Strain-Induced Localization and Electronically Stimulated Desorption and Dissociation

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The small-polaron-like "self-trapping" of a surface electronic excitation plays a central role in electronically stimulated desorption. Two types of desorption, immediate and delayed, are possible. Calculations for hydrogen on silicon surfaces indicates that two-hole excitations produce immediate desorption for H^+ while single holes may produce delayed desorption of neutral H.

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In periodic systems, such as ideal crystal surfaces or polymeric molecules, all electronic excitations are, by symmetry, delocalized. That is, the excitations roam over the entire system, remaining confined at a single site no longer than $\tau \sim \hbar/W$, where W is the excitation bandwidth. For purely electronic excitations, i.e., if atomic displacements (polaron effects) are neglected, such residence times are typically much too short to induce the significant atomic displacements which are necessary for bond cleavage. Yet desorption induced by electronic excitations is routinely observed. Present theoretical discussions of desorption[1,2] do not treat the localization mechanism. What is the process by which a delocalized electronic excitation localizes on one site, thereby causing the emission of an ion or atom from the surface or parent molecule ?

Here we consider how a surface electronic excitation localizes and strains and then ultimately ruptures a surface bond, thereby causing desorption. As in the problem of small-polaron formation,[3] we are concerned with a competition between two effects. The first is the increase of the kinetic energy of an electronic excitation associated with localizing it on a single site on the surface. The competing effect is the lowering of the potential energy of an electronic excitation resulting from the excitation localizing in the potential well produced by appropriate displacements of the atoms surrounding it. The problem of desorption is distinct from that of small-polaron formation (self-trapping) on a surface in that the localization of an excitation on a bond causes destruction, rather than distortion, of the bond. In other words, the potential-energy surface of a bond occupied by a desorption-producing excitation is repulsive. For surface-polaron formation it would be a potential well.

In this Letter we first develop the adiabatic theory of desorption. Two types of desorption are found to be possible: immediate and delayed. Proceeding beyond the adiabatic theory, we find a minimal criterion for immediate desorption. This criterion is used in conjunction with calculations on multihydride silicon surfaces to draw conclusions about the desorption of hydrogen from silicon. We find that two holes on a single surface site (as produced by an Auger or shakeup process)[4] produce the immediate desorption of H^+. However, it is uncertain whether the desorption of neutral hydrogen initiated by a single hole on a site is immediate or involves a time delay. The enhancement of desorption resulting from surface defects and disorder is discussed. Finally, we suggest experiments in neutral-atom desorption which may display predicted temperature and isotope effects.

In order to address the localization of an electronic excitation on a crystal surface we consider a model that is analogous to the molecular-crystal model of polaron studies.[5,6] We treat the localization of an electronic excitation among a regular array of deformable surface bonds. The displacement of each bond from its (excitation-free) equilibrium position, $\vec{g}$, is denoted by $x_{\vec{g}}$. The eigenfunctions of this system are written as linear superpositions of local electronic functions, each associated with localization of the excitation on a particular surface bond. The local electronic functions and the corresponding energies depend on the surface bond distortions. Following the standard projection technique, the coefficients of this tight-binding expansion, the $a_{\vec{g}}$'s (which indicate the extent of the localization), are found to satisfy the following set of coupled equations (equivalent to the stationary Schrödinger equation for the system with eigenvalue E):

$$[E - E_{\vec{g}}]a_{\vec{g}} = -J\sum_{\vec{h}} a_{\vec{g}+\vec{h}}. \qquad (1)$$

Here $E_{\vec{g}}$ is the energy of the system when the electronic excitation is localized at site $\vec{g}$. The terms on the right-hand side of Eq. (1) permit the transfer of the excitation between bonds separated by the nearest-neighbor vector $\vec{h}$. For simplicity we ignore the dependence of the transfer integral,[5,6] $-J$, on the displacements of the two relevant surface bonds.

Adopting the adiabatic approximation, where it is assumed that the electronic excitation adjusts to the instantaneous atomic positions, we seek the eigenstates of the system which minimize the sum of the electronic and the vibrational potential energies. That is, we neglect the vibrational kinetic energy in Eq. (1) and minimize the eigenvalue E with respect to the bond displacements. By an analogous procedure to that of polaron calculations,[5] we find the energy minimization condition to be

$$\sum\nolimits_{\vec{g}'}(\partial E_{\vec{g}'}/\partial x_{\vec{g}})\,|a_{\vec{g}'}|^2=0 \tag{2}$$

for all $\vec{g}$. In the desorption process the presence of a localized excitation eliminates the surface bond, and provides a force to drive the desorbed atom from the surface. Here we model these features by taking

$$E_{\vec{g}}=\sum_{\vec{g}'\neq\vec{g}}\tfrac{1}{2}kx_{\vec{g}'}{}^2-Fx_{\vec{g}}. \tag{3}$$

The first term of (3) is the deformation energy of the unoccupied bonds (which we take to be independent harmonic oscillators of stiffness constant k). The second term provides the force F to expel the atom at the occupied site. With this desorption model the energy minimization condition becomes

$$x_{\vec{g}}=F|a_{\vec{g}}|^2/[k(1-|a_{\vec{g}}|^2)]. \tag{4}$$

Equation (4) differs from the analogous polaron condition[5] by the presence of the factor $1-|a_{\vec{g}}|^2$ in the denominator. It arises because occupation of a bond by an excitation reduces the bond's stiffness. Substituting Eq. (4) into Eq. (1) we obtain the coupled nonlinear equations whose solutions are the adiabatic eigenstates for the desorption model:

$$-J\sum_{\vec{h}}(a_{\vec{g}+\vec{h}}-a_{\vec{g}})=\left\{E+(F^2/k)\left[\frac{|a_{\vec{g}}|^2}{1-|a_{\vec{g}}|^2}+\frac{1}{2}\sum_{\vec{g}'\neq\vec{g}}\left(\frac{|a_{\vec{g}'}|^2}{1-|a_{\vec{g}'}|^2}\right)^2\right]+zJ\right\}a_{\vec{g}}, \tag{5}$$

where z is the number of nearest neighbors. The nonlinearity of this equation reflects the feedback nature of the problem: Electronic localization induces atomic displacements which, in turn, foster localization.

We observe two possible solutions of Eq. (5). With the excitation localized at a site, $a_{\vec{g}}=\delta_{\vec{g},\vec{G}}$, we have desorption: The surface atom is expelled to infinite separation, $x_{\vec{G}}=\infty$, with energy $E=-\infty$ (because of the approximation of the linear repulsive curve). With the excitation extended over the entire surface [$a_{\vec{g}}=N^{-1/2}\exp(i\vec{k}\cdot\vec{g})$, where N is the number of surface sites and $\vec{k}$ is a wave vector], E is given by $-J\sum_{\vec{h}}\exp(i\vec{k}\cdot\vec{h})$.

To gain a deeper understanding of the nature and significance of these solutions, we pass to the continuum limit where the occupation amplitude as a function of the discrete site index, $a_{\vec{g}}$, is replaced by a continuous function of position: $a_{\vec{g}}\rightarrow\psi(\vec{r})$. Equation (5) is then simply the adiabatic wave equation: The term in the curly brackets is the energy eigenvalue minus the effective potential (itself dependent on $|\psi(\vec{r})|^2$) and the kinetic energy operator, $\frac{1}{2}zJa^2\nabla_{\vec{r}}{}^2$, where a is the interbond separation, arises from the left-hand side of Eq. (5). The adiabatic energy is then (after some algebra)

$$E=-(zJa^2/2)\int\psi^*(\vec{r})\nabla_{\vec{r}}{}^2\psi(\vec{r})d^3r-(F^2/2k)\int\{|\psi(\vec{r})|^4/[1-|\psi(\vec{r})|^2]\}\,d^3r-zJ. \tag{6}$$

With $\psi(\vec{r})$ being a solution of the continuum version of Eq. (5), the energy E is at a minimum. Thus, if we alter the length scale of $\psi(\vec{r})$ [i.e., alter the degree to which $\psi(r)$ is spread out on the surface] the energy will be raised.[6,7] Explicitly, we replace $\psi(\vec{r})$ in Eq. (6) by $R^{-1}\psi(\vec{r})$, where R^{-1} is the two-dimensional normalization factor, and seek minima of $E(R)$:

$$E(R)=\frac{-(zJa^2/2)}{R^2}\int\psi^*(\vec{u})\nabla_u{}^2\psi(\vec{u})\,d^3u-\frac{(F^2/2k)}{R^2}\int\frac{|\psi(\vec{u})|^4\,d^3u}{1-|\psi(\vec{u})|^2R^{-2}}-zJ. \tag{7}$$

As shown in Fig. 1 there can be one or two local minima for $E(R)$. For sufficiently small R (corresponding to the dimensions of a single site) the energy approaches $-\infty$, yielding the desorption solution. Expanding the scaling radius, R, to infinity we can (curve I) obtain a delocalized relative minimum with energy $-zJ$, the banding energy.

Thus, on the upper curve of Fig. 1 the delocalized state is metastable with respect to desorption.

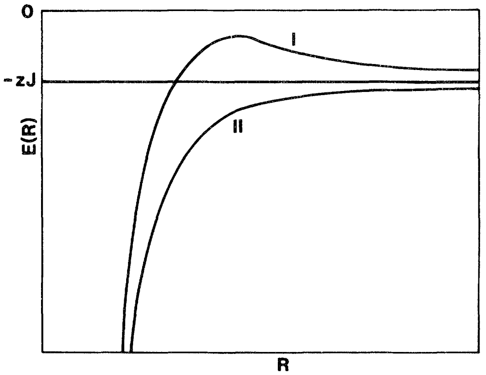

FIG. 1. $E(R)$ vs R for delayed (curve I) and spontaneous (curve II) desorption. Whether a particular system is on a curve like I or II depends upon whether at large R the first term in Eq. (7) initially rises more or less rapidly in magnitude than the second term.

Here an energy barrier must be transcended before a delocalized excitation will localize and produce bond scission. This results in a time delay for desorption (analogous to the time delay for self-trapping in the polaron problem).[3, 6-8] This time delay arises from the requirement that the bonds at and surrounding the desorbing site undergo appropriate displacements before spontaneous desorption [with $dE(R)/dR > 0$] can be initiated. With increasing temperature the energy barrier is more easily overcome and the liklihood of desorption will increase.

On the lower curve there is no impediment to desorption. Here desorption will occur without delay—requiring only the time for the excitation to force the desorbing atom from the surface, typically, 10^{-14} sec.

A sufficient condition for this spontaneous desorption can be inferred from small-polaron formation studies:[6] An electron will spontaneously self-trap to form a small polaron in the three-dimensional molecular-crystal model if the momentum imparted to the bound pair of atoms during the electron's residence at a site exceeds the magnitude of the average vibrational momentum of the bond[6]:

$$F\tau = F\hbar/W > (2ME_v)^{1/2}. \tag{8}$$

Here M is the reduced mass and E_v is the energy associated with the bond's vibrational motion. However, spontaneous desorption from a surface occurs more readily than does small-polaron formation in the bulk. This is because (1) localization occurs more readily in two dimensions than in three, and (2) in electronically stimulated desorption, bonds which are being stretched are also being softened. Thus satisfaction of Eq. (8) guarantees the absence of an energy barrier and time delay for desorption.

It should be noted that surface excitations capable of producing desorption have finite lifetimes. They can decay (usually by Auger processes in 10^{-15}-10^{-14} sec) or diffuse into the bulk. As a result, only those excitations which live long enough on the surface to induce major atomic displacements can produce desorption. Thus, the efficiency of electronically stimulated desorption falls as the excitation's lifetime falls.

Is desorption from an ideal surface likely, or must surface defects be available to catalyze the desorption? As an example we consider desorption of hydrogen chemisorbed on silicon. The relevant parameters of our theory, F and k, are computed by studying both one and two holes on small H-Si clusters. The energies as functions of the H-Si separations were found in the self-consistent Hartree-Fock limit with double-zeta-quality Gaussian basis sets.[9] Comparison with configuration-interaction calculations on similar clusters[10] indicated that our calculations were valid for the quantities of interest.

Desorption is most likely when the excitation may be described by a local (i.e., group) orbital which has a relatively large slope (value of F) and a small intergroup-orbital bandwidth, W. The surface structures which provide the optimal conditions for desorption are the $-SiH_2-$ and SiH_3 groups. This is because some SiH group orbitals of these units have only π-like coupling to the Si atoms which connect the surface groups and hence provide an indirect coupling which contributes to W. Thus these bandwidths are narrower ($\lesssim 2$ eV)[11] than those of the monohydride group whose SiH orbital has a σ-like coupling to the connecting Si atoms.

First we consider the results for two holes; it is known from Auger spectroscopy that the holes are highly correlated on SiH_3, $-SiH_2$, $-CH_3$, and $-CH_2-$ units.[4, 12] The holes then move together between units. In the linear combination of atomic orbitals representation the bandwidth originates from the intersite matrix elements of the Hamiltonian. Thus, while the one-hole bandwidth is linear in the intersite (interunit) overlap, the two-hole bandwidth is reduced by another factor of the intersite overlap. This reduces the two-hole bandwidth, relative to the one-hole bandwidth, by about an order of magnitude.

In calculating k we find a typical Si-H stretch frequency, ω, to be 0.0111 a.u., very close to observed values of ~0.0099 a.u. (2140 cm^{-1}).

For two-hole stimulated desorption, which yields H^+ ions, the slope of the two-hole energy curve (the expelling force) is found to be ~6 eV/Å (0.12 Hartree/Bohr). With these values, and M being the hydrogen atomic mass, spontaneous desorption will occur at low temperature (where $E_v = \hbar\omega/2$) if [from Eq. (8)] the two-hole bandwidth is less than 0.8 eV. This condition is easily met since the two-hole bandwidth is, at most, ~0.2 eV. We conclude that, even though a bandwidth of 0.8 eV implies a rigid-lattice residence time which is too small to break bonds (the H^+ ion would move 0.1 Å in the 10^{-15} sec residence time), as observed,[4] a two-hole excitation immediately undergoes strain localization ("self-traps") upon a site and produces bond scission. This should be characteristic of (highly correlated) two-hole states since these states generally have steep energy surfaces and narrow bandwidths. Thus, since two-hole excitations generally produce spontaneous desorption of (H^+) ions, the critical requirement for the desorption of (H^+) ions is that sufficient hole-hole correlation[12] exists to stabilize two-hole states.

The single-hole case is not definitive. We calculate an expelling force for monohydride and multihydride silicon surfaces of about 3 eV/Å. Satisfying Eq. (8) at low temperature, to guarantee spontaneous desorption, then requires that the single-hole bandwidth be less than 0.4 eV. This is an extremely narrow bandwidth. Hence we cannot predict that single holes produce spontaneous desorption of atoms on either monohydride or multihydride surfaces from Eq. (8)—a sufficient but not necessary condition for spontaneous desorption. Furthermore, the desorption may be of the delayed type (curve I of Fig. 1).

The role of surface defects and disorder in facilitating desorption can be described within the framework of our prior discussion. If we set aside the effect of defects on the decay rates for electronic excitations, defects can aid strain localization in two ways. First, the presence of defects or disorder tends to increase the residence time at some sites, e.g., as a result of Anderson localization.[13] Second, as shown elsewhere (e.g., Ref. 7), in the regions which provide an attractive potential for an electronic excitation the barrier to desorption is generally reduced or may even be eradicated. This decreases or eliminates the time delay for desorption. Thus the presence of surface defect and/or disorder provides centers for strain localization ("self-trapping") and the attendant desorption.

The above considerations imply that in some systems neutral-atom desorption may show a temperature dependence and/or an isotope effect [from Eq. (8)] or may be dominated by defect-site or exciton yields (excitons frequently have comparable F but smaller W than single holes). Positive-ion desorption, originating from the more energetic multihole excitations, is not likely to display these effects (in this case the isotope effect arises from a different mechanism, i.e., reneutralization[1]).

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