Evidence for F⁻ Formation by Simultaneous Double-Electron Capture during Scattering of F⁺ from a LiF(001) Surface

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Slow F⁺ ions ($v < 0.1$ a.u.) scattered from a clean and flat LiF(001) surface under a grazing angle of incidence exhibit a high probability for forming F⁻ ions in the reflected beam, whereas no negative ions are found for neutral F⁰ projectiles. From detailed studies of projectile energy loss and charge transfer, we find evidence for a correlated double-electron capture process in the formation of the F⁻ ions.

Collisions of ions or atoms on surfaces are usually characterized by the transfer or excitation of several electrons. So far, aside from work on Auger [1] and Kondo [2,3] effects, models describing projectile surface charge transfer consider only sequential independent one electron processes. Such has been used to explain exoelectron and O⁻ emission due to the interaction of thermal O_2 with alkali metals [4] or in models for surface neutralization of multiply charged ions [5]. On the other hand, strong correlations can be observed in gas phase collisions for transfer excitation [6] or double electron capture [7] in the sense that each individual electronic transition occurs with a lower probability than the two-electron transition. These types of simultaneous two-electron transitions do not necessarily involve dynamical electron-electron correlation [6–8]. While there is little doubt that similar processes should also exist at surfaces, none seem to have been identified. We address the following question: Can such processes be important for ion-surface collisions and by extension for large molecular targets where detailed collision experiments are scarce?

This Letter presents experimental evidence for a correlated double-electron capture process in grazing scattering of F⁺ projectiles from a LiF(001) surface. The striking result is the observation of large fractions of negative ions in the scattered beam for F⁺ projectiles, whereas for neutral F⁰ projectiles no negative ions are detected. From this finding and from energy loss measurements we conclude that for low incident velocities, F⁻ formation from F⁺ projectiles does not proceed via two independent one-electron capture processes at the surface: (i) F⁺ → F⁰; (ii) F⁰ → F⁻. Instead, two electrons are captured in a correlated manner from neighboring halogen sites. This correlation is attributed to the energy benefit associated with the close location of the holes in an ion-pair mechanism involving a doubly charged surface. The ion-pair mechanism is a central concept in chemical physics; however, such an ion-pair mechanism involving dications has been

mainly conjectured. In the gas phase double charge transfer reactions have been observed only as minor product channels associated with rather low cross sections (see, e.g., [9]) or in very specific conditions via deep UV excitation of molecules (see, e.g., [10]). The observation here that double charge transfer is the dominant product channel suggests that the reaction could be important for large molecular targets.

The experimental data have been collected with two different setups, in Orsay and Berlin, using two different target crystals. In both setups a pulsed fluorine projectile beam is scattered at grazing incidence from a well-prepared LiF(001) single crystal aligned along a high index azimuthal direction. The angle of incidence was chosen close to 1° so that the energy for the projectile motion normal to the surface ($P_\perp^2/2m$) is about 1 eV. Under these conditions projectiles are reflected at a distance of several a.u. above the topmost surface layer. The scattered projectiles are analyzed for charge state, scattering angle, and time of flight. At Berlin scattered particles pass through a thin carbon foil before reaching a channeltron ensuring equal detection efficiency for all charge states. At Orsay the full scattering profiles for all charge states are recorded simultaneously on a position sensitive microchannel plate detector. Also, in both setups the electrons emitted above the target are detected in coincidence. Accordingly, extensive sets of data have been recorded for F⁺, F⁰, and F⁻ projectiles and their products.

Before discussing the present results, recent progress in understanding the formation of negative ions on ionic crystals is briefly recalled. The observation of large fractions of negative ions [11–13] after scattering on ionic crystals was, at first glance, surprising in view of the large energy defect between the projectile affinity level (e.g., 3.4 eV for fluorine) and the binding energies of valence band states (>12 eV for LiF). These observations were interpreted in terms of successive binary collisions with F⁻ ions

embedded in a point-charge lattice. On the time scale of the binary collision, the hole created by the electron transfer remains localized on the halogen site [14,15] so that the Coulomb attraction between this positive charge and the F^- product ion decreases the energy defect to several eV, giving rise to a low velocity threshold for negative ion formation. Such a confluence of energy levels may be related to the ion-pair mechanism routinely invoked in the gas or liquid phase. Once a negative ion is formed, its direct detachment back to the surface is blocked by the wide band gap of LiF. Hence the negative ion population builds up from site to site.

Figure 1 displays negative ion fractions for grazing collisions of F^+, F^0, and F^- projectiles as a function of collision velocity. With neutral F^0 projectiles we find the established threshold behavior for the formation of F^- ions [12]. For incident F^- ions we obtain high negative ion fractions at low velocities. This shows that the electron loss rates are reduced in front of the ionic crystal as a direct consequence of the wide band gap [13]. With increasing projectile velocity, electron capture and loss rates increase so that the scattered negative ion fractions for F^+, F^0, or F^- projectiles merge and any memory of the initial charge is lost. Most striking is the large probability that F^- ions are formed from F^+ projectiles at low velocities. This capture of two electrons cannot be understood by independent sequential one electron capture events (as usually considered in ion-surface interactions), since the final $F^0 \rightarrow F^-$ step is not efficient for low velocities (cf. Fig. 1).

Figure 2 shows energy loss spectra of scattered particles after collisions of 1 keV ($v \approx 0.05$ a.u.) F^+ ions at 1° incidence. The spectra for emerging F^+ and F^- ions both consist of a single peak. The one for F^+ corresponds exclu-

sively to energy loss due to excitation of optical phonons [17,18] and to recoil energies transferred to target atoms [19]. These two contributions to the energy loss should be identical for F^+ and F^- ions [17–19] as confirmed by measurements for $F^+ \rightarrow F^+$ and $F^- \rightarrow F^-$ scattering. Therefore, the additional energy loss $\Delta E = 7.6 \pm 1$ eV observed for emerging F^- ions corresponds to the electronic contribution. Subtracting the energies of the initial and final states, the energy defect for negative ion formation from the F^+ projectile follows from

$$\Delta E = -(I_F^0 + I_F^-) + (E_{\rm vb} + E_{\rm vb} + \Delta E_{h\text{-}h}), \quad (1)$$

where $E_{\rm vb} = 13$ eV is the mean binding energy of the valence electrons at the surface [20–22], $I_F^0 = 17.4$ eV and $I_F^- = 3.4$ eV are the binding energies of free F^0 and F^-, respectively, and $\Delta E_{h\text{-}h}$ is the Coulomb interaction energy between the two holes left on the surface after capture. Equation (1) and the observed energy loss yield $\Delta E_{h\text{-}h} = 2.4 \pm 1$ eV. Comparison of $\Delta E_{h\text{-}h}$ with data obtained for the interaction of the two holes left on the surface after Auger neutralization of light noble gas ions at a LiF surface [23] implies that the two holes have to be created at neighboring halogen sites.

This localization of two holes at adjacent halogen sites separated by $a/\sqrt{2}$ (a = lattice constant) plays a key role in the energy balance associated with the double-electron capture process $F^+ \rightarrow F^-$. In order to evaluate the energy defect ΔE of the charge transfer reaction a point charge model of the surface is used. Such a model was shown to provide a fair estimate of ΔE as compared to Hartree-Fock calculations [12]. The initial state (energy E_I) corresponds to the F^+ projectile at position $\vec{R}$ and the neutral LiF crystal. The two F^- lattice sites participating in the charge transfer are located at $\vec{r}_n$ and $\vec{r}_m$. The final state (energy

FIG. 1. Negative ion fractions of scattered particles for impact of F^+, F^0, and F^- projectiles on LiF(001) under 1° incidence. Open and full symbols correspond to data from Berlin and Orsay, respectively. The solid line is from a calculation [12], whereas the dashed lines are only to guide the eyes. The error bars at low velocity originate from detection efficiency correction estimated from Ref. [16].

FIG. 2 (color online). Energy loss spectra for 1 keV F^+ projectiles after scattering from a LiF(001) surface and emerging as F^+ (□), F^- (△), and F^0 associated without (∘) and with (•) emitted electron. To avoid peak overlap, this last channel is displayed at its actual intensity relative to (∘).

E_{II}) corresponds to the F$^-$ ion at position $\vec{R}$ in front of the LiF crystal with two holes at $\vec{r}_n$ and $\vec{r}_m$. All other sites of the LiF crystal are considered as ± 1 spectator point charges. Neglecting polarization effects we obtain

$$\Delta E(\vec{R}) = E_{II} - E_I = -\{I_F^0 + I_F^-\} + 2[V_{\mathrm{Mad}} + I_F^-]$$
$$+ \frac{1}{|\vec{r}_m - \vec{r}_n|} - \frac{1}{|\vec{R} - \vec{r}_m|} - \frac{1}{|\vec{R} - \vec{r}_n|}$$
$$- 2\sum_i \frac{q_i}{|\vec{R} - \vec{r}_i|}, \tag{2}$$

where $q_i = \pm 1$ is the charge of the ion located at position $\vec{r}_i$ of the crystal. The term in the square brackets gives the binding energy of the F$^-$ ion in the presence of the Madelung potential of the crystal at the position of the halogen site at the surface ($U_{\mathrm{Mad}} = 12.05$ eV). The third term on the right-hand side of Eq. (2) stands for the hole-hole interaction; the fourth and fifth terms, respectively, for the interaction between the negative projectile and two holes formed in the crystal in the final state. The last term arises from the interaction between an external charge and a neutral LiF crystal; for typical distances of closest approach in our grazing experiments it is on the order of an eV. At the instant of charge transfer the local charge of the complex formed by projectile and two active sites is left unchanged as seen from the rest of the crystal. Then the screening effects by the rest of the crystal will not bring sizable polarization corrections to Eq. (2) (see, e.g., [24]). However, when the projectile escapes from the charge transfer region, the crystal polarization given by Mott-Littleton terms [25–27] produces additional screening. This should explain why the measured interaction between the holes is more than 2 eV smaller than the one entering Eq. (2) where, if the two holes are located at adjacent halogen sites ($|\vec{r}_m - \vec{r}_n| = a/\sqrt{2}$), then $\Delta E_{h\text{-}h}$ amounts to 5.07 eV.

According to Eq. (2) the energy defect of the double charge transfer process is drastically reduced if the two holes are located at adjacent halogen sites, and projectiles pass between these two sites. For single electron capture (neutral projectile), the Coulomb attraction of a single hole was shown to reduce the energy defect from about 10 eV at infinite separation down to 3–4 eV on top of a halogen site [11]. Figure 3 shows that for double-electron capture by a F$^+$ projectile from adjacent halogen sites the theoretical prediction for the energy defect goes below 2 eV over a wide region between two halogen sites. From self-consistent field studies we consider this value as an upper bound for the energy defect, since polarization of the scattered F$^-$ ion in the field of the two holes is not taken into account. This implies that, in between two sites, negative ion formation is a quasiresonant double-electron capture process. It proceeds with a much lower energy defect and thus much higher efficiency than the single electron capture F$^0 \rightarrow$ F$^-$. In search for a threshold behavior for double electron capture, charge fractions have been measured
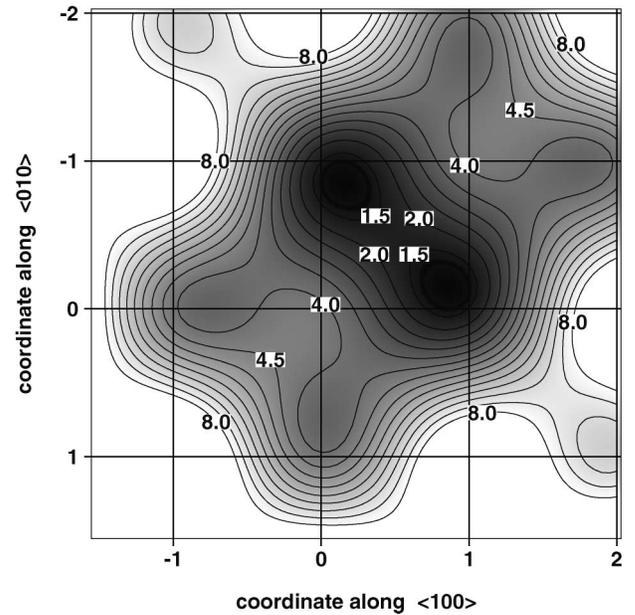
FIG. 3. 2D map of the energy defect (eV) for double-electron capture, F$^+ \rightarrow$ F$^-$ at a distance of 3 a.u. above the LiF surface; the units are in $a/2$ ($a =$ lattice constant). The Li$^+$ and F$^-$ ions are located at the crossings of the grid lines with a Li$^+$ ion sitting in the central position $(0,0)$. The two holes are created at the F$^-$ sites located at $(1,0)$ and $(0,-1)$ positions.

down to 100 eV collision energy. Below 500 eV, the scattered particles hardly penetrate the carbon foil so that the detection efficiency can not be held constant for all charge states. The uncertainty in relative detection efficiency has been estimated from data with O$^+$, O^0, and O$^-$ projectiles [16] and is accounted for by the error bars in Fig. 1. The present results do not indicate a drop of the negative ion fraction at low collision energies suggesting that the energy defect for double-electron capture may amount to sub-eV energies.

The analysis of the neutral products provides important additional information on the electron transfer process. First we emphasize that, at a collision energy of 1 keV, almost 98% of the neutral projectiles are elastically scattered from the surface. Only 2% form negative ions (cf. Fig. 1), and almost no target excitations or electron emission is observed. With F$^+$ projectiles, only neutral scattered particles are detected in coincidence with emitted electrons, and these F^0 were found to originate from detachment of the negative ions formed at the surface. Indeed, considering that F$^-$ ions are formed, on average, at the apex of the trajectory these have twice less the opportunities to detach their electron than incident F$^-$ ions. The detachment probability of 25% ($N_{F^0+e}/[N_{F^-} + N_{F^0+e}]$) derived from Table I is therefore consistent with a detachment probability of about 50% observed with incident F$^-$ (cf. Fig. 1).

When no electron is emitted, the energy loss spectrum of the scattered F^0 reveals two peaks (cf. Fig. 2). The energy lost by the F$^+$ ion via excitation of optical phonons on the ingoing path can be estimated as half that lost by scattered

TABLE I. Energy losses and relative intensities of the processes observed.

F^+ (1 keV) $\rightarrow$	F^+	F^0 1st peak	F^0 2nd peak (excitation)	$F^0 + e^-$	F^-
Energy loss, W (eV)	28.2	12.4	22.7	25.5	36
Intensity N (%)	15	17.3	27.2	10.7	29.6

F^+ (W_{F^+} in Table I) over a complete trajectory. The two peaks in the F^0 spectrum therefore correspond to an energy gain of 2 ± 1 eV and an energy loss of 8.3 ± 1 eV.

The first peak is interpreted as a direct capture from the bottom of the valence band, and the second as the population of a target excited state, an electron bihole complex or trion [23,28]. This state corresponds to an excited electron in the potential of two adjacent holes. Indeed, since at this velocity, F^0 projectiles are scattered elastically, the observed electron capture and target excitation are correlated indicating that the hole and the excitation are created on adjacent halogen sites. Compared with the threshold energy loss associated with electron emission (Table I) a binding energy of 3 ± 1 eV is derived for this state, consistent with previous observations [23]. The population mechanisms could be similar to that demonstrated for single excitons in collision of H or O projectiles [20,29]. When the F^- ion recedes from the (double electron) capture region, its affinity level rises and crosses the level of the trion state.

In summary, three processes are observed involving two electrons: $F^+ \rightarrow F^-$, $F^+ \rightarrow F^0 + e^-$, and $F^+ \rightarrow F^0 +$ trion, representing almost 80% (Table I) of the charge changing processes (or inelastic processes from the electronic point of view). Our observations are consistent with an initial correlated double-electron capture mechanism leading to the formation of F^-, trion population, and electron emission. At present, two possible mechanisms for $F^+ \rightarrow F^-$ conversion have to be considered: either a single bielectronic double capture event or two correlated single electron capture events. By correlation we understand here that the two capture events take place together with the two holes created at adjacent F^- sites. The key feature of the process is the near resonant character of $F^+ \rightarrow F^-$ conversion via the creation of two adjacent holes at the surface, resulting in a drastic reduction of the energy defect for the charge transfer reaction. At low projectile energies, this leads to F^- fractions obtained with F^+ projectiles orders of magnitude larger than for F^0 projectiles. The lack of apparent threshold for this double charge transfer involving dication suggests that this particular type of ion-pair mechanism could also play a role in reaction complex involving large molecules at very low collision energy.

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