Distinguishing attosecond electron–electron scattering and screening in transition metals


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Electron–electron interactions are the fastest processes in materials, occurring on femtosecond to attosecond timescales, depending on the electronic band structure of the material and the excitation energy. Such interactions can play a dominant role in light-induced processes such as nano-enhanced plasmonics and catalysis, light harvesting, or phase transitions. However, to date it has not been possible to experimentally distinguish fundamental electron interactions such as scattering and screening. Here, we use sequences of attosecond pulses to directly measure electron–electron interactions in different bands of different materials with both simple and complex Fermi surfaces. By extracting the time delays associated with photoemission we show that the lifetime of photoelectrons from the d band of Cu are longer by ~100 as compared with those from the same band of Ni. We attribute this to the enhanced electron–electron scattering in the unfilled d band of Ni. Using theoretical modeling, we can extract the contributions of electron–electron scattering and screening in different bands of different materials with both simple and complex Fermi surfaces. Our results also show that screening influences high-energy photoelectrons (~20 eV) significantly less than low-energy photoelectrons. As a result, high-energy photoelectrons can serve as a direct probe of spin-dependent electron–electron scattering by neglecting screening. This can then be applied to quantifying the contribution of electron interactions and screening to low-energy excitations near the Fermi level. The information derived here provides valuable and unique information for a host of quantum materials.

Significance

Electron–electron interactions are among the fastest processes in materials that determine their fascinating properties, occurring on attosecond timescales on up (1 as = 10−18 s). The recent development of attosecond angle-resolved photoemission spectroscopy (atto-ARPES) using high harmonic generation has opened up the possibility of probing electron–electron interactions in real time. In this paper, we distinguish electron–electron screening and charge scattering in the time domain in individual energy bands within a solid. These results open up new possibilities for probing fundamental electron–electron interactions in a host of materials including magnetic, superconducting, and advanced quantum materials.

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from the surface of a material. The RABBITT method (28–30) (reconstruction of attosecond beating by interference of two-photon transitions) has also been very successfully applied to atomic and material samples, where quantum interferences between neighboring two-photon transition pathways can modulate these sidebands as a function of the relative time delay between the HHG pump and IR probe pulses: Any time delay in photoemission from different initial or final states will lead to a phase delay in the interferograms (28, 31).

Very recently, by combining attosecond HHG pulse trains with time- and angle-resolved photoemission (ARPES), we demonstrated the ability to resolve attosecond electron dynamics in different individual final states in materials, with ±20-as time resolution. We used attosecond-ARPES to measure a photoelectron lifetime of ~210 as, which was measured for a final state that coincides with an unoccupied excited state in the band structure of Ni (32, 33). We also showed that the photoelectron lifetime sensitively depends on the band dispersion of the material (i.e., the photoelectron emission angle). That work demonstrated that atto-ARPES can probe intrinsic properties of materials. A great advantage of atto-ARPES is that it achieves good energy resolution (<0.3 eV), to enable band-selectivity as well as angle-resolved studies, combined with the ability to change the HHG polarization, which are all critical for harnessing photoemission selection rules. This makes it possible, in principle, to selectively capture electron dynamics in different initial or final bands in many materials, because the typical separation between neighboring valence bands is <1 eV.

Here, we use sequences of attosecond pulses coupled with time-, energy-, polarization-, and angle-resolved photoelectron spectroscopy (atto-ARPES) to distinguish electron–electron interactions for electrons excited from different initial bands during the photoemission process. The high photoelectron energies ($E - E_F > 20$ eV), combined with attosecond time resolution, allows us to independently measure electron–electron scattering in metals with simple and complex Fermi surfaces, without the influence of screening. To achieve this, we extract the time delays associated with photoemission from individual valence bands in Ni(111) and Cu(111). We find that the lifetime of photoelectrons from a $d$ band of Cu is longer by ~100 as compared with the lifetime of those from the same band of Ni. We attribute this difference to the fact that the $d$ band in Ni is not fully occupied, resulting in enhanced electron–electron scattering and hence a shorter photoelectron lifetime (Fig. 1A). Then, using a spin-dependent scattering model to compare electron–electron interactions in Cu and Ni, we show that the photoexcited electron lifetime in Ni involves enhanced electron–electron scattering throughout the energy range from 0.5 eV to 40 eV. Moreover, because screening influences high-energy photoelectrons ($\sim 20$ eV) significantly less than low-energy photoelectrons (20, 22), they can serve as a direct probe of spin-dependent electron–electron scattering. The resulting Coulomb interaction information we extract is applicable across a broad energy range—from the Fermi energy on up—and can separate and quantify the contribution of screening to low-energy excitations, where both screening and scattering contribute to the signal. Our atto-ARPES approach

![Fig. 1.](image)

**Fig. 1.** Influence of the material band structure on attosecond electron dynamics. (A) Illustration of the photoemission process from Cu(111) and Ni(111) surfaces. Using HHG pulse trains, photoelectrons are excited either from a Cu(111) or Ni(111) surface. Due to the different band structure in these two materials, photoelectrons from Ni(111) experience more electron–electron scattering, which reduces the lifetime of photoelectrons by 100 as compared with Cu(111) as they escape from the material surface. The enhanced scattering also reduces the inelastic mean free path. (B) Band structure of Cu(111) along the $\Gamma$–L direction for DFT calculation (dashed lines), compared with experimental results of band mapping (open symbols; see S3. Static HHG Photoelectron Spectra Analysis of Cu(111)). The interband transition $\Delta_5^+ \rightarrow \Delta_1^+$ is highlighted by the blue arrow, which corresponds to the spectral enhancement of the photoelectron spectrum at harmonic orders $\omega_{15}$ and $\omega_{17}$ as shown in D. (C) Band structure of Cu along the $\Gamma$–L direction for Cu(111), and $\Gamma$–X for Cu(100), showing the evolution of the $\Lambda$ bands to $\Delta$ bands across the $\Gamma$ point. Due to the photoemission selection rules (34), transitions from $\Delta_5^+$ bands are forbidden in the normal emission geometry from Cu(100). The colored areas indicate the perpendicular momentum regions measured in our experiments. Blue arrows indicate the direction in which the HHG photon energy $(\omega_{15})$ increases. (D) Static ARPES spectra excited by an s-polarized HHG field, generated using different noble gases (Xe, Kr, and Ar). Photoemission from two initial bands ($\Delta_5^+$ and $\Delta_1^+$) can be clearly distinguished.
thus makes it possible to independently distinguish the fastest electron–electron scattering and screening dynamics in metals on attosecond time scales, providing valuable information for a host of magnetic materials.

**Experiment**

The concept behind our study is shown in Fig. 1A. Most of the output of a near-IR femtosecond laser is used to generate high harmonics in various noble gases (Xe, Kr, and Ar), which are then focused onto single crystal Cu(111) and Ni(111) surfaces. In the spectral domain, these harmonics span ~15–45 eV (corresponding to $11 \omega_{27} \omega$), each with a linewidth of ~0.3 eV, and separated by $2\omega_{27} \approx 3.2$ eV, where $\omega_{27}$ is the frequency of the driving IR laser. The residual phase-locked laser field is used to simultaneously irradiate the material together with a high harmonic field, which induces sidebands of the photoelectron peaks corresponding to the absorption or emission of an IR laser photon. The photoelectron spectrum is then collected using a hemispherical photoelectron analyzer (Specs Phoibos 100). Note that it has already been shown that RABBITT and attosecond-streaking yield the same temporal information about the photoemission process (31), whereas ARPES adds significant advantages of band specificity (33). Moreover, by simultaneously measuring two photoelectron wavepackets from different initial states excited by the same harmonic orders we can eliminate the influence of the HHG phase (28).

The band structure of Cu(111) is plotted in Fig. 1B. Similar to Ni(111) (33), there are three valence bands along the $\Gamma$–$X$ direction of Cu(111): the $\Delta^*_x$ band with a binding energy of ~2.8 eV, $\Delta^*_y$ with ~3.5 eV, and $\Delta_1$ with ~3.8 eV. By using a s-polarized HHG field we can exclusively excite photoelectrons from the $\Delta^*_y$ and $\Delta^*_x$ bands (34, 35). The band-mapping results are also plotted in Fig. 1B, which shows a strong dispersion of the photoemission peaks as a function of photon energy, indicating that photoemission from bulk states contributes to the signal [S3. Static HHG Photoelectron Spectra Analysis of Cu(111)]. In our experiments, photoemission from the Cu(100) surface is also measured, which corresponds to a band structure along the $\Gamma$–$\chi$ direction (Fig. 1C). As shown in Fig. 1D, photoemission dipole transitions couple different initial and final states (bands) of Cu(111) that can be selected using different harmonic orders and polarizations, by harnessing photoemission selection rules (34, 35). To distinguish the influence of wavefunction localization (excited bulk states vs. free-electron final states) as well as the influence of the fundamental electron interactions on the photoelectron lifetimes, we first identify where the final-state resonances occur in Cu(111). The spectral intensity of $\Delta^*_x$ band photoelectrons excited by the s-polarized HHG field is plotted in Fig. 2A. A strong enhancement of the spectral intensity peaked at the resonant photon energy of ~26 eV can be observed, which can be attributed to the interband transition from the $\Delta^*_x$ initial band to the excited $\Delta^*_x$ final band (Fig. 1B). The Lorentzian linewidth is $\Gamma_{\text{spec}} = 2.13 \pm 0.65$ eV (Fig. 2A), which is consistent with the linewidth recently obtained using high-resolution photoemission at a synchrotron radiation source (36). The predicted final-state lifetime is therefore given by $\tau_{\text{spec}} = h/\Gamma_{\text{spec}} = 309 \pm 94$ as.

The photoemission time delay $\tau_{\text{PE}}(\Delta^*_x) - \tau_{\text{PE}}(\Delta^*_y)$ at the $\Gamma$ point can be extracted from the RABBITT interferogram (Fig. 2D) and is summarized in Fig. 2B. The quantum paths involved in RABBITT interference are illustrated in Fig. 2C. These interferograms (Fig. 2D) were obtained by integrating the photoelectron spectra over $\pm 2.5^\circ$ around the $\Gamma$ point (normal-emission direction). Comparing Fig. 2A and B, we find that $\tau_{\text{PE}}(\Delta^*_x) - \tau_{\text{PE}}(\Delta^*_y)$ at the $\Gamma$ point reaches its maximum value $\tau_{\text{chron}} = 291 \pm 48$ as at the resonant photon energy for the interband transition $\Delta^*_y \rightarrow \Delta^*_x$ in Fig. 1B. This is in good agreement with $\tau_{\text{spec}} \approx 309 \pm 94$ as. This agreement indicates that the lifetime of photoelectrons emitted from the initial $\Delta^*_y$ band [$\tau_{\text{PE}}(\Delta^*_y)$] is short at the $\Gamma$ point. Considering the fact that the spectral intensity of $\Delta^*_y$ is a smooth function of photon energy (Supporting Information, Fig. S4), it allows us to directly assign the measured time delay to the lifetime of photoelectrons from the $\Delta^*_y$ band. Compared with Ni(111) (33), the resonant linewidth from the initial $\Delta^*_y$ band in Cu is narrower, which is consistent with the longer lifetime measured in the time domain (291 ± 48 as for Cu vs. 212 ± 30 as for Ni).

For photoemission through free-electron final states (away from any final-state resonances, > 25 eV in Fig. 3A), we find that the photoelectron lifetime from the $\Delta^*_x$ band of Cu(111) is ~ 100 as in the normal-emission geometry. Moreover, this lifetime is a smooth function of the final-state energy (Fig. 3A). The associated time delay can be clearly seen in the experimentally measured interferograms of Cu(111) as an obvious phase shift in the oscillations of the RABBITT quantum interferences (Fig. 3B), which interestingly is absent in Ni(111) for free-electron final states (33). We note that we can exclude the possibility that the finite photoelectron lifetime in this energy range in Cu(111) is caused by another final-state resonance because we did not observe any photoelectron yield enhancement in this energy range (Fig. 2A), and because it exhibits little momentum (angle) dispersion— unlike the lifetime on resonance (Fig. 3C).

To further reinforce this conclusion, we also measured the photoemission time delay between the $\Delta_x$ and $\Delta_1$ bands along the $\Gamma$–$\chi$ direction for Cu(100) as the two $\Delta_1$ bands cross the $\Gamma$ point of the Brillouin zone (BZ) [Fig. 1C; see S2. Static ARPES Spectra of Cu(111) and Cu(001) for more details]. As shown in Fig. 2B, a similar lifetime difference between $\Delta_1$ and $\Delta_1$ band photoelectrons was measured on the Cu(100) surface when there is no spectral resonance. Excluding final-state effects, the ~100 as lifetime difference of photoelectrons from the $\Delta^*_x$ band for Cu(111) and Ni(111) must be attributed to differences in the fundamental electron–electron interactions experienced by the high-energy photoexcited electrons during photoemission from these two materials.

**Discussion**

The photoexcited electron lifetime for free-electron final states is mainly determined by the competition between dynamic screening and inelastic electron–electron scattering during the photoemission process (18). This is because for highly excited electronic states (> 20 eV) other decay channels, including scattering with photoholes, phonons, and impurities, are expected to have negligible contributions. In Fig. 3A we compare our measured photoelectron lifetime from the $\Delta^*_x$ band of Cu to two empirical models [Goldmann et al. (37) and Eberhardt and coworkers (36)] that are based on bulk excited-state linewidths, as well as a free-electron gas (FEG) model with $\tau_{\text{FEG}} = 2.67$ for Cu (18), where $\tau_{\text{FEG}}$ is the electron-density parameter defined for an electron density $n$ by $n = 3/(4\pi r_{\text{FEG}}^3)$. As shown in Fig. 3A, both empirical models agree well with the photoelectron lifetime on resonance (SB16) as expected; however, they overestimate the photoelectron lifetime off-resonance. This is not surprising—the Goldmann and Eberhardt models are derived from a linewidth analysis of photoemission and inverse photoemission experiments (36, 37) that are mainly based on contributions from resonant (bulk final state) excitations. Compared with steady-state photoemission and inverse photoemission studies, our time-domain approach has unique advantages that allow us to measure the intrinsic high-energy photoelectron lifetime at arbitrary energies (including transitions both on and off final-state resonance). Note that the FEG model cannot reproduce the photoelectron lifetime on resonance, which is also not surprising because it does not account for the real band structure of the material. Most interestingly, the FEG model matches the off-resonance (i.e., free-electron final-state) lifetime measured on Cu(111) very well, but not for Ni(111), which is ~100 as shorter. Note that this trend is very different from the hot-electron lifetimes measured at low energy (< 3 eV above $E_F$), which exhibit a strong...
deviation from the FEG model due to the added presence of screening of d-band electrons (17, 19).

The absence of electron screening effects in high-energy photoemission can be understood by considering two different aspects. First, screening of d band electrons can be estimated by considering an effective dielectric constant \( \varepsilon_d = 1 + \delta\varepsilon_d \), which is induced by the polarizable background of d electrons. At low energies, the corrected lifetime is larger than the value predicted by the FEG model by \( \sqrt{\varepsilon_d} \) (38–40). As pointed out by Quinn (41, 42), \( \delta\varepsilon_d \) reduces as a function of excitation photon energy. As a result, the variation of the photoelectron lifetime due to d-electron screening is estimated to be only a few percent of the FEG lifetime at energies \( \gtrsim 20 \) eV (S8. Approximate Estimate of d-Electron Screening). Second, on \( \sim 100 \)-as time scales, we also need to consider the dynamics of electron screening in metals. As shown in previous theoretical studies, the buildup of charge screening in metals is not instantaneous but takes approximately half of a plasma period to fully develop (43), which corresponds to \( \sim 200 \) as in both Cu and Ni. Because the off-resonance photoelectron lifetimes are much less than this, it seems that photoelectrons from Cu (and Ni) escape before dynamic screening can influence the photoelectron lifetime in this energy range. As a result, dynamic electron screening has negligible influence on the photoelectron lifetimes at energies \( \gtrsim 20 \) eV.

However, the \( \sim 100 \)-as lifetime difference between photoelectrons from the d bands of Cu and Ni can be attributed to the differences in the band structure of these materials, which results in different electron–electron scattering rates between photoelectrons and other electrons in the conduction bands during photoemission. Here, we consider a high-energy photoexcited electron with energy \( E \) above \( E_F \). This electron decays into a lower energy state \( E' \) by exciting one of the other electrons in the band (a scattering partner) from its original state \( \varepsilon \) into an unoccupied state above \( E_F \), \( \varepsilon + \Delta \), where \( \Delta = E - E' \) is the energy transfer (Fig. 44). We note that the scattering process illustrated in Fig. 44 is responsible for removing photoelectron signal from our measurement. Thus, the experimentally measured photoelectrons are those that escape without scattering; nevertheless,
where $\beta$ and $\sigma$ designate the spin (up $\uparrow$ or down $\downarrow$) and orbital that $\alpha$ or $d$-like wavefunction of the scattering partners and the photoexcited electrons, respectively, and

$$\rho_\omega^{\sigma\alpha} (E) = [1 - f(E)] \rho_\omega^{\sigma\alpha} (E)$$

$$\rho_\omega^{\sigma\alpha} (E) = f(E) \rho_\omega^{\sigma\alpha} (E),$$

where $f(E)$ is the Fermi–Dirac distribution function and $\rho_\omega^{\sigma\alpha} (E)$ is the spin- and orbital-dependent density of states (DOS) of the $\sigma$ orbital that is obtained from a density-functional theory (DFT) calculation (Fig. 4C, Inset). We note that because the unoccupied states above the Fermi energy in Ni are dominated by electronic states with minority-spin polarization (1), spin-dependent scattering needs to be taken into account, which results in spin-dependent excited-electron lifetime in the ferromagnetic materials such as Ni (5, 6, 46). Here $M_m$ is the spin-dependent, crystal momentum- and orbital-averaged Coulomb matrix element, assuming $M_1 = M_1$ and $M_1 = M_1$ (see 57. Spin-Dependent Scattering Model for more details). Indeed, as shown in Fig. 3C, we verified experimentally that the assumption of a momentum-averaged Coulomb matrix element $M$ is valid, as originally suggested by Berglund and Spicer (44). Similar models have also been successfully used to explain the hot-electron lifetimes of intermediate states measured using time-resolved two-photon photoemission (Tr-2PPE) (6, 46). Assuming $\rho_1 = \rho_1 = \rho$ and $M_1 = M_1 = M$, Eq. 1 is simply reduced to

$$\frac{1}{\tau(E)} = \frac{1}{\tau(E_F)} \left[ E - E_F \right]^2,$$

which is the well-known $(E - E_F)^2$ scaling of hot-electron lifetimes excited close to the $E_F$ (44).

We first evaluate the influence of the DOS on the available phase space for scattering by assuming $M_1 = M_1 = 1.0$ in Eq. 1. As shown in Fig. 4B, Inset, the phase space increases monotonically as a function of the photoexcited electron energy above $E_F$ for both Ni and Cu, and indeed the phase space of Ni is larger than that of Cu in the energy range of our experiments, indicating that a higher scattering rate and a shorter photoelectron lifetime would indeed be expected. The additional phase space of Ni is dominated by the unoccupied DOS above $E_F$, as evidenced by the fact that the available phase space of Ni moves closer to Cu as its DOS is down-shifted by 1.8 eV to artificially remove the peaked unoccupied DOS (dashed line in Fig. 4B).
photoelectrons and is close to that observed in Cu, whereas the low-energy data (0.5–3 eV) are measured using Tr-2PPE method, extracted from ref. 3 for Cu and ref. 6 for Ni. The high-energy data (15–40 eV) are directly measured in our experiment using atto-ARPES. The data that overlap final-state resonances in both materials are represented by crosses to distinguish them from the off-resonant results of interest here. The yellow area estimates d-electron screening effects by considering the optical constants of Cu (47). The experimentally measured low-energy electron lifetime approaches the bare electron–electron scattering limit (solid blue line, \( M = 1.8 \) for Ni) at an energy \( E_{\text{crit}} \sim 3 \) eV. (Inset) The phase space of the two materials calculated from Eq. 1, assuming \( M^{\text{Cu}} = M^{\text{Ni}} = 1.0 \). The blue dashed line (Ni, \( \Delta \text{DOS} \)) is the results with the DOS of Ni downshifted by 1.8 eV. (C) Lifetime ratio \( \tau_1/\tau_\text{f} \), as a function of excited electron energy \( (E - E_F) \) for Ni obtained using Eq. 1. (Inset) Spin and orbital-dependent DOS of Ni and Cu obtained from DFT calculations.

Fig. 4. Spin-dependent model of electron–electron scattering. (A) Illustration of the electron–electron scattering process described by Eq. 1. The photoexcited electron (red circle) can decay by exciting another unexcited electron (blue circle) to a state above \( E_F \). \( M^{(\sigma \sigma)}(E - E') \) is the Coulomb matrix element, which we find is mostly constant for Cu (at 1.4) across a broad energy range but varies for Ni due to stronger screening at low energies. (B) Comparison between the spin-dependent scattering model [red (Cu) and blue (Ni)] and the experimentally measured lifetime of photoexcited electrons in Cu and Ni. The low-energy data (0.5–3 eV) are measured using Tr-2PPE method, extracted from ref. 3 for Cu and from ref. 6 for Ni. The high-energy data (15–40 eV) are directly measured in our experiment using atto-ARPES. The data that overlap final-state resonances in both materials are represented by crosses to distinguish them from the off-resonant results of interest here. The yellow area estimates d-electron screening effects by considering the optical constants of Cu (47). The experimentally measured low-energy electron lifetime approaches the bare electron–electron scattering limit (solid blue line, \( M = 1.8 \) for Ni) at an energy \( E_{\text{crit}} \sim 3 \) eV. (Inset) The phase space of the two materials calculated from Eq. 1, assuming \( M^{\text{Cu}} = M^{\text{Ni}} = 1.0 \). The blue dashed line (Ni, \( \Delta \text{DOS} \)) is the results with the DOS of Ni downshifted by 1.8 eV. (C) Lifetime ratio \( \tau_1/\tau_\text{f} \), as a function of excited electron energy \( (E - E_F) \) for Ni obtained using Eq. 1. (Inset) Spin and orbital-dependent DOS of Ni and Cu obtained from DFT calculations.
phenomena, including laser-induced demagnetization (8), superdiffusive spin transport, and giant magnetoresistance (49). Low-energy spin-dependent electron lifetimes have been studied, providing much valuable information (5, 6). However, to date it has not been possible to experimentally isolate electron–electron scattering, due to strong contributions to the measured lifetimes from electron screening from localized $d$- and $f$-band electrons, as well as contributions from other interactions (e.g., phonons and impurities). By probing high-energy photoelectron lifetimes, where electron screening becomes negligible, spin-resolved atto-ARPES could probe spin-dependent electron–electron scattering, which could help uncover fundamental magnetic properties.

**Conclusion**

In conclusion, we show that attosecond electron interactions in metals can be studied using energy-, polarization-, and angle-resolved atto-ARPES, allowing us to distinguish the contributions of occupied and unoccupied bands to the photoelectron lifetimes. Strong electron–electron scattering in the unfilled $d$ band of Ni decreases the lifetime of photoelectrons by $\sim 100$ as relative to the photoelectrons emitted from the same band of Cu. Most interestingly, we find that dynamical screening influences high-energy photoelectrons much less than low-energy photoelectrons and is different for Cu and Ni due to the differences in material band structure. As a result, spin-dependent atto-ARPES with high-energy excitation is a unique tool to exclusively study the fundamental processes of spin-dependent electron–electron scattering in magnetic materials and also to quantify the contributions of scattering and screening for low-energy excitations. In the future, atto-ARPES can also be used to extract valuable information about fundamental electron–electron interactions in a host of materials including strongly correlated materials and modern quantum materials.

**Methods**

We use laser-assisted photoemission and RABBITT to measure the photoelectron lifetimes for different initial and final states. Photoemission from the HHG pulse trains are generated in a 150-μm-diameter, 1-cm-long, gas-filled capillary waveguide, driven by $\sim 2$ μJ, 26-fs laser pulses at 780 nm wavelength from a Ti:sapphire amplifier system. We use different noble gases (Xe, Kr, and Ar) to cover a broad extreme ultraviolet (EUV) photon energy range from 16 to 42 eV (corresponding to HHG orders 11–27). A phase-locked linearly polarized IR probe is recombinated collinearly with the HHG pulse trains and focused onto the surface with a FWHM spot size of 250 μm and peak intensity of $2.8 \times 10^{11} \text{W/cm}^2$. The polarization of the IR probe is p-polarized for all our measurements. In the presence of both the attosecond pulse trains and the IR probing field, the angle-resolved photoelectron spectra are modulated as a function of the pump-probe time delays due to quantum-path interference (RABBITT, see Fig. 2C), which is recorded by a hemispherical photoelectron analyzer.

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