

## UNRAVELLING THE MICROSOLVATION FRAMEWORK AROUND PROTOTYPE POLYCYCLIC AROMATIC HYDROCARBON, NAPHTHALENE, BY HIGH-RESOLUTION INFRARED SPECTROSCOPY

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Solvation of aromatic molecules is a fundamental chemical process. Stability and function of almost all biomolecules are governed by the surface water molecules, typically known as biological water. Despite a plethora of reports available for the prototype aromatic molecule, benzene,<sup>1</sup> studies related to the solvation of larger aromatic moieties are rather scarce. Herein, we probe the microsolvated structures of the simplest polycyclic aromatic hydrocarbon, naphthalene (Np), by high-resolution infrared (IR) spectroscopy inside helium nanodroplets and quantum chemical calculations. Our results show that in the monohydrated Np-water dimer, solvent water preferentially binds to the  $\pi$  electron cloud of the two fused phenyl rings via OH- $\pi$  hydrogen bonds (H-bond) and acts as a double H-bond donor. This binding motif is strikingly different from the corresponding cationic Np-water complex, in which water lies in the Np-ring plane and acts as a double H-bond acceptor by the simultaneous formation of two CH-O H-bonds.<sup>2,3</sup> Therefore, we see the presence or absence of charge causes a substantial modification of solvent binding motif. Further stepwise water-addition to neutral Np-water complex leads to evolution of H-bond network as reflected from the IR spectra. In larger Np-(water)<sub>2,3</sub> clusters, hydration motifs mimic the bare water network and thus leads to the formation of linear H-bonded water dimer and cyclic water trimer, which simultaneously interact with Np  $\pi$  electrons. Changing the solvent from water to methanol does not change the qualitative  $\pi$  bonding motif. However, in this case, the solvent only interacts with a single phenyl ring via a OH- $\pi$  H-bond due to the presence of a single proton donor. The addition of the second solvent molecule leads to the formation of H-bonded methanol dimer that interacts with Np.

### References:

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3. K. Chatterjee and O. Dopfer, *Phys. Chem. Chem. Phys.*, 2017, 19, 32262