Electronic Supplementary Material (ESI) for Chemical Science.

Supplementary Information

Structural Characterization of Holo- and Apo-Myoglobin in the Gas Phase by Ultraviolet Photodissociation

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Supplemental Figure:

Figure S1. a) Holo-myoglobin and b) apo-myoglobin sprayed under native conditions (5mM ammonium acetate at pH 5.5) at 1.5-1.7 kV and a capillary temperature of 150°C. c) denatured myoglobin in 49.9% water, 50% acetonitrile and 0.1% formic acid sprayed at 4kV with a 300°C capillary temperature. (H) stands for HOLO, (A) stands for APO and H denotes the free heme group.

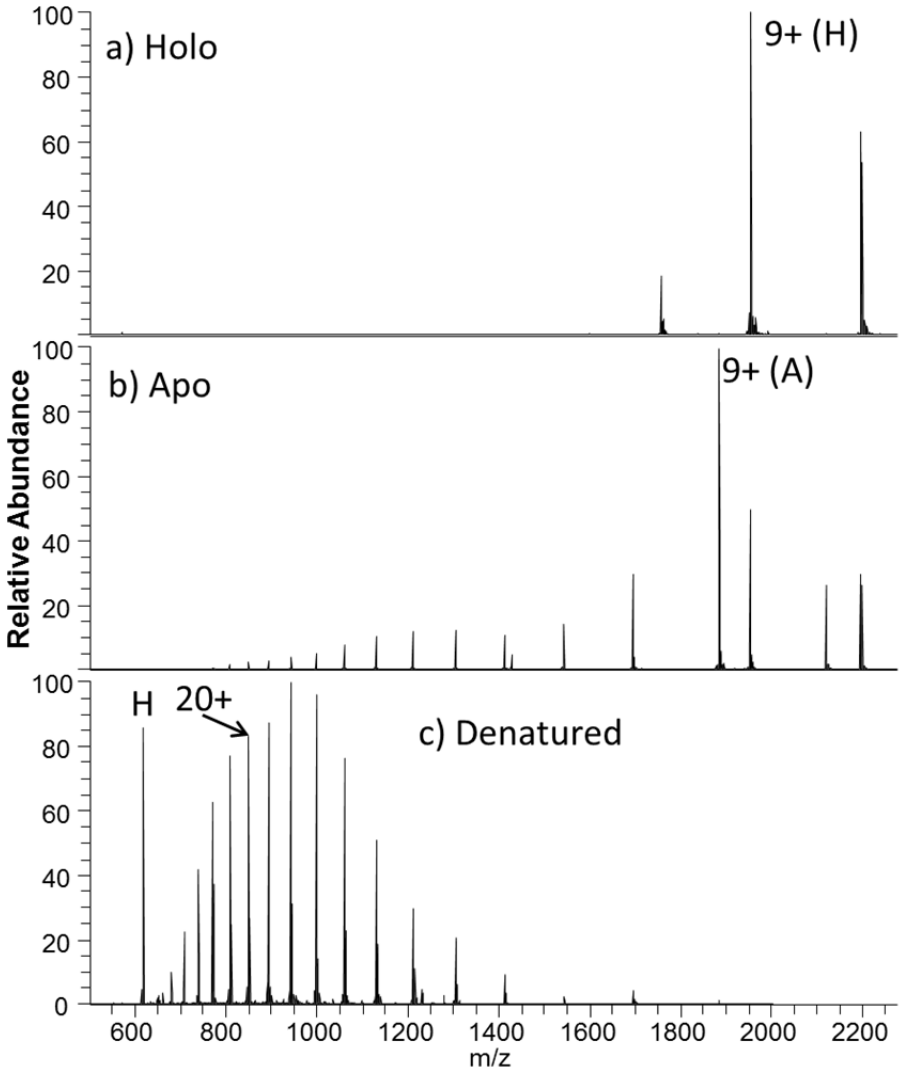

Figure S2. A schematic representation of holo-myoglobin with color coded helices, loops and termini, and the heme is shown in hot pink. The 1DWR crystal structure has been rotated 180° about the x-axis between the top and bottom structures.

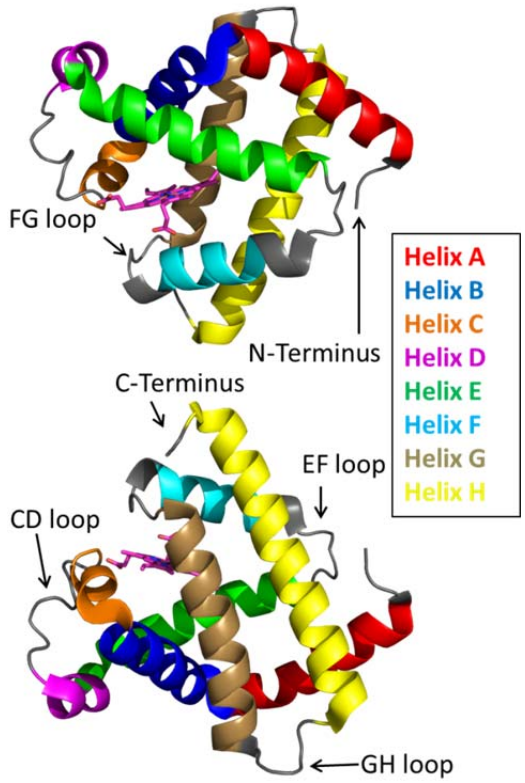

Figure S3. Normalized fragmentation yields averaged over the total number of amino acids in each structural element for charge states 8+ (blue bars), 9+ (red bars), 10+ (green bars) and 20+ (purple bars) of apo-myoglobin with HCD (a) and UVPD (b) fragmentation.

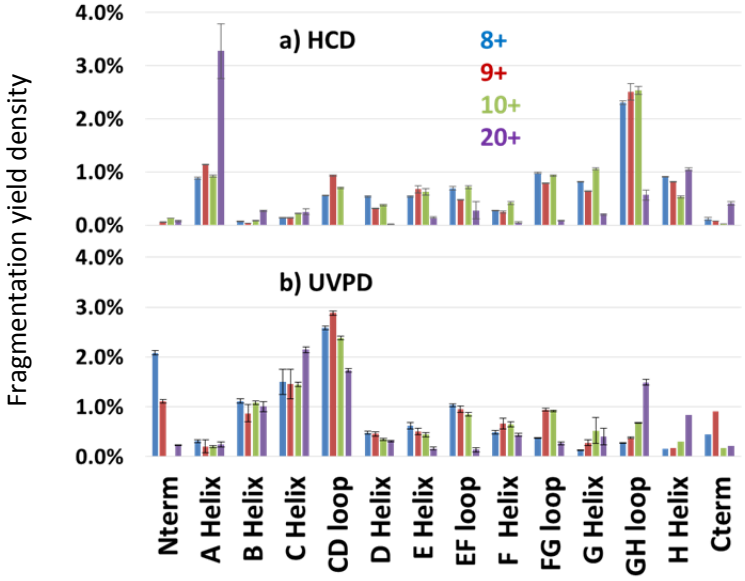

Figure S4. Direct comparison of fragmentation yield densities for holo and apo myoglobin : (a) 8+, (b) 9+, (c) 10+. The key structural elements are labelled. The N- and C-terminii have been removed from the figure.s Standard deviations for fragment yield densities are shown in Figure 4 and Figure S2 for holo and apo forms, respectively.

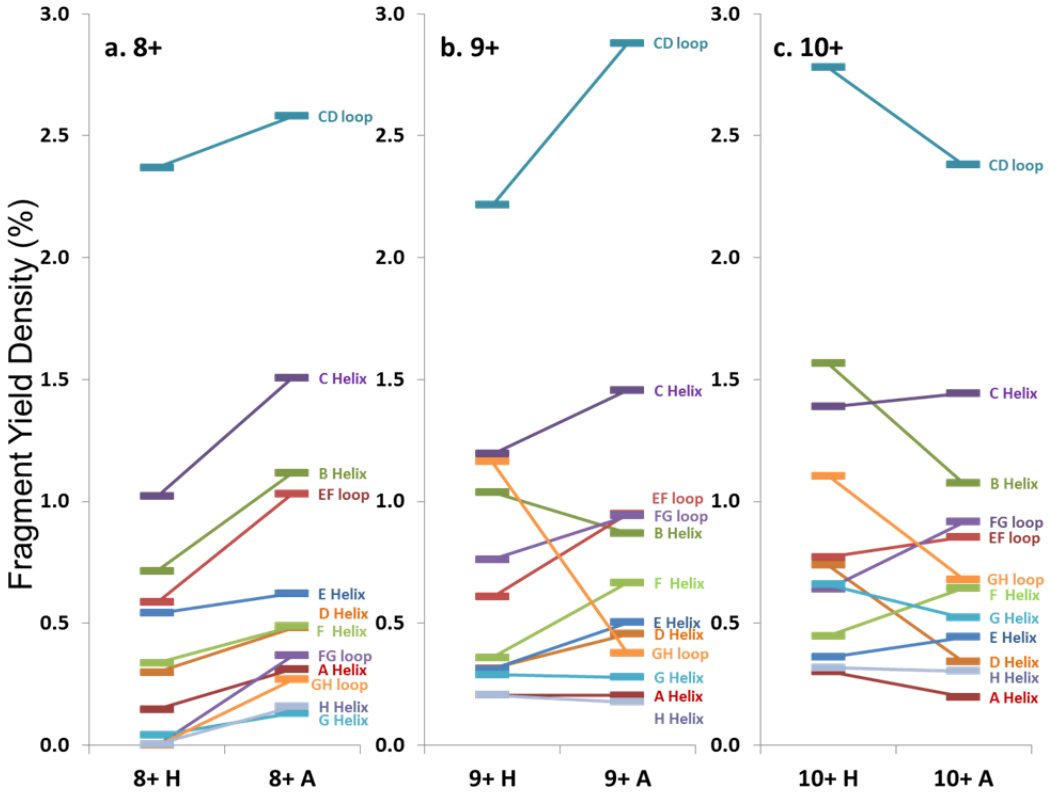

Figure S5. Those residues that were found to have enhanced backbone cleavage frequencies upon UVPD activation are highlighted in red on the holo-myoglobin crystal structure 1DWR and in blue on the apo-myoglobin structure. The heme group is shown as a hot pink color for holo-myoglobin. The 1DWR crystal structure has been rotated 180° about the x-axis between the top and bottom structures. The holo-myoglobin crystal structure is used for the apo-protein to allow easy visualization of the regions that show enhanced UVPD fragmentation.

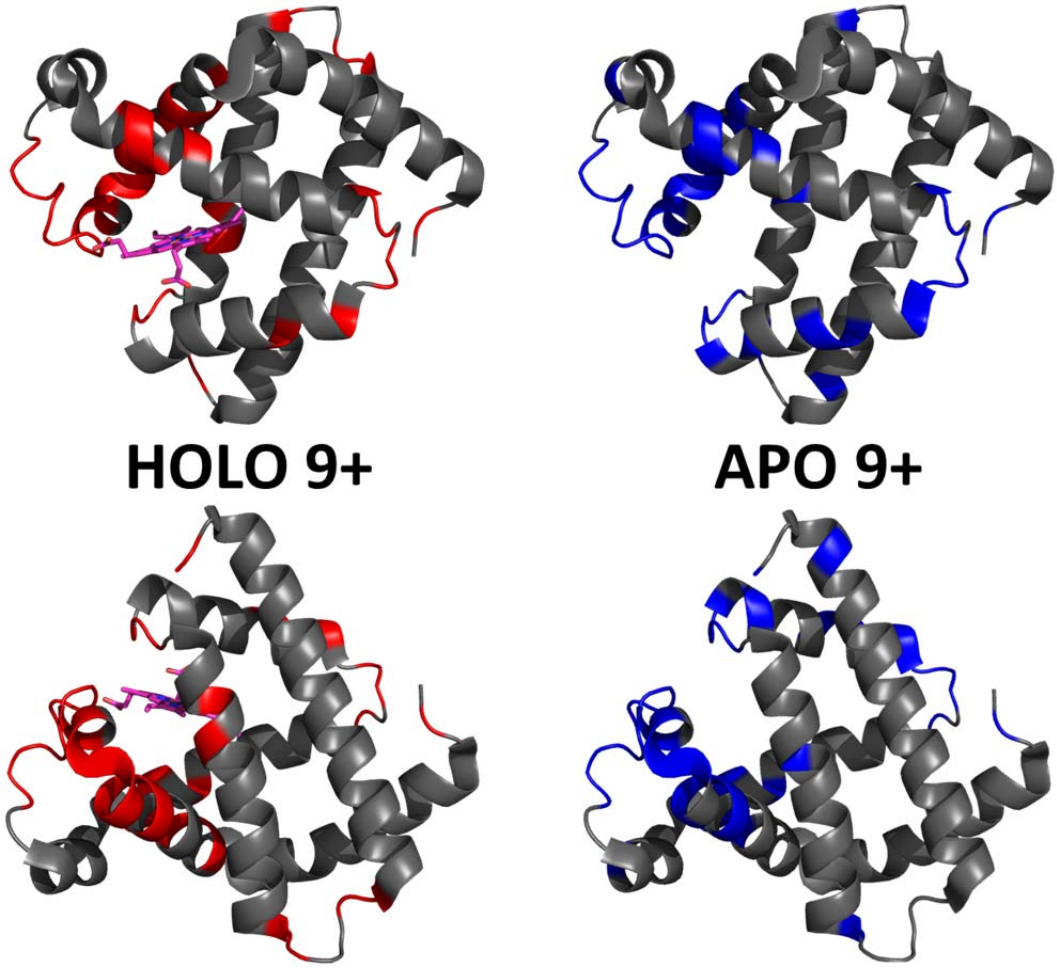

Figure S6. a) Holo-myoglobin fragmentation yields as reported in Figure 2 are presented for comparison with (b) the B-factors from holo-myoglobin crystal structure 1DWR along with (c) solvent accessibility data of both the backbone and side-chains calculated with GetArea. Regions are demarcated below (c). Solvent accessibility data was smoothed by box car averaging of two points.