

**Supporting information
for**

**Multiple Electron Ejection from Proteins Resulting
from Single Photon Excitation in the Valence Shell**

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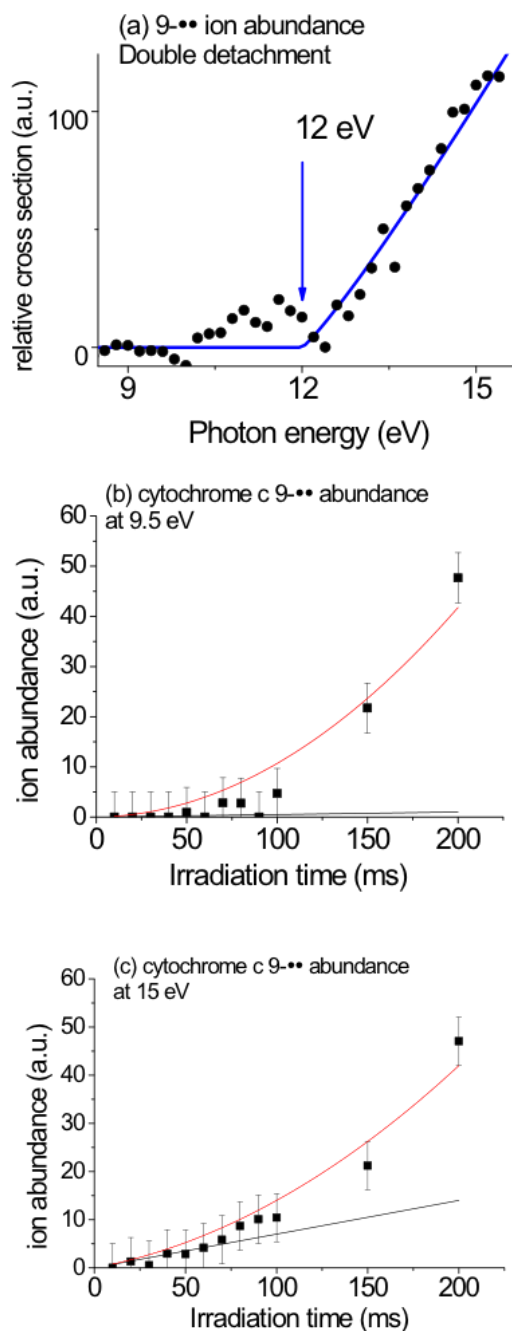


Figure S1.(a) Partial relative cross section in the 8-15.2 eV for 90 ms irradiation duration for double photodetachment of cytochrome c $[M-11H]^{11-}$. The solid line is a Wannier-type linear fit to the data. Ion abundances for the double photodetachment product ion at (b) 9.5 eV and (c) 15 eV recorded as function of the irradiation time in the 10-200 ms range. The data have been least square fitted by a 2nd order polynomial : $a+bt+ct^2$, where a, b, and c are fitting coefficients and t stands for time in ms. The black lines labeled on the graph as linear component represent the linear component of the fit expressed by $a+bt$.

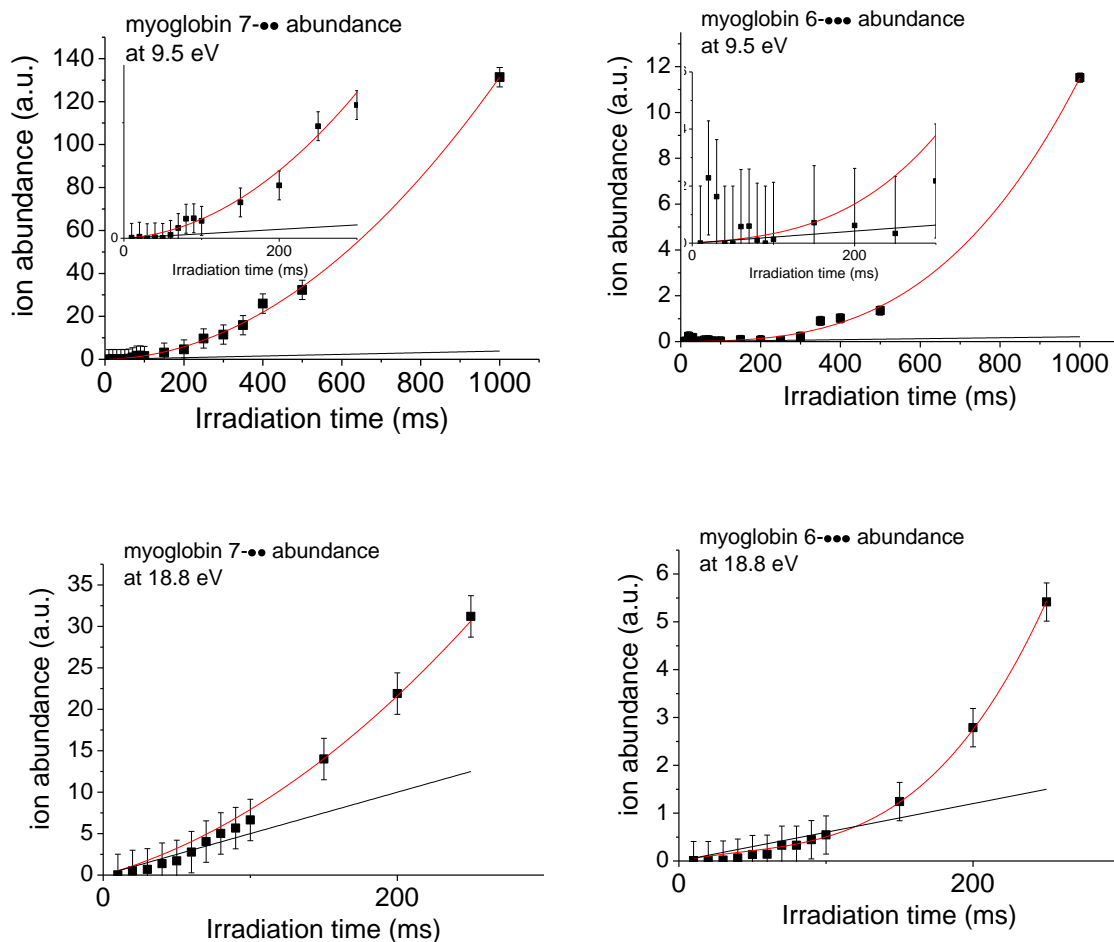


Figure S2. Ion abundances for myoglobin for the double (left) and triple (right) photodetachment product ion at 9.5 eV and 18.8 eV recorded as function of the irradiation time. The data for 7-•• have been least square fitted by a 2nd order polynomial : $a+bt+ct^2$, where a, b, and c are fitting coefficients and t stands for time in ms. The black lines labeled on the graph as linear component represent the linear component of the fit expressed by $a+bt$. The data for 6-•••• have been least square fitted by a 3rd order polynomial : $a+bt+ct^2+dt^3$, where a, b, c and d are fitting coefficients and t stands for time in ms. The black lines labeled on the graph as linear component represent the linear component of the fit expressed by $a+bt$.

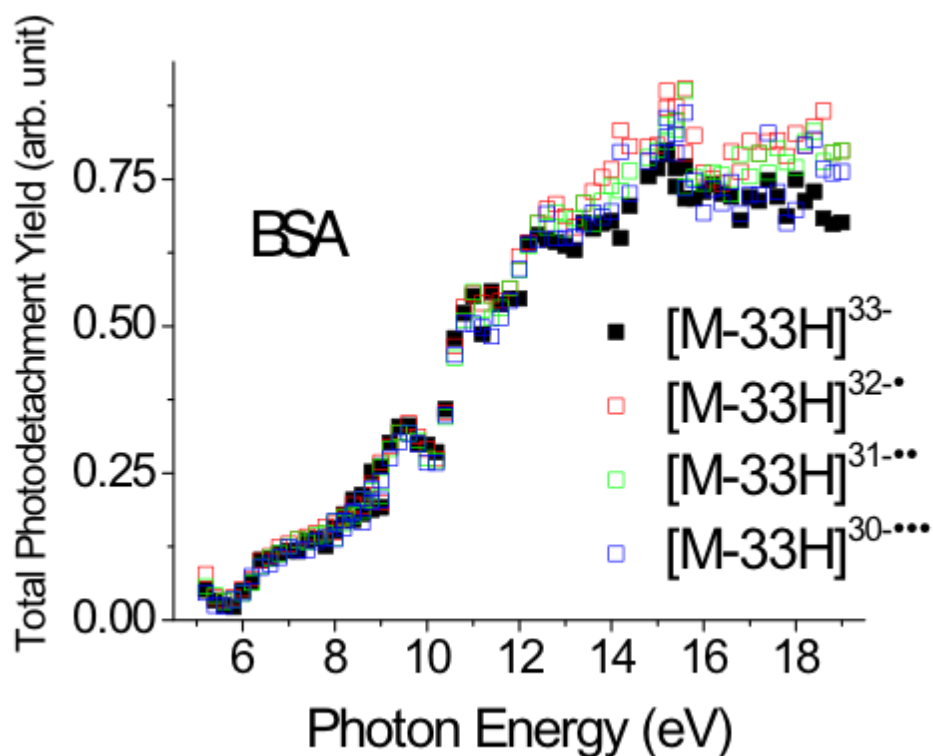


Figure S3. Yields of photodetachment as a function of the SR energy for BSA as a function of the oxidation state. Yields are given by $\ln((\text{parent} + \Sigma_{\text{oxidized}})/\text{parent})/\phi$, where ϕ is the photon fluence, parent is the intensity of the parent peak and Σ_{oxidized} represents the total intensity of the peaks corresponding to oxidized species (i.e. protein that has lost electrons). Oxidized proteins were produced using an additional UV laser in a two-color scheme (see Brunet, C. et al. *Formation and Fragmentation of Radical Peptide Anions: Insights from Vacuum Ultra Violet Spectroscopy*. J. Am. Soc. Mass Spectrom. 2012, 23, 274-281, for experimental for details).

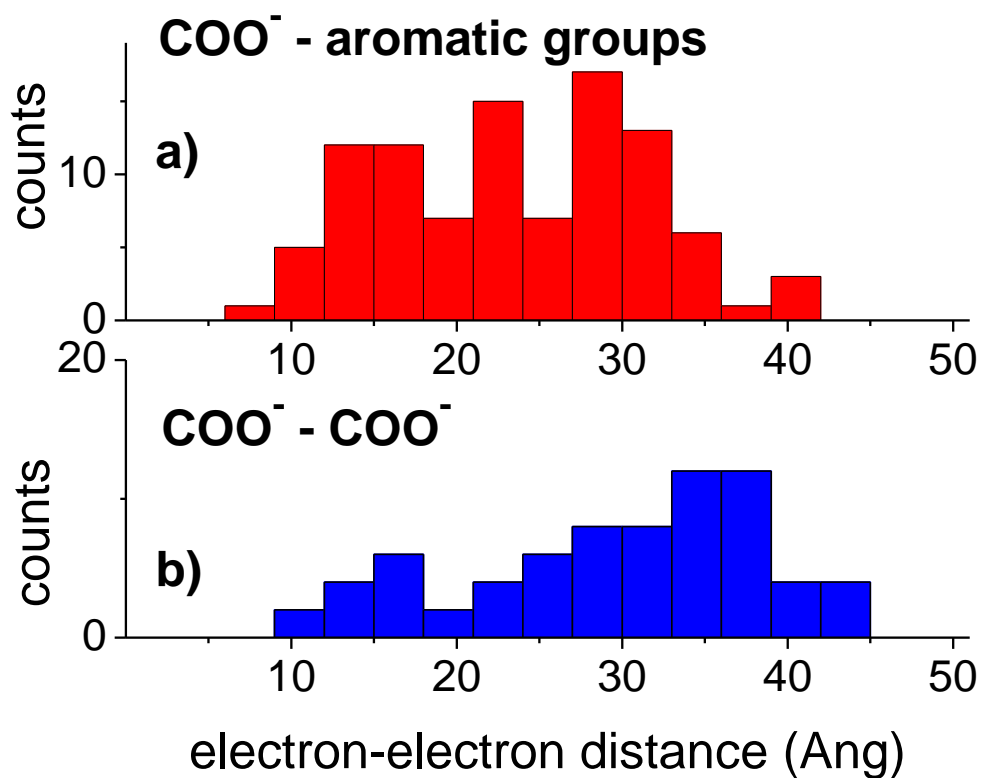


Figure S4. Calculated electron-electron distance distribution in the myoglobin protein (9-charge state) assuming a native structure (1MBN pdb structure). Electron interdistance between (a) two negative charges (held by carboxylate groups) and between (b) a charge on a carboxylate group and an electron from aromatic rings are reported.