

Investigating the photo-relaxation mechanism of 6-azauracil through *ab initio* molecular dynamics simulations

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The excited state dynamics of 6-azauracil (6-AU) were investigated through *ab initio* molecular dynamics simulations.¹ These simulations incorporated nonadiabatic transitions between electronic states using the Zhu–Nakamura trajectory surface hopping method. Previous research has demonstrated that 6-AU differs from its parent molecule uracil in that, following internal conversion from the singlet excited state S_2 to S_1 , relaxation occurs through intersystem crossing to the triplet state T_1 .^{2,3} In a subsequent study employing femtosecond transient absorption spectroscopy, three decay time constants were observed for 6-AU in an acetonitrile solution: $\tau_1 < 0.3$ ps, $\tau_2 = 5.2 \pm 0.1$ ps, and $\tau_3 > 1000$ ps.⁴ This study aims to elucidate the mechanism by which 6-AU decays from S_2 to S_1 via internal conversion, the initial step in its relaxation cascade.

Among the 494 successful trajectories, 451 underwent relaxation from S_2 to S_1 within 500 fs, resulting in the S_2 lifetime of 201 fs for the isolated 6-AU molecule. Further investigation into the physical and structural properties of 6-AU revealed that molecular ring puckering facilitated the internal conversion from S_2 to S_1 by destabilizing the ground state.

¹ Iwasa, N.; Nanbu, S.: Investigating the photo-relaxation mechanism of 6-azauracil through *ab initio* nonadiabatic molecular dynamics simulations;

² Kobayashi, T.; Harada, Y.; Suzuki, T.; Ichimura, T. Excited state characteristics of 6-azauracil in acetonitrile: Drastically different relaxation mechanism from uracil. *J. Phys. Chem. A* **2008**, *112* (51), 13308-13315.

³ Etinski, M.; Marian, C. M. Overruling the energy gap law: Fast triplet formation in 6-azauracil. *Phys. Chem. Chem. Phys.* **2020**, *12* (48), 15565-15671.

⁴ Hua, X.; Hua, L.; Liu, X. Ultrafast excited-state dynamics of 6-azauracil studied by femtosecond transient absorption spectroscopy. *J. Phys. Chem. A* **2015**, *119* (52), 12985-12989.

