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# Laser-Induced Surface Migration via Surface Plasmons

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 of 1 W/cm$^2$, the velocity of migration (61.3 microns/sec) is five orders of magnitude greater than the usual thermal velocities observed at room temperature.
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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 $I \text{ W/cm}^2$, the velocity of migration (61.3 pm/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.\(^1\text{--}^5\) 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, \(\hat{E}\), associated with it above the surface of the form:

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

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 \(\omega\) 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

\[
k_g = \frac{\omega}{c}
\]

\[
k_x = \frac{\omega}{c} \sqrt{\frac{\varepsilon(\omega)}{\varepsilon(\omega) + 1}}
\]
$$k_z = \frac{\omega}{c} \frac{1}{\sqrt{\varepsilon(\omega)} + 1},$$ \hspace{1cm} (4)

where $c$ is the speed of light.

The dielectric function of the metal, $\varepsilon(\omega)$, 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:

$$k_z = i \kappa.$$

(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

$$\frac{\ddot{x}}{m} = \frac{2qE_0}{k_g} \sin(k_x x - \omega t) e^{-\kappa z} - \frac{\partial V(x,y,z)}{\partial x},$$ \hspace{1cm} (6a)

$$\frac{\ddot{z}}{m} = \frac{2qk_x E_0}{k_g} \cos(k_x x - \omega t) e^{-\kappa z} - \frac{\partial V(x,y,z)}{\partial z},$$ \hspace{1cm} (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, 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, $z = z_{\text{eq}}$. 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 an integral form,
\[ x(t) = \frac{2}{\omega} C \int_0^t dt' \int_0^{t'} dt'' \sin[k_x x(t'') - \omega t''], \quad (7) \]

where the constant is
\[ C \equiv \frac{2qE_0 e^{-xZeq}}{mk_q \omega^2}. \quad (8) \]

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/cm²) with a frequency of \( 1.8 \times 10^{14} \) Hz (CO₂ laser at 10.6 μm), 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

\[ \dot{x} = 61.3 \, \mu\text{m/sec}. \]  

(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.
Acknowledgments

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