Charge Density Studies of *in-situ* Crystallized Liquids with Hirshfeld Atom Refinement, Invariom-Model and Multipole-Model

M. Patzer, N. Nöthling, R. Goddard, C. W. Lehmann

Max-Planck-Institut für Kohlenforschung, Kaiser-Wilhelm-Platz 1, 45470 Mülheim an der Ruhr, Germany

patzer@kofo.mpg.de

In-situ crystallization is a powerful tool to obtain the structure of compounds that are liquid at room temperature [1]. The technique involves cooling the sample in a glass capillary below its liquid-solid phase transition temperature, initializing crystallization and using the crystalline powder so obtained as starting material for crystal growth. In favorable cases, a crystal suitable for X-ray analysis can be obtained at the liquid-solid phase boundary by translation of the capillary through the cold nitrogen gas stream (zone melting). If the quality of the *in-situ* grown crystal is sufficiently good, experimental charge density studies (resolution up to 0.5 Å) become possible. Nowadays there are many models used to describe the experimental diffraction intensities (IAM, multipole model, maximum entropy method etc.) [2]. With the appearance of quantum crystallographic methods (Hirshfeld Atom Refinement HAR and X-Ray Constrained Wavefunction analysis XCW) that combine the experimental results with quantum mechanical calculations, it is possible to get precise insights into the "true" nature of the wavefunction and the charge density of a molecule [3]. The charge density of a molecule can also be described as a superposition of theoretical calculated Invariom (*Invaria*nt at*om*) or directly by the theoretically calculated charge density [4]. But which of these methods is best suited for which scientific question or experimental resolution? Different charge density models, such as the multipole-model, HAR and the Invariom-approach, were investigated using experimental diffraction intensities of different *in-situ* crystallized liquids. The residual density in difference Fourier maps as used to evaluate the quality of the theoretical model (Fig. 1) [5]. It was found that multipole parameters derived from fitting to theoretically calculated charge density describe the experiment almost as well as unrestricted multipole refinement. In addition, using theoretical parameters the reflection to parameter ratio is improved.
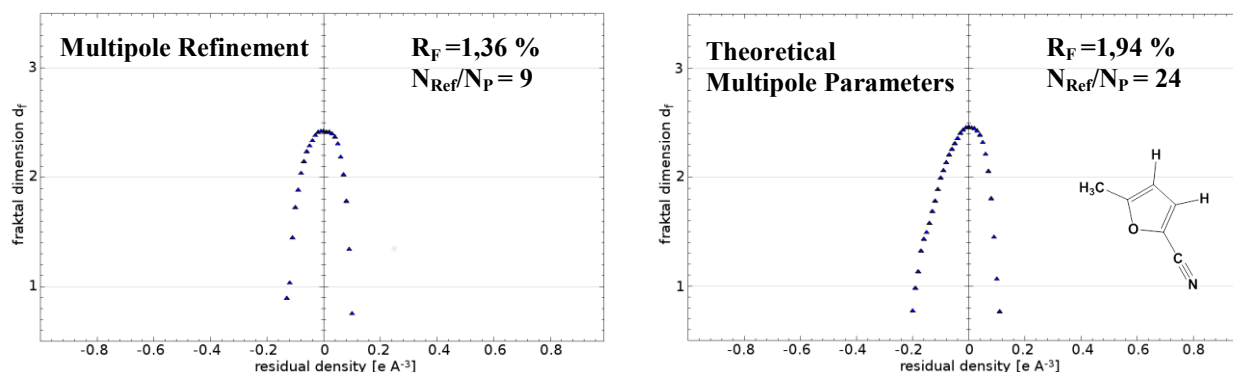

Figure 1. Residual density vs. fractal dimension [5] for 5-methyl-2-furonitrile; multipole parameters derived from least-square fitting of theoretical calculated charge density (B3LYP/6-31G+(d,p)) (resolution 0.66 Å).

[1] Boese, R., (2014). *Zeitschrift für Kristallographie - Crystalline Materials*. 595-601.

[2] Jayatilaka, D. & Dittrich, B., (2008). *Acta Cryst. Section A* **64(3)**, 383-393.

[3] Grabowsky, S., Genoni, A. & Bürgi, H.-B., (2017). *Chem. Sc.* **8(6)**, 4159-4176.

[4] Dittrich, B., Koritsánszky, T. & Luger, P., (2004). *Angewandte Chemie Int. Edition* **43(20)**, 2718-2721.

[5] Meindl, K. & Henn, J., (2008). *Acta Cryst. Section A* **64(3)**, 404-418.

Keywords: Hirshfeld-Atom-Refinement, *in-situ* crystallization