Symposium on Dynamics at Surfaces

July 16-18, 2018

Erfurt, Germany

Monday July 16th

9:00	**Bus Departure from Göttingen**
11:00	**Arrival and registration**
12:00-13:15	**Lunch**
Session Chair:	Prof. Theo Kitsopoulos
13:15-13:30	Prof. Alec Wodtke *Welcoming Remarks*
13:30-14:30	Dr. Heiner Voges, LaVision Göttingen *Life outside Academia*
14:30-15:00	Dima Borodin *Decomposition, Trapping-Desorption and Direct-Scattering of Methanol and Ammonia on Pt(111) Followed via Slice Ion Imaging and Velocity Map Imaging*
15:00-15:30	**Coffee Break**
15:30-16:30	Prof. Daniel Strasser, Hebrew University of Jersualem. *Making Sense of Coulomb Explosion Imaging*
16:30-17:00	Hahn, Hinrich *Hydrogen oxidation on platinum – Revisiting the kinetics of a well-studied catalytic reaction*
17:00-18:00	Prof. Hans Dieter Meyer, University of Heidelberg *Multiconfiguration Time-Dependent Hartree (MCTDH):* *A powerful method for propagating multi-dimensional wave packets*
18:00-20:00	**Dinner**
20:00-	**Poster Session I**

Tuesday July 17th

8:00-9:00	**Breakfast**
Session Chair:	Dr. Sascha Kandratsenka
9:00-10:00	Prof. Jörg Behler, University of Göttingen *High-Dimensional Neural Network Potentials for Complex Systems*
10:00-10:30	**Coffee Break**
10:30-11:30	Prof. Joe Subotnik University of Pennsylvania *Two very different views of dynamics at metal surfaces: surface hopping vs electronic friction*
11:30-12:00	Dr. Oihana Galparsoro *Thermal recombination reactions on metal surfaces: Transition state theory with dynamical corrections.*
12:00-13:30	**Lunch Break**

Session Chair:	Dr. Kai Golibrzuch
13:30-14:00	Jan Geweke *Vibrational Excitation of HCl scattering from Ag(111) vs. Au(111): All Hail The King?*
14:00-14:30	Georg Westphal *Towards photoionization of chiral molecules*
15:00-15:30	**Coffee Break**
15:30-16:30	Prof. Igor Rahinov *On molecule-surface encounters beyond NO/Au(111)*
16:30-17:00	Yvonne Dorenkamp *Inelastic Hydrogen atom scattering from modified Graphene Surfaces*
17:00-17:30	Jascha Lau *Kinetik-Monte-Carlo Simulations of Vibrational Energy Pooling of Monolayer CO on NaCl(100)*
17:30-18:00	Marvin Kammler *Different levels of Theory can describe Hydrogen atom scattering from Graphene*
18:00-20:00	**Dinner**
20:00-	**Poster Session II**

Wednesday July 18th

8:00-9:00	**Breakfast**
Session Chair:	Prof. Alec Wodtke
9:00-9:30	Kim Papendorf *Picosecond-IR-Multiphoton Desorption of H_2 from a Hydrogen Terminated Si(100) Surface*
9:30-10:00	Victoria Walpole *Towards a complete model of bond orientation in the inelastic scattering of NO(X) with Ar*
10:00-10:30	**Coffee Break**
10:30-11:00	**tba**
11:00-12:00	Alec Wodtke *Concepts for detecting reaction intermediates in surface reactions.* *and Closing Remarks*
12:00-13:30	**Lunch**
14:00	**Departure**

ABSTRACTS

FHI-aims AIMD study of scattering of highly vibrationally excited CO from noble metal surfaces

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The experiments recently done in our group show that non-adiabatic effects might play an important role in scattering of highly vibrationally excited CO from metal surfaces [1]. To validate that assertion, we carried out AIMD simulations of scattering of CO(v=22) molecule from Au(111) and Ag(111).

Since, the excited molecule moves very fast it turns out that a DFT code with plane wave basis sets like VASP could not deal with such a situation and the energy conservation is not guaranteed even for a rather small time step.

Using FHI-aims, a code with atom-centered localized orbitals, allows to overcome above convergence problems and produce enough scattering trajectories to produce statistically relevant predictions for the CO scattering outcome.

[1]: R. V. J. Wagner et al., *J. Phys. Chem. Lett.* 8, 19, 4887-4892, **2017**.

High-Dimensional Neural Network Potentials for Complex Systems

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Solid-liquid interfaces pose a significant challenge for atomistic simulations. The very different interactions and bonding situations in water and in solid surfaces are best described by electronic structure methods, which can also take into account the dissociation and recombination of water molecules at the interface. On the other hand, long simulations of large systems are required to obtain converged properties of the liquid phase, which is often computationally very demanding. Machine learning potentials offer a solution to this problem by combining a first principles quality description of the potential-energy surface with the efficiency of simple empirical potentials. In this talk, recent results for the interaction of water with metal and oxide surfaces will be presented, which have been obtained in molecular dynamics simulations employing high-dimensional neural network potentials (NNPs), a typical class of machine learning potentials. NNPs are reactive and thus allow to observe proton transfer processes at the interface, which also play an important role in highly concentrated electrolyte solutions.

Mechanistic investigation of photocatalysed reactions by ps-µs-time-delay OPA-UV-pump-IR-probe-spectroscopy – first results using the example of $Ni(N_3)(PNP)$

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The discovery of photocatalysts and the enhancement of their efficiency is one of the most important research topics of the century. Mechanisms of ultrafast reactions occurring after excitation by UV and visible light can be figured out by observing the temporal evolution of specific IR-bands of educt and/or product vibrations.

Since long-lived species and, compared to simple unimolecular processes, slower bimolecular reaction products like adducts and species formed by diffusion controlled reactions often persist beyond a 1 ns pump-probe delay , an expansion up to 900 µs was constructed using a laser with two interconnected RGA (regenerative amplifier) for pump and probe beam [1].

Moreover, an OPA (optical parametric amplifier) was built for continuous modulation of the pump wavelength, because the mechanism of reactions after photoexcitation is strongly dependent on the incoming photon energy.

First results were attained from a $Ni(N_3)(PNP)$ complex (PNP $=N(CHCHP^tBu_2)_2))$[2] without use of the pump-OPA. This compound might be able to eliminate N_2 eventually creating a rare Ni^{IV} nitrido species able to do 1,2-addition of a C-H bond of benzene.[3] The decay and reconstruction of the azide IR band was observed. Further investigation of N-H and product bands will follow.

[1] S. Kaufmann, D. Schwarzer, C. Reichardt, A. M. Wodtke, O. Bünermann, Nat. Commun. 5, 5373-5378 (2014)
[2] F. Schneck, M. Finger, M. Tromp, S. Schneider; Chem. Eur. J. 23, 33-37 (2014)
[3] V. Vreeken, M. A. Siegler, B. de Bruin, J. N. H. Reek, M. Lutz, J. I. van der Vlugt, Angew. Chem. 127, 7161-7165 (2015)

Decomposition, Trapping-Desorption and Direct-Scattering of Methanol and Ammonia on Pt(111) Followed via Slice Ion Imaging and Velocity Map Imaging

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Currently we investigate the kinetics and dynamics of simple hydrogen carrier molecules – MeOH and NH_3, on Pt(111). Our experimental approach combines typical surface science techniques (UHV, supersonic molecular beams) with a novel approach for ion imaging and velocity map imaging of molecules scattered and/or formed at the surface. This approach allows us to determine the reaction rates and dynamical fingerprints of the reaction from the same measurement, which helps us to identify the underlying chemical processes easily. [1]

For MeOH we observe a sticking coefficient of unity into the molecular adsorption state. On Pt(111) we estimate the decomposition of molecularly adsorbed MeOH to be on the order of 1 %. We find no evidence for other decomposition products than CO and H_2.

The first order desorption rate constants of produced CO (573-773 K) indicates a much slower kinetics than expected for desorption of CO from terraces only. [2] We assign this effect to the non-saturated steps which influence the desorption kinetics of CO even on the Pt(111) surface with 0.25 % step-density. We currently try to describe the step saturation effect quantitatively to make better estimations on the decomposition efficiency of MeOH. No evidence is found for a delayed CO production from MeOH (320-873 K), which indicates that the decomposition process of MeOH to the products is on a smaller time scale than the resolution of our experiment (20 µs).

We were also able to extract kinetic traces for the formation of hydrogen molecules from decomposed MeOH (673-873 K). The form of the kinetic trace indicates a typical second order process which is expected from hydrogen recombination. Unlike for first order processes, for second order rate constants the initial coverage of reactants has to be known. Therefore the decomposition efficiency of MeOH is crucial for the extraction of reliable elementary step rate constants in this experiment.

In contrast to the MeOH in NH_3 we can observe the direct scattering channel, even though this is on the order of few percent for incidence energies between 0.25 and 0.55 eV. In the trapping-desorption kinetics we observe bimodal kinetics, which indicates two molecularly adsorbed states of NH_3. However, we could not observe decomposition of NH_3 so far. The energy distribution of the scattered molecules appears much broader than expected from translational inelastic scattering only. We think that the observed energy distribution might indicate substantial vibrational excitation, which was observed previously from direct-scattering at Au(111). [3] On the example of NH_3 we test the velocity map imaging approach and its advantages to study reaction dynamics at surfaces. We refer here to the poster and the poster abstract of J. Fingerhut.

We plan to investigate the direct scattering channel of NH_3 at Pt(111) with quantum state resolution. This might give new insights on how the chemisorption state influences the vibrational excitation of simple molecules. We plan also to look with more details into the decomposition of NH_3 at Pt(111). We also will extend our studies to the Pt(332) surface for both molecules.

[1] Harding *et al., J. Chem. Phys.* **2017**, *147*, 013939.
[2] Golibrzuch *et al., J. Am. Chem. Soc.* **2015**, *137*, 1465.
[3] Kay *et al., Phys. Rev. Lett.* **1987**, *59*, 2792.

Temperature Programmed Desorption of benzene and aniline from functionalized silica surfaces.

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Biopolymer layer silicates are shown excellent adsorption capacity in textile dye contaminate wastewater treatment. Mainly the functional groups on the composite surface are responsible for the adsorption process. Since the biopolymers are not able to withstand high temperatures it is difficult to perform TPD experiments using the biopolymers. Usually, the textile dyes also have high vapour pressure; thus, it is challenging to transfer typical dye molecules to the gas phase employed in UHV chambers without decomposition. In this study, functionalized silica surfaces were used to mimic the biopolymer layer silicate composite. Anile and benzine was used to mimic the functional groups on the textile dye molecule.

Biopolymers used in studies in liquid phase were alginate and chitosan which contained -COOH and -NH_2 functional groups. For simulating typical surfaces, we used silica wafers, which were cut into 1 cm×1 cm squares (compatible size for UHV chamber sample holders). Thereafter silica surface was cleaned with acetone by sonication for 2 min. The cleaning procedure was repeated for 2 times. Cleaned silica surfaces were heated in a plasma oven for 15 min. Thereafter 2 mL of (3-aminopropyl)dimethylmethoxysilane and (3-Cyanopropyl)dimethylmethoxysilane were added with the TEOS surfactant to the surface. The reaction mixture was heated to 70 °C for 24 h. Thereafter functionalised silica surfaces were washed with acetone and stored in acetone solutions for further use. The silica surface functionalised with ─C≡N group was heated with 50% sulfuric acid for 1h to convert ─C≡N to ─COOH. Thereafter, functionalised silica surface was thoroughly cleaned with acetone and stored in acetone for further use.

The TPD experiments were carried out with a home build UHV chamber and provide information about typical binding energies. From these we deduce information about the binding process of dye molecule at adsorbents in real applications.

Inelastic Hydrogen atom scattering from modified Graphene Surfaces

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Hydrogen atoms can form a covalent C-H bond with a graphene surface. The need to break the conjugated π-system of the graphene layer in the C-H bond formation process and therefore induced reconstruction of the graphene surface gives rise to an adsorption barrier. Graphene can be grown on different metal surfaces. The interaction with the underlying metal layer influences the electronic structure of the graphene layer, and thus alters the H-graphene interaction. For instance, graphene is weakly bound to Pt(111) while a strongly bound (1 x 1) oriented graphene layer can be produced on Ni(111). The interaction strength between the graphene layer and the Ni(111) subsurface can further be tuned by changing the graphene modification on Ni(111).

We performed inelastic hydrogen atom scattering from graphene on Pt(111) and two different graphene modifications on Ni(111): (1 x 1) oriented and partially rotated graphene. Inelastic H atom scattering experiments from graphene on Pt(111) show that for normal incidence energies below the adsorption threshold a quasi-elastic scattering component is observed. However, for normal energies larger than the adsorption threshold a large amount of translational energy of the H atom is transferred. *Ab intio* molecular dynamics (AIMD) simulations qualitatively reproduce the experiments and suggest a very efficient adiabatic energy loss mechanism.

Results for graphene on Ni(111) show certain similarities to the observation for graphene on Pt(111). However, a detailed examination of the obtained data revealed two additional features, which were not observed for Pt(111). Furthermore, the experimental results revealed a significantly lower absorption threshold for both graphene modification on Ni(111) compared to graphene on Pt(111) and a significantly smaller adsorption threshold for (1 x 1) graphene compared to rotated graphene on Ni(111). These observations represent the first experimental evidence for different reactivity of both graphene species due to their different geometric arrangement.

Rydberg-atom tagging of hydrogen atoms scattered from a range of surfaces

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As hydrogen is the simplest reactive species, H-atom scattering on surfaces provides a unique way to study gas-surface interactions in general in order to improve the theoretical models used to simulate them. Analysis of the breakdown of the Born-Oppenheimer Approximation in surface dynamics has long been a barrier to developing accurate, precise models for this. Rydberg-atom tagging (RAT) is an extremely sensitive technique used to study H-atom scattering, the motivation and benefits of which will be discussed in this poster. An introduction to the procedure and the apparatus will be given, followed by a discussion of prior results of H-atom scattering from metallic, insulating, and semiconducting surfaces. Potential new surfaces to study, with reference to other techniques used within this research group, will be highlighted, along with expected issues related to such materials.

Investigation of Ammonia Trapping-Desorption and Direct-Scattering at Pt(111) using Ion Imaging and Velocity Map Imaging

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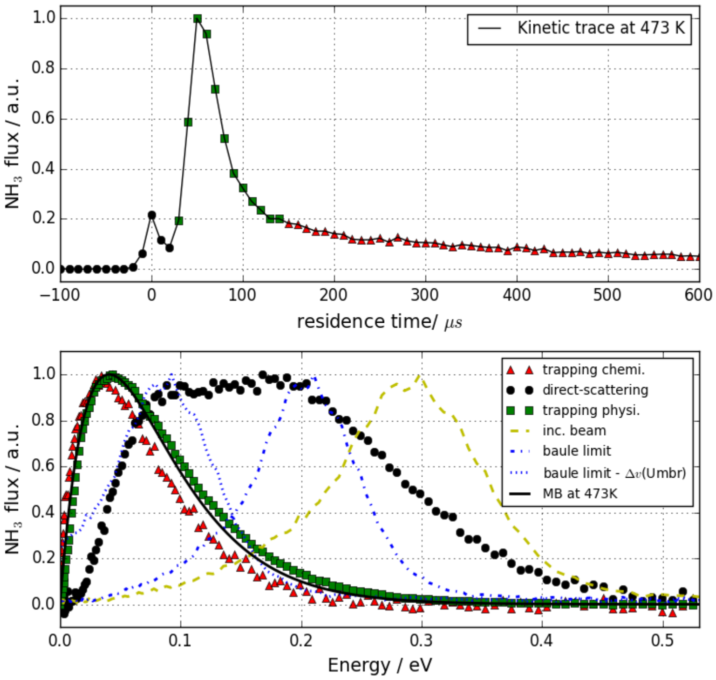
In this work we present a detailed investigation on the interaction of ammonia at the Pt(111) surface. We use classical surface science approach including supersonic molecular beams, ultra-high vacuum (UHV) conditions and a single crystal in combination with laser based techniques (state selective and universal) for ionization and detection via slice imaging and velocity map imaging (VMI).[1]

We investigate different temperatures from 150 °C to 600 °C with incident energies between 0.3 to 0.6 eV. We observe direct scattering and trapping-desorption. Trapping-desorption shows two components in its kinetic trace, a fast, which cannot be resolved, and a slower one. The slower kinetic component shows first order desorption kinetics. The Arrhenius activation energy (~ 0.8 eV) correlates to the binding energy of the molecularly chemisorbed state of NH$_3$. Both kinetic components show dependence on the surface temperature.



The upper panel of the figure shows an exemplary trace for 200 °C. One can observe the three mentioned components. In the bottom panel, one can see the different energy distribution for the three mentioned components. The direct-scattering component is marked with dots, the fast trapping-desorption component is marked with squares and the slow trapping-desorption component is marked with triangles. We added the Baule-limit for the incoming beam and the Baule-limit with vibrational excitation for the NH$_3$ umbrella mode.

At high incident energies, we observe a broad energy distribution of scattered ammonia, which might indicate substantial vibrational excitation of ammonia, previously observed by Bruce D. Kay *et al.* at Au(111).[2] Ammonia on Au(111) is a classic example for pure mechanical vibrational excitation. However, ammonia on gold does not have a chemisorption state, which is present on Pt(111). To investigate the influence of the chemisorption state on direct scattering, we plan to investigate the scattered ammonia with quantum state resolved laser techniques for determination of the vibrational state population.

[1] D. Harding *et al.*, *J. Chem. Phys.* **2017**, *147*, 013939.
[2] B. D. Kay, T.D. Raymond, M.E. Coltrin, *Phys. Rev. Let.* **1987**, *59*, 2792-2794.

Thermal recombination reactions on metal surfaces: Transition state theory with dynamical corrections

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Transition state theory (TST) is undoubtedly the most successful and widely employed theoretical approach for studying reaction rates of rare events at or near thermal-equilibrium conditions. However, there are some critical aspects of this theory that need to be improved in order to access to absolute rate constants theoretically. Just to name some, one one hand, TST is based on the Born-Oppenheimer approximation (BOA) so that it neglects electronic transitions. Although this approximation is well justified for gas phase reactions where electronic transitions require high amount of energy, there is clear evidence of low energy electronic excitations being created on gas-surface reactions. On the other hand, TST assumes that all trajectories passing through the transition state (TS) are successful, i.e, that they lead to the products. The mentioned weaknesses might be corrected by the so-called dynamic factor, which consist in integrating the trajectories from the TS forward and backward in time. To go beyond the BOA, non-adiabaticity might be introduced within the dynamics simulations, and therefore within the dynamic factor that corrects the TST constant rate. An accurate description of the electronic excitations is accomplished with *ab-initio* molecular dynamics with electronic friction (AIMDEF) method [4]. This method is based on the local density electronic friction approximation (LDFA) [5], which was shown to successfully model translational energy loss measurements for H colliding with Au(111) [6].

A model systems for which it appears likely that electronic coupling can influence reactivity is the recombinative desorption of H_2 on Au(111). We study this system by AIMD and AIMDEF simulations in order to rationalize the effect of electronic excitations. The surface temperature effects are also analyzed. In addition, we study the recombinative desorption of H_2 on Cu(111), for which two reaction mechanisms have been recently identified (fast and slow channels) [8]. While the former was well known and have been theoretically modeled successfully within “chemical accuracy”, the later has not been found in theoretical calculations. Several possible origins for this channel are discarded in this work.

[1] M. Born, et al. Ann Phys-Berlin 84, 0457-0484 (1927).
[2] Wijzenbroek, J. Chem. Phys. 145(14), 144701 (2016).
[3] E. Hasselbrink, Surf. Sci. 603, 1564-1570 (2009).
[4] D. Novko, et al. Phys. Rev. B, 92(20), 201411 (2015).
[5] J. I. Juaristi, et al. Phys. Rev. Lett. 100, 116102 (2008).
[6] O. Bünermann, et al. Science 350, 1346–1349 (2015).
[7] Q. Shuai, et al. J. Phys. Chem. Lett. 8(7), 1657-1663 (2017).
[8] S. Kaufmann, et al. J. Chem. Phys. 148(19), 194703 (2018).

Vibrational Excitation of HCl scattering from Ag(111) vs. Au(111): All Hail The King?

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Previous studies comparing the relaxation of vibrationally excited NO scattered from Au(111) and Ag(111) have shown that on the latter the survival probability is lower while the average vibrational energy loss is clearly higher.[1,2] Recent experiments in our group using CO as the probe molecule have revealed similar trends. Although vibrational excitation data for different surfaces is rare, early studies of NO($v = 0 \rightarrow 1$) excitation suggested that vibrational excitation is also stronger on Ag(111) and on Cu(110) than on Au(111).[3–5]

In light of the inferred connection between a surface's work function and the molecule's vertical electron binding energy on the one hand and the non-adiabatic interaction strength on the other hand, the $v = 0 \rightarrow 1$ excitation of HCl on Au(111) fell short of the expectations.[6,7] Thus, I have recently measured $v = 0 \rightarrow 1$ vibrational excitation probabilities for scattering HCl molecules from Ag(111) to compare them to the previously obtained data for Au(111). Will the interaction strength be in line with NO and CO this time? And will silver continue to be the champion of non-adiabatic interactions?

[1] B.C. Krüger, S. Meyer, A. Kandratsenka, A.M. Wodtke, and T. Schäfer, J. Phys. Chem. Lett. **7**, 441 (2016).
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Hydrogen oxidation on platinum – Revisiting the kinetics of a well-studied catalytic reaction

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A study on the CO oxidation on platinum carried out at the *Beamer II* apparatus in our group recently found that the mechanism of this extensively studied reaction is actually more complicated than previously assumed. The reaction of hydrogen and oxygen on a platinum catalyst has been studied over decades as well. However, a look in the literature reveals that although platinum’s ability to serve as a catalyst in this reaction has been known for a long time, the actual reaction mechanism is still controversial. In this experiment we use two pulsed molecular beams to dose a flat or a stepped Pt surface with oxygen (O_2) and probe the pre-covered surface with hydrogen (H_2). Catalytically formed water molecules that leave the surface are subsequently laser-ionized and detected via slice ion imaging in the *Beamer II* apparatus. Time-resolved collection of ion images allows the extraction of dynamic (angular and speed distributions) and kinetic information (velocity resolved kinetics).

Towards a generalized Effective Medium Theory formalism for H atoms interacting with metals surfaces.

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Recently, detailed theoretical and experimental investigations of energy transfer between hydrogen atoms and late *fcc* transition metal (111) surfaces have been made and on the basis of these experiments, it was possible to clarify the role of electron-hole pair excitation during the scattering process. [1-4] However, those investigative efforts excluded metals that tend to crystallize in other crystal structures, such as body centered cubic (*bcc*) and hexagonal close packed (*hcp*), because the theoretical methods in those investigations are based on Effective Medium Theory (EMT) [5], a theory that has been formulated to describe *fcc* metals and their alloys. Here, I present my first efforts to extend the EMT formalism to describe hydrogen atoms interacting with *bcc* metal surfaces. A hydrogen atom at a W(111) surface has been chosen to serve as a test system. In addition, I will briefly outline further research efforts that are planned in future.

[1] O. Bünermann, H. Jiang, Y. Dorenkamp, A. Kandratsenka, S. M. Janke, D. J. Auerbach, and A. M. Wodtke, *Science*, 2015, **350**, 1346-1349.
[2] S. M. Janke, D. J. Auerbach, A. M. Wodtke, and A. Kandratsenka, *J. Chem. Phys.*, 2015, **143**, 124708.
[3] M. Kammler, S. M. Janke, A. Kandratsenka, and A. M. Wodtke, *Chem. Phys. Lett.*, 2017, **683**, 286-290.
[4] Y. Dorenkamp, H. Jiang, H.-J. Köckert, N. Hertl, M. Kammler, S. M. Janke, A. Kandratsenka, A. M. Wodtke, and O. Bünermann, *J. Chem. Phys.*, 2017, *submitted.*
[5] K. W. Jacobsen, P. Stoltze, and J. K. Nørskov, *Surf. Sci.*, 1996, **366**, 394-402.

Threshold Energy and Dynamics of C-H[D] bond Formation on Epitaxial Graphene at Zero Surface Coverage

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Alec M. Wodtke[1,2] , Oliver Bünermann[1,2]
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2. Dept. Dynamics at Surfaces, Max-Planck-Institut für biophysikalische Chemie, Am Faßberg 6, 37077, Göttingen

C-H bond formation on graphene is highly relevant in many research fields and has been intensively studied for decades. However, two key aspects of the adsorption are still experimentally not known, one which is the adsorption threshold and another which is the energy dissipation characteristics of the newly formed C-H bond. We present experiments on H atom scattering from epitaxial graphene under zero surface coverage. Two separated scattering channels are observed, corresponding to scattered atoms that fail and succeed in crossing the adsorption barrier. Together with ab initial molecular dynamics simulations, we show that scattered H atoms that succeed in crossing the barrier lose on average 1 eV energy [half of its incidence energy] in one vibrational period of C-H stretch, pointing to an extremely fast energy dissipation mechanism. Utilizing the dependence of the scattering on the normal incidence energy, the thresholds for initial adsorption are determined.

Different levels of Theory can describe Hydrogen atom scattering from Graphene

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The scattering of hydrogen atoms from quasi free-standing graphene has recently been experimentally investigated in our group [1]. A few hundreds of *ab initio* molecular dynamics (AIMD) simulations were sufficient to elucidate the mechanism by which the incident particles can lose a large portion of their initial kinetic energy during a single collision. Due to the high computational cost, significant statistics in terms of energy loss and angular distributions cannot be obtained via AIMD which would be necessary to compare to experiment.

Based on dispersion-corrected DFT calculations at the GGA level, we constructed two global potential energy surfaces intended for use in MD simulations. One is a parametrized version of the 2nd generation reactive empirical bond order potential (REBO) [2] and the other one is a neural network using atom-centered symmetry functions [3]. Furthermore, another REBO potential was fitted to energies stemming from a hybrid functional/LDA description of the system via the embedded mean-field theory [4].

This talk will focus on similarities and differences between the *ab initio* methods which serve as a basis for fitting the MD potentials. Subsequently, the pros and cons of the global analytical PESs will also be compared to one another and finally, simulations and experimental data will be contrasted.

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Generation of sub-ns H-atom pulses: current limitations and future prospects

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Pump-Probe experiments are conducted routinely in physics, chemistry and biology to study dynamical processes. Such experiments require intense pulses shorter than the dynamic timescales involved. Light pulses easily fulfill these conditions, but chemical reactions are generally initiated by collisions of *matter*. Methods for the generation of matter pulses exist, but their performance is significantly inferior to generation of light pulses. For the specific case of neutral H-atoms the method of bunch-compression photolysis has been demonstrated to improve the duration of matter pulses down to few nanoseconds[1]. Here, we present an approach to implement this method to generate pulses down to <500 ps duration. With these pulses we plan to study the surface dynamics of selected systems. The temporal characterization of such short matter pulses also requires completely new experimental techniques, which remain to be tested, too.

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Why can we use the “simple Baule model” to explain translational inelasticity in diatomic molecule-surface scattering?

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The translational inelasticity in diatomic molecule-surface scattering has been extensively studied for systems like NO/Au(111) and NO/Ag(111). For these systems the translational inelasticity in direct scattering is found to be well described by considering the scattering process as the collision between the projectile with the mass m and the surface atom with the mass M both described by hard spheres. In the case of a collision with normal incidence the final translational energy of the molecule is given by $\frac{(M-m)^2}{(M+m)^2}$ times the incidence translational energy. The good agreement with experimental data is striking. In a real collision the molecule has to be accelerated by the molecule-surface attraction (desorption energies determined by temperature-programed desorption are as high as 0.25 eV) causing a deviation from the prediction of the simple model which should be measurable. As an explanation why this is not observed often effects of the molecule´s orientation are discussed. I would like to discuss with you at my poster if this is plausible and I am looking forward to your ideas.

Hydrogen atom scattering from low temperature surfaces

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Hydrogen atom adsorption at metal surfaces is arguably the simplest reaction in surface chemistry. To adsorb, the H atom must lose its initial translational energy and come to rest at the surface. Because of its light mass, energy and momentum conservation requires that the transfer of translational energy from the H atom to heavy surface atoms is inefficient.

However, it has been shown through scattering experiments that H atom adsorption at metal surfaces involves the conversion of translational energy from the H atom to electronic excitation of the solid. H atoms that are scattered from metal surfaces at room temperature possess a broad and structureless energy loss distribution. Theoretical simulations including electronic excitations can reproduce these findings. Furthermore, the simulations predict that for low surface temperatures ($T \leq 120$ K) several peaks in the energy loss distribution become discernible. In experiment, however, measurements at low surface temperatures are difficult to perform because of the rapid build-up of adsorbate layers. Using our present setup, a Au(111) surface begins to be covered with water in less than five minutes. However, first results of inelastic H-atom scattering from a cold and clean Au(111) surface, as well as those of an adsorbate covered surface, will be presented.

Kinetic Monte Carlo Simulations of Vibrational Energy Pooling in a CO Monolayer on NaCl(100)

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Superconducting nanowire single photon detectors (SNSPDs) have recently been applied to laser-induced infrared fluorescence (LIIF) spectroscopy of adsorbed molecules.[1,2] Their superior sensitivity allows to measure dispersed infrared fluorescence from a CO monolayer on NaCl(100) after excitation of v=1 with a nanosecond laser. While only total fluorescence from this system has been detected with conventional InSb detectors,[3] we were able to measure the temporal evolution of CO in v=4 to 25, populated by vibrational energy pooling, with microsecond resolution.

Using kinetic Monte Carlo simulations, semi-quantitative agreement with the experimental data is obtained. The vibrational energy pooling rate constants are calculated based on a theoretical model introduced by Corcelli and Tully.[4] Several aspects of the model have been refined: The most important extension is to consider interactions over distances of several lattice constants in order to explain population of high vibrational states above v=10. Furthermore, a realistic density of states for the surface phonons of NaCl, also including mode-specific coupling, is used. Combining the highly detailed experimental data and the kinetic simulations provides a profound understanding of the mechanism for vibrational energy pooling in the condensed phase.

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Scattering of highly vibrationally excited NO from thin film VO_2 surfaces

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Vanadium oxides are among the most used heterogeneous catalysts in industrial applications. Vanadium dioxide (VO_2) is also of interest for the understanding of general interactions between surfaces and gas molecules. It shows a Mott transition at 68°C, at which it changes its electrical properties from insulating to conducting.[1] Hence, it provides an adjustable band gap to probe non-adiabatic effects governing vibrational energy transfer between molecules and surfaces.[2,3] This work presents the preparation of VO_2 thin films in a chemical vapor deposition process and subsequent molecule surface scattering experiments.

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Multiconfiguration Time-Dependent Hartree (MCTDH): A powerful method for propagating multi-dimensional wave packets

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The MCTDH algorithm [1-5] is introduced and its multi-layer extension (ML-MCTDH) is briefly discussed. The performance of the MCTDH method is demonstrated by example applications of MCTDH and ML-MCTDH. We shall discuss photo-electron spectra, infra-red absorption spectra, and molecule-surface scattering.

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Vibrational excitation of NO scattered from Au(111): Filling the gap between solid and liquid surfaces

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Direct vibrational excitation of small molecules during a surface collision has been investigated for a long time. Rettner *et al.*[1] found a strong surface temperature dependence of the excitation probability when scattering NO from Ag(111) and used an electronic hole-pair mechanism as the explanation. An Arrhenius like surface temperature dependence was observed for vibrational excitation of NO/Au(111)[2]. These measurements were published up to a surface temperature of 1100 K. Recent experiments from the Nesbitt group for scattering NO from liquid gold seem to agree well with the observed surface temperature dependence at solid surfaces.[3]

In the work presented here, we show measurements of N scattered from solid Au(111) at temperatures close to the metal's melting point. With these measurements we fill the gap between the studies at the solid surfaces[2] and the measurements on liquid gold.[3] We observe excitation probabilities from NO(v=0) to NO(v=1) that seem to increase continuously during the phase transition from the solid to the liquid surface.

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Picosecond-IR-Multiphoton Desorption of H2 from a Hydrogen Terminated Si(100) Surface

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For the investigation of activated reactions on the surface of a semiconductor the most established and well-studied system is the adsorption / desorption of hydrogen on silicon.[1,2] The desorption of H2 from the silicon surface induced by TPD and laser heating is well understood.[3-6] On the other hand, the nature of hydrogen desorption induced by resonant IR excitation of the Si-H stretch-vibration remains unclear and the only reported evidence by Liu et al.[7] has been retracted afterwards.[8]

In an attempt to resolve the mechanism we have found desorption of H2 from a H-terminated Si(100)/H:2x1 surface induced by non-resonant IR absorption from a ps-pulse. The desorbing H2 flux is ionized by (2+1) REMPI via the E, F state and detected by a Multi-Channel Plate. Our preliminary results include quantum-state specific data obtained by scanning the wavelength of the IR pulse or the delay of the REMPI laser pulse.

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Multiphoton Photoelectron Circular Dichroism (MP-PECD) with nanosecond lasers: Resolving effects of the intermediate state

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There is a huge drive to develop heterogeneous catalysts for asymmetric chiral synthesis, which motivates the development of chiral-sensitive spectroscopic techniques, capable of determining enantiomeric excess under UHV molecular beam scattering conditions. Arguably the most sensitive technique is Photoelectron Circular Dichroism (PECD), which measures the forward/backward asymmetry in photoelectrons that are emitted when a chiral molecule is photoionized by circularly polarized light. In a 2+1 Resonance-Enhanced Multiphoton Ionization (REMPI) experiment via the n=3 Rydberg states of fenchone, we demonstrate for the first time that this technique can be performed with nanosecond dye lasers, which brings down the cost by ~2 orders of magnitude. We investigate the dependence of the effect on the electronic and vibrational state used as the REMPI intermediate.

On molecule-surface encounters beyond NO/Au(111)

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NO/Au(111) is perhaps one of the best studied systems that contributed a great deal to our understanding of electronically nonadiabatic influences in gas-surface dynamics [1]. These experiments indicate that energy can be channeled very efficiently from molecular vibration to the electron-hole-pairs of the solid (V-EHP coupling) [1].However, the necessity to make connection between the insights inferred from gas-surface dynamics experiments and heterogeneous catalysis and to gain understanding concerning the importance of electronically nonadiabatic coupling for surface chemistry, calls to take a detailed look to broader scope of collision partners (both gas phase projectiles and surfaces).

One such system is CO/Au(111), where we have shown that CO (v = 1) survives on a Au(111) surface for ~ 100 ps. Such long vibrational lifetimes for adsorbates on metal surfaces are unexpected and pose an interesting challenge to the current understanding of vibrational energy dissipation on metal surfaces [2]. They also suggest that vibrational promotion of Langmuir-Hinshelwood type surface chemistry on metal surfaces might be more common than is generally believed.

Another aspect, concerns extending the experiments yielding basic understanding of molecule-surface dynamics from single crystals of inert metals to catalytic surfaces. Vanadium dioxide, VO_2(M), is of special interest in this respect - as a surface which exhibits sharp transition from insulator to metal at 68^{o}C (Mott transition), a property, expected to have dramatic influence on propensity of V-EHP coupling, which bears on the dissipation of the energy stored in vibrational degrees of freedom of the molecule to the surface, and, eventually on the ability of the molecule to undergo dissociative adsorption. Very recent results on encounters of vibrationally excited NO and electronically excited CO with CVD and PVD fabricated VO_2(M) surfaces will be highlighted.

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Absorption and emission properties of monolayers and multilayers of CO on NaCl(100)

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Recently, laser-induced infrared fluorescence spectra from $^{13}C^{18}O$ multilayers on NaCl(100) have been measured in our group[1]. From a similar experiment after overtone excitation ($\Delta v=2$) of $^{12}C^{18}O$ in a CO multilayer sample with natural abundance, the fluorescence rate constants of the heavy isotopologues could be extracted. Considering local field effects [2],[3] CO in the multilayer structure shows a transition dipole moment similar to CO in the gas phase. Therefore, it would be of interest to compare CO in the monolayer and multilayer structure and to determine the transition dipole moment of the multilayer in absorption. For that purpose we plan to set up the following experiment.

The CO layers on the NaCl(100) surface will be prepared using molecular beam dosing. Compared to dosing with a leak valve, for example, molecular beam dosing provides more defined dosing conditions advantageous for desorption experiments at cryogenic temperatures. The monolayer and the multilayer will then be characterized by FTIR spectroscopy and temperature programmed desorption (TPD) will be used to determine the relative coverage of monolayer to multilayer. Combining the FTIR and the TPD results it is possible to calculate the absorption cross section of CO in the monolayer and multilayer and thus to derive the transition dipole moments directly.

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Making Sense of Coulomb Explosion Imaging

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Coulomb explosion is one of the most fascinating violent processes of molecular fragmentation. Removal of multiple electrons from an isolated stable molecule typically culminates in separation of the excess charges that are strongly repelled by the long range Coulombic repulsion. Assuming purely Coulombic interactions between the charged products of a Coulomb explosion suggests a possibility of direct reconstruction of the instantaneous molecular structure by coincidence imaging of all the cationic fragment momenta. Thus, when combined with ultrafast laser pulses, Coulomb explosion imaging can provide a unique time resolved viewpoint into ultrafast structural dynamics. However, reliable interpretation of Coulomb explosion measurements for polyatomic systems requires both control of the multiple ionization process itself and a detailed understanding of the molecular dynamics that follow, beyond the Coulombic approximation. I will present our recent advances in performing and understanding single-photon Coulomb explosion Imaging of isolated polyatomic molecules, using ultrafast EUV pulses that are produced by high-order harmonic generation (HHG).

Two very different views of dynamics at metal surfaces: surface hopping vs electronic friction

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I will review the two different theories of dynamics at metal surface, one based on weak metal-molecule interactions, the other based on slow nuclear velocities. I will also show how one can extrapolate between these two different theories. In this talk, I will address both vibrational relaxation as well as the possibility of electron transfer. Finally, time permitting, I will show one perverse result highlighting that it can sometimes be very difficult to distinguish between the surface hopping and electronic friction mechanisms.

Implementation of an x-ray photoelectron spectrometer to a surface scattering apparatus

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X-ray photoelectron spectroscopy (XPS) is an ideal method to characterize surfaces. It goes beyond Auger electron spectroscopy AES), so that you cannot only characterize your surface, but can also receive information about your chemical bonding properties. A further advantage of the XPS is, that you can analyze your surface almost damage free, so you don't change your chemical properties of your surface.

During my Bachelor project I have installed an XPS System (Staib) to the surface scattering machine in the Stark Lab. We measured XPS spectra from carbon on Au(111) dependend on the distance to the surface and optimized the experimental geometry. Due to safety restrictions we further modified the experimental setup so that the machine can now be controlled remotely from a desk located in the next room.

A molecular beam-surface scattering study using CO(v = 17)

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The NO/Au(111) system serves as a benchmark system for the detailed study of electronically non-adiabatics dynamics in molecular beam-surface scattering experiments. The experiments suggest that the vibration of the molecule can be excited or de-excited during the collision via coupling to electron-hole-pairs of the solid. These electronically non-adiabatic processes are thought to proceed via an electron transfer from the surface to the molecule forming a transient anion. Since highly vibrationally excited molecules may have an increased vertical electron binding energy, non-adiabatic interactions may become the dominant energy transfer channel at surfaces. Extending the existing work on NO, we succeeded in producing highly vibrationally excited CO in a molecular beam, which is scattered from both metal and insulator surfaces. The comparison of different molecule/surface systems confirms the hypothesis that an electron transfer drives the vibrational de-excitation of small molecules at surfaces. The vibrational relaxation probability clearly depends on the work function of the surface and the vertical electron binding energy of the molecule. Both quantities govern the energetics of the electron transfer reaction. The presented work on highly vibrationally excited CO comprises state-to-state time-of-flight distributions, angular distributions, final rotational state distributions, and final vibrational state distributions for a variety of different incidence translational energies.

Towards a complete model of bond orientation in the inelastic scattering of NO(X) with Ar

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Traditionally, orientation of a molecular bond axis prior to a collision event has focused on the geometry in which collisions occur specifically along one bond or another (an ‘end-on’ collision); for the diatomic NO(X), studied here, this corresponds to collisions at the `N-end’ or `O-end’ of the molecule. There is, of course, the possibility for collisions with the `side’ of the molecule, i.e. when the bond axis is oriented parallel to the incoming collision partner. Whilst it is perhaps not initially obvious that collisions with one ’side’ or another will result in different outcomes, such collisions exhibit a pronounced steric asymmetry. A full experimental and theoretical analysis of both `end-on’ and `side-on’ collisions seeks to unravel the origins of these effects, which are largely quantum mechanical in nature.

Towards photoionization of chiral molecules

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This talk is going to be a progress report on the ongoing measurements at the compact beamer. A brief introduction on the principles of measurement will be given and some of our measurements will be shown.

In this machine a ultra-high vacuum (UHV) chamber is equipped with two nozzles for supersonic molecular beams. One of them contains a heatable reservoir for molecular beams with slow-evaporating organic molecule and a carrier gas. Within the UHV-Chamber a sample holder – equipped with Ag(111) – is installed as well as a Ar^+-sputter gun and a mini-Auger-spectrometer. In the trajectory of the molecular beams an imaging detector is set-up to detect electrons or ions after photoionization of the target molecules. With this set-up experiments were undertaken like:

- - Xenon ionization as a reference measurement (E_{kin} of photoelectrons and velocity mapping)
- Reproduction of the photoelectron circular dichroism (PECD) effect on (+)Fenchone
- Imaging Dynamics of backscattered/trapping and desorption of NO
- Scattering of Benzene on the Ag-surface

Future experiments will combining these methods like:
- Can a PECD-effect be seen on (R)- and (S)-styrene oxide?
- What happens after trapping and desorption on a achiral and chiral Ag-surface?
- Can styrene be oxidized on a Ag-surface?

Concepts for detecting reaction intermediates in surface reactions.

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Knowledge of elementary chemical reaction mechanisms in heterogeneous catalysis is fundamentally important. Such knowledge underlies our ability to construct comprehensive kinetic models of many industrially important systems. This is complicated by the fact that many catalysts exhibit multiple reaction sites and diffusion allows them to be accessed on a rapid time scale. Recently, new methods have become available that begin to push back the veil of darkness on these issues. For example, we now understand quantitatively how CO oxidation on Pt involves reactions at terraces and steps and the elementary reaction mechanism has been elaborated. This was possible due to methods that sensitively probe the reaction products that have desorbed into the gas phase, allowing clear inferences to be made about the processes taking place on the surface. It is clearly important to take the next step and follow reactants and intermediates directly on the surface. Especially for detecting reaction intermediates, high sensitivity is needed as they are likely to be present at small concentrations. Methods like transient infrared absorption (TIR) and sum frequency generation (SFG) have been around for some time, but they suffer from poor sensitivity. In this talk, I will present ideas about how laser-induced-desorption might be used to develop super sensitive detection methods for surface adsorbates.

Controlled Growth of Uniform and High-density Monolayer WS_2 Layers on Sapphire

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We would like to explore how short-lived electronic excitations in the solid state can influence collisional dynamics, a direction of non-Born-Oppenheimer dynamics that has yet to be explored. Semiconductors are clearly the place to start this type of work as lifetimes of excited electronic states of semiconductors are often on the time scale of our H-atom pulse or longer. Unfortunately, traditional semiconductors like Si present problems. They may not have significant coupling to the H-atom, which is interacting at the surface. This is further complicated by the fact that Si surfaces have dangling bonds and must be passivated - often they are passivated by an oxide Another problem arises from the fact that Silicon is an indirect band-gap semiconductor, meaning optical transitions are nominally forbidden. The bulk layered materials are indirect band-gap semiconductors; however, inversion symmetry is broken in the monolayer and many transition metal dichalcogenides (TMDs) become direct band-gap semiconductors; they, therefore, interact strongly with light. Choosing monolayers of tungsten disulfide (WS_2) is a particularly interesting way to overcome these problems. WS_2 is a promising material for future nanoelectronics and optoelectronics. It has remained a great challenge to grow uniform and high surface coverage monolayer WS_2. In this work, we synthesize monolayer WS_2 under various controlled conditions and characterize the monolayer using photoluminescence. We demonstrate that the introduction of hydrogen to the argon carrier gas improves the optical quality and increases the growth area of WS_2, resulting in films exhibiting high density. The addition of hydrogen more effectively reduces the WO_3 precursor and protects against oxidative etching of the synthesized monolayers. It should be noted that great care is taken to position the WO_3 thin film precursor, substrates, and the sulfur source at identical positions for each growth, as the positioning may affect the growth dynamics and resulting film quality. These results demonstrate a strong sensitivity to sample preparation that is important for both a fundamental understanding of these novel materials as well as a reliable reproduction of device properties

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