Nonadiabatic nano-optical tunneling of photoelectrons in plasmonic near-fields

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ABSTRACT

Our work demonstrates nonadiabatic tunneling of photoelectrons in the near-field of gold nanostructures, which occurs in the transition region between the multi-photon-induced photoemission and tunneling emission regimes. Measured kinetic energy spectra at higher laser intensities indicates strong-field electron acceleration and recollision, characteristic for the tunneling emission regime. At the same time, constant scaling of the photoelectron current with the intensity has been measured, a trait of the multi-photon-induced photoemission regime. The Keldysh value of $\gamma \approx 2$ for the transition was determined by analyzing the measured photoemission spectra. This value is in good agreement with the results acquired by the numerical solution of the Time-Dependent Schrödinger Equation.

Keywords: nonadiabatic tunneling, photoemission, plasmonics

1. INTRODUCTION

Contemporary experiments in atomic and molecular physics1-4 and also nano-optics5,6 are conducted in the intensity range between two extremes considering the Keldysh scale parameter $\gamma$: the multi-photon-induced photoemission [MPE] ($\gamma \gg 1$) and the adiabatic tunneling emission [TE] ($\gamma \ll 1$). The $\gamma$ parameter indicates the dominant electron emission process in moderate (MPE) and strong (TE) laser fields. However, systematic experimental research highlighting the nature of this transition itself is missing. There are a few works where one can follow some sort of evolution of the electron emission and rescattering process as the Keldysh parameter is tuned, but either the tuning is implicit and hence not transparent8, or it is explicit but it is confined to a region where only one emission process dominates9,10. The question naturally arises on what happens in the transition region around $\gamma \sim 1$. In this work, we aim to identify the Keldysh value for the onset of tunneling. Previous experimental and theoretical works by other groups11-13 put this onset on a relatively broad intensity range of $0.9 < \gamma < 2.7$.

Here, we demonstrate photoemission between the regimes of multi-photon-induced photoemission and the nonadiabatic tunneling of electrons at the surface of gold nanoparticles. We answer both the question on the stretch of this transition regime and the physical processes taking place there. To accomplish this, we exploit plasmonic methods enabling nanometer-scale field localization and enhancement14,15 as well as near-field probing at the same time16-18. We will show that in the transition region, tunneling/rescattering of electrons take place at the same time when the electron current depends on the photocurrent in a manner that is characteristic for multiphoton-induced emission.

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2. THEORETICAL CALCULATIONS AND RESULTS

It is known of photoionization processes in atomic physics that in the strong-field regime, where tunneling electron emission sets in, photoelectrons are accelerated in a quasi-classical manner in the laser field, and after rescattering from the parent ion, they can acquire a maximum kinetic energy which is roughly ten times the ponderomotive potential \( U_0 \) of the laser field, i.e., the average kinetic energy of a free electron moved by the field of the laser. After small quantum mechanical corrections, the corresponding simple formula for the measurable maximum electron kinetic energy was given by \( E_{\text{cutoff}} = 10U_0 + 0.54I_p \) (see Refs. [19,20]), which is generally considered valid for laser-atom interactions with the ionization potential \( I_p \). At this point, it needs to be validated whether a similar simple relationship can be used in case of photoemission from metals by replacing the \( I_p \) value with the work function, \( W \). For this, we constructed a quantum mechanical model and determined the scaling law that can be applied for our case, i.e., photoemission into plasmonic near-fields. Within our model, we solved numerically the 1D time-dependent Schrödinger equation (TDSE)

\[
i\hbar \frac{\partial \Psi(z,t)}{\partial t} = \left[ \hat{\mathbf{T}} + \hat{V}(z) + \hat{V}_{\text{loc}}(z,t) \right] \Psi(z,t)
\]

by employing a mixed split-operator and Crank-Nicolson approach [21], where for the length-gauge form \( V_{\text{loc}}(z,t) = zE_{\text{loc}}(z,t) \) electron-laser interaction term we have also included a \( Q(z) \) field enhancement factor, i.e., \( E_{\text{loc}} = E_0(t)Q(z) \). Here \( Q(z) \) was a decreasing function and was obtained by fitting an exponential curve after taking into account the average field enhancement values acquired beforehand by finite-difference time-domain (FDTD) and electromagnetic simulations [22]. The incident fields considered for the simulation were Gaussian pulses centered at 800 nm with pulse durations of \( \tau = 5.3 \) fs at full-width at half-maximum (FWHM) intensity. Here, the \( \Psi(=\Psi(z;t=0)) \) initial wavefunction (WF) of the electron, located on the Fermi-level in the bulk and described by the \( V(z) = -\exp(-\beta(z+|z|)) [2(z+|z|) + 1/(E_F + W)] \) potential, was obtained by diagonalizing the field-free \( H_0 = T + V \) Hamiltonian matrix represented on a finite difference grid. The parameter \( \beta \) in the local potential represents the screening constant, that describes the 'shielding-effect' of the bulk electrons on the active electron, and whose value was set to 0.6, yielding good agreement with experimental data [19].
Fig. 1(a) shows the photoelectron spectra (projections of the photoemission WF onto continuum plane wave states) calculated after the passage of the laser pulse for different $I_0$ peak field intensities. As one can observe, a clearly distinguishable plateau feature started to appear from $I_0 \geq 0.12$ TW/cm$^2$. By introducing the concept of the local Keldysh parameter $\gamma_{\text{loc}}$, which is defined by using the maximum of the plasmonically enhanced local field on the nanoparticle’s surface ($z=0$), i.e., $\gamma_{\text{loc}}= \omega(2W)^{1/2}/E_{\text{loc,max}}$, with $E_{\text{loc,max}} = E_0 Q$ ($z=0$), one can observe in Fig. 1 that the aforementioned intensity values correspond to $\gamma_{\text{loc}} \leq 1.8$. For the higher energy part (the plateau and the roll-off region) of these spectra, we fitted a four-parameter model function $f_{\text{mod}}(x) = c-a(x-b)[1-\exp(-d(x-b))]^{-1}$, which, in the limiting case $\lim_{x \to +\infty}(f_{\text{mod}})$ asymptotes, as the photoelectron cutoff energy: $E_{\text{cutoff}} = b$. In Fig. 1(b) we show the obtained cutoff energy values as a function of different peak intensities. By fitting, we determined the scaling

$$E_{\text{cutoff}} = 10U_p + 0.43W$$

(2)

It is worth noting here that the last quantum mechanical correction term was found to be only slightly different from the 0.54W value obtained for atomic targets$^{20}$. This way, we proved the universal applicability of the $10U_p$ scaling. In addition, we also calculated the final total ionization probability as a function of $I_0$ (red circles in Fig. 1(b)) and a transition from multiphoton to strong-field regime could be clearly identified starting from the local Keldysh parameter of $\gamma_{\text{loc}} \leq 1.4$. Also, by considering that the plateau feature started to appear in the spectra from $\gamma_{\text{loc}} \leq 2$, we showed that the transition between the two regimes starts within the region of $\gamma_{\text{loc}} \in [1.4, 2]$, providing a reliable estimate and initial answer to one of our fundamental research questions.

3. EXPERIMENTAL METHODS AND FINDINGS

After having a verified simple scaling law at hand (Eq. (2)), we could study how photoemission from different plasmonic nanoparticles takes place in electromagnetic hot spots of our sample. We used laser pulses with octave-spanning bandwidth that were generated by a commercial Ti:sapphire laser oscillator (Venteon Pulse One) at a repetition rate of 80 MHz. The pulses were compressed to ~10.7 fs duration by a combination of chirped mirrors (Layertec 103366), a pair of fused silica wedges and plane-parallel fused silica slabs. Characterization of the pulse duration was performed using interferometric FROG (IFROG) and d-scan techniques. The sample was housed in a high-vacuum chamber (base pressure: <10$^{-7}$ mbar) and was positioned with nm accuracy in all three dimensions using stacked piezostages (Attocube ECS 3030). Electrons emitted from the surface of the nanostructures entered a hemispherical energy analyzer (SPECS Phoibos 100 R7).

During the measurements, a series of spectra were collected at different incident laser intensities. At low laser intensities, the spectra show a narrow low-energy peak and an exponential ‘tail’ at higher electron kinetic energies (a straight line on a semilogarithmic graph, see Fig. 2(b)). These correspond to direct electrons (i.e. those that are accelerated, but not rescattered in the local fields). As the laser intensity is increased, the spectra develop a distinct plateau-like feature at higher electron kinetic energies, in accordance with our simulation results. This signals the appearance of electrons that are accelerated, but not rescattered in the local fields. We analyze this portion of the electron energy distributions to determine the strength of the local fields with the method presented in Refs. $^{17,18}$. At each laser intensity, the electron cutoff kinetic energy was determined from the associated spectrum.

Fig. 2 shows the overview of the results. In figure 2(a) we show SEM images of the nanotriangles used in the experiment (for designations, see Table 1; the incident laser field is polarized horizontally, along the scale bar). The photoelectron yield vs incident laser intensity (bottom axis) is plotted on a double logarithmic scale in figure 2(d). In the same panels, the local Keldysh parameter ($\gamma_{\text{loc}}$) is indicated (top axis). Linear fit (red solid line) to the raw data (black circles) show slopes between 2.9 and 3.6, indicative of photoelectron emission due to absorption of 3-4 photons from the incident laser field. These are reasonable numbers given that our laser spectrum spans from 630 nm to 1100 nm with a central wavelength of 803 nm (corresponding to 1.54 eV photons) and the nominal value of 5.3 eV for the work function. These are also in accordance with results of our simulations (see Fig. 1(b)).
The shape of the photoemission spectra for increasing laser intensities are shown in Fig. 2(b). For the lowest incident intensities, spectra consist of a low-energy peak and an exponential fall-off (straight line on the semi-logarithmic plot, hence the spectra are ‘triangle-shaped’). Such spectra are well-known to be observed under conditions $\gamma_{\text{loc}} \gg 1$, i.e. in the multi-photon regime. Upon increasing the laser intensity, a plateau feature gradually appears, giving evidence of the appearance of rescattering electrons with substantially increased kinetic energy. The plateau/cutoff feature enables the determination of the field enhancement, for which the resulting value $9.4 \pm 0.6$ is in excellent agreement with the calculated field enhancement value $8.3 \pm 2.2$. This correspondence confirms the existence of rescattering electrons. The magnitude of the local field and the local Keldysh parameter can be calculated from the field enhancement value. Furthermore earlier work also suggests that in case the quiver amplitude of the electrons is much smaller than the local field decay length (i.e. the adiabacity parameter $\delta > 1$), then the appearance of the plateau electrons signifies that the Keldysh parameter is $\gamma_{\text{loc}} < 1$, i.e. tunneling starts to play an important role in the ionization process.

The appearance of the plateau is observed at Keldysh parameter values of about 2. This is in very good agreement with our theoretical results in Fig. 1, showing the appearance of $10U_p$ electrons for $\gamma_{\text{loc}} < 2.2$, representing the onset of strong-field effects. However, at the same time, for $1.35 < \gamma_{\text{loc}} < 2.2$ in the nanoplasmonic near-field, the power-law scaling of the photocurrent with laser intensity also holds true with a constant exponent. Thus, strong-field electron acceleration features and multiphoton scaling laws are present at the same time in this transition region which can be termed as the nonadiabatic tunneling regime. Thus, our work highlights the importance of considering the spectral signatures of the rescattered electrons, in addition to the dependence of the emitted yield on peak intensity.
4. SUMMARY

In summary, we demonstrated nonadiabatic tunneling photoemission in few-cycle near-fields in the vicinity plasmonic nanostructures. By doing so, we pointed out the regime where multiphoton emission scaling laws and strong-field electrons are present at the same time. By analyzing these electron spectra and determining plasmonic field enhancement with spectral cutoffs, we could show the presence of ponderomotively accelerated electrons in this nonadiabatic region which is perfectly characterized by multiphoton emission scaling laws. Nonadiabatic tunneling photoemission takes place for Keldysh-gamma values between ~1.3 and ~2.2. With these experiments and the corresponding support theory, we answered the question of which is the characteristic intensity region where both multi-photon and strong-field emission features are present and what are the typical emission mechanisms in this transition region. For the latter, we showed that measurable rescattering of the electrons can take place even when the emission is perfectly characterized by multi-photon scaling laws.

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