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Contents

Ultrafast Processes

David Phillips

Imperial College London, South Kensington, London, UK SW7 2AZ

Commentary on: **Picosecond jet spectroscopy and photochemistry: Energy redistribution and its impact on coherence, isomerisation, dissociation and solvation,** Ahmed H. Zewail, *Faraday Discuss. Chem. Soc.*, 1983, **75**, 315-330

Ultrafast techniques have really come into their own since the development over the past decade of reliable, relatively inexpensive femtosecond lasers, but in the 1980's, ultrafast still meant picoseconds, and the chosen paper typifies work in this time-domain. The whole subject of course owes its inspiration to George Porter, who with Norrish pioneered flash photolysis,[1] first in the milli-, then micro-, and ultimately nano- and picosecond time-domains.

In the 1960's and 70's, the basic theories of non-radiative decay of photo-excited molecules was put on a firm footing by the pioneering work of Hochstrasser, Jortner, Robinson and many others,[2] and this permitted a broad understanding of decay processes observed experimentally in simple di- and tri-atomic molecules through to large polyatomic systems. However almost all data on large molecules up to this time had been obtained in the condensed phase, or in "bulb" experiments on gases at low pressures in the so-called isolated molecule limit, *i.e.* pressures such that collision with other molecules would not occur during the lifetime of the excited state. These experiments were bedevilled by the fact that at room temperature or the often higher temperatures necessary to maintain a sufficient concentration of molecules in the gas-phase, even a very narrow-line laser excitation source resulted in simultaneous population of a large number of excited -state ro-vibrational levels, since the Boltzmann distribution of ground-state levels led to severe sequence congestion in the spectra.

"Supersonic jet" technology developed by Levy and others[3] was extremely effective in simplifying the electronic *spectroscopy* of complex polyatomic molecules because the narrowing of the Boltzmann distribution by nozzle expansion, reaching effective temperatures well below 1 K allowed single vibrational and even single rotational level excitation for the first time. The technique was rapidly used in conjunction with narrow line-width cw laser excitation to produce high-resolution excited state spectra of many complex molecules, and in some cases their van der Waals complexes and clusters. Ahmed Zewail was one of the first to realise that the use of short-pulse lasers in conjunction with jet cooled molecules could provide similarly revealing information about the *dynamics* of decay of excited states, and the early paper selected here reviews some of the startling successes his group had in this field. The paper acted as an inspiration to many others in the field, and ultimately to work on the femtosecond timescale,[4] and of course, to the award of the Nobel Prize to the author.

Zewail acknowledged early on that he was inspired to work in the dynamics area by amongst others, George Porter's development of "fast" reaction techniques, *viz.* "Flash Photolysis" which is reported elsewhere in this volume. In the early experiments outlined in the present paper, three detection techniques were employed; time-correlated single photon counting, with 30–50 ps time resolution; streak camera detection of fluorescence, with 10 ps resolution, and multiphoton ionisation with resolution determined by the pulse width of the laser, 1 or 15 ps.

Using the former technique, the most significant result was the observation of "quantum beats" in the fluorescence decay of jet-cooled anthracene At low excess energies, the fluorescence and fluorescence excitation spectra of anthracene are very sharp, and the fluorescence decay of single vibronic levels is exponential. At an excess energy of 1400 cm^{-1} however, clear quantum beats were seen, arising from the interference between the initially populated vibronic state, and a state produced

by vibrational redistribution into the small number of weakly coupled background vibrational levels.[5] At higher excess energies, the large number of states interfering renders the quantum interference effects invisible. This first clear observation of these quantum beats led to studies on rotational coherence by Felker and Zewail[6] which in favourable cases permitted estimation of rotational constants, and hence structural information, in large polyatomic molecules where conventional spectroscopy was impossible. After the development of shorter-pulse lasers the way was opened for elegant studies on wave-packet dynamics in simple dissociating systems, such as NaI,[4] and gradually more complex systems in jets, and ultimately to wave-packet dynamics in the condensed phases.

Another major goal of many groups in the late 1970's had been the understanding of the influence of solvent upon the dynamics of excited states in the liquid state. Real progress has of course come with the arrival of femtosecond techniques, and direct studies in solution, but around 1980, it was felt that advances could be made by investigating the spectroscopy and decay characteristics of jet-cooled molecules solvated sequentially by one, two, three, *etc.,* solvent molecules, and higher clusters, which might ultimately mimic condensed-phase behaviour. Large numbers of investigators, including ourselves, entered this field in the 1980's,[7,8] earning from Ed Schlag the irreverent collective title "The Solvation Army", but Zewail was a pioneer, and the work reported in this early paper on dynamics of isoquinoline molecules solvated by water, methanol, and acetone motivated many to follow this path.

Ultrafast dynamics moved on dramatically from the picosecond regime over the 1990's and into this century, but the early work of Zewail outlined in this 1983 review paper of his provided a first glimpse of some of the coherence effects to be studied with ever faster lasers.

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