Electronic Interactions of Electrons, Photons, and Atoms with Material Surfaces

The intent of this research program was to elucidate the microscopic mechanisms by which the energy of incoming beams of atoms, ions, electrons and photons is absorbed, localized and redirected to produce neutral-particle desorption from surfaces and subsequent surface modification or restructuring. The model system LiF was used, and the results compared with measurements of electronically desorbed Li-atoms adsorbed on other substrates. This study explored how the degree of surface metallization influences the choice of the final excitation state of the desorbing particle. Measurements were made to compare the desorption of excited state neutral lithium from lithium fluoride by electron, photon and ion bombardment and from lithium-dosed tungsten and lithium-dosed glass by electron and photon bombardment. In the electron and photon desorption experiments, we observed only the first lithium resonance line. These results contrast with the ion sputtering results, where emissions from higher excited states were observed. This suggests that the presence of a metal rich surface provides a channel for de-excitation of excited lithium states which are above the lithium metal Fermi energy.
COMPLETED PROJECT SUMMARY

TITLE: Electronic Interactions of Electrons, Photons and Atoms with Material Surfaces

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PUBLICATIONS:


**ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:**

The intent of this research program is to elucidate the microscopic mechanisms by which the energy of incoming beams of atoms, ions, electrons and photons is absorbed, localized and redirected to produce neutral-particle desorption from surfaces and subsequent surface modification or restructuring. In particular, we emphasized (1) heavy-particle-, electron-, and photon-induced desorption measurements for the case of the model system LiF, (2) kinematically-complete experiments in which all the neutral species desorbed from a surface are detected, in order to form a complete picture of the energy balance in electronically induced desorption processes for the LiF model system, (3) Parametric and time resolved studies of electronically-stimulated desorption as a function of incident-beam energy, beam intensity, and substrate conditions, and (4) comparison of the results of the above experiments with measurements of electronically desorbed Li-atoms coadsorbed with O-atoms on well defined crystals.

These comparative studies of electron, photon and ion bombardment of the same sample surface probed the various channels through which incident particle energy is dissipated. Electron or photon irradiation of alkali halides results in the swift ejection of halide atoms, leaving behind an enriched alkali metal surface from which the alkali atoms thermally desorb. Ion bombardment involves momentum transfer as well as electronic mechanisms, which results in a different surface stoichiometry at the time of desorption. This study explored how the degree of surface metallization influences the choice of the final excitation state of the desorbing particle. Measurements were made to compare the desorption of excited state neutral lithium from lithium fluoride by electron, photon and ion bombardment and from lithium-dosed tungsten and lithium-dosed glass by electron and photon bombardment.

In the electron and photon desorption experiments, we observed only the first lithium resonance line. These results contrast with the ion sputtering results, where emissions from higher excited states are observed. This suggests that the presence of a metal rich surface provides a channel for de-excitation of excited lithium states which are above the lithium metal Fermi energy. This quenching of the higher excited lithium lines is less likely when the sample is excited by ions. These studies have shown substantial success and have pointed the way for significant future progress. Further studies presently supported by AFOSR on another contract involve careful surface analysis of the stoichiometry of lithium fluoride during ion, electron and photon irradiation. The ultimate aim of this research program is to characterize the final states of all the desorption products and the extent to which they are influenced by the surface, exciting beam and secondary processes.
Electronic Interactions of Electrons, Photons, and Atoms with Material Surfaces

Grant AFOSR 86-0150

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1. Research Objectives

The object of this research program was to address specific questions related to the ways in which energy is absorbed, localized and redistributed in electronically-stimulated desorption processes. Thus an experimental study was carried out of the various energy-transfer channels through which bombardment by energetic electron, heavy-particle, and photon beams leads to (a) surface modification, erosion and macroscopic damage of the LiF model system, and (b) desorption of Li atoms adsorbed on well defined surfaces. In particular, we emphasized (1) heavy-particle-, electron-, and photon-induced desorption measurements for the case of the model system LiF, (2) kinematically-complete experiments in which all the neutral species desorbed from a surface are detected, in order to form a complete picture of the energy balance in electronically induced desorption processes for the LiF model system, (3) parametric and time resolved studies of electronically-stimulated desorption as a function of incident-beam energy, beam intensity, and substrate conditions, and (4) comparison of the results of the above experiments with measurements of electronically desorbed Li-atoms coadsorbed with O-atoms on well defined surfaces.

This research bore directly on a broad spectrum of insulating materials involving considerations of time resolved and spatial energy localization measurements, exciton creation, and the role of defects at surfaces and at interfaces in altering local potentials which are involved in bond-making and breaking processes. In previous studies, we have established that neutral particle desorption via electronic transitions is a dominant effect of low-energy photon, electron and ion irradiation incident on many insulating surfaces, and plays a pivotal role in surface modification and damage in such materials. The mechanisms by which this desorption occurs are even yet only partially understood. However, it is clear that desorption induced by electronic transitions (DIET) is an ubiquitous phenomenon, occurring on the surface of every material thus far studied. The desired end result of this research program was the identification and elucidation of the primary mechanisms through which the deposition of electronic energy in the near surface bulk leads to desorption and consequently to changes in surface structure and composition. Significant progress was made in carrying out the research objectives.

The experiments performed in the program were concerned with the most basic questions of surface physics and chemistry, involving the geometrical structure, electronic structure and dynamics of bond-making and -breaking at surfaces. These comparative studies of electron, photon and ion bombardment of the same sample surface probed the various channels through which incident
particle energy is dissipated. Electron or photon irradiation of alkali halides results in the swift ejection of halide atoms, leaving behind an enriched alkali metal surface from which the alkali atoms thermally desorb. Ion bombardment involves momentum transfer as well as electronic mechanisms, which results in a different surface stoichiometry at the time of desorption. This study explored how the degree of surface metallization influences the choice of the final excitation state of the desorbing particle. Measurements were made to compare the desorption of excited state neutral lithium from lithium fluoride by electron, photon and ion bombardment and from lithium-dosed tungsten and lithium-dosed glass by electron and photon bombardment.

2. Research Status

A. PSD of Li* from Lithium Fluoride

Photon irradiation studies were performed at the University of Wisconsin’s Synchrotron Radiation Center at Stoughton, Wisconsin. Zero order visible and ultraviolet photons from the two meter grazing incidence Brown-Lien-Pruett monochromator (20 - 1200 eV) were incident along the surface normal upon a LiF crystal which was previously cleaved in air and baked under UHV conditions at 600°C. The photon detection system included a 0.3 m McPherson 218 monochromator which has a resolution of 26.5 Å at 1 mm slit width, a photo-multiplier in a cooled housing, and a multi-channel analyzer or CAMAC crate for data acquisition. We scanned the spectral region of 2000-7000 Å using a 1200 lines/mm grating blazed at 5000 Å. Fluorescence radiation was measured at 90° to the surface normal. The base pressure in the experimental chamber was less than 3 x 10⁻¹⁰ Torr throughout these experiments.

The spectrum obtained from irradiation of lithium fluoride (Fig.1) at room temperature shows the first resonance line of lithium at 6708 Å and two broad continua centered at about 3200 Å and 5600 Å. These continua are due to bulk luminescence and scattered light from the irradiating zero order photon beam. No other line radiation was detected above the background noise. We estimate that other spectral lines have maximum intensities that are at least a factor of 100 less intense than the intensity of the observed resonance line.
B. Ion Bombardment of Lithium Fluoride

In further studies, we irradiated a similarly prepared lithium fluoride sample with a 9 keV H$_2^+$ beam from a Colutron ion source. The de-excitation of the desorbed species from the surface and the bulk luminescence were monitored by the signal detection scheme discussed in part A. The ion bombardment was performed at room temperature. Note that in addition to the first resonance line of lithium 6708 Å (2p-2s) there are lithium lines at 3233 Å (3p-2s), 4603 Å (4d-2p) and 6104 Å (3d-2p). The relative intensities of the excitations originating at $n \geq 3$ after correcting for detection system efficiency are greatly enhanced compared to arc discharge data. This indicates a preferential population of these higher excited states via some unknown mechanism.
Fig. 2. Fluorescence spectrum from 9 keV \( \text{H}_2^+ \) bombardment of lithium fluoride

C. ESD of \( \text{Li}^* \) from Lithium Fluoride

It is well known that electron bombardment of alkali halides can desorb generous amounts of excited alkali atoms\(^2\). A typical optical spectrum taken at room temperature is shown in Fig. 3. Here, a 300 eV electron beam was incident along the surface normal on a single crystal LiF sample which had been cleaved in air and baked under UHV conditions at 600\(^\circ\)C. Fluorescence radiation was collected at 90\(^\circ\) from the surface normal; the ambient pressure was less than 10\(^{-9}\) Torr. The 6708 \( \text{Å} \) lithium resonance line is clearly visible as well as a trace signal of hydrogen Balmer alpha at 6563 \( \text{Å} \). As in the photon irradiation studies, no other excited lithium lines were observed above the background noise; any would have to be at least a factor of 100 weaker than the observed line.
D. Lithium Metal Studies

We have observed energetic electron and photon induced desorption of excited lithium neutrals from a thickly dosed lithium film, which was possibly contained oxygen. The experimental setup was similar to that described above. In vacuum we dosed a soda-lime glass plate by means of a SAFS lithium getter. Since the dosed film was opaque (it appeared shiny gray), we conclude from the attenuation length of light in lithium that it had a thickness of at least 1000 Å. At a pressure of $10^{-9}$ Torr we observed electron stimulated desorption of Li* (6708 Å) within 5 minutes of deposition. The electron beam current was 80 μA and energy 300 eV. Figure 4 shows a fluorescence spectrum taken with the sample at room temperature. The spectrum represents 200 signal integrations over five minutes at 1 mm slit width. Previously observed bulk fluorescence of the glass plate had vanished; the plate is viewed as a mechanical support only. The power density of the electron beam was 10 mW/mm² which does not cause appreciable heating or thermal evaporation of the lithium layer.

In another study, we used a tungsten substrate. The base pressure was $10^{-11}$ Torr, thus the environment was much "cleaner" than that for the study described above. The lithium resonance
line was not seen until several hours after the dosing. Subsequently, zero order synchrotron radiation was used to desorb Li*. The results show exactly the same characteristics as those for electrons.

![Fluorescence Yield vs Wavelength](image)

**Fig 4.** ESD of Li* from a lithium layer dosed on glass

E. Discussion

In the DIET experiments (Figs. 1, 3 and 4), we observe only the first lithium resonance line. These results contrast with the ion sputtering results of Fig. 2, where emissions from higher excited states are observed. We therefore propose the following picture.

It has been well established that the surface does not remain stoichiometric during electron or photon induced desorption of alkali halides at room temperature. The halide atoms desorb much faster leaving behind an alkali enriched surface. In our ESD and PSD studies of LiF, we thus expect to have excited lithium atoms desorbing from a surface enriched with lithium metal by a previously discussed mechanism. In the desorption studies of dosed lithium, excited lithium is also desorbing in the presence of a metallic lithium surface. In this case, contamination provides centers of localization for the electronic energy deposited by the incoming electrons or photons leading to desorption of lithium.
We now account for the fact that only the 2p-2s transition is observed in the DIET experiments: as Li* leaves the surface it interacts with the band structure of lithium metal surrounding the desorption site (Fig. 5). Electrons in the 2p level cannot resonantly tunnel to the filled levels of the metal below the Fermi energy. Excitations of Li* to the $n \geq 3$ levels may resonantly ionize ($10^{-15}$s) faster than de-excitation ($10^{-9}$s). Hence, higher transitions are suppressed and we observe only the single 2p-2s line in our spectra.

In contrast to this, we do see higher excited states of lithium upon ion bombardment of LiF. Ion sputtering is much more violent than desorption induced by electronic transitions and proceeds through momentum exchange processes. Under ion bombardment, the surface is more microscopically rugose and a lithium metal band structure will be much less developed. The desorbing Li* departs with a higher velocity and resonant de-excitation of higher excited states by interaction with the band structure is less probable. Consequently, we are able to observe radiative transitions from the higher excited states of lithium.

![Schematic energy level diagram of a lithium atom near lithium metal.](image)

**Fig. 5.** Schematic energy level diagram of a lithium atom near lithium metal.
F. Conclusions

On the basis of the work performed under this grant, the following conclusions may be made:

(A). It is clear that desorption induced by electrons and photons proceeds by different mechanisms than does desorption induced by ion bombardment. For the ESD and PSD processes occurring at LiF and lithium-dosed surfaces at room temperature, the presence of a metal rich surface provides a channel for de-excitation of excited lithium states which are above the lithium metal Fermi energy. This quenching of the higher excited lithium lines is less likely when the sample is excited by ions.

(B). This research has dramatically pointed out the importance of thin surface layers on the final states of desorbed species. Consequently, theoretical and experimental work is presently under way to assess the influence of hydrogen and other overlayers on these processes.

(C). The importance of this approach to further understanding of surface reactions in space and damage in optical systems can not be overstated. Clearly, this is an instance where fundamental studies have significant impact on recognized national needs.

Further studies will include careful surface analysis of the stoichiometry of lithium fluoride, time dependence, and beam energy dependence during ion, electron and photon irradiation. The ultimate aim of these studies is to characterize the final states of all the desorption products and the extent to which they are influenced by the surface, exciting beam and secondary processes. AFOSR is currently supporting work in these research areas through research contracts.

References


3. Personnel

Senior personnel employed under this project included, in addition to the PI's: Professors R. Albridge, J. Tellinghuisen, and A. Barnes; and Drs. D. Russel and P. Nordlander. Junior personnel included the following graduate student Research Assistants: D. Harper, P. Savundararaj, M. Shea, and S. Oyog. In addition B. Pruit, W. Zicko, C. Ricafort, T. Peatman, E. Moore, N. Westlake, K. Haglund, V. Salota, D. Kaplan, and P. Bhorjee were employed at various times as undergraduate research assistants. A collaborative interaction has evolved with personnel from the Institute for General Physics, Technical University, Vienna, Austria. The researchers form Vienna are Drs. Wolfgang Husinsky and Gerhard Betz. A strong theoretical collaboration continues to exist with Dr. John C. Tully of AT&T Bell Laboratories, Murray Hill, New Jersey.

4. Consultative and Advisory Functions (Norman Tolk)

- Consultant to Institute for Defense Analysis, 1988-
- Consultant to Chemistry Division, Los Alamos National Laboratory, 1986-
- Consultant to S-Cubed Corporation
- Consultant to Lockheed Corporation, 1987
5. Publications


6. Papers Presented at Meetings, Conferences, Seminars, Etc.


"Energy Shifts and Broadening of Excited H Levels in the Vicinity of a Metal Surface," P. Nordlander and J. C. Tully, AT&T Bell Laboratories Abstract (1988)


"Electronic Processes at Surfaces" N. H. Tolk, Physics Colloquium, University of Florida, Gainesville, 1/27/86
"Electronic Interactions of Electrons, UV Photons, and Heavy Particles with Surfaces," N. H. Tolk, Argonne National Laboratory Joint Chemistry and Materials Seminar, 2/14/86

"Coherence, Orientation and Alignment Processes in Charge Transfer at Solid Surfaces" N. H. Tolk, Invited Talk, March Meeting of the American Physical Society, 4/3/86

"Energy-Surface Interactions," N. H. Tolk, Ohio State Physical Chemistry Seminar, 4/21/86

"Electronic Optical Damage Mechanisms" N. H. Tolk, Chemistry Seminar, Los Alamos National Laboratories, 4/28/86

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

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

"Electronic Interactions at Surfaces," N. H. Tolk, Chemistry Seminar, Yale University, 4/23/87

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


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