



Department of Inorganic & Physical Chemistry

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Prologue

Born more than a century ago in 1909 along with the Institute, named as “The Department of General and Applied Chemistry” at birth, this department has grown in many ways with the Institute with its eyes focused on both fundamental and applied research in the broad areas of physical and inorganic chemistry. Currently we have 20 faculty members working in rich and diverse areas of chemistry including molecular spectroscopy, chemical dynamics, analytical



and computational theory, electrochemistry, polymer chemistry, transition metal and non-metal chemistry, bioinorganic and biophysical chemistry and functional materials. Other than pushing frontline research, the faculty of the department is equally committed to teaching. New courses are introduced by the departmental faculty frequently at the undergraduate as well as postgraduate levels. Regular student seminars, departmental seminars, colloquia and popular lectures make the department very lively, academic and the place to be in.

The department hosts some of the finest research instruments for carrying out work in advanced competitive areas of chemistry. Some of these instruments such as the FT microwave spectrometer, surface enhanced laser Raman spectrometer, Raman microscope, femtosecond pump-probe experimental set-ups are home-built whereas the high resolution TEM, the AFM, single crystal and powder X-ray and NMR spectrometers have been commercially acquired. Some of these sophisticated facilities were developed under various special programs as well as from individual projects funded by Govt. and private funding agencies. The University Grants Commission had generously supported the department initially under the Special Assistance Program in 1978 and then under the Center for Advanced Studies program since 1980 till today. The Department of Science and Technology of the Ministry of Science and Technology has also supported the department under its FIST program since 2000. Currently the second phase of the FIST program is running.

The Faculty members write projects directly to funding agencies and acquire facilities that are of direct importance to their own research. A large number of projects to individual members have been funded by Govt. agencies such as

CSIR, DST, DRDO, DBT, BRNS, MIT, etc. and private agencies such as Boeing Corp., General Electric, Big Tec, 3M, etc. Some of the projects are interdisciplinary in nature involving faculty members from several departments and addressing problems that have wider implications and importance. Through such collaborative efforts faculty members are able to address harder and deeper problems which are generally difficult to handle by a single research group.

Mentoring students is one of our greatest strengths. We have a very vibrant and dedicated group of students pursuing research career in various fields. Currently about 120 Ph.D. students, 20 research associates, 20 project assistants and a large number of summer trainees constitute the main work force of the department. Selection of Ph. D. entrants to the department is made in two stages. All candidates have to qualify through NET or GATE to apply and be called for interview. After interview the selected students (typically about 20) are invited to join the department. In addition, the integrated Ph. D. program of the chemical sciences division, to which our department is a part, admits about 15 students after B.Sc. The selection of students for the Int. Ph.D. program is done through Joint Admission Test (JAM). The department has an excellent atmosphere for learning where many of the young minds grow up amidst intense discussions with the faculty members of the group or subgroup, regular seminars, group meetings, etc. and enable themselves to face any scientific challenge in the future. There are many international students in the department which enriches the social and cultural lives and experiences of the students.

This brochure contains a two-page write-up of each group headed by one faculty member and description of the work and publications from the group. However, two pages on each group activities are not sufficient. Much more detailed information about the activities in a group may be found in individual faculty web sites.

I hope you enjoy reading this brochure as much as we have enjoyed preparing it!

P. K. Das

Chairman

INORGANIC & PHYSICAL CHEMISTRY





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MICROWAVE SPECTROSCOPY, CHEMICAL DYNAMICS

Chemistry is today identified as 'molecular science'. The main emphasis of our research work is towards fundamental understanding of how molecules interact with each other and how they react to form new products. Our group carries out primarily experimental research work with homebuilt facilities, though theoretical work to support and enhance our understanding is carried out as well.

Molecular and van der Waals Spectroscopy:

We use a home-made pulsed nozzle Fourier transform microwave spectrometer to record rotational spectra of molecules and weakly bound complexes, that are formed in a supersonic expansion. From the rotational spectrum, the moments of inertia of a molecule/complex can be accurately calculated. This leads to the direct determination of the equilibrium structure.

Obtaining the equilibrium structure is the first step towards developing accurate intermolecular potentials, which govern the interaction between molecules. Thus the

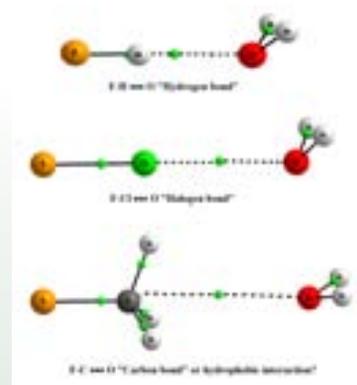
fundamental goal of these studies is to understand intermolecular interactions.

Hydrogen bonding and van der Waals interactions

We have been investigating weakly bound complexes of H_2O and H_2S , as the former is a classic example for hydrogen bonding and the latter is presumed to have van der Waals interactions. Our investigations have convincingly proved that H_2S can form hydrogen bonds as well though, typically weaker than that formed by H_2O . Our group has provided a dynamical criterion for differentiating hydrogen bonding and van der Waals interaction with a universal appeal.¹ Further, our experimental and theoretical work have provided fundamental understanding of hydrogen bonding. This led us to form and chair an international task group approved by the International Union of Pure and Applied Chemistry (IUPAC) to redefine hydrogen bonding. The modern definition we proposed was accepted by IUPAC in 2011.²

Carbon bonding and Halogen bonding

Is hydrogen bonding unique? This is a question that has bothered chemists for a long time. Over the last decade, it has become clear that every element in the periodic table can involve in intermolecular interactions similar to hydrogen bonding. Our group has investigated lithium bonding and halogen bonding extensively, as hydrogen is linked to both the alkali and halogen groups. In 2013, we showed that 'X-C...Y carbon bonding' similar to X-H...Y hydrogen bonding is possible. In particular, the C atom in CH_3X (X is more electronegative than C) can



Pulsed Nozzle Fourier Transform Microwave Spectrometer

Molecular and van der Waals Spectroscopy
Hydrogen bonding and other molecular interactions
Chemical kinetics and dynamics
Shock tube techniques



directly bond with, for example, O of H₂O X-C...O carbon bonds as shown in the figure:

It has now been realized that the 'carbon bonded complexes' would be intermediates in the well-known S_N2 reactions very much like 'hydrogen bonded complexes' being intermediates to proton transfer reactions.³ Carbon bonds can contribute to the ill-defined hydrophobic interactions as well.

Chemical Kinetics and Dynamics:

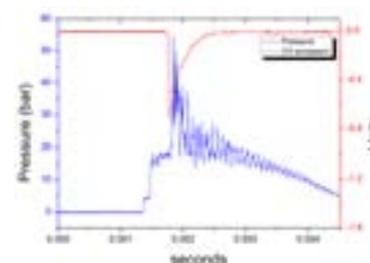
Our group has established a strong collaboration with the Aerospace Engineering Department to develop shock tube facilities for high temperature chemical kinetic studies relevant to combustion. We also carry out fundamental studies on thermal

decomposition of haloethanes and haloethanols. Arrhenius equation has been used to interpret thermal rate constants. Our group has provided the first experimental evidence for a molecular mechanism in thermal decomposition of 1,2-dichloroethane leading to HCl elimination.

Until this work, it was widely believed that the thermal decomposition followed a radical chain mechanism.⁴

Ignition delay measurements on fuels using shock tubes

The single pulse shock tube facility has been used for measuring ignition delay of several fuels of interest to ISRO and DRDL. The ignition delay could be determined by measuring the pressure rise (blue trace) or CH emission (red trace)



at the onset of ignition, as shown in the Figure above.⁵

Results from these studies are useful in developing new and efficient fuels. We have shown recently that there is a strong correlation between the pre-exponential factor A, and the activation energy E_a and one needs to be careful about interpreting them independently. For the HX elimination reactions from haloethanes, experimentally measured A and E_a could be interpreted using both a 'loose' transition state having larger A and E_a or a 'tight' transition state having smaller A and E_a.

Selected publications

- Mani D.; Arunan, E. The X-C...Y Carbon bond and hydrophobic interactions. *Phys. Chem. Chem. Phys.* 2013, 13,14377-14383.
- Arunan, E.; Desiraju, G. R.; Klein, R. A.; Sadlej, J.; Scheiner, S.; Alkorta, I.; Clary, D. C.; Crabtree, R. H.; Dannenberg, J. J.; Hobza, P.; Kjaergaard, H. G.; Legon, A. C.; Mennucci, B.; Nesbitt, D. J. *Pure Appl. Chem.*, 2011,83, 1619-1636 and 1637-1641.
- M. Goswami and E. Arunan, *Phys. Chem. Chem. Phys.* 2009, 11, 8974-8983.
- N. Sharath, K. P. J. Reddy and E. Arunan, Thermal Decomposition of Propargyl Alcohol: Single Pulse Shock Tube Experimental and ab Initio Theoretical Study, *J. Phys. Chem. A.* 2014
- Rajakumar, B.; Reddy, K. P. J.; Arunan, E. Unimolecular HCl elimination from 1,2-dichloroethane: A single pulse shock tube and ab initio study. *J. Phys. Chem.* 2002, 106, 8336-8373.



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LASER SPECTROSCOPY

The goal of our research is to follow (photo-induced) elementary chemical transformations in gas phase and at gas-surface interface in femtosecond (1×10^{-15} second) or picosecond (1×10^{-12} second) time-scales. In particular, we are interested in chemical reactions where the absorbed energy from light is stored in the chemical products or stored chemical energy is released following absorption of light. In the context of growing energy demands, understanding and employing such reactions are crucial for future solar light

harvesting and sustainable energy technologies.

Current Areas of Investigations:

1. Time Resolved Study of Photocatalysis in Ultra-High Vacuum:

The broad objective of this work is to time-resolve (in femtosecond to picosecond time scale) the initial steps in the technologically important and energy/fuel-related photocatalytic processes (i.e., mechanisms and dynamics of energy transfer processes) at NP/semiconductor composite surfaces. In this work femtosecond two-pulse correlation spectroscopy will be employed, as depicted in Figure 1.

2. Decomposition Dynamics of Energetic Materials at Metal Surfaces:

In this project our focus is to explore decomposition mechanisms, kinetics, and dynamics of energetic materials using femtosecond laser spectroscopy.

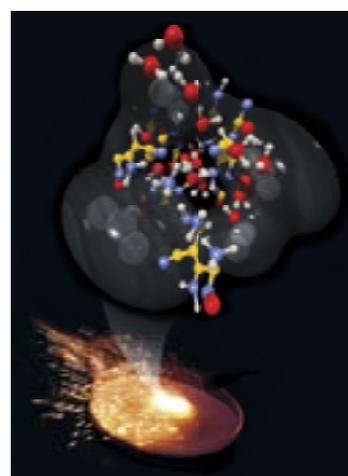


Figure 2: Exploring physical chemistry of explosives/propellants. "What happens at the molecular level when energetic materials burn?" It is still an open question.

3. Micelle Nanolithography: Preparation of Model Catalytic Surfaces

In order to Construct a physically transparent predictive model relating the geometric and electronic structure of metallic NPs to their catalytic activities in energy related catalysis, it is exceedingly important to discover a robust synthetic route for NPs with well-defined size and interparticle distance, maintaining chemical purity and stability with respect to thermal treatment for surface science study. Can

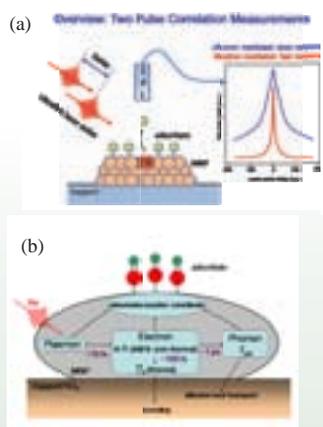
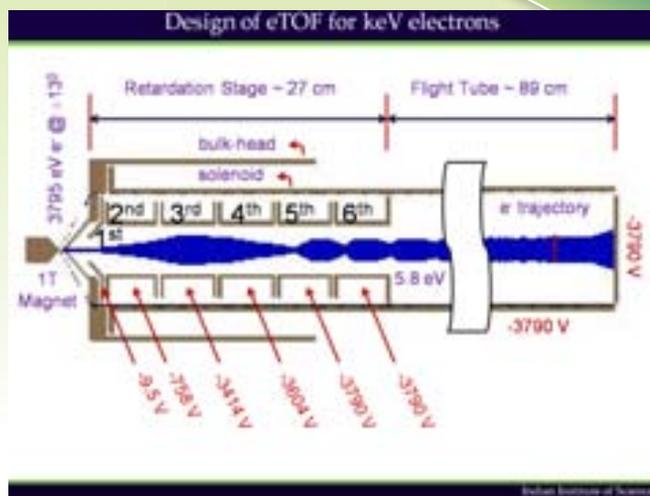


Figure 1: (a) Schematic of ultrafast 2PC measurement. The yield is measured as a function of delay (Δt) by a mass spectrometer(QMS); (b) Schematic of different energy transfer processes at NP surfaces.

Home-built time-of-flight photoelectron spectrometer for liquid surface analysis



micelle nanolithography be the answer? We are working to find that out.

Figure 3: General Synthesis, Deposition and Cleaning Steps in micelle nanolithography technique

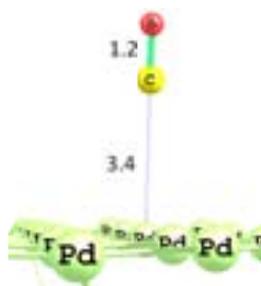
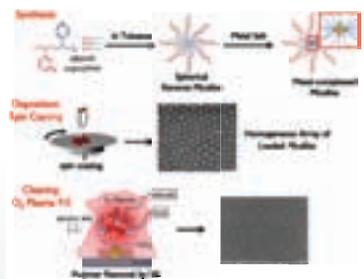


Figure 4: CO binds atop site of Pd(111) facet. Can we employ CASSCF methodology to explore the electronically excited state of Pd-CO complex?

5. Ultrafast X-ray, EUV, VUV Photoelectron Spectroscopy

4. Computation: Local Excited States of Adsorbates at Surfaces

We are employing CASSCF calculation coupled with ONIOM methodology to explore local electronically excited states adsorbates at surfaces.

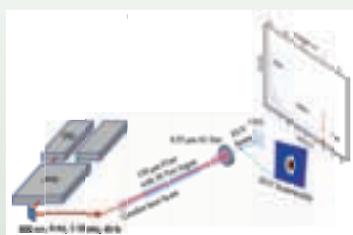


Figure 5: generation Coherent EUV radiation using HHG; EUV grating can separate each harmonics which can be utilized to photoionize species to record transient photoelectron spectroscopy.

Selected publications:

- 1. Sylvinson, D. M. R. and A. Bhattacharya, "Theoretical Prediction of Hole Directed Reactivity in Ammonia Borane Dimer Radical Cation Following Vertical Ionization" submitted to RSC Advances, 2014.
- A. Bera and A. Bhattacharya, "Electronically Nonadiabatic Reaction Mechanisms of a Model Metalized Nitramine Energetic System: Dimethylnitramine-Aluminum Clusters" submitted to Phys. Chem. Chem. Phys., 2014
- A. Bhattacharya and E. R. Bernstein, "Influence of turn (or fold) and Local Charge in the Fragmentation of Peptide Analogue Molecule, CH₃CO-Gly-NH₂ Following Single Photon Ionization at 10.5 eV" J. Phys. Chem. A. 115, 10679 (2011)
- A. Bhattacharya and E. R. Bernstein "Excited Electronic State Decomposition of Gas Phase RDX: An ONIOM-CASSCF Study" J. Phys. Chem. A.115, 4135 (2011)
- A. Bhattacharya, Y. Q. Guo, and E. R. Bernstein "Nonadiabatic Chemistry of Energetic Molecules" Acc. Chem. Res. invited article, 43, 1476 (2010).



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COORDINATION AND BIOINORGANIC CHEMISTRY

The major focus of our research is to develop the hitherto unknown chemistry of bio-essential 3d-metal complexes as potential photodynamic therapeutic (PDT) and anti-metastasis agents. We are designing and synthesizing metal complexes that have DNA and protein binding propensities and such complexes could show photo-induced DNA and protein cleavage activity in visible light. Transition metal complexes with tunable coordination geometry and versatile spectral and redox chemistry offer wide scope of designing new PDT agents as substitutes of organic PDT dyes like porphyrins and phthalocyanines. The metal complexes could also show photo-induced oxidative DNA cleavage activity following different mechanistic pathways, while the organic dyes generally follow only type-II pathway involving formation of singlet oxygen as the cytotoxic species. Our group is currently working in designing and synthesizing different types of coordination and organometallic complexes as photocleavers of protein and DNA in visible light. We are also exploring the photocytotoxicity of such complexes using different

types of cancer cells.

Copper complexes as photocleavers of DNA: Copper(II) complexes with a 3d⁹ electronic configuration show a metal-based electronic transition in the PDT spectral window of 600-800 nm. We have designed and synthesized different types of binary and ternary copper(II) complexes having both DNA binding ligand and photosensitizer. We have shown that the cleavage of DNA in red light occurs via metal-assisted photo-excitation pathway involving the metal-based d-d and/or charge transfer bands. With suitable design of the 3d-metal complexes, the mechanistic pathways could be altered from singlet oxygen to hydroxyl radicals. While redox active copper(II) complexes follow the hydroxyl radical pathway, other copper(II) complexes form singlet oxygen as the reactive species. Copper(II) complexes are also designed as models for restriction enzymes showing hydrolytic cleavage of DNA. We have reported copper(II) complexes showing photo-induced DNA cleavage activity under anaerobic reaction condition. This observation is

of significance since tumors are known to be generally hypoxic in nature.

Vanadium and Iron-based PDT agents: We have designed and synthesized binary and ternary oxovanadium(IV) and iron(III) complexes as photocleavers of DNA and proteins in visible light. The dipyrrophenazine complexes show significant photocytotoxicity in cancer cells.

VO²⁺ complexes with a 3d¹ electronic configuration show a metal-centered electronic band in the near-IR region of ~750 nm. We have designed V(IV) complexes that are redox stable and do not show any significant chemical nuclease activity in the presence of cellular reducing thiols. Significant photocytotoxicity of [VO(dppz)₂Cl]Cl (dppz = dipyrrophenazine) has been observed in HeLa cells on exposure to visible light, while the complex is non-toxic in dark. The oxovanadium(IV) complexes are unique in showing photo-induced DNA cleavage activity in near-IR light. Only lutetium texaphyrin is known to

Metal-based Anticancer Drugs: 3d-Metal Complexes as Photodynamic Therapeutic (PDT) and Anti-metastasis Agents

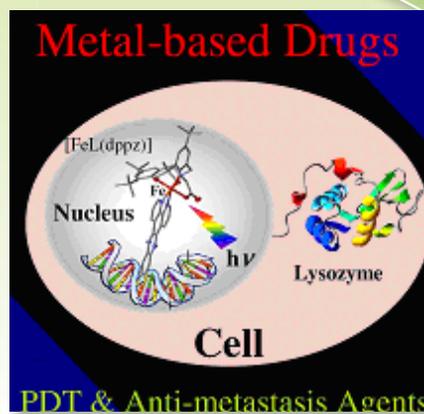


exhibit photocytotoxicity at near-IR wavelength. Vanadium being a bio-essential metal ion, its complexes could be better suited as PDT agents than heavier metal ions like ruthenium and rhodium.

We have explored the photo-induced DNA cleavage activity of several suitably designed mononuclear and binuclear iron(III) complexes. The complexes having photoactive phenanthroline bases show photonuclease activity in visible light. A ternary complex of iron(III) having dipyrrophenazine and phenolate-based tetradentate ligand shows in vitro photocytotoxic activity in HeLa and HaCaT cells forming hydroxyl radicals in a photo-redox pathway. Oxo-bridged diiron(III) complex of L-histidine is found to photocleave bovine

serum albumin (BSA) giving two protein fragments. We are currently working on designing and synthesizing new iron-based PDT and anti-metastasis agents.

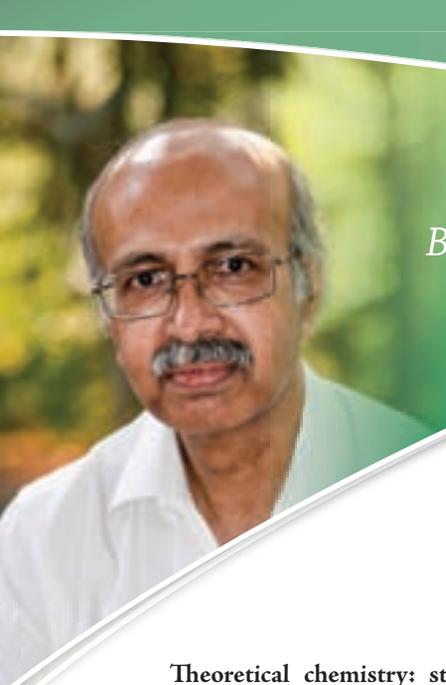
Bioorganometallic chemistry in PDT: Bioorganometallic chemistry is an emerging area in chemical biology due to varied biological applications of organometallic compounds. Among different organometallic systems, those based on ferrocene and its conjugates are of particular importance due to excellent stability of the ferrocene moiety in biological media, its lipophilicity, and its reversible redox chemistry. We are exploring the hitherto unknown chemistry of bioorganometallic complexes of 3d-metal ions for PDT applications. Ferrocene-conjugated ternary copper(II) complexes having photoactive

phenanthroline bases show photo-induced DNA cleavage activity in red light. The dipyrrophenazine complex that shows BSA cleavage activity is a multifunctional model nuclease and protease in the PDT chemistry. The presence of two visible bands due to Fe(II) and Cu(II) makes such systems photoactive over a large spectral window.

Ferrocene-appended 3d-metal complexes that show photo-induced DNA and BSA cleavage activity could be suitably designed for PDT applications targeting both primary and secondary tumors.

Selected publications

- P. Prasad, I. Khan, P. Kondaiah and A.R. Chakravarty, "Mitochondria Targeting Oxidovanadium(IV) Complex as a Near-IR Light Photocytotoxic Agent", *Chem. Eur. J.* 1917445–17455 (2013).
- U. Basu, I. Khan, A. Hussain, P. Kondaiah and A.R. Chakravarty, "Photodynamic effect in near-IR light by a remarkably photocytotoxic iron(III) cellular imaging agent", *Angew. Chem. Int. Ed.* 51 2658-2661 (2012).
- S. Banerjee, P. Prasad, A. Hussain, I. Khan, P. Kondaiah and A.R. Chakravarty, "Remarkable photocytotoxicity of curcumin in HeLa cells in visible light and arresting its degradation on oxovanadium(IV) complex formation", *Chem. Commun.* 487702-7704 (2012).
- A.R. Chakravarty and M. Roy, "Photoactivated DNA cleavage and anticancer activity of 3d-metal complexes", *Prog. Inorg. Chem.* 57, 119-202 (2012).
- S. Dhar, D. Senapati, P.K. Das, P. Chattopadhyay, M. Nethaji and A.R. Chakravarty, "Ternary copper complexes for photo-cleavage of DNA by red light: direct evidence for sulfur to copper charge transfer and d-d band involvement", *J. Am. Chem. Soc.*, 125, 12118-12124 (2003).



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POLYMERS, THEORETICAL CHEMISTRY

Theoretical chemistry: statistical mechanics of complex condensed matter systems

Research in our group encompasses different areas of condensed matter theory, including the statistical mechanics of complex fluids, polymer physics and stochastic processes. Over the last few years, we have been especially interested in developing theoretical models of the dynamics and reactivity of biological macromolecules, with a view to understanding cellular events at the molecular level. Among the problems that we are currently pursuing are the following:

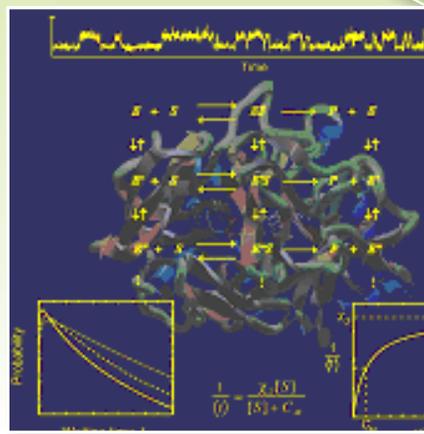
Stochastic gene expression: Like other single-molecule biological processes, gene expression is stochastic, proceeding in fits and starts under the action of random forces in the medium. Yet the fidelity with which information encoded in DNA is copied, translated and passed on is proof of the effectiveness of Nature's strategies to overcome the effects of cellular noise. These strategies involve complex reaction networks whose operations have yet to be fully understood. We have been exploring the implications of a realization of gene expression that is based on just two steps: transcription (the copying of DNA onto RNA) and translation (the synthesis of protein from the DNA

base sequence), both steps competing with RNA and protein degradation, and being subject to thermal noise. We have shown how the steady-state protein distribution – a key determinant of cell viability – can be found for this two-stage process using path integrals. We expect to be able to apply this approach to more complex gene regulatory pathways.

Polymer melt dynamics: Reptation has long been regarded as the mechanism by which polymers in melts move through their surroundings, but only recently have experiments provided evidence that polymer motion under conditions of strong entanglement does follow a curvilinear trajectory. It is now widely accepted that during this motion, individual chains are confined to tube-like channels created by the surrounding chains, but the common assumption that the putative tubes through which polymers reptate have a fixed radius w is no longer tenable. In fact, evidence suggests that the tubes have a fairly broad distribution of w values. But the exact form of this distribution, $P(w)$, has to be still determined, and remains a matter of debate. We have recently discovered that there are close parallels between the locus of the displacements of a confined polymer in the transverse direction and the equilibrium profile of a randomly

growing one-dimensional interface. By exploiting these parallels, we have shown how $P(w)$ may actually be calculated exactly within a path integral formalism. Our suggestion that the statistics of a single, harmonically confined semiflexible polymer adequately explain experimental tube-width heterogeneities in F-actin filaments will need to be tested further.

Confined polymer dynamics: The ability to confine single molecules of DNA or protein to nano-sized domains, and to make measurements of their properties under these conditions, is one of the many recent technological developments that has made it possible to conduct well-defined tests of theoretical polymer models. In this context, we have been trying to understand confinement effects on chain dynamics in rigorous statistical mechanical terms, without appeal to phenomenological methods. These efforts are moving along the following directions: (i) Calculations of the transport and conformational properties of continuum chains in narrow slits. We have been able to show that on length scales of the inter-wall separation, hydrodynamic interactions between different chain segments – usually quite strong – are screened out, and that the diffusivity and relaxation times of Gaussian chains exhibit power laws



in the chain length, with logarithmic corrections. (ii) Calculations of flow effects on polymers in capillaries. Although widely studied in the bulk, polymer-flow interactions have been much less studied in the presence of surfaces. Using a Rouse-Zimm approach, along with a variant of the nonlinear elastic model of chain inextensibility, we have determined the steady-state extension of a sheared polymer in a narrow cylindrical tube, and have found that the chain's fractional extension is much smaller than its bulk value. The result agrees with available experimental data, and appears to originate in the screening of hydrodynamic interactions by the surface. (iii) Calculations of reactivity in enclosed viscoelastic media. Biochemical reactions inside cells are typically subject to the effects both of the cell's boundaries and of the viscoelasticity of its contents. To probe these effects further, we have been studying how they influence one particular reaction – the diffusion-limited cyclization of long polymers. Specifically, we have

determined how the cyclization time of a flexible chain scales with its length when the chain is confined to a sphere, and when its dynamics are modulated by colored Gaussian noise. Our results raise issues that will need further experimental and theoretical elucidation.

Single-molecule thermodynamics: Thermodynamics at the scale of single molecules is characterized by a marked sensitivity of its measurable properties to the effects of fluctuations. As a result, measurements of thermodynamic quantities in different samples prepared under nominally identical conditions do not always yield the same value. However, on the basis of very general principles of non-equilibrium statistical mechanics, it is believed that the *distributions* of these values (for selected stochastic variables) must satisfy certain mathematical constraints that are now referred to as fluctuation theorems. These theorems have been widely applied to the interpretation of thermodynamic

measurements on single molecules, and research in the area of small system thermodynamics is proving to be fertile ground for generating new and interesting mathematical connections between theory and experiment. In this context, we have been using path integrals to explore the nature of the distributions that govern the fluctuations of different single-molecule systems, including the work fluctuations of an elastic dumbbell in planar elongational flow, the force fluctuations of an oscillator model of polymer stretching at constant velocity, and heat fluctuations in a trapped Brownian oscillator. We have found that the distributions in the first two systems satisfy fluctuation theorems of their own.

Selected publications

- *Reaction dynamics under confinement: An exact path integral treatment of a two-stage model of stochastic gene expression*, R. Sharma and B. J. Cherayil, *J. Stat. Mech.* P10029 (2013).
- *The diffusion and relaxation of Gaussian chains in narrow rectangular slits*, P. Bhattacharyya and B. J. Cherayil, *J. Chem. Phys.* 138, 244904 (2013).
- *Interfacial growth as a model of tube-width heterogeneities in melts of stiff polymers*, R. Sharma and B. J. Cherayil, *J. Chem. Phys.* 138, 244911 (2013).
- *Chain extension of a confined polymer in steady shear flow*, P. Bhattacharyya and B. J. Cherayil, *J. Chem. Phys.* 137, 194906 (2012).
- *Exact path integral evaluation of the heat distribution function of a trapped Brownian oscillator*, D. Chatterjee and B. J. Cherayil, *Phys. Rev. E* 82, 051104 (2010).



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NONLINEAR OPTICS, LASER SPECTROSCOPY, BIOPHYSICAL CHEMISTRY

The central objective of our group is to develop and find new applications of single and two-laser based spectroscopic techniques to carry out fundamental studies on molecules and materials. We work in the areas of molecular nonlinear optics, gas phase vibrational spectroscopy and biophysical chemistry of nanoparticle macromolecule interaction.

Nonlinear Optics

In the area of molecular nonlinear optics our aim is to exploit second harmonic generation (SHG) to probe bulk physical properties of molecules in solution. Intensity of incoherent SHG from solution is proportional to the molecular hyperpolarizability ($\chi^{(3)}$) of an analyte, which changes with a physical process as well as symmetry of the molecular specie in solution. Using this principle we measure scattered second harmonic light intensity and relate it to the property which is responsible for causing the change. Chemical

application of second harmonic light scattering is a very active area in our group. Recently polarization resolved second harmonic light scattering has been used in our laboratory to obtain the geometry of weak (1-10 kcal/mol) molecular complexes in solution for which no technique other than small angle neutron scattering is available currently. The origin of large second harmonic generation in noble metal nanoparticles of 5-100 nm diameter is another area of current interest. We have investigated the origin of large nonlinearity in copper nanoparticles. Green routes to the synthesis of nanoparticles of different size and shape are also explored in our laboratory.

Vibrational Spectroscopy

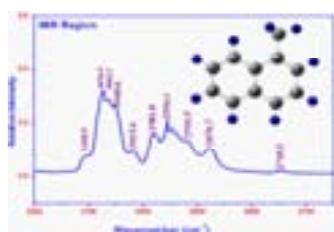
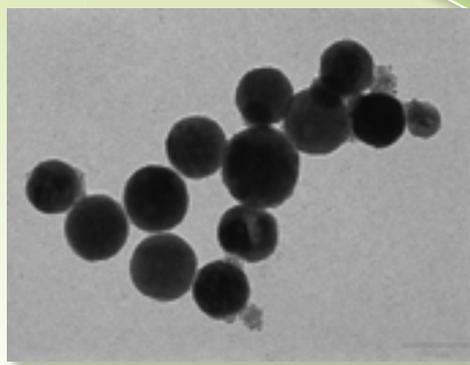
In the area of atmospheric and environmental chemistry our research efforts are currently directed to detection of polycyclic aromatic hydrocarbons (PAH) and their photolysis products at low

concentrations by time resolved FTIR spectroscopy. A series of dimethyl fluorenes and have been studied in the gas phase using FTIR spectroscopy and their vibrational spectra have been assigned. We are currently setting up an apparatus to identify photochemical products generated from PAHs upon ultraviolet irradiation using FTIR spectroscopy, which will help us understand the type and identity of the radicals that are generated in the atmosphere from PAHs by solar radiation. Then we will proceed to investigate scavenger molecules to remove PAHs from the environment. This project is directly related to chemistry of the atmosphere and environment.

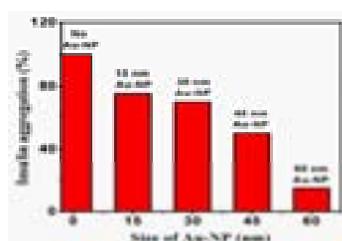
Biophysical Chemistry

We have studied in vitro lipid-protein interaction in the past using physical methods such as FRET, ESR spectroscopy, etc. We are currently investigating adsorption of biomolecules such as proteins and nucleic acids with noble metal

Cu nanoparticles of 55 nm average diameter,
prepared by laser ablation



Gas phase Infrared spectra of
1-methylnaphthalene recorded with 0.2
cm⁻¹ resolution



Effect of size of gold nanoparticles (Au-NP)
on prevention of aggregation of insulin

nanoparticles using a variety
of techniques such as HRS,
DLS, TEM, etc. The objective
of this study is to use these
nanoparticles in modulating
the conformation and activity

of the macromolecules in
the adsorbed state and
thus exploit the surface
of the nanoparticles for
preservation and transport
of the macromolecules.

Selected publications

- Soumi De¹, Manisha Ray, Anusooiya Y. Pati, and Puspendu K. Das Base Triggered Enhancement of First Hyperpolarizability of a Keto-Enol Tautomer J. Phys. Chem. B 117, 15086-15092 (2013)
- Shubhadip Chakraborty, Prasanta Das, Sadasivam Manogaran and Puspendu K. Das Vibrational spectra of fluorene, 1-methylfluorene and 1,8 dimethylfluorene, Vibrational Spectroscopy, 68, 162-169 (2013)
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ORGANOMETALLICS AND MATERIALS CHEMISTRY

Research in our laboratory is carried out in two broad areas: transition metal organometallic chemistry and materials chemistry. Major areas of research in transition metal organometallic chemistry include (a) activation of small molecules, (b) homogeneous catalysis, (c) utilization of small molecules as sources of C_1 synthons, and (d) molecular precursors for certain useful materials. These investigations involve extensive synthetic, structural, and mechanistic studies employing a wide variety of analytical methods, with an emphasis on multinuclear NMR spectroscopy and X-ray crystallography. The areas of research in materials chemistry include (a) materials for hydrogen storage and hydrogen generation and (b) catalysis. This work involves extensive use of microscopy, powder X-ray diffraction methods, and thermal analysis.

Activation of small molecules

The activation of unreactive chemical bonds in small molecules is an area of active current interest. Toward this

goal, our group has been studying the activation of the H-H bond in H_2 , the Si-H bond in silanes, the B-H bond in boranes, and the C-H bond in methane/alkanes using organometallic compounds in the hope of realizing methane conversion catalysts for the transformation of methane into methanol. The partial oxidation of methane in natural gas to a liquid fuel, for example, methanol, is one of the holy grails in the field of catalysis. In addition, our work also involves mapping the reaction coordinate for the oxidative addition of H_2 to a metal center in order to address the question as to what point can the H-H bond be considered to be broken. This is of great significance in homogeneous hydrogenation catalysis.

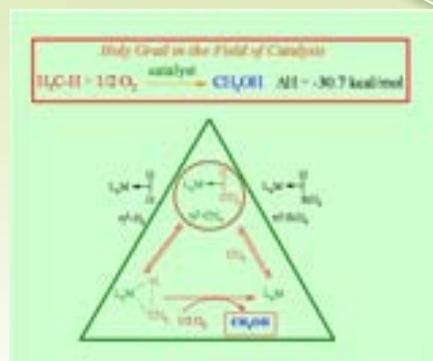
Homogeneous Catalysis

Hydrogen is a molecule used in, perhaps the most massive man-made reactions, namely hydrogenation catalysis. A large number of useful products are derived directly or indirectly from reactions involving hydrogen. While several

homogeneous hydrogenation catalysts are known, research is in progress to improve their performance. Even a slight improvement in the catalytic efficiency will have a significant impact that translates into saving of huge sums of money. Our group is involved in synthesis and activity studies of organotransition metal catalysts with better performance for homogeneous hydrogenation reactions. Current focus of research is toward development of catalysts for the hydrogenation of sterically hindered olefins and alkynes.

Utilization of small molecules as C_1 synthons

The insertion of heterocumulenes such as CO_2 , CS_2 , and COS into metal-hydride and metal-carbon bonds of transition metal fragments and their subsequent functionalization is an area of active interest due primarily to their potential as sources of C_1 chemistry for the generation of useful organic compounds. Currently, efforts in our laboratory are



directed toward inserting these molecules into M-H and M-C bonds, functionalization of the resulting species, and the subsequent elimination of the organics. At the same time, attempts are being made to recycle the metal containing fragments thus making the process cyclic.

Molecular precursors for certain useful materials

Synthesis of high-quality materials by relatively simple and reproducible routes is of both fundamental and technological interest. In this regard, development of soft chemical molecular precursors routes to access such materials has been attracting widespread interest in recent years. Efforts in this area are directed toward development of molecular precursors for Metal Organic

Chemical Vapor Deposition applications as well as metal and intermetallic alloy phases.

Materials for hydrogen generation and storage and catalysis

With the rapid depletion of petroleum resources around the world, there is a strong and urgent need for an alternative fuel to meet the ever increasing energy demands. With a calorific value that is three times as large as that of the liquid hydrocarbons and also its clean burning nature, hydrogen clearly holds immense potential to become a future source of energy. Several key challenges need to be overcome for hydrogen to be employed as a sustainable future energy source in our shift from an economy largely based on carbon to that of hydrogen.

Current efforts in our laboratory are directed toward the development of hydrogen storage materials, primarily monometallic, core-shell, intermetallic and alloy, and composite nanoparticles. In addition, efforts are also focused on the development of nanocatalysts for hydrogen generation from certain substrates and for hydrogenation reactions.

Selected Publications

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- Kumar, R.; Jagirdar, B. R. B-H bond activation using an electrophilic metal complex: insights into the reaction pathway *Inorg. Chem.* 2013, 52, 28-36.
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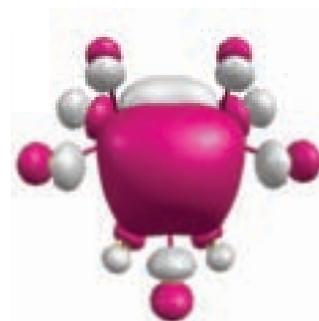
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APPLIED THEORETICAL AND COMPUTATIONAL CHEMISTRY

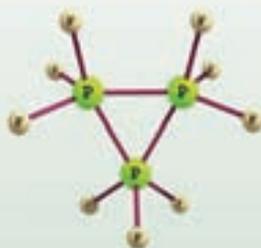
We study the structure and reactivity problems of molecules, clusters and solids using theoretical techniques ranging from the simplest of molecular orbital methods to sophisticated electronic structure theory depending on the system at hand and the questions that are to be answered. We place great importance in not only getting numbers as an answer to a problem, but also in finding out why the numbers turn out the way they do, based on overlap of orbitals, perturbation theory, symmetry, and in devising transferable models. Though an individual student may study specific projects in an area, there is an emphasis in the group to learn everything that goes on through group meetings.

General Areas of Interest at different times have been labeled as Theoretical Inorganic Chemistry, Theoretical Organic Chemistry, Computational Chemistry, Transition Metal Organometallics, Electronic Structure and Electron Counting Rules, Three

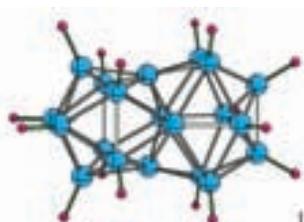
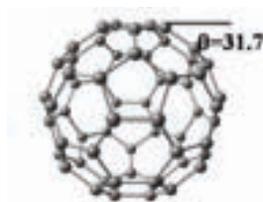
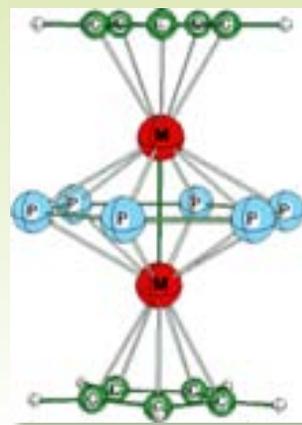
Dimensional Aromaticity, and, Molecular Modeling and Computational Drug Design. Current projects include Reactions of $(C_5H_5)_2Ti$, $(C_5H_5)_2Zr$ Complexes, C-H, C-X, Si-H Bond Activation, Huckel $4n+2$, Wade's $n+1$ and mno Rules: Comparisons and applications, Electronic Structure of elemental boron and boron rich-solids, metallaboranes, heterofullerenes, Metallocene analogs with Phosphorus rings and other heterorings, Electronic Structure Description of weak interactions – blue, red and no shifts in the X-Bond formations where X is hydrogen or any other element, Nickel Mediated Benzyne and Carbonyne coupling with acetylenes, Stabilization of unusual coordination numbers and geometries.



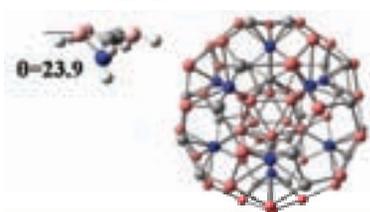
We attempt to relate different areas of chemistry by generating models that are applicable in a variety of contexts. Often these require detailed study of apparently unrelated problems in different branches of chemistry. Relationships are then established between problems in one area to another: e.g. between organic and organometallic chemistry, amongst the chemistry of various main group elements, between allotropes of elements and their compounds and so on. The latter quest has led to several interesting findings with many ramifications. The structural relationship between benzene, benzenoid aromatics and graphite (and now graphene) is well-established. The sp^2 hybridization, the sheet structure of graphite and



Triple-decker sandwich complex with a P_6 middle ring



$B_{20}H_{16}$, mno Rule $m = 2, n = 20$, $o = 0$. $m+n = 22$ electron pairs needed. 16 electron pairs from BH and 6 from 4 B. Hence $B_{20}H_{16}$ is neutral



Hueckel $4n+2$ Rule when restricted to two dimensions. It also helps to explain the structure of large number of boron rich solids. There are several boron rich solids that still defy understanding. Our efforts to understand and to design materials based on boron continue.

the spherical C_{60} which retains the sp^2 hybridization with some strain have all become a part of language of chemists. Similar relationships amongst tetrahedral tetra-coordinate carbon compounds and diamond are taken for granted. It is difficult to imagine an era when these connections were not known. Boron, the element next to carbon, also forms several allotropes which

are covalent solids. These are far more complex than those of carbon. The structural linkages between compounds of boron, say the polyhedral boranes, and the allotropes of boron are not easily made. We have found that the Wade's $n+1$ Rules can be extended to the "mno Rules" which helps in making the connection between $B_{12}H_{12}^{2-}$ and beta-rhombohedral boron. The mno Rule reduces to the

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- K. Sundararajan, N. Ramanathan, K.S. Viswanathan, K. Vidya, E. D. Jemmis, Complexes of acetylene-fluoroform: A matrix isolation and computational study, *J. Mol. Str.* 1049, 69-77 (2013).
- S. Roy, E. D. Jemmis, A. Schulz, T. Beweries, and U. Rosenthal, Stabilization of an Unusual Four-Membered Metallacyclopallene by a Transition Metal Fragment: A Novel Metal-Carbon Bond, *Angew. Chemie*, 51, 5347-5350 (2012).
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BIOINORGANIC AND BIOMIMETIC CHEMISTRY

Medicinally important metalloproteins: Zinc and Antibiotic Resistance

The main focus of our research is to understand the chemistry and biology of naturally occurring and chemically modified metalloproteins (including selenoproteins) and to develop new approaches for modeling/mimicking the enzymatic properties with chemically-designed small molecules. Our group is also interested in the design and synthesis of novel compounds as inhibitors of heme peroxidases and zinc hydrolases. We employ various biophysical methods in combination with chemical synthesis to accomplish these objectives.

Thyroid hormone synthesis and antithyroid drugs:

Thyroxine (T4) is produced on thyroglobulin by thyroid peroxidase (TPO)/hydrogen peroxide/iodide system and deiodinated to its active form (T3) by iodothyronine deiodinase (ID). The activation of thyroid stimulating hormone (TSH) receptor by auto-antibodies leads to "hyperthyroidism", a life-

threatening disease which is treated by anti-thyroid drugs such as 6-n-propyl-2-thiouracil (PTU) and methimazole (MMI). In view of the current interest in anti-thyroid drugs, our group is working on the biological activities of compounds bearing the methimazole pharmacophore. The isosteric substitutions in the existing drugs lead to compounds that can effectively and reversibly inhibit the lactoperoxidase (LPO). These studies reveal that the degradation of the intracellular H₂O₂ by some of the anti-thyroid drugs may be beneficial to the thyroid gland as these compounds may act as antioxidants and protect thyroid cells from oxidative damage. As the inhibition is reversible, the drugs with a more controlled action could be of great importance in the treatment of hyperthyroidism.

Antioxidant activity of organoselenium compounds:

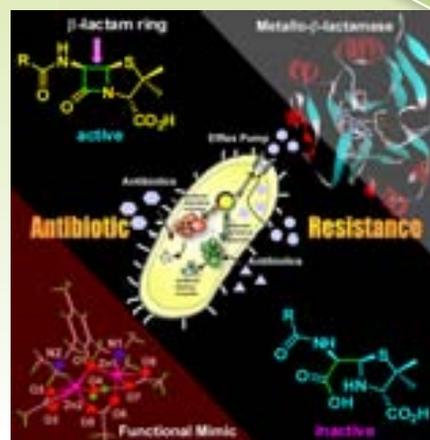
We have recently synthesized selenocystine and aryl-substituted selenocysteine (Sec) derivatives. This study reveals that the introduction of amino/imino substituents capable of

interacting with selenium may stabilize the Sec derivatives. This study further suggests that the oxidation-elimination reactions in Sec derivatives could be used for the generation of biologically active selenols having internally stabilizing substituents. We are also studying the glutathione peroxidase antioxidant activity of ebselen, an organoselenium compound that is currently undergoing phase III clinical trial.

Recently, we have reported a study focusing on the factors that are responsible for the relatively low glutathione peroxidase (GPx)-like antioxidant activity of ebselen. These studies reveal that the relatively poor GPx-like catalytic activity of ebselen and related compounds is due to the undesired thiol exchange reactions that take place at the



Medicinally important
metalloproteins:
Zinc and Antibiotic Resistance



selenium center in the selenenyl sulfide intermediate. This study also suggests that any substituent capable of enhancing the nucleophilic attack of thiol at sulfur in the selenenylsulfide state would enhance the antioxidant potency of organoselenium compounds such as ebselen.

Antibiotic resistance and metallo- β -lactamases: The emergence of microbial resistance to antibiotics is becoming a serious threat to the clinical community. A major problem is the resistance to the β -lactam antibiotics, including the penicillins and cephalosporins, which are among the most widely used class of antibiotics. The most widespread resistance mechanism is the expression of β -lactamases, which inactivate the antibiotics by hydrolysis. The metal-containing enzymes, in particular, hydrolyze a wide range

of β -lactam substrates, such as cephamycins and imipenem that are generally resistant to the serine-containing β -lactamases. Therefore, the clinical application of the entire range of antibiotics is severely compromised in bacteria that produce metallo- β -lactamases (m β l).

Recently, a great deal of effort has been devoted to the development of synthetic zinc complexes as mimics of m β l entities. We have developed a biomimetic system having two zinc(II) ions as a functional mimic of the metalloenzyme. The mimic effectively catalyzes hydrolysis of a variety of β -lactams and the high reactivity of the zinc model is due to the presence of a zinc-bound water molecule that is activated by acetate substituents. The results from the hydrolysis of oxacillin and penicillin G suggest that the second metal

ion is required for a quantitative conversion of the substrates to the hydrolyzed products. This study sheds new light on the possible role of two metal ions at the active site of metallo- β -lactamases and is expected to help in designing novel irreversible inhibitors for the binuclear zinc enzyme.

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- Umayal, M.; Tamilselvi, A.; Mughesh, G. Metallo-beta-lactamases and their Synthetic Mimics: Structure, Function and Catalytic Mechanism. *Prog. Inorg. Chem.*, 2012, 57, 395 - 443.
- Manna, D.; Mughesh, G. A Chemical Model for the Inner-Ring Deiodination of Thyroxine by Iodothyronine Deiodinase. *Angew. Chem. Int. Ed.*, 2010, 49, 9246 - 9249.
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MAGNETIC MATERIALS, MOLECULAR SELF-ASSEMBLY

The primary research interests of our group involve the design, synthesis and functionalization of molecular architectures of finite topologies through directional bonding approach. Our group has been exploring the possibility of finding new single molecule magnets linking smaller magnetic clusters using suitable bridging ligands. We also work on the synthesis of metal-organic hybrid materials using specifically tailored ligands to achieve networks with desired porosity for various gas adsorption and host-guest chemistry.

Coordination driven self-assembly of functional architectures: Coordination driven self-assembly has proven to be an efficient and powerful approach towards the synthesis of large rigid supramolecules of finite shapes, sizes and geometries. These large ensembles have the potential for use in a variety of electronic, photonic, magnetic, catalytic and sensor applications.

In this approach rigid electron poor metal acceptors and rigid electron rich donors are assembled through directional metal-ligand

dative bond. Properties of a molecule are generally guided by the functional group/s present. Thus, incorporation of functional groups into nanostructures may be an efficient way to guide the properties of the resulting assemblies.

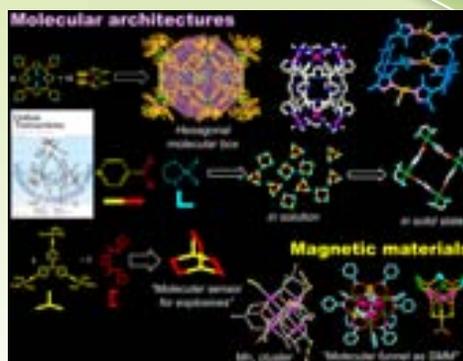
To design advanced materials that incorporate, for example, photonic, magnetic or sensor functionalities it becomes highly desirable to be able to exhibit control over the precise location, orientation and stoichiometry of such functional groups. We have recently introduced ethynyl functionality which introduces fluorescence behavior in a number of 2D and 3D assemblies. These molecules have been found to be efficient chemo-sensors for trinitrotoluene (TNT), dinitrotoluene (DNT) and picric acid which are the chemical signatures of many commercial explosives. Activity towards these nitro compounds shows that these molecular assemblies can be developed as efficient sensors for explosives.

We have also recently designed a $\text{Pt}_{12}\text{Fe}_{12}$ heterometallic open hexagonal box containing six

faces occupied by porphyrin moieties with the internal open void of around $13,550 \text{ \AA}^3$. Such molecules with large cavity can find application in drug delivery process.

Magnetic clusters: The chemistry of high spin paramagnetic metal clusters continues to attract a great deal of interest and has immensely grown during the last two decades. The ability of the ancillary N- and O-donor ligands to assemble novel metal clusters that exhibit complex and varied structural motifs with unusual magnetic properties have prompted researchers to seek new molecular materials. The research in this area is largely driven by the quest for the single-domain magnetic particles exhibiting at the molecular scale, slow thermal and quantum relaxation of magnetization. These materials can find use in quantum-computing.

Our primary interest on this project is to assemble smaller magnetic clusters by bridging polydentate ligands to larger arrays with improved magnetic



properties compared to the starting small clusters. Using this methodology we have recently synthesized a couple of Mn_9 nano-funnels from a simple and known antiferromagnetic Mn_3 triangle using a trihydroxy linker. Detail ac as well as dc magnetic studies revealed that the Mn_9 -larger clusters are new kinds of single molecule magnets. Recently, we have also reported the combination of azide and tris(hydroxymethyl) ethane which yielded a rare μ_6 -oxo centered Mn_6 octahedron. A similar reaction at a relatively higher temperature yielded an azido-linking polycluster with the retention of the Mn_6 core. Thus the presence of sources of small bridging ligands such as O^{2-} , N_3^- , Cl^- or OH^- can lead to an efficient assembly of the low nuclearity cluster into a high nuclearity one.

Metal-Organic Frameworks and gas adsorption studies:

In recent years extensive work has been carried out on inorganic-organic hybrid materials having various tunable functional properties not only for industrial applications, such as host-guest chemistry, heterogeneous catalysis, and gas storage but also because of scientific interest in the formation of molecular assemblies and rationally designed materials. These materials are composed of mostly transition metal ions connected by organic poly-functional ligands. These coordinatively bound assemblies may extend in one-, two- or three-dimensions, while other and weaker interactions such as hydrogen bonds, π - π interactions may keep together chains or layers to form three dimensional solids.

We are currently developing new metal-organic hybrid flexible frameworks containing new polycarboxylate ligands. The primary idea is to use these materials to store hydrogen and perform stereospecific organic reactions in porous frameworks.

Selected publications

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- H-bond driven controlled molecular marriage in covalent cages K. Acharyya and P. S. Mukherjee *Chem. Eur. J.* 2014, 20.
- Role of dicarboxylate linkers in Mn(III)-salicylaldoximate based extended molecular magnets S. Mukherjee and P. S. Mukherjee *Chem. Eur. J.* 2013, 19, 17064.
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- Versatility of azide in serendipitous assembly of Cu(II) magnetic polyclusters S. Mukherjee and P. S. Mukherjee *Acc. Chem. Res.* 2013, 46, 2556.



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ELECTROCHEMISTRY

Investigations of rechargeable lithium, sodium and magnesium batteries:

Among various rechargeable batteries, lithium-ion batteries occupy a special place in terms of energy density and also several applications at present. Research activities on important electrode active materials have been under progress. Both positive and negative electrode materials, which are capable of providing high specific capacity with good structural stability over prolonged charge-discharge cycle life, are considered important for future generation lithium-ion batteries. These compounds need to provide safety and reliability for the battery. Lithium excess manganese oxides have emerged as a promising material for the positive electrodes. These compounds are prepared as sub-micron size particles with porosity for high rate capability. Electrochemical cells in non-aqueous electrolytes are assembled in an argon filled glove box and evaluated for various electrochemical properties. The properties include specific discharge capacity, rate capability, temperature dependence on capacity, ac impedance behaviour, diffusion coefficient and cycle-life test. Li-air

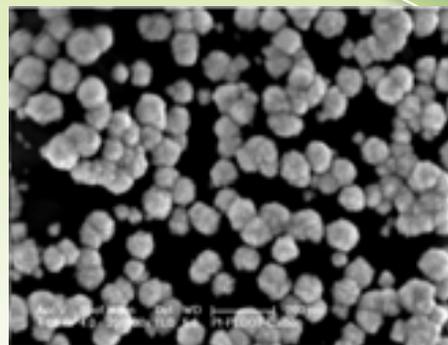
cells are expected to provide very high specific energy. Operation of these batteries in air-breathing mode is an additional attraction. However, rechargeability with high energy efficiency is a crucial issue. Work is in progress on appropriate graphene based catalyst materials for oxygen electrode. Although worldwide research activities on Li-ion and Li-air batteries are intense at present, the resources of Li are limited. Future generation batteries need to depend on raw materials which are plentiful in nature. Sodium and magnesium-based secondary batteries are under investigation. Mg is safe to handle and environmental friendly. Although the electrical performance characteristics of Mg based batteries are likely to be inferior to the batteries based on Li, merits such as enormous resources, safety, environmental compatibility, low cost, etc., of Mg system outweigh its limitations.

Supercapacitors and capacitive deionization:

Electrochemical supercapacitors can withstand higher power than batteries, and deliver higher energy than the conventional electrostatic and electrolytic capacitors. Among the transition metal oxides, MnO_2

with a theoretical capacitance of 1370 F g^{-1} is an attractive material for supercapacitor studies. However, a maximum specific capacitance of 240 F g^{-1} is usually reported in literature. Experimental investigations have been in progress to study various aspects to enhance specific capacitance. In view of this, attempts are made to enhance specific capacitance of MnO_2 by electrochemical deposition in the presence of surfactants. Nano-structured MnO_2 synthesized by inverse microemulsion route is also studied for electrochemical supercapacitors. The effect of crystallographic structure of MnO_2 on the capacitance properties, studies on electrochemical deposition of MnO_2 in acidic and neutral medium using electrochemical quartz crystal microbalance (EQCM) and capacitance characteristics of MnO_2 are studied. From EQCM data of mass variation during cycling, it is observed that the rate of electrodeposition of MnO_2 is higher in the neutral medium than in the acidic medium. As ions present in the solution get adsorbed in the electrode materials of a supercapacitor, deionization of the solution can be achieved conveniently from supercapacitors. These studies are in progress.

SEM image showing the formation of Pt nanoclusters on PEDOT coated carbon paper.



Electrochemical studies of conducting polymers:

Electrochemistry of conducting polymer is an important area of research in view of various applications. Electrooxidation reactions of methanol, formic acid formaldehyde and ethanol on nanocluster of Pd, Pt, Au, Pt-Ru, Au-Pd, etc., deposited on PEDOT/C electrodes are studied in view of their promising applications. Films of PEDOT are electrochemically deposited on carbon paper. Nanoclusters of catalysts are potentiostatically deposited on PEDOT/C electrodes. Catalysts are also prepared on bare carbon paper for studying the effect of PEDOT. The presence of PEDOT film on carbon paper allows the formation of uniform well dispersed nanoclusters of catalysts. Electrooxidation reactions are studied by cyclic voltammetry and chronoamperometry. The data reveal that PEDOT facilitates a

greater catalytic activity for the metallic catalysts.

Photoelectrolysis of water for solar energy storage

Light assisted electrochemical splitting of water to produce hydrogen and oxygen is a promising method for solar energy storage. This solar-to-chemical energy conversion involves the oxidation of water to oxygen and the reduction of resultant protons to hydrogen. The efficiency of the overall reaction is limited by the complex four electron-four proton oxygen evolution reaction (OER). Hence, the design and demonstration of a stable and efficient OER catalyst is a key challenge in solar energy storage. Investigations on the development of efficient catalysts that can operate under ambient conditions with moderate overpotential are in progress.

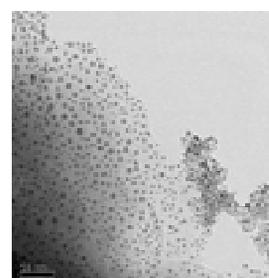


Fig. 1. TEM image of Ag-reduced graphene oxide

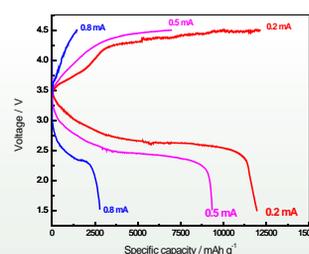
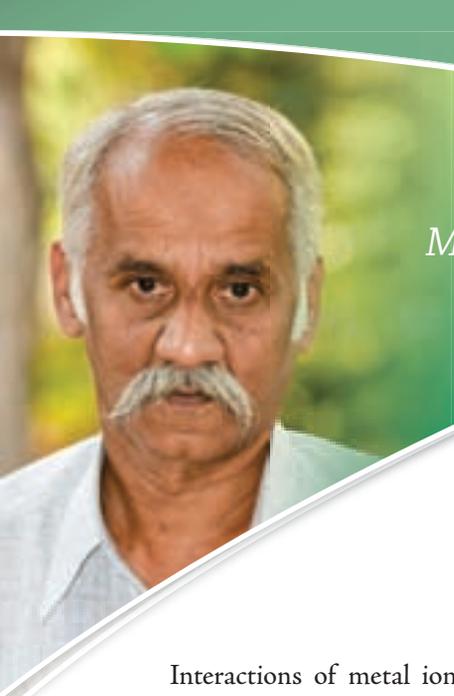


Fig. 2. Charge-discharge profile of Li-O₂ cells with Ag-reduced graphene oxide catalyst at different currents

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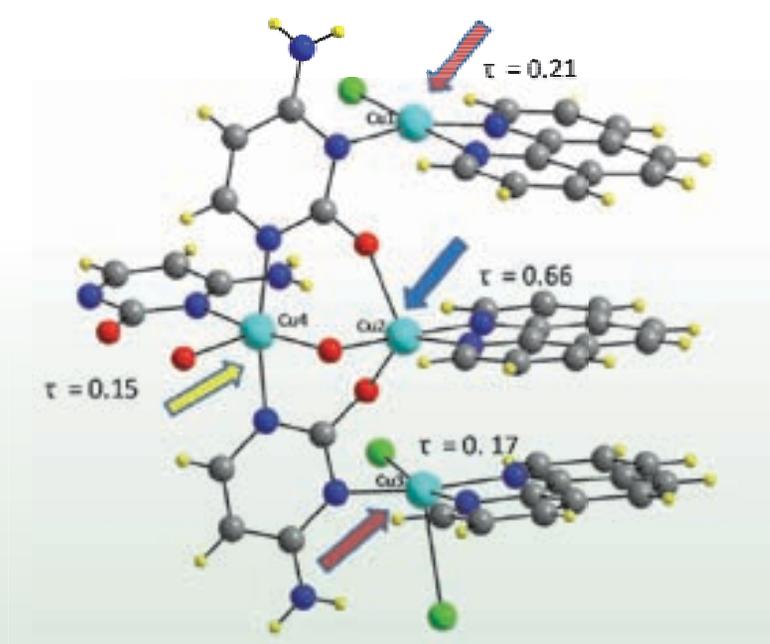
X-RAY CRYSTALLOGRAPHY

Interactions of metal ions with nucleic acid constituents have been a topic of interest for the past few decades. The major interest arises as metal-DNA interactions play a crucial role in DNA stabilisation [bivalent metals like Zn(II), Mg(II)], destabilisation [Cu(II), Co(II), Cd(II)], mutagenesis and also in variety of enzymatic processes. Although all the possible binding sites of pyrimidines with different metals have been

reported by various studies, but only few structural evidences are known. Especially for copper metal only few binary and ternary complexes with the pyrimidine bases are reported in the past four decades.

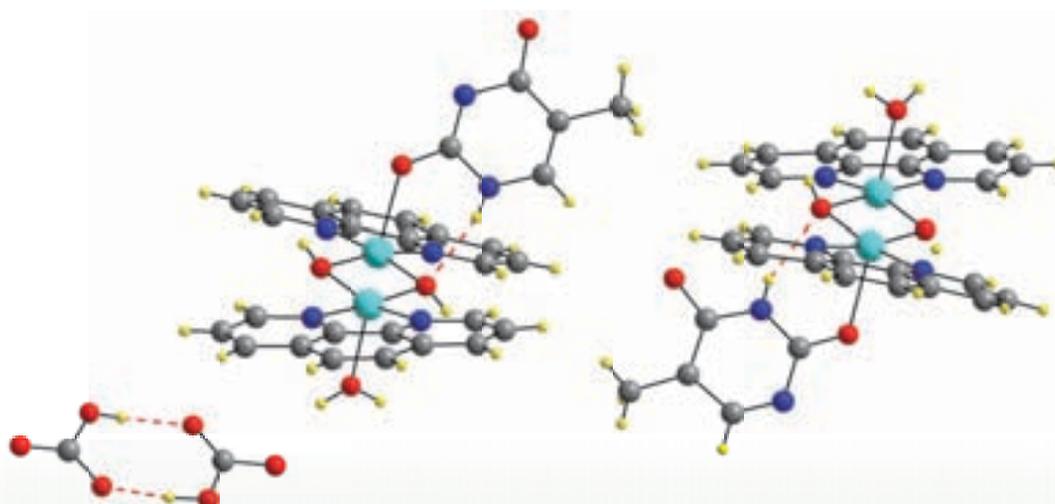
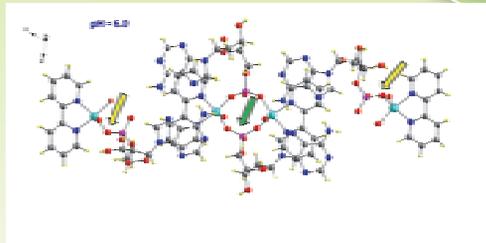
Similar reaction with thymine also resulted in the novel structure which is a unique example wherein two tautomers of thymine are co-crystallized simultaneously.

The reactions done with copper chloride, 2,2'-bipyridine and 5'-adenine monophosphoric acid (5'-AMP) at different pH conditions (3, 6, 9) which resulted in different crystal structures, at pH 3.0 monodentate AMP coordination and at 9.0 bidentate coordination was obtained while at pH 6.0 co-crystal of monodentate and bidentate was observed implying the intermediate formation.



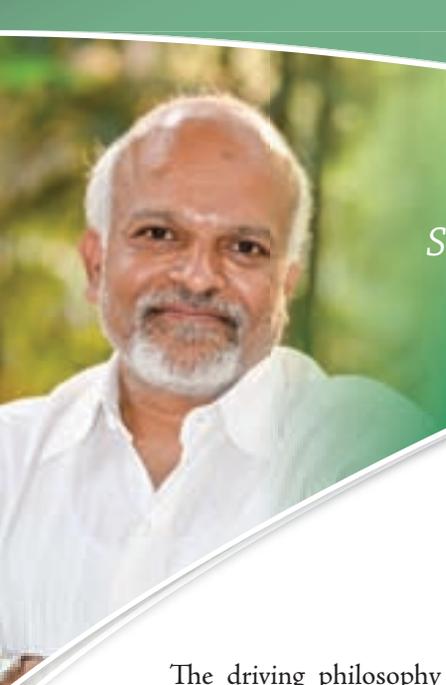
The unusual polymeric ternary copper Cytosine phenanthroline complex, $[\text{Cu}_4(\text{phen})_3(\mu_3\text{-cyt})_2(\mu\text{-OH})(\text{cyt})(\text{OH})\text{Cl}_3]_n \cdot 16\text{H}_2\text{O}$, as a synthetic model for active sites of enzymes wherein for the first time two different tautomers of Cytosine have simultaneously complexed with the copper metal centre was obtained.

X-Ray Crystallography



Selected publications

- S. Pasayat, S. P. Dash, Saswati, P. K. Majhi, Yogesh P. Patil, M. Nethaji, H. R. Dash, S. Das, R. Dinda, *Polyhedron*, 38, 198, (2012)
- D. S. Badiger, R. S. Hunoor, B. R. Patil, R. S. Vadavi, C. V. Mangannavar, I. S. Muchchandi, Yogesh P. Patil, M. Nethaji, K. B. Gudasi, *Inorg. Chim. Acta*, 384, 197, (2012).
- P. Haribabu, Yogesh P. Patil, K. H. Reddy, M. Nethaji, *Inorg. Chem. acta.*, 392, 478, (2012)
- P. Haribabu, Yogesh P. Patil, K. H. Reddy, M. Nethaji, *Trans. Met. Chem.*, 36, 867, (2011)



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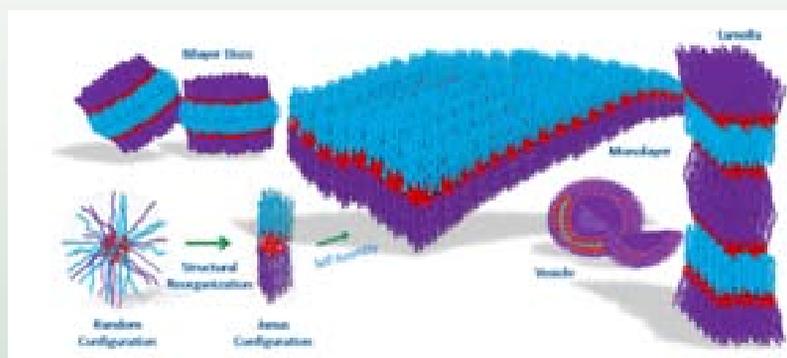
POLYMER CHEMISTRY

The driving philosophy of our research efforts has been to address interesting fundamental questions about the behaviour of new types of macromolecules and/or to design-in specific features into polymeric systems from the viewpoint of eliciting unusual properties. A short description of our efforts in various areas is provided below.

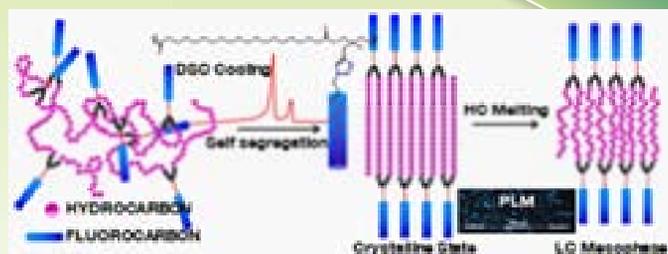
Hyperbranched polymers are highly branched yet soluble structures that closely resemble the more structurally elegant dendrimers that are perfectly branched macromolecules whose topology is such that the number of branching junctions increases exponentially as one moves from the core outwards. Despite the presence of structural defects in hyperbranched polymers (HBPs), the highly branched topology endows them with several unique properties, such as low solution and melt viscosities, absence of chain entanglements and, importantly, they carry a large number of readily accessible end-groups. We have, over the years, developed new straightforward synthetic strategies to prepare a variety of HBPs, such as polyurethanes, polyesters and

polyethers, and have addressed several interesting questions regarding their behaviour, such as the effect of branching density on the compactness of their conformation, on their T_g and crystallization propensities, the variation of T_g in HB copolymer systems, etc. More recently, we have developed several single-step strategies to directly generate HBPs that bear “clickable” entities at the peripheral molecular surface; both for utilizing thiol-ene and azide-yne click reactions. Using these peripherally “clickable” HBPs as nano-dimensional molecular scaffolds, we have been able to demonstrate that randomly hetero-functionalized HBPs self-segregate to generate “Janus” and “tripodal” structures; these then organize in the solid state to form a variety of interesting

nanostructures. Furthermore, we have also developed new approaches to prepare acid-labile and photo-labile HB polyacetals and also unique defect-free HB polydithioacetals; the latter has been used to prepare different types of capped Au-nanoparticles that can be dispersed in either water or organic medium. The photo-labile HB polyacetals, on the other hand, were shown to have use as a photo-resist material for generating photo-patterns. Our current focus in this context is to explore the utility of peripherally hetero-functionalized HBPs for different applications; we are exploring the design of HBPs that have binding ability to specific analytes in an effort to develop sequester-bind-sense type systems. Similarly, we are also exploring the possibility of using HBPs as porogens for



Dendrimer-like Hyperbranched
Polymers; Polymerizable Surfactants
and 2D Polymers; Foldamers.



the creation of interesting porous materials.

Foldamers are polymer chains that can be coerced to adopt specific conformations by inclusion of specific intra-chain interactions between periodically spaced units along the polymer backbone. We have explored several designs to accomplish such folding using a variety of weak non-covalent interactions, such as charge-transfer interactions, metal-ion complexation, and solvophobic effects. To understand the folding process, we use several tools, such as NMR and UV-visible spectroscopies, variable temperature spectroscopic measurements and isothermal titration calorimetry. Translation of such a conformational control into the solid state is key challenge. In this context, we have recently designed polyethylene-like polyesters that

carry hydrophilic polyethylene glycol (PEG) segments at periodic intervals; the immiscibility between the PEG and the backbone alkylene segments drive the chain to fold into a zigzag conformation in polar medium to generate *PEGylated wax-like nanobundles*, which are clearly observable as flat pancake-like entities using AFM imaging. More recently, we have extended this idea to generate periodically grafted polymers bearing alkylene segments in the backbone and pendant fluorocarbon segments; here too folding of the polymer chain enables the unique independent crystallization of both the alkylene and fluoroalkyl segments, which is possible only if the chain folds in the postulated zigzag manner. We are presently exploring the possibility of generating similarly folded polymers that carry dissimilar units on either sides

of the folded chain; this would open up new and exciting possibilities for creating polar structures that are otherwise very difficult to access.

Combining novel design concepts and newer methodologies in distinctly different contexts to evolve polymeric systems that exhibit new and unexpected behaviour will be our guiding research philosophy in the coming years. For instance, realization of Janus Au-particles using HBP-capping, polar ordering of dyes in solution, HBPs for sequestering-binding-sensing, biological applications of HBPs, responsive gels based on amphiphilic HBPs, new approaches for creating 2-D polymers etc., are some of the new directions that we hope will challenge us during the next decade.

Selected publications

- Joydeb Mandal, S. Krishna Prasad, D. S. Shankar Rao and S. Ramakrishnan, "Periodically clickable polyesters: Study of intra-chain self-segregation induced folding, crystallization and mesophase formation" *J. Am. Chem. Soc.* 136, 2538 (2014).
- Ashok Zachariah Samuel and S. Ramakrishnan, "Janus Hybramers: Self-Adapting Amphiphilic Hyperbranched Polymers" *Macromolecules* 45, 2348 (2012)
- Raj Kumar Roy, E. Bhoje Gowd and S. Ramakrishnan, "Periodically Grafted Amphiphilic Copolymers: Nonionic Analogues of Ionenenes" *Macromolecules* 45, 3063 (2012)
- Saptarshi Chatterjee and S. Ramakrishnan, "Hyperbranched Polyacetals with Tunable Degradation Rates" *Macromolecules* 44, 4658 (2011).
- Swati De and S. Ramakrishnan, "Charge-transfer reinforced folding of novel iononenes" *Macromolecules* 42, 8599 (2009).



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THEORETICAL CHEMISTRY

Broadly, we are interested in understanding the vibronic properties of molecular systems in the gas and solution phases. A key driving factor in our studies is the relevance of such properties to the dynamics in the chosen systems.

Aromatic molecules with X-H groups, including pyrrole, phenol, thiophenol, higher fused ring systems, etc. have multiple excited states that are accessibly by standard UV lasers. Upon such excitations, one sees rapid loss of the H atom of the X-H group. It is now widely recognized that this occurs because dissociative states become accessible, either directly or due to crossings with a bright state. Also, these dissociative states encounter the ground state surface at conical intersections. The ultrafast (sub-picosecond) dynamics through these intersections determines the product distributions. Obtaining a theoretical understanding of the processes involved requires high quality multi-coordinate

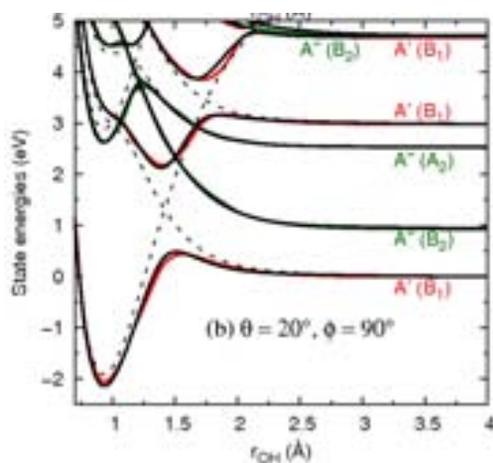
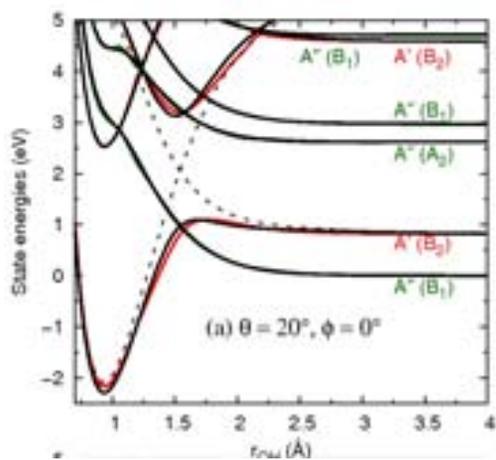
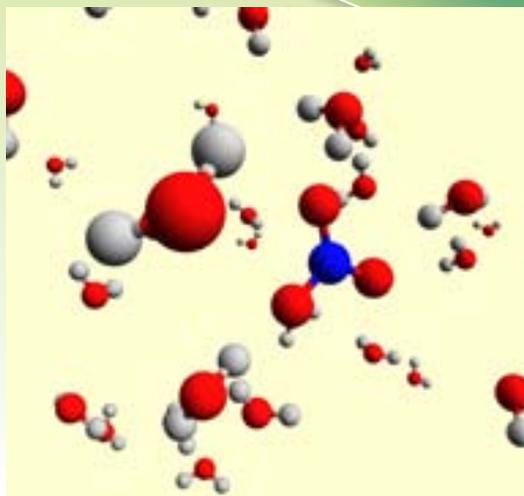
multi-electronic surface potentials for such molecules. We are actively engaged in such tasks. Once obtained, one may carry out wavepacket dynamics to simulate and analyse photoprocesses.

A related branch of our research interests involves understanding energy flow between the vibrational modes in a molecule. An important aspect of any reactive process is for energy to be localized in the reactive modes. However, intramolecular vibrational energy redistribution is a mitigating influence that draws energy away. It is therefore important to understand the intramolecular energy redistribution timescales and pathways of a molecule.

We are also interested in modelling and simulating reaction dynamics in the solution phase, with emphasis on the quantum treatment of the reaction subsystem as well as the role of the solvent in facilitating the process. We

are presently considering some simple H-atom abstraction reactions in this context, where a solute or even the solvent loses an H atom to a reaction partner. Multiple techniques may be used to address such cases, of which our interest is mainly in those that afford a quantum treatment of the H-atom motion. Careful modelling of the reaction surface as well as solute-solvent potential is of essence. In addition to rates, we wish to ultimately understand the extent of influence exerted by the solvent motions on the outcome of reactive processes.

A snapshot of a simulation
of NO_3^- in H_2O



Modelling of multi-electronic state dissociation potential for phenol's OH bond at 0° and 90° CCOH torsions, where the state couplings follow different patterns. The coloured lines show the ab initio data from CASSCF computations, while black solid and dashed lines show the fitted adiabats and diabats, respectively.

Select publications:

- S. G. Ramesh and W. Domcke, "A multi-sheeted three-dimensional potential energy surface for the H-atom photodissociation in phenol", *Faraday Discuss.* 163, 73-94 (2013)
- S. G. Ramesh, S. Re, J. Boisson, and J. T. Hynes, "Vibrational Symmetry Breaking of NO_3^- in Aqueous Solution: NO Asymmetric Stretch Frequency Distribution and Mean Splitting", *J. Phys. Chem. A* 114, 1255-1269 (2010)
- S. G. Ramesh and E. L. Sibert, "Time scales and pathways of vibrational energy relaxation in liquid CHBr_3 and CDBr_3 ", *J. Chem. Phys.* 125, 244512 and 244513 (2006)
- S. G. Ramesh and E. L. Sibert, "A study of the vibrations of fluoroform with a sixth order nine-dimensional potential: A combined perturbative-variational approach", *Mol. Phys.* 103, 149-162 (2005)



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SURFACES, INTERFACES, ELECTROCHEMISTRY

The main focus of our research is to understand interfacial properties involving novel materials and modified surfaces. Our present attention is focused on the following classes of materials. We use a combination of spectroscopy, electrochemistry and microscopy to understand the interfacial properties. Coupled *in-situ* techniques based on electrochemical FTIR, Raman electrochemistry are routinely used to understand various aspects.

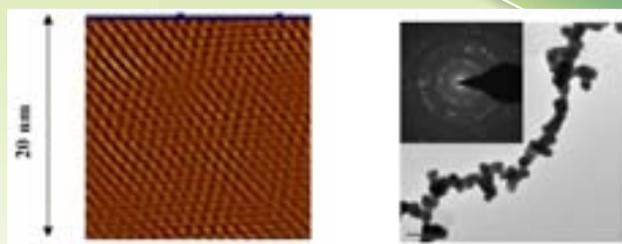
Exfoliated graphite, graphene oxide and graphene: Exfoliated or expanded graphite (EG) is a low dense graphitic carbon with high temperature resistance. The density of the expanded material is very low, of the order of 0.004 g/cm³. The exfoliated graphite particles can be recompressed or re-stacked without any binder. Graphene / graphene oxide is very thin and consists of a monolayer of carbon / (oxidized carbon) atoms tightly packed into a two-dimensional honeycomb lattice. It has gained considerable attention

due to its extraordinary electronic, thermal and mechanical properties. Our interest is on both exfoliated graphite and graphene oxide / reduced graphene oxide. Present focus is on Langmuir and Langmuir-Blodgett films of graphene oxide and graphene oxide-assisted (electro)chemistry at interfaces towards understanding the interfacial properties and to develop new and novel materials. Direct electron transfer of redox active enzymes modified through graphene oxide assemblies and sensors for detection of low concentration of analytes are also pursued. Graphene oxide – nanoparticle composites are being used as catalysts for small molecule oxidation. Intercalation in well-defined number of graphene layers is another area of our current interest.

Organic thin films (SAMs and LB films): In the area of organic thin films, our objective is to prepare stable, compact and well-oriented organic thin

films consisting of donor-space-acceptor assemblies. Intramolecular electron transfer in constrained thin films is studied. Orientation dependent electrocatalysis is pursued using macromolecular thin films.

Transition metal nitrides, carbides and chalcogenides: Towards exploring new electrode materials, we have been working on titanium nitride, titanium carbide, carbonitride – based electrodes. The nitrides and carbides show exceptional stability and good electronic conductivity combined with the ability to support catalyst particles. Transition metal chalcogenides, particularly layered sulphides and selenides are amenable for preparing few layer materials that possess interesting electrical and electrochemical properties. We use nitrides, carbides and various chalcogenides for small molecule oxidation, hydrogen evolution (HER) and oxygen reduction (ORR) studies. Many of the nanostructured nitrides,



carbides and chalcogenides are also tried as electrode materials for secondary lithium ion-, sodium ion- and magnesium-ion batteries.

Nanostructured materials:

Research on nano-particles and nanobimetallics has been quite extensive over the last few decades. Our interest is to prepare nanometallic structures based on Os, Ir, Al etc. Bimetallic and alloy clusters are also prepared and used for electrocatalysis. Use of different (bi)metallic and other nanostructures as substrates for surface enhanced Raman scattering (SERS) studies is one of the main areas of interest.

Molten electrolytes:

Studies on eutectic molten solvents / electrolytes for electrodeposition as well as the preparation of nanostructures are pursued with amide-based solvents. The room temperature deep eutectics are good ionic conductors and are useful as electrolytes in batteries. Molten electrolytes with magnesium, zinc and lithium ion-conductivity are prepared and studied for secondary batteries.

Organic electrode materials:

We have recently initiated work on naturally occurring / synthetic organic electrode materials for secondary

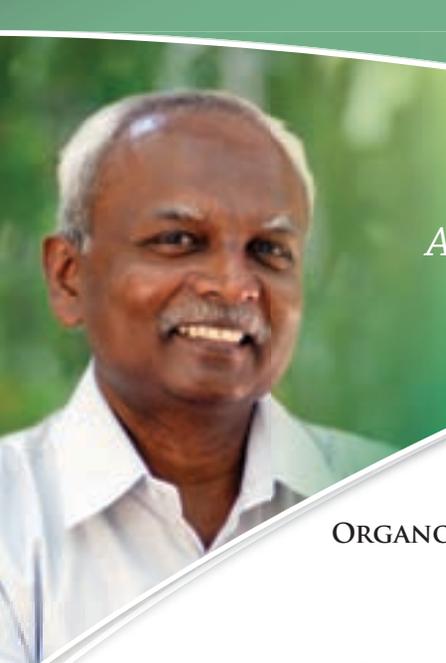
batteries. Ellagic acid, a polyphenol extracted from pomogranate has been recently shown to be a good cathode material for rechargeable lithium batteries. Other quinone and phthalocyanine-based materials are being looked at, as possible candidates.

Selected publications:

- Spontaneous Assembly of Iridium Nanochain-Like Structures: Surface Enhanced Raman Scattering Activity Using Visible Light K Chakrapani and S. Sampath, Chem. Comm. 50 (23), 3061, 2014.
- Ellagic acid: A novel organic electrode material for high capacity lithium ion batteries, Subrahmanyam Goriparti, Harish, M N K and S. Sampath, Chem. Comm., 49, 7234, 2013.
- Facile Synthesis of Carbon Doped TiO₂ Nanowires without External Carbon Source and Its Opto-Electronic Properties and its use as renewable surface SERS substrates, V Kiran and S. Sampath, ACS Appl. Mater. Inter, 4(8), 3818, 2012; Nanoscale, 21(5), 10646, 2013.
- In Situ Electrochemical Polymerization at Air- Water Interface: Surface-Pressure-Induced Orientation of Polyaniline G K Ramesha, A Vijaya Kumara and S. Sampath, J. Phys. Chem. C., 116, 13997, 2012.

Recently granted US patents:

- Composition of electrode material in the form of a coating and a process thereof. US patent 8,343,572
- Low cost electrochemical disposable sensor for measuring glycated hemoglobin. US patent 8,702,931



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ORGANOMETALLICS AND COORDINATION CHEMISTRY, ANTICANCER ACTIVITY

Structure and Reactivity of Organometallic and Coordination Compounds

The study of structure, bonding and reactivity in unusual coordination and organometallic compounds is our primary focus. We restrict our studies to closed shell systems such as zinc(II), titanium(IV) or ruthenium(II) complexes. However, the ligand space that we have explored, ranges from classical ligands of coordination chemistry to some exciting carbene ligands generated *in situ*. Our research methodology involves synthesis of new complexes and their characterization by NMR spectroscopy or X-ray crystallography. Once we know the structure of these compounds, we probe their reactivity and study their catalytic properties. A variety of small molecules including dihydrogen and carbon dioxide (and those that mimic carbon dioxide) are activated by these complexes.

Asymmetric Catalysis

Efficient synthesis of chiral molecules has emerged as one of the greatest challenges in chemical synthesis. To achieve an enantiomeric excess (e.e) of 99% in the product, the difference in energy between

two diastereomeric transition states has to be at least 3 Kcal/mol for a reaction carried out at room temperature. Steric effects are sufficient to tilt the balance in favor of one transition state over the other. Less explored has been the use of hydrogen bonding and the use of weak π - π interactions. We have explored several ligands which are chiral and are capable of carrying out transfer hydrogenation. These ligands are different only in the position of aromatic residues present in them. Their efficiency in transferring chirality has been systematically explored to determine the role of phenyl groups in this process. We are also developing ligands with other weak interactions with the substrate and / or reagents. Mechanistic aspects of these transition metal promoted reactions are confirmed with the help of labeled substrates or reagents.

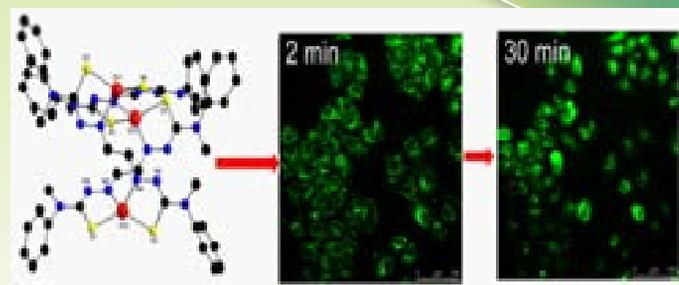
Coordination Chemistry and Anti-cancer Activity

Another area which has caught our attention is the application of organometallic and coordination chemistry to cancer therapy. Cisplatin is the most celebrated inorganic drug. While it is well known that it can cure several forms of cancer, it is also known for its toxicity

to normal cells which causes severe side effects. So the use of coordination and organometallic compounds in medicine is a great challenge, for most metal ions are toxic. Our aim is to look for ways and means to reduce the toxicity of anticancer drugs while retaining their ability to kill cancer cells. To this end we have developed dendrimers and gold nano particles to deliver metal complexes specifically to cancer cells. We have recently shown that bis(thiosemicarbazone) ligands, and their complexes (copper or zinc), can be used in cellular studies. The mononuclear copper complexes of some ligands are quite cytotoxic while the corresponding zinc complexes are not! If only we could deliver these copper complexes selectively to kill them, and then convert them to zinc complexes, we would have a wonder drug! Interestingly, the zinc complexes of these ligands are non-toxic and form trimeric units which are fluorescent. The bright fluorescence of these molecules help us visualize living cells even in the presence of other metal ions. In principle, the ligand can be used for imaging zinc inside a living cell.

To reduce adverse side effects, metal complexes have to be

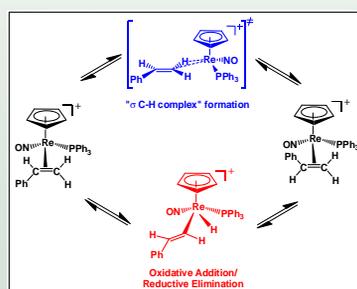
Asymmetric catalysis, Carbon dioxide complexes, Weak interactions, Cuprophilicity, Hydrogen bonding, Anti-cancer activity



delivered to the diseased site in a targeted fashion. Many strategies are being explored by coordination chemists. We have used half-sandwich ruthenium complexes having a variety of heterocyclic ligands bearing the -NH-C(=S)- group to exert cytotoxicity in a selective way. These complexes are internalized through the help of transferrin which functions as a Trojan horse as transferrin receptors which are overexpressed in cancer cells. So any payload on the half-sandwich complex gets into cancer cells more effectively. A second strategy is the use of dendrimers and nanoparticles as delivery vehicles. Our group has linked cytotoxic complexes made from bis(thiosemicarbazone)ligands to large macro molecules to deliver metal complexes selectively through a folic acid or biotin linked macro molecule.

Computational Organometallic Chemistry

From time to time, we use available computational tools to evaluate the organometallic complexes we make for reactivity. Recently, we studied the interaction of half-sandwich complexes of d^6 metal ions which were essentially 16 electron fragments for their interaction / reactivity with small organic ligands, C_nH_m . The interaction of metal fragments with alkanes and alkenes is a matter of great interest for it helps one to effectively use the most common raw material available



to man: petroleum. While activation of alkanes is a great challenge, recent results suggest that even the most unreactive molecule can be activated with an unsaturated metal centre. Interesting reactivity pathways have emerged as a result of our computational study. We have probed the chain walking of metal centres on alkanes and the factors affecting methylene versus methyl binding.

We have also shown that metal centres can migrate from one π face of the olefin to the other. The migration happens through a simple (C-H)···M interaction or through oxidative addition of the metal into the vinylic C-H bond. The process can be tuned by the ligands present on the metal!

Selected publications

- Kumar, A.; Pandiakumar A. K.; Samuelson, A. G.: Titanium promoted reduction of imines with Grignards, silanes, and zinc: identification of a new mechanism with silanes *Tetrahedron* 2014, 70, 3185-3190.
- Thenraj, M.; Samuelson, A. G.: Computational Study of the Migration of Rhenium from One Enantioface of an Olefin to the Other Facilitated by (C-H)center dot center dot center dot Re Interactions. *Organometallics* 2013, 32, 7141-7152.
- Palanimuthu, D.; Shinde, S. V.; Somasundaram, K.; Samuelson, A. G.: In Vitro and in Vivo Anticancer Activity of Copper Bis(thiosemicarbazone) Complexes. *Journal of Medicinal Chemistry* 2013, 56, 722-734.
- Palanimuthu, D.; Shinde, S. V.; Dayal, D.; Somasundaram, K.; Samuelson, A. G.: Imaging Intracellular Zinc by Using a Glyoxal Bis(4-methyl-4-phenyl-3-thiosemicarbazone) Ligand. *European Journal of Inorganic Chemistry* 2013, 2013, 3542-3549.
- Mitra, R.; Das, S.; Shinde, S. V.; Sinha, S.; Somasundaram, K.; Samuelson, A. G.: Anticancer Activity of Hydrogen-Bond-Stabilized Half-Sandwich RuII Complexes with Heterocycles. *Chemistry-a European Journal* 2012, 18, 12278-12291.



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STATISTICAL THERMODYNAMICS AND QUANTUM MECHANICS, AS APPLIED TO CHEMICAL/BIOLOGICAL SYSTEMS

We are interested in understanding complex chemical and biological phenomena using the tools of quantum mechanics and statistical mechanics. Though a large part of the work is analytical, we do numerical calculations too, when it is essential.

The major areas and problems in which we have been interested in are briefly outlined below:

Dynamics of Biophysical Processes

In last 15-20 years, advances in technology have enabled scientists to carry out beautiful experiments on biologically relevant phenomena. Often these are at a single molecule level. Some of these are done in the actual biological systems, while others are done outside the biological system, thus avoiding many of the complexities of the biological systems, but still capturing the essential aspects of the problem. We have been interested in the theory of such experiments. We construct models (usually, nonlinear) for the observed phenomena, using a variety of theoretical tools like Brownian motion and path integrals. Some of the problems studied are outlined below.

Motivated by recent experiments on the translocation of a polymer through a nano-sized pore, we have analyzed the dynamics of barrier crossing by a long chain molecule. We found the exact

solution to this problem, and suggested that the translocation occurs by a kink mechanism, which leads to a translocation time that is proportional to the length of the molecule. We have also analyzed the barrier crossing of short chain as well as star polymers. We are also looking at the barrier crossing problem in a variety of circumstances. We have also looked at the dynamics of the forced unzipping of a DNA molecule, as well as the packaging of a viral DNA into its capsid under the influence of an external force and the dynamics of loop formation of a semiflexible polymer.

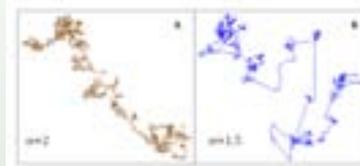
Theory of energy transfer in nano-systems

Fluorescence energy transfer involving molecules is a well understood process and has been extensively used in biological systems. The transfer occurs by dipole-dipole coupling and consequently has a distance⁶ dependence. We have been interested in the distance dependence of such rate, for nano-sized systems. We have analyzed the process theoretically, for energy transfer from the excited state of a dye to (a) a nanoparticle and (b) a sheet of graphene. In the latter we predicted that the energy transfer occurs with a rate that is proportional to distance⁴. This prediction regarding has now been experimentally verified, and the process has been used for a variety of sensing applications. We have

recently studied the vibrational energy transfer to graphene by a similar mechanism and predicted that it can lead to a broadening of IR linewidth, which is observable with the currently available techniques.

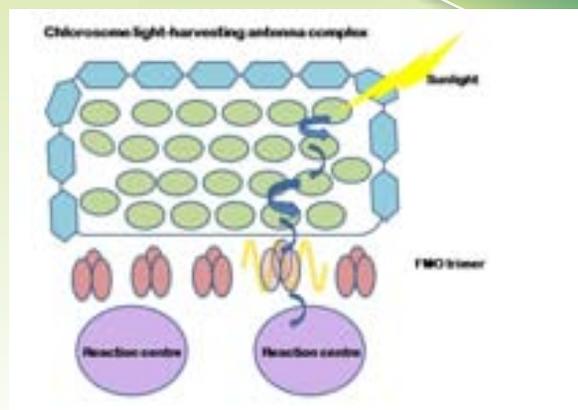
Levy flights

An interesting generalization of Brownian motion is known as Levy flights, which have been observed in a variety of natural processes, like diffusion in micellar systems, foraging of animals, climate change, diffusion in a turbulent medium etc.. These are processes where the particle is subject to an external potential, friction and noise, the noise being characterized by its Levy index α . We have developed a path integral method for the evaluation of the propagator for the process and used it to evaluate the propagator for the case where the motion is overdamped or underdamped, subject to a potential that is at the most harmonic. We are also looking at the dynamics under more complex potentials.



The figure shows typical trajectories accumulated over 5000 steps for (A) Brownian motion ($\alpha=2$) and (B) Lévy flight with $\alpha=1.5$. The trajectory for Lévy flight (B) is composed of clusters of small steps interrupted by long jumps in-between. These huge jumps in the trajectory give rise to the *anomalous diffusive* behaviour in Lévy flights. In contrast, the long jumps are absent in the trajectory for Brownian motion.

Light-harvesting complex of green sulfur bacteria. The chlorosome antenna absorbs sunlight which creates an electronic excitation. This excitation then travels through the antenna and reaches the Fenna-Matthews-Olson trimers. From here, the excitation is transported to the reaction centre where the electron transfer reactions take place.

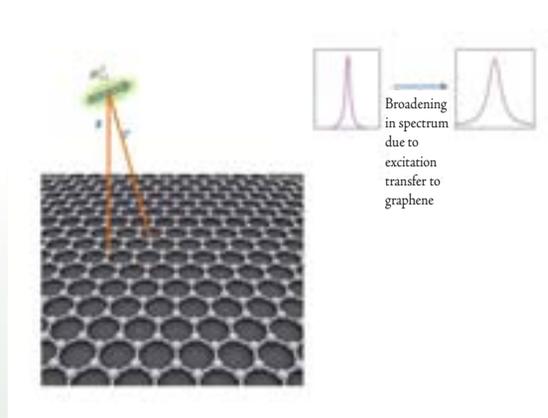


Theory of Energy Transfer in the Photosystem

The FMO complex (part of the photosystem of the green sulfur bacteria), has seven porphyrins, and it has been experimentally demonstrated by Fleming et. al. in 2007 that quantum coherence is important in transferring the energy from the site of excitation to the reaction center. The retention of quantum coherence in the hot and humid surroundings of a biological system is extremely surprising. There have been theoretical approaches which analyze the time evolution of the system using an appropriate Hamiltonian, which show the retention of coherence. The techniques currently available are heavily numerical and hence extremely difficult to apply to bigger systems. We have developed an almost analytical approach to the problem, based on the idea of using the adiabatic eigenfunctions. This allows us to do the calculation in

a fairly easy manner and we find that population relaxation among the adiabatic states is extremely important in determining the efficiency of the process. We have used our method to calculate the time scale of the retention of

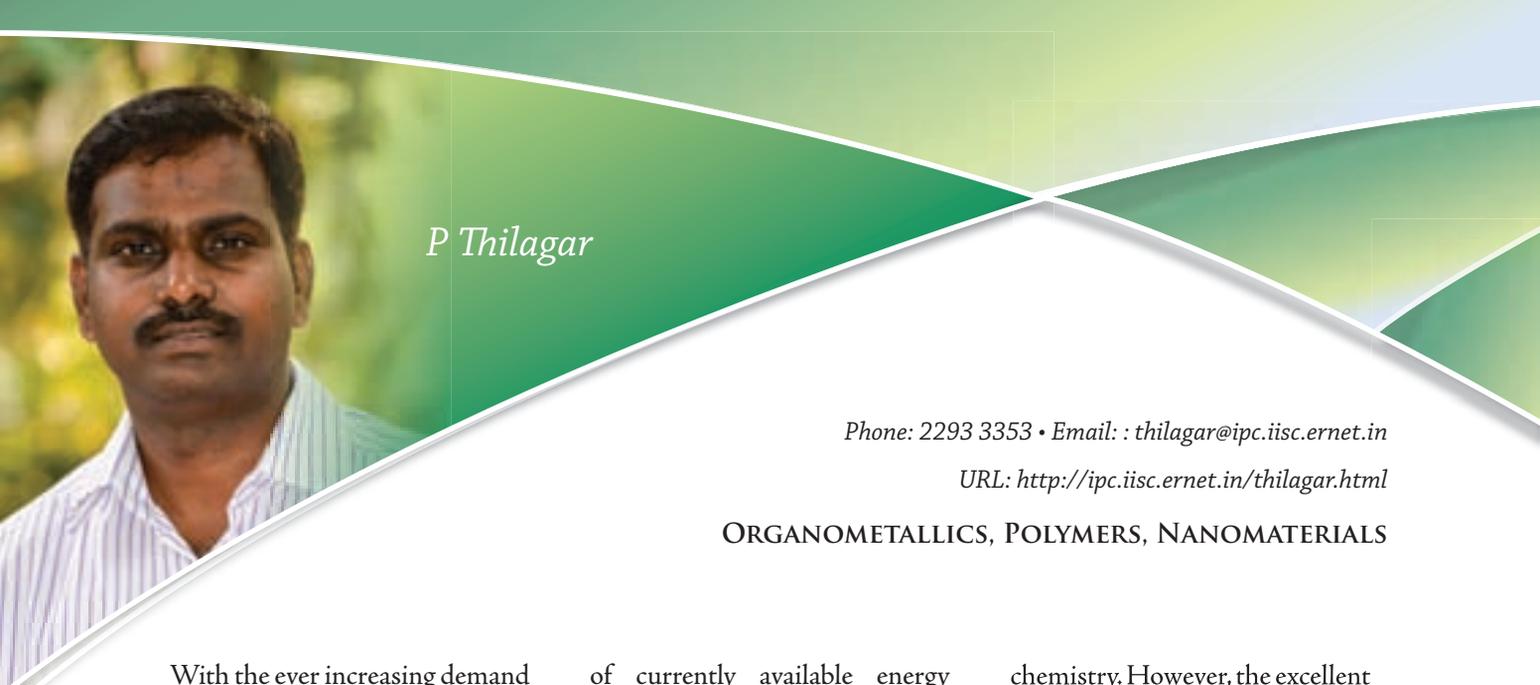
coherence for a Hamiltonian that was obtained from molecular dynamics simulations. For this Hamiltonian, we found the retention of electronic coherence to be much shorter than experimentally observed.



In this image, we show an excited dipole located at a distance z from the graphene sheet. It is possible for the dipole to transfer the excitation energy to graphene, with the dipole getting de-excited and graphene getting electronically excited. This excitation transfer will modify the lifetime of the dipole and will get reflected as a broadening in the spectrum of the dipole.

Selected publications

- Bhattacharyya, Pallavi and Sebastian, K. L. Adiabatic Eigenfunction Based Approach to Coherent Transfer: Application to the Fenna-Matthews-Olson (FMO) Complex and the Role of Correlations in the Efficiency of Energy Transfer, *Journal of Physical Chemistry A*, 117, 8806 (2013).
- Janakiraman, Deepika and Sebastian, K. L., Path-integral formulation for Levy flights: Evaluation of the propagator for free, linear, and harmonic potentials in the over- and underdamped limits, *Physical Review E*, 86, 061105 (2012).
- Santo K P and Sebastian, K L: Dynamics of loop formation in a semiflexible polymer, *Physical Review E*, 80, 061801 (2009).
- Swathi, R. S. and Sebastian, K. L. Long range resonance energy transfer from a dye molecule to graphene has (distance)⁻⁴ dependence, *J. Chem. Phys.*, 2009, 130, 086101 (2009).
- Sebastian, K. L. and Paul, A.K.R: Kramers problem for a polymer in a double well, *Physical Review E*, 62, 927 (2000).



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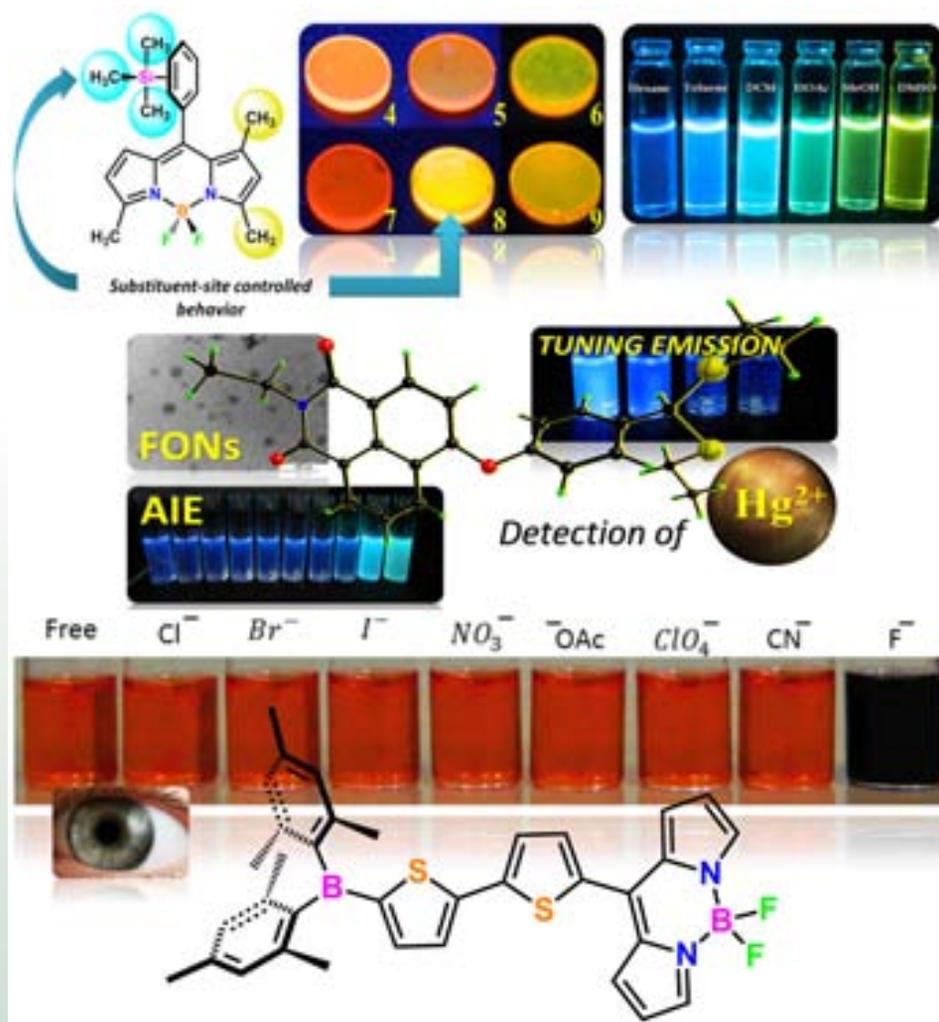
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ORGANOMETALLICS, POLYMERS, NANOMATERIALS

With the ever increasing demand of energy in modern societies and the limited reserves of fossil fuels, mankind have been compelled to search for alternate and sustainable energy resources. Apart from the development of new energy harvesting materials, energy efficient devices are of another primary concern to postpone the exhaustion

of currently available energy resources (fossil fuels). In this regard, organic optoelectronic materials playing major role due to their high efficiency and low production cost with respect to their inorganic analogues. Boron, the neighbour of carbon in periodic table, has been always regarded as an indispensable part of modern synthetic organic

chemistry. However, the excellent optoelectronic properties of boron based materials have only been exploited in modern era. In the relatively small expanse of time, tricoordinate triarylboranes and tetracoordinate BODIPY dyes have emerged as potential and one of the sought after candidates in various fields of "Organic Materials." Combining



Three different aspects of BORON chemistry. Sensing environmentally and biologically important ions and molecules (top). Understanding the energy and electron transfer processes in energy efficiency related materials (right). BORON in biomedical applications (left)



our academic curiosity with quest for developing new materials we are trying to find answer for fundamental questions related to chemistry and chemical biology. Our area of research is highly interdisciplinary, involving aspects of organic, organometallic, polymer and Nanomaterials chemistry. Our

group is engaged in the design and synthesis of new molecules/materials containing *p*-block elements (special attention on BORON) for the potential application in the field of Catalysis, Molecular Electronics (OLEDs, TFTs and solar cells), and Chemosensory materials. We are also involved in design

and synthesis of boronopeptides. In Biology, boronopeptides play a vital role as enzyme inhibitors (special attention on proteasomes), sugar sensors and lectin mimics.

Selected publications

- S. K. Sarkar and P.Thilagar; Chem. Commun., 2013, 49, 8558-8560.
- S. Mukherjee and P.Thilagar; Chem. Commun., 2013, 49, 7292-7294.
- Pagidi Sudhakar, S. Mukherjee, and P. Thilagar; Organometallics, 2013, 32, 3129–3133.
- C. A. Swamy P, S. Mukherjee and P. Thilagar; J. Mater. Chem. 2013, 1, 4691-4698.
- C. A. Swamy P, S. Mukherjee and P. Thilagar; Chem. Commun., 2013, 49, 993-995.



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LASER SPECTROSCOPY AND BIOPHOTONICS

Laser Spectroscopy Group:

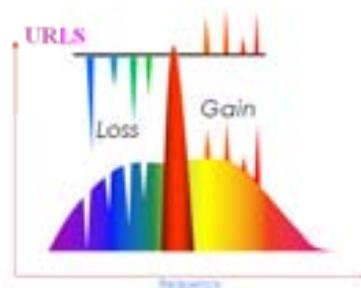
Our research group is interested in the applications of laser spectroscopy in Physics, Chemistry and Biology. In particular, we are interested in understanding the molecular structure, from the point of view of changes in vibrational energies, bond angles and bond lengths during a chemical reaction or a biological process. We use variety of techniques to explore the wide spectrum of questions in physics, chemistry and biology. These techniques include (a) Spectroscopic Imaging (Raman and Infrared imaging), (b) Raman, Resonance Raman, Infrared and fluorescence spectroscopies, (c) Time resolved spectroscopic methods, in nano-second and femto-second time resolution, (d) Terahertz Raman spectroscopy and (e) Instrumentation Development.

Ultrafast dynamics

“Ultrafast” can be defined as any process that occurs in the order of 10^{-15} seconds. There are many photochemical and photophysical processes that occur in this time scale. In order to understand the dynamics of these processes one need to have a time resolution of fs along with a good spectral resolution. Even though the conventional femtosecond Raman spectroscopy may provide fs time resolution but they are limited to a low spectral resolution owing to the broad spectral width constrained by the uncertainty principle. However,

this transform limit can be overcome by Femtosecond Stimulated Raman Spectroscopy (FSRS). It transcends the transform limit by decoupling the spectral and time resolutions and thus enables us to obtain Raman spectra within fs time resolution along with a low spectral resolution ($\sim 15 \text{ cm}^{-1}$). Using this unique combination of spectral and time-resolution of FSRS, we are interested in studying the structural and reactive dynamics of various chemical systems.

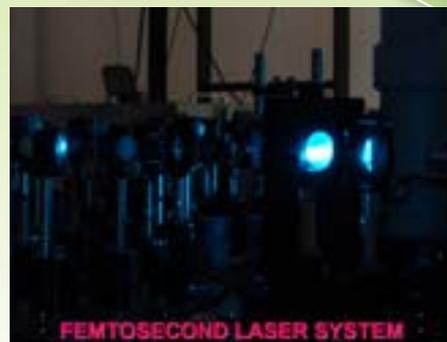
Recently, we have developed a nonlinear technique, which we refer as the “Ultrafast Raman Loss Scattering (URLS)” that has many unique advantages over other methods like, coherent anti-Stokes Raman scattering (CARS), picosecond optical Kerr-gate effect and stimulated Raman scattering (SRS). URLS is an analogue of SRS but more sensitive. It involves the interaction of the two laser sources, *viz.* a picosecond (ps) pulse and white light (WL), with the sample leading to the generation of loss signal on the higher energy (blue) side with respect to the wavelength of the ps pulse unlike the gain signal observed on the lower energy (red) side in SRS. These loss signals are at least 1.5 times more intense than SRS signals. Also, the very prerequisite of the experimental protocol for signal detection to be on the higher energy side by design eliminates the interference from fluorescence, which generally appears on the red side. Unlike CARS, URLS signals are not



precluded by non-resonant background under resonance condition and also being a self-phase matched process is experimentally easier. Thus, the rapid data acquisition, natural fluorescence rejection and experimental ease make the Ultrafast Raman loss scattering (URLS) as a unique valuable structure determining technique.

Resonance Raman spectroscopy

In this area, our objective is to study the fundamental processes in photochemistry and photophysics. We are interested in understanding the molecular architectural changes and its implications to the excited state reactions by applying the combined nanosecond laser flash photolysis (LFP) and time resolved resonance Raman (TR3) techniques. In particular, our interest revolves around, understanding photo induced electron transfer, electronic excited state dependent chemical dynamics, influence of vibronic coupling in photochemical and photophysical processes. Understanding solvent effects on excited state structure and the corresponding reactivity is also an important area of our research interest.



Most of these studies are supported by density functional theory (DFT) and Amsterdam density functional (ADF) programme based computational studies. The computational methods are used to understand the normal mode compositions of a given molecule in the excited state or the intermediate states. The molecular systems of interest include aromatic and heteroaromatic ketones, quinones, xanthenes, polymers, inorganic complexes etc.

Biophotonics

Biophotonics involves application of laser spectroscopy to biology and biomedicine. The activities in this group are devoted to, study of different aspects of brain cancer, from diagnostic as well as prognostic point of view, towards the early detection of cancer, stem cell recognition, study of human neurodegenerative diseases in drosophila as a model, functioning of nerve fibers and dendritic spines, muscles disorders and liver related injuries. Our aim in all these experimental studies is to detect spectroscopic signatures responsible for the disorders as early as possible

and to interpret the molecular structural changes in relation to the mechanism involved. To unravel the biochemistry of life we are using Infrared and Raman imaging systems in all the above-mentioned projects. Apart from disease manifestations we work on pharmacodynamics aspects of diseases too. Here we are trying to identify the effect of existing drugs in curing diseases and their molecular mechanisms, these studies can help in the development of newer and potent drug derivatives.

Terahertz Raman Spectroscopy (THZR)

THZR spectroscopy enables recording of Raman spectra in the spectral range 10 to 300 cm^{-1} . Until recently this region of spectral observation has been either extremely difficult due to Rayleigh scattering or extremely expensive involving multiple spectrometers such as triple monochromators. We have built a simple and robust THZR spectrometer using novel BRAGG filters. The THZR frequency range is of particular importance since the corresponding energy

reflects protein-protein interactions, protein tertiary structural changes, electrostatic interactions, Van der Waal's interactions, solvent librational motions, etc. Thus a study of such low energy contributions to reaction dynamics would lead to fundamental understanding of chemical, physical and biological processes.

Instrumentation Development

Our other research interest is in developing new instrumentation towards security, medical and pharmaceutical applications. We have recently developed a novel technique called the Universal Multiple Angle Raman Spectroscopy (UMARS), which provides the opportunity to measure Raman signals from hidden chemical samples buried inside other chemical materials. This has potential applications in detecting explosives and also in scanning and imaging human tissues and bones.

Selected publications:

- R Pandey and S Umapathy, Solvent induced changes on the polarity of the triplet excited state of 2-chlorothioxanthone from time resolved absorption and Raman spectroscopy, 2014, Chemical Physics, 478, 175.
- S Sil, D Chaturvedi, K B Krishnappa, S Kumar, S N Asthana and S Umapathy, DFT modeling, electrostatic surface potential and SERS studies on biosynthesized silver particles: Observation of 400pM sensitivity to explosives, 2014, J. Phys. Chem.A., 118 (16), 2904.
- A Z Samuel and S Umapathy, Energy funneling and macromolecular conformational dynamics: A 2D Raman correlation study of PEG, Nature Polymer Journal, 2014, 1.
- S Sil and S Umapathy, Raman spectroscopy explores hidden materials in depth: universal multiple angle Raman spectroscopy, 2014, Nature Scientific Reports, 4, 5308.
- Identification of early biomarkers during acetaminophen-induced hepatotoxicity in mice by Fourier transform infrared microspectroscopy, R Gautam, B Chandrasekar, M Deobagkar, S Rakshit, B N Vinaykumar, S Umapathy and D Nandi, 2012, PLoS ONE, 7, e45521.



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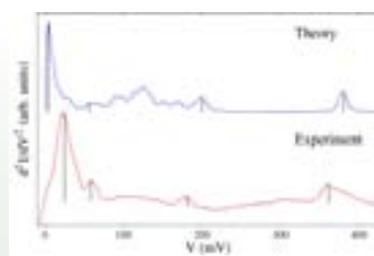
NONEQUILIBRIUM TRANSPORT PROCESSES AND OPTICAL RESPONSE IN NANOFUNCTIONS

Recent advances in technology have provided an unprecedented space-time precision to explore molecules at atomistic level. Quantum effects and thermal fluctuations play a significant role at such small length scales. These effects show up most readily in conductance measurements of single molecular junctions such as scanning tunnelling microscopy (STM). We use statistical models to quantify quantum and many-body effects in the nonequilibrium transport of particles (electrons and phonons) in molecular junctions (quantum junctions). Our approach is based mainly on the quantum master equation and the many-body Green's function formalism. These methods can be easily extended to study nano-scale devices such as quantum heat engines under real working (nonequilibrium) conditions.

Inelastic resonances in molecular current: When an electron tunnels through a molecular junction, it may exchange energy with molecular vibrations. These vibrations have been detected in single molecule experiments. These inelastic interactions show up as peaks in the conductance measurement at vibrational resonances. The inelastic

scattering opens up new pathways for electrons to tunnel from one side of the junction and leads to the enhancement in conductance of the quantum junction. These inelastic resonances are used to study structure of molecules/impurities adsorbed on metal surfaces.

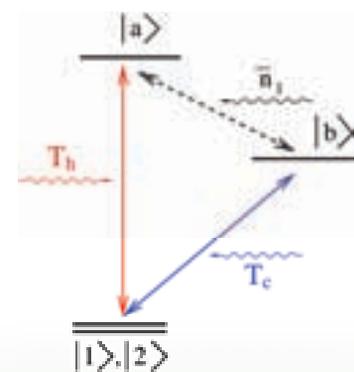
In STM experiments, tunnelling electrons act as a probe for the allowed (empty) density of states (DOS) on the molecule. Several theoretical methods are available to compute the nonequilibrium DOS. In most cases, the nonequilibrium Green's function (NEGF) formulation provides an exact approach to calculate the DOS in presence of many-body interactions.



Experimental (red) and calculated (calculated) inelastic spectra of paracyclophane derivative (3Rd) in STM. The intensities of the peaks are marked by vertical black lines.

Nano scale heat engines: Quantum heat engines (QHE) form basis to

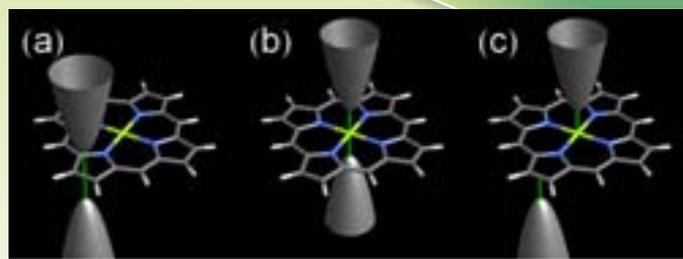
understand the working mechanism of several natural and man-made nanodevices such as photosynthesis cells and photovoltaic (Solar) cells, where the quantum coherences play a significant role in determining the efficiency of heat engines. The basic mechanism of QHE can be understood in terms of simple model systems that convert heat energy to coherent photons. Recent studies show that the quantum effects can be used to manipulate thermodynamic properties of such machines.



A four level QHE model which is coupled to two thermal baths at temperatures T_H and T_C ($T_H > T_C$) and to a cavity mode with occupation n_r .

Unlike in a classical heat engine, where the energy spectrum is continuous, energy exchanged between a quantum working system and a heat reservoir is

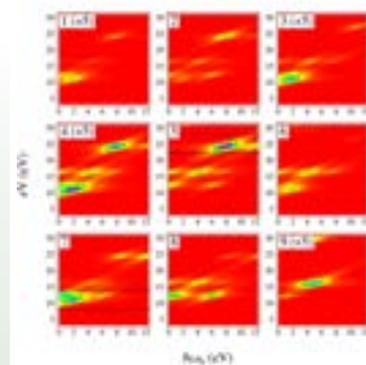
Geometrical configurations of the source (top) and drain (bottom) electrode with respect to MgP molecule



quantized. Therefore the QHEs are modelled as a collection of a finite set of energy levels coupled to two thermal reservoirs at different temperatures. Because of the small size, quantum coherences can be induced and maintained in the (working) system. The quantum coherences provide an extra degree of freedom that can be manipulated to optimize the engine operation and, with suitable tuning, may lead to dramatic changes in the thermodynamics of QHEs. The performance of a practical heat engine is characterized by its power and efficiency. It is desirable to have the maximum efficiency and the output power. Efficiency is maximum for a Carnot heat engine, but the corresponding power is zero (work is done infinitely slowly). In practice, heat engines work away from their equilibrium and therefore have non-zero output power.

Optical response at nano junctions: Optical response of molecules and its effects on the conduction properties at single-molecule junctions is an area of potentially important applications. Although, traditional optical spectroscopy can explore only the micro-meter length-scales, recent developments in instrumentations and new optical techniques have opened new possibilities to study optical response at the level of single molecules. This has allowed better structural characterization of molecular junctions using optical probes. Optical spectroscopy of molecular junctions has a natural advantage of local field enhancement due to plasmon excitation of metal electrons. In a current-carrying state, the molecule is stochastically exchanging electrons with the metal leads. It therefore continuously

explores its various charged (both cation and anion) states. The optical signal comes not only from neutral but also from the charged states of the molecule as well. This opens up a possibility to study the dynamics of molecular charged states and their correlations using two-dimensional spectroscopic techniques.



Two-dimensional current-induced fluorescence spectrum of benzene as a function of photonenergy $\hbar\omega$, and bias energy eV at different lateral tip positions at constant height 1\AA above the molecule.

Selected publications:

- H. P. Goswami, U. Harbola, Phys. Rev. A 88, 013842 (2013).
- S. Rahav, U. Harbola and S. Mukamel, Phys. Rev. A 86, 043843 (2012).
- J. B. Maddox, U. Harbola, N. Liu, C. Silien, W. Ho, G. C. Bazan, and S. Mukamel, J. Phys. Chem A, 110, 6329 (2010).
- U. Harbola and S. Mukamel, Phys. Rep. 465, 191(2008).
- U. Harbola, M. Esposito, and S. Mukamel, Phys. Rev. B 74, 235309 (2006).



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PHYSICAL CHEMISTRY OF MATERIALS

The main focus of our research has been in the area of Physical Chemistry of low dimensional materials with emphasis on the host-guest chemistry in layered and porous host lattices. The insertion of guest molecules and polymers into inorganic host lattices, usually layered or porous solids has been an attractive route for the synthesis of new materials as well as a source of new phenomena. Insertion can, in principle, lead to materials which combine the functionality and reactivity of the guest with the mechanical strength, thermal stability and electronic properties of the host and so possess properties which may not be achieved by either component separately. We have carried out detailed investigations of guest molecules inserted by intercalation into the galleries of the layered solids and by encapsulation in the voids of microporous zeolites. Confinement affects properties of both host and guest and our efforts have been to understand the nature of these changes and how these reflect on host-guest interactions.

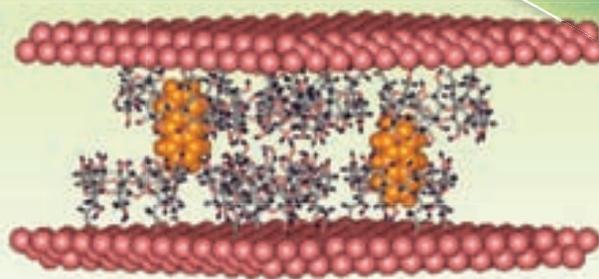
Layered solids The intercalation chemistry of the layered metal chalcogenophosphates, MPS_3 ($M=Mn, Fe, Ni, Zn$ or Cd and $X=S$ or Se) has been investigated.

When M is a paramagnetic ion both crystallographic and magnetic lattices are two-dimensional and exhibit anti-ferromagnetic ordering at low temperatures. We have shown that this family of compounds are unique in that the spin-dimensionality can be controlled either by the choice of the transition metal or the chalcogen. The intercalation chemistry of the MPS_3 compounds is quite different from other layered materials. They undergo a rather unusual ion-exchange intercalation reaction; solvated cationic guest species insert into the interlamellar space with an equivalent loss of divalent metal ions leaving random immobile vacancies in the layer. The guest cationic species and the neutral molecules solvating them may be independently exchanged giving rise to a rich diversity of intercalation compounds. In addition when M is a paramagnetic ion intercalation leads to profound changes in magnetic properties. The organization and motion of guest species confined by intercalation within the galleries of layered solids using a variety of spectroscopic methods as well as dielectric, conductivity and magnetic measurements. The systems that we have looked at include intercalated

hydrated alkali-metal cations and intercalated alkali-metal polymer-electrolytes formed by replacing the hydration shell of the intercalated alkali-metals by polyethylene-oxide or polypropylene oxide. We show that the properties of these guest species confined to the 'flatland' of the interlamellar region are quite different from those exhibited by these molecules in the bulk.

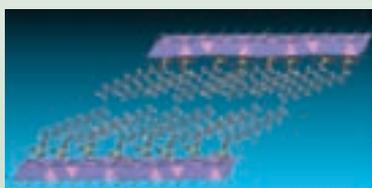
Hybrid materials formed by insertion of guest molecules in nano-structured host lattices constitute a promising class of materials with functionalities that may differ from the either host or guest. Inorganic layered solids in which guest species can access interlamellar space via the intercalation reaction offer a unique route to the design of new hybrids. The host guest chemistry of most layered hosts are restricted to ion exchange reactions; the choice of guest are limited to ionic species since they have to compensate for the charge deficit, either positive or negative, of the layer. We have shown how this limitation may be overcome by functionalizing the internal surface of the host by grafting either long chain surfactants or cyclodextrin cavities to the gallery walls.

Functionalized Layered and Nano-materials



Functionalization converts the essentially hydrophilic interlamellar space into one that has considerable hydrophobic or “organophilic” character. A variety of neutral and non-polar guest molecule may now be introduced within the inorganic solid. These organic-inorganic host lattices combine to provide the best of both worlds; the host – guest chemistry of the anchored organic host with the mechanical and thermal robustness of the inorganic solid.

Different phases of long chain intercalated surfactants - monolayer, bilayer, and interdigitated bilayers - can be realized by altering the grafting density within the galleries of the layered solid. Our efforts have been to establish a quantitative

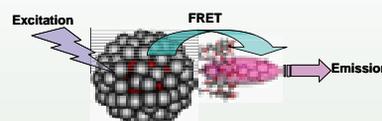


correlation between molecular conformational order and the thermodynamic transitions of the intercalated surfactant bilayer. The techniques developed have been used to understand the conformation, dynamics and melting of the alkyl chains in an anchored bilayer

Functionalized nanomaterials.

The strategies for functionalizing the galleries of layered solids have been extended to nanomaterials. Water soluble nanocrystals of ZnO, MoS₂ and FeO/Fe₃O₄ have been synthesized by capping with cyclodextrin cavities while nanomaterials soluble in non-polar solvents prepared by capping with long chain surfactants. The integrity of the capping cyclodextrins are preserved and available for host-guest chemistry. It is thus possible to include guest molecules within these cavities and thus combine the functionality of the guest with the properties of the nanocrystal in a

single supra-molecular assembly. The functionalized nanomaterials have been used for diverse applications from water remediation to drug delivery. We have shown that the organic chromophore Nile Red may be included within the cyclodextrin cavities capping ZnO nanocrystals and demonstrated that Resonance energy Transfer occur from the ZnO to the Nile red on band gap excitation of the ZnO



Selected publications:

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- Rakshit, S.; Vasudevan, S. Resonance Energy Transfer from β -Cyclodextrin-Capped ZnO:MgO Nanocrystals to Included Nile Red Guest Molecules in Aqueous Media. *ACS Nano* 2008, 2, 1473
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- Mohanambe, L.; Vasudevan, S. Aromatic Molecules in Restricted Geometries: Photo-physics of Naphthalene Included in a Cyclo-dextrin Functionalized Layered Solid. *J. Phys Chem B* 2005, 109, 22523

RESEARCH FACILITIES

The department of Inorganic and Physical Chemistry is equipped to carry out state of the art research in a wide variety of fields. The facilities are constantly upgraded to keep up with modern developments.

Each research group maintains essential instrumental facilities needed for their routine experiments such as metal vapor synthesizer, vibrating sample magnetometer, differential scanning calorimeter, dry-boxes, high pressure reactors, Nd-YAG and dye lasers, nanosecond fluorimeter; CCD detectors; Spex double monochromator, Femtosecond laser and electrochemical systems. A home-built FT microwave spectrometer is the only one of its kind in India. A new Tissue Culture lab to study drugs related to cancer and other related diseases is setup.

In addition, the department maintains UV-Vis, Steady state fluorescence, Time resolved Fluorescence, FT-IR, FT-Raman spectrometers and a multinuclear magnetic resonance (NMR) spectrometer. An atomic absorption spectrophotometer, C H N elemental analyzer and Atomic Force Microscope (AFM) are also available. Other instruments in the department are surface area and pore structure analyzers, simultaneous DTA-TGA and DTG analyzer and a single crystal and powder X-ray diffractometers. Tunneling Electron Microscopy (TEM), HR Mass spectrometer.

An ESI-Mass Spectrometry Facility has been set up as part of the Institute initiative to augment spectroscopic facilities. In addition to the above, several facilities of the Institute are available for use by the Department:

- Spectroscopy and Analytical Test Facility
- Institute X-Ray Facility
- CCD based single crystal X-ray diffractometers
- Super Computers
- Electron Microscopes
- A full fledged Cryogenics Facility
- Bruker 500 and 400 MHz spectrometers
- Bruker DSX 300 MHz Solid-state NMR spectrometers
- SQUID Magnetometer
- Confocal Fluorescence Microscope
- Raman Microscope
- Infrared Microscope

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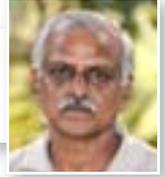


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