

Hydrogen shift in electrostatic potential maps from 3D ED experiments

Paul B. Klar¹, Yaşar Krysiak², Gwladys Steciuk¹, Lukáš Palatinus¹

¹Institute of Physics of the Czech Academy of Sciences, Prague, Czechia, ²Institute of Inorganic Chemistry of the Leibniz University Hannover, Germany

Electron- and X-ray diffraction-based crystal structure models most often ignore the polarisation effects of chemical bonds by applying the independent atom model. As a result, refined hydrogen positions are shifted relative to the actual position of the nucleus of the hydrogen. Therefore, interatomic distances involving hydrogen atoms deviate significantly from reference bond lengths determined, e.g., from neutron diffraction experiments. This is well-known and routinely corrected for in single crystal X-ray diffraction [1]. Structure determination with 3D electron diffraction (3D ED) is a steadily advancing method, which nowadays frequently reveals hydrogen atoms in electrostatic potential maps [2]. In this work we analyse C-H and O-H distances determined from 3D ED experiments.

Five organic and two inorganic compounds were measured with continuous-rotation 3D ED. Structure models were refined taking multiple scattering of electrons into account. With this refinement approach, a very low background noise level was achieved and in total 107 out of 131 hydrogen atoms were detected in the respective electrostatic potential maps. Using the independent atom model and constrained hydrogen positions, a series of refinements with varying distance constraints were performed for each measurement.

The C-H and O-H distances that resulted in the lowest figures of merit (wR_{all}) were compared with reference bond lengths. Distances derived from the 3D ED experiments were systematically longer than respective internuclear distances. The derived C-H bonds were typically 0.03 Å longer, and the O-H distances about 0.10 Å longer. Hence, the shift of the hydrogen atoms relative to the expected position of the proton is more pronounced for the more polar O-H bond. Furthermore, the shift is larger for room temperature measurements than for measurements performed at $T = 100$ K.

Qualitatively, these results are expected within the independent atom model for electron crystallography. The electrostatic potential is dominated by the positively charged nuclei, and a shift of the negative potential of an electron causes a shift of the observed potential maximum away from that electron.

Consequently, refinements that place hydrogen atoms using constraints require new reference distances specific for electron diffraction. The determination of these references is the subject of future work. Higher accuracy may be achieved by implementing the aspherical atom model in a refinement routine that takes multiple scattering into account.

[1] Woinska M *et al.* Hydrogen atoms can be located accurately and precisely by x-ray crystallography. *Sci. Advances*, 2, e1600192 (2016)

[2] Gemmi M *et al.* 3D Electron Diffraction: The Nanocrystallography Revolution. *ACS Central Science*, 5, 1315-1329 (2019)

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