

PROTON DYNAMICS IN SHORT HYDROGEN BONDS: TWO-SITE HOPPING IN A SINGLE-WELL POTENTIAL.

M.R. Johnson, H.P. Trommsdorff, A. Ivanov
(Institut Laue Langevin, Grenoble, France)

I.R. Evans, S.J. Ford
(Department of Chemistry, University of Durham, Durham, UK)

A.J. Horsewill, I. Frantsurov
(School of Physics & Astronomy, University of Nottingham, Nottingham, UK)

Normal hydrogen bonds are characterised by a two-well, potential energy surface (PES) in which the proton can jump from one well to the other [1]. In contrast, short hydrogen bonds are characterised by a single, potential energy well for the proton which, at first sight, would seem to limit the proton dynamics to small amplitude vibrations. Crystallographic measurements reveal however a proton migration effect with increasing temperature in some short hydrogen bonds [2, 3]. Furthermore, short hydrogen bonds are thought to play a key role in important chemical and bio-physical processes (e.g. enzyme catalysis [4]), which would be difficult to understand in terms of a static, albeit anharmonic, single-well potential.

The crystallographic data has been understood with the aid of ab initio molecular dynamics simulations [5,6] which show that fluctuations in the potential energy well, driven by lattice phonons, are responsible for proton migration. In fact, the time-averaged potential energy surface has two minima, resembling the PES of the normal hydrogen bond, and the proton dynamics underlying proton migration can effectively be viewed as two-site hopping, as for a normal hydrogen bond. In order to confirm this model of proton dynamics, two-site hopping in a single-well potential, we have recently undertaken a series of experiments including quasielastic neutron scattering, vibrational spectroscopy and field-cycling NMR.

We will present an overview of the computational results for 3,5-pyridine dicarboxylic acid followed by new experimental evidence for proton hopping in the fluctuating, single-well potential of the short hydrogen bond and the role of entropy on the proton dynamics. A new, more detailed crystallographic study will be presented on a poster.

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