

超高速分光による核酸塩基の光化学素過程の解明

Elucidation of photochemical dynamics of nucleobases by ultrafast spectroscopy

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Nucleobases serve as the fundamental building blocks of life, and their photophysics and photochemistry have attracted sustained scientific interest. Despite extensive investigation, the excited-state dynamics of nucleobases remained incompletely understood. In particular, previous experimental studies employing extreme ultraviolet time-resolved photoelectron spectroscopy (EUV-TRPES) and ultraviolet transient absorption spectroscopy (UV-TAS) had reported conflicting interpretations of the relaxation pathways and lifetimes of key intermediates. To resolve these discrepancies, the objective of this project was to structurally assign the electronic states and transient intermediates involved in the photochemical dynamics of nucleobases using ultrafast time-resolved pump-probe spectroscopy, combining ultraviolet (UV) pump and infrared (IR) probe pulses. In the first phase of the project, ground-state IR spectra of nucleobases were predicted using a range of quantum chemical methods implemented in Gaussian 16. The goal was to identify the computational approach that most accurately reproduces experimentally measured Fourier transform IR (FTIR) spectra of nucleobases in solution. Various exchange-correlation functionals were evaluated, including the hybrid B3LYP and the double-hybrid B2PLYP, along with multiple basis sets. To improve agreement with experiment, solvent effects were incorporated via the Polarizable

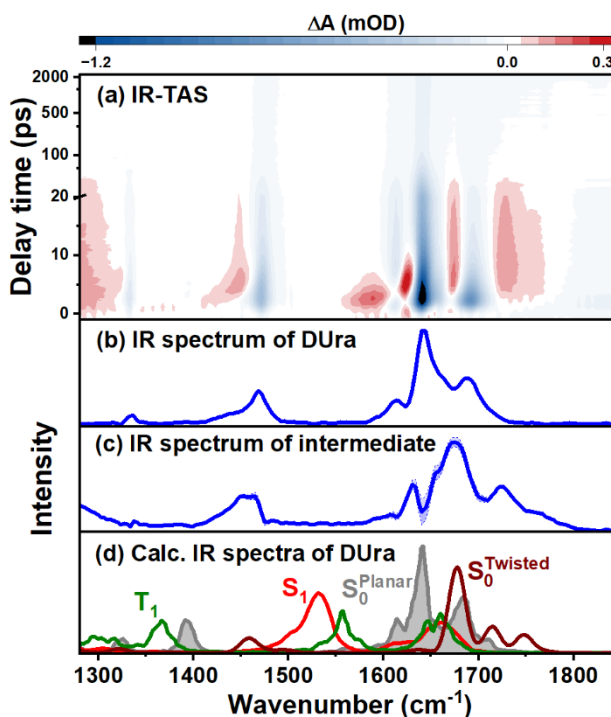


Figure 1. (a) IR-TAS, (b) steady-state IR, (c) IR of the intermediate, and (d) calculated IR spectra of the excited states and intermediate for aqueous uracil in D₂O.