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 garnered significant scientific interest. Despite numerous studies, the excited-state dynamics of nucleobases remain incompletely understood. For instance, prior experimental investigations employing extreme ultraviolet time-resolved photoelectron spectroscopy (EUV-TRPES) and UV transient absorption spectroscopy (UV-TAS) have yielded conflicting results. To address this discrepancy, the objective of this project is to structurally assign the electronic states and intermediates involved in the photochemical dynamics of nucleobases through ultrafast time-resolved pump-probe spectroscopy, utilizing ultraviolet (UV) pump and infrared (IR) probe pulses.

The first phase of the project focused on predicting the ground-state IR spectra of nucleobases using a variety of quantum chemical methods using Gaussian 16 software, aiming to identify the approach that best matches the Fourier transform IR spectra of nucleobases in solution. In this process, different functionals were explored, including the hybrid B3LYP and the double-hybrid B2PLYP, as well as various basis sets. To enhance the accuracy of the theoretical predictions, the Polarizable Continuum Model (PCM) and anharmonic corrections were incorporated, ensuring that the simulations closely align with experimental conditions.

Having identified the most suitable computational method, the current focus of the project is on predicting the IR spectra of the excited states and potential intermediates that are generated following the decay of the initially excited $\pi\pi^*$ state in different nucleobases. The next phase of the research will involve extracting the experimental IR absorption spectra of all transient species generated during the relaxation of photoexcited nucleobases, utilizing advanced ultrafast spectroscopic techniques. These experimental data will then be used to validate and refine the theoretical predictions, facilitating the structural assignment of the observed species and advancing the understanding of the photochemical processes in nucleobases.