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19. ABSTRACT (Continue on reverse if necessary and identify by block number) A central goal of AFOSR sponsored University Research Initiative Program at Vanderbilt University has been to establish a multidisciplinary Center of Excellence concentrating on the atomic-scale dynamics of surface reactions in the space environment. The major research focus of the URI has been the investigation of the ways in which energy deposited by incident atoms, ions, electrons and shortwavelength photons is absorbed and localized to produce bond-making and bond-breaking on surfaces and in the near-surface bulk. Knowledge of these microscopic mechanisms provides detailed clues which lead to an understanding of the macroscopic processes which manifest themselves as surface erosion, modification and damage. This research program bears directly on a broad spectrum of questions germane to the long-term operation of platforms in space, including long-term structural, optical and electronic degradation of materials in the ambient near-earth environment, survivability under and hardening against irradiation from directed-energy weapons, vulnerability in disturbed nuclear atmospheres, and discrimination and sensing techniques based on characteristic radiation (glow) signatures. Significant, and in some cases, startling progress has been made in carrying out the research goals of this effort.			
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FINAL REPORT

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SURFACE REACTIONS IN THE SPACE ENVIRONMENT

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Department of Physics and Astronomy, and Department of Chemistry
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1. INTRODUCTION

A central goal of AFOSR sponsored University Research Initiative Program at Vanderbilt University has been to establish a multidisciplinary Center of Excellence concentrating on the atomic-scale dynamics of surface reactions in the space environment. The major research focus of the URI has been the investigation of the ways in which energy deposited by incident atoms, ions, electrons and shortwavelength photons is absorbed and localized to produce bond-making and bond-breaking on surfaces and in the near-surface bulk. Knowledge of these microscopic mechanisms provides detailed clues which lead to an understanding of the macroscopic processes which manifest themselves as surface erosion, modification and damage. This research program bears directly on a broad spectrum of questions germane to the long-term operation of platforms in space, including long-term structural, optical and electronic degradation of materials in the ambient near-earth environment, survivability under and hardening against irradiation from directed-energy weapons, vulnerability in disturbed nuclear atmospheres, and discrimination and sensing techniques based on characteristic radiation (glow) signatures. The following is a final report of progress in this effort under the URI program.

2. RESEARCH OBJECTIVES AND STATUS OF THE RESEARCH EFFORT

2.1 Scientific Background and Project Summary

The AFOSR sponsored surface physics and chemistry research performed at the Vanderbilt Center for Atomic and Molecular Physics at Surfaces (CAMPS) has emphasized studies of the atomic-scale dynamics of surface reactions in the space environment. We have focused on the ways in which energy deposited by incident atoms, ions, electrons and short-wavelength photons is absorbed and localized to create excitations and make and break bonds on surfaces. Knowledge of these microscopic mechanisms provides detailed clues to the macroscopic processes which manifest themselves as surface erosion, spacecraft glow, surface modification and damage.

Much of scientific and technological significance has been accomplished during the three years of AFOSR/URI support. In particular, we have studied neutral-particle desorption and glow induced by electronic transitions arising from low-energy photon, electron and heavy-particle irradiation of a wide variety of materials. These studies have highlighted the pivotal role of electronically-induced defects and surface states in these phenomena. Substantial theoretical progress has been made for example in calculating particle-surface electron exchange rates at surfaces and in characterizing surface states with the aid of cluster calculations. Finally, fundamental studies of charge-exchange processes

at surfaces have led to the development of the first pure, variable-energy neutral and ionic atomic and molecular beam in the world. Because neutral atomic oxygen and molecular nitrogen are primary constituents of the ambient orbital environment, the availability of low energy oxygen and nitrogen beams open the door to experiments on the effects both of individual irradiation modes and of synergistic effects from the total radiation environment.

The research we have carried out is based on a multidisciplinary approach to surface reactions induced by energetic ions, atoms, photons and electrons, and is at the frontiers of fundamental scientific understanding relevant to critical national needs. The facilities acquired through the URI program has proved to be an excellent base for carrying out the program. This broad approach to surface reaction phenomena using a wide variety of instrumental techniques has provided unique opportunities to train graduate students with the broad perspectives and experience needed to meet the scientific and technological challenges posed by the rapid development of large space-borne manned and unmanned systems.

An important part of our research effort has been to elucidate the atomic-scale dynamics governing glow and erosion processes under irradiation by neutral and ionic oxygen and nitrogen, ultraviolet photons and plasma electrons in the low-earth-orbit (LEO) environment. Important progress has been made in accomplishing that goal. Under this program, pioneering work has been performed at Vanderbilt involving the fundamental microphysics of energy-transfer processes at surfaces, of optical damage in wide-band-gap dielectrics, and of the creation of variable-energy beams of neutral and ionic atoms and molecules. Long-term effective structural and functional operation of space platforms requires a quantum leap in our understanding of surface reactions in the LEO environment. For example, spacecraft glow is an important LEO phenomena. Above 180 km, glow intensity from the atmospheric explorer satellite scales directly as the concentration of atomic oxygen. Below about 160 km, the concentration of molecular nitrogen plays a major role. In the erosion case, evidence from the SolarMax satellite strongly suggests that solar ultraviolet radiation, energetic electrons as well as heavy particles can cause significant synergistic damage perhaps associated with photophysical and photochemical surface reactions. Furthermore, electronic charge-transfer processes determining final states in surface reactions are clearly a major contributing element in the complicated phenomenology of spacecraft charging, multiple surface collision effects and plasma processes. In addition to these long-term threats to the structural, electronic and optical integrity of spacecraft and space-borne sensors from the ambient environment, there is almost no detailed information about the unprecedented and largely unknown insults which can be inflicted on spacecraft either from directed-energy weapons or in a disturbed nuclear environment.

The phenomena occurring at the surfaces of spacecraft, in addition to glow, covers all the variations of desorption: desorption induced by electronic transitions (DIET), desorption arising from momentum exchange (sputtering), and "chemical" sputtering (another variant of DIET) in which the energy necessary for desorption is supplied by surface chemical reactions. Moreover, the energies of interest range from thermal to those of the primary radiation sources (a strong function of altitude). In the case of fast atoms and molecules, the energy scale is set by the velocity of the spacecraft and corresponds to collisions at approximately 5 eV of atomic oxygen and 10 eV for molecular nitrogen-- high enough to initiate DIET processes and still within range of "chemical" interactions. The meaningful sources in surface reactions include:

- neutral atomic oxygen and molecular nitrogen, metastable and ground state, 5 to 10 eV typical energy

- ultraviolet radiation and electrons ranging from a few to many hundreds of eV
- transient incursions of energetic ions (H and He, for example).

These radiation sources inflict varying degrees of mischief. These effects depend on how well and in what form the material supports the creation of localized electronic excitations which relax to form permanent defects. The clues to the dynamical process include photons, electrons, scattered ions or atoms, and substrate particles which have been desorbed from the surface.

Our prior experimental research has focussed on a carefully chosen number of topics including low-energy atomic and ionic oxygen interactions on surfaces, desorption of atomic hydrogen from surfaces, neutralization processes at surfaces, and the role of overlayers and dopants in energy partitioning. Companion theoretical studies have treated nonadiabatic neutralization at surfaces, lifetimes of excited hydrogen and alkali atoms near surfaces, electronic transitions in gas-surface dynamics, and lattice stabilization of excited electronic states of the imbedded pseudo-halogen CN^- .

Our experimental and theoretical research program has been concerned with ultraviolet photon-, neutral particle- and electron-induced electronic processes and has produced significant results of a fundamental nature as described below:

- the first observations of photon stimulated *resonant* bond breaking resulting in the desorption of neutral atoms and molecules;
- the first measurements of the effect of submonolayer contaminants (oxygen and lithium) on electron transfer processes at a metal crystal surface;
- the first measurements of glow spectra arising from variable energy (4 eV to 2 keV) oxygen and nitrogen ion beams;
- the first observations of desorbed excited neutral CN molecules showing anomalous vibrational/rotational distributions from insulator surfaces;
- the first theoretical calculations of the energy shifts and lifetimes of hydrogen-atom excited states in the vicinity of a jellium surface.
- the first theoretical structure calculations for excited electronic states of CN^- in an alkali halide matrix.
- first measurements correlating exciton formation, secondary electron emission and excited state atom desorption.
- the development of a simple theoretical method incorporating electrostatic forces into the extended Huckel scheme applied to ionic systems.
- first measurements elucidating the role of the $Al(2p)$ creation in the ion induced desorption of excited state aluminum atoms

It is clear that the study of desorbed neutrals is essential to a comprehensive understanding of the desorption process itself, as well as of the static and dynamic properties of the surface chemical bond. As a collateral benefit, this more complete

characterization of the bond-breaking processes illuminate potential uses of desorption spectroscopy as an analytical probe both of surface structure and dynamics.

Research performed under this program have made a major impact on the DoD and NASA communities. This is attested to by the fact that two of our graduate students have received NASA fellowships and that either through consulting agreements or through contracts we have received funding from the following organizations: the Institute for Defense Analysis, Wright Patterson Air Force Base, the Acurex Corporation, the Army Strategic Defense Command, Lockheed Missiles and Space Company, S-Cubed, NASA/MSFC, Naval Research Laboratories, Sandia National Laboratories, and Los Alamos National Laboratory.

The work we have carried out, involves both experimental and theoretical studies of the microscopic mechanisms by which surface reactions in the LEO environment lead to erosion, glow, surface modification, and macroscopic damage. As a result of this program we have come closer to our goal to microscopically characterize the interactions of oxygen, nitrogen, electrons and photons with matter.

2.2 Low-Energy Beam-Surface Interactions

2.2.1 Low-energy oxygen and nitrogen collisions with surfaces

Senior Investigators: Albridge (PI), Barnes, Benit, Tolk and Tully
Graduate Students: Qi, Albert

Erosion and glow greatly impede the useful operation and shorten the lifetime of spacecraft in low earth orbit.^{1,2} Attempts to understand, and to eventually control, these macroscopic phenomena require a detailed understanding of the microscopic processes that underlie them; and this detailed understanding must in part rely on laboratory data taken under carefully-controlled ultra high vacuum conditions. Because the environment of the low earth orbit is rich in neutrals and ions,³ laboratory observations of the effects of low-energy atom, molecular and ion beams on surfaces comprise an important subset of the required data. Sufficiently detailed studies can provide information regarding the transfer, storage and redistribution of energy which is brought to the surface and ultimately manifests itself as glow or as the kinetic energy of eroding particles.⁴

Our studies have involved the detection and characterization of species that are eroded from surfaces by atom, molecule, ion, electron or photon irradiation by optical and mass spectrographic techniques.⁵ Thus our primary data relate to individual atomic and molecular processes; and we intend to build a general model of how these processes give rise to damage, erosion and glow.

The desorption of particles from surfaces may occur via *sputtering processes*, which involve a significant transfer of momentum from the bombarding particle to the surface; and via *electronic interactions*, which involve the breaking of electronic bonds and the creation of solid-state defects. At the low energies (~5 eV) of importance to the space environment, desorption induced by electronic transitions (DIET) should be the predominant mode of erosion; and we have seen definite indications of DIET processes in the desorption of excited neutral atoms caused by low-energy ion bombardment.

During the past two and a half years we have constructed a new dedicated low-energy ion source and have used it to study desorption from an Al(Li) alloy. The source delivers ion beams over the energy range from 4 to 5000 eV with significant current and will be used as the basis of our already developed neutral beam source.⁶ We have used the

ion source to systematically study fluorescence due to beam-induced erosion from the oxide layer of an Al(Li) alloy under bombardment by different ionic species. (Because of their low densities, Al(Li) alloys have potential use in structural components of low-orbit spacecraft.) Using ion beams of O, N, N₂, He, Ne, Ar, Kr and Xe we have carefully studied the energy dependences of the strongest line emissions of excited Al* and Li* desorbing from the oxide layer of the alloy surface. In all cases studied the emission spectrum consists of a low, broad and diffuse spectrum on which is superimposed intense emission lines from the desorbing excited Li* and Al*.

The data for Al* are shown in Figure 1a. An interesting and meaningful contrast to this figure is shown in Figure 1b in which the beam energies are referred to the center of mass of the beam-aluminum system. Here a much simpler picture emerges. There is a threshold at an energy of ~75 eV for all but the heaviest of the bombarding species. This energy is the binding energy of the 2p core level in the aluminum atom. Obviously this level plays a central role in the production of the desorbing excited aluminum atoms. The center of mass scaling of this feature allows us to associate it directly with the energy absorption step. Varying the bombarding ion species allows us to unambiguously recognize the process responsible for the initial energy deposition.

Fig. 1a

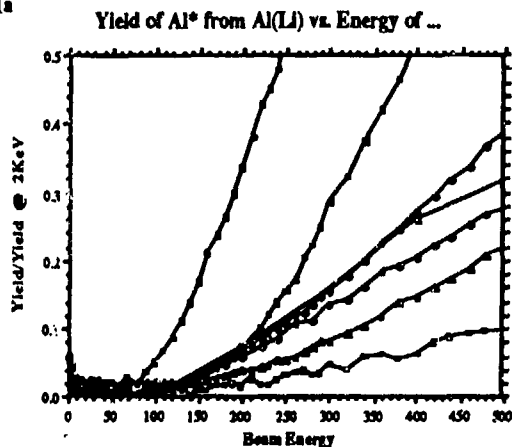
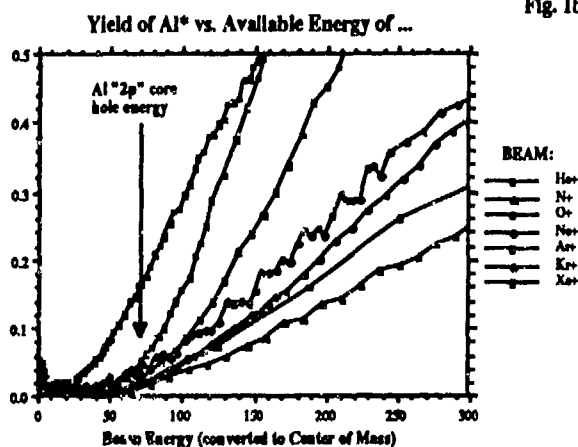


Fig. 1b



The data for the Li* desorption are shown in Figure 2a and once again a meaningful contrast is obtained when the beam energy is determined in the center of mass system (the beam-lithium C of M), as shown in Figure 2b. There is a distinct threshold at ~5.5 eV, which is close to the lithium ionization energy.

Fig. 2a

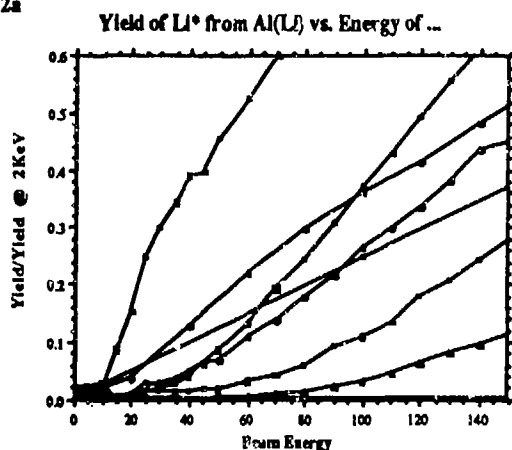
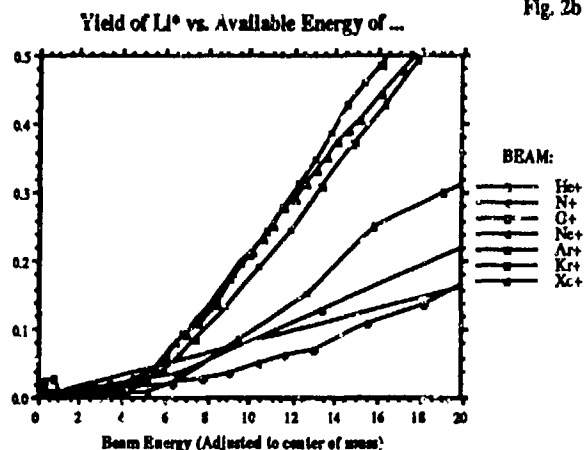


Fig. 2b



These energy-dependent data clearly indicate that the desorption processes are mediated by electronic transitions, and that the processes producing line emission are probably related to the processes producing desorption. This work illustrates how the optical spectra of particles ejected from surfaces as a result of particle bombardment can provide detailed information regarding the atomic-scale processes that mediate particle desorption (erosion) and light emission (glow).

- 1 A.F. Whitaker et al., Proceedings of the AIAA 23rd Aerospace Sciences Meeting, AIAA 85-0416, (1985)
- 2 H.B. Garrett, A. Chutjian, and S. Gabriel, preprint submitted to Journal of Spacecraft and Rockets, in press.
- 3 L.J. Leger, J.T. Visentine, and J.A. Schliesing, in Proceedings of the AIAA 23rd Aerospace Sciences Meeting: AIAA-85-0476, (1985).
- 4 R.F. Haglund et al., Nucl. Instrum. Methods in Phys. Res. B13, 525 (1986).
- 5 R.G. Albridge, R.F. Haglund, Jr., L.T. Hudson and N.H. Tolk, Vuoto 16, 67 (1986)
- 6 R.G. Albridge et al., Nucl. Instr. Methods in Phys. Res. B18, 582 (1987); C.L. Johnson et al., SAMPE Quarterly 18, 35 (1987)

2.2.2 Grazing-incidence neutralization

Senior Investigators: Tolk(PI), Albridge, Nordlander, Russell, Tully
 Graduate Students: Savundararaj, Harper

The study of the interaction of ions with solid surfaces is very important as it gives insight into the fundamental electronic transfer processes at a surface. Scattering energetic ions from solid surfaces at a grazing angle is a special case of ion-surface interaction, and is of particular interest to surface studies as was first reported by Andr ¹. The grazing-incidence geometry results in less penetration into the bulk, hence has increased surface sensitiveness and less damage to the surface under study. A second advantage of this configuration is that it provides for increased probability for interaction with the surface atoms.

From our results² it can be seen that adsorbing an overlayer of oxygen on the nickel surface decreases the orientation of the excited levels, but the alignment of the states are not affected correspondingly. The significance of these results are currently being investigated

further. Also we have to modify our model used in the calculations so that the results of M/I and C/I also agree with the experiments.

We have a new technique for studying the interaction of ions with metal surfaces and also of overlayers on the surface. It has been demonstrated³ that the condition of the surface has effect on the polarization and quantum beats indicating that the changes in the electronic structure of the surface can be studied by this method. We are also in the process of adsorbing other overlayers onto different metal surfaces and studying the effects mentioned above.

¹ H.J. Andr , Phys. Lett. 54A (1975) 315.

² P.M. Savundararaj, R.G. Albridge, D.L. Harper, D.P. Russell and N.H. Tolk, Nucl. Instr. and Meth. in Phys. Res. B40/41 (1989) 262-265.

³ J.C. Tully, N.H. Tolk, J.S. Kraus, C. Rau and R.J. Morris, in : *Inelastic Particle-Surface Collisions*, eds., E. Taglauer and W. Heiland (Springer-Verlag, Berlin, 1981) p. 196.

2.2.3 Beam-tilted-foil neutralization

Senior Investigators: Tolk(PI), Albridge, Nordlander, Russell, Tully
Graduate Students: Harper, Savundararaj

The transmission of ions through thin foils has been studied extensively for quite some time. Andr ¹ first showed that aligned atomic states are produced following the transmission of ions through thin foils at normal incidence. Reducing the symmetry of the beam-foil interaction by tilting the foil with respect to the beam induces an orientation of the final atomic states.² We have extended these early studies to determine the influence of adsorbates on the final states of the beam-tilted-foil interaction in order to better understand the mechanisms involved in the electron-exchange that leads to the neutralization of the beam.

In an ultra-high vacuum environment, a momentum-analyzed proton beam, in the 10 to 50 keV energy range, strikes a very thin amorphous carbon foil. Many of the emerging protons capture an electron from the foil, resulting in the formation of excited hydrogen atoms. Due to the anisotropic distribution of electrons available to the proton in the impulsive beam-foil interaction, the excited state will have an anisotropic distribution of electrons in its magnetic sublevels. The reduced symmetry of the beam-foil interaction will be manifest in the polarization of the light emitted as the hydrogen atom decays to a lower energy state. The polarization of the de-excitation radiation, quantified by a measurement of the relative stokes parameters³ (M/I, C/I, and S/I), is directly related to the distribution of electrons in the magnetic sublevels of the final excited state.

Our preliminary work^{4,5} suggests that the presence of overlayers on the foil exit surface plays a crucial role in the proton-foil electron-exchange interaction. The determination of the final excited states depends strongly on the local electronic environment on the exit surface of the foil. This dependence is demonstrated by the dramatic changes in the polarization of the light emitted by the foil-excited hydrogen atoms which result from applying a few Angstroms of sodium or lithium to the foil exit surface. Further experimental and theoretical studies are necessary in order to quantify the effects of overlayers on the proton-foil interaction and to develop models which describe the mechanisms that lead to the observed final states. These models must include both the electron-capture process at the surface and the evolution of the excited state through the post-capture region.

- ¹ H.J. Andra, "Zero-Field Quantum Beats Subsequent to Beam-Foil Excitation", *Physical Review Letters*, 25(6), 325-7 (1970).
- ² H.G. Berry, L.J. Curtis, D.G. Ellis, and R.M. Schectman, "Anisotropy in the Beam-Foil Light Source", *Physical Review Letters*, 32(14), 751-4 (1974).
- ³ Clarke D. and Grainger J. F., *Polarized Light and Optical Measurement*, Pergamon Press, Oxford (1971).
- ⁴ D.P. Russell, R.G. Albridge, A.V. Barnes, D.L. Harper, P. Nordlander, P.M. Savundararaj, and N.H. Tolk, "Dependence of Alignment and Orientation Induced by Grazing-Incidence and Beam-Foil Electron-Exchange Interactions on Surface Electronic Structure", *Surface Science*, 211/212, 198-206 (1989).
- ⁵ D.L. Harper, R.G. Albridge, D.P. Russell, P.M. Savundararaj, and N.H. Tolk, "The Influence of Adsorbates on Proton Neutralization at Surfaces in a Transmission Geometry", proceedings of the Fourth Annual AFOSR Workshop on Surface Reactions in the Space Environment, Northwestern University, Evanston, IL, (1989).

2.2.4 Status of the photodetachment neutral oxygen beam source

Senior Investigators: Haglund(PI), Becker
Graduate Students: Bunton

Spacecraft surfaces in low-earth orbit experience both erosion and glow due to interactions with the ramming atmosphere. After years of study the mechanisms leading to these processes remain uncertain, although possible explanations have been considered.¹ As atomic oxygen is the primary constituent at low-earth orbital altitudes, most of the laboratory efforts at understanding erosion and glow have concentrated on the production of an oxygen source that is in some way representative of the environment of an orbiting spacecraft. To exactly simulate the oxygen flux alone is a formidable task due to the high flux (of order 10^{15} atoms/cm²/sec.) and low energy of 5 eV. All sources (with the possible exception of the photodetachment source at the Jet Propulsion Laboratory²) fall short in some area such as beam energy, flux or purity of beam. This is of course true of the source to be described here, also. It is not our intention to simulate the environment of space but rather to produce a well-characterized atomic oxygen beam of sufficient intensity to perform mechanistic studies of damage to and fluorescence from surfaces. We will use the tools of optical spectroscopy to monitor fluorescence and excited state atom desorption. We also intend to compare electron, ion, and neutral yields from both model and actual spacecraft materials. It is our hope that such knowledge will enable us to relate the macroscopic processes of damage to such microscopic processes as defect formation and diffusion.

Our atomic oxygen source is based on the photodetachment of the electron from O⁻. One produces a beam of low energy negative ions which are then accelerated (or decelerated) to the desired energy. Afterwards a laser is used to neutralize the beam. The primary advantage of this technique is that it allows for some control over the final state of the atoms. The threshold for photodetachment of O⁻ is 1.47 eV. In the photon energy range of 1.47 to 3.43 eV only ³P ground atoms can result from photodetachment. Above 3.43 eV some atoms will be in the ¹D, first excited state.³ Both the 514.5 nm and the 488.0 nm argon-ion laser lines fall in the range for exclusive production of ground-state atoms. There are two immediate disadvantages. The first is that the cross section for photodetachment is extremely small with the result that only a small percentage of the ions can be neutralized.³ Second, it is generally more difficult to produce negative ions than positive.

The negative ions are produced by the dissociative attachment of nitric oxide. Nitric oxide has a dissociative attachment cross section of $0.0127\pi a_0^2$ (a_0 is the Bohr radius of 0.529 Å) at a relatively high resonance energy of 8 eV.⁴ A barium-oxide coated Pt-Ir filament supplies the electrons for the dissociative attachment. A pair of grids provide a field free region for production of ions at constant potential. Two apertures provide extraction and collimation. After extraction the ions are focused by an einzel lens. This lens is in a six-way cross which was specially constructed with one port at a five degree angle. This allows most of the neutrals from the source to be removed when the ions are deflected by the following deflection plates. The cross is pumped by an Edwards 300 liter/second baffled Diffstak type diffusion pump. The ions are deflected into a second einzel lens which focuses them into a velocity selector (Colutron Wien filter). The velocity selector is followed by a differential pumping aperture and then a third lens for focusing the ions between a pair of plane-parallel mirrors for photodetachment. This lens is contained in a second six-way cross pumped by another 300 liter/second diffstak. After the mirrors, deflection plates remove surviving ions prior to target or current collector. All of the apparatus is assembled excepting the mirrors and the final deflection plates. The mirrors were purchased from Newport Corporation and are coated for reflectivity of greater than 99% for both the strong blue and green argon-ion laser lines. A grid will be placed at the entrance to the photodetachment region providing for deceleration of the ions to the desired energy just prior to neutralization. Ions can be transported and mass selected at higher energy (of order 100 to 300 volts) where the space-charge limited current is greater. Eventually a third cross will need to be added to provide more differential pumping prior to the target chamber.

At this time both positive and negative ions have been extracted with the source acting in discharge mode. Without mass selection, positive currents of 150 nA at 300 V have been extracted which have been sufficient for observation of excited neutral lithium atoms from lithium-aluminum alloy⁵. Negative currents have been smaller. The source will be optimized for negative ions after the mass selection is working properly.

- ¹ B. D. Green, *Proceedings of the Fourth European Symposium on Spacecraft Materials in Space Environment*, Centre d'Etudes et de Recherches de Toulouse, Toulouse, France, 477 (6-9 Sept. 1988). B. D. Green, *et al*, *Planet. Space Sci.*, 34, No. 9, 879-887 (1986); I. L. Kofsky and J. L. Barrett, *Planet. Space Sci.*, 34, No. 8, 665-681 (1986); T. G. Slanger, *Geophys. Res. Lett.* 13, No. 5 431-433 (1986); B. D. Green, *Geophys. Res. Lett.* 11, No. 6, 576-579 (June, 1984).
- ² E. Chutjian, Fourth Annual AFOSR Workshop on Surface Reactions in the Space Environment, Northwestern University, Evanston, IL, 1989.
- ³ L. M. Branscomb, S. J. Smith and G. Tisone, *J. Chem. Phys.* 43, 2906 (1965).
- ⁴ D. Rapp and D. D. Briglia, *J. Chem. Phys.* 43 5, 1480 (1965).
- ⁵ P. Bunton, Fourth Annual AFOSR Workshop on Surface Reactions in the Space Environment, Northwestern University, Evanston, IL, 1989.

2.2.5 Theory of Alkali Atom Neutralization in Ion-Surface Scattering

Senior Investigators: Nordlander, Tully

Recent first principle calculations of the broadening of atomic levels near surfaces have shown that such lifetimes can be very long. We discussed¹ the qualitative consequences of this on the interpretation of neutralization processes in ion-surface collisions, and introduced a new model for charge transfer at surfaces. An application to a recent ion surface neutralization experiment showed good agreement between theory and experiment.

Our finding of long lifetimes of excited atomic levels near metal surfaces has important implications for the interpretation of ion-surface scattering experiments. In particular, the so-called "memory term" cannot be neglected in high energy ion surface collisions. In addition, charge transfer processes will only be probable close to the metal surface where impurity induced electrostatic fields will introduce a lateral corrugation in the shifts of the atomic levels. We have shown that the presence of such a laterally varying electrostatic potential has approximately the same effect on the neutralization efficiency in ion-surface scattering as an increased surface temperature, and therefore can conveniently be included in the finite temperature charge transfer formalism introduced by Geerlings.²

¹ P. Nordlander, J.C. Tully, to appear in Surf. Sci. (1989)

² J. J. C. Geerlings, J. Los, J. P. Gauyacq and N. M. Temme, Surf. Sci. 172 (1986) 257.

2.3 Desorption Induced by Electronic Transitions

2.3.1 Desorption of Atomic Hydrogen from Alkali Metal-Rich Surfaces

Senior Investigators: Tolk (PI), Barnes, Nordlander, Hudson, Russell

In a recent paper¹ submitted to *Physical Review Letters* we reported on first measurements of energy and temperature dependent desorption yields of neutral atomic hydrogen from a surface by photon bombardment. These photon-stimulated desorption (PSD) experiments elucidate the fundamental interactions of hydrogen with alkali metal-rich surfaces. New insights include the preconditions for room temperature hydrogen adsorption, the character of the hydrogen-surface bond, and the wavelength selective mechanism of desorption.

Parks *et al.* have monitored the emission of H^+ from alkali fluorides under photon bombardment.² They postulated that hydrogen, as an intrinsic impurity, was photon activated in the bulk, migrated to the surface, formed a bond with an alkali atom and finally desorbed due to a photon-induced core excitation followed by Auger decay. In contrast, our measurements of the desorption of neutral hydrogen atoms exhibit very different character. The first observation of PSD of H^* from alkali halide surfaces³ required continuous dosing of the surface with gaseous H_2 . To understand the processes leading to the stimulated emission of H^* we have measured these yields from an array of alkali halide surfaces as a function of incident photon energy and sample temperature. A measurement was also performed on an alkali-dosed glass surface which gave identical results. We conclude that a direct wavelength dependent desorption mechanism, not mediated by the bulk, is involved in the photon-stimulated emission of neutral, excited-state hydrogen from these systems, *viz.* a resonant Franck-Condon excitation to neutral dissociative levels of surface alkali hydride molecules.

The temperature and energy dependent results we presented suggest that alkali halide surfaces are initially inert to gaseous H_2 , but as radiation damage produces surface metallization, it is rendered vulnerable to adsorption, dissociatively, and alkali hydride formation. The desorption mechanism postulated here which leads to the emission of neutral hydrogen atoms, namely a direct MGR excitation to a neutral, dissociative state of the surface alkali hydride, is consistent with the energy, shape and width of the observed resonant thresholds and recent theoretical findings⁴ of long-lived antibonding $H^*(n=3)$ states.

¹ L.T. Hudson, A. V. Barnes, J. L. Rose, and N. H. Tolk, "Photon-Stimulated Desorption of Atomic Hydrogen from Alkali Metal-Rich Surfaces," submitted to *Physical Review Letters*.

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- ² C. C. Parks, D. A. Shirley, and G. Loubriel, *Phys. Rev. B* **29**, 4709 (1984).
³ L. T. Hudson, A. V. Barnes, N. J. Halas, R. F. Haglund, Jr., M. H. Mendenhall, P. Nordlander, N. H. Tolk, Y. Wang, and R. A. Rosenberg in *Desorption Induced by Electronic Transitions-DIET III*, 1987, edited by M. L. Knotek and R. H. Stulen, (Springer, New York, 1988), p. 274.
⁴ P. Nordlander and J. C. Tully, *Phys. Rev. Lett.* **61**, 990 (1988).

2.3.2 Photon-stimulated desorption experiments on alkali halides

Senior Investigators: Haglund (PI), Rose
Graduate Students: Bunton

The objective of this work was to clarify the role of surface and near-surface bulk excitations in ultraviolet-photon-induced glow from insulating materials. We carried out a series of experiments using synchrotron radiation to study the correlations between glow and secondary electron emission.

The origin of excited state alkali atoms desorbed from alkali halide surfaces during low energy photon or electron irradiation has remained an area of controversy since its discovery¹. Some of the excited-atom yield is certainly accounted for by secondary electron excitation of desorbed ground state atoms, as proposed for electron-stimulated desorption². The possibility of direct photon-stimulated desorption in excited states - in contrast to indirect mechanisms such as secondary electron excitation - has remained an open question. Such direct mechanisms might include excitation to a repulsive potential³ or excitation to an excited attractive state⁴.

Our results indicate⁵ that excitons play a significant role in the desorption of excited atoms, and that exciton formation competes with broad-band luminescence for flux channeled into excited state desorption and electron emission. We see that the shifts between total electron yields and excited state alkali desorption imply an excited state desorption mechanism in addition to secondary electron excitation, a possibility also supported by the differing lineshapes between the two yields. Simultaneous measurements of ground-state atom, excited-state atom, and secondary-electron emissions under photon irradiation, and of the electron energy distributions at the core exciton energy and away, would provide additional insight.

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- ¹ N. H. Tolk, M. M. Traum, J. L. Kraus, T. R. Pian, W. E. Collins, N. G. Stoffel and G. Margaritondo, *Phys. Rev. Lett.* **49**, 812 (1982).
² R. E. Walkup, Ph. Avouris, and A. P. Ghosh, *Phys. Rev. Lett.* **57**, 2227 (1986).
³ D. Menzel and R. Gomer, *J. Chem. Phys.* **41**, 3311 (1964).
⁴ P. R. Antoniewicz, *Phys. Rev. B* **21**, 3811 (1980).
⁵ P.H. Bunton, R.F. Haglund, and J. L. Rose, in preparation, to be submitted to *Surf. Sci.*

2.3.3 Hot Hole Diffusion in the ESD of Metal Atoms from Alkali Halides

Senior Investigators: Green, Loubriel, Richards, Albridge, Barnes and Tolk
Graduate Students: Hudson, Savundararaj

Within the framework of a realistic theoretical model, diffusion of hot holes in alkali-halide crystals prior to self trapping was shown¹ to have a substantial influence on the time dependence of the flux of desorbed ground state neutral metal atoms resulting from pulsed electron beam bombardment of these crystals. Comparison of results from the model with new time dependent measurements of Li ESD from LiF suggest that substantial

hot hole diffusion occurs in LiF, and that, depending on its preparation, the Li⁺ surface can be an absorber or reflector of hot holes.

It is well known that the desorption of adsorbed species from metal surfaces by electron and photons occurs via the absorption of energy right at the surface.² The same is true of ion desorption from maximally valent ionic solids via the inner-shell Knotek-Feibelman mechanism.³ By contrast, in the rare-gas solids and alkali-halides, desorption occurs following the absorption of energy in the bulk as well as on the surface. The primary mechanism for energy deposition is the production of electron-hole pairs leading to the formation of valence holes. The specific role of hole creation and migration has been discussed as a factor in characterizing absorption and luminescence, but not desorption, in several treatments of alkali halides.^{4,5,6,7} Works dealing with desorption have ignored hot holes by assuming that the holes self trap immediately. These works then dealt with the subsequent defect formation and migration.^{8,9,10,11} Recent work on the desorption of atoms from rare gas solids has demonstrated that hot hole diffusion plays a significant role in these electronically similar systems.² We report on first theoretical and experimental studies which point out the importance of hot hole diffusion in desorption from alkali halide surfaces.

The realization of the importance of the role of fast hot hole diffusion to desorption, coupled with the ideas that (1) hot hole reflectivity can be altered by changing the state of the surface; and that (2) diffusion rates may be influenced by bulk impurities and defects, suggest a wide and fascinating array of experimental and theoretical investigations. These include time, temperature and energy dependent ESD and PSD studies on alkali halides following the introduction of contaminant gasses, deposited alkali metals, and other dopants on the surface and in the near surface bulk.

- ¹ T.A. Green, G.M. Loubriel, P.M. Richards, L.T. Hudson, P.M. Savundararaj, R.G. Albridge, A.V. Barnes, and N.H. Tolk, in *Desorption Induced by Electronic Transitions - DIET IV*, 1989, (in print).
- ² See for example: T. E. Madey and J. T. Yates, Jr., *Surface Sci.* **63**, 203 (1977); D. Menzel, in *Desorption Induced by Electronic Transitions*, eds., N. H. Tolk, M. M. Traum, J. C. Tully and T. E. Madey (Springer Verlag, Heidelberg, 1983).
- ³ M. K. Knotek and P. J. Feibelman, *Phys. Rev. Letters* **40**, 964 (1978).
- ⁴ M. A. Elango, V. N. Kadchenko, A. M. E. Saar, and A. P. Zhurakovski, *J. Lumi.* **14**, 375 (1976).
- ⁵ V. N. Kadchenko and M. Elango, *Phys. Status Solidi A* **46**, 315 (1978).
- ⁶ R. G. Kaufman, W. B. Hadley, and H. N. Hersh, *IEEE Trans. Nucl. Sci.* **17**, 82 (1970).
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- ⁹ H. Overeijnder, M. Szymonski, A. Haring and A. E. De Vries, *Rad. Effects*, **38**, 21, (1978).
- ¹⁰ M. Szymonski, *Rad. Effects*, **52**, 9 (1980).
- ¹¹ T. A. Green, G. M. Loubriel, P. M. Richards, N. H. Tolk, and R. H. Haglund, Jr., *Phys. Rev.* **B35**, 781 (1987).

2.4 Molecular phenomenon in Alkali Halides

Senior Investigators: Tolk, Tellinghusein

Graduate Students: Xu

2.4.1 Experiment

When certain alkali halides are excited with energetic electrons, ions, or photons, a prominent "molecular" emission spectrum is produced, containing about ten regularly spaced bands in the region 220-370 nm. We have succeeded in characterizing the

fundamental spectroscopic properties of this emission system, which is now securely attributed to the CN^- anion, present in the bulk of the crystal or near the surface, probably as a substitutional defect. Although the spectroscopy of this UV transition is now moderately well understood, the mechanism for its occurrence as a "volunteer" in certain (but not all) alkali halides, and its puzzling temperature dependence, remain in question. One paper has been published on this system¹ and work on it is continuing.

In similar experiments one can observe emission from electronically excited atoms and molecules in the gas phase just above the surface of the crystal. One prominent molecular emitter is the OH radical, identified over a decade ago in electron-stimulated desorption from alkali halides. We have conducted preliminary studies of the $A \rightarrow X$ emission spectrum in an attempt to characterize the internal rotational population distribution in the desorbed OH(A) molecules.² The results show that the rotational distribution is anomalously "cool"; however, there are problems in the data which have led us to investigate questions about the theoretical branching ratios in this emission spectrum. This work, still in progress, needs to be completed before the rotational distribution analysis can be given solid footing.

A second molecular emitter produced in ESD -- and first identified in our laboratory -- is the CN radical. A preliminary report of our work on this system has been submitted to *Physical Review Letters*³. A copy of the abstract to this manuscript follows:

Excitation of KBr, KCl, and LiF with electrons of energy 60-1000 eV produces weak emission in the 360-420 nm region, identified as the $B \rightarrow X$ electronic transition in the CN radical. For CN(B) desorbed (via ESD) from LiF, the vibrational populations approximate a temperature of 1500 K, while the rotational abundances can be represented as a sum of two Boltzmann distributions having temperatures of 700 K (80%) and 100 K (20%). For ESD from KBr the rotational distribution is well represented as a single Boltzmann at ~ 600 K.

2.4.2 Theory

In work prompted by the experimental results for the UV spectrum of CN^- , we have carried out the first *ab initio* quantum chemical theoretical calculations on this species in an ionic environment. The latter, which is experimentally essential to stabilize the excited electronic states against autodetachment, is equally important in high-level quantum chemical electronic structure calculations -- and for the same reason: In the absence of the stabilizing ionic environment (which we have simulated with simple truncated point-charge lattices), the highest valence electron wants to "leave" the electronically excited anion. Our point-charge results have sufficed to identify the electronic character of the excited state responsible for the UV emission. We have further investigated more elaborate "real-ion" lattices, but so far for the ground state only. These results have been published in two papers^{4,5}.

In further work on such anionic impurity centers, we have conducted similar calculations on the low-lying electronic states of OH^- and O_2^- . A report on the work on OH^- has been accepted for publication in *Chemical Physics Letters*.⁶ The abstract to this work follows:

Potential curves and spectroscopic constants for the ground and low-lying excited electronic states of OH and OH^- are computed at the MCSCF level, *in vacuo* and in fcc point-charge lattices. Vibrationally bound $^1\Pi$ and $^3\Pi$ states are found 3-4 eV above the ground state of the anion and are probably responsible for the known UV luminescence spectrum of OH^- in alkali halides. The excited states display O-H⁻ character, and their properties depend strongly on orientation in the lattice.

The results for O_2^- are currently being prepared for publication.⁷ For this species, unlike CN^- and OH^- , theoretical potential curves have been obtained previously for several excited electronic states as well as for the ground state. However, the previous results were obtained for O_2^- *in vacuo* only. An interesting result of our calculations is that the excited-state potentials appear to change significantly in the alkali halide point-charge lattice. This may necessitate a re-examination of the interpretation of the experimental spectra for this important impurity center, results for which go back more than three decades in the literature.

An interesting sidelight to our *ab initio* studies on these three anions is our observation of surprisingly large crystal-field splitting of the *II* states when the anions are orientated $\langle 110 \rangle$ in the fcc lattices. This splitting is small in OH^- but quite significant in O_2^- and CN^- . While such splitting has been recognized experimentally in O_2^- , our calculations indicate that it may be a factor of 2-3 larger than previously thought. In CN^- the crystal-field splitting may be as large as 1.5 eV in the 3II state, or four times larger than in O_2^- . Such a large splitting has not been inferred from experimental data for this species to date, but our results may inspire a reinterpretation of experiment -- which seems not to provide definitive values for crystal-field splittings in most work. The results on these crystal-field effects are also intended for publication in the near future.⁸

In related work of a more general nature on diatomic potential curves, we have examined the results of a very simple scaling procedure for obtaining "reduced" potentials - potentials having a common dissociation energy, equilibrium internuclear distance, and force constant. The results of this study show that when examined over a global scale, such reduced potentials often show a surprising similarity, particularly for chemically analogous molecules. This similarity can be much greater than might be predicted from spectroscopic properties based on derivatives of the potentials near their minima, and in fact the latter comparisons are unreliable predictors of agreement on the global scale. This work has already appeared in print.⁹

- 1 "Ultraviolet Spectroscopy of CN^- in Alkali Halides: Dynamics of the Metastable Triplet State," by Marcus Mendenhall, Alan Barnes, Patrick Bunton, Richard Haglund, Larry Hudson, Richard Rosenberg, Dwight Russell, Johannes Sarnthein, Phillip Savundararaj, Norman Tolk and Joel Tellinghuisen, *Chem. Phys. Lett.* 147, 59 (1988).
- 2 "Nonthermal Energy Level Populations in Excited OH Electronically Desorbed from Alkali Halide Surfaces," by Marcus H. Mendenhall, Larry Hudson, Dwight Russell, Joel Tellinghuisen and Norman Tolk, *Nucl. Inst. and Meth.* B33, 834 (1988).
- 3 "Analysis of CN B \rightarrow X Emission in Electron-Stimulated Desorption from Alkali Halides," by Jun Xu, Marcus H. Mendenhall and Joel Tellinghuisen, *Phys. Rev. Lett.* (submitted).
- 4 "Ab Initio Study of Excited States of CN^- Stabilized in Point-Charge Lattices," by Carl S. Ewig and Joel Tellinghuisen, *Chem. Phys. Lett.* 153, 160 (1988).
- 5 "Ab Initio Study of CN^- Impurity Centers in Alkali Halides: Lattice Stabilization of Excited Electronic States," by Joel Tellinghuisen and Carl S. Ewig, *J. Chem. Phys.* 91, 5476 (1989).
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- 7 "Ab Initio Studies of Molecular Anions Stabilized in Point-Charge Lattices: Electronic States of O_2^- ," by Carl S. Ewig and Joel Tellinghuisen (in preparation).

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- ⁸ "Ab Initio Studies of Diatomic Anions in Point-Charge Lattices: Crystal-Field Splitting of Π States in CN^- , OH^- , and O_2^- ," by Carl S. Ewig and Joel Tellinghuisen (in preparation).
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2c. Chronological Listing of Publications Acknowledging URI Support

Publications in or Planned for Referred Journals

1. "Atomic Oxygen Simulation and Analysis," R.K. Cole, R.G. Albridge, D.J. Dean, R.F. Haglund, Jr., C.L. Johnson, H. Pois, P.M. Savundararaj, N.H. Tolk, J. Ye and A.F. Daech, to be published in *Acta Astronautica* (selected by the Int. Academy of Astronautics).
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4. "Laser-Synchrotron Studies of the Dynamics of UV-Photon-Stimulated Desorption in Alkali Halides," R. F. Haglund, Jr. and N. H. Tolk, in *Proceedings of the Conference on Short-Wavelength Radiation: Generation and Applications*, eds. D. T. Attwood and J. Bokor (New York: AIP Conference Proceedings No. 147, 1986), pp. 103-109.
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45. "Exciton Effects in Emission of Secondary Electrons and Excited Atoms from Alkali Halide Crystals under Ultraviolet Photon Irradiation," P. H. Bunton, R. F. Haglund, Jr. and J. L. Rose, in preparation, to be submitted to Surf. Sci.
46. "Hot Hole Diffusion in the Electron-Stimulated Desorption of Metal Atoms from Alkali Halides," T. A. Green, G. M. Loubriel, and P.M. Richards, L.T. Hudson, P.M. Savundararaj, R.G. Albridge, A.V. Barnes and N. H. Tolk, in DIET IV, 4th International Workshop on "Desorption Induced by Electronic Transitions," (1989). In Press.
47. "Hot Hole Diffusion in the Electron-Stimulated Desorption of Metal Atoms from Alkali Halides," T.A. Green, G.M. Loubriel, P.M. Richards, L.T. Hudson, P.M. Savundararaj, R.G. Albridge, A.V. Barnes and N.H. Tolk, in AFOSR IV (Northwestern) 4th Annual Workshop on "Reactions in a Space Environment," (1989). In Press.
48. "Influence of Adsorbates on Ion-Surface Interactions," P.M. Savundararaj, R.G. Albridge, D.L. Harper, D.P. Russell and N.H. Tolk, in AFOSR IV (Northwestern) 4th Annual Workshop on "Reactions in a Space Environment," (1989). In Press.
49. "Laser-Induced Emission of Particles from CaF₂(111) Near the Plasma Threshold," H. Cronberg, W. Muydermann, H. B. Nielsen, E. Matthias and N.H. Tolk, submitted to DIET IV, 4th International Workshop on "Desorption Induced by Electronic Transitions," (1989). In Press.
50. "Photon-Stimulated Desorption of Atomic Hydrogen from Alkali Metal-Rich Surfaces," L.T. Hudson, A.V. Barnes, J. L. Rose and N. H. Tolk, submitted to Physical Review Letters, (1989). In Press.
51. "Secondary Electron Excitation as a Possible Mechanism for Shuttle Glow," P. H. Bunton and R. F. Haglund, Jr., draft manuscript now being considered for submission to Geophys. Lett.
52. "The Influence of Adsorbates on Proton Neutralization at Surfaces in a Transmission Geometry," D.L. Harper, R.G. Albridge, D.P. Russell, P.M. Savundararaj and N.H. Tolk, in AFOSR IV (Northwestern) 4th Annual Workshop on "Reactions in a Space Environment," (1989). In Press.

2d. Professional personnel associated with the URI projects

The researchers associated with the above portions of the URI included:

Patrick Bunton, a graduate research assistant supported by a NASA graduate training grant. He is expected to receive the Ph.D. for portions of this work, and it will be awarded in the summer of 1990.

Douglas Harper, a graduate research assistant

Larry Hudson, a graduate research assistant supported by a NASA graduate training grant. He received his Ph.D. for portions of this work, in December 1989.

Dengfa Liu, a graduate research assistant.

Jining Qi, a graduate research assistant.

Philip Savundararaj, a graduate research assistant. He is expected to receive the Ph.D. for portions of this work, and it will be awarded in the summer of 1990.

Jun Xu, a graduate research assistant.

Klaus Becker, Ph.D., research associate.

Dwight Russell, Ph.D., Post-Doctoral Research Associate.

Paul Wang, Ph.D., Research Assistant Professor of Physics, Vanderbilt University .

Royal Albridge, Ph.D., Professor of Physics, Vanderbilt University.

Alan Barnes, Ph.D., Research Assistant Professor of Physics, Vanderbilt University.

Carl Ewig, Ph.D., Research Associate Professor of Chemistry, Vanderbilt University.

Richard Haglund, Ph.D., Associate Professor of Physics, Vanderbilt University and co-principal investigator on the URI contract.

Marcus Mendenhall, Ph.D., Assistant Professor of Physics.

Joel Tellinghuisen, Ph.D., Professor of Chemistry, Vanderbilt University.

Peter Nordlander, Ph.D.

Janna Rose, Ph.D., Post-Doctoral Research Associate

Norman Tolk, Ph.D., Professor of Physics, Vanderbilt University and co-principal investigator on the URI contract.

John Tully, Ph.D, Bell Labs.

2e. Invited or Refereed Talks Acknowledging URI Support

Dr. R.F. Haglund, Jr.

"The role of bulk and surface band structure in photon-stimulated desorption from alkali halide surfaces," seminar in the Institut für Atom- und Festkörperphysik, Freie Universität, Berlin, November 18, 1988. Host: Prof. E. Matthias

"The Role of Electronic Mechanisms in Electron-, Ion-, Photon- and Laser-Stimulated Desorption," invited lecture series at the University of Osnabrück, Federal Republic of Germany, October 19 to November 17, 1988. Host: Prof. W. Heiland. Titles of individual lectures were as follows:

1. Electronic and non-electronic mechanisms for bond-breaking in dielectrics.
2. Bond-breaking and desorption by electronic excitation.
3. Defect-induced desorption and dissociation.
4. DIET processes in low-energy atom-surface and ion-surface collisions.
5. Electron-stimulated desorption from solid surfaces.
6. Ultraviolet photon stimulated desorption.
7. Laser-induced desorption at low intensities.
8. Laser-induced ablation and surface modification.

"Primary and secondary mechanisms in the ultraviolet photon-stimulated desorption of ground-state and excited-state Li from LiF," Adriatic Conference on Applications of Lasers in Surface Science, International Centre for Theoretical Physics, Trieste, Italy, August 27, 1988.

"Electronic Processes in Electron- and Photon-Stimulated Desorption from Dielectrics," Colloquium in the Department of Electrical Engineering, Princeton University, February 22, 1988. Host: Prof. Phillippe Fauchet

"The Role of Electronic Mechanisms in Thermal, Chemical and Plasma Damage to Intracavity Optics," invited paper for the Symposium of the Society for Photo-optical Instrumentation Engineers, Los Angeles, CA (January 13, 1988)

"The Role of Laser-Plasma Electrons and Photons in Damage to Optical Materials," Seminar in the ring-laser gyroscope group, Litton Industries, Thousand Oaks, CA, January 12, 1988. Host: Dr. Anne Nicol.

"New Results in Electron- and Photon-Stimulated Desorption," Physics Department Colloquium, Universität Osnabrück, Federal Republic of Germany, November 6, 1987. Host: Prof. W. Heiland.

"Electron- and Photon-Stimulated Desorption from Surface Overlayers," Physics Department Seminar, Philipps-Universität, Marburg, Federal Republic of Germany, November 2, 1987. Host: Prof. D. Fick.

"Laser- and Other Photon-Induced Desorption Processes at Dielectric Surfaces," invited paper at the National Meeting of the Optical Society of America, Rochester, NY, October 20-24, 1987.

"Electronic Mechanisms in Thermal, Chemical and Plasma Damage to Intracavity Optics," R. F. Haglund, Jr., Proceedings of the 30th Annual International Technical Symposium of the SPIE, Los Angeles, CA, SPIE 895, 182-193, January 1988.

Dr. N.H. Tolk

"Electronic Processes at Surface," N. H. Tolk, Physics Seminar, University of California, Santa Barbara, 1/6/87

"Desorption Induced by Electronic Processes at Surfaces," Invited Talk, March Meeting of the American Physical Society, 4/16/87

"Electronic Interactions at Surfaces," Chemistry Seminar, Yale University, 4/23/87

"Interactions of Photons, Electrons and Heavy Particles with Surfaces," Physics Colloquium, University of Arkansas, 4/24/87

"Electronic Desorption Processes," Invited Talk, International Workshop on Desorption Induced by Electronic Transitions, DIET-III, Long Island, NY, 4/21/87

"Electronic Processes at Surfaces," Physics Colloquium, Georgia Institute of Technology, 10/28/87

"Mechanisms of Energy-Surface Interactions," Physics Colloquium, Institute for Defense Analysis, Washington, DC, 1/25/88

"Electronic Desorption Processes," Invited Talk, 4th International Symposium on Resonance Ionization Spectroscopy, N.B.S., Gaithersburg, MA, 4/20/88

"Electronic Aspects of Energy Surface Interaction," Physics Seminar, Aerospace Corporation, Los Angeles, CA, 11/1/1988

"Surface Reactions in Space," Physics Seminar, Air Force Geophysical Laboratory, Hancom AFB, MA, 1/30/89

"Atomic Physics at Surfaces," Physics Colloquium, Auburn University, Auburn, AL, 2/3/89

"Collision-Induced Surface Reactions in Space," Workshop on Space Vehicle and Environment Interaction, Johns Hopkins Applied Physics Laboratory, Columbia, MD, 2/21-2/22/89

"Atomic Processes at Surfaces," Seminnarraum 103, des Instituts für Kernphysik, Westfälische-Wilhelms-Universität, Federal Republic of Germany, 8/17/89

"Optical Radiation from Electron, Photon and Heavy Particle Bombardment of Lithium Fluoride and Lithium-Dosed Surfaces," N. H. Tolk, R. G. Albridge, A. V. Barnes, R. F. Haglund, Jr., L. T. Hudson, M. H. Mendenhall, D. P. Russell, J. Sarnthein, P. M. Savundararaj and P. W. Wang, *Proceedings of the Third International Workshop on Desorption Induced by Electronic Transitions (DIET-III)*, May 20-22, 1987, Shelter Island, New York, U.S.A., Eds. R. H. Stulen and M. L. Knotek (Heidelberg: Springer, 1988), pp. 289-294.

Dr. R.G. Albridge

"Atomic Oxygen Simulation and Analysis," R.K. Cole, R.G. Albridge, D.J. Dean, R.F. Haglund, Jr., C.L. Johnson, H. Pois, P.M. Savundararaj, N.H. Tolk, J. Ye and A.F. Daech, 37th I.A.F. Congress (Innsbruck: October 1986)

"The Vanderbilt University Neutral O-Beam Facility," R.G. Albridge, R.F. Haglund, Jr., N.H. Tolk, Poster presentation at NASA Workshop on Atomic Oxygen Effects (Pasadena: November 1986)

"The Electronic Interaction of the Atomic Hydrogen with Surfaces," N. Tolk, R. Haglund, Jr., N. Halas, D. Russell, L. Hudson, P. Nordlander, M. Mendenhall, P. Wang, A. Barnes, J. Wang and R. Albridge, DAMOP Meeting of the Am. Phys. Soc. (Harvard-Smithsonian Ctr. for Astrophysics: May 18, 1987)

Others

"Observation of Excitonic Effects in Excited Neutral Alkali Desorption from Alkali Halides," P. H. Bunton, R. F. Haglund, Jr. and J. L. Rose, to be published in the Proceedings of the Fourth International Workshop on Desorption Induced by Electronic Transitions (DIET-IV), October 2 - 5, 1989, Austria (Berlin: Springer, 1990).

"Neutralization of Ion Beams by Grazing Incidence Scattering from Metal Surfaces," P.M. Savundararaj, R.G. Albridge, D.L. Harper, D.P. Russell and N.H. Tolk, *Bull. Am. Phys. Soc.* **32**, 2148 (1987)

Investigation of Particle-Solid Interactions via Ion and Neutral Beam Bombardment," D.L. Harper, R.G. Albridge, D.P. Russell, P.M. Savundararaj and N.H. Tolk, *Bull. Am. Phys. Soc.* **32**, 2148 (1987)

"Photon Stimulated Desorption of Excited Hydrogen from KCl," L. T. Hudson, A. V. Barnes, N. J. Halas, R. F. Haglund, Jr., L. T. Hudson, D. L. Kinser, M. H. Mendenhall, P. Nordlander, N. H. Tolk, Y. Wang and R. A. Rosenberg, *Proceedings of the Third International Workshop on Desorption Induced by Electronic Transitions* (DIET-III), May 20-22, 1987, Shelter Island, New York, U.S.A., Eds. R. H. Stulen and M. L. Knotek (Heidelberg: Springer, 1988), pp. 274-277.

COMPLETED PROJECT SUMMARY
for
The Air Force Office of Scientific Research
UNIVERSITY RESEARCH INITIATIVE CONTRACT
No. F49620-86-ABC-0125

titled

SURFACE REACTIONS IN A SPACE ENVIRONMENT

*Center for Atomic and Molecular Physics at Surfaces
Department of Physics and Astronomy, and Department of Chemistry
Vanderbilt University, Nashville, TN 37235*

Researchers at Vanderbilt University's Center for Atomic and Molecular Physics at Surfaces have discovered ways in which energy deposited by incident atoms, ions, electrons and shortwavelength photons is electronically absorbed and localized to produce bond-making and bond-breaking on surfaces and in the near-surface bulk. Knowledge of these microscopic mechanisms provides detailed clues which lead to an understanding of the macroscopic processes which manifest themselves as surface erosion, surface modification, damage and glow. This research program bears directly on a broad spectrum of questions germane to the long-term operation of platforms in space, including long-term structural, optical and electronic degradation of materials in the ambient near-earth environment, survivability under and hardening against irradiation from directed-energy weapons, vulnerability in disturbed nuclear atmospheres, and discrimination and sensing techniques based on characteristic radiation (glow) signatures.

These studies have highlighted the pivotal role of electronically-induced defects and surface states in these phenomena. Fundamental studies of charge-exchange processes at surfaces have led to the development of the first pure, variable-energy, neutral and ionic, atomic and molecular beam in the world. Because neutral atomic oxygen and molecular nitrogen are primary constituents of the ambient orbital environment, the availability of low energy oxygen and nitrogen beams open the door to experiments on the effects both of individual irradiation modes and of synergistic effects from the total radiation environment.

The phenomena occurring at the surfaces of spacecraft, in addition to glow, covers all the variations of desorption: desorption induced by electronic transitions (DIET), desorption arising from momentum exchange (sputtering), and "chemical" sputtering (another variant of DIET) in which the energy necessary for desorption is supplied by surface chemical reactions. Moreover, the energies of interest range from thermal to those of the primary radiation sources (a strong function of altitude). In the case of fast atoms and molecules, the energy scale is set by the velocity of the spacecraft and corresponds to collisions at approximately 5 eV of atomic oxygen and 10 eV for molecular nitrogen-- high enough to initiate DIET processes and still within range of "chemical" interactions. The meaningful sources in surface reactions include:

- neutral atomic oxygen and molecular nitrogen, metastable and ground state, 5 to 10 eV typical energy
- ultraviolet radiation and electrons ranging from a few to many hundreds of eV
- transient incursions of energetic ions (H and He, for example).

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These radiation sources inflict varying degrees of mischief. These effects depend on how well and in what form the material supports the creation of localized electronic excitations which relax to form permanent defects. The clues to the dynamical process include photons, electrons, scattered ions or atoms, and substrate particles which have been desorbed from the surface.

Our experimental research has focussed on a carefully chosen number of topics including low-energy atomic and ionic oxygen interactions on surfaces, desorption of atomic hydrogen from surfaces, neutralization processes at surfaces, and the role of overlayers and dopants in energy partitioning. Companion theoretical studies have treated nonadiabatic neutralization at surfaces, lifetimes of excited hydrogen and alkali atoms near surfaces, electronic transitions in gas-surface dynamics, and lattice stabilization of excited electronic states of the imbedded pseudo-halogen CN^- .

This experimental and theoretical research program has produced significant results of a fundamental nature as follows: a) the first observations of photon stimulated *resonant* bond breaking resulting in the desorption of neutral atoms and molecules; b) the first measurements of the effect of submonolayer contaminants on electron transfer processes at a metal crystal surface; c) the first measurements of glow spectra arising from variable energy (4 eV to 2 keV) oxygen and nitrogen ion beams; d) the first observations of desorbed excited neutral CN molecules showing anomalous vibrational/rotational distributions from insulator surfaces; e) the first theoretical calculations of the energy shifts and lifetimes of hydrogen-atom excited states in the vicinity of a jellium surface; f) the first theoretical structure calculations for excited electronic states of CN^- in an alkali halide matrix; and g) the development of a simple theoretical method incorporating electrostatic forces into the extended Huckel scheme applied to ionic systems. As a result of this program we have come closer to our goal to microscopically characterize the interactions of oxygen, nitrogen, electrons and photons with surfaces in space.

Major contributors to this research are Professors Norman H. Tolk, Richard F. Haglund, Royal G. Albridge, Alan V. Barnes, Carl S. Ewig, Marcus H. Mendenhall, and Joel B. Tellinghuisen of Vanderbilt University and John C. Tully, Ph.D. of Bell Labs.