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Comparing the electronic relaxation of pyrimidine bases and nucleosides in aqueous solution STEPHEN BRADFORTH, ASKAT JAILAUBEKOV, University of Southern California, DELMAR LARSEN, University of California, Davis, CHRISTI CHESTER, University of Southern California —
The ultrafast deactivation of DNA bases excited in the ultraviolet is known to occur by rapid nuclear motion through conical intersections between different electronic potential energy surfaces. How the intersections between these surfaces and the dynamics over these surfaces are modified by surrounding the base with water is a significant open question in DNA photophysics. Using a broadband transient absorption apparatus with 30 fs time resolution, we observe dispersed spectra from 300 – 700 nm revealing excited-state dynamics originating for U and T both as nucleobases and nucleosides. New sub-100fs dynamics is observed, including stimulated emission. The deactivation pathways and spectral signatures of the various intermediates are compared to data from gas-phase time-resolved photoelectron spectroscopy and non-adiabatic quantum-classical simulations.

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