Supporting Information

for

Internal Fragments Generated from Different Top-Down Mass Spectrometry Fragmentation Methods Extend Protein Sequence Coverage

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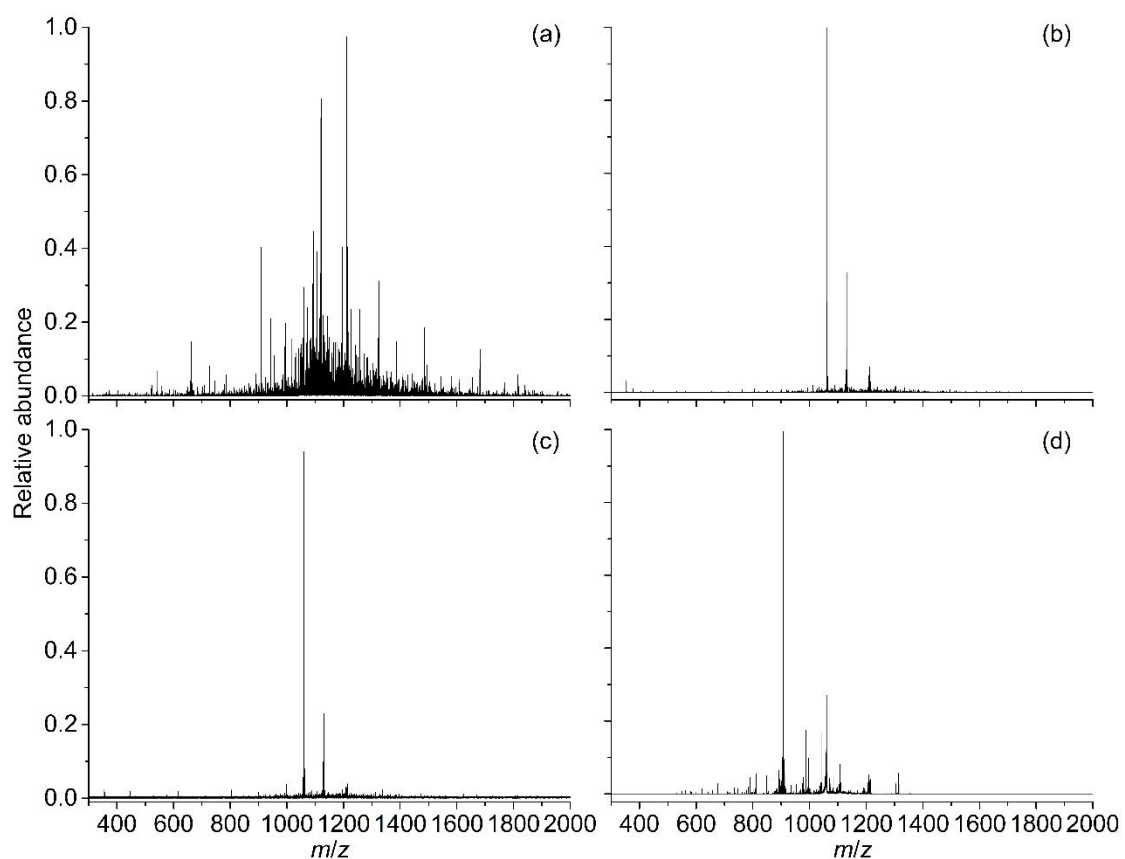
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Figure S1. Representative mass spectra for isolated [myo, 16H]$^{16+}$ formed from 10 μM myoglobin in acidified denatured solution fragmented by (a) collisionally activated dissociation, (b) electron capture dissociation, (c) electron ionization dissociation, and (d) ultraviolet photodissociation.
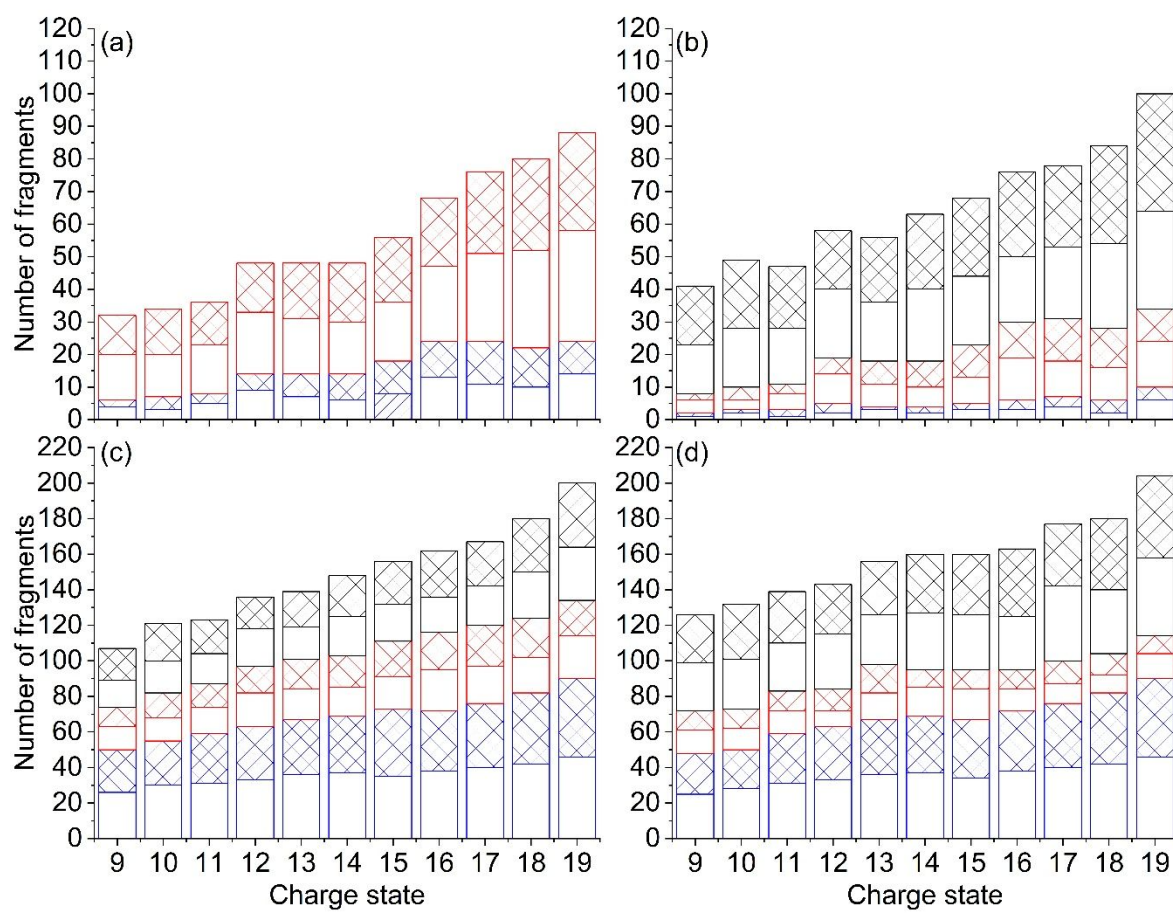
Figure S2. Fragment ion types assigned for [Cyt *c*, zH]$^{z+}$ (cytochrome c), where *z* = 9 to 19 fragmented using (a) collisionally activated dissociation, (b) electron capture dissociation, (c) electron ionization dissociation, and (d) ultraviolet photodissociation. The black bars represent *c* and *z* fragment ions, red bars represent *b* and *y* fragment ions, and blue bars represent *a* and *x* fragment ions.
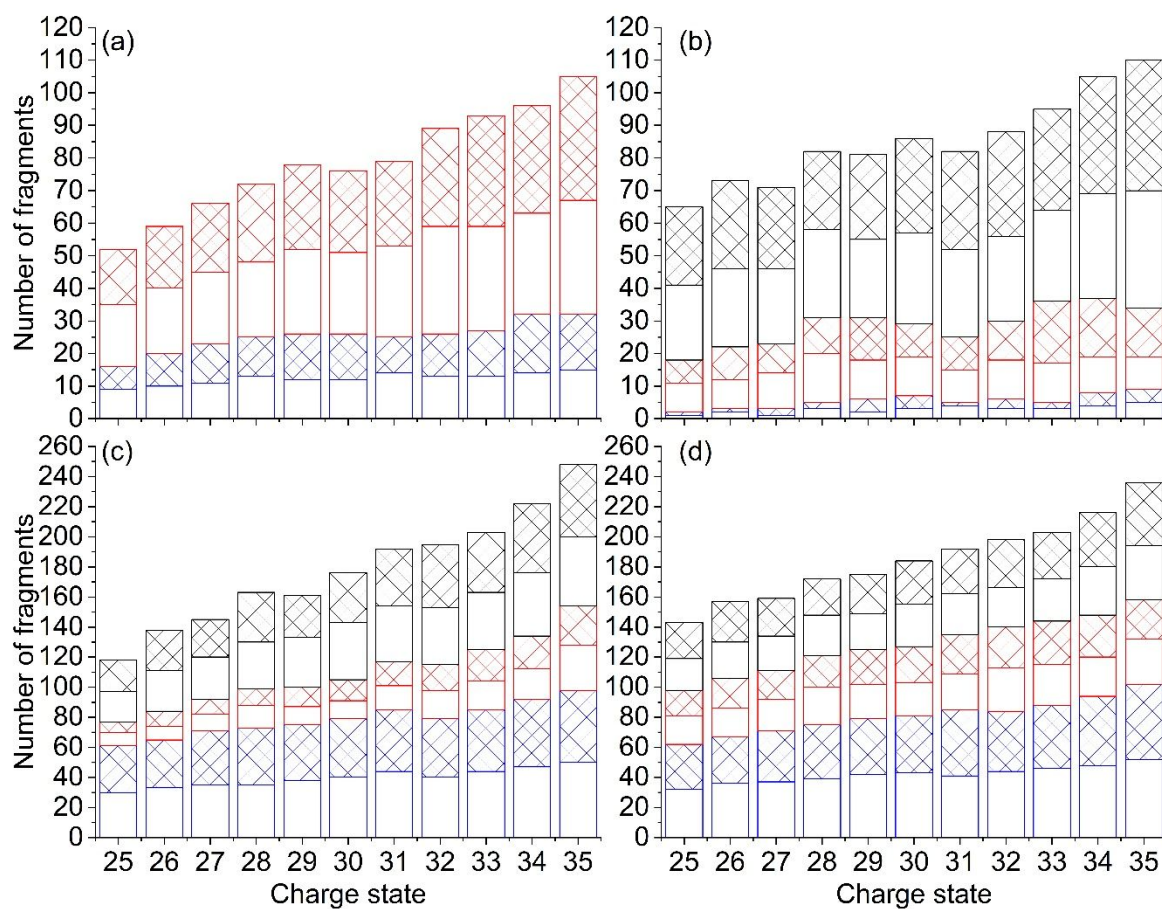
Figure S3. Fragment types assigned for [CAII, zH]$^{z+}$ (carbonic anhydrase II), where $z = 25$ to 35, fragmented using (a) collisionally activated dissociation, (b) electron capture dissociation, (c) electron ionization dissociation, and (d) ultraviolet photodissociation. The black bars represent c and z fragment ions, red bars represent b and y fragment ions, and blue bars represent a and x fragment ions.
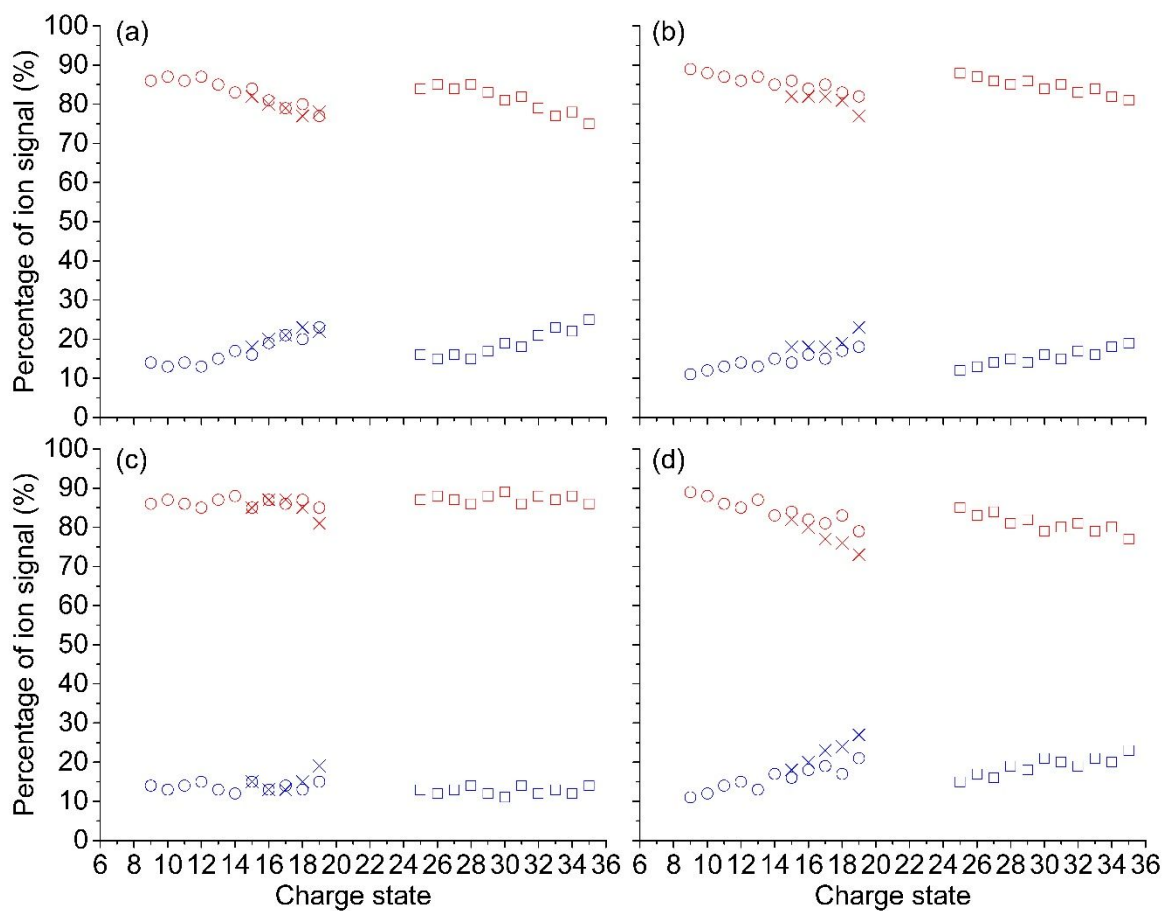
Figure S4. The percentage of ion signal assigned to fragments obtained for cytochrome c (open circles), myoglobin (crosses), and carbonic anhydrase II (open squares) with red markers indicating terminal fragment signals and blue markers indicating internal fragment signals using different fragmentation methods, (a) collisionally activated dissociation, (b) electron capture dissociation, (c) electron ionization dissociation, and (d) ultraviolet photodissociation.
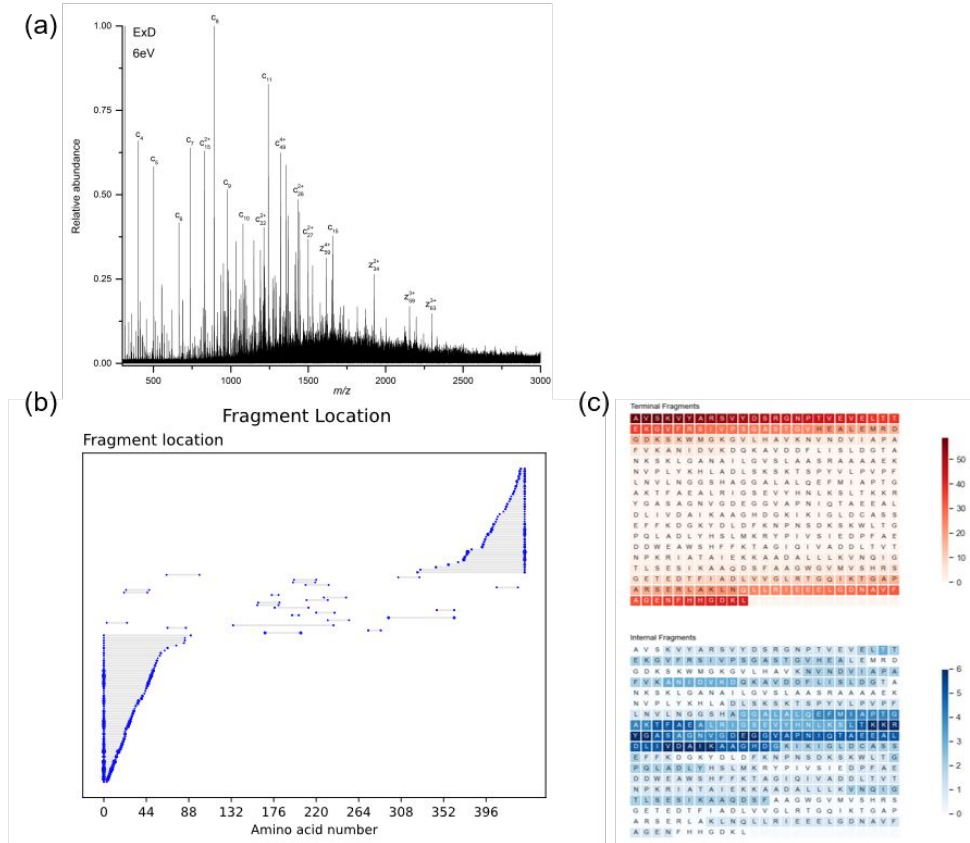
Figure S5. ECD of denatured yeast enolase (46 kDa). (a) Broadband ECD (6 eV) mass spectrum, (b) fragment location map showing both terminal and internal fragments, and (c) heat maps for terminal and internal fragments indicate ca. 40% sequence coverage.

Fragmentation method	Average Terminal Fragment Intensity	Average Internal Fragment Intensity
CAD	3.53×10^6	1.58×10^6
ECD	1.48×10^7	4.42×10^6
EID	8.45×10^6	5.89×10^5
UVPD	5.25×10^5	3.53×10^4

Table S1. Average fragment ion intensities for the most abundant precursor ion charge state of all proteins displayed in Figure S4.