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Editorial

Theoretical aspects of photoinduced processes in complex systems

This special issue of the *Journal of Photochemistry and Photobiology A: Chemistry* addresses the theoretical interpretation, electronic structure characterization and dynamical simulation of photoinduced processes in complex molecular systems. Here, "complex" denotes a wide range of systems, comprising small molecules with complex electronic structure, solute–solvent systems, biological chromophores embedded in a protein environment, extended molecular aggregates with excitonic character and nanostructured aggregates like quantum dot–fluorophore assemblies. Quantum-mechanical effects are ubiquitous in the photochemistry of these systems, and involve both electronic structure and dynamical aspects; this makes the theoretical study a considerable challenge. A paradigm example is ultrafast excited-state processes at conical intersections, which is one of the recurrent themes of this issue.

While many theoretical concepts – e.g., relating to nonadiabatic phenomena and conical intersections, vibrational energy transfer and electronic excitation energy transfer – have existed for quite some time, the development of computational tools allowing for applications to large molecular systems has made enormous strides over the past 10 years. Complementary to the high-level electronic structure calculations and quantum-dynamical simulations that are available for small molecular species, new approximate methods and hybrid strategies make it possible today to address truly "large" systems. These methods include density functional theory (DFT) methods, mixed quantum mechanics–molecular mechanics (QM/MM) methods, "on-the-fly" schemes and efficient approximate quantum dynamics methods that are based upon the propagation of trajectories or Gaussian wavepackets. These developments also pave the way for a detailed understanding of system–environment interactions in photobiological systems, and for the design of coherent control scenarios in high-dimensional situations. The present issue provides a snapshot of the many current developments in this area.

This issue comprises 22 contributions, most of which address both electronic structure and dynamics aspects. The majority of papers focus on applications, even though several contributions put a main emphasis on new methodological developments. The issue starts out with small molecular systems and moves to system–environment interactions, photobiological systems and to extended molecular aggregates and nanostructured assemblies. The series of papers concludes with several contributions on coherent control aspects.

The first three contributions illustrate the complexity of small systems. Gómez-Carrasco et al. present an extensive *ab initio* analysis of OHF in view of interpreting angle-resolved photodetachment spectra, and Ghosal et al. investigate the nonadiabatic dissociation dynamics of the van der Waals complex Cl···HD subsequent to photodetachment of the anionic species. In their study of Br_2 in solid argon, Borowski and Kühn argue that the diatomic's excited-state dynamics in the seemingly inert rare gas environment must be represented in terms of a multidimensional problem involving environmental modes.

The next couple of contributions focus on the role of conical intersections in the nonadiabatic dynamics of polyatomic molecules. Lan et al. investigate the multi-mode nuclear dynamics at two conical intersections of pyrrole, and Worth proposes a model for the complex photochemistry of benzene. Cogan et al. address the role of intersystem crossing at singlet conical intersections. The papers by Bearpark et al. and Barbatti et al. are strongly methodologically oriented and focus on hybrid electronic structure methods and novel on-the-fly dynamics strategies, respectively.

Conical intersections remain a recurrent theme in the following papers, which concern the photochemistry of biological chromophores. Gromov et al. address the electronic structure characterization of the photoactive yellow protein (PYP) chromophore. The following two contributions focus on the ultrafast isomerisation of the retinal chromophore: Conti and Garavelli investigate the role of substituent effects on the excited-state reaction path and S_1–S_0 conical intersection, and Chen and Batista carry out approximate quantum dynamical simulations of the multidimensional nonadiabatic process. The paper by Blancafort and Migani addresses the excited-state decay in cytosine, with a focus on explicit and implicit water solvation effects. Finally, the contribution by Zenichowski et al. studies the excited-state electronic structure of flavins embedded in light-oxygen-voltage domains.

Two contributions specifically address the electronic structure of biological organo-metallic systems, i.e., the study by Schreiber and González on the role of Ag ions in adenine–cytosine mispairs, and the paper by Daniel et al. on the spectroscopy of Ru complexes used as intercalators in DNA.

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The focus of the issue then shifts to the topic of electronic excitation energy transfer, which is a key theme in the study of extended molecular systems and aggregates. Dolghih et al. address fluorescence resonance energy transfer (FRET) in dye-labeled DNA, and Bittner proposes a Frenkel exciton model of ultrafast excited-state dynamics in AT DNA double helices. Saini et al. again address the FRET effect, with a focus on non-Förster behavior. Finally, Kilin et al. provide a comprehensive *ab initio* electronic structure and dynamical study of the exciton transfer dynamics in a quantum dot–dye aggregate.

The issue concludes with a perspective on coherent control scenarios in complex systems. Voll et al. address the laser-induced ring opening in fulgides, as an example of both external and internal control factors at conical intersections. Sugny et al. focus on laser control in the presence of an environment, and the last contribution, by Brüggemann et al., addresses femtosecond laser control of exciton dynamics in photosynthetic antenna systems. (Some of the aspects discussed here connect to another recent special issue, see *J. Photochem. Photobiol. A: Chemistry* 180 (2006), "*Coherent control of photochemical and photobiological processes*".)

Even though this issue can only cover certain aspects of a highly active field, we believe that it illustrates the great variety of systems that can be successfully addressed by today's theoretical approaches. By a combination of theoretical modeling, electronic structure calculations and dynamical simulations, remarkable insight can be gained into the photochemical processes characterizing even complicated biological systems. While the interface between theoretical chemistry and biochemistry and biophysics is certainly one of today's most exciting areas, this special issue also illustrates that many "small" molecular systems continue to pose considerable challenges—and often remain the key to understanding highly complex systems.

My first and foremost thanks go to all contributors, for the excellent and original papers that constitute this issue, and to the referees who provided valuable criticism and advice. I further thank Monique Martin for her assistance in many respects, and Fiona Healy for her reliable help on various technical issues. I hope that many readers will enjoy this collection of papers.

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