

PHOTODISSOCIATION DYNAMICS OF HETEROAROMATIC MOLECULES.

M. N. R. ASHFOLD, B. CRONIN, R. N. DIXON, A. L. DEVINE, G. A. KING, M. G. D. NIX and T. A. A. OLIVER,
School of Chemistry, University of Bristol, Bristol, BS8 1TS, U.K..

Imidazole, pyrrole and phenol are key components of the long wavelength chromophores in nucleobases and aromatic amino-acids like histidine, tryptophan and tyrosine, which dominate the UV absorption spectra of many biological molecules. $\pi^* \leftarrow \pi$ transitions are responsible for these strong UV absorptions, but these heteroaromatic molecules also possess excited states formed via $\sigma^* \leftarrow \pi$ electron promotions. The $\sigma^* \leftarrow \pi$ transitions have much smaller absorption cross-sections, and have only recently started to attract much detailed attention.

We have used high resolution photofragment translational spectroscopy methods to study H atom loss processes following UV photo-excitation of a progressively more complex range of gas phase heteroaromatics^a, including imidazole, pyrrole, phenol and thiophenol, various p-halophenols, cresols, indole and adenine. The studies : (i) confirm theoretical predictions^b that X-H (X = N, O, S) bond fission is an important non-radiative decay process following population of the $^1\pi\sigma^*$ excited states of such molecules, and (ii) reveal that the respective co-fragments (imidazolyl, pyrrolyl, phenoxy, thiophenoxy, *etc*) are formed in a very limited sub-set of the available vibrational state density. Identification of these product states yields detailed insights into the couplings involved in the photo-induced evolution from parent molecule to ultimate fragments.

^aM.N.R. Ashfold, B. Cronin, A.L. Devine, R.N. Dixon and M.G.D. Nix, *Science* **312**, 1637 (2006)

^bA. L. Sobolewski, W. Domcke, C. Dedonder-Lardeux and C. Jouvet, *Phys. Chem. Chem. Phys.* **4**, 1093 (2002)