

Theoretical studies of photophysical events in π -stacked dimers of nucleobases

Spiridoula Matsika,

Department of Chemistry, Temple University, Philadelphia, USA

The excited states of DNA and their fate after UV absorption are of extreme importance because of their biological relevance. Quantum chemistry can help address these problems but one has to limit the size of the system. Dimers of nucleobases are the smallest models one can use to look into the effect of π -stacking and hydrogen bonding on the excited states. We have studied the effect of π -stacking on the photophysical properties of π -stacked dimers of natural nucleobases or their fluorescent analogues. Fluorescent analogues of nucleobases are very useful as probes to study DNA dynamics, since natural DNA does not fluoresce significantly. In many of these analogues, such as 2-aminopurine (2AP), the fluorescence is quenched when incorporated into DNA through processes that are not well understood. So 2AP presents a case where π -stacking changes significantly the photophysical behavior of a base, making it an interesting system to focus on. We will present theoretical studies of the excited states of π -stacked dimers and focus on features of the potential energy surfaces that can describe the fate of the excited state populations. Computed relaxation pathways along the excited state surfaces reveal novel mechanisms that can lead to fluorescence quenching and radiationless decay in the π -stacked dimers [1]. The importance of charge transfer and exciton states will also be discussed.

[1] JX Liang and S. Matsika, *J. Am. Chem. Soc.*, **133**, 6799 - 6808, (2011)