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# Auger decay mechanism in photon-stimulated desorption from sodium fluoride

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Photon-stimulated desorption of $Na^+$ and $F^+$ occurs from a NaF(100) cleaved surface upon Na(1*s*) excitation. These measurements represent the first observation of metal-cation desorption following metal-cation—core excitation. In agreement with the Auger decay model of desorption, both sodium and fluorine positive-ion yields (versus photon energy) are similar to total electron yield in the vicinity of the Na *K* edge, except for a pre-edge peak observed predominantly in $Na^+$ desorption. Intra-atomic Auger decay of the Na(1*s*) core hole followed by charge transfer from adjacent halogens is shown to initiate desorption. The resulting neutral or positively charged halogens provide the driving force for desorption of sodium ions from the surface. Expressions are developed for the maximal energy available to the desorbing $Na^+$ or $F^+$ ions.

## I. INTRODUCTION

Photon-stimulated desorption (PSD) from ionic materials has been shown to occur by ionization of surface-atom core levels followed by Auger relaxation of the core hole.[1] Charge transfer of two or more electrons from the bonding region accompanies the Auger decay cascade, and a surface anion species may become positively charged. If the repulsive multihole final state is sufficiently long lived,[2,3] the species may be expelled as a positive ion from the surface. In this paper we shall develop a description of this mechanism, Auger-stimulated desorption (ASD), to encompass both metal-cation and halogen-anion species desorbing as positive ions. We shall identify the major channels in the Na(1*s*) Auger decay cascade resulting in desorption and derive equations for the maximal energy available to the desorbing $Na^+$ and $F^+$ ions.

Alkali halides have advantages as systems for studying the ASD mechanism. Since the absolute electron-energy thresholds[4] for electron-stimulated desorption (ESD) of ions are high (18 eV for NaCl), ion desorption by secondary-electron ESD should be much less important than the direct ASD mechanism. The ionicity[5] of sodium fluoride and other alkali halides is about 90%, justifying the use of simple bonding concepts. Both anions and cations desorb as positive ions from alkali halides, allowing useful comparisons. Clean samples are prepared easily by cleavage in vacuum.

Alkali halides also have complicating features. Calculations predict surface distortions on the order of 5% of a lattice spacing in alkali-halide and other surfaces.[6–11] The stoichiometry of vacuum-cleaved surfaces may be different from that of the bulk: Gallon *et al.* cleaved alkali-halide crystals and monitored the desorbed species with a mass spectrometer.[12] About one atomic plane of fluorine desorbed from lithium fluoride within 10 sec after cleavage; lithium also desorbed. Both sodium and fluorine desorb from NaF after cleavage. Exposure to radiation can alter the surface. X rays produce *F* centers and other defects in alkali halides. Neutral halogens desorb upon low-energy-electron bombardment,[13,14] enriching the metal content of the surface. At electron and photon energies corresponding to substrate core levels, excited neutral-metal atoms desorb with high intensites, yielding atomic line radiation.[15,16] Since our intent in this work is to develop the Auger decay model for highly ionic systems, we defer discussion of the complex role of defects and hydrogen in ion desorption from alkali halides.

Experimental methods are described in Sec. II. Results are presented and described, under four subsections—yield spectra, the pre-edge feature, mechanisms, and energetics—in Sec. III. In Sec. IV, the major conclusions are summarized.

## II. EXPERIMENTAL

The experiment was performed at beam line III-3 at the Stanford Synchrotron Radiation Laboratory (SSRL) using photons of energies between 1075 and 1155 eV. The monochromator[17] transmitted a flux of $2\times10^9$ photons/sec with a resolution of about 0.7 eV full width at half maximum (FWHM) at 1100 eV. The sodium fluoride crystals, of optical quality, were cleaved *in situ* at a pressure of $4\times10^{-10}$ Torr. To minimize charging, the sides of the crystals were coated with colloidal graphite. The PSD experiments were conducted with the light in *p* polarization at an incident angle of 45°, and employed a time-of-flight mass spectrometer described elsewhere[1] with a modified drift tube designed to avoid saturation of the microchannel plates. This drift tube, biased between $-500$ and $-1500$ V to accelerate the ions, was equipped with two masks and electrostatic deflectors, allowing ions to pass while restricting the line of sight between sample and microchannel plates. Total-electron-yield measurements used a positively biased channeltron electron multiplier. The ion- and electron-yield spectra were normalized to incident photon flux as measured by electron yield from a graphite-coated grid.

## III. RESULTS AND DISCUSSION

In this section, yield spectra, the pre-edge structure, mechanisms, and energetics are discussed separately.

### A. Electron- and ion-yield spectra at the Na *K* edge

Ion and electron yields from a cleaved NaF(100) sample are plotted against photon energy in Figs. 1 and 2. Figure 1 covers a photon-energy range of 80 eV, while Fig. 2 displays a 20-eV range near threshold in more detail. The sums of several scans are shown in the prethreshold region in Fig. 2. The intensity ratio of $I_{\mathrm{Na}^+}:I_{\mathrm{F}^+}:I_{\mathrm{H}^+}$ is about 4:2:7. The electron-yield spectra have the same threshold and gross features as the ion-desorption curves. In Fig. 1 an absorption spectrum[18] of a 20 000-Å NaF film evaporated by Rule shows qualitative agreement with the other spectra and with another published absorption spectrum.[19] Our monochromator was calibrated by shifting the electron-yield peaks and valleys to match these two absorption spectra; an error of ±0.5 eV was estimated in matching these peaks. The valley at 1083 eV is slightly deeper for electron yield and $\mathrm{H}^+$ yield than for $\mathrm{Na}^+$ and $\mathrm{F}^+$ yield. A sharp structure ($\sim 1.3$ eV FWHM) occurs as a resolved peak in $\mathrm{Na}^+$ about 2.3 eV below the inflection point of the electron-yield threshold. The intensity and position of the peak are approximately the same for a freshly cleaved surface as for a surface exposed to the photon beam for many hours. The feature is at least 3 times as weak, if present at all, in $\mathrm{F}^+$, and is absent in $\mathrm{H}^+$ and electron yield.

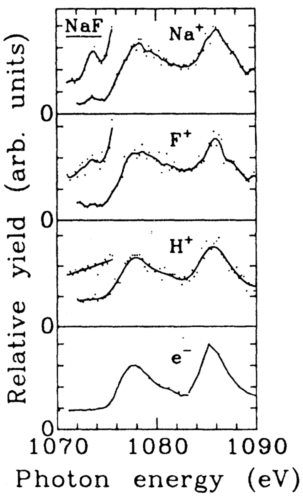

FIG. 2. Comparison of total electron yield to $\mathrm{Na}^+$, $\mathrm{F}^+$, and $\mathrm{H}^+$ desorption. Sums of several scans are shown in the prethreshold region of the ion-desorption spectra. Curves are drawn through the data as a visual aid.

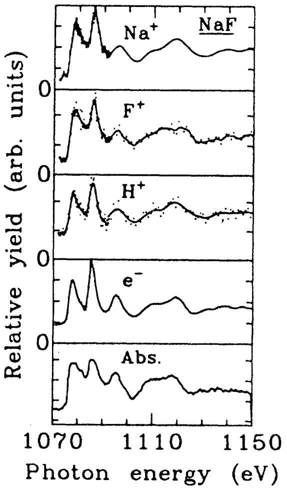

FIG. 1. Comparison of $\mathrm{Na}^+$, $\mathrm{F}^+$, $\mathrm{H}^+$, and electron yield to the absorption spectrum of Rule (Ref. 18). Curves are drawn through the data as a visual aid.

Assuming a photon flux of $2\times10^9$ photons/sec (Ref. 17) and 20% detector efficiency, about $3\times10^{-8}$ $\mathrm{Na}^+$ ions desorb per photon at the $\mathrm{Na}^+$-yield maximum. With the use of Ne or Na photoionization cross sections[20,21] ($\sim 2\times10^5$ b) and arbitrarily considering ionization of only the surface atomic layer, approximately $10^{-4}$ $\mathrm{Na}^+$ ions desorb per surface ionization. By comparison, yields of excited alkali neutrals desorbing from alkali halides are several orders of magnitude larger than ion yields.[15]

In photoabsorption of alkali ions in alkali halides the ionic environment of the alkali ion produces a barrier in the potential of the photoexcited electron. In the approach of Dehmer and Åberg,[22] the barrier partitions the final states into two classes—inner-well (exciton) states and outer-well states. The exciton states have free-ion character and are embedded in the continuum of the outer-well states. For Li(1*s*) absorption[23–25] in LiF, the first prominent structure, assigned to core excitons, lies several eV below the conduction-band minimum. However, for Na(1*s*) absorption in NaF, the first large peak at 1077.7 eV may lie near the conduction-band[19] edge: In the rigid-band approach the Na(1*s*) level to conduction-band transition energy is between 1076.4 and 1078.6 eV (depending on the choice[26–30] of literature values). The rigid-band approach has been discussed previously[25] and gives a reasonable estimate of the position of the conduction-band[23,24] minimum for Li(1*s*) absorption in LiF.

In ASD the ion yield is directly proportional to the core-hole creation rate. Electrons from direct photoexcitation, Auger and exciton decay, and electron scattering contribute to the total-electron yield. Because of electron-electron scattering and multiplication secondary electrons resulting from Auger decay may predominate over those resulting from near-threshold photoelectrons. The charge-transfer process in ASD occurs over a short range and the ions are believed to originate exclusively from the surface layer; the photoionized species responsible for total-electron yield can be many lattice spacings from the surface.[31] Both the ion-yield and the Auger decay component of the total-electron yield are strictly proportional to the absorption cross section and can be compared directly, but the ion yield is more surface sensitive than the electron yield. Assuming that ASD is the primary desorption mechanism, the lack of significant differences (excluding the pre-edge structure) between the PSD and electron yield indicates that the surface sites responsible for PSD are probably similar in electronic structure to those of the bulk.

### B. Pre-edge structure in $Na^+$ desorption

An assignment of the pre-edge structure at 1073.5±0.5 eV must account for both preferential $Na^+$ desorption and the position and shape of the peak. The following possibilities can be rejected.

(1) The high-absolute-energy ESD threshold[4] for $Na^+$ desorption from NaCl eliminates single ionization of a halogen and other low-energy processes as channels for exclusive $Na^+$ desorption from NaCl and, by analogy, from NaF.

(2) A step or edge site (i.e., a site with a low surface Madelung potential) is expected[28,32] to have a *greater* $Na^+(3s^{-1}) \rightarrow Na^{2+}(1s^{-1}3s^{-1})$ binding energy than a bulk site; ionization of such a surface site cannot account for a pre-edge structure.

(3) Atomic Hartree-Fock calculations with relativistic corrections were performed on Na and $Na^+$ using the code of Froese-Fischer[33] as modified by Cowan[34]; good agreement with the experimental 1s binding energy[35] and the $1s \rightarrow 3p$ Rydberg energy was found (i.e., ±0.5 eV) for excitation from the neutral-sodium ground state. The calculated $Na^+(1s^2 2s^2 2p^6)^1S$ to $Na^+(1s^1 2s^2 2p^6 3p)^1P$ energy difference is 1078.6 eV; a core-exciton transition energy may be within a few eV of the corresponding free-ion transition energy. (In LiF the Li 2p exciton is 0.3 eV lower[25] than the corresponding experimental transition energy of the free ion). Therefore, the pre-edge peak at 1073.5 eV is unlikely to be derived from a $Na^+$ $1s \rightarrow 3p$ Rydberg transition.

The dipole-forbidden transition to the $Na(1s^1 2s^2 2p^6 3s)$ state, estimated to have a transition energy of 1072.54 eV in an unrestricted Hartree-Fock calculation[36] of the $NaF_6^{5-}$ cluster, is a possible assignment for the pre-edge structure. A dipole-forbidden Li $1s \rightarrow 2s$ exciton is observed in LiF, allowed[24] by coupling to odd-parity phonons. For preferential $Na^+$ desorption to result, however, the transition would have to occur exclusively on surface sodium ions; it is unknown whether this would be the case.

Defects might give rise to absorption below the main edge. A standard bulk defect is a halogen vacancy. Excitation of a Na(1s) electron to produce an *F* center in such a site, however, may have a low cross section and may not result in preferential $Na^+$ desorption. Sample cleavage may result in a nonstoichiometric surface in which sodium *atoms* are present; electron bombardment can reduce Li in certain lithium salts.[37,38] Sodium metal itself[18] has a low-energy absorption edge (1071.7 eV) and a broad structure after threshold unlike any features in the NaF spectrum. However, if the sodium atoms are isolated on the NaF host lattice, their absorption spectra may more closely resemble the spectrum[35] of atomic Na, which has a sharp dominant Na $1s \rightarrow 3p$ Rydberg peak at 1074.9±0.3 eV followed by weaker structures. For the $Na^+$ pre-edge peak to correspond to this atomic transition, a shift of about −1.4 eV would be required. The Hartree-Fock 3p Rydberg rms orbital radius in $Na(1s^1 2s^2 2p^6 3s 3p)$ is 2.6 Å, while the NaF lattice nearest-neighbor distance[39] is 2.317 Å; we speculate that the transition may therefore only appear in the surface layer and be perturbed in the bulk. A pre-edge Rydberg-type structure has also been observed[40] in $D^+$ desorption from $D_2O$ ice. For this Na $1s \rightarrow 3p$ Rydberg-type assignment to be plausible, subsequent decay of the core hole must occur such that $Na^+$ is produced in a repulsive state on the surface; it is not known whether such a repulsive state will be produced.

### C. Auger decay mechanism

ASD (Refs. 41 and 42) accounts for anions being converted to positive ions and then desorbing, with thresholds at both anion and cation core levels. Following *halogen-ion* photoabsorption in an alkali halide, the halogen decays by the Auger process, becoming positively charged. This positively charged species then experiences a repulsive Madelung potential, and desorbs with a few eV of kinetic energy. Following *metal-ion* photoabsorption the core hole decays with an interatomic charge-transfer step, producing a positively charged halogen which desorbs as before. Although the Auger effect itself is usually regarded as intra-atomic in nature, this latter interatomic decay process has often been represented as interatomic Auger decay. The decay mechanism has been considered previously only in general terms, and has been limited to understanding anions desorbing as positive ions. In the discussion below we shall describe a model for the desorption of *both* $Na^+$ and $F^+$ ions following an interatomic process of Na(1s) hole decay in which the initial Auger step itself is intra-atomic.

Experimental evidence for interatomic Auger decay from core levels is limited. Linewidth broadening originally attributed to interatomic decay was later assigned[43] to phonon broadening. Interatomic Auger decay energies for several ionic systems[44] were estimated and compared to experimental spectra; several weak features were assigned to interatomic Auger decay in NaF. A rough comparison shows the area of the $Na(K)Na(L_{23})F(L_{23})$ structure of Ref. 44 to be about 1% that of the intra-atomic $Na(KL_{23}L_{23})^1D$ structure. Transition rates for Auger decay have been calculated[45]: For solid $CH_4$ and $CF_4$ the intra-atomic rates are a factor of $10^4$ larger than the interatomic rates; only for systems such as Na/O or Mg/O are the calculated interatomic and intra-atomic rates comparable. Clearly, interatomic Auger decay can be considered as a major decay channel only when the normal intra-atomic decay cannot take place.

In NaF the Na(1s) hole produced by photoionization can decay, with a low probability, via a $Na(K)F(L)F(L)$

or Na($K$)Na($L$)F($L$) process, or with much higher probability by an ordinary Na($KLL$) intra-atomic decay. If we consider the latter channel, $Na^{3+}$ is produced within $10^{-15}$ sec (the initial state being $Na^+$). Charge transfer from surrounding fluorine ions must then occur, by the process

$$Na^{3+}+F^{-}\rightarrow Na^{2+}+F^{0} , \tag{1}$$

exothermic by 53 eV, followed by either

$$Na^{2+}+F^{0}\rightarrow Na^{+}+F^{+} \tag{2}$$

or

$$Na^{2+}+F^{-}\rightarrow Na^{+}+F^{0} , \tag{3}$$

which are exothermic by 14 and 28 eV, respectively, as estimated using point-charge lattice corrections to free-ion energies. The energy released in the charge-transfer steps may result largely in fluorescence or in expulsion of electrons from the valence band. The latter process has the net result of an interatomic Auger event; its probability is determined by the extent of polarization about the multihole sodium ion. The quasi-interatomic Auger decay Na($L_3$)F($L_3$)F($L_3$) is endothermic. The experimentally observed[44] quasi-interatomic Auger decay Na($L_3$)F($L_3$) F′($L_3$), where F and F′ are different fluorines, is exothermic by $\sim 7$ eV.

These processes, Eqs. (1)—(3), should proceed on a very fast time scale, leaving the sodium ion that had lost a 1$s$ electron back in its original charge state, as $Na^+$, with, at most, a little excitation energy in the outer shell. The net result, after about $10^{-12}$ sec (a vibrational period) is either that two of the nearest-neighbor fluorine atoms will be neutral $F^0$, or that one will be unipositive $F^+$. In either case the total electrostatic environment of the $Na^+$ ion in question can be repulsive, leading to desorption of the $Na^+$ ion (or of course the $F^+$ ion could desorb).

The real issue to be resolved in discussing this mechanism is therefore not whether the $Na^+$ ion can desorb by Na(1$s$) photoionization at the Na $K$ edge, but the subtler question of whether the electrostatic environment can remain repulsive long enough for this desorption to occur, i.e., for $10^{-12}$ sec or longer. Electronic polarization of the lattice will occur within about $10^{-15}$ sec and will partially screen the repulsive terms in the potential. The effectiveness of this screening depends on the extent of the polarization. Diffusion of the two excess positive charges (on two $F^0$ atoms or one $F^+$) away from one other will be much slower; in a completely ionic material it could occur only by electron hopping, while faster charge transfer through bonds is feasible in a more covalent material. Thus the polarizability and ionicity can both be critical in establishing the feasibility of positive-ion desorption in ionic lattices such as alkali halides.

### D. Ion-desorption energetics

In the limit of complete ionicity, we can readily derive the energies available to both the metal and halogen atoms desorbing as positive ions. Following the approach of Mott and Littleton[46,47] for an ionic lattice in which one anion site is made neutral or positively charged, we combine electrostatic attraction and repulsion, Born repulsion, and polarization relaxation to determine the net repulsion energy. This total repulsion energy can be transferred either to the lattice or to a desorbing ion or both. It thus represents the maximal energy available to a desorbing ion. Unfortunately, a comparison of the repulsion energy to experimental kinetic energies[4] is obviated by the presence of surface charging. The approach taken below may thus be especially valuable in predicting ionic species that *cannot* desorb by a given process.

Consider $Na^+$ desorbing from a sodium chloride lattice site, in which $z$ electrons have been removed from a neighboring halogen ion. We choose NaCl although the energetics of NaF are very similar. The net energy $E^+$ available for desorption of $Na^+$ is the difference between the repulsive energy $U^+$ resulting from an effective charge $z$ on the neighboring halogen and the cohesion energy $W^+$ of the $Na^+$ ion to the lattice. All quantities are defined as positive in sign. The repulsion energy $U^+$ is

$$U^{+}\sim\frac{ze^{2}}{rk_{\text{eff}}} , \tag{4}$$

where $e$ is the electron charge, $r$ is the distance between the $Na^+$ and the halogen under consideration, and $k_{\text{eff}}$ is the effective dielectric constant. For a maximal estimate of repulsive energy, we set $k_{\text{eff}}$ equal to 1. For a nearest neighbor with[39] $r=2.820$ Å we find $U^+$ to be about $5.1z$, measured in eV, for NaCl. The cohesive energy $W^+$ to remove a $Na^+$ ion from the surface is

$$W^{+}=\alpha E_{M}^{+}-E_{\text{BR}}^{+}-0.5e\phi^{+}-E_{S}^{+} , \tag{5}$$

where $\alpha$ is the surface correction to the bulk Madelung energy $E_M^+$. For $Na^+$ in a perfect (100) surface lattice site[48] $\alpha=0.96$ and $E_M^+=8.92$ eV. The second term $E_{\text{BR}}^+$ is the Born repulsion energy, about 1 eV for NaCl. The polarization potential[46] $\phi^+$ in a rigidly held lattice is about 1.5 eV for NaCl; if the removal is on a time scale such that the lattice can relax, the polarization term is about 3.5 eV. For desorption, the time scale is intermediate but closer to the relaxed-lattice case. If we ignore the surface correction $E_S^+$ to the Born repulsion and polarization terms, then $W^+$ is about 4.3 eV. The net energy $E^+=U^+-W^+$ for desorption of a $Na^+$ ion is

$$E^{+}=U^{+}-\alpha E_{M}^{+}+E_{\text{BR}}^{+}+0.5e\phi^{+}+E_{S}^{+} . \tag{6}$$

Production of a positive halogen ion corresponding to $z=2$ is clearly sufficient to expel a $Na^+$ ion from the surface. We see that $U^+$ and $W^+$ are comparable if we maximize the contribution of $U^+$ by setting the dielectric constant equal to 1 for single ionization of a halogen ion. If this latter process could lead to metal-cation desorption, $Na^+$ would have a low-energy threshold at the halogen $np$ binding energy. However, the ESD absolute threshold energy[4] at 18 eV for $Na^+$ desorption from NaCl is too high, eliminating this possibility for NaCl.

The energy $E^-$ available to a desorbing positive halogen ion is

$$E^{-}=\alpha E_{M}^{-}+E_{\text{BR}}^{-}-0.5e\phi^{-}-E_{S}^{-} . \tag{7}$$

For alkali halides, the bulk Madelung energy $E_M^-$ and surface correction $\alpha$ have the same values as those of the cation. The Born repulsion term $E_{\mathrm{BR}}^{-}$ for the positive halogen ion has a smaller value than that of the cation. The polarization term $\phi^{-}$ has two contributions: (1) When the halogen atom $X$ is ionized to $X^{+}$, the lattice relaxes, stabilizing the halogen in the lattice, and (2) as the halogen is removed, polarization stabilizes the vacancy, facilitating removal of the halogen. If the first term is more important, $\phi^{-}$ will be positive in sign. $E_S^{-}$ is the surface Born repulsion and polarization correction term.

Surface Madelung energies ($\alpha E_M$) of many step sites are between 50% and 70% of the bulk values and energies of other sites are even lower.[48] The Madelung-energy term provides the driving force to desorb the halogen ion, making desorption of halogens from majority (high surface Madelung-energy) sites favored energetically. For metal cations, which are repelled from a neighboring ionized halogen, yet bound to the lattice by the Madelung interaction, desorption from minority (step, edge, and other) sites is favored.

## IV. CONCLUSIONS

ASD accounts for $\mathrm{Na}^{+}$ and $\mathrm{F}^{+}$ desorption from NaF. Following photoabsorption of the Na $K$ shell, the sodium ion decays via the $KLL$ Auger process. Relaxation of the $\mathrm{Na}^{3+}$ species to the original charge state $\mathrm{Na}^{+}$ occurs primarily by charge transfer from surrounding fluorines. The net result after about $10^{-12}$ sec is that either two of the nearest-neighbor fluorine atoms will be $\mathrm{F}^{0}$ or that one will be $\mathrm{F}^{+}$. The electrostatic environment of the $\mathrm{F}^{+}$ ion and the neighboring $\mathrm{Na}^{+}$ ions can be repulsive, leading to desorption. The leading term for energies available to the desorbing ions are the surface Madelung energy ($\alpha E_M$) and the electrostatic repulsion $U$, respectively. In particular, desorption of the halogen is preferred energetically from majority surface sites, while metal-cation desorption is preferred energetically from minority sites. In order for desorption to occur the electrostatic environment must remain repulsive for a characteristic time: This time will be controlled by the diffusion rate of the two holes (on two $\mathrm{F}^{0}$ or one $\mathrm{F}^{+}$) away from each other. In fact, the efficiency of the desorption process, about $10^{-4}$ $\mathrm{Na}^{+}$ ions desorbing per surface ionization, is small. The ASD model predicts the observed ESD absolute thresholds [the Cl($3s$) edge at 18 eV for $\mathrm{Na}^{+}$ desorption[4] from NaCl, and the F($2s$) edge at 32 eV for $\mathrm{F}^{+}$ desorption[49] from LiF], the observation of halogen and metal species desorbing as positive ions, and the general agreement of the ion-desorption spectra to the total-electron yield in NaF. In a planned future publication we shall address the limitations of this model.

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