UV multi-photon ionization pathways and fragmentation patterns of clustered nucleobases

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The photophysics of DNA and its constituent molecules has attracted considerable interest for many years, with the central aim to understand electronic excitation and relaxation pathways that can initiate reactivity and lesions [1]. Further interest relates to the mechanisms underpinning the remarkable photo-stabilities of DNA and RNA bases and their evolutionary implications. Experimental studies of isolated biomolecules can precipitate relatively clear photophysical interpretations, while equivalent measurements on hydrogen-bonded complexes enable closer analogies to be drawn with biological environments where different isomeric forms, intermolecular energy transfer processes, and reactivity can be significant.

This seminar will focus on ionization and dissociation pathways via the bright and short-lived ππ* states of adenine and uracil [2,3]. In particular, monomers and hydrated complexes have been probed by ns-timescale multi-photon ionization (MPI) time-of-flight mass spectrometry at 220-270 nm. Photon orders (indicating the number of photons absorbed in the MPI process) were determined by analyzing the production of specific ions and cluster ions as a function of laser fluence on a pulse-by-pulse basis. The differences we have observed in fragment ion production from monomers and hydrated clusters can be interpreted primarily in terms of two effects: (i) energy dissipation from excited nucleobase ions via cluster dissociation, and (ii) distinct fragmentation patterns of protonated nucleobases. Further comparisons will be drawn between the present MPI data and collision experiments on isolated and clustered nucleobases [4,5].

A major challenge in analyzing radiation-induced processes in clusters is the broad distribution of sizes and configurations produced by supersonic expansion sources (or alternative cluster sources, for example utilising laser ablation). The last part of the seminar will discuss a new project to analyze UV and electron interactions with neutral isomers and clusters following selection as a function of dipole moment / mass [6].

[1] Middleton, Crespo-Hernandez and co-workers, Annu. Rev. Phys. Chem. 60 (2009) 217
[2] Schultz and co-workers, PCCP 6 (2004) 2796
[3] Schultz and co-workers, PCCP 12 (2010) 9632
[4] Schlathölter, Huber and co-workers, *ChemPhysChem*, 7 (2006) 2339
[5] Leach and co-workers, *Chem. Phys*. 314 (2005) 263
[6] Eden, EPSRC Career Acceleration Fellowship EP/J002577/1