Introduction: Theoretical Modeling of Excited State Processes

What do plasma, solar panels, and fireflies have in common? The fundamental physics of these phenomena is governed by excited state processes initiated by light. When a photon is absorbed by a molecule, it promotes an electron to a higher energy level leading to a new electron distribution, which often features an open-shell pattern. This event initiates a variety of processes: radiative and radiationless relaxation, photochemical transformations, electron ejection, or attachment. The competition between these processes determines the fate of an electronically excited system—some emit light back, some effectively convert excess electronic energy into heat, some produce charge carriers, and some change their chemical identity. From the quantum-mechanical point of view, these processes entail coupled electronic and nuclear dynamics. Understanding how these quantum processes unfold in systems with many degrees of freedom, usually coupled to the environment, is of great fundamental importance. Ultimately, we want to know how the chemical structure of the molecule and the environment affect branching ratios and time scales of various excited state processes as shown in Fig 1. From a practical point of view, the ability to control these processes is the key to the successful design of new photovoltaic materials, bioimaging probes, photodynamic therapies, and materials for high-energy applications (e.g., fusion reactors). Moreover, precise understanding of light-matter interactions and the ability to describe them quantitatively allows us to utilize radiation as a tool for interrogating properties of molecules and materials. Spectroscopy is indeed the most common and the most powerful tool for deciphering molecular structure. The techniques vary from classic UV−vis and photoelectron spectroscopies to novel nonlinear approaches and high-energy X-ray attosecond pulses. All these phenomena are governed by the same law: the Schrödinger equation: tantalizingly simple, yet notoriously difficult to solve. Although theory has been very successful in developing practical approaches for electronic structure and coupled nuclear-electron dynamics, challenges still abound. This topical issue of Chemical Reviews highlights recent progress as well as outstanding challenges. The review articles written by a worldwide group of experts span the following subjects:

- Chemi- and bioluminescence (Vacher et al.);
- Nonadiabatic and spin-forbidden processes (Penfold et al., Crespo-Otero and Barbatti);
- Photovoltaics and solar energy utilization (Hestand and Spano, Casanova);
- Novel spectroscopies and high-energy radiation (Norman and Dreuw);
- Quantum chemistry methods for excited states:
  - Challenges and solutions (Ghosh et al., Lischka et al.)

We thank all the authors who submitted contributions to this issue. We envision that these comprehensive, deep, and insightful reviews will illustrate the impact of theoretical modeling on the research of light-matter interactions and provide an inspiration for future work.

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Notes

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Figure 1. Excited-state processes. The two main relaxation channels of an electronically excited molecule are fluorescence and radiationless relaxation, a process in which the system relaxes to the ground state by dissipating electronic energy into heat. Other competing processes, such as transition to a triplet state via inter-system crossing (not shown), excited-state chemistry and electron transfer, alter the chemical identity of the molecule. Adapted from: Chem. Rev. 2017, 117, 758–795, DOI: 10.1021/acs.chemrev.6b00238.
Spiridoula Matsika received a B.Sc. in Chemistry from the National and Kapodistrian University of Athens, Greece in 1994 and a Ph.D. in Chemical Physics from the Ohio State University in 2000. After completing her Ph.D. she spent three years as a postdoctoral fellow at Johns Hopkins University working with Prof. David Yarkony. In 2003 she started her independent career in theoretical chemistry at Temple University in Philadelphia, where she is currently a Professor of Chemistry. Spiridoula Matsika’s research focuses on the theoretical quantum mechanical study of excited states, nonadiabatic processes and conical intersections in molecular systems. Her contributions to the theoretical description of photophysics and photochemistry have been recognized by several awards, including the National Science Foundation CAREER award and an Alexander von Humboldt Fellowship. She was the Löwdin Lecturer in 2012 and she is a Fellow of the American Physical Society.

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