Classical-Trajectory Studies of Electron- or Photon-Stimulated Desorption from Ionic Solids

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We present trajectory calculations of electron- or photon-stimulated desorption of positive ions from alkali halides via the "Coulomb explosion" mechanism, in which desorption is due to the repulsive forces resulting from formation of a positive halogen ion (F^+). In many circumstances, the lattice is shown to rearrange within $\sim 10^{-13}$ s and trap the F^+ ion, thus blocking desorption. The dynamic lattice distortions are crucial in the determination of which desorption channels are open, which species desorb, and what final kinetic energies are obtained.

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Photons and electrons can induce electronic transitions to states that are repulsive in character, and the subsequent conversion of potential energy into motion of the lattice atoms can result in the emission of particles from the surface.[1,2] Such processes have significant technological impact in many areas including microfabrication with photon or electron beams, and more generally, in radiation damage of solids. In addition, desorption induced by electronic transitions (DIET) provides the basis for a variety of useful surface diagnostic techniques.[3] In ionic solids such as NaF there is a particularly simple class of electronic transitions which lead to states that are repulsive.[4] Double ionization of an anion, such as F^-, results in the formation of a positive ion, F^+, in a lattice site normally occupied by a negative ion. The Coulomb forces resulting from this ionic charge configuration are repulsive between F^+ and its nearest neighbors (and attractive between F^+ and its next-nearest neighbors). These forces result in motion of the ions in the vicinity of the newly formed F^+, and they provide a possible mechanism for desorption. Double ionization of F^- can be accomplished by a variety of processes including core ionization of F^- followed by intra-atomic Auger decay, core ionization of the alkali cation followed by interatomic Auger decay, or double ionization of the alkali cation followed by transfer of two electrons from a neighboring anion. Desorption resulting from the repulsive Coulomb environment created by Auger decay of a core hole is known as the Knotek-Feibelman mechanism.[5]

Here we report the results of classical-trajectory calculations which explore the dynamics of nuclear motion in desorption processes, using alkali halides as a model system. We focus on positive-ion desorption because most experiments rely on ion detection for sensitivity, and because the desorption mechanism involves simple Coulomb forces. The alkali halides are particularly interesting for two reasons. First, they have been extensively studied experimentally; and there are a number of observations that are difficult to explain simply on the basis of whether or not an ion is stable in the electrostatic environment caused by a reversal of the Madelung (Coulomb) potential. For example, positive-ion desorption from NaCl under low-energy (< 30 eV) electron bombardment appears to occur only after defects have been formed[6]; there is a propensity for M^+ desorption over X^+ desorption where M^+ represents the alkali cation and X^+ the positive halogen ion[6-8]; there are significant numbers of cluster ions [$(M_2X)^+$, etc.] in the ion mass spectrum[6,7]; and the ion kinetic energies tend to be ~ 1 eV,[6] roughly an order of magnitude smaller than the reversed Madelung potential. Second, the ionic nature of the bonding in alkali halides is particularly simple, and reliable interatomic potentials describing the behavior of these systems are available.[9] The repulsive potentials are among the best known for any DIET process because they are dominated by Coulomb interactions.

We have carried out trajectory calculations for fluorides and chlorides of Li, Na, K, and Rb. NaF will be used as a specific example. In the initial phase, a small NaF lattice ($8\times8\times6$ or $10\times10\times4$) is constructed and allowed to relax to minimize the total interaction potential. We assume that double ionization of a single F^- occurs instantaneously and results in the formation of a ground-state F^+ ion plus two electrons. The two electrons are assumed to escape and to have no effect on the nuclear motion. Classical equations of motion are then solved numerically using a third-order predictor-corrector method.[10] We assume that the double-hole state (F^+) stays localized on a single halogen ion for the duration of a trajectory (1–2 ps). The electronic mechanisms responsible for long-lived two-hole localization have been discussed in the literature.[11-14] Ultimately, our assumption of localization is justified since desorption of F^+ would not be possible unless two-hole localization can persist for $> 10^{-13}$ s. With this approach, we can predict whether or not desorption via a specific mechanism can occur, which species can desorb, and what final kinetic energies are expected. We cannot predict absolute desorption yields since neutralization processes are not included.

We will show that substantial new insight into the desorption process is gained by studying the dynamics of nuclear motion caused by a local change in ionic charge state. In addition, our results show that an accurate treatment of electron transfer processes in desorption must also take into account the significant lattice distortions which occur on the 10^{-13}-s time scale.

The potential-energy surface governing ion motion is taken to be a pairwise sum of scalar potentials, where the pair potentials have the form $V_{ij}(R) = V_{ij}^{S}(R) + Q_i Q_j / R$. We include a large enough number of ions in the solid (~ 400) that the Madelung sum converges to the value for an infinite solid to within a few parts in 10^4. The short-range potentials $V_{ij}^{S}(R)$ are taken from the calculations of Gordon and Kim.[9] These potentials are based on superposition of closed-shell Hartree-Fock atomic ions, with the electron kinetic energy, electrostatic overlap, exchange, and correlation terms treated with a local-density-functional approximation. The Gordon-Kim potentials have been shown to reproduce the equilibrium properties of alkali halides (lattice constant, cohesive energy, bulk modulus) to within a few percent.[15] We also use the Gordon-Kim method to obtain approximate potentials involving the open-shell ion F^+, i.e., we treat F^+ as a spherically averaged Hartree-Fock ion ($1s^2 2s^2 2p^4\,{}^3P$). This approximately accounts for the "orbital shrinkage" of F^+ compared to F^-.

We have made extensive tests to determine the sensitivity of the results to changes in the short-range potentials. With a few exceptions, which will be explicitly pointed out, the qualitative outcome is remarkably insensitive to changes in $V_{ij}^{S}(R)$. For example, doubling or halving $V_{ij}^{S}(R)$ for F^+, or replacing the short-range interactions of F^+-I ($I = F^-, Na^+$) with those of F^--I often have only a minor effect. Similarly, adding the asymptotically correct polarization terms, or simulating deviations from spherically symmetric forces, has been found to have little effect. The reason for this lack of sensitivity is that the dominant behavior is determined by the Coulomb terms in the interaction potentials.

Now we turn to a discussion of specific trajectories. In the first sequence, a double ionization process creates ground-state F^+ on the (100) surface of a perfect NaF lattice at $t = 0$. This corresponds to a sudden transition from a bound potential for F^- to the repulsive curve for F^+ shown in Fig. 1. These one-dimensional potential curves are obtained by freezing of the coordinates of all of the other particles, and summing of the interaction potentials as a function of the displacement of the particle of interest from the surface. However, the motion that follows *cannot* be even approximately described as "rolling down" the initially repulsive one-dimensional potential curve. Neutralization[16] may occur at some time, thereby preventing positive-ion desorption. We find, however, that even if neutralization is prevented, e.g., by a correlation bottleneck,[13,14,17] *the newly formed* F^+ *becomes trapped and does not desorb.*

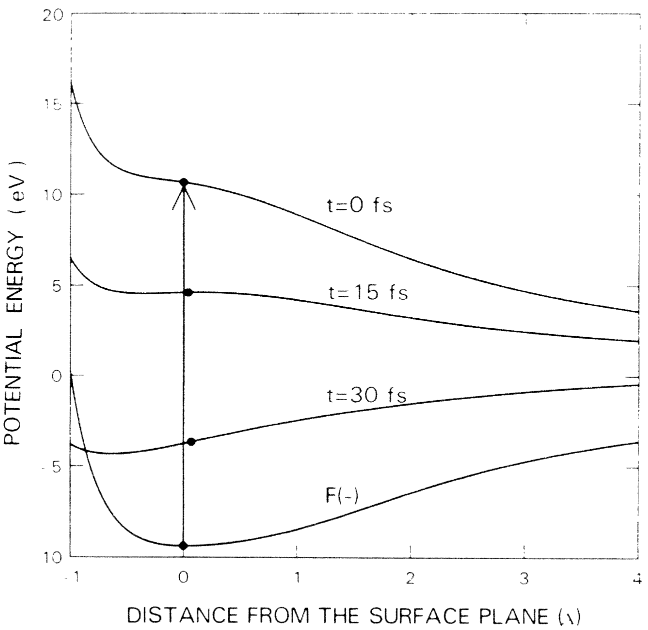

FIG. 1. Interaction potentials are shown for F^- on the surface of NaF (lower curve). $F^- \rightarrow F^+$ at $t = 0$, and the potential is repulsive (upper curve). At later times (15 fs, 30 fs) the lattice distorts and the potentials become attractive. The position of the fluorine ion is indicated by a dot.

In the early stages of the motion, the force acting on F^+ switches from repulsive to attractive. A portion of the lattice adjacent to the F^+ ion is shown in Fig. 2 at $t = 0$ and after 30 fs. After 30 fs, the Na^+ ion below the F^+ has been repelled downward and the nearby F^- ions have been attracted toward the F^+ ion. With this new charge configuration, the forces on the F^+ ion are *attractive,* as illustrated in Fig. 1. *The initially repulsive configuration has been rapidly lost through the displacement of neighboring ions.* A complicated motion follows. The Na^+ ion directly below the F^+ recoils off the third lattice plane and returns toward the surface. This initiates a general displacement in the vertical direction. The F^+ ion becomes displaced ~ 2.5 Å above the surface, but it is held in place by the attraction of F^- ions which were next-nearest neighbors on the surface. The system reaches a mechanically stable configuration, in which the F^+ ion is bridge bonded between two F^- ions, with the F^+ bound by ~ 4 eV. The ability of the lattice to rearrange and trap a double hole (F^+) is somewhat analogous to the process of single-hole trapping (V_k-center formation), which is well known in alkali halides. However, the lattice dis-

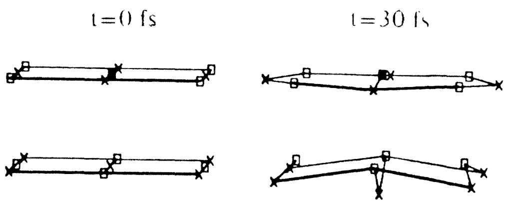

FIG. 2. $F^- \rightarrow F^+$ at $t=0$ on the surface of NaF. The positions of ions adjacent to F^+ are shown at $t=0$ and after 30 fs. Na^+ is indicated by a cross, F^- by an open box, and F^+ by the filled box. In the distorted configuration on the right, the net force on F^+ is attractive.

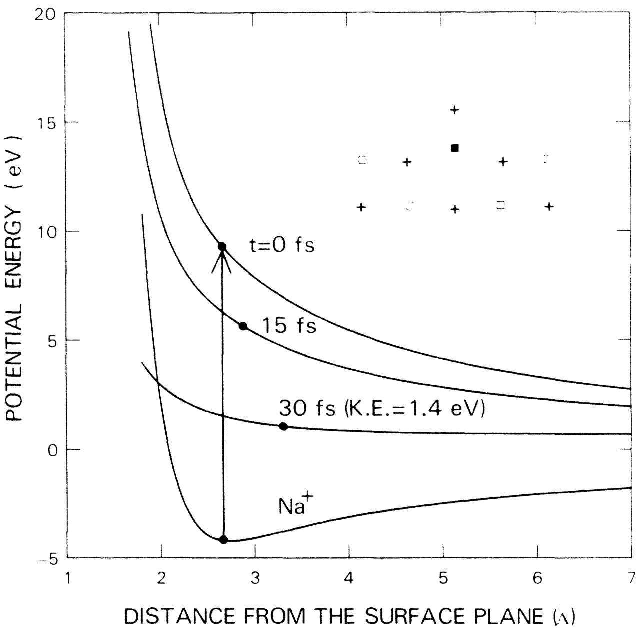

FIG. 3. Interaction potentials are shown for an Na^+ adatom (lower curve). At $t=0$, $F^- \rightarrow F^+$ directly below the adatom, and the potential is repulsive (upper curve). The initial configuration is shown in the inset; Na^+ is indicated by a plus, F^- by an open box, and F^+ by the filled box. Lattice distortions reduce the repulsion at 15 and 30 fs. The position of the Na^+ adatom is indicated by a dot.

tortions required to trap a double hole are much more severe. The end result is a damaged lattice, but no positive-ion desorption.

Next we examine double ionization of an F^- ion in the plane directly below the (100) surface of a perfect NaF lattice. Such an event is considered as a possible mechanism for desorption of the Na^+ ion on the surface directly above the newly formed F^+. Upon formation of F^+, all of the nearest neighbors (Na^+) are repelled, and all of the next-nearest neighbors (F^-) are attracted. The calculations predict that nearest-neighbor F^- ions from the surface layer trap the Na^+, which becomes a mechanically stable adatom. Once again, the initially repulsive configuration has been stabilized by a rearrangement of the lattice which occurs on the $\sim 10^{-13}$-s time scale.

For a perfect NaF lattice, the trajectory calculations predict that creation of ground-state F^+ in a lattice site normally occupied by F^- does *not* result in positive-ion desorption. The ionic charge configuration does not stay repulsive long enough for desorption to occur because the neighboring ions rearrange into a stable configuration. The dynamic lattice distortions can block desorption even under the most favorable assumptions of electronic localization.

A number of factors can increase the ion desorption probability. There may be minority sites, either intrinsic or radiation-induced defects, where geometrical considerations favor desorption. Examples of such site specificity have been previously observed in desorption experiments.[18, 19] Consider a Na^+ adatom directly above a F^- ion on the (100) surface. The initial charge configuration and calculated potential curves are shown in Fig. 3. If the F^- ion becomes doubly ionized, the Na^+ above it experiences repulsive interactions between both its nearest and next-nearest neighbors. In addition, the F^+ ion in the surface plane cannot recoil away since it is surrounded by Na^+ ions. Thus the lattice configuration can remain repulsive long enough for the Na^+ ion to escape. However, the effect of dynamic lattice relaxation is still very significant. The Na^+ ion desorbs with a final kinetic energy of $\simeq 2$ eV. This is only a small fraction of the initial repulsive potential energy of $\simeq 10$ eV.

There are a number of ways of generating stronger repulsive forces. For example, Na^{+3} can be formed by core ionization of Na^+ followed by Auger decay.[8] The neighboring F^- ions will then move toward Na^{+3} because of the increased Coulomb attraction. If two electrons are transferred from one of the F^- ions at the distance of closest approach, very strong repulsive forces would result from the newly formed Na^+-F^+ pair. For double ionization of Na^+ in the second layer, two electrons may be transferred from the F^- ion above it at the distance of closest approach. The classical-trajectory calculations then predict cluster-ion desorption, where the cluster, $Na_4F_5{}^+$, is composed of the F^+ ion plus the eight surrounding surface-layer ions. This large cluster may fragment into smaller clusters upon neutralization of F^+. Cluster-ion desorption is made possible by the strong correlation in the motion of neighboring ions due to the Coulomb interaction. Additional desorption channels are open via this mechanism. For the analogous process with double ionization of Na^+ in the third layer, the trajectory calculations predict that the Na^+ ion directly above in the surface layer is ejected. The desorbed Na^+ ion is predicted to have a final kinetic energy of $\simeq 1.4$ eV. Again, this is only a small fraction of the repulsive potential energy originally available.

We have examined the role of lattice temperature by doing a sequence of calculations in which the ions have (Gaussian) random initial displacements and velocities. For $T = 300$ K, the temperature has little effect on the critical early stages of lattice distortion (< 100 fs). This is expected because the thermal energies ($\simeq 0.025$ eV) are much smaller than the reversed Madelung energy ($\simeq 10$ eV), and the random displacements are much smaller than the subsequent distortions. In our calculations, temperature (300 K) has not been a factor in determining whether or not desorption occurs. This is consistent with observations[7] which show a weak temperature dependence for K^+ and Cl^+ from KCl. However, the thermal fluctuations break the local symmetry and result in displaced configurations for trapped ions at long times.

The trajectory calculations are consistent with available data, and they help explain a number of experimental observations. Pian *et al.*[6] suggested that defect formation may be necessary for positive-ion desorption from NaCl bombarded by electrons with energies above the Cl($3s$) core threshold (18 eV), but below $\simeq 30$ eV. Na^+ was the principal ion observed for low electron energies (< 100 eV), and ion kinetic energies were ~ 1–2 eV. Our calculations provide a *qualitative* basis for an understanding of these results. At higher electron energies, significant yields of Cl^+ and large mass peaks attributed to cluster ions were observed.[6] Similar results have been reported for KCl.[7] For NaF bombarded by ~ 1-keV x rays,[8] both Na^+ and F^+ yields were found to be correlated with Na^+ core ionization. For this system, a large number of decay channels are open because of the ~ 1-keV excitation energy. The observed desorption for this system may be due to two-electron charge transfer from F^- to Na^+[3] at a close distance of approach. This mechanism combines Coulomb and overlap repulsion to achieve a powerful driving force.

According to our calculations, the only example of positive-ion ejection resulting from the formation of a single ground-state positive halogen ion in a *normal* lattice site may be F^+ ejection from LiF.[20] The trajectory calculations predict that F^+ desorption from a LiF surface site is marginal and depends on details of the potentials. The factors favoring F^+ desorption from LiF include the small lattice constant (large Coulomb forces) and the small (but not too small) mass ratio. For all other systems, substantial additional forces were found to be necessary to yield positive-ion desorption. A more detailed discussion of these calculations will be presented elsewhere.

In conclusion we have shown that the dynamic distortions of the lattice can be a crucial factor in photon- or electron-stimulated desorption of ions from ionic solids. The lattice can rearrange and trap an ion even when localization of the electronic excitation is favorable and when the initial configuration is quite repulsive. The ability of the lattice to rearrange has a major effect on desorption yields, on final ion kinetic energies, and on determining the nature of sites where the desorption process may be particularly effective.

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