Electronic excitation energies of pyrimidine probed by synchrotron radiation

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Common constituents of compounds of biochemical interest are mono- or bicyclic aromatics, often with one or several nitrogen atoms substituted for ring carbons. Well-known examples are the five nucleic acid bases, which form the code sequence of *t*-RNA, *m*-RNA and DNA; other examples include the pseudo-amino acid tyrosine and the various azabenzenes. Pyrimidine is though an important precursor system for numerous biologically active compounds, such as nicotinic acid and is a building block in the nucleotides cytosine, uracil and thymine. Research on pyrimidine can therefore serve as a starting point for such studies, especially in order to evaluate the effects of radiation interaction with these systems at the molecular level.

In radiobiology, several models are required to describe a detailed understanding of the underlying interactions between the primary radiation and the cellular environment, in order to quantify the risk of radiation damage on physiological material. Though, the effects of radiation damage within cells, and thence mutagenesis, therefore depends upon our detailed knowledge of the spectroscopy and dissociation dynamics of key components in certain initiation reactions. In this study we are particularly interested to investigate pyrimidine by VUV photoabsorption as an important route to obtain detailed information on the excitation (and ionisation) processes that can lead to degradation.

The electronic sates of pyrimidine have been investigated from 3.0 – 10.8 eV and their lower electronic excitation spectra are due to both ($n \rightarrow \pi$) and ($\pi \rightarrow \pi^*$) valence transitions. The low energy absorption band centred at 4.183 eV and assigned to (π^*) $\leftarrow 5b_2(n_y)$ ($1^1B_1 \leftarrow 1^1A_1$) showing a rich vibrational structure. A strong mixture of the valence and Rydberg ($\pi \rightarrow \pi^*$) excitations was observed for the third valence ($\pi \rightarrow \pi^*$) excited state. Several other Rydberg states converging up to the third ionisation energy have been assigned for the first time [1]. Vibronic coupling plays an important role in the observed patterns which in turn dictates the nature of observable structure of the excited states under investigation, especially the low energy absorption band.

References:

[1] F Ferreira da Silva, D Almeida, R Antunes, A R Milosavljevic, B P Marinkovic, S V Hoffmann, N J Mason and P Limão-Vieira, (2007) *to be submitted*.