# Surface-plasmon–ion interaction in laser ablation of ions from a surface

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(Received 15 March 1993)

Experimental work by Shea and Compton 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 as an inverse bremsstrahlung-type absorption of the SP quantum by an $Ag^+$ ion which undergoes a collision with the surface. We estimate the absorption probability and find it to be consistent with the Shea-Compton results.

Shea and Compton[1] have studied recently 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 $3\times10^7$ W/cm$^2$ with a pulse duration of 30 ps. The energy distribution consists of a peak at an ion energy of $\approx0.5$ eV, which they term the thermal peak, and a broader peak with a mean energy of $\approx3.5$ 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 surface plasmon (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 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.

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 $\approx1$ a.u., 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 the SP, an $Ag^+$ ion, and the surface participate in a three-body collision to yield an $Ag^+$ ion with the SP energy. 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.

A photon, incident from vacuum on a planar, ideal surface of a medium capable of supporting a surface plasmon, cannot create directly a quantum of the SP

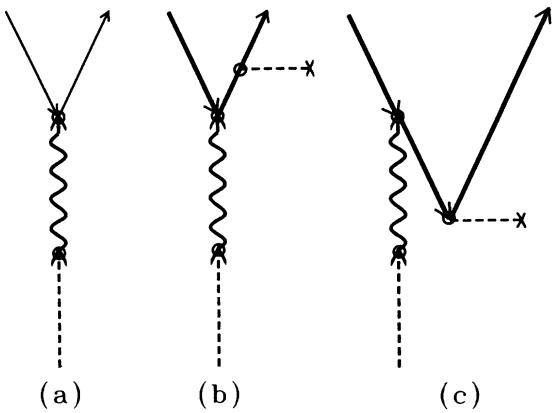


FIG. 1. Open Feynman diagrams representing various processes by which a photon, shown as a vertical dashed line, creates a surface plasmon, indicated by a wavy line, that decays into various final states. Conversion of the photon into a plasmon can be mediated by irregularities in the surface, indicated by the circles. (a) 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. (b) shows plasmon decay through generation of an ion that takes the full plasmon energy by experiencing a momentum-conserving collision with the solid. The horizontal dashed line represents the instantaneous ion-surface interaction. (c) shows the same final state but with time-reversed ordering of the plasmon-ion and the ion-surface interactions.

0163-1829/94/49(4)/2963(4)/$06.00  

field.[2] This is not allowed because the phase velocity of the SP at a vacuum-bounded surface is always less than $c$, 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, e.g., 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 a single $Ag^+$ ion with the SP energy.

The evanescent field associated with a surface plasmon decays away from the surface with an $e$-folding distance that may be as large as the wavelength of a photon with the SP energy. An $Ag^+$ ion in this vicinity can absorb this energy with reasonable probability if it collides with a third body. The ions are assumed to be emitted from the surface independently of the SP field and are taken as due to ordinary evaporation processes occurring in the transiently heated surface region.

The Feynman diagrams of Fig. 1 illustrate two different channels by which a photon can annihilate through creation of a surface plasmon, followed by decay of the latter. In Fig. 1(a), 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 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 the SP-electron conversion process is amply available through an interband transition of the electron or through thermal-diffuse scattering on the phonon field of the solid. Such decay processes give rise to damping of the SP, the extent of which is measured in standard optical determinations of the dielectric properties of the medium. In Figs. 1(b) and 1(c), the final state is one in which an ion is emitted into the vacuum following a collision with the surface. The heavy line represents the ion propagator and the single, dashed-horizontal line the interaction between the ion and the surface.

We use a schematic model to estimate the probability of the SP decay processes shown in Figs. 1(b) and 1(c). 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 SP field itself is approximated here by that appropriate for a plane surface; thus the Hamiltonian describing the SP-ion coupling is

$$H_{\text{SP-ion}}=Ze\sum_{\kappa}\alpha_{\kappa}e^{i\kappa\cdot\rho}e^{-\kappa z}(b_{\kappa}+b^{\dagger}_{-\kappa}) , \tag{1}$$

where $b_{\kappa}$ is an annihilation operator for a surface plasmon with wave vector $\kappa$ and $\alpha_{\kappa}^2=\pi e^2\hbar\omega_s^2/L^2\kappa\omega_{\kappa}$. The normalization area of the surface is $L^2$ and the eigenfrequency of a surface plasmon with wave vector $\kappa$ is $\omega_{\kappa}$, where $\omega_{\kappa}\Longrightarrow\omega_s$ as $\kappa\Longrightarrow 0$. The coordinate system is taken with the $z$ axis perpendicular to the surface and with the vector $\rho$ parallel to it. We employ a momentum eigenfunction basis set to represent the ions in our calculation. This should introduce little error into the final result, since the de Broglie wavelength of an ion with the SP energy is much less than the range of the SP field.

The second-order transition rate corresponding to the decay of the SP through the ion-excitation channel is given by

$$\gamma_{\text{ion}}=\frac{2\pi}{\hbar}\left|\sum_{\mathbf{p}_i}\frac{\langle\mathbf{p}_f|V(\mathbf{r})|\mathbf{p}_i\rangle\langle\mathbf{p}_i|H_{\text{SP-ion}}|\mathbf{p}_0,\kappa\rangle}{E_{\mathbf{p}_0}-E_{\mathbf{p}_i}+\hbar\omega_{\kappa}}+\sum_{\mathbf{p}_i}\frac{\langle\mathbf{p}_f|H_{\text{SP-ion}}|\mathbf{p}_i\rangle\langle\mathbf{p}_i|V(\mathbf{r})|\mathbf{p}_0\rangle}{E_{\mathbf{p}_0}-E_{\mathbf{p}_i}}\right|^2\times\delta(E_{\mathbf{p}_0}-E_{\mathbf{p}_f}+\hbar\omega_{\kappa}) , \tag{2}$$

where we assume that the atoms on the surface have very large effective masses compared with that of the ion. Then we write the matrix element of the ion-atom Hamiltonian as

$$\langle\mathbf{p}_f|V(\mathbf{r})|\mathbf{p}_0\rangle=\frac{V_{\mathbf{p}_{0f}}}{L^3} , \tag{3}$$

where $V_{\mathbf{p}}$ is the Fourier transform of $V(\mathbf{r})$, the ion-surface interaction potential, and $L$ is the length of the side of the normalization volume. The matrix element of the SP-ion interaction Hamiltonian is

$$\langle\mathbf{p}_i|H_{\text{SP-ion}}|\mathbf{p}_0,\kappa\rangle=\frac{\alpha_{\kappa}}{L}\frac{\delta^2(\mathbf{p}^{\parallel}_{0i}+\boldsymbol{\kappa})}{\kappa-ip^{\perp}_{0i}} , \tag{4}$$

where the superscript $(\parallel,\perp)$ represents the component of a vector (parallel, perpendicular) to the surface. After a little reduction one finds,

$$\gamma_{\text{ion}}=\frac{\alpha_{\kappa}^2}{2\pi\hbar L^6}\left|\int_{-\infty}^{\infty}\frac{dp_i^{\perp}V_{\mathbf{p}^{\parallel}_{0f}+\boldsymbol{\kappa},p^{\perp}_{if}}/(\kappa-ip^{\perp}_{0i})}{\frac{\hbar^2}{2M}(\mathbf{p}_0^{\parallel 2}+p_0^{\perp 2}-[\mathbf{p}_0^{\parallel}+\boldsymbol{\kappa}]^2-p_i^{\perp 2})+\hbar\omega_{\kappa}}+\int_{-\infty}^{\infty}\frac{dp_i^{\perp}V_{\mathbf{p}^{\parallel}_{0f}+\boldsymbol{\kappa},p^{\perp}_{0i}}/(\kappa-ip^{\perp}_{if})}{\frac{\hbar^2}{2M}(\mathbf{p}_f^{\parallel 2}-[\mathbf{p}_f^{\parallel}-\boldsymbol{\kappa}]^2+p_f^{\perp 2}-p_i^{\perp 2})-\hbar\omega_{\kappa}}\right|^2\times\delta(E_{\mathbf{p}_0}-E_{\mathbf{p}_f}+\hbar\omega_{\kappa}) , \tag{5}$$

where $M$ is the mass of the ion. The dominant contribution from the integral over $p_i^{\perp}$ is found by taking the residue at the pole at $p_i^{\perp}=p_0^{\perp}-i\kappa$ in the first integral and the residue at $p_i^{\perp}=p_f^{\perp}+i\kappa$ in the second integral.

With this approximation, one finds the result

$$\gamma_{\text{ion}}=\frac{2\pi\alpha_\kappa^2}{\hbar L^6}\left|\frac{V_{\mathbf{p}_{0f}^{\parallel}+\kappa,p_{0f}^{\perp}+i\kappa}}{E_{\mathbf{p}_0}-E_{\mathbf{p}_0^{\parallel}+\kappa,p_0^{\perp}+i\kappa}+\hbar\omega_\kappa}+\frac{V_{\mathbf{p}_{0f}^{\parallel}-\kappa,p_{0f}^{\perp}-i\kappa}}{E_{\mathbf{p}_f}-E_{\mathbf{p}_f^{\parallel}-\kappa,p_f^{\perp}-i\kappa}-\hbar\omega_\kappa}\right|^2$$

$$\times\delta(E_{\mathbf{p}_0}-E_{\mathbf{p}_f}+\hbar\omega_\kappa)\ . \tag{6}$$

It should be an excellent approximation to assume that $\hbar\kappa$ is small compared with the ion momentum. Then keeping only first powers of $\kappa$ in a Taylor expansion, taking $V_{\mathbf{p}}=V_p$ and averaging over all directions of $\mathbf{v}_{0f}$, we find

$$\gamma_{\text{ion}}=\frac{4\pi\alpha_\kappa^2\kappa^2}{3\hbar^3L^6\omega_\kappa^4}\sum_{\mathbf{p}_f}v_{0f}^2V_{p_{0f}}^2\delta(E_{\mathbf{p}_0}-E_{\mathbf{p}_f}+\hbar\omega_\kappa)\ . \tag{7}$$

Converting the sums to integrals and evaluating the integral over $p_f$ by using the $\delta$ function one finds

$$\gamma_{\text{ion}}=\frac{4}{3\pi}\frac{\kappa^2\alpha_\kappa^2p_f}{\hbar^4L^3\omega_\kappa^3}V_{p_f}^2\ . \tag{8}$$

In obtaining this expression it has been assumed that $v_i\ll v_f$. Where $v_f^2$ appears it has been replaced by $2\hbar\omega_\kappa/M$. We now have the damping rate per ion and for scattering on the surface. One now multiplies this rate by $n_IL^3$, where $n_I$ is the density of ions outside the surface. Ion-surface scattering will be represented as independent scattering on the surface layer of atoms, assuming that the latter have very large effective mass. Thus, we take $V_{p_f}^2=\tilde{V}_{p_f}^2\sigma L^2$, where $\tilde{V}$ is the effective scattering potential per surface atom and $\sigma$ is the surface density of scattering centers.

Then using the definition of $\alpha_\kappa$ given just below Eq. (1), the total damping rate of the surface plasmon due to ion emission is found to be

$$\gamma_{\text{ion}}^T=\frac{4}{3}\frac{\kappa e^2\omega_s^2p_f\tilde{V}_{p_f}^2}{\hbar^3\omega_\kappa^4}n_I\sigma\ . \tag{9}$$

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 $\gamma_T$ of the SP due to all processes, viz., $P=\gamma_{\text{ion}}^T/\gamma_T$.

To make an estimate of $n_I$ appropriate to the Shea-Compton experiment, we use the standard evaporation model.[4] In this, the number of atoms $\phi_e$ 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 $\phi_e=fp/Mv$, 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 data[5] 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 $\phi_e$ by $v$ and convert to cgs units to obtain $n_A=(1327.5f/Mv^2)e^{20.4-2.86/kT}$. Taking the effective temperature of the surface to be 0.5 eV during the laser pulse and setting $f=1$, one finds $n_A=2\times10^{21}$ atoms/cm$^3$. We take the ratio $n_I/n_A=\exp[-(\text{IP}-\phi_W)]/2$, where IP is the ionization potential of the Ag atom and $\phi_W$ is the electronic work function of the Ag surface. For the present purposes the values IP=7.6 eV and $\phi_W=3.5$ eV are used. We also average Eq. (10) over the spectrum of surface plasmons generated by the laser, taking $\langle\kappa\rangle\approx\omega_s/v_F\approx0.1$ a.u. and setting $\omega_\kappa\sim\omega_s$.

Substituting into Eq. (10) and using $\tilde{V}_p=4\pi Z^2e^2/(\alpha^2+p^2)$, where $\alpha$ is a screening constant that is negligible in the present application, since $p_f\approx229$ a.u., we find $\gamma_{\text{ion}}^T=8.2\times10^{-7}$ a.u. If one takes $\gamma_T=5.5\times10^{-3}$ a.u., then $P=1.5\times10^{-4}$. This result depends sensitively on the value assumed for the effective temperature of the surface. For example, using $kT=0.4$ eV one finds $P=5.8\times10^{-6}$.

Shea-Compton estimate that a typical yield in their experiments is $\approx10^{-8}$ ions per incident photon.[1] Dividing this value by our computed ratio of ion to total decay rate of the SP at $kT=0.5$ eV, we find that $\approx10^{-4}$ surface plasmons are created per incident photon in their 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 Compton[1] 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 al.*,[6] according to the analysis by Monreal and Apell.[7]

In summary, we have presented a quantitative model of the laser ablation of $Ag^+$ ions possessing the SP energy from a roughened Ag surface. The computed yields are consistent with observations and show a rapidly increasing dependence on laser intensity through the variation of the number of ions existing in the neighborhood of the surface at effective temperature $T$.

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 and the ion-surface interaction more realistically.

Thanks are due to Bob Compton and Mike Shea for many helpful conversations and suggestions during the course of this work. The authors are grateful to Eph Klots for much assistance in conversations about the thermodynamics of this system. This research was sponsored jointly by the Office of Health and Environmental Research, U.S. Department of Energy, under Contract No. DE-AC05-84OR21400 with Martin Marietta Energy Systems, Inc. J.R.M. would like to acknowledge support from the NSF through Grant No. DMR 9114015.

[1]M. J. Shea and R. N. Compton, Phys. Rev. B **47**, 9967 (1993); M. J. Shea, Ph.D. thesis, Vanderbilt University, 1991.

[2]See, e.g., R. H. Ritchie, Surf. Sci. **34**, 1 (1973).

[3]R. H. Ritchie, J. C. Ashley, and T. L. Ferrell, *Electromagnetic Surface Modes,* edited by A. D. Boardman (Wiley, New York, 1982), p. 119.

[4]H. S. W. Massey and E. H. S. Burhop, *Electronic and Ionic Impact Phenomena* (Oxford University Press, New York, 1952), p. 591.

[5]*Handbook of Chemistry and Physics,* 51st ed., edited by R. C. Weast (Chemical Rubber Company, Cleveland, 1970), p. D145.

[6]W. Hoheisel, K. Jungmann, M. Vollmer, R. Weidenauer, and F. Trager, Phys. Rev. Lett. **60**, 1649 (1988).

[7]R. Monreal and S. P. Apell, Phys. Rev. B **41**, 7852 (1990).