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Studies of Dynamic Material Interfaces in Extreme Environments

Steven Sibener UNIVERSITY OF CHICAGO THE

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INTRODUCTION

The scattering of atomic and molecular beams from well-characterized surfaces is an incisive method for studying the dynamics of gas-surface interactions, providing precise information on energy and momentum transfer as well as complex reaction mechanisms. Scanning probe measurements provide a powerful complement to scattering data as SPM measurements give a direct route to the visualization and spectroscopic characterization of interfacial atomic and nanosystems. This AFOSR program examined critical aspects of the chemical and physical behavior of dynamic material interfaces operating in extreme environments. Extreme conditions encompass high and low temperature regimes, high velocity gas flows, optical and charged particle illumination, and severe oxidative environments where interfacial aerodynamic performance (energy and momentum transfer characteristics), morphological change, and chemical stability need to be assessed and quantified. This grant has led to a period of notable discovery and productivity, with experiments complemented by commensurate theory and numerical simulations. We have examined: The vibrational band structure of methyl-terminated Ge(111), a promising new electronic interface; The capture of CO_2 by the recently discovered mechanism of energetic embedding; The growth, structure, and vibrational properties of few layer graphene; Inelastic collisional gas-surface energy transfer involving molecular hydrogen; Temporally and spatially-resolved oxidation of silicon and graphite using energetic supersonic molecular beams combined with scanning tunneling microscopy visualization of the reacting surface - note that a key feature of our activities is to systematically map out site-specific reactivity and morphology changes on the atomic/nano/meso/micro length-scales to accompany our precision measurements of interfacial chemical kinetics, revealing new details of interfacial time evolution such as the key roles that grain boundaries and defects play in materials change; Discovered a new method of enriching and separating isotopes based upon diffraction from an atomic grating; and Elucidated the sticking probability of high kinetic energy methane on crystalline, amorphous, and porous-amorphous ice films. Our experiments on gas trapping into condensed films represent an important new mechanism that contributes to an improved understanding of energy and momentum exchange in high-velocity gas flows at interfaces. Many of these experiments are in direct support of extreme supersonic and hypersonic gassurface interactions.

RELEVANCE TO AFOSR/DOD INTERESTS

This AFOSR program examined critical aspects of the chemical and physical behavior of dynamic material interfaces operating in extreme environments. Extreme conditions encompass temperature regimes, high velocity gas flows, optical and charged particle illumination, and severe oxidative environments where interfacial aerodynamic performance (energy and momentum transfer characteristics), morphological change, and chemical stability need to be assessed and quantified.

A key feature of these efforts was to systematically map out morphology changes on the atomic/nano/meso/micro length-scales to accompany our precision measurements of chemical kinetics occurring at the interface. This allows a comprehensive understanding of how the real-space/real-time morphological changes that occur at the interface are linked to the chemical changes ascertained by our molecular beam and surface spectroscopic studies, processes responsible for surface chemical modification and the release of volatile products emanating from the surface. Such spatio-temporal measurements of surface morphological change and surface chemical change reveal important details about surface modification and the key role that grain boundaries and defects have in determining the time evolution of the interface.

These studies have significantly extended the class of gas-surface collision systems for which energy exchange processes can be verifiably and quantitatively modeled. Such fundamental understanding is needed for the development of advanced flight surfaces, propulsion systems, and reentry vehicles. It is also important for developing a more accurate understanding of momentum accommodation and hence aerodynamic drag in hypervelocity environments, important for high-performance aircraft behavior and, again, the durability and performance of mission-critical reentry flight surfaces. Other studies on embedding/transport/releasing molecules into/from ices and coatings, are also of interest due to the central role such events play in materials passivation and changes in interfacial aerodynamics.

PERSONNEL - CURRENT AND PAST GROUP MEMBERS

Our AFOSR research program has been quite successful in attracting and educating some of the best young scientific talent in the country, including undergraduates, graduate students, and postdoctoral fellows. We also wish to emphasize that we have been quite successful in attracting women and minorities to our program. During the past year 8 of our group members were women, including one under-represented minority. The PI recognizes that the vitality of American science will depend on the involvement of such individuals at all levels of training.

<u>**Current Personnel:**</u> (PD: Postdoc; GS: Grad Student; UG: Undergrad): Steven J. Sibener, Carl William Eisendrath Distinguished Service Professor and PI; Dr. Kevin Gibson (Senior Scientist); Prof. Daniel Killelea (Collaborative Scholar; Assoc. Prof. at Loyola Univ. of Chicago), Jacob Graham (PD), Rachael Farber (PD), Jonathan Raybin (GS), Jeffrey Saylor (GS), Darren Veit (GS), Becca Thompson (GS), Ross Edel (GS), Tim Grabnic (GS), Sarah Brown (GS), Alison McMillan (GS), Michelle Brann (GS), Julia Murphy (GS), Sarah Willson (GS), Caleb Thompson (GS), Ellen Purdy (UG), Laura Duffy (UG), Sammy Allaw (UG).

Recent Sibener Group Alumni Whom Have Graduated and Worked on AFOSR Projects:

- Ms. Wenxin Li (GS), Ph.D. 2015; now at GlobalFoundries
- Zack Hund (GS), Ph.D. 2015; now at UChicago Laboratory High School
- Grant Langlois (GS), Ph.D. 2017; now at Intel basic research
- Kevin Nihill (GS), Ph.D. 2017; now postdoc at MIT

- Bryan Wiggins (PD), now at Intel basic research
- Michelle Chalupnik (UG), now graduate student at Harvard in AMO Physics
- Katherine Oosterbaan (UG), now student at Berkeley in Physical Chemistry

AFOSR SPONSORED DOCTORAL DISSERTATIONS

• Dr. Zachary Michael Hund, Atomic Scattering form Methyl-Terminated Si and Ge, University of Chicago, August 2015 (Note: Much of Zach's AFOSR sponsored research was published during the time period of this report, hence this dissertation's inclusion in this list).

• Dr. Wenxin Li, Interations of Atomic and Molecular Species with Ice and Self-Assembled Monolayers, University of Chicago, December 2015

• Dr. Grant Gregory Langlois, Time-resolved Surface Dynamics: Directed Reactivity, Extraterrestrial Ices, and Nerve Agent Simulants, University of Chicago, March 2017

• Dr. Kevin John Nihill, Atomic and Molecular Beam Scattering: Characterizing Structure and Dynamics of Hybrid Organic-Semiconductor Interfaces and Introducing Novel Isotope Separation Techniques, University of Chicago, December 2017

EXPERIMENTAL METHODS

Our approach utilized four arguably unique and complementary UHV gas-surface scattering instruments, described below, for probing gas-surface interactions involving energy exchange, reactivity, film growth/erosion, including *in situ* FTIR and XPS spectroscopy. These activities were complemented by variable-temperature (20-1000K) UHV-STM/AFM, allowing us to assess local surface structure also with local spectroscopic (scanning tunneling and conductive AFM spectroscopy) capabilities. The first facility is a recently upgraded beam-surface scattering and photochemistry instrument that now includes *in situ* FTIR and XPS spectroscopy. The second is a unique three-supersonic-beam UHV instrument that can carry out studies of interfacial energy transfer and reactivity spanning thermal through hyperthermal energies. The third is a new, combined supersonic beam/STM/AFM scattering facility that allows us to perform imaging studies in direct combination with *in operando* materials oxidation. The fourth is a high-resolution helium scattering instrument that can assess surface structure and phonon states under extreme conditions, also used for isotope enrichment and separation experiments. Taken together, these four facilities give us arguably unique capabilities in the world for executing precision studies of complex reacting interfaces with definitive structural characterization.

EXPERIMENTAL FACILITIES

i) Combined Molecular Beam/Fourier Transform Spectroscopy Facility: The molecular beam/FTIR experiments were conducted in a two-level UHV system, Figure 1, with base pressure 4×10^{-11} torr. The upper level of the chamber is equipped with a double-pass CMA Auger system, low energy electron diffraction (LEED), an XPS source, and a sputter gun. The lower level contains a high-throughput FTIR optics train to monitor on-surface chemical moieties, a 3-fold differentially pumped supersonic beam source, and a mass analyzer to characterize the beam. The geometry is arranged so that the focus of the FTIR spot is coincident with the molecular beam on the crystal surface. Sample temperatures can span the range from 15K to >1000K. This lab is equipped with several functioning supersonic beams for producing a variety of molecular and atomic beams including $O(^{3}P)$, $O(^{1}D)$, or H atoms. Hyperthermal capabilities can be utilized in this facility as well.



Figure 1. Left: Schematic of the Combined Supersonic Beam/Photochemistry/FTIR Apparatus. Center: Photo. Right: Real-time FTIR Spectra of Water Film Growth Using Supersonic Beam Deposition.

ii) Three-Supersonic-Beam Gas-Surface Scattering Facility: The second scattering apparatus, **Figure 2**, consists of three supersonic molecular beam sources, a UHV chamber with rotatable quadrupole mass spectrometer, and the controlling computer system. The molecular beam source chamber contains three quadruply differentially pumped molecular beams horizontally co-planar and aligned and collimated to a single scattering center in the UHV chamber. Each beam has a computer-controlled beam shutter which can be used for modulation experiments or computer-tailored sequential dosing experiments; the center beam also has a 10 to 400 Hz



Figure 2. Triple-Supersonic-Beam UHV Gas-Surface Reactive Scattering Apparatus. Schematic view (left), photo (center) and hyperthermal source (right). Kinetics/dynamical measurements will occur here.

chopper (conventional or cross-correlation) that resides 21.21 cm from the scattering center. The absolute intensities of the three beams can be monitored with flux meters that are mounted in the UHV target chamber. The UHV chamber contains the crystal mount with full polar, azimuthal, and tilt capability, is independently rotatable, and can cooled with LN_2 or LHe. It also contains an independently rotatable and doubly-differentially pumped quadrupole mass spectrometer with electron bombardment ionizer 14.45 cm from the scattering center. There is also a post-collision chopper for time-of-flight measurements *without concern for residence time limitations* that are associated with pre-collision modulation. It is ideally suited for studies where volatile products are generated, or for exposure experiments using an array of energetic beam sources.

(iii) Combined Supersonic Beam/STM/AFM: During the past grant period we completed our new combined supersonic beam/STM/AFM surface scattering/imaging instrument, Figure 3. It can be viewed as consisting of three sections: the triply-differentially pumped beam line, a materials preparation & characterization chamber, and a new variable-temperature SPM that differs from our other SPMs in many critical ways including sample orientation, stability, and

thermal equilibration between the tip and sample; it is based on the ultra-stable design of Shuheng Pan, and has been designed in conjunction with RHK. It has remarkable stability due to its tight mechanical linkages and integral vibrational isolation. This scanner is especially suited for low-T imaging and atom-resolved electronic spectroscopy near liquid helium temperatures. Tip-surface scanner assembly can achieve ca. 10-800 K imaging temperatures with the tip and sample at the same temperature, an essential feature of examining electron transport in molecular & nanoscale systems. Most importantly, it has been constructed to allow the surface plane to be vertical, permitting its use in simultaneous (or sequential but in situ) molecular beam plus scanning probe imaging experiments. The Fig. 3 inset shows a cryogenic image of reconstructed Si(111)-(7x7) taken with this new microscope.

(iv) Specialized Supersonic and Hyperthermal Beams of Atomic Oxygen and Other Radicals with Thermal Through Multi-eV Energies: Supersonic and hyperthermal beam sources will be used in these studies, allowing us to generate intense beams of atoms and radicals covering an extraordinary range of incident energies.

Supersonic Plasma Beam Source: The first of these is our next-generation RF plasma beam source, Figure 4, which generates intense beams of kinetic-energyselected species, e.g., $O({}^{3}P)$, $O({}^{1}D)$, H, OH, and $O_{2}({}^{1}\Delta)$ [16]. Such sources have had great success in exploring gas-phase reaction mechanisms. The source generates beams of variable kinetic energy *via* seeding in rare gases, 0.1-0.5 eV with $\Delta v/v \approx 10-20\%$. Intensities are high, $>10^{18}$ atoms sr⁻¹ sec⁻¹. 30-80% molecular dissociation is typically achieved. The utilization of



Fig. 3. Top: Diagram showing the combined supersonic molecular beam/materials preparation/SPM system. Bottom: Photo of the completed instrument with beam and preparation chambers, SPM, loadlock, manipulator, sample transfer components all connected. Left inset: Si(111) - (7x7) image, T = 78 K. Right inset: photo of the PAN STM/AFM with cryoshields removed.



Figure 4. Left: RF plasma source for generating supersonic beams of atoms and radicals with energies up to ca. 0.5 eV. Right: Hyperthermal laser-ignition beam source. Inset: 5eV beam energy.

dilute O_2 /He mixtures produces both $O({}^{3}P)$ and $O({}^{1}D)$ species, opening opportunities for quantum state specific studies (see below). Ar & Ne seeding produce beams of ground state $O({}^{3}P)$ with energies sufficient to abstract H atoms from primary thru tertiary CH bonds. This beam can produce other energetic species as well, as has been shown by Casavecchia for O, N & other reagents.

Hyperthermal Laser-Detonation Pulsed Beam Source: Figure 4 shows our hyperthermal laser-detonation pulsed beam source (design of Tim Minton MSU, and noting earlier work of Caledonia, Krech, and Green). It works *via* creation of a 20,000 K plasma followed by recombination in an expansion zone to form $O(^{3}P)$ w/o $O(^{1}D)$. Control of the focusing of the 7J CO₂ TEA laser allows tuning of beam energy.

(v) High Energy- and Momentum- Resolution Scattering Facility: The high

energy/momentum resolution neutral particle scattering instrument is shown in Figure 5. It uses a variety of supersonic nozzle beam sources; one is cryogenically cooled with a closed-cycle He refrigerator, giving the capability to "dial" a given nozzle temperature between \sim 40 - 300 K (corresponding to wavevectors from 1.56-0.57 Å⁻¹). The beamline generates intense cw He beams (I \sim $2x10^{19}$ atoms/sr/sec) of extremely narrow velocity dispersion ($\Delta v/v \sim 0.75\%$, speed ratios of over 220) and can be connected in 3 positions, giving wide variability of incident geometry; another source is a high temperature source for operation from 300 K - >1000 K. These beams are chopped into short pulses or a pseudo-random pulse sequence. The crystal chamber has a base pressure in the 10^{-11} torr range, and contains LEED, Auger, XPS, sputtering, and RGA capabilities. The target mount has all necessary degrees of freedom, and can be cooled or heated. Finally, the detector (right side of the photo) is a massive, 2-ton assembly which rotates ca. \pm 22° under computer control with 0.2° resolution and flightpath 100.5 cm. Its mass 4 background of 1-10 Hz corresponds to a He partial pressure of 10^{-14} torr. This instrument was also used for our isotope enrichment and purification experiments.



Figure 5. Overhead photo (A-Top Panel) and schematic view (B-Lower Panel) of the high resolution helium atom scattering instrument with labeled key elements.

AFOSR SPONSORED PUBLICATIONS AND PENDING PATENTS 2015-2019

• Note – This paper acknowledges AFOSR DURIP Support: Size-Dependent Energy Levels of InSb Quantum Dots Measured by Scanning Tunneling Spectroscopy" Tuo Wang, Roman Vaxenburg, Wenyong Liu, Sara M. Rupich, Efrat Lifshitz, Alexander L. Efros, Dmitri V. Talapin, and S.J. Sibener, ACS Nano 9, 725-732 (2015).

• Vibrational Dynamics and Band Structure of Methyl-Terminated Ge(111), Zachary M. Hund, Kevin J. Nihill, Davide Campi, Keith T. Wong, Nathan S. Lewis, M. Bernasconi, G. Benedek, and S. J. Sibener, *J. Chem. Phys.* **143**, 124705/1-10 (2015).

• Capture of Hyperthermal CO₂ by Amorphous Water Ice *via* Molecular Embedding, Grant G. Langlois, Wenxin Li, K. D. Gibson, and S. J. Sibener, Invited Feature Article for the Special Issue: "Dynamics of Molecular Collisions XXV – Fifty Years of Chemical Reaction Dynamics", *J. Phys. Chem. A*, <u>119</u>, 12238-12244 (2015).

• Growth, Structure, and Vibrational Properties of Few Layer Graphene Grown on Rh(111), K. D. Gibson and S. J. Sibener, *J. Phys. Chem. C* <u>120</u>, 24158–24164 (2016).

• Experimental and Theoretical Study of Rotationally Inelastic Diffraction of $H_2(D_2)$ from Methyl-Terminated Si(111), Kevin J. Nihill, Zachary M. Hund, Alberto Muzas, Cristina Diaz, Marcos del Ceuto, Terry Frankcombe, Noah T. Plymale, Nathan S. Lewis, Fernando Martin, and S. J. Sibener *J. Chem. Phys.* <u>145</u>, 084705/1-12 (2016). [J. Chemical Physics Editor's Choice Article for 2016.]

• Temporally and Spatially Resolved Oxidation of Si(111)-(7×7) using Kinetic Energy Controlled Supersonic Beams in Combination with Scanning Tunneling Microscopy, Bryan Wiggins, L. Gaby Avila-Bront, Ross Edel, and S. J. Sibener, *J. Phys. Chem. C.* <u>120</u>, 8191-8197 (2016).

• Separation of Isotopes in Space and Time by Gas-Surface Atomic Diffraction, Kevin J. Nihill, Jacob D. Graham, and S. J. Sibener, *Phys. Rev. Lett.* <u>119</u>, 176001/1-5 (2017). Note Accompanying APS Viewpoint: Atom Scattering Picks Out the Heavyweights, October 23, 2017, Physics <u>10</u>, 116. https://physics.aps.org/articles/v10/116. PATENT PENDING.

• Chemical Dynamics Simulations and Scattering Experiments for O₂ Collisions with Graphite, Moumita Majumder, K. D. Gibson, S. J. Sibener, and William L. Hase, *J. Phys. Chem. C* <u>122</u>, 16048-16059 (2018).

• Exploratory Direct Dynamics Simulations of O₂ Reactions with Graphene Surfaces at High Temperatures, Seenivasan Hariharan, Moumita Majumder, Ross Edel, Timothy Grabnic, S. J. Sibener, and William L. Hase, *J. Phys. Chem. C* 122, 29368-29379 (2018).

• Atomically-Resolved Oxidative Erosion and Ablation of Basal Plane HOPG Graphite Using Supersonic Beams of O₂ with Scanning Tunneling Microscopy Visualization, Ross Edel, Tim Grabnic, Bryan Wiggins, and S. J. Sibener, *J. Phys. Chem. C* <u>122</u>, 14706-14713 (2018).

• Isotope Enrichment *via* Non-Equilibrium Condensation and Reflection during Supersonic Beam Surface Scattering, J. D. Graham, A. A. McMillan, K. J. Nihill, and S. J. Sibener, PATENT PENDING.

• Sticking Probability of High-Energy Methane on Crystalline, Amorphous, and Porous-Amorphous Ice Films, Rebecca S. Thompson, Michelle R. Brann, and S. J. Sibener, J. Phys. Chem. C <u>123</u>, 17855-17863 (2019).

AFOSR SPONSORED RESEARCH PROJECT SUMMARIES

• Note – This paper acknowledges AFOSR DURIP Support: Size-Dependent Energy Levels of InSb Quantum Dots Measured by Scanning Tunneling Spectroscopy" Tuo Wang, Roman Vaxenburg, Wenyong Liu, Sara M. Rupich, Efrat Lifshitz, Alexander L. Efros, Dmitri V. Talapin, and S.J. Sibener, ACS Nano <u>9</u>, 725-732 (2015).

The electronic structure of single InSb quantum dots (QDs) with diameters between 3 nm and 7 nm was investigated using atomic force microscopy (AFM) and scanning tunneling spectroscopy (STS). In this size regime, InSb QDs show strong quantum confinement effects which lead to discrete energy levels on both valence and conduction band states. Decrease of the QD size increases the measured band-gap and the spacing between energy levels. Multiplets of equally spaced resonance peaks are observed in the tunneling spectra. There multiplets originate from degeneracy lifting induced by QD charging. The tunneling spectra of InSb QDs are qualitatively different from those observed in the STS of other III-V materials, for example, InAs QDs, with similar band-gap energy. Theoretical calculations suggest the electron tunneling occurs through the states connected with *L*-valley of InSb QDs rather than through states of the Γ -valley. This observation calls for better understanding of the role of indirect valleys in strongly quantum confined III-V nanomaterials.

• Vibrational Dynamics and Band Structure of Methyl-Terminated Ge(111), Zachary M. Hund, Kevin J. Nihill, Davide Campi, Keith T. Wong, Nathan S. Lewis, M. Bernasconi, G. Benedek, and S. J. Sibener, J. Chem. Phys., 143, 124705/1-10 (2015).

A combined synthesis, experiment, and theory approach, using elastic and inelastic helium atom scattering along with ab initio density functional perturbation theory, has been used to investigate the vibrational dynamics and band structure of a recently synthesized organicfunctionalized semiconductor interface. Specifically, the thermal properties and lattice dynamics of the underlying Ge(111) semiconductor crystal in the presence of a commensurate (1x1) methyl adlayer were defined for atomically flat methylated Ge(111) surfaces. The mean-square atomic displacements were evaluated by analysis of the thermal attenuation of the elastic He diffraction intensities using the Debye-Waller model, revealing an interface with hybrid characteristics. The methyl adlayer vibrational modes coupled with the Ge(111) substrate, resulting in significantly softer in-plane motion relative to rigid motion in the surface normal. Inelastic helium time-of-flight measurements revealed the excitations of the Rayleigh wave across the surface Brillouin zone, and such measurements were in agreement with the dispersion curves that were produced using density functional perturbation theory. The dispersion relations for H-Ge(111) indicated that a deviation in energy and lineshape for the Rayleigh wave was present along the nearest-neighbor direction. The effects of mass loading, as determined by calculations for CD₃-Ge(111), as well as by force constants, were less significant than the hybridization between the Rayleigh wave and methyl adlayer librations. The presence of mutually similar hybridization effects for CH₃-Ge(111) and CH₃-Si(111) surfaces extends the understanding of the relationship between the vibrational dynamics and the band structure of various semiconductor surfaces that have been functionalized with organic overlayers.

• Capture of Hyperthermal CO₂ by Amorphous Water Ice via Molecular Embedding, Grant G. Langlois, Wenxin Li, K. D. Gibson, and S. J. Sibener, Invited Feature Article for the Special Issue: "Dynamics of Molecular Collisions XXV – Fifty Years of Chemical Reaction Dynamics", J. Phys. Chem. A, 119, 12238-12244 (2015). (Note: This was published just as this grant began; such work is now continuing.)

In this work we presented the first study detailing the capture and aggregation of hyperthermal CO₂ molecules by amorphous solid water (ASW) under ultra-high vacuum conditions at 125 K, near the amorphous/crystalline transition. Using time-resolved in situ reflection-absorption infrared spectroscopy (RAIRS), CO₂ molecules with translational energies above 3.0 eV are observed to directly embed underneath the vacuum-solid interface to become absorbed within the ice films despite an inability to adsorb at 125 K; this behavior is not observed for crystalline films. Upon embedding, the mobility of CO₂ within 125 K amorphous ice and the strength of its intermolecular interactions result in its segregation into clusters within the ice films. Tracing the kinetics of CO₂ embedding events under different energetic conditions allows for elucidation of the underlying dynamics, and we draw comparison with other projectiles we have studied to promote generalized conclusions in regards to empirical prediction of a projectile's embedding probability. Through application of a classical model of the entrance barrier for projectiles colliding with amorphous ice, we provide direct evidence for a unified connection between embedding probability and projectile momentum; an account of all embedding data measured by our group traces a unified barrier model. This work highlights the interplay between translational energy and momentum accommodation during collisions with ice in high speed gas flows.

• Growth, Structure, and Vibrational Properties of Few Layer Graphene Grown on Rh(111), K. D. Gibson and S. J. Sibener, J. Phys. Chem. C <u>120</u>, 24158–24164 (2016).

In this paper, we examine the growth of supported multilayer graphene overlayers on a Rh(111) single crystal substrate. At elevated surface temperatures, ethylene dissociates on the surface and carbon is absorbed into the bulk of the Rh. When the crystal is slowly cooled, the carbon diffuses to the surface, and forms multilayer graphene films. The thickness was determined by Auger electron spectroscopy, and the surface ordering by He scattering. The top layer is azimuthally aligned with the Rh(111) surface, and the moiré pattern due to the lattice mismatch between the Rh and graphite is still visible, though greatly attenuated, for thicknesses up to four layers. We also used He scattering to measure the low energy vibrations of the surface for both monolayer and multilayer graphene. One set of experiments measured the thermal attenuation of the elastic He scattering. The result was that the monolayer graphene is much 'stiffer' (a higher Debye temperature) than even ~ 2 layers. We also used time and angle resolved inelastic He scattering to measure the low energy modes near the zone center. Unlike the graphite ZA acoustic mode, which goes to zero frequency at the zone center, the monolayer has a mode that is a nearly constant 7 meV near the zone center. On the other hand, multilayer graphene has a mode that much more closely resembles the ZA mode of graphite. For the low-lying phonons with some degree of polarization perpendicular to the surface, our observations indicate that there is a real difference in the surface dynamical properties as one transitions between a supported two-dimensional monolayer to three-dimensional films consisting of only a few atomic layers in thickness. These findings add important information on how the properties of supported graphene films evolve with dimensional crossover from 2D to 3D systems, knowledge that is needed for achieving targeted properties in thin films of 2D materials.

• Experimental and Theoretical Study of Rotationally Inelastic Diffraction of H2(D2) from Methyl-Terminated Si(111), Kevin J. Nihill, Zachary M. Hund, Alberto Muzas, Cristina Diaz, Marcos del Ceuto, Terry Frankcombe, Noah T. Plymale, Nathan S. Lewis, Fernando Martin, and S. J. Sibener, J. Chem. Phys., 145, 084705/1-12 (2016).

Fundamental details concerning the interaction between H₂ and CH₃-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 $i = 0 \rightarrow 2$ RID intensities for H₂ compared to the strong RID features observed for D₂ 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 CH₃-Si(111) surface atoms. The probabilities of rotationally inelastic diffraction of H₂ and D₂ 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 (D₂) and hence the surface charge density distribution. Specifically, a sixdimensional potential energy surface (PES), describing the electronic structure of the H₂(D₂)/CH₃-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.

• Temporally and Spatially Resolved Oxidation of Si(111)-(7×7) Using Kinetic Energy Controlled Supersonic Beams in Combination with Scanning Tunneling Microscopy, Bryan Wiggins, L. Gaby Avila-Bront, Ross Edel, and S. J. Sibener, J. Phys. Chem. C 120, 8191-8197 (2016).

The site-specific locations of molecular oxygen reactivity on Si(111)-(7 \times 7) surfaces were examined using kinetic energy selected supersonic molecular beams in conjunction with in situ scanning tunneling microscopy. We herein present a detailed visualization of the surface as it reacts in real-time and real-space when exposed to molecular oxygen with translational energy $E_i=0.37$ eV. Atomically-resolved images reveal two channels for oxidation leading to the formation of dark and bright reaction sites. The darks sites dominate the reaction throughout the range of exposures sampled and exhibit almost no preference for occurrence at the corner or inner adatom sites of the reconstructed (7x7) unit cell. The bright sites show a small preference for corner vs. inner site reactivity on the reconstructed (7x7) unit cell. The bright site corner preference seen here at elevated kinetic energies and with selected incident kinematics is smaller than that typically observed for more conventional thermal (background dosed) oxidation These observations suggest that two adsorption pathways, trapping-mediated processing. chemisorption and direct chemisorption, occur simultaneously when using energetic molecular oxygen but with modified relative probability as compared with thermal dosing. These results demonstrate the efficacy of using angle- and energy-selected supersonic molecular beams to gain a topographical diagram of the accessible reactive potential surface energy and precise control of semiconductor oxidation, a process that is of growing importance as we seek to create highquality and precisely-defined oxides having atomic dimensions.

• Separation of Isotopes in Space and Time by Gas-Surface Atomic Diffraction, Kevin J. Nihill, Jacob D. Graham, and S. J. Sibener, Phys. Rev. Lett. <u>119</u>, 176001/1-5 (2017). Note Accompanying APS Viewpoint: Atom Scattering Picks Out the Heavyweights, October 23, 2017, Physics <u>10</u>, 116. https://physics.aps.org/articles/v10/116. PATENT PENDING.

The separation of isotopes in space and time by gas-surface atomic diffraction is presented as a new means for isotopic enrichment. A supersonic beam of natural abundance neon is scattered from a periodic surface of methyl-terminated silicon, with the ²⁰Ne and ²²Ne isotopes scattering into unique diffraction channels. Under the experimental conditions presented in this letter, a single pass yields an enrichment factor 3.50 ± 0.30 for the less abundant isotope, ²²Ne, with extension to multiple passes easily envisioned. The velocity distribution of the incident beam is demonstrated to be the determining factor in the degree of separation between the isotopes' diffraction peaks. In cases where there is incomplete angular separation, the difference in arrival times of the two isotopes at a given scattered angle can be exploited to achieve complete temporal separation of the isotopes. This study explores the novel application of supersonic molecular beam studies as a viable candidate for separation of isotopes without the need for ionization or laser excitation.

• Chemical Dynamics Simulations and Scattering Experiments for O_2 Collisions with Graphite, Moumita Majumder, K. D. Gibson, S. J. Sibener, and William L. Hase, J. Phys. Chem. C <u>122</u>, 16048-16059 (2018).

Energy transfer in collisions of O₂ with a graphite surface was studied by chemical dynamics simulations. The simulations were performed for three collision energies E_i of 2.1, 7.4, and 15 kcal/mol, with the initial incident angle fixed at $\theta_i = 45^{\circ}$. Simulations were performed for each E_i at a surface temperature $T_{surf} = 300$ K. For the higher surface temperature of 1177 K, a simulation was only performed for $E_i = 15$ kcal/mol. The following properties were determined and analyzed for the O_2 + graphite collisions: (1) translational energy distributions of the scattered O₂; (2) distribution of the final polar and azimuthal angle for the scattered O₂; and (3) number of bounces of O₂ on the surface before scattering. The average energy transferred to the graphite surface and that remaining in O₂ translation, i.e. $\langle \Delta E_{surf} \rangle$ and $\langle E_{f} \rangle$, exhibit a strong linear dependence with the initial translational energy, thus providing a window of predictability of their distributions at any E_i . For the O₂ + graphite scattering, the trapping desorption residence time distribution decays exponentially, with an increase in residence time with a decrease in E_i . The rate at which the distribution decreases shows a near linear dependence with an increase in E_i . For the higher collisional energies, O₂ scattering from the surface follows a nearly quasitrapping desorption process. However, for the lowest collision energy it mostly follows conventional trapping desorption. For all the scattering conditions considered experimentally, the relationship between the average final translational energy and average scattering angle for the O₂ molecules found from the simulations is in excellent agreement with the experimental results. This experimental validation of precise simulation outcomes is important as it indicates that collisional energy transfer predictions for this system can be reliably used in assessing interfacial energy flow in a variety of technological applications including high-performance flight systems.

• Exploratory Direct Dynamics Simulations of O₂ Reactions with Graphene Surfaces at High Temperatures, Seenivasan Hariharan, Moumita Majumder, Ross Edel, Timothy Grabnic, S. J. Sibener, and William L. Hase, J. Phys. Chem. C 122, 29368-29379 (2018).

Direct chemical dynamics simulations at high temperatures of reaction between ${}^{3}O_{2}$ and graphene containing varied number of defects were performed using the VENUS-MOPAC code. Graphene was modelled using (5a, 6z)-periacene, a poly aromatic hydrocarbon with 5 and 6 benzene rings in the armchair and zigzag directions, respectively. Up to six defects were introduced by removing carbon atoms from the basal plane. Usage of PM7/UHF (unrestricted Hartree-Fock) method, for the simulations, was validated by benchmarking singlet-triplet gaps of *n*-acenes and (5*a*,*nz*) periacenes with high level theoretical calculations. PM7/UHF calculations showed that graphene with different number of vacancies have different ground electronic states. Dynamics simulations were performed for two ${}^{3}O_{2}$ collision energies, E_{i} of 0.4 and 0.7 eV with an incident angle normal to the graphene plane at 1375 K. Collisions on graphene with one-, two-, three- and four- vacancies (1C-, 2C-, 3C- and 4C-vacant graphene) showed no reactive trajectories, mainly due to the non-availability of reactive sites resulting from nascent site deactivation (NSD), a dynamical phenomenon. On the other hand, ³O₂ dissociative chemisorption was observed for collisions on four- (with a different morphology), five- and sixvacant graphene (4C2-, 5C- and 6C- vacant graphene). A strong morphology dependence was observed for the reaction conditions. On all the reactive surfaces, larger reaction probabilities were observed for collisions at $E_i = 0.7$ eV. This is in agreement with the nucleation time measured by supersonic molecular beam experiments wherein about 2.5 times longer nucleation time for O₂ impinging at 0.4 eV compared to 0.7 eV was observed. Reactivity at both collision

energies viz., 0.4 and 0.7 eV showed the following trend: 5C- < 6C- < 4C-vacant graphene. Formation of carboxyl/semiquinone (C=O) and ether (-C-O-C-) type dissociation products were observed on all reactive surfaces while a higher probability of formation of the ether (-C-O-C-) group was found on 4C- vacant graphene on which dangling carbon atoms are present in close proximity. However, no gaseous CO/CO₂ formation was observed on any of the graphene vacancies even for simulations that were run up to 10ps. This is apparently the result of the absence of excess oxygen atoms that can aid the formation of larger groups, the precursors for CO/CO₂ formation. Although the results of this study do not provide a conclusive understanding of the mechanism of graphene/graphite oxidation, this work serves as an initial study attempting to understand the ${}^{3}O_{2}$ dissociative chemisorption dynamical mechanism on defective graphene/graphite surfaces at high temperatures.

• Atomically-Resolved Oxidative Erosion and Ablation of Basal Plane HOPG Graphite Using Supersonic Beams of O₂ with Scanning Tunneling Microscopy Visualization, Ross Edel, Tim Grabnic, Bryan Wiggins, and S. J. Sibener, J. Phys. Chem. C 122, 14706-14713 (2018).

The detailed mechanism and kinetics for the oxidative erosion and ablation of highly oriented pyrolytic graphite (HOPG) with molecular oxygen has been examined by monitoring the spatiotemporal evolution of the reacting interface. This has been accomplished using a new, unique gas-surface scattering instrument that combines a supersonic molecular beam with a scanning tunneling microscope (STM) in ultra-high vacuum. Using this new instrument, we are able to tightly control the energy, angle, and flux of impinging oxygen along with the surface temperature and examine the reacted surface spanning atomic, nano, and mesocopic lengthscales. We observe that different oxidation conditions produce morphologically distinct etching features: Anisotropic channels, circular pits, and hexagonal pits faceted along crystallographic directions. These outcomes depend upon independent effects of oxygen energy, incident angle, and surface temperature. Reaction probability increased with beam energy and demonstrated non-Arrhenius behavior with respect to surface temperature, peaking at around 1375 K. At the incident collision energies used, it was found that beam impingement angle had only minor effects on the reaction probability and etch pit morphology. Comparison of the relative reactivity of higher grade versus lower grade HOPG indicates that the formation of etched channels largely depends on the presence of grain boundaries. We have also observed the transition to multilayer etching. The influence of structural inhomogeneities such as defects and grain boundaries can now be assessed by real-time visualization of reacting interfaces. For example, the insertion of intentionally created point defects via ion sputtering leads to marked enhancement in interfacial reactivity. The approach used herein has allowed us to correlate timeevolving surface morphology with atomic-level interfacial kinetics and dynamics, providing new insight into the reactivity of materials in aggressive, energetic environments.

• Sticking Probability of High-Energy Methane on Crystalline, Amorphous, and Porous-Amorphous Ice Films, Rebecca S. Thompson, Michelle R. Brann, and S. J. Sibener, J. Phys. Chem. C <u>123</u>, 17855-17863 (2019).

We present research detailing the sticking probability of CH_4 on various D_2O ices of terrestrial and astrophysical interest using a combination of time-resolved, *in situ* reflection absorption infrared spectroscopy (RAIRS) and King and Wells mass spectrometry techniques. As the incident translational energy of CH_4 increases (up to 1.8 eV), the sticking probability decreases for all ice films studied, which include high-density, non-porous amorphous (np-ASW) and crystalline (CI) films as well as porous amorphous (p-ASW) films with various pore morphologies. Importantly, sticking probabilities for all p-ASW films diverge and remain higher than either np-ASW or CI films at the highest translational energies studied. This trend is consistent across all porous morphologies studied and does not depend on pore size or orientation relative to the substrate. It is proposed that in addition to offering slightly higher binding energies, the porous network in the D_2O film is very efficient at dissipating the energy of the incident CH₄ molecule. These results offer a clear picture of the initial adsorption of small molecules on various icy interfaces; a quantitative understanding of these mechanisms is essential for the accurate modeling of many astrophysical processes occurring on the surface of icy dust particles.

CONCLUDING REMARKS

In this Final Technical Report, we have described the accomplishments that have occurred during this AFOSR funded project, a period of ambitious discovery and productivity. The information generated on correlations between reaction kinetics and time-evolving surface structure during materials oxidation is of profound fundamental and technical importance. These results, along with associated collisional energy and momentum transfer experiments and simulations are relevant for the development of new high-performance materials and ultimately flight systems under supersonic and hypersonic flow conditions. Moreover, other experiments dealing with molecule interactions with ices, the growth and characterization of few layer graphene materials, the properties of next generation semiconductors that are coated with passivating organic species, and especially our discovery of a new method for enriching and separating isotopes based upon diffraction from atomic gratings are all notable contributions to furthering our understanding of chemical dynamics related to gas-surface systems and materials. The postdoctoral scholars, graduate students, and undergraduates who participated in this research have all received training that has helped educate the next generation of leaders in areas of direct interest to the AFOSR and DoD.

End of Report