Poster

Hirshfeld atom refinement for polymeric structures: MOFs and COFs

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Metal organic frameworks (MOFs) and covalent organic frameworks (COFs) are polymers which due to their porosity are suitable for various applications, such as gas separation and storage, water harvesting and purification, catalysis, sensing and energy storage. Many of these materials can form crystals amenable to single crystal X-ray diffraction analysis. This provides an opportunity to employ methods from the realm of quantum crystallography, such as Hirshfeld atom refinement (HAR). However, the application of HAR to refine crystal structures of network compounds has been limited thus far with only a few reported cases [1, 2], including one MOF [3]. This group of compounds presents computational challenges not only due to the presence of transition metal atoms but also because quantum crystallography methods tailored to molecular crystals may not be suitable for network compounds.

This work presents a study on the applicability of HAR to MOFs, COFs, and other coordination polymers. In total, successful HARs have been performed for 17 X-ray structures using classical HAR, which involves calculating wave function for a single molecular fragment surrounded by a cluster of atomic monopoles and dipoles. Additionally, for two compounds, HAR employing wave function derived from calculations with periodic boundary conditions (periodic HAR) [4] was carried out. For 10 structures classical HAR was achieved without constraints imposed on hydrogen positions or thermal parameters, while for two structures, hydrogen ADPs were refined. In the case of periodic HAR, one structure (ZOGKUD) could be refined anisotropically, whereas for the other (HOYKUD), only isotropic refinement was feasible (Fig. 1). Compared to IAM, classical HAR resulted in elongated bond lengths formed by H atoms, with a mean absolute difference (MAD) of 0.09 Å. Periodic HAR yielded bond lengths very similar to those obtained with classical HAR. For ZOGKUD, the only structure for which both methods were successful, the MAD between X-H bond lengths obtained with classical HAR and IAM, as well as between periodic HAR and IAM was equal to 0.15 Å. These preliminary findings suggest that for polymeric structures, such as MOFs and COFs, atomic scattering factors provided by classical HAR may be sufficient to obtain structural parameters comparable to those resulting from periodic HAR where the periodicity of the wave function is fully accounted for.

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