Refinement Of Anomalous Dispersion Parameters - More Than Model Improvement

Dr. Michael Bodensteiner[1]
[1]*University of Regensburg*

Correcting for anomalous dispersion takes the inelastic scattering in the diffraction experiment into account.[1] This effect, which relates closely to X-ray absorption, is specific to each chemical compound and particularly sensitive to radiation energies near the absorption edges of the elements in the compound. The widely used tabulated values for these corrections are only approximations, as they are based on calculations for isolated atoms.[2] Features of the unique spatial and electronic environment are ignored, although these can be spectroscopically observed. This significantly affects the fit between the crystallographic model and the measured intensities. 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] The refined parameters are in good agreement with independently recorded X-ray absorption spectra (Fig. 1). Also the impact on the obtained crystallographic model is very significant compared to a model employing tabulated corrections (Fig. 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 different compounds at energies around the absorption edges. It will further show strong deviations observed with home laboratory sources even far from an absorption edge and provide an outlook for determining oxidation states in 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] F. Meurer, O. V. Dolomanov, C. Hennig, N. Peyerimhoff, F. Kleemiss, H. Puschmann, M. Bodensteiner, IUCrJ* ***2022****, 9, 604– 609.*

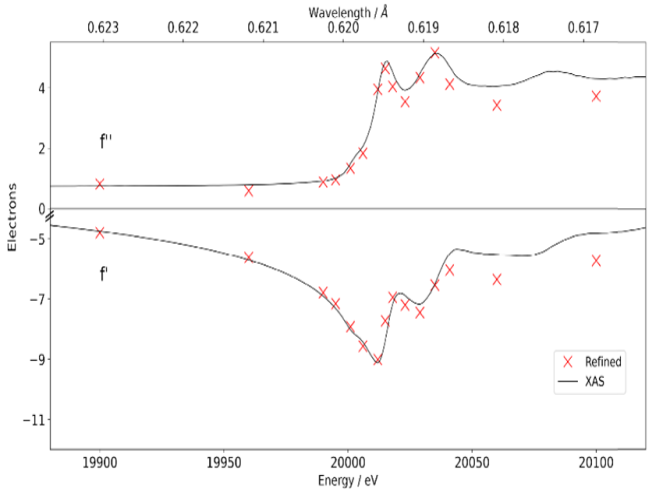

Figure 1

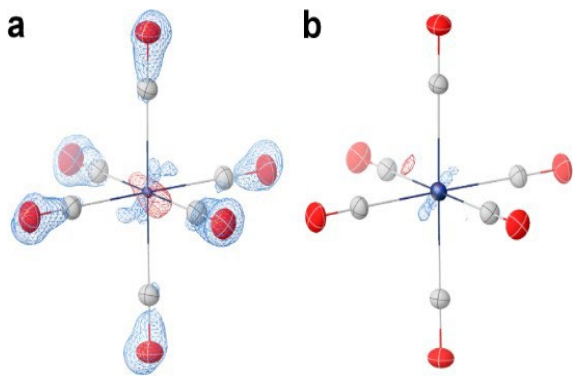

Figure 2