The Effect of Doping in Inelastic H Atom Scattering from Silicon

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Recent inelastic H atom scattering experiments from the semiconducting Ge(111)c(2x8) have shown a bimodal energy loss distribution. One of the components was narrow with a small energy loss. The other component has shown a broad and large energy loss with an onset equal to the surface band gap.[1] While the low energy loss channel is explained by an adiabatic molecular dynamics simulation, the high energy loss component is not described theoretically yet.

To gain a better understanding of the underlying mechanism, we extended our studies to the Si(100)2x1 surface which is semiconducting as well. Despite its electronic structure being similar to the Ge(111)c(2x8) surface, it shows a different H atom energy-loss distribution. The first component is much broader and the second component does not show a clear onset at the surface band gap, both indicators of electronic effects. To further investigate, we carried out scattering experiments from samples with various doping levels. While the second component seems largely unaffected, we observe a clear dopant induced shift in the first component.

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H Atom Scattering Meets Ultrafast Laser Heating: Obstacles, Results and Simulations

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Using spatially chirped high energy femtosecond UV laser pulses for photolysis of hydrogen iodide we generate intense H atom pulses [1] with a measurable pulse duration of down to 1.5 ns. Since the intensity of the H atom pulses is sufficient, we have performed angle- and velocity-resolved H atom scattering experiments on highly oriented pyrolytic graphite (HOPG).

Similarities to the previously conducted experiments on graphene on Ir(111) were observed. Differences can primarily be attributed to the structural differences of the surfaces. Since the obtained signal is well reproducible and the signal of the scattered H atoms is clearly distinguishable from the background signal, the next step towards time-resolved scattering experiments was taken: the simultaneous heating of the surface with a 25 ps, 532 nm laser pulse. I will present first results, experimental challenges encountered along the way, and a possible interpretation of the data.

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Effect of the Substrate on Hydrogen Atom Scattering from Graphene

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Previously, H atom scattering from graphene grown on a Pt(111) substrate was investigated in detail by our group [1]. Depending on the experimental conditions, two energy loss channels were observed, one quasi-elastic and one strongly inelastic. For a C-H bond to form, the delocalized electronic structure of graphene has to be locally destroyed. This gives rise to an adsorption barrier. If the hydrogen atom cannot cross the barrier, it is elastically reflected. However, if the atom can cross the barrier, it loses a large amount of energy, which can lead to it sticking to the surface [1]. Pt(111) was chosen because it is a weakly interacting substrate. This allows comparison of the experimental data with simulations of H atom scattering from free-standing graphene. Although good qualitative agreement is achieved between experiment and theory, quantitative agreement cannot be achieved because of the non-negligible substrate effect.

To experimentally study the substrate effect we chose Ni(111) as an additional substrate and performed the same experiments. Ni(111) is a strongly interacting substrate and a much larger substrate effect is expected.

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Overcoming Limitations of Quasi-Continuous Ion Imaging Experiments: Solutions Instead of Work-Arounds

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Over the last decade, velocity-resolved kinetics (VRK) has shown to be a powerful to investigate the detailed mechanism of surface reactions. In a VRK experiment, two pulsed molecular beams cross at a catalytic surface. While one molecular beam doses the sample with a first reactant, the second molecular beam pulse initiates the reaction. Reaction products desorb from the catalyst and are ionized by a time-delayed ultra-short laser pulse via non-resonant multi-photon ionization. An ion imaging detector measures ions density and velocity, given direct access to the time-dependent product flux called the kinetic trace. Conventional VRK suffers from long measurement time and low-duty cycle since only one beam-laser delay is detected per molecular beam cycle. Recently, we developed an improved version of VRK using a high repetition rate 100kHz ionization laser for quasi-continuous ionization and detecting the ion signal from each single laser pulse via an event-based Timepix3 camera. This high-repetition rate VRK (HRR-VRK) variant increases the duty-cycle of the experiment to 100%, dramatically reducing measurement time and increasing signal-to-noise. Detection of all kinetic times for each molecular beam pulse further allow for non-steady state experiments.

Despite the tremendous advancements of HRR-VRK, the quasi-continuous ion detection revealed severe problems with the standard experimental approach, i.e. (1) strong background from electron bombardment heating of the sample and (2) limitations in detectable ion count rate resulting from gain depletion in the microchannel plate ion-imaging detector. Current "workarounds" significantly limit the possible capabilities of HRR-VRK. Here, we present solution to the existing problems, which will allow lifting HRR-VRK experiments to the next level.

Full-dimensional First-principles Nonadiabatic Dynamics of Energy Transfer in Gas-Surface Scattering

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Energy transfer among different degrees of freedom (DOFs) at gas-surface encounter is of fundamental importance to interfacial chemical processes. Particularly, the energy of incident species can be loss to either surface phonons via an adiabatic mechanism or surface electrons via a non-adiabatic mechanism. A first-principles description of such processes has been challenging as numerous DOFs are involved. By combining the constrained density functional theory (CDFT) to determine charge transfer states at metal surfaces and the independent electron surface hopping approach, we have arrived at a full-dimensional first-principes description of nonadiabatic energy transfer dynamics of highly vibrational excited CO and NO molecules scattered from metal surfaces. Our results emphasize the importance of using a full-dimensional theoretical model and the proper density functional to accurately describe the molecule-surface interaction. It is essential to simultaneously characterizing both adiabatic and nonadiabatic channels for an accurate theoretical description of diverse experimental data. In addition, for H scattering from Ge(111)-c(2×8), we have performed non-adiabatic molecular dynamics simulations based on classical path approximation and surface hopping among Kohn-Sham orbitals. Our results indicate that non-adiabatic electronic transitions from the valence band to the conduction band are more likely to occur at the rest atom site. This mechanism has been recently confirmed by real-time time-dependent DFT simulations, which yield more quantitative results that can be compared with experiment.

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Towards inelastic H atom scattering from cold metal surfaces

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Inelastic scattering experiments of H atoms from metal surfaces have shown that a large amount of kinetic energy can be transferred to electronic excitations of the surface in a collision. The experiments cover a wide range of incidence conditions, both isotopes, various metal surfaces and surface facets. In all cases a very similar behavior was found and only small changes are observed [1-4]. Theoretical models using molecular dynamics simulations with electronic friction show good agreement in all cases. However, recent theoretical studies of the surface temperature dependence revealed that thermal broadening due to thermally exited electron-hole-pairs washes out separate features representing different scattering processes, such as single bounce, multi bounce or subsurface scattering [5]. Furthermore, also details related to the theoretical model, such as the potential energy surface (PES) used or the applied version of friction theory can no longer be distinguished at room temperature [6]. These arguments make it highly desirable to perform H atom scattering experiments on cold metal surfaces.

So far, almost all experiments have been performed at room temperature or higher, and only preliminary experiments were performed at surface temperatures of 110 K. As predicted by simulations, this temperature is not sufficient and we need to achieve surface temperatures well below 100 K, preferably below 10 K. However, there is a major challenge in performing scattering experiments at such low surface temperatures: Physisorption of background gas molecules becomes possible and leads to surface contamination. This has to be suppressed, since H atom scattering experiments on metal surfaces are very sensitive to surface contamination - coverages of << 1% already lead to a visible change of the observed spectrum. Although this represents a major experimental challenge, the prospects of such an effort are to resolve single scattering processes and to provide a more stringent test for theoretical models.

In this talk I will briefly summarize the previous experimental and theoretical work on inelastic H atom scattering from metal surfaces, introduce our approach to realize scattering experiments at very low surface temperatures, and give an update on the current state of the experiment.

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Vibrational energy transfer upon the collision of NO with VO_2 thin films across the insulator-to-metal transition

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Vibrational energy transfer between molecule and metal surface is perhaps one of the most illustrative and chemically relevant examples, where Born Oppenheimer Approximation (BOA) - the cornerstone of molecular level understanding of chemical reactions - is routinely violated. During recent decade tremendous improvements in the state-of-the-art of molecule's preparation and detection yielding overwhelming amount of detailed experimental data that triggered a wave of theoretical advances [1].

However, to the date, the vast majority of our understanding has been gained from scattering experiments conducted on single crystal metal surfaces, while there have not been any fundamental experiments extending our fundamental knowledge on this topic to complex functional surfaces, able to change their electronic properties, bearing on vibrational energy transfer, under external stimuli. In this respect, vanadium dioxide, VO_2, appears to be particularly fascinating as it can morph itself between insulator and metal in only a few degrees temperature range, known as the insulator-to-metal or Mott transition. While this remarkable property of VO_2 triggered numerous technological applications e.g. smart windows, switches, resonators, sensors, field effect transistors, to mention a few, little is known how metal-to-insulator transition impacts vibrational energy transfer. This situation is unfortunate, since vibrational energy transfer in molecule – surface encounters is particularly relevant to understanding the elementary process of bond cleavage, since the vibration of two atoms against one another is precisely the motion needed to induce a reaction.

Here we report clear observations of direct scattering of translationally hyperthermal, vibrationally excited NO from thin VO_2 films across the insulator-to-metal transition [2]. We observed a measurable enhancement of vibrational relaxation probability of NO (v_I=3,11) molecules when the VO_2 transforms from its insulating to metallic phase at 68°C, accompanied by four-order decrease in resistivity. Surprisingly, the enhancement in vibrational relaxation of NO(v_I=3,11) upon insulator-to-metal transition in VO_2 is rather small (order of few percent), in contrast to the stark differences observed between vibrational relaxation probabilities on "typical" metal and insulating surfaces, such as Au or Ag and LiF, respectively. Moreover, the magnitude of vibrational relaxation of the metallic phase of VO_2 is significantly lower than expected, considering the knowledge accumulated for single crystal metal surfaces. We are able to explain the low propensity of NO vibrational relaxation on VO_2 based on electron-transfer mediated vibrational relaxation mechanism, assuming inefficient image charge stabilization of affinity level, as opposed to scattering from coinage metals, which, to the date, shaped our understanding in the field. We believe that our findings will trigger developments in first-principles electronic structure calculations and nonadiabatic dynamics simulations that will promote our understanding of vibrational energy transfer on complex substrates to the level achieved for single crystal metal surfaces

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Towards Nonadiabatic Dynamics Simulations of Carbon Atom Scattering from Metal Surfaces

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The measurements of energy loss spectra of carbon atom scattered off Au(111) surface conducted recently at Dalian Coherent Light Source facility suggest involvement of nonadiabatic effects. In order to construct a theoretical model describing that we are going to use the Independent-Electron Surface Hopping (IESH) approach developed in Tully Lab at Yale University, where the interaction of an incident atom (or molecule) with the surface induces the overlap of atomic and metallic orbitals facilitating energy exchange between projectile's nuclear degrees of freedom and ehp of a metal. The first step here is to produce full-dimensional potential energy surfaces for each single-electron state relevant for the dynamics. In case of C atom, these are triplet (ground state) and singlet spin states of a neutral C, and quartet and doublet states of C anion. We report the preliminary results obtained in pursuing the task above.

Wodtke Retreat Abstract

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Molecular Beam Surface Scattering of O_2 on Au(111)

In the past non-adiabatic vibrational excitation of NO has been observed for systems that are prone to electron transfer for instance NO scattered on Au(111). Since the O_2 molecule has a higher electron affinity, the energy transfer due to electron-hole pair excitation in the system O_2 on Au(111) is assumed to be more intense. In contrast to NO the state-resolved O_2 detection by resonance enhanced multi photon ionization (REMPI) was challenging due to missing REMPI schemes, but a recently developed (2+1') REMPI scheme is suitable even for the detection of scattered or vibrationally excited O_2 molecules.

We measured quantum-state-resolved REMPI-spectra in a supersonic molecular beam of O_2 in the vibrational ground state (v = 0) and in the thermally excited sate (v = 1) at different beam temperatures by two color REMPI and ion imaging. A heatable tube that is mounted in front of the pulsed nozzle addresses the vibrational temperature of the supersonic jet while maintaining its cold rotational temperature and sharp velocity distribution. We have located the corresponding bands in the incident beam. Now we are able to identify state-resolved O_2 in scattered molecular beams. This will allow us to determine the vibrational excitation probability of O_2 on Au(111).

Chemical dynamics in single particle catalysis: observing reactions by correlative *in situ* microscopy

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Keywords: Catalysis, Hydrogen, Microscopy, Spectroscopy, Mikrokinetics

Operando spectroscopy of catalytic reactions has been very successful in mechanistic studies.[1] However, as spectroscopy typically examines large areas/volumes, this averaging "smoothens out" local variations that may be critical to understand how a reaction proceeds. Dynamics in catalyst structure, composition and adsorbate coverage may also go unnoticed by averaged spectral data. A way overcoming these limitations is to use correlative surface microsopy to directly "watch" ongoing catalytic reactions, i.e. to apply several microscopic and spectro-microscopic techniques to the same catalysts locations under identical reaction conditions.[2] Most of the methods herein not only image catalyst structure or composition, but also the adsorbed reactants, so that active and inactive states can be discerned (*kinetics by imaging)*, active regions identified and mechanisms elucidated.[3]

Examples of real-time *in situ* imaging of H_2 oxidation include meso-scale polycrystalline Rh surfaces and Rh nanotips (as small as 30 nm, enabling *single particle catalysis*). For planar catalysts, UV- and X-ray photoemission electron microscopy (UV- and X-PEEM), low energy electron microscopy (LEEM) and scanning photoelectron microscopy (SPEM) were used with resolution up to 3 nm. For nanotips, field emission microscopy (FEM) and field ion microscopy (FIM) were applied with up to atomic resolution.

The direct, real-time and locally-resolved observation of H_2 oxidation on Rh-based catalysts revealed:
(i) the transition from inactive to active states via catalytic ignition and spreading of chemical waves,[4]
(ii) the mechanism of oscillatory H_2 oxidation involving subsurface oxygen,[4]
(iii) how particle size, support and surface composition (decoration, SMSI) affect the local activity,[5]
(iv) whether different facets on a single Rh nanoparticle communicate via hydrogen diffusion or not (coupled monofrequential vs. (uncloupled) multifrequential oscillations),[6]
(v) detecting active sites on a single particle via imaging water molecules,[6]
(vi) that chaos even exists at the nanoscale,[7] and
(vii) how La modifies the reaction dynamics on a Rh nanotip.[8]

Microkinetic modelling and density functional theory (DFT) rationalized the experimental observations. The novel nanoscale insights in the dynamics of reactants and surfaces, including the identification of active regions, may stimulate new ways of catalyst design and operation.

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Hydrogen Oxidation on Platinum Surfaces – A Case of Non-Langmuir-Hinshelwood Chemistry?

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The hydrogen oxidation reaction on platinum surfaces

$$H_{2(g)} + O_{2(g)} \xrightarrow{\text{Pt}} H_2O_{(g)}$$

has been recognized since the early 1800s as a fascinating example of heterogeneous catalysis [1]. Yet, a comprehensive understanding of its reaction mechanism remains elusive [2]. Here, we present water formation kinetics on platinum single crystal surfaces, measured using the high repetition-rate velocity-resolved kinetics method, for two distinct experimental approaches: (1) an excess of atomic hydrogen on the surface, with a molecular beam of O_2 initiating the reaction, and (2) an excess of atomic oxygen on the surface, with a molecular beam of H_2 initiating the reaction. Our analysis identifies the $O^* + H^*$ reaction as the rate-limiting step in experiment (1), while in experiment (2), it corresponds to the $OH^* + OH^*$ reaction. This suggests a change in the reaction mechanism under oxygen-rich conditions, leading to accelerated OH^* formation.

These results are discussed in the context of a previously proposed mechanism for hydrogen oxidation on palladium surfaces [3], which appears unlikely to explain the observations on platinum. Instead, we propose an alternative mechanism in which intact H_2 molecules react directly with adsorbed oxygen atoms, forming OH^* as a competing pathway to hydrogen dissociation on the bare platinum surface. Theoretical insights support this hypothesis: DFT calculations reveal a lower activation barrier for the reaction of H_2 with O^* compared to OH^* formation from adsorbed H^* and O^*. The importance of this process is further confirmed by ab initio molecular dynamics simulations of H_2 adsorption on oxygen-covered platinum surfaces.

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Rate determining processes for ammonia conversion and product formation during oxidation on Pt surfaces

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Ammonia (NH_3) oxidation on Pt involves many experimental challenges, such as catalytic activity over a broad temperature range, coverage-dependent product branching and significant catalytic influence. Exploiting the recently developed method of high repetition-rate velocity-resolved kinetics (HRR-VRK)[1], we present kinetic measurements of NH_3 depletion as well as nitric oxide (NO) and water formation in the range of 443-973 K with focus on the high oxygen coverage conditions that are relevant for the industrial Ostwald process. Two main subjects are addressed:

First, we use stepped Pt single crystals (Pt(332), Pt(10 10 9) and Pt(33 33 32)) to discuss the influence of microscopic NH_3 surface diffusion on the initial NH_3 dehydrogenation and quantify the catalytic effect of atomic steps.

Second, we employ the multi-mass-detection and signal-to-noise reduction capabilities of HRR-VRK to link observed NO formation kinetics on Pt(332) to a rate determining reaction intermediate at different conditions.

The level of understanding of both subjects can be elevated by density functional theory (GGA-DFT) calculations both published[2] and in progress in conjunction with microkinetic modeling. In general, the aim of this project is to compare previous studies[3] with new experimental results in order to understand this example of heterogeneous catalysis in more detail.

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Probing surface dynamics at the solid-liquid interface

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The electrified electrode electrolyte interface is notoriously difficult to study during electrochemical (EC) reactions. Most traditional surface science techniques are disqualified due to the use of electrons, on the other hand, several new in-situ experimental methods have been developed recently. Examples are Electro Chemical X-ray Photoelectron Spectroscopy (ECXPS), Scanning Tunneling Microscopy (STM), Atomic Force Microscopy (AFM), High Energy Surface X-Ray Diffraction (HESXRD) [4] and EC-IRAS [5]. However, each of these methods has limitations in the EC environment. To better understand the electrode surface development and dynamics during EC reactions, a combination of methods is necessary.

In the first part of the talk, the corrosion of an industrial Ni base Ni-Cr-Mo alloy will be addressed. A comprehensive investigation combining several synchrotron-based techniques are used to study the surface region of a Ni-Cr-Mo alloy in NaCl solutions in situ during electrochemical polarization. X-Ray Reflectivity (XRR) and ECXPS were used to investigate the thickness and chemistry of the passive film. Grazing Incidence X-ray Diffraction (GIXRD) was used to determine the change in the metal lattice underneath the passive film. X-Ray Fluorescence (XRF) was used to quantify the dissolution of alloying elements. X-ray Absorption Near Edge Structure (XANES) was used to determine the chemical state of the dissolved species in the electrolyte. Combining these techniques allowed us to study the corrosion process, detect the passivity breakdown in situ, and correlate it to the onset of the Oxygen Evolution Reaction (OER) [6].

In the second part, an alternative approach to study the development of a model electro catalyst surface is presented. By using a combination of Grazing Incidence X-ray Absorption Spectroscopy (GIXAS) [7], 2D Surface Optical Reflectance (2D-SOR) [8] and Cyclic Voltammetry (CV) and a Au(111) electrode model surface, direct surface information during real-time CV can be obtained. Using H_2SO_4 as an electrolyte, our study demonstrate that a thin, passive Au oxide is formed at potentials corresponding to the oxidation peak in the Au CV. This oxide prevents further oxidation of the surface, and not until the onset of the OER, further oxidation of the Au surface occurs leading to the formation of a thick Au oxide.

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Unravelling the interfacial electrolyte structure in the electrochemical double layer with THz spectroscopy and X-ray scattering experiments

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Chemical reactions at the solid-liquid interface are fundamentally governed by the structure of the solid and by the structure and dynamics of the electrochemical double layer (EDL). Hence, to understand and predict electrochemical reactivity and mechanisms, which ultimately can improve our rational-catalyst-design-protocols, detailed experimental characterization of both the electrode surface and the molecular structure of the electrolyte in contact with the electrode is required. Here, I propose to apply spectroscopy at THz frequencies, measured using pulsed electrochemical potentials and a lock-in-amplification scheme, to investigate the interfacial hydrogen-bond (HB) water network at a single crystal electrode under electrochemical conditions.[1] THz-spectroscopy is especially well-suited to probe collective intermolecular vibrations that determine the HB connectivity in interfacial water but are also sensitive to the rattling modes of hydrated ions. Using a lock-in amplifier makes the proposed experimental setup more sensitive than previous designs. Additionally, structural characterization of the metallic surface and the position of ions within the EDL will be measured using in-situ X-ray scattering experiments. This combines the grazing incidence wide-angle X-ray scattering method which probes the crystallographic orientation of the electrode as a function of applied potential, pH and cation/anion concentration with (off-) resonant X-ray diffraction experiments.[2] The combined information of these techniques will be used to find the descriptors than can predict the reactivity of the hydrogen evolution reaction on Au(111). Currently, a huge knowledge gap exists in the order of magnitude decrease in reaction kinetics in alkaline vs. acidic media. While a number of descriptors have been proposed,[3] recently theoretical calculations[4] suggested that the HB connectivity in the interfacial water network is a key factor that determines reactivity but robust and detailed experimental verification is still lacking.

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Taming Complexity in Heterogeneous Catalysis

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The complex and dynamic nature of heterogenous catalytic materials means that even when using high-resolution spectroscopic methods (e.g., XAS, TEM) identification of “active sites” on “technical catalysts” is fraught with difficulties. To circumvent these hurdles, we have developed a method where intrinsic kinetics is used to probe active sites. As the rate at which a species reacts on a catalytic surface is defined by the local environment in which that species is adsorbed, an intrinsic rate constant (i.e., one that has been isolated from thermal and mass transfer constraints) of a chemical transformation is an accurate descriptor of the “active site” on the catalyst surface. In this work, we demonstrate how intrinsic kinetics can be used to quantify and characterise active sites, and how this leads to new discoveries on structure-function relationships.

Decomposition of NO_2 on Palladium: The Kinetics of Oxygen and Nitrogen Atom Recombination at Steps & Terraces of Palladium

NO_2 is a significant environmental pollutant and a key intermediate in catalytic processes such as NOx Storage and Reduction (NSR) and Selective Catalytic Reduction (SCR), making its decomposition a crucial area of study for improving pollution control technologies and understanding surface reaction mechanisms. In addition, oxygen and nitrogen atom recombination plays a crucial role as a competitive process in several key catalytic reactions, but its kinetics have proven challenging to probe at the atomic scale. This study investigates oxygen and nitrogen recombination on two facets of palladium, Pd(332) & Pd(111), under ultra-high vacuum conditions using a novel pulsed molecular beam apparatus capable of collecting high repetition rate, velocity-resolved kinetics. In particular, we examine the decomposition of NO_2 on Pd surfaces as a pathway to study O_2 and N_2 recombination. Notably, surface temperature is controlled by laser heating, allowing access to higher temperatures while completely eliminating the large amounts of background signal that was unavoidable in previous electron bombardment heating methods.

Advancements in Measuring the Thermal Rates of Gas-Surface Reactions

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The accurate determination of gas-surface reaction kinetics requires the measurement of product formation as a function of reaction time, beginning from when reactant reaches the surface. Velocity-Resolved Kinetics (VRK) techniques[1] employ pulsed supersonic molecular beams to deliver time-resolved packets of reactants from the gas-phase to a catalytic surface. Desorbing product fluxes [e.g. $H_{2(g)} + O_{2(g)} \xrightarrow{Pd(111)/Pd(332)} H_2O_{(g)}$][2] are then ionized via a pulsed laser and detected in the form of velocity-sensitive ion images. Analysis of these isothermal time-resolved measurements allows for the determination of elementary rate constants and energetic barriers for desorption, dissociation, or diffusion; thereby providing benchmarks for theoretical predictions to compare against.[3-6]

Recently, a High-Repetition Rate (HRR-) form of VRK has been achieved using a point focused 100 kHz laser system to produce ions from desorbing fluxes via non-resonant multiphoton ionization; an ionization source that begins to approach a universal detection scheme. Resultant ion images are then generated by a gated microchannel plate + phosphor screen detector and recorded in a quasi-continuous manner by a novel event-based camera (ASI Hyperion TPX3CAM) as a collection of ion events with unique pixel-specific timestamps. The combination of high-repetition rate and event-based sensing yields a temporal evolution of multiple reaction products as a function of each individual molecular beam pulse with microsecond resolution. Conversely, conventional VRK measurements were collected by scanning the delay between molecular beam and laser pulses, necessitating steady-state conditions and rebound by the end of each pump-probe cycle. This renders conventional VRK blind to transient behavior on non-stationary catalysts and insensitive to reactions with timescales exceeding 100 milliseconds (i.e. reactions at low temperature); two limitations overcome by HRR-VRK. Notably, HRR-VRK has been successfully employed to monitor the evolving competition between hydrogen oxidation and recombination rates as a function of changing surface oxygen coverage, as well as the coverage-dependent desorption of nitric oxide on palladium. Further advancements include the direct detection of reaction intermediates using laser-induced desorption, improved mass resolution (relevant to isotope studies), and high-sensitivity universal detection using electron bombardment ionization.

Acknowledgments: European Research Council (ERC) under the European Union's Horizon 2020 research and innovation program (grant agreement No. 833404).

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Styrene Epoxidation on Oxidized Silver

Tim Schäfer

Abstract:

The epoxidation of olefins on Ag/O systems is a significant industrial-scale process within heterogeneous catalysis. However, the details of the surface reaction remain controversial, and it has been highly challenging to reconcile the findingsfrom catalytyic studies under reaction conditions with the highly detailed static studies under carefully controlled ultra-highvacuum (UHV) conditions. We combine molecular beam surface scattering and ion imaging techniques to explore the partial oxidation of styrene. This experimental approach enhances the sensitivity to the extent that we can directly observe the partial oxidation product, styrene oxide, under UHV conditions. We note that partial oxidation exclusively occurs at high oxygen coverages, which we attribute to the reaction of styrene with electrophilic oxygen formed specifically at elevated coverages.

Roaming reactions of chiral aldehydes

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Roaming reactions were first identified when the photodissociation of formaldehyde produced vibrationally cold but rotationally hot CO instead of vibrationally hot CO. Hence, the photodissociation of formaldehyde followed two reaction pathways: the direct bond dissociation path, which is associated with the transition state, and the roaming reaction pathway, which involves radicals. In this study, we wanted to study the chirality of the resulting product after photodissociation of a chiral aldehyde and how two different reaction pathways affect the chirality of the final products.

In this study, we investigated the photodissociation of acetaldehyde in the compact beamer to understand how it adapts the experimental conditions. As the initial step, we identified the photodissociation product of acetaldehyde. We determined the optimal beam conditions under which acetaldehyde produced fewer clusters using a femtosecond laser (Spectra-Physics, Solstice Ace, 800 nm, 35 fs, rep-rate 1 kHz). Thereafter, we used the nanosecond laser pulses Nd: YAG laser at 10 Hz (Spectra-Physics, Quanta-Ray)-pumped dye laser (Sirah, Cobra-Stretch) to photodissociate the acetaldehyde and to identify CO. During the two laser experiments, a second Nd: YAG laser at 10 Hz (continuum) pumped dye laser (Liop-Tec) was used to initiate the photodissociation of acetaldehyde. Ionized ions were detected using the ion imaging detector.

Initial experiments with acetaldehyde detected the vibrationally excited CO as the photodissociation product, confirming previous studies' results. As the chiral molecule we selected 1-methyl-3-oxopentane-1-carbaldehyde. Observation of the chiral aldehyde reveals that it also forms CO after photodissociation; however, detection of the rotational and vibrational state interferes with the C_2H_4 fragments of the chiral molecule. As the future direction of the project, we intend to detect the photodissociation of 2-chloro-2-phenylpropanal which has less fragments to interfere with CO detection.

Keywords: Chiral aldehydes, Photodissociation, Roaming reactions

Low-Temperature Scanning Probe Techniques for Studying Spins on Surfaces

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There is increasing interest in quantum science, which promises advances in sensing and computation technology. At the core of quantum science are quantum two-level systems that can act as quantum bits (qubits). For quantum sensors, "sharp" energy transitions that are sensitive to electrostatic and magnetic fields from the environment are desirable. To execute quantum algorithms, long phase coherence times are key, as is the ability to couple multiple qubits. Electron and nuclear spins are ideally suited for this purpose due to their tunable transitions via magnetic fields and well-developed all-electrical control and readout techniques.

A major issue with established nanoscale qubits is their lack of reproducibility and the challenges in coupling them. In this respect, spins in atoms and molecules on a surface are well-defined by their electronic structure. When combined with low-temperature scanning probe microscopy (SPM), it becomes possible to manipulate atomic positions—bringing them close together—and control or read their spin states. Unfortunately, most quantum science efforts have so far been restricted to thin insulating films on metal surfaces, and—until recently—there have been few strategies for studying spins on metals and thick insulators.

In this talk, I will introduce atomic-scale quantum sensing (ASQS) and single-atom magnetic exchange force (MxF) microscopy. In ASQS, a single molecule with an unpaired electron, attached to the metallic tip of an SPM, acts as a sensor. We follow the electron spin resonance of the molecule while approaching single atoms on a metal surface. From changes in the resonance frequency, we can deduce dipolar magnetic and electrostatic coupling between the adatom and molecule with ~100 neV resolution. To detect spins on insulators, a different approach is required, making atomic force microscopy the method of choice. I will show how the MxF between a tip and a single atom on the surface can be determined, as well as how the sign and strength of the interactions can be manipulated. Interestingly, we can track the MxF into a chemical bond formation at the condensed-phase interface and gain insights into the fundamental nature of spin-spin interactions in adsorption.

So far, advanced low-temperature SPM methods have only occasionally been applied to physical chemistry at surfaces and heterogeneous catalysis. I look forward to discussing possible applications and the combination of methods needed to make surface chemistry a more exact science.

Investigation of Initial Phase of Vibrational Energy Pooling of CO_2 adsorbed on NaCl(100)

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Carbon monoxide (CO) adsorbed to NaCl(100) may have the weakest coupling between an adsorbate and a solid surface, thus making it an ideal system to study the interactions between molecules physisorbed to a surface. After saturating the $v = 0 \rightarrow 1$ transition with an infrared laser pulse, CO exhibits vibrational energy pooling (VEP) mediated by dipole-dipole interactions [1]. Here, vibrational quanta are collected in a few CO molecules leading to vibrationally highly excited states up to CO(v = 27) [2]

$$CO(n) + CO(m) \rightarrow CO(n+1) + CO(m-1) + \Delta E(n,m).$$

These highly excited CO molecules can undergo isomerization from the C-bound to a metastable O-bound configuration [3].

We report on time resolved pump-probe infrared transient absorption (IRTA) studies where for the first time the VEP mechanism of *Carbon Dioxide* is observed. The investigated buried $^{13}C^{16}O_2$ monolayer sample adsorbed to NaCl(100) shows - after exciting the 0-1 asymmetric stretch - vibrational state-to-state transitions up to 11-12 and ground state recovery after ~6ns.

Vibrational states up to v=7 are populated within the time resolution (65 ps) of the experiment and stimulated emission arises at transitions 4-5 and 6-7. The frequencies of the corresponding population inversions are consistent with theoretical VEP rates based on a calculated transverse Phonon DOS of NaCl [2].

This observed monolayer pooling process turns out to be faster than previously determined from kinetic-Monte Carlo (KMC) simulations with rate constants derived from perturbation theory [2].

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Towards a Low Temperature FTIR-Spectrometer with SNSPD detector

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For years, our group has been using a grating spectrometer with a superconducting nanowire single-photon detector (SNSPD) to be able to measure very weak laser induced fluorescence in the mid infrared from vibrationally excited molecules. [1]

In this work, I attempt to use a Michelson interferometer instead of the grating. I will discuss the pros and cons of each method and present the current progress of the project.

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Electron Transfer Coupled Spin Transitions in Di- and Tetranuclear Fe/Co Prussian Blue Analogues Revealed by Ultrafast Spectroscopy

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The dynamics of the photodriven electron transfer coupled spin transitions (ETCST) in a dinuclear [FeCo] and a tetranuclear square-type [Fe_2Co_2] Prussian blue analogue (PBA) is investigated by femtosecond IR and UV/vis pump-probe spectroscopy. Both compounds undergo thermal ETCST where the low temperature (LT) diamagnetic species consisting of low-spin Fe(II) and low-spin Co(III) transforms into the high temperature (HT) paramagnetic species consisting of low-spin Fe(III) and high-spin Co(II). Femtosecond pump-probe spectroscopy allows elucidating the time sequence of charge transfer and spin transition and, for the square-type [Fe_2Co_2], demonstrate cooperative ETCST, where a single absorbed photon induces two charge transfer events in both FeCo units.

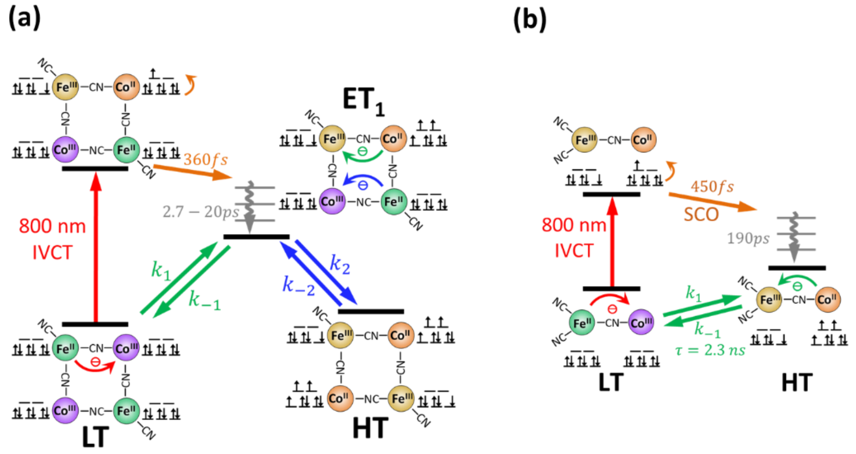

Figure 1: Photo-induced ETCST dynamics for the LT state of the tetranuclear complex (a) and the dinuclear complex (b).

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CO oxidation on Rh(111)/(332)

Arved C. Dorst

Heterogeneous catalysis has implications for our everyday life with examples ranging from Ammonia production in the Haber-Bosch process to automotive exhaust cleaning in modern three-way converters.[1]

In the past, the CO oxidation on platinum has been studied in detail by velocity-map imaging (VMI). A comprehensive comparison between the reaction on the flat (111) surface to the conversion on the stepped (332) surface was done: Two different velocity distributions were observed with the hyper-thermal one originating from terraces while the slower component originates from CO oxidation at steps and defects. The slow component dominated on both surfaces although the step density on Pt(111) is below 1 %.[2] These observations have been used to elucidate site-specific reaction rates of CO oxidation on Pt(111).

Previously, we studied and presented the velocity distributions of oxygen emerging from (sub-)surface states on Rh(111)[3] and Ag(111).[4] In this talk, the results for CO oxidation on rhodium will be presented. The reaction was studied under ultra-high vacuum conditions with VMI on a bisected crystal consisting of a flat (111) and stepped (332) plane. In contrast to *Neugebohren et al.*, only hyper-thermal velocity distributions are observed under steady-state conditions for both, CO oxidation on Rh(111) and Rh(332).

Introducing sub-surface oxygen changes this: A thermal component shows up and it will be shown that this component depends on sub-surface oxygen. Possible explanations and implications of this observation are given during the talk.

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