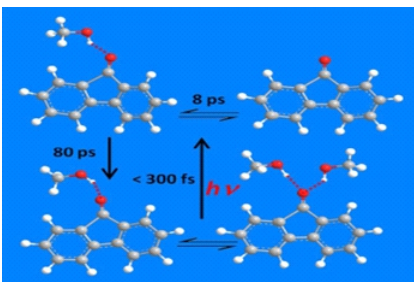## प्रकाश रसायन प्रक्रम

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वास्तविक समय में प्रकाश रासायनिक प्रक्रियाओं की गतिशीलता और स्पेक्ट्रमिकी की निगरानी : 1983-2016 के दौरान रसायन विज्ञान समूह की गतिविधियाँ

दीपक के. पाटिल*

यूएम-डीएई सेंटर फॉर एक्सीलेंस इन बेसिक साइंसेज
मुंबई विश्वविद्यालय (कलिना परिसर), विद्यानगरी, मुंबई-400098, भारत

फ्लोरीन-९-वन की उत्तेजित अवस्था में हाइड्रोजन बंधन विच्छेदन और निर्माण की अल्ट्राफास्ट गतिशीलता।

सारांश

मूलभूत आण्विक प्रक्रियाएँ, जैसे ज्यामितीय विश्रांति और अणुओं के बीच ऊर्जा, इलेक्ट्रॉनों और प्रोटॉनों का अंतरण, उत्तेजित अवस्थाओं में होने वाली गतिशील प्रक्रियाएँ हैं। इनमें से एक या अधिक प्रक्रियाएं प्राकृतिक भौतिक प्रक्रियाओं जैसे दृष्टि और प्रकाश संश्लेषण के साथ-साथ फोटोडिटेक्टर और सौर ऊर्जा भंडारण उपकरणों जैसे फोटोनिक उपकरणों का यांत्रिक हिस्सा हैं, जो इन प्राकृतिक प्रक्रियाओं का अनुकरण करते हैं। ये आण्विक प्रक्रियाएँ परादुत हैं और कुछ फेम्टो- (10^{-15}) से पिको- (10^{-12}) सेकण्ड समय डोमेन में होती हैं। उक्त समय अवधि के दौरान, इन प्रक्रियाओं की क्रियाविधि की जांच के लिए रसायन विज्ञान समूह, बीएआरजी में लेजर स्पेक्ट्रमदर्शिकी तकनीकों को स्वदेशी रूप से विकसित करने के प्रयास किए गए हैं। इस संक्षिप्त विवरण में, कुछ मॉडल अणुओं में इन प्रक्रियाओं के अध्ययन के परिणामों पर चर्चा की गई है।
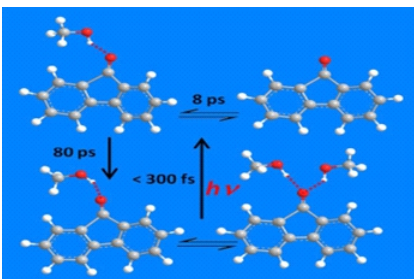
मुख्य शब्दः फेम्टोसेकंड क्षणिक अवशोषण स्पेक्ट्रमदर्शिकी, परादुत गतिकी, समावयवी गतिकी, एच-बॉन्ड गतिकी।

Photochemical Process

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Monitoring the Dynamics and Spectroscopy of Photochemical Processes in Real Time: Activities in Chemistry Group during 1983-2016

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Ultrafast dynamics of hydrogen bond breaking & making in the excited state of fluoren-9-one.

ABSTRACT

The fundamental molecular processes, such as, geometrical relaxation and transfer of energy, electrons and protons between the molecules are the dynamical processes happening in the excited states. One or more of these processes constitute the mechanistic part of the natural physical processes like vision and photosynthesis, as well as the photonic devices, like the photodetector and solar energy storage devices, which mimic those natural processes. These molecular processes are ultrafast and happens in a few femto- (10^{-15}) to pico- (10^{-12}) second time domain. During the said time period, efforts have been put to indigenously develop the laser spectroscopic techniques in the Chemistry Group, BARC, for investigating the mechanism of these processes. In this brief account, results of the studies of these processes in some model molecules have been discussed.

KEYWORDS: *Femtosecond transient absorption spectroscopy, Ultrafast dynamics, Isomerization dynamics, H-bond dynamics.*

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Introduction

Think about synthesizing a molecule using conventional test tube chemistry. It always happens that more than one reaction pathways lead to undesired products as contaminants with reduced yield of the desired product. Hence, chemists strived to device methods for controlling chemical reactions to increase the yield and traditionally, reliance has been on temperature, pressure and use of catalysis to overcome or reduce the energy barrier for the reaction. In the early years of the nineteenth century, knowledge on photochemistry was developed and it was understood that photochemical reactions proceed differently than temperature-driven reactions. Activation energy barrier of a reaction can be bypassed or reduced significantly in the excited state populated following photoexcitation (Fig.1). Photochemical paths access high energy intermediates that cannot be generated thermally, thereby overcoming large activation barriers in a short period of time.

Soon after the discovery of lasers in 1960, Chemists were excited to realize the usefulness of the special properties of the lasers to precisely snip apart molecules and drive difficult reactions. Chemists' idea was to hit a molecule with one frequency of light exciting one specific chemical bond in the molecule until it broke, leaving the other bonds untouched. That means achieving bond selectivity!

But that bond is not isolated from the rest of the molecule. Other parts of the molecule may bend and vibrate interfering with the target bond's absorption of the laser's energy. The degrees of freedom of a large molecule are so efficiently coupled that the energy supplied to one of the bond vibrations is soon distributed among all other vibrational modes. This process is known as *intramolecular vibrational energy redistribution* (IVR). Hence, for several years after discovery of lasers, chemists have been successful only in using the laser as a high-tech Bunsen burner to heat up the molecules, rather than cleave them neatly as they desired. The real Problem was that bond breaking is controlled by the laws of statistical thermodynamics losing the selectivity. The thermodynamically weakest bond was always broken.

So, chemists started asking the question: Is it possible to by-pass the laws of statistical thermodynamics by using intense short laser pulses and break the molecules at our will? The probable solutions discussed were: To use ultra-short laser pulse of high intensity to supply energy to the desired vibrational mode, so that the bond breaks before IVR takes place; or to use sequence of ultra-short pulses to direct the molecular states to the desired direction of the chemical reaction. Therefore, the question of selectivity opened the door to the following fundamental questions: (1) What is the time required to break the Bond? (2) What is the rate of IVR? (3) How the molecules dissipate *excess vibrational energy* to the environment?

Further, many more questions were relevant in this context: What is the mechanism and time scales, in which a molecule changes its geometry (photoisomerization), transfers energy, electron or proton to another molecule? Is it possible to characterize the *'transition state'*? These questions were found relevant to understand the mechanisms of the natural physical processes like vision, the most sensitive natural photodetector, and also the photosynthesis, which has been understood as the most efficient solar energy storage device in nature! These aspects prompted the scientists to look for molecules suitable for applications in Photonic devices, such as molecular switches, optical data storage, optoelectronics, sensors and light emitting diodes, as well as artificial mimicking of the photosynthetic process for solar energy storage. One or more of those photophysical and photochemical processes have been found responsible for operation of these devices.

However, most of the fundamental molecular processes, such as photodissociation, photoisomerization or configurational relaxation and also transfer of energy, electrons and protons between the molecules are the dynamical processes involving the mechanical motion of electrons and/ or atomic nuclei [1, 2]. Considering the speed of atomic motion is ~1 km/s, to record atomic-scale dynamics over a distance of an Angström, the average time required is ~ 100 fs. Hence, using kinetic spectrophotometers having a time-resolution of a few tens of a femtosecond (10^{-15} s), we can freeze the molecular structure far from equilibrium and follow the atomic motions in a molecule in real time to make movies and snapshots capturing the molecular activities of chemical reactions in "slow motion". Furthermore, in a molecule, any of those processes is always happening accompanied by one or more of the other processes and therefore, the overall process responsible for working of any of the devices is quite complex. Lasers have been useful for both as a diagnostic or spectroscopic tool for understanding the rates and mechanism of those processes as well as a chemical reagent for inducing new physical or chemical processes in molecules, materials and devices. Fast (nano- and pico-second) and ultrafast (femto-second) laser spectroscopic techniques have been found to be excellent tools for understanding the mechanism of these processes [3, 4].

Considering the above important aspects of ultrafast photochemistry and possible applications in laser isotope separation and development of materials for energy storage and photonic devices, an urgent need was felt for developing time-resolved laser spectroscopic and complementary techniques in Chemistry Group, BARC. A modest beginning was made in this direction in 1986 by installing three very important kinetic spectrometric techniques, namely, nanosecond laser (excimer) flash photolysis, time-correlated single photon counting (TCSPC) (instrument response was about 1 ns) and nanosecond electron pulse radiolysis. In this article, only a brief account of the studies performed based on laser spectroscopic techniques developed over the next three decades will be discussed.

The excimer laser-based flash photolysis spectrometer was extensively used to study the photo dynamics in the excited states of hydroxy and amino substituted quinones, and the results were complemented by the studies using nanosecond electron pulse radiolysis and TCSPC techniques [5, 6]. This flash photolysis spectrometer was also coupled to a high-power
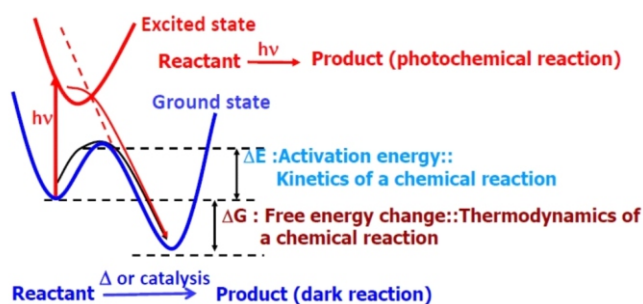
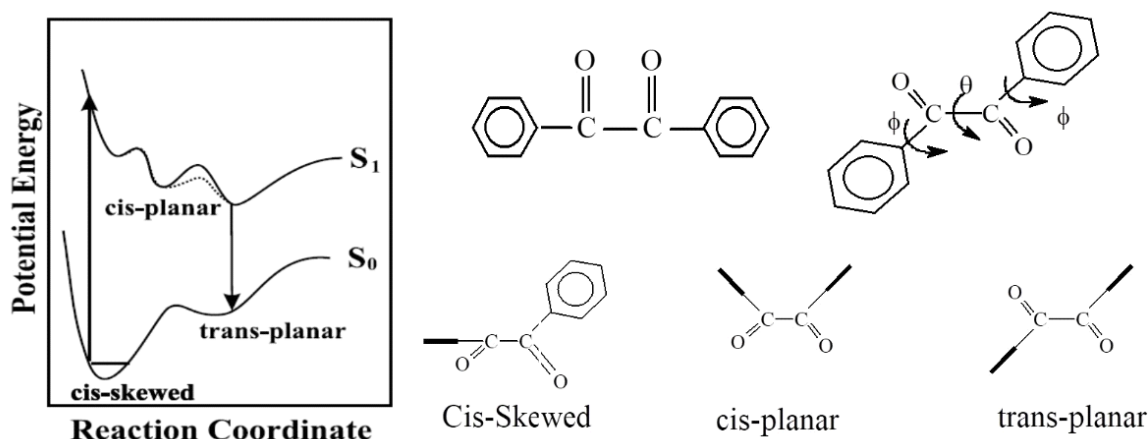*Fig.1: Advantage of a photochemical route for a chemical reaction over the conventional thermal route.*

Fig.2: Schematic presentation of the potential energy surface for the changes in conformation from the cis-skewed form to the more stable trans-planar form in the S₁ state of Benzil. The surface shows that the conformational relaxation process is associated with crossings of two consecutive energy barriers. Dotted line indicates the change in barrier height in polar solvents. Copyright Springer. Adopted from Chem. Phys. Lett. 2002, 360, 443.

CO_2 laser (pulse width 1 ns and 1J/pulse at 10.6 µm) to study the spectroscopy and dynamics of the fragments in infrared multiphoton dissociation (IRMPD) of haloalkanes. This technique was successfully applied to detect and to study the spectroscopy and dynamics of the CF_2 radical in IRMPD of *d*-chloroform [7].

In 1990, first of its kind in India a picosecond transient absorption (TA) spectrometer with the time resolution of about 35 ps was indigenously developed. Development of the spectrometer was very timely to study the photophysical and electron transfer properties of the Fullerenes, which were then very recently discovered and synthesized in laboratories. These results were those among a few other laboratories through the world reported simultaneously [8,9]. This spectrometer has subsequently been used to study photophysical and electron transfer properties of many substituted Fullerenes [10] and many other chemical systems.

Towards our efforts to develop subpicosecond transient absorption (TA) spectrometer in 1993, since no commercial femtosecond laser system and TA spectrometer were then commercially available, decision was taken to indigenously develop an amplified colliding pulsed mode-locked (CPM) dye laser system and the TA spectrometer. In this spectrometer, temporal dynamics could be recorded in the 400 – 1100 nm region with the time resolution of about 200 fs. This spectrometer was then the first one of its kind in India and was extensively used to study the intramolecular charge transfer dynamics in hydroxy and amino-substituted benzophenone derivatives [11] and conformational relaxation dynamics in the excited state of Benzil [12]. The triple exponential decay

dynamics of the S₁ state of Benzil indicated that the process of conformational change from the cis-skewed to the trans-planar form takes place via the formation of a meta-stable intermediate conformer resulting the involvement of two consequent barrier crossing processes. The barrier crossing dynamics is governed by both the polarity of the solvent, which alters the barrier heights by 'static' interactions, as well as the viscosity of the solvent via 'dynamical' interactions.

Considering the limitations (low pulse energy and longer pulse duration) and difficulties in operation of the dye laser
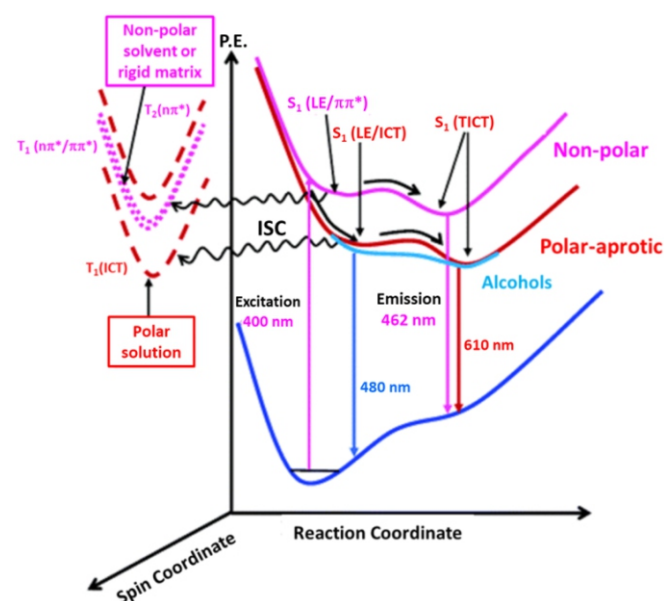

Fig.4: Potential energy surface (PES) diagram for the relaxation dynamics of the excited states of DMABP. S₁(LE) and S₁(TICT) represents the two adiabatically coupled locally excited and relaxed or twisted S₁ states, respectively. In nonpolar solvents, the LE state is an asymmetrically charge-distributed π−π state, but in polar solvents, the LE state is an ICT state. The LE to TICT conversion process via diffusive twisting of the dimethylaminophenyl group is associated with a barrier-crossing process. In alcoholic solvents, the height of the energy barrier is lower than that in aprotic solvents. In alcoholic solvents, the emission maximum at 480 nm arises due to emission from the S₁(LE) state but in aprotic solvents the emission maximum in the 462-610 nm region arises due to emission from the S₁(TICT) state. This diagram also presents the relative positions of different triplet energy levels and possible intersystem crossing processes in rigid matrixes at 77 K. Copyright American Chemical Society, Adopted from J. Phys. Chem. A. 2004, 108, 2583.*
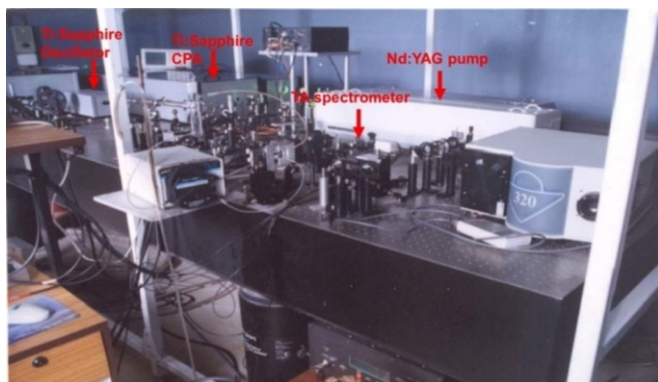

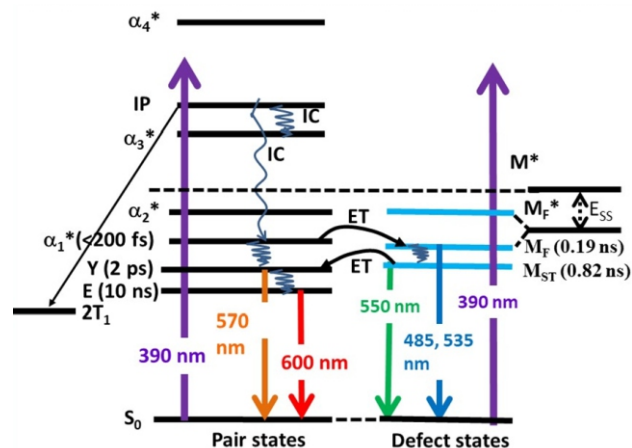*Fig.3: Ti:Sapphire laser based femtosecond TA Spectrometer.*

Fig.5: Schematic energy level diagram of the exciton states in perylene nanoaggregates. Lifetimes of the lower energy exciton states are given in the bracket. Relative positions of the energy levels in pyrene nanoaggregates are very similar. Copyright American Chemical Society, Adopted from J. Phys. Chem. C2020, 124, 24470.

Fig.6: Ultrafast dynamics of hydrogen bond breaking and making in the excited state of fluoren-9-one. Copyright American Chemical Society, Adopted from J. Phys. Chem. B2017, 121, 1068.

based femtosecond oscillator–amplifier system, the femtosecond TA spectrometer was upgraded in the year 2000 by replacing the dye laser based system with a Ti:Sapphire laser oscillator and chirped pulse amplifier (CPA) system delivering optical pulses of 50 fs duration and 500 µJ / pulse energy at 1 kHz repetition rate. This laser system was coupled to a home mode TA spectrometer for which the time resolution (fwhm) was about 120 fs (Fig.3).This spectrometer was upgraded by another Ti:Sapphire laser with 3 mJ/pulse and 35 fs pulse duration. During this time, the TA spectrometer was upgraded by a commercial one.

Over the years these spectrometers have been extensively used to unravel very complex dynamics of ultrafast intramolecular charge transfer processes in the excited states of donor acceptor molecules, like dimethylamino-benzophenone [13] (Fig.4), Michler's Ketone [14], 1-(p-Nitrophenyl)-2-(hydroxymethyl) pyrrrolidine (p-NPP) [15], etc., intramolecular energy transfer dynamics coupled to configurational relaxation in donor–acceptor molecules, photophysics of dye molecules (solar energy materials) on interfaces and electron transfer dynamics from the dyes to the semiconductor nanoparticles [16, 17], the dynamics of the hydrogen bond in the excited state of the fluorenone - alcohol or amine hydrogen bonded complexes [18, 19], exciton dynamics in polyarene nanoaggregates, namely, anthracene, pyrene and perylene (Fig.5) [20, 21].

Several unsolved problems related to our work on the hydrogen bond dynamics studied using time resolved UV–Vis-NIR spectroscopy, led us to think about setting up an ultrafast time resolved IR spectrometer to resolve the bond-specific dynamics by monitoring the spectroscopy and dynamics of vibrational motions. The time-resolved IR spectrometer was used to unravel the ultrafast dynamics of hydrogen bond breaking, making and hydrogen bond reorganization processes in the excited states of fluorenone (Fig.6) and 9-Anthracenaldehyde [22, 23].

Due to limitation of space in this article, detailed discussion on the results of the studies mentioned above and also other studies using ultrafast spectroscopy have not been possible. Interested readers may find the original papers mentioned in the reference section. This article also can no-way be considered as the full account of the research works on ultrafast spectroscopy performed in the Chemistry Group,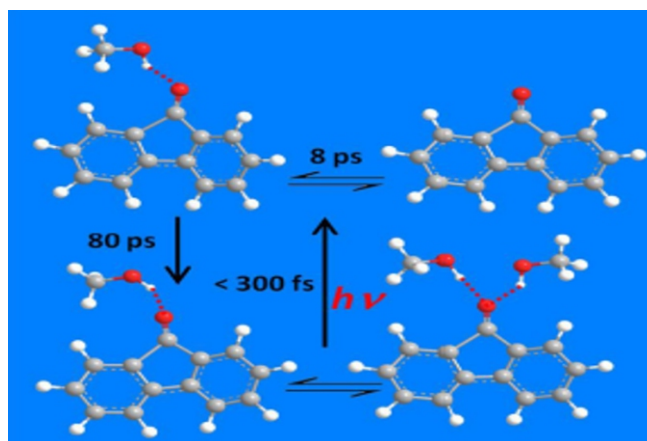 BARC. Without a discussion on the extensive research works using fluorescence up conversion technique; large volume of excellent studies on the carrier dynamics in semiconductor materials, accounting the contributions of the Chemistry Group, BARC to the ultrafast spectroscopy will be far from complete.

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