

## Optical Radiation from Photon-Stimulated Desorption of Excited Atoms

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The first observation of atomic line radiation due to the photon-stimulated desorption of excited neutral atoms is reported. Synchrotron radiation incident on alkali-halide surfaces is found to result in a surprisingly high yield of desorbed excited alkali atoms, more than three orders of magnitude larger than the yield of desorbed ions. Marked structure in the incident-photon-energy-dependent Li\* resonance line intensity suggests that the desorption is induced by secondary electronic processes.

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Over the past few years, much experimental and theoretical effort has been expended on understanding the mechanism of electronically induced desorption.<sup>1</sup> Previous studies have been primarily devoted to photon- and electron-stimulated desorption of ground-state ions. For the case of electron-stimulated desorption (ESD), only recently has optical radiation due to the ejection of excited neutral atoms and molecules been observed.<sup>2</sup> None of the previous studies of photon-stimulated desorption have dealt with the emission of neutral particles either in the ground state or in excited states. We report here the first observation of photon-stimulated desorption (PSD) of excited neutral particles. The desorbed excited neutral particles were detected by monitoring their characteristic atomic line radiation. The measured yields of excited neutrals are found to be surprisingly large, more than three orders of magnitude larger than the measured yields of desorbed ions.

This effect is observed when photons with energy of 40-200 eV are incident on sodium-chloride and lithium-fluoride surfaces. Spectral analysis revealed two general classes of emitted radiation: (a) discrete line radiation from desorbed surface alkali species, and (b) broadband optical radiation arising from the solid which is known to occur when photons in this energy range are incident on some surfaces. For this work, our emphasis was on measurements of discrete line radiation. In addition to spectral studies, the intensity of optical radiation was measured as a function of incident photon energy, revealing significant structure, and as a function of sample temperature (room temperature to 300 °C). PSD measurements of positive ions were also per-

formed on the same alkali-halide samples.

In these experiments, sodium chloride and lithium fluoride targets maintained at ultrahigh vacuum were bombarded with photons (40-200 eV) using the Grasshopper monochromator at the Tantalus storage ring of the University of Wisconsin Synchrotron Radiation Center. The synchrotron radiation beam was incident at 57° to the surface normal. Optical photons were collected at about 90° to the surface normal. Large count rates as high as  $3 \times 10^3$  counts per second were observed from discrete atomic lines. A cylindrical-mirror analyzer was used for measurements of desorbed positive ions. The NaCl and LiF target (100) surfaces were polished prior to introduction into the ultrahigh-vacuum system and then cleaned by heating to 500 °C in vacuum (base pressure,  $5 \times 10^{-11}$  Torr).<sup>3</sup> Optical radiation was observed with the use of a 0.3-m spectrometer with a resolution of 4.8 nm and a spectral range of 200-800 nm.

The field of view of the optical system included both the bulk and up to about 2 mm in front of the surface. Consequently, radiation from desorbed free atoms as well as bulk luminescence was observed as shown in Fig. 1. Note that in addition to the continuum, only the first resonance lines of sodium, the prominent Na *D* doublet at 589.0-589.6 nm, and the lithium first resonance line at 670.7 nm were observed. This is in marked contrast to other means of excitation including photon- or electron-gas excitation and ion bombardment of the alkali-halide surface which result in detection of many atomic lines. The Na *D* photon signal was found to rise linearly with synchrotron photon flux, indicating that the creation of a free excited atom is an isolated single

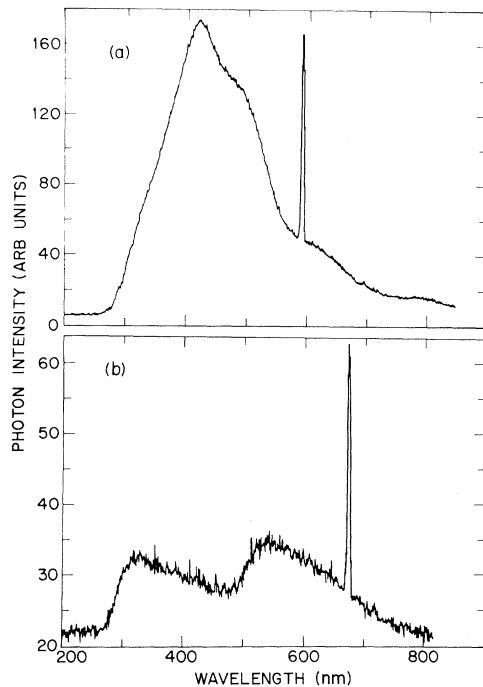


FIG. 1. Spectra of optical radiation produced by zero-order synchrotron radiation transmitted through an aluminum filter (transmits radiation between about 16 and 70 eV) incident on (a) NaCl and (b) LiF, obtained at approximately  $90^\circ$  to the surface normal with a spectral resolution of 2.4 nm.

event. The rate of production of photon-bombardment-induced lithium resonance radiation at 61.5 eV incident photon energy was estimated from our measurements to be  $7.2 \times 10^{-3}$  emitted lithium photon per incident synchrotron photon. This rate is unusually high compared both with previously reported PSD measurements<sup>1</sup> which are typically less than  $10^{-7}$  emitted ion per incident photon, and with the present PSD measurement on lithium fluoride which was found to be approximately  $5 \times 10^{-7}$  emitted positive ion per incident photon. No attempt was made to determine the mass of the emitted ions. The normalized photon and ion signals were found to be quite stable although a gradual dose-dependent decay was observed. Measurements were also obtained as a function of target temperature. For both NaCl and LiF samples, the intensity of resonance radiation was found to decrease monotonically with increasing temperature. All measurements of photon intensity as a function of energy were taken with the target sample at room temperature. All PSD measurements of emitted ions, however, were obtained with a target sample

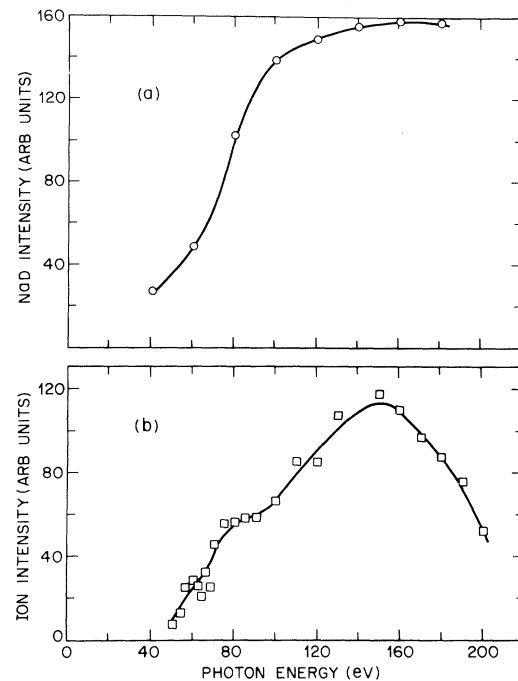


FIG. 2. (a) Na D (588.9–589.6 nm) intensity dependence on incident soft x-ray energy using a room-temperature (100) single-crystal NaCl sample. (b) Positive-ion yield dependence on incident soft x-ray energy with the NaCl sample at approximately  $250^\circ\text{C}$ .

temperature of approximately  $250^\circ\text{C}$  which was found to reduce surface charging.

Figure 2(a) shows the measured intensity of Na D radiation plotted as a function of incident photon energy. Plotted for comparison in Fig. 2(b) are PSD measurements of positive ion yield. These figures along with additional data taken show that the Na D intensity rises smoothly and monotonically with energy, while the ion yield exhibits some structure.

Pronounced energy-dependent structure appears in Fig. 3(a) where the Li resonance radiation intensity is plotted as a function of incident photon energy. Also plotted are our PSD results for positive ions [Fig. 3(b)] and soft-x-ray absorption-coefficient measurements [Fig. 3(c)] obtained by Brown *et al.*<sup>4</sup> The most striking feature common to each measurement in Fig. 3 is a narrow peak at approximately 61.5 eV ( $< 2$  eV full width at half maximum) which is hypothesized to correspond to a Li 1s core exciton.<sup>4,5</sup> Although they have some features in common, the resonance radiation intensity measurements differ somewhat from the PSD ion result and the ab-

sorption data.

To attempt to understand this newly observed phenomenon, both bulk and surface electronic processes must be considered. Electronic sputtering phenomena in alkali halides in the past have been accounted for by invoking the electron- or photon-impact-induced production of defects ( $H$  or  $V_k$  centers) which may diffuse to the surface and result in the ejection of a halogen<sup>6,7</sup> leaving excess metal to evaporate thermally. This phenomenon as traditionally articulated is not adequate to explain the desorption of *excited* neutral alkali atoms but may be an important factor in determining the state of the surface.

Other desorption models currently employed to explain ion ejection include the Menzel-Gomer-Redhead antibonding valence excitation<sup>8</sup> and the Knotek-Feibelman inner-shell excitation models,<sup>9</sup> both of which involve specific excitation mechanisms. As shown in Fig. 3, the desorption of excited neutrals is measured to be roughly proportional to the number of photons absorbed by the target material over a wide range of photon energy. This indicates that the process is nonspecific and does not require a *particular* initial excitation.

It is tempting to try to account for the preferential observation of the first resonance lines by invoking resonance ionization of the higher excited states. This possibility is suggested by the fact that the first resonance levels of Li and Na lie within the forbidden band gaps of LiF and NaCl and all of the other excited states lie near or above the bottom of the unfilled conduction bands. However, if this explanation were true the resulting ion desorption rate would be expected to be *much* higher than actually measured and the energy-dependent photon and ion yields should be in closer agreement. Because of these considerations it is likely that the excited neutral and ion yields must be accounted for by independent desorption mechanisms.

In the light of our observations a plausible three-step desorption scheme for excited neutrals may be hypothesized: (a) The incoming photon creates a core or valence excitation near the surface thereby providing electronic energy to the system in a variety of different ways. (b) One or a series of secondary electronic processes occur, resulting in a long-lived localized-valence excitonic state, which leaves the surface alkali atom in a highly energetic or repulsive state. (c) As the alkali atom departs, the higher excited states, which are more delocalized, preferentially depopulate. As a result, only the first resonance level is observed.

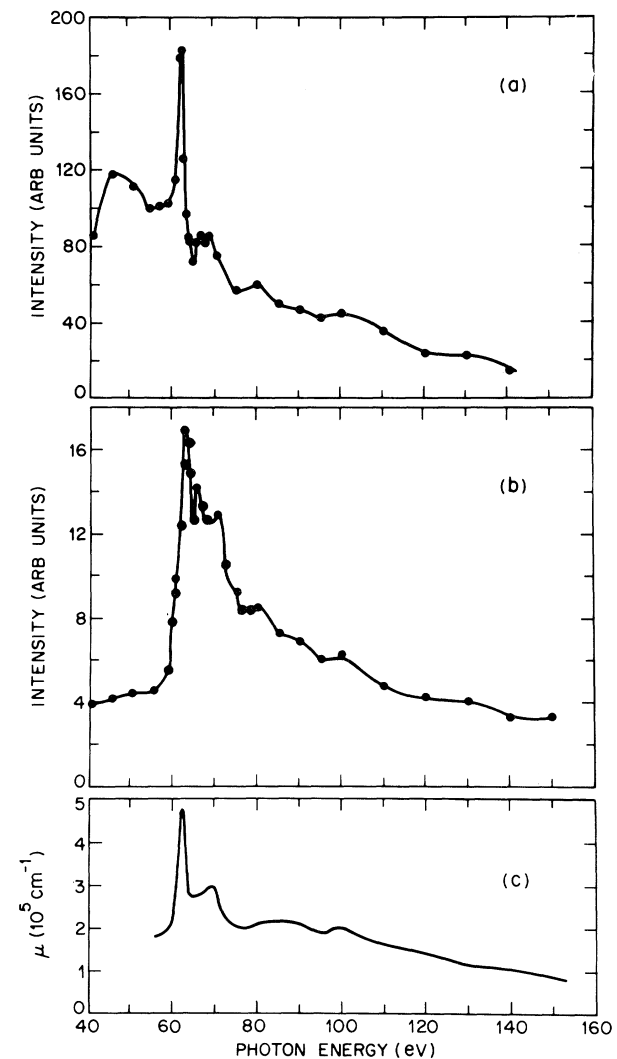


FIG. 3. (a) Li\* (670.7 nm) optical emission dependence on soft x-ray energy using a (100) single-crystal LiF sample at room temperature. (b) Positive-ion yield as a function of incident photon energy using the same sample at about 250 °C. (c) Photon absorption-coefficient measurements (Ref. 4).

erentially depopulate. As a result, only the first resonance level is observed.

These studies, which provide detailed information on final states of desorbed neutrals, promise to provide insight into the electronic mechanisms responsible for photon-stimulated desorption and may constitute a new powerful technique for surface analysis.

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## Cs 5p Absorption Edge in Na-Cs Alloys

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New results for Cs excitation spectra from Na-Cs alloys are presented and the effect of environment on the Cs 5p edge is discussed.

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A number of pure metals including Na, K, Rb, Cs, Mg, and Al yield outer-core excitation spectra which exhibit very sharp absorption edges and have a small overshoot or spike on the shoulder.<sup>1</sup> Mahan and Nozières and de Dominicis (MND) attribute the overshoot to many-body effects in the conduction band.<sup>1</sup> Absorption occurs above threshold because the band states take up energy in electron-hole pair excitations; other effects in the optical matrix elements also contribute to the overshoot.<sup>2</sup> For *pure* metals the theory appears to give at least qualitatively reasonable predictions,<sup>3</sup> but this is not so for *impurities* in metals, to which the theory should also apply. Rare-gas impurities in alkali metals, for example, exhibit profiles which increase linearly from zero at threshold,<sup>4</sup> although MND theory predicts a spike. These phenomena are important because they probe *local* behavior in a conduction-electron liquid. In this Letter we report that the Cs 5p<sup>6</sup> core exhibits a linear threshold at dilution in Na but not in K. We also present the first results showing the transition

from the linear Cs profile to the sharp edge. This occurs with changing composition in Na-Cs alloys. The anomalous effects thus exist in simple monovalent alloys having one electron per atom. Finally, data showing the systematic way 5p<sup>6</sup> excitations depend on environmental factors are assembled and the systematic effects discussed.

Figure 1 shows data for Cs-Na alloys prepared by quench condensing Cs and Na molecular beams simultaneously onto a substrate near liquid-He temperature. A good deal of evidence suggests that such materials are polycrystalline random alloys.<sup>4</sup> The alloys were examined by differential reflectance methods discussed elsewhere.<sup>5</sup> A linear threshold is observed for Cs at dilution in Na (Fig. 1). This behavior echoes profiles reported earlier for Cs adsorbed on Mg,<sup>5</sup> and for rare-gas excitations in alkali metals.<sup>4</sup> Examples of these latter spectra are included in Fig. 1 for comparison. As the Cs content of Cs-Na alloys is increased, a peak grows on the linear profile (Fig. 1). With increasing Cs the peak