MS32 Advanced techniques to disclose Structure-Property Relationships

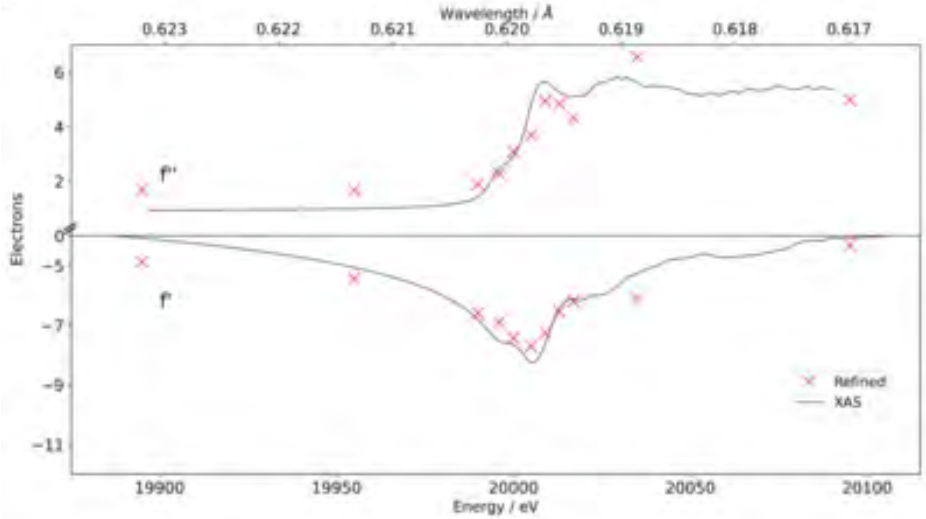
MS32-04
Refinement of anomalous dispersion parameters
F. Meurer [1], O.V. Dolomanov [2], C. Hennig [3], N. Peyerimhoff [4], F. Kleemiss [1], H. Puschmann [5], M. Bodensteiner [1]

[1]University of Regensburg - Regensburg (Germany), [2]OlexSys - Durham (United Kingdom), [3]ESRF/Helmholtz-Zentreum - Grenoble/Dresden-Rossendorf (France), [4]Durham University - Durham (United Kingdom), [5]OlexSys Ltd - Durham (United Kingdom)

Abstract
Correcting for anomalous dispersion is part of any model during an X-ray crystal structure determination. The procedure takes the inelastic scattering in the diffraction experiment into account.[1] 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.[2] Features of the unique spatial and electronic environment that are directly related to the anomalous dispersion are ignored, although these can be spectroscopically observed. 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. The dispersive (f') and absorptive (f") terms of the anomalous dispersion can be refined as independent parameters in the full-matrix least-squares refinement.[3] This procedure has now been implemented as a new feature in the well-established Olex2 software suite.[4] These refined parameters are in good agreement with independently recorded X-ray absorption spectra and the resulting crystallographic models show significant improvement compared to those employing tabulated values (Figs. 1 & 2). The presentation will report on synchrotron multi-wavelength single-crystal X-ray diffraction as well as X-ray absorption spectroscopy experiments which we performed on the molecular compound $Mo(CO)_6$ at energies around the molybdenum K edge (20,000 eV). It will further provide an outlook into the application to determine oxidation states of organometallic compounds.

References
[1] S. Caticha-Ellis, Anomalous Dispersion of X-rays in Crystallography, **1981**.
[2] a) B. L. Henke, E. M. Gullikson, J. C. Davis, *At. Data Nucl. Data Tables*, **1993**, *54*, 181–342; b) S. Brennan, P. L. Cowan, *Rev. Sci. Instrum.*, **1992**, *63*, 850–853; c) S. Sasaki, *KEK Report*, **1989**, *88*, 1-136.
[3] O. Einsle, S. L. A. Andrade, H. Dobbek, J. Meyer, D. C. Rees, *J. Am. Chem. Soc.*, **2007**, *129*, 2210–2211.
[4] O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard, H. Puschmann, *J. Appl. Cryst.*, **2009**, *42*, 339–341.

Experimental (line) and refined (cross) f' and f"



Residual density a) tabulated b) refined dispersion