Collisional Deexcitation at Ion-Bombarded Surfaces

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A new class of inelastic collisional processes accounts for the electron spectra of ion-bombarded sodium halide surfaces. These spectra indicate that the deexcitation process consists of a sequence of lattice-ion collisions in which localized electron transfer occurs. Such collisional processes demonstrate how collisions can initiate electronic change in molecular compounds and that electron-transfer processes must play an essential role in chemistry activated by energetic collisions.

Energetic collisions in solids produce damage, defects, diffusion, and alter the chemical structure of compound materials. Collisional modification of materials is well known both for externally ion-bombarded surfaces as well as for solids that undergo internal nuclear decay. Very little, however, is known of any specific mechanisms responsible for bombardment-activated chemistry—mechanisms where electron capture collisions play a key role. In this Letter we identify a specific inelastic collisional process where we can directly monitor the occurrence of electron capture collisions. This newly identified class of inelastic capture collisions is, we assert, involved in the activated chemistry associated with ion bombardment.

Electron-emission spectra obtained from ion-bombarded ionic compounds provide definitive evidence for a new class of inelastic collisional processes in solids — processes that are basic to defect production and chemical modification in many nonconductive materials. The specific process consists of an inelastic collision sequence within the solid, associated with localized electron transfer and valence change. The electron-transfer step involves collisions between lattice ions that produce displaced, charge-exchanged atoms which are no longer chemically bound. Such collision-induced electron-transfer processes thus can change the chemical state of stable compounds, can switch interaction potentials from attractive to repulsive, and can produce free-atom migration in the solid. They are an essential component of radiation damage mechanisms in compound materials. This type of electron transfer process, which we describe here for ionic solids, is a first example of how collisions in solids can initiate electronic processes that are similar to those stimulated by electron impact excitation [1]. In both cases localized electron transfer accompanied by Madelung potential change can result in atom ejection and diffusion.

Collisional electron capture processes are also of fundamental interest in other technical areas related to bombardment-induced modification of materials and collisionally activated surface chemistry. These include chemical sputtering and plasma-assisted etching [2,3], energetic-ion damage tract formation in insulators [4], and the long-term stability problem of nuclear waste storage materials [5] where internal collisional processes (due to α-recoil nuclei) are similar to those described here and will also alter the chemical integrity of the material.

Inner-shell atomic excitation at surfaces bombarded with keV ions is known to result from orbital interactions and electron promotion processes [6,7] that occur during energetic binary encounters. As a result of such collisional excitation, electron emission due to inner-shell deexcitation processes can take place. Auger electron emission can occur either from excited atoms in the solid or, if the inner-shell lifetime is sufficiently long, from fast excited atoms sputtered from the surface. Such ejection and deexcitation processes resulting in the emission of electrons with characteristic energies are well known and have been extensively investigated in the case of ion-bombarded metal surfaces [8,9].

Inside the solid, however, deexcitation can occur, not only as a consequence of the characteristic lifetime of the excited state, but also as a result of subsequent collisional interactions which can significantly affect the decay process itself. Fast-moving, inner-shell excited atoms that collide with nearby target atoms also experience collisional perturbation and interaction of their excited-state electronic levels. This additional interaction implies new collisional mechanisms in which charge transfer plays a critical role in determining the deexcitation process. Such collisional deexcitation mechanisms can involve excited states, formed by electron capture, which have decay schemes different from that of the initially excited atom; they may also include interatomic Auger deexcitation processes [1,10] where electrons from both colliding atoms participate. These collisional deexcitation mechanisms are due to collisions between moving, inner-shell excited atoms and static atoms of the lattice and can result in nonradiative transitions in which the emitted electrons are characteristic of the deexcitation process.

This concept that nonradiative deexcitation is a consequence of collisional interaction and electron transfer has not been specifically considered in theoretical descriptions of inelastic collisional processes in solids and has not been studied experimentally until now. We present data here for ion-bombarded sodium halide surfaces that can only be interpreted in the context of a collisional deexcitation

event wherein electron-capture processes, which can only occur during a collision, play a critical role. These localized collisional charge-transfer mechanisms can be the key step in collisionally enhanced reactivity and desorption processes at surfaces.

The electron spectra, excited by ion bombardment, that we observe on sodium halide surfaces are very different from what is observed on elemental sodium. For metallic sodium, a single intense transition at about 26 eV has been observed [11]. The spectrum that we obtain, however, on a stoichiometric (100) sodium halide surface consists of three narrow, intense transitions in this same 25–35 eV region [12,13]. These spectral differences imply that the excitation/deexcitation processes in ionic solids are not like those in metals.

A spectrum for NaCl due to 3 keV Ar$^+$ ion bombardment at a 50° angle of incidence is shown in Fig. 1; similar spectra also have been observed on NaF and NaI. These spectra were acquired in the $EN(E)$ mode using a single-pass cylindrical mirror analyzer with an absolute accuracy of about 0.5 eV; additional experimental information will be presented elsewhere [13]. Our results for a number of alkali halides [13] can be summarized as follows.

(A) For stoichiometric surfaces of NaF, NaCl, and NaI collisionally excited with 0.4 to 5 keV ions of either argon or neon. (1) All of the low-energy electron spectra consist of the same three narrow lines (~1 eV, FWHM) at 25.3, 27.9, and 30.9 eV (these line energies are independent of the ion/target combination and of the bombarding energy). (2) The intensities of the three lines decrease with decreasing ion bombarding energy; upper limits of the ion-excitation threshold energies are between 400 and 500 eV for both argon and neon projectile ions. (3) The relative intensities of the three lines are independent of the bombarding ion energy for a specific ion/
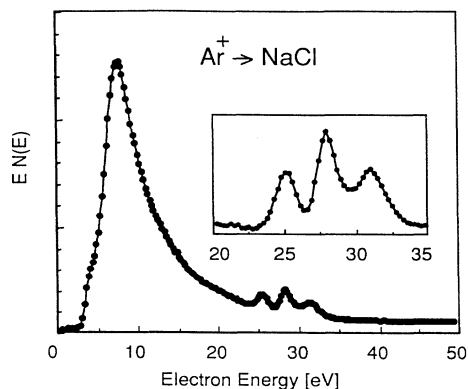
target combination.

(B) For stoichiometric surfaces of NaF, NaCl, and NaI excited by 2.5 keV electron impact (rather than by ion bombardment), we observe (4) no electron-excited features in the 25–35 eV region.

(C) On halogen-depleted sodium halide surfaces, however, (5) the line intensities of the three narrow ion-excited transitions (25–35 eV) are related to the halogen near-surface concentration: the less halogen present, the lower are the line intensities.

(D) For Ar$^+$-ion-bombarded stoichiometric surfaces of KCl, we observe (6) no ion-excited transitions in the 25–35 eV region.

From these results, it is clear that sodium is collisionally excited [(A) 1–3, (D) 6] and that collisions in the lattice [(B) 4], as well as the presence of halogen in the near-surface region [(C) 5], are responsible for the three characteristic transitions that we observe.

Assignment of these three low-energy transitions seen in the sodium halides can be made using free-atom gas-phase spectra for neutral sodium [14–17]. Spectral assignments for Na^{0*} indicate that the three sodium halide lines are due to the following autoionizing transitions in neutral $2p$ core-excited sodium:

$$\text{Na}^{0*}2p^53s^2 \rightarrow \text{Na}^+2p^6 + e^- \ (25.7 \text{ eV}), \qquad (1)$$

$$\text{Na}^{0*}2p^53s\,3p \rightarrow \text{Na}^+2p^6 + e^- \ (28.0 \text{ eV}), \qquad (2)$$

$$\text{Na}^{0*}2p^53s\,3d \rightarrow \text{Na}^+2p^6 + e^- \ (30.9 \text{ eV}). \qquad (3)$$

Deexcitation processes in metals, which involve electron capture, do not reflect the free-atom excitation spectrum of the collisionally promoted electrons. Inner-shell electrons that have been excited to unfilled states (analogous to autoionizing levels in a free atom) are no longer localized on the excited atom but are delocalized in the conduction band. Consequently, the deexcitation spectrum, which involves electrons from the conduction band, would merely reflect the occupied density of states in the valence band (but not that of any specific excited state).

In wide band-gap solids like sodium halides, however, the valence electrons are highly localized and there are no free electrons in the conduction band. Sodium and chlorine, for example, are both essentially closed-shell structures in NaCl: Na$^+$($2p^6$) and Cl$^-$($3p^6$). Here, it is then possible to excite electrons collisionally to a number of localized states each of which can decay by discrete deexcitation transitions.

Collisionally core-excited sodium ions Na^{+*} ($2p^53s$ or higher excited states) can deexcite directly to the $2p^6$ ground state only by a radiative transition (by photon emission). The low-energy electron spectra that we observe are, based on line-energy assignments, due to the nonradiative deexcitation (by electron emission) of $2p$ core-excited neutral sodium Na^{0*} states. For a Na $2p$ vacancy to deexcite and emit an electron, it is necessary that there be at least two electrons in the outer shell. Since the collisionally excited sodium in a sodium halide

FIG. 1. Energy distributions of electrons emitted from a stoichiometric NaCl (100) single crystal surface bombarded with 3 keV Ar$^+$ ions. The inset shows the three peaks (assigned to autoionizing transitions of neutral sodium) after subtraction of a smooth background; energies are referenced to the vacuum level.

is initially an excited lattice Na^{+*} ion, then nonradiative deexcitation implies that electron capture processes are critical in determining the electronic state of the excited sodium and, therefore, its decay channels.

The basic issue, then, is how does an initially collisionally excited sodium Na^{+*} ion (with a single $2p$ vacancy) form the neutral autoionizing states of Na^{0*} that we see for the sodium halides.

Our results on electron-impact-excited Na^{+*} in NaCl show that the excited Na^{+*} does not deexcite by emitting a low-energy electron; however, those excited by ion bombardment do. In the latter case, the excited sodium is moving with hundreds of eV energy; the electron-excited sodium, however, remains static in its lattice site. Therefore, energetic collisions must be involved in the deexcitation process. As we will show, electron capture takes place in subsequent collisions between a moving Na^{+*} and stationary lattice ions to produce the inner-shell-excited neutral Na^{0*} precursor state needed for nonradiative decay to occur.

In sodium halides, collisional electron transfer processes that result in the formation of an inner-shell excited neutral sodium atom Na^{0*} can take place in two ways. First is a one-step formation process, in which electron transfer occurs simultaneously during the primary excitation collision between the projectile (or a fast target recoil ion) and a lattice Na^{+} ion. In this case, the charge state of the projectile is critical since electron attachment can only occur if the projectile ion has already been neutralized prior to the collision in which the lattice Na^{+} ion is excited. Thus the charge state of the projectile can be used to assess the likelihood of such a one-step Na^{0*} formation scheme. Let us consider the possibility of projectile-ion charge neutralization at the surface of a wide band-gap insulator. Because there are no electrons in the conduction band, Hagstrum-type surface neutralization [18] would have to occur by electron tunneling directly from the deep-lying valence band of chlorine (10.9 eV binding energy). For such deep levels, the barrier to tunneling is very large and it seems very unlikely that such neutralization could occur. In addition, Ne excitation spectra on NaCl indicate that the Ne^{+} projectile ion is not neutralized prior to an excitation collision [13]. A detailed discussion of this point will be given elsewhere [13]. Other evidence indicating that the projectile ion is not neutralized comes from gas-phase excitation spectra resulting from the bombardment of neutral gas atoms of Ar, Ne, and He with sodium Na^{+} ions [16,17,19]. We expect for our sodium halide spectra that, if the inert-gas projectile were neutralized, then the transitions we observe would be very similar to the gas-phase transitions observed for corresponding collision partners under single-collision conditions. Such gas-phase sodium electron spectra for collisions between Na^{+} and neutral Ar, Ne, or He [16,17,19] depend on the specific collision partners involved since, in this case, simultaneous electron excitation and electron capture takes place during a single col-

lision. However, the gas-phase Na^{+} collisions with neutral Ar and Ne atoms do not produce spectra that are at all similar to those that we observe for Ar^{+} and Ne^{+} collisions with sodium halides [13]. Therefore the Ar^{+} and Ne^{+} projectiles are not neutralized at the time of impact, and the one-step Na^{0*} formation process must not be the predominant mechanism responsible for the three-line deexcitation spectrum observed on ion-bombarded sodium halides.

A second way to produce a core-excited neutral Na^{0*} is a two-step process involving two sequential inelastic collisions in the solid. This type of collisional sequence forms the basis of our proposed collisional deexcitation model in which collisional electron capture is the fundamental neutralization process. The essential components of this model are presented in Fig. 2 where P^{+} is the projectile and NaCl is the ionic target. In the first step, a projectile ion (or a fast moving Na^{+} recoil ion) collisionally excites a sodium lattice ion (e.g., to $Na^{+*}2p^{5}3s$) and sets it into motion. [Step 1. Collisional excitation: $(P^{+}+Na^{+}) \rightarrow P^{+}+Na^{+*}$.] The lifetime of the $2p$ vacancy (which can only decay radiatively) is sufficiently long for the fast moving Na^{+*} to collisionally interact with a nearby halogen Cl^{-} ion. In the second step, electron capture from the lattice $Cl^{-}3p^{6}$ ion into the M shell of the moving Na^{+*} can occur during an energetic inelastic collision and, thus, produce the three autoionizing states of neutral excited Na^{0*} that yield the observed spectrum. [Step 2. Collisional electron capture: $(Na^{+*}+Cl^{-}) \rightarrow Na^{0*}+Cl^{0}$.] Following this second inelastic collision, nonradiative deexcitation $(Na^{0*} \rightarrow Na^{+}+e^{-})$ can occur and produce the characteristic three-line spectrum observed and ion-bombarded sodium halides. Since we have previously indicated [(B) 4] that no sodium deexcitation transitions are observed under static lattice conditions, the electron capture process responsible for the subsequent nonradiative deexcitation can only occur during a collision.

Electron capture probabilities are, of course, related to the electronic orbital overlap as well as to the energies of the levels involved. Both depend on the distance R between the interacting Na^{+*} and Cl^{-} ions. In the static NaCl lattice, the binding energy of the least-bound $3p$ electron of Cl^{-} is 10.9 eV [20], whereas the binding energy of the $3s$ electron of a moving inner-shell excited atom $Na^{0*}(2p^{5}3s^{2})$ (after electron capture) can be assumed to be very similar to the corresponding gas-phase
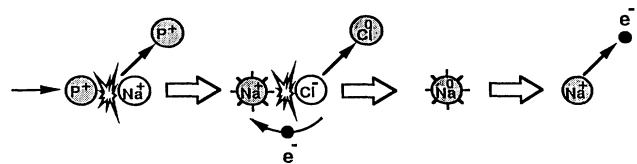

FIG. 2. Collisional deexcitation model for P^{+} ion bombardment of NaCl. Electron capture occurs during the second collision to form an excited Na^{0*} atom.

value of about 7.6 eV. Consequently, from an energetic point of view, electron capture by Na^{+*} from Cl^- can take place only during an energetic collision in which the levels are shifted closer together by about 3 eV. Such shifts are possible in the case of sodium halides where the binding energy of the least-bound p electron of the negative halogen ion is believed to decrease with decreasing R [7]. This shift can result in level crossings which make resonant electron transfer processes [21] not only energetically possible, but which also strongly enhance the probability for collisional electron capture to take place. The occurrence of electron capture collisions in solids has been shown recently by Schippers et al. (Fig. 10 in Ref. [22]) to depend on level crossings.

Similar shifts and level crossings also can occur in chemical compounds other than the alkali halides. For a large group of compounds (e.g., oxides, halides, nitrides) the electron-donor p-level binding energies are typically in the range of 10–15 eV. Electron transfer is highly probable when these collisionally perturbed p levels are degenerate with the energy level of an acceptor (metal) ion. For multiply valent metal ions, this energetic constraint indicates that singly charged ions are the most likely to be involved in such electron transfer processes. We have found recently that collisional electron transfer is indeed dependent on the charge state (valence) of the acceptor ion. Our data show that collisional electron transfer in aluminum compounds, for example, takes place for singly valent Al^+ rather than for triply valent Al^{3+} [23] since level crossing is not possible in the latter case. Even though the description of the system energetics relies on the accuracy of a specific correlation diagram, the use of this basic level-crossing concept makes the prediction of charge-transfer collisions possible.

The bombardment-induced electron spectra described here can be attributed to a specific class of electron transfer and deexcitation mechanisms that only occur during collisions. These localized inelastic interactions are fundamental in collisionally enhanced reactivity and desorption processes at surfaces, and in radiation damage mechanisms in compounds. While we have specifically discussed collisional processes in sodium halides, the electron-transfer process in general is subject to the energy constraint of level crossing. We find this level-crossing condition to be essential in determining whether electron-transfer collisions can take place in specific compounds [23].

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