

CPP 107: Emerging Topics in Chemical and Polymer Physics, New Instruments and Methods

Time: Friday 9:45–12:15

Location: ZEU 255

CPP 107.1 Fri 9:45 ZEU 255

Machine-Learned Polarizabilities: from Molecules to Bulk Raman Spectra — ●DAVID WILKINS, ANDREA GRISAFI, and MICHELE CERIOTTI — Laboratory of Computational Science and Modelling, Institute of Materials, EPFL, Switzerland

The polarizability α of a chemical system is key in theoretically determining the results of spectroscopic experiments. However, α requires a high level of theory as well as extra computational effort on top of the ground-state electronic structure, meaning that to calculate an accurate polarizability can take several days for even a modest-sized molecule. Since an evaluation of spectra requires α to be known for an entire molecular simulation, the expense required would seem to stymie efforts to calculate an accurate spectrum.

The recently developed symmetry-adapted Gaussian process regression (SA-GPR) approach allows the prediction of tensor properties for general systems. I begin by showing that a model based on SA-GPR predicts the molecular α with the accuracy of coupled-cluster calculations, in a matter of seconds. This model can be applied to complex molecules with very high accuracy, suggesting that machine-learning should be the method of first resort for α predictions, rather than density functional theory, which is generally less accurate.

I finally show that SA-GPR is applicable also to the condensed phase, facilitating a prediction of spectroscopic experiments. In particular, I develop a model that allows a fast and accurate calculation of Raman spectra of bulk aqueous systems, as well as paving the way for the simulation of more complex nonlinear spectra.

CPP 107.2 Fri 10:00 ZEU 255

Machine learning the molecular dipole moment with atomic partial charges and atomic dipoles — ●MAX VEIT¹, DAVID WILKINS¹, YANG YANG², ROBERT DiSTASIO JR², and MICHELE CERIOTTI¹ — ¹Laboratory of Computational Science and Modeling, IMX, École Polytechnique Fédérale de Lausanne, 1015 Lausanne, Switzerland — ²Department of Chemistry and Chemical Biology, Cornell University, Ithaca, NY 14853, USA

The gas-phase molecular dipole moment is a central quantity in chemistry. It is essential in predicting molecular infrared and sum-frequency-generation spectra, as well as in describing long-range molecular interactions. Furthermore, it can be extracted directly from expensive, but highly accurate, quantum mechanical calculations, making it an ideal target for machine learning. We choose to represent this quantity with a physically-inspired machine learning model that captures the two distinct physical effects contributing to molecular polarization: Local atomic polarization is captured within the symmetry-adapted Gaussian process regression (SA-GPR) framework, which assigns a dipole moment to each atom, while movement of charge across the entire molecule is captured by assigning a partial (scalar) charge to each atom. These models are fitted together to reproduce the quantum mechanical molecular dipole moment, achieving better results than either model alone. The results show how transparency and physical interpretability can aid not only the understanding of a machine learning model, but allow it to achieve higher accuracy as well, regardless of which physical property is being modelled.

CPP 107.3 Fri 10:15 ZEU 255

Combining experimental and quantum mechanical descriptors to understand chemical bonding in solids — ●STEFAN MAIER¹, SIMON STEINBERG², MICHAEL SCHUMACHER³, PAVLO GOLUB⁴, JEAN-YVES RATY^{5,6}, RYKY NELSON², OANA COJOCARU-MIRENIN¹, RICHARD DRONSKOWSKI², and MATTHIAS WUTTIG¹ — ¹Institute of Physics IA, RWTH Aachen University, 52074 Aachen — ²Institute of Inorganic Chemistry, RWTH Aachen University, 52056 Aachen, — ³Institute for Theoretical Solid State Physics, RWTH Aachen University, 52056 Aachen — ⁴National University of Singapore, Department of Mechanical Engineering, 9 Engineering Drive 1, Singapore 117575 — ⁵CESAM and Physics of Solids, Interfaces and Nanostructures, Université de Liège, B4000 Sart-Tilman — ⁶UGA, CEA-LETI, MINATEC campus, 17 rue des Martyrs, F 38054 Grenoble

How are atoms held together? This question stood at the very beginning of the natural sciences and has played (and still plays) a central role in solid state physics, chemistry and materials science. Exactly

eight decades after Linus Pauling published his famous book: The Nature of the Chemical Bond in 1939, we look at this fundamental question again in a different light. In the meantime, the quantum mechanical methods and experimental techniques available to study chemical bonding have improved tremendously, which allows studying chemical bonding by using new experimental methods combined with advanced quantum-mechanical methods.

CPP 107.4 Fri 10:30 ZEU 255

Operando observation of reaction intermediates above one atmosphere under Fischer-Tropsch conditions — ●PATRICK LÖMKER¹, KEVIN PLONER³, MIKHAIL SHIPILIN², JÖRGEN GLADH², NORBERT KÖPFLE³, THOMAS GÖTSCH⁴, HESHMAT NOEI¹, CHRISTOPH SCHLUETER¹, ANDERS NIELSSON², and PETER AMANN² — ¹Photon Science, DESY, 22607 Hamburg — ²Department of Physics, Stockholm University, 10691 Stockholm — ³Institute of Physical Chemistry, University of Innsbruck, 6020 Innsbruck — ⁴Fritz Haber Institute, Inorganic Chemistry, 14195 Berlin

The quest for a sustainable future poses challenges, especially with regard to the storage and distribution of fuels. The Fischer-Tropsch synthesis and can be part of a sensible production for these fuels. Yet literature detailing the reaction mechanisms is lacking.

As seen by many publications XPS can address the reaction mechanisms in question. However, combining ultra-high vacuum, required for XPS and high pressures above atmosphere have posed significant technical challenges.

We use an instrument designed at Stockholm University utilizing a virtual cell concept, directing a gas flow on the surface to increase the pressure, while minimizing the electron scattering in gas. This instrument is now in operation at the new HAXPES beamline P22 at PETRA III. We present data of CO:H₂ with pressure up to 1025 mbar on a Co(0001) crystal. Intermediates and adsorbed species were identified under the reaction. We clearly observe a transition in the adsorbed species between 500-1000mbar – in line with recent literature.

CPP 107.5 Fri 10:45 ZEU 255

Modulating Selectivity of Nitrites Reduction by Leveraging Polymer-Induced Solvation Effects — ●PENGCHENG HUANG, HUAPING ZHAO, and YONG LEI — Technische Universität Ilmenau, 98693, Ilmenau, Germany.

Closing the nitrogen cycle is essential for mitigating the negative environmental impact of fertilizers run-offs from intensive -crops production and -farming.¹ The key in these processes is to activate nitrogen-containing species (e.g. nitrites, nitrates, and nitro-organic molecules) in heavily diluted aqueous environments into inert products (e.g. nitrogen) in the presence of reducing agents using supported metal catalysts. The modification of the metal and/or support chemistry, nano-architecture, and topology can lead to changes in the transport and binding of the reactive species, which can be leveraged to favor a specific pathway of the reaction.² In this contribution, we propose a strategy to modulate the selectivity of N-O bond activation reactions by tailoring the solvation-microenvironment around the metal cluster. To demonstrate this concept we have developed polymer over-coatings on metal-catalysts that can act as *co-solvents* to simultaneously; 1) control the selectivity and activity of the catalyst towards the desired product to maximize atom-efficiency of the process, and 2) prevent catalyst deactivation by preventing the sintering, lexiviation, and poisoning. In this contribution, we will show the effects of the polymer brushes chemistry (poly(N-isopropylacrylamide) on the molecular transport, catalyst selectivity and activity of Pd-supported on non-porous SiO₂ colloidal particles as model catalysts.

CPP 107.6 Fri 11:00 ZEU 255

The new Small Angle X-ray Scattering Beamline for Materials Research (SAXSMAT) at PETRA III — ●SYLVIO HAAS, ANDRÉ CONCEICAO, XIAO SUN, and SASKIA PFEFFER — Deutsches Elektronen Synchrotron (DESY), Photon Science Division, Hamburg, Germany

Modern applications and basic research in catalysis, biotechnology and materials are often concerned with hybrid and synergetic systems. In other words, systems that brings enhanced properties and performances due to their internal complexity. The challenge is now

in understanding the interactions leading to their assembly and operation. Due to their inherent chemical and structural complexities, a combination of several techniques simultaneously and/or an advanced method is mandatory to determine structural and chemical information of materials.

Small-Angle X-ray scattering (SAXS) is a well-established method to investigate nanostructured materials. Information about particle size distribution, particle shapes, and inter-particle interaction potentials can be determined. Currently, DESY is commissioning a new beamline (P62; SAXSMAT) dedicated to this technique that will be open for user operation in the near future. The X-ray energy can be tuned between 3.5 keV to 35.0 keV. In this presentation the SAXSMAT beamline will be presented including the key features of the beamline:

I.) anomalous SAXS/WAXS: adding element sensitivity II.) SAXS/WAXS computed tomography: adding 3D spatial resolution III.) In situ and In operando SAXS/WAXS: adding time resolution

15 min. break

CPP 107.7 Fri 11:30 ZEU 255

Improved virtual orbitals for the calculation of X-ray absorption spectra for organic molecules — ●ROLF WÜRDEMANN¹ and MICHAEL WALTER^{2,3} — ¹reiburger Materialforschungszentrum, Freiburg, Germany — ²Freiburger Zentrum für interaktive Werkstoffe und bioinspirierte Technologien, Freiburg, Germany — ³Fraunhofer-Institut für Werkstoffmechanik, Freiburg, Germany

X-ray absorption spectroscopy (XAS) is an element specific local probe used for the analysis of materials. One way to compare and interpret experimentally measured spectra is to perform ab initio calculations of XAS spectra for molecules in given geometries. By this different isomers can be distinguished and a deeper understanding of the bonding situation can be gained.

Common ways to calculate XAS spectra by density functional theory (DFT) either utilize fractional charges in the frozen cores or restrict the state-space of linear time-dependent DFT. In our contribution we examine the possibility to utilize the combination of range-separated functionals (RSF) with Huzingas improved virtual orbitals to calculate XAS spectra. This combination has been successful in the calculation of charge transfer excitations[1].

[1] Würdemann, R. and Walter, M., J. Chem. Theory Comput. 2018, 14, 7, 3667-3676

CPP 107.8 Fri 11:45 ZEU 255

Quantum tunnelling in the Marcus inverted regime — ●ERIC R. HELLER and JEREMY O. RICHARDSON — ETH Zürich, 8093 Zürich, Switzerland

Electron transfer rates between weakly coupled states are predomi-

nantly calculated using Marcus theory. Due to its inherent classical character, however, experimental reaction rates can deviate from the Marcus result by several orders of magnitude due to the influence of quantum tunnelling and zero-point energy. These effects prove to be of particular importance in the so called “inverted” regime, where reaction rates become smaller with increasing thermodynamic driving force.

In principle the correct quantum mechanical rate can be obtained by applying Fermi’s golden rule. This, in turn, requires knowledge of the nuclear wavefunctions of the two reactive wells, which are not accessible for all but very small systems.

Semiclassical instanton theory is able to capture nuclear quantum effects in a numerically efficient way allowing application to complex, anharmonic systems. Recently this method has been extended to describe the inverted regime by locating an optimal tunnelling pathway formed by two trajectories, one of which travels in negative imaginary time giving a picture reminiscent of the scattering of particles and antiparticles.

The method thus constitutes a semiclassical path-integral version of Fermi’s golden rule applicable not only to electron-transfer reactions but also light-matter interactions, electrochemistry and many more.

CPP 107.9 Fri 12:00 ZEU 255

3D-printed humidity chamber for neutron scattering on thin films — ●TOBIAS WIDMANN, LUCAS P. KREUZER, and PETER MÜLLER-BUSCHBAUM — TU München, Physik-Department, LS Funktionelle Materialien, 85748 Garching

The investigation of thin soft matter films with neutrons allows a non-destructive probe with good scattering statistics. It entertains a broad field of scientific interest that studies structures and performance of various soft matter systems such as hydrogels or organic solar cells. However, soft matter samples are very sensitive to humidity and temperature and require well-defined ambient conditions. As such, specialized sample environments are needed which provide stable control over the hydrodynamic parameters at the sample position. In the framework of the FlexiProb project, a quickly interchangeable sample environment for experiments at the European spallation source (ESS) is designed. We focus on the design and fabrication of a specialized sample environment for the investigation of thin film samples with grazing incidence small angle scattering (GISANS). At its core stands a 3D-printed humidity chamber that offers the necessary control. The spherical chamber design has well distributed fluidic channels inside its walls which provide a stable and rapidly adjustable temperature. The control over the atmospheric composition around the sample is realized by a remote-controlled gas-flow array that mixes up to three different humidified or dry air streams. The novel chamber design provides a first step into a 3D-printed sample environment for neutron experimentation.