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Effects of electron relaxation on multiple harmonic generation from metal surfaces with femtosecond laser pulses

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Abstract

Calculations are presented for the first four (odd and even) harmonics of an 800 nm laser from a gold surface, with pulse widths ranging from 100 down to 14 fs. For peak laser intensities above 1 GW/cm^2 the harmonics are enhanced because of a partial depletion of the initial electron states. At 10^{11} W/cm^2 of peak laser intensity the calculated conversion efficiency for 2nd-harmonic generation is 3×10^{-9}, while for the 5th-harmonic it is 10^{-10}. The generated harmonic pulses are broadened and delayed relative to the laser pulse because of the finite relaxation times of the excited electronic states. The finite electron relaxation times cause also the broadening of the autocorrelations of the laser pulses obtained from surface harmonic generation by two time-delayed identical pulses. Comparison with recent experimental results shows that the response time of an autocorrelator using nonlinear optical processes in a gold surface is shorter than the electron relaxation times. This seems to indicate that for laser pulses shorter than ~30 fs, the fast nonresonant channel for multiphoton excitation via continuum-continuum transitions in metals becomes important as the resonant channel becomes slow (relative to the laser pulse) and less efficient.

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1. Introduction

In a recent paper [1], we presented a theoretical model using the density matrix formalism to describe multiple harmonic generation (MHG) from a metal surface for laser intensities below the critical value for plasma formation. The metal is treated in the jellium approximation and a smooth model surface potential with the proper Coulombic fall-off is used. Calculations were presented for the case of relatively long laser pulses (290 fs and 35 ps), that had been used in two different experiments on a gold surface [2,3]. Very good agreement was obtained with the experimental results in the case of the 290 fs laser pulses, where thermal effects are not as important as in the 35 ps case. The pulse durations used in these experiments are much longer than the electron relaxation times in gold, which are known to be about 30 fs at 1 eV above the Fermi energy and even faster at higher energies. Second and third-harmonic generation from metal surfaces have been proposed and used for the characterization of 100 fs [4] and 18 fs [5] Ti:sapphire laser pulses by measuring their 2nd- and 3rd-order autocorrelation. One of the advantages in using a metal surface instead of a nonlinear optical crystal is that in the former case one can measure both the 2nd- and the 3rd-order autocorrelation of a laser pulse, and thus obtain a better characterization of it. A second advantage is that, due to the only one skin-depth (~200 Å) effective thickness of the nonlinear surface layer, there are no phase matching problems [1]. In contrast, in the case of nonlinear crystals that are at least a few tens of microns thick, the phase matching condition must be satisfied over the whole

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spectral range of a femtosecond pulse. Moreover, the group velocity-mismatch between the fundamental and 2nd-harmonic in the nonlinear crystal can distort the autocorrelation by lengthening its wings [6]. On the other hand, autocorrelation measurements using surface harmonic generation from a metal surface are expected to be limited by the finite electron relaxation time. Indeed, there is experimental evidence for this in a related recent paper, where the 3rd-order autocorrelation of a 9.5 fs pulse from a Ti:sapphire laser was obtained by measuring the three-photon photocurrent from a gold surface [7]. The interferometric autocorrelation curve exhibits a ~25 fs lengthening in both wings, that is apparently due to the relatively long relaxation time of the one-photon excited electron state. In another experiment with 14 and 29 fs pulses from a Ti:sapphire laser, the dependence of the energy of the generated 2nd-harmonic pulses from a gold surface on the peak laser intensity was investigated [8]. The shape and phase variation of such short femtosecond harmonic pulses cannot be measured directly, and this is one more reason to investigate what the theory predicts about them.

The purpose of this paper is to present calculations on MHG from a gold surface for laser pulse widths in the 100–14 fs range, and to compare them with recent experimental results. In particular, we examine the role of the finite electron relaxation times on MHG and their effect on applications such as measuring the autocorrelations of femtosecond laser pulses.

2. Numerical calculations and discussion

As shown in Ref. [1], the intensity of the coherent component of the reflected Nth harmonic in the case of parallel polarization for the incident laser field is given by

$$I_{N\omega}(t) = 2c\epsilon_0 \frac{(N\omega)^2|F|^2}{(c\epsilon_0)^2} |\langle \hat{\mathscr{P}}_{\mathrm{Nsz}}(t)\rangle|^2, \tag{1}$$

where $F = \sin\vartheta_i/(n_{N\omega}^2\cos\vartheta_i + n_{N\omega}\cos\vartheta_{Nt})$ is a Fresnel coefficient for the Nth harmonic, with $n_{N\omega}$ being the index of refraction of the metal at $N\omega$, and ϑ_{Nt} the angle of refraction for the Nth harmonic field that is transmitted into the metal. The expectation value of the normal to the surface nonlinear surface polarization, $\langle\hat{\mathscr{P}}_{\mathrm{Nsz}}(t)\rangle$, at the Nth harmonic is

$$\begin{aligned}\langle\hat{\mathscr{P}}_{\mathrm{Nsz}}(t)\rangle = {} & \frac{\mathrm{e}}{\mathrm{i}N\omega m}\frac{d}{4\pi^3}\int\int [p_{z,N0}\sigma_{0N}(t) - \mathrm{e}\mathscr{A}(t)\sigma_{0,N-1}(t)]_{\kappa_i,\Omega_i} \\ & \times P(E_i,t)[1-P(E_i,t)][1-P(E_i+\hbar\omega,t)]\cdots \\ & [1-P(E_i+N\hbar\omega,t)]\kappa_i^2\,\mathrm{d}\kappa_i\,\mathrm{d}\Omega_{\kappa_i},\end{aligned} \tag{2}$$

where d is the skin depth of the metal, $p_{z,N0} \equiv \langle N|p_z|0\rangle$ a matrix element of the z-component the electron momentum, $\sigma_{0N}(t)$ the slowly varying part of the off-diagonal density matrix element corresponding to N-photon excitation, and $\mathscr{A}(t)$ the slowly varying complex amplitude of the component of the vector potential normal to the metal surface. The integration is over the Fermi sphere, with E_i, κ_i, and Ω_i being the initial electron energy, wave number, and solid angle, respectively. Note that the first term in the factor $[p_{z,N0}\sigma_{0N}(t) - \mathrm{e}\mathscr{A}(t)\sigma_{0,N-1}(t)]$ inside the integral is associated with harmonic generation following N-photon excitation, while the second term is associated with inelastic scattering of a laser photon from the $(N-1)$-photon excited electron state. $P(E_i,t)$ is the probability that the energy level at E_i is occupied at time t, while $[1-P(E_i+n\hbar\omega,t)]$, $n=0,1,2,\ldots$, is the probability that the energy level at $E_i+n\hbar\omega$ is not occupied. Unlike Ref. [1], where $P(E_i,t)$ is taken to be equal to the Fermi–Dirac distribution, $P_{\mathrm{FD}}(E_i)$, for conduction electrons in thermal equilibrium at 300 K, in this work $P(E_i,t)$ is a non-equilibrium distribution for electrons under multiphoton laser excitation which is calculated numerically. For times much shorter than the electron gas thermalization time (~500 fs), one can show, based on the conservation of the number of electrons, that this non-equilibrium probability distribution is given by

$$P(E_i+n\hbar\omega,t) = \frac{P_{\mathrm{FD}}(E_i)}{N_i}\sum_{j=1}^{N_i}\sqrt{\frac{E_i}{E_i+n\hbar\omega}}\,\sigma_{nn,j}(t), \tag{3}$$

where N_i is the number of representative electrons in the ith energy bin of the initial distribution at $t=0$, and $\sigma_{nn,j}(t)$, with $n=0,1,2,\ldots$, are the diagonal density matrix elements for the jth electron. In obtaining the above expression we have assumed the usual density of states (DOS) for a free electron gas, $D(E) = (2m/\hbar^2)^{3/2}/(2\pi^2)\sqrt{E}$. Note that at time $t=0$, when all the electrons are unexcited, i.e., $\sigma_{nn,j}(0) = \delta_{n0}$, the equation above reduces to $P(E_i,0) = P_{\mathrm{FD}}(E_i)$. For other details of the theoretical model the reader is referred to Ref. [1].

For the calculations presented in this paper we have used the same parameters for modeling a gold surface as in Ref. [1], except if stated otherwise. In particular, for the Drude relaxation rate for multiphoton excitation we use the same relation as in our previous work, $\Gamma_{\mathrm{D}}(j\omega) = [0.3 + 0.01(j\hbar\omega)^2]\times 10^{14}\ \mathrm{s}^{-1}$, where j is the number of photons absorbed and the photon energy is in eV. This empirical formula was obtained by fitting our theoretical values to the experimental values for 2nd- and 3rd-harmonic generation with 290 fs laser pulses in Ref. [2]. The relaxation rate of the ij off-diagonal density matrix element is $\frac{1}{2}\Gamma_{ij} = \frac{1}{2}(\gamma_i^{\mathrm{ee}} + \gamma_j^{\mathrm{ee}}) + \Gamma_{\mathrm{D}}(j\omega)$ with $j > i$, where γ_i^{ee} is the electron-emission rate from the i-photon excited electron state. The relaxation times for the off-diagonal density matrix elements vary from about 30 fs at 1 eV, to 7 fs at 6 eV above the Fermi energy. For the non-radiative decay rates of the diagonal density matrix elements in this paper we use the relation $\gamma_j^{\mathrm{nr}} = \Gamma_{\mathrm{D}}(j\omega)$, which gives good agreement between the value predicted by our theoretical model and the recently measured 60 mA/cm^2 four-photon photoelectron current density from 200 nm thick gold films with 50-fs Ti:sapphire laser pulses of 1 GW/cm^2 peak intensity [9].

Fig. 1 shows the change in the number of electrons per unit energy, $\Delta(\mathrm{d}N/\mathrm{d}E) = D(E)[P(E,t) - P_{\mathrm{FD}}(E)]V$, where