Identification of the Low-energy Shape Resonances of a Nucleobase in Water

Content

Low-energy electrons (<10 eV) have been shown to induce damage to DNA, where the degree of strand breakage increases at distinct electron energies.[1] Excited states of the nucleobases are believed to facilitate electron capture and subsequent breakage, but the responsible states remain to be precisely identified. Whilst many resonance state energies of isolated nucleobases have been measured,[2] these will be perturbed by the surrounding DNA environment.

We use two-dimensional photoelectron spectroscopy to probe the excited states of the uracil anion, selectively bound with a number of water molecules. Using clusters of up to 35 water molecules, detachment energies and resonance locations are extrapolated to the bulk. Both $\pi2 and \pi3$ resonances are observed to decay to the ground electronic state of the uracil anion. Upon extrapolation, the $\pi3$*resonance appears to become near-degenerate with the neutral ground state, but this is from the perspective of electron detachment from the anion. For electron attachment to the neutral, we account for the solvent reorganisation energy, which we measure to be ~1.0 eV. Therefore, the vertical electron attachment energy to the* $\pi3$ state becomes ~2 eV. The lower π2* state may accept electrons too, but of much less energy, and it becomes a bound state in the bulk solvated anion. Both resonances therefore are likely to contribute to the electron accepting abilities of uracil at energies below 2 eV in water.

[1] B. Boudaïffa, P. Cloutier, D. Hunting, M. A. Huels & L. Sanche "Resonant Formation of DNA Strand Breaks by Low-Energy (3 to 20 eV) Electrons" Science 287, 1658-1660 (2000).
[2] K. Aflatooni, G. A. Gallup & P. D. Burrow "Electron attachment energies of the DNA bases" The Journal of Physical Chemistry A 102, 6205-6207 (1998).

Primary authors: CLARKE, Connor (Durham University); VERLET, Jan (Durham University)

Presenter: CLARKE, Connor (Durham University)

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