

Franken Akademie Schloss

May 11 to 14, 2022

Symposium on Dynamics at Surfaces



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'Lichtenfels' train station, we recommend to
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WORKSHOP PROGRAMME

Wednesday 11.05.2022	
16:00-18:00	Arrival and registration
18:00-19:45	Dinner
19:50-20:00	Prof. Dr. Alec M. Wodtke, <i>Welcoming Remarks</i>
20:00-21:00	Prof. Dr. Karl-Heinz Ernst, <i>On-Surface Chemistry of Helicenes</i>
21:00-	Poster Session I
Thursday 12.05.2022	
08:00-9:00	Breakfast
<i>Session Chair:</i>	Prof. Dr. Theo Kitsopoulos
9:00-10:00	Prof. Dr. Sotiris Xantheas, <i>The Many-Body Expansion in Chemistry</i>
10:00-10:30	Coffee Break
10:30-11:00	Dr. Dmitriy Borodin, <i>Benchmark non-reactive Interactions of NH₃ at p(2×2) O/Pt(111) — Consequences for the Ostwald Process</i>
11:00-11:30	Mr. Jan Fingerhut, <i>Formic Acid Decomposition on Pd(111) and Pd(332)</i>
11:30-12:00	Mr. Florian Nitz, <i>The Quantum Rate Model - A Pathway to predict Surface Reactions</i>
12:00-13:30	Lunch Break
<i>Session Chair:</i>	Dr. Oliver Bünermann
13:30-14:30	Prof. Dr. Daniel Killelea, <i>Chemical Speciation and Structural Evolution of Rhodium and Silver Surfaces with High Oxygen Coverages</i>
14:30-15:00	Mr. Arved Cedric Dorst, <i>Velocity Map Images of Recombinatively Desorbing Subsurface Oxygen from Rh(111)</i>
15:00-15:30	Coffee Break
15:30-16:30	Prof. Dr. Saalfrank, <i>Photochemistry and spectroscopy of molecules at surfaces – Insights (mostly) from ab initio molecular dynamics –</i>
16:30-17:00	Ms. Shreya Sinha, <i>Orientational isomerisation of CO on a NaCl(100) surface– Characterization, kinetics and vibrational spectra from ab initio molecular dynamics</i>
17:00-17:30	Mr. Arnab Choudhury, <i>Condensed phase isomerization through tunneling gateways</i>
17:30-18:00	Ms. Ximei Yang, <i>Electronically State-to-State Scattering of O atom from Au(111)</i>
18:00-20:00	Dinner
20:00-	Poster Session II

Friday 13.05.2022	
8:00-9:00	Breakfast
<i>Session Chair:</i> Dr. Kai Golibrzuch	
9:00-9:30	Dr. Jessalyn Devine, <i>Spin-forbidden carbon-carbon bond formation in vibrationally excited α-CO</i>
9:30-10:00	Mr. Michael Schwarzer, <i>Mechanistic Details of Hydrogen Interaction with Palladium</i>
10:00-10:30	Coffee Break
10:30-11:00	Mr. Tianli Zhong, <i>Velocity-resolved laser-induced desorption for kinetics on surface adsorbates and isotherm measurements</i>
11:00-11:30	Mr. Jan-Hendrik Bortler, <i>Photoinduced electron transfer in self-assembled coordination cages: Ligand-to-ligand and host-to-guest charge transfer</i>
11:30-12:00	Mr. Loic Lecroart, <i>DFT reveals correlations between surface and bulk atom energies in fcc-metals</i>
12:00-13:30	Lunch Break
<i>Session Chair:</i> Dr. Sascha Kandratsenka	
13:30-14:00	Ms. Kerstin Krüger, <i>Electronic excitation of a semiconductor surface observed by H atom scattering</i>
14:00-14:30	Dr. Nils Hertl, <i>On the role of surface structure in electronically non-adiabatic H atom scattering from silver</i>
14:30-15:00	Ms. Anna-Maria Schönemann, <i>Towards application of ultrashort H atom pulses in time-resolved surface scattering experiments</i>
15:00-15:30	Coffee Break
15:30-16:30	Prof. Dr. Joost Winterlin, <i>High-speed STM: Technique, Data Analysis, and Applications</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 III

Saturday 14.05.2022	
9:00-10:00	Breakfast
10:15	Departure

ABSTRACTS

(talks)

On-Surface Chemistry of Helicenes

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Surfaces functionalized with helicenes are of interest for chiroptical electronic devices or for electron-spin filtering. While self-assembled layers facilitate studying interesting phenomena, covalently linked chiral modified materials would be much more robust and therefore better suited for applications. We report stereoselective chemistry of different helicene species on noble metal surfaces. The stereochemical analysis of diastereoisomers formed on the surface is performed by scanning tunneling microscopy (STM) and non-contact atomic force microscopy (ncAFM). Depending on the site of bromination at the helical backbone, the Ullmann coupling reaction of different bromohelicenes proceeds stereospecifically to heterochiral or homochiral products. The diastereoselective chemistry is explained by topochemical effects due to the surface alignment of the helicenes during reaction.

Cyclodehydrogenation of bishelicenes was found to proceed also stereo-specifically. Upon annealing the substrate to approximately 670 K and subsequent cooling to 50 K, the characteristic twisted shape of the bis[5]helicenes with protrusions is no longer observed and two-dimensional homochiral domains of planar coronacorone molecular species can be distinguished. The transformation from helical to planar chiral molecules via dehydrogenation and loss of eight hydrogen atoms was confirmed by secondary ion mass spectrometry (ToF-SIMS). Further STM measurements at 7.5 K affirmed the formation of mirror and rotational 2D homochiral conglomerate domains of planar left- and righthanded coronacorone.

The Many-Body Expansion in Chemistry*

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The many-body expansion (MBE) has its origin in combinatorial mathematics and in particular the inclusion-exclusion principle, a counting technique used to obtain the number of elements in the union of finite sets. Its application in Chemistry consists of breaking up a chemical system into nonoverlapping fragments of n “bodies” of increasing size and casting the total energy as a sum of the energies of the constituent fragments up to rank n . The practical application of the MBE lies in cases where it converges at a low rank (typically the 3- or the 4-body term). Its introduction to the Chemical Physics community back in the 1970’s^{[1][2]} – and ever since – consisted of its application to the breaking of hydrogen bonds to define the “bodies” in the expansion.^{[3][4]} We have in recent times revisited the MBE for water and ion-water systems,^{[5][6]} including monatomic and polyatomic ions in the Hofmeister series,^[7] confirmed its fast monotonic convergence at the 4-body term and established the theoretical requirements needed to accurately describe the terms of the expansion. Additionally, we are extending the MBE to account for the breaking of covalent^[8] and metal-metal^[9] bonds in defining the “bodies” of the expansion by introducing a new, novel implementation that is based on the *in situ* electronic structure of atoms in a larger system. I will discuss the implications of this new development in addressing modeling challenges in complex systems such as metal clusters, carbon materials and chemical transformations on metal and metal oxide surfaces in the context of structure and dynamics driven by the MBE.^[10]

[1] D. Hankins, J. W. Moskowitz, and F. H. Stillinger, *J. Chem. Phys.* **53**, 4544 (1970).

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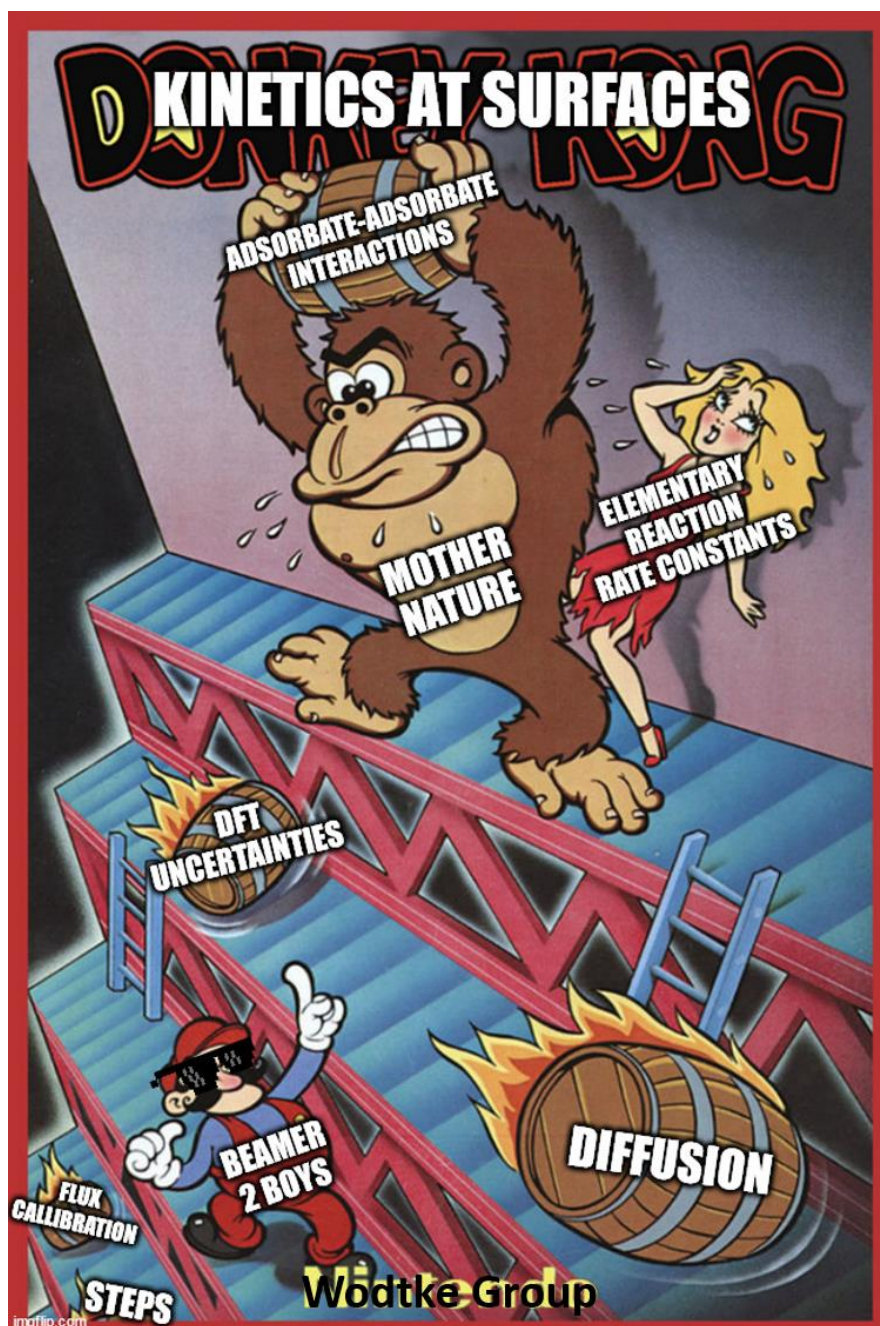
[9] J. Mato, D. T. Tzeli and S. S. Xantheas, submitted (2022).

[10] J. P. Heindel and S. S. Xantheas, *J. Chem. Theor. Comp.* **17**, 7341 (2021).

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Benchmark non-reactive Interactions of NH_3 at $p(2 \times 2)$ O/Pt(111) — Consequences for the Ostwald Process

Dmitriy Borodin, Jan Fingerhut, Michael Schwarzer, Stefan Hörandl, Florian Nitz, Oihana Galparsoro, Igor Rahinov, Dirk Schwarzer, Theofanis N. Kitsopoulos, Alec M. Wodtke.



Formic Acid Decomposition on Pd(111) and Pd(332)

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Understanding heterogeneous catalysis is based on knowing the energetic stability of adsorbed reactants, intermediates, and products as well as the energetic barriers separating them.

Formic acid (HCOOH) for example is a potential hydrogen carrier and its decomposition on transition metals such as platinum or palladium is important to derive insights into the development of direct formic acid fuel cells. While the HCOOH chemistry was investigated especially under oxidative conditions^[1], less attention has been paid to oxygen lean conditions which are more representative to industrial applications. The decomposition on the bare metal surface has been mostly covered by theoretical studies^[2], but critical comparison to experimental rates are rare.

Here, we investigate the interaction of formic acid with atomically flat and stepped palladium surfaces by using Velocity-Resolved Kinetics (VRK)^[3]. We obtain accurate rates for formic acid desorption as well as CO₂ formation. Substitution of the C-end hydrogen with deuterium guides us to the key intermediates participating in the decomposition process. Furthermore, we identify these key intermediates and quantify reaction barriers with support of DFT calculations. Our results indicate that step sites increase the conversion of formic acid to CO₂ and H₂.

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[3] J. Neugeboren, D. Borodin, H. W. Hahn, J. Altschäffel, A. Kandratsenka, D. J. Auerbach, C. T. Campbell, D. Schwarzer, D. J. Harding, A. M. Wodtke and T. N. Kitsopoulos, *Nature* 558, 280 (2018)

The Quantum Rate Model – A Pathway to predict Surface Reactions

Florian Nitz

Thermal desorption rate constants from transition metal surfaces are a central quantity in understanding and predicting heterogeneous catalysis. The recent progress in first-principles calculations (DFT) allows to accurately compute adsorbate surface interactions. However, various approaches to derive the microscopic configuration of adsorbates (free translator, harmonic approximation, hindered translator, ...) have also been described in the literature. As it will be shown, only some of these approaches can be used universally. To provide a critical benchmark, we focus on the recombination of hydrogen atoms at transition metal surfaces and use a fully quantum treatment of the adsorbates in a DFT PES. Therefore we call this method “The Quantum Rate Model”. Desorption rates derived within this framework are tested against experimental results obtained from velocity resolved kinetics and TPD experiments at different transition metal surfaces.

Chemical Speciation and Structural Evolution of Rhodium and Silver Surfaces with High Oxygen Coverages

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Abstract

Understanding the interaction of oxygen with transition metal surfaces is important in many areas including corrosion and catalysis. Of interest to us is the formation and chemistry of subsurface oxygen (O_{sub}); oxygen atoms dissolved in the near-surface region of catalytically active metals. The goal of these studies is to understand how incorporation of O_{sub} into the seldge alters the surface structure and chemistry. The oxygen – Ag system, in particular, has been studied extensively both experimentally and theoretically because of its role in two important heterogeneously catalyzed industrial reactions: the epoxidation of ethylene to produce ethylene oxide and the partial oxidation of methanol to produce formaldehyde. In addition, the O/Rh and O/Ag systems serve as models for the dissociative chemisorption of diatomic molecules on close packed metal surfaces. Despite extensive research, there remain questions about the fundamental chemistry of the O/Ag system. Rh is also used in partial oxidation reactions, and its response to adsorbed oxygen provides an interesting complement to Ag. Where Ag extensively reconstructs, Rh does not. In particular, the structure of the catalytically active surface remains poorly understood under conditions of high oxygen coverages or subsurface oxygen. To improve our understanding of this system, we use ultra-high vacuum (UHV) surface science techniques to characterize Ag and Rh surfaces after exposure to atomic oxygen (AO) to obtain O coverages in excess of 1 ML. AO is generated by thermally cracking molecular O_2 . We then use low-energy electron diffraction (LEED) and UHV Scanning Tunneling Microscopy (UHV-STM) to further characterize the various oxygenaceous structures produced, and quantify the amount of oxygen with temperature programmed desorption (TPD). We have found that the surface temperature during deposition is an important factor for the formation of O_{sub} and the consequent surface structures. Finally, we have recently found that Rh surfaces are significantly more reactive towards CO oxidation when O_{sub} is present. This enhanced reactivity is located at the interface between the less reactive RhO_2 oxide and O-covered metallic Rh. These results reveal the conditions under which O_{sub} is formed and stable, and show that O_{sub} also leads to enhanced reactivity of oxidized metal surfaces.

Velocity Map Images of Subsurface Oxygen Desorbing from Rh(111)

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In heterogeneous catalysis, the reactivity of for example oxidation reactions is often enhanced by transition group metal surfaces as catalysts. After exposure, the oxygen molecules readily dissociate into oxygen atoms on the surface forming characteristic surface reconstruction patterns.¹ However, not only the formation of surface oxygen (O_{surf}) structures but also of subsurface oxygen (O_{sub}) phases is possible, especially when aggressive oxidation agents such as NO_2 or atomic oxygen are used as oxygen source.^{2,3} The O/Rh(111) has been adapted as a benchmark system for O_{sub} formation in the past. In temperature programmed desorption (TPD) experiments, O_{sub} emerges as a narrow desorption feature around 800 K, while O_{surf} forms a subsequent broad desorption feature over several 100 K. Although extensive research has been done on the formed reconstructions of O_{surf} , few is known about the microscopic details of O_{sub} formation.¹

In the here presented work, velocity map imaging (VMI) was applied to the O/Rh(111) system. We combined TPD and VMI to investigate recombinatively desorbing O_{sub} from Rh(111). This allows a precise assignment of high-resolution velocity distributions of desorption products to certain TPD peaks. We observe a hyperthermal velocity distribution for recombinatively desorbing subsurface oxygen. Desorption from surface states appears thermal. These results provide valuable benchmark data, on which theoretical models describing subsurface oxygen dynamics can be developed and tested.

Literature

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Photochemistry and spectroscopy of molecules at surfaces

– Insights (mostly) from ab initio molecular dynamics –

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The interaction of adsorbates on solid surfaces with light is central to surface spectroscopy, surface photochemistry, and non-adiabatic surface science in general. In the present contribution, light-driven molecular adsorbates will be modelled (mostly) by ab initio molecular dynamics. A few examples will be highlighted:

First, we consider femtosecond laser (FL) pulse driven chemistry at metals, e.g., FL-induced, hot-electron mediated desorption, diffusion or reactions. We describe these processes by Langevin Ab Initio Molecular Dynamics with Electronic Friction (AIMDEF) based on Density Functional Theory (DFT), and random forces obtained from a two-temperature model. Our focus is on associative desorption of H₂ and isotopomers from Ru(0001) and its “dynamical promotion”^[1], as well as on desorption, diffusion, reactions of CO on CO:Ru(0001) and CO/O:Ru(0001), respectively^[2].

A second example illustrates how vibrational (IR and Sum Frequency Generation (SFG)) spectra of water-covered aluminum oxide surfaces can be determined with the help of auto- and cross-correlation functions computed from DFT-based AIMD^[3].

Third, the step towards explicitly non-adiabatic surface dynamics is taken in the form of semiclassical, AM1/CI-based “surface hopping”. Specifically, we consider cis-trans isomerizations in densely packed or confined azobenzene molecules, and how they are influenced by excitonic and steric effects^[4].

Finally, briefly “photochemistry without light” will be analyzed with quantum mechanical models, for spectroscopy and simple “reactions” of molecules in cavities^[5].

[1] G. Fuchsels et al., PCCP **13**, 8659 (2011); J.I. Juaristi et al., Phys. Rev. B **95**, 125439 (2017).

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Orientalional isomerisation of CO on a NaCl(100) surface

– Characterization, kinetics and vibrational spectra from ab initio molecular dynamics

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CO adsorbed on NaCl(100) has served as a model system for studying structural and dynamical aspects of weak surface-molecule interaction, for many years now. Several interesting effects have been demonstrated for this system so far, such as vibrational energy pooling, orientational order disorder phenomena, very long vibrational lifetimes of the C-O stretch mode (~ 4 ms), and more recently orientational isomerization after infrared vibrational excitation, wherein the CO molecule adsorbs with the O-end pointing towards the surface rather than the canonical C-end^[1]. We study several aspects of this isomerization process .

First we consider different structures^[2] and energetics of the CO:NaCl(100) system as a function of coverage, map out two- and three-dimensional (global) potential energy surfaces as a function of three vibrational degrees of freedom and minimum energy pathways, particularly for the isomerization reaction. The quantum nature of the vibrations will be highlighted as well^[3].

Next, we go beyond the normal mode picture and look at different vibrational signatures coming from differently oriented CO adsorbates on the NaCl(100) surface and their dependence on temperature and coverage in the framework of ab-initio molecular dynamics coupled with time correlation functions, which include effects like anharmonicity, mode coupling and thermal surface motion.

We also briefly look at the vibrational energy flow between the individual CO adsorbate molecules and also the surface, when one or more of these adsorbates are vibrationally pre-excited by following non-equilibrium molecular dynamic simulations.

Finally, the kinetic aspect of the isomerisation process, mainly the “back-flipping” of “O-bound” CO to “C-bound” CO at temperatures ranging from 0 to 24 K and the importance of thermally mediated heavy-atom quantum tunnelling will be discussed.

[1] J.A Lau et al., Science, 2020, **367**, 175–178.

[2] D. Boese et al., J. Phys. Chem. C, 2016, **120**, 23, 12637–12653

[3] S. Sinha et al., PCCP, 2021,23, 7860-7874 .

Condensed phase isomerization through tunneling gateways

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When a particle crosses a barrier despite lacking the energy to overcome it, the phenomenon is called quantum tunneling. Tunneling is highly mass-dependent and a large isotope effect is often a signature of it. A tunneling rate is generally temperature independent, but it also can be temperature-dependent in special cases. In this work, we present such a tunneling phenomenon for a system of CO molecules undergoing an isomerization reaction following infrared excitation when absorbed on a NaCl surface [1]. The CO molecules “flip” on the surface from an O-bound isomer to a C-bound isomer through tunneling, giving rise to temperature-dependent rates with activation energy less than the predicted barrier height and a very high and non-intuitive kinetic isotope effect. Theoretical quantum rate theory calculation suggests that phonon-assisted accidental state-to-state resonance between the two wells on either side of the barrier opens the “gateways” for the molecules to tunnel. Tunneling through the “gateways” is found to be orders of magnitude faster than predicted by semiclassical models and can have a significant contribution to the making of “molecules of life” in cold interstellar space [2].

References:

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Electronically State-to-State Scattering of O atom from Au(111)

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The experiments use photolysis and discharge to produce three types of O atom beams with energies of 0.1-0.4 eV and different O(¹D) :O(³P) state ratios. The beam strikes an Au(111) surface with a well-controlled angle and surface temperature, we then employ REMPI-based ion-imaging measuring the species that scattering back as a function of angle, velocity, and internal state. No O(¹D) was observed scattering back, only O(³P) was measured. We measured high sticking probabilities for O(¹D,³P), approaching almost unity. The measured mean energy loss for O(³P) atoms scattering back is approximately 40% of the initial energy. The angular and velocity distributions of scattered O(³P) indicate a direct inelastic scattering process.

References

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Spin-forbidden carbon-carbon bond formation in vibrationally excited α -CO

Jessalyn DeVine

As the most abundant carbon-containing compound in the universe, reactions of CO which lead to carbon-carbon bond formation are of critical importance for production of complex carbon-rich molecules in astronomical environments. Carbon-carbon bond formation has been routinely observed in laboratory analogs of astronomical CO ices, where bombardment with high-energy (10-100 keV) irradiation leads to production of a wide range of C_n , C_nO , and C_nO_2 . However, the harsh conditions of such experiments make it difficult to develop a state-specific mechanism by which these molecules form.

Vibrational excitation of CO in the condensed phase is known to lead to vibrational energy pooling (VEP), where vibrational quanta are transferred between neighboring monomers through near-resonant processes described by



Here, we show that the levels of excitation achieved through VEP ($\nu \leq 37$) are sufficient to induce chemical changes leading to production of equal amounts of CO_2 and C_3O_2 , as evidenced by the clear signatures of these species in Fourier transform infrared absorption spectra. Exploration of the reaction pathway using density functional theory shows that the lowest-energy pathway to observed products requires transition to the triplet surface; trajectories remaining on the singlet surface are not productive, but lead back to reactants plus heat. Our results indicate that the required spin-flip occurs within a CO dimer that is consistent with the structural environment of the CO crystal as well as energetic thresholds for states populated through VEP. In addition to shedding light on the mechanism of C-C bond formation in CO ices, this work answers some key mysteries regarding the VEP dynamical framework, and represents an interesting case of vibrationally-driven chemistry.

Mechanistic Details of Hydrogen Interaction with Palladium

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Recently, we developed a detailed model for hydrogen interaction with palladium. The model was fit to velocity resolved kinetics data of HD formation, initiated transiently by a molecular beam pulse of a mixture of H₂ and D₂. The model was parametrized with rate constant expressions which are based on the framework of statistical mechanics and yielded fundamental energy parameters of the system.

In this work, I will apply the model to experiments performed under strongly differing conditions, where one of the isotopologues of hydrogen is supplied as static background gas and the second is used to trigger the reaction.

A good transferability of the model to conditions outside the original validation range underlines the elementary character of the involved processes. This is of high importance for applications to industrial processes performed under markedly different conditions.

Velocity-resolved laser-induced desorption for kinetics on surface adsorbates and isotherm measurements

Tianli Zhong,

Precisely measuring kinetics on surfaces is the key to understand the mechanism of heterogeneous catalysis. Current experimental methods like temperature-programmed desorption (TPD), molecular beam relaxation spectrometry (MBRS) and velocity-resolved kinetics (VRK) rely on thermal desorption of reaction products.[1, 2] However, surface reactions often involve species, i.e. reaction intermediates, which never desorb under reaction conditions. Therefore, we demonstrated a new method, laser-induced desorption velocity-resolved kinetics (LID-VRK), for probing adsorbate coverages on surfaces. In this method, an ultra-short laser pulse irradiates a single crystal surface covered with adsorbates and induces a flux of desorbing particles with typically hyperthermal velocity, which are detected with multi-photon ionization and ion slice imaging. Thereby, the detected LID signal is velocity-resolved by the delay between LID and the ionization, and is proportional to the surface coverage. A detection limit in the order of 10^{-4} monolayer can be achieved. A major advantage is the high surface sensitivity of the LID approach. It allows the measurement of reaction kinetics with microsecond resolution using pulsed molecular beams, which trigger the reaction at the surface. In addition, LID enables the measurement of adsorbate concentrations under steady-state conditions. An example is the measurement of Langmuir isotherms to extract adsorption enthalpies, even at low coverage limits. Lastly, we plan to detect reaction intermediates in surface reactions with LID-VRK, which is important for untangling the complex mechanisms, for example, the elementary steps in H_2 oxidation on catalysis surfaces.

Photoinduced electron transfer in self-assembled coordination cages: Ligand-to-ligand and host-to-guest charge transfer

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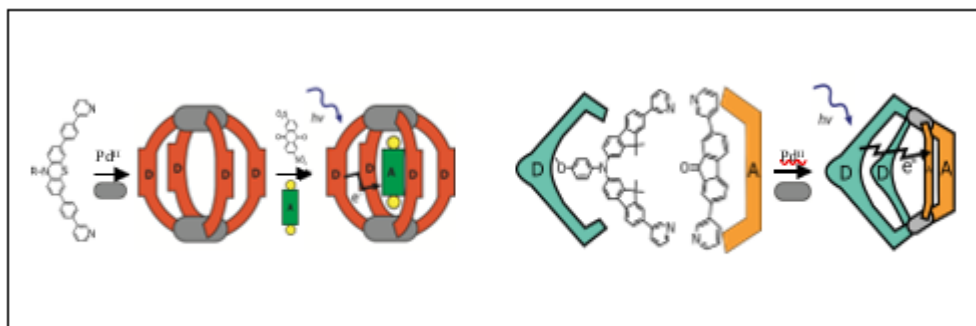


Figure 1: Host-to-guest and donor-acceptor cages capable of charge transfer.

In search for alternatives to highly efficient inorganic solar cells, cheap organic materials with tuneable molecular structure gained popularity, but the synthesis of electron donor-acceptor (D-A) systems is often rather tedious. A versatile yet simple solution is the construction of self-assembling supramolecular D-A structures using transition metals as linkers. These compounds allow precise control of D-A distance crucial to the lifetime of charge separated states after photoexcitation^[1].

Femtosecond-UV/vis-pump-UV/vis- and midIR-probe absorption spectroscopy are extremely powerful tools to elucidate the dynamics of charges after excitation. We already investigated cages of phenothiazine (D) and anthraquinone (A) derivatives^{[2],[3]}, however they formed interpenetrated Pd-double-cages with arbitrary ligand distribution and hence no control of D-A distance. Our new more sophisticated approaches use

- a phenothiazine (D) derivative cage hosting an anthraquinone-2,6-disulfonate (A) guest in its centre
- a triarylamine (D) and fluorenone (A) derivative cage with defined coordination due to restrictions in Pd coordination forced upon by ligands angulated structure

in order to achieve defined morphologies. Both showed clear evidence for charge-transfer.

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DFT reveals correlations between surface and bulk atom energies in fcc-metals

Loic Lecroart

The surface energies values are ambiguous in literature and lack of a general understanding. We propose two one-parameter models to estimate the surface energies for fcc-metals as Ag, Al, Au, Cu, Ni, Pd, Pt, Rh, but not for Pb. The models rely on the bulk energy and on a function that depends on the number of nearest neighbor atoms for the surface atoms. The function parameter was fitted with surface atom energies for (100), (110) and (111) surfaces, which show a strong correlation with bulk energies. The models provide a good comprehension of the energy distribution for (332) surfaces and can predict their surface energies within a relative error of 10% for Ag, Cu, Ni, Pd, Pt and Rh.

Electronic excitation of a semiconductor surface observed by H atom scattering

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Hydrogen atom scattering from various surfaces under ultra-high vacuum conditions is used to investigate the process of translational energy transfer from the impinging H atoms to the well-defined surface samples. The simplicity of the systems makes them particularly interesting for detailed comparisons between high-level experiments and first principle theories.

In the experiment, hydrogen atoms with a well-defined incidence translational energy are scattered from a surface sample, and their translational energy after the collision is probed by the Rydberg-atom tagging time-of-flight method to obtain scattering-angle resolved translational energy-loss spectra. For an insulating surface, it was shown that the collisions are nearly elastic and the observed energy-loss can be reproduced by molecular dynamics simulations based on the Born-Oppenheimer Approximation (BOA). For metals, on the other hand, large translational energy-losses were observed that could not be explained by purely electronically adiabatic energy transfer within the BOA. However, introducing a weak frictional force representing the energy transfer to the electrons successfully captures the physics of the collisions.[1]

In this talk, scattering results for H atoms colliding with a semiconducting Ge(111)c(2x8) surface are presented. Experiments reveal bimodal energy-loss distributions reflecting two scattering channels. Molecular dynamics simulations within the BOA reproduce only one of the two channels quantitatively. The second channel transfers much more energy and is absent in MD simulations. It increases in importance with H atom incidence energy and exhibits an energy-loss onset equal to the Ge surface bandgap. The comparisons between experiment and theory lead us to conclude that H atom collisions at the surface of a semiconductor are capable of promoting electrons from the valence band to the conduction band with high efficiency.

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On the role of surface structure in electronically non-adiabatic H atom scattering from silver

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Without adsorption, heterogeneous catalysis is not possible. A reactant adsorbs only if it transfers enough kinetic energy to the solid[1]; yet we still lack of a clear picture for the energy transfer mechanism between molecules and surfaces.

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.[2-5] However, the influence of the surface structure on the scattering dynamics has not been investigated until recently. In this talk, I present my efforts to adapt the technique used in the above mentioned studies onto other metal surface geometries.

Therefore, I firstly checked, if the potential energy surface (PES) for H at Ag(111) from Kammler et.al.[4] reproduces the energies for H at Ag(100) and Ag(110) without changing the parameterisation. Subsequently, I performed molecular dynamics simulations from those three different silver surfaces and compare probability distribution functions of the final polar angle and kinetic energy to complementary experiments.

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Towards application of ultrashort H atom pulses in time-resolved surface scattering experiments

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In laser-based pump-probe experiments the duration of the pump and probe pulses determine the temporal resolution of the experiment. Therefore, it is essential that the used pulse duration is significantly shorter than the timescale of the process of interest. However, for most chemical reactions to occur, collisions between particles are necessary. Considering collision induced reaction, controlling the exact time of the collision is crucial. Yet, our ability to control this timing is limited to microseconds or several 100 ns. Typically, the shortest neutral matter pulses are H atom pulses, generated by photolysis of hydrogen halides using pulsed UV lasers. But while standard methods yield pulse durations of >100 ns, the recently introduced method of bunch compression photolysis, involving spatially chirped ultra-short UV laser pulses, can produce H atom pulses with a pulse width of only a few nanoseconds [1].

Based on the original bunch compression photolysis approach, we present an improved version by using spatially chirped high energy femtosecond UV laser pulses for photolysis of hydrogen iodide, resulting in intense H atom pulses with a duration of down to 2.5 ns. Since the intensity of the H atom pulses is sufficient, we have performed angle- and velocity-resolved H atom scattering experiments on epitaxial graphene grown on Ir(111) and compared the results with theoretical molecular dynamics simulations.

Literature:

[1] S. Kaufmann, D. Schwarzer, C. Reichardt, A. M. Wodtke, O. Bünermann, *Nature Communications* **2014**, 5 (1), 5373.

High-Speed STM: Technique, Data Analysis, and Applications

Joost Winterlin

Ludwig-Maximilians-Universität, München

High-speed STM has been used to study surface diffusion of adsorbed particles, one of the main steps of a catalytic reaction. In this talk, I first present our STM setup that combines video-rate imaging with temperature variability. It utilizes a beetle-type scanner operated in the constant-height mode, a preamplifier with a high bandwidth, special driving voltages for the scanning piezos, and special software for data acquisition. Imaging rates of 10 to 50 frames per second have been reached. The temperature is varied between 50 and 500 K by simultaneous liquid He cooling and radiative heating. I then present the routine developed for the analysis of the obtained movie data. The routine makes use of a wavelet-based algorithm that detects and tracks adsorbed particles in the presence of the relatively high noise of the high-speed constant-height STM data. Trajectories with a resolution of $\sim 0.5 \text{ \AA}$ have been obtained, allowing us to follow the motion of individual atoms and molecules with atomic resolution. As an application, I present an investigation of the surface diffusion of adsorbed O atoms on a Ru(0001) surface. The O atoms are embedded in a dense layer of CO molecules. The adsorption system models the situation on a catalyst surface that, under actual reaction conditions, is usually fully covered by adsorbed particles. Surprisingly, the O atoms are almost as mobile as on the empty Ru surface. The observations can be understood by a diffusion mechanism that is driven by density fluctuations in the CO layer.

ABSTRACTS

(posters)

Poster Sessions

a/a	Name	Title of Poster
1.	Choudhury, Arnab	Condensed phase isomerization through tunneling gateways
2.	Crowley, Daniel	Investigation of the vibrational decoherence of CO adsorbed on NaCl(100)
3.	Frühling, Tim	Vibrational energy transfer in NO Cu(111) scattering and its possible role in dissociation
4.	Hertl, Nils	H atom scattering from a van der Waals surface.
5.	Hörandl, Stefan	Characterizing the CO formation in Formic Acid Decomposition on Pd(111) and Pd(332)
6.	Kandrantsenka, Alexander	Molecular Dynamics, Friction, and Langevin Force
7.	Lecroirt, Loic	Adsorbate modifies electronic nonadiabaticity: H/D atom scattering from p(2×2) O on Pt(111)
8.	Meyer, Sven	Surface scattering dynamics of graphene and graphite
9.	Schönemann, Anna-Maria	Towards application of ultrashort H atom pulses in time-resolved surface scattering experiments
10.	Tödter, Sophia	Influence of Ge(111) Surface-Hydration on H Atom Scattering Dynamics
11.	Zhong, Tianli	Velocity-resolved laser-induced desorption for kinetics on surface adsorbates and isotherm measurements

Condensed phase isomerization through tunneling gateways

A. Choudhury^{1,2}, *J. A. DeVine*², *S. Sinha*³, *J. A. Lau*^{1,2,4}, *A. Kandratsenka*², *D. Schwarzer*²,
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When a particle crosses a barrier despite lacking the energy to overcome it, the phenomenon is called quantum tunneling. Tunneling is highly mass-dependent and a large isotope effect is often a signature of it. A tunneling rate is generally temperature independent, but it also can be temperature-dependent in special cases. In this work, we present such a tunneling phenomenon for a system of CO molecules undergoing an isomerization reaction following infrared excitation when absorbed on a NaCl surface [1]. The CO molecules “flip” on the surface from an O-bound isomer to a C-bound isomer through tunneling, giving rise to temperature-dependent rates with activation energy less than the predicted barrier height and a very high and non-intuitive kinetic isotope effect. Theoretical quantum rate theory calculation suggests that phonon-assisted accidental state-to-state resonance between the two wells on either side of the barrier opens the “gateways” for the molecules to tunnel. Tunneling through the “gateways” is found to be orders of magnitude faster than predicted by semiclassical models and can have a significant contribution to the making of “molecules of life” in cold interstellar space [2].

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Investigation of the vibrational decoherence of CO adsorbed on NaCl(100)

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CO adsorbed NaCl(100) may have the weakest coupling between an adsorbate and a solid surface, thus making it an ideal system to study structure and dynamics of physisorbed molecules.

The previously estimated lower limit for the dephasing (or decoherence) time of 785 ps [1] had however only been deduced from frequency resolved FTIR measurements and has not directly been obtained in real time measurements. [1] Furthermore, to fully comprehend recent understanding of the mechanism of vibrational energy pooling (VEP) and photoisomerization of CO/NaCl(100) [2][3], we will directly measure the pure vibrational decoherence time of CO by using Sum Frequency Generation (SFG) spectroscopy.

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- [3] J. A. Lau et al., Science 367, 175-178 (2020)

Vibrational energy transfer in NO Cu(111) scattering and its possible role in dissociation

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Scattering diatomic molecules such as NO and CO from well defined metal surfaces (e.g. Au(111) and Ag(111)) has provided a deeper understanding of the underlying energy transfer processes, including non-adiabatic effects that lead to the breakdown of the Born-Oppenheimer-approximation (BOA)^[1]. As the last element in group 11, similar effects are assumed to be important for NO/Cu(111) scattering. Moreover, NO is known to dissociate on Cu(111)^[2], which raises the question of the influence of vibrational motion on this dissociation process. Preliminary experiments indicate a major contribution of trapping desorption in NO/Cu(111) scattering. Furthermore, similar to NO/Au(111) scattering, vibrationally elastic and inelastic scattering of NO($v=3$) is observed. State-to-state time of flight experiments will be conducted and a VMI setup will be added to the experimental setup to gain a deeper understanding of this system.

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H atom scattering from a van der Waals surface.

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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 and surface facets as well as insulators, 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 demonstrate that EMT can also be successfully used to describe the interactions between atomic hydrogen and solid xenon. The fitted potential has an RMSE smaller than 30 meV and MD simulations are capable to reproduce experimental recorded energy loss distributions extraordinarily well. [6] MD simulations performed a simple Lennard-Jones potential fail to describe the experiment.

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Characterizing the CO formation in Formic Acid Decomposition on Pd(111) and Pd(332)

Stefan Hörandl, J. Fingerhut, D. Borodin, M. Schwarzer, T. Kitsopoulos, A. Wodtke

Formic acid decomposition on catalytic surfaces is central to fuel cell technology. On metals, formic acid can decompose to CO and water or to CO₂ and hydrogen. For some time already, we know that on palladium the major pathway of formic acid decomposition yields CO₂ and hydrogen. More recently we found that the formation of CO and water is also present and enhanced at high temperatures.

In this report, we investigate formic acid decomposition on flat and stepped palladium surfaces by using Velocity-Resolved-Kinetics (VRK)[1]. We obtain formation yield of CO and CO₂ in the range of 653 – 873 K. We identify the rate determining step of gaseous CO formation to be the molecular desorption. Furthermore, we observe increasing reactivity of formic acid on step-sites. Monitoring the branching ratio of carbon species, we may further elucidate the understanding of formic acid reactivity on palladium which ultimately leads to a comprehensive microkinetic model.

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Molecular Dynamics, Friction, and Langevin Force

Alexander Kandratsenka

We compare molecular dynamics simulations based on the Langevin equation to experimentally derived energy loss distributions. Despite the fact that the incidence energy is much larger than the thermal energy and the scattering time is only about 25 fs, the energy loss distribution fails to reproduce the experiment if the random force is neglected. Neglecting the random force is an even more severe approximation than freezing the positions of the metal atoms or modelling the lattice vibrations as a generalized Langevin oscillator. This behavior can be understood by considering analytic solutions to the Ornstein–Uhlenbeck process, where a ballistic particle experiencing friction decelerates under the influence of thermal fluctuations.

Adsorbate modifies electronic nonadiabaticity: H/D atom scattering from $p(2 \times 2)$ O on Pt(111)

Loic Lecroart

We report inelastic differential scattering experiments for energetic H and D atoms colliding at a Pt(111) surface with and without adsorbed O atoms. Dramatically, more energy loss is seen for scattering from the Pt(111) surface compared to $p(2 \times 2)$ O on Pt(111), indicating that O adsorption reduces the probability of electron-hole pair (EHP) excitation. We produced a new full-dimensional potential energy surface for H interaction with O/Pt that reproduces density functional theory energies accurately. We then attempted to model the EHP excitation in H/D scattering with molecular dynamics simulations employing the electronic density information from the Pt(111) to calculate electronic friction at the level of the local density friction approximation (LDFA). This approach, which assumes that O atoms simply block the Pt atom from the approaching H atom, fails to reproduce experiment because the effective collision cross section of the O atom is only 10% of the area of the surface unit cell. An empirical adiabatic sphere model that reduces electronic nonadiabaticity within an O-Pt bonding length scale of 2.8 Å reproduces experiment well, suggesting that the electronic structure changes induced by chemisorption of O atoms nearly remove the H atom's ability to excite EHPs in the Pt. Alternatives to LDFA friction are needed to account for this adsorbate effect.

Surface scattering dynamics of graphene and graphite

Sven Meyer, Alec M. Wodtke, T. Schäfer

Since its first successful preparation in 2004, graphene has been extensively studied because of its outstanding mechanical, thermal and electronic properties. Graphene is an especially interesting material because of its zero-bandgap electronic structure, which puts it right on the edge between metals and semiconductors. Up to this point, non-adiabatic interactions have only been observed on metal surfaces. In this work, vibrational excitation of NO was investigated as a probe for non-adiabatic interactions by scattering a molecular beam of NO from epitaxial graphene on Pt(111) (Gr/Pt) and highly oriented pyrolytic graphite (HOPG). No signs of non-adiabatic interactions were found. Instead, thermal vibrational excitation of NO was observed on Gr/Pt as a result of a trapping-desorption scattering mechanism, which is supported by state to state time of flight measurements. In contrast, on HOPG only direct scattering without vibrational excitation has been observed. Further state to state time of flight experiments revealed a very efficient coupling between the surface and the kinetic energy of the NO, resulting in a high translational energy loss of up to 80% for Gr/Pt, and up to 66% for HOPG. An enhanced sticking probability of NO on graphene compared to HOPG was observed that could be modeled using detailed balance. This enhanced sticking probability makes graphene an interesting substrate for catalysts, where it can act as a net to catch the reactands.

Towards application of ultrashort H atom pulses in time-resolved surface scattering experiments

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In laser-based pump-probe experiments the duration of the pump and probe pulses determine the temporal resolution of the experiment. Therefore, it is essential that the used pulse duration is significantly shorter than the timescale of the process of interest. However, for most chemical reactions to occur, collisions between particles are necessary. Considering collision induced reaction, controlling the exact time of the collision is crucial. Yet, our ability to control this timing is limited to microseconds or several 100 ns. Typically, the shortest neutral matter pulses are H atom pulses, generated by photolysis of hydrogen halides using pulsed UV lasers. But while standard methods yield pulse durations of >100 ns, the recently introduced method of bunch compression photolysis, involving spatially chirped ultra-short UV laser pulses, can produce H atom pulses with a pulse width of only a few nanoseconds [1].

Based on the original bunch compression photolysis approach, we present an improved version by using spatially chirped high energy femtosecond UV laser pulses for photolysis of hydrogen iodide, resulting in intense H atom pulses with a duration of down to 2.5 ns. Since the intensity of the H atom pulses is sufficient, we have performed angle- and velocity-resolved H atom scattering experiments on epitaxial graphene grown on Ir(111) and compared the results with theoretical molecular dynamics simulations.

Literature:

[1] S. Kaufmann, D. Schwarzer, C. Reichardt, A. M. Wodtke, O. Bünermann, *Nature Communications* **2014**, 5 (1), 5373.

Influence of Ge(111) Surface-Hydration on H Atom Scattering Dynamics

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Previously H atom scattering experiments have been investigated on insulator and metal surfaces through experiment and theory. It was found, that the Born-Oppenheimer Approximation holds for insulators, but fails for metals. Germanium is a common semiconductor and thus an ideal candidate to investigate H atom scattering processes from semiconductors. A common problem with semiconductors is the complexity of their surface reconstructions, which complicates the theoretical treatment of the surfaces. One potential method for preventing the reconstruction and maintain the sp³ bulk hybridization is through hydration.

Results of scattering experiment from the hydrated and clean Ge(111) surfaces at two incidence energies will be presented and compared to adiabatic molecular dynamics (MD) calculations, which were carried out for the clean, reconstructed Ge(111) surface.

Bimodal energy loss distributions were observed during the experiments for the clean surface at both incidence energies. Adiabatic MD calculations were not able to reproduce the bimodality, only showing a quasi elastic peak. The hydration of the surfaces lead to a loss of the bimodality. The observed energy loss distribution at the lower incidence energy was identical to the adiabatic MD calculations. At the higher incidence energy a broader energy loss distribution was observed. This one results likely from the overlap of the quasi elastic peak with an unknown third component.

Velocity-resolved laser-induced desorption for kinetics on surface adsorbates and isotherm measurements

Tianli Zhong

Current experimental methods like temperature-programmed desorption (TPD), molecular beam relaxation spectrometry (MBRS) and velocity-resolved kinetics (VRK) rely on thermal desorption of reaction products. However, surface reactions often involve species, i.e. reaction intermediates, which never desorb under reaction conditions. Therefore, we present a new method, laser-induced desorption velocity-resolved kinetics (LID-VRK), to probe adsorbate coverages on surfaces. In this method, an ultra-short laser pulse irradiates a single crystal surface covered with adsorbates and induces a flux of desorbing particles with typically hyperthermal velocities, which are detected with multi-photon ionization and ion slice imaging. Thereby, the detected LID signal is velocity-resolved by the delay between LID and the ionization. This two-laser signal is then recorded as a function of time after the dosing molecular beam pulse and it decays exponentially. First-order thermal desorption rate constants are obtained over a range of temperatures and found to be in good agreement with past reports. Since laser induced desorption (LID) produces hyperthermal gas phase molecules, they can be detected with little or no background. This approach is highly surface specific and exhibits sensitivity below 10^{-4} ML coverage. Because the signals are linearly proportional to adsorbate concentration, the method can be employed at lower temperatures than VRK, whose signal is proportional to reaction rate.

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