

Hydrogen atom transfer in radical cations of tryptophan-containing peptides AW and WA studied by mass spectrometry, infrared multiple-photon dissociation spectroscopy, and theoretical calculations

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Electronic Supplemental Information

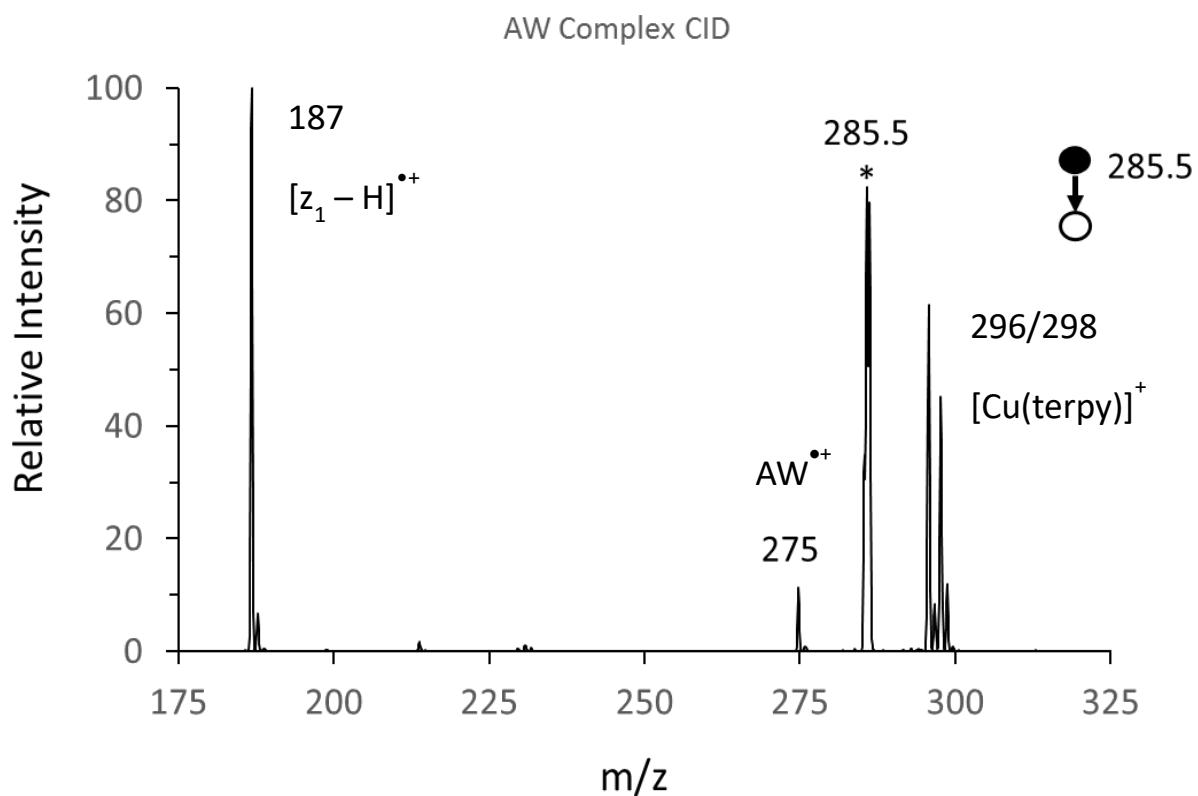


Figure S1. CID spectrum of the $[\text{Cu}^{\text{II}}(\text{terpy})\text{AW}]^{\bullet 2+}$ complex.

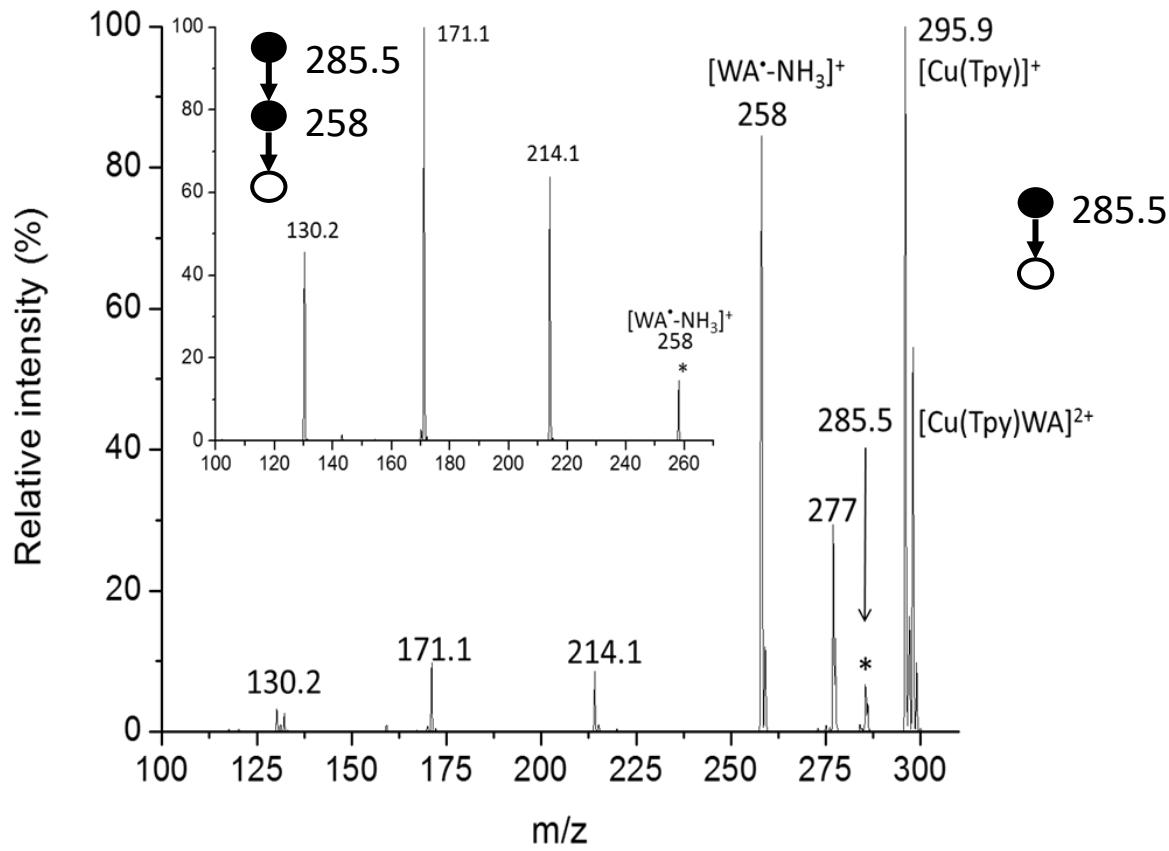


Figure S2. CID spectrum of $[\text{Cu}^{\text{II}}(\text{terpy})\text{WA}]^{2+}$ complex. No $\text{WA}^{\cdot+}$ ion at m/z 275 is seen.
(Spectrum on the inset MS^3 of the m/z 258 ion).

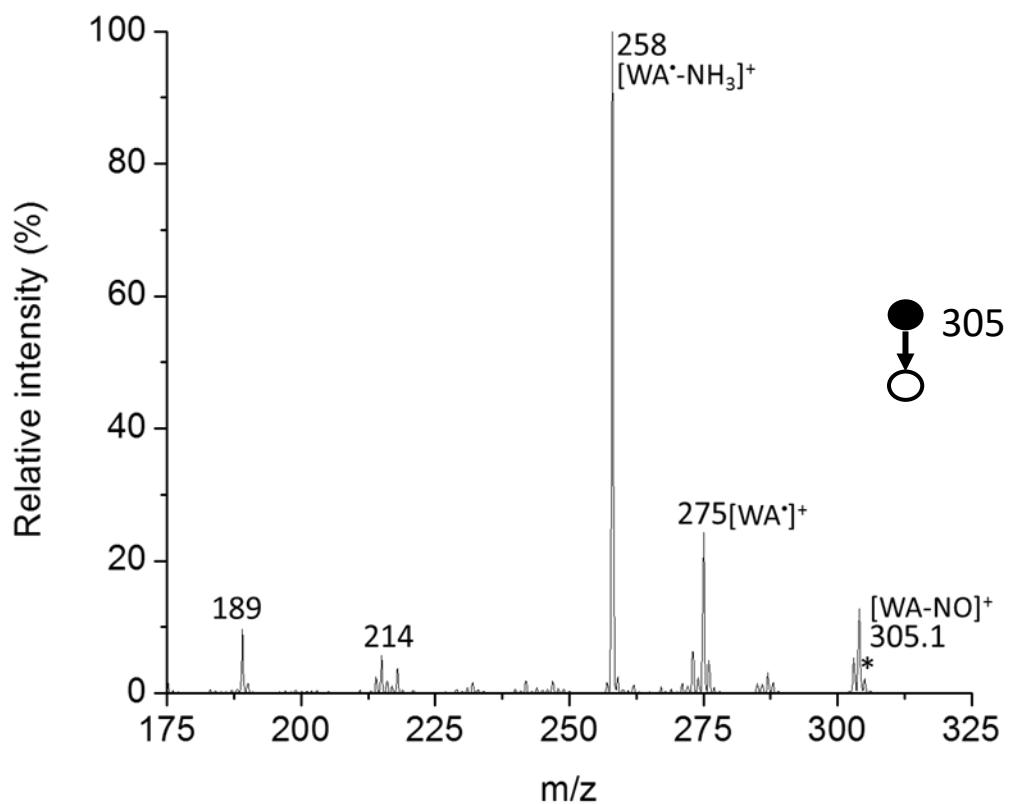


Figure S3. CID spectrum of the protonated N-nitrosylated WA peptide

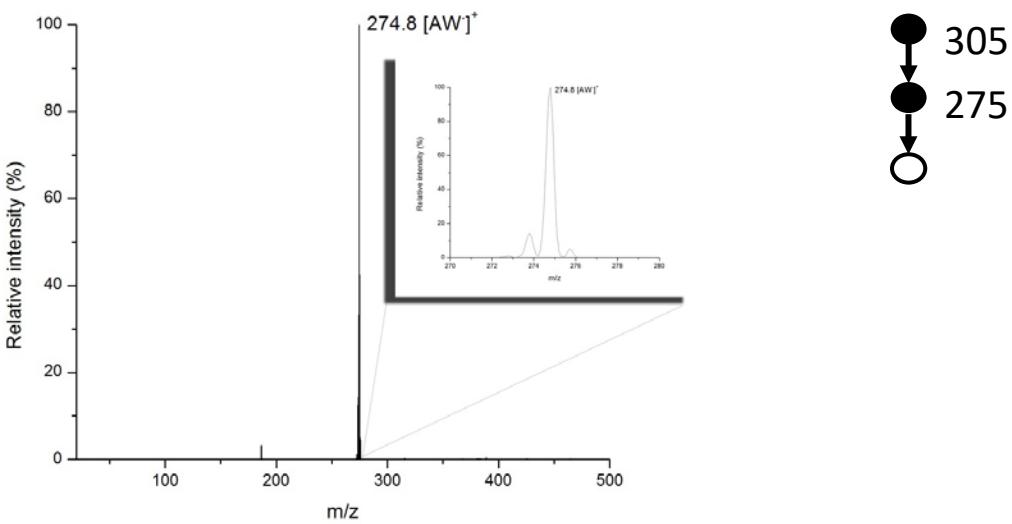
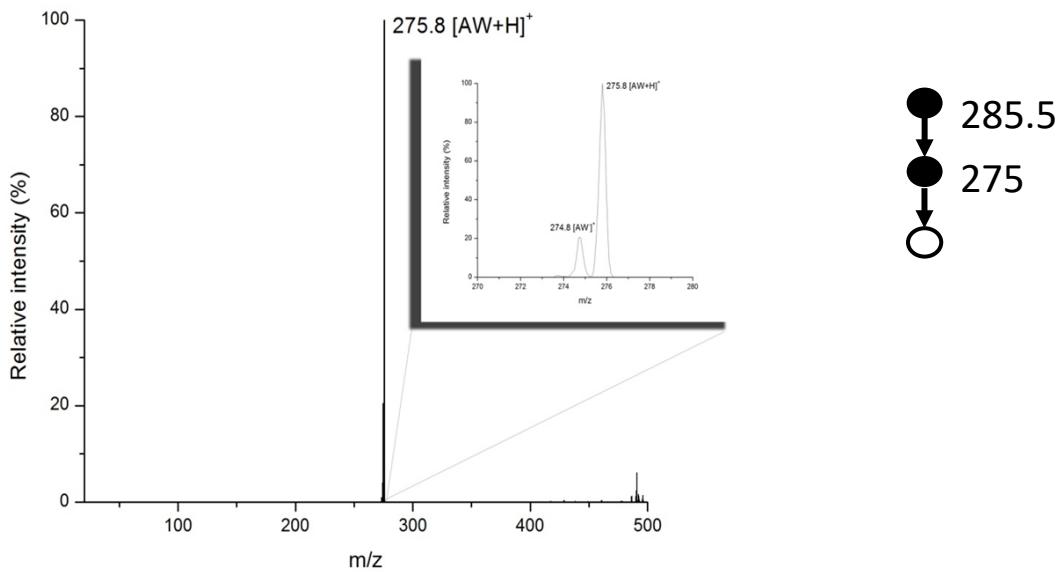


Figure S4. Ion-molecule reaction of $[\text{AW}_\pi^\bullet]^+$ (a) and $[\text{AW}_N^\bullet]^+$ (b) with *n*-propyl thiol. (Zoomed-in portion of the product peak on the inset). (a) shows almost complete hydrogen atom transfer from thiol to $[\text{AW}_\pi^\bullet]^+$ after reacting for 200 ms (eq.3); (b) shows no hydrogen atom transfer reaction for $[\text{AW}_N^\bullet]^+$ after reacting for 2 s.

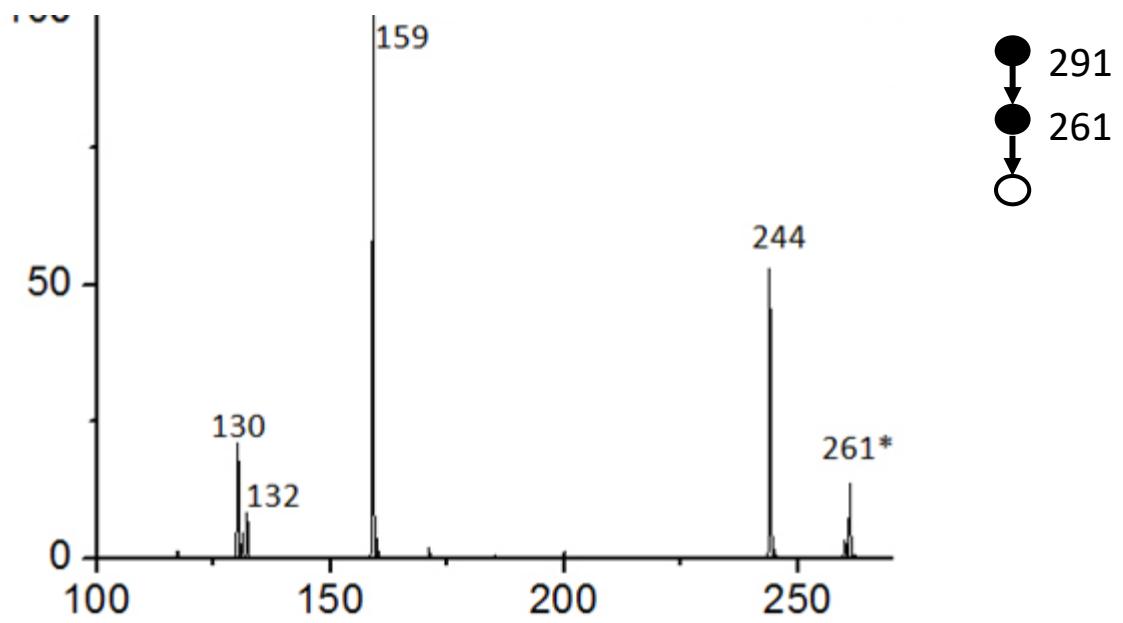


Figure S5. CID fragmentation of $[W_N\cdot G]^+$ radical cation.

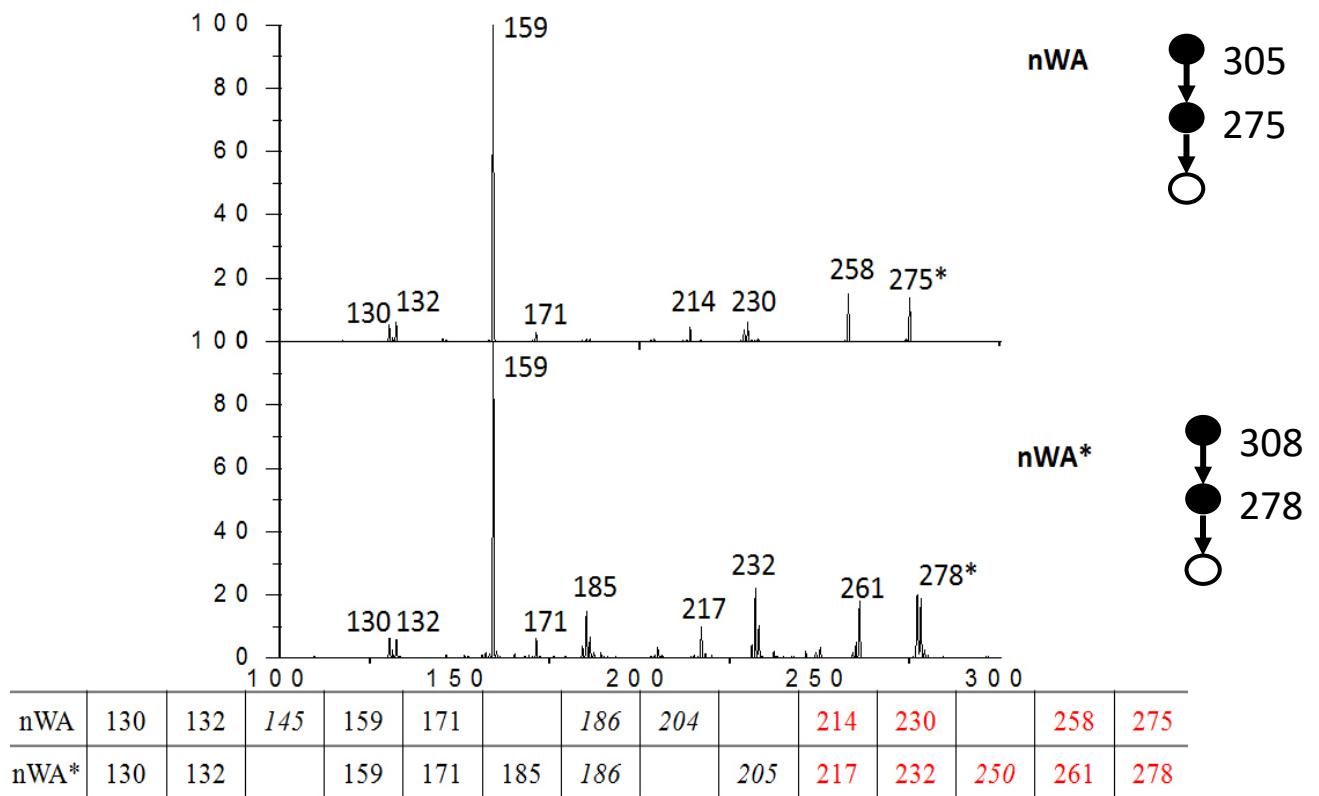


Figure S6. CID spectra of $[W_N\cdot A]^+$ radical cation (top panel) and $[W_N\cdot A^*]^+$ radical cation with d_3 -deuterium-labeled alanine side chain (bottom panel). (*minor fragments are in italic, shifted peaks highlighted with red*).

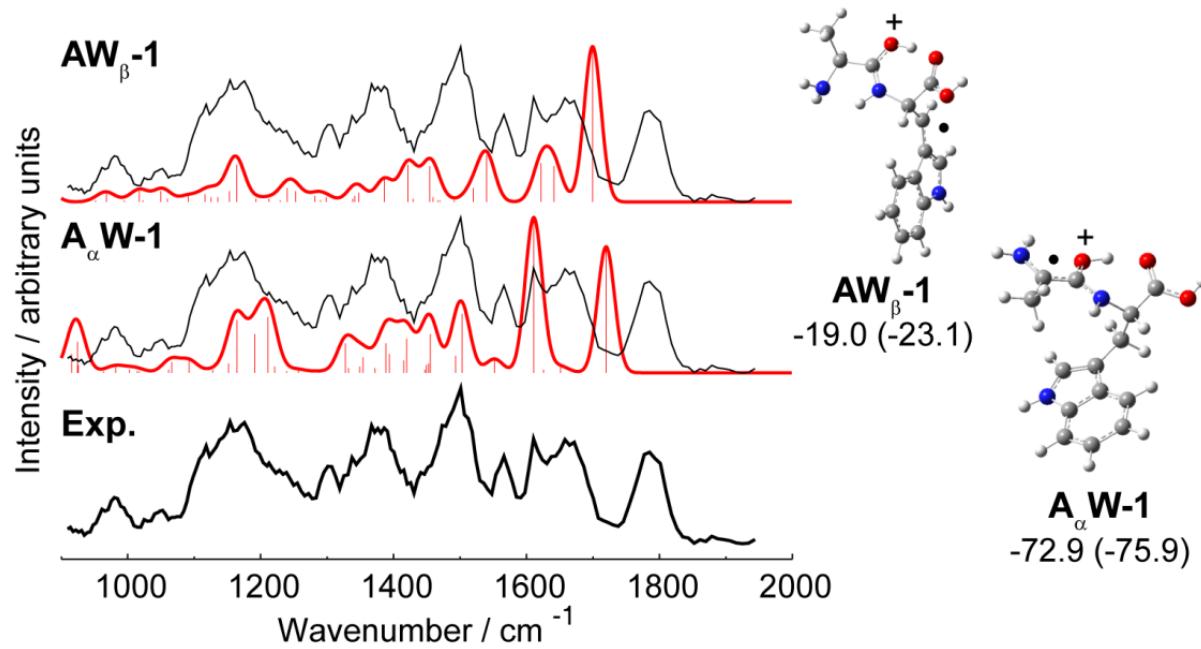


Figure S7. Comparison of the IRMPD action spectrum of $[\text{AW}_N^\bullet]^+$ (black trace) with the predicted IR absorption spectra of $[\text{A}_\alpha^\bullet \text{W}]^+$ and $[\text{AW}_\beta^\bullet]^+$ radical cations. Relative enthalpies (ΔH°_0) and free energies (ΔG°_{298}), in parentheses, in kJ mol $^{-1}$ are shown under the structures.

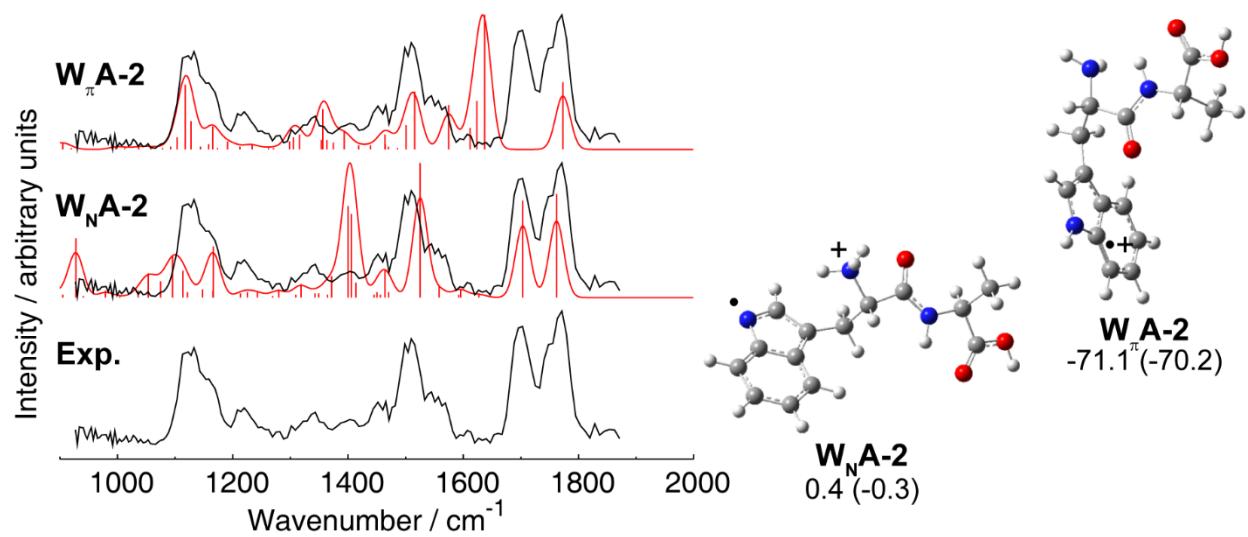


Figure S8. Comparison of the IRMPD action spectrum of $[W_N^\bullet A]^+$ (black trace) with the predicted IR absorption spectra of $[W_N^\bullet A]^+$ and $[W_\pi^\bullet A]^+$ radical cations. Relative enthalpies (ΔH°_0) and free energies (ΔG°_{298}), in parentheses, in kJ mol⁻¹ are shown under the structures.

Table S1. Comparison of CID fragments of protonated WA and $[W_N^\bullet A]^+$ radical cation.
(minor fragments are in italic).

WA					
$[WA+H]^+$			$[W_N^\bullet A]^+$		
Fragment	Loss	Assignment	Fragment	Loss	Assignment
130		3-methyleneindolium	130		3-methyleneindolium
132		$C_9H_{10}N^+$	132		$C_9H_{10}N^+$
144					
159		a_1^+	159		a_1^+
170					
			171		Fig. 4 [131]
			214	61	$[M-NH_3-CO_2]^+$
			230	45	$[M- NH_3-CO]^+$
232	44	$[M+H-CO_2]^+$			
259	17	$[M+H-NH_3]^+$	258	17	$[M-NH_3]^+$
27		$[WA+H]^+$	275		$nW^\bullet A^+$

Table S2. Comparison of CID fragments of protonated AW and $[AW_N\bullet]^+$ / $[AW_\pi\bullet]^+$ radical cations. (*minor fragments are in italic*)

AW						$[AW_\pi\bullet]^+$					
$[AW+H]^{+*}$			$[AW_N\bullet]^+$			$[AW_N\bullet]^+$			$[AW_\pi\bullet]^+$		
Fragment	Loss	Assignment	Fragment	Loss	Assignment	Fragment	Loss	Assignment	Fragment	Loss	Assignment
130		3-methyleneindolium	130		3-methyleneindolium	130		3-methyleneindolium			
132		$C_9H_{10}N^+$									
146											
159		a_1^+	159		a_1^+	159		a_1^+			
187			187		$[z_1\text{-H}]^{\bullet+}$	187		$[z_1\text{-H}]^{\bullet+}$			
188		$\gamma_1\text{-NH}_3$									
			204		$[y_1\text{-H}]^{\bullet+}$				205		γ_1^+
205		γ_1									
213	63	$[M+H\text{-NH}_3\text{-CO}\text{-H}_2O]^+$				214	61	$[M\text{-NH}_3\text{-CO}_2]^+$			
230	46	$[M\text{+H-CO+H}_2O]^+$				231	44	$[M\text{-CO}_2]^+$	231	44	$[M\text{-CO}_2]^+$
258	18	$[M\text{+H-H}_2O]^+$	258	17	$[M\text{-NH}_3]^+$						
276		$[AW\text{+H}]^+$	275		$nAW^{+\bullet}$		275				$\pi AW^{+\bullet}$