Contribution ID: **11** Type: **Oral Communication**

Proton diffusion in a benchmark entangled hydrogen bonding network

Wednesday 6 September 2023 12:30 (15 minutes)

Hydrogen-bonded networks sustain a broad range of structural and charge transfer processes in supramolecular materials. The modelling of the proton dynamics in these systems is challenging and demands insights into prototypical benchmark complexes. Intramolecular H-bonding in 3-hydroxyglutaric acid (M) provides an intriguing case study of entangled proton dynamics. We combine infrared action ion spectroscopy experiments with Born-Oppenheimer Molecular Dynamics computational modeling to expose and rationalize the vibrational signatures of intramolecular Grothuss-like proton diffussion triggered upon either the protonation or the deprotonation of M. Despite the formally similar symmetry of the M·H+ and [M-H]- frameworks, the relative proton affinities of the oxygen centers of the carboxylic and carboxylate groups with respect to that of the central carbohydroxy group lead to differentiated proton dynamics in the two systems. In M·H+, an arrangement of the type HOCO·HOH·OCOH is preferred, with the two protons binding tighter to the central oxygen atom and forming two slightly asymmetric H-bonds. In [M-H]- , the asymmetric OCO·HO· HOCO configuration is most stable, with a stronger H-bonding on the bare carboxylate end. Both systems display nevertheless active backbone and concerted proton sharing dynamics, leading to distinct diffuse band structures in their vibrational spectrum.

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Session Classification: Oral communications