

SCHLOSS RINGBERG

May 15 to 18, 2019

Symposium on Dynamics at Surfaces



For the participants arriving by train at Tegernsee station, we recommend to use a taxi from the train station towards the castle [Taxi Kaufmann](#) phone **+49 (0)8022 / 5555**.

Wednesday May 15th	
16:00-18:00	Arrival and registration
18:00-20:00	Dinner
20:00-21:00	Prof. Dr. Daniel J. Auerbach: <i>Bolometers in Surface Science</i>
21:00-	Poster Session I
Thursday May 16th	
08:00-8:45	Breakfast
<i>Session Chair:</i> Prof. Dr. Theofanis Kitsopoulos	
8:45-9:00	Prof. Dr. Alec Wodtke: <i>Welcoming Remarks</i>
9:00-10:00	Prof. Dr. Bas van de Meerakker: <i>Taming molecular collisions</i>
10:00-10:30	Coffee Break
10:30-11:30	Xuecheng Tao: <i>Microcanonical rates from ring polymer molecular dynamics: direct-shooting, stationary-phase, maximum-entropy approaches</i>
11:30-12:00	Prof. Dr. Dirk Schwarzer: <i>The vibrational lifetime of a molecule physisorbed on a metal surface</i>
12:00-13:30	Lunch Break
<i>Session Chair:</i> Dr. Tim Schäfer	
13:30-14:30	Prof. Dr. Liv Hornekaer: <i>Inducing strong graphene-metal interactions via chemical functionalization</i>
14:30-15:00	Dr. Oliver Bünermann: <i>Hydrogen atom adsorption on surfaces studied in scattering experiments</i>
15:00-15:30	Coffee Break
15:30-16:00	Nils Hertl: <i>H atom scattering from W(110) at low surface temperatures</i>
16:00-16:30	Georg Westphal: <i>Towards photoionization of chiral molecules Part 2</i>
16:30-17:00	Jan Altschäffel: <i>Scattering of highly vibrationally excited CO & NO from noble metal surfaces: An AIMD study</i>
17:00-17:30	Prof. Dr. Pranav Shirhati: <i>Neutral atom/molecule – surface scattering; A soft and universal probe for surfaces</i>
17:30-18:00	
18:00-20:00	Dinner
20:00-	Poster Session I

Friday May 17th	
8:00-9:00	Breakfast
<i>Session Chair:</i> Dr. Sascha Kandratsenka	
9:00-10:00	Prof. Dr. Igor Rahinov: <i>Smart synthesis of nano-materials from the gas phase</i>
10:00-10:30	Coffee Break
10:30-11:00	Dr. Kai Golibrzuch: <i>Towards generation of high intensity sub-ns H atom pulses for study of ultra-fast gas-surface interactions</i>
11:00-11:30	Dima Borodin: <i>Active and Passive Contribution of Atomic Defects towards the Reactivity of NH₃ at Platinum Surfaces</i>
11:30-12:00	Artur Meling: <i>Scattering of NO from thin film VO₂ surfaces</i> RAT Group
12:00-13:30	Lunch Break
<i>Session Chair:</i> Prof. Dr. Dirk Schwarzer	
13:30-14:00	Dr. G. Barratt Park: <i>The quantum-state resolved lifetime of triplet (\tilde{a}^3A_2) formaldehyde</i>
14:00-14:30	Hinrich Hahn: <i>Platinum catalysed hydrogen oxidation dominated by OH recombination</i>
14:30-15:00	Jascha Lau: <i>Reorientation of Physisorbed CO Molecules Induced by Vibrational Energy Pooling</i>
15:00-15:30	Coffee Break
15:30-16:00	<i>Free Time</i>
16:00-16:30	<i>Free Time</i>
16:30-17:00	<i>Free Time</i>
17:00-17:30	<i>Free Time</i>
17:30-18:00	<i>Free Time</i>
18:00-20:00	Dinner
21:00-	Poster Session II

Saturday May 18th	
8:00-9:00	Breakfast
09:15	Departure

ABSTRACTS

(talks)

Bolometers in Surface Science

Daniel J. Auerbach

Bolometers are devices that measure temperature changes due to incident radiation with extraordinary sensitivity. They have applications in many fields including IR spectroscopy, Astronomy, Particle Physics, Thermal Cameras, and Surface Science. I will concentrate on the applications of bolometers in surface science. Early surface scattering experiments with He and H and other atoms and molecules made use of bolometers to provide sensitive, simple detection systems. Bolometers are used in micro calorimetry experiments where the heat of adsorption of molecules are measured. Bolometers provide a state specific detection technique when combined with IR lasers for tagging molecules. This application will be the main focus of my talk. I will describe work underway in Rainer Beck's group in Lausanne, Switzerland to develop a new surface scattering instrument using Bolometer IR tagging for state to state scattering of polyatomic molecules.

Taming molecular collisions

Sebastiaan Y.T. van de Meerakker

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The study of molecular collisions with the highest possible detail has been an important research theme in physical chemistry for decades. Over the last years we have developed methods to get improved control over molecules in a molecular beam. With a Stark or Zeeman decelerator, a part of a molecular beam can be selected to produce bunches of molecules with a computer-controlled velocity and with longitudinal temperatures as low as a few mK. The molecular packets that emerge from the decelerator have small spatial and angular spreads, and have almost perfect quantum state purity. These tamed molecular beams are excellent starting points for high-resolution crossed beam scattering experiments.

I will discuss our most recent results on the combination of Stark or Zeeman deceleration and velocity map imaging. The narrow velocity spread of decelerated beams results in scattering images with an unprecedented sharpness and angular resolution. This has facilitated the observation of diffraction oscillations in the state-to-state differential cross sections for collisions of NO with rare gas atoms^{1,2}, the observation of scattering resonances^{3,4} at temperatures below 1 K revealing the influence of individual partial waves to the scattering dynamics, and product-pair correlations for bimolecular scattering processes⁵.

References

- [1] A. von Zastrow et al., *Nature Chemistry* **6**, 216, (2014).
- [2] J. Onvlee et al., *Nature Chemistry* **9**, 226, (2017).
- [3] S. Vogels et al., *Science* **350**, 787, (2015).
- [4] S. Vogels et al., *Nature Chemistry* **10**, 435, (2018).
- [5] Z. Gao et al., *Nature Chemistry* **10**, 469, (2018).

Microcanonical rates from ring polymer molecular dynamics: direct-shooting, stationary-phase, maximum-entropy approaches

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We address the question of how to calculate microcanonical rates for processes involving significant nuclear quantum effects using ring-polymer molecular dynamics (RPMD), both with and without electronically non-adiabatic transitions. The shortcomings of the naive direct-shooting method, in which the temperature of the internal ring-polymer modes is set to a translational energy scale, are first illustrated. Several strategies are then employed to take advantage of the expression for the RPMD microcanonical rates in terms of the inverse Laplace transform of the thermal reaction rate. It is shown that a simple application of the stationary-phase approximation (SPA) dramatically improves the performance of the microcanonical rates using RPMD, particularly in the low-energy region where tunneling dominates. Using the SPA as a Bayesian prior, numerically exact RPMD microcanonical rates are then stably obtained using maximum entropy inversion of the thermal reaction rates, for both electronically adiabatic and non-adiabatic model systems. Finally, the direct-shooting method is revisited using the SPA-determined temperature for the internal ring-polymer modes, leading to a simple, direct-simulation method with greatly improved accuracy in the low-energy tunneling region.

Keywords: microcanonical reaction rate, ring polymer molecular dynamics, nuclear quantum effects, inverse Laplace transform

The vibrational lifetime of a molecule physisorbed on a metal surface

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Measured relaxation lifetimes of vibrationally excited diatomics chemisorbed on metal surfaces are typically 1-3 *ps*; however, no data is available for physisorbed molecules. We report real-time measurements of the lifetime of CO($v=1$) adsorbed on a Au(111) surface applying the pump-probe sum frequency generation (SFG) technique. We measure a vibrational lifetime of 49 ± 3 *ps*. This confirms recent molecular beam experiments that reported trapping and subsequent desorption of vibrationally excited CO on Au(111). We conclude that vibrational lifetimes of physisorbed molecules on metals can be much longer than those of chemisorbed molecules.

Inducing strong graphene-metal interactions via chemical functionalization

Liv Hornekaer

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Chemical functionalization of graphene on metal substrates is strongly influenced by graphene-substrate interactions. Such interactions have been shown to result in periodic functionalization structures [1] of use for controlling graphene electronic properties, increased graphene-metal interactions [2] for enhanced coating performance, novel adsorption configurations [3] and even dissociative adsorption of molecules [4]. The exact behavior is dependent on both the type of metal substrate and on the degree of functionalization. An overview of the literature and recent results will be given.

1. Richard Balog et al. *Nat. Mat.* 9, 315 (2010); J. H. Jørgensen et al., *ACS Nano* **10**, 10798 (2016)
2. L. Kyhl, R. Balog, A. Cassidy, J. Jørgensen, A. Grubisic-Čabo, L. Trotochaud, H. Bluhm, L. Hornekær, *ACS Applied Nano Materials* 1, 4509 (2018)
3. A. Cassidy, S. Pedersen, H. Bluhm, V. Calisti, T. Angot, E. Salomon, R. Bisson and L. Hornekær, *Phys. Chem. Chem. Phys.* 20, 28370 (2018); Novotny et al., *JACS* 140, 5102 (2018); Jung et al., *JACS* 136, 8528 (2014)
4. L. Kyhl et al., *ACS Nano* 12, 513 (2018)

Hydrogen atom adsorption on surfaces studied in scattering experiments

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Hydrogen atoms can have very large sticking probabilities on certain surfaces; a prominent example is the high sticking probability of hydrogen atoms on metals. This observation is surprising: The kinetic energy as well as the binding energy have to be transferred to the surface efficiently to establish a bond, but due to the low mass of the hydrogen atom only limited energy transfer to lattice vibration is possible. Complex scattering mechanisms or additional dissipation channels could explain the observations. In scattering experiments, we can measure the amount of energy a hydrogen atom loses in a surface collision. Based on such experiments, a theoretical model can be developed and verified that gives us an atomic scale picture of the adsorption process. In the metal case, we could show that the adsorption process involves multiple collisions and that most of the energy is transferred to electron-hole-pair excitations [1].

Another system in which we observe a surprisingly high adsorption probability for hydrogen atoms is graphene. For a C-H bond to form, the delocalized electronic structure of graphene has to be locally destroyed, giving rise to an adsorption barrier. For low translational energies, the hydrogen atom cannot pass the barrier and is elastically reflected. However, for sufficient translational energy, the atom can pass the barrier and a large amount of energy is lost in the collision. Reason is a very rapid energy redistribution from the transient covalent C-H bond into the graphene modes [2]. In our experiments, graphene is grown on metal substrates. We studied the substrate effect comparing platinum and nickel. Furthermore, we can perform experiments with the heavier isotope deuterium to study the isotope effect. Surprisingly, only a minor isotope effect is observed.

[1] O. Buenermann et al., *Science* 350, 1346-1349 (2015)

[2] H. Jiang et al., *Science* 364, 379-382 (2019)

H atom scattering from W(110) at low surface temperatures.

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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] Furthermore, calculations for H on Au(111) at low temperatures predict a clear distinction of different scattering events.[5] Those investigative efforts, however, excluded metals that crystallise in other crystal structures, because the theoretical methods in those investigations are based on Effective Medium Theory (EMT) [6], a theory that has been formulated to describe *fcc* metals and their alloys. In this talk, I present my first efforts to extend the EMT formalism to describe H atoms interacting with *bcc* metal surfaces. The obtained energy formula is fitted to DFT energies for H atoms at W(111). The obtained global EMT-PES is used to perform molecular dynamics simulations to investigate of how the scattering dynamics between H atom and metal surface is affected by the crystal structure and surface temperature.

- [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.*, 2018, **148**, 034706.
- [5] S. M. Janke, PhD thesis, Georg-August-Universität Göttingen, 2016.
- [6] K. W. Jacobsen, P. Stoltze, and J. K. Nørskov, *Surf. Sci.*, 1996, **366**, 394-402.

Towards photoionization of chiral molecules Part 2

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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.

After showing last time that Scattering Experiments of Benzene at Ag-surfaces and PECD-Experiments worked with our homebuild machine – “compact beamer” -, the project of scattering of chiral molecules started. Using styrene oxide and an Ag (111)-surface as the sample system a unexpected behavior was discovered.

With different experimental approaches we're just starting to get to the bottom of the reactivity of styrene oxide.

Used methods and equipment:

- *Kinetic trace experiments*
- *Temperature programmed desorption*
- *Ion imaging*
- *Mass resolved ion detection*
- *ns-dye-Laser*
- *fs-Laser with tunable wavelength*

Future experiments:

- *PECD-effect of styrene oxide*
- *What happens after desorption from Ag(111) or Ag(643)/Ag(-6-4-3)*

Scattering of highly vibrationally excited CO & NO from noble metal surfaces: An AIMD study

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Non-adiabatic effects can play an important role in scattering of diatomics from metal surfaces. This was shown for the system NO/Au(111) [1-2] and more recently for highly vibrationally excited CO scattered from Au(111) & Ag(111) [3-4].

To validate that assertion, we carried out *ab initio* molecular dynamics simulations of scattering of CO($v=17, 22$) & NO($v=16$) from Au(111) and Ag(111). The calculations show that vibrational energy of CO($v=22$) & NO($v=16$) is transferred mostly to the molecular translational and rotational degrees of freedom. A good agreement between experiment and the theory is seen in the translational energy distribution for vibrationally elastic scattering of CO($v=17$) as well as in the scattering angle distribution.

So, adiabatic effects govern the vibrational-translational and vibrational-rotational energy exchange.

The comparison of the experimental and calculated vibrational state distributions shows the importance of accounting for non-adiabatic effects (coupling to the electron-hole pairs). No evidence for molecular dissociation is observed, even for CO($v=22$).

[1]: N. Bartels et al., *Angew. Chem. Int. Ed.* 53, 13690, **2014**.

[2]: R. Cooper et al., *Angew. Chem. Int. Ed.* 51, 4954, **2012**.

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

[4]: R. V. J. Wagner et al., *PCCP* 21, 1650-1655, **2019**.

Neutral atom/molecule – surface scattering

A soft and universal probe for surfaces

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Low energy (thermal) neutral atom/molecular scattering is a promising candidate for developing surface imaging methods offering several unique advantages. In this talk I will discuss our ongoing efforts towards this goal. I will describe the essential concepts involved and highlight the unique features of such an imaging tool. Thereafter, I will focus on the current state of developments with an emphasis on the challenges involved in developing this as a practically useful technique.

One of the key bottlenecks identified is that of preparing atomic/molecular beams with as large intensity as possible, within the constraints imposed by vacuum systems. I will describe our efforts to overcome this hurdle by two approaches, namely (1) Utilizing the ‘mass focusing effect’ in seeded atomic/molecular beams (2) preparing cluster beams. Here, I will describe our recent measurements of angular distribution of seeded atomic beams (Ar + He), measured over a range of stagnation pressures and seeding ratio. Our results show that the mass focusing effect indeed provides narrowing of the angular distribution of the heavier component (Ar), however the enhancement in intensity is not large enough to compensate for decrease in the intensity caused by using dilute mixtures. I will conclude by discussing the idea of using cluster beams to enhance the atomic/molecular beam intensity and the possibility of obtaining sub – 100 nm spatial resolution using this technique.

Smart synthesis of nano-materials from the gas phase

I. Rahinov

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Flame-assisted synthesis of nanomaterials is receiving rapidly growing attention for its capability to produce high-purity nanoparticles of almost all elements in single-step processes and at moderate cost. Production of the nanoparticles with tailored properties by flame-assisted synthesis should rely on detailed understanding of the mechanisms governing their formation and nucleation from the gas phase. Well-defined experiments able to make direct contact with simulations are important prerequisite to elucidating the mechanistic details of particle formation[1,2]. Here we present our recent work comprising experiments and simulations for the synthesis of iron oxide nanoparticles from premixed iron-pentacarbonyl-doped hydrogen/methane/oxygen flat flames[3-5]. The experiments apply molecular-beam sampling with a particle mass spectrometer to measure particle sizes and a quartz microbalance to detect the presence of condensed matter[1]. Laser-Induced Fluorescence (LIF) and Intracavity Laser Absorption Spectroscopy (ICLAS) were applied to monitor gas-phase Fe and FeO, respectively [2,4]. The simulations rely on a finite-rate chemistry approach with detailed diffusion, particle dynamics are described by a bi-modal population balance model. We observe rich and complex flame structure where "prompt" nucleation zone occurs for precursor loads above ~70 ppm - most probably iron clusters[3-5]. These clusters then evaporate and oxidize and giving rise to second, "late" nucleation zone, presumably preceded by FeOOH and Fe(OH)₂ species. We also study how the temperature history can be intentionally modified by orienting flames either in an upward-firing or downward-firing configuration. The results revealed a strong impact of the reactor orientation on the velocity field. It is demonstrated that the downward-burning flame forms a detached stagnation point, causing longer residence times at elevated temperature than an upward- or horizontally firing flame, permitting the growth of larger particles[5].

- [1] Fomin, A., et al., Combined particle mass spectrometer–Quartz crystal microbalance apparatus for in situ nanoparticle monitoring during flame assisted synthesis. *Combustion and Flame*, 2013. 160(10): p. 2131-2140.
- [2] I. Rahinov, A. Fomin, M. Poliak, S. Cheskis, Absorption electronic spectrum of gaseous FeO: in situ detection with intracavity laser absorption spectroscopy in a nanoparticle-generating flame reactor, *Appl. Phys. B* 117, 317-323 (2014).
- [3] M. Poliak, et al., *PCCP* 17 (2015) 680-685
- [4] Kluge, S., Deng, L., Feroughi, O., Schneider, F., Poliak, M., Fomin, A., ... & Dreier, T. (2015). Initial reaction steps during flame synthesis of iron-oxide nanoparticles. *CrystEngComm*, 17(36), 6930-6939
- [5] J. Sellmann, I. Rahinov, S. Kluge, H. Jünger, A. Fomin, S. Cheskis, C. Schulz, H. Wiggers, A. Kempf, I. Wlokas, Detailed simulation of iron oxide nanoparticle forming flames: buoyancy and probe effects, *Proc. Combust. Inst.* 37, 1241–1248 (2019)

Towards generation of high intensity sub-ns H atom pulses for study of ultra-fast gas-surface interactions

Kai Golibrzuch, Victoria Walpole, Sven Kaufmann, Kim Papendorf, Finn-Erik Digulla,
Dirk Schwarzer, Alec M. Wodtke

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In general, chemical reactions are induced by collisions. Despite great progress in the study of ultra-fast phenomena of photon-induced processes with femto-second resolution, collision induced reaction have only been studied on a microsecond time scale. This is mainly due to our limited ability to control the exact time of a collision given by the duration of standard pulsed molecular beams. H atom beams, which can be generated by photolysis of hydrogen halides like HI, HCl or HBr, are usually limited to at pulse durations around 100ns. However, Kaufmann et al[1] showed that HI photolysis using spatially chirped ultra-short laser pulses (bunch compression photolysis) can yield H atom pulses as short as 1.2ns.

Within the ERC founded HBeam project, we try to further develop this method for generation of high-intensity sub-ns H atom pulses which enable the study of gas-surface interactions on an ultra-fast time-scale. Important improvements cover an optimized geometry for photolysis a high-density, cold HI molecular beam, high power photolysis lasers and ion imaging detection.

1. Kaufmann, S., et al., Generation of ultra-short hydrogen atom pulses by bunch-compression photolysis. Nature Communications, 2014. 5.

Active and Passive Contribution of Atomic Defects towards the Reactivity of NH₃ at Platinum Surfaces

D. Borodin, M. Schwarzer, J. Fingerhut, B. G. Park, A. M. Wodtke, T. N. Kitsopoulos.

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Defects can substantially contribute to the reactivity of a metal surface. However, it is not obvious whether defect sites (steps) are more reactive because they stabilize the transition state of a particular reactant (active contribution) or because the reactants residence time at the surface increases (passive contribution) and therefore the reaction probability of the adsorbate increases. A kinetic model for the reaction system can decouple the active and passive contribution of surface defects.

Our experimental approach combines classical surface science techniques, such as ultra-high-vacuum and single crystal surfaces, with supersonic molecular beams for reactant deposition and Laser-based methods for reactant detection. Well-chosen arrangement of the ion imaging detector with respect to the surface allows simultaneous measurement of reaction kinetics (product flux vs. reaction time) and velocity distribution of the products^[1].

In this work we investigate the kinetics of desorption, decomposition and oxidation of NH₃ at Pt(111) and Pt(332) between 400 and 1000 K. We observe that the residence time of ammonia at the clean surface is substantially increases with increasing step-density of the crystal. This is consistent with an energetic preference for ammonia to bind to step sites. In contrast to previous studies from Somorjai and coworkers we cannot observe any decomposition^[2] or oxidation^[3] of NH₃ at Pt(111) surface. Decomposition of NH₃ on clean Pt(332) was so far not observed. The survival probability of NH₃ at Pt(332) decreases with increasing oxygen coverage, indicating that direct NH₃ reaction with atomic oxygen at steps is initiating the oxidation of NH₃. The final products of NH₃ oxidation at Pt(332) yields NO and H₂O. So far we could not observe N₂ formation. The kinetics of all formed products is measured. A kinetic model for NH₃ oxidation is in development.

[1] D. J. Harding, J. Neugeboren, H. W. Hahn, D. J. Auerbach, T. N. Kitsopoulos, A. M. Wodtke, *J. Chem. Phys.* **147**, 013939 (2017).

[2] W. L. Guthrie, J. D. Sokol, G. A. Somorjai, *Suf. Sci.* **109**, 390 (1981).

[3] M. Asscher, W. L. Guthrie, T. H. Lin, G. A. Somorjai, *J. Phys. Chem.* **88**, 3233 (1984).

Scattering of NO from thin film VO₂ surfaces

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Vanadium oxides are among the most used heterogeneous catalysts in industrial applications. Vanadium dioxide (VO₂) 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 VO₂ thin films in a chemical vapor deposition process and subsequent molecule surface scattering experiments.

[1] N. F. Mott, Metal-Insulator Transition, *Review of Modern Physics*, **1968**, *40*, 677-683.

[2] Y. Huang, *et. al.*, Vibrational Promotion of Electron Transfer, *Science*, **2000**, *209*, 111-114.

[3] B.C. Krüger, *et. al.*, Vibrational Inelasticity of Highly Vibrationally Excited NO on Ag(111), *Journal of Physical Chemistry Letters*, **2016**, in submission.

The quantum-state resolved lifetime of triplet (\tilde{a}^3A_2) formaldehyde

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We report state-resolved lifetimes of formaldehyde in the first excited triplet (\tilde{a}^3A_2) electronic state. Pump-laser excitation within 2800 cm^{-1} of the triplet origin is followed by variably delayed F_2 -laser ionization. Lifetimes fluctuate from $> 100\ \mu\text{s}$ to $\sim 100\ \text{ns}$ and a large isotope effect is observed. The average decay rate increases exponentially with increasing vibrational energy above the electronic origin, consistent with a mechanism involving tunneling through the barrier on the electronic ground state to the $\text{CO} + \text{H}_2/\text{D}_2$ continuum. By accessing the triplet state we are able to investigate the molecular elimination reaction down to $\sim 25\ \text{kJ/mol}$ below the zero-point-energy corrected activation barrier. A model based on empirical RRKM rates allows the intersystem crossing matrix elements to be estimated. Surprisingly, the $T_1\text{-}S_0$ intersystem crossing matrix elements are comparable to the $S_1\text{-}S_0$ internal conversion matrix elements observed at similar vibrational excitation.

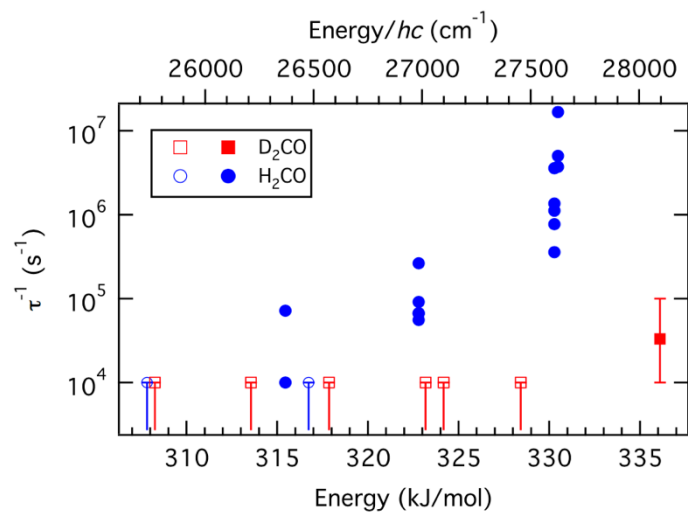


Figure. Measured decay rates of \tilde{a} -state H₂CO (blue circles) and D₂CO (red squares) is plotted as a function of excitation energy (relative to the vibronic ground state). Measured values are indicated by filled markers, and upper limits are indicated by empty markers. The zero-point-energy corrected barrier height is 342 kJ/mol and 348 kJ/mol for H₂CO and D₂CO, respectively.

Platinum catalysed hydrogen oxidation dominated by OH recombination

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The reaction of hydrogen and oxygen on platinum that leads to the formation of water is one of the very first examples of a heterogeneously catalytic reaction, and had been described by the early 19th century. ^{[1][2][3]} Since then, the picture has been established that the first crucial step in the reaction is the formation of the OH intermediate. ^[4] In the second step the hydroxyl molecules form water by the addition of a second hydrogen atom ($\text{H} + \text{OH} \rightarrow \text{H}_2\text{O}$) or by hydroxyl recombination ($\text{OH} + \text{OH} \rightarrow \text{H}_2\text{O} + \text{O}$). The former is usually considered the major reaction path, especially under conditions where the hydrogen coverage exceeds that of oxygen, or both coverages are equal, while the latter is expected to dominate in the limit of excess oxygen. ^{[5][6]} In a recent study on our *Beamer 2* surface scattering apparatus we examined the hydrogen oxidation reaction on platinum in the regime of excess oxygen coverage. Two pulsed molecular beams were used to dose the Pt surface with oxygen (O_2) and probe this with hydrogen (H_2). Desorbing water molecules were laser-ionised and detected via slice ion imaging. ^[7] Reaction dynamics as well as kinetic traces (water formation rate) have been extracted from time resolved ion images. The results show that under these conditions the water formation is actually strongly dominated by hydroxyl recombination, confirming previous predictions. We find that the water formation obeys purely second order kinetics ($\text{A} + \text{A} \rightarrow \text{B}$ type) and we do not find features in the kinetic trace that would be expected for the $\text{H} + \text{OH} \rightarrow \text{H}_2\text{O}$ reaction.

Reorientation of Physisorbed CO Molecules Induced by Vibrational Energy Pooling

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CO adsorbed on NaCl(100) has been intensively studied in the last decades and is considered a prototypical physisorbed molecule.^[1] Recently, we have explored the mechanism for vibrational energy pooling and relaxation in a $^{13}\text{C}^{18}\text{O}$ monolayer on NaCl(100) after excitation to $v=1$ using laser-induced fluorescence (LIF) spectroscopy.^[2] Revisiting the system with an improved experimental setup and higher resolution reveals a second CO monolayer species in the emission spectrum. The dominant species was already observed in Ref. [2] and is consistent with the well-known monolayer structure where CO adsorbs with the C-atom over a Na^+ ion ($\text{O}-\text{C}\cdots\text{Na}^+$). The second species is assigned to CO in a flipped orientation ($\text{C}-\text{O}\cdots\text{Na}^+$). When the $^{13}\text{C}^{18}\text{O}$ monolayer is covered with $^{12}\text{C}^{16}\text{O}$ overlayers, most molecules are in the tilted orientation and a metastable structure that includes tilted molecules is observed with FTIR spectroscopy on macroscopic time scales. The frequency shift of the fundamental $v=1\leftarrow 0$ transition compared to the gas phase is dominated by electrostatic interactions. The experimental shifts for both CO orientations are consistent with those predicted by an electrostatic model based on a molecular multipole expansion.

References

- [1] G. E. Ewing, *Int. Rev. Phys. Chem.* 10, 391-426 (1991).
- [2] L. Chen, J. A. Lau *et al.*, *Science* **363**, 158-161 (2019).

ABSTRACTS

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Non-linear Modelling of dynamics of HEARTBEAT

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The human heart is a complex and yet robust system. The signal that relates to mechanics of human heart is the ECG signal. It is a time-varying signal that reflects the contraction and relaxation of the heart, in a single cycle. Lots of effort has been invested in the development of mathematical models that describe the operation of the human heart, for days [1]. One of the crucial developments is by Zeeman. Starting from a 1D model we have tried to discuss briefly the advantages and disadvantages of Zeeman [2] Model, then we have prescribed a new model.

The focus is mainly on two characteristics of heart. It oscillates at a fixed rate and circulates a fixed amount of blood every minute. So, it must have a stable equilibrium with respect to both frequency and amplitude of vibration. If it gets displaced from equilibrium position, it must come back to equilibrium in some time. The main idea of this work is to justify how and why this equilibrium occurs in the dynamics of heartbeat system, with the help of non-linear differential equations,

References:

1. Loh R. N.K., Thanom W., Nonlinear Control of Heartbeat Models, Oakland University, Rochester, U.S.A.
2. E. C. Zeeman, "Differential equations for the heartbeat and nerve impulse", Towards a Theoretical Biology, Vol. 4, 1972, pp. 8-67.

Synthesis and Analysis of WS₂ using Chemical Vapor Deposition and Time-Correlated Single Photon Counting

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Transition metal dichalcogenides (TMDCs) like MoS₂ or WS₂ form 2D structures graphite-like with weak interlayer interactions. Bulk TMDCs are semiconductors and exhibiting an indirect bandgap. In analogy to graphene, which has been topic of extensive research in the last decade, TMDCs can as well be grown as monolayers where they possess a direct bandgap. This interesting property opens a wide field of possible application for e.g. optoelectronics or nanoelectronics.

The synthesis of large area strictly monolayer TMDCs with high surface coverage remains challenging yet.

We use chemical vapor deposition (CVD) to grow WS₂ on Si/SiO₂ and sapphire substrates. This technique is suitable to create high quality monolayers but crystal size, thickness and quality are highly sensitive to the reaction conditions. We use fluorescence microscopy as a tool to investigate the quality of the samples. Since only monolayer TMDCs exhibit a direct bandgap, which can be efficiently excited with light, the fluorescence intensity is a good measure to discriminate between mono- and multilayer areas. In addition, time-correlated single photon counting (TCSPC) is used to evaluate the fluorescence lifetime of the samples. Long fluorescence lifetime in general indicates good crystallinity and low defect density.

Scattering HCl molecules from Ag(111) and Au(111): Dissociation revisited

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Motivated by a theoretical study presenting quantum dynamic calculations on a neural-network-fitted PES¹, some time ago we investigated the dissociation probability S_0 of HCl molecules on Au(111). Finding dissociation probabilities approximately two orders of magnitude lower than predicted, the publication of our results² triggered vivid discussions and several further DFT studies employing different functionals and degrees of simplification concerning surface rigidity and electronically nonadiabatic effects.³⁻⁶ While more advanced functionals, surface atom motion and electronic friction brought theoretical values for S_0 closer to the experimental ones, the latter still remained a factor of ~ 20 lower.

Recently, I revisited and reanalyzed the experimental data and also searched for evidence of HCl dissociation in dynamical scattering experiments. The results I will present show that the reported experimental sticking probabilities might have been too low. While the revised values for S_0 are still lower than the most recent theoretically predicted ones, the agreement is much better than before.

¹ T. Liu, B. Fu, and D.H. Zhang, *J. Chem. Phys.* **139**, 184705 (2013).

² P.R. Shirhatti, J. Geweke, C. Steinsiek, C. Bartels, I. Rahinov, D.J. Auerbach, and A.M. Wodtke, *J. Phys. Chem. Lett.* **7**, 1346 (2016).

³ G. Fuchsel, X. Zhou, B. Jiang, J.I. Juaristi, M. Alducin, H. Guo, and G.-J. Kroes, *J. Phys. Chem. C* **123**, 2287 (2019).

⁴ G. Fuchsel, M. del Cueto, C. Díaz, and G.-J. Kroes, *J. Phys. Chem. C* **120**, 25760 (2016).

⁵ T. Liu, B. Fu, and D.H. Zhang, *J. Chem. Phys.* **146**, 164706 (2017).

⁶ B. Kolb, X. Luo, X. Zhou, B. Jiang, and H. Guo, *J. Phys. Chem. Lett.* **666** (2017).

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Modelling thermal reactions on 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 involving species that undergo reaction at or near thermal-equilibrium conditions, for which direct dynamical calculations are often unfeasible. However, it is well known that TST gives an upper bound for the rate coefficients since it counts any crossing of the transition state as a reaction. This approximation can be corrected by calculating short time trajectories started at the transition state to obtain the so called dynamical correction factors [1]. Among other reasons, recrossing can originate from the unseparability of the reaction coordinate from all other degrees of freedom. Another dynamical origin might be the excitation of electron-hole pairs, that are well known to happen when molecules interact with metal surfaces.

We study two different gas-surface reactions to evaluate the role of dynamical effects on the reaction rate constants, and therefore, to evaluate the validity of conventional TST. On one hand, a model systems for which appears likely to have a strong electronic coupling: H₂ recombinative desorption on the Au(111) and Cu(111) surfaces. An accurate description of the electronic excitations is accomplished by ab-initio molecular dynamics with electronic friction (AIMDEF) method [2]. This method is based on the local density electronic friction approximation (LDFA) [3], which was shown to successfully model translational energy loss measurements for H colliding with Au(111) [4]. Calculations show that non-adiabaticity do not affect the dynamical factors. However, increasing the temperature decreases the reaction constant up to a factor of 2. On the other hand, we study H adsorption on graphene standing on Pt(111), for which harmonic TST predicts high adsorption probabilities compared to the experimental measurements. Classical dynamics simulations are run on the EMFT-REBO PES that has been validated by comparison of experimental measurements and direct dynamical simulations [5]. Preliminary results predict high corrections to the TST rate constant for this system. The corrected rate is about two orders of magnitude smaller than the TST reaction rate.

[1] C.H. Bennett, *Alg. Chem. Comp.* 46, 63–97 (1977).

[2] D. Novko, et al. *Phys. Rev. B*, 92(20), 201411 (2015).

[3] J. I. Juaristi, et al. *Phys. Rev. Lett.* 100, 116102 (2008).

[4] O. Bünermann, et al. *Science* 350, 1346–1349 (2015).

[5] H. Jiang et al. *Science* 364.6438, 379-382 (2019).

On the dynamics of H atom scattering from tungsten

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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 crystallise in other crystal structures, 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 H atoms interacting with *bcc* metal surfaces. The obtained energy formula is fitted to DFT energies for H atoms at W(111). The obtained global EMT-PES is used to perform molecular dynamics simulations to investigate of how the scattering dynamics between H atom and metal surface is affected by the crystal structure and surface facet.

- [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.*, 2018, **148**, 034706.
- [5] K. W. Jacobsen, P. Stoltze, and J. K. Nørskov, *Surf. Sci.*, 1996, **366**, 394-402.

Hydrogen atom scattering from Graphene

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Experimental results have shown that H-atoms can scatter from quasi free-standing graphene in two distinct ways [1]: depending on incidence angle and energy, there can exist a nearly elastic channel, a high energy loss channel or both at the same time. The basic energy loss mechanism can be revealed using *ab initio* molecular dynamics (AIMD) trajectory simulations. When the projectile comes close to the surface, it causes one carbon atom to re-hybridize. During this process, the targeted C-atom puckers out of the surface plane and the chemical bonds to its neighbors stretch. This structural change causes the H-atom to lose a large portion of its kinetic energy in less than 20 fs and can also lead to the formation of a stable C-H bond.

Since AIMD is computationally too expensive to obtain meaningful statistics, a re-parametrized version of the 2nd generation reactive empirical bond order potential [2] was used to simulate the scattering process. This full-dimensional potential energy surface was trained with energies stemming from a hybrid functional/LDA description of the graphene system utilizing the embedded mean-field theory [3]. This poster focuses quantitatively on the details of the energy loss mechanism. It will be shown how isotope substitution, the addition of a weakly interacting substrate and nuclear quantum effects modeled by ring polymer molecular dynamics [4] influences the scattering process.

References

- [1] H. Jiang *et al.*, *Science*, **364**(6438):379-282, 2019.
- [2] D. W. Brenner *et al.*, *J. Phys. Condens. Matter*, **14**(4):783-802, 2002.
- [3] M. E. Fornace *et al.*, *Chem. Theory Comput.*, **11**(2):568-580, 2015.
- [4] I. R. Craig, D. E. Manolopoulos, *J. Chem. Phys.*, **121**(8):3368-3373, 2004.

Towards laser-induced hydrogen desorption from silicon surfaces

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Mode selective control of covalent bond scission is a long-term goal in surface science^[1]. However, vibrational excitation is thermalized rapidly by energy transfer into combinations of lower frequency modes, followed by energy dissipation into bulk phonons^[2]. Exceptions to this rule are hydrogen terminated forms of silicon, where the large energy mismatch of bulk phonons to the Si-H stretch vibration leads to an unusually long lifetime on the order of 1 ns for Si(111)-1x1-H^[2,3].

For this specific system, desorption of H₂ has been observed upon resonant excitation of the Si-H stretch vibration by free electron laser irradiation^[4,5]. Unfortunately, this experiment could not be reproduced by the authors before their light source was closed^[5]. Here, we present our efforts to reproduce these experiments, expand them towards Si(100)-H - surfaces and compare to thermal laser-induced desorption.

[1] Tully, J. C., *Science* (80). **312**, 1004 (2006).

[2] Harris, A. L. et al., *Faraday Discuss.* **96**, 217 (1993).

[3] Guyot-Sionnest, P. et al., *Phys. Rev. Lett.* **64**, 2156 (1990).

[4] Liu, Z. et al., *Science* (80). **312**, 1024 (2006).

[5] Liu, Z. et al., *Science* (80). **333**, 1824 (2011).

Surface scattering at extreme ultra-violet (XUV) free electron lasers

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The “Mobile Beamer” is designed to make use of the advantageous properties of the radiation produced by the XUV free electron laser in Dalian^[1] for surface scattering experiments on atoms and molecules. The XUV photolysis of small molecules will be used as a novel source of atomic beams, providing fine control over the electronic state and kinetic energy. In addition, the tunable XUV light source will be used for sensitive, isomer-specific detection of molecular scattering products and reaction intermediates at surfaces, via photoionization mass spectrometry with high time of flight as well as spatial and velocity map imaging resolution.

We would like to answer following three fundamental questions: Open-shell atoms can interact strongly with the electrons of a metal surface. For example, it has recently been shown that nonadiabatic "electronic friction" is the dominant energy dissipation mechanism that allows hydrogen atoms to stick to metals.^[2]

1. To what extent do such forces govern the dynamics of heavier high-electron-affinity atoms (O, C, N) at surfaces? Will current theories for non-Born-Oppenheimer dynamics succeed in describing the scattering process of the atom?
2. Can electronic excitation of atoms lead to an increased reactivity with surface adsorbates or is the electronic energy lost to surface degrees of freedom without enhancing a reaction?

Although elementary kinetic models provide invaluable predictive power for gas-phase reactions, they are practically non-existent in surface chemistry due to the complex structure of interfaces. Recent work has provided the first transferrable kinetic model to treat the elementary site-specific processes in CO oxidation on platinum.^[3]

3. By probing surface intermediates, can models based on elementary reaction steps be built for the predictive description of more complex catalytic systems?

[1] Deng Hai-Xiao *et al.*, **2014** Chinese Phys. C 38 028101.

[2] O. Bünermann *et al.*, **2015** Science 350 1346.

[3] J. Neugeboren *et al.*, **2018** Nature 558 280.

New perspectives on hydrogen atom scattering from metal surfaces: Towards high kinetic energies and low surface temperatures

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Hydrogen atoms that are scattered from metal surfaces at incidence kinetic energies of about 1-3 eV possess broad and structureless translational energy loss distributions due to energy transfer to electron-hole-pair excitation. These energy loss distributions were found to be similar for various transition metal surfaces (Au, Ag, Pt, Pd, Cu, Ni).

Recently, we were able to extend the kinetic energy range of the H atoms to up to 7 eV. To produce these H atoms, we dissociate hydrogen iodide using vacuum ultraviolet (VUV) radiation utilizing predissociating Rydberg states. Interestingly, using these higher incidence kinetic energies, we see a significant difference in the translational energy loss distributions for H atoms scattered from Au(111) and Pt(111). H atoms scattered from Pt(111) lose significantly more energy on average than hydrogen atoms that were scattered from a gold surface. An interesting aspect of incidence energies of 6-7 eV is that they exceed the work function of most metal surfaces, making it energetically possible to form exo-electrons and H anions. The corresponding probabilities will provide a sensitive benchmark for theoretical models.

Using high incidence energies in combination with low surface temperatures, theoretical predictions suggest that we can resolve single peaks within the energy loss distribution of the scattered H atoms. These peaks should correspond to different scattering processes like single or double bounce collisions. To perform measurements at low surface temperatures some modifications of the machine are planned to improve the vacuum and thereby prevent a rapid build-up of physisorbed adsorbate layers on the cold metal surfaces.

Controlling the Vibrational Energy Flow at CO Monolayer/Multilayer Interfaces by Isotopic Substitution

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Our recent experimental and theoretical study on the CO monolayer on NaCl(100)^[1] has provided a profound understanding of the vibrational energy pooling process in the monolayer, i.e., the exchange of vibrational quanta $\text{CO}(v) + \text{CO}(v') \rightarrow \text{CO}(v+1) + \text{CO}(v'-1)$. The apparatus for time-resolved and dispersed laser-induced infrared fluorescence measurements^[2] used in that work has been upgraded. It now includes two nozzles for molecular beam dosing, a more compact monochromator inside the detector chamber, which is cooled down to 40 K, a larger superconducting nanowire single-photon detector, and improved spectral resolution (~ 7 nm).

The improved setup provides enough sensitivity for controlled experiments with CO adsorbed on NaCl(100) where we selectively excite CO in the first layer to $v=1$ and fluorescence is observed (a) only from the first layer or (b) only from the overlayers. This can be achieved with isotopically pure $^{12}\text{C}^{16}\text{O}$ and $^{13}\text{C}^{18}\text{O}$ whose vibrational frequencies differ by only ~ 100 cm^{-1} . For the $^{13}\text{C}^{18}\text{O}(\text{monolayer})/^{12}\text{C}^{16}\text{O}(\text{overlayer})$ system (a), the vibrational energy is confined to the first layer while all the energy is transferred to the overlayers in the $^{12}\text{C}^{16}\text{O}(\text{monolayer})/^{13}\text{C}^{18}\text{O}(\text{overlayer})$ system (b).

References

- [1] L. Chen, J. A. Lau *et al.*, *Science* **363**, 158-161 (2019).
- [2] L. Chen *et al.*, *Acc. Chem. Res.* **50**, 1400-1409 (2017).

Nonadiabatic molecular dynamic simulations of H scattering from O-covered Pt(111) surface

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Using Effective Medium Theory, potential energy surface (PES) have been produced to fit DFT data for H-atoms interacting with fcc Pt(111) surfaces. It describes successfully the inelastic scattering of H and D atoms from these surfaces [1, 2]. This allows us to improve the complexity of the studied system by adding to the surface other species as O-atoms at fcc sites corresponding to the coverage of 0.25ML. Experiments of inelastic H-atoms scattering from aluminum oxide films on Pt(111) show two different components in the energy loss spectrum of scattered H atoms: one corresponding to the adiabatic scattering from the oxide layer and one corresponding to the nonadiabatic scattering from the underlying platinum. The ratio of these components is defined by the oxide coverage [3]. To simulate this system, the PES has to be extended to account for the new interactions. We use Morse Potential in order to model the O-Pt interaction. The values of the parameters ($D_e = 1.055\text{eV}$, $\alpha = 2.59\text{\AA}^{-1}$, and $r_e = 2.054\text{\AA}$)

fit the experimental data for vibrational wavelength, desorption energy and equilibrium length for O adsorbed at fcc site [4, 5]. The O-H potential has been found by fitting the analytic form of the energy to ab initio energy values. Our simulations of H- and D-atom scattering from a O-covered Pt(111) surface performed for the incidence energy of 1.92eV and the incidence angle of 45° agree well with the experimental results and support the above energy dissipation mechanism.

[1] M. Kammler et al., Chem. Phys. Lett. 683,286-290 (2017).

[2] Y. Dorenkamp et al., J. Chem. Phys. 148, 034706 (2018)

[3] Y. Dorenkamp et al., J. Phys. Chem. C 122, 10096-10102 (2018)

[4] J.L. Gland et al., Surf. Sci. 95, 587 (1980)

[5] Z. Gu and P.B. Balbuena, J. Phys. Chem. C 111, 9877-9883 (2007)

Scattering small molecules from graphene grown on metal surfaces

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Scattering small molecules from well-defined surfaces is an exceptional way to investigate energy transfer processes at the gas-solid interface and has been investigated thoroughly for metal surfaces. Graphene, a single layer of carbon, can be grown on metal surfaces using CVD and is a promising material for hydrogen and energy storage as well as semiconductor technology. Atoms or small molecules like hydrogen can be intercalated between the graphene and the substrate to reduce the interactions and get closer to free standing graphene.

I will discuss the experiments planned on the Beamer I machine for scattering small molecules like NO and CO with controlled incident conditions from graphene grown on different metal substrates.

Laser-induced desorption of H₂ from Si(111) using a ps-laser – Building a pulse train for visible and infrared light

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Laser-induced desorption (LID) of hydrogen from silicon surfaces mainly has been studied using ns-pulse lasers with photon energies above the band gap which leads to thermal desorption of H₂^[1-3]. With ps-pulses on the other hand, the pulse duration is too short to enable sufficient H₂ desorption which is shown by simulation and experiments. Exposing a Si(111) surface to visible or IR ps-pulses leads to Si ablation rather than H₂ desorption.

We have built up a 4-fold Michelson interferometer^[4] to generate a pulse train consisting of 16 pulses with variable pulse separation. This is advantageous for two applications: The prolonged exposure time should allow the investigation of thermal desorption. It should also be a good imitation of the micropulse structure of the free electron laser used by Liu *et al.*^[5, 6]. This might enable us to investigate H₂ desorption by resonant excitation of the Si-H stretch vibration.

1. Koehler, B.G. and S.M. George, *Laser-induced desorption of H₂ from Si(111) 7 X 7*. Surface Science, 1991. **248**: p. 158-172.
2. Kolasinski, K.W., et al., *Beam investigations of D₂ adsorption on Si(100): On the importance of lattice excitations in the reaction dynamics*. The Journal of Chemical Physics, 1994. **101**(8): p. 7082-7094.
3. Schwalb, C.H., et al., *Real-space investigation of fast diffusion of hydrogen on Si(001) by a combination of nanosecond laser heating and STM*. Physical Review B, 2007. **75**(8).
4. Siders, C.W., et al., *Efficient high-energy pulse-train generation using a 2n-pulse Michelson interferometer*. Applied Optics, 1998. **37**(22): p. 5302-5305.
5. Liu, Z., et al., *Desorption of H from Si(111) by resonant excitation of the Si-H vibrational stretch mode*. Science, 2006. **312**(5776): p. 1024-6.
6. Liu, Z.H., et al., *DESORPTION OF H FROM SI(111) BY RESONANT EXCITATION OF THE Si-H vibrational stretch mode (Retraction of vol 312, pg 1024, 2006)*. Science, 2011. **333**(6051): p. 1824-1824.

Accurate potential energy curves for triplet ground state hetero Alkali dimers

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Accurate potential energy curves for dimeric Alkali species are of great interest in the field of ultra cold physics where quantum effects like Feshbach resonances and Bose-Einstein condensation are studied.[1] For hetero Alkali dimers extensive laser induced fluorescence data is available, allowing for least squares adjustment of potential parameters. In the present investigation it is shown that Tang-Toennies type potential energy curves[2, 3, 4] for triplet ground state hetero Alkali dimers can accurately reproduce spectroscopic observations. These potential energy curves use well known dispersion coefficients from theory with proper damping to describe attractive contributions and a Born-Mayer type repulsive potential including three to five adjustable parameters. The present model is advantageous compared to piecewise defined models with several ten fit parameters appearing in literature, eg [5].

[1] C. Chin et al., Rev. Mod. Phys. 82, 1225 (2010).

[2] K. T. Tang and J. P. Toennies, J. Chem. Phys. 80, 3726 (1984).

[3] J. A. Lau et al., J. Chem. Phys. 145, 194308 (2016).

[4] J. B. Bauer and J. P. Toennies, J. Chem. Phys. 150, 144310 (2019).

[5] A. Pashov et al., Phys. Rev. A 76, 022511 (2007).

Translational Inelasticity of CO $X^1\Sigma^+(v = 17, J = 0)$ Scattered from Metal Surfaces

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State-to-state molecular beam-surface scattering experiments are performed in order to study the dynamics of highly vibrationally excited CO $X^1\Sigma^+(v = 17, J = 0)$ at metal surfaces. The incidence translational energy of the molecular beam is varied between 0.26 eV and 0.57 eV. For both vibrationally and rotationally elastic scattering, the translational energy loss of the scattered molecules agrees with that predicted by the hard-cube model (Baule limit). For rotationally inelastic scattering, the final translational energy decreases with rotational excitation of the scattered molecules. These findings are consistent with a purely mechanical (electronically adiabatically) conversion of energy at the gas-solid interface. However, the observation that the final translational energy is increased for vibrationally relaxed molecules cannot be explained within the electronically adiabatic picture. The underlying mechanism for the vibration-to-translation energy transfer is still debated in literature, especially for the well-studied NO/Au(111) system. Since vibrational degrees of freedom of highly vibrationally excited CO are likely to couple to electronic degrees of freedom of the surface, an electronically non-adiabatic mechanism is proposed in order to understand trends in the final translational energy of vibrationally inelastically scattered molecules. This mechanism considers the image charge stabilization of a transiently formed anion near the surface.

Studying the Hydrogen Atom Interaction with Graphene Using a High-Dimensional Neural Network Potential

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The availability of an accurate full-dimensional potential energy surface (PES) is crucial to study atom-surface interactions. High-dimensional neural networks (HDNNP)[1] provide very accurate PESs for a wide range of systems. They combine the computational efficiency of classical force fields with the accuracy of quantum mechanical calculations. Here, the HDNNP is used to describe the interaction of a hydrogen atom with a graphene sheet. The neural network potential was fitted to DFT data generated in ab initio molecular dynamics simulations. The reactive empirical bond order potential (REBOP)[2] was fitted to the same data and compared to the HDNNP results. Based on these potentials, the scattering under various conditions was examined such as changing the polar angle, the incidence kinetic energy of the hydrogen atom and the surface temperature. Our conclusions overall match with results out of recently performed experiments on hydrogen atom scattering from epitaxial graphene[3]. The potentials properly describe barrier heights and chemisorption wells, the intensities of the two components (Scattering before and after the adsorption barrier) and furthermore temperature- and angle-dependent sticking probabilities, respectively.

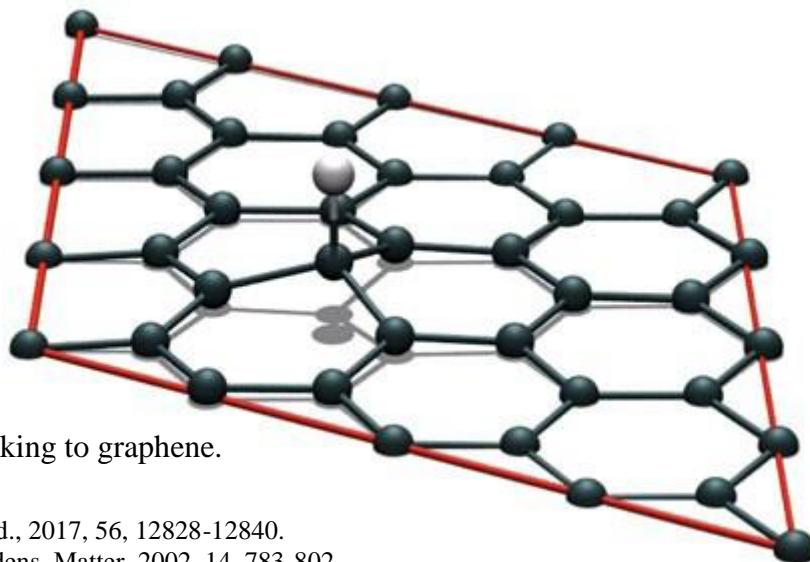


Figure 1: Hydrogen atom sticking to graphene.

References:

- [1] J. Behler, *Angew. Chem. Int. Ed.*, 2017, 56, 12828-12840.
- [2] D. Brenner et al., *J. Phys.: Condens. Matter*, 2002, 14, 783-802.
- [3] H. Jiang, *Dynamics of Hydrogen Atoms Scattering from Surfaces* (Doctoral dissertation), 2016.

Photodissociation Study of O₂ into O(³P₂), O(³P₁), O(³P₀) at the New ‘Mobile Beamer’

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The new atom beam surface scattering apparatus ‘Mobile Beamer’ together with the DCLS free electron laser in Dalian is the ideal tool for producing electronically state-selected atom beams with tunable translational energy, which can be used for many purposes aiming at examining surface science. To demonstrate the design specifications of the new instrument, photodissociation of O₂ at 226.23, 226.06 and 225.65nm has been studied. Employing REMPI based ion-imaging to monitor O(³P₂), O(³P₁), O(³P₀) product-atoms, the relative ion yields as a function of laser power are determined. The results are compared with previously published studies.

Studying photodissociation of O₂ and N₂O as a function of laser fluence at the new “Mobile Beamer”

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The “Mobile Beamer” is designed for the investigation of scattering of atomic and molecular beams from surfaces. The photolysis-generated atomic beams from small molecules can be realized by the VUV free electron laser in Dalian[1], so that the different electronic states and various kinetic energies of atoms can be controlled precisely. Scattering products will be detected by ion-imaging techniques, which have proven to be a powerful tool for measuring the angular and velocity distribution. In order to calibrate the new ion-imaging detector the ultraviolet photodissociation of molecular O₂ and N₂O has been studied. The molecules N₂O and O₂ were photolysed at 203 nm and 225 nm, respectively. The state-selective detection of the generated O (3P₂) and O (1D₂) was achieved by (2+1) REMPI[2] at 225.653 nm and two-photon resonant ionization[3] at 203.813 nm, respectively. The laser fluence dependence for oxygen atom production from O₂ and N₂O dissociation was analyzed.

1] Deng Hai-Xiao et al., Chinese Phys. C 38 028101 (2014).

2] B. Buijsse et al., J. Chem. Phys. 108, 7229 (1998).

3] S. T. Pratt et al., Phys. Rev. A 43, 4702 (1991).

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