Gas-Phase Structure and Dissociation Chemistry of Protonated Tryptophan Elucidated by Infrared Multiple-Photon Dissociation Spectroscopy

Warren K. Mino, Kerim Gulyuz, Da Wang, Corey Stedwell, Nick C. Polfer

Department of Chemistry, University of Florida, P.O. Box 117200, Gainesville, FL 32611, U.S.A.

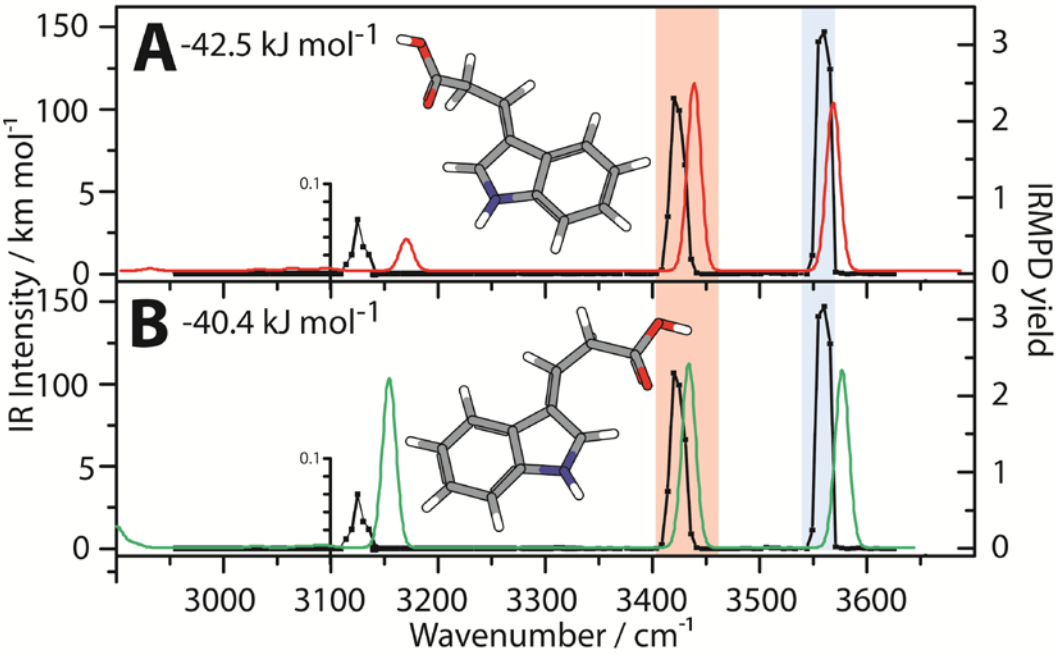


Figure S1. Comparison of $[Trp+H-NH_3]^+$ IRMPD spectrum (black) to calculated spectra (different colors) for lowest-energy benzyl cation conformers. Zero-point energy corrected energies at the B3LYP/6-31+G* level are indicated.

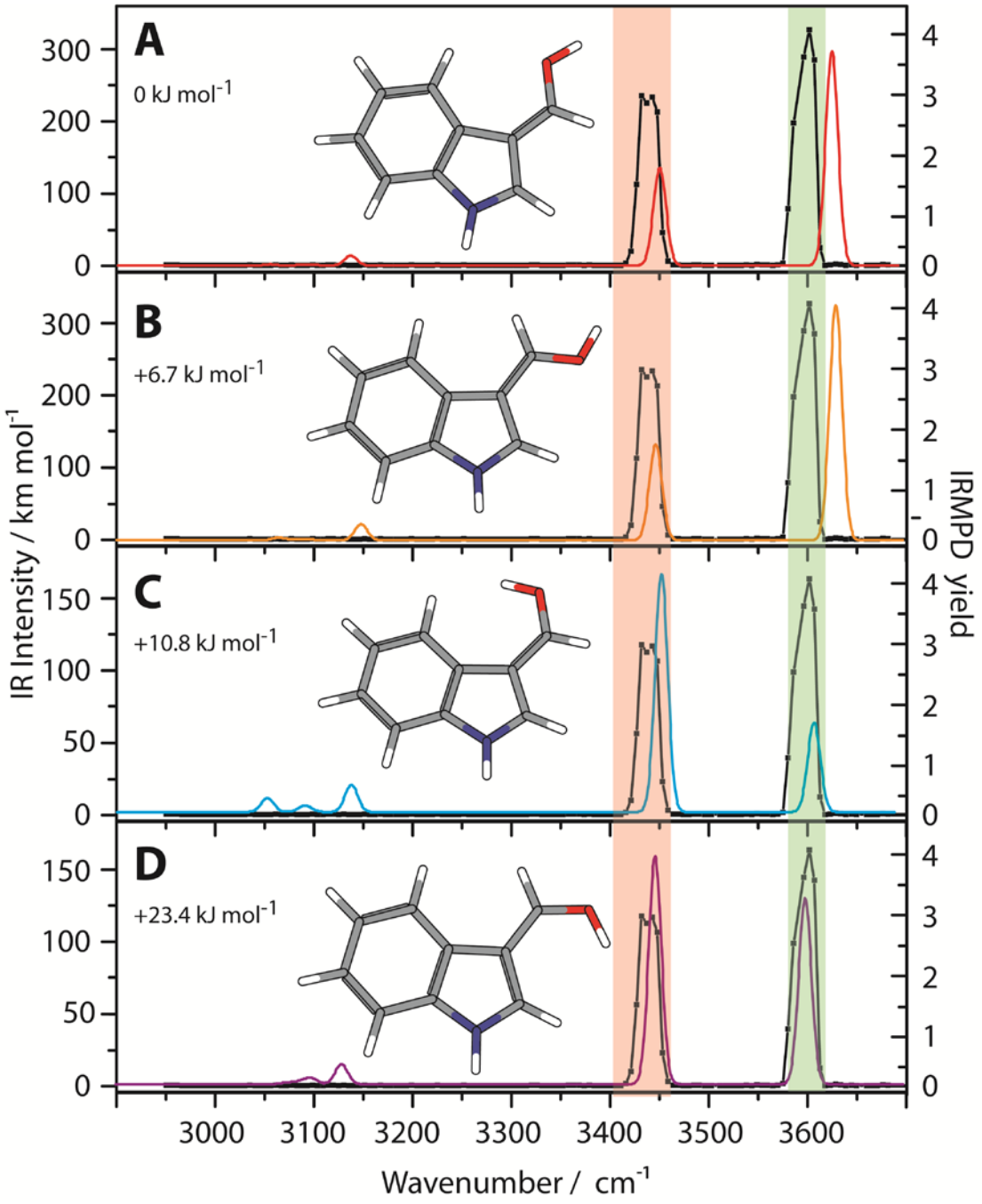


Figure S2. Comparison of $[Trp+H-NH_3-C_2H_2O]^+$ IRMPD spectrum (black) to theoretical spectra (different colors) of putative rotamers. Zero-point energy corrected energies at the B3LYP/6-31+G* level are indicated.

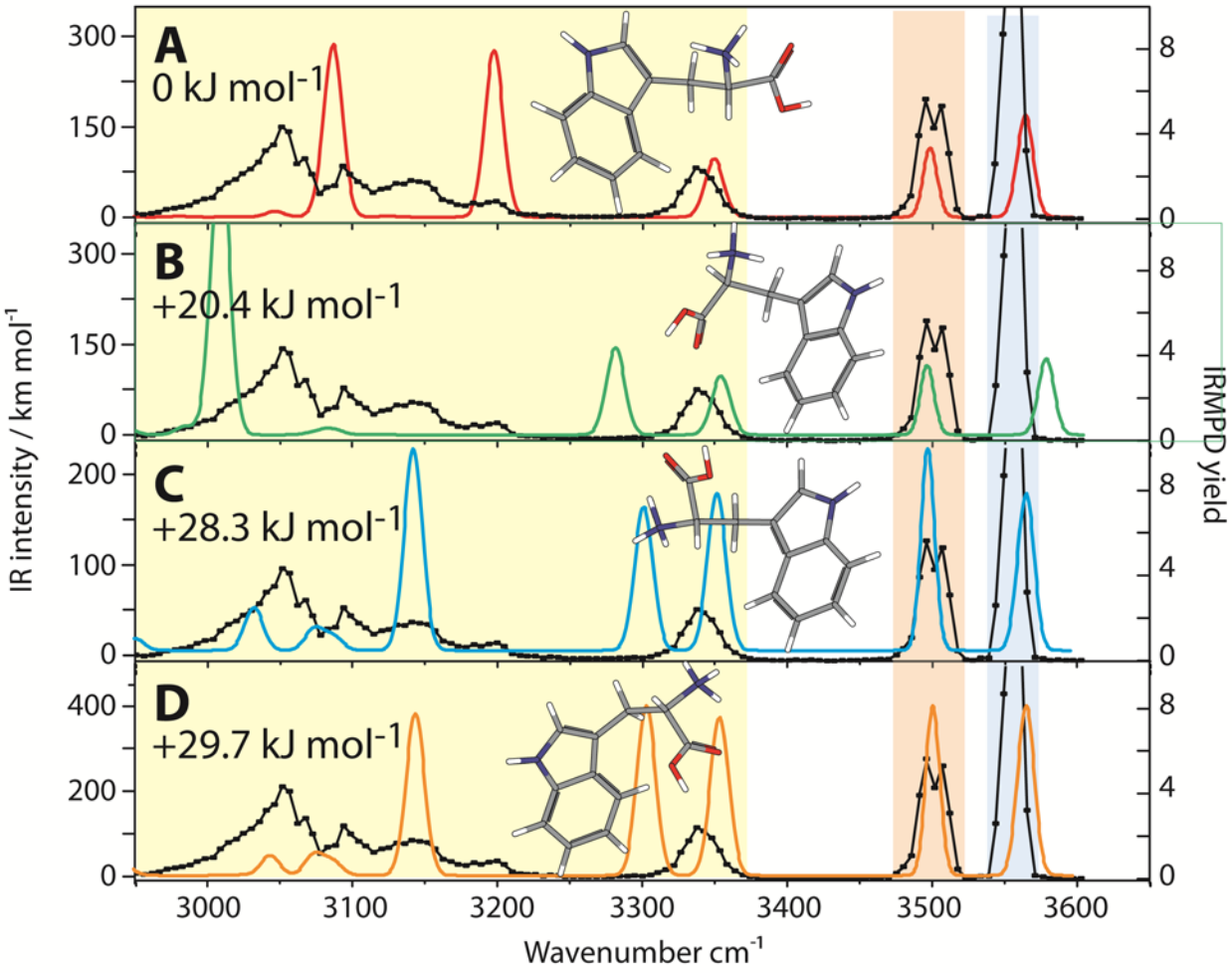


Figure S3. Comparison of $TrpH^+$ IRMPD spectrum (black) to (A) lowest-energy conformer, and (B-D) higher-energy conformers (in different colors). Zero-point energy corrected energies at the B3LYP/6-31+G* level are indicated.

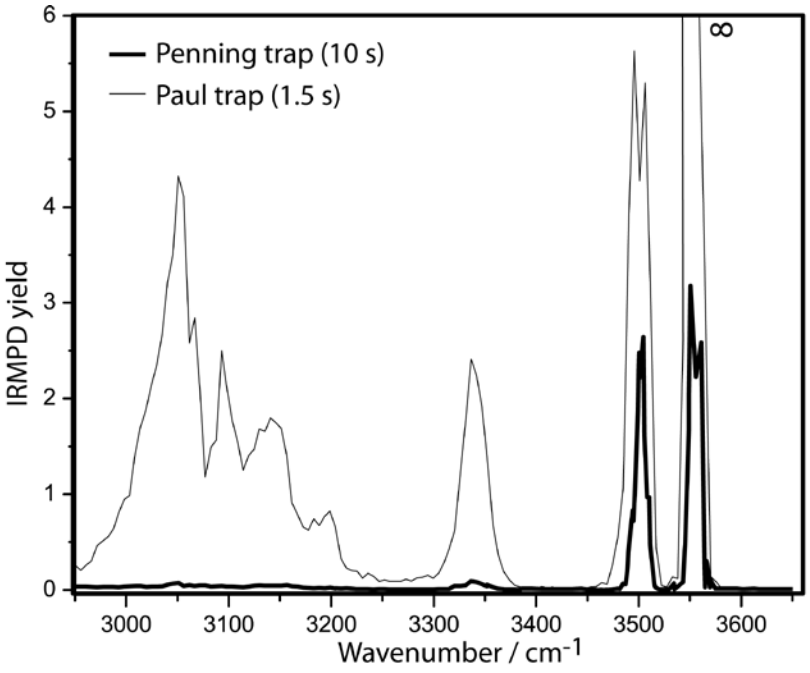
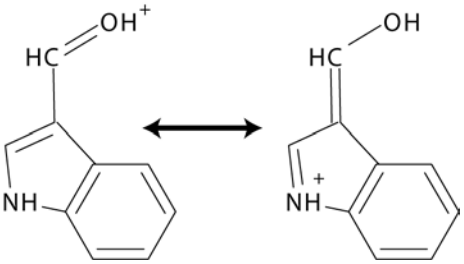


Figure S4. Comparison of IRMPD spectra of $TrpH^+$ in the Penning trap of a commercial Fourier transform ion cyclotron resonance (FTICR) mass spectrometer (4.7 T Apex II, Bruker Daltonics) and the "Paul-type" 3D ion trap of the custom-built mass spectrometer presented here. The ion cloud was irradiated with the tunable cw OPO laser for 10 s and 1.5 s, respectively. The laser fluxes in both experiments were estimated at 280 mW/cm^2 (Penning trap) and 280 W/cm^2 (Paul trap). These values are based on the measured beam waist for a 7.1 cm focal length lens.



Scheme S5. Resonance structures of $[Trp+H\text{-}NH_3\text{-}CH_2CO]^+$ (m/z 146) structure.

Table S6. Summary of B3LYP/6-31+G*, M05-2X/6-31+G* and (single-point) MP2/6-31+G* energies. Note that all zero-point energy (ZPE) and Gibbs (298K) free energy corrections were done using the frequency calculations at B3LYP/6-31+G*. The structures in Fig S3 C+D could not be optimized at the MP2 level of theory.

Structure	B3LYP			M05-2X			MP2	
	Electronic energy / Hartrees	ZPE / kJ mol^{-1}	Gibbs / kJ mol^{-1}	Electronic energy / Hartrees	ZPE / kJ mol^{-1}	Gibbs / kJ mol^{-1}	Electronic energy / Hartrees	ZPE / kJ mol^{-1}
TrpH$^+$								
Fig 3 A	-686.76174	0.000	0.000	-686.68491	2.765	0.627	-682.56524	4.012
B	-686.76170	0.536	1.444	-686.68443	1.405	3.880	-682.56500	2.045
C	-686.76097	2.114	2.631	-686.68620	0.000	0.000	-682.56420	0.000
D	-686.75890	7.341	8.622	-686.68252	8.845	7.848	-682.56080	7.073
FigS3 A	-686.76174	0.000	0.000	-686.68491	2.765	0.627	-682.56524	4.012
B	-686.75379	20.426	21.206	-686.67804	21.177	20.702	-682.55584	17.588
C	-686.75075	28.274	27.219	-686.67280	34.525	31.981	-682.55469	N/A
D	-686.75024	29.734	29.923	-686.67360	32.244	31.104	-682.55435	N/A
[Trp+H-NH$_3$]$^+$								
Fig 2 A	-630.13190	81.782	81.645					
B	-630.15989	9.757	9.848					
C	-630.16351	0.000	0.000					
D	-630.13598	72.561	72.810					
Fig S1 A	-630.17946	-42.491	-46.327					
B	-630.17822	-40.385	-46.311					
[Trp+H-NH$_3$-CH$_2$CO]$^+$								
Fig 2 E	-477.52127	0.000	0.000	-477.46255	0.000	0.000		
FigS3 A	-477.52127	0.000	0.000	-477.46255	0.000	0.000		
B	-477.51846	6.664	6.364	-477.45994	7.126	7.273		
C	-477.51690	10.788	10.056	-477.45841	10.691	9.930		
D	-477.51198	23.370	22.816	-477.45841	24.601	24.349		