Breaking the peptide bond by radiation: Photochemistry at the N atom

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The peptide (or amide) bond is a fundamental bond, common to both proteins (e.g. cytochrome c and bovine serum albumin) and non-biological polymers (e.g. nylon and kevlar). The stability of this bond is important for both biochemistry and commercial fiber applications. Radiation easily damages peptide bonds, evidenced by a reduction of the peptide N 1s π* peak. The simultaneous appearance of a π* doublet at lower energy indicates the formation of new π bonds. Using N 1s NEXAFS spectroscopy we investigate the structural change of the peptide bond. Possible rearrangements of the atomic configuration are discussed, such as dehydrogenation, deoxygenation, and the formation of nitroso or hydroxy groups. To test these mechanisms we examine several simple reference compounds with a chemical structure consistent with the proposed products. Their NEXAFS fingerprints are compared to the irradiated peptide bond spectrum, especially its lower energy π* doublet.