

REPORT DOCUMENTATION PAGE

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4. TITLE AND SUBTITLE Final Technical Report: Fundamental Studies of Molecule-Surface Encounters Relevant to Molecular Adsorption, Size and Chemically Selective Collection, and Trace Identification/C and L (CBT)				5a. CONTRACT NUMBER W911NF-07-1-0103	
				5b. GRANT NUMBER	
				5c. PROGRAM ELEMENT NUMBER 106013	
6. AUTHORS Professor Steven J. Sibener				5d. PROJECT NUMBER	
				5e. TASK NUMBER	
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7. PERFORMING ORGANIZATION NAMES AND ADDRESSES University of Chicago University Research Administration 970 East 58th Street Chicago, IL 60637 -				8. PERFORMING ORGANIZATION REPORT NUMBER	
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES) U.S. Army Research Office P.O. Box 12211 Research Triangle Park, NC 27709-2211				10. SPONSOR/MONITOR'S ACRONYM(S) ARO	
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13. SUPPLEMENTARY NOTES The views, opinions and/or findings contained in this report are those of the author(s) and should not be construed as an official Department of the Army position, policy or decision, unless so designated by other documentation.					
14. ABSTRACT We have addressed many fundamental scientific questions in order to better understand how molecules chemically and physically interact with a wide-variety of surfaces. Such improved understanding is needed as we seek to design, with intent, interfaces for the efficient adsorption, size- and chemically-selective collection, and trace identification of chemical and biological reagents that are present either naturally or not in our environment. We have used the scattering of atomic and molecular beams from well-characterized and intentionally-tailored surfaces,					
15. SUBJECT TERMS Surface Chemistry, Gas-Surface Interactions, Trace Detection, Molecular Films, Polymer Nanostructures					
16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT UU	15. NUMBER OF PAGES	19a. NAME OF RESPONSIBLE PERSON Steven Sibener
a. REPORT UU	b. ABSTRACT UU	c. THIS PAGE UU			19b. TELEPHONE NUMBER 773-702-7193

Report Title

Final Technical Report: Fundamental Studies of Molecule-Surface Encounters Relevant to Molecular Adsorption, Size and Chemically Selective Collection, and Trace Identification/C and L (CBT)

ABSTRACT

We have addressed many fundamental scientific questions in order to better understand how molecules chemically and physically interact with a wide-variety of surfaces. Such improved understanding is needed as we seek to design, with intent, interfaces for the efficient adsorption, size- and chemically-selective collection, and trace identification of chemical and biological reagents that are present either naturally or not in our environment. We have used the scattering of atomic and molecular beams from well-characterized and intentionally-tailored surfaces, coupled with scanning probe microscopy and surface science analysis tools, to delineate atomic-level details of how molecules initially interact with complex surfaces, become adsorbed, exhibit mobility and organization that will depend on molecular size and chemistry with the interface, and, ultimately, be detected in trace quantities using highly-sensitive surface science, optical, or mass spectrometric methods. These studies have also given incisive information on how the physical and chemical nature of polymeric interfaces and SAMs vary as a function of surface temperature, and how these changes influence the probability of molecular adsorption and transport in the condensed phase. Finally, we have also examined the sticking and size/chemically-selective transport of molecules through porous nanostructured thin films, such as photo-modified and spatially-aligned diblock copolymers.

List of papers submitted or published that acknowledge ARO support during this reporting period. List the papers, including journal references, in the following categories:

(a) Papers published in peer-reviewed journals (N/A for none)

Photochemical Study of the Transport Properties of Gases in Polymer Films,

A. L. Cisse, E. Grossman, and S. J. Sibener, *J. Phys. Chem. B*, 112, 7166-7170 (2008).

Modifying Metal-Polymer Nanostructures Using UV Exposure, Nataliya Yufa, Stephanie Fronk, Seth B. Darling, Ralu Divan, W. Lopes, and S. J. Sibener, *Soft Matter*, 5, 1683-1686 (2009).

In-Situ High-Temperature Studies of Diblock Copolymer Structural Evolution, Nataliya A. Yufa, Jason Li, and S. J. Sibener, *Macromolecules* 42, 2667-2671 (2009).

Diblock Copolymer Healing, Nataliya A. Yufa, Jason Li, and S. J. Sibener, *Polymer*, 50, 2630-2634 (2009).

Sputtering of Ordered Ice Ih Adsorbed on Rh(111) Using Hyperthermal Neutral Ar Atoms, K. D. Gibson, D. R. Killelea and S. J. Sibener, *J. Phys. Chem. C*, 113, 13325-13330 (2009).

Hyperthermal Neutral Ar Atom Sputtering of Multilayer Thin Films of p-Xylene Adsorbed on Rh(111), K. D. Gibson and S. J. Sibener, *J. Phys. Chem. C*, 114, 5547-5550 (2010).

DOI: 10.1021/jp906239z, *J. Phys. Chem. C* 114, 5547-5550 (2010).

Self-assembled monolayer-modified block copolymers for chemical surface nanopatterning, N. A. Yufa, S. L. Fronk, S. J. Rosenthal, S. B. Darling, W. A. Lopes, and S. J. Sibener, *Materials Chemistry and Physics*, 125, 382-385 (2011).

Determination of the Sticking Coefficient and Scattering Dynamics of Water on Ice Using Molecular Beam Techniques, K.D. Gibson, Daniel R. Killelea, Hanqiu Yuan, James S. Becker and S.J. Sibener, *J. Chem. Phys.* 134, 034703/1-7 (2011).

Chiral Domains Achieved by Surface Adsorption of Achiral Nickel Tetraphenyl- or Octaethylporphyrin on Smooth and Locally Kinked Au(111), Lieve G. Teugels, L. Gaby Avila-Bront, and S.J. Sibener, *J. Phys. Chem. C* 115, 2826-2834 (2011).

Number of Papers published in peer-reviewed journals: 9.00

(b) Papers published in non-peer-reviewed journals or in conference proceedings (N/A for none)

N/A

Number of Papers published in non peer-reviewed journals: 0.00

(c) Presentations

Presentations, Professor Sibener

Department of Chemistry, Tufts University, Boston, MA

Chicago Area Undergraduate Research Symp. Keynote Opening Address CAURS, Chicago, IL

ACS National Meeting, San Francisco, Symposium on "Interfacial Processes in Energetic Environments"

Hitachi High Technologies America – National Nanotechnology Seminar Series, Burr Ridge, IL

University of Chicago, Department of Chemistry, Chicago, IL

Trends in Chemical Dynamics: From Small Molecules to Biomolecules, Taiwan

Johns Hopkins University, Department of Chemistry, Baltimore, MD

Fermilab, Meeting on Superconducting RF Materials R&D, Batavia, IL

US - China Partnership Workshop on Heterogeneous Catalysis and Surface Chemistry, Dalian, China

2007 Telluride Workshop on Polymer Physics, Telluride, CO

Argonne-Fermilab Collaboration Meeting, Argonne, IL

XVI Symposium on Atomic, Cluster, and Surface Physics – SASP 2008, Les Diablerets, Switzerland

North Carolina State University, Joint Colloquium: Departments of Physics and Chemical & Biomolecular Engineering, Raleigh, NC

Catalyst Program for Gifted Adolescent Students in the Arts and Sciences, Williams College, Williamstown, MA

Co-Organizer, Centennial Symposium of the Physical Chemistry Division of the American Chemical Society: Celebrating the Past,

Embracing the Future, Philadelphia, PA

2008 Chemical and Biological Defense Physical Science and Technology Conference, New Orleans, LA

Invited Lecturer, DOE Nanoscale Science Research Centers Meeting, Annapolis, MD

Joint Meeting of the 13th AACIS International Conference on Surface and Colloid Science and the 83rd ACS Colloid and Surface Science

Symposium, Columbia University, NY

Workshop on the Dynamics and Chemistry of Surfaces and Interfaces, Savannah, GA

Gordon Research Conference on Dynamics at Surfaces, Session Chair and Introductory Remarks on Reaction Dynamics, Proctor Academy,

NH

6th Annual Argonne – U. of Chicago – Fermilab Science Workshop, Chicago, IL

2009 Chemical and Biological Defense Science and Technology Conference, Dallas, TX

Opening of the U. of Chicago Center in Beijing – Science Beyond Borders: Chicago and China, Panelist and Lecturer, Beijing, China.

1st International Workshop on Scattering of Atoms and Molecules from Surfaces, Weizmann Institute of Science, Rehovot, Israel

PACIFICHEM 2010: The 2010 International Chemical Congress of Pacific Basin Societies, Symposium on Materials and

Nanotechnology, Honolulu, Hawaii

University of Wisconsin, Madison, Department of Chemistry, Madison, WI

Number of Presentations: 26.00

Non Peer-Reviewed Conference Proceeding publications (other than abstracts):

Number of Non Peer-Reviewed Conference Proceeding publications (other than abstracts): 0

Peer-Reviewed Conference Proceeding publications (other than abstracts):

Number of Peer-Reviewed Conference Proceeding publications (other than abstracts): 0

(d) Manuscripts

Number of Manuscripts: 0.00

Patents Submitted

Patents Awarded

Awards

Director, The James Franck Institute, July 2001-June 2007.

Director, NSF Center for Chemical Innovation: Center for Energetic and Non-Equilibrium Chemistry at Interfaces

(CENECEI), September 2010 –

Elected Fellow, American Association for the Advancement of Science, 2006.

Elected Visiting Fellow, JILA (Joint Institute for Laboratory Astrophysics), University of Colorado, Boulder, 2007-2008.

Graduate Students

<u>NAME</u>	<u>PERCENT SUPPORTED</u>
Gaby Avila-Bront	
James Becker	
Qianqian Tong	
Tuo Wang	
Hangqiu Yuan	
Nataliya Yufa	
Amadou Cisse	
Lieve Teugels	
FTE Equivalent:	
Total Number:	8

Names of Post Doctorates

<u>NAME</u>	<u>PERCENT SUPPORTED</u>
Daniel Killelea	
FTE Equivalent:	
Total Number:	1

Names of Faculty Supported

<u>NAME</u>	<u>PERCENT SUPPORTED</u>	National Academy Member
Steven J Sibener		No
FTE Equivalent:		
Total Number:	1	

Names of Under Graduate students supported

<u>NAME</u>	<u>PERCENT SUPPORTED</u>
Stephanie Fronk	
William Letsou	
Sam J. Rosenthal	
FTE Equivalent:	
Total Number:	3

Student Metrics

This section only applies to graduating undergraduates supported by this agreement in this reporting period

- The number of undergraduates funded by this agreement who graduated during this period: 2.00
- The number of undergraduates funded by this agreement who graduated during this period with a degree in science, mathematics, engineering, or technology fields:..... 2.00
- The number of undergraduates funded by your agreement who graduated during this period and will continue to pursue a graduate or Ph.D. degree in science, mathematics, engineering, or technology fields:..... 2.00
- Number of graduating undergraduates who achieved a 3.5 GPA to 4.0 (4.0 max scale):..... 2.00
- Number of graduating undergraduates funded by a DoD funded Center of Excellence grant for Education, Research and Engineering:..... 0.00
- The number of undergraduates funded by your agreement who graduated during this period and intend to work for the Department of Defense 0.00
- The number of undergraduates funded by your agreement who graduated during this period and will receive scholarships or fellowships for further studies in science, mathematics, engineering or technology fields: 0.00

Names of Personnel receiving masters degrees

<u>NAME</u>
Total Number:

Names of personnel receiving PHDs

<u>NAME</u>
Nataliya Yufa
Total Number:
1

Names of other research staff

<u>NAME</u>	<u>PERCENT SUPPORTED</u>
Maria Jimenez	No
Kevin Gibson	No
FTE Equivalent:	
Total Number:	2

Sub Contractors (DD882)

Inventions (DD882)

Scientific Progress

There are many fundamental scientific questions that have been addressed in order to better understand how molecules chemically and physically interact with a wide variety of surfaces. We have used the scattering of atomic and molecular beams from well-characterized and intentionally-tailored surfaces, coupled with scanning probe microscopy and surface science analysis tools, to delineate atomic-level details of how molecules initially interact with complex surfaces, become adsorbed, exhibit mobility and organization that will depend on molecular size and chemistry with the interface, and, ultimately, be detected in trace quantities using highly-sensitive surface science, optical, or mass spectrometric methods. Under the auspices of this program, our group: (i) has pioneered a new method for quantifying permeation and diffusion kinetics of volatile small molecules through polymer thin films, including the kinetics for release from such substrates into the gas phase; (ii) has successfully demonstrated trace detection of adsorbates at interfaces via hyperthermal neutral particle sputtering, avoiding complications due to charging and fragmentation; (iii) developed new methods for trace detection in high velocity gas flows by coupling molecular beam surface deposition with Fourier Transform Infrared Spectroscopy - early results demonstrate that sticking coefficients in high velocity flows deviate from unity even when using cryogenic gettering substrates; (iv) has explored the development of improved self-organizing and self-assembling molecular, diblock copolymer, and nano substrates for collection of molecular/biological moieties. Diblock copolymer films are of particular interest as they can create useful self-organizing morphologies, and can be chemically tailored, for selectively arraying chemical and biological species; and (v) utilized state-of-the-art atomic force and scanning tunneling microscopy to examine trace molecules and biological species at interfaces – most recently the formation of chiral molecular interfaces which may have quite significant importance for subsequent adsorption studies centering on chiral discrimination. The ability to look locally, and therefore avoid spatial averaging on the molecular scale, gives details of individual binding sites for molecular and biological systems that is very important for the further development of smart substrates for detection. Such studies have addressed the critical need to design, with intent, interfaces and new methods for the efficient adsorption, size- and chemically-selective collection, and trace identification of chemical and biological reagents that are present either naturally, or not, in our environment.

Technology Transfer

Final Technical Report

Agency Award Number: W911NF-07-1-0103

Final Technical Report: Fundamental Studies of Molecule-Surface Encounters Relevant to Molecular Adsorption, Size and Chemically Selective Collection, and Trace Identification/C and L (CBT)

**Performing Organization:
The University of Chicago**

**Principal Investigator:
Professor Steven J. Sibener
The James Franck Institute and Department of Chemistry
The University of Chicago
929 East 57th Street
Chicago, IL 60637**

**Distribution:
Approved for Public Release; Distribution Unlimited**

**Subject Terms:
Surface Chemistry, Gas-Surface Interactions, Trace Detection, Molecular Films,
Polymer Nanostructures**

Abstract

We have addressed many fundamental scientific questions in order to better understand how molecules chemically and physically interact with a wide-variety of surfaces. Such improved understanding is needed as we seek to design, with intent, interfaces for the efficient adsorption, size- and chemically-selective collection, and trace identification of chemical and biological reagents that are present either naturally or not in our environment. We have used the scattering of atomic and molecular beams from well-characterized and intentionally-tailored surfaces, coupled with scanning probe microscopy and surface science analysis tools, to delineate atomic-level details of how molecules initially interact with complex surfaces, become adsorbed, exhibit mobility and organization that will depend on molecular size and chemistry with the interface, and, ultimately, be detected in trace quantities using highly-sensitive surface science, optical, or mass spectrometric methods. These studies have also given incisive information on how the physical and chemical nature of polymeric interfaces and SAMs vary as a function of surface temperature, and how these changes influence the probability of molecular adsorption and transport in the condensed phase. Finally, we have also examined the sticking and size/chemically-selective transport of molecules through porous nanostructured thin films, such as photo-modified and spatially-aligned diblock copolymers.

Scientific Progress and Accomplishments

There are many fundamental scientific questions that have been addressed in order to better understand how molecules chemically and physically interact with a wide variety of surfaces. We have used the scattering of atomic and molecular beams from well-characterized and intentionally-tailored surfaces, coupled with scanning probe microscopy and surface science analysis tools, to delineate atomic-level details of how molecules initially interact with complex surfaces, become adsorbed, exhibit mobility and organization that will depend on molecular size and chemistry with the interface, and, ultimately, be detected in trace quantities using highly-sensitive surface science, optical, or mass spectrometric methods. Under the auspices of this program, our group: (i) has pioneered a new method for quantifying permeation and diffusion kinetics of volatile small molecules through polymer thin films, including the kinetics for release from such substrates into the gas phase; (ii) has successfully demonstrated trace detection of adsorbates at interfaces *via* hyperthermal neutral particle sputtering, avoiding complications due to charging and fragmentation; (iii) developed new methods for trace detection in high velocity gas flows by coupling molecular beam surface deposition with Fourier Transform Infrared Spectroscopy - early results demonstrate that sticking coefficients in high velocity flows deviate from unity even when using cryogenic gettering substrates; (iv) has explored the development of improved self-organizing and self-assembling molecular, diblock copolymer, and nano substrates for collection of molecular/biological moieties. Diblock copolymer films are of particular interest as they can create useful self-organizing morphologies, and can be chemically tailored, for selectively arraying chemical and biological species; and (v) utilized state-of-the-art atomic force and scanning tunneling microscopy to examine trace molecules and biological species at interfaces – most recently the formation of chiral molecular interfaces which may have quite significant importance for subsequent adsorption studies centering on chiral discrimination. The ability to look locally, and therefore avoid spatial averaging on the molecular scale, gives details of individual binding sites for molecular and biological systems that is very important for the further development of smart substrates for detection. Such studies have addressed the critical need to design, with intent, interfaces and new methods for the efficient adsorption, size- and chemically-selective collection, and trace identification of chemical and biological reagents that are present either naturally, or not, in our environment.

Personnel Associated with this Grant

Faculty:

Prof. Steven J. Sibener

Senior Scientist:

Dr. Kevin Gibson

Visiting Scientist:

Dr. Eitan Grossman

Collaborators:

Dr. Seth Darling

Dr. Ward Lopes

Postdoctoral Scholar:

Dr. Daniel Killelea

Graduate Students:

Gaby Avila-Bront
James Becker
Amadou Cisse
Lieve Teugels
Qianqian Tong
Tuo Wang
Hanqiu Yuan
Nataliya Yufa

Undergraduate Students:

Stephanie Fronk
William Letsou
Sam J. Rosenthal

Administrative Staff:

Tanya Hagerman
Maria Jimenez

Peer-Reviewed Publications and Synopses:

Photochemical Study of the Transport Properties of Gases in Polymer Films, A. L. Cisse, E. Grossman, and S. J. Sibener, *J. Phys. Chem. B*, 112, 7166-7170 (2008).

We describe a general method of finding the transport properties of molecules in polymer films by photolysis. PMMA samples held at different temperatures are exposed to UV radiation at discrete wavelengths and the time-evolution of the volatile photoproducts detected with a quadrupole mass spectrometer. A diffusion model is used to fit the experimental data and deduce diffusion coefficients for the main photoproduct methyl formate. The average value at room temperature was equal to $1.9 \times 10^{-11} \text{ cm}^2 \text{ sec}^{-1}$ at all wavelengths investigated. Together with the values derived at other temperatures, an Arrhenius plot was obtained and the activation energy for methyl formate diffusion within the polymeric thin film calculated from the slope of the graph. We envision that this new method will find application to a variety of problems involving the mass transport of molecules through boundary layers of single or multilayer thin film structures.

Modifying Metal-Polymer Nanostructures Using UV Exposure, Nataliya Yufa, Stephanie Fronk, Seth B. Darling, Ralu Divan, W. Lopes, and S. J. Sibener, *Soft Matter*, 5, 1683-1686 (2009).

Metals have a variety of behaviors when deposited onto diblock copolymer films, in particular, poly(styrene-*b*-methylmethacrylate). Silver is known to form nanowires, whereas gold forms ellipsoidal nanoparticles of different sizes on each of the blocks, and chromium creates a uniform film on PS-*b*-PMMA. We show that with UV light we can alter the separation between silver nanowires, by making each wire narrower. We also demonstrate the effects of UV light on PS-*b*-PMMA coated with thin layers of gold and chromium, as observed with atomic force microscopy and transmission electron microscopy. We have found that UV exposure increased corrugation of such metal-polymer hybrids by removing PMMA domains, but did not remove metal residing on top

of those domains. The ability to manipulate the morphology of these nanomaterials has potential application in areas such as electronics and sensor technology.

In-Situ High-Temperature Studies of Diblock Copolymer Structural Evolution, Nataliya A. Yufa, Jason Li, and S. J. Sibener, *Macromolecules* **42, 2667-2671 (2009).**

We present the results of imaging cylinder-forming poly(styrene-*block*-methylmethacrylate) diblock copolymer at temperatures high enough to show polymer domains evolving. Atomic force microscopy movies of morphological polymer evolution are analyzed to shed light on the formation of domains, as well as the mechanism which drives their subsequent development, such as spatial domain-wall fluctuations.

Diblock Copolymer Healing, Nataliya A. Yufa, Jason Li, and S. J. Sibener, *Polymer*, **50, 2630-2634 (2009).**

The issue of self-healing materials is of paramount importance due to its intrinsic scientific value, as well as potential applications in a wide variety of fields, such as manufacturing, medicine, and electronics. We have investigated the behavior of poly(styrene-*b*-methylmethacrylate) diblock copolymer, following deformation performed by a silicon atomic force microscopy tip. We observed the changes in the polymer as it was subsequently heated *in situ*, and found how diblock “scars” can heal. These observations give important guidance to efforts that seek to create nanostructures using these methods, while also revealing fundamental insights into the mechanisms of polymer repair on the nanoscale.

Sputtering of Ordered Ice I_h Adsorbed on Rh(111) Using Hyperthermal Neutral Ar Atoms, K. D. Gibson, D. R. Killelea and S. J. Sibener, *J. Phys. Chem. C*, **113, 13325-13330 (2009).**

The sputtering of ordered overlayers of water physisorbed on Rh(111) by hyperthermal Ar atoms was investigated. For incident kinetic energies of 10 to 20 eV, the impact of the Ar atoms leads to the desorption of intact single water molecules. This sputtering is sensitive to the crystalline structure of the ice overlayers with the intensity and energy of the sputtered molecules being dependent upon both the final polar and azimuthal angles. The similarity between the results for one and three layers of water strongly suggests that all of the sputtering originates from the exposed topmost layer. In all cases sputtering yields are small, ~10⁻³, and decreases with increasing film thickness; most of the energy transferred during the collision is dissipated into the lattice. These results suggest that sputtering of surfaces with hyperthermal neutrals might be useful as a noncharging and nonchemically destructive adjunct to ion-induced sputtering and secondary ion mass spectroscopy for compositional depth profiling and trace analysis. Intact neutral molecules are ejected, and the molecules left on the surface have not been altered, which is not the case for ion sputtering.

Hyperthermal Neutral Ar Atom Sputtering of Multilayer Thin Films of p-Xylene Adsorbed on Rh(111), K. D. Gibson and S. J. Sibener, *J. Phys. Chem. C*, **114, 5547-5550 (2010).**

Hyperthermal neutral Ar atoms ($\langle E \rangle$) 12 eV) were used to sputter molecules from thin

films of *p*-xylene adsorbed on Rh(111). This was done for several different film thicknesses, and the energy and intensity of the sputtered *p*-xylene was measured as a function of both the incident angle of the Ar and the ejection angle of the sputtered *p*-xylene. The first layer is not sputtered. For thicker films, up to a coverage equivalent to ~16 layers, molecules are ejected from the surface with a yield of at most 0.05 and a translational energy of under 1 eV. For multilayer films, these results show little, if any, dependence on the film thickness. This atom-based technique is envisaged as an alternative to ion sputtering for depth profiling of organic thin films. Since it involves only low-energy neutral species, charging effects are mitigated. Moreover, the incident neutral inert gas species does not react with the surface nor alter the chemical composition of the film.

Self-assembled monolayer-modified block copolymers for chemical surface nanopatterning, N. A. Yufa, S. L. Fronk, S. J. Rosenthal, S. B. Darling, W. A. Lopes, and S. J. Sibener, *Materials Chemistry and Physics*, **125, 382-385 (2011).**

Thin-film poly(styrene-*block*-methyl methacrylate) diblock copolymer (PS-*b*-PMMA) is used to create chemically patterned surfaces via metal deposition combined with self-assembled monolayers (SAMs) and UV exposure. We use this method to produce surfaces that are chemically striped on the scale of a few tens of nanometers. Atomic force and transmission electron microscopies are used to verify the spatially localized organization of materials, and contact angle measurements confirm the chemical tunability of these scaffolds. These surfaces may be used for arraying nanoscale objects, such as nanoparticles or biological species, or for electronic, magnetic memory or photovoltaic applications.

Determination of the Sticking Coefficient and Scattering Dynamics of Water on Ice Using Molecular Beam Techniques, K.D. Gibson, Daniel R. Killelea, Hanqiu Yuan, James S. Becker and S.J. Sibener, *J. Chem. Phys.* **134, 034703/1-7 (2011).**

The sticking coefficient for D₂O impinging on crystalline D₂O ice was determined for incident translational energies between 0.3 and 0.7 eV and for H₂O on crystalline H₂O ice at 0.3 eV. These experiments were done using directed molecular beams, allowing for precise control of the incident angle and energy. Experiments were also performed to measure the intensity and energy of the scattered molecules as a function of scattering angle. These results show that the sticking coefficient was near unity, slightly increasing with decreasing incident energy. However, even at the lowest incident energy, some D₂O did not stick and was scattered from the ice surface. We observe under these conditions that the sticking probability asymptotically approaches but does not reach unity for water sticking on water ice. We also present evidence that the scattered fraction is consistent with a binary collision; the molecules are scattered promptly. These results are especially relevant for condensation processes occurring under nonequilibrium conditions, such as those found in astrophysical systems.

Chiral Domains Achieved by Surface Adsorption of Achiral Nickel Tetraphenyl- or Octaethylporphyrin on Smooth and Locally Kinked Au(111), Lieve G. Teugels, L. Gaby Avila-Bront, and S.J. Sibener, *J. Phys. Chem. C* **115, 2826-2834 (2011).**

The self-assembly of either nickel tetraphenylporphyrin (NiTPP) or nickel octaethylporphyrin (NiOEP) on a reconstructed Au(111) surface is studied using scanning tunneling microscopy in ultrahigh vacuum. Even though the porphyrins are achiral in the gas phase, they are shown to form racemic chiral domains on the surface. For NiTPP we observe the expected roughly “square” unit cell as well as a new “parallelogram” unit cell. For NiOEP we find a hexagonally packed structure in which alternating rows are rotated 15° with respect to each other. We discuss the forces responsible for the formation of chiral domains and find intermolecular interactions to be the dominant factor in the assembly when the porphyrins are on a flat surface. Moreover, we observe that it is possible to break the formation of racemic domains of NiTPP on Au(111) by using a kinked vicinal surface as a symmetry-breaking template to locally lift the structural equivalence of the racemic surface structures. This study shows that a delicate interplay of intermolecular forces and adsorbate-surface interactions leads to the formation of complex structures and chiral phenomena.

PowerPoint Resources

Please see the already submitted quarterly and interim annual reports for PowerPoint slides corresponding to research accomplishments achieved under the auspices of this grant.

Presentations, Prof. Sibener

Department of Chemistry, Tufts University, Boston, MA

Chicago Area Undergraduate Research Symp. Keynote Opening Address CAURS, Chicago, IL

ACS National Meeting, San Francisco, Symposium on “Interfacial Processes in Energetic Environments”

Hitachi High Technologies America – National Nanotechnology Seminar Series, Burr Ridge, IL

University of Chicago, Department of Chemistry, Chicago, IL

Trends in Chemical Dynamics: From Small Molecules to Biomolecules, Taiwan

Johns Hopkins University, Department of Chemistry, Baltimore, MD

Fermilab, Meeting on Superconducting RF Materials R&D, Batavia, IL

US - China Partnership Workshop on Heterogeneous Catalysis and Surface Chemistry, Dalian, China

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North Carolina State University, Joint Colloquium: Departments of Physics and Chemical & Biomolecular Engineering, Raleigh, NC

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Co-Organizer, Centennial Symposium of the Physical Chemistry Division of the American Chemical Society: Celebrating the Past, Embracing the Future, Philadelphia, PA

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New Orleans, LA

Invited Lecturer, DOE Nanoscale Science Research Centers Meeting, Annapolis, MD

Joint Meeting of the 13th AACIS International Conference on Surface and Colloid

Science and the 83rd ACS Colloid and Surface Science Symposium, Columbia

University, NY

Workshop on the Dynamics and Chemistry of Surfaces and Interfaces, Savannah, GA

Gordon Research Conference on Dynamics at Surfaces, Session Chair and Introductory

Remarks on Reaction Dynamics, Proctor Academy, NH

6th Annual Argonne – U. of Chicago – Fermilab Science Workshop, Chicago, IL

2009 Chemical and Biological Defense Science and Technology Conference, Dallas, TX

Opening of the U. of Chicago Center in Beijing – Science Beyond Borders: Chicago and

China, Panelist and Lecturer, Beijing, China.

1st International Workshop on Scattering of Atoms and Molecules from Surfaces,

Weizmann Institute of Science, Rehovot, Israel

PACIFICHEM 2010: The 2010 International Chemical Congress of Pacific Basin

Societies, Symposium on Materials and Nanotechnology, Honolulu, Hawaii

University of Wisconsin, Madison, Department of Chemistry, Madison, WI

End Document