Electronic supplementary information

Figure S1. Tandem mass spectrum of singly protonated Substance P ion measured in the same conditions as that presented in figure 1, but without any photons. Note that the only fragment observed corresponds to loss of 16 Da, which has not been considered in the analysis summarized in table 1.
Figure S2. Photon flux as a function of the photon energy. The blue curve corresponds to the flux measured through a MgF2 window inserted in the optical path, which removes second order radiation in the 5.2 to 10.4 eV. The orange curve has been measured with the gas filter filled with 0.2 mbar of argon, which provides spectral purity in the 8 – 15.5 eV range. The purple curve corresponds to the flux measured without the gas filter. In this configuration, the optics of the beamline act as a filter with a sharp cutoff above 25 eV. Note the orange curve exhibits severe carbon contamination from the optics around 12 eV. This pollution has been now reduced drastically so that the actual flux curves is similar to the nominal one published in [L. Nahon, N. de Oliveira, G. A. Garcia, J.-F. Gil, B. Pilette, O. Marcouille, B. Lagarde, and F. Polack, *Journal of Synchrotron Radiation*, 2012. **19**, 508-520.]
Figure S3. Gas phase ion conformation of substance P singly protonated ion from molecular dynamic simulation. The simulations were performed using the Gromacs software [1] and the Charmm27 force field [2]. The initial conformation was taken from the PDB structure 2KSA, in which only the Substance P chain was keep. The proton was added to the guanidine group of arginine. The structures of protonated substance P was generated via simulated annealing runs that involved heating the system from 50 K to 300 K for 5ps followed by an additional 5ps equilibrium trajectory at 300 K. A trajectory of 200 ps was then recorded for the analysis, in which the distance between the methionine sulfur (in yellow) atom and the N atoms of the guanidine group was calculated and averaged over the last 50 ps of the trajectory. The average distance between the sulfur atom and the protonated nitrogen is 9.65 Å. The last structure of the MD is presented. The molecular structure was obtained using the Chimera software [3]

Figure S4. CID tandem mass spectrum of singly protonated Substance P ion (normalized collision energy = 30). The label ‘ denotes backbone fragment ions having lost NH$_3$. 
Figure S5. Neutral losses from the [M+H]+ precursor ion.
Figure S6. Neutral losses observed from the radical cation \([M+H]^{2+}\).