Effective approaches towards exploring problems ranging from Molecules to Materials

Niharendu Choudhury*

Theoretical Chemistry Section, Chemistry Division
Bhabha Atomic Research Centre, Mumbai-400085, India

ABSTRACT

A brief account of the works carried out in this group in recent years is presented here. A range of fundamental as well as applied problems in Chemistry and related disciplines has been addressed by developing suitable theories, state of the art computer simulation techniques and performing large scale computations. Specifically, the theoretical and computational investigations encompassing broad areas of nuclear materials, waste management, energy and bio-molecular systems have direct relevance to the thrust areas of research in DAE. Research related to exotic chemical/physical problems through development of novel computational techniques have also been discussed. The whole gamut of work described here includes design of new materials with tailor made properties and explaining observed phenomena with electronic and/or atomic scale resolutions through the applications of first principle quantum mechanical methods as well as classical statistical mechanical theories and simulations.

Keywords: Multi scale-modeling, Nanomaterials, Hydrogen storage, Biomacromolecules, Ligand design.

Introduction

With the advent of newer theoretical processes and high performance supercomputing machines along with the availability of many state of the art program suits, applications of theoretical methods in solving complex chemical, physical and biological problems have been an integral part of the modern day research. Any scientific problem can be treated theoretically if the correct lengthscale for tackling the problem can be identified. In that perspective, various lengthscales starting from the most fundamental quantum mechanical domain to atomistic to meso scale to ultimately continuum domain with an underlying hierarchical thread intertwining the domains in the order mentioned above exist. Among all, quantum domain, being the fundamental of all, is governed by the laws of quantum mechanics, whereas all other domains are either based on laws of statistical mechanics or relied on hydrodynamic principles. A true multiscale modelling [1-2] of any material rests on the successful flow of information from the lowest to the higher lengthscales. In the present article, we shall confine ourselves to the problems belonging to the first three domains, namely, quantum, atomistic and meso scale domains.

In what follows, we have described various computational codes used in Sec. 2, various results on Nuclear Materials and Fuel Cycles in Sec. 3.1, Energy and Environment in Sec. 3.2, Soft Condensed Matter in Sec. 3.3, Bio-Inspired Research in Sec. 3.4 and Development of Theoretical Methodologies and Computer Codes in Sec. 3.5. Finally we offer concluding remarks in Sec. 4.

2. Methodology

In dealing with these topics, ab-initio electronic structure calculations for atoms, molecules, clusters and solids, and classical mechanics based molecular dynamics simulations at the atomistic and coarse-grained levels have been extensively used. Standard codes like VASP, GAMESS, ORKA, MOLPRO and many programs developed in-house have been employed for the topics requiring quantum mechanical framework. On the other hand, larger system sizes have been tackled through the uses of classical molecular dynamics (MD) and coarse-grained MD simulations. Standard codes like GROMACS and many in-house developed MD programs along with many analysis codes have been extensively used in many of these cases.

3. Results and Discussions

3.1 Nuclear Materials and Fuel Cycles

In this sub-section, the recent findings on nuclear materials using computational techniques are described.

A. Understanding radiation damages in nuclear structural materials

Ferritic and austenitic steels are the most important structural materials used in industries, in particular, in the nuclear industry. These steels are used mainly for making reactor pressure vessels (RPV) in nuclear reactors, where high temperature and neutron irrradiation can degrade the material properties, and thus limit the lifetime of the reactor's structural components. Steels are alloys of Fe, C and many other small and large solute atoms (SAs) like Ni, Cu, Cr etc. It has been found that the Cu precipitation is one of the primary reasons for the embrittlement of irradiated RPV steels. We have investigated here using first principle electronic structure calculation, in conjugation with the experimental investigation conducted in Material Science Division, BARC about the origin of Cu clustering in steels. The electronic level understanding of such Cu cluster formation reveals [3,4] that Cu-Cu interaction is attractive in nature and the extent of attractiveness increases in presence of the vacancy (V), which is amply generated at high temperatures and
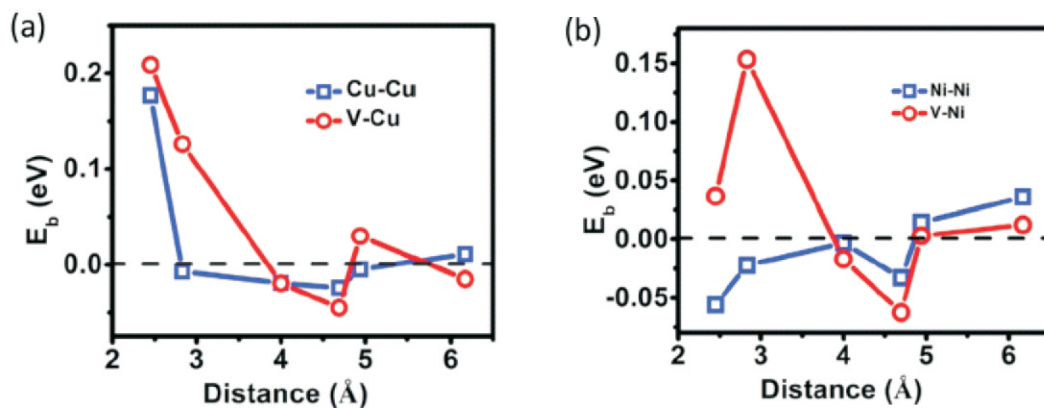
Fig.1: Binding energies of SA–SA and V–SA pairs as a function of the distance in bcc-Fe for (a) Cu–Cu and V–Cu, (b) Ni–Ni and V-Ni.
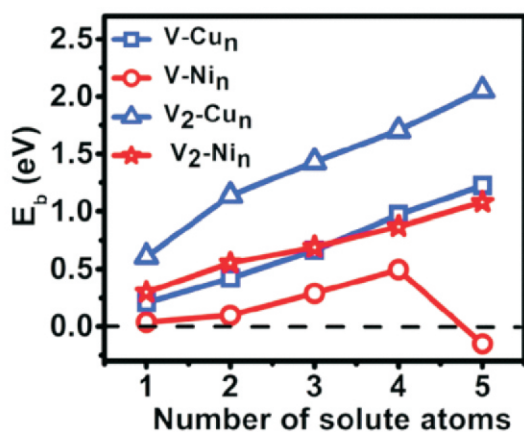

Fig.2: Binding energies of V–Xn and V2–Xn clusters (V stands for vacancy).

irradiation. In Fig.1(a) and (b) we show how SA-SA (SA=Cu, Ni) interaction changes as a function of distance between them. It is to note that the Cu-Cu, V-Cu and V-Ni interactions are attractive (positive energy stands for attraction). The interaction energy of the vacancy-SA clusters shown in Fig.2 demonstrate attractiveness among the SAs increases with number of solute atoms and a vacancy or a di vacancy can bind 5 or more Cu atoms in the Fe matrix. Origin of such interaction was further analysed to reveal a compensatory nature of electronic and distortion energies [4]. It is interesting to explore the different factors that control the nature of the interactions amongst different entities. Components of the total interaction energy, which is split into two major components, namely the electronic effect and the distortion effect are shown in Fig.3. The electronic factor primarily includes the effect of electron redistribution, and the distortion effect is related to the strain induced or relieved upon replacement of Fe atoms by solute atoms. It is observed (Fig.3) that the nature of the two components are very much configuration dependent and the two component energies are compensatory in nature i,e. if one is favourable then another is opposing a particular configuration.

B. Fuel reprocessing

Liquid-Liquid Interface: An important issue at the back end of the fuel cycle is the separation of actinides and lanthanides. Computational design of new ligands and various host molecules based on their interactions with the ions has now become an integral part of the advanced research in this field. Of the fission products, partitioning minor actinides (MAs) such as americium and curium from the bulk are often difficult. We have found that supramolecular host molecules are better candidates for the trivalent separation of Eu and Am due to the favourable host-guest interactions.[5] Of the several hosts, cucurbituril (CB-[n]) hosts are classic cationic binders due to favourable ion-dipole interactions. Our electronic structure calculations show that presence of counter-ions such as nitrate enhances the binding affinities of Am cations as shown in Fig.4.

Solid-liquid Interface: Liquid-liquid extraction have been utilized for many years in the nuclear industry for the reprocessing of the spent fuels [6-7]. Many difficulties associated with the conventional liquid-liquid extraction process such as excessive use of organic solvents, difficulties in separating different phases etc. can be nicely overcome if a heterogeneous solid-liquid interface based method is used. Due to tailor made adsorption properties, the functionalized carbon nanotube (CNT) based membrane separation method will be a very useful alternative to the conventional solvent extraction processes. In order to design a better separation process, thorough knowledge about the structure and dynamics of actinyl ions in water is essential. In a series of investigations using MD simulations, we have investigated structural and dynamical aspects of uranyl ions in water at different temperatures and concentrations of uranyl ions [8,9] and at supercritical conditions [10,11] relevant to supercritical extraction. We have further investigated the adsorption behaviour of the uranyl ions in different functionalized CNTs [12,13]. Detailed analyses demonstrate that the mode of adsorption in –COO–
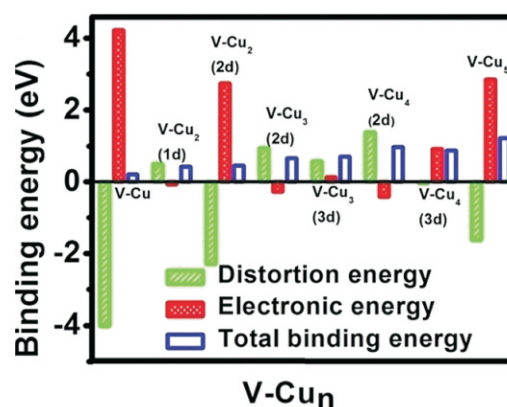

Fig.3: Decomposition of total binding energy of V–Cun complexes into the distortion and electronic binding energies (where V stands for vacancy).
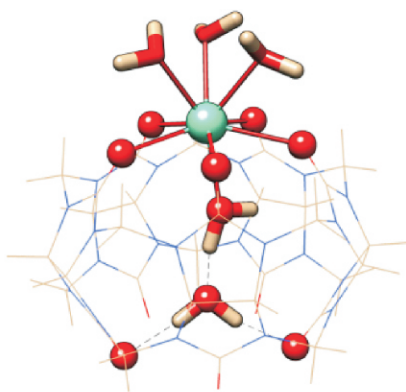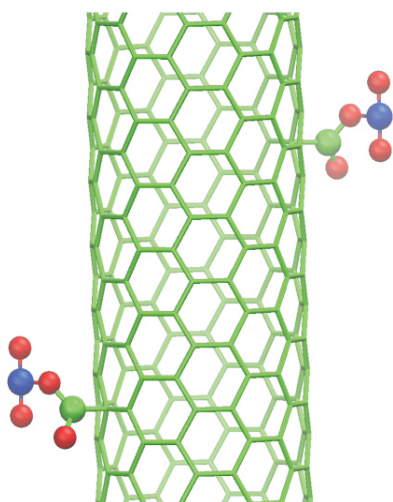
Fig.4: Optimized structure of Am-CB [5].

Fig.5: Carboxylate functionalized CNT.

Fig.6: Adsorption of uranyl ions per unit CNT.

Fig.7: The Ng atoms are adsorbed on the pores of M-MOF-74.

functionalized CNT (Fig.5) is different from bare and –OH/-COOH functionalized CNTs. Calculated adsorption isotherm (Fig.6) for uranyl ion adsorption shows that the carboxylate ion functionalized CNT has the maximum adsorption capacity.

On the other hand, entrapment of radioactive noble gases, Xe and Kr, needs special attention in the context of nuclear fuel reprocessing and nuclear reactor accidents. The generally employed cryogenic distillation process for the separation of noble gases is not cost effective. In recent years, use of porous materials is being actively discussed for adsorption and separation of noble gases. Metal-organic frameworks (MOFs) are considered superior in such applications owing to their high uptake capacity, and superior selectivity. Computational modelling of MOFs through tailoring their properties for noble gas mitigation helps us to identify the suitable candidates. For this purpose, we have investigated the binding of Xe and Kr in M-MOF-74 (Fig.7) employing first principle based electronic structure calculations. Our study [14] has shown that, Xe binds stronger than Kr and adsorption energy changes with the nature of the central metal atom in the MOF. We have also explored the MFM-300 (M) based MOFs for separation and storage of Xe and Kr [15].

Effect of fission products on fuel: For safe and efficient operation of nuclear reactors, gauging the effects of fission products (FPs) on the properties of the host fuel is extremely essential. For this purpose, knowledge of thermo-physical properties of UO_2 fuel in presence of the lanthanide (Ln) FPs is essential. Using DFT with Hubbard-U corrections various properties have been evaluated. The mechanical property viz. bulk modulus of Ln doped UO_2 is found to be directly related to the Ln doping concentration. The thermo-physical properties like heat capacity and coefficient of thermal expansion are also evaluated based on quasi-harmonic approximation to the phonon frequencies. The properties obtained from our *first principle* calculations show a good agreement (Fig.8) with the available experimental and theoretical results [16, 17].

Generating data base for advanced nuclear fuels: Designing advanced fuel materials such as accident tolerant fuels and the management of nuclear waste generated as a result of reactor operations are the two major challenges. Fuel materials like U_3Si_2, UAl_3 and U_2Mo have been projected as advanced fuels for nuclear reactors. Using ab-initio electronic structure calculations within the framework of density functional theory (DFT), various important thermophysical properties of these materials as well as various properties related to heat transport phenomena, such as, thermal conductivity, heat capacity, and thermal expansion coefficient have been calculated and these results will help in developing a database for such materials [18,19].

Energy and Environment

Increasing worldwide energy demands and rapidly depleting fossil fuel resources along with the environmental concerns signify the importance of sustainable and renewable energy options. Hydrogen is considered to be one of the best possible alternative energy carriers. However, to develop an efficient hydrogen energy system, two main hurdles are (a) cost effective generation of hydrogen from renewable resources like water through water splitting and (b) storage of hydrogen by developing efficient hydrogen storage materials and designing more efficient fuel cells to convert the chemical energy to electrical energy. Listed below are some of our efforts in those directions.
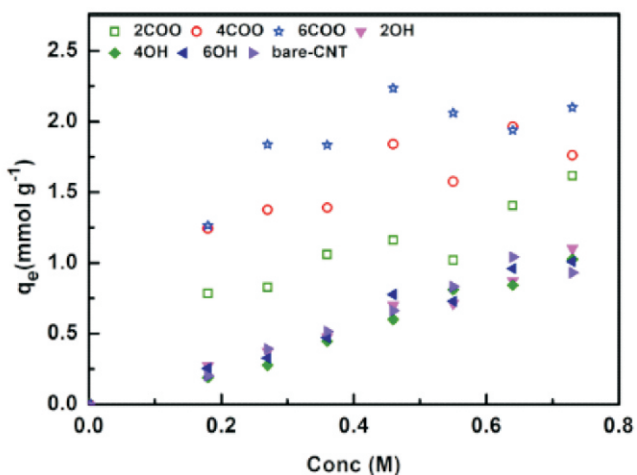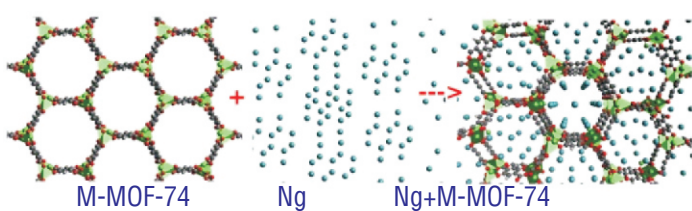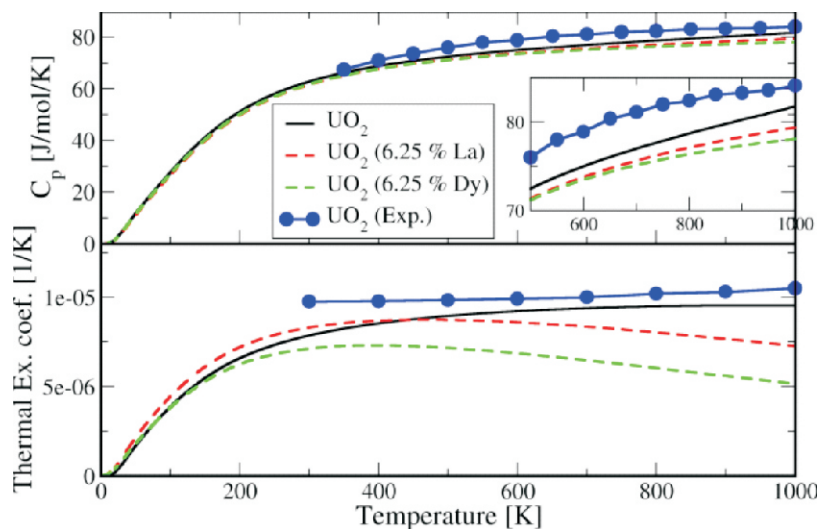
Fig.8: The effect of Ln fission product concentration on thermal properties of Uo₂.

Water splitting: Photocatalytic water splitting reaction using the abundant solar energy and semiconductor materials is an ideal way to generate hydrogen. Large number of semiconductor materials such as TiO_2, ZnO, $SrTiO_3$, $NaTaO_3$, ZnS, CdS, $CdSe$, etc., have been studied for photocatalytic water splitting. Using the periodic density functional theory calculations, we explored [20-21] various oxide based photocatalysts like $SrTiO_3$, $KNbO_3$ and $NaTaO_3$ for their activity towards solar water splitting. Using DFT, we could explain the underlying reasons for the experimentally observed improved photocatalytic activity of Zr doped $KNbO_3$ towards the water splitting reaction [20]. Using DFT, we have explored the poly s-triazine based graphitic carbon nitride as possible photocatalyst for water splitting for the first time[21] and we could propose the hybrid carbon nitride, $g-C_3N_3/g-C_3N_4$ to be a better catalyst, the fact which has been experimentally proved very recently [21].

Hydrogen Storage: Hydrogen storage at ambient conditions is another major bottleneck for hydrogen-based energy systems. We demonstrated varieties of light metal decorated materials, like cyclic carbon molecular systems, fullerenes, boron hydrides, two-dimensional (2D) carbon materials, metal organic frameworks (MOFs) and porous carbon materials for their hydrogen adsorption characteristics based on some of the elegant chemical concepts such as the electrostatic interactions, curvature of carbon nanomaterials and aromatic nature of molecule-based materials, etc. [22-23]. Based on this knowledge, we have put forward [23] the single-walled carbon nano horns as one of the potential candidates for hydrogen storage on the basis of 'intra-curvature'. We have also investigated magnesium clusters for the purpose of hydrogen storage and our results [24] obtained from *ab-initio* molecular dynamic simulation have shown that a complete dehydrogenation from these Mg nanoclusters occurs at ~100⁰C, a significant improvement over bulk MgH₂ (~300⁰C).

3.3 Soft Condensed Matter

There are many exotic structural and dynamical phenomena involving macroscopic many-body systems and these problems should be tackled by using force-field based atomistic and coarse-grained simulations. Below are the depictions of many such topics in which theoretical and computation chemistry have played a major role to understand and unravel many apparently puzzling phenomena and observations.

Patterned C₆₀ Solvation Shell: Accurate description of solvation structure of a hydrophobic nanomaterial is of immense importance to understand protein folding, molecular recognition, drug binding, and many related phenomena. Moreover, spontaneous pattern formation through self-organization of solvent molecules around a nanoscopic solute is fascinating and useful in making template-directed nanostructures of desired morphologies. Here, we show through coarse-grained MD simulation that the patterned solvation layer (Fig. 9) with the imprints of the hydrophobic surface atoms of the C_{60} can be obtained from a completely different mechanism
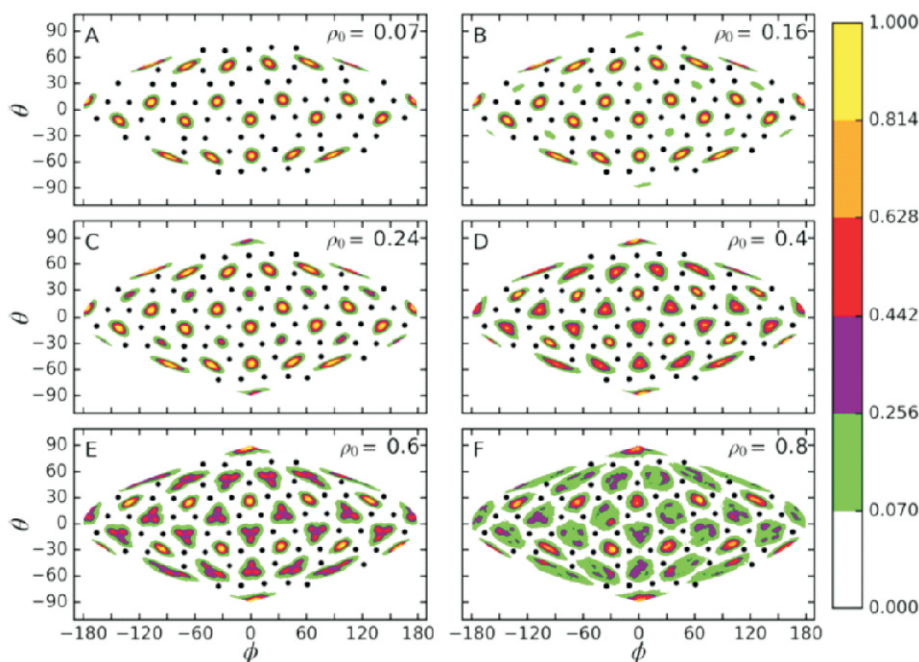
Fig.9: Pattern formation by the surrounding solvents of the C_{60} fullerene at different densities (ρ_0). Black dots are the positions of the C atoms of C_{60}. Pattern shows hexagonal faces have higher solvent densities as compared to pentagonal faces.
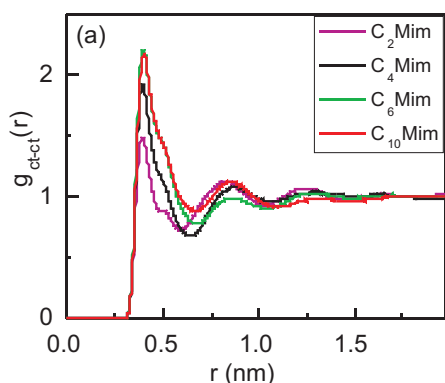
Fig.10: Radial distribution function, g(r) of the terminal carbon atom of the alkyl chain of the RTIL solvent around the same of another RTIL molecule.

arising from a spherically symmetric, short-ranged interaction having two characteristic lengthscales. The nature of the pattern can be modified by adjusting solvent density or pressure. The solute-solvent dispersion interaction is the key to such pattern formation adjacent to the solute surface. In Fig.9, we have shown the pattern of solvent molecules surrounding the C_{60} [25-26] at different bulk densities of the solvent. It is to note that the pattern changes with solvent density or pressure.

Domain Formation in RTIL: Results of our molecular dynamic simulations reveal that self-organization of the room temperature ionic liquid (RTIL) solvent molecules, which creates non-ionic and ionic pockets in RTIL, becomes more significant as the alkyl chain length of the RTIL increases. Apart from observing the self–organisation by structural analysis of the simulated system, preferential solvation of polar and non-polar molecules in the RTIL clearly demonstrates that the polar and non-polar domains are created in the RTIL [27]. With increasing tail length of the RTIL (see Fig.10), alkyl-alkyl (ct-ct) RDF peak increases as a result of nonpolar domain formation by the alkyl chains of the RTIL. The RDFs (Fig.11) (a)-(d) of the nonpolar pyrene (Py) molecules indicates that Py is solvated by the nonpolar chain of the RTIL and charged solute Methyl Viologen (MV^{2+}) is surrounded by the counterions BF_4^-. Therefore the preferential solvation of the Py and MV^{2+} indirectly

corroborates that there is microdomain formation in the RTIL. These simulation results are in consonance with the experimental results [27].

3.4 Bio-Inspired Research

Many of our activities are directed towards understanding the behaviour of water [28] and aqueous solutions [29-32] containing small biological molecules and their action towards bio macromolecules like proteins. Apart from that, large molecular simulations have been used to understand protein drug interaction and structure of viral capsid, which will help in designing new drugs.

TBA & TMAO Hydration and Action: Despite structural similarity and common amphiphilic nature of the two organic molecules, tert-butyl-alcohol (TBA) and trimethylamine-N-oxide (TMAO), their action toward protein structure and stability and their behaviour in aqueous solutions are strikingly different. In the aqueous solution, TBA forms aggregates at a very moderate concentration, whereas TMAO does not. In spite of a large number of experimental as well as simulation studies, many intriguing issues about the behaviour of these two aqueous solutions are either not properly addressed or not addressed at all. We have used extensive MD simulations and novel analyses to address many such issues and also the nature of their interaction with the protein moiety [29]. The Root-mean-square deviation (RMSD) of the Trp-cage mini protein as shown in Fig.12 clearly demonstrates that the TBA helps in denaturation and TMAO tries to keep the folded configuration intact.

Further, TBA molecules interact and get accumulated around the backbone, whereas TMAO prefers to stay away from the backbone (Fig.13). Further analysis (Fig.14) shows accumulation of TBA around the backbone is through hydrophilic OH group. This study also clarifies many points on the behaviour of the aqueous solution. It explains that the anomalous change in the peak height of the RDF as a function of TBA concentration is not really due to anomalous aggregation as predicted in a previous study [30]. The small pre-peak in the TBA-TBA RDF is demonstrated to be exclusively due to inter TBA H-bond formation. One of the most striking observation in the present study is the presence of heterogeneity even in a very dilute ($X_{TBA}=0.04$) TBA solution. However, TMAO solution is found to be homogeneous [29].
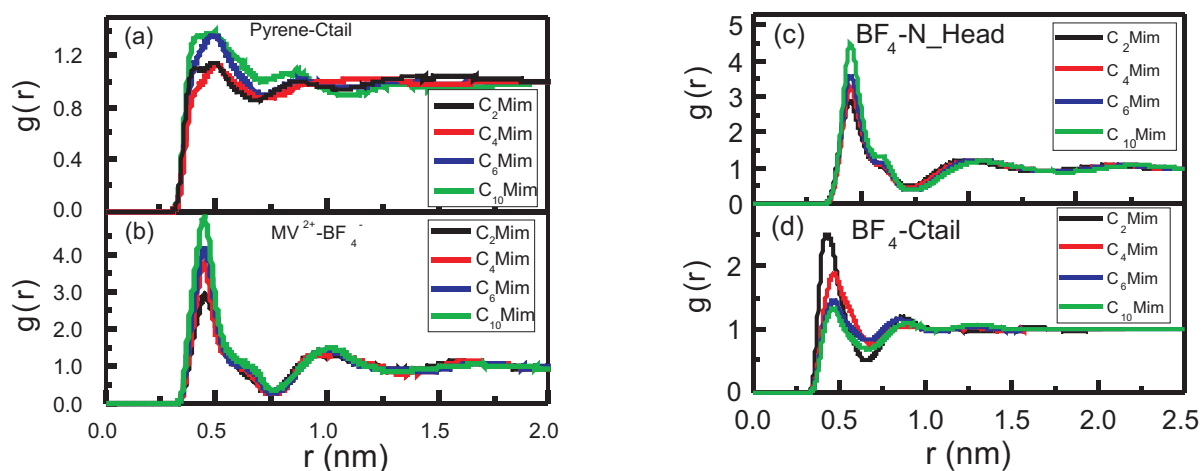

Fig.11: Radial distribution functions of the (a) tail carbon atom of the alkyl chain around the Py molecule and (b) BF_4^- anion around MV^{2+} ion (c)N-atoms of the head group of the cation of the RTIL around the BF_4^- anions (d) tail carbon atom of the alkyl chain of RTIL around the BF_4^--anions.
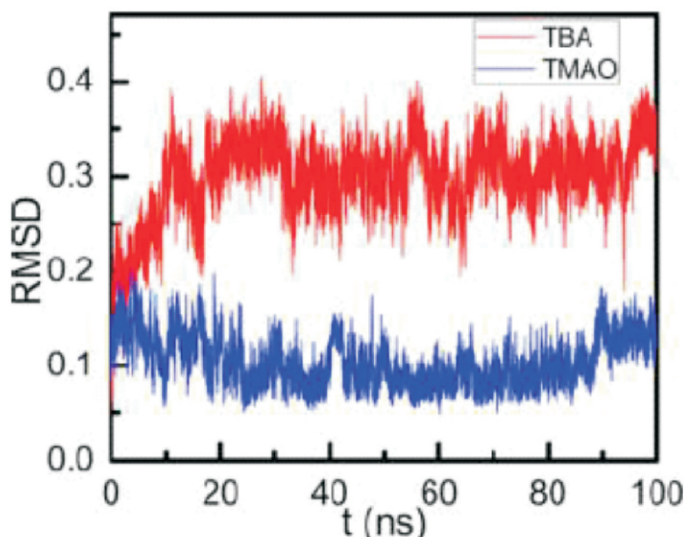
Fig.12: RMSD of the backbone of the Trp-cage miniprotein with respect to initial PDB structure as a function of time in aqueous solutions of TBA (red lines) and TMAO (blue lines).
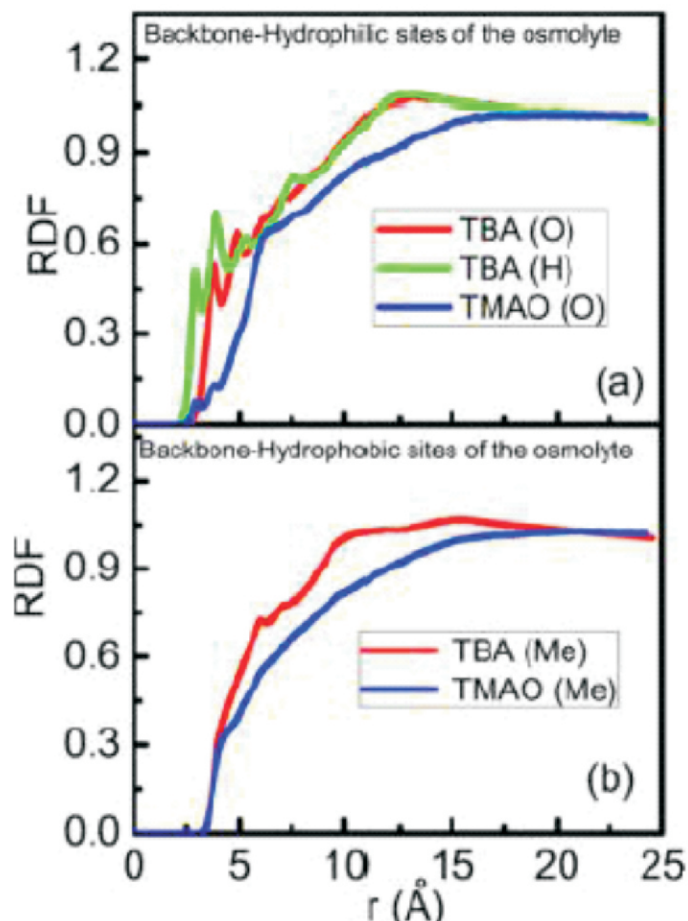
Fig.14: (a) RDF of hydrophilic atoms of TBA and of the TMAO and (b) RDF of the hydrophobic methyl groups of TBA (red line) and TMAO (blue line) around the backbone sites of the Trp-cage miniprotein.
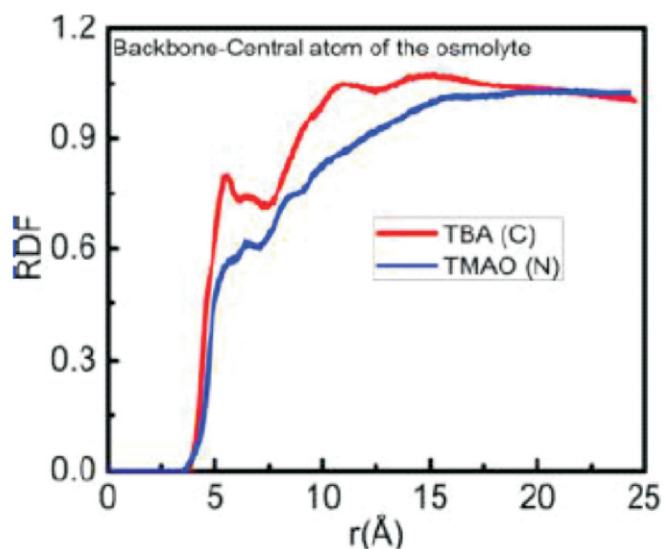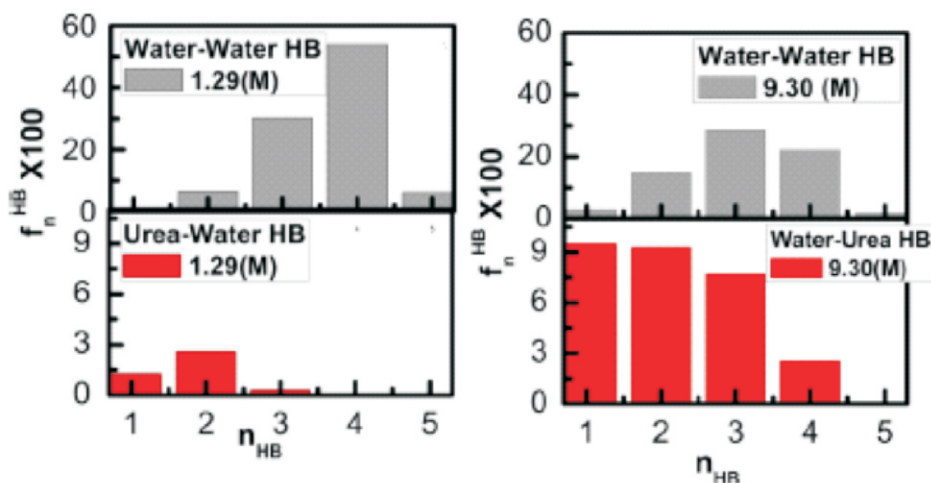

Fig.13: RDF of the central C atoms of TBA (red line) and the central N atoms of TMAO (blue line) around the backbone sites of the Trp-cage miniprotein.

Is Urea Chaotropic?

In another study, using MD simulations we have resolved [31] a long standing questing question: Is urea chaotropic? Through careful analysis, we are able to show that if we account for the fact that urea can also be a neighbour in a concentrated solution of urea, the urea really does not break the water structure, it just replaces one or more water neighbours of a central water molecule. It is shown that in a dilute urea solution (see left panel of Fig.15), most of the water molecules are four hydrogen bonded, but in a concentrated solution (see right panel), most of them are three H-bonded. On the other hand, population of water-urea H-bonds is increased at higher concentrations (see the right panel).

Guanidinium ion and Protein Denaturation: Like TBA, TMAO and urea, guanidinium chloride (GdmCl) is also a biologically important molecule and acts as a protein denaturant. There are reports that Gdm moieties forms aggregate in solution. Using MD simulation, we have investigated [32] the intricacies of aggregate formation and its mode of action on protein to get idea about the mechanism of denaturation. The Parallel stacking of the two Gdm⁺ moieties in
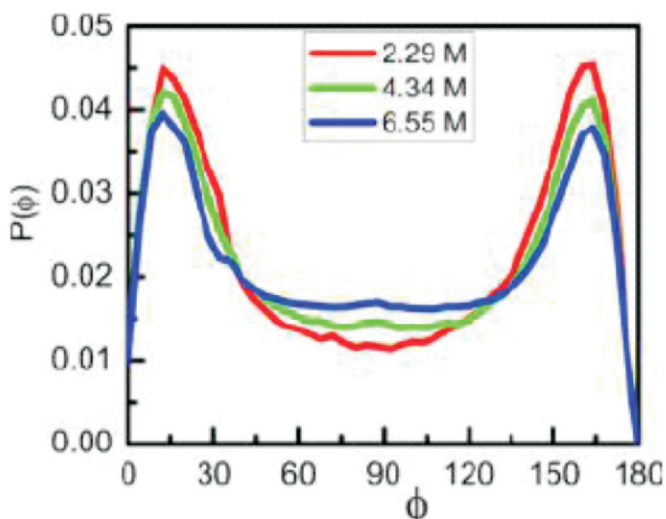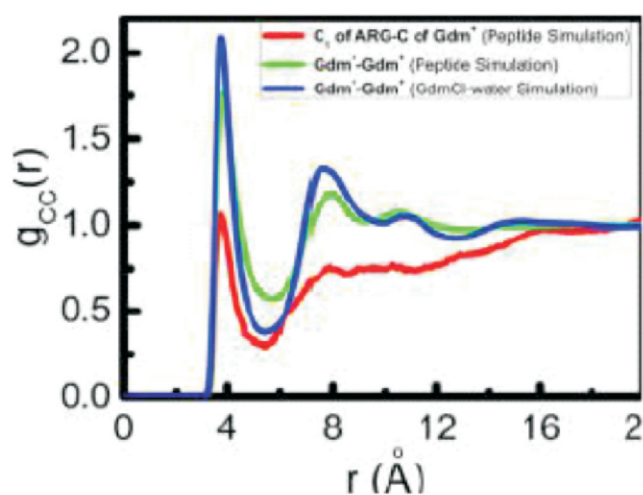

Fig.15: Distribution of water-water (upper panel in each figure) and water-urea (lower panel in each figure) hydrogen bonds at different urea concentrations.
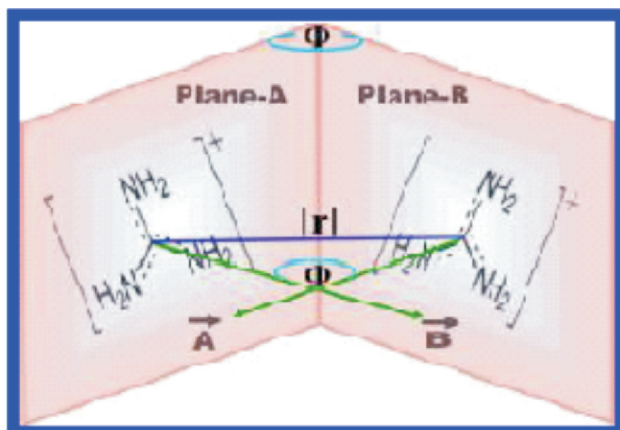
Fig.16: Schematic representation of two molecular planes of guanidinium ions inclined at an angle Φ.

Fig.17: Distributions P(Φ) of the angles Φ between two guanidinium molecular planes.

Fig.18: RDF of the Gdm$^+$ moiety around ARG side chain of the protein, Gdm$^+$ around Gdm$^+$ in the protein- GdmCl- water, and GdmCl- water without protein) systems.
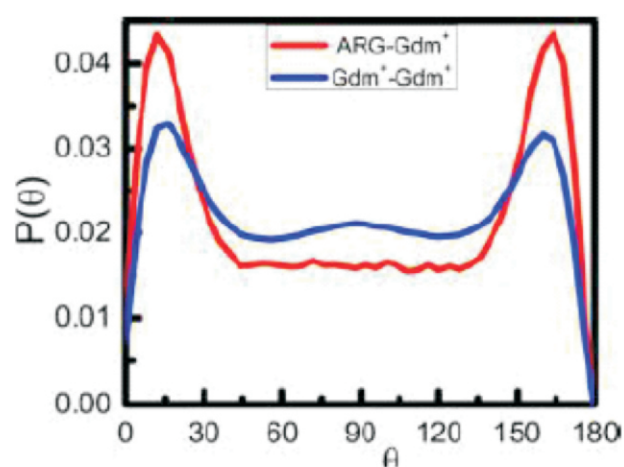
Fig.19: Distributions P(θ) of the angles between Gdm$^+$ moiety and the molecular plane of the ARG side chain of the protein.

concentrated GdmCl binary solution (Figs.16&17) has been observed. The larger peak height of the ARG-Gdm RDF (Fig.18) as compared to other carbon atoms of the protein indicates accumulation of Gdm$^+$ ions around the arginine side chain. Further analysis showed (Fig.19) that the Gdm moiety stacks around structurally similar ARG side chain of the protein [32]. Therefore, parallel staking of the Gdm$^+$ and ARG moieties is the mode by which Gdm$^+$ attacks the protein backbone.

Protein-Drug Interaction: In an effort to understand how a drug molecule accomplish its task interacting with protein molecules, several large-scale computations were performed and compared the efficacy of existing oxime drug molecules towards recovery of free nerve enzyme, acetylcholinesterase from the organophosporous (chemical warfare) intoxications. Present group is instrumental in developing fluorinated drugs for the reactivation of inactivated acetylcholinesterase in both periphery and central nervous system [33]. The effect of heavy water on thermo-stabilization of liquid pharmaceuticals and the inclusion of kinetic isotope effect (Fig.20) are accomplished by carrying out replica exchange MD simulations [34]. Viruses are the simplest

biological systems, essentially composed of a protein shell or capsid that encloses the genetic material. Structural changes in a capsid due to thermal fluctuations play a major role in the deliverance sequel of the confined material and therefore its characterization is essential for providing fresh insights into antiviral/nanomaterial strategies. We have therefore, calculated the heat induced changes in the properties of an empty minute virus of mice particle using large-scale (3.0 million atoms) MD simulations in a year time. The findings have implications in the development of therapeutic inhibitors of viral shells.

Development of Theoretical Methodologies and Computer Codes: Low-Energy Free-Electron Induced Chemistry is a new paradigm in chemical reaction. Negative ion resonance states play a crucial role [35] in low-energy free-electron-induced biomolecular modifications and in the free-electron controlled molecular reactions [36]. The electronic structure and the reaction mechanism of negative ion resonance states are only poorly understood. In fact, one of the most important challenges to current electronic structure theory is the computation of negative ion resonance states. As a major step towards this direction, we have
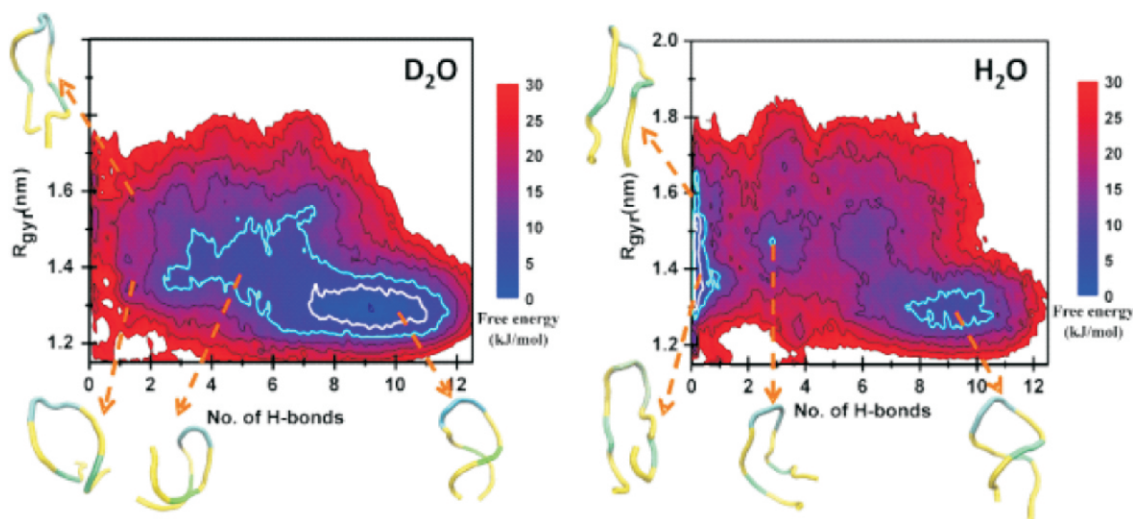
Fig.20: Free-energy surface of polio viral RNA hairpin at 300 K in D_2O and in H_2O.

developed and implemented new state-of-the-art ab initio quantum chemical methods which offer the most accurate computation of negative ion resonances. We have demonstrated [35-36] that the chemical reactions can be initiated, controlled and catalyzed through negative ion resonance states.

Implementations of New Features in DIRAC Code: We describe the theoretical studies [37-38] of symmetry violating properties which are relevant for the search of electron electric dipole moment (EDM) and to probe physics beyond the standard model (SM) of particle physics. In explaining matter-antimatter asymmetry of the universe, there must be CP violation (where C and P mean charge conjugation and parity invariance, respectively). The main emphasis of our research lies in searching for CP violation in atomic and molecular systems. Observation of permanent EDM and magnetic quadrupole moment (MQM) [37] of a system is a signature of simultaneous violation of CP according to the CPT theorem. We are involved in developing highly accurate wave function based relativistic methods for computing the accurate value of CP-odd molecular parameters. In this context, the group has developed many new codes/modules which are integrated with the DIRAC program package and interfaced DIRAC code [39] with many in-house developed advanced computer codes.

Concluding Remarks

In this article, a brief account of varieties of topics requiring quantum to mesoscopic frameworks as carried out in this group has been presented. It shows the usefulness and applicability of modern theoretical and computational chemical physics in solving complex chemical problems. With the advent of newer formalisms and methods, theoretical and computational chemistry will become an indispensible tool for every research group in the world. Amalgamation of state of the art computing technique like machine learning with the existing theoretical and computational tools will bring new era in this field. An application of such machine learning technique in hydrogen storage problem is in progress in our group [40].

Acknowledgements

Corresponding Author*

Niharendu Choudhury (nihcho@barc.gov.in)

References

[1]   J.C. Schön, M. Jansen, *Angew. Chem. Int. Ed.*, 1996, **35**, 1286.

[2]   M. Praprotnik, L. Delle Site, K. Kremer, *Annu. Rev. Phys. Chem.*,2008, **59**, 545-571; Peter, C.;Kremer, K.,*Soft Matter*, 2009, **5**, 4357-4366. DOI: 10.1039/b912027k.

[3]   S. Ahlawat, K. Srinivasu, A. Biswas, N. Choudhury, *Comput. Mater.Sci.*, 2019, **170**, 109167.

[4]   S. Ahlawat, K. Srinivasu, A. Biswas, N. Choudhury, *Phys. Chem. Chem. Phys.*, 2021, **23**, 8689-8704.

[5]   B. Sadhu, M. Sundararajan, T. Bandyopadhyay, *Inorg. Chem.*, 2016, **55**, 598.

[6]   X. Ye, S. Cui, V. de Almeida, B. Khomami, *J. Phys. Chem. B ,* 2009, **113**, 9852-9862.

[7]   G.R. Choppin, M.K. Khankhasayev, Chemical Separation Technologies and Related Methods of Nuclear Waste Management: Applications, Problems, and Research Needs, First Edition. Vol. **320**, Springer, New York, 1999.

[8]   M. Chopra, N. Choudhury, *J. Phys. Chem. B,* 2014, **118**, 14373-14381.

[9]   M. Chopra, N. Choudhury, *Phys. Chem. Chem. Phys.*, 2015, **17**, 27840-27850.

[10]   M. Chopra, N. Choudhury, *J. Mol. Liq.*, 2016, **224**, 599-606.

[11]   M. Chopra, N. Choudhury, *Chem. Phys.*, 2017, **495**, 48-58.

[12]   M. Chopra, N. Choudhury, *J. Phys. Chem. C,* 2013, **117**, 18398-18405.

[13]   M. Chopra, N. Choudhury, *J. Mol. Liq.*, 2019, **294**, 111569.

[14]   T. Vazhappilly, T.K. Ghanty, B.N. Jagatap, *J. Phys. Chem. C,* 2016, **120**, 10968.

[15]   S. Kancharlapalli, S. Natarajan, T.K. Ghanty, *J. Phys. Chem. C,* 2019, 123, 27531-27541.

[16]   Vazhappilly, T.; Pathak, A. K., *J. Nucl. Mat.*, 2019, **519**, 128.

[17]   Vazhappilly, T.; Pathak, A. K., *Comput. Mater.Sci.*, 2020, **185**, 109933.

[18]   K. Srinivasu, B. Modak, T.K. Ghanty, *J. Nucl. Mater.*, 2018, **510**, 360-365.

[19]   B. Modak, K. Ghoshal, K. Srinivasu, T.K. Ghanty, *J. Phys. Chem. Solids* 2020, **136**, 109179.

[20]   K. Srinivasu, S.K Ghosh, *J. Mater. Chem. A,* 2015, **3**, 23011-23016.

[21]   B. Modak, P. Modak, S.K. Ghosh, *Phys. Chem. Chem. Phys.*, 2018, **20**, 20078.

[22]   K. Srinivasu, S.K. Ghosh, *J. Phys. Chem. C,* 2012, **116**, 25184-25189.

[23]   P. Banrjee, R. Thapa, A. Rajkamal, K.R.S. Chandrakumar, G.P. Das, *Int. J. Hydrogen. Ene.*, 2019, **44**, 23196-23209.

[24]   P. Banerjee, K.R.S. Chandrakumar, G.P. Das, *Chem. Phys.*, 2016, **469-470**, 123-131.

[25]   S. Pantawane, D. Bandyopadhyay, N. Choudhury, *ACS Omega,* 2018, **3**, 1060- 1068.

[26]   S. Pant, T. Gera, N. Choudhury, *J. Chem. Phys.* 2013, **139**, 244505.

[27]   B. Manna, D. Bandyopadhyay, N. Choudhury, D.K. Palit, *J. Photochem. and Photobio. A: Chemistry,* 2018, **356**, 81-91.

[28]   D. Bandyopadhyay, S. Mohan, S.K. Ghosh, N. Choudhury, *J. Phys. Chem. B,* 2013, **117**, 8831.

[29]   D. Bandyopadhyay, Y. Kamble, N. Choudhury, *J. Phys. Chem. B,* 2018, **122**, 8220-8232.

[30]   S. Banerjee, J. Furtado, B. Bagchi, *J. Chem. Phys.*, 2014, **140**, 194502.

[31]   D. Bandyopadhyay, S. Mohan, S.K. Ghosh, N. Choudhury, *J. Phys. Chem. B,* 2014, **118**, 11757.

[32]   D. Bandyopadhyay, K. Bhanja, S. Mohan, S.K. Ghosh, N. Choudhury, *J. Phys. Chem. B,* 2015, **119**, 11262-11274.

[33]   A.K. Pathak, T. Bandyopadhyay, *J. Phys. Chem. B,* 2018, **122**, 3876-3888.

[34]   A. K. Pathak, T. Bandyopadhyay, *J. Chem. Phys.*, 2017, **146**, 165104.

[35]   D. Davis, Y. Sajeev. *Chem. Comm.*, 2020, **56**, 14625-14628.

[36.] Y. Sajeev, *Mol. Phys.*, 2019, **117**, 2162-2166.

[37]   T. Fleig, M.K. Nayak, M.G. Kozlov, *Phys. Rev. A,* 2016, **93**, 012505.

[38]   S. Sasmal, H. Pathak, M.K. Nayak, N. Vaval, S. Pal, *Phys. Rev. A,* 2016, **93**, 062506.

[39]   DIRAC, a relativistic ab initio electronic structure program, DIRAC19 (2019), written by A.S.P. Gomes *et al.* (available at http://dx.doi.org/10.5281/zenodo.3572669, see also http://www.diracprogram.org).

[40]   K. Srinivasu, A. Gopalan, M. Haranczyk, R.Q. Snurr, *J. Chem. Theory Comput.*, 2021, **17**, 3052-3064.