

# Accurate hydrogen position from single crystal neutron diffraction

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Neutron diffraction is sensitive to the nuclear density of atoms. Neutron scattering length  $b$  is independent of atomic number, isotopes of the same element can have very different neutron scattering properties, for example, the scattering length is negative for hydrogen ( $^1\text{H}$ :  $-3.742\text{ fm}$ ) and positive for deuterium (D:  $6.67\text{ fm}$ ). The scattering length  $b$  of a nucleus measures the strength of the neutron-nucleus interaction, and it is independent of scattering angle. Unlike X-rays form factors, neutron scattering lengths do not decrease for high Q reflections, advantageous for using neutron diffraction to detect light elements at subatomic resolution. Accurate hydrogen positions from neutron diffraction have been used to facilitate the analysis of chemical bonding and intermolecular hydrogen bonding interactions within the framework of the quantum theory of atoms in molecules (QTAIM) [1]. In this presentation, I will discuss recent developments on locating hydrogen atoms using wavelength-resolved TOF Laue technique employed at the TOPAZ beamline [2] of the ORNL Spallation Neutron Source.

Neutron wavelength-resolved TOF Laue technique expands the measured diffraction pattern from 2D on detector spaces to wavelength-resolved 3D volume in  $(x, y, \lambda)$  along the neutron TOF direction. TOPAZ is capable of volumetric reciprocal space mapping to  $Q_{\text{max}}$  of  $25\text{ \AA}^{-1}$  ( $d_{\text{min}} = 0.25\text{ \AA}$ ). Hydrogen atom positions appear as negative *holes* in Fourier map and can be well resolved from subatomic resolution single crystal neutron diffraction data without the need for sample deuteration. High resolution data measured on TOPAZ uncovered the off-center placement of the disordered methylammonium cation in the hybrid organic-inorganic perovskite  $\text{CH}_3\text{NH}_3\text{PbI}_3$  [3]. The long-proposed dihydrogen bond from the reaction of an iron-based electrocatalyst with  $\text{H}_2$  was confirmed by neutron diffraction [4]. The reaction leads to heterolytic cleavage of the dihydrogen bond into a proton and hydride. The precise location of H atoms revealed an unusually strong “dihydrogen bonding” interaction between the acidic  $\text{N-H}^{\delta+}$  on the pendant amine ligand and hydridic  $\text{Fe-H}^{\delta-}$  in the reaction intermediate. A molecular nanocluster  $\text{Cu}_{32}(\text{H})_{20}\{\text{S}_2\text{P}(\text{O}/\text{Pr})_2\}_{12}$  with a record number of 20 hydrides were found by high-resolution neutron diffraction to exhibit tri-, tetra-, and penta-coordination modes [5].

It is worth noting that large 3D volumes of diffraction data collected on TOPAZ are saved in neutron event mode, which makes it possible to retrieve real-time structural information on material's response to external stimuli (temperature, pressure, electric and magnetic field, etc.). Using this multi-dimensional data collection strategy in 3D diffraction and parameter spaces developed at TOPAZ [6], we have mapped out the key role of hydrogen bonding in the structural phase transitions of a hybrid organic-inorganic perovskite photovoltaic material [7].

## Reference

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