

**03<sup>rd</sup> November 2011 - 10:00 a.m.**  
**DESY building 49 - seminar room (108)**

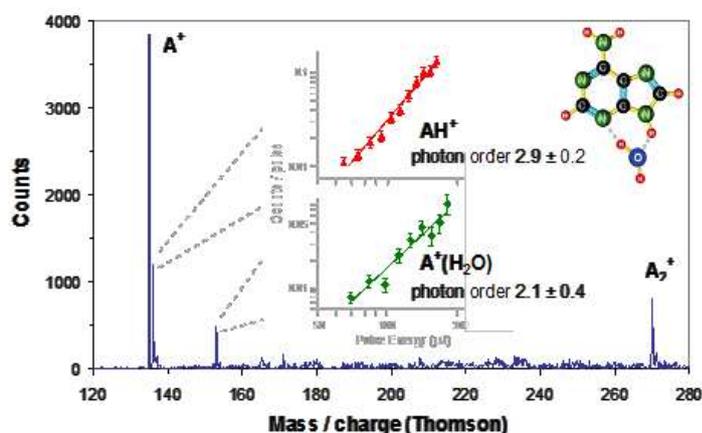
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### Contrasting UV multi-photon ionization pathways in isolated and clustered DNA bases

The photophysics of DNA and its constituents 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 photostability of DNA bases and its 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 the effects of clustering on relaxation from bright  $\pi\pi^*$  states following excitation to a high vibronic level, as well as the subsequent absorption of photons. In particular, adenine monomers and hydrated complexes have been probed by ns-timescale multi-photon ionization (MPI) time-of-flight mass spectrometry at 220-230 nm. Photon orders were determined by analyzing the production of specific ions and cluster ions as a function of laser fluence on a pulse-by-pulse basis. Isolated adenine MPI was observed with a photon order of  $3.1 \pm 0.3$  whereas two photons were energetically sufficient, indicating access to super-excited states (neutral states above the ionization threshold). The photon order for  $A^+(H_2O)$  ( $2.1 \pm 0.4$ ) was compared with  $A^+$  ( $3.2 \pm 0.5$ ) and  $AH^+$  ( $2.9 \pm 0.2$ ). We propose that these results can be understood in terms of  $A^+(H_2O)$  stemming from  $1\pi\pi^*$  excitations followed by intersystem crossing via  $1n\pi^*$  to ns-lifetime  $3\pi\pi^*$  states of  $A(H_2O)_n$  [2].  $AH^+$  production is attributed to photon absorption by  $A_m^+(H_2O)_n$  ions ( $m \geq 2$ ) produced via a excitation to  $3\pi\pi^*$  states and / or excimer states of  $\pi$ -stacked hydrated dimers [3]. Differences in fragment ion production in dry and hydrated conditions provide further evidence for distinct MPI pathways.



[1] Middleton et al., Annu. Rev. Phys. Chem. 60 (2009) 217; [2] Ullrich et al., PCCP 6 (2004) 2796; [3] Smith et al., PCCP 12 (2010) 9632; [4] Kim, J. Mol. Struct. (Theochem) 673 (2004) 121.