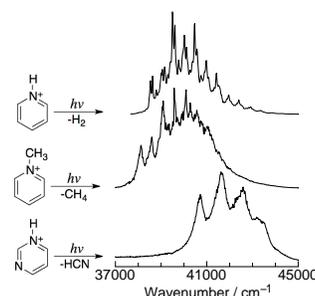


## ULTRAVIOLET PHOTODISSOCIATION ACTION SPECTROSCOPY OF PROTONATED AZABENZENES

**CHRISTOPHER S. HANSEN**, *School of Chemistry, University of Wollongong, Wollongong, New South Wales, Australia*; **STEPHEN J. BLANKSBY**, *Central Analytical Research Facility, Queensland University of Technology, Brisbane, Queensland, Australia*; **EVAN BIESKE**, *School of Chemistry, The University of Melbourne, Melbourne, Victoria, Australia*; **JEFFREY R. REIMERS**, *University of Technology Sydney, School of Physics and Materials Science, Broadway, New South Wales, Australia*; **ADAM J. TREVITT**, *School of Chemistry, University of Wollongong, Wollongong, New South Wales, Australia*.

Azabenzenes are derivatives of benzene containing between one and six nitrogen atoms. Protonated azabenzenes are the fundamental building blocks of many biomolecules, charge-transfer dyes, ionic liquids and fluorescent tags. However, despite their ubiquity, there exists limited spectroscopic data that reveals the structure, behaviour and stability of these systems in their excited states. For the case of pyridinium ( $C_5H_5N-H^+$ ), the simplest azabenzene, the electronic spectroscopy is complicated by short excited state lifetimes, efficient non-radiative deactivation methods and limited fluorescence. Ultraviolet (UV) photodissociation (PD) action spectroscopy<sup>a</sup> provides new insight into the spectroscopic details, excited state behaviour and photodissociation processes of a series of protonated azabenzenes including pyridinium, diazeniums and their substituted derivatives.

The room-temperature UV PD action spectra, often exhibiting vibronic detail,<sup>b</sup> will be presented alongside PD mass spectra and the kinetic data from structurally-diagnostic ion-molecule reaction kinetics. Analysis of the spectra, with the aid of quantum chemical calculations, reveal that many azabenzenes prefer a non-planar excited state geometry reminiscent of the structures encountered in 'channel 3'-like deactivation of aromatics. The normal modes active in this isomerization contribute largely to the spectroscopy of the *N*-pyridinium ion as they build upon totally-symmetric vibronic transitions leading to repeating sets of closely-spaced spectral features.



<sup>a</sup>Hansen, C.S. *et al.*; *J. Am. Soc. Mass Spectrom.* 24:932-940 (2013) <sup>b</sup>Hansen, C.S. *et al.*; *J. Phys. Chem. A* 117:10839-10846 (2013)