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溶液中の核酸塩基の IR スペクトルの理解 Assignment of IR spectra of nucleobases in solution

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The photostability of DNA and RNA is due to their ultrafast relaxation from the photoexcited ¹ $\pi \pi^*$ state to the ground electronic state. However, previous time-resolved IR spectroscopy experiments on uracil in aqueous solution suggested the existence of an intermediate state with a high quantum yield and over 10 ps lifetime. In the literature a debate ensued about whether this unknown "X" state is an electronically excited state, which would be incompatible with the photostability of uracil. Combining time-resolved ultraviolet, infrared and photoelectron spectroscopy with quantum chemical calculations, the elusive "X" state could be assigned to a metastable ground state intermediate with a twisted C=C bond (see Fig. 1 below), which had been proposed recently by Park et al. [J. Phys. Chem. Lett. (2022) 13, 7072]. Since the assignment hinges on the observed blue-shift of the carbonyl stretches, we calculated the IR spectra of possible candidates (electronically excited planar uracil, photohydrates of uracil and the twisted intermediate) using different levels of theory (harmonic and anharmonic DFT frequencies with Gaussian 16, harmonic CASPT2 frequencies with BAGEL, anharmonic IR spectra of uracil in aqueous solution with QM/MM using TeraChem and AMBER). Only the twisted intermediate had an IR spectrum compatible with the experimental observations. The conical intersection (CI) leading from the $1\pi\pi^*$ state to the metastable intermediate was optimized with CASSCF using TeraChem and the barrier to planarity was determined using the nudged elastic band algorithm. The location of the CI is favourable for funneling part of the photoexcited wavepacket to the twisted intermediate and the barrier of 5-10 kcal mol⁻¹ is sufficiently high to explain the lifetime of the "X" state.



1: Schematic diagram of S1/S0 (ethylenic) conical intersection of Ura, molecular structure of 5,6-DHU is also shown.

Publications:

Y. Obara, S. Ghosh, A. Humeniuk, Sh. Kamibashira, Sh. Adachi, and T. Suzuki, *"Formation of Ground-State Intermediate during Electronic Relaxation of Pyrimidine Nucleobases"*, 2024, submitted to JACS.