Editorial

Dynamics in Photoexcited DNA Bases and Related Molecules

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Deoxyribonucleic acid (DNA), the hereditary basis of life's genetic identity, has been of enormous interest for more than a century and particularly since its structure was determined in 1953. Nucleobases are primary building blocks and UV chromophores in DNA. Exposing DNA to radiation in the 200–300 nm range results in strong UV absorption by these bases, which could lead to photochemical reactions causing DNA damage. Fortunately, highly efficient nonradiative decay pathways exist in DNA bases, assuring that most excited molecules quickly relax to the electronic ground state without leading to harmful reactions. The electron dynamics following photoexcitation plays an important role in this deactivation, which is clearly essential for life. Since the development of ultrafast laser pulses and high performance computers, there has been tremendous progress in understanding the electron dynamics of DNA bases, but it is far from complete.

In this special issue, we selected six peer-reviewed research articles which present recent progress in understanding the electronic response of DNA bases excited by laser pulses, mostly through semiclassical dynamical simulations. There is also a brief review of deactivation processes in DNA bases studied with this approach. In the paragraphs below, we provide a brief overview of the key results in each paper.

In “Detailed Photoisomerization Dynamics of a Green Fluorescent Protein Chromophore Based Molecular Switch,” quantum yields were found to be 32% for the *trans*-to-*cis* photoisomerization of BMH and 33% for *cis*-to-*trans*. These simulations indicate that the average excited state lifetime of

trans-BMH is about 1460 fs, which is shorter than that found for *cis*-BMH (3100 fs). For both the *trans*-to-*cis* and *cis*-to-*trans* reactions, rotation around the central C2=C3 bond is the dominant reaction mechanism. Deexcitation occurs at an avoided crossing near a conical intersection which is close to the midpoint of the rotation.

The paper “Competing Deactivation Channels for Excited π -Stacked Cytosines” suggests that the deactivation channel leading to the electronic ground state of stacked bases competes with the path that leads to dimerization. For both pathways, the initial excited state was found to lead to a charge-separated neutral excimer state by charge transfer. Vibrational energy distribution determines the fate of the excimer at the avoided crossing.

The paper “Electron Correlation Effects on the Longitudinal Polarizabilities and Second Hyperpolarizabilities of Polyenes: A Finite Field Study” reports finite-field-based *ab initio* calculations of the longitudinal polarizabilities (α_L) and second hyperpolarizabilities (γ_L) of conjugated polyenes and proposes that electron correlation reduces linear longitudinal polarizability and enhances longitudinal second hyperpolarizability for short polyenes, with the effects decreasing as the chain length increases.

The paper “Constraint Trajectory Surface-Hopping Molecular Dynamics Simulation of the Photoisomerization of Stilbene” extends the trajectory surface hopping (TSH) method from full to flexible dimensional potential energy surfaces by combining the TSH method with constrained molecular dynamics. In this approach, classical trajectories are followed in Cartesian coordinates with constraints in

internal coordinates, while nonadiabatic switching probabilities are calculated separately in free internal coordinates by Landau-Zener and Zhu-Nakamura formulas along the seam.

The paper “Detailed Molecular Dynamics of the Photochromic Reaction of Spiropyran: A Semiclassical Dynamics Study” reports a realistic simulation study for the photoinduced ring-opening reaction of spiropyran. The main results show two different pathways: one involves hydrogen out-of-plane (HOOP) torsion of the phenyl ring nearby the N atom, and the other dominant pathway corresponds to the ring-opening reaction of *trans*-SP to form the most stable merocyanine (MC) product.

In the paper “Bonded Excimer in Stacked Cytosines: A Semiclassical Simulation Study,” the formation of a covalent bond between two stacked cytosines is found to facilitate the deactivation of the electronically excited DNA bases by lowering the energy gap between the LUMO and HOMO.

We believe that the papers published in this special issue represent a significant positive contribution to this general field.

Acknowledgments

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