

**MS22-O4****Investigating short strong hydrogen bonds (SSHBs) with potential proton migration behaviour using experimental charge density analysis**Lucy Saunders<sup>1</sup>, Chris Frampton<sup>2</sup>, Harriott Nowell<sup>1</sup>, Dave Allan<sup>1</sup>

1. I19, Diamond Light Source, Didcot, United Kingdom
2. Wolfson Centre for Materials Chemistry, Brunel University London, Uxbridge, United Kingdom

**email: [lucy.saunders@diamond.ac.uk](mailto:lucy.saunders@diamond.ac.uk)**

Proton migration involves a gradual shift in hydrogen atom position across a hydrogen bond (HB). In the solid-state, this behaviour may occur as a function of an external variable including temperature<sup>1</sup> or pressure.<sup>2</sup> Such behaviour is typically observed in HBs characterised by very short donor-acceptor distances (short strong hydrogen bonds – SSHBs), in the range of 2.5 Å for O—H $\cdots$ O HBs<sup>3</sup> and 2.6 Å for N—H $\cdots$ O HBs,<sup>4</sup> where the barrier to proton transfer is low.<sup>5</sup>

Potentially useful solid-state physical properties including ferroelectrics<sup>6</sup> or thermochromism<sup>7</sup> may result following proton migration across SSHBs. Increasing the understanding of where such behaviour is manifest may allow functional materials to be accessed more reliably in future; correlations to donor-acceptor distances and  $\Delta pK_a$  values of components have previously been made.<sup>8</sup>

In this work, we present variable temperature single crystal synchrotron X-ray diffraction (SCSXR) studies of several potential proton migration materials. These materials are multi-component organic co-crystals/salts (carboxylic acids with urea/*N*-heterocycle co-formers) where SSHBs form the connections between molecules. For the most promising migration materials, we use experimental charge density analysis to investigate the SSHBs across which this behaviour is suggested and attempt to unravel the chemical bonding and/or molecular features that contribute. We present results from multipolar refinements (performed in XD2006<sup>10</sup> using Hansen and Coppens formalism<sup>11</sup>) of charge density data collected on beamline I19, Diamond Light Source (UK).<sup>9</sup> We also discuss aspects of the data collection strategy implemented to obtain the quality high resolution data required for the charge density analysis.

## References:

- [1] C. C. Wilson, K. Shankland and N. Shankland, *Z. Kristallogr.*, 2001, 216, 303-306.
- [2] D. M. S. Martins et al., *J. Am. Chem. Soc.*, 2009, 131, 3884-3893.
- [3] P. Gilli, V. Bertolasi, V. Ferretti and G. Gilli, *J. Am. Chem. Soc.*, 1994, 116, 909-915.
- [4] T. Steiner, I. Majerz and C. C. Wilson, *Angew. Chem. Int. Ed.*, 2001, 40, 2651-2654.
- [5] C. L. Perrin, *Acc. Chem. Res.*, 2010, 43, 1550-1557.
- [6] S. Horiuchi and Y. Tokura, *Nat. Mater.*, 2008, 7, 357.
- [7] C. L. Jones, C. C. Wilson and L. H. Thomas, *CrystEngComm*, 2014, 16, 5849-5858.
- [8] A. O. F. Jones et al., *Phys. Chem. Chem. Phys.*, 2012, 14, 13273-13283.
- [9] D. Allan et al., *Crystals*, 2017, 7, 336.

**Keywords: hydrogen bond, migration, charge density****MS22-O5****Dynamic quantum crystallography**Anders Østergaard Madsen<sup>1</sup>, Anna Hoser<sup>2</sup>, Ioana Sovago<sup>3</sup>

1. Department of Pharmacy, University of Copenhagen, Copenhagen, Denmark
2. Department of Chemistry, University of Warsaw, Warsaw, Poland
3. Department of Chemistry, University of Copenhagen, Copenhagen, Denmark

**email: [a.madsen@sund.ku.dk](mailto:a.madsen@sund.ku.dk)**

From the point of view of X-ray scattering the electron density and the nuclear density are communicating vessels, and it is important to model both in order to get a full picture of the charge density. We use quantum mechanics to construct models of the thermal vibrations in crystals, which can be refined and/or validated against scattering data. Scattering data is here understood in the broadest sense; the traditional methods of X-ray and neutron diffraction could be complemented by other probes, such as ssNMR, Raman and terahertz spectroscopies, as well as inelastic scattering or thermal diffuse scattering, which are all techniques that holds the key to understand the correlated motion of atoms in crystals. The use of quantum mechanics in crystallography has a long history, however in most applications the quantum mechanical modeling has focused on the description of the electron density. Much less attention has been devoted to the nuclear motion, although the atoms in the crystal are of course vibrating, even at the lowest temperatures. This is unfortunate. Not only does the atomic and molecular motion define important physico-chemical properties such as the mechanical and thermodynamic stability of the crystal, but the concerted motion of atoms give rise to thermal diffuse scattering which affects the Bragg intensities. Ultimately, the quantum-mechanical models of electron density distribution and nuclear motion should amalgamate into a common model, which can be compared and refined against the experimental evidence, and which can be used to understand solid state properties at the atomic level. We will present our recent approach to refine lattice-dynamical models against diffraction data [1,2], demonstrate a combined model of normal mode and multipole refinement [3], and give examples of how the dynamics derived from these models can be used to derive heat capacities and free energies in order to investigate the relative stability of polymorphic molecular systems.

## References:

- [1] A. A. Hoser, A. Ø. Madsen, *Acta Crystallogr. Sect. Found. Adv.* 72, 206–214 (2016)
- [2] A. A. Hoser, A. Ø. Madsen, *Acta Crystallogr. Sect. Found. Adv.* 73, 102–114 (2017)
- [3] I. Sovago, A. A. Hoser, A. Ø. Madsen. Manuscript in preparation.

**Keywords: Quantum Crystallography, Lattice dynamics, charge densities**