Evolution of the charge state z and the cross section W of mobility-selected protein ions held for tens of ms at temperatures from 25 to 100 ^{o}C.

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A first differential mobility analyzer (DMA_1) is used to select dimer and tetramers ions of the protein concanavalin A, electrosprayed into CO_2 from water solutions containg 100 mM triethylammonium formate. These selected ions are then subject for tens of ms to heating in an atmospheric pressure flow tube, and finally analyzed in a second DMA (DMA_2)where the drift gas is air at room temperature. The first DMA (DMA_1) flat DMA type (high resolution and high transmission DMA) works in closed loop. The second DMA (DMA_2) half mini type runs in open loop with air of the lab at room temperature.

Approximately 10% reduction in protein cross section (in ambient air) is found for all ions after exposing them to air at 100^{o}C in the transfer tube. This substantial compaction is approximately linear with the change in temperature, and is far from being saturated at 100 ^{o}C. This notion that an even greater compaction would be achieved by further heating is confirmed by estimates of the effective density of the gas phase proteins, which evolves from about 0.85 g/cm^3 at room temperature to about 1 g/cm^3 at 100 ^{o}C. While unusually high for protein ions, this 1 g/cm^3 is still far from the theoretical density of 1.3 g/cm^3 determined based on the volume displaced by proteins dissolved in water.

The thermally induced compaction observed suggests that gas phase proteins are relatively malleable under the action of capillary forces. On the other hand, full compaction, if at all possible, requires substantial heating during substantial periods. This fact confirms the widely held notion that there are substantial barriers resisting conformational changes of proteins following their transfer from solution to the gas phase.

A surprisingly high level of charge reduction takes place in the transfer tube, even at room temperature, which is only moderately accelerated at 100 ^{o}C. For instance, selected dimer ions originally in charge states z =10 (2^{+10}) reach DMA_2 in charge states 10, 9 and 8 (2^{+10}-2^{+8}), with comparable charge loss observed for other dimer (2^{+9} and 2^{+8}) and tetramer ions (4^{+13}). We argue that the observed charge reduction cannot be due just to deprotonation of the protein by triethylamine vapors present. Rather, removal of the protonated amine from the protein must overcome a substantial activation barrier.