Electronic Supplementary Information

Tracking Local and Global Structural Changes in a Protein by Cold Ion Spectroscopy

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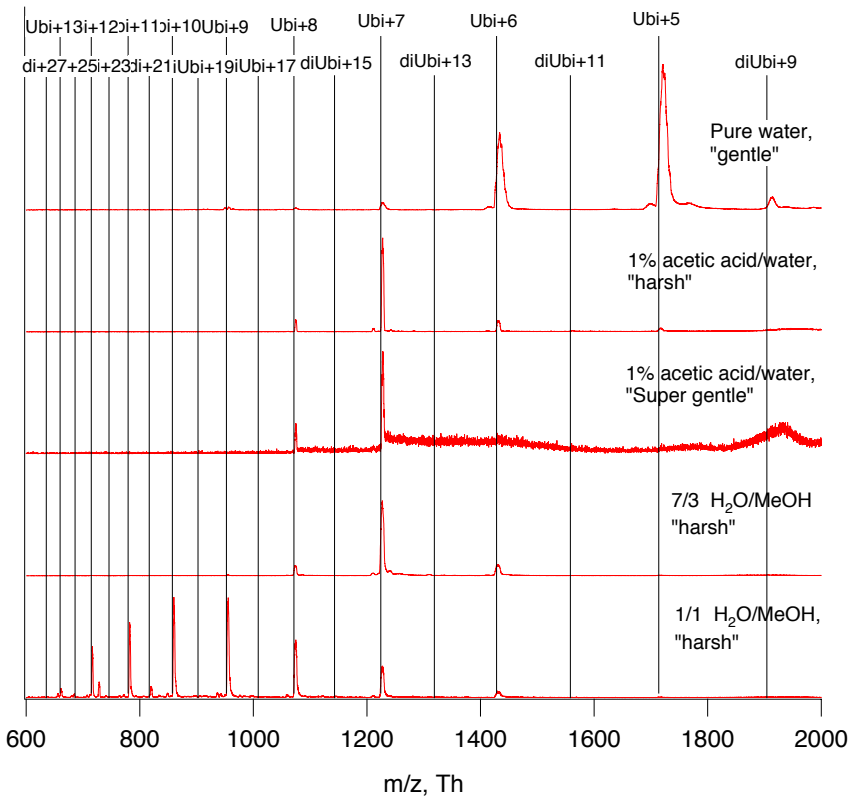

Figure S1a. Mass spectra showing charge-distribution of protonated ubiquitin electrosprayed from different solutions and under different ("super gentle", "gentle" and "harsh") conditions of ESI.

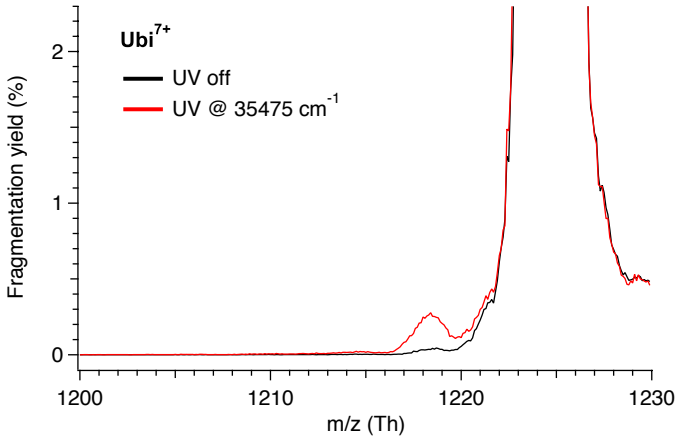

Figure S1b. UV fragment MS of Ubi-$7H^{7+}$ (red trace) and of this protein with UV light blocked (black trace). The ion peak intensity is normalized on the intensity of the parent ion peak (100%).

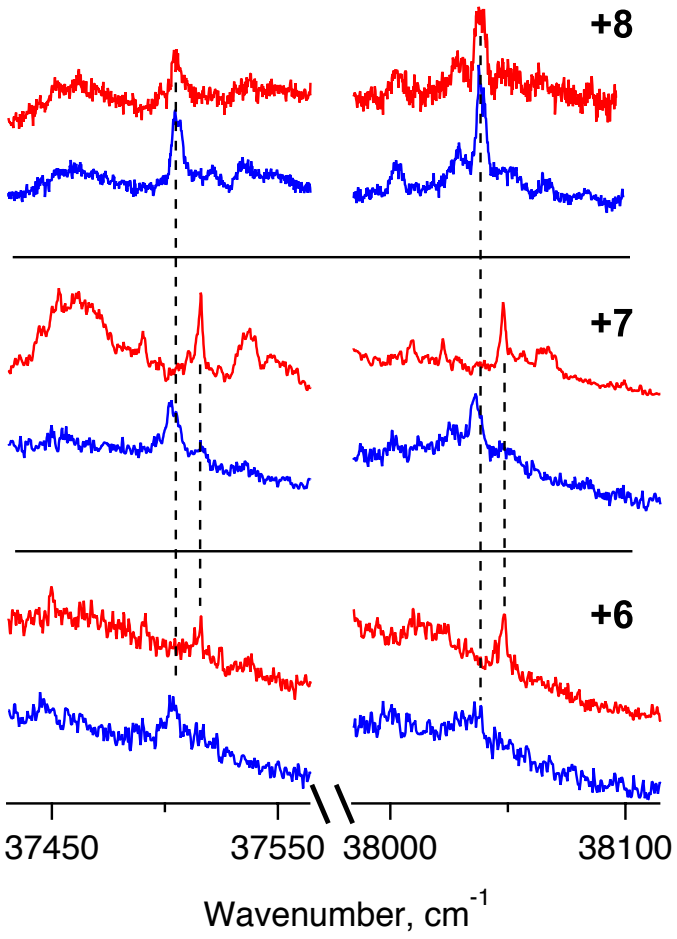

Figure S2. Photofragmentation UV spectra of Ubi^{7+} and Ubi^{8+} in the region of absorption by Phe residue. The protein was electrosprayed from water solution with 1% of acetic acid under the "gentle" (blue traces) and "harsh" (red traces) conditions of ESI.

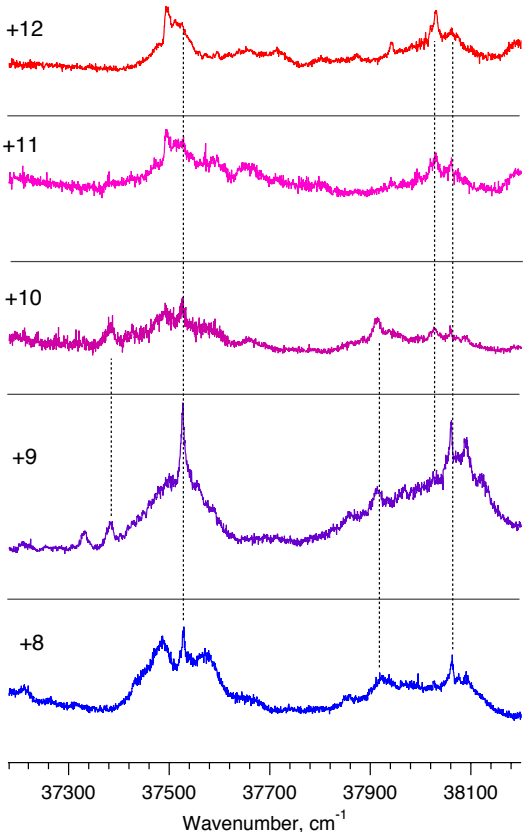

Figure S3. Photo fragmentation UV spectra of Ubi^{n+} for n=8-12 in the region of absorption by Phe residue. The protein was electrosprayed from water/methanol/acetic acid (50/50/1) solution under the "harsh" conditions of ESI. Vertical dashed line show alignment of sharp peaks in different spectra.

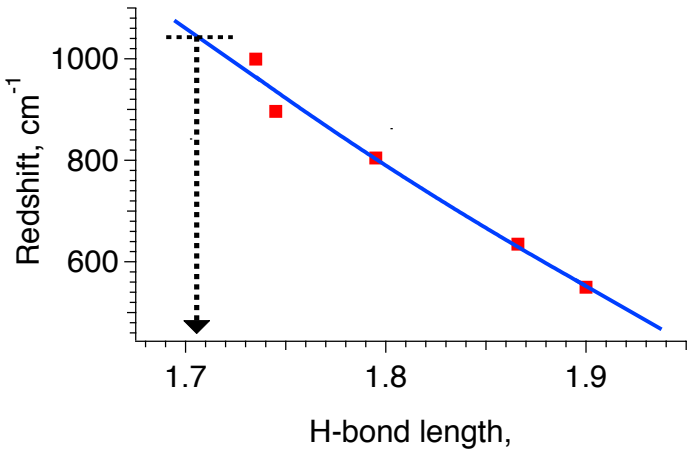

Figure S4. The available data (red squares) for the red shifts of the UV band origin of neutral phenol as a function of the H-bond length between the hydrogen of the phenol hydroxyl and the nitrogen of the acceptor molecules in the studied non-covalent complexes.[1] The data points were fitted by a power function $y(x) = 7300 - 1850 \cdot x^{-1.7}$ that exhibits a nearly linear dependence. The vertical dotted line shows the largerst red shift detected for the UV band origin of Tyr residue in this work for protonated ubiquitin (n=6-8) and its complexes with 5 and 10 water molecules; the dotted arrow line points to the corresponding most likely minimal length of the H-bond (~1.7 Å). The evaluation does not consider the variations of the bond angle.

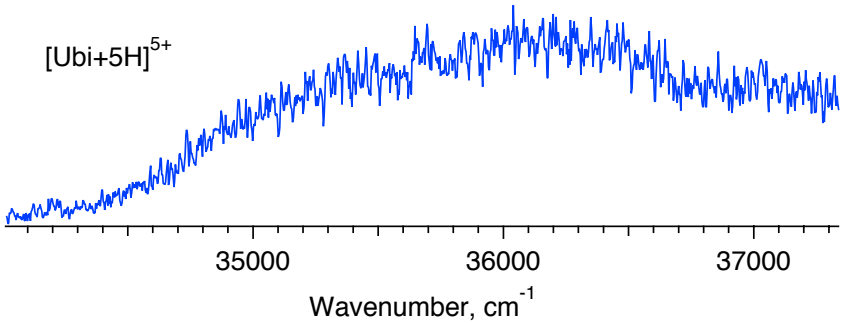

Figure S5. Photofragment UV spectrum of $[Ubi+5H]^{5+}$, produced from pure water solution under "harsh" ESI conditions.

Additional references

[1] a) D. Solgadi, C. Jouvet, A. Tramer, *J. Phys. Chem.* **1988**, *92*, 3313-3315;
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d) H. Tachikawa, T. Iyama, *J. Phys. Chem. A* **2020**, *124*, 7893-7900.