

Far above bandgap photonics: attosecond dynamics of highly excited electrons in materials

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ABSTRACT

Tabletop-scale coherent EUV generated through high-harmonic generation (HHG) produces light in the form of an attosecond pulse train that uniquely combines characteristics of good energy resolution ($\approx 100\text{-}300\text{meV}$) with sub-fs time resolution. This makes HHG an ideal source for studying the fastest dynamics in materials. Furthermore, using angle-resolved photoemission spectroscopy (ARPES), it is possible to extract detailed information about electron dynamics over the entire Brillouin zone. In recently published work, we combined HHG with ARPES to identify a sub-femtosecond excited-state lifetime for the first time. Photoemission occurs as a three-step process: 1) An electron is photoexcited from the valence band to far above the Fermi energy; 2) it transports to the surface, and 3) it overcomes the work function and exits. If the electron is promoted into a highly-excited unoccupied band in the material (as opposed to a free-electron-like state), we observe the electron emission lifetime to increase in a measurable way—the Ni band 22 eV above the Fermi level has a lifetime of 212 ± 30 attoseconds. Furthermore, by comparing photoemission from Cu and Ni, we reveal the influence of attosecond-timescale electron screening vs scattering by the electrons near the Fermi surface. This work for the first time demonstrates the relevance of attosecond spectroscopy to the study of intrinsic properties and band structure in materials, as opposed to the strong-field induced dynamics studied extensively to-date.

Keywords: Materials, Ultrafast phenomena, Angle-resolved photoemission, Time-resolved photoemission

1. INTRODUCTION

Tabletop high-harmonic generation (HHG) produces attosecond pulse trains with the unique characteristics of good energy resolution ($\approx 100\text{-}300\text{meV}$) and sub-fs time resolution, making HHG an ideal source for time-resolved photoemission studies [1,2]. In combination with angle-resolved photoemission spectroscopy (ARPES), it is now possible to extract detailed information about electron dynamics over the entire Brillouin zone [3]. In recent work [4] taking advantage of laser-assisted photoemission [5], we harnessed 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 Ni(111). A significant increase in lifetime of 212 ± 30 as occurs when the final state coincides with an unoccupied excited state in the Ni band structure. Moreover, a strong dependence of lifetime on emission angle is directly related to the final-state band dispersion as a function of electron transverse momentum.

In further work, we have directly extracted the time-domain influence of scattering and screening on the ejected photoelectrons by the electrons near the Fermi level. By taking advantage of the polarization- and angle-resolved sensitivity of photoemission, we can clearly distinguish different photoelectron lifetimes from individual occupied valence bands of Ni and Cu with unprecedented energy and time resolution. This allows us to distinguish different attosecond electron screening and scattering dynamics in Ni(111) and Cu(111)— in the time domain for the first time. We note that our results are distinctly different from previous time-delay measurements in solids, in which multiple valence bands were probed using broad bandwidth isolated attosecond pulses, thus necessarily integrating over multiple bands and photoemission features [2].

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2. Methodology

This work uses a system consisting of a high-harmonic (HHG) source driven by a ti:sapphire laser, and a UHV chamber with a hemispherical analyzer. The physics behind the experiment is explained in Fig. 1A. A comb of linearly polarized high harmonics is focused collinearly with infrared laser pulses (~ 26 fs, 780 nm) onto an atomically clean Ni(111) or Cu(111) surface. We use the entire spectrum of harmonic orders (11th – 41st) as illumination, and any band within the material thus manifests itself as a ladder of direct photoemission bands (Fig. 1B). Addition of the 780 nm laser results in phase-locked laser-assisted photoemission that modulates the photoelectron spectra as a function of relative delay between the EUV pump and IR probe fields (τ_d). This allows us to extract photoelectron dynamics on attosecond time scales and \AA length scales, by analyzing the attosecond-time-scale beating due to the coherent interference of two-photon quantum pathways that lead to the same final photoelectron energy (in a technique combining laser-assisted photoemission and RABBITT) [5-7].

3. Results

We first probed the band structure of Ni(111) by studying how the static photoelectron spectra depend on the EUV photon energy and polarization, as shown in Fig. 1B. Due to photoemission selection rules, we can unambiguously assign the two photoemission peaks that are excited by s-polarized light to the two valence bands with Λ_3 symmetry (Λ_3^α and Λ_3^β). Specifically, the additional spectral weight observed for p-polarized light results from the Λ_1 initial band. Assuming direct transitions to a free-electron-like final state, we can map the momentum in the surface-normal direction for different photon energies. The extracted band structure, compared to DFT calculations, is plotted in Fig. 1C. The most pronounced feature of Fig. 1B is the enhancement photoemission cross section of Λ_3^β when excited by 15th order HHG photons. This spectral resonance is due to direct interband transitions from the Λ_3^β initial band to the high-energy Λ_1^β final band located at ~ 24 eV above the Fermi level, as indicated by the blue arrow in Fig. 1C. The increase in photoemission intensity as a result of this final-state resonance results from an increased lifetime, and consequently increased escape depth for the final-state electron. The energy-dependent photoemission intensity of the Λ_3^β band is summarized in Fig. 2B, together with a fit to a Lorentzian function with width $\gamma = 3.68 \pm 0.88$ eV. This energy bandwidth corresponds to a time-bandwidth limited lifetime of $\tau_{\text{spec}} = 179 \pm 43$ as. However, the origin of the broadening as an actual increase in the lifetime of these electrons is not clear until measured.

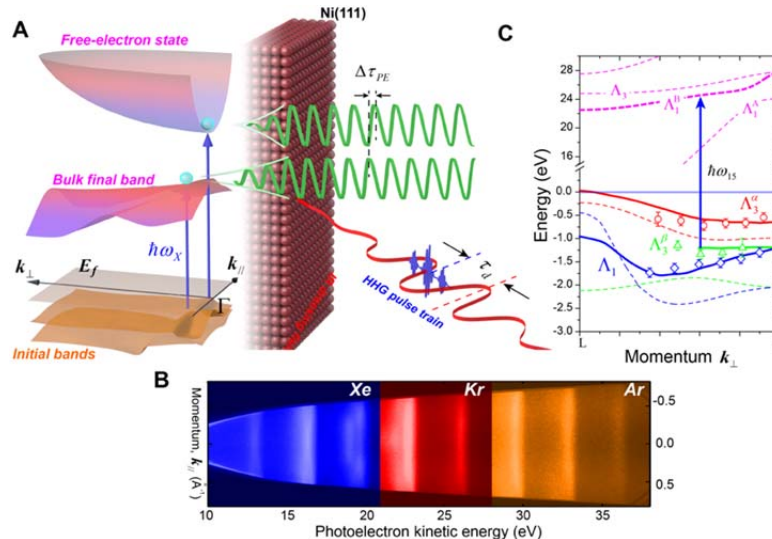


Fig. 1. (A) Using HHG, different photoelectron final states can be accessed, corresponding to free-electron-like states or excited states in the band structure. (B) Static ARPES excited by s-polarized HHG generated in different gas targets. (C) Band structure along Γ -L extracted from our data (open symbols) compared to previous experiments (solid lines) and DFT calculations (dashed lines). The final state resonance in (B) is highlighted.

By using the phase-locked laser-assisted photoemission, we can directly measure photoemission from the surface as a function of time. To take into account the influence of any chirp in the relative time of emission of the harmonics themselves, we use the non-resonant photoemission from Λ_3^α band as the timing reference, and determine the relative photoemission delay of photoemission from the resonant $\tau_{PE}(\Lambda_3^\beta) - \tau_{PE}(\Lambda_3^\alpha)$ and non-resonant $\tau_{PE}(\Lambda_1) - \tau_{PE}(\Lambda_3^\alpha)$ channels. We first s-polarized HHG fields. In Fig. 2C, we plot the experimental RABBITT interferograms obtained by integrating each time-resolved photoelectron spectra over $\pm 2.5^\circ$ around the Γ point. It clearly shows that photoelectrons from the Λ_3^β band are significantly delayed for sideband 16. This time delay gradually vanishes at increasing and decreasing photon energies. The results of $\tau_{PE}(\Lambda_3^\beta) - \tau_{PE}(\Lambda_3^\alpha)$ are summarized in Fig. 2A. We find that the observed maximum in time delay coincides with the spectral peak at the same photon energy (Fig. 2B). Most importantly, the directly-observed time delay, $\tau_{\text{chron}} = 212 \pm 30$ as, agrees with τ_{spec} from the spectral resonance, within error bars (Fig. 2A and B). This result indicates that the spectral peak observed is the result of a resonant lifetime of the highly-excited state in a solid—indeed the first direct observation of a non-trivial attosecond time-scale *event*, as defined by an intrinsic process with a beginning and end and a quantifiable lifetime [4]. Other work has only measured the comparative timing of different long time-scale events.

Compared to Ni, Cu also has an fcc lattice structure, with similar lattice constants. The electronic structure of Cu(111) is also close to Ni(111) (Fig. 1C), but with the Fermi level approximately 2.2 eV higher, due to one more *d* electron in Cu. Because of the difference in Fermi level, Ni has a half-filled *d* band, while Cu has a filled one [8]. We repeated the laser-assisted photoemission measurements on Cu(111); the lifetime of photoelectrons from Cu Λ_3^β band are plotted in Fig. 3A [9]. Similar to Ni(111), a clear increase in the photoelectron lifetime (~ 300 as) due to final-state resonance can be observed around ~ 25.6 eV, which is in good agreement with the linewidth observed in the photoemission yield.

Figure 3 also shows that the time of photoemission for the Λ_3^β band of Cu is ~ 100 attosecond longer than the same band for Ni in the normal-emission geometry, both on- and off-resonance region. This effect cannot be explained by the *final-state* bands of Cu(111), but rather by the screening and scattering of the photoelectrons on exiting the surface. More importantly, the off-resonance photoelectron lifetime of Cu time is in good agreement with a free-electron gas (FEG) model. This is different for Ni, which is ~ 100 as shorter. This result is distinctly different from the photoelectron lifetimes observed at low energies ($< 3\text{eV}$ above Ef) [9]. By comparing the lifetimes obtained from Ni and Cu, we find the photoelectron emission time for Ni is much shorter. This difference can be attributed to the half-filled *d* band in Ni, which enhances electron-electron scattering [10], as shown in Fig. 3B. Because of the enhanced scattering, the electrons are coming from a shallower depth in the material and thus escape the surface more-immediately.

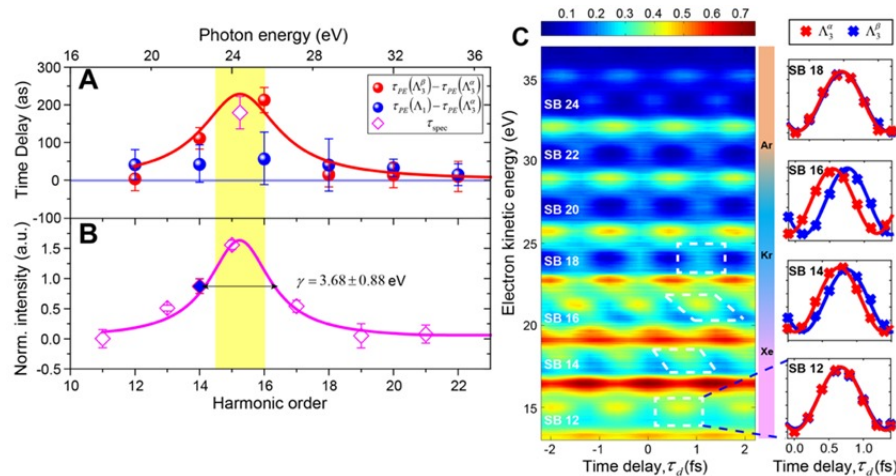


Fig. 2. (A) Measured timing of photoemission $\tau_{PE}(\Lambda_3^\beta) - \tau_{PE}(\Lambda_3^\alpha)$ and $\tau_{PE}(\Lambda_1) - \tau_{PE}(\Lambda_3^\alpha)$ from bands of Ni(111). (B) Spectral intensity of the Λ_3^β initial band as a function of photon energy. The pink line represents a Lorentzian fit, yielding a linewidth of $\gamma = 3.68 \pm 0.88$ eV. (C) 2D map of photoelectron yields as a function of photoelectron energy and pump-probe time delay τ_d , excited by s-polarized HHG. 1D lineouts for Λ_3^α and Λ_3^β initial bands in the corresponding regions are plotted in the right panel.

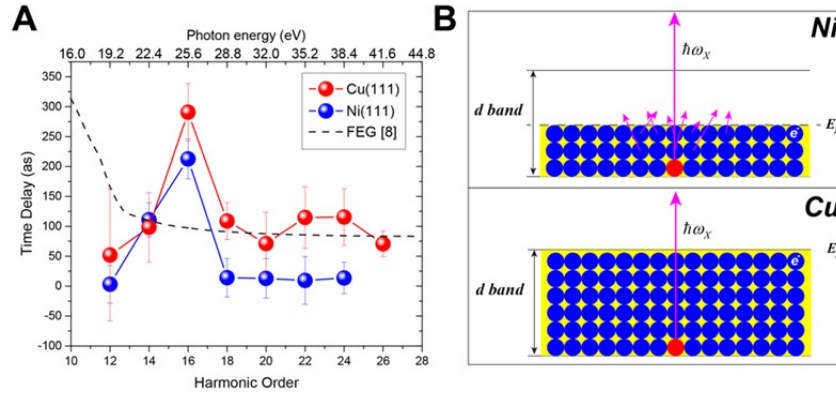


Fig. 3. (A) Lifetime of photoelectrons from d band of Cu(111) and Ni(111) surfaces. The dashed line is the results from FEG model [6]. (B) illustration of the electron-electron scattering in half-filled (Ni) and fully-filled (Cu) d band metals. Half-filled Ni has more unoccupied states in d band, resulting in additional electron-electron scattering channels in the photoemission process.

4. Conclusions

Our results highlight the importance of the material band structure on the timing of photoelectron emission from a surface, and represents the first experimental study of the effects of electron-electron scattering and dynamic screening in metals on attosecond time scales. Thus, it opens new possibilities for ultrafast studies of materials.

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