Time-resolved photoelectron spectroscopy with attosecond precision provides new insights into the photoelectric effect and gives information about the timing of photoemission from different electronic states within the electronic band structure of solids. Electron transport, scattering phenomena and electron-electron correlation effects can be observed on attosecond time scales by timing photoemission from valence band states against that from core states. However, accessing intraband effects was so far particularly challenging due to the simultaneous requirements on energy, momentum and time resolution. Here we report on an experiment utilizing intracavity generated attosecond pulse trains to meet these demands at high flux and high photon energies to measure intraband delays between sp- and d-band states in the valence band photoemission from tungsten and investigate final-state effects in resonant photoemission.
M any important physical properties of solids such as spin magnetism or superconductivity are determined by their electronic valence band. Measurements of the dynamics of valence-band electrons on ultrafast sub-femtosecond timescales reveal important insight into electron–electron correlation,1,2 dynamic hole screening,3 and other multi-electron effects in condensed-matter physics that are still not well understood.

Angle-resolved photoemission spectroscopy (ARPES) grants experimental access to the band-structure dispersion $E(k)$, where the in-band electron momentum $k_i = h^* \sin \alpha \sqrt{2m_e E_{\text{kin}}}$ is conserved upon photoemission and can thus be deduced from the kinetic energy $E_{\text{kin}}$ and the emission angle $\alpha$. Static ARPES measurements have reached energy resolutions below 1 meV5,6, whereas time-resolved ARPES intrinsically requires a larger spectral bandwidth such as several tens to hundreds of meV for the femtosecond regime7–9. Until very recently, attosecond time-resolved ARPES measurements were not possible because of the stringent and seemingly contradicting requirements on the electron energy resolution (~100 meV) and requested time resolution (<100 as).

There are two well-established techniques in attosecond photoelectron spectroscopy (PES): attosecond streaking, which utilizes isolated attosecond pulses10,11, and the reconstruction of attosecond beating by interference of two-photon transitions (RABBITT)12,13, which employs attosecond pulse trains (APTs). In both approaches, photoelectrons are excited by attosecond pump pulses in the extreme ultraviolet (XUV) and their moment of emission is mapped to their final kinetic energy by the electronic field of typically infrared (IR) probe pulses. In a RABBITT spectrogram, this leads to sidebands (SBs) whose intensity depends on the pump–probe delay (Fig. 1a). Usually, the probe pulse duration is about 5 fs for attosecond streaking and a few tens of femtoseconds for RABBITT experiments. The quantitative agreement between attosecond streaking and RABBITT measurements is well established14,15.

Attosecond pulses intrinsically require a large spectral bandwidth from 1.8 eV16 to several tens of eV17 to support their short duration. However, a train of attosecond pulses in the time domain exhibits a comb-like substructure in the spectrum. These well-separated high harmonics in APTs typically have a spectral width of a few 100 meV. The combination of a broad spectral envelope with narrow harmonics enables experiments with attosecond pulses and energy resolution well below 1 eV (Fig. 1b). This characteristic is indispensable for distinguishing between different initial or final states in solid band structures, especially when combined with angular resolution18,19.

However, there is another effect that impairs high energy resolution in attosecond PES experiments on solids: all photoelectrons excited by a single laser pulse are inherently released within very short time and therefore interact with each other. Consequently, space-charge effects lead to shifts and broadening of the photoelectron spectrum (Fig. 1c). Depending on the specific application, this limits the maximum acceptable number of photoelectrons per pulse.

High pulse repetition rates are the obvious solution to this issue: they allow for a high average photoelectron flux with only few released electrons per pulse. Single-pass high-harmonic generation (HHG) systems are typically limited to pulse repetition rates below 100 kHz because of the necessary pulse energies for efficient HHG. Enhancement-cavity-based HHG, however, combines high pulse energies with high repetition rates and is therefore well-suited for (quasi) space-charge free attosecond PES20. Thanks to the 18.4 MHz repetition rate, the high average flux of our HHG source translates to only around 500 emitted photoelectrons per laser pulse. Previous investigations have

![Fig. 1 RABBITT sideband principle and energy resolution in attosecond PES experiments.](image)
shown that space-charge effects at our parameters do not interfere noticeably with the high energy resolution enabled by the narrow high harmonics\textsuperscript{21}.

Although remarkable progress towards the absolute measurement of photoemission timing has been made, it cannot be measured directly either with RABBITT\textsuperscript{22,23} or streaking\textsuperscript{24}. In practice, the timing between the IR and XUV pulse cannot be determined with the necessary precision, e.g., due to uncertainties of the interferometric delay and the exact shape of the electric field of the probe pulse. Therefore, measuring photoemission delays ultimately always comes down to referencing photoemission delays from different states or even different materials with each other. Thus, it is common to compare photoemission time delays from different initial states of the same sample with each other, to extract relative photoemission delays within a single measurement\textsuperscript{25–28}. Attosecond streaking experiments on solid samples often reference valence-band photoemission delays with those of photoelectrons emitted from deeply bound core states with binding energies of several tens of eV\textsuperscript{26,25,29}.

So far, such deeply bound electronic states were not accessible in RABBITT measurements, because it was challenging to obtain the necessary flux of XUV photons with energies in the range of 50–100 eV with many-cycle, high-peak power laser pulses. As the probability of strong-field ionization is proportional to pulse duration, while too much plasma is detrimental for phase matching, HHG with such pulses is less efficient than that with few-cycle pulses, which are used for attosecond streaking. With femtosecond enhancement cavities having reached a maturity that allows for applications in attosecond science\textsuperscript{20}, the high peak power enhancement and repetition rate of our cavity-based HHG setup now allows us, for the first time, to address these electronic core states in solids with APTs, thus combining high photon energies (so far reserved to attosecond streaking) with the high energy resolution of separated individual harmonics at high photon flux.

In this study, we present the first attosecond PES experiment, which overcomes the necessity for a tradeoff between high energy resolution and both high photon energies and high photoelectron flux by means of cavity-enhanced HHG at high flux and high repetition rate. By this means, the influence of both initial and final states on the timing of photoemission is investigated.

Results

Resonant photoemission delay at 62 eV electron kinetic energy.

For high-photon-energy attosecond PES experiments at multi-MHz repetition rate, we generated high harmonics in neon and spectrally filtered them with a molybdenum-silicon multilayer mirror, which had a full width at half maximum bandwidth of 5 eV centered at 65 eV photon energy (Fig. 2a). Although the light source provides photon energies in excess of 120 eV, the energy of ∼65 eV is sufficient to address the 4f states in tungsten, while still permitting the use of high-transmission aluminum filters below their 72 eV absorption edge in order to spatially separate IR and XUV (see “Methods”).

The resulting photoelectron spectrum features several peaks between 50 and 70 eV, which correspond to valence-band photoemission from the individual high harmonics (Fig. 2b). Separated by their binding energy of 31.2 eV\textsuperscript{30}, another set of photoelectron peaks stemming from the 4f electron core state is clearly visible at the low-energy part of the spectrum. An XUV-IR pump–probe PES measurement yields a RABBITT trace (Fig. 2c).

In a RABBITT spectrogram, two-photon transitions give rise to SBs in between the photoelectron peaks originating from the high harmonics (Fig. 1a). As a result of quantum interference between the two possible transitions from its neighboring harmonics, the intensity of $S_q$ of the SB of the order $q$ oscillates at twice the laser frequency, $\omega_{IR}$, as a function of the pump–probe delay $\tau_{PP}$:\textsuperscript{12}

$$S_q(\tau_{PP}) \propto \cos(2\omega_{IR}(\tau_{PP} + \tau_{XUV,q} + \tau_{PE})) + \text{const}.$$ (1)

The phase of this oscillation comprises a delay $\tau_{XUV,q} = (\psi_{q−1} − ψ_{q+1})/2\omega_{IR}$ introduced by the spectral phases of the two neighboring harmonics $\psi_{q±1}$ and the photoemission delay $\tau_{PE}$ introduced by the sample under study. Additional probe field induced delays from continuum–continuum transitions are small compared to the observed delays presented in this work and will be neglected\textsuperscript{19,22}.

According to Eq. (1), we fit a sine function to each SB $q$ and obtain their relative delay, except for the energy- and SB order-independent constant component $\tau_{PP}$ (see “Methods”). Although the 4f-state SB delays are very similar, there is a clear delay anomaly in the SB around 62 eV in the valence band with respect to the others (see open black circles in Fig. 2d). All but this outlier SB closely follow a classical electron transportation model (red line in Fig. 2d), which explains a notable delay in photoemission between the tungsten 4f states and the valence band as reported in previous experiments, based on attosecond streaking\textsuperscript{24,25}. However, the striking increase in photoemission delay by 148 ± 40 asec of SB 56, at 62 eV kinetic energy, has not been observed before and cannot be attributed to the XUV spectral phase of the harmonic comb, as it does not show up in the corresponding 4f SBs at around 30 eV kinetic energy.

Although photoemission delays between different initial states with different orbital momentum have been observed in bulk\textsuperscript{31} and gas\textsuperscript{26,28}, the delay deviation at 62 eV in our experiment is almost by an order of magnitude larger than these and can, thus, not be explained by such an initial-state effect. The tungsten 4f core state consists of a spin doublet separated by 2.2 eV\textsuperscript{30}, whose peaks overlap in the spectrogram. However, simulations according to a recently demonstrated model\textsuperscript{32} have shown that this has hardly any influence on the observed 4f SB delays in our experiment, nor could it explain a resonant delay in the valence band (see Supplementary Note 3).

Having ruled out the influences of initial states and excitation as the reason for the observed discrete increase in photoemission delay at 62 eV, it has to be assumed that this is a final-state effect similar to previously reported findings in other transition metals\textsuperscript{18,19}.

In one case, an observed final-state induced photoemission delay was explained by the reflection and interference of the electron wave packet in the solid, which can occur if the de Broglie wavelength matches the crystal layer distance\textsuperscript{33}. We find not one but two distinct increases in delay and for neither of them the electron wavelength is in agreement with the interlayer distance of 2.24 Å in a W(110) crystal and therefore rule out this explanation for our findings.

In the three-step model of photoemission, the electron transport time to the bulk surface can be modeled by the quotient of the electron inelastic mean free path (IMFP) and the electron wave packet propagation velocity. Tao et al.\textsuperscript{18} attributed a resonant photoemission delay in nickel to the lifetime of the high-lying final state of an excited electron. In the three-step picture of photoemission, they explain this by an increased mean emission depth of the photoelectrons whose energy-velocity relation is not subject to the crystal potential but follows a free-electron dispersion.

Other publications assume that the electron emission depth follows the smooth energy dependence of the universal IMFP curve for all elements\textsuperscript{34} and relate an observed increase in photoemission delay to a decrease in electron propagation velocity induced by the final band structure\textsuperscript{17,19}. We found that
our results are well explained by this approach with the quotient of the general IMFP in tungsten and an electron propagation velocity based on the final band dispersion (see Supplementary Note 1) as displayed in Fig. 2d. For comparison, the resulting delay calculated from the free-electron velocity is also shown.

Both calculations clearly support the experimentally observed relative delay of the core-level photoemission compared to the photoemission from the valence band, leading to a very similar expected delay. It is noteworthy that the actual absolute photoemission delay with respect to the XUV pulse is unknown in this measurement and is chosen such that the relative delays in photoemission delay with respect to the XUV pulse is unknown expected delay. It is noteworthy that the actual absolute delay of the sidebands (predominantly blue) but also the high harmonic peaks (predominantly red) oscillate in intensity. A distinct anomaly in the regularity of the pattern is observed around 62 eV. For better visibility, the displayed spectrogram is background subtracted (see “Methods”). The inset shows the intensities of the sidebands at 59.5 and 61.9 eV (circles), and their fits (lines). Comparison of sideband delays with the electron transport time to the crystal surface. The blue area shows transport times predicted by the final-state group velocities. A classical free-electron propagation results in the red line. Sideband delays extracted from c are indicated by black circles. Sideband delays from another RABBITT spectrogram using argon harmonics (see Supplementary Fig. 2a) is indicated by orange circles. The error bars represent the SD over all traces in each dataset (see “Methods”). As only relative photoemission delays are extracted from the spectrograms, an arbitrary delay offset has been added to each dataset to match the calculated delays.

To further support the validity of our interpretation, we have also performed another RABBITT measurement at a photon energy of ~52 eV addressing the second resonance at the kinetic energy of 43 eV. This resonance is also clearly visible in the measured data (orange solid circles Fig. 2d). The observation of two different surges in photoemission delay (at 43 and 62 eV) predicted by our electron transport time calculations in two independent measurements corroborates our model.

A closer insight into this resonant delay structure at 62 eV is given by analyzing the energy-dependent shapes of the valence-band SBs as indicated by the dashed boxes in Fig. 3a. Each SB has been analyzed by three linecuts: through its center and through its upper and lower margins. The corresponding delays have been plotted in Fig. 3b. The figure shows that the onset of the resonance already appears in the upper margin of the SB below the actual resonance slightly below 60 eV. The intra-SB delay shift of the highest indicated SB around 65 eV can be attributed to the large error bars at these energies.

This SB shape analysis allows for a more precise experimental evaluation of the resonance shape, magnitude, and position. The calculation of the maximum group velocities perpendicular to the surface in the final bands around the resonance area (58–64 eV)

**Fig. 2 Time-resolved photoelectron spectroscopy from tungsten 4f and valence band.** a XUV spectrum generated in neon (black line) and XUV mirror reflectivity (blue filled area). The XUV spectrum is cut off at 72 eV by a 300 nm Al foil filter. b Static photoelectron spectrum with photoelectrons emitted from the tungsten valence band (blue filled area) and the deeper-bound 4f state (red filled area). The comb-like appearance of the excitation spectrum is imprinted in the photoelectron spectrum. Sideband positions are indicated by dashed lines (likewise in c and d). c RABBITT spectrogram. Due to depletion, not only the sidebands (predominantly blue) but also the high harmonic peaks (predominantly red) oscillate in intensity. A distinct anomaly in the regularity of the pattern is observed around 62 eV. For better visibility, the displayed spectrogram is background subtracted (see “Methods”). The inset shows the intensities of the sidebands at 59.5 and 61.9 eV (circles), and their fits (lines). d Comparison of sideband delays with the electron transport time to the crystal surface. The blue area shows transport times predicted by the final-state group velocities. A classical free-electron propagation results in the red line. Sideband delays extracted from c are indicated by black circles. Sideband delays from another RABBITT spectrogram using argon harmonics (see Supplementary Fig. 2a) is indicated by orange circles. The error bars represent the SD over all traces in each dataset (see “Methods”). As only relative photoemission delays are extracted from the spectrograms, an arbitrary delay offset has been added to each dataset to match the calculated delays.
Initial-state photoemission delays within the valence band.

Electronic wave functions in crystals are formed (within the tight binding model) by linear combinations of atomic orbitals, commonly referred to as Bloch waves, which are invariant under lattice translation. Although, in general, any electronic state in a solid corresponds to a superposition of an infinite number of atomic states, often just a few atomic orbitals are dominant in a Bloch wave. In transition metals, a Bloch state $\psi_f(\mathbf{k})$ with a band index $l$ and a wave vector $\mathbf{k}$ may largely consist of atomic $d$-orbitals. The corresponding energy band $E(\mathbf{k})$ is referred to as a $d$-band. Accordingly, energy bands of $sp$-character are formed from atomic orbitals with $s$ and $p$ orbital momentum.

Although the previous section described final-state effects in the resonant photoemission from the tungsten valence band, in the following experiments we focused on the investigation of these different initial bands within the tungsten valence band. As low photon energies are sufficient for this purpose, we generated high harmonics in argon. As compared to neon, HHG in argon provides a significantly higher XUV flux with energies between 33 and 50 eV. The angular acceptance of $\pm 7^\circ$ of our electron spectrometer, the final electron kinetic energy (around 32 eV), and the (110) orientation of the crystal determine the observable part of the tungsten valence band BZ. The resulting partial density of states (DOS) over all populated and accessible band parts is displayed in Fig. 4a. It is composed of a sharp dominating peak of $d$-electron states 1.6 eV below the Fermi energy and a broader and weaker contribution of deeper-bound $sp$-electrons with a band gap of around 2 eV between these two components.

To spectrally resolve these different parts of the tungsten valence bands in a RABBITT experiment, it is thus necessary to choose an excitation bandwidth comparable to the width of the band gap that still allows for at least two strong high harmonics for a well-modulated SB signal. Therefore, we opted for an XUV mirror with a bandwidth of 4 eV centered at 41 eV.

To identify the different $sp$- and $d$-contributions in the valence band by their dispersion, we performed ARPES (Fig. 4b). The data reproduce the key features of the band structure with the upwards open parabola-shaped dispersion of the $sp$-band around 30 eV kinetic energy separated from the flat or downwards open dispersion of the $d$-band around 35 eV. The $k_\|$ projection of the band structure along the $\Gamma$–$P$ and $N$–$P$ directions (black solid lines Fig. 4b) coincides well with the experimental data. As the excitation is not monochromatic, the displayed data consist of a superposition of spectrograms for each harmonic. We simulated this by convoluting the $k_\|$-dependent DOS with the utilized XUV spectrum and accounting for the instrumental resolution. The result is displayed in Fig. 4c and is in qualitative agreement with the experimental data shown in Fig. 4b.

Figure 5a displays the generated XUV spectrum and the reflectivity of the utilized silicon–boron carbide multilayer mirror, which filters out two harmonics of about equal intensity, while further harmonics are suppressed. In the corresponding static photoelectron spectrum, the $sp$- and $d$-electron contributions can be well distinguished (Fig. 5b). Time-resolved pump–probe measurements yield a RABBITT spectrogram (Fig. 5c) where

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Fig. 3 Intra sideband delay evaluation of tungsten valence band photoelectrons around 62 eV. a Magnified view of the RABBITT-spectrogram in Fig. 1c around 62 eV. The dashed boxes represent the energy-dependent shape of each sideband. b For each sideband, we retrieved the delays at its central, highest, and lowest energies (black circles). Note the asymmetric character of the sideband at 60 eV just below the resonance (see text). Calculated classical electron transport time to the crystal surface is indicated by the red line, the group-velocity-based simulation of transport delays by a blue solid line. As the simulation is based on the maximum group velocities at each final energy, contributions from other bands can lead to higher delays (blue filled area). Error bars represent the SD over all traces in each dataset (see “Methods”). c Band energies for electrons photoemitted perpendicularly to the surface (black lines). The classical free-electron dispersion curve is shown in red; the bands with maximum group velocity at each energy are highlighted in blue. The latter are notably more shallow at 60–62 eV, which translates to lower group velocity and therefore higher photoemission delay in b.
As the blueshifted spectral components accumulate in the cavity, this effect is significantly stronger than in regular single-pass HHG setups. A spectral shift of about 0.8 eV leads to an XUV spectrum, which is dominated by a single strong harmonic at the peak of the XUV-mirror reflectivity curve (Fig. 6a). Out-of-bandwidth harmonics are suppressed by the mirror but still visible.

The change from a configuration with two strong harmonics to this spectrum has a strong impact on the measured RABBITT spectrogram (Fig. 6b). As the SB oscillations arise from the interference of the two neighboring harmonics, their modulation depth is determined by the weaker of the two harmonics. Hence, although the central harmonic is by far the strongest, it does not dominate the RABBITT signal to a similar extent and comparably pronounced oscillations can be observed over a relatively broad energy range. This leads to an overlap of lower-order SBs from d-bands with photoelectrons originating from the deeper-bound sp-bands.

The SB delays extracted from this spectrogram closely follow the delay, which is introduced by the group delay dispersion of the XUV mirror (see Fig. 6c). Hence, the observed photoelectrons (and SBs) originate mainly from the same initial state (i.e., the dominant d-band) and about seven different high harmonics such that the SB delays match their spectral phase. A weaker contribution of sp-electrons overlaps with d-band electrons at lower kinetic energies and leads to a certain deviation from the mirror induced delay curve for the SBs at about 27 and 29 eV. This situation is very different from the situation with only two strong harmonics displayed in Fig. 5c, where the spectral phase of the XUV has no influence, because both observed SBs stem from the same high harmonics, but different initial states (sp- and d-band). Consequently, the initial-state induced delay difference between the two SBs (red circles in Fig. 6c) was noticeably smaller than the mirror induced delay difference between the SBs in the blueshifted spectrogram at similar kinetic energies (blue circles in Fig. 6c). The different energy separation between the SBs at around 36 and 29 eV for the unshifted (6.4 eV) and blueshifted spectrogram (7.4 eV), corroborates this interpretation (see Fig. 6c). In the shifted RABBITT trace, this corresponds to three high-harmonic spacings, whereas in the unshifted trace the valence band substructure creates this energy gap.

The possibility of easily shifting SBs to this extent can be a very useful tool for the observation of effects at discrete kinetic energies in future experiments, as well as for distinguishing between initial- and final-state effects.

**Discussion**

We have presented the first RABBITT measurement on deeply bound core states in a solid, which is also the first XUV attosecond experiment at MHz repetition rate. This self-referencing measurement on a W(110) crystal features significant resonant delays in photoemission at electron kinetic energy of 62 and 43 eV, which can be attributed to neither initial-state effects nor the XUV spectral phase. Instead, these two resonances clearly resemble the maximum group velocity in the final bands perpendicular to the surface. A more detailed analysis of the SB shapes around the resonances gives a more detailed insight into...
the position, shape, and magnitude of the resonance, which is linked to the final-state band-structure dispersion. This new technology is thus an extremely powerful tool to investigate the dispersion and group velocities of unoccupied bands on an attosecond timescale. So far, the band structure above the Fermi energy has been hardly accessible in attosecond experiments. This new access allows for the investigation of quasiparticle lifetimes with attosecond precision.

Furthermore, our experiment has shown that different bands within the valence band can be distinguished in a RABBITT spectrogram, which allow for intra-valence band referenced measurements. Angle-resolved photoemission measurements and simulations corroborate these findings and identify the different contributions to stem from $sp$- and $d$-angular orbital-dominated parts of the band structure. An upper limit of $39 \pm 18$ asec of the $sp$-photoemission delay with respect to the $d$-band photoemission is extracted from the measurement, which can be explained in terms of an orbital-momentum-dependent inner-atomic delay. This intra-valence band analysis is not possible for broadband attosecond pulses, as they are utilized in isolated attosecond pulse streaking experiments and have thus not been seen in these previous streaking experiments.

The unique combination of high flux, high photon energy, and high energy resolution together with angularly resolved detection of our experiment will enable further valuable insights into band-structure-dependent electron dynamics, revealing a new understanding of electron–electron scattering and correlation effects upon photoemission of more complex electronic materials on attosecond timescales.

**Methods**

**Cavity-based HHG and PES setup.** The laser system consists of a Ti:Sa oscillator seeding a Yb-doped fiber amplification system with actively stabilized carrier-envelope phase. The repetition rate of 18.4 MHz rate guarantees space-charge-free experimental conditions, avoids cumulative effects in the HHG gas target, and ensures a temporal detection duty cycle of photoelectrons close to 100%. After amplification, the 1030 nm pulses are spectrally broadened in a multi-pass cell and temporally compressed to a final pulse duration of 39 fs at 83 W of average power. These pulses are coupled into a passive resonator with an...
Fig. 6 Tungsten valence band RABBITT-measurement with energy shifted high harmonics. a XUV spectrum measured after the multilayer XUV mirror and corresponding reflectivity curve. The position of the high harmonics is shifted by 0.8 eV compared to previous measurement (Fig. 4). Hence, the spectrum is dominated by a strong high harmonic at the maximum of the mirror reflectivity curve. The other harmonics are significantly weaker and they have similar heights. For better comparability with b and c, their energy plot range is shifted by 6 eV to account for work function and binding energy. b RABBITT spectrogram taken with the excitation spectrum in a. Due to the comparable strengths of most harmonics, many sidebands form (dashed lines), which have similar oscillation amplitudes. c The sideband delays extracted from the spectrogram in b (blue circles) are in good agreement with the calculated sideband delay introduced by the dispersion of the utilized multilayer mirror (black line). The relative delays extracted from the unshifted RABBITT measurement in Fig. 4c (red circles) strongly differ from the delays obtained from the spectrogram in b. The separation between the sidebands at about 29 and 36 eV differs by 1 eV between the unshifted (6.4 eV) and blueshifted spectrogram (7.4 eV). The error bars consist of the SD over all traces in each dataset (see “Methods”) and the errors introduced by the XUV optics (see Supplementary Note 2).

Spectrogram background subtraction and illustration. As the subtraction of a delay-independent background is not necessary for the SB delay analysis and has absolutely no impact on it, static background subtraction is a purely cosmetic affair. However, for illustration, it is very helpful and we have been using two approaches at it. The suppression of the constant fraction of the spectrogram in the Fourier space is very helpful to emphasize the time dependency of the SB intensities. The drawback of this method is that no difference between oscillating SBS and the oscillating harmonic peaks can be discerned after applying the Fourier filter. In contrast, subtracting a delay-averaged and smoothed photoelectron spectrum visualizes well the SB and harmonic peak positions in the spectrogram, because the harmonic peaks clearly emerge over this kind of background. A linear combination of these two backgrounds guarantees optimum visibility of the relevant features of a RABBITT trace and was subtracted from all displayed spectrograms in this work with individually adjusted suitable weighting. To make the spectrograms more pleasing to the eye, additional points were interpolated between the measured data points for a smoother appearance. As an example, the process from the raw data to the spectrogram displayed in Fig. 6b is illustrated in Supplementary Fig. 4.

SB delay evaluation. To extract the phases and thereby the delays from the individual SBS, it is helpful to compensate for drifts that occur during the measurement of a RABBITT trace, e.g., due to slow cavity misalignment, which results in a drift of the spectral envelope of the high harmonics. To minimize the influence of this effect, we measured our spectrograms alternating with increasing and decreasing delay. In addition, we removed the lowest non-constant component of the RABBITT trace and was subtracted from all displayed spectrograms in this work. Identifying the kinetic energies with the highest amplitudes at this SB oscillation frequency. For the SB fit, we average over the photoelectron counts in a total kinetic energy range of 500 meV around the central SB energy, which is well below the separation between high harmonics and SBS of 1.2 eV. In the case of the intra-SB analysis of Figs. 3a and 2b, we chose an integration interval of 300 meV for each slice.

The result of the sine fit is the sum of the three delay components in Eq. (1) of the main text: pump–probe delay \( \tau_{PP} \), XUV spectral phase-induced delay \( \tau_{XY} \), and enhancement factor of 35 and XUV photons are generated via HHG in a noble gas target in a focus and, subsequently, output coupled through a hole in a cavity mirror. Although the setup is optimized for HHG in argon with an output coupled flux of \( 10^{13} \) photons per second at up to 60 eV, it can be run with neon without major modifications at significantly higher photon energies of up to 120 eV at the expense of XUV photon flux (\( 10^{10} \) photons per second). Hence, we can do inter-band-referenced measurements at deeply bound states with neon HHG, while argon HHG is perfectly suited for angular- resolved high-precision studies of valence band dynamics. Due to its low divergence, the XUV beam can be spatially separated from the IR by a 300 nm-thick Al filter in the center of the beam, which is opaque for the fundamental laser light. A two-segment XUV multilayer mirror was used to introduce a variable delay between the IR and XUV components, and focused both beams on a tungsten (110) single crystal. Subsequently, up to \( 10^8 \) photoelectrons per second emitted within a \( \pm 7° \) solid angle are captured by an angle-resolving time-of-flight spectrometer. For wide-angle applications, an additional spectrometer mode with an angle acceptance of \( \pm 15° \) is available and was used for the data presented in Fig. 6b. For more detailed information regarding the setup, please refer to ref. 21.

Tungsten band structure and DOSs. All theoretical data of the electronic structure of tungsten in this work was calculated with the open source software QUANTUM ESPRESSO, which relies on density function theory, plane waves, and pseudopotentials. We assumed a body centered cubic tungsten crystal with a lattice constant of \( a = 3.165 \) Å and used a Perdew-Burke-Ernzerhof functional type ultrasoft pseudo-potential. Our crystallographic orientation is (110) such that the photoelectron emission is centered around \( \Gamma – N \) axis. At a fixed electron spectrometer angle acceptance \( \alpha \), the maximum parallel electron momentum \( k_{\parallel} \) depends on the electron kinetic energy \( E_{\text{kin}} \) according to \( k_{\parallel} = \frac{E_{\text{kin}}}{\hbar} \sin \alpha \sqrt{2mE_{\text{kin}}} \). At \( \pm 7° \) angle acceptance in the electron kinetic energy range from 30 to 65 eV, this leads to a maximum accessible \( k_{\parallel} \) of 0.17–0.25 \( \pi/a \). Hence, the part of the BZ, which contributes to our PES measurements, is at a fixed energy, a cylinder around the emission direction \( \Gamma – N \). Summation over all these states at 32 eV kinetic energy yields the partial DOSs depicted in Fig. 4a. By keeping the \( k_{\parallel} \) information, we obtained a \( k \)-space-resolved DOS, which was used to calculate the simulated angular-resolved photoemission spectrogram in Fig. 4c. For consistency, we confirmed that our DOSs over the entire BZ is in very good agreement with literature.
photoemission delay $\tau_{dp}$. As $\tau_{dp}$ is unknown but identical for all kinetic energies and SB orders, we can only extract the delays of the SBs relative to each other with an arbitrary offset that is equal for all SBs and energies. An upper limit is chosen such that it matches best the calculated delay curves (in Figs. 2d and 6c). Relative delay components, which depend on SB order and the final or initial energy are preserved. As the attochirp delay $\tau_{XUV}$ only depends on the SB order, its non-

constant contribution can be distinguished from the one by $\tau_{dp}$ in measurements with clearly different initial states as for the $4f$ and valence electrons in the neon HHG data in Fig. 2d and the $s$- and $d$-band electrons in Fig. 5d.

The SB sine-fitting is done for all RABBITT spectrograms taken during a measurement campaign at identical parameters. The total SB delay given in the main text and its figure is the mean value of all the delays extracted from the individual spectrograms and their SD is our error bar. As the signal-to-noise ratio in the neon–HHG data in Figs. 2 and 3 is relatively low, we had to merge a total of 54 measurements into 6 subsets of sums over 9 spectrograms, which was not necessary for the argon HHG datasets for the large bandwidth measurement in Fig. 2d (consisting of 73 traces) and the small bandwidth measurement in Fig. 5c (12 traces) and Fig. 6b (82 traces).

**Crystal preparation.** The crystal is mounted in a flag style sample holder, which is held by a frame that is designed to reduce the thermal contact to the vacuum chamber. Hence, the crystal can be heated up to 2200 K by electron impact heating within several seconds and without significantly heating other parts of the vacuum chamber. An actual light-bulb filament is placed about a centimeter behind the tungsten crystal and emits up to 240 mW at a voltage of 1.1 kV when flashing the sample. The X-ray form of the molybdenum crystal is chosen such that it matches best the calculated delay curves (in Figs. 2d and 6c). Relative delay components, which depend on SB order and the final or initial energy are preserved. As the attochirp delay $\tau_{XUV}$ only depends on the SB order, its non-

constant contribution can be distinguished from the one by $\tau_{dp}$ in measurements with clearly different initial states as for the $4f$ and valence electrons in the neon HHG data in Fig. 2d and the $s$- and $d$-band electrons in Fig. 5d.

**Spectrogram acquisition times and step width.** The pump–probe delay step size does not have any influence on the result or the precision of the measurement; however, we are free to choose a value such that the total delay range spans at least two SB oscillation periods, which are well resolved, which results in an intuitively well-understandable spectrogram. In the case of the neon-dataset in Fig. 2c, we opted for traces of 31 delay steps of 167 asec and a total spectrogram exposure time of 174 s each, for all other displayed measurements with argon high harmonics 33 delay steps of 208 asec.

The entire neon HHG dataset presented in this work (Fig. 2) was taken within a net acquisition time of 145 min within two measurement days. The broadband argon HHG RABBITT dataset presented in Fig. 2d of the main text (orange circles) and Supplementary Fig. 2 was measured within a net acquisition time of 195 min in 1 day and the narrowband RABBITT datasets displayed in Fig. 5c and Fig. 6b of the main text in net 28 and 136 min within 1 day, respectively. Because of the cavity-based HHG setup, the gross acquisition time under typical conditions is roughly a factor of 2 longer, as described in the measurement section. Flashing the tungsten crystal will also prolong the actual measurement times. Due to our high background pressure during the photoelectron measurements and the XUV-IR interferometer delay can drift. However, due to the high flux of the system, it is no problem to measure one or even several meaningful RABBITT spectrograms within this time, even when generating high harmonics in neon.

**Data availability**

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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Author contributions

S.H. and T.S. contributed equally to this work. The project was planned by S.H., T.S., M.H., Y.C., U.K. and I.P. The enhancement cavity-based HHG source was designed and set up by T.S., M.H., and I.P. The XUV multilayer mirrors were designed and fabricated by Y.C. The HHG and PES experiments were performed by T.S., S.H., and M.H. Theoretical considerations were done by S.H., M.H., Y.C., V.Y., and U.K. S.H., T.S., U.K., and I.P. wrote the manuscript, which was reviewed by all authors.

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Competing interests

The authors declare no competing interests.

Additional information

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