

Attosecond X-Ray Core-Level Chronoscopy of Aromatic Molecules

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(Received 26 May 2025; accepted 24 October 2025; published 14 November 2025)

Attosecond photoemission or photoionization delays are a unique probe of the structure and the electronic dynamics of matter. However, the spectral congestion of valence photoelectron spectra sets fundamental limits to the complexity of systems that can be studied, and the delocalization of valence electron wave functions blurs the spatial origin of the photoelectron wave packet. Using attosecond x-ray pulses from LCLS, we demonstrate the key advantages of measuring core-level delays: The photoelectron spectra remain atomlike, the measurements become element specific, and the observed scattering dynamics originate from a pointlike source when multicenter interference effects are negligible. We exploit these unique features to reveal the effects of changing functional groups (C-H vs N) and symmetry on attosecond scattering dynamics by measuring and calculating the photoionization delays between N-1s and C-1s core shells of a series of aromatic azabenzene molecules. Remarkably, the delays increase with the number of nitrogen atoms in the molecule and reveal multiple resonances. We identify two previously unknown mechanisms regulating the associated attosecond dynamics, namely the enhanced confinement of the trapped wave function with the replacement of C-H groups by N atoms and the decrease of the coupling strength among the photoemitted partial waves with increasing symmetry. This study demonstrates the unique opportunities opened by measurements of core-level photoionization delays for unraveling attosecond electron dynamics in complex matter.

DOI: [10.1103/dp5w-qxqc](https://doi.org/10.1103/dp5w-qxqc)

Subject Areas: Atomic and Molecular Physics

I. INTRODUCTION

Tracking attosecond multielectron dynamics with atomically resolved spatial information is the current focus of numerous research efforts worldwide. X-ray spectroscopy has established itself as a powerful solution to breaking the complexity barriers faced by valence-shell spectroscopies. These barriers are particularly pronounced in time-resolved studies of the photoelectric effect, known as attosecond chronoscopy [1–3]. This technique has integrated time-domain access to multielectron dynamics into the powerful framework of electron-scattering physics which has created a flourishing research field with applications to molecules

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[4–9], clusters [10,11], liquids [12], and solids [13–16]. Such studies have traditionally made use of attosecond pulses in the extreme ultraviolet (up to 120 eV), which has so far prevented access to atomic core levels.

Here, we demonstrate the unique opportunities that arise from advancing the research field of attosecond chronoscopy from the extreme-ultraviolet to the x-ray domain. This adds element specificity and site selectivity to the method, while simultaneously confining the emission site of the photoelectron wave to a pointlike source, when multicenter interference effects between indistinguishable atoms are negligible. Moreover, core-shell photoelectron spectra have a much simpler structure than valence-shell spectra, which facilitates the extension of the method to complex forms of matter. This advance was made possible by groundbreaking progress in free-electron-laser (FEL) science that has led to the generation of attosecond pulses in the x-ray domain through the x-ray laser-enhanced attosecond pulse generation (XLEAP) technique [17]. The long-standing challenge of temporal jitter between the FEL pulses and laser pulses was solved by using attosecond angular streaking with a circularly polarized infrared laser pulse and detecting the photoelectron momentum distribution in the polarization plane [18–20].

The present experiments establish the unique capabilities of x-ray chronoscopy, recently demonstrated in a diatomic molecule [20], at unraveling the mechanisms of attosecond electron dynamics in complex systems, notably in aromatic molecules (i.e., benzene derivatives). Specifically, our study reveals the multiple-scattering phenomena that lead

to transient trapping of photoelectrons following their release from specific atoms. Our results reveal two previously unknown mechanisms regulating such attosecond scattering dynamics. First, we find that substituting N atoms for C-H functional groups in a ring molecule increases the trapping times. Second, we show that increasing the symmetry of the molecular scaffold also increases the trapping times by suppressing the coupling to the less-trapped partial waves with lower angular momentum. To demonstrate these effects, we chose the azabenzene molecules pyridine, pyrimidine, and *s*-triazine, depicted in Fig. 1(a). We produced attosecond x-ray pulses with energies just above the nitrogen *K* edge located at ~ 405 eV and measured the photoionization delays between the electrons emitted from the nitrogen *K* shell (N-1s) and those emitted from the carbon *K* shell (C-1s). Since the latter have kinetic energies of more than 110 eV, the C-1s electrons are emitted with negligible photoionization delays ($\lesssim 5$ as), defining a self-referenced technique for accessing absolute photoionization delays of the N-1s electrons. We measured N-1s photoionization delays of up to ~ 300 as close to the nitrogen *K*-shell threshold, which generally decrease with increasing kinetic energy but display local maxima at 3–15 eV above the threshold. The measured delays indeed markedly increase from pyridine to pyrimidine. These experimental results are compared with state-of-the-art core-level photoionization calculations, which reveal the presence of several shape resonances in this low kinetic-energy region. The comparison of experiment and theory reveals that the photoelectrons originating

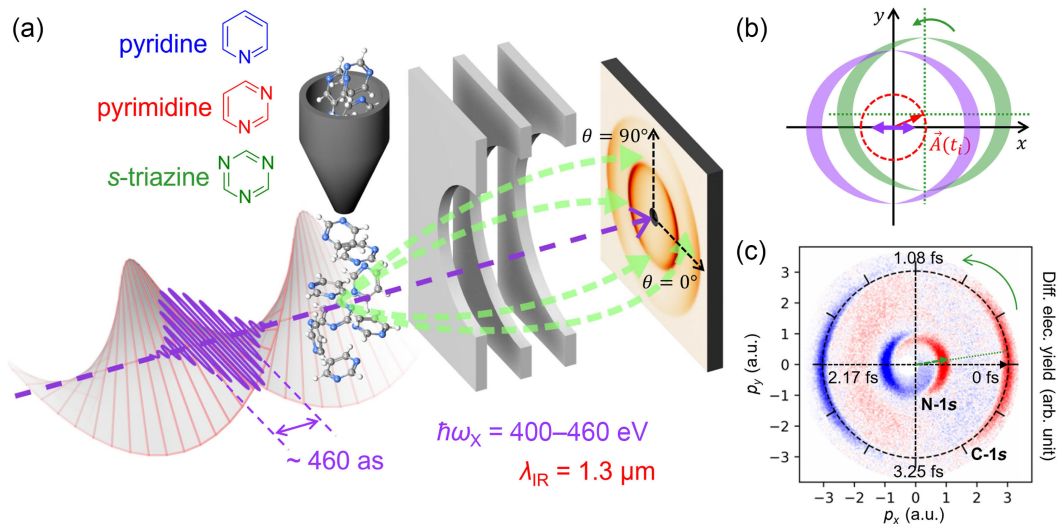


FIG. 1. The principle of measuring core-level photoionization delays with an x-ray free-electron laser (XFEL). (a) Gas-phase azabenzene molecules (pyridine, pyrimidine, or *s*-triazine) are ionized by the attosecond XFEL pulses in the presence of a 1.3- μm circularly polarized streaking laser field. The photoelectrons are collected with a cVMI spectrometer, with θ as the polar angle on the detector. (b) The initial photoelectron momentum distribution (purple) is shifted by the vector potential of the IR field $\vec{A}(t_i)$ at the instant of ionization t_i , where the purple double arrow indicates the x-ray polarization direction. (c) Difference image between streaking within a narrow range of angles and the average over all streaking angles, revealing the angular offset of the N-1s and C-1s electrons, which directly encodes their time delay.

from the nitrogen K shell are trapped with increasing efficiency in the molecular plane in the sequence pyridine, pyrimidine, s -triazine, i.e., with increasing number of nitrogen atoms. Additionally, the increasing symmetry of the molecular scaffold (from C_{2v} in pyridine to D_{3h} in s -triazine) reduces the coupling among the photoelectron partial waves, which frustrates the decay of the trapped partial waves with high angular momentum. Pyrimidine is a building block of the nucleobases thymine, cytosine, and uracil. All three azabenzene molecules are widespread structural motifs in biomolecules, drugs, and molecular optoelectronics [21–24]. The discovered mechanisms therefore suggest guidelines for extending attosecond chronoscopy to biomolecules and molecules used in optoelectronics.

II. EXPERIMENTAL SETUP AND DATA ANALYSIS

Figure 1 illustrates the principle of the present experiments, carried out at the time-resolved, molecular, and optical science (TMO) experimental hutch [25] of the Linac Coherent Light Source (LCLS). Linearly polarized attosecond x-ray pulses with a tunable central energy were obtained using the XLEAP technique [17] and were superimposed with circularly polarized short-wave infrared (IR, 1.3 μm , ~ 40 fs) pulses in the interaction region of a coaxial velocity-map-imaging (cVMI) spectrometer. A continuous molecular beam containing pyridine, pyrimidine, or s -triazine intersected with the overlapping x-ray and IR pulses in the interaction region. The photoelectrons created from nitrogen K -shell ionization of the sample were streaked by the IR pulses and projected onto a position-sensitive imaging detector with a central hole. A photoelectron image recorded by ionizing pyrimidine with x-ray pulses centered at 454 eV is shown in Fig. 1(a), whereby the inner (outer) ring corresponds to ionization of the nitrogen (carbon) K -shell electrons. Figure 1(c) shows how the relative photoionization delays between the N-1s and C-1s photoelectrons were determined. Because each photoelectron was angularly streaked into the direction of the IR-laser vector potential at the instant of photoionization [Fig. 1(b)], the relative angle between the momentum shift of the N-1s and C-1s electrons (the streaking angle) directly encodes their relative photoionization delay. The conversion from relative streaking angle $\Delta\theta$ to the relative photoionization delay $\Delta\tau$ is simply given by $\Delta\tau = T_L \times \Delta\theta/2\pi$, where T_L is the period of the streaking laser [26–32].

Figure 2 illustrates how the relative streaking angles $\Delta\theta$ were obtained from the experimental data. Because of the large temporal jitter (~ 500 fs) between the arrival time of x-ray free-electron laser (XFEL) and IR laser pulses [33], the streaking directions of the core-shell photoelectrons were completely random from shot to shot. The information of relative photoionization time delay is therefore only encoded in the relative streaking angle of the N-1s and C-1s

electrons, which is recorded on a shot-by-shot basis. Figure 2(a) shows the difference image between the average over all shots corresponding to a narrow range of streaking directions from postselection of the images and the average over all streaked images without any sorting and selection. An angular shift $\Delta\theta$ between the streaking directions of C-1s (outer) and N-1s (inner) electrons can be observed, which directly reflects the relative photoionization delays, as described above. To accurately determine the relative streaking angle, we employ a partial covariance analysis that uses the large shot-to-shot variation of streaking directions to directly extract $\Delta\theta$ without estimating and sorting the streaking directions of C-1s and N-1s electrons in every single image. For a given relative streaking angle $\Delta\theta$, the streaking-induced signal fluctuations in C-1s electrons at θ have the most positive covariance with the N-1s electrons around $\theta + \Delta\theta$. By correctly calculating the partial covariance coefficients between streaking-induced signal changes in N-1s and C-1s electrons, the differential streaking angle $\Delta\theta$ manifests itself as a global shift in the partial covariance maps, as shown in Fig. 2(c). Additional details on the partial covariance analysis are given in Sec. II B 1 of Supplemental Material (SM) [34] and systematically explained in Ref. [46]. By comparing Figs. 3(a) and 3(c) to Figs. 3(b) and 3(d), a relative photoionization delay of up to 120 as is observed at 410 eV, as opposed to a negligible delay at 454 eV. We have also developed a complementary data-analysis method (the so-called “center-of-mass” method), which is described in Sec. II. B. 2 of SM. These two independent analysis methods yielded consistent photoionization delays (Fig. S14 in SM). This self-consistency confirms the reliability and robustness of both methods.

Figure 3 summarizes all photoionization delays measured in this work. Figures 3(a), 3(c), and 3(e) show the measured photoionization delays between the N-1s and C-1s photoelectrons for the three molecules, which are excellent approximations to the absolute photoionization delays of the N-1s electrons. These delays are compared to the absolute N-1s photoionization delays from core-level photoionization calculations using the Schwinger variational principle with a correlation-polarization (CP) potential, summed with the Coulomb-laser coupling (CLC) delays. Details on the calculations are given in Sec. III of SM [34]. The comparison of the experimental and theoretical delays among the three molecules can be found in Fig. 3(f) and the inset of Fig. 3(a), respectively. The delays globally decrease with increasing kinetic energy, which reflects the decreasing sensitivity of faster electrons to the potential of the molecular cations. The delays markedly increase from pyridine to pyrimidine, whereas the measured delays of pyrimidine and s -triazine overlap within their respective error bars. The delays of all three molecules feature local maxima between 408 and 420 eV,

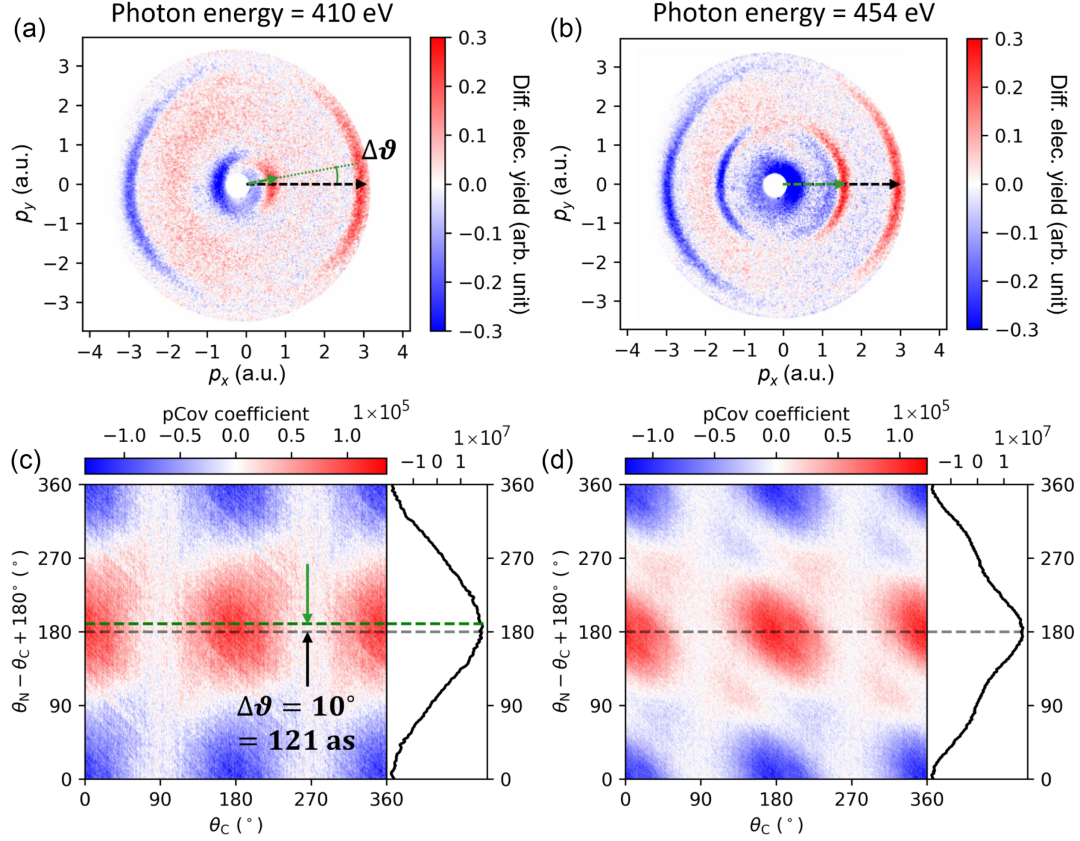


FIG. 2. Using the partial covariance (pCov) analysis to access the differential streaking angles. (a), (b) Difference images obtained as outlined in Fig. 1, illustrating a rather large delay (at 410 eV) and a negligible delay (at 454 eV). The inner (outer) line corresponds to N-1s (C-1s) photoelectrons from pyrimidine, a.u. stands for atomic units. (c), (d) Rotated partial covariance coefficient maps between streaking-induced signal fluctuations in N-1s and C-1s photoelectrons, where the right-hand panels correspond to the sum of the partial covariance coefficients along the θ_C axis. Given a photoionization delay $\Delta\tau = T_L \times \Delta\theta/2\pi$, where T_L is the streaking laser period, the streaking-induced signal fluctuation in C-1s photoelectrons at θ has the most positive covariance with streaking-induced signal fluctuation in N-1s photoelectrons around $\theta + \Delta\theta$. The global shift in the most-correlated region in (c) represents a global differential angle $\Delta\theta$ corresponding to a ~ 120 -as photoionization time delay between the N-1s and C-1s photoelectrons at 410-eV x-ray photon energy. As a comparison, no global shift is observed in (d), indicating a negligible time delay at 454-eV x-ray photon energy.

which are in reasonable agreement with the local maxima in the calculations. These local maxima in both experiment and theory originate from shape resonances, which correspond to a transient trapping of the photoelectron for a few tens to hundreds of attoseconds before it escapes from the molecule.

III. THEORETICAL CALCULATIONS

Since such shape resonances are notoriously sensitive to electron correlations and molecular structure [4,8,9,48], we have carefully benchmarked the core-level photoionization calculations against measured photoionization cross sections [Fig. 3(d) herein and Fig. S22 in SM [34]], as well as photoelectron angular distributions measured in the present work [Fig. 3(b) herein and Fig. S23 in SM]. Comparing the calculations using the equivalent-core (ECO) method with the experimental photoionization cross section [Fig. 3(d)]

revealed very good agreement for the resonance lying below the nitrogen *K* edge and the lowest-lying shape resonance after shifting the calculations to lower energies by 4.3 eV. In comparison, the CP calculations only needed to be shifted by 0.6 eV to agree with the experimental cross sections, and the calculated width of the lowest-lying shape resonance was in better agreement with the experiment than the ECO calculations. The CP calculations also agree better with the angular asymmetry parameters measured in this work [Fig. 3(b) herein and Fig. S23 in SM]. Since both calculations overestimate the energetic position of the upper shape resonance by ~ 3.5 eV, we therefore identified the CP calculations as the more accurate ones and from hereon exclusively discuss these results.

Figures 3(c) and 3(d) demonstrate the two shape resonances of pyrimidine within the energy range, which lead to the local maxima of the cross section. The $^1A'$ symmetry component is dominating in the cross section, which

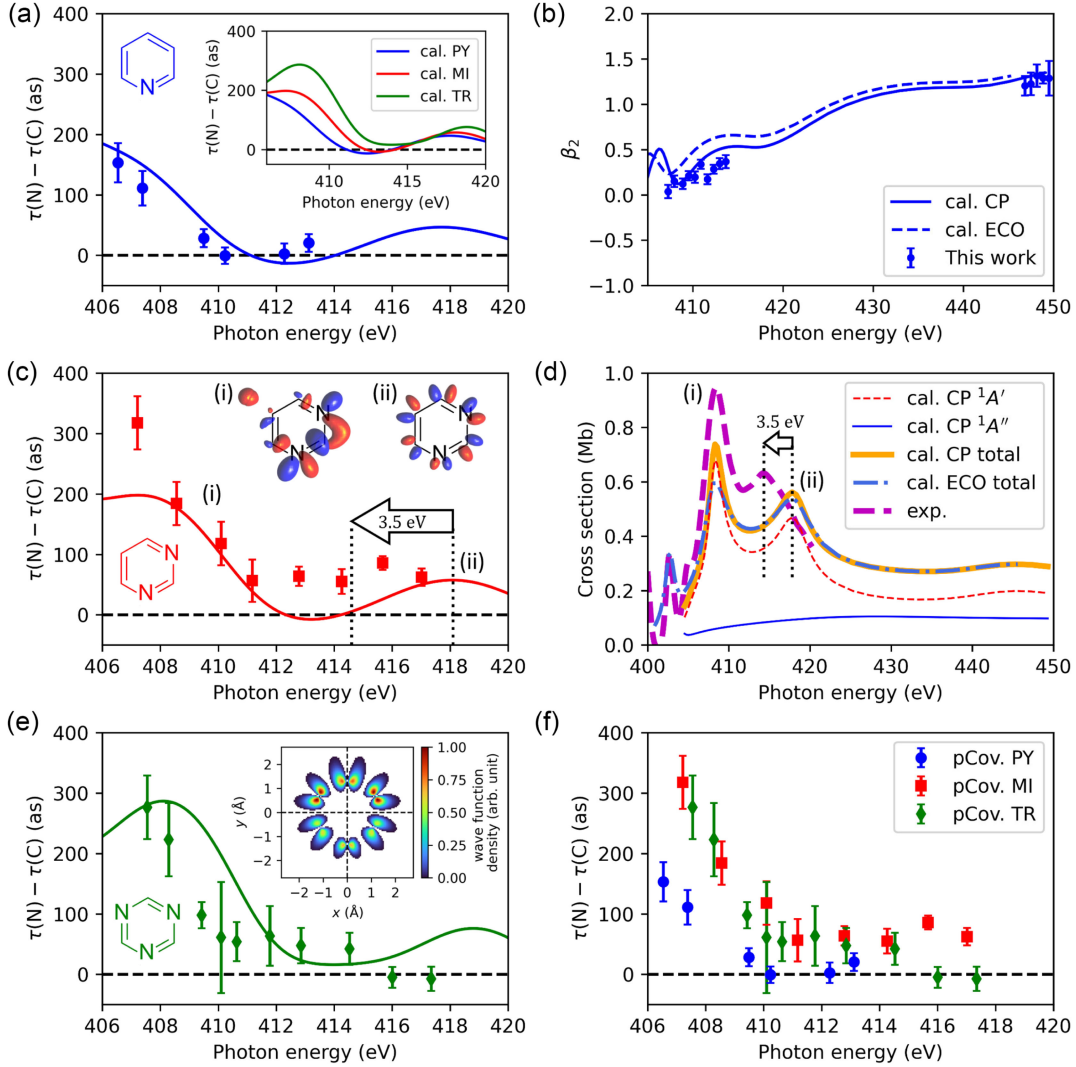


FIG. 3. Energy-dependent photoionization delays and shape resonances. (a), (c), (e) Measured relative photoionization delays ($\tau = \tau_{N1s} - \tau_{C1s}$, symbols) and calculated absolute photoionization delays including CLC delays (full lines) for pyridine (PY, a), pyrimidine (MI, c), and *s*-triazine (TR, e), as a function of the central photon energy of the attosecond FEL pulses. Panel (f) and the inset in (a) compare the relative photoionization delays extracted by the partial covariance method (pCov) and the CP calculations (cal.), respectively. The centers of the photoionization delay data points and the error bars represent, respectively, the mean and 3 times the standard deviation calculated from 100 bootstrapping iterations of the partial covariance analysis, which corresponds to 99.7% confidence interval (3 times the standard deviation). The resonant one-electron wave functions of the two local maxima (i) and (ii) are shown as insets in (c). (b) Photoelectron asymmetry parameter of pyridine measured in the present work, compared to the CP and ECO calculations. (d) The photoionization cross sections of pyrimidine from calculation (cal.) using the ECO and CP methods and experiment (exp.) [47]. The decomposition into partial cross sections corresponding to final states of $^1A'$ and $^1A''$ symmetry of the C_s point group are also shown for the CP calculation. The arrows in (c) and (d) indicate the shift between the calculated and observed position of the higher-lying shape resonance. The inset of (e) illustrates the calculated wave function density of the *s*-triazine at photon energy of 417.7 eV, where the N atom with the core hole is located at $x = 0.00$ Å, $y = -1.35$ Å.

displays an antibonding σ^* character and corresponds to the electron trapping that occurs in the molecular plane in both resonances. The insets in Fig. 3(c) show the one-electron representations of the corresponding resonant wave functions (Kapur-Peierls states; see SM for definition [34]). The lower-lying shape resonance features 5 nodal planes and the upper one 6, showing that partial waves of high angular momentum are dominating the photoelectron

trapping in both cases. The narrower width of the lower resonance nicely correlates with a longer photoemission delay, and the broader linewidth of the upper one correlates with the shorter delay. The partial cross section corresponding to a total final-state wave function of $^1A''$ symmetry, i.e., antisymmetric with respect to the molecular plane and thus a π/π^* -type continuum wave function, does not feature any sharp shape resonances above the ionization

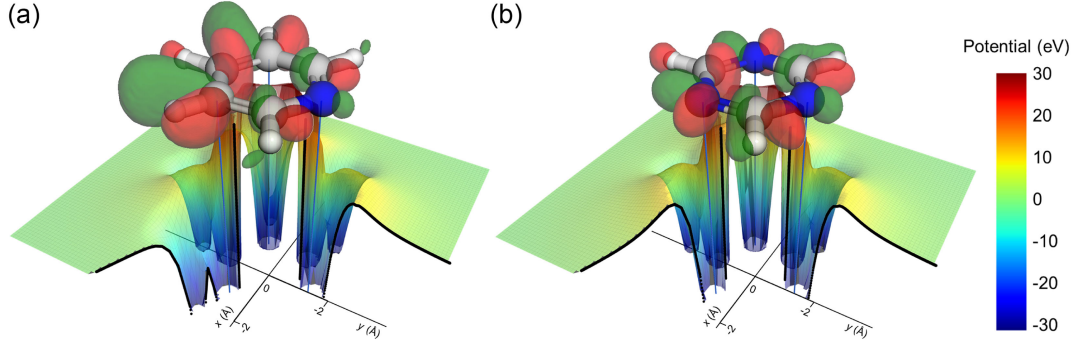


FIG. 4. Illustration of the mechanism of electron trapping. (a) The electrostatic potential of the pyridine cation summed with the centrifugal potential corresponding to $L = 5$ is plotted as the false-colored surface. The shape of the resonant orbital at about 410 eV is illustrated with the ball-stick model [Kapur-Peierls state with isosurfaces of $+0.14$ (red) and -0.14 (green)]. The vertical blue lines map the N atom and the two C atoms located at 120° and 240° with respect to the N atom to their coordinates on the xy plane. The black curves correspond to the tunneling barriers that trap the resonant wave function along the N atom and the meta-C atom. (b) The same plot for the s -triazine cation, where the positions of the three N atoms are labeled.

threshold (~ 404 eV) in the CP calculation. Note, however, the shifted ECO calculation does have a π/π^* narrow feature slightly below the threshold, as shown in Fig. 3(d), which is in agreement with the autoionization feature seen in a previous experimental study [47]. Thus we conclude that in the continuum above the nitrogen K edge the photoelectron trapping is dominated by the σ -type resonances in the molecular plane of pyrimidine. The probability density of the resonant wave function of s -triazine at ~ 418 eV is illustrated in the inset of Figs. 3(e) and in 4. Similar resonances occur in all three molecules, as shown in Fig. S20 in SM.

Since our measurements extend to within ~ 2 eV of the N-1s ionization threshold, they are particularly sensitive to the CLC delays. They therefore provide the opportunity to carefully assess the effects of the measurement on photoionization delays. It has previously been shown that CLC delays in attosecond streaking experiments have the same origin as the continuum-continuum (CC) delays known from reconstruction of attosecond beating by interference of two-photon transitions (RABBIT) measurements [3]. The most commonly used expressions for the CC delays are reported in Ref. [49], which is based on hydrogenlike atoms, and the radial wave functions are approximated considering the asymptotic phase shift (denoted as “P”) or with additional consideration of the long-range amplitude correction (denoted as “P + A”). The approximation of the hydrogenic radial wave function causes errors compared to the time-dependent Schrödinger equation (TDSE), particularly in the low-kinetic-energy region [49], which is relevant in our work. Recently, Ji *et al.* [50] reported using the analytical formula with hydrogenic radial wave functions (confluent hypergeometric functions) [51] instead of their asymptotic forms to calculate the CC transition of the hydrogenlike atoms, which shows excellent agreement with the TDSE in the whole kinetic-energy range. Here, we have adapted the same approach for calculating the CLC delays

with a slight modification, where for the CC transition the increase or decrease of the kinetic energy is a continuous quantity instead of being equal to the energy of one IR photon, and the time delay is defined based on the derivative of the CC-transition matrix element. The details can be found in Sec. IV. B of SM [34]. This new approach yields very good agreement to the TDSE calculations on hydrogenic systems, reported in Ref. [31] (see Fig. S24A in SM). Therefore, we used those results in Figs. 3 and 5, which represent the first application of this new approach to molecular systems. We find that the total photoionization delays including the CLC contribution are in excellent agreement with the experimental results [Figs. 3(a), 3(c), and 3(e)]. Other variants of the CLC correction result in significantly worse agreement (Fig. S24 in SM). We note that regardless of the form of the CLC contribution chosen the trend of increasing time delays from pyridine to pyrimidine and s -triazine, illustrated in the inset of Fig. 3(a).

We also investigated the role of the Auger-Meitner decay and the postcollision interaction (PCI) between the Auger-Meitner electron and the photoelectron. We find that the correction of the Coulomb delay from a singly to a doubly charged cation is nearly compensated by the delay that is caused by the PCI effect (Fig. S25 in SM [34]). Since these corrections are small and do not affect the relative delays between the molecular species that we studied, we refer the interested reader to the SM, and neglect these corrections for the remainder of the present discussion.

IV. DISCUSSION

These results invite an analysis of the mechanisms that govern the trapping of the photoelectron on the attosecond timescale. For this purpose, we analyze the properties of the trapped photoelectron wave function and the potential that

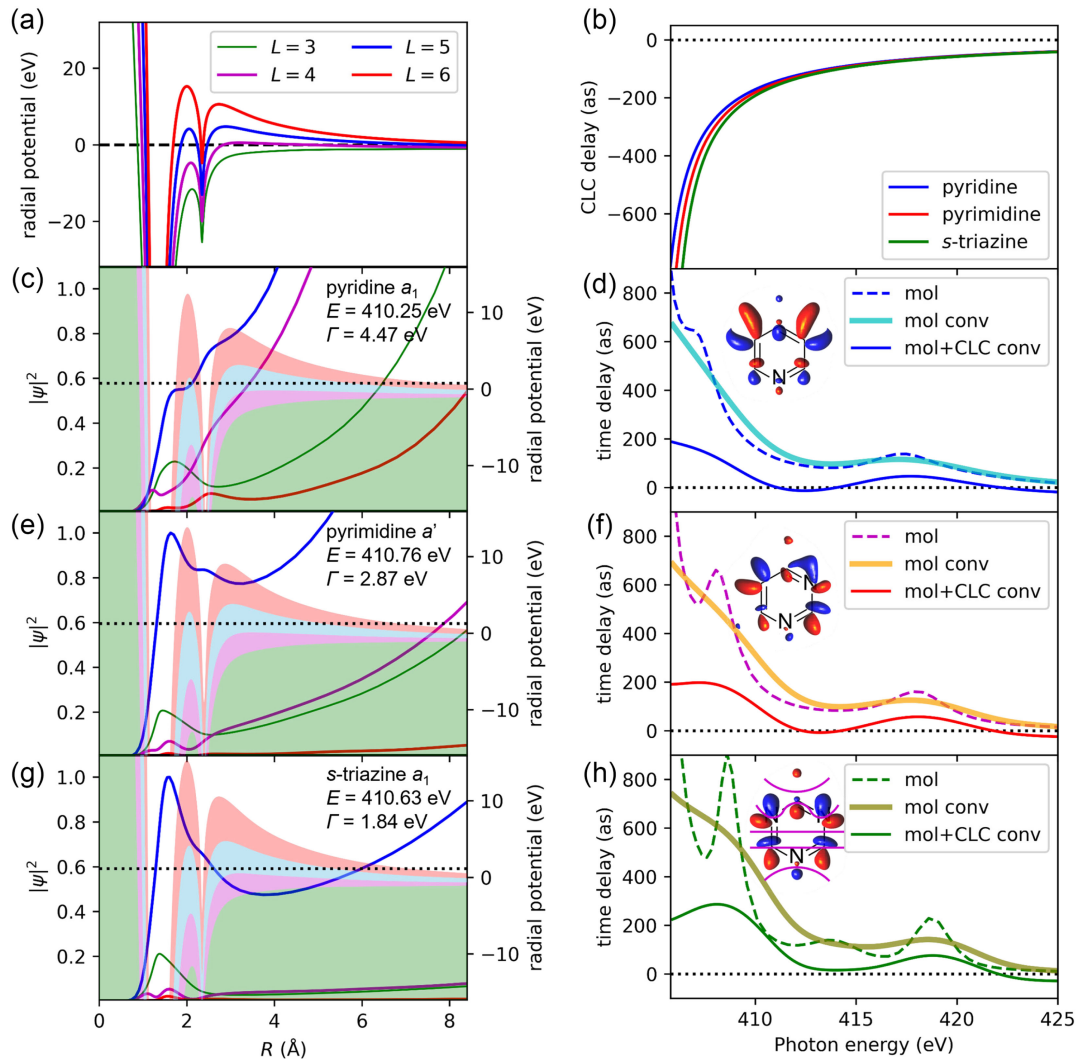


FIG. 5. Mechanisms of photoelectron trapping in the azabenzene molecules. (a) Sketch of radial potentials of s -triazine averaging over the polar angles with the angular-momentum barriers of different L . (b) CLC delays for the three molecules. (c), (e), (g) Resonant wave functions (Kapur-Peierls states) corresponding to the shape resonance centered at the energies indicated in the insets, decomposed into partial waves indicated by the same color code as in (a). Different components corresponding to the same L are summed to obtain the total probability density for a given L . The shaded areas correspond to the radial potentials of the corresponding molecules with the angular-momentum barriers of $L = 3, 4, 5, 6$ along the direction defined in (a) with the corresponding color code, and the dotted lines correspond to the asymptotic energies for the resonant states. (d), (f), (h) Molecular photoionization delays as obtained from the CP calculations (dashed lines), total delays obtained by adding the CLC delays to the molecular delays (thin full lines), and convolution of the total delays with a 3.8-eV FWHM Gaussian line profile (thick full lines). The resonant wave function at about 410 eV for each molecule is illustrated as the inset in the corresponding panel. The magenta curves in (h) qualitatively sketch the location of the nodal surfaces of the resonant wave function for s -triazine.

traps it. Figure 4 compares the trapping of the outgoing photoelectron wave in the resonances at around 410 eV of pyridine and s -triazine. The atomic cores provide attractive potentials in their vicinities, while the centrifugal energy creates a repulsive region centered on the aromatic ring. Their addition results in a potential barrier (black curves in Fig. 4) which traps the resonant wave function. The calculations provide a shape-resonance lifetime of ~ 150 as in the case of pyridine and ~ 360 as in the case of s -triazine. The stark difference in lifetime is reflected in the time-delay difference in the same energy region. The photoelectron

wave initially originates from the $1s$ shells of the nitrogen atoms and then scatters in the molecular potential, which results in comparable amplitudes of the resonant wave function on all atoms of the molecular ring. But what causes the increase of the photoionization delays and resonance lifetimes with increasing number of nitrogen atoms and increasing symmetry [see inset of Fig. 3(a)]?

To answer this question, Fig. 5(a) shows a sketch of effective radial potentials which indicate the height of the angular-momentum barrier for different values of the angular momentum L , and Figs. 5(c), 5(e), and 5(g) show

the absolute square of resonant one-electron wave functions, resolved into partial waves of angular momentum L and irreducible representations of the respective point groups (specified in each panel). Figure 5(b) shows the CLC delays and Figs. 5(d), 5(f), and 5(h) show the calculated delays for all three molecules. We will focus the remainder of this discussion on the shape resonance located at about 410 eV in each molecule.

In all three molecules, the partial-wave components with $L = 5$ dominate the probability density, which is the consequence of the high barrier in the radial potential [Fig. 5(a)] arising from the centrifugal-potential contribution $\hbar^2 L(L+1)/(2m_e R^2)$, where m_e is the mass of the electron and R its distance from the center of charge. The effective potentials of different partial waves are indicated by the shaded areas with different colors in the corresponding panels. It is clear that the main part of the wave function is confined in the quasibound region in the vicinity of the N and C atoms, while a tail indicates tunneling through the barrier. In the case of pyridine [Fig. 5(a)], the dominant $L = 5$ partial wave is least-well trapped compared to the other molecules, which is clear from comparing the modulations of the probability density at the barriers. This identifies tunneling through an angular-momentum barrier as the first mechanism governing electron trapping in the azabenzene series and demonstrates that the trapping strength of the dominant partial wave increases in the order pyridine, pyrimidine, *s*-triazine. Specifically, we see in Figs. 5(c), 5(e), and 5(g) that substituting a C-H group with the N atom increases the $L = 5$ barrier height between the region of the C and N atoms ($R \approx 1.3$ Å) and the location of the H atoms ($R \approx 2.4$ Å). This increases the trapping strength of the effective potential and consequently the lifetime of the resonance. We note that the divergence of the Kapur-Peierls state for large R is a consequence of their mathematical nature, specifically their complex-valued momentum; see SM Sec. III. B [34].

Figure 5 also reveals a second mechanism at play. In addition to the changing probability density ratio between the wave functions in the quasibound and tunneling regions, we also observe the manifestation of molecular symmetry. The reason that the $L = 5$ partial wave prevails in the resonant wave functions can be qualitatively understood from the inset in Fig. 5(h). The resonant wave function displays five nodal surfaces, as qualitatively illustrated in the inset of Fig. 5(h), corresponding to a dominant $L = 5$ partial-wave character. However, the wave function also contains contributions from the other partial waves. As the symmetry of the molecular scaffold of the neutral molecule decreases from *s*-triazine (D_{3h}) to pyrimidine and pyridine (C_{2v}), the relative amplitudes of $L < 5$ to $L = 5$ partial waves increase as a consequence of lower symmetry, which increases the extent of partial-wave mixing. The increasing relative amplitudes of the untrapped $L < 5$ partial waves cause a faster decay of the resonant

state. It is worth noting that although the partial-wave decomposition is useful for the understanding of the physical mechanisms, different partial waves cannot be separately observed.

To summarize, these two mechanisms explain the trend in the resonant photoelectron trapping times in the azabenzene series. This trend is most clearly visualized in Figs. 5(d), 5(f), and 5(h), which show that the photoionization delays in the vicinity of the discussed shape resonance indeed increase in the sequence pyridine, pyrimidine, *s*-triazine.

V. CONCLUSION

In conclusion, we have used the novel attosecond capabilities of LCLS to measure core-level photoionization delays of aromatic molecules. These measurements were made possible by the combination of attosecond x-ray pulses with the angular streaking technique. Absolute N-1s photoionization delays were accessed by using the much faster and therefore prompt C-1s photoelectrons as a time reference. These self-referenced measurements were realized on a fine energy grid and revealed the presence of local maxima at 3–15 eV above the N-1s threshold. The measured delays markedly increase from pyridine to pyrimidine, whereas the measured delays of pyrimidine and *s*-triazine overlap within their error bars. Comparison to advanced, and carefully benchmarked, core-level photoionization calculations identified two dominant shape resonances in each molecule and showed that photoelectron trapping occurs in the plane of the aromatic molecules. Two important mechanisms governing the photoelectron trapping were identified as (i) changes in the barrier height of the molecular potential that lead to an increase of the electron trapping with the replacement of C-H functional groups with N atoms and (ii) the increasing symmetry of the molecular scaffold reduces the coupling between the well-trapped high- L and the not trapped lower- L states. Both effects individually and collectively increase the trapping time in *s*-triazine compared to pyridine. Additional mechanisms may be important. These results demonstrate the promise of performing attosecond core-level photoemission experiments at free-electron-laser facilities for the following reasons. The studied molecules are key building blocks of biologically active molecules and employed in optoelectronics, which opens the perspective of extending attosecond chronoscopy to these systems. The key advantage of core-level photoionization delays over valence-shell photoionization delays is that the photoelectron spectra always remain comparably simple. This will enable the application of the methods described in this work to complex molecules, molecular assemblies, and polymers, such as organic semiconductors, which offers the perspective of studying attosecond electron scattering and trapping in functional materials.

VI. METHODS

A. Experimental methodology

The attosecond soft x-ray pulses were produced using the photocathode shaping method [52]. The mean pulse energy is 39 μJ and the mean FWHM bandwidth is 3.8 eV. From our previous measurements, we can estimate a FWHM temporal pulse duration of 460 as for the x-ray pulses. The x-ray focal spot size is roughly 30 μm in diameter (FWHM). We estimate the intensity of the attosecond x-ray pulse to be $1.2 \times 10^{16} \text{ W/cm}^2$.

The attosecond soft x-ray pulses described above were focused to a spot size of $\sim 30 \mu\text{m}$ in diameter using a pair of Kirkpatrick-Baez focusing mirrors [53]. The 1300-nm streaking pulse with a duration of ~ 40 fs was produced by a commercial optical parametric amplifier (TOPAS-HE, Light Conversion) which is pumped by a ~ 30 -fs, 9-mJ, 800-nm laser source. The signal beam was sent through a superachromatic quarter-wave plate (Thorlabs SAQWP05M-1700) to produce a circularly polarized laser field and was focused with a $f = 600$ mm CaF_2 lens before being reflected from a silver-coated mirror with a 2-mm-diameter hole to copropagate the laser and x-ray fields to the interaction point in the cVMI spectrometer chamber. We estimated the intensity of the IR streaking laser at the interaction point to be $3 \times 10^{13} \text{ W/cm}^2$.

High pressure (6.4 bar) helium gas was bubbled through a vessel heated to 80°C – 140°C to deliver the samples into the cVMI spectrometer chamber, and the photoelectrons ionized from the samples were collected using an electrostatic lens. A variable-line-spacing-grating x-ray photon spectrometer [54,55] was employed downstream of the interaction point to obtain the spectra for individual x-ray shots.

B. Data analysis

The relative photoionization delay between the carbon and nitrogen K -shell photoelectrons $\Delta\tau$ is related to the difference in streaking angle $\Delta\theta$ between the momentum shift of the nitrogen and carbon photoelectrons, $\Delta\tau = T_L \times \Delta\theta/2\pi$, where $T_L = 4.33$ fs is the period of the IR streaking laser. We used two methods to extract the differential streaking angle $\Delta\theta$ from the dataset. The first method uses a partial covariance approach to isolate the correlated changes of streaking-induced variations in the photoelectron momentum distribution, while the second procedure uses a sorting method which tags the arrival time of the attosecond x-ray pulse relative to the IR field. The two approaches are further illustrated and compared in SM [34].

C. Theoretical methodology

The $\text{N } (1s)^{-1}$ photoionization of the three azabenzenes considered here were studied using two methods, the basis-set complex Kohn method [56] and ePolyScat [57,58].

The one-electron basis set used to obtain the occupied molecular orbitals was a correlation-consistent valence triple ζ [59] and the geometry used minimized the Hartree-Fock energy. The ePolyScat calculations used a static-exchange potential with equivalent-core method. An additional CP potential was introduced to approximate the interaction between the emitted electron and the residual molecular cation [60]. The calculated values with and without the CP potential are compared in SM [34]. The multichannel calculation from the delocalized $\text{N } (1s)^{-1}$ holes using the complex-Kohn method [61] with channel coupling and the one-channel calculation using ePolyScat from the localized $\text{N } (1s)^{-1}$ hole show consistency, as demonstrated in SM, Fig. S17A. This also indicates that multicenter interference effects are negligible in the context of this study. Dipole-laser coupling effects [3,62,63] were neglected. The calculated delays were averaged over molecular orientation and the emission direction of the photoelectron.

ACKNOWLEDGMENTS

Use of the Linac Coherent Light Source (LCLS), SLAC National Accelerator Laboratory, is supported by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences under Contract No. DE-AC02-76SF00515. The work of J.-B.J., X.G., D.H., M.Han, S.H., and H.J.W. was supported by ETH Zürich and Projects No. 200021_172946 and No. 200020_204928 of the Swiss National Science Foundation. The work of M.Han was additionally supported by the European Union's Horizon 2020 research and innovation program under the Marie Skłodowska-Curie Grant Agreement No. 801459—FP-RESOMUS. The effort from T.D., J.T.O.A.L.W., J.W., T.J.A.W., and J.P.C. was supported by DOE, BES, Chemical Sciences, Geosciences, and Biosciences Division (CSGB). Z.G., D.C., J.D., P.L.F., R.R.R., and A.M. acknowledge support from the Accelerator and Detector Research Program of the Department of Energy, Basic Energy Sciences division. Z.G., P.L.F., and R.R.R. also acknowledge support from Robert Siemann Fellowship of Stanford University. The effort by R.R.L. and C.W.M. at L.B.N.L. was supported by the U.S. DOE BES, CSGB under Contract No. DE-AC02-05CH11231. Calculations at LBNL made use of the resources of the National Energy Research Scientific Computing Center, a DOE Office of Science User Facility, and the Lawrence computational cluster resource provided by the IT Division at the LBNL. C.S.T. was supported in part by the Berkeley Lab Undergraduate Faculty Fellowship (BLUFF) Program, managed by Workforce Development & Education at Berkeley Lab.

J.-B.J., T.D., K.U., A.M., J.P.C., and H.J.W. conceived the experiment. All authors contributed to the realization of the experiment and discussed the results.

J.-B. J., Z. G., and T. D. developed the data-analysis methodology. J.-B. J. and Z. G. analyzed the data. R. R. L., C. S. T., and C. W. M. performed the calculations of molecular photoionization delays. J.-B. J., Z. G., and H. J. W. wrote the initial draft of the manuscript, which was reviewed and edited by all authors.

The authors declare no competing interests.

DATA AVAILABILITY

The data that support the findings of this article are openly available [64].

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