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# Theory of photodesorption*

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A theory for photodesorption of chemisorbed species is developed. Two cross sections are computed—one for photodesorption in the excited state with subsequent free atomic fluorescence and the other, the total desorption cross section in any state. A decay mechanism involving surface plasmon and particle-hole pair excitations is introduced to account for nonradiative deexcitation processes. A comparison is made to other mechanisms such as photoelectron-stimulated desorption. Estimates show that the cross section is of sufficient magnitude to be readily detected in the laboratory.

## I. INTRODUCTION

It has been known for some time that photons are capable of desorbing chemisorbed (or physiosorbed) species from solid-state surfaces. It may also be possible to desorb substrate atoms. Apart from the technological value of this discovery as a surface preparation technique, photodesorption carries with it the potential of being a useful spectroscopic probe to study the physics of the surface itself. Numerous experimental investigations of photodesorption have appeared in the literature,[1–8] although a comprehensive theory of the phenomenon appears so far to be lacking. The purpose of this paper is to develop such a theory of photodesorption.

The phenomena of photodesorption and electron-stimulated desorption[9] are closely related. In both cases an adsorbed molecule is electronically excited from its ground-state binding configuration to some repulsive excited state. Naturally the nature of the excitation mechanisms differs, but the resulting dynamics bear great similarities. The excited molecule has several options for its behavior. It can desorb from the solid in its electronically excited state and radiatively decay at a later time. Alternately, it can deexcite in a nonradiative manner in the vicinity of the surface and desorb, as a ground-state molecule. On the other hand, the energetics might be such as to prevent the desorption in either the ground or excited states. If one broadens the definition of excited states to include ionized states, then one must also consider neutralization[10] processes in the analysis.

In the following analysis, we will limit our attention to the case of adsorbed atoms which are desorbed in the ground or excited states. It is felt that a thorough understanding of this simple situation is required before attempting to tackle the problems associated with molecular desorption. Due to the complexity of the problem several approximations will be made. First, the motion of the desorbing atoms will be treated classically, although their internal degrees of freedom will be treated quantum mechanically. This approximation has recently been applied to analysis of photodissociation of molecules.[11,12] Second, we will neglect structure of the solid in a direction parallel to the surface and assume translational invariance in this plane. Finally, we limit our attention to the case of weak photon fluxes and disregard nonlinear effects. High-field studies are a topic worthy of study in their own right, but lead to a more complicated formulation of the theory. The thermal-desorption effects will not be considered.

In Sec. II we develop the basic formulas for the photodesorption cross section. This is followed by Sec. III, concerning nonradiative deexcitation, and finally by Sec. IV, the discussion section.

## II. THEORY OF PHOTODESORPTION

Having decided to adopt the approximations listed above, we now proceed to develop the theory. Let $z$ denote the distance of the atom from the surface and $v$ depict the $z$ component of its velocity. The ground electronic state of the atom-solid system will be denoted by the subscript 1, while the state where the atom is excited and the solid (approximately) unperturbed will be denoted by the subscript 2. In the present discussion we limit our attention to the case where only one excited state is relevant to the desorption problem. The analysis may be extended readily to the multistate situation without much difficulty.

The probability of finding the system in the $n$th state with coordinate $z$ and velocity $v$ lying in the range $z$ to $z+dz$ and $v$ to $v+dv$ will be denoted by $P_n(z,v,t)\,dz\,dv$. This distribution obeys the Boltzmann equation,

$$\frac{\partial P_n}{\partial t}+v\frac{\partial P_n}{\partial z}-\frac{1}{M}\frac{d\epsilon_n}{dz}\frac{\partial P_n}{\partial v}=\left(\frac{dP_n}{dt}\right)_E+\left(\frac{dP_n}{dt}\right)_D. \qquad (1)$$

Here $M$ is the atom's mass and $\epsilon_n(z)$ ($n=1,2$) refers to the electronic energy curve of the $n$th state. The first term on the right-hand side of Eq. (1) is the change in the probability distribution due to optical excitation. The second term is the change of $P_n$ due to nonradiative deexcitation processes. These involve a transfer of excitation from the atom to the solid. Deexcitation only occurs when $n=2$. Since the spontaneous-emission lifetime is long compared with other characteristic times in the problem, we will neglect spontaneous emission in the following discussion.

If there were no external radiation field present, then we would have the equilibrium distributions

$$P_1^{(0)}(z,v)=\left(\frac{\beta M}{2\pi}\right)^{1/2}\frac{e^{-\beta[\epsilon_1(z)+(Mv^2/2)]}}{\int_{-\infty}^{\infty}dz\,e^{-\beta\epsilon_1(z)}}, \tag{2a}$$

$$P_2^{(0)}(z,v)\approx 0. \tag{2b}$$

Here we are neglecting the thermal excitation of the excited state, and $\beta=(k_BT)^{-1}$, $T$ being the temperature and $k_B$ being Boltzmann's constant. Introduction of the radiation field perturbs the distributions, so

$$P_n(z,v,t)=P_n^{(0)}(z,v,t)+P_n'(z,v,t). \tag{3}$$

We will only keep those terms appearing to lowest order in intensity in this linear analysis. We will disregard the depletion of the thermal part of the $P_1$ distribution.

The change of the $P_2$ distribution due to optical excitation from the $n=1$ state is given in this classical approach approximately by the Fermi Golden Rule,[11,12]

$$\left(\frac{dP_2'}{dt}\right)_E=\frac{\pi E_0^2}{2\hbar}\,|\langle 2|\,\mu_x|\,1\rangle\,|^2P_1^{(0)}\,\delta[\epsilon_2(z)-\epsilon_1(z)-\hbar\omega], \tag{4}$$

where $E_0$ is the electric field strength, $\langle 2\,|\,\mu_x\,|\,1\rangle$ is the ($z$-dependent) transition moment, and $\omega$ is the radiation frequency. In keeping with our linearization program, we neglect the stimulated deexcitation of state 2. Now $P_1'$ represents the nonthermal portion of the ground-state distribution. Depletion in the thermal part of $P_1$ will not influence the desorption rate, so we take

$$\left(\frac{dP_1'}{dt}\right)_E=0. \tag{5}$$

The nonradiative decay term appearing in Eq. (1) will not be fully specified until later, but for now we assume it can be written in the form

$$\left(\frac{dP_2'}{dt}\right)_D=-D(z)P_2'(z,v,t), \tag{6}$$

$$\left(\frac{dP_1'}{dt}\right)_D=-\left(\frac{dP_2'}{dt}\right)_D. \tag{7}$$

This is consistent with models that have appeared in the literature.[10,13]

The goal is to calculate the rate of atoms desorbing from the surface region in the state $n$, $\dot{N}_n$. Two quantities are of physical interest. One is the total rate of desorbed particles entering the detection system. The other is the rate leaving the surface in the excited state. The former quantity is measurable by counting all particles, while the latter quantity is monitored by detecting the free atomic fluorescent radiation which is emitted at a frequency $\omega_{21}=[\epsilon_2(\infty)-\epsilon_1(\infty)]/\hbar$. The relevant rates are given by

$$\dot{N}_n=N_0\int_0^{\infty}dv\,v\,P_n(\infty,v,t), \tag{8}$$

where $N_0$ is the number of atoms adsorbed on the surface. In $\dot{N}_1$ is included the thermal desorption rate due to the unperturbed distribution of Eq. (2a), although it will be assumed to be negligibly small.

A further simplification will be made by assuming that there exists a unique solution to the resonance condition implied by the argument of the Dirac $\delta$ function in Eq. (4). This approximation may be relaxed at a later time, if necessary, but clouds the formalism somewhat. Thus, let $z_0$ be the root to the equation

$$\hbar\omega+\epsilon_1(z_0)-\epsilon_2(z_0)=0. \tag{9}$$

Combining Eqs. (1), (2), (4), and (6), we have the following Boltzmann equations:

$$\frac{\partial P_1'}{\partial t}+v\frac{\partial P_1'}{\partial z}-\frac{1}{M}\frac{d\epsilon_1}{dz}\frac{\partial P_1'}{\partial v}-D(z)P_2'=0, \tag{10a}$$

$$\frac{\partial P_2'}{\partial t}+v\frac{\partial P_2'}{\partial z}-\frac{1}{M}\frac{d\epsilon_2}{dz}\frac{\partial P_2'}{\partial v}+D(z)P_2' =g(z_0)\delta(z-z_0)\,e^{-\beta Mv^2/2}, \tag{10b}$$

where

$$g(z_0)=\frac{\pi E_0^2}{2\hbar}\left(\frac{\beta M}{2\pi}\right)^{1/2}\frac{|\langle 2\,|\,\mu_x\,|\,1\rangle\,|^2}{|[d(\epsilon_2-\epsilon_1)/dz]|}\,\frac{e^{-\beta\epsilon_1(z_0)}}{\int dz\,e^{-\beta\epsilon_1(z)}}. \tag{11}$$

Let us examine the solution for times sufficiently long that a steady-state behavior has evolved in the neighborhood of the surface, so that the explicit time dependence of $P_n$ may be neglected. Integration of Eq. (10b) proceeds by introducing a new set of variables,

$$\zeta=z, \tag{12a}$$

$$w=\{v^2+(2/M)[\epsilon_2(z)-\epsilon_2(z_0)]\}^{1/2}, \tag{12b}$$

so Eq. (10b) becomes

$$\frac{\partial P_2'}{\partial\zeta}+\left(w^2+\frac{2}{M}[\epsilon_2(z_0)-\epsilon_2(\zeta)]\right)^{-1/2}D(\zeta)P_2' =\frac{g(z_0)}{w}\,\delta(\zeta-z_0)\,e^{-\beta Mw^2/2}. \tag{13}$$

The solution to this is

$$P_2'=\frac{g(z_0)}{w}\Theta(\zeta-z_0)\,e^{-\beta Mw^2/2}\times\exp\left(-\int_{z_0}^{\zeta}\frac{D(\zeta')\,d\zeta'}{\{w^2+(2/M)[\epsilon_2(z_0)-\epsilon_2(\zeta')]\}^{1/2}}\right). \tag{14}$$

If we assume that the curve $\epsilon_2(\zeta)$ has no local maximum, then only those trajectories for which $\frac{1}{2}Mw^2 + \epsilon_2(z_0) - \epsilon_2(\infty)$ is positive will lead to an outward flux from the surface. Those trajectories for which it is negative lead to trapped excited atoms.

The number of atoms desorbing in the excited state per unit time is obtained by combining Eqs. (8), (12), and (14):

$$\dot{N}_2 = N_0 \int dw\, g(z_0)\, e^{-\beta M w^2/2}\, \Theta\left(\frac{Mw^2}{2} + \epsilon_2(z_0) - \epsilon_2(\infty)\right) \times \exp\left(-\int_{z_0}^{\infty} \frac{D(\zeta)\, d\zeta}{\{w^2 + (2/M)[\epsilon_2(z_0) - \epsilon_2(\zeta)]\}^{1/2}}\right). \quad (15)$$

It is convenient to express this in terms of an equivalent cross section for photodesorption. Dividing by the photon flux, $F = cE_0^2(8\pi\hbar\omega)^{-1}$, and the number of adsorbed atoms, $N_0$, we obtain the cross section for producing free atomic fluorescence upon photodesorbing:

$$\sigma_2 = \frac{4\pi^2\omega}{c}\left(\frac{\beta M}{2\pi}\right)^{1/2} \frac{e^{-\beta\epsilon_1(z_0)}}{\int dz\, e^{-\beta\epsilon_1(z)}} \frac{|\langle 2|\mu_x|1\rangle|^2}{|[d(\epsilon_2 - \epsilon_1)/dz]|}\bigg|_{z_0} \times 2\int_0^{\infty} dw\, e^{-\beta M w^2/2}\, \Theta\left(\frac{Mw^2}{2} + \epsilon_2(z_0) - \epsilon_2(\infty)\right) \times \exp\left[-\int_{z_0}^{\infty} D(\zeta)\left(w^2 + \frac{2}{M}[\epsilon_2(z_0) - \epsilon_2(\zeta)]\right)^{1/2}\right]. \quad (16)$$

This formula simplifies considerably if one assumes $k_B T$ small compared with $\epsilon_2(z_0) - \epsilon_2(\infty)$. Then $w \approx 0$ in the last integral and we have

$$\sigma_2 \approx \frac{4\pi^2\omega}{c} \frac{e^{-\beta\epsilon_1(z_0)}}{\int dz\, e^{-\beta\epsilon_1(z)}} \frac{|\langle 2|\mu_x|1\rangle|^2}{|[d(\epsilon_2 - \epsilon_1)/dz]|}\bigg|_{z_0} \Theta[\epsilon_2(z_0) - \epsilon_2(\infty)] \times \exp\left(-\int_{z_0}^{\infty} \frac{D(\zeta')d\zeta'}{\{(2/M)[\epsilon_2(z_0) - \epsilon_2(\zeta')]\}^{1/2}}\right). \quad (17)$$

Physically the last exponential is interpreted as being the probability of surviving to "infinity" without radiative decay. A similar quantity has appeared in the theory of electron stimulated desorption,[9] as one should expect.

We now proceed to integrate Eq. (10a) to find an expression for the cross section for photodesorption in the ground state. We assume immediately that $\beta$ is large, so Eq. (14) becomes

$$P_2' \approx \frac{g(z_0)}{w}\Theta(\zeta - z_0)\, e^{-\beta M w^2/2} \times \exp\left(-\int_{z_0}^{\zeta} \frac{D(\zeta')d\zeta'}{\{(2/M)[\epsilon_2(z_0) - \epsilon_2(\zeta')]\}^{1/2}}\right). \quad (14')$$

Introducing a new set of variables,

$$\zeta = z, \quad (12a')$$

$$u = \{v^2 + (2/M)[\epsilon_1(z) - \epsilon_1(\infty)]\}^{1/2}, \quad (12b')$$

we write Eq. (10a) as

$$\frac{\partial P_1'}{\partial \zeta} = \frac{D(\zeta)P_2'}{v}. \quad (13a)$$

Integration leads to the formula for the ground-state distribution:

$$P_1'(\zeta, u) = g(z_0)\int_{z_0}^{\zeta} d\zeta' \frac{D(\zeta')}{\{(2/M)[\epsilon_2(z_0) - \epsilon_2(\zeta')]\}^{1/2}} \frac{\Theta[\epsilon_2(z_0) - \epsilon_2(\zeta')]}{\{u^2 + (2/M)[\epsilon_2(\zeta') - \epsilon_2(z_0) + \epsilon_1(\infty) - \epsilon_1(\zeta')]\}^{1/2}}$$
$$\times \exp - \left[\frac{\beta M}{2}\left(u^2 + \frac{2}{M}[\epsilon_2(\zeta') - \epsilon_2(z_0) + \epsilon_1(\infty) - \epsilon_1(\zeta')]\right) + \int_{z_0}^{\zeta'} \frac{D(\zeta'')\, d\zeta''}{\{(2/M)[\epsilon_2(z_0) - \epsilon_2(\zeta'')]\}^{1/2}}\right]$$
$$\times \Theta\left(u^2 + \frac{2}{M}[\epsilon_2(\zeta') - \epsilon_2(z_0) + \epsilon_1(\infty) - \epsilon_1(\zeta')]\right). \quad (14a)$$

The cross section is given by

$$\sigma_1 = \frac{4\pi^2\omega}{c} \frac{e^{-\beta\epsilon_1(z_0)}}{\int dz\, e^{-\beta\epsilon_1(z)}} \frac{|\langle 2|\mu_x|1\rangle|^2}{|d/dz(\epsilon_2 - \epsilon_1)|}\bigg|_{z=z_0} \times \int_{z_0}^{\infty} d\zeta' \frac{D(\zeta')\Theta[\epsilon_2(z_0) + \epsilon_1(\zeta') - \epsilon_1(\infty) - \epsilon_2(\zeta')]}{\{(2/M)[\epsilon_2(z_0) - \epsilon_2(\zeta')]\}^{1/2}} \times \exp\left(-\int_{z_0}^{\zeta'} \frac{D(\zeta'')\, d\zeta''}{\{(2/M)[\epsilon_2(z_0) - \epsilon_2(\zeta'')]\}^{1/2}}\right). \quad (18)$$

The total desorption cross section $\sigma$ is simply $\sigma_1 + \sigma_2$.

Evaluation of the above integral is complicated somewhat by the possibility of having $\epsilon_2(z_0) - \epsilon_2(\zeta') < 0$ for some value of $\zeta' > z_0$. This corresponds to trapping in the excited state. The excited atom (which is chemsorbed in an excited state now) emits surface excitations and decays to the ground state. It may desorb if the condition defined by the $\Theta$ function is satisfied.

## III. NONRADIATIVE DECAYS

In the preceding formalism a knowledge of the decay function appearing in Eq. (6) was required. In general, the computation of such a function is rather complex since Coulomb-matrix elements are involved. It was shown recently, however, that in the case where the radiation frequency is greater than the surface plasmon frequency, a nonradiative decay channel involving surface plasmon emission[13] is possible. In this section we apply this formalism to the problem at hand, the calculation of $D(z)$. When the plasmon emission mechanism is operative, one expects it to dominate[13] the decay modes so other contributions will be neglected.

Rather than working directly with the surface plasmon, we choose to work with a hybrid excitation called the surface quasimode.[14] It resembles the surface plasmon at long wavelengths, but incorporates particle-hole excitations at shorter wavelengths. This construct has proven to be of value in other surface-related problems.[15] The Hamiltonian is expressed as

$$H = H_0 + \vec{\mu} \cdot \nabla\Phi(\vec{\mathrm{r}}) + \sum_{\vec{\mathrm{k}}_\perp} \hbar\sigma_{\vec{\mathrm{k}}_\perp}(a^\dagger_{\vec{\mathrm{k}}_\perp} a_{\vec{\mathrm{k}}_\perp} + \tfrac{1}{2}), \tag{19}$$

where $H$ is the Hamiltonian of the atom-solid system, $\vec{\mu}$ is the electric-dipole operator of the perturbed atom, $\Phi$ is the quantized surface-quasimode field, $\sigma_{\vec{\mathrm{k}}_\perp}$ is the frequency of the quasimode excitation with wave vector $\vec{\mathrm{k}}_\perp$ parallel to the surface, and $a^\dagger_{\vec{\mathrm{k}}_\perp}$, $a_{\vec{\mathrm{k}}_\perp}$ are creation and annihilation operators. We are assuming that the surface-quasimode wavelength is typically large compared with the atomic size, so that the dipole approximation is used. For shorter-wavelength excitations this approximation becomes cruder, but still allows us to estimate the magnitude of the decay rate. The quasimode field is given by

$$\Phi(\vec{\mathrm{r}}) = \sum_{\vec{\mathrm{k}}_\perp} g(k_\perp)(a_{k_\perp} e^{-k_\perp|z| - i\vec{\mathrm{k}}_\perp\cdot\vec{\mathrm{r}}} + a^\dagger_{k_\perp} e^{-k_\perp|z| + i\mathrm{k}_\perp\cdot\vec{\mathrm{r}}}), \tag{20}$$

where

$$g(k_\perp) = \left(\frac{\pi\hbar\omega_p^2}{2k_\perp\sigma_{k_\perp}}\right)^{1/2},$$

$\omega_p$ being the plasma frequency of the solid and the quantization area being taken to be unity.

The decay rate $D(z)$ is obtained by using the Fermi Golden Rule again:

$$D(z) = \frac{2\pi}{\hbar} \sum_{\vec{\mathrm{k}}_\perp} |\langle 1, \vec{\mathrm{k}}_\perp | \vec{\mu} \cdot \nabla\Phi | 2, \mathrm{vac}\rangle|^2 \delta(\epsilon_2 - \epsilon_1 - \hbar\sigma_{k_\perp}) . \tag{21}$$

Here the atom makes a transition from the excited state with no surface excitations, $|2, \mathrm{vac}\rangle$, to the ground state with one surface excitation, $|1, \vec{\mathrm{k}}_\perp\rangle$. Thus

$$D(z) = \frac{2\pi}{\hbar} \int \frac{d^2k_\perp}{(2\pi)^2} g^2(k_\perp)(k_\perp^2 |\langle 1|\mu_z|2\rangle|^2 + |\langle 1|\vec{\mu}_\perp|2\rangle \cdot \vec{\mathrm{k}}_\perp|^2) \times e^{-2k_\perp z} \delta(\epsilon_2 - \epsilon_1 - \hbar\sigma_{k_\perp}) . \tag{22}$$

The presence of the $\delta$ function allows us to evaluate the integral and we obtain

$$D(z) = \frac{\pi\omega_p^2}{\hbar} \frac{k^2 e^{-2kz}}{|d\sigma^2/dk|} (|\langle 1|\mu_z|2\rangle|^2 + |\langle 1|\mu_x|2\rangle|^2) \times \Theta(\epsilon_2 - \epsilon_1 - \hbar\sigma), \tag{23}$$

where $k$ is the root to the equation

$$\epsilon_2(z) - \epsilon_1(z) - \hbar\sigma = 0 . \tag{24}$$

We note that $D(z)$ is not simply a decaying exponential. Additional dependence on $z$ enters through $k$ and through the transition-moment matrix elements. It is only for large $z$ that these values approach their free atomic values, so $D(z)$ tends asymptotically to an exponential decay. It should also be noted that the $x$ and $z$ transition moments are not simply related in the neighborhood of the surface. Asymptotically, however, they are related by simple Clebsch-Gordan coefficients. Finally, the above formula for the decay rate is not applicable when $\epsilon_2 - \epsilon_1 < \omega_p/\sqrt{2}$ because then no surface-quasimode emission is possible.

Following arguments presented in the literature,[14] it is possible to obtain an expression for $\sigma_{k_\perp}$ in terms of the dielectric properties of the solid. Thus

$$\sigma_{k_\perp} = \frac{\omega_p}{\sqrt{2}} \left(\frac{1 + \bar{\epsilon}}{1 - \bar{\epsilon}}\right)^{1/2}, \tag{25}$$

where

$$\bar{\epsilon} = \frac{k_\perp}{\pi} \int_{-\infty}^{\infty} dk_z \frac{(k_\perp^2 + k_z^2)^{-1}}{\epsilon(\vec{\mathrm{k}}, 0)} \tag{26}$$

and $\epsilon(\vec{\mathrm{k}}, \omega)$ is the dielectric function of the bulk metal. It is convenient to employ the Lindhard dielectric function in actual computations,

$$\epsilon(\vec{\mathrm{k}}, 0) = 1 + (\pi a_0 k_F x^2)^{-1} \left(\frac{1}{2} + \frac{1 - x^2}{4x} \ln\left|\frac{1 - x}{1 + x}\right|\right), \tag{27}$$

where $k_f$ is the Fermi wave vector, $x = k/2k_F$, and $a_0$ is the Bohr radius.

## IV. RESULTS AND DISCUSSION

As mentioned in the text, two simple photodesorption cross sections are amenable to experiment. The simplest is $\sigma_2$, the cross section for photodesorption into an excited atomic state, which is measured by counting the free atomic fluorescent photons. The cross section for desorption into any state, $\sigma$, is obtained by counting all atoms that stream from the surface under the influence of the light beam. In actual experiments, the source of light could be either synchrotron radiation, vacuum ultraviolet laser, or perhaps some other light source.

In addition to the mechanisms considered in the previous sections, there exist other processes that could result in photodesorption. For example, thermal photodesorption[16] could lead to a contribu-

TABLE I. Typical values for the parameters determing the cross section.

$z_0 = z_1 = 2\times 10^{-8}$ cm

$a_2 = 10^8$ cm$^{-1}$

$A_2 = 2$ eV

$\kappa = 200$ g sec$^{-2}$

$\beta^{-1} = 0.025$ eV

$|\langle 2|\mu_x|1\rangle| = 10^{-18}$ esu cm

$\hbar\omega_p = 5$ eV

$\hbar s = 10^{-8}$ eV cm

$M = 10^{-23}$ g

$V_0 = 2$ eV

$\epsilon_2(\infty) = 4$ eV

$\hbar\omega = 6.3$ eV

$k = 1.5\times 10^8$ cm$^{-1}$

$\hbar\sigma \simeq 5$ eV

tion to $\sigma$, although it is expected to be small at low temperatures. It will not contribute appreciably to $\sigma_2$, however. Another possible contributor is photoemission coupled with electron-stimulated desorption. One may estimate the cross section for this process from the formula

$$\sigma_{\mathrm{PESD}} = f Y \sigma_{\mathrm{ESD}} , \tag{28}$$

where $Y$ is the photoemission yield (number of photoelectrons per incident photon), $\sigma_{\mathrm{ESD}}$ is the cross section for electron-stimulated desorption, and $f$ is a number less than unity to account for the fact that only part of the yield has sufficient energy above threshold to cause electron-stimulated desorption. Values of $Y$ are typically on the order of $10^{-4}$ and $\sigma_{\mathrm{ESD}}$ is[9] on the order of $10^{-20}$ cm$^2$, so an upper limit for $\sigma_{\mathrm{PESD}}$ is $\sim 10^{-24}$ cm$^2$.

Aside from the smallness of these cross sections, they also produce distinctly different energy distributions for the desorbed atoms. Photodesorption produces essentially a monochromatic distribution, while the other processes are expected to result in somewhat broader distributions. Thus they should be experimentally distinguishable by studying the energy distribution of the emitted atoms.

Let us now obtain a crude estimate of the cross sections by plugging in typical order-of-magnitude values for the various parameters. To this end, it is convenient to adopt a simple expression for $\epsilon_2(z)$, such as[9] $\epsilon_2(z) = \epsilon_2(\infty) + A_2 e^{-a_2 z}$. If we furthermore ignore all $z$ dependence in Eq. (23), except for the rapidly varying exponential, the last exponential appearing in Eq. (17) may be evaluated analytically. Furthermore, we might assume for $\epsilon_1(z)$ something of the form $\epsilon_1(z) \doteq -V_0 + \frac{1}{2}\kappa(z-z_1)^2$. The surface-quasimode dispersion formula is assumed to be $\sigma = (\omega_p/\sqrt{2}) + sk_\perp$. Since state 2 is excited by the $x$ component of the dipole operator, we neglect the $z$ component of the dipole linking state 1 and 2. Thus we find

$$\sigma_2 = \frac{4\pi^2\omega}{c}\left(\frac{\beta\kappa}{2\pi}\right)^{1/2} \times \exp\left(-\frac{\beta\kappa}{2}(z_0-z_1)^2\right) \frac{|\langle 2|\mu_x|1\rangle|^2}{|a_2 A_2 e^{-a_2 z_0} + \kappa(z_0-z_1)|} \times \exp\left\{\frac{-\pi\omega_p^2 k^2 |\langle 2|\mu_x|1\rangle|^2}{2\hbar s a_2[(\omega_p/\sqrt{2})+sk]}\left(\frac{M\pi}{2A_2}\right)^{1/2} \times \frac{\Gamma(2k/a_2)}{\Gamma[(1/2)+(2k/a_z)]}\exp\left[z_0\left(\frac{a_2}{2}-2k\right)\right]\right\},$$

where $\hbar\omega = \epsilon_2(\infty) + A_2 e^{-a_2 z_0} + V_0 - \kappa(z_0-z_1)^2/2$. For simplicity we choose $z_0 = z_1$.

Typical values for the various parameters are tabulated in Table I. Because of the wide variation in all the parameters, we elect not to study their full range of possible values. Our main purpose is to obtain a typical estimate for $\sigma_2$ to see if experimental studies are feasible. We find $\sigma_2 = 2\times 10^{-18}$ cm$^2$, which clearly is much larger than $\sigma_{\mathrm{PESD}}$. The $\sigma_1$ cross section has a similar magnitude. For a monolayer of $10^{15}$ atoms/cm$^2$ adsorbed on the surface this would correspond to a quantum efficiency of $2\times 10^{-3}$. Quantum efficiencies of this magnitude have been observed experimentally recently.[7]

A more exact calculation is, unfortunately, not possible at the present time. This is due mainly to the absence of quantitative information concerning the $\epsilon_n$ curves. On the other hand, experiments on photodesorption should enable us to obtain information concerning these curves.

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