Personal and Scientific Reminiscences

Tributes to Ahmed Zewail

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About This Book E-Book Supplementary

A compilation of wonderful tributes to the late Ahmed Zewail (1946-2016), considered the 'Father of Femtochemistry', a long-standing icon in the field of physical chemistry, and the father of ultrafast electron-based methods. The book contains testimonies by friends and relatives of Zewail and by outstanding scientists from around the world who worked or have been affiliated with the Nobel prizewinning professor. Each contribution describes the author's own unique experience and personal relationship with Zewail, and includes details of his scientific achievements and the stories around them. *Personal and Scientific Reminiscences*collects accounts from the most important individuals in the physical and chemical sciences to give us a unique insight into the world and work of one of the great scientists of our time.

Sample **Chapter(s)**

Chapter 1: Ahmed Zewail: Ultra-Scientist and Citizen (1,519 KB)

Contents:

Readership: Students, practitioners and researchers of chemistry, physical chemistry and physics interested in learning about one of the great minds in physical chemistry.

How I lost my funding to Zewail

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I had known Ahmed since he had joined the faculty at Caltech in 1976. Our research has been strongly intertwined and my theoretical work was greatly influenced by his pioneering studies. We had closely interacted throughout his career starting with his picosecond studies of intramolecular vibrational redistributions (IVR), following through his femtochemistry era and finally his 4D ultrafast electron diffraction.

The field of laser chemistry was launched in 1975 by several reports of selective dissociation of SF_6 by intense CO_2 laser (frequency 1000 cm^{-1}). The dissociation, first reported by Abratzumian Ryabov with Letokhov, was a 10-photon process. It generated great excitement and raised the hope that laser selective chemistry might be used to direct and control reactions to different products than are possible thermally, for example, the selective breaking of a stronger bond leaving the weaker one intact. One application that drew considerable scientific and government attention was the possibility of laser-induced isotope separation, leading to many schemes to achieve this goal in atoms and in molecules. In this rapidly-developing field, international conferences were held on almost a weekly basis and results received extensive coverage in the regular press. I had studied and calculated possible mechanisms of selective multiphoton dissociation and how it could compete with intramolecular vibrational redistribution (IVR) so that coherence could be maintained long enough for chemical processes to occur prior to energy thermalization. I had the opportunity in 1977 to collaborate with Nicholas Bloembergen, Eli Yablonovich, and their student Jerry Black at Harvard on the interpretation of their careful multiphoton dissociation study of SF_6. Their experiments and analysis showed that this was a thermal process: due to anharmonicities and the high density of vibrational states, IVR takes place before any bond can break, and the laser was just serving as an expensive heating device. This and many other studies caused the wide interest in laser chemistry to sharply decline. Selectivity and coherence effects were not possible by simply subjecting a molecule to an intense noisy infrared laser.

In 1978, I had collaborated with Rick Smalley at Rice, who had just set up his supersonic beam apparatus to obtain frequency-domain fluorescence measurements of cold molecules at cryogenic temperatures, allowing much better spectral resolution compared to room temperature spectra. His students were focusing on measuring the spin-orbit coupling in the methylene radical before I convinced them that IVR was a much more important issue and suggested they study it in various alkyl-substituted benzenes. Although the frequency domain data showed some indirect evidence of IVR, it was clear that only time-domain measurements could provide clear-cut and unambiguous probes for IVR. When I suggested this to Rick, he said, "Only Zewail can do it!" These experiments were indeed performed a few years later by Zewail.

When I started my faculty position at the University of Rochester, I thought it would help me obtain funding if I were to organize a workshop on intramolecular vibrational redistribution and quantum chaos. This was the hot topic in chemical physics at the time since it held the key for the realization of laser selective chemistry. I contacted several funding agencies who all turned me down right away, but two program directors from the Air Force Office of Scientific Research (AFOSR): Larry Davis and Larry Burggraf, were very enthusiastic, and eager to generously sponsor this conference even beyond what I had requested (this has never happened to me since!). The meeting was held in Rochester in October 1985. I invited about 30 speakers; the meeting went very well and reflected the excitement surrounding the topic and its relevance to coherent laser control of chemical reactions. Zewail, who was doing picosecond measurements in molecular beams at the time, gave a very passionate talk about "IVR and chemical reactivity" forcefully laying out the case for carrying out femtosecond experiments that could directly and unambiguously monitor vibrational motions. To achieve the fs time-resolution, he needed a new laser system. The Air Force grant officers were impressed by Zewail's talk and requested a preliminary proposal immediately. A full proposal was recommended for funding in August of 1986. Frank Wodarczyk was in charge of the Molecular Dynamics portfolio at AFOSR under which Zewail received his initial funding and was involved in the decision. He recalls "At the time I remember being leery of providing so much money to one project, but Davis had enough foresight and faith in Zewail's ideas and in his femtochemistry proposal to commit the funding to start the project". Larry Davis had made sure that Zewail could order the equipment needed right away and AFOSR has continued to support the femtochemistry program ever since.

The outcome of the meeting was that Zewail had received on the spot a positive response to his request for substantial AFOSR funding to build his first femtosecond system, however, when I politely inquired at the end of the meeting for possible support of my ambitious theoretical effort I was told that no funding was left at that time (since it all went to Zewail!). In retrospect, my meeting was too successful. I take some comfort that this was my modest contribution to the birth of the field of femtochemistry.

I recall submitting a referee report to Zewail in his capacity as an editor of Chem Phys Lett. I liked the paper and indicated that it was as impressive as the pyramids, built by the Israelites in Egypt. As soon as he got the report he called me and bitterly complained that the pyramids were in fact built solely by the Egyptians and that my statement (which was based on biblical evidence) is totally false.

Femtosecond lasers in the early 1980s opened up the way to probe photophysical processes of chemical reactions in real time. The field of laser induced chemistry was revived with the development of femtosecond sources with stable phases, and coherent control schemes which allowed for the rational design and realization of laser-selective chemistry. I had worked on developing the density matrix, Liouville space pathway approach to nonlinear spectroscopy, recognizing how the field of ultrafast molecular nonlinear spectroscopy badly needed a unified approach that could describe and compare the various signals. Numerous confusing terminologies and four letter acronyms were commonly used to describe the same measurements, and it was not possible at the time to systematically and rationally design an experiment for probing specific processes. My first paper with Yijing Yan and Larry Fried, on applying the Liouville space formalism to the ICN photodissociation experiments of Zewail, was submitted to J. Chem. Phys. The referees were very skeptical; one referee said something like "Mukamel has a high reputation, and to save this reputation, he should not publish this useless article." The paper was finally published in J. Phys. Chem. In 1989. That paper had started a series of studies that ended up in my book "Principles of Nonlinear Optical Spectroscopy" which appeared in 1995 with Oxford University Press and has helped create a common language that is widely used for the interpretation of signals and for the design of new multidimensional measurements which employ sequences of multiple pulses. These again can be traced back to the stimulating and pioneering work of Zewail.