

SCHLOSS RINGBERG

May 18 to 21, 2014

Symposium on Dynamics at Surfaces



Sunday May 18 th	
16:00-18:00	Arrival and registration
18:00-19:30	Dinner
19:30-20:00	Prof. Alec Wodtke (Göttingen): <i>Welcoming Remarks and Overview.</i>
20:00-21:00	Prof. Xueming Yang (Dalian): <i>Fundamental processes in photocatalysis of methanol and water on TiO₂(110).</i>
21:00-	Poster Session I
Monday May 19 th	
8:00-9:00	Breakfast
<i>Session Chair: Dr. Tim Schäfer</i>	
9:00-10:00	Henrik Haak (Berlin): <i>Design of scientific instruments for experiments in molecular physics.</i>
10:00-10:30	Coffee Break
10:30-11:00	Dan Engelhart (Göttingen): <i>Controlling electron transfer on the atomic scale</i>
11:00-11:30	Kai Golibrzuch (Göttingen): <i>Real-time kinetics from 2D-TOF experiments: A new method for determination of binding energies with high accuracy and application to CO/Pt(111).</i>
11:30-12:00	Prof. Theo Kitsopoulos (Göttingen): <i>Photodissociation of N₂O at 203.5 nm.</i>
12:00-13:30	Lunch Break
<i>Session Chair: Prof. Dirk Schwarzer</i>	
13:30-14:00	Dr. Christoph Bartels (Göttingen): <i>Electron-mediated vibrational energy transfer in NO/Au(111) collisions: comparison of experiment and theory.</i>
14:00-14:30	Dr. Monika Grütter (Göttingen): <i>Inelastic scattering of benzene from Au(111).</i>
14:30-15:00	Dr. Quan Shuai (Göttingen): <i>Preliminary results of D₂ recombination on Au(111) surface</i>
15:00-18:00	Free time
18:00-20:00	Dinner
20:00-21:00	Prof. Beatriz Roldan Cuenya (Bochum): <i>Nanocatalysis: The Shape of Things to Come.</i>
21:00-	Poster Session II

Tuesday May 20 th	
8:00-9:00	Breakfast
<i>Session Chair: Dr. Sascha Kandratsenka</i>	
9:00-10:00	Prof. Arthur Suits (Detroit): <i>Probing Spin-Polarized Hydrogen Atoms with the High-n Rydberg Time-of-Flight Technique</i>
10:00-10:30	Coffee Break
10:30-11:00	Dr. Oliver Bünermann (Göttingen): <i>Inelastic Hydrogen Atom Scattering: Importance of Electron-Hole-Pair Excitations</i>
11:00-11:30	Svenja Janke (Göttingen): <i>H at Au(111): A Potential Energy Surface.</i>
11:30-12:00	Sven Kaufmann (Göttingen): <i>Generation of ultra-short H-atom pulses: A new tool for time-resolved dynamics</i>
12:00-13:30	Lunch Break
<i>Session Chair: Prof. Theo Kitsopoulos</i>	
13:30-14:00	Nils Bartels (Göttingen): <i>Electron-mediated vibrational energy transfer in NO/Au(111) collisions: comparison of experiment and theory.</i>
14:00-14:30	Dr. Pranav R. Shirhatti (Göttingen): <i>CO ($\nu = 0$) scattering from Au(111): Incidence energy dependence of the CO ($\nu = 0-1$) vibration excitation probability.</i>
14:30-15:00	Dr. Li Chen (Göttingen): <i>Phase II: Laser-induced fluorescence spectroscopy of overlayer and monolayer CO/NaCl(100): overtone excitation ($\nu=0 \rightarrow 2$)</i>
15:00-18:00	Free time
18:00-20:00	Dinner
20:00-21:00	Prof. Wolfgang Harbich (Lausanne): <i>Supported metal clusters with a precise number of atoms: stability, optical properties and chemical reactivity</i>
21:00-	Poster Session III
Wednesday May 21 st	
8:00-9:00	Breakfast
<i>Session Chair: Dr. Christof Bartels</i>	
9:00-10:00	Prof. Gerhard Meyer (Zürich): <i>Scanning probe microscopy of atoms/molecules on insulating films: Structure determination and imaging the charge distribution within single molecules</i>
10:00-10:30	Coffee Break

10:30-11:00	Christoph Steinsiek (Göttingen): <i>Towards Molecular Beam Scattering from Ultrathin Metallic Films Growth and Characterization of Ag on Au(111)</i>
11:00-11:30	Dr. Dan. Harding (Göttingen): <i>Beamer II - an advanced machine for surface scattering experiments</i>
11:30-12:00	Dr. Hak Ki Yu (Göttingen): <i>Graphene growth on epitaxial Cu film</i>
12:00-12:15	Prof. Alec Wodtke: <i>Closing Remarks</i>
12:15-13:30	Lunch Break
14:00	Departure

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"Welcome! Today's topic is 'How To Give A Presentation Without Losing Your Audience's Attention'. The End. Thank you for coming."

SPEAKERS' ABSTRACTS

Fundamental Processes in Photocatalysis of Methanol and Water on TiO₂(110)

Xueming Yang

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Heterogeneous photocatalysis is a very important area of research and has received great attentions from chemists, physicists as well as material scientists because of its important applications in energy and environmental sciences and technologies. For many years, surface photocatalysis was viewed as an electron or hole driven event. However, the detailed physical picture of how a specific surface photocatalytic reaction takes place remains unclarified. During the last few years, we have developed a series of new experimental tools (2PPE, TOF-TPD and STM) in our laboratory in effort to study photocatalysis of methanol and water on TiO₂(110) under well defined experimental conditions, and try to understand the fundamental processes of photocatalysis of methanol and water on TiO₂. Using these techniques in combination with laser-surface photocatalysis, we have clarified the fundamental processes of photocatalysis of methanol and water on TiO₂(110). Very interesting experimental results were obtained. For example, we have shown clearly the methanol photocatalysis on TiO₂(110) proceeds in a number elementary steps that can be understood using a ground state reaction picture. Photocatalytic reaction intermediate of methanol photocatalysis on TiO₂(110) has also been observed using high resolution STM. In addition, we have also observed strong photon energy effect on photocatalysis of both methanol and water. Experimental results also show that photocatalysis dissociation of water behaves very differently methanol photocatalysis. These results provide important insights on the dynamics of surface photocatalysis.

Design of scientific instruments for experiments in molecular physics

Henrik Haak

Department of Molecular Physics

Fritz Haber Institute of the Max Planck Society, Berlin, Germany

For novel experiments in science, and molecular physics in particular, specific and complex instruments are required which often cannot be purchased in the market place. Here I describe the technical design and construction of a variety of instruments and related equipment for the deceleration, trapping and analysis of cold molecules. I will explain how 3D computer-aided design (CAD) and finite element methods are used, for example in optimizing Stark decelerators and molecular beam guides, and how the parameter space, e.g. field strength limits, can be expanded. Several projects with their specific problems and solutions are presented.

Controlling electron transfer on the atomic scale

Dan Engelhart

*Georg-August-Universität Göttingen,, Institut für Physikalische Chemie,
Tammannstr. 6, 37077 Göttingen, Germany*

We report measurements of the electron emission probability for electronically excited CO ($a^3\Pi$) scattered from a Au(111) crystal decorated with adsorbed of Ar, Kr, and Xe. Adsorbed layers of each noble gas lead to a significant increase in the electron emission probability. This enhancement is clear evidence that the electronic emission is not a result of an Auger de-excitation process and is consistent with a resonant charge transfer model. For monolayer coverage, electron emission enhancement increases with larger Van der Waals radii of the molecules. Adsorbate induced work function changes do not explain the magnitude of the electron emission enhancement and we suggest that the process leading to electron escape into vacuum depends strongly on distance from the surface during the electron transfer process.

Real-time kinetics from 2D-TOF experiments: A new method for determination of binding energies with high accuracy and application to CO/Pt(111)

Kai Golibrzuch

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The knowledge of binding energies in molecules is a key parameter in chemical transformation. It determines the likelihood to break a specific bond and to form a new bond with another compound of the reaction. The determination of binding energies between molecules and are often determined using temperature-programmed desorption (TPD) at various heating rates and investigating the shape and the peak position in the TPD spectrum. We developed a new approach for the determination of surface temperature dependent rate constants with high accuracy from which we can finally determine the desorption energy E_d and the frequency factor ν . We used a two-dimensional state-to-state time-of-flight technique (2D-TOF) to measure the desorption kinetics CO/Pt(111) in real-time with microsecond resolution. The results are analyzed within a simple kinetic rate model as well as compared to previous studies in this system.

Photodissociation of N₂O at 203.5 nm

Theo Kitsopoulos

Max-Planck-Institut für biophysikalische Chemie, 37070 Göttingen, Germany

I will present our new photofragment/photoelectron imaging spectrometer, which allows for spatial imaging (original ion imaging), velocity mapping and slice imaging of ions of photofragments, including H atoms. The resolution of the apparatus has been demonstrated to be better than 1% in velocity, even when large molecular beams are used such as 5 mm in diameter. We have used this new apparatus to study the photofragmentation of N₂O at ~203.5 nm and we report on the relative absorption cross sections for bending excited state up to $v_2=7$. Our results are in excellent agreement with the theoretical cross sections calculated individual vibrational quantum states up to (0,4,0). We also model our data up to the bending excited level (0,7,0), by assuming that any stretching excitations (pure or combinations) relax entirely into the nearly degenerate bend vibrational levels (0, v_2 ,0). This experiment demonstrates that photodissociation imaging experiments of molecules like N₂O constitute a very sensitive probe of the vibrational state distribution of the parent molecules.

Electron-mediated vibrational energy transfer in NO/Au(111) collisions: comparison of experiment and theory.

Christof Bartels

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The Born-Oppenheimer approximation is known to break down for certain molecule-surface systems, both for adsorbates and in collisions. Particularly direct evidence for the coupling between vibration and electronic excitations comes from the observation that vibrational relaxation is strong when NO($v=15$) scatters from a metallic Au(111) surface, but almost absent when NO($v=12$) scatters from an insulating LiF surface [1]. At least two different theoretical approaches successfully reproduce the experimental results: Molecular dynamics with electronic friction [2] and independent electron surface hopping [3].

In order to test the validity of these models more rigorously, we studied the NO/Au(111) system in more detail, measuring NO($v=0 \rightarrow 1,2,3$) vibrational excitation, NO($v=3 \rightarrow 3,2,1$) vibrational survival and relaxation, NO($v=11,16$) vibrational relaxation, and translational inelasticity for vibrationally elastic and inelastic channels. Comparing the experimental results to the predictions of theory, we find hints on where the theoretical models can be improved.

- [1] Huang, Rettner, Auerbach, Wodtke, *Vibrational promotion of electron transfer*. Science, 290(5489), 111-114, 2000.
- [2] Monturet, Saalfrank, *Role of electronic friction during the scattering of vibrationally excited nitric oxide molecules from Au (111)*. Physical Review B, 82(7), 075404, 2010.
- [3] Shenvi, Roy, Tully, *Dynamical steering and electronic excitation in NO scattering from a gold surface*. Science, 326(5954), 829-832, 2009.

Inelastic scattering of benzene from Au(111)

Monika Grütter¹, Pranav R. Shirhatti^{1,2} and Alec M. Wodtke^{1,2}

¹*Georg-August-Universität Göttingen,, Institut für Physikalische Chemie,
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²*Max-Planck-Institut für biophysikalische Chemie, 37070 Göttingen, Germany*

First experimental results from the inelastic scattering of Benzene (C₆H₆) from a single-crystal gold (111) surface are presented. A beam of cold ($T_{\text{rot}} = 5$ K) molecules in their vibrational ground state were scattered from the surface and subsequently detected by 1-1 REMPI through the $v_6 = 1$ vibrational level of the S₁ state. Various incident beam energies ranging from 0.3 to 2.5 eV were investigated, as well as the scattering from different surface temperatures in the range 100-700 °C. for all incident energies and all surface temperatures, a significant trapping-desorption component was observed. these trapping-desorption signals were analysed with respect to their rotational, vibrational, and translational degree of freedom. Future experiments with improved molecular beam conditions are proposed.

Preliminary results of D₂ recombination on Au(111) surface

Quan Shuai

Max-Planck-Institut für biophysikalische Chemie, 37070 Göttingen, Germany

In this work, we investigated the recombinative desorption of D₂ from Au(111) using a D₂ permeation technique. We used the principle of detailed balance to extract quantitative information about dissociative adsorption dynamics from the time-of-flight (TOF) distributions of molecules desorbed from the surface. As preliminary results, we detected highly translationally excited D₂ molecules of different rotational states for $\nu = 0, 1, \text{ and } 2$. The translational excitation is significantly higher than in D₂/Cu system; like in D₂/Cu the translational excitation goes down as the vibrational excitation increases. This is consistent with there being a much higher barrier on Au than on Cu.^[1] Also we will investigate the dependence of the reaction probability on rotational, vibrational and translational energy of hydrogen molecules. This will be an ideal benchmark data-set for testing modern theories of surface chemistry. Specifically, we wish to know if electronically adiabatic theory can succeed to describe these dynamical measurements. This system was chosen because of recent chemi-current measurements attributed to the recombinative desorption of hydrogen on Au.^[2, 3] The investigations will help us to understand to what extent the Born-Oppenheimer approximation can break down in a simple chemical reaction at a metal surface.

[1] B. Hammer and J. K. Nørskov, *Nature* **376**, 238 (1995).

[2] B. Schindler, D. Diesing, and E. Hasselbrink, *J. Chem. Phys.* **134**, 034705 (2011).

[3] B. Schindler, D. Diesing, and E. Hasselbrink, *J. Phys. Chem. C* **117**, 6337 (2013).

Nanocatalysis: The Shape of Things to Come

Beatriz Roldan Cuenya

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In order to comprehend the properties affecting the catalytic performance of metal nanoparticles (NPs), their dynamic nature and response to the environment must be taken into consideration. The working state of a NP catalyst might not be the state in which the catalyst was prepared, but a structural and/or chemical isomer that adapted to the particular reaction conditions. This work provides examples of recent advances in the preparation and characterization of NP catalysts with well-defined sizes and shapes. It discusses how to resolve the shape of nm-sized Pt, Au, Pd, and PtNi catalysts via a combination of *in situ* microscopy (AFM, STM, TEM), *operando* spectroscopy (XAFS, GISAXS) and modeling, and how to follow its evolution under different gaseous or liquid chemical environments and in the course of a reaction. It will be highlighted that for structure-sensitive reactions, catalytic properties such as the reaction rates, onset reaction temperature, activity, selectivity and stability against sintering can be tuned through controlled synthesis.

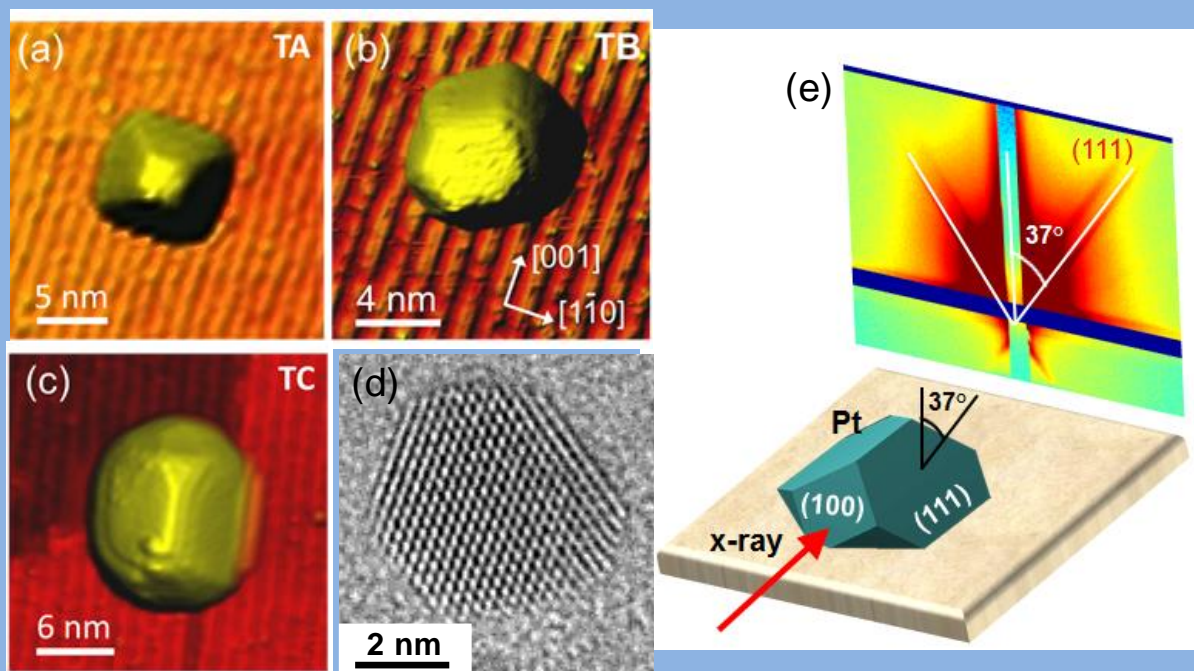


Fig. 1. (a-c) STM images of micellar Pt NPs on $\text{TiO}_2(110)$ acquired at RT after annealing in UHV at 1000°C . (d) High resolution TEM image of a Pt NP deposited on SiO_2/Si obtained at RT after annealing at 800°C in H_2 . (e) GISAXS data from shape-selected Pt NPs on $\text{SrTiO}_3(110)$ acquired in H_2 at 700°C .

Probing Spin-Polarized Hydrogen Atoms with the High-n Rydberg Time-of-Flight Technique

Arthur G. Suits¹, Bernadette M. Broderick¹ and Oleg S. Vasyutinskii²

¹Department of Chemistry, Wayne State University, Detroit MI 48202 USA and ²Ioffe Institute, Russian Academy of Sciences, St. Petersburg 19401 Russia

The production of spin-polarized hydrogen atoms in photodissociation has long been suspected¹, but it is only in recent years that this has been directly observed, first through inferences based on the co-fragment angular momentum polarization², and subsequently through probing of the H atom itself.³ We have recently shown that by adapting the H atom Rydberg Time of Flight (HRTOF) technique, we can measure hydrogen atom spin polarization, and its velocity distribution, with the extraordinary resolution and sensitivity that this method affords.⁴ The spin-sensitive probe scheme combines a linearly polarized Lyman- α laser, a circularly polarized tagging laser, and a photolysis laser. We illustrate this approach with a measurement of the coherent contributions to the H atom spin polarization in photodissociation of HBr at 212.8 nm. We will examine the means to adapt this method to detect the incoherent contribution to the spin polarization in photodissociation as well, and investigate its possible application in crossed-beam scattering and as a unique probe of surfaces and their magnetic properties.

1. O. S. Vasyutinskii, *Sov. Phys. JETP Lett.* 31, 428 (1980).
2. T. P. Rakitzis, P. C. Samartzis, R. L. Toomes, T. N. Kitsopoulos, A. Brown, G. G. Balint-Kurti, O. S. Vasyutinskii, and J. A. Beswick, *Science* **300**, 1936 (2003).
3. D. Sofikitis, L. Rubio-Lago, L. Bougas, A. J. Alexander, and T. P. Rakitzis, *The Journal of Chemical Physics* **129**, 144302 (2008).
4. B. M. Broderick, Y. Lee, M. B. Doyle, O. S. Vasyutinskii, and A. G. Suits, *The Journal of Physical Chemistry Letters* **4**, 3489 (2013).

Inelastic Hydrogen Atom Scattering: Importance of Electron-Hole-Pair Excitations

Oliver Bünermann, Hongyan Jiang, Yvonne Dorenkamp, and
Alec Wodtke

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Obtaining an atomic-level understanding of the dynamics of energy conversion at surfaces remains a richly complex and challenging area of modern research in physical chemistry. A general strategy to this field follows the lessons of gas-phase bimolecular chemical dynamics, where simple model systems are studied experimentally with great care while theoretical simulations are developed.

One of the simplest systems to think of is Hydrogen atom scattering from a single crystalline surface. A new apparatus to experimentally investigate this model system with extraordinary precision is presented. Laser photolysis of Hydrogen Iodide is employed to produce a monochromatic Hydrogen atom beam with well-defined initial directions. Kinetic energies between 100 meV and 7 eV can be produced by tuning the wavelength of the photolysis laser. The final kinetic energy and scattering angle are measured with extraordinary resolution employing Rydberg Atom Tagging. Both techniques are adopted and combined with a state of the art surface scattering machine, introducing an entirely new approach to surface analysis. High control of experimental parameters as well as angular and energy resolved detection give a very detailed picture of the scattering process.

First experiments scattering Hydrogen atoms from an Au(111) surface will be presented. Furthermore, Hydrogen atoms were scattered from a Xeon covered Au(111) surface to allow a comparison between insulator and metal surface. Experimental results are compared to high level theoretical calculations. The importance of electronically non-adiabatic processes and penetrating collisions is discussed.

H at Au(111): A Potential Energy Surface

Svenja Maria Janke

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Tammannstr. 6, 37077 Göttingen, Germany*

I present molecular dynamic simulations for a hydrogen atom scattering from a Au(111) surface. In these simulations, I let the hydrogen atom interact with electron hole pairs and include the phononic motion of the gold atoms. My preliminary results offer not only explanations for experimental results but suggest moreover a strong importance of non-adiabatic effects.

Generation of ultra-short H-atom pulses: A new tool for time-resolved dynamics

Sven Kaufmann

Max-Planck-Institut für biophysikalische Chemie, 37070 Göttingen, Germany

We introduce a new approach to forming ultra-short pulses of neutral atoms: spatially chirped bunch-compression photolysis.

The fragment kinetic energy of most photodissociation processes depends on the frequency of the dissociation light. With spatial chirping, the dissociation laser pulse is tailored in such a way that the position of the dissociation for every frequency component compensates for this fact; faster atoms are forced to travel further to the target. The initially extended bunch of photofragments compresses during flight, producing a short pulse several cm away without the use of any additional electrical or magnetic fields.

With this approach, we demonstrate H-atom pulses 100 times shorter than any previously reported. Using experimentally validated simulations, we show the feasibility of producing 110-ps H-atom pulses."

Multi-quantum vibrational relaxation at metal surfaces – how does it really work?

Nils Bartels

*Georg-August-Universität Göttingen,, Institut für Physikalische Chemie,
Tammannstr. 6, 37077 Göttingen, Germany*

In this talk I will present recent work showing that the efficiency of multi-quantum relaxation of nitric oxide (NO) colliding with a Au(111) surface increases dramatically with enhanced incidence vibrational and translational energy. While these trends can be qualitatively understood by analyzing the energetics of the underlying electron transfer reaction, they contradict predictions from state-of-the-art theoretical models.

CO ($v = 0$) scattering from Au(111): Incidence energy dependence of the CO ($v = 0-1$) vibration excitation probability

Pranav R. Shirhatti

Max-Planck-Institut für biophysikalische Chemie, 37070 Göttingen, Germany

I will be discussing the results of the measurement of CO vibration excitation probability ($v = 0-1$) upon scattering from a clean Au(111) surface. A detailed set of measurements by varying both the incidence energy (0.16 - 0.84 eV) and the surface temperature (473 - 973 K) has been carried out. Our measurements show that the vibration excitation probability increases with increasing incidence energy in the range of 0.3 to 0.84 eV. At the lowest incidence energy (0.16 eV) however, the vibration excitation probability is observed to be much larger than that expected from the above mentioned trend. I will discuss these results in the light of two different pathways for vibrational energy transfer. Namely, the electron hole pair mediated energy transfer and trapping desorption. Our results also suggest that the trapped CO molecules undergo only partial thermal accommodation.

II: Laser-induced fluorescence spectroscopy of overlayer and monolayer CO/NaCl(100): overtone excitation ($\nu=0\rightarrow 2$)

Li Chen

Max-Planck-Institut für biophysikalische Chemie, 37070 Göttingen, Germany

I will describe first the current status of our new machine. The new machine implements the recently available superconducting nanowire single photon detectors (SNSPDs) with high quantum efficiency and low dark-count rate in the mid-infrared wavelength range, to study the vibrational dynamics of adsorbed molecules at submonolayer or even single molecule level using laser-induced fluorescence spectroscopy. Then, I will present our preliminary results of fluorescence as a function of *time (and excitation laser frequency)* from overlayer and monolayer CO on NaCl(100) induced by the *overtone excitation ($\nu=0\rightarrow 2$) with narrow band IR laser* and detected with liquid nitrogen cooled InSb detector. The surface temperature dependent fluorescence decay as well as the different decay kinetics between overlayer and monolayer CO will be discussed. At the end, I will give an outlook of several interesting and refined experiments for the near future.

Supported metal clusters with a precise number of atoms: stability, optical properties and chemical reactivity

W. Harbich

Institute of Condensed Matter Physics, EPFL, CH-1015 Lausanne, Switzerland

Small clusters containing only a handful atoms are a transition state between atomic and molecular properties to one side and solid state properties to the other. After briefly discussing concepts of producing, selecting and depositing such small particles on a substrate, I will focus on the optical properties of the noble metal clusters as a function of size. The birth of the surface plasmon for very small cluster sizes is discussed as well as the fluorescence, well present for metal particles in this size range. In the second part of this contribution I will focus on the chemical reactivity of titania supported transition metal clusters, here Pt_n . Cluster size effects, cluster substrate interaction and cluster stability under reaction conditions will be discussed.

Scanning probe microscopy of atoms/molecules on insulating films: Structure determination and imaging the charge distribution within single molecules

Gerhard Meyer

IBM Zurich Research Laboratory, Säumerstrasse 4 / Postfach, 8803 Rüschlikon, Switzerland

Ultrathin insulating films on metal substrates are unique systems to use the scanning tunneling (STM)/atomic force microscope (AFM) to study the electronic and structural properties of single atoms and molecules, which are electronically decoupled from the metallic substrate. Recent work demonstrates the imaging of molecular orbitals, the molecular structure and the intramolecular charge distribution of single molecules with highest resolution. This opens up the possibility to study molecular processes as bond breaking/formation, conformational switching, charge transfer etc. in utmost detail.

Towards Molecular Beam Scattering from Ultrathin Metallic Films

Growth and Characterization of Ag on Au(111)

Christoph Steinsiek¹, Christof Bartels¹, Dirk Schwarzer², Alec Wodtke^{1,2}

¹*Georg-August-Universität Göttingen,, Institut für Physikalische Chemie,
Tammannstr. 6, 37077 Göttingen, Germany*

²*Max-Planck-Institut für biophysikalische Chemie, 37070 Göttingen, Germany*

NO scattering from bulk Au(111) and Ag(111) has been investigated vigorously and clear evidence for non-adiabatic coupling (between molecular vibration and excitation of surface electrons) was observed. We will extend such experiments to scattering from Ultrathin Metallic Films with atomically defined thickness, looking for a transition from bulk-Au to bulk-Ag and for possible quantum effects. For such investigations a defined and reproducible number of monolayers is desired which can only be achieved via layer-by-layer growth (Frank-van-der-Merwe growth). Therefore it is important to characterize the growth mode and determine the film thickness.

An experimental setup with a home-built electron beam evaporator was setup for the growth of Ag on Au(111). A Quartz Crystal Microbalance and Auger Electron Spectroscopy were employed to determine the thickness of one monolayer.

We have characterized the growth mode and calibrated the films growth by observing characteristic features using AES.

Beamer II - an advanced machine for surface scattering experiment''

Dan Harding

Max-Planck-Institut für biophysikalische Chemie, 37070 Göttingen, Germany

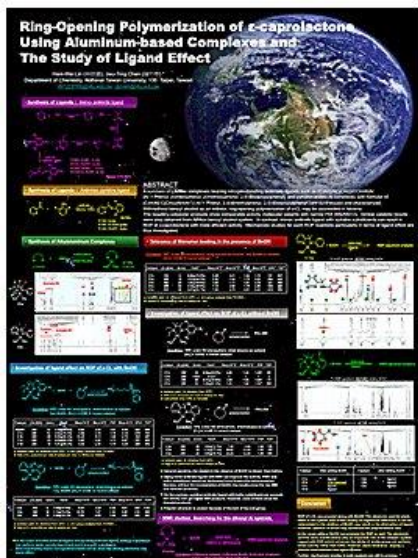
Beamer II is a new machine constructed to study high temperature and reactive surface scattering processes, with both surface-sensitive and gas-phase detection methods. I will outline the new machine and some of the planned early experiments and describe some preparatory work developing vacuum ultraviolet spectroscopic methods.

Graphene growth on epitaxial Cu film

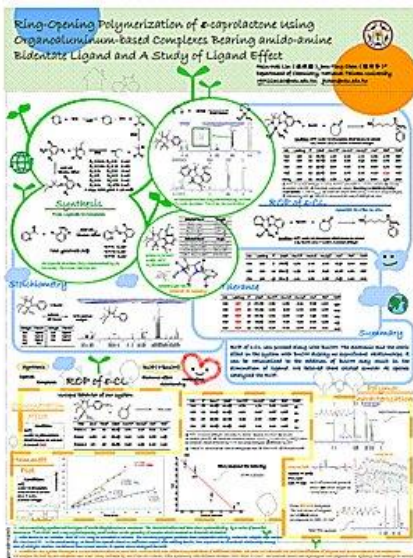
Hak Ki Yu

Max-Planck-Institut für biophysikalische Chemie, 37070 Göttingen, Germany

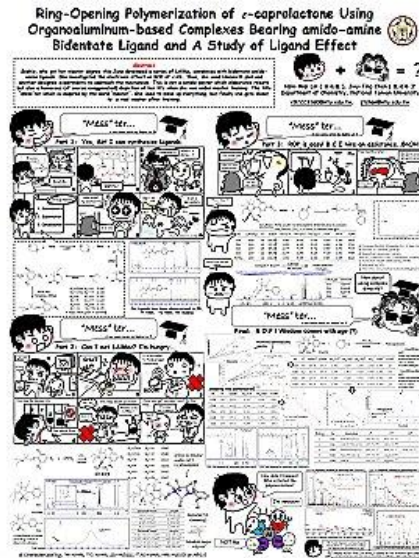
Graphene synthesized by chemical vapor deposition (CVD) on copper (Cu) foil is the best solution for the large scale application compare to other methods such as exfoliation from graphite, epitaxial growth on SiC, and chemical reduction from graphene oxide. However, the several material properites of the so obtained graphene is typically smaller than that of graphene prepared by an exfoliation based method, which is presumably due to multiple domain formation during growth on polycrystalline Cu and several defects such as impurities by oxidation of Cu surface and roughness introduced via the standard commercial copper foil. Here, we will talk about the graphene grown by CVD on Cu (111) surfaces for the high quality of material properties.



Poster 1



Poster 2



Poster 3

POSTER ABSTRACTS

Time-resolved spectroscopy of photoswitchable host-guest interactions

Jennifer Ahrens

Max-Planck-Institut für biophysikalische Chemie, 37070 Göttingen, Germany

In this project light triggered host-guest interactions are examined. Four ligands and two Palladium atoms (Pd^{2+}) build a self-assembled coordination cage $[\text{Pd}_2(\text{L})_4]^{4+}$ - the host complex. This cage can be reversibly converted from a flexible "open-ring" form to a "closed-ring" form by using UV-VIS-light of specific wavelength [1,2]. The two photoisomers show different binding energies to spherical guest molecules such as the $[\text{B}_{12}\text{F}_{12}]^{2-}$ dianion. The ligand is based on a photoswitchable DTE chromophore which are well known with potential applications in data storage and molecular motors [5,6].

The main goal of our project is to elucidate the connection between the light-triggered structural changes of a photochromic coordination cage and its ability to reversibly take up and release guest molecules.

We will investigate the molecular mechanism of this system by the use of a femtosecond-pump(UV)-probe(IR)-experiment [3,4]. In our preliminary results, we detected with a FTIR-spectrometer some characteristic absorptions which can be clearly assigned to the open or the closed form of the cage. Unfortunately we couldn't determine the position of the guest because adding the guest has no effect on the IR-spectra. Neither the IR spectra of the cage, nor the IR spectra of the guest showed any changes by the photoswitching process which could be interpreted as host-guest interactions or used for localizing the guest position. To solve that problem synthesis of modified guests, with particular sensitive IR marker band are planned. A system with a photoswitchable guest instead of a photoswitchable host also seems to be very promising for our purpose [2].

- [1] Light-Triggered Guest Uptake and Release by a Photochromic Coordination Cage; M. Han, R. Michel, B. He, Y. Chen, D. Stalke, M. John and G. H. Clever, *Angew. Chemie.* **52**, 1319-1323 (2013).
- [2] Self-assembled coordination cages based on banana-shaped ligands; Muxin Han, David M. Engelhard and Guido H. Clever; *Chem. Soc. Rev.* **43**, 1848-1860 (2014).
- [3] Femtosecond IR Spectroscopy of Peroxycarbonate Photodecomposition: S1-Lifetime Determines Decarboxylation Rate; C. Reinhardt, J. Schroeder, D. Schwarzer, *J. Phys. Chem. A* **111**, 10111 (2007)
- [4] Ultrafast primary processes of an iron-(III) azido complex in solution induced with 266nm light, H. Vennekate, D. Schwarzer, J. Torres-Alacan, O. Krahe, A. C. Filippou, F. Neese, P. Vöhringer, *Phys. Chem. Chem. Phys.* **14**, 6165 (2012).
- [5] *Molecular Motors*, M. Schliwa, Wiley-VCH, Weinheim (2003)
- [6] *Diarylethenes for Memories and Switches*, M. Irie, *Chem. Rev.* **100**, 1685-1716 (2000).

REAL-TIME DESORPTION KINETICS ON PT(111)

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We investigated the desorption of CO and NO from Pt(111) using a 2D time-of-flight (2D-TOF) method. With this technique it is possible to observe the real-time kinetics of the desorption and thus to determine the binding energy to the surface with high accuracy.

Using a two-laser-system we monitored the temporal decay of the flux of desorbing molecules leaving the surface with a certain velocity. We fit the data obtained for several different surface temperatures T_S to a simple first-order kinetic rate model for which the exponential decay yields the desorption rate constant and therefore the residence time of the molecules on the surface. From an Arrhenius plot of these T_S dependent rate constants we determine the binding energy E_D and the pre-exponential factor (attempt frequency) ν for desorption.

While TPD evaluation using Redhead's equation usually needs a reasonable assumption for ν , our method can in principal deliver both values at once. For future experiments we plan to extend this method to other metal surfaces like Ni and Cu and different adsorbates.

Ultrafast dynamics of a molecular magnetic switch after photo excitation in solution

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The field of molecular switches has been a hot topic among scientist of various professions in recent years. Recently, magnetic bistability and switching was achieved for carefully designed Ni-porphyrin molecules in homogeneous solution ^[1]. The Ni-centered porphyrin moiety undergoes spin crossover (SCO) upon irradiation with light at certain wavelengths, while its tethered azopyridine ligand isomerizes between cis- and trans-forms. The cis-form coordinates in axial position to the metal center, which stabilizes the paramagnetic high spin state. Here, we present the results and first interpretation of our femtosecond broadband transient absorption measurements of the ultrafast relaxation dynamics of this molecular magnetic switch after photo excitation in different solvents. We clearly reveal the steps of intersystem crossing (ISC) and SCO (<200 fs), intramolecular vibrational energy redistribution (IVR) (~1 ps) and vibrational cooling to the solvent (~10 ps). In coordinating solvents, such as acetonitrile, we observe an additional transient relaxation feature on the 150-250 ps time scale, which we attribute to the formation of a singly or doubly solvent-coordinated species. This feature appears to be absent in non-coordinating solvents such as dichloromethane. As the steady-state switching efficiency is largely dependent on the coordinating properties of the solvent, our results indicate the important role of solvent coordination in the stabilization of the excited paramagnetic state and the formation of the relaxed paramagnetic cis species.

- [1] S. Venkataramani, U. Jana, M. Dommaschk, F. D. Sönnichsen, F. Tuczek, R. Herges, *Science*, **2011**, *331*, 445 – 447.
- [2] J. L. Retsek, C. M. Drain, C. Kirmaier, D. J. Nurco, C. J. Medforth, K. M. Smith, I. V. Sazanovich, V. S. Chirvony, J. Fajer, D. Holton, *J. Am. Chem. Soc.*, **2003**, *125*, 32, 9787 – 9800.
- [3] M. Nappa, J. S. Valentine, *J. Am. Chem. Soc.*, **1978**, *100*, 16, 5075 – 5080.

Mind the Gap: Scattering of NO ($\nu=11$) from a Semiconductor

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In this project we investigate the vibrational relaxation of vibration in NO during surface collisions. The vibrational state distributions have been measured exemplarily before for metals (Au(111)) and insulators (LiF).^[1] For each there exists a theoretical model to explain why we find almost every state from $\nu=11$ to $\nu=0$ for relaxation on metal surfaces but only few for insulator surfaces: NO remains mostly in highest vibrational state here.^[2,3] This leads to the assumption, that the mechanism of energy transfer is based on an electron-transfer process. To achieve further information on the influence of the electronic surface structure on vibrational relaxation processes we chose a semiconductor surface with a band gap that corresponds approx. 3 vibrational energy quanta of NO. State distribution data is achieved by exciting molecules to the $\nu=11$ state using Pump-Dump-Sweep^[4], scattering from Ge and subsequent detection of scattered molecules via (1+1) REMPI spectroscopy.

[1] Y. Huang, C.T. Rettner, D.J. Auerbach, A.M. Wodtke, *Science* **290**, 111 (2000).

[2] S. Monturet, P.Saalfank, *Phys. Rev. B* **82**, 075404 (2010).

[3] N. Shenvi, S. Roy, J.C. Tully, *Science* **326**, 829 (2009).

[4] N. Bartels, B.C. Krüger, S. Meyer, A.M. Wodtke, T. Schäfer, *J. Phys. Chem. Lett.* **4**(14) (2013).

Surface scattering of highly vibrationally excited NO from Au(111): new challenges for theory

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Vibrational multi-quantum relaxation is a very efficient process observed during highly vibrationally excited nitric oxide / Au(111) surface scattering.^[1] The most probable scattering channel for NO molecules in the initial state $\nu_1=15$ involves the loss of 8 vibrational quanta. Due to the large energy mismatch between the vibrational spacing in NO and phonon modes in Au a purely mechanical mechanism via coupling to phonons fails to explain the high efficiency of multi-quantum relaxation. Rather, it is thought to proceed nonadiabatically involving the excitation of electrons. Note that the coupling between vibration and electronic motion violates the Born Oppenheimer approximation.^[2]

Experiments on low ν -state NO scattering from Au(111) show that the efficiency of vibrational relaxation is drastically influenced by incidence translational energy and orientation of the molecule with respect to the surface.^[3] Up to now, reported experiments on highly vibrationally excited nitric oxide / Au(111) surface scattering were limited to the investigation of an isotropic ensemble of colliding molecules. Only a single incidence translational energy and one incidence vibrational state were tested.

Here, we report the “missing” experiments on highly vibrationally excited NO ($\nu_1=11$ and $\nu_1=16$): They cover the investigation of final vibrational state distributions as influenced by incidence translational energy and orientation. Additionally, we show the rotational state distributions for selected vibrational elastic and inelastic channels.

We find that incidence vibrational energy promotes vibrational relaxation. For $\nu_1=16$ the relaxation probability is nearly 100 %. Orientation and incidence translational energy do not affect the final vibrational state distribution. In contrast to that, for $\nu_1=11$ the relaxation probability is below 100 % and increases with incidence translational energy. Orienting the N-atom of nitric oxide towards the surface enhances the probability of relaxation. The nonthermal rotational state distributions observed exhibit strong rotational rainbows especially for the vibrational elastic channel. They are influenced by vibrational energy loss, orientation and incidence translational energy.

The findings complete existing data for the “nonadiabatic surface dynamic test case” NO / Au(111). It will be a challenging task for future theories to describe the influence of the molecular parameters on the nonadiabatic dynamics correctly.

[1] Y. Huang, C. T. Rettner, D. J. Auerbach, A. M. Wodtke, *Science* **2000**, 290, 111-114.

[2] M. Born, R. Oppenheimer, *Annalen der Physik* **1927**, 389, 457-484.

[3] N. Bartels, K. Golibrzuch, C. Bartels, L. Chen, D. J. Auerbach, A. M. Wodtke, T. Schäfer, *Proceedings of the National Academy of Sciences* **2013**, 110, 17738-17743.

Introduction to Optical Frequency Combs

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Over the next few years, I will be setting up a new experiment to measure vibrational transitions in light diatomic molecules (in particular, gas-phase OH radicals and CO molecules on a NaCl(100) surface) with unprecedented precision. The goal in these experiments will be to measure the vibrational transitions, which are near 100 THz (3000 cm^{-1} , 0.4 eV, 10 kcal/mol, 40 kJ/mol), with linewidths and absolute accuracies on the order of 1 kHz ($3\text{e-}8\text{ cm}^{-1}$, 4 peV, 100 ncal/mol, 400 nJ/mol) or better. To achieve this level of precision and accuracy, it will be necessary to stabilize the spectroscopy laser against an optical frequency comb. With this poster, I will introduce some of the basic concepts of frequency combs and show how frequency combs can be used to compare the optical frequency of the spectroscopy laser to a radio frequency atomic clock reference to improve the absolute accuracy, as well as transfer the stability of a reference laser to the spectroscopy laser to improve the measured linewidth.

Spectroscopy at VMI and Beamer II

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In order to detect reaction products or scattered molecules we combined laser techniques with a velocity map/slicing imaging setup. Some laser techniques required us to generate light between 110-130 nm via four-wave mixing in Krypton or use the anti-Stokes shift in H₂ to generate (twice) Raman-shifted light at e.g. 187 nm. The imaging setup can not only act as a time-of-flight spectrometer in a Wiley McLaren setup but can also slice an ion cloud using a delayed repeller plate and a gated MCP. In addition to this, we can use photoelectron spectra to obtain information about the ground state (in case of non-resonant ionization) or information about the Rydberg state/ion state used in a resonant transition.

Recent examples include the detection of N₂O, O₂, C₂H₂ and we are exploring possibilities to detect CO₂.

Controlling electron transfer at metal surfaces on the atomic scale

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Electron transfer (ET) is of particular importance for a wide range of biological, physical and chemical phenomena. It plays crucial roles in photosynthesis, dye-sensitized solar cells and heterogeneous catalysis, just to name a few. The efficiency of ET is determined by the displacement between donor and acceptor and decreases at longer distances due to the vanishing overlap of the corresponding wave functions. Especially at surfaces, the distance dependent efficiency of ET is crucial for the means how energy is exchanged between molecules and surfaces. In the here presented work we manipulate the electron transfer efficiency by adsorbing layers of rare gas atoms on a clean Au(111) surface and thus controlling the molecule-metal distance. We monitor the electron emission yield when metastable CO in the $a^3\Pi_1$ state is quenched via an ET mediated mechanism at the surface. The adsorption of rare gases enhances the emission yield drastically, which is in stark contrast to the expected decrease of ET efficiencies at large donor-acceptor distances.

VUV Spectroscopy of Acetylene

Vibrational Excitation in a Heated Supersonic Molecular Beam

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In order to extend our understanding of fundamental processes at surfaces, we plan to undertake state to state surface scattering of acetylene. Here, we describe an investigation of a VUV (1+1') REMPI scheme at different degrees of vibrational and rotational excitation, in search of an efficient and information rich detection method. An electrically heated SiC tube allows the tunable thermal excitation of our supersonic molecular beam. So far, we have measured the VUV spectrum between 124.2 and 126.3 nm. Six transitions were observed, of which four are assigned to transitions through the $\tilde{G}^1\Pi_u$ Rydberg state. They include the origin band $0_0^{0[1-4]}$, 4_1^0 and two of the three 4_1^1 [2]. To quantify the excitation, we determined rotational temperatures by simulation of the origin band and vibrational temperatures by the change in intensity of the bands 0_0^0 and 4_1^0 with temperature. Three different heating settings have been analysed in detail and match best rotational and vibrational temperatures of 40 and 295 K, 70 and 525K and 200 and 685 K.

[1] G. Herzberg, Discuss. Faraday Soc. **35**, 7 (1963).

[2] R. Colin, M. Herman, I. Kopp, Mol. Phys. **37** (5), 1397 (1979).

[3] S. Boyé et al., J. Chem. Phys. **116** (20), 8843 (2002).

[4] S. Boyé et al., Comptes Rendus Physique **5** (2), 239–248 (2004).

Surface Scattering Using Velocity Controlled Molecular Beams of Metastable CO

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The de-excitation of metastable molecules at surfaces was investigated using a new machine that combines a Stark decelerator for accurate velocity control of molecular beams with a beam-surface scattering setup operating under ultra-high vacuum conditions. If the excitation energy of the metastables exceeds the work function of the surface, electrons can be emitted during the process of de-excitation.^[1] The absolute electron yield γ for quenching $a^3\Pi_1$ ($v=0, J=1, +$) metastable CO at an atomically clean Au(111) surface was found to be $\gamma = 0.13 \pm 0.05$.^[2] In order to learn detailed information about the quenching process, the influence of molecular vibration, surface temperature and kinetic energy were investigated. A pronounced enhancement of the electron yield was observed for quenching vibrationally excited metastable CO. Results obtained for two different vibrational distributions accessed by Franck-Condon pumping *via* the states $b^3\Sigma^+$ ($v=0$) and $b^3\Sigma^+$ ($v=1$) suggest an enhancement in electron emission with increasing vibrational quantum number. In addition, surface temperature has been found to have an unexpectedly strong influence on electron emission. The number of ejected electrons increases by $(27 + 7)\%$ when raising the surface temperature from 250 K to 900 K. Within the range of 100 m/s to 500 m/s, the release of electrons was found to be independent of the velocity of metastable CO. These results appear to be in disagreement with existing theories on metastable quenching at surfaces, which are based on the Auger effect. Instead, de-excitation can be explained by formation of a transient anion followed by autodetachment.

[1] H. D. Hagstrum, Phys. Rev. **96**, 336 (1954).

[2] F. Grätz, D. P. Engelhart, R. J. V. Wagner, H. Haak, G. Meijer, A. M. Wodtke, T. Schäfer, Phys. Chem. Chem. Phys. **15**, 14951 (2013).

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