Diabatic Energy Level Confluence: The Mechanism of Negative Ion Conversion of Neutral Atoms in Grazing Scattering from Insulator Surfaces

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The mechanism mediating electron transfer from an alkali halide surface to an atom by bringing diabatically the relevant atomic and surface energy levels into near resonance is elucidated. The mechanism is supported by parameter free calculations on a model F/LiF(100) system where all sites of the crystal lattice but one, the active site, are represented by (polarizable) point charges. The electron transfer interaction between the atom and the active F site of the surface is computed and used in dynamics calculations of negative ion formation in a sequence of binary collisions. [S0031-9007(96)01058-7]

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The interaction of charged particles with alkali halide surfaces has been a subject of intensive research over the past decades. While secondary particle emission has thoroughly been investigated (Refs. [1,2] and references therein), the evolution of the projectile charge state during its interaction with alkali halide surfaces has received attention only recently [3–6]. A striking finding was the formation of *very high fractions of negative ions* in experiments on the grazing scattering of positively charged and neutral H, O, F projectiles from a LiF surface [4,7]. To explain this phenomenon, one should cope with two issues: (i) the production of negative ions by electron transfer from the target surface to the projectile and (ii) the survival of the negative ions in front of the surface. The present contribution deals with the *first problem.* The second problem is still open, though it was indicated in Ref. [4] that, owing to the large energy gap in insulators, the destruction of negative ions, if at all possible, proceeds via kinematic tuning into resonance with unoccupied surface or conduction band states.

Nowadays concepts for electron transfer from a surface to an atom essentially descend from atom–metal surface interaction studies [8,9]. The formation of negative ions is viewed as being due either to the image potential shift of the affinity level of the atom which brings it into resonance with occupied electronic states of the metal, or, in the case of grazing collisions, to kinematically assisted charge transfer [9]. The basic electron transfer mechanism in this context depends crucially on the position of the affinity level of the atom relative to the Fermi level of the solid. Actually, the electron affinities of free projectile atoms (O, F) used in the experiments of Refs. [4,7] (1.47 and 3.45 eV, respectively) strongly differ from typical binding energies of electrons in the valence band of the investigated alkali halide insulators LiF : 12–17 eV [10]). Moreover, image potential effects for a moving charge in front of an alkali halide surface can be estimated to be of the order of 1–2 eV [11]. These features thereby make the observation of Refs. [4,7] incompatible with the mentioned near resonant electron transfer scheme unless a *new mechanism,* involving some specifics of insulators, could shift the energy levels and bring them together to near resonance for the duration of the atom-surface interaction. Such a new mechanism was attributed in Ref. [4] to an influence of the Madelung potential of an ionic crystal on the affinity energy of the impinging atom. However, the mechanism for this *energy level confluence* has remained unexplained so far. This has been one incentive to the present work. Another incentive to this work is that no information is available on the *electron transfer interaction* itself. Our objective in this respect is to obtain this information from parameter free calculations on a realistic model system with a view to perform dynamics calculations of the related negative ion yield. We have thereby focused on the case, investigated experimentally [7] of F atoms scattered from a LiF(100) surface. Yet, the reported computational procedure and the discussion generally apply to a wider class of atom–ionic-crystal interactions.

The proposed electron transfer mechanism is based on the property of ionic crystals to have alternating $+1$ and -1 charge distributions at the lattice sites ($\mathrm{Li}^+_{\mathrm{crystal}}$ and $\mathrm{F}^-_{\mathrm{crystal}}$, respectively). It also takes into account the property that the removal of an electron from an $\mathrm{F}^-_{\mathrm{crystal}}$ site lets the corresponding hole localized at that site [12] on the time scale of the collision. We adopt the simple approach when the projectile $\mathrm{F}_{\mathrm{gas}}$ undergoes a sequence of binary interactions with $\mathrm{F}^-_{\mathrm{crystal}}$ sites (Fig. 1):

$$\mathrm{F}^-_{\mathrm{as}} + \mathrm{F}^0_{\mathrm{gas}} \longrightarrow \mathrm{F}^0_{\mathrm{as}} + \mathrm{F}^-_{\mathrm{gas}} \tag{1}$$

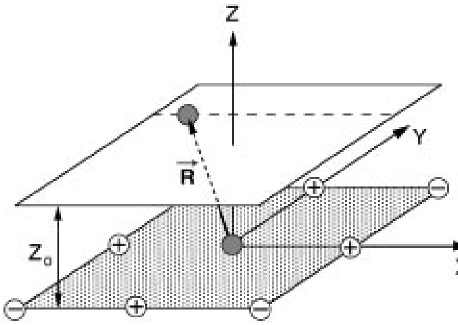

FIG. 1. Sketch of the considered binary interaction model. The shaded plane represents the portion of the ionic surface surrounding the F^-_{as} (dark central circle). The dashed line shows an example of the impinging F_{gas} atom (dark upper circle) trajectory. The model considers parallel trajectories in the plane $(X, Y, Z = Z_0)$: upper white plane.

F_{as} is the "active site" involved in one binary collision; it is taken as the origin of a reference frame in which the vector $\mathbf{R}$ locates the F_{gas} center.

A key feature of the electron transfer mechanism in Eq. (1) is the energy difference:

$$\Delta E(\mathbf{R}) = E(F_{as} + F^-_{gas}) - E(F^-_{as} + F_{gas}) \qquad (2)$$

between final-like and initial-like states. The basic origin of an energy confluence of energy levels is best seen when all relevant centers are considered as *point charges* (PC). In this particular case Eq. (2) is the energy required to bring a negative charge initially located at $\mathbf{R} = \mathbf{0}$ on the neutral surface to a point $\mathbf{R}$ in the gas phase. Clearly

$$\text{for } R \gg a : \Delta E_{PC}(\mathbf{R}) \sim \mathcal{E}_{\text{Madelung}} - 1/R\,, \qquad (3)$$

where a is the lattice constant and $R = |\mathbf{R}|$. Indeed, for point charges, $E(F^-_{as} + F_{gas})$ in Eq. (2) is a constant energy reference related to the initial neutral surface in the presence of a neutral F_{gas}. With this reference, $\mathcal{E}_{\text{Madelung}}$ is the energy of the crystal with a halide hole in it [12]. For a distant -1 charge (representing the formed F^-_{gas}), the halide hole on the surface is seen as a $+1$ charge; this gives rise to the $-1/R$ attraction term in Eq. (3) which initiates the confluence of energy levels. For an *actual system*, one should also take into account the binding energy $\epsilon^{\text{free}}_{\text{binding}}$ of the transferred electron in the *free* initial and final atoms as well as polarization effects noted $\mathcal{P}(\mathbf{R})$; this yields to

$$\text{for } R \gg a : \Delta E(\mathbf{R}) \sim \Delta E_\infty - 1/R + \Delta\mathcal{P}(\mathbf{R})\,, \qquad (4)$$

where $\Delta E_\infty = \Delta\epsilon^{\text{free}}_{\text{binding}} + \mathcal{E}_{\text{Madelung}}$ is the resonance energy defect between the affinity level of the gas atom and the energy level of the valence band of the crystal. $\Delta\mathcal{P}(\mathbf{R})$ contains the polarization of the scattered negative ion by the $+1$ charge at the halide hole on the surface, and vice versa, as well as the interaction of the negative ion with its image charge and the Mott-Littleton contribution from the halide hole [13]. Equation (4) is somewhat reminiscent of the textbook ionic-covalent interactions that play an important role in many gas phase reactions. The dashed curve in Fig. 2 displays $\Delta E_{PC}(\mathbf{R})$ for F/LiF(100) along a straight line path $Y = 0$. Since $\Delta\epsilon^{\text{free}}_{\text{binding}} = 0$ for F/LiF, the observed behavior illustrates the basic mechanism by which the initial-like and final-like energy levels come together when F_{gas} approaches F_{as}.

The above result can be generalized to the case when the projectile A^{q+}_{gas} is a positive ion of charge $+q$. Then, it is easily seen that the $-1/R$ term in Eqs. (3) and (4) becomes $(q - 1)/R$. Thus, save for polarization effects, which are likely to be significant for large q, no confluence of energy levels occurs for singly charged positive ions. Owing to their electron recombination energy of 17.4 eV, F^+ ions are easily neutralized by resonant electron capture from the LiF valence band and can subsequently be converted into negative ions, with the scheme: $F^+ \xrightarrow{\text{1st}} F \xrightarrow{\text{2nd}} F^-$. In contrast, Na^+ and Li^+ ions can hardly achieve the first step in this scheme, thereby hindering the possibility of negative ion formation as indeed observed in Ref. [4].

Figure 2 shows a comparison of $\Delta E_{PC}(\mathbf{R})$ with more realistic $\Delta E_{\text{diabatic}}(\mathbf{R})$ curves for F/LiF. The diabatic initial-like energy levels are obtained from two independent Hartree-Fock-Roothaan calculations (see below): one for an actual F^- ion representing F^-_{as} and one for an actual F atom representing F_{gas} in Eq. (1). Similarly, the diabatic final-like energy levels are obtained from two independent calculations: for an actual F atom and an F^- ion representing, respectively, F_{as} and F^-_{gas} in Eq. (1). By

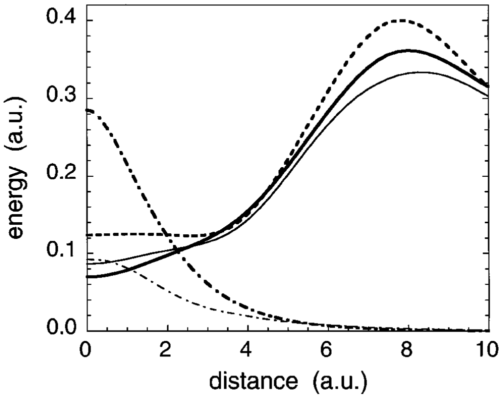

FIG. 2. Computed $\Delta E_{\text{diabatic}}(\mathbf{R})$ diabatic energy difference (full line) and electron transfer interaction $\mathcal{H}_{\text{transfer}}(\mathbf{R})$ (dash-dotted line) in the present F/LiF binary interaction model for the active states (bold lines) and the inert states (thin lines) discussed in the text. The mere point charge estimate $\Delta E_{PC}(\mathbf{R})$ (bold dashed line) is shown for comparison. The results are plotted, as a function of the distance X, along the straight line path $\mathbf{R} = (X, Y = 0, Z_0 = 2.5a_0)$. For $X > 10a_0$, the $\Delta E(\mathbf{R})$ curves keep oscillating about an overall $\mathcal{E}_{\text{Madelung}} - 1/R$ curve due to the alternating ± charges of the lattice.

actual F or F^- it is meant that the atom or ion is described explicitly as a state function corresponding to an electronic configuration of the form: $\psi_{1s}^2\chi_{2s}^2\mu_{2p}^2\nu_{2p}^2\phi_{2p}^n$ with $n = 1$ or 2, respectively. (Lower indices correspond to the orbital labeling of an isolated F or F.) Other centers are not treated explicitly in the but are included as point charges. The orbitals are expanded over a double zeta plus polarization basis [14] extended with diffuse basis functions; this contains part of the $\Delta\mathcal{P}(\mathbf{R})$ term in Eq. (4) by providing freedom for the actual atom or ion to distort in the field of the point charges in each case. Yet, electron transfer is hindered at this stage; this justifies the terminology "diabatic" used for these states [15]. Owing to the open shell structure of an actual F atom, three levels emerge in each (F_{gas} or F_{as}) case; these levels correspond to a permutation of n among the three $2p$-type orbitals in the above electronic configuration. Among the $2p$-type orbitals, the most efficient ones for the electron transfer process lie along $\mathbf{R}$. This justifies the nomenclature "active" and "inert" used in Fig. 2. The computed $\Delta E_{\mathrm{diabatic}}(\mathbf{R})$ curves nicely confirm the $\Delta E_{\mathrm{PC}}(\mathbf{R})$ estimate and lend support to the energy level confluence mechanism.

In order to determine the probability of reaction Eq. (1), one needs to know the corresponding electron transfer interaction $\mathcal{H}_{\mathrm{transfer}}(\mathbf{R})$ [15] that couples the diabatic states. This interaction (Fig. 1) has been determined from the *ab initio* $\Delta E_{\mathrm{adiabatic}}(\mathbf{R})$ curves described below as

$$\mathcal{H}_{\mathrm{transfer}}(\mathbf{R}) = \frac{1}{2}\sqrt{\Delta E_{\mathrm{adiabatic}}^2(\mathbf{R}) - \Delta E_{\mathrm{diabatic}}^2(\mathbf{R})}\,. \tag{5}$$

The adiabatic calculations have been carried out for the actual F_{as}-e^--F_{gas} (19-electron) system in the field of a point charge LiF surface. We use 783 point charges organized in four parallel layers. This gives a precision in the calculated Madelung potential on the active site better than 4×10^{-4} eV. All energy levels are determined, using the HONDO 7 program [16], from SCF-LCAO-CGTO-MO computations which will be described elsewhere [17]. A sample of $\mathcal{H}_{\mathrm{transfer}}(\mathbf{R})$ curves for the active and inert states is shown in Fig. 2.

The electron transfer process Eq. (1) is studied as a function of velocity v for a set of straight line trajectories $\mathbf{R}(t) = (vt, Y, Z_0)$ parallel to the [010] direction in a plane lying at a distance $Z_0 = 2.5a_0$ from the surface. The distance of closest approach to the surface Z_0 is estimated, for the experimental range of normal energies, from the binary atom-atom potentials [18]. The electronic time dependent Schrödinger equation in a 2-state (initial-like, final-like) diabatic representation is solved numerically along each trajectory twice: once for the pair of "active" states and once for a representative pair of "inert" states. The procedure thus disregards any coupling between active and inert states that could arise from the rotation of the $\mathbf{R}(t)$ vector. Figure 3 shows the computed electron transfer probabilities P_{active} and P_{inert} after the averaging over the trajectories in the Y range $[-a/2, +a/2]$ spanning a unit cell width. The statistical average over the open shell of F_{gas} : $P = (P_{\mathrm{active}} + 2P_{\mathrm{inert}})/3$ is also displayed in Fig. 3. The electron transfer probability for the single binary collision Eq. (1) with a point charge surface is already sizable for $v \geq 0.1$ a.u. It is enhanced by taking into account the contribution to $\Delta\mathcal{P}(\mathbf{R})$ that arises, in the exit channel, when the negative point charges on the surface are allowed to polarize in the field of the halide hole-negative ion charge pair (Fig. 3).

In order to obtain from these model calculations an estimate on the F^- ion yield that may be compared with experiment, we consider a small angle θ ($\approx 1°$) F/LiF specular scattering and make two approximations: (i) trajectories within a range d ($\approx 0.5a_0$) from the distance of closest approach to the surface contribute most; and (ii) P can be taken as a mean binary probability in this range. This provides both the effective number of binary collisions $N \approx 2d/(a\tan\theta)$ and the negative ion yield: $\mathcal{Y} = 1 - (1 - P)^N$. Results of this simplified model, for a lower bound estimate on N, are compared with experiment [7] in Fig. 4. The first observation is that the calculations account for a substantial negative ion conversion of neutrals. Yet in view of the simplicity of the model, the detailed shape of the experimental yield is not reproduced. The last two approximations (i) and (ii) are admittedly too crude and may be attenuated by performing calculations at different distances Z from the surface. A weak point of the model is that the states identified as inert in an elemental binary collision may become active when

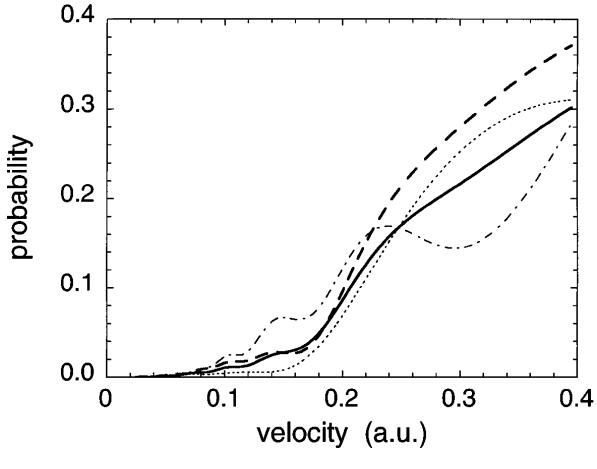

FIG. 3. Computed electron transfer probabilities as functions of the parallel velocity in a single $F_{as}^- + F_{gas}$ binary collision. The P_{active} and P_{inert} curves are plotted using thin dashed-dotted and dotted lines, respectively. The statistical average over the F_{gas} open shell is shown using a bold full line. The bold dashed line shows the effect of letting the point charges on the surface polarize in the field of the formed halide hole–negative ion charge pair in the final-like state.

viewed from adjacent halide sites; this could invalidate the $1/3_{\text{active}}, 2/3_{\text{inert}}$ weights involved in the calculation of P. Having this possibility in mind, we have also plotted in Fig. 4 the yield $\mathcal{Y}_{\text{active}} = 1 - (1 - P_{\text{active}})^N$, assuming the favorable case when all the three possible $2p$ orbitals correlate somehow to an active orbital. The much better agreement of $\mathcal{Y}_{\text{active}}$ with experiment in the onset velocity range is indicative of another track for the improvement of the theory. Other effects related to the actual width ($\approx$4–5 eV) of the valence band have still to be investigated.

In conclusion, we have established that atom–alkali-halide-surface interactions give rise to the remarkable phenomenon of diabatic energy level confluence which favors electron transfer from a halide site of the surface to the gas atom. Focusing on a particular F/LiF model case, we have been able to obtain, from parameter free calculations, unprecedented information on the dynamics of the electron transfer process in this category of atom-insulator interactions. Though not perfect, the proposed approach readily rationalizes the available experimental findings [4,7] that appeared quite astonishing at first sight. Current calculations on similar systems within the proposed model account for the experimental observations [17]. Further research is needed to disentangle the mechanism of F^- destruction causing the high energy falloff in the experimental data (Fig. 4).

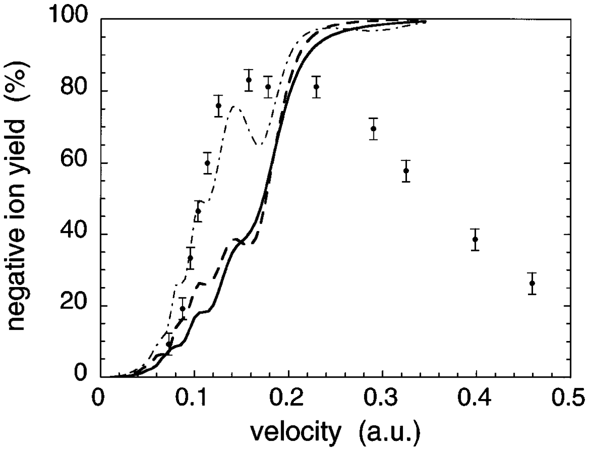

FIG. 4. Comparison of the negative ion yield, versus parallel velocity, as measured for F/LiF(100) in Ref. [7] (data points) with a conservative estimate (sequence of $N = 17$ collisions) of the cumulative charge transfer probability $\mathcal{Y}$. The same symbols are used as in Fig. 3 for corresponding calculations.

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