

## CPP 34: Emerging Topics in Chemical and Polymer Physics, New Instruments and Methods I

Time: Thursday 9:30–13:00

Location: H 0106

**Invited Talk**

CPP 34.1 Thu 9:30 H 0106

**Towards AI-assisted analysis of surface and small-angle x-ray and neutron scattering data** — ●MARINA GANEVA — JCMS, Forschungszentrum Jülich, Jülich, Germany

The long term and sustainable success of Neutron and X-ray community essentially depends on its ability to meet growing challenges in handling and analyzing data of increasing volume and complexity. The arise of new generation of high-intensity x-ray and neutron sources and fast, large area 2D-detectors leads to high data rates and large data volumes, which are not possible anymore to analyze in traditional way. Thus, new fast and reliable approaches are required.

Nowadays AI-assisted approaches are increasingly being developed and applied to address the challenges in our life. They provide a smart solution with potential to accelerate the x-ray and neutron data analysis and facilitate the extraction of valuable insights from large and complex datasets. In the present talk I will discuss challenges and perspectives of AI-assisted data analysis for surface and small-angle x-ray and neutron scattering from soft matter samples and will give an overview of our recent results.

CPP 34.2 Thu 10:00 H 0106

**Deep learning based reflectometry data analysis including prior knowledge** — ●ALEXANDER HINDERHOFER, VALENTIN MUNTEANU, VLADIMIR STAROSTIN, LINUS PITHAN, ALEXANDER GERLACH, and FRANK SCHREIBER — Institut für Angewandte Physik, Universität Tübingen, Auf der Morgenstelle 10, 72076 Tübingen, Germany

Current machine-learning solutions for automatized analysis of X-ray (XRR) and neutron reflectivity (NR) data is constrained by the range and number of considered parameters, making the approach inflexible for applying it to different material and layer configurations. To overcome this, we present an approach that utilizes prior knowledge to regularize the training process over larger parameter spaces. We demonstrate the effectiveness of our method in various scenarios, including multilayer structures with box model parametrization and a physics-inspired special parametrization of the scattering length density profile for a multilayer structure. In contrast to previous methods, our approach scales favorably when increasing the complexity of the inverse problem, working properly even for a several layer multilayer model and an N-layer periodic multilayer model with up to 20 open parameters. We will also discuss autonomous experiments enabled by machine-learning-based online data analysis in synchrotron beamline environments. [1]

[1] L. Pithan et al. *J. Synchrotron Rad.* 30 (2023) 1064

CPP 34.3 Thu 10:15 H 0106

**Deciphering Electron Paramagnetic Resonance Spectra via Machine Learning** — SHENGCHUN WANG<sup>1</sup>, SHUFEI ZHANG<sup>2</sup>, JIHU SU<sup>5</sup>, ●YI LUO<sup>3</sup>, and AIWEN LEI<sup>4</sup> — <sup>1</sup>Department of Medicinal Chemistry, University of Michigan, Ann Arbor, MI, USA — <sup>2</sup>Shanghai Artificial Intelligence Laboratory, Shanghai, China — <sup>3</sup>Institute of Functional Interfaces, Karlsruhe Institute of Technology, Eggenstein-Leopoldshafen, Germany — <sup>4</sup>College of Chemistry and Molecular Sciences, the Institute for Advanced Studies, Wuhan University, Wuhan, China — <sup>5</sup>Department of Modern Physics, University of Science and Technology of China, Hefei, China

Elucidating the properties of spin species is one of central issues in modern chemistry, material and biology science. For understanding these species, the rapid identification of isotropic and anisotropic Electron Paramagnetic Resonance (EPR) spectra is foundational. Conventional simulation methods, though detailed, often lag in efficiency. Here we present a hybrid approach integrating conventional computational method and Multi-Layer Perceptron (MLP) algorithms, leverages an extensive literature-derived EPR database, ensuring both speed and accuracy in species identification from EPR spectra. Evaluations validate its superior efficacy, attributing much to its robust database integration. This tool offers a promising bridge between academic rigor, computational efficiency, and EPR literature.

CPP 34.4 Thu 10:30 H 0106

**JuMPO: A Quantum Optimal Control Library for Robust and Selective Magnetic Resonance Experiments** — ●ARMIN J. RÖMER<sup>1,2</sup>, SIMONE S. KÖCHER<sup>1</sup>, and JOSEF GRANWEHR<sup>1,2</sup> —

<sup>1</sup>Forschungszentrum Jülich GmbH, IEK-9 — <sup>2</sup>RWTH Aachen University

Quantum optimal control is a versatile, powerful method to tailor magnetic resonance experiments both in terms of robustness and selectivity. Nevertheless, the method is not routinely employed in applied science. In order to make the engineering of such experiments more accessible, we have developed a quantum optimal control package adjusted to the language and needs of magnetic resonance spectroscopists. The package, Jülich Magnetic Pulse Optimization (JuMPO), offers a handy toolbox for both robust and highly selective magnetic resonance experiments. It enables optimizing for a range of Larmor frequency offsets and  $B_1$  inhomogeneities, as well as the engineering of pattern pulses, where for each combination of offset and inhomogeneity a separate target state can be specified. Appropriate penalties can guide optimizations towards experimentally implementable pulse shapes. Furthermore, tools for chemically intuitive spin state preparation and spectrometer calibration parameters are featured. As a use case example, we present a set of robust broadband excitation and inversion pulses re-optimized with tighter robustness constraints than with previous pulse sequences. JuMPO can help to devise new, innovative experiments, which provide additional and more detailed information into complex systems, e.g. in catalysis or material science.

CPP 34.5 Thu 10:45 H 0106

**Laser Diffraction for Defectscopy of Cellulose Filaments** — ●DAMIEN PIERCE, KORNELIYA GORDEYEVA, ANASTASIA RIAZANOVA, TOMAS ROSÉN, and DANIEL SÖDERBERG — KTH Royal Institute of Technology, Stockholm, Sweden

Filaments produced from the wet spinning of Cellulose nanofibrils are a promising alternative to those derived from fossil fuels. These filaments are the strongest bio-based filaments currently available, with potential uses in the production of high-performance textiles. However, establishing what the weakest point of such filaments is, has yet to be conclusively determined. We demonstrate the potential of laser diffraction as a defectscopy technique. Tomograms of the apparent width of the filament were measured using laser diffraction and compared with SEM measurements. Tensile testing was performed in order to correlate the observed structures with the breakage point. We expect this technique to provide a rapid, non-destructive method of quality control, greatly speeding up the optimisation of processing conditions.

CPP 34.6 Thu 11:00 H 0106

**Hydration layer ordering effects at gold - electrolyte interfaces confined by an atomic force microscope tip** — ●MARTIN MUNZ<sup>1,2</sup>, WIEBKE FRANSEN<sup>2</sup>, BEATRIZ ROLDAN CUENYA<sup>2</sup>, and CHRISTOPHER KLEY<sup>1,2</sup> — <sup>1</sup>Helmholtz Young Investigator Group Nanoscale Operando CO<sub>2</sub> Photo-Electrocatalysis, Helmholtz-Zentrum Berlin für Materialien und Energie GmbH, 14109 Berlin, Germany — <sup>2</sup>Department of Interface Science, Fritz Haber Institute of the Max Planck Society, 14195 Berlin, Germany

We introduce a correlative microscopy approach, combining in situ conductive atomic force microscopy (c-AFM) with simultaneous friction force and morphology imaging, thus enabling nanoscale physical-chemical interrogation of the catalyst - electrode interface. For the class of bimetallic electrocatalysts, the electric conductivity variations across nanopatterned CuOx islands on Au electrodes can be resolved in air, water and potassium bicarbonate aqueous electrolytes. In line with current contrasts between catalyst surface areas of different composition and oxidation state, I-V curves showed highly resistive CuOx islands. Simultaneously measured friction force images suggested a qualitative contrast variation upon transitioning from water to bicarbonate electrolyte, thus indicating that friction forces respond to hydration layer ordering effects. Complementary in situ AFM friction force measurements, using cantilevers with a high force sensitivity, revealed a decrease in the friction coefficient with increasing ionic concentration, for the low-concentration regime of a potassium perchlorate aqueous electrolyte, thus suggesting a chaotropic effect.

15 min. break

CPP 34.7 Thu 11:30 H 0106

**Using Neural Network Potentials to Predict Thermal Iso-**

**merization Barriers for Spiropyran Derivatives** — ●ROBERT STROTHMANN<sup>1</sup>, JOHANNES T MARGRAF<sup>1,2</sup>, and KARSTEN REUTER<sup>1</sup> — <sup>1</sup>Fritz-Haber-Institut der MPG, Berlin — <sup>2</sup>Universität Bayreuth, Bayreuth

First principles methods like density-functional theory can be used to study reaction barriers and give insights into the influence of chemical modifications on barrier heights and mechanisms. However, their large computational cost hinders their usage in high-throughput settings, which prevents large scale studies including thousands of structures. Surrogate models with reduced costs are therefore of great interest. In this context, neural network potentials (NNPs) have attracted much attention, as their uncertainty can be systematically decreased by increasing the amount and quality of the training data.

In this talk, we will highlight the usage of NNPs to assist in the prediction of thermal isomerization barriers of spiropyran photoswitches. This barrier governs the half-life of the thermal back-reaction, which is one of the key properties in photoswitch design. By utilizing transferability, NNPs trained on only a few spiropyran molecules and fine tuned in active-learning cycles allow the prediction of isomerization barriers for thousands of chemically modified spiropyranes. This not only gives a ranking of suitable photoswitches for a specific application, but also enables a more systematic study on how to tune the thermal half-life via chemical modification.

CPP 34.8 Thu 11:45 H 0106

**Dedoping of PEDOT:PSS using Amines to shift the Threshold Voltage in OECTs** — ●LAURA TEUERLE, HANS KLEEMANN, and KARL LEO — IAPP Dresden

With an increasing importance of organic semiconductors, due to their flexibility, transparency and possible biocompatibility, more applications and device classes emerge.

One of them - the organic electrochemical transistor (OECT) can be utilized in neuromorphic computing and printed digital logic. The most commonly used -PEDOT:PSS is a p-type semiconductor, which leads to normally-on type transistors. However, normally-off type devices are needed for a successful application in logic circuits.

We show that a chemical dedoping method involving amines leads to a shift in threshold voltage to zero and even negative in the corresponding devices.

Different processing methods for the dedoping process and device building are studied, which involve photolithography, inkjet printing and spraycoating. Furthermore, IV measurements for device characterization were taken.

The results show that the studied chemical dedoping of - PEDOT:PSS can be a viable method to create normally-off type transistors for an application in logic circuits.

CPP 34.9 Thu 12:00 H 0106

**On Electron-Photon Correlation in Molecular Cavity QED with Low-Frequency Fields** — ●ERIC W. FISCHER<sup>1</sup> and PETER SAALFRANK<sup>2</sup> — <sup>1</sup>Humboldt-Universität zu Berlin, Institut für Chemie, Brook-Taylor-Straße 2, 12489 Berlin — <sup>2</sup>Universität Potsdam, Institut für Chemie, Karl-Liebknecht-Str. 24-25, 14476 Potsdam

Strong light-matter interaction of molecular systems with quantized field modes of optical micro-resonators form the building block of the rapidly evolving field of polaritonic chemistry.[1] In this contribution, we discuss the role of correlations between electrons and low-frequency cavity fields in molecular cavity QED from a quantum chemical perspective. We show that commonly employed effective ground state models further approximate the cavity Born-Oppenheimer (CBO) framework[2] by neglecting electron-photon correlation.[3] As connection, we introduce a CBO perturbation theory (CBO-PT), which is motivated by distinct electronic and IR cavity excitation energy scales.[3] Illustratively, we discuss the relevance of correlation corrections for reactive systems from the perspective of CBO-PT. Eventually, we show how to address vibro-polaritonic transmission spectra by combining CBO-PT with linear response theory.[4]

[1] T. W. Ebbesen, *Acc. Chem. Res.* **49**, 2403 (2016).

[2] J. Flick et al., *J. Chem. Theory Comput.* **13**, 1616 (2017).

[3] E.W. Fischer, P. Saalfrank, *J. Chem. Theory Comput.* **19**, 7215, (2023).

[4] E.W. Fischer, J.A. Syska, P. Saalfrank, in preparation.

CPP 34.10 Thu 12:15 H 0106

**Thermal expansion on molecular scale: heterogeneity and**

**packing** — ●MARTIN TRESS<sup>1</sup>, JAN GABRIEL<sup>2</sup>, and FRIEDRICH KREMER<sup>1</sup> — <sup>1</sup>Universität Leipzig — <sup>2</sup>Roskilde University, Denmark

While typically used for chemical characterization, infrared spectroscopy also reveals physical properties on molecular scale which are difficult to access otherwise. We study the thermal expansion of molecular bonds in amorphous systems, i.e. a series of polyalcohols as well as liquid water. By analyzing specific molecular vibrations and correlating them with interatomic bond lengths, the thermal expansion of covalent bonds and intermolecular hydrogen(H)-bonds is quantified. Pronounced differences between intra- and intermolecular expansion verify the dominance of the latter. Surprisingly, in polyalcohols the macroscopic thermal expansion (i.e. the cube root of inverse density) is even bigger than that of the strong H-bonds. This suggests that additional weak H-bonds or van-der-Waals contacts dominate the thermal expansion. Since strong H-bonds are the largest barriers to molecular rotation, i.e. they control the structural relaxation time, a clear explanation for the failure of density scaling - an attempt to link structural relaxation time with density - in H-bonding liquids is revealed. Liquid water exhibits an even more complex connection of intermolecular bond expansion and macroscopic expansivity due to the anomalous temperature dependence of its density. Our results demonstrate that heterogeneities in intermolecular contacts play distinct roles in densification and structural relaxation which requires explicit consideration in comprehensive theoretical descriptions of liquids and glass formers.

CPP 34.11 Thu 12:30 H 0106

**A contribution from first principles to understand ageing mechanisms in polyethylene** — ●GUIDO ROMA<sup>1</sup>, YUNHO AHN<sup>2</sup>, YVETTE NGONO<sup>3</sup>, and MURIEL FERRY<sup>4</sup> — <sup>1</sup>Université Paris-Saclay, CEA, S2CM/SRMP, France — <sup>2</sup>Ewha Womans University, Photo-physics Photochemistry Park Lab, Seoul, South Korea — <sup>3</sup>Normandie Univ., CEA, CIMAP Caen, France — <sup>4</sup>Université Paris-Saclay, CEA, SPC, France

The kinetics of radio-oxidation in polymers is still not yet fully elucidated, and polyethylene is a prototypical and important polymer material. In this paper we first developed an interface model in order to try to grasp the main atomic scale features of crystalline and amorphous regions; then we show how first principles calculations can be used to check the reliability of some kinetics schemes proposed in the literature. In particular, calculated energy barriers suggest that bimolecular reactions involving alkoxy radicals cannot be overlooked [1]. We also discuss the mechanisms by which phenolic antioxidants are effective in delaying radio-oxidation in polyethylene. Finally, we show how the prediction of infrared spectra can be a valuable support for experimental investigation of the accumulated carbonyl concentrations through infrared spectroscopy [2].

Bibliography

[1] Y. Ahn, G. Roma, X. Colin, *Macromol.* **55**, 8676 (2022). [2] M. Ferry, Y. Ahn, F. Le Dantec, Y. Ngono, G. Roma, *Polymers* **15**, 1537 (2023).

CPP 34.12 Thu 12:45 H 0106

**Near-surface free volume in polymers characterized by positron annihilation lifetime spectroscopy** — ●CHRISTOPH HUGENSCHMIDT<sup>1</sup>, MAIK BUTTERLING<sup>2</sup>, VASSILY VADIMOVITCH BURWITZ<sup>1</sup>, ADRIAN LANGREHR<sup>1</sup>, LUCIAN MATHES<sup>1</sup>, ERIC HIRSCHMANN<sup>2</sup>, OSKAR LIEDEKE<sup>2</sup>, and ANDREAS WAGNER<sup>2</sup> — <sup>1</sup>Heinz Maier-Leibnitz Zentrum (MLZ), Technical University of Munich, Lichtenbergstr. 1, 85748 Garching, Germany — <sup>2</sup>Helmholtz-Zentrum Dresden-Rossendorf, Institute of Radiation Physics, 01328 Dresden, Germany

Positron annihilation lifetime spectroscopy (PALS) is a powerful technique for characterizing the free volume in polymers. The main drawback of conventional PALS, however, is the presence of a so-called source component due to positrons annihilating in the radioactive source material. By using a pulsed monoenergetic positron beam, as provided by MePS at the HZDR, the variable positron energy allows the depth-resolved PALS and the spectra intrinsically do not contain a source component. In order to investigate the mean pore size in various polymers, we recorded PALS spectra for positron implantation energies between 0.5 and 10 keV. The measured so-called pick-off lifetime of ortho-positronium allowed us to unambiguously determine the mean void size in the bulk. By analyzing the recorded PALS depth profiles changes of the free volume in the near-surface region of, e.g. polypropylene and polycarbonate could be observed.