

MS28-O5 Fast electron diffraction tomography on beam sensitive materials at room temperature: pharmaceuticals and zeolites

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Collecting electron diffraction data suitable for structure solution on beam sensitive materials is a challenging task. Pharmaceuticals and zeolites belong to extremely beam sensitive materials and in most of the cases they amorphize after few minutes when exposed to an electron beam strong enough for collecting a readable electron diffraction pattern with a conventional CCD. Here we present a method that couples the fast electron diffraction tomography (FEDT) [1] procedure with the Timepix single electron detection device [2]. In FEDT the patterns, in precession mode, are collected sequentially by the detector while the crystal is tilting. Due to the fast read-out and high sensitivity of the Timepix detector the FEDT data collection can be carried out with the crystal tilting at a speed of 2°/s or higher without any loss of reciprocal space volume. Crystals can be searched in STEM avoiding beam damage caused by the continuous TEM illumination. During diffraction data collection at room temperature, the electron dose rate can be reduced to the minimum available by the microscope settings, and weak diffraction reflections can be recorded thanks to the zero noise level of the Timepix, after the inelastic background is cut-out by the in-column energy filter. The high stability of the goniometer allows data collection of 90° of reciprocal space coverage in about 30-45 seconds. We demonstrate the efficiency of the method on the structure solution of the cowlesite zeolite, which degrades too fast under the beam for a standard steady-step data acquisition. As a further test for the efficiency of FEDT+Timepix procedure, the structure solution of a pharmaceutical compound is also presented together with the comparison of the crystal model refined by single crystal x-ray diffraction, in order to show the accuracy of electron data on such a compound.

References

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Keywords: precession, electron diffraction tomography

MS29 Molecular interactions in crystal packing and molecular assemblies

MS29-O1 The silver bond

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Hydrogen bonds, halogen bonds and metal coordination are the main tools used by the crystal engineer to design and synthesize new materials. Metal coordination is above all used for construction of metal-organic frameworks (MOFs), where metal ions or metal ion clusters serve as network hubs that are linked by organic, usually bifunctional struts.

Silver is special in being involved in more than one half of all X-M-X fragments (X = O or N, M = any metal) in the Cambridge Structural Database, where the metal is bonded to only two ligands. While this might not be a desirable property for a MOF hub, such links mimic hydrogen bonds, and the "silver bond" could therefore nevertheless represent an interesting addition to the crystal engineering toolbox. Despite the substantial number of Ag-containing crystal structures available, systematic efforts into this matter seem, however, largely to be lacking. The present investigation focuses on the potential of silver in the establishment of robust, three-dimensional structures. As an example, a dipeptide, L-Val-L-Leu, has been crystallized as a normal zwitterion and as the isostructural silver analogue, the latter forming larger and better diffracting crystals.

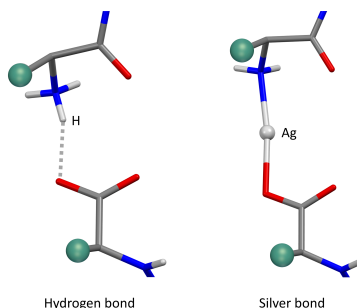


Figure 1. Regular hydrogen bond in the crystal structure of the dipeptide L-Val-L-Leu (left) and a silver bond in the isostructural silver analogue (right). Amino acid side chains are shown as small spheres for clarity.

Keywords: crystal engineering, intermolecular interactions, silver, two-fold coordination

MS29-O2 Molecular interactions and configurational entropy determining the macroscopic polar state of molecular crystals

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Advanced physical characterization of as grown molecular crystals made of dipolar molecules by scanning pyroelectric and phase sensitive second harmonic microscopy has revealed the true macroscopic polar state of molecular crystals: Supported by configurational entropy, i.e. 180° orientational disorder, molecular crystals (and similarly organized materials) grow into a *bi-polar macroscopic state* (for a review, see [1] or basics [2]). This means, experimentally at least two adjacent domains showing opposite average polarization may be observed. Theoretically, this phenomenon is well understood by analytical models (Markov chain, 2D anisotropic Ising model), force field based calculations for defect energies and Monte Carlo (MC) simulations. Both the thermalized state (concerning 180° disorder) of nano sized seeds and e.g. layer by layer grown crystals were investigated by MC. In case of a *seed* undergoing 180° disorder, a bi-polar state is found. In case of a kinetically controlled nucleation of a *mono polar seed*, growth should lead to a *reversal transition*, experimentally confirmed for bi-phenyls [3]. For 4-iodo-4'-nitro-biphenyl (INBP) the reversal of molecular axes 2 takes place over a transition zone of about 150 micron. The combination of anomalous X-ray scattering & pyroelectric measurements allows us to determine the absolute polarity of such bi-polar objects. The experimentum crucis supporting the *reversal* mechanism consisted in the investigation of solid solutions by adding symmetrical molecules (e.g. 4,4'-di-iodo-biphenyl) to the nutrient. Here, the absolute polarity of the as grown bi-polar state was found to be inverted. The result is in agreement with qualitative arguments about main intermolecular interactions at attachment sites [3]. Force field calculations for para substituted benzenes undergoing 180° orientational disorder at growing faces have provided quantitative data in favour of a *reversal transition*. When analysing the source for driving energies, we find that the main part for the electrostatic interaction stems from a dipolar to quadrupole interaction.

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Keywords: macroscopic polar state, orientational disorder, molecular crystals