## REPORT DOCUMENTATION PAGE



AFRL-SR-AR-TR-04-

0507

| 1. AGENCY USE ONLY *(Leave blank)* | 2. REPORT DATE | 3. REPORT TYP |
|---|---|---|
| | 30 SEP 04 | FINAL REPORT 1 APR 01 TO 31 MAR 04 |

**4. TITLE AND SUBTITLE**
REACTION DYNAMICS RELEVANT TO SPACECRAFT IN LOW ORBIT

**5. FUNDING NUMBERS**
F49620-01-1-0276

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AFOSR/NL
4015 WILSON BLVD.ROOM 713
ARLINGTON, VA 22203-1954

**10. SPONSORING/MONITORING AGENCY REPORT NUMBER**

**11. SUPPLEMENTARY NOTES**

**12a. DISTRIBUTION AVAILABILITY STATEMENT**
APPROVE FOR PUBLIC RELEASE: DISTRIBUTION UNLIMITED

**12b. DISTRIBUTION CODE**

**13. ABSTRACT** *(Maximum 200 words)*
The key goal of the project (to improve our understanding of fundamental gas-surface and gas-phase reaction/interaction dynamics that relate directly to orbital and sub-orbital spacecraft or missile missions of direct relevance to the U.S. Air Force) was fulfilled. However, the details of the work performed differed from those proposed. Scientific curiosity, experi mental opportunities, and siscussions with the Program Manager (Dr Michael Berman) led to a modification of some of the detailed objectives of this project. Seminal data were obtained on the hyperthermal reactions of ground-state O(3P) with H2, D2, and small hydrocarbons (methane, ethane, and propane). The hyperthermal atomic oxygen source was confirmed to contain atomic oxygen in its ground O(3P) state by a combination experiment/theory study of the reaction, O+H2 > OH+H, where Prof. George Schatz of Northwestern University conducted the theoretical calculations. A similar study on the reaction of the hypertermal beam with CH4 showed that the molecular oxygen component of the beam is in its ground state.

20041012 044

| 14. SUBJECT TERMS | 15. NUMBER OF PAGES |
|---|---|
| | 16. PRICE CODE |

| 17. SECURITY CLASSIFICATION OF REPORT | 18. SECURITY CLASSIFICATION OF THIS PAGE | 19. SECURITY CLASSIFICATION OF ABSTRACT | 20. LIMITATION OF ABSTRACT |
|---|---|---|---|
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# REACTION DYNAMICS RELEVANT TO SPACECRAFT IN LOW EARTH ORBIT

**Final Technical Performance Report**

**September 29, 2004**

**AFOSR-F49620-01-1-0276**

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## OBJECTIVES

### Proposed Objectives

The general goal of this project was to improve our understanding of fundamental gas-surface and gas-phase reaction/interaction dynamics that relate directly to orbital and sub-orbital spacecraft or missile missions of direct relevance to the U.S. Air Force. Proposed experiments were focused in three areas: (1) gas-surface reactive scattering dynamics of hyperthermal O atoms with partially oxidized carbon and hydrocarbon surfaces, (2) gas-surface inelastic scattering to study the dynamics of microthruster propellant molecules (e.g., $H_2O$) interacting with MEMS surfaces, such as silicon, and (3) prototypical gas-phase reaction dynamics of atomic oxygen with $H_2$ and small alkanes. A new apparatus was to be set up for measuring internal state distributions (by laser-induced fluorescence) from reactive products.

### Proposal Abstract

Atomic oxygen dominates the rarefied upper atmosphere at low Earth orbital altitudes. Orbital and sub-orbital space vehicles collide with ambient oxygen atoms at very high relative velocities that are on the order of 100 times thermal. Such high-velocity collisions occur between O atoms and spacecraft surfaces as well as between O atoms and gas-phase species emitted by the vehicle (from outgassing or thruster firings). Energetic collisions of O atoms with spacecraft surfaces often degrade materials through oxidation and erosion (etching). In addition, the high energy gas-surface and gas-phase collisions typically yield internally "hot" reaction products, which emit radiation from the infrared to the ultraviolet. These emissions (or signatures) are very important for tracking and surveillance. The increasing demand on spacecraft and rockets that reside in or pass through the low Earth orbital space environment means that interactions of ambient atomic oxygen with these vehicles will remain a key long-term technical issue for the Department of Defense.

Underlying the practical problems associated with space vehicle operations in the upper atmosphere are fundamental chemical and physical processes that have remained elusive in laboratory studies. Technical challenges have prevented detailed dynamical investigations of ground-state $O(^3P)$ reactions with simple hydrocarbons. The challenges stem from the difficulty of producing a beam of atomic oxygen, large reaction barriers, and low reaction cross sections. Product detection schemes must also be elaborate. The necessary infrastructure for studying the dynamics of atomic oxygen reactions is thus seldom available, even though such reactions are of extreme importance to scientists and engineers alike. The ability to understand these reactions and then build predictive models for space environmental effects (or combustion) rests on the quality of the data that must come from difficult experiments.

The PI has built a lab and research infrastructure at Montana State University (with DoD support) that is second to none in its capability to study reaction dynamics of hyperthermal atomic oxygen reactions with gaseous and surface hydrocarbons. The proposed work will capitalize heavily on the existing facility to map out the scattering dynamics of a variety of prototypical O + hydrocarbon systems (including O + $H_2$) at collision energies that are representative of those encountered by spacecraft and rockets. In addition, this work will extend the current infrastructure to include a new apparatus that will augment the current capabilities with complementary techniques, providing for product internal state determination and surface analysis. Even with the formidable

capabilities of the upgraded lab and the information that can be obtained there, it will be necessary to marry the O-atom beam technology with equipment on at the Advanced Light Source at Lawrence Berkeley Laboratory in order to fully complete the seminal studies that are proposed. Other work proposed will utilize the experience and capabilities of the PI to provide needed information on energy transfer in the interactions of propellant molecules ($H_2O$) with microelectromechanical (MEMS) surfaces.

The project will bring the PI as well as several students into close contact with collaborators at the Air Force Research Laboratory - Propulsion Directorate and at the LBL Advanced Light Source.

## SUMMARY OF EFFORT

The key goal of the project (to improve our understanding of fundamental gas-surface and gas-phase reaction/interaction dynamics that relate directly to orbital and sub-orbital spacecraft or missile missions of direct relevance to the U.S. Air Force) was fulfilled. However, the details of the work performed differed from those proposed. Scientific curiosity, experimental opportunities, and discussions with the Program Manager (Dr. Michael Berman) led to a modification of some of the detailed objectives of this project. Seminal data were obtained on the hyperthermal reactions of ground-state $O(^3P)$ with $H_2$, $D_2$, and small hydrocarbons (methane, ethane, and propane). The hyperthermal atomic oxygen source was confirmed to contain atomic oxygen in its ground $O(^3P)$ state by a combination experiment/theory study of the reaction, $O + H_2 \rightarrow OH + H$, where Prof. George Schatz of Northwestern University conducted the theoretical calculations. A similar study on the reaction of the hyperthermal beam with $CH_4$ showed that the molecular oxygen component of the beam is in its ground state, $O_2(^1\Delta)$. Crossed-beams experiments on the gas-phase reactions of $O(^3P)$ with $CH_4$, $C_2H_6$, and $C_3H_8$ were completed. Previously unobserved reaction pathways in these reactions were observed. Several experiment/theory publications were written in collaboration with Prof. Schatz, and three more publications based on these results are anticipated. Additional crossed-beams studies were done in order to calibrate a theoretical model of reactive flows (O + Ar) and to study energy transfer in hyperthermal collisions (Ar + $C_2H_6$). Temperature and fluence dependent O-atom exposures of graphite (HOPG) were completed. New erosion morphologies were observed and described in three publications. POSS containg polyimide polymers were exposed to atomic oxygen. The results of this experiment were reported in the first paper to describe the passivating effect of POSS in a polymer that is exposed to atomic oxygen, suggesting the enormous potential of POSS polymers for use as space survivable materials. An O-atom exposure study on the temperature dependent erosion yield of Kapton and FEP Teflon was completed. This experiment represents the first definitive study of the temperature dependence of the erosion of these materials exposed to hyperthermal atomic oxygen, and the results so far have been written up for a conference proceeding. Determination of erosion yields by measurements of etch depth with a profilometer have become standard. A new apparatus which will enable additional sample exposures and *in situ* surface characterization was set up. An AFM instrument was set up and is now routinely used for analysis of sample surfaces. The crossed beams apparatus, which has been used during the past 3 years for studies of hyperthermal gas-phase O-atom reactions is being reconfigured for beam surface

scattering studies involving hyperthermal O atoms. Mounting hardware for a VUV light source has been fabricated and is ready to use for studies of VUV/O-atom synergistic effects on materials.

## ACCOMPLISHMENTS/NEW FINDINGS

### Cross-beams studies of gas-phase reaction dynamics at hyperthermal collision energies

*Atomic-oxygen reactions with hydrogen and small alkanes*

Seminal data have been obtained on the hyperthermal reactions of ground-state $O(^3P)$ with $H_2$ and small alkanes (methane, ethane, and propane).

The study of the $O(^3P) + H_2$ reaction indicated that the reactive atomic oxygen in the 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 and excitation function have been calculated accurately by Prof. George Schatz's group (Northwestern Univ.), and these theoretical calculations have provided a benchmark for comparison with experimental results. We have measured a relative excitation function for the reaction, $O + H_2 \rightarrow OH + H$, and this measured excitation function has the same shape as the excitation function that has been calculated by theory for the reaction of $O(^3P)$ with $H_2$. This experiment/theory comparison confirmed that the atomic oxygen in the hyperthermal O-atom beam is in the $O(^3P)$ state. This is the first experimental observation of the $O(^3P) + H_2(v=0)$ reaction using molecular beams, and this experiment is only possible because the high O-atom velocity in the hyperthermal beam allows the high reaction barrier to be surmounted. Complete sets of data for both the $O(^3P) + H_2$ and $O(^3P) + D_2$ reactions, including product time-of-flight and angular distributions, have been collected, and the analysis is complete. The experimental results on the $O(^3P) + D_2$ reaction dynamics have been published in Donna Garton's thesis, and a joint experiment/theory publication is being prepared in collaboration with Prof. Schatz. The results of experiment and theory agree fairly well that about half the available energy for the reaction goes into internal excitation of the OH product and that this product tends to be backward scattered with respect to the initial direction of the reagent atomic oxygen in the center-of-mass frame. The observed reaction dynamics suggest that the reaction occurs predominantly on the two lowest lying triplet potential energy surfaces and that intersystem crossing to the singlet surface is relatively unimportant.

Detailed crossed-beams experiments were conducted on the reactions of $O(^3P)$ with model hydrocarbon compounds at center-of-mass collision energies in the range 1.5 to 4.0 eV. Data collection for all systems is complete, some results have been published in journals or in Donna Garton's thesis, and some analysis is still ongoing. Concomitant calculations by Prof. George Schatz's group have helped us focus our analysis and interpret our experimental results, and our experimental results have provided a test of the theoretical methods used in the Schatz group. The hyperthermal reactions of $O(^3P)$ with all alkanes show evidence for direct reaction with carbon, in addition to the expected H-atom abstraction reaction to form OH. The direct reactions of O with carbon have not previously been observed experimentally. The most important of these novel reactions is H-atom elimination, resulting in the corresponding methoxy, ethoxy, and propoxy radicals. A less important reaction of O with carbon leads to C–C bond breakage (in ethane and propane). These newly observed reaction mechanisms have also been seen in the theoretical

calculations of George Schatz. For the reaction, $O(^3P) + CH_4 \rightarrow OCH_3 + H$, we have measured the relative excitation function, and we have compared our experimental result with the theoretical result of George Schatz. This study has led to the conclusion that the reaction barrier is 2 eV and that the reaction occurs on both the ground (triplet) and first excited triplet potential energy surfaces. In addition, the reaction proceeds with no crossing from the initial triplet surfaces to a singlet surface. Although we have identified several reaction pathways, we are still in the process of analyzing their dynamics and estimating branching ratios for the various possible reaction channels. An experiment/theory comparison involving the possible reaction of $O_2$ (which is roughly 30 percent of the hyperthermal beam) with $CH_4$ has enabled us to deduce that the $O_2$ in the beam is in the ground $O_2(^3\Sigma_g^-)$ state, as opposed to the excited $O_2(^1\Delta_g)$ state. This was a pleasing result, because ground-state $O_2$ is not nearly as reactive as excited singlet $O_2$ and therefore will not lead to so many complications in the interpretation of experimental data.

The study of the $O(^3P) + H_2$ reaction involves the first direct observation of the reaction of ground-state oxygen atoms with the hydrogen molecule, and it has provided proof that the O-atom beam used in our experiments is composed of ground-state $O(^3P)$ atoms. The follow-on work on the $O(^3P) + D_2$ reaction has allowed the investigation of the dynamics of this model reaction in unprecedented detail. The key novelty of the work with alkanes lies in the regime of atom-molecule collision energies (2.8 - 3.9 eV), which results in the occurrence of a number of reactions, including $S_N2$-like reactions, that have never been observed before in studies of the dynamics of $O(^3P)$ reactions with alkane molecules. The investigations into hyperthermal O-atom reactions so far have indicated that intersystem crossing is not important even though it is clearly possible at the collision energies employed. Not only has the crossed-beams work, in conjunction with theoretical calculations, revealed much fundamental information about hyperthermal O-atom reaction dynamics, but this work is timely and important because energetic $O(^3P)$ reactions with surface and gaseous hydrocarbons associated with spacecraft in the upper atmosphere pose a serious threat to long-term missions in space. Very little is known about the mechanisms by which $O(^3P)$ reacts with hydrocarbons at high collision energies, and this work is helping unravel the complex reaction dynamics that govern these reactions in the extreme environment of low-Earth orbit.

*General hyperthermal gas-phase interactions*

A crossed molecular beams experiment was done on the elastic scattering of $O(^3P)$ with Ar to support theoretical calculations being done by Dr. Matthew Braunstein, who works at Spectral Sciences, Inc. The contribution of this program was to provide Dr. Braunstein with differential cross sections and to collaborate on a publication. Dr. Braunstein is developing codes to simulate reactive flows, such as rocket plumes and their interactions with the ambient environment. The experiment helped anchor his calculations and has helped establish a collaboration with him that will continue with further research into rocket plume chemistry.

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 Prof. 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 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.

**Surface modification by a hyperthermal beam**

*Etching of graphite by atomic oxygen*

An extensive study of the etching of highly ordered pyrolytic graphite (HOPG) by the hyperthermal O-atom beam has been conducted. Samples of (HOPG) were exposed to a variety of O-atom fluences at room temperature and to a single fluence at a variety of sample temperatures. AFM and STM analysis showed a marked change in the erosion mechanism of HOPG with temperature. At low sample temperatures, cylindrical etch pits were observed, but at high temperatures, the eroded surfaces showed random roughness. The occurrence of circular etch pits that are many atomic layers deep has not been observed in the oxidation of HOPG with molecular oxygen or even with thermal atomic oxygen. We have investigated the kinetics of pit formation in detail and have found that anisotropic etch kinetics lead to their nucleation and growth and to their persistence even after several micrometers of material have been removed. We have also found that the erosion rate increases by a factor of three when HOPG is heated from room temperature up to 300°C. Circular pits disappear when the temperature is raised above 150°C, presumably because the overall reactivity increases and the delicate balance between lateral and deepening etch rates that allowed for pit formation becomes lost.

*Passivation of polymer nanocomposite material*

A systematic exposure study (fluence dependence) of samples of polyhedral oligomeric silsesquioxane (POSS) polyimides, supplied by the polymer group at the Air Force Research Laboratory (Edwards AFB), was conducted. These POSS/polyimide hybrid polymers are essentially Kapton-like polymers containing POSS nanoparticles that are chemically bound into the polymer chain. Exposed and control samples were characterized by surface profilometry, atomic force microscopy, and x-ray photoelectron spectroscopy. The data indicate that the POSS-containing polyimides can have erosion rates as low as one percent that of a Kapton H reference sample, because the POSS materials form a surface $SiO_2$ layer which passivates the surface and protects the

underlying polymer from further O-atom attack. These results suggest promise for the use of a POSS polyimide polymer as a "drop-in" replacement for Kapton on spacecraft operating in the low-Earth orbital environment.

*Simulated space environmental effects*

A large body of work, much of it anecdotal, exists on the behavior of Kapton polyimide and FEP Teflon in space and in simulated space environments. The hyperthermal O-atom source at Montana State University is more characterized than any other source used for simulating space environmental effects. With the high level of control and thus confidence of exposure studies, 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 were studied. 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°C), the erosion of both materials appeared to be independent of sample temperature. But above 100°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.

Gas dynamic effects during sample exposures were examined. This study is qualitatively different from a typical "expose and look" study, because it involved monitoring beam intensities on axis with the sample mount in different orientations and even removed altogether. Direct simulation Monte Carlo calculations, performed by Spectral Sciences, Inc., were compared with the data. These calculations showed that gas-phase collisions become important at higher fluxes and may limit the energy and directionality of the O atoms that strike a surface during an exposure. Thus, it is fundamentally not possible to perform accelerated testing beyond a factor of about 10. In light of this new finding, facility operators who perform O-atom testing of candidate spacecraft materials should be mindful that the validity of a test may be compromised when trying to save time by operating at very high O-atom fluxes.

## PERSONNEL SUPPORTED

**Year 1** (4/1/01 - 3/31/02)
a) Timothy K. Minton, Montana State University PI (14%)
b) Donna Garton, graduate student (24%)
c) Deanna Buczala, graduate student (20%)
d) Matt Dorrington, part time undergraduate (100%)
e) Teri Larsen, part-time lab assistant (100%)

**Year 2** (4/1/02 - 3/31/03)
a) Timothy K. Minton, Montana State University PI (21%)
b) Donna Garton, graduate student (100%)
c) Amy Brunsvold, graduate student (30%)
d) Brian Keller, post-doc (66%)
e) Teri Larsen, part-time lab assistant (100%)

**Year 3** (4/1/03 - 3/31/04)
a) Timothy K. Minton, Montana State University PI (21%)
b) Donna Garton, graduate student (100%)

## PUBLICATIONS

### Student Theses

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

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

### Journal Articles

**3.** "Temperature-Dependent Morphological Evolution of HOPG Graphite upon Exposure to Hyperthermal $O(^3P)$ Atoms," K. T. Nicholson, T. K. Minton, and S. J. Sibener, *Progress in Organic Coatings* **47**, 443-447 (2003).

**4.** "A Crossed Molecular Beams Study of the $O(^3P) + H_2$ Reaction: Comparison of Excitation Function with Accurate Quantum Reactive Scattering Calculations," D. J. Garton, T. K. Minton, B. Maiti, D. Troya, and G. C. Schatz, *J. Chem. Phys.* **118**, 1585-1588 (2003).

**5.** "Hyperthermal Reactions of $O(^3P)$ with Alkanes: Observation of Novel Reaction Pathways in Crossed-Beams and Theoretical Studies," D. J. Garton, T. K. Minton, D. Troya, R. Pascual, and G. C. Schatz, *J. Phys. Chem. A* **107**, 4583-4587 (2003).

**6.** "Theoretical Studies of the $O(^3P)$ + Ethane Reaction," D. Troya, R. Z. Pascual, D. J. Garton, T. K. Minton, and G. C. Schatz, *J. Phys. Chem. A* **107**, 7161-7169 (2003).

**7.** "Crossed-Beams and Theoretical Studies of the $O(^3P) + CH_4 \rightarrow H + OCH_3$ Reaction Excitation Function," D. Troya, D. J. Garton, T. K. Minton, and G. C. Schatz, *J. Chem. Phys.* **120**, 731-739 (2004).

**8.** "Measurements and Simulations of High Energy $O(^3P)$ + $Ar(^1S)$ Angular Scattering: Single- and Multi-Collision Regimes," M. Braunstein, A. L. Brunsvold, D. J. Garton, and T. K. Minton, *J. Chem. Phys.* **120**, 2238-2246 (2004).

**9.** "Energy Accommodation in Hyperthermal Gas-Surface Collisions: Relevance to Aerobraking in Planetary Atmospheres," T. K. Minton, M. Tagawa, and G. M. Nathanson, *J. Spacecraft and Rockets* **41**, 389-396 (2004).

**10.** "An Investigation of the Resistance of POSS Polyimide to Atomic Oxygen Attack," A. L. Brunsvold, T. K. Minton, I. Gouzman, E. Grossman, and R. I. Gonzalez, *High Perform. Polym.* **16**, 303-318 (2004).

**11.** "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, *High Perform. Polym.* **16**, 197-206 (2004).

**12.** "Crossed-Beams and Theoretical Studies of the Dynamics of Hyperthermal Collisions between Ar and Ethane," A. L. Brunsvold, D. J. Garton, T. K. Minton, D. Troya, and G. C. Schatz, *J. Chem. Phys.*, in press (2004).

**13.** "Spatially Anisotropic Etching of Graphite by Hyperthermal Atomic Oxygen," K. T. Nicholson, T. K. Minton, and S. J. Sibener, *J. Phys. Chem. B*, submitted September 8, 2004.

**Conference Proceedings**

**14.** "Hyperthermal Reactions of Oxygen Atoms with Saturated Hydrocarbons," T. K. Minton, D. J. Garton, and H. Kinoshita, in *Proceedings of the 6th International Conference on Protection of Materials and Structures from the Space Environment*, Toronto, Canada, May 1-3, 2002. (Refereed)

**15.** "Organic-Inorganic Nano-Hybrid Composite as Atomic Oxygen Durable Coating," Y. Huang, J. Liu, I. Ball, and T. K. Minton, in *Proceedings of the 47th International SAMPE Symposium & Exhibition*, Long Beach, CA, May 12-16, 2002.

**16.** "An Investigation of the Resistance of POSS Polyimide to Atomic Oxygen Attack," A. L. Brunsvold, T. K. Minton, I. Gouzman, E. Grossman, and R. I. Gonzalez, in *Proceedings of the 9th International Symposium on Materials in a Space Environment*, Noordwijk, The Netherlands, June 16-20, 2003 (ESA SP-540, September 2003), pp. 153-158.

**17.** "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," T. K. Minton, D. J. Garton, D. Troya, B. Maiti, R. Pascual, and G. C. Schatz, in *Proceedings of the 9th Inter- national Symposium on Materials in a Space Environment*, Noordwijk, The Netherlands, June 16-20, 2003 (ESA SP-540, September 2003), pp. 129-136.

**18.** "Simulations of Ground- and Space-Based Oxygen Atom Experiments," J. A. Cline, D. Buczala, T. K. Minton, and M. Braunstein, in *Proceedings of the 9th International Symposium on Materials in a Space Environment*, Noordwijk, The Netherlands, June 16-20, 2003 (ESA SP-540, September 2003), pp. 481-485.

**19.** "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, in *Proceedings of the 9th International Symposium on Materials in a Space Environment*, Noordwijk, The Netherlands, June 16-20, 2003 (ESA SP-540, September 2003), pp. 107-112.

**20.** "A Study of Atomic Oxygen Interactions with Protected Silver Surfaces," I. Gouzman, E. Grossman, M. Murat, Y. Noter, N. Saar, G. Zilberman, T. K. Minton, D. J. Garton, D. Buczala, and A. Brunsvold, in *Proceedings of the 9th International Symposium on Materials in a Space Environment*, Noordwijk, The Netherlands, June 16-20, 2003 (ESA SP-540, September 2003), pp. 487-492.

**21.** "Synthesis and Atomic Oxygen Erosion Testing of Space-Survivable POSS (Polyhedral Oligomeric Silsesquioxane) Polyimides," R. I. Gonzalez, S. J. Tomczak, T. K. Minton, A. L. Brunsvold, and G. B. Hofland, in *Proceedings of the 9th International Symposium on Materials in a Space Environment*, Noordwijk, The Netherlands, June 16-20, 2003 (ESA SP-540, September 2003), pp. 113-120.

**22.** "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. (Refereed)

**23.** "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.

## INTERACTIONS/TRANSITIONS

**Participation/presentations at meetings, conferences, seminars, etc.**

*Invited talks*

**1.** "Collision-Induced Chemical Processes on a Chlorinated Surface," *221st American Chemical Society National Meeting*, San Diego, CA, April 1-5, 2001.

**2.** "Gas-Surface Scattering Dynamics in Low Earth Orbit: Polymers under Atomic Oxygen Attack," University of Utah, Salt Lake City, April 9, 2001.

**3.** "Gas-Surface Scattering Dynamics in Low Earth Orbit: Polymers under Atomic Oxygen Attack," University of Colorado, Boulder, April 20, 2001.

**4.** "Collision-Induced Chemical Processes on a Chlorinated Silicon Surface," *AFOSR Molecular Dynamics Contractor's Meeting*, Newport Beach, CA, May 21-23, 2001.

**5.** "Hyperthermal Reactions of Oxygen Atoms with Saturated Hydrocarbons," University of Oregon, Eugene, April 15, 2002.

**6.** "Hyperthermal Reactions of Oxygen Atoms with Saturated Hydrocarbons," Oregon State University, Corvallis, April 16, 2002.

**7.** "Reaction Dynamics Relevant to Spacecraft in Low-Earth Orbit: Novel Reactions of $O(^3P)$ with Gaseous and Surface Hydrocarbons," University of Idaho, February 3, 2003.

**8.** "Reaction Dynamics Relevant to Spacecraft in Low-Earth Orbit: Novel Reactions of $O(^3P)$ with Gaseous and Surface Hydrocarbons," Washington State University, February 4, 2003.

**9.** "Hyperthermal Reactions of $O(^3P)$ with $H_2$ and Saturated Hydrocarbons," *AFOSR Molecular Dynamics Contractor's Meeting*, San Diego, CA, May 18-20, 2003.

**10.** "Hyperthermal Reactions of $O(^3P)$ with $H_2$ and Saturated Hydrocarbons," *XX International Symposium on Molecular Beams*, Lisbon, Portugal, June 8-13, 2003.

**11.** "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.

**12.** "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.

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

*Contributed talks*

**14.** "Hyperthermal Reactions of Oxygen Atoms with Saturated Hydrocarbons," *223rd American Chemical Society National Meeting*, Orlando, FL, April 7-11, 2002.

**15.** "Hyperthermal Reactions of Oxygen Atoms with Saturated Hydrocarbons," *6th International Conference on Protection of Materials and Structures from the Space Environment*, Toronto, Canada, May 1-3, 2002.

**16.** "Hyperthermal Reactions of Oxygen Atoms with Saturated Hydrocarbons," *AFOSR MURI Contractors Meeting*, Chicago, IL, June 17-18, 2002.

**17.** "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.

**18.** "Hyperthermal O($^3P$) Interactions: Beam-Source Characterization, Model Reactions with Small Alkanes, and Erosion Resistance of a POSS Polymer," *AFOSR MURI Contractors Meeting*, Pittsburgh, PA, August 19-20, 2003.

*Posters*

**19.** "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. (presented by student)

**20.** "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. (presented by student)

**21.** "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. (presented by student)

**22.** "Crossed-Beams and Beam-Surface Studies of Hyperthermal O($^3P$) Reactions with Saturated Hydrocarbons," D. J. Garton, J. Zhang, and T. K. Minton, *XX International Symposium on Molecular Beams*, Lisbon, Portugal, June 8-13, 2003. (presented by student)

**23.** "An Investigation of the Resistance of POSS Polyimide to Atomic Oxygen Attack," A. L. Brunsvold, T. K. Minton, I. Gouzman, E. Grossman, and R. I. Gonzalez, *AFOSR MURI Contractors Meeting*, Pittsburgh, PA, August 19-20, 2003. (presented by student)

**24.** "Crossed-Beams and Theoretical Studies of Hyperthermal Reactions of O($^3P$) with $H_2$, $CH_4$, $C_2H_6$, and $C_3H_8$," D. J. Garton, T. K. Minton, D. Troya, B. Maiti, R. Pascual, and G. C. Schatz, *AFOSR MURI Contractors Meeting*, Pittsburgh, PA, August 19-20, 2003. (presented by student)

**25.** "Reactive and Inelastic Scattering Dynamics of Hyperthermal Oxygen Atoms on a Saturated Hydrocarbon Surface," D. J. Garton, J. Zhang, and T. K. Minton, *AFOSR MURI Contractors Meeting*, Pittsburgh, PA, August 19-20, 2003. (presented by student)

**26.** "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)

**Consultative and advisory functions**

*Prof. Masahito Tagawa, Kobe University, Japan*. Prof. Tagawa is the key person in Japan who is studying space environmental effects. He and the PI have collaborated closely on a study of gas-surface energy transfer when energetic $CO_2$ molecules and Ar atoms strike various surfaces. Energy transfer of fast species with surfaces is very important to drag on spacecraft in planetary orbits and for etching of materials in certain environments. The collaboration with Prof. Tagawa led to a post-doc (Hiroshi Kinoshita) from his lab coming to work in the PI's lab for 1 and 1/2 years. Dr.

Kinoshita worked on projects related to the AFOSR grant, although all his funding came from a Japanese scholarship.

*Prof. Gilbert Nathanson, University of Wisconsin*. Prof. Nathanson collaborated with the PI (and Prof. Tagawa, see above) on a study of gas-surface energy transfer when energetic $CO_2$ molecules and Ar atoms strike various surfaces.

*Chemat Technology, Northridge, CA*. The work of the PI on atomic oxygen interactions with polymer surfaces attracted Chemat Technology to collaborate with the PI. Chemat received a NASA SBIR for the development of atomic-oxygen-resistant coatings. These coatings involved the incorporation of silica nanoparticles into silicones. Chemat provided token funding for the PI to test these coatings in his lab. One of the coatings performed exceptionally well, as it showed no erosion upon atomic-oxygen exposure and did not crack or discolor. The results were published as a proceedings paper (#**15** above).

*MURI Center for Materials Chemistry in the Space Environment*. The work supported by AFOSR on this grant has used scientific and financial leverage from an AFOSR-funded MURI center whose focus is on materials degradation in the space environment. The PI is a member of this MURI center that also includes the following people:

Prof. Steven Sibener, University of Chicago (collaborator on HOPG work)
Prof. Luping Yu, University of Chicago
Prof. Dennis Jacobs, Notre Dame University
Prof. George Schatz, Northwestern University (collaborator on O + $H_2$/alkane work)
Prof. John Tully, Yale University
Prof. Barbara Garrison, Penn State University
Prof. Bill Hase, Wayne State University

*Capt. Rene Gonzalez/Dr. Sandra Tomczak, AFRL, Edwards AFB*. Capt. Gonzalez provided samples of POSS polymers to our lab, and we investigated the resistance of these polymers to atomic oxygen attack. Capt. Gonzalez has left AFRL, and the new contact person is Sandra Tomczak, who has prepared a new set of POSS polyimides for further studies of the interaction mechanisms between these materials and hyperthermal O atoms.

*Prof. Judy Yang, University of Pittsburgh*. The PI has conducted sample exposures of semiconductors and metals for Prof. Yang, and she has done analysis with transmission electron microscopy (TEM). Prof. Yang is now preparing to conduct TEM analysis of exposed and unexposed control and POSS polyimide samples, in order to learn more about the structural changes at the surfaces of these materials upon exposure to hyperthermal O atoms.

*Dr. Matt Braunstein, Spectral Sciences, Inc.* Dr. Braunstein is an expert on modeling rocket plume phenomenology. Experiments have been conducted in the PI's lab that help validate the direct simulation Monte Carlo (DSMC) code that has been developed by Dr. Braunstein and his colleagues.

*Dr. Stéphanie Remaury, Centre National des Etudes Spatiales, Toulouse, France*. The PI conducted exposures of samples of candidate thermal control paints 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 traveled to the PI's lab in order to conduct O-atom exposures of protective coatings, and during their visit, they assisted in the setup of an atomic force microscope and in the analysis of exposed POSS-containing samples.

*Dr. Rainer Dressler, AFRL, Hanscom AFB*. The PI provided input to Dr. Dressler who was helping update the MCTL on space survivability.

*Dr. Jacob Kleiman, Integrity Testing Laboratory, Toronto, Canada*. Dr. Kleiman owns a small company that does many types of materials testing. Dr. Kleiman and the PI have had many informal discussions about O-atom sources and about the best way to simulate space environmental effects.

*Dr. Gary Pippin, Boeing Phantom Works, Seattle*. 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 polymer samples to Dr. Pippin for future experiments and is also helping him plan for additional flight experiments.

**Transitions**

*Dr. John Golden (Boeing Defense Systems, Houston)*. Nothing concrete yet; however, discussions are underway with Dr. Golden to conduct collaborative research and development that will lead to eventual replacement of Kapton and carbon fiber reinforced epoxy materials on the space station solar panels with new O-atom-resistant POSS materials.

*Dr. Sandra Tomczak (AFRL, Edwards AFB)*. Dr. Tomczak has recently become manager of a project for DARPA to investigate the use of POSS polyimides to support antennas in low-Earth orbit. The PI is working on this project to conduct O-atom testing on new POSS polyimides that are being developed as part of this program.

*Center for Laboratory Studies of Rocket Plume Chemistry*. The work done in the PI's lab, largely as part of this grant, has attracted the attention of various researchers who are working on rocket plume chemistry relevant to missile defense. Following many discussions with members of this community, the PI submitted a proposal to Senator Conrad Burns (Montana), who obtained a Congressional appropriation that will enable the PI to establish a center at Montana State University for the study of rocket plume chemistry. This center will enhance research infrastructure at Montana State University and should lead to experimental data that will aid in modeling efforts for the Missile Defense Agency.

## NEW DISCOVERIES, INVENTIONS, OR PATENT DISCLOSURES

• POSS-containing polyimide (20 wt%) erodes at a rate as low as 1% that of Kapton when subjected to hyperthermal atomic oxygen attack. This result suggests promise for POSS Kapton as a drop-in replacement for Kapton on spacecraft in low-Earth orbit.

• The laser detonation atomic oxygen beam source that is commonly used to simulate space environmental effects has been proven to contain oxygen atoms only in the ground $O(^3P)$ state. Therefore, this source may be used with confidence to create an environment in which the effect of hyperthermal O atoms reflects interactions involving ground-state O atoms.

• The molecular oxygen in the beam produced from the laser detonation source is in the ground $O_2(^3\Sigma_g^-)$ state, as opposed to the $O_2(^1\Delta_g)$ state. This result is important for the accurate simulation of space environmental effects, because ground-state $O_2$ is much less reactive that excited-state $O_2$.

• The reaction, $O(^3P) + CH_4 \rightarrow OCH_3 + H$, has a barrier of 2 eV and proceeds on the ground and first excited triplet surfaces, with no crossing to the singlet surface, which has a lower barrier.

• The investigations into hyperthermal O-atom reactions with $H_2$ and $CH_4$ have indicated that intersystem crossing (i.e., involvement of the excited singlet potential energy surface) is not significant even though it is clearly possible at the collision energies employed.

• $O(^3P)$ reactions with alkanes at hyperthermal collision energies (1.5 - 3.9 eV) results in the occurrence of a number of reactions, including $S_N2$-like reactions, that have never been observed before in studies of the dynamics of $O(^3P)$ reactions with alkane molecules.

• At relatively low sample temperatures, deep cylindrical etch pits were observed in the surface of highly ordered pyrolytic graphite that was exposed to a beam of hyperthermal atomic oxygen. But at high temperatures, the eroded surfaces showed random roughness. The occurrence of circular etch pits that are many atomic layers deep has not been observed in the oxidation of HOPG with molecular oxygen or even with thermal atomic oxygen.

• Collisions of hyperthermal Ar atoms with ethane can lead to very large energy transfers to the ethane molecule, suggesting the possibility that hyperthermal (5-10 eV) collisions with gas-phase molecules and with polymer surfaces might lead to bond breakage by 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.

• A systematic set of exposures 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°C), the erosion of both materials appeared to be independent of sample

temperature. But above 100°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.

## HONORS/AWARDS

**a) awards received during grant period**

Charles and Nora L. Wiley Faculty Award for Meritorious Research, May 2002

Air Force Research Laboratory, In-House Project of the Quarter: "Space-Survivable Polymers Containing Polyhedral Oligomeric Silsesquioxanes (POSS)", Fall 2002

**b) lifetime achievement honors**

Aurora Illinois Foundation Undergraduate Scholarship, 1976-80

University of Illinois Summer Fellowship, 1979

NASA Award for a Technological Contribution, 1995

MSU Alumni/Bozeman Chamber of Commerce Excellence Award, 1996

Charles and Nora L. Wiley Faculty Award for Meritorious Research, May 2002

Air Force Research Laboratory, In-House Project of the Quarter: "Space-Survivable Polymers Containing Polyhedral Oligomeric Silsesquioxanes (POSS)", Fall 2002

Visiting Associate Professor at the James Franck Institute, University of Chicago, Summer 2004