

Short-Range Electric Interactions of the DNA Surface with its Hydration Shell

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Electric interactions at the interface of native DNA and its aqueous environment are probed with two-dimensional infrared (2D-IR) spectroscopy of backbone vibrations. The fast fluctuations of electric forces from thermal water motions acting on these oscillators are limited in their range to the first two hydration layers.

The interfacial environment of DNA presents a complex interplay of electric forces and hydrogen bonding among water dipoles, counterions and the different charged and polar surface structures of the double helix. Utilizing the vibrational modes of the backbone structure, 2D-IR spectroscopy offers an access to the fast dynamics of thermal equilibrium fluctuations and non-equilibrium energy transfer processes at the interface [1]. This provides insight beyond the current understanding of this environment that is derived primarily from time-averaged techniques and theory [2]. Using a natural DNA sequence of up to 2000 base pairs in its native aqueous environment as a point of departure, step-wise dehydration allows for discerning the contributions and respective time scales of different interfacial species to the fluctuating electric forces that act on the backbone oscillators. We find that water in the first two hydration layers from the DNA surface generates the major part of electric forces, showing thermal fluctuations on a time scale of 300 fs, approximately an order of magnitude slower than bulk water. Contributions from outer water layers to the net forces acting on the DNA surface are screened and, thus, minor as is evident from 2D-IR spectra recorded at different hydration levels. The screening by water dipoles within a 2-3 angstrom radius from the surface is further manifested in the invariance of interfacial electric fluctuations upon switching from mono- to divalent counterions. Furthermore, the 2D-IR spectra demonstrate a quasi-static inhomogeneous broadening that reflects structural disorder of the hydrated interface and lifetimes of DNA-water hydrogen bonds beyond 10 ps. Implications of the results for describing electric interactions at hydrated charged biointerfaces will be discussed.

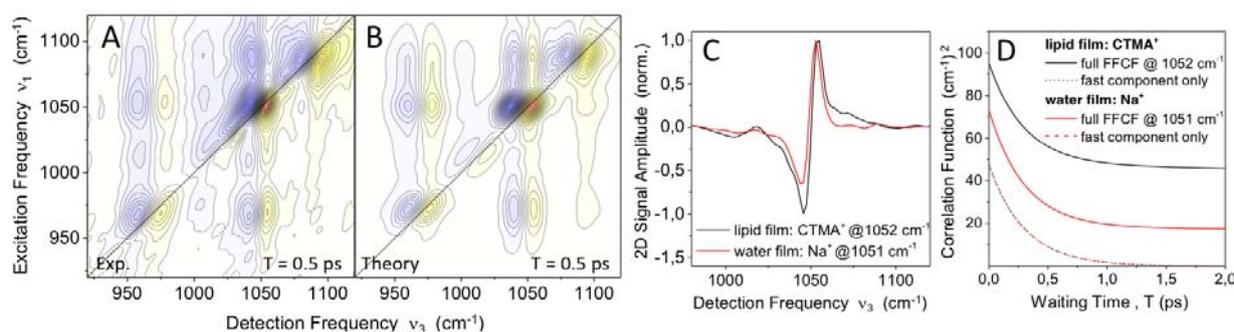


Fig.1 (A) Experimental and (B) simulated 2D spectrum of backbone modes of salmon DNA at full hydration in a water film of a 0.1 M NaCl buffer. (C) Anti-diagonal cross-sections of a phosphodiester linkage mode (L2) of the backbone from (A) and from a CTMA lipid film at partial hydration corresponding to a statistical occupation of the first two water layers. (D) Frequency fluctuation correlation function (FFCF) of the L2 mode obtained from the simulations for full and partial hydration as given in (C), showing the very similar amplitude and correlation time of fast fluctuations from the water shell for both hydration levels.

- [1] T. Siebert et al. *J. Phys. Chem. B* **119**, 9670 (2015); B. Guchhait et al. *Struct. Dynamics* **3**, 043202 (2016).
[2] J. Floisand et al. *J. Phys. Chem. Lett.* **6**, 4012 (2015). K. Andresen et al., *Phys. Rev. Lett.* **93** 248103 (2004); B. Halle et al., *Biopolymer* **48**, 210 (1998); M. Egli et al., *Biopolymers* **48**, 234 (1998).