Capturing Molecules In Transition

ARCHITECT OF FEMTOCHEMISTRY

rof. Ahmed H Zewail

Born in 1946 in Egypt, Ahmed H. Zewail studied MS at the University of Alexandria He obtained his Ph.D from the University of Pennsylvania and did post doctoral work at the University of California, Berkeley.

He is on the faculty at the California Institute of Technology since 1976 and now holds the Linus Pauling Chair professor of chemistry and professor of physics. Prof Zewail is also the director of the Laboratory of Molecular Sciences.

has four children and is married to Dema Zewail. His academic family sists of over 150 students, post-doctorals and visiting associates.

By T. Pradeep

N a 1990 article in *Scientific American*, his year's Nobel laureate in hemistry Prof Ahmed H Zewail efers to a story of American railroad ate Leland Stanford. He in 1872 red $ 25000 that a galloping horse at point is completely off the ground. ove the point British photographer ard Muybridge was employed who pictures of the horse at different s of motion. Muybridge tried various ring mechanisms and finally came ith a camera shutter which opens wo thousandths of a second.

placing cameras at various distances, the photographs demonstrated he horse can indeed be floating in air g its stride as shown in **Figure 1.** ictures also showed that the horse at a speed of about 10 metres per sec-

amera which

more C gets formed. This change was quantitatively described by the classic equation of Svante Arrhenius, a Swedish scientist who received the Nobel Prize for chemistry in 1903.

The birth of molecules was an interesting problem to look at since then. Normally, in a chemical reaction we know the beginning and then the end, nothing in between. The importance of in-between stages in a chemical reaction is made clear by the analogy illustrated by Sture Forsen of Lund university. He compared the scientific community with a theatre audience watching a drastically shortened version of a drama. In the first scene, the curtain raises and the characters are introduced, the curtain falls and raises again to introduce the final scene in which several characters are dead with a few survivors. It is just impossible for the uninformed to 'read' what happened in-between!

Need for femtosecond resolution

The necessary of femtosecond resolution 'to know in-between' can be under-

have only one bond and the potential surface becomes a curve. When two interacting atoms come together, they become bound and a molecule forms in an energy minimum. If the atoms come too close, the repulsion between the nuclei will increase the energy of the system. When they go apart, there again the energy increases and beyond a distance no more change in energy happens and the atoms separate.

Intermediates and transition states

When reactions happen, in several cases the products are formed through intermediates. Some of these intermediates last for sufficiently long time. It is possible to detect these species by various techniques. The presence of free radicals were detected by this method. Free radicals are those with unpaired electrons and are unstable. Fast reaction kinetics studied by R G W Norrish is one example. The processes which occur during molecular collisions could not be understood by such studies of intermediates.

During the 1960s techniques were available with which mono energetic and unidirectional beams of molecules could be produced. Dynamics of collisions were studied by looking at the angular and energy distribution of C when beams of A and B were involved in collision. If C dissociates, properties of the products A and B could be used to derive information about the dynamics.

In molecular beam experiments it is not possible to observe the transition state directly. A more direct approach is to look at the optical properties of the transition state. For example, the transition state will absorb photons at a different frequency compared to the free molecule. There can also be emission of photons or photons

Fig.1

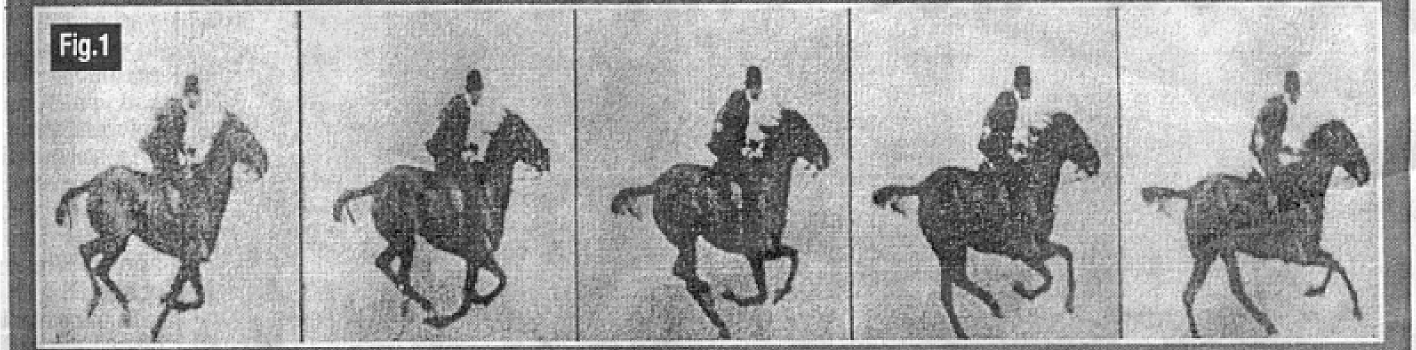


Fig.2

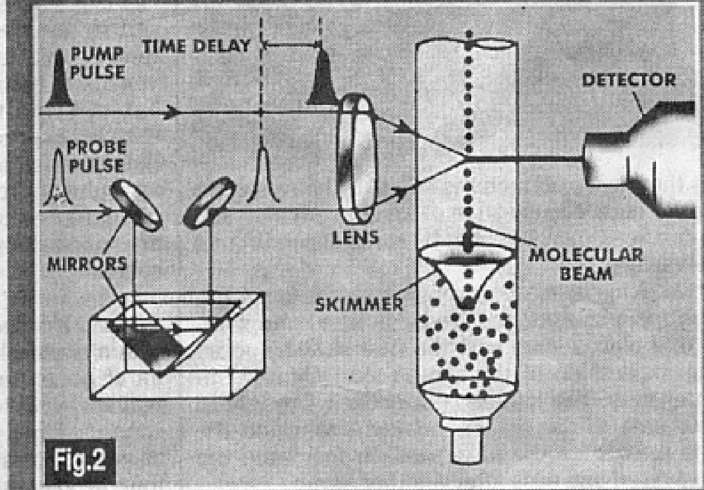


Fig.5

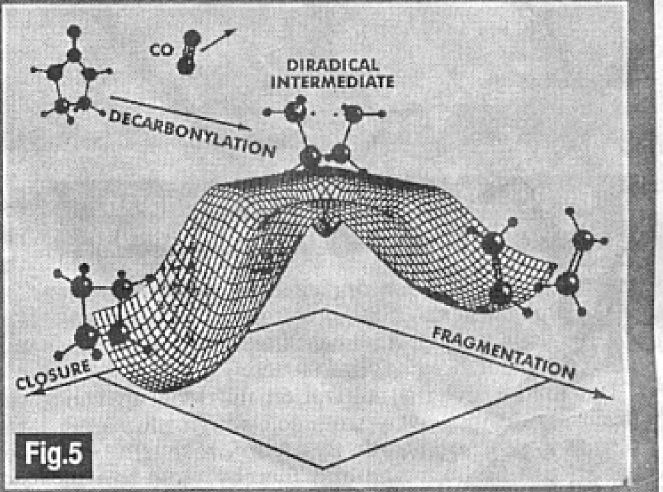


Fig.3

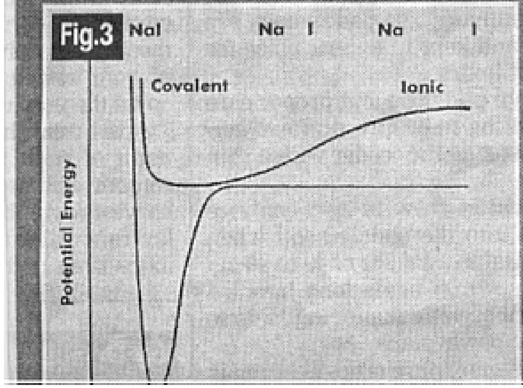
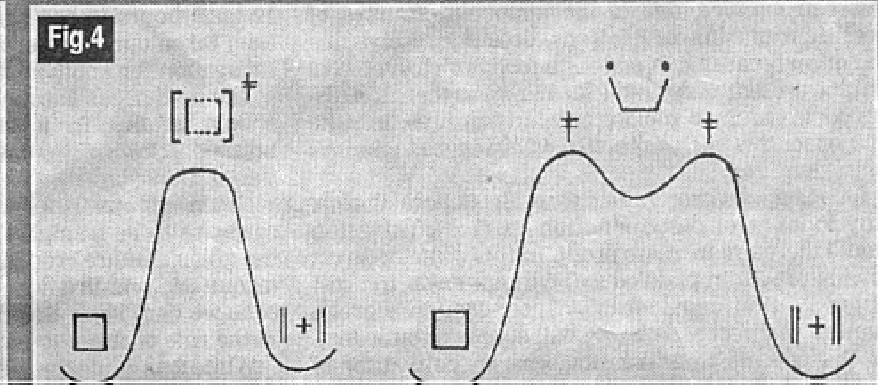


Fig.4



to a second what a second is to 32 million years. It is like one millilitre to a water pool of one cubic kilometre. Time resolution of one fs is not possible even with atomic clocks.

Light travels 300,000 kms a second. In a femtosecond, it travels 0.3 micrometres or the size of a tiny bacterium. By choosing two light pulses with a path difference of 0.3 microns between them, it is possible to get a time difference of one fs. However, it is necessary that the two light pulses themselves are of very short duration, comparable to one fs, only then these pulses will be separately observable. Otherwise we will see only a composite pulse. It is an everyday experience that the distances between objects can be defined more precisely when the objects themselves are small. We cannot define distances between objects more accurately than the dimensions of the objects themselves. This accuracy of measurement is called the resolution. Getting time resolution of a few fs was impossible till some years ago. In early 80's it was state-of-the-art to have picosecond (10^{-12} sec) resolution. In early 70's, scientists were happy with nanoseconds (10^{-9} sec).

How chemical reactions occur?

Chemical reactions happen as a result of collision between interacting species. In most of the collisions nothing significant happens and the colliding partners separate without any change. A very few fraction of the collisions are violent and result in the formation of new species. Such a change, or the chemical reaction can be represented as, A + B ﬁ C where A and B are called the reactants and C is the product. The number of these violent collisions increases with temperature and as a result mass is the lowest and therefore speeds are high. The interaction time is of the order of 10 fs. Generally, the time-scales involved in the birth of molecules is in the range of 10-100 fs.

When a reaction occurs, interacting species go through a transition stage. This can be written as, A + B ﬁ A....B ﬁ C, where A...B means a transition state. This is a situation where the system. A...B as a whole has high energy and is unstable. It can come to a lower energy state A + B (going backwards) or to C (going forward); generally the energy of C is lower than A + B and thus the forward reaction occurs. Molecules go through an activation barrier to reach the products. This idea of Arrhenius also suggests that the transition state is the same in either direction, A + B forming C or C forming A + B.

Potential energy surfaces

The motion of electrons and nuclei in the interacting systems determine the transition state. Looking at all the possible motions in a given system is quite complicated. Therefore, chemists generally understand processes in terms of potential energy surfaces. Corresponding to certain positions of nuclei in a system, we can define an energy point. If we map all the possible positions of nuclei, we get a multidimensional surface which depicts energy as a function of molecular axes. This will look like a map with energy minima and maxima (with hills and valleys as in a geographical map). Along a maximum, a certain chemical bond could be stretched and when the molecule crosses the peak it need not be the same. The conversion of molecules could be depicted in terms of such potential energy surfaces.

In the case of a diatomic molecule, we

called a pump pulse which initiates reaction and sets the clock to zero ti Several fs later, the probe pulse arr and looks at the changes in the molec which will be reflected, for example changes in the absorption of this pulse

It is possible to look at the evolutior the transition state as we probe the syst at different time intervals. To achieve time delay, the finite speed of light can made use of. The pump and probe pul originate at the same time and can be s arated into two beams, one travels slightly longer distance than the other the probe pulse has a path difference of micrometre, it corresponds to a time del of one fs. The schematic of such arrangement is shown in **Figure 2.**

With a difference of 1 to 100 micromet in path difference, a time separation 3.33 to 333 fs can be achieved. This sepa tion can be achieved in the laboratory.

The molecule in the transition state different from the free atoms or the pr uct molecule, C. The light emitted absorbed by the molecule in the transiti state carries its characteristic signatur It is possible to reconstruct an image the transition state from such data. Th branch of physical chemistry is call femtochemistry in which one investigat the making or breaking chemical bon by ultra-short light pulses. The study performed by the tools of femtosecor spectroscopy.

One of the early experiments was t dissociation of cyanogen iodide. The dissociation can be represented as, ICN I...CN ﬁ I + CN. Free cyanide molecul were detected in the early experimen and later the process of transition wa mapped. It was shown that the reactio takes about 200 fs to complete, within th me free CN and I are at a distance of bout 8 Angstrom apart. The real time-cale of molecular dissociations was emonstrated with this experiment.

One of the interesting reactions Zewail nd colleagues looked at was the dissocia-on of the molecule NaI. In the lower ener-y state (ground state), the bond is 'ionic.' fter absorbing the laser pulse, the ion

ir Na$^+$I$^-$ lands itself in a covalent bond ate. This state remains covalent until a a - I distance of 10 - 15 Angstrom, at hich point the bonding becomes ionic. he molecule can flip between the ionic d covalent situations and at an interme-ate point of 6.9 Angstrom, the excited al can decay to the ground state ion pair to the neutral atoms. A schematic of ch a transformation is shown in **Figure**

An important aspect in chemistry is e difference in reactivity of chemical nds. If a molecule contains two identical nds, will they both react at the same ne? In a molecule with two equivalent C-onds, experiments have shown that the nds break at different times.

The molecule used to demonstrate this s tetrafluorodiiodoethane, $C_2I_2F_4$ which ssociates to tetrafluoroethylene, C_2F_4 d two iodine atoms.

Simple chemical reactions can occur in ry complex ways. An example is the ocess occurring in a complex molecule, adduct between benzene and iodine lecule. In the adduct, a pump laser cites a electron from benzene to iodine - harge transfer transition. The negative arge on one iodine end and the positive arge on benzene make them come ether and the bond between the iodines aken and the iodine atom separates thin 750 fs. It is also possible that the electron jumps back, but by that time the bond between the iodines has broken.

Photo isomerisation has also been studied by this methodology. In these processes, light absorption results in the transformation of one structural isomer to another. Zewail and colleagues studied the isomerisation of cis-stilbene to trans-stilbene. They showed that the process occurs as a result of the synchronous motion of the benzene rings. These isomerisation processes are important in biology. For example, the principal process involved in vision is the cis-trans isomerisation of retinal (a compound in the eye) and the concomitant triggering mechanism. It was shown by others that the light that is absorbed is localised and is not redistributed in the molecule. That accounts for the high efficiency of the process of vision. The process is complete in about 200 fs. Several such processes are important in biology, an example is the energy conversion in a chlorophyll molecule.

One of the most well-studied reactions is the ring opening of cyclobutane or the addition of two ethylenes to form cyclobutane. The reaction could proceed through two possible pathways, one in which there is a single transition state and the other in which there is a minimum at the diradical tetramethylene. These two possibilities are shown in **Figure 4**. The two kinds of pathways are central to the understanding of many reactions. Both experimental and theoretical studies suggest that the diradical is not possible. The experiments performed by Zewail and colleagues were aimed at freezing the diradical in time. The compounds chosen to study this were five membered ring systems containing a 'carbonyl' group. When the carbonyl group dissociates by 'decrarbonylation' the desired four-membered ring system can form.

The first pulse decarbonylates a precursor and the probe pulse arriving at different time intervals ionises the species produced and the dynamics is monitored by measuring the mass spectrum. The mass spectra measured indicate that the diradical is observed after giving a time delay of about 300 fs. The course of the reaction is schematically represented in **Figure 5**.

Femtochemistry is practiced by a number of groups world over. Diverse areas are being investigated. Chemistry at interfaces is an important aspect of investigation today. Interfaces between chemistry and biology are also explored.

From the activated states and intermediates used to describe processes, we have come to experimentally observable transition states. We can now see the motion of molecules in real time and map processes. This is where the important application is going to be, relating to bond specific chemistry. Instead of activating all the bonds, a selected bond could be excited, specific products could be formed and reactions may be performed as 'surgical procedures.' These 'operations' are, however, done not with optical microscopes, but with ultra short optical pulses which could 'see' chemical bonds.

From Svante Arrhenius to Ahmed Zewail there was a huge gap of technology. This science was possible with immense developments in molecular beams, optics, lasers, electronics and computing. The cost of seeing the chemical transformation of a bond has been high. As we move forward, the economic input to make a discovery is increasing. It is important that we in India take a serious note of this.

(The author is Asst Prof, Dept. of Chemistry and Regional Sophisticated Instrumentation Centre. IIT. Madras)