

IR multi-photon dissociation spectroscopy of multiply charged oligonucleotide anions

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We report the first infrared spectra of unsolvated multiply-charged anions in the gas-phase - taken on single-stranded homo-oligonucleotides. These multiply-charged oligonucleotide anions are prepared using electrospray, mass-selected in a electrodynamic (Paul) trap and probed via FEL-IR-MPD. Fragmentation upon IR excitation is governed in all the three systems investigated – $[\text{dA}_5\text{-4H}]^{4-}$, $[\text{dT}_5\text{-4H}]^{4-}$ and $[\text{dT}_7\text{-6H}]^{6-}$ – by loss of a corresponding base anion (i.e. A^- or T^- , A= adenine, T= thymine) irrespective of wavelength.

The spectral features observed experimentally are compared with high-level DFT computations for model oligonucleotides multianions (of typically smaller size). They clearly allow to assign bands to vibrational modes of the backbone structure (sugar and phosphate groups) in the spectral region 700-1400 cm^{-1} and to IR bands that can be assigned to vibrational modes which are specific for the particular base. We propose a scheme that may allow to use this mode-selective fragmentation propensity to induce specific cleavage of hetero-oligonucleotide strands. [1]

[1] manuscript in preparation