Oral presentation

# Anisotropic Displacement Parameters from theoretical calculations: where are we now?

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Since the early beginning of the history of X-ray diffraction it was clear that to describe properly experimental results, thermal motion need to be modelled simultaneously with electron density. Peter Debye proposed to model thermal motion using a temperature factor, which is considered by the refinement of anisotropic displacement parameters (ADPs). This approach had not changed much during the last century. Meanwhile, we observe an incredibly fast development of theoretical/quantum chemistry methods, and during the last fifteen years, it became feasible to obtain anisotropic displacement parameters for molecular crystals from theory. This possibility opens the door to understanding materials and their properties better. First, it enables comparing experimental ADPs with those obtained from theory. From such a comparison, one may judge the quality of the theoretical model. When an agreement between ADPs from theory and experiment is good, the theoretical model can be judged as 'correct' and used for further thermodynamic functions estimations (heat capacity, vibrational contributions to free energy-crucial for polymorphs). When computed ADPs differ from experimental ones, it might suggest either that the theoretical model has some deficiencies or that something more is hidden in the X-ray data (*e.g.,* disorder, modulation, anharmonicity).

Currently, ADPs for molecular crystals can be derived from (1) *ab-initio* periodic lattice-dynamics calculations with atom- centered based basis sets[1] or plane-wave[2] (2) molecular dynamics trajectories[3], (3) force fields. We decided to verify and compare those approaches. We used several methods to calculate ADPs for two model compounds, L-alanine, and 4'- hydroxyacetophenone, for which excellent single crystal and neutron diffraction data are available. We conducted state-of-the-art ab-initio DFT periodic supercell calculations (3x2x3 for L-alanine and 3x2x2 for 4'-hydroxyacetophenone) with CRYSTAL17 (atom-centered based basis sets) and with VASP (plane-waves), MD simulations with AMBER and force fields calculations with DMACRYS.

In this contribution, I would like to present the comparison of calculation results with experimental data for all tested methods. Besides comparing obtained ADPs with experimental ones, I will also present comparisons of computed heat capacities with the ones obtained from calorimetry.

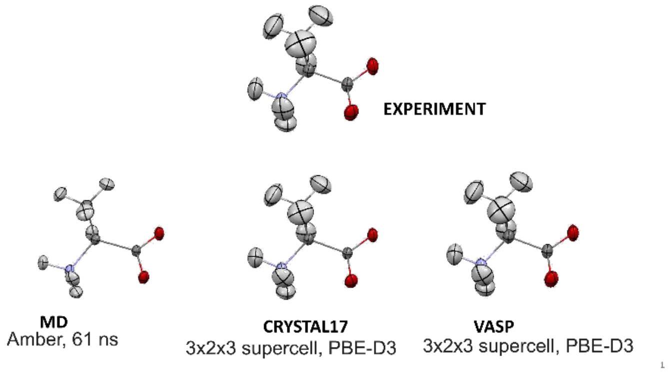

**Figure 1**. Anisotropic displacement parameters for L-alanine from calculations and from experiment.

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[3] Nemkevich A. et al, Phys. Chem. Chem. Phys., 2010,12, 14916-1492