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Electron promotion in collisions of protons with a LiF surface

P. A. Zeijlmans van Emmichoven and A. Niehaus
Utrecht University, Debye Institute, Princetonplein 5, 3584 CC Utrecht, The Netherlands

P. Stracke, F. Wiegershaus, S. Krischok, and V. Kempter
Department of Physics, Technical University Clausthal, Leibnitzstrasse 4, D-38678 Clausthal-Zellerfeld, Germany

A. Arnau
Departamento de Física de Materiales, Universidad del País Vasco, Apartado 1072, San Sebastián 20080, Spain

F. J. García de Abajo
Departamento de Ciencias de la Computación e Inteligencia Artificial, Universidad del País Vasco, Apartado 649, San Sebastián 20080, Spain

M. Peñalba
Departamento de Física Aplicada I, E.T.S.I.I. y T., Universidad del País Vasco, Bilbao, Spain

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Electron spectra arising from grazing incidence collisions in the keV range of protons with a LiF surface grown on a tungsten substrate are analyzed in terms of the mechanism of electron promotion followed by autoionization. The analysis consists in a comparison of the experimental electron spectra with calculated electron spectra. The calculations are based on theoretically obtained molecular potential curves for the H-F$^-$ molecular system in the LiF crystal. We find that molecular potentials which correspond to the promotion of two $2p$ electrons of F$^-$ along the $3d\sigma$ one-electron orbital enter the lowest one-electron continuum at an H-F$^-$ distance of ~2.5 atomic units, so that autoionization at smaller distances becomes possible during the collision. With these potentials, electron spectra are calculated for certain impact parameters using a semiclassical eikonal approximation. Calculated spectra that can be compared to the experimental ones are obtained by integrating over an impact parameter distribution which is extracted from Monte Carlo calculations of trajectories. It is found that satisfactory agreement of experimental and theoretical spectra can be achieved if it is assumed that electron promotion leads with high probability to excitation of autoionizing doubly excited F$^-$ states embedded in the conduction band of LiF. [S0163-1829(99)11915-5]

INTRODUCTION

Kinetic electron emission in low-energy collisions of ions with insulator surfaces is not well understood. For LiF, only a few experimental studies have been carried out that resulted in absolute electron yields[1] and stopping cross sections.[2] These data have recently been discussed in the more general context of electronic transitions at insulator surfaces.[3] Both electron yields and stopping cross sections were found to be unusually high at low kinetic energies. As a possible explanation of the high yields of about two electrons per ion at 1 keV collision energy, and of the low kinetic energy threshold at about 100 eV, it was hypothesized that quasimolecular autoionization in close collisions of the projectiles with the negative halogen ions might be responsible, together with the rather large mean free path for electrons in the crystal.[1] The mechanism of level promotion leading to quasimolecular autoionization in atomic collisions in surfaces has been treated theoretically by Sroubek and Fine.[4] These authors also propose a theoretical expression that would allow one, in principle, to calculate electron spectra due to this mechanism. We found that this expression is equivalent to the so-called ''eikonal approximation'' that had earlier been derived to describe spontaneous electron emission during slow atomic collisions in the gas phase.[5] The latter approximation is based on the so-called ''complex potential'' model developed for the description of Penning ionization processes.[6] To our knowledge, the occurrence of the mechanism of ''electron promotion followed by molecular autoionization (EPMA)'' has not been demonstrated experimentally to occur in particle surface collisions, nor have theoretically obtained spectra for this mechanism been reported. To investigate the role of this mechanism in collisions of protons with a LiF target, we measured electron spectra for this collision system under well-defined experimental conditions, and attempted to analyze these spectra theoretically in terms of the proposed mechanism.

A preliminary presentation of the experimental data was given before.[7] In that paper also an analysis of the spectra in terms of the EPMA mechanism has already been presented. That analysis yielded strong support for the dominance of EPMA at collision energies between 100 eV and 1 keV, but was somewhat incomplete, in that the presented comparison of calculated and measured spectra was only relative, and focused only at an explanation of the general spectral shape. In addition, details of the theoretical analysis were not reported.

In the present paper, we present absolutely normalized

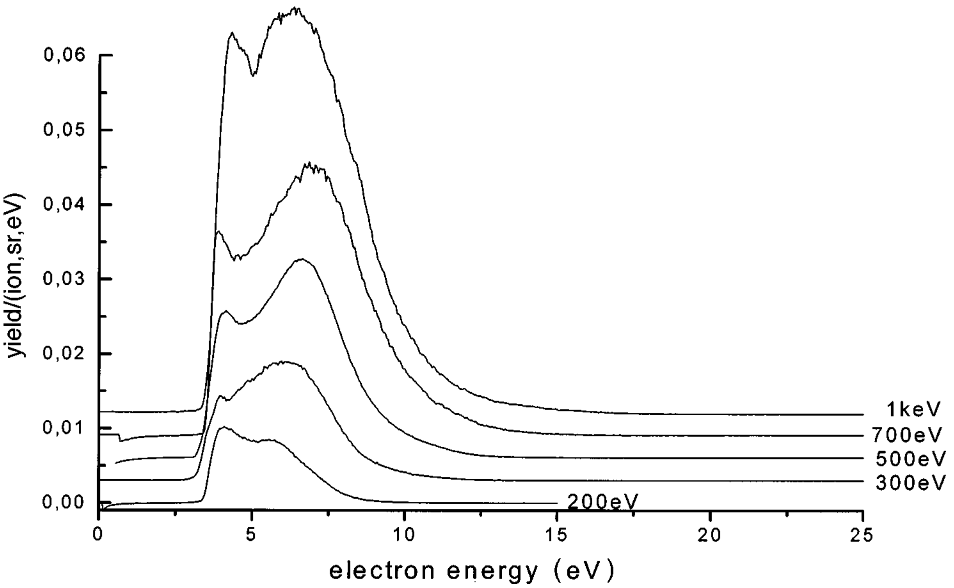

FIG. 1. Experimental electron spectra for 5° grazing incidence H^+-LiF collisions at various laboratory collision energies

experimental electron spectra together with their detailed and quantitative analysis in terms of the electron promotion mechanism. It turns out that details of the spectral shapes not considered in our earlier analysis can only be explained if, in addition to the EPMA mechanism, also electron promotion leading to population and immediate decay during the collision of autoionizing doubly excited F^- states is invoked.

EXPERIMENT

Only the features of importance for the present study are briefly summarized in the following. Details of the apparatus can be found elsewhere,[8,9] as well as details concerning the preparation of the LiF film.[10,11] A mass analyzed H^+ beam impinges on a W(110) surface covered by a LiF film. Prior to the evaporation of the LiF film, the tungsten crystal was cleaned by several cycles of heating in an oxygen atmosphere to 2300 K. The LiF film was produced by thermal evaporation (1100 K) of LiF powder. During the evaporation the W(110) surface was held at room temperature. X-ray photoemission spectroscopy (XPS) measurements showed a film thickness of 10 nm. Metastable ionization electron spectroscopy (MIES) and ultraviolet photoemission spectroscopy (UPS) (He I) measurements showed that the film possesses the electronic structure of a bulk LiF surface.[10] No occupied states could be found with MIES in the band gap of the insulator film. At present, the detection sensitivity is of the order of one defect in 104 lattice sites. The advantage of using LiF films instead of LiF single crystals is the absence of charging phenomena and the easy-to-achieve chemical cleanliness of the film (checked with XPS). The same strategy has been applied by us successfully to study the potential emission in collisions of He*, He^+, and He^{2+} with LiF.[12]

The incidence angle of the ion beam is 5° with respect to the surface; the ejected electrons are energy analyzed under 90° with respect to the beam axis. The spectrometer records the electron spectra at constant pass energy (10 eV) with a resolution of 0.15 eV [full width at half maximum (FWHM)]. Given a constant pass energy of 10 eV, the transmission function of our hemispherical analyzer (Leybold EA 10) is constant over the measured energy range (up to 25 eV electron energy).[13] The difference in the work function of the surface and the analyzer was biased in such a way that electrons leaving the clean W(110) surface with zero kinetic energy arrive at the analyzer with 5.25 eV. Thus, the low-energy cutoff of the spectra for the LiF spectra gives the work function of the LiF film (3.5 eV). Electrons that leave the surface with zero kinetic energy show up at the cutoff energy. The spectra were not compensated for the energy dependence of the collection efficiency introduced by the biasing procedure.

Figure 1 shows the energy spectra of emitted electrons for various collision energies. For reasons of clarity an offset was applied to the various spectra. The electron yield is given in number of electrons per incident ion, eV, and steradians. Due to the biasing procedure and due to the unknown absolute value of our transmission function we are not able to absolutely normalize the spectra with our experimental setup. Therefore, absolute electron yields from the literature have been used[1] to bring our spectra to an absolute scale, thereby assuming that (i) the electron emission is isotropic and that (ii) the total electron yield is the same for perpendicular and grazing incidence. These assumptions need to be verified by future experiments.

The peaklike structure around 4 eV visible in all spectra is due to electrons leaving the LiF surface with close to zero energy. In principle it could be induced by the biasing procedure. Its extreme sensitivity to experimental conditions is also evidenced by the fact that it is somewhat less pronounced in the spectra presented here than in the spectra published in Ref. 7, while the peaklike structure around 6 eV is virtually identical for the two sets of spectra. On the other hand, a similar peaklike structure around 4 eV was also observed in electron spectra induced by electron and photon bombardment.[14,15] Part of it may therefore be real and not an artefact. In our analysis, we will concentrate on an interpretation of the spectra above ~5 eV.

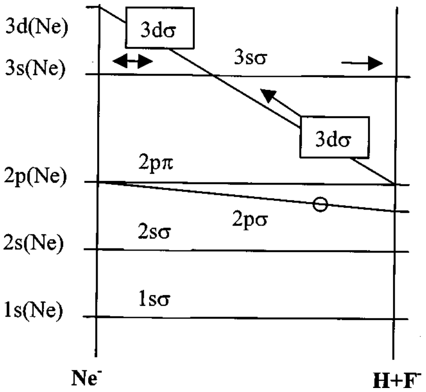

FIG. 2. Schematic diabatic one-electron correlation diagram for the H-F$^-$ system, illustrating the phenomenon of electron promotion via the diabatic $3d\sigma$ orbital.

ANALYSIS

General description

To carry out calculations of electron spectra that can be directly compared to experimental spectra, we have to solve several problems in an approximate way. In the first place, we have to calculate the potential curves relevant for the EPMA mechanism. This has already been discussed in our earlier paper.[7] We consider only collisions between the projectile and the F$^-$ ion in the ionic Li$^+$-F$^-$ crystal. Of the projectile we assume that it has already been neutralized on the grazing trajectory when it reaches small H-F$^-$ distances where ''orbital promotion'' can occur. According to the diabatic one-electron molecular orbital diagram of H-F$^-$, constructed according to the rules given in Ref. 16 and depicted in Fig. 2, the F$^-(2p)$ electrons will be promoted via the $3d\sigma$ orbital, while a ''hole'' will be demoted via the $2p\sigma$ orbital. The potential curve corresponding to this situation can in principle cross into the continuum and lead to autoionization of the transient molecule. The final state of this autoionization would be the ground state of the H-F molecule, with the $2p\sigma,\pi$ orbitals completely filled, and with one electron in the continuum. The EPMA process may therefore be indicated by the following scheme:

$$\mathrm{H}+\mathrm{F}^-\rightarrow(\mathrm{H}-\mathrm{F})^-(\ldots 2p\sigma^1 2p\pi^4 3d\sigma^2)\rightarrow(\mathrm{H}-\mathrm{F})\times(\ldots 2p\sigma^2 2p\pi^4)+e^-(\varepsilon). \quad (1)$$

Here, the molecular states are characterized by their configuration in terms of the *diabatic* one-electron orbitals, as usual. We notice that, according to the correlation diagram, also a transition at the crossing of the $3d\sigma$ orbital with the $3s\sigma$ orbital can occur. In case of such a transition, the two electrons may remain in an excited molecular state that correlates asymptotically with an F$^-$ ion in a doubly excited state with the configuration $(1s^2 2s^2 2p^4 3s^2)$. These states are usually autoionizing and their population can therefore contribute to the electron spectra. To our knowledge, of the three fine-structure states ^3P, ^1D, and ^1S, only the ^1D state has been identified experimentally,[17] and its energy was determined to be $E(^1D)=14.85\,\mathrm{eV}$ above the ground state of F. The ^3P state cannot be populated from the promoted $(\ldots 3d\sigma^2)^1\Sigma$ potential if total spin is conserved, and therefore will not be considered. An estimate of the ^1D-^1S energy difference can be obtained from the known energy difference of the equivalent states of the doubly excited Ne$(\ldots 2p^4 3s^2)$,[18] by scaling according to ''Slaters rules.''[19] In this way we obtain an estimated energy $E(^1S)=16.5\,\mathrm{eV}$, which we will use in our evaluation below. The conduction band of LiF is known from photoemission experiments[14] to start at 14.1 eV above the valence band, and the vacuum level, i.e., the lowest one-electron continuum, at 11.4 eV. Assuming that the excitation energy of an isolated F$^-$ can approximately be taken equal to the energy separation of the corresponding band from the valence band in the LiF crystal, we therefore have to conclude that the band of doubly excited F^{-**} states lies in the conduction band and is embedded in the lowest one-electron continuum of LiF. Population of these states via electron promotion is therefore a possible process and should be considered in the analysis of electron spectra. We will call the corresponding mechanism ''electron promotion followed by atomic autoionization (EPAA)'' to distinguish it from the EPMA mechanism (1). The corresponding scheme is the following:

$$\mathrm{H}+\mathrm{F}^-\rightarrow(\mathrm{H}-\mathrm{F})^{-1}(\ldots 2p\sigma^1 2p\pi^4 3d\sigma^2)\rightarrow\mathrm{H}+\mathrm{F}^{-**}(\ldots 2p^4 3s^2)\rightarrow\mathrm{H}+\mathrm{F}+e^{-1}(\varepsilon). \quad (2)$$

The first arrow in schemes (1) and (2) indicates a *diabatic* path, because H+F$^-$ is the ground state of the system at large H-F distances, and is therefore *adiabatically* connected with the lowest adiabatic molecular Σ state. Similarly, the first excited state of the system at large distances belongs to H$^-$+F, both in their ground states, and is therefore *adiabatically* connected with the first excited adiabatic molecular Σ state.

From the above qualitative discussion it follows that, for a quantitative description of the electron promotion process, the two adiabatic molecular potential curves for the ground and first excited Σ state of the (H-F)$^-$ system are necessary. With these potential curves, the anticipated electron promotion can then be described in terms of a diabatic transition between the two potential curves at some ''avoided crossing.''

We construct the potential curves from calculated molecular orbitals (MO's), which are shown in Fig. 3. The orbitals relevant for the construction of the ground and first excited Σ state are assigned σ, π, and σ^* orbitals, respectively. They relate asymptotically to the atomic H$(1s)$ and F$^-(2p)$ atomic orbitals, and can accommodate eight electrons. The (H-F)$^-$ system has seven outer electrons, so that the highest occupied molecular orbital (HOMO) in the ground state is the σ^* orbital, with one electron in it.

The energy of the Σ ground state we obtain by populating the σ-MO with two electrons, the π-MO with four electrons, the σ^*-MO with one electron, and by adding the corresponding MO energies up to the total energy. Similarly, we obtain the energy of the first excited Σ state by populating the σ-MO with one electron, the π-MO with four electrons, σ^*-MO with two electrons, and by adding up the corresponding MO energies.

In Fig. 4 we show the resulting energy curves relative to the energy curve of the ground state of the ionized system (H-F). The latter is calculated by adding the energies of two electrons in the σ-MO, four electrons in the π-MO, and

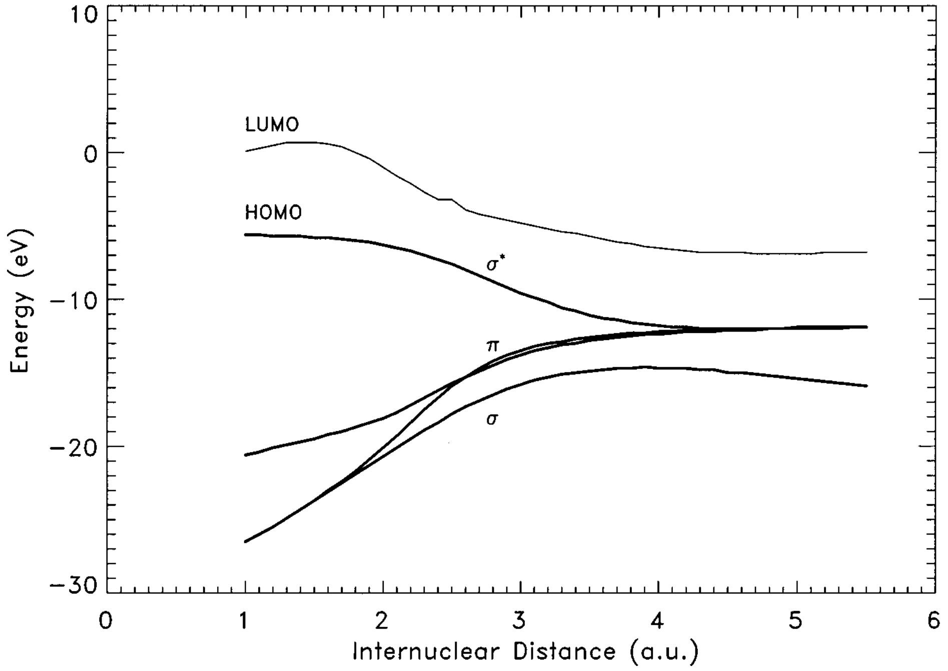

FIG. 3. Calculated molecular-orbital energy levels for the HF$^-$ system as a function of the internuclear distance. HOMO indicates the highest occupied molecular orbital, LUMO the lowest unoccupied molecular orbital. The adiabatic orbitals σ, π, and σ^* are not related in a simple way to the qualitative diabatic orbitals of Fig. 2.

no electron in the σ^*-MO. The energy of the ionized system obtained in this way corresponds in our description to the ''vacuum level'' of the Li-F crystal perturbed by the H atom, and is given in Fig. 4 by the zero-energy line. This ''vacuum level'' relates asymptotically to H+F, both in their ground state, and in the united atom limit to Ne in its ground state.

The ground-state Σ potential at large H-F distances corresponds to the valence band of LiF. The energy of the latter with respect to the vacuum level is known from experiment. In the MO calculations we have made use of this information (see below), so that the asymptotic energy of the H-F$^-$ channel lies at the correct position: at -12 eV, slightly be-

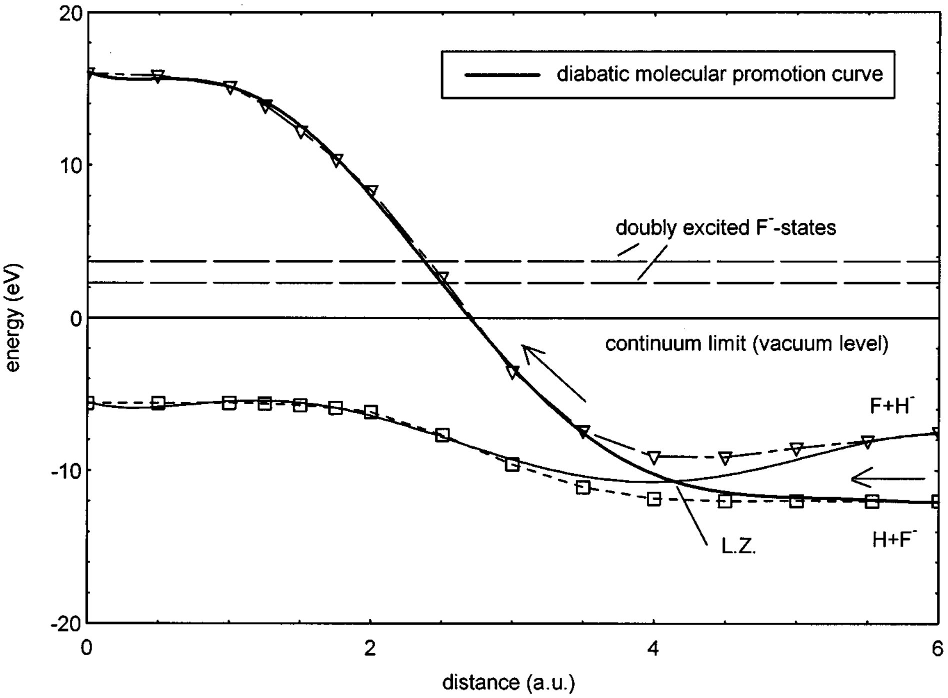

FIG. 4. Ground state and first excited adiabatic molecular Σ potential curves as obtained from the calculated molecular orbitals of Fig. 3 (symbols), and diabatic Σ potential curves (drawn lines). The ''promotion curve'' enters the continuum limit (zero energy line) and crosses the energy region of doubly excited F$^-$ states, where transitions to these states are possible. Also shown is the ''avoided crossing'' (LZ).

low -11.4 eV, where the state density of the valence band starts to rise.[14] The Madelung part of the one-electron binding energy at the F site in this way becomes $E_M = 12 - E_A(\mathrm{F}^-) = 8.6\,\mathrm{eV}$, where $E_A = 3.4\,\mathrm{eV}$ is the electron affinity of F.

In Fig. 4 we show, in addition to the ground and first excited Σ potential curves, also the diabatic molecular curves corresponding to the diabatic transition indicated in the reaction schemes (1) and (2). In the crossing region, these diabatic curves are obtained by interpolation from the relevant adiabatic curves.

We realize of course that the molecular potential curves we obtained in the described way have to be considered as approximations. And, in addition, one has to remember that, in the LiF crystal, the potential curves should generally be replaced by ''energy bands.''

The potential curves that are relevant for the EPAA mechanism [see scheme (2)], and correspond asymptotically to $\mathrm{H}+\mathrm{F}^{-**}$ $(1s^2 2s^2 2p^4 3s^2)$, are not known. The main characteristic of these curves is that they do not involve the promoted orbitals, and therefore should vary with distance in a similar way as the continuum limit. For our calculations we represent the corresponding diabatic potentials by curves running parallel to the continuum limit at the energies estimated for asymptotic distances.

The avoided crossing at which the diabatic transition from the initial $\mathrm{H}+\mathrm{F}^-$ potential into the promoted potential occurs is labeled by ''LZ,'' to indicate that the dynamics at this crossing is treated by us using the Landau-Zener approximation.[20]

The potential curve diagram (Fig. 4) is the basis for our calculations of the electron spectra.

The molecular orbital calculations

The electronic structure of a crystalline solid, i.e., the band structure, shows occupied and empty states with different dispersion relations (energy-momentum relations) depending on band index and wave-vector direction. A detailed calculation that pretends to reproduce band gaps accurately is far from simple and requires the summation over many lattice sites using a large basis set for the electron wave functions. On the other hand, the presence of an impurity ion or atom in the crystal, like H, represents a strong perturbation that modifies the electronic levels in its neighborhood where the interaction takes place or, in other words, most of the electronic transitions (excitation, ionization, and charge exchange). We are mostly interested in studying the electronic coupling between a slowly moving proton and a LiF crystal, and therefore have to make simplifying assumptions. The first assumption is that, as discussed before, the proton is quickly neutralized. The second assumption is that we only need consider the F^- ions as active centers. This is justified since the Li^+ centers are practically inert due to the strength of the binding energy of their *K*-shell electrons (about 50 eV). This means that the relevant atomic states that are considered in the molecular-orbital calculations are the H and F^- states, particularly the $\mathrm{H}(1s)$ and $\mathrm{F}^-(2p)$ levels, which are very close in energy.

We have used the GAUSSIAN-94 computer code to calculate the molecular orbitals of the $(\mathrm{HF})^-$ quasimolecule as a function of the internuclear distance between the H and F centers. The F center is located at the center of an octahedron surrounded by six point charges, which represent the Li^+ ions, at a distance determined by the condition that the Madelung potential at the F^- position is reproduced. The calculation is based on a Hartree-Fock approximation that includes single electron excitations and the basis set used is the $6-31+G(d,f)$. The results of the calculations are shown in Fig. 3. Also indicated in the figure is the lowest unoccupied molecular orbital (LUMO), which asymptotically connects to the $\mathrm{H}(2s)$ level. The molecular orbitals, σ, π, and σ^* shown were used to construct the potential curve diagram as discussed in the preceding section. In this construction only differences between molecular-orbital energies are used, which we expect to be accurate.

At this point we would like to mention that molecular-orbital calculations for the system H-LiF have been performed before[21,22] in connection with an analysis of energy-loss spectra measured for H and H^+ scattering from LiF. The reported results of these calculations, however, we found to be not directly applicable to our present problem.

Calculations of spectra and comparison with experiment

The actual calculations of electron spectra are performed as outlined below. First, a scattering potential is constructed for the purpose of carrying out Monte Carlo type calculations of trajectories occurring for a given experimental situation. It is constructed assuming that the H^+ is neutralized at an estimated distance of four atomic units in front of the surface layer, and it consists of the interaction with a crystal slab containing 1000 Li^+ and F^- ions. The interaction is described as the sum of two terms, a short-range binary part and a long-range part representing the polarization interaction and the ''Madelung-like'' interaction. The short-range part is a potential we calculated for the ground state of the $(\mathrm{HF})^-$ [or $(\mathrm{HLi})^+$] system using the same Hartree-Fock-type molecular-orbital code as used for the calculations of the molecular orbitals. Using the resulting potentials, Monte Carlo calculations are carried out, from which a distribution function $w(b;E_{\mathrm{coll}},\Theta_i,\Phi_I)$ of impact parameters for collisions with F^- centers is retrieved. This function depends on the collision energy (E_{coll}), and on the angles of incidence (Θ_i,Φ_i) with respect to the surface directions.

For the calculation of the electron spectrum arising from a collision with a defined impact parameter, a potential $V_i(R)$ representing the initial state of the ionizing transition is defined. It is composed of the molecular promotion curve shown in Fig. 4, and the Hartree-Fock-type potential V_{HF} for the neutral (HF) system. Within the semiclassical description we use to calculate the electron spectra,[5] the transition probability, or ''width,'' of the initial state is represented as a distance-dependent imaginary part $\Gamma(R)$ of the potential as

$$U_i(R) = V_i(R) - i\Gamma(R)/2. \tag{3}$$

The final state of the autoionization transition leading to a certain electron energy in the lowest one-electron continuum (ε) is represented by a real potential which we indicate by

$$V_f(R,\varepsilon) = V_{\mathrm{HF}}(R) + \varepsilon. \tag{4}$$

Using the so-called ''eikonal approximation''[5] the probability for spontaneous emission of an electron of energy (ε) in a binary collision with a certain impact parameter (b) is calculated by evaluating the following expression:[5,7]

$$P(\varepsilon,b)=\left|\int_{S_1}^{S_2}dS\left[m\sqrt{\Gamma(S)/[2\pi K_i(S)K_f(S,\varepsilon)]}\right.\right.$$
$$\left.\left.\times\exp\left(i\int_{S_1}^{S}[K_i(S')-K_f(S',\varepsilon)]dS'\right)\right]\right|^2. \quad (5)$$

The integration is performed along the trajectory $[S(b)]$ for the particle of reduced mass (m). For each point on S, the corresponding particle distance $R(S)$ is defined, so that the functions can be evaluated for each $S(b)$. The functions $K_i(S)$ and $K_f(S,\varepsilon)$ represent the local momenta of relative motion along the trajectory, and are given by

$$K_i(R)=\sqrt{2m[E_{\text{coll}}-U_i(R)]};$$
$$K_f(R,\varepsilon)=\sqrt{2m[E_{\text{coll}}-V_f(R,\varepsilon)]}. \quad (6)$$

Here E_{coll} is the relative collision energy. Note that the initial-state momentum is a complex number via the complex initial state potential, and that the probability is calculated as a coherent sum of amplitudes along the trajectory. It has been shown that nonclassical effects are well accounted for in the approximation used.[5]

As outlined above, we account for the possible dynamic branching of the population amplitudes in the incoming channel using the Landau-Zener model. This means that we define a probability for the system to choose the diabatic path that leads to promotion. This probability has the form[20]

$$w_{\text{prom}}(b,E_{\text{coll}})=\exp[-2H_{12}^2/(\nu_c(b)\alpha)], \quad (7)$$

with $\nu_c(b)$ the radial velocity at the crossing and H_{12} the electronic coupling matrix element. From the energy separation of the adiabatic curves in Fig. 4 we take that $H_{12}=1.9$ eV. The quantity α is the difference of the slopes of the diabatic curves at the crossing.

To obtain electron spectra from the probabilities $P(\varepsilon,b)$, we have to integrate over the impact parameter. With the distributions defined above, we thus obtain as the final result for the absolute differential electron yield

$$Y(\varepsilon;E_{\text{coll}},\Theta_i,\Phi_j)=\int w_{\text{prom}}(E_{\text{coll}},b)P(\varepsilon,b)$$
$$\times w(b;E_{\text{coll}},\Theta_i,\Phi_i)db. \quad (8)$$

This theoretical differential yield can directly be compared to experimental spectra.

There is one function that is not known in our theoretical description of the process, the width function $\Gamma(R)$. We will use the physically reasonable function

$$\Gamma(R)=A\exp(-R/R_{\text{tr}}), \quad (9)$$

With (A) and (R_{tr}) being free parameters to be determined by comparison with experiment.

It is crucial for the comparison of experimental and theoretical spectra to make sure that the electron energy scale is the same in the two cases. In the experiment, the zero point of the energy scale is fixed at the Fermi level of the crystal. The theoretical electron spectra are calculated relative to the vacuum level of the crystal. Since, according to our measurements, the vacuum level is 3.5 eV above the Fermi level, we fix the zero energy point of the calculated spectra at 3.5 eV of the experimental energy scale.

In a first attempt we tried to reproduce the experimental spectra assuming only the EPMA mechanism to be operative. We found that, in accordance with our previous results,[7] the absolute intensity of the spectra, as well as their ''tailing'' towards high electron energies and their variation with collision energy, can be rather well reproduced in this way. This general agreement becomes especially evident when the intensity is plotted on a logarithmic scale.[7] On the other hand, the spectra show a pronounced peaklike structure around 6 eV, which becomes more visible on a linear intensity scale as used in this paper. This peaklike structure cannot be reproduced on the basis of the EPMA mechanism alone. This is true even if different, less physical, functional forms are used for the width function $\Gamma(R)$. The reason is that the EPMA mechanism can be operative only in the distance region inside the distance at which the promoted curve crosses the continuum limit. This leads to an effective confinement of the transitions in time, and therefore to a minimum broadening of the spectra due to the time-energy uncertainty. For the collision energy region investigated, and for the potentials we used, this broadening exceeds the width of the observed peak structure.

In an attempt to explain the peak structure, we allowed in our calculations for population of the doubly excited F$^-$ states. In principle, one could try to include these channels by treating the transitions at the crossings using again the Landau-Zener model. On the other hand, the electronic coupling matrix elements H$_{12}$ are not known, so that one would have to introduce more free parameters into the calculations. And in addition, the doubly excited F$^-$ states are rather diffuse, so that an appreciable overlap of the corresponding wave functions of neighboring F sites will be present and probably lead to partially delocalized states whose excitation in a diabatic transition in terms of the Landau-Zener model is problematic. In the extreme case that the characteristic ''delocalization time'' is short compared to the time between crossing and recrossing of the potential curves in the collision, we would even expect that the transitions to the excited state band should be described as transitions to an electron continuum, i.e., as irreversible loss to the band from the promoted molecular potential curve. To keep our analysis transparent, we therefore prefer to show spectra that arise under the simple assumption that one of these states is populated with 100% probability ''on the way in'' at the crossing of the promoted molecular potential curve with the curves connecting to the doubly excited F$^-$ states. To realize this kind of a process in the calculations, we simply have to change the quantities relating to the ''initial state'' in relation (5) accordingly at the point of the trajectory where the crossing occurs.

For the calculation, we made the reasonable assumption that $\Gamma(R)$ becomes constant as soon as the transition to the doubly excited state has occurred, and that the constant value is equal to the value of the function $\Gamma(R)$ at the crossing. The two free parameters of the function $\Gamma(R)$ were chosen

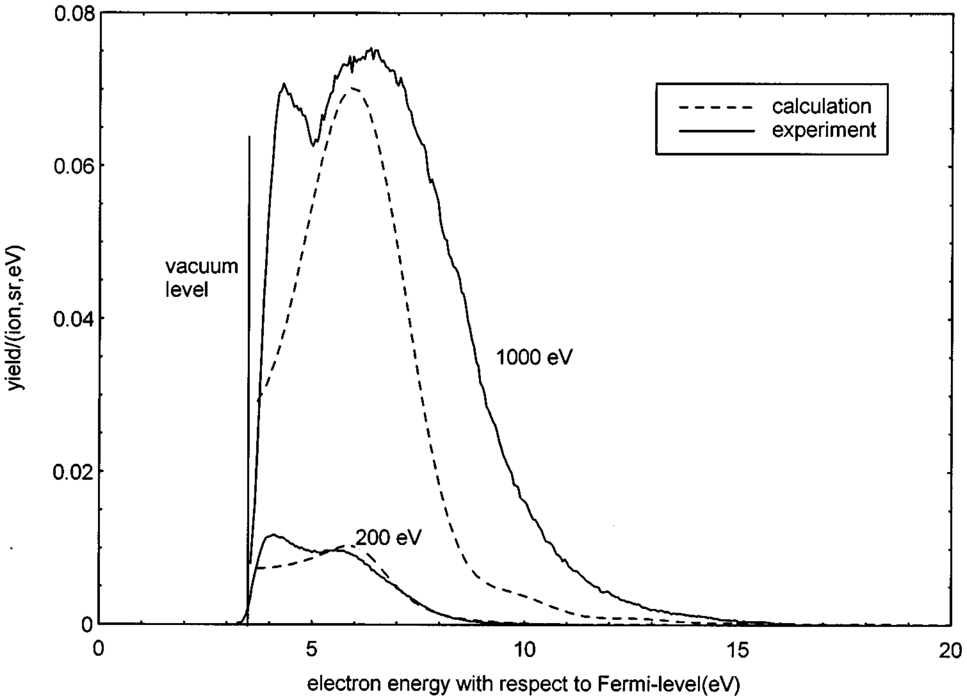

FIG. 5. Comparison of experimental and calculated spectra. The calculations have been carried out assuming 100% population of an excited autoionizing state lying 2.85 eV above the continuum limit, i.e., at the energy of the doubly excited $F^-(1s^2 2s^2 2p^4 3s^2)$ ^{11}D state.

by trial and error to find the best agreement with experiment. In this way the values $A=1$ and $R_{tr}=1$ (both in atomic units) were determined. The result obtained assuming 100% population of the doubly excited molecular state connecting to the ^1D state of the $(\ldots 2s^2 2p^4 3s^2)$ configuration at 14.85 eV is shown in Fig. 5. We notice that the absolute intensity, the variation of the intensity with collision energy, and the characteristic peak structure of the spectra are rather well reproduced. This is especially true for the 200-eV spectrum where also the high-energy exponential tail is well described. In case of the 1000-eV spectrum, the observed peak shape suggests that higher excited states might contribute. In Fig. 6 we

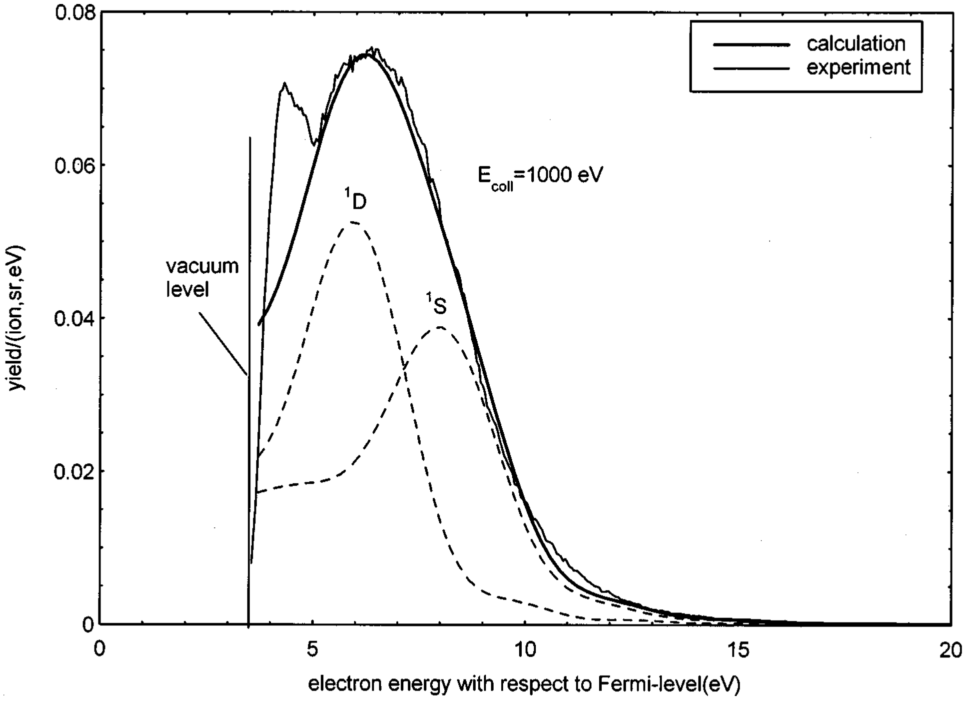

FIG. 6. Comparison of experimental and calculated spectra at 1000 eV collision energy. It is shown that the experimental spectrum can be well reproduced assuming population of two autoionizing states lying 2.85 and 4.5 eV above the vacuum level, i.e., at the energies of the ^1D and the ^1S states of the $F^-(\ldots 2s^2 2p^4 3s^2)$ configuration.

show a comparison of the experimental 1000 eV spectrum with a calculated spectrum resulting if branching from the promoted molecular curve into two doubly excited state curves, the one asymptotically connected to the ^1D state, and the one asymptotically connected to the ^1S state, respectively, is assumed. In the calculation the same parameter values $A=1$ and $R_{\mathrm{tr}}=1$ are used, and the branching—with 50% probability for both channels—is treated in exactly the same way as described above. The agreement between experimental and theoretical spectra is surprisingly good.

Both experimental spectra show an additional peaklike structure just above the vacuum level, i.e., for electrons that start with close to zero energy from the crystal. Such a structure could in principle be reproduced in our calculations by assuming that a state at, or slightly below, the vacuum level, i.e., a surface state in the bulk band gap, is populated by promotion. However, structures of electron spectra close to zero energy can easily be induced by experimental artifacts, so that this interpretation has to be considered very preliminary until more careful measurements that reproduce the structure have been carried out.

DISCUSSION

The main result of the analysis is that the $3d\sigma$-promotion mechanism suggested by the diabatic correlation diagram for the H-F$^-$ system gives the correct absolute intensity and the correct energy dependence of the electron spectra, and therefore may be considered the mechanism that explains the unusually high kinetic emission yields observed for LiF. It is interesting to note that an important part of the promotion mechanism is the diabatic transition from the incoming H+F$^-$ channel at the crossing with the lowest H$^-$+F channel. Only the appropriate incorporation of this transition by the Landau-Zener approximation led to the satisfactory agreement of the energy dependence of the spectra.

The fact that it is possible to reproduce the peaklike structure of the spectra if it is assumed that the promotion ‘‘ends’’ in excited autoionizing states that coincide in energy with the doubly excited F^{-**} (^1D, ^1S) states, whose excitation is predicted by the diabatic correlation diagram, is very strong evidence for the importance of the EPAA mechanism. On the other hand, we would like to emphasize that the occurrence of the EPAA mechanism automatically *implies* the occurrence of the EPMA mechanism if—as in the present case—the crossings between the promoted molecular potential curve with the molecular potential curves connecting to the autoionizing atomic states are embedded in the one-electron continuum (see Fig. 4). Unfortunately the relative importance of the two mechanisms cannot simply be obtained from the electron spectra, because the spectra cannot simply be decomposed into intensity components belonging to the two mechanisms. The reason is that the intensity at a given electron energy and for a certain impact parameter is composed as a coherent sum over amplitudes from different distances, and, in general, from the different potential curves belonging to the different mechanisms [see relation (5)]. On the other hand, a rough estimate of the relative importance of the two mechanisms can be obtained just from the distance-dependent lifetime determined in our model calculations. At the crossing distance of 2.5 Bohr radii the lifetime amounts to about 15 atomic units of time. During this time the H projectile travels over a distance of 3 Bohr radii. As a consequence, for impact parameters that lead to a turning point of the collision well inside the crossing distance of 2.5 Bohr radii, the system in the promoted state decays virtually completely ‘‘during the collision’’ at small distances, with comparable probabilities for transitions inside and outside the crossing. From this—depending on how we define EPMA and EPAA—the relative importance of these mechanisms can be judged.

At this point it appears appropriate to discuss a modification of the definitions of the ionization mechanisms introduced in connection with the diabatic correlation diagram. The main characteristic of EPAA is that the system *stays* in the autoionizing state after the collision. This characteristic becomes important in the collision only after the recrossing, when the collision partners separate. Inside the crossing distance it does not seem sensible to speak of ‘‘atomic autoionization’’ states, one should rather say that the system follows certain molecular potential curves from which molecular autoionization is possible. We therefore propose to ascribe all transitions occurring ‘‘on the way in,’’ as well as those transitions ‘‘on the way out’’ which occur *inside* the crossing distance, to EPMA, and to ascribe only those transitions that occur ‘‘on the way out’’ *outside* the crossing distance, and from the state connected to the autoionizing atomic states, to EPAA. If we adopt this nomenclature; we can state the following qualitative results of our analysis for the H-F$^-$ system: (i) The two mechanisms are approximately of equal importance in the collision energy range investigated; (ii) the relative EPAA contribution increases with increasing collision energy; (iii) the peak structure in the spectra is due to EPAA; (iv) the observed shift and broadening of the peak structure (due to EPAA) with increasing collision energy reflects the population of higher autoionizing states at higher collision energies.

It is interesting to discuss the present results on electron emission in the context of recently published results on the *stopping cross section* for the same H-LiF system.[2] The latter results were obtained for collision energies above 2 keV but they allow an extrapolation down to 1 keV where a value of ~50 eV Å^2 may be estimated from the published data. Our theoretical treatment—using of course the adapted parameter values of the width function—allows a direct calculation of the contribution of the ionization process to the stopping cross section. In a simple, but for the present purpose sufficiently accurate, approximation it is the *ionization cross section* times the energy loss corresponding to the average energy of the emitted electrons. With a calculated ionization cross section of 2.5 Å^2, and with an average energy loss of approximately 16 eV taken from our spectrum, we thus predict a contribution of 40 eV Å^2 to the stopping cross section. In other words, it looks as if the main contribution to the stopping power in the insulator LiF is due to electron emission and can be calculated on the basis of the promotion mechanism.

Finally, we would like to briefly address the relation of the present results to other reported results for the same H/LiF system, namely, on H$^-$ formation[23] and on energy-loss spectra for protons.[21,22] It is obvious that, as part of the electron promotion mechanism identified by us, the initial formation of H^- at the Landau-Zener crossing between the H-F^- potential and the H^--F potential is predicted. Therefore, a theoretical model of H^- formation should contain transitions at this crossing as an important first step. The relation with the energy-loss spectra reported in Refs. 21 and 22 is less clear. The spectra are reported for H^+ ions emerging from the surface in H^+-LiF scattering at large scattering angles. While a clear quasidiscrete peak, labeled *A*, for elastic scattering appears in the spectra, no corresponding peak indicative for a discrete inelastic process can be seen. In Ref. 22 this fact is ascribed by the authors to the absence of $2p(F^-)$ electron promotion. This seems at first sight to be in contradiction to our present results. But we emphasize that this is not the case, because in the energy-loss spectra events are selected that imply a reionization of H, very small impact parameters, possibly multiple collisions, and also elastic collisions with Li targets, and are therefore not comparable with the events represented in the electron spectra. The latter events are characterized by survival of the neutral H projectile, and by rather large impact parameters.

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[1] M. Vana, F. Aumayr, P. Varga, and H. P. Winter, Europhys. Lett. **29**, 55 (1995).

[2] K. Eder, D. Semrad, P. Bauer, R. Golser, P. Maier-Komor, F. Aumayr, M. Peňalba, A. Arnau, J. M. Ugalde, and P. M. Echenique, Phys. Rev. Lett. **79**, 4112 (1997).

[3] V. Kempter, Comments At. Mol. Phys. **34**, 11 (1998).

[4] Z. Sroubek and J. Fine, Phys. Rev. B **51**, 5635 (1995).

[5] A. Niehaus (unpublished).

[6] W. H. Miller, J. Chem. Phys. **52**, 3563 (1970).

[7] P. Stracke, F. Wiegershaus, S. Krischok, H. Müller, V. Kempter, P. A. Zeijlmans van Emmichoven, A. Niehaus, and F. J. Garcia de Abajo, Nucl. Instrum. Methods Phys. Res. B **125**, 67 (1997).

[8] H. Schall, W. Huber, H. Hoermann, W. Maus-Friedrichs, and V. Kempter, Surf. Sci. **210**, 163 (1989).

[9] H. Brenten, H. Müller, K. H. Knorr, D. Kruse, H. Schall, and V. Kempter, Surf. Sci. **243**, 309 (1991).

[10] D. Ochs *et al.*, Surf. Sci. **383**, 162 (1997).

[11] D. Ochs, M. Brause, S. Krischok, P. Stracke, W. Maus-Friedrich, V. Puchin, A. Popov, and V. Kempter, J. Electron. Spectrosc. Relat. Phenom. **88-91**, 725 (1998).

[12] F. Wiegershaus, S. Krischok, D. Ochs, W. Maus-Friedrichs, and V. Kempter, Surf. Sci. **345**, 91 (1996).

[13] K. Berresheim, M. Mattern-Klosson, and M. Wilmers, J. Anal. Chem. USSR **341**, 121 (1991).

[14] D. A. Lapiano-Smith, E. A. Eklund, F. J. Himpsel, and L. J. Terminello, Appl. Phys. Lett. **59**, 2174 (1991).

[15] F. Golek and E. Bauer, Surf. Sci. **369**, 415 (1996).

[16] M. Barat and W. Lichten, Phys. Rev. A **6**, 211 (1972).

[17] J. P. Grouard, V. A. Esaulov, R. I. Hall, J. L. Montmagnon, and Vu Ngoc Tuan, J. Phys. B **19**, 1483 (1986); T. Andersen, Phys. Scr. **T34**, 23 (1991).

[18] J. O. Olsen and N. Andersen, J. Phys. B **10**, 101 (1977).

[19] J. C. Slater, Phys. Rev. **36**, 57 (1930).

[20] L. Landau, Z. Phys. **2**, 46 (1932); C. Zener, Proc. R. Soc. London, Ser. A **137**, 646 (1932).

[21] R. Souda, W. Hayami, T. Aizawa, and Y. Ishizawa, Phys. Rev. B **43**, 10 062 (1991).

[22] R. Souda, T. Suzuki, and K. Yamamoto, Surf. Sci. **397**, 63 (1998).

[23] C. Auth, A. Mertens, H. Winter, and A. G. Borisov, Phys. Rev. Lett. **81**, 4831 (1998).