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Ultrafast vibrational dynamics of water and hydrated DNA

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The unique properties and the biological relevance of liquid water and aqueous environments are closely related to their structure, the extended random network of hydrogen bonds among water molecules and between functional groups of biomolecules and hydrating water. Molecular vibrations are one of the most direct local probes of molecular motions and couplings, structural fluctuations, and energy dissipation in such systems, processes that typically occur on ultrafast, i.e., femto- to picosecond time scales. Nonlinear vibrational spectroscopy in the ultrafast time domain allows for mapping vibrational dynamics in real-time and determining vibrational couplings in a quantitative way [1,2]. In this talk, new insight into structural and vibrational dynamics of neat water and the interaction of DNA with its hydration shell are presented.

Ultrafast vibrational and structural dynamics of neat H_2O

Applying two-dimensional (2D) infrared spectroscopy and two-color pump-probe methods with sub-100 fs time resolution, the intramolecular OH stretch and bend vibrations as well as intermolecular librational modes of neat water are studied. The fastest loss of structural correlations occurs on a sub-50 fs time scale related to fluctuating librational motions in the hydrogen bond network [3,4]. Resonant energy transfer between OH stretch oscillators of different molecules is characterized by time constants of the order of 100 fs. The lifetimes of the OH stretch and bend vibrations are 200 and 170 fs, respectively, with the OH stretch excitation decaying via coupling to the OH bend oscillator [5]. The OH bend vibration decays into librations with the main energy flow into the hindered rotation of the bend-excited molecule [6]. Librations display a sub-100 fs lifetime and play a key role for the dissipation of excess energy into the bulk of the liquid. Such excess energy leads to a (macroscopic) heating of the liquid with an enhanced fraction of broken hydrogen bonds. The characteristic hydrogen bond lifetime is of the order of 1 ps. The ultrafast loss of structural correlations, i.e., loss of structural memory, the femtosecond relaxation of the intramolecular modes and high-frequency librations, and the rapid spreading of excess energy make water a rather inert medium for biological processes.

Ultrafast processes in DNA-water interaction

The interaction with water plays a key role for the structure and function of deoxyribonucleic acid (DNA). So far, there is very limited insight into vibrational dynamics of hydration and the couplings governing the interactions of different parts of DNA helix structures with the surrounding water. Femtosecond nonlinear infrared spectroscopy of DNA oligomers provides new and detailed information on the coupling and relaxation of DNA vibrations and on the role of hydrated phosphate groups for energy dissipation [7,8].

Measurements with DNA-surfactant complex films at different hydration levels allow for discerning the NH stretching bands of the A-T base pairs and the OH stretching band of water. The NH stretching mode of T and the symmetric NH_2 stretching mode of A, both occuring around 3200 cm^{-1}, display a pronounced coupling resulting in a 150 fs anisotropy decay to a constant residual value. At a relative humidity (r.h.) of 0%, corresponding to N≈2 H_2O molecules per base pair, the OH stretching band at 3500 cm^{-1} shows a limited spectral diffusion and a constant anisotropy of 0.4, due to a direct interaction of the H_2O molecules with the phosphate groups of the DNA backbone. At 92% r.h. (N>20), this species is complemented by water molecules interacting weakly with DNA and showing transient properties closer to bulk water.

The antisymmetric $(PO_2)^-$ stretching vibration around 1250 cm^{-1} is a sensitive probe of DNA hydration. The water shells around the phosphates serve as a primary heat sinks accepting vibrational excess energy from DNA on a femtosecond time scale. In contrast, energy transfer within DNA occurs in the 20 ps time domain. Upon heating, the hydrogen bond pattern of a hydration shell undergoes subpicosecond rearrangements, reducing the average number of phosphate-water hydrogen bonds.

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