Theory of the multiphoton photoelectric effect: A stepwise excitation process

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A theory is presented for the multiphoton surface photoelectric effect based on an extension of the Sommerfeld model of a metal that takes into account energy and momentum relaxation. It is shown that the multiphoton photoelectric effect is a stepwise process and not a direct one, as has been assumed for the past 30 years. The theory predicts photoelectron current densities in agreement with experimental results, which are orders of magnitude larger than those predicted by previous theories.

The multiphoton surface photoelectric effect (MSPE) has been the subject of numerous theoretical papers in the past 30 years. Both perturbative[1,2] and nonperturbative[3–6] theories have been developed, which are based on the Sommerfeld model of a metal.[7] Although, in the case of the one-photon photoelectric effect these theories predict values for the photoelectron current density, which agree with the experimental ones,[8] in the case of the multiphoton effect, they predict current densities, which are several orders of magnitude smaller than the experimental values.[9,10] For example, in the case of four-photon electron emission ($\lambda = 1.06\ \mu$m) from a gold surface at 1 GW/cm^2 of laser intensity, the theoretical values for the current density obtained using the results of Refs. 2 and 3 are ten orders of magnitude smaller than the experimental value. The disagreement gets worse with increasing photon order and calls for a more realistic model to describe the process. In all the previous theoretical treatments the MSPE is treated as a direct multiphoton excitation process, and the effects of electron-phonon interaction are ignored. In this paper, we take into account the effect of electron-phonon coupling phenomenologically through the electron-phonon energy (inelastic collisions) and momentum (elastic and inelastic collisions) relaxation rates, $\gamma \sim 10^{11}$ sec^{-1} and $\Gamma/2 \sim 10^{15}$ sec^{-1}, respectively. The rapid dephasing of the bound electronic states makes the optical excitation process incoherent and stepwise, and as we will see, far more efficient than a direct multiphoton process. Since experiments with picosecond laser pulses show that, for laser intesities above a few GW/cm^2, thermionic emission becomes the dominant process,[8–10] we limit ourselves to lower laser intensities for which perturbation theory is adequate. The revised theoretical model predicts photoelectron current densities in qualitative agreement with recent experiments.

We begin with the familiar one-dimensional step potential, $V(z) = -V_0$, $z < 0$, and $V(z) = 0$, $z > 0$ (outside the metal), which is the standard model potential in theoretical studies of the MSPE (Refs. 1–6, and references therein). The unperturbed energy eigenstates of an electron in this potential are[2,5]

$$\phi(z) = \frac{1}{\sqrt{L_z}} \begin{cases} [e^{ik_z z} + re^{-ik_z z}], & z < 0 \\ (1+r)e^{iq_z z}, & z > 0, \end{cases} \tag{1}$$

where L_z is a normalization length, and k_z, $q_z = (k_z^2 - 2mV_0/\hbar^2)^{1/2}$ are the z components of the wave vector for the electron inside and outside the metal, respectively. The latter becomes purely imaginary ($q_z = iq_z''$) for negative electron energies. The parameter $r = (k_z - q_z)/(k_z + q_z)$ is the reflection coefficient. In the x-y plane, the electron is a free particle and its tranverse momentum cannot change from the interaction with the laser field. The effect of electron-phonon interaction is to broaden each bound state in the continuum for negative electron energies by $\hbar\Gamma$ and, thus, causing mixing of the states within this energy range. Therefore, we consider normalized mixed states,

$$\Phi_I(z) = \frac{1}{\sqrt{\mathcal{N}_I}} \sum_{i=1}^{\mathcal{N}_I} w_i^{1/2} \phi_i(z), \tag{2}$$

where $w_i = (\Gamma/2)^2/[\Delta\omega_i^2 + (\Gamma/2)^2]$ are Lorentzian weights, with $\Delta\omega_i$ being the frequency separation of the $|i\rangle$ state from the center frequency ω_I, $\mathcal{N}_I = \pi g(\omega_I)\Gamma/2$ is the effective number of states within a Lorentzian line shape of width Γ, and $g(\omega) = L_z m/2\pi\hbar k_z$ the one-dimensional density of states for each spin state. The excitation of an electron proceeds *resonantly* through such mixed states, and the z component of the electric dipole between two such states is

$$\mu_{IJ} \simeq \frac{\pi}{2} \sqrt{g(\omega_I) g(\omega_J)}\, \Gamma \overline{\mu}_{ij}, \tag{3}$$

where $\overline{\mu}_{ij}$ is the average dipole over the $\mathcal{N}_I\mathcal{N}_J$ pairs of unmixed states.

Consider a laser beam incident at a grazing angle ($\vartheta_i \sim 85°$) on a metallic surface with the electric field, $E(t) = \mathcal{E}e^{i\omega t}$+c.c., linearly polarized on the plane of incidence. The amplitude of the z component of the electric field at the surface is $\mathcal{E}_{z0} = (1+\varrho)\sin(\vartheta_i)\mathcal{E} \simeq 2\mathcal{E}$, where $\varrho \simeq 1$ is the amplitude reflection coefficient. Inside the metal the z component of the electric field is $\mathcal{E}_z = \epsilon^{-1}(\omega)\epsilon_0 \mathcal{E}_{z0} \exp(i\kappa_z' z + \kappa_z'' z)$, where $\kappa_z = \kappa_z' - i\kappa'' z = (\omega/c)[\epsilon(\omega)/\epsilon_0 - \sin^2\vartheta_i]^{1/2}$ is the propagation constant, and $\epsilon(\omega) = \epsilon_0[1 - \omega_p^2/\omega(\omega + i\zeta)]$ is the dielectric constant of a free-electron gas, with ω_p being the plasma frequency and ζ a damping constant. The equation of motion for the slowly varying part, $\sigma_{I,I+1}(t)$, of the off-

diagonal density matrix element $\rho_{I,I+1}(t) = \sigma_{I,I+1}(t)e^{i\omega t}$ is[11]

$$\left[\frac{d}{dt} + \Gamma\right] \sigma_{I,I+1} = \frac{i}{2}\Omega_{I,I+1}\left[\sigma_{I+1,I+1} - \sigma_{II}\right], \quad (4)$$

where $\sigma_{II} \equiv P_I$ is the fractional population of the electrons that have absorbed I photons, and on the right hand side, we have neglected higher order terms associated with coupling to other mixed states. The quantity $\Omega_{I,I+1} = 2\hbar^{-1}\mu_{I,I+1}\mathcal{E}_{z0}$ is the Rabi (interaction) frequency. In the rate approximation the time derivative in the equation above can be neglected, and we obtain $\sigma_{I,I+1} = i\Omega_{I,I+1}(P_{I+1} - P_I)/2\Gamma$. Using this relation, we obtain the following rate equations for the populations $P_I, I = 0, 1, \ldots, N-1$, in the case of the N-photon photoelectric effect:

$$\frac{d}{dt}P_0 = R_{01}(P_1 - P_0) + \gamma(P_1 + P_2 + \cdots + P_{N-1}), \quad (5)$$

$$\frac{d}{dt}P_I = R_{I-1,I}(P_{I-1} - P_I) + R_{I,I+1}(P_{I+1} - P_I) - \gamma P_I,$$

$$0 < I < N-1, \quad (6)$$

$$\frac{d}{dt}P_{N-1} = R_{N-2,N-1}(P_{N-2} - P_{N-1}) - (\gamma + \gamma_{\rm ph})P_{N-1}, \quad (7)$$

where $R_{I,I+1} = |\Omega_{I,I+1}|^2/2\Gamma$ is the rate for the $|I\rangle \leftrightarrow |I+1\rangle$ transition and $\gamma_{\rm ph}$ the one-photon photoemission rate from the last bound state in the excitation ladder, which is smaller than the electron-phonon energy relaxation γ. For simplicity, we have assumed that the excited populations decay to the initial state with the same rate γ. The rate equations above provide a strong field description of the dynamics of the electron populations in the excited states. In the weak field case $(P_1, P_2, \ldots, P_{N-1} \ll P_0 \simeq 1)$ and in the steady state approximation, the population of the $|N-1\rangle$ bound mixed state is given by

$$P_{N-1} = \frac{|\Omega_{01}|^2}{2\Gamma\gamma}\frac{|\Omega_{12}|^2}{2\Gamma\gamma}\cdots\frac{|\Omega_{N-2,N-1}|^2}{2\Gamma\gamma}. \quad (8)$$

Note that, for weak fields, the population depends only on the ratio Γ/γ of the relaxation rates, and not on their absolute values. The photoelectron current density in the presence of a radiation field is given by

$$\vec{J}(\vec{r},t) = \frac{ie\hbar}{2m}\sum_\ell p_\ell\left[\Psi_\ell\nabla\Psi_\ell^* - \Psi_\ell^*\nabla\Psi_\ell + \frac{i2e}{\hbar}\vec{A}|\Psi_\ell|^2\right], \quad (9)$$

where the sum is over the unmixed states that compose the state $|N-1\rangle$, $p_\ell = P_{N-1}w_\ell/\mathcal{N}_{N-1}$ is the probability for an electron to be in one of these states, $\vec{A}$ is the vector potential, and Ψ_ℓ the final state wave function in the continuum for positive electron energies (above threshold) resulting after one-photon absoption from an $|\ell\rangle$ state. Applying first order perturbation to one such $|\ell\rangle$ state, it can be shown that

$$\Psi_\ell(\vec{r},t) = \sum_f \frac{e^{i\vec{k}_\perp\cdot\vec{r}_\perp}}{\sqrt{L_xL_y}}\phi_f(z)e^{iN\omega t}\hbar^{-1} \times\mathcal{E}_{z0}^*\mu_{\ell f}2\pi\delta(\omega_f - N\omega), \quad (10)$$

where the sum is over the final states in the continuum of positive energy states, L_x, L_y are normalization lengths in the x-y plane, and $\vec{k}_\perp$ is the electron wave vector in that plane. Averaging Eq. (9) over an optical period the last term drops out, and the photoelectron current density evaluated at $z \to \infty$ becomes

$$\vec{J}(k_i,\theta_i) = \frac{e\hbar}{m}P_{N-1}\frac{|1+r|^2}{V}4\pi^2|\hbar^{-1}\bar{\mu}_{\ell f}\mathcal{E}_{z0}^*g(\omega_f)|^2 \times[\vec{k}_\perp + q_{zf}\hat{z}]\Big|_{\omega_f = N\omega}, \quad (11)$$

where k_i, θ_i are the initial electron wave number and angle from the z axis, respectively, and V the normalization volume. The total N-photon photoelectron current density is found by integrating the magnitude of $\vec{J}(k_i,\theta_i)$ over the Fermi sphere,

$$J_t = \frac{V}{4\pi^3}\int d\Omega\int J(k_i,\theta_i)P_{\rm FD}(k_i)k_i^2dk_i, \quad (12)$$

where $P_{\rm FD}$ is the Fermi-Dirac distribution and the two spin states are taken into account.

Calculations have been carried out for the cases of one-, two-, and four-photon photoelectric effect on a gold surface at wavelengths $\lambda = 248$, 496, and 992 nm, respectively, chosen so that the photoelectrons have the same energy in the three cases. The parameters which have been used for gold are Fermi energy = 5.51 eV, V_0 = 10.19 eV (work function = 4.68 eV),[8,9] $\omega_p = 1.37\times10^{16}$ rad/sec, and $\zeta = 5.5\times10^{15}$ sec^{-1}. The value for ζ was determined by matching the dielectric constant for a free-electron gas with damping to the experimental value for the complex index of refraction of gold,[12] $n = 1.22+i1.49$, at $\lambda = 248$ nm. For the electron-phonon energy relaxation rate in gold, we have used the experimental value[13] $\gamma \simeq 3\times10^{11}$ sec^{-1}, while the ratio Γ/γ was taken equal to 3×10^4. The temperature in the Fermi-Dirac distribution was set equal to 300 K. Figure 1 shows the theoretical dependence of the total current density on the laser intensity I, in the range between 10^8 and 4×10^9 W/cm^2. For these and lower laser intensities, this dependence is a power law, $J_t \propto I^N$, as expected from perturbation theory. The theoretical result from these calculations is that for laser intensities around a few GW/cm^2, the photoelectron current densities for the MSPE become comparable to that for the one-photon effect and of the order of 1 kA/cm^2, in agreement with recent experiments on the one- and four-photon effects.[8-10] Comparing Fig. 1 with Fig. 2 of Ref. 10, we see that there is qualitative agreement between theory and experiment. For the one-photon effect at $\lambda = 248$ nm, the theoretical value is a factor of 3 larger than the experimental one. This

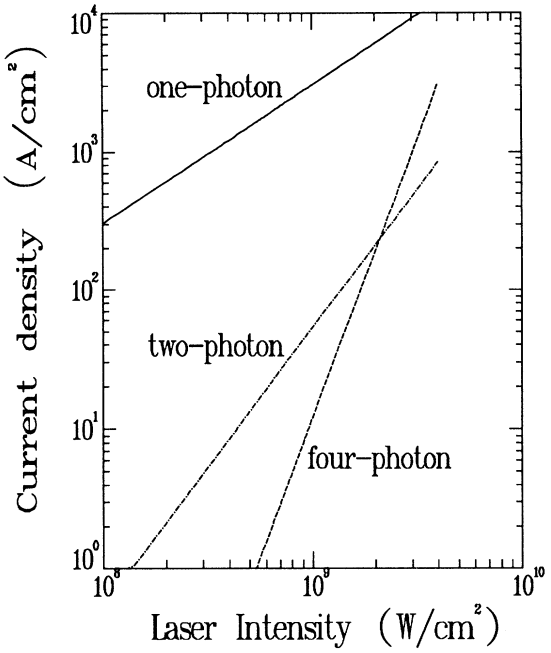

FIG. 1. Photoelectron current density versus laser intensity for the one-photon (solid line), two-photon (dot-dash line), and four-photon (dashed line) photoelectric effect on a gold surface.

can be explained by the fact that after excitation the electrons must travel to the surface, and because of collisions, not all of them escape. The present as well as previous theories[1–6] of the MSPE do not account for this decrease in the current density. At 1 GW/cm^2, the current density for the four-photon effect is lower than that for the one-photon effect by one order of magnitude according to the experiment,[10] by two orders according to our theory, and by ten orders of magnitude according to previous theories.[1–6] The much weaker cross section for the MSPE predicted by previous theories is due to the destructive interference between the different channels in the assumed coherent excitation process. However, the excitation process cannot possibly be coherent in the presence of electron-phonon collisions with momentum relaxation rates of the order of 10^{15} sec^{-1}. The present theoretical model can be improved by taking into account numerically the potential of the image charge, which changes the total potential outside the metal from an abrupt step to a rounded step. Since the electronic wave functions for bound states will extend further outside the metal surface, the effect of the image potential will be to increase the dipole matrix elements for bound-bound transitions and, hence, to enhance the multiphoton photoelectric current density. For example, in the case of the four-photon photoelectric effect, an assumed 30% increase in the bound-bound dipole matrix elements, owing to the image potential, will enhance the current density by about a factor of $1.3^6 \simeq 5$. The exact effect of the potential of the image charge and also of nonabrupt potential models for the surface potential on the MSPE will be investigated numerically in future work.

It should be pointed out that for laser intensities of a few GW/cm^2, there is no evidence of breakdown of perturbation theory, neither from the rate equations (5)–(7) nor the experiments.[8–10] The rate equations predict populations for the excited states that are still smaller than that of the ground state. The slope of the experimental log-log curves for the current vs laser intensity is that predicted by perturbation theory. Note that the larger than unity slope of the experimental log-log curve for the one-photon current density with 500 fs laser pulses, seen in Fig. 2 of Ref. 10 at the highest laser intesity, is due to temperature effects arising from one-photon absorption by electrons as deep as $\hbar\omega$ below the Fermi energy, which do not exceed the threshold for one-photon electron emission. *The point is that even for grazing angles of incidence of the laser beam (minimum absorption) temperature effects set in before purely high intensity effects, such as above threshold electron emission,[6] become important.* At higher laser intensities, when the mutiphoton photoelectron current densities become equal and larger than the one-photon current density, saturation of the bound-bound continuum-continuum transitions takes place. However, this effect will be masked by the expansion of the interaction area on the metal surface (for realistic laser beams with radially dependent intensity) and especially by thermionic emission, which becomes the dominant process at these intensities.[8–10]

The study of dissipative optical processes such as one-, two-, and three-photon absoption from bound-bound transitions, which are responsible for the heating up of the metal, as well as of coherent optical processes such as harmonic generation will be presented elsewhere. The Sommerfeld model of a metal extended to account for energy and momentum relaxation will prove to be as useful in the study of laser-surface interaction as the two-level model of an atom has been in the study of such fundamental optical processes as resonance fluorescence, self-induced transparency, and photon echoes.

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