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TITLE EXPERIMENTAL STUDIES OF PHOTON-SURFACE INTERACTION DYNAMICS IN THE ALKALI HALIDES

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# EXPERIMENTAL STUDIES OF PHOTON-SURFACE INTERACTION DYNAMICS IN THE ALKALI HALIDES

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## Abstract

We describe recent measurements which have provided, in unprecedented detail, insights into the electronic mechanisms through which energy carried into a material by photon irradiation is absorbed, localized and rechanneled to produce desorption, surface modification, erosion and damage. The specific object of these studies has been desorption induced by electronic transitions in alkali halide crystals, with particular emphasis on the dynamics of changes in the surface and near-surface regions. In our experiments, the irradiating ultraviolet photons are provided by a synchrotron storage ring, and the dynamical information about desorption products is obtained from optical measurements of the quantum states, yields and velocity distributions of neutral ground-state and excited-state atoms ejected from the surface of the irradiating material. These studies have shown that the dominant exit channels in photon-induced particle emission are those producing ground-state and excited-state *neutral* atoms. Using dynamical information about these desorbing neutral species, obtained, for example, by laser-induced fluorescence and laser Doppler spectroscopy, we are generating an increasingly comprehensive picture of the dynamics of electronic energy flow into and out of pure crystalline surfaces in these prototypical dielectrics. We are also beginning to be able to relate desorption dynamics to specific materials properties, and to discriminate between pure surface and near-surface effects in these materials. Applications of these techniques to the problem of photon-induced surface damage and to analysis of surface dynamics in dielectric materials are discussed, and the relationships between these nearly ideal model materials and the non-crystalline, covalently bonded materials more typical of real optical elements are pointed out.

## Introduction

The burgeoning development of ultraviolet and soft x-ray light sources is confronting optical designers with unprecedented problems resulting from materials modification and damage under irradiation by short wavelength photons. Notwithstanding the gravity of the problems, however, there exists at present only the most rudimentary understanding of the fundamental mechanisms by which uv- and X-ray-induced surface modifications come about. Moreover, the experience of the past two decades in high-power laser modification and damage to optical materials provides practically no guidance in the present circumstances, because most if not all of the changes to materials induced by ultraviolet and shorter wavelengths are caused by electronic rather than thermal mechanisms.

Motivated by the recent discovery that the dominant products of desorption induced by electronic transitions (DIET) in the alkali halides are neutral atoms and molecules, we have been probing the atomic-scale dynamics of energy absorption, localization and redistribution in dielectric materials subjected to ultraviolet photon bombardment. We have recently identified, for example, the specific excitonic mechanism which leads to desorption of alkali metal atoms from the surface of pure alkali halide crystals. We have also been able to correlate the desorption process with changes in surface composition, and are beginning to match these compositional changes to alterations of geometrical and electronic structure in the surface and near-surface bulk of these materials in their pure crystalline form. Most importantly, however, we have also been able to relate susceptibility to electronically induced desorption to certain generic properties of materials. These properties -- notably, the ability to support the formation of self-trapped excitons which relax into permanent, mobile electronic defects -- are common to many materials encountered in typical ultraviolet and soft X-ray optical elements, including the alkali halides, alkaline earth halides, a number of metal oxides, and fused silica.

Thus these experimental studies, allowing as they do the detailed identification of the quantum states and dynamical characteristics of particles leaving the surface of an irradiated material, are yielding an increasingly comprehensive picture of the electronic mechanisms which operate to produce desorption, and ultimately to material erosion and damage in many optical materials. In this sense, the apparently restricted focus on alkali halides actually provides the kind of broadly useful picture one should expect from detailed studies of model materials. In addition, the variegated techniques of neutral-species desorption spectroscopy developed in this work may be applied not only dynamical studies of photon-induced damage processes, but also to detailed spectroscopic and dynamical studies of surfaces as they are produced in optical fabrication processes.

In this paper, we shall concentrate primarily on recent experimental results of laser-synchrotron experiments in which the detailed mechanisms of photon-stimulated desorption (PSD) have been elucidated by means of techniques borrowed from atomic spectroscopy. We shall show that it is possible, using this class of experimental techniques, to identify desorbing atoms and molecules from their characteristic spectral line radiation and to obtain detailed information on the photon-energy thresholds, time dependence, and velocity distributions of the desorbed particles. The effects of materials properties, such as defect mobilities, can be correlated with surface modification and damage by changing sample properties such as temperature. This detailed characterization of the desorption dynamics allows, in turn, the testing of specific models of electronic excitation mechanisms leading to desorption and hence to the understanding of those generic properties which make given materials more or less susceptible to modification or damage through desorption.

As we shall show, the key to DIET dynamics -- and hence the rate-limiting step in surface damage processes -- turns out to be the efficiency with which self-trapped excitons can form, relax into permanent electronic defects, and then migrate to nearby surfaces or interfaces. *Any* material having these properties will undergo changes in the surface and near-surface bulk which can eventually lead to catastrophic changes under high-intensity or prolonged irradiation by ultraviolet or X-ray photons. Thus, while the specific results presented are derived from experiments on the alkali halides, the work has broad applicability to all materials which can absorb and store incident electronic energy, and then release it through channels which result in bond-breaking.

## Desorption Induced by Electronic Transitions

For a number of years, ions desorbed from materials by energetic electron or photon bombardment have been studied to yield significant information on the mechanisms for bonding and bond breaking in a variety of materials. In the early 1960's, the work of Menzel, Gomer, and Redhead showed that adsorbates on metal surfaces could be removed through electronic rather th thermal transitions, and that the detailed dynamics of the process could be understood by analyzing velocity distributions and other typical dynamical features of the desorbing particles.[1,2] The Menzel-Gomer-Redhead model of desorption from metal surfaces was based on two-body potential models typical of gas-phase chemistry. Interest in the work was awakened further by the work of Madey and Yates, showing that the angular distributions of desorbing ions could provide atomic-scale information on the bonding characteristics of atoms and molecules either adsorbed on surfaces or actually bound in crystal surfaces.[3] In the late 1970's, Knotek and Feibelmann made a major step forward by showing that the preferential electronically-induced desorption of certain species in maximally-covalent covalent solids was related to the enhanced stability of hole pairs produced by deep core-level excitations of those materials.[4] Thus, their work forged a link between the properties of the desorbed species, on the one hand, and the detailed material characteristics, on the other.

Thus, by the end of the 1970's, it was clear that studies of electron- and photon-stimulated desorption (ESD/PSD) provided important clues to both structural and compositional order in optical materials. Indeed, in those instances where the structure or composition could be simply related to specific mechanisms, it was already possible to use ion produced in DIET processes to obtain a limited amount of dynamical information. However, studies of the dynamics of DIET processes received major impetus in 1981 with the discovery by Tolk and co-workers that desorption yields in alkali halides overwhelmingly favored ground-state and excited-state neutral particles, in both electron- and photon-stimulated desorption.[5,6] This work simultaneously advanced the study of DIET dynamics by identifying the major particle desorption channels, as well as making it possible to use a wide variety of optical techniques borrowed from atomic spectroscopy to study the internal quantum states, velocity distributions, angular distributions, and temporal behavior of the desorbing neutral species.[7] Freedom from the constraints of neutral-species mass spectrometry, with its inherent low signal-to-noise ratio, also represented a major step forward from the standpoint of experimental technique in DIET studies.

A typical DIET experiment using neutral-species desorption spectroscopy, as shown schematically in Figure 1, requires an

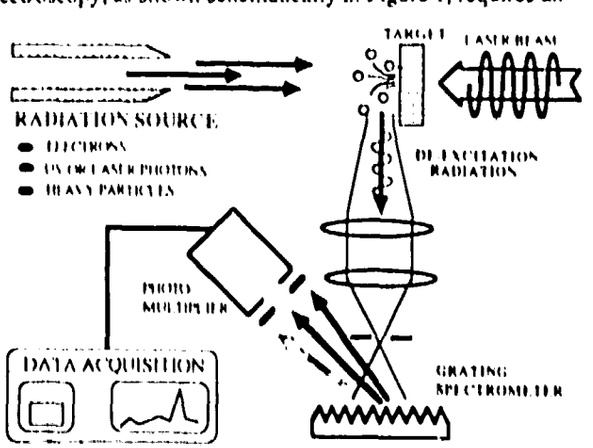



*Figure 1. Schematic diagram of a DIET experiment based on neutral species desorption spectroscopy*

excitation source, a sample, and an optical detection system arranged to view the radiation from particles desorbed from the surface. In the experiments to be described here, the exciting source was the tunable ultraviolet photon beam from a synchrotron storage ring (the Tantalus ring at the University of Wisconsin-Madison). The entire experiment was housed in a ultrahigh vacuum (UHV) chamber (nominal base pressure $4 \times 10^{-10}$ Torr), in which the single-crystal sample was mounted on a precision ultrahigh vacuum manipulator. The photon beam was incident along the surface normal of the (100) surface of a single-crystal alkali halide target which was cleaved and polished prior to its introduction into the UHV system and then cleaned by heating to 400° C. The sample temperature was varied by resistive heating of the copper target holder.

Fluorescence decay signals from desorbing ground-state and excited-state atoms were detected by a spectrometer-photomultiplier combination arranged to view a small region out on front of the surface through an appropriate imaging system. The location of the focal volume with respect to the target surface was varied by translating the horizontal axes of the target manipulator. Fluorescence count rates ranged from a few kHz to a few hundred kHz.

One fine-structure component of the first optical resonance line (589 or 671 nm, respectively, for atomic sodium and lithium) was used to identify the desorbing alkalis. Ground-state neutral atoms were detected from laser-induced fluorescence (LIF) radiation produced by the light from a frequency-stabilized tunable dye laser, transported to a quartz entrance window of the UHV chamber through a single-mode, polarization-preserving optical fiber. To count neutral excited-state atoms, on the other hand, the laser was turned off and the desorbing atoms were detected by setting the spectrometer to the characteristic free-atom wavelength.

To measure relative densities of desorbing alkalis, the laser was injected parallel to and about 1 cm away from the surface, in a direction perpendicular both to the incident beam and to the spectrometer line-of-sight. For velocity distribution or desorption time history measurements, the laser was injected along the rear surface normal of the alkali halide crystal, anti-parallel to and collinear with the photon beam. Velocity distributions of the desorbing ground-state atoms were obtained by scanning the laser through the Doppler-shifted wavelength band resonantly absorbed by the alkali atoms.

A number of surface-diagnostic probes are also available in the UHV chamber, including ion scattering spectroscopy (ISS) and low-energy electron diffraction (LEED). The performance of the experiments to be described here in ultrahigh vacuum is particularly important because, in contrast to many laser-based materials modification studies, these experiments are carried out in an environment in which the contaminants on the surface can be controlled and carefully monitored.

## Early PSD Studies in Alkali Halides

Early in ESD/PSD experiments on alkali halide crystals, it was discovered that desorbed alkali atoms were radiating as free particles out in front of the surface as they flew away from it. Figure 2 shows typical spectra for photon-stimulated desorption of neutral lithium and neutral sodium ejected from the surfaces of LiF (lower spectrum) and NaCl (upper spectrum), respectively. In the figure one sees very clearly the broadband luminescence from the near-surface bulk of the sample, with a sharp spike of line radiation riding on the broad continuum. This line radiation was quickly identified as the Li and Na D lines, and subsequent studies have shown that at low photon or electron energies, the excited species emitting this characteristic line radiation are in fact created in the electronic desorption process, and not in gas phase

interactions with the primary radiation. It has been possible in subsequent PSD and ESD experiments to identify a wide variety of atomic and molecular species desorbed by photon impact, including H, OH, and a radiation from a molecular species (possibly $CN^-$) bound to the surface as a hindered rotor.[8] Thus, as we shall see from the experimental results presented below, neutral-species desorption spectroscopy provides a rich variety of information on particles leaving the surface. This information is sufficient in many cases to determine precisely the channel through which incident photon energy is adsorbed, localized in space and time, and redistributed to neutral-particle desorption channels.

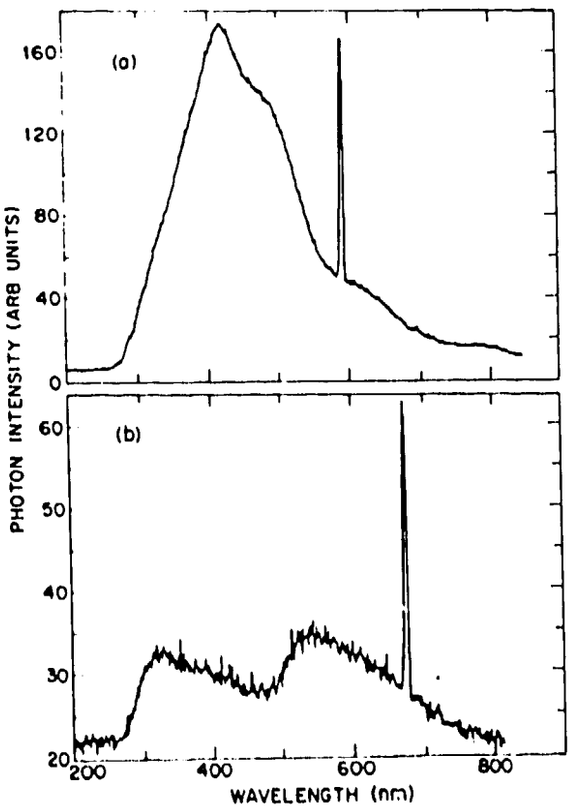



*Figure 2. Fluorescence yield as a function of spectrometer wavelength for PSD from LiF (upper curve) and NaCl (lower curve). The incident uv photons span the complete "white" spectrum of a synchrotron light source. From Ref. 6.*

Another key result from the early PSD experiments on alkali halides was the discovery that even the excited-state neutral yields vastly exceeded the ion yields. Figure 3 shows a comparison of $Li^*$ fluorescence yields (top spectrum) $Li^+$ ion yields (middle spectrum) from photon-stimulated desorption of LiF, and the LiF optical absorption as a function of uv photon energy (bottom spectrum). All three spectra show the influence of the 1s core-level excitation around 61 eV, indicating the formation of an intermediate excitonic state whose precise nature is yet to be clarified. The most important feature of these spectra, however, is the fact that the yield of excited neutral atoms exceeds the yield of Li ions by *five orders of magnitude!* Subsequent experiments in both PSD and ESD have shown that ground-state neutral alkali yields exceed the excited-state yields by an additional two orders of magnitude, driving home the lesson that ground-state neutral desorption is by far the dominant DIET process.

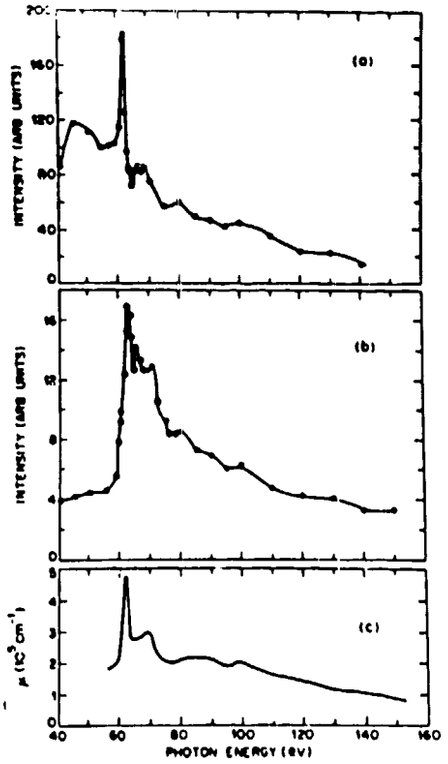



*Figure 3. (a) Fluorescence yield of $Li^*$ desorbed from LiF by ultraviolet photon irradiation, as a function of incident photon energy. (b) Yield of $Li^+$ desorbed from LiF by ultraviolet photon irradiation, taken under the same conditions as the spectrum in (a). (c) Photon absorption coefficient of LiF. The scale factor between (a) and (b) is approximately $10^{-5}$ in favor of the $Li^*$.*

## Recent Photon-Stimulated Desorption Measurements in Alkali Halides

We now consider a number of different measurements in which PSD of neutral alkali atoms from alkali halide crystals was studied in detail in an attempt to understand the physics at the root of the desorption dynamics. These experiments include yields as a function of incident photon energy; velocity distributions; time-resolved desorption yields; and yields of alkali atoms in the presence of surface contaminants. In several cases, striking contrasts can be drawn between the dynamical behavior of ground-state and excited-state neutrals desorbed by ultraviolet photon irradiation. Indeed, we shall see that at this point the process of ground-state neutral desorption appears to be thermal and to stem both from surface and near-surface defect diffusion. The excited-state neutrals, on the other hand, appear to derive purely from a surface excitation process whose precise nature is still under active investigation.

### PSD Yield vs. Photon Energy

Figure 4 shows a measurement of laser-induced fluorescence yield as a function of incident uv photon energy typical of data for ground-state neutral alkali atoms desorbed by photon impact from an alkali halide, in this case for $Na^0$ from NaCl. The temperature of the crystal was approximately 350°C. While the curves do have some structure which appears at the 2p and 2s

core-hole excitation energies of the Na atoms (henceforth denoted $Na^o$), it is likely that core excitations are not directly correlated with the desorption of $Na^o$. The rationale for this statement is that the onsets are rather weak and that similar measurements on other sodium halides (NaBr, NaI and NaF) with significantly different halogen core structures show virtually the same generic yield curves.[9] Hence, it is more likely that these structures result either from secondary yield-enhancing processes such as indirect *valence*-hole excitation due to Auger decay of the Na 2p core holes, or from strong competition between core-hole and valence-hole excitations as the increased bombarding energy opens up new reaction channels. For temperatures in the range shown, the desorption efficiency is on the order of $10^{-3}$ for each photon striking the sample.

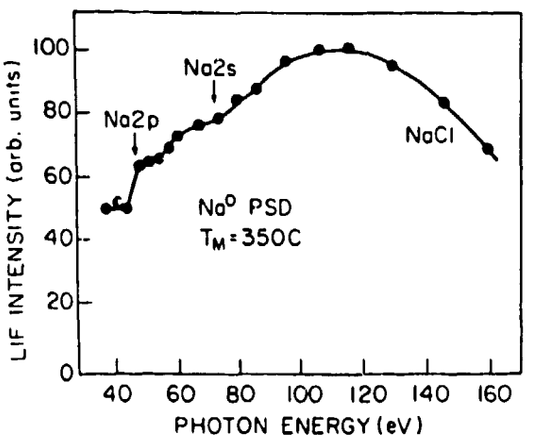



*Figure 3. Laser-induced fluorescence yield for ground-state neutral Na as a function of incident uv photon energy. The sample was pure single-crystal NaCl.*

The relatively featureless yield *vs.* photon energy curve for the ground-state neutral sodium atoms is a striking contrast to the exciton-like spectrum for excited lithium shown in Figure 3. It should also be noticed that the desorption efficiency for the $Na^o$ does not vary by more than a factor of two over the entire photon energy range studied.

## Velocity Distributions

Additional clues to the fundamental character of ground-state neutral desorption dynamics comes from the experimental determination of velocity distributions as a function of surface temperature. The number *vs.* velocity distribution of the neutral desorbing atoms is given by

$$dn/dv = C\ v^2 \exp(-mv^2/2kT), \qquad (1)$$

where the velocity v is related to the measured frequency ν of the emitted photons by the first-order Doppler formula

$$\nu = \nu_0\ [1 + (v/c)\cos\theta]. \qquad (2)$$

The parameter $\nu_0$ is the central frequency for stationary atoms and $\theta = 0$ in the geometry of these experiments.

In the measurements displayed here, the zero-order output of the soft X-ray monochromator was used as the exciting beam, to provide suitably high count rates required for deconvolution and fitting of the data. This zero-order beam contains a continuum of photon energies ranging from 0 to approximately 200 eV, with rather sharply decreasing amplitude at either end of that range. In these measurements, scanning the laser through the appropriate frequency range provides a fluorescence signal from ground-state atoms proportional to the relative population of those atoms able to resonantly absorb the laser photons at the Doppler-shifted frequency in their rest frame.

Figure 5 shows the measured laser-induced fluorescence yield *vs.* laser frequency from PSD experiments on various sodium halide crystals, while Figure 6 shows calculated velocity distributions for desorbed sodium atoms at the temperature best fitting the observed data.[9] The doublet structure in the spectra of Figure 5 arises from the hyperfine splitting (1772 MHz) for sodium D-lines. The velocity distribution is definitely Maxwell-Boltzmann, as fits to the asymmetric broadening of each component of the hyperfine doublet demonstrate. The linearly increasing difference between the fit temperature $T_f$ and the measured temperature $T_m$ (see inset) suggests a systematic error,

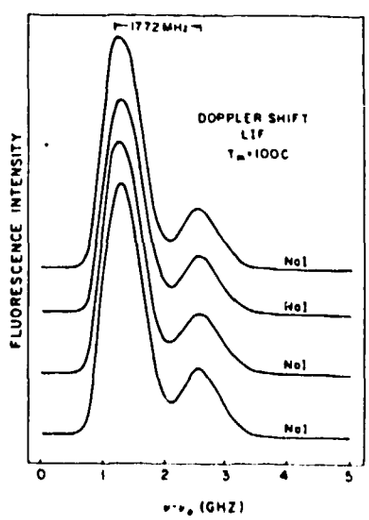



*Figure 5. Measured fluorescence spectra as a function of laser frequency for desorbing $Na^o$ from several sodium halides.*

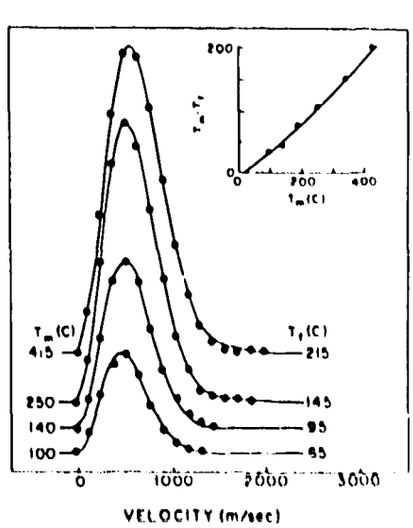



*Figure 6. Calculated velocity distributions for the deconvoluted data of Figure 5; the indicated temperatures $T_f$ represent the best fits to the deconvoluted data assuming a Maxwell-Boltzmann distribution.*

probably arising from a temperature gradient between the thermocouple mount and the crystal surface. Measurements of PSD yield as a function of surface temperature [not shown here] also display an Arrhenius thermal desorption characteristic as a function of increasing surface temperature.

Assuming that the fitted temperatures represent the actual NaCl surface temperature, the desorption of $Na^0$ seems to be completely explained by a thermal process; in particular, there was no evidence at all for the existence of a high-velocity, supra-thermal tail in the velocity distribution. Definitive data on the velocity distributions of the excited state neutrals, such as $Na^*$, do not exist yet; however, there is preliminary evidence from ESD experiments that those distributions are probably not thermal.[10]

### Time Dependence of PSD Yields

We have also measured the time history of ground-state and excited-state lithium desorbing from lithium fluoride crystals. In the case of ground-state lithium (Figure 7), the fluorescence yield showed an initial sharp drop after the beam was turned off, followed by a slowly-decaying emission lasting many seconds.

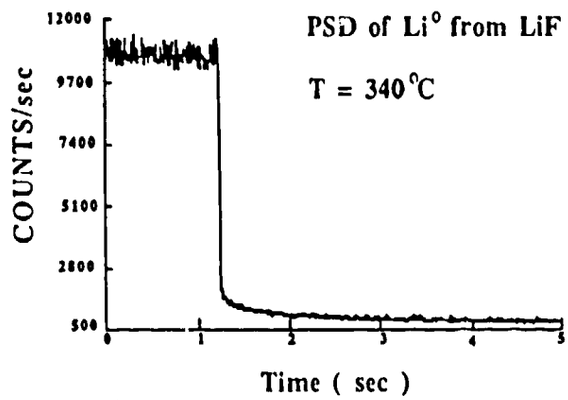



*Figure 7. Time history of Li° yield as a function of time following turning off of an illuminating white-light spectrum of ultraviolet light from a synchrotron storage ring.*

For excited-state atoms, time histories were measured by using the time structure of the synchrotron beam to provide a nanosecond excitation pulse, and routing the fluorescence signals through a time-to-amplitude converter. These data, shown in Fig. 6, indicate that the *excited state* neutral lithium turns on and off with the exciting photon beam. Thus, while the ground-state desorption is consistent with a model in which thermally-driven diffusion transports radiation-induced defects from the near-surface bulk to the surface where thermal desorption occurs,[11] excited-state desorption appears to be a surface-specific process, probably involving direct excitation of surface states.

These data lead to conclusions similar to those drawn from a recent time-resolved study of ESD in LiF.[12] In the case of PSD, however, the typical decay times for the $Li^0$ yields are two to three orders of magnitude slower than those for ESD -- consistent with the much greater effective range of the photons in LiF. In fact, model calculations using realistic energy deposition profiles for electrons and photons appear to be able to fit both the ESD and PSD data with nearly the same diffusion constants, lending credence to the picture of a mechanism whose rate-limiting feature is the diffusion time of defects from the near-surface bulk to the surface.

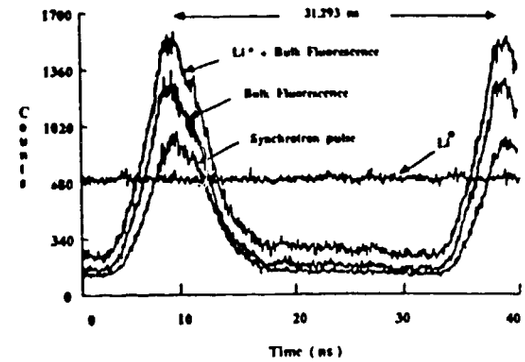



*Figure 8. Time history of Li* desorbed from LiF by ultraviolet photon bombardment (top spectrum), with the bulk luminescence signal and the uv photon beam time spectrum shown for reference. The straight line across the figure is the $Li^0$ desorption yield, which is essentially constant on the ns time scale here.*

### PSD Threshold Energy Measurements

The data of Fig. 2 indicate a rather broad range of photon energies over which the alkalis are desorbed with significant efficiency from alkali halides by PSD. However, as Townsend pointed out in his pioneering paper in ESD on alkali halides,[13] if the creation of a self-trapped exciton is the first step in electronically stimulated desorption, one needs only the energy requried to create the exciton on the dihalide molecule $(X^-_2)^*$ to initiate the process (typically a few eV). However, nearly all measurements of the stimulated desorption process to date have relied on electrons or photons of significantly higher energies than the few electron volts mandated by this requirement. Moreover, until the development of the sensitive optical techniques necessary for tracking neutral desorption, it was not necessarily easy to look for the onset of desorption yields.

We have recently measured the threshold for PSD of $Li^0$ from LiF and found it indeed to be very low in energy. The PSD threshold measurements were made with filters to ascertain the relative yields in different regions of the incident uv photon spectrum. As shown in the bar graph representation in Figure 9, the three spectral bins were from 0-13.2 eV (LiF filter), 20-90 eV (Al filter), and 0-200 eV (full zeroth order spectrum transmitted through the toroidal grating monochromator (TGM) used in this set of measurements). The relative yields shown in Figure 9 for the Al and LiF filters were calibrated by the convolution of the raw yield with a trapezoidal-rule integration of the measured response of a gold photodiode to the tuned spectrum of the TGM. After correcting for the monochromator efficiency, it can be seen that some twenty-five *per cent* of the total neutral yield results from photons below 13.2 eV -- the band gap for the LiF filter. (Indeed, the threshold may be even lower, since this particular filter showed obvious signs of significant color-center formation.) This means that such desorption is likely to take place efficiently even at excimer-laser photon energies, perhaps even without invoking multiphoton transitions.

There is some uncertainty about the upper-end cutoff of photon energies transmitted through the LiF filter, since it showed signs of significant radiation damage (color centers) which would have lowered the cutoff below the nominal value given by the bandgap energy. However, it is evident that nearly

twenty-five *per cent* of the total $Li^o$ yield is produced by photons from the lowest energy bin. The low value of this neutral emission threshold is consistent with results obtained by Schmid *et al.* almost a decade ago using four-photon excitation from a pulsed ruby laser.[14] This is not surprising, since the DIET mechanism producing ground-state neutrals will be efficacious for excitation pulses which are long compared to the energy localization time required to produce the defect.

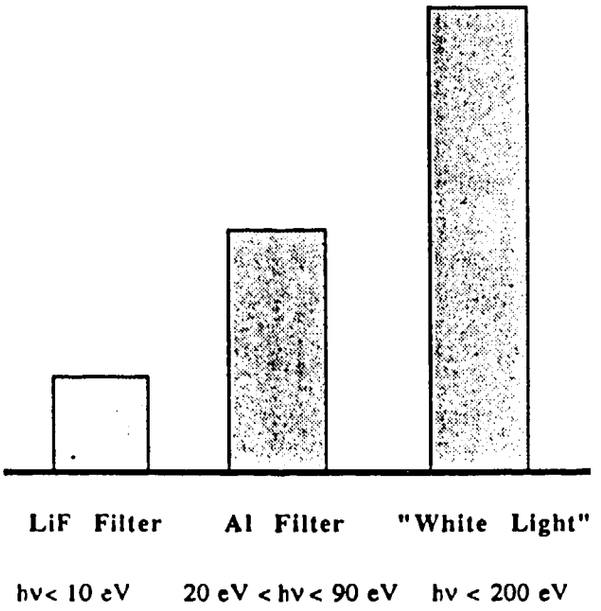



*Figure 9. Relative PSD yields of $Li^o$ from LiF for the photon-energy ranges indicated.*

## Effects of Contaminant Overlayers

In some of the earliest ESD experiments on alkali halides, it was found that samples cleaved in air and then inserted into the UHV environment failed to show neutral alkali desorption until they had received a significant radiation dose. These low alkali yields persisted even when the samples were heated to over 500° C under UHV conditions. When detailed spectral scans over the visible spectrum were taken, it became clear that other species, including H and OH, were desorbing at greater rates than the alkali metals from the sample. Of particular interest was the fact that the *relative* yield of excited H atoms to excited Na atoms was greater than unity for NaF, but less than unity for NaCl.[15] This indicated clearly that the presence of adsorbed species on the surface affected the substrate yields in some complicated manner still not fully understood.

Similar results have now been seen in preliminary experiments on PSD of Li from LiF. Figure 10 shows a spectrum of excited-state neutral lithium desorption in a PSD experiment with white light on LiF. The ground-state $Li^o$ peak is expected, as is the bulk luminescence continuum. But the spectrum also shows two hydrogen lines, indicating that H atoms in the n=2 and n=3 states are also being desorbed with the excited lithium. (It is worthy of note that at low photon and electron energies, adsorbed hydrogen desorbs in several excited states, while only the first excited state of the alkali metals has ever been observed.) Similar results have been seen in ESD experiments in which comparative yields from different alkali halides were measured. Although systematic measurements of these effects are still in the beginning stages, it appears that the *relative* loss of substrate, *vis a vis* the overlayer, material depends both on the details of the overlayer and on the composition of the substrate.

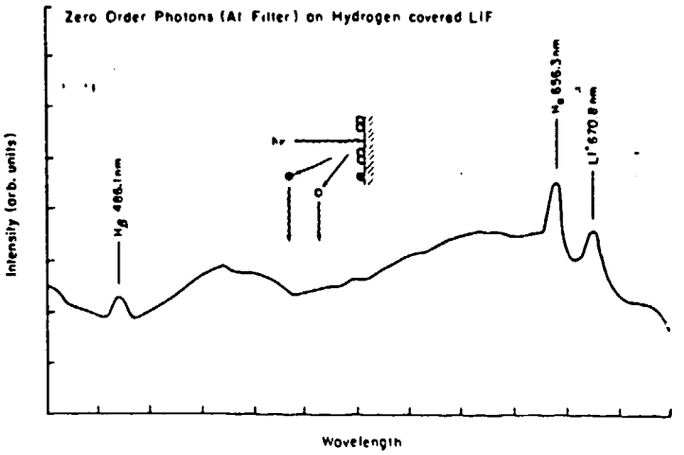



*Figure 10. Fluorescence yield from PSD of LiF as a function of spectrometer wavelength. The excited states of H and Li atoms are identified.*

Further measurements are expected to provide clues as to the exact role of this "protective overlayer" in binding substrate material and preventing surface bond-breaking. More detailed understanding of this physical and chemical properties of the overlayer may have far-reaching implications for solutions to the problem of damage in ultraviolet and X-ray optical materials. This will be a particularly felicitous development if it should prove possible to change the electronic properties of the overlayer-substrate system without affecting the optical properties to any significant degree.

## Desorption, Surface Modification and Damage

The key to a fundamental understanding of the ways in which ultraviolet and X-ray photons modify or damage surfaces is to find the links between the *microscopic* (atomic scale) desorption of individual atoms or molecules from the material, on the one hand, and the *macroscopic* erosion and large-scale modification, on the other. This requires an understanding both of the detailed mechanisms of desorption and of the surface and bulk properties of particular materials. The key questions revolve about the ways in which incident photon energy is absorbed, localized and redistributed through coupling to phonon modes, electronic excitation and particle desorption. Hence, in contrast to thermal desorption processes -- which depend only on the bulk thermodynamic properties of the optical material -- any serious investigation of photon-stimulated materials modification must concern itself with the detailed optical properties of materials, such as band structure. At this point, it is useful to review the general features of electronically stimulated desorption, couple this picture to detailed excitation mechanisms in the alkali halides, and then consider the macroscopic consequences for photon-irradiated surfaces.

## Electronically Stimulated Desorption of Neutral Atoms

DIET processes occur when low-energy photons, electrons, ions or neutral atoms interact with atoms in the surface and near-surface layers of non-conducting materials. It is convenient to characterize such processes as consisting of three stages, illustrated schematically in Figure 11. During the excitation phase, energy from an incoming particle or photon is deposited

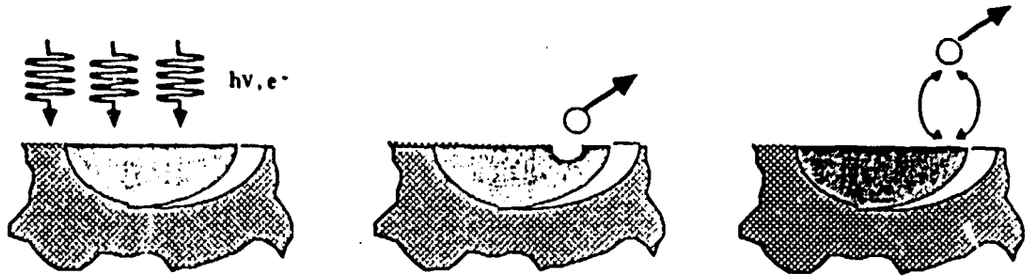



*Figure 11. Illustration of the three phases of a DIET process: (left to right) excitation and localization, ejection and interaction.*

and absorbed *via* an electronic excitation mechanism, generally the creation of electron-hole pairs, and localized for a time on the order of $10^{-12}$ to $10^{-13}$ s. In the second, or **ejection**, stage, the trapped incident energy leaves one or more atoms or molecules in a state which has a net kinetic energy with respect to its neighbors, resulting in movement of the desorbing particle away from its neighbors in the lattice. During the **interaction** phase, as the particle is is in the process of moving away from the surface, it may also undergo other particle-surface electronic interactions, such as charge exchange.

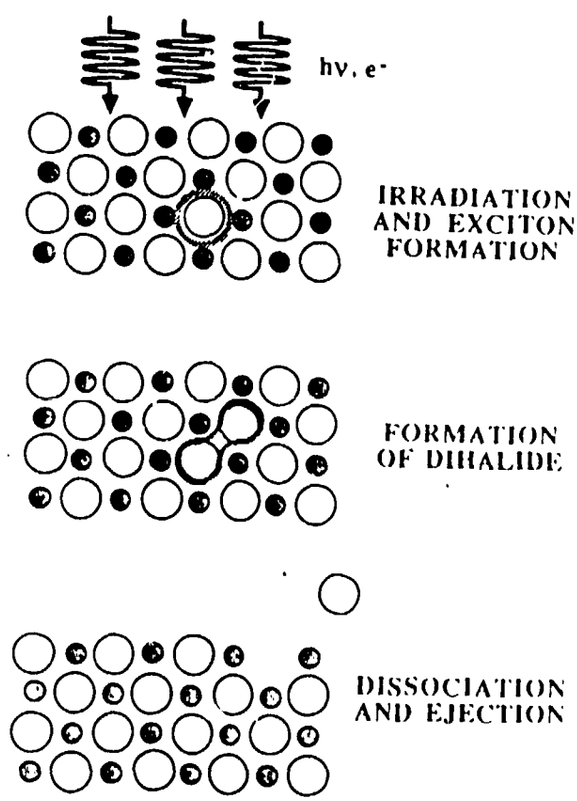
## A Model for Defect-Induced Desorption in Dielectrics

One of the key questions in understanding DIET processes is the identification of specific electronic mechanisms responsible for absorption and localization of energy. The PSD experiments described above show that electronically stimulated desorption of *ground-state* neutral alkali atoms from alkali halide crystal surfaces exhibits a variety of features consistent with thermal desorption at a temperature equal to the surface temperature: a Maxwellian distribution of velocities, a yield *vs.* bombarding energy characteristic which shows relatively few structural features at the known locations of alkali core-hole excitation energies; and a time dependence suggestive of diffusive or thermally-activated movement of defects to the surface. Differences between ground-state ESD and PSD yields do not appear to be significant; those differences that exist probably reflect, as much as anything, either the contrasting energy-deposition profiles or the fact that ESD tends to be a one-step process where PSD can have multi-step effects, including the production of secondary electrons which themselves are capable of effecting ESD.[10]

On the other hand, although the evidence is not as detailed as the results cited here for the alkalis, it has been shown that halogens desorbed from alkali halides under low-energy electron bombardment have suprathermal energies and are emitted in preferential directions along the halogen "strings" in the crystal.[13] This suggests that the formation and relaxation of $V_k$ centers, as originally proposed almost simultaneously by Pooley and by Hersh,[16] is a likely mechanism for the ejection of the halogens from the surface and near-surface layers of the bulk.

The Pooley-Hersh model involves a specific electronic excitation leading to preferential and energetic ejection of halogens along the <110> directions, and is shown schematically in Figure 12. The initial stage localizes the incident electronic energy through the creation of a self-trapped exciton. The transient dihalide molecular ion, formed by the overlap of the excited and a neighboring (normal) halogen ion, relaxes to form H-centers (singly-ionized dihalide ions on halogen vacancies) and F-centers. If formed sufficiently near the surface, H-F-center pairs -- which are extremely stable -- can diffuse to the surface, where a halogen atom is ejected preferentially along the halogen string directions, leaving behind an F center and a defect (halogen interstitial). The F center provides the electron needed for neutralization of the now under- coordinated alkali ion, which then desorbs thermally from the surface. Thus, the Pooley-Hersh picture provides a plausible mechanism for the generation of neutral alkalis to undergo thermal desorption. Moreover, because the Pooley-Hersch mechanism is a simple one-step process -- involving initially only the formation of an exciton -- the creation of neutral alkalis can occur relatively efficiently. In contrast, the Knotek-Feibelman mechanism for creating desorbing ions in maximal-valency covalent solids involves a multi-step inter-atomic Auger decay which is significantly less probable (in the sense of perturbation theory) than an excitonic event. This explains, we believe, the relatively high efficiencies for the production of neutral ground- and excited-state atoms compared to ionic species in DIET from alkali halides.

*Figure 12. Schematic of the Pooley-Hersh defect-induced desorption mechanism.*



No such simple picture appears possible for excited-state alkali desorption, however. For one thing, the time-resolved measurements of PSD for excited-state neutrals shows that the yield of these species drops to background level within 1 ns of the turn-off time of the ultraviolet photon beam. Moreover, the fact that excited-state neutral yields are typically two to three orders of magnitude larger than the ion yields indicates that the mechanism operative in this case must also be relatively simple compared to the Knotek-Feibelman picture, but significantly less efficient than the Pooley-Hersh type of defect-induced desorption. Finally, there is the fact that only the first excited state of alkalis desorbed from alkali halides has ever been observed -- in contrast to the case of hydrogen, for example, where three or four excited states are routinely observed in ESD and PSD experiments.

It is worth while to point out explicitly that these processes can occur in both crystalline and in amorphous materials -- even though, for the sake of simplicity, all of the experimental studies carried out to date have used crystalline samples. The key features of PSD -- namely, the ability to absorb and localize incident electronic energy in a way which allows redistribution of that energy into desorption channels -- arises from the strongly localized electronic charge density in dielectric materials. That charge localization occurs in a random way in amorphous materials, so that it is difficult to predict where (spatially) the defect production will occur. However, the mechanism will operate in much the same way, perhaps with slightly lessened efficiency.

## Surface Modification and Damage Induced by Ultraviolet Photon Bombardment

From these and related ESD experiments, a picture is emerging which clearly demonstrates that electronic mechanisms play a leading role both in *microscopic* desorption processes and in *macroscopic* erosion and surface damage in optical materials of interest in the ultraviolet region of the spectrum. Bearing in mind the influence of surface composition on electronically stimulated desorption dynamics (and the converse!), as well as the model for defect-induced desorption supported by the experimental measurements, it is now possible to consider a credible explanation of surface modification and damage by ultraviolet photon irradiation. In this discussion, it is important to bear in mind that, while the study of color-center formation in *bulk* materials has been a subject of intense study for many years, this work -- as well as its translation into the lore of the uv and X-ray optics community -- has not until now recognized the crucial role played by surfaces and interfaces. It is precisely this feature of real interfaces which our model seeks to incorporate explicitly.

Using the alkali halides as a model material, and considering the effects of the surface overlayer which exists on any surface in a physically realizable environment, we can construct a model of surface damage which takes account of:

-- the operative electronic excitation mechanism;

-- the specific electronic properties of the material; and

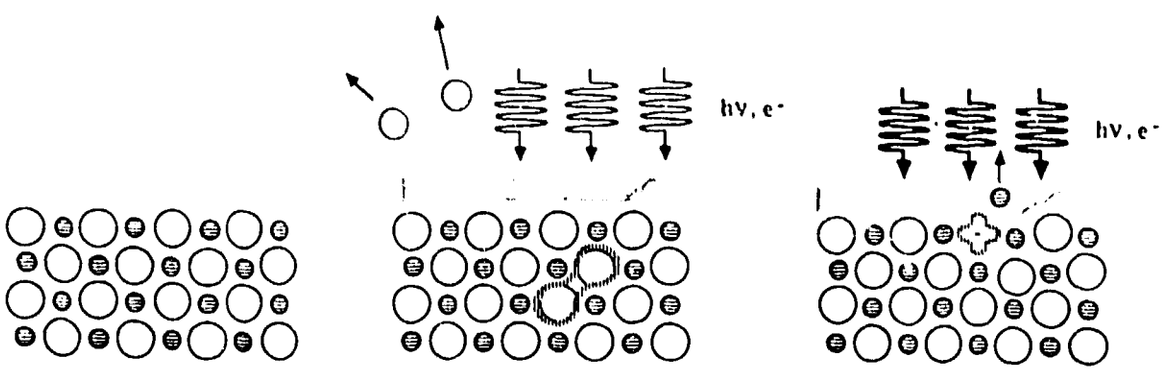
-- the role of overlayers and overlayer-substrate interfaces.

We assume that the Pooley-Hersh mechanism is operative in the substrate, and that the overlayer exhibits photon-stimulated erosion at a rate significantly less than that of the substrate. The model is indicated schematically in Figure 13.

In the **precursor** phase (at left), electronically induced desorption has not begun to take place in significant amounts, but color center formation begins in the bulk, with the net result that halogen ions and atoms are moved to interstitial sites and the alkalis accordingly begin to move from their initial positions, driven by the F-center diffusion mechanism. Defects produced in the substrate bulk will be gettered at the nearest interface, which may either be between substrate and contaminant overlayer, between substrate and any coatings which have been deliberately applied, or between layers of multilayer films. This leads to the evolution of metal-rich interlayers at the boundaries between different materials. Particularly in optical materials coated with multilayer dielectric films, this development of metallic interlayers is portentous.

At some point (Figure 13, middle), there will be significant **overlayer erosion**, either because the photon intensity has reached very high levels or because the total integrated dose has produced a large number of desorption events in the overlayer. (The relationship between desorption and total dose, and between desorption yields and intensity, is not known and is presently the subject of active investigation in a number of laboratories.[17]) At this point, the creation of additional substrate defects occurs with progressively increasing efficiency due to the formation of electron-hole pairs in the near-surface bulk and their diffusively-driven migration to the thinnest part of the overlayer. The precise location of these breaches or gaps in the contaminant overlayer will be determined by a number of statistically-distributed events, including: (1) the migration of defects in the surface overlayer itself; (2) surface rearrangements and reconstructions caused by the desorption of overlayer atoms and molecules; (3) the migration of alkalis and halogens into the overlayer through defect production in the near-surface bulk of the substrate. Hence, the nucleation sites for catastrophic damage may not occur where small-signal-induced defect formation takes place initially.

*Figure 13. Schematic of an electronic model for photon-induced surface damage with thermal consequences in the catastrophic phase.*



When the density of metallic atoms in the gaps or breaches in the contaminant overlayer is sufficiently high, one enters the catastrophic damage phase of surface modification (Figure 13, right). At this point, both electronic and thermal mechanisms can become important. First of all, at sufficiently high surface electric-field densities, it is possible to excite electrons directly into the conduction band even with low-energy photons, so that a surface plasma can be formed. Electrons accelerated by the electric field of the incident photons can easily reach energies required for efficient ESD to occur. Ions can, indeed, be accelerated to energies needed for sputtering -- a process which can under many circumstances occur with greater than unit efficiency. Also, simple thermal absorption by the metals will produce thermal cratering and ablation in the manner only too familiar to the builders of high-energy, high-power infrared lasers for many years. And, while we have not mentioned surface chemistry explicitly, one should not overlook the fact that the presence of reactive species such as oxygen and hydrogen in the contaminant overlayer and near the surface (for materials located in air) will also change the electronic and chemical behavior of the overlayer and exposed substrate materials.

Thus it is possible, starting with isolated desorption events produced by electronic excitations, to arrive at the stage of catastrophic surface erosion and damage where collective, even synergistic, effects become dominant. Moreover, because the detailed study of electronic mechanisms provides the correct description of the energy flow from the incident photons, it is also possible to calculate the rate-limiting features of these surface modification mechanisms in a testable way. It should also be possible, in principle, to look for the most likely synergistic pathways leading to surface modification.

Although our discussion of experimental results has thus far been limited to a specific class of materials -- namely, the alkali halides -- the material properties which allow this type of behavior can now be explicitly identified and extrapolations made to other dielectric materials. Efficient photon-stimulated desorption occurs when two conditions are met:

-- the material in question supports the creation of self-trapped excitons which relax to permanent electronic defects; and

-- those electronic defects are sufficiently mobile to reach the surface and contribute to desorption events.

These conditions are known to be fulfilled not only by the alkali halides, but also by a great many other materials favored as ultraviolet and X-ray optical elements, including alkaline earth halides, many metallic oxides, and fused silica.[18] It may be objected, in the case of X-ray optics, that one is really dealing with multilayer metal films; however, under all realistic conditions, metal films are completely covered with an oxide overcoat which really determines the surface properties. Indeed, it is quite possible that the surface overlayer -- of oxides and whatever other elements, such as hydrogen, that are readily bonded to the surface -- is what really determines the often observed differences between bulk and surface resistance to material modification and damage.

## Summary and Conclusions

In summary, then, recent experiments PSD of *ground-state* neutral alkali desorption in the alkali halides appear to confirm early inferences[13,19] pointing to the formation of self-trapped excitons followed by thermal desorption due to "halogen exhaustion" and defect diffusion. The measurements presented here have provided more detailed experimental answers to basic questions about the mechanisms of DIET processes in insulators than were hitherto available, though some potentially significant features -- *e.g.*, identification of the internal states and the temporal behavior of desorbing halogens -- remain to be studied carefully. In terms of many practical applications, such as radiation damage in alkali halides, it has become clear that the dominant mechanism is ground-state neutral desorption, and that the existence of surfaces and interfaces plays a key role. Hence, the application of optical detection techniques to extract detailed dynamical information on both the desorbing alkalis and halogens will undoubtedly grow in importance in measuring yields, angular and velocity distributions and damage efficiencies. In addition, it is important now to move on to ESD/PSD studies of surfaces with more complex bonding structures to illuminate the role of bond structure on primary desorption characteristics.

In the case of excited-state neutral desorption, however, one can fairly say that the experiments carried out up to the present time have been largely exploratory, and that much of the important dynamical information has yet to be uncovered. Reliable values for relative excited-state *vs.* ground-state neutral yields remain to be extracted, for example, and very little angular distribution data on the alkalis desorbed from alkali halides is presently available. It does not seem possible at this point to guess the specific form of the dynamical mechanisms leading to excited-state neutral alkali desorption.

The one certainty is that many interesting questions about surface-specific bond-breaking mechanisms remain to be studied in these materials. In these studies, neutral species desorption spectroscopy seems destined to continue in a pivotal role, providing both the means for studying the desorption products and the clues to the mechanisms by which optical materials for the ultraviolet and soft X-ray regions are altered by photon-surface interactions -- whether catastrophically or, perhaps, beneficially.

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