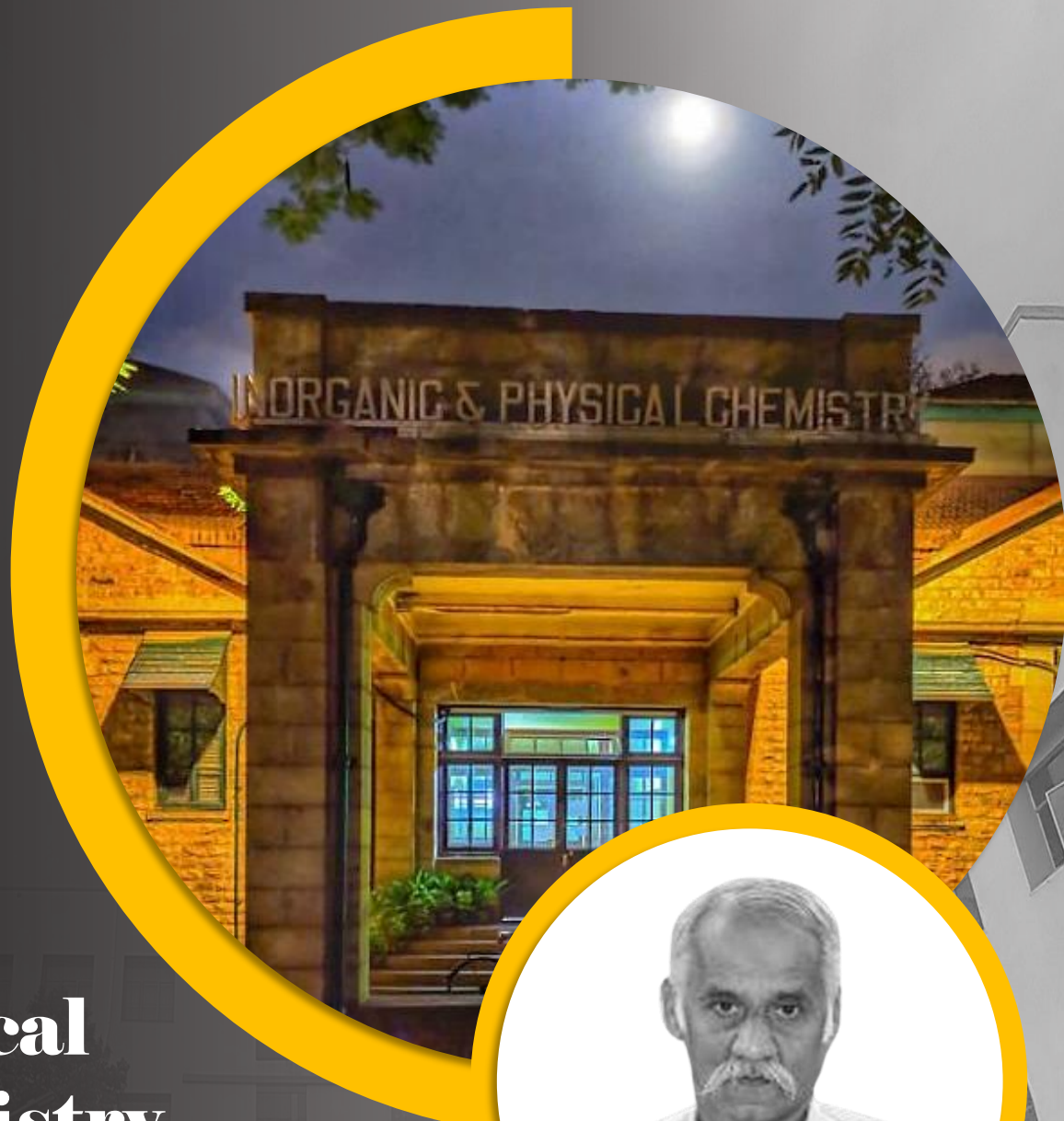




IISc, Bangalore



# Physical Chemistry Symposium 2023

3rd – 5th July

Faculty Hall



Department of Inorganic And Physical Chemistry  
Indian Institute of Science, Bangalore

# Welcome to Physical Chemistry Symposium 2023

A warm welcome to all the participants of the Physical Chemistry Symposium organized by the Department of Inorganic and Physical Chemistry, Indian Institute of Science. This symposium is organized during 3-5 July 2023, to celebrate the contributions of three of our colleagues: Prof. P. K. Das, Prof. B. J. Cherayil and Dr. M. Netaji, who have all served in our Department for several decades.

In 2022, our Department moved from the iconic IPC Building, the first to be built for the Indian Institute of Science, to the Chemical Sciences Building, which houses our Department and the Department of Organic Chemistry and the Solid State and Structural Chemistry Unit. The symposium will be held at the Faculty Hall, right next to the IPC Building and a lunch at the Chemical Sciences Building is planned for the 5<sup>th</sup> July 2023. This will give the participants ample opportunity to visit our old and new homes!

Prof. P. K. Das got his MSc in Chemistry from IIT Kanpur in 1980 and his Ph. D. from Columbia University in 1984. After a postdoctoral stint with Nobel laureate J. C. Polanyi at the University of Toronto, he joined our Department as a Lecturer in 1986. He rose through the ranks and has been serving as a Professor since 2002. He served as the Chair of IPC during 2013-15 after which he served the Institute as the Divisional Chair of the Chemical Sciences Division until 2020. He has established an experimental physical chemistry laboratory with state-of-the-art equipment and has worked on diverse areas starting from gas phase photodissociation dynamics to protein adsorption on nanoparticles. He established a facility for second harmonic generation measurement, which was used by his collaborators from all over the world.

Prof. B. J. Cherayil got his MSc from IIT Madras in 1980. He went on to do an MS from University of Maryland (1983) and Ph. D. from University of Chicago (1987). After a postdoctoral stint at Cornell University, he joined our Department as an Assistant Professor in 1990. He has been serving as a Professor since 2002. He had been a visiting professor at Harvard, Stanford and University of Chicago several times in the last three decades. Prof. Charayil has established a vibrant research group in our Department and trained students in doing research in analytical theory, done by very few today. As a theoretician, he has worked on very diverse problems, including enzyme catalysis showing that Micahelis-Menton mechanism works at a single molecule level.

Dr. M. Netaji did his MSc in Physics from National College, Trichi (Madras University) and went to do Ph. D. at Madras University, submitting his Thesis in 1987. He joined our Department as a Research Associate in 1988 and rose through the ranks to become a Chief Research Scientist. He has trained many students using crystallography in their work. He had helped many groups from the Department, Institute and the Country collecting reliable crystallographic data, which helped them all in improving the quality of research. His group has solved the crystal structures of an extensive range of phosphazanes and phosphazenes, calixarenes and their metal complexes. The results have provided new insights into the nature of the P-N bonds which is one of the most intriguing in chemistry.

The program is listed in the next pages, including the abstracts of all the talks. The talks cover a wide range of topics in physical chemistry. I wish all the participants an exciting three days of stimulating talks, discussions, and informal interactions.



**E. Arunan,  
Chair, IPC**

# Physical Chemistry Symposium 2023

3<sup>rd</sup> – 5<sup>th</sup> July, Faculty Hall, Indian Institute of Science, Bangalore

## Schedule

All talks are in 30 mins + 5 mins Q&A format

Time	Speaker	Title
<b>Monday</b>	<b>3<sup>rd</sup> July 2023</b>	
8:50 am	Welcome	
<b>Session 1</b>	<b>Chair: Priyadarsi De</b>	
9:00 am	<b>Parbati Biswas</b>	Conformation And Relaxation Dynamics Of Ring Polymers In Dilute Solutions
9:35 am	<b>K. Srihari</b>	Isomerization In An Optical Cavity: Lessons From A Simple Model
10:10 am	<b>S. K. Asha</b>	Eco-Friendly Synthetic Strategies For Conjugated Polymers
10:45 am	<b>Tea/Coffee</b>	
<b>Session 2</b>	<b>Chair: Dulal Senapati</b>	
11:05 am	<b>S. Umamathy</b>	Influence Of Solvents In Chemical Reactions: A Raman Study
11:40 am	<b>Ravindra Pandey</b>	Understanding Nanoparticle Membrane Interactions By Probing The Interfacial Water Structure In Response To Surface Charges
12:15 pm	<b>Himangshu P. Goswami</b>	Learning Heat Engines' Quantum Space From Nonequilibrium Fluctuations
12:50 pm	<b>Lunch</b>	
<b>Session 3</b>	<b>Chair: Rohit Srivastava</b>	
2:30 pm	<b>Prasanta Das</b>	Infrared Absorption Of Phenolated Triclosan In Aqueous Solution
3:05 pm	<b>Ananya Debnath</b>	Interface Water Probes Heterogeneity Length And Time Scale Of Membranes
3:40 pm	<b>Tea/Coffee</b>	
<b>Session 4</b>	<b>Chair: Rama Kant</b>	
4:00 pm	<b>Srabanti Chaudhury</b>	Simple Discrete State Stochastic Approaches To Probe Reaction Dynamics In Chemical And Biological Processes
4:35 pm	<b>Priyadarsi De</b>	Amino Acid-Derived Alternating Polyampholytes
5:05 pm	<b>N. Sivakrishna</b>	Crystallography And In Silico Studies Of Cyclin Dependent Kinases (Cdk) And Sulphonamides: For The Development Of Potent Anticancer Drugs
<b>7:00 pm</b>	<b>Conference Dinner (Main Guest House)</b>	
<b>Tuesday</b>	<b>4<sup>th</sup> July 2023</b>	
<b>Session 5</b>	<b>Chair: S. K. Asha</b>	
9:00 am	<b>Paresh Chandra Ray</b>	Influence Of Quantum Confinement On The Linear And Nonlinear Optical Properties Of Nanoscale Materials For Possible Biomedical Applications

9:35 am	<b>Rama Kant</b>	Theory For Electron Transfer On Atomically Stepped Electrode/Electrolyte Interface
10:10 am	<b>P. Elumalai</b>	Tuneable Electrocatalytic Activities Of Nanocomposites As Air-Breathing Electrode For Rechargeable Li-Air Battery
10:45	<b>Tea/Coffee</b>	
<b>Session 6</b>	<b>Chair: Parbati Biswas</b>	
11:05 am	<b>Ganapathy Ayappa</b>	Using Molecular Dynamics Simulations To Study Interactions Of Molecules With The Bacterial Cell Envelope
11:40 am	<b>Dulal Senapati</b>	Concepts Of Physical Chemistry To Design Nanoscale Materials For Energy, Sensing, And Therapeutics
12:15 pm	<b>Debarati Chatterjee</b>	Probing The Facilitated Diffusion Of DNA Target Search By A Binding Protein In A Disordered Background
12:50 pm		
<b>Session 7</b>	<b>Chair: Ravindra Pandey</b>	
2:30 pm	<b>B. Rajakumar</b>	Temperature Dependent Kinetics Of Criegee Intermediate With N-Butyraldehyde And Isobutyraldehyde Using Cavity Ring Down Spectroscopy
3:05 pm	<b>Bedabyas Behera</b>	Detailed Mechanism And Kinetics Of Reactions Of Anti- And Syn-CH <sub>3</sub> CHOO With HC(O)OH: Infrared Spectra Of Conformers Of Hydroperoxyethyl Formate
3:40 pm	<b>Tea/Coffee</b>	
<b>Session 8</b>	<b>Chair: Shubhadip Chakraborty</b>	
4:00 pm	<b>Nandita Maiti</b>	Novel Plasmonic Nanomaterials For Sensing Of Environmental Pollutants And Investigating Light-Induced Surface Reactions
4:35 pm	<b>Pallavi Debnath</b>	A Few Analytical Calculations In Polymers
<b>Wednesday</b>	<b>5<sup>th</sup> July 2023</b>	
<b>Session 9</b>	<b>Chair: Srabanti Chaudhury</b>	
9:00 am	<b>Manabendra Chandra</b>	Harvesting Hot Charge Carriers Via Visible-Light Excitation Of Plasmonic Nanoparticles For Photocatalysis
9:35 am	<b>Rati Sharma</b>	Exploring Signalling Pathways Through Theory And Experiment
10:10 am	<b>Naiwrit Karmodak</b>	Multiscale Modelling Of The Stability And Catalytic Activity Of Materials In Electrochemical Environments
10:45 am	<b>Tea/Coffee</b>	
11:00 am	<b>Group photo</b>	
11:15 am	<b>Visit to Chemical Sciences Building and Lunch</b>	

# Conformation and Relaxation Dynamics of Ring Polymers in Dilute Solutions

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## **Abstract:**

A ring polymer is formed by joining the free ends of a linear polymer. The interest in ring polymers is motivated by the biological relevance of its cyclic architecture. Many biopolymers such as DNA, lipids, polysaccharides, and polypeptides exist naturally in the form of ring. Ring polymers in different solution conditions may be an excellent model system for exploring the properties, interactions, packing and specific functions of these circular biomolecules. The conformational properties, rheology and segmental relaxation dynamics of ring polymers are investigated within the framework of optimized Rouse-Zimm theory. Smaller rings relax faster than larger rings and their respective linear analogues. The hydrodynamic interactions decrease the higher relaxation rates corresponding to the local relaxation modes and increase the smaller relaxation rates which correspond to the collective relaxation modes. The structural properties, like the mean square radius of gyration, static structure factor, scattering intensity, the fractal dimensions, and the mean square intermonomer distances of ring polymers in are calculated in dilute solutions with excluded volume interactions, where the strength of these interactions are evaluated from Flory's mean field theory. The mechanical moduli are dominated by the smaller relaxation rates corresponding to the collective relaxation modes in the low frequency regime, while they are governed by the higher relaxation rates. The characteristic overall relaxation time is found to be same for the rings of various sizes with excluded volume interactions, whereas it shifts to lower frequencies with increasing ring sizes for the Rouse rings.

## References :

1. Handa M., and Biswas P. *Macromols.* **2022**, *55*, 2182.
2. Handa M., and Biswas P. *J. Rheol.* **2021**, *65*, 595.
3. Handa M., and Biswas P. *J. Rheol.* **2021**, *65*, 381.
4. Handa M., and Biswas P. *Soft Mat.* **2019**, *15*, 5896.

# ISOMERIZATION IN AN OPTICAL CAVITY: LESSONS FROM A SIMPLE MODEL

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Theoretical understanding of the mechanism of rate modulation due to vibrational strong coupling is still incomplete[1,2]. A paradigmatic system that has been studied extensively involves an isomerization reaction, modelled by a double well potential coupled to an optical cavity. Explanations ranging from dynamical caging[3] at the transition state to dynamical resonant localisation[4,5] have been put forward to rationalise the sensitivity of the rates to the cavity frequency.

In this talk I will take the simplest model for isomerization[5] in an optical cavity to highlight the dynamical complexity. Although the model is far from representing the actual experimental situation, insights from our study[6] may underscore the importance of accounting for quantum effects[4], solvent dissipation[3,4], and cavity losses[4]. Calculations[6] reveal that even in this simple model one can have nontrivial competition between quantum tunnelling and cavity-system energy flow. As a result, both suppression and enhancement of the isomerization probability can occur depending on the initial reactant state. More specifically, I will show that tuning the cavity frequency results in a chaos-order-chaos transition in the classical phase space with significant consequences for the nature of the quantum polaritonic states that participate in the dynamics of an initial state.

[1] Campos-Gonzalez-Angulo, J. A.; Poh, Y. R.; Du, M.; Yuen-Zhou, J. Swinging between shine and shadow: theoretical advances on thermally activated vibropolaritonic chemistry. *J. Chem. Phys.* **2023**, *158*, 230901.

[2] Mandal, A.; Taylor, M. A. D.; Weight, B. M.; Koessler, E.; Li, X.; Huo, P. Theoretical advances in polariton chemistry and molecular cavity quantum electrodynamics. *10.26434/chemrxiv-2022-g9lr7* **2022**.

[3] Li, X.; Mandal, A.; Huo, P. Cavity frequency-dependent theory for vibrational polariton chemistry. *Nat. Commun.* **2021**, *12*, 1315.

[4] Lindoy, L. P.; Mandal, A.; Reichman, D. R. Quantum dynamical effects of vibrational strong coupling in chemical reactivity. *Nat. Commun.* **2023**, *14*, 2733.

[5] Fischer, E. W.; Anders, J.; Saalfrank, P. Cavity-altered thermal isomerization rates and dynamical resonant localisation in vibropolaritonic chemistry. *J. Chem. Phys.* **2022**, *156*, 154305.

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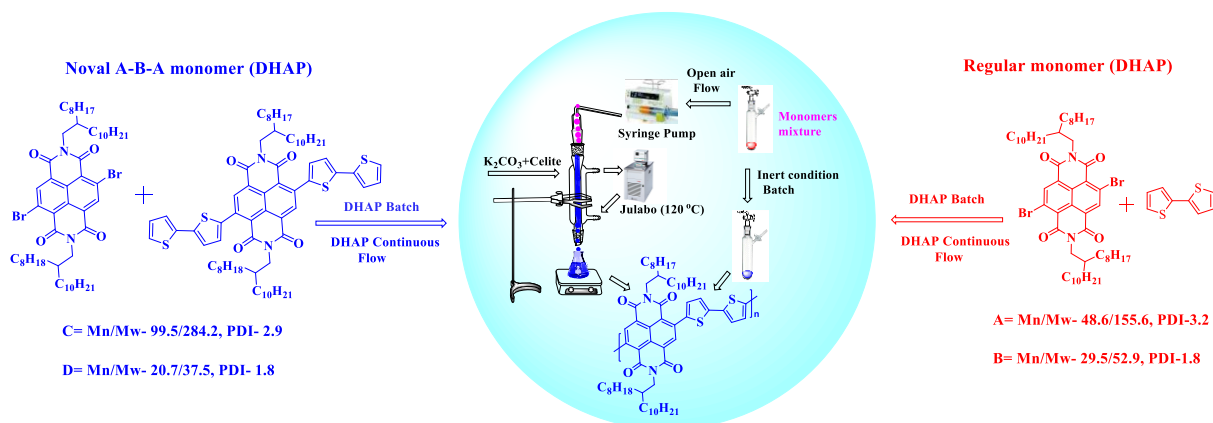
# ECO-FRIENDLY SYNTHETIC STRATEGIES FOR $\pi$ -CONJUGATED POLYMERS

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P(NDI2OD-T2), also known as N2200, is a commercially available donor-acceptor polymer, which is extensively investigated for its high electron mobility ( $> 0.85 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$  in OFET), high power conversion efficiency (PCE)  $\sim 5\%$  in all-polymer solar cells (PSC)s. Recently our group demonstrated the energy storage applications of composites of N2200 with carbon nanotubes (CNTs).<sup>1, 2</sup> The traditional methods for synthesizing these conjugated polymers can be impracticable for industrial-scale production due to the need for toxic pre-functionalized monomers and difficulties in purification. Our research group has been engaged in the development of the versatile acceptor polymers based on naphthalene diimide, by conventional and direct heteroarylation polymerization (DHAP) methods.<sup>3</sup> In my presentation I will discuss the research efforts from our group to develop cost-effective, scalable, and reproducible synthetic routes for P(NDI2OD-T2) polymer. Continuous flow polymerization, direct heteroarylation polymerization and recycling and reusing heterogeneous catalysts are some of the approaches that will be presented.<sup>2-4</sup>



*New A-B-A monomer design to synthesize P(NDI2OD-T2)*

- [1] Sandeep, S.; Roby, S.; Sreekumar, K. and Asha, S. K. *J Phys Chem C*, **2019**, *123*, 2084–2093.
- [2] Wavhal, B. A; Ghosh, M.; Sandeep, S.; Sreekumar, K. and Asha, S. K. *Nanoscale* **2021**, *13*, 12314 – 12326.
- [3] Kakde, N. R; Bharathkumar, H. J.; Wavhal, B. A; Nikam, A.; Patil, S. R.; Dash, S. R.; Vanka, K.; Krishnamoorthy, K.; Kulkarni, A. and Asha, S. K.. *J. Mater. Chem. C*, **2022**, *10*, 13025-13039.
- [4] N. R Kakde and S. K. Asha. *Polym Chem.*, **2023**. <https://doi.org/10.1039/D3PY00183K>



# Influence of Solvents in chemical reactions: A Raman study

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Solvent plays an important role in outcome of various chemical and biological processes. The effect of solvents polarity on the chemical reactions generally be explained through various solvents properties like polarity, viscosity etc. The majority of biological and chemical reactions take place in the solution phase. The solvents effect on the chemical reaction can be well understood from transition state theory. The solvents can affect the reaction rate by changing the relative energies of reactant, product and transition state. Solvents stabilization of the transition state barrier can increase the rate of reaction is often used as a qualitative measure of solvents effect on chemical reaction. Similarly, the solvents can solvate the solute differentially in the ground and excited state which manifested in the absorption and emission spectra as a change in the position, intensity and the bandwidth and known as electronic solvatochromism.

Solute–solvent interaction has significant influence on the structure of the solute. From solute structural point of view, solvation can be divided into static and dynamic processes. The static solvation refers to stabilization of the molecular structure by the solvent to achieve the equilibrium structure, both in the intermediate and ground state. Dynamic solvation relates to the solvent reorganisation-induced dynamics prior to structure reorganization to reach equilibrium geometry. These dynamics effect can influence the rate of ultrafast process such as electron transfer, proton transfer etc. Thus, dynamic solvation contributes to reaction rates that are typically faster than solvent relaxation rates. These dynamics solvation effect also result in vibronic coupling between two different excited electronic states. The solvents induce fluctuations result in mixing of two excited states through molecular vibrations. The strength of vibronic coupling depends solute-solvents interaction. The electronic structure of the solute can lead to change in the molecular structure which can be probed by vibrational spectroscopic techniques. Raman spectroscopy is a powerful technique used for identifying the molecular structure of these intermediate or transient species in solution-phase. It can provide valuable information about the reactivity of intermediate or transient species and its dynamics interactions with solvents.

<sup>1</sup> Mohapatra H; Umaphy S. *J Phys Chem A*. **2009**, *113*(25), :6904-6909.

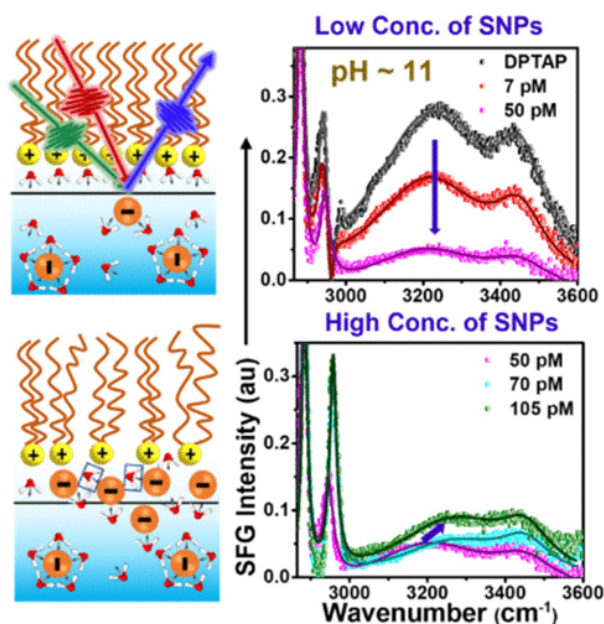
<sup>2</sup> Balakrishnan, G.; Sahoo, S. K.; Chowdhury, B. K.; Umaphy, S. *Faraday Discuss.* **2010**, *145*, 443.

# Understanding nanoparticle membrane interactions by probing the interfacial water structure in response to surface charges

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The spectral responses of interfacial water molecules due to the interaction of charged nanoparticles at different lipid membranes are explored with the help of vibrational sum frequency generation (VSFG) spectroscopy. We observed that the Stern layer configuration dictates the interfacial water structure. In addition, I will also discuss how the interfacial potential can be controlled by altering the pH of the solution. These results provide valuable insights into water molecules' solvation structure and dynamics to exploit for designing and optimizing the delivery system for biomedical applications.



*Schematic and VSFG data for SNP–DPTAP interactions at the interface and molecular reorganization at low (<70 pM) and high ( $\geq 70$  pM) concentration of SNPs.*

## References :

- 1) Gahtori, P.; Varanasi, S. R.; Pandey, R. Spectral Response of Interfacial Water at Different Lipid Monolayer Interfaces Upon Interaction with Charged Gold Nanoparticles. *J. Phys. Chem. C* 2021, 125, 38, 21234–21245.
- 2) Mishra, A.; Gahtori, P.; Pandey, R. Understanding nanoparticle membrane interactions by probing the orientation of interfacial water molecules in response to surface charges. *J. Phys. Chem. B* 2023, 127, 18, 4072–4080.

# Learning heat engines' quantum space from nonequilibrium fluctuations

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The study of fluctuations in coherent heat engines led to the development of quantum thermodynamics whose foundations are based on the fluctuation theorems and thermodynamic uncertainty relationships, quantified by the distributions/moments/cumulants of fluctuating quantities like heat, particle or work<sup>1</sup>. The system space of such quantum heat engines affect the cumulants like flux, noise, skewness, kurtosis etc in nontrivial ways. Although standard theoretical techniques can map the effect of the engines' system space on the fluctuations, analytical understanding is restricted to specific physical regimes and the first cumulant or the flux<sup>2</sup>. Higher order fluctuations, although obtainable, remain numerical and hence depend on the chosen engines' system specifications<sup>3</sup>, or the engines' *quantum space* (a domain of relevant parameters that describe the engine). However, the reverse mapping or relationship, i.e obtaining relevant information about the engines' parameter domain from the nonequilibrium fluctuations is hitherto a completely different story. This question is highly applicable to quantum heat engines where the initial system space or experimental setup isn't fully controllable, eg. with Fano interferences or electromagnetically induced transparencies. This is the subject behind this talk.

In this talk, I shall revisit a popular theoretical quantum heat engine as well introduce an experimentally realized cold atomic heat engine where one can borrow principles from machine learning research (esp. the artificial neural network algorithm) to gain knowledge over the quantum heat engines' system space, eg. noise-induced coherences, ergotropies, efficiencies etc from known values of the nonequilibrium fluctuations: i.e the cumulants<sup>4</sup>.

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<sup>1</sup> Esposito, M, Harbola, U, and Mukamel, S, *Rev. Mod. Phys.*, **2009**, 81, 1665

<sup>2</sup> Sarmah, M J and Goswami, H P, *Phys. Rev. A*, **2023**, 107, 052217.

<sup>3</sup> Giri, S K and Goswami, H P, *Phys. Rev. E*, **2019**, 99, 022014.

<sup>4</sup> Sarmah, M J and Goswami, H P, *arXiv*, **2023**, 2302, 13717.

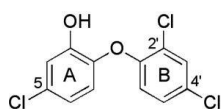
# Infrared Absorption of Phenolated Triclosan in Aqueous Solution

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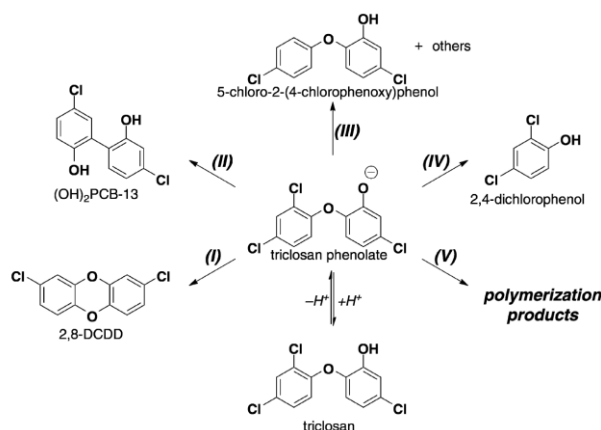
Pharmaceutical development of antibacterial and antifungal agents has lengthened life spans and improved the quality of life, however, their uses have led to rapid growth of environmental contaminants. Triclosan, (5-chloro-2-(2,4-dichlorophenoxy)phenol, **Figure 1**) is a polychlorophenoxy phenol that is designated as TCS. This compound acts as an antibacterial and antifungal agents and is widely used in consumer products such as detergents, dishwashing liquids, soaps, deodorants, cosmetics, lotions, anti-microbial creams, and toothpastes. It is also being used as an additive in plastics and textiles products. As a results, this chemical has been



**Figure 1** Molecular structure of triclosan.

frequently identified contaminant in wastewater sewages, surface waters, sediments cores, fish, human milk, and sludge.<sup>1</sup> It undergoes a variety of degradation processes in the aquatic environment, which includes photo- and thermal-degradation that leads to a variety of products, see some of the examples in reaction **Scheme 1**.<sup>2</sup>

Although, photo-degradation is one of the ways to eliminate contaminants from the environment, however, at the same time it can be a source of toxic products as compared to the parent. Thus, the identification of intermediate and end products in the photochemical transformation of TCS is important. In this talk, I will discuss the conformational analysis of TCS followed by the identification of phenolated intermediate and photodegraded products in aqueous solutions using ATR FT-IR and UV-VIS spectroscopy and DFT calculations.<sup>3,4</sup> In addition, in the second part of my talk, I will briefly discuss another area of my research on “Optimization and validation of various *in vitro* drug release methods based on dissolution apparatuses and HPLC”.<sup>5</sup>



**Scheme 1.** Photochemical degradation of triclosan (TCS).

<sup>1</sup> Anger, C. T., Sueper, C., Blumentritt, D. J., McNeill, K., Engstrom, D. R., and Arnold, W. A., *Environ. Sci. Technol.* **2013**, *47*, 1833.

<sup>2</sup> Kliegman, S., Eustis, S. N., Arnold, W. A., and McNeill, K., *Environ. Sci. Technol.* **2013**, *47*, 6756.

<sup>3</sup> Das, P., Varma, H. D., and Dubey, S. K., Infrared absorption of phenolate form of antibacterial and antifungal agent triclosan in aqueous medium, *ACS Fall 2023 meeting - Optical Spectroscopy and Microscopy Across Biological Scales* (Abstract accepted for presentation).

<sup>4</sup> Das, P. Continuous Scan and Repetitive Mode FT-IR Spectroscopy and Its Application in Isomeric Identification, Conformational Analysis and Photochemistry. In: El-Azazy, M., Al-Saad, K. and El-Shafie, A. editors. *Infrared Spectroscopy - Perspectives and Applications*. London: IntechOpen; 2022, pp. 1 - 21. DOI:10.5772/intechopen.106448.

<sup>5</sup> Gupta, P. K., Pancholi, S. S., and Das, P. *Eur. J. Pharma. Sci.* **2023** (Under review).

# Interface Water probes Heterogeneity Length and Time Scale of Membranes

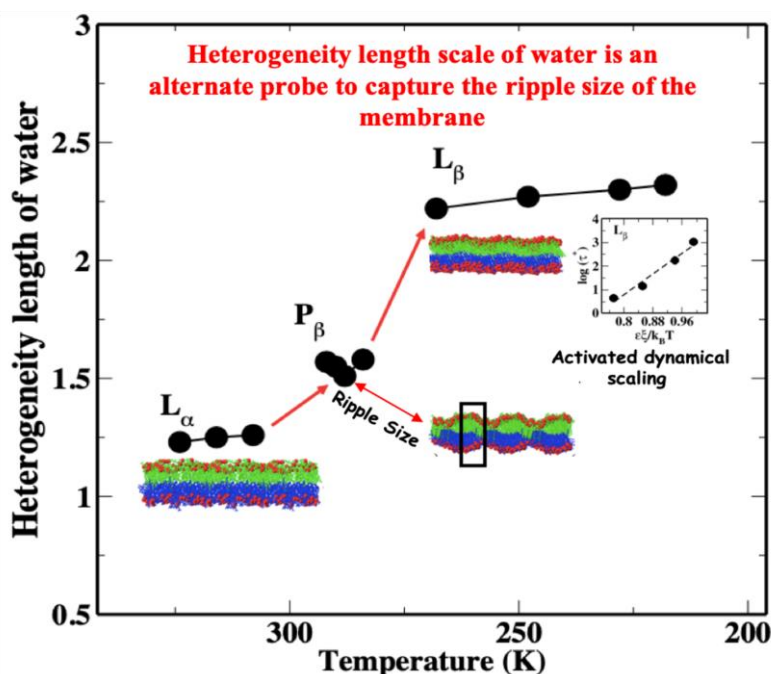
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Water assists in retaining the activity of a cellular membrane under physiological conditions. However, the correlation between the dynamics of water and membrane organization relevant for their activities and survival under physiological and low temperature conditions is not quantified and largely unknown. To this objective, a total of  $\sim 11.55 \mu\text{s}$  all-atom molecular dynamics simulations of 1,2-dimyristoyl-sn-glycerol-3-phosphocholine lipid membranes reveals a *supercooling* driven strong slow-down in heterogeneity time scale and *structure-dictated* drastic growth in heterogeneity length scales of the interface water (IW) at the fluid to the ripple to the gel phase transitions of the membranes. A universal violation and preservation of Stokes-Einstein relation is observed for the time scales derived from different quantities manifesting dynamical heterogeneity.<sup>1</sup> The spatio-temporal scales follow an activated dynamical scaling solely within the gel phase similar to the random first order transition theory. The heterogeneity length scale of the IW becomes temperature invariant at the ripple phase due to the underlying curvature and can capture the ripple size<sup>2</sup>. Thus we demonstrate evidence of probing ripple size of the membrane through the heterogeneity length scale of the interface water. The work opens up a possibility to characterize any domain-associated structural alterations of the membrane through the heterogeneity length scales of the IW in the future.<sup>2</sup>



<sup>1</sup> Sheeba Malik, Smarajit Karmakar, Ananya Debnath; Relaxation time scales of interfacial water upon fluid to ripple to gel phase transitions of bilayers. *J. Chem. Phys.* **2023**; 158 (11): 114503

<sup>2</sup> Sheeba Malik, Smarajit Karmakar, Ananya Debnath; Quantifying dynamical heterogeneity length scales of interface water across model membrane phase transitions. *J. Chem. Phys.* **2023**; 158 (9): 091103.

# Simple Discrete State Stochastic Approaches to Probe Reaction Dynamics in chemical and biological processes

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**Abstract:** The stochastic nature of chemical reactions, fluctuations in thermodynamic and mechanical properties of the systems makes it difficult to clarify the molecular picture of underlying processes. Recent single-molecule experiments have allowed researchers to uncover the molecular properties of biological and chemical systems which are hidden in the ensemble-averaged bulk measurements. The observations stimulated significant theoretical efforts, but the underlying molecular mechanisms are still not properly understood. Our goal is to develop fully quantitative stochastic theoretical frameworks that will allow us to clarify the underlying physical-chemical mechanisms and clarify the molecular picture of underlying processes. In the context of single nanoparticle catalysis, we have introduced a simple theoretical method to provide a comprehensive description of the reaction dynamics on catalysts with multiple active sites based on a discrete-state stochastic description. To establish a link between observed experiments and the theory, we explicitly determine the dependency of the number of active sites, number of intermediate species and the topology of underlying chemical reactions on the dynamics of catalyzed chemical reactions, heterogeneity in chemical reactions. Our theory provides quantitative bounds for realistic dynamic properties of catalytic processes that can be directly applied to analyze the experimental observations and quantitatively describe the effects of heterogeneity in chemical processes. Our analytical and numerical calculations are supported by Monte Carlo computer simulations. This stochastic approach can also be utilized to probe the microscopic mechanism of DNA capture and translocation through biological nanopores strongly influenced by macromolecular bulk crowders. Our results show that apparent electrostatic interactions between the DNA and PEGs control all of the dynamic processes. Our analytical predictions find excellent agreements with existing experiments, thereby strongly supporting our theory.

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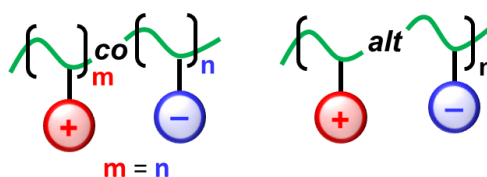
# Amino Acid-Derived Alternating Polyampholytes

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Polyampholytes are polymers containing both cationic and anionic repeating units. Among the different types of polyampholytes, polyzwitterions (such as sulfo-, carboxy-, and phospho-betaines) bearing both cationic and anionic groups together in the same monomer unit are mostly studied in the literature. In addition to the zwitterionic polymers, the development of charge-neutral polyampholytes based on cationic and anionic monomers are extremely challenging as stoichiometric amounts of both the monomers are to be incorporated.

The general strategy for the synthesis of polyampholytes is copolymerization of different unsaturated monomers carrying a positive or negative charge functionality either in a protected or deprotected form. The feed ratio, as well as relative reactivity of the co-monomers, dictate the net charge of the polyampholyte. The inherently different reactivity of co-monomers will result in the compositional drift as well as haphazard placement of the charge units throughout the polymer chain. Thus, it is highly attractive to develop an effective synthetic strategy for polyampholytes without any compositional drift, as the solution performances (e.g., solubility, isoelectric point (IEP)) of polyampholytes are closely related to the composition. In the present lecture, combining the above concerns we outlined a new approach for the synthesis of a novel leucine-derived strictly alternating cationic and anionic moiety based polyampholyte with 1:1 charge balance. To this end, we have engineered an alternating polyampholyte based on poly(styrene-*alt*-maleimide) skeleton by judicious copolymerization of *N*-maleoyl-*L*-leucine *tert*-butyl ester (**M1**) with *tert*-butyl carbamate (Boc)-protected leucine appended styrenic monomer (**M2**) via reversible addition-fragmentation chain transfer (RAFT) polymerization. Since electron donating styrenic monomers undergo copolymerization with an electron accepting *N*-substituted maleimide monomers in an alternating fashion,<sup>1-8</sup> we were able to achieve polymer chains having a cationic and anionic functional moiety in a regular alternating fashion i.e. a charge-neutral polyampholyte on the elimination of the protecting groups.



**Figure:** Polyampholyte from random copolymer versus alternating sequence-controlled polymer.

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# Crystallography and *In Silico* studies of Cyclin Dependent Kinases (CDKs) and Sulphonamides: For the development of potent anticancer drugs

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Cancer is one of the second leading causes of death worldwide. At the same time, there have been several anticancer drugs developed for the treatment of cancer. However, many of these drugs suffer from severe side effects. The major side effects of these chemotherapeutic drugs are due to their poor selectivity towards tumour sites<sup>1</sup>. Hence, the development of drugs that can selectively reach the tumour site can benefit a large number of cancer patients. CDKs have been recognised as key cell cycle regulators<sup>2</sup>. These kinases are over expressed in cancer cells compared to normal cells to promote rapid cell division in cancer cells. Inhibiting CDKs activity through small molecule-based inhibitors can reduce the growth of the tumour. On the other hand, sulphonamides are sulphur-based drugs exclusively used in the treatment of bacterial infections and as antimalarial agents. However, these sulphonamides are not much explored in cancer treatment. Hence, we have designed and synthesized sulphonamides for the inhibition of the activity of CDKs. *In silico* analysis showed that some of these sulphonamides were as potent as known inhibitor (Roscovitine). Further, these molecules successfully crystalized and were subjected to their structure activity relationship. In this talk, the present finding of interaction between CDKs and sulphonamides by *in silico* analysis and crystallography studies of sulphonamides will be discussed.

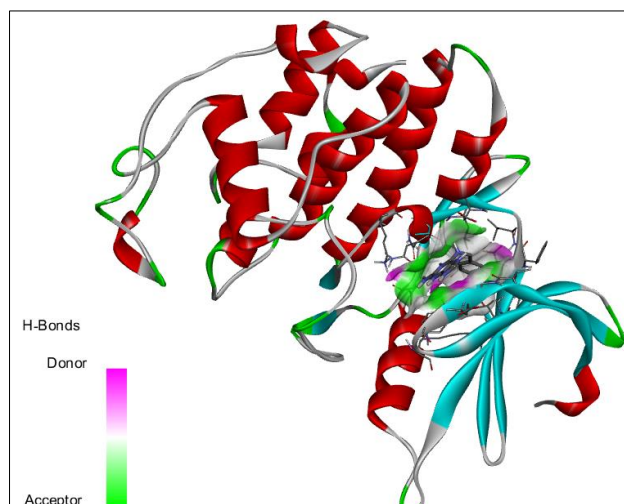


Figure1: Structure depicting active site of the CDK-1 interaction with ligand

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# **Influence of Quantum Confinement on the Linear and Nonlinear Optical Properties of Nanoscale Materials for Possible Biomedical Applications**

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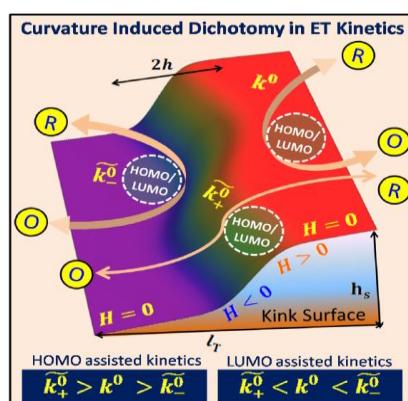
Single and multiphoton absorption such as two, three, four and five photon absorption processes has enabled many technological applications such as quantum photonic technologies, nonlinear photonic devices for information, optical communications, and bio-imaging. Nanoscale materials exhibit strong size-dependent linear and nonlinear optical properties which arise due to the size of the materials, when the size is smaller than the exciton Bohr radius. Here we will discuss our approach to design different multiphoton absorption materials using metal nano cluster, graphene oxide-based quantum dots, carbon dots and perovskite-based quantum dots which exhibit superior single and multiphoton properties, compared with traditional organic and polymeric materials. We will also discuss our group contribution on the application of quantum confined nanoscale material in bio-imaging and biomedical analysis.

# Theory for Electron Transfer on Atomically Stepped Electrode/Electrolyte Interface

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We develop theory for the outer sphere heterogeneous electron transfer (OS-HET) rate constant<sup>1-4</sup> at atomically stepped nanocorrugated metal surface<sup>1</sup>. Theory accounts for the contributions from the nature of metal, local curvature<sup>3</sup> of nanocorrugated atomic step, the density of atomic steps and kinks, dipolar solvents, and the frontier molecular orbital of electroactive molecules. Our theoretical approach models the free energy of activation obtained using the alignment of Fermi energy level in metal with the frontier molecular orbital of electroactive species<sup>5</sup>. The activation free energy, is a function of local curvature dependent work function of nanocorrugated atomic steps, obtained as a product of modified work function (WF) and the fractional electronic charge injected through fluctuations resulting in the alignment of levels. Theory shows that the increase in step density lowers the effective WF of metal compared to the ideal basal plane.<sup>5</sup> The theoretical results highlight the step density-dependent non-monotonic variation in fractional electronic charge therefore activation free energy. Theory shows that the increase in step density results in shift in the Fermi energy level closer to LUMO and away from HOMO energy levels in electroactive species. This causes the reduced (for LUMO) and enhanced (for HOMO) activation free energy for ET kinetics compared to the basal plane. This dichotomic behaviour of LUMO and HOMO results in anomalous enhancement and suppression in the OS-HET kinetics at atomically stepped metal, respectively. Finally, the strong influence of kinks along the step edge on the HET rate constant is predicted to change up to 6 decades (compared to the basal surface of Pt metal). Talk will also highlight some anomalies in experimental results and their theoretical understanding based on our fundamental equations.



Figure(s) caption(s) (Step density dependent electron transfer kinetics at electrode).

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# Tuneable Electrocatalytic Activities of Nanocomposites as Air-breathing Electrode for Rechargeable Li-Air Battery

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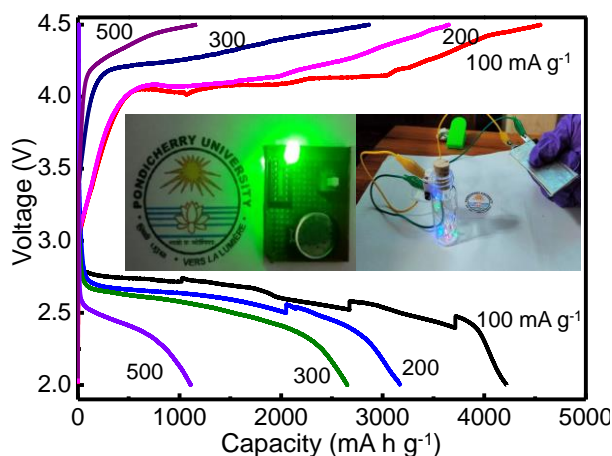
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Electrochemical energy storage has been in the forefront for applications such as consumer electronics and electric traction, especially Lithium-ion battery technology (LIBs). As the energy demand is rising, there is a need to find an alternate energy storage with high energy density. Conversion mechanism-based energy storage systems such as Metal-air batteries were found to be suitable for such scenario. Among them, Li-Air battery with specific energy  $\sim 3000 \text{ kWh kg}^{-1}$  is having an excellent performance compared to other air batteries such as Zinc-Air batteries in terms of capacity, voltage, reversibility on charging etc.<sup>1</sup> Recently, much research is focused on a better bifunctional electrocatalyst that will improve the sluggish  $\text{O}_2$  kinetics of Li-air batteries during charging and discharging. The decomposition of the discharge product,  $\text{Li}_2\text{O}$  results in serious issues due to its insulating nature, reactive superoxide formation and clogging of the pores during discharging. Porous electrodes with homogenous catalytic sites distributed in them is desirable to have better performance as an air-breathing electrodes. We have developed porous carbon network (PCN)<sup>2</sup>, metal oxide-based<sup>3, 4</sup>, Layered Double-Hydroxide based materials as bifunctional catalyst, and their catalytic capability were initially assessed from Tafel Plots and K-L plots derived from RRDE studies. The air-battery was constructed in the form of CR2032 coin cells and was subjected to cyclic voltametric, galvanostatic charge-discharge studies and cycling stability tests. The materials are found to be having better performances in these regards. We have also fabricated large size pouch cell Li-Air battery. Detailed material generation, characterisation ORR/OER and battery performances will be presented.



*Fig. 1. Galvanostatic charge-discharge profiles of Li-Air battery using  $\text{Co}/\text{Co}_3\text{O}_4/\text{NC}$  as electrocatalyst. Inset: Photos of coin and pouch-type air battery powering LEDs.*

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# Using Molecular Dynamics Simulations to Study Interactions of Molecules with the Bacterial Cell Envelope

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With rising bacterial resistance there is a dire need to develop a molecular understanding of the interactions of antimicrobial molecules with the complex topology of the bacterial cell envelope. The translocation pathways associated with molecules from the extracellular environment into the bacterial cell is poorly understood. In this talk I will summarize our ongoing efforts and the challenges involved in understanding the barrier properties of the bacterial cell envelopes. We develop molecular models for peptidoglycan at atomistic as well as coarse-grained scales for the cell walls and assess several structural and mechanical properties as well as insertion free energies of small molecules. We assess the free energy of insertion of antimicrobial peptides and antimicrobial molecules with the outer lipopolysaccharide membrane and compare outer membrane insertion free energy simulations with diffusion coefficients measured using fluorescence correlation spectroscopy to rationalize the selective barrier properties. Our molecular dynamics simulations can potentially open up *in silico* models for the screening and development of novel therapeutics against virulent bacterial infections.

# Concepts of Physical Chemistry to Design Nanoscale Materials for Energy, Sensing, and Therapeutics

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**Abstract:** How important is it to apply concepts of Physics and Physical Chemistry not only to design nanoscale materials but also to apply them for sustainable applications? A few innovative synthetic strategies, which seem unusual in the traditional fabrication of engineered nanomaterials, will be discussed in detail. These synthetic strategies are not only fascinating due to their ability to generate unique structural patterns but also economically sustainable due to their high throughput applications supported by their manipulating physicochemical properties at the interphase. This presentation will describe the fabrication, functionalization, and application of the following nanomaterials which include (i) Resultant Inward Imbalanced Seeding Force (RIISF)-Induced Concave Gold Nanostar (CAuNS) for Non-enzymatic Electrocatalytic Detection of neurotransmitters in human serum, (ii) Fabrication of Bimetallic Multilayered Nanocomposite "(((Au@Ag)@Au)@Ag)@Au" as a dual Electrocatalyst toward Ethanol Oxidation Reaction and Oxygen Reduction Reaction, (iii) Induced capacitor on isolated individual nanoparticles to provide sufficient electric field strength for ultrasensitive Raman sensing, and (iv) Single particle chemical force microscopy to understand viral infectivity. The discussion will also include the traditional strategies of nanomaterial synthesis to highlight their noted differences from our synthetic procedures.

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# Probing the Facilitated Diffusion of DNA Target Search by a Binding Protein in a Disordered Background

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Many fundamental biophysical processes involving gene-regulations and gene editing, at the molecular level, rely on an intricate methodology of searching and locating precise target sites on the genome sequence by specific binding protein moieties. A unique mechanism, known as ‘facilitated diffusion’, which is a combination of 1D sliding along with a 3D movement, is considered to be the key step for such events, and this also accounts for the relatively much faster time scale of target searching process as a whole, than other usual diffusion-controlled biophysical processes. Motivated by recent findings [1] on genome interrogation, we have recently provided a theoretical framework [2] for target search dynamics governed by the sub-diffusive formalism, which agrees well with the experimental observation. Continuing on a similar theme, in this work [3], we aim to probe the modulation of target search dynamics of a protein moiety by estimating the statistics of the search rounds accomplished by the 1D and 3D motion, and its characteristics in various given conditions e.g, when the DNA is considered flexible, when the target is placed at different locations on the DNA, and also in the presence of rearrangements in the surrounding media. We compute and analyze the effect on the rate of target search process in the complex environment [4] following a Mean First Passage Time (MFPT) approach with a Molecular Dynamics (MD) simulation setup, adopting coarse grained models for the DNA and diffusing protein [3].

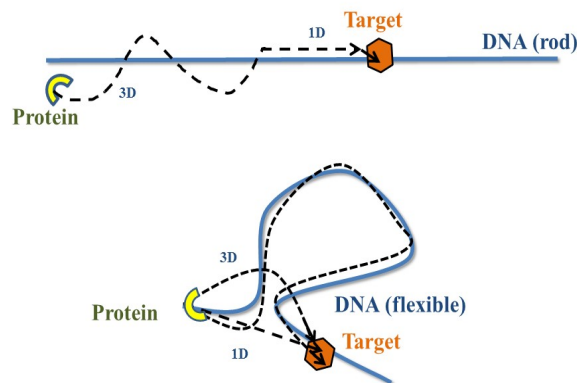


Fig. 1. Schematic representation of the Target Search Problem [3]

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# TEMPERATURE DEPENDENT KINETICS OF CRIEGEE INTERMEDIATE WITH N-BUTYRALDEHYDE AND ISOBUTYRALDEHYDE USING CAVITY RING DOWN SPECTROSCOPY

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Atmospheric ozonolysis of olefins produces short-lived Criegee intermediates (CH<sub>2</sub>OO), which act as a dominant oxidant in the troposphere and get scavenged mostly by the carbonyl compounds. n-Butyraldehyde (nBD) and iso-Butyraldehyde (iBD) are class of oxygenated volatile organic compounds (OVOCs), widely used in the synthetic rubber resins, accelerators, solvents and plasticizers manufacturing industries, flavouring agents in foods like hard and soft beverages, candy, ice cream, baked stuff, etc..[1]. Hence, it is essential to understand their atmospheric removal processes. In this study, the reaction kinetics for CH<sub>2</sub>OO with nBD and iBD were determined by direct probing of CH<sub>2</sub>OO using a highly sensitive custom-built Cavity Ring-down Spectrometer (CRDS) at room temperature and 50 Torr/N<sub>2</sub> of total pressure [2].

A pulsed laser beam of 355 nm was used for the in-situ generation of CH<sub>2</sub>OO at the reaction zone by photolyzing CH<sub>2</sub>I<sub>2</sub> in the presence of excess O<sub>2</sub>. The concentration of the CH<sub>2</sub>OO was monitored by CRDS using another pulsed laser beam at 360 nm. The kinetic decay traces of CH<sub>2</sub>OO from 50 to 1000 ms during the reaction with nBD and iBD are depicted in Figure 1. The  $k_{\text{pseudo}}$  values obtained from the fit of Figure 1 and are plotted against the nBD and iBD concentration, the slope of which give the bimolecular rate coefficient (k).

A negative temperature dependence was observed for the rate coefficient in the studied range of 253-318 K. The Arrhenius equations obtained are  $k_{nBD}(T = 253 - 318 \text{ K}) = (11.51 \pm 4.33) \times 10^{-14} \exp(918.1 \pm 107.2)/T$  and  $k_{iBD}(T = 253 - 318 \text{ K}) = (6.23 \pm 2.29) \times 10^{-14} \exp(1051.4 \pm 105.2)/T \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ . Computational calculations (CVT/SCT and MESMER) were performed to verify the rate coefficients in terms of various possible reaction channels. Atmospheric implication of the studied reactions was also drawn in terms of atmospheric life time of nBD and iBD.

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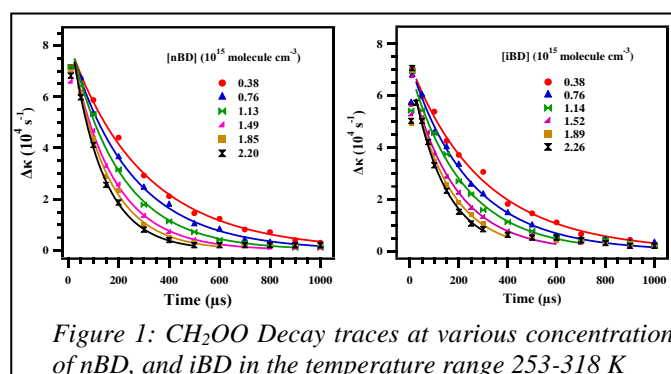
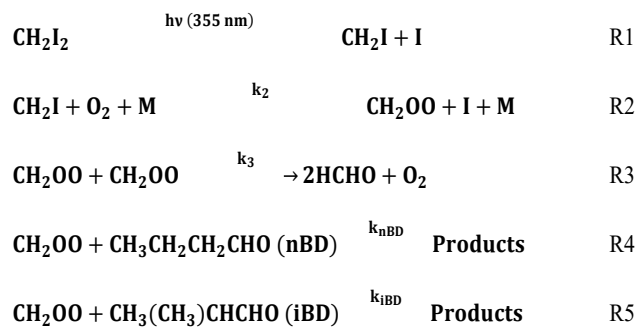


Figure 1: CH<sub>2</sub>OO Decay traces at various concentration of nBD, and iBD in the temperature range 253-318 K

# Detailed Mechanism and Kinetics of Reactions of *anti*- and *syn*-CH<sub>3</sub>CHOO with HC(O)OH: Infrared Spectra of Conformers of Hydroperoxyethyl Formate

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The reaction of CH<sub>3</sub>CHOO with HC(O)OH has a large rate coefficient<sup>1</sup> so that it might play a significant role in atmospheric chemistry, including the formation of secondary organic aerosols (SOA).<sup>2</sup> We investigated the detailed mechanism and kinetics of the reaction of methyl-substituted Criegee intermediate *anti*- and *syn*-CH<sub>3</sub>CHOO with HC(O)OH with a step-scan Fourier-transform infrared spectrometer by recording time-resolved absorption spectra of transient species and end products produced upon irradiation at 308 nm of a flowing mixture of CH<sub>3</sub>CH<sub>2</sub>/O<sub>2</sub>/HC(O)OH at 298 K. Eleven bands due to the formation of hydroperoxyethyl formate [HC(O)OCH(CH<sub>3</sub>)OOH, HPEF], the hydrogen-transferred adduct of CH<sub>3</sub>CHOO and HC(O)OH, were observed. Careful analysis deconvoluted these bands into absorption of three conformers of HPEF, a transient HPEF (P2\*/P3\*) from *syn*-CH<sub>3</sub>CHOO + HC(O)OH, an open-form HPEF (mainly P2) from *anti*-CH<sub>3</sub>CHOO + HC(O)OH, and a stable intra-hydrogen-bonded HPEF (mainly P1). At a later period, the end-product formic acetic anhydride [CH<sub>3</sub>C(O)OC(O)H, FAA], a dehydrated product of HPEF, was observed at 933, 1045, 1200, 1381, 1790, and 1810 cm<sup>-1</sup>; this end-product is the same as that observed in CH<sub>2</sub>OO + CH<sub>3</sub>C(O)OH. Theoretical calculations on the reaction pathway scheme were performed to elucidate their reaction paths. It is likely that *syn*-CH<sub>3</sub>CHOO + HC(O)OH produced conformers P2\*/P3\* initially and were converted to conformers P2 and P3. We derived a rate coefficient for the CH<sub>3</sub>CHOO + HC(O)OH reaction to be  $k' = (2.3 \pm 0.5) \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ . We found also that FAA was produced with a rate coefficient of  $(1420 \pm 71) \text{ s}^{-1}$ .

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# NOVEL PLASMONIC NANOMATERIALS FOR SENSING OF ENVIRONMENTAL POLLUTANTS AND INVESTIGATING LIGHT-INDUCED SURFACE REACTIONS

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Plasmonic nanomaterials exhibit unique optical properties due to the presence of localized surface plasmon resonance (LSPR) band that can be often tuned by varying the size, shape and local environment of these materials. This property of the plasmonic nanomaterials can be exploited for developing nanosensors of high specificity and sensitivity, and also for investigating the surface-catalyzed reactions. The control of chemical reactions on the nanoparticle surface is thus very crucial for understanding the photochemistry of surfaces. In recent times, these surface photochemical reactions were investigated using various techniques, viz. scanning tunneling microscopy (STM)<sup>1</sup>, transmission electron microscopy (TEM)<sup>2</sup>, surface-enhanced Raman scattering (SERS)<sup>3</sup>, etc. In this talk, an overview of the highly sensitive SERS technique will be discussed for monitoring time-dependent oxidation reactions (azo-formation) in 3-hydroxy anthranilic acid capped silver nanoparticles. The formation of the azo derivative was found to undergo isomerization from the trans- to the cis- form. The surface reaction was also dependent on the external conditions; temperature, pH and environment. In another study, the combined results of SERS and density functional theory (DFT) on the anti-thyroid agent, 2-thiazoline-2-thiol, have indicated the predominance of the thione and thiol tautomers in solid and aqueous solution. The selective formation of disulphide dimer and H-bonded dimer on the surface of silver and gold nanoparticles was also observed.

The plasmonic nanomaterials were also exploited recently for the development of nanosensors. In our group, a simple, user-friendly and cost-effective gold nanoparticle based “Colorimetric Sensing Kit” was developed for the detection of the milk adulterant “melamine”. In addition,  $\gamma$ -cyclodextrin capped silver and gold nanosensors were developed for the trace-level sensing of toxic insecticide, chlorpyrifos (CPP), by colorimetry and Raman spectroscopy. The limit of detection of CPP was found to be 1 ppb from SERS. The adsorption behavior of anti-thyroid agent, 2-thiazoline-2-thiol on silver and gold nanoparticles and their response towards toxic heavy metal ions, Hg(II) and Pb(II), were also investigated using colorimetry, SERS and DFT. The results showed that TT thiazoline-2-thiol capped gold nanoparticles could easily detect traces of Hg (II) and Pb(II) in sea and river water samples from different sources.

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## A few analytical calculations in polymers

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In the first part of the talk, I discuss the dynamics in model polymer systems in an attempt to model the relative motion between soft rubbing surfaces at the single polymer level.<sup>1</sup> I briefly present some of our recent results. In the second part, I discuss the dynamics in polymeric liquids, where we generalize the concept of diffusing diffusivity to many-particle systems with localized interactions, a chain of connected beads, namely the Rouse model.<sup>2</sup>

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# Harvesting Hot Charge Carriers via Visible-Light Excitation of Plasmonic

## Nanoparticles for Photocatalysis

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Abstract: Plasmon-mediated multiple charge carrier extraction offers promising potential for enhancing the efficiency of photocatalysis reactions. Substantial research has been carried out on the hot electron-mediated processes; however, the equally significant hot hole-mediated processes are underexplored, primarily owing to the shorter lifetimes of hot holes. In this presentation, I'll go over the outcomes of some of our recent efforts to bridge the gap.<sup>1,2</sup>

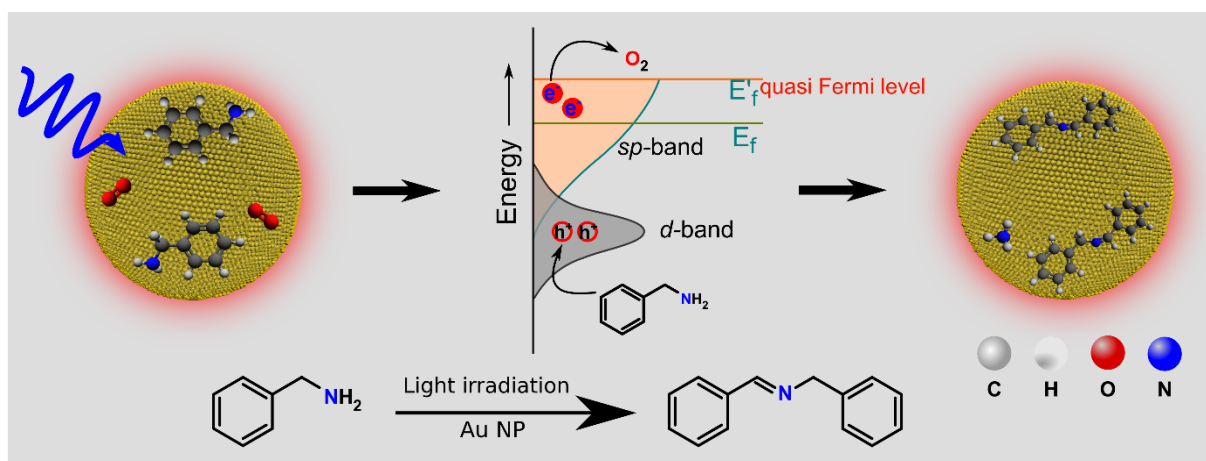


Figure. Simultaneous utilization of hot electrons and hot holes for amine oxidation.

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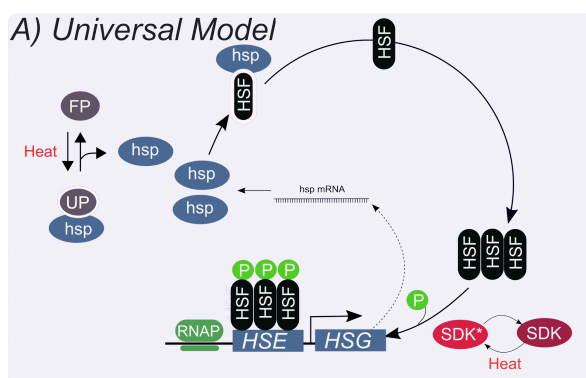
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# Exploring Signalling Pathways through Theory and Experiment

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The kinetics and timescales associated with chemical reactions have important implications in many scientific fields ranging from chemistry to biology. In particular, all the processes inside a biological system, such as a living cell, are governed by when and in what amounts proteins or RNAs can relay the signal downstream and create new molecular entities. Most of these are non-equilibrium processes, and therefore, the participating entities are in non-equilibrium states. The complexity in these systems then arise both due to their dynamical nature and due to the large network of reactions taking place in the cell.



*The Heat Shock Response Mechanism<sup>1</sup>*

I will, in this talk, walk through a few examples of signalling pathways that counter the external stressors and restore balance inside a living cell. Specifically, I will focus on the Heat Shock Response (HSR) pathway, a stress-response mechanism important for proteostasis. The HSR pathway works by increasing the number of heat shock proteins (HSPs) in a cell in response to increased levels of unfolded proteins that are created due to some external stress. The newly produced HSPs then act as molecular chaperones and fold back the unfolded proteins. We have been trying to better understand this process through our research. To this end, I will discuss a modelling study<sup>2</sup> from our group where we show that the Heat Shock Transcription Factor and its complex with HSP play a role in reducing the time lag of response to stress and in re-folding all the mis-folded proteins back to their native state. Further, I will also talk about a complementary experimental study<sup>3</sup> on HSR dynamics in the roundworm, *C. elegans*, where we are looking at how the response is affected when genes associated with the thermosensory neuron are knocked out. These studies will help elucidate the role of the neuron and the key players in regulating the dynamics and also provide intuition about the timescales of response, both at the mRNA and the protein level.

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# Multiscale Modelling of the Stability and Catalytic Activity of Materials in Electrochemical Environments

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Development of inexpensive and efficient electrocatalysts for reduction of oxygen and carbon dioxide is highly desirable to reduce the current dependence on fossil fuels.<sup>1</sup> Recently, computational multi-scale models of solvent and electrolyte environments have opened great opportunities in characterizing the activity and stability of two-dimensional materials and bulk interfaces in a first-principles-based framework.<sup>2,3</sup> In this presentation, a few methodological aspects and the multiscale models developed to understand the physics and chemistry of solid/electrolyte interfaces will be discussed.<sup>4</sup> Applications to the screenings of two-dimensional electrocatalysts for the water splitting reactions and CO<sub>2</sub> reduction reaction will be presented.<sup>5,6</sup> The proposed screening approaches allowed us to identify promising materials with low thermodynamic overpotentials and considerable stability under electrochemical conditions.

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