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Herbert P. Broida Prize Talk: Molecular photofragmentation dynamics in the gas and condensed phase: similarities and differences[1]

MICHAEL ASHFOLD, School of Chemistry, University of Bristol, Bristol, U.K., BS8 1TS

Phenols and azoles are important chromophores in the nucleobases and aromatic amino-acids that dominate the near-UV absorption spectra of many biological molecules. $\pi^* \leftarrow \pi$ excitations are responsible for these strong UV absorptions, but these molecules also possess excited states formed from $\sigma^* \leftarrow \pi$ electron promotions. $\pi\sigma^*$ excited states typically have much smaller absorption cross-sections, but their photochemical importance is becoming ever more widely recognized [1]. We have used photofragment translational spectroscopy (PTS) methods (and complementary *ab initio* theory) to explore X–H bond fission (X = heteroatom) following UV photoexcitation of many such heteroaromatic molecules in the gas phase and, more recently, started ultrafast pump-probe studies of the same (and related) processes in solution. This presentation will (i) summarize the state of knowledge derived from PTS studies of phenol and related molecules in the gas phase [2], (ii) highlight the extent to which such knowledge can inform our interpretation of ultrafast pump-probe studies of the UV photofragmentation of similar molecules ((thio)phenols, anisoles and ethers) in solution [3,4] and (iii) demonstrate how such solution phase studies offer a route to exploring photoinduced ($\pi\sigma^*$-state mediated) ring opening of heterocyclic molecules like furans and thiophenes [5].

[1] See, *e.g.*, M.N.R. Ashfold, G.A. King, D. Murdock, M.G.D. Nix, T.A.A. Oliver and A.G. Sage, *Phys. Chem. Chem. Phys.* **12**, (2010), 1218.
[2] T.N.V. Karsili, A.M. Wenge, S.J. Harris, D. Murdock, J.N. Harvey, R.N. Dixon and M.N.R. Ashfold, *Chem. Sci.* **4**, (2013), 2434.
[3] Y. Zhang, T.A.A. Oliver, M.N.R. Ashfold and S.E. Bradforth, *Farad. Disc. Chem. Soc.* **157**, (2012), 141.
[4] S.J. Harris, D. Murdock, Y. Zhang, T.A.A. Oliver, M.P. Grubb, A.J. Orr-Ewing, G.M. Greetham, I.P. Clark, M. Towrie, S.E. Bradforth and M.N.R. Ashfold, *Phys. Chem. Chem. Phys.* **15**, (2013), 6567.
[5] D. Murdock, S.J. Harris, J. Luke, M.P. Grubb, A.J. Orr-Ewing and M.N.R. Ashfold, *Phys. Chem. Chem. Phys.* **16**, (2014), 21271.

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