![ESRF logo] ESRF	**Experiment title:** Precise Anomalous Dispersion Values extracted from Single Crystal Diffraction Data	**Experiment number:** MI-1430
Beamline: BM-20	**Date of experiment**: from: 03 May 2022 to: 11 May 2022	**Date of report**: 06 Sep 2022
Shifts: 24	**Local contact(s)**: Christoph Hennig, Volodymyr Svitlyk	*Received at ESRF:*

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Report:

Correcting for anomalous dispersion is part of any refinement of an X-ray diffraction crystal structure determination. The procedure takes the inelastic scattering in the diffraction experiment into account. This X-ray absorption effect is specific to each chemical compound and is particularly sensitive to radiation energies in the region of the absorption edges of the elements in the compound. Therefore, the widely used tabulated values for these corrections can only be approximations as they are based on calculations for isolated atoms. Features of the unique spatial and electronic environment that are directly related to the anomalous dispersion are ignored, although these can be observed spectroscopically. This significantly affects the fit between the crystallographic model and the measured intensities when the excitation wavelength in an X-ray diffraction experiment is close to an element's absorption edge.

Synchrotron multi-wavelength single-crystal X-ray diffraction experiments were performed on the molecular compound $Mo(CO)_6$ at energies around the molybdenum K edge. The dispersive (f') and absorptive (f'') terms of the anomalous dispersion can now be refined as independent parameters in the full-matrix least-squares refinement. This procedure has been implemented as a new feature in the well-established *OLEX2* software suite. These refined parameters are in good agreement with the independently recorded X-ray absorption spectrum. The resulting crystallographic models show significant improvement compared to those employing tabulated values. We published this very recently (F. Meurer, O.V. Dolomanov, C. Hennig, N. Peyerimhoff, F. Kleemiss, H. Puschmann, M. Bodensteiner, *IUCrJ* **2022**, *9*, 604).

Therein, we compare our refined values for the real part of the anomalous dispersion correction f' to the parallely obtained spectroscopic data and investigated the dependence of this refinement on the resolution of the data, the level of theory of the underlying crystallographic model, correlations of parameters with the introduced anomalous dispersion refinement, the leverage analysis of the impact of each reflection onto the refinement as well as the agreement of tabulated and refined values for measurements performed on laboratory X-ray diffractometers to these data.

We used some of the data of this MI-1430 experiment in that paper and continued our endeavors to refine the anomalous dispersion correction values from single-crystal X-ray diffraction (SC-XRD) experiments as well as to validate them using X-ray near edge absorption spectroscopy (XANES) and extended X-ray absorption fine structure (EXAFS) spectroscopy, which we started in experiment MI-1364. We revalidated our findings on $Mo(CO)_6$ on different crystals and found both a good reproducibility as well as a strong disagreement between refined and currently used tabulated data, e.g. from Henke (Atom. Nucl. Data Tabl. **1993**, *54*, 181) or Sasaki (KEK Report, **1989**, *88*, 1). New data was obtained at eight additional energies (Fig 1A).

Furthermore, experiments on different other molybdenum compounds ($LMoO_3$ [L=1,2,3-Triazacyclononane], $(MeCN)_3Mo(CO)_3$, and $(TMEDA)Mo(CO)_4$ [TMEDA = tetramethylethylendiamine]) showed that the electronic differences induced by a) oxidation state of Mo and b) ligand field, are visible in both, spectroscopic *and* diffraction data. These results are part of the Master's Thesis of F. Meurer and are currently prepared for publication. We further investigated the influence of anomalous dispersion refinements in an multipole model approach and were also able to show that the refinement of dispersion parameters even gives insight into the electronic environment of an atom even for laboratory diffractometer measurements (Fig 1B).
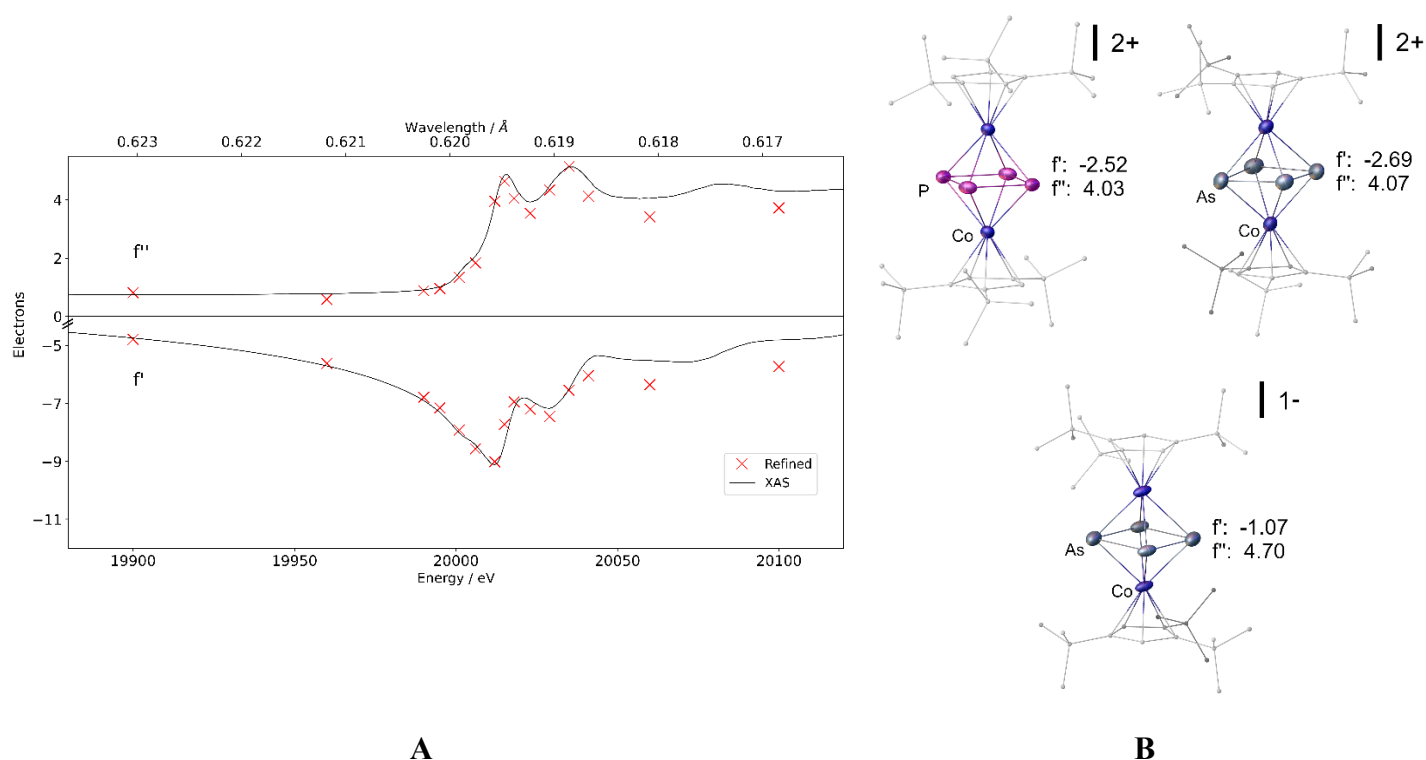

A   **B**

Fig. 1: Comparison of the refined dispersion values for $Mo(CO)_6$ at several energies to the XAS and calculated Spectroscopic *f'* values (**A**) and refined values on published structures measured at laboratory diffractometers (**B**) from (M. Piesch, C. Graßl, M. Scheer, Ang. Chemie Int. Ed. **2020**, *59*, 7154).