

Low Temperature Polarized Spectra of Potassium Bis Oxalato *trans* Diaquo Chromium (III) Trihydrate *

R. DINGLE**

*Chemical Laboratory IV, Department for Physical Chemistry, University of Copenhagen,
Copenhagen, Denmark*

Vibronic coupling mechanisms do not lead to unambiguous assignments of the broad, strongly polarized absorption bands seen in the spectrum. Reasons for this failure are discussed. The sharp lines in the red region, that coincide in absorption and emission, are attributed to magnetic dipole processes. Some peculiarities observed in emission are discussed and some possible mechanisms are considered.

Vibronic intensity gaining mechanisms have been used for many years in the explanation of spectra that are electronically forbidden, particularly in aromatic molecules in gas and solid phases.^{1,2}

Over the past decade, the application of vibronic intensity gaining mechanisms to the question of the source of spectral intensity in the $d-d$ excitations of transition metal complexes has met with mixed success.³⁻⁵ The rather weak spectra, $f \sim 10^{-3}$, their formally forbidden nature ($d-d$) and the usual decrease in intensity on cooling all support a vibronic mechanism. Unfortunately, the wealth of detail seen in many organic molecule spectra is usually absent and rather indirect approaches are employed in order to rationalize the validity of the vibronic model.

The popular mode of analysis has been to utilize the temperature dependence of absorption band intensities (clouded by changes in crystal forces on cooling) and to evaluate the directional properties of the transition dipole moment

$$\langle \psi_{gd}^{el} \varphi_{gd}^{vib} | M | \psi_{excit}^{el} \varphi_{excit}^{vib} \rangle$$

in crystals, in order to assign transitions. At moderately low temperatures φ_{gd}^{vib} , if it is a localized molecular mode, may be neglected and the identity

* Some of the work reported here was done in the Department of Chemistry, University of Western Australia.

** Present address: Bell Telephone Laboratories, Incorporated, Murray Hill, New Jersey, U.S.A.

of the excited *VIBRONIC* state may be established since, except in Jahn Teller configurations, the ground state is usually known.

These methods have been tried on many systems,³⁻⁷ but, even in K_2PtCl_4 crystals, where each unit cell contains only one formula unit, where the ground electronic state is $^1A_{1g}$, where at low temperatures extensive vibrational fine structure is seen^{6,7} and where some transitions are strongly polarized, doubt still exists as to the assignment of the excited electronic states.

The present report concerns the crystal potassium bis oxalato *trans* diaquo chromium(III) trihydrate. In the crystal, the chromium complex is six coordinated, it is near octahedral and is of D_{2h} symmetry. The central chromium ion is at a C_i site and the crystal has a C_{2h} factor group.⁸ In addition, the parent (O_h) energy level scheme is well understood and, in the present case, the noncubic environment should split the degenerate O_h level but not by enough to confuse their parentage.

EXPERIMENTAL

The crystals grow by evaporation from aqueous ethanolic solutions at room temperature. They develop as monoclinic needles extended along the *b* axis and as plates with (001) well developed. (010) can be exposed by cutting the needles normal to the *b* axis. Crystals were identified and oriented by X-ray methods.* Room temperature and 77°K crystal spectra have been obtained on (001), (010), and (100) using pinhole techniques. In addition, spectra have been taken on (001) with the crystal at 4.2° and 1.6°K.

CRYSTAL STRUCTURE

Van Niekerk and Schoening⁸ report *trans* potassium bis oxalato diaquo chromium(III) trihydrate to be monoclinic, space group $P_{21/c}-C_{2h}^4$

$a = 7.85 \text{ \AA}$	
$b = 5.72 \text{ \AA}$	molecular symmetry D_{2h}
$c = 13.88 \text{ \AA}$	factor group C_{2h}
$\beta = 109^\circ 30'$	site group C_i
$Z = 2$	

The coordinated water molecules are *trans*, $Cr-OH_2=2.02 \text{ \AA}$. The $Cr-O_{oxalate}$ bond lengths are 1.92 \AA and the internal chelate angle is 83° . The projection the molecule makes upon principal faces is shown in Fig. 1. Table 1 summarizes the appropriate unit molecular transition moments (*x*, *y*, and *z*) (for the chosen coordinate system) when the molecules are projected upon these faces.

RESULTS

Fig. 2 shows spectra taken on (001) at 300° , 77° , and $4.2^\circ K$. Room temperature results from (010) are shown in Fig. 3. The (100) spectra are very similar to those taken on (001). Tables 2 and 4 summarize the results. The

* Thanks are due to K. J. Watson for this assistance.

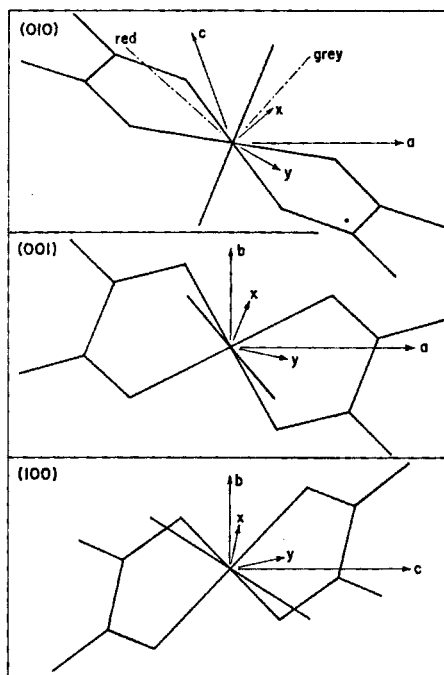


Fig. 1. Molecular projections on the principal crystal faces of $\text{K}[\text{Cr}(\text{III})(\text{C}_2\text{O}_4)_2(\text{H}_2\text{O})_2]3\text{H}_2\text{O}$.

weak sharp lines seen in emission and absorption are summarized in Table 3 and Fig. 4.

All spectra show evidence of six broad bands. The bands are strongly polarized, the intensities are strongly temperature dependent (Fig. 2, Table 2) and the overall intensity is low, $\epsilon \sim 5\text{--}20$ liters mole⁻¹ cm⁻¹. These factors, coupled with the fact that parity should be conserved at all levels of approximation in the crystal, indicate a vibronically induced spectral analysis to be appropriate. From the polarization data the spectra are analyzed and each

Table 1. Projection of unit molecular transition moments upon the principal crystal faces of *trans* $\text{K}[\text{Cr}(\text{III})(\text{C}_2\text{O}_4)_2(\text{H}_2\text{O})_2]3\text{H}_2\text{O}$.

	(001)			(100)			(010)		
	a	b	b/a	b	c	b/c	red	grey	red/grey
<i>x</i>	0.13	0.77	6.0	0.77	0.03	25.7	0.003	0.23	0.01
<i>y</i>	0.74	0.03	0.04	0.03	0.54	0.06	0.93	0.04	23.3
<i>z</i>	0.12	0.17	1.4	0.17	0.43	0.39	0.08	0.68	0.12
<i>xy</i>	0.87	0.80	0.92	0.80	0.57	1.40	0.93	0.27	3.45
<i>xz</i>	0.25	0.94	3.75	0.94	0.46	2.04	0.08	0.91	0.09
<i>yz</i>	0.86	0.20	0.23	0.20	0.97	0.21	1.00	0.72	1.40

Table 2. Spectral characteristics of *trans* K[Cr(III)(C₂O₄)₂(H₂O)₂]3H₂O, face (001), broad bands only.

Crystal face	$\nu_{\max}^{300^\circ}$ cm ⁻¹	ϵ^{300°	$\nu_{\max}^{4.2^\circ}$ cm ⁻¹	$\epsilon^{4.2^\circ}$	$\frac{\epsilon^{4.2^\circ}}{\epsilon^{300^\circ}}$
(001)	17 300 b	6.1	17 850 &_l b	3.8(b)	0.62
	18 750 ⊥b	17.1	19 380 ⊥b	11.5	0.67
	? b	~5-6	19 600 b	4.5	
	23 750 ⊥b	20.0	24 100 ⊥b	15.4	0.77
	24 100 b	10.6	24 630 b	8.3	0.79
	25 400 &_l b	10.2	26 100 &_l b	7.5	0.73
			32 250 ⊥b	~100 cutoff	
			34 500 b	~100 cutoff	

absorption band associated with certain molecular transition moments (Table 4). This selection need not be unique because *x* and *z* are very difficult to separate.

Table 3. Main absorption and emission frequencies associated with sharp lines observed in the spectrum at 4.2°K.

cm ⁻¹	Absorption Assignment	Assignment	Emission cm ⁻¹	
14 432)	(0,0) magnetic dipole	(0,0) magnetic dipole	14 433	unresolved doublet
14 434)				
14 564	+131	-26	14 407	
14 620	+188	-42	14 392	
14 626	+194	-47	14 386	
14 656	+222	-65	14 368	
14 697	+2 × 133	-84	14 349	
14 720	+287	-92	14 341	
14 728	+295	-117	14 316	
14 766	+1 × 194 + 1 × 134	-180	14 253	
		-188	14 245	
14 836	+3 × 134	-194	14 239	
14 887	1 × 187 + 2 × 134	-212	14 221	
14 970	+4 × 134	-218	14 215	
		-257	14 176	
20 860	(0,0)' electric dipole *	-267	14 166	
		-283	14 150	
21 900	(0,0)'' electric dipole			
22 040	+1 × 140	-413	14 020	
22 178	+2 × 139	-428	14 005	
22 275	+2 × 139 + 1 × 108			
22 699	(0,0)''' electric dipole			
22 850	+1 × 151			
~23 000	+2 × 150			

* (0,0)', (0,0)'', and (0,0)''' represent vibronic false origins.

Table 4. Resolution of polarization data into probable molecular transition moments.

Probable transition moments	(001)		(010)		(100)	
	300°K	80°, 4.2°K	300°K	Transition moment	300°K	Transition moment
XZ	17 300 cm ⁻¹ b	17 850 &⊥b	17 300 grey	XZ(not Y)	17 300 b	X,Z?
Y	18 750 ⊥b	19 380 ⊥b	18 700 red	Y(not X)	18 750 ⊥b	Y
X,Z(?)	? b	19 600 b	? red	X,Y(not Z)	19 500 b	X,Y
Y	23 750 ⊥b	24 100 ⊥b	23 700 red	Y(not X)	23 550 ⊥b	Y(not X)
X &/or Z	24 100 b	24 630 b	24 050 grey	X &/or Z (not Y alone)	23 900 b	X &/or Z (not Y alone)
XYZ, maybe Z alone	? &⊥b	{ unresolved 26 100 &⊥b resolved 26 300 &⊥b	25 400 red grey	XYZ	24 500 &⊥b	X,Y,Z ratio suggests Z

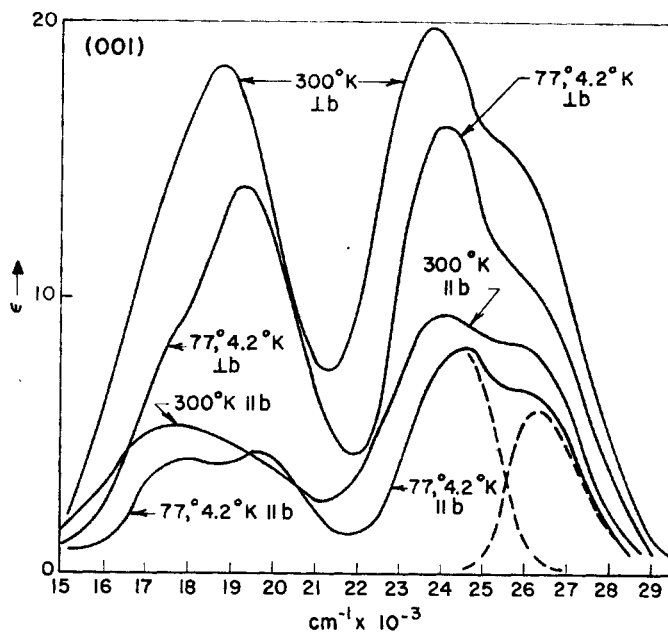


Fig. 2. Absorption spectrum taken on (001) with the crystal at 300°, 77°, and 4.2°K.

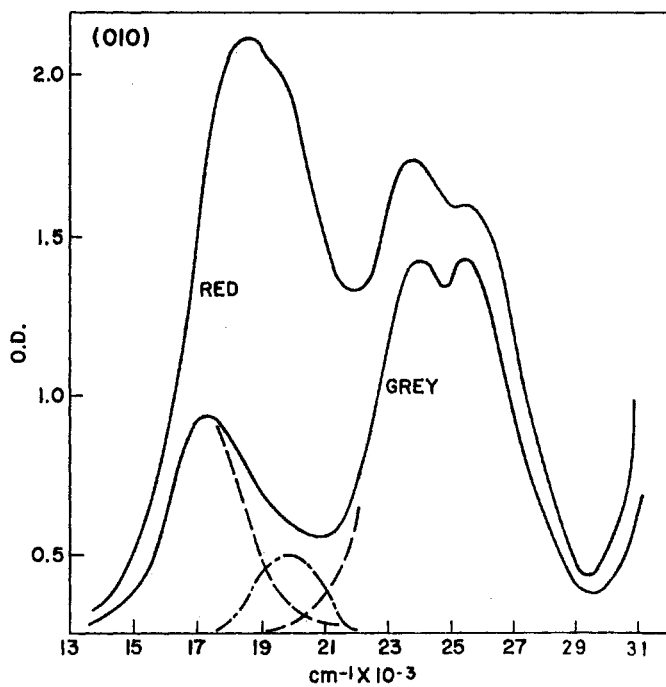


Fig. 3. Absorption spectrum taken on (010), crystal temperature 300°K.

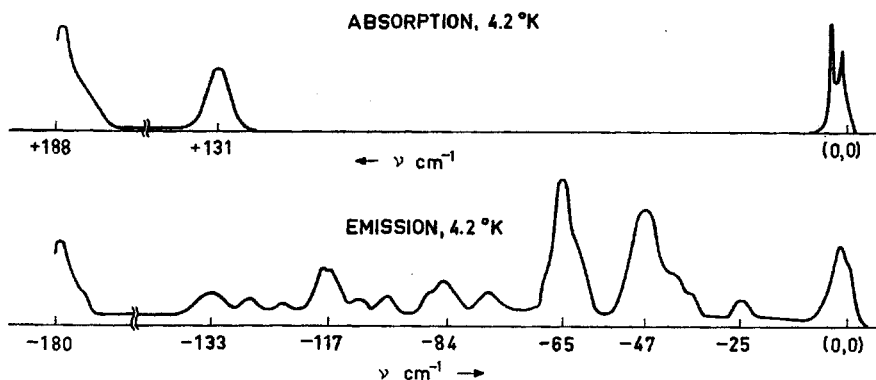


Fig. 4. Absorption and emission (unpolarized on (001)) in the vicinity of the (0,0) line at $14\,433 \pm \text{cm}^{-1}$. Crystal temperature 4.2°K.

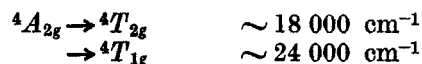
ANALYSIS OF RESULTS

The broad bands

The molecular symmetry, the factor group and the site symmetry all conserve the parity of the d orbital wave functions and hence the parity of the electronic states. The placement of the molecular axes (x , y , and z) is determined by the full molecular structure including ligands and not just by the six atoms coordinated to the chromium ion. The spectra, and especially the $18\,750 \text{ cm}^{-1}$ band, cannot be reconciled with molecular axes along the bond directions.

Should the spectra be considered in an oriented gas model or will crystal effects have to be included?

A solution spectrum in an oxalate buffer (at $\sim 0^\circ\text{C}$) has been obtained and, although in solution the *trans* form goes quickly over to the *cis* form, the extrapolated spectrum (to $t=0$) consists of two asymmetric bands, the higher energy band having the greater asymmetry. The asymmetry supports the model of a distorted electronic structure in solution and comparison with the tris oxalato and hexaquo chromium(III) spectra allows the following correlation



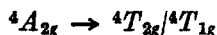
In the crystal, the unique axis of the C_{2h} factor group is parallel to the b crystal axis. Hence, if factor group interaction is to dominate the spectrum, the (010) spectrum should be isotropic. Fig. 3 shows this not to be the case. If the site symmetry determines the spectrum the result should be an isotropic spectrum (all electronic states of the d manifold transforming as A_g , all odd vibrations as a_u). Thus, in view of the spectral anisotropy, it is reasonable to assume that, although the site may have a regulating influence upon the spectrum, the molecular symmetry D_{2h} , *i.e.*, an oriented gas model, should make a good starting point from which to attempt the vibronic analysis.

Table 5. Possible values of the product $\Gamma_{\text{gd},g}^{\text{el}} \times \Gamma_{\text{exc},g}^{\text{el}} \times \Gamma_{\text{exc},u}^{\text{vib}}$ in D_{2h} symmetry.

Odd parity vibrations $\Gamma_{\text{exc},u}^{\text{vib}}$	A_g	$\Gamma_{\text{gd},g}^{\text{el}} \times \Gamma_{\text{exc},g}^{\text{el}}$		B_{3g}
		B_{1g}	B_{3g}	
a_u	A_u	B_{1u}	B_{3u}	B_{3u}
b_{1u}	B_{1u}	A_u	B_{3u}	B_{3u}
b_{2u}	B_{2u}	B_{3u}	A_u	B_{1u}
b_{3u}	B_{3u}	B_{3u}	B_{1u}	A_u

Even in this case, if all odd vibrations are considered equally efficient, an isotropic spectrum would result.

Because six bands are seen in two groups of three, centered more or less about the octahedral



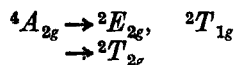
positions, the D_{2h} rhombic environment has led to the total resolution of the degenerate octahedral excited states. At 4.2°K the spectrum is not drastically altered from that seen at 300°K and, excluding such complications as magnetic exchange and/or the influence of acoustical lattice modes at or near $k=0$ in the crystal in the ground state, the vibronic coupling (at 4.2°K) will be in the excited electronic states. Since the bands are broad, electronic/vibrational interaction in these states must be considerable and products $\Gamma_{\text{gd},g}^{\text{el}} \times \Gamma_{\text{exc},g}^{\text{el}} \times \Gamma_{\text{exc},u}^{\text{vib}}$ become important in assigning vibronic symmetries. Table 5 shows possible combinations of odd vibrations and even electronic representations in D_{2h} .

If all vibrations are equally efficient one might expect an isotropic spectrum. Since the spectrum is strongly anisotropic, it is necessary to choose some vibrations to be more effective than others and/or to include more than one ψ_u^{el} state from which intensity can be stolen.* We see later that the latter is necessary and from Tables 4 and 5 it is seen that there are numerous possibilities concerning the choice of vibrations, many of which *may* lead to an explanation of the spectra. Without an independent identification of the excited states, this approach cannot be made unambiguous. From Table 4 some transitions may be analyzed to require only one assisting odd vibration, whereas others appear to be in need of more (two seems adequate).

The sharp lines

These systems, one in the red (lowest line in absorption 14 432 cm^{-1}) and one in the blue/green (lowest line 20 086 cm^{-1}) are thought to correlate with

* See Ref. 9 for details.



respectively. These transitions gain intensity *via* the spin-orbit coupling operator which mixes them with spin allowed transitions according to expressions of the type

$$\frac{\langle \psi_{\text{doublet}}^{\text{el}} | \mathbf{l} \cdot \mathbf{s} | \psi_{\text{quartet}}^{\text{el}} \rangle}{|E_{\text{quartet}} - E_{\text{doublet}}|}$$

This mixing leads to an intensity for the spin forbidden transition

$$f = \frac{f' |\langle \psi_{\text{doublet}} | \mathbf{l} \cdot \mathbf{s} | \psi_{\text{quartet}} \rangle|^2}{|(E_{\text{quartet}} - E_{\text{doublet}})|^2}$$

The operator that corresponds to $\mathbf{l} \cdot \mathbf{s}$ is even and hence this mixing does not result in any breakdown in the parity selection rule for these spin-forbidden transitions.

The absorption and emission results for the red system are not mirror images (Fig. 4). They do, however, have a common origin, at 14 432, 14 434 cm^{-1} in absorption and at 14 433 cm^{-1} in emission.* If electric dipole processes alone are active in the spectrum, then the parity selection rule is broken down. At 4.2°K, this transition must be the (0,0) or (n ,0) in absorption and (0,0) or (0, n) in emission. Only in the case where $n=0$ will the line fall at the same frequency in absorption and emission. For electric dipole processes this would mean a $g-g$ transition which is rigorously forbidden. Magnetic dipole processes are, on the other hand, weakly allowed between states of even parity. The (0,0) transition has an oscillator strength $f \sim 5 \times 10^{-9}$ and is assigned to a magnetic dipole process. This allows the frequencies of the vibrations associated with the vibronic fine-structure to be found, both in the ground and in the excited states. Recourse to Table 3 shows that in absorption there are short progressions in $135 \pm 5 \text{ cm}^{-1}$ and that frequencies 188, 194, 222, 287, and $295 \pm 5 \text{ cm}^{-1}$ also appear built upon (0,0). Some of the latter group may correspond to levels associated with other electronic components of the ${}^2E_g, {}^2T_{1g}$ group. $135 \pm 5 \text{ cm}^{-1}$ is totally symmetric in the excited state. In emission there is some evidence for frequencies at 180, 188, 194, 212, 218, 257, 267, and 283 cm^{-1} . In addition, there are many frequencies below 117 cm^{-1} ! (For further consideration see p. 2225.)

The blue systems show (in absorption) progressions in $135 \pm 5 \text{ cm}^{-1}$. The appearance of this simple progression again indicates the vibration to be totally symmetric in these excited states. If the lowest line in each group in the blue region is assigned as (0,0) magnetic dipole allowed, then the whole of the intensity of these systems must be magnetic dipole in origin and the usually more strongly allowed electric dipole vibronic processes must be completely absent. An alternative, which is more in line with the analysis of the red system, is as follows. Since the complex is essentially octahedral,

* The doublet is not clearly resolved in emission. This, we believe, results from the fact that in order to get a suitable signal to noise level the spectrometer slit was opened to 400 μ whereas for absorption, we typically used 50 μ slits.

many of the selection rules that apply to the octahedron will be transferred over to the lower symmetry, but somewhat modified by the latter environment. Thus, magnetic dipole processes may well be dominated by O_h determined selection rules. In O_h , the transition ${}^4A_{2g} \rightarrow {}^2E_g$ ($14\,433\text{ cm}^{-1}$) is magnetic dipole forbidden. In coupling to ${}^4T_{2g}$ (via spin-orbit interaction), it gains quartet character and magnetic dipole character (${}^4A_{2g} \rightarrow {}^4T_{2g}$ is magnetic dipole allowed) and the (0,0) transition becomes allowed. The blue systems arise from ${}^4A_{2g} \rightarrow {}^2T_{2g}$ which we assume is coupled via spin-orbit forces to the nearby ${}^4A_{2g} \rightarrow {}^4T_{1g}$ transition. The latter is magnetic dipole forbidden in O_h and hence so are the ${}^4A_{2g} \rightarrow {}^2T_{2g}$ transitions. The blue lines then are thought to be electric dipole allowed via a vibronic coupling mechanism which does not allow a (0,0) transition to appear and the lowest lines seen are due to (0,0)+ ν , where ν is an asymmetrical vibration of the excited state. The totally symmetrical mode ($\nu \sim 135 \pm 5\text{ cm}^{-1}$) then builds upon this false origin. Thus the O_h selection rules are not strongly modified in the lower symmetry of this complex.

The results on the red system indicate that there may be as many as five nontotally symmetric vibrations (in absorption) between 188 and 295 cm^{-1} , all of which could be contributing intensity, not only to these spin-forbidden transitions, but also to the spin allowed, but parity forbidden bands nearby. By introducing these results, it is shown that there may be a number of nontotally symmetric vibrations that are active in the *broad band* spectra.

Finally, the sharp line spectra are very strongly polarized. Since they may only couple, via the spin-orbit, with spin allowed states that transform under a similar representation in the appropriate double group, the spin-allowed state to which they couple may also be very strongly polarized. These strong orientation effects are in full accord with the findings in Table 4.

The allowed transition from which intensity
is stolen

Intensity is stolen, in a vibronic model, from transitions that are electronically allowed. If ${}^4A_{2g} \rightarrow {}^4X_u$ is an allowed transition, then the interaction is of the form

$$\langle {}^4A_{2g} | M | {}^4X_u \rangle \langle {}^4X_u | M | {}^4T_{ng} \rangle, \quad n = 1 \text{ or } 2$$

The results in Table 4 show at least two and possibly three different vibronic transition moments, which in turn indicate two and possibly three different allowed transitions to be involved. In the near UV, the absorption is steadily increasing in all polarizations, thus there are transitions allowed in different molecular directions and quite adjacent to the $d-d$ bands. Graddon¹⁰ has reported a weak band $\epsilon \sim 50-100$, near $40\,000\text{ cm}^{-1}$ in solutions of oxalate complexes ($n \rightarrow \pi^*$ in the C=O portions of the ligands?) with strong absorption at higher energies. In a D_{2h} model, these strong absorptions would have to be

$${}^4B_{1g} - {}^4A_u(Z), \quad {}^4B_{2u}(X) \text{ and/or } {}^4B_{3u}(Y)$$

Presumably the $d-d$ transitions gain intensity from this group. Table 4 shows which possible combinations of vibronic levels may lead to a valid result.

From the line spectra there are a number of vibrations active in the excited states; from the band spectra and the last section only one or two symmetry types are needed to explain any one absorption band although more than two are needed to treat the six bands. This is because in D_{2h} and with the chosen coordinate system

$$\begin{array}{l} \text{and} \\ \begin{array}{l} {}^4A_{2g}(O_h) \\ {}^4T_{2g}(O_h) \\ {}^4T_{1g}(O_h) \end{array} \end{array} \text{ becomes } \begin{array}{l} {}^4B_{1g} \\ {}^4A_g + {}^4B_{2g} + {}^4B_{3g} \\ {}^4B_{1g} + {}^4B_{2g} + {}^4B_{3g} \end{array}$$

and in order to get six bands with appropriate polarizations at least three *odd* vibrations are needed (Table 4). It is not possible to make a unique choice of vibrations.

ABSORPTION AND EMISSION IN THE RED SYSTEM

The failure to resolve the $14\,432.1/14\,434.5\text{ cm}^{-1}$ doublet in emission at 4.2°K is due to experimental difficulties. At 1.6°K , absorption measurements demonstrate that the splitting is in the ground state (calculated on a Boltzmann distribution $\Delta\nu=2.2\text{ cm}^{-1}$, observed $2.4\pm 0.2\text{ cm}^{-1}$), Fig. 5. The origin of this splitting is not precisely known. The ${}^4A_2(O_h)$ ground state may split, under the combined action of spin-orbit and low crystalline field effects, into $M_s=\pm 3/2$ and $M_s=\pm 1/2$. These Kramers doublets may only be split further

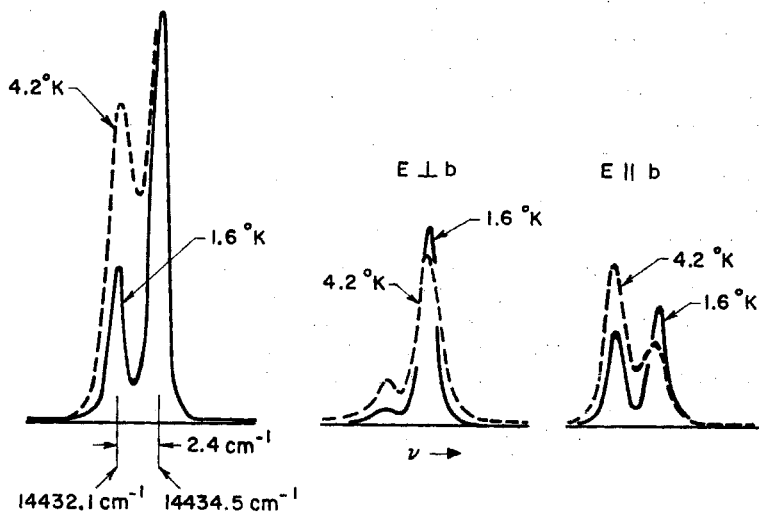


Fig. 5. Variation in relative absorption intensities of the doublet components at $14\,432.1$ and $14\,434.5\text{ cm}^{-1}$ between 4.2°K and 1.6°K . The unpolarized results are scaled to give $14\,434.5\text{ cm}^{-1}$, the same intensity at both temperatures.

by an external magnetic field.* Since the rhombic field is fairly large (as seen in the broad band splittings), the ground state splitting may well arise in the manner just described. An alternative, is that magnetic exchange interaction^{11,12} in the ground state, described by a term in the Hamiltonian, $H' = -J/2(S_1 \cdot S_2)$, where $S_1 = 3/2$, $S_2 = 3/2$, has led to an increased number of ground state levels with total spin quantum numbers $S = 0, 1, 2$ and 3 and with spacings $0, J, 3J$, and $6J$, respectively (antiferromagnetic coupling assumed). Magnetic exchange in the excited state would lead to two levels, but, since the doubling seen has been attributed to the ground state, any effect must be less than the half width of the individual lines and will be neglected.

There is no magnetic susceptibility study on this material so that the presence of exchange in the ground state cannot be substantiated from that point of view. In line with this exchange coupled model of the ground state is the observation (p. 2227) that the emission spectrum is not a mirror image of the absorption and that a complex group of lines appear immediately below (0,0) in emission. If $J \sim 15 \text{ cm}^{-1}$, then lines (or groups of lines, due to the low crystalline field) are expected at (0,0)– 15 cm^{-1} ; (0,0)– 45 cm^{-1} , and (0,0)– 90 cm^{-1} . Fig. 4 indicates a crude agreement between this proposal and the experimental result.

Another possibility would attribute the splitting of 4A_2 to the combined action of spin-orbit coupling and crystal field and then associate all or some of the low frequency emission to excitations trapped at various defects in the crystal. Such phenomena have been seen in $\text{Cr}^{3+}/\text{MgO}$, $\text{Cr}^{3+}/\text{Al}_2\text{O}_3$, pure MnF_2 , and other materials¹³ but are not usually encountered in crystals such as the present one.

More elegant experiments, involving lifetime measurements on individual emission lines and magnetic susceptibility studies at low temperatures are needed before this question of exchange in the ground state can be resolved.

In absorption, we have seen only the sharp doublet at $14\,432.1/14\,434.5$ which is attributed to a single level in the upper state. Unlike ${}^4A_2(O_h)$, the excited ${}^2E_g, T_2(O_h)$ can be split by spin-orbit coupling and/or low crystal fields acting either singly or together. Preliminary magnetic field experiments indicate the $14\,432.1/14\,434.5$ pair to be a Kramers doublet which in turn means 2E has split and that another component should be nearby (splittings in trigonal Cr^{3+} complexes are typically $\sim 60 \text{ cm}^{-1}$ in emerald,¹⁴ $\sim 30 \text{ cm}^{-1}$ in ruby,¹⁴ $\sim 22 \text{ cm}^{-1}$ in $\text{Cr en}_3\text{Cl}_3 \cdot \text{KCl} \cdot 6\text{H}_2\text{O}$ (Ref. 15), and so on). We observe nothing until 132 cm^{-1} above $14\,432 \text{ cm}^{-1}$ where a broadened line appears. It is possible that this is the second component although if this splitting is felt to be too large (in line with this point we observe that $135 \pm 5 \text{ cm}^{-1}$ is a common vibronic spacing in the spectra), the missing component may in fact lie much closer to $14\,432 \text{ cm}^{-1}$, but it may be very broad and weak as a result of a very rapid relaxation to the lower level.**

* Magnetic field experiments in fields up to 60 KG are in progress and will be reported in due course.

** Experiments on lifetimes, magnetic susceptibilities, and magneto-optical properties are in progress and details will be reported at a later date.

CONCLUSIONS

During this study a considerable amount of detailed information has been obtained about the optical properties of the crystal *trans* KCr(III) $(C_2O_4)_2(H_2O)_2 \cdot 3H_2O$. It is indeed rare to see six broad bands, two systems of sharp lines (one in emission as well as absorption), very strong polarization selection rules and very marked intensity variations with temperature in the same crystal of a transition metal complex. Even so, it has not been possible to provide an unambiguous assignment of all the electronic states involved. The general pattern of the results is, however, compatible with a vibronic intensity gaining mechanism in the $d-d$ absorptions. The sharp doublet at $14\,433 \pm 1\text{ cm}^{-1}$ is assigned to a magnetic dipole process, whereas the sharp lines in the blue region are considered to be electric dipole in origin.

The absorption/emission results in the red region, although not yet fully understood, seem to be explicable in terms of excitations bound to defect influenced centers or else by the existence of magnetic exchange in the ground electronic state.

REFERENCES

1. Sponer, H. and Teller, E. *Rev. Mod. Phys.* **13** (1941) 75.
2. Garfoth, F. M., Ingold, C. K. and Poole, H. G. *J. Chem. Soc.* **1948** 406.
3. Ferguson, J. *J. Chem. Phys.* **35** (1961) 1612, and earlier papers.
4. Ferguson, J., Belford, R. L. and Piper, T. S. *J. Chem. Phys.* **37** (1962) 1569.
5. Dingle, R. *J. Chem. Phys.* **46** (1967) 1.
6. Mortensen, O. S. *Acta Chem. Scand.* **19** (1965) 1500.
7. Martin, D. S. and Lenhardt, C. A. *Inorg. Chem.* **3** (1964) 1368; Martin, D. S., Tucker, M. A. and Kassman, A. J. *Inorg. Chem.* **4** (1965) 1682.
8. Van Niekerk, J. N. and Schoening, F. R. L. *Acta Cryst.* **4** (1951) 35.
9. Ballhausen, C. J. *Introduction to Ligand Field Theory*, McGraw, New York 1962, p. 186.
10. Cradon, D. P. *J. Inorg. Nucl. Chem.* **3** (1956) 308.
11. McClure, D. S. *J. Chem. Phys.* **39** (1963) 2850.
12. Ferguson, J., Guggenheim, H. J. and Tanabe, Y. *J. Appl. Phys.* **36** (1965) 1046.
13. For example, Schawlow, A. L., Wood, D. L. and Clogston, A. M. *Phys. Rev. Letters* **3** (1959) 271.
14. Wood, D. L. *J. Chem. Phys.* **42** (1965) 3404.
15. Dingle, R., Vala, M. T. and McCarthy, P. J. *Unpublished*.

Received February 12, 1968.