

Poster Presentation

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Core level crystallography: Probing H-bonding through nitrogen XPS and NEXAFS

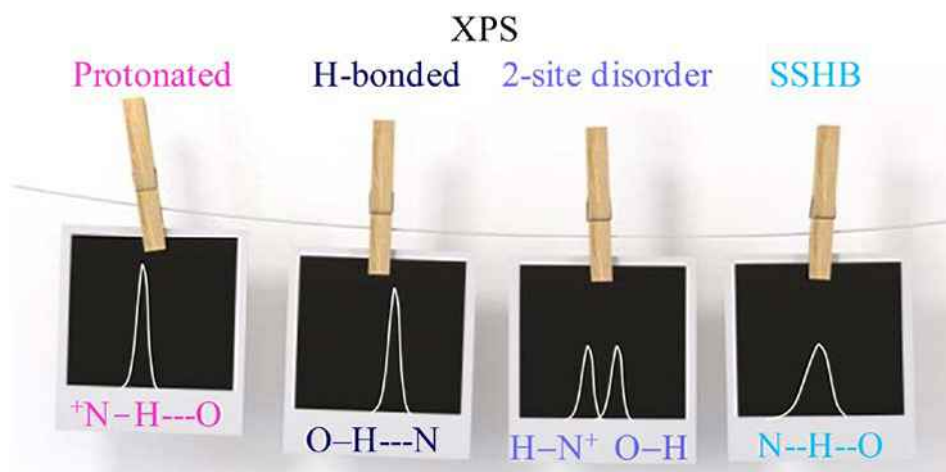
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Determining the location of hydrogen is not always straightforward, despite its potential for wide-reaching effects, such as altering physicochemical properties and biological/chemical processes. Proton transfer can be considered a simple chemical reaction, with a continuum from neutral to protonated states, and short, strong H-bonds (SSHB) and disordered systems between the two extremes. X-ray Photoelectron Spectroscopy (XPS) and Near Edge X-ray Absorption Fine Structure (NEXAFS) intrinsically probe the local environment, with sensitivity to the chemical state of the atom and, importantly, nature of the local chemical and bonding environment. Organic molecular crystals have been studied by nitrogen XPS and NEXAFS, offering an alternative to X-ray and neutron diffraction. Strong chemical shifts occur with proton transfer to nitrogen (+N-H---O vs. N---H-O), unambiguously characterizing protonated and H-bonded systems,[1] leading to direct observation of an unusual solid-state colour change for 4,4'-bipyridine/squaric acid with heating[2] involving proton transfer to nitrogen with temperature-dependent measurements. Correlation between H-bond lengths and chemical shifts indicates potential for predicting H-bond lengths. SSHBs provide an interesting case, as hydrogen can reside midway between donor and acceptor, having a 3-centre, 4-electron bond with quasi-covalent character and atypical properties. Intermediate chemical shifts are found with hydrogen midway between donor and acceptor in 3,5-pyridinedicarboxylic acid, with increased peak width representative of hydrogen's broadened single minimum potential well.[3] This contrasts with conventional 2-site hydrogen disorder, in which signals from both donor and acceptor environments result in 2 peaks reflecting the % occupancy. Valuable electronic and structural information is obtained from the variety of organic systems investigated, with XPS clearly distinguishing different types of crystallographic materials (Fig 1).

[1] J. S. Stevens, S. J. Byard, C. C. Seaton, et al., *Angewandte Chemie International Edition* 2011, 50, 9916-9918., [2] D. M. S. Martins, D. S. Middlemiss, C. R. Pulham, et al., *Journal of the American Chemical Society* 2009, 131, 3884., [3] F. Fontaine-Vive, M. R. Johnson, G. J. Kearley, et al., *The Journal of Chemical Physics* 2006, 124, 234503.



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