

IRMPD ACTION SPECTROSCOPY AND COMPUTATIONAL APPROACHES TO ELUCIDATE GAS-PHASE STRUCTURES AND ENERGETICS OF 2'-DEOXYCYTIDINE AND CYTIDINE SODIUM COMPLEXES

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The local structures of DNA and RNA are influenced by protonation, deprotonation and noncovalent interactions with cations. In order to determine the effects of Na^+ cationization on the gas-phase structures of 2'-deoxycytidine, $[\text{dCyd}+\text{Na}]^+$, and cytidine, $[\text{Cyd}+\text{Na}]^+$, infrared multiple photon dissociation (IRMPD) action spectra of these sodium cationized nucleosides are measured over the range extending from 500 to 1850 cm^{-1} using the FELIX free electron laser. Complementary electronic structure calculations are performed to determine the stable low-energy conformations of these complexes. Geometry optimizations, frequency analyses, and IR spectra of these species are determined at the B3LYP/6-311+G(d,p) level of theory. Single-point energies are calculated at the B3LYP/6-311+G(2d,2p) level of theory to determine the relative stabilities of these conformations. Comparison of the measured IRMPD action spectra and computed linear IR spectra enable the conformations accessed in the experiments to be elucidated. For both cytosine nucleosides, tridentate binding of the Na^+ cation to the O2, O4' and O5' atoms of the nucleobase and sugar is observed. Present results for the sodium cationized nucleosides are compared to results for the analogous protonated forms of these nucleosides to elucidate the effects of multiple chelating interactions with the sodium cation vs. hydrogen bonding interactions in the protonated systems on the structures and stabilities of these nucleosides.