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ADVANCED TECHNIQUES IN RADIATION & PHOTO CHEMISTRY

Guest Editor

Dr. Sisir K. Sarkar

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Editorial

Dear Fellow Members,

We are happy to bring out a special issue on "Advanced Techniques on Radiation & Photochemistry". Our esteemed readers are well aware of the fact that ISRAPS organizes regularly Discussion Meeting on current topic of interest in the field of Radiation & photochemical Sciences. Subsequent to the discussion meting held on September 17, 2008, at CT & CRS building, Anushakti Nagar, Mumbai we have compiled four talks in this issue given by the experts in the field.

The first article discusses the recent development in picosecond pulse radiolysis studies and the efforts currently being put for building one such facility at BARC. In the second article, the authors demonstrate the capability of an indigenously built MB-REMPI-TOF facility and how it can be used as complimentary technique to LP-LIF for gas phase dynamics investigations. The next article brings out how the coherent properties of laser can be used to control various physical and chemical processes and their applications. In the last article innovative way of probing transition states of mechanically activated chemical reactions through single-molecule force-clamp spectroscopy has been presented.

Finally, we want to acknowledge the individual and collective contributions of the authors of this issue. It was a special opportunity to have worked with such an outstanding group. I thank Dr. Tapan K Ghanty for the help provided right from the inception for bringing out the issue.

Wishing you all scientifically rewarding New Year and happy reading.

(Sisir K. Sarkar)

Dr. Sisir K. Sarkar is presently the Head, Radiation & Photochemistry Division, BARC. He is also the Vice President of ISRAPS and Indian Laser Association (ILA). His research interest includes radiation & photochemistry with lasers and accelerators, chemical dynamics, spectroscopy and laser development.

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Message from the President and Secretary

Dear Members of ISRAPS and Readers,

New year greetings from the Executive Council of ISRAPS! The year 2009 started with holding an ISRAPS discussion meeting on "Structure & Dynamics of Complex Chemical Systems: An Interface between Theory & Experiment" held on February 16, 2009 at New Training School Building. National Symposium on Radiation & Photochemistry (NSRP 2009) was organized at Kumaun University, Nainital during March 12-14, 2009. We would like to thank Dr. Dipak K Palit of BARC and Dr. Sanjay Pant of Kumaun University for their effort in making the symposium successful.

All our efforts in recent months have been focussed on the preparation for organising Trombay Symposium on Radiation & Photochemsitry (TSRP-2010) in conjunction with Asia Pacific Symposium on Radiation Chemistry (APSRC-2010) to be held during September 14-17, 2010 at Treasure Island Resort, Lonavala. Preparation for holding an ISRAPS Discussion Meeting on "Design, Synthesis & Photochemistry of Dye sensitized Solar Cell (DSSC) Materials" is also underway.

Finally, we would like to thank Dr. Sisir K Sarkar, the Guest Editor of this special issue, for his efforts in bringing out a scientifically rich issue of ISRAPS bulletin containing four articles of varied interest in the field of advanced techniques in radiation and photochemistry. Thanks are also due to all the authors for contributing articles.

We wish to express our gratitude to each and every member of ISRAPS for their continued support and cooperation in carrying out the activities of the society.

(Dr. Tulsi Mukherjee)
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(Dr. Tapan K. Ghanty)
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Pulse Radiolysis Study in Picosecond Time-domain

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Introduction

The chemical effects of high-energy X-rays, γ-rays or charged particles are being studied since the end of the 19th century [1]. Discovery of the flash photolyis technique by Porter and Norrish in 1947 was an important step towards understanding the mechanism of photochemical reactions by detecting and characterizing the reaction intermediates in real time [2]. This discovery led the radiation chemists also to think about a similar spectroscopic technique for detecting and characterizing the short-lived intermediate radical species in radiation chemical reactions. As a result, the advent of the pulse radiolysis technique in 1962 [3] using pulsed electron accelerators as the radiation source synchronized with time-resolved spectrophotometry permitted the direct identification and reactivity of the transient intermediaries of the reactions. The principle of the technique, which is similar to that of the flash photolyisis technique, is to deliver a high irradiation dose in a the shortest possible time in the form of an electron pulse in order to get detectable concentrations of the short-lived species and to follow directly the evolution of the spectroscopic and kinetic properties during their fast reactions. The earliest but the most important observation was the hydrated electron, followed by the characterization of a large number of short-lived charged or neutral radical species, using microsecond electron pulses [4]. Later, the duration of electron pulse was shortened to a few nanoseconds and the pulse radiolysis has been established to be a well recognized powerful technique for studying the kinetics of high energy electron beam (low LET radiation) induced chemical and biochemical reactions in aqueous solutions, organic liquids, solids and polymeric systems. Truly, it has been used as an indispensible and complimentary to the flash photolysis technique. Bhabha Atomic Research Centre (BARC) has been concerned with the presence of high energy radiation at different sites or its use in different purposes and intensive work has been carried out in many fields using the nanosecond pulse radiolysis as well as the micro to femto second flash photolysis techniques. To mention a few of the most important areas of research, to which BARC has contributed significantly, are:

- Radical reactions in chemistry, biology, medicine and atmospheric chemistry.
- Radiation effects on nuclear materials.
- Radiation chemistry of water in nuclear reactors
- Water chemistry relevant to radioactive waste repositories.

Still there remain fascinating and important problems to be resolved:

- Solvation processes of electrons, cations and anions in the condition of high concentration and high pressure
- Geminate ion recombination and formation of excited states in liquids.
- Charge carrier dynamics in organic semiconducting materials and polymers, and so on. Many of these

processes occur in ultrafast (less than a few nanosecond) time scale. In order to understand the detailed mechanisms of these processes, the need for a pulse radiolysis equipment with pico or sub-picosecond time resolution has been realized.

Electron accelerators

Many electrostatic (e.g., Van de Graaff) and radio frequency (e.g., linac) accelerators with pulse widths on the order of a few nanoseconds are in use worldwide for pulse radiolysis. On the other hand, the number of pulse radiolysis facilities with time resolution shorter than one nanosecond is very small. The first radiolysis installation capable of resolving picosecond time scale kinetics was developed at the University of Toronto in the late 1960s [5]. It took advantage of the fine structure of 30 ps pulses contained within the 30 ns envelope of the accelerator macro-pulse. The stroboscopic transient detection system used optically delayed Cerenkov radiation generated by the individual electron bunches to probe transients created by later bunches within the macropulse. The picosecond time-resolution of the equipment led to many important findings on reactions within spurs [6]. During the 1970s and 1980s, pulse radiolysis facilities based on single-electron-bunch linear accelerators with pulse widths on the order of picoseconds were constructed at Argonne National Laboratory (Illinois), at the Nuclear Engineering Research Laboratory (NERL), University of Tokyo, in Tokai-Mura, Japan, and at Osaka University, Japan [7]. All three installations used a grid-gated thermionic cathode to inject electrons into a radio frequency prebunching section operating at a sub-harmonic of the accelerator frequency [2]. The subharmonic pre-buncher compresses the electron bunch until it can be inserted into the linac section within a single period of the RF frequency. After acceleration, magnetic compression is sometimes used to reduce the pulse width from 30 ps to 0.2–5 ps (vide infra). In addition to the linear accelerator facilities, a Van de Graff-based system in Delft, Netherlands, generates sub-nanosecond pulses [8].

RF photocathode gun based picoseconds accelerator: During the late 1980s and into the 1990s, a new generation of electron accelerators, which consists of a radio-frequency (RF) photocathode electron gun, which can generate an electron beam of sub-picosecond duration with the desired position-momentum relationship for acceptance into the acceleration section, has been developed [9, 10, 11, 12, 13]. Ultrafast accelerators require an injection system which deposits the entire electron bunch in a single RF period. To produce the electron beam a metal (Cu or Mg) or semiconductor (e.g. Cs_2Te) cathode, is struck with an femtosecond laser pulse of ultraviolet wavelength to cause it to emit electrons via the photoelectric effect. The electron pulse emitted from the photocathode is as short as the incident laser pulse (although it tends to expand during beam transport). The key to the RF photocathode gun technology is the existence of laser systems that can be synchronized to the microwave frequency to high precision (i.e., one degree of RF phase, or 1 ps at 2.856 GHz) and stability. Several commercial titanium sapphire (Ti: Sapphire) and Nd:YAG oscillators are available that actively regulate their cavity length to match their frequency to that of an external reference with the required precision and stability. The choice of laser system is governed by the required excitation energy (determined by the work function of the cathode), laser pulse duration (dependent on several factors) and laser pulse energy (determined by cathode quantum efficiency and the required per-pulse charge). Picosecond Nd:YAG systems are economical and may be used in some applications where their fixed pulse width is acceptable, however, femtosecond Ti: Sapphire systems are the prevailing choice because their high bandwidth permits adjustment of the laser pulse width to suit the application and they provide probe and pump beams with femtosecond resolution.

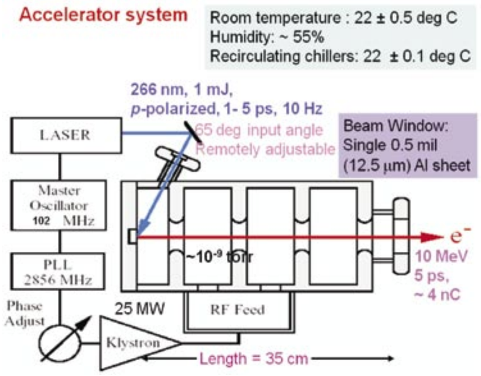

Figure 1: Schematic representation of a laser photocathode electron gun accelerator facility (LEAF) working in Brook Haven national Laboratory, USA..

The electron source and accelerator functions can be combined into a single unit called the photocathode electron gun. Centre portion of the back plate of the photocathode electron gun is coated with the photocathode material. Metal photocathodes such as copper or magnesium are easy to prepare but have low quantum efficiency ($\Phi \sim 10^3 - 10^4$). Semiconductor cathodes such as cesium telluride (Cs_2Te) have higher efficiencies, however, since the material is susceptible to oxygen, they need to bepreapred to be in-situ in high vacuum condition. All of these materials require excitation in the ultraviolet region; typically 266 nm is used because it is the fourth harmonic of Nd:YAG and the third harmonic of the Ti:Sapphire optimum gain region. Measurements on several operating accelerators indicate that approximately 20 microjoules of 266 nm light will excite 1 nanocoulomb of electrons from a clean magnesium cathode or only 70 microjoule of energy / pulse can produce about 7 nanocoulomb charge per pulse. Amplified 10 Hz laser systems can easily produce pulses in excess of 1 mJ at 266 nm, therefore available laser energy is not the limiting factor for charge extraction even with low-efficiency metal photocathodes. However, the high peak power at higher pulse energies can make it more difficult to maintain good mode quality as the laser beam propagates.

The RF photocathode gun consists of one or more conducting resonant cavities, which are filled with several megawatts of microwave power to create transient electric field gradients of 80 to 100 MV/m. The first cavity, or cell, of the electron gun is typically only 50-60% as long as the microwave wavelength, with a disk of photocathode material mounted in the back plate of the gun. When the field gradient is optimal at the photocathode surface, a pulse of laser light is used to generate photoelectrons. The high field gradient accelerates the photoelectrons to MeV energies in a distance of several centimeters. A 1.5 cell photocathode electron gun can accelerate several nanocoulombs of electrons to ~4 MeV using 8 megawatts of RF power. A 3.5 cell gun, such as the one driving the Laser-Electron Accelerator Facility at Brookhaven National Laboratory, uses 15 MW to accelerate electrons to 9 MeV in a distance of 30 cm. Beam energies of 4 – 9 MeV are sufficient for most pulse radiolysis applications, however, additional acceleration stages may be used. RF photocathode guns can generate electron bunches with very clean phase space correlations between their position and momentum distributions. This attribute is very desirable for applications where beam manipulation is important, such as pulse width compression. This type of accelerator is becoming very common as an injector for free electron laser systems, and other applications, where good beam quality is essential.

Beam Transport: Ultimate control of the electron beam pulse width of an ultrafast accelerator system rests with the beam transport system. Space charge effects spread the electron bunch in the longitudinal and transverse directions. Transverse spreading is typically controlled by pairs of quadrupole magnets spaced along the beam line. The primary consideration for transverse focusing is to prevent loss of the beam against the sides of the beam pipe while avoiding compressing the beam into a tight waist until it reaches the target, in order to avoid scrambling the position-momentum correlation which permits strong temporal compression. An aluminium plate of about 5 µm thickness is used at the exit port of the electron beam.

Pulse Compression*:* Longitudinal compression of the electron bunch is used to reduce the pulse width at the target to the shortest value possible. Compression schemes rely on having a correlation between particle velocity and position within the bunch. Such correlations obtain naturally from photocathode injectors; they can be induced in thermionic-generated beams by modulation of the phase and power of accelerating sections. Dipole bending magnets can then be used to make particles of various energies travel paths of different lengths to arrive at the target at the same time. An example of a chicane-type compressor is given in Figure 2 [14]. On the left of the figure, a diagram shows the phase-space distribution of the electron bunch before traverse of the chicane. The velocity of each particle (v_z) is plotted as a function of particle position (z) along the axis of propagation. The leading edge of the bunch is at the lower right (a), meaning that the slower electrons are leading. The bending magnets in the chicane cause the lower energy electrons to take the longest path so that they are delayed to coincide with the faster electrons at the exit to the chicane, as indicated in the phase-space diagram on the right. In actual cases the compression would be slightly less than complete at the exit of the chicane in order to allow for evolution of the packet until it hits the target.

Measurement of the pulse width of an ultrafast electron beam*:* Transition radiation (TR) is generated when an energetic charged particle passes across an interface between regions of substantially different dielectric constants. TR emission occurs over a wide range of wavelengths depending on the particle energy and TR radiator material. Typically, an aluminum plate or foil is used to generate the TR, which has specular optical characteristics and is emitted backward (upstream) and forward (downstream) as the beam crosses the front and back surfaces of the aluminum foil. If the foil surface is oriented at an angle of 45° with respect to the beam, the backward TR will be emitted at an angle of 90° to the beam. Polished aluminium plates that can be inserted into the beam at 45° angles are used as optical TR beam profile monitors. The TR

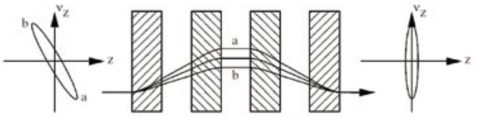

Figure 2. Pulse compression using a chicane configuration.

beam images are collected by ordinary video cameras. Transition radiation is considerably weaker than Cerenkov radiation, however since it is a surface phenomenon it avoids problems with radiator thickness and reflections inherent to Cerenkov-generating silica plates. Optical TR can be measured using a streak camera. An optical TR system has been used to time resolve the energy spread of an electron macropulse in a free-electron laser facility [15]. Interferometry of coherent, far-infrared TR has been used to measure picosecond electron pulse widths and detect satellite pulses at the UCLA Saturnus photoinjector, using charges on the order of 100 pC [16].

Transient detection

With the advent of laser-pulsed photocathode accelerators, a new approach to pulse-probe detection has been possible. Spare output from the laser system which is used to generate the photoelectrons, can be used to create a probe beam synchronized to the electron pulse with resolution on the order of 100 fs. Optical parametric amplification and harmonic generation can be used to generate probe wavelengths from the UV to the near-infrared. Near-infrared wavelengths are important for optical studies of the electron in non-polar solvents. A laser probe beam will have much lower divergence and higher intensity than a Cerenkov probe; both features serve to reduce interference from Cerenkov light generated from irradiation of the sample itself. Figure 3 shows the layout of the dual-beam pulse-probe laser detection system. Placement of the sample photodiode at a distance from the sample allows Cerenkov light from the sample to diverge, reducing its effect on the absorbance measurement. Absorbance measurements can be normalized using the Faraday cup readings to correct for fluctuations in beam intensity. Pulse-probe transient absorption data on the rise time of prompt species such as the aqueous electron can be used to measure the instrument response of the system and deduce the electron pulse width. Figure 7 shows the rise time of aqueous electron absorbance measured with the LEAF system at 800 nm in a 5 mm pathlength cell. Differentiation of the absorbance rise results in a Gaussian response function of 7.8 ps FWHM. Correcting for path length, the electron pulse width is 7.0 ps in this example. The pulse-probe technique can be extended to multi-wavelength detection by using the ultrafast laser pulse to generate a white-light continuum probe, which can be dispersed with a spectrograph across a diode array or CCD detector after traversing the sample. Due to lower probe intensity, Cerenkov emission from the sample would be expected to be more of a complication in this case, but the correction methods developed for stroboscopic Cerenkov detection would also work here.

Time-resolution of the pulse radiolysis set up: It is useful to reiterate the inherent time resolution limitations of techniques that combine charged particle excitation with optical detection. Energetic charged particles travel through a medium at velocity βc, where c is the velocity of light in vacuum, and $\beta = 0.9988$ for 10 MeV electrons, respectively. Light travels through a medium at velocity c/n, where n is the refractive index ($n = 1.33$ for water at 600 nm, for example). In the time it takes 600 nm photons to travel unit distance through water, 10 MeV electrons will travel $\beta n = 1.33$, meaning that the photons will fall 1.1 ps behind for every millimeter of sample depth, if the pulses were pure impulse functions. Empirical measurements with near-Gaussian optical and electron pulses at 800 nm with 8.5 MeV electrons indicate that the FWHM response function broadening increases by 700 fs for every millimeter of travel through water. Therefore, time resolution is ultimately limited by sample depth, the choice of which is affected by considerations such as detection sensitivity, signal strength and the ability of the sample to tolerate signal averaging. Because of this limitation, ultrafast in the context of accelerators refers to timescales from a few hundred femtoseconds to tens of picoseconds.

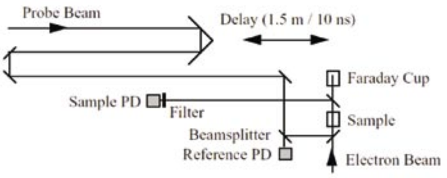

Figure 3. Schematic representation of the LEAF pulse-probe detection system.

It becomes evident that although it has become possible to use femtosecond-pulse electron beam and femtosecond laser light in pulse radiolysis, the resolution is limited by the difference in group velocities of the electrons and the light in sample. However, recently Tagawa and his co-workers have introduced a concept of equivalent velocity spectroscopy (EVS) into pulse radiolysis and demonstrate the methodology experimentally [17]. In EVS, both the electron and the analyzing light pulses precisely overlap at every point in the sample and throughout the propagation time by rotating the electron pulse. The advance allows us to overcome the resolution degradation due to the different group velocity. We also present a method for measuring the rotated angle of the electron pulse and a technique for rotating the electron pulse with a deflecting cavity.

Picosecond pulse radiolysis facility in BARC

Radiation & photochemistry Division, BARC, is presently engaged in setting up a picosecond pulse radiolysis facility. The block diagram of the proposed facility is shown in Figure 4 and the facility lay-out is shown in Figure 5. The followings are the specifications of the proposed picosecond linear accelerator, which is being fabricated under a collaboration project with RRCAT, Indore.

Beam energy: 9 -10 MeV.

Charge: 3 – 6 nano-Coulomb

Electron beam current (peak): 6000 Amps,

Average beam current: 6 x 10^{-5} mA

Pulse duration: 1 to 5 picosecond

Pulse repetition frequency : 10 Hz

Average beam power : 0.6 watts.

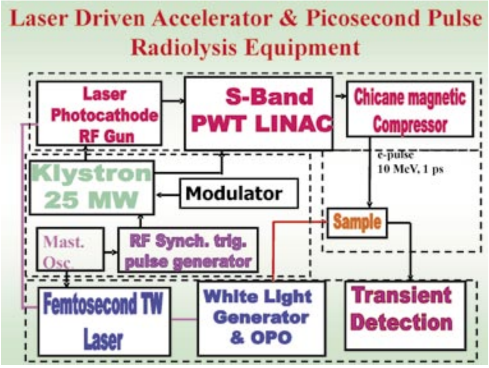

Figure 4: Block diagram of the picosecond pulse radiolysis facility being developed in BARC

Picosecond accelerator will consist of two stages:

A. Photo-cathode RF gun: 3Mev

B. PWT Linac: 7 MeV.

Both the RF gun and the PWT Linac system will be energized by a single 2856 MHz, 25 MW, 5 ms, 10 Hz microwave system driven by a 25 MW Klystron.

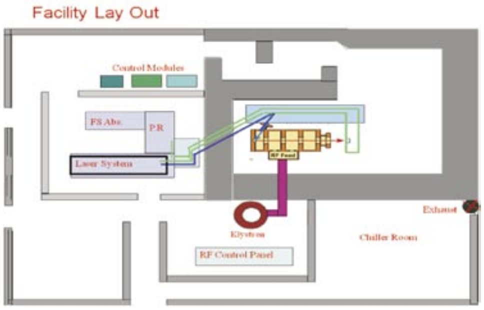

Figure 5: Lay-out of the pulse radiolysis facility being developed in BARC.

Acknowledgement

The author gratefully acknowledges the active collaboration with Dr. S. Krishnagopal, Nuclear Physics Division, BARC, Mumbai, and Dr. Kamal Pant and his group in Beam Physics and Free Electron Laser Laboratory, RRCAT, Indore. The author is also grateful to Dr. S. K. Sarkar, Head, RPCD, BARC and Dr. T. Mukherjee, Director, Chemistry Group, BARC, for their constant encouragements.

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Dipak K. Palit Joined then Chemistry Division of Bhabha Atomic Research Centre, Mumbai, in 1983 after completion of the one-year Orientation Course of the BARC Training School in Chemistry Discipline. Since then he has been associated with the photo & radiation chemistry group of BARC. Over the years, he has developed the ultrafast time-resolved spectroscopic techniques to study the dynamics of light and high energy radiation induced chemical reactions in condensed phase. In recognition to his work in this field, he has been awarded L. M. Yeddanapalli Memeorial Award of Indian Chemical Society (1999), Bronze Medal of the Chemical research society of India (2001), and the Homi Bhabha Award for Science and Technology of DAE, India (2002). He is a fellow of the Indian Academy of Sciences (F. A. Sc.) and the National Academy of Sciences (F. N. A. Sc.)

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Molecular Beam-Resonance Enhanced Multiphoton Ionization: Basic Concepts and Instrumentation

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1. Introduction

Photons have been used extensively as an excitation source for a variety of spectroscopic techniques [1]. Photons from the lamp and other conventional sources can be employed only for the linear optical processes, where a single photon is absorbed. The advent of the lasers has greatly enhanced the capabilities of spectroscopic techniques vis-à-vis conventional techniques, apart from addition of many new techniques. The high intensity of laser beam allows one to develop spectroscopic tools based on even the weak processes, such as Raman scattering and higher order processes, which were not practicable, using conventional light sources. The most important techniques in this category are based on the nonlinear phenomena. It is well known that the contribution of higher order terms to induced polarization becomes significant only at very high photon intensities, since intra-atomic electric field is very high. The contribution of higher order terms in induced polarization, P, can be approximately estimated from the famous Bloembergen expression,

$$P^{(n+1)} / P^{(n)} = E/E_{at,} \qquad (1)$$

where E is the electric field of the incident electromagnetic light wave and E_{at} is the intra-atomic electric field, which is typically of the order 3×10^8 V/cm. Even at high radiation intensities of 10^9 W/cm^2, the ratio of succeeding polarization is small, about 10^{-3}. This shows why non-linear processes are negligible with conventional light sources, and why high intensities of laser radiation are required to exploit such processes. The most widely used spectroscopic techniques in chemistry are based on absorption and emission of electromagnetic radiations. In the above technique, for the measurement purpose, the photons transmitted in the case of absorption process or emitted in the case of emission process, are converted into charged particles, which is an inefficient process, and thus has low sensitivity. For the enhanced sensitivity, it is desirable to have an analytical technique where the charged particles are generated in the process itself. The conventional ionization techniques employed are more sensitive than absorption and emission techniques, however, they lack the selectivity unless coupled with mass separation technique.

Resonance Enhanced Multiphoton Ionization (REMPI), as the name itself suggests, uses multiple photons for the formation of ions, and thus requires high intensity photon sources, such as lasers. In most of the chemical species, the ionization level lies a few eV above the ground state, and thus to reach this level by a single photon absorption either a vacuum-UV or an X-ray photon source is required. However, tunable sources in the above regions are difficult to generate, and also lack selectivity of chemical species in ion formation. To obtain the selectivity, it is desirable to induce ionization by multiphoton absorption, where some of the photons are resonantly absorbed; this gave birth to REMPI. The resonance ionization is a photo-physical process in which electromagnetic radiation is used to ionize atoms, or molecules, via a resonantly-prepared excited state. In this process, an atomic or a molecular system serves as a summing device for storing the energy of resonantly absorbed photons. When the stored energy exceeds the ionization energy, this leads to spontaneous ionization. In most of the chemical species, the resonantly prepared excited state is just one transition below to the ionization continuum.

REMPI is designated as (m+n) REMPI, on the basis of the number of photons (m) employed resonantly to prepare the excited state and that (n) employed to ionize the excited state. Thus, the REMPI process, in which one photon is used for resonant formation of the excited state, and an other for pumping the prepared state into the ionization continuum, is designated as (1+1) REMPI. This process occurs when the excited state prepared by mono-photonic absorption has energy more than half of the molecular ionization energy. The above ionization process requires relatively low laser intensities, and thus leads to the minimal fragmentation of the parent ion. The other variants commonly employed are (2+1) and (3+1) REMPI, where two and three photons, respectively, are resonant with the electronic transitions. Fig. 1 depicts (1+1) REMPI process with a single and two colour photons.

2. Experimental

2.1. Simple REMPI setup

A simple REMPI setup is shown schematically in Fig. 2. In this setup an excimer pumped dye laser is employed for resonance-enhanced ionization. The ionization chamber is made up of stainless steel, with two optical windows on the opposite sides for laser entry and exit. Two plates are mounted at the centre of the chamber, parallel to each other and to the laser beam propagation axis. The analysis chamber has suitable ports with shut-up valves for gas inlet and pumping. A suitable pressure gauge head is mounted on the chamber for pressure measurement. The chamber is pumped to the base vacuum, before filling with the sample for analysis, which is carried out either in a static or in a flow condition. A suitable dye is used in the dye laser to generate wavelength range suitable for exciting the sample molecule of interest for REMPI signal. In most of the cases, the wavelength of interest is generated either by frequency doubling the fundamental of dye laser output or by further mixing frequency doubled output with the pump laser fundamental. A suitable high voltage is applied to the plates, and other connections are made, as shown in the Fig. 2. The dye laser beam is mildly focused at the centre of the two plates, and its wavelength is tuned. In the non-resonant condition, a small signal is obtained, however when the wavelength is in the resonant condition with some transition (either single photonic or bi-photonic), an

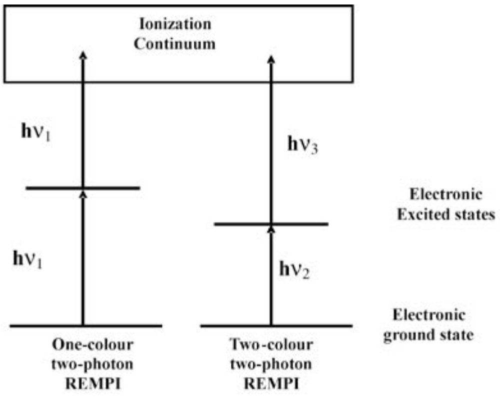

Fig.1: Two variants of (1+1) REMPI technique.

enhanced signal is obtained. By keeping the laser intensity to a moderate value, a very good ratio of the resonant to non-resonant signal can be obtained. The S/N ratio can be further improved on averaging the signal obtained through a charge sensitive detector by a boxcar integrator.

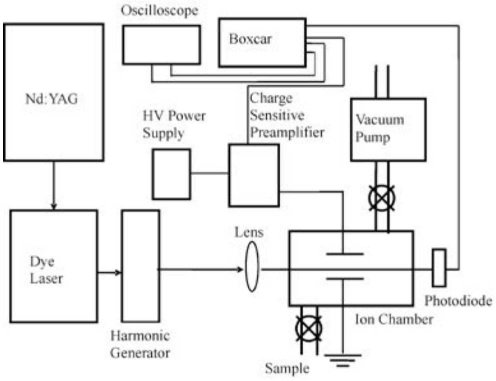

Fig.2: Schematic of simple REMPI setup.

Fig. 3 shows variation in the ion signal as a function of wavelength, for different benzene concentrations. It has been observed that for benzene, a detection limit of 5 ppb can be achieved with S/N=3, on single shot data collection [2]. This can be further improved to sub ppb, by averaging the signal for 100 shots or more. Although the detection limit and sensitivity obtained by the above simple setup can be employed in many applications, however, for the trace analysis of a chemical species in the atmospheric air, a ppt level detection limit is desirable. The obvious question is, whether it is possible to improve the detection limit and selectivity further?

2.2. Supersonic Jet REMPI-TOFMS

In the above analysis, the gas sample is at the room temperature, and, thus, due to a wide population distribution in the ro-vibrational states, given by the Boltzmann expression, only a small fraction of the total available molecules is accessible to the excitation process. This suggests that, in order to improve the REMPI detection limit, the population in the ground state has to be enhanced. Further, to reduce the broadening and to make the transition sharp, collisions between the sample gas molecules themselves, as well as with the background gas molecules are to be minimized. Both the above objectives can be realized by employing a hydrodynamic source, where the sample to be analyzed is expanded through a nozzle into high vacuum. The requisite parameter to obtain hydrodynamic flow is that the source Knudsen number (K_n), $K_n = \lambda/D$, is far less than unity ($K_n << 1$), where λ is the mean free path and D is the characteristic dimension (diameter or width of the nozzle). The above condition ensures sufficient collisions during expansion, and thus, during the expansion, the random thermal energy of the gas or vapour gets converted into directed kinetic energy of the flow through elastic collisions, resulting in a very low temperature, without the perturbation and the spectral broadening inherent in conventional static cooling. In addition, it retains the super-cooled molecules in the gas

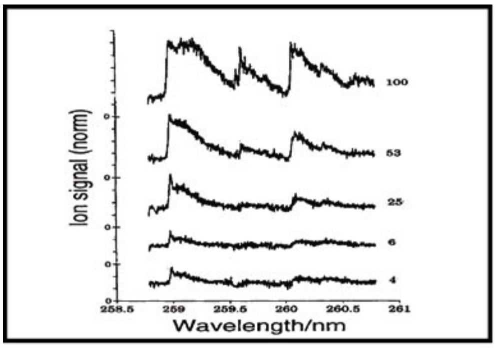

Fig.3: Variation in ion signal as a function of wavelength at different benzene concentrations in ppb.

phase in sufficient density. The process of cooling begins with the translational degrees of freedom of gas molecules through elastic two-body collisions. The cold translational bath subsequently acts as a refrigerant for other degrees of freedom. The distinctive feature of a supersonic expansion is that the molecule of interest is in contact with the cold bath only for a finite duration, and, therefore, the final state of the system is governed by kinetics rather than by thermodynamics. Since condensation is a much slower process than the rotational or even the vibrational relaxation, extensive internal cooling can be achieved, before condensation takes place.

In the hydrodynamic expansion process, the reduction in the transverse velocity component leads to a decrease in the Doppler width, which helps in reducing the spectral congestion and improving the overlap of the laser spectral profile with the molecular transition. The first factor helps in selectivity improvement, while the latter for sensitivity enhancement. The internal cooling leads to a reduction in the population distribution, which makes a higher fraction of the molecules available for excitation by the tuned laser pulse. Fig. 4 shows the schematic of jet part for jet–REMPI-TOF. Here, the gas sample is expanded through a nozzle, and irradiated at the transition region between jet and molecular beam. This configuration has the higher sensitivity than the simple gas sample due to advantage of both high number density (not skimmed) and high cooling [3,4]. This technique has been extensively employed for environmental and pollution monitoring, with its sensitivity at ppt level. The selectivity in the above technique can be further improved by combining it with the TOF detection technique. Here, the ions of different m/z acquire the same kinetic energy, provided by the applied acceleration potential. However, the ions of different m/z have different velocity, and, thus, arrive at the detector as separate pulses of ions. The JET-REMPI-TOF has an advantage of the two-fold selectivity, the selectivity in mass as well as wavelength of excitation.

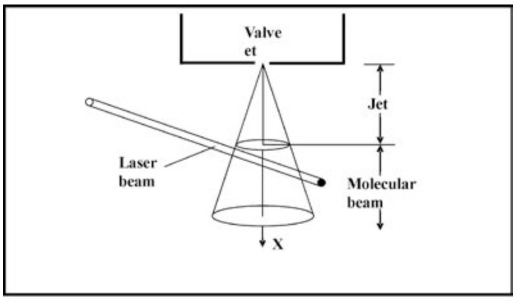

Fig.4: Schematic of jet REMPI setup.

REMPI, being a versatile tool, can be combined with many other techniques for enhancing its analytical ability. It can be employed for both the on-line and the off-line analyses. In many basic research facilities, it is used as an in-situ analytical tool, with time resolution determined by the excitation laser pulse width. We have developed Molecular Beam-Resonance Enhanced Multiphoton Ionization -Time-of-Flight (MB-REMPI-TOF), a highly sophisticated analytical detection system [5], having advantages of the three techniques embedded in its name. In the coming sections, important aspects of the system with basic work on photodissociation dynamics carried out employing the setup are described.

2.3. Molecular Beam REMPI-TOF

The main interest in the development of this system was to carry out studies on photodissociation dynamics. In order to reduce the population of the higher internal states of the dissociating molecules, we have prepared the supersonic molecular beam of chemical species of interest by supersonic expansion of the molecules in a buffer gas, like helium or argon. The ions of different m/z are analyzed on the basis of their flight time to the detector, at a fixed accelerating electric potential. The molecular beam is intersected in the extraction region of a Wiley-McLaren type TOF mass spectrometer [6] by the photolysis laser beam. The stable products and the radicals produced on photodissociation are ionized by a probe (ionization) laser beam, propagating perpendicular to both the photolysis laser and the molecular beams. The generated ions are accelerated, passed through a field-free flight tube, and detected by a pair of microchannel plate (MCP) detector, and identified by their flight time.

The photograph of the integrated system is shown in Fig. 5. The MB-REMPI-TOFMS system consists of differentially pumped two vacuum chambers, the expansion chamber and the ionization-cum-detector chamber. The expansion chamber houses the nozzle-skimmer assembly, and is pumped by a turbo molecular pump (900 l/s, Alcatel, France). The ionization chamber houses TOFMS and fly-through fast ionization gauge, and it is pumped by a turbo-molecular pump of speed 400 l/s (Elettrorava, Italy).

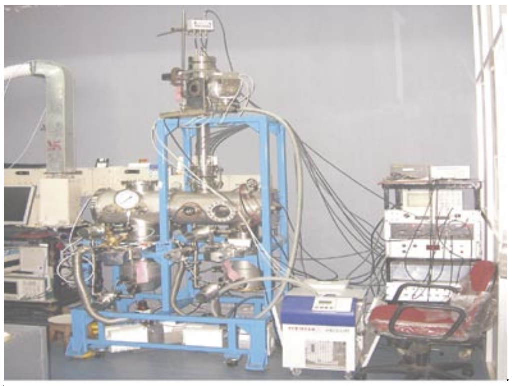

Fig.5: Photograph of the integrated system of MB-Tof-REMPI setup.

In the present system, the TOFMS assembly, similar to Lubman and Jordan design [7], is used. It consists of three parts, ion source, analyzer, and a detector. All the ion optics plates of analyzer are 5 cm square in size, and placed 1 cm apart, using insulator beads. The extraction and the accelerator plates have circular aperture of diameter 1 cm at the centre, which are covered by 50 lines/inch stainless steel grids, having 90 % transmission. To direct the ion beam along the axis of the field-free tube, and thus onto the detector, two pairs of plates are placed orthogonal to the detector axis (z axis). They are located above the accelerator plates. This is followed by the field-free drift tube. At the end of this tub, a T-connector, having 6-inch conflate flanges at the ends, is mounted. Two other to arms of the T-connector are used for connecting Gate valve and 250 l/s Turbo pump (Pfiffer, Germany). A dual microchannel plate (MCP) detector is mounted at the other end of the gate valve, for detecting the arriving ions. The above pump is used for pumping the detector region to obtain better vacuum level in the detector region, and the gate valve to isolate the detector from the other assemblies.

The schematic of the control electronic system is shown in Fig. 6. A digital delay/pulse generator, with pulse resolution of 20 ps, was employed as the master to trigger all the instruments for time synchronization. The time delay between the applied trigger pulse to the pulsed valve and the valve opening was obtained by measuring the delay between the trigger pulse and the fast ionization gauge (FIG) signal, employing a digital oscilloscope. This delay is the sum of the time required to open the pulsed valve from its trigger input and that for the molecular pulse to reach FIG from its generation, i.e., the nozzle exit. By measuring these time delays for different FIG positions with respect to the skimmer, the flow velocity of molecular beam is estimated, and used to obtain the time required for the molecular beam to reach the extraction region of TOF.

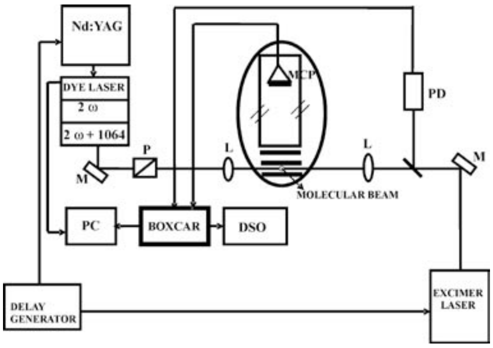

Fig. 6: Schematic of the control electronic system.

Fast photodiodes (Becker-Hickl Model PDM-400) were used to measure the time delays between the external-trigger inputs and the laser outputs for the photolysis laser (excimer laser) and the probe laser (Nd:YAG pumped dye laser). Based on above measured delays, the trigger pulses of different instruments were adjusted, so that the photolysis laser pulse and the molecular beam pulse arrive in the interaction zone at the same time, but at 50-100 ns prior to the probe laser pulse.

2.3.1 Photodissociation Dynamics Studies Employing MB-REMPI-TOF

The main aim of photodissociation dynamics studies presented here, employing MB-REMPI-TOF, is to explore capability and versatility of the system. For this purpose, we have chosen $CHBr_3$, a molecule having different dissociation pathways, depending on the excitation wavelength. It has been estimated by Sturges and co-workers [8] that bromoform contributes about 3% of the total bromine measured in both the troposphere and the lower stratosphere. However, it accounts for more than 9% of the reactive bromine in the stratosphere, due to its high absorption cross section. Therefore, from the point of view of stratospheric ozone destruction, the photodissociation of $CHBr_3$ has received a lot of attention. The following are some of the important dissociation pathways based on energetics,

$$CHBr_3 \rightarrow CBr_2 + HBr \;\; 245 \text{ kJ/mol}, \quad (2)$$

$$\rightarrow CHBr_2 + Br \;\; 258 \text{ kJ/mol}, \quad (3)$$

$$\rightarrow CHBr + Br_2 \;\; 349 \text{ kJ/mol}, \quad (4)$$

$$\rightarrow CBr + HBr + Br \;\; 530 \text{ kJ/mol}. \quad (5)$$

Further, in reactions 3 and 5, Br atom may be formed in the ground state $Br_{3/2}=(4P^5\ ^2P_{3/2})$ or the spin-orbit excited state $Br_{1/2}=(4P^5\ ^2P_{1/2})$, hereafter, referred to as Br and Br*, respectively. It is well known that in photolysis of bromoform [9], Br atom elimination is a major channel. Hence, the present study is directed to measure the Br/Br* ratio in photodissociation of bromoform at ~ 234 and 248 nm. For this purpose, the molecular beam of $CHBr_3$ was generated by flowing helium through a bubbler, containing $CHBr_3$ at room temperature and at total stagnation pressure of 1.5 bar. The photodissociation dynamics experiments were performed by combining REMPI and TOF mass spectrometer to state-selectively monitor Br and Br* atoms. The (2+1) REMPI transitions of Br and Br* atoms, in the wavelength region of 230-235 nm, were used to probe Br and Br* atoms. The laser pulses were generated from a Quantel dye laser, TDL 90, using rhodamine 101 (LC 6400) dye solution in methanol, pumped by a Quantel seeded Nd:YAG laser, YG-981-C-20. The fundamental dye laser output is frequency-doubled in a KDP crystal and mixed with the fundamental output of the Nd:YAG laser, to obtain an output in 230-235 nm range. The final output was separated from the rest of laser beams, using a set of four Pellin-Broca prisms. In most of the experiments, the same laser beam, one-colour, employed as the pump and the probe laser, i.e., for photodissociation of the parent molecule and ionization of the photoproducts Br and Br* atoms. In this case, the laser beam was focused by a lens of 280 mm focal length, and the distance of the lens from the molecular beam axis varied to obtain the best ratio of on- and off-resonance signal. Fig.7 shows a typical TOF spectrum of the Br product from $CHBr_3$.

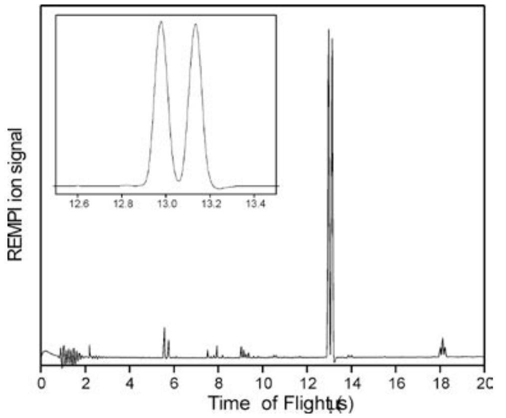

Fig.7: A typical TOF spectrum of photoproduct Br atom from $CHBr_3$ in time domain; ^{79}Br and ^{81}Br can be seen at 12.95 and 13.15 µs, respectively.

In two-colour experiments, the photolysis laser (248 nm excimer laser) beam was overlapped with the molecular beam and the counter propagating probe laser (dye laser) beam at the ionization region of TOF. The photolysis laser beam was focused with a lens of focal length 500 mm. The typical delay between the photolysis and the probe laser was 50 ns.

The REMPI spectra was obtained by recording the TOF signal at m/z=79 and 81, as a function of the probe laser wavelength. The typical spectrum obtained is shown in Fig.8. The assignments to the resonance transitions obtained in the present study are given in the Table 1, which match very well with the literature reported values.

Table 1: REMPI transitions of Br

Peak No	Experimental wavelength	Literature wavelength	Two photon Transition From 4p
1	233.74	233.70	$6p\,{}^4P_{3/2} \leftarrow 4p\,{}^2P_{3/2}$
2	234.09	234.04	$6p\,{}^2S_{1/2} \leftarrow 4p\,{}^2P_{1/2}$
3	234.41	234.35	$6p\,{}^2D_{5/2} \leftarrow 4p\,{}^2P_{1/2}$
4	234.61	234.57	$6p\,{}^4S_{3/2} \leftarrow 4p\,{}^2P_{1/2}$
5	234.92	234.86	$6p\,{}^2D_{3/2} \leftarrow 4p\,{}^2P_{1/2}$
6	235.30	235.32	$5p\,{}^2F_{5/2} \leftarrow 4p\,{}^2P_{1/2}$
7	235.93	235.66	$5p'\,{}^2P_{1/2} \leftarrow 4p\,{}^2P_{1/2}$
8	236.00	235.87	$5p'\,{}^2P_{3/2} \leftarrow 4p\,{}^2P_{1/2}$

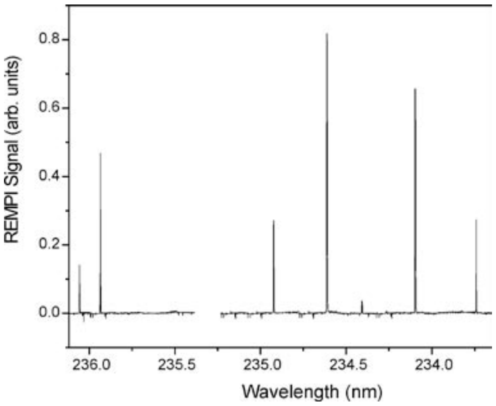

Fig.8: REMPI spectra of Br produced from $CHBr_3$.

The relative quantum yields of Br and Br* were extracted from the relative integrated signal intensities in the TOF spectrum.

$$\frac{N_{Br*}}{N_{Br}} = p\frac{I_{Br*}}{I_{Br}} \qquad (6)$$

$$\Phi_{Br} = \frac{N_{Br}}{N_{Br}+N_{Br*}} = \left(1+N_{Br*}/N_{Br}\right)^{-1} \qquad (7)$$

$$\Phi_{Br*} = \frac{N_{Br*}}{N_{Br}+N_{Br*}} = \left(1+N_{Br}/N_{Br*}\right)^{-1} \qquad (8)$$

where N_X and I_X are number and integrated signal, respectively, for the species indicated in the subscript. The parameter *p* is the ratio of the oscillator strengths for Br and Br* transitions. The ratio of integrated areas for two-photon transitions of Br* and Br is found to be 3.1 (depicted in Fig. 9), which estimates Br* ($^2P_{1/2}$)/Br ($^2P_{3/2}$) ratio to be 1.4, using *p*=0.46 [10]. Similar value (1.38) for the relative yield of Br* ($^2P_{1/2}$)/Br ($^2P_{3/2}$) was observed in photodissociation of BrCl at 235 nm [11]. In a purely statistical process, the ratio should be the same as the ratio of 2J+1 values, which is 0.5. The wide difference between the observed and the statistically estimated values can not be accounted for by the Boltzmann factor. Thus, it seems that there are some interactions between states in the exit channel.

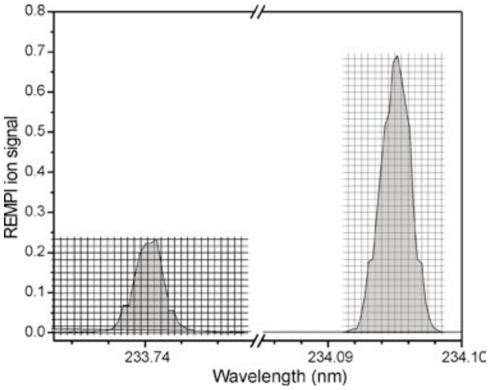

Fig. 9: Ratio of integrated areas for two-photon transitions of Br* and Br.

3. Conclusions

REMPI, being an ionization based technique, is very sensitive, and used for trace analysis, either standalone or in combination with other techniques. It can be employed for both on-line and off-line analyses. In many basic research facilities, it is used as an in-situ analytical tool, with time resolution determined by the excitation laser pulse width. Of particular interest and promise for the real-time characterization of atmospheric pollutants is the combination of a pulsed supersonic molecular jet with REMPI and time-of-flight mass spectrometry (TOFMS). We have developed Molecular Beam-Resonance Enhanced Multiphoton Ionization -Time-of-Flight (MB-REMPI-TOF) technique, a highly sophisticated analytical detection system, having advantages of three techniques embedded in its name. This system is being used for photodissociation dynamics of halogenated hydrocarbons.

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Coherent Control Technologies and its Applications

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Abstract

Coherent control of molecular dynamics deals with the steering of quantum mechanical systems with suitably shaped femtosecond (fs) laser pulses. The coherence properties of the laser are exploited to achieve constructive interference for a predefined target wave function via a phase corrected superposition of wave functions. The goal of coherent control, the selective preparation of a target state, is an important prerequisite for mode-selective chemistry. Controlling the outcome of chemical reactions by specifically tailored fs laser pulses is a fascinating perspective, which has recently become experimentally feasible and successful control experiments have been demonstrated the great versatility of this technique to selectively influence light matter interaction in complex systems. The required shape of the laser field is determined in a feedback-controlled regulation loop which uses a signal derived from the experiment as feedback. The loop is repeated until a pulse that suits the requirements is obtained. The concept of coherent control is to adjust the spectral and temporal characteristics of the excitation light to the molecular resonances and dynamics, such that these can be selectively addressed and manipulated. This has implications on enriching our understanding on mode selective chemistry and control of molecular dynamics. This technique has the potential to control chemical reactions and develop various exciting future applications.

Introduction

The laser-induced control of chemical or physical processes has been one of the major goals in the field of chemical physics for a long time [1]. The practical reasons for such control are to suppress unwanted products and synthesize new structures and new materials. Macroscopic parameters such as temperature, pressure, and concentration etc. have been used for decades in the chemical industry to alter reaction rates. The field of catalysis is devoted to enhance the natural yield of a reaction. But these are nonselective methods, and cause the breaking of the weakest bond due to an equipartition of the activation energy over all bonds. With the invention of lasers, mode-selective chemistry aimed to minimize the amount of byproducts by activating only those bonds which are essential for the reaction. This goal has been achieved only in a few small systems for two reasons: First, it is usually necessary to excite the system to a higher vibrational state in order to overcome the activation energy. The anharmonicity of the potential, however, impedes the excitation of more than one vibrational transition with a narrow-band laser. Second, intramolecular vibrational energy redistribution in highly excited molecules dissipates the energy into other vibrational modes on an ultrashort time scale. Therefore, simple excitation schemes proved to be ineligible to focus the excitation energy in a certain mode over a sufficiently long time. Nevertheless, phase of light be used as a photochemical tool to control the outcome of a chemical reaction based on a simple and very general concept of wave interference. Coherent control can be defined as the ability to control any optical driven process using the coherent properties of lasers and samples.

The availability of commercial fs laser systems with better performance/ specifications make the development of new techniques and applications of time-domain spectroscopy even more attractive. Femtosecond laser pulses are promising tool for coherent control. Coherent control attempts to control a chemical reaction with shaped fs laser pulse. Excitation with shaped fs laser pulse can cause a molecule to vibrate in such a way as to break the bond of our choice and produce the desired products. However, Control is hampered by fast relaxation, complicated mode structure, imperfect knowledge of the inter-nuclear potentials. From a theoretical point of view, optimum electric field can be found through quantum mechanical calculation. The optimal electric field E(t) is found such that the target is maximized. This electric field then can be synthesized in the laboratory. This scheme is called open loop and it requires the knowledge about the Hamiltonian of the system, which is feasible for small molecules and not for complex molecules. To overcome this difficulty, Judson and Rabitz [2] in the seminal paper "Teaching lasers to control molecules", proposed to use a learning algorithm, which optimizes the laser pulse shape in an iterative manner based on actual experimental result. The laser field adapts to the given molecule and the control objective. This is called closed loop, automated loop or self learning loop.

The experimental realization of feedback controlled self learning loop requires a high power femtosecond laser system, frequency conversion units to have suitable wavelengths for the molecular system under investigation, a computer controlled pulse shaper, and an optimization algorithm based on evolutionary strategies. The wide spectra inherent to femtosecond laser pulses is manipulated in the pulse shaper to generate an electric field profile, which adapts to the desired result. The search of the optimal field will be guided by an automated learning loop, which employs a direct feedback from the experimental output. The optimized pulse will provide physical insight into the control process. The feedback-controlled pulse shaping has been successfully applied to control the molecular dynamics in complex systems. The closed-loop process is shown in figure 1.

Coherent control techniques have proliferated over the last few years and many successful control experiments demonstrate the great versatility of this technique to selectively influence light matter interaction in complex systems [3]. In the quantum control process, molecular dynamics are guided with specifically designed light fields. Recent works of the groups of Gerber [4], Dantus [5] and Silberberg [6] illustrate several fundamental and practical aspects of coherent control in gas as well as liquid phase.

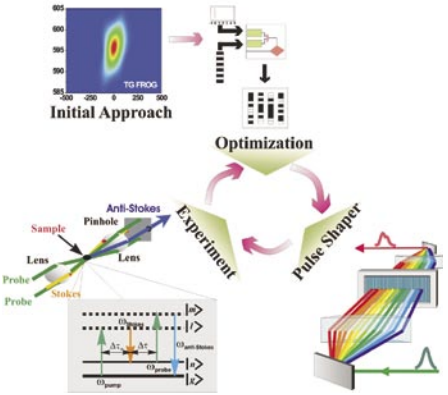

Fig. 1. Optimal Control Setup: Schematic description of the various components of the optimal control experiments using coherent anti-Stokes Raman scattering (CARS) technique. The Stokes laser pulse of CARS process (bottom, left) is shaped by a phase modulator setup (bottom, right). The spectrum resulting from this experiment serves as feedback for the evolutionary algorithm (top, right), which controls the pulse shaper during the optimization.

Feedback Controlled Femtosecond Pulse Shaping

Femtosecond pulse shaping is one of the important technical developments in the field of coherent control. By femtosecond pulse shaping, one should be able to manipulate the phase, amplitude, and possibly also the polarization state properties with a large number of degrees of freedom. Ultrashort laser pulses can be described in the time domain and in the frequency domain which are connected via Fourier transforms, thus shaping of an ultrashort laser pulse can in principle be achieved either in the frequency or time domain. A very successful technique for femtosecond pulse shaping is based on a so-called 4f-setup which allows one to modulate laser pulses in the frequency domain (fig 1, bottom right). The incoming laser beam gets dispersed by a grating. The dispersed beam is then collimated by a lens with a focal length f. The grating itself is positioned in the focal plane of this lens. In this way, the individual frequency components will be focused individually, but spatially displaced with respect to each other, into the focal plane of the lens. In this ''Fourier plane'' the different frequency components can be influenced separately by various methods. A symmetrically arranged second lens and grating recombine the different spectral components. In the ideal case and without further optical components, a laser pulse leaves this geometry without modification. This setup is hence called ''zero-dispersion compressor'' [7].

The actual pulse shaping occurs by suitable spectral modifications in the Fourier plane, employing a spatial light modulator (SLM). Depending on the type of SLM, the zero dispersion compressor setup may have to be modified slightly with respect to the principal description given above. The most widely used SLM is a liquid crystal display (LCD). It consists of two glass plates that are coated with small areas of indium–tin oxide, a transparent but conducting substance. These areas represent individual pixels to which electric voltages can be applied. The resulting electric field reorients the long-stretched liquid crystal molecules between the two glass plates and thus modulates the refractive index for transmitted light. The resulting optical path difference is thus adjustable for each wavelength in the Fourier plane and enables spectral phase modulation. For pure phase shaping, the power spectrum of the pulse is unchanged. polynomial representation of the phase function is chosen to reduce the number of free parameters [8]

$$\phi_n = \sum_{k=2}^{k} c_k \left(\frac{n-N_0}{N}\right)^k \quad n = 0, 1, 2, \ldots, N-1;\ N = 640$$

with quadratic terms as lowest polynomial order *k* since constant (*k* = 0) or linear (*k* = 1) phase terms only produce a phase or time shift, respectively. The taylor coefficients parameters c_k and N_0 are optimized by the algorithm. N_0 has been included as a parameter to ensure that the offset of the phase function coincides with the center of the spectrum after the optimization has been accomplished. Apart from polynomial phase function, one can also have periodic phase function for physical systems sensitive to symmetry properties in the phase functions. With the help of two LCD layers and polarizers, one can also achieve independent phase and amplitude control over the wavelength components by applying suitable voltages to individual pixels of LCD mask.

However, physical systems such as molecules are three-dimensional. One can therefore ask if it is possible to make use of the vectorial properties of light as well and to additionally "pull" along the correct spatial directions. This requires controlling the polarization state of light on a femtosecond time scale. Femtosecond polarization pulse shaping can be considered to be a novel spectroscopic technique, because the temporal as well as three-dimensional spatial properties of quantum wave functions can potentially be addressed and controlled. Only recently such a technique called femtosecond polarization pulse shaping has been realized. For the first time, temporal intensity, momentary frequency, degree of ellipticity and orientation of elliptical principal axes can be varied in a complex manner within a single laser pulse.

Of critical importance in the concept of feedback controlled experiments is a reliable optimization algorithm which searches for the global optimum in a multidimensional parameter space. The algorithms typically used for these experiments are termed evolutionary as they mimic the process of biological evolution. This imitates the classical picture of evolution in a computer code, which simulated selection, mutation and recombination within a feedback regulation loop. Minimizing the data acquisition time in complicated control experiments, which may be running stably for only a short time, is essential. Therefore, an efficient algorithm is highly desirable (i.e. finding the global optimum, fast convergence). Evolutionary algorithms have been proven robust under such condition.

Another important step in laser control experiments with shaped pulses is an accurate phase characterization of the optimized pulse. This information cannot be obtained from simple autocorrelator which provides just the temporal profile of the pulse. In principle, any autocorrelation measurement in which the autocorrelator signal beam is spectrally resolved is a frequency resolved optical gating (FROG) measurement. FROG [9] is extensively used for complete characterization of the pulse. This technique operates in the time-frequency domain involving both temporal and frequency resolution simultaneously. Basically, it has two steps time gate for temporal information, and a frequency gate for spectral information. Scanning all delays and frequencies, a so-called *spectrogram* is obtained, which completely determines the Electric field. The first step of FROG is to measure the spectrogram of the pulse; the second is the reconstruction of $I(t)$ and ö(t) from the spectrogram.. Depending on the type of nonlinearity used for the temporal gating, several types of FROG exist. A spectrogram of the pulse is constructed and analyzed using FROG software obtained from femtosoft technology.

Nonlinear optical processes like four-wave mixing (FWM) are ideally suited for the study of coherent interaction of light and matter. Due to the coherent nature of this process, the phase and the amplitude of the femtosecond pulses directly influence the FWM response. Also FWM is an ideal method for optimal control studies as it can be used to monitor ground as well as excited state dynamics [10]. It has been demonstrated that a change of the chirp of femtosecond laser pulses has a striking influence on the frequency-selective spectroscopy with spectrally broad ultrashort pulses. Especially, coherent anti-Stokes Raman scattering (CARS) [11] is a widely used technique for the study of the vibrational motion in a molecule, where the molecule is prepared by two coherent lasers and probed by another laser (bottom left of Fig. 1). The CARS process is initiated with the spatial and temporal overlap of three pulses in the sample. For an electronically resonant excitation the frequencies ω_{pump} and ω_{probe} of the pump and probe pulses, respectively, can be tuned to electronic transitions of the molecular system in order to resonantly enhance the signal intensity. The third pulse is the so-called Stokes pulse with frequency ω_{Stokes}. In Raman resonance, the difference $\Delta\omega = \omega_{pump} - \omega_{Stokes}$ corresponds to the energy of a vibrational transition in the electronic ground state. Pump and Stokes pulses interact nonlinearly with each other. This interaction coherently excites the vibrational modes. The probe beam is scattered from this coherent motion and results in an anti-Stokes signal, which is coherent and directed. Again, due to the broad spectral bandwidth of the femtosecond pulses, several molecular vibrational modes are excited simultaneously. These modes contribute to the CARS spectrum but they are poorly resolved.

A femtosecond laser system in combination with two optical parametric amplifiers is used to create the three femtosecond pulses required for the four-wave mixing process. The Stokes pulse and was phase modulated in a feedback-controlled loop by means of a folded *4f*-arrangement of two gratings and a liquid crystal spatial light modulator (SLM-640/d, Jenoptik) [8]. The evolutionary algorithm responsible for the optimization is restricted to a search of the phase function without changing the power spectrum of the Stokes pulse by amplitude modulation. The pulses interacted with the sample in a folded BoxCARS geometry. The anti-Stokes signal was measured as a function of probe delay time by means of a single monochromator equipped with a CCD camera for broadband detection.

Control of Multimode Dynamics

Coherent control techniques have been applied to influence the multi-mode dynamics. In the first experiment, fs-CARS was applied to liquids consisting out of one molecular species. In the following, results from optimizations of the nonlinear spectrum obtained from toluene are discussed. Toluene does not absorb in the visible spectral region. Therefore, the CARS process does not involve any excited electronic state. Centering the stimulated Raman excitation at approximately 1090 cm^{-1} results in an excitation of a variety of vibrational modes. In the CARS spectrum three bands can be detected, which for simplicity are labeled by ① (≈1000 cm^{-1}), ② (≈800 cm^{-1}), and ③ (≈1200 cm^{-1}) (left part of Fig. 2). The fs-CARS spectrum obtained for transform-limited laser pulses is dominated by band ① and only shows weak shoulders at the positions of lines ②, and ③ (see panel A of Fig. 2). Performing an optimization of the Stokes phase shape resulted in dramatic changes of the anti-Stokes spectra. Here, the Raman band ratio served as fitness function for the evolutionary algorithm used to control the spectral phase of the Stokes pulse. Panels B and C of Fig. 2 depict the spectra obtained after optimization of bands ②, and ③, respectively. In both cases the formerly very weak bands clearly dominate the spectra [8,12]. The corresponding Stokes laser pulses are shown next to the spectra. They were measured using a transient grating frequency resolved optical gating (TG-FROG) setup. The spectral selection was observed to persist for the full coherence lifetime (not shown here).

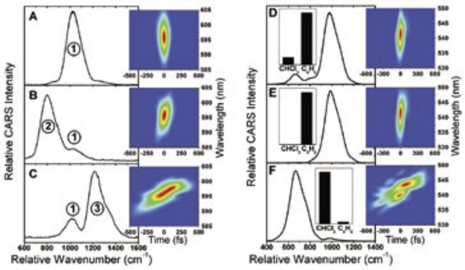

Figure 2: fs-CARS spectra taken with transform-limited (A,D) and phase-shaped (B,C,E, and F) Stokes pulses from toluene (left side) and a mixture of chloroform and benzene (right side). For each spectrum the TG-FROG trace of the associated Stokes laser pulse is shown.

The second experiment introduced here, demonstrated the control of CARS spectra obtained from mixtures of different molecules. As an example, in the right part of Fig. 2 the result for a binary mixture of benzene and chloroform is shown. Again, the CARS excitation is not resonant with the molecular electronic transitions. The difference between pump and Stokes laser wavenumbers was set to 800 cm^{-1}. The spectrum displayed in panel D of Fig. 2 was obtained with transform-limited laser pulses. It shows a strong line at 992 cm^{-1}, which can be assigned to the ring breathing mode of benzene. The weaker line at 670 cm^{-1} belongs to chloroform. Again, an optimization is possible, which is shown in panels E and F. Here, a selection of the benzene and the chloroform bands was successfully performed, respectively (see also bar diagrams comparing the CARS intensities of both molecules) [12,13]. The FROG traces of the corresponding Stokes laser pulses are given for each spectrum. Like for toluene, also for the mixture, the spectral selection persists during the observable lifetime of the signal. Additionally, the optimized laser pulses were also applied to the pure substances. In each case, the pulses suppressing the respective substance contribution in the mixture also resulted in a drastic reduction of the signal intensity in the liquid containing only these molecules.

The above observed spectrum control has far reaching effects. On the one hand, the selective excitation of specific molecular modes is an important stepping stone towards the realization of the control of chemical reactions. On the other hand the targeted suppression of Raman lines in the CARS spectrum would have considerable advantages for frequency-resolved spectroscopy. Here, one would still be able to obtain mode-specific information with femtosecond time resolution. These results are significant as new ways of spectral filtering as well as exciting possibilities of mode-selective study of chemical reaction dynamics. The spectral filtering is also shown to be molecule specific, which is of interest to for filtering out spectral contributions of specific molecules in mixtures. This concept has significant impact on background free spectroscopy and imaging. Since changes in chemical bonding involve a superposition of several modes, control of multimode wave packets may lead to selective control over reactions.

Applications of Quantum Control

Application of coherent control to quantum systems is relatively recent. We will look at how these concepts are applied to manipulate the dynamics of a variety of quantum systems, chemical reactions, and, perhaps most pertinently for us, semiconductor nanostructures. The first broad class of applications addresses the chemist's dream: to create novel stable or meta-stable products by selectively making or breaking chemical bonds to drive the chemical system toward the desired (quantum) state. These applications take advantage of the enormous strides in recent times of femtosecond laser pulse-shaping capabilities. The hope is that the laser-driven coherent manipulation of the molecular motion-induced quantum interferences (between different pathways from one state to another) will facilitate products or molecular states, not accessible by conventional chemical or photo-chemical means [14].

(i) **Control of Energy Transfer and Isomerization:** In a very significant work in the quantum control of chemical systems, Herek et al. [3] have used coherent learning control over the energy flow pathways in the light-harvesting molecular complex in a photosynthetic bacterium. Their experiment on a condensed phase system not only proves that molecular complexity need not preclude the possibility of coherent control, but also opens up the new application area of the quantum control of biological systems. The first adaptive control of a liquid phase isomerization reaction was demonstrated in a dye molecule (NK488) dissolved in methanol by Gerber and his group [4], where both enhancement as well as reduction of the isomerization efficiency could be achieved.

(ii) Chemical Reactions: Quantum control with light is an interesting approach, where selective chemical reactions with photons can be performed. Using a multiparameter control approach to control the population of different dissociation channels has been demonstrated in gas phase [4] but not yet in condensed phase systems. Since the reaction timescale on which such photodissociation processes take place is very fast, there is no reason why such processes should not be controllable in the condensed phase. If the system is chosen in a way that the triggered photodissociation is the initial step for a bond activation, the subsequent bond-formation processes will automatically lead to the desired products, depending on the initial photodissociation fragments. The selective control of unimolecular photodissociation reactions in the condensed phase is a very interesting field for future experiments. For unimolecular reactions, especially those involving bond cleavage or isomerization, it is conceivable that an electric field does exist to achieve the desired chemical change. However, for bimolecular reactions, those involving bond formation between two separate atoms or molecules, controllability of the outcome by an electromagnetic field can be questioned. There have been a few experimental successes in this extremely challenging problem.

(iii) Imaging and Spectroscopy: One of the major goals in coherent control is to achieve the greatest contrast between different pathways following optical excitation of a sample. In microscopy, as well as in imaging in general, the goal has always been to achieve the greatest contrast possible. A number of new developments in the area of imaging that can be traced to advances in the field of coherent control [5].

(iv) Molecular Switch: Molecular switches are especially interesting because of their scale and cost. Switching between different conditions is required for many applications such as data storage. In order for the molecule to be used as switch, the change between the stated must be fast and reversible by external stimuli. The two states must be thermally stable and be able to switch back and forth many times. The two states must be distinguishable by some probe. For reliable applications it is necessary to switch efficiently between the different states, which can be accomplished by adaptive femtosecond quantum control methods.

(v) Laser Distillation (Stereoselectivity): Another field in which adaptive femtosecond quantum control can provide the necessary concepts is stereoselectivity. For example, the selective control of enantiomer concentration in initially racemic mixtures is an important application in chemistry. Naturally, the liquid phase is the most suitable environment for high product yields. Ultrafast feedback signals can be provided by measuring the optical activity. Due to the high relevance of selective control of enantiomer concentrations, several approaches have been developed theoretically often incorporating the influence of the polarization of the light. Although first experiments without complex pulse shaping techniques have been conducted on this topic, efficient conversion under standard laboratory conditions has not been demonstrated yet. With the recent advances in shaping the polarization, adaptive femtosecond quantum control could provide the key concepts to achieve selectivity of enantiomers [4].

(vi) Optical Centrifuge: Lasers are routinely used to nudge, trap, and stir atoms to perform Nobel-prize winning feats, but so far molecules have avoided being subject to the same level of control. Now short laser pulses can be used to create large rotational forces on molecules, causing them to rapidly spin around at speeds that can be extremely well controlled. A molecule placed in a polarized laser field will align itself along the direction of polarization. If the polarization of the field were made to slowly rotate, the molecule would follow. Finally, if the rotation of the polarization is accelerated, the molecule would experience centrifugal forces that could either distort or even break some of its bonds. Now by placing a cloud of chlorine gas in such an optical centrifuge, the molecules begin to spin about 6 trillion times a second [15]. At such a high speed the centrifugal forces are enough to snap the bonds holding each molecule together and the molecules shatter into a shower of chlorine atoms. Potential uses of such optical centrifuge include separating gases of different molecules, or even isotopes of the same molecule.

Since heavier molecules break apart at slower spin rates because of a tiny difference in their moments of inertia which measures how they respond to rotation. This could also be used to break only selected bonds in a molecule, leaving bonds away from the centre of rotation intact, and thus opening the door to direct 'bond-by-bond control' of molecular chemistry. More speculatively, a dense gas of spinning molecules might provide a new source of intense high-frequency radiation easily 'tunable' to frequencies not available from lasers.

(vii) Nanoscience and Technology: The application of coherent control to semiconductors and their nanostructures, has not yet witnessed a serious experimental demonstration. The novel size-dependent properties exhibited by nanomaterials are at the origin of the large fundamental and technological interests they receive. Most of these are associated to modifications of the electronic and vibrational degrees of freedom by quantum confinement. Its impact on the electronic properties has been extensively investigated during the last decade in both semiconductor and metal nanosystems. Quantum control is an exciting new field with great potential for nanoscience/nanotechnology. The control of quantum systems might be a highly useful tool for nanoscience and is still evolving [16].

Challenges and Future directions

In the above we have shown the experimental demonstrations in which laser pulses are used to control a number of physical and chemical processes. These include processes such as isomerization, fragmentation, photo-association, bio-molecular reactions charge transfer, ionization, high harmonic generation, frequency mixing etc. which involves manipulation of nuclear and electron dynamics as well as non-linear optical phenomena. The systems can range from atoms or small molecules to complex bio molecules, nanoparticles, aerosols etc. In addition, the control environment may be isolated molecules, solutions and even trapped particles in solids.

Applications in the future will build upon the current successes. Potential applications include isotope separation, prototype molecule synthesis, the creation of ultra-cold molecules, manipulation of molecular switches, controlled bio-molecular dynamics, photo-dynamic therapies, amongst other possibilities. Looking even further down the road, laser sources of increased energy could allow for manipulating core electron dynamics in atoms and possibly even nuclear reactions.

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Single-molecule force-clamp spectroscopy: Probing transition states of mechanically activated chemical reactions

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Abstract

Knowledge of the transition state (TS), the high energy bottleneck *en route* from reactants to products, is the key to molecular level understanding of chemical reactivity. Atomic level description of such short-lived TSs, although for gas phase reactions involving only few atoms, has previously been achieved through femtosecond laser spectroscopy and quantum chemical calculations. It is experimentally challenging to directly obtain such information from solution-phase reactions. Here, we use a novel single-molecule technique based on a custom-built atomic force microscope (AFM) to study the bimolecular disulfide reduction (S_N2 type). Using this technique, we apply a constant stretching force to individual disulfide bonds over long periods of time and examine its effect on the reaction kinetics. The stretching force mechanically activates the disulfide bond and exponentially accelerates the reduction reaction by lowering the energy of activation. In this experiment, disulfide bond length serves as the one-dimensional reaction coordinate and allows us to measure the disulfide bond elongation at the TS with an unprecedented sub-ångström resolution. The single-molecule force spectroscopy measurements do not require the knowledge of the lifetime of the TSs and yet provide their structural information. This novel technique not only demonstrates to be a powerful tool to study chemistry at the single-molecule level but also shows that mechanical force, in addition to light, electricity and heat, can be used as a means of activating chemical reactions.

Introduction

Why single-molecules?

It has been well known that chemical reactions can be activated (or catalyzed) by heat, electricity and light and the underlying chemistry is called thermochemistry, electrochemistry and photochemistry, respectively. In principle, mechanical forces, which are ubiquitous in nature, can also be used to study chemical reactions under the phenomena 'mechanochemistry'.[1] Mechanochemistry is defined as the chemistry of molecules under the influence of a stretching force and studying its effect on the reaction pathways. However, the details of this branch of chemistry have largely been unexplored, mainly for the following reasons. Mechanical force is a vector quantity as it has a magnitude as well as a direction associated with it along which it acts. In general, the molecules in solution are oriented along all directions and the mechanical force needs to be applied along different directions for different molecules. Hence, there is no simple way to apply mechanical forces to individual molecules in bulk solution. As a result, one would have to work with one molecule at a time to study the effects of a mechanical force (or stretching force). With the advent of atomic force microscopy (AFM)[2] it has become possible to measure forces in the range of 10 pN to 10 nN. Further developments led to single-molecule force-clamp technique[3] with which mechanical forces could be applied to individual molecules for longer times.

Single-molecule force-clamp technique

Single-molecule force-clamp technique is an experimental tool with which a constant stretching force between 10 pN and 1nN can be applied to single-molecules and any deviations from this set force, either due to a chemical reaction or due to protein mechanics, are corrected. The force can be maintained constant for very long times (from a few seconds to couple of minutes) by a very fast feedback mechanism (<5 ms) making it possible to study the effect of the mechanical force on a wide range of force-sensitive phenomena. These phenomena can range from the mechanochemistry of a single bond[4] to the forced unfolding of a large molecule such as a protein.[3] The principle of force-clamp technique utilized in AFM to apply force on single-molecules is described in Figure 1. Briefly, octameric polyproteins, which are tandem repeats of eight identical single-domain proteins attached in head-to-tail fashion, have been used in single-molecule experiments. Polyproteins are very important and give their characteristic fingerprints. They also aid in identifying the molecule of interest from 'impurities', unwanted molecules and even molecular aggregates in solution. A small volume of solution (~50 - 100 µl) containing the molecule (~0.1 - 10 µM) of interest is placed on a substrate (gold-coated glass cover-slip). A cantilever (200 µM) with a small tip (~20 nm), which can sense the forces in the range of 10 pN – 10 nN, is brought into contact with the substrate by moving the substrate towards the cantilever. The substrate can be moved towards and away from the cantilever with high precision (~1 nm) by using a piezoelectric positioner. The substrate is then retracted away from the cantilever and force on the cantilever is measured with the help of a laser and split-photodiode system. The laser beam is focused onto the angular-end of the V-shaped cantilever and the reflected beam falls onto the split-photodiode such that the intensities on both diodes are equal when there is no external pulling or pushing force on the cantilever. When the substrate is retracted, any molecule tethered between the tip and the substrate would experience the applied stretching force. The exact force on the cantilever can be quantified from the photodiode output by noting the corresponding bending in the cantilever (calibrated by equipartition theorem).[5] Furthermore, if the force on the molecule as reported by the cantilever is changed either due to a chemical reaction or due to protein unfolding, the force feedback system brings back the force to the set force. A force differential, which is the difference between the force on the molecule and the set force, is sent to the feedback amplifier (PID). The amplifier amplifies the signal proportionally to the differential which is then sent to the piezoelectric positioner to counter act the change in the force and bring the force back to the set value by retracting or approaching, which will depend on the sign of the differential.

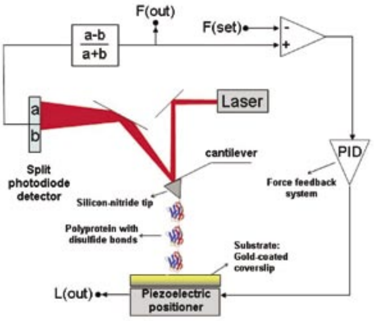

Figure 1. Schematic diagram of the single-molecule force-clamp technique. Force-clamp technique can be used to stretch single-molecules and study chemistry and protein mechanics at the single-molecule level. When come into contact, the tip of the cantilever picks up molecules (polyproteins with engineered disulfide bonds) placed on the substrate. When the substrate is retracted by piezoelectric positioner, the molecule is stretched and the force on the molecule is measured by the amount of deflection of the laser beam on the photodiode. Whenever a protein is unfolded or a disulfide bond is reacted, the force on the molecules drops as the molecule elongates. To keep the force on the molecule constant, the force on the molecule is brought back to the set force by the force feedback system, which instructs the piezoelectric position system to retract such that the force on the molecule is restored.

Identification of single disulfide bonds in force-clamp experiments

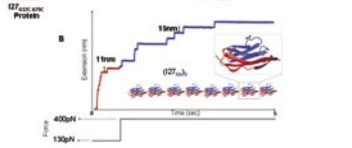

Figure 2. Identification of single protein disulfide bonds in force-clamp AFM. (A). Cartoon diagram showing the sequence of events that occur during a single-molecule mechanochemistry experiment. A polyprotein containing a disulfide bond in each protein domain is stretched under a constant force of 130 pN. The disulfide bond is initially buried and the application of force unfolds the protein to expose the disulfide bond to the bulk. This unfolding process manifests as a step in the extension vs time graph (B) indicating the elongation of the molecule by 11 nm. Further stretching of the protein at 400 pN results in a staircase of steps ~15 nm resulting from the elongation of polypeptide chain between cysteines 32 and 75 following the reduction of disulfide bond by DTT.

Chemical molecules are much smaller (<1 nm) compared to the tip of the cantilever (~20 nm), so it is technically very challenging to hold single-molecules and perform mechanochemsirty by AFM. To circumvent this problem, we utilize much larger molecules such as proteins which have well-defined three dimensional structures. We engineer single disulfide bonds in proteins by inserting two cysteines as point mutations. The inserted cysteines are in vicinity of each other and readily form a disulfide bond at ambient conditions. The polyprotein used in our experiments is an octameric version of ($I27_{G32C\text{-}A75C}$), where the cysteines are at positions 32 and 75 in the protein consisting of 89 amino acids. The disulfide bond formed between the two cysteines (32-75 disulfide bond) is buried and is not accessible to the bulk solvent molecules.[6] When a single polyprotein is picked up by force-clamp AFM and stretched at a constant force of 130 pN (for ~0.5 sec), the protein unfolds in a single-step and the unfolded protein unravels resulting in an 11 nm elongation step as measured by the piezoelectric positioner. However, due to the unraveling of a protein domain, the force on the molecule drops from 130 pN and this is brought back to 130 pN by the force feedback system (Figure 1). Further stretching of the polyprotein unravels all other protein domains and these events result in a staircase pattern where each step is 11 nm. At the end of this stage, the disulfide bond in each domain is exposed, with the force on them maintained at 130 pN. However, to perform the force-dependent kinetics of the disulfide bond, we change the force between 100 pN and 400 pN and keep it constant for 4.5 sec and continue measuring the molecular extension. In the second stage, where the force is changed from 130 pN to 400 pN, the disulfide bond would be exposed to the bulk containing the disulfide bond reducing agent dithiothreitol (DTT) and the reduction manifests as a step of 15 nm in the extension vs time graph (Figure 2B). It is important to note that the disulfide bond does not reduce or undergo homolytic cleavage in the absence of the reducing agent. The disulfide bond is mechanically rigid and very stable below 1 nN.[4] Thus, the 15 nm step is due to the disulfide bond reduction by DTT and the following elongation of the polypeptide between the cysteines (amino acids between 32 and 75), which was initially sequestered from the stretching force by the mechanically strong disulfide bond. The time at which this bond breakage occurs after changing the force can easily be determined in the extension vs time graph (Figure 2B). When all the disulfide bonds that are exposed to the bulk in the first stage are reduced under force in the second stage, the extension vs time graph results in a staircase where the step size is of 15 nm indicating the disulfide bond reduction. So, in force-clamp experiments with polyproteins it is possible to identify single disulfide bonds and perform mechanochemistry on them.

Force-dependent kinetics of the disulfide bond reduction

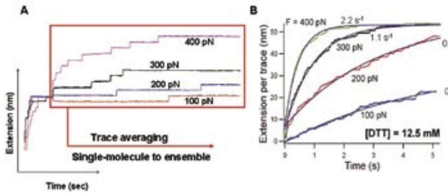

Figure 3. Force-dependent kinetics of the disulfide bond reduction. (A). single-molecule recordings of extension vs time at different stretching forces (100 pN – 400 pN). It is evident from these recordings that the reaction is accelerated with the stretching force, there are more disulfide bonds reduced in 5 sec at 400 pN compared to 300 pN and so on. (B). Averaged extension vs time curves for the disulfide bond reduction at four different forces. The trace averaged data is fitted with a single-exponential function to get the reaction rate constant. The disulfide bond reduction rate is increased from 0.2 sec^{-1} at 100 pN to 2.2 sec^{-1} at 400 pN and the increase in the reaction rate is not linear with the stretching force.

In the previous section, it was shown that single-molecules can be unambiguously identified and a constant stretching force can be applied to them to study their mechanochemistry. However, the effect of the applied force on the chemical reactivity needs to be quantified. As described in the previous section, it would be possible to perform the disulfide bond reduction under a varying stretching force and study the force-dependent kinetics of the disulfide bond reaction in detail. The experimental results of the force-dependent kinetics of the disulfide bond reduction by DTT are shown in Figure 3. The mechanochemical reduction, reduction under the influence of a reducing agent as well as a stretching force, of the disulfide bond is force sensitive. For example, in the extension vs time trace at 100 pN (Figure 3A), there is just one disulfide bond reduced in 5 sec. On increasing the force to 200 pN and 300 pN, two and three disulfide bonds, respectively, are reduced in 5 sec. However, on increasing the force to 400 pN, seven disulfide bonds are reduced in 5 sec period. It is an indication that the reaction rate is not linearly dependent upon the applied stretching force. However, it is not possible to quantify the force-dependency of reaction rates from individual single-molecules recordings as each recording does not contain sufficient number of reduction events (Figure 3A). We experimentally measure many single-molecule traces at any given force and then average the extension vs time traces of the second stage (Figure 2B). In trace-averaging, we use more than 25 traces and the resulting data is shown in Figure 3B. The averaged traces are exponential in nature with very small steps resulted because of the trace averaging. The data could be well fitted with single-exponential functions without invoking any need for multiple exponential functions. The rates of the reaction at 100, 200, 300, and 400 pN are 0.2, 0.3, 1.1, and 2.2 sec^{-1}, respectively. Hence, it can be concluded that the disulfide bond reduction is force-sensitive and the reduction rate exponentially increases with the applied force (Figure 4).

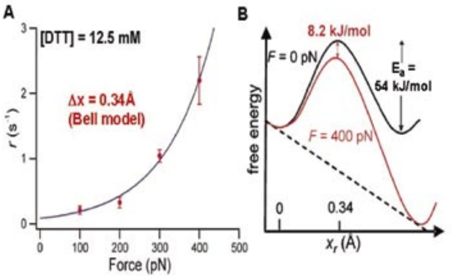

Figure 4. Mechanochemical reduction rate of the disulfide bond is exponentially dependent on the applied force. (A). The reaction rates of the disulfide bond reduction at four different forces 100, 200, 300, and 400 pN are 0.2, 0.3, 1.1, and 2.2 sec^{-1}, respectively. The thick line is a fit of the Bell (Arrhenius like) model to the experimental data. The Bell model is given by $r(F) = r_0 \exp(F\Delta x/k_BT)$ (see text for more details). Bell model yields a value of 0.34 Å for Δx, the distance to the transition state. (B). Simplified illustration of the free energy landscape of the disulfide bond reduction by DTT under stretching force. The transition state as measured by the Bell model locates at 0.34 Å. The activation barrier for the bimolecular S_N2 type disulfide bond reduction is 54 kJ/mol. However, application of stretching force lowered the mechanical activation barrier, explaining the force-accelerated disulfide bond reduction. For example, the barrier is lowered by 8.2 kJ/mol by applying a force of 400 pN (see text for more details).

Bell model to explain the force-dependency of reduction

We use a very simple model to explain the experimental data of force-accelerated disulfide bond reduction. In the first approximation, these results can be explained by the Bell model.[7,8] In this model, the force-dependent rate process is described as $r(F) = [\mathrm{DTT}]\ A \exp((F\Delta x - E_a)/k_BT)$. Here, A is a constant with units of $M^{-1}s^{-1}$, E_a is the activation energy of the reaction, k_B is Boltzman constant and Δx is the distance to the transition state. This model in fact resembles the Arrhenius-like model. Fitting the Bell model to the force-dependent rate constant of the disulfide bond reduction yields a distance to the transition state value of Δx = 0.34 Å, and the energy barrier of 54 kJ/mol.[4,9]

Measuring the disulfide bond length at the TS with sub-ångström resolution

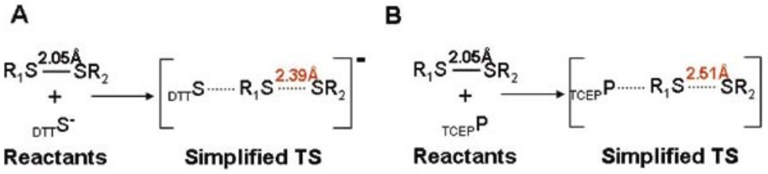

Figure 5. Simplified illustration of the transition state (TS) structures for the disulfide reaction initiated by thiolate (A) and phosphine (B). The equilibrium disulfide bond length is 2.05 Å and it is elongated by 0.34 Å at the TS for the thiolate (DTT) initiated reduction. The disulfide bond elongation at the TS is longer (0.46 Å) for the phosphine (TCEP) initiated reduction. These bond elongations are measured by the Bell model fit to the mechanochemical reduction of the disulfide bond performed by force-clamp spectroscopy.

It is well known in literature that the disulfide bond reduction by DTT proceeds via an S_N2 mechanism.[10] In this biomolecular nucleophilic substitution reaction, the thiolate anion of DTT is nucleophile and it attacks the disulfide bond almost along the disulfide bond axis. In the TS, the three sulful atoms are collinear and the attacking thiolate is in the process of making a bond with the central sulfur atom whereas the original disulfide bond between the central atom and the leaving sulfur lengthens (Figure 5). Indeed, theoretical simulations predicted that the disulfide bond elongates at the TS and the theoretical prediction of the bond elongation (0.37 Å)[11] is in agreement with the experimental observation of the disulfide bond elongation at the TS (0.34 Å). Further experiments on the mechanochemical reduction of the disulfide were performed with a different class of reducing agents known as phosphines. Phosphines also reduce the disulfide bond via a bimolecular nucleophilic substitution.[12] Force-clamp experiments on the mechanoreduction of the disulfide bond by tris-(2-caroxyethyl)phosphine (TCEP) revealed that the disulfide bond elongation (Δx) at the TS is 0.46 Å.[9] Results from our preliminary quantum chemical calculations using the density functional theory showed that the disulfide bond length at the TS is much longer when TCEP is used compared to DTT in the calculations.[9] This is in qualitative agreement with the results from force-clamp experiments. However, we would have to perform more rigorous calculations and test other theoretical models to achieve a higher level quantitative agreement with the experiments. Nevertheless, our experiments measure the bond lengths of the disulfide bond at the TS with an unprecedented sub-ångström resolution.

Challenges in probing the transition state structure

Knowledge of the TS is the key to the molecular level understanding of chemical reactivity. Atomic level description of TS geometries have previously been achieved for chemical reactions in gas phase by femto-second laser spectroscopy.[13] These reactions consisted of few atoms and devoid of any solvent interactions, which is very common in solution phase reactions. Furthermore, high intensity and ultrafast femto-second laser technology was required as the TSs are very short lived as their lifetimes are in the range of 1-10 ps. Chemical reactions that normally occur in solution are more complex and involve many atoms, and there is growing evidence that solvent molecules also influence reaction kinetics by directly participating in the reaction. Although studies such as linear free energy relationships and heavy atom kinetic isotope effects indirectly probe the potential TS geometry of solution phase reactions, atomic-level details of the TS has been until now only gained through quantum chemical calculations. Our experiments demonstrate that the experimentally measured distance to the TS, Δx, during the mechanochemical disulfide bond reduction is related to bond elongation at the TS predicted by quantum chemical calculations. In our experiments, we do not need to know or measure the lifetime of the TS. In spite of its transient nature, we are able to measure the bond lengths with sub-ångström resolution. This was primarily possible due to the application of the constant stretching force throughout the time evolution of the reaction and the direct proportionality between the reduction in the energy barrier and the distance to the TS.

Conclusion and perspective

Our experiments provide a platform for testing different theoretical models as well as quantum chemical calculations. The field of mechanochemistry is undergoing an exciting transformation, owing to the development of new tools for probing, manipulating, and studying single-molecules. Force-clamp spectroscopy has emerged as a compelling technique, providing new opportunities to rigorously study chemical reactions at the single-molecule level. We anticipate that this technique will become an important tool in the chemist's arsenal and unravel more mysteries of the nano-world in the near future.

Acknowledgement

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A. Sri Rama Koti *received his M.Sc. in Chemistry from University of Hyderabad in 1997 and Ph.D. in Physical Chemistry from the Tata Institute of Fundamental Research (TIFR) in Mumbai, with Prof. Periasamy in 2002. His dissertation topic was "Fluorescence spectroscopy and dynamics of organic molecules in complex systems". He was a post-doctoral research scientist with Prof. Julio Fernandez during 2003-2007 in the Department of Biological Sciences at Columbia University where he acquired expertise in single-molecule protein mechanics and mechanochemistry. He joined as a Reader in the Departments of Chemical and Biological Sciences at TIFR in February, 2008. He has set-up a custom-built atomic force microscope for single-molecule manipulation at TIFR and he currently works on mechanical properties of proteins and biopolymers.*

NSRP-2009 Report

National Symposium on Radiation & Photochemistry (NSRP-2009) was held at the Department of Physics, DSB campus of Kumaun University, Nainital, during March 12-14, 2009. This symposium, organized by Kumaun University in collaboration with ISRAPS, was the 8th in the NSRP series. We convey our sincere thanks to the Kumaun University, our colleagues at BARC, and all ISRAPS members for their kind cooperation to make the symposium a great success. In particular, we would like to thank Dr. D. K. Palit, Convener and Dr. Sanjay Pant, Local Organizing Secretary for their hard work towards the success of NSRP-2009. We are also grateful to DAE-BRNS for its continuous support to this effort of the society. Thanks are also due to other funding agencies like DST, CSIR, DRDO, AERB for their help. We are grateful to Prof. C. P. Barthwal, Ex-Vice-Chancellor of Kumaun University and Prof. T. Mukherjee, Director, Chemistry Group, BARC for their help and overwhelming support in conducting the symposium. The main objective of this symposium was to discuss the recent developments in the field of radiation and photochemistry and their applications. Several specific topics like interaction of radiation with matter, fast radiolytic and photolytic processes, applied research in radiation & photochemistry, atmospheric photochemistry, laser photophysics & photochemistry, role of radiation chemistry in nuclear technology, dosimetry & safety aspects in high energy radiation and lasers, photo and radiation chemistry of nanoparticles & quantum dots, theoretical aspects of radiation and photochemistry were covered during the symposium. About 125 scientists including two from abroad participated in the symposium. Various experts in the field of radiation and photochemistry have delivered altogether 19 invited talks. There were 77 contributory papers in photochemistry and 35 contributory papers in radiation chemistry. One special ISRAPS bulletin edited by Prof. Anunay Samanta of Central University, Hyderabad was released during this symposium. During NSRP-2009, Best Poster Presentation's cash awards along with certificates were given to 7 participants below the age of 32, and certificates were given to 11 participants. . Dr. D. Amilan Jose of CSMCRI, Bhavnagar, was awarded the "P. K. Bhattacharya Memorial Award". Dr. Hari Mohan Memorial Award for best poster in Radiation Chemistry was initiated and the first award was given during NSRP-2009.

Announcement

Third Asia Pacific Symposium on Radiation Chemistry (APSRC-2010) and DAE-Tenth Biennial Trombay Symposium on Radiation & Photochemistry (TSRP-2010)

The 3rd Asia-Pacific Symposium on Radiation Chemistry (APSRC-2010) incorporating 10th Trombay Symposium on Radiation & Photochemsitry (TSRP-2010), organized by Bhabha Atomic Research Centre under the auspices of the Indian Society for Radiation and Photochemical Sciences (ISRAPS), will be held from September 14, 2010 (Tuesday) to September 17, 2010 (Friday) at Treasure Island Resorts, Lonavala, INDIA. The resort is a luxurious holiday location about 130 Kms away from Mumbai and 65 Kms from Pune, near the famous Karla Caves off Mumbai-Pune motorway (Website: www.treasureislandindia.com). While the APSRC will gather scientists at the forefront of research on radiation chemistry to share information on recent progress in this field, the TSRP is intended to discuss the fine prints of both Radiation & Photochemistry on a single platform. The proceedings of the symposium will constitute keynote addresses, invited talks, and presentation of contributory papers as posters. The symposium will bring together not only the experts around the world but also young researchers in both the areas, yielding fruitful discussions and setting the course of future direction.

Scientific Scope

Fundamental Radiation Chemical Issues for Advanced Nuclear Energy Systems:

- Water Coolant System, Fuel Reprocessing & Waste Management
- Radiation Chemistry at Elevated Temperature & Pressure

Next Generation Radiation Sources & Applications in Radiation and Photochemistry:

- Synchrotron Radiation, Laser Driven Accelerator, Pico & Femto Second

Pulse Radiolysis

Radiation Processing of Food and Industrial Products (Radiation Chemistry Aspects)
Polymer Design and Processing
Radiation Biochemistry: Antioxidants, Radioprotectors, Drugs
Ultrafast Spectroscopy & Dynamics of Photoinduced Chemical Processes
Gas Phase Reaction Dynamics in Bulk and Beams
Radiation & Photochemistry of Atmosphere &Environment
Radiation and Photochemistry in Ionic liquids and Supercritical fluids
Role of Radiation & Photochemistry in Nano Sciences
Theoretical Aspects of Radiation and Photochemistry

For further details please log on to
http://www.barc.gov.in/symposium or **www.israps.org** (Under Construction)
Dr. TulsiMukherjee, Chairman, APSRC-2010 & TSRP-2010
Chemistry Group, Bhabha Atomic Research Centre, Trombay, Mumbai 400 085, INDIA.
Tel: 91-22-2559 5234, Fax: 91-22-2550 5331/2550 5151 Email: apsrctsrp2010@gmail.com

Call for Nominations

Dr. P. K. Bhattacharyya Memorial Award

Indian Society for Radiation and Photochemical Sciences (ISRAPS) has instituted the 'Dr. P.K. Bhattacharyya Memorial Award' to be awarded annually to a young Indian scientist, who has made outstanding contributions in the field of radiation and photochemistry.

Dr. Pijush Kanti Bhattacharyya (1935 - 2002), the 'Founder Secretary' of the Indian Society for Radiation and Photochemical Sciences (ISRAPS) during 1984 -1992, was a major force behind its formation. ISRAPS is an organization devoted to promote education, advancement and applications of radiation and photochemical sciences in India. He was one of those few scientists, who initiated research in the field of radiation- and photochemistry in India. He contributed significantly to the study of radiation effects on materials used in the reprocessing of spent nuclear fuel, radiation processing of materials, radiation induced colouring of diamonds and radiation- and photochemical investigations on many organic and inorganic molecules.

The award carries a citation, a bronze medal and cash, which will be presented to an awardee every year during either the Trombay Symposium on Radiation and Photochemistry (TSRP) or National Symposium on Radiation and Photochemistry (NSRP).

Eligibility

Citizens of Indian nationality below 32 years of age as on December 31, 2009 and working at least for five years to make significant contributions in the field of photo and radiation chemistry are eligible to be nominated. It may be noted that the award would be given for the research work carried out only in India.

Nominations

Name of the candidate may be proposed by a member of the Executive Council of ISRAPS, Head of the Institution to which the candidate belongs or a Bhatnagar Prize winner in the field of radiation and photochemistry. The nomination should be as per the proforma given below. The nomination, complete in all respects should reach the Secretary, ISRAPS, on or before June 01, 2010.

Selection

An expert panel will scrutinize the applications for the award. The awardee has to present her / his work during APSRC-TSRP-2010 which will be held at Lonavala during September 14-17, 2010. The awardee will be provided with DA and to-and-fro train-fare by AC-3-tier, if the awardee can not get the same from any other source. It may please be noted that the decision of the expert panel is final and canvassing in any form is a disqualification.

Completed application may please be forwarded to
Dr. Tapan K. Ghanty, Secretary, ISRAPS
C/o Theoretical Chemistry Section, Chemsitry Group,
Bhabha Atomic Research Centre, Mumbai 400 085.

Proforma for Application

1. Name of the nominee in full
2. Date and place of Birth (Enclose certificate of age duly attested)
3. Address (With Telephone and e-mail)
   (a) Office (b) Residence
4. Academic Qualifications (in tabular form)
5. Details of Employment
6. Awards / Recognitions
7. List of publications