

ELECTRONIC SPECTROSCOPY AND THE
PHOTOCHEMISTRY OF COMPOUNDS
WHICH CONTAIN
QUADRUPLE METAL-METAL BONDS

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ABSTRACT

The electronic spectra and structures of binuclear transition metal compounds which contain a quadruple metal-metal bond are discussed. Experimental results are presented for the electric-dipole forbidden transitions of $(n\text{-Bu}_4)_2[\text{Re}_2\text{Cl}_8]$, $(n\text{-Bu}_4)_2[\text{Re}_2\text{Br}_8]$, $\text{Mo}_2(\text{O}_2\text{CCH}_3)_4$, $\text{Mo}_2(\text{O}_2\text{CCD}_3)_4$, $\text{Mo}_2(\text{O}_2\text{CH})_4$, and $\text{Mo}_2(\text{O}_2\text{CCF}_3)_4$. The near infrared absorption system in $\text{K}_3\text{Mo}_2(\text{SO}_4)_4 \cdot 3.5 \text{H}_2\text{O}$ has also been analyzed.

Aqueous acid solutions of $\text{Mo}_2(\text{SO}_4)_4^{4-}$, $\text{Mo}_2(\text{aq})^{4+}$, and $\text{Mo}_2\text{Cl}_8^{4-}$ yield molecular hydrogen and oxidized molybdenum products upon ultraviolet irradiation. The compounds $\text{Mo}_2\text{Cl}_4\text{P}_4$ ($\text{P} = \text{P}(n\text{-Bu})_3$, $\text{P}(\text{Et})_3$ and $\text{P}(\text{Et})(\text{Ph})_2$) undergo photooxidation to chloride bridged binuclear Mo(III) compounds subsequent to 254 nm irradiation in chlorocarbon solvents. The nature of these photooxidation reactions are examined.

TABLE OF CONTENTS

	PAGE
CHAPTER 1. ELECTRONIC SPECTRA OF COMPOUNDS WHICH CONTAIN QUADRUPLE METAL-METAL BONDS.	1
I. Electronic Spectra and Structures of Compounds Containing Quadruple Metal-Metal Bonds. An Overview of the Field.	2
II. Further Studies of the Electronic Spectra of $\text{Re}_2\text{Cl}_8^{2-}$ and $\text{Re}_2\text{Br}_8^{2-}$. Assignment of the Weak Bands in the 600-350 nm Region. Estimation of the Dissociation Energies of Metal-Metal Quadruple Bonds.	32
III. Emission Spectra and Lifetimes of $\text{Re}_2\text{Cl}_8^{2-}$, $\text{Re}_2\text{Br}_8^{2-}$, and $\text{Mo}_2\text{Cl}_8^{4-}$ at 1.3 K Upon Excitation of the $\delta \rightarrow \delta^*$ Transition.	52
IV. Studies of the Polarization Behavior, Temperature Dependence, and Vibronic Structure of the $23,000\text{ cm}^{-1}$ Absorption System in the Electronic Spectra of $\text{Mo}_2(\text{O}_2\text{CCH}_3)_4$ and Related Compounds. Emission Spectrum of $\text{Mo}_2(\text{O}_2\text{CCF}_3)_4$ at 1.3 K.	65
V. Electronic Structure and Spectrum of $\text{Mo}_2(\text{O}_2\text{CH})_4$ and Related Compounds.	99

	PAGE
CHAPTER 2. THE PHOTOCHEMISTRY OF COMPOUNDS WHICH CONTAIN A QUADRUPLE MOLYBDENUM- MOLYBDENUM BOND.	112
I. Production of Hydrogen by Ultraviolet Irradiation of $\text{Mo}_2(\text{SO}_4)_4^{4-}$ in Aqueous Sulfuric Acid. Electronic Absorption Spectrum of $\text{K}_3\text{Mo}_2(\text{SO}_4)_4 \cdot$ 3.5 H_2O at 15 K.	113
II. Photochemical Oxidation Reactions of Binuclear Molybdenum(II) Complexes in Aqueous Acids and in Chlorocarbons.	124

CHAPTER 1
ELECTRONIC SPECTRA OF COMPOUNDS WHICH CONTAIN
QUADRUPLE METAL-METAL BONDS

Electronic Spectra and Structures of Compounds Containing Quadruple
Metal-Metal Bonds . An Overview of the Field

Parallel spectroscopic and theoretical studies of diatomic molecules¹ have provided a basis for molecular bonding theory. The electronic structure of many polyatomic molecules² may be adequately described by postulating diatomic-like σ and π bonds between s and p orbitals on different atomic centers. An attempt to extend this model to explain metal-metal bonding in transition metal cluster compounds must recognize several new features. The most important is the presence of metal d orbitals in the valence shell. Now the spectroscopic manifestation of strong metal-metal bonding will be explored.

Binuclear compounds M_2L_8 (M = Mo(II), Re(III) or Tc(III); L = ligand donor atom) of second and third row Group VI and VII B transition metal ions with the d^4 electronic configuration are systems well-suited for examining the consequences of metal-metal bonding. Chemical and structural properties of these compounds are consistent with the presence of an unusually strong metal-metal bond.³ Both the net positive charge and high atomic numbers of these ions are expected to effect large (n-1) d - (n)s and (n)p orbital energy separations.⁴ Therefore, the valence shell of the metal ion approximately consists of partially occupied d-like orbitals, and consequently the bonding between two metal ions primarily involves the d orbitals.

From a more practical viewpoint, the high symmetry (D_{4h}) of the M_2L_8 compounds is particularly favorable for spectroscopic investigations. We will now consider the electronic structure of these compounds with a special emphasis on the near infrared-visible-ultraviolet absorption bands associated with the M_2 chromophore.

Simple MO Diagram for d Orbital Splittings

The qualitative splitting pattern expected for the d orbitals of a homonuclear diatomic molecule is depicted in Figure 1a. If the internuclear axis is chosen as the z axis of right and left-handed coordinate systems, respectively for the two atoms, then σ , π and δ bonds are generated from the appropriate linear combinations of the (d_z^2), (d_{xz} , d_{yz}) and (d_{xy} , $d_{x^2-y^2}$) orbitals in that order. Introduction of the eight ligands as for example in $Re_2Cl_8^{2-}$ along the x and y axis will dramatically raise the energy of the δ and δ^* orbitals composed of the $d_{x^2-y^2}$ components (Figure 1b). This pair of orbitals is primarily metal-ligand σ -antibonding in character. A similar but less pronounced destabilization would also occur for the σ and σ^* orbitals in a crystal field approach. According to the model $Re_2Cl_8^{2-}$ would contain a quadruple metal-metal bond and so it was proposed by Cotton⁵ to explain the diamagnetism, the eclipsed geometry and the unusually short Re Re distance which is obtained. This qualitative MO diagram suggests that the lowest energy electric-dipole-allowed transition in such compounds is $^1A_{1g} \rightarrow ^1A_{2u}$ ($\delta \rightarrow \delta^*$). Our discussion of electronic spectra will be centered around $Re_2Cl_8^{2-}$ as it has been the most extensively studied of those compounds which contain a quadruple metal-metal bond.

For $\text{Mo}_2\text{Cl}_8^{4-}$ a z polarized transition is observed at $19,128 \text{ cm}^{-1}$ and at low temperatures a vibrational progression in a 336 cm^{-1} vibration (a_{1g} (MoMo) in ground state is 346 cm^{-1})¹¹ is observed.¹⁴ The compound $\text{Mo}_2(\text{SO}_4)_4^{4-}$ exhibits a structureless absorption at $19,400 \text{ cm}^{-1}$.¹⁵ From the polarization data¹⁵ a ${}^1A_{1g} \rightarrow {}^1A_{2u}$ ($\delta \rightarrow \delta^*$) assignment is indicated; however, the intensity of this absorption is rather low¹⁶ with an $\epsilon_{\text{max}} \sim 170$.

A confusing characteristic of the $\delta \rightarrow \delta^*$ absorption band has been its relatively low intensity. Generally, one-electron $N \rightarrow V$ excitations of the bonding to antibonding kind are among the most intense molecular transitions.¹⁷ Recently it was suggested¹⁸ that the diminished intensity of the $\delta \rightarrow \delta^*$ transition is a consequence of weak orbital overlap. Mulliken has shown¹⁷ that the oscillator strength (f) of a one electron $N \rightarrow V$ diatomic-like transition in a weak coupling or valence bond formalism is approximated by

$$(f) = 1.096 \times 10^{11} \nu s^2 r^2$$

where ν is the transition energy in cm^{-1} , s is the orbital overlap, and r the bond length in cm. As the δ overlap is on the order of 0.1 or less, a valence bond description is more appropriate than the MO model. Employing the valence bond formula, oscillator strengths in the neighborhood of 10^{-2} are predicted for typical values of r and ν .

One further point of interest is the location of the triplet state ${}^3A_{2u}$ or more correctly, the A_{1u} and E_u spin orbit components of the $\delta \rightarrow \delta^*$ excitation. It was originally proposed¹⁹ that a weak structured

absorption at 6250 cm^{-1} in the diffuse reflectance spectra of some, but not all $\text{Mo}_2\text{Cl}_8^{4-}$ salts was ${}^1\text{A}_{1g} \rightarrow {}^3\text{A}_{2u}$. As we shall discuss shortly, oxidized Mo species may exhibit a structured absorption in the $6000\text{-}8000 \text{ cm}^{-1}$ region. More recently, a single crystal polarized spectral study¹⁵ of $\text{K}_4\text{Mo}_2\text{Cl}_8 \cdot 2\text{H}_2\text{O}$ revealed an (x,y) polarized shoulder (ca. $17,500 \text{ cm}^{-1}$) on the lower energy shoulder of ${}^1\text{A}_{1g} \rightarrow {}^1\text{A}_{2u} (\delta \rightarrow \delta^*)$. It was suggested that this resulted from a transition to the E_u spin-orbit component of ${}^3\text{A}_{2u}$. Subsequently, the emission spectra of $\text{Re}_2\text{Cl}_8^{2-}$, $\text{Re}_2\text{Br}_8^{2-}$, and $\text{Mo}_2\text{Cl}_8^{4-}$ were recorded at 1.3 K upon excitation of the ${}^1\text{A}_{1g} \rightarrow {}^1\text{A}_{2u}$ absorption.²⁰ Lack of overlap between the emission spectrum and the O-O line of the $\delta \rightarrow \delta^*$ absorption was observed for all three compounds. The emission band shape was similar to that of the $\delta \rightarrow \delta^*$ absorption and the luminescent lifetimes were all on the order of 100 ns. It was concluded²⁰ that the emission probably originated from one of the spin-orbit components of ${}^3\text{A}_{2u}$. Therefore, a ${}^1\text{A}_{2u} - {}^3\text{A}_{2u}$ separation of $1000 - 3000 \text{ cm}^{-1}$ is indicated.

Upon one-electron oxidation or reduction of binuclear group VI or VIIB transition metal compounds, one would expect an electron to be removed from a δ bonding orbital or added to a δ antibonding orbital, respectively. A series of epr studies by Cotton and Pedersen²¹ have shown that this is indeed the case for oxidized species such as $\text{Mo}_2(\text{SO}_4)_4^{3-}$ and $\text{Mo}_2(\text{O}_2\text{CC}_3\text{H}_7)_4^+$ and for the reduced species $\text{Tc}_2\text{Cl}_8^{3-}$, $\text{Re}_2(\text{O}_2\text{CC}_6\text{H}_5)_4^+$ and $\text{Re}_2\text{Cl}_4(\text{P}(\text{C}_2\text{H}_5)_3)_4^+$. It is now becoming apparent that a near infrared electronic absorption band is characteristic of these single electron reduction and oxidation products. Ebner and

Walton²² have noted the presence of an absorption at 7100 cm^{-1} (1400 nm) with a molar extinction coefficient greater than 2000 for $\text{Re}_2\text{X}_5(\text{PRPh}_2)_3$ (X = Cl or Br).²² Similar behavior obtains for $[\text{ReCl}_3(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2)]_2$ and $[\text{ReCl}_3(\text{Ph}_2\text{PCH}_2\text{PPh}_2)]_n$.²³ Another reduced species $\text{Tc}_2\text{Cl}_8^{3-}$ has been studied and an absorption at 6200 cm^{-1} ($\epsilon_{\text{max}} 630$) was observed.²⁴ At low temperatures, a well resolved 320 cm^{-1} vibrational progression is detected.

An absorption at 7100 cm^{-1} ($\epsilon_{\text{max}} 143$) was also observed¹⁶ in the electronic spectrum of the oxidized species $\text{Mo}_2(\text{SO}_4)_4^{3-}$. At low temperatures the band displays well resolved vibrational progressions of 350 cm^{-1} . For comparison, the ground state value²⁵ of a_{1g} (MoMo) for $\text{Mo}_2(\text{SO}_4)_4^{3-}$ is ca. 380 cm^{-1} . On the basis of the sharp molecular vibronic structure observed for $\text{Mo}_2(\text{SO}_4)_4^{3-}$ and the lack of any observable splitting of Mo signals in the X-ray photoelectron spectrum, a $\delta \rightarrow \delta^*$ assignment for the near infrared absorption system rather than an intervalance charge transfer assignment was proposed.¹⁶ A $\delta \rightarrow \delta^*$ assignment was also suggested²⁴ for $\text{Tc}_2\text{Cl}_8^{3-}$ with the aid of an $X\alpha$ calculation. An analogous assignment therefore appears likely for the compounds examined by Walton, et al.^{22, 23} It is interesting to note that the ϵ_{max} of the near infrared absorption is similar to that of the $\delta \rightarrow \delta^*$ absorption in corresponding compounds which possess a full metal-metal quadruple bond. These results suggest a $\delta \rightarrow \delta^*$ assignment for the $13,000\text{ cm}^{-1}$ ($\epsilon_{\text{max}} 2600$) absorption of $\text{Mo}_2(\text{O}_2\text{CCF}_3)_4^-$ rather than the metal to ligand charge transfer (MLCT) assignment which was originally suggested.²⁶ Although this absorption

is at higher energy (ca. 6000 cm^{-1}) than in the other examples cited, the position of the $\delta \rightarrow \delta^*$ absorption of the unreduced compound is also (ca. $15,000 \text{ cm}^{-1}$) at an increased energy.²⁷

Electronic structure simulations have been attempted employing a variety of theoretical techniques. The earliest studies of $\text{Re}_2\text{Cl}_8^{2-}$ and $\text{Mo}_2(\text{O}_2\text{CCH}_3)_4$ were of the Extended Hückel type.^{28, 29} Although these calculations qualitatively accounted for the bonding features, they were inadequate for a description of the excited states. In particular, the lowest unoccupied virtual orbitals were incorrectly predicted to be σ -nonbonding orbitals which were localized along the metal-metal axis. New impetus on the theoretical front was provided when Mortola, Moskowitz, and Rösch³⁰ applied the multiple scattering $X\alpha$ method to $\text{Re}_2\text{Cl}_8^{2-}$. Although underestimating the energy of the ${}^1A_{2u}$ state by some $10,000 \text{ cm}^{-1}$, the qualitative ordering of the excited states was consistent with experiment.^{6, 10} Calculations of the SCF- $X\alpha$ SW type³¹ for $\text{Mo}_2\text{Cl}_8^{4-}$ supported the earlier $\delta \rightarrow \delta^*$ assignment¹⁰ for the $19,128 \text{ cm}^{-1}$ absorption. Once again, the energy of the transition was underestimated by $10,000 \text{ cm}^{-1}$. For $\text{Mo}_2(\text{O}_2\text{CH})_4$ SCF- $X\alpha$ -SW calculations incorrectly predict the $\delta \rightarrow \delta^*$ excitation to be the lowest excited singlet state.³² Also, the energy of the ${}^1A_{2u}$ state again was underestimated by some $15,000 \text{ cm}^{-1}$. An accurate prediction of a $\delta \rightarrow \delta^*$ excitation energy was recently accomplished,²⁴ with an $X\alpha$ calculation of $\text{Tc}_2\text{Cl}_3^{3-}$. The success in this instance was ascribed to the fact that calculation of doublet to doublet excitations

for the odd electron system are free of the ambiguities associated with estimating triplet and singlet energies for the closed shell system. This cannot be the entire explanation as experimental evidence²⁰ suggests a small singlet-triplet splitting of $\delta \rightarrow \delta^*$ (vide supra). Another possible explanation would be the failure of the $X\alpha$ method to adequately account for electron repulsion contributions to the $\delta \rightarrow \delta^*$ excitation energy of the closed shell systems. With regard to this point it should be recalled that the $\delta \rightarrow \delta^*$ transition energies are much less in both the singly oxidized and reduced species. For these cases the ground and excited states contain equal numbers of singly occupied orbitals so that electron repulsion effects will be similar for both the ground and excited states. In the closed shell systems, the $\delta \rightarrow \delta^*$ excited state contains two singly occupied δ -like orbitals whereas the ground state contains one doubly occupied δ orbital. A considerable amount of ionic character in the ${}^1A_{2u}$ state would effectively place both δ electrons on the same atom with a large electron repulsion term between them. It seems likely that unfavorable electron repulsion effects contribute to the high energy of the ${}^1A_{2u}$ state for these systems. Since the metal-metal bond length only changes slightly upon one-electron oxidation or reduction, the magnitude of the unfavorable electron repulsion terms can be estimated from the energy separation between the $\delta \rightarrow \delta^*$ transition in the closed shell case and either the oxidized or reduced case. Values of 12,000, 8000, 17,000 cm^{-1} are obtained for $\text{Mo}_2(\text{SO}_4)_4^{4-/3-}$, $\text{Tc}_2\text{Cl}_8^{3-/2-}$, and $\text{Mo}_2(\text{O}_2\text{CCF}_3)_4^{0/1-}$, respectively. The

exact origin of these electron repulsion energies remains as a problem for future theoretical studies.

The Metal Localized $\delta \rightarrow \pi^*$ Excited State

Four regions of weak absorption are observed between the more intense $\delta \rightarrow \delta^*$ ($14,700 \text{ cm}^{-1}$) and $\pi(\text{Cl}) \rightarrow \delta^*$ (vide infra; $32,600 \text{ cm}^{-1}$) bands of $\text{Re}_2\text{Cl}_8^{2-}$ (Figure 2). The first weak band of $(\underline{n}\text{-Bu}_4\text{N})_2[\text{Re}_2\text{Cl}_8]$ maximized at $17,675 \text{ cm}^{-1}$ and at 15 K consists of three progressions in a 225 cm^{-1} excited state $a_{1g}(\text{ReRe})$ stretching vibration built on three origins.⁷ Two of the progressions are polarized parallel and one perpendicular with respect to the ReRe molecular axis. The band red shifts by only 200 cm^{-1} in $(\underline{n}\text{-Bu}_4\text{N})_2[\text{Re}_2\text{Br}_8]$.⁷ These data are consistent with a metal localized state which possesses greater antibonding character than ${}^1A_{2u}(\delta \rightarrow \delta^*)$ as reflected by the diminished value of $a_{1g}(\text{ReRe})$. Recall that this vibration was 248 cm^{-1} in the ${}^1A_{2u}$ state. The presence of several vibronic origins and the weakness of this band suggest an electric-dipole-forbidden, vibronically-enabled transition. The $\delta \rightarrow \pi^*$ (${}^1A_{1g} \rightarrow {}^1E_g$) assignment was adopted⁷ as it would be expected to lie lower than $\pi \rightarrow \pi^*$ (vide infra; $39,215 \text{ cm}^{-1}$). A $\delta \rightarrow \pi^*$ assignment was preferred over $\pi \rightarrow \delta^*$ since the π orbital possesses substantial halogen character (% Cl, π , 44; π^* , 19).

The $\delta \rightarrow \pi^*$ absorption system plays a particularly prominent role in the electronic spectra of $\text{Mo}_2(\text{O}_2\text{CR})_4$ ($\text{R} = \text{H}, \text{CH}_3, \text{CD}_3, \text{CF}_3$) compounds. These complexes, which are isostructural with $\text{Cu}_2(\text{O}_2\text{CCH}_3)_4$, contain four bridging carboxylate ligands. Unlike the other compounds which contain a quadruple metal-metal bond, there is no absorption

in the 14,000 - 21,000 cm^{-1} range. Furthermore, no electronic absorption bands of appreciable intensity were detected at lower energy.³² The first feature in the solution electronic absorption spectra of these species^{29,32,33} is a weak band centered at 22,700 cm^{-1} ($\epsilon_{\text{max}} \sim 100$) and the frozen solution spectrum³² of $\text{Mo}_2(\text{O}_2\text{CH})_4$ is shown in Figure 3. Dubicki and Martin²⁹ observed a single vibrational progression of 350 cm^{-1} for the 22,700 cm^{-1} band in the 77 K diffuse reflectance spectrum of $\text{Mo}_2(\text{O}_2\text{CCH}_3)_4$. They were not able to identify whether the progressional mode was MoMo or MoO stretching and no firm assignment for the 22,700 cm^{-1} absorption system was reached; however, it was concluded that this absorption was not the $\delta \rightarrow \delta^*$ transition, which therefore must be at higher energy. More direct evidence that this weak absorption system was not $\delta \rightarrow \delta^*$ came from the polarized crystal spectra of $\text{Mo}_2(\text{O}_2\text{CCH}_2\text{NH}_3)_4(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$ and $\text{Mo}_2(\text{O}_2\text{CH})_4$.^{34,15}

A study¹⁸ of the polarized spectra of a crystal of $\text{Mo}_2(\text{O}_2\text{CCH}_3)_4$ as well as films of $\text{Mo}_2(\text{O}_2\text{CCD}_3)_4$, $\text{Mo}_2(\text{O}_2\text{CCF}_3)_4$, and $\text{Mo}_2(\text{O}_2\text{CH})_4$ at 15 K provided a definitive assignment for the 22,700 cm^{-1} absorption band. The energy of this transition was found to be essentially independent of the carboxylate ligand (Figure 4) implying a metal-localized excitation. From a comparison of the shifts of the progressional frequency and ground state infrared and raman fundamentals, it was established¹⁸ that the vibration responsible for the excited state progression was a_{1g} (MoMo). The direct observation of the 190 cm^{-1}

hot band related to the first intense vibronic component conclusively showed that the transition was allowed in the Herzberg-Teller sense and therefore was electric-dipole forbidden.¹⁸ Comparison with the infrared spectra of these compounds identified the 190 cm^{-1} vibration as an a_{2u} (MoO) bending vibration.¹⁸ As this vibration lowers the symmetry of the Mo_2L_3 chromophore, it is reasonable that such a vibration would be important in a vibronic coupling mechanism. The presence of two kinds of perpendicular polarization was interpreted¹⁸ as a low symmetry site splitting of a degenerate electronic state. For $\text{Mo}_2(\text{O}_2\text{CCF}_3)_4$, a structured emission was observed¹⁸ at 1.3 K. As for the weak absorption system, a progression in a_{1g} (MoMo) is observed. Because of the 1800 cm^{-1} gap between the O-O band of the absorption and emission spectra, and the long luminescent lifetime (2 ms) it was suggested that triplet emission from the state related to the weak absorption was observed. It was concluded¹⁸ that only a ${}^1A_{1g} \rightarrow {}^1E_g$ transition can account for the $22,700\text{ cm}^{-1}$ absorption system. Of the available low-lying excitations, only $\delta \rightarrow \pi^*$ or $\pi \rightarrow \delta^*$ yield 1E_g states. The latter assignment was rejected, as $X\alpha$ calculations³² on $\text{Mo}_2(\text{O}_2\text{CH})_4$ have indicated that $\delta \rightarrow \pi^*$ falls below $\pi \rightarrow \delta^*$ and more importantly, only the former transition is metal localized (% Mo: δ 89; π^* , 96; π , 65; δ^* , 86). Furthermore, the calculations suggest that the shoulder at $30,600\text{ cm}^{-1}$ (Figure 3) with an oscillator strength of approximately 0.03 should be assigned to the $\delta \rightarrow \delta^*$ excitation.

The anomalous spectral behavior of the $\text{Mo}_2(\text{O}_2\text{CR})_4$ compounds may be a manifestation of strong covalent Mo-O π bonding. Calculations³² suggest that strong metal ligand bonding can indirectly strengthen the metal-metal bond. Vibrational studies³⁵ of binuclear Mo(II) compounds with various ligand systems tend to support this conclusion. Photoelectron spectra^{36,37} have also been measured for $\text{Mo}_2(\text{O}_2\text{CR})_4$ compounds and the energy ordering of the bonding orbitals $\text{MoMo } \delta > \text{MoMo } \pi > \text{MoO} \sim \text{MoMo } \sigma$ was consistent with the $X\alpha$ description.

Other Metal Localized Excited States

The next absorption band, in order of increasing energy, for $\text{Re}_2\text{Cl}_8^{2-}$ is another weak ($\epsilon_{\text{max}} 65$) band centered at $20,940 \text{ cm}^{-1}$ (Figure 2).⁷ Only perpendicularly polarized progressions of ca. 400 cm^{-1} are observed.⁷ This high frequency clearly is not attributable to a_{1g} (ReRe), and was assigned to an excited state a_{1g} (ReCl) stretch (ground state¹¹ 359 cm^{-1}). This suggests a transition to an unoccupied, metal-chlorine orbital. The vibronic nature of the transition is supported by the low intensity, the presence of several vibronic origins and the red shift and intensity increase between 15 and 298 K. A corresponding absorption was observed⁷ at $19,150 \text{ cm}^{-1}$ in $(n\text{-Bu}_4\text{N})_2[\text{Re}_2\text{Br}_8]$. It was pointed out that this 1790 cm^{-1} red shift upon halide substitution parallels the $1400 - 1500 \text{ cm}^{-1}$ red shift of the $d_{xy} \rightarrow d_{x^2-y^2}$ transition in $(n\text{-Bu}_4\text{N})_2[\text{OsNX}_4]$ ($X = \text{Cl}, \text{Br}$).⁷ Therefore, a ${}^1A_{1g} \rightarrow {}^1A_{1u}$ ($\delta \rightarrow d_{x^2-y^2} (b_{2u})$) assignment was adopted.⁷ Weak absorptions observed in the $22,000 - 24,000 \text{ cm}^{-1}$ region of $\text{K}_4\text{Mo}_2\text{Cl}_8 \cdot 2\text{H}_2\text{O}$ have been in part ascribed to the ${}^1A_{1g} \rightarrow$

${}^1A_{2g}$ ($\delta \rightarrow d_{x^2-y^2}$ (b_{1g})) transition.^{14,31}

Proceeding to higher energy in the electronic spectrum of $\text{Re}_2\text{Cl}_8^{2-}$ (Figure 2), an extremely weak progression is seen at about $23,650 \text{ cm}^{-1}$ superimposed on more intense absorption. The progressional frequency of 185 cm^{-1} was attributed⁷ to the symmetrical bending mode a_{1g} (ReReCl). This band was tentatively assigned⁷ to the electric-dipole forbidden transition $\pi \rightarrow \delta^*$ (${}^1A_{1g} \rightarrow {}^1B_{1u}$). Excitation of a_{1g} (ReReCl) was pointed out⁷ as consistent with the considerable halogen character of the π orbital shown by the $X\alpha$ calculation.⁶ Part of a weak absorption system at $22,000 - 24,000 \text{ cm}^{-1}$ in $\text{Mo}_2\text{Cl}_8^{4-}$ has been assigned to ${}^1A_{1g} \rightarrow {}^1E_g$ ($\pi \rightarrow \delta^*$) on the basis of an $X\alpha$ calculation.³¹

Before moving to the subject of charge transfer excitations, the second lowest "allowed" metal-localized excitation will be considered. A transition centered at $39,215 \text{ cm}^{-1}$ in the 5 K polarized crystal spectrum of $((\underline{n}\text{-C}_4\text{H}_9)_4\text{N})_2[\text{Re}_2\text{Cl}_8]$ (Figure 2) has been attributed to the ${}^1A_{1g} \rightarrow {}^1A_{2u}$ ($\pi \rightarrow \pi^*$) transition.⁶ The modest red shift of this band to $37,735 \text{ cm}^{-1}$ in the crystal spectrum of $((\underline{n}\text{-C}_4\text{H}_9)_4\text{N})_2\text{-Re}_2\text{Br}_8$ is consistent with the 44.4% Cl character of the π orbital predicted⁶ by an $X\alpha$ calculation for $\text{Re}_2\text{Cl}_8^{2-}$. Intense absorption greater than $34,000 \text{ cm}^{-1}$ in $\text{K}_4\text{Mo}_2\text{Cl}_8 \cdot 2\text{H}_2\text{O}$ was in part assigned to the $\pi \rightarrow \pi^*$ excitation with a calculated energy³¹ of $39,400 \text{ cm}^{-1}$. A well resolved band with an oscillator strength of 0.02 occurs at about $44,000 \text{ cm}^{-1}$ in the solution spectra of $\text{Mo}_2(\text{O}_2\text{CR})_4$ compounds.^{27,29,32}

On the basis of an $X\alpha$ calculation³² this was assigned to the ${}^1A_{1g} \rightarrow {}^1A_{2u}$ ($\pi \rightarrow \pi^*$) transition. The relative order of the $\pi \rightarrow \pi^*$ energies for the compounds discussed parallels that of the $\delta \rightarrow \delta^*$ transition energies.

A metal localized $\sigma \rightarrow \sigma^*$ type transition has never been observed experimentally and $X\alpha$ calculations consistently predict this excitation to lie in the as yet unexplored vacuum ultraviolet region of the spectrum.

Ligand $\rightarrow \delta^*$ and $\delta \rightarrow$ Ligand Charge Transfer Excitations

Next the charge transfer states which are possible for the M_2L_8 compounds will be discussed. The δ and δ^* orbitals are respectively the highest occupied and lowest unoccupied molecular orbitals in these compounds. Therefore, it is not surprising that metal to ligand charge transfer (MLCT) and ligand to metal charge transfer (LMCT) transitions which originate or terminate in the δ or δ^* orbitals have been observed.

First, the LMCT excitations will be considered. If the symmetry adapted ligand π and σ -like orbitals are considered, one obtains:

$$\begin{aligned}\sigma_L &= \pi_{\parallel} = a_{1g} + b_{1g} + e_g + a_{2u} + b_{2u} + e_u \\ \pi_{\perp} &= a_{2g} + b_{2g} + e_g + a_{1u} + b_{1u} + e_u\end{aligned}$$

where σ_L denotes ligand σ orbitals and π_{\parallel} denotes ligand π orbitals which lie in a plane containing the metal-metal axis and π_{\perp} represents ligand π orbitals which lie in a plane perpendicular to the metal-metal axis. Only LMCT transitions from the b_{2g} or one of the three e_g

ligand orbitals to the lowest unoccupied b_{1u} (δ^*) orbital are electric-dipole allowed. Intense (x,y) polarized absorption at 30,870 (ϵ_{\max} of 6000 - 9000 in solution) and 23,630 cm^{-1} in the 5 K polarized crystal spectra of $((\underline{n}\text{-C}_4\text{H}_9)_4\text{N})_2[\text{Re}_2\text{Cl}_8]$ (Figure 2) and $((\underline{n}\text{-C}_4\text{H}_9)_4\text{N})_2[\text{Re}_2\text{Br}_8]$ respectively, were assigned to the LMCT transitions ${}^1A_{1g} \rightarrow {}^1E_u$ ($\text{Cl}(e_g \pi_{\parallel} \text{ and } \pi_{\perp}) \rightarrow \delta^*$).⁶ Consistently, an MCD A term is associated with these bands.¹³ The halide dependence of the transition, of course, substantiates the LMCT assignment.

An $X\alpha$ calculation of the electronic structure of $\text{Mo}_2\text{Cl}_8^{4-}$ predicted the ${}^1A_{1g} \rightarrow {}^1E_u$ ($\pi(\text{Cl}) \rightarrow \delta^*$) transitions to fall at 37,500 and 38,600 cm^{-1} , respectively. In accord with this prediction, an A term was observed at 37,000 cm^{-1} in 6 \underline{N} HCl solutions containing the $\text{Mo}_2\text{Cl}_8^{4-}$ ion.¹³ To lower energy of the intense LMCT absorptions of $\text{Re}_2\text{Cl}_8^{2-}$, there are two sharp parallel polarized peaks at 27,000 and 28,100 cm^{-1} (ϵ_{\max} of 400 in CH_3CN solution).⁷ These absorptions shift to 21,290 and 22,080 cm^{-1} , respectively, in the analogous bromide derivative.⁷ Because of the small separation between the two transitions, their LMCT behavior and the polarization along the metal axis, the $e_g \pi_{\parallel}$ and π_{\perp} (halide) $\rightarrow \delta^*$ (${}^1A_{1g} \rightarrow A_{2u}$ (a, b³, E_u)) assignments were proposed.⁷ Similar absorptions have not been observed for $\text{Mo}_2\text{Cl}_8^{4-}$, perhaps in part because spin-orbit coupling should be smaller for Mo(II) than for Re(III).

Complex absorption systems at 35,700 cm^{-1} (Figure 2) in $\text{Re}_2\text{Cl}_8^{2-}$ and 26,300 cm^{-1} in $\text{Re}_2\text{Br}_8^{2-}$ also appear to be electric-

dipole allowed LMCT transitions.¹³ Because of the mixed z and (x,y) polarization and the complex MCD signal observed, it was suggested¹³ that the absorption system was due to the overlapping transitions ${}^1A_{1g} \rightarrow {}^1A_{2u}$ ($Cl(\pi_{\perp}) \rightarrow \delta^*$) and ${}^1A_{1g} \rightarrow {}^1E_u$ ($Cl(\sigma) \rightarrow \delta^*$).

A LMCT transition to a metal orbital other than δ^* has been proposed¹⁴ for $Mo_2Cl_8^{4-}$. The relatively weak absorption band at $28,800\text{ cm}^{-1}$ was polarized along the MoMo axis; its intensity was independent of temperature. Therefore, a ${}^1A_{1g} \rightarrow {}^1A_{2u}$ ($Cl(\pi) \rightarrow d_{x^2-y^2}$) assignment was adopted.¹⁴ Examination of the crystal spectrum of $(NH_4)_4Mo_2Br_8$ ³⁸ should provide useful additional information about the charge transfer states in the binuclear Mo(II) halides.

Transitions of the MLCT type have so far only been identified for binuclear Mo(II) carboxylate compounds. The most intense feature ($\epsilon_{\max} \sim 7000$, $f = 0.19$) in the spectrum of $Mo_2(O_2CH)_4$ (Figure 3) is an intense peak at $41,900\text{ cm}^{-1}$.³² An $X\alpha$ calculation³² has supported a $\delta \rightarrow (C-O)\pi^*$ assignment, specifically ${}^1A_{1g} \rightarrow {}^1E_u$ ($b_{2g} \rightarrow e_u$). Similar bands are observed for $Mo_2(O_2CCH_3)_4$,²⁹ $Mo_2(O_2CCF_3)_4$,³³ $Mo_2(O_2CC_6H_5)_4$.²⁹ As the ionization potential³⁹ of the corresponding carboxylic acid increases, the energy of this band decreases which is consistent with the MLCT assignment.

Implications of the Spectroscopic Studies with Respect to Metal-Metal Bond Strengths

Resonance enhancement of a_{1g} (ReRe) and a_{1g} (MoMo) have been observed for $Re_2Cl_8^{2-}$, $Re_2Br_8^{2-}$,¹² and $Mo_2Cl_8^{4-}$ ¹⁹ salts. As many

as 10 overtones of the a_{1g} metal-metal stretching vibration were observed for $\text{Mo}_2\text{Cl}_8^{4-}$.¹⁹ This allowed Clark and Franks^{12,19} to evaluate the anharmonicity constant, that is, how the spacing between adjacent vibrational levels decreases with increasing vibrational quantum numbers. The lack of sensitivity of $a_{1g}(\text{ReRe})$ to halide substitution suggested to us that this vibration corresponds to almost pure ReRe stretching with little contribution from the other vibrational modes of a_1 symmetry. Because of this and the success of the diatomic metal chromophore description of the electronic spectrum, we suggested⁷ that the Birge-Sponer extrapolation technique, well known in the vibrational spectroscopy of diatomic molecules,⁴⁰ might apply in this instance. Simply stated, the decrease of the vibrational level separation with increasing vibrational quantum number is used to extrapolate to a dissociation limit. Employing this technique, values of 115 - 130 and 110 - 160 kcal/mole were estimated⁷ for ReRe and MoMo quadruple bond energies.

As pointed out earlier, the electron repulsion contribution to the $\delta \rightarrow \delta^*$ excitation may be factored out by examining the single electron oxidized and reduced species. It is this value which more nearly corresponds to a simple bonding-antibonding orbital splitting. Recall that the spectroscopic studies^{6,21} and calculations^{6,30,31,32,41,42,43} consistently indicate that the δ and δ^* orbitals are almost pure linear combinations of metal d_{xy} orbitals. Because of these facts, an upper limit of the δ - δ bond energy should be equal to the electron repulsion

corrected bonding-antibonding separation. With the O-O energies of 6314 and 5900 cm^{-1} for the $\delta \rightarrow \delta^*$ transition in the odd electron compounds $\text{Mo}_2(\text{SO}_4)_4$ ³⁻¹⁶ and Tc_2Cl_8 ³⁻¹⁵ estimates of 18 and 17 kcal/mole for the maximum strength of the δ - δ bond are obtained.

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Compound	Sample condition	Polarization	Energy max. ${}^1A_{1g} \rightarrow {}^1A_{2u}(\delta \rightarrow \delta^*)$ in cm^{-1}		ϵ_{max}	f	${}^2A_{1g}(M-M)$ cm^{-1}	
			${}^1A_{2u}$	${}^1A_{1g}$			${}^1A_{1g}$	${}^1A_{2u}$
$\text{Re}_2\text{Cl}_8^{2-}$	x-tal ^a /Methanol-HCl ^b	z^a	14,654 ^a		1530 ^b	0.023	274 ^c	248 ^a
$\text{Re}_2\text{Br}_8^{2-}$	x-tal ^a	z^d	14,104 ^d				277 ^c	255 ^d
$\text{Mo}_2\text{Cl}_8^{4-}$	x-tal ^e /6M HCl ^f	z^e	19,128 ^e		1050	0.015 ^f	346 ^e	336 ^e
$\text{Tc}_2\text{Cl}_8^{4-}$	x-tal ^h		14,290					
$\text{Re}_2\text{Cl}_8(\text{PEt}_3)_2$	x-tal ^{a, d}	z^a	14,363 ^d				278 ⁱ	289 ^d
$\text{MoCl}_4(\text{PEt}_3)_4$	KBr/ CH_2Cl_2 ^j		16,955		3015		342 ⁱ	320 ^j
$\text{Mo}_2(\text{SO}_4)_4^{4-}$	x-tal ^k /5M H_2SO_4	z^k	19,400		170			
$\text{Mo}_2(\text{aq})_4^{4+}$	10^{-2} M HSO_3CF_3 ^m		19,840		337			
$\text{Mo}_2(\text{en})_4^{4+}$	10^{-3} M HSO_3CF_3 ^m		20,920		483			
$\text{Mo}_2\text{Cl}_4(\text{SMe}_2)_4$	CH_3Cl_2 ⁱ		17,090		1100			
$\text{Mo}_2\text{Cl}_4(\text{bipy})_2$	CHCl_3 ⁱ		18,870		2200			
$\text{Mo}_2\text{Cl}_4(\text{CH}_3\text{CN})_4$	CH_3CN ⁱ		16,610		1800			
$\text{Mo}_2\text{Br}_4(\text{bipy})_2$	KBr ⁱ		17,390					
$\text{Re}_2(\text{CH}_3)_8^{4-}$	Et_2O^n		18,600		≤ 1500			
$\text{Cr}_2(\text{CH}_3)_8^{4-}$	Et_2O^n		22,000		≤ 700			
$\text{Mo}_2(\text{CH}_3)_8^{4-}$	Et_2O^n		19,500		≤ 1500			

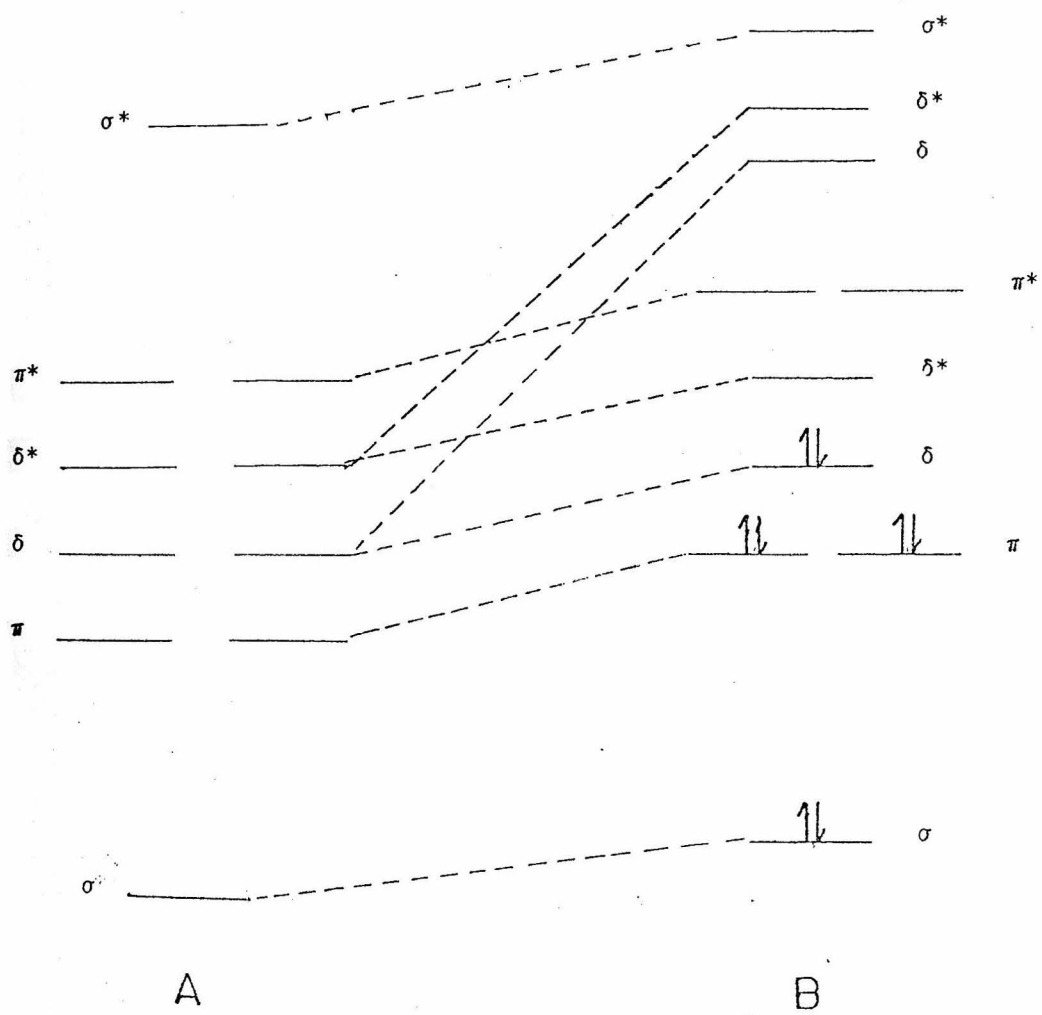
Table I Footnotes

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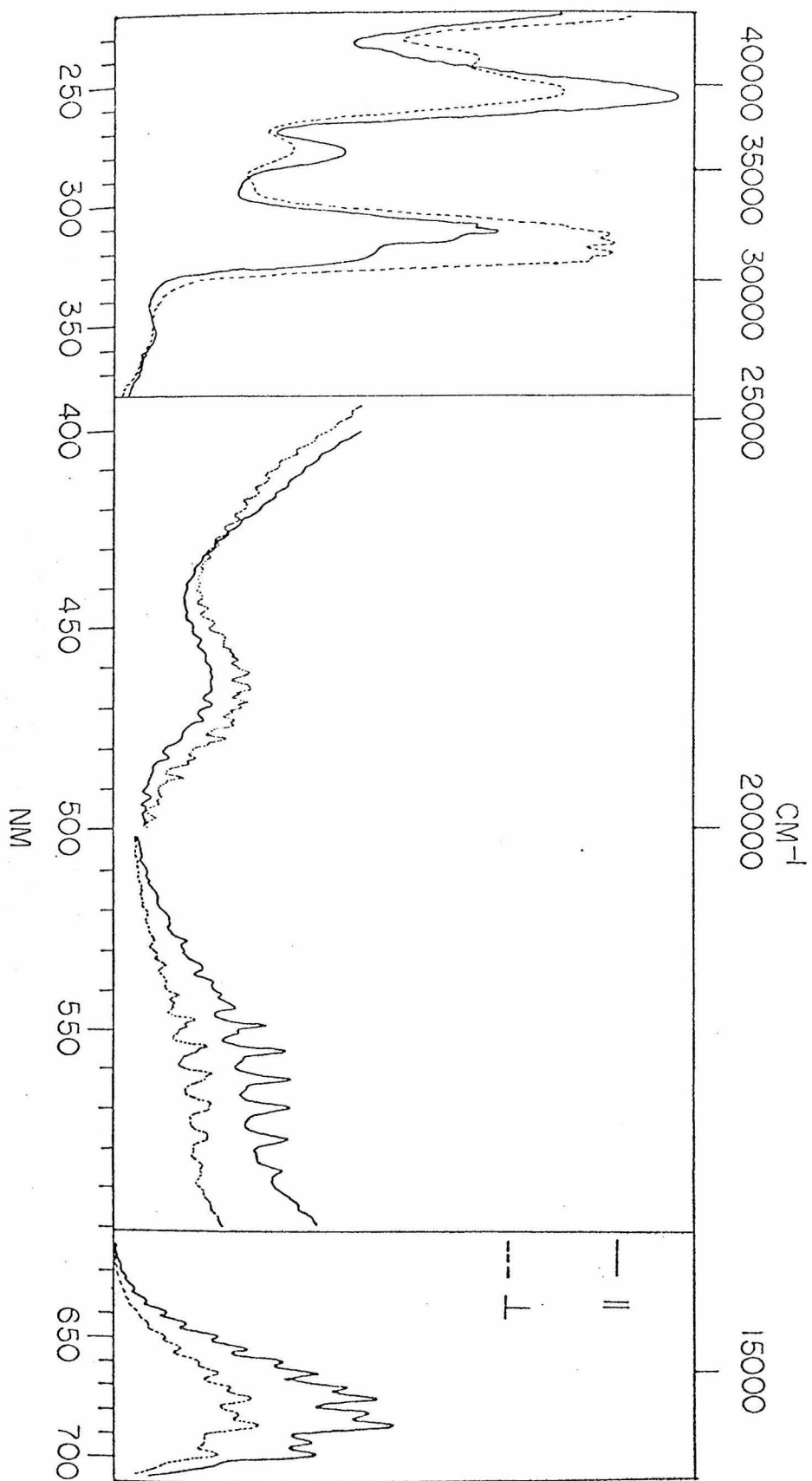
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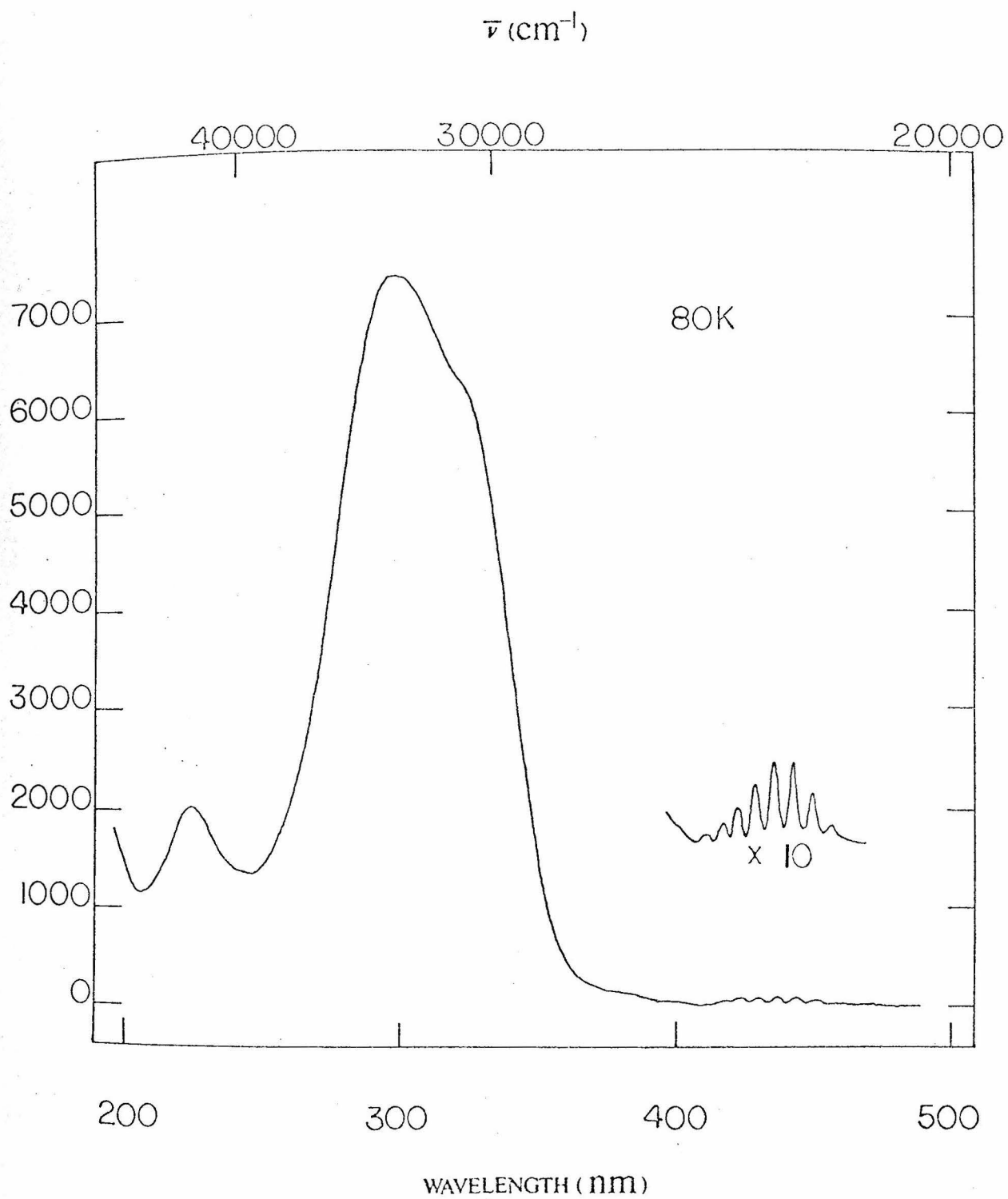
Figure Captions

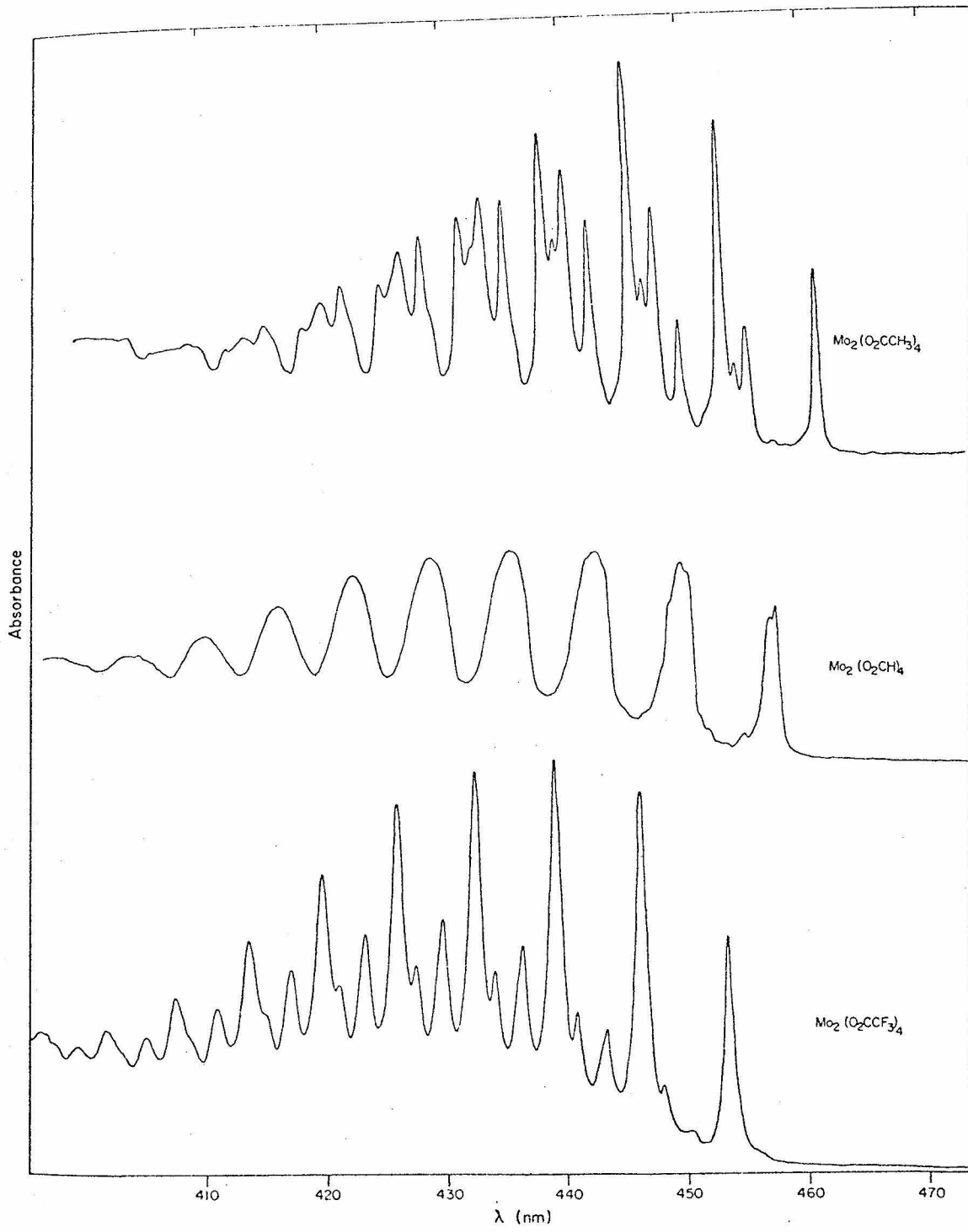
- Figure 1. Simple MO diagram for the d orbital splittings in a homonuclear diatomic molecule (A) and in a M_2L_8 compound with D_{4h} symmetry (B).
- Figure 2. Single crystal polarized electronic absorption spectra of $(n\text{-Bu}_4\text{N})_2[\text{Re}_2\text{Cl}_8]$ at 5 K (outer spectra) and 15 K (central portion). Three different crystals were used to obtain these spectra.
- Figure 3. Electronic absorption spectrum of $\text{Mo}_2(\text{O}_2\text{CH})_4$ in a 4:1 ethanol:methanol glass at 80 K.
- Figure 4. Electronic absorption spectra of the $\delta \rightarrow \pi^*$ band in $\text{Mo}_2(\text{O}_2\text{CCH}_3)_4$, $\text{Mo}_2(\text{O}_2\text{CH})_4$ and $\text{Mo}_2(\text{O}_2\text{CCF}_3)_4$. Spectra were obtained at 15 K for samples which had been sublimed onto a quartz window.



ABSORBANCE







Further Studies of the Electronic Spectra of $\text{Re}_2\text{Cl}_8^{2-}$ and $\text{Re}_2\text{Br}_8^{2-}$.
Assignment of the Weak Bands in the 600-350 nm Region. Estimation
of the Dissociation Energies of Metal-Metal Quadruple Bonds.

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Abstract: Previously published evidence bearing on the polarizations and assignments for the strong bands in $\text{Re}_2\text{Cl}_8^{2-}$ and related species is synthesized and it is shown that work from our two laboratories gives a consistent picture. New polarized spectra of thick crystals of $(\underline{n}\text{-Bu}_4\text{N})_2[\text{Re}_2\text{Cl}_8]$ and $(\underline{n}\text{-Bu}_4\text{N})_2[\text{Re}_2\text{Br}_8]$, measured at 15 K, are reported and discussed. Four new regions of weak absorption between the more intense $\delta \rightarrow \delta^*$ ($14,700 \text{ cm}^{-1}$) and $\pi(\text{Cl}) \rightarrow \delta^*$ ($32,600 \text{ cm}^{-1}$) bands of $\text{Re}_2\text{Cl}_8^{2-}$ have been characterized. The first weak band of $(\underline{n}\text{-Bu}_4\text{N})_2[\text{Re}_2\text{Cl}_8]$ maximizes at $17,675 \text{ cm}^{-1}$ and consists of three progressions in a 225 cm^{-1} excited state a_{1g} (ReRe) stretching vibration built on three origins. Two of the progressions are polarized parallel and one perpendicular with respect to the ReRe molecular axis. The band red shifts by only 200 cm^{-1} in $(\underline{n}\text{-Bu}_4\text{N})_2[\text{Re}_2\text{Br}_8]$. The results indicate that the band is attributable to the electric-dipole-forbidden, metal-

localized transition $\delta \rightarrow \pi^*$ (${}^1A_{1g} \rightarrow {}^1E_g$). A second absorption at $20,940 \text{ cm}^{-1}$ exhibits only perpendicularly polarized progressions on several vibronic origins with a common vibrational spacing of ca. 400 cm^{-1} (a_{1g} (ReCl) stretch). This band also intensifies and red shifts upon warming (15 to 300 K). The 1790 cm^{-1} red shift of this band in $(n\text{-Bu}_4\text{N})_2[\text{Re}_2\text{Br}_8]$ pinpoints it as a $\delta \rightarrow d_{x^2-y^2}$ (b_{2u}) (${}^1A_{1g} \rightarrow {}^1A_{1u}$) transition. The third band, which is at $23,645 \text{ cm}^{-1}$, is extremely weak and only one perpendicularly polarized progression in the a_{1g} (ReReCl) skeletal bending mode was detected. A $\pi \rightarrow \delta^*$ (${}^1A_{1g} \rightarrow {}^1B_{1u}$) assignment is suggested. The fourth absorption system is comprised of two sharp peaks at $27,000$ and $28,100 \text{ cm}^{-1}$, which are parallel polarized. These peaks shift to $21,290$ and $22,080 \text{ cm}^{-1}$ in $(n\text{-Bu}_4\text{N})_2[\text{Re}_2\text{Br}_8]$, consistent with a ligand to metal charge transfer (LMCT) assignment. As the LMCT transitions to a^1E_u and b^1E_u states are not split appreciably in $\text{Re}_2\text{Cl}_8^{2-}$, it is suggested that the fourth weak band system is derived from the corresponding $e_g \pi(\text{Cl}) \rightarrow \delta^*$ (${}^1A_{1g} \rightarrow A_{2u}$ (a, b^3E_u)) excitations. Dissociation energies of $\text{Re}^{\frac{4}{2}}\text{-Re}$ and $\text{Mo}^{\frac{4}{2}}\text{-Mo}$ bonds have been estimated from a Birge-Sponer extrapolation, giving values of 115-130 kcal/mol for the former and 110-160 kcal/mol for the latter.

Introduction

The earliest, tentative suggestions^{1,2} as to how to assign the electronic spectrum of $\text{Re}_2\text{Cl}_8^{2-}$, the species in which the existence of quadruple bonds was discovered,^{1,3} as well as the extension of such assignments to the spectra of closely related complexes, have not withstood recent experimental⁴⁻¹⁰ and theoretical^{6,10-12} scrutiny. Work done within the past few years⁴⁻¹² has provided new spectral assignments that seem certain to be correct in their essentials and bring us to a point of departure for delving more deeply into the details of the spectra and bonding in the entire class of compounds¹³ containing quadruple M-M bonds, and other multiple bonds between metal atoms. One purpose of this paper is to present some new and pertinent facts concerning the spectra of the $\text{Re}_2\text{X}_8^{2-}$ ($\text{X} = \text{Cl}, \text{Br}$) ions.

In the past it has appeared that there have been disagreements between publications from our two laboratories as to observations and interpretations regarding the electronic structural properties of $\text{Re}_2\text{Cl}_8^{2-}$ and related species containing quadruple bonds. In actual fact, we are in essentially complete agreement as to the observations and their interpretation. In view of the importance of establishing a clear picture of the situation regarding the prototypal^{1,3} quadruple bond, *i. e.*, that in $\text{Re}_2\text{Cl}_8^{2-}$, we also present in this report a synthesis of some isolated observations recorded in earlier publications, as well as a needed critique of our previous estimates of the bond dissociation energies (BDE's) of quadruple bonds.

Contrary to the impression created in a recent publication⁵ from one of our laboratories, there was in fact a sound basis for the claim, which was advanced^{4,6} first by Cowman and Gray, that the $14,000 \text{ cm}^{-1}$ absorption band in $\text{Re}_2\text{Cl}_8^{2-}$ is polarized parallel to the Re-Re axis. The crystallographic

results, showing as they do the existence of a disorder in the crystals, taken together with the earlier crystal spectra,^{4,7} confirmed in the most direct way the aforementioned assignment of polarization. The misunderstanding between our laboratories was in large part attributable to the fact that the logic of the Cowman-Gray argument was not presented in full form in either of the two published documents.^{4,6} To set the record straight, we shall now outline the main parts of the argument.

It should be recalled that each of the three complexes, $(\underline{n}\text{-Bu}_4\text{N})_2\text{-}[\text{Re}_2\text{Cl}_8]$, $(\underline{n}\text{-Bu}_4\text{N})_2[\text{Re}_2\text{Br}_8]$, and $\text{Re}_2\text{Cl}_6[\text{P}(\text{C}_2\text{H}_5)_3]_2$, exhibits a moderately intense band at about $14,000\text{ cm}^{-1}$; in each case the integrated intensity of the band is independent of temperature (between 5 and 300 K) and a vibrational progression in a_{1g} (ReRe) is exhibited at 5 K. Studies on single crystals of $\text{Re}_2\text{Cl}_6[\text{P}(\text{C}_2\text{H}_5)_3]_2$ showed conclusively that the $14,000\text{ cm}^{-1}$ band is ReRe-axis (parallel or z) polarized.⁴ Starting with this incontestable result, three important points should be emphasized: (1) There is an obvious analogy of the $14,000\text{ cm}^{-1}$ bands in $\text{Re}_2\text{Cl}_8^{2-}$ and $\text{Re}_2\text{Br}_8^{2-}$ with that in $\text{Re}_2\text{Cl}_6[\text{P}(\text{C}_2\text{H}_5)_3]_2$. (2) The fact that the solution MCD spectra of $(\underline{n}\text{-Bu}_4\text{N})_2[\text{Re}_2\text{Cl}_8]$ and $(\underline{n}\text{-Bu}_4\text{N})_2[\text{Re}_2\text{Br}_8]$ show that the intense bands at $32,600$ and $23,630\text{ cm}^{-1}$, respectively, exhibit A terms.^{6,7,14} These results, which show that the excited state is degenerate, establish that the intense bands are ${}^1A_{1g} \rightarrow {}^1E_u$, and therefore that they must be polarized perpendicular to the molecular axis. As the crystal spectra show,^{4,7} the $14,000\text{ cm}^{-1}$ band displays polarization character opposite to that of ${}^1A_{1g} \rightarrow {}^1E_u$. It must therefore be parallel polarized. (3) The previously unpublished observation that a few crystals of $(\underline{n}\text{-Bu}_4\text{N})_2[\text{Re}_2\text{Br}_8]$ possess a nondichroic orange-yellow face, with the $14,000\text{ cm}^{-1}$ band absent.⁷ No such face

would be possible if the band were perpendicularly polarized.

The early reports^{2,15} of the electronic absorption spectrum of $(\underline{n}\text{-Bu}_4\text{N})_2[\text{Re}_2\text{Cl}_8]$ did not concern themselves with the region of weak absorption between the 14,700 and 32,600 cm^{-1} bands. By examining concentrated solutions containing $\text{Re}_2\text{Cl}_8^{2-}$, we have now shown that there are four weak bands in this region. We shall first describe here the single crystal spectra and assignments of these new band systems for $(\underline{n}\text{-Bu}_4\text{N})_2[\text{Re}_2\text{Cl}_8]$, and also report related spectroscopic results for $(\underline{n}\text{-Bu}_4\text{N})_2[\text{Re}_2\text{Br}_8]$.

Experimental Section

Crystals of $(\underline{n}\text{-Bu}_4\text{N})_2[\text{Re}_2\text{Cl}_8]$ and $(\underline{n}\text{-Bu}_4\text{N})_2[\text{Re}_2\text{Br}_8]$ were grown and oriented as previously described.⁴ Low temperature polarized spectra were recorded on a Cary 17 spectrometer using a Cary liquid helium dewar and tandem Glan-Taylor air-spaced calcite polarizers. The 0.2 and 0.5 absorbance slidewires were used to record the weak bands. Temperature was measured with a calibrated carbon resistor. Polarizations are denoted \parallel and \perp along the extinction directions of the (100) crystal face, corresponding to projections predominantly \parallel and \perp to the ReRe molecular axis.^{4,7}

Results and Discussion

The electronic spectrum of $(\underline{n}\text{-Bu}_4\text{N})_2[\text{Re}_2\text{Cl}_8]$ in acetonitrile solution at 298 K (Figure 1) shows four absorption bands (I - IV) between the electric-dipole-allowed $\delta \rightarrow \delta^*$ (${}^1A_{1g} \rightarrow {}^1A_{2u}$) and $\pi(\text{Cl}) \rightarrow \delta^*$ (${}^1A_{1g} \rightarrow {}^1E_u$) systems at 682 and 314 nm, respectively. In a crystal at 15 K, band I, which is centered at 17,675 cm^{-1} , consists of three vibrational progressions (Figure 2 and Table 1). Owing to overlap with the $\delta \rightarrow \delta^*$ band at lower energy, it is not possible to locate the true progressional origins with certainty. A strong

parallel polarized progression in a 225 cm^{-1} vibration originates at $17,062\text{ cm}^{-1}$, and a less intense one begins at $17,452\text{ cm}^{-1}$. The weaker progression could either represent a new vibronic origin or a single quantum of a_{1g} (ReCl) built on the one at $17,062\text{ cm}^{-1}$. A perpendicularly polarized progression of the same frequency is built on a vibronic origin at $17,117\text{ cm}^{-1}$. The 225 cm^{-1} progression is assigned to the excited state a_{1g} metal-metal stretching mode. For comparison, the ground and $\delta \rightarrow \delta^*$ state values are 274^{16} and $248^{4,6,7}\text{ cm}^{-1}$, respectively. A maximum in the progression is reached at the fourth band, or third vibration, in contrast to the $\delta \rightarrow \delta^*$ system, which peaks at the first vibration.^{4,7} This indicates a greater distortion of the Re_2 bond in the excited state associated with band I than that accompanying $\delta \rightarrow \delta^*$ excitation. The reduced value of a_{1g} (ReRe) for band I is also consistent with a transition to an orbital that possesses a large amount of metal-metal antibonding character. The mixed polarization, the presence of at least two vibronic origins, and the weakness of band I suggest an electric-dipole-forbidden, vibronically-enabled transition. A similar band, with unresolved, overlapping vibronic structure, is observed at $17,475\text{ cm}^{-1}$ for $(\underline{n}\text{-Bu}_4\text{N})_2\text{-}[\text{Re}_2\text{Br}_8]$. Such insensitivity to halide substitution confirms the metal-localized nature of the excitation. The transition $\delta \rightarrow \pi^*$ (${}^1A_{1g} \rightarrow {}^1E_g$) is consistent with the experimental data, and would be expected to lie lower than $\pi \rightarrow \pi^*$, which is at $39,215\text{ cm}^{-1}$ in a crystal of $(\underline{n}\text{-Bu}_4\text{N})_2[\text{Re}_2\text{Cl}_8]$ at 5 K.⁶ We prefer $\delta \rightarrow \pi^*$ to $\pi \rightarrow \delta^*$ for the $17,675\text{ cm}^{-1}$ band, as the π orbital possesses a substantial halogen character.⁶

Band II, which is centered at $20,940 \text{ cm}^{-1}$ (Figure 2 and Table 1), exhibits only perpendicularly polarized components with several vibronic origins, complex overlapping progressions, and a common vibrational spacing of ca. 400 cm^{-1} . This high frequency progression clearly is not attributable to $a_{1g}(\text{ReRe})$, and is assigned to an excited state $a_{1g}(\text{ReCl})$ stretch (ground state $^{16}359 \text{ cm}^{-1}$), which suggests a transition to an unoccupied, metal-chlorine orbital. The vibronic nature of the transition is supported by the low band intensity, the presence of several vibronic origins, and the red shift and approximately twofold increase in intensity upon increasing the temperature from 15 to 298 K. (It was not possible to assess the temperature dependence of bands I or III, owing to concomitant thermal broadening of the more intense systems with which they overlap.) A corresponding band was observed at $19,150 \text{ cm}^{-1}$ in $(\underline{n}\text{-Bu}_4\text{N})_2[\text{Re}_2\text{Br}_8]$. This modest (1790 cm^{-1}) red shift upon halide substitution parallels the $1400 - 1500 \text{ cm}^{-1}$ red shift of the $d_{xy} \rightarrow d_{x^2-y^2}$ transition in $(\underline{n}\text{-Bu}_4\text{N})[\text{OsNX}_4]$ ($X = \text{Cl}, \text{Br}$).¹⁸ The above data support a $\delta \rightarrow d_{x^2-y^2}$ assignment for band II. In a D_{4h} complex such as $\text{Re}_2\text{Cl}_8^{2-}$, there are b_{1g} and b_{2u} linear combinations of the $d_{x^2-y^2}$ orbitals, yielding $^1A_{2g}$ and $^1A_{1u}$ excited states, respectively, for promotion of a δ electron. A transition to either of these states is orbitally forbidden. In the Herzberg-Teller coupling scheme,¹⁹ $^1A_{1g} \rightarrow ^1A_{2g}$ can gain vibronic intensity both parallel and perpendicular, but $^1A_{1g} \rightarrow ^1A_{1u}$ can only be allowed in perpendicular polarization, as a $D_{4h} \text{ M}_2\text{X}_8$ unit does not possess an a_{2g} vibrational mode. As band II exhibits only perpendicular polarization, the assignment $\delta \rightarrow d_{x^2-y^2} (b_{2u}) (^1A_{1g} \rightarrow ^1A_{1u})$ is adopted.

Band III, which is centered at $23,645 \text{ cm}^{-1}$, is barely detectable on the low energy tail of band IV (Figure 2 and Table 1). There is only one clear progression in a 185 cm^{-1} vibration, and it is perpendicularly polarized;

however, the presence of parallel components cannot be ruled out, as the intensities are very low. The 185 cm^{-1} vibration is attributed to the symmetrical bending mode, a_{1g} (ReReCl). One striking aspect is the length of the progression, which, despite its weakness, is detectable for 12 to 13 vibrations. Band III is not observable in $(\underline{n}\text{-Bu}_4\text{N})_2[\text{Re}_2\text{Br}_8]$, owing to the presence of interfering charge transfer absorption. We tentatively assign band III to the electric-dipole-forbidden transition $\pi \rightarrow \delta^*$ (${}^1A_{1g} \rightarrow {}^1B_{1u}$). The fact that an $X\alpha$ calculation has shown⁶ that the π orbital of $\text{Re}_2\text{Cl}_8^{2-}$ possesses considerable halogen character is consistent with the assignment, as excitation of a_{1g} (ReReCl) is reasonable for a transition to ${}^1B_{1u}$.

Band system IV, which consists of two sharp, parallel polarized peaks at $27,000$ and $28,100\text{ cm}^{-1}$, shifts to $21,290$ and $22,080\text{ cm}^{-1}$, respectively, in $(\underline{n}\text{-Bu}_4\text{N})_2[\text{Re}_2\text{Br}_8]$. This constitutes conclusive evidence for a ligand to metal charge transfer (LMCT) assignment. Two closely-spaced, allowed $e_g\pi(\text{Cl}) \rightarrow \delta^*$ (${}^1A_{1g} \rightarrow {}^1E_u$) transitions have been predicted^{6,10} for $\text{Re}_2\text{Cl}_8^{2-}$ and $\text{Mo}_2\text{Cl}_8^{4-}$ by $X\alpha$ calculations, and the intense band observed in a crystal of $(\underline{n}\text{-Bu}_4\text{N})_2[\text{Re}_2\text{Cl}_8]$ at $30,870\text{ cm}^{-1}$ is split into two components.⁶ We suggest that band IV comprises the transitions to the two A_{2u} spin-orbit components derived from the LMCT states a^3E_u and b^3E_u .

Previous estimates made by us of the BDE for $\text{Re}^{\frac{4^{\circ}}{2}}\text{-Re}$ in $\text{Re}_2\text{Cl}_8^{2-}$ now seem likely either to be too low²⁰ (ca. 80 kcal/mol), because solvation contributions to excited state reactivity could be substantial,^{20,21} or too high² (ca. 360 kcal/mol) because of accumulated errors in the MO calculation.²² It is interesting to note that for the Re-Re double bonds in Re_2Cl_9 and Re_3Br_9 the BDE's have been estimated from thermochemical data to be 85 and 103

kcal/mol, respectively.²³ This suggests that for the quadruple bond a value somewhat over 100 kcal/mol might be sensible.

As another approach to this problem, we have utilized available vibrational data for $\text{Re}_2\text{Cl}_8^{2-}$, $\text{Re}_2\text{Br}_8^{2-}$, and $\text{Mo}_2\text{Cl}_8^{4-}$. Data first reported for these species^{16,17a, 24,25} have recently been improved and extended by Clark and Franks for $\text{Re}_2\text{X}_8^{2-}$ ^{26a} ($\text{X} = \text{Cl}, \text{Br}$) and for $\text{Mo}_2\text{Cl}_8^{4-}$.^{26b} In each case the Raman band that is due principally to totally symmetric metal-metal stretching was observed not only as the fundamental, but through several overtones. For the $\text{Re}_2\text{X}_8^{2-}$ ions, the first three overtones and for $\text{Mo}_2\text{Cl}_8^{4-}$ the first ten overtones were observed. From these overtone progressions Clark and Franks were able to evaluate ω_e and χ_e , the harmonic frequency and anharmonicity constant, respectively, for each of the $\text{M}_2\text{X}_8^{n-}$ species. It is well known in the vibrational spectroscopy of diatomic molecules^{27,28} that such information may be used to estimate BDE's by a method known as the Birge-Sponer extrapolation. Specifically, the BDE is estimated as $(\omega_e^2/4\chi_e) - \omega_e/2$. This is only an approximation, even for diatomics; it can give results either too high or too low, but usually too high.²⁷ Its reliability in a polyatomic system is uncertain; the main difficulty arises because the "bond stretching mode", so-called, for a given bond will in general be coupled to other modes of the same symmetry and it is not clear whether the degree of coupling will vary with the state of excitation of the vibration. In the $\text{M}_2\text{X}_8^{n-}$ ions, with D_{4h} symmetry, there are two other totally symmetric (a_{1g}) vibrations besides " ν_{MM} ", namely " ν_{MX} " and " ν_{MMX} ". Thus we apply the Birge-Sponer extrapolation in these cases with considerable circumspection.

Table 2 gives the input data from Clark and Franks²⁶ and the BDE's estimated. The uncertainty intervals on the latter derive solely from those listed for the χ_e values. It can be seen that all of the BDE's obtained are in a range we consider reasonable. If we assume that the values obtained are more likely to be too high than too low, we might say, allowing for an error in this direction of 15-20%, that the BDE for $\text{Re}^{4^\circ}\text{-Re}$ may be 115-130 kcal/mol, whereas that for $\text{Mo}^{4^\circ}\text{-Mo}$ is probably in the range 110-160 kcal/mol. It should be noted that these are very substantial bond energies. The only homonuclear units with BDE's that are clearly higher are $\text{C}\equiv\text{C}$ (196) and $\text{N}\equiv\text{N}$ (226), and beyond the first short period only $\text{P}\equiv\text{P}$ (125 kcal/mol) has a BDE in the same range.²⁹

Conclusions

(1) There exists excellent experimental evidence of several kinds for the entire assignment of band polarizations for $\text{Re}_2\text{Cl}_8^{2-}$ given previously.^{4,6} This leads, in turn, to reliable transition assignments for these bands, including four weak features, as has been detailed above. No significant disagreements exist between our two laboratories in these respects.

(2) Earlier estimates of the $\text{Re}^{4^\circ}\text{-Re}$ bond energy based on photochemical observations²⁰ and a crude MO calculation² are recognized to be, respectively, too low and too high. We suggest, very tentatively and with full awareness of the dangers inherent in the method, that by a Birge-Sponer extrapolation using Clark's Raman data on overtones of the $\text{M}_2\text{X}_8^{n-}$ species, the $\text{Mo}^{4^\circ}\text{-Mo}$ and $\text{Re}^{4^\circ}\text{-Re}$ bond dissociation energies most likely lie in the ranges 110-160 and 115-130 kcal/mol, respectively.

Acknowledgment

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Table 1.

Band	$\nu(\pm 0.3)$	$\nu(\pm 0.3)$	Species (cm^{-1})	polarization	$A_{1g} \rightarrow$ E_g			
I	586.1	17052						
	584.2	17117		226		⊥		
	578.2	17205		235				
	576.6	17343		231		⊥		
	573.0	17452		234				
	570.1	17541		222		⊥		
	568.9	17576		231				
	565.8	17674		234		⊥		
	562.7	17771		231				
	561.5	17809		234		⊥		
	558.4	17908		201				
	556.0	17986		231		⊥		
	555.3	18010		231				
	551.3	18139		248		⊥		
	549.4	18202		213				
	547.7	18258		213		⊥		
	544.9	18352		199				
	543.6	18396		199		⊥		
	II	541.8		18457			⊥	
		497.3		20109			414	
493.8		20251	414	⊥				
492.3		20313	419	⊥				
490.4		20391	414	⊥				
488.7		20462	400	⊥				
487.4		20517	408	⊥				
483.9		20665	406	⊥				
482.5		20725	397	⊥				
480.6		20807	438	⊥				
478.9		20881	438	⊥				
477.6		20938	438	⊥				
474.4		21079	438	⊥				
473.1		21137	438	⊥				
471.2		21222	438	⊥				
469.9		21281	438	⊥				
468.6		21340	438	⊥				
466.7		21427	438	⊥				
465.4		21487	438	⊥				
464.4		21533	438	⊥				
462.2		21636	438	⊥				
461.1		21687	438	⊥				
460.1		21734	438	⊥				
458.2		21824	438	⊥				
456.9		21887	438	⊥				
455.6		21949	438	⊥				
454.2		22017	438	⊥				
452.6		22095	438	⊥				
449.2	22262	438	⊥					
445.1	22467	438	⊥					
442.2	22614	438	⊥					

III	439.2	22769		193		1E_g
	435.5	22962		150		
	432.7	23111		177		
	429.4	23288		164		
	426.4	23452		194		
	422.9	23646		169		
	419.9	23815		200		
	416.4	24015		192		
	413.1	24207		183		
	410.0	24390		198		
	406.7	24588				
IV	370.	27000				$A_{2u}(a^3E_u)$
	356.	28100				$A_{2u}(b^3E_u)$

Table 2. Birge-Sponer Extrapolated Re_2 and Mo_2 Bond Dissociation Energies in $\text{M}_2\text{X}_8^{n-}$ Complexes

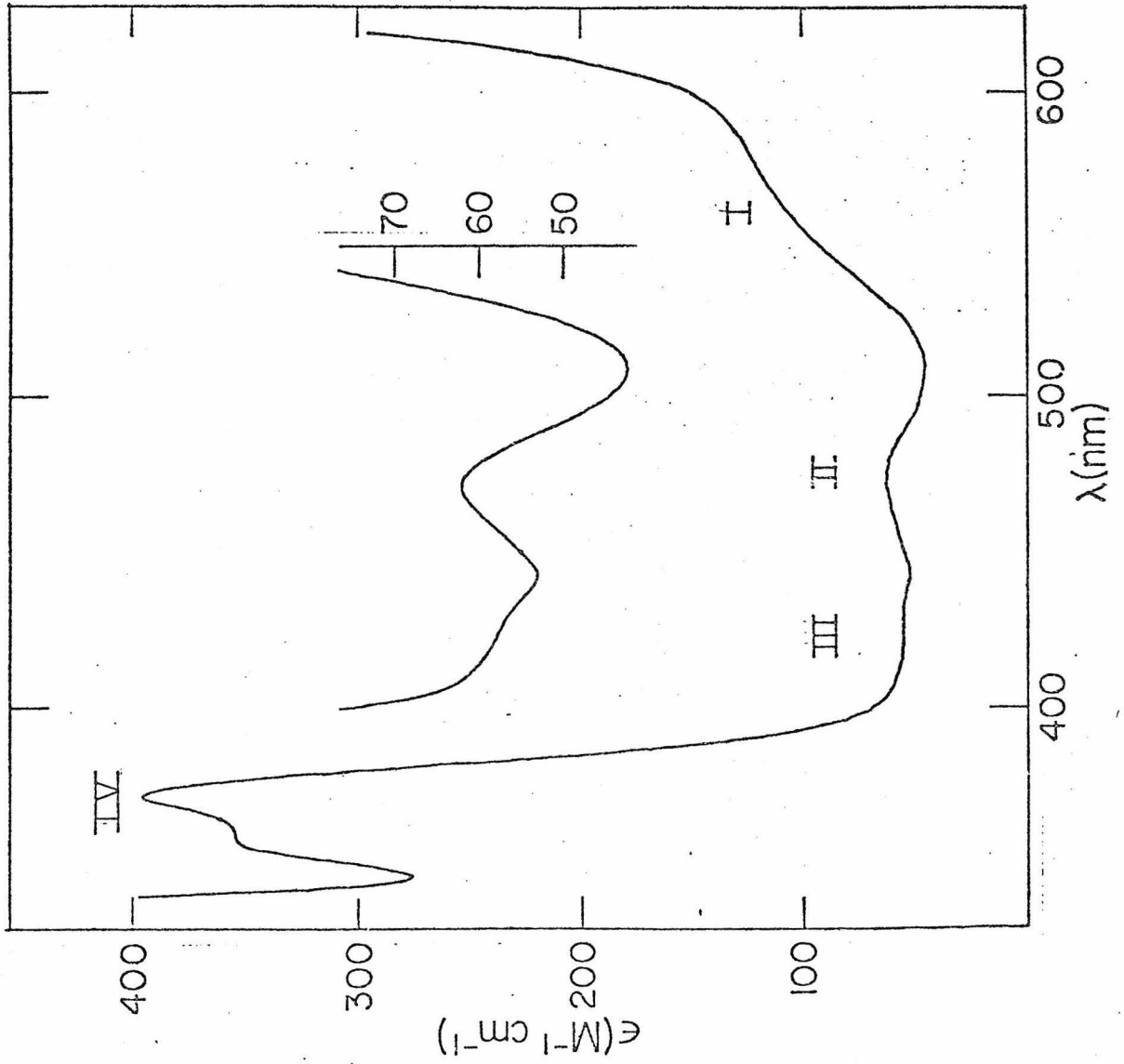
<u>Compound^a</u>	<u>ω_e (cm⁻¹)</u>	<u>χ_e (cm⁻¹)</u>	<u>BDE (kcal/mol)</u>
$\text{K}_4[\text{Mo}_2\text{Cl}_8]$	347	0.50 ± 0.05	172 ± 20
$\text{Rb}_4[\text{Mo}_2\text{Cl}_8]$	339	0.43 ± 0.05	190 ± 25
$\text{Cs}_4[\text{Mo}_2\text{Cl}_8]$	342	0.66 ± 0.07	127 ± 15
$(\underline{n}\text{-Bu}_4\text{N})_2[\text{Re}_2\text{Cl}_8]$	273	0.35 ± 0.05	152 ± 20
$(\underline{n}\text{-Bu}_4\text{N})_2[\text{Re}_2\text{Br}_8]$	276	0.39 ± 0.06	139 ± 25

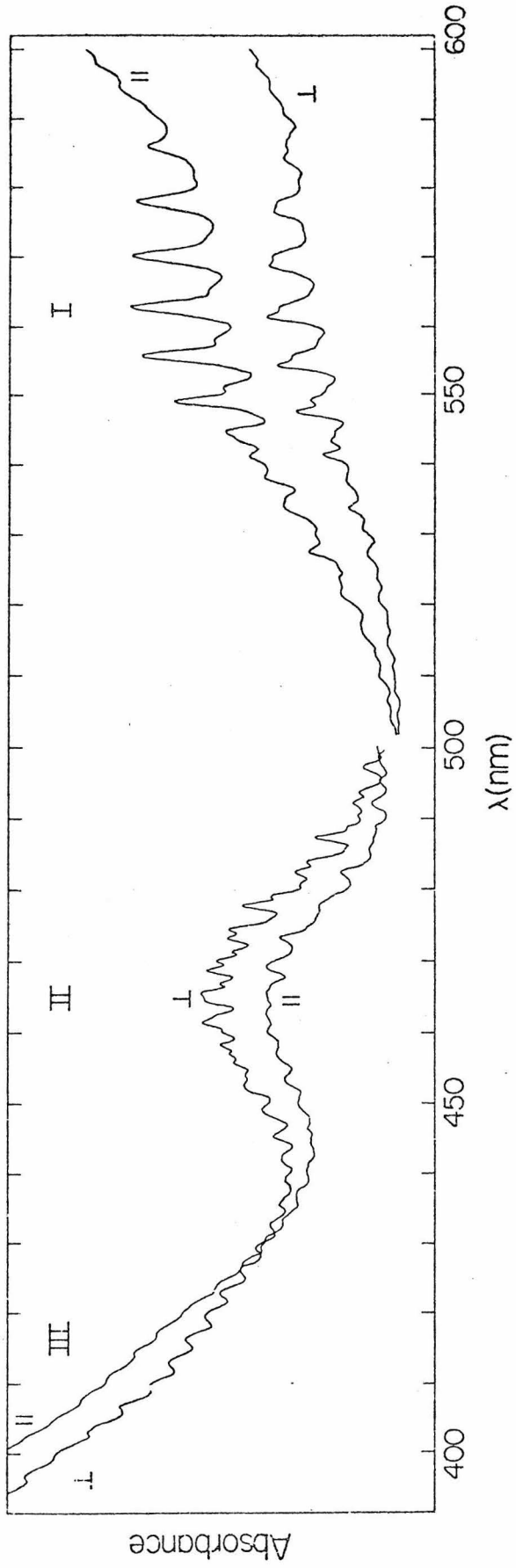
^a Data from ref. 26.

Figure Captions

Figure 1. Electronic absorption spectrum of $(n\text{-Bu}_4\text{N})_2[\text{Re}_2\text{Cl}_8]$ in acetonitrile solution at 298 K in the region 600-350 nm.

Figure 2. Single crystal polarized spectra of bands I - III in $(n\text{-Bu}_4\text{N})_2[\text{Re}_2\text{Cl}_8]$ at 15 K. Bands II and III were recorded at a vertical scale expansion 2.5 times that used for band I. The measurements were made at a spectral bandwidth less than 0.75 nm.





Emission Spectra and Lifetimes of $\text{Re}_2\text{Cl}_8^{2-}$, $\text{Re}_2\text{Br}_8^{2-}$ and $\text{Mo}_2\text{Cl}_8^{4-}$
at 1.3 K Upon Excitation of the $\delta \rightarrow \delta^*$ Transition

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Abstract: Excitation (650 nm) of $(\underline{n}\text{-Bu}_4\text{N})_2[\text{Re}_2\text{Cl}_8]$ and $(\underline{n}\text{-Bu}_4\text{N})_2$ -
 $[\text{Re}_2\text{Br}_8]$ in KBr disks at 1.3 K gives broad emission centered at
13,020 and 12,530 cm^{-1} , respectively. Emission lifetimes are as
follows: $\text{Re}_2\text{Cl}_8^{2-}$, 150 ns; $\text{Re}_2\text{Br}_8^{2-}$, 110 ns. Luminescence was
also recorded for the $\text{Mo}_2\text{Cl}_8^{4-}$ ion doped into a crystal of $(\text{enH}_2)\text{Cl}_2$.
Again a broad, structureless emission band was observed (14,950 cm^{-1}
 τ 75 ns, 1.3 K). Owing to the lack of overlap of the emission
with the 0-0 transition in absorption, it is proposed that the
luminescent state is one of the spin-orbit components of ${}^3A_{2U}$. This
places the $\delta \rightarrow \delta^*$ singlet-triplet splitting in the range 1000-3000 cm^{-1} .

Absorption spectroscopy has been employed to characterize the lowest spin-allowed transitions in compounds that contain a metal-metal quadruple bond.¹ With the exception of dimolybdenum(II) carboxylates,² the lowest singlet excited state in dinuclear complexes of Mo(II) and Re(III) is $^1A_{2u}$ (in D_{4h} microsymmetry) derived from the one-electron excitation $\delta \rightarrow \delta^*$. The location of $^3A_{2u}$ ($\delta \rightarrow \delta^*$) (or, more properly, its A_{1u} and E_u spin-orbit components) in these complexes, however, has been the subject of some speculation. And, although scattered wave $X\alpha$ calculations have been performed for $Re_2Cl_8^{2-}$,³ $Mo_2Cl_8^{4-}$,⁴ and $Mo_2(O_2CH)_4$,⁵ it is generally agreed that the level of sophistication is not sufficient to predict singlet-triplet splittings with any confidence.

Clark and Franks⁶ noticed a weak, structured absorption at 6250 cm^{-1} in the diffuse reflectance spectra of some but not all of the $Mo_2Cl_8^{4-}$ salts they examined, and the suggestion was made that this near IR band might be attributable to the $^1A_{1g} \rightarrow ^3A_{2u}$ ($\delta \rightarrow \delta^*$) transition. However, it has been pointed out⁷ that the $12,000\text{ cm}^{-1}$ singlet-triplet splitting that follows from such an interpretation is unexpectedly large, and the possibility of near IR impurity absorption has been raised.^{7,8} An alternative placement of $^1A_{1g} \rightarrow ^3A_{2u}$ in $Mo_2Cl_8^{4-}$ could be $17,500\text{ cm}^{-1}$, where Fanwick *et al.*⁷ found a weak shoulder in one polarized absorption spectrum of a single crystal of $K_4Mo_2Cl_8 \cdot 2H_2O$.

In an attempt to gather more evidence concerning the position of the $^3A_{2u}$ state in quadruply-bonded dinuclear complexes, we have measured the emission spectra and lifetimes at 1.3 K of $(n\text{-Bu}_4\text{N})_2\text{-}[\text{Re}_2\text{Cl}_8]$, $(n\text{-Bu}_4\text{N})_2[\text{Re}_2\text{Br}_8]$, and 0.2% $\text{Mo}_2\text{Cl}_8^{4-}$ in a single crystal of $(\text{enH}_2)\text{Cl}_2$. The results reported herein support a relatively small singlet-triplet splitting of the $\delta \rightarrow \delta^*$ excited states.

Experimental Section

The compounds $(n\text{-Bu}_4\text{N})_2[\text{Re}_2\text{Cl}_8]$ and $(n\text{-Bu}_4\text{N})_2[\text{Re}_2\text{Br}_8]$ were prepared by the literature method.⁹ Crystals of $(\text{enH}_2)\text{Cl}_2$ doped with $\text{Mo}_2\text{Cl}_8^{4-}$ were prepared by the following modification of the literature synthesis¹⁰ of $(\text{enH}_2)_2[\text{Mo}_2\text{Cl}_8]$. $\text{Mo}_2(\text{O}_2\text{CCH}_3)_4$ ¹¹ was added to a 6N HCl solution saturated with $(\text{enH}_2)\text{Cl}_2$. The solution was filtered before slowly cooling to 5°C, yielding a crop of translucent purple crystals. Calculated for $\text{C}_2\text{H}_{10}\text{N}_2\text{Cl}_2$: C, 17.93%; H, 8.22%; N, 20.91%; Cl, 52.93%. Found: C, 17.82%; H, 7.48%; N, 20.47%; Cl, 54.13%; Mo, 0.35%. The Mo analysis corresponds to a mole fraction of $\text{Mo}_2\text{Cl}_8^{4-}$ of ca. 0.2% (assuming $\text{Mo}_2\text{Cl}_8^{4-}$ is the only Mo species present). The C, H, N, and Cl analyses were obtained from Chemalytics, Inc., and the Mo analysis was performed by Schwarzkopf Micro-analytical Laboratory.

Emission spectra were obtained at the λ point of liquid He in an optical dewar. A pulsed nitrogen laser was used to pump a dye laser (output pulse width of 32 ns) and excitation wavelengths of 650 and 540 nm were used for the Re(III) and Mo(II) compounds, respectively. Emission lifetimes were recorded at the wavelength of maximum emission intensity. Boxcar integration techniques were applied to the signal from a GaAs phototube for data collection. A resolution of

0.6 nm was maintained for the emission spectra. Emission spectra were corrected for phototube and monochromator response before plotting. Samples of $(\underline{n}\text{-Bu}_4\text{N})_2[\text{Re}_2\text{Cl}_8]$ and $(\underline{n}\text{-Bu}_4\text{N})_2[\text{Re}_2\text{Br}_8]$ consisted of crystals suspended in 13 mm diameter KBr pressed disks. The low-temperature single crystal polarized absorption spectra of the crystal doped with $\text{Mo}_2\text{Cl}_8^{4-}$ (vide supra) were recorded employing experimental conditions as previously described.¹ Parallel polarization is for the long axis¹² (c), which was also an extinction direction of the $(\text{enH}_2)\text{Cl}_2$ crystal. The crystal was mounted over a pinhole on a copper disk with heat-conducting copper grease.

Results

Upon 650-nm excitation of the ${}^1A_{1g} \rightarrow {}^1A_{2u}$ ($\delta \rightarrow \delta^*$) transition of $(\underline{n}\text{-Bu}_4\text{N})_2[\text{Re}_2\text{Cl}_8]$, a broad emission centered at $13,020\text{ cm}^{-1}$ is observed (Figure 1) with a lifetime of 150 ns at 1.3 K. Two features of the emission spectrum are extremely important. Firstly, it is evident that a mirror symmetry relationship does not exist between the emission band and the ${}^1A_{1g} \rightarrow {}^1A_{2u}$ absorption system. Notably, the sharp vibronic structure observed in absorption is not present in emission. Secondly, and more importantly, there is no overlap between the emission band and the 0-0 transition of ${}^1A_{1g} \rightarrow {}^1A_{2u}$ that has been positioned from single crystal polarized absorption measurements.¹³

Similar 650-nm excitation of $(\underline{n}\text{-Bu}_4\text{N})_2[\text{Re}_2\text{Br}_8]$ results in broad emission centered at $12,530\text{ cm}^{-1}$ with a lifetime of 110 ns at 1.3 K. The 490-cm^{-1} red shift of the emission maximum from that in $\text{Re}_2\text{Cl}_8^{2-}$ is reasonable for a $\delta \rightarrow \delta^*$ type transition, considering the fact that ${}^1A_{1g} \rightarrow {}^1A_{2u}$ ($\delta \rightarrow \delta^*$) in $\text{Re}_2\text{Br}_8^{2-}$ is red-shifted in absorption by 586 cm^{-1} .¹⁴

The related species $\text{Mo}_2\text{Cl}_8^{4-}$ behaves analogously to the Re(III) compounds, as excitation at 540 nm gives a broad, structureless emission centered at 14950 cm^{-1} (Figure 2) with a 75 ns lifetime at 1.3 K; however, the separation between the emission and absorption systems is nearly twice that in the Re(III) compounds. It is also evident in this case that the emission band does not overlap the 0-0 transition reported⁷ at 18083 cm^{-1} for a single crystal of $\text{K}_4\text{Mo}_2\text{Cl}_8 \cdot 2\text{H}_2\text{O}$. As the polarization of this band has been established⁷ to be parallel to Mo-Mo, the results for the doped crystal prove that the $\text{Mo}_2\text{Cl}_8^{4-}$ ion orients with Mo-Mo directed primarily along the needle axis of the crystal.

A broad absorption centered at 405 nm, which is not attributable to $\text{Mo}_2\text{Cl}_8^{4-}$, is present in the doped crystal. This absorption does not occur in a pure $(\text{enH}_2)\text{Cl}_2$ crystal. When a 6N HCl solution containing $\text{K}_4\text{Mo}_2\text{Cl}_8$ is allowed to stand overnight under anaerobic conditions, the 530 nm absorption decreases at the same time a new band grows in at 418 nm. The latter absorption is present in solutions of $\text{Rb}_3\text{Mo}_2\text{Cl}_8\text{H}$ prepared¹⁵ from oxidation of the $\text{Mo}_2\text{Cl}_8^{4-}$ ion in concentrated HCl. Therefore it is likely that $\text{Mo}_2\text{Cl}_8\text{H}^{3-}$ or a related species is trapped during growth of the doped crystals. Because the 405 nm band was found not to be polarized, it appears that this species is randomly incorporated into the $(\text{enH}_2)\text{Cl}_2$ lattice. Emission related to this second component was not observed, as only the lowest absorption was pumped using 540 nm radiation. Observation of emission in a doped crystal, where the rate of resonance energy transfer should be small, shows

that impurity emission from an exciton trap probably does not occur.

Discussion

For $\text{Re}_2\text{Cl}_8^{2-}$ and $\text{Mo}_2\text{Cl}_8^{4-}$ the lack of overlap between the emission band and the 0-0 peak in absorption strongly rules against an assignment of simple fluorescence from the $^1A_{2u}$ state. Unfortunately, the emission lifetimes are not definitive in this respect, as they are consistent with either fluorescence and little radiationless decay¹⁶ or "phosphorescence" with a large contribution from nonradiative deactivation pathways. However, two additional observations are inconsistent with a $^1A_{2u}$ emitting state, namely, the absence of vibronic structure for the $\text{Re}_2\text{Cl}_8^{2-}$ emission and the increased emission/absorption separation in $\text{Mo}_2\text{Cl}_8^{4-}$. Ligand substitution effects in the Re(III) complexes, as well as the similarity of the absorption and emission half-bandwidths and the overall band profiles, suggest that luminescence occurs from a state that is bonding to the same extent as is $^1A_{2u}$. For the reasons just stated, then, we believe the emitting state is one of the spin-orbit components of $^3A_{2u}$ (A_{1u} or E_u). Assignment of the emission to $^1A_{2u} \rightarrow ^1A_{1g}$, however, is not entirely out of the question, as a large geometrical distortion in the $^1A_{2u}$ state of $M_2X_8^{n-}$ complexes could lead to nonoverlapping emission and absorption systems. The Duschinsky effect¹⁷ could then operate to give an emission band shape that is considerably distorted from that of the corresponding absorption.¹⁸ For the $M_2X_8^{n-}$ ($M = \text{Re}, \text{Mo}; X = \text{Cl}, \text{Br}; n = 2 \text{ or } 4$) compounds, the excited state distortion most likely would involve an eclipsed (D_{4h}) to noneclipsed (D_{4d}) conformational change. Even if this type of distortion occurs, it apparently does not affect the a_1 vibrational modes to a large extent, as the ground-to-excited

state frequency shifts of a_1 (ReRe) and a_1 (ReReCl) are small.¹³ Additionally, the calculations of Norman and Kolari^{4,5} for $\text{Mo}_2\text{Cl}_8^{4-}$ suggest that chloride-chloride attractions contribute to the stabilization of the eclipsed geometry. Thus there is doubt whether the ${}^1A_{2u}$ state would distort at all from the eclipsed configuration.

The evidence favors assignment of the emission to one of the transitions $A_{1u}({}^3A_{2u})$ or $E_u({}^3A_{2u}) \rightarrow {}^1A_{1g}$. This interpretation places the singlet-triplet (${}^1A_{2u} - {}^3A_{2u}$) separation in the range 1000-3000 cm^{-1} . This range is quite in line with the only documented singlet-triplet splitting in a dinuclear Re(III) or Mo(II) compound, which is 1800 cm^{-1} for the ${}^3, {}^1E_g(\delta \rightarrow \pi^*)$ excited states of $\text{Mo}_2(\text{O}_2\text{CCF}_3)_4$.² Further elucidation of the nature and position of the low-lying triplet excited states in $\text{M}_2\text{X}_8^{n-}$ complexes will require much additional theoretical and experimental effort.

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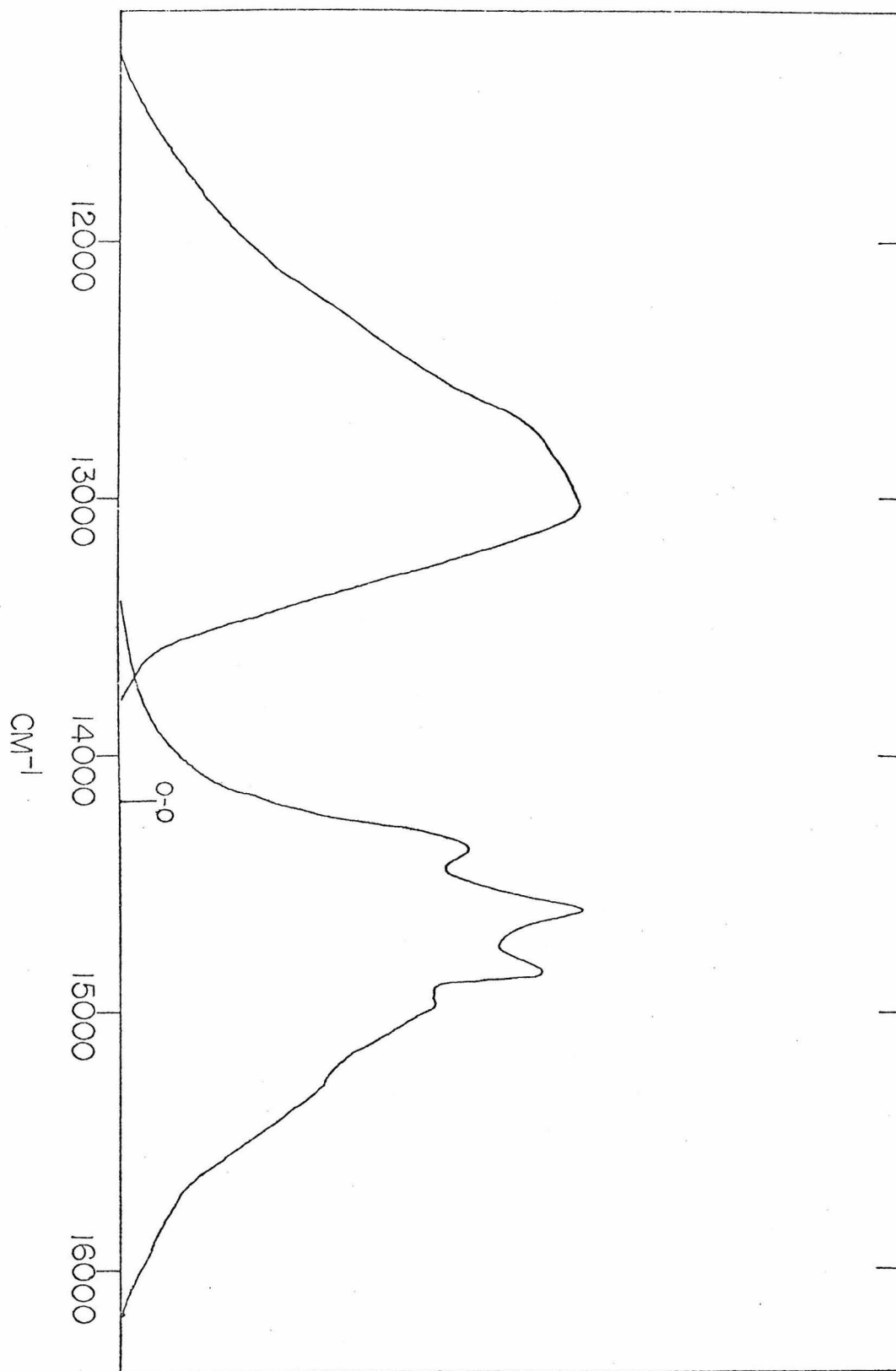
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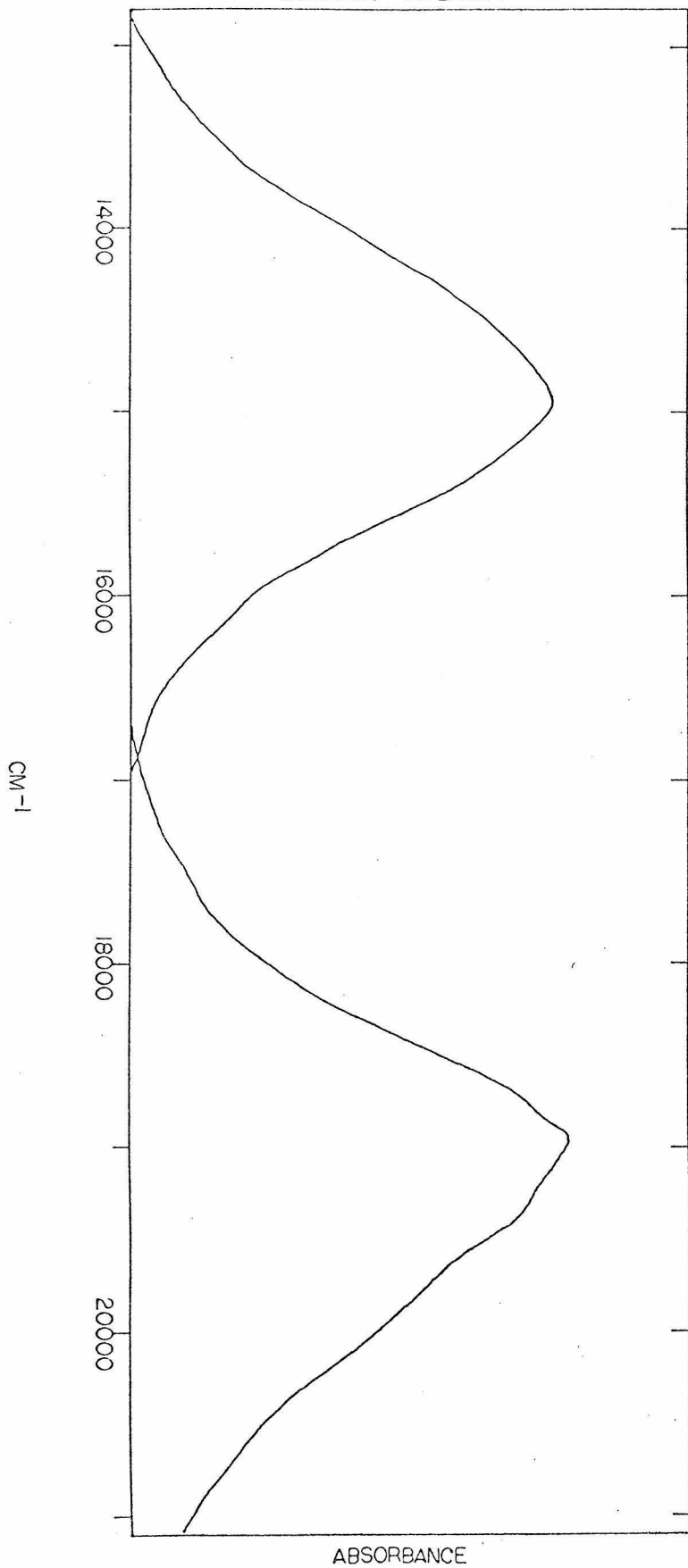
Figure Captions

- Figure 1 Corrected emission (1.3 K) and absorption (15 K) of $(n\text{-Bu}_4\text{N})_2[\text{Re}_2\text{Cl}_8]$ in a KBr disk.
- Figure 2 Corrected emission (1.3 K) and absorption (15 K) spectra of a single crystal of $(\text{enH}_2)\text{Cl}_2$ doped with $\text{Mo}_2\text{Cl}_8^{4-}$ (0.2 mol%).
- Figure 3 Single crystal polarized absorption spectra at 15 K of a single crystal of $(\text{enH}_2)\text{Cl}_2$ doped with $\text{Mo}_2\text{Cl}_8^{4-}$ (0.2 mol%). Polarizations are denoted parallel and perpendicular to the crystal needle axis.

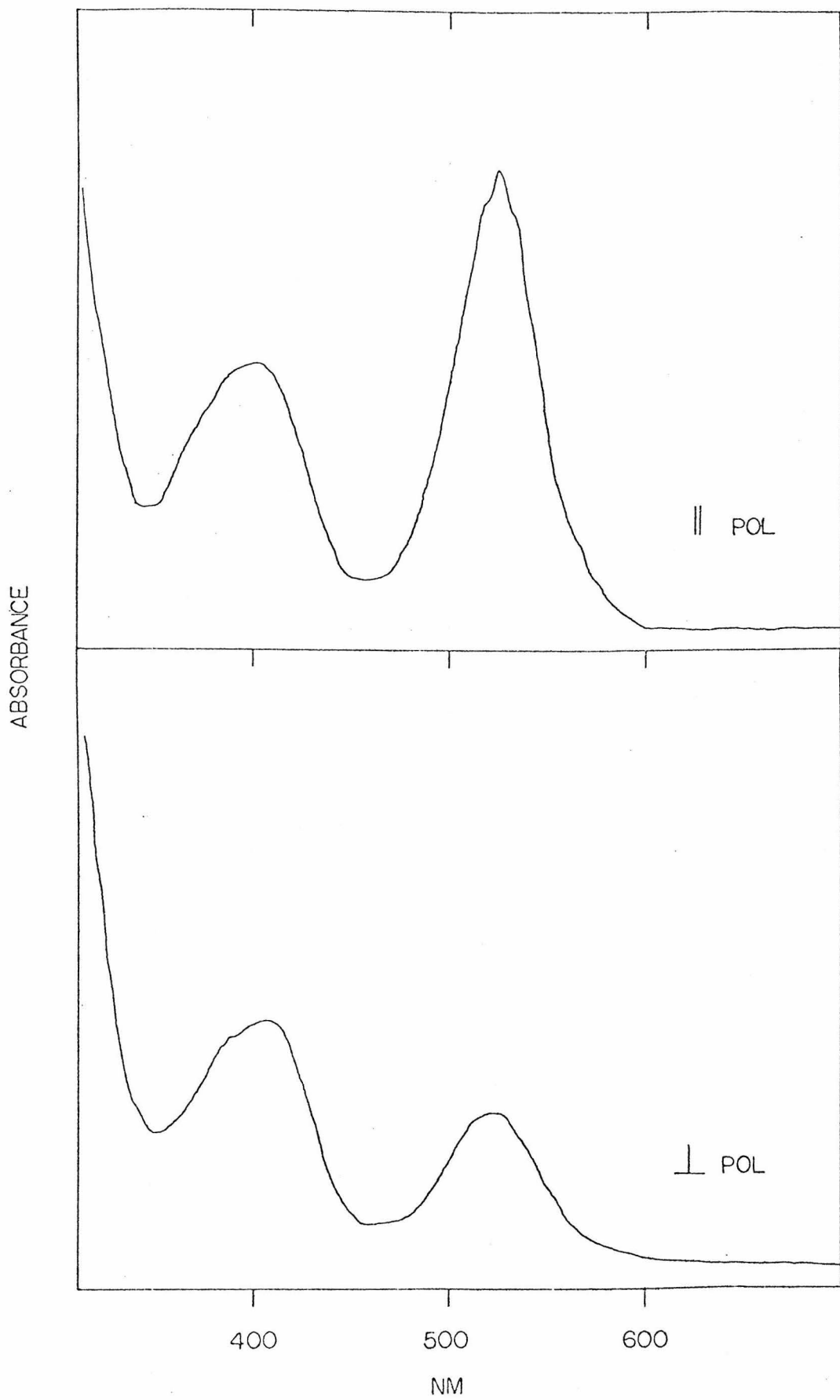
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Studies of the Polarization Behavior, Temperature Dependence,
and Vibronic Structure of the $23,000\text{ cm}^{-1}$ Absorption System in
the Electronic Spectra of $\text{Mo}_2(\text{O}_2\text{CCH}_3)_4$ and Related Compounds.
Emission Spectrum of $\text{Mo}_2(\text{O}_2\text{CCF}_3)_4$ at 1.3 K

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Abstract: The $23,000\text{ cm}^{-1}$ absorption band in the electronic spectrum of $\text{Mo}_2(\text{O}_2\text{CCH}_3)_4$ is primarily polarized perpendicular to the metal-metal axis. Rich vibronic structure is observed for this absorption system in the spectra of $\text{Mo}_2(\text{O}_2\text{CCH}_3)_4$, $\text{Mo}_2(\text{O}_2\text{CCD}_3)_4$, $\text{Mo}_2(\text{O}_2\text{CCF}_3)_4$, and $\text{Mo}_2(\text{O}_2\text{CH})_4$ at 15 K. Analysis of the temperature dependence of the hot bands in the spectrum of $\text{Mo}_2(\text{O}_2\text{CCF}_3)_4$ has established that the transition is vibronic, being allowed primarily by an $a_{2u}(\text{MoMoO})$ bending vibration ($\sim 190\text{ cm}^{-1}$). Interpretation of the vibronic structure in the spectrum of $\text{Mo}_2(\text{O}_2\text{CCH}_3)_4$ suggests that the 0-0 transition is split by 275 cm^{-1} into x- and y-polarized components. This splitting, which is much larger in $\text{Mo}_2(\text{O}_2\text{CCF}_3)_4$, correlates with departures from ideal D_{4h} symmetry that are evident from crystal structure determinations. A dominant progression in the MoMo totally symmetric

stretch is observed on each of several vibronic origins in the spectrum of $\text{Mo}_2(\text{O}_2\text{CCH}_3)_4$. Franck-Condon analysis demonstrates that a 0.1 \AA elongation of the MoMo bond occurs in the excited state. From the lowest energy vibronic origin in $\text{Mo}_2(\text{O}_2\text{CCF}_3)_4$, an estimate of 90 cm^{-1} for the metal-metal torsional frequency is obtained. Structured emission is observed for $\text{Mo}_2(\text{O}_2\text{CCF}_3)_4$ at 1.3 K ($\tau \sim 2 \text{ ms}$). The emission origin lies 1800 cm^{-1} lower than that of the absorption system. The results are consistent with the assignment of the absorption band to the orbitally-forbidden, metal-localized transition ${}^1\text{A}_{1g} \rightarrow {}^1\text{E}_g$ ($\delta \rightarrow \pi^*$), and the emission to the corresponding triplet \rightarrow singlet.

Introduction

It is now well established that the low-energy absorption system of moderate intensity ($\epsilon \sim 10^3$) in the electronic spectra of $\text{Re}_2\text{Cl}_8^{2-}$, $\text{Re}_2\text{Br}_8^{2-}$, $\text{Re}_2\text{Cl}_6[\text{P}(\text{C}_2\text{H}_5)_3]_2$, and $\text{Mo}_2\text{Cl}_8^{4-}$ is attributable to the electric-dipole-allowed transition $\delta \rightarrow \delta^*$ (${}^1\text{A}_{1g} \rightarrow {}^1\text{A}_{2u}$).²⁻⁴ By contrast, spectra of $\text{Mo}_2(\text{O}_2\text{CR})_4$ (R \neq aromatic) exhibit only a weak low-energy band ($\epsilon \sim 10^2$) which peaks at about 440 nm ($\sim 23,000 \text{ cm}^{-1}$).⁵ Recently, Cotton, Martin, and coworkers have examined the polarized crystal spectra of $\text{Mo}_2(\text{O}_2\text{CCH}_2\text{NH}_3)_4(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$ ⁶ and $\text{Mo}_2(\text{O}_2\text{CH})_4$.⁷ Although a firm assignment of the weak system was not made, it was shown⁶ conclusively that the transition in question in the $\text{Mo}_2(\text{O}_2\text{CR})_4$ -type compounds could not be $\delta \rightarrow \delta^*$ (${}^1\text{A}_{1g} \rightarrow {}^1\text{A}_{2u}$).

We have examined the polarized spectra of a crystal of $\text{Mo}_2(\text{O}_2\text{CCH}_3)_4$ as well as films of $\text{Mo}_2(\text{O}_2\text{CCD}_3)_4$, $\text{Mo}_2(\text{O}_2\text{CCF}_3)_4$, and $\text{Mo}_2(\text{O}_2\text{CH})_4$ at 15 K. Particular attention has been paid to the elucidation of the hot bands in the spectra of $\text{Mo}_2(\text{O}_2\text{CCH}_3)_4$ and $\text{Mo}_2(\text{O}_2\text{CCF}_3)_4$. The emission spectrum of $\text{Mo}_2(\text{O}_2\text{CCF}_3)_4$ at 1.3 K has also been measured. Our data suggest that the $23,000 \text{ cm}^{-1}$ system in molybdenum(II) acetate is derived from a metal-localized, electric-dipole-forbidden transition to an excited state of ${}^1\text{E}_g$ symmetry.

Experimental Section

The compounds $\text{Mo}_2(\text{O}_2\text{CCH}_3)_4$,⁸ $\text{Mo}_2(\text{O}_2\text{CCF}_3)_4$,⁹ $\text{Mo}_2(\text{O}_2\text{CH})_4$,¹⁰ and $\text{K}_4\text{Mo}_2\text{Cl}_8$ ¹¹ were prepared and purified by standard literature methods. Satisfactory elemental analyses were obtained in all cases.

The deuterated complex $\text{Mo}_2(\text{O}_2\text{CCD}_3)_4$ was prepared by suspending 0.6 g (0.93 mmol) of $\text{Mo}_2(\text{O}_2\text{CCF}_3)_4$ in 10 ml of deuterated acetic acid. After warming and stirring for 2 h, the pale yellow powder was filtered and washed with ethanol, pentane, and dried in vacuo. Calcd for $\text{Mo}_2(\text{O}_2\text{CCD}_3)_4$. C, 21.83; D, 5.49. Found. C, 21.4; D, 5.2.

Low energy ($100\text{-}500\text{ cm}^{-1}$) infrared spectra were recorded on a Perkin Elmer 180 spectrometer. Sample temperatures of 40 K were attained in a Cryogenics Technology Model 20 Cryocooler, which was equipped with polyethylene windows. Samples of molybdenum(II) carboxylates for the low energy IR spectra were Vaseline mulls spread on a thin polyethylene disk. Infrared spectra in the range $300\text{-}4000\text{ cm}^{-1}$ were recorded on samples of KBr pellets using a Perkin Elmer 225 instrument. All samples were prepared under a nitrogen atmosphere. Electronic spectra were recorded on a Cary 17 spectrometer. Low temperatures (15 or 80 K) were obtained with a Cary liquid helium dewar. Temperature was monitored with a calibrated carbon resistor next to the sample on the cooling block. The temperature dependence study was performed by allowing controlled increases from 80 to 300 K over a 5 h period. Spectra of $\text{Mo}_2(\text{O}_2\text{CCH}_3)_4$, $\text{Mo}_2(\text{O}_2\text{CCF}_3)_4$, $\text{Mo}_2(\text{O}_2\text{CH})_4$, and $\text{Mo}_2(\text{O}_2\text{CCD}_3)_4$ were obtained from sublimed films on optasil quartz disks (1/2 in. diameter; 1/32 in. thick) that were mounted in the dewar using heat-conducting copper grease for good thermal

contact. Pellet spectra (KBr) were also recorded and resembled the film spectra but were of lower quality. Slitwidth and lamp settings were such that a spectral bandwidth of less than 0.07 nm was maintained for all low temperature optical spectra. The emission spectrum was measured at 1.3 K, obtained by pumping on liquid helium in an optical dewar. A pulsed nitrogen laser (337 nm) was used to excite the sample whose emission was recorded at 0.6 nm resolution using boxcar integration techniques. The spectrum was corrected for phototube response before plotting.

Both $\text{Mo}_2(\text{O}_2\text{CCH}_3)_4$ ¹² and $\text{Mo}_2(\text{O}_2\text{CCF}_3)_4$ ⁹ crystallize in the triclinic space group P1. Crystals of reasonable size were obtained only for $\text{Mo}_2(\text{O}_2\text{CCH}_3)_4$. The needlelike crystals were observed to grow with two kinds of well-formed faces. These types were readily distinguished, as one face exhibited extinction directions nearly parallel (within 2°) and perpendicular to the needle axis, whereas the extinction directions for the other face made an approximately 15° angle with the needle axis. Polarized spectra were recorded for the former type of crystal face. Subsequent X-ray oscillation, Weissenberg, and precession photographs showed conclusively that the needle axis was the crystallographic b axis, and that polarized spectra were taken || and ⊥ to b within 10° of the bc crystal face.

Polarization ratios were calculated for transitions assumed to be polarized along the MoMo(z) and the mutually perpendicular

MoO(x,y) axes. These calculations were performed by projecting the molecular axes along the extinction directions. Adopting the same notation used in the crystal structure analysis,¹² we report the following polarization ratios $\mu_b/\perp b$ for the bc crystal face: $z = 3.61$, $x = 0.004$ (MoO(1), 0.008; MoO(3), 0.000), $y = 0.55$ (MoO(2), 0.618; MoO(4), 0.476). The calculations show that the assumption that the principal absorption directions lie along the MoMo and MoO axes does not hold rigorously for the molecule in the low-symmetry crystal environment, and we emphasize that uncertainties are to be associated with the reported polarization ratios; nevertheless, the calculations are entirely consistent with the observation of strong parallel- and both strong and weak perpendicularly-polarized features.

The oscillator strength of the $23,000 \text{ cm}^{-1}$ band in $\text{Mo}_2(\text{O}_2\text{CCF}_3)_4$ was determined from measurements on an oxygen-free acetonitrile solution at room temperature. From a plot of the spectrum on an energy scale, the oscillator strength was found by cut-and-weight integration of the peak, allowing for the overlapping tails of intense bands at 297 and 335 nm. For $\text{K}_4\text{Mo}_2\text{Cl}_8$, a freshly-prepared, degassed (20° C , 6 N HCl) solution was employed to obtain an oscillator strength.

Results and Discussion

The oscillator strength of the $22,700 \text{ cm}^{-1}$ band in the absorption spectrum of $\text{Mo}_2(\text{O}_2\text{CCF}_3)_4$ in acetonitrile solution at 298 K is 0.0011. This value is an order of magnitude less than that (0.015)¹³

obtained for the $\delta \rightarrow \delta^*$ band at $19,300 \text{ cm}^{-1}$ in $\text{K}_4\text{Mo}_2\text{Cl}_3$. Examination of the spectra of $\text{Mo}_2(\text{O}_2\text{CCF}_3)_4$ and $\text{Mo}_2(\text{O}_2\text{CH})_4$ at 40 K between 4000 and $22,000 \text{ cm}^{-1}$ revealed no lower energy electronic bands of appreciable intensity ($\epsilon > 10$). Upon cooling, the $23,000 \text{ cm}^{-1}$ band in each of four complexes ($\text{Mo}_2(\text{O}_2\text{CCH}_3)_4$, $\text{Mo}_2(\text{O}_2\text{CCD}_3)_4$, $\text{Mo}_2(\text{O}_2\text{CCF}_3)_4$, and $\text{Mo}_2(\text{O}_2\text{CH})_4$)⁷ shows remarkable vibronic structure (Figures 1, 2; Tables 1-4). The integrated intensity of this band increases slightly (10-15%) and a red shift is exhibited between 15 and 300 K. It is unlikely that the weak band represents a spin-forbidden transition, as a similarly-structured emission system (τ 2 ms) was observed at lower energy (0-0 gap of 1800 cm^{-1}) in a film of $\text{Mo}_2(\text{O}_2\text{CCF}_3)_4$ at 1.3 K (Figure 3; Table 5). From the oscillator strength of the absorption band, a radiative lifetime of $2 \mu\text{s}$ is estimated.¹⁴ Therefore, the long-lived emission is logically assigned to a transition from the triplet state that is related to the singlet excited in absorption at $23,000 \text{ cm}^{-1}$. The $\text{Mo}_2(\text{O}_2\text{CCH}_3)_4$ complex does not emit, which may reflect the more efficient radiationless processes expected for a molecule possessing high frequency (CH) vibrations in the weak coupling limit.¹⁵

Upon examination of the low-energy side of the first intense vibronic component in the spectrum of $\text{Mo}_2(\text{O}_2\text{CCF}_3)_4$ ($22,064 \text{ cm}^{-1}$; A, Figure 4), using a thick sample, additional weak features were observed at $21,950$ and $21,862 \text{ cm}^{-1}$ (B, C, Figure 4). At 15 K these weak features cannot be hot bands on the $22,064 \text{ cm}^{-1}$ "origin", as their intensities are several orders of magnitude too large. This

observation implies that there must be a lower energy forbidden origin. When the temperature is increased to 80 K, hot bands (D, E, Figure 4) are exhibited at 21,773 and 21,671 cm^{-1} . The temperature dependence of the latter hot band is clearly resolved over a large temperature range (80 - 260 K), whereas the 21,773 cm^{-1} hot band was obscured by broadening of the more intense 22,064 cm^{-1} component at higher temperatures. As a hot band arises from thermal population of ground state vibrations, its temperature dependent intensity should follow a Boltzmann distribution. In Figure 5 the Boltzmann plot for the 21,671 cm^{-1} hot band is shown. The slope obtained corresponds to a ground state vibrational spacing of $206 \pm 20 \text{ cm}^{-1}$. This means that the hot band is built on a weak electronic origin (i.e., the true 0-0 energy for the transition) approximately midway between 21,671 cm^{-1} and the first intense vibronic component (22,064 cm^{-1}) of the transition. In fact, a weak feature is observed at 21,862 cm^{-1} (C, Figure 4), where the hot band analysis predicts the 0-0 transition to occur. Moreover, the intensity of this weak peak is temperature independent (observable between 15 - 80 K), ruling out its assignment to a low frequency, vibronically-allowed transition. Therefore, we conclude that 21,862 cm^{-1} is the 0-0 transition energy, and that its intensity is derived from magnetic-dipole allowedness.¹⁶ The 0-0 feature is about 100 times less intense than the vibronic portion of the system, which places its oscillator strength at about 10^{-5} (a reasonable order of magnitude for a magnetic-dipole transition).¹⁷ As will be shown later, the excited state is 1E_g

in D_{4h} , and ${}^1A_{1g} \rightarrow {}^1E_g$ is allowed as a magnetic-dipole transition. Because the crystallographic symmetry is C_i ¹² and the 0-0 transition will be shown to be even \rightarrow even, the electric-dipole forbiddenness and magnetic-dipole allowedness are rigorous. Similar hot bands are observed in the spectrum of $Mo_2(O_2CCH_3)_4$, and their polarizations are shown in Figure 6. Unfortunately, resolution of the vibronic structure was not sufficient to observe the 0-0 band directly. The $21,302\text{ cm}^{-1}$ hot band (A, Figure 6) and the first intense vibronic component at $21,696\text{ cm}^{-1}$ (A, Figure 1) are polarized similarly. This provides additional evidence that this hot band and first intense component derive their intensities by coupling the same non-totally symmetric vibration (ground state 191 cm^{-1} for the hot band and excited state energy of 202 cm^{-1} for the first intense component) with an electric-dipole-forbidden 0-0 transition approximately midway between them. The spectrum of $Mo_2(O_2CH)_4$ also exhibits a similarly-behaved hot band $\sim 375\text{ cm}^{-1}$ to lower energy of the first intense peak of the system (Table 4). Therefore, the allowedness of the first vibronic component of the $23,000\text{ cm}^{-1}$ band in $Mo_2(O_2CCH_3)_4$, $Mo_2(O_2CCF_3)_4$, and $Mo_2(O_2CH)_4$ is attributed to coupling with a $\sim 190\text{ cm}^{-1}$ vibration.

An important feature of the polarized spectra (Table 1) of $Mo_2(O_2CCH_3)_4$ is the presence of vibronic components with three different polarization ratios. For example, the first intense component (A, Figure 1) is strongly polarized perpendicular, the weak

feature at $21,870\text{ cm}^{-1}$ (C, Figure 7) is polarized parallel, and the intense peaks at $21,969$ and $22,244\text{ cm}^{-1}$ (C, E, Figure 1) are weakly polarized perpendicular to the metal-metal axis. The presence of two perpendicularly polarized bands (strong and weak) suggests a low symmetry splitting into x and y components with different polarization ratios, as expected (see Experimental Section), owing to the alignment of the molecule with respect to the crystallographic axes. There are two possible explanations for the low symmetry splitting. If the excited state involved in the forbidden transition were orbitally degenerate (i. e., 1E_g) in D_{4h} symmetry, then in the C_i site of the crystal a splitting of the electronic origin would occur, producing two different components with x and y polarization ratios (a Davydov splitting can be ruled out, as there is only one molecule in the unit cell¹²). Alternatively, the split transition could arise as a result of a nondegenerate electronic excited state (${}^1A_{1g}(u)$, ${}^1A_{2g}$, ${}^1B_{1g}(u)$, or ${}^1B_{2g}(u)$) coupling with a low-symmetry-split $e_u(g)$ vibration of the molecule. To investigate the latter possibility, we have examined the infrared spectra of mulls of $\text{Mo}_2(\text{O}_2\text{CCH}_3)_4$, $\text{Mo}_2(\text{O}_2\text{CCF}_3)_4$, and $\text{Mo}_2(\text{O}_2\text{CH})_4$ in the $100\text{-}500\text{ cm}^{-1}$ region at 40 K. An intense band system centered at 360 cm^{-1} is exhibited in the spectrum of $\text{Mo}_2(\text{O}_2\text{CCH}_3)_4$. This system is split by 25 cm^{-1} into a sharp component at 372 cm^{-1} and a somewhat broader one at 347 cm^{-1} . Force constant calculations¹⁸ have shown that this intense system arises from the IR active a_{2u} and e_u MoO stretching vibrations. The broader band, which presumably represents the e_u vibration, has a linewidth

of ca. 30 cm^{-1} . Bands were also observed in the MoMoO bending region at 175 and 228 cm^{-1} for $\text{Mo}_2(\text{O}_2\text{CCH}_3)_4$, at 170 and 232 cm^{-1} for $\text{Mo}_2(\text{O}_2\text{CH})_4$ and 190 and 216 cm^{-1} for $\text{Mo}_2(\text{O}_2\text{CCF}_3)_4$. Force constant calculations for $\text{Mo}_2(\text{O}_2\text{CCH}_3)_4$ have suggested that these bands are attributable to a_{2u} and e_u MoMoO bending vibrations.¹⁸ As none of the e_u vibrations is split sufficiently to explain the separation of the x and y polarized vibronic components, the electronic transition must be to a split 1E_g state. Of interest is the fact that all three compounds show a vibrational band in the energy range ($170\text{-}190 \text{ cm}^{-1}$) where the hot band analysis placed the vibronically active fundamental for the first intense origin. Our analysis suggests an a_{2u} assignment for this band, as a_{2u} would induce x and y polarized components in a transition to a split 1E_g state, according to the Herzberg-Teller coupling scheme.¹⁹

The vibrational fine structure of the $23,000 \text{ cm}^{-1}$ band may be assigned after proper account is taken of the following: As the pure electronic transition is forbidden, all of the strong features at 15 K must arise from excitation of a quantum of one of several possible antisymmetric vibrations in the excited state (Table 6). A progression of spacing $355\text{-}370 \text{ cm}^{-1}$ is built on each vibronic origin (three strong ones for $\text{Mo}_2(\text{O}_2\text{CCH}_3)_4$ and only one for $\text{Mo}_2(\text{O}_2\text{CCF}_3)_4$). Weak features pose a problem, as they can be either new vibronic origins or progressions on one of the intense vibronic bands with a small Franck-Condon factor. For example, if the Franck-Condon factor is 0.4, a progression with relative intensities of $1:0.4:0.08:0.01\dots$

is expected. Therefore, in a complex spectrum, only the first two bands would be observable.

Only one dominant progression, which must represent quanta of a totally symmetric vibration, is exhibited by $\text{Mo}_2(\text{O}_2\text{CCF}_3)_4$ (ca. 355 cm^{-1}) and $\text{Mo}_2(\text{O}_2\text{CCH}_3)_4$ (ca. 370 cm^{-1}). There are only two a_{1g} modes of the Mo_2O_8 unit that fall in this energy region. Bands attributable to the a_{1g} (MoMo) stretch were observed in the Raman spectra of $\text{Mo}_2(\text{O}_2\text{CCH}_3)_4$ (406 cm^{-1})¹⁸ and $\text{Mo}_2(\text{O}_2\text{CCF}_3)_4$ (397 cm^{-1}).⁹ A Raman peak also was observed²⁰ at 322 cm^{-1} for $\text{Mo}_2(\text{O}_2\text{CCH}_3)_4$, where force constant calculations place a_{1g} (MoO).¹⁸ As the average MoO bond length in $\text{Mo}_2(\text{O}_2\text{CCF}_3)_4$ is shorter than that in $\text{Mo}_2(\text{O}_2\text{CCH}_3)_4$ (vide infra), we would expect the a_{1g} (MoO) stretch to occur at higher energy in the former complex; however, the progressional energies display the opposite trend. For this reason, the spacings of 355 and 370 cm^{-1} are logically attributable to an excited state a_{1g} (MoMo) stretch that is reduced somewhat from the ground state value. The emission system of $\text{Mo}_2(\text{O}_2\text{CCF}_3)_4$ exhibits one major progression with a spacing of ca. 390 cm^{-1} , which is in good agreement with the Raman band at 397 cm^{-1} assigned to a_{1g} (MoMo).⁹

A progression in the metal-metal stretching frequency reflects a displacement of the excited state geometry from the ground state along this normal coordinate. The intensity I_n of the n'th member of a vibrational progression is given by the Poisson distribution²¹:

$$I_n = I_0 S^n / n!$$

The Franck-Condon factor S is most simply obtained from the ratio I_1/I_0 . This is related to the distortion, Q_0^α , from equilibrium along an a_{1g} mode of frequency ω_α by:

$$S = (1/2)k(Q_0^\alpha)^2/h\omega_\alpha.$$

Force constant calculations on $\text{Mo}_2(\text{O}_2\text{CCH}_3)_4$ have given $k_{\text{MoMo}} \cong 3.73 \text{ mdyne/\AA}$ for the 406 cm^{-1} a_{1g} mode ($\sim 75\%$ MoMo stretching).¹⁸

Using these parameters and a value $S = 2.2$ obtained from the electronic spectrum, we calculate $Q_0^{\text{MoMo}} \cong 0.1 \text{ \AA}$.

As mentioned above, the most intense vibronic component is allowed by coupling the 0-0 transition with an a_{2u} vibration. In the ground state, the $a_{2u}(\text{MoMoO})$ vibrational quantum for $\text{Mo}_2(\text{O}_2\text{CCF}_3)_4$ is 191 cm^{-1} , and similar values are found for $\text{Mo}_2(\text{O}_2\text{CCH}_3)_4$ and $\text{Mo}_2(\text{O}_2\text{CH})_4$. According to vibronic selection rules (Table 6), either an a_{1u} , a_{2u} , b_{1u} , or b_{2u} mode can induce perpendicularly polarized intensity into ${}^1A_{1g} \rightarrow {}^1E_g$. If we assume that the molecular symmetry is reduced to D_{2h} , we note that a_{1u} and b_{1u} (a_{2u} and b_{2u}) correlate with an a_u (b_{1u}) vibration, which induces x (y) polarization in the ${}^1A_g \rightarrow {}^1B_{2g}$ component of the parent ${}^1A_{1g} \rightarrow {}^1E_g$ transition, and y (x) polarization to ${}^1A_g \rightarrow {}^1B_{3g}$, thereby accounting for the observed behavior. The a_{1u} metal-metal torsional vibration is expected to be of low frequency. In fact, the lowest energy weak feature ($21,950 \text{ cm}^{-1}$; B, Figure 4) in $\text{Mo}_2(\text{O}_2\text{CCF}_3)_4$ might be the a_{1u} vibronic origin, which would place the metal-metal torsional frequency at about 90 cm^{-1} . The related hot band is observed at $21,773 \text{ cm}^{-1}$ (D, Figure 4). Polarization of the corresponding feature ($21,428 \text{ cm}^{-1}$; B, Figure 6)

in $\text{Mo}_2(\text{O}_2\text{CCH}_3)_4$ is consistent with the proposed assignment.

The a_{2u} , b_{1u} , and b_{2u} modes are all MoMoO deformations, calculated to lie near 200 cm^{-1} in $\text{Mo}_2(\text{O}_2\text{CCH}_3)_4$.¹⁸ We favor a_{2u} as the dominant, vibronically active mode, particularly in view of the close agreement between the vibrational quantum derived from the hot band (191 cm^{-1}) and the 190 cm^{-1} peak in the low temperature IR spectrum of $\text{Mo}_2(\text{O}_2\text{CCF}_3)_4$. The parallel polarized component of low intensity at $21,870\text{ cm}^{-1}$ (or ca. 370 cm^{-1} from the estimated position of the 0-0 band) in the spectrum of $\text{Mo}_2(\text{O}_2\text{CCH}_3)_4$ (C, Figure 7) must represent another vibronic origin (rather than a quantum of an a_{1g} vibration built on $21,696\text{ cm}^{-1}$). It is likely that coupling with the e_u (MoO) stretching vibration induces the z polarization (ground state 347 cm^{-1}).

A weak band at $21,818\text{ cm}^{-1}$ that is strongly xy polarized in the spectrum of $\text{Mo}_2(\text{O}_2\text{CCH}_3)_4$ is assigned to a transition involving a quantum of a_{2u} (MoO) built upon the 0-0 component at about $21,500\text{ cm}^{-1}$. The two intense features at $21,969$ and $22,244\text{ cm}^{-1}$, which are polarized weakly perpendicular, are attributed to vibronic origins on the second component of the 0-0 ${}^1A_{1g} \rightarrow {}^1E_g$ (vide supra). As the second 0-0 component, unlike the first, could not be located with certainty, definitive assignments are not possible. If we assume that the $21,969\text{ cm}^{-1}$ peak represents a quantum of a_{2u} (MoMoO) built upon the second 0-0 component, then the low symmetry splitting of 1E_g is about 275 cm^{-1} (i.e., second 0-0 at $\sim 21,775\text{ cm}^{-1}$).

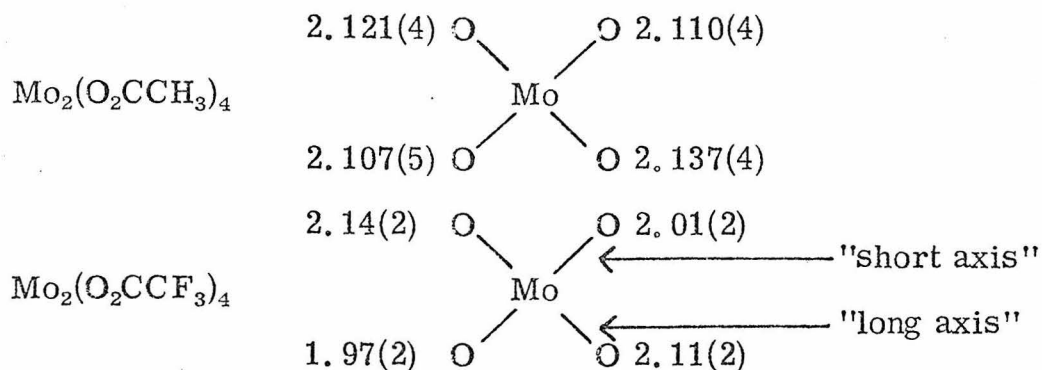
The 22,244 cm^{-1} peak (E, Figure 1) is not a member of an a_{1g} progression on either of the intense vibronic origins, because the third member of such a progression is not observed. Therefore, it is a vibronic origin on one of the two 0-0 components, corresponding either to a 469 or 744 cm^{-1} vibration. Such high energies cannot result from MoO vibrations, but must involve a carboxylate ligand deformation that lowers the symmetry of the Mo_2O_8 unit, thereby allowing the transition. Support for this suggestion comes from a comparison with the spectrum of the deuterated complex, $\text{Mo}_2(\text{O}_2\text{CCD}_3)_4$ (Figure 2). Relative to the positions of the other peaks in the spectrum, only the 22,244 cm^{-1} band (E, Figure 2) displays a noticeable red shift ($\sim 40 \text{ cm}^{-1}$) in the deuterated complex. Band D (Figure 1) is absent in $\text{Mo}_2(\text{O}_2\text{CCD}_3)_4$, which implies either a low or high energy shift to a position at which it is obscured by more intense peaks at 21,981 (C, Figure 2) or 22,095 cm^{-1} .

In IR spectra measured in KBr pellets at ambient temperature, a band attributable to OCO bending shows a similar red shift (675 to 645 cm^{-1}). Although an absorption assignable to the $\rho_r(\text{OCO})$ deformation was not observed in the IR spectrum of $\text{Mo}_2(\text{O}_2\text{CCH}_3)_4$, one such feature occurs at 460 cm^{-1} in acetate ion.²² Therefore, we assign the 22,244 cm^{-1} peak to a vibronic origin involving a 469 cm^{-1} OCO deformation built on the second 0-0 component. Band D is attributed to a transition involving a similar OCO deformation built on the first 0-0 component. We assume that the apparent absence

of band D in the spectrum of $\text{Mo}_2(\text{O}_2\text{CCD}_3)_4$ is due to a 40 cm^{-1} red shift, which results in the weak absorption being buried beneath band C (Figure 2).

Bands F and G (Figure 1), which occur 318 and 320 cm^{-1} above C and E, respectively, are assigned to transitions involving a quantum of the $a_{1g}(\text{MoO})$ stretching vibration built on the two strong vibronic origins. The polarizations of F and G match C and E, as expected, and force constant calculations predict $a_{1g}(\text{MoO})$ to be about 320 cm^{-1} in the ground state.¹⁸ This a_{1g} progression has a small Franck-Condon factor (ca. 0.3), and therefore diminishes according to $1:0.3:0.045$. Hence, the third member in the progression would not be observable. The small Franck-Condon factor for the symmetric MoO stretch indicates that the excited state distortion along the normal coordinate is minimal.

Because no polarization data or force constant calculations for $\text{Mo}_2(\text{O}_2\text{CCF}_3)_4$ are available, the vibrational assignments given in Table 2 are less certain. Assignments are made by analogy with the interpretation of the spectrum of $\text{Mo}_2(\text{O}_2\text{CCH}_3)_4$. Discussion of the differences in the spectra of $\text{Mo}_2(\text{O}_2\text{CCH}_3)_4$ and $\text{Mo}_2(\text{O}_2\text{CCF}_3)_4$ is facilitated by recalling the reported^{9,12} bond distances in the two complexes, as follows:



The relative simplicity of the spectrum of $\text{Mo}_2(\text{O}_2\text{CCF}_3)_4$ may be associated with the substantial distortion of the Mo_2O_8 unit from D_{4h} symmetry. Only one strong component is exhibited in the spectrum, and the medium intensity component (A, Figure 2) actually is comprised of two overlapping weak progressions (Table 2). The spectrum of $\text{Mo}_2(\text{O}_2\text{CCH}_3)_4$ exhibits, by contrast, three strong progressional origins of comparable intensity, and band C (Figure 2), which does not red shift appreciably in $\text{Mo}_2(\text{O}_2\text{CCD}_3)_4$ (10 cm^{-1} or less), and which has no counterpart in $\text{Mo}_2(\text{O}_2\text{CCF}_3)_4$, is one of the more intense vibronic features. It is logical to propose that, in the distorted Mo_2O_8 unit of $\text{Mo}_2(\text{O}_2\text{CCF}_3)_4$, one of the components of ${}^1A_{1g} \rightarrow {}^1E_g$ is moved to higher energy and is buried under more intense peaks, whereas the other component, which is associated with the "long-axis" $(\text{OMoO})_2$ plane, occurs at approximately the same energy as in $\text{Mo}_2(\text{O}_2\text{CCH}_3)_4$. The lack of sensitivity of this 0-0 component to ligand substituents (CH_3 or CF_3) rules out any interpretation based on charge transfer to or from the ligand π or π^* orbital. Considering the energies of the metal δ and δ^* orbitals,²³

the transition must be $\delta \rightarrow \pi^*$ or $\pi \rightarrow \delta^*$. The latter assignment may be rejected, as X α calculations²³ on $\text{Mo}_2(\text{O}_2\text{CH})_4$ have indicated that $\delta \rightarrow \pi^*$ falls below $\pi \rightarrow \delta^*$, and, more importantly, that only the former transition is metal-localized (% Mo: δ , 89, π^* , 96; π , 65, δ^* , 86). We conclude, therefore, that the 23,000 cm^{-1} system in $\text{Mo}_2(\text{O}_2\text{CCH}_3)_4$ is attributable to the transition ${}^1\text{A}_{1g} \rightarrow {}^1\text{E}_g$ ($\delta \rightarrow \pi^*$), which is low-symmetry-split by about 275 cm^{-1} .

It has been shown²⁴ that the $\delta \rightarrow \pi^*$ band in the electronic spectrum of $\text{Re}_2\text{Cl}_8^{2-}$ lies only 3700 cm^{-1} above that attributable to $\delta \rightarrow \delta^*$. Apparently, in the molybdenum(II) carboxylates, splitting of the δ levels has increased to the point where $\delta \rightarrow \pi^*$ is now slightly lower in energy than $\delta \rightarrow \delta^*$, and it has been suggested²³ that the latter transition in $\text{Mo}_2(\text{O}_2\text{CH})_4$ be associated with an intense shoulder at 30,800 cm^{-1} . The difference in the spectral behavior of $\text{Mo}_2(\text{O}_2\text{CH})_4$ and $\text{Mo}_2\text{Cl}_8^{4-}$ may be related to the fact²³ that the metal-metal bond distance is 0.05 Å shorter in the former complex, but further studies will be needed to clarify why the $\delta \rightarrow \delta^*$ splitting is affected more than $\delta \rightarrow \pi^*$.

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Table 1. Vibronic Structure of the Lowest Energy Visible Band in the Spectrum of $\text{Mo}_2(\text{O}_2\text{CCH}_3)_4$ at 15 K.

nm	cm^{-1}	Polarization ^d	Assignment ^e
469.44	21302 ^a	1s	$\nu_0 - a_{2u}(g)$
466.68	21428 ^a	1w	$\nu_0 - a_{1u}(g)$
	21500 ^b		ν_0
460.91	21696	1s	$\nu_0 + a_{2u}$
459.66	21755 ^c	1w	$\nu_0 + \Gamma_u$
458.78	21797 ^c	1w	$\nu_0 + \Gamma_u$
458.34	21818 ^c	1s	$\nu_0 + a_{2u}'$
457.25	21870		$\nu_0 + e_u$
455.19	21969	1w	$\nu_0' + a_{2u}$
454.19	22017	1s	$\nu_0 + 1_u'(\text{OCO})$
453.19	22066	1s	
451.16	22165	1w	
449.56	22244	1w	$\nu_0' + \Gamma_u(\text{OCO})$
448.69	22287	1w	$\nu_0' + a_{2u} + a_{1g}$
447.51	22346	1w	
446.61	22391	1s	
445.71	22436	1s	
443.18	22564	1w	
442.13	22618	1w	
441.00	22676	1w	
440.18	22718	1w	
439.23	22767	1s	
438.29	22816	1s	
435.81	22946	1w	
434.84	22997	1w	
433.05	23092	1w	
431.35	23183	1s	
429.00	23310	1w	
427.88	23371	1w	
426.24	23461	1w	
424.59	23552	1s	
422.42	23673	1w	
421.25	23739	1w	
419.46	23840	1w	
418.01	23923	1s	

^a Hot bands were not detected at 15 K, but were evident in a thick crystal at 80 K.

^b O-O energy estimated from the hot band (but not observed in the spectrum).

^c Weak features observed in a thick crystal at 15 K.

^d || denotes polarization along the MoMo axis. 1w signifies weak polarization perpendicular to the MoMo axis. 1s signifies strong polarization perpendicular to the MoMo axis.

^e Only the origins for progressions in the totally symmetric MoMo stretch are shown since higher members of the progression are indicated by the hash marks. The ground state MoMoO bending mode is $a_{2u}(g)$, and $a_{1u}(g)$ is the corresponding metal-metal torsional vibration. The two pure electronic origins are denoted by ν_0 and ν_0' . Excited state MoO stretching modes are a_{2u}' , e_u , and a_{1g} , and a_{2u} is an excited state MoMoO bending mode. An excited state antisymmetric carboxylate deformation is $\Gamma_u(\text{OCO})$, and $\nu_0 + \Gamma_u$ denotes an unassigned vibronic origin.

Table 2. Vibronic Structure of the Lowest Energy Visible Band in the Spectrum of $\text{Mo}_2(\text{O}_2\text{CCF}_3)_4$ at 15 K.

nm	cm^{-1}	Assignment ^e
461.45	21671 ^a	$\nu_0 - a_{2u}(g)$
459.28	21773 ^a	$\nu_0 - a_{1u}(g)$
457.41	21862 ^{b,c}	ν_0
455.58	21950 ^b	$\nu_0 + a_{1u}$
455.10	21973 ^b	$\nu_0 + \Gamma_u$
453.23	22064	$\nu_0 + a_{2u}$
451.22	22162 ^b	$\nu_0 + \Gamma_u$
450.11	22217 ^b	$\nu_0 + \Gamma_u$
449.46	22249 ^b	$\nu_0 + \Gamma_u$
447.89	22327	$\nu_0 + \Gamma_u(\text{OCO})$
445.93	22425	
443.16	22565 ^d	$\nu_0 + a_{2u} + a_{1g}$
440.70	22691	
438.77	22791	
436.17	22927	
433.86	23049	
432.10	23143	
429.50	23283	
427.30	23403	
425.68	23492	
423.08	23636	
420.86	23761	
419.46	23840	
416.91	23986	
415.00	24096	
413.36	24192	
410.83	24341	
408.76	24464	
407.35	24549	
404.87	24699	

^aHot bands were not detected at 15 K, but were evident at 80 K in a thick sample.

^bWeak bands observed in thick path length sample.

^cO-O band observed in the spectrum and confirmed as such by the hot band temperature dependence.

^dThis band is broad with a distinct high energy shoulder and remains as such throughout the progression, indicating two overlapping weak progressions.

^eNotation as in Table 1; a_{1u} is an excited state metal-metal torsional vibration.

Table 3. Vibronic Structure of the Lowest Energy Visible Band in
the Spectrum of $\text{Mo}_2(\text{O}_2\text{CCD}_3)_4$ at 15 K.

nm	cm^{-1}		Assignment ^a
460.29	21725	370	$\nu_0 + a_{2u}$
456.76	21893		$\nu_0 + e_u$
454.94	21981		$\nu'_0 + a_{2u}$
452.59	22095		
449.76	22234		
447.29	22357	377	$\nu'_0 + \Gamma_u(\text{OCO})$
445.00	22472		
442.35	22606		
440.00	22727	368	
437.82	22840		
435.14	22981		
432.94	23098	368	
430.88	23208		
428.26	23350		
426.11	23468	354	
424.41	23562		
421.59	23720	355	
419.29	23850		
418.12	23917		
415.17	24087		

^a Notation as in Table 1.

Table 4. Vibronic Fine Structure of $\text{Mo}_2(\text{O}_2\text{CH})_4$ at 15 K

<u>nm</u>	<u>cm⁻¹</u>	<u>Assignment^e</u>
465.27 ^a	21 493	$\nu_0 - a_{2u}(g)$
457.29	21 868	$\nu_0 + a_{2u}$
456.79	21 892	
456.50 ^b	21 906	
454.65	21 995	
451.94	22 127	
451.21 ^b	22 163	
449.82 ^b	22 231	
449.26 ^c	22 259	
448.33 ^b	22 305	
447.53 ^b	22 345	
444.80 ^b	22 482	
444.08 ^b	22 518	
442.88 ^b	22 579	
442.16 ^b	22 616	
441.45	22 653	
440.53	22 700	
436.29 ^d	22 920	
429.59 ^d	23 278	
423.06 ^d	23 637	
416.71 ^d	23 997	
410.71 ^d	24 350	
405.18 ^d	24 680	

^a Broad hot band observed at 80 K.

^b Shoulder.

^c Not resolved.

^d Maximum of a broad peak that contains many unresolved components.

^e Notation as in Table 1.

Table 5. Vibronic Structure in the Emission Spectrum of $\text{Mo}_2(\text{O}_2\text{CCF}_3)_4$ at 1.3 K.

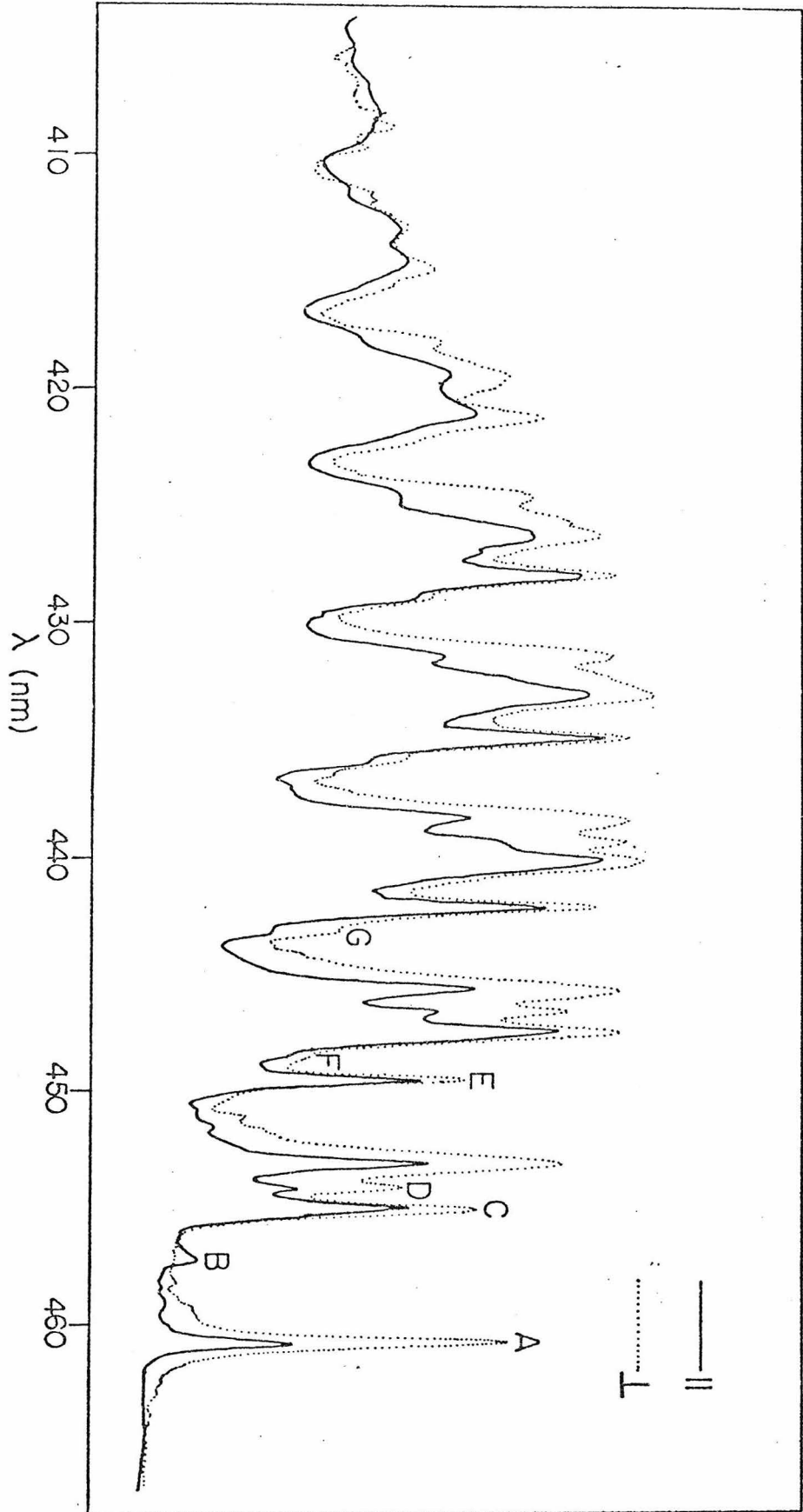
nm	cm^{-1}
498.80	20048
499.73	20011
501.61	19936
503.88	19846
506.95	19726
508.57	19663
509.92	19611
512.11	19527
513.82	19462
517.41	19327
519.61	19262
520.51	19212
522.55	19137
524.27	19074
528.26	18930
529.80	18875
531.26	18823
533.28	18752
535.62	18670
538.94	18555
540.98	18485
542.62	18429
544.25	18374
546.78	18289
547.41	18268
550.60	18162
	obscured
554.08	18048
555.56	18000
558.47	17906
559.79	17864
562.46	17779
564.02	17730
566.70	17646
568.41	17593
572.18	17477
574.38	17410
576.27	17353
578.87	17275
580.89	17215
585.58	17077
587.54	17020
590.07	16947
594.32	16826
599.88	16670

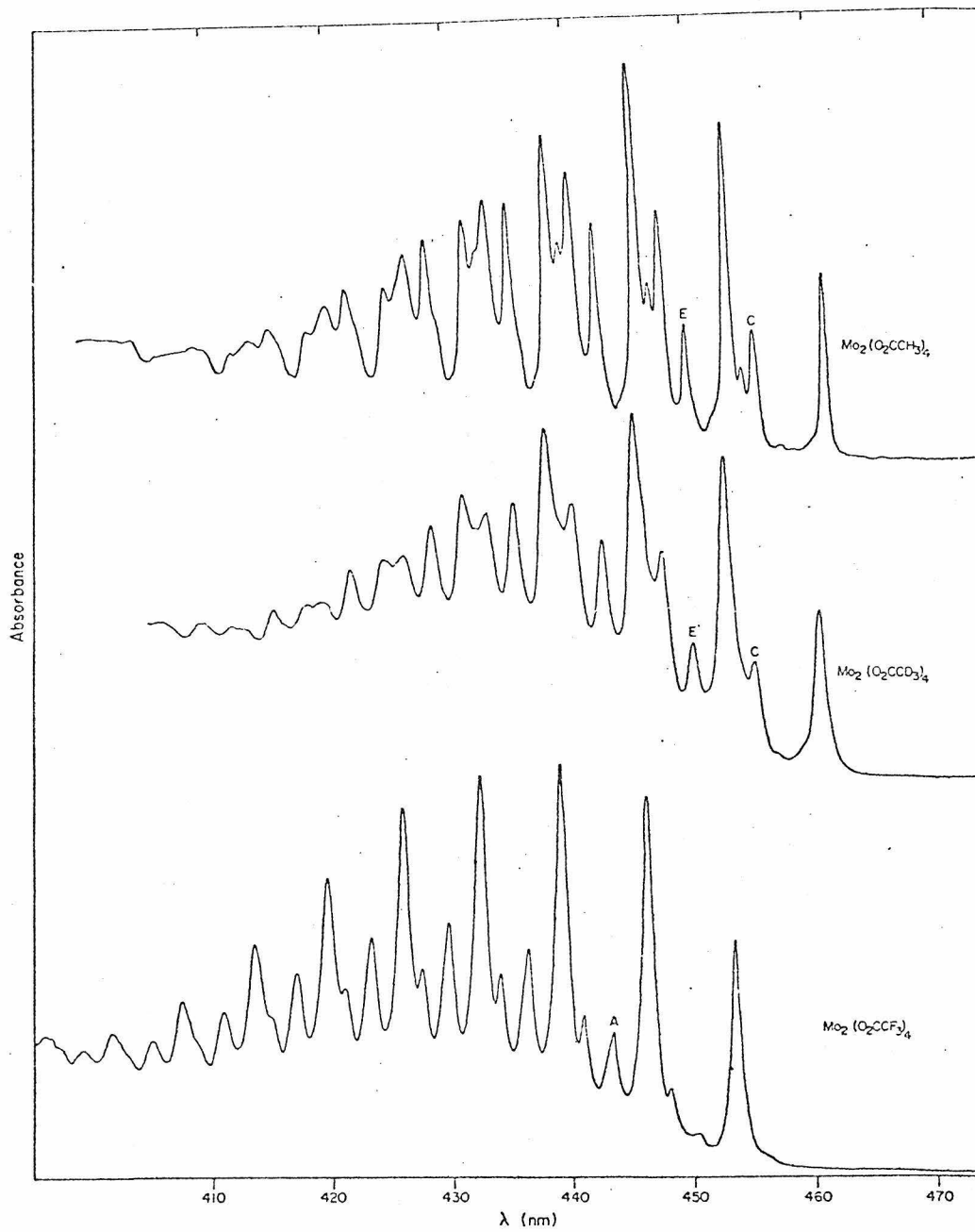
Table 6. Vibronic Intensity Inducing Vibrations (${}^1A_{1g}$ Ground State)

Polarization Direction	Excited States		
	D _{4h} Symmetry	D _{2h} Symmetry	
	1E_g State	${}^1B_{2g}$ State	${}^1B_{3g}$ State
x	a_{1u}		a_u
	a_{2u}	b_{1u}	
	b_{1u}		a_u
	b_{2u}	b_{1u}	
y	a_{1u}	a_u	
	a_{2u}		b_{1u}
	b_{1u}	a_u	
	b_{2u}		b_{1u}
z	e_u	b_{3u}	b_{2u}

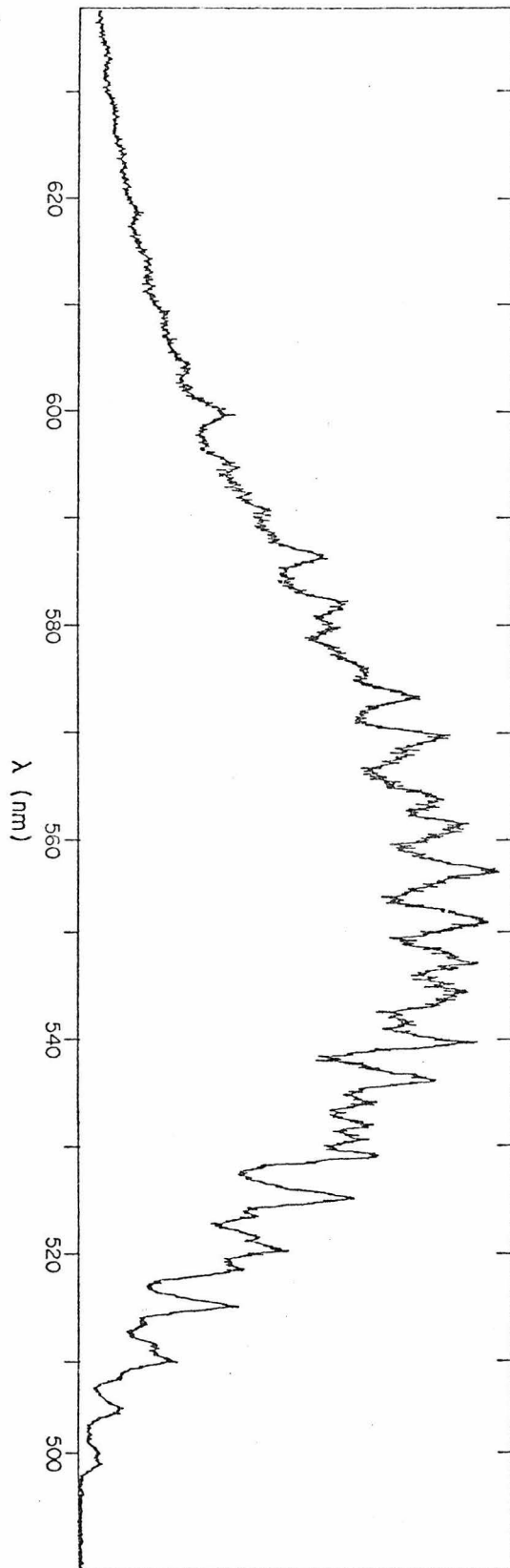
Figure Legends

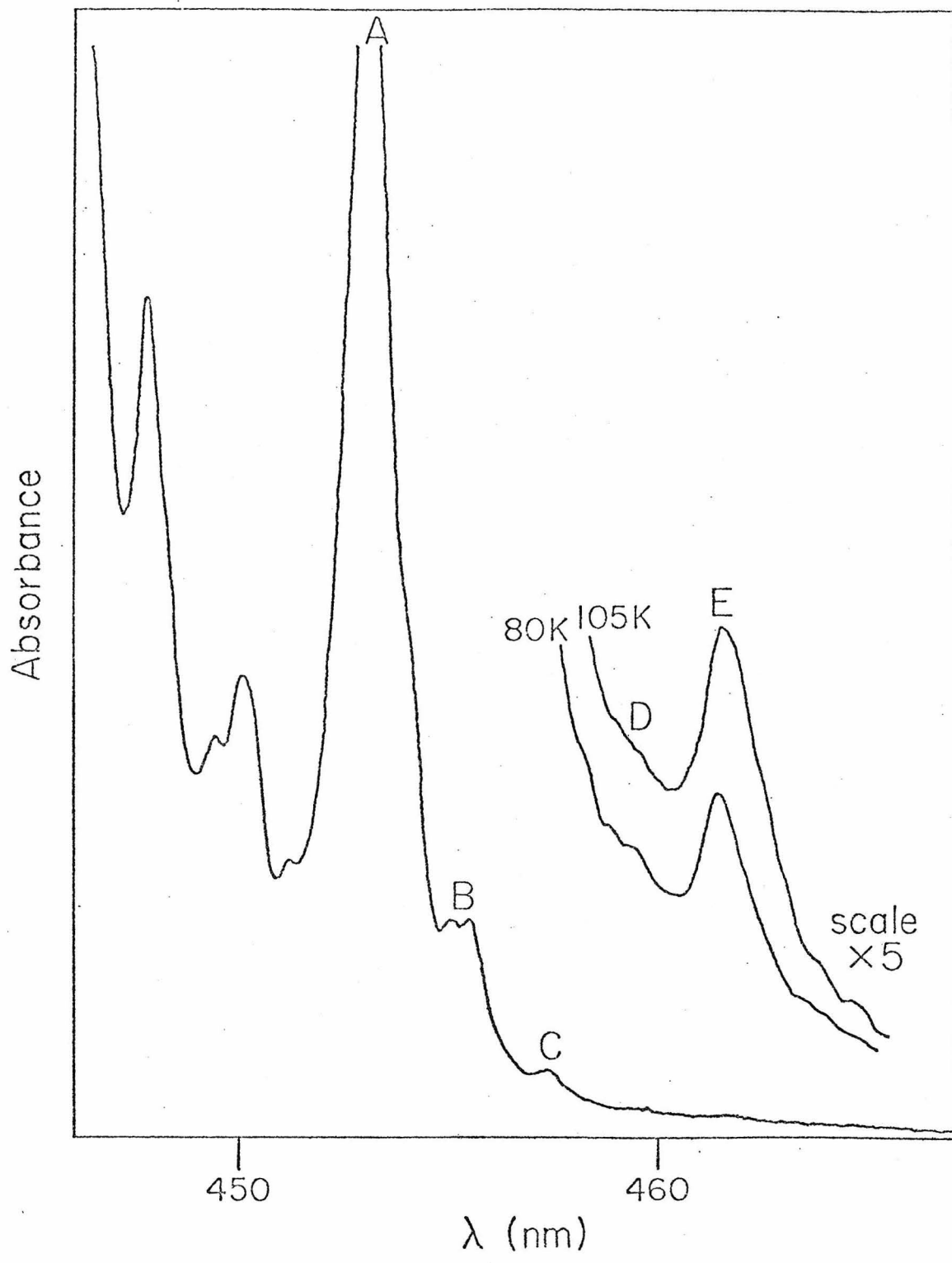
- Figure 1. Single crystal polarized spectra of $\text{Mo}_2(\text{O}_2\text{CCH}_3)_4$ at 15 K. Polarizations are denoted \parallel and \perp to the b crystallographic axis on the bc crystal face. Spectral bandwidth was 0.07 nm.
- Figure 2. Electronic spectra of $\text{Mo}_2(\text{O}_2\text{CCH}_3)_4$, $\text{Mo}_2(\text{O}_2\text{CCD}_3)_4$, and $\text{Mo}_2(\text{O}_2\text{CCF}_3)_4$ at 15 K. Spectra of sublimed films on quartz disks at 0.07 nm bandwidth were recorded.
- Figure 3. Corrected emission spectrum of a thick sublimed film of $\text{Mo}_2(\text{O}_2\text{CCF}_3)_4$ on quartz at 1.3 K. The sample was irradiated at 337 nm with a pulsed nitrogen laser and the spectrum was recorded at 0.6 nm bandwidth.
- Figure 4. The band origin in the electronic spectrum of $\text{Mo}_2(\text{O}_2\text{CCF}_3)_4$ at 15 K. Hot bands (80 and 150 K) are shown at a vertical scale expansion of 5. The spectra were recorded at 0.07 nm bandwidth.
- Figure 5. Boltzmann plot of the temperature dependence of the hot band intensity (I_r) for $\text{Mo}_2(\text{O}_2\text{CCF}_3)_4$.
- Figure 6. Hot bands in the single crystal polarized spectra of $\text{Mo}_2(\text{O}_2\text{CCH}_3)_4$ at 80 K. Polarizations are denoted \parallel and \perp to the b crystallographic axis on the bc face.
- Figure 7. Weak features in the single crystal polarized spectra of $\text{Mo}_2(\text{O}_2\text{CCH}_3)_4$. Polarizations are denoted \parallel and \perp to the b crystallographic axis on the bc face. The spectra were recorded at 15 K with 0.07 nm bandwidth.

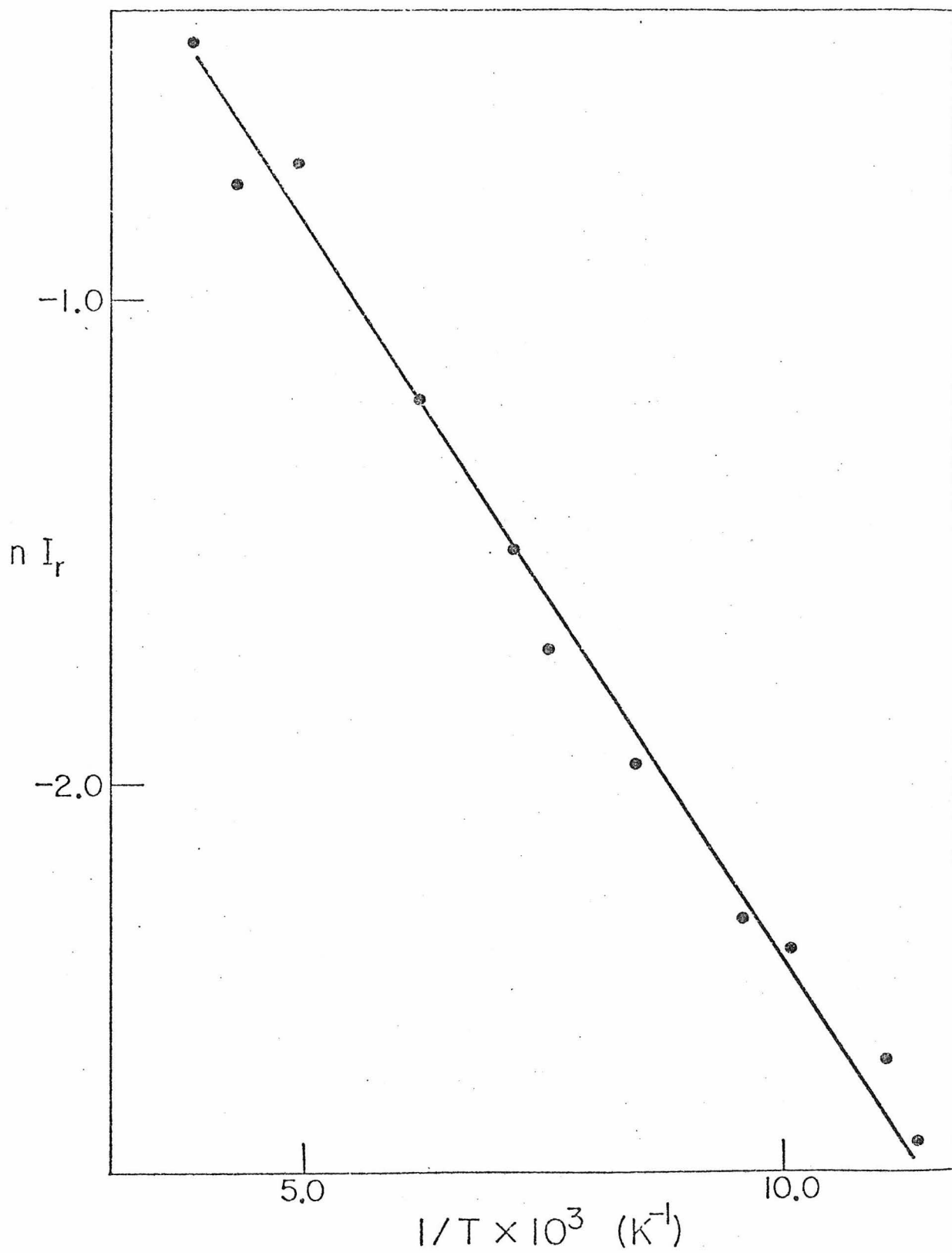


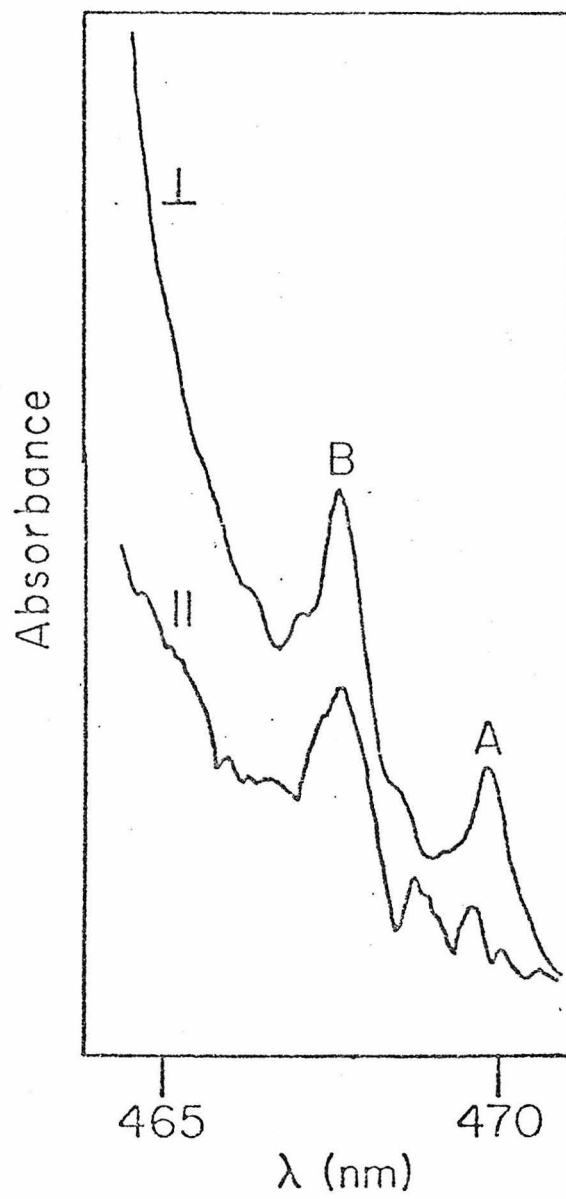


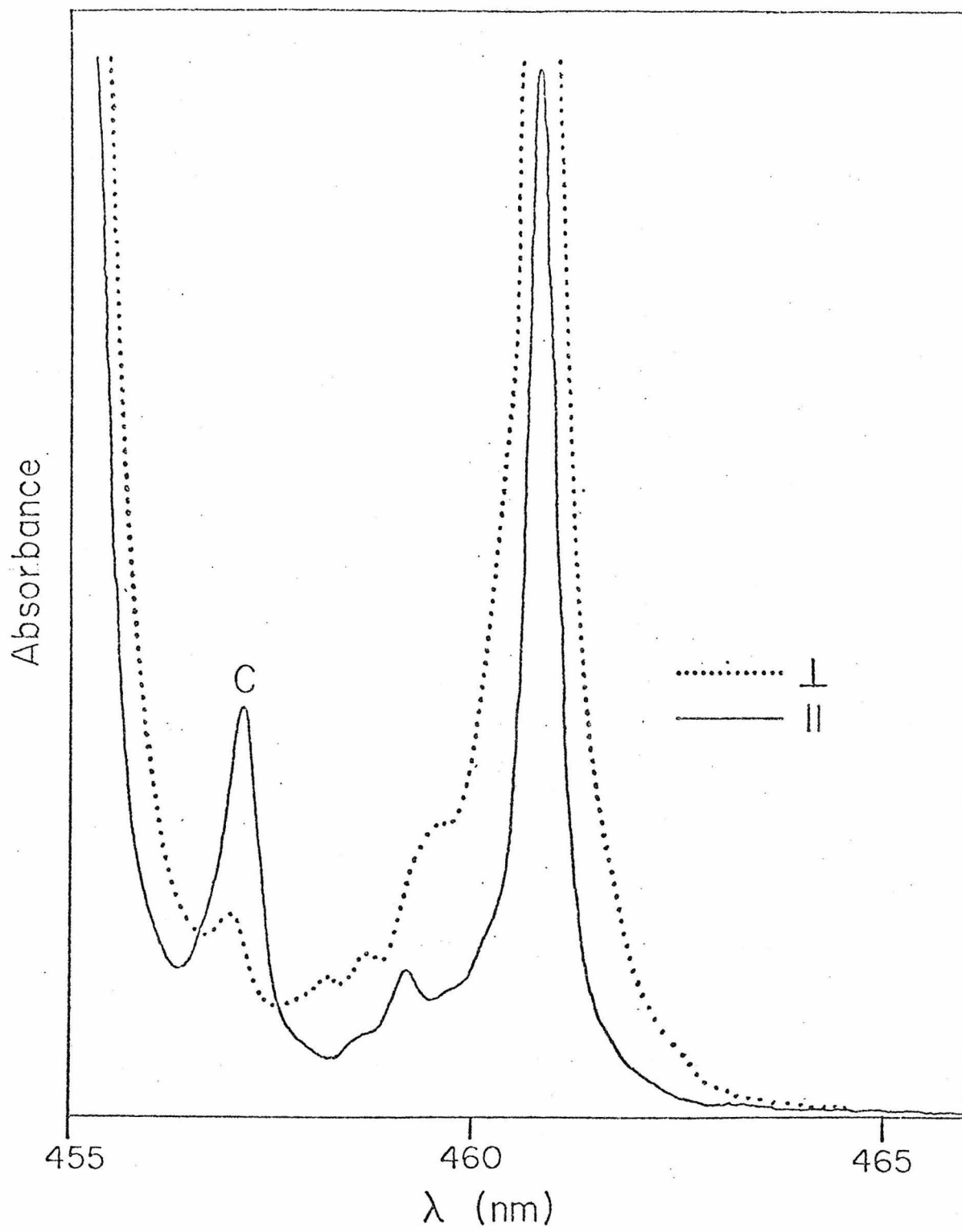
Intensity











Electronic Structure and Spectrum of $\text{Mo}_2(\text{O}_2\text{CH})_4$ and Related Compounds*

Introduction

The quadruple-bond formulation¹ of the strong metal-metal interactions in binuclear Mo(II) complexes has been confirmed by X α calculations on $\text{Mo}_2\text{Cl}_8^{4-}$ and $\text{Mo}_2(\text{O}_2\text{CH})_4$.² There is some evidence that the lowest excited states in the two complexes are different, however.² In this paper, we present an analysis of the electronic spectrum of $\text{Mo}_2(\text{O}_2\text{CH})_4$, and make comparisons with $\text{Mo}_2\text{Cl}_8^{4-}$ as well as with other binuclear Mo(II) carboxylate complexes.

Experimental

The compound $\text{Mo}_2(\text{O}_2\text{CH})_4$ was prepared from $\text{Mo}_2(\text{O}_2\text{CCH}_3)_4$ and formic acid.² Calcd. for $\text{C}_4\text{H}_4\text{Mo}_2\text{O}_8$: C, 12.92; H, 1.08. Found: C, 12.99; H, 1.10. $\text{K}_4\text{Mo}_2\text{Cl}_8$ was prepared by a published method.³

Far infrared spectra were obtained for vaseline mulls on polyethylene disks using a Perkin-Elmer model 180 spectrometer. A Cryogenics Technology model 21 cryocooler equipped with polyethylene windows was employed for measurements at 40 K.

All electronic spectra were recorded on a Cary 17 double beam instrument. Low temperature spectra were obtained for a

*W. C. Trogler's contribution to the joint paper by J. G. Norman, H. J. Kolari, H. B. Gray, and W. C. Trogler, Inorg. Chem., 16, 987 (1977).

thin film of $\text{Mo}_2(\text{O}_2\text{CH})_4$ sublimed onto a quartz disk. Temperatures of 80 or 15 K were obtained for the sample mounted in a Cary liquid helium dewar through use of either liquid nitrogen or helium as coolant. Sample temperature was measured with a calibrated carbon resistor secured to the cooling block. For the 15 K spectrum slits were controlled so that a resolution of 0.05 nm was achieved.

Oscillator strengths were measured at room temperature by preparing oxygen-free methanol solutions so that the band to be measured had an absorbance of 0.4 - 0.8. The spectrum was replotted on an energy scale and cut and weigh-integrated to obtain an oscillator strength.

Results and Discussion

The electronic spectra of $\text{Mo}_2(\text{O}_2\text{CH})_4$ (Figure 1) and $\text{K}_4\text{Mo}_2\text{Cl}_8$ (Figure 2) are clearly different. For example, the low temperature spectrum of $\text{K}_4\text{Mo}_2\text{Cl}_8$ shows bands at 18,200 and $41,670 \text{ cm}^{-1}$, which may be attributed to ${}^1A_{1g} \rightarrow {}^1A_{2u} (\delta \rightarrow \delta^*)$ and ${}^1A_{1g} \rightarrow {}^1A_{2u} (\pi \rightarrow \pi^*)$ transitions.² The former band contains a progression in the a_{1g} Mo-Mo stretch at 40 K (360 cm^{-1}). These assignments are consistent with those proposed for analogous bands in the spectrum⁴ of $\text{Re}_2\text{Cl}_8^{2-}$. The UV-VIS spectrum of $\text{Mo}_2(\text{O}_2\text{CH})_4$ (Figure 1) displays four bands, all of which are at considerably higher energy than $\delta \rightarrow \delta^*$ in $\text{Mo}_2\text{Cl}_8^{4-}$. Band I, at $22,990 \text{ cm}^{-1}$ has an oscillator strength of only 8×10^{-4} . Bands III and II overlap

but are resolved into a peak at $33,780 \text{ cm}^{-1}$ and a shoulder at $30,580 \text{ cm}^{-1}$ at 80 K in a 4:1 ethanol-methanol glass (Figure 3). The oscillator strengths of bands II and III are estimated to be 0.03 and 0.19, respectively. Finally, band IV with an oscillator strength of 0.021 occurs at $44,250 \text{ cm}^{-1}$.

At 15 K band I (Figure 3) shows considerable vibronic structure. Analogous bands occur in $\text{Mo}_2(\text{O}_2\text{CCH}_3)_4$ and $\text{Mo}_2(\text{O}_2\text{CCF}_3)_4$.⁵ Polarized spectral studies including full vibronic analysis⁵ have suggested that band I be assigned to the vibronically-allowed transition ${}^1\text{A}_{1g} \rightarrow {}^1\text{E}_g (\delta \rightarrow \pi^*)$. The 40 K low energy ir spectrum of $\text{Mo}_2(\text{O}_2\text{CH})_4$ was obtained (Figure 4) and peak positions and assignments are listed in Table 1. Identification of Mo-O modes were possible by comparison with $\text{Mo}_2(\text{O}_2\text{CCF}_3)_4$ ⁶ and $\text{Mo}_2(\text{O}_2\text{CCH}_3)_4$, with force constant calculations⁷ available for the latter complex.

With this information detailed assignment of band I is possible. The distortion of the M_2O_8 moiety in $\text{Mo}_2(\text{O}_2\text{CCH}_3)_4$ and $\text{Mo}_2(\text{O}_2\text{CCF}_3)_4$ from ideal D_{4h} to D_{2h} symmetry has been noted.⁵ This is manifested in low symmetry splitting of the electronic (and hence vibronic) origins for the ${}^1\text{E}_g$ state. The small (24 cm^{-1}) splitting of band A in $\text{Mo}_2(\text{O}_2\text{CH})_4$ implies that distortion from D_{4h} symmetry is not significant. In fact, such a small splitting could be a factor group effect as there are four molecules per unit cell.⁶

A temperature dependent hot band similar to that observed for $\text{Mo}_2(\text{O}_2\text{CCH}_3)_4$ and $\text{Mo}_2(\text{O}_2\text{CCF}_3)_4$ occurs 385 cm^{-1} to lower energy of band A above 80 K. This is expected since the Mo-O a_{2u} vibration

(which vibronically enables the transition) is essentially the same energy (170, 183, and 190 cm^{-1}) in all three complexes. Therefore the true (24 cm^{-1} split) O-O band for $\text{Mo}_2(\text{O}_2\text{CH})_4$ lies at about $21,685\text{ cm}^{-1}$. The sole vibrational progression is attributed to the Mo-Mo a_{1g} stretch (360 cm^{-1}). This excited state distortion in the Mo-Mo bond is appropriate for the antibonding 1E_g ($\delta \rightarrow \pi^*$) state. Other weaker features are assigned by analogy with $\text{Mo}_2(\text{O}_2\text{CCH}_3)_4$.⁵

We have carefully examined the spectrum of $\text{Mo}_2(\text{O}_2\text{CH})_4$ from 80 to $20,000\text{ cm}^{-1}$ at 40 K and find no electronic absorption bands of appreciable intensity. Therefore we must look to higher energy for a band attributable to the δ - δ^* transition. In fact, band II with an oscillator strength of 0.03 is a reasonable candidate, as it is of comparable intensity to the δ - δ^* bands in $\text{Re}_2\text{Cl}_8^{2-}$ (0.023)⁹ and $\text{Mo}_2\text{Cl}_8^{4-}$ (0.015).⁵

Band II, as well as bands I and IV, do not appear to depend on the nature of the coordinated carboxylate (Table 2). This suggests a metal-localized transition assignment for all three bands. Band III, on the other hand, depends drastically on the nature of the carboxylate. The huge shift observed for the benzoate compound hints at a transition involving carboxylate π or π^* orbitals. As the IP¹⁰ of the corresponding carboxylic acid increases the energy of band III decreases, suggesting assignment to a charge transfer transition $\delta \rightarrow L(\pi^*)$. Since the transition apparently is allowed it must be either ${}^1A_{1g} \rightarrow {}^1A_{2u}$ or ${}^1A_{1g} \rightarrow {}^1E_u$. It is likely that band I derives its vibronic

intensity (which is chiefly polarized perpendicular to the Mo-Mo axis⁵) from band III, suggesting a ${}^1A_{1g} \rightarrow {}^1E_u$ assignment for the latter. Band IV, considering its oscillator strength and slight carboxylate dependence, is reasonably assigned to ${}^1A_{1g} \rightarrow {}^1A_{2u}$ ($\pi \rightarrow \pi^*$).

The δ - δ^* and π - π^* transitions are proposed to lie 4700 and 2200 cm^{-1} to higher energy in the carboxylate complexes (as compared to $\text{Mo}_2\text{Cl}_8^{4-}$). We take this to be an indication of the stronger metal-metal interactions in the carboxylate complexes, which are reflected in the considerably shorter Mo-Mo bond length of 2.09 Å in $\text{Mo}_2(\text{O}_2\text{CR})_4$ compounds. The Mo-Mo bond length¹ in other non-bridged complexes is ca. 2.15 Å. The δ - δ^* transition is affected most by this change of bond length. We infer that it is primarily the δ^* level which is affected. This helps rationalize the relatively low energy position of the $\delta \rightarrow \pi^*$ transition. Electron repulsion factors will also need to be considered, as they could easily be larger in Mo_2O_8 than in $\text{Mo}_2\text{Cl}_8^{4-}$.

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Table 1. Far Infrared Spectrum of $\text{Mo}_2(\text{O}_2\text{CH})_4$ at 40 K.

<u>cm⁻¹</u> ^a	<u>Assignment</u>
471 s	a_{2u} (Mo-O stretch)
445 s	e_u (Mo-O stretch)
410 m	
384 m	
371 s	
345 w	
231 m	e_u (Mo-O bend)
170 w	a_{2u} (Mo-O bend)
128 w	e_u (Mo-O bend)
78 w	

^a s = strong, m = medium, and w = weak intensity.

Table 2. Comparison of the electronic absorption spectra of $\text{Mo}_2(\text{O}_2\text{CR})_4$ complexes for $\text{R} = \text{CH}_3, \text{H}, \text{CF}_3,$ and C_6H_5 .

	<u>Band I^a</u>	<u>Band II</u>	<u>Band III</u>	<u>Band IV</u>
$\text{Mo}_2(\text{O}_2\text{CCH}_3)_4$ ^b	22,730	n. o.	34,010	42,900
$\text{Mo}_2(\text{O}_2\text{CH})_4$ ^c	22,990	30,580	33,780	44,250
$\text{Mo}_2(\text{O}_2\text{CCF}_3)_4$	23,000 ^c	30,210 ^c	32,360 ^c	44,200 ^d
$\text{Mo}_2(\text{O}_2\text{CC}_6\text{H}_5)_4$ ^b	n. o.	n. o.	23,700	44,300
Oscillator strength ^e	0.0008	0.03	0.19	0.021
Assignment	$\delta \rightarrow \pi^*$	$\delta \rightarrow \delta^*$	$\delta \rightarrow \text{L}(\pi^*)$	$\pi \rightarrow \pi^*$

^a Band energies in cm^{-1} .

^b L. Dubicki and R. L. Martin, Aust. J. Chem., 22, 1571 (1969).

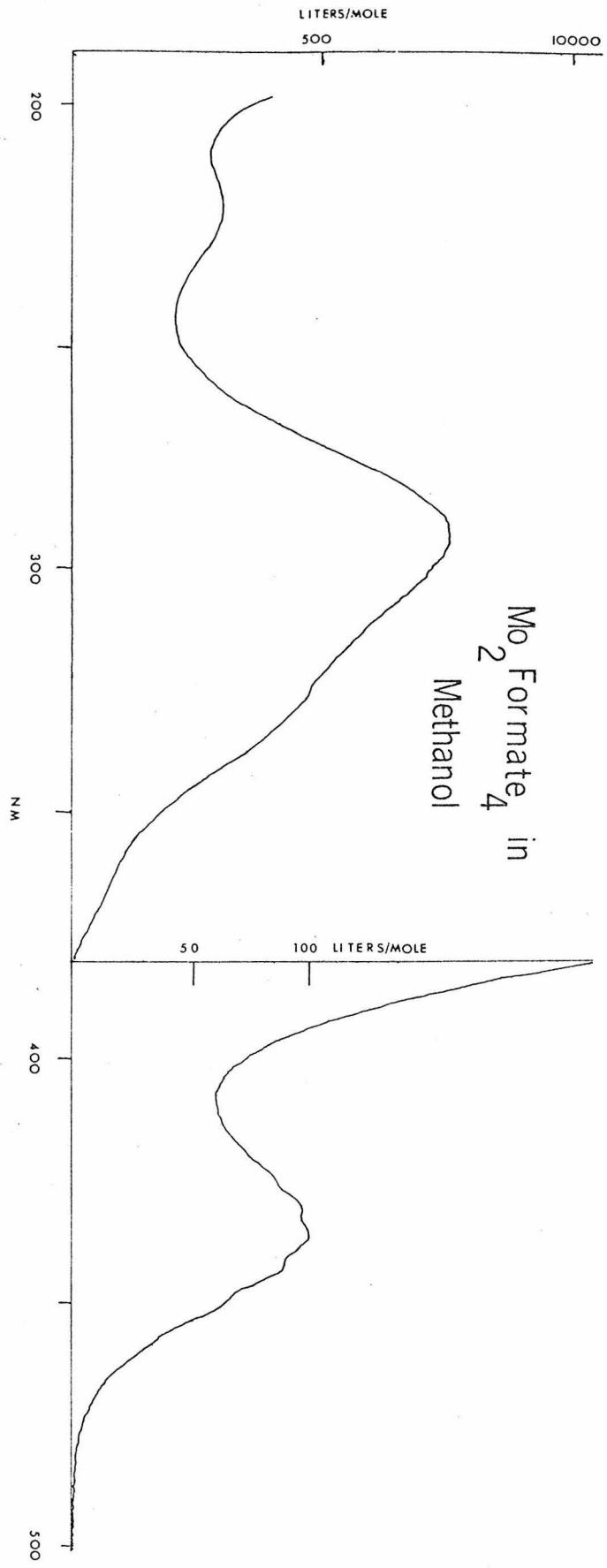
^c This work.

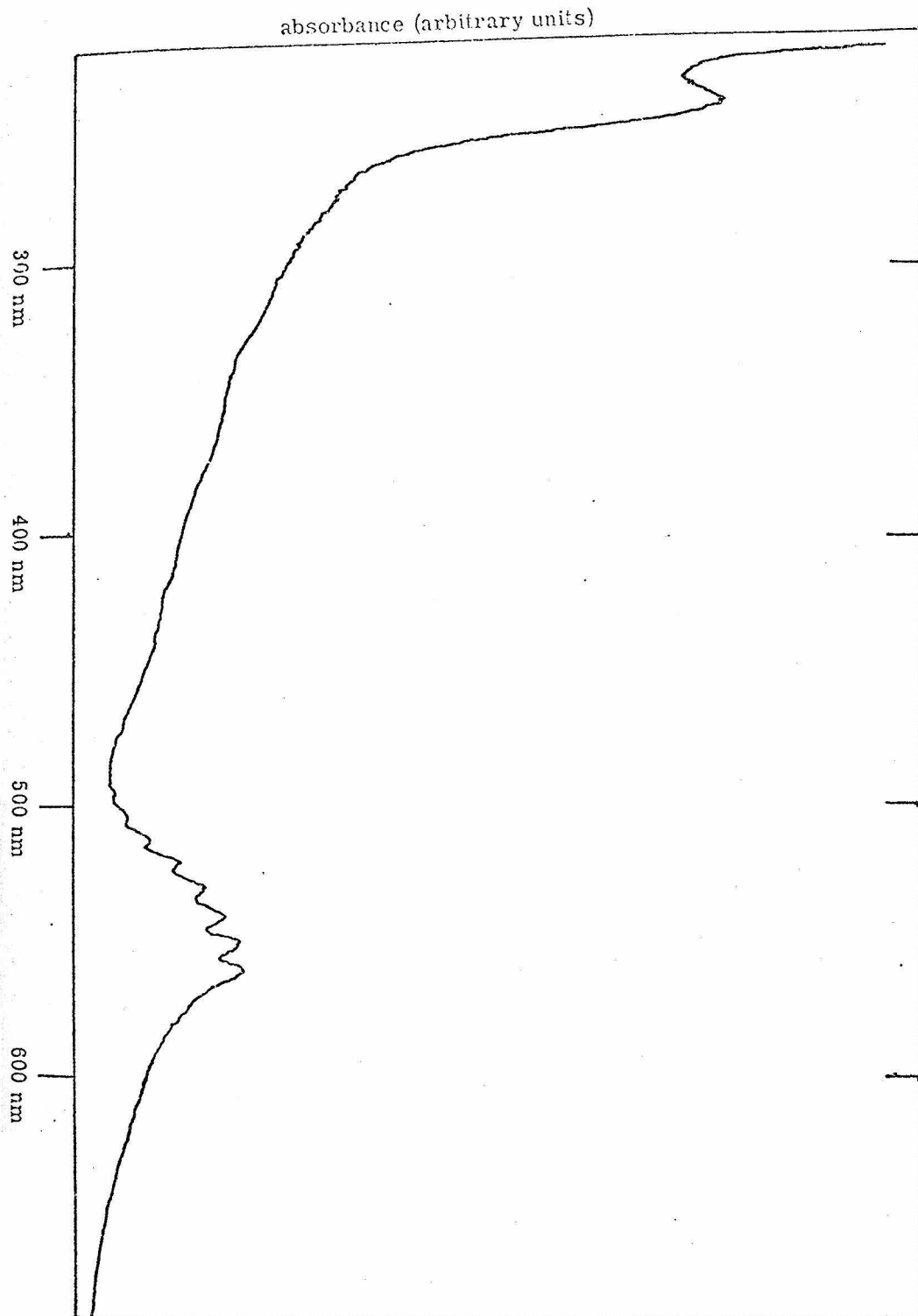
^d Reference 6.

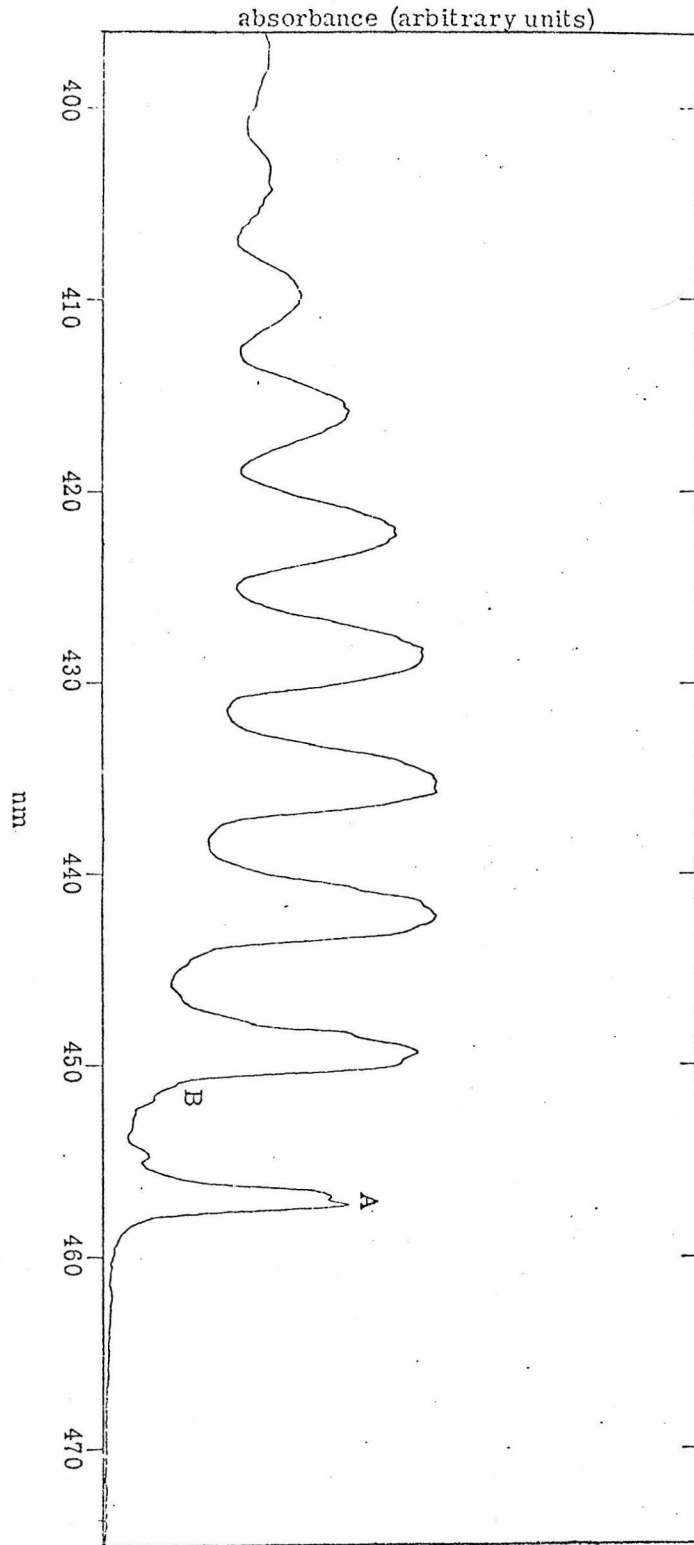
^e Our values for $\text{Mo}_2(\text{O}_2\text{CH})_4$

Figure Captions

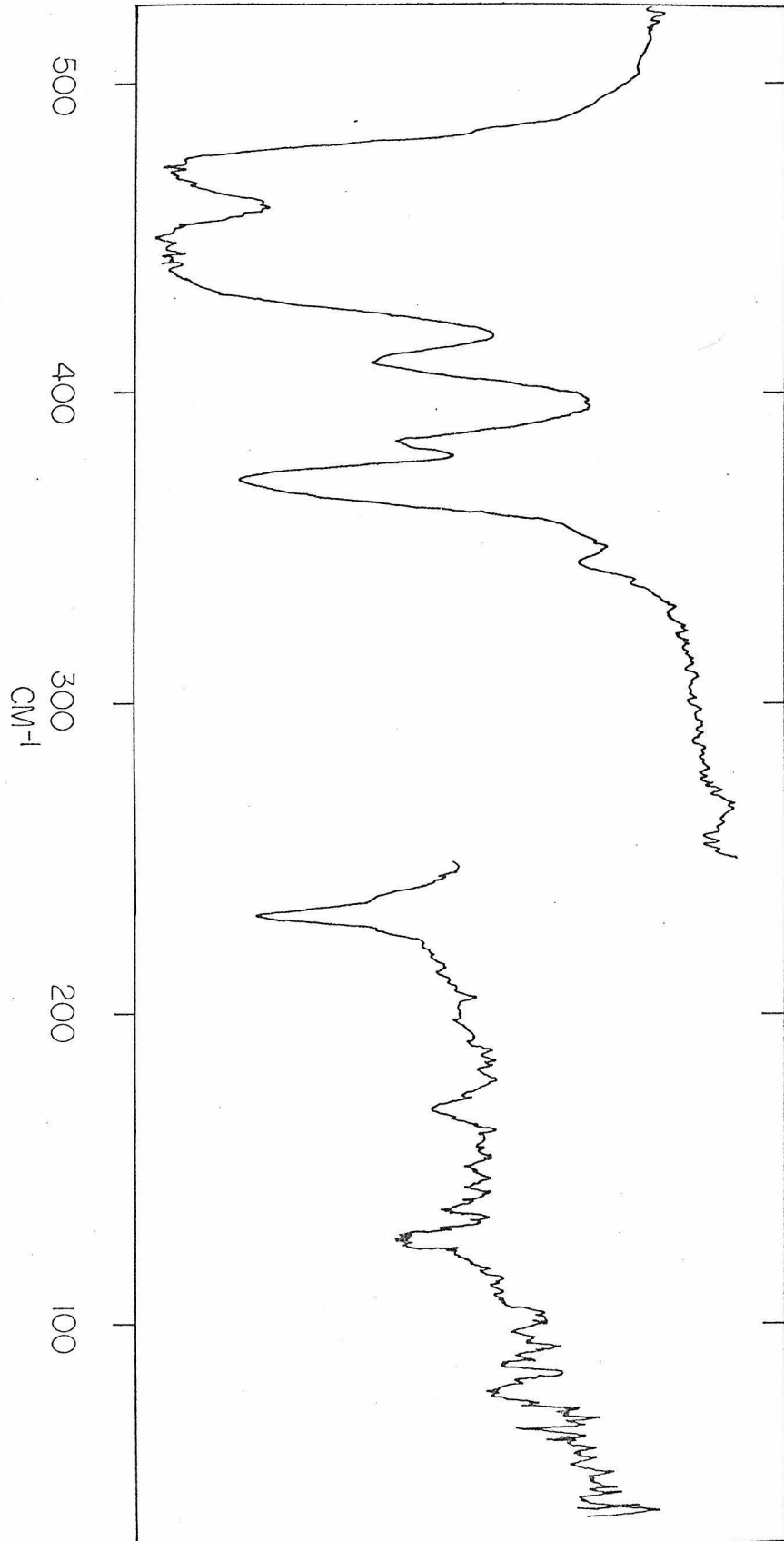
- Figure 1. Electronic absorption spectra of $\text{Mo}_2(\text{O}_2\text{CH})_4$ in methanol solution at room temperature.
- Figure 2. Electronic absorption spectrum of $\text{K}_4\text{Mo}_2\text{Cl}_8$ at 40 K in a mineral oil mull.
- Figure 3. Electronic absorption spectrum of $\text{Mo}_2(\text{O}_2\text{CH})_4$ at 15 K for a sample sublimed onto a quartz window.
- Figure 4. Low energy infrared spectrum of $\text{Mo}_2(\text{O}_2\text{CH})_4$ at 40 K. The sample consisted of $\text{Mo}_2(\text{O}_2\text{CH})_4$ powder suspended in vaseline on a polyethylene disk.







TRANSMITTANCE



CHAPTER 2.
THE PHOTOCHEMISTRY OF COMPOUNDS WHICH CONTAIN
A QUADRUPLE MOLYBDENUM - MOLYBDENUM BOND

Production of Hydrogen by Ultraviolet Irradiation of $\text{Mo}_2(\text{SO}_4)_4^{4-}$ in Aqueous Sulfuric Acid. Electronic Absorption Spectrum of $\text{K}_3\text{Mo}_2(\text{SO}_4)_4 \cdot 3.5 \text{H}_2\text{O}$ at 15 K.

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Abstract: Ultraviolet irradiation (λ 254 nm) of $\text{Mo}_2(\text{SO}_4)_4^{4-}$ in 5 M H_2SO_4 produces H_2 and the one-electron oxidation product $\text{Mo}_2(\text{SO}_4)_4^{3-}$. The disappearance quantum yield of $\text{Mo}_2(\text{SO}_4)_4^{4-}$ is 0.06 at 254 nm. The spectrum of $\text{K}_3\text{Mo}_2(\text{SO}_4)_4 \cdot 3.5 \text{H}_2\text{O}$ exhibits an absorption band at 1405 nm (ϵ 143); this band shows a vibrational progression in a 350 cm^{-1} fundamental even in 5 M D_2SO_4 solution at room temperature. At 15 K additional vibronic structure is resolved. This band is assigned to the $N \rightarrow E$ type transition $\delta \rightarrow \delta^* (^2B_{2g} - ^2B_{1u})$.

Introduction

It has been shown previously that ultraviolet irradiation of aqueous acidic solutions containing one-electron reductants such as Fe^{2+} yield hydrogen.² We are presently exploring the photoredox behavior of low-valent molybdenum complexes containing strong metal-metal bonds, and in particular are directing our attention to systems that are capable of reducing hydronium ions. Herein we report the results of an investigation of the photoreactivity of $\text{Mo}_2(\text{SO}_4)_4^{4-}$ in aqueous sulfuric acid. The near infrared spectrum of $\text{K}_3\text{Mo}_2(\text{SO}_4)_4 \cdot 3.5 \text{H}_2\text{O}$ at 15 K has also been studied.

Experimental Section

The compounds $\text{K}_4\text{Mo}_2(\text{SO}_4)_4^{3,4}$ and $\text{K}_3\text{Mo}_2(\text{SO}_4)_4 \cdot 3.5 \text{H}_2\text{O}^5$ were prepared according to standard procedures. All manipulations with the molybdenum complexes were conducted under nitrogen or in degassed solution. For the irradiations, the appropriate solution was placed in a special vacuum-tight, 1-cm quartz spectrophotometer cell and degassed through three freeze-pump-thaw cycles. Low pressure Hg lamps were used for the 254 nm irradiations. The electronic absorption spectra of the reaction solutions were monitored using a Cary 17 spectrophotometer. Quantum yields at 254 nm were determined using ferrioxalate actinometry such that the sample absorbed 5.77×10^{-7} einsteins/min. Mass spectral analyses of the gas above the irradiated solutions were obtained with an AEI-MS-902 high resolution mass spectrometer. The low temperature near IR spectrum of $\text{K}_3\text{Mo}_2(\text{SO}_4)_4 \cdot 3.5 \text{H}_2\text{O}$ was obtained by positioning a sample in a Cary Liquid Helium Dewar. X-ray photoelectron spectra were obtained with a HP5950A spectrometer from powdered samples on double stick tape.

Evolution of H_2 was measured for exhaustively photolyzed samples of $\text{Mo}_2(\text{SO}_4)_4^{4-}$ in vacuum-tight 1 cm spectrophotometer cells equipped with

a glass side-chamber and needle valve. The amount of evolved H_2 was determined by Toepler pumping the stirred photolyzed solution through three liquid nitrogen traps into a calibrated volume and manometrically measuring the pressure. To insure that only H_2 was collected, the gas was then passed over hot copper oxide, yielding water that was condensed in a liquid nitrogen trap, leaving no detectable gas.

Photochemistry of $Mo_2(SO_4)_4^{4-}$

Irradiation (254 nm) of $Mo_2(SO_4)_4^{4-}$ in 5 M D_2SO_4 results in the spectral changes shown in Figure 1. As irradiation proceeds, small gas bubbles are formed. The band at 515 nm ($\epsilon \sim 170$) characteristic^{3,4} of $Mo_2(SO_4)_4^{4-}$ decreases in intensity, whereas a structured absorption system diagnostic (vide infra) of $Mo_2(SO_4)_4^{3-}$ grows in at 1200-1600 nm (ϵ_{max} of 143). Isosbestic points are initially maintained at 578 and 420 nm and shoulders develop at 570 and 405 nm. A quantum yield of 0.06 was obtained for disappearance of $Mo_2(SO_4)_4^{4-}$.

Mass spectral analysis of the gas formed by irradiating $Mo_2(SO_4)_4^{4-}$ in 5 M H_2SO_4 solution confirmed that H_2 was produced. Thus the principal photoreaction must correspond to Eq. 1:



An exhaustively-photolyzed solution yielded 0.31 moles of H_2 per mole of $K_4Mo_2(SO_4)_4$. The fact that this is less than the theoretical amount of H_2 (0.5 moles) is not unexpected, as isosbestic points are not maintained (Fig. 1); that is, the reaction observed upon 254 nm irradiation is not stoichiometric at high conversion.⁶

Near Infrared Spectrum of $\text{Mo}_2(\text{SO}_4)_4^{3-}$

We have found that $\text{Mo}_2(\text{SO}_4)_4^{3-}$ exhibits a previously unreported⁵ absorption band in the near IR at 1405 nm (ϵ_{max} 143 for a 5 M D_2SO_4 solution). Remarkably, a vibrational progression with a spacing of 350 cm^{-1} attributable to a_{1g} (MoMo) was observed even in solution at room temperature. In contrast, the lowest energy electronic absorption band of $\text{K}_4\text{Mo}_2(\text{SO}_4)_4$, which occurs at 519 nm (ϵ 170), has been shown⁷ to be due to the transition $\delta \rightarrow \delta^*$ (${}^1A_{1g} \rightarrow {}^1A_{2u}$). There are two plausible explanations for the near IR band of $\text{K}_3\text{Mo}_2(\text{SO}_4)_4 \cdot 3.5 \text{ H}_2\text{O}$. As the compound is formally of mixed valence, the transition could be assigned intervalence charge transfer in the weak interaction description.^{8,9} Alternatively, the transition could be viewed as the N \rightarrow E type¹⁰ transition $\delta \rightarrow \delta^*$ (${}^2B_{2g} \rightarrow {}^2B_{1u}$). The former description seems inappropriate for several reasons. Firstly, the MoMo bond lengths¹¹ and stretching frequencies¹² are approximately equal in $\text{K}_4\text{Mo}_2(\text{SO}_4)_4$ and $\text{K}_3\text{Mo}_2(\text{SO}_4)_4 \cdot 3.5 \text{ H}_2\text{O}$. Therefore, the δ bonding model applicable to $\text{K}_4\text{Mo}_2(\text{SO}_4)_4$ would be expected to obtain for $\text{K}_3\text{Mo}_2(\text{SO}_4)_4 \cdot 3\text{H}_2\text{O}$ as well. EPR measurements for $\text{K}_3\text{Mo}_2(\text{SO}_4)_4 \cdot 3.5 \text{ H}_2\text{O}$ suggest that the odd electron occupies a δ orbital delocalized over both metal centers.¹³ We also have examined the X-ray photoelectron spectrum of $\text{K}_3\text{Mo}_2(\text{SO}_4)_4 \cdot 3.5 \text{ H}_2\text{O}$ and have found no splitting of the Mo $3p_{\frac{1}{2}}$ signal. One final point, and most convincing, is the fact that the 1405 nm band in the spectrum of $\text{K}_3\text{Mo}_2(\text{SO}_4)_4 \cdot 3.5 \text{ H}_2\text{O}$ shows sharp vibronic structure at 15 K (Figure 2, Table 1). An intervalence charge transfer band, because the transition is a multiphonon excitation,^{9,14} would not be expected to exhibit well resolved molecular

vibronic structure. Both the vibrational progression in quanta of 350 cm^{-1} and the Franck-Condon factor of about 1.5 are more consistent with the $\delta \rightarrow \delta^*$ assignment.

The vibrational structure of the 1405 nm band in the spectrum of $\text{K}_3\text{Mo}_2(\text{SO}_4)_4 \cdot 3.5 \text{ H}_2\text{O}$ is assigned as follows: There are five (A-E, Figure 2, Table 1) origins for progressions in $a_{1g}(\text{MoMo})$. Conspicuous is the presence of the two major components A and C with slightly different Franck-Condon factors. The progression that begins at C has a slightly higher progressional frequency than that beginning at A. These split components are interpreted to result from the $\delta \rightarrow \delta^*$ transition of two crystallographically nonequivalent $^{11} \text{Mo}_2(\text{SO}_4)_4^{3-}$ ions in the unit cell. Previously, it has been noted¹² that this nonequivalence results in slightly different ground-state values of $a_{1g}(\text{MoMo})$ (373 and 386 cm^{-1}). The two weak peaks, B and E, might possibly represent transitions involving quanta of a_{1g} modes built on A and C, respectively. Alternatively, these weak peaks could result from Davydov splitting of the pure origins (A and C). The other weak peak, D, may be attributed to a transition involving a quantum of an a_{1g} mode built on either A or C. It is apparent, however, that definitive assignments of the three weak peaks cannot be made with the limited data available.

Acknowledgment

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c) University of California at Santa Cruz.
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Table 1. Vibronic Structure of the Near IR Band in the Spectrum of $K_3Mo_2(SO_4)_4 \cdot 3.5 H_2O$ in a KBr pellet at 15 K

<u>nm</u>	<u>cm⁻¹</u>	<u>A</u>	<u>B</u>	<u>C</u>	<u>D</u>	<u>E</u>		
1583.7	6314							
1575.6	6347							
1558.2	6418							
1520.0	6579						351	
1500.3	6665							
1492.3	6701						354	
1482.4	6746						358	
1475.9	6776						351	
1442.9	6930						353	351
1425.0	7018						354	
1417.3	7055						363	
1406.7	7109						355	
1402.3	7131						348	
1374.0	7278						350	348
1357.2	7368						359	
1339.0	7468						359	
1312.9	7616						347	
1296.2	7715						347	

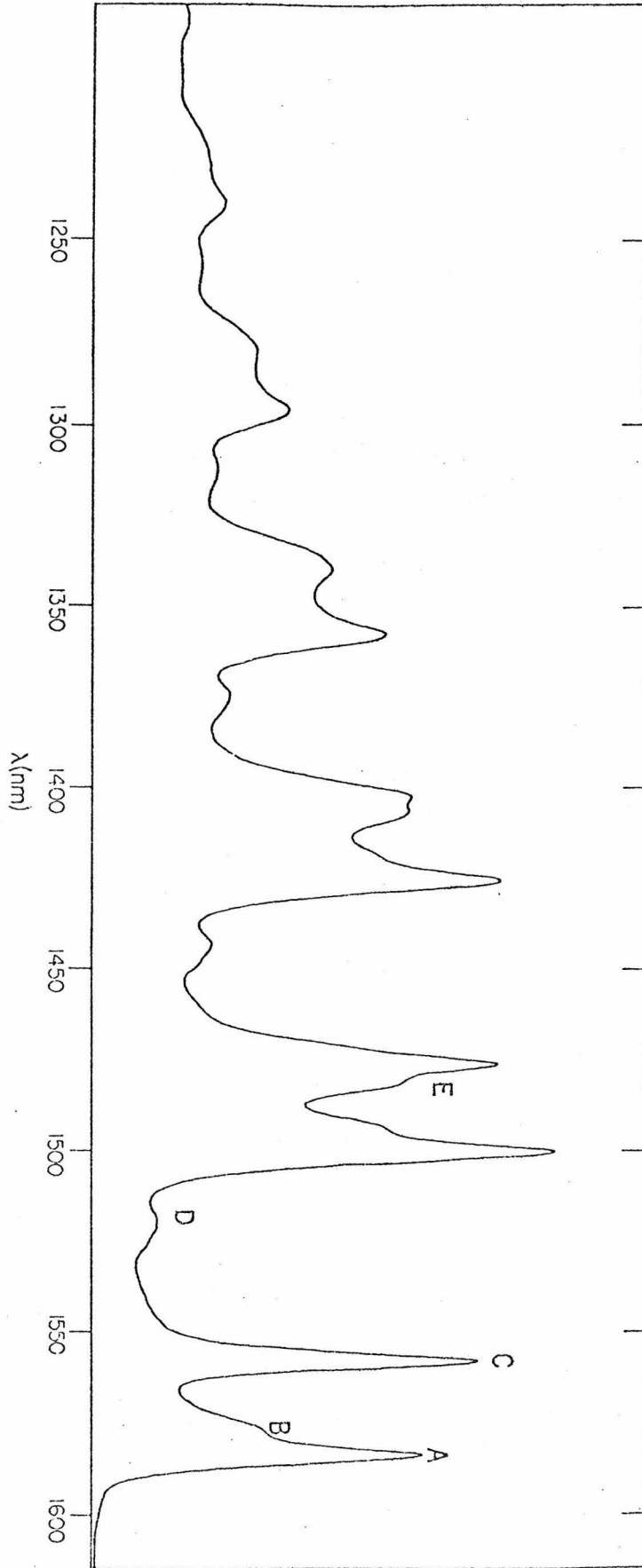
Figure Captions

- Figure 1. Electronic absorption spectral changes during 254 nm irradiation of $\text{K}_4\text{Mo}_2(\text{SO}_4)_4$ in 5 M D_2SO_4 solution.
- Figure 2. Electronic absorption spectrum of $\text{K}_3\text{Mo}_2(\text{SO}_4)_4 \cdot 3.5 \text{H}_2\text{O}$ in a KBr pellet at 15 K.



123

Absorbance



Photochemical Oxidation Reactions of Binuclear Molybdenum(II)
Complexes in Aqueous Acids and in Chlorocarbons.

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Abstract: The disappearance quantum yield at 254 nm of $\text{Mo}_2(\text{SO}_4)_4^{4-}$ in aqueous H_2SO_4 to yield one-half mole of H_2 and $\text{Mo}_2(\text{SO}_4)_4^{3-}$ is independent of acid concentration (0.001 - 5 M H_2SO_4). Ultraviolet irradiation of $\text{Mo}_2(\text{aq})^{4+}$ in 1 M HO_3SCF_3 produces one mole of hydrogen and $\text{Mo}_2(\mu\text{-OH})_2(\text{aq})^{4+}$. The quantum yield for this process is 0.035 upon 254 nm excitation. When $\text{Mo}_2\text{Cl}_8^{4-}$ is irradiated at 254 nm, $\text{Mo}_2\text{Cl}_8\text{H}^{3-}$ is initially formed with a quantum yield of 0.13. Eventually $\text{Mo}_2\text{Cl}_8\text{H}^{3-}$ thermally decomposes to yield one mole of hydrogen gas and $\text{Mo}_2(\mu\text{-OH})_2(\text{aq})^{4+}$. No reaction was observed when $\text{Mo}_2(\text{O}_2\text{CH}_2\text{NH}_3)_4^{4+}$ in 0.25 M HCl was subjected to uv irradiation. Irradiation (254 nm) of $\text{Mo}_2\text{Cl}_4\text{P}_4$ ($\text{P} = \text{P}(\text{Et})_3$, $\text{P}(\underline{n}\text{-Bu})_3$, and $\text{P}(\text{Et})(\text{Ph})_2$) in chlorocarbon solvents yield triply chloride bridged molybdenum(III) compounds. Quantum yields for these reactions are reported. Consideration of the spectra of these compounds suggests that the photoactive excited state has considerable LMCT character.

Introduction

Photooxidation reactions have been observed for a variety of metal ions in aqueous media.¹⁻³ Frequently, molecular hydrogen is the reduction product of the redox process. For example, ultraviolet excitation of $\text{Cr}^{2+}(\text{aq})$, $\text{Fe}^{2+}(\text{aq})$, $\text{Eu}^{2+}(\text{aq})$, and $\text{Ce}^{3+}(\text{aq})$ results in a one-electron oxidation of the metal center concomitant with dihydrogen formation.¹ Recently we reported⁴ the first example of an analogous reaction for a metal cluster compound. It was shown that 254 nm irradiation of aqueous sulfuric acid solutions of $\text{K}_4\text{Mo}_2(\text{SO}_4)_4$ yielded H_2 and $\text{Mo}_2(\text{SO}_4)_4^{3-}$. In order to test the generality of this process for binuclear Mo(II) compounds we have examined the photochemistry of $\text{Mo}_2(\text{aq})^{4+}$, $\text{Mo}_2\text{Cl}_8^{4-}$, and $\text{Mo}_2(\text{O}_2\text{CCH}_2\text{NH}_3)_4^{4+}$ in aqueous acid solutions.

Although photooxidation reactions in aqueous media are often loosely described as the result of charge transfer to solvent (CTTS) excitation, solvated electron production has only been established (e. g., $\text{Cr}^{2+}(\text{aq})$, $\text{Fe}(\text{CN})_6^{4-}$, $\text{W}(\text{CN})_8^{4-}$, and $\text{Mo}(\text{CN})_8^{4-}$)¹⁻³ for those compounds where independent spectroscopic studies also indicate a low-lying CTTS absorption. This is to be compared with the fact that a solvated electron intermediate has not been observed subsequent to flash photolysis of aqueous ferrous solutions.³ Mechanistic studies⁵ have implicated the presence of H atoms during photolysis of $\text{Fe}(\text{aq})^{2+}$. An investigation⁶ of the reaction of H atoms with $\text{Fe}^{2+}(\text{aq})$ had suggested the formation of an unstable hydride complex FeH^{2+} . Kinetic evidence⁷ for the photooxidation reaction was consistent with a mechanism involving hydrogen evolution from a FeH^{2+} species. Herein we present evidence that photochemical production of

hydrogen from binuclear Mo(II) ions occurs via an intermediate hydride complex. It is proposed that the photoactive state results from excitation of a LMCT transition.

Organometallic compounds have also been observed to undergo photooxidation reactions in halocarbon solvents. Irradiation of ferrocene⁸ in the presence of CCl₄ and CHCl₃ and of ruthenium⁹ in CCl₄ and CH₂ClCH₂Cl yield the ferricenium and ruthenicenium ions. A net photooxidation also obtains for the photo-declusterification of metal-metal bonded compounds in halocarbon solvents.¹⁰ In order to further elucidate the photochemistry of binuclear Mo(II) compounds the reactions of Mo₂Cl₄P₄ (P = P Et₃, P(n-Bu)₃ and P(Et)(Ph)₂) have been examined in chlorocarbon solvents upon 254 nm irradiation.

Experimental

The compounds K₄Mo₂Cl₈ · 2H₂O,¹¹ K₄Mo₂(SO₄)₄,¹² Rb₃Mo₂Cl₈H,^{13,14} Mo₂(O₂CCH₂NH₃)₄(SO₄)₂ · 4H₂O,¹⁵ Mo₂Cl₄[P(Et)₃]₄,¹⁶ Mo₂Cl₄[P(n-Bu)₃]₄,¹⁷ and Mo₂Cl₄[P(Et)(Ph)₂]₄¹⁷ were prepared by published methods. The phosphine derivatives were recrystallized from CH₂Cl₂ by the addition of methanol to filtered solutions and cooling to 0° C and satisfactory C, H analyses were obtained. Solutions of Mo₂(aq)⁴⁺ in 1 M HO₃SCF₃ were prepared as described by Bowen and Taube.¹⁸ Although binuclear Mo(II) compounds are air stable for short (3 h) to long (1 yr) periods of time in the solid state, they are exceedingly oxygen sensitive in solution. For the Mo₂Cl₄P₄ compounds we noticed that traces of moisture are also detrimental. Therefore the following procedures were adopted. Solids were stored under N₂ prior to use. Solution spectra were measured in special evacuable

cells. The apparatus consisted of a 1.0 or 0.1 cm quartz cuvette attached to a pyrex tube which in turn was connected to a teflon needle valve and either a 10 ml pyrex bulb or a 5 ml pyrex calibrated volume tube. A 24/40 ground glass joint after the needle valve allowed attachment to a vacuum line. Solid samples weighed in room atmosphere were transferred to the cuvette sidearm. For aqueous solutions 5 ml of the appropriate acid mixture was pipeted into the 10 ml bulb. Solutions of $\text{Mo}_2(\text{aq})^{4+}$ were transferred in a nitrogen filled glove bag. The cell was then sealed, attached to the vacuum line and freeze-pump-thaw degassed for three to four cycles and only then was the solution mixed with the solid in the sidearm. Extinction coefficients were determined in 0.1 cm cells so that a sufficiently large amount (0.02 g) of material could be used for an accurate weighing. No correction for sample volume was made as it is an insignificant source of error. Molar extinction coefficients were reproducible to $\pm 5\%$ and are believed precise to $\pm 10\%$. A similar procedure was employed with chloro-carbon solvents except that excess solvent was vacuum distilled from CaH_2 into the cooled (77 K) pyrex sidearm of the solution cell. The sidearm was calibrated to either 3 or 7 ml. After warming, excess solvent was slowly removed until the volume was reduced to a calibration line. The solvent was then subjected to three freeze-pump-thaw cycles before mixing with the solid in the quartz sidearm. Failure to take these precautions may account for the anomalously low ϵ_{max} value reported¹⁹ for the 588 nm absorption band of $\text{Mo}_2\text{Cl}_4[\text{P}(\underline{n}\text{-Bu})_3]_4$.

Irradiations at 546, 505 and 436 nm were obtained from the output of a 1000 W Hg-Xe arc lamp which was collimated before passing through the appropriate interference filter. For some 546 nm irradiations light from a 450 W Hanovia medium pressure Hg lamp was passed through a Corning 4-102 glass filter combination. The focused beam from a 200 W Hg-Xe arc was used for some "broad band" UV photolysis. A 30 W low pressure Hg (Hanovia Germicidal) lamp with a Vycor envelope was used as a source of 254 nm radiation. Because of competing thermal side reactions it often was vital to have an intense source of 254 nm radiation. Therefore the output of the low pressure Hg lamp was not filtered. The only other spectral line of appreciable intensity is at 578 nm.²⁰ In each instance we have shown that the compounds examined were not photoactive in this spectral region.

Quantum yields were determined at 254 nm employing the ferrioxalate actinometer.²⁰ The procedure was modified to adopt the precautions recently suggested by Bowman and Demas.²¹ Disappearance quantum yields of the binuclear Mo(II) compounds were obtained by monitoring the decrease of the visible $\delta \rightarrow \delta^*$ absorption band. Aqueous solutions of binuclear Mo(II) ions decompose thermally.^{13,14,18} Correction for these thermal background reactions was necessary for the quantum yield determinations. This was accomplished by alternating periods of time with and without irradiation for each sample. In most instances this correction was less than 5-10%. We have also observed an initial slow decomposition of the $\text{Mo}_2\text{Cl}_4\text{P}_4$ compounds in CH_2Cl_2 , even with the aforementioned precautions. Presumably traces of oxygen or the presence of adventitious moisture

account for this observation. Chloroform reacted with the $\text{Mo}_2\text{Cl}_4\text{P}_4$ compounds thermally and amounted to a 10-30% correction in the quantum yields in this instance. No corrections for inner filter effects were applied as the quantum yields were obtained for less than 10% photolysis. Typically three measurements were obtained with an internal consistency of $\pm 5\%$. Except in those cases where the thermal correction was large (i. e., the photochemical reactions in chloroform, 0.001 M H_2SO_4 and 6 M HCl) reproducibility of the quantum yields was $\pm 15\%$.

Hydrogen evolution was measured for photolyzed samples in the vacuum-tight 1 cm spectrophotometer cells. The amount of evolved H_2 was determined by Toepler pumping the stirred photolyzed solution through three liquid nitrogen traps into a 12.2 ml volume and manometrically measuring the pressure. To insure that only H_2 was collected, the gas was then passed over hot copper oxide, yielding water that was condensed in a liquid nitrogen trap, leaving only traces ($< 5\%$) of residual gas. Typically 0.03-0.07 mmoles of hydrogen gas were collected and the measurements were reproducible to $\pm 5-10\%$.

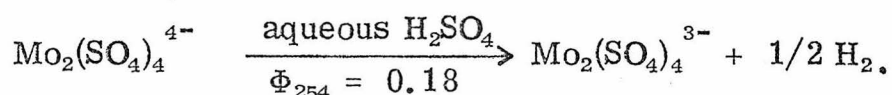
The compound $\text{Mo}_2\text{Cl}_3(\mu\text{-Cl})_3[\text{P}(\text{Et})(\text{Ph})_2]_3$ was prepared photochemically by the following method. One quarter gram of Mo_2Cl_4 - $[\text{P}(\text{Et})(\text{Ph})_2]_4$ and a teflon stir bar were placed in a quartz tube (3.5 diameter, 14 cm height) which could be sealed with a teflon needle valve and attached to a vacuum line via a 24/40 ground glass joint. The cell was evacuated and ca 50 ml of CH_2Cl_2 (which was stored in vacuo over CaH_2) was distilled into the tube. The solution was then irradiated with the unfiltered light from a 200 W Hg-Xe lamp (ca 5 hr)

until the blue colored solution changed to a bright maroon. After reattaching to the vacuum line the volume was reduced to 10 ml and ~ 30 ml of diethylether (stored in vacuo over LiAlH_4) was distilled into the tube. A maroon oil formed and the mixture was stirred for one day until a maroon powder was obtained. The tendency of the compound to form an oil made purification very difficult. This powder was collected, redissolved in CH_2Cl_2 , and precipitated again to yield 0.15 g of product. The solution spectrum of the compound in CH_2Cl_2 was similar but not identical to that of the photoproduct. A molecular weight of 950 g/mole was measured in chloroform solution. Anal: Found C, 46.88 ; H, 4.42; P, 9.7. Calcd for $\text{Mo}_2\text{Cl}_6[\text{P}(\text{C}_2\text{H}_5)(\text{C}_6\text{H}_5)_2]_3$: C, 48.17; H, 4.33; P, 8.87; MW = 1047 g/mole. The infrared spectrum measured in a KBr pellet showed two strong Mo-Cl stretches at 315 and 332 cm^{-1} .

Ultraviolet-visible absorption spectra and spectral changes were recorded utilizing a Cary 17 spectrometer. Infrared spectra were recorded with a PE 225 instrument. Molecular weights were determined using an HP 301A vapor pressure osmometer and benzil as a calibrant. Elemental analyses were obtained from Chemalytics, Inc. and the Caltech microanalytical laboratory.

Results

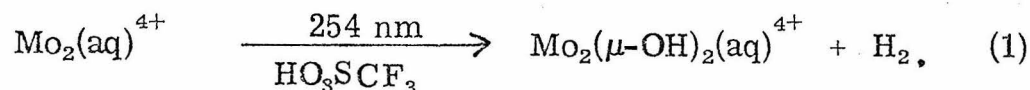
Photooxidation Reactions in Aqueous Media - Previously we demonstrated⁴ that ultraviolet irradiation of $\text{Mo}_2(\text{SO}_4)_4^{4-}$ in 5 M H_2SO_4 yielded H_2 and $\text{Mo}_2(\text{SO}_4)_4^{3-}$. At high conversion this reaction was not stoichiometric. Therefore we have measured the amount of H_2 evolved in partially photolyzed (ca 80%) solutions and find 0.49 moles of H_2 literated per mole of $\text{Mo}_2(\text{SO}_4)_4^{4-}$ consumed. When considered together with the earlier⁴ results, the initial stoichiometry is unambiguously defined as



The quantum yield of this process is essentially independent of acid concentration from 0.001 M to 5.0 M H_2SO_4 (Table 1). Attempts to extend the measurements to lower acid concentrations were hampered by increasingly rapid hydrolysis. It should also be noted that a regular increase in ϵ_{max} of the $\delta \rightarrow \delta^*$ transition was observed for decreasing acid concentrations. This may result from either partial substitution of the sulfate ligand by water or a change in the solvation structure of the $\text{Mo}_2(\text{SO}_4)_4^{4-}$ ion.

Excitation (254 nm) of $\text{Mo}_2(\text{aq})^{4+}$ in 1 M trifluoromethanesulfonic acid results in the electronic absorption spectral changes shown in Figure 1. As the irradiation proceeds, the color of the solution changes from red to green, and the band at 505 nm, characteristic of $\text{Mo}_2(\text{aq})^{4+}$,⁴ decreases in intensity. Absorption bands attributable to product occur at 620, 570, 490, and 362 nm, and isosbestic points at 568 and 424 nm are maintained throughout the conversion. No

reaction was observed under similar conditions in the dark or when the wavelength of irradiation was 366 nm. As 254-nm irradiation proceeds, small gas bubbles are formed and mass spectral analysis confirmed the presence of H₂. Measurement of the hydrogen evolved yielded 1.06 ± 0.1 moles per mole of Mo₂(aq)⁴⁺ for solutions 5×10^{-3} to 1.4×10^{-2} M in Mo₂(aq)⁴⁺. Furthermore, the absorption spectrum of the green photoproduct is identical to that of a Mo(III) species first prepared by Hartmann and Schmidt²³ and formulated as a hydroxybridged dimer by Ardon and Pernick.²⁴ The overall photochemical reaction may be formulated as in Eq. 1:



The disappearance quantum yield for Mo₂(aq)⁴⁺ at 254 nm is 0.036.

Concentrated HCl solutions of the Mo₂Cl₈⁴⁻ ion are readily oxidized to Mo₂Cl₈H³⁻.^{13,14} The rate of this reaction is dramatically decreased in dilute HCl solutions. For example, in 3 M HCl at ambient temperature only 15% reaction occurs over a period of 18 hr. We shall refer to the acid solutions of K₄Mo₂Cl₈·2H₂O as containing the Mo₂Cl₈⁴⁻ ion although it should be realized that in solution an equilibrium among partially aquated species obtains. Irradiation (254 nm) of Mo₂Cl₈⁴⁻ in 3 M HCl induces the electronic absorption spectral changes shown in Figure 2. As the reaction proceeds the color of the solution changes from red to green; however, there are no isosbestic points. The first absorption band attributable to products

appears at 415 nm. Upon further irradiation this peak grows slightly, a new band appears at 369 nm and bubbles of gas are evolved. The 369 nm band is also found if a photolyzed solution containing the 415 nm absorption is allowed to stand in the dark. If an authentic sample of $\text{RbMo}_2\text{Cl}_8\text{H}$ is dissolved in 3 M HCl, an absorption band is initially observed at 415 nm (Figure 3). Subsequently, the intensity of this band decreases concomitant with the growth of a new band at 369 nm. Cotton and Kalbacher¹⁴ have shown that the reaction of $\text{Mo}_2\text{Cl}_8\text{H}$ with D_2O yields HD. We find that 0.92 moles of H_2 are evolved per mole of $\text{Rb}_3\text{Mo}_2\text{Cl}_8\text{H}$ in 3 M HCl. When a solution of $\text{Mo}_2\text{Cl}_8^{4-}$ in 3 M HCl is photolyzed to completion 1.16 moles of H_2 were evolved per mole of $\text{Mo}_2\text{Cl}_8^{4-}$ consumed.

The electronic spectrum of the green product derived from the decomposition of $\text{Rb}_3\text{Mo}_2\text{Cl}_8\text{H}$ in 3 M HCl exhibits bands at 369 ($\epsilon \sim 820$) and 655 ($\epsilon \sim 85$) nm and a shoulder at 600 ($\epsilon \sim 75$) nm. A dimeric formulation of the products was assumed to calculate the extinction coefficients. This spectrum appears identical to that reported²³ for $\text{Mo(III)(H}_2\text{O)}_6^{3+}$ in 2 M HCl which was later shown²⁴ to be $\text{Mo}_2(\mu\text{-OH})_2(\text{aq})^{4+}$. As for $\text{Mo}_2(\text{aq})^{4+}$, photolysis of $\text{Mo}_2\text{Cl}_8^{4-}$ ultimately yields one equivalent of H_2 and the hydroxy-bridged molybdenum(III) dimer.

Consistent with the observations of Cotton and Kalbacher¹⁴ we find that $\text{Mo}_2\text{Cl}_8\text{H}_3^{3-}$ is stable in more concentrated acid solutions. Photolysis (254 nm) of $\text{Mo}_2\text{Cl}_8^{4-}$ in 6 M HCl initially (< 5% reaction)

quantitatively produces $\text{Mo}_2\text{Cl}_8\text{H}^{3-}$ with a disappearance quantum yield of 0.092. At greater than 10% conversion, the production of $\text{Mo}_2\text{Cl}_8\text{H}^{3-}$ levels off and then decreases upon further irradiation. This is most likely a result of secondary photolysis. In fact, $\text{Mo}_2\text{Cl}_8\text{H}^{3-}$ in 6 M HCl disappears with a quantum yield of 0.040 when excited at 254 nm. The photoproduct in this instance possesses an intense absorption at 305 nm and a weaker band at 512 nm. An isosbestic point is maintained at 490 nm throughout the photolysis. Because $\text{Mo}_2\text{Cl}_8\text{H}^{3-}$ absorbs more strongly than $\text{Mo}_2\text{Cl}_8^{4-}$ at 254 nm the secondary photolysis rationale is vindicated. Similarly, secondary photolysis can account for the fact that conversion to $\text{Mo}_2(\mu\text{-OH})_2(\text{aq})^{4+}$ is not quantitative at high conversions for the photolysis carried out in 3 M HCl. In fact, the development of a shoulder at 300-305 nm at long irradiation times (Figure 2) is evidence for the product of secondary photolysis.

No spectral changes were observed when a solution of $\text{Mo}_2(\text{O}_2\text{CCH}_2\text{NH}_3)_4^{4+}$ in 0.25 M HCl was irradiated for 12 hr with the unfiltered radiation of a 200 W Hg-Xe lamp.

Photooxidation Reactions in Chlorocarbon Solvents - When a solution of $\text{Mo}_2\text{Cl}_4[\text{P}(\text{Et})_3]_4$ is photolyzed at 254 nm, the spectral changes shown in Figure 4 occur. A band attributable to the $\delta \rightarrow \delta^*$ absorption decreases concomitant with the growth of an intense absorption at 314 nm and a shoulder develops ca 400 nm. In more concentrated solutions at long irradiation times two weak absorptions

are found at 515 and 570 nm. An isosbestic point is initially (< 50% photolysis) maintained at 525 nm. Similar spectral changes are observed when $\text{Mo}_2\text{Cl}_4[\text{P}(\text{Et})_3]_4$ reacts with CCl_3 and CHCl_3 by a thermal pathway. In both cases an intense absorption appears at 314 nm, a shoulder develops ca 400 nm, and broad weak absorptions peaking at 510 and 570 nm are detected. Initially, an isosbestic point obtains between 525 and 530 nm. Clearly the thermal and photochemical processes yield very similar or identical products.

Walton and coworkers²⁵ have shown that workup of the reaction mixture of $\text{Mo}_2\text{Cl}_4[\text{P}(\text{Et})_3]_4$ with CCl_4 in CH_2Cl_2 yields 29% of $(\text{Et}_3\text{PCl})_3\text{Mo}_2\text{Cl}_9$; however, this product will not redissolve in CH_2Cl_2 . We have observed the formation of small amounts of this compound when the product of the photochemical reaction (see Experimental Section) is recrystallized from $\text{CH}_2\text{Cl}_2\text{-CCl}_4$. Addition of ether to the photolyzed solutions of $\text{Mo}_2\text{Cl}_4[\text{P}(\text{Et})_3]_4$ yielded an oil which eventually could be induced to form a powder with irreproducible elemental analysis. The infrared spectrum of this compound (KBr pellet) in the Mo-Cl stretching region showed bands at 330 (s), 309 (s), and 280 (m) very similar to those at 334 (s), 307 (s), 275 (m), and 250 (w) in $(\text{Et}_3\text{PCl})_3\text{Mo}_2\text{Cl}_9$.

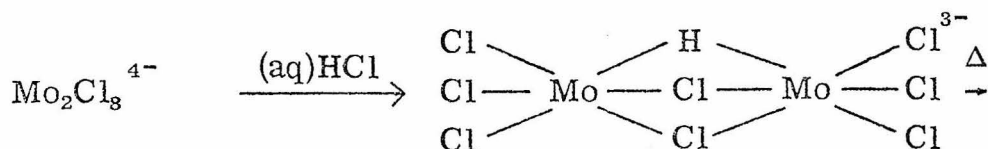
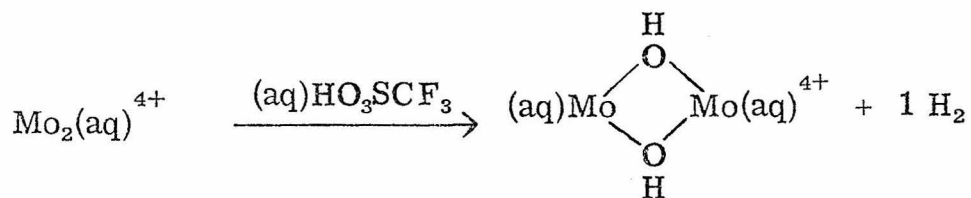
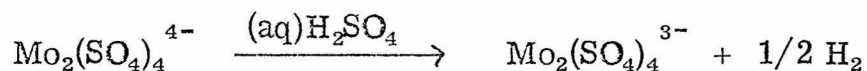
Photolysis (254 nm) of $\text{Mo}_2\text{Cl}_4[\text{P}(\text{n-Bu})_3]_4$ and $\text{Mo}_2\text{Cl}_4[\text{P}(\text{Et})(\text{Ph})_2]_4$ in CH_2Cl_2 results in spectral changes similar to those observed for the photochemical reaction of $\text{Mo}_2\text{Cl}_4[\text{P}(\text{Et})_3]_4$ with CH_2Cl_2 . The spectra of the photoproducts from the reaction of $\text{Mo}_2\text{Cl}_4[\text{P}(\text{n-Bu})_3]_4$ with CH_2Cl_2 , EtCl , and CHCl_3 were identical. It was possible to isolate a CH_2Cl_2 soluble product from the photochemical reaction of $\text{Mo}_2\text{Cl}_4[\text{P}(\text{Et})(\text{Ph})_2]_4$ with CH_2Cl_2

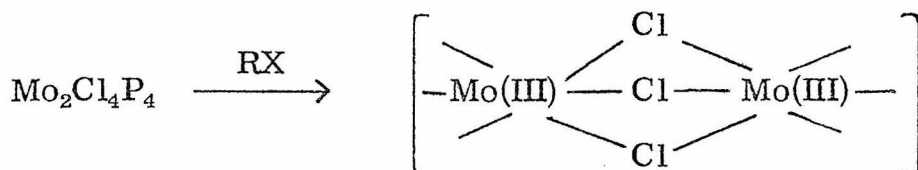
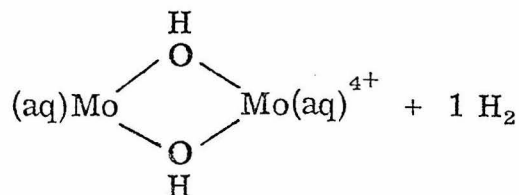
whose elemental analysis and molecular weight were consistent with an $\text{Mo}_2\text{Cl}_6[\text{P}(\text{Et})(\text{Ph})_2]_3$ formulation; however, its electronic spectrum was not identical to that of the photolyzed solution. It therefore appears likely that photolysis of $\text{Mo}_2\text{Cl}_4\text{P}_4$ compounds initially yields an $\text{Mo}_2\text{Cl}_5\text{P}_4$ or a similar species which subsequently can lose phosphine ligands ultimately producing the $\text{Mo}_2\text{Cl}_9^{3-}$ ion.

Quantum yields at 254 nm for the photochemical reactions of $\text{Mo}_2\text{Cl}_4\text{P}_4$ ($\text{P} = \text{P}(\text{Et})_3$, $\text{P}(\text{n-Bu})_3$, and $\text{P}(\text{Et})(\text{Ph})_2$) with various chlorocarbon solvents are presented in Table 1. For all photooxidation reactions both in aqueous (vide supra) and chlorocarbon solvents, no appreciable photoactivity (i. e., $\Phi > \sim 0.0005$) was observed when samples were excited at 546, 505, and 436 nm. As for the photochemistry of $\text{Re}_2\text{Cl}_8^{2-26}$ no reactivity occurs when the lowest energy $\delta \rightarrow \delta^*$ transition is excited.

Discussion

In summary, the photochemical processes of binuclear Mo(II) compounds upon 254 nm excitation are





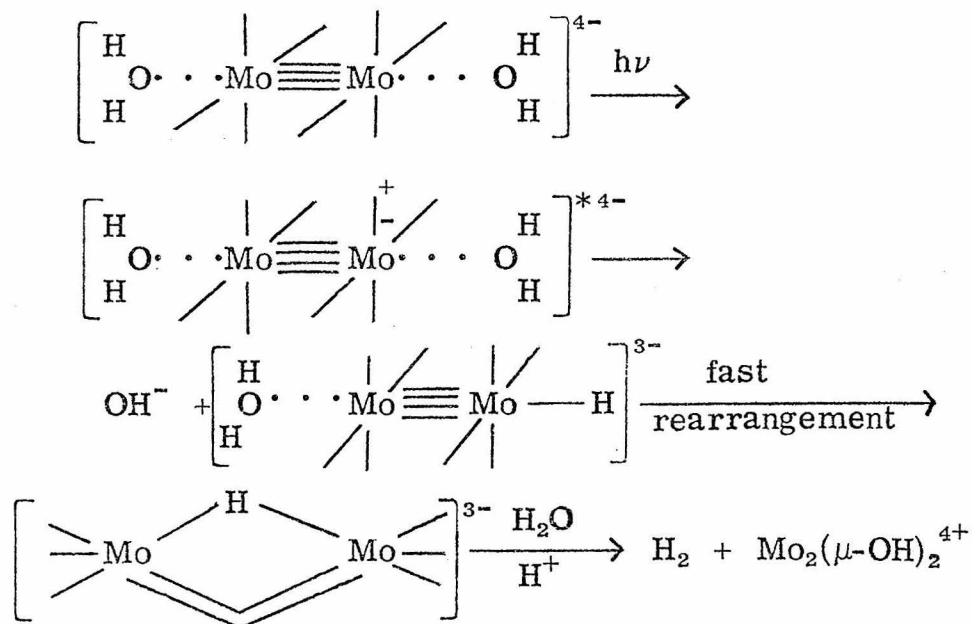
Spectroscopic studies²⁷⁻³⁰ of compounds which contain quadruple metal-metal bonds have demonstrated that the lowest energy visible absorption band arises from the metal localized one-electron $N \rightarrow V$ excitation $\delta \rightarrow \delta^*$. Irradiation of this absorption band in $\text{Re}_2\text{Cl}_8^{2-}$ and in those compounds studied in this work does not lead to metal-metal bond cleavage. When $\text{Re}_2\text{Cl}_8^{2-}$ in CH_3CN is subjected to ultraviolet irradiation ($\lambda < 366 \text{ nm}$) rupture of the quadruple bond is observed.²⁶ This is now thought³¹ to proceed by a solvent assisted pathway rather than by homolytic cleavage of the ReRe bond. As shown herein, UV irradiation of binuclear molybdenum (II) compounds yields oxidized metal species and a binuclear structure is maintained in the products. These results are in sharp contrast to the photochemical reactions of other compounds which contain metal-metal bonds where, in general, homolytic bond cleavage obtains.^{10,32} For example, excitation of the $\sigma \rightarrow \sigma^*$ transition³³ in $\text{M}_2(\text{CO})_{10}$ ($\text{M} = \text{Mn}, \text{Tc}, \text{Re}$) compounds leads to efficient metal-metal bond cleavage.^{10,32}

A recent spectroscopic analysis³⁴ suggested values of 115-130 and 110-160 kcal/mole for the metal-metal bond energies in $\text{Re}_2\text{Cl}_8^{2-}$ and $\text{Mo}_2\text{Cl}_8^{4-}$, respectively. Also, the low lying (700 - 350 nm) metal-localized electronic absorption bands of these compounds often exhibit well-resolved vibronic structure^{27-30, 34, 35} and the excited state value of a_{1g} (MM) is consistent with strong, residual metal-metal bonding in these excited states. The large metal-metal bond energy and the absence of an appreciable weakening of this bond in low lying metal-localized excited states explains the absence of photolytic fragmentation in compounds which contain a quadruple metal-metal bond.

The magnetic circular dichroism (MCD) spectrum of $\text{Mo}_2\text{Cl}_8^{4-}$ in 6 M HCl shows an A term at 270 nm which has been attributed to an allowed $\text{Cl}(\pi) \rightarrow \delta^*$ ligand to metal charge transfer (LMCT) transition. Therefore it is likely that a LMCT state is initially produced when $\text{Mo}_2\text{Cl}_8^{4-}$ and $\text{Mo}_2\text{Cl}_4\text{P}_4$ are photolyzed at 254 nm. Because intersystem crossing between charge transfer and metal localized states may be slow^{36, 37} it is possible that a LMCT state is responsible for the photochemistry. The LMCT absorption bands of $\text{Mo}_2(\text{aq})^{4+}$ and $\text{Mo}_2(\text{SO}_4)_4^{4-}$ have not been identified yet. Using the difference in optical electronegativities³⁸ between Cl^- and H_2O and between Cl^- and SO_4^{2-} the LMCT bands are estimated at 190 and 230 nm, respectively. The quantum yields (Table I) for $\text{Mo}_2\text{Cl}_8^{4-}$ and $\text{Mo}_2(\text{SO}_4)_4^{4-}$ are similar while that of

$\text{Mo}_2(\text{aq})^{4+}$ is much less. This is consistent with the proximity of the LMCT band with respect to 254 nm excitation. It is interesting to note that $\text{Mo}_2(\text{O}_2\text{CCH}_2\text{NH}_3)_4^{4+}$ did not react when irradiated in the ultraviolet ($\lambda \geq 200$ nm). For $\text{Mo}_2(\text{O}_2\text{CH})_4$ the lowest energy charge transfer transition centered at 300 nm has been assigned³⁹ to a metal to ligand charge transfer (MLCT) transition. No LMCT transitions were found for $\text{Mo}_2(\text{O}_2\text{CH})_4$ for $\lambda \geq 200$ nm. The solution spectrum reported¹⁵ for $\text{Mo}_2(\text{O}_2\text{CCH}_2\text{NH}_3)_4^{4+}$ is virtually identical to that of $\text{Mo}_2(\text{O}_2\text{CH})_4$. Therefore, there is strong circumstantial evidence which suggests that the photoactive state possesses substantial LMCT character.

A particularly significant observation is the intermediacy of a metal hydride for the photochemical production of hydrogen from $\text{Mo}_2\text{Cl}_8^{4-}$. One reasonable mechanism for the formation of the hydride is as follows



An analogous scheme could be drawn for $\text{Mo}_2(\text{aq})^{4+}$ and $\text{Mo}_2(\text{SO}_4)_4^{4-}$ except that for the latter compound attack of $\text{Mo}_2(\text{SO}_4)_4^{2-}$ on $\text{Mo}_2(\text{SO}_4)_4^{4-}$ to yield $\text{Mo}_2(\text{SO}_4)_4^{3-}$ must obtain. The oxidation state of molybdenum in the LMCT state is formally 1.5. Binuclear Mo (1.5) compounds have never been isolated. An extremely unstable $\text{Mo}_2(\text{O}_2\text{CCF}_3)_4^-$ species has been generated by pulsed radiolysis of methanol solutions containing $\text{Mo}_2(\text{O}_2\text{CCF}_3)_4$.⁴⁰

Mechanisms for the reactions of $\text{Mo}_2\text{Cl}_4\text{P}_4$ with chlorocarbons can be imagined similar to the above or involving electron transfer to solvent. There is no reason to favor any mechanism at this point. Flash photolysis studies would be of help in the further elucidation of these reactions.

Acknowledgments

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Table 1. Disappearance Quantum Yields at 254 nm for
Photooxidation Reactions of Binuclear Mo(II) Compounds

<u>Compound</u>	<u>[Compound]</u> <u>Moles/l</u>	<u>Solvent</u>	ϵ_{\max} ($\delta \rightarrow \delta^*$)	Φ_{254}
$K_4Mo_2(SO_4)_4$	4.41×10^{-3}	5.0 <u>M</u> H_2SO_4	150	0.19
$K_4Mo_2(SO_4)_4$	3.90×10^{-3}	2.5 <u>M</u> H_2SO_4	207	0.17
$K_4Mo_2(SO_4)_4$	3.90×10^{-3}	0.5 <u>M</u> H_2SO_4	230	0.16
$K_4Mo_2(SO_4)_4$	3.72×10^{-3}	0.05 <u>M</u> H_2SO_4	237	0.15
$K_4Mo_2(SO_4)_4$	3.84×10^{-3}	0.001 <u>M</u> H_2SO_4	250	0.18
$Mo_2(aq)^{4+}$	2.15×10^{-3}	1 <u>M</u> HO_3SCF_3	337 ^a	0.035
$Mo_2(aq)^{4+}$	1.93×10^{-3}	1 <u>M</u> HO_3SCF_3 / 0.15 <u>M</u> CH_3OH	337	0.031
$K_4Mo_2Cl_8 \cdot 2H_2O$	1.71×10^{-3}	3 <u>M</u> HCl	960	0.14
$K_4Mo_2Cl_8 \cdot 2H_2O$	1.06×10^{-3}	3 <u>M</u> HCl	960	0.13
$K_4Mo_2Cl_8 \cdot 2H_2O$	9.33×10^{-4}	6 <u>M</u> HCl	1050	0.092
$Rb_3Mo_2Cl_8H$	5.37×10^{-4}	6 <u>M</u> HCl	1400 ^b	0.040
$Mo_2Cl_4[P(Et)_3]_4$	3.06×10^{-4}	CH_2Cl_2	3065	0.055
$Mo_2Cl_4[P(Et)_3]_4$	4.54×10^{-4}	CH_2Cl_2 / $\sim 10^{-5}$ <u>M</u> in galvinoxyl	3065	0.055
$Mo_2Cl_4[P(Et)_3]_4$	3.04×10^{-4}	$CHCl_3$	3065 ^c	0.060
$Mo_2Cl_4[P(Et)_3]_4$	1.70×10^{-4}	$CHCl_3$	3065 ^c	0.063

Table 1 (Continued)

Compound	[Compound] Moles/l	Solvent	ϵ_{\max} ($\delta \rightarrow \delta^*$)	Φ_{254}
$\text{Mo}_2\text{Cl}_4[\text{P}(\underline{n}\text{-Bu})_3]_4$	2.47×10^{-4}	EtCl	3150 ^c	0.016
$\text{Mo}_2\text{Cl}_4[\text{P}(\underline{n}\text{-Bu})_3]_4$	4.20×10^{-4}	CH_2Cl_2	3150	0.058
$\text{Mo}_2\text{Cl}_4[\text{P}(\underline{n}\text{-Bu})_3]_4$	4.29×10^{-4}	CHCl_3	3150 ^c	0.054
$\text{Mo}_2\text{Cl}_4[\text{P}(\text{Et})(\text{Ph})_2]_4$	5.31×10^{-5}	CH_2Cl_2	3125	0.019
$\text{Mo}_2\text{Cl}_4[\text{P}(\text{Et})(\text{Ph})_2]_4$	1.62×10^{-4}	CHCl_3	3125 ^c	0.035

^aValue of ϵ_{\max} taken from ref. 18.

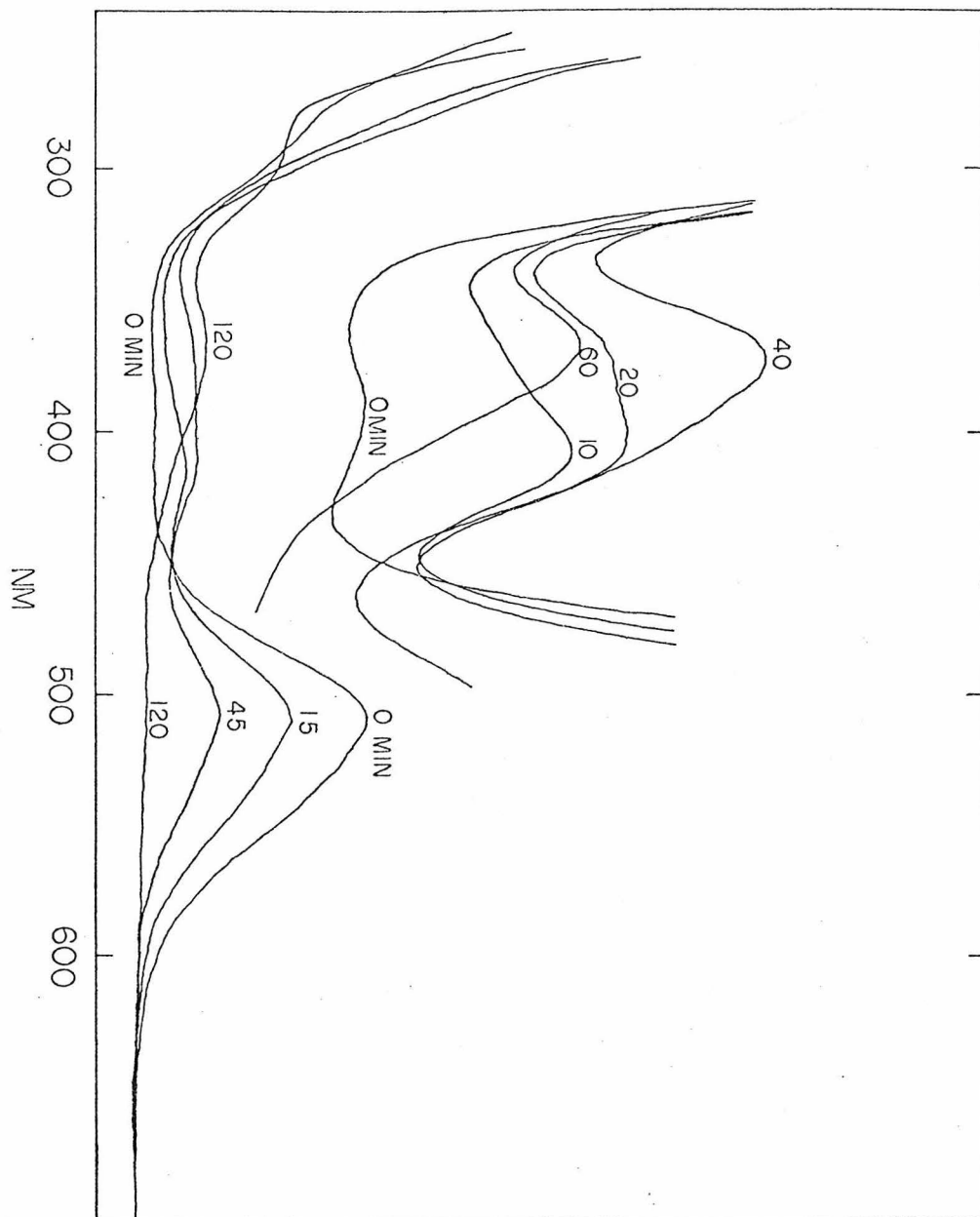
^bThe ϵ_{\max} value is for the band centered at 419 nm which is not $\delta \rightarrow \delta^*$ in this compound.

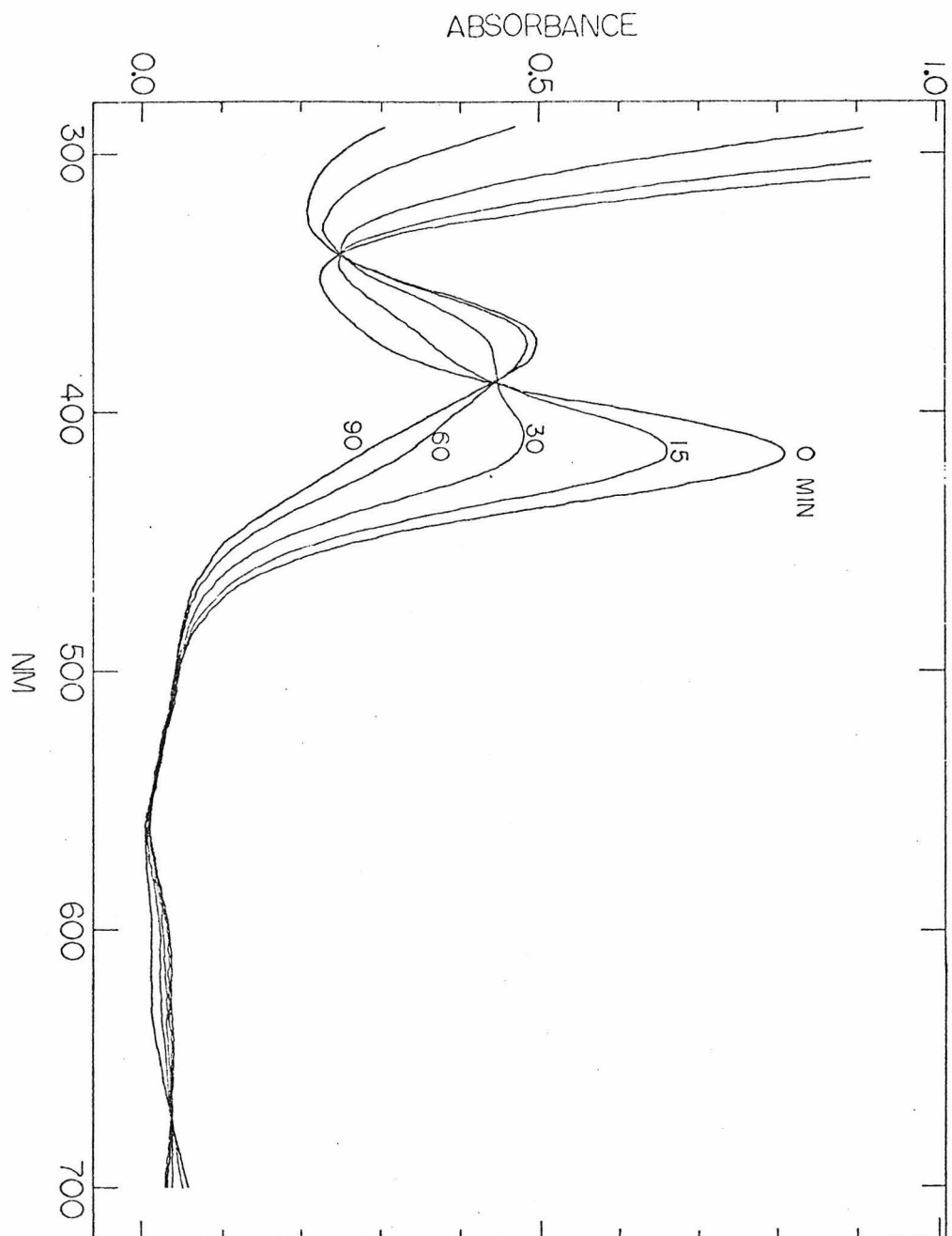
^cThese values assumed identical to those obtained in CH_2Cl_2 .

Figure Captions

- Figure 1. Electronic absorption spectral changes during 254 nm irradiation of $\text{Mo}_2(\text{aq})^{4+}$ in 1 M HSO_3CF_3 solution. Spectral changes were observed to be more complex for concentrations of HO_3SCF_3 less than 0.1 M.
- Figure 2. Electronic absorption spectral changes during 254 nm irradiation of $\text{Mo}_2\text{Cl}_8^{4-}$ in 3 M HCl solution. For the 300-500 nm region spectra for a more concentrated sample are also shown.
- Figure 3. Electronic absorption spectral changes of a 5.84×10^{-3} M solution of $\text{Rb}_3\text{Mo}_2\text{Cl}_8\text{H}$ in 3 M HCl subsequent to mixing. The cell path length was 0.1 cm.
- Figure 4. Electronic absorption spectral changes during 254 nm irradiation of $\text{Mo}_2\text{Cl}_4[\text{P}(\text{Et})_3]_4$ in CH_2Cl_2 .

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