BUNSEN-TAGUNG 2025

Physical Chemistry
of the Climate and the Atmosphere

Leipzig University
March 17-19, 2025

BOOK
OF ABSTRACTS

POSTERS

Deutsche Bunsen-Gesellschaft
für physikalische Chemie

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Atmospheric online ion chromatograph

SH-GIC 7000

The atmospheric online ion chromatograph analyzes the soluble components of the air through online collection and liquefaction systems to achieve the function of continuous monitoring of air quality, providing comprehensive and accurate monitoring data for air quality monitoring and pollutant tracing. This equipment adopts a fully plasticized flow system, electrolytic self-regeneration suppression mode, all-weather continuous operation, remote control, remote data transmission, etc., so that the atmospheric online ion chromatograph has perfect and stable testing performance while bringing users an automated and humanized application experience.

Outstanding performance

- It can detect anions in the atmosphere in real time and stably, including but not limited to (F^-、Cl^-、NO_2^-、Br^-、NO_3^-、SO_4^{2-})；
- It can detect cations in the atmosphere in real time and stably, including but not limited to (Li^+、Na^+、NH_4^+、K^+、Mg^{2+}、Ca^{2+})；
- It can detect small molecular acids in the atmosphere in real time and stably, including but not limited to ($HCOO^-$、CH_3COO^-、$C_2O_4^{2-}$)；
- Simultaneously read ⩾10 sets of particle chromatographic data and images, and obtain online detection data.

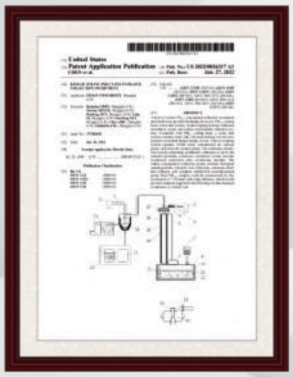
Atmospheric particulate matter concentration -soluble component analysis system


DIPLÔME

inventions Geneva

SALON INTERNATIONAL DES INVENTIONS GENÈVE

Geneva International Invention Award
Silver Award


United States
Patent Application Publication

US20220026317A1
US Patent

Product Features

- 🟩 Particle enrichment multiples 3-10 times, small fluctuation, high stability
- 🟩 Effective particle concentration diameter 30~3000nm
- 🟩 Input airflow 10-200L/min flexibly adjustable
- 🟩 Saturation temperature is close to room temperature
- 🟩 Install a drying tube to eliminate the influence of humidity
- 🟩 Sampling time can be set as needed
- 🟩 Dual systems run independently
- 🟩 Concentrated samples can be tested online and automatically retained at the same time

Product patents and papers

Shang, X., Li, L., Zhang, X., Kang, H., Sui, G., Wang, G., Ye, X., Xiao, H., and Chen, J.*: A semicontinuous study on the ecotoxicity of atmospheric particles using a versatile aerosol concentration enrichment system (VACES): development and field characterization, Atmos. Meas. Tech., 14, 1037–1045, https://doi.org/10.5194/amt-14-1037-2021, 2021.
Shang X, Kang H, Chen Y, Abdumutallip M, Li L, Li X, Fu H, Wang X, Wang L, Wang X, Ouyang H, Tang X, Xiao H, George C, Chen J.
PM1.0-Nitrite Heterogeneous Formation Demonstrated via a Modified Versatile Aerosol Concentration Enrichment System Coupled with Ion Chromatography. Environ Sci Technol. 2021 Jul 20;55(14):9794-9804. doi: 10.1021/acs.est.1c02373

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ddd

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P06_31	**Accessing Sn≥2 States of OLED Emitters by Femtosecond NIR Spectroscopy** B.E.N.B.E.N. de Faria, Düsseldorf/DE, W. Haselbach, Düsseldorf/DE, A. Prüfer, Dortmund/DE, J. Matthes, Düsseldorf/DE, S. Zimmermann, Düsseldorf/DE, Prof. Dr. P. Gilch, Düsseldorf/DE
P06_32	**Revealing excited state properties of Cu(I) photosensitziers by time- and temperature dependent step-scan FTIR spectroscopy** F.F. Drexlmeier, Kaiserslautern/DE, K. Rediger, Kaiserslautern/DE, M. D. Mandourah, Braunschweig/DE, M. Wolf, Braunschweig/DE, K. Haselhoff, Braunschweig/DE, M. Karnahl, Braunschweig/DE, S. Tschierlei, Braunschweig/DE, G. Niedner-Schatteburg, Kaiserslautern/DE, M. Wächtler, Kaiserslautern/D
P06_33	**Exploring Defect-Engineered Metal-Organic Frameworks with 1,2,4-Triazolyl Isophthalate and Benzoate Linkers for Dihydrogen Adsorption.** S.S. Chetry, Leipzig/DE, Muhammad F Lukman, Leipzig/DE, Volodymyr Bon, Dresden/DE, Rico Warias, Leipzig/DE, Daniel Fuhrmann, Leipzig/DE, Jens Möllmer, Leipzig/DE, Detlev Belder, Leipzig/DE, Chinnakonda S Gopinath, Pune/IN, Stefan Kaskel, Dresden/DE, Andreas Pöppl, Leipzig/DE, Harald Krautscheid, Leipzig/DE
P06_34	**Spectroscopic Studies on the Photoadditions of Psoralens and Angelicins to DNA** M. P.M. P. Rademacher, Düsseldorf/DE, A. T. Ott, Düsseldorf/DE, T. Rohn, Düsseldorf/DE, L. T. Leusch, Düsseldorf/DE, T. J. J. Müller, Düsseldorf/DE, P. Gilch, Düsseldorf/DE
P06_35	**Time-Resolved Spectroscopic Studies on the Net Heterolysis of Homopolar Selenium-Carbon Bonds** D.D. Grenda, Regensburg/DE, A. Tiefel, Regensburg/DE, C. Allacher, Regensburg/DE, E. Harrer, Regensburg/DE, C. Nagel, Regensburg/DE, R. Kutta, Regensburg/DE, J. Rehbein, Regensburg/DE, A. Breder, Regensburg/DE, P. Nuernberger, Regensburg/DE
P06_36	**Optical Spectroscopy of Diamondoid Derivatives** D.D. Schleier, Berlin/DE, M. Hörtnagl, Berlin/DE, P. Crandall, Berlin/DE, A. Breier, Berlin/DE, S. Stahl, Berlin/DE, S. Völz, Berlin/DE, O. Dopfer, Berlin/DE
P06_37	**Stimulated Emission in Liquid Core Fibers and Quasi-Isotropic Charge Carrier Confinement Effects of Cadmium Chalcogenide Nanoplatelets** D. A.D. A. Rudolph, Hannover/DE, V. Adolfs, Hannover/DE, A. Antanovich, Hannover/DE, S. Spelthann, Hannover/DE, D.H. Chau, Hannover/DE, M. Chemnitz, Jena/DE, M. Schmidt, Jena/DE, M. Steinke, Hannover/DE, J. Lauth, Tübingen/DE
P06_38	**Plasmon-assisted near-infrared photoluminescence of quantum dots** V.V. Alabusheva, Dresden/DE, A. Saha, Dresden/DE, V. Shilovskikh, Dresden/DE, V. Lesnyak, Dresden/DE

P06_39	**Exploring CO2 adsorption in Flexible MOF $[Cu_2(Me\text{-}trz\text{-}ia)_2]$ using in situ EPR spectroscopy** P.P. Das, Leipzig/DE, Sibo Chetry, Leipzig/DE, Muhammad Fernadi Lukman, Leipzig/DE, Harald Krautscheid, Leipzig/DE, Andreas Pöppl, Leipzig/DE
P06_40	**Quantitative spectroscopy of non-thermal molecular plasmas using a mid-infrared frequency comb** I.I. Sadiek, Bochum/DE, Norbert Lang, Greifswald/DE, Jean-Pierre H. van Helden, Bochum/DE
P06_41	**Quantifying Polymer, Water and Salt in Complex Coacervates by Femtosecond Stimulated Raman Microscopy (FSRM)** F.F. van Riel Neto, Düsseldorf/DE, C. Borbeck, Düsseldorf/DE, P. Gilch, Düsseldorf/DE
P06_42	**Using an organic dye to probe interfaces of perovskite optoelectronics with optical spectroscopy** S. M.S. M. Stepping, Uppsala/SE, G. Boschloo, Uppsala/SE
P06_43	**Conventional X-ray source-based time-resolved X-ray photoelectron spectroscopy (TR-XPS)** C.C. Groothuis, Oldenburg/DE, L. Mohrhusen, Oldenburg/DE
P06_44	**Exploring Structure-Property Relationships in Perovskite Supercrystals by Spatially-resolved X-ray Scattering and Optical Spectroscopy** J.J. Hiller, Tübingen/DE, R. Thalwitzer, Tübingen/DE, A. Bozkurt, Tübingen/DE, M. Scheele, Tübingen/DE
P06_45	**Raman-Spectroscopic Mapping of Structural Preferences in Lateral Shock Regions of Supersonic Jet-Expansions** N.O.B.N.O.B. Lüttschwager, Göttingen/DE,
P06_46	**Operando Spectroscopy of Pd and PdAu Laterally Condensed Catalysts during Selective Acetylene Hydrogenation Reaction** E.E. Öztuna, Berlin/DE, T. Götsch, Berlin/DE, D. Cruz, Berlin/DE, P. Zeller, Berlin/DE, O.V. Vinogradova, Berlin/DE, Z. Li, Berlin/DE, C. Rohner, Berlin/DE, Z. Gheisari, Berlin/DE, A. Steigert, Berlin/DE, M. Hävecker, Berlin/DE, M. Gorgoi, Berlin/DE, B. Roldán Cuenya, Berlin/DE, M. Muske, Berlin/DE, A. Knop-Gericke, Berlin/DE, T. Lunkenbein, Berlin/DE, K. Skorupska, Berlin/DE, V.J. Bukas, Berlin/DE, D. Amkreutz, Berlin/DE, M. Bär, Berlin/DE, R. Schlatmann, Berlin/DE, K. Reuter, Berlin/DE, A. Efimenko, Berlin/DE, R. Schlögl, Berlin/DE
P06_47	**Chiral Selector Ion Vibrational Spectroscopy on Amino Acid Enantiomers** F.F. Horn, Leipzig / Berlin/DE, K. R. Asmis, Leipzig/DE, S. Schmahl, Leipzig/DE
P06_48	**Probing the Temperature of Single Quantum Dots Confined in a Nanoparticle Ion Trap by Fluorescence Thermometry** K.K. Papagrigoriou, Leipzig/DE, S.C. Leippe, Leipzig/DE, F. Johst, Hamburg/DE, B. Hoffmann, Leipzig/DE, S. Zeller, Hamburg/DE, K.R. Asmis, Leipzig/DE, A. Mews, Hamburg/DE, B. Bastian, Leipzig/DE
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P06_50	**Determining the Orientation of NV- Color Centers in Heteroepitaxial Diamond by Optically Detected Magnetic Resonance (ODMR) Spectromicroscopy** J.J. Weippert, Freiburg im Breisgau/DE, C. Wild, Freiburg im Breisgau/DE, V. Lebedev, Freiburg im Breisgau/DE, J. Engels, Freiburg im Breisgau/DE, J. Kustermann, Freiburg im Breisgau/DE, T. Luo, Freiburg im Breisgau/DE, L. Lindner, Freiburg im Breisgau/DE, N. Mathes, Freiburg im Breisgau/DE, J. Jeske, Freiburg im Breisgau/DE, P. Klar, Freiburg im Breisgau/DE, C. Giese, Freiburg im Breisgau/DE, T. Fehrenbach, Freiburg im Breisgau/DE, M. Ohnemus, Freiburg im Breisgau/DE

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P07_04	**Hydrogen Atom Scattering from Graphene on Nickel** S.S. Tödter, Göttingen/DE, Y. Dorenkamp, Göttingen/DE, O. Bünermann, Göttingen/DE
P07_05	**Chemistry of charge-imbalanced layers generated by Ion Soft-Landing** K. A.K. A. Behrend, Leipzig/DE,
P07_06	**Switching Photoresponsive Metal-Organic Frameworks with Polarized Light** T.T. Al Najjar, Berlin/DE, C. Li, Karlsruhe/DE, Y. Jiang, Karlsruhe/DE, L. Heinke, Berlin/DE
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P07_08	**Investigation of Emulsification in Lab-on-a-Chip Systems for Efficient T-Detection via Liquid Scintillation Counting** J. P.J. P. Bäcker, Leipzig/DE, A. Becker, Leipzig/DE, H. Lippold, Leipzig/DE, C. Fischer, Leipzig/DE, D. Belder, Leipzig/DE
P07_09	**Development of a photocatalytic microreactor to investigate oxide-based model catalysts in NAP conditions** F.F. Li, Oldenburg/DE, Lars Mohrhusen, Oldenburg/DE
P07_10	**Adsorption and Structure Formation of the Carbonyl-Functionalized Ionic Liquid [5-oxo-C_6C_1Im][NTf_2] on Au(111) and Pt(111)** L.L. Knörr, Erlangen/DE, H. Bühlmeyer, Erlangen/DE, J. Steffen, Erlangen/DE, S. Trzeciak, Erlangen/DE, J. Hauner, Erlangen/DE, R. Eschenbacher, Erlangen/DE, D. Zahn, Erlangen/DE, A. Görling, Erlangen/DE, J. Libuda, Erlangen/DE
P07_11	**The Research Training Group GRK 2721: Hydrogen Isotopes ^{1,2,3}H** K.R.K.R. Asmis, Leipzig/DE, J. Warneke, Leipzig/DE, J. Westermayr, Leipzig/DE, K. Zeitler, Leipzig/DE, B. Abel, Leipzig/DE, D. Belder, Leipzig/DE, C. Fischer, Leipzig/DE, R. Gläser, Leipzig/DE, T. Gulder, Leipzig/DE, T. Heine, Leipzig/DE, H. Krautscheid, Leipzig/DE, A. Kuc, Leipzig/DE, A. Pöppl, Leipzig/DE, R Tonner-Zech, Leipzig/DE
P07_12	**Chemical interaction within novel carbon-silica composites studied by X-ray photoelectron spectroscopy** L.L. Rasmussen, Leipzig/DE, B. Lilli, Leipzig/DE, R. Denecke, Leipzig/DE, D. Enke, Leipzig/DE, S. Wassersleben, Leipzig/DE
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P07_14	**Water adsorption on doped single crystal $SrTiO_3$ and $BaTiO_3$ for the oxygen evolution reaction** M.C.M.C. Neumann, Darmstadt/DE, J.P. Hofmann, Darmstadt/DE
P07_15	**Carbon nanomembranes (CNMs) for separation of the gases relevant for green energy technologies** D.D. Hüger, Jena/DE, A.-L. Gaus, Ulm/DE, M. Frey, Jena/DE, M. Klein, Jena/DE, J. Picker, Jena/DE, C. Neumann, Jena/DE, M. Hager, Jena/DE, U. S. Schubert, Jena/DE, M. von Delius, Ulm/DE, A. Turchanin, Jena/DE

P07_16	**Structure and reactivity of MgO single-crystal surfaces studied by IRRAS with CO and CO_2 as probe molecules** W.W. Li, Eggenstein-Leopoldshafen/DE, Z. Yu, Eggenstein-Leopoldshafen/DE, A. Nefedov, Eggenstein-Leopoldshafen/DE, Y. Wang, Eggenstein-Leopoldshafen/DE, C. Wöll, Eggenstein-Leopoldshafen/DE
P07_17	**High-pressure hydrogen reduction of single crystalline iron surfaces - XPS/UPS and LEED** S.M.S.M. Kim, Darmstadt/DE, I. Dirba, Darmstadt/DE, O. Gutfleisch, Darmstadt/DE, J.P. Hofmann, Darmstadt/DE
P07_18	**Structural Anisotropy of Water at Charged Aqueous Interfaces Probed by Depth-Resolved SFG/DFG Spectroscopy** A.A. Diaz Duque, Berlin/DE, A. Fellows, Berlin/DE, S. Kaur, Berlin/DE, M. Wolf, Berlin/DE, M. Thämer, Berlin/DE
P07_19	**Aqueous Phase Transfer of Colloidal 2D Lead Chalcogenide (PbS, PbSe and PbTe) Nanoplatelets Preserving their Near-Infrared Photoluminescence** M. T.M. T. Vochezer, Tübingen/DE, L. Biesterfeld, Tübingen/DE, J. Lauth, Tübingen/DE
P07_20	**Ice Nucleation and Ice Binding Activity of Organic Molecules** C.C. Aleff, Bielefeld/DE, M. Sudbrock, Bielefeld/DE, T. Koop, Bielefeld/DE
P07_21	**Quantitative Analysis of the Kinetics of Recrystallization in Polycrystalline Ice Discs** M.M. Sudbrock, Bielefeld/DE, C. Aleff, Bielefeld/DE, T. Koop, Bielefeld/DE
P07_22	**^1H / ^2H / ^3H separation using nanoporous materials investigated by Thermal Desorption Spectroscopy** H.H. Lippold, Leipzig/DE, A. Becker, Leipzig/DE, M. Hirscher, Stuttgart/DE, J. Liu, Leipzig/DE, C. Fischer, Leipzig/DE
P07_23	**InAs Quantum Dots with tunable Absorptions up to ~ 2500 nm: Synthesis and mechanistically Insights** E.E. Salikhova, Hamburg/DE, S. Becker, Hamburg/DE, A. Mews, Hamburg/DE, J. S. Niehaus, Hamburg/DE
P07_24	**M(Cu,Ag)InX$(S,Se)_2$ Nanoparticles for Novel Transistor Structures** N.N. Günther, Dresden/DE, A. Eychmüller, Dresden/DE
P07_25	**The Charge State of Single Nanoparticles in the Gas Phase** S. C.S. C. Leippe, Leipzig/DE, K. Papagrigoriou, Leipzig/DE, K. R. Asmis, Leipzig/DE, B. Bastian, Leipzig/DE
P07_27	**Carbon Nanomembranes with Atomic Layer Deposited Al_2O_3: Unlocking High Selectivity and Scalability in Membrane Separations** Z.Z. Yao, Bielefeld/DE, J. Biedinger, Bielefeld/DE, M. Wortmann, Bielefeld/DE, N. Meyerbröker, Bielefeld/DE, M. Westphal, Bielefeld/DE, A. Hütten, Bielefeld/DE, G. Reiss, Bielefeld/DE, Y. Yang, Bielefeld/DE, A. Gölzhäuser, Bielefeld/DE

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P08_03	**On the Complex Hydrogen-Bond Network Structural Dynamics of Liquid Methanol: Chains, Rings, Bifurcations and Lifetimes** S.S. Blach, Bochum/DE, Dominik Marx, Bochum/DE, Harald Forbert, Bochum/DE
P08_04	**Strong Anisotropic Electronic Coupling between Gold Surfaces and Interfacial Water** C.C. Park, Bochum/DE, S. Ghosh, Telangana/IN, H. Forbert, Bochum/DE, D. Marx, Bochum/DE
P08_05	**Energy decomposition analysis for excited states** F.F. Kreuter, Leipzig/DE, R Tonner-Zech, Leipzig/DE
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P08_07	**Towards Accurate Modeling of Thermally Activated Delayed Fluorescence Emitters: Computational Investigations of Cyanoarenes** J.J. Weiser, Augsburg/DE, C. Wiebeler, Augsburg/DE
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P08_09	**Simulating Ion Diffusion in Perovskites: Application of Curvature Constrained Cubic Spline-Based Potentials in Molecular Dynamics** J.J. Jacoby, Aachen/DE, M. J. Wolf, Aachen/DE, J. Kullgren, Uppsala/SE, R. A. De Souza, Aachen/DE
P08_10	**Quantum Solvation of H_2O and H_3O^+ in ^{4}He and p-H_2 Bosonic Environments at Ultralow Temperature.** S.S. Maity, Bochum/DE, L. D. Caballero, Bochum/DE, H. Forbert, Bochum/DE, D. Marx, Bochum/DE
P08_11	**Intrapore and interpore diffusion of water in MOF-303** V.V. Karpov, Berlin/DE, F. Berger, Berlin/DE, J. Sauer, Berlin/DE
P08_12	**Water-Induced Linker Isomerization of MOF-303** V.V. Karpov, Berlin/DE, M. Debansh, Odisha/IN, F. Berger, Berlin/DE, J. Sauer, Berlin/DE
P08_13	**Temperature Dependence of the Methyl Group Dynamics of Ethanol in a Glycerol-Water Environment** M.M. Brandt, Rostock/DE, E. Bensons, Rostock/DE, T. Biedenbänder, Rostock/DE, B. Corzilius, Rostock/DE, R. Ludwig, Rostock/DE, D. Paschek, Rostock/DE
P08_14	**Ab Initio Studies on the Location and Stability of Bronsted Acid Sites in zeolite H–MOR** P.P. Neuendorf, Berlin/DE, H. Windeck, Berlin/DE, F. Berger, Berlin/DE, J. Sauer, Berlin/DE

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P09_02	**Program suit for modeling ion transport in solid electrolytes** M.M. Schäfer, Marburg/DE, K.-M. Weitzel, Marburg/DE
P09_03	**Temperature Dependence of Ionic Conductivity of Yttria-Stabilized Zirconia (YSZ) Crystals** A.A. Kumari, Marburg/DE, K.-M. Weitzel, Marburg/DE
P09_04	**Advancement of the Charge Attachment Induced Transport Technique** M.M. Fritz, Marburg/DE, Victor H. Gunawan, Marburg/DE, Timo Kassubek, Marburg/DE, Kevin Rein, Marburg/DE, Karl-Michael Weitzel, Marburg/DE
P09_05	**Quantification of chemical replacement zones by means of ToF-SIMS, NRA and nanoindentation** K.K. Rein, Marburg/DE, A. Korn, Göttingen/DE, T. Schwarz-Selinger, Garching/DE, C. Volkert, Göttingen/DE, U. v. Toussaint, Garching/DE, K.-M. Weitzel, Göttingen/DE

Physical Chemistry of the Climate and the Atmosphere

Bromine explosions and catalytic ozone depletion in the Arctic springtime boundary layer

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Ozone (O_3) volume mixing ratios (VMR) below 5 ppb are observed frequently during springtime in the polar boundary layer. This is related to bromine (Br_2) release from salty ice and snow. Br_2 VMR grows exponentially during so called Bromine Explosions (BEs). Consequently, increased amounts of vertical column densities (VCD) of BrO are observed in situ as well as by remote sensing. These BE events have been discussed serving as a source of tropospheric BrO at high latitudes, which is often underestimated in global chemistry-climate models (GCMs). We have implemented a treatment of bromine release and recycling on sea-ice- and snow-covered surfaces in the GCM ECHAM/MESSy Atmospheric Chemistry (EMAC).
We compare EMAC model predictions with observed O_3 and BrO VMR during the MOSAiC campaign (Spring 2020), from Arctic ozone monitoring stations and BrO VCD observations from satellite (TROPOMI). Bromide concentrations extracted from snow samples taken at Spitzbergen (Ny Ålesund) are compared with modeled bromine deposition on ice and snow. Based on these results, we present improvements to the release mechanism in EMAC and possible applications in ICON will be discussed.

Kinetics of the reaction of OH with CF_3CHO at different temperatures

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Hydrofluoroolefins (HFOs) are increasingly being used in applications such as refrigeration and foam blowing, where they replace substances that have larger ozone-depletion potentials and global-warming potentials. In the atmosphere, HFOs rapidly react with the OH radical to form a number of products including trifluoroacetaldehyde (CF_3CHO) the fate of which is either reaction with OH or photolysis. The OH-initiated degradation of CF_3CHO can lead to the formation of trifluoroacetic acid (TFA, $CF_3C(O)OH$) which is believed to be detrimental for the environment.

$$OH + CF_3CHO\ (+\ O_2) \rightarrow H_2O + CF_3C(O)O_2 \qquad (1)$$

$$CF_3C(O)O_2 + HO_2 \rightarrow CF_3C(O)OH + O_3 \qquad (2)$$

To date, the reaction of CF_3CHO with OH is poorly characterised, with no published data on the rate coefficient at temperatures other than room temperature which precludes accurate assessment of its role in e.g. TFA formation in different parts of the atmosphere.[1]

In this work we determine temperature dependent rate coefficients for reaction (1) using the pulsed-laser-photolysis, pulsed-laser-induced fluorescence (PLP-LIF) technique with various OH precursors and CF_3CHO concentrations measured online by UV- and IR-absorption spectroscopy and use these to assess the atmospheric lifetime w.r.t reaction with OH of CF_3CHO at different altitudes.

Literature:
[1] R. Atkinson, D. L. Baulch, R. A. Cox, J. N. Crowley, R. F. Hampson, R. G. Hynes, M. E. Jenkin, M. J. Rossi, J. Troe, T. J. Wallington, Atmos. Chem. Phys. 2008, 8, 4141.

The viscosity and surface tension of supercooled levitated droplets determined by excitation of shape oscillations

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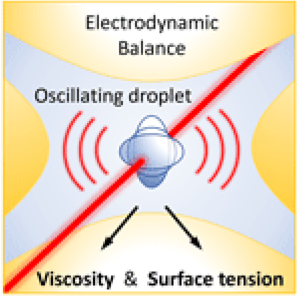
Atmospheric aerosols impact the radiative budget of the climate, air quality and human health [1]. Viscosity and surface tension are important physical properties of aerosol that influence numerous atmospheric processes, such as the rate of heterogeneous and photochemical reactions, the lifetimes of chemical species, the evaporation and growth processes leading to CCN formation, and the ability to act as IN. Due to the complex chemical composition of atmospheric aerosol, viscosity and surface tension evolve during an aerosol lifetime.



We report a new method for determining the viscosity and surface tension of supercooled liquid droplets using electrodynamic levitation and phase analysis of shape oscillations. The method uses a high-frequency alternating electrical potential to excite shape oscillations in a levitated droplet, and the phase shift in the oscillations is used to determine droplet viscosity and surface tension simultaneously. The advantages over existing contactless methods include its applicability to atmospherically relevant temperatures and the possibility of continuously monitoring changes in real-time. We demonstrate proof-of-concept measurement for supercooled water droplets and dilute sucrose solution droplets. The technique is especially well-suited for investigating the role of atmospheric processing in the viscosity and surface tension of solution droplets in equilibrium with a given or changing relative humidity or temperature.

Literature:
[1] M. Shiraiwa et al. Environ. Sci. Technol., 51, 13545–13567, **2017**
[2] M. Singh, S. H. Jones, A. Kiselev, D. Duft and T. Leisner, Atmos. Meas. Tech., 16, 5205–5215, **2023**

Laboratory Investigation of the Influence of NO and NO_2 on the measurement of organic nitrates in a simulation chamber by thermal dissociation cavity-ring-down spectroscopy (TD-CRDS)

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Measurement of total peroxy nitrates (∑PNs) and alkyl nitrates (∑ANs) by instruments that use thermal dissociation (TD) inlets to convert the organic nitrate to detectable NO_2 can suffer from systematic bias (both positive and negative) resulting from unwanted secondary chemistry in the hot inlets. Here we report experiments using (for the first time) atmospherically relevant, unsaturated, biogenic alkyl nitrates generated in a simulation chamber as well as two different PAN sources. We show that the widespread use of a commercially available C3-alkyl nitrate (isopropylnitrate, IPN) to characterise inlet chemistry for detection of ANs is not appropriate for air-samples that contain nitrates of biogenic origin. By detecting NO_X rather than NO_2, we provide a simple solution to avoid the bias caused by conversion of NO to NO_2 by primary and secondary peroxy radicals formed in the thermal degradation of long-chain, alkyl nitrates in air at TD-temperatures. We also highlight pitfalls in the use of photochemical sources of PAN to characterise the TD-inlets which is related to the presence of thermally labile trace gases such as peracetic acid ($CH_3C(O)OOH$) and hydrogen peroxide (H_2O_2).

Accurate Property Data from Theory for Small Molecules relevant to Atmospheric Chemistry

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Data for properties of isolated small molecules in their electronic ground state, like molecular structure (r_e, r_0, r_g, … structure) or fundamental frequencies, are of importance in many branches of science, e. g. astrochemistry, atmospheric chemistry, heterogeneous catalysis, matrix isolation vibrational spectroscopy under cryogenic conditions, to name just a few. The importance of high-quality data for *isolated* molecules is in their role as reference data for situations where these same molecules are found in some sort of environment. The influence of an environment on some molecular property cannot be judged without reference data for the same property for the isolated molecule.

Calculated property data compare very well with data from experiment (for the latter see, e. g., [1,2] and references therein), if (i) the system under study – the molecule in a given electronic state – is composed of only few and of only light atoms (say, $Z < 10$) and if (ii) the calculated property data derive from a sufficiently high level of quantum chemical theory (typically from an explicitly correlated coupled-cluster method like CCSD(T)-F12 for electronic structure).

This contribution shows, by comparison between experiment and theory, that accurate property data for small molecules and molecular ions relevant to atmospheric chemistry can be obtained, consistently and with good success, from a valence-only treatment.

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Health effects of Saharan dust particles and associated pollutants

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The Sahara Desert generates the most mineral dust (MD) content globally, contributing roughly 200 million tons of MD to the atmosphere each year. Saharan dust events, particularly in North Africa, contribute to the long-range transport of numerous chemicals and biological species, affecting biogeochemical cycles and exacerbating pollution in the atmosphere, water, and soil. Despite the large amount of MD released annually, few studies have explored its chemical compositions and associated harmful effects. The DUSTRISK project, which focuses on assessing the health risks associated with mineral dust and its associated pollutants, aims to enhance understanding of how the composition of Saharan dust impacts human health and its role in the long-range transport of other aerosol species, such as organic compounds and metal ions. Thus, a thorough analysis of the chemical composition of Saharan dust, including the assessment of its oxidative potential (OP) and toxicity in PM10 and PM2.5 samples are done to understand their effects.

During dust events, the OP increases significantly, with both coarse and fine particles showing values 3 to 4 times higher than on non-dust days. PM10 OP is about 73% higher than that of PM2.5, highlighting the importance of coarse Saharan dust particles. This increase in OP is linked to elevated levels of trace elements and organic compounds, including copper, iron, manganese, and zinc, which reached ten times higher concentrations during dust events. These substances are known to strongly deplete antioxidants and promote acute oxidative stress in the body. On average, organic (2.73 $\mu g/m^3$) and elemental (0.25 $\mu g/m^3$) carbon concentrations are 10 and 21 times higher on dusty days, respectively. Likewise, particle-bound mercury (PBM) also increases by about 74% during dust events, with average concentrations of 35.2 pg/m^3 for PM10 and 16.1 pg/m^3 for PM2.5, posing an addition health risk associated with coarse dust particles. When exposed to A549 cells for 24 hours, Saharan dust induced oxidative stress more strongly than quartz dusts. In addition, Saharan dust events appear to enhance the inflammatory potential of PM2.5, linked to the presence of endotoxins. Iron and manganese are identified as key factors contributing to PM2.5's inflammatory effects. This study underscores the complex chemical and biological interactions of Saharan dust and its effects associated with the transport of other atmospheric pollutants, highlighting its significant impact on human health and air quality in Africa.

Oxidation of Isoprene in the Atmosphere and the Effect of Temperature

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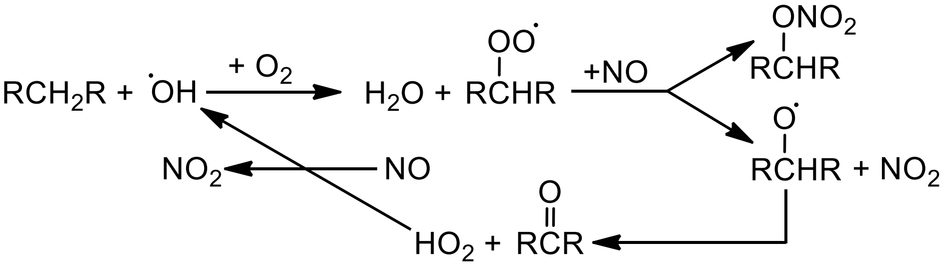
Isoprene (C_5H_8) represents the most important primary biogenic emission into the atmosphere, where (at 500 Tg Year^{-1}) it accounts for about half the emission of all biogenic VOCs (BVOCs) [1]. An understanding of its oxidation at different temperatures is essential in order to understand the formation of secondary pollutants such as ozone and secondary organic aerosol. In the atmosphere, the oxidation of organic trace gases, initiated by hydroxyl radicals (OH) and subsequent reactions with oxygen, produces peroxy radicals (RO_2), which react with NO to form nitrates and alkoxy radicals (RO) plus NO_2. Pressure, temperature, molecular size and structure determine the branching ratio between these two reaction pathways. As the alkoxy radical can react with O_2 to form HO_2 (which can further react to form OH), it is a key intermediate in the OH/HO_2 recycling mechanism [2,3]. In contrast, the formation of an organic nitrate is chain terminating.



In this work, we investigate the reaction of the isoprene peroxy radical (HOIsopOO) with NO using pulsed laser experiments (PLP-LIF and PLP-TAS) with real-time detection of NO_2 formation and off-line detection of organic nitrates.

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Biomass burning emission characterization before and after chemical aging in an atmospheric reaction chamber

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Biomass burning (BB) emissions are a major source of primary aerosols as well as aerosol precursors in the atmosphere. The plume consists of a complex mixture of inorganic and organic aerosol species and vapors that change during transport and aging, altering the mass, composition and properties of the aerosol. Field campaigns allow a characterization of plumes under realistic conditions, but the complex, incontrollable conditions lead to a large variability and studies have observed both particulate matter increases and decreases with aging. [1]

Here, we present a data set studying emissions from different biomass (beech, birch, wheat straw) under varying aging conditions: The focus of this work is daytime aging via OH oxidation or photolysis, however NO_3 oxidation was also explored. Furthermore, for each aging condition relative humidity and NO_x addition were varied. The experiments were performed at the Leibniz Biomass Burning Facility (LBBF) in combination with the Atmospheric Chemistry Department Chamber (ACD-C) at the Leibniz Institute of Tropospheric Research. A large suite of measurement instruments (online and offline) was used to characterize the gas and particle phase of the plume before and after aging.

The large parameter space and overall number of experiments allow us to show the variability both in the characterization of the fresh plume as well as post-aging. We aim to improve the understanding of how the chemical aging mechanism affects the volatility of compounds in both gas and particle phase. This, in turn, determines the aerosol composition and properties, which influence air quality and climate.

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Investigation of the impact of atmospheric pollution on air quality and ecosystems

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Particulate matter (PM) has profound implications for climate change, human health, and ecosystem sustainability. While many studies have explored particulate pollution globally, limited research exists on PM composition and distribution in Africa. This study investigates PM impacts in two distinct African contexts: urban air quality in Fez, Morocco, and ecosystem interactions in the Namib Desert, Namibia. Through intensive field campaigns, PM samples were collected and analysed for inorganic ions and trace metals using various analytical techniques.

In Fez, PM10 mass concentrations ranged from 37 to 107 µg m^{-3}, with traffic emissions, particularly from diesel engines, contributing 30% of PM mass. Biomass burning accounted for an additional 14% of total PM, primarily from local anthropogenic activities as evidenced by polar plot analysis. In the Namib Desert region, the study revealed that atmospheric aerosols serve as crucial nutrient vectors, supplying essential elements including phosphorus, iron, zinc, manganese, nickel, and copper to desert flora.

This comprehensive analysis provides valuable insights into both the environmental challenges and ecological services of PM in Northern and Southern Africa. The findings support targeted air quality management strategies for urban areas while highlighting the complex role of atmospheric particles in sustaining desert ecosystems. These results contribute to our understanding of PM dynamics in understudied African regions and contribute in developing evidence-based environmental policies.

Machine Learning-Based Prediction of the Glass Transition Temperature

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Knowledge of the glass transition temperature of molecular compounds in atmospheric aerosol particles is important for chemical reaction kinetics and phase state. While there is a great diversity of organic compounds present in aerosol particles, experimental glass transition temperatures are known for only a minor fraction of them. [1,2] Therefore, we have developed a machine learning model to predict the glass transition temperature of organic molecular compounds based on molecule-derived input variables. The extremely randomized trees (extra trees) procedure was chosen for this objective. The model generates descriptors from a SMILES (Simplified Molecular Input Line Entry System) string and reaches a mean absolute error (MAE) of about 11-13 K. [2]

For improved results, the model can use the melting temperature of the compound as an additional input variable, if known. In case no melting temperature is available, a separate machine learning model can be used to obtain a prediction for the missing melting temperature value. This model was also developed by our research group and was built on the Bradley Good data set, in combination with a histogram-based gradient boosting algorithm. Just like the glass transition temperature model, the melting temperature model needs a SMILES string as an input. [3]

Furthermore, we also show that the model's performance exceeds that of previous parametrizations developed for this purpose and also perform better than existing machine learning models. We believe that this combined model is a powerful tool for many applications in atmospheric aerosol science and material science.

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Glass Formation of Organosulfates

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Atmospheric aerosols significantly influence the Earth's radiation budget. They can act directly through scattering, reflection and absorption of light or indirectly by acting as nuclei for the formation of liquid water and ice clouds. For these processes, the phase state of the aerosol particles is an important parameter. Many atmospherically relevant volatile organic compounds (VOC) contribute to the formation of secondary organic aerosols (SOA), which may form amorphous solids, i.e. glasses, depending on the ambient conditions. [1,2]

Organosulfates represent the largest fraction of sulfur-containing organic compounds in atmospheric aerosol particles and have been detected in a variety of field studies. [3] Unfortunately, knowledge of the phase state of such compounds is sparse.

In our work, we present experimental results on the glass formation of selected atmospherically relevant organosulfates. The glass transition temperatures (T_g) were determined using differential scanning calorimetry (DSC). By spray drying aqueous solutions containing organosulfates employing the MARBLES technique, [4] amorphous phase states were observed for some of the compounds. This is surprising, as small ionic molecules generally have a high tendency to crystallize upon drying. In addition, binary mixtures of organosulfates with organic glass formers were investigated. In this way, the T_g for substances that did not form glasses upon spray drying in pure form was determined by extrapolation using the Gordon-Taylor equation. We show that organosulfates can contribute to amorphous aerosol particles in the atmosphere and can form glasses despite their ionic character.

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On the interference of laser-induced fluorescence from CH_2I and OH in kinetic studies of CH_2O_2 reactions

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Criegee intermediates are important reactive species generated during the ozonolysis of unsaturated hydrocarbons in the atmosphere. Rudolf Criegee proposed a mechanism in which ozone initially reacts with an alkene through a 1,3-dipolar cycloaddition, resulting in the formation of a primary ozonide.[1] This primary ozonide then rapidly decomposes into a stable carbonyl compound and a so-called carbonyl oxide, also known as a Criegee intermediate (CI). The CI can further react, and many of these reactions form OH radicals, the major oxidative species in the troposphere. An effective and by now widespread method to produce the simplest Criegee intermediate, CH_2OO, for kinetic laboratory studies is the reaction $CH_2I + O_2 \rightarrow CH_2O_2 + I$ with the iodomethyl radical, CH_2I, formed by photodissociation of CH_2I_2.[2–4]

In our contribution, we report on measurements of the laser-induced fluorescence after laser-flash photolysis of neat CH_2I_2 and CH_2I_2-O_2 mixtures. The experiments were carried out at 293 K and 10 mbar in different bath gases. The fluorescence intensity-time profiles observed near 310 nm, after excitation at 282 nm, can be explained in terms of superimposed vibrational relaxation of CH_2I and formation of OH. The results will be compared with existing literature data, and consequences for laboratory kinetic studies of Criegee intermediates will be discussed.

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The reactivity of peroxy radicals

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Peroxy radicals, RO_2, are key species in the atmosphere. They are formed from a reaction of OH radi-cals with hydrocarbons:

$$RH + OH + O_2 \rightarrow RO_2 + H_2O$$

In polluted environments, RO_2 radicals react predominantly with NO, leading to formation of NO_2, and eventually through photolysis of NO_2 to formation of O_3.

At low NOx concentrations such as in the marine boundary layer or the background troposphere, the life-time of RO_2 radicals increases and other reaction pathways such as self- and cross reaction with other RO_2 or with HO_2 radicals become competitive. To study these reactions, UV absorption spectroscopy has been employed in the past: this technique gives good sensitivity for peroxy radicals, but poor selectivity as these radicals have broad absorption features in the UV. We have established a technique allowing to follow peroxy radicals with a better selectivity compared to UV, but with still good sensitivity by cou-pling laser photolysis to cw-Cavity Ring Down Spectroscopy in the near IR.

Here, we will present some recent results on measurements of rate constants and branching ratios of the self-reaction of selected peroxy radicals [1-4]. Radicals are generated by laser photolysis, and the detection of the peroxy radicals is done be cw-Cavity Ring Down Spectroscopy in the near IR, a rather selective method compared to UV absorption spectroscopy.

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Peroxy radicals and Criegee intermediates in β-pinene ozonolysis at different temperatures

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Stabilized Criegee intermediates (SCIs) and organic peroxy radicals (RO_2) are critical in atmospheric oxidation processes and secondary organic aerosol (SOA) formation. However, the influence of temperature on their corresponding reaction mechanisms in SOA formation is unclear. Through utilizing formic acid as a SCI scavenger and regulating the ratio of ($[HO_2]/[RO_2]$) from ~0.3 to ~1.9 using different concentrations of CO, the roles of RO_2 and SCIs in SOA formation were investigated from 248 to 298 K, particularly for dimer formation in β-pinene ozonolysis [1]. The SOA yield increased by 21% from 298 to 273 K, while it decreased by 40% from 273 to 248 K. Both, changing $[HO_2]/[RO_2]$ and scavenging SCIs, significantly affect SOA yield and composition. SCI reactions accounted for more than 40% of dimer and SOA mass formation for all temperatures. Increasing $[HO_2]/[RO_2]$ inhibited dimer and SOA formation, and this inhibition became larger with decreasing temperature. Compared to low $[HO_2]/[RO_2]$ (0.30–0.34), the dimer abundance at high $[HO_2]/[RO_2]$ (1.53–1.88) decreased by about 31% at 298K and 70% at 248 K. $[HO_2]/[RO_2]$ has a specific impact on SCI-controlled dimers at lower temperatures by especially influencing the C_9–SCI reactions with RO_2. The dimers formed from C_9–SCI reactions with RO_2 were estimated to decrease by 61% at high $[HO_2]/[RO_2]$ compared to low $[HO_2]/[RO_2]$ at 248 K. The high reactivity and substantial contribution to SOA of β-pinene-derived SCIs at lower temperatures observed in this study suggest that monoterpene-derived SCI reactions should be accounted for in describing colder regions of the atmosphere.

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First comprehensive high resolution study of the $^{28}SiH_4$ octad bending bands

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High resolution spectra of silane can be interesting for the investigation of the atmospheres of giant gas-planets, such as Jupiter and Saturn, Ref. [Tre78], especially for studying their atmospheric composition and chemistry.

We present the infrared spectrum of mono-silane which was measured at varied experimental conditions with a Bruker Fourier transform infrared spectrometer IFS125HR and analyzed for the first time in the 2600–2950 cm^{-1} region of the octad where 16 strongly interacting triply excited bending bands are located [Ule25]. The 3505 transitions belonging to fourteen sub-bands of the octad (with the exception of unappeared $3\nu_4(A_1)$ and $3\nu_2(A_2)$) were assigned ($J^{max} = 20$) and theoretically analyzed in the frame of the effective Hamiltonian model. The obtained set of 139 fitted parameters reproduces the initial 3505 experimental line positions with the $d_{rms} = 7.3 \times 10^{-4}$ cm^{-4}. A list of assigned experimental transitions is presented as the Supplementary data 2 in the corresponding paper [Ule25].

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Formation of extremely low-volatility products from the aqueous oxidation of terpenoic acids derived from α-pinene and δ-3-carene by OH

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The atmospheric aqueous phase has been recognized in recent years as an important reaction media for the processing of water-soluble organic compounds. A large amount of water dispersed in the atmosphere in various forms, including fog, rain, clouds, and wet aerosol, makes it an important medium in which the volatile precursors are degraded and form aqueous secondary organic aerosols (aqSOA). The currently poorly characterized monoterpenes aqueous-phase processes are becoming an emerging topic of interest in the field of atmospheric chemistry.[1]

Here, we study reaction rate coefficients (k_{OH}), for the aqueous-phase reaction of pinic acid, caric acid, caronic acid, norpinic acid, and norpinonic acid with OH radicals. Additionally, quantitative analysis of the studied reaction markers, mainly, known α-pinene and δ-3-carene SOA components was performed.

The k_{OH} values measured were between 1.0×10^{9} and 4.4×10 9 M^{-1} s^{-1}. The highest reaction rate constant was measured for caric and caronic acids in temperature equal to 308K and pH=10, reaching kOH= 4.4×10^{9} for both compounds. The calculated activation energies, EA, fall in a range of 9-21 kJ mol^{-1}. Moreover, the enthalpy of activation (7.1–18.8 kJ mol-1) entropy of activation (0.7–39.0 J K-1 mol-1) of OH radical oxidation, as well as the lifetimes of studied compounds in the atmosphere, were calculated. Moreover, we found that terpenylic and terebic acids are important products not only of α-pinene oxidation, but also δ-3-carene oxidation.

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Secondary Organic Aerosol Formation through Uptake of Isoprene and alpha-Pinene Oxidation Products

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Oxidation of isoprene and monoterpenes have been shown to contribute significantly to the formation of secondary organic aerosol (SOA) in recent decades. [1] However, the involved SOA formation pathways are not clearly understood. In particular, kinetic investigations of the corresponding SOA formation through uptake are largely missing, leaving huge uncertainties in evaluating their impact on atmospheric chemistry, and thus, discrepancies in observed and predicted formation rates and spatial distributions of SOA by atmospheric chemistry models. [2]

Within the present work, the two most abundant isomers of isoprene-derived hydroxy hydroperoxides (ISOPOOHs) have been synthesized. Subsequently, to elucidate gas-particle interactions, the partitioning behaviour of 1,2-ISOPOOH was investigated in more detail for various seed particles using online MS techniques, namely PTR-ToFMS, AMS and CI-ToFMS. For acidic seed particles, a reactive uptake of 1,2-ISOPOOH with a specific uptake coefficient of $\gamma = (9\pm4) \times 10^{-3}$ was observed.

Furthermore, the OH oxidation of 1,2 ISOPOOH as well as alpha-Pinene under low-NO_x conditions was studied. The formation of numerous highly oxygenated organic molecules was observed. Subsequently, the uptake coefficients of the individual compounds were determined for two different seed particle compositions for both precursor compounds and analysed using a resistance model which considers limitations by gas- or particle-phase processes. Finally, overall trends for specific uptake coefficients depending on molecular properties, such as vapor pressure, molecular mass or their respective O/C ratio were investigated.

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Photochemical induced Aerosols Redox Chemistry leads to Mass Losses during Atmospheric Aging

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Secondary organic aerosols (SOA) are ubiquitous in the atmosphere and contribute to a large fraction of the total aerosol mass. These aerosols undergo chemical and physical transformations that change the amount of organic present [1]. In addition, light absorbing compounds in the aqueous/organic aerosol phase can initiate photochemical reactions that influence the aging of SOA. Traditionally, the growth and ageing of aerosols is primarily based on the transfer of organic matter and oxidants from the gas to the particles. However, the oxidation can fragment SOA components and release volatile organic compounds (VOCs). The complexity of these processes leads uncertainty as to how photosensitizers influence the ageing of aerosols in the atmosphere [2,3].

In the present study, photo-oxidation experiments were performed in the ACD-C twin chamber using anthraquinone-2-sulfonate (AQS) as a model photosensitizer, and mixtures of sucrose and glycine as a surrogate for organic particles. The photo-oxidation of sucrose by reactive species formed by excited AQS decreased the particle volume, while the oxidation state of the particle increased and VOCs were released into the gas phase. In the presence of the amino acid glycine, this effect was significantly enhanced. This emphasizes the influence of chemical composition on SOA ageing and the volatility of SOA in the presence of chromophoric organics.

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Experimental and model studies of the multiphase chemical processing of glyoxal at the CESAM cloud chamber

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Chemical processes in clouds were suggested to contribute substantially to secondary organic aerosol (SOA) mass [1]. However, considerable uncertainties still exist, e.g. with regards to the nature of the resulting aerosol particles [1,2]. Thus, the project PARAMOUNT aimed at investigations of chemical cloud processing of organic constituents such as glyoxal in the CESAM chamber. To study the multiphase processing, a large set of online instruments was used. The chamber results demonstrated the feasibility of such adiabatic experiments for the first time and, even if the cloud lifetime remains short, an aqueous-phase processing was studied. Under aerosol conditions, the OM formation was observed including various higher molecular weight compounds. The glyoxal-related experiments revealed an active chemical processing occurring interestingly after the droplet evaporation. There, e.g., a rapid formation of formic acid was observed. Finally, the performed CESAM experiments were modeled with a multiphase chemistry model using MCM/CAPRAM investigating chemical processing in deliquesced aerosol and cloud droplets. The measured AMS mass was reproduced by the model, however, sensitivity studies also demonstrated that the modeled OM concentration is very sensitive to the applied kinetic forward and backward rate coefficients of the glyoxal hydration process. Interestingly, the simulations revealed that the water evaporation proceeds on a faster timescale than the adjunct repartitioning of dissolved glyoxal. Thus, the kinetically delayed evaporation of glyoxal leads to higher aqueous-phase concentrations after the cloud evaporation fostering the formation of dimers and formic acid during the post-evaporation period.

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Impact of HOMs on ambient monoterpene SOA formation in a German forest

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Secondary organic aerosols (SOA) are formed by the reaction of volatile organic compounds (VOCs) from either anthropogenic or biogenic sources. The mechanism of SOA formation is a complex system involving a large number of reactions and chemical species, leading to large uncertainties in modelling predictions and potential climate impacts. In recent years, the importance of highly oxygenated organic molecules (HOMs) in SOA formation has been demonstrated. In order to better assess this issue, an intensive field campaign took place in July 2014 at the Forest Research Station of the University of Bayreuth (Germany) where two sites were equipped. [1] A complementary set of real-time mass spectrometers was deployed. To fully depict the chemical composition of the particles, offline chemical analysis based on a day-night regime of High-Volume quartz filter samples was performed, focussing on biogenic SOA tracers as well as particulate HOMs tracers. The different sources of particles including several biogenic SOA factors as well as transport-related factors were identified from source apportionment analysis on combined AMS organic and inorganic mass spectra, supported by the offline analysis results. Combining these results with the gas and particulate HOMs results, allowed us a unique opportunity to investigate the relationship between HOMs and monoterpene SOA as well as new particle formation.

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Atmospheric Aerosol Dynamics in Central Europe: Insights from Project TRACE

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European PM10 concentrations have stagnated over two decades despite emission reductions, possibly due to particle aging and long-range transport. Project TRACE assesses these factors in Central Europe, focusing on coal and wood combustion. Using combined online (Aerosol Mass Spectrometer and Aethalometer) and offline (GC-MS, Ion Chromatography) methods, it examined aerosol transport and transformation at three sites: Melpitz, DE; Kosetice, CZ; and Frydlant, CZ.

Measurements were taken in winter (Feb 1–Mar 10) and summer (Jul 1–Aug 20) of 2021. Winter aerosols were dominated by nitrate and sulfate, while organics prevailed in summer. Melpitz recorded winter nitrate and sulfate concentrations of 24 $\mu g/m^3$ and 9 $\mu g/m^3$, respectively, versus 9 $\mu g/m^3$ and 5 $\mu g/m^3$ in summer. Seasonal differences appeared in brown carbon absorption at 370 nm; winter absorption coefficients were 11.87 Mm-1 for Frydlant, 9.07 Mm-1 for Melpitz, and 8.77 Mm-1 for Kosetice, with a coefficient of variation of 14.09%. Frydlant's brown carbon was more absorbing, suggesting a darker source type. The NOAA-HYSPLIT model provided 96-hour back trajectories at 500 m altitude, linking sites to emission sources and identifying geographic origins.

Results from the First CIMS Intercomparison Workshop at TROPOS in ACTRiS CiGas

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Secondary organic aerosol (SOA) can constitute a major fraction of atmospheric aerosol mass with implications for the ecosystems, climate and human health. Condensable vapors are formed via atmospheric oxidation processes. The improved detection of these group of compounds with online mass spectrometric techniques has led to massive progress in the understanding of atmospheric processes in the last decades. The large variety of instruments and techniques, however, limits the comparability of the results.

In March 2023, ten API-ToF CIMS instruments took part in an intercomparison workshop at TROPOS in Leipzig, Germany within the organisational frame of ACTRiS CiGas UHEL. Our ACD-C twin chamber setup with two 19 m³ FEP-foil simulation chambers was used to host five of the instruments each. A unified inlet system was designed to improve the comparability of the results and minimize the differences during the sampling process. In the experiments we focused on the detection of sulfuric acid and different oxidized organic compounds that are the target compounds of CiGas-UHEL unit. Two calibration compounds were used: 4-nitrophenol (4-NP) and 1,2-ISOPOOH (1,2-IP) that were introduced in various concentration steps at dry and high RH conditions. We measured oxidation of α-pinene with OH and ozone also with high RH and NO in the chamber. Lastly, we measured different concentrations of sulfuric acid with dry and high RH conditions and with and without α-pinene in the chamber.

The intercomparison workshop provided critical information about variation of the detection of CIMS instruments. The response of the instruments to the changes in chamber conditions was not uniform which underlines the importance of intercomparison workshops.

Biophysical Chemistry and Biophotonics

Surface Enhanced Infrared Absorption Spectroscopy on the Interaction of Cell Penetrating Peptides with Lipid Bilayers

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Cell-penetrating peptides (CPPs) are short amino acid sequences capable of efficiently traversing cell membranes, facilitating the intracellular delivery of diverse therapeutic agents, including drugs and nucleic acids. Their versatile applications in drug delivery, gene therapy, and imaging make CPPs promising candidates for enhancing the efficacy of biomedical interventions [1]. Despite the widespread use of cell-penetrating peptides (CPPs) for intracellular cargo delivery, the precise mechanism of their interaction with cell membranes remains inconclusive. In order to shed light on this topic, we have utilized Surface-Enhanced Infrared Absorption Spectroscopy (SEIRAS) for the mechanism of peptide-lipid interactions between the novel class of cell-penetrating peptides (CPPs) and the solid-supported lipid bilayer (1-palmitoyl-2-oleoyl-glycero-3-phosphocholine, POPC) [2]. The CPPs primarily consisted of ten arginine molecules (R10) with perfluorinated tags. By comparing the spectra of different peptide samples, we have observed disparities in the way that non-fluorinated CPPs (R10C9 and R10C12) and fluorinated CPPs (R10F13 and R10F17) interact with POPC regarding their binding to the artificial lipid bilayer. We anticipate that this research will assist in elucidating the mechanism behind peptide-lipid interactions within the field of peptide-based intracellular delivery techniques.

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Quantum chemical study of non-covalent bonding in gentiodelphin

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Much of the beauty of nature's plants relies on the large variety of colorants present in their leaves and blossoms. The intensive blue color of *gentiana makinoi* is ascribed to the presence of gentiodelphin, an exceptionally stable di-acylated, tri-glucosated anthocyanidin [1]. It is generally assumed that the highly flexible molecular structure allows for many conformations with only small energetic barriers [2]. Interestingly, in the case of gentiodelphin, a partially closed structure was proposed from NMR data [1]. Acylation with aromatic acids is thought to shield the central benzopyrylium structure against water nucleophilic attacks by orienting face-to-face to it. Another proposed functional motive of such a stacked geometry is the possibility of intra-molecular energy transfer from the central structure to the acyl group [3]. In general, a subtle balance between hydrogen-bonding, dispersion interaction and bond-twisting can be a assumed to govern the molecule's low-energy structure. Using dispersion-corrected density functional theory (DFT-D), we have identified several minimum geometries of gentiodelphin with similar energy, in majority closed structures with both acyl groups in near face-to-face orientation with the molecular center. An energy decomposition analysis is facilitated by means of fragment molecular orbital (FMO) approach. In contrast to the findings in [1], we cannot identify a unique low-energy conformation of the molecule. Instead, using a set of appropriate structural descriptors and the extended tight binding (xTB) method implemented within the package CREST [4], we present a statistical analysis of the gentiodelphin molecule in closed and partially-closed conformations.

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The Entropy of Mixing in Self-Assembly and the Role of Surface Tension in Modeling the Critical Micelle Concentration

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A theory for the micelle formation of nonionic head-tail amphiphiles (detergents) in aqueous solutions is derived based on the traditional molecular thermodynamic (TMT) modeling approach and a variant of Flory-Huggins (FH) theory [1,2] that goes beyond lattice models [3,4]. The theory is used to analyze experimental values for the critical micelle concentration (CMC) of n-alkyl-ß-D-maltosides within a mass action model based on a refined definition of the CMC [4, 5]. To correlate those parts of the micellization free energy, which depend on the transfer of hydrophobic molecule parts into the aqueous phase, with molecular surfaces, known data for the solubility of alkanes in water [6] are reanalyzed [4]. Use is made of the concept of the pseudo-chemical potential introduced by Ben-Naim [7]. In this way, it is shown that modeling of the micellization free energy in the TMT approach combined with FH theory requires a term describing the change in liberation free energy upon micelle formation. The latter contains contributions from the kinetic energy of the micelles as well as the free/accessible volume in the solution. Implications are discussed for processes involving a change of hydrophobic molecular surfaces in contact with water such as membrane protein solubilization [8], protein folding, and protein channel opening [9,10].

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Influence of Initial High Molecular Weight Levels on Monoclonal Antibody Particle Formation Kinetics

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Protein based drugs may form proteinaceous particles that vary in size from nanometers to millimeters [1]. Monitoring the kinetics of protein particle formation, e.g., through accelerated degradation studies, is an attempt to understand and assess the rate and progression of particle populations. Little is known about whether the initial level of high molecular weight species of a protein solution influences the propagation of protein particle formation, and thus affects the storage stability (2-3 y at 5 °C required for drugs) of proteins. In this study, we have established a method to generate stable protein solutions of different high molecular weight levels (IHL). We have evaluated a 16-week thermal stability study at 40 °C of two monoclonal antibodies at different high molecular weight levels using chromatographic and particle analysis. We have performed an isothermal stress study with guanidinium hydrochloride at room temperature to evaluate the formation of high molecular weight species. The application of the Finke-Watzky (F-W) two-step nucleation model allowed us to mathematically describe the kinetics of high molecular weight formation and to extract kinetic parameters of this process [2]. For mAb-A, above a threshold of ≥ 7 % IHL, we observed that the formed trimers/tetramers undergo conversion into higher-order oligomers at 40 °C. This is not observed at lower high molecular weight levels. In contrast, mAb-B exhibited an increased IHL formation rate above a threshold of ≥ 4 % IHL, which was reflected in the monomer decay rates at 40 °C and the F-W kinetic parameters of the chemical stress study. This case study shows that the IHL exerts a differential influence on the progression of HMW formation. The reason for this difference is under investigation. The results of our short-term chemical stress study are in accordance with those of a classical 40 °C storage stability study, which evaluated different IHLs. The aim of this analysis related to the high molecular weight level formation kinetics will enhance our understanding of the protein particle formation process and facilitate the stabilisation of protein-based drugs.

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Investigation of Pressure-Induced Dimerization in a Pyrene-based Dyad Crystal: Associated with Auxiliary exhibition of thermally Induced Intramolecular Charge Transfer

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We report the design and photophysical properties of a D-B-A dyad composed of electron-rich N,N'-dimethylaniline (DMA) as the electron donor and pyrene (Py) as the acceptor, linked via a -CH=CH- chain. The molecule crystallizes in the triclinic space group *P*-1 with four symmetry-independent molecules in the asymmetric unit at 80K, undergoing a reversible structural phase transition at different temperatures depending on the solvent where it crystallized, where the unit cell volume reduces by half and the number of molecules in the unit cell decreases to two. For example, the transition temperatures for the crystals that were crystallized in cyclohexane, toluene, and dichloromethane are 200K,198K, and 209K respectively. Structural differences between the molecules, including pyramidalization at the tertiary nitrogen atom and variations in bond lengths, were observed during this transition. Notably, strong π···π stacking interactions were present at all temperatures. TDDFT calculations revealed a smaller HOMO-LUMO gap (3.06 eV) compared to other Py-bridge-DMA systems.[1] Temperature-dependent emission spectra collected at the P66 beamline in PETRAIII show dual fluorescence originating from locally excited (LE) and intramolecular charge transfer/excimer (ICT) states, with the ICT/excimer emission diminishing above 220K. The photophysical behavior correlates with the single crystal XRD result which shows a structural change over 190K while raising the temperature from 80K. Additionally, under hydrostatic pressure (0.5–2.0 GPa) using a diamond anvil cell (DAC), the crystals exhibited piezochromic behavior, characterized by a redshift and gradual quenching of emission. These findings demonstrate the potential of Py-CH=CH-DMA crystals as multifunctional materials responsive to temperature, pressure, and light stimuli, offering insights into the design of tunable luminescent molecular crystals for applications in optoelectronics and pressure sensors.

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Spectroelectrochemical investigation of heme protein axial ligand exchange variants in solution and in immobilized state

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Developing artificial metalloproteins is a promising research field that offers the possibility of creating novel catalysts for reactions that are either not catalyzed by natural enzymes or of superior properties tailored for technological or medical applications. The composition of the active site, including the coordination of the metal atom, is known to determine the enzyme selectivity regarding substrate activation. Here, we examine how structural variations correlate with the redox properties of the active site and, as such, serve as a parameter governing biocatalysis of specific reactions. Heme proteins are excellent model systems for these investigations as they are involved in many fundamental cellular processes, covering a wide range of redox potentials.

In this study, we employ a small multi-heme protein HTHP[1][2][3] (hexameric Tyr-coordinated heme protein) as a model for engineering the cofactor axial coordination. The catalytic heme bs are solvent-exposed, making them accessible to even bulk potential substrates. We examine HTHP variants displaying Tyr-, Met, or His-coordination. We use cyclic voltammetry to assess the redox potential of the enzyme variants electrostatically immobilized on an electrode, while UV-Vis spectroelectrochemistry allows us to determine the redox potential of the proteins in solution. (Surface-enhanced) Resonance Raman spectroscopy enables us to elucidate the spin and coordination of the cofactor to correlate structural ligand effects to its redox properties.

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Bioanalytical application of IR- and 2D-IR Spectroscopy: Tracking the enzymatic activity of hexokinase by monitoring the PO_3^-− and PO_2^-− vibrations.

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Hexokinase plays a crucial role in the glycolysis pathway, catalyzing the phosphorylation of glucose to glucose-6-phosphate. Infrared (IR) spectroscopy provides a non-invasive and precise methodology for monitoring enzymatic reactions by analyzing the characteristic vibrational modes of functional groups. This study examines the potential of linear and two-dimensional IR spectroscopy for the analysis of hexokinase enzymatic activity, with a particular focus on the phosphate stretch vibrations PO_3^- (1110 cm^{-1}) and PO_2^-(1150 cm^{-1}) motivated by recent works on isolated phosphate ions[1].

Real-time spectral analyses were conducted to monitor the conversion of a PO_2^- into a PO_3^-, which was induced by the reaction of ATP with glucose in the presence of hexokinase. The study validated the specificity of the PO_3^- and PO_2^- vibrations as reliable markers for phosphate group transformations, as previously proposed by Barth[2]. These findings demonstrate the potential of IR spectroscopy as a robust analytical tool for biochemical studies, enabling precise monitoring of enzymatic reactions.

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Ultra-short carbon nanotube channels incorporated into lipid membranes

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Single-walled carbon nanotubes (SWCNTs) are used as building blocks for fluorescent biosensors that can be used to detect small molecules. They emit light in the near-infrared region (> 1000 nm), enabling deeper tissue penetration and higher sensitivity than optical sensors in the visible range. [1] However, SWCNTs can also be seen as nanofluidic channels with novel properties. They have been incorporated into membranes to transport liquids and ions. [2]

Here, we synthesize short SWCNTs down to 10 nm and find a length-dependent red shift in the E_{11} absorption for shorter SWCNTs. We show that ultra-short SWCNTs with a length of 10 nm incorporate themselves into lipid membranes and act as nanochannels for small molecules, enabling the detection of membrane transport. Furthermore, we quantify how transport of small biomolecules through these channels changes SWCNT fluorescence. In summary, we use fluorescent carbon nanotubes as channels in lipid membranes and explore optical sensing of mass transport.

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Catalysis

Hydrogenation of α,β-unsaturated aldehydes over Pd, Cu and Pd/Cu Surfaces

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Previous works on the hydrogenation reaction of acrolein over Pd (111) single crystal surfaces have demonstrated an almost 100% selectivity on the formation of the unsaturated propenol. This selectivity arises from a surface oxopropyl-species formed by acrolein during the initial stage of the reaction.[1] In our recent studies[2-3], we showed that Pd(111) can be functionalized with different types of ligand that promotes chemoselectivity without being dependent on the spontaneous formation of the oxopropyl-species by acrolein itself. This was identified by the change in the kinetic of the reaction and a spectroscopic identification of a new reaction intermediate.

In this contribution, we present initial insights into a systematic theoretical study of the hydrogenation reaction of acrolein over Pd(111) and ligand-functionalized Pd(111), alongside preliminary results from our experimental investigation on the hydrogenation reaction of the α,β-unsaturated aldehyde methacrolein over Pd(111), Cu(111) and Pd/Cu(111) surfaces. We employ a combination of surface-sensitive tools along with the molecular beam techniques to obtain detailed information on the mechanisms and kinetics of methacrolein partial hydrogenation to 2-methyl-propenol. Specifically, infrared reflection absorption spectroscopy (IRAS) is employed to identify and follow the evolution of the surface species under the reaction conditions. Complementary, their spacial distribution on the catalytic surface is monitored by scanning tunneling microscopy (STM). Although still in an early stage, we aim to obtain a deeper understanding of the fundamental surface processes that results in selective hydrogenation of α,β-unsaturated aldehydes, paving the way for more tailored catalytic strategies in selective hydrogenation reactions.

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Investigations of vanadium doped $Co_3O_4(111)/Au(111)$ and mixed $V_xCo_{3-x}O_4(111)$ ultrathin films

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Vanadium is of high interest in oxidation catalysis due to its multiple oxidation states, which allow for selective oxidation processes. Especially when combined with Co_3O_4, it has shown catalytical improvements in the selective partial oxidation of alcohols in the test studies on powdered catalysts. In this contribution, we report on the recent progress in development of V-doped $Co_3O_4(111)$ and mixed $V_xCo_{3-x}O_4(111)$ oxide in form of ultrathin films that should serve as well-defined model catalysts in selective partial oxidation of alcohols. Specifically, the distribution and incorporation of V into $Co_3O_4(111)/Au(111)$ thin films was studied via a combination of scanning tunnelling microscopy (STM) and low energy electron diffraction (LEED) as a function of deposited amounts of Vanadium and preparation conditions. For this purpose, $Co_3O_4(111)/Au(111)$ thin films were prepared via physical vapor deposition (PVD) under controlled oxygen pressure at elevated temperatures followed by vanadium deposition and oxidation. The amounts of vanadium and the exact preparation procedure we systematically varied in such a way that a broad variety of V,Co-containing oxide structures were formed, ranging from $Co_3O_4(111)$ surface doped with a little amount of V up to mixed $V_xCo_{3-x}O_4(111)$ oxides or vanadium oxide islands formed on top of the $Co_3O_4(111)$ films.

STM and LEED analyses show that the stage in which the vanadium deposition and oxidation takes place plays a crucial role in the resulting V-containing cobalt oxide structures.

This study provides deep structural insights into different types of V-containing $Co_3O_4(111)$ surfaces and offers the preparation routes for a variety of model catalysts for partial selective oxidation of alcohols. Our findings build the basis for mechanistic understanding of structure-reactivity-selectivity relationships in mixed and doped Co_3O_4 oxides.

In-Situ Electrochemical Raman Spectroscopy of Fe,N-Doped Templated Carbon and Self-Adsorbed Fe-Phthalocyanine for Enhanced Oxygen Reduction Reaction Activity

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Reaching the goal of a green society and especially green industry calls for new energy carriers and other forms of energy transformation to be established. Amidst this transition, hydrogen and therefore fuel cells are one of the most promising topics to date with many attempts to incorporate it into daily life [1]. To catalyze the sluggish oxygen reduction reaction (ORR), less expensive and abundant catalysts have to be developed [2]. While heteroatom doped carbons are known for their good performance, a deeper understanding of the molecular interaction between heteroatoms like N, Fe and O in a carbon matrix during ORR is vital for platinum group metal-free (PGM-free) catalyst development [3].

This work is focused on in-operando analysis of self-adsorbed Fe-Phthalocyanines (FePc) on synthesized Fe,N-doped carbon. A self-adsorption of FePc on the porous Fe,N-doped carbon support material was used to generate a catalytic improvement on ORR activity in regards to its components acting alone. To understand this behavior, electrochemical and especially spectroelectrochemical methods are applied. Samples with different ratios were characterized by cyclic voltammetry, rotating ring disc electrode (RRDE) experiments and electrochemistry coupled Raman spectroscopy. From the results, the crucial influence of support porosity and the catalytic mechanism can be discussed. The Data suggest a cooperative mechanism for a non-planar interaction between macromolecular bound Fe, porous nitrogen doped carbon and Fe dopings.

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Insights on the effect of water in the isothermal partial oxidation of methanol on gold surfaces

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Nanoporous gold (npAu) is a highly selective catalyst for the partial oxidation of methanol to methyl formate (MeFo), an important precursor for various chemicals.[1] Water, a byproduct of the oxidation reaction and a common methanol impurity, significantly lowers MeFo formation for liquid phase methanol oxidation over npAu, but for gas-phase reaction, npAu demonstrates high selectivity even at high conversions and thus, high water contents in the feed.[1,2] These results indicate a complex role of water in the reaction mechanism which makes a microscopic understanding critical for using water-containing feeds allowing for lower purity constraints.

The aim of this study is to gain atomistic level insights of the role of water in the partial oxidation of methanol on Au surfaces. For this purpose, isothermal pulsed molecular beam (MB) experiments using time-resolved mass spectrometry and in-situ infrared reflection absorption spectroscopy under ultra-high vacuum (UHV) conditions were carried out with and without added water. By comparing reactivity of flat Au(111) and stepped Au(332) surfaces, moreover, the effect of low-coordinated sites was addressed. These investigations showed an overall decrease in MeFo formation when adding water. On the one hand, water affects methanol (or methoxy) adsorption and on the other hand, it alters the reactivity of the oxygen species on the surface by OH formation which exhibit different reaction barriers and mobilities, as shown by DFT and AIMD simulations. This also affects undesired overoxidation. The negative effect of water is nearly absent under oxygen-poor, low coverage conditions in the presence of low-coordinated sites. Thus, this study further enhances the microscopic understanding of the effect of water on the complex reaction mechansim for methanol oxidation on npAu catalysts.

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Novel Photocatalytic Pathway for the Selective Activation and Deuteration of specific α-C-H bonds for alcohol late-stage deuteration

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Most traditional methods for the deuteration of molecules are still based on the usage of well-known acid/base based promoted protocols. The downsides of these methods are poor selectivity and rather harsh reaction conditions.[1] Other more selective methods are using noble transition-metal based catalysts to activate specific positions to gain the deuterated compounds.[2] This is often coupled with high costs for the transition-metal based catalysts as well as a huge waste production. Nevertheless, selective deuteration of compounds is becoming more interesting for several reasons like some medical applications or as internal mass standards.[3]

Herein, we report a novel photocatalytic pathway for the selective deuteration of small organic molecules. The activation is achieved by the combination of a tertiary catalytic system which includes a previously unknown HAT acceptor, a thiol-based HAT donor and a commercially available photocatalyst.[4] We are able to directly activate C(sp^3)-H bonds in small alcohol molecules for selective late-stage transformation.

The exact mechanism is yet still unknown. The formation of the C(sp^3)-radical is mainly based on hydrogen abstraction due to *in situ* formed thiyl-radical which is acting as an HAT acceptor. However, higher yield is achieved by adding a novel HAT acceptor. In combination with the thiol as an HAT acceptor and donor we are able to achieve incorporation up to 99% of deuterium while remaining yields of the alcohol up to 99%.

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Heterostructured nanostars for photocatalytic water splitting

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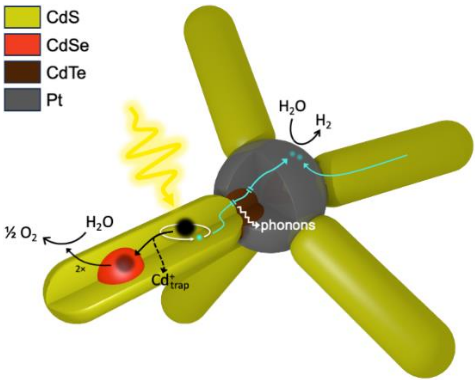
Nanosized hybrid semiconductor-metal materials are particularly promising for sustainable photocatalytic water splitting due to their intrinsic nanostructure advantages.[1] Both a high surface-to-volume ratio and the quantum size effect enable highly efficient light absorption with precise adjustment of the band edge to match the water redox potentials.

We have developed a synthesis for heterostructured nanostars with one central platinum particle.[2] Multiple cadmium chalcogenide nanorods function as efficient light-harvesting antennas, funnelling electrons to one platinum centre for multielectron hydrogen evolution reaction.



Here, we present the potential of these heterostructured nanostars for driving sustainable multielectron photocatalytic water splitting reaction. Catalytic performance is evaluated after a successful ligand exchange of the hydrophobic phosphorus-based ligands. This is achieved by photoreactor test experiments under controlled conditions, testing short surface ligands to determine their effect on the hydrogen evolution reaction.

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Heterogeneously Catalyzed Energy Release of Azaborine based Molecular Solar Thermal Systems

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Molecular solar thermal (MOST) systems combine the conversion, storage and release of solar energy using switchable photoisomers.[1] Azaborine/BN-Dewar couples are a relatively new class of MOST systems that show promising properties for energy storage applications such as portable devices.[2] However, so far only homogeneous catalysts are available to trigger the energy release,[3] which does not allow for a straightforward catalyst-photoisomer separation. In this work, we investigate the heterogeneously catalyzed energy release of azaborine/BN-Dewar based MOST systems with different substituents, namely 1-(tert-butyl)-2-mesityl-1,2-dihydro-1,2-azaborinin/Dewar (Aza1/Dew1), 1-(tert-butyldimethylsilyl)-2-mesityl-1,2-dihydro-1,2-azaborinin/Dewar (Aza2/Dew2) and 1-(tert-butyl)-2-mesityl-1,2-dihydro-1,2-azaborinin/Dewar (Aza3/Dew3), using Au(111) as a potential catalytic material. We tested different solvents (cyclohexane and dichloromethane) and used highly oriented pyrolytic graphite (HOPG) as an inert reference surface. In our study, we combined photochemical infrared reflection absorption spectroscopy (PC-IRRAS) with density functional theory (DFT). We show that Au(111) is active in releasing the energy stored in a BN-Dewar isomer. However, the catalytic activity strongly depends on the substituents and the solvent used. Although the activity of the Au catalyst is too low to be implemented in applications, our study provides proof of principle that a heterogeneously catalyzed approach is applicable.

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Advancing PFOA Remediation: Gas-Phase Photothermal Catalysis with Z-Scheme Systems

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Perfluorooctanoic acid (PFOA), valued for its thermal and chemical stability, has become a global environmental concern due to its persistence and toxicity.[1] PFOA is highly resistant to degradation and is frequently detected in rainwater, freshwater, sediment, and air.[2] Significant challenges remain, particularly in optimizing photocatalytic activity by improving charge separation and minimizing charge recombination. Overcoming these limitations is essential to enhance performance for PFOA degradation.

This study investigates the use of a direct Z-scheme photocatalyst comprising Fe_2O_3 and Cu_2O nanoparticles for the photothermal degradation of PFOA in the gas phase. PFOA was released from a carbon-based material through heating, then carried via helium gas into a photocatalytic chamber containing the Z-scheme catalyst, irradiated with simulated sunlight. The Z-scheme photocatalyst demonstrated enhanced PFOA removal efficiency due to its superior carrier charge separation and strong redox potential. The unique bandgap properties of Fe_2O_3 and Cu_2O contributed to this enhanced photocatalytic performance, providing a cost-effective and environmentally friendly solution for PFOA degradation.

Comprehensive characterization using XRD, XPS, photoluminescence, and TEM revealed that the Fe_2O_3 and Cu_2O combination within the Z-scheme architecture significantly improved charge separation and reduced recombination, promoting higher PFOA degradation rates. This approach represents a promising pathway for the efficient photocatalytic remediation of persistent organic pollutants like PFOA.

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A ternary (semiconductor nanoparticle):(redox polymer):(molecular catalyst) hybrid material for versatile photocatalyis

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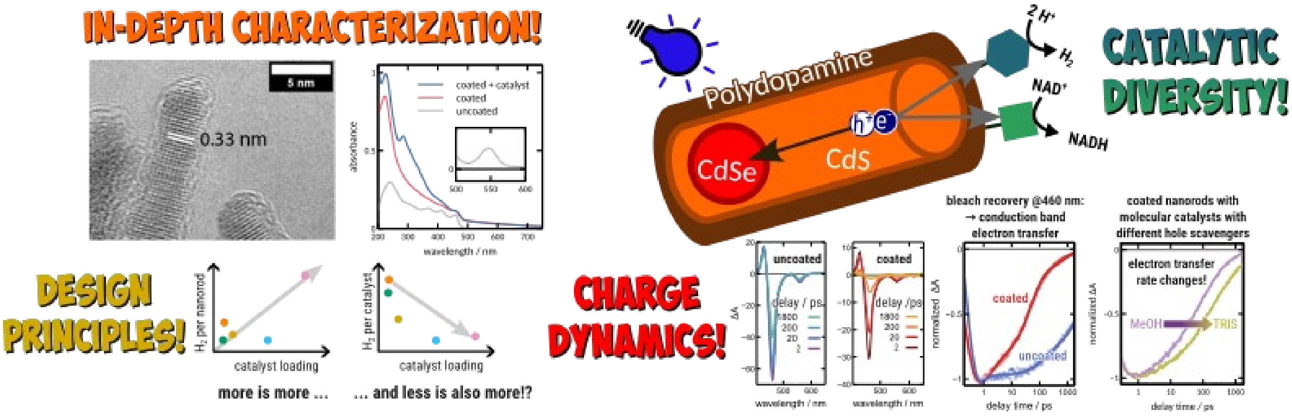
CdSe@CdS dot-in rod nanostructures are ideal photoactive materials for use in solar energy conversion because of their high absorption in the visible spectrum. With suitable catalysts, they can sustain many redox reactions such as solar water splitting. However, they suffer from poor longterm stability and only limited surface functionalization options. Therefore, we recently introduced a ternary hybrid system in which nanorods are coated with a polydopamine shell.[1,2] This shell acts as a scaffold with multiple options to bind different molecular catalysts, and protects the nanorods from photooxidation.

In this contribution, we deliver a comprehensive overview on this photocatalytic system. We cover an in-depth characterization of the synthesized material, incuding electron microscopic, UV/Vis, and elemental analysis, and use it in two different photoinduced redox reactions. From this, we generalize design principles to maximize the photocatalytic efficiency of this ternary photocatalyst. Last, we investigate the material *via* transient absorption spectroscopy to understand the underlying photo-induced charge transfer processes and gain mechanistic understanding of the photocatalytic cycle.



Acknowledgement: Financial support is acknowledged by the German Research Foundation (DFG) – TRR234 CataLight (project number 364549901) and the Federal Ministry of Education and Research (BMBF) – SINATRA: Py-Pho-Hybrid-Energy (project number 033RC035).

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COCoS: A contactless operando conductivity setup for measurement of dielectric properties

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The activity of surface catalytic sites depends on the number of active sites and the migration and rearrangement of active sites during the reaction [1]. Previous studies have demonstrated catalytic performance can be described using dielectric properties [2]. Therefore, it is essential to measure dielectric properties under operando conditions.

In this work, a device based on the microwave cavity perturbation technique (MCPT) was developed following the ideas of Eichelbaum et al. [3]. This technique facilitates real-time and non-contact monitoring of samples under various atmospheric conditions at temperatures up to 500°C.

Fig.1 COCoS: experimental set-up using MCPT.

The COCoS set-up was calibrated at room temperature using single crystals of $SrTiO_3$, $LaAlO_3$, Al_2O_3, TiO_2, and SiO_2 under a nitrogen atmosphere. The results indicated that the present COCoS setup can accurately measure the relationship between the resonance frequency and the permittivity. The device was subsequently used to test and analyze conductivity and catalytic performance of the binary metal oxides MoO_3, Nb_2O_5, TeO_2 and V_2O_5, laying a solid foundation for further research on the Mo-V-O and Mo-Nb-O ternary oxide catalysts.

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Catalytic Hydrogen Production from Ammonia Using Inconel Reactors

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Through NH_3 to H_2 conversion, green hydrogen production enables carbon-free energy storage and supply. We aim to produce H_2 from NH_3 using a reactor fabricated from Inconel acting as a catalytic support. Moreover, we develop an additively manufactured (AM) combustor capable of burning NH_3 and N_2/H_2 mixtures [1], as shown in Figure 1, contributing to H_2 combustion methods without generating environmentally harmful NO_x byproducts.

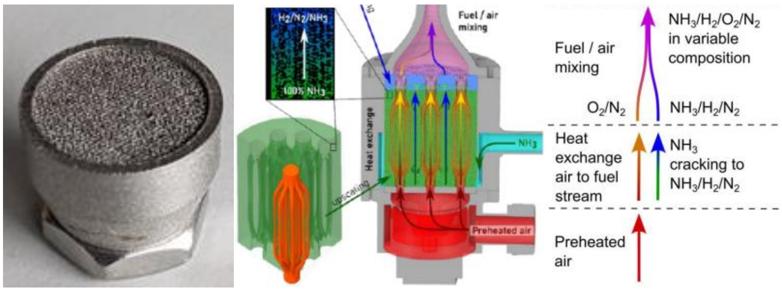

Figure 1. Left: catalytic fabricated using AM; middle: schematic visualizing the proposed low-NO_x thermochemical conversion process for NH_3. Preheated Air Supply (red), NH_3 Supply (light blue), Fuel Reformer (green), Micro Mixer (blue), Fuel/Air Mixing (violet) and Heat Transfer Pipe (orange); right: gas streams and mixing

According to the Sabatier principle, Ni and Co exhibit weak adsorption energy (E_{ad}) with N_2, while Fe and Mo exhibit strong E_{ad} with N_2 [2]. The combination of weakly adsorbing elements (Ni, Co) and strongly adsorbing elements (Fe, Mo) demonstrates significant potential as a catalyst for NH_3 decomposition [3]. The Sabatier principle suggests Inconel may be a good catalytic candidate. High-entropy alloys containing Co, Mo, Fe, Ni, and Cu exhibit higher catalytic activity than Ru for NH_3 decomposition [4], further supporting Inconel as a candidate catalyst.

We evaluate catalytic reactors fabricated from Inconel using AM technology, reporting on both the catalytic activity of various Inconel alloys and the development of a thermodynamically efficient catalytic reactor for NH_3 reforming.

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Partial oxidation of 2-Propanol on Co_3O_4 (111) model catalyst: the role of co-adsorbed water

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Partial oxidation of alcohols to their aldehyde counterparts is gaining considerable attention as a promising reaction system for reversible storage of green hydrogen in molecular systems. In this study, we investigate the mechanisms of 2-Propanol oxidation to acetone over model Co_3O_4(111)/Au(111) catalyst following a rigorous surface science approach. Employing a powerful combination of molecular beam techniques, reflection-absorption infrared spectroscopy (IRAS) and scanning tunnelling microscopy (STM), we address the evolution of the reaction intermediates and the desired product acetone on the surface under the reaction conditions and establish detailed correlations with the microscopic structure of the catalyst. The specific focus of this study lies at the understanding of the role of solvents, such as water or Acetonitrile, on the mechanisms and kinetics of acetone formation.

Specifically, our studies revealed that by a pre-treatment of Co_3O_4(111) with H_2O at elevated temperatures it becomes possible to substantially enhance the formation rate of acetone, while water deposition in the low temperature range rather suppresses the reaction. This result is in line with the observations obtained on the powdered Co_3O_4-based catalysts. The preliminary IRAS results suggest that the origin of the reactivity enhancement upon high temperature treatment with water can be most likely related to formation of isolated OH-groups. To clarify this hypothesis, we performed a comprehensive study, in which different reaction parameters, such as the amount of deposited water, the pretreatment temperature and 2-Propanol coverages were varied in a systematic way. Additionally, the possible role of surface defects, which can be potentially formed upon high temperature pretreatment of the catalytic surface, was investigated both by STM and IRAS.

The results of this study provide deep atomistic-level insights into the mechanisms of alcohol partial oxidation on oxide surfaces and the role of aqueous solvent in the related surface reactions.

Electrochemistry

Photoelectrochemical water splitting performance of the ZnONiO nanocomposite under visible solar light

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Solar photoelectrochemical (PEC) water splitting depends highly on catalyst materials. Among the most considered semiconductor materials, Zinc oxide (ZnO) is an excellent candidate due to its unique properties. However, the high recombination rate of pristine ZnO hinders PEC applications. This could be overcome by using an efficient co-catalyst such as Nickel oxide (NiO). Our research aims to develop ZnONiO nanocomposite using different concentration of NiO for PEC water splitting using the hydrothermal chemical growth method.

The result showed improvement on the PEC water splitting when NiO impeded into the ZnO which is attributed to the higher electron-hole pairs separation rate, high density of the active surface sites, and synergetic effect of ZnO and NiO. By using the hydrothermal chemical growth method, NiO can be grown into the semiconductor surface which can lead to efficient PEC water splitting activities.

Carbonized Biomass Electrode for Electrochemical Degradation of PFOA

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Per- and polyfluoroalkyl substances (PFAS), commonly referred to as "forever chemicals," are a significant global pollutant in drinking water [1]. Their persistence in the environment and resistance to degradation pose serious risks to human health, including fertility issues and cancer [2]. While several methods have been developed to reduce PFAS contamination, such as traditional adsorbents [3], thermal treatments [4], and plasma technologies [5], these approaches are often prohibitively expensive and energy-intensive.

In this study, we developed a sustainable and cost-effective solution by utilizing a free-standing electrode derived from biomass waste for the electrochemical degradation of perfluorooctanoic acid (PFOA), a prevalent PFAS compound. Biomass waste was pyrolyzed at different temperatures, which allowed the tuning of the band gap and surface area. Additionally, the electrodes were impregnated with metal nanoparticles to facilitate the reduction of PFOA.

Key parameters, including pH, stirring speed, and pyrolysis temperature, were systematically analysed to optimize performance. Notably, higher pyrolysis temperatures resulted in an increased band gap and BET surface area, both of which contributed to superior degradation rates. The results demonstrated that the carbonized biomass electrode not only achieved effective PFOA reduction but also offered a scalable, environmentally friendly alternative to conventional PFAS treatment methods. This work highlights the potential of free-standing biomass-derived electrodes as a promising candidate for addressing PFAS contamination, advancing the development of sustainable technologies for water purification.

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Manganese oxide-based electrocatalysts for oxygen evolution reaction and electrochemical reforming of organic compounds in acidic media

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Over the past decade, the frequency of extreme climate events has increased due to rising greenhouse gas emissions, underscoring the urgency of decarbonizing energy systems and transitioning to sustainable sources. Hydrogen production via the oxygen evolution reaction (OER) represents a promising pathway, but efficient OER electrocatalysts rely on scarce, noble metals like Pt, Ir, and Ru. [1] In contrast, Manganese oxides (MnOx) offer a sustainable alternative due to their abundance, non-toxicity, and catalytic activity in acidic conditions - crucial for PEM electrolyzers. [2] However, their stability above 1.75 V_{RHE} is limited by formation of permanganate ions and subsequent dissolution. To enable practical applications, it is crucial to improve the stability to extend the operational potential window. [3]

In this study, we investigated the activity, stability, and faradaic efficiency (FE) for O_2 during OER on manganese oxide and its combinations with antimony, tin, titanium, niobium, and silicon oxides. FEs were measured using differential electrochemical mass spectrometry (DEMS), with trends in stability and FEs analyzed. The most stable electrocatalysts were further tested for electrochemical oxidation of formic acid, methanol, ethanol, and ethylene glycol using DEMS and EC-IRRAS.

Finally, we discuss the factors governing selectivity and stability for these species, offering insights into the development of more efficient, selective, and stable earth-abundant electrocatalysts for electrolyzers.

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An in-situ IR spectroscopy study of N-methylphtalimide as anolyte for organic redox flow batteries

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The concept of redox flow batteries (RFBs) decouples power delivery from the battery capacity providing scalable energy storage. One promising anolyte for organic RFBs is N-methylphthalimide (MePh). In this study, we investigated the charging and discharging of MePh in MeCN *in-situ* using highly oriented pyrolytic graphite (HOPG) electrodes. We employed cyclic voltammetry (CV), electrochemical reflection-absorption infrared spectroscopy (EC-IRRAS) and density functional theory (DFT).

We observed the onset potential for the reduction at -1.9 V_{fc}. The reduced species were identified spectroscopically as a $MePh^{\bullet}$ radical. At -2.5 V_{fc}, an additional species forms, which we assigned to a decomposition product. The formation of this decomposition product limits the cyclability.

Finally, we demonstrated that degradation occurs only in solution, and no electrode fouling or dimer formation occurs. Based on our results, we propose two possible reaction mechanisms contributing to the degradation of the $MePh/MePh^{\bullet}$ couple: first, $MePh^{\bullet-}$ is able to deprotonate MeCN due to its strong basicity, forming a $MePhH^{\bullet}$ radical; second, MePh undergoes a radical reaction with MeCN, which abstracts an $H^{\bullet}$ radical, forming $MePhH^{-}$.

Electrochemical Insights into the Radical Scavenging Mechanism of DOPA Residues in Collagen Fibers

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DOPA (dihydroxyphenylalanine) residues are known to form in collagen fibers, the main structural protein of all connective tissues, by post-translational oxidation of tyrosine residues [1]. Recently, it has been suggested that whenever the collagen fibers undergo mechanical stress, then free radicals can form in them and the DOPA residues can function there as radical scavengers [1],[2]. In such a mechanism, the electrons from the DOPA residue migrate to the free radical site and quenches the free radical which simultaneously oxidizes the DOPA to DOPA-semiquinone. In the presence of O_2, it can further get oxidized to Dopaquinone with the formation of H_2O_2 as a side product [1]. In our current project, we are employing electrochemical techniques to investigate the free radical scavenging properties of DOPA residues in anaerobic and aerobic conditions. We have electrochemically oxidized the DOPA residue in a peptide with sequence G-DOPA-D to Dopaquinone. Here, the electrons are transferred from the DOPA residue to the electrode which resembled the migration of electrons from DOPA to the site of free radicals in the collagen fibers. By performing Cyclic Voltametric measurements, we identified the potential at which DOPA oxidizes to Dopaquinone and with the help of Chronoamperometry we were able to show that in the presence of O_2, the semiquinone intermediate formed during the electrooxidation of DOPA on the working electrode reacts with O_2. Comparative experiments conducted with the peptides G-Tyr-D and G-Phe-D revealed that the Tyr residue in G-Tyr-D is oxidized to DOPA at approximately 800 mV with respect to Ag/AgCl reference electrode, whereas no similar oxidation was observed for the Phe residue in G-Phe-D.

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Bio-inspired materials for energy storage applications

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Biomaterials, whether naturally occurring or derived as by-products from industrial processes, have gained increasing importance in recent years. Beyond their advantages of abundance, renewability, sustainability and non-toxicity, biomaterials exhibit unique structures and chemical properties that make them highly promising for green applications [1]. For example, naturally occurring compounds such as anthraquinone and riboflavin can serve as electrocatalysts for processes like carbon dioxide capture and oxygen reduction [2-5]. Additionally, biomaterials find applications in fields such as medicine, transistors and battery research. [1,6].

One particularly promising area of application for biomaterials is in energy storage technologies, for example in supercapacitors. Supercapacitors in general are characterized by their high-power density, rapid charge and discharge capabilities, and long cycle life. However, the development of sustainable and cost-effective materials for their electrodes and electrolytes remains a critical challenge [7]. Our approach is to investigate and develop green energy storage devices using biomaterials. With their tuneable structures, excellent electrochemical properties, and environmental benefits, biomaterials offer a compelling solution to these challenges, paving the way for greener and more efficient energy storage devices.

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Reaction Kinetics and Dynamics

Ab-Initio Simulation of Photoreactions

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Ab initio molecular dynamics (AIMD) involves describing the motion of the nuclei using classical Newtonian mechanics while treating the electron cloud quantum mechanically via density functional theory. This approach was pioneered by Roberto Car and Michele Parrinello with the development of the Car- Parrinello Molecular Dynamics (CPMD) program. Simulating photoreactions, presents a significant challenge compared to ground-state simulations. Here, we combine restricted open-shell Kohn-Sham theory (ROKS) with AIMD to simulate photochemical reactions. Our method successfully confirms a textbook principle for photochemically induced halide substitution of aromatic compounds. Photochemical reactions are also used in the synthesis of silver nanoparticles. We simulate the photochemical reduction of trisilver citrate with AIMD and expand our system to study the formation of silver nanoparticles. [1] [2]

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Ion Molecule Reactions with state-selected ions: Combined experimental and theoretical studies

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Kazuumi Fujioka, Honolulu/US; Rui Sun, Honolulu/US;
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In previous work the ion molecule reaction **HBr^+ + HCl** has been investigated experimentally as a function of the center of mass collision energy and the ion external rotation and compared to AIMD simulations.[1, 2] Resonance-enhanced multiphoton ionization (REMPI) was used to prepare rotationally state-selected ions in distinct vibronic states. Cross sections σ were measured inside a guided ion beam apparatus as a function of the rotational energy, E_{rot}, and of the collision energy, E_{cm}.

In this contribution we extend that work by studying the reaction system **HBr^+ + CH_4**. Data will be presented for the proton transfer (PT), charge transfer (CT), hydrogen abstraction (HA) and bromine transfer (BT). σ_{PT} decreases monotonically with increasing E_{cm} as well as with increasing E_{rot}. The cross section of the endothermic HA-reaction exhibits a distinct maximum at E_{cm}=1 eV and is independent on the ion rotation. The CT- and BT-reaction are independent on the ion rotation and both increase with increasing E_{cm}. As a function of E_{cm} the BT channel features a concave up behavior whereas the CT-channel shows a concave down behavior. The concave up behavior suggests an angular dependency of the reaction mechanism. The conducted AIMD simulations agree qualitatively with the experimental data.[3]

We also studied the reaction system **HCl^+ + Kr**. Here, the PT- and CT-channel are both endothermic. σ_{PT} exhibits a distinct maximum originating from the dissociation of HKr^+ in a consecutive reaction. σ_{CT} increases with increasing E_{cm}. The ion rotation has no pronounced influence on the reaction dynamics.[4]

Current efforts aim for the analysis of the reaction dynamics of the HA-reaction in the astrochemical relevant reaction system **NH_3^+ + H_2/D_2**. Preliminary results suggest that tunneling through a barrier occurs as postulated by theoretical work.[5, 6]

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Simulated Atmospheric Transformation of Tire Additives in an Aqueous Environment

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As traffic-related non-exhaust emissions, tire and road wear particles (TRWP) are an important contributor to synthetic polymer-based materials in aerosols. Besides the tire rubber itself, various chemicals, e.g. antioxidants, are added [1]. However, little is known on abundance, fate, and transport of airborne TRWP and their chemicals [2]. In the tropospheric multiphase system chemical conversion may take place through radical species such as hydroxyl- or sulphate-radicals [3].

The antioxidant 6-PPD and its transformation product (TP) 6-PPDQ have been studied for their degradation by light, hydroxyl- and sulphate-radicals in a photoreactor to simulate atmospheric liquid-phase conditions. TPs were tentatively identified by ultra-performance liquid chromatography high resolution mass spectrometry (LC-HRMS) and pseudo first-order rate constants were determined.

6-PPD was degraded by sulphate-radicals most rapidly, followed by hydroxyl-radicals, and finally by light. In contrast, 6-PPDQ was degraded by hydroxyl-radicals, only. The determined rate constants and tentatively identified TPs may further support the understanding of the atmospheric fate of tire-related chemicals.

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Aqueous OH aging of brown carbon aerosols emitted by pyrolysis of woody biomass

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Biomass burning (BB) is one of the major sources of emission of greenhouse gasses, non-methane volatile organic compounds, black carbon aerosols, and light-absorbing brown carbon aerosols (BrC) into the atmosphere. Biomass-related pollution is also projected to increase in the foreseeable future due to the widespread residential and industrial uses of wood and pellet fuel, and more frequent wildfires. BB emissions affect the air quality, and climate and harm human health. [1]

The chemical composition of BrC is not only extremely complex but also dynamic and, evolves during transport and chemical processing (aging) in the atmosphere. [2] Furthermore, poorly characterized chemical composition of fine BrC aerosols is strongly connected with their chemical, toxicologic, and optical properties [2, 3].

This work aimed to investigate the chemical aging of BrC inside the hydrometeors by the OH, which is the most important daytime atmospheric oxidant. BrC was generated in a benchtop combustor, extracted into water, and oxidized by the OH in the aqueous photoreactor. The molecular-level characterization of BrC was carried out with ultra-performance liquid chromatography coupled with electrospray ionization time-of-flight mass spectrometry. The metric data was processed using a non-targeted analysis workflow based on MS-DIAL data-mining software. This approach provided new, detailed insights into the chemical composition of the fresh and chemically aged BrC generated by pyrolysis of woody biomass.

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Probing the Vibrational and Rotational Wave-Packet Dynamics of Mass-selected Neutral Clusters

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Studying the spectroscopy and dynamics of size-selected neutral clusters remains challenging due to the difficulties associated with mass-selection for these clusters and the lack of intense and easily accessible radiation sources. Here, we report our setup and results on vibrational and rotational wave packet dynamics for mass-selected neutral clusters which allow us to obtain detailed vibrational and rotational information. We employ a cryogenic ion-trap tandem mass spectrometer in combination with a femtosecond laser system to perform femtosecond pump-probe spectroscopy involving with the negative-neutral-positive excitation scheme (fs-NeNePo). We have obtained detailed and accurate information on the molecular vibrations for the ground electronic states of neutral silver clusters via probing their vibrational wave-packet dynamics.[1,2] Additionally, we have recently investigated the rotational coherence in the mass-selected small boron clusters in the time-domain.

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Femtosecond Spectroscopy on the Oxidative Cleavage of Alkenes via Photoexcited Nitroarenes

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The oxidative cleavage of alkenes via ozonolysis is a common transformation in organic chemistry. Due to safety concerns alternative approaches are sought after. As demonstrated recently [1,2], photo-excited nitroarenes are selective agents for this cleavage. Here, femtosecond transient absorption experiments and quantum chemical computations on the photoreaction of 4-cyanonitrobenzene (4CNNB) with cyclooctene in acetonitrile will be presented. Cyclooctene is shown to quench the triplet state of 4CNNB with a bimolecular rate constant slightly below the diffusion limit. Quenching goes along the formation of a transient species which we tentatively assign to the depicted triplet biradical (Figure 1). Our results indicate that the short triplet lifetimes of nitroarenes and reformation of starting materials by the biradical hamper the efficiency of the photoreaction.

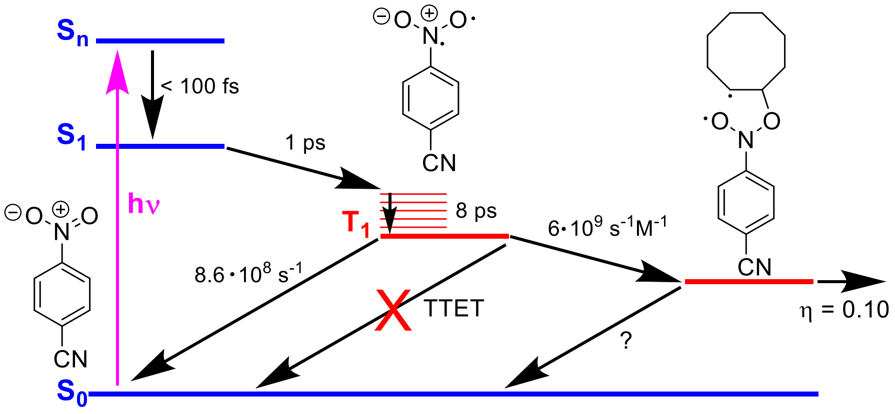

Figure 1. Preliminary kinetic scheme of the early processes in the oxidative cleavage.

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Investigation of reaction intermediates and heat flow by 2D-IR spectroscopy

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Within the newly funded CRC 1636 [1] we aim to study reaction intermediates and dynamics of plasmon-catalysed reactions or in the presence of a strong electric field (i.e. of vibropolaritons) by employing nonlinear and 2D spectroscopies.

In addition, IVR/VET can be efficiently followed by cross-peak dynamics in 2D-IR spectroscopy [2], following the assignment of vibrations by FTIR. In particular, heat or temperature changes can modulate the reaction dynamics. Here, 2D-IR is well suited to observe the local heat flow on a molecular scale via the time dependence of the cross peaks.

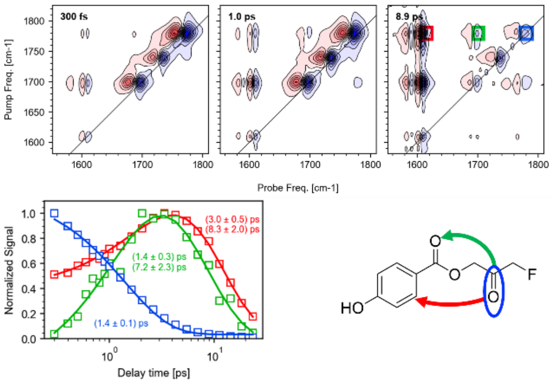

Figure 1: 2D-IR spectra showing a) snapshots of different waiting times between the pump-pulse pair and probe. b) Analysis of the vibrational lifetime of the C=O signal at 1700 cm^{-1} and c) a schematic of the vibrational energy transport (VET).

This contribution summarises our current efforts towards a detailed mechanistic study of heat- or plasmon-catalysed reactions by transient IR and 2D-IR and shows the application potential of these methods within the framework of CRC 1636.

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Colloidal synthesis of 2D klockmannite copper selenide nanocrystals and their plasmonic properties

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The family of copper chalcogenides is currently of significant interest in optoelectronic research due to their unique combination of semiconducting and metallic properties. These materials exhibit very strong ang highly tuneable surface plasmon bands in the near-infrared (NIR) region and excitonic absorption in the visible range. This dual behavior allows for a wide range of customisable combinations of plasmonic and excitonic properties within a single monolithic system, enabling adjustable nonlinear coupling. Controlling the size and shape of nanocrystals allows precise tailoring of these properties.

Copper selenides represent one such significant metal chalcogenides, however, the synthesis of single-phase copper selenide (CuSe) is challenging due to its complicated klockmannite structure and the intrinsic variable valence states of Cu and Se. Herein, we report a simple, phosphine- and thiol-free, effective hot-injection synthesis of colloidal 2D CuSe nanocrystals. We show the successful shape control simply by tuning the injection temperature and precursor concentrations without introducing additional ligands. We also demonstrate the strong absorbances of the CuSe nanocrystals in the NIR region which can be tuned by changing the shape and size. The spectral features in the NIR have been analysed by comparing them with theoretical calculations using the complex-scaled discrete dipole approximation (CSDDA) method.

Investigation of the temperature dependence of the photoinduced electron transfer reaction of excited singlet pyrene and indole using a tertiary solvent mixture

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Photo-induced electron transfer (PET) plays an important role in many areas of chemistry. The physical properties of the solvent influence the rate constant of PET reactions in many ways. The classical electrodynamical description of the solvent reorganization energies in electron-transfer theories use the Pekar factor $\gamma=(1/n^2-1/\varepsilon)$ as the solvent parameter. The dielectric constant ε and refractive index n influence the solvent dipole reorientations and contribute to the activation energy of the electron transfer reactions [1]. Unfortunately, most published measurements use different solvents in an inconsistent manner, e.g. Ref. [2]. The results of polar and non-polar solvents are compared together with high- and low viscosity solvents. We have presented recently results of experiments carried out in a series of solvent mixtures comprising propyl acetate, butyronitrile, and diethyl phthalate [3], covering a wide range of dielectric constants while keeping the refractive index and the viscosity constant [4]. The quenching rate constants were obtained from Stern-Volmer diagrams based on both static and dynamic (TCSPC) measurements. Fluorescence lifetimes, quenching rate constants k_q, and the ΔG-dependence of $\ln k_q$ are reported at different temperatures, with all solvent parameters kept nearly constant in a range from 15 to 55 °C.

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Monitoring of chemical reactions by single-molecule SERS using DNA origami-based plasmonic nanoantennas

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DNA origami nanostructures are ideally suited to arrange both plasmonic nanoparticles as well as receptors for analyte molecules with nanometer precision. In this way they can provide optimized substrates for surface-enhanced Raman scattering (SERS), where the strongest signal enhancement is localized in nanometric hot spots and where the DNA origami can be used to precisely position the molecules of interest. In recent years we have demonstrated the few- and single-molecule SERS detection in different nanoparticle arrangements.[1-5]

The monitoring of chemical reactions on a single-molecule level is particularly interesting, because relevant intermediates can be identified and elementary reaction steps can be revealed. As an example for a rather complex molecular system we studied the enzymatic activity of horseradish peroxidase (HRP) on the single-molecule level by SERS and identified single reaction steps within a catalytic cycle in-situ.[6] However, a major complication in the interpretation of single-molecule SERS data is a potential interaction of the excited surface-plasmon resonance and the molecules detected by SERS. Consequently, we have studied in detail, how plasmon-induced chemical reactions take place in small organic molecules. First results on single-molecule SERS measurements of plasmon-induced chemical reactions will be shown.

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Spectroscopy

Ion Effects on THz Spectra of Microsolvated Clusters

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Halide ions play a key role in atmospheric chemistry, yet little is known about their impact on the structure of water clusters that transport them. Despite various attempts, determining the effect of ions – in particular due to their location in the clusters – remains a daunting task. Terahertz (THz) spectroscopy has recently emerged as a powerful tool for the direct investigation of intermolecular vibrations perturbed by ions. Here, we performed extensive ab initio molecular dynamics simulations on finite-size Cl^- ion clusters in order to showcase its potential in structure elucidation. We investigated whether THz spectroscopy can be exploited to detect subtle rearrangements in water clusters, resulting due to different locations of Cl^- ions.

Temperature effects in aminoalcohols from vibrational spectroscopy of soft jet expansions

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For the purpose of spectral simplification, molecules are frequently cooled using supersonic jet expansions. Moderate cooling is rarely explored, although it encodes the evolution of hot transitions up to room temperature. Despite the non-equilibrium nature of adiabatic expansions, one can assign effective average Boltzmann temperatures for every rotational and vibrational degree of freedom that can be analysed. For this analysis, aminoethanol, dimethylaminoethanol and dimethylaminopropanol were studied by FTIR spectroscopy in pulsed supersonic slit jet expansions. [1] For rotational temperatures, the band contour and its broadening due to rotational contributions was analysed and the rotational temperature was estimated using a simple interpolation formula. [2] Vibrational temperatures were estimated by an intensity analysis of fundamental, sum and difference transitions. We focus on trends rather than accurate absolute temperatures, because the latter are anyway averages over different expansion regions and depend on model assumptions.

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Microhydration of tertiary amines:
Resonances and how to remove them by isotope substitution

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Tertiary amines are strong hydrogen bond acceptors towards an OH group of a water molecule. The hydrogen bonded OHb stretching vibration wavenumber is lowered and comes close to the water bending overtone b2. This gives rise to anharmonic resonance with b2 and states building on it, or to combination transitions of OHb with low frequency intermolecular modes [1]. These effects are investigated for 10 tertiary amines with FTIR [2] and Raman [3] spectroscopy in supersonic slit jet expansions. OHb is found to share intensity with b2 and up to two other states. Four different coupling models are explored. When regular water is replaced by partially deuterated water (DOH), the anharmonic resonances and the combination bands disappear and there is only one signal for the OHb stretching vibration left.

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Infrared spectroscopic markers of fluorous interactions

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Fluorination is one of the most common substitutions in molecular design, with the stability of C–F bonds ensuring that fluorinated molecules are often biologically inert. However, fluorine atoms are more than “fat hydrogens”; they significantly alter molecular properties such as polarity, acidity, and particularly hydrophilicity. Highly fluorinated molecules often segregate from both aqueous and non-polar environments into a distinct fluorous phase, an occurrence termed the “fluorous effect.” This phenomenon has gathered extensive interest, with some proposed mechanisms involving unusually weak dispersion forces [1], dipole-dipole forces [2], and unfavorable molecular geometries [3].

In this work, we investigate the vibrational responses of fluorinated molecules across different environments. We begin by examining the influence of electrostatics on simple fluorinated probes through the Vibrational Stark Effect (VSE), employing a solvatochromic approach. Next, we assess the vibrational characteristics of perfluorinated alkanes (PFAs) in various media, identifying specific markers indicative of PFAs under fluorous interactions. We further explore the molecular conformations of PFAs in solid-supported self-assembled monolayers (SAMs), observing trends that suggest a nonlinear dependence of the fluorous effect on molecular length. Finally, using these systems, we characterize the organization of interfacial water by Surface-enhanced infrared spectroscopy (SEIRAS) and detect a distinct dangling-water band, providing insight into water structuring at fluorous interfaces.

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Probing the Adsorption of CO_2 Molecules by Model Sorbent Materials with Infrared Photodissociation Spectroscopy

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As carbon dioxide emissions from fossil fuel combustion and deforestation continue to rise, developing effective CO_2 capture technologies has become a critical component in efforts to curb greenhouse gas levels. Among these technologies, direct air capture (DAC) has sparked considerable debate among researchers over the past decade, with discussion centered on its potential viability and significance as a greenhouse gas mitigation strategy. Moreover, the main challenge remains CO_2's low reactivity and stable structure, which hinders its transformation into value-added products. Addressing these, we focus on the initial adsorption and activation steps of CO_2 by catalysts, a necessary process to facilitate its conversion. By employing gas-phase studies on well-defined model systems, combined with infrared photodissociation spectroscopy and quantum chemical calculations, we can reveal molecular-level details of CO_2 binding and activation.

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IRPD Spectroscopy of $[Fe_2AlO_4]^+$ and $[Co_2AlO_4]^+$: Unexpected Structural Isomers upon Transition Metal Substitution

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Studies on metal oxide clusters in the gas phase are aimed at gaining a better atomistic understanding of single-site catalysts. Here, we study the structure and reactivity of cationic model systems using a combination of mass spectrometry, infrared photodissociation (IRPD) spectroscopy, ion mobility and electronic structure calculations ranging from density functional theory to multi-reference electron correlation methods.

The reactivity of the aluminium oxide cation $[Al_3O_4]^+$ is studied upon the sequential substitution of an Al atom by a transition metal atom, either Fe or Co. The electronically closed-shell $[Al_3O_4]^+$ has a cone-like structure and is unreactive towards methane,[1] while $[FeAl_2O_4]^+$ and $[CoAl_2O_4]^+$ show a planar bicyclic structure with a terminal oxygen radical ($Al{-}O^{\bullet-I}$) that activates CH_4.[2]

However, the doubly substituted species, $[Fe_2AlO_4]^+$ and $[Co_2AlO_4]^+$, are unreactive towards methane, and a structure assignment is not possible on the basis of a comparison of IRPD spectra to vibrational spectra derived from harmonic frequency calculations for different isomers. Therefore, we also performed ion mobility spectrometry (IMS) and ab initio molecular dynamics simulations to unambiguously determine the structure of these systems. The IMS results confirm a “key-like” structure with a planar four-membered ring connected to a nearly linear terminal $O{-}TM^{+III}{-}O^{-II}$ unit, that displays large amplitude motion and which can only be captured by simulations that also consider anharmonic effects.

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Spectroelectrochemical studies on CdS nanowires

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CdS is a promising material for photocatalysis due to its suitable valence and conduction band energies. Previous reports showed the use of CdS-based photocatalysts in the hydrogen evolution reaction, but the underlying charge transfer is poorly understood and the durability of the catalysts is severely limited due to corrosion by photogenerated holes. [1] Therefore, it is crucial to study the charge carrier dynamics inside CdS-based photocatalysts and the charge transfer to analyte molecules.

Photoluminescence (PL) spectroelectrochemistry is a tool to study the charge carrier transfer processes in semiconductor materials and to gain insight into the types and energies of states involved. [2,3] In this work, we study solvothermally synthesized CdS nanowires deposited onto a working electrode substrate of a three-electrode set-up in aqueous electrolytes. The nanowires are investigated by time-resolved PL spectroscopy in dependence of an applied potential, which varies the charge carrier concentration in the semiconductor states. In an electrochemically inert potential window, we find interesting changes in the PL signal, which originate from electrochemical filling of electron trap states. We have developed a rate equation model that successfully explains the changes in the trap band emission intensity and decay dynamics. Our study provides an understanding of charge transfer processes inside the nanowires. Future work will include the study of charge transfer to analyte molecules that exhibit reduction potentials in the same range in which the PL changes occur.

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Formation of Long-Lived Charge transfer states in PM6:Y6 Bulk-Heterojunction by Langmuir Schaefer deposition technique

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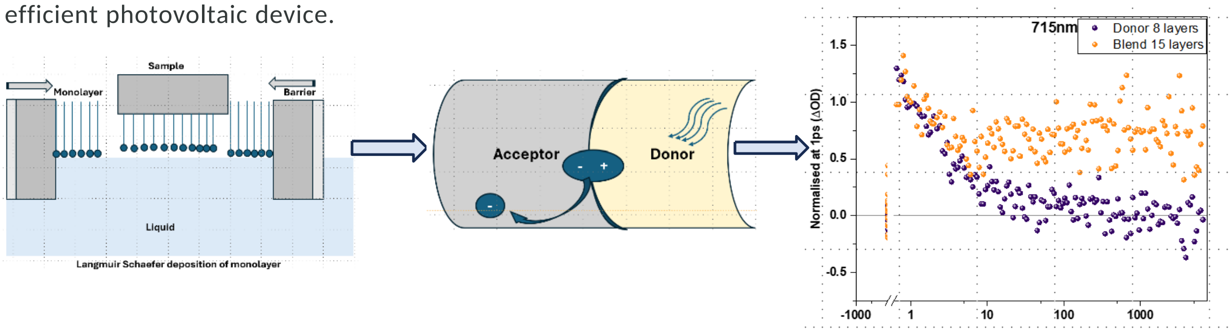
Non-fullerene acceptors along with different donor molecules have driven significant enhancements in device efficiencies for photovoltaic devices based on organic thin films, reaching an impressive 18.01 % efficiency[1].PM6(donor) has strong light absorption (it allows to capture of a broader spectrum of sunlight) and good charge mobility, which helps generate more excitons when exposed to light, and Y6 (acceptor) efficiently accepts electrons to allow current flow [2].

However, the aggregation and film non-homogeneity, influenced by the deposition method, can have a crucial impact on both the optical absorption and electronic properties. Langmuir Schaefer films exhibit more organized supramolecular arrangements than drop-casted and spin-coated films, which is significant for optimizing electronic performance in photovoltaic devices [3]. In our recent work, we have shown the crucial role of the Langmuir Schaefer film deposition technique in improving the lifetime of the charge transfer states in PM6:Y6 bulk heterojunction by transient absorption spectroscopy.

To investigate excited state dynamics of PM6(donor) and Y6(acceptor), different Langmuir film layers of donor and acceptor in a blending ratio of (1:1) have been prepared by Langmuir Schaefer deposition, and excited state dynamics are investigated by femtosecond transient absorption spectroscopy. Pristine donor (PM6) shows exciton decay within 10 picoseconds at 715nm; however, the donor-acceptor blend shows non-decaying behavior at 715nm. The lifetime of the charge transfer state is increased by 6 nanoseconds. Which shows efficient electron transfer from donor to acceptor.

This work along with further experimentation involving I-V characterization can give better insights into an efficient photovoltaic device.



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Stepwise Argon Decoration of Alcohols in Jet Expansions

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The cryogenic matrix shift of vibrational spectra relative to the cold gas phase is challenging to model and may have contributions in different directions - an experimental stepwise microsolvation approach can be useful in this context. Motivated by earlier exploratory studies in our group on argon-induced spectral shifts in alcohol spectra, this work tries to understand these shifts and their causal interactions between quest molecules and matrix atoms.

In this work FTIR spectra in supersonic expansions of (1,1,1,3,3,3)-hexafluoropropan-2-ol (HFIP) and (2,2,2)-trifluoroethanol (TFE) and their dimers [1][2] are investigated. By gradual addition of argon gas to the expansion, individual steps of Ar attachment can be observed in favourable cases despite the low spectral resolution. The OH stretching fundamentals, shifted from the Ar-free values, are assigned by their evolution with respect to the concentration of argon and compared to harmonic DFT calculations. Limitations of harmonic calculations for predicting these subtle shifts are revealed.

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Vibrational signatures of carboxylic acid microhydration

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In microhydrated carboxylic acids, both the acid and water act as hydrogen bond donors and acceptors. In the present work these hydrogen bonded complexes of formic and acetic acid with water were studied focussing on the hydrogen-bonded OH-stretching vibrations as sensitive indicators of cluster formation. Experimental Raman- and FTIR-jet spectra were assigned to the mixed dimer (1:1) as well as trimers (1:2, 2:1) with the assignments supported by DFT calculations. The observed spectra of formic and acetic acid with water show noticeable similarities.

We explored possible resonances in the formic acid/water dimer analogous to those occurring in complexes of ketones with water [1] as well as the elusiveness of in phase OH-stretching vibrations in all formic acid/water complexes, a behaviour also reported for formic acid/methanol clusters [2]. In contrast, the in phase OH-stretching vibration was clearly detected in the acetic acid/water dimer.

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Charge Carrier Diffusion in Colloidal MAPBBr$_3$ Perovskites

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Metal halide perovskites are promising light-harvesting components for future optoelectronic applications such as solar cells, light-emitting diodes, and photodetectors. [1,2] The applicability of such devices is subject to the bound electron-hole pair (exciton) properties. In addition to the exciton generation and decay, one should also understand their transport and diffusion behavior.

The examined nanostructured organic-inorganic perovskites are provided by colloidal synthesis, leading to a high defect tolerance and tuneable optical properties. Additionally, it enables shape and size control of the structures, allowing the growth of nanostripes, nanosheets, and nanoplatelets. [3] This reduced dimensionality and changed crystal structure influences the exciton dynamics and needs to be understood in terms of their applicability as optoelectronic devices.

A double-path confocal fluorescence-lifetime imaging microscope (FLIM) visualizes exciton migration under ambient conditions. The separation of excitation and detection path enables a time- and space-resolved mapping of the excitons. This technique gives insight into the exciton dynamics, such as the type of diffusion, the diffusion path, and the diffusion length.

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Sub-micrometer particle analysis using nanoelectromechanical systems-based Fourier-transform infrared spectroscopy (NEMS-FTIR)

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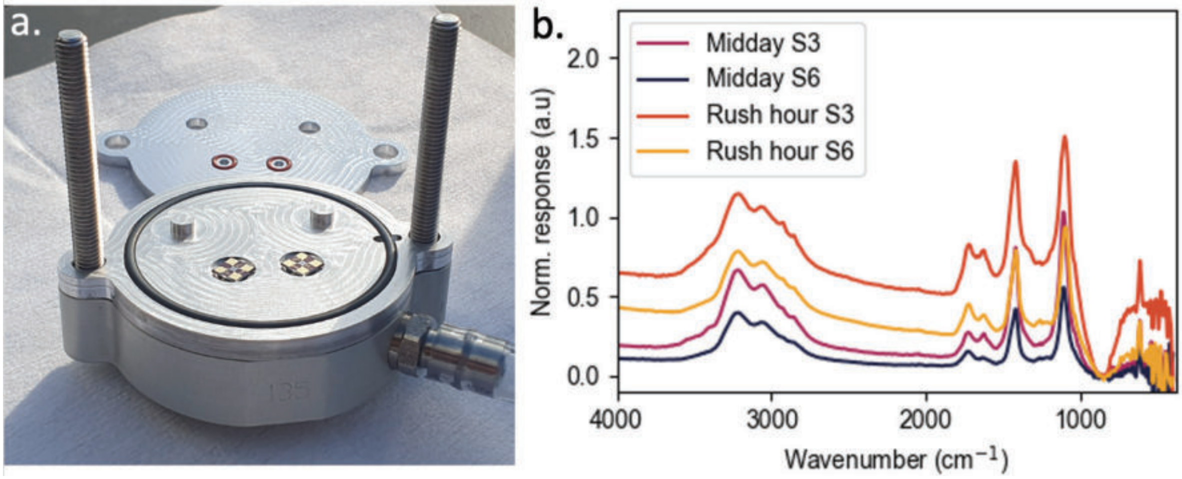
Airborne ultrafine particles (UFPs) have a high number concentration in urban environments but low total mass, complicating chemical analysis [1]. Traditional methods like FTIR spectroscopy and mass spectrometry require lengthy sampling or preparation. We propose NEMS-FTIR spectroscopy (EMILIE™ from Invisible-Light Labs GmbH) for rapid chemical characterization of sub-micrometer aerosols.

Figure 1a shows a MOUDI™ cascade impactor (TSI GmbH) with a custom adaptor plate used to pre-select aerosols and accommodate two nanomechanical sampling chips. Four duplicate samples of urban aerosol were collected each 2 min at 2 l/min, with particle cut-offs at 3.2 µm and 560 nm. The recorded spectra in Figure 1b show several peaks that can be attributed to organic and inorganic-based aerosols [1]. These results show, that nanomechanical sampling and sensing chips can be effectively implemented in a cascade impactor and used for the rapid chemical characterization of different particle fractions down to UFPs.



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Thin-film-based EC-SERS substrates for spectroelectrochemical applications in microfluidic flow cells

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Surface-enhanced Raman spectroscopy (SERS) is a highly promising technique for detecting analytes in small sample volumes and at low concentrations, due to its ability to enhance Raman signals by several orders of magnitude compared to classical Raman spectroscopy. [1] Additionally, the combination of electrochemical methods with surface-enhanced Raman spectroscopy (EC-SERS) enables the direct correlation of electrochemical processes with changes in molecular optical properties. [2] Particularly, the implementation of these techniques as a "lab-on-a-chip" technology enhances its applicability for environmental research and on-site analysis.

To this end, we have developed a chip-integrated three-electrode system, with the working electrode functionalized as the SERS-active surface. A thin-film-based approach was employed to fabricate the nano-structured SERS substrate, involving electrochemical deposition of silver nanoparticles onto a sputtered silver thin film. To ensure a homogeneous nanoparticle distribution and reproducible SERS spectra, we optimized a double-potentiostatic deposition protocol. [3]

The resulting chip-integrated three-electrode system, featuring a nano-structured silver working electrode, provides a compact, miniaturized platform for on-chip spectroelectrochemistry. Using 1,1′-Dimethyl-4,4′-bipyridinium dichloride as a model system, we demonstrated the voltage-dependent optical detection of its three distinct oxidation states [4] via EC-SERS in preliminary experiments.

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Hydrophobic cations reshape the Electric Double Layer at a gold/water interface.

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Using large hydrophobic cations as electrolytes has been shown to enhance several reactions, such as the hydrogen evolution reaction. However, the impact of such cations on the electric double layer (EDL) [1] and the hydrogen bond network of the electrode solvate interface is still incompletely understood.[2] Here, we investigate the impact of tetrabutylammonium cations (TBA^+) as hydrophobic cations at a gold surface on the EDL by a THz spectroscopic and combinational study via MD simulations.

Our findings indicate a partial desorption of TBA^+ at high potentials, leading to surface rehydration. Simultaneously, we observe the formation of a film primarily consisting of TBA^+ accumulated at the surface that transitions into a highly structured film of coadsorbed TBA^+ and Cl^-, demonstrating the strong impact of such electrolytes on the structure of the EDL.

Overall, the results highlight the significance of hydrophobic cations in structuring and modifying the electrode water interface. These results advance our understanding of the electrolyte effects on the electrochemical double layer and provide a new angle for future studies to understand reaction pathways, especially the proton transport from the bulk solution to the reactive site.

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Influence of the Hydrogen Concentration on the *ortho*/*para* Ratio for Benzonitrile Complexes

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Rotational spectroscopy and astrochemistry go hand in hand, as constants derived from Fourier transform microwave spectroscopy have been used on numerous occasions to identify molecular species in the interstellar medium (ISM). [1] Benzonitrile is an important example of a molecule that was identified in the ISM using rotational spectroscopy. [2] Its complex with hydrogen has a large dipole moment and is of particular interest, as it may serve as a precursor for hydrogenation reactions which could result in the formation of benzylamine or toluene. [3,4] The formation of said complex is possible because hydrogen itself is ubiquitous in the interstellar medium.

Our work was inspired by studies of the complex of hydrogen and OCS. [5] Using cavity Fourier transform microwave jet spectroscopy with helium as the carrier gas, we found large deviations of the *ortho* and *para* hydrogen ratios from the theoretical 3:1 ratio at room temperature prior to complexation, with ratios reaching up to 50:1. By systematically varying the hydrogen concentration ranging from 0.264 % to 35.1 %, we were able to not only identify an optimum concentration for the formation of the weakly bound *para*-hydrogen complex, but also to energetically rank the different species.

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Solving the Synthetic Riddle of Colloidal 2D PbTe Nanoplatelets with Tunable Near-Infrared Emission

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The colloidal synthesis of two-dimensional (2D) lead chalcogenide semiconductors yields near-infrared emissive materials with strong excitonic contribution at room temperature.[1-6] They are model systems for efficient charge carrier multiplication and hold potential as intriguing candidates for fiber-based photonic quantum applications. However, synthetic access to the third family member, 2D lead telluride (PbTe), remains elusive due to a challenging precursor chemistry. Here, we report a direct synthesis for 2D PbTe nanoplatelets (NPLs) with tunable photoluminescence (PL, 910 – 1460 nm (1.36 – 0.85 eV), PLQY 1 – 15 %), based on aminophosphine precursor chemistry.[1] Our NMR study underpins the synthetic importance of an *ex-situ* transamination of tris(dimethylamino)phosphine with octylamine to yield a reactive tellurium precursor for the formation of 2D PbTe NPLs at temperatures as low as 0 °C. Associated GIWAXS measurements confirm the 2D geometry of the NPLs and the formation of superlattices. The importance of a post-synthetic passivation of PbTe NPLs by PbI_2 to ensure colloidal stability of the otherwise oxygen sensitive samples is supported by X-ray photoelectron spectroscopy. Our results expand and complete the row of lead chalcogenide-based 2D NPLs, opening up new ways for further pushing the optical properties of 2D NPLs into the infrared and toward technologically relevant wavelengths.

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Insights into the optical and electronic properties of colloidal $MoSe_2$ semiconductors

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Transition metal dichalcogenides (TMDCs) are layered materials of the form MX_2 (M = Mo, W; X = S, Se, Te) which possess a direct band gap and strong spin-orbit coupling. [1,2] A reduced Coulomb screening of excitons in ultrathin TMDC monolayers results in large binding energies with values of ~500 meV at room temperature.

As a result of these interesting photophysics, a wide range of applications including sensors, nanoelectronics, energy harvesting, catalysis, superconductors and spintronics have been proposed. A critical step toward the realization of these applications is the scalable production of processable quantities of 2D semiconductor monolayers. [3-7]

We use colloidal bottom-up synthesis methods for obtaining $MoSe_2$, which we have established for different TMDCs [5-9] to yield processable inks, which are characterized by Transmission Electron Microscopy, X-Ray Diffraction, X-Ray Photoelectron Spectroscopy and Raman spectroscopy. From the inks we deposit $MoSe_2$ films and perform femtosecond transient and potential modulated absorption spectroscopy to determine the optical and electronic properties of the material. We are able to extract the optical and electronic band gaps of 1.55 eV and ~2.1 eV respectively, resulting in an exciton binding energy of ~0.5 eV matching published theoretical calculations (0.47 eV [10]). Our insights help bridge the gap between the synthetic process and desired optoelectronic properties of the material.

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Model Studies of the Electrode Processes of Organic Redox Flow Batteries using In-situ Spectroscopy – the Effect of Water and Oxygen

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The concept of redox flow batteries (RFBs) decouples power delivery from battery capacity, providing scalable energy storage. In our study, we model a system of an all-organic RFB half-cell using *N*-methylphthalimide (MePh) as the redox-active medium, which has been investigated so far only by purely electrochemical techniques. [1] We used electrochemical IR spectroscopy (EC-IRRAS) combined with CV techniques to investigate the influences of water and oxygen on the cyclability and decomposition of MePh.

Oxygen drastically affects the reduction of MePh in CVs and EC-IRRAS spectra. We propose that oxygen undergoes a reduction reaction at the working electrode at less negative potentials than the onset potential of MePh reduction. This leads to a $O_2^{\bullet-}$ radical, which attacks and decomposes MePh. The presence of water also leads to increased decomposition of MePh during reduction. Quantitative analysis shows that at low water concentrations, only a fraction of MePh decomposes, while at stoichiometric water concentrations, no reduction of MePh to $\text{MePh}^{\bullet-}$ takes place. We propose a decomposition pathway, in which $\text{MePh}^{\bullet-}$ reacts with water due to its strong basicity, abstracting a proton (H^+) and rendering the product redox-inactive, much faster than for MeCN.

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The x-ray absorption spectrum of the *tert*-butyl radical

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Hydrocarbon radicals play an important role in atmospheric chemistry and combustion processes. They have been detected in interstellar space[1] where they are key intermediates for the formation of complex species. However, spectroscopic information on radical species in the x-ray regime is scarce.

Here we present an investigation of the *tert*-butyl radical C_4H_9 by x-ray absorption spectroscopy (XAS), where carbon 1s electrons are excited into unoccupied orbitals. For open shell species this method is able to probe transitions into a singly occupied molecular orbital. The experiments were performed at the soft x-ray beamline GASPHASE at the synchrotron Elettra where electrons and ions resulting from the same ionization process are detected in coincidence. The *tert*-butyl radical was generated by pyrolysis of azo-*tert*-butane and the spectrum of the pure radical was obtained by the subtraction of spectra measured at different temperatures. The lowest energy signal is assigned to the excitation of the 1s electron at the central carbon into the SOMO. Transitions of the terminal C1s electrons are shifted to higher energies. The signals in the XAS were assigned by *ab initio* calculations that show a very good agreement with the experimental data.

Furthermore, we investigated the fragmentation of the core excited molecule after excitation at different photon energies. Fragmentation products were identified and the observed differences in the relative yield of the fragmentation products could qualitatively be explained.

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Cryo Resonance Raman spectroscopy of catalytic intermediates of Lytic Polysaccharide Monooxygenases

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Lytic polysaccharide monooxygenases (LPMOs) are a family of mono-Cu enzymes capable of introducing chain breaks in insoluble polysaccharides like cellulose. This functionality has made them a prime candidate in industrial production of biofuels. However, with their function only identified in 2010, and their preferred co-substrate being H_2O_2 only known since 2017 [1], much has yet to be uncovered about their reaction mechanism.

In this work, we aim to investigate several reoxidation mechanisms implicated in protection of the active site against oxidative stress using Resonance Raman spectroscopy at cryogenic temperatures. The reduced enzyme is treated with an excess of hydrogen peroxide to generate catalytic intermediates that are also Raman-active [2,3], and flash frozen at different time points during the reoxidation reaction using Rapid freeze quench stopped-flow. Accumulation of spectra at cryogenic temperatures has the advantage of increasing sample stability against photolytic damage even upon prolonged measurement time.

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Gas-Phase Vibrational Spectroscopy of Halide – Hexafluoroisopropanol Complexes: Hydrogen Bond Strength and Aggregation

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1,1,1,3,3,3-hexafluoroisopropanol (HFIP), an increasingly popular organic solvent, is known for its exceptional hydrogen-bond (HB) donor ability and HB network-formation, making it useful for applications ranging from protein structure determination to electrochemical reactions.[1] However, understanding HFIP's solvation properties and the HBs formed is far from trivial. Valuable insights can be gained by studying isolated, microsolvated ions in the gas phase, which are tractable by sophisticated computational models.[2]

Here, we study the gas-phase vibrational spectroscopy of the halide anion ($X^- = Cl^-$, Br^-, I^-) – HFIP complexes and compare it to that of the corresponding complexes with isopropanol and water in order to characterise the interactions in place. Infrared photodissociation (IRPD) spectra of the messenger-tagged complexes are obtained in the O-H(D) stretching region (2000 to 3800 cm^{-1}), where we observe the OH red-shift. We find that the red-shifts, which also reflect the extent of charge transfer along the coordinate of the proton transfer reaction $X^- + HY \rightarrow XH + Y^-$, correlate qualitatively with the difference in the proton affinities $\Delta PA = PA(X^-) - PA(Y^-)$.

In a second part, we examine the interactions in $F^-(HFIP)_n$, n = 1-3 complexes exploring the effects of aggregation on the HBs formed. The red-shift of more than 2000 cm^{-1} when n = 1, is reduced upon addition of new solvent molecules. The nature of all these interactions is evaluated using energy decomposition analysis methods demonstrating that the greater covalent character of the two bonds in F-H-O moiety for n = 1 decreases with increasing n also revealing the competition between these HBs in the first solvation shell concomitantly with the stabilization of the anion.

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In-situ Electron Paramagnetic Resonance Investigation of Isotope-selective Breathing in MIL-53 during Dihydrogen Adsorption

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The development of smart materials capable of separating dihydrogen isotopologues has risen recently.[1,2] Among potential candidates, the flexible MIL-53 (Al) has been gaining attention due to its structural flexibility providing the so-called ''breathing mechanism'' that can be useful to separate hydrogen isotopologues selectively. In the present work, an *in situ* continuous wave electron paramagnetic resonance investigation has been proven as a sensitive technique to follow the isotopologue-selective adsorption-desorption of dihydrogen species[3] on the paramagnetic metal-doped MIL-53 ($Al_{0.99}$ $Cr_{0.01}$) and MIL-53 ($Al_{0.99}$ $V_{0.01}$), respectively. The presence of paramagnetic spin probes such as Cr^{3+} and V^{4+} inside the MIL-53 framework allows for monitoring the framework transition including the 2nd transition step that selectively occurs at $p > 100$ mbar when D_2 gas is adsorbed on the pores at 23 K.

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Photodissociation of Triiodide in Solution Detected by Time-Resolved THz Spectroscopy

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The photodissociation of the triiodide anion (I_3^-) is an ideal model reaction for studying the dynamic effects of the solvent on chemical reactivity. The ultrafast photodissociation dynamics have been extensively studied by probing the photo-fragments following dissociation. In this work we have studied the photodissociation of I_3^- in solution using optical pump THz probe (OPTP) spectroscopy. The THz (50-200 cm^{-1}) probe allows us to follow the response of the solvent following photodissociation. We observe a ground state bleach signal at 143 cm^{-1}, this corresponds to the antisymmetric stretch of the ground state I_3^-. The bleach signal is recovered by geminate recombination of the photo-fragments in timescales of ~2ps and ~10 ps in aqueous solution. We also observe the excess energy release into the solvent in a timescale ~40 ps. Experiments were also done in methanol mixtures. The details of the role of solvents on the fate of the photo-fragments following photodissociation are discussed in detail in the poster.

Complex FFC NMR insights into the dynamics of ionic liquids

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Our project focuses on the study of rotational and translational motion in ionic liquids (ILs) by means of fast field cycling (FFC) NMR relaxometry over broad temperature ranges. The spectrometer frequency can be swept between 10 kHz and 40 MHz for ^{1}H nuclei, yielding NMR dispersion profiles which allow for the simultaneous observation of several molecular processes at different timescales in one single experiment. Depending on the atomic composition of the ILs it is mostly possible to measure ^{1}H NMR dispersion profiles for the cations as well as ^{19}F NMR dispersion profiles for the anions. In order to dissect the spin lattice relaxation rates into their inter- and intramolecular contributions, relaxation models are required. While translational diffusion coefficients can be extracted using the force free hard sphere model, the determination of rotational correlation times strongly depends on the molecular structure of the ions. As long as the rotating identity can be considered a rigid sphere, the simple Bloembergen Purcell Pound model can be applied. This is the case for example for the triethylammonium [TEA]+ cation. However, if the ions are better described as ellipsoids (e.g. N-pentylpyridinium $[C5Py]^+$ cation), or show additional internal rotation, (e.g. bis(trifluoromethylsulfonyl)imide $[NTf2]^-$ anion) more complex relaxation models are required. [1, 2] Finally, molecular dynamics (MD) simulations are a useful complement to FFC NMR relaxometry, since they do not only provide comparable values for both quantities, but can also mechanistically verify the applied relaxation models by computing the inter- and intramolecular frequency-dependent dipolar NMR relaxation and reconstructing the total NMR dispersion profiles.[3]

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Quantum Cascade Laser in IR Difference Spectroscopy: Photoresponses of the Blue-Light Receptor Cryptochrome

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Quantum Cascade Lasers (QCLs) have been established for time-resolved IR spectroscopy as high-power radiation source with a broadly tunable wavelength, complementing existing globar applications. Implemented methods provide an effective tool for the structural and kinetic investigation of protein mechanisms, achieving time resolutions across extensive time scales from nanoseconds up to seconds.

We present high-resolution kinetic measurement data generated by a novel EC-QCL transmission setup, showcasing its application in studying the kinetics of protein photoreactions in aqueous solution by time-resolved vibrational spectroscopy in a flow cell. The setup has been specifically developed for handling protein samples in flow with a low sample consumption of nanoliters per minute [1]. Recently, a coverage in a range of 8 ns to 35 ms at a repetition rate of 2 Hz per acquisition was achieved. We performed characterization experiments and performance assays using the irreversible photoreduction of flavin mononucleotide in aqueous solution. We provide here an overview of the complex measurement procedures and encountered challenges such as coping with the acquisition and evaluation of large amounts of data. This setup provides a method for unraveling protonation mechanisms of irreversible systems as exemplified by data acquired on the blue light receptor protein cryptochrome, featuring the chromophore flavin as a cofactor.

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Phosphorus atomic resonance absorption spectroscopy for application in shock tube experiments

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Atomic resonance absorption spectroscopy (ARAS) is a versatile and well-established method to detect atomic species in kinetic shock tube experiments.[1] For ARAS, a suitable precursor containing the particular atomic species is diluted in a carrier gas and flowed through a microwave discharge burning in a quartz tube. The emitted radiation, after filtering, is resonantly absorbed by the corresponding atoms in the reaction mixture, and the narrow linewidths in combination with the usually large absorption cross-sections make the method very selective and sensitive.

The absorbance behind the shock front can be measured time-resolved and converted into a concentration-time profile by suitable calibration. Elements for which ARAS was successfully applied in shock tube experiments are e.g. H(D), C, N, O as well as the halogens Cl and I.[2] To the best of our knowledge, the method has not yet been used to monitor P atoms.

In our contribution, we report on work in progress to adopt ARAS to quantitatively detect P atoms in shock tube experiments. As a precursor, PCl_3 diluted in He was used, and the lamp emission properties were investigated and optimized with respect to lamp gas pressure and precursor concentration. The characterization of the lamp spectrum as well as the search for suitable calibration systems and alternative precursors will be discussed; an application to PH_3 pyrolysis will be presented.

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Exploring the long-lived excited states of backbone substituted copper(I) sensitizers by temperature-dependent and time-resolved luminescence spectroscopy

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Photoactive transition metal complexes play a crucial role in various light-driven applications, e.g. photocatalytic water splitting. While the catalytic center in these reactions can already be synthesized based on abundant elements like iron, the light-sensitizing unit still often contains rare precious metals. Photosensitizers based on more abundant elements, e.g., copper are more sustainable but usually less effective. In order to improve the performance and efficiency of light-induced processes by these complexes, it takes to develop structures that sustain suitable long-lived excited states. In this context, copper(I) complexes that coordinate a bidentate xantphos and methoxy-substituted bathocuproine ligand show promising results [1].

To further explore the nature of the long-lived excited states and the impact of the backbone bathocuproine substitution on the function-determining manifold of long-lived excited states temperature and time-dependent luminescence spectroscopy is performed. The results suggest contributions of at least two long-lived, presumably triplet states separated by an energetic barrier. This barrier is influenced by steric hindrance as well as mesomeric and inductive effects from the methoxy substituents leading to strong modulation of excited states' lifetime. The insights gained from the spectroscopic studies are amended with the performance of the complexes in singlet oxygen and hydrogen production to derive rules for optimal sensitizer design.

We acknowledge funding by the Fonds der Chemischen Industrie (FCI) and the German Research Foundation (DFG) under project number 364549901–TRR234 CATALIGHT.

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Study of Exciton and Phonon Properties in Quantum Dots via Temperature-Dependent Photoluminescence

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Colloidal quantum dots (QDs) are the subject of intense research due to their exceptional size-tunable optoelectronic properties, due to spatial confinement of electron and hole motion. Colloidal QD surfaces are passivated by surface ligands, which make the QDs dispersible in different solvents (depending on the functional group of the ligand), and enable processibility into thin films. Further, surface ligands can modify the electronic structure via introducing or passivating defects at the surface and hence impacting the presence of trap states within the bandgap or enabling a control of electronic coupling between neighboring QDs via ligand length and to control carrier mobility in a QD thin film. Finally, surface ligands can influence acoustic phonon modes and exciton-phonon coupling, which impacts radiative and non-radiative processes such as surface-trapping, and carrier mobility.

In this work, we present a strategy to investigate radiative and non-radiative carrier relaxation and the exciton-phonon coupling in colloidal CdSe QDs using temperature-dependent photoluminescence spectroscopy (ranging from 5 K – 290 K). A series of CdSe QDs with varying surface functionalization is studied to analyze the impact of surface ligands. A quantitative analysis of the temperature-dependent change in the photoluminescence peak position, linewidth, and intensity can simultaneously deliver information about the energetic position of the surface traps. Further, the exciton-phonon coupling is determined from the photoluminescence linewidth which requires knowledge on the phonon energy. To determine the acoustic phonon energy which is typically observed at ~ 20 cm^{-1} in dependence on the respective surface ligands we utilize Raman spectroscopy applying a special volume holographic notch filter to suppress the Rayleigh line.

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Accessing $S_{n\geq2}$ States of OLED Emitters by Femtosecond NIR Spectroscopy

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Efficient emitters for OLEDs showed harvest singlet and triplet excitons. In the TADF (thermally activated delayed fluorescence) approach, dark triplet excitons are converted into emissive singlet ones by reverse intersystem crossing (rISC). Efficient TADF emitters need to exhibit small singlet-triplet energy bandgap (ΔE_{ST} ~ 25 meV) and higher states ($S_{n\geq2}$ and $T_{n\geq2}$) that contribute to spin vibronic mixing to enable ISC and rISC [1]. These states can be localized energetically by time resolved near-infrared (NIR) spectroscopy [1][2].

Here, femtosecond (fs) NIR spectroscopy is utilized to characterize the $S_{n\geq2}$ states of a prototypical TADF emitter (TAA-DCN [3]). The respective NIR transitions (Figure 1, right) exhibited a dynamic shift on the same time scale as the stimulated emission. From the results, vertical and adiabatic energies of $S_{n\geq2}$ states can be assembled.

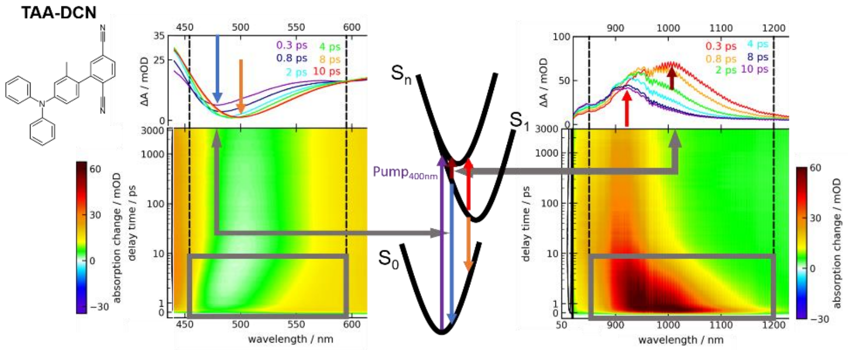

Figure 1: fs UV/Vis (left) and NIR (right) measurements on TAA-DCN dissolved in toluene. The diagram in the centre rationalizes the observed dynamic shifts.

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Revealing excited state properties of Cu(I) photosensitziers by time- and temperature dependent step-scan FTIR spectroscopy

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Photoactive transition metal complexes play an important role as photocatalysts and photosensitizers in photochemical processes, e.g. water splitting or carbon dioxide reduction. Heteroleptic Cu(I)-complexes with xantphos and modified bathocuproine ligands have shown dark and emissive long-lived excited states with photosensitizing ability and may be a sustainable alternative for rare noble transition metals.[1] However, exploiting the potential requires gaining deeper insight into these long-lived excited states. Here we show the effect of the structure on the photophysical properties, e.g. the location and lifetime of the excited states using time- and temperature-dependent step-scan FTIR spectroscopy. Our results indicate a strong effect of modifications in the electronic density at the bathocuproine ligand tunable via the substitution pattern. Compared to the reference sample without methoxy groups we observed a decrease in the lifetime for the *ortho*-substituted sample and an increase for the *meta*-substituted sample. DFT calculations were used to gain a better understanding of the triplet states involved, their relative energetic position and their location at the bathocuproine structure to understand the source of these observations. These results highlight the significant impact of ligand substitution patterns on the excited state properties of heteroleptic Cu(I) complexes, providing valuable insights for optimizing their photosensitizing performance.

We acknowledge funding by the Fonds der Chemischen Industrie (FCI) and the German Research Foundation (DFG) under project number 364549901–TRR234 CATALIGHT.

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Exploring Defect Engineered MOFs with 1,2,4-Triazolyl Isophthalate and Benzoate Linkers for Dihydrogen Adsorption.

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This work reports the synthesis and characterization of defect-engineered metal-organic frameworks (DEMOFs) with coordinatively unsaturated sites (CUS) which can be utilized for gas adsorption, catalysis, and separation.[1] Defects are introduced into $[Cu_2(Me\text{-}trz\text{-}ia)_2]$[2] by replacing up to 7% of the 3-methyl-triazolyl isophthalate linker with 3-methyl-triazolyl m-benzoate, creating uncoordinated equatorial sites (see Fig. 1). Materials were thoroughly characterized using PXRD, IR, and Raman spectroscopy, confirming phase purity with minimal structural changes. NMR and HPLC analyses quantified the effective incorporation of defective linkers within the MOF framework. XPS and X-band EPR spectroscopy provided valuable insights into the local structure and charge balance of the synthesized materials, suggesting two types of defects and an increase in Cu^I concentration leads to H_2 / D_2 higher isosteric heat of adsorption.[3] This approach offers valuable insights into CUS creation in MOFs which can be utilized further for hydrogen isotopologue separation.

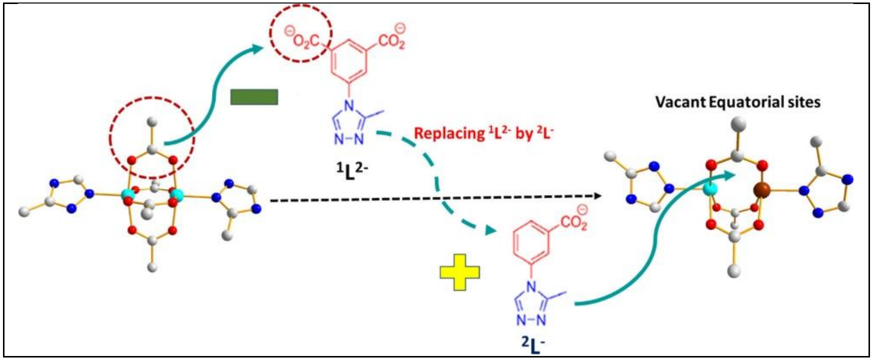

Fig. 1: The Strategy Implemented for the Development of DEMOFs is Based on Partial Replacement of the Regular Linker $^1L^{2-}$by the “Defective Linker” $^2L^-$ Lacking One Carboxylate Group[a]

[a]The diagram focuses on Cu–Cu paddlewheel unit changes due to 2L– incorporation. Color coding: CuI, brown; CuII, turquoise; C, gray; O, red;and N, blue. Additional structural specifics are excluded for the sake of simplicity.

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Spectroscopic Studies on the Photoadditions of Psoralens and Angelicins to DNA

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Angelicins are an alternative to linear analogs (psoralens) in PUVA (psoralen + UVA) therapy for treating autoimmune skin disorders due to two promising properties [1]: After reversible intercalation between DNA bases, psoralens only photoreact with thymine (T) bases and “suffer” from a picosecond photoinduced electron transfer (PET) with guanine (G) (Figure 1a) [2]. Contrary to that, angelicins can form photoadducts with T *and* cytosine (C) bases (Figure 1b) [3]. Unlike psoralens, angelicins are postulated not to form interstrand-cross-links within DNA after photoexcitation due to sterical hindrance. This monofunctionality is associated with significantly reduced phototoxic side effects [4].

Here, the interaction of the parent compound angelicin (ANG) and a novel derivative (AMBA) with synthetic DNA is studied. First results show indications for a (weak) photoreactivity of both angelicins with respect to C bases, which is absent in psoralens [5] such as AMO [6].

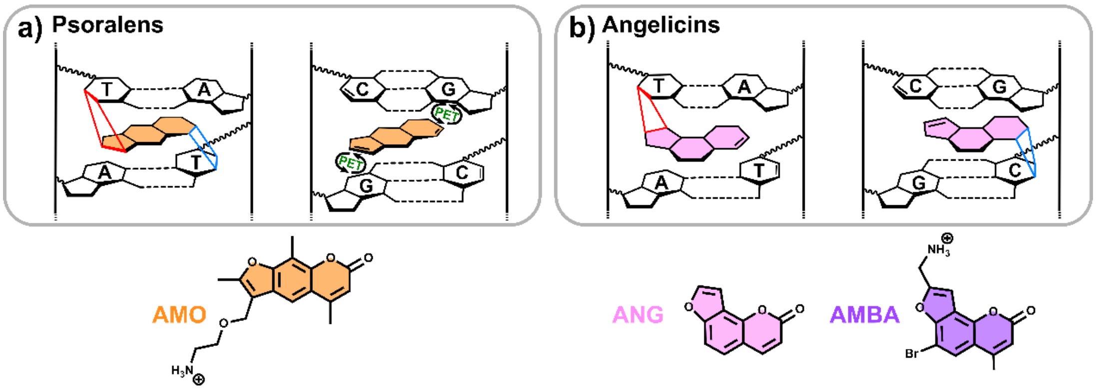

Figure 1. Photoinduced interaction of psoralens (a) and angelicins (b) with DNA.

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Time-Resolved Spectroscopic Studies on the Net Heterolysis of Homopolar Selenium-Carbon Bonds

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When chemical bonds break one distinguishes between homolysis and heterolysis, i.e., forming either a radical pair or an ion pair, respectively. The difference between electron affinity and first ionization energy of the respective bonding partners determines about the mode of bond breaking, which is negative in the case of heterolysis. Therefore, homopolar bonds, with small or only marginal differences in electronegativity between their constituents, exclusively undergo the energetically lower lying homolysis, both in thermal groundstate processes, but also from low excited states. [1] This limits the reactivity of a given bond, since the electron affinity and ionization energy, linked to electronegativity by the Mulliken definition [2], are intrinsic properties of the bond constituents. However, in a two step process, with thermal homolysis as the first and photoexcitation of only one of the filial radicals as the second step, these restrictions would no longer apply, since the ionization energy and electron affinity will differ between an excited and ground state radical, thus allowing for a net - heterolysis of homopolar and even symmetrical bonds. [3]

$$\mathbf{A{-}A} \longrightarrow \mathbf{2\,A^{\bullet}} \xrightarrow{\textbf{light}} \mathbf{A^{\bullet *}} + \mathbf{A^{\bullet}} \xrightarrow{\textbf{SET}} \mathbf{A^{-}} + \mathbf{A^{+}}$$

Using transient absorption spectroscopy on different timescales [4, 5], conjoined with synthetic and theoretical investigations, this study exemplary demonstrates a two-step net-heterolysis for homopolar selenium-carbon as well as symmetrical selenium-selenium bonds.

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Optical Spectroscopy of Diamondoid Derivatives

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Diamondoids are three dimensional organic molecules that are derived from the diamond lattice structure. As such, they contain no aromatic system, rendering their electronic structure distinctly different from polycylic aromatic hydrocarbons. Nonetheless, they exhibit broadly tunable optical properties as well as a high chemical and thermal stability, making them suitable for applications in photonics, material science and medicine.[1]

Nanodiamonds have also been detected in meteorites and consequently diamondoid derivatives have also been suggested to play a decisive role in astrochemistry. Early interstellar ice experiments detected tetra-aza-adamantane, an adamantane where all four CH units have been substituted for an isoelectronic nitrogen atom.[2] So far, a mechanism for its formation is unknown, but nitrogenated hydrocarbons are becoming increasingly more important to describe the chemistry of the extraterrestrial environments.[3]

In order to use diamondoids in photonics and detect them in space, knowledge of their electronic structure is required. We use a cryogenic ion-trap to record high resolution optical spectra of various diamondoid cations like tetra-aza-adamantane and oxa-adamantane. In contrast to admantane, the incorporation of heteroatoms into the cage disturbs the electronic structure significantly, resulting in longer excited state lifetimes and the observation of vibrational progressions for tetra-aza-adamantane and oxa-adamantane. We attribute this behavior to a reordering of the molecular orbitals and the absence of conical intersections, that contribute to an ultrafast deactivation in adamantane.

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Stimulated Emission in Liquid Core Fibers and Quasi-Isotropic Charge Carrier Confinement Effects of Cadmium Chalcogenide Nanoplatelets

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The colloidal synthesis of 2D nanoplatelets (NPLs) based on cadmium chalcogenides allows a precise control of their optical properties due to variation in atomic monolayer thickness and the formation of heterostructures. Particularly, CdSe/CdS core-crown NPLs exhibit exceptional optical properties such as high photoluminescence quantum yields, large absorption [1] and gain cross-sections [2], as well as reduced rates of Auger recombination [3]. Such characteristics position these colloidal nanoemitters as highly promising candidates for optical technologies, such as LEDs and lasers [4]. However, their anisotropic emission pattern, directed along the lateral surface normal, typically requires an alignment of the NPLs in potential devices. Current applications often depend on thin films where NPLs are oriented flat-on, which enables high concentrations in a small volume, but also leads to a decreased photoluminescence due to effects like Förster resonance energy transfer [5].

Here, we report on two different projects. One focuses on the stimulated emission of bright CdSe/CdS core-crown NPLs by incorporating them in liquid core silica glass fibers as colloidal dispersion. We employ a nanosecond pulsed laser with a line focus in a longitudinal configuration to pump the NPLs in the fibers. Further, by usage of high refractive index solvents, the waveguiding effect of the fiber core is enabled. While there are still emission losses by NPLs oriented above the critical angle for total internal reflection and an overall lower NPL concentration in the liquid dispersion, these losses can easily be overcome by upscaling the fiber length. This increases the light interaction path and allows us to avoid the need for a directed orientation of the NPLs in our setup and to observe stimulated emission.

In a second project we investigate the charge carrier confinement of CdSe core-only NPLs with different lateral dimensions. While NPLs with a large lateral surface area only show difference in confinement almost only due to differences in platelet thickness, laterally small NPLs blur the boundary between anisotropic confinement in one direction and isotropic 3D confinement. Here we utilize transient absorption spectroscopy in order to shed light on the exciton behavior of such edge cases.

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Plasmon-assisted near-infrared photoluminescence of quantum dots

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Colloidal quantum dots (QDs) experience gradual transition from laboratories to real-world optical devices, promoted by their pure, bright, and stable light emission across visible to infrared wavelengths. Near-infrared (NIR) QDs are of particular interest for optoelectronic devices, [1] such as Cu-Zn-In-Se (CZISe) nanocrystals (NCs), that have narrow NIR emission and a photoluminescence quantum yield (PLQY) of 20%. [2] The application of these NIR QDs is, however, still limited by domination of non-radiative recombination for the emitters with a smaller bandgap. Localized surface plasmon resonance (LSPR) can accelerate radiative recombination rate through the Purcell effect and increase photoluminescence (PL) intensity by near-field enhancement and directional light extraction. [3] Plasmonic nanomaterials have already proven to be effective in the visible range, [4] as well as in NIR. [5,6]

In this work, we investigate the influence of electromagnetic field, produced by large silver nanoplates, on core/shell CZISe/ZnS NCs in the NIR region. The prioritized condition for this type of plasmon-exciton coupling is overlapping of QDs emission wavelength with the resonance absorption of metallic nanoparticles. The expected enhancement of the PL intensity was achieved with almost 7-fold increase. We also studied the influence of a dielectric transparent poly(methyl methacrylate) (PMMA) spacer between Ag triangles and CZISe/ZnS NCs, which allowed us to control the distance between two types of NCs. It was found that the addition of PMMA layer led to smaller PL enhancements in comparison with NC layers without a spacer. We refer this effect to the influence of surface ligands of both types of NCs, which provide a dielectric layer between QDs and Ag particles. This layer most likely may be sufficient to suppress charge transfer and has optimal thickness to contribute to enhancement by the Purcell effect.

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Exploring CO_2 adsorption in Flexible MOF $[Cu_2(Me\text{-}trz\text{-}ia)_2]$ using *in situ* EPR spectroscopy

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Metal-organic frameworks (MOFs) are well explored for their tunable properties like gas storage, band gap, catalysis, etc. We have considered a flexible MOF $[Cu_2(Me\text{-}trz\text{-}ia)_2]$ which contains Cu(II)-Cu(II) paddle-wheel units, and studied its local properties upon CO_2 adsorption using *in situ cw* EPR spectroscopy [1]. Upon CO_2 adsorption, it is observed that the local structure changes can be identified by the changes in the EPR signal from Cu(II)-Cu(II) paddle-wheel units [2]. Depending on the pressure, the spectra show different weights of the magnetically coupled Cu(II)-Cu(II) units vs. the uncoupled Cu(II), which can be directly linked to the effect of the adsorbed gas molecules onto the metal-organic framework. This gives us insight into the process of gas adsorption in the framework. Further understanding of the adsorption process could potentially contribute to the application of gas molecules separation and storage using metal-organic frameworks.

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Inorganic Chemistry **2024** *63* (23), 10843-10853
DOI: 10.1021/acs.inorgchem.4c01589

Quantitative spectroscopy of non-thermal molecular plasmas using a mid-infrared frequency comb

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Non-thermal molecular plasmas play a crucial role in technological applications, yet their non-thermal characteristics, such as molecular state population distributions, remain insufficiently understood. Here, we apply a mid-infrared frequency comb-based Fourier transform spectrometer to measure high-resolution spectra of plasmas containing hydrogen, nitrogen, and methane in the 2800 – 3400 cm^{-1} range. This spectrally broadband, high-resolution method enables quantum-state-resolved spectroscopy of plasma-generated such as CH_4, C_2H_2, C_2H_6, HCN, and NH_3 species simultaneously.

Using the line-by-line fitting approach, we accurately determined the population of rovibrational transitions within different vibrational bands of the probed molecular species. For example, for HCN in the 3200 – 3400 cm^{-1}, we could probe four vibrational transitions: the fundamental $\nu_1 \leftarrow \nu_0$ band, (ii) the $\nu_1 + \nu_2 \leftarrow \nu_2$ hot band, (iii) the $\nu_1 + 2\nu_2 \leftarrow 2\nu_2$ hot band, and (iv) the $\nu_2 + \nu_3 \leftarrow \nu0$ combination band. The results revealed a significant non-thermal distribution of the populations among the rotational molecular states, with distinct temperatures observed for lower and higher rotational quantum numbers [1]. A detailed analysis of the population distributions of other molecular species is underway, aiming to establish correlations between the determined rotational temperatures of the different vibrational states and the vibrational-vibrational and vibrational-translational relaxation rates. Broadband comb spectroscopy offers unprecedented fundamental insights into the non-thermal nature of molecular plasmas – a detailed picture that has never been accomplished before for such complex environments

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Quantifying Polymer, Water and Salt in Complex Coacervates by Femtosecond Stimulated Raman Microscopy (FSRM)

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Solutions of two polyelectrolytes with opposing charges can undergo liquid-liquid phase separation (LLPS) forming polymer-rich droplets (complex coacervates), surrounded by a polymer-depleted supernatant. This behaviour strongly depends on salt concentrations. The Voorn-Overbeek theory predicts salt enrichment in the coacervate phase during LLPS, but recent experiments show salt enrichment in the supernatant, driving new theories and experimental studies [1]. Here femtosecond stimulated Raman microscopy (FSRM) [2] is introduced to quantify the partitioning of polymer, water and salt in complex coacervates. Experiments were conducted on a "classical" complex coacervate forming pair, consisting of PDADMAC and PSS (structures in Figure 1) and the Raman active salt NH_4SCN. The chemical maps (Figure 1) reveal polymer enrichment, water depletion, and salt enrichment in the droplet.

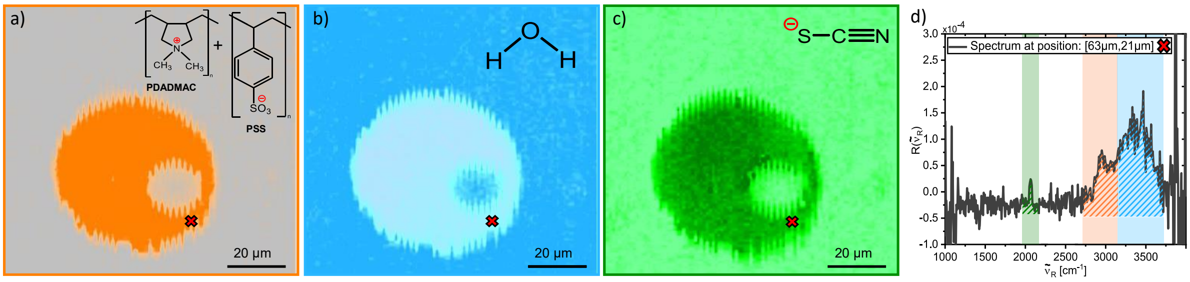

Figure 1. Chemical maps showing the distribution of polymer (a), water (b) and salt (c) obtained from FSRM measurements on a PDADMAC/PSS – NH_4SCN coacervate sample, color-coded as shown in the Raman spectrum (d).

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Using an organic dye to probe interfaces of perovskite optoelectronics with optical spectroscopy

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Lead halide perovskites are semiconductors with excellent optoelectronic properties that are promising for solar cell applications to approach the increasing demand for energy on earth. High defect densities and ion conductivity have a significant effect on the device performance and its insufficient long-term stability. In former work, a Stark shift was observed for dye-sensitized solar cells (DSC) with solid and liquid electrolytes. [1, 2] It is caused by movement of the containing ions. However, ion movement can be monitored in time. Light excitation causes charge-transfer states in common DSC dyes. This results in a built-in electric field across the dipole moment of the dye that leads to a spectral shift (Stark effect). Ions in perovskites screen electric fields by ion movement. In perovskite solar cells, this can happen upon applying electrical bias or light excitation. [3] The ion movement changes the field the dye observes and leads to a reversal Stark shift.

We use the Stark effect of the probing dye to study the hidden interface of an organic halide perovskite with TiO_2 as an electron-transport layer. The TiO_2-perovskite interface is modified by inserting an organic dye which is probed by time-resolved absorption (TA) and emission spectroscopy. The ion movement is further observed by photo-induced absorption spectroscopy (PIA). The charge-transfer from the perovskite is monitored with the spectral Stark shift of the dye allowing us to probe the TiO_2-perovskite interface.

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Conventional X-ray source-based time-resolved X-ray photoelectron spectroscopy (TR-XPS)

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Understanding dynamic surface processes such as reaction kinetics, segregation or even simple adsorption/desorption is an important goal in surface science. To obtain a deeper understanding, different chemical species on the surface and their changes in the millisecond to second timescale have to be identified. A commonly used method for this is time-resolved X-ray photoelectron spectroscopy (TR-XPS). [1,2] Pertubation-based synchrotron XPS or pump-probe like XPS using e.g. free electron lasers have successfully been employed for time-resolved measurements. However, such techniques take high efforts, including high costs and limited availability.

Here, we evaluated a method for time-resolved measurements using a conventional X-ray source (Al Kα) along with a DLD detector. This has potential to simplify (photochemical) TR-XPS experiments. Inspired by recent synchrotron AP-XPS studies, we tested event averaging, in which individual time-resolved measurements are synchronized by a defined trigger event and then averaged. [3, 4, 5] In our case, this procedure improves the signal-to-noise ratio and thus increases the sensitivity, while allowing for a time resolution on the few second range.

Figure 1 presents the single and time-resolved C1s XPS spectra of CO adsorption on Pt(111) (pulse of CO at a time of 0s, time resolution 7s), as individual experiment (left a,b) and after event averaging of 20 individual experiments (right, c,d).

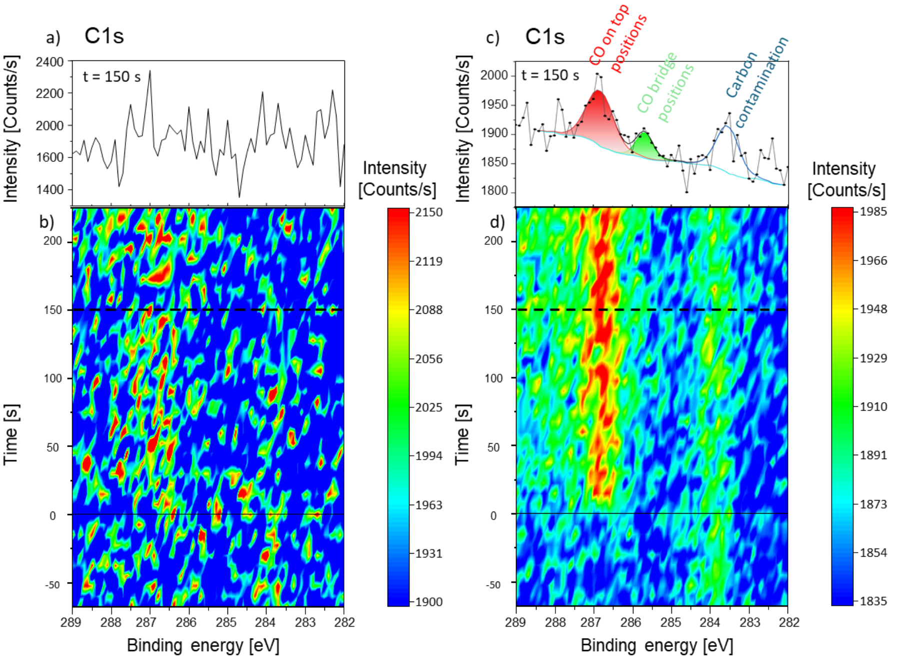

Figure 1: *a) individual C1s photoelectron spectra of Pt(111), 150 s after a CO pulse, b) time-resolved measurement of C1s spectra with CO-dosing at t = 0 s, c) final C1s spectra after event averaging of 20 measurements, t = 150 s after CO-dosing, d) time-resolved measurement of C1s spectra after event averaging of 20 measurements with CO-dosing at t = 0 s.*

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Exploring Structure-Property Relationships in Perovskite Supercrystals by Spatially-resolved X-ray Scattering and Optical Spectroscopy

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Supercrystals extend the excitonic properties of colloidal solutions of microscopic quantum dots to the macroscopic realm and are of significant interest for optoelectronic device applications such as LEDs, solar cells, and electro-optic modulators. [1]

Our lab recently achieved reliable mechanical control over self-assembled $CsPbX_3$ supercrystals, enabling us to relocate, stack, and deform these systems with high accuracy. We believe these mechanical manipulations will be instrumental in studying how disturbances to the highly ordered structure of the mesocrystals influence their emergent properties. [2,3] Additionally, these manipulations allow us to expose them to conditions that are otherwise inaccessible through self-assembly from colloidal solutions.

The presentation details our approach of combining spatially-resolved X-ray nanodiffraction with diffraction-limited optical spectroscopy to investigate the relationship between mesoscopic structure and macroscopic functionality of perovskite supercrystals.

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Raman-Spectroscopic Mapping of Structural Preferences in Lateral Shock Regions of Supersonic Jet-Expansions

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Despite the relative weakness of the Raman effect, Raman spectroscopy has proven to be a valuable tool for the investigation of structural preferences of small molecules and their aggregates in supersonic jet expansions. To counteract the relative weakness of the Raman effect, a powerful laser with several watt optical output power is typically required. However, weak signals may still need considerable exposure times to be detected with sufficient signal to noise level, increasing substance consumption in traditional “one-pass” jet-setups. To mitigate this, we recently developed a gas-recycling Raman jet-spectrometer, which reduces substance consumption and facilitates measurements of weak signals and expensive substances [1]

Gas-recycling also paves the way for mapping experiments, where the number of required measurements quickly increases with increasing spatial resolution. Spatially resolving the jet-expansion is possible thanks to the small laser beam diameter (on the order of a few 10 µm) and the motorized vacuum chamber and nozzle which move with micrometer resolution relative to the static laser beam.

In this contribution, we present the first mapping application results from our new setup, focusing primarily on the small molecules *n*-pentane and ethanol. We examine conformational and clustering preferences within the lateral shock of slit-jet expansions, a region characterized by an effective temperature intermediate between the cold zone-of-silence of the jet and the regular room temperature gas phase. Notably, while rotational temperature and density increase (the latter to the benefit of linear Raman spectroscopy), many jet-spectra properties are retained. We investigate whether “off-axis” jet-spectroscopy is something to consider for broader application in the jet-spectroscopic tool belt.

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Operando Spectroscopy of Pd and PdAu Laterally Condensed Catalysts during Selective Acetylene Hydrogenation Reaction

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The pyrolysis of methane from fossil fuel sources produces hydrogen and solid carbon along with different pyrolysis gases. Acetylene, which forms as a side-product of the Hüls' arc pyrolysis reaction [1], needs to be converted into ethylene with high efficiency for its safe removal and to close the carbon cycle. Thus, selective acetylene hydrogenation into ethylene is a crucial catalytic reaction which is also widely studied in academia as a model reaction. The catalyst of choice is Pd which has high activity, and its selectivity for ethylene production can be further enhanced by addition of a second element, e.g. carbon in the near-surface [2] or metals such as Ag, Ga, or Au.[3,4] In this study, we have investigated the surface chemistry and the electronic structure of Pd and PdAu laterally condensed catalysts (LCC) [2] via near ambient pressure X-ray photoelectron spectroscopy (NAP-XPS) and Near Edge X-ray Absorption Fine Structure (NEXAFS) during the selective acetylene hydrogenation. The operando experiment involved dosing the reaction feed of acetylene and hydrogen mixture (1 mbar) at various temperatures from room temperature to 100 °C while tracking the evolution of Pd 3d, C 1s core levels and valence band spectra by NAP-XPS, along with NEXAFS Pd L_3-edge. The quantification of Pd 3d spectra suggested that Pd can incorporate more carbon atoms in the near-surface region and in the bulk compared to the PdAu alloy, which was supported by Density Functional Theory (DFT) calculations. NEXAFS Pd L_3-edge spectra of Pd LCC also showed an increase in the whiteline energy along with broadening of the peak upon dosing the reaction feed and with increase in temperature, indicating Pd:C phase formation[5], whereas these changes in the whiteline were not observed in the PdAu LCC. The NEXAFS results validated that the presence of Au hinders the incorporation of C in the Pd lattice.

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Chiral Selector Ion Vibrational Spectroscopy on Amino Acid Enantiomers

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Molecular chirality plays a central role in how the building blocks of life, like amino acids, sugars, or nucleotides, interact. The stereochemistry and conformational flexibility of chiral molecules have a strong impact on their biological, biochemical, and pharmacological properties. A central analytical challenge is the generally applicable differentiation of enantiomers, as well as the fast and accurate determination of the enantiomeric excess of a chiral sample. Gas phase vibrational action spectroscopy is a highly sensitive, selective, and fast tool for this purpose.

Chiral ionic analytes are transferred into the gas phase, where they interact with volatile chiral selector molecules in a gas-filled ion guide under the formation of diastereomeric complexes. These are then mass-selected, cryogenically cooled, messenger-tagged and an infrared photodissociation (IRPD) spectrum is measured. The spectra of the vibrationally cold diastereomers exhibit sufficiently different IR fingerprints, such that they can be spectrally distinguished and quantified.

Different intermolecular non-covalent interactions can be present in diastereomers, among them H-bonds, π-π interactions and steric hindrance. We study a set of different chiral selector molecules and chiral amino acid analytes with different structural motifs to identify the decisive interactions in the present complexes. We aim at maximizing the differences in the vibrational action spectra of the diastereomers and gain insights into the interactions governing chiral recognition by characterizing the molecular level forces at work. We also study, how well chiral selector ion vibrational spectroscopy is applicable to more complex analytes by increasing the number of stereocenters in the chiral analyte.

Probing the Temperature of Single Quantum Dots Confined in a Nanoparticle Ion Trap by Fluorescence Thermometry

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To obtain pristine information on the intrinsic, size-dependent properties of nanoparticles, characterizing individual nanoparticles isolated in the gas phase is a prerequisite. This approach avoids both the heterogeneity of an ensemble and perturbing interactions with the surrounding environment. Single nanoparticle mass spectrometry (NPMS) has proven to be a viable concept for probing properties of single, charged particles by enabling the non-destructive determination of mass, charge, and optical properties. [1,2]

Here, we report on a novel approach to determine the temperature of individual quantum dots in an ion trap at cryogenic conditions by fluorescence thermometry. The quantum dot temperature represents a crucial intrinsic property (e.g., for modeling the sorption behavior) that is notoriously difficult to determine for single particles isolated in the gas phase. In the present study, CdSe/CdS quantum dots are excited by a continuous 532 nm laser and the temperature is derived from the temperature-dependent fluorescence emission wavelength using the empirical Varshni relation. The experimental findings are in satisfactory agreement with a simple heat balance model that describes the particle temperature as a function of light absorption, fluorescence, and collisional cooling. [3]

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The influence of heteronuclear interactions on translational diffusion coefficients studied by NMR relaxometry

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Using fast-field-cycling NMR relaxometry it is possible to measure frequency-dependent relaxation rates of NMR-active nuclei. Fitting of these dispersion profiles provides access to translational and rotational dynamical properties, such as self-diffusion coefficients and rotational correlation times. The fitting procedure becomes increasingly complex as the number of parameters increases with more types of interaction between all the NMR active nuclei in the sample. However, the translational diffusion coefficients can also be extracted directly from the experimentally obtained relaxation data, by using a linear dependence of the relaxation rates at low frequencies. [1] We show, that heteronuclear interactions play a crucial role when applying this so-called low-frequency approach (LFA). Therefore, three different ionic liquids (ILs) have been synthesized. By selective deuteration of either the cation or the anion, two of the ILs represent a one-spin system with only ^{1}H-^{1}H interactions on the cation or ^{19}F-^{19}F interactions on the anion. In the third IL there are additional ^{1}H-^{19}F interactions between cations and anions. It is an ongoing debate under which circumstances these heteronuclear contributions can be neglected. We can show that the low-frequency approach holds when being applied to the experimentally obtained relaxation data of one-spin systems. In contrast, by neglecting the heteronuclear contribution, the LFA will yield falsified self-diffusion coefficients when being applied to two-spin systems without any further data evaluation. Here, a proper dissection of the total relaxation rates into inter- and intramolecular parts is essential before applying the LFA only to the intermolecular contribution. [2]

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Determining the Orientation of NV^- Color Centers in Heteroepitaxial Diamond by Optically Detected Magnetic Resonance (ODMR) Spectromicroscopy

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The negatively charged nitrogen vacancy (NV^-) color center is of great interest with respect to applications in quantum sensing and computing. For some of these applications, large substrate sizes are required for which heteroepitaxial diamond constitutes the only viable option at the moment. The transfer of growth and fabrication processes from mm-scale homoepitaxy to wafer-scale heteroepitaxy, however, is not straightforward and brings a large number of challenges with itself, e.g. because the doping in the overgrown substrate has substantiate effects on growth modes and orientation-dependent rates.

Depending on the application it is important to ensure whether the process incorporated the NV^- centers with an equal distribution or only one of their four magnetically relevant orientations which are parallel to the diamond crystals' <111> directions. Optically Detected Magnetic Resonance (ODMR) has been established as a technique for such measurements. It consists of laser excitation, which induces a spin polarization to the system, a resonant excitation of the polarized spin system by microwave irradiation and a fluorescence detection probe. This can be applied both in continuous wave and pulsed measuring sequences.

In this contribution, the application of ODMR is demonstrated for two examples: (a) full and truncated pyramidal microstructures on heteroepitaxial diamond(001) with NV centers in the side surfaces (b) as-grown heteroepitaxial diamond(111) wafers with bulk NV doping.

Surfaces and Interfaces

Quantitative LEED analysis of the system CO/NaCl(100): Anisotropic vibrational amplitudes and effect of partial ‘flipping’ of molecules

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The monolayer CO adsorbed on the NaCl(100) surface continues to be an intensively investigated model system of physisorption, both experimentally and theoretically [1-3]. A recent structure analysis based on quantitative low-energy electron diffraction (LEED) beam intensities confirmed the antiparallel ordering of CO molecules in the p(2x1) phase proposed by various models [4]. While thermal effects are important in this system, indicated by the notable temperature dependence of half-ordered beam shapes, standard LEED I(V) analysis usually treats thermal effects using isotropic vibrational amplitudes of atomic centers, while recent model caculations clearly indicate anisotropic thermal motions of carbon and oxygen [5].

In order to treat anisotropic vibrational amplitudes within the adsorbate layer, the iterative procedure proposed by Fritzsche [6] was implemented and applied to the system NaCl(100)-p(2x1) CO. In addition, the recently addressed possibility of a partial flipping of molecules within the adlayer was investigated. While CO binds to the NaCl substrate via carbon, a flipped orientation is only slightly higher in energy [3], and LASER-induced inversion of molecules was demonstrated only recently [1]. It is shown that anisotropic thermal vibrations, in comparison to the isotropic treatment, affect LEED-I(V) spectra predominantly in the energy range below 100 eV. Furthermore, while a complete inversion of the monolayer significantly changes the reliability factor of the LEED analysis and thus proves the chemical sensibility of the method, a mixing of one percent flipped molecule basically has no effect on the I(V) curves.

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The Effect of Doping in Inelastic H Atom Scattering from Silicon

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Recent inelastic H atom scattering experiments from the semiconducting Ge(111)c(2x8) have shown a bimodal energy loss distribution. One of the components was narrow with a small energy loss. The other component has shown a broad and large energy loss with an onset equal to the surface band gap.[1] While the low energy loss channel is explained by an adiabatic molecular dynamics simulation, the high energy loss component is not described theoretically yet.

To gain a better understanding of the underlying mechanism, we extended our studies to the Si(100)2x1 surface which is semiconducting as well. Despite its electronic structure being similar to the Ge(111)c(2x8) surface, it shows a different H atom energy-loss distribution. The first component is much broader and the second component does not show a clear onset at the surface band gap, both indicators of electronic effects. To further investigate, we carried out scattering experiments from samples with various doping levels.

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Hydrogen Atom Scattering from Graphene on Nickel

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Previously, H atom scattering from graphene grown on a Pt(111) substrate was investigated in detail by our group [1]. Depending on the experimental conditions, two energy loss channels were observed, one quasi-elastic and one strongly inelastic. For a C-H bond to form, the delocalized electronic structure of graphene has to be locally destroyed. This gives rise to an adsorption barrier. If the hydrogen atom cannot cross the barrier, it is elastically reflected. However, if the atom can cross the barrier, it loses a large amount of energy, which can lead to it sticking to the surface [1]. Pt(111) was chosen because it is a weakly interacting substrate. This allows comparison of the experimental data with simulations of H atom scattering from free-standing graphene. Although good qualitative agreement is achieved between experiment and theory, quantitative agreement cannot be achieved because of the non-negligible substrate effect.

To experimentally study the substrate effect we chose Ni(111) as an additional substrate and performed the same experiments. Ni(111) is a strongly interacting substrate and a much larger substrate effect is expected. Furthermore, the influence of the crystal orientation on hydrogen atom scattering was studied and allowed the separation of various scattering channels.

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Chemistry of charge-imbalanced layers generated by Ion Soft-Landing

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Ion Soft-Landing (ISL) is used to deposit mass-selected molecular ions and their fragments onto surfaces.[1] The deposition of multilayers of one type of pre-charged, electronically stable ions (which retain their charge in the soft-landing process) raises fundamental questions about the charge-balancing processes in the formed layers. We demonstrate the formation of counterions (ammonium in the case of anion) in these charge-imbalanced layers. We show that the exact chemical composition of the counterions is dependent on the deposition parameters (e.g. ion current) which influence the coaccumulation of contaminations present in the background of the vacuum chamber.

Additionally, we show that highly reactive fragment ions formed via CID can bind at the surface to a previously deposited ion of same polarity, resulting in highly charged clusters, which were analyzed by analytical mass spectrometry.[2]

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Switching Photoresponsive Metal-Organic Frameworks with Polarized Light

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Nanoporous metal-organic frameworks (MOFs) are a promising class of materials with unique properties, suitable for diverse applications such as gas separation and controlled diffusion. The incorporation of photochromic (or photoswitchable) molecules into the MOF structure results in photoresponsive MOFs.[1] The structural or functional properties of such photoresponsive MOFs can be modified by light irradiation in a reversible and remote controlled manner.[2] By using linker molecules with fluorinated azobenzene side groups, photoswitchable MOF films were prepared whose chirality can be reversibly modified by irradiation with circularly polarized light of specific wavelengths.[3] The effect is based on the selective photoisomerization of the embedded chiral photochromic molecules upon irradiation with light. In this poster, we present the next step for the use of photoswitchable MOFs as smart materials and show its potential by using polarized light.

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Metal-Organic Framework Sensor Arrays for Highly Selective and Sensitive Sensing

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Metal-organic frameworks (MOFs) are crystalline nanoporous materials made of organic linkers connected by metal ions. MOFs are well-known for their large surface area, adjustable porosity and tunable functionality. Therefore, they seem perfectly suited as active material for sensing a broad range of molecules, in particular of the large group of volatile organic compounds (VOCs). For the molecule detection, MOF-films can be used in sensors with gravimetric transducers (based on a quartz crystal microbalance, QCM) [1] or in a colorimetric approach[2]. While many similar VOC molecules have similar responses in each individual MOF-sensor, the use of arrays of MOF-sensors with different affinities offers an exceptional selectivity and even allows the discrimination of similar complex VOC mixtures[3].There the data of the MOF sensor array are analyzed by simple machine learning algorithms. The versatile MOF-film approach and their adaptability makes such sensors ideally suited for various tasks, including food quality evaluation[2] and environmental monitoring.[4] On the poster, the state of art of optical MOF-film based sensors is presented.

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Investigation of Emulsification in Lab-on-a-Chip Systems for Efficient T-Detection via Liquid Scintillation Counting

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Tritium is a low-energy β^--emitter that can be well-detected using liquid scintillation counting (LSC). To do so the tritiated sample is mixed with a scintillation cocktail mainly composed of an organic solvent, and, if aqueous samples are to be measured, great amounts of surfactants [1][2]. Different micromixing structures as part of a lab-on-a-chip-platform were evaluated on their capability to accomplish fast emulsification even with reduced surfactant concentration and therefore enabling more efficient detection by lowering quenching effects.

A comparison of counting efficiencies after LSC measurement showed that micromixing units, such as a herringbone mixer (Darwin Microfluidics), can keep up with conventional emulsification by shaking a vial of sample and scintillation cocktail. Even when the ratio of cocktail to tritiated water (HTO) was changed to a lower cocktail fraction the counting efficiency decreased only slightly [3].

Another approach for forming a cocktail-water-emulsion was introducing additional energy in the form of sound waves leading to acoustic streaming. To do so the chip system was equipped with a piezo element. Different piezo elements, chip designs and materials as well as scintillation cocktail mixtures were evaluated on their performance to find an optimized system configuration.

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Development of a photocatalytic microreactor to investigate oxide-based model catalysts in NAP conditions

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Recently, solar fuel production by CO_2 photocatalytic conversion over semiconductors, such as TiO_2, has been proposed to be a promising alternative for handling with the increasing CO_2 concentration in the global atmosphere. [1-4] The investigations by spectroscopy and microscopy approaches on well-defined model catalysts within ultrahigh vacuum (UHV) can deepen our understanding of the fundamental mechanisms and structure-property relationships at atomic-level, while further extending to near ambient pressure (NAP) can make the reaction system closer to applied catalysis. [5-8]

In Su_2nCat-CO_2, we develop new, noble metal free hybrid catalyst materials consisting of abundant elements for the thermal and photochemical conversion of small molecules and especially CO_2 using sunlight. This project is focused on the development of a **photocatalytic microreactor** to probe the performance of well-defined model systems synthesized and characterized in a UHV environment under a more realistically simulated catalytic conditions. We target an apparatus that is capable of online, real time catalytic testing in the pressure regime between UHV and ambient conditions (1 atm). Our design creates the microreactor volume by sealing on the sample surface with an O-ring. Thus, the surrounding chamber stays in vacuum, while only the surface is exposed to the reactive environment. This decreases the internal (dead) volume, and allows for subsequent atomic level characterization and avoids substantial contamination of the UHV sample holder.

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Adsorption and Structure Formation of the Carbonyl-Functionalized Ionic Liquid [5-oxo-C_6C_1Im][NTf_2] on Au(111) and Pt(111)

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Catalytic activity and selectivity can be precisely tuned by combining heterogeneous catalysts with ionic liquids. Recently, significant research has focused on the fundamentals of Solid Catalysts with Ionic Liquid Layers (SCILL). The analysis of the interaction between atomically specified model systems and functionalized ionic liquids (ILs) is the next stage of this study.

We have studied the carbonyl-functionalized ionic liquid [5-oxo-C_6C_1Im][NTf_2] on Au(111) and Pt(111) surfaces. Using physical vapor deposition under ultrahigh vacuum (UHV) conditions, we deposited the IL to study its adsorption, interactions, and thermal behavior. For this, we performed in situ experiments using scanning tunneling microscopy and time-resolved and temperature-programmed infrared reflection absorption spectroscopy, along with molecular dynamics simulations and density functional theory calculations to support the interpretation of the experimental results.

We observed that the weakly bound multilayer of [5-oxo-C_6C_1Im][NTf_2] remains stable on Au(111) and Pt(111) up to about 390 K under UHV conditions. The more strongly bound monolayer desorbs at around 500 K. On Pt(111), we observe decomposition and partial desorption of the [5-oxo-C_6C_1Im][NTf_2] monolayer starting at 260 K, while we observe no decomposition on Au(111). Furthermore, we find that the orientation of the IL sub-monolayer on Au(111) is strongly dependent on both coverage and temperature.

The Research Training Group GRK 2721: Hydrogen Isotopes $^{1,2,3}H$

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Hydrogen's three naturally occurring isotopes, protium (H), deuterium (D) and tritium (T) lie at the focus of the DFG-funded Research Training Group $^{1,2,3}H$ (GRK 2721). $^{1,2,3}H$ combines the expertise of Leipzig University, the Helmholtz-Zentrum Dresden-Rossendorf/Research Site Leipzig, and the Leibniz Institute of Surface Engineering in the fields of laser spectroscopy, materials science, lab-on-a-chip technology, advanced organic synthesis and radiochemistry. It fosters fundamental research in the field of hydrogen isotopes to gain an atomic-level understanding of nuclear quantum effects in nanostructured materials and ^{n}H-bonded networks. $^{1,2,3}H$ thereby advances methods for H/D/T separation, D/T labelling and T detection while educating tomorrow’s workforce in emerging technologies that exploit the unique properties of the hydrogen isotopes.

Chemical interaction within novel carbon-silica composites studied by X-ray photoelectron spectroscopy

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Both silica and activated carbon are known for their use as adsorbents for the purification of wastewater. A promising strategy in modern wastewater treatment is the combination of these two adsorption materials. [1] It is also assumed that a homogeneous arrangement of the compartments in the larger nanometer dimension range is associated with an increase in adsorption performance. For this purpose, carbon-silica composites were produced from rice husks using novel synthesis methods. X-ray photoelectron spectroscopy (XPS) measurements were carried out to demonstrate successful bonding between the two components. In Si 2p spectra, which could be assigned to silica, both conducting and non-conducting species could be recognized by differential charging resulting from the electron emission. To distinguish these components more precisely, additional measurements were carried out with a flood gun. As expected, the charged (non-conducting) species shifted, while the signals of the uncharged (conducting) silica species remained at the previously determined binding energies. These effects were not observed in comparative measurements with only mechanically homogenized reactants of the same composition, which is why a successful linking between carbon (providing the conductive contact) and part of the silica can be assumed. Uncharged silica species could be observed for composites with carbon to silica atomic rations ranging from 95:5 up to 65:35.

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Nucleation mechanism of TDMAH on CoO nano-islands

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Atomic Layer Deposition (ALD) has emerged as a promising technique for fabricating high-quality thin films with atomic precision, enabling advancements in electronics, nanotechnology, and catalysis. [1-2] Understanding nucleation mechanisms in ALD is crucial for ensuring quality, optimizing reaction efficiency, tailoring substrate compatibility, and enabling the development of advanced materials with precise properties. [3-4]

This study investigates the nucleation mechanisms and initial thin film growth stages using tetrakis(dimethylamido)hafnium (TDMAH) on cobalt oxide (CoO) nano-islands under ultra-high vacuum conditions. Infrared Reflection Absorption Spectroscopy (IRAS) was employed to monitor surface reactions during nucleation at 300 K and 400 K, along with experiments on D_2O pre-saturated surfaces.

As a result of this study, we identified that at 300 K the presence of hydroxyl groups was critical for initiating nucleation, facilitating hydrolysis, and forming Hf-O bonds. In contrast, at 400 K, Lewis's acid-base interactions with cobalt and oxygen ions dominated, leading to distinct adsorption dynamics with the decomposition of precursor and formation of -OH groups on the surface which served as nucleation sites afterwards. Experiments on the D_2O-pre-saturated surface revealed that -OD groups at island edges serve as essential adsorption sites for TDMAH. TDMAH reacts with surfaces containing -OD groups, forming hafnium oxide and adsorbed -NCH_x species, inhibiting further adsorption of additional hafnium precursor molecules.

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Water adsorption on doped single crystal $SrTiO_3$ and $BaTiO_3$ for the oxygen evolution reaction

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The oxygen evolution reaction (OER) introduces large overpotentials in water electrolysis because of its sluggish kinetics due to the four-electron transfer process. By heterovalent substitution in oxide electroceramics (doping), different compensation mechanisms (electronic, ionic, valence changes…) can be enabled. A description of how the catalyst surface can be modified in terms of doping, substitution, or defect engineering so that a specific catalyst OER active surface phase forms and which role the Fermi Level, as well as the occupied and unoccupied states of the surface, plays in this transformation is still missing.

The *collaborative research center FLAIR* (SFB 1548) is working on being able to predict and apply these different compensation mechanisms. We propose that the Fermi Level can be used as a universal descriptor for these compensation mechanisms and will be integral for creating efficient and stable perovskite OER catalysts in the future on the principles of *Fermi Level engineering* [1].

For systematically checking the influence of the electronic structure changes due to doping of $SrTiO_3$ (100) and $BaTiO_3$ (001) single crystals, we have performed lab-based x-ray photoelectron spectroscopy (XPS) in our Cluster Tool DAISY-FUN as well as synchrotron-based XPS, x-ray absorption spectroscopy (XAS) and resonant photoemission spectroscopy (resPES) at BESSY II, beamline PM3.

There, water adsorption experiments were performed on single crystal $SrTiO_3$ (undoped, doped with 0.05 wt.% Nb, 0.1 wt.% Nb and 0.7 wt.% Nb), as well as reduced single crystal $BaTiO_3$ (undoped and doped with 0.05 wt.% Mn and 0.05 wt.% Fe). The results of these measurements will be presented.

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Carbon nanomembranes (CNMs) for separation of the gases relevant for green energy technologies

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Due to the global climate changes, there is an urgent demand for advancements in separation of the gases relevant for development of green energy technologies. 2D materials, such as *carbon nanomembranes* (CNMs), are promising candidates for these purposes. CNMs are 1 nm thick, mechanically stable molecular nanosheets synthesized *via* electron irradiation of aromatic self-assembled monolayers (SAMs). By choosing the precursor molecules, properties of these molecular 2D materials – such as their permeance and selectivity for gases – can be tailored by orders of magnitude. [1] In this work, we prepare CNMs from molecularly designed SAMs and study their basic properties by complementary surface sensitive techniques including X-ray photoelectron spectroscopy (XPS), scanning tunnelling microscopy (STM), low-energy electron diffraction (LEED) and polarization modulation infrared reflection absorption spectroscopy. The permeation and separation properties of the formed CNMs, for such gases as H_2, H_2O and CO_2, were characterized by highly sensitive mass spectroscopy measurements.

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Structure and reactivity of MgO single-crystal surfaces studied by IRRAS with CO and CO_2 as probe molecules

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MgO, a low-cost alkaline metal oxide material, has been widely used as a catalyst or support in heterogeneous catalysis. Achieving a thorough understanding of the structure and chemical properties of MgO-based catalysts requires reliable reference data from surface-science studies on MgO model systems (e.g., single crystals). Compared to extensive investigations on metal surfaces, the application of reflection absorption spectroscopy (IRRAS) to oxide single-crystal surfaces poses substantial challenges due to the very low reflectivity of dielectric substrates in the infrared range. Here, we present the first polarization-resolved IRRAS data obtained for CO and CO_2 adsorption on MgO(100) single-crystal surfaces using a sophisticated UHV apparatus (THEO).[1,2] The surface ligand IR (SLIR) approach has proven to be a surface-sensitive, non-destructive technique well-suited for investigating the surface chemistry of pure and metal-decorated oxide catalysts.[3,4] The systematic IRRAS results reveal that exposure of MgO(100) to both CO and CO_2 at low temperatures leads to weak physisorption, characterized by the typical C-O stretching vibrations at 2150-2170 cm^{-1} for CO and the asymmetric OCO stretching vibrations at 2134-2370 cm^{-1} for CO_2 in a linear geometry. The corresponding binding energies are determined from temperature-dependent IRRAS measurements. The adsorption sites and configurations will be discussed in detail, based on polarization-resolved IRRAS data, theoretical analysis, and previous transmission IR results.[5,6] Furthermore, in the p-polarized spectra, we observe a significant polarization-dependent band splitting of about 20 cm^{-1} with a sign reversal, consistent with the theoretical predictions.[7]

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High-pressure Hydrogen Reduction of Single Crystalline Iron Surfaces – XPS/UPS and LEED

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We present a procedure that enables fast and swift reduction of iron. Scientists have been challenged to measure pure iron's properties due to its oxidation in air and bulk contaminants originating from the manufacturing process. Thus, samples were either directly grown in vacuum via physical vapour deposition, or commercial samples were subdued to long and repetitive reduction methods because of bulk contaminants segregating to the surface [1]. One such example is the application of numerous sputtering-annealing cycles as well as hydrogen treatments lasting for weeks [2,3].

Our method demonstrates the completion of the reduction of single crystalline iron surfaces in less than a few hours, resulting in a clean surface as proven by LEED. This can be achieved by a high-pressurised hydrogen autoclave at elevated temperatures [4]. Contaminations are observed and identified by XPS, with samples before the reduction showing carbon, oxygen and sulphur and the absence thereof after. The displayed results include the LEED reconstruction of the contaminants as well as the clean p(1x1) surface of Fe(100), Fe(111) and Fe(110). Finally, the results are rounded off by valence band and work function measurements.

In summary, we present a quick method for the reduction of iron oxides and LEED and XPS/UPS data of oxidised and clean single crystalline iron. These surfaces are then used to study their interaction with e.g. water or oxygen, or other gases uncovering possible reaction mechanisms.

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Structural Anisotropy of Water at Charged Aqueous Interfaces Probed by Depth-Resolved SFG/DFG Spectroscopy

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Charged aqueous interface are subject of extensive investigation due to their relevance in both natural and industrial processes, for instance, ion transport across biological membranes, or artificial energy conversion and storage. At charged aqueous interfaces, the excess surface charge induces a modification of the water structure right at the phase boundary, which is dominated by field-induced reorientation. According to the Gouy-Chapman (GC) theory, the decay length of field penetration into the electrolyte ranges between the sub-nanometer scale and 10s of nanometers i.e., up to ~100s of molecular water layers. Even though such theory gives valuable information about the electrostatic properties of water interfaces, less is known about its influence in the water structure, nor how the water itself contributes to the formation of the electrochemical double layer.

In this work, we directly probe the anisotropic water structure using our recently developed depth-resolved vibrational spectroscopy technique that combines the phase-resolved sum- and difference-frequency generation (SFG and DFG) responses (1,2). By studying the depth-dependency of the water response, we demonstrate that the interfacial water structure features at least two distinct dielectric regimes, akin to the compact layer / diffuse layer distinction of the Gouy-Chapman-Stern (GCS) model. Beyond this, we extract and analyze the spectra of the compact and diffuse layers for different electrolyte concentrations, showing that they generally report distinctly different molecular structures and environments.

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Aqueous Phase Transfer of Colloidal 2D Lead Chalcogenide (PbS, PbSe and PbTe) Nanoplatelets Preserving their Near-Infrared Photoluminescence

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Colloidally synthesized two-dimensional (2D) lead chalcogenide (PbX; X = S, Se, Te) nanoplatelets (NPLs) exhibit efficient tunable photoluminescence (PL) at near-infrared up to shortwave-infrared wavelengths (PbS at ~720 nm, PbSe 860 – 1510 nm, PbTe 910 – 1460 nm, depending on the NPL thickness), where optical glass fibers exhibit negligible attenuation.[1-5] These NPLs are synthesized from lead oleate and the respective chalcogenide source at low temperatures and are colloidally stable in organic solutions due to a saturating hydrophobic mixed oleate and octylamine layer chemically bound to their surface. However, relying on post-synthesis processing of the hydrophobic NPLs (e.g. incorporation into polymer fibers by electrospinning)[6] from organic solvents is limiting their applicability. Here we present a general aqueous phase transfer protocol for 2D PbS, PbSe, PbTe NPLs that preserves their PL at technologically relevant wavelengths.[7] We exchange the non-polar ligand shell of 2D PbX with hydrophilic 11-mercaptoundecanoic acid,[8] which yields bright and water soluble NPLs. Our results extend the possibilities for encapsulating near-infrared-emitting lead chalcogenide NPLs and pushing them toward solid state applications, e.g. the fabrication of polymer-encapsulated inorganic-organic nanocomposite thin films.[9]

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Ice Nucleation and Ice Binding Activity of Organic Molecules

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While ice binding and ice nucleation induced by molecular species has gradually garnered more attention over the last few years, the molecular mechanisms by which they act remains controversial in many cases. While some studies already examined molecular ice binding or ice nucleation activities, a more comprehensive approach of these substances on both these properties is desirable. [3,4] These effects are of importance as such molecules may contribute to environmentally relevant ice formation processes. For instance, ice nucleation plays a pivotal role in climate-relevant processes such as precipitation that may alter the Earth's radiative balance, while ice growth inhibition is part of the response to freezing conditions in both flora as well as fauna. [1,2]

We studied water-soluble organic molecular substances as model species for ice binding as well as ice nucleation processes to gain a deeper understanding of the mechanisms of these interactions. Here, we present ice nucleation results from the micro- and nanolitre sized droplet freezing arrays BINARY and nanoBINARY built in our laboratory, [5, 6] as well as ice recrystallisation inhibition measurements from the sucrose-sandwich technique and the splat cooling approach. Furthermore, we performed ice shaping measurements to gain insights into the mode of interaction and discuss the results in the context of their structure.

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Quantitative Analysis of the Kinetics of Recrystallization in Polycrystalline Ice Discs

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Ice recrystallization (IR) is an important phenomenon in various contexts. For example, in living organisms, IR is often undesirable, as the formation of large ice crystals poses a threat to cells and tissues. Conversely, recrystallized ice can serve as a template for creating porous materials [1]. Understanding the mechanisms of ice growth and its inhibition—both by natural and synthetic substances—is therefore a highly relevant area of current research [2-5].

Assessing the extent of IR often remains challenging and time-consuming, particularly in the absence of automated image analysis tools. One commonly used method to investigate IR is the splat-cooling assay, which generates thin discs of polycrystalline ice [3-4,6]. The shape and size of the ice crystallites and their temporal evolution are determined from microscopic images. However, poor contrast and the simultaneous presence of other features of varying sizes make an automated analysis difficult. Hence, image analysis is often performed manually, with areas and crystals being selected subjectively rather than based on their statistical occurrence. To address these limitations, we have developed a multi-step automated image analysis routine that ensures high precision, reproducibility, and an unbiased evaluation of ice crystals. This routine enables the investigation of large areas of ice discs, thereby allowing for the determination of an almost complete size distribution. As a result, it is sensitive enough to detect and verify even minor effects induced by small molecular compounds, an example of which will be presented.

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^{1}H / ^{2}H / ^{3}H separation using nanoporous materials investigated by Thermal Desorption Spectroscopy

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The heavy hydrogen isotopes, deuterium (^{2}H) and the radioactive tritium (^{3}H), are widely used for labeling organic compounds to investigate reaction mechanisms or drug metabolism. In recent times, they are attracting much interest in view of the development of nuclear fusion as a carbon-free solution to cover the energy demand of the future. Novel strategies for more efficient isotope separation are being explored. For $^{1}H_2$ / $^{2}H_2$ separation, the utilization of quantum sieving effects in nanoporous materials, such as modified zeolites or metal-organic frameworks (MOFs), has proven fruitful. [1, 2]

In this work, we have investigated the $^{1}H_2$ / $^{2}H_2$ / $^{3}H_2$ separation efficiency of an Ag-exchanged zeolite type Y by Thermal Desorption Spectroscopy. [1] The gas outlet was equipped with a CuO flow reactor to convert the ejected $^{3}H_2$ to $^{3}H_2O$ for safe disposal. Isotopologue mixtures were separated via selective adsorption at ~80 K and temperature-controlled desorption. Our results show strongly preferred adsorption in the order $^{3}H_2 > ^{2}H_2 > ^{1}H_2$, explained by chemical affinity quantum sieving based on the different zero-point energies. [1-3] In consideration of its easy synthesis and radiation stability, the zeolite proved to be a promising candidate for large-scale applications of H isotope separation, specifically including tritium.

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InAs Quantum Dots with tunable Absorptions up to ~ 2500 nm: Synthesis and mechanistically Insights

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RoHS-compliant Indium Arsenide (InAs) Quantum Dots (QDs) are highly promising for infrared (IR) applications, including consumer devices, optical communication, bioimaging, and sensing. However, compared to established II-VI and IV-VI semiconductor nanoparticle systems, the wet-chemical synthesis of less toxic III-V systems remains underexplored.[1] Notably, the largest reported non-elongated InAs QDs exhibit absorption maxima of only up to 1700 nm [2], whereas theoretical calculations suggest potential values up to ~3500 nm.

Herein, we present a novel reaction pathway to synthesize ultra-large InAs QDs with record nanoparticle sizes and record-breaking absorptions up to ~ 2500 nm. Using our controlled method, we can produce single non-elongated quantum dots in a defined matter.

Additionally, we provide significant mechanistic insights into the formation process of these ultra-large InAs QDs, paving the way for further advancements in this field.

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$M(Cu,Ag)InX(S,Se)_2$ Nanoparticles for Novel Transistor Structures

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Smartphones, computers, televisions, radios, power chargers - transistors can be found in almost every electronic device. Nowadays, such electronic components are expected to become smaller, flexible, and more powerful. However, a high-performance, flexible, thin-film transistor technology is still missing.

Semiconductor nanocrystals (NCs) have the potential to achieve a breakthrough in transistor performance, as they are processed solution-based and can overcome the intrinsic low carrier mobility of organic semiconductors. In the last decades, different functional NCs have been successfully fabricated. It is possible to precisely control the physical and electronic properties of NCs via parameters such as size, shape and composition. Using them in different transistor architectures is promising, as studies with CdSe NCs have shown recently. [1]

In this work, we strive to use different NCs for thin film field-effect transistors (FET), which allow to easily realize high-performance devices without nanostructuring. Therefore, $M(Cu,Ag)InX(S,Se)_2$-NCs like $CuInSe_2$ are synthesized to replace the widely studied but more toxic Cd- or Pb-containing materials. To improve the electronic communication, the insulating organic ligands necessary for the synthesis are exchanged with inorganic ligands (I^-, Br^-, S^{2-}, SCN^-) in simple solution-based phase transfer ligand exchanges. Different FET-architectures were successfully fabricated and further analysed. [2,3]

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The Charge State of Single Nanoparticles in the Gas Phase

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Obtaining information on the intrinsic properties of single nanoparticles (NPs) remains a major challenge in nanoscience. While ensemble experiments suffer from chemical and physical heterogeneity, most single-particle techniques involve the characterization of supported NPs on a support. In contrast, we use a single nanoparticle trap to non-destructively determine the absolute mass and charge of individual NPs isolated in the gas phase.[1] The instrument also allows to perform visible and fluorescence spectroscopy to further characterize the NPs.[2,3,4]

Being able to change the NP charge state in a controlled way is crucial for faster experiments and to investigate its influence on other NP properties. However, until now we were not able to reduce the NP charge. By probing the charging dynamics of single 100 nm SiO_2 NPs while varying the gas pressure, gas type and NP charge state we could elucidate the influence of these parameters on the charging dynamics and gain full experimental control of the NP charge state. This makes it possible to investigate how the charge state of a NP affects its behavior, for example when it interacts with light and gas molecules. Furthermore, based on the results, we validated a model of the charging dynamics that provides a deeper mechanistic understanding of the processes taking place on the NP.

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Carbon Nanomembranes with Atomic Layer Deposited Al_2O_3: Unlocking High Selectivity and Scalability in Membrane Separations

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Efficient membrane separations require precise control over pore size and surface properties, challenges that conventional polymer membranes often cannot meet. Our work demonstrates the enhanced selectivity and scalability of carbon nanomembranes (CNMs) functionalized via atomic layer deposition (ALD) of Al_2O_3. Initially fabricated from electron-induced cross-linking of amorphous poly(4-vinylbiphenyl) (PVBP) layers, these CNMs exhibit an ultrathin structure with sub-nanometer pore size, enabling rapid water transport and selective ion rejection.[1] Al_2O_3 deposition through ALD further refines the pore structure, achieving a remarkable balance between permeance and selectivity. Al_2O_3 functionalization introduces hydrophilicity and further refines the pore dimensions, resulting in a water vapor permeance rate of 1.9×10^{-5} $mol\cdot s^{-1}\cdot m^{-2}\cdot Pa^{-1}$ with water vapor/nitrogen selectivity exceeding 1×10^{4}, performance that surpasses conventional polymer-based membranes and graphene oxide membranes. This combined approach demonstrates the effectiveness of ALD for tuning CNM properties, advancing their application in gas separation, air dehumidification, and molecular filtration.

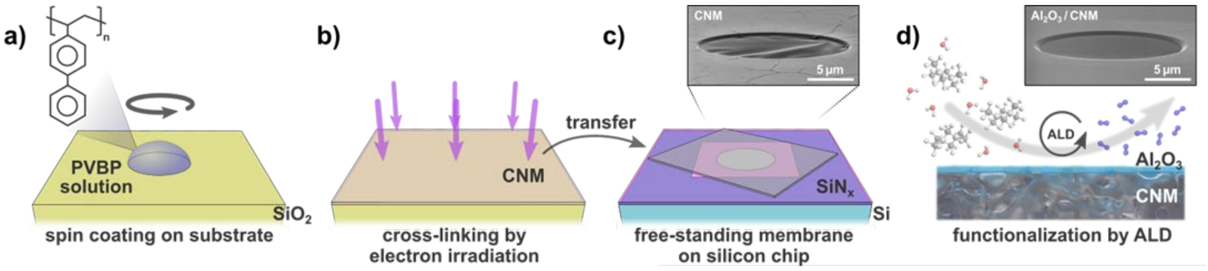

Figure 1. Steps for the preparation of CNM and subsequent Al2O3 functionalization via ALD.

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Theory and Data Science

Electrochemical Oxidation of UV Filters: A First-Principles Molecular Dynamics Study – Part 2

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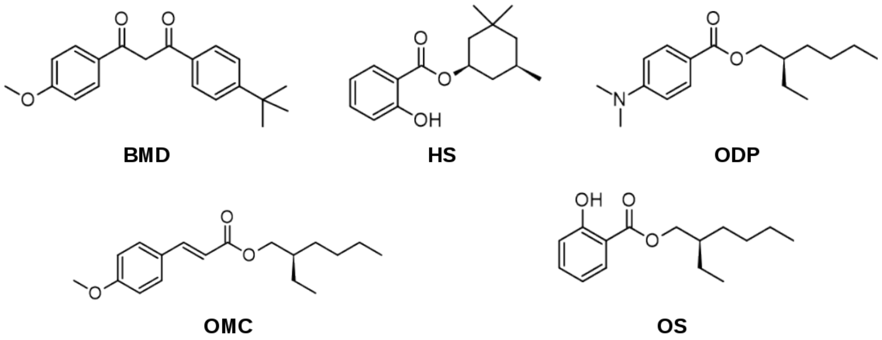
The global demand of sunscreens had raised due to awareness of the risk that solar overexposure represents, implying the contamination of large amounts of water with UV filters. It was found that their current environmental concentrations can produce adverse effects [1]. For this reason, there is a growing interest in the development of wastewater treatment methods (**WWTMs**) that remove these compounds. Electrochemical oxidation is a promising WWTM, since it provides a versatile, efficient, cost-effective, easily automatable, and clean process [2]. Car-Parrinello Molecular Dynamics (**CPMD**) is used to determine reaction mechanisms at the ab-initio level of theory: the electronic cloud is computed using the **DFT** approximation and the nuclear motion is treated classically using Newton dynamics. [3].

Continuing with our work [4], a theoretical model of the electrochemical oxidation of organic UV filters as pollutants using CPMD was employed to the case of five of the most used UV filters: **BMD**, **HS**, **ODP**, **OMS** and **OS** (Figure 1). In this model, the organic compound is introduced in a suitable water box and then 8 OH radicals are produced by removing H atoms from the solvent, thus simulating the anodic environment after the electric discharge.



BMD **HS** **ODP**

OMC **OS**

Figure 1 Structure of the five UV filters.

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Deconvoluting impedance spectra of sodium-ion cells by distribution of relaxation times analysis with dispersed analytical basis functions

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Electrochemical impedance spectroscopy (EIS) is a powerful technique for investigating various electrochemical systems, including sodium-ion batteries (SIBs), which are emerging as a cost-effective and sustainable alternative to lithium-ion batteries for large-scale energy storage and electric vehicle applications. However, interpreting EIS data is often cumbersome because of the overlapping nature of electrochemical processes in the frequency representation, making it difficult to distinguish individual contributions to the overall impedance.

In the present study, a robust approach for the deconvolution of impedance spectra of alkali metal-ion cells is proposed. This approach is based on the distribution of relaxation times (DRT) technique in combination with analytical basis functions derived from empirical relaxation models [1]. The DRT method transforms EIS data into a spectrum of relaxation times, effectively separating the underlying processes based on their characteristic time constants. By incorporating analytical basis functions, the DRTs can be reconstructed without the need for regularization and by using fewer processes. This improves the systematic and automated classification and interpretation of impedance spectra significantly.

The presented approach is used on experimentally acquired impedance data of commercial SIB cells comprising sodium nickel manganese iron oxide cells ($NaNi_{0.33}Mn_{0.33}Fe_{0.33}O_2$) as active cathode material. The aim is to fingerprint degradation mechanisms in a cycle-ageing phase following a repeated early-life overdischarge, which is known to affect the cell's characteristics [2].

Using analytical discretization bases, the separation and quantification of the changes in the impedance of the tested SIBs implied that the repeated overdischarge led to significant alterations in the properties of the cell's solid electrolyte interphase (SEI). This finally led to irreversible changes in the cell characteristics, compromising the performance of the cells in the long term.

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On the Complex Hydrogen-Bond Network Structural Dynamics of Liquid Methanol: Chains, Rings, Bifurcations and Lifetimes

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The H-bond network of water has been extensively studied for decades by now, however the exploration of methanol as a closely related associated solvent is very limited by comparison. The scarcity of accurate simulation data was a motivation to strive for a comprehensive investigation of the structural dynamics of liquid methanol including some electronic properties. In this computational study, extensive ab initio molecular dynamics simulations were performed for bulk methanol at ambient condition in order to reveal the intricacies of the H-bond network topology including the associated lifetimes. We show that methanol predominantly forms large filamentary aggregates incorporating numerous bifurcations and smaller rings which are stable up to several picoseconds according to the intermittent lifetimes of such H-bonded aggregates depending on size. Most notably, the effective molecular dipole moments of the individual methanol molecules in the liquid state obtained on-the-fly from the full electronic structure, which thus include electronic polarization and charge transfer effects, are found to be very sensitive to both, topology and specific structure of the H-bond network in which they are embedded. In particular, they show pronounced non-additivity effects on the order of 20 to 25% depending on the length of linear chains or the size of cyclic rings, a phenomenon that is not accessible in force field simulations relying on fixed point charge models.

Strong Anisotropic Electronic Coupling between Gold Surfaces and Interfacial Water

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Understanding the intrinsic properties of solid/electrolyte interfaces is crucial for comprehending the behavior of catalysts, capacitance, reactivity, and the anomalous behavior of confined water. However, probing electrochemical interfaces buried between electrodes and electrolytes is notoriously challenging. In particular, the intrinsic properties at metal/water interfaces remain unclear. Using ab initio molecular dynamics (AIMD) simulations with a large supercell we find that strong electronic interactions between water molecules and gold metal surfaces govern the structure of water molecules and charge transfer. Specifically, dangling OH groups adjacent to the gold surface exhibit orientation-dependent electronic polarization and charge transfer. These findings hold significant importance for tailoring the electrochemical properties of metal-aqueous interfaces, with broad implications ranging from sensing to electrochemistry.

Energy decomposition analysis for excited states

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Chemical bonds are crucial concepts in chemistry, often used to explain reactivity. These bonds are typically classified as ionic, covalent, etc., but most have a mixed character and that is not an observable. Therefore, model methods like Energy Decomposition Analysis (EDA) are needed, which breaks down bonding energy into chemical meaningful components such as electrostatic, Pauli repulsion, and orbital interaction. By comparing these components, the bonding character can be revealed. However, most EDA methods are limited to ground states and only few can apply to excited sates. Excited states are also important, especially in photochemistry, where light alters properties like structure and orbital occupation. Reactions in excited states may not occur in the ground state, so EDA for excited states is valuable.

Our approach combines the Morokuma-Ziegler-EDA scheme with linear response TDDFT. The method calculates excitation energies for various intermediate states using two variants: the first variant uses excitation coefficients of fragments to calculate excited states, while the second optimizes these coefficients

Exciplexes were used as a test system, where only one fragment is excited, leading to bonding with the other fragment, so splitting the excitation is not a concern. After testing, the method was applied to pentacene oligomers, known for their singlet fission properties. In singlet fission, an excited singlet monomer interacts with others, forming two coupled triplets that later decouple. This excitation is spin-allowed, but de-excitation is spin-forbidden, making the system potentially useful for more efficient charge separation in solar cells. We aimed to use the new method to understand the interaction between the excited monomer and others and gain insights into the mechanism.

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Nuclear quantum effects (NQEs) in charge inverted hydrogen bonded and dihydrogen bonded systems

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The quantum nature of light nuclei influences the chemical bonding properties which is the focus of this study. Hydrogen isotope effects predominantly emerge due to variations in atomic mass when moving from hydrogen (1.0073 u) to deuterium (2.0141 u) to tritium (3.0160 u). Thus, hydrogen isotope substitution leads to a change in the stretch vibrational frequencies (n (H_2): 4161.2 cm^{-1}, n (HD): 3632.2 cm^{-1} and n (D_2): 2993 cm^{-1}) and consequently a change in ZPE [1], which is given as E(ZPE) = ½ h n. This means that isotope substitution directly impacts the strength of the bonding.

We studied NQEs on molecular geometries and chemical bonding in charge inverted hydrogen bonded (CIHB) and dihydrogen bonded (DHB) systems by substituting hydrogen (H) with deuterium (D) and tritium (T). We applied nuclear electronic orbital-density functional theory (NEO-DFT) [2] to capture nuclear quantum effects and energy decomposition analysis (EDA) methods to analyze the changes in electronic structure due to geometric isotope effects. For all complexes, the intermolecular as well as intramolecular distances gradually decrease with heavier hydrogen isotope substitution. In the case of boron clusters interacting with AlH_3, HF and NH_3 the major stabilizing contributions comes from the electrostatic interaction while in case of carbene it is the orbital contribution. In most of the complexes, isotope substitution enhances the electrostatic as well as orbital contribution but at the same time cause sufficient large increase in the Pauli term which overcompensate the above mentioned two stabilizing contributions resulting in the destabilization of interaction energy. NOCV deformation densities show the charge depletion from the partially negative charge hydrogen side towards the vacant orbital on the neighboring molecule in CIHB systems which confirms the formation of CIHB.

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Towards Accurate Modeling of Thermally Activated Delayed Fluorescence Emitters: Computational Investigations of Cyanoarenes

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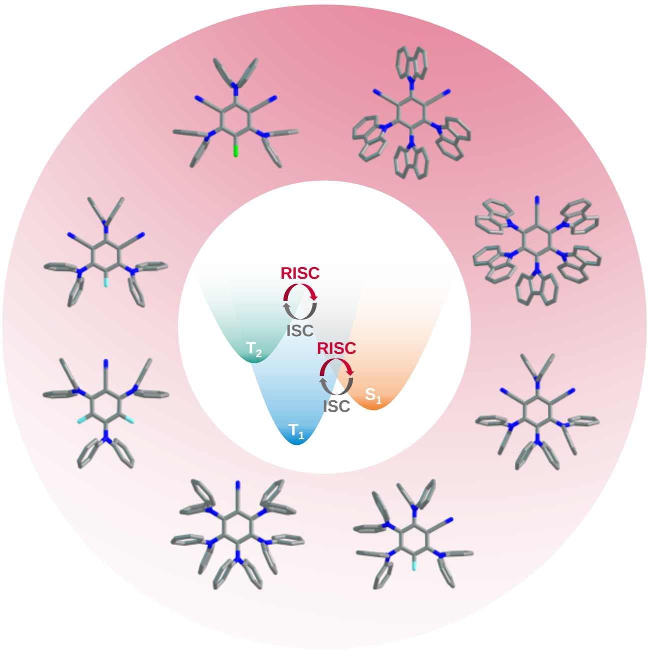
Due to the low efficiency and high cost of many conventional fluorescent and phosphorescent materials, the field of organic light-emitting diodes (OLEDs) has recently shifted to a new generation of OLEDs using thermally activated delayed fluorescence (TADF) emitters. The facilitating mechanism involves a thermally active reverse intersystem crossing (RISC) process between singlet and triplet states, converting the triplet population into a singlet population and enabling delayed fluorescence with high quantum yields.[1]



Preliminary work on this topic could already show good agreement of computed singlet-triplet gaps with experimental results in a straightforward time-dependent density functional theory (TD-DFT) framework for 4CzIPN and a halogenated derivative.[2] Ongoing computational investigations into cyanoarene systems have revealed trends that enable the systematic tuning of these molecules to achieve desired properties, paving the way for targeted design of more efficient TADF emitters. Additionally, this work provides valuable insights into the RISC mechanism and identifies active interconversion channels present in cyanoarenes.

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Benchmarking electrical properties of transition metal oxides using various functionals

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Last year, we presented the impact of different pseudopotentials (PPs) on the electrical properties of TMOs such as TiO_2, MoO_3, MoO_2, ZnO, V_2O_5, and V_2O_3. The findings indicated that the effect of PPs on the bandgap and conductivity were negligible; while the effect on the dielectric permittivity was significant. This year, we extend our study to benchmark the performance of various exchange-correlation (XC) functionals across a broader set of TMOs.

Our benchmark demonstrates the performance of standard generalized gradient approximation (GGA) [1] functionals e.g., PBE [2], meta-GGA functionals e.g., SCAN [3], and hybrid functionals e.g., HSE06 [4]. The Hubbard correction [5] was used for better localisation of electrons interaction. The materials cover a wide conductivity range from very low conductivity [~10^{-7} (S/m)] e.g., TiO_2-Rutile [6] to high conductivity [~10^{6} (S/m)] e.g., ReO_3 [7]. We calculated key electronic properties, including band gaps, dielectric permittivity, and electrical conductivity using Wannier functions (with BoltzWann [8]). We used an efficient workflow that enables systematic benchmarking for diverse set of materials, and implemented it using the automated workflow manager AiiDA [9] ensuring a reproducible output.

We report the preliminary results of benchmarking that the effect of different XC functionals on the electrical properties of different materials.

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Simulating Ion Diffusion in Perovskites: Application of Curvature Constrained Cubic Spline-Based Potentials in Molecular Dynamics

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Molecular Dynamics (MD) is a powerful tool for studying ion transport in solids, but it requires reliable effective potentials to be available for the target system. If no such potentials exist, then new ones must be derived and validated, and this is a highly non-trivial task that requires a large investment of computational resources, time, and care.

Traditionally, effective potentials consist of analytic terms, which can limit their accuracy; furthermore, the terms are non-linear, which make it challenging to find the globally optimal parameter set. One potential approach to overcome these problems is the Curvature Constrained Cubic Splines (C^3S) method [1]. In C^3S, cubic splines are used to provide greater flexibility of the functional form, while the global curvature is constrained to avoid unphysical oscillations due to over-fitting; moreover, the optimisation problem is linear.

In this study, we applied the C^3S method to generate two-body potentials for perovskite magnesium silicate ($MgSiO_3$) using structures, energies and forces from density functional theory (DFT) calculations as training data. $MgSiO_3$ is one of the most abundant materials in the Earth's mantle, and it adopts a perovskite phase under the high pressure and temperature conditions found in the lower mantle [2]. From the MD simulations with the C^3S-potentials, we determined the thermal expansion coefficient, and oxygen tracer diffusion coefficient as a function of temperature and pressure.

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Quantum Solvation of H_2O and H_3O^+ in ^4He and *p*-H_2 Bosonic Environments at Ultralow Temperature

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Nanodroplets of ^4He atoms feature manifestations of superfluidity. Either as a nanodroplet or as a gentle tag, ^4He is used for spectroscopic investigation of a target molecule at ultralow temperature. In this regard, in search of other superfluid solvents, *p*-H_2, due to its bosonic spin-statistics, has been investigated both by theoretical as well as experimental methods. However, in these cases, the onset of superfluidity is either debated or suggested to be dependent on *p*-H_2 cluster size. Hence, investigating these properties of solutes in ultracold solvents through computational approaches has gained increased recent interest. Theoretical descriptions of bosonic solvent particles requires the inclusion of bosonic exchange while the molecular flexibility must be accounted for as well. We apply a hybrid path integral methodology combined with highly accurate neural network potentials of CCSD(T) quality to simulate quantum solvation of neutral and charged molecular species in both ^4He and *p*-H_2 bosonic environments. We not only compare the microsolvation behavior of these molecules and its connection to the superfluid response of the solvent up to larger clusters, but also search for interesting behavior such as supersolidity as discovered recently for CH_5^+ in ^4He clusters.

Intrapore and interpore diffusion of water in MOF-303

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Water scarcity is a global challenge, and metal-organic frameworks (MOFs) show potential for addressing it by capturing water from ambient air. Of particular interest is MOF-303, featuring aluminum-oxide nodes connected by PZDC (1-H-pyrazole-3,5-dicarboxylate), due to its exceptional water-harvesting capabilities.[1] To further optimize this material it is essential to understand the adsorption structures and the diffusion of water molecules within and between the MOF pores.

We apply quantum chemical techniques to gain an atomistic understanding of water diffusion in MOF-303, focusing on intrapore and interpore pathways. We localize transition structures (TS) for these processes at PBE+D3 level with the help of climbing image nudged elastic band (CI-NEB), eigenvector following, and the improved dimer method (IDM) implemented in VASP and MonaLisa.[2] The final transition structures are validated by vibrational analysis and the proper connectivity by the intrinsic reaction coordinate (IRC) method. From the calculated diffusion barriers self-diffusion coefficients of water are derived.

Our results show that water diffusion barriers exhibit a non-monotonic dependence on the water content for different diffusion pathways. Upon addition of water, intrapore diffusion becomes slower, while interpore diffusion becomes faster. The former arises from the rigidity of water clusters at hydrophilic sites, where an established hydrogen bond network prevents water molecules from easily adapting to assist diffusion. In contrast, the latter is due to water-MOF interactions causing structural distortions in the MOF, which open interpore channels and promote diffusion along water chains.

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Water-Induced Linker Isomerization of MOF-303

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The metal organic framework MOF-303, consisting of Al(OH)(PZDC) units, where PZDC is 1-H-pyrazole-3,5-dicarboxylate, shows exceptional promise for atmospheric water harvesting. According to X-ray diffraction experiments, the pyrazole linkers in the framework undergo *trans*-to-*cis* isomerization as the loading with water increases.[1] Understanding this isomerization and its driving forces is not only crucial for accurate predictions of adsorption structures in MOF-303, but will also deepen our knowledge of MOF-water interactions in general.

We optimized the structures and compared the energies of both the *cis* and *trans* isomers of MOF-303 for loadings from 0 to 8 water molecules per asymmetric unit (asym. u.) using the PBE+D3 functional. We also calculated the barriers for the *trans*-to-*cis* isomerization reactions based on transition structures localized with the climbing image nudged elastic band (CI-NEB) method.

We show that filling the pores with water triggers the *trans*-to-*cis* isomerization in MOF-303 by changing the most stable form from *trans* to *cis*, which is accompanied by a lowering of the barriers for this reaction. In the bare MOF, *cis* and *trans* isomers are separated by a large barrier, with the *trans* isomer being more stable than the *cis* isomer by 24 kJ/mol per asym. u. At low water loading (1 to 6 water molecules per asym. u.) the energy difference remains within the range of 4 to 19 kJ/mol per asym. u. and displays a non-monotonic change, with the *trans* isomer remaining more stable. The stability order reverses upon adsorption of the 7th water molecule, rendering the *cis* isomer more stable than the *trans* isomer for the higher loadings of 7 and 8 H_2O per asym. u. This aligns with the experimental observations.[1]

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Temperature Dependence of the Methyl Group Dynamics of Ethanol in a Glycerol-Water Environment

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Methods which induce site-specificity and sensitivity enhancement in solid-state magic-angle spinning NMR spectroscopy become increasingly important for structural biology applications due to the size of the molecules under investigation. Recently, several strategies have been developed to improve site specificity and thus reduce signal overlap. Under dynamic nuclear polarization (DNP) for NMR signal enhancement, it is possible to use cross-relaxation transfer induced by select dynamic groups within the molecules which is exploited by SCREAM-DNP (Specific Cross Relaxation Enhancement by Active Motions under DNP).[1] Here ^{1}H DNP-based transfer with site-specific heteronuclear transfer is used, resulting in a fast build-up of polarization sufficiently distant to the radical and thus avoiding paramagnetic broadening.

Here, we study the dynamics of the methyl group using molecular dynamics (MD) simulations and *ab initio* calculations. As a model system, we have chosen ethanol in a glycerol-water environment, where both an undeuterated and a deuterated variant of ethanol have been investigated. Since SCREAM-DNP measurements are performed at low temperatures, it is especially relevant to understand the temperature dependence of these dynamics. Investigating the methyl group dynamics may lead to a better understanding of the mechanistic details of the polarization transfer, therefore enabling a more efficient application of SCREAM-DNP.

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Ab Initio Studies on the Location and Stability of Brønsted Acid Sites in zeolite H–MOR

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Acidic zeolites play a vital role in heterogeneous catalysis. Mordenite in its acidic form (H–MOR) is one of the most widely used catalysts for a variety of reactions. The acidity mainly derives from the presence of Brønsted acid sites (BAS). Knowledge about the location and stability of BAS is of critical importance when designing catalysts and optimising catalytic processes.

This study uses a chemically accurate (± 4kJ/mol) QM:QM embedding scheme (QM = quantum mechanics) to determine the relative stability of all possible BAS in H–MOR. Further, we predict IR and ^{1}H-NMR features for a set of most stable BAS and compare them with experimental spectra. Additionally, we investigate the amount and stability of H-bonded BAS.

We find that the predicted IR and ^{1}H-NMR features fall within the experimental full width at half maximum intervals of 3608 ± 21.4 cm^{-1} [2] and 4.3 ± 0.9 ppm. [3] We also find that although there are many possibilities for H-bonded BAS in H–MOR, they are energetically disfavoured compared to BAS that point into empty pore space, due to framework distortion involved in the formation of H-bonds. This is at variance with other zeolites such as H–MFI. Here, the most stable BAS also include H-bonded BAS, [4] clearly demonstrating a key difference in the zeolite frameworks.

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Transport and Storage

The Effect of Hydrogen on Model Lubricants from Multi-Phase Molecular Dynamics Simulations

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We study the effect of dissolved molecular hydrogen on a variety of linear alkanes acting as model lubricant systems exposed to a hydrogen atmosphere at elevated pressures. Single-phase and multi-phase molecular dynamics simulations are used to determine both the thermodynamic properties and the fluidity of the alkane-hydrogen mixtures under varying temperature and pressure conditions. Widom's particle insertion technique is employed to map out the free energy of solvation and to determine the solubility of molecular hydrogen in terms of the inverse Henry constant for those systems. Two-phase simulations are used to directly determine the hydrogen content as a function of pressure in addition to the interfacial properties of the alkane/hydrogen systems. The computed thermodynamic bulk and interfacial properties are found to be generally in good agreement with available experimental data. The recently introduced OrthoBoXY-technique [1-2] is employed to determine the viscosity of the hydrogen-containing alkane systems as well as the system-size independent self-diffusion coefficient of its constituents. A major observation is that the presence of dissolved hydrogen leads to a fluidisation of the lubricant, exactly counteracting the effect of the increased pressure of the hydrogen atmosphere.

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Program suit for modeling ion transport in solid electrolytes

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Significant progress in the understanding of ion transport in solid electrolytes, i.e. in glasses and polymers, has been reached in recent years by the analysis of spatial concentration profiles arising from chemical diffusion or electro-diffusion of charge carriers in such solids. There is a wide variety of transport experiments applicable, including classical diffusion experiments as well as the Charge Attachment induced Ion Transport (CAIT) technique and the Alkali Proton substitution (APS) technique [1,2,3]. Concentration depth profiles can e.g. be quantified by means of secondary ion mass spectrometry (SIMS). Here, the modeling of concentration depth profiles is based on the numerical solution of coupled Nernst-Planck and Poisson equations.

The program suit introduced here is capable of modeling concentration depth profiles from all transport experiments mentioned above. In the case of amorphous ionic solid materials the analysis yields concentration dependent diffusion coefficients reflecting the potential energy landscape of such materials [3,4,5].

The program suit is based on a python code that is capable to determine the concentration depth profiles based on a given concentration dependence of the diffusion coefficients with the help of an underlying Fortan95 simulation. The program package also provides information on the ion current and the local electrical potential. One pivotal input parameter is the number of electrodes, N, in contact with the sample. N is equal to 1 in a CAIT experiment, N is equal to 2 for an APS or an electro-poling experiment.

The program allows multiple instances to be started at the same time, which then run locally in the background. In addition, it includes evaluation routines that make it possible to display calculations graphically and compare them with experimental profiles.

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Temperature Dependence of Ionic Conductivity of Yttria-Stabilized Zirconia (YSZ) Crystals

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Yttria-Stabilized Zirconia (YSZ) is widely used for its ionic conductivity and its stability over a wide range of temperatures. YSZ has in particular high relevance as a key component in solid oxide fuel cells (SOFCs) [1]. This study investigates the temperature-dependent conductivity of YSZ crystals in the range of 25-450°C, using an electric field assisted proton introduction into a sample.

To this end the YSZ sample is sputter-coated with 100nm thin Pt layers on both sides. It is placed into Hydrogen and deuterium atmosphere at 200 mbar pressure. The setup is exposed to a potential gradient of typically 0 to 20 Volt. Two types of experiments have been conducted.

1. On a very short time scale (typically minutes), current voltage plots have been measured for a series of temperature between room temperature and 450°C. This allows determining the total electric conductivity of the samples. The results show that this conductivity exhibits a minimum around 90°C, implying that the conductivity increases with decreasing temperature below 90°C and increases above 90°C with increasing temperature. A similar observation has been reported by Kim et al. [2]. The current information suggests that the conductivity might be dominated by protons below 90°C but be dominated by oxygen anions above 90°C.
2. In addition to the short-term experiments, also long-term experiments have been conducted. Here, the electric field induced transport experiment is being conducted typically over a day or even longer. Subsequent to the transport experiment concentration profiles of the different constituents of the YSZ plus the externally offered ion are measured by means of time-of-flight secondary-ion-mass-spectrometry (ToF-SIMS).

In this contribution we will report on the current progress in measuring ionic conductivities of YSZ and concentration replacement profiles employing two different kinds of external ions. In one experiment we use protons or deuterons, generated from molecular hydrogen or deuterium at a thin platinum electrode [3]. In another experiment we plan to use oxygen anions generated in a fs-laser plasma experiments (similar to ref. [4]) as external foreign ions. This work sheds new light on the identification of charge carriers in energy conversion materials.

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Advancement of the Charge Attachment Induced Transport Technique

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The Charge Attachment induced Transport (CAIT) technique is based on bringing a solid electrically conducting sample in contact with a single metal electrode and shining a charge carrier beam at the opposite side, inducing a well-defined electrochemical surface potential and as a consequence charge carrier transport in the sample. One powerful aspect of this approach is associated with the ability to quantify potential energy landscapes of ion conducting solids as elaborated in the DFG research unit Energy Landscapes and Structure in Ion conducting Solids (ELSICS) [1, 2].

Here we report on current efforts to further advance the CAIT technique towards investigation of mixed ionic electronic conductors (MIECS). As the next step we describe the following series of experiments.

1. A Lithium-ion beam is shining at a pure Lithium-ion conductor, which is in contact with a platinum electrode at the backside. The current-voltage data are measured with focus on the x-axis intercept and the faradaic Lithium deposition between the sample and the metal electrode.

2. A Lithium-ion beam is shining at a pure electronic conductor leading to Lithium deposition at the front side of the sample.

3. An electron beam is shining at a MIEC (e.g. $LiCoO_2$ or $LiMn_2O_4$), which is in contact with a platinum electrode at the backside. Here attention is focused on Lithium deposition at the front side of the sample.

4. A Lithium-ion beam is shining at a MIEC in contact with a Pt electrode on the backside. Here, we expect to observe Lithium deposition both at the fronts side and at the backside (between sample and Pt electrode).

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Quantification of chemical replacement zones by means of ToF-SIMS, NRA and nanoindentation

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Chemical replacement zones in solid state materials have relevance in many fields of material science. The most powerful approach for generating such replacement zones is the electric field assisted ion exchange (EFAIE) which induces uni-directional transport in solids and allows to manipulate the physical properties of solid electrolytes, especially near the sample surface [1]. Native alkali cations such as Na^+ can, e.g., be exchanged by foreign cations introduced with, e.g., sputtered/molten electrodes [1, 2]. The ion exchange can lead to, among other things, chemical hardening, improvement of antimicrobial properties or the formation of waveguides structures [2, 3, 4].

In this contribution we demonstrate the formation of pronounced replacement zones, and the quantification of the replacement zones by three different techniques. The alkali deuteron substitution (ADS) is a special form of the EFAIE, where Deuterium is converted to D^+ ions at a thin platinum electrode. An electric field applied drives the D^+ ions into the sample and induce replacement of the native (and mobile) alkali ions. This technique is an adaptation of the alkali proton substitution technique firstly introduced by Omata et al. [5]. We have implemented a modified version of this in our group recently [6].

In this contribution, we present the results of an ADS experiment on an ion conducting D263T borosilicate glass, for which the native properties have been established before in a CAIT experiment [7]. As a result of the ADS experiment, the native Na^+ and K^+ are replaced by D^+ ions up to a depth of 2 micrometer from the surface. The replacement zones are quantified by means of ToF-SIMS, nanoindentation and Nuclear Reaction Analysis (NRA). We compare the quality of the results of the different techniques. Ultimately, all three techniques arrive at the same width of the replacement zone, however, with complementary information content.

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