PHYSICAL REVIEW A **79**, 030901(R) (2009)

Ultrafast studies of electronic processes at surfaces using the laser-assisted photoelectric effect with long-wavelength dressing light

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(Received 22 December 2008; published 30 March 2009)

We show that ultrafast surface science studies using the laser-assisted photoelectric effect can benefit from longer-wavelength infrared dressing beams. We compare soft-x-ray photoemission from a Pt(111) surface dressed by 1300 and 780 nm light. Using 1300 nm light, the amplitude of the laser-assisted photoelectric signal is enhanced sevenfold compared with 780 nm. This allows lower dressing laser intensity to be used, which dramatically suppresses undesirable processes such as above-threshold photoemission, desorption, and distortion of the photoemission spectrum due to space charge. This work enables ultrafast studies of surface-adsorbate systems and attosecond electron dynamics over a wider energy range.

DOI: 10.1103/PhysRevA.79.030901 PACS number(s): 42.50.Hz, 42.65.Ky, 42.65.Re, 79.60.−i

Atomic and molecular dynamics at surfaces is a topic important to many processes of both practical and fundamental interest, including catalytic chemical reactions [1], the development of photocathodes for detectors and accelerator electron sources [2,3], and fundamental explorations of image potential states on surfaces [4,5]. In many of these processes, nuclear and electronic dynamics are coupled: thus the relevant time scales span from picoseconds to attoseconds. The ability to generate extremely short duration light pulses using high-order harmonic generation now makes it possible to observe even the fastest surface dynamics. Different experimental methodologies have also played a key role in this work. In particular, the development of laser-assisted photoemission (LAPE) and laser-assisted Auger decay (LAAD) has made it possible to study high-energy electronic processes where the dynamics are particularly fast.

First explored in the case of atomic photoionization [6,7], LAAD and LAPE have been used to characterize soft-x-ray (xuv) pulses [8,9] and to measure atomic core-hole lifetimes in free atoms [10]. In previous work, we reported the observation of the laser-assisted photoelectric effect in solid-state systems [11]. LAPE from surfaces has since been successfully combined with attosecond soft-x-ray pulses [12] and with femtosecond xuv pulses from the FLASH free-electron laser [13]. This discovery has opened up possibilities for studying ultrafast electron dynamics in solids and surface-adsorbate systems. Recently, we reported direct time-resolved observation of core-level relaxation dynamics in a complex surface-adsorbate system by combining LAAD and LAPE [14]. A different approach for the study of electron dynamics on metals has been proposed by Bovensiepen and co-workers [15].

When ionizing radiation is absorbed by matter, electron emission can either occur directly via the photoelectric effect, or indirectly via Auger decay of a core-excited state created by inner-shell photoionization. When this electron emerges into a strong light field, it is accelerated by the laser. If the interaction occurs continuously over several optical cycles, the electron undergoes oscillations. In the presence of atomic nuclei or solids that can absorb momentum, this leads to the generation of sidebands in the photoelectron and Auger spectra corresponding to the absorption and stimulated emission of photons from the laser field. The amplitudes of these sidebands depend on the profile of the laser and xuv pulses, the time delay between both pulses, and any dynamical processes in the sample. Therefore, by measuring the temporal evolution of these sidebands, information about the ultrafast dynamics of the system can be extracted.

For ultrashort Ti:sapphire laser pulses at an infrared (ir) wavelength of 780 nm, intensities of $\approx 10^{11}$ W/cm^2 are typically required to generate observable LAPE signals. At such high intensities, the ir laser can itself lead to electron emission through multiphoton and above-threshold ionization (ATI), or in the case of emission from a solid surface, above-threshold photoemission (ATP). These multiphoton emission processes often result in a large flux of electrons from the sample that can obscure the detection of LAPE sidebands. These processes are so-called initial state effects (i.e., signal originates overwhelmingly from atoms that have not interacted with the xuv light), whereas LAPE is a *final state* effect in that these processes are specific to the xuv-excited atoms.

The ATP process is particularly problematic for ultrafast measurements of surface electron dynamics. In ATI and ATP processes, electrons can absorb many more photons than the photoionization threshold, and thus are ejected at high kinetic energies. In the case of ATI in atoms, generally these electrons still have sufficiently low kinetic energies that they are separated in energy from the xuv-induced electrons, and thus are not a major problem. However, past work has shown that ATP from surfaces can be significant at much lower laser intensities than in atoms due to field enhancement effects [16]. These ATP electrons can make it impossible to detect LAPE signals for dynamic processes that generate free electrons with low kinetic energies. In our previous work studying electron dynamics in surface-adsorbate systems [14], using the correct ir dressing laser intensity was a critical issue, since the range of intensities over which a LAPE signal could be observed without introducing too much ATP was quite narrow. Moreover, processes such as Auger decay and

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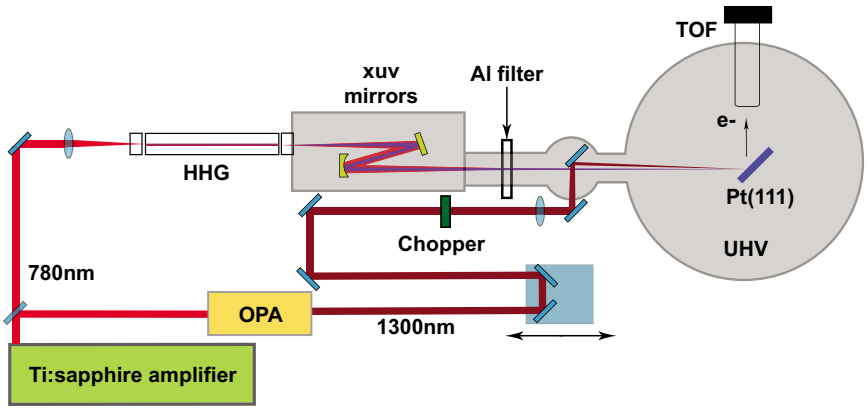

FIG. 1. (Color online) Experimental setup for observing the laser-assisted photoelectric effect from a Pt surface.

interatomic Coulombic decay [17] often result in low-energy electrons, and thus their spectroscopic signatures are buried in a large background of ATP electrons. Furthermore, the high flux of ATP electrons from a very small surface area leads to a Coulomb explosion of the electron cloud, in which fast electrons are accelerated and slow electrons are decelerated because of Coulomb repulsion between them [18,19]. This space-charge effect can distort the photoelectron energy spectrum and also smear the LAPE signal [20]. Thus, for many studies in time-resolved surface electronic dynamics, it is critical to reduce ATP and space-charge initial state effects. Moreover, even in the case of time-resolved studies in isolated atoms, there are cases where a reduction in ATI signal is desirable.

In this Rapid Communication we show that using a dressing laser at longer wavelengths dramatically reduces ATP and space-charge effects while enhancing the surface LAPE signal. By comparing LAPE photoemission spectra from a clean Pt(111) surface taken using 780 and 1300 nm dressing wavelengths, we demonstrate that the LAPE signal is significantly enhanced while dramatically reducing the number and kinetic energies of ATP electrons, and also suppressing space-charge effects. This improvement results from the favorable wavelength scaling of both the LAPE and ATP effects, which, when combined, result in a very remarkable improvement. This approach to laser-assisted photoemission allows us to probe ultrafast dynamics in solids and surface-adsorbate systems over a large final-state energy range. In particular, this methodology promises to make it possible to study time-resolved low kinetic-energy processes on surfaces that have been impossible to probe until now.

In the case of LAPE using relatively low-intensity ir light, careful comparison of theory and experiment [21,22] has shown that the sideband height can be modeled by the square of a Bessel function $A_1 = J_1^2(x)$, with the argument given by $x = \sqrt{\frac{16\pi\alpha}{m_e\hbar}\frac{IE_{\mathrm{kin}}}{\omega_{\mathrm{ir}}^4}}$. Here, E_{kin} represents the kinetic energy of the photoemitted electron, I the intensity of the ir laser pulse, and $\hbar\omega_{\mathrm{ir}}$ the ir photon energy. For a small argument x, A_1 can be approximated by $A_1 \approx x^2/4$ leading to

$$A_1 \propto (IE_{\mathrm{kin}}/\omega_{\mathrm{ir}}^4). \tag{1}$$

From Eq. (1), we see that the amplitude of the LAPE sidebands can be increased by (1) increasing the laser intensity I, (2) increasing the kinetic energy E_{kin} of the electron to be dressed, or (3) decreasing the frequency ω_{ir} of the dressing field. Considering (1), increasing the laser intensity is generally undesirable because it increases the ATP electron flux and may also damage or induce desorption from the surface [16]. For (2), increasing the photoelectron kinetic energy is not generally applicable since for processes such as Auger decay or interatomic Coulombic decay, the ejected electron kinetic energy is determined by the energy level structure of the system and cannot be varied by changing the energy of the incoming photons. Therefore, the best option for increasing the LAPE signal level is to tune the wavelength of the ir dressing pulses to wavelengths longer than the 780 nm wavelength typical of a Ti:sapphire laser. This approach is particularly compelling given the λ^4 dependence of the LAPE signal strength [from Eq. (1)]. However, heretofore, the predicted scaling of the LAPE process to longer wavelengths has not been verified experimentally. Recently, this wavelength scaling has been shown in the case of high-harmonic generation (HHG) [23], and in phase matching the HHG process [24].

Our experimental setup is shown in Fig. 1. A temperature-controlled Pt(111) sample is mounted on a translation and rotation stage inside an ultrahigh vacuum chamber (pressure $\approx 2\times10^{-10}$ mbar). The xuv and dressing pulses are generated from a Ti:sapphire multipass amplifier producing 2 mJ pulses at a repetition rate of 2 kHz and with a duration of 30 fs. The pulses are centered at a wavelength of 780 nm, with a bandwidth of 50 nm. Approximately 80% of the laser energy is used to generate high harmonics in an argon-filled hollow waveguide [25]. A 200-nm-thick aluminum filter is used to block any residual ir beam. A pair of Mg:SiC multilayer mirrors (one flat, one curved) are used to spectrally select the 27th harmonic (29 nm wavelength or 43 eV energy) and focus the xuv beam onto the Pt surface. The remaining 20% of the laser energy is either used directly as the 780 nm ir dressing beam, or sent through a home-built optical parametric amplifier [26] to produce a 1300 nm dressing laser beam with a pulse duration of 31 fs. The ir pulses are directed through a variable delay stage and a focusing lens before overlapping with the xuv beam on the sample, at a small 1° angle. The kinetic energy of the photoemitted electrons ejected at 90° with respect to the xuv beam is analyzed using a time-of-flight detector. A more detailed description of the experimental setup can be found in [20].

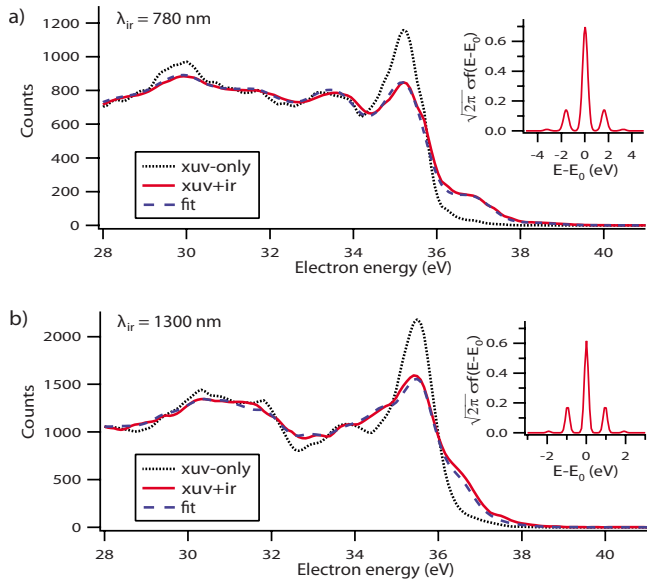

FIG. 2. (Color online) Laser-assisted photoelectric effect with (a) 780 and (b) 1300 nm dressing pulses. Both spectra are measured at zero time delay between the xuv and ir pulses. In (a) the 780 nm pulses with peak intensity $I_{780\ \mathrm{nm}}=1.4\times10^{11}$ W/cm^2 generate sidebands $A_{1(780\ \mathrm{nm})}=0.13\pm0.01$, while in (b) the 1300 nm pulses with peak intensity $I_{1300\ \mathrm{nm}}=2.4\times10^{10}$ W/cm^2 generate sidebands $A_{1(1300\ \mathrm{nm})}=0.18\pm0.01$.

Figure 2 shows the observed photoemission spectra in the energy region near the Fermi edge in the case of illumination of a clean Pt(111) crystal. Here, the xuv and ir pulses are temporally coincident, so that the photoemitted electrons experience the peak dressing laser intensity. To quantitatively extract the LAPE sideband amplitude from our experimental spectra, we model the absorption and emission of up to two ir photons by a laser-assisted response function given by

$$f(E-E_0)=\frac{1-2A_1-2A_2}{\sqrt{2\pi\sigma^2}}e^{(E-E_0)^2/2\sigma^2}+\sum_{\pm}\left(\frac{A_1}{\sqrt{2\pi\sigma^2}}e^{(E-E_0\pm\hbar\omega)^2/2\sigma^2}+\frac{A_2}{\sqrt{2\pi\sigma^2}}e^{(E-E_0\pm2\hbar\omega)^2/2\sigma^2}\right),\qquad(2)$$

where A_1 and A_2 represent the first- and second-order sideband intensities, σ the width, and $\hbar\omega$ the peak separation. The LAPE response function from Eq. (2) can be considered to be independent of the electron kinetic energy over a range of a few electron volts. Thus within this range, the photoemission spectrum when both ir and xuv beams are present can be assumed to be a convolution of the xuv-only spectrum with the LAPE response function. We fit this convolution to the xuv+ir spectrum, allowing the sideband intensities, width, and peak separation to serve as fitting parameters.

The insets of Fig. 2 show the LAPE response function associated with the resulting fit parameters. In Fig. 2(a), we use 780 nm pulses to drive LAPE, while in Fig. 2(b) we use 1300 nm light. We see that LAPE driven by 1300 nm light shows notably larger sidebands compared with 780 nm, even though the 1300 nm laser intensity was much lower than the 780 nm laser intensity. These data directly demonstrate that the use of 1300 nm pulses very significantly enhances the LAPE signal. In addition to increasing the strength of the LAPE signal, the lower intensity of the 1300 nm pulses also dramatically reduces ATP photoelectrons. This is because the laser intensity is lower, and because a larger number of lower energy photons are required for ATP, leading to a considerably smaller cross section. Detailed discussions of the ATP cross section can be found in [27–30]. Figure 3 shows the photoemission spectra using 780 and 1300 nm light alone. By comparing the difference in the low-energy range in both spectra, we see that the lower-intensity 1300 nm pulses introduce significantly fewer electrons with lower kinetic energies than in the case for the higher-intensity 780 nm pulses. Thus, ATP is suppressed when lower-intensity longer-wavelength pulses are applied.

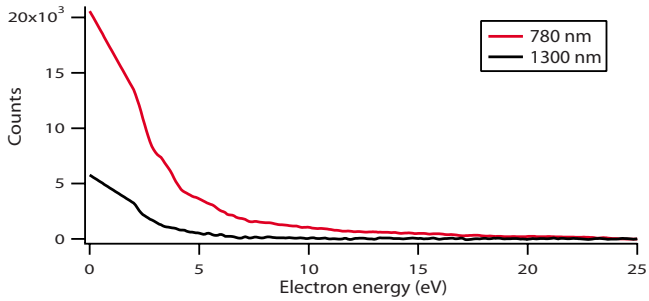

FIG. 3. (Color online) Multiphoton photoemission spectra using 780 nm (upper red line) and 1300 nm (lower black line) pulses alone. At the intensities of $I_{780\ \mathrm{nm}}\approx10^{11}$ W/cm^2 required for 780 nm pulses to obtain observable LAPE signal, a large ATP photoelectron flux is observed in the energy range up to 23 eV. In contrast, using 1300 nm pulses, the intensity of $I_{1300\ \mathrm{nm}}\approx10^{10}$ W/cm^2 required for good LAPE signals produces ATP photoelectrons with kinetic energies less than 7 eV.

The suppression of ATP, without a reduction in the LAPE signal, is especially useful for studying dynamics in surface-adsorbate systems. In many interesting processes in these systems, the electrons to be studied are photoemitted with low kinetic energies. When longer-wavelength ir light is used, ATP generates fewer low-energy electrons, therefore offering a wider energy range in which to detect an unobscured LAPE signal. Furthermore, ir-induced multiphoton or thermal desorption of the adsorbate will also be strongly suppressed.

Moreover, we also observe strongly reduced space-charge effects using 1300 nm dressing beams (see Fig. 4). In the combined xuv+ir spectrum using 780 nm dressing light, we can observe a clear shift of the photoemission spectrum to higher energies with respect to the xuv-only spectrum. In contrast, space-charge effects are suppressed in the 1300 nm spectrum. This leads to a more accurate calculation of the LAPE signal. This eliminates the need to correct for space-charge shifts in the LAPE sideband fit, as was done with the data shown in Fig. 2(a).

In addition to the advantages mentioned above, our results

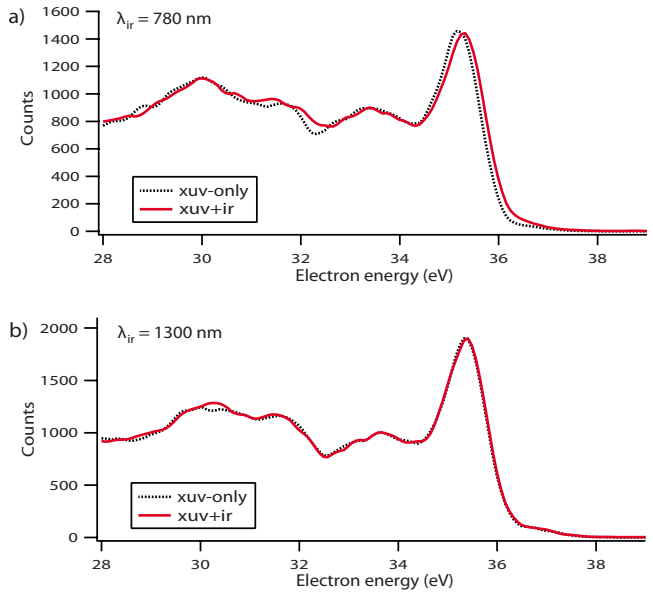

FIG. 4. (Color online) Comparison of space-charge effects around the Fermi edge at −100 fs time delay between the xuv and ir pulses. For 780 nm pulses, the large number of low energy photoelectrons generated through ATP causes a shift of the entire photoemission spectrum around the Fermi edge. This effect is greatly suppressed with 1300 nm pulses, because of the smaller number of ATP photoelectrons.

allow us to experimentally verify the ω_{ir}^{-4} dependence of the LAPE sideband strength. From Eq. (1) we see that at low dressing laser intensities, the first-order sideband height is directly proportional to the intensity of the driving pulse and inversely proportional to the frequency of the driving pulse to the fourth power. Using our experimental results from Fig. 2, we can verify the relationship,

$$\frac{\omega_{780\ \mathrm{nm}}^4}{\omega_{1300\ \mathrm{nm}}^4} = \frac{A_{1(1300\ \mathrm{nm})} I_{780\ \mathrm{nm}}}{A_{1(780\ \mathrm{nm})} I_{1300\ \mathrm{nm}}}. \tag{3}$$

The predicted frequency ratio yields 7.7, while the experimentally determined factor on the right of Eq. (3) yields 8.0 ± 0.4. This excellent agreement between our experimental data and Eq. (3) proves that the theoretical model presented in [31] is the correct one for describing LAPE from surfaces. The 4% discrepancy we find in our data is mainly caused by errors in the measurement of the beam size and the spatial overlap between the xuv and ir beams on the sample.

In summary, our data clearly demonstrate several advantages to using longer-wavelength pulses to drive the laser-assisted photoelectric and Auger effects from surfaces. By moving to a dressing wavelength of 1300 nm, the enhanced LAPE signal and suppressed ATP and space-charge background dramatically improve the range of laser intensities over which good LAPE signals can be observed, as well as enhancing the LAPE signal for a given laser intensity and reducing space-charge and multiphoton effects. This approach to LAPE and LAAD will therefore be critical for enabling time-resolved studies of ultrafast electronic processes at surfaces. Finally, longer wavelengths may also reduce the laser intensity required for the study of subcycle processes by streaking of electrons through the laser electric field. The corresponding drastic reduction in ATP promises the extension of the streaking technique to the investigation of attosecond dynamics in surface-adsorbate systems.

The authors gratefully acknowledge support for this work from the NSF through its Physics Frontiers Centers Program and Engineering Research Center on EUV Science and Technology.

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