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LASER-INDUCED SURFACE MIGRATION VIA SURFACE PLASMONS

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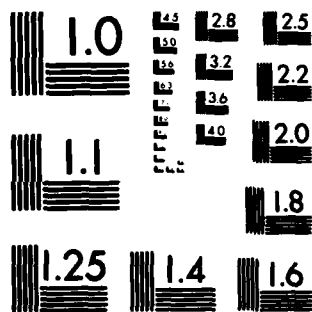
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Laser-Induced Surface Migration
via Surface Plasmons

by

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LASER-INDUCED SURFACE MIGRATION VIA SURFACE PLASMONS

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→ A classical model coupling a charged adspecies to a laser-induced surface plasmon is presented. Such coupling can enhance the rate and specify the direction of surface migration. For the particular case of an atomic oxygen ion of charge -1 adsorbed on aluminum which is exposed to CO_2 laser radiation of intensity 1 W/cm^2 , the velocity of migration ($61.3 \text{ } \mu\text{m/sec}$) is five orders of magnitude greater than the usual thermal velocities observed at room temperature. ←

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Migration of adsorbed particles on a solid surface is an important process in catalytic reactions.¹⁻⁵ Such motion has been observed even for adsorbates with very high binding energies at relatively low temperatures.¹ This surface migration is essentially random motion that proceeds at a typical adsorbate velocity of a few angstroms per second.^{1,2}

Adsorbed particles on a surface, however, can be strongly influenced by the existence of surface plasmons. For example, it has been theoretically argued that the interaction between adspecies can be enhanced by these surface waves.⁶ Furthermore, laser-induced periodic surface structure has been explained in terms of surface plasmons.⁷ In the following, we shall examine the effect that a surface plasmon can have on the motion of a charged adspecies at low temperatures. We shall discuss the possibility of using a laser-excited surface plasmon to control both the rate and direction of surface migration.

If a smooth metal surface is exposed to laser radiation of an appropriate frequency, a surface plasmon can be excited via frustrated reflection.⁸ This plasmon will have an electric field, $\vec{E}$, associated with it above the surface of the form⁹

$$\frac{\vec{E}}{E_0} = \left(\frac{k_x}{k_g}, 0, -\frac{k_z}{k_g} \right) \exp[i(k_x x + k_z z - \omega t)] + \text{c.c.}, \quad (1)$$

where the z -direction is perpendicular to the surface, x is parallel and in the direction of the plasmon propagation, and E_0 is the amplitude and ω the frequency of the laser field. The wavenumber k_g for the laser in the gas medium above the metal and k_x and k_z for the surface plasmon are given by

$$k_g = \frac{\omega}{c} \quad (2)$$

$$k_x = \frac{\omega}{c} \sqrt{\frac{\epsilon(\omega)}{\epsilon(\omega)+1}} \quad (3)$$

$$k_z = \frac{\omega}{c} \frac{1}{\sqrt{\epsilon(\omega)+1}} , \quad (4)$$

where c is the speed of light.

The dielectric function of the metal, $\epsilon(\omega)$, will in general be less than negative one for the plasmons excited. Under this condition, the x-component of the wavevector, Eq. (3), will be real and the z-component, Eq. (4), will be imaginary:

$$k_z \equiv i\kappa . \quad (5)$$

If a particle of charge q is now introduced above the surface, it will couple to the plasmon electric field. The equations of motion for this particle can be readily obtained from Eq. (1) as

$$m\ddot{x} = \frac{2q\kappa E_0}{k_g} \sin(k_x x - \omega t) e^{-\kappa z} - \frac{\partial V(x, y, z)}{\partial x} , \quad (6a)$$

$$m\ddot{z} = \frac{2q\kappa_x E_0}{k_g} \cos(k_x x - \omega t) e^{-\kappa z} - \frac{\partial V(x, y, z)}{\partial z} , \quad (6b)$$

where m is the mass of the adspecies and $V(x, y, z)$ is the interaction potential between the adspecies and the surface. This interaction can be quite complicated,^{10,11} especially in the presence of the surface plasmon. We shall assume that the interaction is sufficiently strong to confine the charged particle to an equilibrium distance from the surface, $z = z_{eq}$. However, it will be free to move along the plane of the surface. These conditions would be characteristic of a physisorbed state.

Under these assumptions, Eq. (6a) can be simplified and converted to and integral form,

$$x(t) = \omega^2 C \int_0^t dt' \int_0^{t'} dt'' \sin[k_x x(t'') - \omega t''], \quad (7)$$

where the constant is

$$C \equiv \frac{2q\kappa E_0 e^{-\kappa z_{eq}}}{m k_q \omega^2}. \quad (8)$$

We now change the variable of integration in Eq. (7) to

$$u'' = k_x x(t'') - \omega t'' \quad (9)$$

and similarly for t' . Furthermore, we note that the velocity of the particle will be much slower than the plasmon:

$$\dot{x}(t'') \ll \frac{\omega}{k_x}. \quad (10)$$

Under these conditions, we can readily integrate Eq. (7) to give

$$x(t) = C \{k_x x(t) - \omega t - \sin[k_x x(t) - \omega t]\}. \quad (11)$$

However, for any time greater than a few periods of the laser frequency, the oscillatory term will be insignificant. Therefore,

$$x(t) = \frac{C\omega}{k_x C - 1} t. \quad (12)$$

Consequently, coupling a charged adspecies to the plasmon will produce a linear motion parallel to the plasmon.

If an aluminum surface is exposed to a laser of low intensity (1 W/cm^2) with a frequency of $1.8 \times 10^{14} \text{ Hz}$ (CO_2 laser at $10.6 \text{ }\mu\text{m}$), surface plasmons

can be excited. We now consider an atomic oxygen ion of charge -1 adsorbed on the surface, which will couple to this plasmon. The resultant velocity can be obtained from Eqs. (8) and (12) as

$$\dot{x} = 61.3 \text{ } \mu\text{m/sec.} \quad (13)$$

This is substantially larger than the usually thermal velocities of a few angstroms per second that are observed at room temperature. Furthermore, we can easily increase this speed by using a laser of higher intensity. It should also be noted that the velocity of a negatively charged particle is with the plasmon; the positive particle will move against it. Thus, the plasmon-induced motion has a preferred direction.

We have shown that a laser-excited surface plasmon can impart substantial motion to a charged adspecies. However, we have only considered this effect for weakly-bound adsorbates at low temperatures. The exact form of the surface interaction potential was not considered, and the phenomena of surface relaxation that often accompanies migration^{2,12} was not examined. Finally, it should be noted that the interplay of the surface plasmon with the adspecies/surface potential could have a substantial effect on surface migration. Research to overcome these limitations in this model is now in progress.

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