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Electromagnetic-field-enhanced desorption of atoms

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We present a description of how the collective electronic excitation in a small metal particle leads to a large field enhancement in the surface region which induces electronic transitions resulting eventually in the desorption of atoms. Our results for the frequency and radial dependence of the desorption yield are in good agreement with recent experimental findings for sodium particles, and make it possible to extract information about the effective number of desorption sites for a small particle.

INTRODUCTION

During the last decade we have seen an accelerated development in the studies of electronic and optical properties of clusters and small particles,[1,2] especially in the field of photostimulated desorption.[3,4] The small particle has the unique feature, compared to a smooth metal surface, of providing a strong enhancement of the "stimulating" laser light giving rise to photodesorption also for very low power cw lasers. The present paper is intended to make a qualitative and quantitative treatment of this phenomenon and to investigate its consequences for the particular experiment in Ref. 4, where desorption of sodium atoms for small sodium particles supported on a LiF single crystal was investigated using light with a broad frequency range.

The main findings in Ref. 4 were the following.

(1) No threshold for desorption is seen, and the desorption rate increases linearly with light intensity I_0: 40 $\text{mW/cm}^2 < I_0 < 160\ \text{W/cm}^2$.

(2) The desorption rate depends strongly on the frequency of the incident light, peaking around 2.54 eV, with a full width at half maximum (FWHM) of 0.46 eV, for particles with an average radius of 500 Å.

(3) The signal depends on the particle size. For $R < 100$ Å, it is almost negligible, reaches a maximum around $R \approx 400$ Å, and then drops off for larger values of R.

(4) The desorption signal indicates that atoms at certain "exposed" positions desorb preferably, with an upper limit for the desorption yield of one atom per 10^5 photons, and that the desorption sites are uncorrelated.[5]

(5) The desorption signal is nonthermal in nature.

In this paper we will present a simple theory based on a photon-induced electronic transition (absorption). Hence we utilize (5) and the scaling with incoming intensity (1) in setting up our theoretical description of the electrodynamics of the process. Based on this we can explain the main features seen in (2) and (3), i.e., the frequency and radial dependence by carefully treating the total field in the surface region of the small particle. Furthermore, the upper limit for the desorption yield in (4) and our calculated efficiency of the process yields a gross estimate for the number of "effective" sites on a small metal particle. In order to be able to predict this number more accurately, one has to be more specific with respect to the wave functions involved and the possible desorption sites. In other words, when we calculate the electronic transition rate $1/\tau$, induced by light of frequency ω, using the Fermi's golden-rule formula:

$$1/\tau=(2\pi/\hbar)\sum_{i,f}|\langle i|(e/2mc)(\mathbf{A}\cdot\mathbf{p}+\mathbf{p}\cdot\mathbf{A})|f\rangle|^2 \times\delta(E_f-E_i-\hbar\omega)\ . \quad (1)$$

We need not only to restrict the summation by prescribing information about the bonding and antibonding nature of the states $|i\rangle$ and $|f\rangle$, but also we have to know which subgroup of these states is effective in the desorption of *neutrals* from the surface region. However, since this is a formidable task, outside the scope of this Brief Report, in what follows we will assume that *all* electronic transitions are effective in producing electrons in orbitals leading to desorption, but using an effective restriction on the set $\{i,f\}$ by only using the *surface* part of the electromagnetic field in the particle. This procedure gives an estimate for the efficiency of the process which, when compared to the experimentally extracted efficiency, gives an upper bound for the number of surface atoms (sites) which really do contribute. Furthermore, for computational ease and because of the lack of specific experimental information regarding the actual shape and size distribution of the particles, we will make our calculation for a perfectly spherical particle.

THEORY AND EXPERIMENTAL COMPARISON

As stated in the introduction, our basic desorption mechanism is that the incident light is absorbed by the small particle, primarily by the surface region.[6] This is most important for very small particles ($R \leq 100$ Å), but is still of importance for larger ones.[7] The electronic transition taking up the photon energy goes between bonding (valence-band) and antibonding (conduction-band) levels. For an atom at the surface this can be critical because it is in an unsymmetrical environment, and hence, it is easier to break off from the small particle than from bulk atoms. Furthermore, in a small particle the effective field inside can be strongly enhanced close to the so called Mie frequency. This corresponds to a collective excitation of the confined electron gas which is spatially localized in the surface region. Again this gives a stronger perturbation in the electronic structure in the surface region which can affect the binding of the outermost atoms. Notice that this field enhancement is much weaker for a semi-infinite solid with a *smooth* surface. However, by using an attenuated-total-reflection geometry, providing the necessary momentum conservation, Al desorption from aluminum films has recently been reported.[8]

The experiment in Ref. 4 is made on a sample having 10^{13} particles/m^2 with a size range of 10 to 150 nm. Therefore, in most cases it is enough to study one particle when it comes to the electrodynamical behavior, since they are rather far apart and we can neglect their mutual interaction. Clearly the local electromagnetic field is different for each "exposed" position. However, taking into account that there are approximately 1000 sites per particle (see below) and 10^{13} particles/m^2 and that sites are independent, we can safely assume that those "exposed" positions are placed at random on the particle surface. Thus, to calculate the efficiency of the desorption process, i.e., the number of atoms we get per incoming photon, we define an area A_{eff}. This area is the apparent area on a particle taken up by desorbing atoms. It therefore includes in principle such factors as the general surface conditions of importance for the existence of particular site prone to desorption as well as the branching ratio to other processes where the excited electron decays giving rise to an Auger electron before the desorbing atom gets the kinetic energy necessary to escape.[9] However, in the experiments in Ref. 4 the difference between the excitation energy and the energy to break the surface bond is observed as kinetic energy of the desorbed atoms. Other relaxation channels therefore seem to play a minor role in this situation. Therefore, the main part of A_{eff} is really related to the general surface conditions of the small particles.

Using the concept with an apparent area A_{eff} and letting I_0 be the intensity of the incoming light of frequency ω and ϵ_0 the vacuum dielectric constant,

$$I_0 = \tfrac{1}{2} c \varepsilon_0 |E_0|^2 , \tag{2}$$

we can write the following for the number N_d of desorbed atoms per unit time and particle:

$$N_d = \frac{a(\omega) I_0}{\hbar\omega} A_{\text{eff}} , \tag{3}$$

$a(\omega)$ being the fraction of the incoming radiation which is absorbed in the surface region (≤ 1). This should be compared with the number N_i of incident photons per unit time and particle

$$N_i = \frac{I_0}{\rho_0 \hbar\omega} , \tag{4}$$

where ρ_0 is the density of particles. From Eqs. (3) and (4) we can now define an efficiency:

$$\eta \equiv N_d / N_i = a(\omega) \rho_0 A_{\text{eff}} . \tag{5}$$

We will later see that $a(\omega) \sim 0.01$. From the experimentally found upper bound for the efficiency $\eta \leq 7 \times 10^{-6}$ and the particle density $\rho_0 = 10^{13}$/m^2, we can therefore estimate $A_{\text{eff}} \approx 7000$ Å^2. This corresponds to approximately 1000 surface sites (7 Å^2 each) or 0.2% of the surface area of a 500-Å-large particle.

We now continue by giving a more detailed discussion for N_d and show that it gives the main physics of the experimental results with respect to the radial dependence and the general frequency characteristics. By the equivalence between the Fermi's golden-rule formulation in Eq. (1) and the Joule heating,[10] it is possible to pick out the part of $1/\tau$ which is related to the surface part of the electromagnetic field. This has been done earlier[11] for small metal particles, and we only quote the result for the surface part of the total absorptance:

$$a(\omega) = \tfrac{4}{3} qR |\epsilon E_r(R,\omega)/E_0|^2 \operatorname{Im} \left[\frac{1-\epsilon}{\epsilon} \frac{d_r}{R} \right] , \tag{6}$$

where $q = \omega/c$, $\epsilon = \epsilon(\omega)$ is the *bulk* dielectric function of the metal sphere, and the length $d_r = d_r(R,\omega)$ is the center of gravity of the induced electron density, being in the angstrom range. Since we will be looking at values of $R \gg d_r$, we can estimate d_r by its counterpart for a planar surface, $d_\perp(\omega)$, for which there are very good calculations available.[12]

When calculating the ratio between the total radial field at the surface $E_r(R,\omega)$ and the incoming field strength E_0, we have to use the expression from a retarded formalism since qR is not small. We have the following (for the dipolar mode $l = 1$):

$$E_r(R,\omega)/E_0 = 3 j_1(\rho_t) \frac{h_1^{(1)}(\rho)\partial j_1(\rho)/\partial\rho - j_1(\rho)\partial h_1^{(1)}(\rho)/\partial\rho}{h_1^{(1)}(\rho)\partial[\rho_t j_1(\rho_t)]/\partial\rho_t - \epsilon j_1(\rho_t)\partial[\rho h_1^{(1)}(\rho)]/\partial\rho} , \tag{7}$$

where $\rho = qR$ and $\rho_t = q_t R$; $q_t^2 = q^2 \epsilon(\omega)$. ρ and ρ_t characterize the retarded regime ($\rho \sim 1$), but for very small particles ($R \ll \lambda$) where ρ and $\rho_t \ll 1$ we get the well-known nonretarded limit of Eq. (7):

$$E_r(R,\omega)/E_0 = \frac{3}{\epsilon + 2} . \tag{8}$$

The calculation of Eq. (7) is done with the following model dielectric function of the sodium particle:

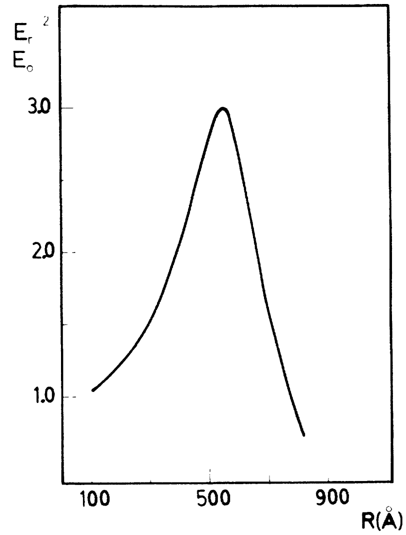

FIG. 1. The dependence of the surface electromagnetic field in a small particle, in units of the external field strength E_0, as a function of particle radius (R). Notice the peaking of the curve in the region where $\lambda R \sim 1$, λ being the wavelength of the incoming radiation (514 nm or $\hbar\omega = 2.41$ eV).

$$\epsilon = 1 - \frac{\omega_p^2}{\omega(\omega + i/\tau)} \tag{9}$$

using a plasma frequency $\omega_p = 5.89$ eV and a Drude damping $\omega_p \tau = 10^3$.

The ratio $|E_r(R,\omega)/E_0|^2$ is shown in Fig. 1 for a large range of R values and with a fixed frequency $\omega = 2.41$ eV to facilitate a comparison with the experimental conclusions. We can clearly reproduce the general trend found in the experiments with an increase for small R, then a peak before it decays for larger values of R. The experimentally found radial dependence is therefore a consequence of the interplay between R and λ, whether we are in the nonretarded or the retarded regime of the electrodynamical response of the small particle. Since we do not know the exact particle distribution, except for the information about a large spread in particle size, it is difficult at this stage to draw any conclusions from the fact that the peaking of the experimental curve around 40 nm is slightly different from the theoretical value in Fig. 1 (53 nm).

Going now back to Eqs. (2)–(6), coupled with the very weak R dependence of d_r for R values exceeding 10 nm, and comparing the experimental results for the radial dependence with Fig. 1, we come to the conclusion that $\rho_0 A_{\text{eff}}$ is rather independent of R for the experimentally investigated range of R values. Provided ρ_0 has a weak radial dependence (if any), we conclude that the number of effective desorption sites are about the same, independent of the particle size. In other words the particles get more and more smooth as they grow in size.

We now switch to a discussion of the frequency dependence of the desorption yield N_d. With a realistic value for Im $d_r \approx 0.1$ Å (Refs. 2 and 12) and $|E_r(R)/E_0|^2 \approx 10$ at maximum, the typical maximum value for $a(\omega)$ is ($R = 500$ Å):

$$a(\omega) \approx 0.01 \tag{10}$$

which is an important number setting the scale of N_d. In the calculation to be discussed in what follows we will of course use the full frequency dependence of d_r. In Fig. 2 we show a calculation $N_d(\omega)$ using $a(\omega)$ from Eq. (6). To facilitate a comparison with the shape of the experimental curve the two curves are scaled to have the same maximum value. It should be noted that in the retarded regime $E_r(R,\omega)/E_0$ [Eq. (7)] always has a nonzero imaginary part even if $\epsilon(\omega)$ is real. Then the position and the width of the theoretical curve is mainly due to the interplay between the real and the imaginary parts of $E_r(R,\omega)/E_0$. It is obvious from Fig. 2 that the electrodynamical model based on the field enhancement around the Mie plasma frequency works very well for predicting the overall frequency dependence of the process. This calculation therefore confirms the speculations in Ref. 4 of the importance of the surface-plasmon excitation for the desorption process. However, instead of stressing that stimulated desorption is the consequence of a surface-plasmon absorption leading to desorption, we would like to stress the role of the surface plasmon in creating a high electromagnetic field in the surface region, analogous to the surface photoelectric effect, and hence creating many bonding-antibonding pairs leading to desorption.

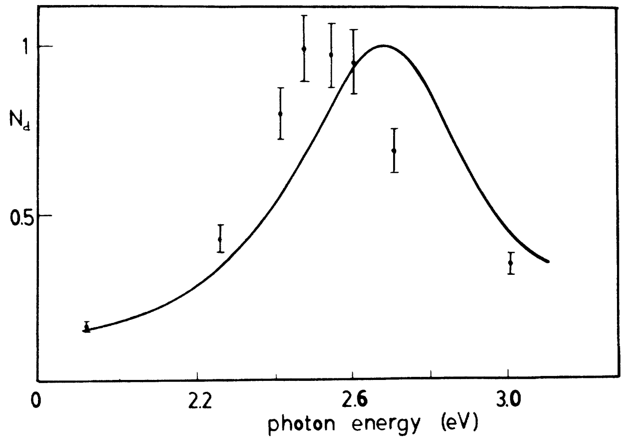

FIG. 2. The frequency dependence of the experimentally determined desorption yield (Ref. 4) is compared to a theoretical calculation of the frequency-dependent field (enhancement) factors, cf. Eqs. (2)–(6), i.e., $N_d(\omega)$. N_d and the experimental results are scaled to their maximum values to facilitate an easy comparison.

CONCLUSIONS

Our main emphasis in this work has been to extract the part of the physics we have a rather good understanding of, i.e., the electrodynamical part. What is left then in the desorption signal is important information as to the efficiency of the process: the number of desorption sites on a small particle.

Based on the field enhancement taking place in a small metal particle and especially the field behavior close to the surface, we can account for the radial and frequency dependence of the observed yield essentially in terms of the field factor $|E_r(R,\omega)/E_0|^2$, the ratio between the total radial field in the surface region and the external field E_0 impinging on the particle.

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