

High Pressure Behaviour of Small hydrogen Bonded Molecules: A Neutron Diffraction Study

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The advantages of neutron radiation in diffraction, compared to those of X-rays, have been well documented as has the role of high pressure in neutron diffraction experiments.[1,2]

PEARL – the dedicated high pressure neutron instrument at ISIS – was designed around the PE press and has, for the past 21 years, formed a significant part of the user programme at the ISIS Neutron and Muon Facility [3].

In this presentation we will provide a brief introduction into the capabilities of the PEARL instrument in particular for studying hydrogen bonded materials as a function of temperature and pressure. We will then provide two examples of hydrogen bonded systems in which the application of high pressure modifies the crystal structure and by using neutron diffraction in conjunction with computational modelling we have been able to understand the driving forces involved in phase transitions.

In the first example we will describe the high-pressure structural behaviour of phosphoric acid [4]. A compression study of the monoclinic phase, using neutron powder diffraction and X-ray single-crystal diffraction, shows that it converts to a previously unobserved orthorhombic phase on decompression. Compression of this new phase is reported up to 6.3GPa. We find the orthorhombic phase is more efficiently packed, with reduced void spaces, resulting in a larger bulk modulus. Molecule–molecule interaction energies reveal a more extensive network of increased attractive forces in the orthorhombic form relative to the monoclinic form, suggesting greater thermodynamic stability.

In a second example we show recent results from the non-planar biurea molecule ($C_2H_6N_4O_2$) which can be described as two monomer urea units related to each other by 2-fold symmetry running the connecting N–N bond. At room pressure and temperature biurea crystallises in a monoclinic structure. The molecular network is held together using N–H...O intermolecular hydrogen bonds and results in each oxygen atom having a close contact with three N–H groups with three distinct distances.

At ~0.55GPa we observe an isosymmetric phase transition [5] where the biurea molecule changes both its shape and reorientates within the unit cell (Figure 1 resulting in a reduction in the overall unit cell volume of 4.4% and a lengthening of the hydrogen bond. Using a combination of calculations to determine the inter and intra-molecular energies we show that despite what

may first appear to be a phase driven by unfavourable hydrogen bond interactions the phase transition is actually driven by dispersion effects.

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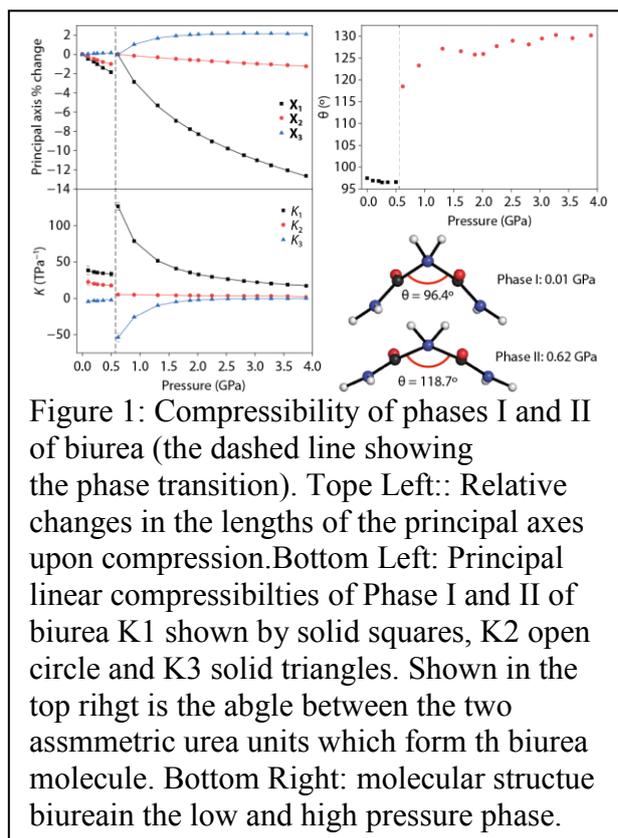


Figure 1: Compressibility of phases I and II of biurea (the dashed line showing the phase transition). Top Left: Relative changes in the lengths of the principal axes upon compression. Bottom Left: Principal linear compressibilities of Phase I and II of biurea K_1 shown by solid squares, K_2 open circle and K_3 solid triangles. Shown in the top right is the angle between the two asymmetric urea units which form the biurea molecule. Bottom Right: molecular structure biurea in the low and high pressure phase.

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