Electronic Supplementary Material (ESI) for Faraday Discussions.

Investigation of the position of the radical in z_3-ions resulting from electron transfer dissociation using Infrared Ion Spectroscopy

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Supplementary Information

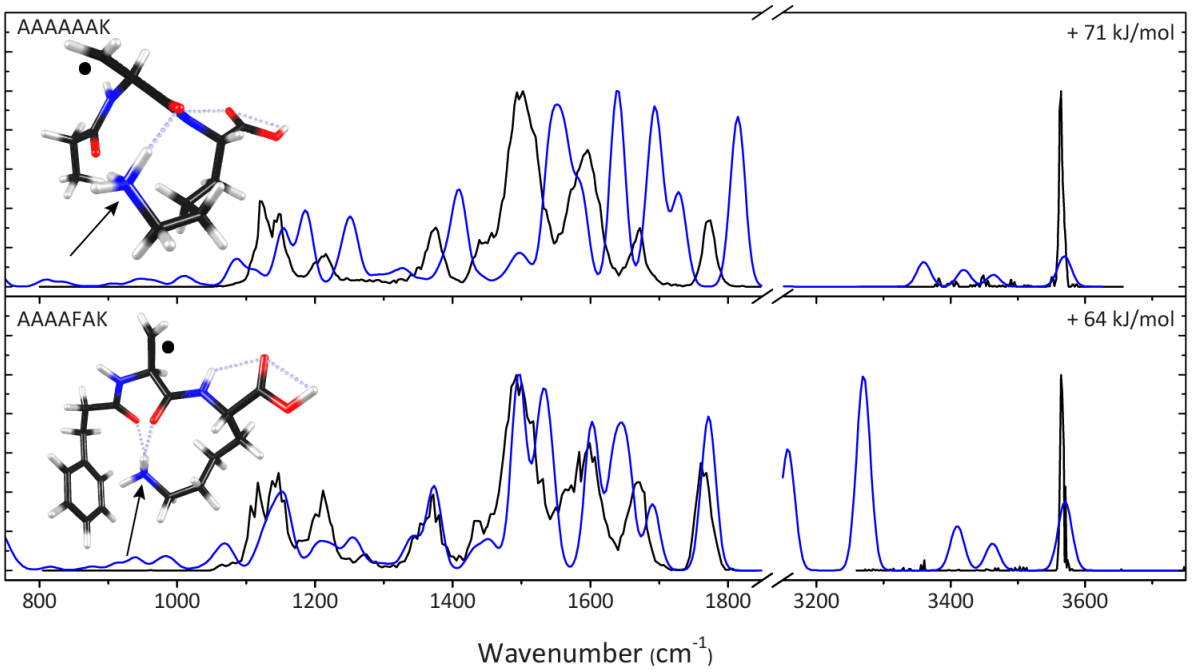
The additional figures show the comparison between the experimental spectra of the z_3-ions of $[AAAAAAK+2H]^{2+}$ and $[AAAAFAK+2H]^{2+}$ (Figure S1) and of $[KAHA+2H]^{2+}$ (Figure S2) with calculated spectra where the radical is positioned at the C_β-atom of the second residue counted from the C-terminus. This is an alanine residue in Figure S1 and a histidine residue in Figure S2. Table S1 lists the calculated relative Gibbs energies for all presented z-ion structures at three different levels of theory (B3LYP, B3LYPD and M06-2X).

Supplementary Information Table S1. *Overview of relative energies of the z-ions with radicals positioned at the C_α, C_β and C_γ positions of the first, second and third residue (counted from the C-terminus). The energies are computed at the B3LYP, MP2, B3LYPD and M06-2X levels of theory.*

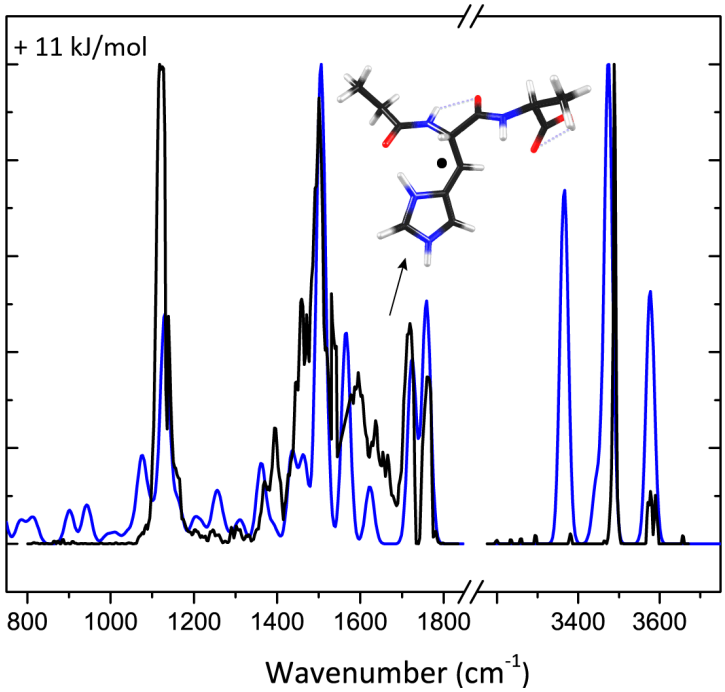
B3LYP	3rd residue			2nd residue		1st residue
Peptide|fragment	C_α	C_β	C_γ	C_α	C_β	C_α
AAAA|AAK	+ 21	+ 63	-	0	+ 71	+1*
AAAA|FAK	+ 32	+ 3	+ 102	0	+ 64	+8*
AAAA|HAK	+ 22	+ 17	+ 153	+ 8	+ 68*	0*
AAAA|WAK	+ 31	+2	-	0	+ 72*	+56*
AAAA|YAK	+ 33	0	+ 111	+ 15	+ 77*	+7*
K|AHA	+ 15	+ 66*	-	0*	+ 11*	+ 17*

B3LYP-D	3rd residue			2nd residue		1st residue
Peptide:	C_α	C_β	C_γ	C_α	C_β	C_α
AAAA|AAK	+17	+58	-	+3	+ 63	0*
AAAA|FAK	+ 32	+2	+ 105	**0**	+ 63	+14*
AAAA|HAK	+ 16	+ 8	+ 147	+ 6	+ 63*	0*
AAAA|WAK	+ 26	0	-	0	+ 63*	+51*
AAAA|YAK	+ 36	0	+ 108	+ 19	+ 74*	+12*
K|AHA	+ 13	+ 62		0	+ 10*	+ 17*

M06-2X	3rd residue			2nd residue		1st residue
Peptide:	C_α	C_β	C_γ	C_α	C_β	C_α
AAAA|AAK	**+ 13**	+ 51		**+ 8**	+ 56	+0*
AAAA|FAK	+ 32	+5	+95	**0**	+ 58	+16*
AAAA|HAK	+15	+12	+142	+8	+ 63*	**0***
AAAA|WAK	+ 28	+ 9		**0**	+ 63*	+50*
AAAA|YAK	+ 33	**0**	+ 93	+ 21	+ 68*	+10*
K|AHA	+ 12	+ 61		**0**	+ 14*	+ 17*



Supporting Information Figure S1. *Experimental spectra of the z_3-ions from $[AAAAAAK+2H]^{2+}$ and $[AAAAHAK]^{2+}$(black) compared with calculated spectra (blue) for structures with the radical at the C_β position of the second residue (Ala). These structures are relatively high in energy due to the absence of resonance stabilization of the radical.*



Supporting Information Figure S2. *The calculated spectrum (blue) for radical migration to the C_β position of the second residue (histidine) compared with the experimental spectrum (black) of the z_3-ion from $[KAHA+2H]^{2+}$.*