

Photofragmentation of small peptides containing tyrosine at 263 nm: role of the Charge transfer state on the CO

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The mass spectrometry of molecules of biological interest, based on their fragmentation, help to characterize their structures and properties. Different fragmentation techniques are currently used as CID, IRMPD and ECD. More recently, the UV photodissociation has been applied to these molecules and show some specific fragmentation channels [1, 2].

The photofragmentation pathways at 263 nm of several small peptides containing tyrosine as the UV chromophore have been characterized using a multi-coincidence technique [3,4]. Fragmentations occurring or initiated in an excited state are distinguished from those occurring after internal conversion to the ground electronic state by their rapid fragmentation times and binary nature. For the studied systems, it is shown that fragmentations occurring after internal conversion to the ground state are the dominant processes compared to fragmentations occurring in the excited state. The UV photospecific channels, *i.e.* C_aC_b bond breakage in YGH⁺ and YAH⁺ and direct z-type bond breakage in GYGH⁺, respectively, can be rationalized upon consideration of charge transfer states accessible after absorption of one UV photon. Indeed, excited state calculations performed at the RI-CC2 level of theory indicate that charge transfer on the active CO group is a prerequisite for photospecific bond ruptures. The fragmentation mechanisms and the localization of the charge on the side chain after fragmentation are discussed in terms of the ionization energies of the fragments.

References:

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