EXCITED STATE DYNAMICS IN 2-AMINOPURINE RIBONUCLEOSIDE: FROM FEMTOSECOND TO MICROSECOND TIME SCALE

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2-aminopurine is a structural isomer of adenine that is widely used as fluorescence probe in DNA because its fluorescence lifetime and quantum yield respond sensitively to local DNA duplex conformation and neighboring microenvironment. Despite its broad utilization in biochemical and biophysical studies, there is ongoing debate about the mechanism by which fluorescence is quenched in 2-aminopurine in different solvents. Establishing the excited-state relaxation pathways that lead to fluorescence quenching is essential for a meaningful interpretation of the experimental data in terms of local structure and dynamics. In this contribution, the excited state dynamics in 2-aminopurine ribonucleoside is investigated by using broad-band transient absorption spectroscopy in different solvents. Excitation is performed at 320 nm and the spectral evolution is monitored in the spectral region from 330 nm to 700 nm. Three exponential functions are required to fit globally the transient absorption signals from femtosecond to microsecond time scale. The first lifetime is assigned to solvent relaxation dynamics in the excited singlet state. The singlet state population then bifurcates to two different decay channels. The first channel is the well-documented fluorescence emission while the second channel is assigned to intersystem crossing to the triplet manifold. The extent of participation of this nonradiative decay channel depends sensitively on the polarity and hydrogen bonding ability of the solvent. The triplet state population decays back to the ground state in hundreds of nanoseconds and is quenched by molecular oxygen. Our results unequivocally show that the excited-state dynamics in 2-aminopurine is more complex than previously thought.