Two-dimensional and transient absorption spectroscopies of single-stranded DNA in the deep UV

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Ultrafast electronic dynamics in DNA and its nucleobases are studied with 2D-UV photon echo and transient absorption spectroscopies, covering a spectral range of 250-300 nm. Increasing the DNA length leads to significant changes in their 2D spectra.

It is well established that in single nucleotides photoexcitation decays within a few ps or even faster, whereas in DNA it takes a much longer time (from tens to hundreds of ps) [1]. However, the underlying mechanism of such significant difference in deactivation of electronic population is not fully understood and remains debated. All experimental transient absorption (TA) DNA-studies in the lowest absorption peak (240-300 nm) reported in the literature have been conducted using narrow-band UV-sources in one- or two-color fashion [1-2]. To date, no electronic 2D spectroscopy of DNA has been reported. In this study, performed with a broadband UV-source covering a 250-300 nm UV spectral range [3], we were able to collect the 2D spectra of DNA oligomers (dA_n and dT_n) in the spectral width of ~ 6000 cm^{-1} and to resolve several peaks and cross-peaks. As an example, Fig. 1 compares the 2D spectra of single nucleobase (Ade), dimer (dA_2) and tetramer (dA_4) taken at 200 fs "waiting time" delay. A remarkable difference in the cross-peaks at the red side of spectra can be recognized immediately. Increasing the DNA length leads to decreasing the spacing between these peaks (along ω_τ) and overall blurring of the structures in the 2D spectra.

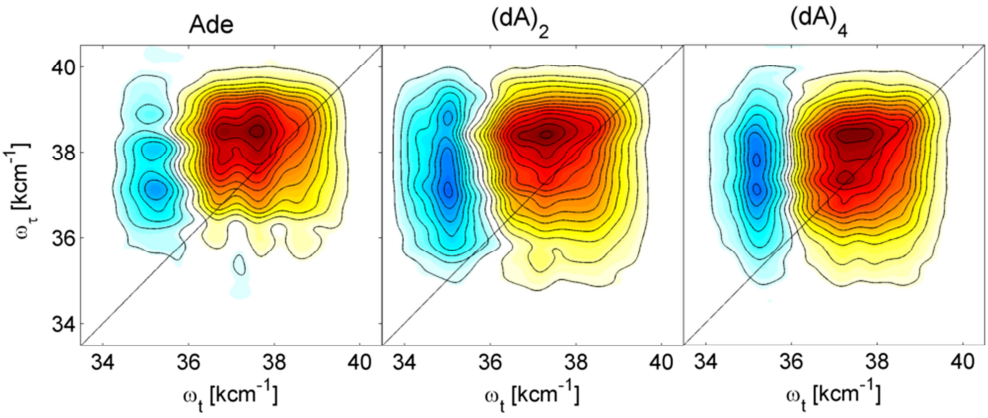

Fig. 1. Two-dimensional spectra (real part) of Ade and it oligomers dA_2 and dA_4 at waiting time T = 200 fs. Contours are drawn at 5% intervals.

However, the main feature – the presence of two lobes in the 2D spectra with the opposite signs – remains unchanged. TA studies conducted in the same spectral range show gradual increase in the lifetimes and a systematic growth of the magnitude for the longest decay component. A spectroscopic model, capable for the explanation of these observations, is proposed.

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[2] C. Su, C.T. Middleton, B. Kohler, J. Phys. Chem. B **116**, 10266 (2012).
[3] V. I. Prokhorenko, A. Picchiotti, S. Maneshi, and R. J. D. Miller, Springer Proc. Phys. **162**, 432 (2015).