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Ten Years of Femtochemistry: A Historical Perspective

In 1987 the field of femtochemistry had its beginning with the publication of a series of pioneering pump−probe studies of chemical reactions on the femtosecond time scale by Ahmed Zewail and co-workers. The field struck at the very heart of chemistry. From the days of Svante Arrhenius (late 19th century) to the eras of Henry Eyring and Michael Polanyi (1930s), and that of molecular beam collision experiments (1960s), all methods of studying the fundamentals of reaction dynamics were, in a sense, indirect. Indeed, the evolving dynamical phenomena could not be seen in action and instead had to be inferred from the observation of ensuing events. The advent of femtochemistry changed all of this, enabling a direct observation of the elementary processes of bond breaking and bond making and the study of the cornerstone of reactivity, the fleeting transition states. This was the important breakthrough of 1987 which opened a new door to investigating the reaction dynamics of chemical events with atomic-scale resolution.

Prior to this, the last important step reached in time resolution was in the 1940s and early 1950s when R. G. W. Norrish, George Porter, and Manfred Eigen introduced the millisecond-to-microsecond time scale. The 10 orders of magnitude improvement in time resolution enabled by the femtosecond methodology (spectroscopy, mass spectrometry, and other probes) has brought chemistry and biochemistry to a new level of understanding. The impact of femtochemistry has been evident in many ways in all phases and in molecular systems of varying complexity from the two-atom system to clusters and the condensed phase. Rich and important applications followed through the study of numerous complex systems in gases, liquids, fluids, and clusters. The work has had broad implications, opening up, for example, the organic world to femtochemistry, reviving the field of physical-organic chemistry by addressing questions that could only be asked 50 years ago, but which no one dreamed of conceiving an appropriate approach to obtaining the answers. Indeed, the field has added the dimension of time to structure, enabling a true view of the dynamics of the chemical bond to be attained. The experimental foundations of Zewail and co-workers, first introduced with simple systems, established the methods to bring to fruition predictions and concepts for the entire field, which before that time could only be envisioned theoretically.

The enormous growth of the field since 1987 is evident from the broad range of papers and the numerous contributing groups that are attested to by the selection of some papers presented at the 1997 conference in Lund, and collected herein, in this special issue of the *The Journal of Physical Chemistry A* devoted to this increasingly active field of chemical research which encompasses virtually every topic that lies at the forefront of modern chemistry.

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