FA4-MS33-T01

Structural Evolution in Molecular Materials by Diffraction and Related. Chick C Wilson
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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, with effect on optical and non-linear optical properties; 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.

Keywords: hydrogen bonding, solid-state structural changes, structure and properties

FA4-MS33-T02

On quantitative structural and electron density studies of interactions in molecular crystals. Anna Hoser, Paulina M. Dominiak, Krzysztof Woźniak.
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This contribution is focused on quantitative relationships between interacting atoms in molecular crystals resulting from experimental charge density studies. The role of factors influencing the quality of such relationships - in particular, treatment of H-atoms and assumptions blindly applied during refinement process - will be discussed. Details of refinement of single crystal X-ray data in order to achieve the final structural results of the same quality as those resulting from neutron data will be presented. Will demonstrate how to refine high resolution single crystal X-ray diffraction data only to obtain electron densities as reliable as in the case of joint neutron/X-ray multipole refinement. Improvement of data collection and processing and extension of electron density models used allow to detect even the finest interactions in the solid state. These are key steps toward quantitative relationships in the field of crystal engineering.

Keywords: molecular crystals, experimental electron densities, quantitative relationships

FA4-MS33-T03

Crystallographic elucidation of structure-properties relationships in molecular spin-crossover crystals. P Guionneau[a], H Shepherd[b], S Lakhloufi[a,c], A Kaiba[a], F. Le Gac[a], MH Lemée-Cailleau[c], JF Létard[a], AE Goeta[b], P Rosa[a]. [a]*CNRS, Université de Bordeaux, ICMCB, France.* [b]*Chemistry Department, Durham University, U.K.* [c]*Institut Laue-Langevin, ILL, Grenoble, France.*
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The fascinating spin-crossover phenomenon concerns many fields as diverse as the dynamic of Earth mantle, human biology and the race to new materials for the future with potential industrial applications in information storage, display devices and molecular electronics in general. To this aim, the spin-crossover phenomenon in molecular materials has been extensively studied worldwide which results in a large amount of data and a fine knowledge of this phenomenon [1], revealing in particular the paramount role of the structural properties on the magnetic and optical properties. However, whilst new molecular spin-crossover materials are designed, intricate behaviours are encountered deserving deeper crystallographic analysis. In such context, we will present the structure-properties relationship in some recently studied molecular spin-crossover materials. These studies concern the investigation of complicated phase diagrams where pure structural transition and spin-crossover act in synergy. Notably, we will show how crystal structure modifications induced by external constraints allow to control the spin conversion rate, and thus the magnetic response, in dinuclear iron(II) molecular complexes [2]. We will also show for instance how a reversible non destructive metal-ligand bond break can drive the magnetic features in a family of hepta-coordinated iron(II) molecular crystals [3] as well as how the interactions between the solvent and these molecular complexes appear crucial. These results, based on X-ray and neutron diffractions in various experimental environments such as high pressure, low temperature and light irradiation on molecular single crystals, not only elucidate the peculiar behaviour of the related compounds but also bring global information on the spin-crossover mechanism itself and on structure-properties relationship in molecular materials.

[1] Eds. P. Gütlich, H.A. Goodwin, Spin Crossover in Transition Metal Compounds, Topics in Current Chemistry, Springer Verlag, Berlin-Heidelberg-New York, 2004, vols. 233-235. [2] Kaiba A. et al. *Dalton trans*. (2010), 39, 2910-2918. [3] Guionneau P. et al. *Chem. Comm.* (2007), 3723-3725.

Keywords: X-ray single-crystal diffraction, structural relationships, molecular crystals