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14. ABSTRACT
MURI research activities, involving strong interactions between experiment and theory, including interactions with AFRL, NASA, and Boeing, have advanced knowledge of condensed-phase and gas-phase reactions relevant to materials reactivity in LEO. We have: elucidated the mechanism by which graphite is eroded by high-kinetic energy atomic oxygen; quantified the pathways by which organic molecules react with atomic oxygen in regimes not found in the terrestrial environment; explored hyperthermal O chemistry with gas-phase model organic compounds to delineate quantum chemical reaction dynamics appropriate to LEO; discovered a new gas-surface collisional energy-transfer mechanism in which atoms become embedded and re-emitted from thin organic films with specific directionality and excess momentum, contributing to a refined understanding of collisional energy transfer; developed new theoretical methodologies for treating rare events which can dominate the morphological evolution of eroding interfaces - including the first three-dimensional code that incorporates realistic interfacial chemical reactions with large surface area processes; explored synergistic effects in polymer degradation involving atomic oxygen and short-wavelength radiation commensurate with LEO solar illumination; collaborated with AFRLs to understand the efficacy of hybrid organic/inorganic POSS materials; and are important partners in orbital experiments, MISSE-5 and -6, which seek to better define materials degradation in LEO.

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MURI Center for Materials Chemistry in the Space Environment

Final Technical Report for May 1, 2001 – November 30, 2006

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Contents

1. Cover Sheet..... 1
2. Objectives..... 2
3. Status of Effort..... 3
4. Accomplishments/New Findings..... 6
5. Personnel Supported and Associated with this Program..... 19
6. Publications..... 20
7. Interactions/Transitions..... 28
8. New Discoveries, Inventions, or Patent Disclosures..... 45
9. Honors/Awards..... 46
End of Document..... 48

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2. Objectives

2a. Strategic Objectives

The primary objective of this MURI was to elucidate the critical chemical and physical processes which are responsible for the degradation of materials in space environments. The scientific achievements of this MURI, exemplified by its notable list of publications, have indeed advanced the state-of-the-art in this field of endeavor. The knowledge so generated will become the foundation for developing predictive models for materials degradation and failure. This fundamental knowledge will, ultimately, enable the intelligent design of new materials and protective systems with enhanced durability for use in spacecraft. We shall also use this knowledge to help design improved ground-based test standards for candidate spacecraft materials. Moreover, this MURI effort has augmented our understanding of gas-surface collisional energy and momentum transfer, supplying data needed to accurately assess orbital decay in the space environment. This MURI Center has had significant impact on DoD's urgent need to develop advanced, time-stable materials for use in space, leading, ultimately, to reduced system failure due to materials degradation in long-duration LEO operations.

2b. Program Abstract

The MURI Center for Materials Chemistry in the Space Environment seeks to develop a quantitative and predictive understanding of how materials degrade or become passivated in the space environment. This is a critical research area for the DoD and NASA given the large and increasing dependence on satellites and manned spacecraft that reside in, or pass through, the low-earth orbit (LEO) space environment. The physical and chemical environment at LEO is not benign, but rather presents a highly aggressive materials oxidation and degradation situation, ensuring that this will remain a key long-term technical issue for the DoD and NASA as long-duration space activities become even more common than at the present time. For such orbits the interaction of atomic oxygen with thin-film coatings and both structural and nonstructural materials plays a dominant role in the long-term viability and performance of orbiting spacecraft. This situation is further complicated by: (i) the high kinetic energy of gas-surface collisions in LEO, (ii) the synergistic chemical effects which will occur due to the presence of intense levels of solar radiation, (iii) the presence of electronically excited neutral and charged particles, which may further perturb the expected interfacial chemistry, and (iv) the presence of nanoscale interfacial defects produced via sputtering by high-energy particles. This MURI Center brings together, arguably, the leading chemical researchers who, acting together, and in conjunction with DoD, NASA, and Industrial partners, can realistically tackle this complex materials problem. Delineation of the fundamental materials effects due to particle impingement and irradiation on materials used in LEO vehicles is a likely outcome of this effort. Recent developments in advanced experimental methods, theoretical methodology, computer modeling, and synthesis suggest that the time is now appropriate to launch such a concerted multidisciplinary effort to develop a predictive understanding of the surface and materials chemistry which dominate the time-evolution of materials behavior and failure in the harsh LEO environment. This MURI Center assembles the needed capabilities to have significant impact on this topic, including: experimental atomic beam gas-surface scattering and imaging studies involving neutral and ionic species in relevant reaction environments, surface photochemistry expertise, synchrotron-based measurement and irradiation, synthesis of structural and conducting polymers, and theory involving realistic molecular-level models using quantum chemical methods, rate calculations, and simulations of morphological interface

evolution. The 8 members, located at the U. of Chicago, Montana State, Northwestern, Notre Dame, Penn State, Texas Tech, and Yale, have the required complementary expertise, in many instances having pioneered the experimental, theoretical and synthetic methods in use today, to address the underlying chemical and physical issues which are needed to predict materials evolution in the LEO environment. Such understanding is presently lacking, and is needed for a wide-range of metallic, organic, polymeric, semiconductor, and insulating materials. As an added benefit, this MURI effort will further augment our understanding of gas-surface collisional energy and momentum transfer, supplying data needed to accurately assess orbital decay in the space environment. To summarize, this MURI Center is well positioned to have significant impact on DoD's urgent need to develop advanced, time-stable materials for use in space, leading, ultimately, to reduced system failure due to materials degradation in long-duration LEO operations.

3. Status of Effort

This section begins with the required 200 word MURI Status of Effort Summary Statement. It is followed by Status of Effort Statements for each MURI faculty member.

3a. MURI Status of Effort Summary (200 Word Summary)

MURI research activities, involving strong interactions between experiment and theory, including interactions with AFRL, NASA, and Boeing, have advanced knowledge of condensed-phase and gas-phase reactions relevant to materials reactivity in LEO. We have: elucidated the mechanism by which graphite is eroded by high-kinetic energy atomic oxygen; quantified the pathways by which organic molecules react with atomic oxygen in regimes not found in the terrestrial environment; explored hyperthermal O chemistry with gas-phase model organic compounds to delineate quantum chemical reaction dynamics appropriate to LEO; discovered a new gas-surface collisional energy-transfer mechanism in which atoms become embedded and re-emitted from thin organic films with specific directionality and excess momentum, contributing to a refined understanding of collisional energy transfer; developed new theoretical methodologies for treating rare events which can dominate the morphological evolution of eroding interfaces – including the first three-dimensional code that incorporates realistic interfacial chemical reactions with large surface area processes; explored synergistic effects in polymer degradation involving atomic oxygen and short-wavelength radiation commensurate with LEO solar illumination; collaborated with AFRLs to understand the efficacy of hybrid organic/inorganic POSS materials; and are important partners in orbital experiments, MISSE-5 and -6, which seek to better define materials degradation in LEO.

3b. MURI Faculty Individual Status of Effort Statements

Barbara J. Garrison

We have developed a comprehensive model which allows us to model the complex physical and chemical effects of UV irradiation of materials to complement the studies of the Sibener group. Using high-quality electronic structure calculations, we have determined the essential activation and reaction energies necessary to describe the degradation pathways of PMMA after photon absorption. Additional pathways of degradation were calculated for O atom reactions with the UV fragmented PMMA. A Monte Carlo (MC) scheme was embedded into molecular dynamics (MD) simulations to perform activated chemical reactions after photolytic scissions. The microscopic understanding of the conditions that lead to the degradation and loss of material

following UV irradiation has been elucidated. Further studies will include the synergistic effects of oxygen bombardment and related chemistry in the MD simulation.

William L. Hase

A model has been developed which can be used, with the VENUS chemical dynamics computer program, to study energy transfer in projectile collisions with hydrocarbon films. Accurate intermolecular potential energy functions are required between the projectiles and the film, and they were developed for the interaction of $O(^3P)$ atoms with alkane surfaces, Ne atoms with alkane surfaces, Ar-atoms with alkane surfaces and with hydroxylated, per-fluorinated, and fluorinated alkane surfaces, and CO_2 with perfluorinated alkane surfaces. These models were used to study energy transfer in collisions of Ne, $O(^3P)$, and Ar atoms with alkythiolate self-assembled monolayers (H-SAMs), Ar atoms with hydroxylated HO-SAMs, and CO_2 molecules with perfluorinated F-SAMs. Near quantitative agreement is obtained with experiments of the Sibener, Nesbitt, and Morris research groups. High-level ab initio calculations were performed to determine energies, transition state properties, and intrinsic reaction coordinates for reactions associated with $O(^3P)$ processing of hydrocarbon materials. This ab initio information was used to fit PM3 semi-empirical electronic structure theory with specific reaction parameters (SRPs), so that the resulting PM3-SRP model represents reactions for $O(^3P)$ processing of hydrocarbons. The PM3-SRP model was incorporated into the VENUS/MOPAC software package and used to study the dynamics of $O(^3P)$ + ethane reactions at 5 eV collision energy. Exploratory simulations at the B3LYP and MP2 levels of theory were used to study H^+ and CH_3^+ reactions with hydrocarbon molecules. QM/MM methods will be used to extend these simulations to collisions with surfaces.

Dennis Jacobs

We have studied the reaction of 5-20 eV O^+, O_2^+, and Ne^+ ions with dodecanethiolate and semifluorinated dodecanethiolate self-assembled monolayers (SAM), polyhedral oligomeric silsesquioxane (POSS) monolayers, and highly oriented pyrolytic graphite (HOPG) surfaces. To better understand the dynamics of polymer degradation under ion irradiation, we have deposited SAM layers to which Prof. Luping Yu has substituted the hydrogen atoms located on the C-12, C-11, and C-10 positions of 1-dodcanethiol with deuterium atoms. The dose-dependent signal for abstraction from isotopically labeled positions reveals a strong energy-dependence to the rate at which surface order decays. To simulate degradation of silicon-containing polymers in LEO and examine their self-passivation properties, we have applied in-situ X-ray photoelectron spectroscopy (XPS) to measure surface composition changes of POSS films at various stages during O^+ exposure. It was shown that a multilayer of POSS is required for films to form a protective layer and develop resistance to further oxidation. Defect initiation on graphite was studied for 5-20 eV O^+, O_2^+, and Ne^+ ion bombardment. Scanning Tunneling Microscopy (STM) reveals the relatively low probability for defect initiation on graphite; however, XPS and temperature programmed desorption (TPD) shows that oxygen can be rapidly incorporated into defects on graphite. This family of ion/surface scattering experiments has helped establish the mechanisms by which O^+, the dominant ion in LEO, erodes and degrades carbon-based materials.

Timothy K. Minton

The general goal of our component of the MURI center has been to understand in detail how atomic oxygen leads to the erosion and degradation of materials on spacecraft in low Earth orbit. To this end, we have conducted crossed molecular beams experiments on the fundamental interactions between hyperthermal atomic oxygen and hydrogen, deuterium, methane, ethane, and propane. In addition, we conducted beam-surface scattering experiments

and O-atom exposures on various surfaces, including metals, hydrocarbon polymers, POSS polymers, and graphite. Furthermore, we investigated synergistic effects in polymer degradation involving atomic oxygen and VUV light and/or collision-induced dissociation. To help understand energy transfer in hyperthermal collisions, we conducted a crossed-beams experiment on the inelastic scattering of Ar and ethane. To ensure that the reactions studied reflect the chemistry that occurs between spacecraft and the space environment, we improved and characterized a hyperthermal O-atom source. In order to compare lab and space data, samples were provided for two International Space Station experiments. Many papers, conference proceedings, talks, and posters resulted from this work, and the PI helped organize relevant scientific meetings. Close collaborations with other MURI investigators as well as NASA, AFRL, and industry personnel have ensured that our work has truly been part of a unified approach to learning the details of how materials react to various space environments.

George C. Schatz

Schatz has performed theoretical studies of the interaction of hyperthermal atomic oxygen with isolated molecules and with surfaces to establish the basic reaction mechanisms associated with materials degradation in the Low Earth Orbit environment. These studies have included studies of oxygen reactions with hydrocarbons, fluorinated hydrocarbons, water, HCl, hydrogen, and POSS/Kapton models as gas phase species, and with alkane thiol self assembled monolayers on gold surfaces, and with liquid squalane. We have also studied reactions of hyperthermal O^+ and H atoms with small molecules.

Steven J. Sibener

The Sibener Group has used molecular beams, scanning probe microscopy, quantum scattering calculations, and molecular dynamics simulations to address materials degradation and collisional gas-surface energy transfer/orbital decay issues of relevance to the LEO environment. Experiments involving metals, self-assembling monolayers (SAMs) of hydrocarbons, polymers, graphite, and diamond have been carried out; several publications have resulted from these efforts. We have had strong collaborations with the Minton group on graphite, diamond, and hydrocarbon oxidation, and the Hase group with respect to gas-surface collisional energy transfer, as well as the Schatz and Tully groups which have joined the theory effort in graphite reactivity. We have also had projects in photochemical synergistic effects, with the Garrison Group providing relevant theory. Time-lapse scanning tunneling microscopy of metals and AFM measurements of SAMs and polymers subjected to terrestrially simulated orbital environments was part of this effort. MURI instrumentation has been completed successfully: we have established the ability to carry out variable-temperature and atomically-resolved UHV-STM imaging of reacting films and interfaces between 25 K and 1000 K. During the past year we constructed, and are now testing, a 5 eV $O(^3P)$ source based on the laser-detonation methods pioneered by the Minton group. This new capability, coupled with our extant ability to generate supersonic beams of $O(^3P)$ and $O(^1D)$ atoms, gives us unprecedented control over reactivity studies involving these reagents. Our experiments during the past year have continued to involve graphite erosion including the exploration of synergistic effects involving ion bombardment, directional etching, polymer erosion with atomic oxygen including synergistic effects involving VUV illumination, metallic oxidation, and our first generation of "geometry-restricted" O + hydrocarbon reactions in which chemically modified end-groups on even and odd chain-length SAMs are used in conjunction with our angle and velocity selected beams of atomic oxygen. Experiments have also been launched on Teflon model compounds (perfluorinated SAMs) and model polymer thin films that were synthesized

by the Yu Group. Finally, we have completed a massive study of collisional energy transfer involving Ne, Ar, and Xe colliding with crystalline SAM interfaces. These experiments, in conjunction with relevant theory from the Hase Group, are shedding new light on energy and momentum exchange mechanisms which occur at hyperthermal energies, a topic of direct relevance to orbital decay. In particular, we have discovered a new gas-surface collisional energy-transfer mechanism in which atoms become embedded and re-emitted from thin organic films with specific directionality and excess momentum, contributing to a refined understanding of collisional energy transfer.

John C. Tully

We developed and implemented a number of new theoretical and computational tools for simulating and predicting the rates and pathways of chemical reactions with surfaces. One emphasis of this work was on nonadiabatic processes; reactions involving more than one electronic potential energy surface. Nonadiabatic events often dominate the dynamics of hyperthermal collisions with surfaces, collisions of open shell species and ions, and even thermal interactions with metallic surfaces. We implemented an ab initio Ehrenfest method for propagating nuclear motion when electronic transitions are occurring. Using this tool, we explored the reactions of O^+ ions with graphite surfaces, with emphasis on the differences in reactivity between neutral O atoms (studied by Minton and Sibener) and positively charged O^+ ions (studied by Jacobs). We developed a "wide-band" theory of charge exchange at metal and semiconductor surfaces, valid when the energy of an adsorbate electronic level lies within the conduction band of the substrate. We developed a kinetic Monte Carlo computer code for simulating the erosion of surfaces in low Earth orbit, and applied this method to elucidate the mechanisms of erosion of graphite by 5 eV oxygen atoms(with Minton and Sibener).

Luping Yu

Alkane thiols with various functional groups have been synthesized. These compounds have been shipped to Minton, Jacobs and Sibener's labs for degradation studies. We have synthesized thiol model compound with ferrocene moieties, that was delivered to Sibener's group. Isotopically labeled SAMs have proved particularly useful for the mechanistic studies of SAM reactivity conducted at Notre Dame, while odd and even 1-ene SAMs are being examined by the Sibener group at Chicago for geometry-restricted reactions.

4. Accomplishments/New Findings

Barbara Garrison

The goal of our component of the MURI project is to model the synergistic effects of solar UV radiation and oxygen bombardment of materials. The model that we have developed allows us to extract the microscopic details of the irradiation process and understand the subsequent degradation of material. The model consists of three stages: (1) defining the material and choosing pathways which are indicative of the material degradation, (2) calculating the activation and reaction energies of the pathways, and (3) incorporating the reactions in a MD simulation to understanding the microscopic details leading to ejection of material.

To complement the experiments of the Sibener group, we have performed our simulations with a poly(methyl methacrylate), or PMMA, substrate. In addition, much experimental work and many analytical models are available to aid in the understanding effects of UV radiation with

PMMA. The pathways of degradation were chosen to represent those which are relevant at UV wavelengths and include the main chain and side chain scissions. Following the main chain scission, the polymer can undergoing unzipping, while following the side chain scission, small particles and gases can be released.

Electronic structure calculations were used to determine the reaction energetics of chemical pathways. The hybrid CBS-QB3 approach lends itself well toward calculating highly accurate values of the reaction states of small molecules. Relative to the radical species created by the photon induced bond cleavage, the release of carbon dioxide was determined to be exothermic whereas the unzipping of a monomer and the release of CO was endothermic. Further calculations showed the synergistic effects of $O(^3P)$ atoms. The reaction of atomic oxygen with any of the radical species is highly exothermic and leads to the formation of a stable molecule and another radical species.

Coarse-grained MD simulations of UV irradiation of PMMA were then performed using the set of reactions and energetics from the electronic structure calculations. The MD simulation uses a probabilistic (Monte Carlo) scheme to execute the activated chemical reactions following photolytic scissions during the dynamics calculations. Our studies show that a certain conditions lead to ejection of material from a PMMA substrate. If the photon is absorbed thermally (no photolytic scission event), material ejection occurs when the energy density in the surface layer is large enough to cause a critical number of bonds to thermomechanically break. In addition, photochemical events are able to eject material from the substrate. Following the photon absorption and subsequent bond break, the polymer integrity is disrupted decreasing the cohesive density and the substrate transforms and fragments. In one pathway of degradation, the release of small molecules, such as CO_2, CO, methane, and methanol, hollows out the material and then low velocity polymer clusters eject. In another pathway of degradation, MMA monomers are unzipped from the polymer chains and ejection of clusters of material occurs in a layer-wise manner. In both photochemical pathway, the substrate ejection is a two-step process with the chemical transformation of material preceding the thermally induced release of large clusters.

William L. Hase

a. Energetics, transition states, and intrinisic reaction coordinates for reaction associated with $O(^3P)$ processing of hydrocarbon materials.

Electronic structure calculations based on multiconfiguration wave functions were used to investigate a setoff archetypal reactions relevant to $O(^3P)$ processing of hydrocarbon molecules and surfaces. They include $O(^3P)$ reactions with methane and ethane to give OH + methyl and ethyl radicals, $O(^3P)$ + ethane to give $CH_3O + CH_3$, and secondary reactions of the OH product radical with ethane and ethyl radical. Where comparison of computed barriers and energies of reaction with experiment is possible, the agreement is good to excellent.

b. Semi-empirical model for $O(^3P)$ reaction with alkane molecules and surfaces. Application to $O(^3P) + C_2H_6$.

A*b initio* information was used to fit PM3 semi-empirical electronic structure theory with specific reaction parameters (SRPs), so that the resulting PM3-SRP model represents, as accurately as possible, the reactions involved in the high energy $O(^3P)$ processing of hydrocarbons. The PM3-SRP model was incorporated into our VENUS/MOPAC software package and used to simulate the dynamics of $O(^3P)$ + ethane reactions at a 5 eV collision

energy using QM direct dynamics. The reaction cross sections calculated for the primary reaction channels are in good agreement with the prior results of Troya and Schatz. Our trajectories were integrated for the relatively long time of up to 500 fs and, in addition to the three primary reaction channels, an additional 19 reaction channels were observed. It was found that the PM3-SRP model does not accurately represent all the many possible reaction channels that may occur at the high collision energy of 5 eV. A more detailed semi-empirical electronic structure theoretical model is needed, with multi-reference characteristics, to accurately represent the many possible reactions. Work to develop such a model is in progress.

c. Energy transfer in O(^{3}P) collisions with alkylthiolate self-assembled monolayer surfaces

Energy transfer was simulated for collisions of O(^{3}P) with the decanethiolate SAM at collision energies of 2.3, 11.2, 71.0, and 120.0 kcal/mol, and for a variety of incident angles with respect to the surface normal. For the 2.3 kcal/mol collision energy the O-atom physisorbs on the surface and desorbs with a Boltzmann distribution in accord with the surface temperature. For the high energy collisions, the nature of the energy transfer is strongly dependent on the incident angle. For near normal incident angles, the O-atoms penetrate the surface and sixty to eighty percent are accommodated by the surface. For glancing collisions, with an incident angle of 75 degrees, there is negligible energy transfer to the surface and there is not a Boltzmann component in translational energy distribution of the scattered atoms. This finding illustrates the efficiency of energy transfer in collisions of high energy projectiles with polymer surfaces depends on the angle it which the projectile strikes the surface, and suggests that the surface structure will be an important component in the energy transfer. The following can be investigated by simulating collisions with disordered surfaces, such as liquid alkanes.

d. Analytic intermolecular potentials for Ar-atom collisions with hydroxylated and fluorinated alkane surfaces

CCSD(T) electronic structure calculations, extrapolated to the complete basis set (CBS) limit, were used to calculate intermolecular potentials for the Ar-CF_4 and Ar-CH_3OH systems. Accurate and physically meaningful fits to these potentials were obtained with a sum of 2-body Buckingham potentials. These potentials may be used to construct potentials for Ar-atoms colliding with hydroxylated and fluorinated hydrocarbon surfaces.

e. Dynamics of O(^{3}P) reaction with propane and propane tetramer

Direct Dynamics quasiclassical trajectory simulations were performed, with a PM3-SRP potential energy surface (PES), to study the dynamics of O(^{3}P) reactions with propane and propane tetramer. The PM3-SRP PES was developed by using specific reaction parameters (SRPs) to fit PM3 to high level *ab initio* calculations for O(^{3}P) reactions with alkanes; *i.e.* T. Yan, W. L. Hase, and C. Doubleday, *J. Chem. Phys.* **120**, 9253 (2004). The simulations were performed at relative translational energies E_{rel} of 40 kcal/mol or less, for which the only open reaction channels are H-atom abstraction to form OH and an ensuing additional H-atom abstraction by OH to form H_2O. The properties investigated in the simulations are:

- Probability of forming OH and H_2O versus impact parameter, b, and E_{rel}.
- Probability of forming OH in different vibrational and rotational states versus b and E_{rel}.
- Relative probability of secondary versus primary H-atom abstraction by O(^{3}P).
- Differential reaction cross sections for forming all product states at different relative translational energies.
- Distribution of OH rotational states for the OH v = 0, 1, and 2 vibrational states.

There are two primary differences between the O(^{3}P) reaction dynamics with propane and propane tetramer. There is a higher probability of secondary H-atom abstraction for the

tetramer, which appears to be due to a greater accessibility of its secondary hydrogen atoms. The rotational energy distribution of the OH product is colder for the tetramer, which may result from secondary collisions with the tetramer reactant.

f. Direct dynamics software for $O(^3P)$ reactions

We have developed the VENUS/MOPAC computer program with specific reaction parameters (SRPs) to model $O(^3P)$ reactions with alkane molecules and materials. This program will be made available to others (e.g. for Spectral Sciences, Inc.) who want to model $O(^3P)$ chemical dynamics. The VENUS/NWChem and VENUS/GAMESS packages have been developed to perform $O(^3P)$ direct dynamics simulations at higher levels of electronic structure theory.

g. Ne + H-SAM scattering

Ne atom collisions with the n-hexyl thiolate self-assembled monolayer (H-SAM) surface were simulated. The energy distribution of the scattered Ne-atoms has both a Boltzmann component (BC) and a non-Boltzmann (NB) component. For almost all initial conditions the BC component does not arise from a trapping desorption intermediate and the effective temperature of this component is higher than the surface temperature. It is suggested there is an efficient IVR between the a subset of the surface modes as the Ne atom collides which gives rise to the Boltzmann component.

h. CO_2 + F-SAM scattering

Chemical dynamics simulations were performed to study energy transfer in collisions of CO2 with a perfluorinated octanethiol self-assembled monolayer (F-SAM) surface. Three types of collision events were observed: direct scattering, physisorption on the top of the surface, and penetration of the surface. Penetration leads to near thermal accommodation with the F-SAM, whereas accommodation is not reached for either the direct or physisorption trajectories. The distributions of the translational energy and rotational angular momentum of the scattered CO_2 molecules were analyzed for the different trajectory types. The results found from the simulations are in excellent agreement with experiments for carbon dioxide scattering off perfluoropolyether.

i. Chemical dynamics software and simulation (CDSSIM) system website

The computer programs and simulation models, developed as part of this grant, are documented and released so they can be used by other research groups; see the Chemical Dynamics Software and Simulation (CDSSIM) website: cdssim.chem.ttu.edu.

Dennis C. Jacobs

Hyperthermal energy ions can inflict significant damage on a SAM through impulsive energy transfer, charge-transfer induced electronic excitations, and a variety of chemical reactions. A complement of experiments has documented many of the degradation pathways by which a SAM is eroded and structurally modified under ion bombardment. Mass spectrometry identifies the scattered ionic products when hyperthermal Ne^+/O^+ impacts an alkanethiolate or semifluorinated alkanethiolate SAM. In addition to physical sputtering from Ne^+ or O^+ ion bombardment, O^+ will directly abstract hydrogen or fluorine atoms from predominantly the topmost layer of the SAM. (Site-Selective Abstraction in the Reaction of 5- to 20-eV O^+ with a Self-assembled Monolayer. Xiangdong Qin, Tochko Tzvetkov, Xin Liu, Dong-Chan Lee, Luping Yu and Dennis C. Jacobs. *J. Am. Chem. Soc.* 2004, *126*, 13232.) Removal of an atom from a hydrocarbon SAM chain will initiate facile hydrogen migration along the chain and create opportunities for cross-linking between chains. In addition, an O^+ ion can remove carbon from the chain or incorporate oxygen into the SAM with significant probability (38% and 18%,

respectively, for a 5-eV O^+ ion). (Qin, X.; Tzvetkov, T.; Jacobs, D. C. *Nucl. Instrum. Meth. B* 2003, *203*, 130.). Prof. George Schatz has used direct dynamics quasiclassical trajectory methods for simulation of O^+ reactive scattering on an alkanethiolate SAM. The favorable comparison with experimental results suggests the mechanisms by which oxygens atoms or ions degrade a hydrocarbon surface. The site dependence to ion erosion not only demonstrates a strong propensity for abstraction to occur near the vacuum interface but also is manifested in the preferential attack of molecules adsorbed at domain boundaries or near defect sites in contrast to those packed internally within a structural domain.

Comparatively, Ne^+ is less destructive than O^+ when the ions are targeted at a SAM. Fewer scattered products emerge from a Ne^+-bombarded SAM, and the resulting layer is less disordered than a SAM exposed to an equivalent amount of O^+. These results underscore the important influence of chemical effects as O^+ stabilizes reaction intermediates and lowers activation barriers far better than its Ne counterpart. (Xiangdong Qin, Tochko Tzvetkov and Dennis C. Jacobs, *J. Phys. Chem. A,* **110** (4), 1408 -1415, 2006)

POSS is found to decrease AO erosion rate when incorporated into polymers on a nano-scale. Because POSS molecules constitute the core part in copolymers to prevent oxidation, it is critical to understand the mechanism by which POSS degrades in LEO. We have deposited a monolayer of POSS molecules on a Au (111) surface, and directed a 5-eV O^+ beam to collide with the monolayer under ultrahigh vacuum (UHV) conditions. The recession rate of a POSS monolayer and the surface chemical environment are measured by XPS. It is found that the number of Si atoms remains constant, and SiO_2 is produced during O^+ bombardment. The rate of carbon removal of a POSS monolayer is comparable to that of a decanethiolate SAM. It is shown that more than one layer of POSS is required for the SiO_2 layer to be dense enough to prevent further oxidation. These findings will provide valuable information for the design of functionalized polymers for next-generation spacecraft materials.

HOPG is an ideal surface for modeling carbon composites. The present study is focused on elucidating the mechanism by which 5-20 eV O^+ initiates defects within the basal plane of a graphite surface. We found that impurities on a graphite surface (most likely water since it cannot be imaged by STM) can charge during O^+ bombardment and repel incident O^+. Correspondingly, charged impurities locally protect regions of the graphite surface, and STM reveals clusters of defects only where impurities are absent on the surface. Contaminants can be minimized, if the graphite sample is annealed above 400 °C prior to ion bombardment. STM, XPS and TPD are applied to characterize the modified HOPG surface at various stages during O^+ exposure.

STM imaging of an irradiated HOPG surface at low ion fluencies provides information about the initial rate at which individual defects are formed on a pristine graphite surface, where all C-C bonds within a basal plane are intact. In the low dose limit, we are able to identify, count, and measure the size of defects induced by ion impacts. The results demonstrate that the probability with which an individual ion creates a defect scales dramatically with incident ion energy, and the probability of forming new defects on an intact region of the basal plane increases proportionally with total ion dose. Complementary to STM, XPS measures the chemical composition of HOPG during O^+ bombardment at higher ion fluencies. The oxygen uptake rate depends strongly on the incident energy of O^+ ions; however, the coverage of oxygen at the saturation point is independent of the incident ion energy. TPD spectra show that only CO_2 desorbs from O^+-sputtered graphite at a temperature near 400^0C. The second-order desorption peak suggests that CO_2 is not a chemisorbed molecule on the surface but forms upon heating as a gas-phase product from a bimolecular surface reaction.

Kinetic Monte-Carlo simulations performed by Prof. John Tully allow us to test various

mechanisms for the oxidation of graphite and compare the predicted rate constants with independent experimental findings. Although our experiments are performed with O^+ at low fluence, they can also shed light on the high-fluence, O-atom experiments previously conducted by Profs. Steve Sibener and Tim Minton.

Together, these MURI studies shed light on some of the complex mechanisms operative when hyperthermal energy ions bombard organic thin films. In particular, the results help increase our understanding of how polymeric materials and carbon composites degrade in the harsh low-earth orbit environment where the external surfaces of a spacecraft are bathed relentlessly in atomic oxygen, O^+ ions, electrons and photons.

Timothy K. Minton

Hyperthermal Reactions of Oxygen Atoms with CH_4, CH_3CH_3, and $CH_3CH_2CH_3$

We have conducted detailed crossed beams experiments on the reactions of $O(^3P)$ with model hydrocarbon compounds at center-of-mass collision energies in the range 2.8-3.9 eV, which are representative of those encountered on spacecraft in low Earth orbit when an incident O-atom interacts with a localized effective mass on a hydrocarbon surface. The hyperthermal reactions of O atoms with methane, ethane, and propane showed evidence for direct reaction with carbon, in addition to the expected H-atom abstraction reaction to form OH. Reactions leading to H-atom elimination and the corresponding methoxy, ethoxy, or propoxy radical are possible, and reactions involving breakage of the C-C bond in ethane and propane may also occur. While the H-atom abstraction channel has a modest barrier in the range 0.1-0.3 eV, the other observed reactions have barriers greater than 1.8 eV and therefore might become important at the high collision energies between atomic oxygen and spacecraft surfaces in low Earth orbit. H-atom elimination and C-C bond breakage in the reaction of $O(^3P)$ with saturated hydrocarbons has never been observed before. These newly observed reaction mechanisms have also been seen in the theoretical calculations of George Schatz.

Hyperthermal Reactions of Oxygen Atoms with H_2 and D_2

We carried out a crossed beams study of a relatively simple system in order to validate the assumption that the reactive atomic oxygen in our hyperthermal beam is in the ground $O(^3P)$ state and not in an excited state, such as $O(^1D)$, or in a mixture of excited and ground states. The reaction dynamics of $O(^3P)$ with molecular hydrogen can be calculated almost exactly; thus theoretical calculations of George Schatz provide a benchmark for comparison with our experimental results. We have studied the O + H_2 reaction at center-of-mass collision energies just above threshold for the $O(^3P)$ reaction with H_2, which is about 10 kcal mol^{-1}, and we have observed OH product signal that appears to rise dramatically above this threshold energy, which is expected behavior near threshold. In addition, product angular distributions for OH or OD, depending on the collision partner of the O atom, drop off precipitously at lab angles that would be expected for an $O(^3P)$ reaction. We therefore confirmed that at least most of the observed reactive signal arises from ground-state $O(^3P)$ reactions with H_2 (or D_2). This was the first experimental observation of the $O(^3P)$ + H_2 reaction using molecular beams, and this experiment was only possible because the high O-atom velocity in our beam allowed the high reaction barrier to be surmounted.

Exposure of Samples to the Hyperthermal O-Atom Beam

A temperature-controlled sample mount was constructed, and we have used it extensively to carry out exposures of model materials in our hyperthermal O-atom beam at different

temperatures, ranging from 25°C to 300°C. Many samples of highly-ordered pyrolytic graphite (HOPG) and Kapton have been exposed throughout this temperature range, and after the erosion yields were measured with the use of profilometry, the samples were sent to Steve Sibener's Lab at the University of Chicago, where extensive AFM and STM analysis showed a marked change in the erosion mechanism of HOPG with temperature but not that of Kapton. Many samples of POSS polymers were exposed, and it was found that certain POSS-containing polyimides eroded less than one hundredth the erosion rate of Kapton control samples. These results suggest that POSS loading of polymers may be a viable approach to making polymers resistant to atomic oxygen attack in low Earth orbit. Exposures of other model polymers (e.g., polyethylene and FEP Teflon) have been carried out in order to determine the erosion yields of these well-studied polymers following exposure to our atomic-oxygen beam. The erosion yields were similar to those reported when these polymers were exposed to the low Earth orbital environment. We have studied the linearity of the fluence dependence of Kapton H erosion and the dependence of sample temperature on the erosion of Kapton H and FEP Teflon. A systematic set of exposures, which eroded room-temperature Kapton H from 1.4 to 25 microns, showed that the erosion of Kapton H is linearly dependent on O-atom fluence. This result helps validate the use of Kapton H mass loss or erosion depth as a linear measure of the O-atom fluence of a materials exposure. The erosion of both Kapton H and FEP Teflon exhibited a strong temperature dependence. At lower temperatures (<100 deg. C), the erosion of both materials appeared to be independent of sample temperature. But above 100 deg. C, the erosion yield of Kapton H and FEP Teflon exhibited an Arrhenius-like temperature dependence, with apparent activation energies of 0.3 and 0.24 eV, respectively. These observations suggest that O-atom-induced erosion of these dissimilar polymers proceeds through direct, nonthermal gas-surface reactions and through reactions that depend on surface temperature, perhaps involving reactions of O atoms that become trapped (thermalized) at the surface.

Energy Transfer in Hyperthermal Collisions of Ar with Ethane

Crossed-molecular beams experiments have been done to study the dynamics of Ar + ethane collisions at hyperthermal collision energies. Experimental time-of-flight and angular distributions of ethane molecules that scattered into the backward hemisphere (with respect to their original direction in the center-of-mass frame) have been collected. Translational energy distributions, derived from the time-of-flight distributions, reveal that a substantial fraction of the collisions transfer abnormally large amounts of energy to internal excitation of ethane. The flux of the scattered ethane molecules increased only slightly from directly backward scattering to sideways scattering. The experimental results were compared to the results of theoretical calculations by George Schatz's group. The calculations show angular and translational energy distributions which are in reasonable agreement with the experimental results. These calculations have been used to examine the microscopic mechanism for large energy transfer collisions ("supercollisions"). Collinear ("head-on") or perpendicular ("side-on") approaches of Ar to the C-C axis of ethane do not promote energy transfer as much as bent approaches, and collisions in which the H atom is "sandwiched" in a bent Ar···H-C configuration lead to the largest energy transfer. The conclusions of this study have important implications for materials degradation in low-Earth orbit. Gas-surface collisions occur between the outer materials (often polymers) of a spacecraft and ambient O atoms and N_2 molecules. The relative velocities are comparable to those used in the Ar + ethane studies. Center-of-mass collision energies with a heavy surface may be as high as 10 eV, and large energy transfers in the gas-surface collisions may result in collision-induced dissociation. Collision-induced dissociation would produce

radical sites that would make a polymeric material much more susceptible to atomic-oxygen attack. Thus, strongly inelastic collisions may act synergistically with atomic oxygen to degrade spacecraft materials.

Beam-Surface Scattering Studies of the Individual and Combined Interactions of VUV Radiation, Hyperthermal O, O_2, or Ar with Fluorocarbon Surfaces

Surfaces of spacecraft traveling in low-Earth orbit (LEO) collide with atomic oxygen and molecular nitrogen in the Earth's residual atmosphere at average relative velocities of ~7.4 km s^{-1}. These high velocities lead to gas-surface collisions with many electron volts of collision energy in the center-of-mass reference frame (perhaps 8 eV or more in the case of N_2 collisions). The hyperthermal collision energies are in excess of many bond dissociation energies and may promote materials degradation through reaction or collision-induced dissociation. Spacecraft in LEO are also exposed to high fluxes of vacuum ultraviolet (VUV) radiation, which might contribute to the degradation of materials through photodissociation of bonds near the material's surface. Fluorinated ethylene-propylene copolymer (FEP Teflon) is used as a thermal blanketing material to protect spacecraft from direct solar heat. It has been reported that FEP Teflon erodes under the combined exposure of VUV light and atomic oxygen, while erosion by atomic oxygen alone is negligible. We conducted a study to understand the mechanisms by which CID and VUV light act either alone or in synergy with atomic oxygen to degrade a fluorocarbon surface. These studies employed our hyperthermal beam source, operated either with our "standard beam" of ~70% O and ~30% O_2 or with pure Ar, and a deuterium (D_2) lamp that provides a source of VUV light. The energy of the hyperthermal beam pulse that strikes the target surface is selected with the use of a chopper wheel that is synchronized with the firing of the hyperthermal source. The D_2 lamp is on a sliding mount, such that the distance from the lamp to the target surface can be varied, thus allowing the VUV flux at the surface to be varied. The distance from the lamp to the surface was varied from a few inches to >10 inches, depending on whether or not a band-pass filter was used to select a narrow wavelength range of VUV light. Two types of fluorocarbon surfaces were used: FEP Teflon and a liquid analog, perfluoropolyether (PFPE, Krytox 1618). The liquid surface is continuously refreshed so we can study the initial interactions of the incident beam with a fluorocarbon surface. The FEP Teflon surface is static, and our data reflect a steady-state situation in which the surface is continuously bombarded by the incident beam (at a repetition rate of 2 Hz). Although the hyperthermal beam is pulsed, the D_2 lamp is continuous. Products were detected with a rotatable mass spectrometer detector.

Findings:

- FEP Teflon that was exposed to VUV light alone yielded volatile reaction products (C_nF_m fragments) that were detected with a mass spectrometer. Observed products indicate that VUV light leads to C–C bond breakage.
- $O(^3P)$ atoms with up to ~6 eV of translational energy did not react with a pristine FEP Teflon surface, but there was an indication of O-containing products in the presence of VUV light.
- Scattered products (e.g., C_2F_4, CF_3, F) were detected when Ar atoms with energies greater than ~8 eV were directed at pristine FEP Teflon and continuously refreshed PFPE surfaces, indicating that a CID mechanism may lead to mass loss from a fluoropolymer surface.
- The CID signal increased significantly when both Ar atoms and VUV light bombarded an FEP Teflon suface, suggesting a synergistic mechanism between CID and VUV in the mass loss of FEP Teflon.

- The similarity between the CID dynamics on FEP Teflon and continuously refleshed liquid PFPE surfaces suggests that volatile products come from single collisions at the gas-surface interface.

Conclusions

- Atomic oxygen alone contributes negligibly to fluoropolymer degradation in LEO.
- VUV light may act synergistically with atomic oxygen to degrade fluoropolymers in LEO.
- CID from hyperthermal collisions (e.g., from N_2 bombardment) may act synergistically with atomic oxygen to degrade fluoropolymers in LEO.
- VUV light may act synergistically with CID to degrade fluoropolymers in LEO.
- The dominant synergistic effect leading to fluoropolymer degradation in LEO will depend on the altitude (i.e., flux of N_2 versus O atoms) and the VUV light flux.

Space Flight Experiments

We have been actively involved in two Materials International Space Station Experiments (MISSE5 and MISSE-6) For MISSE-5 we worked with Prof. Luping Yu to provide samples of hydrocarbon polymers with different carbon-oxygen functional groups for exposure in space. The experiment was delayed because of the Columbia disaster, and we only received the exposed samples recently so they have not yet been analyzed. Nevertheless, we conducted ground-based exposures with our O-atom source. In this ground-based study, we tested an empirical model of O-atom-induced polymer erosion that had been developed by a group at the University of Toronto. We found that the erosion yields of the tested materials were not predicted quantitatively by the empirical model and concluded that the relative erosion yield of each polymer might be dependent on rate limiting processes other than formation of CO and CO_2 (the basic assumption of the model). Such a rate limiting process might only apply to a temperature-dependent mechanism which occurs concomitantly with a temperature-independent mechanism. A candidate rate limiting reaction is H-atom abstraction. Our results suggested that a quantitative model of the erosion yield of a polymer should consider the chemical environments of the atoms which may be involved in rate-limiting reactions with atomic oxygen. We plan to study the erosion yields of the same polymers that were exposed in space and determine if the conclusions of the laboratory experiment match those of the space experiment.

We became involved with the MISSE-6 experiment, an AFOSR-funded experiment which is to be deployed by the end of 2007. This is an "active" experiment where data will be recorded in real time on data loggers. Our key involvement was to prepare polymer films on quartz crystal microbalances for real-time measurements of erosion rates. We became very familiar with the use of a quartz crystal microbalance in our lab and with coating polymers on the quartz discs. Eventually, we delivered 30 quartz crystal microbalance sensors to Boeing for flight on MISSE-6. We provided some of our own polymer samples for testing, and we also prepared samples of POSS polyimide from polyamic acids that were provided by Dr. Sandra Tomczak of AFRL, Edwards AFB. In addition, we provided support to the Jacobs group, who also developed active experiments for MISSE-6. Our support consisted of conducting O-atom exposures of prototype experiments, such as an atomic oxygen dosimeter based on a conducting polymer and a magnetic deflector designed to prevent ions from striking a sample.

George C. Schatz

We have used direct dynamics quasiclassical trajectory methods to model the hyperthermal reaction dynamics of several gas phase reactions, including most recently the

reaction of O^+ with methane and of O with HCl. In both of these studies, we found that products which are unimportant for the thermal energy reaction dynamics can become dominant at high energies. For O + HCl, we found that the hydrogen elimination channel (H + OCl) dominates over hydrogen abstraction to give O + HCl at collision energies above 3.5 eV, and then fragmentation to give O + H + Cl becomes dominant above 5 eV. Both of these results are in agreement with preliminary results from Tim Minton's measurements. Further, our theoretical calculations have enabled us to develop qualitative models that can be used to predict the behavior of other hyperthermal reactions, and we have been able to use this to model O + H_2O (unpublished).

We have developed a QM/MM approach for simulating the reaction of hyperthermal atomic oxygen with surfaces. Both solid and liquid surfaces have been studied, and our most recent work has concerned the reaction of oxygen with squalane. This required developing a new code which combines the MSINDO electronic structure model for describing portions of the system where reaction occurs with the OPLS force field for describing regions where bond breaking is not important. We have done extensive modeling of the Minton experiments on O + squalane, and the results are in excellent agreement. This enables us to provide a detailed mechanistic study of this system

Steven J. Sibener

During the past grant periods we have been active in several MURI projects, encompassing instrument design and construction, scattering and scanning probe imaging experiments and related numerical simulations. The molecular beam and scanning probe microscopy experiments seek to address materials degradation and collisional gas-surface energy transfer/orbital decay issues of relevance to the LEO environment. These activities include experiments on graphite, diamond, metals, self-assembled monolayers, and polymers.

(a) Instrumentation Development

During the last year we have constructed successfully a pulsed hyperthermal 5eV atomic oxygen beam source based upon the design used at Montana State. This source has been successfully installed in our reactive scattering laboratory, and has generated intense beams of 5 eV $O(^3P)$ atomic oxygen. It forms a wonderful complement to our extant supersonic source, which covers thermal through ca. 1 eV energies. This laser ignition source, based on a 7J CO2 TEA laser, has also been used to make hyperthermal Ar beams up to 10 eV for hyperthermal scattering experiments on graphite subsrates.

(b) Hyperthermal Oxidation of Graphite (Joint Effort with Chicago, Montana State and Yale)

An understanding of the fundamental chemical reactivity and dynamics behind hyperthermal (0.1-20 eV) collisions of gaseous species with organic thin films and carbon composites is needed in order to predict the long-term behavior of materials in LEO and to design more durable materials for use on future spacecraft. Highly-ordered pyrolytic graphite (HOPG) is a viable model surface for this kind of investigation. An HOPG surface is essentially a collection of compressed sheets of basal-plane carbon. In a joint endeavor, the Minton Group at Montana State (responsible for hyperthermal atomic oxygen exposure) and the Sibener Group at Chicago (responsible for precision scanning probe imaging and analysis) have combined their capabilities to examine the chemical reactivity and morphological evolution of highly-ordered pyrolytic graphite upon exposure to hyperthermal (5 eV) $O(^3P)$ atoms. The Minton and Sibener groups are writing several papers on this topic. A combined experiment and simulation paper is also in process with the Tully group. We delineated the mechanisms responsible for the

spatially anisotropic etching of graphite by hyperthermal atomic oxygen. We are currently preparing to study the angle dependence of etching using our new 5 eV source in Chicago. Complementary measurements on diamond, based in Montana and Chicago, are also ongoing. Synergistic effects experiments involving ion-induced material defects have now been completed. These latter experiments are being supported by numerical simulations from the Garrison Group (ion damage simulations) and the Tully Group (KMC simulations of morphology evolution).

(c) Photo-oxidation of Polymers

We have continued and expanded our experiments which probe the reactivity of model polymers in LEO. The first system is PMMA, which we have examined with AFM imaging and FTIR spectroscopy following exposure to $O(^3P)$ and $O(^3P)$+VUV. To accomplish these measurements we have purchased and installed the D2 lamp used at NASA Glenn so that we can relate our results to prior efforts at NASA. Preliminary results show profound differences in the morphological evolution and reactivity of the polymer with vs. without VUV. Changes in film thickness during VUV illumination are being used to assess changes in polymer composition and structure. The importance of parallel reaction channels such as materials erosion and skeletal oxidation will be delineated using FTIR spectroscopy. Associated calculations from the Garrison Group are helping support these measurements.

These activities now include quartz microbalance measurements of materials erosion. This new detector was purchased with support from Boeing, and provides a wonderful complement to our scattering measurements. Here, we monitor the rate of materials removal in real time due to exposure to atomic oxygen and VUV irradiation. We are hopeful that these experiments will allow us to probe subtle but important details of synergistic effects during polymer erosion. Finally, we are also starting to explore how to spatially deploy metallic nanoparticles on photo-modified polymeric substrates, a necessary first step for the intentional creation of high-performance interfaces.

(d) Experiments with Organic Self-Assembling Monolayers

We are continuing to examine the reactivity of SAMs. During the past year, in conjunction with Yu's group, we have initiated new studies on the reactivity of even and odd chain length 1-ene SAMs. These experiments will shed information on geometry-restricted oxidation reactions, providing critical tests of theories which simulate such reactive encounters. *In situ* spectroscopy measurements are being set up to allow us to probe the interface after reaction without the need to expose surfaces to atmospheric pressure.

(e) Gas-Surface Collisional Energy Transfer

We completed and published our analysis of how energy is accommodated in hyperthermal collisions of Xe with decanethiol SAMs/Au(111). *This project has revealed the existence of a new scattering channel in which the incident atom becomes embedded in the film and then is emitted with high kinetic energy along, preferentially, the chain-tilt polar angle of the film.* We term this new mechanism directed ejection. Analysis involved classical trajectory calculations using a code originally provided to us by Bill Hase as part of this MURI program. This work, when taken with our prior work on Ar and Ne scattering, gives fresh insights for modelling orbital decay in LEO. This project is also revealing new details of how thin-film microstructure influences the dynamics of such collisions. This series of experiments/simulations is likely the most extensive study of collisional gas-surface energy transfer carried out for a complex organic

interface. These efforts have recently been extended to include rare gas collisions with disordered molecular films of SF_6. These latter studies have revealed the importance of multiphonon events in characterizing the probability of energy transfer from disordered interfaces, as well as the collision regime at which elastic reflection becomes a visible scattering channel. Our newest efforts are now focusing on collisional energy transfer from polymeric interfaces, with PMMA being our initial choice for study. As these experiments mature, we anticipate increasing theoretical support from both Garrison (MD) and Hase (scattering calculations).

(f) Influence of Dissolved Oxygen on the Oxidation Kinetics of Stepped Nickel

We have completed a thorough study that demonstrated how dissolved oxygen influences the subsequent oxidation behavior and surface structure of stepped Ni. Dissolution history directly influences structural phase stability by altering the driving forces governing oxygen absorption. This occurs via modification of the chemical potential of the sub-surface region of the interface. Interestingly, the modifications in dissolution thermodynamics and kinetics are irreversible. Oxygen absorption into the stepped crystals has been modified permanently even though the crystal structure has not been altered by faceting. Cross-talk between bulk, i.e. selvedge, and surface oxygen is remarkably influential in determining phase stability with ramifications extending to equilibrium morphology and rates of metallic oxidation.

John C. Tully

a. Ab Initio electronic structure studies of oxygen atoms with graphite surfaces.

The $O(^3P)$ ground state of oxygen interacts weakly with the graphite surface, with a binding energy too low to support a significant coverage of oxygen at ambient temperatures. By contrast, the excited $O(^1D)$ state interacts more strongly, with a binding energy of about 2 eV, sufficient for a high coverage of oxygen to be maintained on the surface. Since almost all atmospheric oxygen atoms in LEO are in the $O(^3P)$ ground state, it requires a transition from $O(^3P)$ to $O(^1D)$ in order for oxygen to strongly bind. Since graphite is a semi-metal, it requires a vanishingly small energy to remove an electron of up spin from just below the Fermi level, and replace it with a down spin electron just above the Fermi level; spin-orbit interaction is not required to switch the state of the O atom. Proper description of this effect is critical but difficult. We have found that, with finite cluster *ab initio* methods, accurate potential energy surfaces can be obtained only if the size of the graphite slab is chosen so that the energies of the lowest singlet and triplet states of the isolated slab are about equal in energy. The "special" aromatic slabs employed in calculations by others produce incorrectly weak binding. This may have important implications not only to erosion of graphite, but also to interaction of oxygen with carbon nanotubes.

b. Ab Initio "on-the-fly" dynamics of oxygen atom and ion interactions with graphite.

We have developed algorithms for carrying out *ab initio* self-consistent-field (Ehrenfest) dynamics "on the fly". This has been implemented in the Gaussian suite of electronic structure programs at the Hartree Fock and density functional theory levels. We have applied this theory to study the transition from $O(^3P)$ to $O(^1D)$ as a 5 eV oxygen atom approaches the graphite surface. Even though this process is allowed, as discussed above, it appears to be of relatively small probability, at least in a direct scattering event. This may contribute to the low reactivity of the basal plane of graphite with oxygen atoms.

c. Interaction of O^+ ions with graphite surfaces.

We have carried out Ehrenfest simulations of the collisions of 5 eV O^+ ions with graphite surfaces. The O^+ ions are incompletely neutralized to $O(^3P)$ atoms on the incoming part of the trajectory, suggesting that ions will exhibit different reactivity from neutrals. We have also carried out kinetic Monte Carlo simulations of the erosion of graphite surfaces by 5, 10 and 20 eV O^+ ions, in collaboration with the Jacobs group. In order to reproduce the observed etching rates and etch pit sizes, it is necessary to assume that O^+ ions have a higher initial reactivity than neutral oxygen atoms, but once a pit begins to form, the reactivities of ions and neutrals appear similar.

d. Electron transfer at metal and semiconductor surfaces.
We have developed a theory of electron transfer between atoms or molecules and solid surfaces. Electron transfer frequently dominates the chemistry between ionic or open shell species with surfaces. Reactions of energetic O atoms and O^+ ions are examples. Our theory applies to cases where energetically resonant electron transfer can occur from or into the conduction band of the solid. Initial tests of the approach are very promising, suggesting that the method will have wide applicability.

Luping Yu
Yu's group focused their attention to the development of efficient synthetic approaches to preparation of model compounds functionalized with thiol. These model compounds mimic the structural features in Teflon, polystyrene, polyacrylate and polyimides and allowed detailed mechanistic studies of polymer erosions. These molecules were fully characterized structurally to ensure the monolayer formation.

An efficient approach to prepare mixed disulfide compounds was developed, which allowed us to prepare several alkyl-ss-perfluoroalkyl compounds.
An effective approach was developed to prepare alkanethiol compounds labeled at specific carbon with deuterium. This approach allowed us to introduce deuterium to specific site in alkylthiols and other similar compounds. These are the first series of alkanethiol compounds with site-defined deuterium labels and offered unique opportunities for the studies of kinetic profiles of polymer erosion.

Various types of model alkanethiols for polyketone, polystyrene, polymer containing silicon, poly(methyl methacrylate), and polybutadiene have been synthesized. The most effective synthetic routes to prepare these model compounds have been established. These alkanethiols are designed to present functional groups corresponding to polymers on the surface after assembly so that interaction with atomic oxygen can be studied. Several compounds are designed so that insightful studies on the dependency of interaction dynamics on the alignment direction of reactive functional group can be carried out. Finally, alkanethiol with highly reactive functional group, oxyamine, has also been synthesized to compare with relatively inert functional groups toward oxygen scattering.

We have carried out a detailed study of immobilization of isocyanide compounds on the surface of nickel substrate. Molecules with ferrocenyl moiety and different functional groups were synthesized and tested for surface reaction with Ni substrate. Surface electrochemistry was used as a tool to characterize the surface assemblies. Various other techniques are also used to characterize SAMs. A strong chemisorption on the Ni surfaces was found when the ferrocene terminated isocyanide molecules are used. The resulting SAMs were shown to exhibit a dense

packed structures and a high thermal stability in a solution of boiling ethanol. This self-assembling approach will be useful in the preparation of stable coating on nickel surface.

Finally Yu's group initiated effort to synthesize new metal-containing polymers. These polymers are multifunctional materials. They are photoconductive and contain transition metal complexes that can be converted into metal oxides. The sample was studied for their reaction with atomic oxygen in Minton's lab.

5. Personnel

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7. Interactions/Transitions

7a) Presentations at Meetings

All MURI faculty spoke at the MURI meeting held at The University of Chicago, June 17, 18 2002, as well as at The University of Pittsburgh, August 19, 20 2003. These meetings introduced the MURI Team's capabilities and projects to a wide variety of interested DoD, NASA and Industrial researchers. Students and postdocs from all MURI groups were also present and gave posters. The most recent meeting in this series was held at Montana State University, January 27-28, 2005.

Barbara Garrison

2001-2002

Working seminar at Northwestern University, Evanston, IL, January 14 and 15, 2002 Marina Medvedeva presented the talk about the molecular dynamics simulations of the interaction of low energy H and C atoms with a diamond surface. Discussion about possible computational methods to model a material degradation in the space has been performed with George C. Schatz group.
M. Medvedeva, B. J. Garrison, "Molecular Dynamics Study of Impact of Low Energy Atoms in Erosion of a Hydrocarbon Surface," talk.
6th International Conference "Protection of materials and Structures from the Low Earth Orbit Space Environment", Toronto, Canada, May 1-3, 2002
The kick-off meeting, The University of Chicago, Chicago, June 17 and 18, 2002
B. J. Garrison, "Molecular Dynamics Simulations of Low Energy Atom and UV Radiation Interactions with Surface," talk.
Y. G. Yingling, B. J. Garrison, "Influence of Photochemical Processes on Laser Ablation Mechanism. Molecular Dynamics Study," poster.
M. Medvedeva, B. J. Garrison, "Molecular Dynamics Study of Low Energy Atom Impact on Hydrocarbon Surfaces," poster.
M. Medvedeva, B. J. Garrison, 'Molecular Dynamics Study of Low Energy Atom Impact on Hydrocarbon Surfaces," talk.
6th International Conference on Computer Simulation of Radiation Effects in Solids (COSIRES'2002), Dresden, Germany, June 23-27, 2002 Y. G. Yingling, B. J. Garrison, "Photochemical Processes in Laser Ablation of Organic Solids," invited talk

2002-2003

Gordon Research Conference on Laser Interactions with Materials, New Hampshire, July 21-26, 2002. Y. G. Yingling, B. J. Garrison, "The influence of photochemical processes on laser ablation mechanism. Molecular Dynamics Study," poster.
Dennis Jacobs visited Penn State to exchange information about the study of 5 eV O atom and SAMs reactions, October 2002.
American Chemical Society National Meeting, New Orleans, March 2003. B. J. Garrison, Y. G. Yingling, L. V. Zhigilei, "Mesoscopic Modeling of Laser Ablation" invited talk.

2003-2004

Course Grain Modeling of Degradation of PMMA," MURI Annual Review, Pittsburgh, PA, August 18-20, 2003.
Conference on Laser Ablation, Crete, Greece, October 5-6, 2003, "Photochemical Processes in Laser Ablation of Organic Materials," " invited talk.
American Physical Society, Montreal, Quebec, Canada, March 22-26, 2004, "Photochemical Ablation of Organic Solids" invited talk.
Acireale, Sicily, Italy, May 30-June 4, 2004, Coarse Grained Chemical Reaction Model (CGCRM): A new protocol for including chemical reactions in large-scale MD simulations", invited talk.

2004-2005

Gordon Research Conference on Laser Interactions with Materials, New Hampshire, August 1-5, 2004. Y. G. Yingling, P. F. Conforti, T. Nedelea, B. J. Garrison, "Theoretical Studies of Laser Ablation of Polymers," poster.
American Chemical Society, Philadelphia, PA, August 22-26, 2004. P.F. Conforti, B. J. Garrison, "Molecular Dynamics Simulation of Laser Ablation," poster.
American Chemical Society Meeting, Philadelphia, PA, August 22-26, 2004. B.J. Garrison, "Molecular Dynamics Simulations of Laser Ablation," invited talk.
Loughborough University, Loughborough, UK, September 24, 2004. B.J. Garrison, "Mesoscale Modeling of Laser Ablation," invited talk.
Conference on Laster Ablation, Banff, Canada, September 11-16. P.F. Conforti, Y. G. Yingling, B. J. Garrison, "Simulations of Laser Ablation of Poly (methyl methacrylate," poster.
LPM2005, Williamsburg, VA, April 4-6, 2005, B. J. Garrison, "Photochemical Ablation of Organic Solids," invited talk

2005-2006

American Chemical Society, Washington, D.C., August 28 – September 1, 2005. P.F. Conforti, B. J. Garrison,"Simulations of Laser Ablation of Polymers," poster.
Workshop on Laser Interface Interactions and Laser Cleaning, Konstanz, Germany, June 4-7, 2006. B. J. Garrison, M. Prasad, P. F. Conforti, Y. G. Yingling, "Photochemical Ablation of Organic Solids from a Computer Modeling Prospective," invited talk.

2006-2007

International Conference on Photo-Excited Processes and Applications, Charlottesville, VA, September 3-7, 2006. P. F. Conforti, M. Prasad, B. J. Garrison, "Techniques for simulating photochemical reactions in PMMA," poster.
International Conference on Photo-Excited Processes and Applications, Charlottesville, VA, September 3-7, 2006. Y. G. Yingling, B. J. Garrison, "Computational study of the onset of ablation: Molecular versus polymeric solids," talk.
International Conference on Photo-Excited Processes and Applications, Charlottesville, VA, September 3-7, 2006. M. Prasad, P. F. Conforti, B. J. Garrison, "Computational investigation into the mechanisms of UV ablation of poly (methyl methacralate)," talk.
American Chemical Society, Chicago , Ill, March 25-29, 2007. M. Prasad, P. F. Conforti, B. J. Garrison, "Modeling light interaction with materials: Techniques to successfully incorporate chemistry and physics in molecular simulation," invited talk.

William L. Hase

2001-2002

Presented invited lectures at the Atomic and Molecular Interactions Gordon Conference (July 2002), Telluride Workshop on Chemical and Optical Properties of Atmosperic Aerosols (August 2002), and Symposium on Classical and Quantum Statistical Mechanics Studies of

Solvation at the 224th ACS National Meeting (Boston, August 2002), in which simulations of rare gas atom collisions with alkyl thiolate self-assembled monolayers (SAMs) were presented.
Tianying Yan, a graduate student in the Hase Group, presented a paper on simulations of Ne-atom collisions with alkyl thiolate self-assembled monolayers (SAMs) at the 224th ACS National Meeting (Boston, August 2002).

2002-2003

Presented invited lectures at the ACS Symposium on Classical and Quantum Statistical Mechanics Studies of Solvation at the 224th ACS National Meeting (Boston, August 2002) and the 19th Conference on the Dynamics of Molecular Collisions (Lake Tahoe, July, 2003), in which simulations of rare gas and $O(^3P)$ atom collisions with alkyl thiolate self-assembled monolayers (SAMs) were presented.
Tianying Yan, the graduate student in the Hase Group working on this project, presented a paper on simulations of Ne-atom collisions with alkyl thiolate self-assembled monolayers (SAMs) at the 224th ACS National Meeting (Boston, August 2002) and presented a lecture on this work at Virginia Tech University in April, 2003.

2003-2004

Talks at Meetings/Conferences:
"Dynamics of Energy Transfer and Chemical Reaction in Gas-Surface Collisions", 19th Conference on the Dynamics of Molecular Collisions, Granlibakken Conference Center, Lake Tahoe, California, July 13-18, 2003 (invited).
"Studying Microscopic Reaction Mechanisms by QM, QM+MM, and QM/MM Direct Dynamics Simulations", Conference on Theory and Applications of Computational Chemistry (TACC-2004), Gyeongju, Korea, February, 15-20, 2004 (invited).
"Energy Transfer and Chemical Reaction in Collisions of Rare Gas and Triplet Oxygen Atoms with Hydrocarbon Surfaces", 227th ACS National Meeting, Symposium on Computational Approaches to Problems in Environmental Chemistry, Anaheim, California, March 29-April 1, 2004 (invited).
"Applications of QM, QM+MM, and QM/MM Direct Dynamics Simulations", 227th ACS National Meeting, Symposium on Mixed Quantum, Classical, and Semiclassical Dynamics, Anaheim, California, March 29-April 1, 2004 (invited).
Talks at Universities/Colleges:
Virginia Tech University, Chemistry Department Seminar, Virginia, August 29, 2003.
Wayne State University, Physics Department Seminar, Detroit, Michigan, September 16, 2003.
Kalamazoo College, Chemistry Department Seminar, Kalamazoo, Michigan, November 3, 2003.
Korea National University of Education, Chemistry Department Seminar, Chongwon, Korea, February 13, 2004.
Nagoya University, Computational Chemistry Seminar, Nagoya, Japan, February 23, 2004.
Michigan State University, Physical Chemistry Seminar, East Lansing, Michigan, April 15, 2004.

2004-2005

Talks at Meeting/Conferences:
"Chemical Dynamics Simulations of Energy Transfer and Reaction in Collisions of Projectiles with Self-Assembled Monolayers", 230th ACS National Meeting, Symposium on Applications of Self-Assembled Monolayers (SAMs) in Surface and Interface Science, Washington, DC, August 28 – September 1, 2005.

"Energy Transfer and Chemical Reraction in Collisions of Rare Gas and O(^{3}P) Atoms with Hydrocarbon Surfaces", 2005 AFOSR Contractor's Meeting in Molecular Dynamics and Theoretical Chemistry, Monterey, California, May 22-24, 2005.
"VENUS. A Computer Program for Simulating Atomic-Level Motions and Properties of Nanomaterials", West Texas Nanotechnology Forum, Lubbock, Texas, April 19, 2005.
Talks at Universities/Colleges:
Baylor University, Chemistry (November 5, 2004); Texas Tech University, Mathematics (November 18, 2004); University of Maryland, Center for Scientific Computation and Mathematical Modeling (February 16, 2005); Universtity of North Texas (May 6, 2005).

2005-2006

Talks at Meetings/Conferences
"Chemical Dynamics Simulations of Energy Transfer in Collisions of CO2 with a Perfluorinated Alkyl Thiolate Self-Assembled Monolayer Surface", 2006 AFOSR Contractor's Meeting in Molecular Dynamics and Theoretical Chemistry, Arlington, Virginia (June 5-7, 2006).
"Chemical Dynamics Simulations of Carbon Dioxide Scattering off a Fluorinated Self-Assembled Monolayer Surface", 232nd ACS National Meeting, Symposium on Frontiers in Molecular Dynamics, San Francisco, CA (September 10-14, 2006).
Talks at Universities/Colleges
University of New Mexico (September 23, 2005); Texas Tech University, Physics (November 10,2005); Oklahoma State University, Physics (April 11, 2006); Texas A&M University (April 18, 2006).

Dennis Jacobs

2001-2002

Dennis Jacobs presented his work on O^+ incorporation into silicon oxide films in a seminar at Montana State University on Oct. 25, 2001. Xiangdong Qin gave an oral presentation on the O^+/SiO_x system at the National Meeting of the American Chemical Society in Orlando, FL on April 9, 2002. Tochko Tzvetkov gave an oral presentation on the O^+/SiO_x system at the National Meeting of the American Physical Society in Indianapolis on March 22, 2001. Xiangdong Qin presente a poster on O^+/SAM etching at the National Meeting of the American Chemical Society in Boston, MA on Aug. 20, 2002.

2002-2003

"Reaction of Hyperthermal O^+ with Self-Assembled Monolayers," 14th International Workshop on Inelastic Ion Surface Collisions, Netherlands, September, 2002 (contributed).
"Dynamics of ion/surface reactions at hyperthermal energies", Department of Chemistry seminar, Pennsylvania State University, October, 2002 *(INVITED)*.
"Dynamics of ion/surface reactions at hyperthermal energies", Chemical Engineering Department Colloquium, University of Florida, Gainseville, FL, January, 2003 *(INVITED)*.
"Dynamics of ion/surface reactions at hyperthermal energies", Gordon Research Conference, New Hampshire, August, 2003 *(INVITED)*.

2003-2004

"Dynamics of Ion/Surface Reactions in a Low-Earth Orbit Environment," Department of Chemistry Colloquium, University of Akron, Akron, OH, September, 2003 *(INVITED)*.
"Dynamics of Ion/Surface Reactions in a Low-Earth Orbit Environment," Department of Chemistry Colloquium, Carleton College, MN, March, 2004 *(INVITED)*.

"Structural Damage of Self-Assembled Monolayers Induced by 5-eV O^+ Bombardment", T.Tzvetkov, X.Qin, and D.C.Jacobs, 51st Annual AVS Symposium, Anaheim, California, 2004 (T. Tzvetkov gave oral presentation).
"Structural Damage of Self-Assembled Monolayers Induced by 5-eV O^+ Bombardment," T. Tzvetkov, X. Qin and D. C. Jacobs, Prairie Chapter of the American Vacuum Society Annual Meeting, Chicago, IL (2004).
"Site-Selective Abstraction in the Reaction of 5- to 20-eV O^+ with a Self-Assembled Monolayers," Xiangdong Qin, T. Tzvetkov and D. C. Jacobs, Prairie Chapter of the American Vacuum Society Annual Meeting, Chicago, IL (2004).

2004-2005

"Reaction of Hyperthermal Energy O^+ with Hydrocarbon Self-Assembled Monolayers (SAM)", Inelastic Ion Surface Collisions (IISC-15) Workshop, Ise-Shima, Japan, October, 2004 *(INVITED)*.
"Site-Selective Abstraction in the Reaction of 5- to 20-eV O^+ with a Self-Assembled Monolayer", X.Qin, T.Tzvetkov, D.C.Jacobs, D.Lee, and L.Yu, 51st Annual AVS Symposium, Anaheim, California, November 2004. (X. Qin gave oral presentation).
"Reactive Ion/Surface Collisions at Hyperthermal Energies," Gordon Conference on Molecular Energy Transfer, Santa Ynez, CA, January 2005 (*INVITED*).
"The Hostile Environment of Space: A Fundamental Look at How Satellite Materials are Eroded," Colloquium Series, Virginia Tech. University, Blacksburg, VA, February 2005 (*INVITED*).
"Reaction of Hyperthermal Energy Oxygen Ions with Hydrocarbon Self-Assembled Monolayers", D.C.Jacobs, T.Tzvetkov, X.Qin, and X.Liu, 2005 MRS March Meeting, San Francisco, CA (T. Tzvetkov gave oral presentation).
"The Hostile Environment of Space: A Fundamental Look at How Satellite Materials are Eroded," 25th Donald G. Davis Memorial Lecture, University of New Orleans, New Orleans, LA April 2005 *(INVITED)*.
"Ion etching of graphite: Defect initiation by 5-20 eV O^+ and Ne^+ bombardment", Xin Liu, Tochko Tzvetkov, Xiangdong Qin, Dennis C. Jacobs, Natasa Mateljevic, and John C. Tully, 230th ACS National Meeting, Washington, DC, 2005 (X. Liu gave oral presentation).

2005-2006

"Defect Initiation on Graphite by Hyperthermal Ion Beams," X. Liu, T. Tzvetkov, L. Zeng, X. Qin, and D. C. Jacobs, 232nd ACS National Meeting, San Francisco, CA, 2006 *(INVITED)*.
"Hyperthermal O^+ induced etching of polyhedral oligosilsequioxane (POSS) monolayers on Au(111)" X. Liu, T. Tzvetkov and D. C. Jacobs, 232nd ACS National Meeting, San Francisco, CA, 2006.

Timothy K. Minton

2001-2002

"Hyperthermal Reactions of Oxygen Atoms with Saturated Hydrocarbons," Physical Chemistry Seminar, University of Oregon, Eugene, April 15, 2002. (invited seminar)
"Hyperthermal Reactions of Oxygen Atoms with Saturated Hydrocarbons," Physical Chemistry Seminar, Oregon State University, Corvallis, April 16, 2002. (invited seminar)
"Hyperthermal Reactions of Oxygen Atoms with Saturated Hydrocarbons, "T. K. Minton, D. J. Garton, M. R. Dorrington, H. Kinoshita, J. Manso, G. C. Schatz, and R. Pascual, *223rd American Chemical Society National Meeting*, Orlando, FL, April 7-11, 2002. (contributed talk)
"A Crossed Beams Study of the Reaction of Hyperthermal Oxygen Atoms with CH_4, CH_3CH_3, and $CH_3CH_2CH_3$," D. J. Garton, M. R. Dorrington, H. Kinoshita, J. Manso, and T. K. Minton,

223rd American Chemical Society National Meeting, Orlando, FL, April 7-11, 2002. (poster presented by student)
"Reactive and Inelastic Scattering Dynamics of Hyperthermal Oxygen Atoms on a Hydrocarbon Surface," J. Zhang, D. J. Garton, and T. K. Minton, *223rd American Chemical Society National Meeting*, Orlando, FL, April 7-11, 2002. (poster presented by student)
"Erosion of Graphite and Kapton Surfaces by Hyperthermal Oxygen Atoms," J. Manso, H. kinoshita, M. R. Dorrington, D. J. Garton, T. K. Minton, K. Nicholson, and S. J. Sibener, *223rd American Chemical Society National Meeting*, Orlando, FL, April 7-11, 2002. (poster presented by student)
"Hyperthermal Reactions of Oxygen Atoms with Saturated Hydrocarbons," T. K. Minton, D. J. Garton, and H. Kinoshita, *6th International Conference on the Protection of Materials and Structures from the Space Environment*, Toronto, CA, May 1-3, 2002.

2002-2003

Talks

"Reaction Dynamics Relevant to Spacecraft in Low-Earth Orbit: Novel Reactions of $O(^3P)$ with Gaseous and Surface Hydrocarbons," Departmental Seminar, University of Idaho, February 3, 2003.
"Reaction Dynamics Relevant to Spacecraft in Low-Earth Orbit: Novel Reactions of $O(^3P)$ with Gaseous and Surface Hydrocarbons," Departmental Seminar, Washington State University, February 4, 2003.
"Hyperthermal Reactions of $O(^3P)$ with H_2 and Saturated Hydrocarbons," *AFOSR Molecular Dynamics Contractor's Meeting*, San Diego, CA, May 18-20, 2003.
"Hyperthermal Reactions of $O(^3P)$ with H_2 and Saturated Hydrocarbons," *XX International Symposium on Molecular Beams*, Lisbon, Portugal, June 8-13, 2003.
"Model Atomic Oxygen Reactions: Detailed Experimental and Theoretical Studies of the Reactions of Ground-State $O(^3P)$ with H_2, CH_4, CH_3CH_3, and $CH_3CH_2CH_3$ at Hyperthermal Collision Energies," *9th International Symposium on Materials in a Space Environment*, Noordwijk, The Netherlands, June 16-20, 2003.
"Hyperthermal $O(^3P)$ Interactions: Beam-Source Characterization, Model Reactions with Small Alkanes, and Erosion Resistance of a POSS Polymer," *AFOSR MURI Review*, Pittsburgh, PA, August 19-20, 2003.

Posters

"Crossed-Beams and Beam-Surface Studies of Hyperthermal $O(^3P)$ Reactions with Saturated Hydrocarbons," *XX International Symposium on Molecular Beams*, Lisbon, Portugal, June 8-13, 2003. (presented by student)
"An Investigation of the Resistance of POSS Kapton to Atomic Oxygen Attack," *9th International Symposium on Materials in a Space Environment*, Noordwijk, The Netherlands, June 16-20, 2003. (presented by student)
"Crossed-Beams and Theoretical Studies of Hyperthermal Reactions of $O(^3P)$ with H_2, CH_4, C_2H_6, and C_3H_8," *AFOSR MURI Review*, Pittsburgh, PA, August 19-20, 2003. (presented by student)
"Reactive and Inelastic Scattering Dynamics of Hyperthermal Oxygen Atoms on a Saturated Hydrocarbon Surface," *AFOSR MURI Review*, Pittsburgh, PA, August 19-20, 2003. (presented by student)
"An Investigation of the Resistance of POSS Polyimide to Atomic Oxygen Attack," *AFOSR MURI Review*, Pittsburgh, PA, August 19-20, 2003. (presented by student)

2003 – 2004

Conference Proceedings

"Erosion of Kapton H by Hyperthermal Atomic Oxygen: Dependence on O-Atom Fluence and Surface Temperature", D. M. Buczala and T. K. Minton, in *Proceedings of the 7th International Conference on the Protection of Materials from the Space Environment*, Toronto, Canada, May 10-13, 2004.

"Simulations of Hyperthermal Oxygen Beam Exposures," J. A. Cline, T. K. Minton, and M. Braunstein, in *Proceedings of the 37th AIAA Thermophysics Conference*, Portland, OR, 2004. AIAA Paper No. 2004-2685.

Talks

"Hyperthermal Reactions of $O(^3P)$ with Hydrogen and Methane," Dalian Institute of Chemical Physics Symposium on Molecular Dynamics (IV), Dalian, China, July 21-23, 2004. (Invited)

"Reaction Dynamics Relevant to Spacecraft in Low-Earth Orbit: Atomic-Oxygen Reactions with Gaseous and Surface Hydrocarbons," James Franck Institute Colloquium, The University of Chicago, Chicago, IL, June 1, 2004. (Invited)

"Studies of the Erosion of Kapton H, FEP Teflon, and Hybrid Inorganic/Organic Polymers in an Atomic Oxygen Environment," *7th International Conference on the Protection of Materials from the Space Environment*, Toronto, Canada, May 10-13, 2004. (Contributed)

"Hyperthermal Reactions of $O(^3P)$ with Hydrogen and Methane," *227th American Chemical Society National Meeting*, Anaheim, CA, March 28 - April 1, 2004. (Invited)

"Reactive and Inelastic Scattering Dynamics of Hyperthermal Oxygen Atoms on a Liquid Hydrocarbon Surface," American Physical Society Annual Meeting, Montreal, Quebec, Canada, March 22-26, 2004. (Invited)

"Hyperthermal $O(^3P)$ Interactions: Characterization of an O-Atom Source, Model Reactions with Small Alkanes, and O-Atom Resistance of a POSS Polymer," Air Force Research Laboratory, Edwards AFB, CA, September 8, 2003. (Invited)

Posters

"Energy Transfer in Hyperthermal Collisions of Ar with Ethane," A. L. Brunsvold, D. J. Garton, T. K. Minton, D. Troya, and G. C. Schatz, *227th American Chemical Society National Meeting*, Anaheim, CA, March 28 - April 1, 2004. (presented by student)

"Hyperthermal Reactions of $O(^3P)$ with Hydrogen and Methane," D. J. Garton, A. L. Brunsvold, T. K. Minton, D. Troya, and G. C. Schatz, *AFOSR Molecular Dynamics Contractor=s Meeting*, Newport, RI, May 24-26, 2004.

Student Theses

"Temperature Dependent Study of FEP Teflon and Kapton H Erosion in a Simulated LEO Atomic Oxygen Environment," Deanna M. Buczala, M.S. thesis, May 2004.

"Hyperthermal Reactions of $O(^3P)$ with Hydrogen and Methane," Donna J. Garton, Ph.D. thesis, May 2004.

2004-2005

Meeting Organization

Host of the AFOSR MURI Program Review ("Materials Chemistry in the Space Environment") held in Bozeman, MT, 27-28 January, 2005.

Co-organizer of symposium ("*In Situ* Studies of Gas-Solid Surface Reactions") held at the Materials Research Society National Meeting in San Francisco, CA, March 28 - April 1, 2005.

Talks

"Atomic Beam-Surface Scattering Studies of the Combined Effects of VUV Radiation and Hyperthermal O or Ar Atoms on the Erosion of FEP Teflon Surfaces," *National Meeting of the Materials Research Society*, San Francisco, CA, March 28 - April 1, 2005. (invited, presented by student)

"Hyperthermal Reactions of $O(^3P)$ with Hydrogen and Methane," *Gordon Research Conference on Molecular Energy Transfer*, Jan. 9-14, 2005. (invited)
"Reaction Dynamics Relevant to Spacecraft in Low-Earth Orbit: Atomic-Oxygen Reactions with Gaseous and Surface Hydrocarbons," University of California – Davis, November 16, 2004. (invited)
"Reaction Dynamics Relevant to Spacecraft and Missiles: Hyperthermal Atomic Oxygen Reactions," Montana State University, October 22, 2004. (invited)
"Reaction Dynamics Relevant to Spacecraft in Low-Earth Orbit: Atomic Oxygen Reactions with Gaseous and Surface Hydrocarbons," University of Hawaii, October 11, 2004. (invited)

Posters

"Beam-Surface Scattering Studies of the individual and Combined Interactions of VUV Radiation and Hyperthermal O, O_2, or Ar with Fluorocarbon Surfaces," A. L. Brunsvold, H. P. Upadhyaya, J. Zhang, and T. K. Minton, *Gordon Research Conference on Dynamics at Surfaces*, Andover, NH, 14-19 August, 2005.
"Hyperthermal $O(^3P)$ Reactions with a Saturated Hydrocarbon Surface," J. Zhang, D. J. Garton, T. K. Minton, D. Troya, and G. C. Schatz, *XXth Conference on the Dynamics of Molecular Collisions*, Pacific Grove, CA, 10-15 July, 2005.
"Beam-Surface Scattering Studies of the Individual and Combined Effects of VUV Radiation and Hyperthermal O, O_2, or Ar with Fluorocarbon Surfaces," A. L. Brunsvold, H. P. Upadhyaya, J. Zhang, and T. K. Minton, *XXth Conference on the Dynamics of Molecular Collisions*, Pacific Grove, CA, 10-15 July, 2005.
"Reaction Dynamics Relevant to Spacecraft in Low-Earth Orbit: Atomic-Oxygen Reactions with Gaseous and Surface Hydrocarbons," T. K. Minton, D. J. Garton, J. Zhang, A. Brunsvold, D. Troya, B. Maiti, and G. C. Schatz, *2005 AFOSR Molecular Dynamics Contractors' Meeting*, Monterrey, CA, 22-24 May, 2005.
"Collision-Induced Desorption of Chlorine from a Chlorinated Silicon Surface," J. Zhang and T. K. Minton, *Gordon Research Conference on Molecular Energy Transfer*, Buellton, CA, 11-14 January, 2005.
"Energy Transfer in Hyperthermal Collisions of Ar with Ethane," A. L. Brunsvold, D. J. Garton, T. K. Minton, and G. C. Schatz, *AFOSR MURI Program Review*, Bozeman, MT, 27-28 January, 2005.
"An Investigation of the Resistance of POSS Polyimide to Atomic-Oxygen Attack," A. L. Brunsvold, T. K. Minton, I. Gouzman, Eitan Grossman, S. J. Tomczak, and R. I. Gonzalez, *AFOSR MURI Program Review*, Bozeman, MT, 27-28 January, 2005.
"Atomic Beam-Surface Scattering Studies of the Individual and Combined Effects of VUV Radiation and Hyperthermal O, O_2, or Ar on the Erosion of FEP Teflon Surfaces," A. L. Brunsvold, H. P. Upadhyaya, J. Zhang, and T. K. Minton, *AFOSR MURI Program Review*, Bozeman, MT, 27-28 January, 2005.
"Energy Transfer in Hyperthermal Collisions of Ar with Ethane, A. L. Brunsvold, D. J. Garton, T. K. Minton, D. Troya, and G. C. Schatz, *Gordon Research Conference on Molecular Energy Transfer*, Buellton, CA, 11-14 January, 2005.
"Beam-Surface and Crossed-Beams Studies of Hyperthermal $O(^3P)$ Reactions with Saturated Hydrocarbons," D. J. Garton, J. Zhang, T. K. Minton, D. Troya, and G. C. Schatz, *Gordon Research Conference on Molecular Energy Transfer*, Buellton, CA, 11-14 January, 2005.

2005-2006

Meeting Organization

Organizer of Symposium ("Chemical Dynamics in Extreme Environments") held at the ACS National Meeting, San Francisco, September 10-14, 2006.

Invited Talks

"Laboratory Studies of Hyperthermal O-Atom Reactions," *2005 Maui Analysis of Upper Atmosphere Injections (MAUI) Space Experiment Workshop*, Wailea, Maui, HI, Sept. 5, 2005.

"Crossed-Beam and Beam-Surface Scattering Studies of Hyperthermal O and Ar Interactions," *International Symposium on Application of Quantum Beams 2005*, Kobe University, Kobe, Japan, Oct. 18-19, 2005.

"Hyperthermal Reactions of Oxygen Atoms with Spacecraft Materials and Rocket Plumes," Texas Tech University, Lubbock, TX, October 4, 2006.

"Crossed-Beams Studies of Hyperthermal O(^3P) Reactions," *Dalian Institute of Chemical Physics Symposium on Molecular Dynamics*, Dalian, China, October 18-21, 2006.

"Crossed-Beams Studies of Hyperthermal O(^3P) Reactions," *Trends in Chemical Dynamics: From Small Molecules to Biomolecules*, Chiao Hsi, Yi-Lan County, Taiwan, December 10-15, 2006.

Contributed Talks

"Atomic Beam-Surface Scattering Studies of the Individual and Combined Effects of VUV Radiation and Hyperthermal O or Ar Atoms on FEP Teflon Surfaces," *International Chemical Conference of Pacific Basin Societies (Pacifichem) 2005*, Honolulu, HI, Dec. 19, 2005.

"Beam-Surface Scattering Studies of the Individual and Combined Interactions of VUV Radiation and Hyperthermal O, O_2, or Ar with Fluorocarbon Surfaces," *10th International Symposium on Materials in a Space Environment*, Collioure, France, June 19-23, 2006.

Posters

"Reaction Dynamics Relevant to Spacecraft in Low-Earth Orbit: Atomic-Oxygen Reactions with Gaseous and Surface Hydrocarbons," T. K. Minton, D. J. Garton, J. Zhang, A. Brunsvold, D. Troya, B. Maiti, and G. C. Schatz, *2005 AFOSR Molecular Dynamics Contractors= Meeting*, Monterrey, CA, 22-24 May, 2005.

"Beam-Surface Scattering Studies of the Individual and Combined Effects of VUV Radiation and Hyperthermal O, O_2, or Ar with Fluorocarbon Surfaces," A. L. Brunsvold, H. P. Upadhyaya, J. Zhang, and T. K. Minton, *XXth Conference on the Dynamics of Molecular Collisions*, Pacific Grove, CA, 10-15 July, 2005. (presented by student)

"Hyperthermal O(^3P) Reactions with a Saturated Hydrocarbon Surface," J. Zhang, D. J. Garton, T. K. Minton, D. Troya, and G. C. Schatz, *XXth Conference on the Dynamics of Molecular Collisions*, Pacific Grove, CA, 10-15 July, 2005. (presented by student)

"Beam-Surface Scattering Studies of the individual and Combined Interactions of VUV Radiation and Hyperthermal O, O_2, or Ar with Fluorocarbon Surfaces," A. L. Brunsvold, H. P. Upadhyaya, J. Zhang, and T. K. Minton, *Gordon Research Conference on Dynamics at Surfaces*, Andover, NH, 14-19 August, 2005. (presented by student)

"Hyperthermal Reactions of O and O_2 with a Hydrocarbon Surface: Direct C–C Bond Breakage by O and H-Atom Abstraction by O_2," J. Zhang, H. P. Upadhyaya, A. L. Brunsvold, and T. K. Minton, *2006 AFOSR Molecular Dynamics Contractors= Meeting*, Arlington, VA, 5-7 June, 2006.

"Effect of Polymer Structure on the Erosion of Hydrocarbon-Based Polymers by Atomic Oxygen," D. J. Garton, D. P. Stockdale, D.-C. Lee, L. Yu, and T. K. Minton, *10th International Symposium on Materials in a Space Environment*, Collioure, France, June 19-23, 2006.

"Effect of Polymer Structure on the Erosion of Hydrocarbon-Based Polymers by Atomic Oxygen," D. J. Garton, D. P. Stockdale, D.-C. Lee, L. Yu, and T. K. Minton, *2006 National Space & Missile Materials Symposium*, Orlando, FL, June 24-30, 2006. (presented by student)

"Erosion Kinetics of Polyimides Exposed to Atomic Oxygen," R. Cooper, H. P. Upadhyaya, A. L. Brunsvold, J. Zhang, T. K. Minton, and S. J. Tomczak, *2006 National Space & Missile Materials Symposium*, Orlando, FL, June 24-30, 2006. (presented by student)
"Surface Modification of Novel Metal-Containing Polymers by Hyperthermal Atomic Oxygen," T. Horne, D. J. Garton, L. Yu, and T. K. Minton, *2006 National Space & Missile Materials Symposium*, Orlando, FL, June 24-30, 2006. (presented by student)
"Crossed-Beams and Beam-Surface Scattering Studies of Hyperthermal O(^3P) Reactions," D. J. Garton, J. Zhang, A. L. Brunsvold, H. P. Upadhyaya, T. K. Minton, W.-F. Du, G. C. Schatz, and D. Troya, *Trends in Chemical Dynamics: From Small Molecules to Biomolecules*, Chiao Hsi, Yi-Lan County, Taiwan, December 10-15, 2006.

George C. Schatz
2001-2002
American Chemical Society, Spring Meeting, Orlando, April 1-6, 2002.
"A Direct Trajectory Dynamics Investigation of Fast O + Alkane Reactions", R. Z. Pascual, D. J. Garton, and G. C. Schatz (Invited talk)
6th International Conference on Protection of Materials and Structures from Space Environment, Toronto, May 1-3, 2002
"A Direct Trajectory Dynamics Investigation of Fast O + Alkane Reactions", R. Z. Pascual, D. J. Garton, and G. C. Schatz, MURI review meeting, Chicago, June 13, 2002
2002-2003
9th International Symposium on Materials in a Space Environment, June 16-20, 2003, Noordwijk, The Netherlands
"Model atomic oxygen reactions: detailed experimental and theoretical studies of the reactions of ground-state O(^{3}P) with H_2, CH_4, CH_3CH_3 and $CH_3CH_2CH_3$ at hyperthermal collision energies" (given by Diego Troya)
NATO Advanced Research Workshop on the Theory of the Dynamics of Elementary Chemical Reactions, Balatonfoldvar, Hungary, June 7-12, 2003
"Dynamics Studies of O(^{3}P) + CH_4, C_2H_6, C_3H_8 Reactions" (given by Diego Troya)
Workshop on Quantum Reactive Scattering, San Lorenzo El Escorial, Spain, June 21-23, 2003
"Reactions of Hyperthermal Oxygen: From hydrocarbons to polymers" (given by GCS)
International Quantum Chemistry Symposium, Bonn, Germany, July 21-15, 2003 "Reactions of Hyperthermal Oxygen: From hydrocarbons to polymers" (given by GCS)
Seminar at the University of Hanover, Germany July 23, 2003 "Modeling chemical reactions using MSINDO" (given by GCS)
2003 – 2004
"Supercollisions and Self Assembled Monolayers", Columbia University, June 12, 2004.
"Carbon Nanotube Fracture and Hyperthermal Chemistry," Conference on Theoretical and Computational Chemistry, Feb. 16-19, Giongiu, Korea
"Hyperthermal Chemistry," ACS National Meeting, Anaheim CA March 28-31, 2004
7th International Conference on Protection of Materials and Structures from Space Environment, Toronto, May 9-13, 2004
"A Direct Dynamics Studies of Hyperthermal O atom Reactions with Alkane Thiol Self-Assembled Monolayers"
"Studies of Hyperthermal O Atom reactions with Fluorinated Hydrocarbons" (presented by D. Troya)

"Reactions of O^+ with methane and with alkane thiol self-assembled monolayers" (presented by L. Sun)
"Hyperthermal Chemistry," 27th Free Radical Symposium, Taipei, July 25-30, 2004
"Hyperthermal Chemistry," 18th Gas Kinetics Symposium, Bristol, England, August 8-12, 2004

2004-2005

"Reactions of Atomic Oxygen, from small molecules to polymers", University of Wisconsin, Sept. 21, 2004
Truhlar Fest, Computational Chemical Dynamics, University of Minnesota, Oct. 8,9, 2004
"Reactions of Hyperthermal Atomic Oxygen" (invited)
SERS Workshop, Wright Patterson Air Force Base, Nov. 11-12, 2004.
"Theoretical Studies of SERS"
MRS Fall National Meeting, Boston, Nov. 29-Dec. 2, 2004
"Fracture in Carbon Nanotubes" (invited)
Space Effects MURI Meeting, Bozeman, MT January 27-28, 2005
"Modeling Polymer Erosion by Hyperthermal O and O^+"
BOSS Review Meeting, Ritz-Carson, Tyson's Corner, McLean VA, Feb. 7-8, 2005
"Optimizing Gradient Index Lens Performance"
ACS National Meeting, San Diego, CA March 12-17, 2005
"New Uses for Electronic Structure and Molecular Dynamics Calculations"
MRS Spring Meeting, San Francisco, March 31, 2005
"QM/MM Studies of Polymer Degradation due to Hyperthermal Atomic Oxygen" (invited)
CCP6 Workshop, Belfast UK April 1-5, 2005-07-14
"Reactions of atomic oxygen and sulfur with H_2 and hydrocarbons" (invited)
IAMS Retreat, Taipei, Taiwan, June 16-17, 2005
"Reactive Collision Dynamics; Metal Nanoparticle Optical Properties" (invited)
Quantum Reactive Scattering Workshop, Santa Cruz, CA July 15-18, 2005
"Direct Dynamics Calculations" (invited)

Steven J. Sibener

Gordon Research Conference on Thin Film & Crystal Growth Mechanisms, Invited Participant, Williams College, Williamstown, MA
XVIIIth Conference on the Dynamics of Molecular Collisions, Copper Mountain, CO
University of Wisconsin, Department of Physics, Madison, WI
University of Southern California, Department of Chemistry, Los Angeles, CA
University of California at Irvine, Department of Chemistry, Irvine, CA
National Meeting of the Materials Research Society, Fall 2001, Symposium on Current Issues in Heteroepitaxial Growth: Stress Relaxation and Self Assembly, Boston, MA
MURI review meeting, Chicago, June 13, 2002
Gordon Research Conference on Atomic and Molecular Interactions 2002, Roger Williams University, Bristol, RI
Workshop on Nanoscale Approaches to Multifunctional Coatings, Keystone, CO, 12-16 August, 2002.

2002-2003

NSF-MRSEC and UC-Argonne Consortium for Nanoscience Research Workshop on "Nanohybrid Structures", University of Chicago, Chicago, IL
Department of Chemistry "Highlands in Chemistry Seminar Series", Virginia Tech, Virginia
March 2003 Meeting of the APS, "Symposium on Structure and Properties of Organic Thin Films", Austin, Texas

March 2003 Meeting of the APS, Organizer, Symposium on "Dynamics, Assembly, Reactivity and Function Across Extended Length-Scales", Austin, Texas
Princeton Materials Institute, Princeton University, Princeton, NJ
University of Notre Dame, Department of Chemistry and Biochemistry, Notre Dame, IN
35th Great Lakes Regional Meeting of the ACS, "Symposium on Nanoscience and Nanotechnology", Loyola University, Chicago, IL
Talk given by Ken Nicholson: Nucleation and Growth of Nanoscale to Microscale Cylindrical Pits in Highly-Ordered Pyrolytic Graphite upon Hyperthermal Atomic Oxygen Exposure, K.T. Nicholson, T.K. Minton, and S.J. Sibener, *9th International Symposium on Materials in a Space Environment*, Noordwijk, The Netherlands, June 16-20, 2003.
Telluride Science Research Center Meeting, "Polymers: Theory vs. Experiment", Telluride, CO
Gordon Research Conference on Dynamics at Surfaces, Proctor Academy, Andover, NH

2004

XIVth Symp. on Atomic, Cluster & Surface Physics (SASP2004), La Thuile, Val d'Aosta, Italy
Montana State University, Department of Chemistry and Biochemistry, Bozeman, MT
NNI Interagency Workshop: Nanoscience Research for Energy Needs, Discussion Leader and and Speaker -- Catalysis and Nanoparticles, Arlington, VA
Invited Guest Lecturer, AFOSR Contractor's Meeting on Molecular Dynamics and Theoretical Chemistry, Newport, RI
Prairie Chapter of the American Vacuum Society, University of Illinois, Urbana-Champaign, IL
Argonne National Laboratory, Colloquium, Materials Science Division, Argonne, IL
University of Rochester, Department of Chemistry, Rochester, NY
University of Texas at Austin, Distinguished Lecturer, Center for Nano and Molecular Science and Technology, Austin, Texas
National Meeting of the Materials Research Society, Symposium on Materials for Space Applications, Boston, MA

2005

Gordon Research Conference on Molecular Energy Transfer, Buellton, CA
National Meeting of the ACS, Symposium on Dynamics and Conductivity of Nanoparticles and Their Assemblies, San Diego, CA
Pennsylvania State University, Department of Chemistry, University Park, PA
Telluride Meeting on Polymer Theory vs. Polymer Experiment, Telluride, CO
ACS National Meeting, Washington, D.C., Symposium on "Applications of Self-Assembled Monolayers and Organized Thin Films n Surface and Interface Studies"
ACS National Meeting, Washington, D.C., Polymers
ACS National Meeting, Washington, D.C., Symposium on "Influence of Local Structure and Reagent Energy on Chemical Reactions at Solid Surfaces"
Workshop on In-Situ Characterization of Surface and Interface Structures and Processes, Advanced Photon Source and Center for Nanoscale Materials, Argonne National Laboratory, Argonne, IL.
International Symposium on Creation of Nanoscale Designed Surfaces and their Electronic and Catalytic Properties (JST-JIS-NDS), Keio University, Mita Campus, Minato-ku, Tokyo, Japan
21st Century COE KEIO-LCC International Symposium on Frontiers of Nanoscale World: From Nanoclusters to Nanomedicine, Keio University, Yagami Campus, Yokohama, Japan
Department of Chemistry and Chemical Biology, Cornell University, Ithaca, NY
National Meeting of the Materials Research Society, Symposium on "Degradation Processes in Nanostructured Materials", Boston, MA

2006

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

John C. Tully

2002-2003

Invited Talks at Meetings

International Academy of Quantum Molecular Sciences, Menton, France (7/70/2)

Workshop on Currents and Trajectories in Quantum Mechanics, Lyon, France (9/9/02)

XIth International Congress of Quantum Chemistry, Bonn, Germany (7/24/03)

Gordon Research Conference on Dynamics at Surfaces (8/13/03)

Talks at Universities

Northwestern University (5/10/02), Wayne State University (10/7/02), University of Sherbrooke (11/13/02), Montana State (3/7/03), Emory University (5/4/03), Georgia Tech (5/5/03)

Posters

"Graphite erosion by low-earth orbit O(^{3}P) and Metal nanoparticle near-field optics", Gordon Research Conference on Clusters, Nanocrystals & Nanostructures, Aug 3-8, 2003 (presented by Lance Kelly)

"Kinetic Monte Carlo model of macroscopic graphite erosion by O(3P) in low-earth orbit", Gordon Research Conference on Dynamics at Surfaces, Aug 10-15 (presented by Lance Kelly)

"Random Roughness Model of Scattering and Accommodation at Surfaces", Gordon Research Conference on Dynamics at Surfaces, Aug 10-15 (presented by John Tully)

2003 – 2004

Invited Talks at Meetings

XIth International Congress of Quantum Chemistry, Bonn, Germany (7/24/03)
Gordon Research Conference on Dynamics at Surfaces (8/13/03)
American Chemical Society Local Meeting, Pittsburgh (10/9/03)
American Physical Society, Montreal (3/22/04)
American Chemical Society, Anaheim (3/30/04) Award Lecture
American Chemical Society, Anaheim (3/31/04)
Faraday Society, Oxford, England (4/7/04)
Canadian Symposium on Theoretical Chemistry, Quebec (7/14/04)

Talks at Universities

Montana State (3/7/03), Emory University (5/4/03), Georgia Tech (5/5/03), University of Montreal (9/17/03), Bridgewater State College (11/13/03), MIT/Harvard (12/9/03-12/11/03), Trinity College (1/30/04), University of Michigan (5/6/04)

Contributed Talks and Posters

"Graphite erosion by low-earth orbit O(^{3}P) and Metal nanoparticle near-field optics", Gordon Research Conference on Clusters, Nanocrystals & Nanostructures, Aug 3-8, 2003 (presented by Lance Kelly)

"Kinetic Monte Carlo model of macroscopic graphite erosion by O(3P) in low-earth orbit", Gordon Research Conference on Dynamics at Surfaces, Aug 11, 2003 (presented by Lance Kelly)
"Random Roughness Model of Scattering and Accommodation at Surfaces", Gordon Research Conference on Dynamics at Surfaces, Aug 12, 2003 (presented by John Tully)
"Kinetic Monte Carlo model of macroscopic graphite erosion by O(3P) in low-earth orbit", American Chemical Society, New York, Sept 10, 2003 (presented by Lance Kelly)
"Theoretical Studies of Graphite Erosion in Low Earth Orbit", American Chemical Society, New Haven, June 21, 2004 (presented by Natasa Mateljevic)

2004-2005

"Ab initio studies of the interaction of oxygen with perfect and defective graphite surfaces", M. Mateljevic and J. C. Tully, AMERICAN CHEMICAL SOCIETY 228: August, 2004
"Kinetic Monte Carlo model for graphite slabs exposed in low-earth orbit", K.L. Kelly and J. C. Tully, AMERICAN CHEMICAL SOCIETY 228: August, 2004
"Study of chemical dynamics at surfaces using molecular dynamics simulations", S. Roy and J. C. Tully, AMERICAN CHEMICAL SOCIETY 228: August, 2004
"Time-dependent density functional theory for studying the energies and lifetimes of excited adsorbate states on metal surfaces", X.S. Li, H. B. Schlegel, M. J. Frisch and J. C. Tully, AMERICAN CHEMICAL SOCIETY 228: August, 2004
Mixed Quantum/Classical Dynamics, J. C. Tully, AMERICAN CHEMICAL SOCIETY 228: August, 2004 (invited).
Mixed Quantum/Classical Dynamics, J. C. Tully, Truhlar Symposium, October, 2004 (invited)
Mixed Quantum/Classical Dynamics, J. C. Tully, Summer Course on Theoretical Chemistry, Park City, June, 2005 (invited)

2005-2006

Mixed Quantum/Classical Dynamics, J. C. Tully, International Academy of Quantum Molecular Sciences, Menton, Fr, July, 2005 (invited)
Mixed Quantum/Classical Dynamics, P. V. Parandekar and J. C. Tully, American Conference on Theoretical Chemistry, July, 2005 (invited)
"Equilibrium and Detailed Balance in Mixed Quantum/Classical Dynamics", P. V. Parandekar and J. C. Tully, American Conference on Theoretical Chemistry, July, 2005.
"Erosion of Graphite Surfaces by 5 eV Oxygen Atom Impact", N. Mateljevic, H. Cheng and J. C. Tully, American Conference on Theoretical Chemistry, July, 2005.
"Chemical Dynamics", J. C. Tully, Mercury Conference on Computational Chemistry, Clinton, NY, July, 2005 (invited)
Chemical dynamics at metal surfaces, J. C. Tully, AMERICAN CHEMICAL SOCIETY 231: March, 2006 (invited).
Energy transfer at metal surfaces: the role of electronic excitations, N. Shenvi, H. Cheng and J. C. Tully, AMERICAN CHEMICAL SOCIETY 232: August, 2006 (invited).
Nonadiabatic dynamics at metal surfaces, N. Shenvi, S. Roy, H. Cheng and J. C. Tully, AMERICAN CHEMICAL SOCIETY 232: August, 2006 (invited).
Dynamics at metal surfaces: the role of electronic excitations, J. C. Tully, Gordon Research Conference on Atomic and Molecular Interactions, July 2006 (invited).

Luping Yu

2004-2005

ACS Meeting, Philadelphia, 08/22/2004. (Invited talks)
Towards Molecular Electronics, the University of Ulm, November 26-27, 2004

Bolling Green State University, 09/15/2004
Brookhaven National Lab, 10/06/2004
University of South Florida, 10/15/2004.
Iowa State University, 2005
"Modeling Polymer Erosion by Hyperthermal O and O^+", Space Effects MURI Meeting, Bozeman, MT, January 27-28, 2005.

7b) Consultations

William L. Hase

Tianying Yan (Nankai, China) – collisions of rare gas atoms with per-fluorinated, fluorinated and hydroxylated SAMs.
John Morris Group (Virginia Tech University) - rare gas atom scattering off hydroxylated, per-fluorinated, and fluorinated SAM surfaces.
Chuck Doubleday (Columbia University) - develop semi-empirical electronic structure theory models which are flexible enough and have a sufficient theoretical foundation to accurately represent high-level *ab initio* calculations for multiple-reaction complex chemical systems.
David Nesbitt Group (University of Colorado) - collisions of CO_2 with per-fluorinated hydrocarbon surfaces.
Emilio Martínez-Núñez (Universidad de Santiago de Compostela, Spain) - collisions of CO_2 with per-fluorinated hydrocarbon surfaces.
Robert Shroll (Spectral Sciences, Inc.) - $O(^3P)$ reaction dynamics.

Dennis C. Jacobs

Dennis Jacobs collaborated with Dr. Rainer Dressler (AFRL/VSBXT) in comparing experimental results on the scattering of O^+ on decanethiolate SAMs (Jacobs Lab) with O^+ on gas-phase propane molecules (Dressler lab). Remarkable similarities were observed in the dissociative charge-transfer channels. Continued collaborations will involve larger alkane molecules and functionalized SAM layers. These efforts will help establish links between the vast gas-phase ion-molecule literature and the virtually unexplored field of ion scattering on organic surfaces. Collaborations are also underway with Dr. Sandra Tomczak (AFRL/Space and Missile Propulsion) and Dr. Gary Pippin (Boeing Phantom Works) to launch MISSE-6. We are coordinating experiments to expose various materials, including POSS polyimide materials, to modified LEO environments around the International Space Station. In particular, synergistic effects will be assessed by comparing recession rates for samples in full LEO with those for samples in LEO where photons, ions, or electrons have been eliminated. *In situ* monitoring of the film thickness will be recorded on data loggers throughout the mission.

Timothy K. Minton

Dr. Matthew Braunstein, Spectral Sciences, Burlington, MA. Dr. Braunstein and his company perform calculations to model reactive flows. The PI has collaborated with Dr. Braunstein on a number of publications involving hyperthermal atomic-oxygen interactions with gaseous species and with surfaces. The PI has also had many discussions with Dr. Braunstein about the role of hyperthermal atomic oxygen reactions in rocket plume chemistry and signatures. These discussions led to the PI requesting and receiving two Congressional appropriations for the establishment of a Center for Laboratory Studies of Rocket Plume Chemistry at Montana State University. In addition, Dr. Braunstein has funded the PI to study a plume-related O-atom

reactions that were part of Phase II SBIR and Phase I STTR projects. In general, the experiments done at Montana State University have helped validate direct simulation Monte Carlo (DSMC) codes that have been developed by Dr. Braunstein and his colleagues.

Dr. Rene Gonzalez and Dr. Sandra Tomczak, Air Force Research Laboratory, Space and Missile Propulsion Branch, Edwards, AFB. Dr. Gonzalez provided samples of POSS polymers to the PI's lab, where the resistance of these polymers to atomic-oxygen attack was investigated. Dr. Gonzalez left AFRL, and a collaboration continued with his successor, Dr. Tomczak. Dr. Tomczak has provided many samples to the PI for studies of the O-atom interaction mechanisms with POSS materials. In addition, Dr. Tomczak became the PI for a DARPA funded effort to make space structures from new POSS polyimide materials. The award of this project depended in part on the results of work done by the PI that showed how exposure of a POSS polyimide produced a passivating layer that protected the underlying material from further O-atom attack. Based on O-atom exposures done in the PI's lab, a new POSS polyimide has been selected as a base material for fabricating a new multifunctional material for use in low-Earth orbit. The PI continues to collaborate with Dr. Tomczak on the DARPA project, which includes both space- and ground-based testing of POSS polyimides.

Dr. Judith Yang, Department of Materials Science and Engineering, University of Pittsburgh (also director of the "Pittsburgh MURI"). Samples provided by Prof. Yang were exposed at various times to atomic oxygen at Montana State University and sent to her for analysis. The PI has collaborated with Prof. Yang on several publications involving the oxidation of silicon and silver by hyperthermal atomic oxygen. The PI joined with Prof. Yang as a co-organizer of a symposium, "*In Situ* Studies of Gas-Solid Surface Reaction Dynamics," which was part of the spring 2005 Materials Research Society meeting.

Dr. Gary Pippin, Boeing Phantom Works. Dr. Pippin has organized many space flight experiments and is currently involved in several MISSE (Materials International Space Station Experiment) experiments. The PI has provided samples to Dr. Pippin for two such experiments (MISSE-5 and MISSE-6) and has received samples back from MISSE-5 for analysis. In 2006, the PI delivered 30 samples of polymer films on quartz crystal microbalances to Dr. Pippin for the upcoming MISSE-6 experiment.

Dr. Stephanie Remaury, Centre National des Etudes, Spatiales, Toulouse, France. The PIs lab conducted exposures of samples of candidate thermal control paints that were to be used for ESA missions. Dr. Remaury evaluated a number of exposed samples and made her recommendations in a report.

Drs. Eitan Grossman and Irina Gouzman, Soreq NRC, Israel. Drs. Grossman and Gouzman have visited the Pi's lab multiple times and have provided samples of various materials for testing in the lab. In two cases, they paid for extensive tests of some materials. The PI has written a refereed paper and several conference proceedings in collaboration with Drs. Grossman and Gouzman.

Dr. Rainer Dressler, AFRL, Hanscom AFB. The PI provided input to Dr. Dressler who helped update the Military Critical Technologies List (MCTL) on space survivability. In addition, Dr. Dressler has organized telescope imaging of rocket plume firings in low Earth orbit. The crossed-beams experiments in the PI's lab complement these field experiments.

Dr. Jacob Kleiman, Integrity Testing Laboratory, Toronto, Canada. Dr. Kleiman owns a small company that does many types of materials testing. Dr. Kleiman organizes a major space environmental effects meeting every two years, and the PI has been on the organizing committee. In addition, the PI has helped find funding for this meeting. Dr. Kleiman has recently built an O-atom source for space environmental effects testing in Canada, and he spoke regularly to the PI about O-atom sources for a period of time.

Prof. Steven George, University of Colorado. Prof. George and the PI have teamed up on a project to use atomic layer deposition (ALD) coatings to protect polymer substrates from atomic-oxygen attack and VUV-induced photochemistry. Funding has been applied for under the STTR program.

George Schatz

Schatz has had extensive collaborations with Minton (MURI team member). He has also collaborated with Rainer Dressler (AFRL) – O^+ reactions with hydrocarbons (and a joint paper written)
Karl Jug, Thomas Bredow (Hanover) – exchanged visits (collaboration continued)
Dick Zare (Stanford) – exchanged visits and people (collaboration initiated)
Sandra Tomczak (Edwards) – collaboration initiated
Matt Braunstein (Spec. Sciences) – O collisions with H_2O, in progress

Steven J. Sibener

We have initiated QCM experiments at Chicago with the support of Dr. Gary Pippen of Boeing to establish terrestrial experiments on materials of high interest to LEO operations. We are initially focusing on atomic oxygen/VUV degradation of polymers. We are also participants in the MISSE-5/6 activities.

We have also been in close contact with NASA Glenn as we implement vacuum-ultraviolet (VUV) measurements in our laboratory. Identical lamps have been procured and installed as those used by Joyce Dever and colleagues, ensuring relevance of our synergistic VUV measurements to prior work at NASA.

Interactions continue between Wright-Patterson AFB and the University of Chicago in which Dr. Robert Mantz of the nonstructural materials division and the Sibener Group will use their complementary experimental capabilities to develop an improved fundamental understanding of volatilization mechanisms of LEO coatings.

Collaborated with Adam Kollin, President, RHK Technologies in the design and implementation of an improved cryogenic and elevated temperature scanning probe microscope.

Have given invited lectures at the past two Materials Research Society meetings in symposia dealing with environmental effects in the space environment.

John C. Tully

The Tully group has established continuing interactions with Matthew Braunstein and his collaborators at Spectral Sciences Incorporated. Braunstein and Jason Cline visited Yale on

July 29, 2003, to coordinate a number of parallel theoretical efforts. Braunstein's group is carrying out molecular dynamics simulations of reactions of oxygen with graphite surfaces, using an extension of the Brenner Potential to approximate the forces. These simulations are complementary to those being carried out by Hongzhi Cheng in the Tully group on the same systems, but using the MSINDO semiempirical force field. Both groups are simultaneously carrying out ab initio calculations to test the approximate force fields, the Braunstein group using the GAMESS code and Natasa Mateljevic in the Tully group using the plane wave pseudopotential VASP code and the Gaussian code. In a separate effort, Jason Cline and Matthew Braunstein are carrying out hydrodynamic simulations of gases colliding with surfaces for a number of applications, including the characterization of Tim Minton's O-atom source. Currently their codes assume complete accommodation upon collision with the surface. They plan to upgrade their simulation codes to incorporate incomplete momentum accommodation using the Tully group's Random Roughness Model. The Tully group also partnered with Gaussian, Inc., to implement ab initio Ehrenfest dynamics into the Gaussian electronic structure code.

Luping Yu

Model compounds were sent to experimental groups for use in atomic oxygen and synergistic effects experiments. Synthetic techniques for preparing selectively deuterated alkanethiols were shared with other groups.

7c) Transitions

George C. Schatz

Matt Braunstein (Spec. Sciences) – O reactions with H_2 (joint project: vibrationally excited H_2)

8. New Discoveries, Inventions, or Patent Disclosures

Illustrative advances from our MURI activities include:

Identification of POSS polyimide as space survivable material
Minton

Graphite Oxidation: Paradigm for Materials Erosion including Synergistic Effects
Minton, Sibener, Garrison, Schatz, Tully

Reaction Pathways of Gas-Phase Organic Molecules
Minton, Hase, Schatz

Reaction Pathways of Organic/Inorganic Solids and Films
Jacobs, Minton, Sibener, Yu, Garrison, Hase, Schatz, Tully

Collisional Gas-Surface Energy/Momentum Transfer
Neutrals: Hase, Minton, Sibener, Tully, Yu; Ions: Garrison, Jacobs

Synergistic Photo-Effects: Polymer Degradation/Reactivity, O Atom Reactivity with PMMA
Garrison, Sibener

New Class of Stable SAMs Synthesized and Demonstrated Involving Isocyanides on Ni
Yu

Instrumentation Development by Experimental Group
Unique Scattering Instruments and O-Sources, Variable-Temp STM, Synergistic Effects

Methodology Development by Theory Group
Rare Events, Energy Transfer, Reactivity, Morphology Evolution

Example: Elucidating the role of singlet-triplet spin transitions and of charge neutralization in collisions of oxygen atoms and ions with surfaces is fundamental to

understanding reactions in low earth orbit, and may have much broader implications, e.g., reactivity of carbon nanotubes (Tully).

Example: Use of direct dynamics using the PM3 semiempirical method to describe O^+ reactions with methane. This very simple approach works well, providing us with a tool that can be used to study many other similar ion-molecule reactions. Among the surprising results from this study is that the CH_3^+ product is produced readily as in a triplet excited state (a spin-allowed product) at low energy, under circumstances where the corresponding singlet ground state product is spin-forbidden (Schatz).

Example: Successful theoretical models for hydrocarbon surfaces, including a wide variety of alkyl thiolate SAMs; most detailed studies to date of collisional energy transfer at organic interfaces (Hase).

9. Honors/Awards

Barbara J. Garrison

Penn State Materials Research Institute 2003 Best Ph.D. Thesis Award to Yaroslava G. Yingling,
former student and postdoc, now at the National Cancer Institute.
Shapiro Professor of Chemistry, 2002
Vice-chair elect of the Physical Chemistry Division of the American Chemical Society
Francis P. Garvan-John M. Olin Medal from the American Chemical Society, 1994
American Physical Society Fellow, 1994
American Vacuum Society Fellow, 1994
Penn State Faculty Scholar Award for Outstanding Achievement in Physical Sciences and Engineering, 1990
Akron Section Award, American Chemical Society, 1990
Peter Mark Award, American Vacuum Society, 1984

William L. Hase

60th Birthday Festschrift of the Journal of Physical Chemistgry A, Volume 110, No.4, 2006
60th Birthday Special Issue of the International Journal of Mass Spectrometry, Volume 241, Nos. 2-3, 2005
Robert A. Welch Chair in Chemistry, Texas Tech University, 2004
Distinguished Professor of Chemistry, Wayne State University, 1997
Fellow, American Association for the Advancement of Science, 1997
Leader in Chemistry, College of Arts and Sciences, University of Missouri, Columbia, Missouri, 1996
Fellow, American Physical Society, 1991
Recognized as one of the 100 outstanding graduates of the College of Arts and Sciences during New Mexico State University's Centennial year 1987-88

Dennis C. Jacobs

25th Donald G. Davis Memorial Lecture (2005)
CASE U.S. Professor of the Year for Doctoral and Research Universities (2002)
U.S. Professor of the Year for Doctoral and Research Universities, Carnegie Foundation (2002)
Kaneb Teaching Award (2002)
Carnegie Scholar at the Carnegie Foundation for the Advancement of Teaching (1999-2000)
Shilts/Leonard Teaching award for outstanding teacher in the College of Science at the University of Notre Dame (1999)
Thomas P. Madden award for outstanding teacher in the first year of studies at the University of

Notre Dame (1998)
Alfred P. Sloan Research Fellow (1993-1995)

Timothy Minton

Graduate Student, Amy Brunsvold: Amelia Earhart Fellowship, 2005—2007; Montana Space Grant Consortium Fellowship, 2006—2007
Promoted to the rank of Full Professor – July 1, 2005
Air Force Research Laboratory, In-House Project of the Quarter (Fall 2002): "Space-Survivable Polymers Containing Polyhedral Oligomeric Silsesquioxanes (POSS)"
Charles and Nora L. Wiley Faculty Award for Meritorious Research, 2002

George C. Schatz

Cherry Emerson Lecture, Georgia Tech, Feb. 2007
Thomas Lecture, University of Missouri, Dec. 2006
Kilpatrick Lecture, IIT, Sept. 2006
Schatz was elected to the National Academy of Sciences, 2005
Appointed Editor-in-Chief of the Journal of Physical Chemistry
Elected to American Academy of Arts and Sciences, 2002
Named Morrison Professor of Chemistry, Northwestern University 2002
Elected to International Academy of Quantum Molecular Science, 2001

Steven J. Sibener

Elected Fellow of the American Association for the Advancement of Science, 2006
Member, Editorial Board, Advances in Chemical Physics (2007-2012).
Chair, APS Irving Langmuir Prize Committee (2004)
Member, Advisory Board, Center for Nanoscale Materials, Argonne National Lab (2001-2003)
Carl William Eisendrath Professor, The University of Chicago, appointed July 2001
Director, The James Franck Institute, appointed July 2001
Member, NSF-MRSEC Directors' Executive Committee (1998-2000)
Director, Univ. of Chicago Materials Research Science and Engineering Center, 7/1997-6/2001
Elected Fellow of the American Physical Society, 1997
Chairman, Div. of Chemical Physics, American Physical Society, 1996
Visiting Fellow, Joint Institute for Laboratory Astrophysics, U. of Colorado, Boulder, 1992-93
Marlow Medal of the Faraday Division of the Royal Society of Chemistry, 1988
Member, Board of Trustee's Visiting Committee for the College of Arts and Science, University of Rochester (July 1, 1987 - June 30, 1993).
IBM Faculty Development Award, 1984-86
Alfred P. Sloan Foundation Research Fellow, 1983-87
Camille and Henry Dreyfus Young Faculty in Chemistry Award, 1980
Gulf Oil Research Fellow, University of California, Berkeley
American Institute of Chemists Award, University of Rochester
Phi Beta Kappa

John C. Tully

2001-2006:

Appointed Sterling Professor, Yale University, 2006
Yale Science and Engineering Association Award in Basic Science, 2006.
McElvain Lecturer, University of Wisconsin, Madison, November14, 2006.
Maurice Shock Visiting Fellow, University College, Oxford University, 2005
J. S. Guggenheim Fellowship, 2005
Nieuwland and Peter C. Reilly Lecturer, Notre Dame University, December 6-9, 2004
Highlands in Chemistry Speaker, Virginia Tech, October 22, 2004

2004 American Chemical Society Award in Theoretical Chemistry
Arthur D. Little Lecturer, MIT, December 2003
Special Issue of the *Journal of Physical Chemistry*: "Tully Festschrift", August 2002
Chair, Division of Chemical Physics, American Physical Society, 2001-02
Frontiers in Chemistry Lecturer, Wayne State University, 2002
E. G. Young Lecturer, University of Sherbrooke, 2002
Arthur William Davidson Lecturer, University of Kansas, 2001
Class of 1960 Speaker, Williams College, 2001

Selected Other Awards and Activities:

National Academy of Sciences, 1997
American Chemical Society Peter Debye Award in Physical Chemistry, 1995
American Chemical Society Madison Marshall Award, 1999
Named Arthur T. Kemp Professor, 1997
AT&T Bell Laboratories Affirmative Action Award, 1992
American Academy of Arts and Sciences, 1997
International Academy of Quantum Molecular Sciences, 2000
Connecticut Academy of Science and Engineering, 1998
AT&T Bell Laboratories Distinguished Technical Staff Award, 1982
American Physical Society Fellow, 1978
National Research Council Board on Chemical Sciences and Technology, 2000-
Nominating Committee, National Academy of Sciences, 2001-
Chair, Division of Physical Chemistry, American Chemical Society, 1993-94
Advisory Board, Alfred P. Sloan Foundation, 2001-
Advisory Board, Camille and Henry Dreyfus Foundation, 2003-
National Science Foundation Advisory Committee for Chemistry, 1987-90
Petroleum Research Fund Advisory Board, 1988-90
Chemistry Evaluation Panel, Air Force Office of Scientific Research, 1979-82
Board of Directors, The Sheffield School, Yale University, 2003-
Chemistry Council, Department of Energy Basic Energy Sciences, 2004-

Luping Yu

NSF Special Creativity Award. (2004)
Mr. &Mrs. Sun Chan Memorial Award in Organic Chemistry. (1998)
National Science Foundation Young Investigator Award. (1994-1999)
Arnold and Mabel Beckman Foundation Young Investigator Award. (1993-1995)
Camille and Henry Dreyfus Foundation New Faculty Award. (1991-1996)
Award for Research Excellence in Fundamental Science from the Ministry of Education, P. R. China. (1987)
Award for Research Excellence in Science and Technology from Zhejiang University, P. R. China. (1986)

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