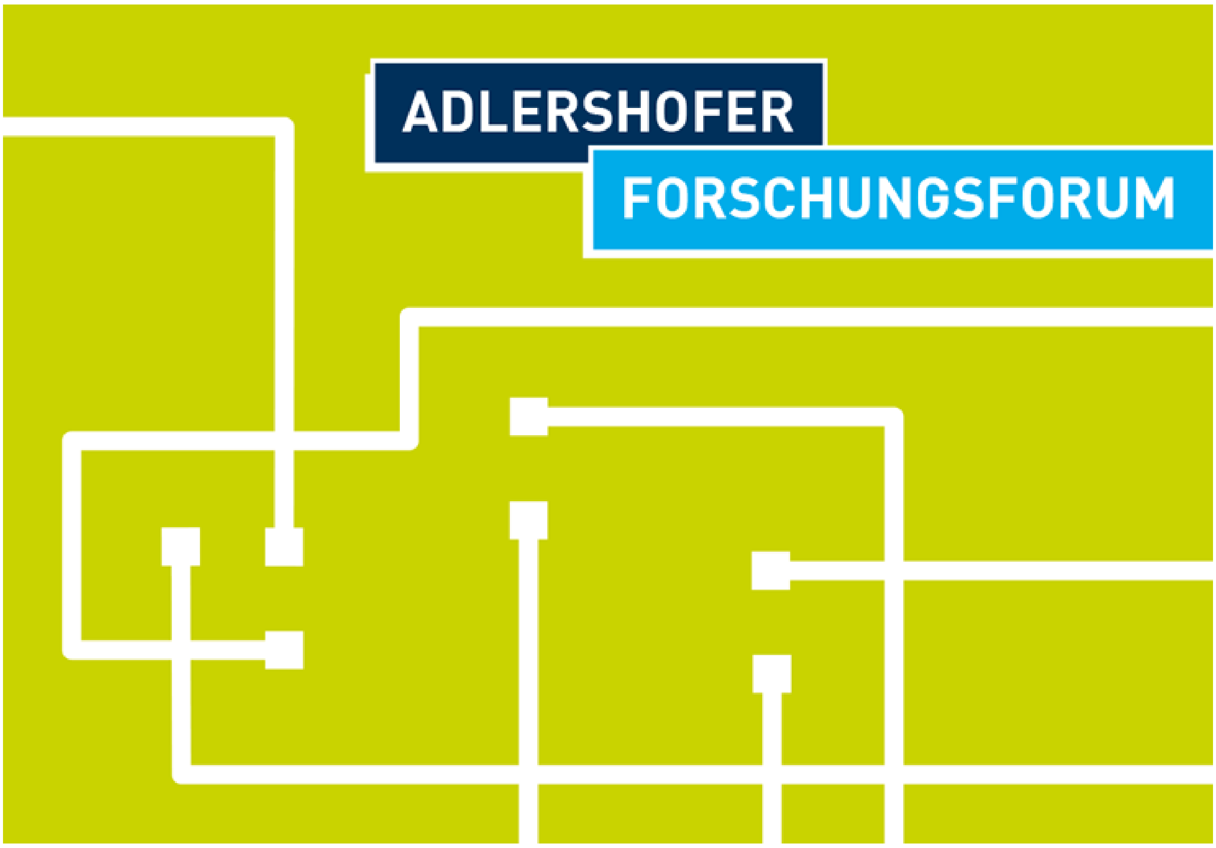

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ABSTRACTS ZUR POSTERSCHAU

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Redefining stable isotope analysis by molecular absorption spectrometry

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Variations in the isotope amount composition of some elements like lithium, boron, magnesium, calcium, copper and strontium have been used as proof of provenance of a sample and to describe geological processes. Routinely, isotope compositions are determinate by mass spectrometry; the working horse of the isotope analysis. However, mass spectrometric methods are expensive, time consuming and they require a high qualified analysist.

Here an alternative faster and low cost optical method for isotope ratio determination is proposed: high-resolution continuum source molecular absorption spectrometry (HR-CS-MAS). Stable isotope amount composition of X= Li, B, Mg, Ca, Cu and Sr have been determined by monitoring the absorption spectrum of their monohydride (XH) in graphite furnace HR-CS-MAS. For example, for the three Mg isotopes (^{24}Mg, ^{25}Mg and ^{26}Mg) band (0→0) for the electronic transition $X^1\Sigma+ \rightarrow A^1\Pi$ was evaluated around wavelength 513.4 nm (Fig. 1). Partial least square regression (PLS) for analysis of samples and reference materials were applied. For this, a spectral library with different isotopes ratios for PLS regression were built. Results are metrological compatible with those reported by mass spectrometric methods. [1,2]

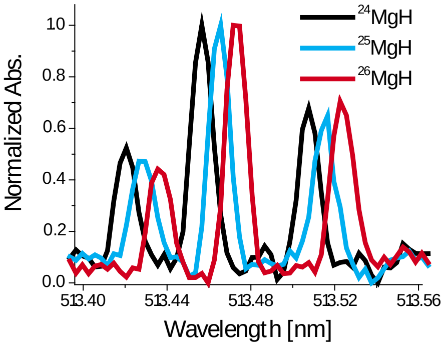

Fig.1. Comparison of the average spectra of ^{24}MgH (^{24}Mg relative isotope abundance 99%), ^{25}MgH (^{25}Mg 99 %) and ^{26}MgH (^{26}Mg 99 %) around wavelength 513.45 nm.

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In situ monitoring of mechanochemical syntheses of metal phosphonates

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Keywords: mechanochemistry, in situ, metal phosphonate, metal organic compound

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The exploration of metal phosphonates chemistry has gained great interest during the last decades, because of their structural diversity. Transition metal phosphonates are promising candidates for an application as electrocatalysts in oxygen reduction reactions (ORR).[1,2]
Here, we present the in situ investigation of mechanochemical syntheses of different metal phosphonates by synchrotron X-ray diffraction.[3] Nitrilotri(methylenephosphonic acid) and *N*,*N*-Bis(phosphonomethyl)glycine were chosen as ligands. The milling process can be divided into different steps. Some of the products have not been obtained by classical solution chemistry before.
These metal phosphonates and/or their derivatives are considered to be active in electrochemical energy conversion.[4] The verification of their applicability is one of the topics of our resent research.

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Electronic structure of intercalated MXene: towards next generation supercapacitor

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Abstract

MXenes are a new class of 2D materials consisting of transition metals carbides and nitrides that demonstrated extraordinary features for electrochemical energy storage.[1] However, the electronic structure and the mechanism leading to energy storage are largely unexplored so far.[2]

In this work, we have investigated MXene (Ti_3C_2) in water using soft X-ray absorption spectroscopy (XAS) at the O K-edge and Ti L-edge before and after urea intercalation. The samples were characterized not only as dried state in vacuum but also in aqueous dispersion solution using a flow cell system. Pure urea was compared as reference. For liquid samples, total fluorescence yield measurements have been performed whereas total electron fluorescence measurements were done for dry samples.

The impact of intercalation of urea molecules between the MXene planes as well as the effect of aqueous dispersion on their electronic structure will be discussed. In addition, correlation with the electrochemical properties of MXene-based supercapacitor, will be investigated.

This study provides new insights toward the understanding of MXene modification after urea intercalation. It demonstrates that XAS performed directly in aqueous media is a powerful method for the characterization of energy-related materials and future experiments related to *in operando* characterization of MXene-based supercapacitors will also be mentioned.

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Two-State Effective Potential Approximation for Time-Dependent ICD Simulations in Quantum Dots

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The electron dynamics of the interatomic Coulombic decay (ICD) between two singly-charged nanostructured semiconductors, i.e., quantum dots (QD), has accurately been described in a model based on the conduction-band effective-mass approximation, employing a properly antisymmetrized two-electron wave function, for which the TDSE is solved [1-3]. During ICD, an electronically excited QD relaxes through ionization of a neighboring QD. Since for large inter-QD distances the exchange part of the el.-el. interaction becomes negligible, the ICD dynamics may approximately be described via the dynamics of the electron in the ionized QD, while the two states of the relaxing QD are described by effective potentials. The coupling between the two states is expressed via transition Coulomb-interaction matrix elements. The ICD time scales and the directionality of the leaving electron obtained from the effective single electron dynamics were found to compare well to accurate results from two-electron dynamics for a variety of paired QD geometries. In the future, we want to apply the method to paired metal-nanoparticle - QD systems.

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Abstract for „Anonymous Communication over DNS“

Adlershofer Forschungsforum 2017

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Anonymous communication in the Internet is considered a solved problem since the advent of onion routing. Wide usage of the TOR protocol indicates that anonymity is in high demand in today‘s connected world.

In certain use cases, TOR‘s circuit establishment is quite expensive and constitutes a significant communication overhead. Also, the mandatory usage of TCP requires several round trip times of transmission until the actual content can be sent to its target.
For processing small amounts of data in both the request and its response we propose an anonymous communication system based on the domain name system (DNS). We evaluate the usage of UDP as transport protocol and show that existing concepts like DNS tunnels can be adapted to this use case. We also provide a proof of concept of our system in a real world scenario using public wifis for enhanced anonymity control.

Multiplex suspension array fluorescence immunoassay (SAFIA) for environmental screening of bioactive compounds in wastewater.

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Due to the demand of monitoring the water quality regarding emerging pollutants, such as drug residues, selective, high-throughput and multi-target analytical methods must be established. On the one hand, the influence of sewage on natural surface waters must be routinely monitored. On the other hand, estimation of removal efficiencies of pollutants, such as drug residues, is in the focus of industrial and public wastewater treatment. [1] Immunoassays, such as ELISA, offer the possibility to be highly sensitive and selective due to the high target affine and specific recognition of antibodies to target molecules. Batch-wise processing in microtiter plates allow the necessary high-throughput, but only a single analyte can be determined within one measurement.

To overcome these disadvantages, we developed a four-plex micro-bead based flow cytometric assay, which is adaptable for the microtiter plate format. The modular and self-prepared bead support consists of polystyrene-core-silica-shell particles. While the polystyrene core is used for encoding, by introducing different amounts of fluorescent dyes, the silica-shell creates a solid-support for the immunoassay: The target analytes, three drugs, carbamazepine, diclofenac and caffeine and the f ecal marker isolithocholic acid are covalently coupled to amino-groups on the surface via NHS-chemistry. A competitive immunoassay is subsequently conducted in a simple mix-and-read procedure. Finally, we could use SAFIA to assess the influent of treated and untreated waste water on the Douro river estuary in Portugal. The results of the analysis are comparable to ELISA. However, measurements could be carried out in 25% the time of analysis.

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Templated bilayer self-assembly of π-expanded macrocyclic oligothiophenes complexed with fullerenes.

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Three-dimensional (3D) self-assembly of molecular multilayer systems represents a major challenge towards engineering more complex molecular structures and functional devices. Fully conjugated π-expanded macrocyclic oligothiophenes exhibit a combination of highly attractive structural, optical and electronic properties, making them suitable for multifunctional molecular thin film architectures. A self-assembled monolayer of hydrogen-bonded trimesic acid at the interface between graphite and its heptanoic acid solution provided host-sites for the epitaxial ordering of Saturn-like complexes[1] of C_{60} with oligothiophene macrocycles in mono- and bilayers. Bias set-point imaging (STM tomography) verified the formation of the template layers and molecular dynamics simulation corroborated the conformational stability and helped to assign the most energetically favorable adsorption sites. Using scanning tunneling spectroscopy we could determine the rectification properties of the adlayers and showed the modification of the rectifying properties of the macrocycles by the formation of donor-acceptor complexes in a densely packed all-self-assembled supramolecular nanostructure.[2]

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2D-materials covering and replicating single dendronized macromolecules

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Abstract

Graphene can replicate the topography of a substrate with a precision down to single macromolecules [1]. Here we use this capability and investigate graphene and other 2D-materials for covering and replicating single macromolecules with increasing cross-sections. We deposited dendronized polymers (denpols) onto mica substrates and covered them with graphene oxides (GO), reduced graphene oxides (rGO), and graphenes. Denpols consist of a linear backbone surrounded by a cladding of structurally regular dendritic branches (dendrons), anchored to each repeat unit. The diameter of denpols can be systematically tuned by varying the dendron generation. The height of the molecular imprints in GO agrees well with the height of uncovered molecules. The height of molecular imprints in graphenes is smaller than the height of uncovered molecules with the difference growing with the dendron generation. First results for rGO indicate that the heights of molecular imprints in rGO are in between those for graphene and GO. We attribute the smaller heights under graphenes and rGO to a larger interaction between the sheets and the substrate, effectively squeezing the molecules, implying that it may be possible to measure the interaction forces between 2D sheets and substrates by using the macromolecules as force sensors.

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In situ monitoring of mechanochemical Knoevenagel condensations

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Keywords: in situ, C-C coupling, Knoevenagel condensation

Mechanochemical C-C bond forming reactions gained increasing interest in the past decades. The Knoevenagel condensation as a special Aldol condensation is an important reaction for synthesizing α,β-unsaturated compounds.[1]

Here, we present in situ investigations on the mechanochemical Knoevenagel condensation by combined X-ray diffraction and Raman spectroscopy.[2-4] The milling process was performed under solvent-less conditions.

The first crystalline product formation can be detected after 36 minutes, a complete conversion is reached after 50 minutes. Stopping the milling process after first indication of product reflexions still leads to a complete conversion. Both reactions result in highly crystalline material. The process can be described as a melt-mediated reaction since the aldehyde remains crystalline until the beginning of product formation, whereas the malononitrile melts during the milling process due to its low melting point.[3]

The information gained in this study lead to experiments with different benzaldehyde derivates.

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Estimation of the mean radiant temperature
within a street canyon using an urbanized regional climate model

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Abstract

Mean radiant temperature (Tmrt) strongly influences the thermal comfort of the human body during sunny weather. In this work, we study the effect of direct solar radiation and shadowing from it on Tmrt during the extreme heat event in 2003. To this end, we apply the regional climate model COSMO-CLM coupled with the urban parameterization scheme DCEP driven by ERA-Interim. We extend DCEP to that it calculates the Tmrt within a street canyon. In particular, we consider the human body as a box that is characterized by an emissivity of 0.97 and an albedo of 0.3, and that absorbs longwave and shortwave radiation from the sky and other surfaces. Mean radiant temperature is then defined as the uniform temperature of an assumed black-body surface around the human body yielding the same radiant heat transfer as in the actual case. In this study, we place the human body in different positions within a street canyon and compare the corresponding mean radiant temperatures.

Kristallzüchtung: Prozessentwicklung mithilfe der Lateral-Photovoltage-Scanning-Methode

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Die Kristallzüchtung in Adlershof hat eine lange Tradition. Jan Czochralski ließ hier 1916 seinen Federkiel versehentlich in ein Fass geschmolzenes Zinn gleiten und begründete damit eine neue Methode der Kristallzüchtung: dem Ziehen von Einkristallen aus der Schmelze. Erst diese Entwicklung ermöglichte den Computer im Alltag von jedermann. Mit der Weiterentwicklung diese Hochleistungselektronik wuchsen auch die Anforderungen an die Kristalle. Einen Ansatz hierzu liefert das IKZ indem es die Entwicklung von neuartigen Züchtungsmethoden vorantreibt. Gemeinsam haben alle Züchtungsmetho-den, dass Silicium verflüssigt und anschließend gerichtet erstarrt wird. Hierbei sind Simulationen der Temperatur in einem wachsenden Kristall Stand der Technik. Das Augenmerk liegt auf dem Designen der Isothermen $T = 1687\,\mathrm{K}$, bei der Silicium kristal-lisiert. Die einzige Methode um die Form dieser Isothermen in einem gewachsenen Kristall zu bestimmen, und somit einen Vergleich der Temperatursimulationen mit der realen Erstarrungsfront zulässt, ist die Lateral-Photovoltage-Scanning-(LPS)-Methode. Hierbei wird davon profitiert, dass die Kristalle minimale Schwankungen in der Dotierstoff-konzentration aufweisen. Dotierungen sind bewusste Verunreinigung mit Phosphor oder Bor um den elektrischen Widerstand des Kristalls manipulieren zu können. Das Ziel meiner Promotion ist es den physikalischen Effekt, den die LPS-Methode nutzt, zu simulieren um den Messaufbau weiter zu optimieren.

An einer simulierten Siliciumprobe wurde zunächst gezeigt, dass die detektierte elektrische Spannung proportional dem Dotierstoffunterschied ist, was dem Messprinzip entspricht. Nach dieser Validation des verwendeten Models konnte das Auflösungsvermögen der Messmethodik untersucht werden. Hierbei zeigte sich, dass eine Verbesserung der verwendeten Optik keine Verbesserung der Ortsauflösung zur Folge hätte. Stattdessen erhärten sich die Indizien, dass das Erwärmen einer Probe bei der Messung zu eine höheren Auflösung führe. Damit ließe sich die Form der Isothermen zukünftig präziser bestimmen und eine bessere Korrelation zu den Temperatursimulationen beobachten.

Silver Nanowires as Model Systems for Novel Applications in Nanooptics

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In this contribution, recent results and perspectives for the use of silver (Ag) nanowires (NWs) in nano-photonic experiments and applications are presented.

Ag NWs can be fabricated with ultimate quality through chemical synthesis resulting in crystalline Ag and consequently with lowest surface roughness and without grain boundaries.

Results are presented, showing that such a nanowire can be trapped freely levitating in air in a Paul trap which enables studying its optical response without disturbing effects from supporting structures.
Spectral resonance features are found. These analysis is combined with a post-analysis after trapping where one of the NWs has been landed onto a clean fiber facet. With an atomic force microscope, the shape of the NW specimen is determined with high precision. Finally, the optical response is modeled with a simple and well-fitting Fabry-Pérot model yielding overall a coherent analysis of spectra, shape and model.

The fact, that such simple NWs act as resonators which can be modeled with the easiest models motivates further work in which these NWs are envisioned as resonators for lasing and strong coupling. Recent results on these prospects are shown and discussed.

In situ investigations of a mechanochemical cocrystal formation by X-ray diffraction for two different milling jar materials

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Mechanochemistry has become a valuable method for the synthesis of new materials, especially for pharmaceutical cocrystals.[1] The Advantages of fast reactions in high purity and yield face a lack of understanding the underlying mechanism. Therefore, *in situ* setups to study mechanochemical reactions have been established.[2,3] Herein, we present an *in situ* investigation of the mechanochemical cocrystal formation of pyrazinamide (PZA) with pimelic acid (PM) using synchrotron XRD. Two new polymorphs of PZA:PM (1:1) were synthesized by milling the starting materials in milling jars of different materials. While Form I is only obtained using a steel jar, Form II can be obtained purely in jars made of Perspex. In situ XRD experiments reveal a direct formation of Form II in Perspex and an intermediate formation of Form II in steel jars converting to Form I upon further grinding. Heating experiments and DFT calculations predict that Form II is the thermodynamically more stable polymorph. Therefore, the reaction progress in the steel jar contradicts Ostwald's rules of stages[4] as the more stable Form II converts into the metastable Form I. Hence, mechanochemistry offers the possibility to synthesize new materials that cannot be obtained using conventional methods.[5]

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Insight into the wetting of a graphene-mica slit pore with a monolayer of water

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Scanning force microscopy (SFM) and Raman spectroscopy allow the unraveling of charge doping and strain effects upon wetting and dewetting of a graphene-mica slit pore with water.[1] Graphene-mica slit pores are prepared by mechanical exfoliation of graphite onto a freshly cleaved muscovite mica surface in dry nitrogen. SFM reveals a wetting monolayer of water, slightly thinner than a single layer of graphene. The Raman spectrum of the dry pore exhibits the D’ peak of graphene, which practically disappears upon wetting, and recurs when the water layer dewets the pore. Based on the 2D- and G-peak positions, the corresponding peak intensities, and the widths, we conclude that graphene on dry mica is charge-doped and variably strained. A monolayer of water in between graphene and mica removes the doping and reduces the strain. We attribute the D’ peak to direct contact of the graphene with the ionic mica surface in dry conditions, and we conclude that a complete monolayer of water wetting the slit pore decouples the graphene from the mica substrate both mechanically and electronically.

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Surface enhanced hyper-Raman scattering of biomolecules on silver nanostructures

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In the local optical fields of plasmonic nanostructures, many vibrational spectroscopic effects such as the incoherent, spontaneous Raman scattering or its nonlinear analogue hyper-Raman scattering can benefit from strong surface enhancement. Surface-enhanced hyper-Raman scattering (SEHRS) follows different selection rules and different enhancement mechanism compared to surface-enhanced Raman scattering (SERS), and thus it can provide complementary chemical and structural information about the molecule-nanostructure system under investigation [1, 2].

Here, we present SEHRS experiments at near-infrared excitation (1064 nm) for nucleic acid bases and aromatic amino acids with electronic transitions off-resonance with the laser wavelength. We compare the data with SERS spectra at 532 nm and discuss the observed variations in relative signal strengths of many molecular vibrations in terms of the different selection rules for the one- and two-photon excited Raman process. In particular, we investigated the influence of variation in pH and molecule concentration on the SEHRS and SERS spectra. The results support the high sensitivity of SEHRS spectra with respect to small environmental changes, and strongly suggest SEHRS as a tool to probe biomolecule-nanoparticle interactions.

Financial support from FCI (Chemiefonds Fellowship), ERC (Grant No. 259432), and DFG GSC 1013 (SALSA) is gratefully acknowledged.

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Strong Coupling between Surface Plasmon Polaritons and Molecular Vibrations

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The hybridization of different quasi-particles is an extensively studied subject; both from a practical as well as fundamental point of view. The resultant hybrid excitations exhibit new properties that are not available by the isolated constituents.

Here, we report on strong coupling of surface plasmon polaritons and molecular vibrations in an organic/inorganic plasmonic hybrid structure. The structure consists of a poly-vinyl-methyl-ketone layer deposited on top of a silver layer. Attenuated-total-reflection measurements in Kretschmann configuration reveal a clear anticrossing behavior in the dispersion relation in vicinity of the carbonyl stretching vibration of the polymer. The experimental spectra are nicely reproduced by transfer matrix calculations. A finite energy splitting of upper and lower polariton branch up to 14 meV is obtained and the dispersion relation is in good agreement with the numerical calculations.

This new hybrid state is not only interesting from a fundamental point-of-view but also of direct practical relevance. Recently, it has been demonstrated that hybridization of microcavity photons and molecular vibrations in organic compounds offers the possibility to modify chemical reaction rates [1, 2]. By coupling to SPPs instead of microcavity photons, this approach can be transferred into a large-area and geometrically simple setting.

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GISAXS on small sample volumes using large beams

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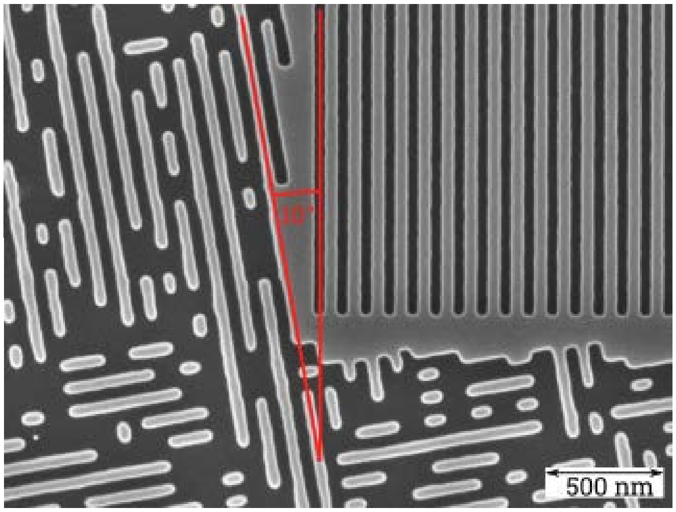
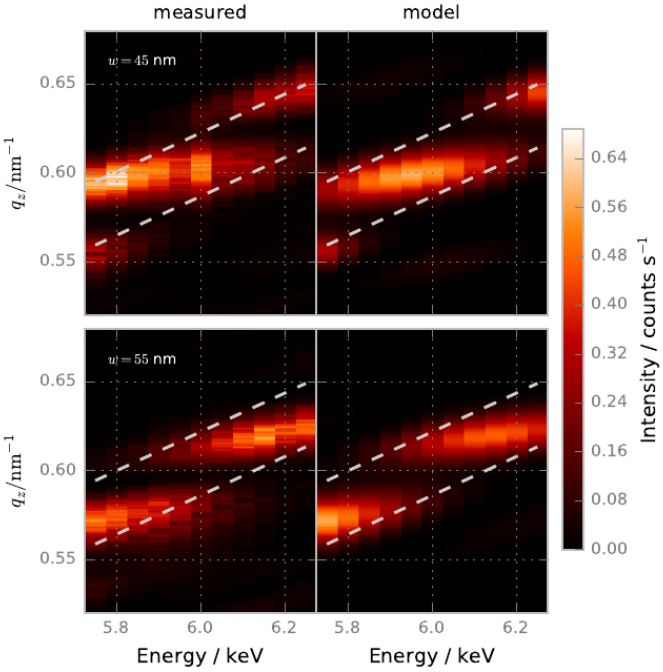
Grazing-incidence small-angle X-ray scattering (GISAXS) is often used as a versatile tool for the contactless and destruction-free investigation of nano-structured surfaces. However, due to the shallow incidence angles, the footprint of the X-ray beam is significantly elongated, limiting GISAXS to samples with typical target lengths of several millimetres. For many potential applications, the production of large target areas is impractical, and the targets are surrounded by structured areas. Because the beam footprint is larger than the targets, the surrounding structures contribute parasitic scattering, burying the target signal.





In this poster, we present GISAXS measurements of isolated as well as surrounded grating targets in Si substrates with line lengths from 50 mm down to 4 mm. For the isolated grating targets, we explain the changes in the scattering patterns due to the reduced target length. For the surrounded grating targets, the scattering signal of a 15 mm x 15 mm target grating structure is separated from the scattering signal of 100 mm x 100 mm nanostructured surroundings by producing the target with a different orientation with respect to the predominant direction of the surrounding structures. As virtually all lithographically produced nanostructures have a predominant direction, the described technique allows GISAXS to be applied in a range of applications, e.g. for characterization of metrology fields in the semiconductor industry, where up to now it has been considered impossible to use this method due to the large beam footprint.

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Studies on the Effect of Nanoparticles on Laser Ablation Processes

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Abstract. Laser Induced Breakdown Spectroscopy (LIBS) is an analytical technique based on the emission by atoms in local thermal equilibrium, inside a plasma created, after the interaction between a sample and a laser. Thanks to some of its characteristics, like straightforward or no sample preparation, simple set-up and high sensitivity, its use and interest has spread widely in the industrial and academic sectors. Starting from the research of De Giacomo et al. [1], the aim of this work was to increase our knowledge about Nanoparticle-Enhanced LIBS (NELIBS), a modified version that results in an amplified signal when metal NPs are deposited on the specimen.

While the first part of the work was concerned with the study of the increase in sensitivity by comparing calibration curves for the same element obtained with both LIBS and NELIBS, the second part of the work was focused on having a more profound insight in the differences of the plasmas created by the two different techniques. This was achieved by applying for the first time a numerical algorithm, called Abel Inversion [2], to imaging measurements made on the whole plasma plume or on single atomic lines. This approach was then transferred to 3D images with information about emissivity in every point of the image, giving us the chance to evaluate the emitting distribution in the whole plasma body. By analysing different temporal frames we could study the plasma evolution in detail, confirming the initial hypotheses that plasmas from NELIBS experiments appear brighter and wider. However, the latter do not seem to be the only decisive parameter for the observed enhancement phenomenon.

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Growth and mechanical properties of a monomolecular layer of water wetting a flexible quasi-2D graphene-mica slit pore – fluid or ice-like?

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Graphene deposited onto atomically flat muscovite mica makes a flexible, yet impermeable slit pore[1]. Water molecules can move in and out of the slit pore through the edges, with the graphene conforming to the water layer. Its topography can be detected with sub-Angstrom vertical resolution using Scanning Force Microscopy (SFM)[2]. It has been argued that water in the slit pore exists in highly ordered ice structure[3]. In this work, we follow the monomolecularly thick layer of water as it wets the slit pore. Wetting propagates from edges as finger like water islands of irregular shapes. Additionally, nano-indentation maps reveal that at constant indentation forces monomolecularly thick water islands exhibit marked differences in deformability. We suggest that this variation in mechanical properties maybe due to a variation in the packing density of water molecules within individual islands. On a soft island the SFM tip can indent deeper by pushing the mobile water molecules away from the indentation spot. The difference in the lateral density suggests that during wetting, water can exist in a fluid-like state in the slit pore.

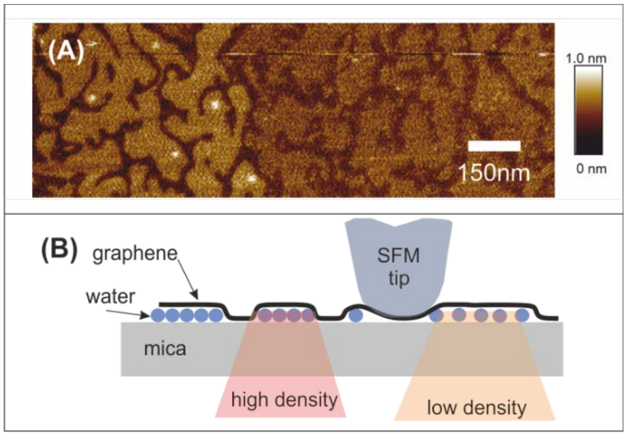

Fig. ***(A)*** *SFM topography image of a partially filled graphene-mica slit. Layers of monomolecularly thick water under a single graphene layer are visible as irregularly shaped islands separated by thin channels. Right half of the image shows domains of lower heights compared to domains in left half.* ***(B)*** *Schematic representation of a possible explanation for the difference in deformability of the islands. At constant indentation force the tip indents low density islands more than high density islands.*

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Development of a Quick Test to Screen for Bisphenol A Release from Polymer Materials

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Bisphenol A (BPA) is a common industrial chemical that is widely used as a monomer or additive in the production of polymer materials. This substance causes impairment of the childbearing function, acceleration of sexual aging, negatively impacts the brain, and also contributes to the development of certain oncological diseases, as well as increasing the risk of a fetus developing the Down syndrome. But the biggest downside of bisphenol is the fact that it accumulates in the system during its use, as well as after[1]. Many methods have been proposed for the determination of BPA, in particular gas and liquid chromatography[2-3]. The main disadvantages of such approaches are the high cost of the equipment, the significant duration of an analysis, and difficulties in screening a large number of samples. Immunoanalytical techniques' attributes are high throughput, high specificity and sensitivity, as well as low cost and simplicity. Particularly interesting as a quick test for screenings is the lateral flow immunoassay (LFIA), a format widely in use for the detection of pregnancy[4]. LFIA for BPA have been described before, but lack sensitivity[5] .

In this work, the focus was on the decoration efficiency (by passive adsorption)[6] of monoclonal antibodies on 40 nm gold nanoparticles. Using spectral methods, it could be shown that adding 10% NaCl induced gold nanoparticle aggregation. Consequently, nanoparticles should be labeled with antibody under optimal pH value and antibody concentration. Additionally, stability of the antibody layer has to be assessed in view of the determination of bisphenol A in matrices like water from different sources, leachates and extracts.

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Determination of plant essential nutrients in soils using DP-LIBS

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LIBS (laser-induced breakdown spectroscopy) is known as a fast and simultaneous multi-element analysis with little or no sample preparation. In the last few years there has been a growing interest in applications of LIBS in the field of agriculture. As part of the National Research Strategy BioEconomy 2030 the German Federal Ministry of Education and Research (BMBF) started an innovation programme called BonaRes. BonaRes consists of ten interdisciplinary research project associations which are dealing with soil as a sustainable resource for the bio-economy. One of these research projects is I4S (intelligence for soil) which has the goal to develop an integrated system for site-specific soil fertility management. This system includes a sensor platform, which contains different sensors, like XRF, VIS-NIR, Gamma and LIBS. The main task of LIBS measurements in this project is the real time determination of the elemental contents of nutrients in soils, like calcium, magnesium, potassium. For this purpose, a special setup has been designed. The sample uptake operates with the help of a rotatable sample plate which circulates with different velocities to simulate the application on the field. To provide a higher intensity and a better reproducibility of the obtained signal, a double-pulse Nd:YAG laser (λ = 1064 nm) was used. In order to minimize dust formation from the soil during the operation of the laser, a dust removal by suction has been integrated.[1] When using relative methods such as LIBS, a suitable calibration curve is needed for absolute quantification. With the help of 16 certified reference soils, calibration curves for different elements were initially calculated and used for the quantification of seven soil samples from different testing grounds in Germany. The complex matrix of soils, as well as the influence of moisture and grain size in soils makes the absolute quantification by LIBS challenging. To overcome these influences, a calibration curve based on multivariate analysis (partial least square regression) was generated.

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Coupling a Single Nitrogen-Vacancy Center in Nanodiamond to Superparamagnetic Nanoparticles

(Nikola Sadzak, Martin Héritier and Oliver Benson)

Single Nitrogen-Vacancy (NV) defect centers in diamond have been exploited as single photon sources and spin qubits due to their room-temperature robust quantum light emission and long electron spin coherence times. They were coupled to a manifold of structures, such as optical cavities, plasmonic waveguides, and even injected into living cells to study fundamental interactions of various nature at the nanoscale. Of particular interest are applications of NVs as quantum sensors for local nanomagnetometry. Here, we employ a nano-manipulation approach to couple a single NV center in a nanodiamond to a single few-nm superparamagnetic iron oxide nanoparticle in a controlled way. After measuring via relaxometry the magnetic particle spin-noise, we take advantage of the ground state spin level separation to detect the superparamagnetic particles in presence of a driving AC magnetic field. Our experiments provide detailed insight in the behavior of such particles with respect to high frequency fields. The approach can be extended to the investigation of increasingly complex, but controlled nanomagnetic hybrid particle assemblies. Moreover, our results suggest that superparamagnetic nanoparticles can amplify local magnetic interactions in order to improve the sensitivity of diamond nanosensors for specific measurement scenarios.

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Title: Trees as Indicators of the Urban Heat Island (UHI)

Abstract: The project BIWi (trees as indicators of the UHI) investigates different tree-ring parameters (tree-ring width, pointer year catalogs, wood anatomical features) in Berlin. About 150 trees from 12 urban-ecologically different sites are analyzed. In Germany, Berlin is the city with the most pronounced UHI. The project's goal is to attribute specific growth features to effects of the UHI.

Established techniques of measurement and data processing in dendroecology are used. Applied are time series analysis such as correlation and regression analysis, principal component analysis and extreme year's statistics. A set of methods useful and applicable for urban areas are being developed. The approach aims at determining and prioritizing the growth factors for mean climatic and extreme weather conditions (dry seasons, heat waves, smog) at different sites. For this purpose, tree-ring chronologies as well as catalogs addressing extreme growth reactions and specific wood anatomical features (frost rings, density fluctuations, etc.) are compiled.

The effects of the UHI will be identified by comparing tree-ring patterns and climate-growth correlations at urban sites in Berlin with those at rural sites in Köpenick and at Telegrafenberg in Potsdam. In addition to the analysis of urban tree species (*Acer*, *Tilia,* etc.) the differentiating process particularly also requires the analysis of basic forest tree species such as *Quercus*, *Fagus* or *Pinus* to prevent the identified urban-rural diversities from being blurred by species-specific differences.

The ultimate aim is to develop a general procedure investigating the spatial distribution and spatio-temporal evolution of UHIs using dendroclimatological data. The poster shows the sampling approach, the data processing, and preliminary results.

Investigating nano-structured surfaces with grazing incidence soft X-ray fluorescence combined with a Maxwell solver based on finite-elements

Victor Soltwisch, Philipp Hönicke, Yves Kayser, Janis Eilbracht, Jürgen Probst, Frank Scholze and Burkhard Beckhoff

A lamellar Si3N4 grating produced with e-beam lithography was experimentally investigated with reference-free grazing incidence X-ray fluorescence analysis (GIXRF) and theoretical evaluated with the finite-element method. While simulations based on the matrix formalism allow investigating simple layered systems, this approach will fail if a periodic 3D structure, e.g. a grating is present. In this case the interference due to the periodic arrangement must be taken into account in the modeling. Maxwell solvers based on finite-elements are ideally suited for modeling of electric field intensities for any arbitrary 2D or 3D structure. This allows for the simulation of induced fluorescence intensities by integrating field intensities in specific regions in the computational domain. We will validate this approach by comparison to experimental GIXRF measurements obtained from a layer system in order to demonstrate that this approach is able to deliver a reconstruction of the geometrical line shape of a structured surface with a high sensitivity. This combined toolset of GIXRF and finite-element simulations paves the way for a versatile characterization of nanoscale 3D structured surfaces.

Novel thermographic methods using structured laser-based illumination

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Photothermal imaging is commonly used for the characterization of material properties, the determination of layer thicknesses or the detection of inhomogeneities such as voids or cracks. For this purpose, the solid specimen is externally heated, e.g. by using a light source. The resulting transient heat flows interact with the inner structures of the specimen, which in turn is measured as a transient temperature distribution at the surface.

Novel array-shaped, high-power laser light sources allow to control the heating of the surface arbitrarily, both temporally and spatially. This enables us to shape the heat flows within the material in a very specific way. In a first application, we demonstrate how to apply destructively interfering thermal wave fields in order to detect subsurface defects with a very high sensitivity. A similar technique, although originating from a very different physical domain, is already in use for medical 3D imaging showing the high potential of this approach.

Application of fluoride nanoparticles in wood protection

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Alkaline earth metal fluoride nanoparticles have been investigated for application in wood protection. Sols of MgF_2 and CaF_2 were synthesized and their efficacy was tested against fungi and termites. The sols were characterized by XRD and SEM. The wood specimens were vacuum impregnated with nanoparticles and then exposed to fungi and termites according to EU certified test conditions. Our results show that wood impregnated with metal fluoride nanoparticles significantly reduce cellulose hydrolysis by fungi and termites. The wood samples were exposed to brown rot fungi; *Coniophora puteana* and *Poria placenta*. Between the two fungi, the overall mass lost due to fungal degradation was lower for treated (MgF_2 and CaF_2) wood samples exposed to *Coniophora puteana*. Thus, the metal fluoride nanoparticles impregnated in the wood samples were more efficient in reducing cellulose degradation from *Coniophora puteana* than from *Poria placenta*. However the mass loss in samples treated with MgF_2 was similar to those treated with CaF_2, irrespective of type of fungi. Therefore, it is likely that fungal degradation in treated samples was dependent on the biocidal action of fluorides rather than on the differences in chemical and physical properties of MgF_2 and CaF_2, respectively. Conversely, for termite exposure, wood samples treated with MgF_2 had lower mass loss compared to those treated with CaF_2. A possible explanation for this difference in results could be fungi and termites use separate mechanisms for cellulose hydrolysis which will be further investigated. Future experiments include testing the leaching potential of MgF_2 and CaF_2 nanoparticles from wood. The results from the leaching experiment will test if metal fluoride nanoparticles can provide long term and environmentally safe protection to wood.

Urban Mobile Instruments for Environmental Monitoring URBMOBI 3.0

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Urban climate research is primarily based on point or location-based measurements of climate and air quality data. With the development and implementation of the third generation of an urban mobile measurement device, abbreviated as URBMOBI 3.0, we aim to amend this scenario. The URBMOBI 3.0 is a relatively small sensor unit equipped with micro-sensors for measuring the following meteorological parameters: temperature, relative humidity, and solar radiation. Additionally it measures ambient air pollutant concentrations of particulate matter (PM) from 0.30 to 17 µm with a typical flow rate of 1.2L/min, nitrogen dioxide (NO_2), nitrogen oxide (NO), and ozone (O_3) up to 20 ppm. Geo tagging of the measured data is enabled via a Global Positioning system (GPS) device and the acquired data is stored in a built in SD card. It is expected that by 2018 vehicles such as trams, buses and/or cars will be mounted with URBMOBI 3.0 prototype devices in order to measure climate and air quality data at high spatial and temporal resolutions (2 sec). These measurements can then take place on a regular basis, where conventional measurements systems are not built up or cannot be set up. Urban climate models and simulation tools will be fed with the acquired data, which in turn may provide a better understanding of the status and reasons of existing urban climate conditions. This will provide an opportunity to improve the urban climate by providing tools for enhanced city planning and air quality management. A high temporally and spatially resolved data set over a longer period will be of major importance for validation, testing and usage when microscale climate models and other simulation tools come into being.

Speeding up microplastics analysis with modern NIR spectroscopy

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Annually vast amounts of plastics are produced world-wide. However, recycling and waste management is still insufficient resulting in large quantities of plastics being released into the environment. By convention plastic fragments smaller than 5 mm are referred to as microplastics (MP). The occurrence of MP has been reported by researchers virtually all around the globe. Gaining knowledge on MP is currently a time-consuming process because analysis mainly relies on micro-infrared [1,2] and micro-Raman [3] methods. Prior to that the particles need to undergo purification and enrichment. Thus, only small numbers and volumes of samples can be investigated. Here we tested NIR spectroscopy combined with a multivariate data analysis as a means of speeding up the process of MP analysis.

Experiments were performed using the most abundant polymers polyethylene, polypropylene, polyethylene terephthalate and polystyrene. MP samples were obtained by adding the cryomilled and sieved (<125 µm) particles to approximately 1 g of standard soil at 0,5–10 mass%. Spectra were recorded with a fiber optic reflection probe connected to a FT-NIR spectrometer. 5–10 spectra recorded of each sample were used for the calibration of chemometric models (partial least squares regression, PLSR). “Unknown” test samples were then used to test the model’s capability to predict the type and amount of polymer.

In samples containing 1–5 % of the polymers the prediction yielded the highest degree of agreement with the gravimetric reference values. At low polymer loads some false positive results in the identification were observed. Large amounts of polymers limited the prediction capability by a nonlinear behaviour of the absorption. Further testing was done with real world samples such as compost and washing machine filters. Even though the calibration did not account for these highly complex sample compositions, satisfactory results could be achieved.

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In-situ and operando X-ray absorption spectrometry of new liquid and solid battery materials

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The complete understanding of the functionality of battery components requires the correlation with underlying physical and chemical properties which is the challenge for most analytical methods due to a lack of reference materials. For this purpose, PTB implemented physically traceable methods based on X-ray spectrometry.

Lithium Sulfur (Li-S) batteries are promising candidates for improved batteries offering up to 5 times higher capacity than conventional lithium ion batteries. For a better understanding of battery degradation processes in-situ and operando characterization techniques are required [1]. By means of operando near sulfur K-edge X-ray absorption spectrometry recorded during galvanostatic cycling with potential limitation (GCPL) measurements we could determine the different sulfur species for 8 cycles of a Li-S battery with DOL/DME (1:1 wt.%) 1 Mol TFSI electrolyte. In particular, the formation of polysulfides could be revealed. We used CR-2032 coin cell formed Li-S batteries modified with thin windows enabling the transmission of excitation and fluorescence radiation. Traceable X-ray spectrometric measurements were performed using radiometrically calibrated instrumentation in the PTB laboratory at BESSY II synchrotron radiation facility. While for the first cycles the polysulfides convert almost entirely we see for further cycles a permanent appearance.

NCM (nickel, cobalt, manganese) based Lithium-Ion batteries (LIBs) are well working systems and under steady development. Some degradation processes of the cathode result in the deposition of manganese at the separator and the graphite anode. With reference-free X-ray fluorescence spectrometry we can quantify the mass deposition of manganese on the anode and the separator. With additional manganese K-edge and L-edge NEXAFS we also can conclude to the present species of manganese.

To investigate fluid systems such as electrolyte solutions we designed in collaboration with TU Berlin a fluid cell with a 150 nm thin silicon nitride entrance window that enables soft X-ray studies to probe even light elements such as fluorine. With fluorine K-edge NEXAFS of the electrolyte solution in the fluid cell we can investigate the different behavior of Ionic Liquids in the present of lithium hexafluorophosphate.

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Combined surface-enhanced hyper-Raman and surface-enhanced Raman spectra of tricyclic antidepressants using gold and silver nanostructures

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Tricyclic antidepressants (TCA) are an interesting group of molecules because of the many functions they can have. In therapy of a range of diseases, they can be used by different ways of interaction with the molecular constituents of different cell types. However, the molecular interaction of TCA with different bioorganic molecules and cells must be elucidated.

Vibrational spectroscopy is an ideal tool for studying the interaction of drug molecules in biological environments. Specifically, surface-enhanced hyper-Raman scattering (SEHRS), the spontaneous, non-coherent two-photon analogue of surface-enhanced Raman scattering (SERS) has been shown to be particularly sensitive to the interaction of molecules with surfaces and cells. SEHRS spectra of several organic compounds as well as of complex biological materials such as cells are known and suggest micro-probing of native, non-labeled organic structures and materials.[1] SERS spectra of some tricyclic antidepressants obtained with silver nanoparticles have been reported and suggested a way for detection of the molecules.[2]

We will discuss the SERS spectra of desipramine, imipramine, and amitryptiline using biocompatible gold nanostructures, as well as different types of silver nanoparticles and combine them with two-photon excited SEHRS spectra of the molecules, thereby providing a very comprehensive vibrational characterization of the nanoparticle-drug interactions. The data were obtained in different model environments, e.g., in the presence of other biological molecules, under varied antidepressant concentration, and at different pH. All measurements were carried out in aqueous solutions containing nanoparticles, the drug molecules, and potential additional bioorganic compounds.

The combined SEHRS and SERS data indicate that the molecules interact with the silver nanostructure mainly via their ring moiety. In contrast, in the interaction with gold, the methylaminopropyl side chain plays a very important role, together with parts of the ring system.[3] Understanding the interaction of the drugs with the surface of gold and silver nanostructures will have implications for drug delivery and for investigations of drug-biomolecule interactions.

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