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L-EDGE SPECTRA of Mo COMPOUNDS & ENZYMES

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To evaluate the utility of L-edge spectrosocopy as a probe of molybdenum enzyme structure, we have recorded (using SSRL Beam Line VI) spectra of a variety of Mo compounds and lyophilized enzyme samples. The observed $d - d$ splittings are compared with optical spectra or calculations for the same Mo complexes and Tc analogues in Table 1.

Table 1 - Mo X-Ray Splittings *vs.* Optical Splittings for Mo Compounds and Tc Analogues

Mo Complex	Tc Analog	Optical Transition or Splitting	Mo Optical Energy (eV)	Tc Optical Energy (eV)	L_3 Splitting (eV)
MoO_4^{2-} d^0	TcO_4^- d^0	$E - T_2$	1.68	2.36	2.48
MoS_4^{2-} d^0	TcS_4^- d^0	$E - T_2$	1.25		1.41
$MoOCl_4^-$ d^1	$TcOCl_4^-$ d^2	$d_{xy} \rightarrow d_{xz,yz}$ $d_{xy} \rightarrow d_{x^2-y^2}$ $d_{xy} \rightarrow d_{z^2}$	1.77 2.80	1.59	1.21 2.83 4.28
$MoOCl_5^{2-}$ d^1	$TcOCl_5^{2-}$ d^2	$d_{xy} \rightarrow d_{xy,yz}$ $dxy \rightarrow d_{x^2-y^2}$ $d_{xy} \rightarrow d_{z^2}$	1.71 2.78	1.32 2.07,2.55	1.21 2.85 4.49

In Figure 1 the orientation dependence of the $L_{2,3}$ edges of a single crystal of $[N(Et)_4][MoOCl_4(H_2O)]$ is illustrated . Three distinct components are visible in the second derivative spectra, and based on analogy with the optical data, they can be assigned in order of decreasing energy as $p \rightarrow d_{z^2}$, $p \rightarrow d_{x^2-y^2}$, and $p \rightarrow d_{xz,yz}$ respectively. For the uppermost transition, the minimum intensity occurs when the $\vec{E}$-vector is parallel to the b-axis. If the d_{z^2} orbital lies along the short Mo - O bond axis, then this is consistent with the tentative assignment, since all the Mo - O bonds in this crystal lie nearly parallel to the ac plane. The orientation dependence of the other transitions also agrees qualitatively with theory. A distinct feature can even be observed in the L_3-edge third derivative for the $p \rightarrow d_{xy}$ transition.

The L_3 edges for active and desulfo xanthine oxidase and sulfite oxidase are compared with model compound spectra in Figures 2a and 2b. For xanthine oxidase, two major features are resolved, whereas for sulfite oxidase four distinct bands are observed. The 1.4 eV active xanthine oxidase splitting is much smaller than the 3.0 eV total splitting for sulfite oxidase. This is consistent with a smaller ligand field with a terminal sulfur as opposed to terminal oxo group. The desulfo xanthine oxidase splitting pattern is similar to that of a dioxomolybdenum compound with roughly octahedral geometry, while the sulfite oxidase profile has some resemblance to a skew trapezoidal Mo complex.

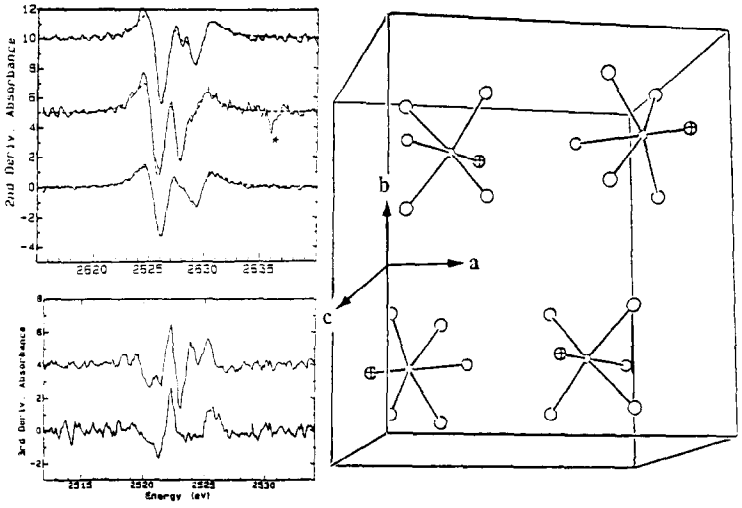

Figure 1: Polarized spectra for a $[N(Et)_4][MoOCl_4(H_2O)]$ crystal. Diffraction peaks are indicated by *. Left panel, top to bottom: L_2-edge 2nd derivative: $\vec{E} \perp c$, $\vec{E} \parallel b, \vec{E} \parallel a$, (—) data and (- - -) best fit. L_3-edge 3rd derivative: $\vec{E} \parallel b, \vec{E} \parallel a$. Right panel, orientation of anions within the unit cell. Oxygen atoms are highlighted.

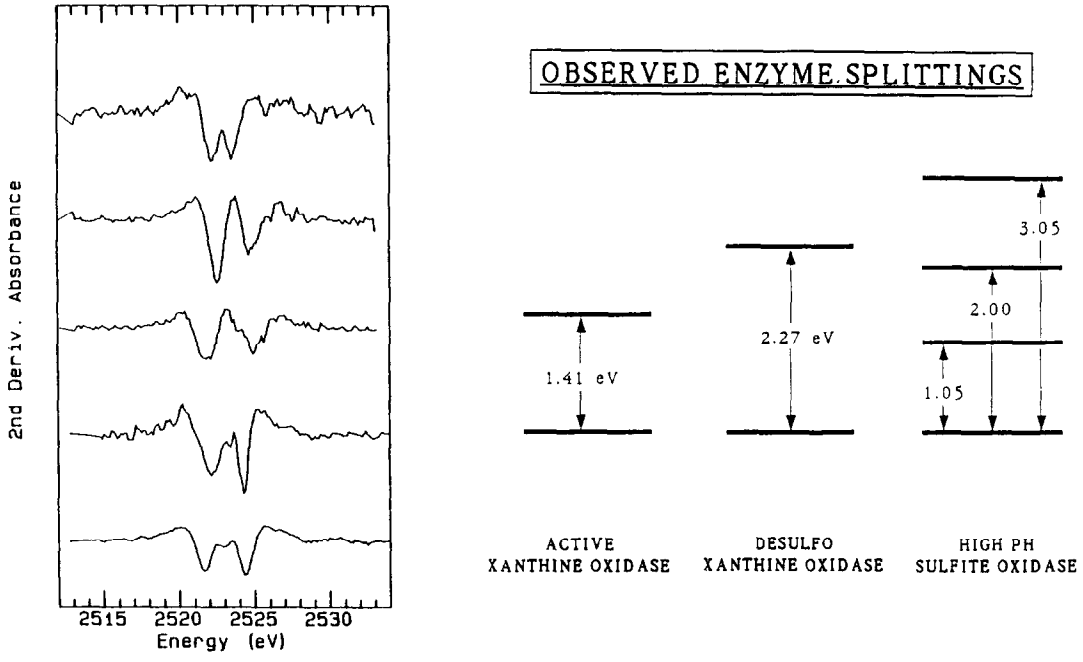

Figure 2: A comparison of L_3 edges for (top to bottom) oxidized active xanthine oxidase, desulfo xanthine oxidase, octahedral model, sulfite oxidase, skew trapezoidal model.

We find that a ligand field approach qualitatively explains Mo L edge spectral features. However, despite the utility of L edge spectroscopy as a fingerprint probe for characterizing metal centers, we do not find good quantitative agreement between x-ray and optical splittings. Presumably, more detailed analysis of the observed splittings has to account for the perturbations by the core-hole as well as d-d interactions.