

Computational Modelling

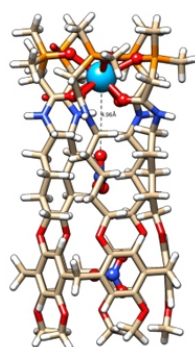
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Multiscale Modelling and Simulations for Nuclear Fuels, Waste Management, and Radiation Damages

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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: Multiscale 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, $^{99\text{m}}\text{Tc}$ 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 $18.19 \times 10^{-6} \text{ K}^{-1}$ which is consistent with the previously reported values (15.2×10^{-6} to 17.3×10^{-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

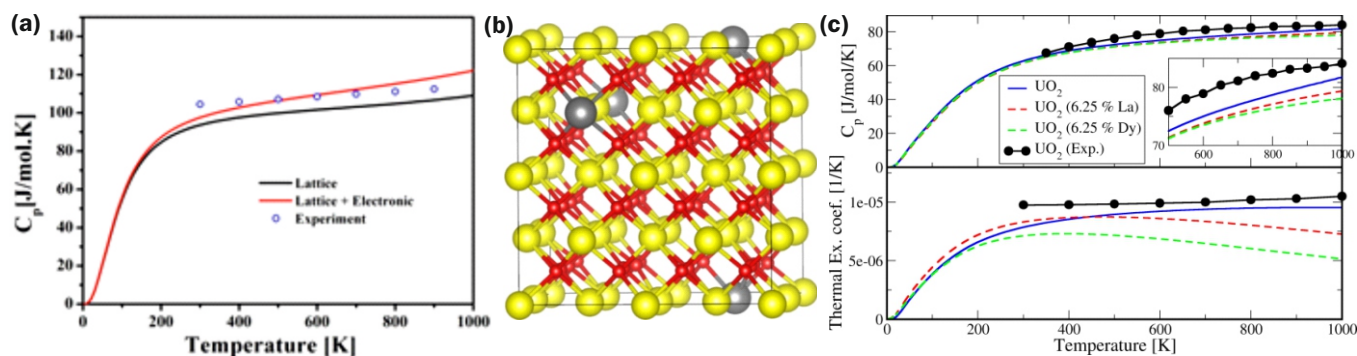


Fig.1: (a) Molar specific heat of UO_2 with and without the electronic contributions along with experimental results. (b) Optimized crystal structures of UO_2 with 6.25% Dy doping. U, Dy and O atoms are represented by the yellow, grey, and red coloured spheres, respectively. (c) The specific heat at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

pressure (C_p) 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 (C_p) is calculated for $U_2Ln_2O_8$ which show deviation at higher temperature from C_p 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 C_p 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

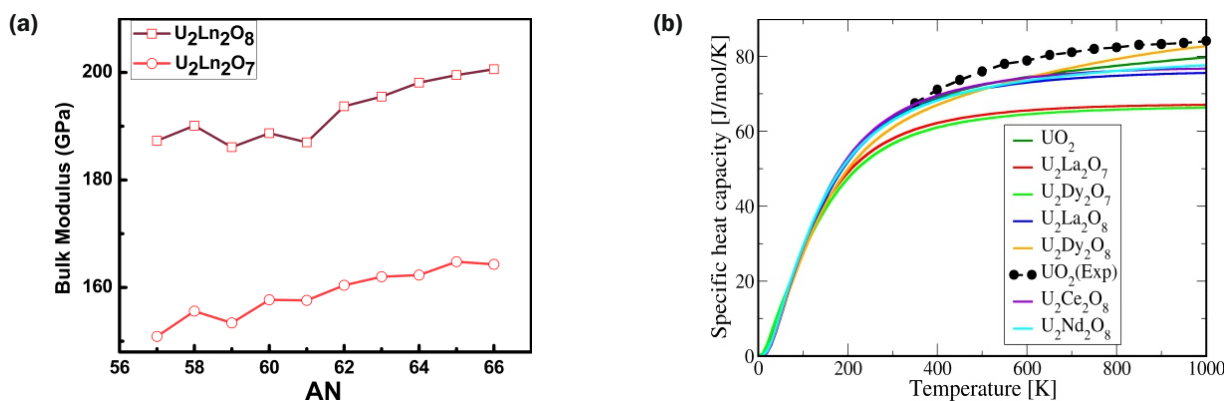


Fig.2: (a) The bulk modulus for different $U_2Ln_2O_8$ and $U_2Ln_2O_7$ structures are plotted with respect to the atomic number of lanthanides. (b) The specific heat C_p of pure UO_2 and Ln substituted UO_2 without oxygen vacancies ($U_2Ce_2O_8$, $U_2La_2O_8$, $U_2Nd_2O_8$, $U_2Dy_2O_8$) and with oxygen vacancies ($U_2La_2O_7$, $U_2Dy_2O_7$) are plotted.

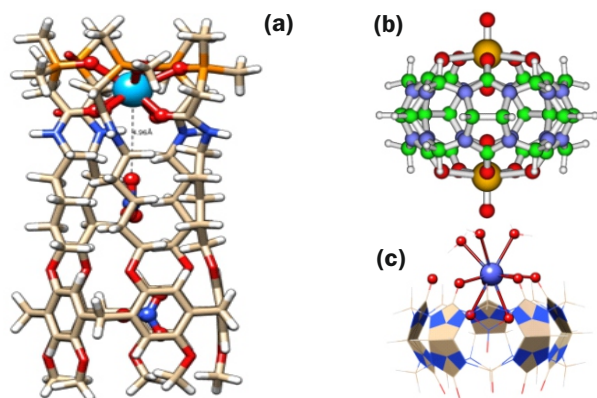


Fig.3: Optimized structures of (a) Th(IV) binding to functionalized PA[5], (b) uranyl and (c) Am(III) binding to CB-[5].

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 [UO₂]²⁺, [NpO₂]²⁺ and [PuO₂]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 PuO₂ 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 [PuO₂(H₂O)₆]²⁺ formed with water is shown in Fig.4 (a). The overall structure including PuO₂ is pentagonal bi-pyramidal. When betaine is added, the most stable structure formed is [PuO₂(Bet)₄(H₂O)]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

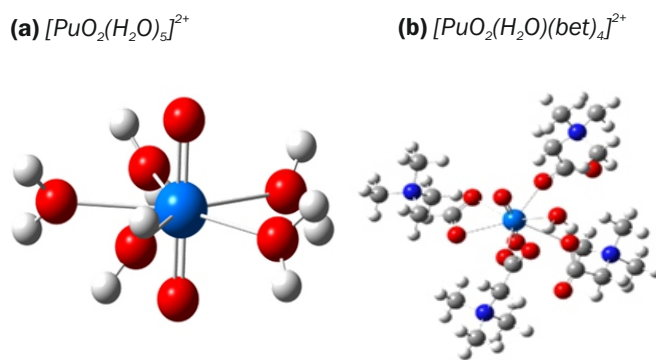


Fig.4: Optimized structures of PuO₂²⁺ with (a) water and (b) with betaine and water.

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, La₂Hf₂O₇ [32], Lu₂Hf₂O₇ [33], Y₂Zr₂O₇ materials show impressive features related to the

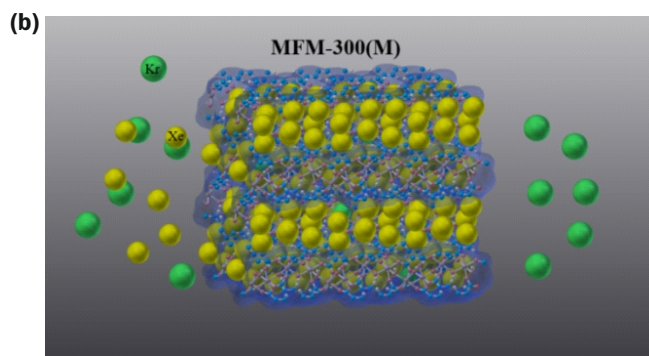
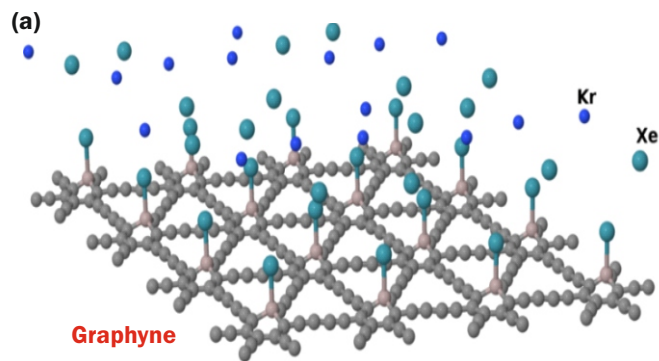


Fig.5: Schematic representation of Xe/Kr separation by (a) graphyne and (b) MFM-300(M) MOFs.

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 $^{241}\text{Am}^{3+}$ 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.

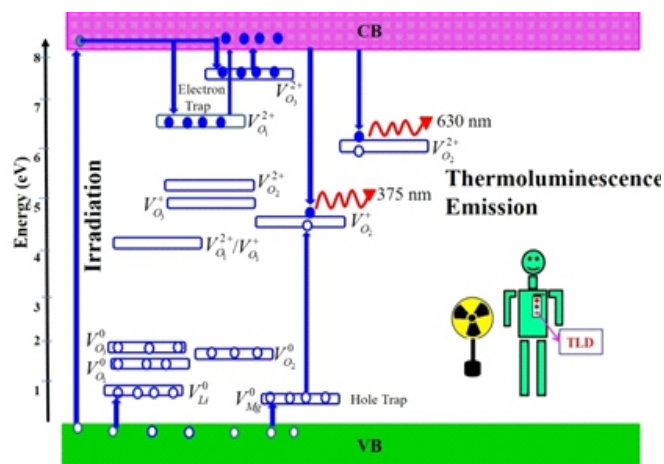


Fig.6: Electronic transitions due to different defect states.

Radiation Damages in Nuclear Structural Materials

Neutron irradiation of steel creates a large number of 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

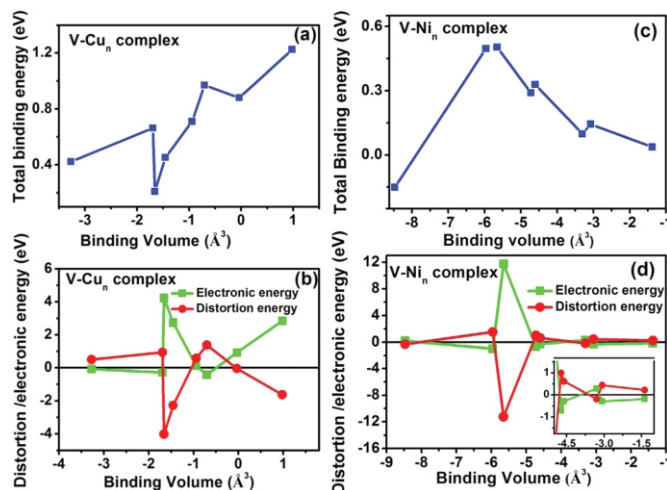


Fig.7: Total binding energy and constituent distortion and electronic energy as a function of binding volume for V-Cu_n complexes (where V stands for vacancy). The figure is reproduced from Ref. 40.

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.

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