

Electronic supplementary information

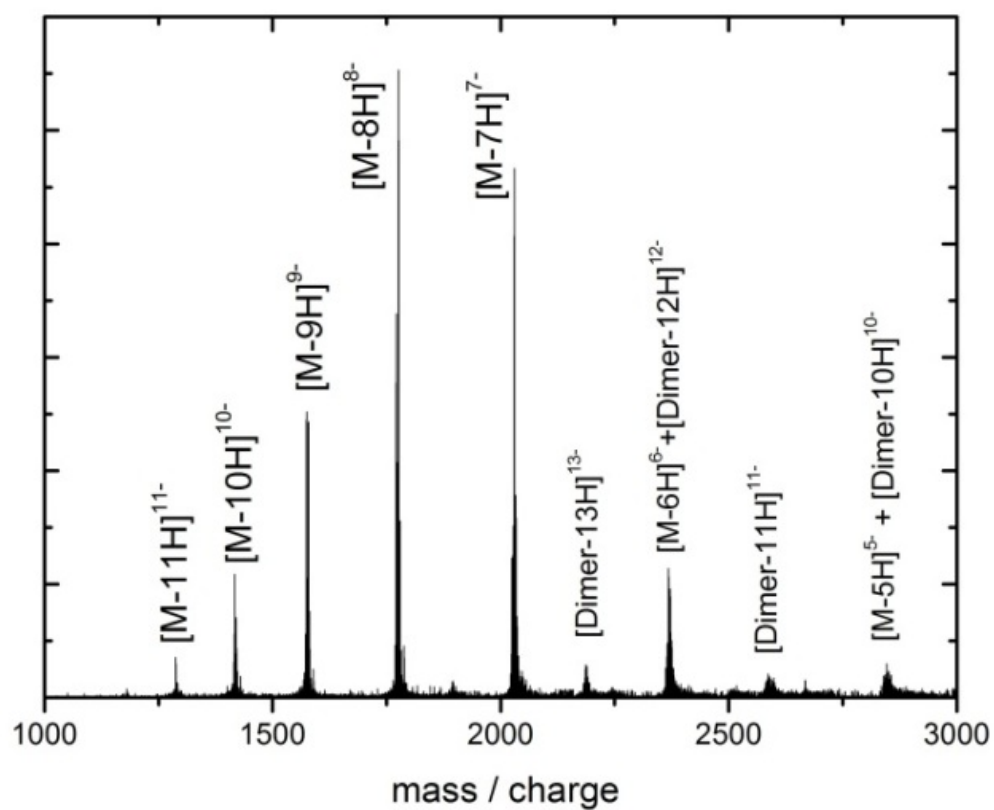


Figure S1. Orbitrap LTQ overview mass spectrum in negative ion mode obtained by electrospraying a 0.1 mM water/methanol 1:4 solution of native bovine α -Lactalbumin (pH 10, see experimental). Peak assignments are based on analysis of high resolutions scans.

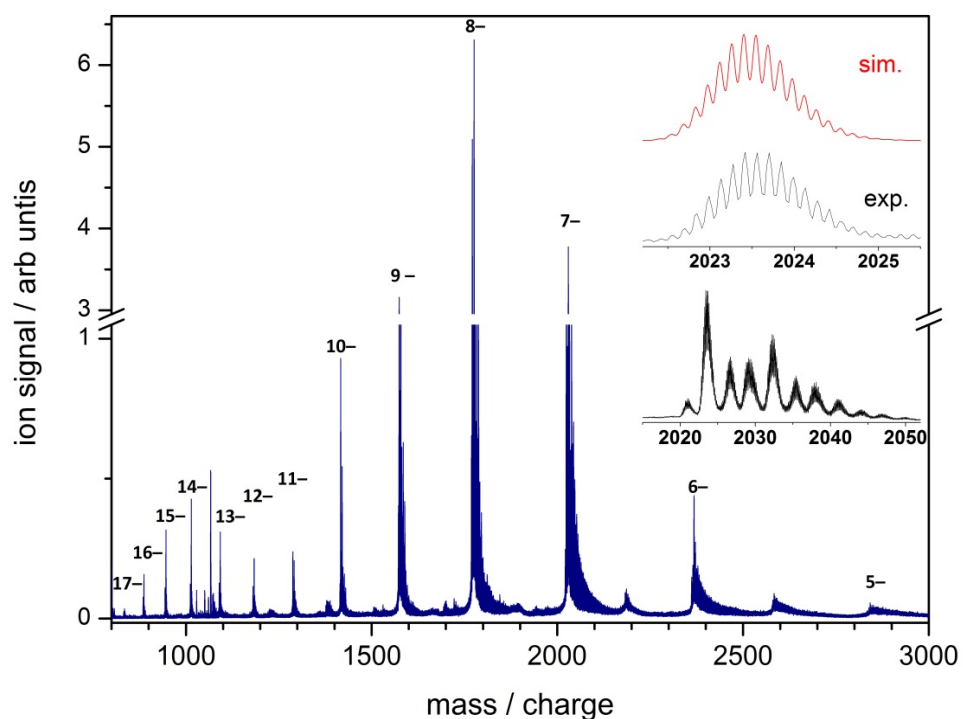


Figure S2. Nanospray-ReTOF mass spectrum in negative ion mode obtained by electrospraying a 0.1 mM water/methanol 1:4 solution of bovine α -Lactalbumin reduced by adding a tenfold excess of DTT (100 mM NaOH, see experimental). The lower inset shows a higher resolution segment of the overview scan illustrating that multianions can also contain some Na^+ counterions (substituting for H^+). Also shown in the upper inset is an isotopomer-resolved portion of the spectrum (upper inset).

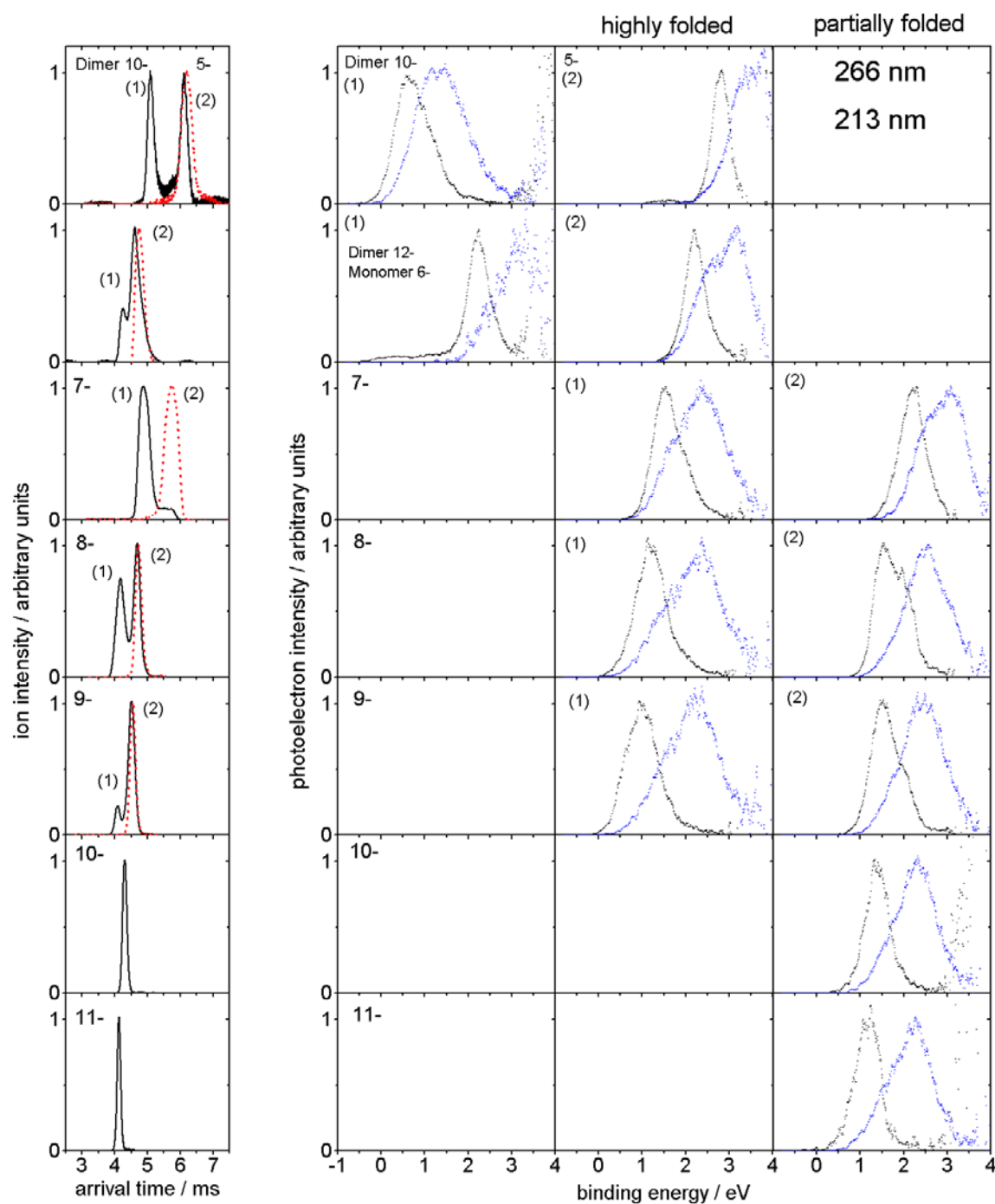


Figure S3. PE spectra of the native/non-reduced protein at 213 (blue) and 266 nm (black) normalized to their most intense feature. Analysis of threshold regions yields comparable ADEs. The effective detachment cross section is significantly higher at 213nm than at 266nm. Cut-offs at high EBE values are due to the repulsive Coulomb barrier.

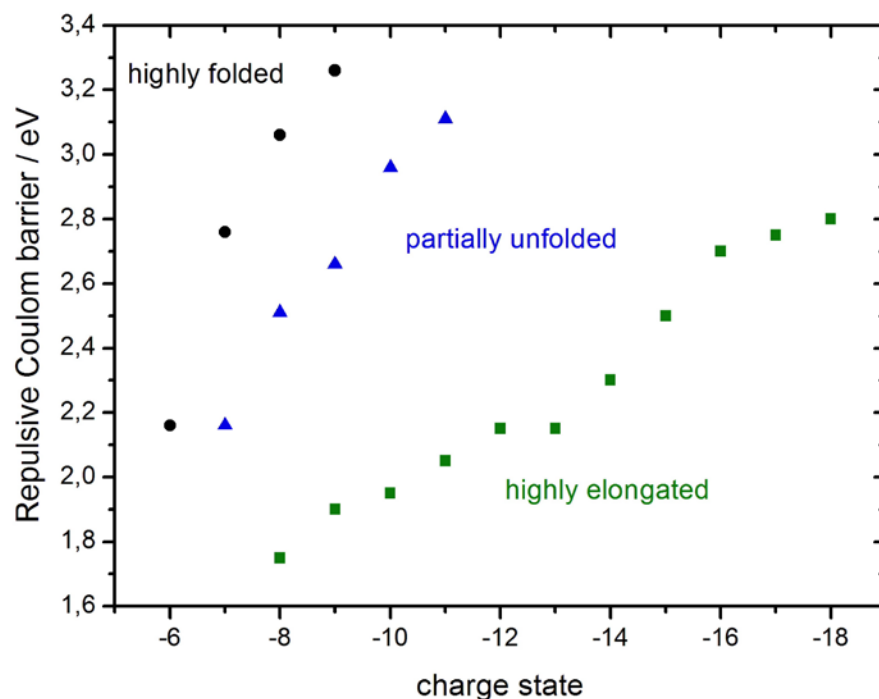


Figure S4. Experimentally determined repulsive Coulomb barriers as a function of charge state. These show the same trends as the adiabatic detachment energies. Note, that the RCB of the quintuply charged state of the highly folded conformer type has not been determined because of dominant noise above an EBE of 3 as described in the experimental section. Additionally, the same RCBs were determined for the two conformations of the 6- charge state.

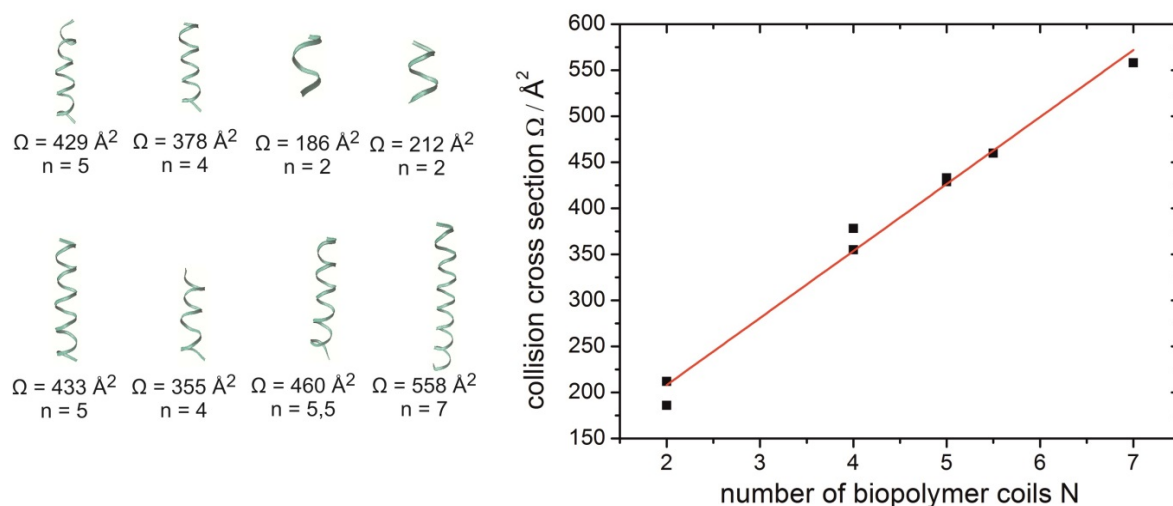


Figure S5. Illustration of the procedure used to calibrate the parameter c in equation (3) of the main text. Helical fragments were obtained from the pdb structure file of horse heart myoglobin. Their collision cross sections were determined by the projection approximation. Structures, corresponding cross sections and characteristic numbers of helical coils, n , are shown on the left. The coil diameter is assumed to be constant, 5 \AA . A plot of collision cross section versus n shown on the right indicates a roughly linear dependence. The corresponding slope was used to determine c .

Table S1: Predicted collision cross sections for denatured α -Lactalbumin multianions as a function of excess charge state based on a helical model as described in the main text.

<i>Charge</i>	<i>Cross section / \AA^2</i>	<i>Screw pitch / \AA</i>	<i>Diameter/ \AA</i>
8-	1992	4,1	5,1
9-	2147	4,5	5,1
10-	2286	4,8	5,1
11-	2379	5,0	5,0
12-	2502	5,3	5,0
13-	2626	5,6	5,0
14-	2766	5,9	4,9
15-	2895	6,3	4,9
16-	3001	6,6	4,9
17-	3128	6,9	4,8
18-	3231	7,2	4,8