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Molybdenum X-Ray Absorption Edges from 200 – 20,000 eV, The Benefits of Soft X-Ray Spectroscopy for Chemical Speciation

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Abstract

We have surveyed the chemical utility of the near-edge structure of molybdenum x-ray absorption edges from the hard x-ray K-edge at 20,000 eV down to the soft x-ray M_{4,5}-edges at ~230 eV. We compared, for each edge, the spectra of two tetrahedral anions, MoO₄ and MoS₄²⁻. We used three criteria for assessing near-edge structure of each edge: (i) the ratio of the observed chemical shift between MoO₄²⁻ and MoS₄²⁻ and the linewidth, (ii) the chemical information from analysis of the near-edge structure and (iii) the ease of measurement using fluorescence detection. Not surprisingly, the K-edge was by far the easiest to measure, but it contained the least information. The L_{2,3}-edges, although harder to measure, had benefits with regard to selection rules and chemical speciation in that they had both a greater chemical shift as well as detailed lineshapes which could be theoretically analyzed in terms of Mo ligand field, symmetry, and covalency. The soft x-ray M_{2,3}-edges were perhaps the least useful, in that they were difficult to measure using fluorescence detection and had very similar information content to the corresponding L_{2,3}-edges.

Interestingly, the soft x-ray, low energy (~230 eV) M_{4,5}-edges had greatest potential chemical sensitivity and using our high resolution superconducting tunnel junction (STJ) fluorescence detector they appear to be straightforward to measure. The spectra were amenable to analysis using both the TT-multiplet approach and FEFF. The results using FEFF indicate that the sharp near-edge peaks arise from 3d → 5p transitions, while the broad edge structure has predominately 3d → 4f character. A proper understanding of the dependence of these soft x-ray spectra on ligand field and site geometry is necessary before a complete assessment of the utility of the Mo M_{4,5}-

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Supporting Information

(1) Crystallographic data of Na₂MoS₄ in CIF format.

(2) Additional figures illustrating calculations: (a) TT-multiplet simulations of M_{4,5}-edge pre-edge structure assuming 3d → 4f transitions. (b) FEFF simulations of all MoO₄²⁻ K, L and M edges.

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edges can be made. This work includes crystallographic characterization of sodium tetrathiomolybdate.

Keywords

Molybdenum; XANES; near-edge spectra; XAS; x-ray absorption spectroscopy; soft x-ray spectroscopy; L-edge spectroscopy; M-edge spectroscopy; superconducting tunnel junctions; STJ X-ray detectors; molybdate; thiomolybdate; sodium tetrathiomolybdate; crystal structure

Introduction

X-ray absorption spectroscopy (XAS) has proven to be a powerful tool for diagnosing the structure and chemistry of molybdenum containing materials. It has, for example, played a major part in our understanding of Mo active sites in metalloenzymes ([1-3] and references therein), been extensively applied to catalyst systems, especially MoS₂-based hydrodesulfurization catalysts [4], and provided insights into Mo-based industrial materials [5]. This variety of applications has arisen because XAS is one of the few techniques that can provide both structural details and electronic information on metal coordination sites under almost any experimental condition: it is straightforward to examine concentrated or dilute samples, crystalline or amorphous materials, molecular gases, liquids or frozen solutions. XAS provides structural information through analysis of the extended x-ray absorption fine structure (EXAFS) region, which is the oscillating part of the XAS spectrum that extends above the absorption edge. An EXAFS study allows the determination of the number, distance and element of neighboring atoms with respect to the absorbing atom as well as the thermal or structural disorder of their positions. Indeed, EXAFS is often the only practical way to study the arrangement of atoms in materials where traditional diffraction techniques cannot be used because they have no long-range order. The extensive literature employing Mo K-edge EXAFS is a testament to the success of the technique ([1-5] and references therein).

A less commonly appreciated, but nevertheless valuable part of the XAS spectrum is the near-edge region (also known as the x-ray absorption near-edge structure or XANES), which comprises about a 30 eV span immediately before the absorption edge. This region contains transitions to bound states and thus provides spectra that can be interpreted in terms of electronic structure and oxidation state. However, the ease of observation and information content of the near-edge region critically depends upon whether the observed transitions are formally allowed and whether or not they involve the valence orbitals. For example, the K-edge spectra of the *p*-block element sulfur comprise allowed $1s \rightarrow 3p$ transitions to bonding and antibonding *p* orbitals, and these spectra can therefore be readily interpreted in terms of the sulfur chemical environment [6,7]. In contrast, the first row transition metals coordinate through *3d* orbitals. Hence their K-edges exhibit relatively weak and uninformative near-edge spectra as $1s \rightarrow 3d$ transitions are formally dipole forbidden. However, the L_{2,3}-edges of first transition metals comprise dipole allowed $2p \rightarrow 3d$ transitions, which are intense and structured and which exhibit changes with oxidation state and significant magnetic x-ray circular dichroism. These spectra can be analyzed to yield chemically useful information such as ligand field, site symmetry, spin-state and covalency [8,9].

Molybdenum is a second-row transition metal, and hence there are a number of edges available as potential probes of the Mo chemical status. Perhaps easiest to measure are the Mo K-edges which are found in the x-ray region at approximately 20,000 eV. For these, the near-edge structure arises from dipole forbidden $1s \rightarrow 4d$ transitions, and thus, apart from a much smaller quadrupole contribution, the strength of any pre-edge structure is proportional

to the amount of Mo p - d mixing in the lowest empty orbital. The Mo L_1 -edge, at about 2866 eV, is the $2s$ analogue of the Mo K-edge and has a similar information content. By contrast, the Mo L_2 and L_3 -edges, which occur around 2626.0 eV and 2523.2 respectively, comprise dipole allowed $2p \rightarrow 4d$ transitions. These have been measured for a number of systems including selected Mo enzyme systems [10,11] and related model compounds (for example, [12]) and they have been shown to be sensitive to the ligand field about the Mo as well as the Mo oxidation state.

Perhaps the most interesting are the higher order M-edges. Apart from the relatively uninformative M_1 -edge which, like the L_1 -edge is the $3s$ analogue of the K-edge, there are the $M_{2,3}$ -edges which arise from allowed $3p \rightarrow 4d$ transitions and the $M_{4,5}$ -edges which comprise transitions from the $3d$ shell. These edges have been little studied and their chemical sensitivity and ease of measurement is not well established. Calculations, however, have shown that the $M_{4,5}$ -edges in particular may possess low natural linewidths [13], and if they have a relatively large chemical shift this could make them good potential probes of electronic structure and oxidation state.

Measurements of Mo M-edges are technically challenging. The Mo $M_{2,3}$ and the Mo $M_{4,5}$ -edges occur at around 400 eV and 230 eV respectively, both well within the so-called “soft” x-ray region (< 2000 eV). Soft x-rays have a short pathlength in most materials, including air, which necessitates the use of ultra-high vacuum chambers and windowless sample handling. In addition, the region is crowded with the light element (B, C, N, O, F) K-edges, and this raises a real possibility that the Mo spectrum will be obscured. A further problem is the relatively low fluorescence yield of these edges [14,15]. It is well established that many XAS measurements on a “real-world” dilute material require energy-discriminating fluorescence detection. The technically more straightforward electron-yield measurements are not only limited by the high electron cross-section to the surface of any sample, but they also often contain large distorted background contributions due to the absorption of adjacent edges and charging effects which limit both the precision of the measurements and the ability to obtain spectra from materials that are dilute in the absorbing atom. Unfortunately, the low reported fluorescence yields of Mo M-edges, $\sim 3.5 \times 10^{-3}$ for the $M_{4,5}$ -edges and $\sim 2.0 \times 10^{-4}$ for the $M_{2,3}$ -edges [14,15], raises the possibility that fluorescence detection is statistically unfeasible or likely to be obscured by adjacent edges. However, over the past decade, there have been considerable advances in soft x-ray fluorescence detector technologies and these include development of high-resolution superconducting tunnel junction (STJ) detectors [16,17] that facilitate the measurement of near-edge spectra from these higher order edges on relatively dilute materials. In short, M-edges have become experimentally accessible and are potentially useful probes of Mo environment. While calculations concerning the energy, fluorescence yield and other physics of the Mo M-edges have been performed, experiments are needed to determine both the utility and ease of measurement of these edges and whether they can be used to study dilute samples such as metalloproteins.

In this paper, we survey the interaction of Mo with x-rays, from the K-edge at 20,000 eV to the M_5 edge at ~ 228 eV. For a XAS experiment on a dilute Mo sample, such as a metalloprotein, the factors that need to be considered include the ratio of Mo cross-section to background cross-section, the Mo fluorescence yield, the Mo edge natural linewidth, and the ratio of chemical shift range to linewidth. We use spectra obtained from various salts of the molybdate (MoO_4^{2-}) and tetrathiomolybdate (MoS_4^{2-}) anions to illustrate how these properties change for x-ray absorption edges over nearly two orders of magnitude in binding energy in order to help illustrate some general trends for x-ray spectra. In order to facilitate measurements in the soft x-ray region, we chose to use the sodium salts of both anions, and we hence prepared and crystallographically characterized Na_2MoS_4 . Finally, we comment

on the ease of measurement for each edge and outline the potential of the various edges, in particular the M-edges, as probes of Mo chemical environment.

Experimental

XAS Sample Preparation

$\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$ and $(\text{NH}_4)_2\text{MoS}_4$ were purchased from Sigma-Aldrich and stored sealed in an anaerobic dry box until use. Na_2MoS_4 was prepared as described below.

K-edge measurements employed either ~ 2 mM solutions frozen in $3 \times 10 \times 10$ mm acrylic cuvettes or finely ground powders diluted with an appropriate quantity of boron nitride pressed into 1 mm sample holders sealed with Mylar tape. L-edge measurements were prepared as finely ground powders mixed with graphite and dusted onto Mylar tape. The soft x-ray M-edge samples were prepared as finely ground powders spread on carbon adhesive tape and then sealed inside a capped sample-holder for transfer into the vacuum chamber as described elsewhere [18].

Preparation and Crystallography of Na_2MoS_4

Orange-red Na_2MoS_4 was prepared according to the method described by Laurie et al [19]. A solution of $(\text{NH}_4)_2\text{MoS}_4$ in an ice cold solution of NaOH (0.85 g) in water (10 mL) was stirred and cooled in ice for 2 h under a vacuum generated by a Schlenk line vacuum pump. The mixture was then stirred at room temperature under vacuum until dry. The solid formed was extracted with acetone (ca. 30 mL) and filtered to remove insoluble material. Addition of ether to the filtrate precipitated red crystals of product. Samples were recrystallized three times from acetone/ether.

The X-ray crystal structure was obtained from black-red single crystals of Na_2MoS_4 prepared by allowing ethanol to diffuse into a solution of the compound in water. Intensity data were collected on a Bruker SMART Apex CCD detector using graphite monochromatized Mo $K\alpha$ ($\lambda = 0.71073 \text{ \AA}$) radiation. A single black-red crystal of dimensions $0.3 \times 0.4 \times 0.45 \text{ mm}^3$ was mounted on a glass fiber and transferred to the goniometer for data collection. The crystal was cooled to 130(2) K under a cold nitrogen gas stream. Data were reduced using the program SAINT [20]. The structure was solved by direct methods (SHELXTL) and difference Fourier syntheses. Absorption corrections were made using the program SADABS [20]. The structure was refined by full-matrix least-squares on F^2 . Thermal ellipsoid plots were generated using the program ORTEP-3 [21] integrated within the WinGX [22] suite of programs. Main crystallographic data: Na_2MoS_4 , $M = 270.16$, orthorhombic, space group $Pnma$, $a = 9.5832(6) \text{ \AA}$, $b = 6.9550(5) \text{ \AA}$, $c = 12.2258(8) \text{ \AA}$, $V = 814.86(9) \text{ \AA}^3$, $Z = 4$, number of reflections = 1010, number of unique reflections = 975, $2\theta_{\text{max}} = 55.14^\circ$, $R1 = 0.0418$, $wR2 = 0.095$, $GOF = 1.092$.

XAS Measurements

Mo K-edge x-ray absorption data were measured at Stanford Synchrotron Radiation Laboratory (SSRL) beamline 9-3, with a Si(220) double-crystal monochromator and two rhodium-coated mirrors: one flat premonochromator mirror for harmonic rejection and vertical collimation and one toroidal postmonochromator mirror for focusing. Fluorescent x-rays were measured using a 30-element Ge fluorescence detector (Canberra Industries), fitted with Soller slits and a Zr filter to minimize the relative contribution of scattered radiation. An Oxford Instruments CF1208 liquid helium cooled sample cryostat was used to maintain the sample temperature at 9K. The x-ray energy was calibrated using the first and major inflection point of a standard Mo foil, measured at the same time as the sample

spectrum using two ion chambers positioned downstream of the cryostat. The Mo K-edge structure and position were monitored to ensure that no x-ray photochemistry occurred.

Mo L-edges were measured using SSRL beamline 6-2 using a Si(111) monochromator and a bent-flat nickel coated mirror to reject harmonics. Samples were maintained in an atmosphere of helium to minimize attenuation of the X-ray beam, and commercial electron yield and Ar-filled fluorescence ion chamber detectors (EXAFS Co. Pinoche NV) were used. The x-ray energy was calibrated by separate measurements of the sulfur K-edge of a finely powdered sodium thiosulfate sample and assuming the initial maximum to be at 2469.2 eV.

Mo M-edge spectra were recorded using the soft x-ray undulator beamline 4.0.2 at the Advanced Light Source (ALS). This beamline uses a variable included angle grating monochromator and a vertical focusing mirror as detailed elsewhere [23]. Samples were mounted on a liquid helium cooled cold finger (Janis Research, Wilmington, MA) in UHV vacuum chamber. Electron yield detected x-ray absorption spectra were recorded using a CEM4716 channeltron electron multiplier (Burle Electrooptics, Sturbridge, MA). Fluorescence detected x-ray spectra were measured using a 9 or 36-element superconducting tunnel junction (STJ) detector array [16,17]. A complete fluorescence spectrum was collected for each detector element and for each incident energy data point, allowing optimization of the fluorescence energy windows after data collection. Fluorescence spectra were energy calibrated by reference to the C and O K-edge fluorescence at 277.0 and 524.9 eV respectively. Absorption spectra were normalized to the incident radiation intensity measured either by using the photocurrent from a gold mesh or, optionally the integrated intensity of the carbon fluorescence peak. Energy calibration measurements for the $M_{2,3}$ spectra were performed assuming the second, more intense M_3 peak of $\text{NaMoO}_4 \cdot 2\text{H}_2\text{O}$ to be 397.3 eV as well as using the pre-edge peak of boron nitride at 401.5 eV or the first pre-peak of $\text{K}_3\text{Fe}^{\text{III}}(\text{CN})_6$ at 399.85 eV. $M_{4,5}$ spectra were calibrated by fixing the M_5 peak of $\text{NaMoO}_4 \cdot 2\text{H}_2\text{O}$ at 231.0 eV. When used, standard spectra were measured immediately before and after each Mo M-edge measurement. Samples were measured either at room temperature or at ~ 130 K; using temperatures below this limit caused interference from frozen N_2 . For the electron yield data, appropriate corrections usually had to be made for baseline offsets arising from a combination of light-element x-ray absorption and charging effects. By contrast, the high energy discrimination of STJ detector meant that fluorescence detected data required no baseline correction.

XAS Calculations

The energies of the K, L and M-edges were determined by using the centroid of the full-width half-maximum area of the pre-edge peak as illustrated in the supporting information.

L-edge and M-edge spectra were simulated using the TT-multiplet simulation program [24]. For the $L_{2,3}$ -edges the calculation described the electronic transitions from the $\text{Mo(VI)} 2p^6 4d^0$ ground state to $2p^5 4d^1$ (the intermediate filled orbitals we excluded for clarity). For the $M_{2,3}$ -edges the transitions from a $3p^6 4d^0$ ground state to a $3p^5 4d^1$ excited state were used, while for the $M_{4,5}$ -edges the ground state used was $3d^{10}$ and transitions to both $3d^9 5p^1$ as well as $3d^9 4f^1$ excited states were each investigated. First, coulomb and exchange interactions and spin-orbit interactions were calculated for both the initial and final states. Atomic multiplets were used to account for the ground and final state electronic spin-orbit L–S interactions and the final state core hole J–J coupling. The *ab initio* Hartree-Fock values of Slater integrals and spin-orbit coupling were used as tabulated values, and charge transfer and electron correlation effects were accounted for by reducing the Coulomb and exchange integrals. For the $L_{2,3}$ and $M_{2,3}$ edges a T_d crystal field was included which split the $4d$ orbitals into t_2 and e classes with an energy difference of $10Dq$. In addition, ligand-

to-metal charge-transfer (LMCT) contributions producing final state configurations $4d^1\bar{L}$, (where $\bar{L}$ represents a ligand based electron hole) were considered for these edges by performing additional monopole calculations for the initial (between Np^64d and $Np^64d^1\bar{L}$, where $N = 2$ or 3 for the $L_{2,3}$ and $M_{2,3}$ -edges respectively) and the final (between Np^54d^1 and $Np^54d^2\bar{L}$) states, with an energy difference Δ . For the comparison with the experiment, the lifetime broadening of the core hole and the resolution of the spectrometer were accounted for with Lorentzian and Gaussian lineshapes respectively. An arbitrary energy correction was included to align the experimental and calculated spectra.

Calculations were also performed using the program FEFF 8.40 [25,26]. Unlike the TT-multiplet, this approach does not sum individual transitions but instead uses an *ab initio* full multiple scattering formalism, based on self-consistent muffin-tin potentials. We note that the calculation is currently limited to the continuum spectrum beyond the Fermi level. As a result, bound states are not generally included, however, in molecules, weakly bound states that are below the vacuum but above the muffin-tin zero will show up as resonances. The calculations presented here used crystallographic coordinates restricted to a single MoO_4^{2-} or MoS_4^{2-} anion.

Results

Crystal Structure of Na_2MoS_4

In this work we compare spectra for various salts of MoO_4^{2-} and MoS_4^{2-} anions to determine chemical shifts for each Mo x-ray edge, and as it is known that the *d*-level splittings of molybdates can vary with anion geometry [27] it is important to ensure the salts used in this study are essentially isostructural. For MoO_4^{2-} , the structure of the anion in $\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$ is well known to be tetrahedral [28]. For MoS_4^{2-} the ammonium salt [29,30] has been structurally characterized and, along with the heavier Group 1 salts, M^I_2MoS_4 ($\text{M}^I = \text{K}^+$ [31], Rb^+ [32], Cs^+ [33]), shown to adopt the β - K_2SO_4 structure [34] with discrete cations and tetrahedral tetrathiomolybdate anions. Other MoS_4^{2-} compounds including NEt_4^+ [35], polyammonium [36-42] and metal-complex [43,44] salts, have also been structurally characterized, the polyammonium salts exhibiting extended $\text{N-H}\cdots\text{S}=\text{Mo}$ hydrogen bonded structural motifs. However, neither the structure of the Na_2MoS_4 salt used here for the soft x-ray work, nor the related light Group 1 Li salt, have been reported.

The crystal structure of Na_2MoS_4 confirms that the compound is isostructural to the ammonium and heavier Group 1 salts. A view of the structure is shown in Figure 1. It consists of isolated Na^+ cations and discrete MoS_4^{2-} anions. The Mo atom is tetrahedrally coordinated by four terminally bonded sulfido ligands with Mo-S distances in the range 2.172(1)–2.193(2) Å and S-Mo-S angles in the range 108.14(8)–110.47(8)°. These distances and angles are consistent with those found in other salts containing the MoS_4^{2-} complex. The compound contains two crystallographically unique Na^+ cations, both of which are encircled by an irregular polyhedron of sulfur atoms. Atom Na(1) is surrounded by nine sulfur atoms from six symmetry related MoS_4^{2-} ions, with $\text{Na}\cdots\text{S}$ distances ranging from 3.25–3.54 Å. Atom Na(2) is surrounded by eight sulfur atoms from five $[\text{MoS}_4]^{2-}$ anions, with $\text{Na}\cdots\text{S}$ distances in the range 3.50–3.64 Å, with two longer $\text{Na}\cdots\text{S}$ interactions at 3.92 Å. The compound is isostructural with other simple tetrathiomolybdate salts, $\text{M}^I_2[\text{MoS}_4]$ ($\text{M}^I = \text{NH}_4^+$, [29,30] K^+ [31], Rb^+ [32], Cs^+ [33]) with all compounds adopting the β - K_2SO_4 structure. The linear relationship between the sum of the ionic radii of the component elements and the unit cell volume, observed by Gattow and Franke [45] and Müller and Sievert [46,47] for compounds of this general type, does not extend to Na_2MoS_4 . The sizable thermal parameters for the Na^+ ions and the $\text{Na}\cdots\text{S}$ distances, that exceed the sum of the ionic and van der Waals radii of Na^+ and sulfur, respectively, suggest that the

Na⁺ ions occupy oversized voids in a structure comprised of closely packed tetrathiomolybdate anions.

Survey of X-ray Near-Edge Spectra

Figure 2 summarizes the available x-ray absorption spectra for MoO₄²⁻ and MoS₄²⁻ as a function of the edge. In this figure we have aligned each spectrum relative to the measured centroid energy (E') of the pre-edge peak. These energies are summarized in Table 1. We have omitted L₁ and M₁ edges, since these edges are similar to the K-edge, with broad pre-edge features but also with much smaller fractional edge-jumps, the worst possible combination of properties. Leaving aside the obvious observation that the higher order edges occur at lower energies, some clear trends are apparent. First, the linewidths are substantially reduced with higher edge orders, the splitting of the L and M_{2,3}-edges is greater for MoO₄²⁻ compared to MoS₄²⁻ and for both anions, the sharp M₄ and M₅-edges do not show any significant splitting pattern. We now consider the properties of each edge in detail.

K-edge Spectra

Figure 2 shows that a broad pre-edge peak dominates both Mo K-edges. K-edges originate at the *1s* level, and by the dipole selection rule, the final state has to have *p* symmetry. Thus, apart from a very small quadrupole contribution, the strength of this pre-edge feature is proportional to the amount of Mo *p-d* mixing in the lowest unoccupied orbital. Detailed calculations of MoO₄²⁻ and MoS₄²⁻ K-edges have been reported elsewhere so we limit ourselves here to noting that both pre-edge peaks have a broad linewidth of around 5.5 eV (FWHM), which is in good agreement with the expected natural linewidth of 4.5 eV [13]. In addition, the observed chemical shift of these peaks between the MoO₄²⁻ and MoS₄²⁻ is 3.70 eV. We note that this is significantly smaller than the 7.60 eV chemical shift observed for the first inflection point of the K-edge.

L-Edge Spectra

The L₃ and L₂ edges for MoO₄²⁻ and MoS₄²⁻ are shown in Figure 3, along with simulations using the TT-multiplets package with parameters given in Table 2. Both of these edges show a split main peak that corresponds to a *2p* → *4d* transition to the empty valence orbitals of the tetrahedral ion. Despite the limitations of a ligand field model for such covalent complexes, the splittings used in the simulations, 2.0 and 1.3 eV respectively, agree with previous observations [11] and correspond reasonably well to values predicted from uv-visible spectra; 1.68 and 1.25 eV respectively [48,49]. Similarly the measured linewidths for MoO₄²⁻ average 2.2 eV for both edges, which is consistent with the expected natural linewidths of 1.69 eV for the L₃ edge and 1.83 eV for the L₂-edge. We estimate the MoO₄²⁻ to MoS₄²⁻ chemical shift for both edges to be very similar at 2.40 eV for the L₃-edge and 2.35 eV for the L₂.

M-Edge Spectra

The M₃ and M₂ edges MoO₄²⁻ and MoS₄²⁻ are shown in Figure 4, along with simulations using the TT-multiplets package with parameters given in Table 2. Unlike the K and L-edge spectra, these data were recorded using total electron yield, and a substantial arbitrary background has been subtracted from each spectrum. The M₃ and M₂ edges occur at ~ 400 eV and are separated by approximately 17 eV and are thus sufficiently close in energy so that they are routinely measured together. A major technical issue in measuring the M_{2,3}-edges is the proximity of the nitrogen K-edge, which is found between the two M-edges at a nominal 409.9 eV and can thus obscure the Mo M₂-edge. For this reason, the MoS₄²⁻ M-edge measurements employed Na₂MoS₄ instead of the commercially available ammonium

salt. The $M_{2,3}$ -edges are visually similar to the corresponding L-edges, with both M-edges showing split main peaks that reflect transitions with $3p \rightarrow 4d$ character. As with the L-edges, the splittings used in the simulations, 2.0 and 1.3 eV respectively, correspond reasonably well to values predicted from uv-visible spectra [48,49]. Similarly, the measured linewidths suggested by the TT-multiplet calculations (Table 2) are similar to the expected 2.1 eV [15]. The MoO_4^{2-} to MoS_4^{2-} chemical shifts are less than the corresponding L-edges at 2.25 eV for the M_3 -edge and 2.08 eV for the M_2 -edge.

The M_5 and M_4 edge spectra for MoO_4^{2-} and MoS_4^{2-} together with their TT-multiplet simulations are also shown in Figure 4 with simulation parameters in Table 2. Again these spectra were recorded using total electron yield, and a substantial arbitrary background was subtracted from each spectrum. These edges occur close together slightly above 200 eV, a low energy region that chemists rarely investigate. However, the spectra in this region have some valuable properties that merit further investigation. In particular, the calculated natural M_5 linewidth is reported to be only ~ 0.12 eV, about 40-fold sharper than the K-edge [13].

Our measurements show that both $M_{4,5}$ -edges have sharp unsplit main peaks with linewidths significantly broader than the calculated values at ~ 0.4 eV. The MoO_4^{2-} spectrum reproducibly shows an asymmetric lineshape. The MoO_4^{2-} to MoS_4^{2-} chemical shifts are larger than both the $M_{2,3}$ and the $L_{2,3}$ -edges, with 2.54 eV for the M_5 -edge and 2.64 eV for the M_4 -edge. The large ratio of chemical shift to natural linewidth suggests that the $M_{4,5}$ -edges will be the most sensitive region for determination of the Mo electronic structure and for the characterization of mixtures, even without ligand field splitting information. This lack of any significant splitting is consistent with an assignment to $3d \rightarrow 5p$ character, as a tetrahedral field does not split the $5p$ level. However, we note that for other geometries the ligand field produces a p -splitting that could well be much larger than the natural line width. It is important to point out that TT-multiplet analysis does not rule out the alternative assignment to $3d \rightarrow 4f$ transitions (see, for example Table 2 and Figure S1). This will be addressed further in the discussion.

Measurement of M-edges using Fluorescence Detection

Monitoring the intensity of fluorescence subsequent to x-ray absorption is a well-established method of measuring x-ray spectra, particularly for materials dilute in the absorbing atom. With regard to the Mo M-edges, we note that the reported fluorescence yields for the $M_{4,5}$ -edges at 3.5×10^{-3} , while low, are not unreasonable for a fluorescence detected measurement. By contrast, those for the $M_{2,3}$ -edges are more than an order of magnitude smaller at $\sim 2 \times 10^{-4}$, making measurement of these edges potentially a much more difficult proposition. Moreover, as all these M-edges occur in the crowded soft x-ray region there is potential for interference from fluorescence from many other elements, especially the light element K-edges. Hence, a high-resolution energy discriminating detector is essential to isolate the various Mo fluorescence regions.

Figure 5 shows example soft x-ray fluorescence spectra recorded of MoO_4^{2-} using our high-resolution (~ 15 eV FWHM) STJ fluorescence detector [16,17]. These spectra were measured as a consequence of our fluorescence detected XAS data collection and in order to achieve good signal-to-noise the incident x-ray energy is averaged over a span of several eV. In the figure, the average incident x-ray energy of each spectrum has been chosen to illustrate the change in the x-ray fluorescence as a given x-ray edge is scanned. Figure 5a shows spectra recorded during a $M_{2,3}$ -edge scan with incident energies immediately below both edge peaks (378 – 391.2 eV), at the M_3 -edge peaks (392.6 – 399.8 eV) and at the M_2 -edge peak (409.8 – 417.0 eV). Figure 5b shows analogous spectra recorded during a $M_{4,5}$ -edge scan; immediately below the $M_{4,5}$ -edge peak (225.8 – 228.8 eV), averaged over the M_4 -edge peak (232.9 – 235.9 eV) and significantly above the $M_{4,5}$ -edge peaks (246 – 258

eV). We note that inspection of Figure 5 clearly demonstrates the crowded nature of this region of the x-ray spectrum, with a small adventitious C K-edge fluorescence as well as an O K-edge peak, both indicating the presence of harmonics in the incident x-ray beam.

There are clearly three Mo fluorescence windows suitable for detection of x-ray spectra and these are indicated on Figure 5 by grayed boxes denoted Mo_a, Mo_b and Mo_c. Mo_a, observed at ~ 194 eV, is most likely dominated by the M_{4,5} $5p \rightarrow 3d$ fluorescence, while Mo_b and Mo_c at ~ 335 eV and ~ 398 eV probably arise from $4s \rightarrow 3p$ and M_{4,5} $4d \rightarrow 3p$ transitions respectively. Not surprisingly, Mo_a is the only Mo fluorescence observed during M_{4,5}-edge and this exhibits substantial change in intensity concomitant with M_{4,5} absorption measurements (Figure 5b). By contrast, for the Mo_{2,3}-edge spectra all three Mo fluorescence windows show changes across the absorption bands. Interestingly, significant changes in lineshape are apparent within Mo_b and Mo_c windows on scanning the Mo M₃ and Mo M₂ bands, indicating that irradiation at the M₂-edge produces a distinct fluorescence spectrum from the M₃-edge which includes significant fluorescence from the 3p_{1/2} initial state. Surprisingly, the biggest intensity changes on scanning the M_{2,3}-edges are seen within the Mo_a window, indicating the presence of substantial Coster-Kronig transitions. In fact, it is clear from Figure 5 that the Mo_a fluorescence is by far the strongest observed Mo M-fluorescence band, especially as the transmittance of the infrared absorbing windows on our STJ detector at 200 eV is 20% of the transmittance at 400 eV. Hence, the relative fluorescence intensity at Mo_a compared to Mo_b and Mo_c is about 5 times greater than suggested by Figure 5.

The Mo_{2,3}-edge x-ray absorption spectra of solid Na₂MoO₄•2H₂O recorded using each of the Mo fluorescence windows are compared in Figures 6a-c and the M_{4,5}-edge spectrum measured using the Mo_a fluorescence window is presented in Figure 7. To our knowledge these data represent the first fluorescence detected Mo M-edge spectra to be reported. It is instructive to compare these spectra with the electron yield data in Figure 4. First we note that, unlike the electron yield spectra, no arbitrary background has been subtracted from these data. All three windows give good Mo_{2,3}-edge spectra, however the lineshapes of the spectra from Mo_b (Figure 6c) and Mo_c (Figure 6b) appear distorted, particularly at the M₃-edge. This may be due to fluorescence saturation effects that may well become less apparent at lower Mo concentrations. The spectrum from Mo_c is offset compared to that from Mo_b. While the origin of this is unclear, it is important to note that this window also contains the N K-edge fluorescence at 392.4 eV, suggesting that this window is not useful in any nitrogen containing sample as any N K-fluorescence will almost certainly overwhelm the much weaker Mo contribution. The largest change in absolute count-rate was measured using the Mo_a window (Figure 6a). However, despite the high count-rate, this spectrum has increased noise arising from inherent offset from the Mo_{4,5} fluorescence; we observe a signal-to-background ratio of 0.22 in Figure 6a compared to 1.7 in Figure 6c. In addition, when comparing this spectrum to the electron-yield data in Figure 3 and the other two fluorescence spectra, it is clear that the M₃-edge intensity is reduced compared to the M₂-edge. While this may arise from fluorescence saturation effects that should be reduced at lower Mo concentrations, it may well arise from different Coster-Kronig efficiencies for the M₂ and M₃ final states.

Figure 7 shows the M_{4,5}-edge spectrum of solid Na₂MoO₄•2H₂O recorded using the Mo_a fluorescence window. It is clear from comparing the partial fluorescence yield spectrum Figure 7a with the electron-yield data in Figure 4 that fluorescence detection produces good quality M_{4,5}-edge spectra. Figure 7b shows the full M_{4,5}-edge region showing that the observed pre-edge peaks have a relatively low intensity compared to the overall edge-jump. That this edge-jump is a real part of the M_{4,5}-spectrum is apparent from the dramatically increased Mo_a fluorescence at energies above the M₄-edge apparent in Figure 5b and Figure

6a. The broad edge-jump was not observed using electron-yield as it was impossible to distinguish it from the substantial background contributions.

As TT-multiplets cannot simulate continuum structures, we used the multiple scattering program FEFF to calculate the MoO_4^{2-} $M_{4,5}$ -edge, and the results are shown in Figure 7. Unlike the TT-multiplet, this approach does not sum individual transitions but instead uses an *ab initio* full multiple scattering formalism. We note that FEFF calculations provide good simulations of the MoO_4 K and $L_{2,3}$ -edges, and for the $M_{2,3}$ -edges the simulations are also good, however, the spectra are broadened so the d-orbital splitting is not resolved (Figure S2 in the supporting information). For the $M_{4,5}$ -edges, FEFF provides a reasonable simulation of the both edge region (Figure 7b) and pre-edge peaks (Figure 7a), although the simulated resonances are weaker and broader than the observed bands.

As FEFF gives a reasonable simulation of the $M_{4,5}$ -edges it can be used to provide an assignment of the main features of the $M_{4,5}$ -edge spectrum. $M_{4,5}$ transitions originate from the $3d$ level and hence both $3d \rightarrow 5p$ or $3d \rightarrow 4f$ transitions are allowed. FEFF allows separate calculations for these two cases and the results are shown in Figure 7. It is clear from Figure 7a that the sharp resonances arise largely from $3d \rightarrow 5p$ transitions, with only a small contribution from f -states, while Figure 7b shows that the bulk of the broad edge region arises from $3d \rightarrow 4f$ transitions with only limited p -character. We note that much greater intensity of the f -character relative to the p -character is consistent with TT-multiplet calculations of the transition cross sections, which are achieved by multiplying the relevant matrix element by the number of vacancies in the final state level. These suggest that the total transition intensity for a $3d \rightarrow 5p$ transition should be about 2.3% of the $3d \rightarrow 4f$ value.

Discussion

In this paper we are comparing the utility of the pre-edge structure of the various Mo x-ray edges as probes of Mo chemical environment. To this end, we have measured the hard x-ray K and $L_{2,3}$ -edges as well as the soft x-ray $M_{2,3}$ and $M_{4,5}$ -edges of the tetrahedral anions, MoO_4^{2-} and MoS_4^{2-} . For each edge we have measured the chemical shift between molybdate and tetrathiomolybdate and estimated the observed linewidth. We also have simulated these data using both TT-multiplet and FEFF approaches. Finally, we have examined the fluorescence properties of Mo M-edges from the viewpoint of measuring x-ray absorption spectra of dilute materials using fluorescence detection.

Table 3 summarizes the Mo K-, L- and M-edge X-ray absorption spectra of molybdate and thiomolybdate salts, together with the Mo partial cross section for each absorption edge (as determined from ENDF/B evaluated nuclear data library [50]), the oxygen total cross section at the same energies, the published fluorescence yields [14,15,51,52] and the published natural linewidths [13]. Clearly, for the easiest experiment, one desires the highest possible Mo to background cross-section ratio, together with the highest attainable fluorescence yield. For simplicity, we neglect the impact of instrumentation and calculate the quantity d^* for each edge, which is the fluorescence yield multiplied by the ratio of the Mo to O cross-sections. This quantity is a useful gauge of the ease of fluorescence-detected measurement for dilute Mo in an oxygen matrix, such as a metalloprotein sample in aqueous solution. The ideal experiment will also have the largest chemical shift and the sharpest linewidths. We therefore use the data in Table 3 to calculate the chemical sensitivity, which we define as the chemical shift to linewidth ratio, or Δ/Γ and $\Delta/\Gamma_{\text{obs}}$ for the natural and observed linewidths respectively. Not surprisingly, the observed chemical sensitivity $\Delta/\Gamma_{\text{obs}}$, is lower than $\Delta/\Gamma_{\text{obs}}$ using the natural linewidths, but the overall trends with the different Mo edges are the same.

The near-edge peak of the Mo K-edge has by far the largest d^* , at 85.6, and this edge clearly exhibits the greatest overall sensitivity. This is not surprising as K near-edge spectra can be measured on less than micromolar concentrations. However, the chemical sensitivity is the poorest of all the edges. The chemical shift is significantly less than both the observed and natural linewidths, and for the compounds studied here, the near-edge peak is essentially unstructured.

The $L_{2,3}$ -edges are about 3 orders less sensitive than the K-edge, but, there is still sufficient sensitivity to be measured on dilute samples using an appropriate energy discriminating detector. The chemical sensitivity is significantly greater than the K-edge, with Δ/Γ and $\Delta/\Gamma_{\text{obs}}$ for the L_3 -edge peak equaling 1.39 and 1.09 respectively. In addition, the $L_{2,3}$ -edge spectra contain d -splitting information that can be rationalized theoretically, using, for example TT-multiplet calculations, to yield chemically useful information such as ligand field, site symmetry, spin-state and covalency. Hence, it is not surprising that several Mo L-edge studies are present in the literature (for example: [10-12,27]). Finally, for paramagnetic compounds, $L_{2,3}$ -edges in general are known to exhibit a large x-ray magnetic circular dichroism which can probe magnetic properties of the Mo center [9].

The $M_{2,3}$ -edges prove to be a difficult measurement using fluorescence detection. First, they give the lowest d^* values of all the edges, being a further 3 orders of magnitude less sensitive than the $L_{2,3}$ -edges. Second, as Figure 5 shows, the $M_{2,3}$ fluorescence is complex and it is split over 3 very different energy regions. The majority of the fluorescence is within the low energy Mo_a window at ~ 194 eV and this therefore faces both an O cross section about 4 times greater than the absorbing photon as well as a substantial inherent fluorescence background from $M_{4,5}$ -edge absorption. Hence d^* over-estimates the ease of measurement of the $M_{2,3}$ -edges by at least a factor of 5 for the Mo_a window, and, from Figure 5 and Figure 6, by about an order of magnitude for the Mo_b and Mo_c windows. Finally, the nitrogen K-edge absorbs between the M_3 and M_2 edges at 409.9 eV, and fluoresces at 392.4 eV, just below the M_3 absorption and within the Mo_c window. The N K-edge fluorescence yield, 5.2×10^{-3} , is at least 25-fold greater than the total M_2 fluorescence. Hence, while fluorescence detected measurements in the Mo_a and Mo_b windows would still be feasible, the presence of a significant nitrogen component will obscure the Mo_c fluorescence window. Similarly, the increased background cross section above the N K-edge could mask any Mo M_2 absorption.

The information content of the $M_{2,3}$ -edge peaks is very similar to the $L_{2,3}$ -edges. While the chemical sensitivity is lower, they still exhibit d -splitting that can be analyzed using the TT-multiplet approach and presumably exhibit a strong x-ray magnetic circular dichroism. However, it is not immediately clear from the spectra presented here whether an $M_{2,3}$ -edge study has any appreciable advantage over the corresponding $L_{2,3}$ -edge spectra, particularly as the $L_{2,3}$ -edges are considerably easier to measure than the soft x-ray M-edges.

In contrast to the $M_{2,3}$ -edges, the low energy Mo $M_{4,5}$ -edges are relatively straightforward to measure using fluorescence detection. Although the Mo to O cross-section ratio is lower than for the Mo $M_{2,3}$ -edges, the fluorescence yield is higher, giving the $M_{4,5}$ -edges a higher overall d^* . Moreover, the fluorescence spectrum is much simpler and occurs mostly within the Mo_a window, and it is clear from figure 6 that, so long as the sample is not too dilute, these edges can be readily measured using modern high-resolution energy discriminating instruments like our STJ detector. The $M_{4,5}$ -edges are also less prone to interference by other edges. The only light element with a K-edge that is likely to obscure the $M_{4,5}$ absorption or fluorescence is boron, which absorbs at 188 eV and fluoresces at 183.3 eV. Fortunately, boron is not likely to be a significant component of normal biological samples. Carbon K-edges absorb at 284.2 eV and fluoresce at 277 eV, and while these energies are

above the Mo $M_{4,5}$ -edges they may still present a problem for biological samples where carbon is expected to be in substantial excess if there is significant harmonic content in the x-ray beam. Hence it is important to ensure that these harmonics are minimized before attempting measurements on such samples. The chlorine $L_{2,3}$ -edges at ~ 200 eV are only about 35 eV below the Mo $M_{4,5}$ -edges and these could present problems in particular systems. However, our STJ detector has a resolution of < 15 eV and should readily discriminate the Mo M from the Cl fluorescence. In addition, the Cl $L_{2,3}$ -edge fluorescence yields are about an order of magnitude lower than those of the Mo $M_{4,5}$ -edges at 2.3×10^{-4} [53], and the Cl total cross section at 228 eV is about 6×10^{-4} cm²/g, only six times greater than the already large oxygen background cross section. Hence, while it is probably prudent to attempt to eliminate Cl from samples, low or moderate levels of chlorine should not, in general, present a significant problem to measuring Mo $M_{4,5}$ -edge spectra.

In terms of information content, the Mo $M_{4,5}$ -edges are also promising. The sharp pre-edge peaks exhibit by far the largest chemical sensitivity with observed $\Delta/\Gamma_{\text{obs}}$ of 6.14 and 6.35 for the M_4 and M_5 edges respectively. The reported natural linewidths are much smaller than the 0.4 eV we observe, with the M_5 -edge in particular having a reported value of 0.12 eV [13]. If sustained by further experiment, this low value offers the prospect of a chemical sensitivity $\Delta/\Gamma_{\text{obs}}$ of ~ 21 , about 25 times greater than the Mo K-edge. For the tetrahedral MoO_4^{2-} and MoS_4^{2-} anions studied here the pre-edge peaks do not show any obvious ligand-field splitting. As noted above, this is consistent with the assignment of these transitions to $3d \rightarrow 5p$ character in a tetrahedral field. However, other geometries do produce significant p -splitting which, if observed, would substantially improve the utility of these near-edge spectra. In addition, the fluorescence-detected spectra also clearly show broad intense $3d \rightarrow 4f$ transitions, which may also prove to be chemically useful. In any case, further experiments designed to reveal ligand field splitting patterns are clearly desirable to clarify the utility of the Mo $M_{4,5}$ -edges.

Conclusion

We have surveyed the chemical utility of the near-edge structure of Mo x-ray absorption edges from 200 to 20,000 eV by comparing, for each edge, spectra of two tetrahedral anions, MoO_4^{2-} and MoS_4^{2-} . We used three criteria for assessing near-edge structure of each edge: the ratio of the observed chemical shift between MoO_4^{2-} and MoS_4^{2-} and the linewidth, the chemical information from analysis of the near-edge structure and the ease of measurement using fluorescence detection.

Not surprisingly, the K-edge are by far the easiest to measure, but contain the least information. The $L_{2,3}$ -edges, although harder to measure, have benefits with regard to selection rules and chemical speciation in that they have a greater chemical shift and detailed lineshapes enabling theoretical analysis in terms of Mo ligand field, symmetry, and covalency. The soft x-ray $M_{2,3}$ -edges are perhaps the least useful, in that they are difficult to measure using fluorescence detection and have very similar information content to the corresponding $L_{2,3}$ -edges.

Interestingly, the soft x-ray, low energy (~ 230 eV) $M_{4,5}$ -edges have greatest potential chemical sensitivity and it turns out that they are straightforward to measure using our high resolution STJ fluorescence detector. They are also not likely to be obscured by light element K or L-edges, although if the sample contains a substantial amount of carbon, it is important to ensure that the incident x-ray beam is largely free of higher energy harmonics. The $M_{4,5}$ -edge spectra were amenable to analysis using both the TT-multiplet approach and FEFF 8.40, and the results indicate the sharp near-edge structure arises from $3d \rightarrow 5p$ transitions while the broad edge feature at higher energy has predominately $3d \rightarrow 4f$

character. A proper understanding of the dependence of these soft x-ray spectra on ligand field and site geometry is necessary before a complete assessment of the utility of the Mo M_{4,5}-edges can be made.

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Figure 1.
Crystal structure of Na_2MoS_4 . This is a perspective view with displacement ellipsoids drawn at the 50% probability level.

Figure 2.

A survey of x-ray absorption edges for MoO_4^{2-} (left) and MoS_4^{2-} (right) compounds. Each spectrum has been aligned at the measured centroid energy (E') of the pre-edge peak, as listed in Table 1. The K-edge and L-edge spectra were measured using fluorescence detection while the M-edges used electron-yield detection. K-edges were measured using solutions, while the L and M-edges employed powdered solids. MoO_4^{2-} spectra were all measured on $\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$. For MoS_4^{2-} , the hard x-ray spectra the K and L-edge spectra were measured using $(\text{NH}_4)_2\text{MoS}_4$ while the soft x-ray M-edge spectra (d – g) used Na_2MoS_4 to avoid interference from N K-edge absorption as detailed in the text.

Figure 3.

Mo L_{2,3}-edge X-ray absorption spectra and TT-multiplet simulation data of diluted powders of Na₂MoO₄ and (NH₄)₂MoS₄ recorded in fluorescence mode. Left panel: L₃ data, right panel: L₂ data. For each panel, top: MoO₄²⁻, bottom: MoS₄²⁻, solid line: x-ray spectrum, broken line: simulation, vertical solid lines: simulated stick spectra. Simulation parameters are given in Table 2. For both L₃ calculations, 2 transitions have < 2% intensity and are hence too small to be readily observed.

Figure 4.

Mo M-edge X-ray absorption spectra and TT-multiplet simulation data of solid $\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$ and Na_2MoS_4 recorded in electron-yield mode. Left panel: $M_{2,3}$ data, right panel: $M_{4,5}$ data. For each panel, top: MoO_4^{2-} , bottom: MoS_4^{2-} , solid line: x-ray spectrum, broken line: simulation, vertical solid lines: simulated stick spectra. An arbitrary background has been subtracted from each spectrum. Simulation parameters are given in Table 2. The $M_{4,5}$ edge was simulated using $3d \rightarrow 5p$ transitions. A $M_{4,5}$ edge simulation using $3d \rightarrow 4f$ transitions is presented in the supporting information (Figure S1).

Figure 5.

Soft x-ray fluorescence spectra of Na_2MoO_4 recorded using an STJ detector. These spectra were recorded as part of M-edge data collection for the spectra in Figure 6. (a) $\text{M}_{2,3}$ -edge scan: (solid line) below edge; 378 – 391.2 eV (broken line) M_3 -edge peak; 392.6 – 399.8 eV (dotted line) M_2 -edge peak 409.8 – 417.0 eV. (b) $\text{M}_{4,5}$ -edge scan: (solid line) below edge; 225.8 – 228.8 eV (broken line) M_4 -edge peak 232.9 – 235.9 eV (dotted line) above the M_4 and M_5 peaks 246 – 258 eV. The light element K-edge fluorescence energies are indicated. Suitable windows containing the Mo M fluorescence bands are shown by gray shading and are discussed in the text. Peaks arising from elastic scattering in (b) are indicated by a non-shaded box as discussed in the text. No correction has been made for the energy-dependence of the transmission of the Al infrared shielding windows in from of the STJ detector.

Figure 6. Fluorescence detected $M_{2,3}$ -edge x-ray absorption spectra of Na_2MoO_4 recorded using an STJ detector using different fluorescence energy windows. The spectra have been normalized to the M_3 -edge peak intensity. No offset has been applied to the data.

Figure 7.

Fluorescence detected $M_{4,5}$ -edge x-ray absorption spectra of Na_2MoO_4 recorded using an STJ detector. The spectra have been normalized to the M_5 -edge peak intensity. (a) The pre-edge peak region. (b) The full spectrum showing the broad edge feature not apparent in electron-yield measurements. For each panel: (i) spectrum (ii) FEFF simulation (iii) $3d \rightarrow 4f$ contribution to the FEFF simulation (iv) $3d \rightarrow 5d$ contribution to the FEFF simulation. (iii) and (iv) have been offset for clarity. No offset has been applied to the data.

Table 1

Centroid energy (E') in eV for the pre-edge peak for the MoO_4^{2-} and MoS_4^{2-} spectra in Figure 2.

	K	L ₂	L ₃	M ₂	M ₃	M ₄	M ₅
MoO_4^{2-}	20010.5	2628.0	2523.5	413.7	396.5	234.2	231.0
MoS_4^{2-}	20006.8	2620.6	2521.7	411.8	394.5	231.7	228.7

Table 2

TT-multiplet simulation parameters for the calculated L-edge and M-edge spectra shown in Figure 3, Figure 4 and Figure S1. In general good fits could be obtained with the given 10 Dq $\pm$ 0.15 eV. The satellite features seen in the M_{2,3} spectra were accounted for by assuming LMCT transitions with $\Delta = 0$ eV and a 60% 4d⁰ : 40% 4d¹L ground state. In order to correctly simulate the M_{4,5} edge separation using 3d $\rightarrow$ 5p transitions the 5p L-S coupling was not included for MoO₄²⁻ and was reduced to 20% of the atomic value for MoS₄²⁻ as discussed in the text.

		MoO ₄ ²⁻				MoS ₄ ²⁻			
Edge	Transition	10Dq	Slater Reduction	Lineshape FWHM (eV)		10Dq	Slater Reduction	Lineshape (FWHM) (eV)	
				Lorentzian	Gaussian			Lorentzian	Gaussian
L _{2,3}	2 <i>p</i> → 3 <i>d</i>	2.0	5%	2.2 (e, L ₂) 2.1 (t ₂ , L ₂) 1.8 (e, L ₃) 2.5 (t ₂ , L ₃)	0.7	1.3	5%	2.8 (e, L ₂) 2.2 (t ₂ , L ₂) 2.6 (e, L ₃) 2.4 (t ₂ , L ₃)	0.6
M _{2,3}	3 <i>p</i> → 4 <i>d</i>	2.0	30%	1.8 (e) 2.6 (t ₂)	0.04	1.3	30%	2.5 (M ₃) 3.1 (M ₂)	0.04
M _{4,5}	3 <i>d</i> → 5 <i>p</i>	–	80%	0.40	0.04	–	30%	0.40 (M ₅) 0.46 (M ₄)	0.04
M _{4,5}	3 <i>d</i> → 4 <i>f</i>	–	1%			–	10%		

Table 3

Summary of the properties of the Mo x-ray absorption edges. The nominal energy refers to elemental Mo. The Mo partial cross sections are derived from the ENDF/B evaluated nuclear data library [50] and refer to the specific Mo sub-shell only. The fluorescence yield and natural linewidths are determined from published values using the cited references. The observed linewidth is that determined for MoO₄²⁻ and MoS₄²⁻ pre-edge structures as described in the text. The chemical shift is the energy difference of the MoO₄²⁻ and MoS₄²⁻ pre-edge structure centroids determined in this work.

Edge	Nominal Energy (eV)	Mo Partial Absorption Cross section σ (cm ² /g)	O Total Cross section σ (cm ² /g)	Fluorescence Yield ω	$d^* = \frac{\sigma_{Mo}}{\sigma_O} \times \omega$	Natural Linewidth Γ (eV)	Observed Linewidth Γ_{obs} (eV)	Chemical Shift Δ (eV)	Natural $\Delta\Gamma$	Observed $\Delta\Gamma_{obs}$
K (1s)	20000.4	67.5	0.603	0.765	85.6	4.52	5.5	3.70	0.82	0.67
L ₁ (2s)	2865.5	287	247	0.010	1.16E-02	3.80				
L ₂ (2p _{1/2})	2625.1	669	317	0.034	7.18E-02	1.83	2.2	2.40	1.31	1.09
L ₃ (2p _{3/2})	2520.2	1410	396	0.037	0.132	1.69	2.2	2.35	1.39	1.07
M ₁ (3s)	506.3	872	1430	3.6 × 10 ⁻³	2.19E-03	6.3				
M ₂ (3p _{1/2})	411.6	957	2380	2.0 × 10 ⁻⁴	8.05E-05	2.1	2.2	2.08	0.99	0.95
M ₃ (3p _{3/2})	394.0	2460	2680	1.9 × 10 ⁻⁴	1.75E-04	2.1	2.2	2.25	1.07	1.02
M ₄ (3d _{3/2})	231.1	630	9810	3.5 × 10 ⁻³	2.25E-04	0.22	0.43	2.64	12.0	6.14
M ₅ (3d _{5/2})	227.9	904	1.01 × 10 ⁴	3.5 × 10 ⁻³	3.13E-04	0.12	0.40	2.54	21.2	6.35
Reference	[53, 54]	[50]	[50]	[14,15,51,52]		[13]	This work	This work		