The Evolution of Hydrogen Bonds in Molecular Materials Under Changing External Conditions by Neutron Diffraction and Complementary Methods

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Much of our recent experimental work has focused on the use of X-ray and neutron diffraction to study the structural evolution of hydrogen bonded molecular systems, including polymorphic materials, molecular complexes, tautomeric molecular materials, systems exhibiting hydrogen atom transfer and disorder, and magnetic systems coupled through hydrogen bond motifs. In particular we have focused on multi-temperature and pressure approaches to these studies, revealing often subtle behaviour of the hydrogen bonding, the structural evolution and on some cases of evolution of physical properties. Some of these effects are sufficiently subtle as to challenge the limits of current experimental diffraction, and also to challenge our theories of hydrogen bond formation.

As a complementary approach to understanding these systems, we have for some years been applying developing plane-wave (periodic) density functional theory calculations for studying hydrogen bonds in the solid state. These are shown to have real potential in the study of a variety of hydrogen bonding systems. In addition MD approaches have been developed for these calculations, which allow us to examine the temperature evolution of molecular structures in the solid state and to quantify proton transfer effects. This leads to a fuller understanding of hydrogen bond formation and offers an improved description of the structural evolution observed in experiments.

These approaches will be illustrated by results from a range of studies including: proton transfer systems, including examples in which the rational design and control of the degree of proton transfer is achieved; materials with potentially cooperative hydrogen bonding; tautomeric hydrogen bonded systems in which very small experimental energy differences can be reproduced and understood; prediction of energy scales for polymorphism in hydrogen-bonded molecular complexes, and optimisation of magnetic coupling in inorganic materials by design of simple hydrogen-bonded linkages.