The official bi-monthly publication of Bhabha Atomic Research Centre

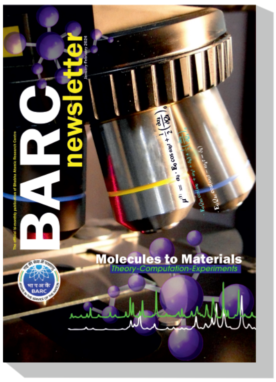
# BARC newsletter

January-February 2024

## Molecules to Materials

### *Theory-Computation-Experiments*

राष्ट्र की सेवा में परमाणु
भा प अ कें
BARC
ATOMS IN THE SERVICE OF THE NATION



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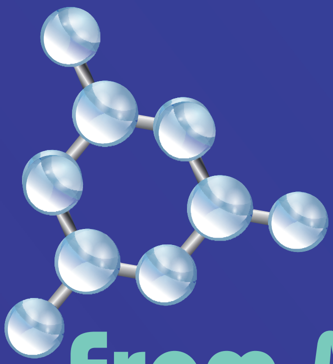


## foreword

# From Molecules to Materials

## Unlocking new synergies in Theory, Computations and Experiments

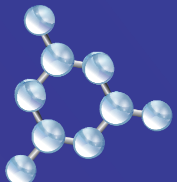
I am delighted to write this foreword for the thematic issue of BARC Newsletter on "Theoretical & Computational Chemistry at BARC" to be published on the important occasion of National Science Day. The research on theory, computations and simulations has been an integral component of all scientific and technological research, of late. With the advent of newer and efficient theoretical methods and availability of high performance supercomputing machines, importance and scope of theory and computations have expanded many folds, as real life challenges can be tackled now very efficiently and accurately in a highly economical way. With the need to understand the structure and energetics of the complex molecules as well as materials and their behavior under extreme conditions, the quantum and classical mechanical methods have now become the most indispensable tools not only in chemistry but in chemical, biological and material sciences as well. In recent years, the cutting edge research in theoretical and computational modeling of materials at different length and time scales have provided an in-depth understanding and rationalization of various chemical processes. Moreover, the capability for discovering and designing new materials, predicting the unknown structure and tailor-made properties of materials that cannot be probed directly by the experiments has made the theoretical and computational methods even more beneficial. This has been possible solely due to the development of advanced theoretical methods, simulation tools and high performance supercomputing machines. The discovery of the state-of-the-art techniques such as machine learning and high-throughput screening methods has further empowered the theoretical and computational methods to tackle real-life problems with greater complexity. Two Noble prizes awarded in the years 1998 and 2013 have demonstrated the increasing importance and vast spread of this branch of research in Chemistry.

In this regard, this issue of BARC Newsletter provides a glimpse of theoretical and computational research in BARC relating to the development of sophisticated theoretical methods, energy storage materials, catalysis, health care etc. Interestingly, the design of newer fuels for advanced nuclear reactors, the evaluations of the physicochemical properties of nuclear fuels and structural materials under extreme conditions and suitable ligand and solvent design for the reprocessing of the spent nuclear fuels have been covered in this issue.

I sincerely hope this collection of research articles will provide a brief idea of the role of theoretical and computational methods in chemistry. It will definitely motivate and encourage the researchers from different areas of scientific field, in particular those involved in experimental studies in DAE related problems to use theoretical methods through collaboration to understand the fundamental concepts from the ab initio level.

I take this opportunity to thank all the authors and associate editors for their time and efforts in preparing this issue.

**Dr. A. K. Tyagi**
Director, Chemistry Group
Director, Bio Science Group
Bhabha Atomic Research Centre



# Theoretical and Computational Chemistry @BARC

We are extremely happy to showcase this special issue of the BARC Newsletter on the very important occasion of National Science Day. Each year, February 28 is celebrated as National Science Day to commemorate the Nobel Prize-winning work, the 'Raman Effect', discovered by Professor C. V. Raman. We are honored to work on this special issue of BARC Newsletter in the capacity of associate editors. This issue highlights some of the ongoing and important research outcomes in BARC in the field of theoretical and computational chemistry.

Over the years, theoretical and computational chemistry has emerged as an essential and integral part of experimental research not only in chemistry but also in other areas encompassing physical, biological, and engineering sciences. It plays a central role in modern society to design and study new products with important applications in food, healthcare, energy, and environment. Discovering new functional molecules and materials has been accelerated to a great extent with the advent of advanced and sophisticated theoretical and computational chemistry tools and methodologies. Apart from providing an in-depth understanding and rationalization of experimental observations, theoretical and computational studies are also helpful in designing novel molecules and materials with tunable properties. Development and implementation of advanced theories, formulation of fast and accurate simulation techniques, establishing structure-property relations, extending applicability of these techniques in various fields like energy, in particular nuclear energy, environment and healthcare has been the major focus of theoretical and computational research in BARC. With the advent of data mining techniques like artificial intelligence and machine learning, the scope and applicability of theoretical and computational methods to tackle real-life challenges with greater complexity, have expanded manifold.

This newsletter issue comprises 13 articles on varied topics of contemporary theoretical chemistry research-contributed by seasoned scientists from different divisions of BARC. It starts with the interview of Dr. Swapan K. Ghosh, former Head of Theoretical Chemistry Section, BARC, followed by an introductory article on the importance of Theoretical and Computational Chemistry in modern day chemistry research. As this special issue is being published coinciding with the National Science Day events in BARC - to commemorate the great discovery of the 'Raman Effect' - the first technical article of this issue is on the use of experimental Surface-enhanced Raman scattering (SERS) spectroscopy and computational approach in the modern day Raman spectroscopy research. The other articles deal with theoretical chemistry research in varied domains, including nuclear energy, energy conversion and storage, catalysis, exotic chemistry, material properties at extreme conditions and developments of new theoretical and computational methods.

All these articles provide a great deal of knowledge in the respective fields of current theoretical chemistry research at BARC. We hope that the present issue of the BARC newsletter would provide a scientifically stimulating environment for innovative ideas to address current problems in modern society related to food, healthcare, energy, and the environment. On behalf of Theoretical Chemistry Section, Chemistry Division, we sincerely acknowledge and thank all contributors and reviewers of this special issue for their active cooperation and support. We sincerely thank Dr. Swapan K. Ghosh, Dean UM-DAE CEBS for giving his valuable time for the interview. Special thanks to Dr. S. Adhikari, Associate Director, KMG, for giving us the opportunity to serve as the associate editors for this special issue. His novel ideas, encouragement, and support made it possible to bring this issue into a reality in a very short time. We take this opportunity to thank Mr. Manoj Singh, Head, SIRD and the Editorial Team of SIRD, in particular, Mr. Madhav N, Mr. Dinesh J. Vaidya and Smt. Jyoti Panda for their hard work and painstaking efforts in carrying out content curation, design and preparation of proofs of all the articles. We sincerely thank Dr. A. K. Tyagi, Director, Chemistry Group and Director, Bio Science Group for his constant support and encouragement.

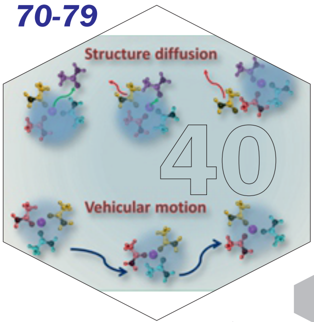
| **Dr. M. Sundararajan** | **Dr. B. Modak** | **Dr. K. Srinivasu** | **Dr. A. K. Pathak** | **Dr. K. R. S. Chandrakumar** | **Dr. N. Choudhury** |
|---|---|---|---|---|---|
| TCS, BARC | TCS, BARC | TCS, BARC | TCS, BARC | TCS, BARC | TCS, BARC |

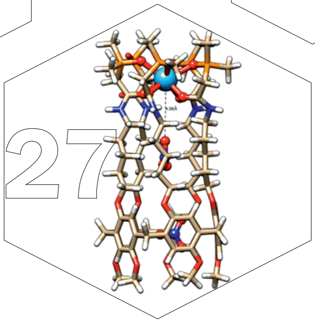
## RESEARCH AND DEVELOPMENT IN THEORETICAL AND COMPUTATIONAL CHEMISTRY

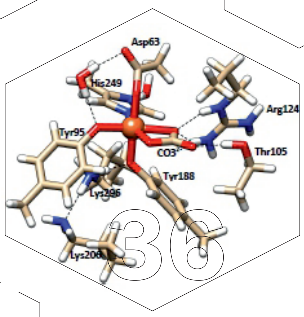
## RESEARCH HIGHLIGHTS

## NEWS & EVENTS

## AWARDS & HONORS







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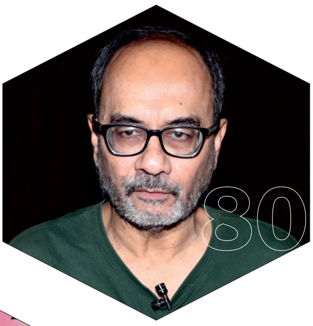

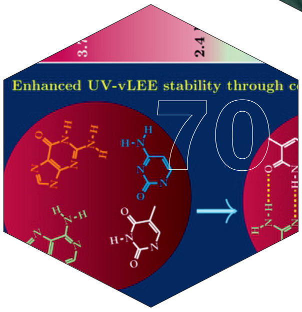

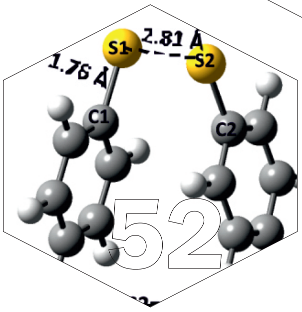

## ARTICLES OF FORTHCOMING ISSUE

- Wet Chemical Synthesis of Hydroxyapatite Powder and Estimation of Curcumin...
- Dosimetric characterization of 10 MeV electron accelerator for food irradiation
- Optical Power Enhancement of High Repetition Rate Copper Vapor Laser MOPA Chains
- Cold Atmospheric Pressure Plasma Device for Multipurpose Applications
- Radiation Induced Mutation Breeding for Improvement & Revival of Rice Landraces

# सैद्धांतिक एवं अभिकलनात्मक रसायन विज्ञान विषय पर बीएआरसी न्यूज़लेटर जनवरी-फरवरी 2024 अंक में सम्मिलित तकनीकी आलेखों के सारांश

**1**

## अत्याधुनिक रसायन विज्ञान अनुसंधान में सैद्धांतिक और अभिकलनात्मक रसायनिकी का महत्व

निहारेंदु चौधरी[1,2]
[1]सैद्धांतिक रसायन विज्ञान अनुभाग, रसायन विज्ञान प्रभाग, भाभा परमाणु अनुसंधान केंद्र (भापअ केंद्र), ट्रॉम्बे-400085, भारत
[2]होमी भाभा राष्ट्रीय संस्थान, अणुशक्तिनगर , मुंबई-400094, भारत

### सारांश

रसायन विज्ञान में अनुसंधान निस्संदेह रूप से हमारे दैनिक जीवन में अत्यंत महत्वपूर्ण भूमिका निभाता है। उदाहरण के लिए, कुछ उत्पाद जिनका हम नियमित रूप से उपयोग करते हैं, जिनमें टूथपेस्ट, साबुन, कपड़े, दवाएं और हमारा भोजन भी शामिल हैं, वे सभी किसी न किसी तरीके से रसायन विज्ञान से संबंधित हैं। इसलिए, रसायन विज्ञान में अनुसंधान हमारे दैनिक जीवन के विभिन्न पहलुओं को विकसित करने और आगे बढ़ाने में हमारी मदद करता है। परम्परागत रूप से रसायन विज्ञान को एक प्रायोगिक विषय माना जाता है। इसलिए, यह सवाल उठाना काफी प्रासंगिक है कि क्या और कैसे सैद्धांतिक और अभिकलनात्मक रसायनिकी वास्तव में काम करता है, और यह भी कि क्या रसायन विज्ञान अनुसंधान की इस शाखा की आवश्यकता है। इस लेख में, हम इन मुद्दों पर संक्षेप में चर्चा करेंगे और इस प्रक्रिया में, रसायन विज्ञान में आधुनिक शोध के शुरुआती दौर में सैद्धांतिक और अभिकलनात्मक रसायनिकी की जरूरतों पर भी प्रकाश डालेंगे। परमाणु ऊर्जा विभाग के कार्यक्रमों से संबंधित अंतर-विषयक अनुसंधान के क्षेत्रों में सैद्धांतिक और अभिकलनात्मक रसायनिकी की महत्वपूर्ण भूमिका पर भी प्रकाश डाला गया है।

**(पूरे लेख के लिए पृष्ठ संख्या 15 देखें।)**

**2**

## न्यूरोट्रांसमीटर, सिल्वर नैनोकणों की सतह पर सेरोटोनिन का अधिशोषण: एक सतह-संवर्धित रमन स्कैटरिंग और डीएफटी अध्ययन

रिधिमा चड्ढा[1,2], अभिषेक दास[1,2] और नंदिता मैती[1,2]
[1] विकिरण एवं फोटोकैमिस्ट्री प्रभाग, भाभा परमाणु अनुसंधान केंद्र (भापअ केंद्र), ट्रॉम्बे-400085, भारत
[2] होमी भाभा राष्ट्रीय संस्थान, अणुशक्तिनगर , मुंबई-400094, भारत

### सारांश

अधिशोषण में बेहतर जानकारी के साथ-साथ फिजियोलोजी स्तर विशेष के लिए कम सांद्रता पर न्यूरोट्रांसमीटर का पता लगाने के लिए सेरोटोनिन के सतह-संवर्धित रमन स्कैटरिंग (एसईआरएस) और घनत्व अभिलक्षकीय सैद्धांतिक (डीएफटी) अध्ययनों की जांच की गई। चांदी के नैनोकणों की सतह पर सेरोटोनिन की संवेदन संसूचन के अतिरिक्त, संगणित और प्रयोगात्मक रमन स्पेक्ट्रम के बीच अच्छे सहसंबंध ने क्रमशः ठोस और जलीय विलयन में तटस्थ और ज़्विटरियोनिक रूपों में सेरोटोनिन की उपस्थिति दर्शायी। एसईआरएस और डीएफटी परिणामों ने ऑक्सीजन/हाइड्रॉक्सिल साइट के माध्यम से संभावित अधिशोषण के साथ चांदी के नैनोकणों की सतह पर मुख्य रूप से अपचयित तटस्थ (ऋणायन) रूप में विश्लेष्य की उपस्थिति को भी दर्शाया।

**(पूरे लेख के लिए पृष्ठ संख्या 20 देखें।)**

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## नाभिकीय ईंधन, अपशिष्ट प्रबंधन, और विकिरण क्षति के लिए मल्टीस्केल मॉडलिंग और सिमुलेशन

तिजो वज़ालप्पिल्ली*[1,2], अरूप के. पाठक[1,2], महेश सुंदरराजन[1,2] , बृंदाबन मोदक[1,2],
श्रीनिवासु कंचर्लापल्ली[1,2] और निहारेंदु चौधरी*[1,2]
[1]सैद्धांतिक रसायन विज्ञान अनुभाग, रसायन प्रभाग, भाभा परमाणु अनुसंधान केंद्र (भापअ केंद्र), ट्रॉम्बे - 400085, भारत
[2]होमी भाभा राष्ट्रीय संस्थान, अणुशक्तिनगर , मुंबई-400094, भारत

### सारांश

नाभिकीय पदार्थों का कम्प्यूटेशनल मॉडलिंग अपरिहार्य है क्योंकि इनमें से अधिकतर पदार्थों का उपयोग उच्च तापमान, उच्च दाब, उच्च विकिरण प्रवाह और संक्षारक रासायनिक पर्यावरण जैसी चरम स्थितियों में किया जाता है, जो सतत प्रयोगात्मक अध्ययन को कठिन बनाता है। अब, मजबूत सैद्धांतिक विधियों और उन्नत कम्प्यूटेशनल तकनीकों के विकास के साथ, विभिन्न प्रयोगात्मक अनुसंधान के समर्थन के लिए सुरक्षित और लागत प्रभावी पद्धति से सैद्धांतिक और अभिकलनात्मक रसायनिकी का उपयोग करके नाभिकीय पदार्थों के गुणधर्मों का सफलतापूर्वक निर्धारण किया जा सकता है। नाभिकीय अनुप्रयोगों से संबंधित पदार्थों को, प्रारंभिक, अर्ध-अनुभाविक इलेक्ट्रॉनिक संरचना गणना, शास्त्रीय आण्विक गतिकी, गतिज मोंटे कार्लो सिमुलेशन, परिमित तत्व और मशीन लर्निंग विधियों की सहायता से, इलेक्ट्रॉनिक से लेकर परमाणु से लेकर मेसोस्कोपिक तक, विभिन्न लंबाई के पैमाने पर प्रतिरूपित किया जा सकता है। वर्तमान लेख में, नाभिकीय ईंधन चक्र के पश्च एवं अग्र भाग दोनों को शामिल करते हुए पऊवि के मुख्य क्षेत्रों पर रासायनिकी वर्ग, भापअ केंद्र में किए गए विविध अभिकलनात्मक रसायनिकी अनुसंधान की एक झलक प्रदान की गई है। विशेष रूप से, हमारा शोध एक तरफ प्रगत नाभिकीय ईंधन के अभिकलनात्मक अभिकल्पन, भुक्तशेष ईंधन पुनर्प्रसंस्करण और अपशिष्ट प्रबंधन के लिए नए लिगैंड और विलायकों के विकास और दूसरी तरफ विकिरण क्षति और ईंधन प्रदर्शन में निम्नन की अंतर्निहित उत्पत्ति को समझने से संबंधित है। **(पूरे लेख के लिए पृष्ठ संख्या 24 देखें।)**

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## ऊर्जा रूपांतरण और भंडारण के लिए कम्प्यूटेशनल मॉडलिंग

बृंदाबन मोदक*[1,2] , श्रीनिवासु कंचर्लापल्ली[1,2] , तिजो वज़ापिल्ली और केआरएस चंद्रकुमार
[1] सैद्धांतिक रसायन विज्ञान अनुभाग, रसायन प्रभाग, भाभा परमाणु अनुसंधान केंद्र (भापअ केंद्र), ट्रॉम्बे - 400085, भारत
[2] होमी भाभा राष्ट्रीय संस्थान, अणुशक्तिनगर, मुंबई- 400094, भारत

### सारांश

इस आलेख में निवल-शून्य लक्ष्यों की दिशा में हरित ऊर्जा मिशन से संबंधित सैद्धांतिक रसायन विज्ञान अनुसंधान गतिविधियों का एक संक्षिप्त विवरण प्रस्तुत किया गया है। विशेष रूप से, सौर ऊर्जा रूपांतरण के लिए नवीन पदार्थों के अभिकल्पन से संबंधित सैद्धांतिक और कम्प्यूटेशनल अध्ययन, जिसमें फोटोकैटलिटिक जल विपाटन के माध्यम से सौर हाइड्रोजन उत्पादन, उपयोगी ईंधन के रूप में सौर $CO_2$ का रूपांतरण, और फोटोवोल्टाइक अनुप्रयोग, हाइड्रोजन के प्रतिवर्ती भंडारण के लिए दक्ष पदार्थों का विकास शामिल है और सॉलिड-स्टेट बैटरी पर चर्चा की गई है। यहां चर्चा किए गए कार्य के पूरे स्पेक्ट्रम में समायोजनीय गुणधर्मों के साथ नवीन पदार्थों का अभिकल्पन और प्रथम सिद्धांत क्वांटम यांत्रिक विधियों का उपयोग करके जटिल परिघटनाओं का निरूपण शामिल है। **(पूरे लेख के लिए पृष्ठ संख्या 30 देखें।)**

5

## स्वास्थ्य सेवा अनुसंधान: कंप्यूटर सहायतित औषधि निर्माण

महेश सुंदरराजन[1,2] एवं ए.के. पाठक*[1,2]
[1] सैंद्धांतिक रसायन विज्ञान अनुभाग, रसायन विज्ञान प्रभाग, भाभा परमाणु अनुसंधान केंद्र (भापअ केंद्र), ट्रांबे-400085, भारत
[2] होमी भाभा राष्ट्रीय संस्थान, अणुशक्तिनगर, मुंबई- 400094, भारत

### सारांश

हमारे समूह में हाल के वर्षों में किए गए स्वास्थ्य सेवा से संबंधित अनुसंधान का एक संक्षिप्त विवरण यहां प्रस्तुत किया गया है। सुपर कंप्यूटर, सुदृढ़ सांख्यिकीय यांत्रिकी आधारित विधियों और द्रुत सैद्धांतिक एल्गोरिदम के आगमन के साथ, अभिकलनात्मक रसायनिकी अनुसंधान अब स्वास्थ्य सेवा में एक अभूतपूर्व भूमिका निभाता है और परमाणु ऊर्जा विभाग के कार्यक्रमों से इसकी सीधी प्रासंगिकता है। जैविक परिघटनाओं और जैविक प्रक्रियाओं के अंतर्निहित भौतिक सिद्धांतों की समझ जो अन्यथा प्रयोगों के माध्यम से प्राप्त करने योग्य नहीं हैं, को बड़े पैमाने पर ऑल-एटम आणविक गतिशीलता सिमुलेशन और क्वांटम यांत्रिक विधियों को नियोजित करके अनुसंधान किया जाता है।

**(पूरे लेख के लिए पृष्ठ संख्या 34 देखें।)**

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## गहन गलनक्रांतिक विलायकों में सूक्ष्म विसरण तंत्र

एच. श्रीनिवासन[1,2], वी.के. शर्मा[1,2] और एस. मित्रा*[1,2]
[1]ठोस अवस्था भौतिकी प्रभाग, भाभा परमाणु अनुसंधान केंद्र (भापअ केंद्र), ट्रॉम्बे-400085, भारत
[2]होमी भाभा राष्ट्रीय संस्थान, अणुशक्तिनगर , मुंबई-400094, भारत

### सारांश

औद्योगिक और फार्मास्युटिकल अनुप्रयोगों में व्यापक रूप से उपयोग किए जाने वाले गहरे गलनक्रांतिक विलायकों (डीईएस) में अभी भी सूक्ष्म दृष्टिकोण से उनके भौतिक रासायनिक गुणधर्मों की पूरी समझ का अभाव है। डीईएस का उपयोग करने वाले अनुप्रयोगों का नियंत्रण व दक्षता उनके अभिगमन गुणधर्मों पर महत्वपूर्ण रूप से निर्भर करती है। इस लेख में, हम सूक्ष्म विसरण क्रियाविधि को उजागर करने वाले डीईएस पर हमारे अनुकरण और सैद्धांतिक अध्ययनों को प्रस्तुत करते हैं जो उनके सूक्ष्म अभिगमन गुणधर्मों के निर्गमन में अंतर्दृष्टि प्रदान करते हैं। आण्विक अंत:क्रिया द्वारा निभाई गई महत्वपूर्ण भूमिका पर ध्यान केंद्रित करते हुए हम जांच करते हैं कि डीईएस के गुणधर्म उनके घटकों और संरचना पर कैसे निर्भर करते हैं। इसके अतिरिक्त, हम इन प्रणालियों में जल की सांद्रता और आण्विक विसरण दर के बीच सह-संबंध का विश्लेषण करने के लिए जल द्वारा इन अंत:क्रिया के मॉडुलन का पता लगाते हैं। हमारे निष्कर्ष बताते हैं कि डीईएस में जटिल निर्माण और बलगतिकी की गहन समझ आण्विक विसरण से निर्गमन संमष्टि अभिगमन गुणधर्मों की व्याख्या करने के लिए आवश्यक कड़ी प्रदान कर सकती है।

**(पूरे लेख के लिए पृष्ठ संख्या 38 देखें।)**

**7**

## रसायन विज्ञान के भविष्य को आकार देती नई सैद्धांतिक रसायन विज्ञान विधियाँ

वाई. सजीव[1,2] , तिजो वज़हपिल्ली[1,2] , श्रीनिवासु कंचर्लापल्ली[1,2] , अरूप के. पाठक[1,2], और मलाया के. नायक[1,2]
[1] सैद्धांतिक रसायन विज्ञान अनुभाग, रसायन प्रभाग, भाभा परमाणु अनुसंधान केंद्र (भापअ केंद्र), ट्रॉम्बे - 400085, भारत
[2] होमी भाभा राष्ट्रीय संस्थान, अणुशक्तिनगर , मुंबई - 400094, भारत

### सारांश

नवीनतम सैद्धांतिक पद्धतियों और कम्प्यूटेशनल एल्गोरिदम का उपयोग आज रसायन विज्ञान अनुसंधान को नई ऊंचाइयों पर ले जा रहा है। इन उल्लेखनीय नई प्रगति ने सैद्धांतिक रसायन विज्ञान को छोटे आण्विक प्रणालियों के आद्यावस्था रसायन विज्ञान के परंपरागत क्षेत्र से आगे बढ़ने में सक्षम बनाया है, जिससे नवीन प्रयोगों को प्रस्तावित करने की अनुमति मिली है। अधिक सटीकता के साथ, यह अब इलेक्ट्रॉनों की सापेक्ष गति को ध्यान में रखते हुए बड़े आण्विक प्रणालियों की उत्तेजित-अवस्था और यहां तक कि निरंतर-अवस्था रसायन विज्ञान का निर्धारण किया जा सकता है। इन नए सैद्धांतिक विकासों के साथ कृत्रिम बुद्धिमत्ता और मशीन लर्निंग के एकीकरण ने सैद्धांतिक रसायन विज्ञान को विज्ञान का एक शक्तिशाली और स्वतंत्र क्षेत्र बना दिया है। यह लेख सैद्धांतिक रसायन विज्ञान अनुभाग, रसायन विज्ञान प्रभाग, भापअ केंद्र द्वारा इन क्षेत्रों में की गई नवीनतम क्रमगत प्रगति पर प्रकाश डालता है।

**(पूरे लेख के लिए पृष्ठ संख्या 42 देखें।)**

**8**

## एकल परमाणु मिश्र धातु उत्प्रेरण: प्रत्यक्ष ज्ञान और अभिकल्पन

संदीप निगम*[1,2] और चिरंजीब मजूमदार[1,2]
[1]रसायन विज्ञान प्रभाग, भाभा परमाणु अनुसंधान केंद्र (भापअ केंद्र), ट्रॉम्बे-400085, भारत
[2]होमी भाभा राष्ट्रीय संस्थान, अणुशक्तिनगर , मुंबई-400094, भारत

### सारांश

उत्प्रेरक पदार्थ ऊर्जा एवं पर्यावरणीय संधारणीयता के लिए महत्वपूर्ण हैं। अभिकलनात्मक पदार्थ विज्ञान नवीन और कुशल उत्प्रेरक पदार्थ को अभिकल्पित करने के लिए अपरिहार्य उपकरण रहा है। एकल परमाणु उत्प्रेरण, उत्प्रेरक की दक्षता को अधिकतम करने के सिद्धांत पर आधारित है। वर्तमान लेख नए उभरते क्षेत्र 'सिंगल एटम अलॉय कैटलिस्ट्स (SAAC)' का सामान्य परिचय प्रदान करता है। इसके बाद सल्फ्यूरिक एसिड अपघटन अभिक्रिया (सल्फर -आयोडीन (एसआई) ताप रसायन चक्र का सबसे ऊष्माशोषी चरण) के लिए एकल परमाणु मिश्रधातु उत्प्रेरक को अभिकल्पित करने में हमारा अभिकलनात्मक प्रयास प्रस्तुत किया गया है।

**(पूरे लेख के लिए पृष्ठ संख्या 47 देखें।)**

**9**

## डाइफिनाइल डाइचैल्कोजन प्रणाली की संरचना और गुणधर्मों पर अतिरिक्त इलेक्ट्रॉन का प्रभाव

दिलीप कुमार मैती[1,2]
[1]निदेशक का  कार्यालय, भाभा परमाणु अनुसंधान केंद्र (भापअ  केंद्र), ट्रॉम्बे-400085, भारत
[2]होमी भाभा राष्ट्रीय संस्थान, अणुशक्तिनगर , मुंबई-400094, भारत

### सारांश

अतिरिक्त इलेक्ट्रॉन की उपस्थिति में $(R\text{-}X)_2$ (R=Ph, $PhCH_2$ ; X=S, Se) प्रकार के सल्फर और सेलेनियम आधारित डाइचाल्कोजन प्रणाली की संरचना और गुणधर्मों को स्पष्ट करने के लिए मूलाधार  क्वांटम रासायनिक तरीकों को नियोजित किया जाता है।  जल माध्यम में इन दो-केंद्र तीन-इलेक्ट्रॉन (2c-3e) 3बंधित प्रणालियों की स्थिरता पर फिनाइल रिंग में इलेक्ट्रॉन निकालने वाले ($-NO_2$) और इलेक्ट्रॉन प्रदान करने वाले ($-CH_3$) समूहों के प्रभाव पर चर्चा की गई है। यह रिपोर्ट दर्शाती है कि इलेक्ट्रॉनिक प्रभाव और ज्यामितीय लचीलेपन का संयोजन इन प्रणालियों में 2c-3e बंधन का  सामर्थ्य निर्धारित  करता है और यह अध्ययन ऋणात्मक डाइचाल्कोजन प्रणाली के एंटीऑक्सीडेंट गुणधर्मों को समझने में भी सहायता करता है । **(पूरे लेख के लिए पृष्ठ संख्या 51 देखें।)**

**10**

## नाभिकीय पदार्थों की अभिकलनात्मक ऊष्मागतिकी

पी.एस. घोष[1,2], के. अली[1,2] और एके आर्य*[1,2]
[1]ग्लास और प्रगत पदार्थ प्रभाग, भाभा परमाणु अनुसंधान केंद्र (भापअ केंद्र), ट्रॉम्बे - 400085, भारत
[2] होमी भाभा राष्ट्रीय संस्थान, अणुशक्तिनगर , मुंबई - 400094, भारत

### सारांश

वर्तमान पीढ़ी के नाभिकीय रिएक्टरों के बेहतर प्रदर्शन और प्रगत पीढ़ी-IV रिएक्टरों की प्राप्ति के लिए, वांछित गुणधर्मों वाले नए पदार्थों का विकास अत्यंत महत्वपूर्ण है। नाभिकीय ईंधन चक्र के विभिन्न चरणों के लिए नए पदार्थों का अभिकल्पन और विकास चुनौतीपूर्ण है क्योंकि, संवृत्त ईंधन चक्र के अग्र और पश्च भाग के लिए नाभिकीय ईंधन के प्रहस्तन में रेडियो-विषाक्तता की संभावना होती है। अभिकलनात्मक ऊष्मागतिकी, किसी तापमान और संरचना श्रेणी में नाभिकीय पदार्थों के मौलिक ऊष्मागतिकी गुणधर्मों को निर्धारित करने के लिए एक अद्‌वितीय अवसर प्रदान करता है जो अन्य प्रयोगों द्‌वारा प्राप्त नहीं किया जा सकता है। नए पदार्थों के अभिकल्पन करने, संरक्षा पहलुओं का विश्लेषण करने और रिएक्टर प्रचालन स्थितियों में पदार्थों के प्रदर्शन का अनुकरण करने के लिए उच्च तापमान ऊष्मागतिकी गुणधर्म आवश्यक हैं। वर्तमान लेख में, घनत्व अभिलक्षकीय सिद्‌धांत (डीएफटी) और शास्त्रीय आण्विक गतिशीलता (एमडी) आधारित अनुकरण कार्यनीतियों का उपयोग करके पदार्थों के अभिकल्पन और विकास के तीन पहलुओं पर विस्तृत चर्चा की गई है। सबसे पहले, $U_{1-x} Np_x O_2$ / $Th_{1-x} Np_x O_2$ मिश्रित ऑक्साइड ईंधन के तापीय गुणों का अध्ययन व्यापक तापमान और संरचना श्रेणी पर तापीय गुणधर्म डेटासेट विकसित करने के उद्‌देश्य से प्रस्तुत किया गया है। दूसरे, नई पीढ़ी के रिएक्टरों के लिए नई संरचनात्मक पदार्थ खोजने के उद्‌देश्य से नए न्यून-सक्रियण उच्च उत्क्रम माप मिश्रधातुओं के अभिकल्पन सिद्‌धांतों को विस्तारपूर्वक प्रस्तुत किया गया है। अंत में, Fe-Zr अंतर-धातुक मिश्रधातुओं में विखंडन धातुओं के समावेश/विलयन के ऊर्जाविज्ञान पर,  उच्च स्तरीय नाभिकीय धात्विक अपशिष्टों के अंतर्गत Fe-Zr मिश्रधातुओं को अपशिष्ट के रूप में प्रोफाइल करने के उद्‌देश्य से, चर्चा की गई है। **(पूरे  लेख के लिए पृष्ठ संख्या 56 देखें।)**

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## परमाण्विक प्रतिरूपण संचालित (गंध रहित, धूम्र रहित और शून्य विषाक्तता) प्रयोगशाला प्रयोग

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### सारांश

परमाण्विक प्रतिरूपण (मॉडलिंग) के उपकरणों का उपयोग करके आण्विक संयोजन का नाभिकीय अभिकल्पन एवं अभियांत्रिकी, विज्ञान और अभियांत्रिकी के विभिन्न क्षेत्रों में अनुप्रयोग के लिए बहुत उपयोगी और लोकप्रिय हो गया है। इस अभिकलनात्मक परमाण्विकी प्रतिरूपण संरचनात्मक, यांत्रिक, तापभौतिकी और गतिशील गुणधर्मों के मात्रात्मक निर्धारण करने की क्षमता के कारण बहुत मांग बन गई है जो प्रयोगात्मक निष्कर्षों की व्याख्या करने और नए प्रयोगों की योजना बनाने में उपयोगी हैं। वर्तमान लेख परमाण्विकी प्रतिरूपण के प्रदर्शन पर केंद्रित है जिसमें परमाणु ऊर्जा विभाग के अनुप्रयोगों से संबंधित क्वांटम इलेक्ट्रॉनिक संरचना गणना, परंपरागत और मूलाधार आण्विक गतिशीलता अनुकरण और सांख्यिकीय यांत्रिकी शामिल हैं जो परमाण्विक प्रतिरूपण एवं रासायनिक विश्लेषण अनुभाग, भापअ केंद्र के रसायन अभियांत्रिकी वर्ग में किए गए।

**(पूरे लेख के लिए पृष्ठ संख्या 61 देखें।)**

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## सैद्धांतिक रसायन विज्ञान: आधुनिक प्रवृत्तियों पर एक अवलोकन

चंद्र एन. पात्रा
विश्लेषणात्मक रसायन विज्ञान प्रभाग, भाभा परमाणु अनुसंधान केंद्र (भापअ केंद्र), ट्रॉम्बे-400085, भारत

### सारांश

सैद्धांतिक और अभिकलनात्मक रसायनिकी, रसायन विज्ञान में अनुसंधान का एक अभिन्न अंग है और अब यह संबद्ध विषयों के साथ अपने अंतरापृष्ठ के माध्यम से अंतर्विषयी अनुसंधान के अग्रणी क्षेत्रों में एक प्रमुख योगदाता के रूप में भी उभर रहा है। शक्तिशाली कम्प्यूटेशनल संसाधनों की उपलब्धता के साथ, जटिल प्रणालियों की संरचना और गतिशीलता का निर्धारण करना और विभिन्न अनुप्रयोगों के लिए वांछित गुणधर्मोंके साथ नए अणुओं और पदार्थों को अभिकल्पित करना अब एक सपना नहीं रह गया है। इस प्रयास में एक बड़ी चुनौती पदार्थों और घटनाओं के विवरण में निहित विभिन्न लंबाई और समयमान के लिए विभिन्न उपकरणों का उपयोग करने की आवश्यकता से उत्पन्न होती है। वर्तमान समीक्षा का उद्देश्य सभी प्रक्षेत्रों को एकीकृत करना है; सूक्ष्मदर्शी प्रक्षेत्र, जहां क्वांटम यांत्रिकी के श्रोडिंगर समीकरण के समाधान के माध्यम से प्राप्त होने वाली इलेक्ट्रॉनिक संरचना प्रासंगिक है, जबकि मध्यवर्ती मध्याकार लंबाई पैमाने में, गति के परंपरागत समीकरण, सांख्यिकीय यांत्रिक विवरण और परमाण्विकी अनुकरण आमतौर पर उपयोग किए जाते हैं और स्थूल लंबाई पैमाने में, सांतत्यक यांत्रिकी पर्याप्त हो सकती है।

**(पूरे लेख के लिए पृष्ठ संख्या 66 देखें।)**

# Tete-à-tete with

## Dr. Swapan K. Ghosh

Distinguished Professor, Dean of Academic Affairs
UM-DAE Centre for Excellence in Basic Sciences (CEBS)
&
Former Head, Theoretical Chemistry Section, BARC

*Dr. Niharendu Choudhury**: **You were instrumental in synergizing Theoretical Chemistry Community in BARC. Starting your journey as a training school graduate in Heavy Water Division (HWD), which was not a pure basic research division, how did you establish yourself amongst the ranks of the most renowned theoretical chemists in the country? What were the significant challenges and opportunities during your journey in BARC?**

*Dr. Swapan K. Ghosh*: Thank you for your kind invitation and positive words. Earlier, there was a theoretical chemistry community, with several excellent scientists (mostly physicists) nurtured by Dr. P. G. Khubchandani, who were pursuing theoretical research, covering diversified areas such as formalism development, work on molecular orbitals, issues related to solid state physics, etc. Many of these scientists were my teachers in the BARC training school, and have provided encouragement and inspiration to me.

After graduating from the BARC training school, I joined the Heavy Water Division (HWD), where there was a need for theoretical calculation of separation factors in deuterium isotope exchange reactions, in addition to the need for understanding the chemistry of corrosion behavior of components used in heavy water plants. It was great pleasure to work on some of the teething problems faced by heavy water plants of that time and also to carry out theoretical investigations on various existing as well as new possible deuterium exchange reactions for the future. There was good camaraderie among the colleagues, all of whom were geared up to problem solving mode. The work although didn't belong to basic research as such but the work I was involved in (both theoretical and experimental) was the need of the hour and working on them gave me ample satisfaction.

Gradually, I drifted towards theoretical chemistry research riding on the support extended by senior colleagues of HWD. I soon completed my Ph.D. from IIT Bombay under the supervision of Prof. Bidyendu Mohan Deb, an eminent theoretical chemist, followed by post-doctoral research with Prof. Robert Parr in USA, and later came back and started almost full time theoretical chemistry research in HWD on density based theories. Support for my work came not only from my Division Head, Mr. H. K. Sadhukhan but also from the then BARC Director Dr. R. Chidambaram. I was instrumental in developing a computer code (published as a BARC Report) for calculation (based on a density based parametric equation) of thermodynamic as well as transport properties of heavy water at any given temperature and pressure, which proved quite useful to several scientists of BARC and DAE.

Due to strong support to my activities from senior colleagues from BARC, all major challenges proved to be almost surmountable. The opportunities that came in my way stem from the faith the seniors had in my capabilities; and the ensuing journey was quite smooth besotted with minor ups and downs, as is the case most of the time. Gradually, a research group,focusing on theoretical approach, nucleated in HWD, with a few very talented young people who joined us from the ranks of BARC training school. In summary, the BARC system played a positive role in

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*...Superannuation is a state of transition that sets into everybody's life, but scientists actually never retire! I keep myself busy by teaching at University of Mumbai-DAE-CEBS, and also carry out some research (whatever is possible with me)...*

**Dr. Swapan K. Ghosh**

supporting my endeavors in theoretical chemistry research besides transforming me into what I am today. I am truly grateful to BARC and DAE system for that.

*Dr. Niharendu Choudhury*: **From being a young scientist in HWD, BARC, you have resurrected a full-fledged Theoretical Chemistry Section and later an independent Section. In fact, you were instrumental in establishing a thriving theoretical chemistry community beyond the theoretical chemistry section in BARC. Elucidate the challenges you might have faced in this journey?**

*Dr. Swapan K. Ghosh*: My interest in theoretical chemistry emanated from the excellent academic teaching by Prof S.C. Rakshit in quantum chemistry in the M.Sc. Class at the University of Burdwan, West Bengal. Additionally, I consider myself fortunate enough to have got an opportunity to work in a thriving atmosphere prevalent in BARC.

I had developed a passion for theoretical chemistry and strongly believed that if one is passionate and poised to work hard, success beckons him. However, I also felt that if one would like to pursue research in a subject more vigorously and fruitfully, the first requisite is to convince oneself as well as others who provide support to this research. Along with me, most of my senior colleagues believed that theoretical research is an integral part of multi-diversified scientific research.

The next challenge is that one needs to have sustained scientific interactions for which there should be a good research team of like-minded people. I started teaching in the Training School quite early in my career and was able to inspire a few very talented young people from the training school to join us. Thus, a research team of theoretical chemistry took shape in HWD. I am extremely thankful to Dr. R. M. Iyer, Dr. J.P. Mittal, Dr. C. Manohar and Mr. H.K. Sadhukhan.

Mr. Alok Samanta, who had a keen interest in mathematics and chemistry at the fundamental theoretical level, was the first to join us from the ranks of training school. He is not only very highly gifted and brilliant but is also an excellent human being who had been admired for his selfless and extremely helpful nature. Mr. Tapan Ghanty, Mr. Chandra Patra and Mr. Niharendu Choudhury joined our team one after the other. All of them have worked on different research problems and have established themselves in their respective fields. This helped us immensely to take up more responsibilities, and address diverse challenging research problems.

Subsequently, we moved to the chemistry group, where the formal theoretical chemistry section was formed with the help of Dr. J. P. Mittal, and also later as an independent section by the then Director of BARC Dr. Srikumar Banerjee. Two more colleagues, Dr. Tusar Bandyopadhyay and Dr. Dilip Maity, who were in the chemistry division initially, also joined us. Dr. Chandrakumar, followed by Dr. Mahesh, Dr. Malaya, Dr. Sajeev and later Dr. Tijo joined us through KSKRA. Three more persons from the training school joined the team - Mr. K. Srinivasu, Mr. Brindaban Modak - and later Dr. Arup Pathak. The team was thus enlarged, and the research areas were also diversified,

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> **Dr. Swapan K. Ghosh**

covering problems encompassing quantum as well as classical systems through theoretical approaches spanning over the whole range of microscopic to mesoscopic to macroscopic length scales. Collaboration with experimentalists was also taken up by my colleagues. The help coming from multiple quarters played a vital role in our activities. I have been fortunate to have received whole hearted support and encouragement from Dr. R. Chidambaram, Dr J.P. Mittal, Dr. Srikumar Banerjee, Dr. Tulsi Mukherjee and several others.

*Dr. Niharendu Choudhury*: **You have superannuated from BARC in 2013, but you are still well aware of the work and the nature of research being carried out in the Theoretical Chemistry Section (TCS), Chemistry Division, BARC.**

**(a) How do you compare the research carried out at the Theoretical Chemistry Section with that in other institutes in India and abroad?**

*Dr. Swapan K. Ghosh*: Superannuation is a state of transition that sets into everybody's life, but scientists actually never retire! I keep myself busy in teaching at UM-DAE-CEBS, and also carry out some research (whatever is possible with me). I am grateful to Prof S.M. Chitre and the Chairman, AEC for their support for my association at CEBS. I like reading scientific literature and am fond of being aware of what is going on in my field of research. Moreover, whatever little I could do is due to the help from my colleagues in theoretical chemistry section, and as a result of this, I have cultivated close bonds of friendship with them.

The work being done in TCS is of high quality and is at par with the work of many other research groups in the country and elsewhere. One of the main challenges faced by them is lack of sufficient number of PhD students. This has affected the productivity of TCS in comparison to the faculties in other institutes. However, this can at least partially be compensated by the vibrant research atmosphere created by the presence of so many brilliant scientists of diverse expertise under one umbrella, providing an opportunity of learning from each other through discussion and collaboration.

**(b) Do you have suggestions/advices to the members of the Theoretical Chemistry Section for improving the quality of their research and visibility?**

*Dr. Swapan K. Ghosh*: Let me start with the general advice by Peter Medawar "Work on important problems" in his book, Advice to a Young scientist, which is always applicable. The TCS community in BARC is already working on important research problems. Of course, there is always scope for further improvement in everything that people do, and the same is true here as well. The best possible thing is to leave it to individual researchers who are well equipped to ask important questions and find suitable solutions. Fortunately, the support for this freedom is usually made available by the senior colleagues.

Visibility of research to the outside world is not an issue today. In this era of high speed information communication good quality work becomes public in no time, thanks to the media! One can also use online platforms of various

> *… in BARC we have a pool of highly competent scientists under the same roof, with expertise in different areas, which are often complementary. Thus, intra collaboration among the scientists will aid in addressing problems of more diverse nature and collective wisdom might generate novel ideas…*
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> **Dr. Swapan K. Ghosh**

forums, websites etc to make their work available to others. The quality of the work is the only important aspect, and in my opinion there is no well formulated recipe, although it is often said that the work should be important enough in some sense to the researcher to generate an honest urge to pursue the work.

Still I would like to mention a few points that might be worth considering for the members of TCS in BARC. The most important challenge the team members (or the leadership) of research groups usually confront is the sustainability of the team. For which, one has to work constantly towards maintaining (i) excellence of work at the intellectual level (which will always be respected), (ii) richness and originality of scientific content of the work, (iii) importance of the questions addressed and the answers generated, (iv) usefulness of the work to the people in the immediate neighborhood, other people in the organization, or the society at large in the long term, and finally, (v) selflessness of the leadership and members of the team (always respected). This is of course my personal view within my limited understanding.

In general, I would like to mention a few things about the advantages of being in BARC. Here, we have a number of highly competent scientists under the same roof, with expertise in different areas, which are often complementary. Thus, collaboration among the scientists within TCS (or even discussion and scientific interaction) and also with others will be very helpful to address problems of more diverse nature and also collective wisdom might generate novel ideas. Particularly, for interdisciplinary research, BARC is an excellent place. Walking an extra mile beyond one's comfort zone might be easier in BARC in comparison to elsewhere. Also this might enlarge one's vision. One can also do self-evaluation through a 'SWOT (Strength, Weakness, Opportunities, and Threat) Analysis' for improvement.

*Dr. Niharendu Choudhury*: **Of late, a majority of the research groups are shifting towards applications of computational tools in different areas of their research rather than pursuing formalism developments. What is your opinion?**

*Dr. Swapan K. Ghosh*: Theoretical chemistry research consists of using theoretical and computational tools for addressing scientific problems, and provides rationalization and prediction of results of chemical interest. Undoubtedly, development of new theoretical tools or reformulation and modification of existing formalisms or development of new computational strategies etc. forms an integral part of this research. Similarly, calculation of results through computational means constitute another valuable component. Thus, theory and computation are intertwined and represent two sides of the same coin.

Computation and theoretical insights together can provide a true picture of the reality. Thus, both are equally important to dissect a problem for complete understanding and for arriving at solution to a problem.

To summarize, theoretical research has two wings, one dealing with development of new theoretical tools or computational strategies or even interpretative aspects unifying several

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> **Dr. Swapan K. Ghosh**

existing approaches, while the other dealing with generating new data through computation, which can be compared with experimental results, if available, or can be interpreted using existing or new formalisms. The individual interest or ability usually determines what a person prefers to do.

*Dr. Niharendu Choudhury*: **What are the different areas of research in DAE in which theoretical and computational chemistry can play a significant role, and what are the future prospects?**

*Dr. Swapan K. Ghosh*: Theoretical and computational chemistry research has the potential to provide valuable insights and direction to almost any problem related to molecules, and materials and various physico-chemical phenomena. In particular, when experiment is difficult to perform due to requirement of conditions of high temperature, pressure or radioactivity, computational approach is the only practical solution. Analogously, when a few molecular candidates have to be shortlisted from a large set, such as drug design, solvent design etc, computational screening is a very valuable tool and can potentially save a lot of energy and resources. In this sense, theoretical or computational chemistry research can certainly play a significant role by providing valuable inputs in different areas of research in DAE.

In biological research, computational biology is very useful along the lines of computational chemistry. Since many of the biological processes are chemical in nature and therefore computational chemistry tools will be very relevant for use in computational biology. Computational chemistry based study of soft matter and active matter is also very useful in biology related research. For waste management research, as mentioned before, solvent selection can be done using computational chemistry. Similarly, development of suitable glass system for radioactive waste disposal, theories of glass transition can be studied within the framework of theoretical chemistry. Quite often, need arises for using both microscopic length scale (involving quantum mechanical investigation) and the atomistic length scale (involving classical MD simulation), which necessitates bridging of the length scales, which is an important area of research (multi-scale modeling) in theoretical chemistry/physics.

Catalysis is another important area of research in DAE. The aspects of single atom catalyst, which are of much interest now, can be studied using computational chemistry. The research on hydrogen energy through development of catalyst for water splitting and also hydrogen storage materials can be done using computational chemistry. In materials science, computational chemistry has been of much help through computational design of novel materials with desired properties. Thus, there are many areas of research in DAE which can be enriched by proper use of computational chemistry tools.

*Dr. Niharendu Choudhury*: **Now-a-days "publish or perish" is the 'mantra' of a successful research career. Therefore, young researchers are focusing on the quantum of publications rather than fundamental developments. How do you look into this.**

*Dr. Swapan K. Ghosh*: In my opinion, publication is not an objective but a by-product in the sense that it is a vehicle or platform to declare research results, thus making them

> *…ML or AI has a bright future in all areas of research. It basically extracts science out of generated data sets, through systematization and essentially brings order out of chaos. But, AI can never be able to exceed the power of human intuition or intelligence…*
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> **Dr. Swapan K. Ghosh**

available to the scientific world. If one concentrates on the research problem, asks meaningful and important questions, results (and hence publications) will automatically follow. Of course the outcome is not always linearly dependent on the effort and hence the number of papers may not be uniformly distributed in time. In this regard, DAE has been very considerate by encouraging scientists to take up challenging problems in preference to handling relatively easy problems giving rise to faster publications. Also "Publish or Perish" has never been the prime motivation for BARC, to the best of my knowledge.

*Dr. Niharendu Choudhury*: **With Artificial Intelligence (AI) and Machine Learning (ML) making rapid strides in Computational Chemistry arena, do you think conventional computational chemistry research methodologies based on quantum and statistical mechanics, becoming redundant?**

*Dr. Swapan K. Ghosh*: ML and AI are now promising new areas which have pervaded almost all domains of research. A simpler version QSAR (Quantitative Structure Activity Relationship), however, had been well known in the chemical field, where one can predict Properties (Reactivity) of molecules in terms of several structural parameters. ML is a sophisticated and highly versatile version of this, if I am permitted to say so. In general, ML or AI has a bright future ahead in all areas of research. It basically extracts science out of generated data sets, through systematization and essentially bringing order out of chaos. I have very limited expertise and knowledge about this area and hence these are only general comments. Of course, AI can never be able to exceed the power of human intuition or intelligence. Also, ML or AI will never make quantum mechanics or statistical mechanics based approaches redundant. On the other hand, one cannot rule out the possibility of new developments by considering a suitable combination of the theoretical formalisms with some of the concepts behind ML or AI, leading to the emergence of new directions of research.

*Dr. Niharendu Choudhury*: **What do you envisage about the future of Theoretical and Computational Chemistry in India and abroad in the next 25 years?**

Dr. Swapan K. Ghosh: I am a highly optimistic about an extremely bright future for Theoretical and Computational Chemistry research both in India and abroad. I wish I was younger to witness the growth of these fascinating developments and participate in these during the coming years.

The rapid growth of computational resources with immense computing power as well as the developments of data science, ML or AI based approaches are truly fascinating. Thus, it is very difficult to predict what would be the situation in next 10, 15 or 20 years. There may be a paradigm shift in the overall scenario of research in computational chemistry or physics. But one can definitely say that this field is poised for a much higher momentum, and the predictive ability will be enhanced many-fold, although the understanding level may have a rather slow rise. Also, since more people might be inclined to foray the ML or AI field, efforts towards further development of the conventional theoretical approaches might receive less attention, thus making their growth rather slow.

**Dr. Niharendu Choudhury is currently heading Theoretical Chemistry Section in BARC. Dr. Choudhury specializes in diversified areas of research in theoretical and computational chemistry. He is recipient of DAE Scientific and Technical Excellence Award (2010).*

# Theoretical and Computational Chemistry

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# Importance of Theoretical and Computational Chemistry in State-of-the-art Chemistry Research

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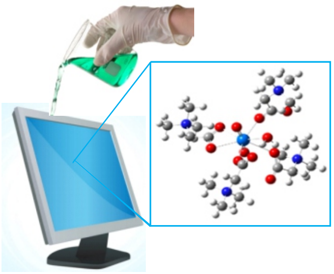

ABSTRACT

There is no doubt that research in chemistry plays an extremely important role in our day-to-day lives. For example, some of the products we use routinely, including toothpaste, soaps, clothes, medicines, and also the food we consume are all related in some or the other manner to chemistry. Therefore, research in chemistry helps us in developing and advancing various aspects of our daily life. Conventionally, chemistry is considered as an experimental subject. So, it is pertinent enough to raise the question – whether and how Theoretical and Computational Chemistry actually works; and also whether there is a need for a specialized branch of theoretical chemistry research. In this article, we shall briefly discuss these issues and, in the process, also highlight the needs of Theoretical and Computational Chemistry in the modern-day start-of-the-art research in chemistry. The important roles that Theoretical and Computational Chemistry can play in areas of interdisciplinary research related to the programs of DAE are also highlighted.

KEYWORDS: *Theoretical and Computational Chemistry, Medicines*

## Introduction

Theoretical Chemistry is a branch of chemistry in which generalizations based on theoretical principles and concepts are developed and these doctrines are used to understand the fundamental physical principles in underlying chemical processes. Within the framework of theoretical chemistry, one can construct chemical laws, principles and their modifications and their hierarchy. A major place in theoretical chemistry is occupied by the dogma of the interconnection between the structure and the property of chemical systems. Theoretical chemistry uses mathematical methods with appropriate physical assumptions to explain the structures, dynamics and thermodynamics of a chemical system and correlate between them. In doing so, theoretical chemists often use computers and computational methods to solve equations numerically wherever analytical solution is not possible or perform simulations of the actual system and phenomena. However, the bottleneck in early years was the non-availability of supercomputing machines to handle large chemical systems.

With the advent of high-performance supercomputing (HPC) machines, the field of theoretical chemistry has seen a paradigm shift and has changed into Theoretical and Computational Chemistry. Because of the availability of large-scale computational facilities, now fairly large and complex chemical and physical systems can be handled computationally. However, extent of largeness of the system depends on the computational technique we use. The first step in any theoretical method is to map the actual physical system into a model system by choosing constituent basic units appropriately. Depending on the chosen length scale of the basic unit, various branches of theoretical chemistry have evolved. If electrons and nuclei of the atoms constituting the system are the basic units, the methods we need to apply should be based on the principles of well-known Quantum Chemistry/Mechanics and the system size that we can handle in such cases can be up to a few hundred atoms. However, due to the inherent periodicity of the lattice structure, some of the computational methods such as periodic density functional theory (DFT) [1] using plane waves can be used to study bulk solids. Similarly, in atomistic lengthscales in which atoms are the basic units, statistical mechanical principles are used for any many-body system and larger system sizes such as proteins and DNAs in water or for that matter any macromolecule in a solvent can be handled in this domain. At the mesoscopic length scale, where clusters of atoms are the basic units, statistical mechanical principles are used to describe and the system sizes relevant to biological systems like cell membranes, complete cell, multi protein interactions in the cell matrix can be studied easily. The question that we ask here is whether Theoretical and Computational Chemistry is important in chemistry research.

Here, I list a number of important reasons why Theoretical and Computational Chemistry (TCC) is important and an integral part of modern chemistry research

### Computational Chemistry Predicts Reaction Mechanisms and Transition States

For any newly discovered chemical reaction, establishing the mechanism by identifying the transition state (TS) and the pathway connecting the reactants to the products via TS is a very important step in chemistry. Identifying the TS and the reaction pathway using experiments is not so easy. Here arises the need of quantum chemical calculations to understand the reaction mechanism, which helps chemists to modify the reaction and thereby improve the yield, productivity and

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specificity of the reaction [1-8]. The citation of 2013 Noble prize in Chemistry, which was awarded to three theoretical scientists Martin Karplus, Michael Levitt and Arieh Warshelon their works on Theoretical and Computational Chemistry reads, *"Today the computer is just as important a tool for chemists as the test tube. Simulations are so realistic that they predict the outcome of traditional experiments."*

### Computational Chemistry Is Used for Calculating Reaction Rates

Not only the detailed chemical reaction pathway, but the rate and direction of a chemical reaction, which occurs at lightning speed of the order of picoseconds or fem to seconds can also be predicted from quantum mechanical calculations. Aided by advanced theoretical methods, computers can now unveil chemical processes independently, and also can complement data obtained from expensive experimental laser spectroscopy to a meaningful conclusion [9-11].

### Computational Chemistry Is Key for Designing Newer Molecules and Exotic Materials

Computational chemistry can predict new molecules of importance. It helps us to design new ligands, and molecules with tunable properties.By a-priori deducing the structure-property correlations, ne wer and unconventional molecules and compounds with exotic chemistry and properties can be designed. The use of modern day periodic DFT based quantum mechanical methods has made the application of Computational Chemistry possible towards design of suitable materials for energy, healthcare and catalysis. A tremendous amount of peer reviewed research papers [12-15] is coming out recently on computational design of materials in those fields. Better predictability with respect to experimental results have been established in these studies.

### Computational Chemistry helps in Analyzing and Rationalizing Experimental Data

Many experimental results in chemistry require theoretical and computational chemistry to interpret the experimental data and the observation. Be it experiment on thermodynamics, or kinetics, or spectroscopy, theoretical and computational chemistry assists in interpreting experimental results. Most of the experimental observations are macroscopic in nature and therefore an atomic or molecular level understanding of those observations require theoretical and/or computational supports. Here theoretical and computation chemistry works in consonance with the experimental research [16].

### Computational Chemistry in Drug Design in the Pharmaceutical Industry

Theoretical and Computational Chemistry plays an astounding role in the pharmaceutical industry. Computational chemistry, in particular, is extensively used in many stages of drug development. Computational Chemistry using QM calculations, docking and simulations provides a complete in-silico route to design a new drug. Computational chemistry can very accurately predict the binding site of a drug in a protein molecule and thereby helps in sensing a disease or deactivating a particular enzyme causing a disease [17-20]. Computational chemistry has devised method like QSAR (Quantitative Structure Activity Relationship), through which a few molecular candidates are chosen form a large library of compounds suitable to be drug molecules and any other molecules with suitable characteristics.

### Theoretical and Computational Chemistry enables us to venture into experimentally inaccessible or difficult to access domains.

One of the profound roles of Theoretical and Computational Chemistry has been to pervade those domains either not accessible or difficult to access by experiments.[21-23]Evaluating physic-chemical properties of materials at high temperature, pressure and radiation through experimental research is difficult to achieve but Theoretical and Computational research can easily predict those properties with extremely high predictability. This kind of theoretical and computational research is very important in nuclear industry. Any experiment at astro-physical condition is very difficult to perform, but theory and simulations can easily mimic those condition in computers and predict useful results [24]. That's why Theoretical and Computational chemistry plays a vital role in astronomical chemistry research, cloud formation etc.

### Theoretical and Computational Chemistry enables us to understand bio-molecular phenomena in Biochemistry and Biophysics.

Biomolecules are macromolecules such as proteins, DNA, lipids etc. Due to their large size, the exact conformational structure of such molecules very much depends on environment such as salt concentration, pH, temperature, pressure etc. The properties of these molecules also depend on their structure. Phenomenon like protein folding can be better understood using molecular simulation. Molecular simulations using classical force field are now extensively used to study protein-ligand interaction, protein aggregation, drug binding etc. Therefore, theoretical and computational chemistry is a major tool to study biophysical systems [25-27].

### Theory and Computations in Nuclear Energy

Roughly 15% of the electrical power in the world is produced from nuclear reactors, without significant emissions of CO2,one of the major components of greenhouse gas. That's why nuclear energy is the most attractive avenue to achieve Net Zero Emission target within a reasonable timeframe. One of the major components in the nuclear reactor operation is the formulation of a proper fuel cycle. Below are the different stages of nuclear reactor operation, in each of which Theoretical and Computational Chemistry can play a major role [28-33]. The advancement in computational chemistry has reached a stage where it can be used for a process design. [34].

#### In front-end of the fuel cycle:

Theory and computation can be applied to various problems of nuclear energy. This methodology can be used efficiently in both front end and back end of the fuel cycles [35,36]. In the front end of the fuel cycle, computational methods can predict the properties of fuels at extreme conditions of temperature, pressure and radiation almost accurately without performing any experiment, which is, in any way, very difficult to perform. Similarly, this method can be very successfully used to design newer fuels[37-38] for advanced nuclear reactors.

#### In operating phase of nuclear reactors

When a nuclear reactor runs for a longer time, because of the extreme condition at which it runs, a number of problems arises, such as, the degradation of fuel quality due to presence of fission products in the fuel matrix, radiation damages in nuclear structural material like RPV steel. In both the cases theoretical and computational chemistry/physics plays a very vital role in identifying the root cause of the degradation or damage process. By performing computational and experimental studies at tandem, such problems can be solved very cost effectively. In fact, many computational studies have been conducted in the above two areas. In fact, a large number of investigations is carried out in our section in evaluating fuel properties in presence of fission products [39,40]. Computational chemistry using DFT has also been used in finding the origin of early onset of Cu precipitation causing radiation damages in RPV steel [41,42].

### *In front-end of the fuel cycle:*

Although, nuclear energy is a very sustainable source of energy with very little emissions, but the wastes produced in nuclear reactors are radio toxic in nature and therefore isolation and safe disposal of both low-level and high level wastes (HLWs) are extremely essential [43]. In a close fuel cycle like the one in India, nuclear fuel recycling is an essential and integral part of it. In order to extract useful fuel materials from the spent nuclear fuel, liquid-liquid solvent extraction process is one of the most widely used techniques. Use of an organic ligand for complexation with the ions is an essential step in this method. Although Tri Butyl Phosphate (TBP) is a very effective ligand for complexation of actinide ions, there are many drawbacks associated with the use of TBP. Therefore, the search for a better ligand for the extraction of these ions is a major field of research in DAE. In fact, apart from many experimental investigations [44], many computational investigations [45] have also been employed to design novel ligands for better efficiency. In fact, a seamless use of experimental and computational methods will make the progress faster.

The liquid-liquid biphasic solvent extraction technique uses a large amount of organic solvent like dodecane, and after the extraction, the radiotoxic solvents are to be discarded to the environment, causing an environmental concern. Therefore, search for an alternative technique is going on. For example, solid-liquid extraction using a solid adsorbent like carbon nanotubes, graphene, graphene oxide etc. with suitable functionalization can be used as an alternative. In this method, actinide ions adsorbed on the adsorbent can be easily separated from the rest of the solution without going through the cumbersome liquid-liquid extraction process. In a recent molecular dynamics study, adsorption of uranyl ions on -$COO^-$ functionalized carbon nanotubes has been shown[46] to follow Langmuir type of isotherms. Such studies are now in the R&D stage and theoretical and computational techniques are of huge help in designing suitable adsorbent. It also can screen a large number of possible candidates to a smaller set, on which experiments can be performed. In this way, theory and computation can make the process cost effective and hassle free contributing significantly to the circular economy of the nation.

### *In nuclear waste disposal and environmental safety*

Due to long-lived radioactivity associated with the remains of the recycled fuels, the safe disposal of these high-level remnants is an extremely important matter and therefore, a lot of research and development is underway in this direction. There are two major areas of nuclear waste disposal, in which theoretical and computational chemistry can contribute significantly. The HLW are generally vitrified by mixing it with a suitable material capable of forming a glass, a state of matter, in which diffusion of atoms, molecules and ions are extremely slow. However, there are many lacunas in the fundamental knowledge about the diffusion mechanism and other properties of the glass. Therefore, theoretical and computational chemistry [47] can be used to get atomistic level understanding of these processes. The vitrified HLW is finally disposed in deep geological repositories, whereas low and intermediate level wastes are deposited in surface disposal facilities. In these facilities, waste containers are placed in constructed vaults made up of protective cover walls of a few meters thick to avoid leaching of radioactive ions into the ground water confined in clay layers. The knowledge of interaction with clay and the diffusion of these ions in the interlayer clay spaces are extremely important in assessing the environmental issues. Theoretical and computational chemistry plays [48] a dominant role in such studies before any actual experiments are carried out.

## Summary

Why theoretical and computational chemistry is an important component of the modern chemistry research is discussed in details. Applicability of theory and computations in various fields of chemical research are discussed. There are many facets of nuclear energy research in each of which theory and computations can be used and in fact, a few areas in which theoretical and computational chemistry has already been used are discussed. As Artificial Intelligence (AI) and Machine Learning (ML) have now pervaded the world of chemistry research, future years will see a huge upsurge in the applications of AI-ML in energy materials [49], in particular nuclear materials [50], catalysis [51,52], biology [53,54], biophysics [55], drug discovery [56] and other fields of research. Now the newer AI-ML techniques for the high throughput screening of materials required for a particular job has become a regular process and thereby reduces the experimental work, which in turn reduces the use of man powerand the cost. It is very heartening to see that not only the drug industry, but all other industries are now using AI/ML for their respective research and development.

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## Density Functional Theoretical

## 2

# Adsorption of Neurotransmitter, Serotonin on the Surface of Silver Nanoparticles: A Surface-enhanced Raman Scattering and DFT Study

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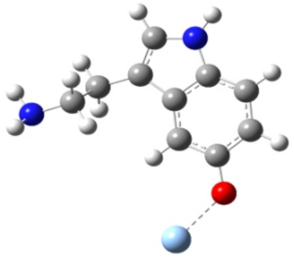

*5HT (anion)-Ag. The colour codes used to identify the atoms are N (blue), O (red), C (grey), H (white) and Ag (sky blue)*

ABSTRACT

Surface-enhanced Raman scattering (SERS) and density functional theoretical (DFT) studies of serotonin were investigated in order to have a better insight into the adsorption as well as the detection of the neurotransmitter at low concentrations specific to physiological levels. In addition to the sensitive detection of serotonin on the silver nanoparticles surface, the good agreement between the computed and experimental Raman spectrum indicated the presence of serotonin in the neutral and zwitterionic forms in solid and aqueous solution, respectively. The SERS and DFT results also revealed the presence of the analyte predominantly in its reduced neutral (anion) form on the silver nanoparticles surface with the probable adsorption through the oxygen/hydroxyl site.

KEYWORDS: *Serotonin; Surface-enhanced Raman scattering (SERS); Density functional theory (DFT); Structural and vibrational analysis; Conformers*

### Introduction

Serotonin (5-hydroxytryptamine, 5HT) is an important neurotransmitter which controls various physiological and behavioural functions in the body, such as mood, anxiety, sleep and cognition functions [1]. It is well known that the serotonin (5HT) levels in the body can be correlated to several diseases such as depression, anxiousness, sleep and digestive problems, panic disorders, etc. [2]. Therefore, it is of prime importance to detect the neurotransmitter, 5HT at low concentrations, specific to physiological levels. Among the various methods used for detecting the 5HT biomarker, the surface-enhanced Raman scattering (SERS) technique has attracted great attention due to its high selectivity, sensitivity, cost-effectiveness and ease of operation [3]. In addition, to the amplified sensitivity in the Raman detection limit, the SERS technique has the potential to identify and fingerprint biomarkers, drugs, proteins, etc. [4-6]. SERS also provides valuable structural information regarding the interaction viz. the sites of binding and the orientation of the analytes on the nanomaterial substrates [7-9]. However, sensitive and precise detection of the 5HT levels using SERS require the fabrication of novel nanosubstrates.

In the present work, novel silver nanosubstrates, viz. colloidal silver nanoparticles (AgNPs) as well as nanostructured silver-coated films (NSCFs) were prepared for the detection of traces of the neurotransmitter, 5HT using the SERS technique. In addition to fingerprinting and detection of 5HT, the adsorption characteristics of the analyte on AgNPs and NSCFs were investigated. The binding characteristics were probed by monitoring the observed changes in the Raman spectral features measured on the surface of AgNPs and NSCFs relative to that in aqueous solution. 5HT probably exists in the cationic, neutral, zwitterionic and anionic conformations at neutral to alkaline pH. The prevalent conformers of 5HT in solid and solution as well as the adsorbed species on AgNPs and NSCFs were identified by comparing the experimentally observed normal Raman and SERS spectrum with the DFT computed Raman spectrum of various conformers of 5HT and their Ag complexes. This study reveals that trace levels of the biomarker, 5HT can be easily detected using the SERS technique and the variation in its levels under physiological conditions can be correlated to mood swings, anxiety, and sleep as well as digestive disorders.

### Materials and Methods

AgNPs were prepared using modified Creighton method [10]. NSCFs were fabricated using formamide as the reducing agent [11,12]. 5HT functionalized AgNPs (5HT-Ag) and 5HT capped NSCFs (5HT-NSCFs) were prepared by the addition of 5HT solution to AgNPs for the former and by dipping the NSCFs on the 5HT solution for 15 min for the latter, respectively. The AgNPs, NSCFs, 5HT-Ag and 5HT-NSCFs were then characterized using UV-vis absorption and Raman measurements. An insight into the experimental results was obtained by performing geometry optimization for all the conformers of 5HT using DFT (Gaussian 03 program) [13] with B3LYP functional and aug-cc-pVDZ basis set [14]. The molecular vibrations were computed for the optimized conformers and compared with the experimentally observed

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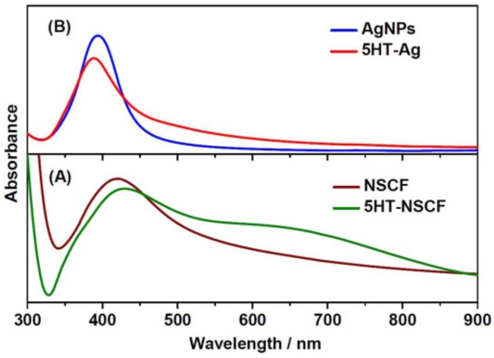

*Fig.1: Absorption spectrum of (A) NSCF and 5HT (10 nM) functionalized NSCF (5HT-NSCF); (B) AgNPs and 5HT (10 nM) capped AgNPs (5HT-Ag).*

Raman spectra of 5HT in solid and aqueous solution. The geometry optimization was also performed for the possible 5HT-Ag complexes with B3LYP/LANL2DZ for Ag atom. The computed vibrations at the optimized geometries were then compared with the SERS spectrum of 5HT-AgNPs and 5HT-NSCFs.

### Results & Discussion

The UV-vis absorption spectrum of NSCF and 5HT-NSCF with 5HT concentration of 10 nM is shown in Fig. 1 (A). In NSCF, a broad band appears with maximum at 420 nm, which is attributed to the bulk-like surface plasmon resonance (BL-SPR) band [4,15,16]. It is known that the BL-SPR band of metal NPs strongly depends on the shape, size, extent of aggregation and dielectric constant of the medium [17]. The absorption spectrum of 5HT-NSCF (Fig.1(A)) displays reduced absorbance in the BL-SPR band which is also red-shifted to 430 nm. In addition, a lower energy band with maxima around 618 nm is observed, which is attributed to the surface-like surface plasmon resonance (SL-SPR) peak [4,15,16]. The SL-SPR band arises due to the dipole-dipole interactions of the higher aggregated particles. The UV-vis absorption spectrum of AgNPs and 5HT-Ag with 5HT concentration of 10 nM is shown in Fig.1 (B). A single sharp peak at 394 nm attributed to the BL-SPR band is observed for the AgNPs. In case of 5HT-Ag, the spectrum is broad with reduced absorbance at 394 nm along with the appearance of a shoulder around 450-600 nm. The red-shifted band is attributed to the SL-SPR band that appears due to 5HT induced aggregation of AgNPs.

The optimized (B3LYP/aug-cc-pVDZ) molecular structures of cationic, neutral, zwitterionic and anionic conformers of 5HT are shown in Fig.2 (I-IV). In order to know the relative stability of the conformers, the minimum energies at their respective optimized geometries were compared. The relative energies of the 5HT conformers computed at the B3LYP/aug-cc-pVDZ level of theory indicated that the cationic conformer is the most stable followed by neutral, zwitterionic and anionic forms. The relative energies of the cationic, neutral, zwitterionic and anionic conformers are 0, 10.46, 11.17 and 23.17 kcal $mol^{-1}$, respectively. The Raman vibrations for all the conformers of 5HT were computed at their optimized geometries and compared with the normal Raman spectrum in solid and aqueous solution. The acid dissociation constant (pKa) of 5HT is known to be 9.97 and 10.73 [18]. Thus, 5HT may exist in solid and aqueous solution in either of the possible conformation, viz. cation, neutral, zwitterion or may get deprotonated (anion) in solution and on the surface of AgNPs and NSCFs.

The Raman spectrum of 5HT in solid is shown in Fig.2 (A). The Raman bands are assigned based on comparison of the experimental spectrum with the theoretically computed (B3LYP/aug-cc-pVDZ) Raman vibrations of the cationic, neutral, zwitterionic and anionic forms of 5HT. The Raman spectrum (Fig.2 (A)) exhibits strong and medium intensity peaks at 1540, 1428, 1353, 1307, 1238, 941, 842, 773, 754 and 462 $cm^{-1}$, which are assigned to indole ring C=C stretch, NH in-plane (ip) bend, indole ring C-C stretch combined with OH ip bend, CH ip bend, indole ring distortion combined with $CH_2$ rock, C-$NH_2$ stretch, CH out-of-plane (oop) bend, indole ring breathing and indole ring bend, respectively. The experimental and theoretical results clearly suggest that 5HT in solid remains predominantly in the neutral form although slight contributions from other conformers cannot be completely ignored. The Raman spectrum of aqueous solution of 5HT ($10^{-1}$ M) as shown in Fig.2 (B) displays intense peaks at 1554, 1438, 1349, 1241, 939, 826 and 762 $cm^{-1}$ that are assigned to indole ring C=C stretch, NH in-plane (ip) bend, indole ring distortion combined with $CH_2$ rock, indole ring C-C stretch combined with CH ip bend, C-$NH_2$ stretch, CH out-of-plane (oop) bend and indole ring breathing, respectively. The Raman spectrum of 5HT in aqueous solution when compared with the computed Raman vibrations indicated the predominance of the zwitterionic conformer in solution.

The SERS spectrum of 5HT-NSCF and 5HT-Ag with 10 nM concentration of 5HT at neutral pH is shown in Fig.3 (A) and

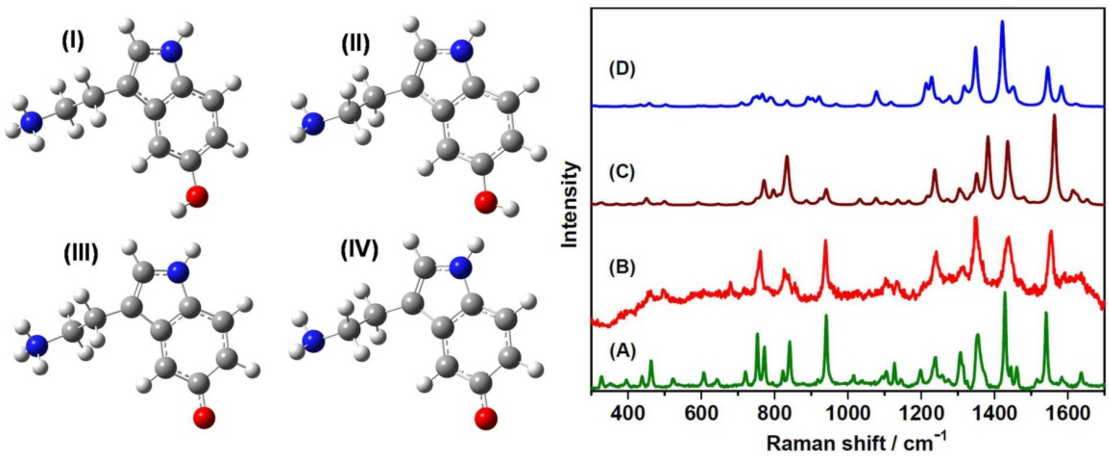

*Fig.2: Optimized molecular structures of (I) cationic, (II) neutral, (III) zwitterionic and (IV) anionic conformers of 5HT. The colour codes used to identify the atoms are N (blue), O (red), C (grey) and H (white). Normal Raman spectrum of 5HT in (A) solid, (B) aqueous solution and simulated Raman spectrum of (C) neutral and (D) zwitterionic conformers.*

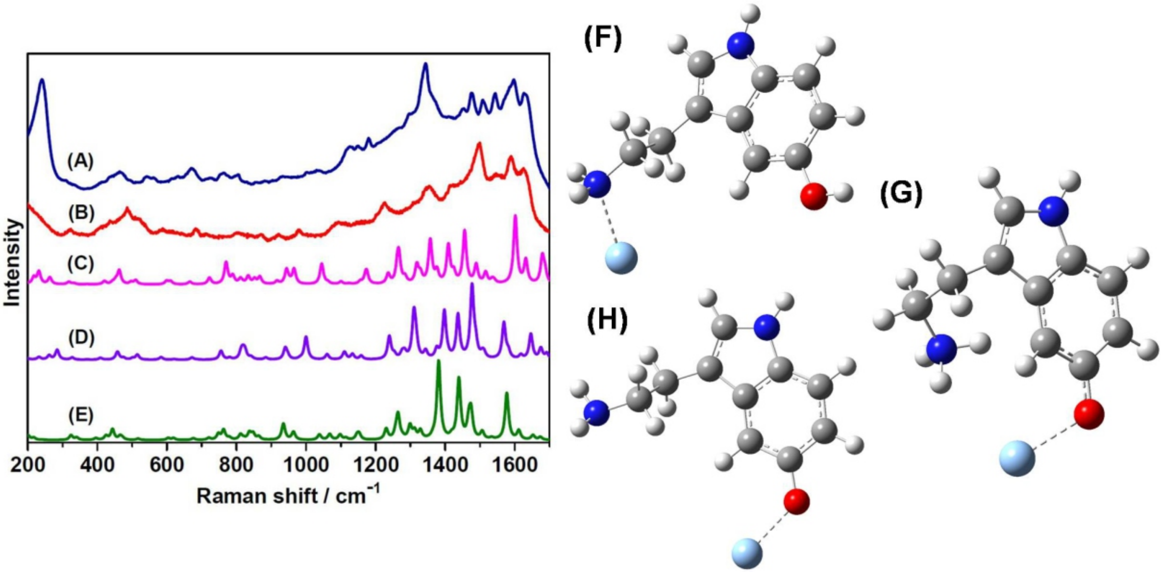

*Fig. 3: SERS spectrum of (A) 5HT-NSCF, (B) 5HT-Ag and simulated Raman spectrum of (C) 5HT (neutral)-Ag, (D) 5HT (zwitterion)-Ag and (E) 5HT (anion)-Ag. Optimized molecular structures of (F) 5HT (neutral)-Ag, (G) 5HT (zwitterion)-Ag and (H) 5HT (anion)-Ag. The colour codes used to identify the atoms are N (blue), O (red), C (grey), H (white) and Ag (sky blue).*

3 (B), respectively. The SERS spectrum shows good signal to noise (S/N) ratio. The SERS spectrum recorded for 1 nM concentration of 5HT (figure not shown) also showed reasonable S/N ratio. In case of 5HT-NSCF, intense SERS bands were observed at 1597, 1343 and 242 cm$^{-1}$ that are assigned to indole ring C=C stretch, indole ring distortion combined with CH$_2$ rock and Ag-O stretch, respectively. Medium intensity peaks observed at 1626, 1544, 1508, 1475, 669 and 464 cm$^{-1}$ are assigned to indole ring C=C asymmetric stretch, CH$_2$ twist, CH$_2$ twist combined with CH and NH ip bend, NH oop bend, indole ring breathing and indole ring CH bend, respectively. Similarly, the SERS spectrum of 5HT-Ag as shown in Fig.3 (B) displays strong and medium intensity peaks at 1589 (indole ring C=C stretch combined with C-N stretch), 1499 (CH$_2$ twist), 1353 (indole ring distortion combined with CH$_2$ rock), 1226 (indole ring distortion combined with CH$_2$ rock) and 485 (indole ring CH ip bend) cm$^{-1}$, respectively. The SERS spectrum of 5HT-Ag and 5HT-NSCF were compared with the computed (B3LYP/LANL2DZ) Raman spectrum of the zwitterion, neutral and deprotonated neutral (anion) conformer of 5HT-Ag complex as shown in Fig.3 (F-H). The computed relative energies suggest that the 5HT (neutral)-Ag is most stable, followed by 5HT (zwitterion)-Ag and the 5HT (anion)-Ag is least stable and their relative energies are 0, 1.01 and 10.78 kcal mol$^{-1}$, respectively. Thus, any of the three conformers, viz. neutral, zwitterion and the deprotonated neutral (anion) may be adsorbed on the surface of AgNPs and NSCFs. Comparison of the SERS spectrum and the computed Raman spectrum of the Ag-complexes indicate the presence of the analyte predominantly in its reduced neutral (anion) form on the silver nanosurface with probable adsorption through the oxygen/hydroxyl site.

## Conclusions

In this study, a detailed investigation of serotonin (5HT) detection using AgNPs and NSCFs as the SERS nanosubstrate is presented. The results suggested that trace concentrations of 5HT (1-10 nM) could be easily detected using SERS, which may be useful for the prediction of various disorders that arise due to the variation in serotonin levels in the body under physiological conditions. In addition to the detection of 5HT, the agreement between normal Raman and computed (B3LYP/aug-cc-pVDZ) Raman spectrum indicated the presence of serotonin in the neutral and zwitterionic conformers in solid and aqueous solution, respectively. The SERS and DFT results also revealed the presence of the analyte predominantly in its reduced neutral (anion) form on the silver nanosurface with the probable adsorption through the oxygen/hydroxyl site.

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## Computational Modelling

## 3

# Multiscale Modelling and Simulations for Nuclear Fuels, Waste Management, and Radiation Damages

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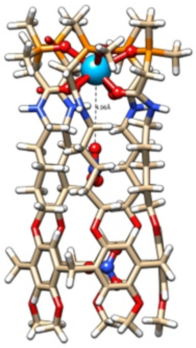

*Optimized structures of Th(IV) binding to functionalized PA [5]*

ABSTRACT

Computational modelling of nuclear materials is indispensable because most of these materials are used in extreme conditions such as high temperature, high pressure, high radiation fluxes and corrosive chemical environments, which makes frequent experimental studies difficult. Now, with the development of robust theoretical methods and advanced computational techniques, the properties of nuclear materials can be successfully predicted using theoretical and computational chemistry in a safe and cost effective manner to supplement various experimental researches. The materials pertaining to nuclear applications can be modelled at different lengthscales starting from electronic to atomic to mesoscopic lengthscales with the help of *ab initio*, semi-empirical electronic structure calculations, classical molecular dynamics, kinetic Monte Carlo simulations, finite element and machine learning methods. In the present article, a glimpse of the diverse computational chemistry research carried out in Chemistry Group, BARC on core areas of DAE encompassing both back end and front end of the nuclear fuel cycles has been provided. In particular, our research deals with computational design of advanced nuclear fuels, development of novel ligands and solvents for spent fuel reprocessing and waste management in one hand and understanding underlying origins of radiation damage and fuel performance degradation on the other hand.

KEYWORDS: *Mutliscale modelling, Nuclear fuel, Nuclear waste management, Back end fuel cycle, Radiation damage*

## Introduction

The extensive use of nuclear energy is among the only viable way to meet the growing energy demands without increasing any carbon footprint to the already polluted environment. Bhabha's vision of the Indian nuclear energy program embedded with utmost safety precautions has enabled India to run the program safely for more than 50 years and become self-reliant in this arena. In order to maintain a sustained, smooth operation, many challenges are faced in different parts of nuclear fuel cycle, namely, front end, back end of it. One of the advanced research goals in the front end is the design and development of novel fuels for newer generation reactors. In particular, post Fukushima nuclear event driven by an intense earthquake followed by a tsunami, quest for advanced nuclear fuels that are more tolerant to accidents is on the rise. In this front, computational modelling plays a very crucial role as repeated experimental studies are rather difficult due to the inherent radiotoxic nature of these nuclear fuels. By understanding the electronic structure of advanced nuclear fuels such as $UAl_3$ and $U_3Si_2$, it is easy to calculate various thermo-physical properties computationally and therefore, such computational studies will aid immensely in the design and development of these newer fuels.

On the operational front of the nuclear energy production, one of the primary challenges is the degradation of nuclear fuel quality and behavior under extreme conditions of the reactors. In particular, the interaction of fuel with fission products modifies fuel properties significantly. In this context, substitution of lanthanide (Ln) fission products in the uranium dioxide ($UO_2$) fuel matrix and subsequently their impact on the thermo-physical properties of $UO_2$ fuel is investigated using atomistic models. Another challenge in the operational front of the nuclear energy production is the degradation of the nuclear structural material viz. steel. The high quality reactor pressure vessels (RPV) steel used in nuclear reactors [1,2] can withstand high temperature and neutron irradiation. However, due to sustained effect of the high irradiation dose, the lifetime of the reactor's structural components is reduced. Here too, repeated experimental investigations to understand the basics behind such degradation is severely limited due to underlying high radiotoxicity associated with these materials and thus, use of theoretical methods comes handy to identify the root cause of such degradation processes. In this context, we have used first-principle electronic structure calculations to investigate the origin of such radiation damage in RPV steel.

On the other hand, in the back end of India's closed nuclear fuel cycle, it is mandatory to recover useful part of the un-spent fuels and safe removal of other harmful radiotoxic constituents of the spent fuel. Radioactive waste is a hazardous waste that contains radioactive isotopes of different atoms that are, if not managed properly, can come out in ecological environment and pose a very dangerous threat to

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human life.The radioactive Xe and Kr are produced from nuclear reactors, spent nuclear fuel reprocessing plants and postulated nuclear accident scenarios. Currently, the expensive cryogenic distillation process is employed for the entrapment of noble gases (Ng). Adsorption of Xe and Kr on porous materials can provide a cost effective technology for the capture of these volatile fission gases. In this direction, use of computational chemistry along with artificial intelligence and machine learning can speed up the search for a suitable porous material for the adsorption of Xe and Kr. With efficient reprocessing, we can selectively recover several radionuclides that are useful for societal applications such as $^{137}$Cs for food irradiation, $^{60}$Co for treating cancer, $^{106}$Ru for treatment of ophthalmic cancer, $^{99m}$Tc as Nuclear medicine, and $^{90}$Sr as a radioactive tracer. Moreover, the un-fissioned fuel material can be reprocessed as fuel. The speciation of radioactive ions through the use of supramolecular containers (SCs) is an active field of research in which state of the art DFT calculations can be used to design efficient SCs. Conventionally, one of the major techniques that has been utilized over the decades in the nuclear industry for the reprocessing [3,4] of the spent fuels is the two-phase liquid-liquid extraction process. However, there are many difficulties and environmental concerns associated with this conventional method such as, disposal of excessively used radiotoxic organic solvents, difficulties in separating different phases due to third phase formation etc. Therefore, search for newer techniques that overcome these difficulties is essential. Here too, computational chemistry has a big role to play in designing superior techniques. Increasing applications of radiation technology drives us to develop efficient devices for the measurement of radiation dose and theoretical chemistry can play a vital role in designing suitable material for this purpose.

The main purpose of the present article is to highlight the theoretical and computational work carried out on various aspects of front end and back end of nuclear fuel cycle at the Theoretical Chemistry Section, Chemistry Division, BARC. In what follows, modeling and methods used are mentioned in Sec. 2, a few salient results from our group are listed in Section 3 and finally the summary and future directions are outlined in Sec. 4.

## Methodology

The ab initio electronic structure calculations used in different research topics mentioned here are based on density functional theory (DFT). For this purpose, state-of-the-art computational programs like VASP, ORCA and TURBOMOLE have been used. The RASPA simulation code has been used for Grand Canonical Monte Carlo (GCMC) simulations for the calculation of adsorption isotherms of noble gases on porous materials. The classical molecular dynamics(MD) simulations are performed using GROMACS package for the design of novel materials for the actinide extraction from spent fuel. Apart from these standard codes, many in-house codes are developed and used for the post processing and analyses of large amounts of data obtained from simulations.

## Results and Discussion

### *Computational modeling of advanced nuclear fuels $UAl_3$ and $U_3Si_2$*

Among the intermetallic compounds of uranium, U-Al alloy is found to be promising nuclear fuel for high-power research reactors due to its high thermal conductivity and structural stability. U-Al system can form three different intermetallic compounds namely, $UAl_2$, $UAl_3$ and $UAl_4$. The calculated electronic density of states indicate that $UAl_3$ is metallic in nature and states near the Fermi energy are predominantly coming from U 5f states. Various thermal properties like, free energy, molar specific heat (Fig. 1(a)), bulk modulus, thermal expansion coefficient have been computed and compared with the available experimental results [5]. It is revealed that the contribution of electronic component to the molar specific heat becomes significant at high temperature. Both the electronic and phonon components of thermal conductivity have been measured using the Boltzmann transport theory. Thermal conductivity results indicate that the phonon contribution is important at very low temperatures and becomes insignificant as the temperature increases. The stability of different types of point defects in $UAl_3$ has been predicted by calculating their defect formation energies. Incorporation energies of fission products (Kr, Xe, Sr, Cs, and I) into different possible pre-existing vacancies like, U, Al and divacancy containing both U and Al vacancy sites in $UAl_3$ crystal lattice have been calculated to find the most favorable sites. We have also investigated the structural changes in $UAl_3$ influenced by the incorporation of different fission products. The results from current study can be helpful in gaining valuable insights into the behavior of $UAl_3$ fuel in a nuclear reactor.

Uranium silicide materials are projected as one of the possible accident tolerant fuels (ATF) and among different silicides of uranium, $U_3Si$, and $U_3Si_2$ are having the high uranium density [6-8]. $U_3Si_2$ has been found to have better stability and lower swelling as compared to $U_3Si$. In one of our studies, we explored the electronic structure and thermo-physical properties of $U_3Si_2$ within the framework of quasi-harmonic approximation (QHA) [9]. The measured mean thermal expansion coefficient between 0 K to 1200 K was found to be $18.19 \times 10^{-6}$ $K^{-1}$ which is consistent with the previously reported values ($15.2 \times 10^{-6}$ to $17.3 \times 10^{-6}$). Other thermo-physical properties viz. free energy, heat capacity, bulk modulus, etc. have been evaluated. The molar specific heat calculated from vibrational contribution alone was found to be underestimated compared to the experimental results. However, incorporation of the electronic contribution improved the results significantly. Electronic component of the thermal conductivity was calculated using the Boltzmann transport theory and the results were comparable to the reported experimental results.

### Effect of Lanthanide Fission Products on $UO_2$ Fuel

A large number of fission products are generated during the nuclear fission of uranium atoms in $UO_2$ fuel where lanthanide (Ln) ions constitute a significant portion. The interaction of fission products with $UO_2$ can impact its fuel properties and thus have significant consequences for reactor operation. For this purpose, the mechanical and thermal properties of $UO_2$ fuel in the presence of lanthanide (Ln) fission products are calculated using periodic density functional theory [10,11].The trivalent Ln atom substitution and presence of oxygen vacancies distort the $UO_2$ lattice (Fig.1 (b)). Among different Ln atoms, the values of these elastic moduli are increasing from La to Dy and inversely related to their Shannon ionic radii. We notice that there exists a linear relationship between doping concentration (atom %) and volume of doped $UO_2$ lattice. In general, bulk modulus of doped $UO_2$ lattices shows reduced bulk modulus values compared to pure $UO_2$. The magnitude of reduction is linearly correlated to the extent of Ln substitution in the $UO_2$ lattice. Our results are matched well with the available experimental observations reported for Ln substituted $UO_2$. The La and Dy atom doping also modifies the electronic energy levels of $UO_2$ by introducing new energy bands near the band gap region. The specific heat at constant

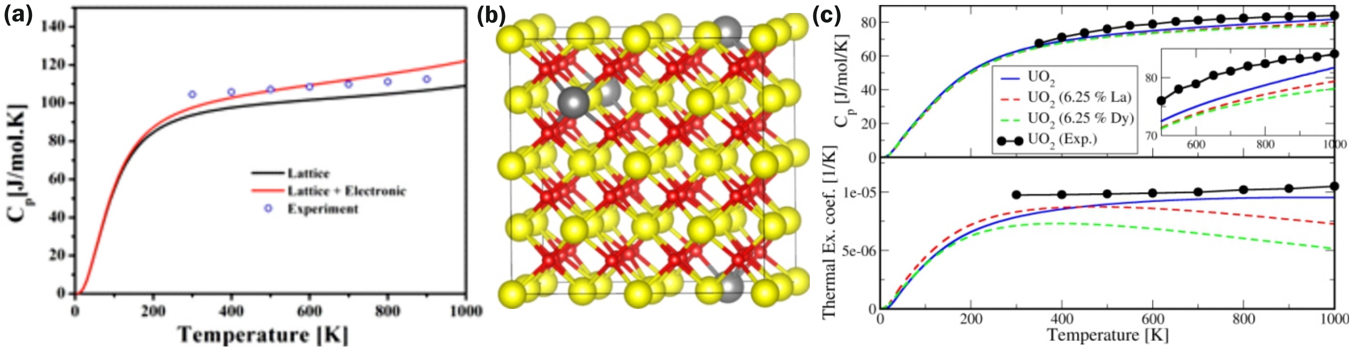

*Fig.1: (a) Molar specific heat of $UAl_3$ with and without the electronic contributions along with experimental results. (b) Optimizedcrystal structures of $UO_2$ with 6.25 % Dy doping. U, Dy and O atoms are represented by the yellow, grey, and red coloured spheres, respectively. (c) The specific heat at constant pressure, Cp and thermal expansion coefficient, α(T) of pure $UO_2$ and with La and Dy fission product doped (6.25%) $UO_2$. Enlarged figure for Cp from 500K to 1000K are shown in the inset for better comparison of $C_p$ values.*

pressure (Cp) and coefficient of thermal expansion of $UO_2$ fuel are reduced at higher temperatures due to the Ln atom substitution (Fig.1 (c)). The extent of the reduction is directly related to the amount of Ln fission products present in the $UO_2$ fuel.

The substitution of $U^{4+}$ ions by $Ln^{3+}$ ions creates a charge imbalance in the lattice which will be neutralized by either oxidation of U atoms from +4 to +5 state ($U_2Ln_2O_8$) or creation of oxygen vacancies ($U_2Ln_2O_7$). In the former case, the lattice volume is reduced in $U_2Ln_2O_8$ structures compared to that of pure $UO_2$ [12,13]. The substitution of lanthanide fission products in the $UO_2$ fuel amends the bulk and Young's moduli of the fuel (Fig.2 (a)). Further, specific heat capacity (Cp) is calculated for $U_2Ln_2O_8$ which show deviation at higher temperature from Cp of $UO_2$. However, these deviations are minor compared to Ln-doped $UO_2$ ($U_2Ln_2O_7$) structures with oxygen vacancies(Fig. 2(b)). The overall specific heat capacity of the $UO_2$ fuel matrix with the Ln fission product has contributions from Cp values of Ln-$UO_2$ where U in U(V) state ($U_2Ln_2O_8$) and Ln-$UO_2$ with oxygen vacancy ($U_2Ln_2O_7$). In another study [14], the trivalent and tetravalent Ce atom substitution in $UO_2$ and their effect on thermophysical properties is investigated. Further, the effect of Ce doping concentrations in $UO_2$ is assessed by varying the Ce ion concentrations in the lattice (6.25%, 12.5%, 25%, and 50%) for various charge balancing mechanisms. The lattice volumes of Ce doped $UO_2$ structures show higher or lower values compared to undoped $UO_2$ depending upon the oxidation state of Ce and U atoms. The electronic density of states analysis shows that Ce substitution levels as well as the oxidation state of Ce/U atoms strongly influences the band structure of the $UO_2$ lattice. The specific heat capacity of Ce doped $UO_2$ structures are calculated at different Ce doping concentrations and for disparate charge balancing procedures. Our results are helpful in the assessment of fuel properties of $UO_2$ with fission products in a more complex situation where multivalent oxidation states are present and different Ln replacement levels in the fuel.

## Nuclear Fuel Reprocessing and Waste Management

***Macrocycles*:** Designing novel ligands for the complexation of various fission products and long lived actinides have gained significant attention due to their environmental importance [15]. Strategies for reducing the mobility of these species usually center on their reduction to less soluble, lower oxidation state species, which in the case of uranium involves reduction of soluble U(VI) to insoluble U(IV). This process is facilitated by Multi-heme cytochromes in Bacteria and Iron containing mineral surfaces [16]. To design an efficient extractant, it is mandatory to know the speciation of the heavy metal ions in different environment at the molecular level. The rigid cavity of macrocycles modulates the speciation and binding of heavy metal ions that are similar to those of protein backbones. Pillar-arenes (PA) are largely hydrophobic in nature and upon functionalization with carbamoylmethylphosphine oxides (CMPO), they can be used for the selective extraction of Th(IV) ion in nitric acid and room temperature ionic-liquid medium [15]. DFT calculations are carried out to understand the speciation. DFT calculations clearly suggest the binding is stronger and the nitric acid weakly interacts with Th(IV) ion (Fig.3 (a)).Unlike PA, Cucurbiturils (CB[n]) are classic host molecule that can bind cations with large association constant (log $K_a$). In a theory-inspired study, we have shown that uranyl ion can bind strongly with CB-[5] host molecule [16]. We have studied the binding in several conformers, and we note that μ-5 binding is the most

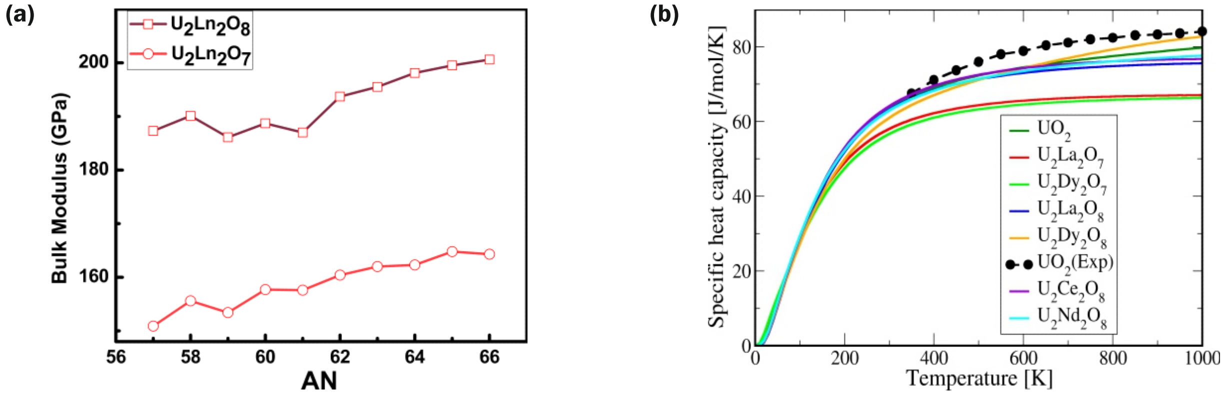

*Fig.2: (a) The bulk modulus for different $U_2Ln_2O_8$ and $U_2Ln_2O_7$ structures are plotted with respect to the atomic number of lanthanides. (b)The specific heat Cp of pure $UO_2$ and Ln substituted $UO_2$ without oxygen vacancies ($U_2Ce_2O_8$, $U_2La_2O_8$, $U_2Nd_2O_8$,$U_2Dy_2O_8$) and with oxygen vacancies ($U_2La_2O7$, $U_2Dy_2O_7$) are plotted.*

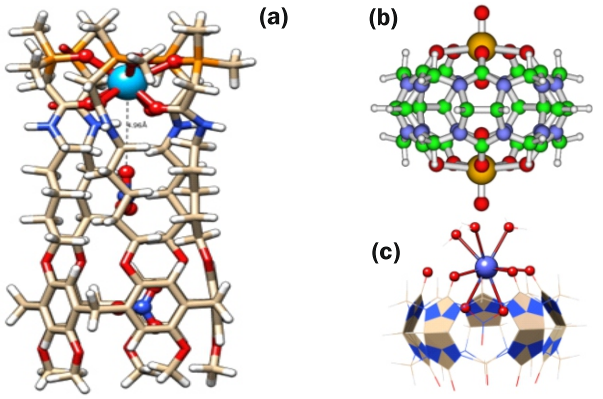

Fig.3: Optimized structures of (a) Th(IV) binding to functionalized PA[5], (b) uranyl and (c) Am(III) binding to CB-[5].

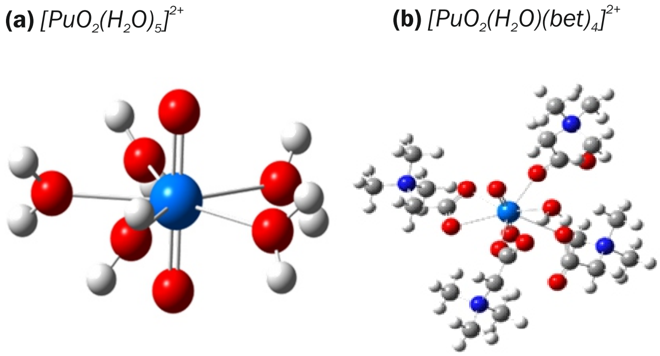
**(a)** $[PuO_2(H_2O)_5]^{2+}$ **(b)** $[PuO_2(H_2O)(bet)_4]^{2+}$

Fig.4: Optimized structures of $PuO_2^{2+}$ with (a) water and (b) with betaine and water.

favorable one (Fig.3 (b)). Experiments are conducted in parallel and surprisingly, X-ray data was released that our conclusions matched nicely [17]. We have also provided the structure and binding affinities of several functionalized CB-[5] with $[UO_2]^{2+}$, $[NpO_2]^{2+}$ and $[PuO_2]^{2+}$ species. Experiments are yet to be conducted on these radionuclides with functionalized CB-[5]. We have also studied the Lanthanide/actinide separation with CB-[5] host molecule [18]. The portal oxygens of CB-[5] are hard-donors favorably bind Eu(III) ion compared to the soft-nature of Am(III) ion. The counter-anions dictate the binding energies that are elucidated from electronic structure calculations (Fig.3 (c)). Our calculations are later experimentally proved by Tomar and co-workers [19].

***Deep Eutectic Solvents*:** In order to design suitable substance for extraction of uranyl ion, knowledge of structural and dynamical properties of uranyl ions in water is essential. Using MD simulation, various structural and dynamical properties of uranyl ions in water at different temperatures and concentrations of uranyl ions [20-23] are investigated. Our work on solid-liquid extraction using functionalized carbon nanotubes (CNT) demonstrated [24,25] that $COO^-$ functionalized CNT is a better candidate as compared to hydroxyl and amine functionalized CNTs. On the other hand, green solvents like Task Specific Ionic Liquids (TSIL), which has the specific complexing ability for the actinide ions, are excellent alternatives to the conventional solvents. Recently, direct dissolution of solid $PuO_2$ in betaine, a TSIL, is shown by Jayachandran et al. [26]. In order to get insight into this phenomenon, we have used electronic structure calculations. The structure has been optimized with the def-TZVP basis set and B3LYP functional with GD3-BJ dispersion correction in TURBOMOLE set of program. The optimized structure of the most stable aqua complex $[PuO_2(H_2O)_5]^{2+}$ formed with water is shown in Fig.4 (a). The overall structure including $PuO_2$ is pentagonal bi-pyramidal. When betaine is added, the most stable structure formed is $[PuO_2(Bet)_4(H_2O)]^{2+}$ with the optimized structure as shown in Fig.4 (b). It is interesting to observe that the presence of one water molecule provides extra stability to the mixed complex as compared to pure betaine complex. Investigations on various other aspects of complexation are in progress.

***Metal-organic frameworks*:** The conventional porous materials like charcoal, alumina and zeolites lack a superior selectivity and uptake capacity for the capture of Ng. Recently, metal-organic frameworks (MOFs) has been shown excellent selectivity and intake capacity for the separation of gas mixtures including noble gases. In our study, the noble gas adsorption properties of all the experimentally reported M-MOF-74s (M= Mg, Mn, Fe, Co, Ni, Cu and Zn) and yet to synthesize early transition metal M-MOF-74s (M=Ti, V, Cr) are investigated [27]. The computed lattice constants from our study matched well with the available experimental data. In any uptake capacity, Xe binds stronger than Kr in all M-MOF-74s. Analyzing the binding energies in 6 Xe/Kr + M-MOF-74 systems, Ti and Ni show highest binding energies while Mn and Cu have the least binding energies. For example, the binding energy for Xe follows this trend Ti > Ni > Co > Zn >Cr > Fe > V > Mg >Mn> Cu among different metal atoms in M-MOF-74s for a uptake capacity of six(per unit cell). In our calculations as well as in experiments, open metal sites are found to be the strongest binding sites for Xe/Kr. In another study, a new SBMOF-2 with Mg as central metal atom and polarizable groups with significant Xe/Kr adsorption have been proposed [28]. Computational modelling of 2D carbon allotropes such as graphene, graphdiyne and graphyne (Fig.5 (a)) with different dopants show that Xe/Kr adsorption is on a par with efficient MOFs [29,30].

In one of our studies, a series of MOFs, MFM-300(M) (M = Al, In, Ga, Sc, V, Cr, and Fe) were explored for selective capture of Xe from a Xe/Kr mixture [31]. Structural parameters calculated from the DFT optimized structures of the MOFs are consistent with the available experimental results. Various textural properties such as surface area, void fraction, largest cavity diameter, pore-limiting diameter, etc., were calculated. From the adsorption energies calculated through DFT calculations at varied loading capacities, the adsorption strength of Xe was found to be stronger as compared to that of Kr, and the adsorption energies were found to increase with increase in loading. Grand Canonical Monte Carlo (GCMC) simulations were carried out at different pressures to get the isotherms and the results indicated that the considered MOFs have significantly higher uptake capacities for both Xe and Kr and are selective for Xe over Kr. Based on the energy decomposition analysis, strong adsorbate−adsorbate interactions were observed at higher loading and that is more significant for Xe as compared to Kr. The observed strong adsorbate−adsorbate interactions were attributed to the confinement effects of the one-dimensional channels in considered MOFs. Among the series of MOFs considered, MFM-300(In) was found to have the best Xe/Kr selectivity factor and the Xe/Kr separation by the MOF is schematically represented in Fig.5 (b).

***Radioactive waste immobilization*:** Selecting a material, which can serve the purpose of both lanthanide hosts for photoluminescence and actinide host for nuclear waste immobilization, would be a great step in the area of advance materials technology. Extensive research has been carried out to explore efficient pyrochlore materials for radioactive waste immobilization. As for example, $La_2Hf_2O_7$ [32], $Lu_2Hf_2O_7$ [33], $Y_2Zr_2O_7$ materials show impressive features related to the

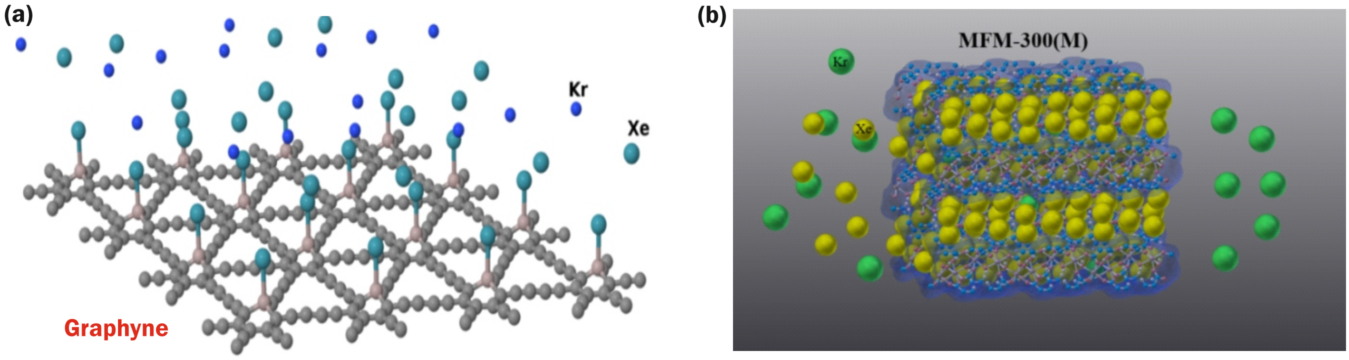

*Fig.5: Schematic representation of Xe/Kr separation by (a) graphyne and (b) MFM-300(M) MOFs.*

solubility of heavy metal in the host structure. Recently, calcium fluorapatite compound has been demonstrated as a potential host for radioactive waste immobilization. A special focus in this work has been given to $^{241}Am^{3+}$ion, which is highly radioactive and hazardous in nature and exists in the high-level radioactive nuclear waste [34].

### Design of Novel Phosphor Materials for Radiation Detectors

Among different phosphor materials, $LiMgPO_4$ shows many attractive features, like good sensitivity to ionising radiation, linear in dose response, radiation stability, low fading rate, reusability, so on. It has been explored that the presence of hole trapping centers, electron trapping centers, and recombination centers is very crucial for achieving good thermoluminescence efficiency [35]. The origin of experimentally observed thermo luminescence bands at 354 and 630 nm has been explained by the recombination of the stimulated electrons at defect states of singly and doubly charged oxygen vacancies, respectively (Fig.6). In a different study, for the first time using DFT, we have systematically investigated using the defect structures of LiF in the presence of Mg and Ti, commercially known as TLD-100, which has been extensively studied by various experimental groups worldwide [36]. We have explored the crucial role of each dopant element, as well as lattice vacancy defects and successfully explained the origin of observed optical spectrum of Mg, Ti-doped LiF. Thus, an unambiguous and ultimate clarification of the fundamental absorption, and emission processes in these materials has been accomplished.

### Radiation Damages in Nuclear Structural Materials

Neutron irradiation of steel creates a large number defects such as vacancies that modify the effective interaction between two large solute atoms (Sas). Smaller SAs like C, N, B, O has already been investigated by us [37]. Copper precipitations [38,39] in steel under neutron irradiation has been experimentally observed using Atom Tomography. How defects generated due to irradiation cause Cu-Cu interaction to be attractive has been investigated using first-principle electronic structure calculations within the framework of density functional theory (DFT). The present work [40] demonstrated the attractive interactions between a vacancy (V) or di-vacancy and the SAs (mainly Cu and Ni) in the bcc-Fe lattice. The attractive binding energy (BE) in case of V-$Cu_n$ and V-$Ni_n$ clusters, where V stands for vacancy and n is the number of SA atoms (Cu or Ni) vs. n is shown in Fig.7. By decomposing the binding energy into distortion energy and electronic energy using a novel algorithm [40], it is demonstrated that these two energies are compensatory in nature (see Fig.7(b) and (d)).

### Conclusion

In this article, multi-scale and multi-disciplinary research problems related to nuclear materials using different computational techniques are summarized. The structure-property relations derived here for different fuel materials allow the fuel performance assessment, which is relevant for the fuel design and nuclear safety. Several materials are designed based on multi-scale modelling to selectively extract actinide ions from a mixture of fission products. Moreover, the computer simulations can give relevant information in

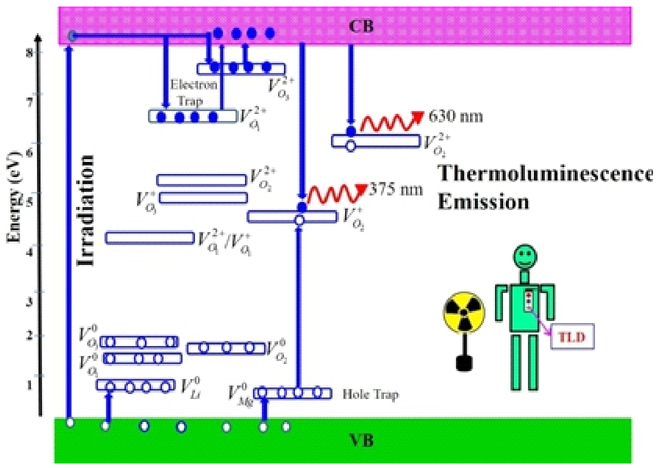

*Fig.6: Electronic transitions due to different defect states.*

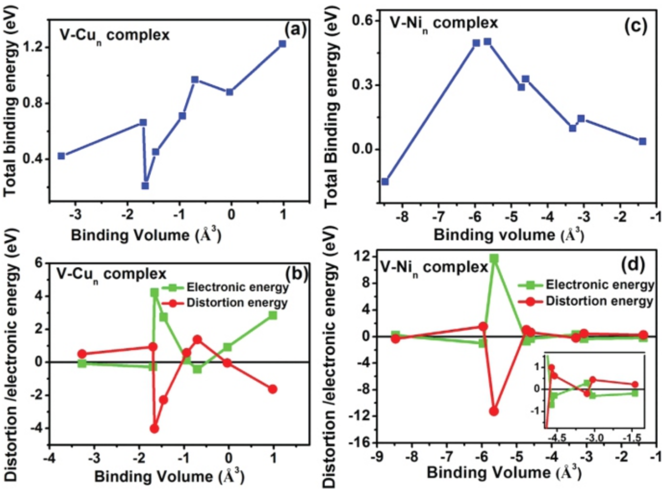

*Fig.7: Total binding energy and constituent distortion and electronic energy as a function of binding volume for V–$Cu_n$ complexes (where V stands for vacancy). The figure is reproduced from Ref. 40.*

designing significant materials for the storage/separation of radioactive noble gases. By performing systematic first-principles electronic structure calculations, we have analyzed in detail the radiation damage in steel. Now, computational modelling of nuclear materials is accelerated utilizing machine learning and artificial intelligence tools in our section.

## Acknowledgements

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## Target of Net-Zero Emission

4

# Computational Modeling for Energy Conversion and Storage

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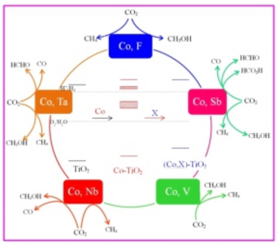

*$CO_2$ conversion behavior of $TiO_2$ in the presence of different dopant*

ABSTRACT

In this article, a brief account of the theoretical chemistry research activities related to green energy mission towards the net-zero targets has been presented. Specifically, the theoretical and computational studies related to the design of novel materials for solar energy conversion, including the solar hydrogen generation through photocatalytic water splitting, solar $CO_2$ conversion to usable fuels, and photovoltaic applications, development of efficient materials for reversible storage of hydrogen, and solid-state battery have been discussed. The whole spectrum of work discussed here includes design of novel materials with tunable properties and explaining complex phenomena using first principle quantum mechanical methods.

KEYWORDS: *Green energy, Solar energy, Quantum mechanical, DFT*

## Introduction

Development of alternate energy sources have become one of the major areas of interests due to limitation of long term availability of fossil fuels as well as environmental issues. There has been a growing interest on hydrogen energy as a renewable source. During past few decades extensive research activities including both experimental and theoretical are going on to make hydrogen energy realizable [1]. However, there are few challenges for the so called hydrogen economy viz., designing efficient strategy for the generation of hydrogen, developing cost effective, durable, safe, and environment friendly storage system. In this article, we have focused on both the important aspects related the hydrogen economy as mentioned above. Using the density functional based electronic structure calculations, we have designed wide variety of photocatalyst for the generation of hydrogen via visible light driven water splitting. To develop efficient materials for hydrogen storage, we have investigated different light metal decorated carbon porous nanostructures which can adsorb molecular hydrogen. The other major renewable energy source that has been used extensively is the photovoltaic (PV) systems/solar systems. Unlike the other renewable energy generation, where it is required to have continuous monitoring, maintenance and geographical limitations, solar cells system can be left unattended and require very minimal maintenance. However, the major disadvantage of solar panel to date is its low efficiency, which is affected by different parameters, including, the panel temperature, cell type, panel orientation, irradiance level, etc. In this regard, computational modeling of novel materials has been found to be very popular. Finally, we will present a brief discussion related to energy storage technologies, using rechargeable lithium/sodium ion battery, which are superior to all other secondary batteries due to their high energy density.

## Computational Details

Spin polarised DFT calculations for the material systems have been carried out using PAW based electronic structure code, viz. the Vienna ab initio simulation package (VASP) [2]. During geometry optimization, we use generalized gradient approximation (GGA) with Perdew–Burke–Ernzerhof (PBE) functional for the exchange correlation contribution [3]. On the other hand, electronic structure calculations have been carried out using Heyd–Scuseria–Ernzerhof (HSE) hybrid density functional to overcome the limitations of standard density functional [4].

## Results and Discussion

### *Computational Design of Novel Materials for Hydrogen Energy*

This section focuses mainly on both the important aspects related to the hydrogen energy, viz., design of efficient photocatalyst for water splitting to generate hydrogen, and developing materials for efficient reversible storage of hydrogen.

*$H_2$ Generation*: One of the most promising ways to produce hydrogen is the photocatalytic water splitting using solar energy. However, finding a suitable catalyst which can split water and produce hydrogen under visible light is a major challenge in this field of research. Till now, a wide range of photocatalysts have been developed, most of which are oxide based semiconductors, and recently various perovskite type materials have also attracted immense interest due to their potential catalytic property to split water. Among them, $NaTaO_3$, $KTaO_3$, $KNbO_3$, $NaNbO_3$, $SrTiO_3$ have been shown to be an excellent photocatalyst for the generation of hydrogen. However, their large band gap limits the photoactivity only to the range of UV light, which covers ~5% of the solar spectrum. Hence one of the biggest challenges is to modify its band gap so that it can utilize the visible light of solar spectrum for the photocatalytic applications. The introduction of foreign

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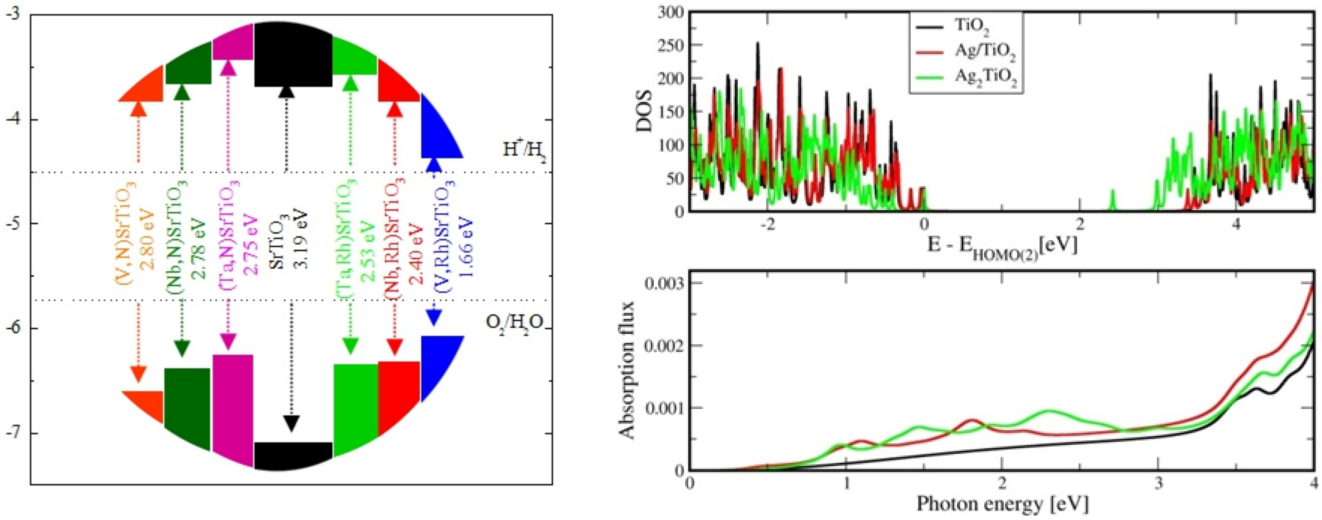

*Fig.1: (a) Change of band gap and band edge of $SrTiO_3$ in the presence of different dopant. (b) Density of states and absorption spectra of $TiO_2$ and $Ag/TiO_2$*

elements in the crystal lattice to change the band structure is observed to be one of the most promising ways to improve the visible light activity of the wide band gap semiconductor photocatalysts. Significant contribution has been made to enhance the photocatalytic activity of a wide range of perovskite based photocatalyst, viz. $NaTaO_3$, $KTaO_3$, $KNbO_3$, $NaNbO_3$, and $SrTiO_3$ [5,6]. An efficient strategy has been demonstrated to engineer the band structure of the photocatalyst in a controlled manner through doping with foreign element. It has been revealed that the choice of dopant atoms is highly material specific. Thus, it is shown that doping of (Mo, N) pair into $NaTaO_3$ is one of the most promising ways to improve the water splitting activity under solar light, while, (W, N) pair has been found to be most effective for enhancing visible light photocatalytic activity of $KNbO_3$, and $NaNbO_3$. However, in case of $KTaO_3$, (N, F) pair is found to be the most preferred one because of significant band gap lowering and the unique advantages of F for accelerating photocatalytic water splitting activity. The (V, Rh) pair is shown to be very effective for $SrTiO_3$ due to remarkable reduction in band gap with capability of releasing both hydrogen and oxygen during water splitting reported to date. Interestingly, these dopant pairs are chosen so that they form charge compensated system, thus greatly reducing the unwanted vacancy formation. More importantly, these dopant pairs result into the formation of clean band structure without any localized defects states in the forbidden region, which is very much essential for achieving higher photo-conversion efficiency. It is interesting to note that the reported results are found to be of great interest and beneficial to the researchers involved in the synthesis of new photocatalyst with improved features.

Recently, polymeric materials like graphitic carbon nitrides were also reported as potential catalysts for solar water splitting reaction to generate molecular hydrogen. Through our first-principles calculations, we proposed two-dimensional graphitic carbon nitride (g-CN) composed of the s-triazine units as a potential candidate for photocatalytic water splitting reaction [7]. The measured electronic band gap of the single layer g-CN through the more efficient hybrid energy density functionals is found to be 2.89 eV, which was found to further decrease to ~2.75 eV in multilayered structure. To further improve the visible light activity of g-CN, doping with different non-metal elements like B, O, P and S was considered to fine tune its electronic structure. Among the various dopants considered, phosphorus doping was found to be more effective in reducing the band gap to 2.31 eV. In a different study, effect of decorating with metal and metal cluster on the photocatalytic activity of graphitic carbon nitride has been investigated. Interestingly, Ag and $Ag_4$ cluster deposition on g-CN does not lead to any mid gap states which can be a better candidate. Calculated optical absorption spectra also indicate that the metal decoration leads to a clear shift in the absorption peak towards the visible region [8].

We also attempted to understand the overall photocatalytic water splitting reaction mechanism over the g-CN surface and calculate the associated overpotentials for both oxygen and hydrogen evolution reactions (OER and HER) [9]. OER over g-CN becomes completely downhill at and above the potential of 2.16 V and since the valence band of g-CN was located at a potential of 2.64 V, the photo-generated holes in the valence band of g-CN should be able drive OER without the aid of any co-catalyst. However, HER on g-CN was found to have an overpotential of around 1.1 V while the conduction band minimum of g-CN was at around 0.26 V above the hydrogen reduction potential and hence the HER needs a co-catalyst. Since the g-CN can be efficient for the OER and $g\text{-}C_3N_4$ was known to be a better candidate for HER, we also proposed a composite of these two materials as a better photocatalyst and was later experimentally realized.

The metal oxide surfaces with metal clusters play crucial role in photocatalytic applications. $TiO_2$ is extensively used in photocatalytic applications. Especially, the decoration of Ag clusters on the surface is a successful strategy to improve the efficiency. The Ag and $Ag_2$ adsorbates added new states near the bandgap region (Fig.1 (b)).The absorption flux is significantly increased in the 0.75 – 2.5 eV photon energy region for $Ag/TiO_2$ and $Ag_2/TiO_2$ which is important in photocatalytic and photovoltaic applications. The new states created by adsorption of Ag clusters are localized in nature, which prevents the hole carriers from recombination with electron carriers [10]. The relaxation lifetimes for electrons are comparable in the three structures. However, hole relaxation lifetimes are higher than electrons. The lifetimes of photo induced charge carriers such as electrons and holes amends the reduction and oxidation of molecular adsorbates, and reaction yields of their fragments and are very significant to photocatalysis.

*$H_2$ Storage*: Hydrogen has high chemical energy per mass (142 MJ $kg^{-1}$) and it is environmentally friendly, has infinite

reserve in the form of water. For the successful implementation of hydrogen as one of the alternative fuels, developments have been focused on a safe, efficient and reversible hydrogen storage medium which works at ambient conditions. In this regard, we have proposed few materials for hydrogen storage using the concepts such as electrostatics, curvature and aromaticity of the material [11,12]. The new predictions reported in our work demonstrate that the s-block metal cations can adsorb molecular hydrogen (without dissociation into atomic hydrogen) and form $MH_{16}$ complexes. It may be noted that the number of hydrogen atoms (nH=16) interacting with s-block ions is more than that for any transition metal cations and is the highest ever reported in the literature. The interaction of this kind is shown to be mediated by the simple electrostatic interactions and these concepts of ion-molecule interactions have been explored in utilizing to design the suitable materials for hydrogen storage purpose by considering the alkali metal doped fullerenes. Accordingly, it has been demonstrated that achievement of forming a stable complex of sodium doped fullerene molecule along with 48 hydrogen molecules is possible, corresponding to 9.6 wt %. Since the important requirements for the hydrogen storage materials, namely, weak interaction between the ion and molecular hydrogen and larger number of hydrogen molecules surrounding the ions, are met with the s-block elements, it can have important implications in designing the alkali metal ions based hydrogen storage materials. Although the synthetic procedures and applications of these metal hydride complexes are still at the embryonic stage, the present theoretical predictions and other experimental studies are likely to pave the way to the hydride chemistry of s-block elements, leading to better hydrogen storage materials. Very recently, we have put forward the single-walled carbon nanohorns as one of the potential candidates for hydrogen storage on the basis of 'intra-curvature'. An attempt has also been made to investigate magnesium clusters for the purpose of hydrogen storage and our results have shown that a complete dehydrogenation from these Mg nanoclusters occurs at ~100$^{o}$C which is a significant improvement over bulk $MgH_2$ (~300$^{o}$C) through *ab-initio* molecular dynamic simulation. The understanding gained from the above works has led to the development as well as rational design of hydrogen storage materials especially on the basis of carbon based nanomaterials.

### Efficient Materials for Photovoltaics Applications

We investigate the photovoltaic properties of two-dimensional (2D) cesium lead bromide($CsPbBr_3$) perovskite nanoplatelets (NPL) with thickness of few monolayers (ML) [13]. The photovoltaic properties of $CsPbBr_3$ NPLs are changing with layer thickness and show variation from bulk $CsPbBr_3$ perovskite. The band gap values for Pb-Br surface terminated $CsPbBr_3$ NPLs are 2.17 eV, 2.12 eV, 2.10 eV and 2.04 eV for 1 ML, 2 ML, 3 ML, and 4 ML, respectively from our DFT calculations. The band gap is reduced with increasing thickness of the NPLs due to the quantum confinement effects. The band gap obtained for 1 ML thickness from HSE06 calculations is 3.29 eV. Similarly, the band gap for bulk perovskite structure is 3.08 eV. Thus, the confinement along z-axis for 2D NPL can also affect other photovoltaic properties such as light absorption, binding energy of excitons and charge transport.

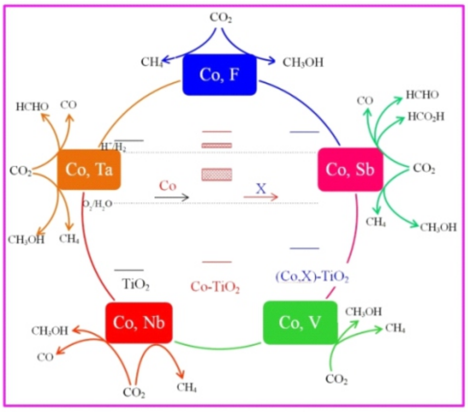

*Fig.2: $CO_2$ conversion behavior of $TiO_2$ in the presence of different dopant.*

### Computational Design of Efficient Catalyst for $CO_2$ Conversion to Fuels

Solar energy conversion of carbon dioxide to hydrocarbon fuels ($CH_4$, $CH_3OH$, CO, HCHO, and HCOOH) is considered as one of the promising approaches to reduce global warming and generation of sustainable energy. The mission for utilization of the sunlight to the maximum extent for these purposes has provided motivation to find efficient materials. Interestingly, codoping with (F/Nb/Ta) into Co-doped $TiO_2$ successfully reduce the band gap without forming any localized defect states, which is very much important for good charge carrier mobility and longer life time of the photogenerated charge carriers [14]. More interestingly, these materials show enhanced photoactivity for the $CO_2$ conversion processes under visible light irradiation (Fig.2). In a recent study, it has been predicted that the codoping of (Ni, La) or (Ni, W) pair into $SrTiO_3$ can lead to improved $CO_2$ conversion activity under sunlight.

### Development of Materials for Next-generation Li-ion Batteries

During the past few decades, there has been an emerging trend in energy storage technologies. An excellent example of energy storage devices includes the rechargeable lithium battery, which is superior to all other secondary batteries due to their high energy density. With experimental group biomass-derived carbon has been explored as versatile anodes for high-performance sodium and lithium-ion batteries using $Na_2Ti_3O_7$ nanorods, layered oxide material, $LiNi_xMn_yCo_zO_2$. The structural changes in the $Fe_3O_4$ electrode due to Li intercalation and de-intercatalation process in the electrodes during charging and discharging of the batteries have also been revealed. Sodium super ion conductors based structures are being explored as cathode materials for application in sodium ion battery technology. Doping with W has been found to enhance the structural integrity and enhanced Na-ion mobility significantly. Interestingly, Phosphorous/Fluorine-codoped carbon has been explored for enhanced both sodium ion and lithium ion storage [15].

## Conclusion

Under the present global climate of having large demand for developing a sustainable energy supply and effective environmental solutions, the utilization of solar energy holds a bright future for simultaneously addressing the energy demand and environmental challenges. In addition to the experimental approach in photocatalyst development, theoretical prediction and high throughput material screening should provide very powerful tools to guide the experimental community for rationally designing better materials with enhanced light harvesting, improved charge separation, transfer, and appropriate redox potential to drive the redox reactions. The principal objectives of our theoretical studies are to play a predictive role in the development of promising new materials, to provide fundamental understanding of processes that are difficult to extract from experiment alone, and to assist in the analysis of experimental results, and to elucidate the key atomic-scale features.

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# Healthcare & Biomaterial

## 5

# Healthcare Research: Computer Aided Drug Design

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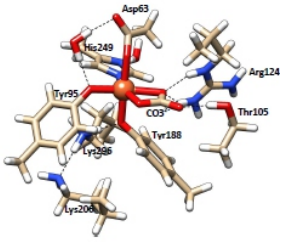

*Active site of iron-transferrin*

ABSTRACT

A brief account of research related to healthcare carried out in recent years in our group is portrayed here. With the advent of supercomputers, robust statistical mechanics based methods, and fast theoretical algorithms, computational chemistry research now plays an unprecedented role in healthcare and have direct relevance to the programs of DAE. The understanding of physical principles underlying biological phenomena and biological processes that are not otherwise achievable through experiments is investigated by employing both large-scale all atom molecular dynamics simulations and quantum mechanical methods.

KEYWORDS: *Biomaterial, Heavy water, Drug design, Decorporation, Targeted drug delivery, Bio-nanocontainer*

## Introduction

It is pertinent to pose a few questions, e.g., when and why a biomolecule (protein, RNA, DNA, etc.) folds, unfolds, or changes its conformation; why a drug stops working, etc. Answers to these questions can open up potentially important new avenues with immense healthcare, engineering, and societal applications. Successfully solving them might lead to the next super-drug or molecule with targeted, cost-effective applications in healthcare with minimal unwanted side-effects. However, the biological processes are so slow that studying them on the best supercomputers would take almost the age of the universe by employing conventional molecular dynamics simulation. One can overcome the uphill task by employing a biased simulation protocol. This will help in designing new decorporating agents for actinide contaminations, the use of heavy water in pharmacies, the design of drugs with better efficacy in reactivating intoxicated acetylcholine esterase, and the speciation of radionuclides in humic substances. In what follows, various codes used in biophysical research are described in Sec. 2. Various results, namely, thermo-stabilization of polio viral vaccine by using $D_2O$ in Sec. 3.1, use of viral capsid as bio-nanocontainer in Sec. 3.2, mechanistic insight into designing decorporation agents for actinides in Sec. 3.3, reactivation of organophosporous intoxicated acetylcholinesterase in Sec. 3.4, interaction of fission products with humic substances in Sec. 3.5 and biospeciation of actinides with blood serum transferrin in Sec. 3.6 are depicted. Finally, a brief summary is presented in Sec. 4 as a conclusion.

## Methodology

At present, *ab initio* electronic structure calculations for bio-molecules, and classical mechanics based all atom molecular dynamics simulations have been extensively used. GAMESS, TURBOMOLE and ORCA codes have been used for electronic structure calculations, in-house codes have been employed for analysis of mined data, and GROMACS has been used for all atom molecular dynamics simulations of biological systems to understand the observed phenomena and predict the mechanism of bio molecular action.

## Results & Discussion

### *Thermostabilization of Polio Viral Vaccine by using $D_2O$*

Heat plays a detrimental role in the therapeutic activity of many thermolabile liquid pharmaceuticals. This demands the maintenance of an uneconomical and logistically challenging cold chain, i.e., to maintain the pharmaceutical within a specified low temperature, and this is a billion-dollar industry. The majority of the live vaccines are stored at 2-8°C in order to sustain optimal cold temperatures, accounting for 80% of the financial cost of vaccination. The oral polio vaccine is considered to be the most thermo-labile of all the common childhood vaccines. Despite heavy water ($D_2O$) having been known for a long time to stabilize attenuated viral RNA against thermo-degradation, the molecular underpinnings of its mechanism of action are still lacking. Whereas, understanding the basis of $D_2O$ action is an important step that might reform the way other thermolabile drugs are stored and could possibly minimise the "cold chain" problem, thus making them more economical and reaching places with a scarcity of proper logistics. Here, using a combination of parallel tempering and well-tempered metadynamics, a biased MD simulation in both light water ($H_2O$) and $D_2O$, we have fully described the free energy surface associated with the folding or unfolding of a RNA hairpin of poliovirus-like enteroviruses. Parallel tempering meta-dynamics simulations reveal that in $D_2O$ there is a considerable increase in the stability of the folded state as monitored through the intramolecular hydrogen bond, size, shape, and flexibility of RNA structures. This transforms into a higher melting temperature ($T_m$) in $D_2O$ by 41 K (see Fig.1) when compared to that of light water ($H_2O$) [1]. Simulation in heavy water clearly showed that $D_2O$ strengthens the HB network in the solvent, lengthens inter-residue water-bridge lifetime, and weakens the dynamical coupling of the hairpin to its solvation environment, which enhances the rigidity of solvent-exposed

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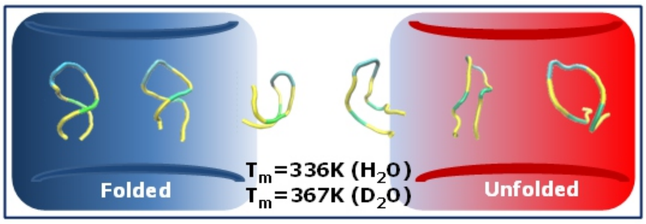

*Fig.1: Folding and unfolding behavior of RNA hairpin in $D_2O$ along with respective melting temperatures.*

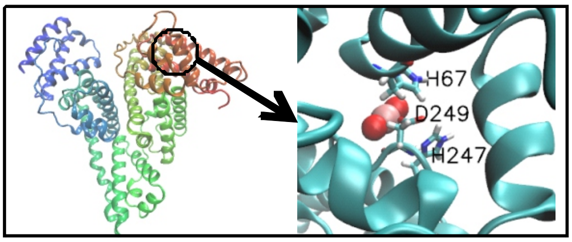

*Fig.2: Structure of the human serum albumin and its binding with $UO_2^{2+}$*

sites of the native configurations. The results suggest that, like other added osmoprotectants, $D_2O$ can act as a thermostabilizer when used as a solvent for storing polio vaccine. Liquid heavy water in place of light water has the tremendous potential to break the “cold chain” problem.

### *Viral Capsid as Bio-Nanocontainer*

Viruses are the simplest biological systems, essentially composed of a protein shell or capsid that encloses the packaged genetic material. The infection process and release of packaged materials depend on the structural changes of the capsid, which are sometimes induced by thermal fluctuations. Thermal fluctuations that induce structural changes in a capsid play a major role in the delivery of the confined material. Characterising the successive structural changes as a function of temperature may provide fresh insights into antiviral and nanomaterial strategies. We have calculated the heat-induced changes in the properties of a virus capsid using large-scale ($3.0 \times 10^6$ atoms) all-atom MD simulations, which was accomplished in the CPU-GPU architecture of the BARC Anupam system in a year time – by far this is a national standard. We focus on two heat-induced structural changes of the viral shell, namely, the dynamical transition (DT) [2] and the breathing transition (BT) [3]. DT (222K) brings forth the flexibility in the shell, which ceased to exist at cryogenic conditions and is measured through the sudden and sharp changes in the collective motion of hydrogen atoms. It is observed that at BT temperature (318K), the capsid changes from a non-functional form to a flexible and functional state, such that the breathing motions of virus particles become large enough to initiate disassembly and infection process [3]. The distribution of equilibrium atomistic stresses in the peptide fragments of the capsid reveals a largely asymmetric nature and suggests that structural breathing may actually represent large dynamic changes in the hotspot regions, far from the capsid pore, which bears remarkable resemblance to the recently conducted hydrogen-deuterium exchange coupled to mass spectrometry experiment. The findings have possible fallout in the development of therapeutic inhibitors of viral shells in general, the design of novel bio-nanocontainers, improved vaccines, targeted drug delivery, inactivation procedures for viruses in the food and pharmaceutical industries, heat-induced sanitization of public places, etc.

### *Mechanistic Insight into Designing Decorporation Agents for Actinides*

Radionuclides, mostly actinides are regularly handled in various routes of the nuclear fuel cycle, ranging from mining and power production to the reprocessing of spent nuclear fuel. Although there are stringent safety measures during the regular handling of radionuclides at all stages, the possibility of internal contamination due to these radionuclides cannot be ignored. Due to the growing applications of radionuclide-based materials in nuclear energy, defence, space industries, and medical applications, the danger of exposure to these radionuclides is a mounting concern for human health. During the handling of actinides, accidental discharge into the environment can cause severe health risks to human beings, ranging from minor problems like nausea and vomiting to more severe effects like failure of vital organs, cancer, and even death due to both radiological and chemical toxicity. These radionuclides can enter the human body via four major pathways: inhalation, through a wound (including an accidental injection), ingestion, or absorption through intact skin. Certain radionuclides, e.g., uranium, exhibit long biological lifetimes and are excreted at variable rates from the body. Recently, it was shown that human serum albumin (HSA), a major zinc carrier protein, can also bind with uranyl ions (see Fig.2); however, their behaviour with different biological ligands remains obscure. It is interesting to mention that environmental factors like pH plays very important role in the dynamics of proteins [4-6]. Thus effect of pH is included to understand the metal ion binding with HSA. Our MD study reveals that uranyl ions cannot associate to the zinc ion bound HSA protein but can be captured by free HSA at all pH values, i.e. endosomal, alkaline, and physiological pH [7]. The findings will provide important contributions in designing potential candidates for the decorporation of actinides from the human body.

### *Reactivation of Organophosporous Intoxicated Acetylcholinesterase*

In an effort to understand how a drug molecule accomplishes its task of interacting with protein molecules, several large-scale computations were performed and compared the efficacy of existing oxime drug molecules towards the recovery of the free nerve enzyme, acetylcholinesterase (AChE) from organophosporous (OP) or chemical warfare agent intoxications [8-9]. AChE is a serine hydrolase that catalyses the breakdown of the neurotransmitter acetylcholine. It hydrolyzes the choline ester into choline and acetic acid in order to terminate synaptic transmission in neuromuscular junctions and in chemical synapses of the cholinergic type, e.g., cholinergic brain synapses. AChE, the primary cholinesterase enzyme, is highly efficient, but its catalytic activity is limited by the diffusion of the substrate. The very high catalytic activity of AChE is attributed to a catalytic triad, which consists of a serine, a glutamate, and a histidine residue. The catalytic triad of the AChE is a vulnerable target of OP compounds [8-9]. The OP compounds bind to the serine of the catalytic triad and subsequently inhibit its catalytic activity. Despite the fact that fluorination makes a drug more lipophilic, the molecular level understanding of protein-fluorinated drug interaction is obscure [9-11]. Due to their enhanced ability to penetrate the blood-brain barrier, they are suitable for reactivation of OP-inactivated AChE in the central nervous system. Our MD studies show that the fluorinated oximes (FOBI/FHI-6) interact more strongly with the protein residues than the non-fluorinated oximes (OBI and HI-6); this is also verified from

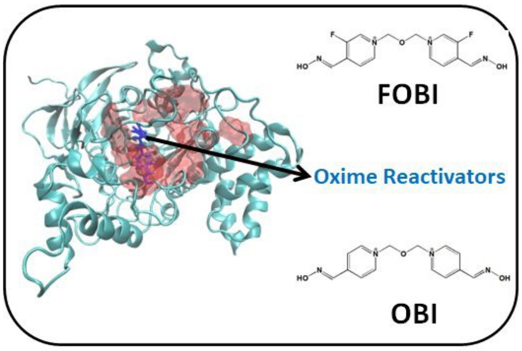

*Fig.3: Catalytic site of Acetylcholinesterase, and fluorinated and non-fluorinated oxime drugs.*

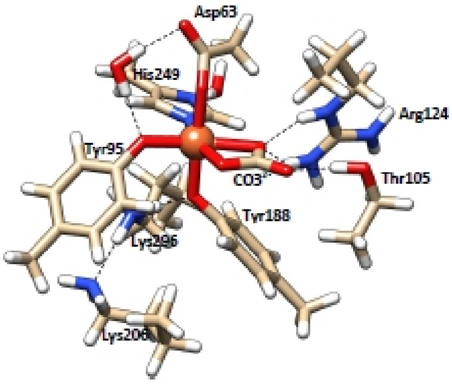

*Fig.4: Active site of iron-transferrin.*

quantum mechanical calculations. Distinct unbinding pathways for FOBI/FHI-6 and OBI/HI-6 are observed, as evident from the potential of the mean force profiles (see Fig.3) of unbinding process [11-12]. It is suggested that FOBI/FHI-6 drugs are held more firmly in the gorge of the AChE in comparison to OBI/HI-6 and may lead to higher reactivation efficiency of the OP-inactivated enzyme [11-12].

### *Interaction of Fission Products with Humic Substances*

Heavy metal ions such as uranyl ($UO_2^{2+}$), cesium ($Cs^{137}$) and strontium ($Sr^{90}$) radionuclides are one of the high level wastes generated from the back end of nuclear fuel cycle. The migration of these radionuclides in soil largely depends on chemical and biological reactivity of soil components. Natural Organic matter (NOM) is one of its essential components which are known to modulate the mobility of radionuclide cations like $Cs^+$ and $Sr^{2+}$. Humic (HA) and fulvic acids (FA) with varying oxygen contents can interact with heavy metal ions. HA itself can have few amino acids in their macromolecular structure. The NOM has several binding sites and identifying the probable binding pockets is a humongous task. To shed light on the possible binding sites and their transport behavior at the molecular level multi-scale model approach is used. We have used metadynamics, MD simulations and density functional theory based calculations to understand the binding mechanism of $Sr^{2+}$ and $Cs^+$ cations to FA, a model for NOM [13-14]. We find that $Sr^{2+}$ binds stronger through inner sphere mechanism, whereas $Cs^+$ binds weaker with outer sphere mechanism. These variation lead to $Cs^+$ is ready for plant uptake even in the presence of humic substances, whereas $Sr^{2+}$ does not. Our simulations reveal that water molecules modulate the speciation of $Sr^{2+}$ and $Cs^+$ ions. Very recently, we have reported the structures and binding of iodine species to HA. Iodine exist in two anionic forms namely iodide and iodates [15]. We proposed that iodate binds stronger than iodide and the former binding is less pH dependent than that of iodide. Our theory driven experiments based on UV-vis spectroscopic measurements of iodide and iodate with HA proved the computational predictions are indeed true.

### *Biospeciation of Actinides with Blood Serum Transferrin*

Blood serum Transferrin (sTf) metalloprotein mobilizes iron to the cell. The Fe(III) ion is surrounded by carbonate, asparate, tyrosines and histidine as shown in Fig.4 [16]. The active site is strongly specific to Fe(III).

Only 30% of the protein is saturated with iron, whereas the remaining 70% is ready for binding other metal ions including actinides. Radionuclides such as Th, Cm, Pu ions are known to bind transferrin, but their geometric structures are not known [17-19]. The bio-speciation of actinides in transferrin is challenging due to the following reason. The coordination number for Fe(III) is six, whereas for An(III) or Ln(III) is larger than six. Thus, transferrin is tailer made for Fe(III), whereas for Ln and An, the coordination number needs to be expanded. These variations can be scrutinized with multi-scale modeling techniques that were performed here. The predicted octa-coordinated structure of Th(IV) and hepta-coordinated Cm(III) species are comparable with the EXAFS data [17-19]. The vacant coordination number of actinides is saturated by solvent water molecules which are only possible through polarizable water force-field parameters implemented in our MD simulations. The effects of pH are also investigated in detail with quantum chemical and MD simulations.

Further, the possible decorporation of radionuclides using HOPO and CAM based decorporating agents are investigated in detail [18]. We have taken Pu(IV) ion as an example to understand the Pu–sTf interaction is a primary step toward future design of its decorporating agents. Due to the obvious experimental difficulties, such as, handling of radionuclides associated with health and safety concerns, we have explored the use of multi-scale computational techniques to understand the Pu(IV) binding with sTf and look out for its decorporation at extracellular pH using suitable ligands. Until now, we have screened two decorporating agents for Pu(IV); hydroxypyridinone (HOPO) and catechol (CAM)-based ligands. Pu(IV) at protein binding site is found to be strong that it was not detached with the docked HOPO, whereas CAM is found to facilitate dislodging the heavy ion from the protein's binding influence.

## Conclusion

In this article, theoretical research essential to (i) understand observed biological phenomena, (ii) predict mechanisms of bio-molecular action, and (iii) design new drugs with better efficacy is briefly discussed. The present results suggest the importance and necessity of the use of advanced statistical mechanics based strategies and sophisticated computational codes in a synchronised manner. The present-day amalgamation of the existing state-of-the-art computational techniques with artificial intelligence and machine learning-based algorithms will open up a new possibility in all facets of healthcare research in near future.

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# Molecular Diffusion

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# Microscopic Diffusion Mechanisms in Deep Eutectic Solvents

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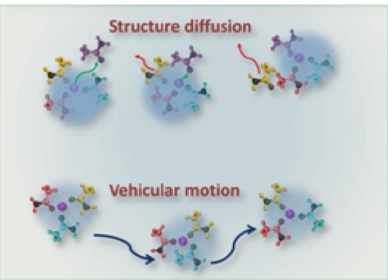

*Schematic representing structure diffusion and vehicular motion mechanisms of lithium transport*

ABSTRACT

Deep eutectic solvents (DESs), widely used in industrial and pharmaceutical applications, still lack a complete understanding of their physicochemical properties from a microscopic perspective. The control and efficiency of applications utilizing DESs hinge significantly on their transport properties. In this article, we report our simulation and theoretical studies on DESs unravelling the microscopic diffusion mechanisms which provide an insight into the emergence of their macroscopic transport properties. We investigate how the properties of DESs depend on their components and composition, with a focus on the pivotal role played by molecular interactions. Additionally, we explore the modulation of these interactions by water to analyze the correlation between water concentration and molecular diffusion rate in these systems. Our findings suggest that a thorough understanding of complex formation and kinetics in DESs can provide the necessary link to interpret the emergence bulk transport properties from molecular diffusion.

KEYWORDS: *Deep eutectic solvents, Molecular dynamics simulations, Diffusion, Neutron scattering*

## Introduction

Over the past two decades, deep eutectic solvents (DESs) have garnered significance due to their expanding applications across various industrial sectors [1,2]. Their popularity is driven by enhanced eco-friendliness and preparation protocols when compared to ionic liquids (ILs). Despite sharing similar physicochemical properties with ILs, DESs differ as they are not exclusively composed of ions; rather, they contain a substantial molecular component. Further, the constituents of the DESs are typically sustainable and biodegradable, as a result they are considered as green solvents [3]. Generally, DESs are created through mixtures of hydrogen bond donors (HBDs) and salts, offering versatility through the diverse options of HBDs (based on amides, glycols, phenols) and salts available for their preparation [1,4].

Deep eutectic solvents (DESs) have become valuable in a wide array of applications, including nanoscale synthesis [3,5], electrochemical processing [1,6], drug solubilization [7], and serving as electrolytes in batteries [4,8,9]. The intriguing functional aspects of DESs have ignited interest in exploring their fundamental properties. Understanding the molecular mechanisms responsible for their unique functionalities is essential for designing and synthesizing new DESs with tailored properties. Transport properties, particularly in non-aqueous solvents, play a crucial role in various industrial and pharmaceutical processes utilizing DESs. For example, in catalytic applications, achieving lower solvent viscosity is favourable for improving reaction rates, especially in diffusion-controlled reactions. Similarly, for electrochemical processes such as electroplating/ batteries, ionic conductivity, which is the key parameter, is also significantly controlled by solvent viscosity. Hence, understanding the microscopic diffusion processes that lead to their emergence is essential for gaining insights into the adjustability of their overall transport properties. These properties hold significance across various applications.

As a multicomponent mixture comprising both ions and molecules, DES displays complex microscopic transport phenomena due to the various intermolecular interactions present in the solvent. Furthermore, it exhibits glass-forming features, suggesting a strong interplay between structural relaxation and transport phenomena. These structural relaxations are facilitated by the relaxation of extensive intermolecular H-bond networks and complexes formed within the DES. Consequently, adjusting the intermolecular interactions within the DES emerges as a valuable approach to modulate its transport properties. In this context, water, being a strongly polar compound, serves as an effective agent for controlling molecular interactions and, consequently, adjusting both microscopic and bulk transport properties within the system.

This article unveils a collection of research conducted by our group, delving into the microscopic diffusion landscape and its origins arising from molecular interactions within DESs. The exploration is undertaken through a combination of molecular dynamics (MD) simulations, the theory of stochastic processes, and neutron scattering [4,8,10-13]. Our studies are focussed primarily on DESs based on acetamide and lithium salts. These DESs are shown to be potential candidates for electrolytes in lithium-ion batteries and supercapacitors [9,14,15]. It is observed that diffusion of acetamide in these systems exhibit a cage-jump mechanism which is linked to the nature of complexes formed in the DES. Further, at the microscopic level, the DESs exhibit dynamical heterogeneity which inherently emerges as a consequence of cage-jump mechanism. Owing to the ability of water to disrupt the hydrogen bond network and complexes, it is observed that addition of water makes the systems significantly more

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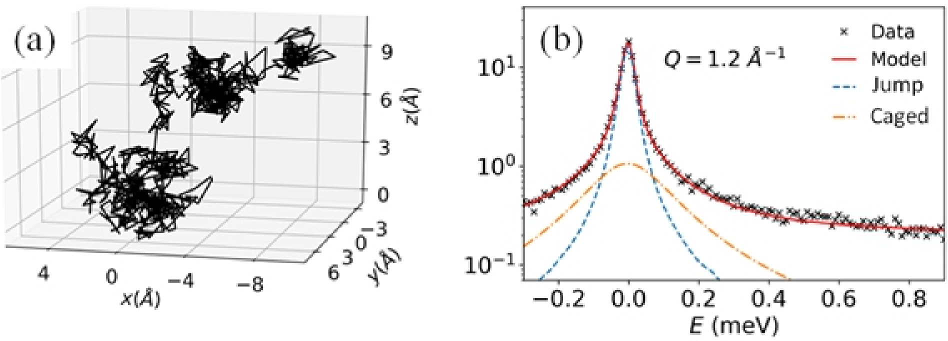

*Fig.1: (a) Simulated trajectory of acetamide COM molecules in DES. (b) QENS spectra of acetamide + $LiClO_4$ DES at Q = 1.2 Å$^{-1}$. The model function is based on cage-jump mechanism and the individual components for jump and caged diffusion are also indicated.*

dynamic. Studying the dynamics at different water concentrations offers a pathway to investigate the correlation between diffusivities and complex lifetimes in DESs. This becomes particularly relevant due to notable impact of water on the transport properties of DESs.

## Cage-jump Mechanism of Diffusion

Classical molecular dynamics (MD) simulations on DES based on acetamide and lithium perchlorate were carried out to understand the microscopic diffusion within the system [10]. In Fig.1 (a), we present the centre of mass (COM) trajectories of acetamide in the DES, revealing distinct patterns of local clustering and jump-like motions. This diffusion behaviour is characteristic of liquids with an extensive network of hydrogen bonding (H-bonding). The rationale behind this behaviour can be explained by considering the following arguments: At any given time, molecules within the system are typically either complexed or H-bonded with their neighbours, leading to localized caged diffusion. However, this cage is transient and is influenced by the lifetime of the formed complex or H-bonds. Subsequent to the relaxation of the cage, the molecules undergo jump-like translations, after which they reform their complexes with a different set of neighbours.

The cage-jump diffusion model can be verified using quasielastic neutron scattering (QENS) experiments [10], which distinctly probe the diffusion of acetamide molecules. This sensitivity is primarily attributed to the significant incoherent scattering cross-section of hydrogen atoms, making QENS particularly adept at probing the dynamics of hydrogen within the system. In fact, cage-jump diffusion model was also used to explain the QENS data of supercooled water and glycerol based DES. In Fig.1 (b), we show the data from QENS experiments on the DES and its model description based on a combination of jump and localized caged diffusion. The suitability of the data with the model clearly vindicates the presence of the cage-jump diffusion mechanism in this system. To comprehend the mechanism of cage-jump diffusion, it is crucial to explore the formation of various complexes within the deep eutectic solvent (DES) using molecular dynamics (MD) simulation data.

## Formation of Complexes

Our analytical approach centers on categorizing acetamide molecules into distinct states determined by their interactions with neighbouring molecules and ions. Two states of acetamide molecules were predominantly found – one corresponding complexes with lithium and the other free acetamide [8] – classified as bound and free acetamide, respectively. Typically, 35% of acetamide molecules were found to be in bound state and around 60% in the free state. Notably, the diffusion of bound acetamide in DES was observed to be ~ 3 times slower than the free acetamide molecules in the system. The formation of these complexes vindicated the transient caging of acetamide molecules during the diffusion process. This could be validated through studying the distribution of acetamide molecules around each lithium ion in the system. The typical time-evolution of number of acetamide molecules ($N_{ACM}$) in the first solvation shell of lithium ions is shown in the inset Fig.2 (a). The complete probability distribution, P($N_{ACM}$) calculated from MD simulations are also shown in Fig.2 (a), indicating that 3 and 4 are the most dominant coordination of acetamide around lithium ions. The snapshots of these complexes are indicated in Fig.2 (b).

The formation of complexes has important consequences to the mechanism of lithium transport within

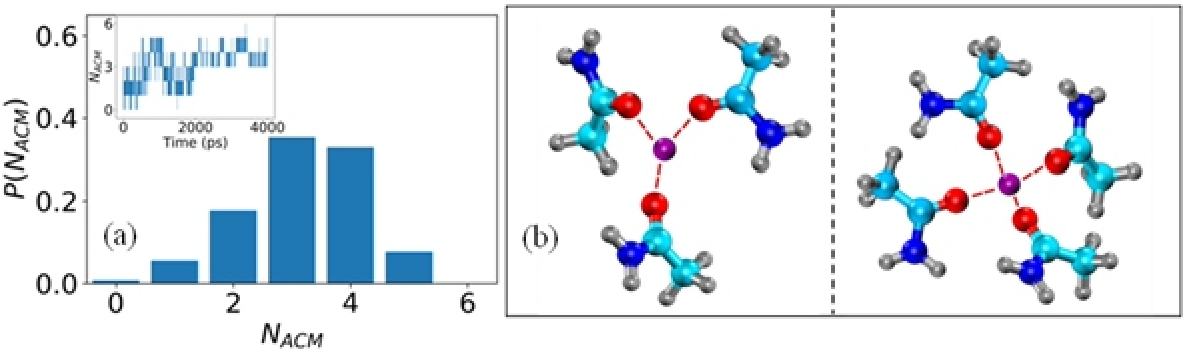

*Fig.2: (a) Probability distribution of $N_{ACM}$ for the lithium ions in the DES. (inset) Time evolution $N_{ACM}$ of a random lithium ion the system. (b) Simulation snapshots of lithium ion complexed with 3 and 4 acetamide molecules.(hydrogen – gray; oxygen – red; carbon – cyan; nitrogen – blue; lithium – magenta; chlorine – purple).*

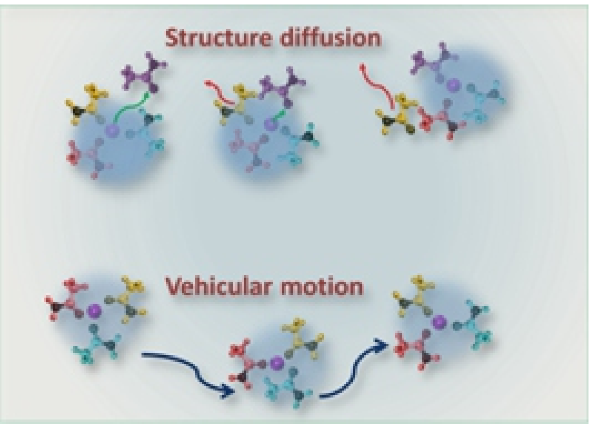

*Fig.3: Schematic representing structure diffusion and vehicular motion mechanisms of lithium transport.*

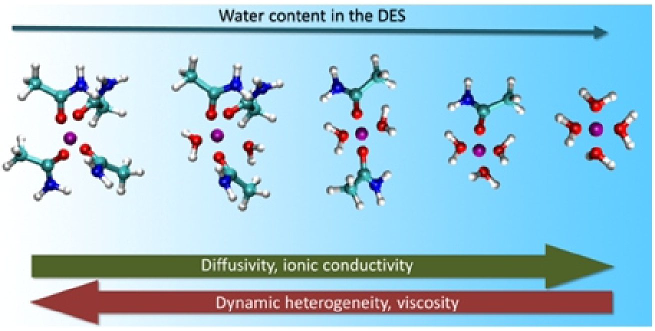

*Fig.4: Schematic showing the evolution of the complexes between lithium ions, water and acetamide in aqueous mixtures of acetamide based DES. As the concentration of water increases, dynamic heterogeneity and viscosity of the DES decrease, and diffusivity and ionic conductivity increase.*

DESs. In liquid electrolytes, there are two typical mechanisms through which lithium ions are transported–structure diffusion and vehicular motion, as represented in Fig.3. In structure diffusion, the lithium ions are transported by exchanging its neighbours and forming new complexes in the process of diffusion. Meanwhile, in vehicular motion, the lithium ions diffuse along with their first solvation shell without breaking the complex with acetamide. In the DES, it was observed that all the lithium ions were complexed with the different acetamide molecules in the DES and they're found to follow the diffusion of the bound acetamide molecules in the system [8]. This striking observation indicated that the mechanism of lithium transport in this system is most likely propagated by vehicular motion. In order to validate this, we also calculated the lifetime of these complexes using bond autocorrelation functions obtained from MD simulations. The typical lifetimes of these complexes between acetamide and lithium was estimated to be ~ 1 ns, suggesting that majority of lithium diffusion is propagated while the complex is intact [8].

## Modulation of Diffusion by Water

MD simulations of aqueous mixtures of the DES (acetamide + $LiClO_4$) were also carried out to investigate the effect of water on microscopic diffusion in the system [11,12]. Our studies revealed that the underlying solvation structure of lithium ions substantially changed due to the addition of water in the system. With increasing water content, acetamide molecules were displaced from the lithium solvation shell, replaced by water molecules, leading to availability of free acetamide. This change in lithium complexes leads to an increased diffusion of both acetamide and lithium in aqueous DES. The diffusion of different species in the DES more than doubled for water at 20 wt% [11]. It was observed that the diffusivity of acetamide, lithium, and perchlorate increases at least by a factor of two at just 5% water by weight. Subsequently, they continue to increase with water content and become about 4 times of their values at 20 wt% of water. The addition of water alters the nature of the complexes formed in the DES and also destabilizes the complexes resulting in a decreased lifetime. These two effects comprehensively lead to substantially enhanced diffusion within the DES. Further, the decrease in their diffusivities can also be associated to increase in the ionic conductivity and decrease of bulk viscosity.

The presence of dynamical heterogeneity in deep eutectic solvents (DESs), associated with a significant deviation from Brownian motion, is a well-established phenomenon [13,16]. By characterizing dynamical heterogeneity through the non-Gaussian parameter computed from molecular dynamics (MD) simulations, it was observed that the introduction of water led to a reduction in non-Gaussianity within the system [11]. This implies that the addition of water contributes to restoring homogeneity in the dynamics of the system. The impact of water concentration on diverse dynamical and structural properties of the DES is illustrated in Fig.4.

## Conclusions

Our comprehensive simulation studies on deep eutectic solvents (DESs) reveal a non-Brownian diffusion behaviour characterized by a cage-jump mechanism. The transient cages formed during diffusion result from the prolonged lifetimes of ion-molecule complexes. The formation of these complexes hinders the free movement of molecules, significantly slowing down the diffusive motion and thereby contributing to poor transport properties in DESs. To address this issue, we investigate the addition of water to the solvent, finding that water disrupts and destabilizes these complexes, leading to increased diffusion rates and reduced viscosity. The insights gained from our studies provide a mechanism for understanding how the controlled addition of water can finely adjust the microscopic diffusion properties of DESs. Moreover, these findings support the notion that the intricate molecular relaxation processes within the system are interconnected with the bulk transport properties that manifest as a consequence of such relaxation behaviour.

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## Theoretical Chemistry

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# New Theoretical Chemistry Methods: Shaping the Future of Chemistry

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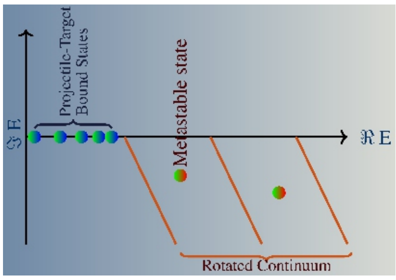

*Metastable states are obtained as complex eigenvalue solutions of the Schrödinger equation by imposing outgoing boundary conditions.*

ABSTRACT

The use of the latest theoretical methodologies and computational algorithms is driving chemistry research to new heights today. These remarkable new advances have enabled theoretical chemistry to move beyond the traditional field of ground-state chemistry of small molecular systems, allowing for innovative experiments to be proposed. With greater accuracy, it can now predict the excited-state and even the continuum-state chemistry of larger molecular systems by taking into account the relativistic motion of electrons. The integration of artificial intelligence and machine learning with these new theoretical developments has made theoretical chemistry a powerful and independent field of science. This article highlights the latest methodological advances made by Theoretical Chemistry Section, Chemistry Division, BARC in these areas.

KEYWORDS: *Theoretical methodologies, Computational algorithms, Artificial intelligence, Machine learning*

### Introduction

Theoretical chemistry, which was originally intended to provide conceptual and mathematical support for chemical and spectroscopical observations, became an independent field in the last century. Computers and computational algorithms have infused theoretical chemistry with remarkable predictability, accuracy, and enriched chemical reaction modeling. Current developments in theoretical chemistry enable it to expand the frontiers of chemistry in unprecedented ways. It has made significant original predictions in challenging fields including continuum-state chemistry, cold-chemistry, attosecond electron relaxation dynamics in molecules, light-matter interactions, modeling of astrochemical and prebiotic chemical evolution and validating the existence of symmetry violating interactions in nature originating from relativistic effects in many body systems. The symmetry violating interactions reveal 'a new physics' beyond the standard model of elementary particles, which are essential to understand the matter-antimatter asymmetry in our universe. The recent infusion of artificial intelligence and machine learning algorithms into theoretical chemistry has been instrumental in translating these developments to large chemical systems such as chemical solutions, bulk materials, and biological molecular systems. The contributions made by the *Theoretical Chemistry Section, Chemistry Division, BARC* towards these directions in recent times are briefly discussed here.

### Nuclear Metastability to Electronic Metastability: New Quantum Chemical Methods

Radioactive decay of metastable states of nuclei is of primary importance in nuclear physics and nuclear industry. Experimentally, the resonance structures observed in neutron-nucleus collision cross sections at low incident energy of neutron are associated with these metastable states. Consequently, they are also referred to as resonance states. In analogy to metastable nuclei, electronically metastable molecules can be prepared by low-energy electron (LEE)-molecule collisions [1]. Metastable negative ion states of a molecule, which are analogous to metastable nuclei created by neutron capture, are selectively and resonantly created simply by tuning the kinetic energy of the LEEs to the corresponding resonant electron attachment energy of the neutral molecular targets. Our focus here is on how electronic metastability is computed and how it helps us uncover a new area of chemistry, which we refer to as metastable-state chemistry. Quantum mechanically, metastable states are described by Gamow-Siegert wave functions, which are complex eigenvalue solutions of the Schrödinger equation obtained when imposing purely outgoing boundary conditions [2]. They do not belong to the Hermitian domain of the Hamiltonian. However, several mathematical methods have been developed to obtain these scattering solutions that correspond to metastable states in the Hermitian domain of the Hamiltonian itself [3,4]. The unbounded similarity transformation of the Hamiltonian is one of the most accurate mathematical approaches that map the scattering domain to the Hermitian domain. Like the unbounded similarity transformation, several analytic continuations of the Hamiltonian approaches have been used to extend the complex energy eigenvalue domain [3, 4].

Multiple analytical continuation approaches, including continuum remover complex absorbing potentials [5], complex back rotation transformation approaches [6], real-valued continuum remover potentials [7] and reflection free complex absorbing potentials [8] have been derived from our research. These methods are designed to utilize the advancements made by state-of-the-art bound state methods to directly calculate metastable states [3, 4, 9]. The continuum remover potentials which we developed are particularly interesting as they directly partition the continuum spectrum into the

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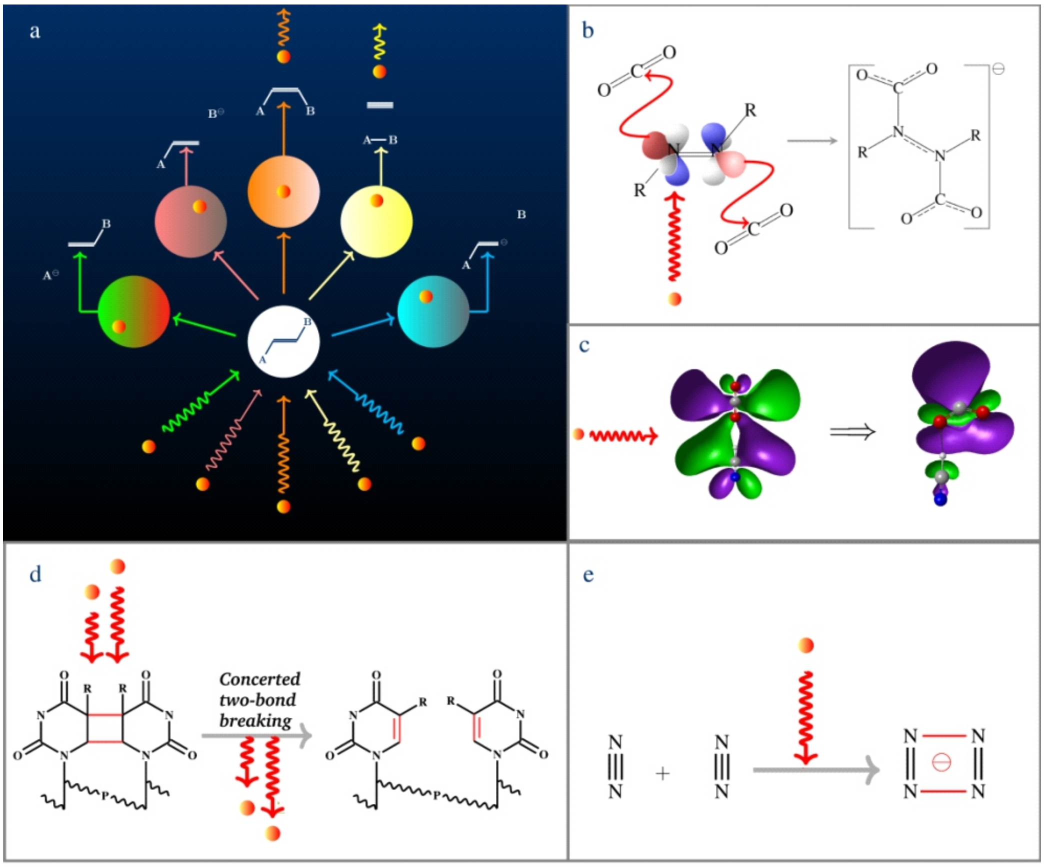

*Fig.1: (a) Electron controlled chemistry: An illustration of the use of LEE as a chemical tool to perform state-specific and site-specific chemical reactions is shown using a substituted ethylene molecule as a target molecule. Each colour wavy-arrow represents the kinetic energy of the electron that is resonantly captured by the target molecule and the corresponding negative ion meta stable state is shown using the same colour. (b) LEE induced chemical synthesis(See ref. 12). (c) LEE induced chemical activation of $CO_2$ (See ref. 13). (d) LEE as a chemical catalyst and an agent for DNA repair(See ref. 18). (e) Chemical synthesis of theoretically predicted molecules (See ref. 11).*

so-called Q-space and P-space wave functions, where the Q-space wavefunction is a projection of the metastable state wavefunction in the interaction region of the Hamiltonian. This partitioning of the discretized continuum domain helps us use this method in conjunction with the well-known Feshbach projection theory of nuclear metastable states for electronic resonance states [10]. In short, these new quantum chemical theoretical methods enable us to study the electronic metastability of molecules and their implications in chemistry, which has never been explored before.

### *Metastable-state chemistry*

The resonant capture of low energy electrons (LEEs, 0-30 eV) into the molecular field allows for chemical transformations to be made possible through metastable negative ions states of molecules. In practice chemical transformations specific to metastable negative ion states are triggered [11–14] and catalyzed [15–19] by tuning the kinetic energy of the LEEs to be the resonant electron capture energy of the molecules. Most remarkably, in addition to being state-specific, resonance attachment is an incredible tool for site-specific chemical reactions. This ability to create localized negative ion metastable states, in principle, can provide selectivity towards a site or even to a bond, which is one of the most attractive and ultimate goals of synthetic chemistry. The exploration of these experimental possibilities in molecular science to perform state-specific and site-specific chemical reactions has resulted in the use of LEE as a powerful quantum tool for controlling the chemistry of molecules (see Fig.1 (a)).

A remarkable theoretical demonstration of LEE as a chemical catalyst was achieved through our new quantum chemical methodology for electronic metastable states [15, 17–19]. This theoretical prediction, later proven experimentally [16], is believed to have a revolutionary impact on synthetic chemistry in the future. A few of the theoretical predictions we made based on this experimental possibility of using LEE as controlling and catalyzing chemical reactant are illustrated in Fig.1 (b-e). One of the immediate consequences of the LEE controlled chemical synthesis is that the theoretically possible chemical structures can be prepared through the resonant attachment of a low energy electron (LEE) through state specific reaction dynamics that have previously been unavailable [11, 14]. This possibility is discussed in Fig.1 (e).

Metastability can also occur when multiple photoexcited molecules are in the interaction region. Intermolecular Coulomb interactions facilitate the photoexcited metastable system to relax very rapidly via a new electronic relaxation channel available to the system, i.e., by ionizing an electron, and this mechanism is therefore known as intermolecular Coulombic decay (ICD). Since π-molecular systems are ideal chromophores for resonant electron excitation, and their $\Pi^*$ excited state wavefunctions are diffused, this mechanism will be operative when a π-molecular system is photoirradiated with UV light. This mechanism in a π-molecular system was successfully demonstrated for the first time in literature by our theoretical and experimental efforts [20]. We have also unravelled a few of its revealed its remarkable implications in chemistry [21–23].

## Development and Implementation of Relativistic Electronic Structure Methods for Atomic and Molecular Systems

Our research activity deals with the theoretical studies of symmetry violating properties which are relevant for the search of electron electric dipole moment (eEDM) and to probe physics beyond the standard model (SM) of particle physics. In this context, we developed many new codes/modules which are integrated with the DIRAC program package from time to time, and interfaced DIRAC code with many in-house developed advanced coupled cluster (CC) codes for the highly accurate/precise calculations of electronic structure and relevant properties of experimentally promising atomic and molecular systems. The matter-antimatter asymmetry of the present-day universe is one of the biggest mysteries to scientists. In 1967, Sakharov [24] showed that the dominance of matter over antimatter in our universe can only be explained if these conditions are fulfilled- (a) there must be *CP* violation (where *C* and *P* means charge conjugation and parity invariance, respectively), (b) there must be non-conservation of baryon number, and (c) there must be interactions out of thermodynamic equilibrium. Our research activity deals with the first condition of Sakharov's proposal, i.e., searching for *CP* violation in atomic and molecular systems.

Observation of permanent electric dipole moment (EDM) [25] of a non-degenerate quantum system (i.e. stationary atomic or molecular state) arising from both the lepton as well as the hadron sector of matter such as the electron EDM, the nucleon-electron scalar-pseudoscalar (S-PS) interaction, the nuclear Schiff moment and the nuclear magnetic quadruple moment (MQM) [26] is a signature of simultaneous violation of time-reversal (T) and parity (P) invariance. The T violation is equivalent to CP violation according to the CPT theorem. However, CP violation within the SM of elementary particles fails to explain the observed imbalance between matter and antimatter. Such CP-violating properties, viz., the EDM of electron and nucleons, the scalar-pseudoscalar (S-PS) [27-28] nucleon-electron neutral current interaction, and the nuclear MQM etc. can contribute to the permanent EDM of an open-shell paramagnetic molecular system, which, in principle, can be measured experimentally. To extract the values of electron EDM, nuclear MQM and S-PS coupling constants from the experimental data, various electronic structure parameters of potential molecular candidates are essential. These parameters cannot be obtained from any experiment but can be calculated from highly accurate ab initio methods that can treat the effects of both electron correlation and special relativity. The JILA [25] and the ACME [29] have performed electron EDM experiments using YbF and ThO, respectively. An experiment with BaF is underway by the NL-eEDM [30] collaboration. In 2014, we put an upper bound on the electron EDM as $d_e \leq 9.7 \times 10^{-29}$ e-cm from our theoretical studies on ThO [31] and with the experimental data obtained from the ACME collaboration. A triatomic molecule, YbOH has also been proposed as a candidate for MQM experiment.

### *Relativistic ab initio methods for symmetry violating and properties*

We are involved in developing highly accurate wave-function-based methods that incorporates the electron correlation effects as well as the relativistic motion of electrons and then computing the accurate values of CP-odd molecular parameters. Property modules for the study of various symmetry violating interactions and the configuration interaction (CI)-based expectation value methods are implemented as new features and released with the open-source code DIRAC program package [32]. The truncated CI-based methods are not size-extensive, which demands more robust wave-function-based methods for accurate prediction of CP-violating molecular parameters. On the other hand, coupled cluster methods at any level of truncation are always size-extensive and thus are more reliable than the truncated CI methods. In particular, the four-component relativistic CC-based methods are best suited for this purpose as it can simultaneously take care of the effects of electron-correlation and relativistic motion of electrons in an efficient way. We have been involved in the implementation of a number of relativistic single reference coupled cluster (SRCC)-based analytical methods, viz., Z-vector, expectation-value and extended coupled cluster (ECC) approaches for the precise calculations of molecular properties [33-35]. Out of these three methods, the Z-vector approach has been found to be the most reliable and efficient in predicting the said CP-odd molecular properties. Within the CC-based Z-vector approach, properties of interest can be computed by the following equation:

$$\Delta E' = \langle \Phi_{DHF} | (O_N e^T)_c | \Phi_{DHF} \rangle + \langle \Phi_{DHF} | [\Lambda (O_N e^T)_c]_c | \Phi_{DHF} \rangle$$

where, $O_N$ is the normal-ordered property operator and T($\Lambda$) is the excitation (de-excitation) operator whose amplitudes can be determined by solving the respective amplitude equations. $|\Phi_{DHF}\rangle$ is the four-spinor-based Dirac-Hartree-Fock wave-function and is used as the reference function for constructing the CC wave-function $|\Psi\rangle = e^T |\Phi_{DHF}\rangle$,The *c* in the subscript of the above equation means the connectedness that ensures the size-extensivity of the method.

The new modules developed and implemented in DIRAC program package by us are one of the essentials tools for theoretical studies of CP violation. Furthermore, using our in-house developed relativistic coupled cluster methods, one not only can accurately predict the symmetry violating molecular properties but also can understand the role of electron correlation and special relativity in precise calculations of energy and properties of atomic and molecular systems.

## Mesoscopic Model for Plasmons of Noble-metal Clusters on a Solid Surface

Clusters of noble-metal atoms with 10 to 100 atoms adsorbed on a solid surface show electronic structure properties representative of molecules, and they can display collective electronic phenomena resembling to plasmons in metal solids. Our study shows the optical absorption by the nanostructured silicon (111) surface with large silver (Ag) clusters $Ag_n$, n=33, 37 (open shell) and n=32 (closed shell), (Fig.2 (a)) adsorbed on the slab surface [36]. Adsorption of Ag clusters on Si surface increases the light absorption by large percentages with surges in absorption peaks in the regions of photon energies corresponding to localized plasmons (Fig.2 (b)). Absorption spectrum of metal cluster/solid surface structures is modelled employing a mesoscopic Drude-Lorentz model. A general description of the location and shapes of the absorption peaks related to plasmon frequencies can be related to the electron densities of finite metallic clusters. Therefore, plasmon frequency $\omega_{pl}$ for the solid silver metal is connected to the electronic density per unit volume. We have derived a mesoscopic model connecting the electronic polarizability generated by plasmon oscillations and the applied electric field. These plasmon oscillations are dependent on the Lorentz restoring force due to the distribution of ion and electron charges in the system and to a dissipative Drude friction. The restoring force is directly related to the plasmon frequency ($\omega_{pl}$)and friction term is connected to the plasmon relaxation time (lifetime) ($\pi_{pl}$) Finally, an

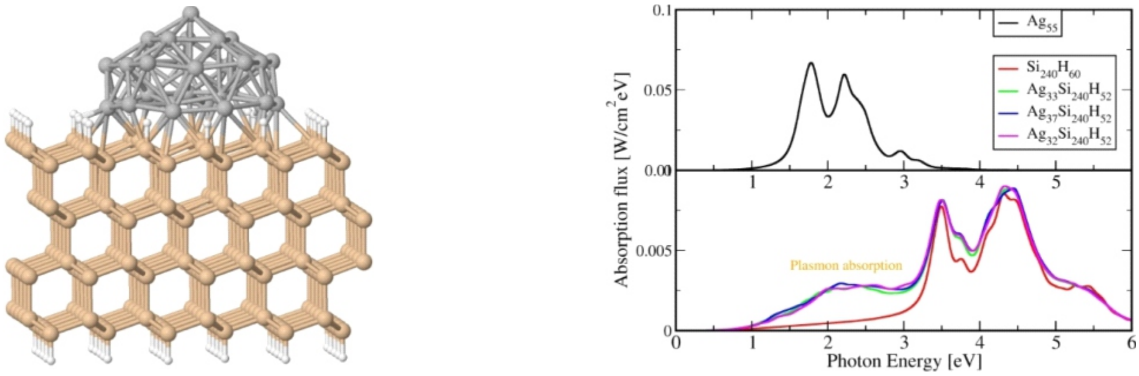

*Fig 2: (a) The $Ag_{32}Si_{240}H_{52}$ structure where $Ag_{32}$ cluster is adsorbed on a Si surface. (b) Absorption spectrum for the $Ag_n$/Si(111)structures, Si surface and $Ag_{55}$ cluster.*

expression for the plasmon light absorbance per unit length is derived as follows [36].

$$\alpha_{pl}(\Omega) = \frac{1}{c\eta}\frac{\omega_{pl}^2\,\Omega^2/\tau_{pl}}{(\Omega^2-\omega_{pl}^2)^2+(\Omega/\tau_{pl})^2}$$

which shows a Lorentzian line shape. Here, the plasmon absorption peak (line shape) provides the frequency and lifetime of the plasmon. These two values can be extracted from our calculated absorption spectrum given in Fig.2 (b), which gives adsorbate ($Ag_n$ cluster) plasmon frequency of $\omega_{pl} = 3.9 \times 10^{15}\ s^{-1}$ ($h\omega_{pl}$ = 2.56eV) and lifetime of $\pi_{pl} = 0.5\text{x}10^{-15}$ s = 0.5*f*s. The calculated plasmon energies overlap with the appropriate solar photon energies, making the present structures and properties relevant to applications for solar cells and photocatalysis.

### Bridging Finite Size Properties to that of Bulk

Understanding the process of solvation in the condensed phase has been fundamental to diverse areas of research in chemistry, physics, biology, and related disciplines of science and engineering. Despite enormous interest, a precise quantification of the solvation energy for finite as well as bulk systems with unknown interaction potential remains elusive. Recently, with the advent of supersonic expansions and nozzle-beam techniques, solvation in finite-size hetero clusters has been amenable to experimental observation, and renewed interest has grown in the theoretical arena to connect the finite-size cluster properties to the bulk properties, viz., solvation energy, electron-detachment energy, and charge-transfer-to-solvent spectra [37-39]. A new general relation for the size-dependent solvation energy, electron-detachment energy, and charge transfer-to-solvent energy (CTTS) of finite size solvated negatively charged clusters is derived based on a microscopic theory with unknown interaction potential (see Fig.3). It is shown that the new extrapolation formula, when fitted to finite-size cluster data, yields significantly more accurate results for bulk values of X.n$H_2O$ (X= $F^-$, $Cl^-$, $Br^-$, I-, $SO_4^{2-}$, $C_2O_4^{2-}$, $Po_4^{3-}$etc) and X. n$CO_2$ (X=F-, Cl-, Br- and I-) systems. Our present study reveals that the maximum error on the calculated bulk values, as compared to the experimentally measured ones is 5%. More importantly, the robust scheme proposed here provides a route to obtain bulk values from the knowledge of electron-detachment energy and CTTS for finite and complex systems whose inter-particle potentials are unknown (see Fig.5). The general microscopic theory-based expression can also predict instability ranges of multiply charge anions e.g $SO_4^{2-}$, $C_2O_4^{2-}$, $PO_4^{3-}$etc [39].

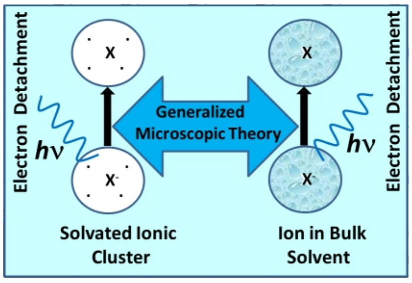

*Fig.3: Connecting finite size properties to that of bulk*

Statistical mechanics and generalised linear response theory-based approaches are also employed to derive the analytical expressions for the size dependent dielectric constant and normalised orientation polarisation of solvents from the knowledge of the bulk value [40]. As an illustrative example, water is considered, and the dielectric constants for the same are calculated over the entire range of water clusters. Our results reveal that the dielectric constant and normalised orientation polarisation are monotonically increasing with the increase in the number of solvent molecules and converge to the respective bulk values in the thermodynamic limit. More importantly, the size dependent dielectric constant is found to be independent of the nature, geometry, and microscopic charges of the non-spherical ions, which offers a new platform for calculating the hydration energy and orientational polarisation based on linear response theory for different kinds of ions in the solvent medium.

### Machine Learning Models and Data Mining Tools for Large Scale Materials Exploration

Data Science along with advanced machine learning (ML) algorithms have shown potential applications in exploring new molecules and materials at a much faster pace as compared to the conventional methods [41]. In recent years, computational high-throughput screening of molecules and materials are shown to be promising to screen large database of molecule/materials for a particular application [42]. For such a large-scale screening, fast and accurate computational tools with optimum speed and accuracy are required. Quantum chemical or density functional theory (DFT) based methods can be more accurate, but these methods are computationally expensive and impractical for large scale studies. On the other hand, empirical and semi-empirical methods can be faster, but the accuracy and transferability can be poor. Hence, training machine learning models using reliable data can optimize the computational time and accuracy. In one of our recent studies, where the target was to screen a large database of metal organic frameworks (MOFs) for $CO_2$ capture applications, accurate atomic charges were required to treat the host-guest interactions in a force field simulation. Since the atomic charges from DFT are very expensive and the empirical charge methods were reported to give inaccurate charges for certain atoms, we trained a machine learning model for assigning atomic charges to the atoms in MOFs [43]. A Random Forest ML algorithm has been trained using a limited set of features representing both the elemental properties and the local bonding environment around that atom. Database of about 380,000 atomic charges were calculated using the Density Derived Electrostatic and Chemical (DDEC) method on a subset of the Computation-Ready Experimental Metal-Organic Framework (CoRE MOF-2019) were used to train, test and validate the model. Random forest regression algorithm was found to perform better among the considered models with $R^2$ and mean absolute error values of 0.995 and 0.019 respectively. Our model has been deployed as open-source software, Partial Atomic Charges in Metal-Organic Frameworks (PACMOF) [44] and the package has been extensively used by the researchers in the field.

## Summary

We are consistently at the forefront in developing newer theoretical methods. Our in-house developed *ab initio* theories for metastable states have made remarkable original contributions in a yet-to-be explored area of chemistry. We have made a valuable contribution to the international joint initiative to develop a state-of-the-art *ab initio* method for the electron-correlated description of atomic and molecular systems including relativistic effects. New theoretical methodologies have also been developed and implemented for the *ab initio* computation of light absorption and subsequent dissipative dynamics in metal clusters. By incorporating statistical mechanics and generalized linear response theory-based approach, a better understanding of the process of solvation in the condensed phase is achieved. By developing a Python-based open-source machine learning code for large scale screening of metal organic framework, we are also confidently advancing into the future of data science. All these developments in our Section can lead to proposals for new experiments in different areas of science. To sum up, ourSection has made significant accomplishments by developing new theoretical methodologies for frontier and interdisciplinary fields of science.

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## Design and Development

**8**

# Single Atom Alloy Catalysis: Perception and Design

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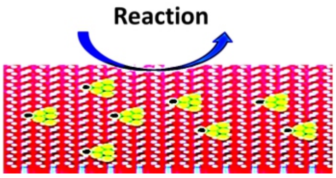

*Atoms are dispersed on support*

ABSTRACT

Catalytic materials are crucial for energy and environmental sustainability. Computational material science has been indispensable tool to design novel and efficient catalytic material. Single atom catalysis is based on the philosophy maximizing the efficiency of catalyst. The present article provides a general introduction to newly emerging area 'Single-Atom Alloy Catalysts (SAAC)'. Afterwards our computational attempt in designing single atom alloy catalyst for sulfuric acid decomposition reaction (*most endothermic step of Sulfur-Iodine (S-I) thermochemical cycle*), is presented.

KEYWORDS: *Single Atom Alloy catalyst, DFT, SI cycle, Ag-Pt cluster, Pt(111) slab*

### Introduction

Catalysis is a kinetic phenomenon where catalytic material alters the rate of a chemical reaction, ideally without being chemically changing itself. Catalysis and Catalytic material designing are strategic field for development of newer technologies benefiting the society and this field play key role in reducing energy consumption/cost in industry. Well-known examples of catalysis are Haber process for the ammonia synthesis, contact process for sulfuric acid production, utilization of catalysts for petroleum cracking. Other than energy applications, catalytic materials are also equally important for environmental applications such as abatement of pollutants, volatile organic compounds (VOC). Industry uses various catalytic converters and smokestack scrubbers to help keep sulphur pollutants out of the atmosphere. Transport vehicle uses automotive catalytic converters to reduce the content of toxic gases and pollutants in their exhaust gas.

According to the phases in which a catalyst and the reactant(s) are present, catalysis can be classified as homogeneous, heterogeneous or biological/enzymatic. The areas of catalysis, surface chemistry have been of interest in the departmental activities of DAE i.e. catalysts for hydrogen mitigation under LOCA condition in nuclear reactor, or catalyst for D/H isotope exchange under bi-thermal condition. Schematic presented in Fig.1 summarizes the various catalysis processes being pursued in Department of Atomic Energy (DAE). In past, both homogenous Catalysis (Suzuki C–C cross coupling case) and heterogeneous catalysis (nanoparticles on oxide support) has been pursued in the DAE and presently also, department has various programs to design and development of novel catalytic materials with improved efficiencies for various energy and environmental application.

Homogeneous catalysts usually possess superior activity and/or selectivity but the major issue of separating catalyst from raw materials and products limits their real application. Molecular-level understanding of heterogeneous catalysis tells that when a solid catalyst is used to speed up a chemical process, the overall reaction usually consists of a series of elementary steps such as adsorption of the reactants on the surface of the solid, diffusion on the surface, breaking of some reactant bonds, and the creation of new ones to form the product molecules, which eventually desorb from the surface. Due to this heterogeneous catalyst always exhibit lower atom efficiency in the catalytic process. To combine the advantages of both heterogeneous and homogeneous catalysts, Single-atom catalysts (SAC) emerging as a new area in the catalysis community [1-4].

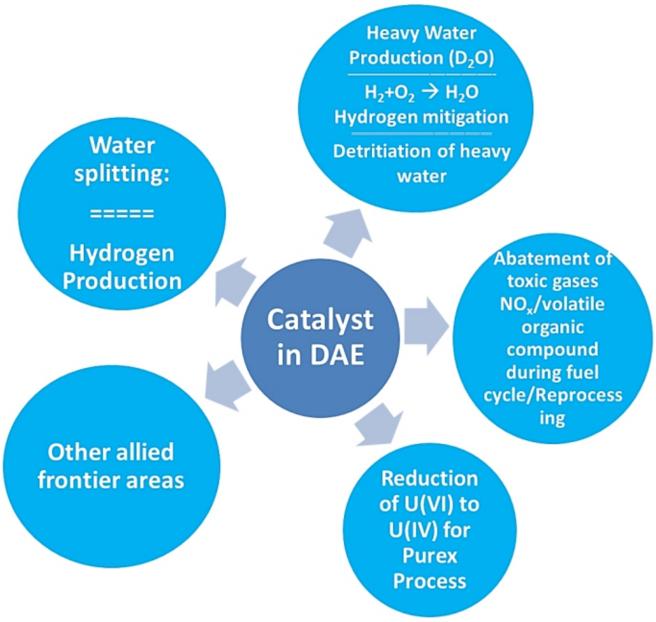

*Fig.1: Schematic diagram showing some of the catalytic processes being pursued in DAE.*

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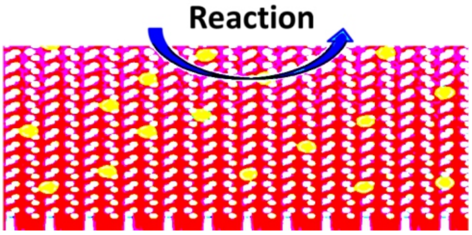
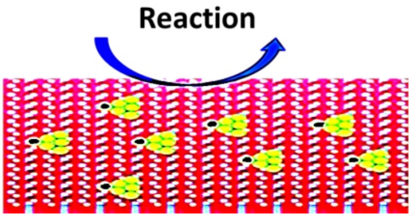
Single atom catalyst (SAC) is a catalyst where isolated atoms are dispersed over a support [1-3]. During the last decade this field of research has attracted a great deal of attention because of two reasons (1) High catalytic activity (2) Selectivity. More importantly, the dramatic development in this research activity can be explained by two reasons; (a) It can bridge the homogenous and heterogeneous catalysis (b) Linking the theoretical results with experimental observation more efficiently. While the higher selectivity can be linked to the geometrical feature like reducing ensemble effect, the higher catalytic activity is linked to the electronic structure of the narrow (localized) band d-orbital electrons of metal. Therefore, single atom catalysts are emergent catalytic materials that have the promise of merging the scalability of heterogeneous catalysis with higher activity of homogenous catalysts.

Broadly the SAC-field can be divided into three classes:

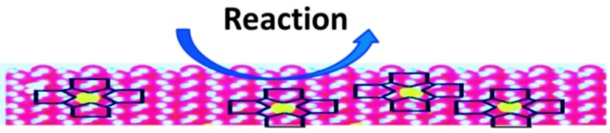
(1) Atoms are dispersed on support (metal oxide, carbon materials etc.)



(2) Active metal atoms are embedded into another less reactive host metal matrix i.e., Single Atom Alloy (SAA) catalyst. The alloy may be utilized as such or on some support. The following schematic shows black circle as active atom alloy with reactive host metal matrix presented in yellow.



(3) Organometallic compounds with active metal atoms connected to ligands are deposited on support like metal oxide, carbon, $MoS_2$ etc.



In the coming sections we will be summarizing our previous effort in designing the single atom alloy catalyst for $SO_3$ decomposition reaction, the most endothermic step of Sulfur-Iodine (S-I) thermochemical cycle [4].

### Computational Method

Calculations under Density Functional Theory (DFT) formalism were performed using Vienna ab initio Simulation Package (VASP) software. Plane wave based pseudo-potential approach has been utilized for calculations. The full-potential all-electron projector augmented wave (PAW) method were used to define electron–ion interactions. The PAW pseudo-potential was generated taking scalar relativistic corrections

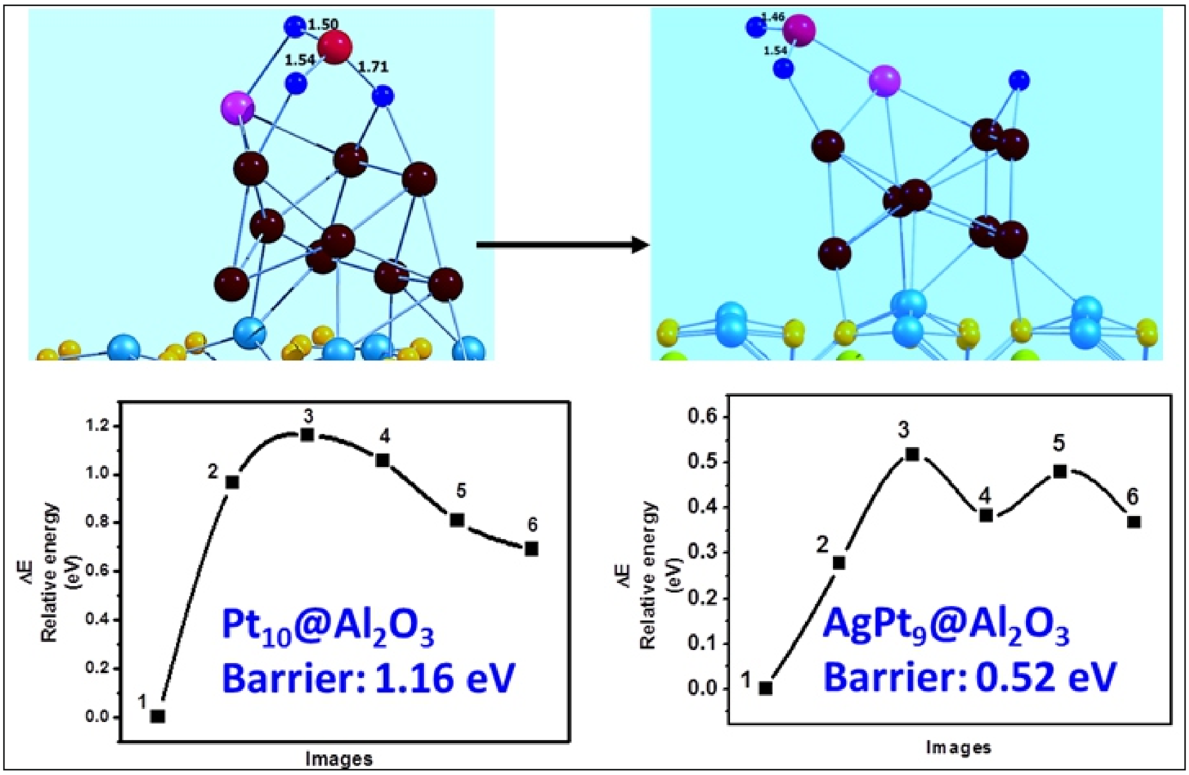


*Fig.2: Reaction barrier for $SO_3$ decomposition for $Pt_{10}$@$Al_2O_3$ and $AgPt_9$@$Al_2O_3$ clusters.*

into account. Spin polarized generalized gradient approximation has been employed to calculate the exchange-correlation energy. After spin polarized calculations, all the obtained structures were re-optimized by including spin orbit coupling (SOC). The plane wave basis set cut off energy was fixed at 400 eV. The total energy convergence was tested with respect to simulation cell size and plane-wave basis set size. The geometry optimization has been carried out by using conjugate gradient method. The geometries are considered to be converged when the forces on each ion becomes 0.01eV/ Å or less. The total energy was found to be accurate within 1 meV.

## Results and Discussion

The Sulfur-Iodine (S-I) thermochemical cycle is being pursued in the DAE for large scale hydrogen generation. Chemistry Division, BARC has been working on design and development of catalyst for sulfuric acid decomposition reaction, the most endothermic step of Sulfur-Iodine (S-I) thermochemical cycle [5]. Comparative studies on iron oxide-based catalysts ($Fe_2O_3$ & $Fe_{1.8}Cr_{0.2}O_3$) and Pt catalyst ($Pt/Al_2O_3$) have been demonstrated previously [5]. Even though, commercial Pt-based catalysts are considered to be the most promising candidates, thermal sintering and loss of Pt in the corrosive reaction environment limits their application and hunt for alternative are on. Another possible way to avoid sintering can be doping in the platinum catalyst itself. It is well known that the incorporation of an impurity atom can lead to reordering of the energy levels and thereby altering the geometry and chemical properties of catalyst. Thus, by appropriate doping the platinum catalyst, one can have the possibility of reducing the activation barrier, and simultaneously one can play with nanocluster support interaction as well. Reduction of activation barrier can help in reducing the reaction temperature, while improved platinum support interaction can enhance the binding and its sustainability during the reaction condition. In this context, single atom alloy catalyst can play a big role in optimizing the performance of Pt catalyst for $SO_3$ decomposition. Specific question attempted were

(1). Can one bring down the $SO_3$ decomposition reaction temperature by reducing the activation barrier?

(2). Can one increase the sintering resistance?

With this motif, we theoretically investigated the potential of single Ag site embedded Pt catalyst towards $SO_3$ decomposition [4]. Two types of substrate were considered (i) Pt nanocluster supported on alumina i.e. $Pt_{10}$@$Al_2O_3$ (ii) Pt(111) surface. The selection of substrates was guided by the fact that Pt nanoparticle (~2-3 nm) on alumina support have been successfully employed as catalysts for sulfuric acid decomposition reaction and (111) facet of Pt surface is thermodynamically most stable facet therefore any platinum nanoparticle is expected to have majority of its surface as (111) facet. In order to create single atom alloy (*very low molar fraction*) catalyst from supported $Pt_{10}$ cluster, substitutional doping of single Ag atom into $Pt_{10}$ was carried out.

Implanting single Ag atom in alumina supported platinum cluster $Pt_{10}$@$Al_2O_3$ i.e. $AgPt_9$@$Al_2O_3$ leads to significantly reduced activation barrier for S-O bond breaking [4]. After interaction, S-O bond length of $SO_3$ molecule connected to trigonal face of metal cluster ($AgPt_9$@$Al_2O_3$) increases from 1.44 to 1.71 Å (~19% elongation). Reaction enthalpy for the decomposition reaction ($DH_{diss}$-AgPt) was found to be +0.37 eV which was much lower than that of $Pt_{10}$@$Al_2O_3$ counterpart ($DH_{diss}$-Pt = +0.69 eV). Moreover, the S-O bond breaking reaction barrier (activation barrier) for $SO_3$—($AgPt_9$@$Al_2O_3$) obtained under similar methodology was 0.52 eV only, i.e.; almost half of barrier obtained for $SO_3$—($Pt_{10}$@$Al_2O_3$) complex. Alloying the alumina supported platinum nanocluster with single Ag atom, lowered the activation barrier for S-O bond breaking by more than 50% in comparison to pristine platinum counterpart. At variance with pure $Pt_{10}$@$Al_2O_3$ which tries to detach with support during decomposition reaction, single atom alloy nanocluster $AgAgPt_9$@$Al_2O_3$ enhances binding with support, strengthening sintering resistance. Ag weakens the binding of reaction product $SO_2$ with cluster which can help in easy desorption (Better recyclability). During the interaction of $SO_3$ with $AgAgPt_9$@$Al_2O_3$, decrease in the metal cluster–alumina surface separation was observed i.e., stronger grip of cluster on substrate. Hence, one can infer that $AgPt_9$ cluster remains immobilized on $Al_2O_3$ support during the reaction and expected to be resilient towards possible sintering.

After establishing the fact that presence of single Ag atom in the Pt nano cluster significantly improves its potential as catalyst for $SO_3$ decomposition, in order to further ascertain the role of single Ag site, interaction of $SO_3$ was investigated with Pt(111) surface before and after single atom alloying (substitutional doping with Ag). For single atom alloy catalyst, one of platinum atom in the uppermost layer was replaced with silver atom leading to 1% silver concentration in total slab. Results reveal that activation barrier for $SO_3$ decomposition on $Ag_1Pt(111)$ surface was 1.22 eV reduced by ~30% to facilitate the S-O bond breaking and simultaneously presence of Ag leads to weaker binding of reaction product. Notable influence of single Ag atom was also observed at both length scale i.e. $AgPt_9$@$Al_2O_3$ cluster and Pt(111) slab, where it was found that single Ag atom substitution shows significant reduction in activation barrier in contrast to pristine counterpart. Single Ag atom plays dual role as it not only reduced the activation barrier but simultaneously adsorbs reaction product $SO_2$ weakly, signifying relatively easier desorption and better recyclability. In order to rationalize the role of silver attention was focused on bonding in $SO_3$ molecule with catalyst and deeper location of silver *d*-electrons and lesser electronegativity of silver were attributed for better performance of single Ag atom alloy Pt catalyst. When $SO_3/SO_2$ molecule interacts with silver atoms, higher binding energy of *d*-electron of silver prevents its effective interaction with LUMO of incoming molecule which in turn weakens bonding. At the same time, the higher electronegativity difference between Ag and S leads to injection of more (relative to Pt-case) charge into sulphur atom of $SO_3$ [4]. The more injection of charge populates an antibonding molecular orbital of $SO_3$, leading to elongation of the S–O bond and hence weakening of bond i.e., reduction of bond cleavage barrier.

## Conclusions

In summary, the present article has provided a brief introductory overview of Single Atom Alloy Catalyst (SAAC) and further, design of SAAC catalyst for SI-thermochemical cycle using state of the art density functional theory (DFT) has been presented. Alloying the platinum catalytic particle with single Ag atom significantly reduced the activation barrier for $SO_3$ decomposition with better prospects of recyclability and sintering resistance. In the context of disintegrative leaching and sintering issues of the supported platinum nanoparticle catalyst, it is predicted that alloying the Pt-catalyst with low concentration Ag implanting can be very fruitful.

## Acknowledgements

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# Density Functional Theory

9

# Effect of Excess Electron on Structure and Properties of Diphenyldichalcogen Systems

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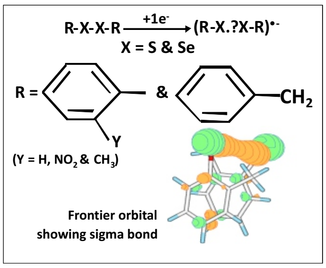

ABSTRACT

Ab initio quantum chemical methods are employed to elucidate structure and properties of sulfur and selenium based dichalcogen systems of the type $(R\text{-}X)_2^-$ (R=Ph, $PhCH_2$; X=S, Se) in presence of an excess electron. Effect of electron withdrawing ($-NO_2$) and electron donating ($-CH_3$) groups in phenyl ring on the stability of these two-center three-electron (2c-3e) bonded systems in water medium is discussed. This report illustrates that the combination of electronic effect and geometrical flexibility decides the strength of 2c-3e bond in these systems and this study also helps to understand antioxidant properties of anionic dichalcogen systems.

KEYWORDS: *Antioxidant, Chalcogen, Radical anion, Structure and properties*

## Introduction

Sulfur and selenium based diaryldichalcogenes are eco-friendly oxidizing agents and important drugs in pharmaceutical industry mainly due to their antioxidant properties [1]. One electron reduction of neutral disulfides and diselenides may lead to the formation of *two-center three-electron (2c-3e)* bonded radical anion systems [2]. The extra electron in such systems is accommodated in the lowest unoccupied molecular orbital which is often an antibonding sigma orbital. Due to the presence of this electron in a repulsive antibonding orbital, such three electron bonded species are not very stable and may dissociate easily. Electron capture dissociation (ECD) with Fourier transform ion cyclotron mass spectrometry (FTICR MS) has been used for direct measurement of sulfur and selenium centered 2c-3e bonded complexes [3]. Areal time probing of 2c-3e bonded sulfur system has also been performed following femtosecond laser spectroscopy. Recently, transient anion states of gas-phase diphenyldisulfide are characterized by means of electron transmission (ET) and dissociative electron attachment (DEA) spectroscopic methods. Quantum chemical calculations play a major role in understanding the nature of this type of three electron bonding. Mixing of two sulfur valence p-orbitals from the respective radical anion, $RS^-$ and free radical, RS form disulfide radical anion $(R\text{-}S.^{\cdot}.S\text{-}R)^-$ having a three electron bond between two sulfur atoms. Bond strength of such a bond is expected to depend on the combined effects of structural parameters, substitution patterns and electronic interactions. The combined effects are expected to control the extent of p-orbital interaction that in turn is expected to influence the strength of the newly formed bond.

Over the years several chalcogen based radical cation and anion systems are studied applying theoretical and pulse radiolysis based experimental techniques to understand nature of bonding and antioxidant properties. At present, electron acceptor properties of dichalcogen systems, namely, diphenyldisulfide and diphenyldiselenide of the type R-X-X-R (X = S, Se; R= Ph, $PhCH_2$) are discussed and the newly formed 2c-3e bonds in their anionic $(R\text{-}X\text{-}X\text{-}R)^-$ states are characterized as a case study. These are model systems for understanding the antioxidant behavior of sufur and selenium based biological systems.

## Computational Methods

First principle based quantum chemical calculations are performed to find out the most stable structure of different $(Ph\text{-}X\text{-}X\text{-}Ph)^-$ radical anion systems under gas phase isolated condition. Further optimization of such geometries is carried out including solvent effects following a macroscopic solvation model following SMD model in water medium. To calculate geometrical and energy parameters of these systems, a long range corrected DFT functional including dispersion correction (ω-B97XD) and MP2 method are employed along with 6-311++G(d,p) set of atomic basis functions. Restricted Open Shell HartreeFock (ROHF) formalism is applied to avoid any spin contamination in these doublet radical anionic systems.

## Results and Discussion

### *Structure& Stability of $(R\text{-}S)_2$ and $(R\text{-}S)_2^{\cdot-}$ (R=Ph, $PhCH_2$)*

Two minimum energy equilibrium structures are obtained for neutral diphenyldisulfide system and these structures differ mainly in spatial orientation of two phenyl rings. To calculate gas phase geometrical parameters of $(PhS)_2$ system more accurately, geometry optimization is also carried out at CCSD level of theory which is known to recover dynamic correlation accurately. Geometrical parameters of neutral $(PhS)_2$ and $(PhCH_2S)_2$ calculated at ω-B97XD/6-311++G(d,p) level agrees well with that obtained at MP2 as well as CCSD level of theory. Geometry of the most stable structures are recalculated in water medium applying a continuum model for

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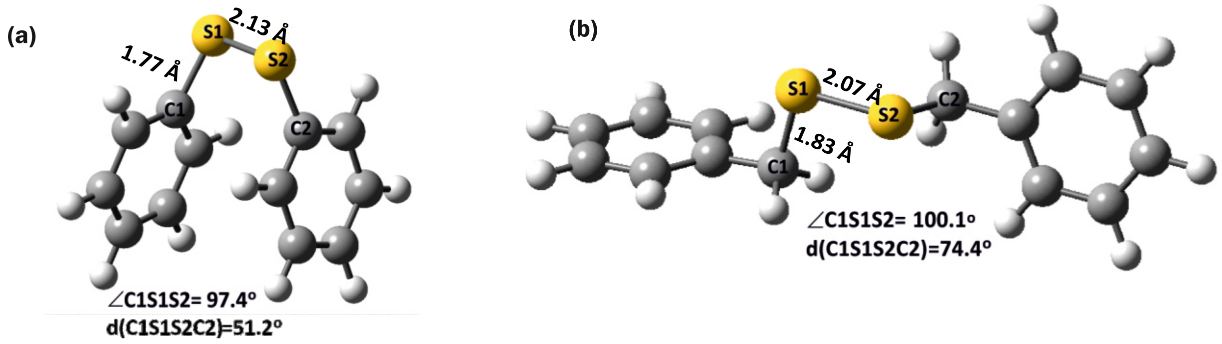

*Fig.1: Most stable equilibrium structure of (a) $(PhS)_2$ and (b) $(PhCh_2S)_2$ systems calculated at MP2/6-311++G(d,p) level in water medium. Selected bond lengths, bond angle and dihedral angle are also shown.*

hydration. Most stable structures of $(PhS)_2$ and $(PhCH_2S)_2$ calculated at MP2 level in water medium are provided in Fig.1 (a-b). In case of the most stable structure of $(PhCH_2S)_2$ system, two benzyl rings are in anti-position as can be seen from the figure. Table 1 summarizes the changes in selected geometrical parameters and molecular properties of $(PhS)_2$ and $(PhCH_2S)_2$ systems produced upon capture of an electron.

Two minimum energy structures are obtained for diphenyldisulfide, (PhS)2and the two structures differ mainly in spatial orientation of two phenyl rings. In the first case, one phenyl ring is displaced over the other phenyl ring and due to partial interactions of pi orbitals from two phenyl rings, the first structure is more stable than the second one by 3.8 kcal/mol at Mp2 level. Calculated S1-S2 and C1-S1 bond distances are 2.87 Å and 1.77 Å respectively and these are very close to MP2 values. The respective bond angle, C1S1S2, dihedral angles, δ(C1S1S2C2), δ(S1S2C2C2') and δ(S2S1C1C1') are predicted as 91.6°, 41.8° and 78.8° and -99.8°. Calculated distances C1-C2 and C3-C4 at MP2 level (see Fig.2 (a) for atom labels) are 3.0 Å and 4.4 Å respectively. Respective bond distances S1-S2 and C1-S1 are 2.82 Å and 1.77 Å and the bond angle, C1S1S2 and dihedral angle, δ(C1S1S2C2) are 87.7° and 49.5° respectively in water medium. The distance between C1 and C2 atoms 3.0 Å and the same between C3 and C4 atoms is 4.4 Å. Calculated dipole moments are 7.24 D and 10.97 D in the gas phase and water medium respectively. Thus, MP2 results on geometrical parameters suggest that on attachment of an excess electron, the dichalcogen bond, S1-S2 elongates by 0.7 Å and C1-S1 bond distance remains practically unchanged in the gas phase and in water medium for (PhS)2 system. Along with that, bond angle(<C1S1S2) and dihedral angle, δ(C1S1S2C2) remain unperturbed on electron attachment in $(PhS)_2$ in the gas phase as well as in water medium.

Now a $-CH_2-$ group is added to the structure of radical anion $(PhS)_2^-$ between each phenyl ring and the chalcogen S atom to provide molecular flexibility and the calculations are carried out for $(PhCH_2S)_2^-$ radical anion. Optimized structures are different than those of diphenyl disulfideradical anion. Calculated S1-S2 and C1-S1 bond distances are 2.76 and 1.82 Å respectively. It may be noted that S1-S2 bond is shorter in $(PhCH_2S)_2$ by 0.07 Å than that in $(PhS)_2$. The obtained bond angle, <C1S1S2 and dihedral angle, δ(C1S1S2C2) are 90.5° and 71.8° respectively (see Fig.2 (b) for atom labels). The distance between the two phenyl rings and their orientations do not allow any pi-pi interactions. The dipole moment of this radical anionic system is calculated as 7.3 D. The other equilibrium structure having all anti-structure and is less stable than the most stable one by 8.6 kcal/mol.

It is observed that sulfur atoms are more negative in water medium than in gas phase for both the radical anions. It may be noted that the calculated bond order between two S atoms is close to 0.5 in these negatively charged systems. The odd electron spin is observed to be equally localized on two S atoms. On addition of an excess electron to $(PhS)_2$, the distance between two sulfur atoms is increased by 25% and binding energy is decreased by 57% as compared to the neutral counterpart, $(PhS)_2$ at Mp$_2$ level. Electron affinity (adiabatic) of $(PhS)_2$ is -0.7 eV in gas phase and the same in water medium is -2.5 eV. This suggests that the excess electron can easily bound to the system in water medium. It is noted that calculated binding energy of $(PhS)_2$ is reduced by 7.8 kcal/mol in water medium compared to the same in gas phase. This indicates that solvents play a significant role on the stability of these systems having an excess electron. In water medium, with respect to neutral $(PhS)_2$ system, the distance between two sulfur atoms is calculated to be increased by 24% and binding energy is decreased by 70% when an extra electron is

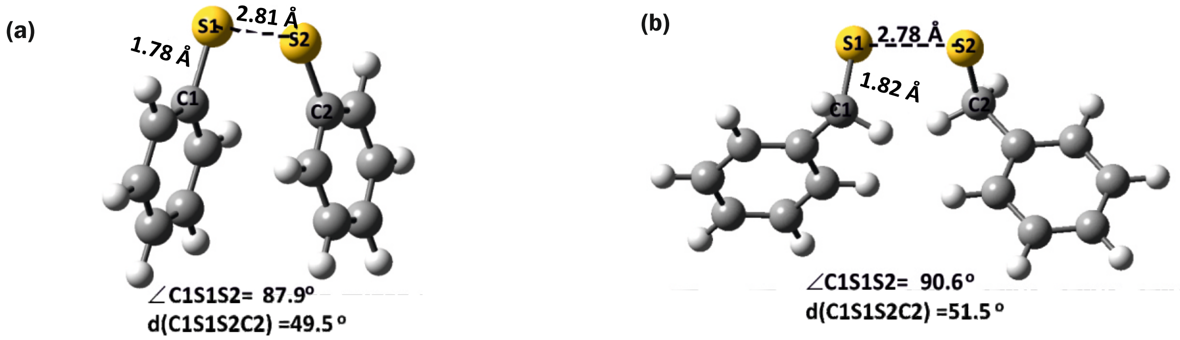

*Fig.2: Most stable equilibrium structure of (a) $(PhS)_2$ and (b) $(PhCH_2S)_2$ systems calculated at MP2/6-311++G(d,p) level in water medium. Selected bond lengths, bond angle and dihedral angle are also shown.*

*Table 1: Selected geometrical and molecular parameters of $(R\text{-}X)_2$ in water medium calculated at MP2/6-311++G(d,p) level of theory. Values in the braces show the parameters in presence of an excess electron, $(R\text{-}X)_2$, (R=Ph, $PhCH_2$, o-$NO_2$Ph, o-$CH_3$Ph; X=S, Se).*

| rX1X2 (Å) | rC1X1 (Å) | ∠C1X1X2 (degree) | d(C1X1X2C2) (degree) | d(X1X2C2C2') (degree) | d(X2X1C1C1') (degree) | Atomic charge on Sulfur (a.u.) | Electron Affinity (eV) | Binding Energy (kcal/mol) |
|---|---|---|---|---|---|---|---|---|
| diphenyldisulfide, $(PhS)_2$ | | | | | | | | |
| 2.13,<br>(2.81) | 1.77,<br>(1.76) | 97.6, (88.0) | 47.7, (49.5) | 74.5, (70.1) | -101.7, (-110.9) | -0.49, (-0.91) | -2.5 | 68.8, (20.5) |
| dibenzyl disulfide, $(PhCH_2S)_2$ | | | | | | | | |
| 2.07,<br>(2.78) | 1.82,<br>(1.82) | 100.7, (90.6) | 81.1, (71.7) | -178.0, (-141.6) | -177.9, (-141.6) | -0.34, (-0.83) | -2.3 | 61.6, (16.3) |
| diphenyldiselenide, $(PhSe)_2$ | | | | | | | | |
| 2.41,<br>(3.05) | 1.92,<br>(1.92) | 94.7, (92.4) | 42.3, (22.8) | 73.7, (47.3) | -102.6, (-131.7) | -0.20, (-0.54) | -3.0 | 92.4, (23.2) |
| dibenzyldiselenide, $(PhCH_2Se)_2$ | | | | | | | | |
| 2.35,<br>(2.97) | 1.98,<br>(1.99) | 99.3, (90.0) | 81.1, (69.7) | -177.1, (-133.6) | -177.1, (-133.4) | -0.20, (-0.70) | -2.7 | 61.7, (21.1) |
| ortho-nitro-diphenyldiselenide, $(o\text{-}NO_2\text{-}PhSe)_2$ | | | | | | | | |
| 2.40,<br>(2.41) | 1.93,<br>(1.92) | 97.2, (95.3) | 34.0, (37.7) | 49.6, (75.1) | -123.1, (-101.1) | -0.09, (-0.10) | -2.9 | 60.7, (21.0) |
| ortho-methyl-diphenyldiselenide, $(o\text{-}CH_3\text{-}PhSe)_2$ | | | | | | | | |
| 2.41,<br>(3.03) | 1.92,<br>(1.94) | 96.6, (87.9) | 37.8, (40.0) | 77.0, (77.1) | -99.9, (-105.3) | -0.22, (-0.55) | -3.0 | 94.9, (26.5) |

added to the system. The binding energy of dibenzyl disulfide radical anion is calculated to be lower by 4.2 kcal/mol compared to that in $(PhS)_2$, S1-S2 distance is shorter by 0.05 Å though. This indicates that geometrical flexibility incorporated by adding a –CH2- group does not play any significant role to stabilize these radical anions and electronic effects are expected to play a major role to stabilize/destabilize these systems.

### *Structure & Stability $(R\text{-}Se)_2$ (R=Ph, $PhCH_2$, o-$CH_3$Ph, o-$NO_2$Ph)*

Calculated geometrical parameters of the most stable structures of $(PhSe)_2$ and $(PhCH_2Se)_2$ systems in presence of an excess electron are provided in Table 1. Two minimum energy structures are also obtained in these systems similar to diphenyldisulfide system discussed before. Such observations are also reported in the literature for diphenylchalcogen systems including $(PhTe)_2$ based on conformation analysis On geometry optimization, two equilibrium structures are obtained for diphenyldiselenide radical anion and the most stable structure obtained in water medium is displayed in Fig.3(a) along with selected geometrical parameters. One can see that one phenyl ring is displaced over the other phenyl ring to a lesser extent compared to the most stable structure of diphenyldisulfide radical anion. The most stable structure is more stable than the second equilibrium structure by 9.4 kcal/mol. This extra stability may be attributed to pi orbital interactions from two phenyl rings. Calculated gas phase Se1-Se2 and C1-Se1 bond distances 3.04 Å and 1.92 Å respectively and are longer than the sulfur system as expected. Bond angle, C1Se1Se2 and dihedral angle, δ(C1Se1Se2C2) are predicted as 92.2° and 28.2° respectively. It may be noted that calculated dihedral angle, δ(C1Se1Se2C2) is significantly smaller than the sulfur systems suggesting morepi-pi interaction in Se systems. The Se1-Se2 and C1-Se1 bond distances are 3.03 Å and 1.93 Å respectively in water medium showing no significant effect of solvent water medium. The obtained bond angle, <C1Se1Se2 and dihedral angle, δ(C1Se1Se2C2) are 92.4$^0$ and 21.2$^0$ respectively in water medium. Calculated dihedral angle suggests that two phenyl rings in the radical anion, $(PhSe)_2$ become less displaced in water environment. The distance between the C1 and C2 atoms is 3.3 Å and that between C3 and C4 atoms is 3.8 Å. Calculated dipole moments are 5.6 D and 10.7 D in the gas phase and water medium respectively. When a -CH2- group is added between each phenyl ring and Se atom to the structure of radical anion $(PhSe)_2$, again only two stable equilibrium structures are obtained. These structures are very different from those of $(PhSe)_2$. One structure is more stable than the other one by 9.1 kcal/mol. Structure and selected geometrical

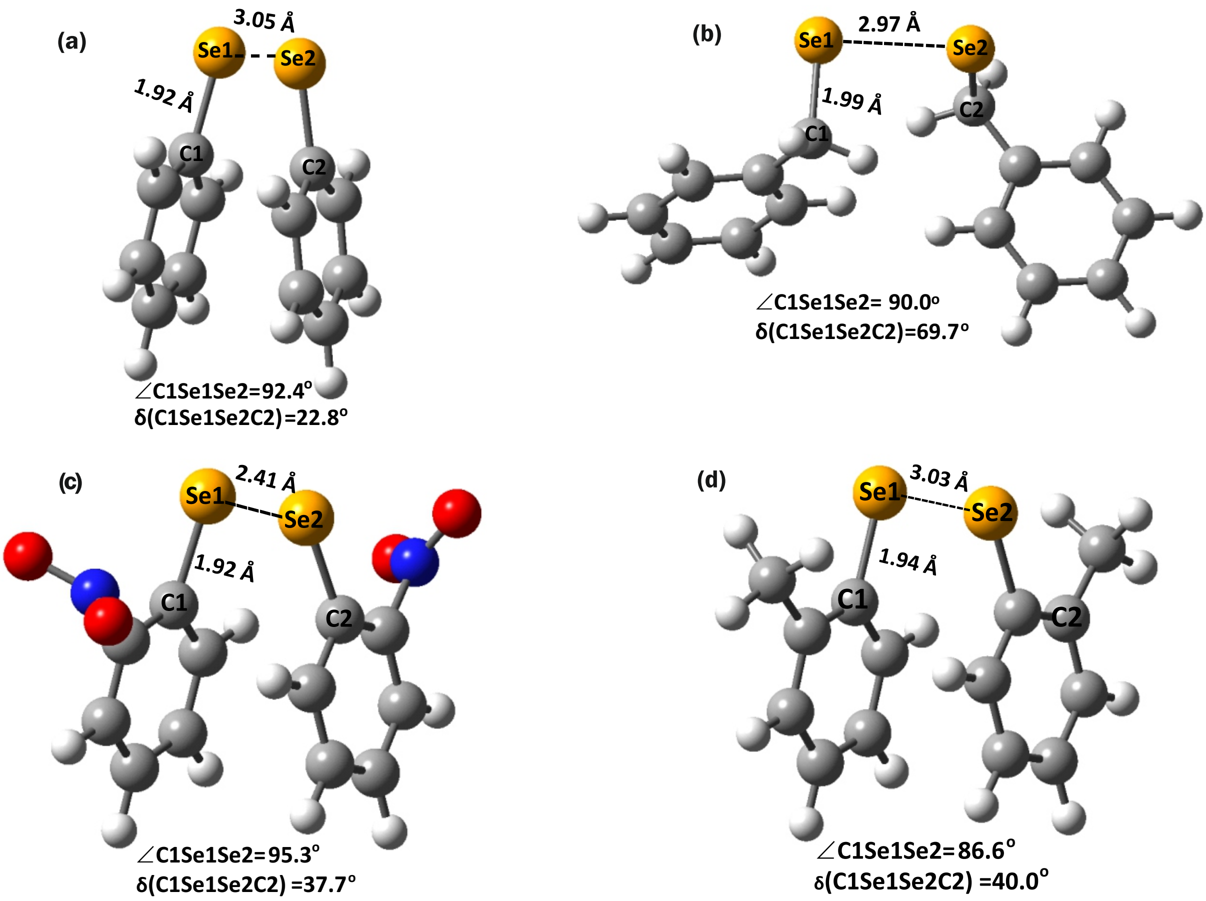

*Fig.3: Most stable equilibrium structure of (a) $(PhSe)_2$, (b) $(PhCH_2Se)_2$, (c) $(o\text{-}NO_2PhSe)_2$ and (d) $(o\text{-}CH_3PhSe)_2$ systems calculated at MP2/6-311++G(d,p) level in water medium. Selected bond lengths, bond angle and dihedral angle are also shown.*

parameters of the most stable one as calculated in water medium is given in Fig.3 (b). Calculated Se1-Se2 and C1-Se1 bond distances are 3.10 and 2.01 Å respectively. It may be noted that Se1-Se2 bond is longer in $(PhCH_2Se)_2$ by 0.07 Å than that in $(PhSe)_2$ in contrast to its sulfur counterpart. The obtained bond angle, <C1Se1Se2 and dihedral angle, δ(C1Se1Se2C2) are 93.9° and 78.8° respectively. Calculated data suggests that on the addition of $-CH_2$- group, molecular geometry and properties are similar to corresponding S system. The dipole moment of this dimer radical anionic system is calculated as 12.7 D.

Effect of electron withdrawing/donating group on structure and stability of the radical anion, $(PhSe)_2$ is also studied by substituting one of the ortho- positions of the two phenyl rings. Structures with $-NO_2$ and $-CH_3$ substitutions only in anti-positions of the most stable structure of diphenyldiselenide radical anion are considered as input geometries to locate equilibrium structure. The most stable structure of $(o\text{-}NO_2\text{-}PhSe)_2$ radical anion along with certain geometrical parameters is shown in Fig.3 (c). It is interesting to note that adding an electron withdrawing group like $-NO_2$ to each phenyl ring in their ortho position has made the distance between two Se atoms shorter by 0.64 Å in water medium. However, dihedral angle, δ(C1Se1Se2C2) is increased by 15.8 degree indicating less pi-pi interaction. On addition of an electron donating group like $-CH_3$ to the phenyl ring, no notable change in the distance between two Se atoms is obtained and the structure is displayed in Fig.3 (d). However, dihedral angle, δ(C1Se1Se2C2) is increased by $18^0$ compared to that in the radical anion with unsubstituted phenyl rings. This increase in dihedral angle reflects the displacement between the two phenyl rings may be due to bulky nature of $-NO_2$ and $-Ch_3$ groups.

In short, the structures obtained for radical anions of $(o\text{-}CH_3\text{-}PhSe)_2$ and $(o\text{-}NO_2\text{-}PhSe)_2$ are very similar to the parent radical anion. The binding energy of $(PhSe)_2$ radical anion with respect to its dissociative products PhSe and PhSe is calculated as 34.2 kcal/mol. The calculated increase in the distance between two selenium atoms in the radical anion is 21% and decrease in binding energy is 63% as compared to the neutral system, $(PhSe)_2$. Binding energy of $(PhSe)_2$ is significantly smaller in water medium compared to the gas phase data (see Table 1). On substituting by $-CH_3$ group at ortho position of the phenyl rings, binding energy of the radical anion is increased by 3.3 kcal/mol compared to the unsubstituted radical anion, $(PhSe)_2$. However, in case of $(o\text{-}NO_2\text{-}PhSe)_2$ system, binding energy is decreased by 2.2 kcal/mol, the distance between the two Se atoms is reduced significantly though. Thus, substitution by an electron withdrawing group in the phenyl ring decreases the stability of $(PhSe)_2$ showing strong electronic effect in the binding characteristics of these *hemi* bonded systems. Calculated atomic charges do support this observation. Though in case of $(o\text{-}CH_3\text{-}PhSe)_2$ system, odd electron spin is equally localized over two Se atoms; for $(o\text{-}NO_2\text{-}PhSe)_2$ system, the odd electron spin is not localized over Se atoms.

Visualization of selected molecular orbitals in these radical anions is important to understand the nature of bonding features. Selected molecular orbitals involved in electronic transition of the major optical band of these radical anion systems are visualized. These orbitals are based on the most stable structures of the radical anions in water medium and involved in the most prominent electronic transitions in the visible region [4]. It is clearly seen that in case the highest doubly occupied orbitalexcept for $(o\text{-}NO_2\text{-}PhSe)_2$, two p-orbitals from two sulfur/selenium atoms of these radical anion mixes head-on showing the presence of a bonding sigma (σ) orbital. In case of the lowest singly occupied orbital, two p-orbitals having opposite symmetry are orientated towards each other indicating the presence of an anti-bonding sigma (σ*) orbital. Thus, the optical absorption band obtained in these radical anion systems are due to σ→σ* transition as known to occur in a *two-centre three-electron* bonded system. In case of $(PhSe)_2$ system, a better mixing of the two p-orbitals from two Se atoms is observed.

## Conclusion

The effect of an excess electron on geometry, nature of bonding and stability of diaryldichalconides, namely, $(PhS)_2$, $(PhSe)_2$, $(PhCH_2Se)_2$, $(o\text{-}NO_2\text{-}PhSe)_2$ and $(o\text{-}CH_3\text{-}PhSe)_2$ is studied. These dichalcogens have high electron affinity in water medium and should be able to capture electron efficiently suggesting their antioxidant property. It is shown that in presence of an excess electron, these diaryldichalcogen systems are bound by *two-centre three-electron* bond between two chalcogen (S/Se) atoms. Visualization of frontier molecular orbital of the most stable equilibrium structures suggests that sulfur and selenium valence p-orbitals are mixed head-on indicating sigma character of the three electron bond between two S/Se atoms in these radical anions. Atomic spin populations are equally distributed over two S or Se atoms in these systems except for $(o\text{-}NO_2\text{-}PhSe)_2$. Solvent water medium induces red shifts in absorption maxima of these systems with excess electron when solvent effect is introduced through a macroscopic model. The origin of the strong absorption bands in the visible region are assigned to be electronic transition from sigma bonding orbital to antibonding sigma* orbital.

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# Nuclear Materials

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# Computational Thermodynamics of Nuclear Materials

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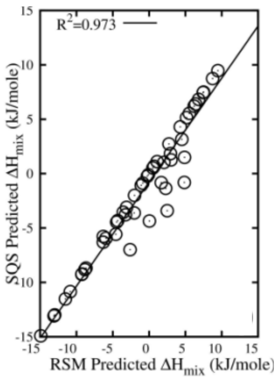

*Correlation between the enthalpy values calculated from regular solution model (RSM) and those of the full SQS*

ABSTRACT

For improved performance of present generation nuclear reactors and realization of advanced Generation-IV reactors, development of new materials with desired properties is of utmost importance. Design and development of new materials for various stages of nuclear fuel cycle is challenging due to associated radio-toxicity involved in the handling of nuclear fuels for front- and back-end of closed fuel cycle. Computational thermodynamics provides a unique avenue to determine fundamental thermodynamic properties of the nuclear materials in a temperature and composition range which are otherwise not attainable by experiments. High temperature thermodynamic properties are essential to design new materials, to analyse safety aspects and to simulate performance of the materials in reactor operating conditions. The Present article elaborates on three aspects of design and development of new materials using density functional theory (DFT) and classical molecular dynamics (MD) based simulation strategies. Firstly, the study of thermal properties of $U_{1-x}Np_xO_2$/ $Th_{1-x}Np_xO_2$ mixed oxides fuels are presented with an aim to develop thermal property dataset over a wide temperature and composition range. Secondly, design principles of new low-activation high entropy alloys are elaborated with an aim to find new structural material for new generation reactors. Finally, energetics of incorporation/solution of fission metals in Fe-Zr intermetallics is discussed with an aim to profile Fe-Zr alloys as a wasteform for high level nuclear metallic wastes.

KEYWORDS: *Molecular dynamics (MD), Density functional theory (DFT)*

## Introduction

Nuclear energy is a clean source of energy and a promising alternative to the fossil fuels. Generation-IV reactors design concepts aim to provide nuclear power facilities that are safer, resistant to proliferation and economically sustainable. The most important factor in the development and implementation of Gen-IV reactors is the dependability and performance of structural materials for both in-core and out-of-core applications [1]. Design and development of new materials for various stages of nuclear fuel cycle is challenging due to associated radiotoxicity. Computational thermodynamics provides a unique avenue to determine fundamental thermodynamic properties of the nuclear materials in a temperature and composition range which are otherwise not attainable by experiments. In this article, we have discussed three studies based on computational thermodynamics, viz., study of thermal properties of mixed-oxide fuels, high throughput screening of single phase high entropy alloys and assessment of Fe-Zr alloys as a host for the high level metallic wastes.

## Computational Methods

Classical molecular dynamics (MD) simulations were carried out using Large-scale Atomic Molecular Massively Parallel Simulator (LAMMPS) package to determine thermal properties of $U_{1-x}Np_xO_2$ and $Th_{1-x}Np_xO_2$ systems. The interaction potential between the atoms was modelled by a combination of Buckingham-Morse and many-body potentials. NPT ensemble, using the Nosé-Hoover thermostat and barostat, was used in the MD runs. For calculations of thermal conductivity within LAMMPS, the Green-Kubo formalism was adopted [2]. Nudge elastic band method as implemented in LAMMPS was used to calculate the migration barrier of O vacancies. To capture substantial oxygen diffusion on the limited MD timescale, 1% oxygen vacancies were introduced in the supercell.

Spin-polarized density functional theory (DFT) calculations, as implemented in Vienna Ab-initio Simulation Package [3,4], were employed. The interaction between the atoms were modelled using projector augmented wave (PAW) potentials [5] with generalized gradient approximation (GGA) based exchange-correlations, as parametrized by Perdew, Burke and Enzerhof (PBE) [6]. Optimized k-point mesh and cut-off energy were used for all the calculations. To model disordered alloys, special quasi-random structures (SQS) were generated using Monte Carlo method as implemented in ATAT package [7].

## Thermal Properties of Transmutation Fuels

Increasing energy efficiency by recycling the spent fuel along with major actinides Np, Pu and Am is one of the main objectives of future nuclear program. $NpO_2$ based mixed oxide (MOX) transmutation fuels are specifically important because of their high yield during the burn-up and 106 years of half life [8,9]. Because of the related radio-toxicity of these materials, the impact of adding MAs to MOX on thermal and diffusional characteristics has not been well investigated through experiments. Therefore, thermal and diffusional properties, viz., thermal expansion, thermal conductivity and oxygen diffusivity of $NpO_2$ based MOX using atomistic simulations [2,10] were evaluated.

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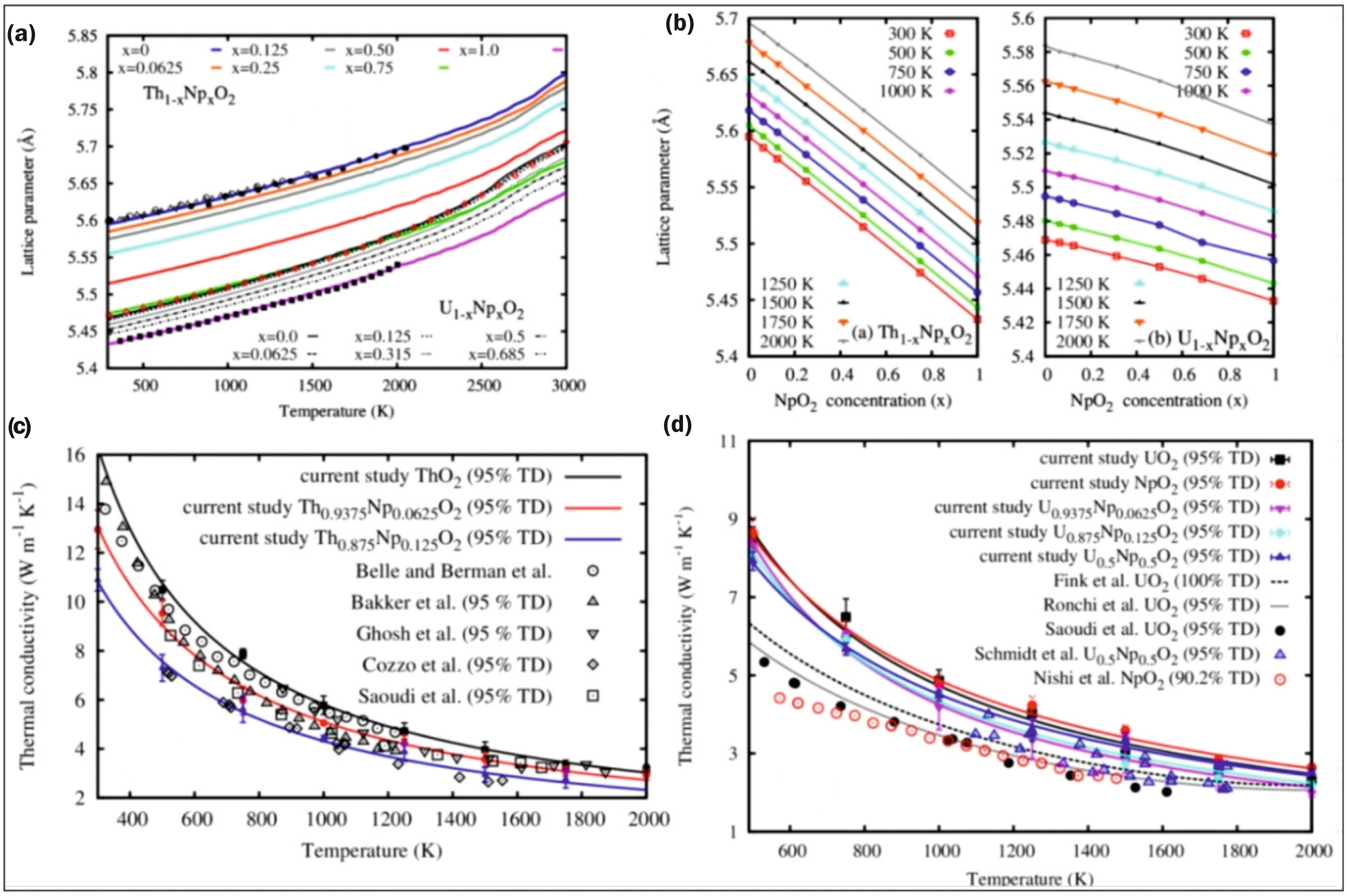

*Fig.1: Variation of (a) lattice parameters of $Th_{1-x}Np_xO_2$ and $U_{1-x}Np_xO_2$ (x=0.0, 0.0625, 0.125, 0.25, 0.50, 0.75 and 1.0) as a function of temperature, (b) lattice parameters as a function of $NpO_2$ concentration. Variation of thermal conductivity of (c) $Th_{1-x}Np_xO_2$ (x=0.0, 0.0625 and 0.125) and (d) $U_{1-x}Np_xO_2$ (x=0.0, 0.0625, 0.125, 0.5 and 1.0) as a function of temperature. Lines present MD calculated values and points present high temperature XRD values.*

The lattice parameters of $Th_{1-x}Np_xO_2$ and $U_{1-x}Np_xO$ decrease with temperature at all the studied compositions (see Fig.1 (a)). The overall trend in lattice parameters, which follow Vegard's law, is in good agreement with the experimental results. The lattice parameters of $Th_{1-x}Np_xO_2$ and $U_{1-x}Np_xO_2$ MOX decrease with the $NpO_2$ content (see Fig.1 (b)). Further, it can be seen from Fig.1 (b) that the rate of decrease in the lattice parameter of $Th_{1-x}Np_xO_2$ is higher than that of $U_{1-x}Np_xO_2$, which suggest that $NpO_2$ has a greater influence on lattice parameters for $Th_{1-x}Np_xO_2$ than $U_{1-x}Np_xO_2$. This phenomenon can be explained by the differences in ionic sizes of $Th^{4+}$ (1.19 Å), $U^{4+}$ (1.14 Å) and $Np^{4+}$ (1.12 Å) in an 8-fold coordination. Further, the variation of lattice parameters (in Å) of $Th_{1-x}Np_xO_2$ & $U_{1-x}Np_xO_2$ MOX can be presented as a function of $NpO_2$ concentration (x, $1.0 \geq x \geq 0.0$) and temperature (T, $2000 \geq T \geq 300$):

$$a(\mathrm{Th}_{1-x}\mathrm{Np}_xO_2) = -0.160777\mathrm{x}+4.44721\times10^{-5}\mathrm{T}+6.87589\times10^{-9}T^2+5.57487$$
$$a(U_{1-x}\mathrm{Np}_xO_2) = -0.0397186\mathrm{x}+4.56747\times10^{-5}\mathrm{T}+8.35801\times10^{-9}T^2+5.45702$$

The calculated thermal conductivity (TC) of $Th_{1-x}Np_xO_2$ (x=0.0, 0.0625 and 0.125) and $U_{1-x}Np_xO_2$ (x=0.0, 0.0625, 0.125, 0.5 and 1.0) along with the experimental values of $ThO_2$, $UO_2$, $NpO_2$ and $U_{0.5}Np_{0.5}O_2$ are plotted in Fig.1 (c) and 1 (d). The TC values of $UO_2$ and $NpO_2$ are quite close across this temperature range. However, MD calculated TC values of both $UO_2$ and $NpO_2$ are grossly overestimated at lower temperature (<1000 K) compared to experimental values (see Fig.2 (d)). In order to improve the accuracy of the thermal-conductivity predictions for $UO_2$, MD results need to be corrected for the spin-phonon-scattering mechanism by adding the corresponding relaxation time derived from existing experimental data. Fig.2 (d) also indicates a small reduction in TC values for $U_{1-x}Np_xO_2$, even at low temperatures, due to reduction in the phonon mean free path coming from scattering associated with a non-uniform cation sub-lattice. The degradation of the $UO_2$ TC due to Np substitutional defects is relatively small compared to the addition of Np in $ThO_2$.The calculated TC values of $Np_{0.5}U_{0.5}O_2$ are lower than those of pure $UO_2$ and $NpO_2$ due to higher impurity-phonon scattering at low temperatures (<750K). The calculated TC values of $Np_{0.5}U_{0.5}O_2$ also match the experiments well throughout the temperature range with maximum deviation of 15%. This is consistent with the experimental observation that the TC of $NpO_2$ with 95% theoretical density (TD) was close to that of $Np_{0.5}U_{0.5}O_2$ above 1098K. At higher temperatures (above 750K), the TC values are almost independent of the NpO2 concentration and the TC values for $UO_2$, $NpO_2$ and $U_{1-x}Np_xO_2$ MOX almost superimpose at high temperatures [2].

The mean square deviations (MSD) of pure $ThO_2$, $UO_2$, $NpO_2$ and $Th_{1-x}Np_xO_2$, $U_{1-x}Np_xO_2$ MOX at five intermediate compositions for a temperature range from 750K to 2000K were calculated (Fig.2). The higher slope of MSD for $NpO_2$ can be attributed to the lower oxygen migration energy ($E_m$) in $NpO_2$ than in the $ThO_2$. By assuming Arrhenius relationship, the D is related to the migration energy ($E_m$) as $D=D_0 \exp(E_m/k_BT)$, where $D_0$ is the pre-exponential term, $k_B$ and $T$ is Boltzman constant and temperature, respectively. From the logarithmic plot of $D$ as a function of $1/T$, $E_m$ is determined over the $NpO_2$ concentration in MOX and those values are shown in Fig.2. Moreover the sequence of the $E_m$ values of the pure oxides is consistent with that determined from NEB calculations. Fig.2

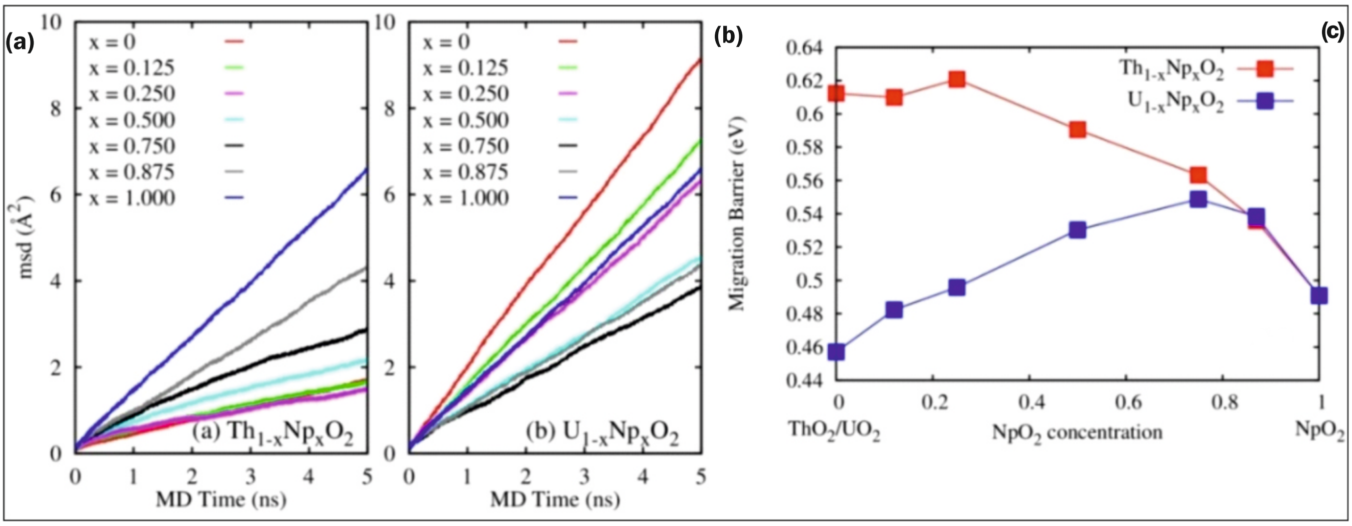

*Fig.2: Mean square displacement (MSD) of oxygen as a function of MD simulation time in (a) $Th_{1-x}Np_xO_2$ and (b) $U_{1-x}Np_xO_2$ MOX calculated at 750K. (c) The migration barriers ($E_m$) of oxygen vacancy in $Th_{1-x}Np_xO_2$ and $U_{1-x}Np_xO_2$ MOX as a function of $NpO_2$ concentration evaluated from MD calculated oxygen diffusivity as a function of temperature (Arrhenius plot).*

shows slight increase of $E_m$ with increase of $NpO_2$ concentration for $Th_{1-x}NpO_2$ MOX up to x=0.25 followed by continuous decrease up to x=1.0. On the contrary, the $E_m$ increases continuously with increasing $NpO_2$ concentration up to x=0.75 followed by decreasing trend up to x=1.0. Fig.2 clearly shows nonlinear variation of the $E_m$ with $NpO_2$ concentration and maxima lies around x=0.25 and 0.75 for $Th_{1-x}NpO_2$ and $U_{1-x}NpO_2$ MOX, respectively.

### High throughput screening of High-entropy Alloys

The structural materials of Gen-IV reactors must withstand conditions that are far harsher than what the nuclear power plants of today can handle, including a higher neutron flux, a more corrosive environment and higher operating temperatures. The existing alloys, viz., ferritic/martensitic steels, austenitic stainless steels, nickel-base alloys are not suitable for next generation reactors. High-entropy alloys (HEA), a new class of material, is a promising structural material for Gen-IV reactors. Present article elaborates a design principle of new low-activation single phase HEA using a computational high-throughput screening followed by experimental validations [11,12].

Designing of a HEA with desired properties from a vast composition space only by experimental means is a formidable task. Therefore, computational approaches can be efficiently used to explore this vast composition space. In literature, there are a number of empirical models [see ref. 12] which were proposed to predict the formation of single phase HEA. The precise value of mixing enthalpy ($\Delta H_{mix}$) for a HEA holds significant importance, as it serves as a crucial parameter in all the empirical models. The $\Delta H_{mix}$ can be calculated using Miedama model which is quick but not accurate. On the other hand DFT calculations using SQS can be employed to calculate the $\Delta H_{mix}$, which is accurate but time consuming (as we need big supercell to handle the configurational disorder of the system). The following method was employed in this study to calculate the mixing enthalpy of the HEAs:

(I) $\Delta H_{mix}$ of all the binary alloys (AB solid solutions) formed by the low activation elements (Ti, V, Cr, Mn, Fe, Ta, and W) have been calculated at 3 different compositions, viz., 25:75, 50:50 and 75:25, using 32 atom-SQS. (ii) using the binary $\Delta H_{mix}$, the interaction parameters of the binary combinations are calculated by using a regular solution model (RSM) $\Delta H_{mix}^{ij} = \sum_{i=1,j>i}^{No.of\,elements} \Omega_{ij} c_i c_j$, where $\Omega_{ij}$ and $c_{i(j)}$ are the interaction parameter between i and j atoms and concentration of i(j) atom. (iii) $\Omega_{ij}$ values are used to calculate the $\Delta H_{mix}$ of ternary, quaternary and quinary alloys. To check the accuracy of the above methodology, we have compared the $\Delta H_{mix}$ of few ternary, quaternary and quinary alloys calculated using the above mentioned RSM to the $\Delta H_{mix}$ computed using bigger SQS cell. It has been found that accuracy of $\Delta H_{mix}$ of RSM is similar to the SQS cell method ($R^2$ value of 0.973) leading to conclusion that the $\Delta H_{mix}$ calculated using RSM enough for calculating the $\Delta H_{mix}$ of HEAs (Fig.3 (a)).

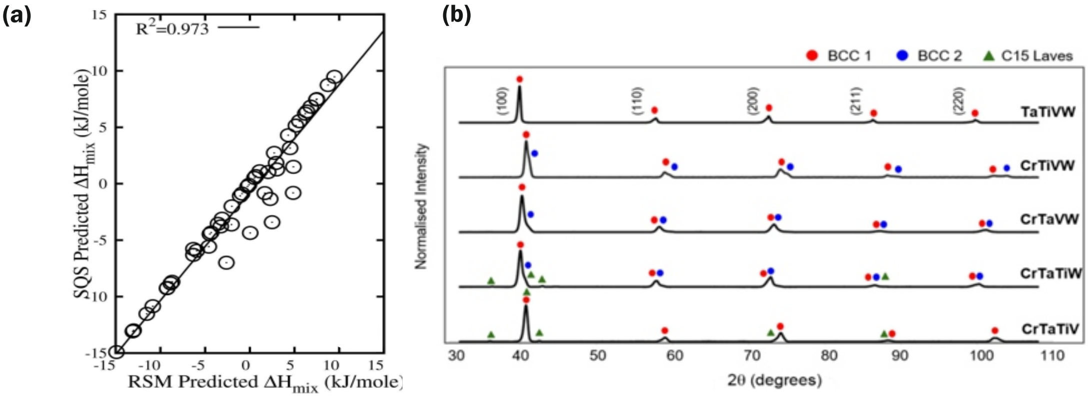

*Fig.3: (a) Correlation between the enthalpy values calculated from regular solution model (RSM) and those of the full SQS and (b) XRD pattern of high-entropy alloys.*

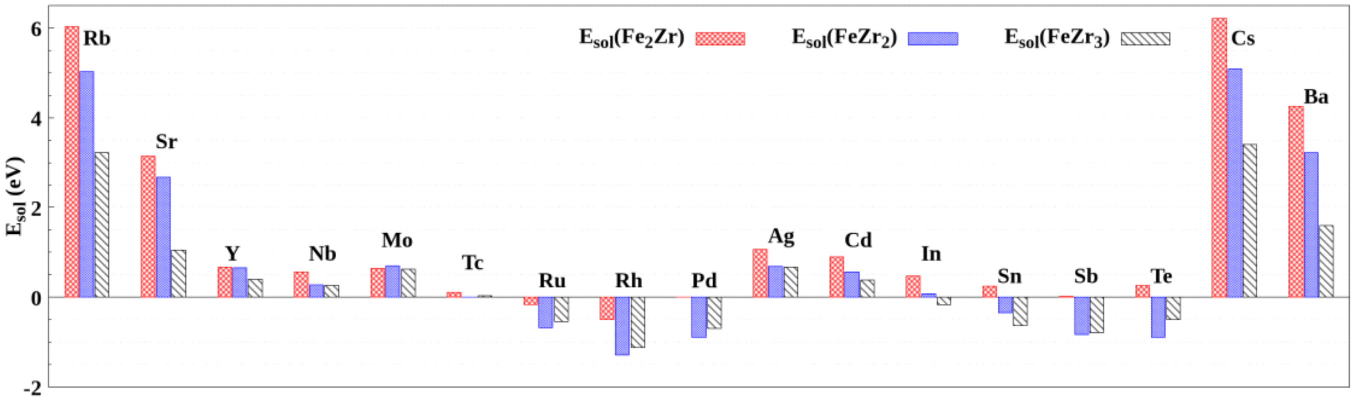

*Fig.4: Solution energies of the s-, p- and d-block FMs in c-$Fe_2Zr$, t-$FeZr_2$ and o-$FeZr_3$ intermetallics.*

In the literature, 8 different empirical models (details are in Ghosh et al. [12]) are available, which are used to predict the formation of single phase HEA. But it is important to mention that not a single parameter is 100% fail-safe in this prediction. Therefore, bench-marking of all the models have been carried out against the experimentally reported 36 distinct quaternary/quinary as-cast HEAs from the palette of seven low-activation elements. It has been found that the model proposed by Ye et al. [13] is the most suitable in our alloy palette, therefore, further predictions were made using the same model. We have predicted the probability of single phase formation in all the 35 and 21 equiatomic quaternary and quinary alloys, respectively. To validate our predictions, experimental studies are carried out on 5 near-equiatomic alloys, viz., TaTiVW, CrTiVW, CrTaVW, CrTaTiW and CrTaTiV. Experimental studies suggest that TaTiVW, CrTiVW and CrTaVW alloys do form single/two bcc phase; while CrTaTiW and CrTaTiV alloys form bcc+Laves phase (Fig.3 (b)). These observations are in very good agreement with our predictions.

## Fe-Zr Alloys as Host Matrices for High Level Nuclear Metallic Waste

The growth of the nuclear power industry is also contingent upon the efficient management of nuclear wastes. While there is proper wasteforms available for immobilizing high-level (radioactivity>$3.7\times10^{11}$Bq/L) liquid waste, a suitable wasteform for the immobilization of high-level metallic wastes, viz., hulls, grids, spacers, etc., generated from reactors, remains lacking. Experimental findings have identified stainless steel (SS) and Zirconium (Zr) based alloys, such as SS-15wt% Zr, Zr-16wt% SS, and Zr-8wt% SS, as promising materials for metallic wasteform [14]. Notably, Fe-Zr intermetallic phases, viz., (c)ubic-Fe2Zr, (t)etragonal-$FeZr_2$, and (o)rthorhombic-$FeZr_3$, are predominant in SS-Zr alloys and play a crucial role in accommodating actinides present in metallic wastes [15]. In view of these considerations, our study explores the potential of Fe-Zrintermetallics to function as a wasteform for fission metals (FMs).

The thermodynamical, mechanical as well as dynamical stability of c-$Fe_2Zr$, t-$FeZr_2$ and o-$FeZr_3$ phases were first established from their formation energy, single crystal elastic constants and phonon dispersions [16]. Further, to study the feasibility of incorporation of the s-, p- and d-block FMs, viz., Rb, Sr, Cs, Ba, In, Sn, Sb, Te, Y, Nb, Mo, Tc, Ru, Rh, Pd, Ag and Cd in the Fe-Zrintermetallics, we have calculated the incorporation and solution energy of the FMs in c-$Fe_2Zr$, t-$FeZr_2$ and o-$FeZr_3$ intermetallics [16-18]. The calculated incorporation energies of the FMs suggest that the incorporation of all the FMs, except Rb and Cs, is exothermic in nature. The incorporation of Rb and Cs in all the three intermetallics is endothermic, which indicates that they are difficult to incorporate in these intermetallics. Interestingly, it is also observed that the Zr-rich intermetallics (t-$FeZr_2$ and o-$FeZr_3$) are energetically more preferred as hosts for all the FMs, except Tc, Ru and Rh atoms as compared to Fe-rich c-$Fe_2Zr$ owing to their larger negative incorporation energies.

However, it has been found that the vacancy formation energy of Fe/Zr in all the intermetallics are greater than 1 eV, which suggest that the equilibrium concentration of vacancy is very low in the system. Therefore, solution energies are more appropriate to assess the potential of these intermetallics to incorporate the fission metals. The calculated lowest solution energies ($E_{sol}$) of *s*-, *p*- and *d*-block FMs in the c-$Fe_2Zr$, t-$FeZr_2$ and o-$FeZr_3$ intermetallics are shown in Fig.4. At first, the site preferences of the FMs were determined based on their solution energies at the Fe and Zr sites. It has been found that s-block FMs, In, Sn, Y, Nb, Mo, Ag and Cd prefer to occupy Zr site; while the remaining FMs, viz., Tc, Ru, Rh, Pd, Sb and Te prefer to occupy Fe site. The calculated $E_{sol}$ of s-block FMs are higher than 1 eV suggesting that the s-block FMs can be easily segregated from the intermetallics. The solution energies of p- and d-block FMs in the three intermetallics are 0.5 and 1.0 eV, respectively, possibly making them soluble at higher temperatures due to lattice modulations. Overall, the solution energies of the FMs in the t-$FeZr_2$ and o-$FeZr_3$ phases are less than those in the c-$Fe_2Zr$ phase except for the Mo atom which has almost equal solution energy in the three intermetallics.

## Conclusions

The Present study elaborates on the usage of computational thermodynamics to determine fundamental thermodynamic properties of nuclear materials in a temperature and composition domain which are otherwise not attainable by experiments alone. Major conclusions arrived at are as follows:

(I)A database of thermal expansion, thermal conductivity and oxygen diffusion parameters has been developed for Np-based transmutation fuels which can be used to design new generation fuels, to analyse safety aspects and to simulate performance of the materials in reactor operating conditions.

(ii) The Occurrence of new single-phase high-entropy alloys and composition ranges are determined where they remain in single-phase. Further mechanical and defect properties of those alloys are ongoing with an aim to develop ductile radiation-resistant HEAs.

(iii) Fe-Zr alloys are suitable for the incorporation of p- and d- block fission elements with limited solubility.

(iv) We believe that limited experimental efforts are required to validate some of our predictions.

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## Density Functional Theory

11

# Atomistic Modeling (Odourless, Fumeless and Zero Toxicity) Driven Laboratory Experiments

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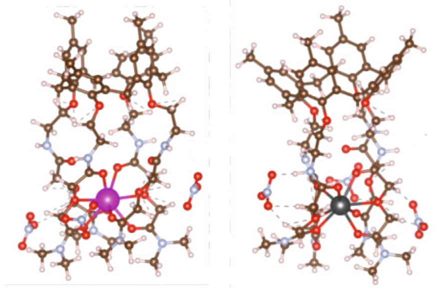

$Eu(NO_3)_3(C4DGA)$ and $Am(NO_3)_3(C4DGA)$

ABSTRACT

Atom by atom design and engineering of a molecular assembly using the tools of atomistic modeling nowadays has become very useful and popular for application in the various fields of science and engineering. This computational atomistic modeling has become very demanding due to its ability to predict quantitatively the structural, mechanical, thermo-physical and dynamical properties which are useful in interpreting the experimental findings and planning the new experiments. The present article focuses on the demonstration of atomistic modeling consisting of Quantum electronic structure calculations, classical and ab-initio molecular dynamics simulations and statistical mechanics carried out in Atomistic Modeling and Chemical Analysis Section, Chemical Engineering Group of BARC pertinent to DAE application.

KEYWORDS: *Atomistic modeling, DFT, Molecular dynamics, SX and IX, Multi-component glass, Barrier materials*

## Introduction

Atomistic modeling consisting of electronic structure calculations, classical molecular dynamics simulations, on the fly force based molecular dynamics simulations has become very powerful tool to design and develop the tailor made molecular architecture for varieties of application. The use of atomistic modeling driven molecular engineering is growing exponentially with continuing advance of CPU-GPU accelerated parallel computing, innovative and robust algorithms and accessibility of parallelized software [1]. Atomistic modeling (AM)predicts the properties of materials before their manufacture and determines the parameters and behavior needed to develop the advanced chemical process [2]. Tri-n-butyl phosphate (TBP) is extensively used in the PUREX process. In spite of great success, there is a demand and continuing search for an alternative of TBP. Due to inherent chemical similarities of Ln and An, identification of a suitable extractant for separation of the minor actinides (MA) from Ln is a major challenge in reprocessing of spent fuel. Similarly, separation of Zr and Hf is very difficult due to similar chemical properties and thus poses a challenge. Currently TBP is used on a commercial scale to separate Hf from Zr ions though it has low separation factor. There is a continuing search for finding an alternative of TBP. The finding of a right ligand-solvent system for selective metal ion extraction and enrichment is quite time consuming and a tiresome which can be cost-effective if the screening is done beforehand of the experiment. Since, the fabrication methodologies of nano membrane using graphene are yet to be simplified, computational investigations are the only means for advancing the progress. The screening of cost effective titanium alloy as neutron targets keeping its high absorption of hydrogen can be conducted by AM. Selection of suitable glass composition for vitrification of HLLW can be predicted with the guide of AM. Therefore, to achieve this goal, a strategy has been conceived employing the concepts of AM for solvent extraction, isotope separations, desalination, hydrogen storage materials and multi-component glass. First, a computational modeling strategy has been envisaged to design the molecular system followed by synthesis and characterization and finally, testing of the synthesized materials for targeted applications.

## Computational Methods

Density functional theory (DFT) with generalized gradient approximation and appropriate basis set (SVP, TZVP etc.) were used for structural relaxation, energy and hessian calculations for isolated molecules. COSMO solvation modeling was used to account for the solvent effect in the energetics and thus in thermodynamics. Classical and ab-initio molecular dynamics simulations using the appropriate ensembles (NVT, NPT etc) and boundary condition were used for evaluating the structural, thermophysical, mechanical and dynamical properties of molecules and materials in different state of matters. For periodic system, PBE functional including projector augmented wave potentials with an energy cut-off of 350 eV were employed. Monkhorst–Pack k-points were used for the Brillouin zone integration. The forces on all the atoms are kept less than $0.01 eVÅ^{-1}$.

## Results and Discussion

Density functional theory at the B3LYPlevel [3] was used to establish that ditertiary butyl dicyclohexano 18-crown 6 (DTBDCH) was the right extractant for removal of $Sr^{2+}$ ion. The preferential extraction of Zr over Hf towards organophosphorus extractant has been established using DFT and experimental results [4]. The optimized complexes of Zr and Hf ions with b is

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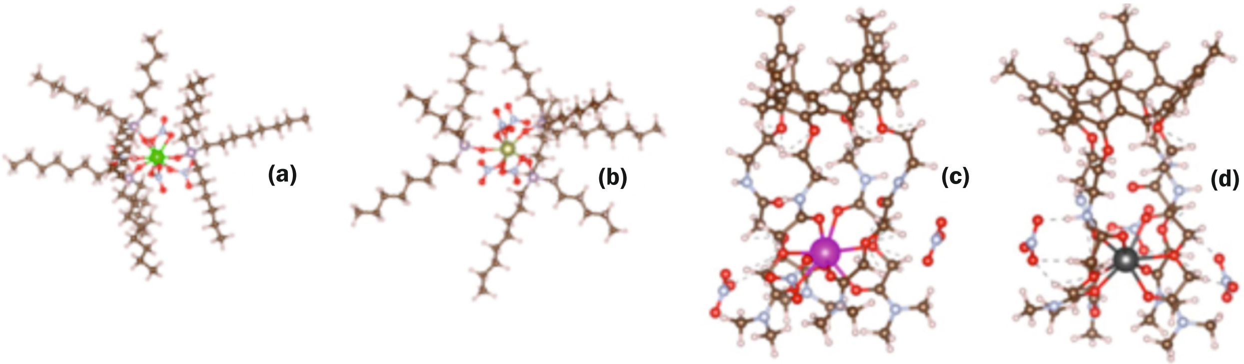

*Fig.1: Structures of (a) $Zr(NO_3)_4$ $(Cyanex923)_3$ (b) $Hf(NO_3)_4$ $(Cyanex923)_3$, (c) $Eu(NO_3)_3(C4DGA)$ and (d) $Am(NO_3)_3$ (C4DGA).*

(hexyl)-octyl phosphine oxide (Cyanex923) are displayed in Fig.1 (a,b). DFT successfully captures the complexation stability order as Cyanex923>Cyanex925 for both Zr and Hf ions. Cyanex923 is the best extractant in terms of high distribution constant and displays higher selectivity over Cyanex925 for Zr which is in excellent agreement with the experimental results. As per recent experimental results, TODGA (*N,N,N',N'*-tetra-*n*-octyldiglycolamide) is shown to be promising for actinides extraction. Computational studies of An/Ln complexes are rather limited [5].The optimized complexes of $Eu^{3+}/Am^{3+}$ ions with TODGA are depicted in Fig.1 (c,d). The $\Delta G_{ext}$[5] was higher for Eu ion than Am ion. The structures, energy and thermodynamics were calculated to investigate coordination mode, reaction energy and extraction ability of DGA appended calix[4]arene (C4DGA) [5]. The $\Delta G_{ext}$ for Eu ion was higher over Am ion which corroborates the experiments. The entropy of complexation, S was seen to be reduced for DGA to large extent compared to C4DGA. The ΔG was found to be negative and higher for Eu ion in absence of nitrate ion. The S was found to be negative in the presence of nitrate ion for 1:4 stoichiometry whereas slightly positive for 1:3. The role of nitrate was shown to be indispensable.

MD simulations were conducted to assess the uranyl extraction using LAMMPS package [6]. The extent of ion transfer from aqueous to organic phase is defined in terms of distribution constant, $K_d$ which is an important process parameter for plant design. Therefore, $K_d$ of $UO_2^{+2}$ ion by varying uranyl and acid concentration were estimated. The results in Fig.2 (a) show the non-linear increase in $K_d$ with increase in $UO_2^{+2}$ ion. There is a rise in $K_d$ with increase in acid up to 6M, thereafter a fall in $K_d$ with further increase in acid (Fig.2 (b)) as observed in the experiments. It is expected that the initial increase in $HNO_3$ concentration facilitates $UO_2^{+2}$ migration from interface to the organic phase by increasing the interfacial roughness, and so creating pathways for $UO_2^{+2}$ ion migration from interface to the organic phase. However, at very high acid concentration (>6M), the decrease in $K_d$ might be possible from two reasons: first, the competition between $UO_2^{+2}$ ions and $HNO_3$ molecules to be picked by TBP and second, the increased accumulation of $HNO_3$ molecules near the interface, which actually blocks the pathways for $UO_2^{+2}$ ion migration from aqueous to the organic phase.

DFT calculations were conducted to design functionalized resins for isotopic enrichment of Gd [7] using vibrational frequency of hydrated $Gd^{3+}$ ion and $Gd^{3+}$-crown ether complex ion by evaluating separation factor (α) (Fig.3). The results show that the separation factor with DB18C6 is higher than B18C6 and DCH. Because of comparatively high , DB18C6 is considered to be promising for isotopic enrichment of Gd, and hence DB18C6 was functionalized with chloromethylated polystyrene (CMPS) resin. Experiments were conducted by column chromatography and the separation factor was found to be in good agreement with the calculated results and thus hold promise for the future isotopic enrichment technology.

Using MD and DFT calculations, the binding affinities of graphene-embedded 18-crown-6, 16-crown-5 and 14-crown-4 for $Li^+$, $Na^+$, $K^+$, $Mg^{2+}$ and $Ca^{2+}$ metal ions were investigated [8]. The binding preference of these membranes depends on the crown ether cavity and the stability of hydration shell of the binding ion. The adsorption capacity of simulated crown ether graphene membranes for different cations is shown in Fig.4. 18C6 was found to be highly selective for $K^+$ ions. The order of selectivity was : $K^+>Na^+>Li^+$ for graphene embedded 18C6 with a strong competition between $Na^+$ and $K^+$ whereas for 14C4

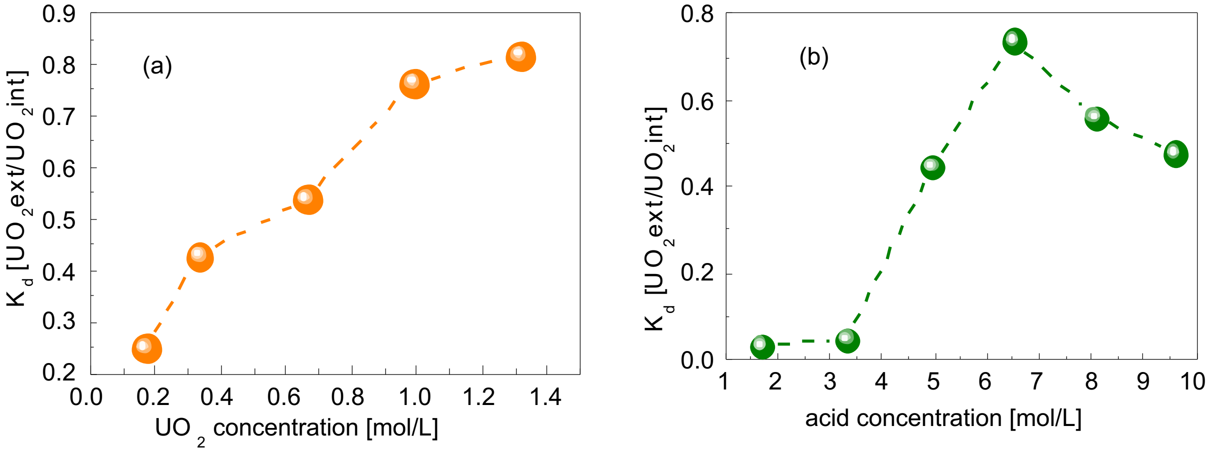

*Fig.2: Calculated values of $K_d$ for uranyl as a function of (a) uranyl concentration and (b) acid concentration in the system.*

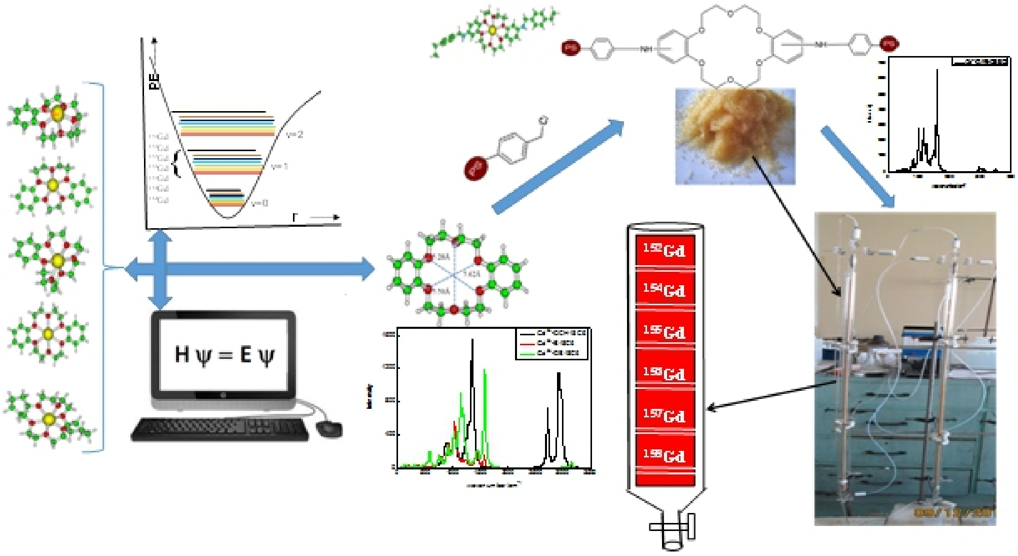

*Fig.3: Computer aided molecular engineering for isotope separation of gadolinium using column chromatography.*

and 16C5, the order of selectivity was: $Na^+ > K^+ > Li^+$.In spite of strong interaction of $Na^+$ and $K^+$ with 16C5-graphene and 14C4-graphene, no permanent trapping of ions was noted for $K^+$ with graphene-18C6. The results show Langmuir type adsorption profile, where one site can be occupied only by single cation. The adsorption capacity of ions/pore was always smaller than 1.0, which indicates that only one ion can be adsorbed by single crown ether pore, corresponding to 1:1 crown ether pore: cation ratio. Fig.4 (a,b) shows hydration number of cation as a function of distance from membrane surface. Fig.4 (c) shows the ions hydration w.r.t. distance from graphene-16C5. Results show reducing hydration number of ions while their transfer from bulk solution to crown ether. The maximum hydration number of metal ions was noted not in bulk but at few distance away from graphene membrane.

Titanium is preferred as neutron targets due to high hydrogen storage capacity and is of importance to understand the interaction of hydrogen with Ti. The calculations are conducted using PBE with GGA using linear combination of atomic orbitals (LCAO) and projector augmented wave (PAW) potential as implemented in the Atomistic Toolkits (ATK). The climbing image nudged elastic band technique was employed to find the minimum energy paths for H atom migration. The activation energy barrier from top to bridge and top to hollow sites was negative for H atom indicating barrier less diffusion. The calculated barrier height for dissociation was 0.4eV at surface coverage of $\theta_H > 0.5$ML whereas the barrier height for recombination was found to be much higher than that of dissociation (Fig.5). In case of recombination the H atom has to be detached from the binding of Ti atom and it recombines with another H atom to form $H_2$ molecule and this requires higher activation energy which is generally provided by applying external temperature.

Combined experiments and MD simulations were performed to understand the improved durability of borosilicate glass with addition of ZnO [10-13]. The MD results were found to be in good agreement with the experimental data for Young's Modulus, glass transition temperature and leaching. Both experiments and MD simulations report the enhanced chemical durability of glass with addition ZnO. Low R ($Na_2O/B_2O_3$) and high K ($SiO_2/B_2O_3$) of ZnO doped sodium borosilicate (Zn-NBS) glass surface compared to bare NBS represents the more stable structure of glass surface for Zn-NBS than NBS. During simulation, $Na^+$ ions were found to diffuse from bulk glass region to the interface and some of them were even migrated to the bulk side of the aqueous phase. The results in Fig.6 show that the leaching of Na+ ions can be reduced with ZnO doping and similar trend was noticed

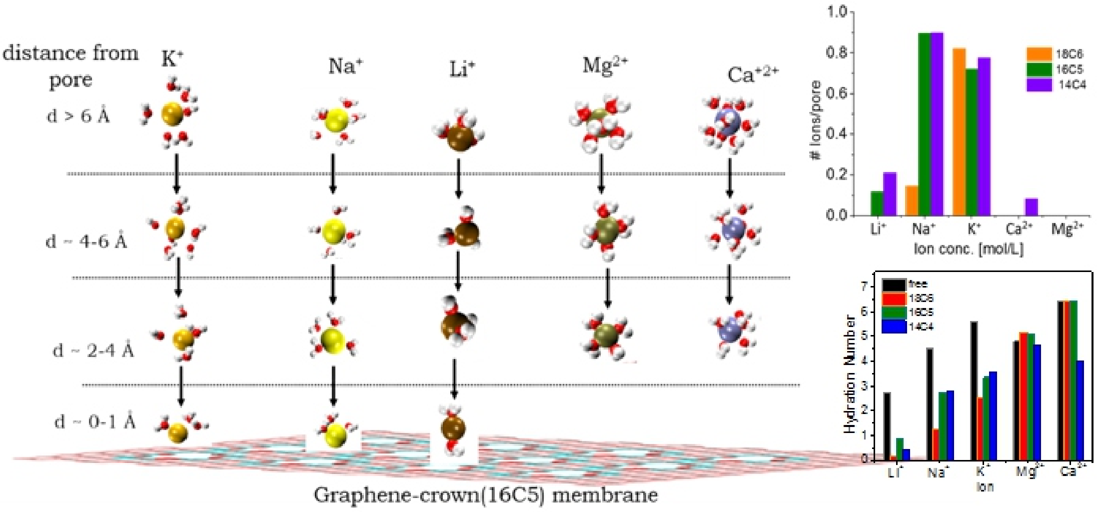

*Fig.4: Dehydration of metal ions on graphene-16C5 membrane. Hydration number of metal ions as a function of ion distance.*

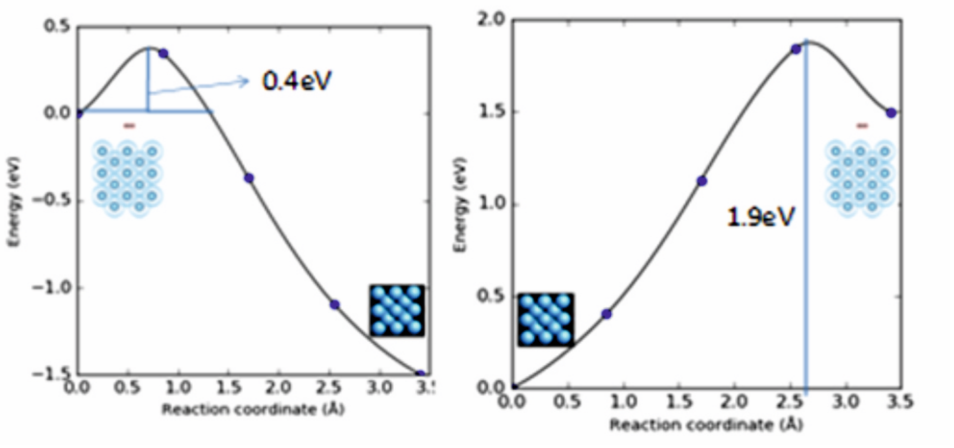

*Fig.5: (a)barrier for dissociation and recombination of $H_2$ molecule on the Ti (100) surface using LCAO basis set.*

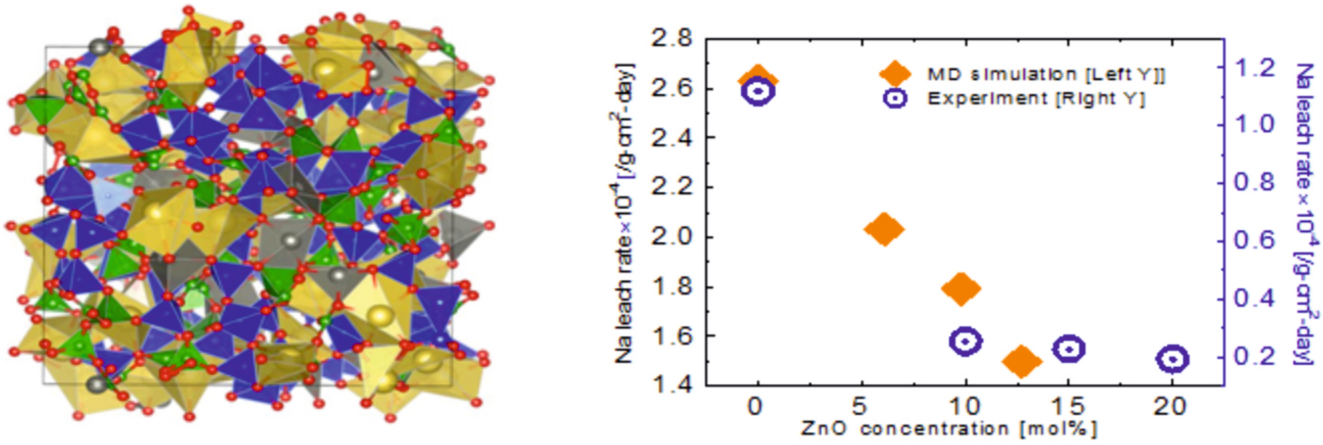

*Fig.6: ZnO-NBS (9.8% ZnO) glass andNa leaching rate from MD simulation (left Y) and experimental (right Y) studies.*

in experimental studies. MD simulations as well as experimental observations support the fact that ZnO would increase the chemical durability of glass. Low R and high K of ZnO doped NBS glass surface compared to bare NBS represents the more stable structure of glass surface with Zn doping, in which atoms will remain intact with the bulk structure of glass and would be less prone to leaching. The water adsorption in glass was found to affect the glass structure significantly at surface region while marginally in bulk region. The enhanced chemical resistivity of Zn-NBS was also established from the reduced diffusivity and higher activation energy for diffusion of Na+ ions while Zn doping or increasing ZnO concentration in NBS glass.

## Conclusion

DFT in combination with COSMO solvation model can be used as a pre screening tool for the selection of ligand-solvent systems. It can be stated that DFT-based computational methods have played and are still playing a key role in understanding the separation mechanism of various metal ions and isotope separation. High-fidelity MD simulations were shown to capture the experimentally observed migration of uranyl nitrate from the aqueous to the organic phase andultrafast water transport in graphene based membranes and thus are useful in planning the experiments. The identification of neutron generator and glass composition for waste immobilization can be predicted by atomistic calculations. To conclude, presently atomistic modeling is indispensable in the development of molecular engineering based nuclear technology.

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## Interdisciplinary R&D

12

# Theoretical Chemistry: An Overview on Modern Trends

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$$H\psi = E\psi$$
$$\vec{F} = m\frac{d^2\vec{x}}{dt^2}$$
$$\Omega \leq \Omega_0$$

ABSTRACT

Theoretical and Computational Chemistry forms an integral component of research in chemistry and is now also emerging, through its interface with allied disciplines as a major contributor to frontier areas of interdisciplinary research. With the availability of powerful computational resources, it is no longer a dream to predict the structure and dynamics of complex systems, and to design novel molecules and materials with desired properties for various applications. A major challenge one faces in this endeavor arises from the need to use different tools for different length and time scales inherent in the description of materials and phenomena. The current review is aimed at integrating all the domains; The microscopic domain, where the electronic structure obtainable through the solution of Schrodinger equation of quantum mechanics is relevant, while in the intermediate mesoscopic length scale, classical equations of motion, statistical mechanical description and atomistic simulation are commonly used and in the larger macroscopic length scale, continuum mechanics might suffice.

KEYWORDS: *Interdisciplinary research, Novel molecules, Microscopic domain, Atomistic simulation*

## Introduction

The school chemistry book starts with the concept 'Chemistry: An experimental Science', this has taken a new direction with the advent of Computational Chemistry, where theoretical and experimental research go hand-in-hand. This not only impacted the subject of chemistry in public domain but also emboldened the chemists to work along the seamless boundaries of molecules to materials. In recent years, the development of fundamental concepts and mathematical foundations has increased tremendously without any ambiguity, especially with the advancement of computational techniques along with state-of-the-art computational tools.

The genesis of 'Theoretical Chemistry', started nearly 400 years ago, when in the seventeenth century, Johannes Kepler [1] speculated on the symmetry of snowflakes and also on the close packing of spherical objects. The symmetrical arrangement of closely packed structures in the late nineteenth century led to many theories of crystallography and solid-state inorganic chemistry. John Dalton [2] represented compounds as aggregations of circular atoms, and Johann Josef Loschmidt [3] created diagrams based on circles using two-dimensional analogues. August Wilhelm von Hofmann is credited [4] with the first physical molecular model that was essentially topological. Joseph Le Bel [5] and Jacobus Henricus van't Hoff [6] introduced the concept of stereochemistry, with Van't Hoff showing tetrahedral molecules representing the three-dimensional properties of carbon. John Desmond Bernal gave [7] the first model of liquid water. It is now over 30 years since the first computer simulation of a liquid was carried out [8] at the Los Alamos National Laboratories, using the most powerful MANIAC computer.

## Electronic Structure Theory Describes the Motions of the Electrons and Produces Energy Surfaces

### *Hartree-Fock Theory & Beyond*

The shapes and geometries of molecules, their different energy levels and wavefunctions, as well as the interactions of these states with electromagnetic fields lie within the realm of structure theory. In the Born-Oppenheimer model of molecular structure, it is assumed that the electrons move so quickly that they can adjust their motions instantaneously with respect to any movements of the heavier and slower moving atomic nuclei. This assumption motivates us to view the electrons moving in electronic wave functions within the molecule's atomic framework. These electronic functions are found by solving a Schrödinger equation [9].

$$\mathrm{H}_k\Psi_k = E_k\Psi_k$$

thus, depend on the locations $\{Q_i\}$ at which the nuclei are sitting i.e. the $E_k$ and $\Psi_k$ are parametric functions of the coordinates of the nuclei and this dependence of electronic energies on the positions of the atomic centers cause them to be referred to as electronic energy surfaces.

The electronic energies $E_k(Q)$ allow one to determine the geometries and relative energies of various isomers that a molecule can assume by finding those geometries $\{Q_i\}$ at which the energy surface $E_k$ has minima, $\partial E_k/\partial Q_i=0$ with all directions having positive curvature (as monitored by the Hessian matrix, $H_{ij} =\partial^2 E_k/\partial Q_i\partial Q_j$, with no negative eigen values) [10]. Such geometries describe stable isomers. Also produced in electronic structure simulations are the electronic wave functions $\{\Psi_k\}$ and energies $\{E_k\}$ of each of the electronic states. The separation in energies can be used to make predictions about the spectroscopy of the system. Not only can electronic

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wave functions tell us about the average values of all physical properties for any particular state (i.e., $\Psi_k$ above), but they also allow us to tell how a specific "perturbation" (e.g., an electric field in the Stark effect, a magnetic field in the Zeeman effect, light's electromagnetic fields in spectroscopy) can alter the specific state of interest. The late Professor John Pople, made developments leading to the suite of Gaussian computer codes [11] that now constitute the most widely used electronic structure computer programs. For his contributions, he shared the 1998 Nobel Prize in Chemistry.

The full *N*-electron Schrödinger equation governing the movement of the electrons in a molecule is

$$\left(-\frac{\hbar^2}{2m_e}\sum_i \nabla_i^2 - \sum_a \sum_i \frac{Z_a e^2}{\mathbf{r}_{ia}} + \sum_{ij} \frac{e^2}{\mathbf{r}_{ij}}\right)\Psi = E\Psi$$

However, by approximating the full electron-electron Coulomb potential $\sum_{ij} e^2 / r_{ij}$ by a sum of terms, each depending on the coordinates of only one electron $\sum_i V(r_i)$, one arrives at N separate Schrödinger equations:

$$\left(-\frac{\hbar^2}{2m_e}\nabla_i^2 - \sum_a \frac{Z_a e^2}{\mathbf{r}_{ia}} + \frac{e^2}{\mathbf{r}_{ij}}\right)\phi_i = \varepsilon_i \phi_i$$

one for each of the N so-called orbitals $\ddot{O}_i$ whose energies$\varepsilon\varepsilon_i$ $\varepsilon$are called orbital energies. It turns out that much of the effort going on in the electronic structure area of theoretical chemistry has to do [12] with how one can find the "best" effective potential *V*®; that is, the *V*®, which depends only on the coordinates r of one electron, that can best approximate the true pairwise additive Coulomb potential experienced by an electron due to the other electrons. The approximation in different forms along with the symmetries led to Hartree-Fock (HF) and other high-level theories for accurate description of solution of Schrödinger equations. The CI, [13] MCSCF, [14] MPPT/MBPT, [15] and CC [16] methods move beyond the single-configuration picture by adding to the wave function more configurations whose amplitudes they each determine in their own way. This can lead to a very large number of CSFs in the correlated wave function, and, as a result, a need for extraordinary computer resources.

### *Density Functional Theory (DFT)*

Here one solves a set of orbital-level equations

$$\left(-\frac{\hbar^2}{2m_e}\nabla_i^2 - \sum_a \frac{Z_a e^2}{\mathbf{r}_{ia}} + e^2 \int d\mathbf{r} \frac{\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} + U(\mathbf{r})\right)\phi_i = \varepsilon_i \phi_i$$

in which the orbitals $\phi_l$ 'feel' potentials due to the nuclear centers (having charges $Z_a$), Coulombic interaction with the total electron density $\rho(r')$ and a so-called exchange-correlation potential denoted $U(r')$. The particular electronic state for which the calculation is being performed is specified by forming a corresponding density $\rho(r')$. Before going further in describing how DFT calculations [17] are carried out, let us examine the origins underlying this theory.

The so-called Hohenberg-Kohn theorem [18] states that the ground-state electron density $\rho(r)$ *describing an N-electron system uniquely determines the potential V(r) in the Hamiltonian*

$$H = -\sum_j \left(-\frac{\hbar^2}{2m_e}\nabla_j^2 + V(\mathbf{r}_j) + \frac{e^2}{2}\sum_{kj} r_{j,k}\right)$$

and, because *H* determines the ground-state energy and wave function of the system, the ground-state density $\rho(r)$ determines the ground-state properties of the system. It is also likely that extensions of DFT to excited states (many workers are actively pursuing this) be placed on more solid ground and applicable to molecular systems. Because the computational effort required in DFT approaches are smaller than that for conventional (SCF, MCSCF, CI, etc.) methods, DFT offers great promise and is expanding its applicability beyond atoms and molecules to materials and biomolecules. Useful implementations of DFT using plane wave basis sets and pseudopotentials replacing the core electrons as employed in Car-Parrinello molecular dynamics (CPMD) and Vienna *Ab-initio* Simulation Package (VASP) codes find wide applications in material science and solid states.

## Statistical Mechanics

### *Classical Theories*

The goal of statistical mechanics is to interpret and predict the properties of macroscopic systems in terms of their microscopic counterparts [19]. It provides the basis for understanding numerous natural phenomena and for design and optimization of chemical processes [20]. The importance of statistical mechanics in many different branches of basic and applied chemistry has long been realized, although its tunability to specific structural and dynamical problems has become feasible only in recent times [21]. The obvious reason for such a systematic development is its versatile applicability and suitability to cover the entire spectrum of physicochemical problems, thereby providing an inherent proximity to real experimental data [22]. As a corollary, a number of approximate and semiempirical methods [23] emerge which use ingenious combinations of basic concepts from statistical mechanics.

The quanta of sophistication in statistical mechanical methods are naturally driven by the specificity of problems used to represent various physicochemical systems. So far a number of more rigorous theoretical methods have been devised, which are based on molecular simulations, liquid-state theories, self-consistent field theory, and classical density functional theory. Thus, efficient lattice-Boltzmann methods have been developed for predicting the structure and dynamics of charged colloidal systems, integral equation theory has been established for equilibrium phase behavior of fluids involving virtually any system of practical interest, density functional theory in various versions has been formulated [24] to study the conformational behavior of polymer solutions at interfaces. With the rapid increase of computational capabilities, molecular simulation and *ab initio* quantum mechanics started providing the major impetus in statistical mechanics. However, simulation itself has a long way to go for the actual realization of the fundamental concepts in chemistry, not only because significant progress has yet to be made about the strategies for modeling multiple length and timescale phenomena but, more importantly, interpretation of simulation data, much like experimental results, often requires theoretical tools for analysis and representation. Thus, the present and the next decade is going to have an amalgamation between the analytical and simulation methodologies for predicting the molecular constituents of a system with "tailored" properties, commonly used in practical applications including control of gene expression, synthesis of biomacromolecules, and fabrication of nanomaterials [28].

### *Basic Concepts and New Developments*

Statistical mechanical description of classical systems [1] involves the concept of an ensemble, which is an arbitrarily large collection of imaginary systems, all of which are characterized by the same macroscopic parameters, but have different sets of coordinates and momenta of the particles. The system dealing with an interface is an open system in general, and is characterized by fixed values of volume *V*, temperature

*T*, and chemical potential μ with the ensemble designated as a grand canonical ensemble. Theoretical description of classical fluids at an interface starts with the description of the single particle density $\rho(\mathrm{r})$, of the fluid, conveniently expressed as [3]

$$\rho^{(1)}(\mathbf{r}) = \rho(\mathbf{r}) = \langle \hat{\rho}(\mathbf{r}) \rangle = \left\langle \sum_{i=1}^{N} \delta(\mathbf{r} - \mathbf{r}_i) \right\rangle$$

The determination of this fundamental quantity has led to a large number of methodologies, which can be broadly classified, into four categories. The first one is based on the integral equation theory (IET), which has been found to be quite successful in both homogeneous and inhomogeneous forms of description. The second one belongs to methods based on density functional theory (DFT), which has been applied to simple and complex fluids in its various forms of description, viz. perturbative and non-perturbative methods like weighted density approaches (WDA). The hybrid methods that include both the density functional and the integral equation theory constitute the third method, which has been applied quite recently to study the fluid mixtures and the electric double layer. The fourth one involves the Monte Carlo (MC) and molecular dynamics (MD) simulations,7 which provide direct physical insights into different important aspects of the structure of fluids.

Alongside the developments of versatile theoretical tools, the past two decades have seen a phenomenal growth in computer *experiments* [25] mainly because they provide essentially exact, quasi-experimental data on well-defined models, hence theoretical results can be tested unambiguously in a manner that is generally impossible with data obtained in experiments on real liquids. It is also possible to obtain information on quantities of theoretical importance that are not readily measurable in the laboratory. In a conventional MD simulation, a system of N particles is placed within a cell of fixed volume. A set of velocities is also assigned, usually drawn from a Maxwell-Boltzmann distribution corresponding to the temperature of interest. It was several years before a successful attempt was made to solve the equations of motion for a set of Lennard-Jones particles [26].

The subsequent trajectories of the particles are then calculated by integration of the classical equations of motion

$$m\ddot{r}_i = -\nabla_i V_N(\mathbf{r}^N).$$

The particles are assumed to interact through some prescribed force law and the bulk of the computational labor is concerned with the calculation at every step of the forces acting on each particle. The static and dynamic properties of the system are then obtained as time averages over the dynamical history of the system

$$\mathrm{A}_{obs} = \langle \mathrm{A} \rangle_t = \lim_{\tau\to\infty} \frac{1}{\tau} \int_0^{\tau} dt \mathrm{A}\left[\Gamma(t)\right]$$

where $\Gamma$ represents a particular point in phase space. Apart from the choice of initial conditions, a molecular dynamics simulation is, in principle, entirely deterministic in nature. By contrast, as the name suggests, a probabilistic element is an essential part of any Monte Carlo computation. In a classical Monte Carlo simulation, a system of *N* particles interacting through some known potential is again assigned a set of arbitrarily chosen initial coordinates; a sequence of configurations of the particles is then generated $[\Gamma(t) \rightarrow \Gamma(t+1)]$ by successive random movements with the probability density $\rho_{\mathrm{ens}}(\Gamma)$ of the ensemble. Any reasonable initial distribution should lead to the same average value.

$$\mathrm{A}_{obs} = \langle \mathrm{A} \rangle_{ens} = \langle \mathrm{A} \mid \rho_{ens} \rangle = \sum_{\Gamma} \mathrm{A}(\Gamma)\rho_{ens}(\Gamma)$$

with the ergodicity holding good for the specified system of interest. A number of hybrid methods are also in rolling, viz. the self-consistent density functional approach (SCDFA) [27] from DFT and IET and the Monte Carlo density functional theory (MCDFT) [28] from MC and DFT. Whereas the former is based on the calculation of density functional quantities from IET and mostly applied to simple fluids including the ionic systems, the later requires single chain simulation with enumeration of configurations and finds applications in complex polymeric fluids.

## Concluding Remarks and Future Directions

The goal of materials design is the optimization of specific properties such as high strength and low density together with a number of other critical aspects including manufacturing cost and environmental acceptability. Computational materials design help in addressing all these aspects. The present decade is passing through an evolution of methodologies [29] for designing new materials through multiscale materials modeling [30]. At the quantum scale, ground state (and sometimes the excited state) energies as well as other properties (e.g., molecular geometry, vibrational and NMR spectroscopic data, multipolar moments, etc.) are calculated. Currently, ab initio molecular orbital theory [31] provides the most accurate prediction of molecular properties. The results of quantum mechanical calculations are often used in the design of molecular force fields providing a connection to the next scale, that of atomistic simulations. Using statistical mechanics, the results of atomistic or molecular scale calculations can then be applied to describe behavior at the mesoscopic and macroscopic scale (e.g., process or bulk properties). Mesoscale computations describe behavior and properties of systems that reflect the molecular composition of materials. Some current predictive approaches include linear statistical modeling, fractal models, re-normalization models, lattice-Boltzmann approaches, wavelets, homogenization solutions of partial differential equations, self-consistent mean field theory, dynamic mean-field density functional methods, and dissipative particle dynamics. Application of statistical mechanical theories in physicochemical problems has opened a new vista in understanding microscopic structural and dynamic properties and linking the same to macroscopic phenomena occurring in real time. Many developments like SCF, IET, DFT, MD and MC as well as combination of these methods like SCDFA and MCDFT have strengthened the field.. The practical value of all these developments is reflected not only by its generality but also by its versatility for solving complex problems. This review gives some specific examples of recent developments hovering around these methods. The applicability of the present methods demands the scope for new methodologies as well as versatile numerical algorithms.

The contents discussed in the present review are illustrative rather than exhaustive. The methods described above could be reliably applied for studying a number of current topics like the DNA salt binding, the molecular self-assembly, the solvation dynamics, the wetting transition. The organization of nanostructures within self-assembled templates has attracted a great deal of attention in recent years as this method can possibly be used in developing hybrid composite materials [32] Molecular simulations corroborate the fact that by tethering oligomers to specific locations on nanoparticle surfaces could facilitate the self-assembly of nanoparticles into specific structures which will eventually be dependent upon the complex geometry and topology of the tethered nanoparticles [33].

Future applications of the methods discussed above depend on continuing progress in the representation of real systems and, more importantly, on their clever implementations. Further, efficient algorithms and faster data processing are the need of the hour and quite a good number of works on artificial intelligence and machine-learning techniques are worth mentioning. [34,35] Although much current work in the literature concerns relatively simple models, much of it in the coming years will depend upon the development of more realistic force fields for more complex systems. Important advances are already emerging in applications of these methods to material fabrication, environmental protection, biomolecular engineering, and nanotechnology for various high-end applications in space, atomic energy, and defence equipment. Modeling and simulation in general and theoretical chemistry in particular will play an extremely crucial role in all these areas of developments for mankind in the foreseeable future!

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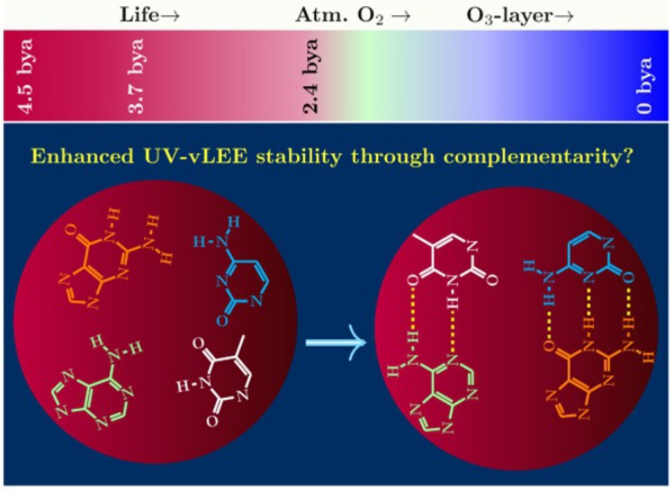
## Biomolecular Complementarity

# *Prebiotic Origin of Biomolecular Complementarity*



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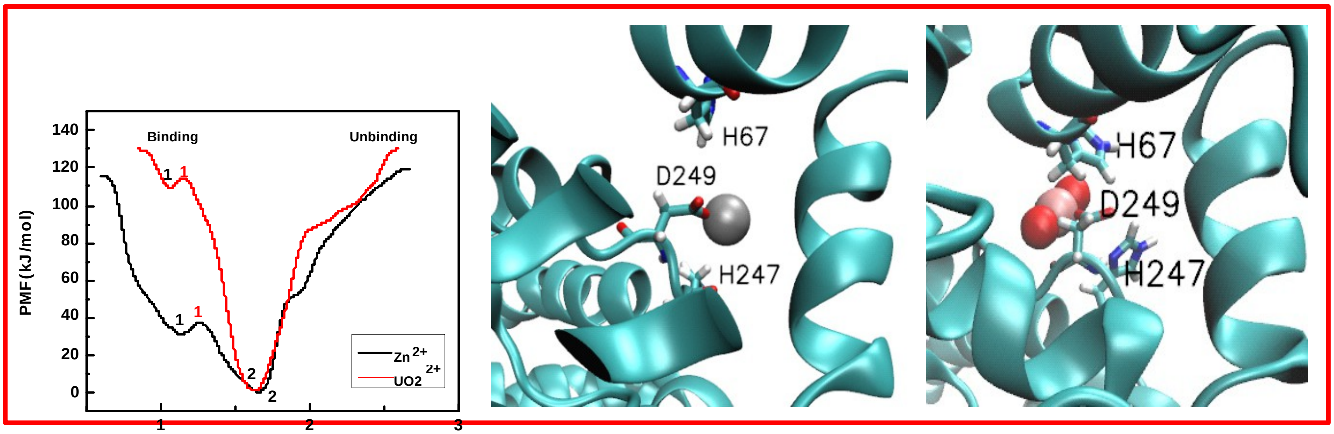
The long-held notion that complementarity based on intermolecular hydrogen bonding confers thermodynamic stability to DNA has recently been experimentally disproved. This experimental refutation made the origin of complementarity an enigma in the chemical origin of life. Our published article (*Commun. Chem.2023, 6, 259*) presents a hypothesis that complementarity based on intermolecular hydrogen bonding originates from the broader molecular stability necessitated by the ambient physicochemical conditions of a prebiotic medium in which it chemically evolved. Due to the absence of a protective stratospheric ozone layer, a continuous flow of unattenuated shortwave UV photons reached the early Earth's surface and greatly intensified its prebiotic physico-chemical conditions.

A prebiotic chemical medium that constantly receives short-wave UV photons eventually becomes a breeding ground for very low-energy electrons (vLEEs). In other words, the prebiotic medium was intensified by two of the most efficient molecular deleterious agents, i.e., shortwave UV photons and vLEEs. We have reviewed the molecular stability inherent in nucleobases and in their chemically advanced structures against two of these most prominent prebiotic molecular deleterious agents. Our efforts revealed that the inherent ability of complementary bases to survive adverse conditions of prebiotic medium rather than individual bases leads to their proliferation and consequently to the chemical evolution of their advanced molecular complements.

Our studies revealed that the inherent ability of complementary bases to survive adverse conditions of prebiotic medium rather than individual bases leads to their proliferation and consequently to the chemical evolution of their advanced molecular complements.

## An All Atom Molecular Dynamics Study

# Binding of Human Serum Albumin with Uranyl Ion at Various pH



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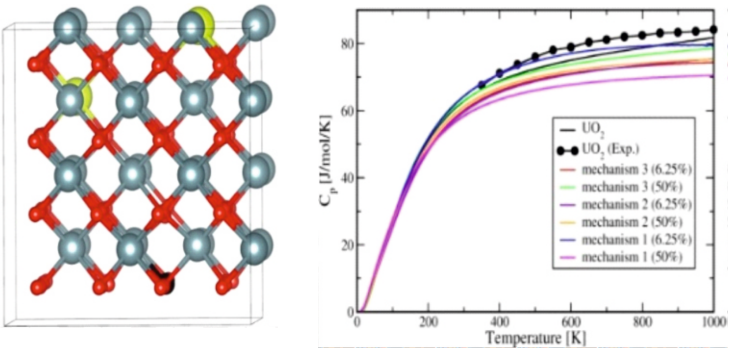
It is observed that the binding of metal ions with HSA is the result of the dynamical balance between metal-HSA and metal-water short range Coulomb interactions.

Actinide, namely, uranium, poses a two-fold risk once it enters the human body. On the one hand, the major risk is due to their nuclear radiation, and on the other hand, it is a consequence of their heavy metal toxicity. Irrespective of the intake pathway, i.e., inhalation, ingestion, or cutaneous absorption, actinides are resorbed and transported by the bloodstream prior to deposition in target organs or tissues. The actinides exhibit long biological lifetimes of 20–50 years and are excreted at slower rates. They link with different biological ligands (proteins, amino acids, etc.) and mimic natural biological elements (iron, calcium, etc.). Uranium is routinely handled in various stages of the nuclear fuel cycle, and its association with human serum albumin (HSA) has been reported in the literature; however, their binding characteristics still remain obscure. Understanding binding characteristics is important for a better understanding of the mechanisms controlling their specific target deposition, the toxic effects, and the design of suitable decorporating agents. However, no efforts are given to understand the phenomenon at molecular level. For the first time, the enhanced sampling method, namely, well-tempered meta-dynamics, is employed to study the binding processes of uranyl and zinc ions with HSA at the molecular level (published in *J. Biomole. Struct.Dyna. 2023, 41, 7318-7328*). It is observed that the binding of metal ions with HSA is the result of the dynamical balance between metal-HSA and metal-water short range Coulomb interactions. It can be inferred that the uranyl ion cannot associate with the zinc bound HSA protein but can be captured by free HSA at all pH values, i.e., endosomal, alkaline, and physiological pH.

## Effect of Oxidation States

# Computational Study of Thermophysical Properties of Cerium doped $UO_2$



*J. Nucl. Mater.2024, 588,154791.*

**Tijo Vazhappilly and Arup K. Pathak**
Scientific Officers, Chemistry Group
Bhabha Atomic Research Centre, Trombay-400 085, INDIA

Our calculations were helpful in evaluating the fuel properties of $UO_2$ with fission products in a complex environment where cations with multivalent oxidation states are present.

The interaction of fission products with $UO_2$ fuel, which is generated during the nuclear fission, can amend the fuel behaviour. Among different lanthanide (Ln) fission products produced, Cerium (Ce) shows considerable yield. In this work, the trivalent and tetravalent cerium (Ce) atom substitution in $UO_2$ and their effect on thermophysical properties is investigated using density functional theory. Further, the effect of Ce doping concentrations in $UO_2$ is assessed by varying the Ce atom concentrations in the lattice (6.25%, 12.5%, 25%, and 50%) for various charge balancing mechanisms. The lattice charge balance in the Ce doped $UO_2$ structure is attained through different processes such as oxygen vacancy creation, accommodating excess oxygen in the lattice, and by altering the oxidation of state of U atoms. The volume of Ce doped $UO_2$ lattices show higher or lower values compared to pure $UO_2$ depending upon the oxidation state of Ce and U atoms. The mechanical properties tend to reduce for Ce substituted $UO_2$ as compared to pure $UO_2$. The Ce dopant concentration and the electronic charge on Ce and U atoms effect the band structure of Ce doped $UO_2$. Thermal properties such as specific heat capacity are evaluated using quasi-harmonic approximation. Our results show good agreement with the reported experimental values (*published in J. Nucl. Mater.2024, 588,154791*). Especially, the effect of oxidation state of Ce on fuel properties of $UO_2$-$CeO_2$ matrix has never been investigated. Our calculations are helpful to evaluate the fuel properties of $UO_2$ with fission products in a complex environment where cations with multivalent oxidation states are present.

# Quantifying the Role of Counter-Ions

## *Redox Potentials of Uranyl Ions in Macrocyclic Complexes*

ACS Omega, 2023, 8, 18041-18046.

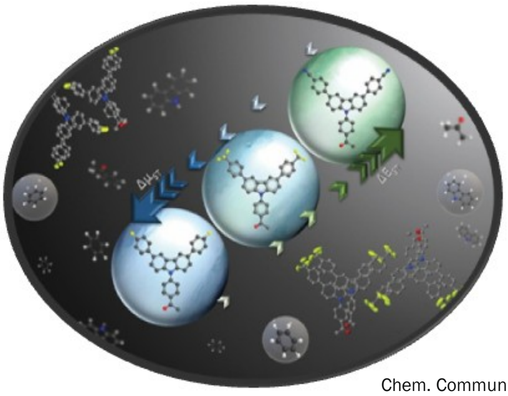
**Mahesh Sundararajan**
Scientific Officer, Chemistry Group
Bhabha Atomic Research Centre, Trombay-400 085, INDIA

The study showed that triflate anion can contribute more than 50% to the predicted redox potentials, suggesting that their vital role in the overall reduction processes cannot be neglected.

Several uranyl ions strapped with Schiff-base ligands in the presence of redox innocent metal ions are synthesized, and their reduction potentials are recently estimated. The change in Lewis acidity of the redox-innocent metal ions contributes to ~60 mV/pKa unit quantified which is intriguing. Upon increasing the Lewis acidity of metal ions, the number of triflate molecules found near the metal ions also increases whose contributions toward the redox potentials remain poorly understood and not quantified until now. Most importantly, to ease the computational burden, triflate anions are often neglected in quantum chemical models due to their larger size and weak coordination to metal ions. Herein, we have quantified and dissected the individual contributions that arise alone from Lewis acid metal ions and from triflate anions with electronic structure calculations (published in *ACS Omega, 2023, 8, 18041-18046*). The triflate anion contributions are large, in particular, for divalent and trivalent anions that cannot be neglected. It was presumed to be innocent, but we here show that they can contribute more than 50% to the predicted redox potentials, suggesting that their vital role in the overall reduction processes cannot be neglected.

## Phosphorescence in Carbazole Derivatives

# Modulation of $\Delta E_{ST}$ and Room Temperature Phosphorescence in Carbazole Derivatives



Chem. Commun., 2024, 60, 1408.

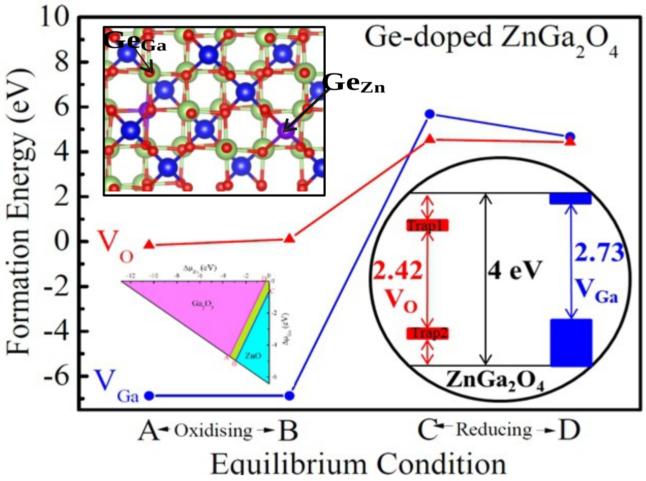
**K. V. Barhate, A. P. Wadawale, *K. R. S. Chandrakumar, and N. Agarwal**
*Scientific Officer, Chemistry Group
Bhabha Atomic Research Centre, Trombay-400 085, INDIA

> The results would be of interest in developing the metal free organic molecular systems having the property of room temperature phosphorescence.

For the first time in the literature, a correlation between the (i) difference in the dipole moment values of the singlet and triplet states $\Delta\mu_{ST}$ and their respective energy gaps $\Delta E_{ST}$ and (ii) HOMO-LUMO gap, $\Delta E_{gap}$ with the $\Delta E_{ST}$ values. In case of $\Delta\mu_{ST}$, $\Delta E_{ST}$ is found be correlated inversely whereas there is a linear correlation with the $\Delta E_{gap}$ values. These correlations have been observed with the molecular systems which exhibit room temperature phosphorescence. Materials with high ground-state polarity are capable of stabilizing the charge transfer excited states of emitters by having electrostatic interactions with its (emitter) excited-state dipole moment. This results in lowering of the singlet excited state (S1) of the emitter; therefore, the energy gap between S1 and the lowest triplet excited state (T1) is reduced. Similar to this, we believe that large $\Delta\mu_{ST}$ will stabilize the charge transfer state to reduce the S1 level, which results in reduction of $\Delta E_{ST}$. These results would be of interest in developing the metal free organic molecular systems having the property of room temperature phosphorescence (*Chem. Commun., 2024, 60, 1408*).

## Insight from DFT Study

# Intrinsic Charge Carrier-Trapping Defects in Ge-Doped $ZnGa_2O_4$



J. Phys. Chem. C 2023, 127, 13918–13928.

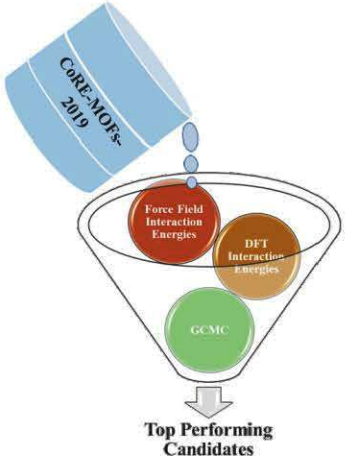
**Brindaban Modak**
Scientific Officer, Chemistry Group
Bhabha Atomic Research Centre, Trombay-400 085, INDIA

Wide band gap semiconductors with high dielectric constant and good thermal dissipation are very popular for wide range of optical and electronic devices. In the recent studies $ZnGa_2O_4$ has been projected as an alternative to $Ga_2O_3$. The structural simplicity (face-centered-cubic spinel structure) results into isotropic electronic and optical properties for $ZnGa_2O_4$, in comparison to the large anisotropic properties for the β-monoclinic variety of $Ga_2O_3$. Recent experimental observation indicates that the doping with Ge into $ZnGa_2O_4$ improves the optical properties. However, an unambiguous and ultimate explanation on microscopic origin of the experimentally observed optical property and the limiting factors has not been accomplished so far. This drives us to gain a detailed knowledge of the defect chemistry in Ge-doped $ZnGa_2O_4$. The present study explains the experimental observation of colour variation property of $ZnGa_2O_4$ by oxidation-reduction process. The experimental observation of poor optical behaviour in the presence of oxygen vacancy and improvement due to doping with Ge have been explained. Present study showed that the presence of Ge favors formation of gallium vacancy, which can reduce the band gap significantly without the involvement of discrete mid gap trap states, resulting into enhanced optical output (*J. Phys. Chem. C 2023, 127, 13918−13928*). This unique strategy can be applied to large number of materials for the enhancement of their optical properties.

> The study showed that the presence of Ge favors formation of gallium vacancy, which can reduce the band gap significantly without the involvement of discrete mid gap trap states, resulting into enhanced optical output.

# Porous Materials for Carbon Capture

## Computational High-throughput Studies to explore porous materials for carbon capture



ACS Appl. Mater. Interfaces 2023, 15, 28084–28092

***S. Kancharlapalli and R.Q. Snurr**
*Scientific Officer, Chemistry Group
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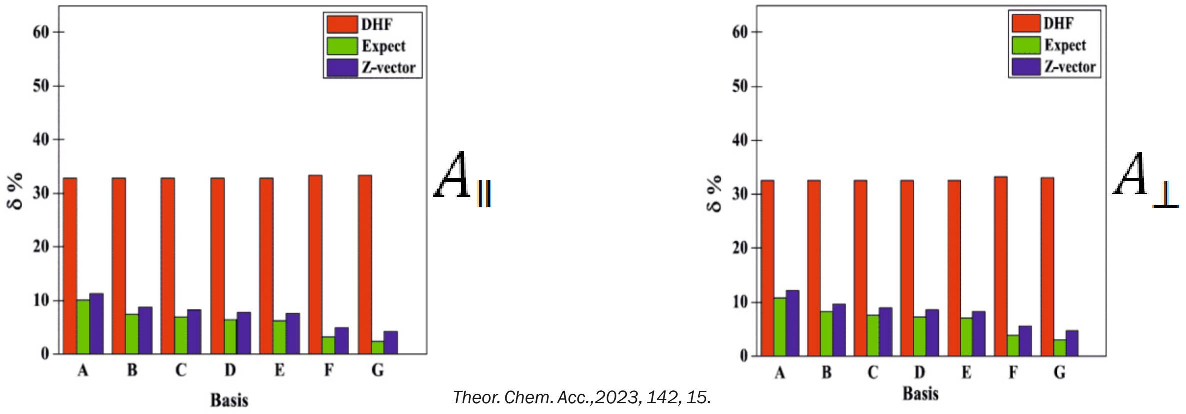
Our study identified MOFs that show selective $Co_2$ adsorption under wet flue gas conditions with significant $CO_2$ uptake capacity and $CO_2/N_2$ selectivity.

Computational high-throughput screening (HTS) has the potential to identify top-performing materials for a particular application, like gas storage and separation applications, from large database of materials. For such large scale studies, fast and efficient computational tools are in high demand. For screening metal–organic frameworks (MOFs) for $CO_2$ capture from wet flue gas, a random forest machine learning model that can predict the partial atomic charges in MOFs was developed and deployed as python library that has been extensively used. Model was trained and tested on a collection of about 320000 atomic charges calculated through density-derived electrostatic and chemical (DDEC) on a subset of the Computation-Ready Experimental Metal–Organic Framework (CoRE MOF-2019) database. Using the trained model and other state-of-the-art computational techniques, a systematic computational HTS of the all-solvent-removed version of the CoRE-MOF-2019 was carried out for selective adsorption of $CO_2$ from a wet flue gas mixture. Our screening study identified MOFs that show selective $CO_2$ adsorption under wet flue gas conditions with significant $CO_2$ uptake capacity and $CO_2/N_2$ selectivity (*JACS Appl. Mater. Interfaces 2023, 15, 28084–28092*). We also analyzed the nature of pore confinements responsible for the observed CO2 selectivity.

## Low-energy Precision Tests

# *Relativistic Coupled-cluster Study of SrF for Low-energy Precision Tests of Fundamental Physics*



*Theor. Chem. Acc.,2023, 142, 15.*

**K. Talukdar, H. Buragohain, *M. K. Nayak, N. Vaval and S. Pal**
*Scientific Officer, Chemistry Group
Bhabha Atomic Research Centre, Trombay-400 085, INDIA

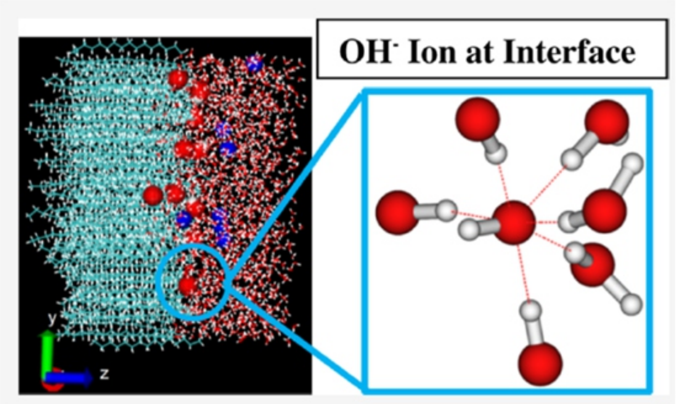
A Laser-coolable molecule, SrF, can be an interesting system for spectroscopic tests of fundamental physics. We present an electronic structure study of this molecule within the four-component relativistic coupled-cluster singles and doubles (RCCSD) framework and employ the RCCSD-based methods to compute its molecular-frame dipole moment and core properties such as hyperfine structure coupling constant and molecular P, T-odd electronic structure parameters that are of great importance for the high-precision tests of fundamental physics.

The impact of basis set size, Hamiltonian and nuclear model on the property calculation of SrF is also investigated. The computed results are in good agreement with the available experimental values. The present study shows that the SrF molecule could be useful for high-precision molecular experiments to explore physics beyond the Standard Model of elementary particles (*Theor. Chem. Acc., 2023, 142, 15*).

The study showed that the SrF molecule could be useful for high-precision molecular experiments to explore physics beyond the Standard Model of elementary particles.

# Propensity of Excess Hydroxide Ions

# On the Propensity of Excess Hydroxide Ions at the Alcohol Monolayer–Water Interface



J. Phys. Chem. B 2023, 127, 783–793.

**D.Bandyopadhyay, K. Bhanja and N. Choudhury**
Scientific Officers, Chemistry and Chemical Engineering Groups
Bhabha Atomic Research Centre, Trombay-400 085, INDIA

Air–water and oil–water interfaces are ubiquitous in many natural and technological processes. Understanding the distributions of different ions at such interfaces relative to bulk is of fundamental as well as technological importance. A large number of investigations have been devoted to understand structure and orientation of water and the distributions of different ions at the air-water interface through vibrational sum frequency generation spectroscopy (VSFG) and molecular dynamics (MD) simulations. However, interfaces between long-chain organic molecules and water are also of utmost importance because of their ubiquitous presence in several systems, such as various electrochemical systems, biological membranes, atmospheric aerosols and fuel cells. Knowledge on the alcohol–water interface is also essential to understand the formation of sea spray aerosol, which has significant influence in cloud formations and climate change. In the present work, using extensive molecular dynamics simulations and advanced techniques, the distributions of self-ions ($H^+$ and $OH^-$) of water at the cetyl ($C_{16}$) alcohol – water interface have been studied. Present study demonstrates that hydroxyl ions accumulate at the interface, but hydronium ions are distributed homogeneously throughout the bulk and the interface (*J. Phys. Chem. B 2023, 127, 783–793*). It is also observed from the present study that these two self-ions of water are entirely different in terms of their ability to act as H-bond acceptors or donors. These results are to be experimentally verified by VSFG or 2D-IR spectroscopy.

The study showed that the two self-ions of water are entirely different in terms of their ability to act as H-bond acceptors or donors. These results are to be experimentally verified by VSFG or 2D-IR spectroscopy.

## Futuristic Battery Materials

# *Exploring Solid-State Battery Materials using Neutron Spectroscopy and ab-initio Simulations*

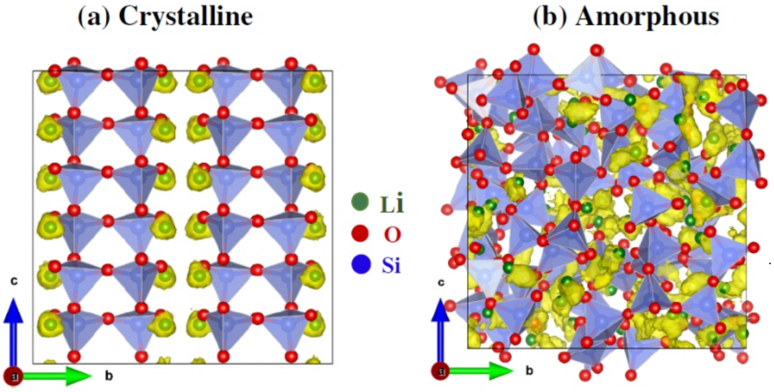


Fig.: The structure of (a) *crystalline*-$Li_2Si_2O_5$ and (b) *amorphous*-$Li_2Si_2O_5$ used in simulations. The Li probability iso-surface plot (yellow dots) from AIMD simulations at 1000K. The disjoint iso-surface plots in *crystalline*-$Li_2Si_2O_5$ shows absence of $Li^+$ diffusion, while connected iso-surface plots in amorphous phase reveal $Li^+$ diffusion.

**Dr. R. Mittal and Dr. M. K. Gupta**
Scientific Officers, Solid State Physics Division, Physics Group
Bhabha Atomic Research Centre, Trombay-400 085, INDIA

> Our studies showed that manipulating the ionic stoichiometry of these materials and prompting the formation of the amorphous phase can significantly improve the diffusion process, improving the material's potential performance in a battery.

Renewable energy produced by solar and wind technologies is intermittent, so there is a need for economical storage devices that have long life cycles. Electrochemical batteries are a promising solution for renewable energy storage. The scientists are studying a range of battery materials and their properties, including conventional lithium-ion batteries and the next-generation battery materials. Solid-state batteries have higher energy density compared to traditional Li-ion batteries and have the potential to offer great advantages as batteries in electric vehicles.

Understanding the diffusion process of Li or Na ions in these electrolytes is important, as the faster movement of these ions increases the battery's storage capacity. For a battery material, high ionic diffusion is favourable for the charge/discharge process. We have proposed a few strategies (*J. Mater. Chem. A11, 1712, 2023; J. Mater. Chem. A 11, 23940, 2023*) to enhance the Li/Na-ion conductivity and tune the operating temperature in solid-state electrolytes, such as doping, amorphization, reducing dimensionality, etc. Quasi-elastic neutron spectroscopy is a spectroscopic technique that is a great tool for investigating these diffusion processes, as the motions of particles can be explored at the atomic scale. Ab-initio molecular dynamics simulations alongside the experiments were extremely helpful in enabling to interpret the data.

In the solid electrolyte material $Li_2Si_2O_5$, we have shown (*J. Mater. Chem. A11, 1712, 2023*) that the dynamics of silicon polyhedral units play an important part in the lithium diffusion process. It has been shown that amorphous phase of $Li_2Si_2O_5$ facilitates the fast motion of lithium. We have identified that the specific topology of Na zig-zag chains in $Na_3ZnGaX_4$ (X=S, Se) provides (*J. Mater. Chem. A 11, 23940, 2023*) the low-barrier energy pathways for Na-ion diffusion. We bring out the role of specific zig-zag Na chains topology in the framework structure and its dynamics, leading to Na diffusion.

Our studies showed that manipulating the ionic stoichiometry of these materials and prompting the formation of the amorphous phase can significantly improve the diffusion process and also material's potential performance in a battery. This is an important consideration which needs to be taken into account in designing future solid-state battery materials.

# Prof. Ashoke Sen visits BARC

## How false vacuum is different from ether...

*It is not really ether. I mean one cannot distinguish false vacuum from ordinary vacuum. Ether makes sense if there's an experiment which you can do to distinguish it from the usual vacuum. Actually, one doesn't need ether to explain the propagation of matter. Finally, one cannot distinguish false vacuum from real vacuum...*

## Devising phase diagram for different false vacua...

*In String Theory or for that matter in a fundamental theory, it is pertinent to have a phase diagram. In String Theory what happens is that we have many different phases and near each phase we can have a phase diagram. But there are many many phases that you've and still you don't know how the whole thing fits together. You can study phase diagrams in individual regions and we can see that there is true vacuum and false vacuum in individual regions but we still don't have a way to fit everything together. Basically, what we have to do is to merge all of them. Firstly, we have not discovered all these phases. We are finding newer and newer phases almost every day. So, we need to first find all these phases and see how these different phases fit together. It is certainly a problem. But in principle, it can be solved. But we haven't been able to solve it yet...*

## Expansion of the Universe...

*For a most part of the universe, expansion is adiabatic i.e. entropy is conserved. But, in the early universe, there were phases in which it was not adiabatic. There is a first order phase transition which actually leads to entropy production. However, for most parts it is adiabatic. Also, the density of Dark Energy is uniform...*

## Discovery of Higgs Field and the existence of other states...

*By doing an experiment the kind of environment you're producing was already there in the early universe. In the early universe (when it underwent an extremely high temperature phase) it did not trigger the production of killer bubble. Otherwise, we wouldn't have existed. This tells us that by doing low energy experiments in accelerators, we are not going to produce the killer bubble...*

# 'The Future of our Universe'

**Select edited excerpts of Prof. Ashoke Sen's talk at Trombay Colloquium in BARC in February**

## 5

## Big Bang Theory and the Origins of Potential...

*The potential is a part of the Theory. It is not dependant on Time. Big Bang, of course, is a time dependant phenomenon. The potential is a property of the Theory which is there forever. Once you have a given fundamental theory, we can calculate what that potential is. This is the potential of scalar field, which is a part of the Theory. The Higgs potential, for example, is part of the Theory. It doesn't depend on the Big Bang phenomenon...*

## 6

## Interlink between Dark Matter and Normal Matter, and Energy and Dark Energy...

*Dark energy, as I understand, doesn't exchange energy with anything - that's again part of Einstein's Equations. Normal Matter and Dark Matter could exchange energy. However, experimentally, we know that it doesn't, because if it could exchange energy we might have already seen the Dark Matter. We can expect there's a small interaction between the Dark Matter and the Normal Matter but insofar we have not yet detected such a thing actually taking place...*

## 7

## Gravitational pull stronger than the Dark Energy expansion force...

*Dark energy is on account of gravity. The expansion of the Universe is controlled by gravitational force. Gravity depends on the kind of energy density. Dark Energy density tells us what is the source of gravity that is produced. The Dark energy density gives an overall accelerated expansion. The gravitational force between the matter and the galaxy is larger than the Dark Energy expansion...*

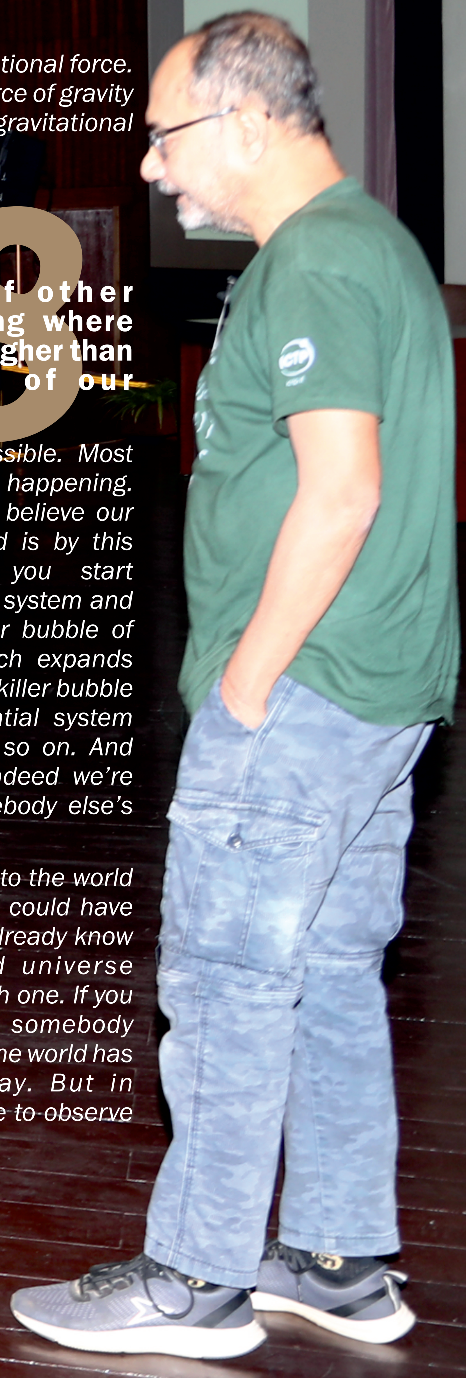

Vivek Bhasin, Director, BARC handing over a memento to Prof. Ashoke Sen. Dr. A.K. Tyagi, Director Chemistry Group and Bio Science Group is standing next to him.

## 8

## Possibility of other universe existing where the potential is higher than the potential of our universe...

*This is certainly possible. Most likely that is what is happening. One of the ways we believe our universe is produced is by this cascading effect i.e. you start from a high potential system and then produce a killer bubble of lower potential, which expands and then produces a killer bubble of even lower potential system and it expands and so on. And according to that, indeed we're expanding into somebody else's universe.*

*If we had been close to the world of the expansion, we could have observed it. But we already know that the observed universe doesn't have any such one. If you are expanding into somebody else's universe then the world has gone very far away. But in principle it is possible to observe this...*



# National Science Day 2024 in BARC

## *Atoms for Society: Securing Water, Food, and Health*

National Science Day (NSD) is celebrated every year on 28 February to commemorate the discovery of Raman Effect by renowned Indian Scientist and Nobel Laureate Prof. C.V. Raman. The aim of this celebration is to provide a platform for fruitful interactions between students from various schools/colleges and leading scientists of BARC and DAE, as well as to emphasize on the significant role of science for the societal benefit.

The theme of NSD-2024 in BARC during February 28-1 March is ‘Atoms for Society: Securing Water, Food, and Health’, to spread awareness about research development work and associated technological outcomes in these vitally important domains of science and technology.

Audio-visual presentations, skit performance, quiz competition, invited talks by eminent scientists on topics related to the theme, technology exhibition, visit to various state-of-art laboratories and research facilities in Trombay were organized for the benefit of students as part of the 3-day event.

# BARC scientist awarded Chemical Research Society of India medal

Dr. K.R.S. Chandrakumar, Scientific Officer/G, BARC was awarded the “Chemical Research Society of India-Bronze Medal” for the year 2023. Dr. Chandrakumar joined BARC, Trombay soon after completing his Ph.D in the year 2003 from National Chemical Laboratory, Pune. His noteworthy contributions include the conceptual density functional theory based chemical reactivity descriptors, development of hydrogen storage materials and structure-reactivity relationship in carbon based nanostructured materials. His research interests are in the areas of nanostructured materials, growth mechanism of carbon nanotubes & fullerenes. Recently, he initiated the activity on investigating nanocatalysis for hydrogen generation from water, $CO_2$ reduction, the fundamental mechanisms of assembled complex nanostructures, including DNA-Origami and their functionalities.

Dr. Chandrakumar is deeply interested in science popularization and basic education programs. He is also a Visiting Faculty at the Center for Excellence in Basic Sciences (CEBS), University of Mumbai.

He is a recipient of the Young Scientist Award from Indian Science Congress Association (2002), Young Scientist Medal from Indian National Science Academy (2005) and Young Scientist Award from Department of Atomic Energy (2007). He was also awarded the Scientific & Technical Excellence Award (2015) from Department of Atomic Energy.

# BARC scientist selected as a Member of INYAS

Dr. Brindaban Modak, Scientific Officer/F of Theoretical Chemistry Section, Chemistry Division, BARC, has been selected as a member of the prestigious Indian National Young Academy of Sciences (INYAS) for a period of 5 years (2024-2029).

The major thrust of his research activities include developing novel materials for hydrogen generation through solar water splitting, Li/Na-ion batteries, tuneable materials for optoelectronics and light-emitting devices, modeling of thermophysical properties of advanced nuclear fuels, materials for nuclear waste immobilization and phosphor materials for radiation dosimetry. Dr. Modak has 77 publications in reputed international journals to his credit which are well cited in literature. He is also a recipient of Young Scientist Platinum Jubilee Award (2019) of The National Academy of Sciences, India (NASI), Outstanding Doctoral Student Award of HBNI (2019), DAE Young Scientist Award (2018), Homi Bhabha Prize (2008), and Four Best Poster Presentation Awards. He is also a member, NASI (2021); and Young Associate of Maharashtra Academy of Sciences (2021).

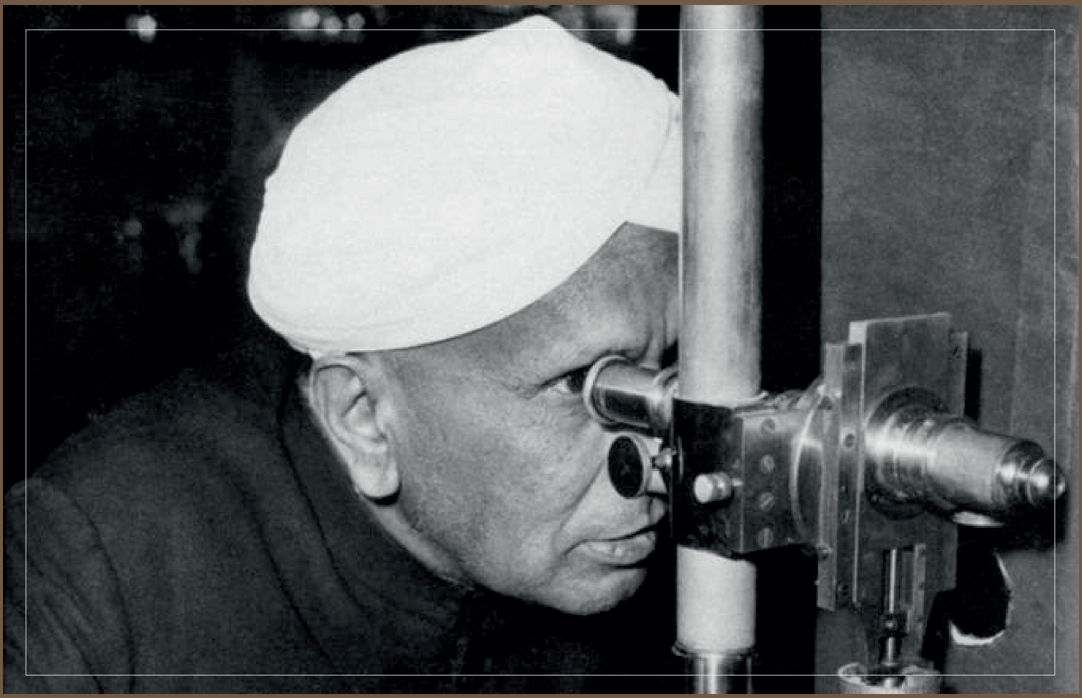


Photo courtesy of Raman Research Institute, Bangalore.

Sir C.V. Raman looking into the Spectrograph.

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