

Development of an Ablation Spectrometer for Calcium Isotope Analysis via High-Resolution Optical Spectroscopy

Termeh Bashiri, Simon Blume, Phelan Yu, Nicholas Hutzler, Timothy Steimle, Carlos Abad Andrade, Jens Riedel, Mitchio Okumura
Caltech

The analysis of calcium isotopes is essential in diverse fields such as medicine, environmental science, and geology. For instance, calcium isotope ratios are proposed as biomarkers for bone-related diseases, while they also serve as proxies for paleo-environmental changes. However, current mass spectrometry techniques face challenges due to isobaric interferences, particularly between $^{40}\text{Ca}^+$ and $^{40}\text{Ar}^+$. These methods also require large, specialized instruments, limiting their broader application. To address these limitations, we propose the use of high-resolution optical spectroscopy, combined with a laser ablation source for calcium isotope analysis. By generating a laser-induced plasma from a CaF_2 target, our method circumvents common interferences through absorption and emission spectroscopy for isotope measurements.

Preliminary cold molecular beam laser-induced fluorescence experiments on CaF isotopologues have already laid the groundwork for this experiment. The development of this spectrometer has the potential to revolutionize calcium isotope analysis in fields such as diagnostics and environmental research, making high-precision isotope measurements more accessible for clinical and field applications.

Structure-property relationships in functionalized metal organic framework from first-principles high-throughput screening

Joshua Edzard, Holger-Dietrich Saßnick, Julia Santana Andreo, Caterina Cocchi
Carl von Ossietzky Universität Oldenburg
Institute of Physics

Metal organic frameworks (MOFs) are novel materials with high potential in many fields of application, ranging from gas storage and catalysis to optoelectronics [1,2]. Thanks to their unique structural characteristics, the electronic properties of MOFs can be tuned by chemical modifications of their building blocks (metal ions and linker molecules), leading to an enormous variety of systems with customized features.

In this work, we focus on MOF-5 and using automatized first-principles calculations, we scan all possible structures that arise by exchanging the native Zn ion with metal atoms having the same oxidation state, and by functionalizing the organic ligand 1,4-benzodicyclohexadiene with common functional groups of varying electro-donating ability. From the analysis of the resulting 56 structures, we clarify that the atomic radius of the metal node defines the lattice constant and therefore the pore size. The presence of earth-alkali metals and of the hydrogen bonds generated by ligand substitution with COOH and OH mostly stabilize the structure. Linker functionalization affects the electronic structure by tuning the band-gap size over a range of a few eV. In particular, substitution with NH_2 , NO_2 , and OH groups lead to compounds with favorable characteristics for visible-light absorption.

[1] Z. Wang and S. M. Cohen, Chem. Soc. Rev., 2009, 38, 1315–1329.

[2] J.-L. Wang, C. Wang and W. Lin, ACS Catalysis, 2012, 2, 2630–2640.

Reactivity of CO₂ with solvated electrons at the NH₃/Cu(111) interface.

Maya Heine, Lukas Gierster, Julia Stähler
Humboldt Universität zu Berlin

Institute of Chemistry

When electrons are photoinjected from a metal substrate into D₂O or NH₃ adlayers they can be stabilised and exhibit lifetimes from femtoseconds to minutes. The energetics and dynamics of such trapped and solvated electrons have been studied across femtosecond to minute timescales using time-resolved two-photon photoelectron spectroscopy and are well understood [1]. An exciting next step is to investigate the interactions of such electrons with molecules and observe possible reactions of femtosecond timescales. For example, solvated electrons have already been shown to reduce O₂ at a model DMSO/Cu electrode [2]. We investigate the interaction of CO₂ with the amorphous NH₃/Cu(111) interface, as much remains to be understood regarding the timescales and energetics of possible reactions of this important molecule. We show first results where we observe ultrafast effects of CO₂ on the solvated electron lifetimes and work function modifications upon CO₂ addition, suggesting reactions of the solvated electrons with CO₂.

[1] Stähler et al. Chemical Science 2, no. 5, 907-16 (2011)

[2] Demling et al. The Journal of Physical Chemistry C 127 (6), 2894-2900 (2023)

Mechanochemically synthesized COF for PFAS adsorption

Maroof Arshadul Hoque, Thomas Sommerfeld, Jan Lisec, Prasenjit Das, Carsten Prinz, Christian Heinekamp, Tomislav Stolar, Martin Etter, Biswajit Bhattacharya, Franziska Emmerling

Bundesanstalt für Materialforschung und -prüfung
Structural Analysis

Since the 1950s, per- and polyfluoroalkyl substances (PFAS) have been widely used in a range of consumer products, including clothing, paints, cookware and fast-food packaging. Properties such as high thermal resistance and water and oil repellency contribute to their wide usage. After decades of production, these substances have eventually found their way into our drinking water. Given the adverse effects of PFAS molecules on human health, the removal of these substances from our drinking water is a matter of urgency. This study employs the use of materials known as covalent organic frameworks (COFs) to adsorb PFAS molecules from an aqueous medium. COFs are crystalline, highly porous, two- or three-dimensional polymers with tunable topology and functionalities. For the purposes of this study, a COF was synthesised using 1,3,5-tris(4-aminophenyl)benzene (TAPB) and 1,3,5-triformylbenzene (TFB) via a mechanochemical process. Mechanochemistry represents a green synthesis method that uses mechanical energy to initiate chemical reactions, as opposed to using harmful solvents and heat. Adsorption tests were carried out to test the effectiveness of the material in question against PFAS. The COF was exposed to a solution of perfluorooctanoic acid (PFOA) and perfluorooctanesulfonic acid (PFOS). Following a 13-hour period, it was observed that 90% of PFOA and 99% of PFOS had been adsorbed by the COF. Most of the adsorption appeared to have occurred within the first 10 minutes of exposure. It can therefore be concluded that the TAPB-TFB COF is a promising material for the adsorption of PFAS molecules.

Use Your Time (Domain) Wisely: Streamlined Analysis of Complex Mixtures with Pulsed-Laser Techniques

Josefin Hufgard, Yi You, Jens Riedel

Bundesanstalt für Materialforschung und -prüfung
Instrumental Analytics

Analyzing complex mixtures with mass spectrometry (MS) usually requires extensive sample preprocessing and separation techniques such as high-pressure liquid chromatography (HPLC). This approach allows for one analyte to be detected at a time but at a cost of throughput. Recently, increasing attention is on the rapid and simultaneous ionization of all analytes in complex mixtures without extensive preprocessing, aiming to streamline the analysis process. Among those, pulsed laser-based ablation on single droplets, allows for contactless chemical investigation and reaction monitoring in situ, with minimal sample pretreatments. Specifically, the mid-infrared lasers encompass the fundamental vibrational resonances of typical biological matrices and solvents; their use results in efficient material removal from the bulk phase during the ablation process. Interestingly, the resulting analyte chronograms during the ablation process showed that the analytes were not detected concomitantly similar to that of a shotgun analysis. Instead, chronograms offered time-domain information by being detected at different timestamps. In this study, the distinctive time-domain profiles of each analyte were used to flag, recognize and group mass-spectral peaks that stem from the same chemical origin.

Here, we applied a pulsed diode-pumped solid-state (DPSS) laser at 3- μm wavelength to 10 μL hanging droplets of analyte. A secondary electrospray ionization (SESI) source was built in-house to ionize ablated analytes. With a model sample, i.e. a mixture of three antibiotics, remarkable differences in their chronograms were observed. In fact, the time-domain information reflects the chemical signature of the analytes and can provide an additional data dimension for accurate interpretation. With a phase-sensitive algorithm, the modified cross-correlation (mXcorr), the similarity between chronograms can be gauged. Consequently, mass-spectral peaks that shared the same chronogram features were grouped together, yielding clean analyte-specific mass spectra sets that can aid analyte identification. Finally, the applicability for biological samples, such as peptides, will also be discussed.

Mechanochemistry as a New Synthetic Route for the Synthesis of APIs

Caitlin Moss, Lucia Casali, Franziska Emmerling

Bundesanstalt für Materialforschung und -prüfung
Structural Analysis

Mechanochemistry offers a sustainable and innovative approach to synthesizing active pharmaceutical ingredients (APIs) by driving chemical reactions through mechanical force, such as milling or grinding, instead of traditional solvents. This technique aligns with green chemistry principles by reducing or eliminating solvent use, minimizing waste, and lowering energy consumption. Mechanochemical synthesis simplifies purification processes and often achieves higher atom economy, contributing to cleaner production methods. Additionally, the unique reaction environments accessible through mechanochemistry can unlock new pathways and improve yields for APIs that are challenging to synthesize conventionally. This poster highlights key applications and case studies that demonstrate the potential of mechanochemistry to replace environmentally taxing processes, providing an efficient, scalable, and eco-friendly alternative for pharmaceutical development.

Alkali antimonide photocathodes: Thermodynamic stability and vibrational properties from first principles

Julia Santana Andreo, Caterina Cocchi, Holger-Dietrich Saßnick

Carl von Ossietzky Universität Oldenburg
Institute of Physics

Modern advancements in generating ultrabright electron beams have ushered in innovative experimental techniques in particle accelerators. However, the current challenge lies in improving the quality of electron sources, primarily with novel photocathode materials, such as alkali-based semiconductors. In this work, we employ density functional theory combined with machine learning techniques to probe the thermodynamic stability of various alkali-based crystals, emphasizing the role of the approximations taken for the exchange-correlation (xc) functional. Our results reveal that SCAN offers the optimal trade-off between accuracy and computational costs to describe vibrational properties in these materials. Furthermore, it is observed that systems with a higher concentration of Cs atoms exhibit enhanced anharmonicities, which are accurately predicted and characterized with the employed methodology.

Structural, Electronic, and Optical Properties of Tin-Halide Monomers

Freerk Schütt, Ana M. Valencia, Caterina Cocchi

Carl von Ossietzky Universität Oldenburg
Institute of Physics

The growing interest in tin-halide semiconductors for photovoltaic applications demands in-depth knowledge of the fundamental properties of their constituents, starting from the smallest monomers entering the initial stages of formation. In this first-principles work based on time-dependent density-functional theory, we investigate the structural, electronic, and optical properties of tin-halide molecules SnX_{n-2} , with $n=1,2,3,4$ and $\text{X}=\text{Cl}, \text{Br}, \text{I}$, simulating these compounds in vacuo as well as in an implicit solvent. We find that structural properties are very sensitive to the halogen species while the charge distribution is also affected by stoichiometry. The ionicity of the Sn-X bond is confirmed by the Bader charge analysis albeit charge displacement plots point to more complex metal-halide coordination. Particular focus is posed on the neutral molecules SnX_2 , for which electronic and optical properties are discussed in detail. Band gaps and absorption onset decrease with increasing size of the halogen species, and despite general common features, each molecule displays peculiar optical signatures. Our results are elaborated in the context of experimental and theoretical literature, including the more widely studied lead-halide analogs, aiming to contribute with microscopic insight to a better understanding of tin-halide perovskites.

The role of glutamic and glutaric acid in Fenton-like reactions and implications to the aqueous particle phase of the atmosphere

Nazanin Taherkhani, Daniele Scheres Firak, Thomas Schaefer, Hartmut Herrmann

Leibniz Institute for Tropospheric Research

The Earth's atmosphere contains a large number of chemical compounds from various sources, and their concentrations vary greatly in the atmospheric particle phase. Reactive oxygen species (ROS) are chemical compounds that initiate chemical reactions and are fundamental to the effects of aerosols on public health, air quality, and climate. The Fenton reaction has gained significance in atmospheric chemistry due to its role in the oxidation of various atmospheric constituents. The Fenton and associated reactions involve the interaction of peroxides, typically hydrogen peroxide, with Fe(II) , leading to the generation of ROS. The reactivity of the Fenton reaction can be influenced by a variety of factors, including iron ligands which potentially inhibit or enhance the radical generation. In this investigation, the objectives were to determine second-order rate constants of Fenton reactions using the phenanthroline method based on the monitoring of Fe(II) conversion, and also elucidate the impact of glutamic and glutaric acid ligands on the reaction rate. We selected glutamic acid as a ligand owing to its prevalence as an amino acid found in atmospheric aerosols, hypothesizing its significance in atmospheric redox chemistry. In contrast, glutaric acid was chosen for its structural similarity to glutamic acid, allowing for a comparative investigation of ligand-specific effects. A significant outcome of this study was the determination of second-order rate constants for the Fenton-like reaction under pH 5 condition. Initially, the rate constant for the reaction in the absence of any ligand was measured at $68 \pm 2 \text{ M}^{-1} \text{ s}^{-1}$, serving as a reference for comparison. The rate

constant with the introduction of glutamic acid was $102 \pm 5 \text{ M}^{-1} \text{ s}^{-1}$ and of glutaric acid was $82 \pm 2 \text{ M}^{-1} \text{ s}^{-1}$. The observed differences underscored the crucial role of ligand coordination in modulating the reactivity of iron complexes on the reaction kinetics in Fenton-like reactions.