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Sulfate speciation analysis using soft x-ray emission spectroscopy

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ABSTRACT: The chemical and electronic structure of fifteen different sulfates is studied using S L\textsubscript{2,3} soft x-ray emission spectroscopy (XES). Sulfur L\textsubscript{2,3} XES spectra of sulfates are distinctively different from those of other sulfur compounds, which make XES a powerful technique for sulfate detection. Furthermore, subtle but distinct differences between the spectra of sulfates with different cations are observed, which allow a further differentiation of the specific compound. Most prominently, the position and width of the emission from “S 3s” derived bands systematically varies for different compounds, which can be understood with electronic structure and spectra calculations based on density functional theory.

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INTRODUCTION

Sulfur compounds play important roles in a large number of applied material systems. They are used, e.g., as active materials in lithium-sulfur batteries\textsuperscript{3}, CdTe- or Cu(In,Ga)(S,Se)\textsubscript{2}-based thin-film solar cells\textsuperscript{2}, metal sulfide catalysts\textsuperscript{3} (e.g., FeS\textsuperscript{4}, CuS\textsuperscript{5}, CoS\textsuperscript{6}), and also have high relevance in geology, the coal and oil industries, and many other fields. To understand and optimize these materials, a detailed knowledge of their chemical structure (including secondary phases) is important, in particular as a function of external parameters under operating conditions. This includes surface phases, diffusion processes in multilayer structures, as well as surface stability under operation, and calls for a thorough characterization of the different sulfur-containing phases in the material.

Often, the materials are exposed to environments that contain oxygen and/or humidity, possibly under illumination, which in turn can lead to the formation of sulfate phases. These sulfate phases are important to detect and characterize, as they can impact the device performance. As an example, sulfate formation can be observed for Cu(In,Ga)(S,Se)\textsubscript{2} thin-film solar cells after exposure to humidity and light\textsuperscript{7-9} in experiments that investigate the long-term stability of the cells. Sulfates also play an important role as part of the electrolyte in a number of electrochemical applications, in which the interaction and absorption of sulfates on the material’s surface also need to be taken into account\textsuperscript{10}.

For a chemical speciation of the involved compounds, photoelectron spectroscopy is a very powerful and surface-sensitive tool that has been intensively employed in the past. Significant core level shifts are observed in S 2p x-ray photoelectron spectroscopy (XPS) for different sulfur compounds, loosely following the formal sulfur oxidation state\textsuperscript{11,12}. Particularly, the shift between sulfides and sulfates is found to be on the order of 7 eV. Several groups have also attempted to differentiate between sulfides with different cations using XPS and Auger electron spectroscopy\textsuperscript{13-16}. Systematic shifts in S 2p binding and Auger kinetic energies in dependence on the specific sulfate compounds were described\textsuperscript{12,13}. However, comparing the different studies and further literature values from the NIST data base\textsuperscript{12}, the available data are inconsistent. This might be related to the large band gap of sulfates, which can lead to charging in the experiments and also gives a high variability in binding energy depending on the Fermi level position within the band gap. Thus, the modified Auger parameter $\alpha’$ of sulfur, which is not affected by charging and Fermi level variations, was also investigated; unfortunately, it exhibits only small variations between the different sulfates\textsuperscript{13,15}. Finally, the XPS valence band spectra of a variety of sulfates and bisulfates were explored\textsuperscript{13,14,16}. After careful subtraction of the valence band contributions of the cations, small absolute\textsuperscript{13,14,16} and relative\textsuperscript{14} energy shifts were observed. However, while such
an analysis works reasonably well with well-defined surfaces of reference compounds, a similar analysis becomes very challenging in a more complex “real-world” system, where many other contributions in the valence region are present.

To analyze the electronic and chemical structure of sulfur compounds with bulk sensitivity, x-ray spectroscopy techniques are a uniquely suited choice. Most commonly, the S K edge has been investigated in the past using both x-ray absorption17,18 (XAS) and emission spectroscopy17,19 (XES). In these studies, significant energetic shifts of the absorption edge and the Kx x-ray emission energy are observed, which follow the formal oxidation state of the respective compound17,19. Among the sulfates, changes are much less pronounced; small energy shifts and changes in spectral shape are observed in XAS, while the energy position as well as the shape of the S Ka XES spectra are mostly independent of the cation17.

The information content of XES increases significantly as compared to core to core transitions as in S K, when investigating transitions involving valence states, i.e., for S Kα20-25 (probing states with p symmetry) and S L2,3 (probing states with s and d symmetry) XES17,26,27. In addition to the observed chemical line shifts, the spectral shapes now vary for different compounds offering high sensitivity for the differentiation of sulfur compounds. Together with the suitable photon attenuation lengths in the soft x-ray range, this makes S L2,3 XES a very versatile technique for the investigation of fundamental and applied material systems like thin-film solar cells7,8,26-29, CdS nanoparticles30, or CdS/ZnSe superlattices31.

Already in early pioneering work, the S L2,3 XES spectra of sulfates were investigated and found to be very distinct from other sulfide compounds20-32. In later studies, improved energy resolution allowed a better distinction between different sulfur species, but the spectra of different sulfates still are very similar, as is the case for their Kα spectra22,25. This is understandable, given the fact that XES is a very local probe (as defined by the wave function of the initial core hole) and that sulfates are ionic compounds, with the sulfur located in the center of the sulfate ion, i.e., not in direct proximity to the cation partner. Notably, small but distinct energy shifts and changes in line width have been observed in the S Ka XES spectra of different sulfates21.

In this paper, we present an in-depth experimental and theoretical study of the S L2,3 XES spectra of a variety of different sulfates. We show that sulfates not only exhibit very specific S L2,3 XES spectra when compared to other sulfur-containing compounds, but that there are distinct differences among the spectra of different sulfates that allow a more detailed and insight-based identification of the particular compound.

EXPERIMENT

Sulfate powders were purchased from Spectrum Chemical (K₂SO₄) and Alfa Aesar (all other sulfates). In most cases, anhydrous materials were available, with the exception of ZnSO₄·7H₂O and FeSO₄·7H₂O. The powders were unpacked and further processed in a nitrogen-filled glove box. From the pure powders, pellets were pressed using pressures between 50 and 300 bars. The pellets were then mounted on a sample holder using double-sided tape compatible with ultra-high vacuum. The ZnSO₄·7H₂O and FeSO₄·7H₂O pellets were afterwards degassed in the rough vacuum of the glove box loading chamber for several hours, presumably losing a good fraction of the water of crystallization. Samples were afterwards transported in a nitrogen-filled container from the glove box to the experimental station and introduced into the loading vacuum chamber of the experimental station with a short air exposure of approx. 10 seconds. The base pressure of the experimental station was better than 10⁻⁹ mbar.

XES experiments were performed at beamline 8.0.1 of the Advanced Light Source (ALS), Lawrence Berkeley National Laboratory (Berkeley, USA) with the dedicated Solid And Liquid Spectroscopic Analysis (SALSA) roll-up experimental station38. Spectra were collected using a high-transmission soft x-ray spectrometer37 with a variable line space (VLS) grating, achieving a resolving power E/ΔE of about 1500. The energy scales of the beamline and the spectrometer were carefully calibrated using the well-documented absorption energies of highly oriented pyrolytic graphite (HOPG)38, TiO₂39, and N₂40 references. The necessary x-ray absorption scans were measured using the iRIXS endstation41 at beamline 8.0.1. The detailed calibration procedure is described in the supporting information; it results in an emission energy scale that is precise to better than 0.1 eV in absolute energies and 0.03 eV in relative energies between the measurements.

In earlier studies at beamline 8.0.1, it was observed that prolonged exposure of sulfates (here: CdSO₄) can cause radiation damage, and a small fraction of sulfide (here: CdS) was found after several tens of minutes of exposure42. For the present study, such possible changes were characterized for CaSO₄ after exposing the sample to increasing radiation doses, as described in more detail in the supporting information. For high radiation doses, we find beam-induced sulfite and a small degree of sulfide formation. We avoid this by reducing the exposure time per sample spot to one second by...
continuously scanning the sample under the synchrotron beam. While no additional sulfite formation can be observed at these settings, a small sulfite signal remains (visible for the alkali and alkaline earth metal sulfates, as well as FeSO₄), which we attribute to sulfite species present in the as-prepared samples.

**THEORY**

For a detailed understanding of the experimental spectra, we use electronic structure and spectra calculations based on density functional theory (DFT). For this we have approached the sulfates from two “directions”: First, the XES spectrum of an isolated SO₄²⁻ ion was calculated using the StoBe-DeMon 3.1 DFT code. Second, the investigated sulfates were described correctly as periodic crystals, and their electronic structure and XES spectra were calculated using the Wien2k program package.

StoBe-DeMon is based on self-consistent solutions of the Kohn-Sham DFT equations using Linear Combinations of (Gaussian type) Atomic Orbitals (LCAO). For our XES calculations, we used the Becke Perdew gradient-corrected exchange and correlation functionals. The valence electrons were described with triple-ζ bases and effective core potentials (ECPs) with 7111/411/1 and 73111/6111/1 basis sets for oxygen and sulfur, respectively. The auxiliary basis sets were comprised of five s and two spd functions for oxygen, and five s and four spd functions for sulfur, to fit the Coulomb and exchange-correlation potentials. The XES transition probabilities were calculated based on dipole matrix elements and the ground state Kohn–Sham eigenstates.

WIEN2k is based on the full-potential augmented plane wave plus local orbitals (APW+lo) method to solve the Kohn-Sham DFT equations. To describe the electronic exchange-correlation effects, the generalized gradient approximation (GGA) as parameterized by Perdew, Burke, and Ernzerhof (PBE) was used. The plane-wave cutoff was defined by setting the product of the largest atomic sphere radius $R_{MT}$ times the largest $K$-vector $K_{max}$ to 7. The self-consistent field (SCF) cycle was run with 1000 $k$ points, while 10000 $k$ points were used for calculating the projected density of states (PDOS) and the XES spectra. XES spectra were calculated in the dipole approximation using Fermi’s golden rule with the formalism described by Neckel, Schwarz, et al. and implemented in WIEN2k. While delivering no absolute emission energies, this “ground state approach” leads to a very good description of the XES spectra, since the core-hole is filled and the valence-hole well screened in the final state. The crystal structures of the investigated sulfates were obtained from the Materials Projects Database.

**RESULTS AND DISCUSSION**

The S L₂,₃ XES spectra of all investigated sulfates are shown in Figure 1 and compared with the spectrum of an isolated SO₄²⁻ as calculated with the StoBe-DeMon package. Due to the ionic nature of sulfates, all spectra contain the same main features, independent of the cation. In the following, we first assign these features based on the calculated spectrum of the tetrahedral SO₄²⁻ ion (point group T₄) in a molecular orbital picture. This is similar to the early work by Dolenko et al., who investigated the electron-excited S K, O K, and S L₂,₃ XES spectra of Li₂SO₄ and (NH₄)₂SO₄. The subsequent discussion of the differences between the spectra of the different sulfates will then need to take into account the respective cation and the band nature of the valence states.
Figure 1: S L2,3 XES spectra of the investigated fifteen sulfates, normalized to the maximum of the “S 3d” emission line at ~162 eV. An excitation energy of 200.9 eV was used in all cases, with the exception of ZnSO4, for which an excitation energy of 184.5 eV was used. Up to an emission energy of 148 eV, the spectra are also shown magnified by a factor of 5 (red). On the bottom, the calculated spectrum for the SO2+ ion is shown for comparison. The calculated energy positions and intensities are depicted by red (L2) and blue (L3) bars. The green curve is calculated by including a symmetric Voigt-shaped line broadening. Above the calculated spectrum, the isodensity surfaces of selected orbitals are shown (colors denote the sign of the wave function).

The molecular valence orbitals of the SO2+ ion are formed by hybridization of the O 2s, O 2p, S 3s, S 3p, and S 3d atomic orbitals, forming the 4a1, 3t2, 5a1, 4t2, 1e, 5t2, and 1t1 molecular valence orbitals. In the S L2,3 XES spectrum, only orbitals with an appreciable overlap with the S 2p core levels and s and d symmetry (to obey the dipole selection rules) will be seen, i.e., only those molecular orbitals that have significant contributions from the S 3s and S 3d atomic orbitals.

We find that the calculated XES spectrum gives a reasonable qualitative description of the experimental spectra. Most prominently, the line doublet at ~155 eV can be assigned to transitions involving the 5a1 molecular orbital, which, while dominated by O 2s and O 2p (see discussion of Figure 3), also includes contributions from the S 3s atomic orbital and thus is denoted as “S 3s” derived states or bands. Due to the spin-orbit splitting of the S 2p core levels, this one valence state leads to two spectral lines (L2 and L3 emission) that are separated by the S 2p spin-orbit splitting of 1.20 eV\(^{55,56}\) and have an intensity ratio of about 2:1 (L2: L3), according to the 2j+1 multiplicity of the core levels. Generally, all spectral features show this splitting, but only the 5a1 line is sufficiently narrow that the two lines are clearly separated.

Similarly, the broad peak at ~162 eV can be assigned to transitions involving the 1e and 5t2 molecular orbitals, which both have S 3d contributions. We will hence also denote this as “S 3d” derived states/bands in the following. Furthermore, we find two weak and very broad peaks at ~140 eV and ~144 eV (in the experimental spectra), which can be assigned to the 4a1 and 3t2 molecular orbitals, respectively. The 4a1 orbital contains S 3s and O 2s contributions. The 3t2 orbital is dominated by O 2s and S 3p contributions, but also has some admixture of S 3d\(^{55}\). In a simplified picture, these two orbitals will be denoted as “O 2s” derived states/bands.

While the calculated spectrum of SO2+ allows the above assignment of the main spectral features and gives a qualitative agreement with the experimental spectra, distinct quantitative differences are found. The SO2+ calculation shows a significantly lower relative “S 3d” intensity than is found in the respective spectral region of the experimental spectra. Similarly, the intensity of the 3t2 feature at ~144 eV, relative to the 4a1 feature at ~140 eV, is stronger in the experimental spectrum than predicted for the ion.

Most strikingly, the experiment shows distinct differences between the spectra of the different sulfates, which naturally cannot be explained by the simplified picture of an isolated SO2+ ion. We find that the emission energy and widths of the “S 3s” emission lines vary significantly (the corresponding values are given in Table S1 in the supporting information). Furthermore, more subtle shape changes can be observed for the “S 3d” and the “O 2s” emission. The intensity ratios of these features also vary for the different compounds, most prominently for Cs2SO4 and BaSO4, where it is strongly reduced. All these changes create a powerful tool to distinguish the different sulfates. They can only be understood by correctly describing the compounds as crystalline solids with different cations, as will be discussed in the following.

While the variations of the relative intensities of the “S 3d” and “O 2s” emission could contain information on variations in the hybridization between the S and O bands, we find that in the present case the intensity changes are dominated by different degrees of self-absorption, which describes the absorption of the incoming and outgoing photons\(^{58,59}\). This modifies the XES intensity by a factor \(c_\lambda\), which depends on the absorption lengths of the incoming (\(\lambda_\text{in}\)) and outgoing photons (\(\lambda_\text{out}\)) in the following way:

\[
c_\lambda = \frac{\cos \theta_\lambda}{\lambda_\lambda} \int_0^\infty \exp \left(-x \cos \theta_\lambda\right) \exp \left(-x \cos \theta_\text{out}\right) dx
\]

where \(\theta_\lambda\) and \(\theta_\text{out}\) are the angles between the sample surface normal and the directions of the in- and out-going photons, respectively. For the geometry in our experiment (\(\theta_\text{in} = 0^\circ\) and \(\theta_\text{out} = 45^\circ\)), \(c_\lambda\) becomes \(\lambda_\text{out} / (\lambda_\text{out} + \sqrt{2} \lambda_\lambda)\). Both, \(\lambda_\lambda\) and \(\lambda_\text{out}\), are different for the different sulfates; in addition, \(\lambda_\text{out}\) also varies as a function of emission energy across the spectrum. In the case of Cs2SO4 and BaSO4, \(\lambda_\text{out}\) is significantly smaller at ~140 eV than at 162 eV, which leads to the observed suppression of the “O 2s” emission. Using tabulated values for \(\lambda^{60}\), this is quantified for all samples in Figure 2, where the intensity ratio...
between the “O 2s” and the “S 3d” emissions is plotted as a function of \( c_j(O\ 2s) / c_j(S\ 3d) \).

\[ \lambda_{out} \]

**Figure 2:** Blue data points represent the intensity ratio of the “O 2s” and “S 3d” emission lines as a function of \( c_j(O\ 2s) / c_j(S\ 3d) \). The red line shows a linear fit of the data (including the origin). Next to the data points, the corresponding compounds are given.

In most cases, \( \lambda_{out} \) increases as a function of emission energy (i.e., from 140 to 162 eV) and \( c_j(O\ 2s) / c_j(S\ 3d) \) is smaller than 1, reducing the relative intensity of the “O 2s” emission. The exceptions are Rb\( _2 \)SO\( _4 \) and SrSO\( _4 \), for which \( \lambda_{out}(O\ 2s) \) is larger than \( \lambda_{out}(S\ 3d) \), due to the Cooper minimum in the ionization cross section of the nearby Rb and Sr M\( _{1,4} \) absorption edges. We find that the data points all lie close to a line that includes the origin, which suggests that self-absorption is indeed the dominating factor causing the observed intensity behavior. The slope of this line (0.69) then corresponds to the corrected average intensity ratio of the “O 2s” and “S 3d” emission in the investigated sulfates. We note that this is a “matrix effect” – it does not primarily depend on the character of the emitting atom (or sulfate ion) and its immediate chemical environment, but rather on the composition of the “surroundings” that the outgoing photon needs to traverse on its way to the surface and the XES detector. Overall, the influence of self-absorption is too strong to allow to extract information on variations in the hybridization between the S and O bands for the different sulfates. These variations can be much better studied by K\( _\alpha \) XES where self-absorption plays a much smaller role. However, no variations in the relative intensity of the “O 2s” derived band is mentioned by Sugiura or visible in the data of his careful study on 12 different sulfates, indicating that this effect is indeed small.

For the further discussion of the spectra, we will now switch from describing the electronic structure with the simplified picture of the SO\( _4^{2-} \) ion to the correct description of a crystal that also includes the electronic impact of the respective cations. To do this, we have calculated the electronic structure and the XES spectra of the investigated compounds using Wien2k. In the following, we will use the calculations in Figure 3 to exemplarily analyze the S L\( _{2,3} \) emission of CaSO\( _4 \). At the bottom of the graph, the calculated band structure of CaSO\( _4 \) is shown with the energy relative to the valence band maximum (VBM) on the abscissa and the position in reciprocal (k-) space on the ordinate. The k-resolved band structures for all sulfates investigated in this paper are shown in the SI (Figures S5, S6, and S7). The bands show a comparably small dispersion, owing to the ionic nature of the crystal, and are bundled in small groups of bands that can be related/assigned to the corresponding states in the molecular SO\( _4^{2-} \) picture discussed above.

Above the band structure, the electronic density of states projected onto the three atomic species of the compound (“PDOS”) is depicted. We find that the PDOS is dominated by the contribution of the oxygen atoms. In the region of the upper valence bands (between 10 and 0 eV), only a very small sulfur and nearly no calcium contribution is present. At higher binding energies, the situation is similar, but significant contributions from calcium are visible that can be attributed to Ca 3p states that form a band with the 3\( _t \) states of the sulfate ion. Above the PDOS, the (small) contribution from S (“S PDOS”) is shown magnified and further projected onto their orbital angular momentum (s, p, and d). The situation is analog to the situation of the molecular orbitals of SO\( _4^{2-} \) discussed above, reflecting the sulfur atomic orbital contributions to the different bands (i.e., S 3s contributing to the bands around 8.5 eV and 23 eV, S 3p to the ones around 6 eV and 19 eV, and S 3d to the ones around 3 eV). From this, we can calculate an L\( _3 \) XES spectrum, shown in red above (“calc. (L\( _3 \))”). The L\( _2 \) contribution can be included by adding a scaled (x0.5) and shifted (by 1.2 eV) version of the L\( _3 \) spectrum. Here, the result was convoluted with Voigt functions to account for experimental and lifetime broadening (“calc. (L\( _{2,3} \) with broadening)”). The Gaussian widths were set to the experimental resolution (0.1 eV) and the Lorentzian widths were adjusted to fit the experimental spectrum. We find a good agreement between the calculated and experimental spectra. This calculations now includes the dispersive nature of the bands and is in particular improved with respect to that of the SO\( _4^{2-} \) calculation in terms of relative intensities and shapes of the spectral features. To correctly reproduce the relative energy separations, the
energy scale of the calculated spectrum had to be stretched by a factor of 1.06.

On the low energy side of the “S 3s” emission, we find a small contribution from CaSO₄ contamination (labeled in Figure 3), which is discussed in the experimental section and the supporting information.

For comparison, the top panel of Figure 3 depicts the experimental (black, digitized from Ref.²¹) and our calculated (red) S Kβ XES spectrum of CaSO₄. In contrast and complementary to S L₂,₃ XES, which probes bands with s and d symmetry, the bands with p symmetry are probed by S Kβ XES. This leads to two emission lines that can be attributed to the “O2s”/“3t₁” (hybridized with S 3p states) and “S 3p”/“4t₁” derived bands at 2453.8 eV and 2467.4 eV, respectively. The spectrum is well reproduced by our calculation (energy scales were aligned at the “S3p” peak and the scale of the calculation was stretched by a factor of 1.06).

The spectra of all investigated sulfates were calculated with the same procedure as described for CaSO₄ - Figure 4 gives a comparison of the experimental and calculated spectra. For each pair, the calculated spectra were shifted to align the emission energy of the “S 3d” derived bands (at ~162 eV) with that of the experiment. For all calculated spectra, the emission energy scale was stretched by the same factor of 1.06. In most cases, the calculation accurately reproduces the relative shift of the “S 3s” emission, which shifts by about 1 eV from CdSO₄ (L₂ at 154.65 eV) to Rb₂SO₄ (L₂ at 155.71 eV). This demonstrates that the lines shifts are related to the band structure of the specific compound, i.e., involving the specific cation.

In addition to the spectra, Figure 4 shows the DOS projected onto the cation for each compound, which allows to get an intuitive qualitative view of the observed “S 3s” line shifts. Whenever the cation contributes with significant PDOS below/above the “S 3s” derived band, the latter is shifted up/down, i.e., towards/away from the VBM. The closer the cation-induced state to the “S 3s” derived band, the stronger the shift. This can be nicely seen for the alkali and alkaline earth metal sulfates, where the p levels of the outer shell of the cation gradually approach the “S 3s” derived band, which also gradually shifts upwards. Eventually, in the case of Cs₂SO₄, the cation p levels cross the “S 3s” derived band, which then appears at a lower emission energy than for all other alkaline metal sulfates. Likewise, the lowest “S 3s” emission energy is observed for CdSO₄ where the “Cd 4d” derived band is just above the “S 3s” derived band.

In some cases, the cation-derived band hybridizes with the “S 3s” derived band, giving a wave function overlap with the S 2p core level, and consequently directly showing up in the S L₂,₃ XES spectra. We observe this for Rb₂SO₄ and BaSO₄ as a shoulder on the low emission energy side, and for Cs₂SO₄, ZnSO₄, and CdSO₄ as additional intensity on the high emission energy side (see magnified regions in Figure 4). Note that for ZnSO₄ and, to a lesser extent, CdSO₄, the calculation places the “Zn 3d” and “Cd 4d” contributions at higher emission energies than we observe in the experiment. This is caused by an underestimation of the calculated binding energy

**Figure 3**: Analysis of the S L₂,₃ XES spectra of CaSO₄ and comparison with Kβ XES. Lower panel from bottom to top: Calculated k-resolved band structure, density of states projected onto the different atomic species (PDOS), density of states projected onto s, p, and d symmetry for the sulfur atom (S PDOS), calculated S L₁ emission spectrum, calculated S L₂,₃ emission spectrum including experimental and lifetime broadening, and the experimental spectrum (top, black). For better visibility, the S PDOS and the calculated L₂ spectrum is shown magnified by a factor of 3 for energies smaller than 22 eV (relative to the VBM). Note that the energy axis of the calculation was stretched by a factor of 1.06 relative to the experimental energy axis for optimal alignment. Upper panel: Experimental (black, digitized from Ref.²¹) and calculated (red, energy rel. VBM) S Kβ XES spectrum of CaSO₄.
The energy shifts of the “S 3s” emission line thus create a sensitive tool to distinguish between different sulfate compounds. In practical applications, either the absolute emission energy of the “S 3s” emission line (as listed in Table S1), or the energy difference between the “S 3s” and the “S 3d” emission lines can be used to differentiate between different sulfates. Due to its narrow line width, the “S 3s” position can be determined more precisely (in particular for data with lower signal-to-noise ratio than presented here), but a good absolute energy calibration is required to compare with the values in Table S1. Nevertheless, this can be easily facilitated by measuring a suitable sulfate reference (e.g., CaSO₄) immediately before or after the sample that contains the unknown sulfate compound.

**Figure 4:** Experimental (black) and calculated (red) $L_{2,3}$ XES spectra of a) alkali metal sulfates, b) alkaline earth metal sulfates, and c) other sulfates. Below each calculated spectrum, the DOS projected onto the respective cation is shown in blue. In the cases where the cation contributes with a significant PDOS outside of the plotted energy window, the corresponding state is given, together with the energetic distance ($dE$) to the “S 3s” band. To better visualize line shifts, vertical dashed lines mark the position of the “$S\text{ 3s}$” and “$S\text{ 3d}$” emission of Li$_2$SO$_4$.

Similar emission energy shifts have also been observed for the features in the $K_{\beta}$ XES of different sulfates$^{21}$ and it is worth comparing these with the shifts of the “$S\text{ 3s}$” feature in the $L_{2,3}$ emission. As shown in Figure S3, we find a linear correlation between the shifts of the “$3s$” feature of the $L_{2,3}$ emission and the “$3p$” feature of the $K_{\beta}$ emission. The shifts of the “$3s$” feature are about double that of the “$3p$” feature, which together with the much smaller line width, make $S\text{  L}_{2,3}$ the more sensitive tool for sulfate speciation. In analogy to the shifts of the “$3s$” $S\text{  L}_{2,3}$ emission, the shifts of the “$3p$” feature in the $K_{\beta}$ emission are cause by the influence of the electronic states of the cation on the band structure. For all sulfates in which data was available for both $S\text{  L}_{2,3}$ and $S\text{  K}_{\beta}$, this shifts the “$S\text{ 3s}$” and “$S\text{ 3p}$” derived bands (and thus emission lines) in the same direction as is visible in the band structure calculations presented in Fig. S5, S6, and S7. In the case of Cs$_2$SO$_4$ and CdSO$_4$, a different behavior is expected due to the position of the “$Cs\text{ 5p}$” respectively the “$Cd\text{ 4d}$” derived bands just above the “$S\text{ 3s}$” derived band but no corresponding Cs$_2$SO$_4$ or CdSO$_4$ $K_{\beta}$ data was available to us.

As mentioned above, we observe significant differences of the line widths of the “$S\text{ 3s}$” emission lines for the different sulfates, which are shown in Figure 5. Factors that contribute to the line width are the experimental broadening, the band width of the “$S\text{ 3s}$” derived band, and the lifetime broadening. While the experimental broadening is identical for all samples, the band width and the lifetime broadening can vary significantly. To understand this, we assume that the (“$S\text{ 3 s}$”)$^1$ final state decays mainly through Auger transitions. With a simple phase-space...
argument, more Auger channels become available for higher binding energies of the “S 3s” derived band (assuming that the bands above do not change considerably). This reduces the lifetime of the (“S 3s”) \(^1\) state, leading to an increase in lifetime broadening. In fact, when plotting the width of the “S 3s” emission as a function of its emission energy in Figure 5, we find a decrease of the line width with increasing emission energy for most of the sulfates, which can even be described with a linear relationship (as indicated by the red fitted line). The line widths for the compounds that do not follow this trend (FeSO\(_4\), In\(_2\)(SO\(_4\))\(_3\), SnSO\(_4\), BaSO\(_4\), and Rb\(_2\)SO\(_4\)) exclusively lay above the red line, which suggests that other broadening effects play a significant role in their case. In fact, all of these compounds exhibit a significantly stronger dispersion for the “S 3s” derived band than the other compounds (see Figures S5, S6, and S7). This is caused by a stronger hybridization with states contributed by the cation that are close in energy for these compounds and broadens the “S 3s” emission line. Again, similar changes in the line width of the “S 3p” emission in K\(_x\) XES has been observed\(^2\) and we compare with this data in Fig. S4. A linear correlation between the FWHM of the “S 3s” → S 2p\(_{3/2}\) and “S 3p” → S 1s transitions is observed, with the exception of the data points for BaSO\(_4\), Rb\(_2\)SO\(_4\), and FeSO\(_4\), where the “S 3s” bands are affected by hybridization with cation bands.

CONCLUSIONS

We use a series of high-quality S L\(_{2,3}\) XES spectra of fifteen different sulfates to describe and understand their spectral specificity, hence creating a unique tool for sulfate differentiation. The overall spectral signature of the sulfates is very unique, as compared to other sulfur compounds. Comparing with the calculated spectra of an isolated SO\(_4\) ion, the main spectral features can be assigned based on a molecular orbital model. We find distinct differences between the spectra of the different sulfates, namely changes in relative peak intensities and the widths and positions of the “S 3s” derived emission line. These changes can be attributed to self-absorption, differences in valence hole lifetimes, and, based on the comparison with calculated spectra of the individual compounds, energy shifts of the “S 3s” derived band, respectively. In particular, the energy shifts of the “S 3s” derived band make S L\(_{2,3}\) XES a direct and sensitive tool for the differentiation of sulfate species in a large variety of fundamental, natural, and applied material systems.

Figure 5: Line width of the “S 3s” → S 2p\(_{3/2}\) transition as a function of its emission energy (blue filled circles). The compounds are given next to the data points. The red line shows a fit illustration of the linear dependency between width and line position excluding the data points of FeSO\(_4\), In\(_2\)(SO\(_4\))\(_3\), SnSO\(_4\), BaSO\(_4\), and Rb\(_2\)SO\(_4\).

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website. The supporting information gives details on the spectrometer and beamline calibration procedure, the characterization and mitigation of beam-induced spectral changes, a table summarizing emission energies, intensities, and widths, and the k-resolved electronic band structures of the investigated sulfates (PDF).

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REFERENCES


(3) Wang, G.; Li, C.; Shan, H. Highly Efficient Metal Sulfide Catalysts for Selective Dehydrogenation of Isobutane to


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