

Comparison of soft X-ray absorption spectra of transition metal sulfates

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The 3d transition metal (Fe, Co, Ni, Cu, and Zn) sulfates make an octahedral structure with 6 coordination containing some water molecules. Those complexes have various numbers of the coordinated water such as FeSO₄·7H₂O, NiSO₄·6H₂O, and CuSO₄·5H₂O. Only copper combines directly with SO₄²⁻ in five elements. Four H₂O are coordinated in the same plane and two SO₄²⁻ are coordinated out of plane (Figure 1). To investigate how the electronic states of coordinated water molecules are affected by the central metal atoms, soft X-ray absorption spectra have been measured in the energy range of 530~545 eV (O1s) and 690~1050 eV (metal 2p) of the 3d transition metals at BL-6 [1] of the HiSOR.

Figure 2 shows the total electron yield (TEY) spectra of the 3d transition metal sulfates in the O1s edge. The lowest peaks are observed around 532.8 eV and their energies depend on the 3d transition metals. There are two kinds of oxygen atoms (H₂O and SO₄²⁻) in the present complexes. To distinguish them, the TEY spectrum of anhydrous copper sulfate (CuSO₄) is also measured and compared with CuSO₄·5H₂O (Figure 3, top panel). The lowest peak observed only in CuSO₄·5H₂O is thus ascribed to contribution of the coordinated water molecules. The difference spectrum is calculated by normalizing the two spectra with the number of oxygen atoms (Figure 3, middle panel) and compared with the spectrum of a gaseous water molecule [2] (Figure 3, bottom panel). Comparing to the 4a₁ peak of gaseous water molecule, the lowest peak of the coordinated water is shifted to lower energy side by about 1 eV and broadened. The lowest peak energies of the 3d transition metals are summarized in Table 1 with the average bond length of X-OH₂ (X= Fe, Co, Ni, Cu, and Zn). The shorter the average bond length of X-OH₂, the higher the lowest peak energy except Ni.

TEY spectra are also measured at metal 2p edge. There observed spin-orbit separation peaks of 2p_{3/2} and 2p_{1/2} to 3d transitions with the energy separation of 13~21 eV except Zn, which has no hole in the 3d orbit. Comparing the experimental transition energies of 2p_{3/2} to 3d with the calculated differences of binding energies between 2p and 3d electrons, the largest discrepancy for Cu is considered to be ascribed to direct coordination of SO₄²⁻ to the central metal.

REFERENCES

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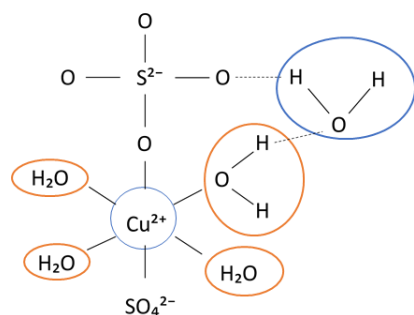


FIGURE 1. Schematic diagram of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$.

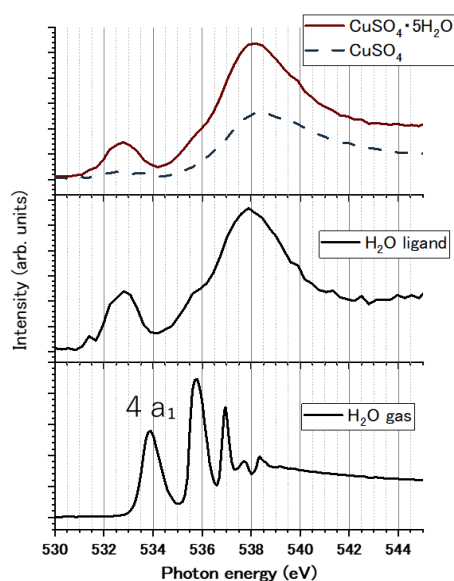


FIGURE 3. TEY spectra of (top) $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ and CuSO_4 , (middle) calculated ligand (H_2O) component, and (bottom) H_2O (gas).

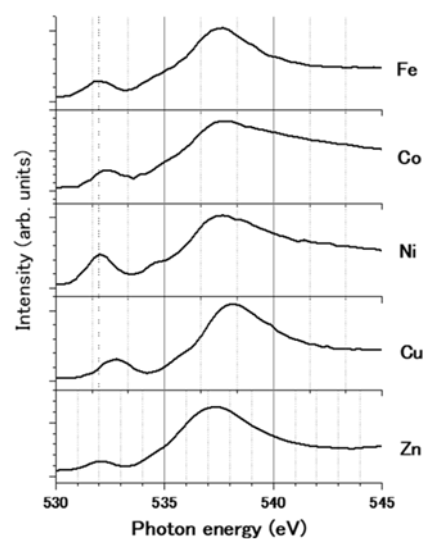


FIGURE 2. TEY spectra of $3d$ transition metal (Fe, Co, Ni, Cu, and Zn) sulfates at the $\text{O}1s$ edge.

TABLE 2 The lowest peak energies of the $3d$ transition metal sulfates and the average bond length of $\text{X}-\text{OH}_2$ ($\text{X} = \text{Fe}, \text{Co}, \text{Ni}, \text{Cu}, \text{and Zn}$).

	Peak energy (eV)	Average bond length (Å)
$\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$	532.0	2.123
$\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$	532.4	2.092
$\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$	532.0	2.051
$\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$	532.8	1.956
$\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$	532.0	