Photon-induced ionization and dissociation of gas-phase biomolecules

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Investigating the interaction of light with biologically relevant molecules has gained interest for a wide variety of research fields including photochemical reactions such as light harvesting as well as radiation damage in proteins and DNA related to cutting-edge cancer treatment techniques. However, in the condensed phase, disentangling direct and indirect radiation effects is often difficult. Electrospray ionization introduces biomolecular ions from solution into the gas phase, allowing for studies of molecular systems in a well-defined state.

The coupling of electrospray ionization sources with synchrotrons [1, 2] and free-electron lasers [3] opens the way to the investigation of the electronic structure of biomolecular systems and of a fine description of their relaxation mechanisms in the VUV and soft X-ray energy range. The wide-ranging photon energy available at the synchrotrons enables systematic studies of ionization and dissociation as a function of the photon energy. Inner-shell excitations provide a localized site of energy deposition. The extremely high photon flux and fs pulse duration offered by free-electron lasers allow studying the molecular properties in intense fields. Furthermore, using the assets of free-electron lasers in a pump-probe scheme enables the study of the dynamics of charge migration and charge transfer within gas-phase biomolecules.

Near edge X-ray absorption fine structure spectroscopy (NEXAFS) probes transitions between atomic core levels and orbitals of the molecular bonding states of intra-molecular neighbours. Therefore, NEXAFS is a powerful structural tool that provides information on the electronic structure. Data taken by near edge X-ray absorption mass spectrometry (NEXAMS) of gas-phase oligonucleotides, peptides and proteins show π^*, σ^* transitions and Rydberg states similar to conventional NEXAFS spectra of thin films and liquids. Additional structural and dissociation dynamics within the molecules can be extracted from the NEXAMS information of the different individual ionization and dissociation products. For instance, a sugar fragment from the backbone of the oligonucleotide GCAT reveals totally different dissociation dynamics than a nucleobase fragment from the same molecule. Moreover, the gas-phase NEXAMS method can be sensitive to the secondary structure of proteins [4]. Further results on site-selective photo absorption of sulphur or metal atoms in complex biomolecules will also be discussed.

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