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A SURFACE PLASMON MODEL FOR LASER ABLATION OF Ag^+ IONS FROM A ROUGHENED Ag SURFACE

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ABSTRACT- Experimental work by Shea and Compton¹ suggests that Ag^+ ions emitted from a roughened Ag surface irradiated by a nanosecond or picosecond laser beam may absorb the full energy of the Ag surface plasmon (SP). We have modeled this process under the assumption that it proceeds through an inverse bremsstrahlung-type absorption of the SP quantum by an Ag^+ ion which also undergoes a small-impact parameter collision with another ion or atom in the vicinity of the surface. We give a quantitative estimate of the absorption probability and find reasonable agreement with the Shea-Compton results.

I. Introduction

In a very interesting recent set of experiments, Shea and Compton¹ have studied the distribution in energy of Ag^+ ions emitted from a roughened Ag surface irradiated by photons. They find copious emission of Ag^+ ions when they use a picosecond laser with a photon energy of 3.49 eV at a power level of $3 \times 10^7 \text{ W/cm}^2$ with a pulse duration of 30 ps. The energy distribution consists of a peak at an ion energy of $\approx 0.5 \text{ eV}$, which they term the thermal peak, and a broader peak with a mean energy of $\approx 3.5 \text{ eV}$. The yield of ions in the higher energy peak is found to scale approximately as the third power of the laser power level, while the emission of ions in the thermal peak is linear in the laser power. When the photon energy is increased to 4.66 eV the thermal peak is observed but the peak at 3.5 eV (the 'SP' peak) is not seen. At a photon energy of 2.33 eV both the thermal and the SP peaks are observed. Shea and Compton hypothesize that the higher-energy peak in the ion distribution is due to the decay of the well-known Ag surface plasmon. This is made plausible by the observed polarization dependence of the yield.¹ To account for the dependence of the emission probability on photon energy, they argue that the SP is excited with only small probability at the higher energy and that at the lower energy, a complex, two-photon absorption may be occurring. Their data at the lower energy are not sufficiently

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detailed to show whether or not the yield of ions in the higher peak scales as a higher power of the laser power level. Observation of such a dependence would tend to support the mechanism that they propose.

We have made a quantitative estimate of the probability that the peak in the ionic distribution at ≈ 3.5 eV is due to the annihilation of surface plasmons through the decay channel that yields ions possessing the full SP energy.

Direct conversion of the SP energy into the kinetic energy of an Ag^+ ion is quite unlikely due to the strong mismatch in momentum between the SP and an ion. The SP carries momentum ranging from zero to less than $\approx 1 \text{ \AA}^{-1}$, while that of an Ag^+ ion with the SP energy is several hundred times larger than this maximum value. To conserve momentum, collision with a third body is necessary. We assume that a second Ag^+ ion or an Ag atom is present to participate in a three-body collision with the SP and the ion. We evaluate the decay rate of the SP through this channel using quantal perturbation-theoretic methods and compare the computed probability of ion emission with that measured by Shea and Compton.

Theory

A photon, incident from vacuum on the plane surface of a medium capable of supporting a surface plasmon, cannot create a quantum of the SP field by annihilation.² This is not allowed because the phase velocity of the SP at a vacuum-bounded surface is always less than the velocity of light in vacuo. Speaking quantally, there is a mismatch in momentum; the photon momentum is always less than that of the SP. Such an interaction is not forbidden: (a) if the photon is incident on the surface from a medium in which its speed is less than c , (b) if there are irregularities in structure (roughness) on a planar surface, (c) or if the surface plasmon exists on a finite body, such as a spheroid.³

Here we assume that in the Shea-Compton work the Ag surface has been sufficiently roughened by prior laser irradiation that the conversion of a photon to a surface plasmon is readily accomplished. We are not concerned here with the details of this process, but will focus on the SP-ion transformation, deriving an analytical expression for the damping rate of the SP to a final state consisting of at least one Ag^+ ion.

Figure 1 shows schematically: (a) a portion of a metal surface, (b) an evanescent SP field associated with the metal, and (c) Ag^+ ions and atoms emerging from the surface. The latter are assumed to be emitted from the surface independently of the SP field and are due to ordinary evaporation processes occurring in the transiently heated surface region. The electric field associated with the SP decreases in strength with increasing distance from the surface. At a plane surface, or at the surface of a cluster of atoms with radius large compared with the wavelength of light at the SP eigenfrequency, the field strength is expected to decrease exponentially with distance from the surface.

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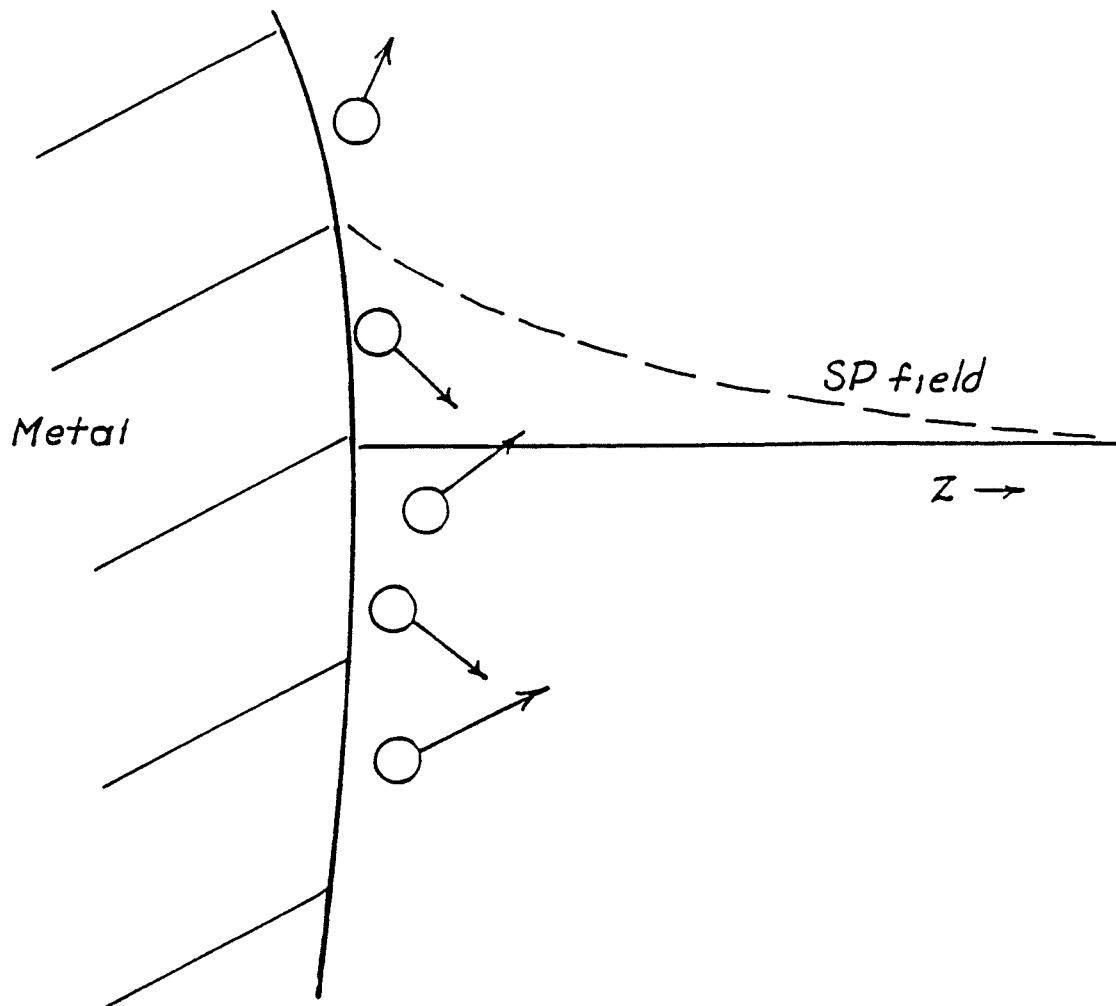


Figure 1. A schematic picture of a section of a metal surface, subjected to laser irradiation, that supports a surface plasma oscillation. The z axis is taken normal to the surface. The surface plasmon field decreases in strength with increasing distance from the surface and is indicated by a dashed line. Atoms and ions evaporating from the surface are shown as circles with quasi-randomly directed velocities. An ion may gain the energy of the surface plasmon under the influence of its electric field if a momentum-conserving collision with another ion or atom takes place.

The Feynman diagrams of Fig. 2 illustrate two different channels by which a photon annihilates through creation of a surface plasmon, followed by decay of the latter. In Fig. 2a the final product is an electron-hole pair, the electron of which goes to a final state of the solid or can be emitted into the vacuum. The diagonal dashed line represents the photon propagator, the wavy line that of the SP, and the solid line that of an electron. The double horizontal line depicts the interaction between the SP and the photon that can be mediated, e. g., by surface irregularities. The momentum necessary for this process is amply available through an interband transition of the electron or through thermal diffuse scattering on the phonon field of the solid. In Figs. 2b and 2c the final state is one in which an ion and an atom or another ion are emitted into the vacuum. The double lines represent ions or atoms that participate in the interaction and the single dashed horizontal line the interaction between them.

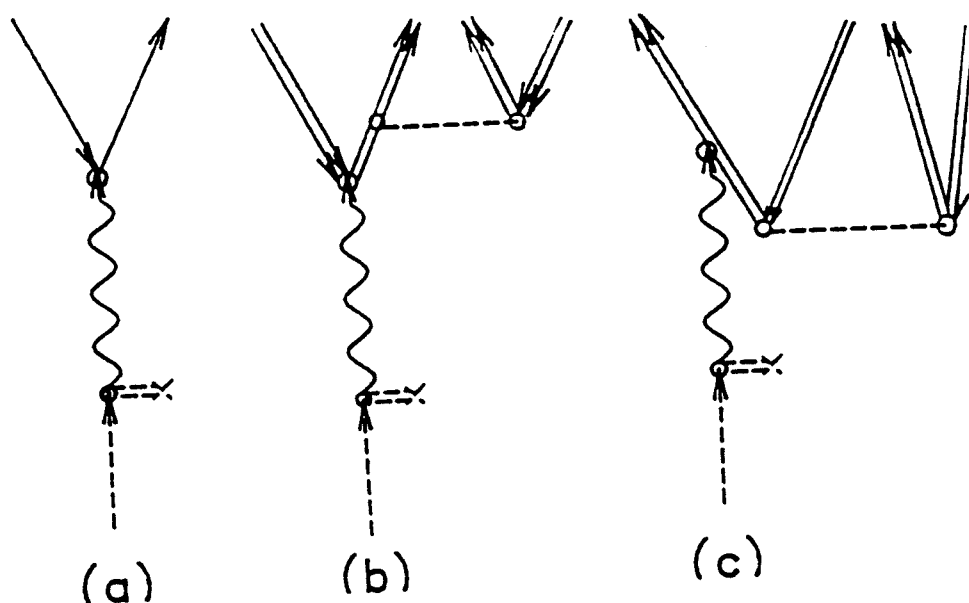


Figure 2. Open Feynman diagrams representing various processes by which a photon, shown as a diagonal dashed line, creates a surface plasmon, indicated by a wavy line, that decays into various final states. Conversion of the photon into a plasmon can be mediated by irregularities in the surface, indicated by the crosses. Figure 2a depicts decay of the surface plasmon into a single electron-hole pair. The solid line represents an electron if it is directed upward, denoting propagation forward in time. If directed downward, a solid line denotes a hole in the solid. Momentum is conserved between the plasmon and the electron-hole pair through collision of the electron with the lattice. Figure 2b shows plasmon decay through generation of an ion that takes the full plasmon energy by experiencing a momentum-conserving collision with another ion or an atom outside of the solid. The horizontal dashed line represents the instantaneous ion-atom or ion-ion interaction. Figure 2c shows the same final state but with time-reversed ordering of the plasmon-ion and the ion-atom interactions.

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We use a schematic model to estimate the probability of the processes shown in Figs. 2b and 2c. The coupling between the SP field and the ion is taken to be linear in the field coordinates and in the charge on the ion.

The second-order quantal decay rate of the SP due to ion emission is found to be

$$\gamma_{ion} = \frac{4}{3} \frac{e^2 p_f V_{p_f}^2}{\hbar^3 \omega_s^2} n^2. \quad (1)$$

In obtaining this result we have made a number of approximations. A full account of this theory will appear elsewhere.⁴ In this equation: (a) ω_s is the eigenfrequency of a surface plasmon, here taken to be dispersionless, (b) V_{p_f} is the momentum representation of the interaction potential for ion-atom scattering evaluated at the momentum $\hbar \vec{p}_f$ of an ion with the full SP energy, and (c) n is the density of ions or atoms in the neighborhood of the surface.

The probability that a surface plasmon will decay by giving its energy to an ion through the process under consideration, is given by the ratio of the rate calculated above

to the total decay rate γ_T of the SP due to all processes, viz., $P = \frac{\gamma_{ion}}{\gamma_T}$.

To make an estimate of n appropriate to the Shea-Compton experiment, we use the standard evaporation model.⁵ In this, the number of atoms ϕ_e evaporated from a solid surface per unit area per unit time is given in terms of p , the vapor pressure of the solid, M , the mass of the atoms evaporated, and their speed v . The relation is $\phi_e = \frac{fp}{Mv}$, where f is the fraction sticking to the surface upon striking it. The usual expression for p is $p = Ce^{-W/kT}$, where W is the binding energy of the atom in the solid, and C is a constant. Fitting experimental data⁶ we find $p = e^{20.4 - 2.86/kT}$, where p is in mm Hg and kT is in eV. To find the density of atoms in the neighborhood of the surface we divide ϕ_e by v

and convert to cgs units to obtain $n = \frac{1327.5f}{Mv^2} e^{20.4-2.86/kT}$. Taking the effective temperature of the surface to be 0.5 eV during the laser pulse and setting $f=1$, one finds $n=2.3 \times 10^{21}$ atoms/cm³.

Substituting into Eq. 1, using atomic units and employing a screened Coulombic form for the interaction potential, we find $\gamma_{ion} = 1.9 \times 10^{-7}$ a.u. If one takes $\gamma_T = 1.5 \times 10^{-2}$, then $P = 4.3 \times 10^{-2}$. This result depends sensitively on the value assumed for the effective temperature of the surface. Using $kT = 0.4$ eV one finds $P = 3.8 \times 10^{-3}$.

Shea and Compton estimate that a typical yield in their experiments is $\approx 10^{-8}$ ions/incident photon.¹ Dividing this value by our computed ratio of ion to total decay rate of the SP, we find that $\approx 10^{-5}$ surface plasmons are created per incident photon in the Shea-Compton experiments. This value is perhaps not unreasonable considering that scanning electron microscope pictures show that the structures on the Ag surfaces used by Shea and Compton¹ that are assumed to be responsible for absorption of photons into surface plasmon oscillations are, on the average, quite large compared with the photon wavelength and that they cover only a few percent of the surface. These surfaces are apparently quite different from those used in the experiments of Hoheisel, et al⁷, according to the analysis by Monreal and Appel.⁸

SUMMARY

Using quantal perturbation theory we have made an estimate of the probability of decay of a surface plasmon at an Ag surface through an inverse bremsstrahlung-type process. The decay is taken to be to a final state in which an Ag⁺ ion gains the energy of the surface plasmon and collides with an atom or another ion to conserve momentum. We argue that these results are consistent with observations that the emission of Ag⁺ ions in the laser irradiation of a roughened Ag surface is proportional to the third power of the intensity of the photon field and with the absolute emission probability measured by Shea and Compton.¹

The approximations used here limit our theory to prediction of the total number of ions in the SP peak. We plan to extend this work to account for the finite width of the Ag⁺ energy distribution; this will involve including damping of the SP and collisional and Doppler broadening of the ion peak, as well as representing the SP field more realistically.

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