

- (17) R. L. Armstrong and C. A. Martin, *Phys. Rev. Lett.*, **35**, 294 (1975).
 (18) K. R. Jeffrey, *J. Magn. Reson.*, **7**, 184 (1972).
 (19) A. Sasane, D. Nakamura, and M. Kubo, *J. Magn. Reson.*, **3**, 76 (1970); B. I. Swanson and B. C. Lucas, to be submitted for publication.
 (20) B. I. Swanson and B. C. Lucas, to be submitted for publication.
 (21) J. Rafalko, B. I. Swanson, and B. Schwartz, to be submitted for publication.
 (22) J. F. Scott and J. P. Remeika, *Phys. Rev. B*, **1**, 4182 (1970).
 (23) B. I. Swanson and R. R. Ryan, *Inorg. Chem.*, **12**, 285 (1973); R. R. Ryan and B. I. Swanson, *ibid.*, **13**, 1681 (1974).
 (24) G. G. Schlessinger, *Chemist-Analyst*, **56**, 48 (1967).
 (25) B. I. Swanson and L. H. Jones, *Inorg. Chem.*, **13**, 313 (1974).
 (26) J. J. Rafalko, B. I. Swanson, and L. H. Jones, *J. Chem. Phys.*, **67**, 1 (1977).
 (27) J. M. Worlock, Proceedings of NATO Advanced Study Institute, Structural Phase Transitions and Soft Modes, Geilo, Norway, April 1971, p 329.
 (28) S. R. Fletcher and T. C. Gibb, *J. Chem. Soc., Dalton Trans.*, 309 (1977).
 (29) R. W. Schwartz, S. F. Watkins, C. J. O'Connor, and R. L. Carlin, *J. Chem. Soc., Faraday Trans. 2*, **72**, 565 (1976).
 (30) The critical temperature for the second phase change in $\text{Cs}_2\text{NaFe}(\text{CN})_6$ was observed at 499 K via optical microscopy: B. Swanson unpublished results.
 (31) L. H. Jones and B. I. Swanson, *Acc. Chem. Res.*, **9**, 128 (1976).
 (32) B. I. Swanson, S. Hamburg, and R. R. Ryan, *Inorg. Chem.*, **13**, 1681 (1974).
 (33) L. H. Jones, *Inorg. Chem.*, **2**, 777 (1963).

Contribution from Ames Laboratory, ERDA, Iowa State University, Ames, Iowa 50011, and the Department of Chemistry, Auburn University, Auburn, Alabama 36803

Polarized Single-Crystal Electronic Spectra for Tripotassium Tetrasulfatodimolybdate-3.5-Water

PHILLIP E. FANWICK,^{1a} DON S. MARTIN, JR.,^{*1a} THOMAS R. WEBB,^{1b} GARY A. ROBBINS,^{1a} and ROBERT A. NEWMAN^{1a}

Received February 14, 1978

Low-temperature polarized spectra for the band of $\text{K}_3\text{Mo}_2(\text{SO}_4)_4 \cdot 3.5\text{H}_2\text{O}$ in the near-infrared region, between 5700 and 9000 cm^{-1} , are reported. This band has rather remarkable vibrational structure which provides an exceptional picture of vibrations in the excited state. The data are consistent with an assignment of the band as the $\delta^* \leftarrow \delta$, ${}^2\text{B}_{1u} \leftarrow {}^2\text{B}_{2g}$, dipole-allowed transition. The information, including hot bands developed in spectra above 80 K, indicate that the 0-0 lines of the two crystallographic sites are at 6311 and 6418 cm^{-1} . However, there is no observed splitting of symmetry-related crystal (Davydov) states. Extended Franck-Condon progressions for each site based on a metal-metal stretching vibration of 350 cm^{-1} are observed. In addition, Franck-Condon terms of three other vibrations are seen. There are also weak featureless bands in the visible region at 16800 and 24000 cm^{-1} .

Introduction

Single-crystal electronic absorption spectra have been reported by now for several compounds which contain dimeric complexes of transition elements with quadruple metal-metal bonds. Studies²⁻⁴ of crystals with $\text{Re}_2\text{Cl}_8^{2-}$ together with results⁵ for $\text{Mo}_2\text{Cl}_8^{4-}$ have confirmed that the lowest energy observed electronic absorption is polarized in the direction of the metal-metal bond. In the D_{4h} symmetry of the $d^8 \text{M}_2\text{Cl}_8^{n-}$ ion, the spin-allowed $\delta^* \leftarrow \delta$ transition involves the excitation $b_{1u}^* \leftarrow b_{2g}$, so the transition is ${}^1\text{A}_{2u} \leftarrow {}^1\text{A}_{1g}$ and should be dipole-allowed along the z axis which is coincident with the metal-metal bond. Therefore, this first transition can be reasonably assigned as $\delta^* \leftarrow \delta$. Such an assignment is predicted by $X\alpha$ scattered wave calculations,³⁻⁶ although the calculated energies for the transition have rather generally been much lower than those observed.

Polarized crystal spectra⁷ of $\text{K}_4\text{Mo}_2(\text{SO}_4)_4 \cdot 2\text{H}_2\text{O}$ have indicated a band with its maximum at 19400 cm^{-1} and also a polarization consistent with a $\delta^* \leftarrow \delta$ assignment. On the other hand, the lowest energy electronic transitions in crystal spectra for the molybdenum alkylcarboxylate dimers⁷⁻⁹ have exhibited much lower intensities. Vibrational structure for these absorption bands at liquid-helium temperature have indicated components in both the z and x,y polarizations which imply some excitation by vibronic (Herzberg-Teller) perturbations.

In the synthesis of the red $\text{K}_4\text{Mo}_2(\text{SO}_4)_4 \cdot 2\text{H}_2\text{O}$, blue crystals are frequently encountered,¹⁰ especially if oxygen has not been rigorously excluded. In this compound, $\text{K}_3\text{Mo}_2(\text{SO}_4)_4 \cdot 3.5\text{H}_2\text{O}$, the $\text{Mo}_2(\text{SO}_4)_4^{4-}$ anion has been subjected to a one-electron oxidation to form the $\text{Mo}_2(\text{SO}_4)_4^{3-}$ anion. The crystal structure of both the red and blue compounds was reported by Cotton et al.,¹¹ and the present work was undertaken to obtain polarized crystal spectra for the oxidized dimeric anion. In the meantime, Gray and co-workers¹² have reported a richly structured absorption band for KBr pellets of $\text{K}_3\text{Mo}_2(\text{S}-$

$\text{O}_4)_4 \cdot 3.5\text{H}_2\text{O}$ in the near-infrared region between 1200 and 1600 nm which they tentatively assigned as the $\delta^* \leftarrow \delta$ transition.

Experimental Section

The preparation of $\text{K}_3\text{Mo}_2(\text{SO}_4)_4 \cdot 3.5\text{H}_2\text{O}$ has been described previously.¹¹ The compound crystallizes with a monoclinic lattice $C2/c$, $a:b:c = 30.654:9.528:12.727$, and $\beta = 97.43^\circ$. A number of very thin crystals, suitable for spectroscopy, were found. Several crystals were mounted on the goniometer head of a computer controlled four-circle X-ray diffractometer. From preliminary oscillation photographs, the crystallographic axes were determined by standard programs to be in agreement with the reported values. From observations of the crystals as various reflections were called into the diffracting position, it was determined that the large faces of thin rectangular crystals were 100 with the c axis aligned in the direction of the long dimension. Other crystals in the form of prismatic needles had developed 100 and 010 faces. For the 100 face of monoclinic crystals, electric vectors of the two transmitted plane polarized light waves are exactly aligned with the b and c crystallographic axes so it has been possible to obtain absorption spectra for these b and c polarizations. The indices of refraction for the 100 face were determined for Na D to be $n_b = 1.581$ and $n_c = 1.552$ by the Becke line method with the use of calibrated immersion liquids purchased from the Cargille Co. The thickness for the crystals was determined from the interference colors between crossed polarizers and the indicated birefringence. The thickness of one crystal with optical faces could be confirmed as well by an interference method from the wavelengths of a series of absorbance maxima and minima in a region of low absorptions.¹³ Uncertainty in the thickness was about 10%. For the near-infrared region, where detection is much less sensitive than in the visible and near-ultraviolet region, it was possible to find crystals with faces sufficiently large (0.5-1.0 mm) for the instrumental sensitivity and to mount these crystals over slits in metal plates so the long dimension could be aligned with the slit images in the sample compartment of the spectrophotometer.

The experimental procedures for measuring polarized spectra at liquid-helium temperatures have been described previously.^{5,14} For the study of hot bands, the temperature of the sample holder was measured by means of a platinum resistance thermometer. The

eccentricity of our polarizers had not been determined previously in the infrared region, and the eccentricity does decrease with increased wavelength of the light. Accordingly, the absorbance of crossed polarizers was recorded from 2000 to 600 nm. The results indicated that the eccentricity increased linearly with wave number from a value of 40 at 5000 cm^{-1} to 220 to 16700 cm^{-1} . The eccentricity is high enough to provide satisfactory polarized spectra if the absorbances and polarization ratios are not too high.

Results and Discussion

Considerations of the Crystal Structure. In the monoclinic $C2/c$ unit cell there are eight $\text{Mo}_2(\text{SO}_4)_4^{2-}$ ions. However, since this is a side-centered cell, there are only four ions in a primitive cell. There are, therefore, four crystal states for each molecular excitation. Each of the ions is related to only one of the other three by space group symmetry operations. Thus, there are two types of ions in the structure. In one type there is an H_2O molecule bonded terminally to each Mo in the ions; these are designated as the isolated ion type. In the second type an H_2O molecule, bonded terminally to an Mo, is also bonded to the Mo of another ion to give chains of ions linked together by H_2O bridges. These are designated as the chain-type ions.

The structures of the isolated and chain-type ions are virtually identical. For example, the Mo-Mo distances are respectively 2.167 (1) and 2.162 (1) Å which is some 0.05 Å longer than the 2.111 Å of $\text{Mo}_2(\text{SO}_4)_4^{4-}$. The longer bond is consistent with the loss of an electron from the δ bond in the oxidized species. The distance from Mo to a terminally bonded water oxygen is 2.550 (4) and 2.545 (3) Å, respectively, for the isolated and chain ions. This fairly long distance, compared to the 2.046–0.084 Å distances for the molybdenum-sulfate oxygens, is indicative of rather weak terminal bonds to the waters.

Loewenschuss et al.¹⁵ have reported Raman and IR spectra for the crystals and noted that many of the vibrational bands occurred as pairs separated by 10–25 cm^{-1} . They attributed these separations to the different crystal sites for the molecules. For example, the Mo-Mo stretching frequencies were 373 and 386 cm^{-1} which is surprisingly close to the 371- cm^{-1} value for $\text{Mo}_2(\text{SO}_4)_4^{4-}$, considering that the bond order has been reduced from 4 to 3.5.

A Frenkel exciton band of states should exist for each molecular transition of each molecule in a primitive lattice cell.¹⁶ For each pair of molecules, equivalent by space group symmetry operations, these Frenkel states for the sites (1) and (2) may be designated $\Phi_1'(\mathbf{k})$ and $\Phi_2'(\mathbf{k})$ where \mathbf{k} is the wave vector. The two Davydov bands may then be represented by

$$\Phi_1'(\mathbf{k}) = (\Phi_1'(\mathbf{k}) + \Phi_2'(\mathbf{k}))\sqrt{2} \quad (1a)$$

and

$$\Phi_{II}'(\mathbf{k}) = (\Phi_1'(\mathbf{k}) - \Phi_2'(\mathbf{k}))/\sqrt{2} \quad (1b)$$

Transitions are electric dipole allowed only to the two Davydov states $\Phi_1'(0)$ and $\Phi_{II}'(0)$.

If (μ_1) and (μ_2) are the usual electric dipole operator for molecules at these symmetry related sites, there will be the corresponding transition moment vectors, μ_1 and μ_2

$$\mu_1 = \int \varphi_1'(\mu_1)\varphi_1^\circ d\tau \quad (2a)$$

and

$$\mu_2 = \int \varphi_2'(\mu_2)\varphi_2^\circ d\tau \quad (2b)$$

where φ_1° and φ_1' are the ground- and excited-state molecular wave functions for site 1, etc. The vector μ_1 can be represented as the vector

$$\mu_1 = x\hat{a} + y\hat{b} + z\hat{c} \quad (3)$$

where \hat{a} , \hat{b} , and \hat{c} are unit vectors along the crystallographic axes. The glide and reflection operation converts the transition

moment vector μ_1 into vector μ_2 for the site (2) which is

$$\mu_2 = x\hat{a} - y\hat{b} + z\hat{c} \quad (4)$$

The transition moment from the ground state, Φ° , to the Davydov state $\Phi_1(0)$ is accordingly

$$\mu_1 = \int \Phi_1'(0)(\mu_1 + \mu_2)\Phi^\circ d\tau = \mu_1 + \mu_2 = \sqrt{2}(x\hat{a} + z\hat{c}) \quad (5)$$

For the Davydov state $\Phi_{II}(0)$ the moment is

$$\mu_{II} = \int \Phi_{II}'(0)(\mu_1 + \mu_2)\Phi^\circ d\tau = \mu_1 - \mu_2 = \sqrt{2}y\hat{b} \quad (6)$$

For spectra measured in the 100 face the transition to Davydov state $\Phi_1(0)$ will be allowed in c polarization and forbidden in b whereas the transition to Davydov state $\Phi_{II}(0)$ will be allowed in b polarization and forbidden in c . In each polarization therefore there will be possible only two peaks for each molecular transition, one from the chain-type site and the other from the isolated ion-type site.

Polarization ratios for the absorption of light were calculated for the oriented gas molecule model in the following way. For a D_{4h} molecule either a transition moment will be oriented along the fourfold symmetry axis z or else there will be two orthogonal and equal moments, which are both orthogonal to z for a degenerate pair of transitions, i.e., for x,y polarization. From analogy with the absorption in uniaxial crystals the z molecular polarization is commonly labeled π while the x,y polarization is designated σ . For light linearly polarized along the z axis of a collection of noninteracting molecules, a molar absorptivity, ϵ_π , can be defined, and for light polarized perpendicular to z , there is a molar absorptivity, ϵ_σ . However, for the 100 face of the crystal the light must be polarized along only either the b or c crystallographic axes. The crystallographic molar absorptivities are then computed by the expression¹⁷ in matrix form

$$\begin{pmatrix} \epsilon_c \\ \epsilon_b \end{pmatrix} = \begin{pmatrix} \cos^2 \theta_1 & \sin^2 \theta_1 \\ \cos^2 \theta_2 & \sin^2 \theta_2 \end{pmatrix} \begin{pmatrix} \epsilon_\pi \\ \epsilon_\sigma \end{pmatrix} \quad (7)$$

where θ_1 is the angle between the z molecular axis and c and θ_2 is the angle between the z and b .

For the isolated ions, in this compound θ_1 is 49.09° and θ_2 is 89.65° so for z polarization $(\epsilon_c/\epsilon_b)_{1,\pi} = 1.3 \times 10^4$ and $(\epsilon_c/\epsilon_b)_{1,\sigma} = 0.536 = 1/1.86$. For the chain-type ions, $\theta_1 = 67.50^\circ$ and $\theta_2 = 23.00^\circ$ so $(\epsilon_c/\epsilon_b)_{2,\pi} = 5.79$ and $(\epsilon_c/\epsilon_b)_{2,\sigma} = 0.179 = 1/5.59$. In case there was no difference in the energy or in the molecular intensities, a polarized intensity can be calculated by simply adding the intensities contributed from each site. The ratios from such combined intensities would be $(\epsilon_c/\epsilon_b)_\pi = 8.95$ and $(\epsilon_c/\epsilon_b)_\sigma = 0.374 = 1/2.70$.

The sites for both types of ion possess only the inversion symmetry element. Hence the D_{4h} molecular symmetry is compromised by the crystal fields. The extent of the disruption of the selection rules will depend upon the relative strength of the crystal fields. If the crystal perturbations are small, there may be no significant differences from the calculated polarization ratios, and it may be possible to infer molecular polarizations. However, the crystal field does have the potential to split the degeneracies which occur under D_{4h} . In that case the two σ transitions will be split in energy and appear separately with their individual transition moments which no longer need to be orthogonal to each other or to the metal-metal axis.

Crystal Spectra for $\text{K}_3\text{Mo}_2(\text{SO}_4)_4 \cdot 3.5\text{H}_2\text{O}$. At the present, there are no theoretical computations of orbital or of transition state energies for the sulfato complexes. Accordingly, as a qualitative guide to aid in predicting possible molecular polarizations of the observable transitions, the one-electron orbital energies are plotted in Figure 1 for the $\text{Mo}_2(\text{O}_2\text{CH})_4$ complex

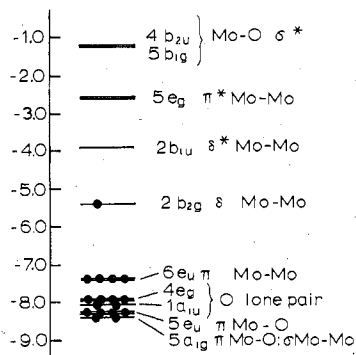


Figure 1. One-electron orbital energies in electron volts for the $\text{Mo}_2(\text{O}_2\text{CH})_4$ molecule from $X\alpha$ scattered wave calculations of Norman et al.⁶ The orbitals are filled as expected for $\text{Mo}_2(\text{SO}_4)_4^{3-}$.

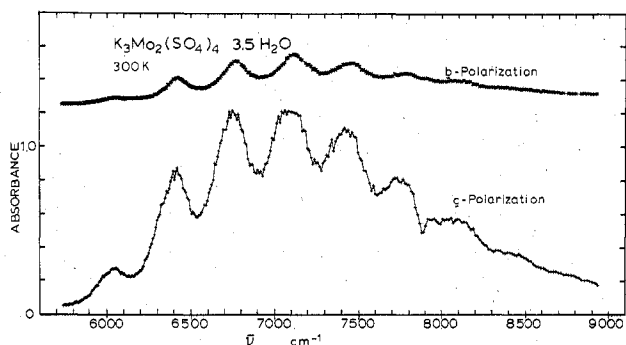


Figure 2. Room-temperature polarized spectra in the near-infrared region for the 100 face of $\text{K}_3\text{Mo}_2(\text{SO}_4)_4 \cdot 3.5\text{H}_2\text{O}$. Crystal thickness was 14μ . Absorbances can be converted to molar absorptivity by multiplying by $190 \text{ cm}^{-1} \text{ M}^{-1}$.

from $X\alpha$ scattered wave calculations by Norman et al.¹⁸ The formate complex possesses the four bridging ligands with Mo-O bonds as does the tetrasulfato complex and also possesses D_{4h} symmetry. The orbitals in the figure have been filled as expected for $\text{Mo}_2(\text{SO}_4)_4^{3-}$; i.e., there is only one electron in the $b_{2g}-\delta$ bonding orbital. The lowest energy transition predicted from Figure 1 would be $b_{1u}(\delta^*) \leftarrow b_{2g}(\delta)$, ${}^2B_{1u} \leftarrow {}^2B_{2g}$. This transition is electric dipole allowed in z polarization. In the case where vibrational structure to the band can be resolved, there are expected to be Franck-Condon progressions seen in z polarization based on totally symmetric molecular vibrations. Generally, the progression for the metal-metal bonded complexes has been based on the metal-metal stretching vibration although for $\text{Re}_2\text{Cl}_8^{2-}$ the appearance of a second progression, also with spacings of the metal-metal stretch, demonstrated the involvement of a second vibration.² The intensity of these dipole-allowed transitions will be dependent upon the overlap of the radial portions of the b_{1u} and b_{2g} orbitals.

With only single-electron occupancy of the b_{2g} orbital the transition $b_{2g}(\delta) \leftarrow e_u(\pi)$, ${}^2E_u \leftarrow {}^2B_{2g}$ is a possibility. Such a transition would be dipole allowed in x, y polarization, and in this case the Franck-Condon progression based on the metal-metal stretching mode would be seen in x, y polarizations. Other possible low-energy transitions, e.g., $e_g(\pi^*) \leftarrow b_{2g}(\delta)$, $b_{2g}(\delta) \leftarrow e_g(0)$, both ${}^2E_g \leftarrow {}^2B_{2g}$, and $b_{2g}(\delta) \leftarrow a_{1u}(0)$, ${}^2A_{1u} \leftarrow {}^2B_{2g}$, are electric dipole forbidden. Such transitions could be excited by the vibronic perturbations. They would be expected to appear as low-intensity progressions with separations of the metal-metal stretch which originate $\bar{\nu}_1 \text{ cm}^{-1}$ above the unobserved 0-0 transition, where $\bar{\nu}_1$ is the wavenumber of the exciting vibration in the excited electronic state.

The room-temperature spectra for both b and c polarizations in the near-infrared spectra for a crystal of $\text{K}_3\text{Mo}_2(\text{SO}_4)_4 \cdot$

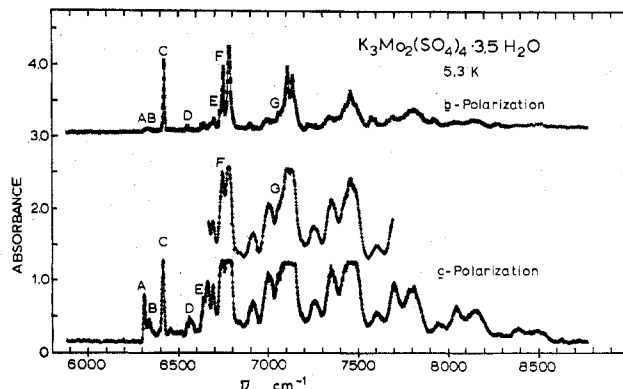


Figure 3. Polarized spectra in the near-infrared region at 5.3 K for the 100 face of $\text{K}_3\text{Mo}_2(\text{SO}_4)_4 \cdot 3.5\text{H}_2\text{O}$. Crystal thickness was 14μ . Absorbances can be converted to molar absorptivities by multiplying by $190 \text{ cm}^{-1} \text{ M}^{-1}$.

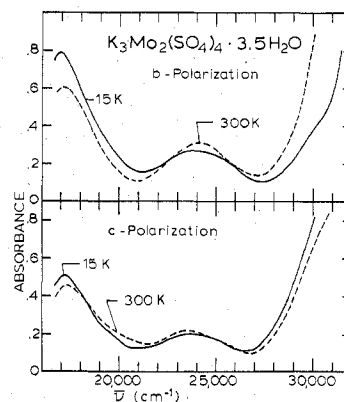


Figure 4. Polarized spectra in the visible and near-ultraviolet region for $\text{K}_3\text{Mo}_2(\text{SO}_4)_4 \cdot 3.5\text{H}_2\text{O}$. Crystal thickness was 76μ . Absorbances can be converted to molar absorptivities by multiplying by 37.

$3.5\text{H}_2\text{O}$ are shown in Figure 2. The spectra show remarkable vibrational detail for room-temperature spectra, there being eight broad peaks discernible between 6040 and 8400 cm^{-1} for an average spacing of 349 cm^{-1} . The c polarized spectrum was approximately five times as intense as that for b polarization. Indeed, the two most intense peaks for c polarization were off the recorder scale.

Figure 3 shows the wealth of vibrational detail developed in this electronic band when the crystal was cooled to 5.3 K which is in contrast to the weak and broad featureless bands in the visible and near-ultraviolet region which are shown in Figure 4. The short central spectrum in Figure 3 was recorded for c polarization with somewhat wider slit widths than the lower section. Although resolution was reduced by the larger slits, it was possible to demonstrate the multiple components in the regions of high absorption. Even so, peaks at 6780 , 7103 , and 7135 cm^{-1} were off-scale. The b polarization was recorded at approximately the same slit widths as the lower c spectrum and only the 6780-cm^{-1} peak was off-scale.

Every component had a higher intensity in the c polarization than in the b . In every feature which was sharply resolved, the agreement in wave number between the two polarizations was quite generally within $\pm 1-2 \text{ cm}^{-1}$, about the limit of resolution. Since such components arise from transitions to different Davydov states, no splitting of Davydov states originating from a single molecular state of a common crystal site was detectable.

There are seven Franck-Condon progressions with moderate to high intensity which are clearly discernible in the spectra. The first observed member of each progression is labeled in

Table I. Resolved Vibrational Components in the Near-IR Band of $K_3Mo_2(SO_4)_4 \cdot 3.5H_2O$

component	$\bar{\nu}$, cm^{-1}	$\Delta\bar{\nu}$, ^a cm^{-1}
A1	6311	0-0 (isolated)
B1	6339	(28)
C1	6418	0-0 (chain)
	6455 vw	(145)
	6545 vw	(234)
D1	6561	(250)
	6577 vw	(266)
E1	6640 sh	(329)
A2	6660	349
B2	6691	352
F1	6746	(328)
C2	6780	360
D2	6917	356
E2,A3,B3	7003 ^b	343
G1	7066 sh	(648)
F2	7103	357
C3	7135	355
D3	7252 ^c	335
E3,A4,B4	7350 ^b	348
G2	7431 sh	365
F3	7456	353
C4	7487 sh	352
D4	7602	350
E4,A5,B5	7699 ^b	349
G3	7784 sh	352
F4	7810	354
D5	7947	346
E5,A6,B6	8046 ^b	348
G4	8134	350
F5	8156	347
E6,A7,B7	8386 ^b	340
G5	8484	350

^a Values of $\Delta\bar{\nu}$ in parentheses give the energy in wave numbers above the indicated 0-0 line for the first observed member in a progression. Values without parentheses give the separation from the preceding member in the progression. ^b A merged peak.

^c A broad peak in vicinity of high quartz absorption.

Figure 3. Wave numbers for each component are listed in Table I.

The lowest energy feature in the helium spectra is the sharp peak, A, at 6311 cm^{-1} in *c* polarization. Therefore the band at 6040 cm^{-1} in the room-temperature spectrum is clearly a hot band. A shorter but perhaps broader peak, B, occurs at 6339 cm^{-1} , only 28 cm^{-1} higher in energy. The A and B transitions are virtually absent in the *b* spectrum where there is a very weak absorption with a maximum at about 6330 cm^{-1} . The *c:b* intensity ratio is very high and appears consistent with *z* polarization for the isolated ion site. The second members of the A and B progressions are clearly resolved in *c* polarization and a weak shoulder, E1, occurs at 6640 cm^{-1} . The three components E2, A3, and B3 have merged, and five additional merged peaks continue as a major progression in the *c* spectrum. The $\Delta\bar{\nu}$ (343 cm^{-1}), indicated for the merged E2, A3, B3 peak, was calculated from the wave number of the A2 peak. Hence, this rather low $\Delta\bar{\nu}$ has probably resulted because the maximum of the merged peak did not coincide with A3 transition.

Another transition, very strongly polarized in the *c* direction, appears as the peak D at 6561 cm^{-1} . D is a fairly broad peak, not as intense as A or B, which seems to contain at least three closely spaced transitions of which only the one at 6545 cm^{-1} has appreciable *b* intensity. Seven D peaks are clearly seen in Figure 3. The third peak at 7252 cm^{-1} is close to a quartz absorption and may be abnormally broadened.

The C progression has the most intense peaks in the spectra, the C1 peak being very sharp. A strong F progression begins just 34 cm^{-1} before the C2 peak so there is a very intense pair at 6746 and 6480 cm^{-1} . The first member of the G progression appears as a shoulder at 7066 cm^{-1} , just 37 cm^{-1} below F2.

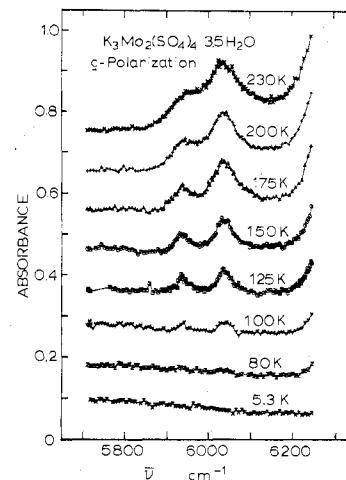


Figure 5. Absorption spectra in *c* polarization for $K_3Mo_2(SO_4)_4 \cdot 3.5H_2O$ for various temperatures in the hot-band region of the infrared band.

The G2 shoulder at 7431 cm^{-1} is about as intense as C4 at 7487 cm^{-1} , and G3 at 7784 cm^{-1} is comparable to F4 at 7810 cm^{-1} . The C, F, and G progressions have high intensity in both polarizations. It is clear that the vibrational features seen at room temperature are primarily due to the merged C, F, and G peaks. It is also clear that these transitions are much stronger in *c* than in *b* polarization. Although some *c* peaks are badly off-scale, it appears that the polarization ratio is consistent with the 5.8 calculated for the *z* polarization of the chain ion site.

Recordings of the *c* spectra in the hot-band region below 6250 cm^{-1} are shown in Figure 5 for a series of temperatures ranging from 5.3 to 230 K. As the temperature increases, a pair of bands develop centered at $5936\text{--}6040\text{ cm}^{-1}$. At room temperature, only one broad absorption could be seen in this region which was strongly *c* polarized. The two peaks lie just 375 and 378 cm^{-1} below the A1 and C1 peaks in the helium spectra which agree closely with the values of 373 and 386 cm^{-1} reported for the metal-metal stretch from the Raman spectrum.¹⁴ In addition a logarithmic plot of the integrated absorbance $\int A d\nu$ for the two components in Figure 5 vs. $1/T$ gave a Boltzmann factor corresponding to $320 \pm 30\text{ cm}^{-1}$. These results appear consistent with the assignments of A1 and C1 as the 0-0 transitions, respectively, for an electric dipole-allowed *z*-polarization transition in the isolated and chain-type ions, respectively. The 107-cm^{-1} separation of A1 and C1 can be attributed to the effect of the sites on the transition energies. Such results preclude the assignment of the transition as the $\delta \leftarrow \pi$ transition which would be *x,y* polarized and is consistent with the $\delta^* \leftarrow \delta$ transition.

The origins of the other progressions seen in the spectra then will result from the addition of a totally symmetric vibration to the 0-0 energy. Each of these other totally symmetric transitions can give rise to a separate Franck-Condon progression, but apparently the intensity of higher terms is not observable. Only the metal-metal stretch suffers a sufficient relaxation in the excited state to give extended progressions on each of the other vibrations.

There is no detectable difference in the spacing of the observed progressions. The average of the 22 spacings $\Delta\bar{\nu}$ in Table I is $350 \pm 6\text{ cm}^{-1}$. The uncertainty appeared to arise primarily from merging of components such as the A, B, E in some peaks or from weak poorly resolved shoulders in some instances.

The pattern of totally symmetric vibrations for the isolated and chain-type sites can now be compared. The F1 occurs 328 cm^{-1} above C1, and E1 is 329 cm^{-1} above A1. They can

apparently be associated with 256- and 274-cm⁻¹ Raman bands attributed to Mo-O stretches.¹⁵ The D1 peak is 250 cm⁻¹ above A1. The component 250 cm⁻¹ above C1 would fall at 6658 cm⁻¹ which would superimpose it on the A2, B2 peak so the intensity in this region may be in part due to this vibration. The G1 peak is 648 cm⁻¹ above C1. If this energy is added to A1, it would place a component at 695 cm⁻¹ which is under the edge of the EAB merged peak. The 648-cm⁻¹ line would probably be correlated with the fairly strong 618-638-cm⁻¹ peaks of the Raman spectrum.

The one feature for the isolated site which does not appear for the chain site is the peak B1. This occurs only 28 cm⁻¹ above A1, and from its shape and intensity it would seem appropriate to assign it to phonon excitation on the 0-0 transition of the isolated ion site which does not occur on the chain site.

This electronic band therefore has provided tentative frequencies for four of the six possible totally symmetric molecular vibrations in the excited electronic state under D_{4h} symmetry. A number of weak peaks can be seen in the first 300 cm⁻¹ above A1 origin. Three of these are listed in Table I. Some may originate in phonon effects, but it seems that the component at 6545 cm⁻¹ has an appreciable b intensity and might correspond to a transition excited vibronically by an E_g vibration in x,y polarization.

The relative intensity of the C transition to the A transition deserves some comment. From eq 1 and the orientation of the z axes with respect to the b and c crystallographic axes it can be calculated that the chain site, giving the C progression, gives over 99% of the molecular absorption intensity to the b and c polarizations. The isolated ion, giving A, places only 46% of its intensity in c polarization and virtually nothing in b . The C transition is indicated to be the more intense. Even so, from the height of the very narrow C1 peak, part of the A1 intensity appears to be concealed in some broadness of the peak and also to have been drawn off into the B phonon band.

There seems but little doubt that this infrared band is the $\delta^* \leftarrow \delta$ transition for the $\text{Mo}_2(\text{SO}_4)_4^{3-}$ ion. This band appears at much lower energies in this ion than in $\text{Mo}_2(\text{SO}_4)_4^{4-}$ because the δ -bonding orbital is only half occupied so the splitting of the bonding and antibonding orbitals has been reduced. A similar effect should also occur on reduction from the d^8 configuration upon oxidation. The dimeric ion $\text{Tc}_2\text{Cl}_8^{3-}$ is a known species,¹⁹ in which the bond order has been lowered to 3.5 by the addition of an electron into the δ^* orbital. A spectroscopic study and $X\alpha$ scattered wave computation²⁰ indicated a band in the infrared region with maximum at 6500 cm⁻¹ which was assigned as the ${}^2B_{2g} \leftarrow {}^2B_{1g} (\delta^* \leftarrow \delta)$.

The oscillator strength for the $\text{Mo}_2(\text{SO}_4)_4^{3-}$ infrared band was estimated from the integrated intensity of the room-temperature c polarized spectrum. Since the c polarization is predicted by the oriented molecule model to have 67% of the molecular absorption, the factor ($1/3 \times 0.67$) was used to predict a value of 8×10^{-4} for an isotropic medium. This value is somewhat lower than the oscillator strength⁵ of 2×10^{-3} observed for $\text{K}_4\text{Mo}_2\text{Cl}_8 \cdot 2\text{H}_2\text{O}$. However, it is rather close to the value of 1.1×10^{-3} indicated for $\text{K}_4\text{Mo}_2(\text{SO}_4)_4$ despite the 0.05 Å longer metal-metal bond which is expected to reduce the orbital overlap and accordingly the transition moment.

One intriguing puzzle which remains is the absence of any vibrational structure whatsoever to the 19400-cm⁻¹ band of $\text{K}_4\text{Mo}_2(\text{SO}_4)_4 \cdot 2\text{H}_2\text{O}$ while the oxidized compound provides such a richly structured band. The behavior for $\text{K}_4\text{Mo}_2(\text{SO}_4)_4 \cdot 2\text{H}_2\text{O}$ is quite exceptional in view of the highly structured spectral bands observed with the other chloride, sulfate, and

carboxylate dimeric complexes of Mo, Re, and Tc with strong metal-metal bonds.

The weak absorptions in the visible region cannot be assigned with any certainty. The band with maximum at 16800 cm⁻¹ is responsible for the characteristic blue of the crystals. It is more intense in b than in c polarization which would be consistent with molecular x,y polarization. However, it seems too weak to be associated with the $b_{2g}(\delta^*) \leftarrow e_u(\pi), {}^2E_u \leftarrow {}^2B_{2g}$ transitions which are dipole allowed and expected to be stronger than the $\delta^* \leftarrow \delta$ band. The oscillator strength without reduction to account for random orientation amounts to just 3.5×10^{-4} . Thus its intensity is close to what might be expected for an excitation by a vibronic perturbation. However, its intensity does not fall off at lower temperatures which usually occurs for vibronic transition. It may be that crystal field perturbations contribute to the transition intensity. It might conceivably be the transition $e_g(\pi^*) \leftarrow b_{2g}(\delta)$ or possibly $\sigma^*(\text{Mo-O}) \leftarrow \delta$. The still weaker band at 24000 cm⁻¹ also does not possess the temperature dependence of a vibronic transition. This might be the spin-forbidden transition, ${}^4E_u \leftarrow {}^2B_{2g}$, associated with the very strong transition beyond the range of the measurements at 32000-33000 cm⁻¹. This intense band could then be the $\delta \leftarrow \pi, {}^2E_u \leftarrow {}^2B_{2g}$ transition. With the occurrence of the $\delta^* \leftarrow \delta$ transition at about 6300 cm⁻¹ it seems somewhat surprising that the $\delta \leftarrow \pi$ transition has such high energy. Perhaps the high energy of the 2E_u electronic state above the ground state may be related to the high electron correlation energy required to move an electron from a filled to a half-filled orbital in comparison to removal from a filled to an empty orbital.

Acknowledgment. This work received support from the Energy and Mineral Resources Research Institute of Iowa State University and National Science Foundation Grant CHE76-83665. It also received support from the Auburn University Grant in Aid Program. The spectra were measured in the Ames Laboratory of the U.S. Department of Energy.

Registry No. $\text{K}_3\text{Mo}_2(\text{SO}_4)_4$, 63311-41-1.

References and Notes

- (1) (a) Iowa State University. (b) Auburn University.
- (2) C. D. Cowman and H. B. Gray, *J. Am. Chem. Soc.*, **95**, 8177 (1973).
- (3) A. P. Mortola, J. W. Moskowitz, N. Rosch, C. D. Cowman, and H. B. Gray, *Chem. Phys. Lett.*, **32**, 283 (1975).
- (4) F. A. Cotton, B. A. Frenz, B. R. Stults, and T. R. Webb, *J. Am. Chem. Soc.*, **98**, 2768 (1976).
- (5) P. E. Fanwick, D. S. Martin, F. A. Cotton, and T. R. Webb, *Inorg. Chem.*, **16**, 2103 (1977).
- (6) J. G. Norman and H. J. Kolari, *J. Am. Chem. Soc.*, **97**, 33 (1975).
- (7) F. A. Cotton, D. S. Martin, P. E. Fanwick, T. J. Peters, and T. R. Webb, *J. Am. Chem. Soc.*, **98**, 4681 (1976).
- (8) F. A. Cotton, D. S. Martin, T. R. Webb, and T. J. Peters, *Inorg. Chem.*, **15**, 1199 (1976).
- (9) W. C. Trogler, E. I. Solomon, I. Trajberg, C. J. Ballhansen, and H. B. Gray, *Inorg. Chem.*, **16**, 828 (1977).
- (10) F. A. Cotton, B. A. Frenz, and T. R. Webb, *J. Am. Chem. Soc.*, **95**, 4431 (1973).
- (11) F. A. Cotton, B. A. Frenz, E. Pedersen, and T. R. Webb, *Inorg. Chem.*, **14**, 391 (1975).
- (12) D. K. Erwin, G. A. Geoffroy, H. B. Gray, G. S. Hammond, E. I. Solomon, W. C. Trogler, and A. A. Zagars, *J. Am. Chem. Soc.*, **99**, 3620 (1977).
- (13) R. M. Rush, D. S. Martin, Jr., and R. G. LeGrand, *Inorg. Chem.*, **14**, 2543 (1975).
- (14) D. S. Martin, Jr., *Inorg. Chim. Acta, Rev.*, **5**, 107 (1971).
- (15) A. Lowenschuss, J. Shamir, and M. Ardon, *Inorg. Chem.*, **15**, 238 (1976).
- (16) D. P. Craig and S. H. Walmsley, "Excitons in Molecular Crystals", W.A. Benjamin, New York, N.Y., 1966, Chapter 3.
- (17) Although this expression is in somewhat different form, it is equivalent to that used by T. S. Piper, *J. Chem. Phys.*, **35**, 1240 (1961).
- (18) J. G. Norman, M. Kolari, H. B. Gray, and W. C. Trogler, *Inorg. Chem.*, **16**, 987 (1977).
- (19) J. D. Eakins, D. G. Humphreys, and G. E. Mellish, *J. Chem. Soc.*, 6012 (1963).
- (20) F. A. Cotton, P. E. Fanwick, L. D. Gage, B. Kalbacker, and D. S. Martin, *J. Am. Chem. Soc.*, **99**, 5642 (1977).