Laser-Assisted Photoelectric Effect from Surfaces

L. Miaja-Avila,[1] C. Lei,[1] M. Aeschlimann,[2] J. L. Gland,[3] M. M. Murnane,[1,*] H. C. Kapteyn,[1] and G. Saathoff[1]

[1]*Department of Physics and JILA, University of Colorado, Boulder, Colorado 80309-0440, USA*
[2]*Department of Physics, University of Kaiserslautern, Kaiserslautern, Germany D-67663*
[3]*Department of Chemistry, University of Michigan, Ann Arbor, Michigan 48109-1055, USA*

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We report the first observation of the laser-assisted photoelectric effect from a solid surface. By illuminating a Pt(111) sample simultaneously with ultrashort 1.6 eV and 42 eV pulses, we observe sidebands in the extreme ultraviolet photoemission spectrum. The magnitude of these sidebands as a function of time delay between the laser and extreme ultraviolet pulses represents a cross-correlation measurement of the extreme ultraviolet pulse. This effect promises to be useful to extend extreme ultraviolet pulse duration measurements to higher photon energies, as well as opening up femtosecond-to-attosecond time-scale electron dynamics in solid and surface-adsorbate systems.

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Recent progress in high-harmonic generation (HHG) [1–3] has opened up a new era of ultrafast x-ray science that takes advantage of the femtosecond-to-attosecond pulse duration of this light source. HHG can produce ultrafast, coherent beams that span the entire extreme ultraviolet (EUV) region of the spectrum, making it an attractive light source for investigating dynamical processes in atoms, molecules, plasmas, materials, and surfaces. To date, high-harmonic beams have been used extensively in pump-probe geometries, where a visible pump pulse excites dynamics and a time-delayed EUV probe monitors changes in the sample. This approach has been successfully used to study electron relaxation in materials [4,5], surface-adsorbate dynamics [6], photoacoustic dynamics [7], and molecular dissociation [8].

Another recent critical discovery that has made it possible to study high-energy and attosecond time-scale atomic dynamics is the laser-assisted photoelectric effect (LAPE). In this process, an atom is simultaneously irradiated by EUV and intense infrared (ir) light; the presence of the ir laser modifies the normal EUV photoelectron spectrum. This effect can be described as the simultaneous absorption or stimulated emission of one (or several) ir photons with the EUV photon, which leads to sidebands in the EUV photoelectron spectrum. Alternatively, LAPE can be considered as due to ''dressing'' of the free-electron continuum; i.e., the photo-ionized electron is born into a state where the free electron is driven by the ir laser field. The oscillation of this field results in energy sidebands in the photoelectron spectrum when the interaction occurs over several optical cycles. Alternatively, a continuous shift of the spectrum is observed in the suboptical cycle regime. The magnitude and shape of these shifts or sidebands as a function of time delay between the EUV and ir beams can be used to measure the duration of short EUV pulses. This process was first studied in the context of Auger electron emission by Schins *et al.* [9], and was extended to the direct photoionization process by Glover *et al.* [10]. The laser-assisted photoelectric effect in atomic systems has been extended to the study of attosecond time-scale structure in EUV emission [11,12], and to study core-level atomic dynamics [13].

However, to date LAPE has been observed only in gas-phase atomic systems. This limits its current applicability to the study of isolated atoms or molecules. Furthermore, this limitation also represents a practical limit to the use of LAPE for EUV pulse characterization, since both atomic photoionization cross sections and the obtainable photon flux from high-harmonic sources decrease rapidly with increasing photon energy. The result has been that current EUV pulse duration measurements are limited to the energy range of $\lesssim$100 eV. Other approaches for characterizing ultrashort EUV pulses, such as the autocorrelation using two-photon absorption [14,15], are experimentally challenging at very high photon energies, and to date have been demonstrated only at photon energies $<$50 eV.

In this work we present the first demonstration that the physics of the laser-assisted photoelectric effect can be extended to solid-state systems. This result represents the laser-assisted version of the original manifestation of the photoelectric effect—in which photons strike a solid surface and result in ejection of electrons with energy up to $\hbar\omega - W_f$, where $\hbar\omega$ is the EUV photon energy and W_f is the work function. In our work, a clean Pt(111) single crystal was used as the solid surface, since it exhibits a large density of states at the Fermi edge, with a characteristic peaklike structure in the photoelectron spectrum. In the presence of an intense laser field, sidebands appear in the Pt(111) photoemission spectrum. The modification of the photoelectron spectrum by LAPE can be distinguished from simple heating of the electrons by the pump beam by varying the laser polarization, by measuring the mean energy of the photo-ejected electrons and showing that it does not change, and by successfully fitting the photoelectron spectrum to a dressed continuum state model.

We also demonstrate that surface LAPE can be used to measure the EUV pulse duration.

This result is significant for three reasons. First, surface LAPE has the potential to study ultrafast, femtosecond-to-attosecond time-scale electron dynamics in solids and in surface-adsorbate systems—where complex, correlated, electron relaxation processes are expected. This is in contrast with measurements in atomic systems, where dynamics are generally homogeneously broadened and where time-domain studies have duplicated information that can be obtained from spectroscopy. Second, surface LAPE will make it possible to characterize lower-flux and higher-energy EUV pulses, because of the orders-of-magnitude higher density of target atoms, which is typically limited to $\ll$1 Torr pressure to allow for sufficient electron mean-free path in the experiment. Finally, this result represents new physics—the extension of laser-assisted photoemission from atoms to the case of a surface.

Figure 1 shows the experimental setup. A regularly cleaned, temperature-controlled Pt sample is mounted on a translation and rotation stage inside a UHV chamber. The localized d-band peak at the Fermi edge, which is 0.9 eV wide, is a very useful characteristic peak for observing sidebands. At the base pressure of 2×10^{-10} torr, the Pt surface stays clean for several hours. For these measurements, the sample was cooled down to $-180\,^{\circ}$C using liquid nitrogen. A Ti:sapphire multipass amplifier laser system producing 1.5 mJ, 780 nm pulses at a repetition rate of 2 kHz and with a duration of 25 fs is used to generate the ir pump and EUV probe beams [16]. Approximately 30% of the laser energy is used for the ir pump, while the remaining 70% of the laser energy is upconverted by phase-matched high-harmonic generation in an argon-filled hollow waveguide [17]. An Al filter of 200 nm thickness and a pair of a flat and a curved Si:Mo multilayer mirror are used to block the ir light and to spectrally select the 27th harmonic (at a wavelength of 30 nm corresponding to a photon energy of 42 eV) and to focus this probe beam onto the Pt surface in a beam spot size of 0.4 mm in diameter. A small residual contribution from the 29th harmonic is below 1%.

The ir pump beam is directed through a variable optical delay stage as well as a focusing lens, and overlapped with the probe on the sample at a small angle of 1°. Its pulse duration is broadened to ≈35–40 fs by dispersion as it propagates through optics in the delay line. The maximum power is 300 mW, and the beam radius can be varied from 0.1 mm to 1.2 mm by moving the lens, to produce an intensity of $>10^{12}$ W/cm^2. The EUV probe beam, containing about 10^6 photons per pulse, irradiates the sample at 45°. The kinetic energy of the photo-emitted electrons are analyzed at 90° with respect to the probe beam, using a 600-mm-long time-of-flight detector (TOF).

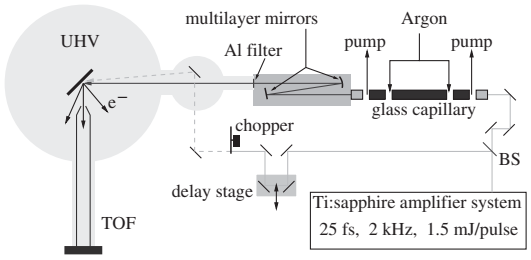

FIG. 1. Experimental setup for observing the laser-assisted photoelectric effect from surfaces.

Figure 2 shows a series of photoelectron spectra around the Fermi edge at a moderate pump beam intensity of 2×10^{12} W/cm^2 and for relative time delays of -100 fs to $+100$ fs between the ir pump and EUV probe beams. Negative time delays mean that the pump arrives after the probe. The ir pump beam polarization was chosen parallel to the direction of detection. For the -100 fs measurement, the probe-only spectrum is also shown (dashed line). At this time delay, both the probe-only as well as the pump-probe spectra show the typical d-band structure of clean Pt(111). While the spectral shape is unaffected by the presence of the pump, the pump-probe spectrum is slightly shifted to higher electron energies as compared to the probe-only spectrum. This is due to the negative space charge created on the surface by the pump that accelerates the photo-emitted electrons. We observe this shift for time delays between at least -1 ps and $+1$ ps. This can be explained by the fact that the photo-emitted electrons slowly move away from the surface and escape the space-charge field, so that they are affected even for rather large negative time delays. At very high pump

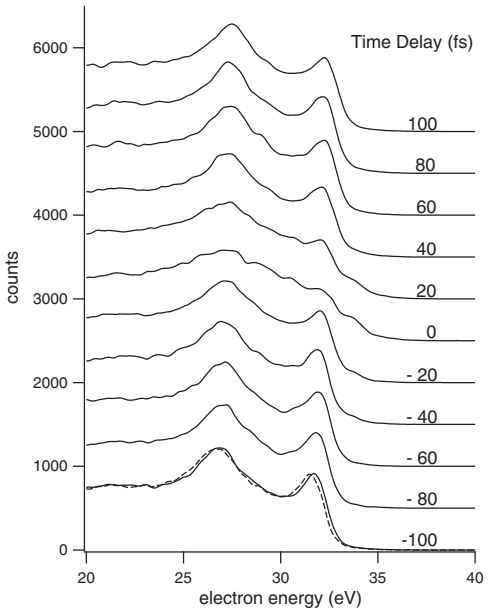

FIG. 2. Observed photoelectron spectra from Pt(111) as a function of time delay between the ir pump and EUV probe beams, and at moderate ir pump powers. For -100 fs time delay, the probe-only spectrum (dashed line) is also shown. A slight shift of the spectrum due to pump-induced space charge can be seen that does not change the shape of the spectrum and that can be corrected for.

intensities, the space-charge effect also changes the shape of the pump-probe photoelectron spectra. However, for the moderate intensity used here, only a small shift occurs ($\sim$100 meV), that is determined from the -100 fs curves and corrected for in all pump-probe spectra.

In a narrow time window of a few tens of fs around zero time delay, we observe a very strong change in the shape of the photoelectron spectra near the Fermi edge. To determine if this shape change was due to the presence of hot electrons excited by the pump pulse, we calculated the average kinetic energy of the photoelectrons above 20 eV, both with and without the ir pump pulse present. (Below 20 eV photoelectron kinetic energies, the pump-probe spectrum is dominated by low-energy electrons from above threshold photoemission [18].) No significant pump-induced increase of the average kinetic energy was found around zero fs. Indeed, the calculated average photoelectron kinetic energies with and without the ir pump were identical, within 0.1 eV, at all time delays. This indicates an essentially equal redistribution of electrons to higher *and* to lower kinetic energies in the presence of the ir field. The shift to lower energies, however, cannot take place by a modulation of the initial photoelectron states because the lower energy states below the Fermi level are filled. Moreover, an interpretation of the modulation arising as a result of hot electrons [19] is ruled out, because this would increase the average kinetic energy of the photoelectron distribution. We can also exclude a laser-induced change of the band structure, which is not possible on this ultrafast time scale. As discussed above, the effects of space charge are small and also do not explain the observed large modulations near time zero. The expected ponderomotive shift at the applied pump intensity is about 0.1 eV. Since this shift is only present around time zero, it is dominated by the observed Fermi edge modification and cannot be resolved.

Our results can only be explained as dressing of the continuum photoelectron states by the applied laser pump field. In an atomic system, the EUV photoelectron spectrum consists of discrete atomic peaks. In the presence of an intense laser field, the laser-assisted photoelectron emission sidebands are easily distinguished, and are separated from the main photoemission peaks by the ir photon energy. Their amplitudes have been found consistent with a description of the final state by a Volkov wave function, i.e., a free electron oscillating in the laser field, with no significant influence from the initial state [10]. In the case of photoemission from a surface, the spectrum consists of a continuous distribution due to the band structure of the solid. However, the unperturbed spectrum of Pt(111) has a d-band peak near the Fermi edge of width 0.9 eV, that can be used to discern sideband peaks. To quantitatively predict the expected sideband intensities in the case of photoemission from Pt in the presence of an intense ir field, we model the absorption and emission of up to two ir photons by a photoelectron of kinetic energy E_0 by

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

The convolution of this LAPE response function with the probe-only photoelectron spectrum is then fit to the pump-probe spectrum. Here $f(E-E_0)$ contains the amplitudes A_1 and A_2 of the first two sidebands, as well as the width σ and the peak separation $\hbar\omega$ as fit parameters. The factor in front of the first Gaussian peak is chosen to normalize the response function to 1. The parameters A_1 and A_2 thus give the fraction of electrons scattered into the first and second sidebands, respectively. Figure 3 shows the result for zero time delay between the pump and probe beams. The dotted line gives the photoemission spectrum without the ir pump pulse present. The solid line shows the photoemission spectrum with the ir pump pulse present. Finally, the dashed line shows the fit. There is excellent agreement between the experimentally measured photoemission spectrum in the presence of the ir field, and the curve obtained by convolving Eq. (1) with the unperturbed photoemission spectrum. Although this model neglects the effects of the solid on the final continuum state, the excellent agreement indicates that the observed change of the spectrum is essentially caused by a modulation of the final continuum state, which can be described as Volkov-like under our experimental conditions.

The inset of Fig. 3 shows the LAPE response function associated with the fit parameters: $A_1 = 0.241 \pm 0.004$; $A_2 = 0.012 \pm 0.005$; $\sigma = 0.23 \pm 0.03$ eV; and $\hbar\omega = 1.59 \pm 0.02$ eV. Here the response function is plotted so that the peak heights are given by $A_{1,2}$ and thus directly reflect the fraction of electrons scattered into the respective sideband. Our fit indicates the same order of magnitude for the sideband amplitudes as in atomic LAPE observed at comparable laser intensity [10]. About 50% of the photoemitted electrons are redistributed in energy in the pres-

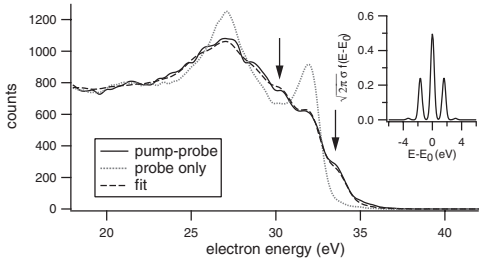

FIG. 3. Observed photoemission spectrum with (solid line) and without (dotted line) the ir pump pulse present. The dashed line shows the fit to the pump-probe curve by convolving the LAPE response function from Eq. (1) with the unperturbed spectrum. The expected sideband position is indicated by arrows. The inset shows the LAPE response function associated with the fit.

ence of the pump pulse. Such a redistribution would be unlikely to be achieved from a modulation of the initial state, but is consistent with our picture. The fit to the sideband separation of $\hbar\omega = 1.59$ eV corresponds very well to the photon energy of the ir pump beam, while the width σ reflects well the convolution of the laser bandwidth ($\approx$0.1 eV) and the detector resolution at the high-energy part of the photoelectron spectrum ($\approx$0.2 eV). A less constrained fit that allows asymmetric sidebands gives nearly identical results.

In a separate data set, we fixed the pump-probe delay and varied the laser intensity. We observed a clear linear dependence of the A_1 sideband amplitude on laser intensity, until saturation is reached when the second sideband A_2 becomes significant. As the intensity is further increased, A_1 levels off and peaks at a value of $\sim$0.33. This behavior is identical to the atomic case, where the intensity dependence of A_1 follows the square of a Bessel function [20]. Surface LAPE is the only explanation of our experimental data. This is further corroborated by the fact that no sidebands are observed when the pump polarization is perpendicular to the direction of detection.

By fitting the photoelectron spectra for all other time delays, with $h\omega$ and σ fixed to the values derived from the zero fs spectrum, we determine the strengths A_1 of the first-order sideband as a function of delay between the pump and probe. Figure 4 plots A_1 versus time delay, to show the measured cross-correlation between the ir pump and EUV probe beams. The small error bars indicate a large sensitivity of the fit to the sideband heights, which is due to the fact that the positive sidebands show up in a region well beyond the Fermi edge, where the probe-only spectrum only exhibits a small count rate. A Gaussian fit yields a full width at half maximum of 37 ± 3 fs, in agreement with the expected EUV pulse duration of $\sim$10 fs and the pump duration of 35–40 fs, respectively.

In our present data, we do not see evidence of more-complex physics such as rapid modification of the valence band by the laser. This is consistent with the atomic LAPE case, where the ground state is relatively little affected by the electric field because the electron is tightly bound to the ion. In a solid, the valence band electrons are tightly bound to the solid, with only a small number of electrons near the Fermi surface able to react to a low intensity incident field. Although electron heating and other possible valence band effects without doubt occur, these are minor compared with LAPE when very short pulses (i.e., high peak intensity but relatively low fluence) are used to avoid these effects. Nevertheless, further theoretical and experimental investigation is needed to explore over which regimes an atomiclike model is applicable to solids, and to extract solid-state dynamics.

In conclusion, we report the first observation of the laser-assisted photoelectric effect from a solid surface. In the presence of an ir pump pulse, the EUV photoelectron spectrum from a Pt(111) sample exhibits a sideband structure at the Fermi edge that can only be interpreted as laser-assisted photoemission. Since the observed sidebands arise from electrons that escape from the first few atomic layers, the time resolution of this surface-LAPE should be extremely high (comparable to the attosecond time resolution observed in gas-phase LAPE), presenting new possibilities for studying femtosecond-to-attosecond correlated electron dynamics in solids. Compared with laser-assisted photoemission from atomic systems, surface LAPE has the advantage of much higher target atom densities and may thus be well-suited to characterizing high-energy femtosecond-to-attosecond EUV pulses, where the photon flux from high-harmonic generation is much lower.

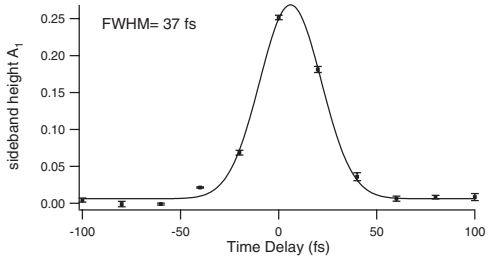

FIG. 4. Measured cross correlation of the ir pump (35–40 fs) and $\approx$ 10 fs EUV probe, that was determined by plotting the height of sideband A_1 as a function of time delay between the pump and probe. A Gaussian fit yields 37 ± 3 fs, limited by the duration of the ir pump pulse.

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*Email address: murnane@colorado.edu

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