

Elastic and inelastic processes in the scattering of positive ions of hydrogen and helium from a LiF surface

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A theoretical calculation that allows for a fairly complete description of the charge-exchange and surface electronic excitation processes occurring in the H^+ and He^+ scattering by ionic surfaces is presented. The interaction parameters required to describe the collisional process are calculated by using a model Hamiltonian that has proved to provide a systematic good description of the properties like binding energy, equilibrium distance, and vibrational frequency of several dimers and atom-surface systems. The formalism is applied to the comparative study of the scattering of H^+ and He^+ by the fluorine atom of a LiF surface. The ion survival probabilities by elastic and inelastic processes are calculated, and the general trends of the experimental findings are reproduced. Very satisfactory results concerning the electron-hole pair excitations in the He^+ scattering are obtained when the charge fluctuation on the active F site is considered. The role of the surface core states is found to be decisive for the $e-h$ pair excitation by He^+ scattering, and for the neutralization of H^+ projectiles.

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I. INTRODUCTION

A great deal of low-energy ion scattering from solid surface experiments have been performed in order to elucidate the mechanisms of ion neutralization and electronic excitation.¹⁻⁵ The energy spectra of ions scattered along trajectories close to the normal direction to the surface show a peak related with the ions that have only suffered an elastic collision with the target atom (elastic peak corresponding to elastic scattering) and other peaks shifted to lower energies with respect to the elastic peak, that correspond to ions that have lost energy by inelastic processes such as reionization, electron-hole pair, or core-electron excitations in the surface (inelastic peaks corresponding to inelastic scattering). It is observed that for several target elements the inelastic peaks dominate over the elastic peak. The usual treatment of ion-surface charge exchange is based first, on considering the ion trajectory divided into three segments; i.e., the incoming region, the close atomic encounter, and the outgoing region, and second, on the surface assumed as a jellium. In this case the ion neutralization occurs by either a resonant or by an Auger process, where the relative importance of each one is determined by the energy position of the ion level relative to the valence band. An alternative approach is to assume that electron transitions take place during the violent collision with individual target atoms. Clear evidence has been presented that violent collisions play a key role in determining the final charge state of the scattered ions, although clear band effects that mark some crucial discrepancies between surface scattering and gas-phase collision are also observed. The ion level promotion due to the hybridization with localized states on the surface opens a possibility of resonance with valence-band states, this being highly favored by the continuum nature of them.

A theoretical description of the scattering process that aims to provide answers about the role of the extended and

localized states of the solid target in the ion neutralization and electronic excitation, must contemplate (i) a model of the ion-surface interaction that allows for the calculation of the projectile energy level and the hopping between the projectile state and the states of the surface atoms, (ii) a time-dependent model Hamiltonian that incorporates these atom-atom interaction terms, and (iii) a formalism accounting for the amplitude interferences in the calculation of ion neutralization and electronic excitation probabilities, allowing also to infer about the role of the interaction with the core states of the target. A theoretical description along these lines has already been presented in previous works.⁶⁻⁸ The results obtained for several ion-target combinations have allowed to understand the different mechanisms of charge-transfer and electronic excitation in terms of the interaction of the projectile state with the band and core states of the surface. It has also been shown from these results that a quantitative and systematic description of the experimental findings depends strongly on a reliable calculation of the parameters that account for the projectile-surface interaction.

In this paper we perform a comparative study of the H^+ and He^+ scattering from fluorine of a LiF surface. For He^+ scattered by the F atom, the experimental data show three subpeaks assignable to elastic scattering and to inelastic scattering due to single and double electron-hole pair excitations. While in the case of H^+ scattering by F, the elastic peak and a remarkable background due to multiple scattering from the deeper layers are only observed.⁵ The experimental scattering geometry corresponds to a 160° scattering angle and an incident angle with respect to the surface equal to 80° . The formation of negative ions in the scattering of hydrogen from a LiF surface has been studied within a time-dependent Hartree-Fock approximation, by using a charged cluster $(Li_5F)^{4+}$ plus the residual point-charge field of the LiF surface to account for the Madelung potential effect on the projectile and substrate energy levels.⁸ One important result ob-

tained in this paper was the enhanced H^- formation in the scattering by the alkali Li^+ ions due to the presence of the F^- nearest neighbors. This conclusion agrees with the more prominent H^- peak observed in the scattering by Li^+ in the $LiCl$ surface,⁹ although these results do not reproduce the experimental findings of Souda *et al.*⁵ concerned with the H^+ neutralization and electronic excitations.

An Anderson-like Hamiltonian is used in this case to describe the collisional time-dependent process. In this way the interactions between the extended and localized states on the surface and the localized states on the projectile site are well contemplated. It has been found that the extended nature of the valence bands is decisive for a good description of the electronic excitations of the surface and the ion neutralization. The different terms of the Anderson Hamiltonian are obtained from a model proposed for describing the adiabatic interaction between the projectile and the target atoms. This implies that the hopping with the band states is written in terms of the hopping with the surface atoms by using a linear combination of atomic orbitals (LCAO) expansion of the solid states, while the energy term related with the energy of the active projectile level is obtained as the difference between the total energies of the corresponding electronic configurations of the interacting system.

We consider that one main question comes from the model Hamiltonian used to obtain the atom-atom interaction terms. This Hamiltonian is derived from a many-body Hamiltonian written in terms of the symmetrically orthonormalized atomic basis set where only those terms leading to bond-pair interactions are retained. Up to this point two options are open: (i) to adopt a Hartree-Fock (HF) approximation with parameters given in terms of one- and two-electron integrals calculated by using the orthonormal basis set, and (ii) to perform an expansion of the parameters up to second order in the overlap over the many-body Hamiltonian followed by a HF approximation. In this case, only the hopping parameters are calculated by using the orthonormalized basis set defined within the dimeric subspace. These two options of the interaction Hamiltonian have been discussed previously and applied to the description of dimeric systems, and also to the interaction of atoms with surfaces.^{10,11} The parameters obtained from the option (i) have been adopted for the description of the ion scattering by surfaces in all our previous works. However, after an extensive analysis of new dimeric systems,¹² we have arrived at the conclusion that the option (ii) provides a more delicate balance among the different interactions involved that leads to a very systematic good description of the properties of the analyzed dimers (binding energies, equilibrium distances, and vibrational frequencies). The main difference between the two options rests on the diagonal terms of the model Hamiltonian, leading to different proposals for the variation of the energy levels with the distance between atoms.

To describe the interaction between the projectile and a clusterlike LiF surface, we calculate the Hamiltonian parameters by using the option (ii). The ion energy level is obtained as the difference between the total energy of the neutral projectile-surface interacting system and the total energy of the ion-surface interacting system.¹³ Another new and im-

portant ingredient is to allow for the charge variation on the active fluorine ion due to the electron capture by the projectile, as a way to take into account the localization of a hole created in this ionic surface.¹⁴ Finally, the extended nature of the band states is taken from a semi-infinite linear-chain model calculation of the ionic compound surface.

Section II A is devoted to a detailed description of the calculation of the interaction parameters, while Sec. II B introduces the model Hamiltonian for the collisional process and discusses the proposal to account for the localized nature of the hole created at the active fluorine ion. The time-dependent formalism for calculating the ion survival probabilities by elastic and inelastic processes is presented in Sec. II C. Also in this section we describe how to calculate the average charge in the active fluorine ion at the surface in a consistent way with the dynamical evolution of the collisional process, and the variation of the projectile velocity accordingly with the electronic transitions. Our results are presented and discussed in Sec. III, and the concluding remarks in Sec. IV.

II. THEORY

A. A model for the atom-surface interaction

The molecular orbitals (MO) of the $(Li_5F)^{4+}$ cluster embedded in the residual point-charge field of the LiF semicrystal are obtained from a full electron self-consistent Hartree-Fock calculation.¹⁵ The projectile-cluster interacting system is then considered as a ‘‘giant dimeric system’’ with the isolated cluster described in terms of its own eigenstates, and the interaction described by a bond-pair model Hamiltonian:¹⁰

$$H = \sum_{i,\sigma} E_{i\sigma}(R) \hat{n}_{i\sigma} + \sum_{i \neq j, \sigma} (V_{ij,\sigma}(R) \hat{c}_{i\sigma}^+ \hat{c}_{j\sigma} + \text{H.c.}) + V_{n-n}, \quad (1)$$

where the i and j states are obtained from a symmetric orthogonalization of the MO Φ_α of the isolated cluster and the atomic state Φ_a centered at the projectile site. A mean-field approximation on the two-electron interactions allows for the following expressions of the Hamiltonian parameters after a second-order expansion in the overlaps S_{ij} is performed:

$$\begin{aligned} E_{i\sigma} = & \epsilon_i^0 - \sum_j S_{ij} V_{ij,\sigma} + (1/4) \sum_j S_{ij}^2 \Delta E_{ij,\sigma} + \tilde{U}_i \langle \hat{n}_{i-\sigma} \rangle \\ & + \sum_{j \neq i} [\tilde{J}_{ij} \langle \hat{n}_{j-\sigma} \rangle + \tilde{G}_{ij} \langle \hat{n}_{j\sigma} \rangle] + \sum_{k \neq j} [h_{ikj} \langle \hat{c}_{k-\sigma}^+ \hat{c}_{j-\sigma} \rangle \\ & + \Lambda_{ikj} \langle \hat{c}_{k\sigma}^+ \hat{c}_{j\sigma} \rangle], \end{aligned} \quad (2)$$

$$\begin{aligned} V_{ij,\sigma} = & t_{ij} + \sum_k [h_{kij} \langle \hat{n}_{k-\sigma} \rangle + \Lambda_{kij} \langle \hat{n}_{k\sigma} \rangle] - \tilde{G}_{ij} \langle \hat{c}_{i\sigma}^+ \hat{c}_{j\sigma} \rangle \\ & + \tilde{J}_{ij}^x \langle \hat{c}_{i-\sigma}^+ \hat{c}_{j-\sigma} \rangle - \sum_k [\Lambda_{ikj} \langle \hat{c}_{k\sigma}^+ \hat{c}_{i\sigma} \rangle + \Lambda_{jik} \langle \hat{c}_{j\sigma}^+ \hat{c}_{k\sigma} \rangle], \end{aligned} \quad (3)$$

where

$$\begin{aligned} \Delta E_{ij,\sigma} &= \left[\epsilon_i^0 + \sum_k (J_{ik}^0 \langle n_{k-\sigma} \rangle + G_{ik}^0 \langle n_{k\sigma} \rangle) \right] \\ &\quad - \left[\epsilon_j^0 + \sum_k (J_{jk}^0 \langle n_{k-\sigma} \rangle + G_{jk}^0 \langle n_{k\sigma} \rangle) \right], \\ \tilde{G}_{ij} &= (J_{ij}^0 - J_{ij}^{x0})(1 + S_{ij}^2), \\ \tilde{J}_{ij} &= J_{ij}^0 - S_{ij}^2 J_{ij}^{x0}, \\ \Lambda_{kij} &= h_{kij} - h_{kij}^x. \end{aligned}$$

All two-electron integrals come from the general expression:

$$V_{ijkl} = \langle \Phi_i(\vec{r}) \Phi_k(\vec{r}') | 1/|r-r'| | \Phi_j(\vec{r}') \Phi_l(\vec{r}) \rangle,$$

where in particular $U_i = V_{iii}$, $J_{ij} = V_{iij}$, $J_{ij}^x = V_{ijj}$, $h_{kij} = V_{kkij}$, and $h_{kij}^x = V_{kikj}$.

The zero superindex refers to the integrals calculated by using the atomic states to differentiate them from the same ones obtained by using orthogonalized atomic functions. This model Hamiltonian has been used for the description of several dimers, leading to very satisfactory results concerning with binding energies, equilibrium distances, and vibration frequencies.¹⁰ The one-electron integrals ϵ_i and t_{ij} include the electron interaction with the nuclei and with the point-charge field of the LiF semicrystal. While V_{n-n} accounts for the projectile nucleus interaction with the nuclei of the (Li₅F) cluster as well as with the point-charge field of the LiF surface.

The hopping parameters $V_{a\alpha}(R)$, where the subscripts a and α denote the orthogonalized states that asymptotically tend to the atomic state of the projectile and the MO of the isolated cluster, respectively, are obtained from the total-energy calculation of the ionic projectile interacting with the clusterlike surface without allowing charge-transfer between them (E^+). The more relevant hoppings correspond to those between the atom state and the MO states that are practically pure $1s$ -F state (V_{a1}), $2s$ -F state (V_{a2}), and $2p_z$ -F state (V_{a3}). The values obtained for these hopping parameters are practically the same as the ones corresponding to the dimer F-H.

The total energy of the neutral projectile-surface interacting system (E^0) is calculated similarly, and the ionization energy of the projectile atom (ϵ_a) is obtained from the difference $E^0 - E^+$.

B. Model Hamiltonian for the collisional process

An Anderson-like time-dependent Hamiltonian within a spinless model is used for describing the collisional process. The interaction of the state localized on the projectile site with the extended and localized band states of the surface is well contemplated in this form. The spinless model is appropriate when it may be assumed that there is only one active atom state involved in the charge-exchange process. This is

clearly the case of the resonant neutralization of He^+ , where the He- $1s$ state for the second electron [$\epsilon_a(\infty) = -24.6$ eV] is the active one. In the case of H^+ , taking into account the energy difference between the affinity level (-0.7 eV) and the ionization level (-13.6 eV), the spinless model may be applied in two steps: first, the neutralization of H^+ , and then the negative-ion formation from H^0 .

The expression of the Hamiltonian is the following one:

$$\begin{aligned} H(t) &= \sum_k \epsilon_k \hat{n}_k + \sum_c \epsilon_c(t) \hat{n}_c + \epsilon_a(t) \hat{n}_a \\ &\quad + \sum_k [V_{ak}(t) \hat{c}_a^+ \hat{c}_k + \text{H.c.}] \\ &\quad + \sum_c [V_{ac}(t) \hat{c}_a^+ \hat{c}_c + \text{H.c.}] + V_{res}(t), \end{aligned} \quad (4)$$

where the k states refer to the valence-band states, and the c states to the core band states that hybridize appreciably with the projectile atomic state of energy given by $\epsilon_a(t)$. The core bands are assumed of zero width. The time dependence of the parameters comes from the classical trajectory $R=R(t)$ described by the projectile. An LCAO expansion of the hopping with the valence-band states leads to

$$V_{ak} = \sum_{i,R_s} c_{i,R_s}^k V_{ai}$$

with the index i summing over the valence states of the surface atom at position R_s . Within a nearest-neighbor approximation, the only interaction maintained is the one with the fluorine atom on the surface:

$$V_{ak} \approx \sum_{i=2p} c_{i,F}^k V_{ai}$$

and the significative V_{ai} corresponds to the V_{a3} hopping parameter obtained from the stationary calculation described in Sec. II A. The coefficients $c_{i,F}^k$ are calculated by using a linear model of the ionic compound surface. The hopping with the core states included in Eq. (4) are the more relevant ones V_{a1} and V_{a2} , as it was discussed in Sec. II A. In Fig. 1, the hoppings V_{a1} , V_{a2} , and V_{a3} are shown as a function of the distance R from the projectiles H^+ and He^+ to the fluorine atom at the surface. The core-level energies $\epsilon_1(R)$ and $\epsilon_2(R)$ are also assumed to depend on the projectile's trajectory according with the adiabatic interaction described by the Hamiltonian (1).

The ion level energy $\epsilon_a(R)$ calculated as the difference $E^0 - E^+$ takes into account the electron interaction with the alternating $+1$ and -1 charge distribution at the lattice sites. This interaction appears in the ϵ_a^0 one-electron term of the expression (2) (atomic units are used):

$$\epsilon_a^0 = \left\langle \varphi_a \left| - (1/2) \nabla^2 - \sum_{\alpha} \frac{Z_{\alpha}}{|r-R_{\alpha}|} - \sum_{i=0}^N \frac{q_i}{|r-R_i|} \right| \varphi_a \right\rangle,$$

where the first two terms correspond to the kinetic energy and the electron-nuclei interaction, while the third represents

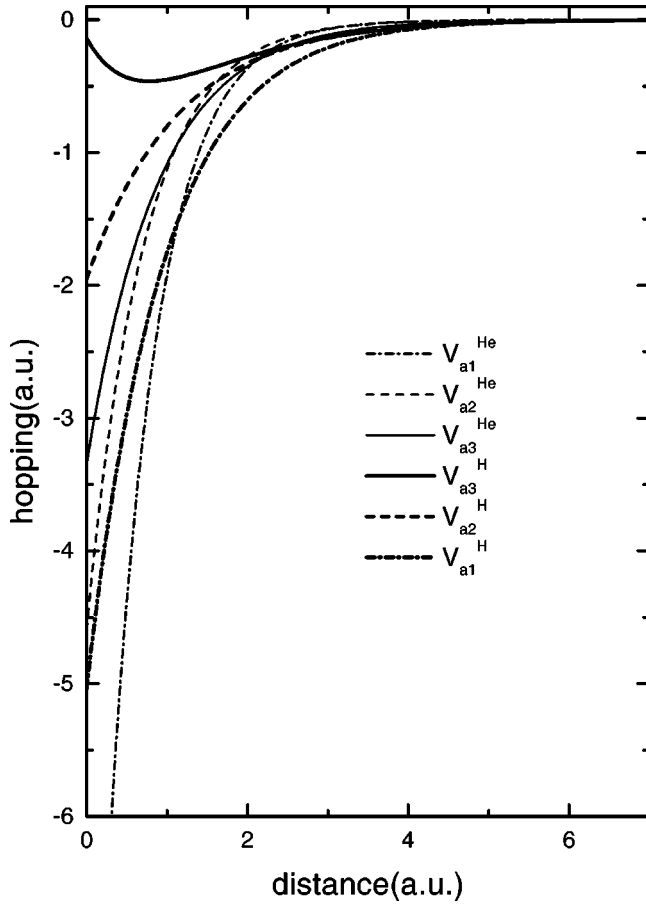


FIG. 1. Hopping interaction terms between the projectile state (a) and the active MO ($\alpha=1,2,3$) of the target, as a function of the ion-surface distance.

the interaction of the electron with the point-charge distribution. In our case the active site $i=0$, $R_0=0$, corresponds to the fluorine atom at the surface with charge $q_0=-1$ participating in the charge-transfer process. A good approximation of ϵ_a^0 is the following:

$$\epsilon_a^0 = \left\langle \varphi_a \left| -\frac{1}{2}\nabla^2 - \sum_{\alpha} \frac{Z_{\alpha}}{|r-R_{\alpha}|} - \sum_{i \neq 0}^{N-1} \frac{q_i}{|r-R_i|} \right| \varphi_a \right\rangle + \frac{1}{R} \quad (5)$$

The repulsive contribution $1/R$ to $\epsilon_a(R)$ implies to assume that the charge of the active site at the surface does not change. In the binary collision the electron capture by the projectile (H^+ , He^+) leaves the corresponding hole localized at the active site within the time scale of the collision process, as it has been already pointed out by Borisov *et al.*¹⁴ In our description we can take into account the dynamical charge fluctuation on the active F^- site along the projectile trajectory defined by $R=R(t)$ as the formalism allows to calculate the average occupation number $\langle n_0(t) \rangle$ for the second electron in the $2p_z$ state of the active fluorine, according with the excitation and charge-transfer processes taking place during the collision. The repulsive contribution $1/R$ in Eq. (5) is then replaced by $\langle n_0(t) \rangle / R$, leading to a less repulsive effect as $\langle n_0(t) \rangle$ becomes smaller than one due to the

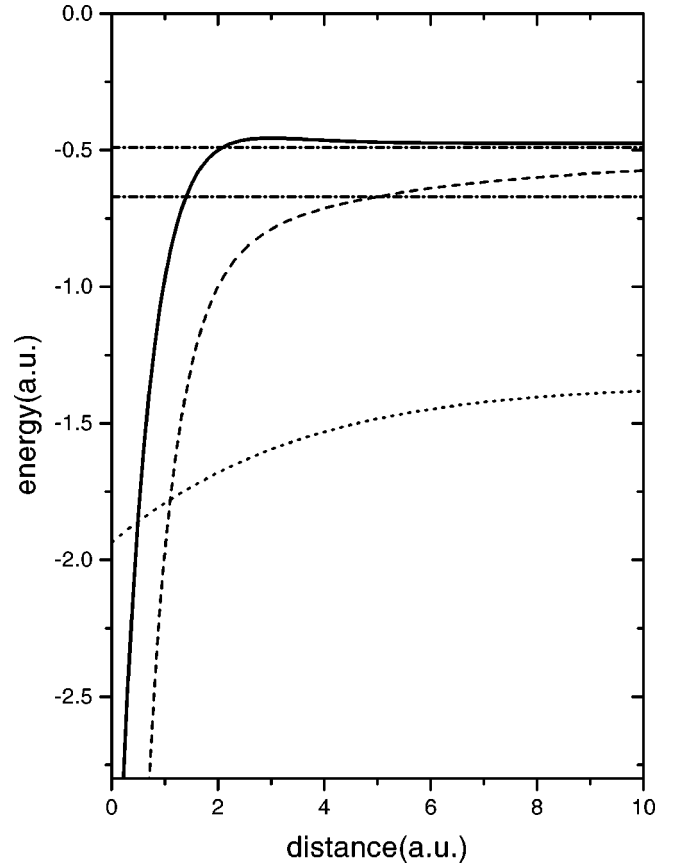


FIG. 2. The H^+ energy level ϵ_a as a function of the ion-surface distance: the solid curve corresponds to the calculation with $\langle n_0 \rangle = 1$ while the dashed curve to $\langle n_0 \rangle = 0$. The dotted curve corresponds to the F-2s core-level energy; and the dot-dashed straight lines delimit the valence-band edges of LiF.

charge-exchange process occurring along the time evolution. The energy levels $\epsilon_a(R)$ for H^+ and He^+ are shown in Figs. 2 and 3, respectively, for two limit situations: $\langle n_0 \rangle = 1$ and $\langle n_0 \rangle = 0$. The energy level in the dynamical calculation is defined between these two limit values depending on the value of $\langle n_0(t) \rangle$ along the ion trajectory. The variation of the hydrogen energy level with the distance from the surface shows a pronounced difference with the one calculated in Ref. 8 by using the option (i) for the interaction Hamiltonian. It is found that the electron-electron repulsion energy is overestimated in the option (i), leading to an upward shift of the level energy for small separation distances and consequently to a systematic underestimation of the binding energies of the analyzed systems.¹⁰ In Figs. 2 and 3 the only core-level energy that shows an important variation as a function of R : ϵ_2 that tends to the $2s$ F state, is also shown.

The “residual” potential included in Eq. (4) is required to calculate the variation of the projectile velocity along the trajectory and the turning points for the collision. We define this potential as

$$V_{res}[R(t)] = \langle H \rangle_{full} - \langle H \rangle_{dynamic} + Z_p \sum_{i=0}^N \frac{q_i}{|R-R_i|},$$

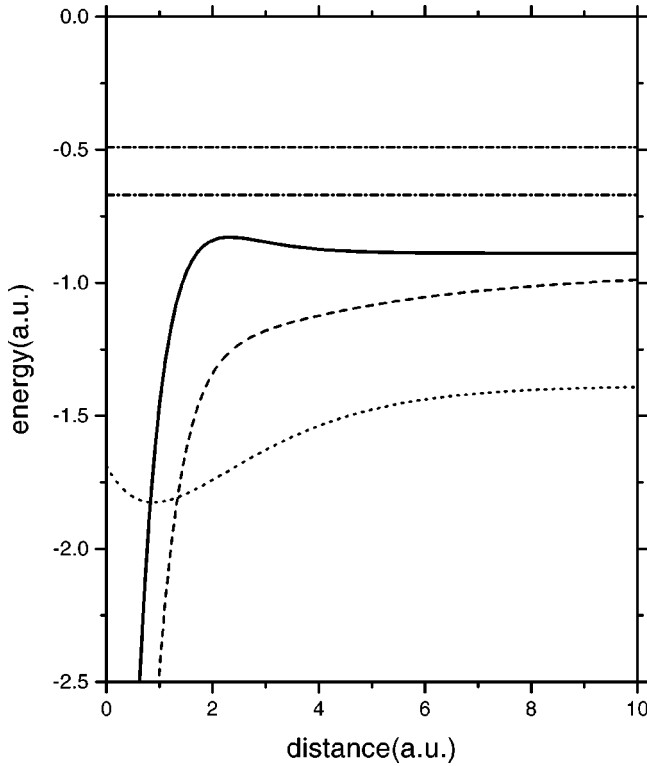


FIG. 3. The same as in Fig. 2 for the case of a He^+ projectile.

where $\langle H \rangle_{full}$ is the mean value of the full Hamiltonian [Eq. (1)], but without the interaction between the projectile nucleus and the point-charge distribution that is written explicitly in the third term, and $\langle H \rangle_{dynamic}$ is the mean value of the Hamiltonian terms maintained for describing the dynamical collision process according with the Anderson-like model. Both $\langle H \rangle_{full}$ and $\langle H \rangle_{dynamic}$, are calculated without allowing charge transfer between the projectile and the surface. By making the same considerations as in the case of the energy level $\varepsilon_a(R)$ with respect to the effect of the charge fluctuation on the active fluorine site, the final expression of $V_{res}(R)$ may be written as

$$V_{res}[R(t)] = \langle H \rangle_{full} - \langle H \rangle_{dynamic} + Z_p \sum_{i \neq 0}^{N-1} \frac{q_i}{|R - R_i|} - \frac{Z_p \langle n_0(t) \rangle}{R}. \quad (6)$$

In Fig. 4 this potential for both projectiles, H^+ and He^+ , is also shown for the two limit values of $\langle n_0 \rangle$.

C. Time-dependent formalism

1. Elastic and inelastic ion survival probabilities

We use the same Green's function technique used in previous works,⁶⁻⁸ which in our opinion is quite convenient when the solid eigenstates are known as in the case of the linear-chain model. The time-dependent Green functions proposed are

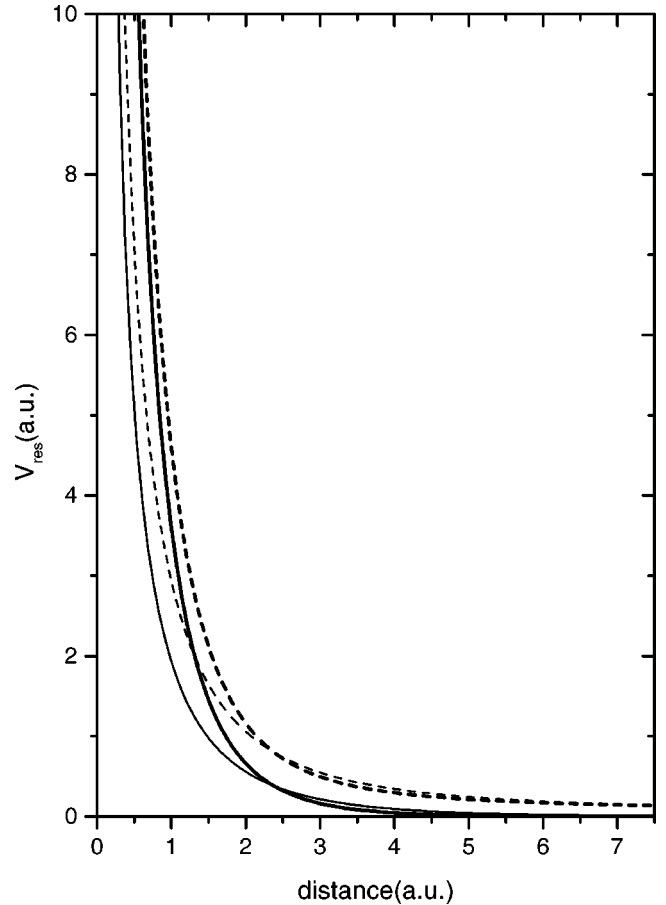


FIG. 4. The “residual” potential V_{res} as a function of ion-surface distance. H^+ scattering: (—) for $\langle n_0 \rangle = 1$, (- -) for $\langle n_0 \rangle = 0$. He^+ scattering: (—) for $\langle n_0 \rangle = 1$, (- -) for $\langle n_0 \rangle = 0$.

$$G_{qm}(t, t_0) = i \Theta(t - t_0) \langle c_m^+(t_0) c_q(t) + c_q(t) c_m^+(t_0) \rangle,$$

where q and m refer to the surface and projectile states that diagonalize the system without interaction. Thus, $c_m^+(t_0)$ creates an electron at the initial time t_0 in an eigenstate Φ_m of the noninteracting system, while $c_q(t)$ destroys an electron at the time t in an eigenstate Φ_q . It is straightforward to see that the average occupation number in the q state is given by

$$\langle n_q(t) \rangle = \sum_{\alpha(\text{occupied})} |G_{q\alpha}(t, t_0)|^2, \quad (7)$$

where the initially occupied α states are the surface valence and core band states for an incoming positive ion. Within the spinless model we are using, the probability of a positive charge state for the projectile results to be:

$$P^+(t) = 1 - \langle n_a(t) \rangle \quad (8)$$

It is important to notice that $P^+(t)$ involves the elastic and inelastic-scattering processes. The probability of surface electron excitation is given by the average occupation of the conduction band:

$$P_{ee}(t) = \sum_{k \in \text{cond. band}} \langle n_k(t) \rangle = P_{ee}^{ce}(t) + P_{ee}^{ve}(t), \quad (9)$$

where the core (P_{ee}^{ce}) and the valence (P_{ee}^{ve}) electron excitation probabilities can be distinguished accordingly with Eq. (7). In order to compare with the experimental data of Souda *et al.*,⁵ we need to evaluate the probabilities for positive ions that correspond to the elastic and inelastic peaks. Within the independent electron approximation we are performing, it is possible to define the inelastic ion survival probability as

$$P_{inelastic}^+ = \sum_{k \in \text{cond.band}} \langle (1 - c_a^+ c_a) n_k \rangle = P^{+*} P_{ee} - \sum_{k \in \text{cond.band}} |\langle c_a^+ c_k \rangle|^2,$$

where P^+ and P_{ee} are obtained from Eqs. (8) and (9), respectively, and $\langle c_a^+ c_k \rangle$ is obtained from

$$\langle c_a^+(t) c_k(t) \rangle = \sum_{\alpha \text{ occupied}} G_{a\alpha}^*(t, t_0) G_{k\alpha}(t, t_0).$$

It is also possible to distinguish between the ion probability for inelastic processes related to valence electron excitations ($P_{inelastic}^{+(B)}$) and those related to core electron excitations ($P_{inelastic}^{+(C)}$):

$$P_{inelastic}^{+(B)} = P^{+*} P_{ee}^{ve} - \sum_{k \in \text{cond.band}} \sum_{\alpha \in \text{valence band}} G_{a\alpha}^*(t, t_0) G_{k\alpha}(t, t_0),$$

$$P_{inelastic}^{+(C)} = P^{+*} P_{ee}^{ce} - \sum_{k \in \text{cond.band}} \sum_{c \text{ (core states)}} G_{ac}^*(t, t_0) G_{kc}(t, t_0).$$
(10)

Thus, the elastic ion survival probability ($P_{elastic}^{+(A)}$) results are

$$P_{elastic}^{+(A)} = P^+ - P_{inelastic}^{+(B)} - P_{inelastic}^{+(C)}. \quad (11)$$

Here we have adopted the notation that Souda *et al.*⁵ use for classifying the inelastic and elastic peaks in the ion energy spectra: *A* denotes the elastic peak, *B* is the inelastic peak concerned with the excitation of an electron of the valence band, while *C* denotes the inelastic peak related with the excitation of a core electron, and also with the simultaneous excitation of two valence electrons and the reionization process, when these three inelastic processes mean similar energy losses. The reionization process by a resonant mechanism during the violent collision takes place in the case of a neutralization of the ion projectile along the incoming trajectory by another mechanism like the Auger process. The reionization probability can be computed within our formalism by considering an incoming neutral projectile. But the description of the excitation of two simultaneous electron-hole pairs is not possible within the assumed independent electron approximation. Nevertheless the formalism allows for the inclusion of the two-electron terms that ac-

count for these processes, that can be treated within a perturbative way.¹⁸ Basically the two-electron terms we would need to include are

$$\sum_{k_1 k_2 k_3} (V_{k_1 k_2 k_3 a} \hat{c}_{k_1}^+ \hat{c}_{k_2}^+ \hat{c}_{k_3}^+ \hat{c}_a + \text{H.c.}) + \sum_{k_1 k_2 k_3 k_4} V_{k_1 k_2 k_3 k_4} \hat{c}_{k_1}^+ \hat{c}_{k_2}^+ \hat{c}_{k_3}^+ \hat{c}_{k_4}.$$

In the same way, the electron-electron repulsion in the projectile site given by the term $U n_{a\uparrow} n_{a\downarrow}$, must be included in the Anderson-like Hamiltonian for a correct description of the all final charge states (H^+ , H^- , H^0) in the H^+ scattering case. A perturbative calculation of this correlation term that goes beyond the time-dependent HF approximation is also possible within the Green's function technique.¹⁹ The inclusion of these terms in the Hamiltonian is an improvement left for a future work.

2. The charge at the active fluorine site

The average occupation number $\langle n_0(t) \rangle$ for the second electron in the $2p_z$ state of the active fluorine atom is calculated from the expression:

$$\langle n_0(t) \rangle \approx \sum_k |c_{i,F}^k|^2 \langle n_k(t) \rangle$$

with $\langle n_k(t) \rangle$ given by Eq. (7).

3. The variation of the projectile velocity along the trajectory

We assume a rectilinear trajectory $R(t)$ that is calculated by integrating the velocity $v(t) = dR/dt$ at each time. The projectile velocity varies along the trajectory due to the coupling between the electronic transitions and the nuclear motion in order to maintain constant the total energy E (nuclei + electrons). This variation can be taken into account by an average potential constructed as the sum of the energies of the different electronic channels weighted by the corresponding probabilities of occurrence.^{16,17} The approximation of an average potential is a good one for incident kinetic energies (E_k) not too low as to invalidate the assumption of an unique trajectory. In our case this potential is directly given by

$$V(t) = \langle H(t) \rangle$$

and for a constant value of the total energy $E = E_k + \langle H(\infty) \rangle$, the velocity is determined as

$$v(t) = \sqrt{2[E - V(t)]/M}.$$

The calculation of $\langle H(t) \rangle$ requires to know the different average occupation numbers $\langle n_q(t) \rangle$ and the cross terms $\langle \hat{c}_a^+(t) \hat{c}_q(t) \rangle$, which can be calculated from the Green's functions $G_{qm}(t, t_0)$. The turning point is determined when $v(t)$ becomes zero.

4. Motion equations for the Green is functions

Defining $g_{qm}(t, t_0)$ as

$$g_{qm}(t, t_0) = G_{qm}(t, t_0) \exp \left[i \int_{t_0}^t \varepsilon_q d\tau \right]$$

the required Green's functions are found by solving the integral-differential equations given by

$$idg_{a\alpha}(t, t_0)/dt = \int_{t_0}^t d\tau \Sigma(t, \tau) g_{a\alpha}(\tau, t_0) + \sum_{\beta} \tilde{V}_{a\beta}(t) g_{\beta\alpha}(t_0, t_0) + \delta(t - t_0) \delta_{a\alpha}$$

$$idg_{K\alpha}(t, t_0)/dt = \tilde{V}_{K\alpha}(t) g_{a\alpha}(t, t_0) + \delta(t - t_0) \delta_{K\alpha},$$

where α runs over the projectile and surface states, K and β only over the surface states, and the new functions introduced are

$$\Sigma(t, \tau) = -i\Theta(t - \tau) \sum_{\beta} \tilde{V}_{a\beta}(t) \tilde{V}_{\beta\alpha}(\tau),$$

$$\tilde{V}_{\beta\alpha}(t) = V_{\beta\alpha}(t) \exp \left[i \int_{t_0}^t (\varepsilon_{\beta} - \varepsilon_{\alpha}) d\tau \right].$$

III. RESULTS AND DISCUSSION

The band energies of the ionic surface are determined from the dispersion relation of a semi-infinite linear chain of alternate F^- and Li^+ atoms. The top of the valence band is located at -0.49 a.u., the bandwidth is 0.19 a.u. and the energy gap is 0.49 a.u. The $c_{2p,F}^k$ coefficients are normalized to obtain a projected charge of 0.9 on the $F-2p_z$ state. The noncomplete electron transfer from Li to F is contemplated in this form, and consequently the small but not vanishing participation of the $F-2p$ state in the conduction band is preserved. This also means that the maximum value of $\langle n_0 \rangle$ is actually 0.9 instead of 1 . The core bands that are included correspond to the $2s-F$ state located at -1.38 a.u., and to the $1s-F$ state with an energy of -25.7 a.u. The core state energies are obtained from the HF calculation of the isolated cluster $(Li_5F)^{4+}$ embedded in the residual point-charge field of the LiF semicrystal.

A. He^+ scattering

In Fig. 5 we can see the occupations of the surface and projectile states as a function of the ion-surface distance (negative values of distance only indicate the incoming part of the trajectory). These occupations are calculated through Eq. (7), $\langle n_c \rangle$ correspond to the two core states considered, $\langle n_{vb} \rangle$ to the valence band, $\langle n_{cb} \rangle$ to the conduction band, and $\langle n_a \rangle$ to the occupation of the projectile state. The sum of all the $\langle n_q(t) \rangle$ has to be equal to the total number of active electrons, and this becomes a good test of our numerical calculation. The results shown in this figure correspond to an incoming ion with a kinetic energy of 300 eV. The variations

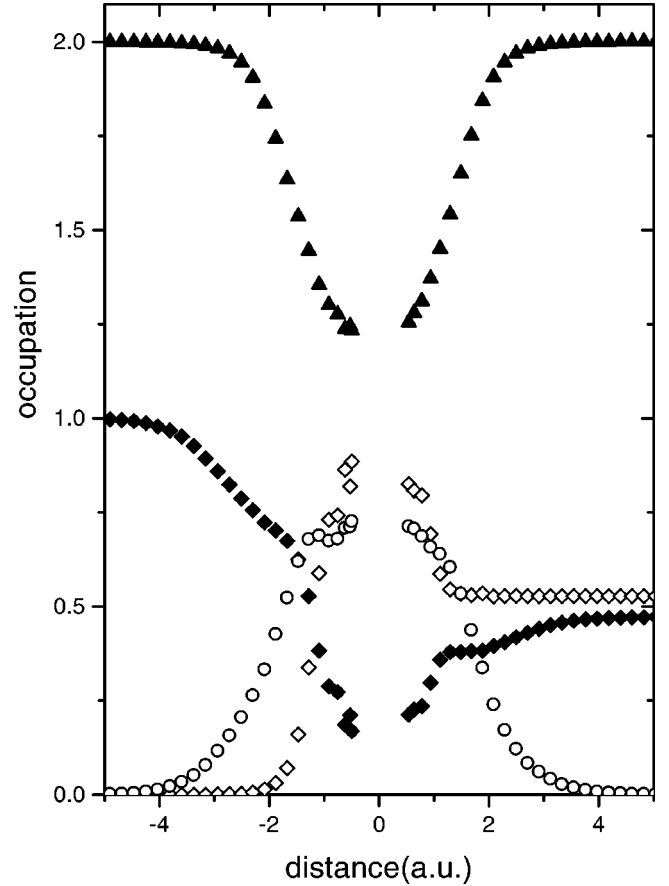


FIG. 5. Average occupations as a function of ion-surface distance. (\blacktriangle) surface core states $\langle n_c \rangle$; (\blacklozenge) valence-band states $\langle n_{vb} \rangle$; (\diamond) conduction-band states $\langle n_{cb} \rangle$; (\circ) projectile state $\langle n_a \rangle$.

of the occupations according with the hybridizations among the surface and projectile states that take place along the ion trajectory can be observed. Thus, the core state occupation shows a pronounced adiabatic variation suggesting an intermediary role in the inelastic and charge-transfer processes. The projectile and conduction-band states become occupied along the incoming part of the trajectory at the expense of falling down the core and valence-band occupations. In the outgoing part a redistribution of the electronic charge occurs giving place asymptotically, to a negligible neutralization of the ion projectile and to an appreciable electron-hole pair excitation on the surface ($\langle n_{cb} \rangle \approx 0.53$ and $\langle n_{vb} \rangle \approx 0.47$).

The elastic and inelastic ion survival probabilities as a function of the incoming ion kinetic energy are shown in Fig. 6. We found that for all the energy values analyzed, the core electron excitation probability P_{ee}^{ce} is zero. Then the inelastic ion survival probability corresponds only to $P_{inelastic}^{+(B)}$ [Eq. (10)]. Also, in Fig. 6, we compare the results obtained by either including or not the variation of the charge $\langle n_0 \rangle$ on the active F site at the surface. Only when the localized nature of the hole created at the active F site is included, the energy dependencies of $P_{inelastic}^{+(B)}$ and $P_{elastic}^{+(A)}$ are in good coincidence with the experimental results.⁵ As it has been already mentioned, Souda *et al.* find three peaks (A, B, and C) in the energy ion spectra coming from the He^+ ions scattered from

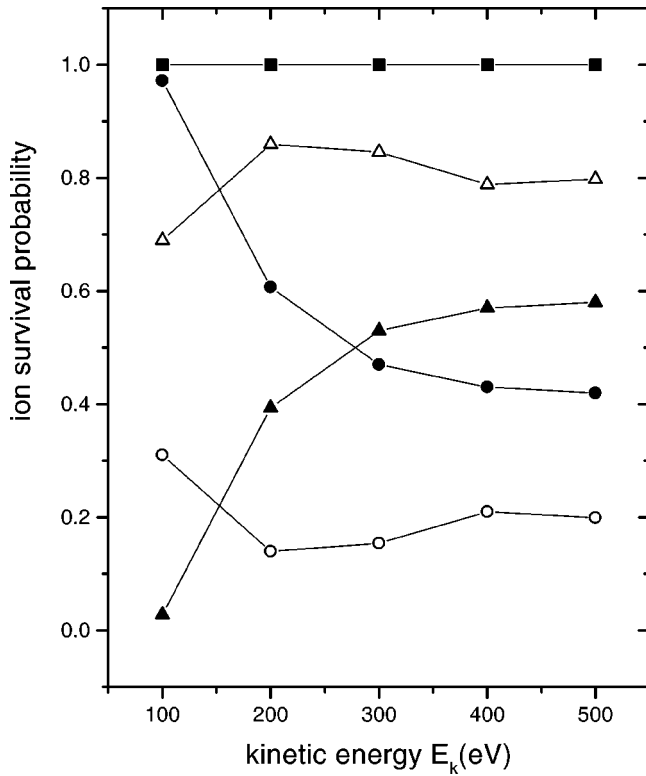


FIG. 6. The ion survival probabilities as a function of E_k for He^+ scattering. The circles correspond to elastic processes ($P_{elastic}^{+(A)}$), and the up triangles to inelastic processes ($P_{inelastic}^{+(B)}$). The open symbols correspond to results obtained by ignoring the charge fluctuation $\langle n_0 \rangle$ on the active F site. (■) the final positive charge-state probability P^+ giving the same result independently of the charge fluctuation $\langle n_0 \rangle$.

the topmost layer F atoms. The peak B is assignable to the He^+ ions, which excite one electron-hole pair since the energy-loss value relative to the elastic peak A corresponds well to the band-gap energy of LiF. The peak C is thought to be caused by simultaneous excitation of two $e-h$ pairs according with the energy-loss value that is twice the one for the peak B. It is also found a negligible ionization probability from the He^+ spectrum obtained with He^0 incidence. Then it is not expected an important contribution of reionization processes to the peak C. It is also observed that the inelastic peaks become dominant with increase of energy: for 100 eV the elastic peak dominates in intensity, while for energies around 300 eV the intensity of the inelastic peaks begins to be larger. The measured intensities of the elastic peak (A) and inelastic peak (B) are proportional to the probabilities of ions scattered elastically ($P_{elastic}^{+(A)}$) and inelastically ($P_{inelastic}^{+(B)}$), respectively. We found that our results for $P_{elastic}^{+(A)}$ and $P_{inelastic}^{+(B)}$ exhibit the same behavior with the incident ion energy when they are compared with the intensities of the elastic (A) and inelastic (B) peaks. As P^+ is constant and equal to 1 within the whole energy range, we can conclude that there are only inelastic processes without neutralization in the scattering of He^+ from the fluorine atom at these energy values. The ionization probability for incoming He^0 atoms has also been calculated, and found negligible

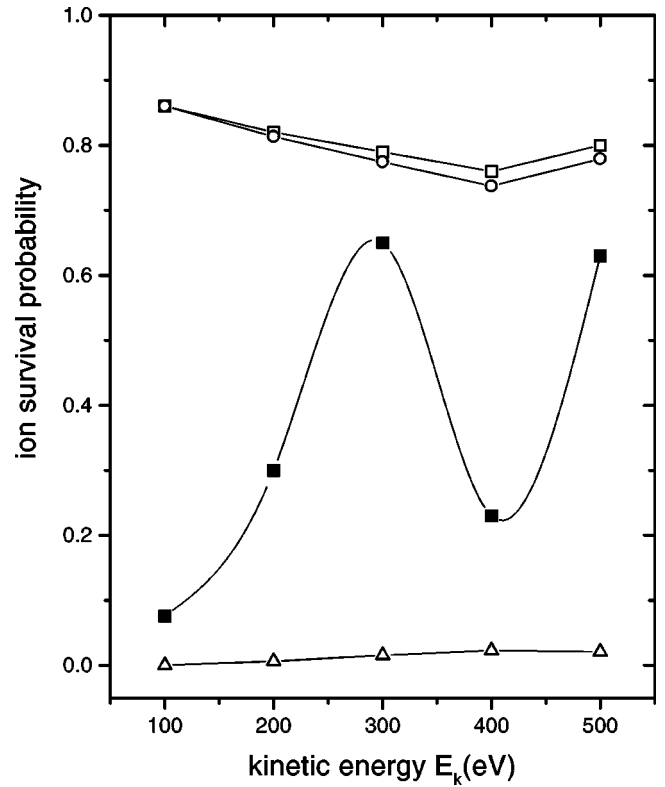


FIG. 7. The same as in Fig. 6 for H^+ scattering. (□) P^+ by ignoring the charge fluctuation on the active F site. In this case $P_{elastic}^{+(A)}$ coincides with P^+ when the effect of this charge fluctuation is included.

in all the energy range, as it has been observed from the ion spectrum for He^0 scattering. Within the approximation used in this paper, it is not possible to calculate the probability for the simultaneous excitation of two $e-h$ pairs. We expect that a more pronounced decrease of the elastic ion survival probability with increasing energy will be obtained by including this reaction channel.

Another significant result is concerned with the role played by the core states; the hybridization with the $2s$ -F state makes possible the excitation of the $e-h$ pair, while the inelastic scattering is suppressed when this core state is not included in the description of the ion-surface interaction. This indicates the formation of quasimolecular states during the collision whose promoted energy levels allow for resonant capture and loss processes leading finally to excitations of a valence electron.

B. H^+ scattering

By considering the charge variation on the active F site our results indicate a negligible electron-hole pair excitation, then P^+ corresponds in this case to the probability of elastically scattered ions; the results obtained by ignoring this variation gives also a small inelastic ion survival probability as it is seen from Fig. 7. For the scattering of neutral atoms we found an increasing ionization probability with the increase of the kinetic energy [Fig. 8(a)]. The measured energy spectra of H^+ ions show a broad background due to multiple

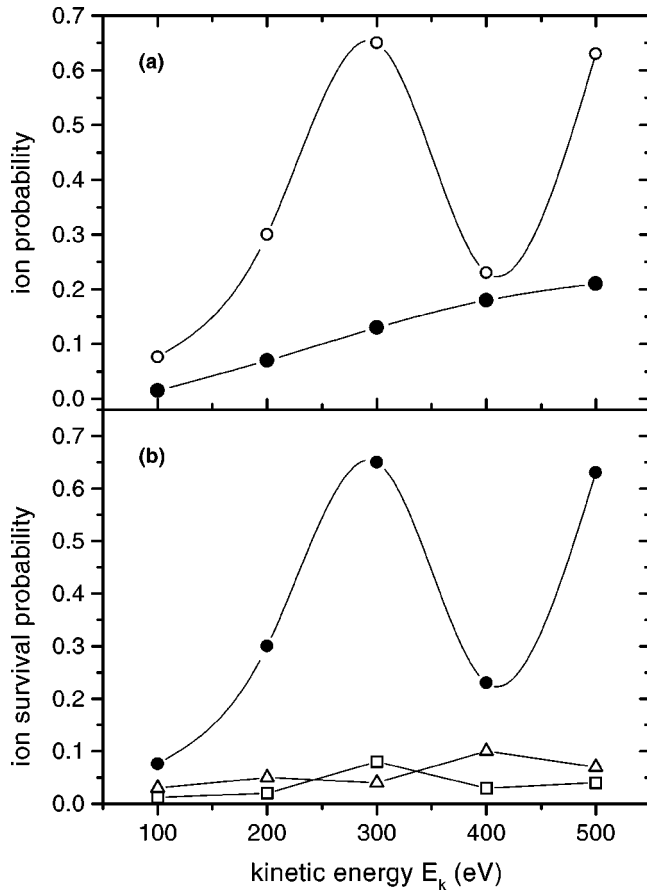


FIG. 8. (a) The positive charge-state probability P^+ as a function of the kinetic energy. Empty circles correspond to P^+ for an incoming ion H^+ while full circles correspond to P^+ for an incoming neutral hydrogen atom. (b) The full circles correspond to the calculation including the surface core states; (Δ) results where the interaction with the $2s$ -F state has been neglected; (\square) results where the interactions with both $1s$ -F and $2s$ -F states have been neglected.

scattering from deep layers, indicating a low probability of valence electron capture by the H^+ ion. Our calculation leads to an oscillatory behavior of P^+ as a function of E_k , but it does not take into account neither multiple-scattering processes nor the negative charge state for the projectile. The energies of affinity and ionization levels of hydrogen near the surface are not separate enough as to expect that the spinless approximation provides a completely satisfactory description of the charge-transfer process. A calculation beyond the Hartree-Fock approximation is required to describe more correctly the all possible final charge states for an incoming H^+ ion.

In Fig. 8(b) we can observe P^+ as a function of kinetic energy when the core states are left out from the calculation. The ion survival probability falls down due to the resonance of the ion level with the valence states, which in this case has not been altered by hybridizations with the core states. The presence of a core state so deep in energy as the $1s$ -F state only introduces a shift in the oscillations with E_k , but it does not substantially affect the values of P^+ . The e - h pair excitation is also negligible when the core states are not consid-

ered. We conclude that the electronic excitations at the surface depend strongly on the coupling between the H - $1s$ state and the F - $2p$ state, and this coupling value is small as it can be seen from Fig. 1. Then the result concerned with the lack of e - h pair excitation will be independent of the better description of the charge states of the projectile that we can do.

IV. CONCLUSIONS

We have presented a parameter-free calculation of the ion-surface scattering process that accounts for

(i) A description of the interaction based only on the properties of the atoms involved.

(ii) The analysis of the surface core states that hybridize appreciably with the projectile state.

(iii) A dynamical one-particle Anderson-like Hamiltonian that includes the extended band states and the localized core bands that participate in the collision process.

(iv) A description of the dynamical evolution that allows for the calculation of the probabilities for the different elastic and inelastic channels.

(v) A classical ion trajectory that includes the velocity variation of the projectile accordingly with an average time-dependent potential that involves the coupling between the nuclear motion and the electronic transitions.

(vi) The possibility to examine the role played by the localized nature of the hole created at the active anion site of an ionic surface, and its effect on the projectile level shift along the trajectory in a consistent way.

These ingredients make the formalism a powerful tool towards a complete description of the elastic and inelastic processes that take place in ion-surface collision.

The results obtained provide a very satisfactory explanation of the differences observed in the energy spectra for H^+ and He^+ scattering by fluorine in a LiF surface. The role of the adiabatic interaction with the F core states is clearly evidenced, being the presence of the $2s$ -F state decisive for a high e - h pair excitation in the scattering of He^+ , and for a neutralization of H^+ lower than that expected for the case of a projectile level quasisonant with the valence-band states. Another important result is that good agreement with the experimental trends is only achieved when the charge fluctuation on the active fluorine ion is taken into account in a consistent way with the excitation and charge-transfer processes along the trajectory. Finally, our formalism opens the possibility of including correlation terms that are important to describe the simultaneous excitation of two e - h pairs, and the negative charge state for H^+ scattering.

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