



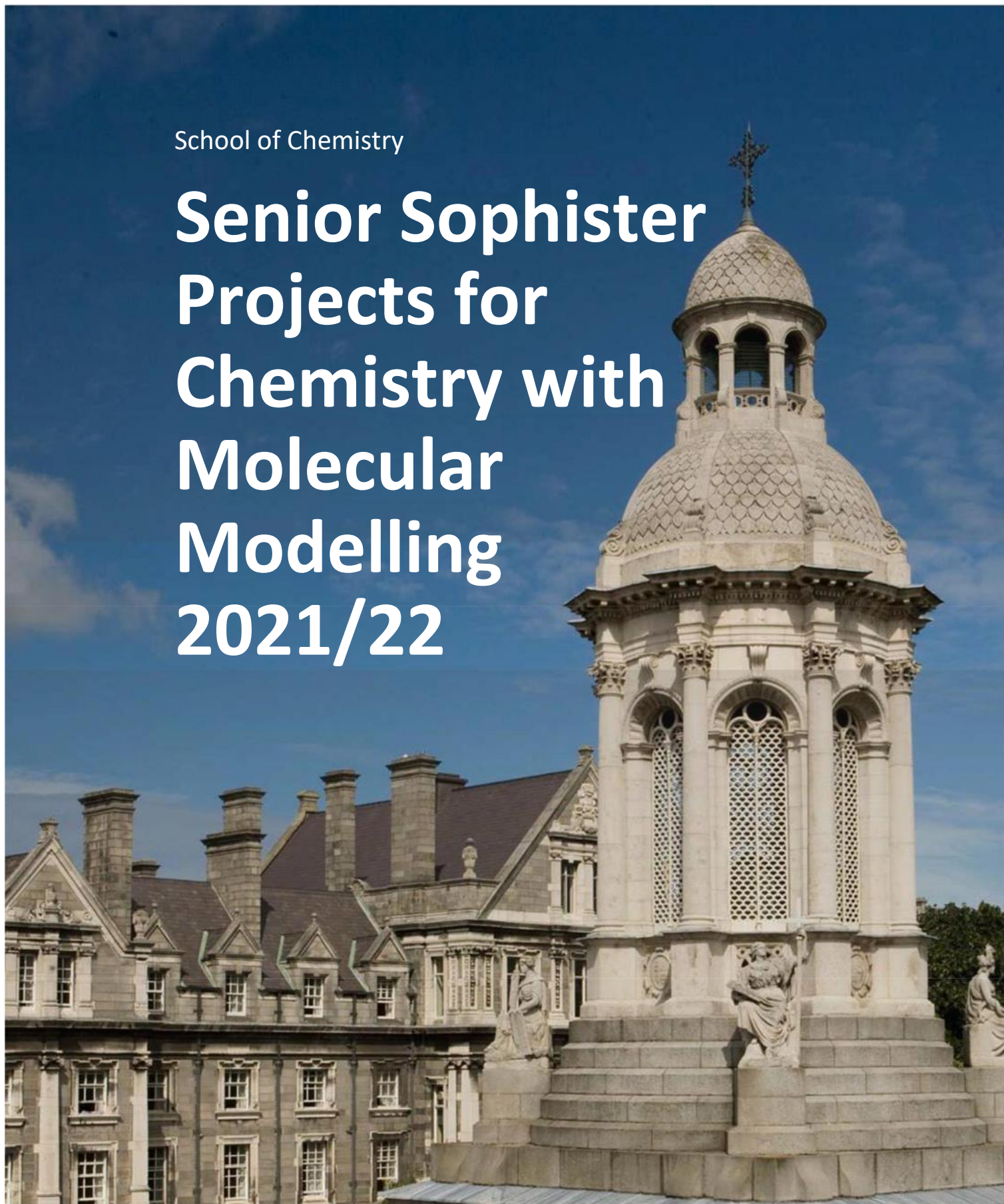
Trinity College Dublin

Coláiste na Tríonóide, Baile Átha Cliath

The University of Dublin

School of Chemistry

Senior Sophister Projects for Chemistry with Molecular Modelling 2021/22



School of Chemistry Senior Sophister Research Project 2021

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**Organic, Medicinal and Biological
Chemistry**

School of Chemistry Senior Sophister Research Project 2021

Theoretical Study of Phase-Transfer Catalysts for Asymmetric Conjugate Additions of Cyanide

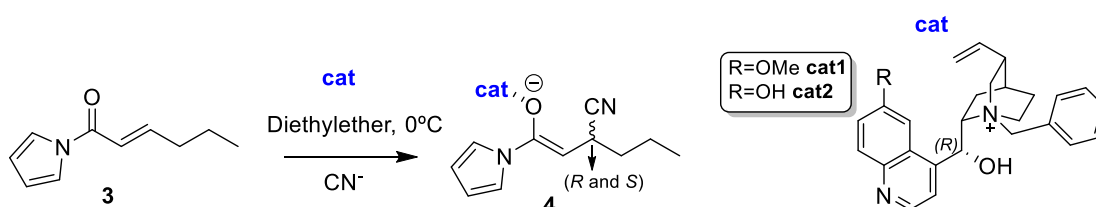
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Research Project Description:

A wide variety of asymmetric transformations catalysed by chiral catalysts were developed for the synthesis of valuable organic compounds in the past several decades. Within asymmetric catalysis field, phase-transfer catalysis was recognized as a powerful method for establishing useful procedures for organic synthesis.

While the field of asymmetric organocatalysis is currently growing exponentially, an understanding of the mechanistic details involved in most of these reactions has often lagged far behind the pace of catalyst development, which in return retards rational catalyst design. Therefore, continuous efforts should be made toward the design and development of new catalysts classes, as well as understanding existing relationships between the structure of the catalyst and its ability to transfer stereochemical information.

Catalytic asymmetric cyanation of prochiral unsaturated compounds were extensively studied in recent years as their reaction products are considered highly desirable building blocks for pharmaceutical compounds. Here in, the mechanistic picture of the enantioselective conjugate cyanation of unsaturated ketone catalysed by a *Cinchona* alkaloid quaternary salt will be studied. An improved PTC derivative to the existing system is proposed in order to increase the enantioselectivity of a model reaction and therefore a theoretical study of the free-energy profile will be performed.



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Study of Tuneable Bioactive Anion Transporters

Dr. Cristina Trujillo (CT2)

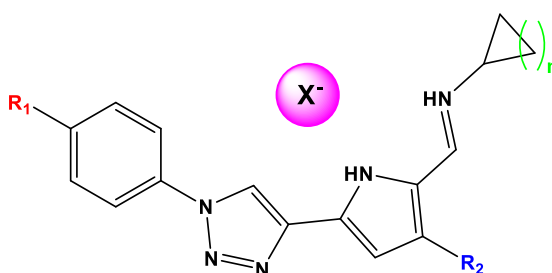
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Research Project Description:

The development of supramolecular anionophores for transmembrane ion transport is driven by their potential utility as tools for studying ion transport processes and as therapeutics for diseases arising from mis-regulation of protein ion channels.

Significant effort has been devoted to designing mobile carrier systems with high anion transport activity in vesicles (particularly for chloride), and more recently, in cells. Transmembrane ion transport by synthetic anionophores is typically achieved using polar hydrogen bonding anion receptors. As with naturally occurring ion transporters, anion selectivity is crucial, and depends on the delicate balance between transporter anion binding selectivity and anion desolvation.

A theoretical study of the different non-covalent interactions established between anions and bioactive anion transporter molecules is proposed. An analysis of the anion-anionophore encounter and characterisation of the different interactions established are crucial to induce variations within the anion-transporter molecule to increase the affinity and therefore improve the anion transporter process.



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Physical, Computational and Materials
Chemistry

School of Chemistry Senior Sophister Research Project 2021

High-Throughput Modelling of Surface Coverages and Electronic Structure of 2D-Materials for (Electro)Catalysis

Prof. Max García-Melchor (MGM2)

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Research Project Description

Two-dimensional carbides or MXenes¹ are known to be readily functionalized with a variety of adsorbates such as O, OH, F, and H. These functional groups have been proven to confer a superior thermodynamic stability, which can be attributed to the similar electronic structure that functionalized MXenes adopt compared to their bulk counterparts. Functionalized MXenes are typically obtained by etching of a MAX phase (Figure 1A) with the general formula $M_{n+1}AX_n$, where n ranges from 1 to 4, M denotes an early transition metal (e.g. Ti, Zr, Hf, V, Mo), A stands for an element from groups 13–16 (e.g. Al, Ga, In, Tl, Si, Ge, Te), and X for carbon or nitrogen. Because of their high tunability and electronic properties, MXenes have been employed in a myriad of applications such as supercapacitors,² wireless communications,³ as well as in a number of electrochemical reactions, including the oxygen evolution reaction,⁴ and hydrogen evolution reaction.⁵ These applications are often governed by the surface termination of MXenes, which depends on the reaction conditions.

This project aims to leverage state-of-the-art computational methods to conduct a high-throughput investigation of the surface coverages and electronic structure of experimentally reported MXenes (Figure 1). These new theoretical insights are expected to identify promising MXenes as (electro)catalysts for relevant industrial applications. By the end of this project students should demonstrate a deep knowledge of surface catalysis, electronic structure of 2D materials, and density functional theory methods.

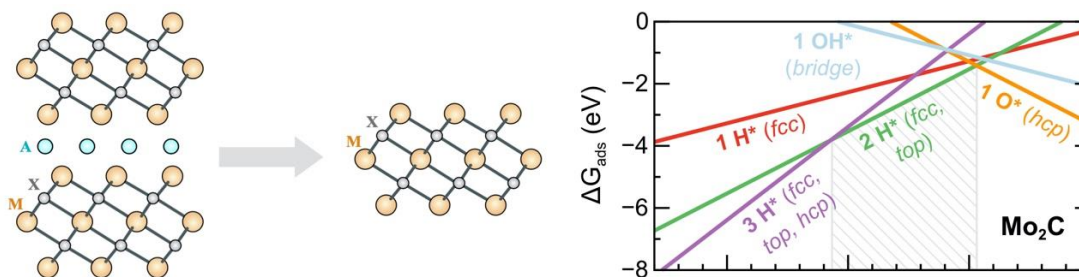


Figure 1. Side view representation of a M_3AX_2 phase along with its resulting MXene, M_3AX_2 (left). Predicted surface coverages for Mo_2C at different applied potentials (right).

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School of Chemistry Senior Sophister Research Project 2021

Bonding and Repulsion in Hydrogen Donor-Acceptor Pattern Recognition

Prof. Dónall A. Mac Dónaill (DMacD1)

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Research Project Description:

The accepted role of hydrogen-bonding in nucleotide recognition has been questioned by Kool at al. [1] who have suggested that complementary shapes, mimicking nucleotides, may alone be sufficient for discrimination (Fig. 1). Seddon and Evans however have questioned this view [2]. It is not necessarily a binary choice; the role of hydrogen donor-acceptor patterns in nucleotide recognition may be regarded as twofold, serving to bind associating complementary pairs, while simultaneously opposing non-complementary associations [3].

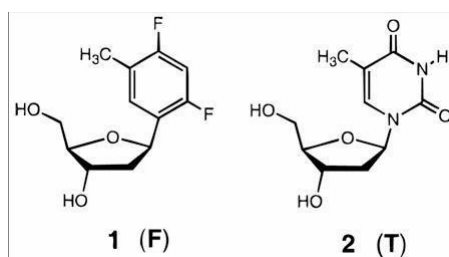


Figure 1. Difluorotoluene (F), a Nonpolar Isotere for Thymine (T) [2].

The evolutionary theoretician Eörs Szathmáry has developed a model for assessing the biological fitness of alternative alphabets with a view to explaining the particular genetic alphabet employed by nature [4]. While the results were interesting, the interactions energies he employed were very approximate. In this project Szathmáry's model will be revisited, adapted where necessary, and using improved estimates of interaction energies. The project will involve Quantum Chemical calculations and a small amount of programming (though Excel may suffice).

The objective of the project will be to gain further quantitative insight into the relative importance of the repulsive and attractive components in nucleotide recognition, and thereby better understand the factors underlying the particular composition of the genetic alphabet (A, T, C and G) and as well as possible alternatives. The project should inform us on the robustness of Szathmáry's model and his conclusions.

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School of Chemistry Senior Sophister Research Project 2021

Tautomeric Instability and the Composition of the Nucleotide Alphabet

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Research Project Description:

Piccirilli *et al* [1] have demonstrated the chemical feasibility of incorporating novel base pairs into the genetic alphabet (Fig 1). The question therefore arises as to why nucleic acid sequences are assembled from the four bases G, C, A and U as opposed to an alternative or larger alphabet.

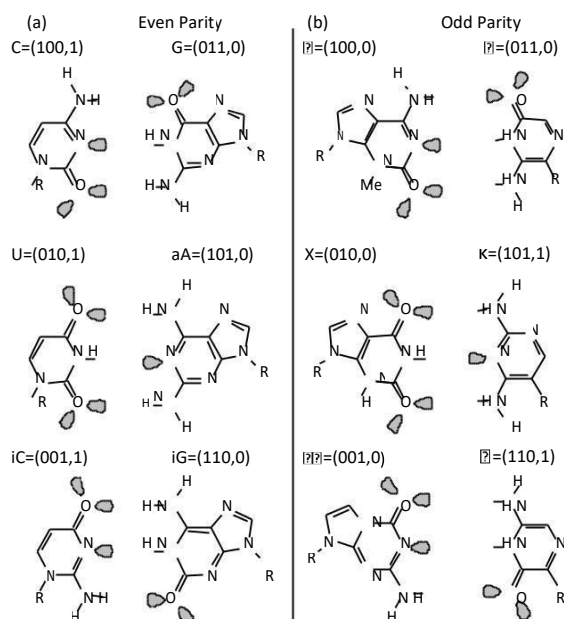


Figure 1. Potentially viable nucleotides divided by parity (a) the even-parity subset and (b) the odd-parity subset.

Some potential members of the genetic alphabet are rendered non-viable by reason of tautomeric instability. For example, the donor/acceptor pattern in iG is unstable, in contrast to that of G. The project will employ a variety of *ab initio* and semi-empirical quantum-chemical approaches to explore the underlying basis of the instability and will attempt to identify stable alternatives to A, T, C and G.

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<http://dx.doi.org/10.1038/343033a0>

School of Chemistry Senior Sophister Research Project 2021

Doping Cu₂O – towards low cost photovoltaic cells.

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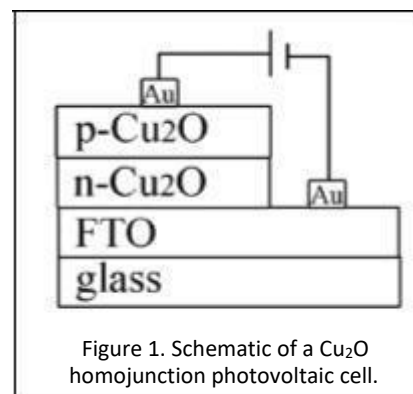
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Research Project Description:

The sun offers an immense amount of free and clean power, which we have not yet begun to seriously exploit. Metal oxides are ideal candidates owing to their combination of low cost and high stability in aqueous solutions. Unfortunately the optical band-gaps of many metal oxides generally lie outside the visible range (> 3 eV) making them bad for solar applications. Despite immense effort, attempts to reduce the band-gaps of active oxides such as TiO₂ through dyes, doping or co-doping have not succeeded in providing a viable material.

Cu₂O was the first material for which a patent was granted for a photovoltaic material but despite its historical importance, Cu₂O never gained great interest. With a band gap of 2.1 eV the maximum efficiency predicted from the Shockley-Queisser limit [1] is around 20% with the current interest stemming from its natural p-type conducting properties [2] and potential for very low cost photovoltaic devices [3]. To generate the most efficient device, a homojunction cell [figure 1] in which both n-type and p-type Cu₂O are present would need to be fabricated, [3] although currently no viable way of creating (through doping) n-type Cu₂O has been found [4].

In this project we will use density functional theory to examine the defect chemistry of Cu₂O to determine (i) if improved p-type properties can be generated (e.g. by N doping) and (ii) if simple doping can generate n-type Cu₂O (e.g. by Cl doping). In addition we will look at the native defects (Cu and O vacancies, Cu and O interstitials) to determine if these defects can form in opposition to the doped defects.



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The impact of grain boundaries on the ionic conductivity of doped CeO₂

Prof. Graeme Watson (GWW2)

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Research Project Description:

The grain boundaries within multi-crystalline materials give rise to structural discontinuities which result in specific GB structures, potential non-stoichiometry and the segregation of point defects, all of which can significantly alter the macroscopic properties [1]. As a consequence, grain boundaries and interfaces can control the properties of materials and hence they are vital to understanding and optimising their performance. Despite this, there is little understanding of the structure and even less on the effects of these interfaces on materials properties due to the inherent complexity of the issues and limited experimental techniques.

We have recently developed a method of predicting the structure of tilt grain boundaries using sophisticated polarizable forcefields and applied this to CeO₂ [2] and demonstrated the segregation of oxide ion vacancies to the interface resulting in enhance 2D diffusion (figure 1). This project seeks to determine the impact of dopant segregation to the boundary on the ionic conductivity. Such data is important in understanding the impact of material processing in multi-crystalline materials for the electrolyte of solid oxide fuel cells.

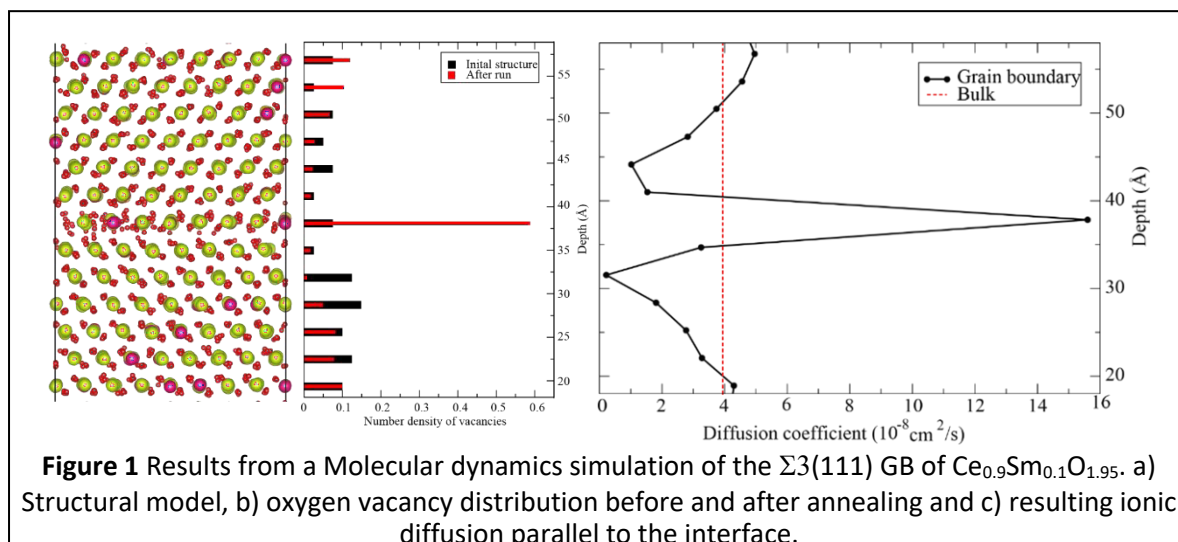


Figure 1 Results from a Molecular dynamics simulation of the $\Sigma 3(111)$ GB of Ce_{0.9}Sm_{0.1}O_{1.95}. a) Structural model, b) oxygen vacancy distribution before and after annealing and c) resulting ionic diffusion parallel to the interface.

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