Surface Science Division
Room 25 - Session SS+HC+NS-WeA
Dynamical Processes at Surfaces

Moderators: Ashleigh Baber, James Madison University, Kathryn Perrine, Michigan Technological University

3:00pm **SS+HC+NS-WeA-3 Quantum Molecular Machines***, **Saw-Wai Hla,*** Ohio University and Argonne National Laboratory **INVITED**

One of the goals of nanotechnology is the development of complex molecular machines that can be operated with atomic level control in a solid-state environment. Most biological molecular machines have the sizes from tens of nanometers to a few microns –a range where classical machine concepts hold. However, artificially designed molecular machines can be in the size range down to a few nanometers or less, which is in the range of quantum processes. In this talk, we will present various artificial molecular machines such as molecular motors and linear transport devices such as molecular cars operating in the quantum regime on materials surfaces. Fundamental operations of these synthetic molecular machines are investigated at one molecular machine-at-a-time in an atomically clean environment using low temperature scanning tunneling microscopy (STM), tunneling spectroscopy, and molecular manipulation schemes [1,2]. These investigations reveal how charge and energy transfer are taken place within single molecular machines as well as among the molecular machines in the molecular networks. Moreover by introducing dipole active components in the rotor arms of the molecular motors, communication among the molecules can be introduced via dipolar interaction. In addition to single molecule operations, synchronization of molecular motors can be achieved depending on the symmetry of the molecular assemblies on surfaces and the strength of applied electric field energy. Here, all the molecular motors can be rotated in a synchronized manner using 1V or higher electric field supplied from the STM tip. Below this bias, the rotor arms of the molecular motors can reorient into different directions. Careful analyses reveal that such reorientations of the molecular motors are not random, but they are coordinated to minimize the energy. Furthermore, individual molecular motors can be charged using the inelastic tunneling scheme with the STM tip. This introduces spin-active components within the molecular motors and enables us to investigate spintronic properties of individual molecular motors at the sub-molecular scale using tunneling spectroscopy. For the controlled linear transport at the nanoscale, we will present the latest development of molecular nanocars.This work is supported by US DOE grant DE-FG02-02ER46012.

[1] U.G.E. Perera . F. Ample, H. Kersell, Y. Zhang, G. Vives, J. Echeverria, M. Grisolia, G. Rapenne, C. Joachim, and S.-W. Hla. ***Nature Nanotechnology 8***, 46-51(2013).

[2] Y. Zhang, H. Kersell, R. Stefak, J. Echeverria, V. Iancu, U. G. E. Perera, Y. Li, A. Deshpande, K.-F. Braun, C. Joachim, G. Rapenne, and S.-W. Hla. ***Nature Nanotechnology*** **11**, 706-711 (2016).

4:20pm **SS+HC+NS-WeA-7 Collective, Multi-atom Diffusion in Epitaxially Grown Metallic Films***, **Matt Hershberger**, M Hupalo, P Thiel,* Iowa State University Ames Laboratory –USDOE*; M Man, M Altman,* Hong Kong University of Science and Technology, Hong Kong*; C Mullet, S Chiang,* University of California-Davis*; M Tringides,* Iowa State University Ames Laboratory –USDOE

Surface diffusion is the main process controlling mass transport of many important phenomena such as nucleation, nanostructure growth, pattern formation, and chemical reactions. In practically all cases, it is described as a random walk of independently moving adatoms. Such process is inherently stochastic and therefore very slow as a route to self-organization in nature.

A series of experiments in different epitaxially grown metallic films over the last 5 years using different techniques has challenged the classical picture. The experiments have shown unusually fast, collective diffusion is present in nature, observed in a range of experiments over different length and time scales.

STM experiments show that fully completed Pb crystalline islands emerge “explosively” out of the compressed wetting layer on Si(111) after a critical coverage q_c=1.22ML is reached. The unexpectedly high island growth rates and directional correlations show that mass transport is through the correlated motion of the wetting layer.[1] Additional deposition of Pb shows island density that does not reach steady state; it shows abrupt jumps in island density with new generations of smaller islands continuing to nucleate (in contrast to classical nucleation). Real time experiments with LEEM, monitoring the refilling of an initial vacant area in Pb/Si(111), show that the initial steep profile does not disperse and that the profile propagates at constant velocity x~t. The profile follows a non-Fickian form with two moving highly correlated fronts, one inward and the other outward.[2] The formation of long anisotropic multi-height Ag islands on Ge(110) is exceedingly fast, when compared to the rates expected from random walk Ag diffusion barriers. A wetting layer is also present prior to the crystallization and is responsible for the fast growth rates, although the temperature is above room temperature.[3] Evidence for collective diffusion has been seen in Pb/Si(100), Pb/Ge(111), Pb/Ni(111), Pb/W(110), Ag/Si(110).

A better understanding of these processes can guide the search of collective transport in other systems, especially to identify the relevant growth “window” (of temperature and coverage). It can further clarify the role of stress since the compression of the non-crystalline wetting layer is critical for these effects.[4]

References:

1. M. T. Hershberger et al., .Phys. Rev. Lett. 113, 236101 (2014)

2. K. L. Man et al., Phys. Rev. Lett. 110, 036104 (2013)

3. C. H. Mullet et al., manuscript submitted.

4. E. Granato et al., Phys. Rev. Lett. 111, 126102 (2013)

4:40pm **SS+HC+NS-WeA-8 Quantitative Molecular Beam Study for CO_2 Hydrogenation on Cu (111) and Cu(100) Surfaces***, **Jiamei Quan**, T Kondo, T Kozarashi, T Mogi,* University of Tsukuba, Japan*; J Nakamura,* University of Tsukuba, Japan, Japam

Catalytic conversion of CO_2 into valuable fuels and chemicals such as methanol, especially if activated by a precise energetic control, represents a potentially economic strategy for utilization of fossil feedstock and reducing CO_2 emissions and their contributions to climate changes. The formation of formate intermediates ($2CO_2 + H_2 \rightarrow 2H\ COO_a$) on Cu catalysts is an important initial step, in which the reaction probability is reported as low as 10^{-12} at 340 K.[1] Our previous reports suggested that the reaction proceeds via an Eley-Rideal type mechanism, where CO_2 directly reacts with pre-adsorbed H to form $HCOO_a$.[2] Recently, we have clarified using supersonic molecular beam apparatuses that the reaction probability is promoted up to ~10^{-3} by increasing both translational and vibrational energies, while insensitive to the Cu surface structure (Cu(111) and Cu(100)) and the surface temperature (120 - 210K). The energy efficacy on the reaction probability is found to be larger as much as 100 times for the vibrational energy compared to the translational energy, suggesting that the vibrational excitation significantly enhances the formate formation. Based on the comparison with DFT calculations, we conclude that the excitation of the bending mode of CO_2 at the transition is crucially important to form the C-H bond of HCOO via lowering LUMO level of CO_2. The small pre-exponential factor derived by the experiment is ascribed to the preferential orientation of the CO_2 molecule (C-end collision to H_a on Cu) for the reaction. The discovered thermal non-equilibrium channel in CO_2 conversion, which doesn’t require the heating of catalysts, is expected to provide a prototypical surface reaction dynamics and open up novel industrial pathways of efficient CO_2 conversion into useful chemicals and fuels.

[1] (a) T. Fujitani, J. Nakamrua et al., *App. Surf. Sci.* 121–122 (**1997**) 583; (b) H. Nakano, J. Nakamrua et al., *J. Phys. Chem. B* 105 (**2001**) 1355.

[2] (a) J. Quan, J. Nakamrua, et al., Angew. Chem. Int. Ed. 56 (**2017**) 3496; (b) G. Wang, J. Nakamura, et al., *J. Phys. Chem. B* 110 (**2005**) 9.

5:00pm **SS+HC+NS-WeA-9 A New Approach for Controlling the Rotational Orientation of a Molecule and Studying the Stereodynamics of a Molecule-Surface Collision***, **Gil Alexandrowicz,*** Technion – Israel Institute of Technology, Israel **INVITED**

The interaction between a molecule and a solid surface is fundamental to a huge variety of research fields and applications, ranging from industrial heterogeneous catalysis to ultra-cold astrochemical reactions on cosmic dust. One molecular property that affects molecule-surface interactions, but is also particularly difficult to control and resolve, is the orientation and alignment of the rotational axis of the molecule i.e. the quantum rotation projection states. The existing paradigm is that control over this molecular property can be obtained either by photo-excitation schemes and/or by deflecting experiments using strong electric or magnetic fields. Using these approaches valuable insight was obtained and the crucial role the rotation projection states have on the outcome of molecule-surface collision was demonstrated. However, the two approaches mentioned above can only be applied to a very small sub-group of systems (typically excited/paramagnetic species). In this presentation I will describe a completely different approach which utilizes the rotational magnetic moment, which is a general molecular property, to control and resolve the projection rotation states of ground-state molecules.

Our new experimental approach combines an atomic interference setup, originally built to perform ultra-fast surface diffusion measurements[1], with magnetic manipulation techniques we developed for separating quantum states of molecular beams[2]. The result is a unique setup which can both control and resolve the rotational orientation of a molecule as it collides with a solid surface. In this presentation I will show some recent experiments where we controlled the rotational orientation of a ground state hydrogen molecule, and correspondingly modified the outcome of a collision event with flat and stepped copper surfaces[3].The possibilities this new technique opens for studying the stereodynamic nature of molecule-surface interactions as well as ultra-fast surface dynamics will be briefly discussed.

[1] Progress in Surface Science, 84, 323 (2009).

[2] Science, 331, 319 (2011).

[3] Nature communications, (DOI: 10.1038/ncomms15357), in press (2017).

5:40pm **SS+HC+NS-WeA-11 Surface Temperature Effects in CH_4 Dissociation on Flat and Stepped Nickel Single Crystals***, **Eric High**, E Dombrowski, A Utz,* Tufts University

A modified King and Wells molecular beam reflectivity method was used to obtain thermal and quantum state resolved initial sticking probabilities (S_0) for CH_4 on nickel single crystals at elevated surface temperatures (500 to 1000K). We recorded the reactivity of a supersonic molecular beam of methane with and without laser excitation to v=1 of the v_3 antisymmetric C-H stretching vibration. Square wave modulation of the laser source during CH_4 deposition provided simultaneous real-time measurement of $S_0^{LaserOff}$ and S_0^{v3}, resulting in a dramatic reduction in data acquisition time, a significant reduction in experimental error, and the opportunity to measure S as a function of accumulating surface coverage. On a Ni(111) surface, both laser-off and vibrational state-resolved measurements of S_0 were essentially independent of surface temperature, within error, from 1000 to 800K and then decreased linearly as T_{surf} dropped from 800 to 500K. These findings are consistent with the predictions of Reaction Path Hamiltonian calculations by Jackson and Guo over a wide range of incident kinetic energies (96 to 167 kJ/mol). The calculations suggest that at low incident energies, reactivity occurs predominantly at on-top sites, but as energy increases, reactions begin to occur at bridge sites as well. We will also present more recent measurements on the low step density Ni(997) surface that provide insight into the role of step-edge nickel atoms at these industrially relevant surface temperatures.

6:00pm **SS+HC+NS-WeA-12 Experimental and Theoretical Study of Rotationally Inelastic Diffraction of $H_2(D_2)$ from Methyl-Terminated Si(111)***, **Kevin Nihill**[1], Z Hund,* University of Chicago*; A Muzas, C Diaz, M del Cueto,* Universidad Autónoma de Madrid, Spain*; T Frankcombe,* University of New South Wales, Australia*; N Plymale, N Lewis,* California Institute of Technology*; F Martin,* Universidad Autónoma de Madrid, Spain*; S Sibener,* University of Chicago

Fundamental details concerning the interaction between H_2 and CH_3-Si(111) have been elucidated by the combination of diffractive scattering experiments and electronic structure and scattering calculations. Rotationally inelastic diffraction (RID) of H_2 and D_2 from this model hydrocarbon-decorated semiconductor interface has been confirmed for the first time *via* both time-of-flight and diffraction measurements, with modest $j = 0 \rightarrow 2$ RID intensities for H_2 compared to the strong RID features observed for D_2 over a large range of kinematic scattering conditions along two high-symmetry azimuthal directions. The Debye-Waller model was applied to the thermal attenuation of diffraction peaks, allowing for precise determination of the RID probabilities by accounting for incoherent motion of the CH_3-Si(111) surface atoms. The probabilities of rotationally inelastic diffraction of H_2 and D_2 have been quantitatively evaluated as a function of beam energy and scattering angle, and have been compared with complementary electronic structure and scattering calculations to provide insight into the interaction potential between H_2 (D_2) and hence the surface charge density distribution. Specifically, a six-dimensional potential energy surface (PES), describing the electronic structure of the $H_2(D_2)/CH_3$-Si(111) system, has been computed based on interpolation of density functional theory (DFT) energies. Quantum and classical dynamics simulations have allowed for an assessment of the accuracy of the PES, and subsequently for identification of the features of the PES that serve as classical turning points. A close scrutiny of the PES reveals the highly anisotropic character of the interaction potential at these turning points. This combination of experiment and theory provides new and important details about the interaction of H_2 with a hybrid organic-semiconductor interface, which can be used to further investigate energy flow in technologically relevant systems.

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[1] **Morton S. Traum Award Finalist**

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