Cryogenic infrared spectroscopy of radical cations relevant in astrochemistry: isomerization, reactivity, and vibronic coupling

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Reactive molecular ions play a central role in the chemistry of planetary atmospheres and the interstellar medium. Laboratory astrophysics studies on their formation and reaction pathways under astronomically relevant conditions are crucial to interpret astronomical observations and as input for simulations in astrochemical networks. Of similar importance are spectroscopic studies of the often elusive, but essential, ionic reaction partners, intermediates and products that yield fundamental insights on their geometric and electronic structure, and provide spectroscopic signatures needed for their identification in space [1].

Cryogenic ion traps have proven to be ideal tools for studying ion-molecule reactions under controlled conditions and allow for sensitive spectroscopic studies of mass-selected, cold, and isolated molecular ions. Here, I will describe the combination of such a cryogenic 22-pole ion trap instrument with the free electron lasers at the FELIX Laboratory [2]. It allows for wide-range infrared vibrational action-spectroscopy of molecular ions such as hydrocarbon and nitrogen-substituted hydrocarbon radical cations ranging in size from comparatively small systems to polycyclic aromatic hydrocarbons.

One focus will be on infrared experiments and methods to disentangle the isomeric composition of ionic samples [3], and how we use and extend these methods to investigate isomerization processes in dissociative ionization [4,5] and isomer-selective reaction kinetics of radical ion-neutral reactions at astronomically relevant temperatures [6]. Radical molecular ions are also of fundamental interest in molecular physics. The wide tunability of the FELIX lasers allows to probe directly the low-lying vibrational modes of linear open-shell ions that are subject to vibronic coupling, mainly due to the Renner-Teller effect, as will be illustrated on the examples of the linear HC_3H^+ ($^2\Pi_g$) isomer [3] and the linear radical cation of cyanoacetylene, HC_3N^+ ($^2\Pi$).

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