

$\text{FA}_{x-1}\text{Cs}_{1-x}\text{PbI}_y\text{Br}_{3-y}$ (24–26). We obtained an excellent PCE of close to 18.0% in the initial trial; detailed PV metrics are listed in table S6.

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ACKNOWLEDGMENTS

Supported by King Abdulaziz City for Science and Technology (M.G. and S.M.Z.), an EPFL Fellowship co-funded by a Marie Curie stipend from the European Union's Seventh Framework Programme (no. 291771) (J.L.), the Swiss National Science Foundation, NRP 70 “Energy Turnaround,” SNF-NanoTera (SYNERGY), and the Swiss Federal Office of Energy. We thank F. Zhang for experimental aid with the preparation of some perovskite solutions and TiO_2 films, I. Dar and G. J. Jacopin for assistance with the photoluminescence experiments, and W. Tress for help with the curve fitting. X.L., D.B., C.Y., S.M.Z., A.H., and M.G. have applied for a European patent for the VASP process.

SUPPLEMENTARY MATERIALS

www.sciencemag.org/content/353/6294/58/suppl/DC1
Materials and Methods
Supplementary Text
Figs. S1 to S8
Tables S1 to S6

2 April 2016; accepted 25 May 2016
Published online 9 June 2016
10.1126/science.aaf8060

ULTRAFAST DYNAMICS

Direct time-domain observation of attosecond final-state lifetimes in photoemission from solids

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Attosecond spectroscopic techniques have made it possible to measure differences in transport times for photoelectrons from localized core levels and delocalized valence bands in solids. We report the application of attosecond pulse trains to directly and unambiguously measure the difference in lifetimes between photoelectrons born into free electron-like states and those excited into unoccupied excited states in the band structure of nickel (111). An enormous increase in lifetime of 212 ± 30 attoseconds occurs when the final state coincides with a short-lived excited state. Moreover, a strong dependence of this lifetime on emission angle is directly related to the final-state band dispersion as a function of electron transverse momentum. This finding underscores the importance of the material band structure in determining photoelectron lifetimes and corresponding electron escape depths.

The electronic band structure of materials consists of occupied and unoccupied bands that emerge as the electron wave functions of adjacent atoms in the lattice overlap with each other. In general, valence bands will have more wave function overlap and will therefore be wider than, for example, the core levels. The periodicity of a crystal lattice imposes an energy-momentum relation that is described as the dispersion relationship for electrons in each band, making the electronic structure of solids quite complex. Fortunately, angle-resolved photoemission spectroscopy (ARPES) can resolve both the energy and momentum of photoelectrons by probing photo-

emission from materials at well-defined angles. This information is related to the energy and momentum of electrons populating distinct bands, providing a direct measurement of the band dispersion and the Fermi surface (1). When combined with ultrafast lasers, time-resolved ARPES makes it possible to capture fast changes in the band structure of materials near the center of the Brillouin zone (i.e., low electron momenta) on picosecond and femtosecond time scales (2). More recently, advances in tabletop high-harmonic generation (HHG) (3, 4) have resulted in coherent extreme ultraviolet (EUV) and soft x-ray beams that are ideally suited for ARPES, opening up time-resolved studies over the entire Brillouin zone (5, 6). HHG is emitted as a series of attosecond pulse trains with unique characteristics of good energy resolution (~100 to 300 meV) combined with sub-femtosecond time resolution. These capabilities have made it possible to observe and control the fastest electron dynamics in molecular and mate-

rial systems (7, 8). Recent work probed how fast a material can change its magnetic state or transition from insulating to metallic (5, 9), uncovering which microscopic mechanisms were responsible for driving fast phase or state transitions in materials. Other work probed the ~7-fs lifetime of core-excited states of adsorbates on surfaces (10).

HHG has also been used to probe the time delay associated with the photoemission process itself in isolated atoms and materials (11–17) by taking advantage of laser-assisted photoemission (18). Although some discrepancy remains between experiment and theory (17, 19), it is generally agreed that the photoemission time delay from isolated atoms arises from convolution of a Wigner time delay due to scattering of photoelectrons in the atomic potential and a measurement-induced delay due to propagation of the photoelectrons in the laser field (20). Unlike the case of isolated atoms, interpreting photoemission time delays from solids requires consideration of complex band structures and various many-body interactions that photoelectrons can experience as they approach the surface. Previous attosecond-streaking studies of a transition-metal W(110) surface revealed a considerable time delay (~110 as) between photoemission from core-level and valence-band states (11). In contrast, no delay was measured for the free-electron metal Mg, although a time delay similar to that of W was expected (13). Various theoretical models have been proposed to explain the photoemission time delay from solids in terms of transport time (21, 22), degrees of initial-state localization (21, 23), and band-structure effects (24, 25). The use of isolated attosecond pulses in these experiments was necessarily accompanied by a broad EUV bandwidth, which then gave rise to an integrated broadband photoemission feature comprising multiple valence bands (11, 13, 14). Other recent work used synchrotron sources to measure the final-state linewidths of photoemission from Cu, finding pronounced variations in the ARPES spectra with small changes in photon energy that could not be assigned to a free-electron final state. This work identified the direct transitions and

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measured very broad linewidths of >3 eV for unoccupied excited final states in the band structure within the photon energy range 20 to 150 eV (26).

Here, we directly and unambiguously measured the influence of the band structure of a material on the lifetime of photoelectrons. To accomplish this, we used attosecond pulse trains of well-defined harmonics to measure the photoemission time delays for free-electron final states as well as final states corresponding to the unoccupied bulk bands of the transition metal Ni(111). We were able to distinguish photoelectron lifetimes from individual valence bands and final states in Ni(111), with additional help from selection rules for photoemission for EUV fields with different polarizations (1, 27). Our results show that when the final state corresponds to an unoccupied excited state in the Ni band structure, photoelectrons experience an abrupt delay of $\sim 212 \pm 30$ as. This delay corresponds to the lifetime of the excited state and can be interpreted physically as a variation of the attenuation length of the final-state wave function inside the crystal. Therefore, through a direct time-domain measurement of attosecond photoelectron dynamics, our results provide insights into the fundamental concepts of photoelectron lifetime, inelastic mean free path (IMFP), and group velocity. Moreover, we observed large angle-dependent (i.e., momentum-dependent) variations in photoemission time delay, which are directly related to the final-state band dispersion.

The basic principle underlying our experiments is illustrated in Fig. 1A. Linearly polarized high harmonics are focused collinearly with infrared laser pulses (~ 26 fs, 780 nm) onto an atomically clean Ni(111) surface. The HHG spectra consist of multiple harmonic orders (11th to 41st) spanning from 17 to 66 eV, which are generated using different noble gases (Xe, Kr, Ar, and Ne). The corresponding HHG pulse train comprises EUV

bursts with durations of ~ 200 as [full width at half maximum (FWHM)] within a ~ 15 -fs (FWHM) envelope (28) in the time domain. Photoelectrons with sufficiently large momenta along the surface-normal direction escape the surface and are detected by a hemispherical electron analyzer. In the angle-resolved photoelectron spectrum, the same initial Bloch wave packet is excited to multiple final states with different kinetic energies, manifesting as a ladder of direct photoemission bands, each separated by twice the fundamental photon energy $\hbar\omega_L$ (where $\hbar$ is the Planck constant divided by 2π and ω_L is the frequency of the fundamental driving laser) (Fig. 1B). Laser-assisted photoemission in the presence of the phase-locked infrared (IR) laser field (3×10^{11} W/cm²) modulates the photoelectron spectra as a function of τ_d , the relative delay between the EUV pump and IR probe fields. This allows us to extract photoelectron dynamics on attosecond time scales and angstrom length scales by analyzing the attosecond beating due to the interference of two-photon quantum pathways that lead to the same final photoelectron energy (in a technique called RABBITT) (16, 28). RABBITT and attosecond streaking have been shown to yield the same temporal information about the photoemission process (19, 20).

We first probed the electronic band structure of Ni(111) by studying the dependence of the static photoelectron spectra on the EUV photon energy and polarization (Fig. 2A). Striking differences can be observed for photoemission excited by s- and p-polarized EUV fields, which can be understood in terms of the selection rules for direct interband transitions (1, 27). Taking these selection rules into account and considering our experimental geometry (45° angle of incidence of the HHG beam), we can unambiguously assign the two photoemission peaks in Fig. 2A that are excited by s-polarized light to the two valence bands with Λ_3 symmetry (Λ_3^a and Λ_3^b , with respective binding

energies of ~ 0.6 eV and ~ 1.25 eV). The additional spectral weight observed for p-polarized light is from the Λ_1 initial band (~ 1.7 eV) (Fig. 2B). Both s- and p-polarized photoemission exhibit peak shifts when excited by different photon energies; this is clear evidence of contributions from bulk band transitions. Assuming direct transitions to a free electron-like final state, we can map the electron momentum in the surface-normal direction $k_\perp$ for different photon energies (1, 29, 30). The extracted band structure is plotted in Fig. 2B. The good agreement of our photoelectron spectra with previous studies using synchrotron light covering a similar energy range (30) (Fig. 2B) verifies that high harmonics are ideal for capturing electron and band structure dynamics with subfemtosecond time resolution, good energy resolution (100 to 300 meV), easy manipulation of the photon energy and polarization (31), and perfect synchronization to the driving laser. Note that the valence bands calculated using density functional theory (DFT) are ~ 0.7 eV deeper than experiment because of the presence of strong correlations for Ni 3d electrons (30, 32).

The most pronounced feature of Fig. 2A is the enhancement in the intensity of the low-energy spectral peak (~ 1.25 eV) upon excitation by ~ 24 -eV HHG photons (15th order). This resonant feature clearly appears in the spectra that emerge from excitation by an s-polarized EUV field, indicating that the Λ_3^b band is the initial band. Considering the band structure of Ni(111) along the Γ -L direction, we can assign this spectral resonance to direct interband transitions from the Λ_3^b initial band to the high-energy unoccupied Λ_1^b final band located at ~ 24 eV above the Fermi level, as indicated by the blue arrow in Fig. 2B.

In photoemission theory, the matrix element responsible for photoelectron spectra can be written as $M_{fi} = \langle f | H^{\text{int}} | i \rangle$, where $|i\rangle$ is the initial state, $|f\rangle$ is the final state, and $H^{\text{int}} = \mathbf{A}_X \cdot \mathbf{p} + \mathbf{p} \cdot \mathbf{A}_X$

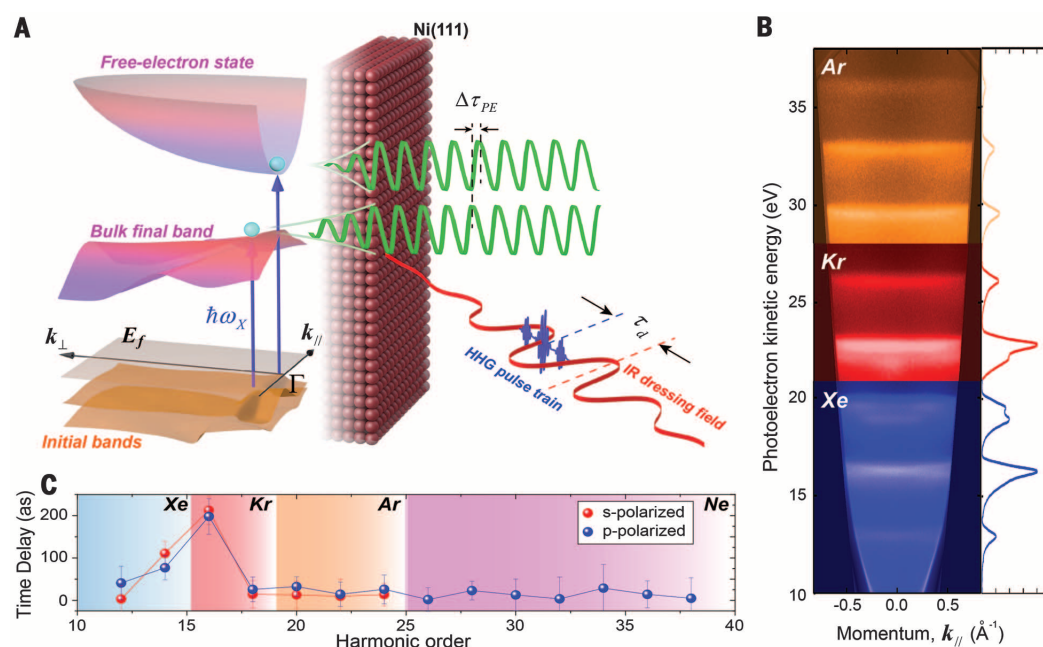


Fig. 1. Photoemission time delay on and off a resonance in the band structure. (A) Using high-order harmonics, different photoelectron final states can be accessed, corresponding to free electron-like states or excited states in the band structure. The damping length of the final-state wave function inside the crystal is increased when the transition coincides with a final-state resonance. (B) Static ARPES excited by s-polarized HHG. The energy resolution is ~ 0.3 eV, which is sufficient to distinguish photoemissions from two initial bands (Λ_3^a and Λ_3^b). (C) Photoemission time delays from laser-dressed harmonic sidebands for s- and p-polarized HHG for noble gas targets. A notable delay is introduced at sideband SB16, attributable to the >200 -as lifetime of the excited state in the material band structure.

represents the interaction Hamiltonian between an electron and EUV electromagnetic radiation with vector potential $\mathbf{A}_X$. The final-state wave function can be represented as a time-reversed low-energy electron diffraction (LEED) state, composed of a free-electron wave arriving at the detector and a damped Bloch wave inside the crystal (1, 33), with a characteristic damping length directly related to the IMFP and photoelectron lifetime. The increase in photoemission intensity as a result of this final-state resonance can be attributed to an increase in photoelectron lifetime, with associated elongation of the characteristic damping length of the final-state wave function, which strongly enhances the spatial overlap between the initial and final-state wave functions, and hence the transition probability. The energy-dependent photoemission intensity of the Λ_3^B band is summarized in Fig. 3B, together with a fit to a Lorentzian function with width $\gamma = 3.68 \pm 0.88$ eV and centered at 24.40 eV, which is consistent with previous studies (26). Thus, the characteristic lifetime of this final state can be extracted from $\tau_{\text{spec}} = \hbar/\gamma = 179 \pm 43$ as.

To directly measure the difference in photoelectron lifetimes between electrons excited into high-energy final bands (i.e., on resonance) and those excited into free-electron final states located in the band-gap region (1, 33), we introduced an IR laser field to dress the photoelectrons. In the presence of the dressing laser field, there are two distinct quantum paths from an initial state to the same sideband, namely (i) absorption $\hbar\omega_{2n-1} + \hbar\omega_L$ and (ii) emission $\hbar\omega_{2n+1} - \hbar\omega_L$ of an IR photon (fig. S1B). When the relative time delay τ_d between the

HHG pump and the IR probe is changed, the intensity of sidebands from a given initial band is modulated as a result of quantum-path interferences (16, 28):

$$S_{2n}(\tau_d) = A_0 \sin[2\omega_L(\tau_d - \tau_X - \tau_{\text{PE}})] \quad (1)$$

where A_0 is the intensity of modulation, $\tau_X = (\phi_{2n+1} - \phi_{2n-1})/2\omega_L$ represents a time delay contributed by the phase chirp between neighboring harmonics ($\phi_{2n+1} - \phi_{2n-1}$), and τ_{PE} is the photoemission delay. Simultaneous measurement of two photoelectron wave packets excited by the same harmonic orders allows us to cancel the influence of attochirp (τ_X). This method was first implemented and validated for isolated atoms (16). In our experiments, we use the nonresonant photoemission from the Λ_3^a band as the timing reference and determine the relative photoemission delay of the resonant $\tau_{\text{PE}}(\Lambda_3^B) - \tau_{\text{PE}}(\Lambda_3^a)$ and nonresonant $\tau_{\text{PE}}(\Lambda_1) - \tau_{\text{PE}}(\Lambda_3^a)$. This allows us to compare time delays for comparable photoelectron energies and to cancel effects arising from the attochirp- or dressing field-induced phase delays.

We first measured the time delay $\tau_{\text{PE}}(\Lambda_3^B) - \tau_{\text{PE}}(\Lambda_3^a)$ using s-polarized HHG fields. In Fig. 3C, we plot a set of experimental RABBITT interferograms for τ_d in the range -2 to 2 fs. The interferograms were obtained by integrating the photoelectron spectra over $\pm 2.5^\circ$ around the Γ point and subtracting the background spectrum obtained well before time zero. We intentionally selected a small angular region in the analysis to avoid the ambiguities resulting from

angle-dependent photoemission time delay (see below). Figure 3C clearly shows that photoelectrons from the Λ_3^B band are notably delayed for sideband SB16 (corresponding to a photon energy of 25.6 eV), which manifests as a large offset in oscillations in the interferograms. This time delay gradually vanishes at increasing and decreasing photon energies, showing a nonmonotonic change of $\tau_{\text{PE}}(\Lambda_3^B) - \tau_{\text{PE}}(\Lambda_3^a)$ as a function of photon energies. One-dimensional (1D) lineouts corresponding to the Λ_3^a and Λ_3^B bands in the sideband region are extracted in the panel on the right side of Fig. 3C, making it possible to determine the precise values of $\tau_{\text{PE}}(\Lambda_3^B) - \tau_{\text{PE}}(\Lambda_3^a)$ as a function of energy. The results are summarized in Fig. 3A (see supplementary materials for detailed analysis). By comparing this relative photoemission delay with the spectral resonance (Fig. 3B), we find that the observed maximum in time delay coincides with the spectral resonance at the same photon energy, strongly indicating that the observed photoemission time delay originates from the excited-state band structure of Ni(III). Most important, the time delay measured using laser-assisted photoemission, $\tau_{\text{chiron}} = 212 \pm 30$ as, agrees (within error bars) with the value from the spectral resonance, $\tau_{\text{spec}} = 179 \pm 43$ as.

To extract the photoemission time delay $\tau_{\text{PE}}(\Lambda_1) - \tau_{\text{PE}}(\Lambda_3^a)$, we used p-polarized EUV fields for photoemission (Fig. 1C). We note that in this situation, the low-energy sideband intensity of the RABBITT oscillations has contributions from both Λ_1 and Λ_3^B bands. With the knowledge of the intensity contributions from these two initial bands, the time delay $\tau_{\text{PE}}(\Lambda_1) - \tau_{\text{PE}}(\Lambda_3^a)$ can be extracted (see supplementary materials), as shown in Fig. 3A. In strong contrast to the Λ_3^B band, photoemission from the Λ_1 band exhibits a very small time delay relative to that from the Λ_3^a band and varies smoothly across the photon energy range.

In photoemission theory, the photoelectron lifetime can be understood as the time taken for the wave function to evolve from a Bloch wave inside the material into a free-electron wave function outside the solid. Semiclassically, this is also the time the photoelectron spends moving a distance corresponding to an IMFP (33, 34). As we show below, the on-resonance time delay measured in our experiments can be directly related to the lifetime of the final-state high-energy band. The fact that our measured time delay agrees well with the lifetime extracted from the spectral linewidth indicates that the lifetimes of photoelectrons originating from the initial Λ_3^a band are very small (within experimental error, $\sim \pm 53$ as). At the same time, the photoelectron lifetimes corresponding to the Λ_1 band are longer by ~ 50 as (Fig. 3A). Because both bands exhibit a smooth variation in photoemission cross section over the photon energy range used here (see supplementary materials), it is reasonable to assume that their photoelectron lifetimes are slowly varying as a function of photon energies. Thus, the results shown in Fig. 3A can be interpreted as an abrupt increase of ~ 212 as in photoelectron lifetime from the Λ_3^B band when the direct transition approaches a bulk final band (Λ_1^B), resulting in a final-state resonance.

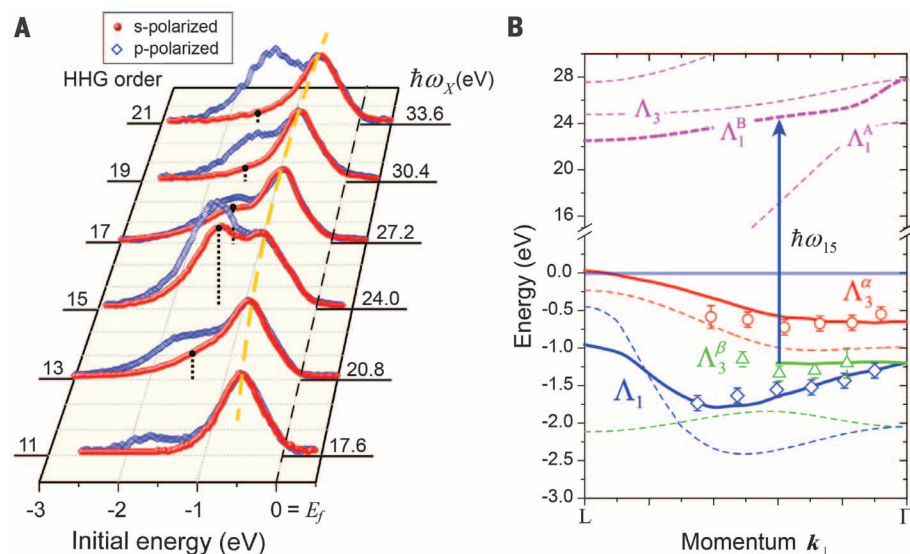


Fig. 2. Final-state resonance in photoemission from Ni(III). (A) EDC curves excited by s- (red) and p-polarized (blue) HHG in a normal emission geometry (integrated $\sim \pm 2^\circ$ around the Γ point). The position of the Fermi level (black dashed line) is determined from the laser photon energy (~ 1.6 eV) and analyzer work function (4.25 eV). The orange dashed line shows the shift of the high-energy peak with HHG photon energy, emphasizing the contribution of bulk band transitions. The intensity of the Λ_3^B band clearly shows a spectral resonance at ~ 24 eV. (B) Band structure along the Γ -L direction (normal to the surface) extracted from our data (open symbols) compared with results of previous experiments (30) (solid lines) and DFT calculations (dashed lines). A free-electron final state in a constant inner potential (30) is assumed and is used to map the electron momentum normal to the sample surface $\mathbf{k}_\perp$. The final-state resonance observed in (A) corresponds to a direct transition from the Λ_3^B initial band to the Λ_1^B final band, as highlighted by the blue arrow.

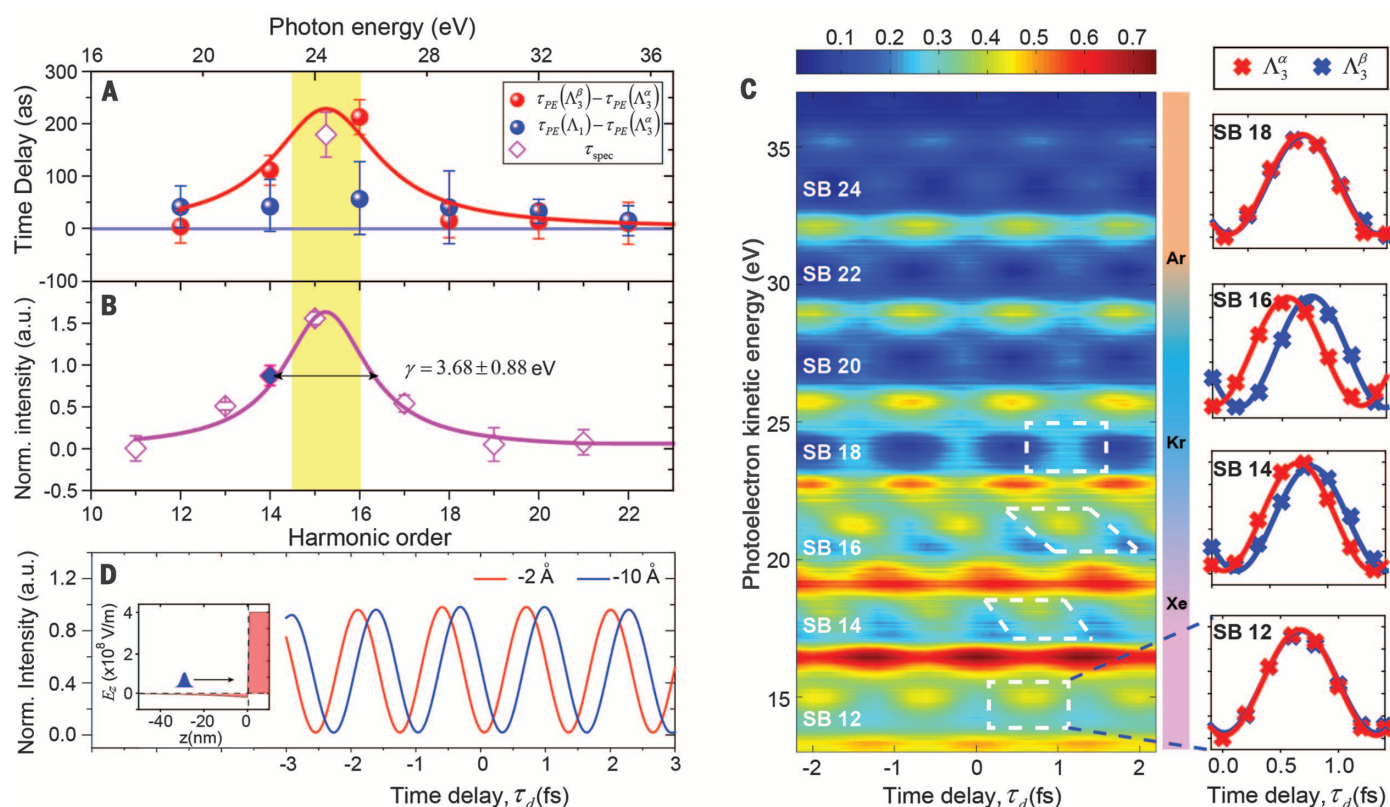


Fig. 3. Direct time-domain measurement of the final-state lifetime.

(A) Photoemission time delays $\tau_{PE}(\Lambda_3^\beta) - \tau_{PE}(\Lambda_3^\alpha)$ and $\tau_{PE}(\Lambda_1) - \tau_{PE}(\Lambda_3^\alpha)$ as a function of photon energy, clearly showing an increase in lifetime (by 212 ± 30 as) when the final state corresponds to a short-lived excited state in the band structure. Error bars represent SD of time delays extracted from more than 200 individual scans. The red solid line is a Lorentzian curve with the same linewidth as in (B). (B) Spectral intensity of the Λ_3^β initial band as a function of photon energy. The blue point (14th order) is obtained from HHG driven by 390-nm laser field. Error bars represent the fitting uncertainties of the photoelectron yield from individual photoelectron spectra that were used to extract each point (see supplementary materials). The pink line represents a Lorentzian fit, yielding a

linewidth of $\gamma = 3.68$ eV. (C) Two-dimensional map of photoelectron yields as a function of photoelectron energy and pump-probe time delay τ_d , excited by s-polarized HHG. To enhance the color contrast, 90% of the ground-state spectrum is subtracted to visualize the interferogram. The relative delays between photoelectrons from the Λ_3^α and Λ_3^β initial bands are manifested as a large offset in oscillations in the sidebands (white dashed boxes). A zoom-in view in both energy and time delay at the resonant energy is plotted in fig. S5D. Right panel: 1D lineouts for Λ_3^α and Λ_3^β initial bands in the corresponding regions. (D) Results of 1D semiclassical simulations. Relative to photoelectrons emitted from $2 \text{ \AA}$ below the surface, those emitted from $10 \text{ \AA}$ below the surface are delayed by 267 as. Inset: Profile of the dressing field strength normal to the surface (E_z) across the interface.

To physically interpret our measurements, we used a 1D semiclassical model (35) to calculate the RABBITT interferograms of photoelectrons with the same final energy but emitted from different depths (e.g., $2 \text{ \AA}$ and $10 \text{ \AA}$) below the surface to simulate photoelectrons with different IMFPs. This model considers the quantum phases accumulated as the photoelectrons scatter from the IR dressing field and crystal potential (see supplementary materials). The IR dressing field inside the metal is mostly screened (see supplementary materials and inset of Fig. 3D) and has negligible influence on photoelectrons as they travel to the surface (36). One-dimensional lineouts of the RABBITT oscillations are plotted in Fig. 3D for photoelectrons with a free-electron velocity corresponding to an energy of 25.5 eV inside the crystal. We find that the RABBITT oscillation traces of photoelectrons emitted $10 \text{ \AA}$ below the surface are delayed by 267 as relative to those corresponding to photoelectrons originating $2 \text{ \AA}$ below the surface; this is consistent with the measured lifetime difference between them. In turn,

this allows us to directly relate our time-domain measurements to the lifetimes and IMFPs of photoelectrons, which determine the surface and bulk contributions (1, 33).

Determining the IMFP involves selecting a photoelectron velocity to be used in calculating it. In a periodic crystal lattice, the elastic interaction with atoms strongly modifies the electron energy-momentum relationship, giving rise to the electronic band structure. It is generally believed that the velocity of photoelectrons can be represented by the group velocity of the corresponding final bands, which is given by the derivative of the energy with respect to the momentum wave vector $\mathbf{k}_\parallel$ (11, 13, 14). To determine the final-state group velocity, we used an ab initio calculation for the bulk band structure of Ni along the Γ -L direction, including the high-energy valence bands (~ 24 eV). We found that the final band involved in the resonant transition (highlighted in Fig. 2B) has a narrow bandwidth (~ 4 eV), consistent with our experimental spectra. The corresponding group velocity is given by $|\partial E_{\text{fin}}/\partial(\hbar\mathbf{k}_\parallel)| \approx 3.0 \text{ eV}\text{\AA}/\hbar$, which

is much smaller than the velocity of a free electron with the same kinetic energy ($\sim 19.1 \text{ eV}\text{\AA}/\hbar$). Using the calculated group velocity, we obtain an IMFP of at most $1 \text{ \AA}$, which is much smaller than values reported in other studies (37, 38). We believe that this discrepancy arises because the group velocity is not the transport velocity for high-energy photoelectrons. As pointed out in previous studies (34), high-energy (>20 eV) photoelectrons leave the crystal before they are subject to the influence of the crystal lattice, so they behave more like plane waves with a free-electron dispersion. By using the corresponding free-electron velocity in our analysis, we extract an IMFP of $\sim 6 \text{ \AA}$ for photoelectrons that are emitted on resonance, consistent with previous studies (29). In contrast, the IMFPs of photoelectrons from the Λ_3^α and Λ_1 bands, as well as those from the Λ_3^β band away from the spectral resonance, are estimated to be $\sim 3 \text{ \AA}$, manifesting their surface-emission nature.

Other important evidence that the band structure of the material strongly influences the photoemission lifetime can be seen from the angle

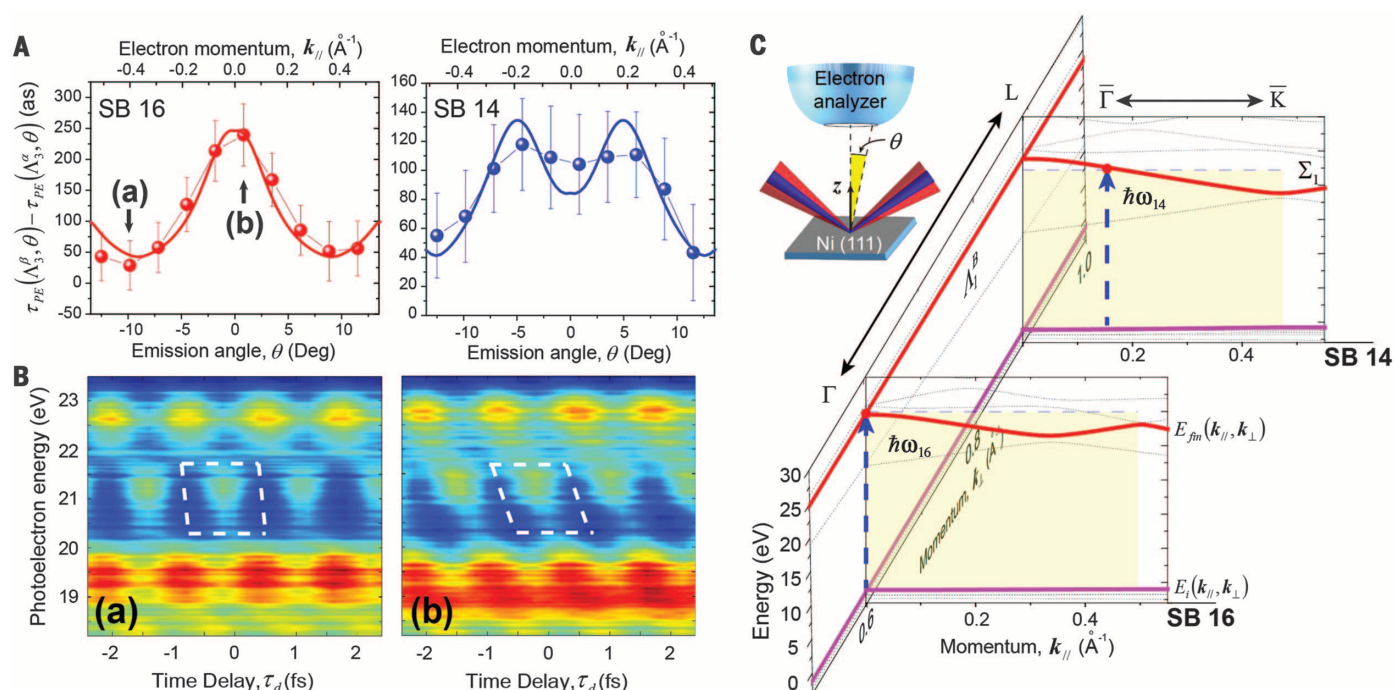


Fig. 4. Angle-dependent photoemission time delays. (A) Angle-dependent photoemission time delay $\tau_{PE}(\Lambda_3^B, \theta) - \tau_{PE}(\Lambda_3^A, \theta)$ for SB16 and SB14 obtained using s-polarized HHG. The experimental data are points; the solid lines are a fit to the final-state band structure obtained from our model and DFT calculations (see supplementary materials). Error bars represent SD of the time delays extracted from more than 200 individual scans. (B) Typical RABBITT interferograms for SB16 with emission angles [(a) and (b)] labeled in (A). The offset in oscillations is highlighted with white dashed boxes. (C) Illustration of direct transitions in the Γ - $\bar{K}$ direction for SB14 and SB16.

dependence of the lifetime as a function of electron transverse momentum $k_{\parallel}$. To cancel any time delays imposed by the incident and reflected laser fields (35, 36) and to extract the contribution due to band-structure effects, we used the RABBITT oscillations from the Λ_3^A band as the timing reference at different emission angles (θ) for each sideband (see supplementary materials). The angle-dependent results of $\tau_{PE}(\Lambda_3^B, \theta) - \tau_{PE}(\Lambda_3^A, \theta)$ are summarized in Fig. 4A for SB16 and SB14 (near the resonance). As shown in Fig. 4A, the time delay $\tau_{PE}(\Lambda_3^B, \theta) - \tau_{PE}(\Lambda_3^A, \theta)$ at SB16 reaches its maximum value of ~ 220 as at $\bar{\Gamma}$ point ($\theta = 0$), whereas it reduces to ~ 30 as when the emission angle approaches $\theta = \pm 15^\circ$. The overall trend is symmetric around the $\bar{\Gamma}$ point, which strongly suggests the band-structure origin of this angle-dependent photoemission time delay. The most interesting feature is that $\tau_{PE}(\Lambda_3^B, \theta) - \tau_{PE}(\Lambda_3^A, \theta)$ exhibits a double-peak shape at SB14 (Fig. 4A) as the time delay increases to its maximum on-resonance value at $\theta \approx \pm 6^\circ$ and then decreases for larger emission angles.

To quantitatively interpret this angle-dependent photoemission lifetime, we compared the predicted time delays associated with our model and DFT calculations (see supplementary materials) with the experimental data (Fig. 4A). Our results show that for SB16, the HHG photon energy closely matches the resonant excited state at the $\bar{\Gamma}$ point,

Because different photon energies are used for these two sidebands, different $k_{\parallel}$ along the Γ - $\bar{K}$ direction are assigned according to the band-mapping results in Fig. 2B. The initial and final bands are highlighted by thick solid lines; the binding energy of the initial band (purple) is corrected according to the binding energy obtained in our experiments. Transitions corresponding to sideband photon energies are labeled as dashed arrows. Inset: Experimental geometry. IR and HHG beams are focused onto a Ni(111) surface at a 45° incident angle; θ is assigned to the emission angle of photoelectrons relative to the sample normal direction ($\mathbf{z}$) along the $\bar{\Gamma}$ - $\bar{K}$ direction.

yielding a maximum time delay for $\theta = 0$. Moreover, the time delay monotonically decreases at larger emission angles, since final-state band dispersion causes the transition to be off resonance. On the other hand, for SB14, in which the photon energy is ~ 3.2 eV lower, the resonant transition is not accessible at the $\bar{\Gamma}$ point, but is on resonance and yields a maximum time delay at a $\sim 6^\circ$ emission angle (Fig. 4C). The key factor for this agreement is the dispersion of the Σ_1 final band along the $\bar{\Gamma}$ - $\bar{K}$ direction (with a group velocity of ~ 14 eV $\bar{A}/\hbar$), which determines the slope of the time delay as a function of θ .

Our results highlight the importance of the material band structure in determining photoemission time delays, which must also be taken into account even at higher photon energies. In the future, this approach can be used to experimentally access quasi-particle lifetimes, electron mean free paths, electron-electron scattering, and dynamical screening, all of which represent grand challenges for condensed matter theory. Moreover, other effects, including Cooper minima (39) and Fano resonances (40), could also lead to notable delays, making attosecond studies of metal valence bands a challenging but also a rich and interesting problem.

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ACKNOWLEDGMENTS

We thank A. Carr, P. Matyba, G. D. Mahan, G. B. Arnold, G. F. Mancini, H. X. Li, Z. Zhu and Y. Cao for helpful discussions. This work was done at JILA. The JILA authors gratefully acknowledge support from the National Science Foundation through the JILA Physics Frontiers Centers Program and a Gordon and Betty Moore Foundation EPIQS Award through grant GBMF4538. T.S. and M.Ma. gratefully acknowledge support from Air Force Office of Scientific Research under a Basic Research Initiative grant (AFOSR FA9550-12-1-0481)

and DOE-BES, the Division of Chemical Sciences (grant DE-FG02-05ER15731). The authors declare that they have no competing interests. H.K. and M.Mu. have a financial interest in a laser company, KMLabs.

SUPPLEMENTARY MATERIALS

www.sciencemag.org/content/353/6294/62/suppl/DC1
 Supplementary Text
 Figs. S1 to S9
 References (41–72)

13 March 2016; accepted 11 May 2016
 Published online 2 June 2016
 10.1126/science.aaf6793

MALARIA MOSQUITOES

A maleness gene in the malaria mosquito *Anopheles gambiae*

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The molecular pathways controlling gender are highly variable and have been identified in only a few nonmammalian model species. In many insects, maleness is conferred by a Y chromosome-linked M factor of unknown nature. We have isolated and characterized a gene, *Yob*, for the M factor in the malaria mosquito *Anopheles gambiae*. *Yob*, activated at the beginning of zygotic transcription and expressed throughout a male's life, controls male-specific splicing of the *doublesex* gene. Silencing embryonic *Yob* expression is male-lethal, whereas ectopic embryonic delivery of *Yob* transcripts yields male-only broods. This female-killing property may be an invaluable tool for creation of conditional male-only transgenic *Anopheles* strains for malaria control programs.

Animals have evolved a variety of mechanisms for sex determination. In insects, a common pattern requires a primary sex-determining signal that in early embryos activates a short cascade of sex-specifically spliced genes. The products of these genes modulate differentiation of an individual into either male or female, depending on the sex determination system (1). In the absence of the primary signal, a default pattern of gene splicing leads to the development of the opposite sex. Only the final element of the cascade, the *doublesex* gene, is well conserved, whereas upstream genes are highly evolutionarily labile (2) and are difficult to identify with comparative genomics tools.

Drosophila melanogaster has an XX/XY chromosomal sex determination system, in which a double dose of X chromosome-linked signal elements (XSE) represents the primary signal that initiates female-specific pre-mRNA splicing in a cascade of subordinate genes *sex lethal* (*Sxl*), *transformer* (*tra*), and *doublesex* (*dsx*) (3, 4). The resulting transcripts yield functional female-specific proteins, of which SXL regulates splicing of *tra*, and TRA, along with its

cofactor TRA2, promotes splicing of *dsx*. In males, a single dose of XSE is insufficient to initiate this female-specific cascade, and the three genes are spliced by a default male-specific mode, with only *dsx* encoding a functional protein. The male and female forms of DSX regulate sex-specific morphologies by modulating the expression of genes involved in downstream sexual differentiation processes.

The dipterans *Ceratitis capitata*, *Lucilia cuprina*, and *Musca domestica*, and the beetle *Tribolium castaneum*, also possess an XX/XY chromosomal system. However, in these insects an unidentified Y chromosome-linked M factor constitutes a primary signal that determines maleness (5–8). In none of these species is *Sxl* involved in sex determination. Instead, maternal *tra* mRNA is sufficient to direct default female development in the absence of the Y-linked factor, whereas in males the M may be preventing establishment of *tra* function by an unknown mechanism (9–12). The XX/XY system incorporating a dominant Y-linked M factor is common in many insect groups (13–15). However, with the exception of *Nix* (a homolog of *tra2*) from a mosquito *Aedes aegypti* (16), genes encoding M factor have remained enigmatic.

In anopheline mosquitoes, the only described element of the (morphological) sex determination cascade is *dsx* (17). To elucidate the initial steps of sex determination in the African malaria mosquito, *Anopheles gambiae*, we analyzed transcriptomes of male and female embryos (18), whose sexual

identity was determined by polymerase chain reaction (PCR) (fig. S1). Separate pools of mRNA were sequenced, yielding ~500,000 Roche 454 reads from each sex. From the male pool, 21 reads uniquely mapped to the previously characterized scaffold AAAB01008227 derived from the *A. gambiae* Y chromosome (19).

The corresponding gene (hereafter called *Yob*) consists of three exons and produces transcripts differing in size because of intron retention (fig. S2). *Yob* likely represents the same gene as *gYG2* (20), which partially overlaps *Yob*, but its annotation lacks over half of the *Yob* gene sequence. Among the *A. gambiae* Y-linked genes, only the *Yob/gYG2* locus is Y-linked across the examined species from the *A. gambiae* complex (21), indicative of an important sexual identity function. Consistent with the chromosomal location, transcription of *Yob* is limited to males. Transcription begins in embryos between 2 and 2.5 hours after oviposition, before blastoderm formation (22) and expression of other Y-chromosome genes (20, 21), and continues throughout the life of the mosquito (Fig. 1A and fig. S3A). Onset of the *Yob* transcription is nearly contemporaneous with that of orthologs of *even skipped* (AGAP010279) and *hunchback* (AGAP010777) (fig. S3B), whose transcripts mark the beginning of zygotic expression in *Drosophila* (23, 24). We

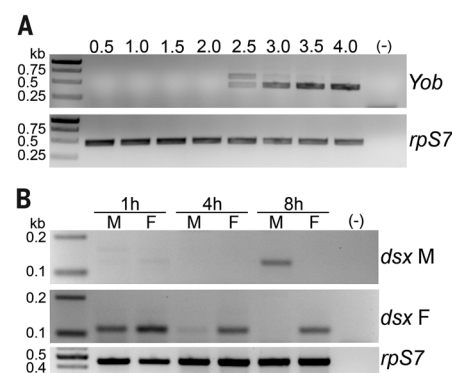


Fig. 1. Transcription of *Yob* and *dsx* in *A. gambiae* early embryos. (A) Onset of zygotic *Yob* transcription. (B) Establishment of the sex-specific expression pattern of *dsx*. Time of RNA sample collection (in hours after oviposition) are shown above gel images; (–) negative control; ribosomal protein S7 (*rpS7*) transcript levels were used as a gel loading control.

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Direct time-domain observation of attosecond final-state lifetimes in photoemission from solids

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Science **353** (6294), 62-67.

DOI: 10.1126/science.aaf6793 originally published online June 2, 2016

Clocking electrons as they exit a metal

Einstein earned his Nobel Prize for a quantum-mechanical explanation of electron ejection from metals by light. More than a century later, attosecond spectroscopy has let researchers explore that process in real time. Tao *et al.* used attosecond pulse trains to distinguish the dynamics of electrons excited from a nickel surface into discrete states versus free space (see the Perspective by Bovensiepen and Liggues). They succeeded in resolving a time delay of ~200 as that was associated with excitation into unoccupied band states.

Science, this issue p. 62; see also p. 28

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