PHOTODISSOCIATION DYNAMICS OF HETEROAROMATIC MOLECULES.

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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, phenoxyl, thiophenoxyl, *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.

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

[b] A. L. Sobolewski, W. Domcke, C. Dedonder-Lardeux and C. Jouvet, *Phys. Chem. Chem. Phys.* **4**, 1093 (2002)