Insights into S_2 population trapping of uracil using trajectory surface hopping dynamics

Pratip Chakraborty[a] and Spiridoula Matsika[a]

[a] *Temple University*
pratip.chakraborty@temple.edu

The photophysics and photochemistry of DNA/RNA nucleobases have been extensively investigated during the past two decades, both experimentally and theoretically. The ultrafast relaxation of the canonical nucleobases following photoexcitation is of significant interest when it comes to understanding how nature has ensured their photostability. Here we study the excited state dynamics of uracil which is a nucleobase found in RNA. Although theory and experiment have shed a significant light in understanding the photoexcited dynamics of uracil, there are still disagreements in the literature about specific details. The population trapping in the S_1 minimum is universally accepted. However, the trapping in S_2 has been a contentious topic because the height of the barrier on the S_2 state calculated using different electronic structure methods varies widely depending on the method. In order to examine how the dynamics is influenced by the underlying electronic structure theory, we have performed the excited state dynamics of uracil using on-the-fly trajectory surface hopping method on potential energy surfaces calculated at different electronic structure theory levels to investigate the effect of the barrier on the decay dynamics.