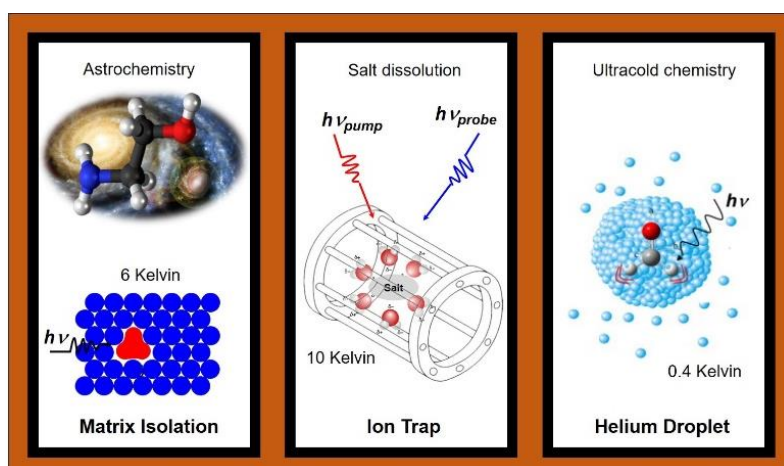


Cryogenic spectroscopy of reaction intermediates and molecular clusters in solid- and gas-phases

Structural characterization of reaction intermediates is highly crucial for understanding the mechanistic pathways of chemical reactions. However, capturing and analysing these fleeting entities posed a persistent challenge. Therefore, specialized instrumentation is necessary to both generate and trap the intermediates for thorough examination. Our matrix-isolation spectroscopy technique involving electron impact ionization of organic precursors followed by mass-selected co-deposition of transient intermediates with neon onto a cold (6 Kelvin) surface has done electronic characterization of isolated species. The UV-Vis spectrum of fulvenallenyl radical (**c-C₅H₄C≡CH**), intermediate in the formation of polycyclic aromatic hydrocarbons, has been recorded.¹ This highly resonance stabilized radical has prospect to be identified in interstellar medium.

The hydrogen-bonded network of water is disrupted by the introduction of salt ions which has direct impact on processes like catalysis, cloud chemistry and human body functions. However, no consistent molecular picture is available describing these affects. So, I probed archetypical salt-water complexes isolated in the gas-phase in order to analyse the interaction between salt ions and a few water molecules. The microhydrated lithium halide cluster anions, **[LiX₂(H₂O)_n]⁻**, were studied by cryogenic ion vibrational spectroscopy at 13 K in the O-H stretching region.² The spectroscopic fingerprints of individual isomers were discriminated by IR/IR double-resonance **pump-probe** experiments. This work revealed that increasing anion polarizability in salts enhances dynamics of surrounding water molecule, facilitating interconversion among isomers even at cryogenic temperatures.



Understanding on the generation of molecular complexes at ultra-low temperature is in incipient stage. These cryogenic molecular aggregations play a significant role in atmospheric aerosol and cosmic ice chemistry. Helium nanodroplets, with a temperature of 0.4 Kelvin, provide a condition where local minimum structures are often promoted during molecular association. By employing mass-selective IR spectroscopy and comparing the experimental results to computational models, structure of the pyruvic acid dimer **[CH₃COCOOH]₂** has been determined. Consistent with previous findings regarding organic acid dimers, an isomer lying +10 kJ/mol higher than the global minimum species is formed inside helium droplet.

1. Chakraborty et al., *Angew. Chem. Int. Ed.* 2016, **128**, 236
2. Chakraborty et al., *Chem. Sci.* 2022, **13**, 13187.