DISSOCIATIVE ELECTRON ATTACHMENT TO GAS PHASE BIOMOLECULES

Abstract

by

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Radiation damage to living cells is initiated with a variety of molecular lesions which are mostly resulted from the attacks of secondary species generated by the raw high-energy quanta. Since the seminal experiments by Sanche’s group demonstrating that low-energy electron (LEE) attachment to DNA can incur strand breaks through resonant processes, copious amount of research works has been devoted to study the dissociative electron attachment (DEA) to biomolecules initiated from resonance anionic states.

Biomolecules include nucleobases, sugars, phosphates, amino acids and et al. Five-membered ring is a widely existing structure in biomolecules and also plays an active role in various biochemical processes. My work in this dissertation shows DEA can induce ring opening for aromatic five-membered ring compounds, such as isoxazole, oxazole, and thiazole. Especially, for isoxazole the observation that all the ring opening pathways were conducted through O-N bond cleavage. This observation is of special interest to pharmaceutic engineering
because the biotransformation of several isoxazole substructure containing drugs are found downstream from O-N bond cleavage.

Besides the five-member ring compounds, LEE destructive impact on peptide linkage was studied through DEA studies with peptide model molecules, formamide and its methylated derivatives. Peptide bond cleavage induced by DEA clearly presents the bond selectivity, which is susceptible when the LEE energy falls between 5 to 8 eV. Resonance states responsible for the cleavage were found by my stabilization calculations which show an anti-bonding force was exerted on the peptide bond by the attaching electron through forming a \( \pi^* \) type orbital around this bond.

In addition to the conventional DEA study through measuring the anion yields, an experimental methodology called stepwise electron spectroscopy for detection of neutral products from DEA was proposed and successfully applied to detect and characterize neutrals formed via DEA to \( \text{CCl}_4\). This experimental procedure can be extended to investigate more radicals resulted from DEA processes.