Title: The Structures of Protonated and Alkali Metal Cationized Nucleobase Self-Assemblies by Infrared Multiphoton Dissociation Spectroscopy and Computational Methods

Abstract:

*In vivo*, genetic information storage relies on the sequence of nucleobases and the recognition of base pairs. The complementary pairing interactions between nucleobases contribute to form stable structures of DNA/RNA such as duplexes, triplexes, quadruplexes, and hairpins. The G-quadruplex, one of the self-assembled nucleobase structures, is stabilized by the presence of alkali metal cations.\(^1\) In addition to the well-known biological roles of nucleobases, they are also widely applied in synthesizing biomaterials, which stems from their ability to form the homo- and hetero-adducts by their characteristic non-covalent interactions following Watson-Crick, Hoogsteen and Wobble base pairs.\(^2\) To reveal the intrinsic binding properties of these biomolecules with cations, mass spectrometric methods have been used to study the physical and chemical properties of these ionic complexes composed of nucleic acid bases in the gas phase. Computational methods provide further insights into electronic structures and thermodynamic properties of molecules, and afford a deeper interpretation of the experimental data.

In this talk, the nucleobase self-assemblies, Uracil\(_n\)Ca\(^{2+}\) (\(n=4,5,6\)) and 1-methylcytosine dimers with alkali metal cations, were studied by infrared multiphoton dissociation (IRMPD) spectroscopy and computational methods. Thermodynamic and experimental results were compared for different optimized isomers to reveal the real structures of these complexes. Furthermore, a discussion of the structure and dissociation properties of protonated 9-ethylguanine:1-methylcytosine base pair will be provided. There is an explanation about an *anomaly* that exists due to a contradiction between the experimental dissociation product ratio for protonated 9-ethylguanine:1-methylcytosine and that predicted by computed gas basicities.