



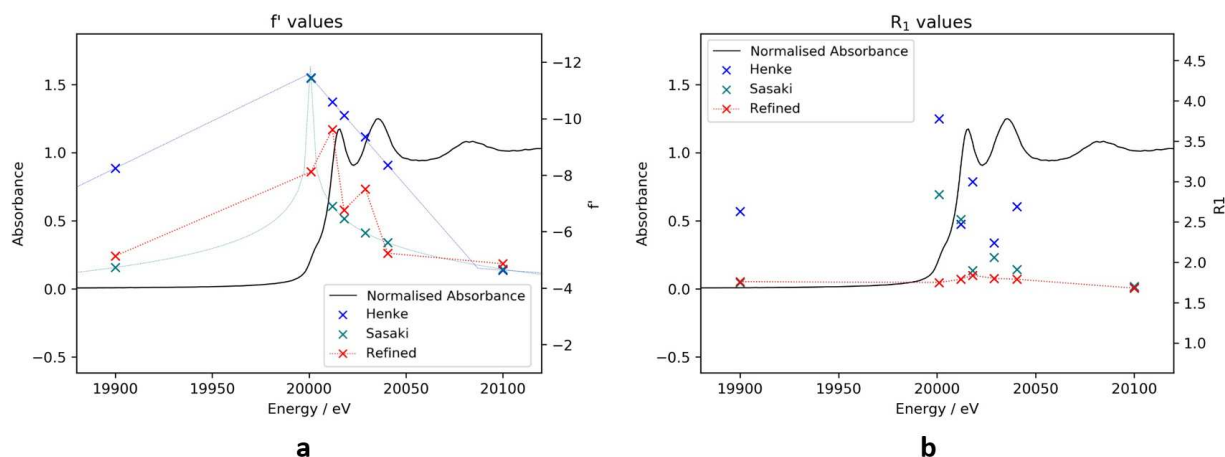
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|  | <b>Experiment title:</b><br>Multi-wavelength experiments in the range of the absorption edge to refine dispersion values and from single crystal X-ray data | <b>Experiment number:</b><br>MI-1364    |
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| <b>Shifts:</b><br>6  | <b>Local contact(s):</b><br>Dr. Christoph Hennig  | <i>Received at ESRF:</i>                |
| <b>Names and affiliations of applicants</b> (* indicates experimentalists):<br><br>Dr. Michael Bodensteiner*, Florian Meurer*<br>X-ray Structure Analysis, University of Regensburg, Universitätsstraße 31,<br>93053 Regensburg, Germany<br><br>Dr. Christoph Hennig*<br>Rossendorf Beamline (BM20-CRG), European Synchrotron Radiation Facility<br>71, Avenue des Martyrs, 38043 Grenoble, France |   |   |

#### Report:

Single Crystal X-ray Diffraction (SC-XRD) uses tabulated dispersion values to account for inelastic interactions between incident photons and the electrons of atoms in a crystal structure, which reduce the scattered radiation intensity observed in the diffraction pattern. These dispersion values correct the atomic form factors  $f_n = f_{0,n} + f' + if''$  with  $f_n$  being the atom's corrected form factor,  $f_{0,n}$  being the classical form factor,  $f'$  and  $f''$  being the real and imaginary part of the correction. Tabulated values from different sources are always pre-calculated for neutral, isolated atoms and remained unchanged for decades. Therefore, those dispersion values are not well-suited for chemical compounds and their unique electronic environments. For instance, different formal oxidation states of a given element lead to a significant shift of the absorption edge itself and influence the pattern after the edge. This effects are well known and used in methods such as X-ray absorption near edge spectroscopy (XANES) or extended X-ray absorption fine structure (EXAFS).

With these considerations in mind, our goal was to obtain information on the chemical and electronic environment of a compound by collecting SC-XRD data and *refining* its dispersion values at the heaviest atom's absorption edge. For this purpose, we collected XANES data of the compound  $\text{Mo}(\text{CO})_6$  and compared the data to an absorption spectrum of metallic Molybdenum to specify the actual edge of absorption. We then carried out seven SC-XRD experiments at different energies based on the determined absorption edge on the  $\text{Mo}(\text{CO})_6$  compound and compared our refined dispersion values to the ones being tabulated by Sasaki (KEK Report **1989**, 88, 1) and Henke (Atom. Data Nucl. Data Tabl. **1993**, 54, 181).

As shown in **Fig. 1 a** even 100 eV below the absorption edge of Molybdenum (20,000 eV) the  $f'$  value according to Henke differs significantly from both our refined and the tabulated Sasaki value.



**Fig. 1:** Refined values for  $f'$  with the tabulated values from Sasaki and Henke over the X-ray absorbance of  $\text{Mo}(\text{CO})_6$  with values from SC-XRD measurements at seven different energies (**a**) and their resulting  $R_1$  (**b**).

The biggest difference was observed at 20,000 eV: At this point both tables assume, that the absorption edge has already been passed, because they are based on elemental Molybdenum. In spite of the identical formal oxidation state  $\text{Mo}(0)$ ,  $\text{Mo}(\text{CO})_6$  is electronically different compared to the pure element. It reveals the absorption edge of Molybdenum to be shifted to 20,013 eV, which was approved by XANES measurements of both, Molybdenum foil and the  $\text{Mo}(\text{CO})_6$  crystal. Most noticeably, the refined dispersion value peaks only at 20,013 eV, whereas both tabulated dispersion values are already decreasing at this energy. To validate these findings, we also compared the resulting  $R_1$  values for the respective models in **Fig. 1 b**. It was found to be constantly low for our refined dispersion values, indicating a consistently good agreement of our modelled and measured data. In contrast, the  $R_1$  values for the tabulated dispersion values deviate significantly in the energy range around the absorption edge of Molybdenum. This suggests, that the assumed dispersion values used in X-ray Crystallography have to be individually revised for experiments with elements near an absorption edge. Additionally, a correlation between refined dispersion values and the shift of an absorption edge may be used to draw conclusions on the electronic and chemical environment of an element of interest or even allow to derive its formal oxidation state from SC-XRD experiments.

In our investigations we could demonstrate that the dispersion corrections  $f'$  and  $f''$  can be refined for measurements near Molybdenum's absorption edge and that this procedure benefits the quality of the structure model. Furthermore, we observed that the dispersion values are heavily influenced by both - the shift of the edge of absorption and the extended X-ray absorption fine structure. Further studies of this kind also heavily rely on synchrotron radiation for simultaneous SC-XRD and XANES/EXAFS measurements.