

# Chronicles of Chemical Dynamics

Sukhendu Nath, Awadhesh Kumar and Sisir K. Sarkar

## Preamble:

The present article examines the evolution of the field of Chemical Dynamics pursued at Chemistry Group, BARC. During this journey, it has been pursued and recounted chronologically a few contemporary stories on setting up world class research facilities for carrying out studies on solution phase to gas phase to interface, millisecond to femtosecond time domain and macromolecules to single molecules. This journey involves development of various challenging laser spectroscopic methods.

## Introduction:

Radiation chemistry research at BARC, which was started in 1950s, catalyzed complementary photochemical research for an in-depth study of a chemical process in Chemistry Group. The gained importance of these areas of research led to creation of Radiation Chemistry Section in Chemistry Division in 1958, and Radiation Chemistry & Chemical Dynamics (RC&CD) Division in 1999, which was renamed as Radiation & Photochemistry Division (RPCD) in the Chemistry Group in the year 2005. Initial photophysical and photochemical studies remained confined to the solution phase. These studies got a boost on introduction of time-resolved studies, when a microsecond flash photolysis system was developed indigenously first in 1970s and then in early 1980s. Subsequently, a kinetic laser flash photolysis set up installed in the year 1985, which facilitated investigation of short-lived species. Time-resolved evolution of a species could be monitored, and characterized by its UV-Visible spectral features. At the same time, nanosecond pulsed CO<sub>2</sub> laser was installed in the year 1986, which promoted gas phase studies and initiated chemical dynamics research. The ultrafast laser facilities boosted chemical dynamics research in the condensed phase. Then there was a rapid progress in the field of ultrafast dynamics, and the Chemistry Group scientists were in sync with the development globally.

## Chemical dynamics:

One of the most fundamental problems in chemistry is to understand how chemical reactions occur: that is, how reagents are transformed to products. Chemistry is traditionally performed by applying heat, pressure, agitation, etc. to the reactants. Chemists start by studying the thermodynamics of a reaction, then its rate, and finally postulate its mechanism.

However, all along it has been easy to focus on the state before and after the reaction, i.e. on the reactants and products. Gradually, there has been a change in the curiosity of chemists, and they started asking how and why reactants transform to products. The present chronicle will examine the evolution of the field of chemical dynamics pursued in RPCD, Chemistry Group. Chemical dynamics essentially describes how reagent molecules approach, collide, exchange energy, sometimes break bonds and make new ones, and finally separate into products. During this journey a few contemporary departmental programs, such as laser isotope separation followed by ultrafast spectroscopy was pursued. Chemical dynamics has become increasingly interdisciplinary and nurtured a large number of areas like photochemistry and laser chemistry; laser isotope separation; ultrasensitive detection; atmospheric, combustion, plasma chemistry, photocatalysis, cluster chemistry, many more.

### ***Molecular laser isotope separation:***

With the introduction of laser in early 1960s, chemists have a reliable ideal light source at their disposal. About fifty years ago, BARC ventured into a new frontier of scientific research. Molecular Laser Isotope Separation (MLIS) program was based on the interaction of lasers with molecules. It was the beginning of Laser Chemistry- which brings to mind the proposition that it should be possible to provide lasers tuned to a given energy level which can break specific bonds as required. This process can induce specific rearrangements with a minimum of side reactions.

The MLIS program was formally initiated with MDRS (multidisciplinary research scheme) activities in 1974, in which Chemistry Group was also actively involved under the leadership of Dr. J. P. Mittal. The activity could be pursued successfully. However, the process is quite involved and complex requiring several gadgets, like lasers, molecular beam apparatus, etc. In mid 1980s, a phenomenon of Infrared Multiphoton Excitation (IRMPE) leading to dissociation (IRMPD) of a polyatomic molecule was discovered. This method of excitation was expected to selectively dissociate a bond being excited, and hence created a lot of euphoria about selective bond dissociation leading to successful separation of desired isotopes (<sup>34</sup>S, <sup>13</sup>C, D, T, <sup>235</sup>U). However, only a limited success could be achieved, since the energy pumped into a molecule gets randomized fast to all the vibrational modes. Subsequently, the weakest bond breaks irrespective of the vibrational mode of excitation.

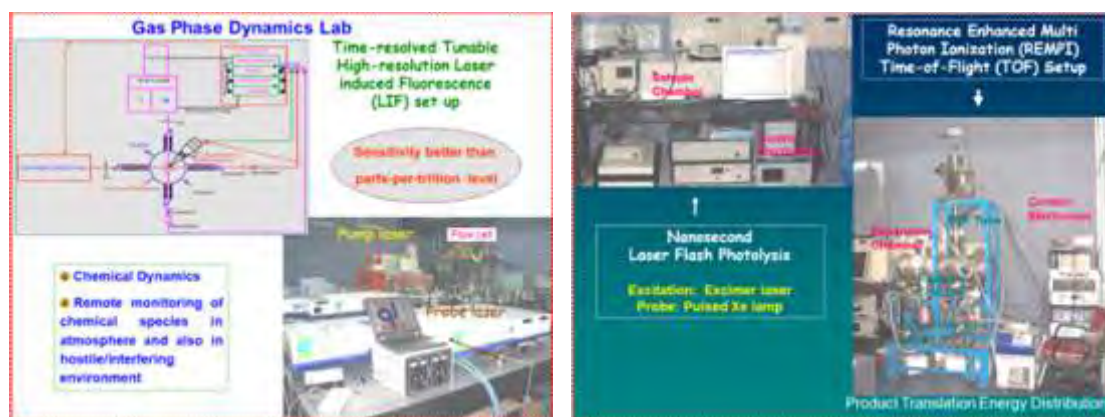
### ***Multiphoton excitation:***

Probably none of the phenomena in laser photochemistry discovered in the past is as exciting as IRMPE and IRMPD, wherein polyatomic molecules can dissociate by absorbing many single-frequency infrared photons. Since vibrational energy is quantized, this absorption is treated as a match between the photon energy and the energy levels gap. It is surprising since the energy difference between vibrational energy levels goes on decreasing as one move up the vibrational ladder. At the top, the levels are close enough to be continuous, the bond breaks and the molecule dissociates. Pulsed CO<sub>2</sub> laser facility in Chemistry Group was very useful in initiating IRMPE and IRMPD in several polyatomic molecules. Several organic compounds containing C-F bond, which have high absorption cross-section in the laser emission region, were investigated. Although dissociation occurs

mostly from the ground electronic state of the molecule, many times dissociation channels with unusual products or yields were observed. In a few cases, polyatomic molecules in the ground electronic state, but with very high vibrational excitation, relaxed to an excited state (lowest singlet state,  $S_1$ ) and emitted electronic fluorescence. This process of unusual relaxation ( $S_0$  to  $S_1$ ) is aptly known as Reverse Electronic Relaxation. Sulfur hexafluoride ( $\text{SF}_6$ ) was an ideal molecule for testing IRMPE and IRMPD. This molecule was also used to sensitize other molecules, not absorbing in the  $\text{CO}_2$  laser region, for investigating their dissociation dynamics. Some of the transient molecules (such as  $:\text{CF}_2$ , vibrationally excited benzene) formed during IRMPD could be detected with laser flash photolysis set up in UV/Visible region. The kinetics and spectral features of these molecules could be investigated, but with much difficulties because of small concentration of molecules in the gas phase. Some of the transients with vibrational excitation were also studied by measuring infrared fluorescence (IRF), and information on intramolecular and intermolecular vibrational energy transfer could be obtained. It was a real challenge to measure IRF spectra of a vibrationally excited product employing variable IR filters.

### *Frontiers in chemical dynamics:*

Real research in chemical dynamics i.e., obtaining microscopic details of a gas phase chemical reaction, started by developing molecular beam set up along with laser spectroscopic techniques in RPCD during 2000-2008. Various time-resolved and highly sensitive and selective laser techniques, namely LP-LIF (Laser Photolysis-Laser induced Fluorescence) and REMPI-TOF-MS (Resonance Enhanced Multiphoton Ionization-Time of flight Mass Spectrometer), were developed utilizing nanosecond lasers in the year 2000 and 2008, respectively. These two setups commissioned in the Gas Phase Dynamics laboratory (Fig. 1) are presented below.



**Fig. 1: Gas Phase Dynamics Laboratory**

Employing LIF and REMPI, laser-induced dissociation dynamics of several polyatomic molecules could be investigated. Nascent population distributions over rotation and vibration of the transient product OH radical were measured with LIF. Thus, partitioning of the available energy among various degrees of freedom of OH and its co-fragment was

estimated, and dynamics of dissociation could be predicted as statistical, impulsive or a combination of both mechanisms (hybrid). Energy distribution of the OH product is useful, because it determines reactivity of this radical with other molecules. Moreover, OH is an important tropospheric oxidant and known as tropospheric scavenger or detergent.

REMPI-TOF-MS technique was employed to investigate dynamics of formation of halogen atoms (mostly Cl and Br), important atmospheric oxidants next to OH, photodissociation of halogen-containing volatile organic compounds, which are atmospheric pollutants.

To study the transient dynamics in time region from microsecond to femtosecond, different spectrometers were developed in Chemistry Group. Initially, a flash lamp based photolysis setup was developed in 1970s to study the reaction dynamics in the microsecond time domain. A concentric cell filled with argon gas at high pressure was used for the generation of light flash with duration of  $\sim 15 \mu\text{s}$  full width half maxima (FWHM). The transient produced due to this flash lamp excitation was monitored using a CW-high pressure xenon lamp. Such setup was used to study the reaction dynamics between uranium and plutonium ions with carbonate ions. To further improve the time-resolution of the setup, a nanosecond laser flash photolysis setup was developed in 1985 to study the dynamics in the sub-microsecond time domain. Different excimer lasers were used for the excitation of the sample and broad band white light from a xenon arc lamp was used to probe the transient species. Such setup was used to study photoinduced processes of chemical species to understand their fate in the atmosphere. This setup was workhorse to identify and characterize triplet states of different classes of organic molecules.

### ***Ultrafast dynamics-Femtochemistry:***

Success in understanding nanosecond chemical dynamics made Chemistry Group scientists more ambitious, and encouraged them to take up a challenge to develop a femtosecond pump-probe setup indigenously for the first time in the country to initiate and record snapshots of chemical reactions with femtosecond ( $10^{-15}$  s) time resolution. An Argon-ion laser pumped colliding-pulse-mode (CPM) locked dye laser oscillator (70 fs, 620 nm and 100 pJ energy pulse) was developed in the year 1997. Pulse from CPM dye laser was amplified in a five stage Nd:YAG laser pumped amplifier to produce pulses of 300 fs, 30 Hz and 300 mJ energy. Using a  $\beta$ -barium borate (BBO) crystal the fundamental light was converted to 310 nm laser (second harmonic generation) pulse for the sample excitation. A white light continuum, generated in a water cell using 620 nm laser pulses, was used to probe the transients. Transient spectra were recorded using a dual-diode array detector. This home built femtosecond setup was used to understand some of the fundamental processes in the excited states, like conformational dynamics, H-bond reorganization, solvent relaxation, electron and energy transfer, etc.

The success of home built femtosecond spectrometer opened up the research in the femtosecond timescale in Chemistry Group. Subsequently, two state-of-the-art ultrafast spectroscopic facilities (Fig. 2), namely femtosecond transient absorption spectrometer and femtosecond fluorescence up-conversion setup were inducted in the year 2006 to expand the research in the ultrafast dynamics. The transient absorption spectrometer with a temporal

resolution of 100 fs was deployed to study the excited state dynamics by monitoring the spectral properties of transient species in wide spectral range (350-1100 nm and 3-8  $\mu\text{m}$ ). Use of optical parametric amplifier (OPA) along with a difference frequency generator (DFG) widened the scope of excitation of molecules to different energy levels (electronic, vibrational, etc.), and subsequently different molecular processes could be investigated. Such experimental facility was instrumental in embarking in the area of cutting edge research, like dye-sensitized solar cell (DSSC), biosensors, etc.

The femtosecond fluorescence up-conversion setup, with temporal resolution of 100 fs, was introduced in the Chemistry Group in the year 2006. Utilizing fluorescence as the probe, the up-conversion setup was used to study ultrafast electron, proton, charge transfer and solvation dynamics in homogeneous and heterogeneous media. This setup was instrumental in understanding the torsional dynamics of molecular rotors which lead to the development of very efficient and selective sensors for different bio-analytes.



**Fig. 2: Two ultrafast facilities to study the condensed phase chemical dynamics: Left- Transient absorption; Right-Fluorescence up-conversion**

In the year 2015, a two-dimensional infrared (2D-IR) spectrometer was developed indigenously for the first time in India (Fig. 3) to study the real time coupling between different chemical bonds which determines the structure and activity of chemical systems. A 1 kHz amplified femtosecond laser system along with two OPAs was used for the generation of mid-IR pulses (3-8 micron) with pulse duration of  $\sim 80$  fs. A simple and cost effective beam splitter based Mach-Zender interferometer was used for the generation of two collinear pump pulses, which were used to create perturbation in the sample which was further probed with another IR laser pulse. The instrument response function (IRF) of the set-up is  $\sim 150$  fs. Using this 2D-IR spectrometer, the layer wise hydrogen bond reorganization dynamics in confined water pool was investigated. From detailed spectral diffusion study, using an ultra-small IR probe (azide ion), it was demonstrated for the first time that the water molecules in a confined water pool behave quite similar to bulk water even in significantly smaller pool size than predicted by time-dependent fluorescence measurements. 2D-IR study also reveals a hidden anomalous solvation region in DMSO-water mixed solvent.



**Fig. 3: 2D-IR Spectrometer set up**

Femtosecond Laser-Induced Breakdown Spectroscopy (fs-LIBS) has also been set up in Chemistry Group in the year 2013 for detection of trace elements in bulk materials. This setup helped chemist to understand the interaction of high energy femtosecond laser pulses with matters of different origin and nature, which finds various applications such as in fuel reprocessing, and understanding rock composition and their formation, etc.

### ***Interfacial dynamics:***

After having fairly good understanding of dynamics in the gaseous and solution phase, scientists in Chemistry Group further widened the scope of studies at interfaces between air and solution. A highly selective and sensitive nonlinear sum-frequency generation (SFG) spectroscopic technique has been developed in the year 2012 to investigate structure, orientation and dynamics of a molecule at an interface. Both conventional and heterodyne detected SFG provide rich information on atmospheric pollutants, and biological molecules (drugs, amino acids, etc.) on phospholipids (mimic cell membrane) by measuring vibrational spectra of adsorbed molecules at an interface.

### ***Control science:***

The motivation to achieve reaction control is to suppress unwanted by-products, and synthesize new structures and new materials. Macroscopic parameters such as temperature, pressure, concentration and catalyst have been used for decades in the chemical industry to alter reaction rates. But all these are nonselective methods, and break the weakest bond due to an equipartition of the excitation energy into all the bonds. With the advent of lasers, mode-selective chemistry aimed at by activating only those bonds which are essential for the reaction. However, this goal was achievable only in a few small systems for mainly two reasons: First, it is essential to excite the molecular system to a higher vibrational state in order to overcome the activation energy. However, the anharmonicity of the potential impedes the excitation of more than one vibrational transition with a narrow-band laser. Second, intramolecular vibrational energy redistribution (IVR) in highly excited molecules is

highly efficient and equilibrates the energy into other vibrational modes on an ultra-short time scale. Therefore, simple excitation schemes are not suitable to accumulate the excitation energy in a certain mode over a sufficiently long time for carrying out bond selective chemistry. Some involved excitation schemes are required to accomplish the bond selectivity. Knowledge of overtone spectra of a polyatomic molecule is important for such a scheme of bond selective chemistry in the molecule. A molecule can be selectively excited to an overtone, which can be further pumped to a repulsive state of the molecule. To investigate the overtone vibrational bands of molecules, photoacoustic spectroscopy technique was also set up in the year 2001, and overtone spectra of water molecules were measured.

These constraints can be circumvented by an experimental set up of feedback-controlled self-learning loop which requires (i) high power fs-laser system and frequency conversion units to generate required wavelengths matching the absorption of the targeted molecule (ii) a computer-controlled pulse shaper, and (iii) an optimization scheme based on evolutionary algorithm.

Encouraged with all these developments, RPCD has built a facility called ‘Femto Cave’ to further pursue various activities in the control science regime of chemical dynamics (Fig.4) in the year 2013.



Fig. 4: Control science set up

### ***Single molecule fluorescence spectroscopy & imaging:***

All experimental techniques discussed above involve the interrogation of a large number of molecules which provide spectroscopic properties which is an ensemble average of all interrogated molecules. However, all such molecules may not behave exactly similar way, particularly in a heterogeneous media. Dynamic studies of individual molecules carry much detailed information about the system. Hence, Chemistry Group also embarked on single molecule spectroscopy (SMS) to understand the dynamics at a single molecule level (Fig. 5). This technique not only provides dynamical and spectroscopic information of a single molecule but also improves the sensitivity of detection to the single molecular level. This experimental facility was used to elucidate the coupling and interplay between the kinetics of photophysics, quenching, diffusion, and solute exchange from picosecond to seconds,

stitching all possible stages of molecular interaction in a single experiment. A state-of-the-art super-resolution orientation imaging setup was developed in the year 2015 to study the single molecule dynamics at nanoscale in a multi-dimensional spectroscopy scheme to extract not only rates but also reaction site and molecular orientation in 3D space. This setup has also been used to study the complexation kinetics of actinides, conformational changes of proteins at Angstrom scale due to complexation with metal, origin of fluorescence in carbon dots, photon antibunching, etc.



**Fig. 5: A home-built single molecule multi-parameter fluorescence spectroscopy setup**

### **Way forward:**

The sustained work during this period produced adequate new knowledge-base in laser induced chemistry, which is being applied and will be further intensely pursued for useful deliverables relevant to environment, energy and health. Some of these deliverables are: Measurement of environmental impact of volatile organic compounds (VOC), degradation of pollutants, green hydrogen generation, development of solar energy materials, development of photo-sensors, bio-sensors and radiation sensors, ultra-sensitive detection of single molecule, etc.