The application of pressure provides a unique method of perturbing the hydrogen bond. The application of high pressure allows the hydrogen bond length to be altered cleanly and continuously within the same phase, and changing pressure can produce much larger changes in geometry than can changing temperature.

We present recent developments in high pressure technology and neutron instrumentation which now make it possible to measure the changes of the proton behaviour of the hydrogen bond at hydrostatic pressures up to and beyond 10 GPa. By making use of examples of materials containing hydrogen bonds for example water, squaric acid, KDP and gas hydrates, we will demonstrate the application of these techniques and how they provide insight into the nature of the hydrogen bond at high pressure.

Keywords: hydrogen-bond, high-pressure, neutron diffraction

### MS.90.4

**Stereochemistry & charge density of hydrogen bonds with oxygen acceptor**

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Hydrogen bonds play a crucial role in the structure and function of many bioactive molecules. They combine the strength of an electrostatic interaction with the directionality of a dipole interaction to produce specific bimolecular interactions [1]. An understanding of the relative strengths and geometries of the hydrogen bonds is required for the design of new supramolecular materials including the engineering of synthetic supramolecular crystal engineering and of novel drug molecules, supramolecular crystal engineering and molecular mechanics.

Putting the Squeeze on Hydrogen Bonds

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### MS.90.5

**Water structure is important – OH···π hydrogen bonds in p-sulfonatocalix[4]arene**

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Hydrogen bonding in the solid state is a well recognised and widely studied phenomenon. The simplest model systems to probe hydrogen bonding are hydrated crystal forms, since water can act both as a hydrogen bond donor and acceptor while being a rigid and very small molecule. On the other hand, the incorporation of water into the crystal lattice can cause serious problems in, for example, pharmaceutical compounds due to considerably lower solubility and thus lower bioavailability, making crystalline hydrate research more than an academic interest. Investigating the interactions of water in crystal structures gives vital information about conventional hydrogen bonds as well as the relevance of short and long range interactions which stabilise crystalline hydrates.

The compound p-sulfonatocalix[4]arene is reported to crystallise in a triclinic pentasodium salt[1] and an orthorhombic tetrasodium salt,[2] both highly hydrated with 14 and 12 water molecules, respectively. The tetrasodium salt hydrate is reported to contain one water molecule in the host’s cavity, making this substance the perfect model to study water in hydrophobic environments. During our investigations, we found two novel monoclinic polymorphs of the tetrasodium salt hydrate, also showing the embedded water molecule. Using X-ray and neutron single crystal diffraction, accurate hydrogen positions for two of the coordinated water molecules. The hydrogen bond preferential stereochemistry is correlated to the π electrons of the cavity proving the existence of OH···π interactions. In addition, the molecules are ‘compressed’ with short OH bonds, a direct consequence of the hydrogen bonded water network in the crystal structure. The pentasodium salt hydrate exhibits an intra-cavity water engaging in both OH···π and OH···O hydrogen bonding, with the OH covalent bond forming the interaction with the aromatic ring shortened. Using the ab initio lattice energy calculation algorithm PACHA,[3] based on the neutron coordinates, gives an OH···π interaction energy of 6.9 – 7.5 kJ mol⁻¹, and reveals the dominance of the charge assisted interactions to the Na⁺ coordinated water molecules. The p-sulfonatocalix[4]arene crystal forms thus represent a model system to investigate water interactions involving comparison of hydrophilic and hydrophobic entities. Such interactions are especially important in protein/water systems but are not trivial to study, either due to the size of the protein or the difficulty in producing crystals suitable for neutron work, mesoscale systems such as p-sulfonatocalix[4]arene represent an accessible simplified model compounds.

The application of pressure provides a unique method of perturbing the hydrogen bond. The application of high pressure allows the hydrogen bond length to be altered cleanly and continuously within the same phase, and changing pressure can produce much larger changes in geometry than can changing temperature.

### MS.90.6

**Water structure is important – OH···π hydrogen bonds in p-sulfonatocalix[4]arene**

Katharina Fucке, Judith A. K. Howard, Jonathan W. Steed, Department of Chemistry, Durham University, Durham, (UK). E-mail: katharina.fucke@durham.ac.uk

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### Keywords:

- Hydrogen bonding, hydrate, water structure
- Electron density, interactions