z polarization is consistent with the selection rules for C_{4v} point symmetry. The origin of the average spacing of 700 cm^{-1} displayed by this band envelope is attributed to the totally symmetric Cr–O(terminal) stretching mode in the electronic excited state.

However, the irregular spacings of this band system, in xy polarization, relative to the VO^{2+} complexes[1] suggests that spin–orbit or further vibrational coupling is being observed. Under the influence of spin–orbit coupling the excited state arising from the $(3d_{xz},3d_{yz})^1$ orbital occupation splits into two components with Γ_6 lying below Γ_7 (see Table) by the value of the spin–orbit coupling constant (to first order) which has a free-ion value[5] for Cr^V of 380 cm^{-1}. The feature at *ca.* 11 800 cm^{-1} in both polarizations and the appearance of the additional structure in *xy* polarization is consistent with the assignment of band II to the spin–orbit split ^2E state. Thus, the experimental evidence agrees with the results of both the *ab initio* CI[5] and the SCF MS-Xα calculations[7] in assigning the lowest energy absorption band to a *d–d* transition of the type $^2B_2 \rightarrow {}^2E$ (the calculated values being 9 900 and 8 300 cm^{-1}, respectively, being close to the electronic origin of 11 800 cm^{-1} observed experimentally).

Band I.—The absorption at *ca.* 18 000 cm^{-1} is assigned to the one-electron promotion $3d_{xy} \rightarrow 3d_{x^2-y^2}$, on the basis of a comparison with the assignment of VO^{2+} spectra[1] and the inherent vibrational fine structure of this band. This transition is equivalent to 10 *Dq* for the equatorial chloride ligands and the assignment is compatible with the expected increase in the crystal-field splitting parameter, for a concomitant decrease in ionic radii and increased oxidation state from VO^{2+} to CrO^{3+}.

None of the features classified[1] as band I in the VO^{2+} series displayed a vibrational progression, although a band showing a M–Cl mode only has been observed for $[OsNCl_4]^-$.[14,15] Thus, the vibrational progression of *ca.* 300 cm^{-1}, observed in both polarizations, implies a Cr–Cl stretching mode, this value being reduced from that of the ground state due to promotion into the Cr–Cl σ^* orbital. In the ground state of $[CrOCl_5]^{2-}$, a totally symmetric metal–halogen mode has been reported[10] at 343 cm^{-1}. From the selection rules, it is evident that, for $[CrOCl_4]^-$ in C_{4v} point symmetry, the intensity in *z* polarization can only be due to spin–orbit coupling (*i.e.* by utilization of the C_{4v}' group), since this anion possesses no A_2 vibrational mode (see Table). Therefore, the first feature in *xy* polarization should not be lower in energy than the first feature in *z* polarization. However, in both polarizations the band profile is broad and the intensity of the envelope *below* the shoulder at 17 700 cm^{-1} in *z* polarization may contain the $\Gamma_7 \rightarrow \Gamma_7$ electronic origin of the absorption. The well resolved visible bands of the $[VOX_2(tmu)_2]$ (X = Cl or Br; tmu = *N,N,N′,N′*-tetramethylurea) complexes[1] demonstrated that, for $3d^1$ oxo systems, a vibronic relaxation of the selection rules can dominate over a spin–orbit mechanism. This could extend to CrO^{3+}, given the comparable free-ion spin–orbit coupling values of V^{IV} and Cr^{V} [13] and the similar band position for this transition for VO^{2+} and CrO^{3+} chloro complexes. Furthermore, since there are vibrational *E* modes[8] available for coupling in $[CrOCl_4]^-$, it is suggested that the features seen between 17 550 and 19 060 cm^{-1} in *xy* polarization derive their intensity vibronically.

The assignment proposed here for the band commencing at *ca.* 17 600 cm^{-1} is at variance with those postulated earlier.[5,7] However, the *ab initio* calculation[5] placed the equivalent *d–d* transition at 22 400 cm^{-1} and the Xα calculations[7] estimated this transition to be at 19 400 cm^{-1}.

Conclusions

The major debate, regarding the interpretation of the electronic spectra of the d^1 oxo complexes of Cr, Mo, and V, has been the interpretation of the 'second' or 'visible' absorption band and the location of the $d_{xy} \rightarrow d_{x^2-y^2}$ transition. For $[CrOCl_4]^-$ the previous theoretical results have suggested that the 'second' band is due either to an oxygen (π) to metal (σ^*) transition (*ab initio* CI)[5] or a halogen (π) to a metal (π^*) transition (SCF MS-Xα).[7] This paper presents a new and important argument in favour of the $d_{xy} \rightarrow d_{x^2-y^2}$ transition being assigned to the 'second' or 'visible' band of CrO^{3+} (and MoO^{3+}).[15] This assignment is in full accord with that originally proposed by Gray and Hare[4] and further substantiated by the studies of Winkler and Gray.[2b]

The new observation is the identification of *ca.* 20 270 cm^{-1} as the origin of the $d_{xy} \rightarrow d_{z^2}$ transition for $[CrOCl_4]^-$. This places an upper limit on the energy span of the *d–d* transitions for this ion and presents a different perspective than the ones resulting from the theoretical calculations. Thus, the $d_{xy} \rightarrow d_{z^2}$ transition was estimated at 33 100 and 26 600 cm^{-1} by the *ab initio*[5] and Xα[7] calculations, respectively.

The assignments of the polarized single-crystal electronic spectral data for $[AsPh_4][CrOCl_4]$, proposed herein, are consistent with the earlier[1] assignments for $[VOCl_4]^{2-}$. The three *d–d* transitions have been located and their origins are 11 900, 17 550, and 20 270 cm^{-1}, for $d_{xy} \rightarrow d_{xz},d_{yz}$, $d_{xy} \rightarrow d_{x^2-y^2}$, and $d_{xy} \rightarrow d_{z^2}$, respectively.

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