Electronic Supplementary Material (ESI) for Faraday Discussions.

Selecting and identifying gas-phase protonation isomers of nicotineH^+ using combined laser, ion mobility and mass spectrometry techniques

Samuel J. P. Marlton,[1] Benjamin I. McKinnon,[1] Boris Ucur,[1] Alan T. Maccarone,[1] William A. Donald, [2] Stephen J. Blanksby,[3] Adam J. Trevitt.[1]

[1.] School of Chemistry, University of Wollongong, Wollongong, AUSTRALIA

[2.]School of Chemistry, University of New South Wales, Sydney, AUSTRALIA

[3.] Central Analytical Research Facility, Institute for Future Environments, Queensland University of Technology, Brisbane, AUSTRALIA

SUPPORTING INFORMATION

Table S1: Relative energies of different conformers of PYRO-nicH$^+$ relative to the PYRI-nicH$^+$ (*S, trans, anti*) global minimum in kcal/mol as calculated with four different DFT levels of theory with the aug-cc-pVDZ basis set as well as the MP2 method with the cc-pVDZ basis set. Omitted values converged to another structure upon optimisation. Labels are according to the naming system implemented by Yoshida *et al*. [REF 34 in main text] and represents (pyrrolidine ring conformational region, relative placement of the methyl group to the pyridine ring, χ angle region).

PYRO	**M06-2X**	**CAM-B3LYP**	**ωB97X-D**	**MP2**
(N, cis, anti)	3.1	-	4.2	-
(W, cis, anti)	2.7	5.3	4.1	-
(W, cis, syn)	2.4	5.1	3.8	-
(W, trans, anti)	0.5	2.5	1.6	0.7
(W, trans, syn)	0.5	2.5	1.6	-

Table S2: Relative energies of different conformers of PYRI-nicH$^+$ relative to the PYRI-nicH$^+$ (*S, trans, anti*) global minimum in kcal/mol as calculated with four different DFT levels of theory with the aug-cc-pVDZ basis set as well as the MP2 method with the cc-pVDZ basis set. Omitted values converged to another structure upon optimisation. Labels are according to the naming system implemented by Yoshida *et al*. [REF 34 in main text] and represents (pyrrolidine ring conformational region, relative placement of the methyl group to the pyridine ring, χ angle region).

PYRI	**M06-2X**	**CAM-B3LYP**	**ωB97X-D**	**MP2**
(N, cis, anti)	6.0	6.0	5.7	-
(N, cis, syn)	5.6	5.9	5.4	-
(S, cis, anti)	5.4	-	5.3	-
(E, cis, anti)	5.1	6.3	5.2	-
(W, trans, syn)	1.1	1.0	1.1	-
(W, trans, anti)	0.2	-	-	-
(S, trans, anti)	0	0	0	0

Table S3: Experimental and Calculated vertical transition energies for the *(W, trans, anti)* isomer of PYRO-nicH^+. TD-DFT calculations were performed with M06-2X and ωB97X-D with the aug-cc-pVDZ basis set.

PYRO	**M06-2X**		**ωB97X-D**	
PYRO Transition from S_0 to:	**Transition Energies (eV)**	**Calculated Oscillator Strength (f)**	**Transition Energies (eV)**	**Calculated Oscillator Strength (f)**
S_1	4.67	0.0030	4.88	0.0034
S_2	5.04	0	5.01	0.0001
S_3	5.59	0.043	5.52	0.040
S_4	6.23	0.079	6.15	0.062
S_5	6.69	0.066	7.02	0.39

Table S4: Experimental and Calculated vertical transition energies for the *(S, trans, anti)* isomer of PYRI-nicH$^+$. TD-DFT calculations were done with M06-2X and ωB97X-D with the aug-cc-pVDZ basis set.

PYRI	**M06-2X**		**ωB97X-D**	
PYRI Transition from S_0 to:	**Transition Energies (eV)**	**Calculated Oscillator Strength (f)**	**Transition Energies (eV)**	**Calculated Oscillator Strength (f)**
S_1	3.41	0.0018	3.30	0.0005
S_2	4.40	0.0014	4.34	0.0012
S_3	5.24	0.13	5.19	0.13
S_4	5.79	0.0004	6.04	0.010
S_5	6.10	0.016	6.13	0.0027

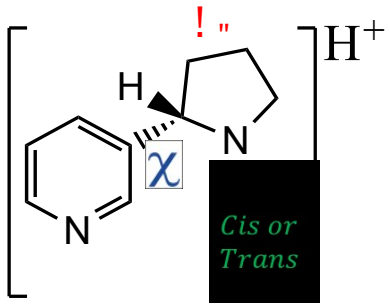


Figure S1: Structure of (*S*)-(-)-Nicotine including degrees of freedom which differentiate the conformers.

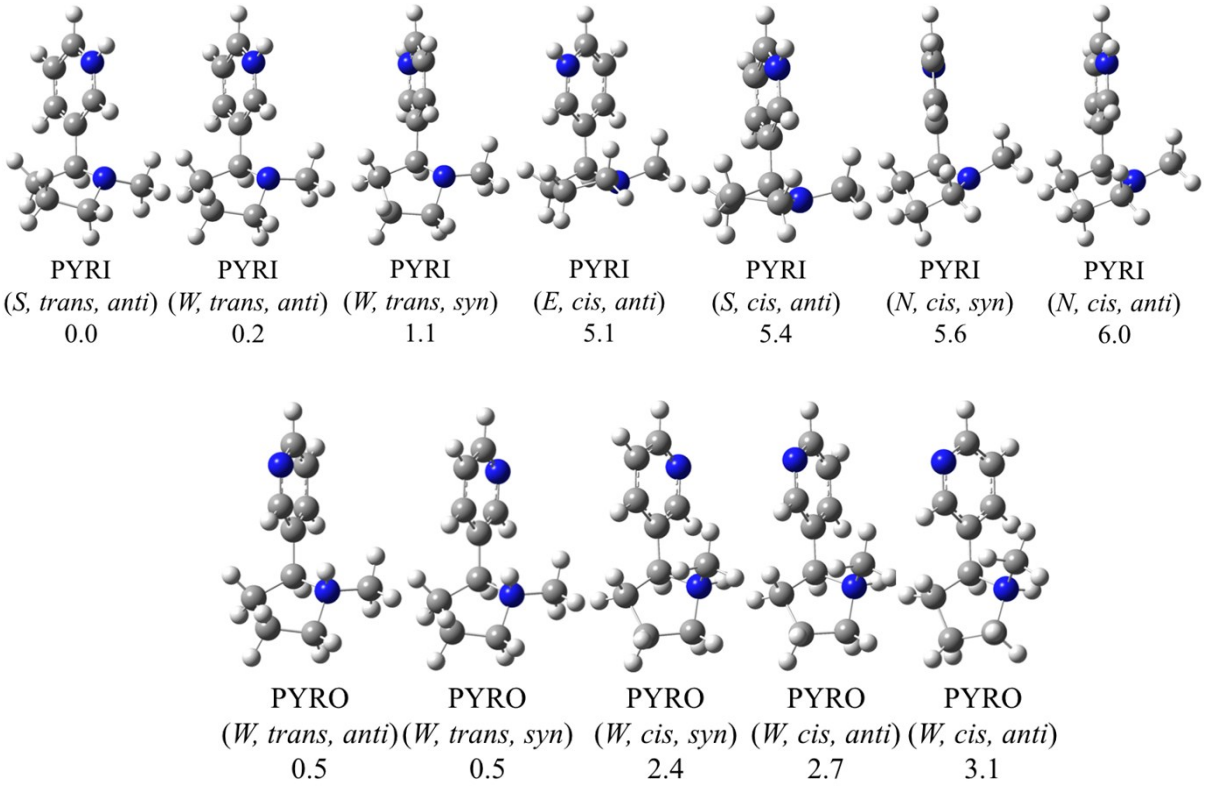


Figure S2: Optimised structures for twelve conformers of nicH$^+$ their relative energies in kcal/mol as calculated using M06-2X/aug-cc-pVDZ.

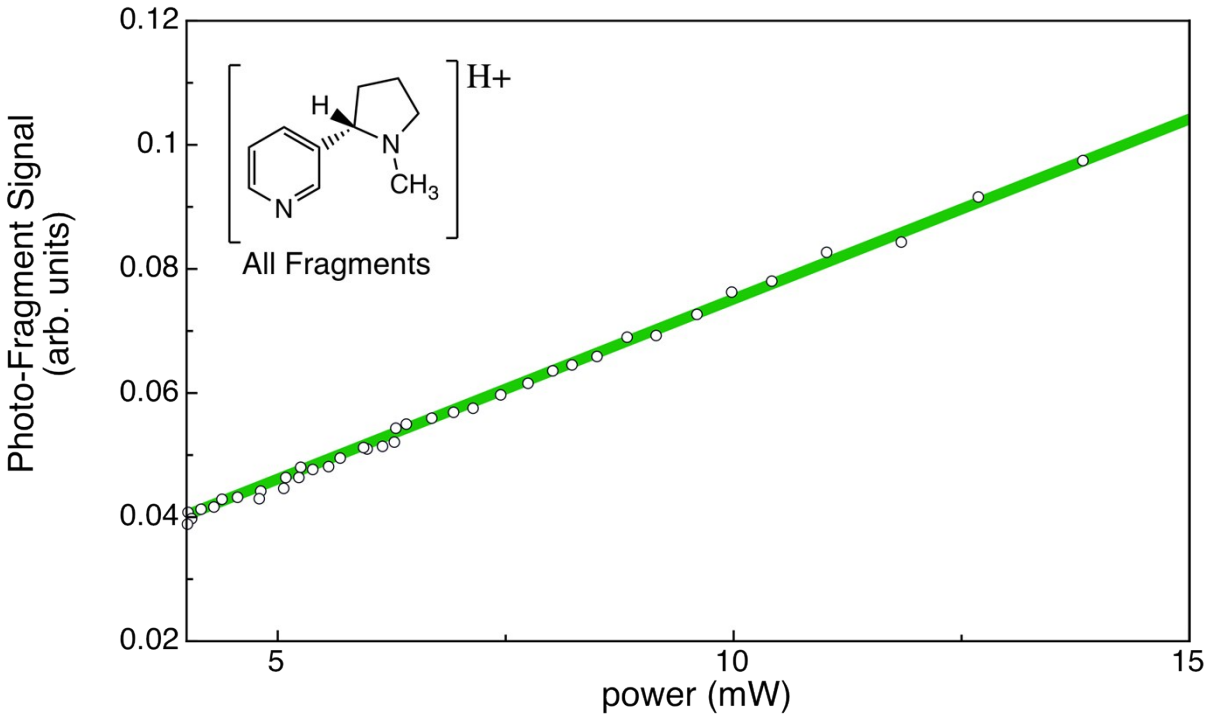


Figure S3: Power dependence experiments showing change in 266 nm photo-fragment signal with increasing laser power for all photoproduct ions.

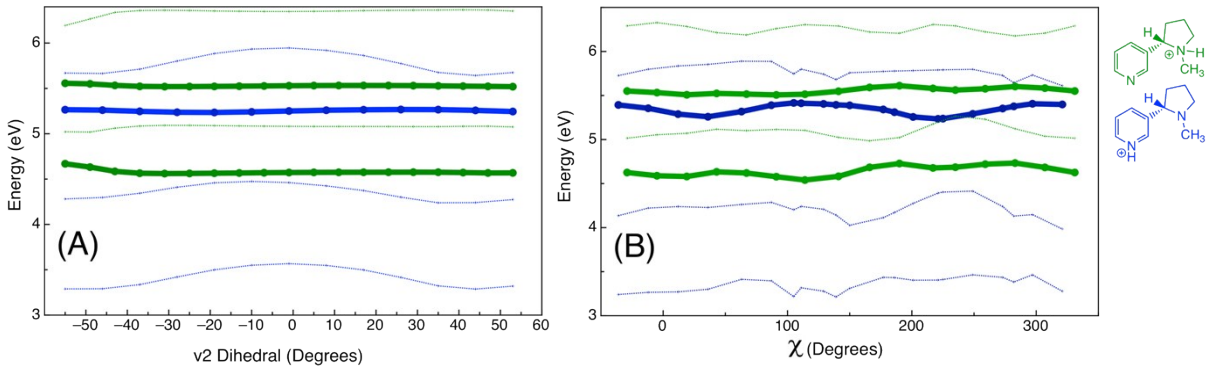


Figure S4: Electronic excitation energies of the first four states of protonated PYRI-nicH+ (blue) and PYRO-nicH+ (green) as the pyrrolidine ν_2 angle (A) or χ angle (B) was scanned. Transition energies were calculated using M06-2X/aug-cc-pVDZ. States of interest are plotted with bold lines. The -0.5 eV shift applied in the TD-DFT simulated electronic spectra was not applied to values presented in this table.

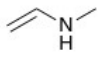
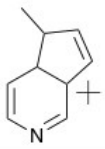
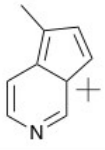
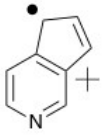
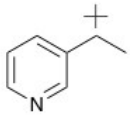
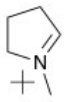
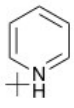
Dominant Precursor	PYRO-nicH$^+$			Both	PYRI-nicH$^+$	
Neutral Fragment(s)	NH_2CH_3	NH_2CH_3 H_2	NH_2CH_3 H_2 $\bullet CH_3$			
Product Ion						
m/z	132	130	117	106	84	80

Figure S5: Product ion assignments proposed by Williams *et al.* [REF 35 in main text] and assignment of the corresponding neutral fragment. The precursor ion assignment is based on experimental results presented here in the present study.

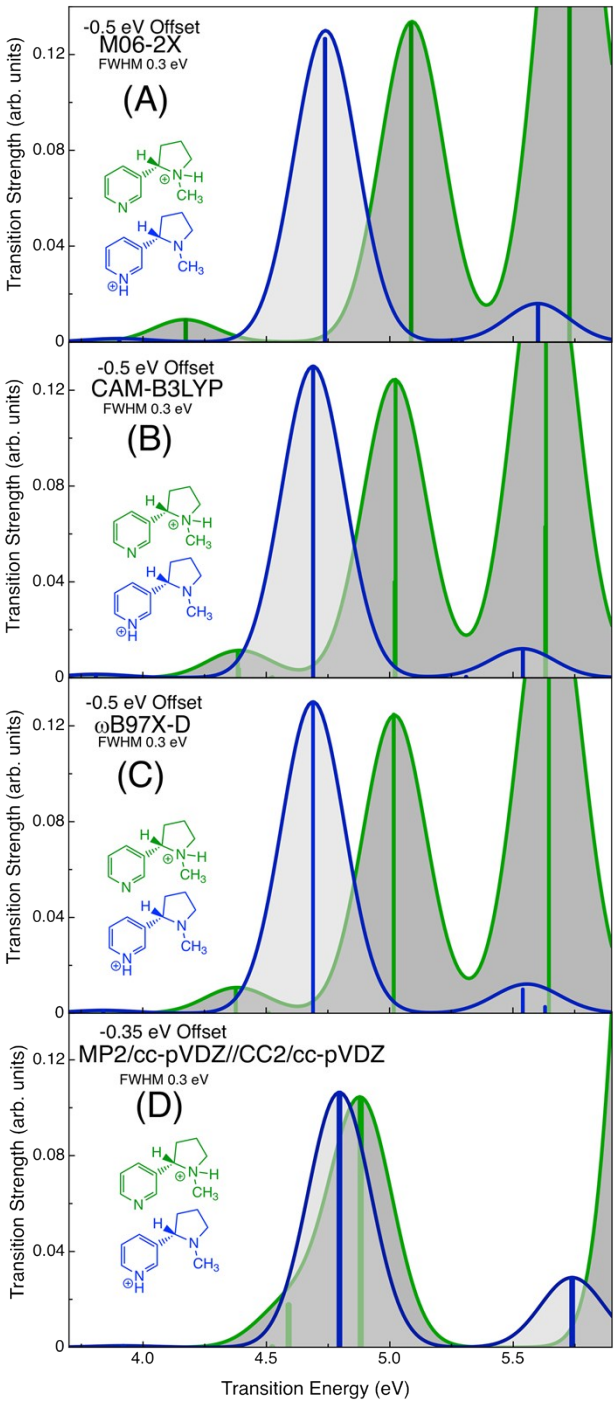


Figure S6: Calculated TD-DFT vertical transition energies for PYRI-nicH$^+$ (blue) and PYRO-nicH$^+$ (green). Three TD-DFT levels of theory were used (A) M06-2X, (B) CAM-B3LYP, (C) ωB97X-D, all with the aug-cc-pVDZ basis set. The transitions were fitted with Gaussian functions with a FWHM of 0.3 eV. Transitions have been offset -0.5 eV, as explained in the text. (D) Shows transitions calculated using CC2/cc-pVDZ from geometries which were optimised using MP2/cc-pVDZ. CC2 transitions have been offset by -0.35 eV as explained in the text.

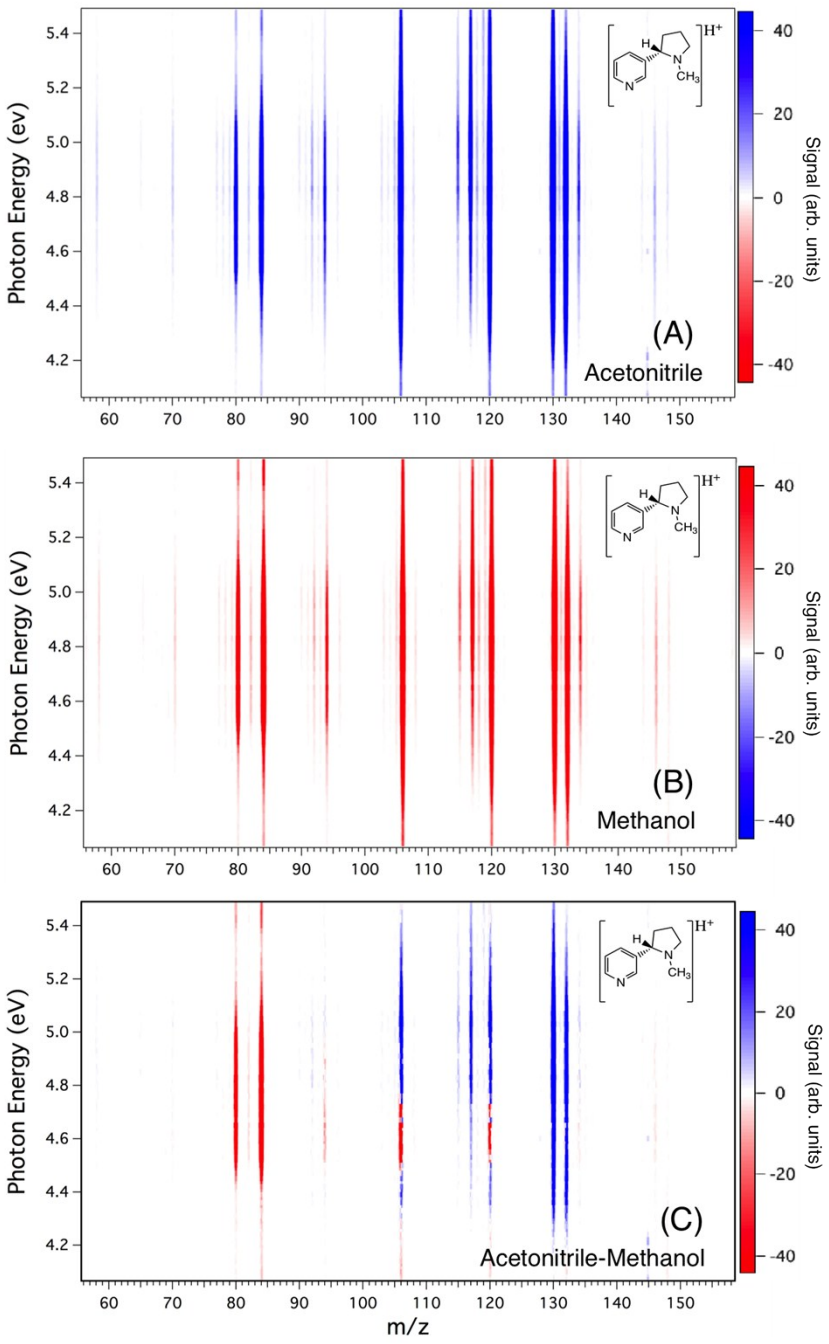


Figure S7: Intensity photodissociation action plots showing the changing intensities of all nicH$^+$ photodissociation fragments between 60 m/z and 150 m/z. ESI solvents (A) acetonitrile and (B) methanol were used. The difference between image (A) and (B) is plotted in (C).

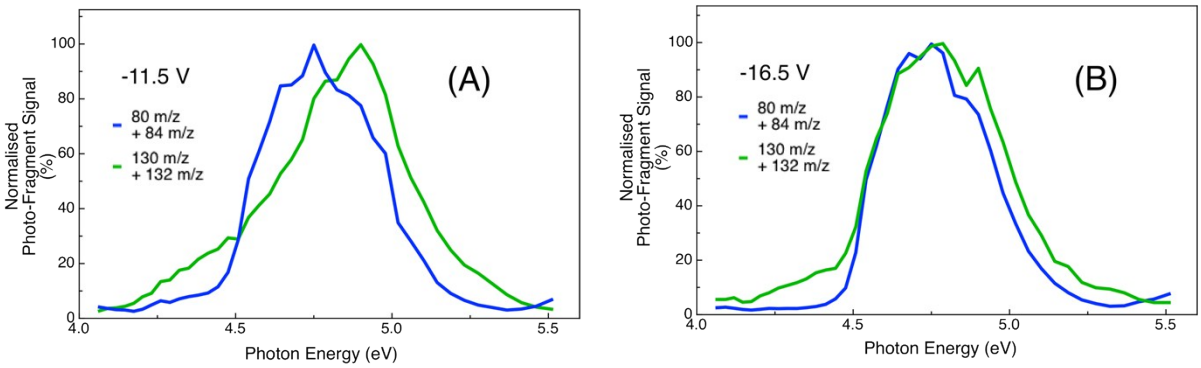


Figure S8: Normalised action spectra of fragments of $nicH^+$ after partial separation of the protomers of $nicH^+$ by FAIMS at -11.5 V (A) and -16.5 V (B).