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Introduction: Femtochemistry

Only a few years after femtochemistry was first established as a field of research did we witness an explosion of research in all phases of matter and in biological systems. The reason behind this explosion is fundamental—chemical bonds form and break on the femtosecond time scale, and on this scale of time we can freeze the transition states at configurations never seen before. Even if there is no reactants-to-products transformation—physical change—one is observing the most elementary of all molecular processes. On a time scale shorter than the vibrational and rotational periods, the ensemble behaves coherently as a single-molecule trajectory.

Theory has enjoyed a similar explosion in related areas dealing with ab initio electronic structures and molecular dynamics. Progress has been made for calculations of potential energy surfaces (PES), especially for the ground state of reactions. On excited-state surfaces, it has become feasible to map out regions of PES where transition states and conical intersections are important for the outcome of reactions. For dynamics, new methods have been devised for direct viewing of the motion by formulating the time-dependent picture, rather than solving the time-independent Schrödinger equation and then constructing a temporal picture. The coupling between theory and experiment has reached a profound state, and elsewhere Jörn Manz has given an overview describing evolutions and revolutions in the field, from genesis, the early days of quantum theory by Schrödinger, to the emergence of quantum control.

But these developments in femtochemistry did not reach this level without the crystallization of some new concepts that were, in the beginning, shrouded in fog. First was the issue of the "uncertainty principle", which had to be decisively clarified. Second was the question of whether one could sustain a wave packet motion throughout the reaction. In other words, could the de Broglie wavelength of the atom define a "classical motion" without quantum spreading? This too had to be clearly demonstrated and followed from reactants to products, not only in elementary chemical reactions but also during biological changes. And finally, there were some questions about the uniqueness and generality of the approach. For example, why not deduce the information from high-resolution frequency-domain methods and then Fourier transform to obtain the dynamics? It was clear then and certainly now that transient species cannot be isolated this way, and there is no substitute for direct "real-time" observations that fully exploit the intrinsic coherence of molecular motions.

In this thematic issue on Femtochemistry, the comprehensive contributions are diverse and wide-ranging, elucidating the scope of applications and the disparate areas of research, maturing and emerging. Of particular significance is the outreach to the world of complexity highlighted by studies of the liquid state, biological systems, and nanostructures. Equally important is the continued development of new techniques for the gas and condensed phases, and methods exploiting nonlinear spectroscopy, reaching beyond the conventional linear analogue. Elementary processes can now be directly probed in mesoscopic systems (clusters) with the goal of understanding the transition from the gas to the liquid phase. And, new direct structural methods are emerging with success. Most invitees accepted the request to contribute to this special issue of *Chemical Reviews*. Some could not make it, but we hope their work on 2D spectroscopy, photosynthesis, and other topics is in part covered by the articles published here. Some of these articles may appear in future regular issues of *Chemical Reviews*, and if so, they will be linked to the thematic issue in the Web edition.

The multifaceted nature of femtochemistry touches a number of scientific disciplines from physics to chemistry to biochemistry. This issue includes reviews that describe state-of-the-art methods for probing chemical reaction dynamics with femtosecond time resolution. Bragg, Stolow, and Neumark review time-resolved photoelectron spectroscopy, a method that allows one to follow changes in electronic structure in processes such as intersystem crossing. Schmuttenmaer has reviewed the use of ultrashort pulses in the far-infrared end of the spectrum, while Bressler and Chergui have reviewed the use of ultrashort X-ray pulses, at the other end of the electromagnetic spectrum. Dantus and Lozovoy have reviewed a number of laser-based methods for controlling laser—matter interactions, thus affecting the dynamics and outcomes of physicochemical processes.

Early studies in femtochemistry were concerned with the dynamics of small isolated molecules. At

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present, studies focus on the more complex systems, and this has led to new directions of research for clusters and in the condensed phase. Dermota, Zhong, and Castleman review the ultrafast dynamics of clusters elucidating the power of studying mesoscopic systems. The condensed phase adds additional complexity, providing a sink for energy relaxation, in addition to dynamic intramolecular forces. Nibbering and Elsaesser review the ultrafast vibrational dynamics of hydrogen bonds in the condensed phase. Rey, Møller, and Hynes give us a theoretical perspective on the ultrafast vibrational population dynamics of water and related systems. Glasbeek and Zhang review femtosecond studies of solvation and intramolecular configurational dynamics of fluorophores in liquid solution. Douhal reviews the ultrafast guest dynamics in the confined environment provided by cyclodextrin nanocavities.

Biological systems, although inherently more complex, provide an exciting direction for ultrafast studies. Crespo-Hernández, Cohen, Hare, and Kohler have reviewed studies on the excited-state dynamics of nucleic acids. Polívka and Sundström have given a comprehensive review of the ultrafast dynamics of carotenoid excited states, from solution to natural and artificial systems. Mukamel and Abramavicius have reviewed many-body approaches for simulating coherent nonlinear spectroscopies of electronic and vibrational excitons. Kumar Pal and Zewail have reviewed the dynamics of water in biological recognition.

We take this opportunity to thank the Editor-in-Chief, Professor Josef Michl, for his timely decision on this thematic issue for the broader community of all chemists, for his thorough editing, and for all the care taken by him and his staff to make it possible to produce such a high-level contribution. We hope it will be of value not only to researchers in femtochemistry but also to those working in the adjacent sciences of femtobiology and femtophysics.

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