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Probing molecular processes in collagen peptidic models with ionizing radiation and mass spectrometry

Jean-Christophe Pouilly¹, Lucas Schwob¹, Mathieu Lalande¹, Jimmy Rangama¹, Lamri Adoui¹, Alain Mery¹, Violaine Vizcaino¹, Rodolphe Antoine², Philippe Dugourd², Dmitrii Egorov³, Ronnie Hoekstra³ and Thomas Schlathöller³

¹Université de Caen Normandie, France

²Institut Lumière Matière, France

³University of Groningen, Netherlands

Collagen is the most abundant protein in the human body. Cartilage and tendons owe their special mechanical properties to the fibrous collagen structure. These strong fibrils are aggregates of a sub-unit consisting of three collagen proteins wound around each other in a triple helix. The response of this protein to ionizing radiation has never been studied, despite its fundamental importance. Recently, we probed the effect of UV, VUV and soft X-ray photon absorption on an isolated peptidic sequence of type-1 collagen, as well as a model of the collagen triple helix by coupling tandem mass spectrometers to an OPO laser and a synchrotron beamline. For UV photon energy below the ionization threshold, photoabsorption is found to induce electronic excitation followed by peptidic backbone cleavage. Increasing the photon energy around the ionization threshold, a smooth transition from excitation to ionization occurs and we observe inter-followed by intra-molecular fragmentation. The latter is strongly reduced for the triple-helix model compared to the isolated peptide. This is consistent with conversion of the photon energy into molecular rotational-vibrational energy. Besides, our results show that proline hydroxylation, a typical post-translational modification of collagen, induces strong H₂O loss from the peptides studied. We want to push further our work on collagen by irradiating the model peptides with heavy ions, by using a unique home-built experimental apparatus recently developed in Caen. In this set-up, molecular ions are produced by an electrospray ionization source, mass-over-charge selected and accumulated in a Paul trap, before being extracted and they finally cross the ion beam. Products of the interaction are analyzed by a time-of-flight mass spectrometer. Very recently, we validated our set-up by irradiating the leucine-enkephalin peptide with He⁺ ions at 7 keV. The next step will be to compare results for collagen peptides to those obtained with photons and look for ion-induced specific molecular processes such as deprotonation.

pouilly@ganil.fr