Ion beam spectroscopy of DNA strands

L.M. Nielsen\textsuperscript{1} and S. Brøndsted Nielsen\textsuperscript{1}

\textsuperscript{1}Department of Physics and Astronomy, Aarhus University, DK-8000 Aarhus C, Denmark

\textit{E-mail: Lisbeth@phys.au.dk.}

Electronic coupling between photo-excited bases in nucleic acids is a topic of high current interest since it is of importance in photobiology for self-protection against solar UV light and for the employment of DNA strands as conductors in nanotechnology.

For single bases the photophysics is well established. After photoexcitation the internal conversion back to the electronic groundstate proceeds via conical intersections in an ultrafast process (hundreds of femtoseconds). Hereafter the excess energy is distributed to the surrounding water in picoseconds\cite{1}. This scheme protects the molecules, while in vacuum they are photodestroyed on the microsecond time scale.

For longer strands and "real" DNA the situation is more complicated and less understood. Here two stacked bases are separated by 3.4 Å, and the π-electrons are close enough in space to couple, which alters their photophysics compared to the single bases. The coupling gives rise to new quantum states as linear combinations of single-base wavefunctions; they are denoted Frenkel excitons and represent collective excitation of more bases. The spatial extent of the excitons is hotly debated. The extent is relevant for DNA photoprotection but also for the ability of DNA strands to conduct current as the strength of π-stacks and the presence of delocalized domains determine the efficiency of electron hopping over long distances.

The absorption spectra of DNA strands resemble those of single bases with no splitting of the band located at around 260 nm. Recent nontrivial calculations by Markovitsi and coworkers\cite{2} on model strands indicated that the change in absorption induced by excitation to exciton states is to the blue as upper eigenstates carry high oscillator strengths but that the shift is small. In this talk I present action spectra recorded at the electrostatic ion storage ring in Aarhus (ELISA) of short singly negatively charged strands of adenine bases, (dA)\textsubscript{2}−, (dA)\textsubscript{3}−, and (dA)\textsubscript{4}−. A comparison with the spectrum of dAMP published by Weber and coworkers\cite{3} show that the base-stacking interactions cause a small blueshift in agreement with the theoretical predictions. From the action spectra it is also established that internal conversion can compete with electron detachment when the excitation energy is above the detachment energy. Future developments will be discussed.

\textbf{References}


