"Diffraction Spectroscopy" - Refinement of Anomalous Dispersion

Florian Meurer[1], Oleg V. Dolomanov[2], Christoph Hennig[3], Nobert Peyerimhoff[4], Florian Kleemiss[1], Horst Puschmann[2], Michael Bodensteiner[1]

[1]Universität Regensburg, Röntgenstrukturanalyse, Fakultät für Chemie und Pharmazie, Universitätsstr. 31, 93053 Regensburg, Germany, michael.bodensteiner@ur.de, [2]OlexSys Ltd, Chemistry Department, Durham University, DH1 3LE, UK, [3]Rossendorf Beamline (BM20-CRG), European Synchrotron Radiation Facility, 71, Avenue des Martyrs, 38043 Grenoble, France, [4]Department of Mathematical Sciences, Durham University, DH1 3LE, UK,

Recent developments in the field of quantum crystallography have led to the user friendly "NoSpherA2" implementation of Hirshfeld Atom Refinement (HAR) into the "Olex2" software.[1] However, individual non-spherical formfactors calculated at high level of theory often still reveal unmodelled electron density, especially in the vicinity of heavy atoms.[2] Radiation damage is a common explanation to this artifacts and originates from inelastic scattering, i. e. absorption.[3] From the point of view of X-ray spectroscopy, absorption is very individual for each compound and different electronic transitions as well as interactions with neighboring atoms can be assigned in the corresponding spectra.[4] Absorption is also closely related to the anomalous dispersion term, best known in crystallography in context with absolute structure determination.[5] Those values used in crystal structure determinations are usually taken from tables that are calculated for neutral spherical atoms and do not take into account many spectral features. Hence, structural models suffer from these shortcomings especially when an absorption edge of an involved element is close to the X-ray energy of the primary beam.

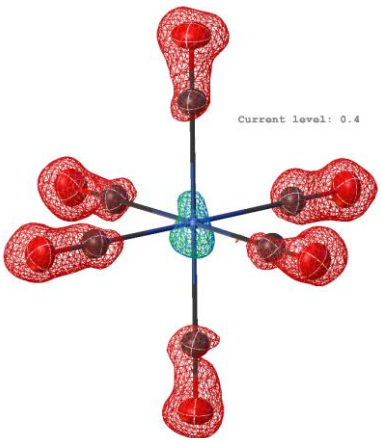

Figure 1: Residual density from data acquired at the Mo-K-edge energy and corrected for anomalous dispersion according to the Sasaki table.[6]

The presentation reports on our results of the inclusion of anomalous dispersion refinement into crystal structure determinations. Synchrotron experiments were carried out at different energies around the K-edge of Molybdenum. A very good correlation between the absorption spectrum of a given element and the refined dispersion values was achieved. The structure model remains unchanged before, after and even at the absorption edge, whereas the employment of tables from literature leads to high residual density, bad displacement parameters and overall poor-quality factors, in any case.

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