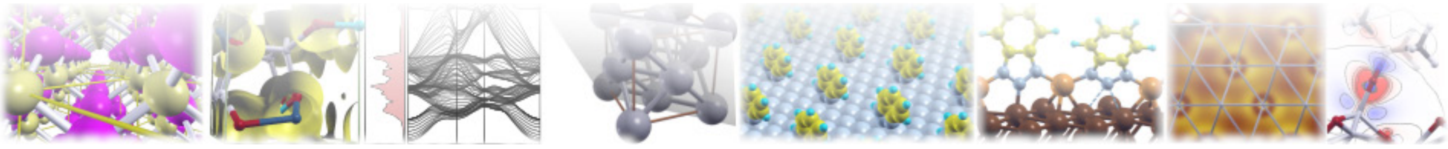
QUANTUM ESPRESSO

September 15–20, 2019
Ljubljana, Slovenia

Summer School on Advanced Materials and Molecular Modelling



# BOOK OF ABSTRACTS

September 15 – 20, 2019
Jožef Stefan Institute, Ljubljana

QUANTUM ESPRESSO FOUNDATION

MAX DRIVING THE EXASCALE TRANSITION

Jožef Stefan Institute
Ljubljana, Slovenija

cecam
Centre Européen de Calcul Atomique et Moléculaire

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BOOK OF ABSTRACTS: Quantum ESPRESSO Summer School on Advanced Materials and Molecular Modelling

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Ljubljana, Slovenia, 2019

# School Motivation

The aim of the ***Summer School on Advanced Materials and Molecular Modelling with Quantum ESPRESSO*** is to introduce students, postdocs, and other researchers to materials and molecular modelling with Quantum ESPRESSO. The school covers basic concepts as well as recent advances and developments, with emphasis on density-functional-theory based methods and high-performance computing. It follows a two-decade-long tradition of Quantum ESPRESSO training courses that have been held all over the world and is part of an ongoing effort of the MaX CoE to widen the scope of its action to European countries outside the consortium.

# Sponsors

QUANTUM ESPRESSO FOUNDATION

MAX DRIVING THE EXASCALE TRANSITION

Jožef Stefan Institute Ljubljana, Slovenija

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# Organizers

***Stefano Baroni*** *(SISSA, Trieste)*

***Anton Kokalj*** *(Jožef Stefan Institute, Ljubljana)*

***Ivor Lončarić*** *(Ruđer Bošković Institute, Zagreb)*

***Antun Balaž*** *(Institute of Physics Belgrade)*

# Acknowledgments

*A special acknowledgment goes to:*

***Matic Poberžnik*** *(organization & logistics, implementation of school virtual-machine),*
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***Barbara Kapun, Dolores Zimerl****,* ***Tatjana Močnik*** *and* ***Francesca Garofalo*** *(administration),*

*Networking Infrastructure Centre for making the HPC facilities available for the school,*

*Department of Knowledge Technologies (E8) and Department of Communication Systems (E6) for making their video-classroom available for the school,*

*and all others who contributed.*

*Help from personnel of the Department of Physical and Organic Chemistry at Jožef Stefan Institute is much appreciated and acknowledged.*

# Special Guest Lecturers

***Željko Šljivančanin*** *(Institute of Nuclear Sciences, Vinča)*

***Iurii Timrov*** *(EPLF, Lausanne)*

***Dino Novko*** *(Institute of Physics, Zagreb)*

# Lecturers

***Stefano Baroni*** *(SISSA, Trieste)*

***Anton Kokalj*** *(Jožef Stefan Institute, Ljubljana)*

***Paolo Giannozzi*** *(DMIF, Udine)*

***Pietro Delugas*** *(SISSA, Trieste)*

***Iurii Timrov*** *(EPLF, Lausanne)*

***Giovanni Pizzi*** *(EPLF, Lausanne)*

***Carlo Cavazzoni*** *(CINECA, Bologna)*

***Pietro Bonfa*** *(Università degli Studi di Parma, Parma)*

# Tutors

***Andrea Urru*** *(SISSA, Trieste)*

***Yusuf Shaidu*** *(SISSA, Trieste)*

***Oscar Baseggio*** *(SISSA, Trieste)*

***Nicola Spallanzani*** *(CINECA, Bologna)*

***Matic Poberžnik*** *(Jožef Stefan Institute, Ljubljana)*

***Matej Huš*** *(National Institute of Chemistry, Ljubljana)*

***Drejc Kopač*** *(National Institute of Chemistry, Ljubljana)*

***Andrijana Solajić*** *(Institute of Physics, Belgrade)*

***Jelena Pešič*** *(Institute of Physics, Belgrade)*

***Milan Jocić*** *(Institute of Physics, Belgrade)*

***Srđan Stavrić*** *(Institute of Nuclear Sciences, Belgrade)*

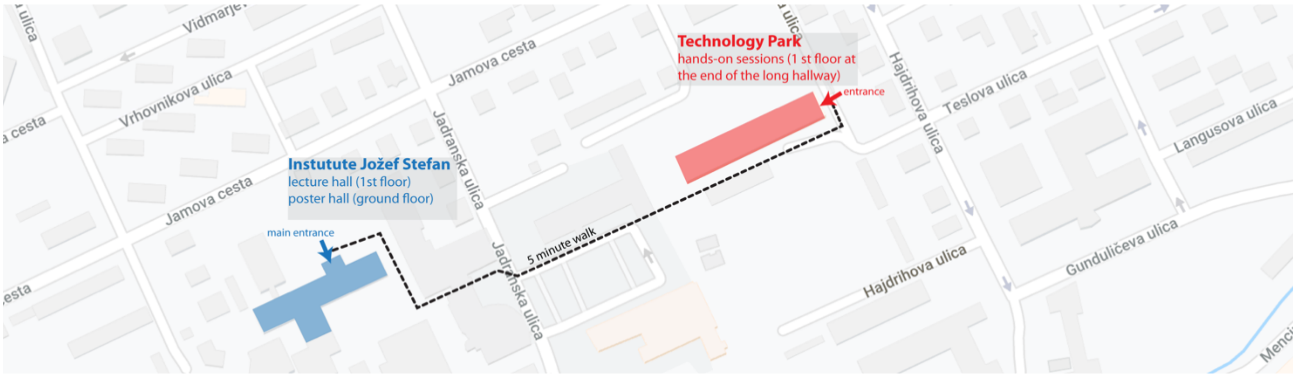
# Where & When?

***QE 2019 Summer School Summer School on Advanced Materials and Molecular Modelling with Quantum ESPRESSO*** takes place at the Jožef Stefan Institute (Jamova 39, Ljubljana, Slovenia) from 15 to 20 September 2019.

In particular:

- **lectures** take place at lecture hall @ Jožef Stefan Institute (blue colored on below map),
- **hands-on exercises** take place at video classroom @ Technology Park (red colored).

# Venue map



# Map of restaurants and canteens

# Program of the QE-2019 Summer School

Color code: ***Lecture*** (lecture-hall) ***Hands-on*** (classroom)

## DAY 0: Sunday, September 15 *(Basic introductory lectures)*

| | |
|---|---|
| **14:00 – 14:45** | **Anton Kokalj**<br>*A chemist view of bonding & a very informal intro to Bloch theorem: from molecules to solids and back* |
| **14:45 – 15:00** | *Coffee break* |
| **15:00 – 18:00** | **Stefano Baroni**<br>*Broad overview of theoretical methods: DFT, pseudopotentials, plane waves. Finite vs. infinite systems: supercells and k-points. Signal analysis: FFTs and the Nyqvist-Shannon theorem.* |
| | *Registration* |
| **18:00 – 19:00** | *Small welcome party: snacks & beverages* |

## DAY 1: Monday, September 16

| | |
|---|---|
| **8:00 – 8:50** | *Registration & participant's computer setup check* |
| **8:50 – 9:00** | *Opening remarks & general instructions* |
| **9:00 – 10:30** | **Paolo Giannozzi and Pietro Delugas**<br>*Quantum ESPRESSO: overview and basic functionalities. The self-consistent cycle. PBC: supercells and k-point sampling.* |
| **10:30 – 11:00** | *Coffee break* |
| **11:00 – 12:30** | **Paolo Giannozzi and Pietro Delugas (contd).**<br>*Charge densities and potentials. Systems in 0-1-2-3D. Metals vs. insulators. Non-magnetic vs. magnetic systems.* |
| **12:30 – 14:00** | *Lunch* |
| **14:00 – 14:30** | *Participant's computer setup check (contd).* |
| **14:30 – 18:00** | Hands-on. **Anton Kokalj, Pietro Delugas, Andrea Urru, Matic Poberžnik, Andrijana Solajić, Jelena Pešić**<br>*Installation. SCF + basic post-processing. XCrySDen, PWgui, QE-emacs-modes, PWTK (basics). Exercises.* |
| **18:00 – 18:30** | *Coffee break* |
| **18:30 – 19:30** | Special guest lecture – **Željko Šljivančanin**<br>*A short introduction to physics and chemistry at crystalline surfaces* |

## DAY 2: Tuesday, September 17

| | |
|---|---|
| **9:00 – 10:30** | **Paolo Giannozzi and Anton Kokalj**<br>*Forces, stresses, geometry optimisation. Chasing saddle points: the NEB method* |
| **10:30 – 11:00** | *Coffee break* |
| **11:00 – 12:30** | **Paolo Giannozzi**<br>*Advanced functionals: higher accuracy (hybrids), strongly correlated materials (DFT+U), weakly bound systems (van der Waals)* |
| **12:30 – 14:00** | *Lunch* |
| **14:00 – 18:00** | Hands-on. **Anton Kokalj, Iurii Timrov, Yusuf Shaidu, Matic Poberžnik, Matej Huš, Srdjan Stavrić**<br>*Optimizations, NEB, functionals. Automating the workflow with PWTK.* |
| **18:00 – 18:30** | *Coffee break* |

| | |
|---|---|
| **18:30 – 19:30** | Special guest lecture – **Iurii Timrov**<br>*First-principles quantum simulations of correlated materials using Hubbard-corrected density-functional (perturbation) theory* |

## DAY 3: Wednesday, September 18

| | |
|---|---|
| **9:00 – 10:30** | **Stefano Baroni**<br>*Density-functional perturbation theory: phonons* |
| **10:30 – 11:00** | *Coffee break* |
| **11:00 – 12:30** | **Iurii Timrov**<br>*Time-dependent density-functional (perturbation) theory: optical absorption and electron energy loss spectroscopies* |
| **12:30 – 14:00** | *Lunch* |
| **14:00 – 18:00** | Hands-on. **Iurii Timrov, Oscar Baseggio, Andrea Urru, Milan Jocić**<br>*(TD) DFPT* |
| **18:00 – 18:30** | *Coffee break* |
| **18:30 – 21:00** | **Elevator pitches + poster session (part I)** |

## DAY 4:Thursday, September 19

| | |
|---|---|
| **9:00 – 10:30** | **Giovanni Pizzi**<br>*High-throughput computing with the AiiDA platform* |
| **10:30 – 11:00** | *Coffee break* |
| **11:00 – 12:30** | Hands-on. **Giovanni Pizzi, Nicola Spallanzani, Pietro Bonfà**<br>*Hands-on AiiDA* |
| **12:30 – 14:00** | *Lunch* |
| **14:00 – 16:30** | Hands-on. **Giovanni Pizzi, Nicola Spallanzani, Pietro Bonfà**<br>*Hands-on AiiDA* |
| **16:30 – 17:00** | *Coffee break* |
| **17:00 – 18:00** | Special guest lecture – **Dino Novko**<br>*Equilibrium and ultrafast vibrational dynamics from first principles* |
| **18:00 – 18:30** | *Coffee break* |
| **18:30 – 21:00** | **Elevator pitches + poster session (part II)** |

## DAY 5: Friday, September 20

| | |
|---|---|
| **9:00 – 10:30** | **Carlo Cavazzoni and Pietro Bonfà**<br>*Quantum ESPRESSO on HPC and GPU systems: parallelisation and hybrid architecture* |
| **10:30 – 11:00** | *Coffee break* |
| **11:00 – 12:30** | Hands-on. **Pietro Bonfà, Carlo Cavazzoni, Pietro Delugas, Drejc Kopač, Milan Jocić**<br>*Hands-on QE on HPC and GPU systems* |
| **12:30 – 14:00** | *Lunch* |
| **14:00 – 16:30** | Hands-on. **Pietro Bonfà, Carlo Cavazzoni, Pietro Delugas, Drejc Kopač, Milan Jocić**<br>*Hands-on QE on HPC and GPU systems* |
| **16:30 – 16:45** | *Break* |
| **16:45 – 17:00** | **Poster prize award & Closing remarks** |

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# Invited special guest lectures

### Invited special guest lecture

## A short introduction to physics and chemistry at crystalline surfaces

Dr. ŠLJIVANČANIN, Željko [1]

[1] *Institute of Nuclear Sciences, Vinča*

**Corresponding Author**: zeljko@vinca.rs

After a brief account of the most common ideal crystalline surfaces and their basic properties, I will describe the interaction of surfaces with atomic and molecular adsorbates. This will include modeling of simple chemical reactions at metal surfaces and the role played by structural defects. Then I will focus on graphene and efforts to modify its electronic properties via controlled hydrogenation.

Results from DFT calculations will be compared with those from the experiments, obtained using techniques such as scanning tunneling microscopy and temperature programmed desorption.

### Invited special guest lecture

## First-principles quantum simulations of correlated materials using Hubbard-corrected density-functional (perturbation) theory

Dr. TIMROV, Iurii [1]

[1] *École Polytechnique Fédérale de Lausanne*

**Corresponding Author**: iurii.timrov@epfl.ch

DFT+U and DFT+U+V are simple and powerful tools to model correlated systems containing partially-filled manifolds of localized d and f states [1]. However, the Hubbard U (on-site) and V (inter-site) parameters are often treated semi-empirically, which is a somewhat unsatisfactory approach. Conceptual and practical methods to determine e.g. the Hubbard U parameter from first principles have nevertheless been introduced long ago, based either on the constrained random-phase approximation or on linear-response theory [2]. Nonetheless, these approaches are often overlooked due to their cost and/or complexity. Here, we introduce a computationally inexpensive and straightforward approach to determine on-site U and inter-site V [3], hitherto obtained from the difference between bare and self-consistent inverse electronic susceptibilities evaluated from supercell calculations. By recasting these calculations in the language of density-functional perturbation theory (DFPT) [4] we remove the need of supercells, and allow for a fully automated determination of Hubbard parameters. Such developments open the way for deployment in high-throughput studies, while providing the community with a simple tool to calculate consistent values of U and V for any system at hand. The approach has been implemented in the Quantum ESPRESSO package [5] and is showcased with applications to selected transition-metal compounds. Lastly, we will discuss the effect of Hubbard corrections on the calculation of formation energies of systems with defects [6], phonons [7], and near-edge X-ray absorption fine structure [8].

References:
[1] V.I. Anisimov, J. Zaanen, O.K. Andersen, Phys. Rev. B 44, 943 (1991).
[2] M. Cococcioni and S. de Gironcoli, Phys. Rev. B 71, 035105 (2005).
[3] I. Timrov, N. Marzari and M. Cococcioni, Phys. Rev. B 98, 085127 (2018).
[4] S. Baroni, S. de Gironcoli, A. Dal Corso, P. Giannozzi, Rev. Mod. Phys. 73, 515 (2001).
[5] P. Giannozzi et al., J. Phys.: Condens. Matter 29, 465901 (2017).
[6] C. Ricca, I. Timrov, M. Cococcioni, N. Marzari, U. Aschauer, Phys. Rev. B 99, 094102 (2019).
[7] A. Floris, I. Timrov, B. Himmetoglu, S. de Gironcoli, N. Marzari, M. Cococcioni, in preparation.
[8] I. Timrov, P. Agrawal, S. Erat, A. Braun, M. Cococcioni, M. Calandra, N. Marzari, D. Passerone, in preparation.

**Invited special guest lecture**

## Equilibrium and ultrafast vibrational dynamics from first principles

Dr. NOVKO, Dino [1]

[1] *Institute of Physics, Zagreb*

**Corresponding Author**: dino.novko@gmail.com

Raman spectroscopy is a powerful and widely used technique for structural characterization and quality assessment of quasi-two-dimensional and layered materials. This tool under ultrafast transient conditions can as well be utilized to investigate the photo-induced phonon or nuclear dynamics. Here I present a theoretical framework based in first principles that is able to simulate both equilibrium and non-equilibrium dynamics of phonons in metallic systems. The main relaxation mechanism in this approach is coupling between thermalized/hot electrons and system phonons (i.e., nonadiabatic electron-phonon coupling). Using this general theory I explain the anomalous Raman spectrum of MgB2 and further reveal a laser-excited non-equilibrium dynamics of E2g phonon mode in this superconductor [1,2]. As another exciting example, I simulate Raman spectra of several single-layer transition metal dichalcogenides doped with field-effect technique [3] and show how the adiabatic Born-Oppenheimer approximation breaks down unexpectedly in these cases as well.

References:

[1] D. Novko, Phys. Rev. B 98, 041112(R) (2018).
[2] D. Novko, F. Caruso, C. Draxl, E. Cappelluti, arXiv:1904.03062, (2019)
[3] B. Chakraborty et al.,Phys. Rev. B 85, 161403(R) (2012)

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# List of lectures and hands-on sessions

### Lecture 1

A chemist view of bonding & a very informal intro to Bloch theorem: from molecules to solids and back

Anton Kokalj
*Jožef Stefan Institute, Ljubljana, Slovenia*

### Lecture 2

Broad overview of theoretical methods: DFT, pseudopotentials, plane waves. Finite vs. infinite systems: supercells and k-points. Signal analysis: FFTs and the Nyqvist-Shannon theorem.

Stefano Baroni
*SISSA, Trieste, Italy*

### Lecture 3

Quantum ESPRESSO: overview and basic functionalities. The self-consistent cycle. PBC: supercells and k-point sampling.

Paolo Giannozzi [1] and Pietro Delugas [2]
[1] *DMIF, Udine, Italy;* [2] *SISSA, Trieste, Italy*

### Lecture 4

Charge densities and potentials. Systems in 0-1-2-3D. Metals vs. insulators. Non-magnetic vs. magnetic systems.

Paolo Giannozzi [1] and Pietro Delugas [2]
[1] *DMIF, Udine, Italy;* [2] *SISSA, Trieste, Italy*

### Lecture 5

Forces, stresses, geometry optimisation. Chasing saddle points: the NEB method

Paolo Giannozzi [1] and Anton Kokalj [2]
[1] *DMIF, Udine, Italy;* [2] *Jožef Stefan Institute, Ljubljana, Slovenia*

### Lecture 6

Advanced functionals: higher accuracy (hybrids), strongly correlated materials (DFT+U), weakly bound systems (van der Waals)

Paolo Giannozzi
*DMIF, Udine, Italy*

### Lecture 7

Density-functional perturbation theory: phonons

Stefano Baroni
*SISSA, Trieste, Italy*

### Lecture 8

Time-dependent density-functional (perturbation) theory: optical absorption and electron energy loss spectroscopies

Iurii Timrov
*EPLF, Lausanne, Switzerland*

### Lecture 9

High-throughput computing with the AiiDA platform

Giovanni Pizzi
*EPLF, Lausanne, Switzerland*

### Lecture 10

Quantum ESPRESSO on HPC and GPU systems: parallelisation and hybrid architecture

Carlo Cavazzoni [1] and Pietro Bonfà [2]
[1] *CINECA, Bologna, Italy;* [2] *Università degli Studi di Parma, Parma, Italy*

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### Hands-on session 1

SCF + basic post-processing. XCrySDen, PWgui, QE-emacs-modes, PWTK (basics). Exercises.

Anton Kokalj, Pietro Delugas, Andrea Urru, Matic Poberžnik, Andrijana Solajić, Jelena Pešić

### Hands-on session 2

Optimizations, NEB, functionals. Automating the workflow with PWTK.

Anton Kokalj, Iurii Timrov, Yusuf Shaidu, Matic Poberžnik, Matej Huš, Srdjan Stavrić

### Hands-on session 3

(TD) DFPT

Pešić Iurii Timrov, Oscar Baseggio, Andrea Urru, Milan Jocić

### Hands-on session 4

Hands-on AiiDA

Giovanni Pizzi, Nicola Spallanzani, Pietro Bonfà

### Hands-on session 5

Hands-on QE on HPC and GPU systems

Pietro Bonfà, Carlo Cavazzoni, Pietro Delugas, Drejc Kopač, Milan Jocić

# Poster session (part I)

**Poster session (part I)** / ①

## DFT calculation of dielectric properties for alloys

BUBAŠ, Matej [1]; Dr. SANCHO PARRAMON, Jordi [1]

[1] *Ruđer Bošković Institute*

**Corresponding Author:** mbubas@irb.hr

Electromagnetic response of a metal can be modified by changing its shape and thickness, within the limits defined by properties of that metal. Key properties of electromagnetic response can be inferred from the dielectric function.

Alloying can be another way of tuning the electromagnetic response, and thus the dielectric function of a metal. However, without any prior knowledge of the dependence of dielectric function on the alloy composition, cumbersome experimental exploration of that dependence has to be undertaken. Therefore, a theoretical approach to dielectric function determination using density functional theory (DFT) can prove to be very useful. For that purpose, we are presenting a theoretical framework for dielectric function calculation for alloys, with preliminary results comparing different methods.

**Poster session (part I)** / ③

## Co-transformation of methane and water using atomically precise gold clusters on titania

**Author:** Ms. MADRIDEJOS, Jenica Marie [1]

**Co-Authors:** Dr. LI, Nannan [2]; Prof. METHA, Gregory [1]

[1] *The University of Adelaide*

[2] *Sungkyunkwan University*

**Corresponding Author:** jenicamarie.madridejos@adelaide.edu.au

Regarded as the principal component of natural gas, methane (CH4) is usually converted into longer hydrocarbons via syngas route which requires high temperatures ($T > 800^{\circ}C$). To lower the energy required for direct methane to methanol (DMTM) process, a suitable catalyst that promotes C-H bond activation is required. In theory, it has been established that gold nanoparticles can promote the delicate oxidation of CH4 by oxygen (O2) due to charge transfer. Our current experimental studies have shown the efficiency of chemically synthesised, ligand-stabilised gold clusters on TiO2 in transforming methane to desired higher valued products. In addition, we propose two mechanistic pathways of the adsorption and co-conversion of methane and water into our desired products using density functional theory.

### Poster session (part I) / ⑤

## A first-principles study of the switching mechanism in InSbTe-GeTe superlattices

**Author**: Dr. RIBALDONE, Chiara [1]

**Co-Authors**: Dr. DRAGONI, Daniele [2]; Prof. BERNASCONI, Marco [2]

[1] *University of Milano - Bicocca*

[2] *University of Milano-Bicocca*

**Corresponding Author**: c.ribaldone1@campus.unimib.it

Interfacial phase change memories (iPCMs) based on Sb2Te3-GeTe superlattices have been recently proposed as an alternative candidate to conventional GST-based PCM for the realization of device with improved performances. The switching mechanism was proposed to involve crystalline to crystalline structural transitions, associated with a rearrangement of the stacking sequence in the GeTe bilayers. Density functional theory calculations have shown that such rearrangement could be achieved by means of a two-step process with an activation barrier for the flipping of Ge and Te atoms which is sensible to the biaxial strain acting on the GeTe bilayers. Within this framework, strain engineering on GeTe bilayers in Sb2Te3-GeTe superlattices could be exploited to further reduce the activation barrier for the switching process, improving iPCMs performances. In the present work, InSbTe-GeTe superlattices with different compositions are studied by means of density functional theory as implemented by the Quantum Espresso suite of programs, aiming at exploit the large mismatch (3.8\%) in the in-plane lattice parameters between In3SbTe2 and GeTe to reduce the activation barrier for the Ge/Te rearrangement as compared to Sb2Te3-GeTe.
Among the compositions studied, the In3SbTe2-(GeTe)3 superlattice features the most promising properties for applications in iPCMs: it exhibits a biaxial tensile strain of GeTe bilayer equal to 1.95\%, retaining at the same time a crystal structure similar to the low resistance state of Sb2Te3-(GeTe)2 superlattice, with the GeTe bilayers block separated by the In3SbTe2 layers. The transformation into a possibly high resistance state was therefore investigated, following the same path proposed by Yu and Robertson for the Sb2Te3-(GeTe)2 superlattice. As expected, the activation barriers for the switching process are indeed lower than those obtained for the Sb2Te3-(GeTe)2 superlattice. In order to verify the existence of a contrast in the electric conductivity between the proposed high and low resistance configurations, the electric conductivity tensors for the two structures were computed as implemented in the BoltzWann code. The two configurations display a contrast in the electric conductivity of about an order of magnitude along the growth direction, that is sufficient to distinguish the high and the low resistance states.

These results show that it is indeed possible to exploit strain engineering, by properly selecting different blocks in chalcogenide superlattices, to reduce the activation barriers for the switching process, and thus the power consumption in interfacial phase change memories.

**Poster session (part I)** / 7

# Scrutinizing the bonding of 2-mercaptobenzimidazole on Cu(111) by STM and DFT

**Author**: Ms. VAN MIDDEN, Marion Antonia [1]

**Co-Authors**: Dr. LOZINŠEK, Matic [2]; Dr. ZUPANIČ, Erik [1]; Dr. KOKALJ, Anton [2]

[1] *Jožef Stefan Institute, Ljubljana*

[2] *Jožef Stefan Institute*

**Corresponding Author**: marion.van.midden@ijs.si

Interfacial structures resulting from the interaction between the Cu(111) surface and a well-known corrosion inhibitor 2-mercaptobenzimidazole [1] were investigated by a combined experimental and computational-modeling approach employing scanning tunneling microscopy (STM) and density functional theory (DFT), respectively.
For STM studies the molecules were evaporated on an atomically flat clean Cu(111) substrate in ultra high vacuum (UHV). Varying the deposition rate and substrate temperatures resulted in different self-assembled structures on the surface which were studied using a Nanonis JT STM operated in UHV at temperatures close to liquid helium. Spectroscopy measurements taken on different compositions of molecules clearly show strong coupling with the substrate resulting in smeared HOMO and LUMO orbitals.
Several different models of 2-mercaptobenzimidazole bonding to the Cu(111) surface have been evaluated by DFT calculations. Comparison of simulated and experimental images allowed us to determine the structures of the self assembled monolayers elucidating the bonding mechanisms of 2-mercaptobenzimidazole on Cu(111).

### Poster session (part I) / 9

# Superhydrophobic surface on aluminium based on alkyl and perfluoroalkyl silanes

**Author:** Dr. RODIČ, Peter [1]

**Co-Author:** Prof. MILOŠEV, Ingrid [1]

[1] *Jožef Stefan Institute*

**Corresponding Author:** peter.rodic@ijs.si

Aluminium is one of the most important metals in modern engineering industry due to superior physical and mechanical properties. Its corrosion resistance is based on compact and chemically stable passive oxide film that is spontaneously formed on the surface. However, in more corrosive environments such as sodium chloride solution, chloride ions may attack aluminium surface, therefore, it is prone to corrosion.

To delay such corrosion event, various methods have been suggested. One of the most appropriate is surface modification to obtain the superhydrophobic surface [1]. In such a case, the water contact angle is greater than 150° and a sliding angle less than 10°. Such extreme water-repellent properties show self-cleaning and anti-icing effects, therefore superhydrophobicity has been attracted over the last decade in both academic and industrial areas [1,2].

The superhydrophobic surface can be obtained in accordance with two key factors: micro-nanoscale structure and low surface energy. The micro-nanoscale structure can be achieved by well-accepted chemical etching method in acidic solution. The low surface energy can be achieved by surface treatment with (perfluoro)alkyl silanes [3] which are chemically bonded on the aluminium surface with Al-O-Si bonds [4,5].

The goal of this research was to reveal the mechanism of surface treatment using (perfluoro)alkyl silanes, followed by performing surface characterisation. The coatings were prepared by a two-step process during etching process in HCl/H2O2 solution. Then samples were immersed in ethanol solution containing octyltrimethoxysilane (AS-8) or 1H,1H,2H,2H-perfluorooctyltrimethoxysilane (FAS-8). The surface characterization was performed using contact profilometry, scanning electron microscopy (SEM), ATR-FTIR spectroscopy and optical tensiometer. The corrosion properties were evaluated using electrochemical measurements.

Both modified aluminium surfaces provide highly efficient corrosion-resistant properties during immersion in 0.1 M NaCl solution. However, higher water repellence shows aluminium modified with perfluoroalkyl silane, that also shows self-cleaning and icing delay.

References:

[1] N. J. Shirtcliffe, G. McHale, S. Atherton, M. I. Newton, An introduction to superhydrophobicity, Adv. Colloid. Interface. Sci., 161 (2010) 124–138.

[2] I. Milošev, T. bakarič, S. Zanna, A. Seyeux, P. Rodič, M. Poberžnik, F. Chiter, P. Cornett, D. Costa, A. Kokalj, P. Marcus, Electrochemical, surface-analytical, and computational DFT study of alkaline etched aluminium modified by carboxylic acids for corrosion protection and hydrophobicity, J. Electrochem. Soc., 166 (2019) C1–C6.

[3] P. Rodič, I. Milošev, One-step ultrasound fabrication of corrosion resistant, self-cleaning and anti-icing coatings on aluminium, Surf. Coat. Technol., 369 (2019) 175–185.

[4] M. Poberžnik, D. Costa, A. Hemeryck, A. Kokalj, Insight into the Bonding of Silanols to Oxidized Aluminum Surfaces, J. Phys. Chem. C., 122 (2018) 9417–9431.

[5] M. Poberžnik, A. Kokalj, Implausibility of bidentate bonding of the silanol headgroup to oxidized aluminum surfaces, Appl. Surf. Sci., In press (2019).

### Poster session (part I) / 11

## Symmetric spin initialization: a new powerful tool for computational materials discovery

**Author:** Mr. GALASSO, Michele [1]

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We present a new method that has been recently implemented in the evolutionary algorithm USPEX for the initialization of magnetic moments in crystals. The method is based on an empirical observation: the majority of the antiferromagnetic materials known today has a ground state in which the different atomic spin states break symmetry only up to a subgroup of index 2 with respect to the parent space group of the paramagnetic phase. Therefore, with our method, magnetic structures are generated in USPEX by imposing this symmetry criterion. In addition, a new calculation regime has been implemented in USPEX for the search of the ground magnetic state with fixed geometry. Two tests of our method have been performed, respectively for the optimization of structural and magnetic degrees of freedom and for the optimization of only magnetic degrees of freedom in the newly implemented calculation regime. The first test shows an improved sampling of the free energy surface of Fe12O18 , while the second test correctly reproduces the ground state of hematite at the first generation. The problem of computing the U correction for DFT+U has also been addressed. Using linear response theory, a value of U = 7.6 eV has been obtained for hematite.

### Poster session (part I) / 13

## Understanding trends in lithium binding at two-dimensional materials

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Layered structure and peculiar electronic properties of two-dimensional (2D) materials foster the concept of utilizing them as main components of lithium-ion batteries. Understanding basic physical mechanisms governing the interaction of Li with 2D crystals is of key importance to succeeding in a rational design of cathode and anode materials with superior functionalities. Study of Li atoms adsorbed at graphene clearly shows that Li atoms, featuring a long-ranged electrostatic repulsion, are individually dispersed across the surface [1]. This was a motivation for the further investigation of Li adsorption at a number of different 2D materials. In this study density functional theory was applied to reveal the microscopic picture of Li interaction with 15 2D crystals, including several transition metal oxides and dichalcogenides, carbides of Group XIV elements, functionalized graphene, silicene, and germanene, as well as black phosphorus and Ti2C MXene [2]. We found that the general trend in Li binding can be estimated from positions of conduction band minima of 2D materials since the energy of the lowest empty electronic states shows a nice correlation with the strength of Li adsorption. At variance to the majority of studied surfaces where the electron transferred from Li is spread across the substrate, in monolayers of carbides of Group XIV elements the interaction with Li and the charge transfer are well localized. This gives rise to their capability to accommodate Li structures with a nearly constant binding energy of alkaline atoms over Li coverages ranging from well-separated adatoms to a full monolayer.

References:

[1] S. Stavrić, M. Belić, Ž. Šljivančanin, Carbon 96, 216 (2016)
[2] S. Stavrić, Z. S. Popović, Ž. Šljivančanin, Phys. Rev. Mater. 2, 11407 (2018)

Poster session (part I) / ⑮

# Electron-phonon interaction and superconductivity in graphene doped with metal atoms

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With its outstanding mechanical and electrical properties [1,2], graphene is predicted to have a plenty of applications and has gained enormous research focus in last years. Furthermore, its already superb properties can easily be tuned by various structure manipulations including the applied strain, controlled defects, exposure to electrical or magnetic field, or doping. As opposed to pristine graphene, when doped with some alkali metal atoms adsorbed on its surface in a manner similar to the graphite intercalation compounds, graphene becomes superconducting, with critical temperatures up to 11K [3,4]. This raised an interest in research of superconductivity in graphene, which is not present in its pristine form. Here we investigate the electron-phonon interaction several structures based on graphene doped with metal atoms. In the framework of density functional theory and Eliashberg theory, we calculate the electron-phonon coupling and estimate the superconducting critical temperatures.

References:
[1] Katsnelson, M., Novoselov, K., Geim, A., Nat. Phys. 2(9), 620–625 (2006)
[2] Bolotin, K., Sikes, K., Jiang, et al., Solid State Commun. 146(9), 351–355 (2008)
[3] Profeta, G., Calandra, M., Mauri, F., Nat. Phys. 8(2), 131–134 (2012)
[4] Pešić, J., Gajić, R., Hingerl, K., Belić, M., EPL 108(6), 67005 (2014)

Poster session (part I) / 17

# Identification of potential human proteins responsible for anticarcinogenic and anti-neuroinflammatory effects of curcumin by inverse molecular docking

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Research efforts are placing an ever increasing emphasis on identifying signal transduction pathways related to the chemopreventive activity of curcumin. Its anticarcinogenic effects are presumably mediated by the regulation of signaling cascades, including nuclear factor κB (NF-κB), activator protein 1 (AP-1), and mitogen-activated protein kinases (MAPK). By modulating signal transduction pathways, curcumin induces apoptosis in malignant cells, thus inhibiting cancer development and progression. Due to the lack of mechanistic insight in the scientific literature, we developed a novel inverse molecular docking protocol based on the CANDOCK algorithm. For the first time, we performed inverse molecular docking of curcumin into a collection of 13,553 available human protein structures from the Protein Data Bank resulting in prioritized target proteins of curcumin. Our predictions were in agreement with the scientific literature and confirmed that curcumin binds to folate receptor β, DNA (cytosine-5)-methyltransferase 3A, metalloproteinase-2, mitogen-activated protein kinase 9, epidermal growth factor receptor and apoptosis-inducing factor 1. We also identified new potential protein targets of curcumin, namely deoxycytidine kinase, NAD-dependent protein deacetylase sirtuin-1 and -2, ecto-5′-nucleotidase, core histone macro-H2A.1, tyrosine-protein phosphatase non-receptor type 11, macrophage colony-stimulating factor 1 receptor, GTPase HRas, aflatoxin B1 aldehyde reductase member 3, aldo-keto reductase family 1 member C3, amiloride-sensitive amine oxidase, death-associated protein kinase 2 and tryptophan-tRNA ligase, that may all play a crucial role in its observed anticancer effects. Moreover, our inverse docking results showed that curcumin potentially binds also to the proteins cAMP-specific 3′,5′-cyclic phosphodiesterase 4D and 17-β-hydroxysteroid dehydrogenase type 10, which provides a new explanation for its efficiency in the treatment of Alzheimer’s disease. We firmly believe that our computational results will complement and direct future experimental studies on curcumin’s anticancer activity as well as on its therapeutic effects against Alzheimer’s disease.

### Poster session (part I) / ⑲

# Magnetic interaction of Mn and Cr atoms on Ag(001) modified by graphene adsorption

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We study the magnetic exchange interaction between Mn or Cr atoms adsorbed on Ag(001) surface by DFT as implemented in Quantum Espresso package. First we relax the structures in ferromagnetic spin configuration. Then, we calculate the total energies of various spin configurations in the obtained geometric configurations and obtain that the lowest energy spin configuration is antiferromagnetic for both kinds of adatoms. The same is obtained by fitting the Hamiltonian of Ising form to the DFT energies and obtaining the exchange parameters.

We then turn to case of same system as before, but with graphene adsorbed on the adatoms. The structure is again relaxed in the ferromagnetic configuration and energies of various spin configurations are again calculated. The result is that the lowest energy spin configuration remains antiferromagnetic for Cr adatoms, while it changes for Mn adatoms.

Since bonding with graphene broke symmetry between the adatoms, the system is relaxed in the minimum energy spin configurations and the energies are calculated again for sake of self-consistency, which is obtained already in first step. The relaxation however shows that the relation between the DFT energies of different spin configurations in same geometric configuration changes drastically with relaxation, as do the distances between the adatoms, which points to strong magnon-phonon coupling in the system. The Ising model may not be as appropriate in this case as in the case without graphene, but it follows the DFT results for the some part, and also shows that the exchange parameters change significantly upon change of geometry.

### Poster session (part I) / 21

## Electron scattering on impurities characterized by a strong electron-phonon coupling

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In semiconducting materials, like transition-metal oxides [1-3] and organic semiconductors [4,5], one may easily imagine impurities characterized by a strong electron-phonon coupling (polaronic impurities), as a source of scattering for electrons. Although similar problems have been investigated before in the context of electron tunneling across microscopic junctions, nanowires and quantum dots [6,7], to the best of our knowledge, effects of polaronic impurities on the charge transport in bulk systems have not been addressed so far. Thus, we described, in a close form, the exact solutions of the electron scattering on a phonon degree of freedom within the Green function formalism, establishing a connection between the T-matrix and Feynman diagrams to all orders in electron-phonon interaction. Using this formalism, we calculated electron partial scattering cross sections for elastic and inelastic processes and analyzed dependence of the total scattering cross section on the impurity orbital energy and strength of electron-phonon coupling. In addition, temperature dependence of the electron mobility is analyzed for various model parameters.

References:

[1] A. J. Bosman, H. J. van Daal, Adv. Phys. 19, (1970) 1.
[2] M. Reticcioli, U. Diebold, G. Kresse, C. Franchini, Handbook of Materials Modeling: Applications: Current and Emerging Materials (eds. W. Andreoni, S. Yip, Springer, 2019).
[3] F. De Angelis, C. Di Valentin, S. Fantacci, A. Vittadini, A. Selloni, Chem. Rev. 114 (2014) 9708.
[4] F. Ortmann, S. Roche, Phys. Rev. B 84 (2011) 180302.
[5] I. Salzmann, G. Heimel, M. Oehzelt, S. Winkler, N. Koch, Acc. Chem. Res. 49 (2016) 370.
[6] N. A. Zimbovskaya, M. R. Pederson, Phys. Rep. 509 (2011) 1.
[7] N. B. Zhitenev, H. Meng, Z. Bao, Phys. Rev. Lett. 88 (2002) 226801.

### Poster session (part I) / 23

## The effect of copper coverage on perovskite support for catalytic reverse water-gas shift reaction

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The size of the active copper area on top of the SrTiO3 perovskite support can affect the selectivity and activity of the catalytic CO2 hydrogenation. Structure sensitivity has an experimentally confirmed effect on the catalytic activity relevant to industrial methanol synthesis. Here, we present a detailed theoretical study on methanol synthesis sub-reaction, the reverse water-gas shift (RWGS). We present DFT results for the RWGS pathway on 3 surfaces, namely Cu(111), SrTiO3, and the Cu/SrTiO3 interface between both surfaces. Adsorbate-adsorbate lateral interactions are taken into account for surfaces which show high intermediate coverage, and the effective cluster expansion Hamiltonian is constructed for the most abundant hydrogen adatom on Cu(111) surface. The detailed mechanism is then used in the meso-scale kinetic Monte Carlo simulations, to study the selectivity and activity for CO production in the RWGS reaction, depending on the size of Cu(111) island and Cu/SrTiO3 interface areas.

## Poster session (part I) / 25

# Probing the fluoride ion donor properties of KrF2

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The lightest reactive noble gas that forms compounds, which can be isolated in macroscopic amounts, is krypton [1]. The only compound of krypton that can be synthesised directly from the elements is KrF2. This binary fluoride is thermodynamically unstable and a very powerful oxidising and fluorinating agent. Krypton difluoride is the starting material from which all other compounds of krypton are derived [2]. Specialised low-temperature techniques for synthesis, crystallisation, isolation, and characterisation of reactive oxidising fluorine-bearing compounds are therefore required for the krypton chemistry research. The fluoride ion donor properties of KrF2 can be exploited for the synthesis of novel krypton compounds. In this work, the interaction of Lewis base KrF2 with Lewis acids of various strengths was investigated and resulted in novel coordination complexes [3] and co-crystals of KrF2. The synthesised compounds and co-crystals were characterised in the solid state by low-temperature single-crystal X-ray diffraction, low-temperature Raman spectroscopy, and additionally by quantum-chemical calculations. These compounds and co-crystals represent a significant extension of the rather limited synthetic and structural chemistry of krypton.

References:
[1] M. Lozinšek, G. J. Schrobilgen: The world of krypton revisited. Nat. Chem. 2016, 8, 732.
[2] J. F. Lehmann, H. P. A. Mercier, G. J. Schrobilgen: The chemistry of krypton. Coord. Chem. Rev. 2002, 233–234, 1–39.
[3] M. Lozinšek, H. P. A. Mercier, D. S. Brock, B. Žemva, G. J. Schrobilgen: Coordination of KrF2 to a Naked Metal Cation, Mg2+. Angew. Chem. Int. Ed. 2017, 56, 6251–6254.

### Poster session (part I) / 27

# Adsorption of azole-type corrosion inhibitors in the presence of coadsorbed corrosion-relevant species on Cu(111)

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Azoles, compounds characterized by a five-membered aromatic ring containing one nitrogen atom and at least one other heteroatom (N, S, or O), are well known for their ability to decelerate corrosion processes on copper surfaces, i.e., they often act as corrosion inhibitors. The formation of a strong inhibitor-surface bond is believed to be an essential step in achieving inhibition. However, as important as it might be, other factors, such as lateral cohesive intermolecular forces or effects of inhibitor adsorption on surface electronic properties (e.g. work-function, band-gap), should be considered as well.

In this study we utilized DFT calculations and an implicit solvent model to investigate, how coadsorbtion of some corrosion relevant species, O(ads), H(ads), OH(ads), and Cl(ads) affect intermolecular interactions and the strength of the inhibitor-surface bond both in the presence and absence of water solvent. The first three species are typically involved in cathodic corrosion reactions, either oxygen reduction or hydrogen evolution, while Cl is a well-known corrosion activator. Our calculations show that coadsorption of a $(4\times4)$ overlayer of O(ads) increases a magnitude of the binding energy of the chemisorbed azole molecule on Cu(111) by up to $0.6$ eV. Increasing the coverage of O(ads), increases the magnitude of binding energy even further and in the presence of a $(2\times2)$ overlayer of O(ads) it is by $1.0$ eV greater than on pristine Cu(111). According to our analysis, two factors contribute to this stabilization. The first is the formation of an H-bond between O(ads) and the NH fragment of the azole molecule. The second is the O(ads) induced enhancement of a direct covalent-like bond between the N atom of the chemisorbed organic molecule and the surface Cu atom. On Cu(111), coadsorbtion of O(ads) leads to the greatest enhancement of the bonding of adsorbed azole molecules, followed by Cl(ads). In contrast, OH(ads) weakens the adsorption of inhibitors and the presence of H(ads) does not significantly affect it.

Calculations further reveal, that in some cases coadsorbed O(ads) is able to promote inhibitor's N--H bond cleavage, resulting in a more stable and strongly adsorbed inhibitor molecule. These findings raise intriguing questions regarding the nature and extent of the effect that some corrosion relevant species have on the adsorption of inhibitor molecules.

# Poster session (part II)

**Poster session (part II)** / ②

# Evidence for a Linear Coordination of Ag+ in Water: a X-Ray Absorption Spectroscopy, Classical and Ab Initio Molecular Dynamics Study

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Even though many experimental and theoretical works have been devoted so far to the study of the Ag+ ion in aqueous solution, a general agreement on its coordination structure seems not to have been reached yet. In particular, its coordination number (CN) as well as the average bond distance with coordinating water molecules are far from being unambiguously determined. The picture arising from the earliest spectroscopic studies is that of a tetrahedral coordinated Ag+ in water,[1] but this structure has been more recently questioned by some X-ray absorption (XAS) works proposing higher (5 – 6) or even lower CNs, as in the case of the tetrahedrally-distorted "2+2" model.[2,3] CNs higher than four have also been obtained in many theoretical works employing both classical and ab initio molecular dynamics simulations (MD and AIMD).[4,5]

In this work, we present the results of a study combining XAS measures with MD and AIMD in which we obtained evidence for a linear coordination of the Ag+ ion in water (CN = 2). In particular, fitting procedures of the XANES (X-ray absorption near edge structure) and EXAFS (extended X-ray absorption fine structure) parts of the spectrum collected on an Ag+ solution in water have been performed and indicate the preference for a linear coordination. This structure has been obtained also by Car-Parrinello molecular dynamics simulations. In addition, a new three-site model for the Ag+ ion was developed in order to correctly reproduce the linear coordination in classical MD simulations.

References:

[1] Y. Tsutsui, K.-I. Sugimoto, H. Wasada, Y. Inada and S. Funahashi, J. Phys. Chem. A, 1997, 101, 2900–2905.

[2] J. L. Fulton, S. M. Kathmann, G. K. Schenter and M. Balasubramanian, J. Phys. Chem. A, 2009, 113, 13976–13984.

[3] I. Persson and K. B. Nilsson, Inorg. Chem., 2006, 45, 7428–7434.

[4] R. Vuilleumier and M. Sprik, J. Chem. Phys., 2001, 115, 3454–3468.

[5] R. Spezia, C. Nicolas, P. Archirel and A. Boutin, J. Chem. Phys., 2004, 120, 5261–5268.

**Poster session (part II)** / ④

# HRTEM and DFT Study of Translation States in Sb- doped ZnO

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Zink oxide crystallizes in a noncentrosymmetric wurtzite structure, s.g. P63mc, with a lattice parameters: a = 3.253 Å, c = 5.213 Å. The polar vector points along the c-axis from Zn to O atom directly above (αA). Some dopants, such as In2O3, Fe2O3, Mn2O3, Ga2O3, SiO2, SnO2, TiO2 and Sb2O3, are known to induce inversion of polarity in ZnO by generating inversion boundaries (IBs). Besides stacking faults (SFs) that are present in pure ZnO, IBs are the most common type of planar defects. Depending on the type of inversion the polar axis can be head-to-head or tail-to-tail oriented across IB. IBs predominantly lie in basal planes (b-IB), but with some dopants, such as Ga2O3, they extend along the pyramidal planes of ZnO structure (p-IB).

Here, we investigated the atomic structure of b-IBs in Sb-doped ZnO by density functional theory (DFT) calculations and high-resolution transmission electron microscopy (HRTEM). We first reviewed all the models that were reported in the literature regarding inversion boundaries and stacking faults. After a detailed analysis of the literature data, five different translational states for IBs were identified, wherein three of them were experimentally observed [1-3]. Using DFT implemented in the Quantum-ESPRESSO package, the IBs models were structurally optimized and analyzed in terms of stability for Sb-doping. In the examined cases we obtained a good match between the experimental results and the calculated ones for two of the translations. By combining theoretical results with experimental ones, we discovered a new model for Sb-doped ZnO.

References:
[1] A. Rečnik et al., J. Am. Ceram. Soc., 84 (2001) 2657.
[2] A. Goldstein et al., ACS Nano, 7 (2013) 10747.
[3] J. Hoemke et al., J. Am. Ceram. Soc., 100 (2017) 4252.

**Poster session (part II)** / 6

## Ab-initio study of proton transfer reactions between the H3O+ ion and volatile organic compounds related to cork-taint in wine

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Abstract: Cork-taint in wine has long been a serious issue for the wine industry causing large economic loses. Cork-taint is mainly caused by chloro-anisoles and bromo-anisoles while other compounds such as geosmin, guaiacol, and Sesquiterpenes contribute to a lesser degree [1, 2]. These volatile organic compound's (VOC's) are transferred from the cork of the wine bottle, and are considered objectionable and have a characteristic smell resembling a moldy newspaper, wet dog, damp cloth or damp basement that lead to wine spoiling and economic losses even at very low concentrations at few mg/L to ng/L. Determining the concentration of such VOC's in the present context (wine) requires detection techniques to be fast and real-time (~with in sec) and quantitative determination of VOC's with a detection limit as low as few parts per trillion by volume (pptv). Proton transfer reaction mass spectrometry (PTR-MS)[3] can be a technique of choice because it allows for the online monitoring of compounds with ultra low detection limits and fast response time < 100 ms. Moreover, If the proton transfer reaction rate is given, then the VOC concentration can be determined without calibration using the following equation: $\Delta[\mathrm{RH}+]\approx\kappa[\mathrm{H3O}+]0[\mathrm{R}]\Delta t$ within the drift tube of the PTR-MS instrument.

This study aims at determining the reaction rate constants of the reaction between hydronium ion and several VOC's which are considered imperative in cork-taint. We have used average dipole orientation (ADO) [4] theory of ion-neutral molecule collision to calculate rate coefficients of H3O+-VOC's reaction. ADO predicts the ion-molecule collision rate constant based on permanent dipole moment and Polarizability of organic species. We performed DFT calculations implemented in Quantum-espresso code [5] to determine electric dipole moment and Polarizability of isolated molecules and used them to estimate rate constants using ADO, classical trajectory method by Su & Chesnavich [6, 7, 8]. Also, the capture collision rate coefficients of the proton transfer reaction are calculated. Calculations have been performed at different center-of-mass energy and expressed in terms of E/N. Experimental determination of ion-molecule collision rate constants, usually associated with large errors [3]. The present calculations of rate constants using ADO theory and parameterized trajectory calculations will be preferred in the determination of absolute VOC concentrations for future experiments using PTR-MS on cork-taint and other off-flavor compounds in wine.

References:

[1] Marıa Luisa Alvarez-Rodrıguez et al, App. and Env. Micro. , p. 5860–5869 (2002).
[2] Andrii Tarasov et al, Talanta Vol 175, 82-92 (2017).
[3] W. Lindinger et al, Int. J. of Mass Spec. and Ion Proc. Vol. 173, 3 p. 191-241 (1998).
[4] T. Su and M.T. Bowers, J. Chem. Phys. 58, 3027 (1973).
[5] https://www.quantum-espresso.org/
[6] W. J. Chesnavich, T. Su, and M.T. Bowers, J. Chem. Phys. 72, 2641 (1980).
[7] T. Su and W. J. Chesnavich, J. Chem. Phys. 76, 5183 (1982).
[8] T. Su, J. Chem. Phys. 100 (6), (1994).

### Poster session (part II) / ⑧

# Response of GaN to sequential ion irradiation

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Behavior of materials in radiation harsh environment is an important issue because damage build-up within material in such environment can exhibit complex behavior. Therefore, as one of the candidate materials that can be used in radiation harsh environments, response of GaN to ion irradiation should be studied in detail.

Dense electronic excitation in the wake of the swift heavy ion (mass > 20 amu, kinetic energy > 1 MeV/amu) can lead to nanoscale material damage along ion trajectory called ion track. Thermal spike scenario describes this process as transfer of the deposited swift heavy ion energy from the electronic subsystem into phonon subsystem via electron-phonon coupling. Permanent damage can be formed upon rapid quenching of the molten material if the density of deposited energy (usually expressed in terms of electronic energy loss of the swift heavy ion) is sufficient to induce melting.

Irradiation with heavy ions in the keV energy range can also produce defects via different energy dissipation channel, namely nuclear energy loss. This process is known to introduce defects up to several hundred nanometers in depth. Depending on the applied ion fluence, damage build-up can lead even to complete amorphisation of the material within the ion range.

Recently, synergistic effects of nuclear and electronic energy loss came into research focus. By means of molecular dynamics simulations, response of damaged wurzite GaN (defects introduced by keV ion irradiation) was studied when subjected to swift heavy ion irradiation, in order to investigate role of defects with respect to the ion track formation.

**Poster session (part II)** / 10

# DFT study of hydrogen bonding between metal hydroxides and common organic functional groups

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Under several realistic conditions relevant to corrosion, metal surfaces are not only oxidized but also hydroxylated. In such cases, adsorption of molecules may proceed via H-bonding interactions. Hence, hydrogen bonding between small molecules with common functional groups and metal hydroxides were investigated using DFT calculations as to analyze the effect of different atoms on hydrogen bond strength. Discrete Al(OH)3 and Cu(OH)2 clusters were used as simple models of metal hydroxides, whereas the H-bond between two water molecules was used as a reference for comparison. According to calculations, both metal hydroxides are good H-bond donors and Cu(OH)2 is also a good H-bond acceptor. The calculations of H-bond strength, formed by small molecules with common functional groups, show that imidazole is both a very good H-bond donor (N--H--O bonding) and acceptor (N--H—O bonding); the same is true for Me2POOH (O--H--O donor and O--H--O acceptor bonding), where Me stands for methyl (CH3). In contrast, MeSH is a bad H-bond acceptor and donor. To assess whether the calculated hydrogen bond energies, obtained from small clusters, can be used to estimate molecular adsorption via H-bonding on hydroxylated surfaces, the calculations were also performed for imidazole and Me2POOH on boehmite--AlOOH(010) and Cu(OH)2(001) surfaces. The comparison between the two sets of calculations reveals that simple cluster calculations can give a rough estimate of adsorption energy, but only under provision that one guesses the correct number of H-bonds that a molecule forms with a hydroxylated surface.

**Poster session (part II)** / ⑫

# Investigation of lattice anhamonicities in bulk lonsdaleite: hexagonal diamond using first principles approach

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Carbon offers a wide variety of allotropes, each exhibits a unique electronic and vibrational properties and hence, attracts the researchers to study them extensively for several applications.

Lonsdaleite, also known as hexagonal diamond, is an allotrope of carbon and is widely being studied since years owing to its interesting structural, vibrational and thermodynamical properties. The exhaustive calculations and analysis of the aforementioned properties are yet to be performed to explore the future prospects of this material as a potential thermoelectric material.

In the present work, we demonstrate a zero-point motion and lattice thermal expansion in bulk hexagonal diamond using ab-initio theory. We start our calculations with the structure relaxation at any temperature by minimizing the Helmholtz free energy and then periodic perturbation is considered for phonon calculations. In order to understand the anharmonicities, we calculate the Grüneisen parameters for each phonon mode that contributes to the lattice anharmonicities. The thermal expansion is found to be positive for hexagonal diamond and thus the mode- Grüneisen parameters. We also calculate the bulk modulus and find that the bulk modulus is almost 414 GPa and an expansion of 4x10-6 K-1 at 300 K. The zero point motion contribution results in a 1.2% increment of the corresponding frozen-atom lattice constant.

The ab-initio calculations thus performed to study the lattice anharmonicities in hexagonal diamond opens up future research directions for this material with respect to its thermoelectric applications.

We are also exploring the structural, vibrational and thermodynamical properties of several other 1D, 2D and bulk materials. Presently the work is going on towards investigation of these properties of silicon nanowire with orientation and dimension dependencies, silicene, all inorganic halide perovskites, etc.

**Poster session (part II)** / 14

# Computational study of vibrational properties of chemically exfoliated titanium carbide MXenes - Ti3C2 and TiC2

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With the increased attention to 2D materials beyond graphene a new large family extending the world of 2D materials was discovered in 2011 [1]. This is the group of early transition metal carbides and/or carbo-nitrides labeled as MXenes. MXenes are synthesized by exfoliating MAX phase ternary carbides, nitrides, or carbonitrides: Mn+1AXn, where M is an early transition metal, A is a III or IV A-group element and X is carbon/nitrogen. Acid etching is used to remove the A layer, resulting in the formation of Mn+1Xn MXene [2]. The rich chemistries and unique morphologies of MXenes, in addition to their good electronic conductivities, render them strong candidates for many applications that range from sensors and electronic device materials, conductive reinforcement additives to polymers, electrochemical energy storage materials, among many others [3, 4]. MXenes can potentially be used as additives to polymers to fabricate composites with outstanding mechanical properties and good electrical conductivities [5].

We present a comparative study on the vibrational properties of Ti3C2 and TiC2 using density functional theory (DFT) calculations. Both Raman and infrared-active vibrational modes are predicted and conclusively assigned to experimental spectra as a guide for characterization. After the synthesis, HF etched MXenes were characterized using Raman spectroscopy and then further processed as additive to poly(methyl methacrylate) (PMMA) [6].

The computational analysis enabled proper assignation of MXenes modes in spectra but also modes of residual products of synthesis, TiO2 and amorphous carbon. Further comparative analysis of DFT calculations with Raman spectra of MXene/PMMA composite offers insight in effects of PMMA matrices on MXenes modes.

References:

[1] M. Naguib, et al.,Two-Dimensional Nanocrystals Produced by Exfoliation of Ti3AlC2, Advanced Materials, 23, 4248 (2011)

[2] A. Alhabeb, et al., Guidelines for Synthesis and Processing of Two-Dimensional Titanium Carbide (Ti3C2TxMXene), Chemistry of Materials, 29, 7633 (2017)

[3] B. Anasori, et al., 2D Metal Carbides and Nitrides (MXenes) for Energy Storage, Nature Reviews Materials, 2, 16098 (2017)

[4] K. Hantanasirisakul, et al., Fabrication of Ti3C2Tx MXene Transparent Thin Films with Tunable Optoelectronic Properties, Advanced Electronic Materials, 2, 1600050 (2016)

[5] X. Zhang et al. Ultrathin nanosheets of MAX phases with enhanced thermal and mechanical properties in polymeric compositions: Ti3Si(0.75)Al(0.25)C2 Angew. Chem. Int. Ed. 52, 4361, (2013)

[6] J. Pešić et al., Structural and Optical Characterization of MXene Ti3C2 /PMMA (Polymethyl methacrylate) nanocomposite, manuscript in preparation

**Poster session (part II)** / ⑯

## Determination of beryllium point-defects elastic characteristics for nuclear fusion

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In the frame of nuclear fusion, reactors should present parts in beryllium in order to produce tritium, one of the fuel for fusion. Studies have to be conducted for both understanding how tritium can move in beryllium and how beryllium-related parts can withstand an environment such as a nuclear fusion reactor.
Based on ab-initio methods, computations of beryllium hexagonal close packed bulks have been processed, in order to determine the elastic dipole tensors associated to several point-defects present in beryllium. These tensors could then be used to describe several physical values such as the stress or strain fields.

**Poster session (part II)** / ⑱

## Bis(amino acid) fumaramides as small molecular weight gelators: X-ray diffraction and calculation of NMR properties

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Supramolecular gel chemistry reveals highly potential application of oxalamide, fumaramide and various amino-acid units as organisational elements in the design of gelling systems [1]. Here, we present the structures and computed solid-state NMR parameters for two bis(amino-acid)-fumaramide esters amino-acid = Leucine (1) or Valine (2), to be used as a benchmark data for analyses of ssNMR measurements from gel phases.
Parameters were calculated by "gipaw.x" module in Quantum Espresso. [2] Prior to GIPAW calculation, geometry optimizations have been performed by pseudopotential plane-wave "pw.x" module. [2] For Valine derivative 2, disorder of one isopropyl and ester group were detected from the x-ray crystallography, so GIPAW calculations were performed on two different structural models to simulate disorder. Single crystal data: (1) space group: P212121, a = 4.9701(2) Å, b = 14.7298(4) Å and c = 28.278(2) Å; (2) space group: P212121, a = 4.9093(3) Å, b = 13.1211(12) Å and c = 30.031(3) Å. Quantum Espresso calculation: “PBE-rrkjus-gipaw” pseudopotentials from Ceresoli [3], k-point sampling: (6, 2, 1) for both 1 and 2, unit cell parameters fixed.

References:
[1] L. Frkanec and M. Žinić, Chem. Commun. (2010) 46, 522-537.
[2] P. Giannozzi et al., J. Phys.:Condens. Matter (2017) 29 465901.
[3] https://sites.google.com/site/dceresoli/pseudopotentials

**Poster session (part II)** / ⑳

# Non-oxidative catalytic dehydrogenation of propane and butane over Cr2O3: a DFT study

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Dehydrogenation of alkanes is becoming an increasingly important industrial process due to the rising demand for alkenes, such as propylene and butadiene. As the traditional methods of steam cracking and fluid-catalytic-cracking are insufficient to satisfy the growing demand, the use of catalytic dehydrogenation is increasing. Industrially, Cr2O3 is in addition to Pt/Sn the most commonly used catalyst. The reaction is endothermic and only proceeds at elevated temperatures. Industrially, the process runs at 600 °C.

We have studied the non-oxidative catalytic dehydrogenation of propane and butane Cr2O3, using plane-wave DFT formalism and the Grimme D3 correction for the van der Waals interaction. To account for strong correlation, the Perdew-Wang 91 exchange correlation with the Hubbard U parameter for Cr was used.

We found that on the (0001) surface of α-Cr2O3, propane and butane bind to the surface moderately strongly (0.3 eV) and non-specifically. Upon binding, they can undergo hydrogen stripping. The rate-determining step is the removal of the first hydrogen atom (barrier of 1.5 eV), which is in both instances cleaved off from the terminal carbon atom. The hydrogen atoms bind to the oxygen atoms of the catalyst, where they eventually recombine into gaseous hydrogen and desorb.

In the case of propane, the hydrogen atom from the secondary carbon atom is stripped in the second step, yielding propylene. Further dehydrogenation to propyne is not favourable. Butane is dehydrogenated first to 1-butene and to a lesser extent further to butadiene. No dehydrogenation, which would yield triple bonds, is observed.

**Poster session (part II)** / ㉒

# Lateral interactions between electronegative adatoms on metal surfaces: a high-throughput computational study

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As an electronegative atom approaches a metal surface, charge is transferred and the adatom becomes negatively charged. As more such adatoms accumulate on the surface, repulsive lateral interactions are expected (and in most cases found) between them. However, in a previous study [1], we found that the lateral interactions between oxygen adatoms on aluminum surfaces are instead attractive and concluded that they are a consequence of an interplay between simple geometric and electrostatic effects and that they can emerge when bonding is sufficiently ionic and the height of the adatoms above the surface is low enough. Since this model is purely geometric it stands to reason that it should be generally applicable, provided that the conditions for stabilization are met. Hence we have extended the study and consider, by means of DFT calculations, four different electronegative adsorbates (N, O, F and Cl) on 44 different metals to see if this type of lateral interactions can be identified there as well. The atoms were adsorbed at hollow sites on the (001) surface of hcp metals, (111) and (100) surfaces of fcc metals, and (110) and (100) surfaces of bcc metals.

Our calculations show that lateral interactions between electronegative adatoms can be classified into three different categories: (i) the expected case where repulsive interactions are found between the negatively charged adsorbates, (ii) attractive interactions are found between the adatoms, and (iii) conditions for attractive interactions are met, however, surface reconstruction occurs in the low coverage case and it is found to be more stable. Repulsion is typical for most transition (d-block) metals with very few exceptions. Attractive interactions are predominately found for p-block metals, whereas surface reconstruction was mainly identified for the alkali metals, which crystallize in bcc lattices and have a very large lattice parameter. In addition, we also provide a simple means of estimating which type of interaction is expected for each adatom-metal combination, via the quantity termed “vacant” surface area. This quantity is calculated by subtracting the surface area occupied by the metal cation in the lowest oxidation state from the surface area of the metal’s surface unit cell.

References:

[1] M. Poberžnik, A. Kokalj, J. Phys. Chem. C, 2016, 120, 25915–25922

### Poster session (part II) / ㉔

## CHIVES - Simulating laser excitations

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Intense femtosecond-laser pulses can induce ultrafast structural phenomena in solids by creating a highly non-equilibrium state, which is characterized by high temperature electrons (~ 10 000 K) and near room temperature ions.
In order to compute and simulate these laser-induced structural phenomena we developed an electronic-temperature-dependent density-functional-theory Code for Highly excIted Valence Electron Systems, short CHIVES. Basically, the hybrid parallel implementation (MPI + OpenMP) of most of the subroutines used in CHIVES and the use of a norm-conserving basis set for the valence electrons enables us to perform ab initio molecular dynamics simulations with supercells
containing up to 1440 atoms in bulk and/or thin film geometry. Besides technical details of CHIVES, we present preliminary results on the influence of vacancies on laser-induced ultrafast structural phenomena in diamond like nonthermal melting.
Additionally, we would like to discuss the possibility to
create or modify NV centers in diamond by femtosecond-laser pulses.

### Poster session (part II) / ㉖

## Experimental and theoretical study of dimerization of α-pinene peroxides

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α-Pinene is the second most abundant biogenic non-methane hydrocarbon emitted into the atmosphere, produced particularly by conifers. In the atmosphere it undergoes successive reactions, forming less volatile products, called secondary organic aerosols (SOA). Atmospheric aerosols influence the climate and they can be damaging to health, causing acute and chronic diseases. SOA quantities in the air are underestimated by the current atmospheric models which suggests missing or neglected reaction mechanisms. For example, the singlet oxygen is not yet included in the global atmospheric models and may be one of the atmospheric oxidants, which could fill the gap between the modelled and the measured SOA.
Preliminary experiments were done in acetonitrile with photochemically generated singlet oxygen. The oxidation products were four isomeric α-pinene peroxides, determined with LC-APCI-IT-TOF and 2D NMR. Additionally, after short heating of peroxide mixture, organic peroxide dimers were identified. Oxidation mechanisms were verified using quantum mechanical methods (so far only semi-empirical methods AM1, PM3 and PM6).
Quantitation and determination of kinetic rates of these oxidation products will be our next step. Study suggests that singlet oxygen can play a significant role in atmospheric oxidation processes and can be the missing part of current SOA chemistry.