High Pressure Structural Studies of Hydrogen Bond Centring

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Pressure provides a powerful means to explore the effects of H-bond centring. Easily available pressures can make large changes in H-bond geometry, allowing studies of H-bonds under a wide range of strengths. In addition, pressure makes these geometric changes cleanly by varying the density without the complications introduced by chemical substitution when geometry changes are made by ''chemical pressure''. As a result, ice, one of the simplest H-bonded systems, has been intensively studied. Here, the aim has been to observe the transition to centred ice X, where the proton reaches the centre of the hydrogen bond. Raman and infra-red studies report the onset of the transition at ~70 GPa, but find that the transition is not complete until ~120 GPa [1]. Ab-initio molecular dynamics studies support this view and find evidence of quantum smearing of the protons over a pressure range of ~50 GPa around the centring transition [2].

Direct structural information on the proton distributions in this pressure range would greatly improve our understanding of the centring transition in ice. However, the pressures involved remain much too high at present for neutron diffraction which is the only technique able to make such measurements. H-bonded ferroelectrics such as potassium dihydrogen phosphate (KDP), potassium dideuterium phosphate (DKDP) and squaric acid ($H_2C_4O_4$, H_2SQ) provide more tractable analogues for structural studies of H-bond centring. Their structures have been studied in detail at ambient pressure and up to ~2 GPa by high resolution neutron diffraction [3], and are estimated to undergo hydrogen-bond centring at pressures between 5 and 10 GPa [3]. Recent developments to the Paris-Edinburgh cell have now extended the maximum pressure for single-crystal neutron diffraction studies to 10 GPa and hence make it possible to determine structures at pressures close to the centring transition.

We will present the results of neutron diffraction studies of KDP, DKDP and H_2SQ up to 10 GPa. These studies reveal that the proton/deuteron distributions remain strongly elongated at pressures where the H-bond appears to be centred.

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