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Model for electron- and photon-stimulated desorption

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A model for electron and photon desorption of neutral and ionized molecules from metal surfaces is presented. The novel features of this model are that desorption can take place from excited bonding states, and that the desorbing particle starts its motion toward the substrate, in contrast to the usual assumption. A discussion of the qualitative consequences of this model and their comparison with experiment is presented.

I. INTRODUCTION

When slow electrons (about 20 eV and up) or photons impinge on an adsorbate covered metal surface, desorption of ions and neutrals, together with other processes, can occur. There have been many investigations of desorption phenomena using electrons (electron-stimulated desorption, ESD)[1,2] but few using photons of sufficient energy.[3] The discussions of experimental results[1-4] and theoretical refinements[5-7] have been in terms of a theory which was proposed by Menzel and Gomer[8] and by Redhead.[9] In this paper a new mechanism is proposed in which transitions between bonding states lead to neutral atom or ion desorption from metal surfaces.[10]

A basic problem in understanding stimulated desorption is to understand the process by which an ion or a neutral atom or molecule desorbs from a metal surface with an acquired energy of 10 eV or more.[4] Direct momentum transfer to an adsorbate by a low-energy electron or photon is negligible. Therefore, desorption of the adsorbate involves energy transfer to the electronic structure of the adsorbate-substrate system. This excited state of the system must, however, persist for a sufficiently long time so that the particle has time to acquire the kinetic energy and desorb.

The microscopic model used to discuss electron desorption is due to Menzel, Gomer, and Redhead (MGR).[8,9] A similar model was proposed for photodesorption by Adams and Donaldson.[11] In the MGR model an excitation causes a Frank-Condon transition from the ground state of the adsorbate-substrate system to antibonding states which lead to neutral or ionic desorption. The model has basically two steps[12]: one, the electronic excitation of the complex and two, the subsequent evolution of the complex, taking place on a much slower time scale, leading some of the time to ionic or neutral particle desorption. The MGR model is based on a model for molecular dissociation.[13] However, there is evidence[14] that excited states of atoms on a metal surface have a very short lifetime (of the order 10^{-16} sec). It takes a 10-eV ion, say oxygen, approximately 10^{-14} sec to move 1 Å. The electronic relaxation processes on a metal surface are about two orders of magnitude faster. Consequently there is a serious question as to the existence of a long-lived antibonding state.

Recently a suggestion has been put forward by Feibelman and Knotek[15] that electron stimulated desorption (for instance of oxygen) from metals requires a core-hole excitation with an Auger transition. This argument is strictly on the basis of observed threshold energies and requirement of charge removal from electronegative adsorbates, but it does not suggest a process by which the ion or neutral particle is desorbed. Their argument in an earlier paper[16] that in oxides an ionized oxygen finds itself in a repulsive Madelung potential and is therefore expelled with considerable energy, is plausible. On metals, however, the potential would be screened long before the particle would have had time to move and to acquire the large kinetic energy. The observed desorption of neutrals and negative ions[17-20] (in particular oxygen) is also difficult to account for by way of a Madelung potential.

II. DESCRIPTION OF THE MODEL

The model being proposed here has a two step process: the excitation of the excited adsorbate substrate complex, which will not be considered here, and the desorption sequence. It is argued that an excited complex, which leads to desorbed neutrals, is an adsorbate ion produced by the initial excitation process and that a complex leading to desorption of positive ions is an excited absorbate ion. Neutrals or ions may be desorbed from both.

As an example, an oxygen adsorbed on a tungsten substrate will be considered. It is assumed that the particles follow classical trajectories. In the excitation process an ion is created at the position of the adsorbed particle. The ionic radius is smaller, and in some cases much smaller, than the atomic radius. For instance, the oxygen atomic radius is 0.66 Å and the O^+ radius is 0.22 Å.[21] The ion created in the excitation process sees an attractive image potential. The new equilibrium position of the ionized adsorbate is at about the surface atom radius plus adsorbed ion radius. This is considerably closer to the substrate than the ground-state adsorbate equilibrium position (see Fig. 1). The ion therefore starts moving toward the substrate. Ion neutralization via electron tunneling from the substrate is represented by a vertical jump from the upper to the lower curve in Fig. 1. The kinetic energy that the ion had at the time of neutralization is unchanged so that the total energy of the neutral is the kinetic energy before neutralization plus the potential energy of the lower curve at the position of the neutralization. If this total energy is greater than the binding energy, then the neutral is desorbed after bouncing from the substrate.

The neutralization can take place by resonance tunneling from the conduction band of the metal or by Auger neutralization.[22] It should be noted that if the tunneling electron originates from a state below the Fermi level, the metal is left in an excited state and the surface complex loses that energy as far as desorption energies are considered. This is represented by the vertical jump in Fig. 1 and mentioned above.

The crossing of the neutral and ion potential-energy curves represents the crossing of the Fermi level by the atomic energy level, reversing the direction of allowed electron tunneling. Resonance tunneling from energy levels in the filled band below the Fermi level could be represented in Fig. 1 by a continuum of neutral energy curves, above the one shown there, with an energy width equal to the bandwidth.

It is seen in the above discussion that the creation of an ion is required in order that a neutral be desorbed. This agrees with the observation that neutral desorption does not take place at low excitation energies.[3]

III. ION DESORPTION

The desorption process for ions in this model is more complicated, requiring at least two tunneling processes to occur. The initial state with the lowest threshold energy, which leads to positive-ion desorption, is an excited positive ion on the surface referred to as V_2 in Fig. 2. A core hole, for instance the $2S$ state in oxygen, may be produced in the excitation process. The desorption sequence which leads to a positive-ion desorption requires that the excited ion move toward the substrate, be neutralized sufficiently close to the substrate to be high up on curve V_0 in Fig. 2 and then be ionized again by electron tunneling to the substrate and find itself on curve V_1 before it leaves the close vicinity of the substrate. V_1 is the ground-state-ion-potential-energy curve.

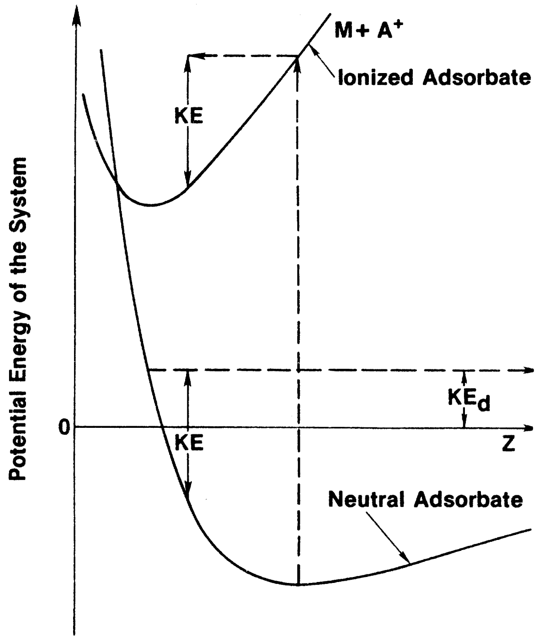

FIG. 1. Depiction of a sequence leading to the desorption of a neutral atom.

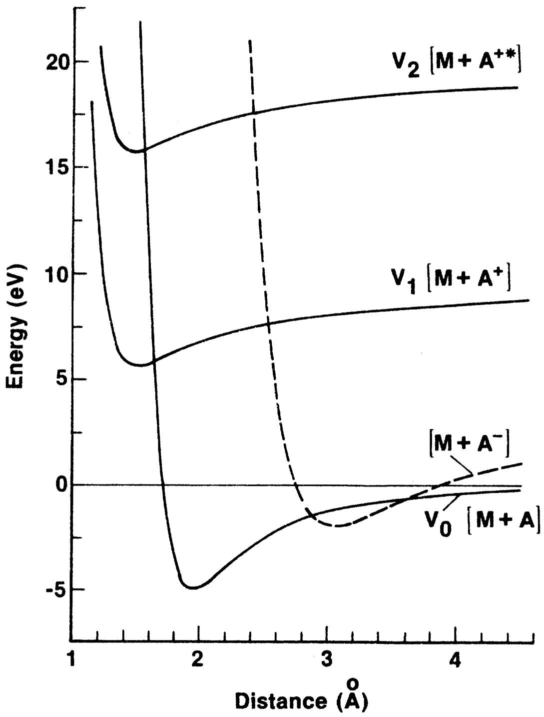

FIG. 2. Approximate potential-energy curves involved in oxygen ion desorption from tungsten. V_2 is the potential-energy curve of the excited ion with a $2S$ core hole; V_1, the ground-state ion; V_0, the neutral atom; and the dashed curve, the negative ion.

The rate R at which electrons tunnel between the substrate and adsorbate and vice versa, depends on the relative positions of the atomic or molecular energy level of the adsorbate and the Fermi level of the metal substrate. At a distance from the substrate where V_0 in Fig. 2 has a higher energy than V_1, the tunneling takes place from the adsorbate to the substrate and vice versa. In this simplified model the energy levels of the atom are assumed not to be broadened by the interaction with the substrate. Energy losses of the ions due to interaction with the substrate are also not considered.

A particular path for the desorption of an ion, following Fig. 2, will be considered next, with the further simplification that the atom is initially at rest. After excitation to the potential energy curve labeled 2, the particle moves toward the substrate with a classical velocity

$$v(z) = \{2[V_2(z_0) - V_2(z)]/M\}^{1/2} \quad . \tag{1}$$

If the probability per unit time of an electron tunneling from the metal onto the ion is $R_2(z)$, then the probability that the ion is not neutralized at the position z is

$$\begin{aligned} p_2(z) &= \exp\left\{-M^{1/2}\int_z^{z_0} \frac{R_2(z')dz'}{\{2[V_2(z_0) - V_2(z)]\}^{1/2}}\right\} \\ &= \exp[-M^{1/2} f_2(z,z_0)] \quad , \end{aligned} \tag{2}$$

provided the ion has not yet reached the classical turning point. When considering a different path, the ion might have reflected from the hard-core part of the potential and that would have to be included in Eq. (2). It might be mentioned that when the ion is inside the neutral potential curve V_0, it cannot be neutralized; it can only be de-excited to the lower ionic potential energy curve, V_1. An ion making that transition, however, will not have sufficient energy to desorb as an ion.

The neutralized particle might desorb as a neutral, but if the particle has sufficient total energy, then it can be reionized. The neutral has sufficient energy if

$$V_2(z_0) - V_2(z_n) + V_0(z_n) \gtrsim I \quad , \tag{3}$$

where z_n is the position of the ion at the time of neutralization. Consequently, for the particle to desorb as an ion, it has to be neutralized in the region $z_2 < z_n < z_1$, where z_1 is the solution of the equation $V_2(z_0) - V_2(z_1) + V_0(z_1) = I$ and z_2 is the solution of the equation $V_2(z_2) = V_0(z_2)$, where the two potential-energy curves cross.

The probability that the neutral is not reionized to potential-energy curve 1 while traveling from z_n to $z_{\min}$ to z is

$$p_0 = \exp\left\{-M^{1/2}\int_{z_{\min}}^{z_n} \frac{R_0(z')dz'}{\{2[V_0(z_{\min}) - V_0(z')]\}^{1/2}} - M^{1/2}\int_{z_{\min}}^{z} \frac{R_0(z')dz'}{\{2[V_0(z_{\min}) - V_0(z')]\}^{1/2}}\right\} \quad , \tag{4}$$

where R_0 is the probability of electron tunneling from the atom to the substrate. Then

$$p_0(z) = \exp[-M^{1/2} f_0(z,z_n,z_0)] \quad , \tag{5}$$

and where $z_{\min}$ is the nearest point of approach found from

$$V_2(z_0) - V_2(z_n) + V_0(z_n) - V_0(z_{\min}) = 0 \quad . \tag{6}$$

The probability for the ion created at z_i to leave the surface without being neutralized is

$$p_1(\infty) = \exp\left\{-M^{1/2}\int_{z_i}^{\infty} \frac{R_1(z')dz'}{\{2[V_0(z_{\min}) - V_0(z_i) + V_1(z_i) - V_1(z')]\}^{1/2}}\right\} = \exp[-M^{1/2} f_1(z_i,z_n,z_0)] \quad . \tag{7}$$

Finally, the probability that an ion, created at z_0 neutralized at z_n to $z_n + dz_n$ and reionized at z_i to $z_i + dz_i$ to curve 1, leaves the surface is

$$\begin{aligned} p_i(z_i,z_n,z_0)\,dz_i dz_n = {} & \frac{M}{2\{[V_2(z_0) - V(z_n)][V_0(z_{\min}) - V_1(z_i)]\}^{1/2}} \\ & \times \exp\{-M^{1/2}[f_z(z_n,z_0) + f_0(z_i,z_n,z_0) + f_1(z_i,z_n,z_0)]\} R_2(z_n) R_0(z_i)\,dz_i dz_n \quad . \end{aligned} \tag{8}$$

with the restrictions on z_i and z_n described previously and noting that if the neutral is reionized before "bouncing" from the surface, appropriate changes have to be made in the above expressions.

The total desorption probability is found by integrating over z_n, the place of neutralization of the initial ion, and z_i, the position of reionization of the desorbing neutral: There are contributions to the total desorption probability from other paths, e.g., several bounces before desorbing, but it is assumed that they are small.

The lowest excited state from which positive oxygen ion desorption takes place is the $2S$ core-hole excited state as discussed above. However, ion desorption may also take place from higher-energy excited states. For instance, a doubly ionized oxygen in a desorption sequence, similar to neutral desorption with a single electron tunneling from the substrate will also lead to a positive-ion desorption.

IV. NEUTRAL DESORPTION

To have a neutral desorb from state 2 the ion has to move toward the substrate sufficiently so that its kinetic energy plus the ground-state potential energy exceed the binding energy of the neutral atom. That is

$$[V_2(z_0) - V_2(z)] + V_0(z) \geqslant 0 \ . \tag{9}$$

If the ion is neutralized when $z < z_d$, where z_d is the position where the above expression is zero, then a neutral atom will desorb. Some of the neutrals with sufficiently high energy will desorb as ions as discussed in the previous section. However, since the number of ions is small ($\sim$1%) there is little effect on neutral desorption and will be ignored here. The probability for one or more round trips from the point of creation to the repulsive-core port of the potential-energy curve and back is small and is also ignored.

The probability for neutral desorption then is

$$\begin{aligned} p_{n2} &= \exp\left(-M^{1/2} \int_{z_d}^{z_0} \frac{R_2(z')\,dz'}{\{2[V_2(z_0) - V_2(z')]\}^{1/2}}\right) \\ &= \exp[-M^{1/2} f_{n2}(z_d, z_0)] \ . \end{aligned} \tag{10}$$

In electron-stimulated desorption the surface complex may also be excited to potential-energy curve 1. Excitation to potential-energy curve 1 can lead only to neutral desorption as was discussed in the first section dealing with the model. The probability for neutral desorption from that energy level is the same as Eq. (10) with the proper changes in labels. It should be noted that energies of the neutrals desorbed from the curve 2 can be substantially larger than the maximum energies from curve 1 suggesting that the positive-ion current should be proportional to the high-energy neutral current. Excited neutrals have been observed in carbon monoxide desorption from tungsten by Newsham and Sandstrom.[23] They observed CO^+ ions with a maximum energy of 3 eV and excited neutrals with a maximum kinetic energy of 11 eV.

V. NEGATIVE ION DESORPTION

The dotted curve in Fig. 2 represents the potential-energy curve for a negative ion interacting with the substrate. In the region where the dotted curve is below curve V_0 there exists the probability that an electron tunnels from the substrate to the neutral, leading to a possible negative-ion desorption. Negative-ion desorption has been observed by Hock and Lichtman[17] and more recently by Yu.[20] It should be noticed that in the present model, negative ions with large energy may be desorbed. Negative-ion energies larger than positive-ion energies have indeed been observed by Yu for oxygen desorption from tungsten.[20] Also in agreement with the model presented here, Yu[20] observed both negative- and positive-ion species being desorbed from the same surface site.

VI. ISOTOPE EFFECT

From Eqs. (8) and (10) it can be seen that the probability for desorption depends sensitively on the mass of the desorbing ion. The heavier isotope is slower moving for any given kinetic energy available to the system and since desorption is dominated by rate dependent processes, it has a larger probability of not desorbing. This isotopic dependence was predicted by the MGR model and first observed experimentally by Madey *et al.*[24] The present model shows without any extra assumptions that the isotope dependence of ions is larger than that of neutrals[25] since ion desorption is a two-electron tunneling process.

VII. CONCLUSION

To recapitulate, the present model of desorption agrees qualitatively with the major experimental observations; the high threshold energies for neutral desorption to take place are due to the requirement of initially creating an ionized adsorbate, the dependence of the probability for desorption on the isotopic mass and its larger effect in ion desorption is a consequence of the desorption sequence. The tunneling rates and lifetime of excited states necessary in this model are compatible with rates in other experiments, i.e., neutralization spectroscopy. The present model also predicts the presence of high-energy neutrals desorbing along with the ions, and negative-ion desorption from the same initial excited state.

It can be seen that the desorption probabilities depend very sensitively on the shape and positions of the potential-energy curves relative to each other and the Fermi level and where on the curve the ion starts its voyage. This tends to agree with the observed sensitivity of the desorption cross section on the adsorption sites and temperature.[26] Although it has not been considered here explicitly, the effect of the three-dimensional structure of the potential-energy curves plus, to some extent, the vibrational motion[7] of the adsorbate before ionization will lead to angular distribution[26] of the desorbed ions.

Qualitatively therefore, this model agrees with the available experimental data. The added benefit is that one can attempt to calculate the potential-energy curves from which desorption takes place. The model also points out correlations between the various particles desorbed from the same initial excited state.

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