

Electronic Supplementary Information for:
“Electronic Spectroscopy of Differential Mobility-selected
Prototropic Isomers of Protonated Para-Aminobenzoic Acid”

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S1 Experimental apparatus

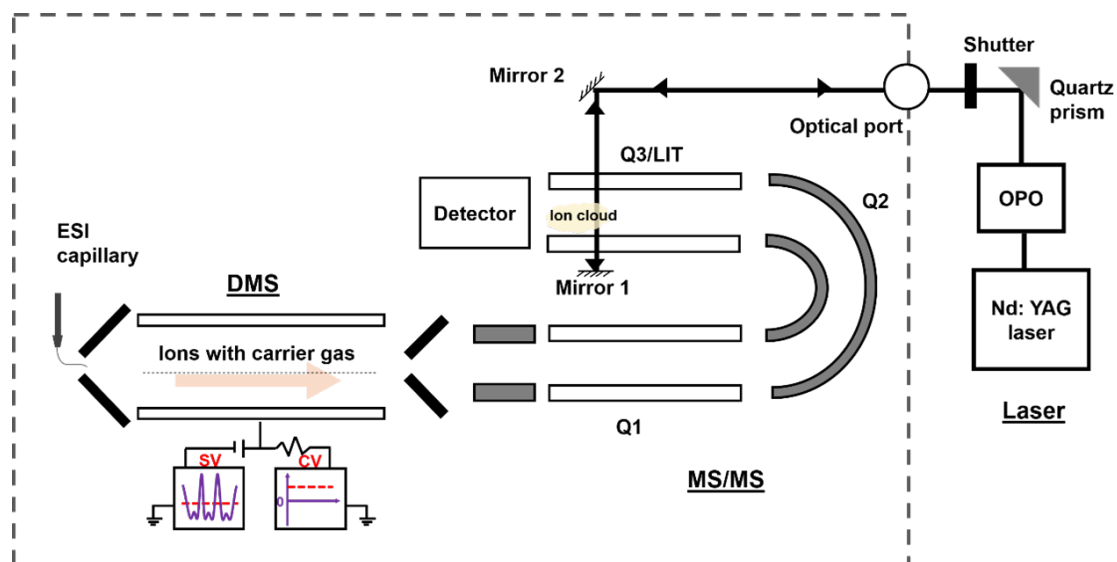


Figure S1: A schematic illustration of the experimental apparatus used for DMS-MS experiments and for photodissociation experiments presented in the main article.

As shown in Figure S1, electrosprayed ions traverse through the DMS cell in the same direction as the carrier gas (N_2 , 1 atm.) under the influence of an applied electric field. The electric field consists of an asymmetric radiofrequency potential (separation voltage, SV), superimposed on top of a DC potential (compensation voltage, CV); for a given SV above the high-field limit, every ion will elute at a unique CV value required to correct its trajectory toward the exit orifice. The DMS cell is housed in front of the entrance to a triple quadrupole mass spectrometer. DMS-selected ions are mass-selected in the first quadrupole (Q1), pass through a second quadrupole in RF-only mode (Q2), and are accumulated in the third quadrupole (Q3). Here, DMS-gated, mass-selected ions are irradiated by the output of a tunable Nd:YAG-pumped OPO. Ions with electronic transition energies resonant with the incoming light can undergo photodissociation inside Q3. Parent and fragment ions are ejected from the trap following a mass-selective axial ejection protocol before detection at a channeltron ion detector.

S2 Photodissociation action spectra

See below for spectroscopy data cited in the main text.

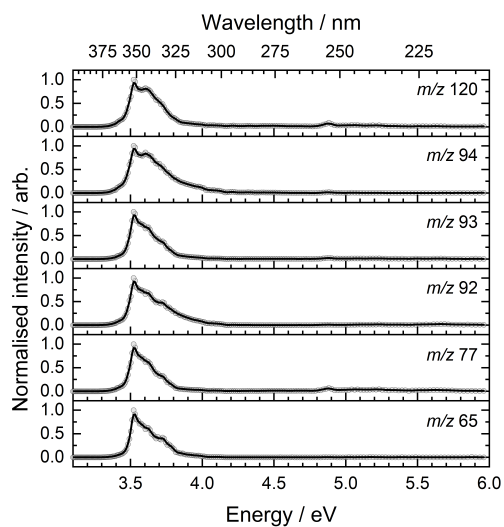


Figure S2: UVPD spectra for individual fragmentation channels corresponding to photodissociation of the O-protonated isomer in response to UV photon absorption.

S3 DMS data

See below for differential mobility spectrometry data cited in the main text.

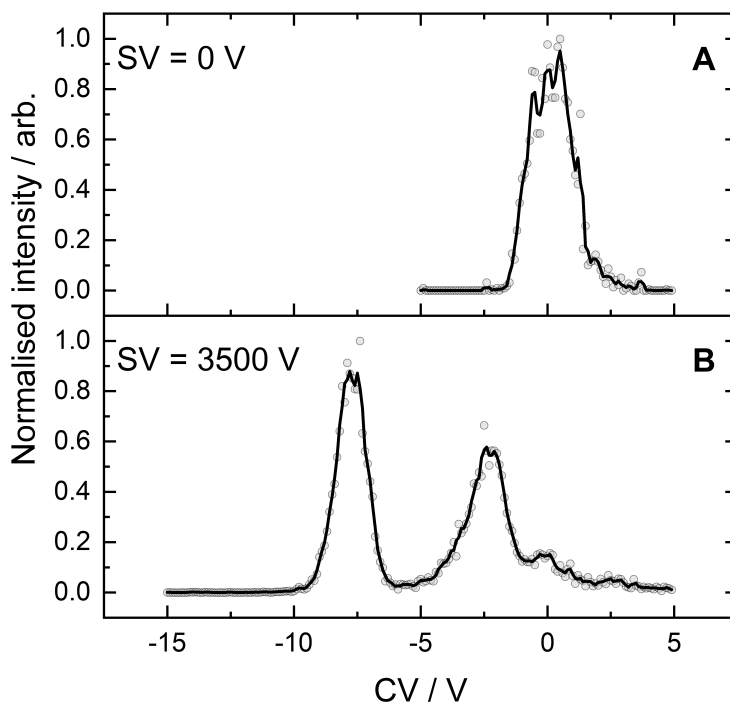


Figure S3: Ionograms for electrosprayed PABA dissolved in H₂O. A: SV = 0 V; B: SV = 3500 V. The raw data (open circles) are overlaid with a 3-point adjacent-average smoothed curve.

S4 Calculated transition orbitals

Figure S4 & Figure S5 below show the calculated molecular orbitals with the highest contributions for the first three transitions for both the O- and N- protonated isomers of protonated para-aminobenzoic acid. In all cases the transitions are predominantly π - π^* character.

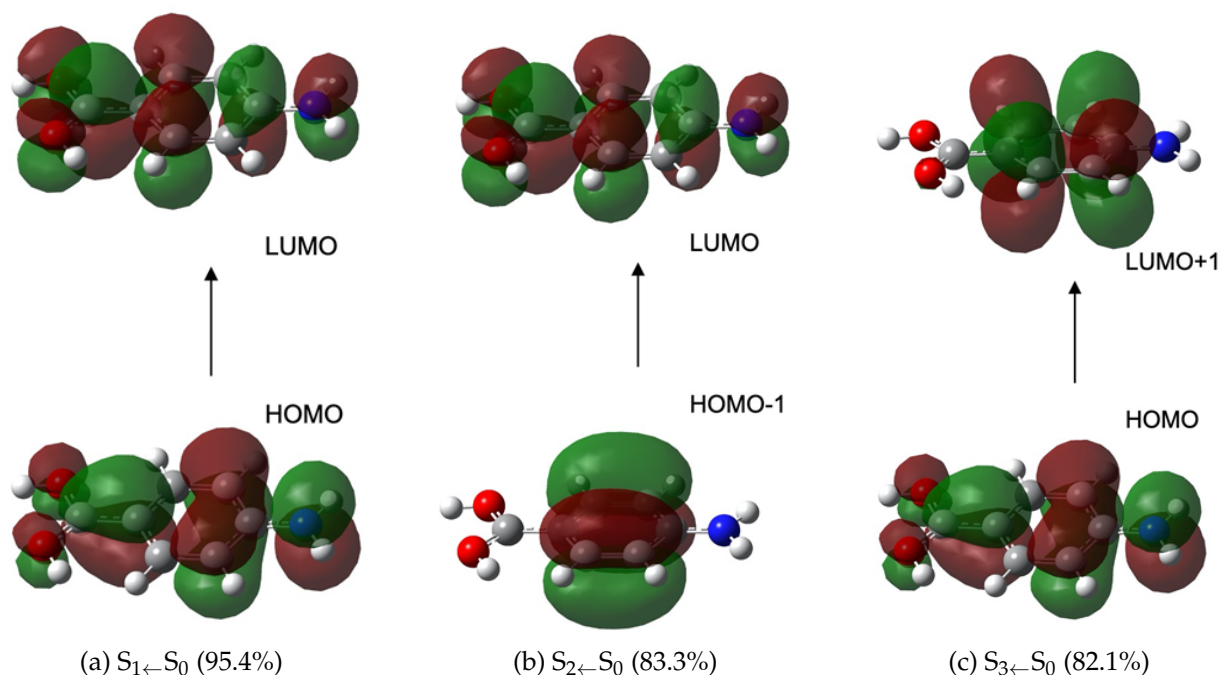


Figure S4: The calculated TD-DFT molecular orbitals for the O-protonated isomer for corresponding to electronic transitions from the ground state (S_0) to the n^{th} excited state, with percentage contributions shown in parentheses.

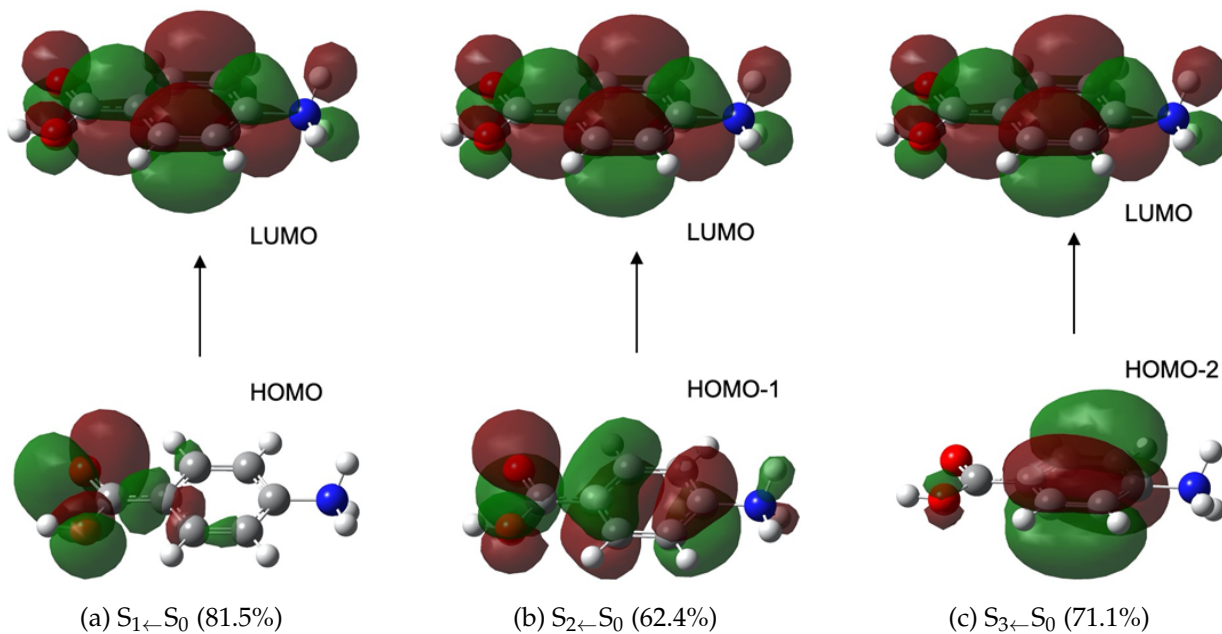


Figure S5: The calculated TD-DFT molecular orbitals for the N-protonated isomer for corresponding to electronic transitions from the ground state (S_0) to the n^{th} excited state, with percentage contributions shown in parentheses.