Clocking Auger electrons

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Intense X-ray free-electron lasers (XFELs) can rapidly excite matter, leaving it in inherently unstable states that decay on femtosecond timescales. The relaxation occurs primarily via Auger emission, so excited-state observations are constrained by Auger decay. In situ measurement of this process is therefore crucial, yet it has thus far remained elusive in XFELs owing to inherent timing and phase jitter, which can be orders of magnitude larger than the timescale of Auger decay. Here we develop an approach termed ‘self-referenced attosecond streaking’ that provides subfemtosecond resolution in spite of jitter, enabling time-domain measurement of the delay between photoemission and Auger emission in atomic neon excited by intense, femtosecond pulses from an XFEL. Using a fully quantum-mechanical description that treats the ionization, core-hole formation and Auger decay as a single process, the observed delay yields an Auger decay lifetime of $2.2^{+0.2}_{-0.3}$ fs for the KLL decay channel.

This non-radiative decay mechanism is the dominant decay mechanism for elements with a low atomic number. In these cases, the core-hole decay lifetime is essentially equivalent to the Auger decay lifetime, and on the order of femtoseconds. When the core-hole is created by photoionization, the Auger decay lifetime is related by the uncertainty principle to the spectral linewidth of the photoemission line. High-resolution electron spectra, mostly measured using high-brightness synchrotron sources, have therefore been used to infer Auger decay lifetimes.

Alternatively, it is possible to access these dynamics directly in the time domain, using X-ray pulses with a duration comparable to, or shorter than, the Auger decay lifetime. For example, in proof-of-principle experiments in krypton using relatively weak, table-top attosecond XUV pulses, core-holes were created by photoionization. The corresponding Auger decay was then temporally resolved by dressing the electron emission with an optical laser pulse. In these experiments, the photoemission profile essentially matches the temporal profile of the exciting attosecond XUV pulse, as photoemission occurs on attosecond timescales. In contrast, the Auger emission is extended over a longer duration—typically on a femtosecond timescale.

In a number of attosecond investigations of Auger decay, the temporal profile of Auger emission has been approximated by a convolution of the XUV pulse profile with an exponential decay curve. This phenomenological ad hoc model using rate equations is based
on a two-step description of Auger decay, and treats the ionization and Auger emission as distinct processes. More recently, an alternative, fully quantum-mechanical model has been proposed\textsuperscript{25,26}, which treats the time-dependent Schrödinger equation within the strong-field approximation. Within this approach, the Auger process is considered as a single-step excitation-decay of the vacancy, or Auger, state. Both creation of the vacancy and its subsequent decay into the non-stationary wavepacket of the Auger electron are considered as a single quantum-mechanical process. A similar approach was developed earlier for resonant Auger processes in molecules\textsuperscript{21,22}. The quantum-mechanical model treats Auger decay in terms of the amplitudes of the states involved—that is, the vacancy state and the continuum of states of emitted Auger electrons—while the ad hoc rate-equation approach treats the process in terms of the real-valued populations of those states. The two models give similar results when the exciting pulse is much shorter than the Auger lifetime. However, as the exciting X-ray pulse becomes comparable to or even longer than the Auger decay lifetime, a substantial difference appears in the emission profiles predicted by the two models.

In the context of our experiment, the difference in the emission profiles is manifested in terms of the quantity we intend to measure: the time delay between the centres of mass of the photoemission and Auger emission bursts. The profiles predicted by the ad hoc two-step model have their centres of mass displaced exactly by the Auger decay lifetime, but this is not so in the quantum-mechanical model we used to determine our final results, and we must perform an additional step to retrieve the decay lifetime from the observed time delay.

In this paper, we present an experimental study of photoinduced Auger emission in the time domain, using intense, femtosecond soft X-ray pulses from an XFEL of duration commensurate with the core-hole lifetime. Under these conditions, the ad hoc two-step model fails, and a full quantum-mechanical treatment must be used, resulting in an Auger decay lifetime that is consistent with past high-resolution spectroscopic measurements. Therefore, our work represents an experimental demonstration of the quantum effect in the delay between photoionization and Auger decay, and emphasizes the general importance of treating the Auger process as a single-step quantum-mechanical process when performing future XFEL experiments.

**Ultrafast science at XFELs**

XFELs provide extremely intense pulses across the soft and hard X-ray spectral domains, permitting the interrogation of a wide range of systems that are not accessible via other X-ray light sources. In principle, the pulses delivered at XFELs can be short enough to explore few- or even subfemtosecond dynamics\textsuperscript{27}, including Auger decay\textsuperscript{28}. Furthermore, XFEL pulses are many orders of magnitude more intense than X-rays from other sources, and consequently can be used to pump and probe highly excited states of matter\textsuperscript{1−4,29−33}, many of which are constrained or influenced by Auger decay.

Despite these favourable characteristics, existing attosecond time-resolved spectroscopies have hitherto been impossible to apply at XFELs. Even with modern electronic and optically distributed reference signals\textsuperscript{34,35}, it is currently not feasible to perfectly synchronize an XFEL pulse with the field of a streaking laser pulse; experiments at XFELs suffer from ever-present timing and phase jitter which places limits on the achievable time resolution. Independent time-of-arrival measurements can be used in post-processing to dramatically improve the effective time resolution\textsuperscript{36−41}, but their implementation is challenging, and in many cases the jitter remains more than an order of magnitude larger than the timescales of Auger decay. The past decade has seen the establishment of the attoclock technique\textsuperscript{42}, based upon angular streaking, which offers an alternative to linear streaking for the attainment of few-attosecond resolution using a table-top source. Recent efforts to apply angular streaking at XFELs have shown promise as a diagnostic tool for mitigating jitter\textsuperscript{43}, but these techniques have yet to see broader application for experimental measurements at XFEL facilities.

As a result, direct time-resolved studies of most electron dynamics at XFELs have generally not yet been accomplished. There is thus a need for a straightforward technique that can unite the advantages of two very disparate light sources: whereas XFELs are the only sources able to deliver intense, ultrashort X-ray pulses and create highly excited states of matter, it is so far primarily table-top attosecond sources that have been able to provide adequate time resolution with which to probe the electronic dynamics underpinning those states.

Here, we develop and use a self-referenced streaking approach that circumvents timing jitter and allows for the extension of table-top attosecond spectroscopy to XFELs. This will enable a class of experiments benefiting from highly intense X-ray pulses alongside attosecond time resolution. As a demonstration, we have measured the delay between photoemission and Auger emission for KLL Auger decay in atomic neon, enabling us to deduce the Auger decay lifetime of K-shell vacancies in neon. These measurements were made in the time domain and with subfemtosecond precision, paving the way for the extension of the technique to a variety of ultrafast measurements at XFELs worldwide.

**Time-resolved electron spectroscopy**

A schematic of the experimental apparatus at the Linac Coherent Light Source free-electron laser is shown in Fig. 1. We induce 1s core-level photoemission and subsequent Auger decay with an XFEL pulse whose photon energy is centred at 1,130 eV with 5 eV of bandwidth. From the average pulse energy, the fluence is estimated to be below 40 J cm\textsuperscript{-2}. The pulse is directed into a dilute neon gas target, and the photoelectrons and Auger electrons are analysed using a time-of-flight spectrometer equipped with an electrostatic lens to increase the collection efficiency. We perform single-shot measurements of both peaks simultaneously, taking advantage of the fact that the KLL Auger spectrum of neon is dominated by the strong emission line associated with the Ne\textsuperscript{2+} 2p\textsuperscript{4}D\textsubscript{2} final state\textsuperscript{44}. Acquiring both peaks simultaneously requires that they be sufficiently close together in energy; indeed, our spectral resolution is lower on the Auger peak than on the photoelectron peak owing to its higher kinetic energy.

An important prerequisite for streaking measurements is that the dynamics must occur within a half-cycle of the streaking laser field\textsuperscript{45}. From the peak current in the bunch compressor, the X-ray pulse duration in our experiment was estimated to be less than 10 fs full-width at half-maximum (FWHM), so that an infrared streaking field with a correspondingly long optical cycle is required. To this end, a titanium:sapphire 800 nm femtosecond laser is used as the pump source to generate the infrared signal and idler pulses in a barium borate crystal via optical parametric amplification. These pulses are mixed in a gallium selenide crystal for difference-frequency generation, producing mid-infrared streaking pulses with a wavelength of 17 μm. The streaking period, therefore, is 57 fs, so we can be confident that the exciting X-ray pulse and the few-femtosecond Auger dynamics will be fully encompassed within a half-cycle of the streaking field.

The linearly polarized streaking laser has a time-dependent electric field

\[ E_{IR}(t) = E_0(t) \cos(\omega_{IR} t), \]

and vector potential

\[ A_{IR}(t) = \frac{E_0(t)}{\alpha_{IR}} \sin(\omega_{IR} t), \]

such that \( E_{IR}(t) = -\frac{\partial A_{IR}(t)}{\partial t} \). The symbols \( E_0(t) \) and \( \omega_{IR} \) represent the slowly varying amplitude of the streaking field and its angular frequency,
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and phase of the streaking field acting on the emitted electrons must
with the condition that $\Delta E_i$. Consequently, advanced by some amount in the time between emissions, owing to photoelectrons. As a result, the phase of the streaking laser will have equation (3), the Auger electrons are generally emitted later than the with the streaking laser. We note that, whereas the photoelectrons shot by simultaneously measuring shifts in the kinetic energy of two both the amplitude and phase of the streaking laser field for each Using our experimental technique, we can potentially determine on the stationary target. The resultant streaked photo and Auger electron emission is measured using a large-acceptance time-of-flight (TOF) spectrometer.

respective. In this experiment the maximum amplitude of the streaking field is around $5.6 \text{ MV m}^{-1}$, and the corresponding intensity is $40 \text{ GW cm}^{-2}$.

Upon interaction with the streaking laser field, the emitted photoelectrons’ change in kinetic energy $\Delta E_i$, can be approximated by

$$\Delta E_i \approx \sin(\theta) \sqrt{8E_{el} U_p}, \quad (3)$$

where $\theta$ is the phase of the streaking pulse at the moment of photoemission $t$, and $E_{el}$ is the electrons’ field-free kinetic energy. This equation is central to streaking spectroscopy and follows from the classical expression for the electron kinetic energy in the laser field with the condition that $U_p < E_{el}$. The ponderomotive potential $U_p$ is given by

$$U_p = \frac{e^2 E_0^2}{4m_e^2 \omega^2}, \quad (4)$$

where $e$ and $m_e$ are the charge and mass of the electron. Examination of equations (2)–(4) reveals that the change in the final kinetic energy $\Delta E$ experienced by the observed electron is proportional to the vector potential $A(t)$ of the streaking field at the moment of interaction. For extended emission, the streaking laser in effect maps the time domain onto the sheared electron spectrum. This approach provides a route towards reconstructing the temporal characteristics of the electron emission with the potential for attosecond resolution. A crucial requirement is that the amplitude and phase of the streaking field acting on the emitted electrons must be known with sufficient precision.

Self-referenced streaking spectroscopy

Using our experimental technique, we can potentially determine both the amplitude and phase of the streaking laser field for each shot by simultaneously measuring shifts in the kinetic energy of two types of electrons. In this experiment, we observe the kinetic energies of both the photoemission and Auger peaks after interaction with the streaking laser. We note that, whereas the photoelectrons and Auger electrons are both shifted in kinetic energy according to equation (3), the Auger electrons are generally emitted later than the photoelectrons. As a result, the phase of the streaking laser will have advanced by some amount in the time between emissions, owing to the pulse’s propagation through the stationary target. Consequently, the Auger electrons’ energy shift will be a function not only of $\theta$, but of $\theta + \theta_\alpha$, where $\theta_\alpha$ represents the phase advance between the instants of photoemission and Auger emission. The result is that the change in energy experienced by photoelectrons and Auger electrons will generally differ in magnitude and even sign, depending on the temporal overlap and absolute carrier-envelope phase of the mid-infrared pulse. It should be noted that since the field-free kinetic energies $E_i$ of the two types of electrons are different, there would always be a difference in the magnitude of their energy changes, even if the emissions were simultaneous, due to the factor of $\sqrt{E_i}$ in equation (3)).

Conceptually, if one were to smoothly vary the overlap between X-ray-stable and carrier-envelope-phase-stable streaking pulses, the sinusoidal curves traced out by the two emission peaks’ centres of energy would be temporally displaced by the time elapsed between the two events, as illustrated in Fig. 2a and Fig. 2b. In effect, each peak in the electron energy spectrum independently samples the oscillation of the streaking vector potential. When plotting the two streaked centres of energy against each other, as in Fig. 2c, the resultant ring has an ellipticity determined by the phase shift between the two sine curves. A phase shift of 0 (that is the case where both emissions were simultaneous) would result in a straight line, as both emissions would experience the same vector potential in each shot. If the shift were $\pi/2$, the graph would be a wide ellipse with major and minor axes parallel to those of the coordinate system, because whenever one emission interacted with a zero crossing of the streaking field, the other would interact with an extremum. Finally, a phase shift between 0 and $\pi/2$ would lead to a sheared ellipse.

In reality, the carrier-envelope phase of the mid-infrared streaking pulse cannot be controlled during experiments at XFELs. Therefore, each single-shot measurement is made with a random streaking phase. Nevertheless, if a large enough set of measurements is accumulated, the entire parameter space will be explored, and a scatter plot forming an ellipse like that in Fig. 2c can be constructed.

In addition to its randomly varying phase, the precise arrival time of the streaking pulse with respect to the X-ray pulse fluctuates. Therefore, the strength of the streaking effect varies from shot to shot, depending on the temporal overlap between the X-ray pulse and mid-infrared intensity pulse envelope. Whereas variation in the streaking field phase leads to the characteristic ellipse, these timing-jitter-induced variations in streaking strength result in a broadening of the elliptical distribution, since for any given angle around the ellipse there are a range of possible displacements from its centre. If the jitter were very small, the ellipse would collapse to a single line like that shown in the idealized plot in Fig. 2c. In this case, all shots would overlap with the same part of the streaking field envelope, although the carrier-envelope phase would still vary between shots. If the timing jitter increases relative to the streaking pulse duration, the centre of the ellipse becomes filled.

In principle, the shape of the ellipse may also be influenced by photon energy jitter, which causes corresponding variations in the initial kinetic energy of each burst of photoelectrons. This occurs prior to and independent of the interaction of the photoelectrons with the streaking field, and manifests as a small offset in the measured photoelectron kinetic energy spectra. The Auger spectra are immune to energy jitter, because the initial kinetic energy of the Auger electrons is independent of the X-ray photon energy.

The elliptical distribution, generated by correlating the streaking-induced shift in kinetic energy of the photoelectron and Auger peaks in single-shot measurements made over a complete set of streaking field parameters, is the key to our technique. In effect, the correlation plot is a map, with each position pinned to a unique set of streaking field parameters. Once this distribution has been obtained, all subsequent single-shot measurements can be mapped to retrieve the instantaneous streaking phase and amplitude. Single-shot measurements performed with desired streaking parameters can be identified and isolated, even though those
parameters are uncontrolled during the experiment. This is how we have extended the techniques of table-top attosecond spectroscopy to be applied at XFELs, allowing a dramatic increase in achievable time resolution to the subfemtosecond regime.

**Experimental results**

In the experiment, the streaked kinetic energies of the photoelectron and Auger electron peaks are determined by numerically fitting the recorded spectra in each single-shot measurement and calculating the centre of energy of each peak. In addition to the streaked measurements, we also obtained thousands of spectra in the absence of the streaking laser. By comparing the streaked energies to the corresponding streaking-field-free values, we determine the changes in kinetic energy, ΔE_{Aug} and ΔE_{c}, induced by the streaking field in each single-shot measurement. These field-free kinetic energies can also be used to determine the photon energy jitter. In our experiments this jitter follows a distribution with a root-mean-square width of 1.2 eV, which was small in comparison to the total change in the photoelectron kinetic energy induced by the streaking field. This, in conjunction with its normally distributed nature and the fact that we average over many thousands of shots in the following treatment, allows it to be neglected. In future experiments, if the photon energy jitter were found to be non-negligible, there are multiple approaches that might be taken to mitigate or eliminate its effect. The most straightforward of these would be simultaneous reference measurements of the single-shot X-ray photon energy.

Figure 3 shows the correlation between ΔE_{Aug} and ΔE_{c}, obtained from tens of thousands of streaked measurements, revealing a characteristic elliptical distribution. Specific regions of the ellipse are highlighted, with sketches of the corresponding measurement conditions shown in the subplots on the right. The subplots indicate how the correlation map can be used to navigate to previously inaccessible streaking parameters: the angular coordinate of each point identifies the streaking phase for that shot, and its radial coordinate is a function of the streaking field amplitude.

The characteristic elliptical distribution in Fig. 3 will be used to measure the delay between photoemission and Auger emission, which itself will be used to calculate the Auger decay lifetime. The distribution also provides access to important diagnostics.

The data in Fig. 3 make it simple to identify those shots for which the photoemission burst coincides with a zero crossing of the streaking vector potential. Such shots appear on the ‘equator’ of the ellipse, since the photoelectrons experienced a minimal energy shift. After identifying these shots, it is possible to calculate the average duration of the X-ray pulse by comparing the width of the photoemission line in these maximally broadened shots to the width of the field-free photoemission lines. Using this method, we determined the average X-ray pulse FWHM to be \(7 \pm 1\) fs, as detailed in the Methods.

Further, by analysing the widths of the distributions in our data and given the pulse duration of the mid-infrared laser, which was approximately 300 fs root-mean-square, we calculated that the timing jitter has a root-mean-square width of 110 fs. One of the chief strengths of self-referenced streaking is that it enables resolution that would ordinarily be impossible with jitter this severe; we will use these data to measure a temporal delay with subfemtosecond precision despite the presence of timing jitter that is orders of magnitude larger.

**The delay in Auger emission**

As an alternative to examining features in the individual or averaged streaked Auger spectra, which is not possible here owing to limited energy resolution, the degree of ellipticity in the distribution can provide access to the delay between the two emission bursts. We note that any ellipse can be described using the set of parametric equations

\[
x(\theta) = A \sin(\theta + \phi_A), \quad y(\theta) = B \sin(\theta).
\]

In our case, \(x\) and \(y\) correspond to the change in kinetic energy of the Auger and photoelectrons respectively. As described in detail in the Methods, the angle \(\phi_A\) is the phase advance that occurs between the two instants of electron emission. It is given by

\[
\phi_A = \sin^{-1}\left(\frac{y}{y_2}\right),
\]
where $y_1$ is the ellipse’s $y$ intercept, and $y_2$ is its maximum value of $y$. By examining the angular sectors of the ellipse corresponding to $y_1$ and $y_2$ we can calculate them, obtaining values of $8.0 \pm 0.1$ eV and $20.9 \pm 0.1$ eV, respectively. Using these values in conjunction with equation (6) enables us to calculate the phase advance $\phi_A$ to be $0.39 \pm 0.01$ radians. Details of the selection of the sectors containing the points, and the calculation of the uncertainty on these values, can be found in the Methods. The corresponding time-delay, $\tau_{\text{delay}}$, between the photoemission and Auger emission bursts can then be calculated using the observed phase shift $\phi_A$ and $T_{\text{IR}} = 56 \pm 3$ fs, the period of the streaking pulse:

$$\tau_{\text{delay}} = \frac{\phi_A}{2\pi} T_{\text{IR}} .$$

Applying this algorithm to the distribution shown in Fig. 3, we obtain a delay of $3.5 \pm 0.3$ fs. The subfemtosecond uncertainty on this value was obtained by propagating the uncertainties on $\phi_A$ and $T_{\text{IR}}$ using a standard functional approach, as detailed further in the Methods. Notably, by extracting information from a large amount of individual shots, our technique enables us to measure this delay despite using an X-ray pulse whose duration is longer. However, in this case, we must avoid using a theoretical model of Auger decay which assumes a very short ionizing pulse.

**Evaluation of the Auger decay lifetime**

We will apply a fully quantum-mechanical theoretical model of the Auger emission process to interpret our measurement of the delay between photo- and Auger emission bursts. This model of laser-assisted Auger decay was originally developed in reference 20, and is based on the solution of the time-dependent Schrödinger equation describing atomic ionization by an X-ray pulse and corresponding Auger decay in the presence of a strong laser field. A complete mathematical description can be found in the Supplementary Information.

We can use this model to calculate time-dependent Auger emission profiles and examine their dependence on experimental and physical parameters. We are interested in the time delay between the centres of mass of the photoemission and Auger emission profiles, which is the experimentally measured quantity $\tau_{\text{delay}}$. In our calculations we find that $\tau_{\text{delay}}$ is dependent not only on the Auger decay lifetime $\tau_A$, but also on the ionizing X-ray or XUV pulse used in the experiment. This stands in contrast to the predictions of the ad hoc two-step model used in past work5, in which the quantities $\tau_{\text{delay}}$ and $\tau_A$ are identical regardless of ionizing pulse duration. The quantum-mechanical model shows that this is only accurate when extremely short ionizing pulses are used. In most XFEL experiments with femtosecond pulses, this condition is not met, and $\tau_{\text{delay}}$ can...
only be correctly related to the Auger decay lifetime by using the quantum-mechanical model.

By calculating the delays $\tau_{\text{delay}}$ associated with a variety of possible Auger decay lifetimes $\tau_{\text{A}}$ and accounting for the $7 \pm 1$ fs X-ray pulse duration measured in our experiment, the model allows us to map between $\tau_{\text{delay}}$ and $\tau_{\text{A}}$. This procedure led to the conclusion that the observed delay $\tau_{\text{delay}} = 3.5 \pm 0.5$ fs between the emission bursts corresponds to an Auger decay lifetime $\tau_{\text{A}} = 2.2 \pm 0.2$ fs. The uncertainty on this value incorporates that on $\tau_{\text{delay}}$ and the X-ray pulse duration, which were propagated using a functional approach. Our final result for the Auger decay lifetime is in agreement with measurements reported from spectral linewidth studies, which have found values in the range 2.0–2.6 fs (refs. 7,15,40,49).

To illustrate the importance of the theoretical model, we have performed additional simulations with variable X-ray pulse duration. Keeping the Auger decay lifetime fixed at the retrieved value of 2.2 fs, we increased the X-ray pulse duration from 100 as to 12 fs. The results are shown in Fig. 4. Although the observed delay is close to the Auger decay lifetime for attosecond pulses, a substantial difference appears as the ionizing pulse duration increases. This difference between $\tau_{\text{delay}}$ and $\tau_{\text{A}}$ demonstrates the necessity for a full quantum-mechanical treatment for experiments such as ours, where the exciting X-ray pulse duration is comparable to or longer than the Auger decay lifetime.

Conclusion and outlook
This measurement, which was performed at an XFEL, was made possible via self-referenced attosecond streaking. Following this successful demonstration of its efficacy, self-referenced streaking will enable experiments to take advantage of the extreme-intensity X-ray pulses at XFELs while simultaneously exploiting the unrivalled time resolution provided by attosecond streaking spectroscopy.

In conjunction with the technique, the measurement was made possible via the application of a consistent quantum model of Auger decay. Through the application of this more advanced model, we demonstrated that the older, ad hoc two-step model overestimates the extracted lifetime by more than 1 fs under the present experimental conditions. This will have major ramifications for future studies of Auger decay, especially those applying our self-referenced streaking to make the measurement at XFELs.

Because so many highly excited states of matter relax via Auger decay, this result may also help to inform future studies on double-core-hole spectroscopy26–31, XFEL-pumped X-ray lasers2,3, and other innovative techniques dependent upon the timescales of Auger processes. Beyond simple atomic systems, our self-referenced Auger measurements could pave the way for investigations into the effect of a system’s chemical environment on Auger decay2; a comparison could, for example, be made between decay rates of carbon in CF$_3$ and CO. Studies of Auger decay in molecules would require high energy resolution in order to resolve structures in these more complicated Auger spectra, and the quantum model used for the interpretation of the data would need to be expanded to encompass molecular structures. Nevertheless, this is a promising avenue for future experiments. Furthermore, we expect that precise temporal characterisation of Auger decay processes in complex systems will be crucial in interpreting diffraction and scattering patterns in single-molecule imaging experiments, where a large proportion of Auger electrons are known to deposit energy into molecular samples after emission7,51,52.

Online content
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Methods

Calculation of the average pulse duration. The duration of the X-ray pulse is an important parameter in this experiment, as it influences the emission profile of both types of electrons. We will calculate it following the methods described in ref. 13. Our method is facilitated by the correlation plot shown in Fig. 3, and provides similar resolution to established non-invasive measurements of pulse duration14. In streaking experiments such as ours, the duration of an X-ray pulse can be calculated using the relation

\[ \tau_x = \frac{\sigma_{DC}}{s}, \]  

where \( \sigma_{DC} \) represents the breadth of the streaked photoemission peak after deconvoluting that of the field-free peak, and \( s = \frac{dy}{dt} \) is the streaking speed. The latter represents the rate of change of the peak’s kinetic energy with respect to the timing of the streaking pulse. Where the X-ray and streaking pulses are well overlapped, the final energy of photoelectrons emitted at time \( t \) is given by

\[ E_{k}(t) = \frac{\Delta E_{\text{max}} - \Delta E_{\text{min}}}{2} \sin(\alpha_k t) + E_{k0}, \]  

where \( \Delta E_{\text{max}} - \Delta E_{\text{min}} \) is the difference between the most positive and most negative changes in photoelectron energy throughout the experiment, \( \sigma_k \) is the angular frequency of the streaking field, and \( E_{k0} \) is the field-free kinetic energy of the photoelectrons. Therefore, at the zero-crossing of the streaking field,

\[ s = \frac{\Delta E_{\text{max}} - \Delta E_{\text{min}} \times \pi}{T_{IR}}, \]  

where we have used the relation \( T_{IR} = \frac{\pi}{\omega} \) and set \( t = 0 \).

The value of \( \Delta E_{\text{max}} - \Delta E_{\text{min}} \) is calculated from angular sectors corresponding to the maxima and minima of the streaking phase. All shots within a given angular sector interact with the same streaking phase, but the final kinetic energy of the electrons will still vary according to the streaking field amplitude—which will itself vary according to timing jitter. Clearly, the largest possible change in kinetic energy will occur when the streaking amplitude is maximal and the phase causes the electrons to interact with a peak of the streaking vector potential. Because timing jitter results in a normal distribution of streaking amplitudes, it is most likely that a given shot will interact with the centre of the streaking pulse envelope. These conditions are identified by numerically fitting the distribution of absolute photoelectron kinetic energies within both sectors and extracting its peak, as shown in Extended Data Fig. 1. Using this method, we determine that \( \Delta E_{\text{max}} - \Delta E_{\text{min}} = 48 \pm 1 \) eV.

The first step towards finding \( \sigma_{DC} \) is to calculate the spectral width of the photoemission peak at the zero crossing of the streaking field. These shots can be swiftly identified using the elliptical distribution: they must lie on its equator, where the kinetic energy of the photoelectrons was largely unchanged. Further, the shots closest to the edge of the ellipse interacted with the peak of the streaking pulse envelope, resulting in a maximized change in Auger electron kinetic energy. Therefore, we restrict our consideration to shots for which the final photoelectron kinetic energy was within 1 eV of its field-free value. Within this group, we take the 300 outermost shots on each side of the ellipse, corresponding to the strongest streaking effect. Recall that, as illustrated in Fig. 3, the left and right sides of the ellipse correspond to zero crossings of the streaking pulse with opposite slopes. Since the shots do not display any irregular structure, they can each be fitted using Gaussian functions, and the width of these functions can be computed. The average breadth of the 300 shots on the left of the ellipse is \( \sigma_L = 8.9 \pm 0.2 \) eV and that of the 300 shots on the right is \( \sigma_R = 9.8 \pm 0.2 \) eV. Here and in the following, we have used the standard error on the mean value of \( N \) repeated measurements, given by

\[ \sigma_m = \frac{\sigma}{\sqrt{N}}, \]  

where \( \delta \) is the statistical width of the distribution. We must deconvolve the bandwidth of the field-free photoemission peak \( \sigma_p \) from that of the peak at a zero crossing using the relation

\[ \sigma_{DC} = \sqrt{\sigma^2 - \sigma_p^2} = 7.9 \pm 0.2 \text{ eV}. \]  

Here, \( \sigma^2 = \frac{\sigma_{DC}^2}{s^2} \) represents the average of the squares of the mean bandwidth at each zero crossing. The average field-free photoemission bandwidth is \( \sigma_p = 4.95 \pm 0.01 \) eV. The uncertainty on \( \sigma_{DC} \) is much smaller than that on \( \sigma_p \) because there are many more unstacked shots available to use in the calculation of the former. The average XFEL pulse duration can be calculated using these quantities, propagating the uncertainties on each one using a standard functional approach. The average full width at half maximum (FWHM) duration of the X-ray pulse is given by

\[ \tau_x = 2.2 \ln(2) \frac{\sigma_{DC}}{s} = 7 \pm 1 \text{ fs}, \]  

where the factor 2.2ln(2) is used to convert from root-mean-square width to FWHM.

Extraction of the phase shift. As noted in the main text, the two equations

\[ x(t) = A \sin (\theta + \phi_k), \quad y(t) = B \sin (\theta) \]  

describe an ellipse and plotting them against each other will allow us to measure \( \phi_k \). A generalized plot of the two equations is shown in Extended Data Fig. 2. In this plot the y intercept, \( y_2 \), as well as the maximum value of \( y, y_p \), are highlighted. From equation (14), it is clear that

\[ y_1 = B \sin (-\phi_k), \quad y_2 = B. \]  

It follows that

\[ \phi_k = \sin^{-1} \left( \frac{y_1}{y_2} \right). \]  

Therefore, we can measure the magnitude of \( \phi_k \) simply by measuring the y intercept and maximum value of \( y \) in our data. In fact, the same principle can be applied to the negative y intercept and extremum, and both positive and negative pairs on the x axis. All four possible measurements were made and showed little disagreement. For the result shown in the paper, the positive y pair was used. The motivation for choosing \( y_1 \) and \( y_2 \) as opposed to \( s_1 \) and \( s_2 \) comes from the fact that our spectral resolution on the photoemission (y) peak is better than that of the Auger peak. Furthermore, \( s_1 \) ought to be measured at a zero crossing of the photoemission peak. Under these conditions the peak will be substantially broadened, and its position will be more uncertain. In contrast, the Auger peak—and therefore measurements using points on the y axis, which is at a zero crossing of the Auger peak—is less sensitive to broadening-induced noise.

Error analysis. The method lends itself to straightforward error analysis. If we are able to quantify the uncertainties on \( y_1 \) and \( y_2 \) as \( \sigma_1 \) and \( \sigma_2 \), respectively, we could define a parameter \( K = \frac{y_2}{y_1} \), whose uncertainty will be given by the following expression:

\[ \sigma_K = K \left( \frac{\sigma_1}{y_1} \right)^2 + \left( \frac{\sigma_2}{y_2} \right)^2. \]  

From here it is simple to quantify the uncertainty on \( \phi_k \) using a functional approach and equation (16), as follows:

\[ \sigma_{\phi} = \sin^{-1} (K) - \sin^{-1} (K \pm \sigma_K). \]  

Recall that \( \phi_k \) corresponds to the streaking phase advance, which occurs between the centres of energy of the photoemission and Auger emission bursts. As described in the main text, the centre-of-mass delay between the two emissions \( \tau_{\text{delay}} \) is a scalar product of \( \phi_k \) and the mid-infrared streaking laser wavelength \( \lambda_\text{IR} \):

\[ \tau_{\text{delay}} = \frac{\phi_k \lambda_{\text{IR}}}{2\pi c}. \]  

The constant \( 2\pi c \) can be assumed to be known to an infinite degree of precision. It is now straightforward to calculate \( \sigma_{\text{delay}} \), the uncertainty on \( \tau_{\text{delay}} \), which is given by

\[ \sigma_{\tau_{\text{delay}}} = \frac{\phi_k \lambda_{\text{IR}}}{2\pi c}. \]  

The wavelength \( \lambda \) was measured at Linac Coherent Light Source to be \( 17.1\pm2 \) μm. Therefore, we need only identify \( \sigma_1 \) and \( \sigma_2 \) to determine the precision of our measurement of the centre-of-mass delay. The quantities \( y_1 \) and \( y_2 \) and their uncertainties, were measured by examining the distribution of data, in particular angular sectors of the ellipse.

Selection of ellipse sectors. It is clear that, when measuring from the origin, the ellipse’s y intercept \( y_2 \) is contained within a sector aligned with the positive y axis. It is less obvious to determine which sector contains \( y_1 \), the maximum value of y. From the general equation of an ellipse,

\[ \begin{pmatrix} x(t) \\ y(t) \end{pmatrix} = \begin{pmatrix} \cos(\alpha) & -\sin(\alpha) \\ \sin(\alpha) & \cos(\alpha) \end{pmatrix} \begin{pmatrix} a \cos(t) \\ b \sin(t) \end{pmatrix} + \begin{pmatrix} x_0 \\ y_0 \end{pmatrix}, \]  

one can derive the angle \( \theta \), for which \( y \) is maximal:

\[ \theta = \tan^{-1} \left( \frac{b}{a} \cot(\alpha) \right). \]  

It follows that \( y = y(\theta) \). An initial approximation to \( \theta \) was made using a least-squares fit of the elliptical data, which provided the necessary constants \( a \) and \( b \) and resulted in a value of \( \theta = 0.6612 \) rad. To support this choice of \( \theta \), \( y_2 \) was measured for a range of critical angles \( \theta \). The results are in Extended Data Fig. 3. The value of \( \theta \) that maximizes \( y_2 \) was found to be very close to that determined from the fit. Furthermore, \( y_2 \) shows little variation in the region of \( \theta \) space close to \( \theta \). One can infer that this was a good choice of \( \theta \), and further that any uncertainty on \( \theta \) will have a small impact, because it will result in only a small change to \( y_2 \).
The next step is to identify $y_i$ from the distribution of points in the sector at $\theta_i$. The two sectors are highlighted in Extended Data Fig. 4.

Let the sector from which we obtain the value $y_i$ be called $Y_i$, such that $y_i$ is given by the mean of all the $y$ coordinates of the points in $Y_i$. The sectors $Y_i$ and $Y_j$ are defined in a subtly different way. By definition, $y_j$ is the y intercept of the ellipse, and as such the sector $Y_j$ is identified by taking the set of points closest to the $y$ axis, so that:

$$y_j = \{(x,y) : |x| < e_j, \ e_j \in \mathbb{R}, e_j > 0 \}.$$  

(23)

The sector $Y_i$, conversely, is defined as the points whose angular coordinate is closest to the critical angle $\theta_i$. In terms of polar coordinates, we can define $Y_i$ as follows:

$$Y_i = \{(r, \theta) : |\theta - \theta_i| < e_i \} , \ e_i \in \mathbb{R}, e_i > 0 \}.$$  

(24)

A polar sector is ill-suited for determining $y_i$, as it incorporates outliers at the edge of the cone, causing the algorithm to overestimate $y_i$ and therefore $\theta_i$, when tested with simulated data. However, as we make the sectors wider and wider, the width of the distribution $\Delta Y_i$ begins to increase. The sector sizes were chosen to minimize $\Delta Y_i$.

Accounting for this using equation (20) results in the value of $\tau_{\text{final}}$. The dominant source of uncertainty in the experiment is in the measurement of the streaking wavelength, which was only known within a 3% range.

The procedure described above can now be used to go from these uncertainties to those of the COE delay $\tau_{\text{COE}}$. The sector sizes were chosen to minimize $\Delta Y_i$.

The quantum-mechanical model. In this semiclassical approach, making use of the full quantum-mechanical numerical simulation: for a given set of experimental parameters, each Auger decay lifetime results in a unique value of the phase shift. To determine the Auger decay lifetime, it is iterated over until the simulated phase shift matches the observed phase shift, as described in the main text.

**Data availability**

The data that support the plots within this paper and other findings of this study are available from the corresponding authors on request.

**Code availability**

Interested parties may contact A.K.K. (kazan356@rambler.ru) to obtain a copy of the simulation code used to verify the quantum treatment of Auger decay for our experiment.

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**Author contributions**

L.F.D. and G.D. proposed the measurement of Auger lifetimes at the Linac Coherent Light Source and A.L.C. conceived the self-referenced streaking approach that enabled these measurements. The experiment and supporting experiments were performed by A.A.-H., C. Bostedt, J.R., H.E., M.B., A.C., S.C., A.L.C., R.C., J.T.C., L.F.D., G.D., K.E., G.D., D.C.H., M.C.H., M.I., R.K., A.R.M., F.T., W.H., T. Mazza, M.M., H.P., C.R., A.S., P.A.W., M.M., R.S. and A.L.C. acknowledge funding through the Clusters of Excellence 'The Hamburg Centre for Ultrafast Imaging' (EXC 1074 project ID 194651731) and 'CUE: Advanced Imaging of Matter' (EXC 2056 project ID 390719949) of the Deutsche Forschungsgemeinschaft. J.T.C. acknowledges support by Science Foundation Ireland (grant number 16/R/3696) and the SEAT (grant number 19/R/1525). L.C. and C.R. acknowledge support from the National Science Foundation under grant number 1605042 and the US Department of Energy under grant DE-FG02-04ER15164. WH. acknowledges financial support from a Marie Curie International Outgoing Fellowship and by the BaCaTeC programme. M.I. acknowledges funding from the Volkswagen Foundation within a Peter Paul Fwheel Fellowship. N.M.K. acknowledges hospitality and financial support from the theory group in cooperation with the SWS project package of European XFEL (Hamburg). A.R.M. and S.J. acknowledge financial support from the German Science Foundation (DFG) (Grant No. 2752/1-1). M.I., R.S., C.Behrens and A.L.C. were supported by the US Department of Energy, Office of Science, Basic Energy Sciences, Chemical Sciences, Geosciences, and Biosciences Division under contract AC-02-06CH11357.

**Competing interests**

The authors declare no competing interests.

**Additional information**

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Extended Data Fig. 1 | Distribution of maximally streaked kinetic energies. The changes in photoelectron kinetic energy in the sector corresponding to maximal streaking phase are plotted in the histogram. The red line shows the numerically determined least-square fit, from which we extract the peak of the distribution. By the normally distributed nature of timing jitter, highest number of shots will overlap at or near the peak of the pulse envelope, so that the peak of the histogram ought to correspond to those conditions.
Extended Data Fig. 2 | Generalized ellipse. An arbitrary ellipse is shown (blue line) with the x- and y-axes highlighted (black lines), in addition to the parameters $y_1$ and $y_2$ (red dotted lines).
Extended Data Fig. 3 | Critical angle $\theta_c$. The measured value of $y_2$ is shown (blue line) for a range of critical angles $\theta_c$. The red dotted line represents the value of $\theta_c$ that was used in the final analysis.
Extended Data Fig. 4 | Sectors for calculation of the parameters $y_1$ and $y_2$. A zoomed-in section of the data is shown. Overlaid on the density map, the red points are those contained in each of the sectors used to find the parameters. The black crosses represent the measured values $y_1$ and $y_2$, which are highlighted by the red dotted lines. From these data, $y_1$ and $y_2$ were measured at 7.9 eV and 20.9 eV respectively.
Extended Data Fig. 5 | The distribution of parameters $y_1$ and $y_2$. The red dashed lines highlight the mean value and the black dashed lines display the statistical width of each distribution.