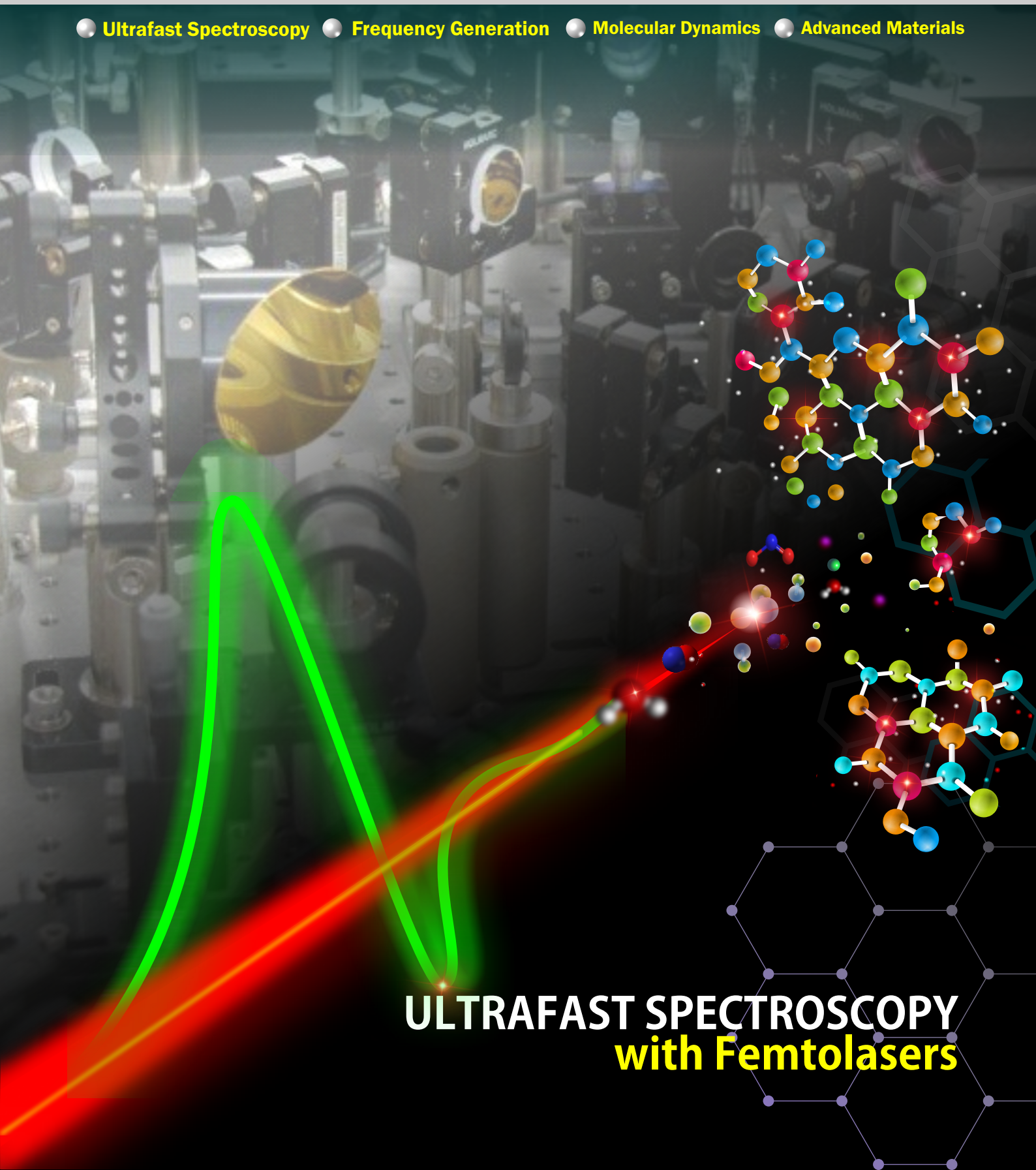
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BARC newsletter

September-October 2024 ISSN: 0976-2108

PLATINUM JUBILEE YEAR 70 Glorious Years 1954-2024

Ultrafast Spectroscopy | Frequency Generation | Molecular Dynamics | Advanced Materials



ULTRAFAST SPECTROSCOPY with Femtolasers

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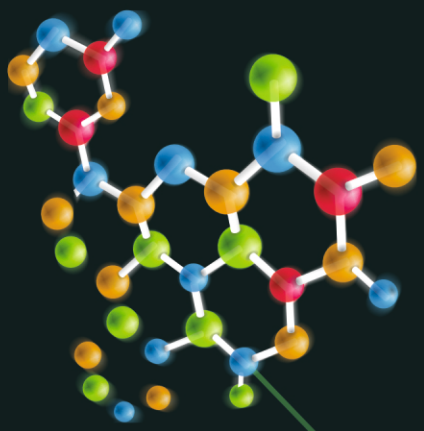
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foreword

Frontiers in Femtochemistry

I am indeed very pleased to write this foreword for the special thematic issue of the BARC Newsletter on the spectroscopic research using femtosecond laser in the Chemistry Group, BARC. Laser based time-resolved spectroscopic research was initiated in the Chemistry Group to generate short-lived reactive species and study their reaction kinetics and dynamics by following their time evolution. These studies have helped to unearth the mechanistic insights of important chemical and biological processes. Considering its immense applications in several fields like photosynthesis, light harvesting and other photochemical reactions, this frontier research area has grown rapidly in a very short time in the Chemistry Group keeping pace with the international standard. Chemistry Group has gained reach experience in the research area of spectroscopy and chemical dynamics by setting up various research facilities from millisecond to femtosecond timescales. To compete with international laboratories against all the odds, our scientists in the Chemistry Group took up the challenges and indigenously developed a femtosecond laser-based multistage dye amplifier and a transient absorption (TA) spectrometer, which is the first of its kind in India. This spectrometer records snapshots of chemical reactions with femtosecond time resolution.

The successful development of such a spectrometer has significantly boosted the femtosecond laser-based spectroscopy research in the Chemistry Group. Subsequently, several state-of-the-art picosecond and femtosecond laser laboratories have been developed indigenously to study not only the chemical structure and dynamics in bulk, but also at interfaces. The advantage of the high peak power of these lasers has been exploited for different spectroscopic applications, like Vibrational-Sum-Frequency-Generation (VSFG) spectroscopy to study the molecular interaction and their orientation at the interface; and Laser-Induced-Breakdown-Spectroscopy (LIBS) for elemental analysis with high sensitivity and selectivity. Recently, a tabletop setup for the generation of short-pulse electrons in water has been developed to study the reaction of electrons in femtosecond time scale.

Femtolasers are now invaluable not only for observing chemical processes in real time but also for manipulating the chemical reaction to produce a desired product. These are also very commonly being used by industry for critical material processing and the medical fraternity for treatment and diagnosis purposes. Inputs from these spectroscopic studies are the basis for such deployment of the femtolasers for the benefit of mankind.

This special thematic issue will enrich the scientific community about the expertise on the femtosecond laser spectroscopy available in Chemistry Group. I am confident that with this awareness the scientific community will be in a position to explore the possible use of these facilities for departmental activities. This will also encourage collaborative work with other organizations. I congratulate all the authors and the SIRD editorial team for the timely release of this special issue on femtosecond spectroscopy.

Awadhesh Kumar
Director, Chemistry Group
Bhabha Atomic Research Centre

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ASSOCIATE EDITOR'S *message*

Femtolasers & Ultrafast Spectroscopy

It gives me immense satisfaction to be associated with this special BARC Newsletter on "Ultrafast Spectroscopy with Femtolasers". Femtosecond laser has fundamentally changed our concept of chemical reaction and made it possible to see the movement of every atom during the chemical reaction using the world's fastest camera. Such development not only helps us to understand the fundamental chemical and biological processes in real time but is also important in the development of modern tools for industrial applications. The importance of femtochemistry research is reflected in the Nobel Prize in Chemistry awarded to Prof. Ahmed H. Zewail in 1999 for his work on the transition states of chemical reactions using femtosecond spectroscopy.

This special issue provides a glimpse of the spectroscopic research initiated in Chemistry Group, BARC and the effort for indigenous development of state-of-the-art experimental facilities using high power femtolaser in accordance with the country's "Atmanirbhar Bharat" mission. I sincerely hope that this thematic issue will enrich the scientific community and inspire further development and deployment of femtolaser for the benefit of mankind.

This special issue comprises nine articles covering a wide range of research activities from time-resolved spectroscopy to analytical applications of femtolaser. The first two articles provide a historical perspective on the femtochemistry research in the Chemistry Group. The first article showcases our effort to develop a transient absorption spectrometer using a home built amplified femtolaser for the first time in India and the application of this technique in understanding the chemical processes, like solvent relaxation, proton transfer, electron transfer, H-bond rearrangement, etc. which are ubiquitous in chemistry and biology.

The next three articles cover the research area involving the use of femtosecond spectroscopy to understand the ultrafast dynamics of charge carriers in a wide range of nanomaterials, like dye-sensitized nanoparticles, quantum dots (QD), QD-molecule composite, perovskites, organic semiconductors, etc. having direct relevance to solar energy conversion and photocatalysis. The development of modern state-of-the-art spectroscopic setup is presented in the next two articles. A brief account of the design and development of a two-dimensional infrared (2DIR) spectrometer, a first of its kind in India, and its application to unravel the hidden information on the dynamic coupling between molecules with femtosecond time resolution is presented. Molecular interaction at interfaces has wide technological importance. The next article describes a unique technique based on the Vibrational Sum Frequency Generation (VSFG) and discusses its applications in environmental and biological studies at aqueous interfaces. The generation of plasma using a femtolaser and its application in the mapping of elemental composition in intricate matrices has been presented in the next article. The final article of the issue describes our recent effort for the generation of ultrashort electrons by multiphoton ionization of water using a high power femtolaser to study the reactivity of electrons at the early stage of their birth.

The sincere effort of our colleagues, past and present, in this frontier area of research, helped us to reach a new height which is reflected in more than a hundred publications in reputed high impact international journals and more than 30 PhD theses using femtolaser based spectroscopic techniques.

Finally, I would like to thank each of the contributors for their cooperation in preparing this special issue. I also thank my colleagues in Ultrafast Spectroscopy Section, RPCD, Chemistry Group, for their help and encouragement during the preparation of this special issue. I sincerely acknowledge the Newsletter editorial team of SIRD for their untiring effort in bringing out this special issue in a time-bound manner.

Sukhendu Nath
Head, Ultrafast Spectroscopy Section
Radiation & Photochemistry Division
Chemistry Group

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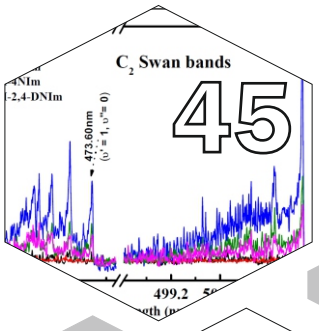
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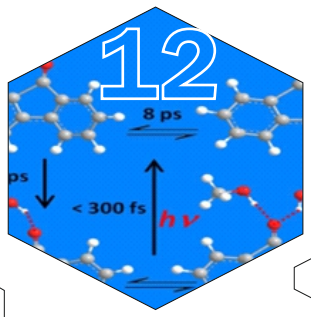
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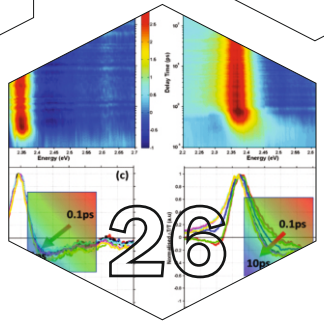
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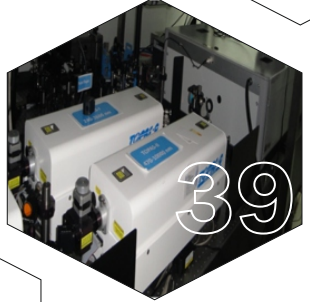
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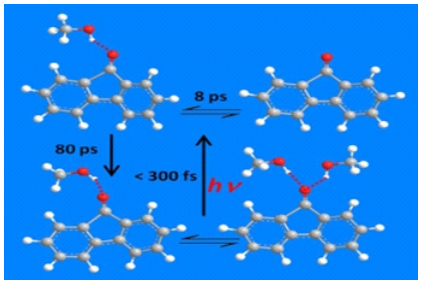
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प्रकाश रसायन प्रक्रम

1

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

दीपक के. पाटिल*
यूएम-डीएई सेंटर फॉर एक्सीलेंस इन बेसिक साइंसेज
मुंबई विश्वविद्यालय (कलिना परिसर), विद्यानगरी, मुंबई-400098, भारत



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

सारांश

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

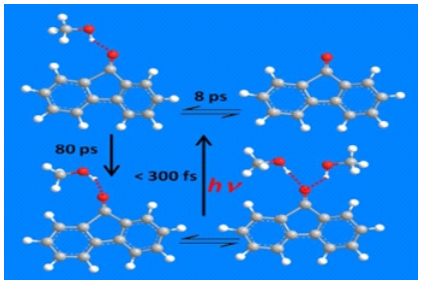
मुख्य शब्दः फेम्टोसेकंड क्षणिक अवशोषण स्पेक्ट्रमदर्शिकी, परादुत गतिकी, समावयवी गतिकी, एच-बॉन्ड गतिकी।

Photochemical Process

1

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

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

ABSTRACT

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

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

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Introduction

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

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

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

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

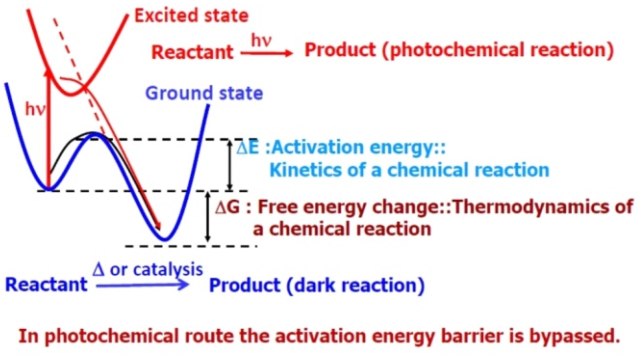


Fig.1: Advantage of a photochemical route for a chemical reaction over the conventional thermal route.

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

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

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

The excimer laser-based flash photolysis spectrometer was extensively used to study the photo dynamics in the excited states of hydroxy and amino substituted quinones, and the results were complemented by the studies using nanosecond electron pulse radiolysis and TCSPC techniques [5, 6]. This flash photolysis spectrometer was also coupled to a high-power

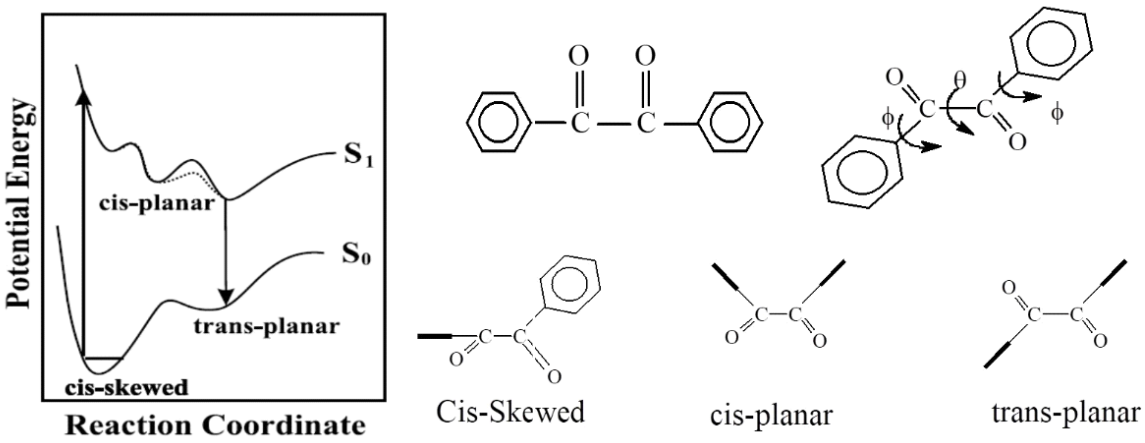


Fig.2: Schematic presentation of the potential energy surface for the changes in conformation from the cis-skewed form to the more stable trans-planar form in the S_1 state of Benzil. The surface shows that the conformational relaxation process is associated with crossings of two consecutive energy barriers. Dotted line indicates the change in barrier height in polar solvents. Copyright Springer. Adopted from Chem. Phys. Lett. 2002, 360, 443.

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

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

Towards our efforts to develop subpicosecond transient absorption (TA) spectrometer in 1993, since no commercial femtosecond laser system and TA spectrometer were then commercially available, decision was taken to indigenously develop an amplified colliding pulsed mode-locked (CPM) dye laser system and the TA spectrometer. In this spectrometer, temporal dynamics could be recorded in the 400 – 1100 nm region with the time resolution of about 200 fs. This spectrometer was then the first one of its kind in India and was extensively used to study the intramolecular charge transfer dynamics in hydroxy and amino-substituted benzophenone derivatives [11] and conformational relaxation dynamics in the excited state of Benzil [12]. The triple exponential decay dynamics of the S_1 state of Benzil indicated that the process of conformational change from the cis-skewed to the trans-planar form takes place via the formation of a meta-stable intermediate conformer resulting the involvement of two consequent barrier crossing processes. The barrier crossing dynamics is governed by both the polarity of the solvent, which alters the barrier heights by 'static' interactions, as well as the viscosity of the solvent via 'dynamical' interactions.

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

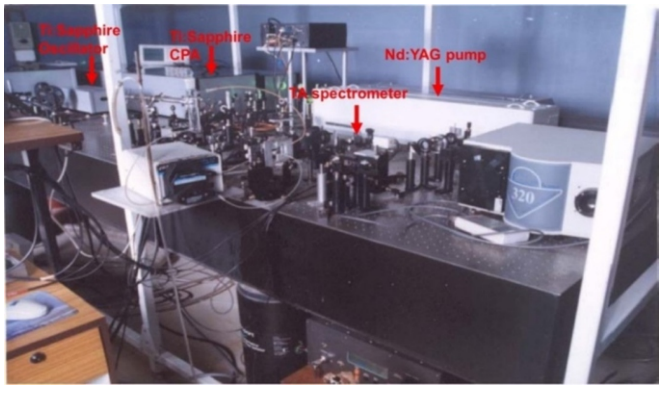


Fig.3: Ti:Sapphire laser based femtosecond TA Spectrometer.

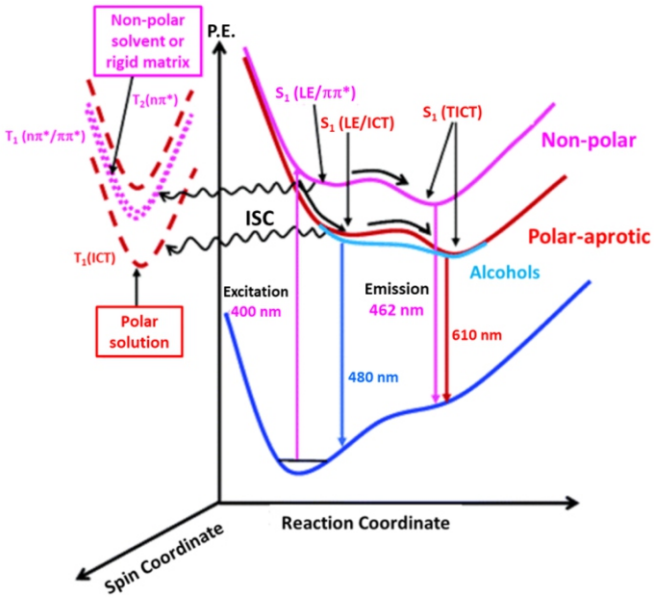


Fig.4: Potential energy surface (PES) diagram for the relaxation dynamics of the excited states of DMABP. S_1(LE) and S_1(TICT) represents the two adiabatically coupled locally excited and relaxed or twisted S_1 states, respectively. In nonpolar solvents, the LE state is an asymmetrically charge-distributed π–π state, but in polar solvents, the LE state is an ICT state. The LE to TICT conversion process via diffusive twisting of the dimethylaminophenyl group is associated with a barrier-crossing process. In alcoholic solvents, the height of the energy barrier is lower than that in aprotic solvents. In alcoholic solvents, the emission maximum at 480 nm arises due to emission from the S_1(LE) state but in aprotic solvents the emission maximum in the 462-610 nm region arises due to emission from the S_1(TICT) state. This diagram also presents the relative positions of different triplet energy levels and possible intersystem crossing processes in rigid matrixes at 77 K. Copyright American Chemical Society, Adopted from J. Phys. Chem. A. 2004, 108, 2583.*

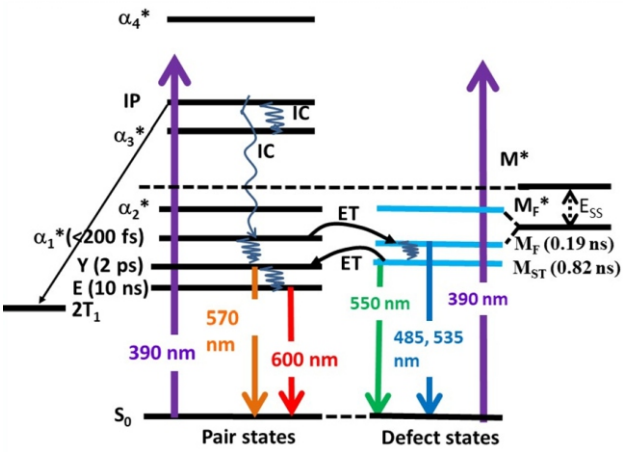


Fig.5: Schematic energy level diagram of the exciton states in perylene nanoaggregates. Lifetimes of the lower energy exciton states are given in the bracket. Relative positions of the energy levels in pyrene nanoaggregates are very similar. Copyright American Chemical Society, Adopted from J. Phys.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

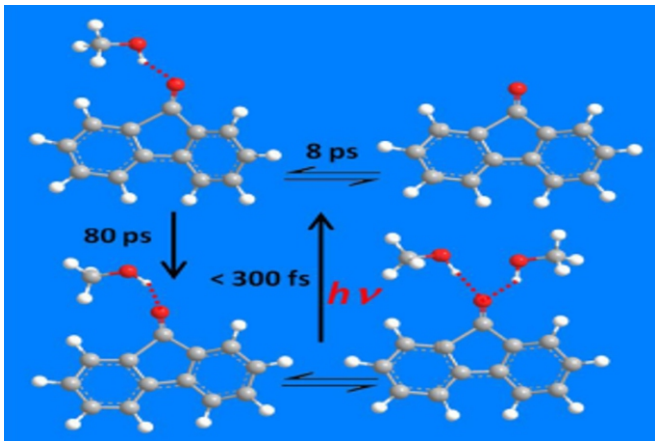


Fig.6: Ultrafast dynamics of hydrogen bond breaking and making in the excited state of fluoren-9-one. Copyright American Chemical Society, Adopted from J. Phys. Chem. B2017, 121, 1068.

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

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

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

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

Acknowledgments

It is my pleasant duty to acknowledge the kind guidance, help and encouragement of Prof. J. P. Mittal and Prof. T. Mukherjee in development of the facilities and important contributions of my divisional colleagues, collaborators and students, number of whom is too large to make individual mentioning here. But their active contributions are clearly evident in the list of references given here.

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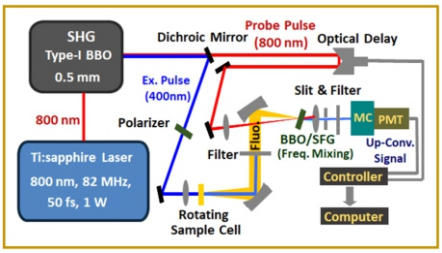
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पराद्रुत प्रतिदीप्ति अपकन्वर्जन

2

पराद्रुत फोटोइंड्यूस्ड प्रक्रियाओं के यांत्रिकी और गतिज विवरण के अन्वेषण में प्रतिदीप्ति अपकन्वर्जन तकनीक

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राजा रमन्ना फेलो, परमाणु ऊर्जा विभाग



आरपीसीडी, बीएआरसी में विकसित फेमटोसेकंड एफयूसी सुविधा का व्यवस्था आरेख।

सारांश

वर्तमान लेख का उद्देश्य विकिरण और प्रकाश रसायन विभाग (आरपीसीडी), रसायन विज्ञान वर्ग (सीजी), भापअ केंद्र में विकसित अत्याधुनिक पराद्रुत प्रतिदीप्ति अप-कन्वर्जन (एफयूसी) सुविधा का एक संक्षिप्त विवरण प्रस्तुत करना और विभिन्न पराद्रुत फोटोइंड्यूस्ड प्रक्रियाओं के अंतर्गत अन्वेषण में इस सुविधा के उपयोगों पर चर्चा करना है, जो पूर्व के कम समय विभेदन वाले पारंपरिक प्रकाश भौतिकी मापों का उपयोग करके संभव नहीं हैं। इस लेख में, आरपीसीडी में विकसित एफयूसी सुविधा पर चर्चा की गई है, और बाद में इस सुविधा का उपयोग करके किए गए कुछ चयनित पराद्रुत अध्ययनों को संक्षेप में प्रस्तुत किया गया है, जिससे यह पता चलता है कि यह सुविधा इन प्रक्रियाओं के जटिल यांत्रिकी अंदरूनी पहलुओं को ज्ञात करने के लिए कैसे उपयोगी थी, जो कई व्यावहारिक अनुप्रयोगों के लिए सीधे प्रासंगिक हैं।

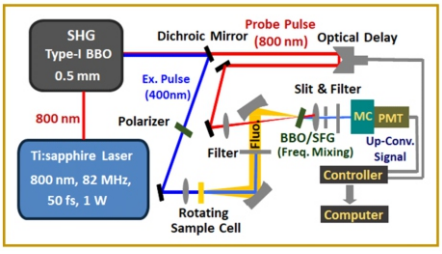
मुख्य शब्दः प्रकाश रसायन, पराद्रुत फोटोइंड्यूस्ड, जटिल यांत्रिकी

Ultrafast Fluorescence Up-conversion

2

Fluorescence Up-Conversion Technique in Investigating Mechanistic and Kinetic Details of Ultrafast Photoinduced Processes

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Schematic diagram of the femtosecond FUC facility developed in RPCD, BARC

ABSTRACT

Present article is aimed to provide a brief account of the state-of-the-art ultrafast fluorescence up-conversion (FUC) facility developed in the Radiation & Photochemistry Division (RPCD), Chemistry Group (CG), BARC, and to discuss the usages of this facility in exploring the insides of different ultrafast photoinduced processes, which are otherwise not possible by using conventional photophysical measurements having lower time resolutions. In this article, the FUC facility as developed in RPCD is discussed fist, and subsequently a few selected ultrafast studies carried out by using this facility have been presented in brief, bringing out how this facility was useful to get intriguing mechanistic insides of these processes, which are having direct relevance to many practical applications.

KEYWORDS: *Photochemistry, Ultrafast photoinduced processes, Intriguing mechanistic insights*

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Introduction

In Bhabha Atomic Research Centre (BARC), R&D activities in chemistry had started since the formation of this advanced research institute in 1954. In the initial years, major chemistry activities of the institute were oriented towards the development of infrastructures and facilities for advanced chemical analysis, to support different nuclear research programs of the Department of Atomic Energy (DAE). Alongside, chemistry fraternities also started perusing fundamental research to understand various radiation induced chemical processes. During mid-eighties, fundamental research in photochemical sciences was also initiated, as photoinduced processes are often complementary to radiation induced processes, and also because many photoinduced processes have direct relevance to different applied areas, namely, exotic photochemical synthesis, luminescence-based sensor development, solar energy conversion, photovoltaics applications, understanding excited state properties, and many others. Though in the initial years, photochemical studies were carried out using steady-state measurements mainly, due to the lack of time-resolved techniques, subsequently, however, different time-resolved techniques were developed in BARC for advanced photochemical studies [1-3]. In this respect, development of ultrafast photochemical techniques require to mention, and one of such technique is the femtosecond fluorescence up-conversion (FUC) facility [3]. Present article aims to discuss the important features of the state-of-the-art FUC facility developed in the RPCD, and to bring out how this facility was used fruitfully in exploring the intriguing mechanistic insides of ultrafast photoinduced processes. In the following sections, thus, we present and discuss in brief the aforementioned aspects of the FUC facility and its uses, justifying the perspective of the present article.

Fluorescence up-conversion setup: Basic aspects and instrumentation

FUC is a nonlinear frequency mixing process whereby two photon energies (ω_1 and ω_2) are mixed together to produce a sum-frequency light ($\omega_s = \omega_1 + \omega_2$) [4]. The block diagram of the femtosecond FUC facility developed in the RPCD, BARC, is shown in Figure 1. In this experimental setup, a mode-locked Ti:sapphire laser (CDP, Russia), which is optically pumped by a solid state semiconductor laser (Verdi, 5W, 532 nm; Coherent, USA) and produces ~50 fs laser pulses at a frequency of 82 MHz with central wavelength at ~800 nm and tunability range of 770-950 nm, is used as the fundamental ultrafast laser source.

In the FUC facility, the fundamental laser pulses from the Ti:sapphire laser (~800 nm) are first routed through a harmonic generator (1 mm Type-I BBO) to generate the 2nd harmonic (around 400 nm) or the 3rd harmonic (around 266 nm) light, which are used for sample excitation. A Berek compensator was used in the path of excitation light to adjust its polarization with respect to the fundamental 800 nm light which was used as gate pulse (vide infra). The excitation pulses excite the sample taken in 1 mm thick rotating quartz cell, and the emanating fluorescence from the sample is then focused onto a nonlinear mixing crystal (0.5 mm Type-I BBO) with the help of two off-axis parabolic mirrors. Meanwhile, the gate pulses are routed through a stepper motor driven optical delay line and then focused onto the same mixing crystal, overlapping spatially with the focused fluorescence light. The optic axis of the mixing crystal is tuned suitably for the best phase-matching condition to achieve efficient sum-frequency generation [4].

The sum-frequency pulses thus generated are having temporal width similar to that of the gate pulses. These pulses are separated from the residual gate pulses by using a UV band pass filter (UG 11) and focused at the slit of a double monochromator and detected eventually by using a photon counting setup (CDP, Russia). For the recording of the fluorescence decay trace of the sample, the gate pulses are delayed temporally with respect to the excitation pulses, by moving the optical delay line placed in the path of gate light. For each of the delay positions of the gate pulses, the integrated intensity (count) of the sum-frequency light is recorded for a fixed period of time, and the process is repeated with the sequential movement of the delay line, covering the whole region of the desired fluorescence trace. The plot of the counts obtained for the integrated sum-frequency light as a function of the time delay τ of the gate pulses, reproduces the

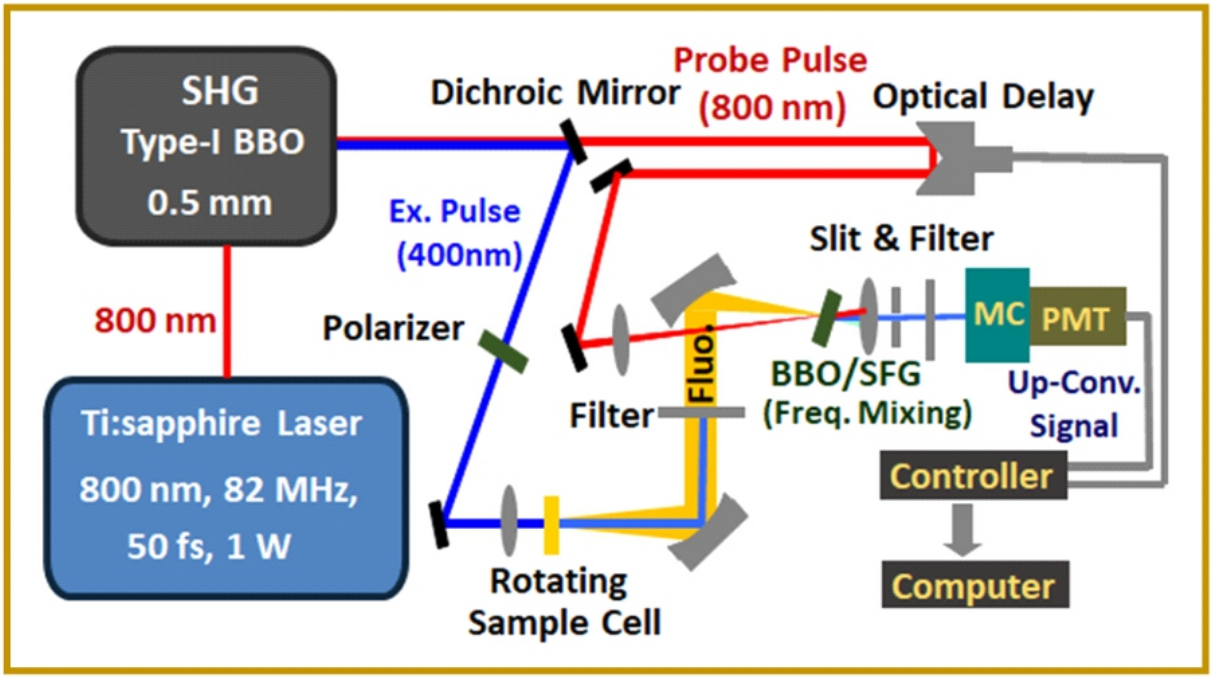


Fig.1: Schematic diagram of the femtosecond FUC facility developed in RPCD, BARC.

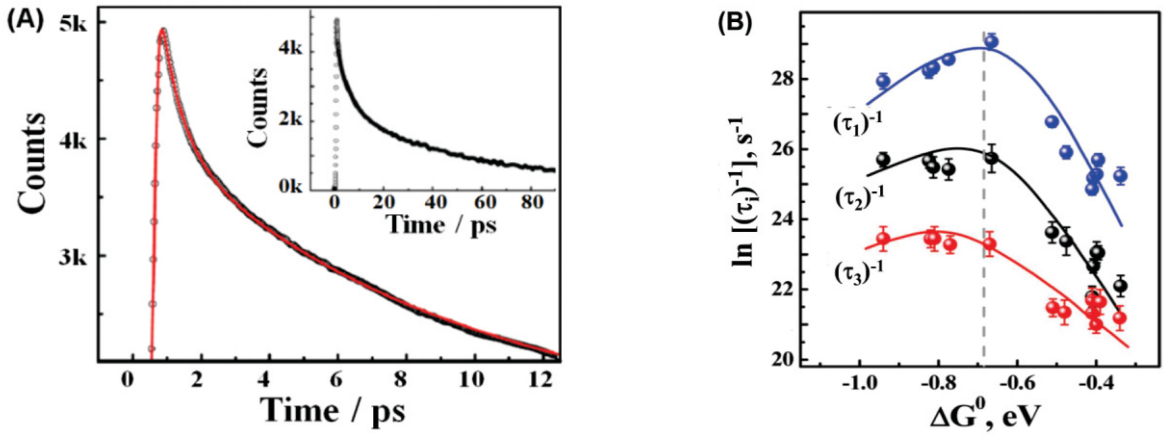


Fig.2: (A) Ultrafast fluorescence kinetic trace of donor dye coumarin 102 in cetylpyridinium chloride (CPC) micelle, where pyridinium moiety of CPC acts the electron acceptor. Initial part of the trace is zoomed in the main figure, while the full trace is shown in the inset of the figure. (B) MI behavior shown by the inverse of all the decay components (τ_1, τ_2 and τ_3) on correlating with reaction exergonicity. Figures are redrawn from reference [13].

fluorescence kinetic trace of the sample, with a time resolution similar to the temporal width of the gate pulses.

Selected ultrafast studies carried out using the present up-conversion setup

In the last about 40 years, many exciting ultrafast studies have been reported in the literature to understand the detailed insight of many chemical and physiochemical processes like, solvent relation, intramolecular relaxation, intra and intermolecular charge transfer, tortional relaxation, excited state proton transfer, photoinduced electron transfer (PET), charge recombination (CR) in ion-pairs, and so on. To be mentioned that most of these processes are directly or indirectly associated with many natural systems as well as in many practical applications. Due to space limitation, discussion on all these processes is beyond the scope of this article. Consequently, in the following we limit our discussion solely on a few of the selected ultrafast studies caried out by us using the FUC facility developed in RPCD, BARC, bringing out the intriguing results thus obtained on the concerned photoinduced ultrafast processes.

Ultrafast bimolecular photoinduced electron transfer processes

Photoinduced electron transfer (PET) is an important research topic in chemical sciences for long, especially since the development of conventional ET theory by Marcus in 1956, predicting the unique inversion behavior for the ET rates (k_{et}) on correlating with reaction exergonicity ($-\Delta G^0$), i.e. k_{et} would follow a bell-shaped curve with $-\Delta G^0$, displaying its increasing trend in the normal region ($-\Delta G^0 < \lambda$), a decreasing trend in the inverted region ($-\Delta G^0 > \lambda$), and the maximum k_{et} at the barrierless condition ($-\Delta G^0 = \lambda$), where λ is the total reorganization energy for the reaction [5]. Following this theory, enormous experimental studies were carried out, but the Marcus inversion (MI) behavior remained elusive for almost 30 years, till it was first reported by Miller and co-workers in 1984 for intramolecular charge shift reactions in radiolytically produced radical species involving donor-spacer-acceptor type of bi-functional molecules [6]. Later on, many other ET systems were found out to display MI behavior, but interestingly only for intramolecular ET and CR reactions. For bimolecular ET in conventional solvents, however, the observed reaction rates (k_{obs}) did not show the MI behavior, rather follow the Rehm-Weller behavior [7], where k_{obs} effectively saturates to the bimolecular diffusion-controlled rate (k_d) at the higher exergonicity region [5].

First report of MI behavior for bimolecular ET reaction was first reported by our group following the PET reactions in micellar systems [8-10]. In these cases, k_{obs} is found to be faster than the concerned k_d values, which are significantly lower due to constrained nature of the medium. Observed MI behavior in these cases is attributed to the non-diffusive nature of the reaction, which is understood to follow two-dimensional ET (2DET) mechanism, as proposed by Sumi and Marcus in 1986, to refine the conventional ET theory for reactions occurring under the non-equilibrium solvent relaxation condition [11]. As our initial studies were carried out using the sub-nanosecond resolved time-correlated single photon counting (TCSPC) measurements, the limited time resolution (~100 ps) of the TCSPC setup restricted us to record the ultrafast part of the kinetic traces, essential to substantiate the involvement of the 2DET mechanism. Accordingly, bimolecular PET reactions in micelles and in other constrained media were explored further, recording the ultrafast fluorescence kinetic traces of the acceptor or donor dyes in the PET reactions using FUC measurements (Fig.2 A) [12-14]. Correlating the inverse of the decay components extracted from the observed kinetic traces, we could observe clear MI behavior, not only for the fastest ET component (τ_1) but also for the other relatively slower ET components (τ_2 and τ_3) as well (Fig.2 B). These results unequivocally established that bimolecular ET in constrained media indeed progressed through 2DET mechanism than following the conventional 1DET mechanism, which is applicable only for ET reactions in low viscosity and fast relaxing solvents.

Ultrafast torsional relaxation process in molecular rotors

Molecular rotors are the fluorogenic molecules that undergo tortional relaxation in the excited state to dissipate their excitation energy in a fast non-radiative manner. The fluorescence emissions of the molecular rotors are thus extremely weak in low viscosity solvents. As the tortional relaxation are retarded very largely on increasing the solvent viscosity or on making the rotor molecules to bind with macromolecules or supramolecular assemblies, their fluorescence intensity undergoes a huge enhancement, making these dyes to be very useful fluorescence probes for various applications. Further, molecular rotors possessing target specific recognition groups can find applications in biological imaging and therapeutics. Understanding the modulations of the torsional relaxation dynamics in different microenvironments is very essential to explore the usefulness

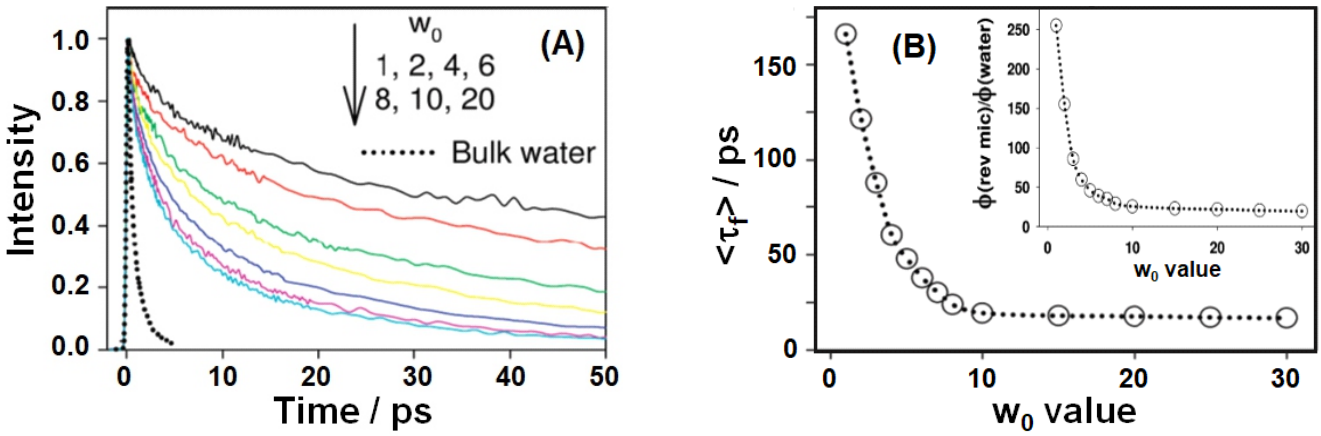


Fig.3: (A) Ultrafast fluorescence kinetic traces of ThT dye in AOT RMs with varying w_0 values. Kinetic trace for the dye in bulk water is also shown for a comparison. (B) Changes in the $<\tau_f>$ and Φ_f (inset) values of ThT in AOT RMs as a function of the w_0 values. Figures are redrawn from reference [15].

of the molecular rotors in different chemical and biological applications. In this context, good number of studies has been carried out in RPCD, BARC, following FUC measurements. Giving an account of all these studies is certainly not possible in the present article, however, in the following sub-sections we briefly present a few of these studies, highlighting the effect of supramolecular confinements and that of binding with bio-macromolecular systems on the ultrafast torsional relaxation dynamics of an important molecular rotor dye, Thioflavin-T (ThT).

Torsional relaxation of molecular rotors in confined media

In one of our studies, ultrafast deexcitation process of ThT dye was investigated in the confined water pools of aerosol-OT (AOT) reverse micelles (Rms), following FUC measurements [15]. In an earlier study, it was reported that the inverse of the fluorescence yield of ThT correlates quite linearly with the inverse of the viscosity of RMs, suggesting the usefulness of ThT for fluorescence-based micro-viscosity sensing [16]. In our study, steady-state fluorescence and ultrafast FUC measurements (Fig.3 A) were caried out to follow the changes in the fluorescence yields (Φ_f) and average fluorescence lifetimes ($<\tau_f>$) of ThT as a function of the increasing water pool size (w_0 values; water to AOT molar ratio) of the AOT RMs. Both Φ_f and $<\tau_f>$ values decreased in an asymptotic manner, approaching the limiting values in the respective cases (Fig.3 B), which are substantially higher than the corresponding values in bulk water. Observed results thus provide an intriguing inside of the confinement effect, suggesting that due to electrostatic interaction of cationic dye ThT with the negatively charged AOT head groups, and also because the water molecules in the water pools of RMs are bound to AOT head groups, the torsional relaxation of the dye in the RMs were substantially sluggish even in the cases where water pool sizes are very large, causing the torsional relaxation process in the confined environments to be quite slower than in the bulk water.

Subsequently, the w_0 depended changes in the Φ_f and $<\tau_f>$ values for ThT dye were also investigated in the cationic and neutral RMs of benzyl-hexadecyl-dimethyl ammonium chloride (BHDC) and Triton X-100 (TX-100), respectively [17,18]. In cationic RMs, the Φ_f and $<\tau_f>$ values decreased asymptotically with w_0, similar to the anionic RMs, however, the results interestingly indicated that the sluggishness introduced to the torsional relaxation is always much higher than in the anionic RMs. This observation intriguingly suggested that in RMs the principle of electrostatic interaction is largely overruled by the constitution of the nanoconfined space in the RMs [18]. Compared to cationic and anionic RMs, in neutral RMs, even though the Φ_f and $<\tau_f>$ values are much higher than in bulk water, these values and consequently the sluggishness in the torsional relaxation is quite invariant of the w_0 values [18]. This observation thus substantiated that the nature of constitution of the nanoconfined space and the localization of the probe therein determine the observed effect on the torsional relaxation of a molecular rotor in the concerned supramolecular systems.

Torsional relaxation of molecular rotors on binding with bio-macromolecules

With the perspective that the torsional relaxation of molecular rotors would be retarded significantly on binding to bio-macromolecular systems, in one of the studies, Nath and coworkers [19] used ThT as the fluorescence probe to investigate the possible structural changes of calf thymus DNA (*ct*-DNA) in the premelting temperature (T) region, i.e. $T < T_m$, the melting temperature. While primary structure of DNA changes form helix to coil form at around T_m (~75° C), there are also minor changes in the secondary structures of DNA in the premelting region, and these changes around the physiological temperature (~37° C) particularly are realized to play a very significant role in controlling many biological activities. In the literature not much studies are reported on the structural changes of DNA in the premelting region. Following steady-state and sub-nanosecond fluorescence measurements, Nath and coworkers demonstrated that both fluorescence intensity and average fluorescence lifetime of the ThT-*ct*-DNA system undergo significant changes with temperature in the premelting region, which are otherwise not observed with the standard DNA binder dyes like ethidium bromide (EB) and 4',6-diamidino-2-phenylindole (DAPI), suggesting the usefulness of ThT as a fluorescence probe to monitor the secondary structural changes of DNA as well.

Subsequent to the above study, Nath and coworkers further extended the investigation to explore the insight of the binding interaction of ThT with *ct*-DNA [20]. Ground state absorption and steady-state fluorescence of ThT showed large changes with the varying concentration of *ct*-DNA, which allowed to estimate the binding constant value for the dye-DNA system as about 3.9×10^3 M^{-1}, indicating that the dye binds very strongly with *ct*-DNA. Binding interaction in the ThT-*ct*-DNA system is perturbed very strongly by the addition of a salt, suggesting that electrostatic interaction between cationic ThT and highly negatively charged DNA plays a major role in stabilizing the dye-DNA complex. Ultrafast fluorescence kinetic

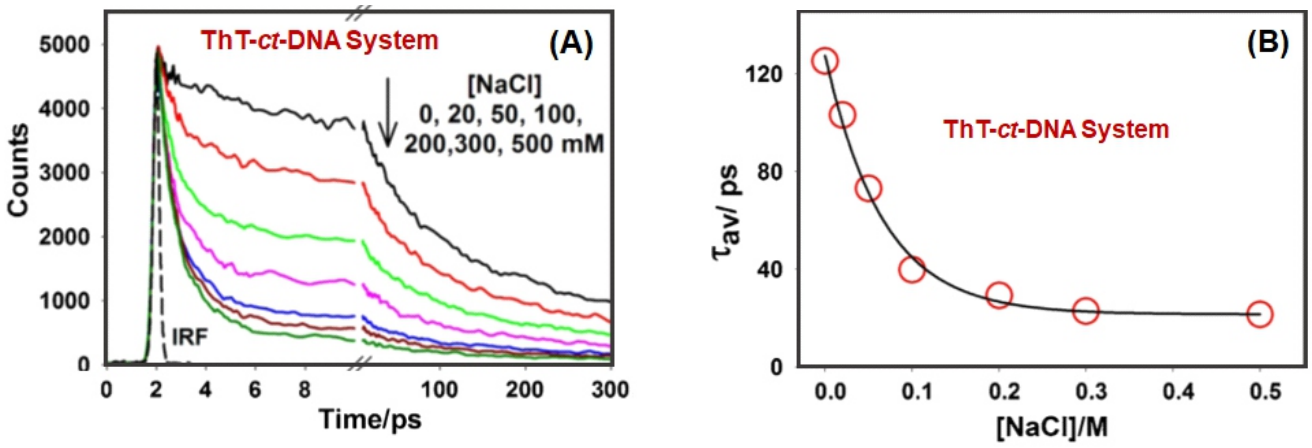


Fig.4: (A) Changes in the ultrafast fluorescence kinetic traces for ThT-ct-DNA system in the presence of varying salt concentration. (B) Changes in the <τ> values for the ThT-ct-DNA system with the changing salt concentration. Figures are redrawn from reference [20].

traces for the ThT-*ct*-DNA system as recorded through FUC measurements in the presence of varying salt concentration provided more intriguing insight of the binding interaction in this system. With the gradual addition of the salt, since the binding interaction is perturbed systematically, the ultrafast kinetic traces also concomitantly become faster (Fig.4 A) and accordingly the $<\tau_f>$ values also decrease asymptotically, approaching towards a limiting value (Fig.4 B). Interestingly, however, even in the presence of the highest salt concentration used, the limiting $<\tau_f>$ value (~20 ps) remains evidently much higher than that of the free ThT in aqueous solution (~0.61 ps). Additionally, for all the salt concentrations used, the fluorescence kinetic traces always show quite a sizeable and apparently invariant contribution of an exceptionally long (~1.4 ns) decay component. From these ultrafast results, it is evidently indicated that along with electrostatic mode of binding, a good fraction of the ThT molecules also experience the intercalative mode of binding with the DNA base pairs. Observed results also clearly indicated that while the electrostatically bound ThT molecules are slowly released from their bound state by the addition of salt, the intercalated dye molecules are hardly become free from their bound state by the influence of the salt used in the solution.

Overall, the results discussed in section 3 clearly indicate that the measurements using ultrafast FUC technique help tremendously to get intriguing insights of ultrafast photoinduced processes. Accordingly, the FUC facility developed in RPCD, BARC was used extensively to explore many other ultrafast processes, and the discussion on all these ultrafast systems is beyond the scope of the present article.

Conclusion

In the present article we provide a brief account of the ultrafast FUC facility developed in the RPCD, BARC. We also discuss the fruitful usages of this state-of-the-art facility in exploring the intriguing mechanistic insides of different ultrafast photoinduced processes studied in our group, citing and discussing the important results briefly, as obtained for some of the selected ultrafast photosystems, using the aforementioned experimental facility. In this discussion, we have tried to highlight how the ultrafast measurements helped in exploring the mechanistic and kinetic insides of the concerned photoinduced processes, which would otherwise have not been possible using conventional photochemical measurements. To be mentioned that the understanding of the mechanistic and kinetic details of ultrafast photoinduced processes are very important as these processes are directly or indirectly involved in large number of practical applications.

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प्रगत पदार्थों में स्पेक्ट्रमिकी

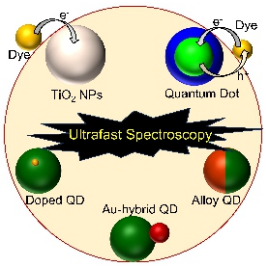
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सौर सेल पदार्थों पर अल्ट्राफास्ट स्पेक्ट्रमिकी यात्रा की कहानी

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उन्नत सामग्रियों में अल्ट्राफास्ट सस्पेक्ट्रमिकी

सारांश

अर्धचालक नैनोपार्टिकल्स एवं क्वांटम डॉट्स (क्यूडी) पर हमारी परादुत स्पेक्ट्रमिकी यात्रा का रोडमैप 1998-2017 की अवधि में तैयार हुआ। इस दौरान, हमने TiO_2 नैनोकणों में इंटरफेसियल इलेक्ट्रॉन स्थानांतरण प्रक्रियाओं और डाई सेंसिटाइज्ड सोलर सेल अनुप्रयोगों के लिए विशेष रूप से डिजाइन किए गए डाई अणुओं के बारे में महत्वपूर्ण जानकारी प्रदान की। कई विशेष रूप से डिजाइन किए गए QD/अणु संयोजन में अल्ट्राफास्ट हॉट और थर्मलाइज्ड इलेक्ट्रॉन और होल ट्रांसफर डायनेमिक्स का मूल्यांकन किया गया है।Mn- और Cu-डोपिंग, Auहाइब्रिड और मिश्रधातु क्यूडी सहित कई उन्नत कार्यात्मक क्यूडी की परादुत वाहक विश्रांति गतिकी पर हमारी मौलिक समझ का वर्णन किया गया है जो सौर सेल दक्षता के साथ एक सीधा संबंध दर्शाता है।

मुख्य शब्दः परादुत स्पेक्ट्रमदर्शिकी, क्वांटम डॉट्स, नैनोपार्टिकल्स, इलेक्ट्रॉन एवं छिद्र स्थानांतरण, सौर सेल

Spectroscopy in Advanced Materials

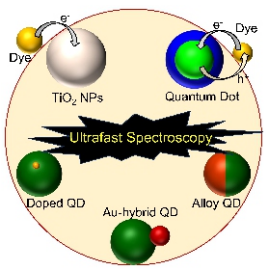
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A Tale of Ultrafast Spectroscopic Journey on Solar Cell Materials

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Ultrafast Spectroscopy in Advanced Materials

ABSTRACT

The roadmap of our ultrafast spectroscopic journey on semiconductor nanoparticles and quantum dots (QDs) is described over the period of 1998–2017. Over this time, we provided significant insights into the interfacial electron transfer processes in TiO_2 nanoparticles and tailor designed dye molecules for dye sensitized solar cell applications. Ultrafast hot and thermalized electron and hole transfer dynamics in several tailor designed QD/molecule composite is summarized. Our fundamental understanding on the ultrafast carrier relaxation dynamics of several advanced functional QDs including Mn- and Cu-doping, Au-hybrids and alloy QDs is described which provides a direct correlation with the solar cell efficiency.

KEYWORDS: *Ultrafast spectroscopy, Quantum dots, Nanoparticles, Electron and hole transfer, Solar cell*

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Introduction

Semiconductor nanomaterials, including quantum dots (QDs) are of immense interest in the field of solar cells, light emitting diodes, photocatalysis etc. due to their easy solution processability and bandgap tunability [1]. To successfully utilize such tiny materials in certain devices, it is extremely important to understand the fundamentals of the exciton (bound electron-hole pair) relaxation-recombination dynamics within these materials which often falls in fast to ultrafast timescale [2]. In this regard, during our journey in BARC from 1998–2017, we have extensively investigated the ultrafast charge transfer dynamics in several oxide semiconductor and metal nanoparticles, and chalcogenide QDs, after sensitizing with a series of molecules. We also fabricated several chalcogenides QD-based heterostructures and investigated their ultrafast photophysical dynamics and showed that they have a direct correlation with the solar cell efficiency. In this article, we aim to summarize some of the key findings of our journey in BARC from 1998–2017 which includes 13 PhD thesis and 121 peer-review research publications (Fig.1).

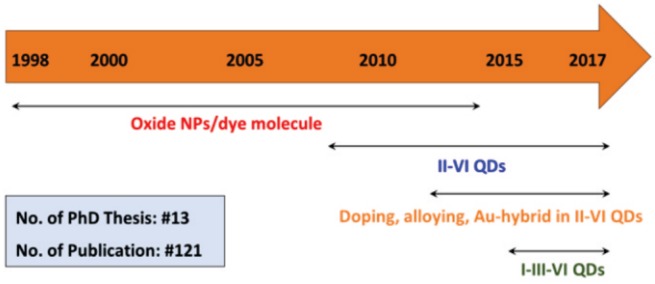


Fig.1: Timeline showing our progress in different fields over the two decades in BARC.

One of our early works on the interfacial electron transfer dynamics was reported in surface modified TiO_2 nanoparticles sensitized by the molecule Alizarin (Fig.2a, b) [3]. Ultrafast electron injection from the Alizarin molecule to TiO_2 has been confirmed by direct detection of the electron in the conduction band of TiO_2, as well as the corresponding Alizarin cation, along with the bleaching of the dye molecule. The back electron transfer (BET) dynamics is found to be slower on the surface modified TiO_2 than the unmodified one, which has been explained on the basis of electron transfer in the Marcus inverted region. Similar interfacial electron transfer and BET dynamics has been demonstrated extensively involving TiO_2 and ZrO_2 nanoparticles and several molecules [4]. We provided detailed insight into the electron injection dynamics of intramolecular charge transfer and twisted intramolecular charge transfer (TICT) states of coumarin molecules to TiO_2 NPs (Fig.2c, d) [5-6]. Our result provides information on the extremely slow BET process in the TiO_2/coumarin system involving TICT states, being TICT is a charge separated state, and could serve as a very good system for the dye sensitised solar cells (DSSC).

We demonstrated the kinetic model of the exciton decay of porphyrin J and H-aggregates which are suitable for light harvesting antenna due to their wide range of coverage of the solar energy spectrum [7-8]. Further, we showed that these aggregates form complexes with TiO_2 NPs and improve the photoinduced charge separation (Fig.2e, f). We attributed higher yield of the charge separation is due to exciton-coupled charge transfer dynamics in porphyrin aggregates and their complexes with TiO_2 NPs. We further demonstrated the ultrafast interfacial charge transfer and BET dynamics to TiO_2 and ZrO_2 nanoparticles involving several tailor made catechol and resorcinol Ru- and Os-porphyrin based dye and BODIPY molecules [9-11]. Our result suggests that although strong catechol coupling may be favourable for interfacial electron injection to TiO_2 NPs in <100 fs timescale, the stronger coupling reduces the spatial separation between TiO_2 and the dye, causing faster BET reactions compared to the corresponding resorcinol derivatives, where slower BET is

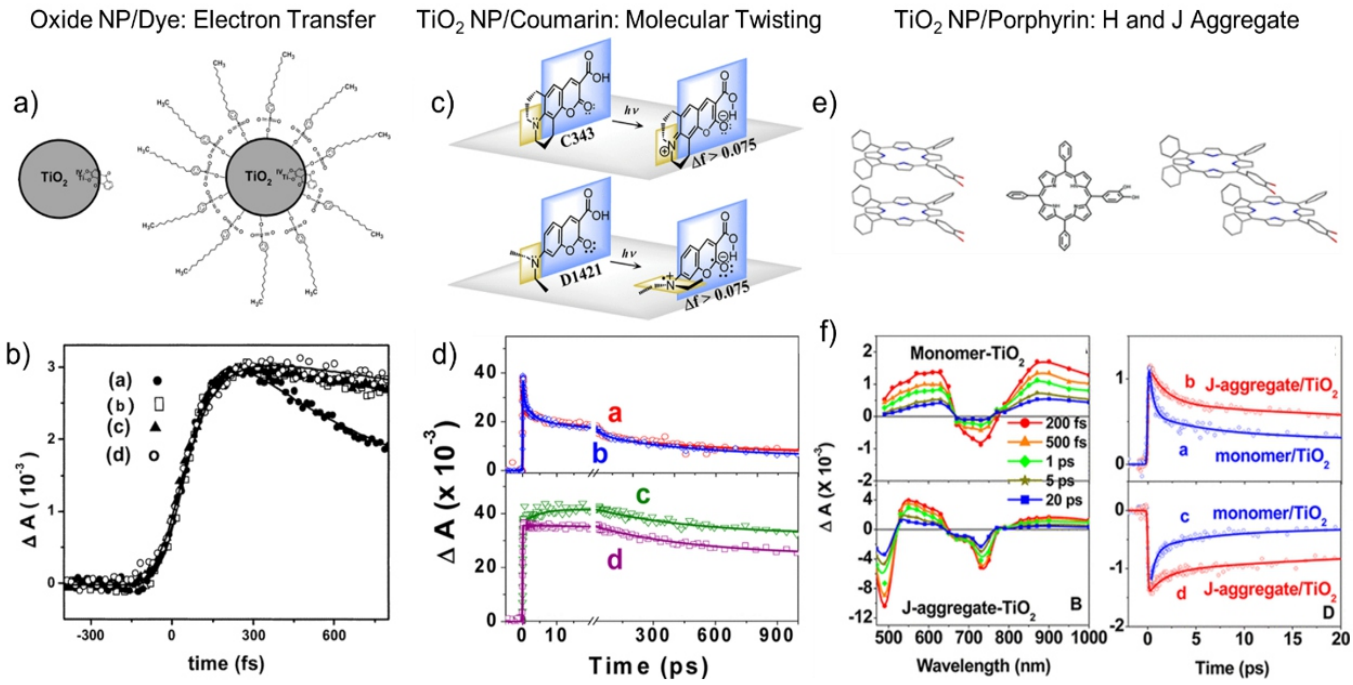


Fig.2: a, b) Schematic of TiO_2 NPs without and with alizarin molecule, and corresponding ultrafast transients (in different solvent for the nanocomposite in b-d) respectively [3]. c, d) Molecular structure of two coumarin (C343 and D1421) and corresponding transients in upper and lower panel respectively. Reproduced from J. Phys. Chem. C 2014, 118 (20), 10661-10669. e) Molecular structure of the porphyrin monomer and H and J aggregates, and f) transient absorption spectra of the monomer and J aggregates in the presence of TiO_2, and corresponding transients, respectively [7].

observed. We proposed that such slowing down of the BET processes may lead to significant boosting of the solar cell performance in the DSSC devices made with resorcinol derivatives. We also demonstrated electron transfer and proton-coupled electron transfer reactions in Ru-polypyridyl complexes where water plays an important role [12].

Following demonstration of the ultrafast interfacial processes in a variety of oxide semiconductor NPs and dye molecules for their proper utilization in DSSCs, we turned our attention to work on the emerging chalcogenide quantum dots (QDs) in 2009. We prepared several thiol capped water soluble MX QDs where M = Cd, Zn and X = S, Se, Te, and their core/shell heterostructures, and investigated their ultrafast charge carrier dynamics [13]. The cooling and population dynamics of mercaptopropionic acid capped CdTe QDs in different quantized states of the charge carriers were monitored by following the growth kinetics of the bleach at different excitonic positions upon above bandgap excitation with a 400 nm femtosecond pump pulse. The carrier cooling time to the second and first excitonic state was measured to be 150 fs and 500 fs respectively, which increases with increasing the size of the CdTe QDs, and has a strong dependence on the defect states [13]. Electron and hole cooling time of the first excitonic state of CdTe QDs was determined using electron and hole quencher and measured to 700 fs and 150 fs respectively. Electron and hole trapping dynamics were also measured to in the range of 1 ps. We further compared the ultrafast charge transfer dynamics of the CdTe QDs with type-II CdTe/CdS core/shell QDs [14]. In the type-II CdTe/CdS core/shell, the electron is transferred to the CdS shell while the hole is localized in the CdTe core due to their band alignment. Using a femtosecond transient absorption study, we corroborated the above ultrafast processes in the core/shell QDs using individual electron and hole quencher molecules. Importantly, we observed slow carrier relaxation to the band edge states and increased carrier lifetime due to charge separation which may have profound usage of these materials in photovoltaics. We further extend our idea on increased charge separation of CdTe QDs upon decoration with graphene where extremely longer charge recombination time (>1 ns) was observed, as compared to ~50 ps in CdTe QDs (Fig.3a, b). The observation reflects efficient charge separation on the graphene surface and can serve as an efficient quantum dot solar cell (QDSC) material [15].

We then extend our idea on charge separation in several tailor made QDs and QD core/shell systems by sensitizing them with a large number of organic and inorganic molecules, which often form strong charge transfer (CT) complexes. For example, one of our early works in this direction was reported in CdS QDs/ 4´, 5´-dibromofluorescein (DBF) nanocomposite, followed by strong ground state CT complex formation [16]. The strong CT complex formation in <100 fs timescale results in efficient interfacial hole and electron transfer processes from one component to another in the nanocomposite (Fig.3c, d). Here, the nanocomposite forms a type-II like structure, in which the photoexcited CdS QDs can transfer the hole to the DBF molecule in 800 fs, while the photoexcited DBF can transfer electrons to the CdS domain in 100 fs timescale which we have revealed by ultrafast experiments. Strong CT complex formation is also observed in CdSe QDs and CdSe based type-I and type-II core-shell NCs and aurin tricarboxylic acid (ATC) nanocomposite where the effect of shell materials on the CT process has been described [17]. While the electron injection dynamics was observed in <150 fs in all three cases, the hole transfer process has been found to be facilitated in CdSe/CdTe type-II structure (~3 ps) and it is retarded in CdSe/ZnS type-I structure (~6 ps) due to their electronic band alignment. We further provided important information about the hot carrier

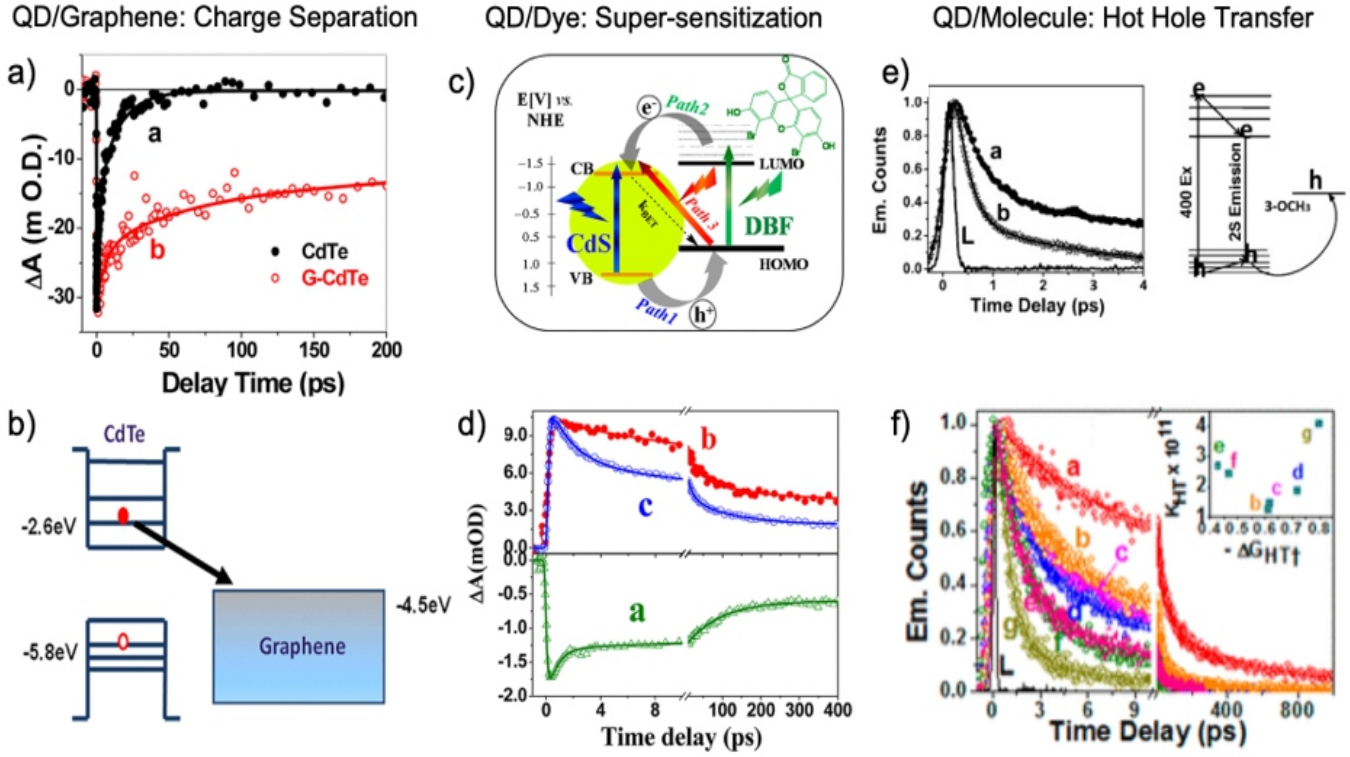


Fig.3: a, b) Ultrafast transients of CdTe QDs without and with graphene, and corresponding schematic of electron transfer [15]. c, d) Schematic of electron, hole transfer in the CdS QDs/DBF molecule super-sensitized system, and a few transients of the system, respectively [16]. e) Hot hole transfer dynamics of CdSe QDs in the presence of 3-methoxycatechol [18]. f) Hole transfer dynamics of CdSe QDs in the presence of different catechol derivatives [18].

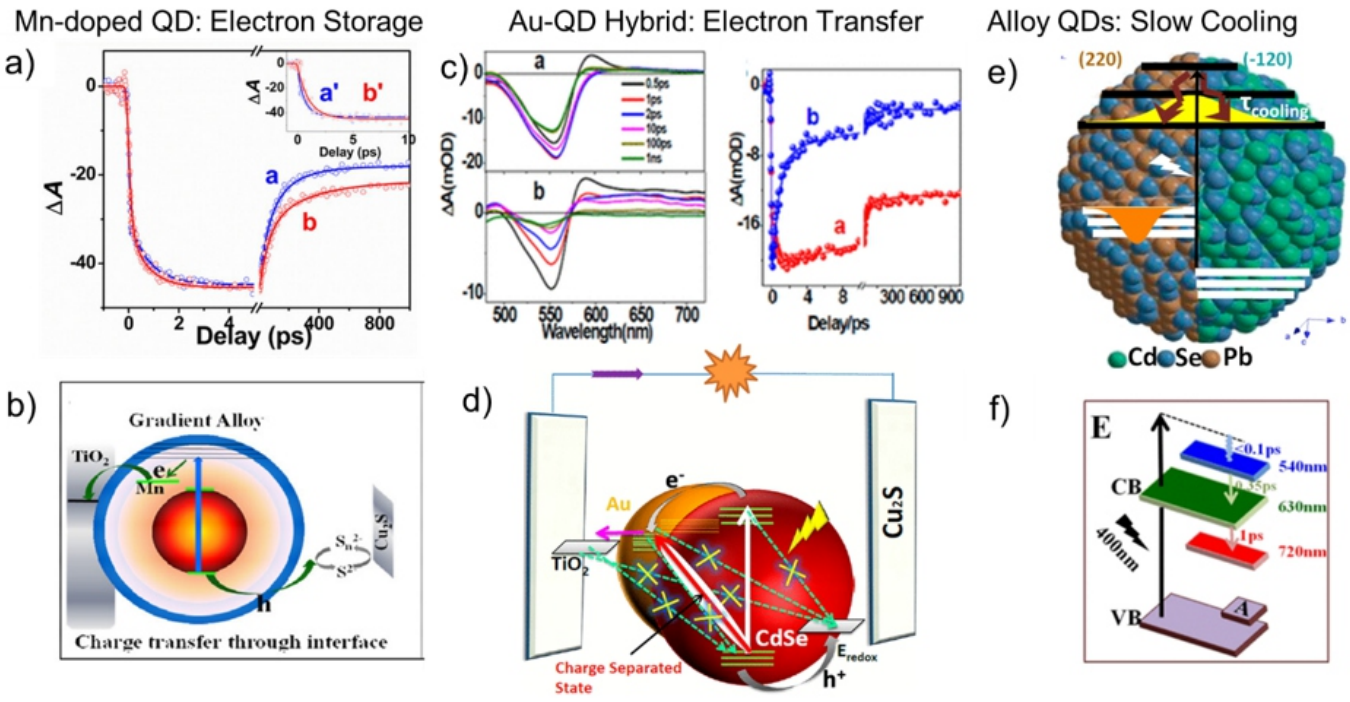


Fig.4: a, b) Ultrafast transients of undoped and Mn-doped alloy QDs, and corresponding schematic of Mn-mediated electron transfer process, respectively [20]. c, d) Transient absorption spectra and kinetics of CdSe and Au-CdSe hybrids, and corresponding electron transfer to Au domain schematic, respectively [22]. e) Slow electron cooling process in the CdSe/PbSe Janus structure [24]. f) Slow carrier cooling process via intra bandgap donor-acceptor states in $CuInS_2$ QDs [25].

(hole) extraction from QDs to different molecular adsorbates using combination of femtosecond transient absorption and upconversion spectroscopy (Fig.3e, f) [18]. The hot hole dynamics was probed by monitoring higher exciton states which takes place in only 250 fs timescale, in comparison to the thermalized hole transfer timescale of 2-10 ps. Our results suggest electron donating moiety in these molecular adsorbates helps in boosting the hot hole extraction. Overall, the nanocomposites were claimed to be a super-sensitizer which can boost the QDSC efficiency drastically by simultaneous extraction of electrons and holes.

We then switched our research direction on ultrafast processes in Mn- and Cu-doped QDs, Au-hybrid QDs, and different alloy QDs and nanocrystals (Ncs), all of which show a direct relevance to the QDSC performance. In particular, Mn-doped CdSe QDs and related NCs were investigated, which show introduction of structural defects in the doped QDs than the undoped QDs, leading to ultrafast recombination [19]. However, upon functionalization with bromo-pyrogallol red (Br-PGR) molecule, which forms a strong CT complex, the Mn-state can act as an electron storage centre within the QDs. We propose such electron storage capacity of the Mn-dopant may boost the QDSC performance tremendously. In fact, by developing Mn doping in tailor designed alloyed QDs that supports a CT state within the material, we show such electron storage capacity can boost the solar cell efficiency from ~3.3 % to 4.5 % from undoped to Mn-doped QDs (Fig.4a, b) [20]. Along with Mn-doping in QDs, we also investigated ultrafast carrier dynamics in Au-hybrid CdSe Qds [21]. Our results show that both hot and thermalized electron transfer to Au domain takes place from the CdSe QDs in a timescale of 150 fs and 300 fs respectively which has a Au NP size dependence. We further show that the ultrafast electron transfer to Au-domain and subsequent slow charge recombination process has a direct consequence on enhancing the photocatalytic dye-degradation of rhodamine B, as well as enhancing the solar cell efficiency from 3.4 % to 4.4 % (Fig.4c, d) [22].

We also developed different alloy QDs, which includes CdS_xSe_{1-x}, $CdPb_xSe_{1-x}$, $Cd_xZn_{1-x}S_ySe_{1-y}$, $CuInS_2$, $AgInS_2$, etc., and studied the ultrafast exciton and carrier dynamics for improved QDSC efficiency. As compared to sub-ps carrier cooling in CdSe and CdS QDs, extremely slow electron cooling of ~8 ps is observed in the $CdS_{0.7}Se_{0.3}$ QDs, which is one of the slowest reported carrier cooling in QDs, due to efficient electron-hole decoupling [23]. We also explored the electronic cross-talk dynamics in CdSe/PbSe Janus NCs where too we observed slow electron cooling of 5 ps due to hole localization in the PbSe domain (Fig.4e) [24]. Importantly, sub-picosecond exciton and biexciton dynamics has been demonstrated in $CuInS_2$ and $AgInS_2$ QDs, where the sub-bandgap antisite states play a significant role (Fig.4f) [25]. All these slow electron cooling dynamics have a direct relevance to the final outcome of the QDSC efficiency which also we have demonstrated in some of the above systems.

In summary, in the above-mentioned time frame, we have contributed ultrafast interfacial charge transfer dynamics as well as sub-picosecond exciton and carrier dynamics in a wide range of materials, including oxide semiconductor nanoparticles, II-VI and I-III-VI chalcogenide QDs and corresponding doped, alloyed and core/shell QDs. Our understanding provides important fundamental insight into the ultrafast processes that may lead to design of higher efficient DSSCs and QDSCs. Overall, we believe we have contributed significantly to the development of several solar cell materials for photovoltaic applications via providing important insights into the ultrafast photophysical processes.

Acknowledgments

Hirendra N. Ghosh (HNG) acknowledges all his younger colleagues and PhD scholars who have contributed to this journey.

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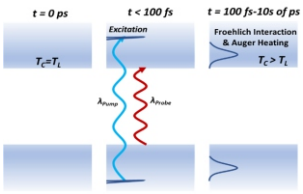
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तप्त आवेश वाहक गतिशीलता

4

हैलाइड पेरोव्स्काइट्स में तप्त वाहकों और हम फेमटोसेकंड क्षणिक अवशोषण स्पेक्ट्रमिकी के साथ उनका अनुसरण कैसे करते हैं?

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पेरोव्स्काइट्स में गर्म वाहक शीतलन

ABSTRACT

पेरोव्स्काइट्स के अद्वितीय गतिकी गुणधर्मों में से एक धीमी गति से तप्त वाहक का ठंडा होना है। वर्तमान लेख में, हमने चर्चा की है कि तप्त वाहक क्या है? और फेमटोसेकंड क्षणिक अवशोषण स्पेक्ट्रमिकी का उपयोग करके इस घटना का अध्ययन हम कैसे कर सकते हैं, को दर्शाया है। इसके अतिरिक्त हमने, तप्त वाहकों के ठंडा होने में शामिल तंत्रों और शीतलन गतिकी को नियंत्रित करने वाले कारकों पर चर्चा की है। हमने इसे लीड हैलाइड पेरोव्स्काइट्स कहे जाने वाले पदार्थ वर्ग के शीतलन को तप्त वाहकों के उदाहरण के साथ भी स्पष्ट किया है।

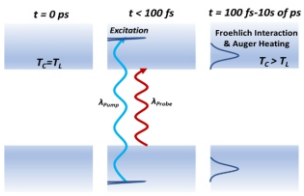
मुख्य शब्द : क्षणिक अवशोषण , नैनोकण , तप्त वाहक , पेरोव्स्काइट्स।

Hot Charge Carrier Dynamics

4

Hot Carriers in Halide Perovskites & How do we follow them with Femtosecond Transient Absorption Spectroscopy?

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Hot Carrier Cooling in Perovskites

ABSTRACT

One of the unique dynamics properties of perovskites is slow hot carrier cooling. In the present article, we discuss, what hot carriers are? and show how we can study this phenomenon using femtosecond transient absorption spectroscopy. We additionally discuss the mechanisms involved in cooling of hot carriers and factors governing the cooling dynamics. We also illustrate this with example of hot carriers cooling from class of materials called lead halide perovskites.

KEYWORDS: *Transient Absorption, Nanoparticle, Hot Carriers, Perovskites*

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Introduction

Lead Halide perovskites have shown immense potentials in thin film photovoltaics with high power conversion efficiency (PCE) of ~26% [1-2]. While Shockley Queisser (S-Q) limit sets a theoretical maximum for a single junction solar cell of 31%, there are avenues that one can explore to achieve a high PCE by mitigating carrier heat losses in photovoltaic devices. However, in a semiconductor extracting hot carriers (HC) before cooling is a futile exercise unless one can either extract carriers 'fast' or 'slowing' HC cooling. However, above mentioned approaches are easier said than done in a typical solar cell where cooling takes place in a time scale of <100 fs and extraction times in 10-100s of ps. The present article attempts to introduce the phenomena of HC cooling and is not an exhaustive report on the topic.

In the present article, we introduce what hot carriers are and discuss factors governing HC cooling and we attempt to show that HC in lead halide perovskites sustain for a longer period of time 10-100s of ps and possibility of extraction remains a distinct 'reality'. The HC cooling is followed by femtosecond Transient Absorption (fs-TA) Spectroscopy.

Carrier Cooling in Semiconductors

A semiconductor is defined by a forbidden gap between the Valence and Conduction Band also called as band gap as shown in Fig.1, with the band composed of energy levels spacing of less than thermal energy. Typical above band gap excitation leads to higher kinetic energy on carriers and non-equilibrium distribution of carriers. These carriers subsequently relax via intervalley scattering, carrier-carrier scattering etc. leading to establishment of quasi equilibrium. Since these energy levels are closely spaced in individual bands with energy separation < E_{Phonon} (Energy of phonons), interaction with phonons help release this energy in form of heat within the system. Typical cooling mechanism involving e-phonon interaction in a polar semiconductor is called Froehlich interaction or e-LO phonon interaction or polaron formation and takes place in a time scale of <100 fs [5-6]. Subsequent cooling in typical semiconductors happens by decay of optic phonons to acoustic phonons as shown in Fig.2. Therefore, the carrier temperature (TC) decays until it equals lattice temperature leading to a quasi-equilibrium. In case of a confined semiconductor the cooling is hindered due to discreteness in energy levels of individual bands with energy spacing within individual bands > E_{Phonon}. This occurs due to quantum confinement effect and cooling takes place in a time scale of 100 fs-few ps. This is called phonon bottleneck. This is the typical cooling observed under low pump intensity, however under high pump intensity the rate of relaxation like phonon-phonon scattering rates, Auger heating, hot phonon bottleneck play a major role in HC cooling. The mechanisms involved in these HC cooling are described in Fig.1.

Carrier Cooling Mechanisms

Typical mechanisms involved in HC cooling are described below.

Hot Phonon Bottleneck

Most common mode of relaxation in a polar semiconductor, like lead halide perovskites, is Froehlich interaction which is essentially interaction between macroscopic electric field due to longitudinal optic (LO) phonon and electrons with subsequent decay of LO phonons into 2 longitudinal acoustic (LA) modes also called Klemens mode. However, under high pump intensity carrier reheating occurs due to competition between phonon decay rate and carrier density dependent e-LO scattering leading to a non-equilibrium phonon population and hindered cooling. This process is called hot phonon bottleneck. This HC cooling can be modelled based of Froehlich interaction with the energy loss rate as given below,

$$\left(\frac{dE}{dt}\right)_{Phonon} \approx -\frac{\hbar\omega_{LO}}{\tau_{LO}}\left\{\left(e^{-\frac{\hbar\omega_{LO}}{k_bT_C}}\right)-\left(e^{-\frac{\hbar\omega_{LO}}{k_bT_L}}\right)\right\} \quad (1)$$

where $\hbar\omega_{LO}$ is the phonon energy, τ_{LO} is the HC cooling time or LO phonon lifetime and T_C and T_L are the carrier and lattice temperatures respectively [4].

Modelling HC cooling in Halide perovskite under low carrier density <<10^{18}/cm^3 reveals a rate of <1 ps. However a typical Froehlich interaction times are of the order of lifetimes of LO phonons which is <100 fs. Therefore, the typical modelling based on the above energy loss rates indicate cooling time of ~300-1000 fs indicating hot phonon bottleneck at play.

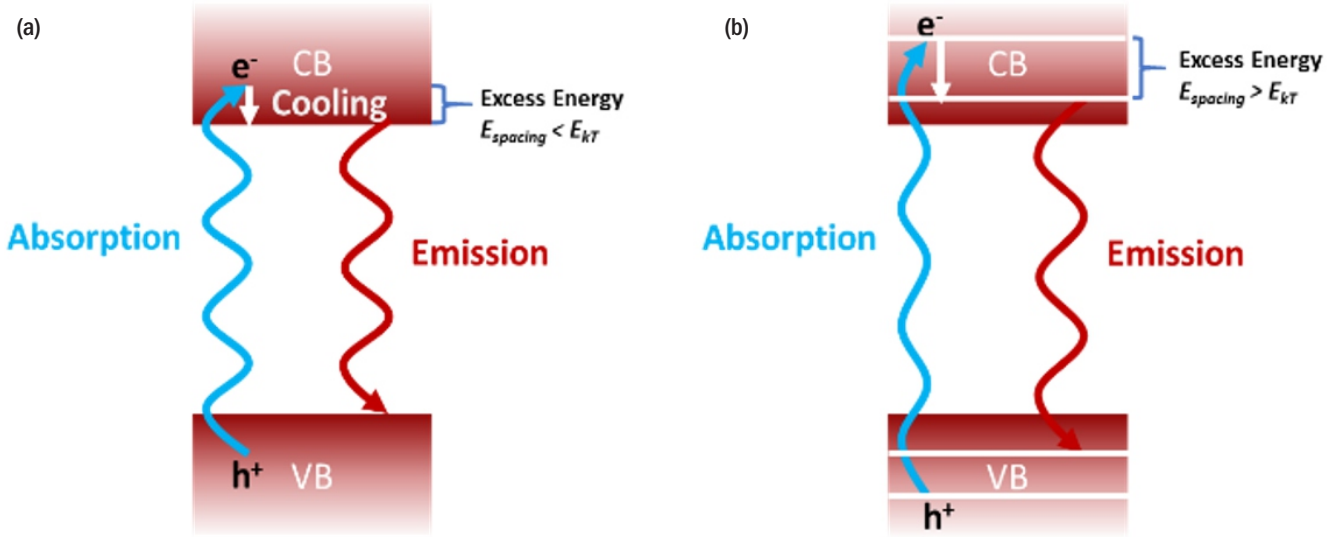


Fig.1: Typical carrier relaxation processes in semiconductors (a) Bulk semiconductor (b) Quantum Dot. Note: Carrier Trapping and other relaxation modes not shown.

Auger Heating

Under high pump intensities, <*N*>=*jσ* where *N* is the average number of excitons/crystal, *j* is pump fluence and *σ* absorption cross section, is greater than 1, therefore possibility of single nanocrystal containing multiexciton increases. These carriers interact via coulomb interaction and undergo fast carrier-carrier scattering with scattering times, governed by size, shape, composition of etc. Therefore, if a particular nanocrystal harbors a biexciton, then energy associated with exciton recombination is transferred to the other exciton forming a hot exciton in the nanocrystal. These HC release the energy via carrier-LO phonon interaction subsequently heating the system. The Auger heating rates are therefore directly proportional to the number of particles within the system as given below in equation 2.

$$\left(\frac{dE}{dt}\right)_{Total} = \left(\frac{dE}{dt}\right)_{e-Phonon} + k_3(E_g + E)n^2 \qquad (2)$$

where k_3 is the Auger recombination coefficient E_g is the band gap.

$\left(\frac{dE}{dt}\right)_{Total}$ and $\left(\frac{dE}{dt}\right)_{e-Phonon}$ are energy loss rates

Therefore, under heating due to Auger recombination, while the initial carrier cooling proceeds via Froehlich mode and hot phonon bottleneck, the energy loss rate decreases as cooling proceeds and eventually matched with Auger heating rate and this form a negative feedback leading to cooling rate governed by Auger process which had a ΔT^2 dependence [5-7].

Acoustic-Optic Phonon Up-conversion

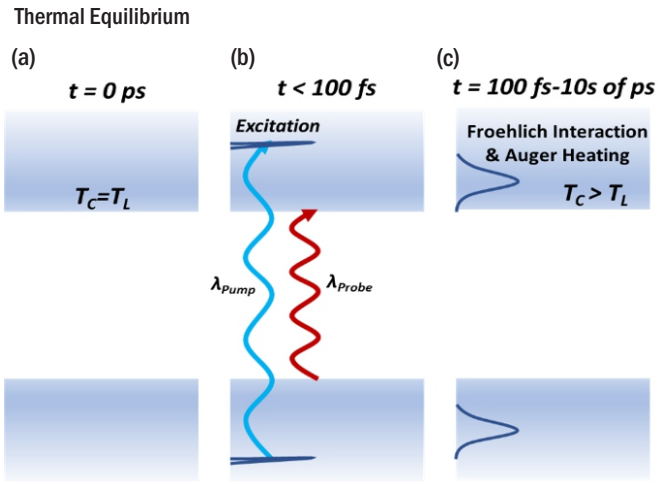


Fig.2: Schematic representation of HC cooling processes (a) Before excitation (b) On photoexcitation, electrons and holes in conduction and valence bands respectively with narrow energy distribution above the individual band minima (or maxima) from conduction (or valence) band are created (c) Subsequent cooling via Froehlich interaction Auger heating etc.

Under still higher carrier densities >10^{18}/cm^3, LO phonons decay to Acoustic modes and these Acoustic phonons propagate through the solid and dissipated heat. However, if a given material has a low thermal conductivity, propagation of the Acoustic modes is hindered. This in turn leads to localization and therefore longer lifetime for Acoustic phonons thereby increasing the probability of up-conversion of Acoustic phonons back to optic phonons by a process called Acoustic-Optic phonon up-conversion. The probability of up-conversion is also enhanced if there exists a significant overlap between low energy optic modes and acoustic modes. In a lead halide perovskite with organic a cation, a substantially low thermal conductivity accompanied by the strong overlap between low frequency modes of the organic cation with lead halide phonon modes lead to a high probability for an up-conversion to occur.

How to Monitor Carrier Cooling using fs-TA Spectroscopy?

Here we are interested in monitoring HC dynamics using femtosecond transient absorption spectroscopy (fs-TA). In a typical excitation, with a fs pulse the non-equilibrium distribution of carriers are generated by 400 nm pump pulse with pulse width of <100 fs. The carriers are monitored through visible wavelengths using a probe pulse spanning the entire visible region from 400-750 nm. The primary focus here is to monitor charge carrier dynamics. This is accomplished by tracking bleach of the ground state exciton after pump pulse excitation. The bleach is created due to depletion of the ground state and state filling. The schematic in Fig.2 represents the events with respect to time on photoexcitation. The initial state before excitation represents an equilibrium between the TC and the lattice temperature (T_L). On photoexcitation, a non-equilibrium carrier distributions is established which is pulse limited or instantaneous. Subsequently the system cools in the time scale of 100 fs-10 s of ps via Froehlich interaction and phonon-phonon interaction. The depletion in the ground state as monitored at bleach wavelength shows an asymmetry towards blue side due to HC as shown in the Fig.3. Since the bleach tracks the population of carriers, it can be used as index for TC. HC absorption is at blue side compared to ground state bleach position, leading to asymmetry of the bleach towards the higher energy region. Therefore, the HC population distribution can be fitted with a Maxwell Boltzmann distribution as given below to retrieve T_c.

$$\Delta A(E) = -A_0 e^{\frac{-E}{k_b T_C}} \qquad (3)$$

ΔA is change in absorbance, T_c is the carrier temperature. TC for individual delay time is used to extract TC decay.

Below we illustrate how this is accomplished using fs-TA spectroscopy for Methylammonium lead bromide ($MAPbBr_3$) quantum dots (QD). Fig.3 gives the pseudo color TA spectra with respect to time. The Figure shows TA spectra with a bleach at 2.35eV and which could be assigned to first exciton transition based on comparison between ground state absorption of $MAPbBr_3$ QDs. As shown in the Fig.3 a, c and b, d for TA spectra for low and high intensities as labelled indicates considerable broadening towards the blue side of the bleach at high pump intensity. This bleach broadening decrease slower

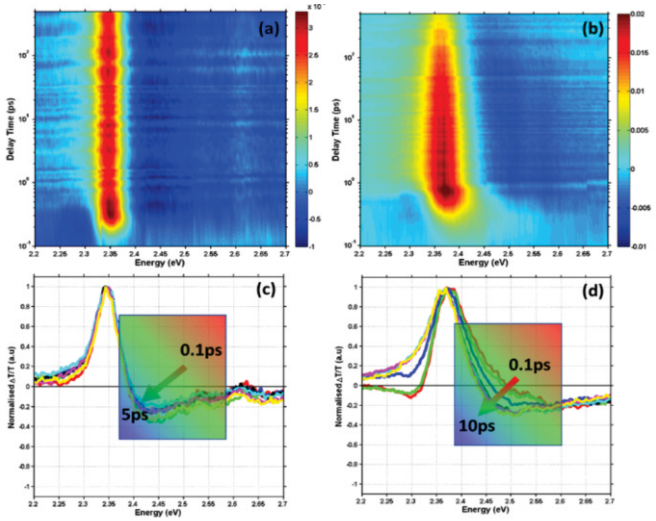


Fig.3: (a) & (c) Pseudocolor TA ΔT/T spectra, (b) & (d) Normalised ΔT/T spectra for $MAPbBr_3$ NCs at carrier density of 1.5×10^{17}/cm^3 and 10^{18}/cm^3 respectively.

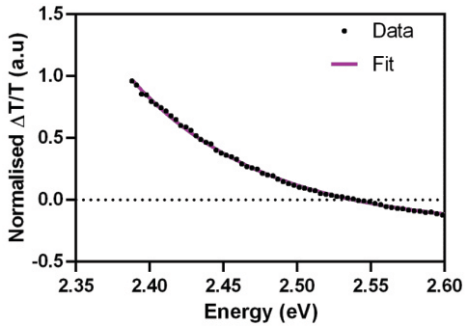


Fig.4: Data (open circles) & Exponential Fits (line) for a typical time delay.

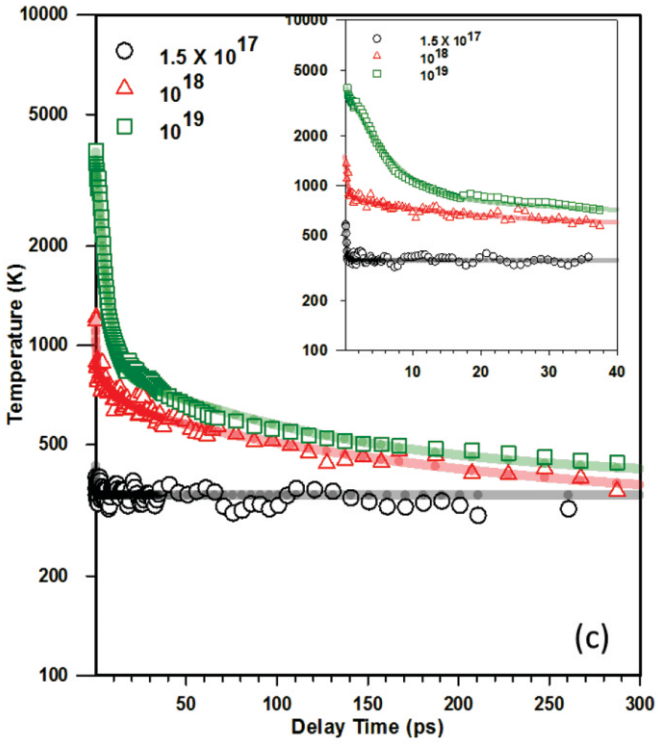


Fig.5: HC cooling dynamics at initial carrier densities 1.5×10^{17}, 10^{18} & $10^{19}/cm^3$.

at higher pump intensity. To quantitatively understand the above observation, we have fitted the wings of the bleach as described above using Maxwell Boltzmann statistics using expression 1. A typical fit is represented in Fig.4. The time slices of TA spectra are used to build T_c vs time curve which is shown in Fig.5. The T_c vs t shows that under low pump intensity the T_c decay is fast and cooling occurs < 1ps indicating role of Froehlich interaction and hot phonon bottleneck. However, under higher intensity HC cooling is slow with times of 11 ps and ~100 ps, indicating different regimes of cooling operational. As mentioned earlier under high pump intensity the Auger heating could be one possible reason for slow HC cooling. We verified the same from measurement of biexciton Auger recombination time (τ_{Auger}) which was ~30 ps. The HC cooling times scaling is in accordance to Auger heating time with a ~τ_{Auger} / 3 scaling. The slowest component indicates that the cooling is hindered in this system with the slowest component of ~100 ps. In hybrid lead halide perovskite the thermal conductivity for these perovskites are low due to anharmonic phonon-phonon scattering leading to possibility of up-conversion of acoustic phonon to optic phonon leading to reheating of carriers. This up-conversion explain slow HC cooling in $MAPbBr_3$ [8-9].

Conclusion

Here we have attempted to show how a novel phenomenon like slow HC cooling in Lead halide perovskites can be followed using fs-TA spectroscopy. The possibility of slow HC cooling offers some hope towards achieving the goal of breaking S-Q limit. The study shown here is not extensive however some of our recent results indicate modulation of HC cooling using different variants of halide perovskite structure. Some of these works demonstrate immense potential of halide perovskites in HC solar cells.

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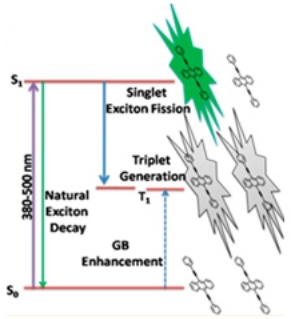
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एकल विखंडन पदार्थ

5

एकल विखंडन पदार्थ की परादु्त स्पेक्ट्रमिकी: जैविक प्रकाश-वोल्टिक में संभावनाएँ

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कार्बनिक अर्धचालक में एकल विखंडन

सारांश

एकल विखंडन (एस. एफ.), कार्बनिक पदार्थों में एक स्पिन अनुमत प्रक्रिया है जो एकल ऐक्साइटॉन को तीन गुना के जोड़े में खंडित करती है तथा संभावित रूप से शॉकले-क्विसर सीमा से परे कार्बनिक फोटोवोल्टिक उपकरण दक्षता में सुधार कर सकती है। हालांकि, ऊर्जावान और गतिकी बाधाओं के कारण, एसएफ केवल कुछ चुनिंदा कार्बनिक अणुओं तक ही सीमित है। मौजूदा और नए कार्बनिक पदार्थों में एसएफ प्रक्रिया को अनुकूलित करने के लिए एसएफ गतिकी का स्पेक्ट्रमिकी मूल्यांकन और संरचना-गतिकी संबंध को समझना अनिवार्य है। इस लेख में, हमने कार्बनिक अर्धचालक पदार्थों की पॉलीसीन श्रृंखला में एकल विखंडन के प्रकाश भौतिकी और परादु्त गतिकी का वर्णन किया है। एसएफ प्रक्रिया की स्पेक्ट्रमिकी पहचान, एसएफ गतिकी के संरचनात्मक तथा आकृति विज्ञान ट्यूनिंग के महत्व और प्रकाश-वोल्टिक उपकरणों में इन पदार्थों के उपयोग के संभावित दायरे पर चर्चा की गई है।

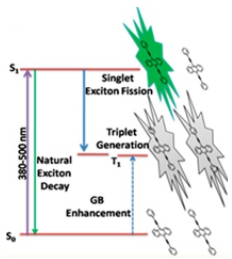
मुख्य शब्दः कार्बनिक प्रकाश-वोल्टिक्स, एकल विखंडन, तीन गुना ऐक्साइटॉन, परादु्त स्पेट्रमदर्शिकी

Singlet Fission Materials

5

Ultrafast Spectroscopy of Singlet Fission Materials: Prospects in Organic Photovoltaics

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Singlet Fission in Organic Semiconductor

ABSTRACT

Singlet fission (SF), a spin allowed process in organic materials splits singlet exciton into a pair of triplets which can potentially improve organic photovoltaic device efficiency beyond Shockley-Quisser limit. However, due to energetic and kinetic constraints, SF is restricted to only a few selected class of organic molecules. Spectroscopic assessment of SF kinetics and understanding the structure-dynamics relation is imperative to optimize SF process in existing and new organic materials. In this article, we provide an overview of photophysics and ultrafast dynamics of singlet fission in polyacene series of organic semiconducting materials. Spectroscopic identification of SF process, importance of structural and morphological tuning of SF dynamics and potential scope of utilization of these materials in photovoltaic devices has been discussed.

KEYWORDS: *Organic photovoltaics, Singlet fission, Triplet excitons, Ultrafast spectroscopy*

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Introduction

Photovoltaics (PV), the direct solar-to-electrical conversion route is the backbone of renewable and sustainable energy resources. While silicon based solar cell is currently dominating the photovoltaic industry, development of cheaper and more efficient solar-electricity devices, such as organic photovoltaics, has been a persistent quest. Though organic semiconductor based PV systems has not reached competitive efficiency and long term stability as compared to silicon solar cells; lower cost, tunability, flexibility and foldable architecture has attracted great deal of research interest in organic photovoltaics (OPV). In the context of OPV, singlet fission (SF) has come up as a golden opportunity to cross the Shokley-Quisser (S-Q) efficiency limit [1]. In a single junction solar cell, theoretical efficiency is limited to about 33% of incident solar energy due to several loss factors; thermalization loss of above-band gap-energy being one of the dominant contributor (Fig.1). SF converts a singlet exciton to a pair of triplets by an efficient spin allowed mechanism, which can produce two charge-carriers per absorbed photon providing a potential route to increase organic photovoltaics efficiency. If fully exploited, theoretical efficiency of singlet fission sensitized PV device can reach up to 45%. This prospect has attracted a great deal of research interest on SF photophysics in past one decade.

In singlet fission, singlet exciton energy is redistributed to generate a pair of triplet excitons. Thus, a potentially good SF molecule must satisfy thermodynamic criterion of $E(S_1) \geq 2E(T_1)$ [2]. Unlike intersystem crossing (ISC), SF being a spin allowed process, can proceed at fast enough rate to outcompete other de-excitation channels. However, SF requires spin exchange and sharing of singlet energy which introduce the requirement of strong intermolecular coupling to facilitate SF in ultrafast timescale. Requirement of isoergic or exoergic condition restricts SF process to be limited to a class of organic molecules, such as polyacenes (Fig.2). In addition, strong electronic coupling necessitates favorable intermolecular interaction in the solid state and kinetics of SF process is very much susceptible to crystal structure, sample morphology, defects and presence of polymorphs. Femtosecond resolved transient pump-probe spectroscopic measurement is imperative to assess the rate of SF vs other relaxation channels and to quantify the yield of triplets generated by SF route.

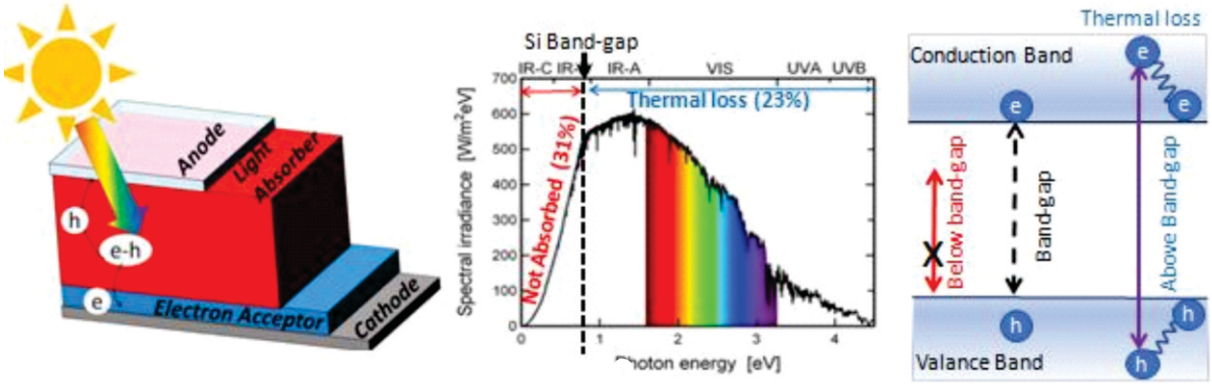


Fig.1: Schematic of single junction solar cell and energy loss mechanism due thermal loss of above band gap photon energy and no absorption of below band gap photon energy limiting theoretical efficiency to about 33%.

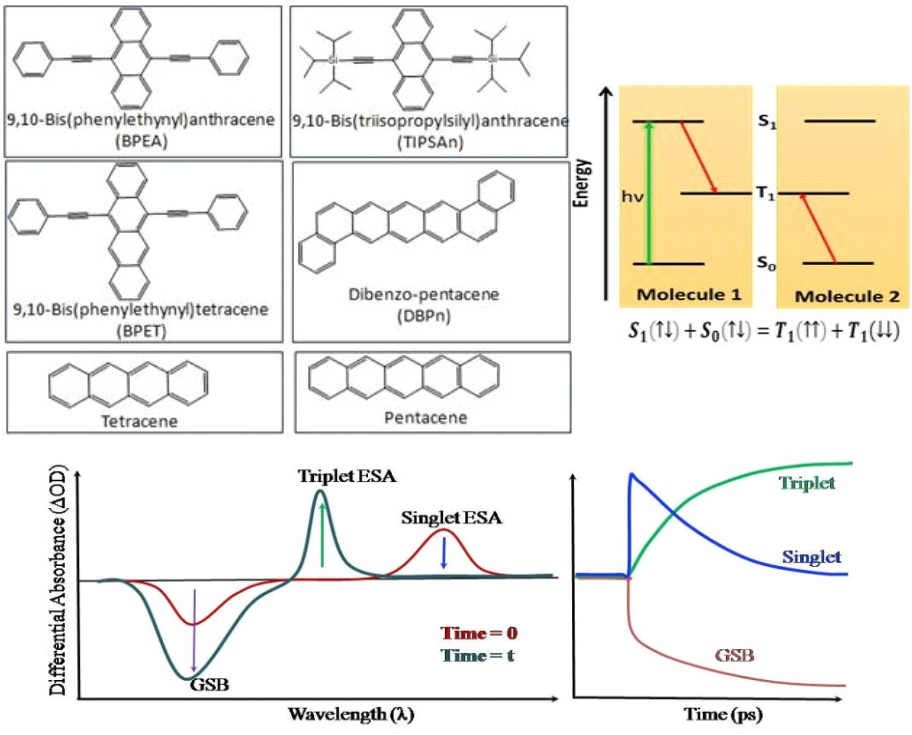


Fig.2: Molecular structure of a few representative polyacene based SF molecules and energy sharing diagram of singlet exciton to a pair of triplet excitons. Typical transient spectroscopic signature in SF process is illustrated.

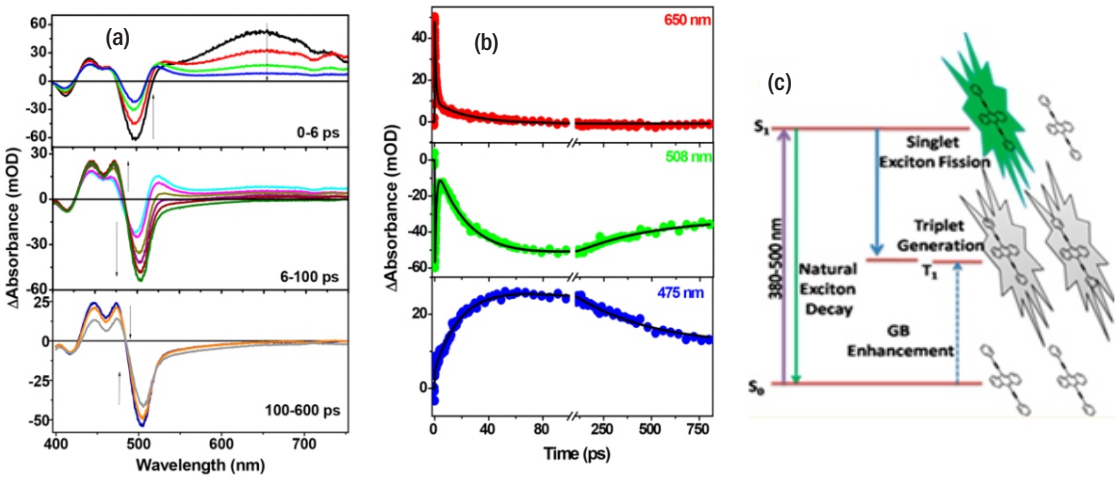


Fig.3: (a) Transient absorption spectral evolution of BPEA NA following singlet excitation by 390 nm 100 fs laser pulse. (b) Temporal kinetic profiles along with fitted data recorded at important wavelengths. (c) Schematic of transition associated with singlet fission process in BPEA. Adapted with permission from J. Phys. Chem. C, 122, (2018): 21047−21055.

Observation of excited state absorption (ESA) decay of singlet exciton, rise of triplet exciton ESA and concomitant rise in ground state bleach (GSB) signal is hallmark of SF process (Fig.2). In this article, we present ultrafast spectroscopic evaluation of SF dynamics in a few polyacene class of molecules (Fig.2) with an emphasis of structure and morphology dependence of SF rate and SF yield.

Singlet Fission in 9,10-bis (Phenylethynyl) Anthracene (BPEA): Our First Case Study

Due to endothermicity, anthracene is known to be an inefficient SF material. However, incorporation of phenylethynyl substitution in 9 and 10 position meets thermodynamic criterion of SF and is experimentally shown to facilitate fast SF with high yield [3]. Detailed photophysical and time resolved spectroscopic studies adopted to discern SF chemistry in BPEA nanoaggregate (NA) is described as follows. BPEA nanoaggregate prepared by flash precipitation in aqueous media display strongly perturbed absorption as compared to monomer suggesting strong intermolecular interaction in NA. On the other hand, strong quenching of emission (> 50 times) and fast decay of single exciton states in NA served as preliminary hint of SF process. To confirm fast deactivation pathway of singlet exciton, ultrafast pump-probe transient absorption spectroscopic studies were conducted. Transient absorption data (Fig.3) of BPEA NA shows broad singlet excited state absorption (ESA) at 650 nm region and ground state bleach (GSB) at 500 nm region. In very early timescale, fast decay of both ESA and GSB is due to singlet exciton-exciton annihilation due to fast exciton diffusion. In later time, we observed rise of ESA at 475 nm corresponding to triplets of BPEA and rise of bleach at 520 nm.

Rise of bleach helped us to identify SF mechanism in this molecule for the first time. Quantitative estimation yielded triplet formation of 140-160% (depending on sample morphology) which corresponds to SF yield of 70-80% (Triplet yield = 2 x SF yield). Long lived nature of the triplets generated from SF process was verified from nanosecond transient absorption spectroscopy which showed SF generated triplet excitons of BPEA lived for more than 32 µs.

Effect of Bulky Substituent

Molecular structural modification can alter the energetics and molecular packing, incurring significant effect on SF yield. To exemplify influence of molecular packing on SF process, phenyl groups of BPEA was replaced by bulky isopropylsilyl group in 9, 10-Bis [(triisopropylsilyl) ethynyl] anthracene (TIPSAn). This molecular structural change imparted negligible absorption shift and emission quenching in TIPSAn, rather a red shifted broad emission from long lived excimer state is idendified [4]. Notably, triplet yield found to be very low (<20%) which suggests inhibition of SF process and dominance of excimer state relaxation in TIPSAn. Absence of SF in TIPSAn is attributed to weak intermolecular interaction due to bulky substituent which does not provide necessary electronic coupling required for ultrafast SF. Thus molecular structure and consequent intermolecular packing in solid state plays a critical role in SF dynamics in polyacenes.

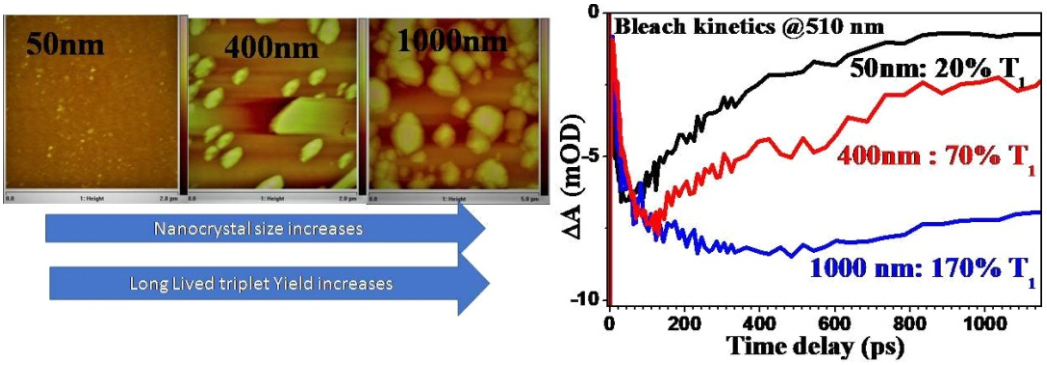


Fig.4: AFM image and bleach recovery kinetics of different sized nanocrystals of BPEA. As particle size increases, yield of long-lived triplets increases.

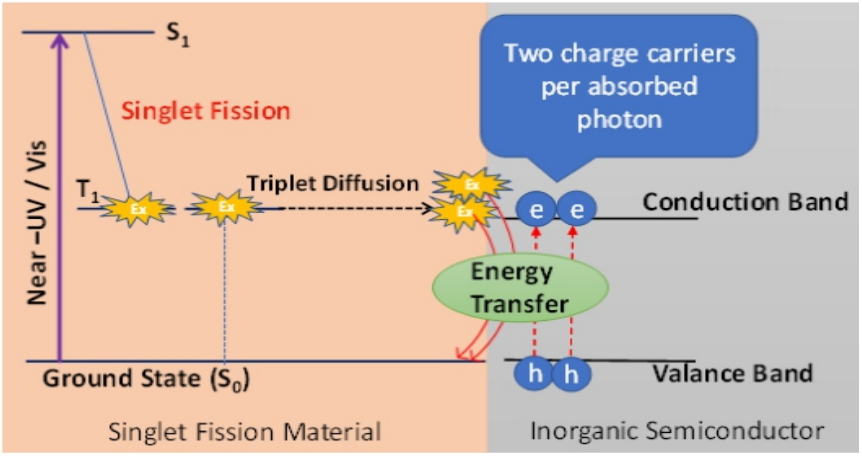


Fig.5: Proposed scheme of harvesting SF generated triplets in photovoltaics.

Importance of Extended Conjugation

While TIPSAn does not offer favourable packing for SF process, other structural modification on BPEA was explored by incorporating additional fused benzene ring. This extended conjugated derivative of BPEA, abbreviated as BPET (Fig.2) is shown to enhance SF yield [5]. Thin-film of BPET displays strong red shift of absorption band covering solar spectrum up to 650 nm and exhibits several orders of magnitude of emission quenching. Femtosecond pump-probe spectroscopy quantified SF yield of 90% (triplet yield=180%) occurring within a few picosecond timescale. Detailed analysis of transient absorption data led us to propose ultrafast triplet pair formation (< 200 fs) followed by separation into free triplets with a time constant of 1.4 ps.

Influence of Energetics

Longer π-conjugation in ployacenes is generally expected to impart faster SF kinetics due to stabilization of triplet states over singlet, resulting favorable thermodynamic driving force. However, when the conjugation length is moved beyond pentacene, additional factors comes into picture. In pentacene, SF process is exothermic by ~0.12 eV and proceeds with rate constant of 80 fs, making it the fastest known SF material [6]. Extending conjugation beyond pentacene, such as hexacene and heptacene, SF rate is reported to slow down. In a nonlinearly fused heptacene (DBPn) derivative, we established that exothermicity exceeds 1 eV and SF process occurs with a time constant of 5.2 ps, more than 50 times slower than in pentacene [7]. Highly exothermic SF in DBPn requires multiphonon relaxation to dissipate excess energy released in SF process, resulting in slower SF rate. Thus, excessive exothermicity is shown to be detrimental for fast SF process.

Role of Sample Morphology

While ultrafast rate of SF is prerequisite of a good SF material to outcompete other nonradiative decay channels of singlet exciton, SF generated triplet excitons need to live long to convert them into charge-carriers. However, SF generated triplet excitons may undergo triplet-triplet annihilation and can disappear before energy extraction. Sample morphology is shown to play important role dictating fate of triplet exctions in BPEA nanoaggregate and thin film (Fig.4). While ultrafast singlet exciton fission kinetics is measured to be independent of particle size, SF generated triplet lifetime is shown to decrease with decrease in particle size. Transient absorption kinetics of small particles shows growth in bleach band up to 40 ps due to fast SF but subsequent ground state bleach recovery in hundreds of ps highlights recombination of triplets before they separate into free triplets (Fig.4). Only a small fraction of signal (about 20%) survives beyond 1 ns which corresponds to free triplets. As particle size increases to several hundred nanometers, long-lived triplet yield increases to 70%. On the other hand, larger domain size in thin film exhibits almost negligible bleach recovery up to ns time scale with a triplet yield of 170%. Thus yield of free triplets is shown to be strongly dependent on particle size due to sample morphology dependent triplet separation kinetics.

Summary and Outlook

In summary, spectroscopy and ultrafast dynamics of singlet fission in polyacene class of molecules have been thoroughly investigated. We have described methodology of characterization SF process and different factors influencing the SF rate and yield. Ultrafast spectroscopic analysis on a series of polyacene derivatives led us to understand role of molecular structure and intermolecular interaction on SF process. Our study identified a first ever anthracene derivative with strong blue light absorption and high SF yield. Nanocrystal size and sample morphology is shown to play important role in SF dynamics. Structural tuning of thermodynamic and kinetics parameters of SF process in polyacenes have been thoroughly assessed. Systematic analysis of nanocrystal and thin film samples prepared under varied condition led us to optimize SF yield close to desirable value of 100%.

While high SF yield is demonstrated in many organic materials, the basic challenge associated with SF induced triplet exciton harvesting is finding suitable acceptor materials. Exploration of different semiconductor quantum dots as triplet harvester is necessary to find best acceptor material for SF sensitization (Fig.5). Diversity in synthetic methodology to add functionalities on existing SF chromophores is also required, not only to control SF energetic and electronic coupling (by crystal packing engineering) but also imparting required chemical stability and solution processibility. It is also important to note that apart from photovoltaics, SF generated triplet excitons may be leveraged to generate reactive singlet oxygen for photodynamic therapy or in other light harvesting methods such as photocatalysis.

Acknowledgment

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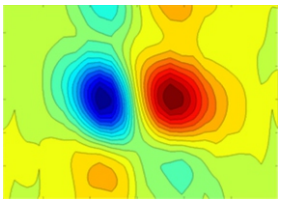
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पराद्रुत बहुविमीय स्पेक्ट्रमिकी

6

2D अवरक्तन स्पेक्ट्रमिकी: पराद्रुत टाइम स्केल में आण्विक गतिकी के अन्वेषण की एक नवाचार तकनीक

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पानी का 2D स्पेक्ट्रा

सारांश

पराद्रुत 2D अवरक्त (2DIR) स्पेक्ट्रमिकी ने आण्विक गतिकी की हमारी समझ में क्रांतिकारी परिवर्तन किया है, जो जटिल वातावरण में अणुओं के संरचनात्मक और गतिशील गुणधर्मों के बारे में गहन जानकारी प्रदान करता है। यह लेख, विभिन्न सीमित माध्यमों में पानी के अणुओं की गतिशीलता को समझने के लिए 2DIR स्पेक्ट्रमिकी के स्वदेशी विकास और अनुप्रयोग पर प्रकाश डालता है।

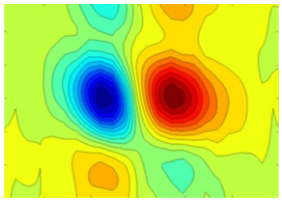
मुख्य शब्द : पराद्रुत 2D अवरक्त स्पेक्ट्रमिकी आण्विक गतिकी ; हाइड्रोजन बंध ; सीमित जल प्रणालियां ; डीएमएसओ- जल मिश्रण।

Ultrafast Multidimensional Spectroscopy

6

2D Infrared Spectroscopy: An Innovative Technique for Probing Molecular Dynamics in Ultrafast Time Scale

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2D Spectra of Water

ABSTRACT

Ultrafast 2D infrared (2DIR) spectroscopy has revolutionized our understanding of molecular dynamics, offering deeper insight into the structural and dynamic properties of molecules within complex environments. This article highlights the indigenous development and application of 2DIR spectroscopy to understand the dynamics of water molecules in different confined media.

KEYWORDS: *Ultrafast 2D infrared spectroscopy, Molecular dynamics, Hydrogen bonding, Confined water systems, DMSO-water mixtures*

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Introduction

The exploration of molecular dynamics lies at the heart of deciphering the complex mechanisms driving chemical reactions, biological functions, and material properties. Traditional spectroscopic techniques often struggle with limitations when targeted for elucidating the intricate behavior of molecules on ultrafast timescales or within complex environments. Techniques such as nuclear magnetic resonance (NMR) and fluorescence spectroscopy, despite their invaluable contributions, offer a trade-off between temporal resolution and structural detail. This trade-off becomes particularly pronounced in scenarios involving rapid dynamic events in confined environments, such as electron transfer processes, protein folding, or solvent interactions, highlighting a critical gap in our experimental arsenal [1]. Ultrafast 2DIR spectroscopy emerges as a possible solution, bridging the experimental gap between time and structure resolution that has long constrained our ability to fully comprehend molecular dynamics [2]. Its unparalleled capacity for providing bond-specific structural resolution across a broad spectrum of timescales from femtoseconds to tens of picoseconds depending on the vibrational lifetime sets a new standard for spectroscopic inquiry [1]. The versatility of the technique extends to a wide array of samples, including dilute solutions, solid-state systems, and complex biological membranes, underscoring its universal applicability [3].

Ultrafast 2D infrared (2DIR) spectroscopy, pivotal since its inception in 1999, uniquely captures interactions between vibrational modes, manifested as infrared bands and cross-peaks, which serve as molecular fingerprints. This technique integrates experimental data with molecular dynamics simulations, offering profound insights into molecular structures and transient states with high temporal and spectral resolution. It is particularly transformative in studying the dynamic behaviors of water molecules in confined environments like reverse micelles(RMs) or biological systems, and in tracking solvent dynamics, electron transfer, and interactions at interfaces or within chemical reactions and protein folding processes. The extensive applications of 2DIR spectroscopy range from materials science to life sciences, interrogating protein, enzyme, and DNA dynamics in solutions, and advancing our understanding of complex chemical systems and disease mechanisms. This integration into interdisciplinary research continues to catalyze significant scientific breakthroughs, influencing fields from drug discovery to the design of novel biomaterials[4].

Experimental Set-up

A Fourier transform spectroscopy-based two-dimensional infrared (2DIR) spectrometer (cf. Fig.1a) was developed indigenously for the first time in India around an amplified femtosecond laser system (800 nm, 1 mJ, 1 kHz)[5]. Two optical parametric amplifiers (OPA) in combination with difference frequency generator (DFG) were used to create mid-IR (3-10 μm) femtosecond pulses. A schematic diagram of the 2DIR setup developed in Chemistry Group, BARC is presented in Fig. 1b. The mid IR pulse from DFG was divided into pump (~ 96%) and probe (~ 4%) pulses using a CaF_2 wedge window. A simple Mach-Zehnder interferometer was used to create a collinear pump pair using two CaF_2 based 50:50 beam splitters ensuring uniform dispersion for both pump pulses. One of the pump pulses was traversed through a computer controlled retroreflector to control the time-delay between two collinear pump (τ). The interference between pump pulses was monitored through signal intensity fluctuations with τ using a PbSe photodiode. The probe pulse was directed through another retroreflector on a computer-regulated translational stage defining the pump-probe delay (T_w), also known as waiting time.

Both pump and probe pulses was focused onto the sample using a 2-inch off-axis parabolic (OAP) mirror and subsequently made parallel using a similar OAP mirror. The probe beam was detected using an Mercury Cadmium Telluride (MCT) dual array detector after passing through a scanning monochromator. The precise spatial overlapping of the pump and probe beams at the sample was ascertained using a pinhole (0.1 mm) on a XYZ translation stage, while their temporal alignment was monitored via the nonlinear signal produced in a 50 μm thick Germanium window. The sample, positioned between two CaF_2 windows with a 50 μM Teflon spacer, was subject to data collection by varying the time delay between pump pair pulses (τ) in 4 fs increments for a given T_w. The interferogram, generated as a function of the τ-axis upon Fourier transformation, generated the excitation frequency within the 2DIR spectrum.

Results and Discussion

Water is crucial in almost all chemical and biological processes happening on the earth, particularly at the solid-liquid interface, impacting heterogeneous catalysis and biomolecular activity in ion channels. At these interfaces, it shows significant changes in hydrogen bonding due to the disruption from the interface, leading to unique molecular

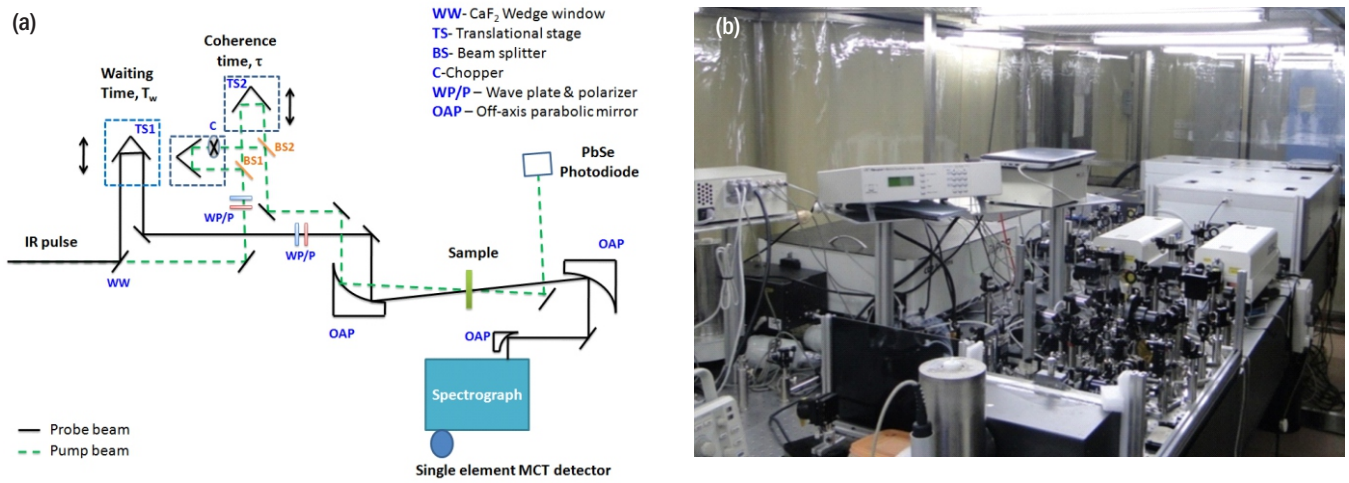


Fig.1: (a) Optical lay-out and (b) Photo of the 2DIR spectrometer developed in Chemistry Group, BARC.

behaviors [6]. Although extensively studied, many questions remain about the changes in the structure and dynamics of interfacial water, especially how these perturbations extend from the interface to resemble bulk combine these two paragraphs.

The dynamics of water at various chemical and biological interfaces have been extensively investigated to understand the impact of the chemical nature of these interfaces on the structure and hydrogen bond dynamics of water [7-8]. Traditional spectroscopic methods such as time-dependent fluorescence Stokes' shift (TDFSS) have been widely used to explore these dynamics [9-10]. However, TDFSS is limited by the size of the fluorescent probe used which are unable to predict actual dynamics of water due to the use of large probe molecules which perturb the system largely from its equilibrium configuration [9]. Further, the involvement of excited state molecules also make the system far from equilibrium.

To address these limitations, time-resolved vibrational spectroscopy, particularly infrared (IR) spectroscopy, offers a more refined approach. Unlike electronic excitation in TDFSS, vibrational excitation in IR spectroscopy causes negligible perturbation to the molecular system, allowing studies under thermal equilibrium conditions [11]. While time-resolved IR spectroscopy has improved our understanding of the hydrogen bond structure and re-orientational dynamics of interfacial water, it often lacks sensitivity to subtle molecular motions. The advent of 2DIR spectroscopy has revolutionized this field. With its ability to disperse spectral information across two dimensions coupled with ultrafast time resolution, 2DIR spectroscopy excels in unraveling complex structural and dynamic information in intricate environments [1].

Dynamics of water in AOT reverse micelle

The power of 2DIR spectroscopy to unravel the complexities of confined water dynamics is exemplified in its application to study water in AOT RMs. These micelles serve as a model system for biological water, offering a controlled environment to investigate the influence of confinement on the structural and dynamic properties of water. The study involved a detailed investigation into the dynamic behavior of water confined within Aerosol-OT (AOT) RMs, utilizing ultrafast 2DIR spectroscopy. Through the use of azide ions as an ultrasmall infrared (IR) probe, the study reveals critical insights into how molecular dynamics of water are altered by confinement, thereby challenging the prevailing notion that water in smaller RMs behaves akin to bulk water [5].

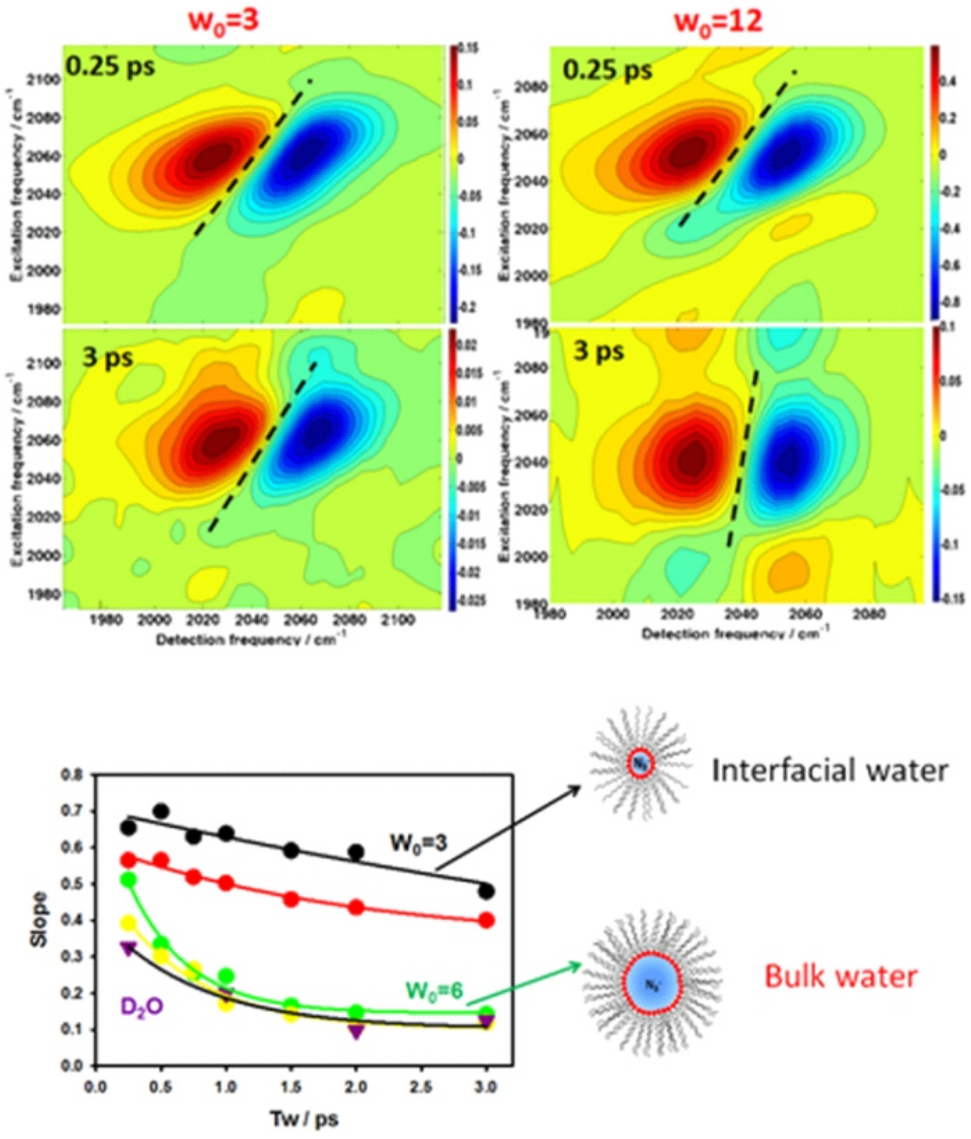


Fig.2: Upper panel: 2DIR spectra for antisymmetric stretch of azide in AOT RMs for w_0=3 (left) and w_0=12 (right) at waiting time of T_w= 0.25 ps (top) and 3 ps (bottom) the parameter w0 is defined as the ratio of water concentration to surfactant concentration, [H2O]/[AOT]. Lower panel: Variation in slope as a function of waiting time for w_0=3 (D_w = 2 nm), w_0=4.5 (D_w = 2.45 nm), w_0=6 (D_w = 2.9 nm), w_0=12 (D_w = 4.7 nm) and bulk D_2O.

Initial experiments on linear IR spectroscopy and vibrational lifetime measurements of azide ions in various sized AOT RMs revealed shifts in spectral features like peak position and width with changes in the water pool's radius, suggesting environmental variations for the azide ion. Despite these shifts, the vibrational lifetime of the azide ion remained consistent across different water pool sizes [5]. This suggested that azide ions were centrally located in the water pools, similar to bulk water, although this interpretation did not fully account for the complex dynamics of confined water molecules, especially hydrogen bond reorganization dynamics.

Notably, 2DIR spectroscopy revealed that for smaller water pools, the dynamics and structural characteristics of water molecules deviated substantially from those of bulk water. This observation starkly contrasted with previous interpretations based on vibrational lifetime measurements, underscoring the enhanced sensitivity of 2DIR spectroscopy to the complexities of confined water dynamics. 2DIR spectra analysis at various waiting times for different water pool sizes uncovered a pronounced sensitivity of the frequency-frequency correlation function (FFCF) to the size of the water pool. For smaller water pools (diameter, D_w = 2 nm), the FFCF measurements indicated a significant slowdown in the hydrogen bond reorganization dynamics compared to bulk water [5]. This slowdown was attributed to the confinement effects exerted by the interface of the Rms on the water molecules, a phenomenon that becomes progressively less pronounced as the size of the water pool increases [5]. The findings of this study through 2DIR spectroscopy illuminate the profound impact of confinement on molecular dynamics of water within RMs. Unlike vibrational lifetime measurements, which could not differentiate between the dynamics of water molecules in small and large water pools, 2DIR spectroscopy provided compelling evidence of the unique behavior of confined water. This behavior includes the extensive slowdown of hydrogen bond relaxation dynamics in smaller water pools, highlighting the superiority of the technique in capturing the subtle dynamics of confined water molecules. Moreover, the study advocates for the use of ultrasmall IR probes, like the azide ion, in investigating the dynamics of biologically relevant confined water molecules [5].

Investigation of H-bond Dynamics in DMSO-water mixture

In another study, we embarked on a comprehensive exploration of the structural dynamics within aqueous solutions of dimethyl sulfoxide (DMSO) and water, employing sodium nitroprusside (SNP) as a local vibrational probe [12]. Through a combination of infrared (IR) absorption spectroscopy, vibrational pump-probe spectroscopy, and 2DIR, the research illuminates the complex interplay of molecular interactions that define the behavior of DMSO-water mixtures, highlighting the presence of two distinct anomalous regions of hydrogen bond dynamics that were hitherto not fully elucidated by previous studies [12].

The study meticulously identified two anomalous concentration regions within the DMSO-water mixtures, characterized by distinctive hydrogen bond dynamics. The first region, occurring at a DMSO mole fraction (X_{DMSO}) of approximately 0.2, and the second region, around X_{DMSO} of 0.4, signify the existence of varied hydrogen-bonded structures influenced by the concentration of DMSO. 2DIR spectroscopy furnished a detailed perspective on the time scales of hydrogen bond reorganization dynamics across different compositions of the DMSO-water mixture. The study notably highlighted the slower dynamics in intermediate DMSO concentrations and elucidated the structural dynamics in both anomalous regions, which had remained elusive in prior

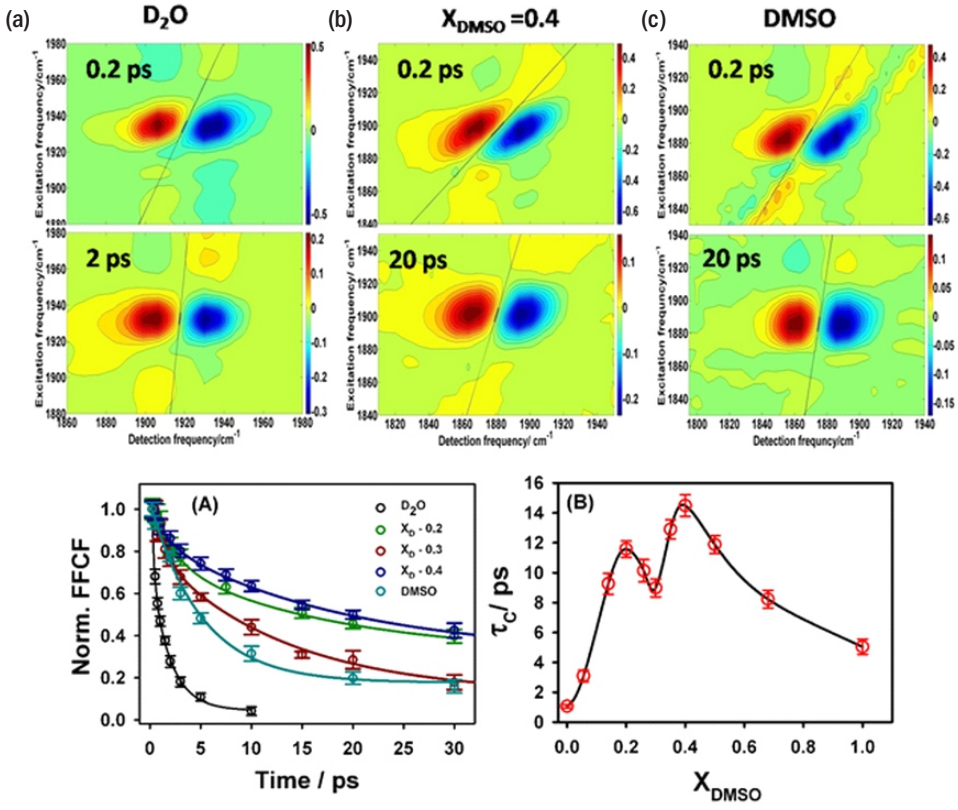


Fig.3: 2D-IR spectra of nitrosyl band of SNP in (a) D_2O at waiting times of 0.2 and 2 ps (b) In DMSO-water with X_{DMSO}~0.4 at waiting times 0.2 and 20 ps. (c) in DMSO at waiting times 0.2 ps (upper panel) and 20 ps (lower panel). (A) The FFCF decays of SNP in DMSO-D_2O solvents at various compositions. Circles represent the data points and solid lines represent their multi-exponential fits. (B) Variation in the correlation time with X_{DMSO}. The error bars represent the standard deviation of the measurements (n=3).

investigations. The analysis of FFCF decay times provided a nuanced understanding of the hydrogen bonding dynamics and the structural heterogeneity within the mixtures [12].

In summary, this research presents a pioneering examination of the structural dynamics and hydrogen bond interactions within DMSO-water mixtures, leveraging the sensitivity of SNP as a vibrational probe. The discovery of two anomalous regions of hydrogen bond dynamics enriches our understanding of the molecular mechanisms underpinning the unique properties of these mixtures [12].

Conclusion and Future Perspectives

Our studies have shown significant deviations in the behavior of water molecules confined within AOT reverse micelles, notably a slowdown in hydrogen bond reorganization dynamics compared to bulk water. This demonstrates the profound impact of confinement on molecular dynamics and highlights the capability of 2DIR spectroscopy to detect subtle molecular phenomena. Additionally, our research into DMSO-water mixtures has identified regions with unique hydrogen bond dynamics, offering new insights into molecular interactions in these mixtures. The use of 2DIR spectroscopy has proven invaluable in deciphering molecular dynamics, enhancing our understanding of chemical and biological systems. Looking forward, one potential direction is to extend 2DIR spectroscopy to other confined systems like biological membranes or nanostructured materials, potentially impacting drug delivery and materials science. This technique could also investigate electrolyte behaviors in supercapacitors or charge dynamics in photovoltaic materials, aiding in the development of efficient energy systems.

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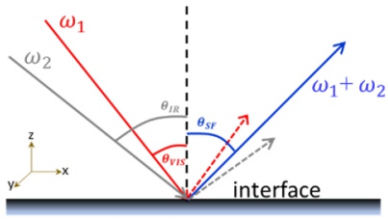
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अंतरापृष्ठ पर स्पेक्ट्रमिकी

7

परादृत लेजर का उपयोग करके सॉफ्ट अंतरापृष्ठ पर अंतरापृष्ठ-चयनात्मक अरेख स्पेक्ट्रमिकी

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इंटरफेस पर सम फ्रीक्वेंसी पीढ़ी

ABSTRACT

अंतरापृष्ठ पर रसायन विज्ञान, जहां दो अमिश्रणीय स्थूल माध्यम मिलते हैं, विषमदैशिक वातावरण के कारण स्थूल चरणों से काफी भिन्न होते हैं। अंतरापृष्ठ-चयनात्मक स्पेक्ट्रमदर्शिकी, विशेष रूप से कंपन योग आवृत्ति जनन (वीएसएफजी), अंतरापृष्ठ पर आण्विक व्यवहार में अंतर्दृष्टि प्रदान करता है। वीएसएफजी, जैसे कि तरल सतह "नरम अंतरापृष्ठ" के लिए विशिष्ट रूप से अनुकूल है, कंपन संक्रमणों के माध्यम से अणुओं की अंतरापृष्ठ-चयनात्मक अन्वेषण को सक्षम बनाता है। चयनात्मकता की कमी या कठोर परिस्थितियों से बाधित पारंपरिक तरीकों के विपरीत, वीएसएफजी ऐसे नरम अंतरापृष्ठ की विशेषता बताने में उत्कृष्ट है। यहां, हम वीएसएफजी के सिद्धांत की रूपरेखा तैयार करेंगे, इसकी अंतरापृष्ठ-चयनात्मकता का पता लगाएंगे, और जलीय अंतरापृष्ठ पर पर्यावरण और जैविक अध्ययनों में इसके अनुप्रयोगों पर चर्चा करेंगे।

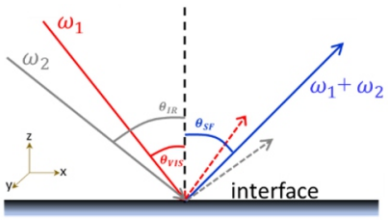
मुख्य शब्द : सतह और अंतरापृष्ठ , कंपन योग आवृत्ति उत्पादन (वीएसएफजी) , स्थायी कार्बनिक प्रदूषक (पीओपी) , फॉस्फोलिपिड।

Spectroscopy at Interface

7

Interface-Selective Nonlinear Spectroscopy at Soft Interfaces using Ultrafast Laser

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Sum frequency generation at interface

ABSTRACT

Chemistry at interfaces, where two immiscible bulk media meet, differs significantly from the bulk phases due to the anisotropic environment. Interface-selective spectroscopy, particularly vibrational sum frequency generation (VSFG), offers insights into molecular behaviors at interface. VSFG, uniquely suited for "soft interfaces" like liquid surfaces, enables interface-selective probing of molecules through vibrational transitions. Unlike traditional methods hindered by lack of selectivity or stringent conditions, VSFG excels at characterizing such soft interfaces. Here, we outline the theory of VSFG, explores its interface-selectivity, and discusses its applications in environmental and biological studies at aqueous interfaces.

KEYWORDS: *Surface and Interface, Vibrational sum frequency generation (VSFG), Persistent organic pollutant (POP), Phospholipid*

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Introduction

Interfacial chemistry is associated with intricate molecular interactions transpiring at the juncture between two immiscible media, where the symmetries of bulk materials are disrupted. With water pervading as Earth's most abundant liquid, aqueous interfaces manifest ubiquitously across biotic and abiotic realms, from the ocean's surface (air-water interface) to mineral surfaces (gas-solid or liquid-solid interface), and within cellular domains (lipid or protein-water interface). Water as well as other reactants exhibit preferential orientation and non-uniform distribution across interfaces, leading to the various interface-selective physicochemical phenomena. Achieving a molecular-level comprehension of these interfacial processes necessitates precise probing of interface with molecular specificity.

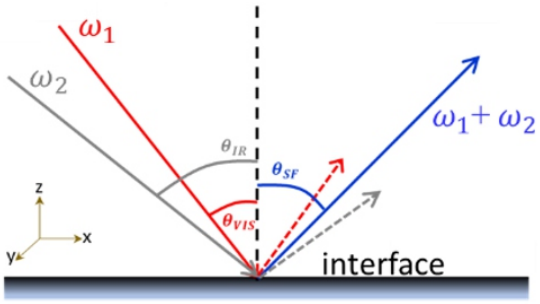
Even-order nonlinear spectroscopy, such as Vibrational Sum Frequency Generation (VSFG), emerges as a potent tool for interface-selective analysis of molecular interactions under ambient conditions. [1] Recent advancements, like phase-sensitive i.e., heterodyne detected-VSFG, enable precise recording of absorption spectra and absolute orientation of interfacial molecules. [2]

Theory of Vibrational Sum Frequency Generation (VSFG) and Interface-selective Spectroscopy

VSFG is one of the outcomes of nonlinear interaction of light with matter. The second-order polarization, P^2 generates the sum frequency signal from an anistropic media where the constituting molecules have a preferred orientation.

$$\boldsymbol{P}^{(2)} = \epsilon_o \chi^{(2)}\, \mathbf{E}\omega_1\, \mathbf{E}\omega_2 \qquad (1)$$

where, ϵ_o is the dielectric constant in vacuum; $X^{(2)}$ is the second-order electric susceptibility corresponding to the molecular hyper-polarizability, $E\omega_1$ and $E\omega_2$ are the electric fields of the interacting intense lights having angular frequencies ω_1 and ω_2, respectively. The spectroscopy associated with $P^{(2)}$ or with the higher order polarizations (e.g., $P^{(3)}$, $P^{(4)}$ etc) are known as *nonlinear spectroscopy*. For an isotropic medium, $X^{(2)}= 0$ and hence, $P^{(2)}= 0$. Thus, in a centrosymmetric media, which is the case with isotropic bulk media, there is no VSFG signal, under electric-dipole (ED) approximation. However, at an interface, the inversion symmetry breaks down and $X^{(2)} \neq 0$ and hence $P^{(2)} \neq 0$. In other words, the sum frequency signal is generated only at the interface, making VSFG an inherently interface specific nonlinear spectroscopy technique (Scheme I). In reflection geometry, the sum frequency is generated at a particular direction (Θ_{SF}) which is different from the reflection angles of ω_1 and ω_2. This has a technical advantage in selective detection of the SFG signal by spatial separation from the ω_1 and ω_2.



Scheme I: Sum frequency generation (SFG) at interface in non-collinear reflection geometry.

Following equation (1), the intensity of the sum frequency light can be expressed as [3]

$$I_{SFG} \propto \left|\boldsymbol{P}^{(2)}\right|^2 \propto \left|\chi^{(2)}\right|^2 I_{\omega_1} I_{\omega_2}$$

Or

$$\frac{I_{SFG}}{I_{\omega_1} I_{\omega_2}} \propto \left|\chi^{(2)}\right|^2 \qquad (2)$$

Thus, a plot $\frac{I_{SFG}}{I_{\omega_1} I_{\omega_2}}$ against ω_2 (let ω_2 correlates to the vibrational transition of interfacial molecules and hence corresponds to IR light) provides the squared-$X^{(2)}$ spectrum of interfacial molecules. This is what is done in conventional VSFG measurement. The VSFG-intensity spectra at different polarization combinations (SSP, SPS, PSS and PPP) are used to deduce information about orientational distribution of interfacial molecules. [4] In the case of phase-sensitive VSFG, the sum frequency is detected by interferometric method, known as heterodyne-detection. The heterodyne-detection provides the real and imaginary components of $X^{(2)}$ independently.

Broadband *Heterodyne-Detected* VSFG Spectrometer Based on a Femtosecond Laser System

Fig.1 shows a picture of the broadband *HD*-VSFG setup at Radiation & Photochemistry Division, Chemistry Group, BARC. The spectrometer is based on a femtosecond Ti:sapphire regenerative amplifier system with specifications: central wavelength 800 nm, pulse width ~50 femtosecond, energy

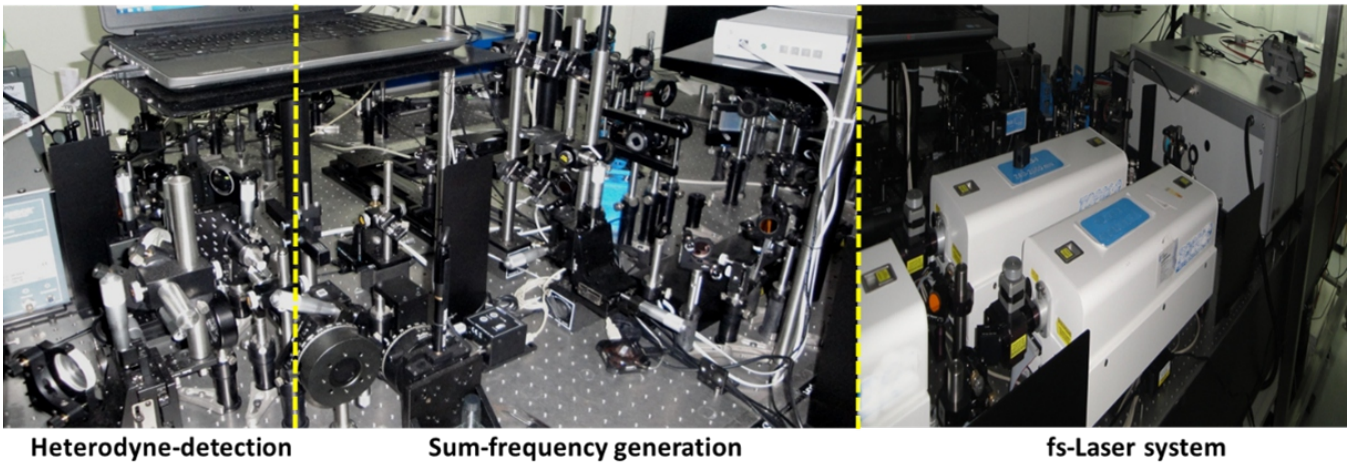


Fig.1: Indigenously developed broadband HD-VSFG setup at Radiation & Photochemistry Division, Chemistry Group, BARC. The spectrometer is based on a femtosecond Ti:Sapphire amplified laser system.

~3mJ/pulse, and pulse repetition rate 1.0 kHz. One part of the amplified output (~ 1 mJ/pulse) is passed through a narrow band pass filter (center wavelength 800 nm) that converts the broad band femtosecond pulse into a narrow band picosecond pulse (fwhm ~ 16 cm^{-1}, energy ~ 15 µJ/pulse), known as the visible pulse (ω_{VIS} or ω_1). The second part of the amplifier output (~1 mJ/pulse) is frequency converted to a broad band IR pulse (ω_{IR} or ω_2 pulse; fwhm ~ 300 cm^{-1} @ 3400 cm^{-1}) using an optical parametric amplifier (OPA) followed by a difference frequency generator (DFG). The spatio-temporal overlap of the ω_1 and ω_2 pulses on the sample surface generates the sum frequency signal. For the *heterodyne detection* of the generated sum frequency, it is mixed with a local oscillator (LO) signal which has a constant phase-difference from that of the former. The mixing generates an interference pattern. The interference pattern from the sample surface is compared with that from a reference surface (Z-cut quartz) to obtained the *Re* [$X^{(2)}$] and *Im* [$X^{(2)}$] spectra [5,6] The *Im* [$X^{(2)}$] spectrum thus obtanined provides the accurate absorption characteristics of interfacial molecules while the real component, *Re* [$X^{(2)}$], shows a dispersive band shape. Thus, unlike in conventional VSFG spectrocopy, the sign of $X^{(2)}$ is retained in the *Im* [$X^{(2)}$] spectra, which reveals the absolute orientation of molecule at the interface. [7]

Interaction of Perfluorinated Persistent Organic Pollutant (f-POP) with Biological Lipid Monolayer/Water Interface

This section discusses the interfacial interaction of perfluorinated persistent organic pollutant (*f*-POP) with biological lipids and their surface prevalence using heterodyne detected VSFG spectroscopy. Unlike a degradable pollutant which has a short-term effect on the environment, persistent organic pollutants (POPs) have a long-term effect on aqueous interface and the associated biotic/abiotic systems. Cationic lipid, 1,2-dipalmitoyl-3-trimethylammonium-propane (DPTAP), monolayer/water interface shows an intense negative band in 3000 – 3560 cm^{-1} region and a positive band above 3600 cm^{-1} (Fig.2) which corresponds to the H-down oriented water (3000 – 3560 cm^{-1}) in the electric double layer (EDL) generated by cationic head group of DPTAP and the H-up oriented weakly interacting topmost water (> 3600 cm^{-1}) above the lipid head group region, respectively. [8,9] In presence of perfluorohexanoic acid (PFHA), amplitude of the OH stretch signal is significantly reduced (red curve, Fig.2) due to neutralization of the surface charge by the anionic carboxyl group of $PFHA^-$, making the DPTAP/water interface nearly net neutral. The amplitude of the weakly interacting OH (above 3600 cm^{-1}) is also reduced in the presence of $PFHA^-$, which indicates that PFHA not only affects the water below the DPTAP head group (EDL associated water) but also the topmost water in the hydrophobic region of DPTAP monolayer. These perturbations are qualitatively similar to that of NaCl at the DPTAP interface (compare the purple and red curves, Fig.2).

The anionic lipid, 1,2-Dipalmitoyl-sn-glycero-3-phosphoglycerol (DPPG), monolayer/water interface (black curve, Fig.3) shows an intense positive band in 3000 – 3600 cm^{-1} region and a negative band above 3600 cm^{-1}, pertaining to the H-up oriented water in the EDL and the H-down oriented weakly interacting water (>3600 cm^{-1}) in the hydrophobic region above the lipid head group. In the presence of PFHA, the water signal is decreased at the DPPG/water interface. From the perspective of electrostatics, this is unexpected as the head groups of both DPPG and PFHA are negatively charged. These observations suggest that PFHA exhibits different modes of interactions with DPPG than that with DPTAP at the aqueous interface.

We propose an acid-base reaction between DPPG and PFHA (dppg-PO_4^- + pfha-COOH dppg-PO_4H^+ pfha-COO^-) as the reason of such observation at the interface. The neutralization reaction makes the DPPG/water interface effectively uncharged. In addition, the oleophobic perfluorinated alkyl chain of $PFHA^-$ experience repulsive interaction with the alkyl chains of the lipid. Hence, $PFHA^-$ is expelled from the DPPG/water interface. [10]

Summary

Vibrational Sum Frequency Generation (VSFG) spectroscopy is an inherently interface-selective technique applicable at ambient condition to variety of surfaces and interfaces that are accessible to light. This technique provides a deeper understanding of the structure and orientation of molecules at surface and interface. Study of the f-POP-lipid/water interface as discussed here for example, demonstrates head group-specific interaction of f-POP with biological lipids at

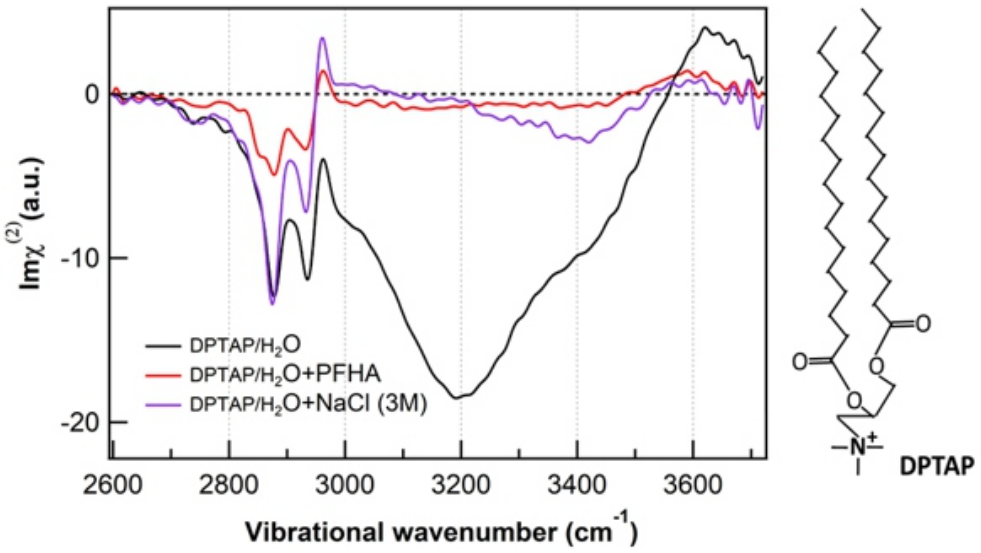


Fig.2: Effect of PFHA and NaCl (3.0 M) on the Im$\chi^{(2)}$ spectrum of the anionic DPPG monolayer/water interface (Surface pressure 30 ± 2 mN/m). Adapted with permission from ref 10.

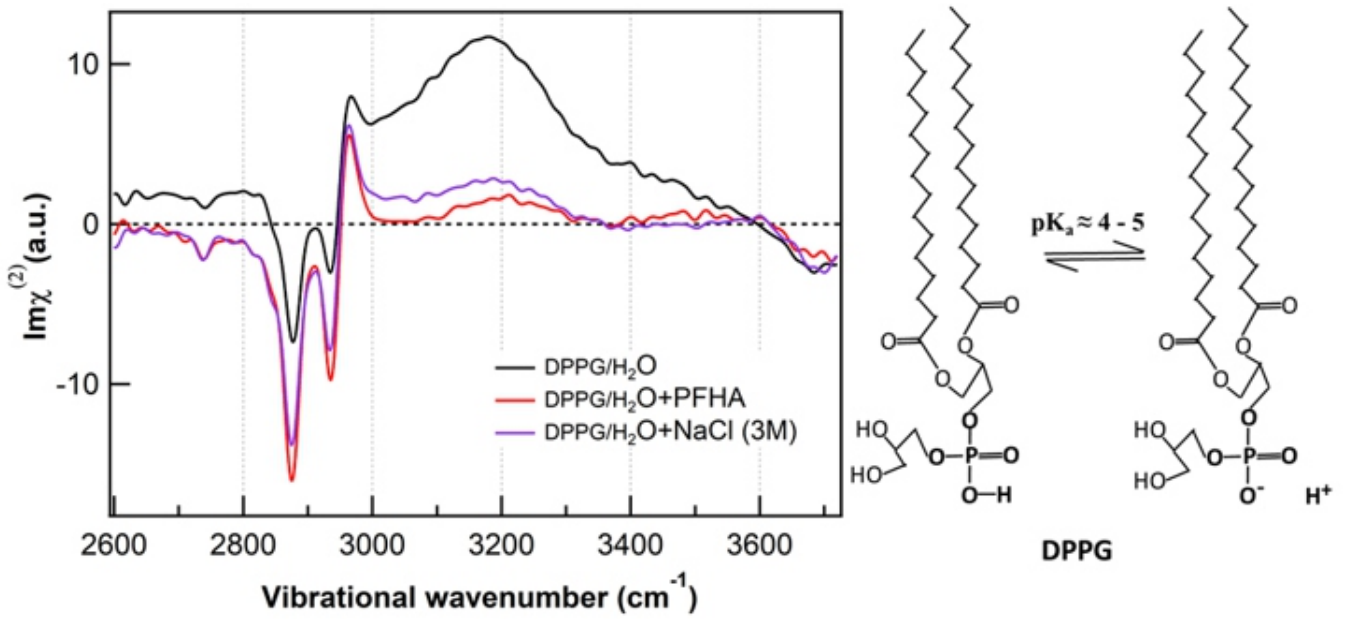


Fig.3: Effect of PFHA and NaCl (3.0 M) on the Im$\chi^{(2)}$ spectrum of the anionic DPPG monolayer/water interface (Surface pressure 30 ± 2 mN/m). Adapted with permission from ref 10.

aqueous interface. Specifically, the expulsion or penetration of PFHA into the phospholipid monolayer depends on the charge and chemical nature (e.g., pK_a) of the lipid head group, which has implications to the f-POP-induced perturbation of membrane fluidity and transmembrane electric potential.

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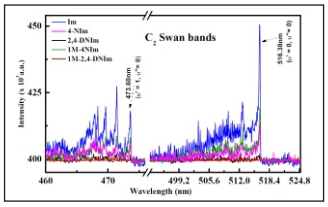
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जटिल पदार्थों का विश्लेषण

8

फेमटोसेकंड लेजर-प्रेरित ब्रेकडाउन स्पेक्ट्रमिकी: जटिल पदार्थों का उन्नत विश्लेषण

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विकिरण एवं प्रकाश रसायन प्रभाग, भाभा परमाणु अनुसंधान केंद्र, ट्रांब-400085, भारत
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इमिडाज़ोल सीरीज़ के लिए वायु में अंकित C_2 स्वान बैंड उत्सर्जन तीव्रता में प्रवृत्ति।

सारांश

फेमटोसेकंड (fs) स्पंद प्रगत तत्व उष्मा प्रभावित क्षेत्र और मैट्रिक्स प्रभावों को कम करके विश्लेषण को आगे बढ़ाते हैं ,जिससे सटीक संरचना निर्धारण संभव होता है। केस स्टडीज़ जटिल मैट्रिक्स के भीतर तत्व संरचना को मैप करने में फेमटोसेकंड लेजर प्रेरित ब्रेकडाउन स्पेक्ट्रमदर्शिकी (f s - L I B S) की प्रभावकारिता को रेखांकित करते हैं। (f s - L I B S) पारंपरिक तरीकों के बराबर पूर्वानुमान सटीकता के साथ ,अक्रिय धातु उत्प्रेरकों की मात्रा निर्धारित करने के लिए एक अर्ध-गैर-विनाशकारी उपकरण के रूप में कार्य करता है। इसके अलावा ,इसका अनुप्रयोग विस्फोटक की पहचान करना है ,जो रासायनिक संरचनाओं के साथ वर्णक्रमीय उत्सर्जन के सहसंबंध के कारण होता है। यह तकनीक विश्लेषणात्मक

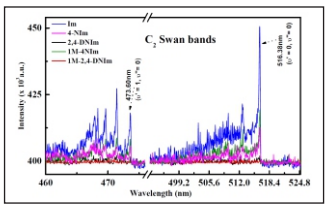
मुख्य शब्द : फेमटोसेकंड ,ताप प्रभावित क्षेत्र ,प्लाज्मा ,उत्प्रेरक ,उच्च ऊर्जा पदार्थ।

Analysing Complex Materials

8

Femtosecond Laser-Induced Breakdown Spectroscopy: Advancing Analysis of Complex Materials

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Trend in C_2 Swan band emission intensities for the imidazole series recorded in air.

ABSTRACT

Femtosecond (fs) pulses advance elemental analysis by minimizing heat affected zone and matrix effects, enabling precise composition determination. Case studies underscore the efficacy of femtosecond laser induced breakdown spectroscopy (fs-LIBS) in mapping elemental compositions within intricate matrices. fs-LIBS serves as a quasi-nondestructive tool for quantifying noble metal catalysts, with predictive accuracy comparable to conventional methods. Furthermore, its application extends to explosive detection, leveraging spectral emissions' correlation with chemical structures. This technique holds significant implications for analytical chemistry and security applications.

KEYWORDS: *Femtosecond, Heat affected zone, Plasma, Catalyst, High energy materials*

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Introduction

Over the past two decades, LIBS has become a widely used analytical technique with broad applications, spanning pharmaceuticals, environmental monitoring, cultural heritage preservation, and water quality assessment [1]. Its allure lies in its adaptability across solid, liquid, and gaseous samples, remarkable sensitivity, minimal sample preparation, and real-time analysis capability. LIBS also presents an enticing opportunity for remote analysis, opening new avenues for hazardous material detection and industrial monitoring.

Traditionally, LIBS employs nanosecond lasers, but these suffer from drawbacks such as plasma reheating and large heat-affected zones (HAZ) that extends beyond the irradiated volume due to thermal diffusion thereby limiting spatial and depth resolution. In contrast, ultrashort femtosecond pulses offer enhanced spatial and depth resolution by minimizing HAZ formation. Furthermore, fs-ablation reduces matrix effects, facilitating more precise elemental composition determination. The distinctive attributes of fs-laser ablation present valuable prospects for mapping elemental compositions in intricate matrices and characterising a variety of physical and chemical processes. The case studies discussed in this article will elucidate several of these capabilities.

Experimental Setup

The LIBS system comprises of several components: femtosecond laser system (Amplitude Systems), a high resolution echelle spectrometer (Mechelle, ME5000, Andor), an Intensifier Charge Coupled Device (ICCD), (Andor DH734-18mm-CCI-01U) outfitted with gate/delay generator and optomechanical components. The fs-laser system comprises of Ti:Sapphire oscillator, chirped pulse regenerative amplifier, and a grating compressor. This system operates at a repetition rate of 1 kHz, delivering 3 mJ per pulse at a central wavelength of 800 nm with a pulse duration of 50 fs, and pulse-to-pulse energy fluctuation of <5%.

The fs-LIBS experiments were carried out by focusing 1 mJ of energy onto the sample surface using a BK7 plano-convex lens (f = 10 cm). Samples were securely mounted on a motorized Y-Z translational stage, seamlessly integrated with LabVIEW for automated sample translation during data acquisition. Plasma emission was collected using a collimator, fiber-coupled to a cross-dispersion Echelle spectrograph, which covers the spectral range of 230–830 nm in a single scan with 0.1 nm wavelength resolution. This, in conjunction with a thermoelectric cooled intensified charge-coupled device (ICCD), is used for the acquisition of spectra. The ICCD is gated in synchronization with the fs laser pulse to get the maximum S/N ratio. The gate delay, gate width, and the detection system are controlled through a digital delay generator.

Case study I - Quantitative Analysis of Noble Metal Catalysts on Cordierite Substrates using Femtosecond Laser-Induced Breakdown Spectroscopy

The distinctive advantages of fs-LIBS such as a small HAZ and pronounced reduction in matrix effects are effectively leveraged for trace elemental analysis in complex matrices such as catalyst surfaces. An illustrative instance is the assessment of Pd and Pt concentrations in a cordierite ($2MgO\ 2Al_2O_3.5SiO$) supported xPd-yPt bimetallic catalyst [2]. These noble metal-based catalysts play a pivotal role in the combustion of unburnt hydrocarbons. To better comprehend the catalyst's functionality, it is imperative to extract analytical insights concerning both the substrate surface and the concentration of platinum group metals. Analyzing cordierite-supported catalysts via LIBS poses specific challenges. Cordierite contributes to a complex LIBS spectrum, while the unpolished nature of the support further complicates the quantitative analysis of noble metals.

The time and space integrated fs-LIB spectra are recorded for characterizing both the cordierte matrix and the bimetallic catalysts supported on cordierite. The use of an Echelle spectrometer allows for simultaneous multi-element measurements, facilitating the selection of the most appropriate emission line for analysis within the range of 240 – 830 nm.

The spectral emission of the cordierite matrix and noble metals are systematically studied to identify 270.2 nm and 340.4 nm lines for quantitative estimation of Pt and Pd respectively (Fig.1a, b). Quantification of the LIBS signal is further aided by measurement of excitation temperature and electron density of the laser ablated plasma. Further assuming local thermodynamic equilibrium, the fs-LIP source is characterized for excitation temperature and electron number densities by using the Boltzmann plot method and Saha equation respectively. Time resolved LIBS under optimized conditions is employed for evaluating the analytical predictive ability of this technique. Calibration curves for Pt and Pd exhibit

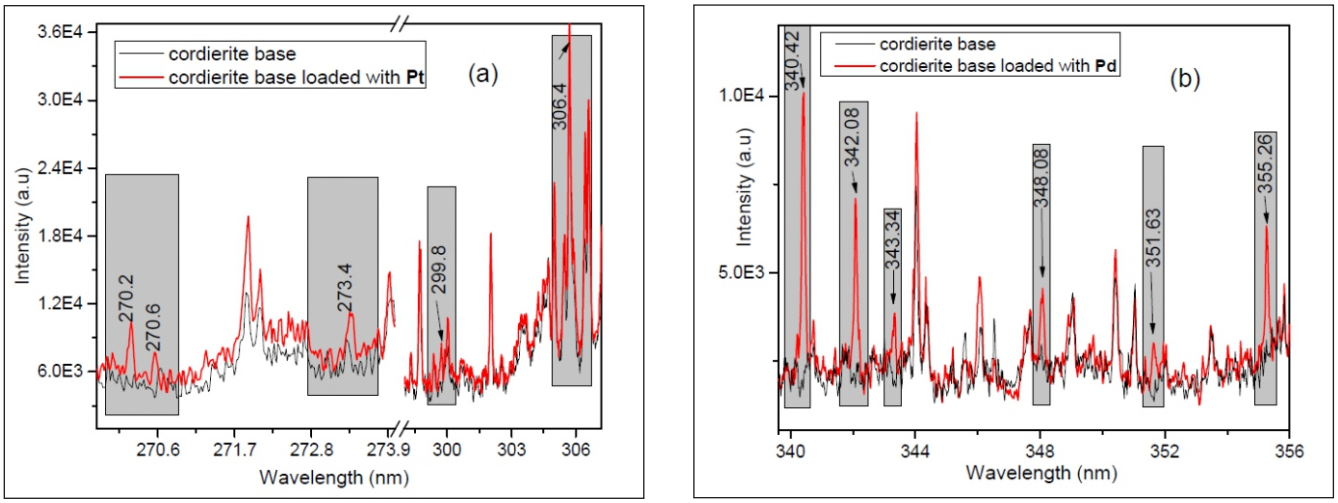


Fig.1: (a), (b) fs-LIB spectra (red curve) showing prominent emission lines of Pt(I) and Pd (I) loaded on the cordierite substrate. Spectrum of cordierite base (black curve) is also shown for the purpose of comparison.

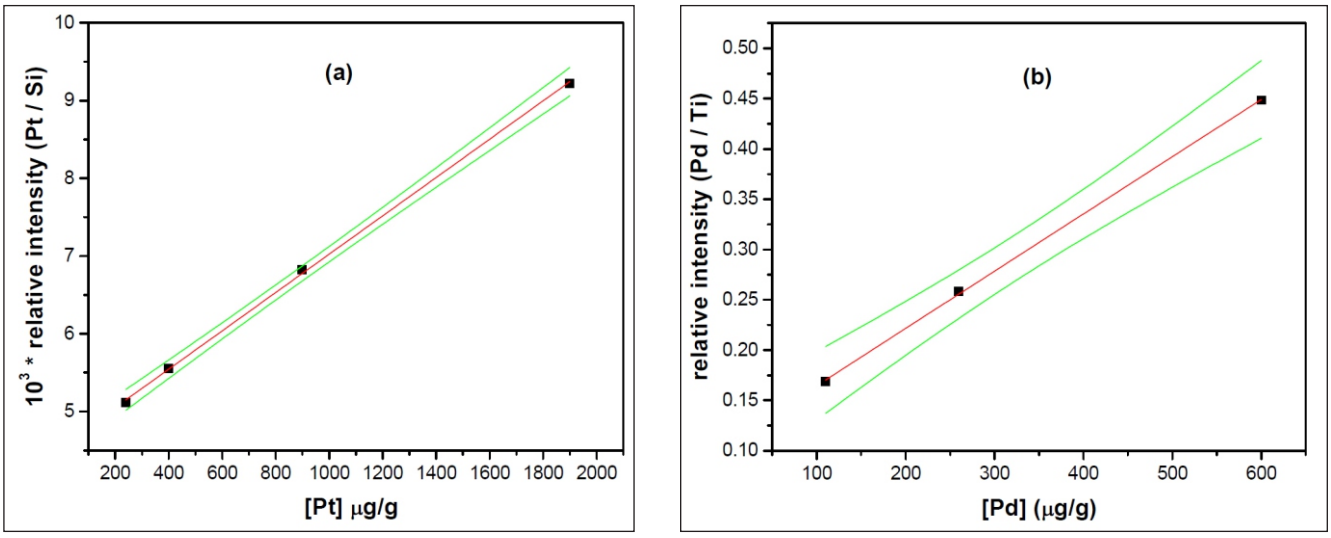


Fig.2: Calibration curve: (a) Pt on Cordierite support; (b) Pd on Cordierite support. Red curve: linear fit, green curve: prediction bands at 95%.

good linearity. The limit of detection for Pt and Pd is estimated to be 55 µg/g and 17 µg/g of cordierite respectively (Fig.2a, b). Further the predictive accuracy of this method in good agreement with results from conventional neutron activation analyses. fs-LIBS, a quasi non-destructive analytical tool can therefore be employed for quantification of noble metal catalysts.

Case study II- Bridging Molecular Structures to Spectral Signatures of high energy materials (HEMs)

The precise identification and discrimination of explosive materials using LIBS faces a formidable obstacle from the matrix effect, especially when detecting explosive molecules across diverse substrates, including paper, metal, polymer, and leather. Fortunately, using fs-pulses for ablation effectively mitigates these matrix effects, rendering them negligible. Furthermore, femtosecond excitation is marked by lower continuum and plasma temperatures due to the absence of plasma re-heating, along with minimal plasma-atmosphere interaction, which favours molecular fragmentation. These unique attributes make fs-LIBS an attractive method for explosive detection.

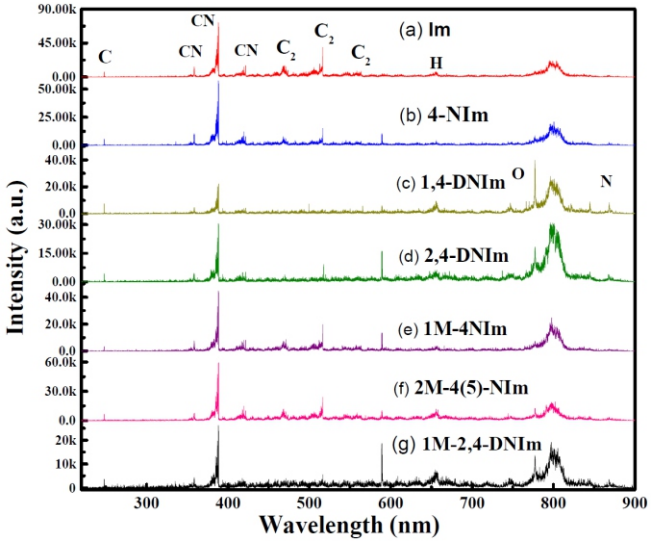


Fig.3: fs-LIB spectra recorded in air at gate delay 100 ns and gate width 800 ns at 1 mJ pulse energy (a) Im (b) 4-NIm (c) 1,4-DNIm (d) 2,4-DNIm (e) 1M-4NIm (f) 2M-4(5)-NIm and (g) 1M-2,4-DNIm.

Organic HEMs, characterized by common elements of C, H, N, and O, yield similar emission spectra, featuring prominent CN and C_2 molecular emission bands alongside atomic emissions reflecting their elemental constituents. This similarity poses a challenge for utilizing fs-LIBS for explosive discrimination. Our primary research thrust revolves around elucidating the correlation between the molecular structures of these compounds, focusing on the type, position, and number of substituents, and their impact on the intensity ratios of molecular and atomic species. To achieve this, we have selected imidazole and its nitro derivatives for study, as they show promise for both civil and military applications due to their exceptional thermal stability, impact and shock insensitivity, superior performance, as well as their cost-effective and environmentally friendly synthesis. The selected HEMs are (a) Imidazole (Im), (b) 4-Nitroimidazole (4-NIm), (c) 1,4-Dinitroimidazole (1,4-DNIm), (d) 2,4-Dinitroimidazole (2,4-DNIm), (e) 1-Methyl-4-Nitroimidazole (1M-4NIm), (f) 2-Methyl-4(5)-Nitroimidazole (2M-4(5)-NIm), and (g) 1-Methyl-2,4-Dinitroimidazole (1M-2,4-DNIm).

The emission spectra prominently feature CN and C_2 molecular bands (Fig.3). CN bands, characterized by Δv values of -1, 0, and +1, were observed within ranges of 357–360 nm, 384–389 nm, and 414–423 nm, respectively, with the highest intensity at 388.3 nm corresponding to CN violet band. C_2 molecular bands, corresponding to Δv=-1, 0, and +1 transitions, were observed in the spectral regions spanning 460–475 nm, 510–520 nm, and 550–565 nm, respectively; the most intense being the Swan band at 516.4 nm. Conversely, atomic emissions linked to elemental constituents C(I), Hα, O(I), and N(I) triplet lines appeared comparatively subdued. While robust CN molecular emissions were observed for all compounds, C_2 molecular bands were only observed in Im, 4-NIm, 1M-4NIm, and 2M-4(5)-NIm, with decreasing emission intensity across the series. Notably, the dinitroimidazoles (1,4-DNIm, 2,4-DNIm, and 1M-2,4-DNIm) exhibited notably feeble C_2 emissions (Fig.4).

The remarkable disparity in C_2 yield between Imidazole and its derivatives, particularly 4-NIm and 2,4-DNIm, stems from structural nuances. In case of Imidazole, the unsubstituted C=C bond undergoes fragmentation following ring opening, thus contributing to high C_2 yield. 4-NIm, despite the absence of this structural motif, exhibits markedly higher C_2 intensity compared to 2,4-DNIm. The discrepancy is partly due to the nitro group's inductive effect, inducing significant charge

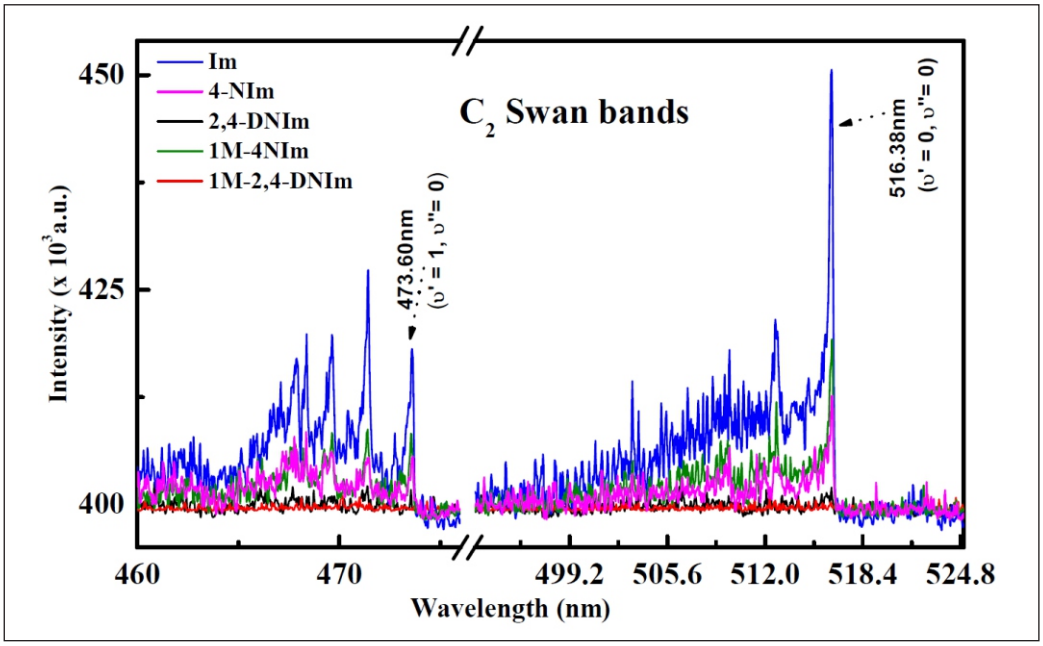


Fig.4: Trend in C_2 Swan band emission intensities for the imidazole series recorded in air. Reproduced from Ref. 3 with permission from the Royal Society of Chemistry.

separation on the carbon atom. Additionally, the electronegative oxygen atom reduces electron density in the aromatic ring, leading to varied canonical forms. Consequently, resonance effects diminish electron density within the Imidazole ring. Both the resonance and inductive effect act in a synergistic fashion rendering it more susceptible to atomization. This structural fragility in 4-NIm results in diminished C_2 and pronounced CN intensity. Conversely, 2,4-DNIm, with additional electron-withdrawing nitro moieties, exhibits near-absent C_2 emission. These findings suggest a clear correlation between spectral emissions and chemical structures, highlighting the potential use of the atomization-to-fragmentation ratio as a performance indicator for high-energy materials.

Expanding on these findings, we have examined a new set of high-energy materials, focusing on triazole-substituted nitroarenes with various functional and structural isomers. These compounds, feature methyl (CH_3), methoxy (OCH_3), and amino (NH_2) groups in ortho and para positions. Despite their apparent similarity, correlation analysis of their spectra reveals significant differences based on molecular structure, including the types of bonds and the position of substituents within the aromatic ring. Moreover, detonation parameters including oxygen balance, detonation velocity, detonation pressure, and chemical energy of detonation were observed to correlate strongly with the $(CN + C_2)/(C + H + N + O)$ ratio [4]. Consequently, the ratio of the sum of molecular emission intensities to the sum of atomic emission intensities emerges as a dependable performance metric for energetic compounds. Such correlation studies are anticipated to enhance comprehension and refine discrimination methodologies for hazardous materials of this nature.

Conclusion

In summary, fs-LIBS emerges as a pivotal tool in the realms of analytical chemistry and security applications. It serves as a quasi-nondestructive means for assessing noble metal catalysts, with predictive precision akin to established methods. Furthermore, its scope encompasses explosive detection, leveraging spectral emissions' correlation with chemical structures. The proposed metric, measuring the ratio of molecular to atomic emission intensities, showcases promise in refining discrimination methodologies for identifying high-energy materials.

Acknowledgments

The author sincerely acknowledges the support and valuable insights provided by Dr. Ajay K. Singh, BARC. This work would not have been possible without the collaborative efforts of Dr. Salil Verma, BARC and Prof. S. Venugopal Rao, University of Hyderabad. Their contributions are sincerely appreciated.

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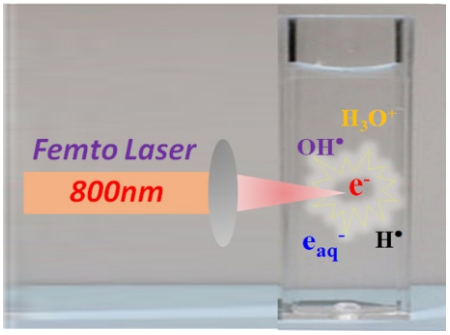
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मल्टीफ़ोटॉन आयनीकरण-लघु इलेक्ट्रॉन स्पंद

9

पानी के मल्टीफ़ोटॉन आयनीकरण द्वारा अल्ट्राशॉर्ट इलेक्ट्रॉन स्पंद का मूलस्थानस्थ जनन

अमिताभ नंदी[1], राजीब घोष[1,2], अरुणा के .मोरा [1,2] और सुखेंदु नाथ *[1,2]
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फेमटॉलिसिस

ABSTRACT

विकिरण रसायन विज्ञान और जीव विज्ञान अनुसंधान से संबंधित विकिरण प्रेरित रासायनिक परिवर्तनों की गतिकी का अध्ययन करने के लिए नियमित रूप से स्पंदित विकिरणी अपघटन प्रयोग किया जाता है। मानक स्पंदित विकिरणी अपघटन सुविधाएँ नैनोसेकंड समय पैमाने में समय विभेदन को सीमित करती हैं। फेमटोसेकंड और पिकोसेकंड समय पैमाने में विकिरण प्रभाव की प्रारंभिक घटनाओं तक पहुँचने के लिए एक अल्ट्राशॉर्ट इलेक्ट्रॉन स्रोत की आवश्यकता होती है जिसके लिए एक फेमटोसेकंड लेजर संचालित फोटोकैथोड-आधारित इलेक्ट्रॉन त्वरक की आवश्यकता होती है। हालाँकि ,तकनीकी चुनौतियाँ और अत्यधिक लागत ऐसे जटिल उपकरणों के विकास को सीमित करती हैं। यहाँ हम एक प्रवर्धित फेमटोसेकंड लेजर का उपयोग करके पानी के मल्टी फोटॉन आयनीकरण द्वारा सब-पिकोसेकंड इलेक्ट्रॉन स्पंद की मूलस्थानस्थ जनन के लिए एक अपेक्षाकृत सरल वैकल्पिक तकनीक प्रस्तुत करते हैं। टेबल-टॉप कमर्शियल फेमटोसेकंड लेजर का उपयोग करके ,हमने सब-पिकोसेकंड विभेदन वाले इलेक्ट्रॉनों के जनन और अस्थायी पहचान के लिए एक कॉम्पैक्ट पंप-प्रोब स्पेक्ट्रोमीटर विकसित किया है।

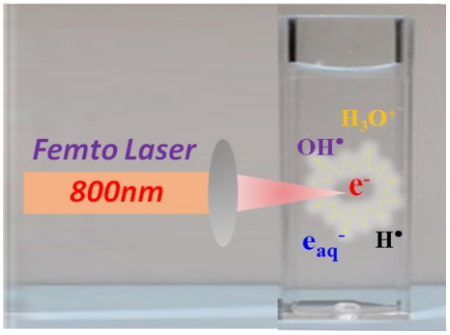
मुख्य शब्द : अल्ट्राफास्ट स्पेक्ट्रोस्कोपी, मल्टीफ़ोटॉन आयनीकरण; इन-सीटू इलेक्ट्रॉन उत्पादन; इलेक्ट्रॉन विलयन

Multiphoton Ionization-Short Electron Pulse

9

In-Situ Generation of Ultrashort Electron Pulse by Multiphoton Ionization of Water

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Femtolysis

ABSTRACT

Pulsed radiolysis experiment is routinely employed to study kinetics of radiation induced chemical changes relevant to radiation chemistry and biology research. Standard pulsed radiolysis facilities limit the time resolution in nanosecond time scale. Accessing early events of radiation effect in femtosecond and picosecond timescale requires an ultrashort electron source which demands a femtosecond laser driven photocathode-based electron accelerator. However, technological challenges and exorbitant costs limit the development of such complex instrumentation. Herein we present a relatively simpler alternative technique for in-situ generation of sub-picosecond electron pulse by multiphoton ionization of water using an amplified femtosecond laser. Using a table-top commercial femtosecond laser, we have developed a compact pump-probe spectrometer for the generation and temporal detection of electrons with sub-picosecond resolution.

KEYWORDS: *Ultrafast spectroscopy, Multiphoton ionization; In-situ electron generation; Electron solvation*

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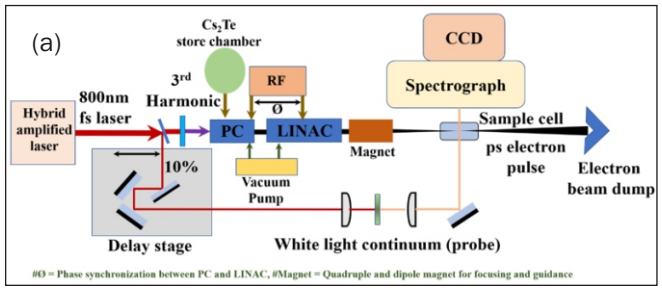
Introduction

The ionizing radiations have a severe impact on chemical and biological species due to radiation induced generation of energetic electrons and radicals which induce chemical modification such as DNA damage. Understanding radiation induced chemical and biological effects requires the study of electron and ion induced chemical kinetics in real time. To extract dynamic information and to identify the radiolytic product, an electron based pulsed radiolysis setup is commonly being used? Thermionic gun based few MeV pulsed electron linear accelerator (LINAC) is now an established technology and is routinely employed for pulsed radiolysis experiments with nanosecond time resolution [1]. However, a complete understanding of radiation induced damage in chemistry and biology requires early timescale information in picosecond and femtosecond timescale. Accessing femtosecond and picosecond timescale information in a pulsed radiolysis study needs a femtosecond electron pulse which can only be generated by a photocathode gun driven by a femtosecond laser [2]. A high current photocathode gun requires use of Cesium-telluride (CsTe) material which is susceptible to atmospheric degradation. Thus, a CsTe photocathode needs to be prepared, transported and maintained at high vacuum (< 10^{-9} mbar) and requires frequent replacement. In addition, the time synchronization of the laser and radiofrequency (RF) field and phase synchronization of RF in photocathode and LINAC are important technological barriers for the implementation of femtosecond pulse radiolysis facility. Fig.1(a) & Fig.1(b) shows the original photograph of the ELYSE facility [3], which gives an idea of the complexity of a picosecond accelerator setup. In addition, the exorbitant cost involved in such multi-component complex instrumentation limits the widespread development of such facilities.

Herein we show an alternative approach for in-situ generation of sub-picosecond electron pulse in water using a femtosecond amplified laser through multiphoton ionization (photolysis) process [4]. By using moderate energy (100-300 µJ/pulse) commercially available femtosecond laser pulse, we generate and detect sub-picosecond electron pulse in water as a table-top facility. The dynamics of pre-solvated and solvated electrons have been monitored in 350-1100 nm region by pump-probe technique. Broadband measurement of transient absorption spanning visible and near IR region allowed us to probe the relaxation of semi-solvated electrons, which mainly absorb beyond 900 nm and the reaction kinetics of both pre-solvated and solvated electrons. This setup is proposed to act as a viable alternative to a picosecond electron accelerator-based pulse radiolysis facility, at least in the aqueous medium.

Method

The sub-picosecond photolysis setup was developed by modifying the existing ultrafast transient absorption (TA) spectrometer as shown in Fig.2. The setup is coupled to a commercial amplified femtosecond laser 50 fs, 800 nm, kH1z from Amplitude Technologies, France. About 200 µJ/pulse laser energy is strongly focused within a quartz cuvette filled with water. A small fraction of the remaining pulse energy (about 1 µJ) is used to generate a broadband white light continuum (350-1100 nm) in a rotating calcium fluoride plate which is used as probe light. In the present setup, the probe pulse is propagated perpendicular to the pump pulse to minimize the interference from the pump induced light generated in the optical cell. The pump induced changes in the probe light were monitored using a dual diode array detector coupled with a spectrograph. The relative temporal delay between the pump and probe pulse was controlled using a computer controlled optical translational stage. Considering strong absorption at ~800 nm, IR-140 dye was used as a reference sample for the determination of zero time of the setup. IR-140 has an excited state absorption (ESA) band in 500-650 nm region which is due to the absorption of its first excited singlet state (S_1). The appearance of the ESA signal of IR-140 provides information about the zero time of the setup.



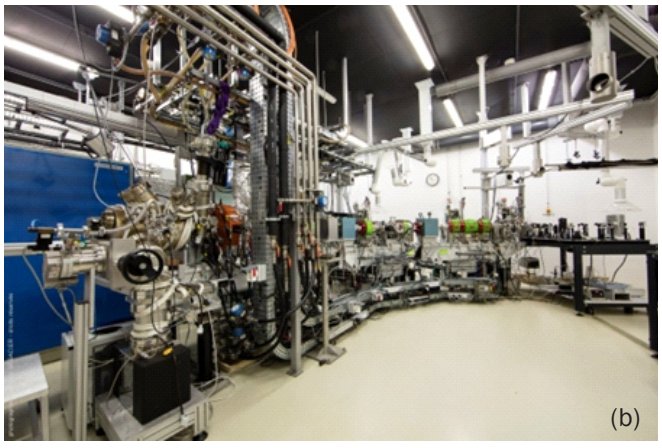
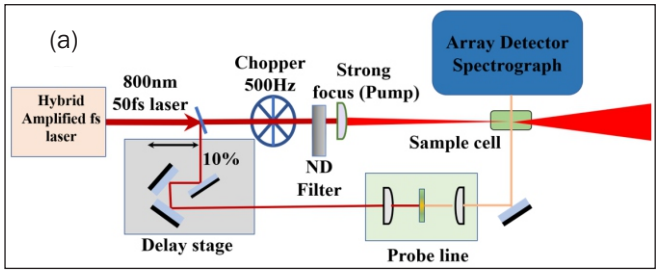


Fig.1: (a) Schematic of the conventional picosecond pulse radiolysis setup, (b) Actual facility of ELYSE [Source: https://www.icp.universite-paris-saclay.fr].



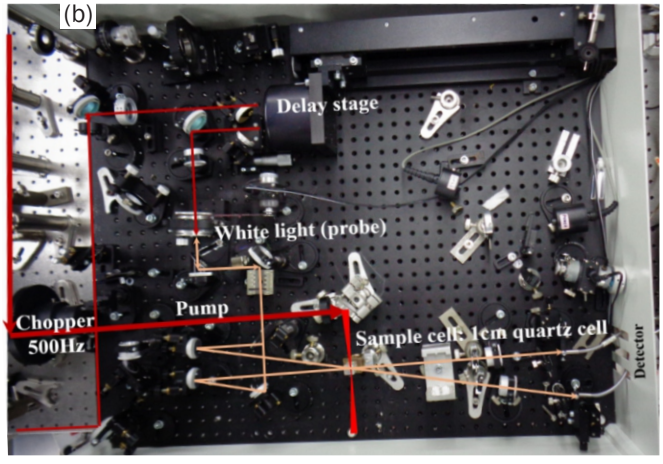


Fig.2: (a) Schematic of the broad band pump-probe setup to measure the dynamics of electrons generated in-situ by multiphoton ionization of water. (b) Photograph of the modified transient absorption setup.

Results & Discussion

The transient absorption (TA) spectra recorded at 1 ps and 5 ps with pure water as a medium of ionization are shown in Fig.3(a). The omission of the data in the 770-870 nm region is due to the large scattering of the pump light. The pure water spectrum at 5 ps time delay closely matches the solvated electron spectrum recorded with a LINAC based nanosecond pulse radiolysis facility. This result suggests the formation of electrons by multiphoton ionization of water using an intense femtosecond laser. Whereas pure water spectrum recorded at 1 ps time delay shows a significant absorption in the 1000-1070 nm region, which is a signature of the pre-hydrated electron. However, we could not see the signature of the dry electron due to the limited temporal window of our setup. The decay kinetics (Fig.3(b)) of the pre-hydrated electron (1050 nm) and hydrated electron (710 nm) were analysed with multiexponetial decay function. Our analysis shows a rise component at 710 nm with a time constant of 0.83±0.2 ps and a correlated decay at 1050 nm with a time constant of 0.86±0.2 ps. This observed time scale suggests the growth of solvated electron at 710 nm at the cost of the decay of the pre-hydrated electrons.

Thus, the present setup has the capability of detecting pre-hydrated electrons and solvated electrons separately. Some electron quenchers can be added to the medium and their reaction can be monitored in real time using our setup. We have shown that the decay of pre-solvated electrons leads to the rise of solvated electron signals which are correlated with each other. In the presence of an electron quencher, the surviving probability of pre-hydrated electron will be dependent on the concentration of the electron quencher. Hence the solvated signal strength at 710 nm will be dependent on the quencher concentration. Thus, we have investigated the reaction of pre-hydrated electrons with a well-known electron quencher, nitrate ion. The effect of nitrate ions on the yield of solvated electrons is shown in Fig.4. It is evident from the figure that the addition of potassium nitrate (KNO_3) results in a gradual decrease in the signal of the hydrated electron at 710 nm. The scavenging of pre-hydrated electrons by nitrate ions will compete with the solvation of electrons. The reciprocal of the surviving (S) percentage of pre-hydrated electron will be in a linear relation with scavenger's concentration (C) as shown in equation 1.

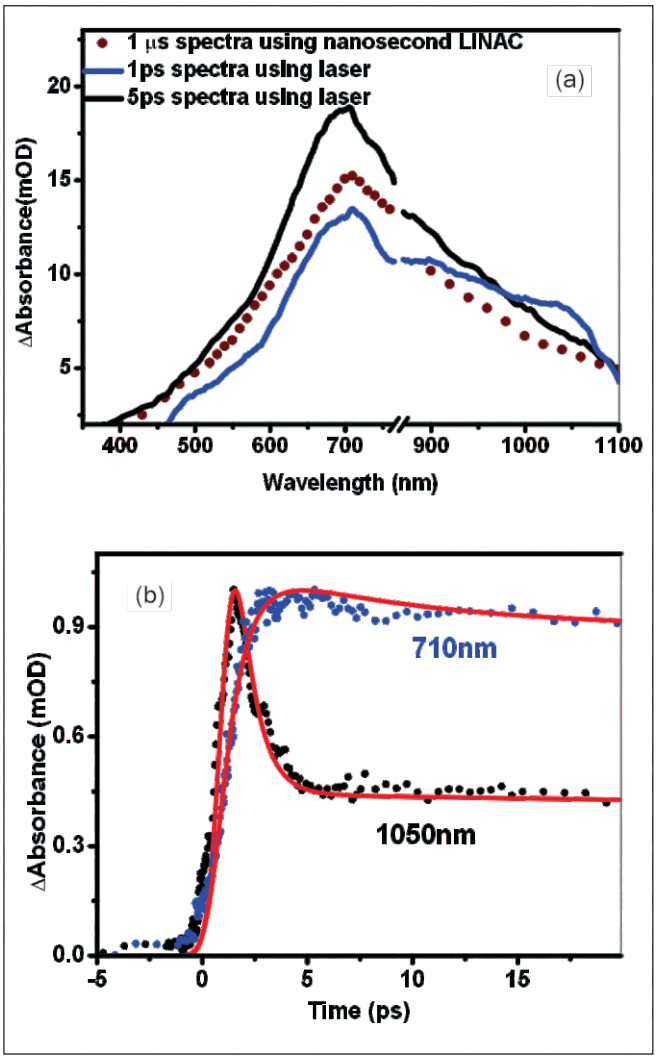


Fig.3: (a) Time-resolved spectra of electron (350-1100 nm) recorded by multiphoton ionization of water at 1 and 5 ps time delay. Solvated electron spectrum measured at 1μs using LINAC based nanosecond pulse radiolysis setup is also shown for comparison. (b) Normalized transient decay kinetics at 1050 nm and 710 nm. The solid lines through experimental data points are fitting using multiexponential decay function.

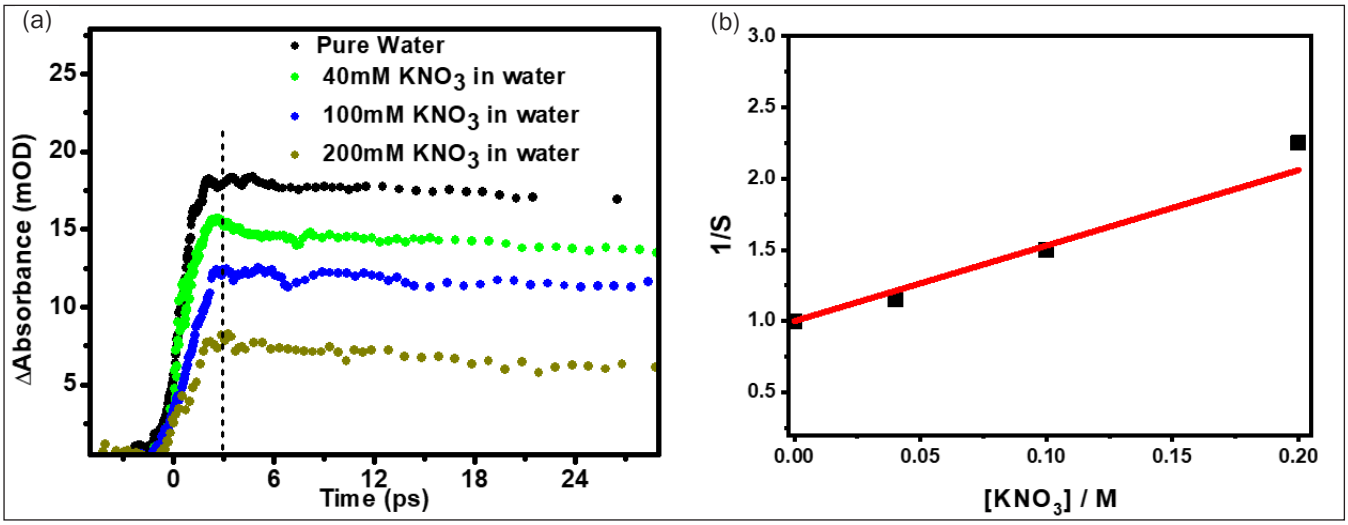


Fig.4: (a) Real time observation of 710 nm kinetics in presence of different concentrations of KNO_3 (b) Variation in the survival probability(S) of pre-hydrated electron with the concentration of KNO_3. The solid line is the fitting of the experimental data by equation 1.

$$\frac{1}{S} = \tau_{pre} k_{pre}[C] + 1 \quad (1)$$

Where τ_{pre} is the lifetime of the pre-hydrated electron and k_{pre} is the rate of reaction between pre-hydrated electrons and the nitrate ions. The reported average lifetime of pre-hydrated electrons (τ_{pre}) is about 540 fs [5]. The variation in the survival probability of pre-hydrated electron with the concentration of nitrate ion is shown in Fig.4(b). The fitting of the experimental data with equation 1 results in the rate constant (k_{pre}) value of 1 x 10^{13} $M^{-1}s^{-1}$. This large value of the rate constant clearly indicates the strong electron scavenging ability of nitrate ion. Thus, our setup was able to measure the very fast reaction of electron with a suitable scavenger.

Conclusion

In conclusion, we report development of a compact table top sub-picosecond resolved broadband transient absorption spectroscopic set up for generation and study of pre-hydrated solvated and hydrated electron produced by multiphoton ionization of water using femtosecond 800 nm laser pulse. Our set up can be employed to record temporal evolution of electron dynamics over full visible and NIR spectral window (350 to 1100 nm) and can act as a viable alternative to picosecond electron accelerator-based pulse radiolysis facility, at least in aqueous medium.

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PhD Thesis Using Femtosecond Laser Facility in Chemistry Group

Sr. No	Ph. D. Students	Title of Thesis	Guide	Institute & Year
1	Ajay K. Singh	Ultrafast Relaxation Dynamics in Some Organic Molecules in Solution Phase	Jai P. Mittal	University of Mumbai, 2002
2	Sukhendu Nath	Fast and Ultrafast Photoinduced Processes in Fullerene and Other Organic Molecules	A. V. Sapre	University of Mumbai, 2002
3	Guda Ramakrishna	Study of Interfacial Electron Transfer Dynamics in Dye sensitized Wide Bandgap Semiconductor Nanoparticles	Jai P. Mittal	University of Mumbai, 2005
4	Jahur A. Mondal	Ultrafast Dynamics Of Photoinduced Intra- And Intermolecular Processes In Condensed Phase.	Dipak K. Palit	University of Mumbai, 2010
5	Vaishali Samant	Ultrafast Hydrogen Bond and Electron Transfer Dynamics in the Excited States 9-Fluorenonen and Its Amine Derivatives.	Dipak K. Palit	University of Mumbai, 2010
6	Prabhat K. Singh	Studies on the Dynamics of Ultrafast Photoinduced Processes in Condensed Phase Using Thioflavin-T and Coumarin as the Probes	Haridas Pal	HBNI, 2011
7	Chandralekha Singh	Investigation of Ultrafast Dynamics of the Excited States of Donor-Acceptor Molecules in Condensed Phase.	Dipak K. Palit	University of Pune, 2012
8	Sachin R. Rawalekar	Ultrafast Charge Transfer Dynamics of II-VI Semiconductor Nanostructure Materials.	Hirendra N. Ghosh	University of Pune, 2012
9	Sreejith Kaniyankandy	Charge Transfer Dynamics in Quantum Dot and Quantum Dot Based Nanostructures.	Hirendra N. Ghosh	HBNI, 2012
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19	Mohammed Ahmed	Spectroscopic Studies on Interactions of Ions, Water and Bio-molecules and Applications.	Ajay K. Singh	HBNI, 2016
20	Biswajit Manna	Dynamics of Excited States and Transient Species in Self Assembled Media	Dipak K. Palit	HBNI, 2017
21	Jayanta Dana	Ultrafast Charge Transfer Dynamics of Dye-Semiconductor and Metal Nano-composite Material.	Hirendra N. Ghosh	HBNI, 2017
22	Sourav Maiti	Ultrafast Charge Carrier Dynamics of Semiconducting Nanocrystalline Materials.	Hirendra N. Ghosh	University of Pune, 2017
23	Aruna K. Mora	Understanding the Ultrafast Dynamics of Molecular Rotor Based Amyloid Probes.	Sukhendu Nath	HBNI, 2017
24	Vijay Beniwal	Non-linear Polarity Scales, Interfacial Diels-Alder and ESIPT Reactions in Ionic Liquid Media.	Anil Kumar	NCL, Pune, 2017

25	Pallavi Singhal	Synthesis of Nanomaterials for Energy Conversion and Environmental Applications.	S. K. Jha	HBNI, 2019
26	Rahul Kalel	Photophysical Properties of Organic Molecules in Constrained Biological and Chemical Media.	Sukhendu Nath	Savitribai Phule Pune University, 2019
27	Papu Samanta	Photoinduced Electron Transfer Processes in Homogeneous and Microheterogeneous Media Involving Organic and Inorganic Donor Acceptor Systems.	Haridas Pal & Sharmistha Dutta Choudhury	HBNI, 2021
28	Ananta Dey	Role of Noncovalent Interactions in Proton-Coupled Electron Transfer (PCET) and Designing Supramolecular Assemblies.	Amitava Das	NCL, Pune, 2021
29	Sunil Aute	Synthesis, Characterization and Photophysical Studies of Dyes for Dye Sensitized Solar Application.	Amitava Das	CSMCRI, Bhavnagar, 2021
30	Subhadip Roy	Studies of Metabolites and Ions at Aqueous Interfaces by Surface-Sensitive Spectroscopic Technique.	Jahur A. Mondal	HBNI, 2021
31	Amitabha Nandi	Ultrafast Dynamics of Exciton and Charge Carriers in Thin Film and Nanoaggregates of Polyaromatic Molecules.	Sukhendu Nath	HBNI, 2022
32	Nishith Ghosh	Interface-Selective Vibrational Spectroscopic Study of Aqueous Interfaces: Application to Atmospheric and Biological Systems	Jahur A. Mondal	HBNI, 2023

Evaluation of Rate of Dissolution of UNF for Indian PHWR

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Dissolution of used spent nuclear fuel (UNF) of Indian PHWR is a key step for fuel reprocessing and the plant through put is guided by the rate of reaction. The rate of reaction depends on the reactant concentration and reaction temperature. The rate of the dissolution reaction can be calculated by shrinking core model because the reaction takes place at the surface of the solid and the reaction zone moves into the solid core leaving behind the converted material. Further, a few methods available in the literature [1] are also applied to compute the rate of reaction for irradiated PHWR fuel. The rate of reaction is only controlled by reaction and the reaction is pseudo-first order with respect to HNO_3 [2]. The schematic representation of dissolution with typical chopped fuel piece has been shown in Fig.1.

The heterogeneous reaction has been carried out in several steps and the rate constant of the dissolution reaction can be calculated from the slope of the equation given below:

$$\left(1-\frac{[U]_t}{[U]_f}\right)^{\frac{1}{3}} = 1-\frac{2}{3}\,\frac{kC_B}{n\delta\rho_B R}\,t$$

The rate of dissolution has been computed using shrinking core model (SCM) and found to be in the range of 5.27×10^{-3} to 5.70×10^{-3} m/s using zone averaging method. The calculated value is in well agreement with the reported value. Further, the rate has been improved for irradiated fuel in presence of cracks and the rate of reaction is obtained as 4.1×10^{-2} m/s. Hence, the present calculation method can be applied to calculate the rate of dissolution for fast reactor fuel reprocessing.

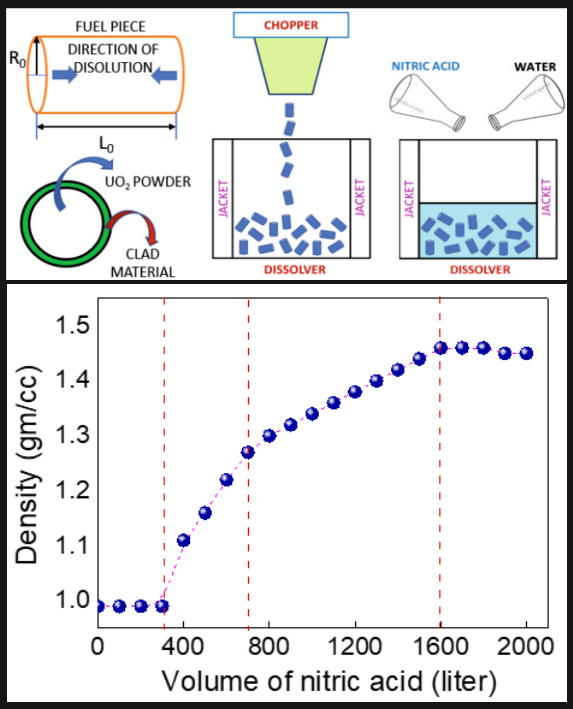


Fig.1: Schematic representation of a typical chopped fuel piece of SNF and the chopper dissolver system where the chopped pieces are dropped into water and the concentrated nitric acid has been added for dissolution. The profile represents the density of dissolved solution as a function of volume of 12M nitric acid.

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Predictive Analytics in Occupational Health and Safety

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Introduction

In today's dynamic work environments, predictive analytics has emerged as an effective mechanism for anticipating and mitigating probable risks before they manifest as an incident or accident. By combining statistical techniques, machine learning algorithms, and historical data, predictive analytics facilitates a proactive approach to Occupational Health and Safety (OHS). This not only helps in identifying emerging hazards but also provides practical insights that enhance decision-making, optimize operations, and improve overall safety performance. Predictive Safety Analytics goes beyond traditional safety measures, which primarily respond to incidents after they occur. Instead, it leverages data, technological and analytical tools to predict potential risks, thus facilitating preventive strategies and cultivate a safer workplace. This shift from reactive to proactive strategies marks a significant progress in workplace safety management, allowing organizations to foresee and rectify safety concerns before they deteriorate into incidents.

One of the key advantages of predictive analytics is its ability to identify patterns, trends, and anomalies that may indicate potential hazards and risks. By utilizing historic data, organizations can proactively monitor worker behavior, equipment performance, and environmental conditions in real-time. It can reveal patterns, such as unsafe work practices, equipment malfunctions, or environmental hazards, enabling timely interventions before they lead to accidents. For example, while real-time monitoring of machinery can detect minor defects that could develop into significant safety risks if left unaddressed, predictive algorithms, using maintenance history and sensor data, ensure machinery is serviced before failures occur, minimizing downtime and reducing the risk to employees.

Predictive analytics is not limited to understanding past incidents (descriptive analytics) or explaining why they occurred (diagnostic analytics). It focuses on forecasting what is likely to happen by pattern and relationships analysis in historical data. Such capability allows organizations to develop data-driven safety programs, optimize resource allocation, and implement preventive measures that reduce workplace risks. In addition to enhancing operational efficiency, predictive analytics can help foster a culture of health and wellness within organizations. It reduces absenteeism, improves employee retention, and lowers workforce-related costs by providing insights into potential risks that can be addressed before they result in accidents or health issues. Turning data into actionable strategies enables organizations to address these risks, creating a safer, more resilient workplace.

Critical Components of Predictive Analytics in Occupational Health and Safety

Predictive analytics in workplace safety is a proactive, data-driven method designed to identify and mitigate hazards before they occur. This approach relies on thorough data collection, drawing from multiple sources like safety reports, audits, and inspections. Incident reports provide insights into the factors responsible for past accidents, near-misses, and violations, while safety audits highlight compliance and probable risks. Sensors monitor environmental factors such as temperature, equipment performance, etc. Feedback from workers further enriches this data, contributing valuable perspectives on safety concerns and near-miss incidents. This often requires compiling and processing raw data from various departments to produce actionable safety metrics. Effective data preparation is essential to guarantee the correctness and dependability of the insights produced.

Managing this wealth of data requires a robust system for organizing, storing, and maintaining its accuracy and usability. Data protection and hassle-free accessibility can be ensured by secure and safe storage preferences like cloud services or

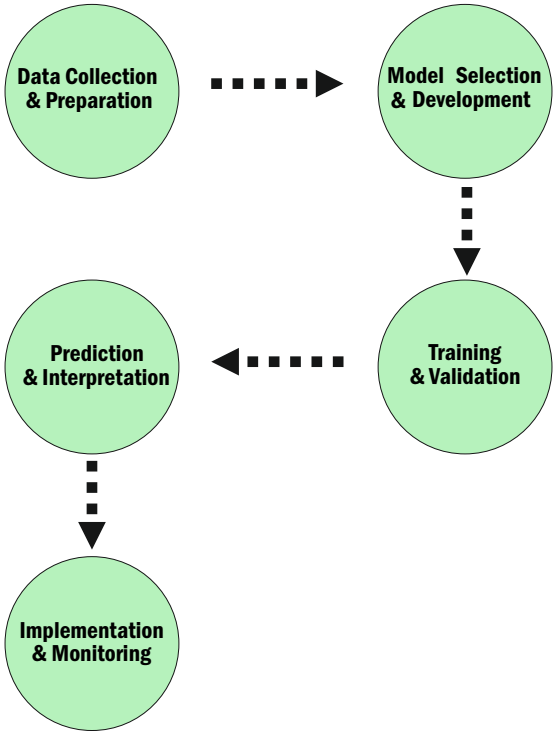


Fig.1: The process of Predictive Analytics .

Table: Salient Components of Predictive Analytics and Their Impact on Occupational Health and Safety.

Key Component	Description	Impact on Occupational Health and Safety
Data Collection	Gathering relevant safety data (incident reports, safety audits, sensors, etc.).	Ensures comprehensive information is available for risk analysis, helps in identifying trends and emerging hazards.
Data Management & Preparation	Organizing, storing, and cleaning data for analysis.	Enhances data accuracy and reliability, ensures the proper integration of diverse data sources for better predictive outcomes.
Analytical Methods	Statistical techniques (e.g., regression, time-series analysis) and machine learning algorithms.	Identifies relationships between variables, detects trends, and predicts potential risks, leading to proactive safety measures.
Predictive Modelling & Risk Assessment	Developing models to forecast future safety risks.	Enables proactive risk management by identifying where and when accidents are likely to happen, facilitating targeted interventions and safety strategies.
Interpretation & Implementation	Turning predictive insights into actionable safety strategies.	Allows organizations to implement preventive measures based on predictions, optimizing safety protocols and reducing incidents.
Training & Communication	Educating employees about interpreting insights and fostering participation in preventive measures.	Promotes a culture of safety, empowering employees to actively engage in hazard prevention, increasing the overall effectiveness of safety initiatives.

databases. Data cleaning processes, which involve removing duplicates and standardizing formats, are essential to ensure the consistency and reliability of the data. Data from multiple sources must be integrated into a integrated format to permit comprehensive analysis and ensure that no important data is overlooked in the analytical model. Before conducting analysis, data must be prepared, which includes transforming raw data into a suitable format for predictive modelling. This process involves aggregating data points, normalizing values, and selecting the most critical variables, or features, that have the greatest impact on safety outcomes. High-quality data is crucial for precise predictions, and systematic audits, along with validation, help maintain the integrity and relevance of the data. Validation is particularly important to evaluate the efficacy of safety measures and prioritize issues that need to be addressed.

Predictive analytics uses various advanced analytical methods to process this data. Standard techniques such as regression and correlation analysis to examine relationships between variables, classification algorithms, and time series analysis to find out trends over a period of time are commonly employed. The nature of the data and particular analysis objectives dictate the model selection. Machine learning algorithms, such as classification and clustering methods, further enhance the predictive capabilities. These algorithms categorize safety risks or cluster similar incidents to identify patterns, offering a deeper understanding of potential hazards. By applying powerful statistical techniques, organizations can uncover relevant relationships between safety outcomes and operational metrics, allowing for predictions about where and when accidents are likely to occur, and under what circumstances. Once the data is prepared, the selection of appropriate models is critical.

Predictive models, which are developed from historical data, forecast future safety risks and help organizations implement preventive measures. These models consider a number of factors, including employee behavior, workplace conditions, and external influences, making it possible to predict safety-related events and adjust operational strategies accordingly. The selected models are trained on historical data in order to recognize patterns and relationships, with performance validated using different datasets to ensure accuracy and reliability. By continuously refining these models to adapt to evolving workplace dynamics, organizations can enhance their ability to prevent accidents and optimize resource allocation. An essential part of predictive safety Analytics is assessing risks by evaluating the likelihood and severity of potential hazards. Techniques such as Failure Modes and Effects Analysis (FMEA) and Fault Tree Analysis (FTA) to identify potential failure points in processes or equipment, and the root causes of incidents respectively. These assessments allow organizations to prioritize risks and focus resources on areas of concern with the highest probable safety impact.

Once insights are generated, interpreting the results is critical for translating data into actionable strategies. The model forecasts future events, probabilities and trends, and the output is translated to get actionable insights. Organizations must identify trends and patterns, and then develop recommendations to mitigate the identified risks. Implementing these strategies requires integrating predictive insights with existing safety protocols, aligning new data-driven approaches with traditional safety measures like incident reporting and safety training programs.

Successful implementation of predictive safety Analytics also depends on employee training and involvement.



Fig.2: Benefits of Predictive Analytics.

Employees need to be educated on interpreting predictive insights and understanding potential risks so that they can actively participate in preventive measures. Encouraging workers to report observations and engage with safety data fosters a collective responsibility for workplace safety. Moreover, effective communication strategies are vital to ensure that insights are shared clearly and concisely with all stakeholders. Using visualization tools and regular briefings can help convey complex predictive data in an accessible format, ensuring that everyone from safety professionals to frontline workers understands the implications of predictive insights.

The decision-making activities must integrate predictions and insights generated from predictive analytics. Ongoing monitoring is crucial for evaluating the model's effectiveness should be evaluated by means of continuous monitoring so as to find and deficiency and requirements of any suitable adjustments and amendments during the course of implementation and utilization of model. This cycle of refinement ensures that predictive analytics remains applicable and impactful, strengthening the organization's safety culture over time.

Benefits of the Predictive Analytics in Occupational Health and Safety

Predictive analytics offers a wide array of benefits that enhance decision-making, operational efficiency, and risk management across various industries. In occupational health and safety, its application is even more profound, transforming traditional safety practices into a proactive, data-driven approach that focuses on prevention, optimization, and long-term strategic benefits.

Predictive analytics provides safety managers with data-driven insights for more informed decision-making. By utilizing historical as well as real-time data, it is possible to forecast future outcomes, anticipate risks and take preventive measures. This proactive approach helps in identifying vulnerabilities and mitigating them before they escalate into serious incidents. In the realm of workplace safety, this translates into better management of risks associated with occupational hazards and equipment malfunctions, ultimately reducing accidents and ensuring a safer work environment.

One of the biggest applications of predictive safety Analytics is in workplace accidents prevention. Organizations can identify potential hazards early with the help of predictive analytics and implement targeted preventive measures. This proactive strategy not only minimizes the likelihood of accidents but also contributes to a safer and more positive workplace culture. Moreover, predictive models help organizations focus on high-risk areas, allowing for timely interventions that reduce occupational hazards before they become critical.

Predictive analytics also plays a crucial role in improving operational efficiency. By forecasting demand, optimizing processes, and predicting equipment failures, organizations can streamline operations, reduce downtime, and improve maintenance scheduling. In the context of workplace safety, predictive tools enable companies to allocate resources more effectively by focusing on areas and activities where risks are most likely to occur. This optimization not only reduces operational disruptions but also enhances overall productivity.

The financial implications of predictive safety analytics are substantial. Both direct costs, e.g., medical expenses and workers' compensation, and indirect costs, such as production delays, equipment downtime, and potential legal penalties can be minimized by preventing accidents and minimizing workplace hazards. Furthermore, companies that maintain a strong safety record often experience long-term benefits, such as improved operational efficiency, enhanced reputation, and reduced insurance premiums. These savings contribute to the overall financial success of the organization.

Continuous monitoring and predictive insights not only enhance safety but also help ensure compliance with

regulatory requirements. Predictive models can flag potential compliance issues before they result in violations, reducing the risk of legal and financial penalties. Additionally, predictive analytics helps in long-term planning by providing futuristic insights into trends and safety risks. Organizations can use these insights to develop more effective safety strategies, align resources with high-risk areas, and implement proactive measures that foster a culture of safety and resilience.

By identifying and addressing risks before they pose a threat to employees, predictive safety Analytics helps create a healthier and safer occupational space. This ensures employees' well-being as well as enhanced job satisfaction and retention, as workers feel more secure in their roles. A safer work environment promotes higher levels of productivity, improves morale, and reduces absenteeism, further contributing to the organization's overall success.

The Impact of Predictive Analytics on Occupational Health and Safety in India

India's diverse occupational landscape, with its mix of organized and unorganized sectors, faces significant challenges in maintaining workplace safety and employee well-being. Predictive analytics, which has transformed occupational health and safety globally, offers immense potential for addressing these challenges in the Indian context. By leveraging data-driven insights, predictive analytics can help Indian organizations anticipate risks, reduce workplace accidents, and improve overall productivity.

In Indian industries, especially high-risk sectors such as construction, mining, and manufacturing, frequent workplace injuries and health issues can lead to lost workdays, higher insurance costs, and productivity losses. Predictive analytics enables organizations to identify vulnerable worker populations based on factors like demographics, job roles, and workplace conditions. For example, analyzing anonymized data related to worksite claims, employee turnover, and health surveys can reveal patterns indicating employees at greater risk of injury or illness. In a typical Indian factory, where manual labor often plays a significant role, predictive models can detect early signs of health issues such as musculoskeletal disorders due to repetitive tasks. By identifying these risks early, organizations can implement targeted interventions like introducing ergonomic tools or adjusting workloads reducing both absenteeism and presenteeism (where employees work while unwell, impacting both safety and productivity).

India's workforce is often impacted by socio-economic factors like long commutes, lack of access to quality healthcare, and family responsibilities. Predictive analytics can integrate these social determinants of health, offering a more holistic view of the workforce's well-being. For instance, employees living in remote or poorly connected areas may face additional challenges in attending work during bad weather or transportation strikes. By factoring in such societal data, Indian employers can design more flexible work arrangements, such as staggered shifts or remote work options, tailored to the needs of the workforce. This approach helps Indian companies better manage employee absenteeism, presenteeism, and productivity, offering solutions such as childcare assistance or healthcare access programs that address specific challenges.

In India's rapidly evolving industrial landscape, where unforeseen circumstances like extreme weather, infrastructure failures, or natural disasters can disrupt operations, predictive analytics can be a vital support. By analyzing patterns in workplace data and external factors such as weather conditions, organizations can forecast disruptions and manage risks effectively. For example, during monsoon season, construction companies in India can use predictive models to anticipate delays or accidents caused by heavy rains and plan safety measures accordingly. Predictive analytics can also help organizations prepare for other unforeseen events, such as employee shortages during strikes or pandemic outbreaks, ensuring organization continuity in critical industries like transportation or healthcare.

One of the major benefits of predictive analytics in the Indian occupational landscape is its ability to tailor health and safety programs to the specific needs of the workforce. By analyzing demographic and operational data, employers can develop focused interventions. For instance, in industries where female workers are predominant, such as textiles, predictive models may highlight health issues like anemia or reproductive health concerns that could lead to higher absenteeism rates. Employers can then design programs that address these specific health needs, improving employee retention and productivity. In hazardous sectors like mining, predictive models can identify which equipment failures or operational procedures are likely to cause accidents, enabling organizations to implement preventive maintenance schedules and targeted safety training for workers handling risky tasks.

For Indian organizations, the financial benefits of predictive analytics extend beyond accident prevention. By reducing occupational hazards, companies can lower medical and compensation costs while also avoiding potential legal issues. Organizations with robust safety records often enjoy improved reputations and reduced insurance premiums, all of which contribute to long-term financial sustainability. By leveraging predictive analytics, Indian industries can move from reactive to proactive safety management, ensuring that they not only comply with regulations but also create a safer, healthier work environment. This proactive approach is essential in protecting India's workforce while driving operational efficiency and long-term economic growth.

Challenges in Implementing Predictive Analytics in Occupational Health and Safety

As organizations integrate predictive analytics for workplace safety, it is vital to recognize and tackle the challenges that may accompany this initiative. The introduction of predictive analytics raises significant ethical questions that organizations must navigate thoughtfully. Utilizing employee data to forecast safety risks can lead to apprehensions about security of personal information, privacy, and consent. While the aim is to bolster workplace safety, ensuring transparency is critical. Organizations should effectively communicate how predictive models operate, the data being collected, the purposes for which it is used, and the safeguards in place to safeguard employee privacy. Developing ethical guidelines and securing informed consent are essential steps in fostering trust and addressing these ethical issues.

The deployment of predictive analytics requires extensive data collection and analysis, making the protection of data privacy and security very important considerations. Strong and effective measures such as encryption protocols, secure storage solutions, and stringent access controls must be put in place to prevent any unauthorized access, misuse or breaches vis a vis sensitive information. Adherence to data protection regulations is crucial in predictive analytics (Zarsky, T. Z. (2017)). Regular audits of data security practices, investments in encryption technology, and educating employees about data confidentiality are necessary to instil trust in the minds of employees and stakeholders regarding the ethical use of predictive analytics.

Although predictive models yield important and useful insights, an excessive reliance on them can create challenges. Occupational safety is dynamic and affected by several factors that can shift rapidly. Organizations should strive to not depend on predictive models exclusively and instead incorporate real-time situational awareness into their safety strategies. Striking a balance between predictive insights and continuous monitoring and adaptability is essential for effectively responding to emerging safety challenges. This approach ensures that organizations can exploit the predictive capabilities of data even though maintaining flexibility in dealing with the evolving situations.

Addressing these challenges requires a comprehensive and broad-based approach that includes ethical standards, robust data security measures, and a clear understanding of predictive analytics' role in safety management. By proactively tackling these ethical issues and obstacles, organizations can create a safe, responsible, and reliable work environment.

Conclusion

Predictive analytics offers transformative benefits in occupational health and safety, enhancing decision-making, risk mitigation, operational efficiency, and cost savings. By adopting proactive safety measures, organizations can prevent accidents, reduce hazards, and ensure regulatory compliance while fostering a safer, more positive work environment. This data-driven approach allows for better risk assessment, the optimization of resources, and the prevention of incidents, ultimately leading to improved safety outcomes and sustained success. However, it's crucial to address ethical concerns like data privacy and transparency when integrating predictive models into safety strategies. As predictive analytics continues to evolve, its potential to reshape occupational safety practices grows, enabling organizations to anticipate and prevent workplace risks before they occur.

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Aiming High

India's Aspirations in the Global Space Economy by Shri A.S. Kiran Kumar

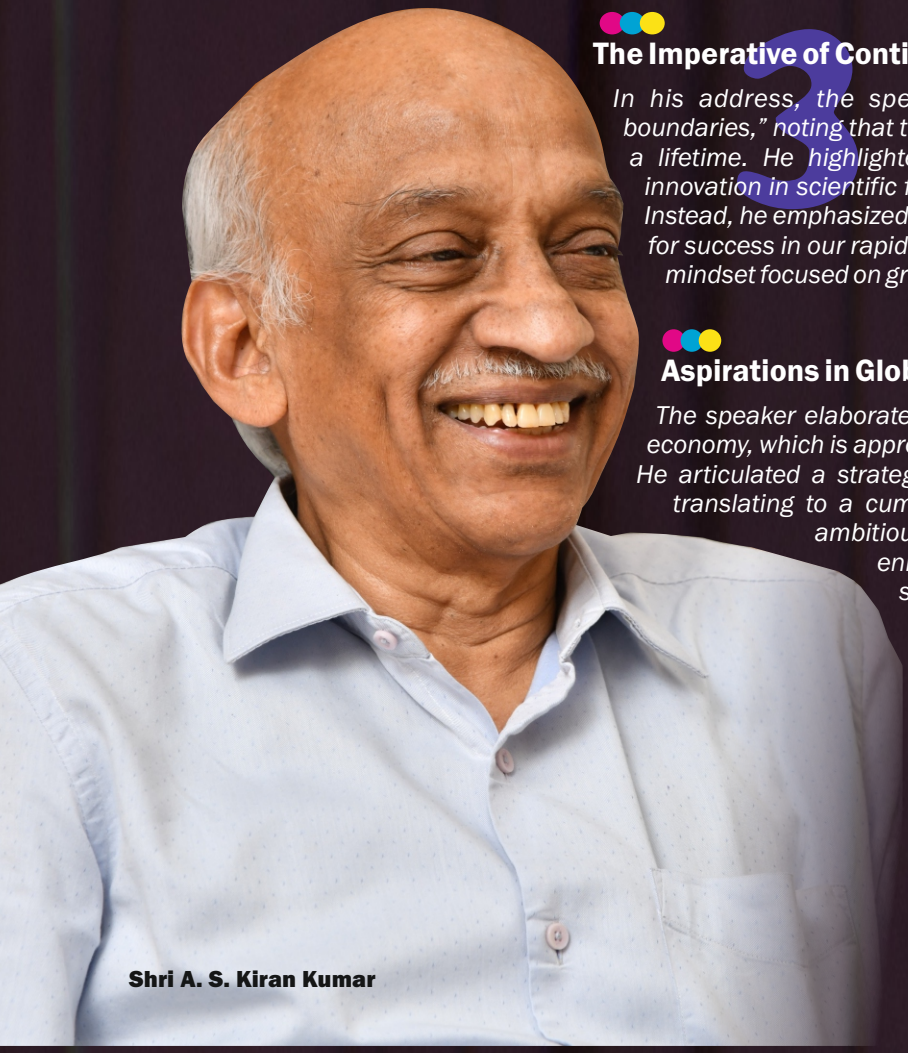
In a recent address to Trombay Colloquium audience (on September 13, 2024) on the topic 'Indian Lunar Mission', the former Secretary of the Department of Space (DoS), Shri A.S. Kiran Kumar, articulated several key advancements and strategic initiatives undertaken by India in space exploration and allied areas.

1 Evolution of Domestic Rocket Technology...

In his address, Shri Kiran Kumar highlighted the evolution of domestic sounding rocket technology, tracing its origins from the Rohini series RH200 to the advanced RH-560 Mark II. He emphasized this technological progression as a testament to India's growing capabilities in aerospace engineering and its strategic relevance in global space endeavors.

2 Chandrayaan-I Mission...

Reflecting on ISRO's Chandrayaan-I mission, the speaker highlighted its key role in confirming water molecules on the Moon and noted that findings from Chandrayaan-III were shared globally on National Space Day 2023, reinforcing India's significant contribution to lunar research.



Shri A. S. Kiran Kumar

3 The Imperative of Continuous Learning and Innovation...

In his address, the speaker urged attendees to "push beyond your boundaries," noting that true learning from mistakes may require more than a lifetime. He highlighted the importance of continuous learning and innovation in scientific fields, asserting that "experience is less relevant." Instead, he emphasized that knowledge and the ability to adapt are crucial for success in our rapidly evolving landscape, underscoring the need for a mindset focused on growth and progress.

4 Aspirations in Global Space Economy...

The speaker elaborated on India's current standing in the global space economy, which is approximately 2%, valued at $8.4 billion as of 2022-23. He articulated a strategic vision aimed at increasing this share to 8%, translating to a cumulative value of $44.4 billion by 2032-33. This ambitious goal, he said, reflects India's commitment to enhancing its role in global space activities through sustained investment and innovation.

5 Media Engagement with Space Research ...

When asked about the Department of Space's favorable media coverage compared to other departments, he noted that DoS' popularity stems from the intrinsic human fascination with space, rather than from efforts to secure positive coverage. Additionally, he stated that the groundbreaking work of the organization naturally attracts public interest due to its significance and impact.

6 Active Engagement at DoS...

In his address, Shri Kumar emphasized that DoS personnel are consistently engaged with new challenges, fostering an environment conducive to innovation and problem-solving. This active involvement is essential for sustaining momentum in India's ambitious space initiatives.

Through these discussions, the former Secretary of the DoS illuminated both the achievements and aspirations of India in space exploration, reinforcing the nation's commitment to advancing scientific knowledge and innovation on a global scale.

Reports from conferences, theme meetings, symposia, and outreach



Program dignitaries unveiling the Book of Abstracts on PPSTA-2024.

Participants to the symposium.

PPSTA-2024

National Conference on Pulsed Power Science, Technology & Applications

The DAE-BRNS maiden National Conference on "Pulsed Power Science, Technology & Applications" (PPSTA-2024) took place from September 12-14, 2024, at the BARCF Facility in Visakhapatnam, organized by the Pulsed Power & Electro-Magnetics Division in collaboration with the Power Beam Society of India. Dr. Ashish Kumar Ray, former Director of BTDG, was the Chief Guest; Dr. Archana Sharma served as Chairperson, and Dr. Rishi Verma was the Convener.

Approximately 170 participants attended from various institutions including DAE, DRDO, CSIR-CEERI Pilani, IIT-BHU, IISc Bangalore, BITS Pilani, and several industries.

Among them were 113 from R&D (92 from DAE and 15 from DRDO), 44 from academia, and 13 from industry. A total of 113 submissions were received for presentations, with 45 delivered as oral talks and the rest as posters.

The conference highlighted advancements in pulsed power science and technology while fostering knowledge exchange among researchers, academics, and industry professionals across diverse fields. It also featured the release of a Book of Abstracts on papers submitted for discussion at the conference.

Reports from conferences, theme meetings, symposia, and outreach



Group photograph of participants to MCQAAM-2024 held at NCCCM-BARC, Hyderabad.

Program dignitaries unveiling MCQAAM-2024 souvenir during the inaugural session.

MCQAAM-2024

Material Characterisation - Quality Assurance in Analytical Measurements

A one-day theme meeting titled “Material Characterization - Quality Assurance in Analytical Measurements” (MCQAAM-2024) was held on September 13, 2024, at NCCCM-BARC, Hyderabad, marking 30 years of excellence in analytical measurements.

Dr. Awadhesh Kumar, Associate Director of the Chemistry Group at BARC and Chairman of the meeting, welcomed attendees and discussed the vision behind NCCCM's establishment, emphasizing the efforts to set up a clean room facility for ultra-trace analytical measurements. He expressed gratitude to former leaders and the current Director of BARC for their support.

The chief guest, Dr. Komal Kapoor, Chief Executive of NFC, acknowledged the foundational contributions of Shri K. Balaramamoorthy and Dr. S. Gangadharan in establishing NCCCM in 1993. He highlighted collaborative programs with Control Lab and stressed the importance of producing Certified Reference Materials (CRMs) for validating analytical measurements.

Dr. Balamuralikrishnan, Director of DMRL, underscored the significance of material characterization from a metallurgical perspective and called for collaboration between NCCCM and DMRL in producing CRMs and analyzing strategic materials.

Shri K. Srinivas, Director of ESG at BARC, reminisced about his early experiences with the project and detailed the complexities involved in constructing India's first non-metallic clean lab at NCCCM.

Dr. K. Dash, Head of NCCCM-BARC, outlined key activities over the past three decades, particularly focusing on CRM production in analytical measurements.

The meeting featured invited talks from eminent scientists across various topics, including materials development using high-energy radiation, chemical sensors, quality assurance in materials characterization, and more. A souvenir commemorating NCCCM-BARC's significant activities over the past thirty years was released during the event.

Reports from conferences, theme meetings, symposia, and outreach



Release of BTDG Colloquium Book of Abstract.

ALA-2024

One day Theme Meeting on Advancements in Laser Applications

The Advancements in Laser Applications (ALA-2024) technical theme meeting convened leading researchers from prestigious institutions, including NPL, TIFR, RRCAT, IIT Delhi, IIT Bombay, and BARC, to explore the latest developments in laser technology.

The meeting featured six invited lectures and a keynote address, covering a diverse range of topics such as:

1. Advances in Laser-based Instrumentation
2. Laser-based Terahertz Generation and Applications
3. Laser-based Quantum Computation

The event attracted over 100 participants, all of whom engaged enthusiastically throughout the day. In the inaugural session, chief guest of the meeting Prof. Jayaram Chengalur, Director, TIFR, Mumbai addressed the audience by his exemplary speech. Next was the inaugural address by Dr. Archana Sharma, Director, BTDG which was followed by overview of the Theme meeting by Shri Martin Mascarenhas, AD, BTDG and Head, LPTD. The keynote address, titled "Laser in Metrology," was delivered by Prof. Venu Gopal Achanta, Director of NPL, Delhi.

The morning sessions concentrated on Laser-Based Instrumentation. Dr. S. K. Dubey from IIT Delhi delivered a compelling presentation on Electro-optic Sensing and Imaging, emphasizing its applications in both medical and strategic fields while discussing potential collaborations between BARC and IIT Delhi. Following him, Dr. Jolly Xavier, also from IIT Delhi, presented on Quantum Enhanced Optical Imaging and Sensing, detailing innovative techniques such as quantum microscopy of biological organisms utilizing spatial and polarization entanglement. Shri A. S. Rawat from BARC concluded the morning session with an insightful talk on Laser-Based Vibration Measurement, highlighting significant advancements in measurement techniques.

The first session after lunch was focused on Applications of Ultra-intense Lasers in THz Generation. Dr. J. A. Chakera from RRCAT shared insights into recent achievements in High-energy X-rays, Attosecond Pulse Generation, and Advanced Particle Accelerators, including updates on collaborative programs with CERN for their LHC project. Following this, Dr. S. S. Prabhu from TIFR Mumbai elaborated on Far-Field and Near-Field Terahertz (THz) Spectroscopy of Materials, underscoring its critical role in material analysis.

In the last session, the topic of Lasers in Quantum Computing was discussed. Dr. Gopal Dixit from IIT Bombay presented on the Alley-Transistor for Quantum Technologies at Ambient Conditions, exploring novel approaches for integrating quantum technologies. This was followed by Dr. Sourav Dutta from TIFR Mumbai, who discussed Laser Cooling and High-resolution Spectroscopy using External Cavity Diode Lasers built at TIFR. The session concluded with Dr. B. Dikshit from BARC presenting on Ion/Atom Trapping for Quantum Computing, emphasizing the transformative potential of laser technologies in advancing quantum computational capabilities.

The meeting was concluded by Dr. S Baruah, Scientific Secretary, ALA-2024 by summarizing the important points of the invited talks. Dr. Padma Nilaya, also attended and served as Co-chairperson of the theme meeting ALA-2024.

Overall, ALA-2024 served as a vital platform for knowledge exchange and collaboration among experts in laser applications, focusing on advancements in instrumentation, THz applications, and quantum computing technologies. The meeting not only highlighted current research but also paved the way for future innovations in these dynamic fields.

Reports from conferences, theme meetings, symposia, and outreach



Mr. Gashaw G. Wolde (Section Head, Division for Asia and the Pacific, IAEA) speaks at the Mid-Term Review Meeting.

Participants of the Mid-Term Review Meeting for the IAEA technical cooperation project (RCA RAS-7040) pose for a group photograph.

IAEA RCA PROJECT RAS-7040

Water Resources Management through Environmental Isotope Analysis & Applications

The Isotope and Radiation Application Division of Radiochemistry and Isotope Group (RC&IG), BARC held a Mid-Term Review Meeting for the IAEA technical cooperation project (RCA RAS-7040) titled "Improving Water Resources Management Practices by Enhancing Regional Collaboration in Environmental Isotope Analysis and Applications" from October 21 to 25, 2024 in Mumbai, India.

The project's goal is to enhance water resource management through improved regional collaboration in isotope analysis. Considering the uncertain future of many agrarian regions across the world due to global warming and its associated threats water resources, this regional collaborative project assumes a greater importance.

Twenty-two representatives from National Project Teams (NPTs) and National Project Coordinators (NPCs) from countries including Australia, Fiji, India, Indonesia, and others participated in this event. Notable attendees included Mr. Gashaw G. Wolde (Section Head, Division for Asia and the Pacific, IAEA), Mr. U. D. Saravana Kumar (Technical Officer, IAEA) and Dr. Y.K. Bhardwaj (Associate Director, RC&IG, BARC), who inaugurated the event. Mr. Dang Duc Nhan, the lead country coordinator, from Vietnam Atomic Energy Agency (VINATOM) presented the project's objectives and expected outcomes. Dr. K. Tirumalesh, Scientific Officer-G, IRAD, BARC acted as local coordinator for this event.

During the five-day meeting, the national project work plans and the achievements were reviewed, the work plan for the remaining period was finalized and upcoming regional training programs were discussed.

Additionally, delegates visited BARC's low-level counting facility at BARC Hospital on October 24 to observe radiocarbon sampling from natural water. The meeting concluded with remarks from Dr. R. Acharya, Head of IRAD at BARC.

The Regional Cooperation Agreement (RCA) aims to enhance research, development, and training in nuclear science and technology across Asia and the Pacific. Among its various initiatives, the current program specifically promotes the application of nuclear techniques to identify groundwater sources and pollutants, thereby facilitating effective remedial actions.

Reports from conferences, theme meetings, symposia, and outreach



Participants to the symposium pose for a group photograph at the venue.

(From left): Dr. N. Choudhury (Head, Chemistry Division), Dr. Swapan K. Ghosh (Distinguished Professor and Dean, UM-DAE-CEBS), Dr. J. P. Mittal (Former Director, Chemistry Group), Dr. A. K. Tyagi (Dean, HBNI) and Dr. Awadhesh Kumar (Associate Director, Chemistry Group).

CTTC-2024

Symposium on Current Trends in Theoretical Chemistry

The Chemistry Division, BARC in collaboration with the Society for Materials Chemistry (SMC), organized the DAE-BRNS symposium on Current Trends in Theoretical Chemistry (CTTC-2024) from September 26-28, 2024, at the DAE Convention Centre, Anushakti Nagar. The event was chaired by Dr. A. K. Tyagi (Dean, HBNI), with Dr. Awadhesh Kumar and Dr. N. Choudhury serving as Co-Chairman and Chairman of the Local Organizing Committee, respectively. The symposium aimed to foster academic interactions and discussions on contemporary trends and future directions in theoretical and computational chemistry. Key topics included: Theoretical formalisms and simulation strategies; Electronic structure and spectroscopic properties; Chemical dynamics, reactivity, and catalysis; Soft matter; Computational biology; Energy; Nuclear waste management; and Machine learning applications in chemistry.

The event attracted participants from various institutes across India, featuring eminent researchers in theoretical chemistry. The inaugural session was enlightened by the Chief Guest address by Prof. J. P. Mittal. Three plenary lectures were delivered in the symposium by three distinguished speakers: Prof. Sourav Pal, Prof. Rajeev Ahuja, and Prof. Swapan K. Ghosh. Over the three days, the symposium included: 3 Plenary Lectures; 22 Perspective Talks; 12 Short Talks; 9 Lightning Talks; and 3 Technical Talks.

In order to encourage and include more number of young researchers, many short and lightning talks were arranged. Approximately 126 contributory papers were presented as posters and awards were given for the best contributions. The proceedings of CTTC-2024 include abstracts from all invited talks and contributory papers. After 3 days of intense deliberation, the symposium concluded successfully, with participants expressing appreciation for the platform it provided for meaningful interactions and collaborations among leading research groups in theoretical chemistry across India.

Reports from conferences, theme meetings, symposia, and outreach



Empowering Students through Science

The team of BARC scientists with the Students & Faculties of Guru Ghasidas University.

BARC's Nuclear Outreach in Raipur

The BARC team that visited colleges in Raipur from August 5 to 10, 2024, as part of an outreach program, meticulously crafted the initiative to enhance understanding of advancements in nuclear technology and to dispel common myths regarding nuclear energy.

The participating institutions in this program included

1. Guru Ghasidas University, Bilaspur 2. Government Bilasa Girls' P.G. College, Bilaspur 3. Dr. C.V. Raman University, Bilaspur 4. Government G.N.A.P.G. College, Bhatapara 5. Pandit Ravishankar Shukla University, Raipur.

Approximately 1,200 students and faculty members from these five colleges engaged in the program, which featured a variety of activities including a written test, scientific and technical lectures, edutainment skits, and an audio-visual quiz.

Program Activities

1. *Written Test*: A preliminary quiz covering physics, chemistry, biology, mathematics, and radiation science, for the selections of top students for a final quiz round.

2. *Lectures*: Topics included myths about radiation, reactor technology, food irradiation, and career opportunities within the Department of Atomic Energy (DAE).

3. *Interactive Sessions*: Engaging Q&A sessions followed the lectures and skits to foster active participation from students and faculty.

4. *Edutainment Skits*: Performances designed to illustrate the benefits of nuclear technology while addressing misconceptions.

5. *Final Quiz Round*: Conducted with audio-visual elements showcasing BARC technologies and encouraging student interaction.

Prizes were awarded to quiz winners, with appreciation expressed by participating colleges.

Lecture Topics during the program included

1. "Radiation: Myths and Misconceptions" by Shri R.K.B. Yadav (Scientific Officer, Health, Safety and Environment Group).

2. "Reactor Technology" by Shri S.K. Mondal (Scientific Officer, Reactor Group).

3. "Food Irradiation: Need of the Hour" and "Career Opportunities in DAE and BARC" by Shri S.P. Prabhakar (Scientific Officer, Reactor Design and Development Group).

Dr. S. Adhikari, Group Director of the Knowledge Management Group at BARC, served as the convener for the outreach program.

The strong interest shown by attendees in lecture sessions and inquiries regarding recruitment and higher education opportunities within DAE and BARC underscored the program's success in promoting scientific knowledge and dispelling myths about nuclear energy.



The lecture on "Radiation: Myths and Misconceptions" by Shri R.K.B. Yadav for the students of Govt. G.N.A.P.G. College.



Interactive session moderated by Shri S.K. Mondal for the students of C.V. Raman University.



Written quiz test at Govt Bilasa Girls P. G. College being supervised by Shri S.P. Prabhakar and others.

BARC Scientist Elected Fellow of National Academy of Sciences, India (NASI)



Dr. Sukhendu Nath, Scientific Officer/H and Head, Ultrafast Spectroscopy Section, Radiation and Photochemistry Division, has been elected as a Fellow of the prestigious National Academy of Sciences, India (NASI) for his pioneering contribution to the indigenous development of femtosecond two-dimensional infrared (2DIR) spectrometer, which is a first-of-its-kind in India. Dr. Nath is recognized internationally for his outstanding contribution to the area of ultrafast dynamics in molecular systems and the development of amyloid sensors. His recent contribution is unraveling the mechanism of photocatalysts for green hydrogen generation and reduction of CO_2 to useful chemicals. Recently, he has developed a tabletop setup for the generation and reaction of ultrashort electron pulse by multiphoton ionization process. Dr. Nath is also the recipient of the prestigious INSA Young Scientist Award, the Distinguished Lectureship Award by the Chemical Society of Japan and the DAE Science and Technology Excellence Award.



BARC Training School

Cultivating Excellence in Nuclear Science & Technology

The Atomic Energy Training School, now recognized as the BARC Training School, was established in 1957 at the Bhabha Atomic Research Centre (BARC) in Mumbai. Its primary objective is to provide specialized technical education to talented youth across India in the fields of nuclear science and technology, subsequently recruiting them into the Department of Atomic Energy (DAE). Since its inception, the BARC Training School has been effectively managed by the Human Resource Development Division (HRDD), fulfilling Dr. Homi Bhabha's vision of a secure energy future for the nation. Currently, the training programmes offered have attained iconic status and have expanded to meet the diverse needs of the DAE. From its first batch in 1957-58 to the 67th batch in 2023-24, nearly ten thousand trainees in science and engineering have graduated from this esteemed institution.

The recruitment process begins with advertisements published in national newspapers, ensuring coverage across all states and union territories. Each year, HRDD conducts outreach activities alongside an online examination for recruitment under the Orientation Course for Engineering Graduates and Science Postgraduates (OCES) and the DAE Graduate Fellowship Scheme (DGFS). Candidates are screened based on their GATE scores or their performance in an online computer-based test (CBT) administered by HRDD. This CBT is conducted over a weekend at approximately 123 centers located in 49 cities throughout India, with one examination session dedicated to each discipline. Those who qualify for interview based on their GATE scores or CBT results must are called to attend the selection interview held in Hyderabad for geology applicants and in Mumbai for other disciplines. The rigorous technical interview is conducted by a panel of experts. Selected OCES Trainee Scientific Officers (TSOs) undergo a comprehensive one-year training programme at the BARC Training School in Nuclear Science & Technology, while DGFS Fellows pursue an M.Tech degree at selected Indian Institutes of Technology (IITs). Upon successful completion of their respective programmes, both OCES TSOs and DGFS Fellows are absorbed into the DAE.

Currently, all faculty members involved in training programmes are sourced from within the department, ensuring a wealth of qualified educators who meet academic standards. The courses and syllabi are regularly updated to align with current trends, particularly in nuclear science and engineering. The final merit list for TSOs is determined by performance in weekly exams, end-of-semester exams, project work, and viva-voce assessments, which ultimately influence



Graduation Function for 67th (OCES-2023) Batch Trainees.



Inauguration Function for 68th (OCES-2024) Batch Trainees.

their postings within various DAE units. Beyond academic pursuits, HRDD organizes evening lectures featuring eminent personalities discussing cutting-edge research topics in science and engineering. Additional activities include sports meet, yoga sessions, cultural programme, publication of the TSO magazine "Karvaan," study tours to other DAE units, administrative workshops, and soft-skill development workshop all aimed at fostering holistic development for the TSOs.

HRDD also supports the BARC Ph.D programme by accepting Junior Research Fellows (JRFs) for basic sciences and various engineering disciplines under the DAE Doctoral Fellowship Scheme (DDFS) for engineering postgraduates. The Ph.D programme at BARC combines classroom instruction with significant research components. The BARC Training School provides essential infrastructure and logistical support for Ph.D coursework across all disciplines.

In its ongoing efforts to engage with young minds regarding DAE's advanced activities and maintain connections with academia, HRDD offers internship and project opportunities to deserving students pursuing degrees in Science and Engineering from universities across India. Applications are processed by HRDD based on eligibility criteria, leading to allocations of guides and research labs according to candidates' disciplines and topic preferences. This initiative is mutually beneficial: it supplies short-term manpower to BARC while igniting a passion for STEM research among students, guiding them toward careers in research.

Additionally, HRDD organizes QUEST under its Continuing



Inauguration Function for 3rd Batch of BARC-Ph.D programme (JRFs) under HBNI.

Education Programme. QUEST is an innovative initiative that allows Homi Bhabha National Institute (HBNI) Ph.D students and employees from DAE units to enhance their knowledge through advanced courses approved by HBNI's Board of Studies (BoS). This programme serves as a platform for knowledge transfer where experienced DAE professionals share their expertise with aspiring scientists and technologists, including Ph.D candidates. Over recent years, HRDD has successfully executed numerous advanced courses through QUEST, further solidifying its commitment to education and professional development within India's nuclear research landscape.

-The article has been compiled by HRDD and SIRD Newsletter Editorial Team.



Valedictory function of Quest course on Nuclear Power Project Management.

Industry

BARC's Nuclear

The spinoff technologies developed through research and development in nuclear energy at BARC are regularly transferred to industry for commercialization. BARC provides comprehensive support to licensees by offering technology training, field demonstrations, consultancy, and detailed documentation that includes procedures, flowcharts, diagrams, troubleshooting guides, and lists of raw materials, equipment, and suppliers. During the period from September to October 2024, BARC transferred five technologies to various industries.

By TT&CD and SIRD Newsletter Editorial Team

Technology Transfers

BARC has transferred the technology of Atmospheric pressure portable catalytic air plasma system for fast synthesis of aqueous Nitrate & Nitrite fertilizers to M/s. Nano Fertilizers Pvt. Ltd., Delhi. It also transferred the technology of Radiation Assisted Adsorbent0 for Textile Effluent Decolouration (Rad-TED) to M/s. Synco Industries Ltd., Jodhpur.

Other key technologies transferred to industry include;

A Rapid Composting Technology for decomposition of dry leaves, kitchen waste and temple waste: Transferred to M/s. Swayambhar Producer Company Limited, West Bengal.

NISARGRUNA Biogas Plant for Processing Biodegradable Waste: Transferred to M/s. Watech Greepo Systems Pvt. Ltd., Lucknow, Uttar Pradesh.

Pulsed UV Disinfection System: Transferred to M/s. Faith Innovations, Delhi.

Besides, **the license period of BARC's AnuSpect Gamma Spectrum Analysis Software (Source Code and Binary Version) technology for** M/s. Nucleonix Systems Pvt. Ltd., Hyderabad has been renewed. This is the first renewal to the firm; **Fluoride Detection Kit for Ground Water has been** renewed to M/s. Orlab Instruments Pvt. Ltd. Hyderabad. This is the third renewal for the firm.

Technology Overview: Nitrate and nitrites are essential nutrients for the crops. The present invention offers a portable thermal plasma device for fast synthesis of nitrate and nitrite in high concentration, via a catalyst based green process leaving zero carbon footprints. A highly reactive thermal plasma environment facilitates the synthesis process at a power level of 20 kW at atmospheric pressure, does not use any additional chemical, and directly converts atmospheric air into nitrate and nitrite through interaction with water in a very efficient and controlled manner. This system offers a clean, sustainable, decentralized, flexible alternative method for generation of nitrates and nitrites that may be used as nitrogen-based crop fertilizer. Achieved concentration is several orders of magnitude higher than that achievable in competing non-thermal plasma processes.

Technology Overview: The indiscriminate release of coloured dye wastewater from cotton/viscose textile industries into water streams not only spoils aesthetics but also affects the ground water quality adversely, posing serious health risks to diverse forms of life. Strict environmental norms have pushed these industries to the brink of shutdown owing to non-compliance. Therefore, non-expensive, environment-friendly viable technologies are the need of hour to mitigate this ever-escalating problem, particularly for small and unorganized industries with limited financial resources. 'Radiation assisted Adsorbent technology for Textile Effluent Decolouration (RAd-TED)', developed by BARC, aids in removal of anionic dyes from cotton/viscose textile dyeing/printing wastewater streams. The technology offers a simple, efficient and cost-effective solution to decolorize and recycle cotton/viscose textile wastewater.

beckons

Spin-off technologies



Signing of MoU for Utilization of Neutron Imaging Facility at BARC for Archaeometric Analysis..

Memorandum of Understanding

A MoU titled Utilization of Neutron Imaging Facility at BARC for Archaeometric Analysis: Signed on 02/09/24 for 3-year period between BARC, Directorate of Archaeology and Museums, Mumbai, Maharashtra. The MoU explores the potential of neutron-based non-destructive techniques set up at the Dhruva and APSARA-U nuclear research reactors by Technical Physics Division of Physics Group, BARC in characterizing archaeological artefacts. The technique, because of its large penetration depth aims at deciphering the internal morphology, providing the conservation scientists with deep insight into the craft ship and manufacturing practices of our ancestors.

AKRUTI

For Phase-II activities at AKRUTI Kendra in Tarapur, a tripartite MoU was inked by NPCIL, BARC and SVERI on 27/09/24 in Tarapur.Signing of Tripartite MoU between SVERI, Pandharpur, NPCIL and BARC at AKRUTI Kendra - Tarapur for Phase-II activities.

Activities of AKRUTI:

A tripartite Memorandum of Understanding (MoU) was signed among NPCIL, BARC, and SVERI to advance Phase-II activities at the AKRUTI Kendra located in Tarapur. This facility is dedicated to fostering entrepreneurship development specifically targeted at rural households. The initiative aims to positively impact approximately 5,000 students and 25,000 farmers, among other beneficiaries.

The existing MoU for Phase-I focused on enhancing community awareness through the display and demonstration of DAE-BARC technologies for residents near NPCIL's Tarapur Atomic Power Station (TAPS).

In addition to these developments, the BARC AKRUTI Team has actively engaged with various educational institutions across India over the past quarter to promote and popularize DAE technologies among students.

Notable institutions involved in this outreach include Jaihind College in Mumbai, Savitribai Phule Pune University, Dr. D. Y. Patil Arts, Commerce and Science College in Pune, Mahatma Gandhi University in Kottayam, Kerala, and Uttar Banga Krishi Vishwavidyalaya in Cooch Behar, West Bengal.

This comprehensive approach not only aims to equip students with knowledge about advanced societal technologies of DAE but also seeks to bridge the gap between academia and practical applications in rural entrepreneurship, thereby fostering a sustainable ecosystem for innovation and growth within these communities.

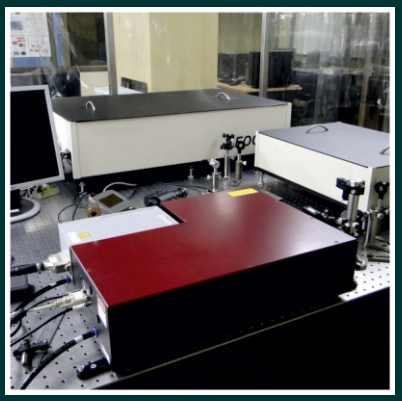
Atal Incubation Centre-BARC

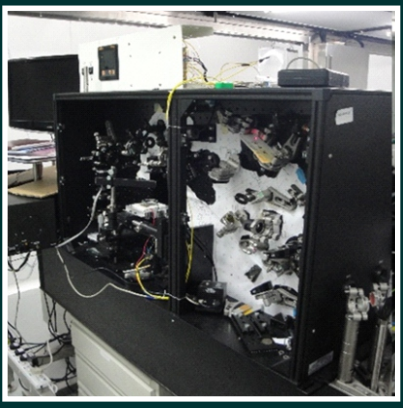
AIC-BARC and HBNI jointly announced the second cohort of the Start-up Pre-Incubation Program for aspiring young innovators, early-stage entrepreneurs, and students. Eligible STEM and non-technical students can form teams to jointly develop a start-up idea. The program will run between November 2024 and early February 2025 with six weeks of online sessions in between, aimed at boosting ideas to make the first prototype.



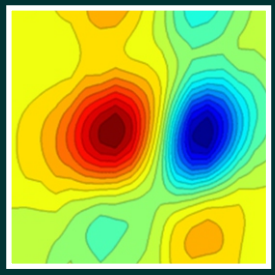
Signing of Tripartite MoU between SVERI, Pandharpur, NPCIL and BARC at AKRUTI Kendra - Tarapur for Phase-II activities.

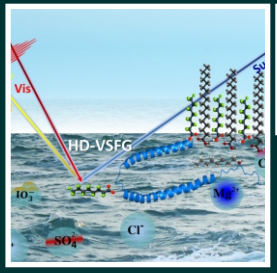












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