

Ultrafast vibrational dynamics of hydrated DNA

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The interaction with water plays a key role for the structure and function of deoxyribonucleic acid (DNA). While the time-averaged equilibrium structure of hydrated DNA has been studied in detail by x-ray diffraction and nuclear magnetic resonance, there is very limited information on vibrational dynamics^{1,2} and the couplings governing the interaction of water molecules with base pairs and with ionic phosphate groups in the DNA backbone. In this paper, we present new insight into the interaction of DNA oligomers with their hydration shell, originating from femtosecond nonlinear infrared spectroscopy. Both pump-probe data and two-dimensional infrared spectra will be presented for a wide range of DNA hydration levels. The ultrafast dynamics and the transient spectra of NH and (PO₂)⁻ stretching vibrations of DNA and of the water OH stretching mode are determined in DNA oligomers containing 23 alternating adenine (A) – thymine (T) base pairs in Watson-Crick geometry.

Measurements with DNA-surfactant complex films allow for discerning the NH stretching bands of the A-T base pairs and the OH stretching band of water^{3,4}. The NH stretching mode of T and the symmetric NH₂ stretching mode of A, both occurring around 3200 cm⁻¹, display a pronounced coupling. At 0% relative humidity (r.h.), corresponding to N₂ ≈ 2 H₂O molecules per base pair, the OH stretching band of water at 3500 cm⁻¹ shows a negligible spectral diffusion and a constant anisotropy of 0.4, due to a direct interaction of individual H₂O molecules with the phosphate groups of the DNA backbone. At 92% r.h. (N > 20), the DNA hydration shell displays transient properties closer to bulk water^{5,6,7}.

The antisymmetric (PO₂)⁻ stretching vibration around 1250 cm⁻¹, a sensitive probe of DNA hydration, allows for mapping energy dissipation processes and changes of hydrating structures in real-time. The water shells around the phosphate groups accept excess energy from DNA on a femtosecond time scale, much faster than the picosecond energy transport within DNA. Transient heating of the water shells reduces the number of hydrogen bonds between water and DNA.

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