Femtosecond broadband spectroscopy: From ultrafast photophysics, via femtochemistry to bimolecular reactions in a single picosecond

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The celebrated experiments of A. H. Zewail and coworkers have paved the way to the exciting new field of ultrafast spectroscopy of molecules and molecular reactions. A major part of the investigations has, however, relied on the accidental coincidence of given laser lines with molecular absorptions, both in the spectrum of the educt and the transient spectrum of the intermediates or products. A fair amount of "chemical intuition" was then added to resolve any ambiguities.

The last years have now witnessed the upgrowth of low noise and sufficient intensity excitation sources freely tunable from the deep UV into the MIR with pulse durations in the 10 fs regime. These allow the selected molecular excitation with a speed that matches the nuclear motion within the molecules. Associated probe pulses and foremost femtosecond continua spanning from below 300 nm well into the NIR routinely warrant true transient spectroscopy with a temporal resolution of 50 femtoseconds or better.

In parallel to these methodical advancements, the systems under investigation became more complex and relevant to interdisciplinary research. Help in the understanding and interpretation comes from the evolving quantum chemistry and dynamics that add unprecedented insight. In the talk I will discuss this evolution by means of examples starting from the nonradiative relaxation, progressing through intramolecular electron and proton transfer to the dissociation of complex molecules, to finally demonstrate the first observation of a bimolecular reaction that proceeds in as little as 1 ps.