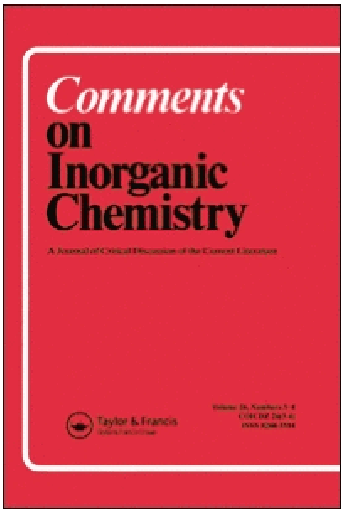

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On the Interpretation of the Electronic Spectra of Complexes Containing the Molybdenyl Ion

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On the Interpretation of the Electronic Spectra of Complexes Containing the Molybdenyl Ion

Assignments of the electronic transitions responsible for the two relatively weak visible-absorption systems in the spectra of tetragonal molybdenyl ions, MoO^{3+}, are considered in the light of available experimental data. Solution spectra of sulfato, phosphato, and chloro molybdenyl complexes as well as studies of the low temperature polarized spectra of $MoOCl_4^-$ in a single crystal establish that the two transitions are ${}^2E(xz, yz) \leftarrow {}^2B_2(xy)$ ($\sim$15 500 cm^{-1}) and ${}^2B_1(x^2 - y^2) \leftarrow {}^2B_2(xy)$ ($\sim$22 500 cm^{-1}).

Oxo complexes play a prominent role in the chemistry of metal ions in high oxidation states. Electronic structural studies of species such as UO_2^{2+}, VO^{2+}, and MoO^{3+} have been numerous, and the ground states of simple complexes of these cations are fairly well understood. Although countless studies have been made, differences of opinion still surface over the interpretation of the electronic absorption spectra of many of these complexes. Our Comment deals primarily with one issue in this area, namely, the interpretation of the spectra of simple complexes of the molybdenyl cation, MoO^{3+}.

Nineteen years ago one of us interpreted the electronic absorption spectrum of $MoOCl_5^{2-}$ based on the assumption that in such an axially compressed tetragonal field the ground state would be ${}^2B_2(xy)$, and the *d–d* excited states would be ordered ${}^2E(xz, yz) < {}^2B_1(x^2 - y^2) < {}^2A_1(z^2)$.[1] Thus the relatively weak bands observed at 14 000 (ϵ 12 M^{-1} cm^{-1}) and 22 500 cm^{-1} (ϵ 14 M^{-1} cm^{-1}) were assigned to the ${}^2E(xz, yz) \leftarrow {}^2B_2(xy)$ and ${}^2B_1(x^2 - y^2) \leftarrow {}^2B_2(xy)$ transitions, respectively. More intense bands were found at 28 000 and 32 500 cm^{-1} in the $MoOCl_5^{2-}$ spectrum, and these were attributed to $\pi O \rightarrow Mo$ charge transfer transitions. There are compelling reasons to reject the $\pi O \rightarrow Mo$ assignments, however, not the least of which is the fact that the electronic spectra of two nonhalo MoO^{3+} species, $MoO(HSO_4)_4^-$ and $MoO(H_2PO_4)_4^-$, do not exhibit intense absorption systems below 35 000 cm^{-1} (Figure 1).[2,3] It is apparent from these observations that $\pi O \rightarrow Mo$

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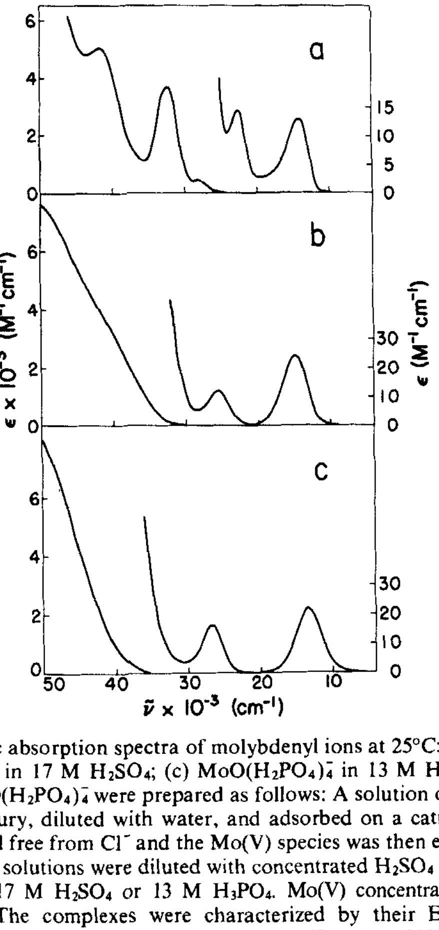

FIGURE 1 Electronic absorption spectra of molybdenyl ions at 25°C: (a) $MoOCl_5^{2-}$ in 12 M HCl; (b) $MoO(HSO_4)_4^-$ in 17 M H_2SO_4; (c) $MoO(H_2PO_4)_4^-$ in 13 M H_3PO_4. The complexes $MoO(HSO_4)_4^-$ and $MoO(H_2PO_4)_4^-$ were prepared as follows: A solution of Mo(VI) in 3 M HCl was reduced with mercury, diluted with water, and adsorbed on a cation exchange column. The column was washed free from Cl^- and the Mo(V) species was then eluted with 1 M H_2SO_4 or H_3PO_4. These Mo(V) solutions were diluted with concentrated H_2SO_4 or H_3PO_4 to yield 10^{-2} M Mo(V) solutions in 17 M H_2SO_4 or 13 M H_3PO_4. Mo(V) concentrations were determined by Ce(IV) titrations. The complexes were characterized by their EPR spectra (Ref. 2): $[MoO(HSO_4)_4]^-$, $g_\parallel = 1.889$, $g_\perp = 1.941$; $[MoO(H_2PO_4)_4]^-$, $g_\parallel = 1.892$, $g_\perp = 1.927$.

charge transfer in MoO^{3+} complexes falls at much higher energies than originally suggested, and that the 28 000 and 32 500 cm^{-1} bands are due to πCl → Mo transitions.

Recent theoretical work by Weber and Garner[4] on $MoOCl_4^-$ has raised the possibility that πCl → Mo charge transfer transitions may fall at lower energies than 28 000 cm^{-1}. $X\alpha$ calculations performed by these authors placed the $^2E(xz, yz) \leftarrow {}^2B_2(xy)$ and $^2B_1(x^2 - y^2) \leftarrow {}^2B_2(xy)$ transitions at 15 600 and 23 300 cm^{-1}, respectively, whereas the lowest πCl → Mo transition ($^2E \leftarrow {}^2B_2$) was predicted at 18 700 cm^{-1}. Weber and Garner concluded that the lowest band in $MoOCl_4^-$ (15 500 cm^{-1}) was indeed $^2E(xz, yz) \leftarrow {}^2B_2(xy)$, but that the second weak feature [peaking at 22 600 cm^{-1} in the spectrum of a crystal of $(Ph_4As)(MoOCl_4)$] was attributable to the lowest πCl → Mo transition ($^2E \leftarrow {}^2B_2$). The evidence offered in Figure 1, however, strongly supports the original $^2B_1(x^2 - y^2) \leftarrow {}^2B_2(xy)$ assignment for the second weak band in the $MoOCl_4^-$ (or $MoOCl_5^{2-}$) spectrum, because analogous absorptions are present in the spectra of $MoO(HSO_4)_4^-$ and $MoO(H_2PO_4)_4^-$. The fact that the $^2B_1(x^2 - y^2) \leftarrow {}^2B_2(xy)$ band appears at slightly higher energy (~26 000 cm^{-1}) in the latter two complexes is entirely consistent with simple theoretical considerations, because the equatorial ligand field generated by four oxygen-donor ligands should exceed that of four chlorides [the observed increase of 3000–4000 cm^{-1} in the $x^2 - y^2/xy$ splitting is in line with the ratio $Dq(O)/Dq(Cl)$ ~1.2 (Ref. 5)]. What is more, the equatorial ligand-field splitting in $MoOCl_4^-$ (or $MoOCl_5^{2-}$), as deduced from the $^2B_1(x^2 - y^2) \leftarrow {}^2B_2(xy)$ assignment of the 22 600 cm^{-1} band, agrees closely with the analogous splitting in $MoCl_6^-$ ($^2E_g \leftarrow {}^2T_{2g}$ at 24 000 cm^{-1}).[6] Thus there is little doubt that the original interpretation of the 22 500 cm^{-1} band in the spectrum of $MoOCl_5^{2-}$ was correct.

We have taken the analysis one step farther by examining the polarized absorption spectra of a single crystal of $(Ph_4As)(MoOCl_4)$ at 5 K (Figure 2). Spectra recorded on the axial face of a tetragonal $(Ph_4As)(MoOCl_4)$ crystal[7] are identical with the σ spectra, indicating that the absorption bands are due to electric dipole transitions. The lowest energy absorption band in the $MoOCl_4^-$ spectrum maximizes near 15 500 cm^{-1} and is strongly, though not completely, xy polarized (i.e., perpendicular to the Mo–O axis). A great deal of vibrational fine structure is observed in both xy and z polarizations, consisting of progressions in 900, 170, and 50 cm^{-1} modes. The former two modes correspond to the totally symmetric Mo–O stretching and O–Mo–Cl bending vibrations, whose energies in the ground electronic state are 1008 and 184 cm^{-1}, respectively.[8] The $^2E(xz, yz) \leftarrow {}^2B_2(xy)$ transition is electric-dipole allowed in xy polarization, but can acquire z polarized intensity via vibronic and spin-orbit coupling mechanisms. In a molecular orbital sense the transition involves the promotion of an electron from π^*(Mo–Cl) to a π^*(Mo–O) orbital. This excitation should be accompanied by an increase in the equilibrium Mo–O bond length, which in turn should decrease the equilibrium O–Mo–Cl bond angle, resulting in the vibrational progressions of 900 and 170 cm^{-1}. Thus the assignment of the observed vibrational progressions to the $^2E(xz, yz)$ state seems secure.

It is apparent from Figure 2 that the $^2E(xz, yz) \leftarrow {}^2B_2(xy)$ band is spilt into two components: one highly structured absorption envelope and an apparently unstructured band at lower energy. Both bands are more intense in xy polarization (the fine structure in the higher energy component, however, is identical in xy and z polarizations). To account for these observations, we propose that the two components are attributable to transitions

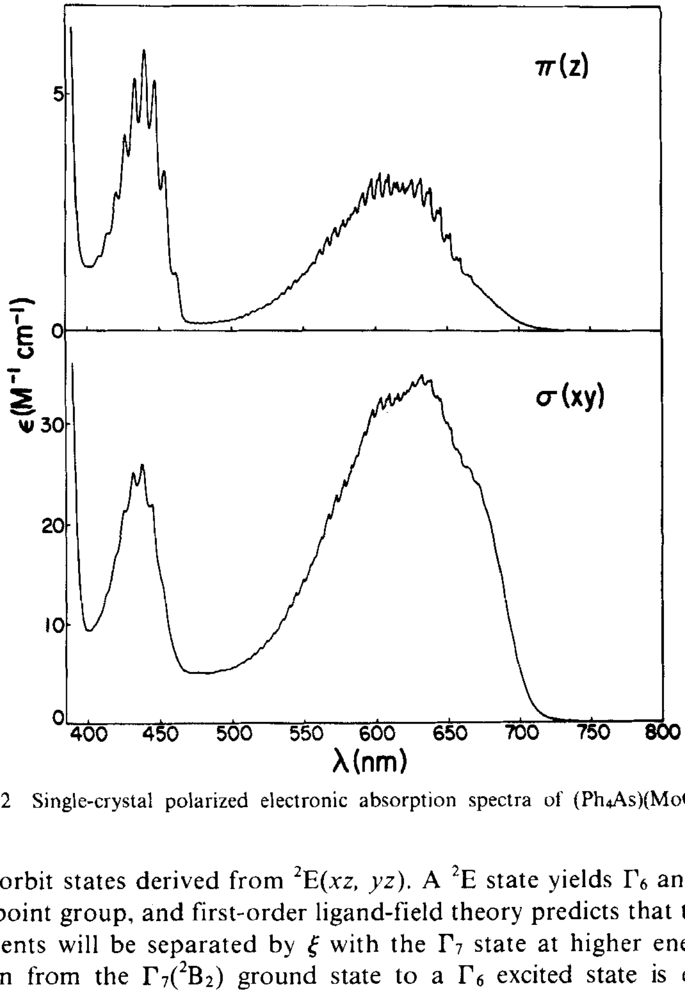

FIGURE 2 Single-crystal polarized electronic absorption spectra of $(Ph_4As)(MoOCl_4)$ at 5 K.

to spin–orbit states derived from $^2E(xz, yz)$. A ^2E state yields Γ_6 and Γ_7 in the C_{4v}' point group, and first-order ligand-field theory predicts that the two components will be separated by ξ with the Γ_7 state at higher energy. A transition from the $\Gamma_7(^2B_2)$ ground state to a Γ_6 excited state is electric-dipole allowed in xy polarization, whereas a transition to a Γ_7 state is allowed in both xy and z. The highly structured component of the 15 500 cm^{-1} absorption system in $(Ph_4As)(MoOCl_4)$ can therefore be assigned to the $\Gamma_7(^2E) \leftarrow \Gamma_6(^2B_2)$ transition, and the lower energy component to $\Gamma_6(^2E) \leftarrow \Gamma_7(^2B_2)$. The progression in ~50 cm^{-1} quanta built on $\Gamma_7(^2E) \leftarrow \Gamma_7(^2B_2)$ probably represents a lattice mode.

As noted earlier, the second weak band peaks near 22 600 cm^{-1} in the single crystal spectrum of $(Ph_4As)(MoOCl_4)$. At low temperature a ~350 cm^{-1} vibrational progression with an apparent origin at 21 780 ± 20 cm^{-1} is resolved in xy polarization. The oscillator strength of this band in xy polarization decreases by approximately a factor of 2 upon cooling the crystal from room temperature to 5 K [$f_{xy}(300\ \mathrm{K}) = 2.9 \times 10^{-4}$; $f_{xy}(5\ \mathrm{K}) = 1.6 \times 10^{-4}$]. The behavior of the band in xy polarization is consistent with a vibronic mechanism in which the $^2B_1(x^2 - y^2) \leftarrow {}^2B_2(xy)$ transition in $MoOCl_4^-$ gains intensity through a promoting mode of e symmetry. A much better resolved vibrational progression of ~350 cm^{-1} is observed in z polarization [$f_z(300$ and $5\ \mathrm{K}) = 3.6 \times 10^{-5}$], but with an origin at 21 680 ± 20 cm^{-1}. The blue shift of the xy relative to the z polarized vibrational components would then correspond to the energy of the vibronic promoting mode in the excited state.[9] Finally, a distortion along the symmetric Mo–Cl stretching coordinate in the $^2B_1(x^2 - y^2)$ excited state is expected, thereby explaining the ~350 cm^{-1} vibrational progression observed at low temperature ($\nu_{Mo\text{-}Cl} = 354\ cm^{-1}$ in the ground state[8]).

Our interpretation of the electronic absorption spectrum of $MoOCl_4^-$ differs from that based on the $X\alpha$ calculation[4] only on the question of the position of the lowest energy charge-transfer band. It is clear from our analysis that excited states from $\pi Cl \rightarrow Mo$ transitions fall above $^2B_1(x^2 - y^2)$, and it follows that the calculated ($X\alpha$) energy for

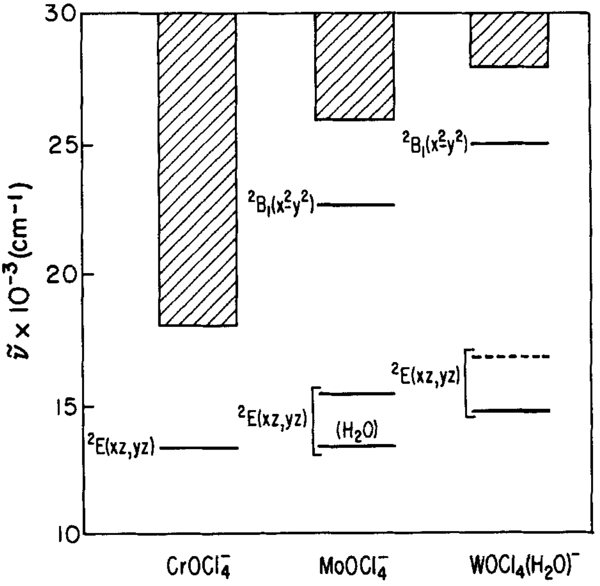

FIGURE 3 Relative energies of selected electronic excited states of $MOCl_4^-$ and $MOCl_4(H_2O)^-$ (M = Cr, Mo, W) complexes. Energies of the $^2E(xz, yz)$ and $^2B_1(x^2 - y^2)$ states refer to absorption maxima in the room temperature spectra of single crystals of $(Ph_4As)CrOCl_4$ (Refs. 4, 10), $(Ph_4As)MoOCl_4$ (this work), $(Ph_4As)MoOCl_4(OH_2)$ (Ref. 11), and a nujol mull of $(Ph_4As)WOCl_4(OH_2)$ (Ref. 12). The dashed line indicates the energy predicted for the $^2E(xz, yz)$ state of $WOCl_4^-$. Shaded areas represent regions of charge transfer absorption.

$^2E \leftarrow {}^2B_2(\pi Cl \rightarrow Mo)$ is too low by several thousand wavenumbers. It is possible that this discrepancy is related to the neglect of two-electron Coulomb repulsion terms in the calculation.

Finally, several points may be made in the general context of *d–d* and charge-transfer excited state energies of closely related oxometal(V) species (Figure 3).[4,10–12] The placement of the $^2E(xz, yz)$ and $^2B_1(x^2 - y^2)$ excited states provides clear evidence for the expected increases in $\pi O \rightarrow M$ and $\sigma Cl \rightarrow M$ bonding interactions in the series 3d < 4d < 5d. The strength of the $\pi O \rightarrow M$ interaction is reflected in the $^2E(xz, yz)$ energy, and two analogous sets of complexes [$CrOCl_4^- < MoOCl_4^-$; $MoOCl_4(H_2O)^- < WOCl_4(H_2O)^-$] follow the expected trend. The limited data on the $^2B_1(x^2 - y^2)$ energy suggest that equatorial σ-bonding interactions are stronger in WO^{3+} than in MoO^{3+} systems. Extension of this comparison to $CrOCl_4^-$ is precluded at the present time owing to the uncertainty in the position of $^2B_1(x^2 - y^2) \leftarrow {}^2B_2(xy)$ in that case. A rough extrapolation based on Figure 3 places the $^2B_1(x^2 - y^2)$ state of $CrOCl_4^-$ in the 18000–20000 cm^{-1} range, which is just above the onset of absorption attributable to $\pi Cl \rightarrow CrO^{3+}$ transitions.

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9. The blue shift of vibronic maxima in *xy* polarization averages 70 cm^{-1}, but varies widely from peak to peak. It is unlikely, therefore, that a single promoting mode is involved ($MoOCl_4^-$ possesses three vibrational modes of *e* symmetry that could give *xy* polarized intensity to a $^2B_1 \leftarrow {}^2B_2$ transition). In addition, spin–orbit mixing of $^2B_1$ *with* ^2E states could lead to temperature independent intensity in *xy* polarization.

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