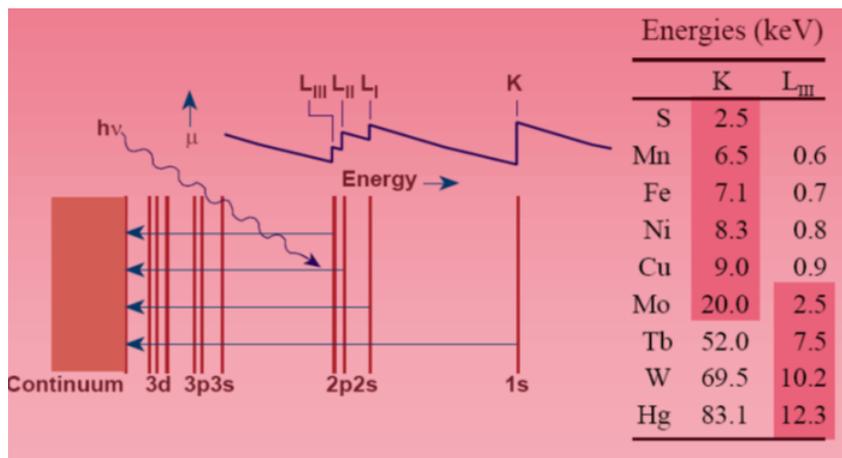


4.9: X-Ray Absorption Near Edge Structure (XANES)

The X-ray photon absorbed results in transitions within the atomic energy levels of the absorbing atom. During the spectroscopic scan, no absorption occurs until the photon has an energy equal to the ionization energy of core electrons. At lower X-ray energies, X-ray induced ionization of 2p or 2s electrons gives rise to what are called L_{III} , L_{II} , and L_I absorption edges. At significantly higher X-ray energies, photoionization of a 1s electron gives rise to the K X-ray absorption edge. The photon energies required for these edges of several selected elements are summarized above. X-ray sources provide a spectral distribution between 2 - 25 keV, giving access to K edges of elements through the second transition series. For elements in the remainder of the periodic table, these X-ray sources can access their L edges. Thus, all elements from ca. S throughout the periodic table can be probed.



For a given element, K edge energies depend slightly (\pm a few eV) on the chemical environment of the element. For example, higher oxidation state metals have higher positive charge, making it slightly more difficult to photodissociate a 1s electron, shifting the K edge to higher energy. Shifts of 1-2 eV per oxidation state are typical for first-row transition metals. **Also, spectroscopic transitions from the 1s orbital to orbitals just below the continuum (Fermi level), such as 3d, 4s, 4p, etc., obey electric dipole selection rules like any other electronic transition and assignments of such features can provide information about molecular symmetry.**

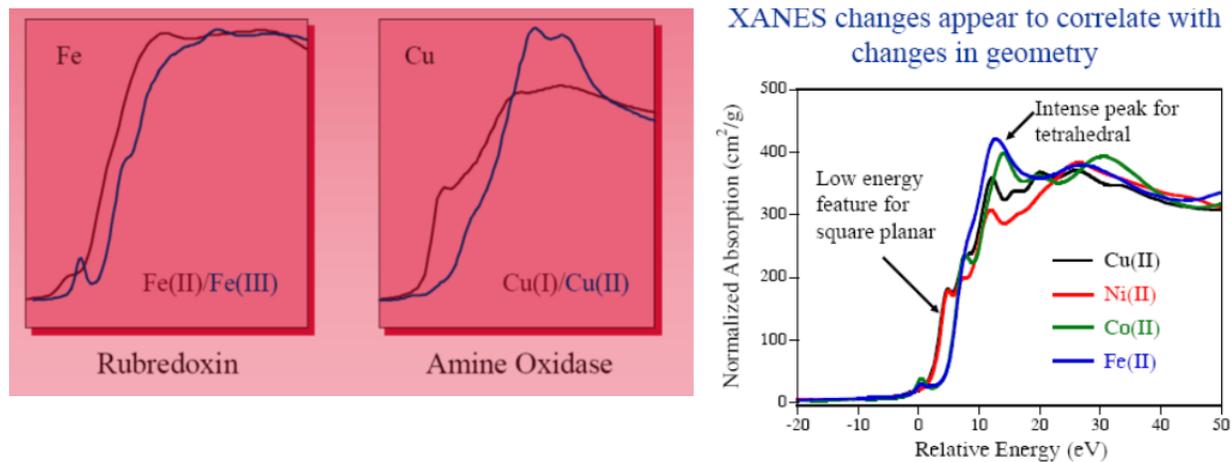


Figure 4.9.1: XANES sensitivity to oxidation state and geometry

The shape of the edge and the pre-edge resonances are characteristic for the local symmetry of the investigated atom sites and can be used as fingerprints in identification of its local structure. Tetrahedrally coordinated Cr materials, lacking an inversion center, exhibit a single intense pre-edge peak which can be assigned to a dipole allowed transition of 1s electron to an unoccupied anti-bonding t_2^* tetrahedral orbital.

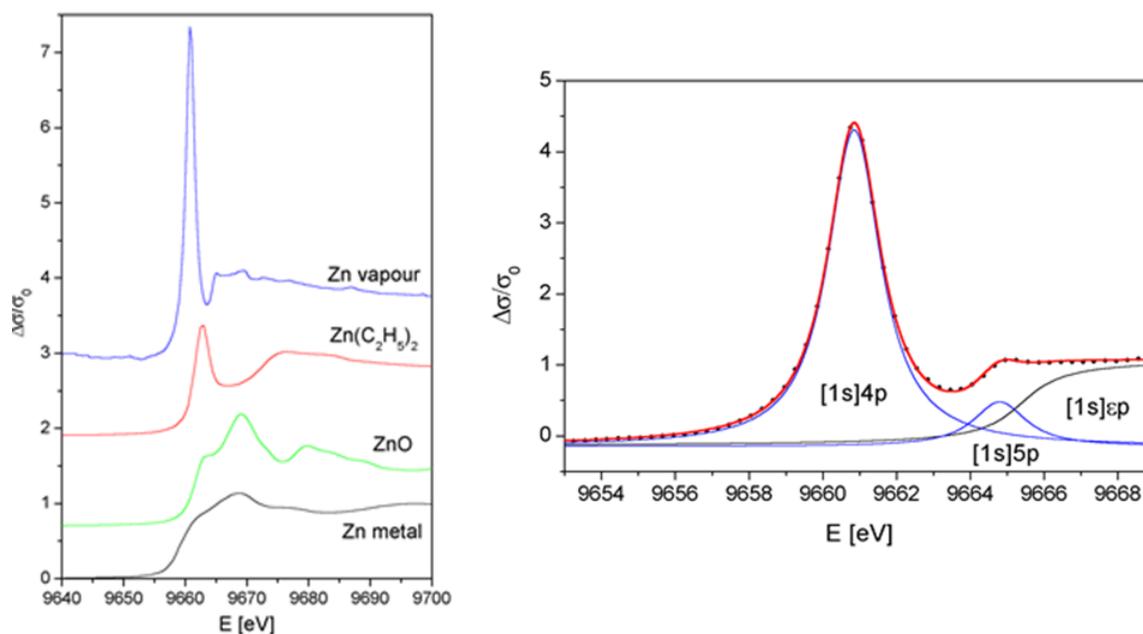
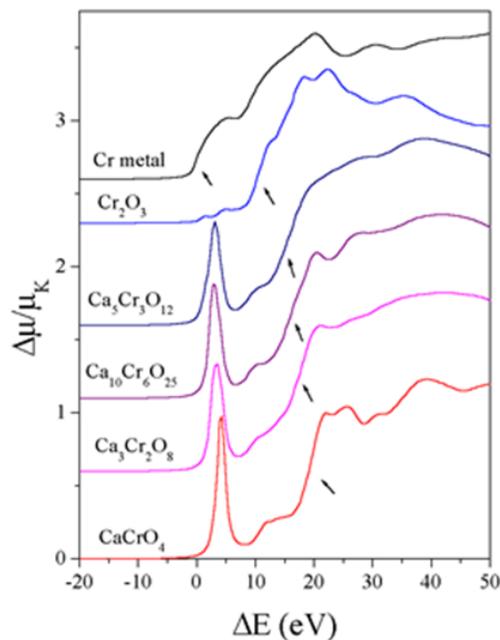


Figure 4.9.1: **Left:** Zn K-edge XANES measured on free and bound Zn atoms. Contains information on the unoccupied valence orbitals. **Right:** Atomic XANES can be described by pre-edge resonances due to transitions from 1s initial state to Rydberg final states below 1s ionization threshold and absorption edge due to transitions into continuum states above 1s ionization threshold.

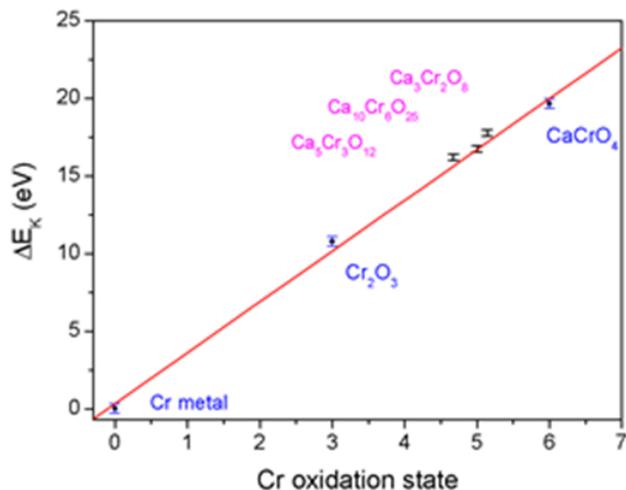
Determining Oxidation state from XANES

The binding energies of the valence orbitals and therefore the energy position of the edge and the pre-edge features are correlated with the **valence state** of the absorbing atom in the sample. With increasing oxidation state each absorption feature in the XANES spectrum is shifted to higher energies.



Normalized Cr K-edge profiles, displaced vertically, for the calcium chromate samples and Cr₂O₃, CaCrO₄, and Cr metal. Energy scale is relative to the Cr K-edge in metal (5989.0 eV). These spectra were measured at EXAFS 2 beamline in HASYLAB at DESY

in Hamburg.



Energy positions of the Cr K-edge in chromates (|) and reference samples (o) vs. Cr oxidation state. Linear dependence based on the reference samples is shown by solid line

The energy shifts vary linearly with the valence of the absorbing atom. The largest shifts, up to a few eV per oxidation state, are observed at the edge position. Shifts of the pre-edge peaks are considerably smaller, of the order of a few tenths of eV.

📌 The Take-home lesson about EXAFS utility

XANES tell Researchers what types of atoms and their oxidation states in a sample?

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