Surface Science
Room 305 - Session SS-TuM

Dynamics

Moderators: Sara Mason, Brookhaven National Laboratory, **Dr. Zbynek Novotny**, Pacific Northwest National Laboratory

8:00am **SS-TuM-1 Hyperthermal Atomic-Oxygen Scattering Dynamics on Representative Satellite Surfaces**, ***Timothy Minton***, *Pedro Jorge,* University of Colorado Boulder **INVITED**

There is intense interest in the utilization of very low Earth orbit (VLEO, 100 – 350 km in altitude); a few missions in this region have been flown and more are planned. Despite the advantages of VLEO satellite operation (e.g., enhanced image resolution, faster data transfer rates, reduced development and launch costs, and straightforward demise scenarios), VLEO altitudes have long been avoided because of the high density and harsh oxidizing environment of the residual atmosphere. VLEO environments contain predominantly oxygen atoms and nitrogen molecules, which collide with ram surfaces on spacecraft at relative velocities of ~7.5 km s^{-1}. Momentum exchange between these atmospheric atoms/molecules and satellite surfaces results in an aerodynamic drag force on the vehicle. For VLEO operation, the drag is significant enough to require propulsion to counteract drag and maintain orbit, resulting in increased energy and also size (typically from solar panels and propellant storage) to operate the propulsion system. Increased size results in increased drag forces and the need for more energy and propellant, creating a vicious cycle. Beyond the clear necessity of minimizing drag for feasible flight in VLEO, the quantification of drag allows for orbital path determination and collision avoidance. Thus, minimizing and predicting drag are crucial for proliferated VLEO operation.

We have conducted molecular beam-surface scattering experiments with O atoms, traveling at orbital velocities of ~8 km s^{-1}, to investigate their inelastic scattering dynamics on several realistic and ideal material surfaces as a function of both polar (*q*) and azimuthal (*f*) scattering angles. The velocity and angular distributions of scattered O atoms depend strongly on the incident angle of the impinging atoms and the roughness of the surface in ways that are not *a priori* predictable. Using on the scattering dynamics data, a new gas-surface scattering model has been formulated, based on a washboard approach which uses a gamma function roughness model and a coupled Cercignani-Lampis (CL) model to describe the local atom-surface scattering dynamics. When parametrized to give the optimum fit to the molecular beam-surface scattering data, the model may be used for the determination of overall energy and momentum accommodation and for simulations of satellite drag.

8:30am **SS-TuM-3 Beyond the Binary Collision Approximation: Approximate Modeling of Low-Energy Impingement Events Using Classical Molecular Dynamics**, ***Carson Mize***, *Jörg Meyer,* Leiden University, Netherlands

Since their development in the 1970s, Binary Collision Approximation (BCA) models are widely applied tools to help validate ion and atom implantation processes on materials, such as deposition, diffusion, and damage in good agreement with experimental data at high incidence energies (> 1 MeV). BCA codes are practical and useful due to their computational efficiency to account for nuclear and electronic contributions to the stopping of the impinging particles, however, the approximations are expected to break down completely within the low energy regime (< 1 keV). Considering recent advances in molecular dynamic (MD) models commonly used in gas-surface dynamics, we aspire to answer the following two questions: 1) Do BCA models have any validity in the low energy regime? 2) Can we develop a classical-MD based model that still is computationally inexpensive for common applications with considerably improved accuracy?

To this end, we focus on bombarding a tungsten surface with low energy hydrogen atoms (5 – 100 eV) as a showcase system due to the availability of an EAM potential designed to model H absorption in W and the associated defects caused by H.[1] While our dynamical models based on a "grand-canonical"-like MD are still a work in progress due to the modeling challenge of accounting for energy dissipation to electrons and phonons, here, we mimic the respective approximations inherent to the BCA to reduce the model comparison into the respective binary and many-body approaches. Our additive MC calculations provide us with high resolution snapshots, allowing us to capture surface evolution effects like implantation and damage, which are typically neglected in BCA models. Additionally, the model establishes a framework for future improvements such as replacing electronic stopping with a more robust electronic friction description or additional ability to describe the evolution of the surface at increasing exposure.

References

[1] D. R. Mason, D. Nguyen-Manh, V. W. Linblad, F. G. Granberg, M. Y. Lavrentiev J. Phys.: Condens. Matter 2023, *35*, 495901.

8:45am **SS-TuM-4 Influence of Subsurface Oxygen on the Energetics of CO Oxidation on Planar and Stepped Rhodium Surfaces**, ***Dan Killelea***, Loyola University Chicago; *Tim Schäfer,* Georg-August Universität, Göttingen, Germany

The ability to obtain velocity distributions of molecules desorbing from surfaces with both high temporal precision and angular resolution provide newfound insight into both the kinetics and the dynamics of recombinative desorption and subsurface emergence.

I will discuss our observations of the influence of subsurface oxygen on CO oxidation on both Rh(111) and Rh(332) and how the velocity distributions of the product CO_2 shifts when O_{sub} is present. I will discuss these observations and their potential impacts in oxidation reactions in heterogeneously catalyzed reactions over transition metal surfaces.

9:00am **SS-TuM-5 Unexpectedly Weak Vibrational Energy Transfer in O_2/Au(111) Collisions**, ***Igor Rahinov***, The Open University of Israel; *Itai Kallos,* Ben Gurion University Be'er Sheva, Israel; *Kerim Benfreha,* University of Goettingen, Germany; *Joshua Baraban,* Ben Gurion Uni. Be'er Sheva, Israel; *Tim Schäfer,* University of Goettingen, Germany; *Alexander Kandratsenka, Alec Wodtke,* Max Planck Institute for Multidisciplinary Sciences, Germany

Vibrationally inelastic scattering of molecules from metal surfaces provides a sensitive probe of electronically nonadiabatic energy transfer accompanying breakdown of the Born–Oppenheimer approximation. Previous studies established an intuitive semi-quantitative framework in which vibrational excitation and relaxation probabilities approximately scale with the energetic accessibility of transient electron transfer between molecule and metal. Within this framework, O_2 has long been an intriguing missing case: because of its high electron affinity, and the relatively small image-charge stabilization energy required for transient-anion-formation-driven vibrational energy transfer upon collision with Au(111), it should be among the strongest electronically nonadiabatic scatterers [1]. Yet this expectation could not be tested directly because effective quantum-state-resolved detection schemes for O_2 were not available.

Here we report quantum-state-resolved measurements of vibrational excitation in O_2(v = 0-->1) scattering from Au(111), enabled by a recently developed REMPI detection scheme for vibrationally excited O_2 [2]. Rotationally resolved detection of scattered O_2(v = 1) was achieved via two-color REMPI through the 3dπ Rydberg states, allowing direct determination of O_2(v = 0 → 1) vibrational excitation probabilities under direct scattering conditions.

Contrary to expectations based on electron affinity/work function considerations and trends established for NO, CO, and HCl scattering from noble metals [1], the measured vibrational excitation probabilities for O2/Au(111) are remarkably low. We discuss a physical picture in which O_2/Au(111) represents a frustrated strong-coupling system: although only modest image-charge stabilization is required to transiently access the anion formation, the repulsive interaction potential prevents the molecule from approaching sufficiently close to the surface for efficient electron-transfer-mediated vibrational energy uptake.

[1] I. Rahinov et al., Phys. Chem. Chem. Phys. 26, 15090 (2024).
[2] I.S. Kallos et al., J. Chem. Phys. 162, 051103 (2025).

9:15am **SS-TuM-6 High Temperature Annealing Dynamics and Surface Recovery of (3x1)-O Nb(100) Elucidated by Helium Atom Scattering**, ***Michael Van Duinen***, University of Chicago; *Cristobal Mendez, Tomas Arias,* Cornell University; *Steven Sibener,* University of Chicago

Superconducting radio frequency (SRF) cavities are the fundamental accelerating components of linear particle accelerators. Niobium is the material of choice for SRF cavities due to its high malleability, thermal conductivity, and superconducting critical temperature (T_C). Despite Nb having a T_C of ~9 K, the practical operating temperature of a Nb SRF cavity is ~2 K, below the boiling point of He and consequently quite expensive to operate. The improvement of Nb SRF cavities and the lowering of operating costs has focused primarily on the development of new materials on the Nb

surface. One of the primary limitations to both Nb SRF cavities and the new materials under study is the presence of a thermally stable and robust oxide. Understanding the formation, stability, and dynamics of the oxide and its effects on the operation of Nb SRF cavities requires study of atomic-scale surface material chemistry. Helium atom scattering (HAS) is a surface diffraction technique that has the ability to probe surface structure, bonding, and dynamics. The chemically inert He and an ultra-high vacuum (UHV) environment make HAS an ideal probe for the chemically reactive and sensitive Nb surface. High-temperature HAS studies have revealed that the (3x1)-O NbO phase that forms readily on Nb(100) is stable and intact for surface temperatures as high as 1100 K. This phase of the oxide forms readily from high-temperature dissolution of the Nb_2O_5 pentoxide phase and forms optimally when annealed at 1900 K. However, little is known about the dynamics of the formation of the (3x1)-O, annealing timescales, or the effectiveness of annealing temperatures below 1900 K. The studies presented seek to take an in-depth look at the recovery of (3x1)-O surfaces that have been sputtered to disorder. High-surface-temperature helium diffraction allows for a closer look in to the temperatures relevant to the recovery of the (3x1)-O surface from sputtered defects. High-temperature diffraction also reveals the kinetics and activation energy of (3x1)-O recovery. Auger and LEED further explore the extent that elemental composition and structure influence (3x1)-O recovery from sputtering. These studies overall strengthen our understanding of the dynamics of oxides on the Nb surface that will assist in the development of new materials formed on Nb SRF cavity surfaces.

9:30am **SS-TuM-7 Isotopic, Structural, and Surface Dependencies in Non-Equilibrium Gaseous Condensation***, **Francisco Lizano**, Elizabeth Jamka, Steven Sibener,* University of Chicago

Gas-surface interactions mediated by adsorption dynamics are key to many necessary formation reactions in both astrophysical and terrestrial environments. This dynamic process of gas molecules colliding with a surface and losing energy through adiabatic and non-adiabatic interactions, however, remains poorly understood, especially regarding the mechanisms that govern the energy exchange between the impinging molecules and the interface. Factors such as the kinematics of the incident molecules, molecular structure, and surface phonon density of states can affect the rate of condensation and molecular formation efficiencies. This is especially important within the interstellar medium (ISM), where reactions between gaseous species and dust grains or ice mantles are necessary to explain the chemical evolution and formation of molecules in the ISM. Accurate simulations of the chemical evolution of ISM environments require accurate binding energies and adsorption probabilities from experimental data. Discrepancies in the $^{12}C/^{13}C$ abundance ratio between the solar system and the ISM can possibly be attributed to mass-dependent adsorption or desorption of CO that leads to isotope fractionation. It has been shown that CO molecules are known precursors to many complex organic molecules detected in the ISM, the formation of which requires both gaseous CO and solid CO adsorbed onto a dust grain. Our work employs molecular beams to study the dynamics of gas-surface interactions and adsorption probabilities of a wide range of systems. In situ spectroscopic characterization of the surface via reflection-absorption infrared spectroscopy (RAIRS) coupled with the King and Wells mass spectrometry technique allows us to determine sticking probabilities of impinging molecules onto a well-characterized surface. This has allowed for the investigation of isotopic dependencies in non-equilibrium gaseous condensation for systems such as $^{12}CO_2/^{13}CO_2$ and $^{12}CO/^{13}CO$, as well as structural dependencies using isomers of butene, at a wide range of incident energies. Ongoing work is investigating the impact surface phonon modes have on the sticking of these molecules. Understanding the factors that influence the propensity of a gas molecule to adsorb to the surface will improve models of interstellar events and further our knowledge of non-equilibrium condensation in fields such as heterogeneous catalysis, thin film growth, and aircraft icing in cold environments.

9:45am **SS-TuM-8 Effects of Subtle Temperature Fluctuations on Surface Mobility of Atomic Steps and Oxidation Dynamics in High-Temperature Alloys***, **Shyam Patel**,* Brookhaven National Laboratory*; Chaoran Li,* Binghamton University*; Abdullah Al-Mahboob, Jerzy Sadowski,* Brookhaven National Laboratory*; Guangwen Zhou,* Binghamton University

In contrast to the traditional perspective that minute thermal fluctuations are inconsequential in surface dynamics, here we report the remarkable impact of subtle temperature changes on altering surface oxidation behavior. Using real-time low-energy electron microscopy imaging of the initial-stage oxidation process on NiAl(100), we investigate the interplay between minute temperature variations and surface reaction dynamics at the atomic scale. Our findings reveal that even minor fluctuations in temperature can exert significant influence on the dynamic process of oxide formation and surface mobility of atomic steps. Specifically, these nuanced temperature changes induce the nucleation of oxide islands, which subsequently locally pin the surface migration of atomic steps, leading to the lengthening of surface steps. Furthermore, our results demonstrate that persistent temperature variations have the ability to counteract the pinning effect imposed by oxides on the migration of atomic steps. These results underscore the profound effect of minute temperature changes in inducing significant alternations to surface reaction dynamics and highlight the critical importance of considering thermal fluctuations in understanding and dynamically manipulating surface processes.

11:00am **SS-TuM-13 Theoretical Investigation of the Adsorption and Diffusion of Co and Ni on Ceria***, Nusrat Jahan Rifat, Md. Saeedur Rahman, **Ye Xu**,* Louisiana State University **INVITED**

Transition metal nanoparticles supported on ceria are widely studied to catalyze technologically important reactions such as three-way catalysis, water-gas shift, and hydrocarbon reforming. There is ample evidence in the literature that base metals such as Co and Ni exhibit unique, superior catalytic activity when supported on ceria compared to other oxides. This is generally explained in terms of bifunctionality, interfacial effects involving metal-oxygen and metal-vacancy sites as well as charge transfer, and spillover / reverse spillover of surface species between the metals and oxide. Understanding the configuration and stability of nanoparticles of these catalytic metals on ceria is therefore of importance in heterogeneous catalysis.

We theoretically study and analyze the energy, geometry, and electronic configuration of Co and Ni clusters of up to several dozen atoms adsorbed on the $CeO_2(111)$ surface based on density functional theory (DFT) calculations. Furthermore, potential diffusion mechanisms of small Co and Ni species up to tetramers on $CeO_2(111)$ are investigated, and additional factors that enhance or hinder the diffusion of these metals on ceria are explored. The broad similarities and subtle differences between the two metals are revealed and discussed. The implications of the stability and diffusivity of the clusters to particle size distribution, stability, and growth are discussed in the context of mathematical and kinetic models. The totality of these findings is used to rationalize the findings of recent surface science studies, including STM and XPS, of Co and Ni deposited on model ceria thin film surfaces. Our work provides fundamental insights to the understanding of ceria-supported Co- and Ni-catalyzed reactions and guidance to improved catalyst design based on the Co- and Ni-ceria materials systems.

11:30am **SS-TuM-15 Stimulus-Driven Catalysis: Surface Reactions under Oscillatory Pressure Conditions***, Esteban Fornero,* Instituto de Desarrollo Tecnológico para la Industria Química, Argentina*; Gengnan Li,* Brookhaven National Laboratory*; Zubin Darbari, Eliseo Perez Gomez, Jay Shukla, Ignacio Vargas,* Brookhaven National Laboratory and State University of New York at Stony Brook*; Dario Stacchiola, Qin Wu, **J. Anibal Boscoboinik**,* Brookhaven National Laboratory

Periodic external stimuli provide a promising route for manipulating catalytic activity and accessing reaction pathways unavailable under steady-state conditions. Here, I present an in-situ experimental approach that combines synchronized pressure-wave perturbations with fast time-resolved spectroscopy to investigate catalytic dynamics on well-defined surfaces. Using CO oxidation on Pt(111) as a model system, we demonstrate how square-wave modulation of the CO partial pressure drives periodic changes in surface coverages and reaction kinetics. Infrared reflection absorption spectroscopy (IRRAS) and online mass spectrometry with millisecond time resolution directly track transient CO_2 production and reveal how controlled perturbations of the reaction environment can dynamically overcome CO poisoning. The measurements expose the formation of non-equilibrium surface states associated with enhanced catalytic turnover and provide direct insight into the coupling between gas-phase forcing and surface reaction dynamics. Beyond CO oxidation, this methodology is readily extendable to other catalytic systems and operando spectroscopic techniques, particularly to reactions governed by competitive adsorption processes where dynamic modulation of surface populations can strongly influence catalytic performance, reactivity, and selectivity.

11:45am **SS-TuM-16 Dynamic Metal–Support and Bimetallic Interactions in Ru Catalysts during Ammonia Decomposition***, **Soomin Kim**,* Korea Advanced Institute of Science and Technology, Republic of Korea*; Yujin Jeon,* Korea Advanced Institute of Science and Technology (KAIST) & Institute for Basic Science (IBS), Republic of Korea*; Kwangjin An,* Ulsan National Institute of Science and Technology, Republic of Korea*; Mu-Hyun Baik,* Korea Advanced Institute of Science and Technology (KAIST) & Institute for Basic Science (IBS), Republic of Korea*; Jeong Young Park,* Korea Advanced Institute of Science and Technology, Republic of Korea

Ammonia decomposition is a cornerstone of the green hydrogen economy, requiring highly active and durable catalysts. Ruthenium (Ru) is recognized as the most efficient catalytic candidate; however, its high cost, scarcity, and sensitivity to surface electronic structure necessitate precise optimization of Ru-based systems. To achieve this, fine-tuning the metal-support interface and surface composition is paramount. In this study, we investigate two distinct surface engineering strategies: leveraging facet-dependent Strong Metal-Support Interactions (SMSI) in Ru/TiO_2 and exploring bimetallic synergy in RuCo/MgO catalyst.

For Ru/TiO_2 catalysts, anatase TiO_2 supports exposing predominantly (101) or (001) facets were employed to regulate SMSI during ammonia decomposition. In situ ambient-pressure X-ray photoelectron spectroscopy (AP-XPS) and in situ DRIFTS reveal that NH_3 induces temperature-dependent formation of a TiO_x overlayer on Ru nanoparticles, accompanied by substantial modulation of Ru electronic states. The Ru/bipyramid-TiO_2 forms a thinner and partial TiO_x overlayer that preserves accessible Ru surface sites while generating an electron-rich Ru–TiO_x interfacial structure favorable for NH_3 dehydrogenation and N≡N recombination. In contrast, the Ru/nanosheet-TiO_2 undergoes more extensive encapsulation, resulting in reduced surface accessibility and lower catalytic activity. Complementary DFT calculations demonstrate that the oxide–metal interfacial sites lower the activation barriers for N–H bond cleavage through oxygen-assisted dehydrogenation pathways. In parallel, RuCo/MgO catalysts exhibit enhanced catalytic stability and reactivity arising from dynamic bimetallic surface interactions. The incorporation of Co modifies the electronic environment of Ru, stabilizing the surface ensembles under ammonia decomposition conditions and suppressing sintering while promoting NH_x activation and nitrogen recombination.

Our findings reveal that ammonia decomposition relies on dynamic surface and interfacial changes in Ru-based catalysts. In situ techniques uncover SMSI evolution, interfacial charge transfer, and bimetallic synergy, providing actionable design principles to optimize Ru-based catalyst efficiency for hydrogen production from ammonia.

12:00pm **SS-TuM-17 Vibrational Excitation in Plasma Catalysis: How Important Are Dynamical Effects?***, **Floris van den Bosch**, Jörg Meyer,* Leiden University, Netherlands

Plasma catalysis offers to be a promising alternative to current ammonia production processes, due to the combination of high selectivity of heterogeneous catalysis and efficient activation of nitrogen in the plasma. However, the theoretical understanding of how various plasma processes contribute to efficiency improvements remains limited. The pioneering work of Metha et al. [1] extended the standard formulation of transition state theory by making it vibrational state-specific through the use of the Fridman-Macheret α model [2]. The resulting microkinetic model accounted for vibrational contributions under the non-equilibrium conditions of a plasma reactor. In this work, we critically examine the prototypical chemical process of activated N_2 reactivity on ruthenium through explicit rate coefficient calculations using state-of-the-art molecular dynamics, based on a potential energy surface previously validated against molecular beam experiments. Our findings reveal that vibrational activation is significantly more effective in promoting surface reactivity than predicted by the Fridman-Macheret α model, which fails to capture the full complexity of state-specific contributions. Furthermore, our calculations indicate that vibrational activation is also the primary driver of highly activated thermal catalytic reactions. These results provide a valuable benchmark to guide the development of future state-specific microkinetic models for heterogeneous and plasma catalysis.

[1] Metha, P., et al. Nat. Catal., 2018. 1: p. 269-275
[2] Fridman, A. Plasma Chemistry. Cambridge University Press, 2008. ISBN: 978-0-521-84735-3

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