AHMED ZEWAIL
NOBEL LAUREATE IN CHEMISTRY
In order to describe the scientific contributions of Professor Zewail, the 1999 Nobel Laureate in Chemistry, it is important to describe the field of chemistry prior to his groundbreaking experiments. In 1986, the Nobel Prize in Chemistry was awarded to Professors D.R. Herschbach, Y.T. Lee and J.C. Polanyi for advances in Molecular Beams and Chemiluminescence techniques for studying chemical reactions. These powerful methods were being developed to measure the outcome of chemical reactions given a well-parameterized set of initial conditions such as collision energy and in many cases with initial quantum state selection. Professor Lee wrote in his Nobel address:

«If the motion of individual atoms were observable during reactive collisions between molecules, it would be possible to understand exactly how a chemical reaction takes place by just following the motion of these atoms. Unfortunately, despite recent advances in microscope technology that allow us to observe the static arrangement of atoms in a solid, we are still far from being able to follow the motion of atoms in the gas phase in real time.»

Zewail's main scientific contribution was to demonstrate that direct observation of atomic motion during a gas-phase chemical reaction was possible using femtosecond laser pulses.

Zewail's breakthrough experiment reported on the observation of the Transition State of a chemical reaction in 1987 [1]. In that article, the dissociation reaction of triatomic iodocyanide, ICN, was studied in the gas phase. Prior experiments on that photodissociation reaction were focused on measuring the product state distributions and a kinetic rate for the emergence of the product fragments. Zewail's experiment, using femtosecond laser pulses (one femtosecond = $10^{-15}$ s), showed that probing of the intermediate species, those that are no longer reagents but are not yet products, could be achieved. That experiment drastically changed what chemists thought possible, and opened new horizons in the understanding of chemical reactions. From that day observing molecular reaction dynamics to elucidate a reaction mechanism was no longer a dream.

The existence of the transition states in chemical reactions was predicted by Arrhenius in 1889. Calculations on reaction trajectories involving the potential energy surface, as well as numerous spectroscopic measurements, indicated that the relevant time scale for bond formation and bond breakage was in the picosecond to femtosecond range. Femtosecond technology did not become available until 1981, when laser pulses shorter than 100 femtoseconds were announced by a group at Bell Laboratories. By the mid-eighties, scientists were applying femtosecond lasers to study the response of semiconductors and large organic molecules in solution. Zewail adopted the advanced femtosecond-laser technology and brought it to bear upon the fundamental steps of chemistry, namely the breaking and forming of chemical bonds. The initial observations were
carried out on isolated molecules containing a well-defined reaction coordinate. This permitted a relatively simple explanation for the results. In fact, Zewail demonstrated that following a femtosecond excitation, the motion of heavy atoms in a molecule could be described according to the rules of classical mechanics. This observation allowed an intuitive classical interpretation of the experiments. The quantum mechanical calculations that closely followed the experiments confirmed the observations.

The experiments are carried out using two ultrafast laser pulses. First, a powerful pump pulse excites the molecule to a higher energy state. Then a weaker pulse, at a wavelength chosen to detect how the original molecule is transformed as the reaction proceeds, probes the system. The pump pulse determines the starting time for the reaction while the probe pulse examines what is happening at a certain point in time. By varying the time interval between the two pulses it is possible to obtain snapshots of the progress of the reaction and to see how the original molecule is transformed in time.

Some scientists were concerned about how the uncertainty principle affected the femtosecond measurements from Zewail's group. The energy bandwidth of the ultrashort pulses was much broader than had ever been used in spectroscopic measurements. Spectroscopists were used to working with nearly monochromatic lasers. Undaunted by the criticism, Zewail published a series of papers where he demonstrated some very important points:

- Transition states can be probed directly and efficiently with ultrashort pulses.
- The dynamics of potential energy curve crossing are best studied in the time domain.
- The saddle point in more complex reactions can be studied directly.
- The products of a fast reaction can exhibit vibrational coherence.
- Femtosecond pulses can be used to obtain very high spectroscopic resolution.

The complexity of the molecular samples that Zewail's group has studied continues to increase. One of the more important aspects of his work has been the study of a number of inorganic and organic chemical reactions. These experiments have demonstrated that gas phase measurements can provide valuable insights into the reaction mechanism. Using a high-pressure vessel, Zewail studied systematically the transition from the isolated, dilute-gas conditions to the high buffer-gas pressure condition, which mimics the liquid phase.
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Most femtosecond measurements monitor changes in the spectroscopy of the chemical species involved as a function of time. In an effort to make a more direct observation of the molecular dynamics, Zewail’s group has been developing a method involving ultrafast electron diffraction. Chemical reactions are initiated with a femtosecond laser pulse, the evolution of the reaction, however, is probed with a very short pulse of electrons. The electron diffraction pattern obtained as a function of time delay from the initiation pulse provides snapshots of the entire structure with sub-Angstrom resolution. The diffraction patterns as a function of time delay provide the dynamic changes in structure as the chemical reaction proceeds in time. Zewail commented in his Nobel Prize address that Femtobiology remains as one of the most significant frontiers. Already there are a number of important experimental contributions from his group on this field. Based on his previous achievements, we can expect exciting results from Zewail’s group in the near future.

Zewail was educated in Egypt where he received the B.S. and the M.S. from Alexandria University. He received his Ph.D. from the University of Pennsylvania (with Prof. R.M. Hochstrasser), and his postdoctoral training at the University of California, Berkeley (with Prof. C.B. Harris). Zewail’s current research is devoted to developments of ultrafast lasers and electron pulses for studies of dynamics of complex systems with atomic-scale resolution. Time-resolved studies with ultrafast electron diffraction and the dynamics of biological processes are amongst his areas of major interest.

Literature:


Further Information:

www.nobel.se/chemistry/laureates/1999/press.html


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