

Poster Presentations

[MS24-P05] Influence of Chemical and Crystallographic Environment on Solid-State Proton Transfer.

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Proton transfer can be considered the simplest example of a chemical reaction and plays a key role in many chemical and biological processes such as acid/base catalysis or enzyme activity. The majority of studies into the mechanisms and the controlling factors of these processes have focused on the solution state, with less work on understanding these factors in the solid-state. However, proton transfer in a crystal influences a range of physicochemical properties, such as colour or conductivity, through changes to the crystal structure. One route for the investigation of these factors is through the creation of multi-component crystalline materials. Such materials offer a continuum of structural types from neutral co-crystals to charge separated salts with proton disordered and mixed systems between the two extremes. Studies into the influence of chemical changes in the components on the final phase have often utilised the ΔpK_a rule, [1, 2] while recent work has demonstrated the influence of the local environment of proton location [3-5]. Understanding how the interplay of these factors influences the level of proton transfer in the final crystal is vital to achieve the aim of controlled creation of crystalline materials with task-specific properties. The creation of multi-component crystals of 4-phenylpyridine and isonicotinamide with differing benzoic acids was undertaken to investigate proton transfer in an acid to pyridine hydrogen bond through changes in the chemical and crystallographic environment. The influence of the local bonding environment and functional

group choice on proton transfer was examined through crystallographic structure determination and by molecular modelling. In most cases, while the choice of chemical species contributed to the level of proton transfer, the local environment was a significant factor. Ab initio quantum mechanics calculations on dimers and small molecular clusters confirms the influence of neighbouring intermolecular interactions on the proton transfer energy surfaces by adjusting the shape and size of the low energy minima. Thus to create new materials with desired properties, reproducibility of both intermolecular interactions and crystal environment are of equal importance. In this case the isonicotinamide system displays greater consistency in crystal environment compared to the 4-phenylpyridine case, with 78% of all known structures sharing the same hydrogen bonding motifs.

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