Electronic Supplementary Information for: "UVPD spectroscopy of differential mobility-selected, adenine prototropic isomers"

Fiorella Villanueva Heldmaier,[a,b] Neville J. A. Coughlan,[a,b] Alexander Haack,[a,b] Rebecca Huard,[a,b] Mircea Guna,[c] Bradley B. Schneider,[c] J. C. Yves Le Blanc,[c] J. Larry Campbell,[a,d] Marcel Nooijen,[a] and W. Scott Hopkins*[a,b,e,f]

[a] *Department of Chemistry, University of Waterloo, 200 University Avenue West, Waterloo, Ontario, Canada; E-mail: shopkins@uwaterloo.ca*
[b] *Waterloo Institute for Nanotechnology, University of Waterloo, 200 University Avenue West, Waterloo, Ontario, N2L 3G1, Canada*
[c] *SCIEX, Four Valley Drive, Concord, Ontario, L4K 4V8, Canada*
[d] *Bedrock Scientific Inc., Milton, ON, Canada.*
[e] *Centre for Eye and Vision Research, Hong Kong Science Park, New Territories, Hong Kong*
[f] *Watermine Innovation, Waterloo, Ontario, Canada*

*email:shopkins@uwaterloo.ca

S1 Photodissociation action spectra

See the figure below for additional action spectra cited in the main text.

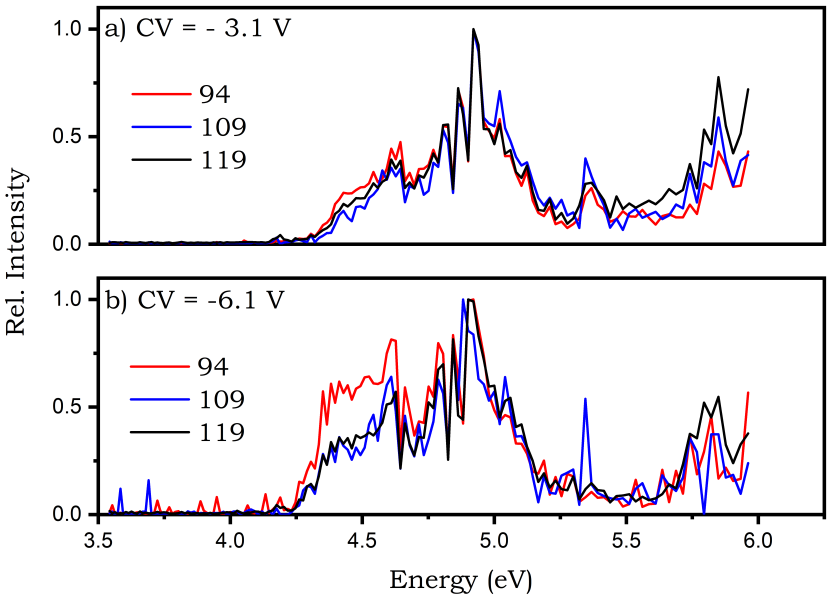

Figure S1: The photodissociation spectra for each of the three main fragmentation channels (*m/z* 94, 109, and 119) for the two peaks found at CV = –3.1 V (top) and CV = –6.1 V (bottom) at SV = 3500 V.

S2 Optimised structures and energies

All calculated structures, i.e., the four tautomers (gas phase and solution phase), the fragments ($m/z = 119, 109, 94$ and NH_3, HCN, NHCNH and NH_2CN) and all intermediates and transition states along fragmentation pathways (see next section) are uploaded to the *iochem-bd* database,[1,2] where they are publicly accessible via https://doi.org/10.19061/iochem-bd-6-93. These also show all vibrations obtained by normal mode analysis (thus, also the transition state mode for transition state structures), thermal energy corrections as well as the high level single point energies obtained at the CCSD(T)/6-311++G(d,p) level of theory.

S3 Fragmentation pathways

Fragmentation pathways were obtained using the Nudged-Elastic Band (NEB) method,[3–5] implemented in ORCA 4.2.1.[6] We changed the method to B3LYP-D3(BJ)/def2-TZVPP for a more accurate description of non-minimum geometries. For consistency reasons with respect to the electronic energy, also the reactants and fragmentation products were re-optimised on that level of theory. Geometries and vibrational frequencies showed no significant differences to the previous calculations.

Starting from either A1 or A4, three pathways are shown in Fig. S2. In particular, it can be seen that the pathway starting from A4 is always below the fragmentation threshold energy and thus, the threshold itself is the rate determining energy and not a high-lying barrier (e.g., for intramolecular proton transfer). The orange path corresponds to a mechanism, where first the N1-C2 bond is cleaved (first energy step) and after cleaving the C5-C6 bond, the proton transfer occurs. This pathway was found by MD simulations[7] but is clearly higher in energy than the other ones found, where C5 is protonated initially.

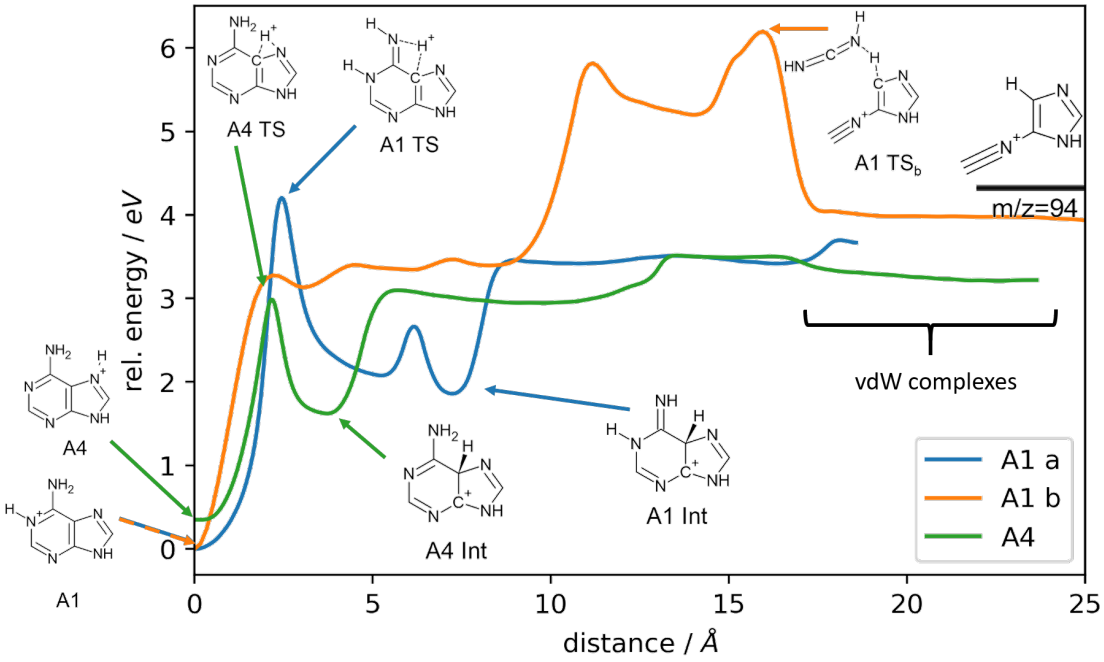

Figure S2: Reaction path profiles for the fragmentation of A1 and A4 towards the *m/z* 94 fragment. A1 leads to NHCNH and A4 to NH_2CN. Important structures along the way are depicted, the threshold energy is shown to the right (black line).

S4 Predicted CV values

Table S1: Comparison of measured and computed CV shifts at a SV = 3500 V.

Tautomer	A1	A2	A3	A4
Computed	–1.22	–2.42	–2.09	–0.34
Measured	–3.1	–6.1		—

References

[1] Álvarez-Moreno, M.; de Graaf, C.; López, N.; Maseras, F.; Poblet, J. M.; Bo, C. *J. Chem. Inf. Model.* **2015**, *55*, 95–103.

[2] Bo, C.; Maseras, F.; López, N. *Nat. Catal.* **2018**, *1*, 809–810.

[3] Jónsson, H.; Mills, G.; Jacobsen, K. W. Nudged elastic band method for finding minimum energy paths of transitions. Class. Quantum Dyn. Condens. Phase Simulations. 1998; pp 385–404.

[4] Henkelman, G.; Jónsson, H. *J. Chem. Phys.* **2000**, *113*, 9978–9985.

[5] Henkelman, G.; Uberuaga, B. P.; Jónsson, H. *J. Chem. Phys.* **2000**, *113*, 9901–9904.

[6] Neese, F. *Wiley Interdiscip. Rev. Comput. Mol. Sci.* **2017**, *8*, 73–78.

[7] Giacomozzi, L.; D'Angelo, G.; Diaz-Tendero, S.; De Ruette, N.; Stockett, M. H.; Alcamí, M.; Cederquist, H.; Schmidt, H. T.; Zettergren, H. *J. Chem. Phys.* **2019**, *151*, 044306.