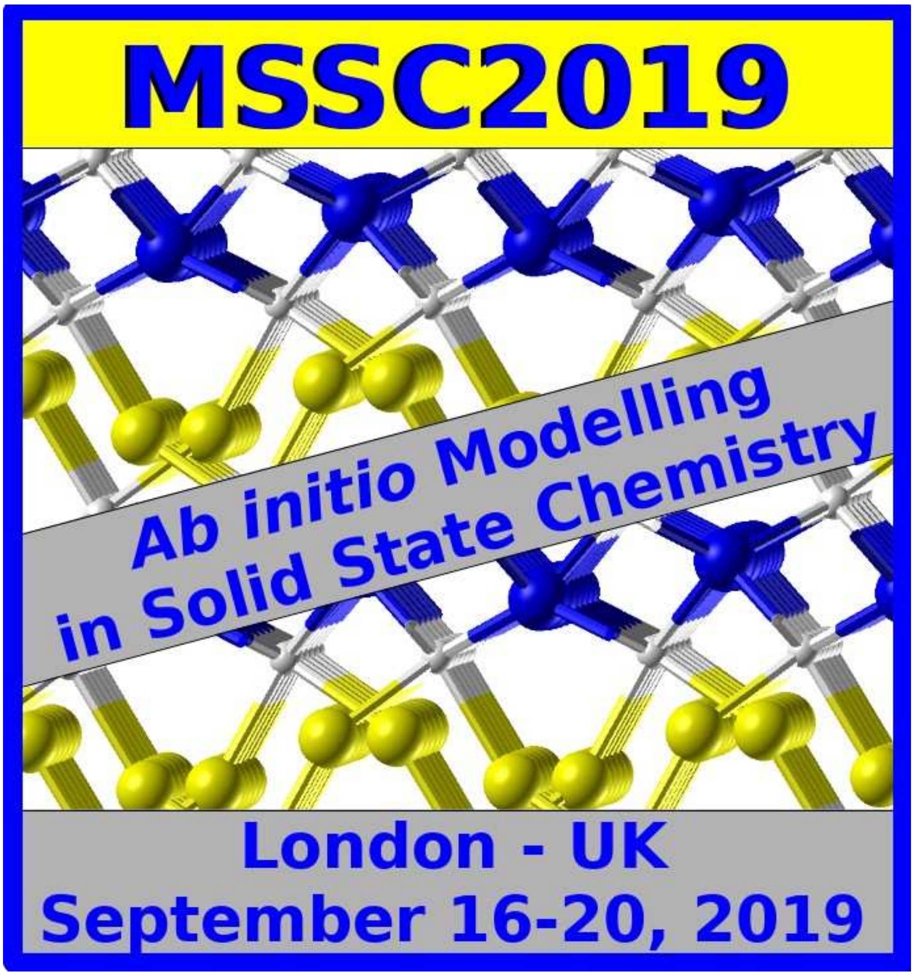
WORKSHOP REPORT



http://www.imperial.ac.uk/mssc2019/

Abstract

The Department of Chemistry and the Thomas Young Centre at Imperial College London and the Theoretical Chemistry Group of the University of Torino, in collaboration with the Computational Materials Science Group of the Science and Technology Facilities Council (STFC), organized the 2019 MSSC Summer School on the "ab initio modelling of crystalline and defective solids with the CRYSTAL code".

CRYSTAL is a general-purpose program for the study of periodic solids. It uses a local basis set comprised of Gaussian type functions and can be used to perform calculations at the Hartree-Fock, density functional or global and range-separated hybrid functionals (e.g. B3LYP, HSE06), double hybrid levels of theory. Analytical first derivatives with respect to the nuclear coordinates and cell parameters and analytical derivatives, up to fourth order, with respect to an applied electric field (CPHF/CPKS) are available.
The structure, thermodynamics, vibrational states and a wide range of properties can be computed for crystals, surfaces, polymers and molecules. In addition to its long standing use in solid state chemistry and condensed matter physics CRYSTAL is also used by a rapidly growing community of non-specialized users (material scientists, crystallographers, geologists, ...).

The school provided an overview of the underlying theory and fundamental issues affecting use of the code, with particular emphasis on practical issues in obtaining reliable data efficiently using modern computer hardware.

The capabilities of CRYSTAL was illustrated with hands-on tutorials organized in the afternoon sessions.

All information about the school can be found on this website:
http://www.imperial.ac.uk/mssc2019/

Attendees

Speakers

- Ehsan Ahmad - Imperial College London (UK)
- Maria L. Alfredsson - University of Kent (UK)
- Leonardo Bernasconi - Center for Research, Computing University of Pittsburgh (USA)
- Gerit Brandenburg - Heidelberg University (Germany)
- Ian J. Bush - Oxford e-Research Centre, University of Oxford (UK)
- Silvia Casassa - Università di Torino (Italy)
- Bartolomeo Civalleri - Università di Torino (Italy)
- Furio Corà - University College London (UK)
- Atreyi Dasmahapatra - Università di Torino (Italy)
- Klaus Doll - University of Stuttgart (Germany)
- Alessandro Erba - Università di Torino (Italy)
- Anna Ferrari - Università di Torino (Italy)
- Andrea Ferretti - S3 Center, Istituto Nanoscienze, CNR, Modena (Italy)
- Nic M. Harrison - Imperial College London (UK)
- Sandrine E. M. Heutz - Imperial College London (UK)
- Giuseppe Mallia - Imperial College London (UK)
- Ruth Martínez - Universidad Complutense de Madrid (Spain)
- Lorenzo Maschio - Università di Torino (Italy)
- Barry G. Searle - STFC Daresbury Laboratory (UK)

Tutors

- Zainab Alaithan - Imperial College London (UK)
- Carles Ràfols i Bellés - Imperial College London (UK)
- Paolo Restuccia - Imperial College London (UK)

Delegates

	Title	First name(s)	Surname	Affiliation
1	Dr	Aidin	Ahmadi	University of Birjand
2	Mr	Fedor	Akhmetov	NRNU MEPhI, Moscow, RU
3	Mr	Kamal	Belbase	TU Vienna
4	Mr	Mohamed	Bensifia	MSME-UPEM, Paris-France
5	Dr	MARIA VICTORIA	CASTILLO SCHEUERMANN	UNT-TUCUMAN-ARGENTINA
6	Miss	Maria	Čebela	INN Vinca, Serbia
7	Mr	Tsz Hin	Chan	University of Exeter
8	Mr	Ivan	Clayson	UCL, UK
9	Mr	Benjamin	Craig	Uni of Southampton
10	Dr	Thomas	Darden	OpenEye SantaFe USA
11	Mr	Xindi	DIAO	UCL
12	Mr	Sergio	Gámez-Valenzuela	Málaga (Spain)
13	Dr	Jacob	Gavartin	Schrodinger Inc
14	Dr	De-Bo	Hu	NCNST, Beijing, China
15	Dr	Safia	IZZAOUIHDA	LS3MN2E-CERN2ED
16	Dr	Adam	Jackson	STFC, Harwell, UK
17	Ms	Agnieszka	Jamróz	University of Warsaw
18	Mr	Dan-Marian	Joita	BabesBolyai ClujNapoca R
19	Dr	Ali	Kachmar	QEERI, Qatar Foundation
20	Miss	Manaswita	Kar	University of Southampto
21	Mr	Gideok	Kim	MPI-FKF, Stuttgart, DE
22	Ms	Johanna	Kolbel	University of Cambridge
23	Prof	Timothy	Korter	Syracuse University USA
24	Dr	Tarek	Larbi	Tunis El Manar Universit
25	Mr	rabii	larhlimi	UniversitÃ© of poitiers
26	Miss	Qi	Li	University of Cambridge
27	Dr	Mark	Light	Southampton UK
28	Miss	Lyra	Lin	Imperial College London
29	Mr	François	Mairesse	UNamur, Belgium
30	Dr	Jefferson	Maul de Andrade	University of Turin
31	Miss	Iuliia	Melchakova	KNU, Daegu, South Korea
32	Mr	Mohamad	Muhieddine	Imperial College London
33	Miss	Manasi	Mulay	University of Sheffield
34	Dr	Jan	Novotny	CEITEC MU, Brno, CZ
35	Dr	Matthew E.	Potter	Southampton University
36	Mr	Conor	Price	University of Exeter, UK

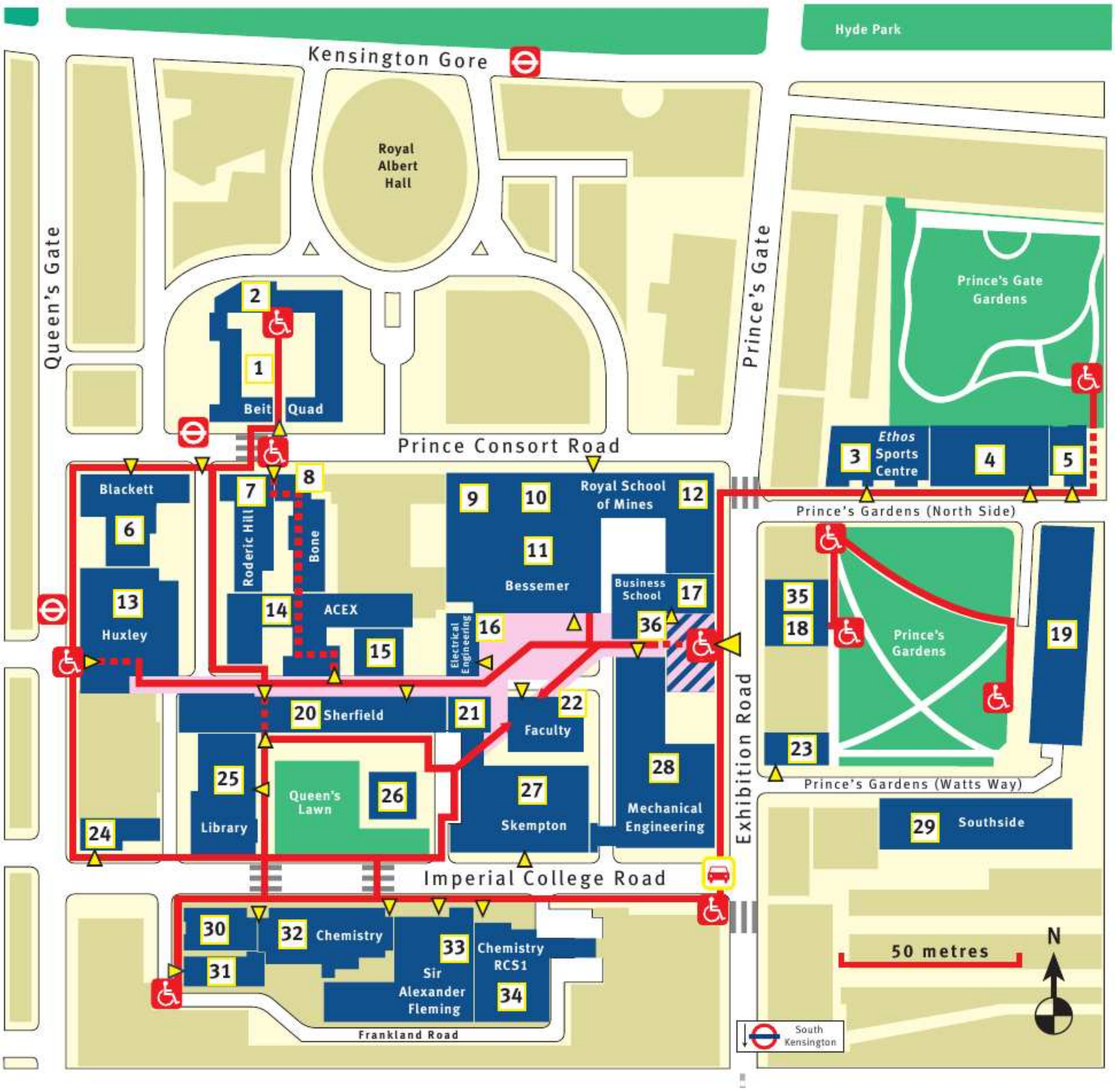
37	Miss	rana	riahi	Düsseldorf, HHU
38	Mr	Adrien	Richard	UCL
39	Ms	Eleonora	Romeo	University of Turin
40	Dr	Pralok	Samanta	UCD, Dublin
41	Mr	Sergey	Shteingolts	IOPC Kazan Russia
42	Ms	Laura I.	Tenelanda-Osorio	Universidad Eafit, Col
43	Miss	Nisa	Ulumuddin	Washington State Uni
44	Mr	Roman	Voronkov	LPI RAS, Moscow, Russia
45	Miss	Lisette	Warren	University of Edinburgh
46	Dr	Adam	Zaczek	University of Cambridge
47	Dr	Pezhman	Zarabadi-Poor	CEITEC-MU, Brno, Czechia
48	Dr	Liviu	Zarbo	INCDTIM Romania
49	Dr	Andy	Zeng	University of Liverpool
50	Mr	Yizu	Zhang	Imperial College London
51	Dr	Tianqi	Zhao	Dept. of Chemistry, UCL

Location

MSSC2019 took place from Monday 16 – Friday 20 September at...

- **Registrations and Morning Sessions - Royal School Of Mines, Prince Consort Rd, Kensington, London SW7 2BP (Building 12)**

- **Afternoon Sessions - Department of Chemistry/Biochemistry, South Kensington Campus, London SW7 2AZ (Building 32)**



Programme

MORNING SESSIONS: RSM - Room 1.31

Coffee Break: Royal School of Mines (RSM) / Department of Materials - Room 1.31

	Monday 16th	Tuesday 17th	Wednesday 18th	Thursday 19th	Friday 20th
9:00 - 9:45	Translation symmetry, space groups. Geometry **G. Mallia**	Vibrational frequencies calculation and tools for their analysis **A. Ferrari**	Local defects in crystalline materials **G. Mallia**	Ab initio modelling of Metal Organic Framework with CRYSTAL **B. Civalleri**	Dielectric and optical properties of solids **L. Bernasconi**
9:45 - 10:30	How to Model Crystals: Periodic Boundary Conditions **S. Casassa**	Quasi-harmonic Approximation: Thermal Effects on Structural and Thermodynamic Properties **A. Erba**	Modeling low-dimensional systems with CRYSTAL: Nanotubes and Fullerenes **A. Ferrari**	Post-HF techniques and the CRYSCOR project **L. Maschio**	Excited states. TD-DFT **L. Bernasconi**
	Coffee Break	*Coffee Break*	*Coffee Break*	*Coffee Break*	*Coffee Break*
10:50 - 11:35	Hamiltonians and basis sets **K. Doll**	From bulk to surface. Relaxation and reconstruction **K. Doll**	Infrared and Raman Spectra of Solids **L. Maschio**	CRYSCOR: studied cases **R. Martinez-Casado**	Ab initio transport properties and thermoelectric materials **A. Dasmahapatra**
11:35 - 12:20	Geometry optimisation of solids **A. Erba**	One-electron properties **F. Corà**	Ab initio thermodynamics **E. Ahmad**	Van der Waals interactions in the DFT framework **G. Brandenburg**	Quantum transport in nanojunctions **A. Ferretti**
12:20 - 13:05	The structure of the CRYSTAL code. CRYSTAL input/output **G. Mallia**	TOPOND: topological analysis of the electron charge density of solids **S. Casassa**	The effect of pressure: equations of state; bulk modulus; elastic constants ***M. Alfredsson***	CRYSTAL in parallel **I. Bush**	Predictive simulation and materials characterisation ***S. Heutz***

AFTERNOON SESSIONS: Chemistry/Biochemistry Building

Coffee Break and Poster Session: Department of Chemistry
Chemistry Cafe' (Room 232)

BASIC TUTORIALS : ROOM 311 – BIOCHEMISTRY BUILDING

	Monday 16th	Tuesday 17th	Wednesday 18th	Thursday 19th	Friday 20th
14:30 - 16:15	Geometry input	DLV: visulisation of structures and properties. **B. Searle** Total energy (Single-point)	13:05 - 15:45 *Lunch* & *Poster Session*	Geometry optimisation	Basic modelling of surfaces and defects
	Coffee Break	*Coffee Break*		*Coffee Break*	*Coffee Break*
16:45 - 18:30	Basis set input & basis set editing	One-electron properties. TOPOND: electon denssity analysis	16:00 ... *Self-guided Tour*	Vibrational frequencies	Nanotube systems

ADVANCED TUTORIALS : ROOM 310 – BIOCHEMISTRY BUILDING

	Monday 16th	Tuesday 17th	Wednesday 18th	Thursday 19th	Friday 20th
14:30 - 16:15	Advanced options in geometry optimisation and frequencies calculation	Magnetic properties	13:05 - 15:45 *Lunch* & *Poster Session*	CRYSTAL in Parallel Mode: Pcrystal vs. MPPcrystal	Dielectric properties
	Coffee Break	*Coffee Break*		*Coffee Break*	*Coffee Break*
16:45 - 18:30	Advanced options in geometry optimisation and frequencies calculation	Magnetic properties	16:00 ... *Self-guided Tour*	CRYSCOR	Dielectric properties

Social Dinner

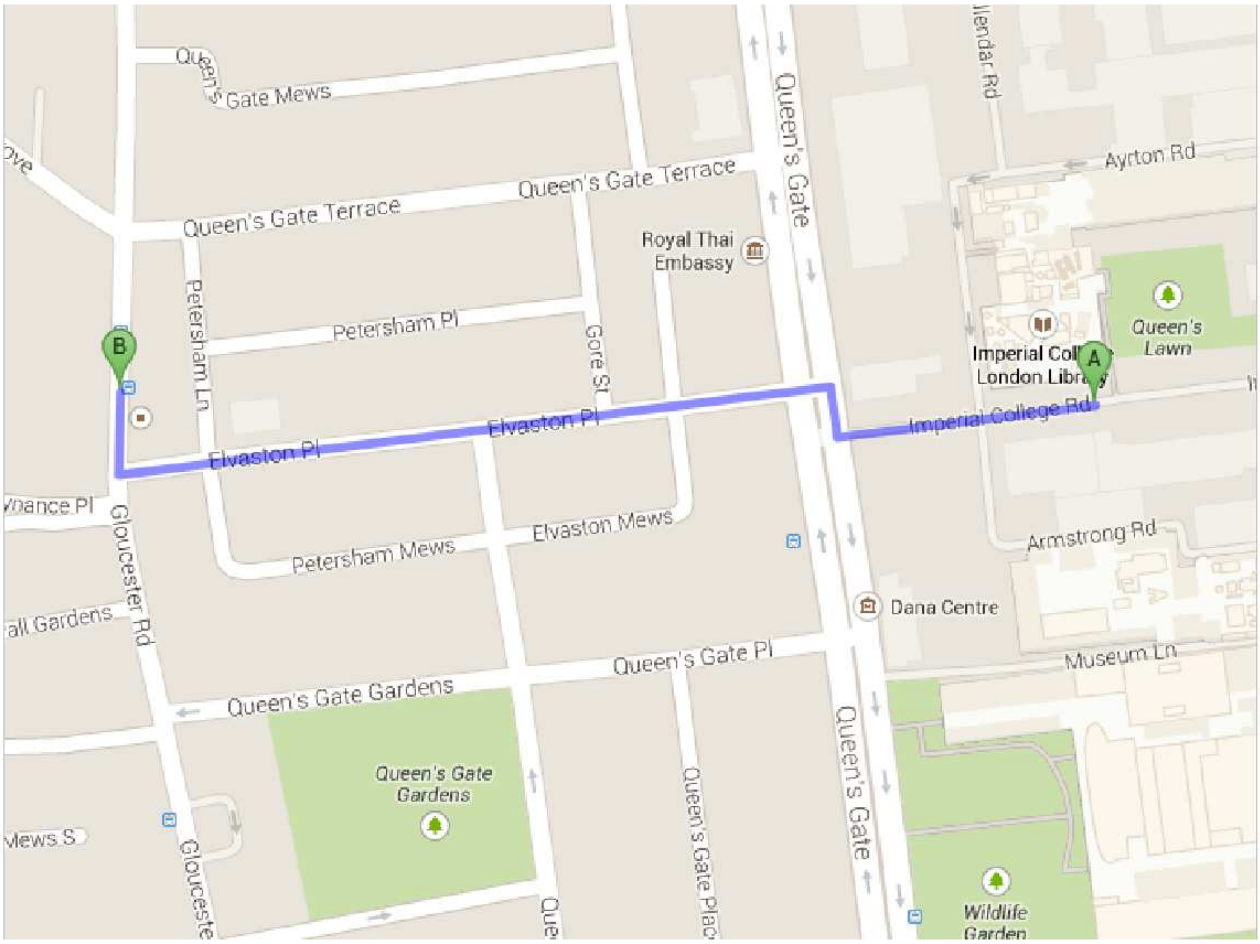
The MSSC Dinner took place on Wednesday 18 September at...

MED KITCHEN RESTAURAN
25–35 Gloucester Road
London SW7 4PL

The meeting point for those walking to the restaurant was at 18:45 at the entrance to the building in which the MSSC afternoon sessions were held (point A in this map below with the directions).

The three winners of the Best Poster Awards were announced.

The feedback about the dinner was very positive and attendees enjoyed the social interaction and to know each other. The atmosphere was very friendly and relaxed.



Imperial College London

Science & Technology Facilities Council

THE THOMAS YOUNG CENTRE
LONDON CENTRE FOR THEORY AND SIMULATION OF MATERIALS

MSSC2019
Ab initio Modelling in Solid State Chemistry
London - UK
September 16-20, 2019

MSSC2019
Ab initio Modeling in Solid State Chemistry
September 16-20, 2019 - London, UK
http://www.imperial.ac.uk/mssc2019/

London, September 18th, 2019

Best Poster #1

Ms Agnieszka Jamróz

”Predicting Ground-State Configurations and electronic properties of monolayer hexagonal C-B-N alloys: Cluster Expansion Method”

MSSC2019
Ab initio Modeling in Solid State Chemistry
September 16-20, 2019 - London, UK
http://www.imperial.ac.uk/mssc2019/

London, September 18th, 2019

Best Poster #2

Miss Lisette Warren

”Towards understanding the role
of lead-based modifiers
in rocket propellants”

MSSC2019
Ab initio Modeling in Solid State Chemistry
September 16-20, 2019 - London, UK
http://www.imperial.ac.uk/mssc2019/

London, September 18th, 2019

Best Poster #3

Mr Sergio Gámez-Valenzuela

”Modelling the Optical Properties
of Benzochalcogenodiazole-based Copolymers
using Tuned Range-Separated
Hybrid Functionals.”

Poster Titles and Abstracts

Structural and Vibrational Characterization of powerful insecticide dichlorodiphenyltrichloroethane, 2,4-DDT

María V. Castillo[a], Maximiliano A. Iramain[a], Lilian Davies[b], María E. Manzur[a], Silvia Antonia Brandán[a]

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[a]*Cátedra de Química General, Instituto de Química Inorgánica, Facultad de Bioquímica. Química y Farmacia, Universidad Nacional de Tucumán, Ayacucho 471, (4000) San Miguel de Tucumán, Tucumán, Argentina.*

[b]*Instituto de Investigaciones para la Industria Química (INIQUI, CONICET), Universidad Nacional de Salta, Av. Bolivia 5150, 4400 Salta, Argentina.*

Abstract

The powerful insecticide dichlorodiphenyltrichloroethane (2,4-DDT) have been characterized by using the experimental FT-IR and FT-Raman spectra in the solid state. The complete vibrational assignments were performed combining hybrid B3LYP/6-311++G** calculations with the internal coordinates and the scaled quantum mechanical force field (SQMFF) methodology. The structural, electronic, topological and vibrational properties were studied for the most stable structure by using natural bond orbital (NBO) and atoms in molecules (AIM) analyses. Also, the Mulliken and Merz-Kollman (MK) charges were evaluated in gas phase together with the molecular electrostatic potential (MEP) in order to predict the potential nucleophilic and electrophilic reaction sites. In this work, the force fields and the complete assignments of the 78 vibration normal modes expected for 2,4-DDT are reported. In addition, the force constants are reported. Here, the properties for 2,4-DDT were compared with those reported for other chlorinated and toxicant agents.

KEYWORDS: 2,4-DDT, vibrational spectra, molecular structure, descriptor properties, DFT calculations.

Towards understanding the role of lead-based modifiers in rocket propellants

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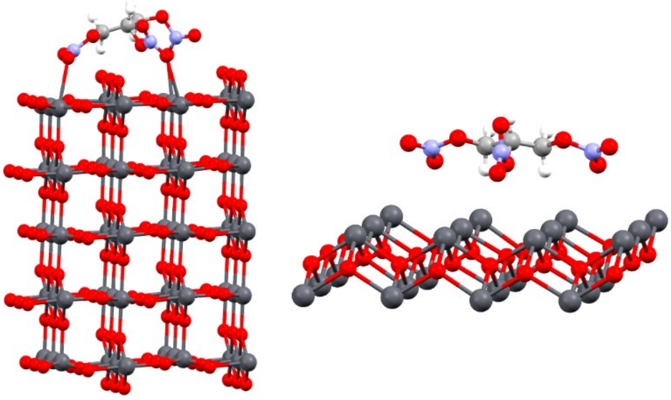
Lead-based compounds, such as lead salicylate, are commonly used additives in double base rocket propellants containing nitroglycerin and nitrocellulose mixtures, where they are attributed with generating a steady fuel burn rate. European legislation seeks to restrict the use of lead in propellants due to land and wildlife contamination, and to minimise health risks to personnel handling and operating propellants. However, as the behaviour of lead-based additives within the propellant system is poorly understood, and attempts to simply replace the lead with other materials has met with limited success, there is now a need for a fundamental investigation into the effects of lead-based compounds on the chemical reactivity of double base rocket propellants.

This research thus aims to establish whether lead oxide (α-PbO and β-PbO_2) can provide catalytically active surfaces for the binding of nitroglycerin compared to tin oxide (SnO_2), which in contrast shows only modest catalytic function as a ballistic modifier.

The bulk electronic structure of each system has been deduced, and the most stable surface identified, to which a nitroglycerin molecule was attached in a binding study. The optimised structures have been extensively analysed, with outcomes focusing on adsorption energies and changes in electronic band structure diagrams. Results thus far indicate preferential binding of nitroglycerin to the PbO_2 surface versus the PbO surface. This is due to nitroglycerin binding to Pb and O vacancies exposed on the PbO_2 surface allowing for bond formation. In contrast, the inert and diffuse Pb lone pair located on the PbO surface prevents approach of the molecule so that only long-range interactions form.

This work has made use of the ab initio CRYSTAL17 code, with the range separated hybrid HSE06 functional and localised basis sets utilised alongside the Grimme D3 dispersion correction scheme. Future work intends to study a metallic Pb surface, and other lead-free modifiers to provide fundamental insight in the search for a non-toxic replacement.



Optimised adsorption structures; Nitroglycerin bound to PbO_2 (left) and PbO (right) in the most stable adsorption mode.

Free Energy Landscape of Sodium Solvation into Graphite

Ali Kachmar[1], William A. Goddard III[2]

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[2]Materials and Process Simulation Center, California Institute of Technology, Pasadena, California 91125, United States

Abstract

Sodium Ion Batteries (SIBs) are the most cost-effective alternative to current generation lithium ion batteries (LIBs), [1-3] but Na is known to deliver very low energy capacity for sodium intercalation compared to Lithium. In order to improve the performance for SIB, we want to understand at the atomistic level how the metal ion changes its coordination to the solvent in positioning itself for insertion into graphite or adding at the metal surface [4,5]. Previous studies (force fields with fixed charges) ignored the coupling of electronic states with the changing charge and solvation. We report here Density Functional Theory molecular metadynamics simulations [6-8] to obtain the free energy landscape including changes in the electronic coupling as a sodium ion in Dimethyl sulfoxide solvent intercalates into graphite, the first step in understanding how the local environment affects the free energy of solvation [9]. We analyze the free energy landscape for all the possible sodium solvation scenarios, while quantifying their free energy barriers. Our simulations indicate that solvent plays an important role in stabilizing the sodium intercalation into graphite through shielding of the sodium while modulating the interaction of the solvent with the graphite sheets [10]. In order to facilitate this intercalation we propose solvents with negatively charged groups and aromatic cores (e.g., cyclic ethers) that could allow a greater rate of anion exchange to increase Na^+ mobility.

References

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Interfaces based on g-CN: features of interaction and electronic properties.

Carbon nitride (C_3N_4) pays attention due to its promising application as a material for electronic devices after prediction of its special properties. It’s not only ultrahard material, but also the material with special electronic properties that allow to use C_3N_4 as a material for LED. Unlike most organic molecules g-C_3N_4 is chemical and thermal stable. It’s insoluble and could be synthesized in different ways: CVD, PVD, solvothermal method etc. There are two polymeric states of such materials that differ with the shapes of holes (vacancies) and their size (see Figure 1): constructed from triazine as g-CN_1(a), while the one constructed from tri-s-triazine is referred to as g-CN_2(b).

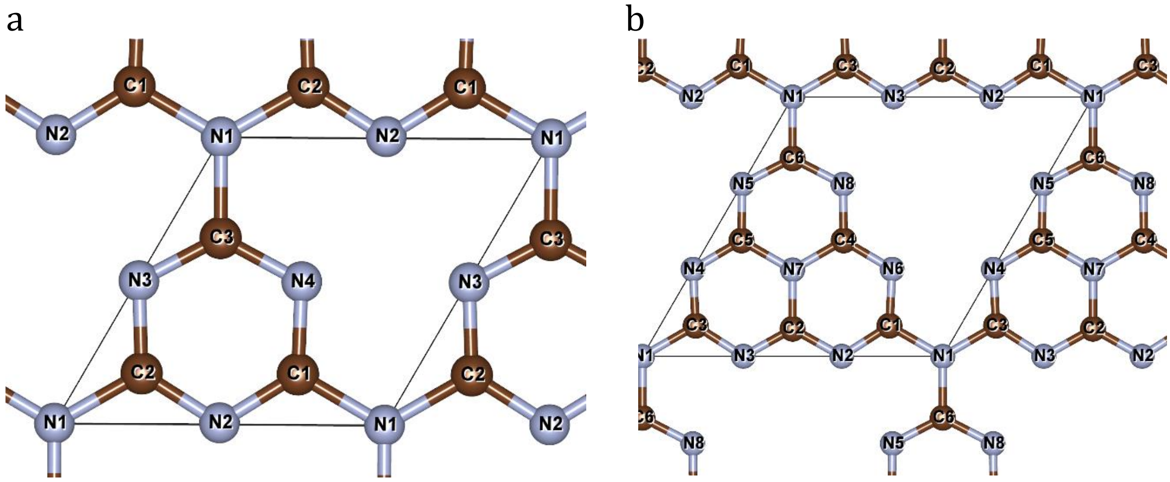

Figure 1. Geometry of g-CN1 (a) and g-CN2 (b). Unit cell is indicated with parallelogram

Lone electron pair of nitrogen and π-bonding system form valence band so it could be tuned with changing chemical environment. Electronic properties of pure g-C_3N_4 were investigated from different points, but modifications of such plane structures wasn’t paid attention. This work is held to explore an impact of adding rich row metals (Cr, Mn, Fe, Co, Ni) on electronic properties and to make predictions about its potential sphere of use from the first-principles density functional theory (DFT) studies.

Abstract

Developing Stability Criteria of Isolated Metal Adatoms on a Well-Defined Copper Oxide Film

Nisa Ulumuddin[1], Kyle Groden[1], Alex C. Schilling[2], E. Charles H. Sykes[2] and Jean-Sabin McEwen[1],

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Single-site catalysts (SSC) are attractive materials due their high selectivity and atomic efficiency.[1] In the case of SSC's consisting of supported metal adatoms, strong interactions between the metal species and the support are required to anchor the adatom on the surface. Oxides are found to be effective supports for metal adatoms, preventing their agglomeration and thus promoting the catalyst's thermal stability.[2-3] Despite this, adatoms can still diffuse into the bulk, causing the catalyst to deactivate. STM measurements of a thin surface oxide film, specifically the "29" $Cu_xO/Cu(111)$ surface oxide, with atomically dispersed Pt after CO oxidation, found that some Pt adatoms previously planted on its surface were missing, suggesting that Pt was able to go subsurface after the reaction.[2] This brings us to the investigation of the segregation tendencies of various metal adatoms on a thin-film copper oxide surface, using a model "29" $Cu_xO/Cu(111)$ surface oxide as an example.

In this work, we determine the segregation tendencies of Ag, Au, Pd, Pt and Rh adatoms on a pristine "29" $Cu_xO/Cu(111)$ surface from first principles using density functional theory based calculations (schematics in Figure 1). To deconvolute the properties which govern the segregation of the metal (M) adatom from the surface, we first correlate the adatom segregation energy (Figure 1) to the formation energy of a bulk Cu_3M alloy, the bulk metal surface energy, and the strain energy induced from fitting the metal adatom into a fixed Cu lattice. We also perform a differential charge analysis and oxygen binding energy calculations to determine how oxygen adatoms affect the segregation tendencies on the surface of an oxide film. The oxide film's influence is further isolated through a comparison of the segregation energy trends on a Cu surface in the presence and in the absence of a surface oxide. We find that metals with surface energies that are lower than that of Cu result in favorable adatom segregation energetics. The ability of a metal adatom to segregate from Cu increases in the following order: Rh, Pt, Pd, Au, and Ag, where Ag is the least likely to diffuse into the bulk. A density of states (DOS) analysis confirms that segregation is favorable for metal adatoms with d-band centers that are further away from the Fermi level than Cu. A more segregated adatom also binds weaker to CO. We thus propose the difference between the surface energy of the bulk adatom metal and that of Cu as a descriptor for its segregation tendency on the "29" $Cu_xO/Cu(111)$ surface. Using this information, we can now predict stable adatoms to be supported on "29" $Cu_xO/Cu(111)$ before investing into more computationally expensive calculations.

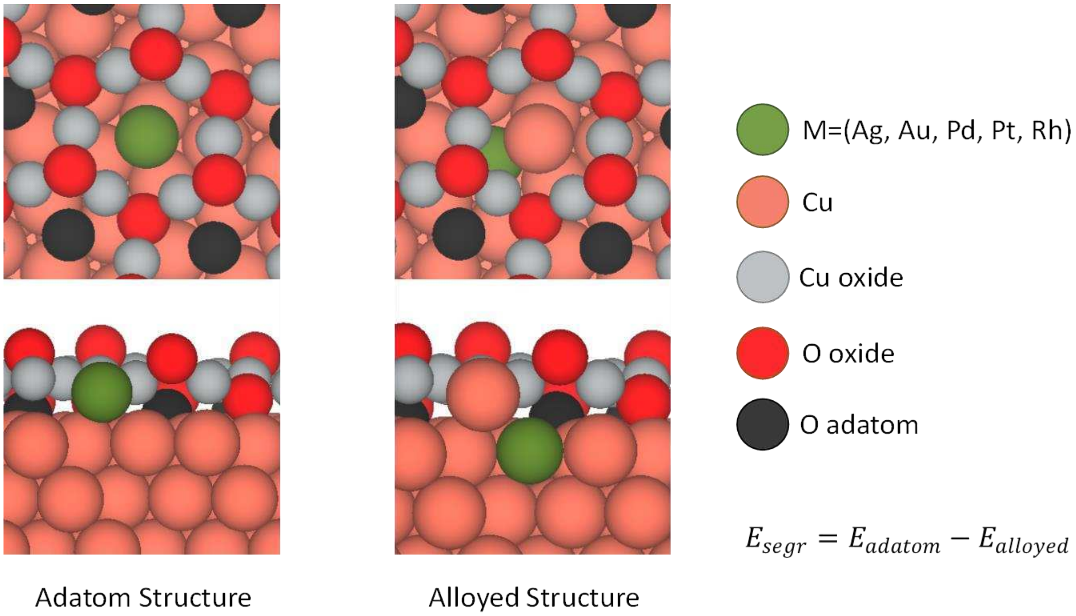

Figure 1: Schematic of the adatom and alloyed structures used to calculate segregation energies.

References:

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Title: The ion-exchange mechanism of transition metals into zeolites

I. Clayson,[1] N. Collis,[2] J. Kilmartin, [2] M. Sarwar[2] and B. Slater[1]

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Oxides of nitrogen (NO_x) are harmful pollutants produced predominantly anthropogenically,[1] where NO_x has been found to have a causal link with cardiac and respiratory disease[2] as well as a damaging effect to the environment.[3] Globally, a total of 47.5×10^9 kg of nitrogen from NO_x was produced in 2014, where this amount has been effectively unchanged from the previous 10 years, with much of the growth in production occurring in high population density areas in Asia.[4] Given the substantial amounts of NO_x produced and the risks it possesses both to the ecosystem and human health, NO_x production must be tackled. A significant area for NO_x production are automotive vehicles. Current approaches to reduce vehicle NO_x emissions depend on NO_x reducing catalysts with Cu docked in various aluminosilicate zeolites.[5–9] In order to deposit the catalytically active metal ions into the zeolite, they must be exchanged with the original synthesis counter-cation. However, the metal species deposited is dependent on: (i) the zeolite topology, (ii) the exchange procedure, and (iii) the zeolite Si/Al ratio.[10–12] These differing species can have different catalytic activities.[13] The exchange mechanism is not currently fully understood and therefore in order to make effective NO_x reducing catalysts, the pathway and energic profile of the ion-exchange must be investigated.

This work aims to focus on elucidating the effects of: (i) solvation, (ii) metal reagent choice, (iii) metal identity, (iv) Al distribution, (v) Si/Al ratio and (vi) zeolite topology. Current work has suggested that solvation enables greater Cu(II) mobility within bulk SSZ-13 but reduces uptake at the surface whilst unsolvated Cu(II) cations are predicted to be mobile on the surface and thus may have a tendency to aggregate as seen with solid-state exchange methods.[11] On-going work is focused on further exploring the effects of solvation on ion uptake and mobility at the surface and within the bulk of SSZ-13 for Cu(II) reagents by introducing a continuum solvation model for water molecules beyond the 1st solvation shell. Moreover, the Pd(II), Fe(II/III) and Co(II) species as well as the formation energy profile for multi-nuclear metal species and their dependency on the aforementioned effects will be studied.

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Title:

Artificial Photosynthesis from Perovskite Materials: A $SrSnO_3$ Case Study

Abstract:

Photoelectrolysis offers a mechanism for long term, clean energy storage via hydrogen production. Recently, several perovskites have shown promise for this application [1,2]. Perovskites, ABX_3, are highly customisable, with several options for the A, B and X ions. This results in a large range of tailorable properties, such as the band gap and the relative stability, making them highly suitable for photoelectrolysis. The bulk properties of many perovskites have been explored [2,3]. However, their potential for photocatalysis is mainly governed by surfaces, making their study critical. Using techniques such as density functional theory, we develop a large scale theoretical screening process to tackle the large range of candidates for A, B and X.

Here we present a method for screening a list of potential perovskites for water splitting, and present here $SrSnO_3$ as a case study. We examine the effect of forming surfaces and the introduction of adsorbants (hydrogen and oxygen) onto the surface, taking note of the band alignment with respect to the evolution potentials.

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Oxide and silicide thermoelectric thin films

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Abstract. The band structure of some oxides and silicides of some transitional metals presents unusual features such as flat bands near the Fermi level. Such flat bands have been associated [1] with improved thermoelectric properties. In order to verify this hypothesis experimentally, and futher search for novel thermoelectric materials, we developed the procedure for the pulsed laser deposition of thin crystalline films of copper and titanium oxides, and iron and chromium silicides. We present the current status of this work, along with our extensive tests of the quality of our films by X-Ray diffraction, scanning electron microscopy, atomic force microscopy, etc.

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Optimisation of Band Gap Tuning of Hybrid Organic – Inorganic Perovskite Solar Cell

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Hybrid perovskite solar cells (with chemical formula ABX_3) are of great interest due to the recently measured power conversion efficiency (PCE) of greater than 20% (but theoretically, 30%). Perovskite structures are easily customisable, with a range of options for A, B and X. This enables us to both tune the electronic band gap and the stability by varying the composition. Two promising perovskites are the $CH_3NH_3PbI_3$ (MAPI) and $CH(NH_2)_2PbBr_3$ (FAPB) structures. By varying the ratio of FA and MA and doping with Br, we can potentially tune the band gap and effective masses (and hence electronic transport).

We present a theoretical investigation of the structural and electronic properties of $MA_xFA_{1-x}PI_yBr_{1-y}$, performed using first–principles density functional theory (DFT). Our results show that decreasing fractions of x and y increase the band gap, and we present a composition phase diagram showing how these two values (x & y) change the band structure. We discuss how the variation in these compositions, including the effects of the rotation of the organic groups, affect the effective masses and, ultimately, the transport. We also explore the effects of clustering and intermixing on these structures and their stability.

Modelling the Optical Properties of Benzochalcogenodiazole-based Copolymers using Tuned Range-Separated Hybrid Functionals.

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Since the discovery of organic semiconductors, these systems have been deeply investigated and many strategies to module their optical and electronic properties have been established. In this sense, Donor-acceptor (D−A) approach to conjugated polymer design has become a widely used method for preparing conjugated polymers with narrow band gaps. This approach involves synthesizing a polymer with a delocalized π-electron system that comprises alternating electron-rich (donor) and electron-deficient (acceptor) repeat units. The combination of high-lying HOMO levels (residing on the donor units) and low-lying LUMO levels (residing on the acceptor units) results in an overall narrow band gap for the polymer (see **Figure 1**).[1] In this sense, poly(cyclopentadithiophene)benzothiadiazole, (PS in Figure 1) is a D−A polymer for which power conversion efficiencies in solar cells of 5-6% are reported.[2] In this work, we use density functional theory (DFT) calculations to investigate the tuning of the electronic and structural properties of cyclopentadithiophene-benzochalcogenodiazole D−A polymers, wherein a single atom in the benzochalcogenodiazole unit is varied from sulfur to selenium to tellurium [3] (**Figure 1**). Resonance Raman (RR) spectroscopy is also used to describe the nature of the electronic excitations. Improved prediction of the optical properties has been obtained by using long-range corrected functionals, considering both tuned and default range-separation parameters, aiming at predicting their optical and charge transport properties.

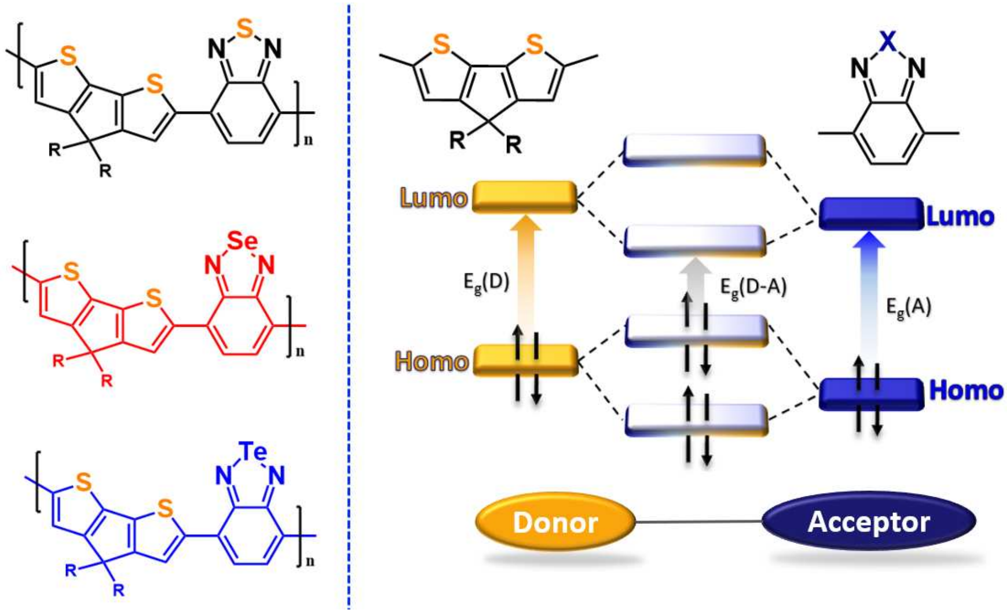

Figure 1. D-A copolymers under study (a). HOMO-LUMO gap decrease upon D-A approach.

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Poster Title:
Prediction and Ranking of Different Polymorphs of Pharmaceutical Molecules using Basin Hopping Model and Electronic Structure Theory

Abstract:
The goal of crystal structure prediction methods is to identify the possible polymorphs of a molecule based on minimal information (e.g., its two-dimensional chemical diagram) available. In this work, we have developed a new basin hopping methodology to predict low energy polymorphs and rank the polymorphs using high level electronic structure calculations.

Interaction of anatase with water pollutants

Keywords: TiO_2, Photocatalyst, DFT, Water

Scarcity of clean useable water is driving attention towards recycling and reusing of waste-water across the globe. Pharmaceuticals as well as personal care products constitute large number of pollutants causing severe human health and environmental hazards. Unlike other wastewater treatments involving separation of water pollutants, photocatalytic water treatment destroys pollutants using light energy and a photocatalyst. The adsorption of pollutants on the photocatalyst surface is one of the rate determining steps governing performance of a photocatalytic water purification. Titania (TiO_2) is a popular commercial photocatalyst, commonly synthesised as anatase, but it has poor adsorption of hydrophobic pollutants. Experimental techniques to determine the pollutant interactions with the photocatalysts are restricted by the dynamic nature of interactions of a range of water pollutants. On the other hand, theoretical simulations allow to selectively study interactions of organic molecules with the TiO_2 surface.

This study investigates the interaction of model water pollutants, such as salicylic acid, with the most stable (101) surface of TiO_2 anatase. Interaction energies were calculated using density functional theory (DFT, using the PBE functional), to determining stable adsorption configurations. Theoretical calculations provide information about the strength and selectivity of adsorption of pollutants. Further research will explore the dynamic nature of anatase-pollutant interactions. The information obtained via DFT calculations will be validated by experimental measurements and will further be used as design guidelines for photocatalyst surface modification strategies for enhancing efficiency of photocatalytic water treatment.

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Predicting Ground-State Configurations and electronic properties of monolayer hexagonal C-B-N alloys: Cluster Expansion Method

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Graphene-like C-B-N layered alloys constitute intriguing class of materials exhibiting short and even long-range order and ranging from B- and/or N-doped graphene, through mixtures of graphene and hexagonal boron nitride (h-BN) domains, to C-doped h-BN systems. Despite of considerable scientific interest and numerous experimental and theoretical studies, overall understanding of the equilibrium morphology, stability, phase diagrams, and electronic structure of such two-dimensional ternary alloys is far of being complete. Our previous Monte Carlo studies within valence force field (VFF) scheme with Tersoff's reactive potential have revealed that C-B-N ternary alloys deviate strongly from random alloys, exhibit short-range ordering, and have tendency to form graphene and h-BN domains [1]. We have also found out on the basis of tight-binding (TB) calculations that the energy band gap in C-B-N alloys decreases very quickly with the growing concentration of carbon [2]. In the combined VFF-TB studies, it has been necessary to consider systems with thousands of atoms and search through a huge configuration space, which is not accessible in any direct *ab initio* approach.

In the present study, we aim at providing the predictions for ternary C-B-N alloys on the level of the density functional theory calculations, which would allow us to assess the accuracy of our previous results based on the VFF scheme. The method of choice is the *cluster expansion* (CE) approach that has been employed in numerous studies of alloys [3]. In the CE method the alloy Hamiltonian is mapped on the Heisenberg-like lattice model with pair, triplet, and quadruplet interactions and the constants of these interactions are established from a series of *ab initio* calculations for carefully chosen set of clusters. However, in typical CE calculations this expansion is arbitrarily truncated neglecting higher order interactions, and the estimation of the resulting error in total energies gets impossible. In the present studies, taking advantage of the VFF calculations, we are able to determine the required order in the cluster expansion, just comparing the CE calculations with a given degree of clusters with the full total energy calculations for the alloy system, just consistently employing the Tersoff's potential in both types of calculations. Having determined the required degree of the CE, we are now in position to calculate the energies of all required clusters employing the DFT calculations and further employ Monte Carlo sampling method for the effective Hamiltonian to find the energetically most favorable configurations of C-B-N alloys.

In the present study, we employ CELL package [3] for derivation of cluster expansion model for C-B-N monolayer alloys and *ab initio* all-electron package *exciting!* [4] to calculate cluster's energies. The employed procedure delivers the most accurate up to now results for the C-B-N alloys in the whole range of concentrations, which generally exhibit qualitative agreement with predictions based on VFF model.

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Photocatalytic Reduction of CO_2 on ZIF-2 enhanced perovskite

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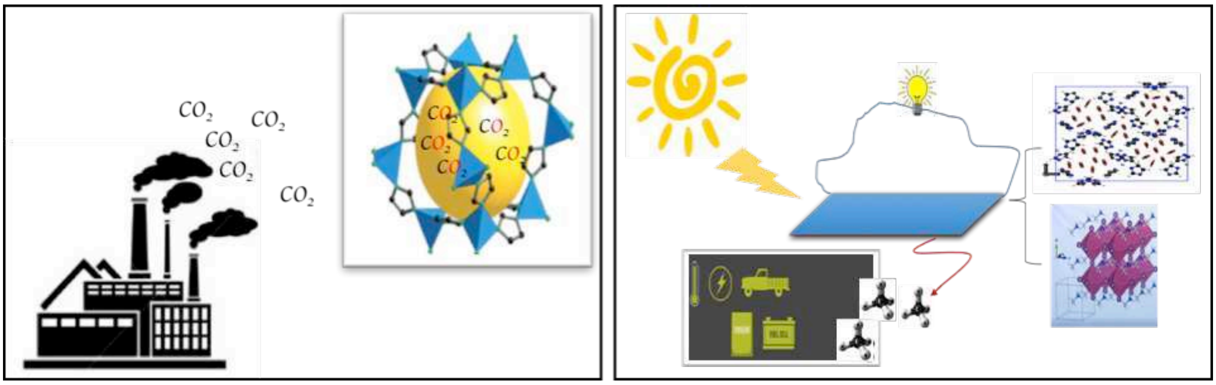
Metal organic frameworks (MOFs) thin films, a novel form of nanomaterials, have attracted recently enormous interest in nanotechnology fields. Different methods are used to produce such thin films by deposing MOFs, obtained in the form of powders, on solid surface (e.g. TiO_2, SiO_2, ZnO nanowire, …). However, the application of the later in such fields as electronics and energy storage devices are not a mature field yet. [1]

In the few decades, the demand of devices converting solar energy into electrical power have been growing with accelerating speed. In this work, we are conceiving a new perovskite solar cell witch the zeolitic imidazolate frameworks ZIF-2, a subclass of metal organic frameworks (MOFs), deposit on methylammonium lead halides (MALHs) surface. The ZIF-2 is evaluated for their ability to speed-up the transfer of excited electrons in upon illumination. [2]

Furthermore, zeolitic imidazolate frameworks (ZIFs) material as they hold great promise as porous materials for several potential applications such as gas storage, molecular catalysis and gas separating, we aim to evaluate whether our ZIF-2@ MALHs perovskite solar cell can also reduce CO_2 to methane. [3-4]



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Prediction of novel high-pressure Tin/Silicon nitride phase

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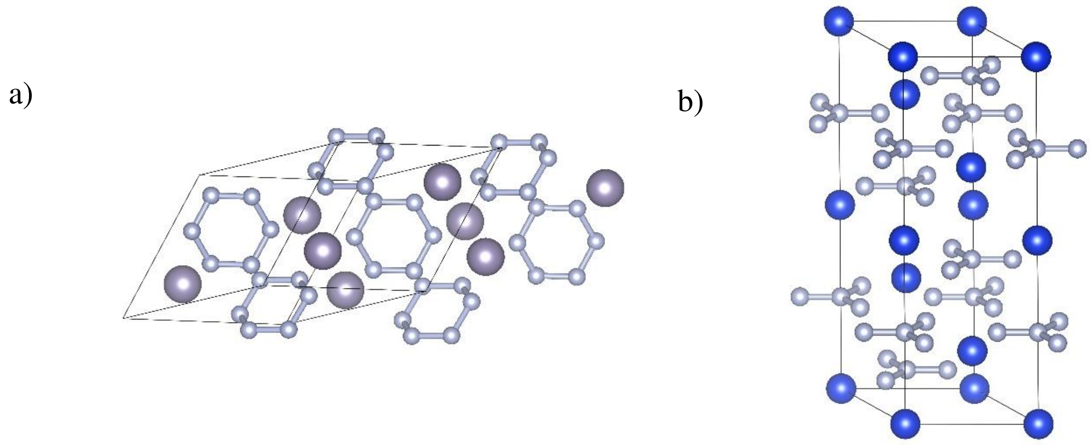
Although the potential of polynitrogen as a high energy density material (HEDM) has attracted attention, the difficulty of preserving polynitrogen towards attempts to discover molecular and extended nitrogen structures.

New stoichiometries and stable structures were identified using crystal structure prediction code (USPEX) based on evolutionary algorithms combined to DFT calculations (VASP). DFT calculations are done to make link between structural and electronic structure to understand the new arrangements. We explored binary phase diagram (Sn-N and Si-N) from ambient pressure up to 200 GPa and we proposed 6 stoichiometries for Sn-N system and 5 stoichiometries for Si-N system. 13 stable phases and several metastable phases have been studied at different pressure for given system, and they are dynamically stable.



a) SnN_6 at 100 GPa contains 6-N rings. b) SiN_4 at 200GPa contains 4-N stars

Studying mechanical properties and phase transitions of aspirin polymorphs with terahertz spectroscopy and ab initio simulations

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Keywords: THz-TDS, DFT, aspirin, mechanical properties, phase transitions.

Abstract: The crystal structure of aspirin form I was first determined in 1964. Although there was evidence of a second polymorph (form II), its structure was not confirmed and accepted until 2005,[1] mainly because forms I and II show very close structural similarity and frequently disordered intergrowths of the two polymorphs.[2] Terahertz time-domain spectroscopy (THz-TDS) explores dynamics in the far-infrared region, and it is useful for polymorph differentiation, as terahertz radiation can detect both inter and intramolecular vibrations within a solid. Density functional theory (DFT) simulations enable detailed interpretation and assignment of the complex molecular motions acquired from the THz-TDS. Combining these results with ab initio molecular dynamics (AIMD), temperature-dependent conformational changes can be resolved to provide information into the deformations and phase transitions within the crystal structures of small organic molecules such as aspirin.

Geometry optimisations and frequency analyses were performed with the CRYSTAL17 software package using the PBE-D3 density functional and the Ahlrich-VTZ basis set. The lattice and cell parameters were fully relaxed within their corresponding symmetry group. Geometry optimisation results showed total volume errors of less than 1.7% for both polymorphs. The energies from these results showed that form I was predicted to have a lower energy than form II by only 0.34kJ/mol, which corresponded well with previous studies.[3] The simulated spectra for both form I and form II are shown in Fig.1. Experimental samples were prepared by mixing 1 wt% of aspirin (form I) with polytetrafluoroethylene (PTFE). The spectrum was acquired with a commercial TeraPulse 4000 spectrometer (TeraView Ltd. UK) at 80 K. The satisfactory match between the experimental and simulated spectra of aspirin form I validates the simulated results. The only feature in the experimental spectrum that is not seen in the simulated spectrum is the peak at approximately 1.55 THz (marked by the grey line in Fig. 1). This is suspected to arise from form II domains, either as individual crystals within the bulk sample or intergrown within the form I structure.[2] Further THz-TDS measurements are to be carried out on form II.

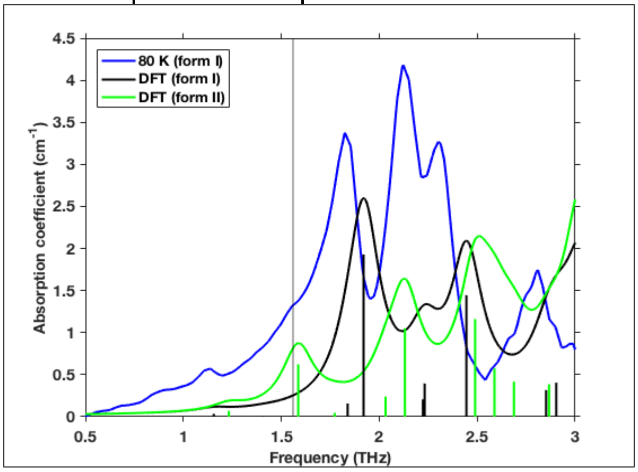

Fig. 1. The simulated spectra of form I (black), form II (green) and the experimental spectrum of form I (blue). Ticks represent the corresponding active modes. The grey vertical line indicates the feature that likely corresponds to the form II polymorph in the 80K form I spectrum.

A 2×1×2 supercell model of the form I aspirin structure was generated and an aspirin dimer was removed from the supercell as a first effort to simulate the defect that may cause the deformations and changes of stacking that lead to polymorph conversion. Large crystals were grown to perform single-crystal THz-TDS measurements at various angles that will provide more information on the nature of specific modes.

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Theoretical developments of new gas detection devices

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Abstract

This work is carried out as part of the impulsion Isite FUTURE project "CAPTEUR", which aims to develop experimentally and theoretically a new generation of reliable and selective gas sensors based on functionalized carbon nanotubes (CNTs). CNTs have excellent characteristics for gas detection [1]. Several types of single-wall CNTs exist, the experimental devise is based on the use of semiconductors CNT. Moreover, since the imidazole molecule [2] has a strong interaction with CO_2, the NTC [(5,5) or (8,0)] – imidazole - CO_2 systems have been chosen as test systems to set up the theoretical methodology. The theoretical modeling of such a device involves an accurate description of the interaction of the molecules with the surface of the carbon nanotube, two calculation codes based on DFT are used: CRYSTAL [3] and GAUSSIAN [4], using the ONIOM method for geometry optimization.

The most relevant type of bonding between Imidazole and CNT is being sought (H-Bonding, van der Waals, π-staking). In order to understand the effect of imidazole CNT functionalization and interaction of the whole system with CO_2, band diagrams, Fermi levels and state densities (DOS) of CNT, CNT - imidazole and CNT – imidazole - CO_2 have been determined.

In perspective, for a realistic modeling, it is proposed to use a more approximate method like DFTB [5]. Also, other semiconductor CNTs, other functionalizing molecules (triazol, bisalophen, dipyrin phenol) and other polluting gases will be tested (NO_2, NH_3...) according to the suggestions of our experimental collaborators (F. Bouanis , IFSTTAR).

Key words:

Functionalized CNT, Imidazole-CO_2, DFT, ONIOM

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Intermolecular Head-to-Head Interactions of Carbonyl and Thiocarbonyl Groups

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In this study, we report unusual head-to-head carbonyl–carbonyl (Fig. 1) and thiocarbonyl–thiocarbonyl interactions explored for crystalline β-hydroxyketones and drug thiamazole, respectively. Three studied β-hydroxyketones display an ability to form dimensionally different crystal formative motifs ranging from 1D to 3D. Despite the structural differences, primarily in intermolecular interactions, the studied ketones are arranged by the same bicyclic hydrogen-bonded twelve-membered supramolecular synthon, where the C=O···O=C contact plays a key role. Thiamazole molecules form an analogous C=S···S=C contact, but observed outside the cyclic N–H···S bonded supramolecular synthon. These unusual interactions along with all the others that are present in the crystal structures, for instance, classical H-bonds, were investigated by means of quantum-topological analysis of the calculated and experimental electron densities.

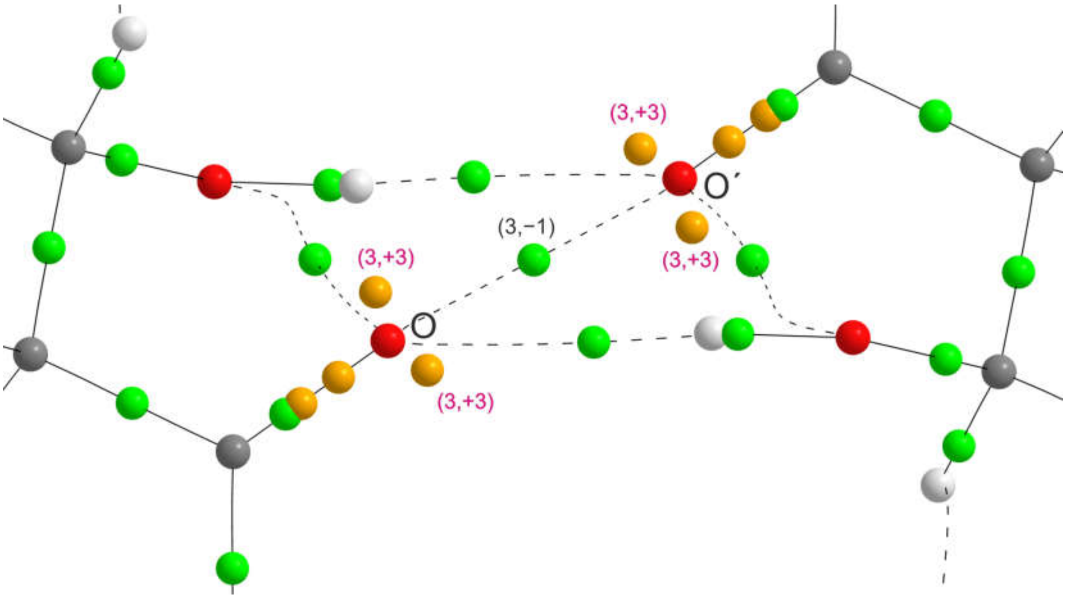

Figure 1. Twelve membered supramolecular synthon according to gas-phase quantum-chemical calculations (PBE0/cc-PVTZ). Critical points (3, –1) in $\rho(r)$ and (3, +3) in $\nabla^2\rho(r)$ are displayed by green and orange dots, respectively.

This work was financially supported by the Russian Science Foundation (grant No. 17-13-01209).

High-Throughput Screening of Metal-Organic Frameworks for Xenon Recovery from Exhaled Anesthetic Gas using AiiDA Smart Workflows †

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Although xenon has been introduced as an efficient ansthetic gas due to its excellent properties such as zero metabolism, low blood to gas ratio, rapid recovery time, and hemodynamic stability, its world-wide usage is limited because of high production and consequently market costs. It is resulting from the current technology, *ie.* cryogenic distillation, to extract xenon from containing gas mixture. Thus, finding alternative solutions to avoid energy-expensive production process or implementing recovery steps can remedy this issue and deliver xenon at lower costs. In this regard, likewise other cryogenic separation processes, solid adsorbents and more specifically metal-organic frameworks (MOFs) can be considered as excellent candidates to be designed/identified to replace the current expensive separation processes. Recently, Elsaidi *et al.*[1] reported the possible room temperature recovery of xenon from exhaled anesthetic gas as an alternative approach to remedy above-mentioned concerns. We also published[2] a follow-up computational study on the application of five analogues of Cu-BTC for the same purpose and also investigated the possibility of boosting the recovery performance by lowering the temperature (Figure1).

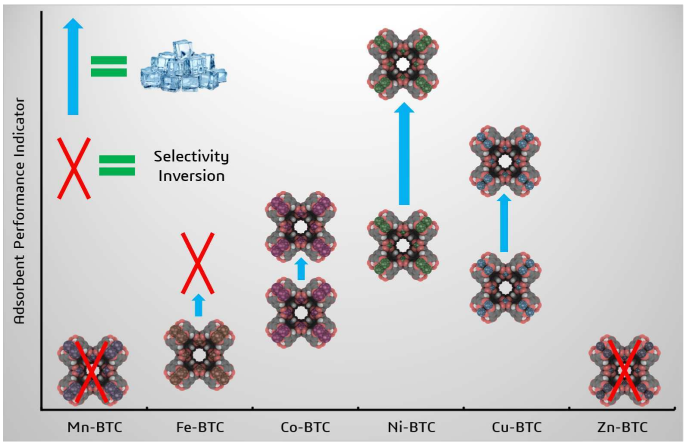

Fig. 1 Schematic representation of adsorbent performance indicator of Cu-BTC analogues for xenon recovery from exhaled anesthetic gas as 298 and 273 K[2]

In the current account, we continue the aforementioned line of research to provide sustainable solution for facilitating the medical application of xenon. To achieve this, we included several MOF databases (hypothetical and experimental) in our studies. However, dealing with four component mixtures in combination with thousands of structures make the in-silico study complicated. Therefore, we benefited from AiiDA[3] in combination with in-house smart workflows to improve both the efficiency and accuracy as well as possibility of fair sharing procedures and results. We implemented several computational, inspection, and validation steps within our workflow to benefit from the combination of easy-to-get descriptors and approving properties for selection of top-performing candidates. The identified MOFs were further scrutinized and validated through advanced geometry optimization algorithms.

Key References

1 S. K. Elsaidi, D. Ongari, W. Xu, M. H. Mohamed, M. Haranczyk and P. K. Thallapally, *Chemistry–A European Journal*, 2017, **23**, 10758–10762.
2 P. Zarabadi-Poor and R. Marek, *ACS Sustainable Chemistry & Engineering*, 2018, **6**, 15001–15006.
3 G. Pizzi, A. Cepellotti, R. Sabatini, N. Marzari and B. Kozinsky, *Computational Materials Science*, 2016, **111**, 218–230.

Some Feedback

A survey was conducted at the end of the workshop and a feedback form was distributed too; the outcome of both was very positive. Attendees appreciated the quality of the lectures in the morning, of the tutorial sessions in the afternoon and of the organisation of the workshop.
They were happy and enthusiastic about the learning experience.
They would recommend this event to a friend/colleague.

Some positive comments have been reported below.

1) Everything was very clear. Lecturers tried to explain topics carefully and illustrated challenging parts with everybody known examples.

2) A huge variety of quantum chemistry topics are covered in a very systematic way easy to adsorb. Very clear, communicative, approachable friendly environment. Looking forwards for more like these.

3) Thanks for the fantastic workshop.

4) Excellent talks by S. Casassa, G. Mallia, M. Alfredsson. Very useful information for understanding fundamentals concepts. Tutorial session was a great opportunity to gain hand-on experience.

5) Lectures were very nice.

6) Thanks a lot for organizing the workshop and taking care of us.

7) Very interesting talks!

8) Very good organisation. Thank you a lot for this very nice week full of knowledge and interested exchange.

9) Good tutorial content and very useful insights.

10) Good venue overall for a workshop this size.

11) Very nicely designed and a very useful course.

12) Overall the workshop was very rich and provides the ground and the tools to start running crystal.

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