Universal Photochemical Breaking of the Peptide Bond

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The photochemical breaking of the peptide (amide) bond is investigated by x-ray absorption spectroscopy at the C 1s, N 1s, and O 1s edges. Interestingly, the product of the photochemical reaction leaves a clear and universal signature, i.e. two well-defined $\pi^*$ peaks at the N 1s edge which grow while the $\pi^*$ peak of the peptide bond shrinks. This signature is found for a wide variety of amides, ranging from the smallest peptides to large proteins and including non-biological polyamides, such as nylon. An additional characteristic is the overall intensity reduction of both the $\pi^*$ and $\sigma^*$ features at the O 1s edge, which indicates loss of oxygen. The product of the photochemical reaction is stable in vacuum. Possible models for the bond cleavage mechanism are considered systematically, and their predictions for the reaction product are tested against the N 1s spectra of many model compounds. No obvious choice is found, however, leaving the intriguing question about the mechanism of this well-defined photochemical reaction.