

High-resolution attosecond interferometry reveals spin-orbit and electron-correlation effects in photoionization delays

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We introduce an experimental technique for achieving an unprecedented energy resolution in attosecond interferometry. Using a second-harmonic bandwidth compressor, we create narrow-band (<1 nm), tunable femtosecond pulses that generate high harmonics with a bandwidth of 50–73 meV, achieving the highest energy resolution in any attosecond time-resolved measurement, sufficient to resolve the spin-orbit splitting of the ^2P ground state of Ar^+ . The fine tunability of these pulses resolves a 10-as variation of the spin-orbit photoionization delay across the $[Ne]3s^1 3p^6 5p$ resonance of neutral Ar. Calculations based on the relativistic random-phase approximation with exchange, with qualitative inclusion of shakeup configurations, reveal the importance of spin-orbit and electron-correlation effects to accurately reproduce and interpret photoionization delays.

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I. INTRODUCTION

Attosecond spectroscopy appears to be fundamentally limited by the trade-off between temporal and spectral resolution, imposed by Fourier relations. Consequently, resolving ever shorter timescales seemingly deteriorates the available spectral information. However, interferometric approaches can overcome this apparent limitation, as demonstrated in the femtosecond-visible [1] and attosecond-extreme-ultraviolet [2] domains, as well as in stimulated Raman spectroscopy [3]. Attosecond interferometry opens the exciting possibility of combining high spectral resolution with the highest temporal resolution, as realized in the measurement of photoionization delays [4,5]. The applications of this technique have recently grown tremendously, accessing ionization time delays in atoms and molecules with a variety of techniques [6–8]. The relative delay between different shells has often been studied [2,4,5,9], but comparisons between different atoms and molecules [10,11] and between size-resolved molecular clusters [12] have also been reported.

The limited spectral resolution has so far restricted such measurements to isolated resonances [6,13,14] and well-separated final states of the atomic or molecular cations [5,6]. Achieving higher spectral resolution opens the door to study novel effects, such as the influence of vibrational structure [15,16], the fine structure [17–19], or even weaker interactions in the final cationic states. Very few studies have been able to

resolve the delay difference between final ion spin-orbit states. The possibility to highlight relativistic aspects of the temporal delay between photoelectron wave packets in such measurements has been established, but such studies remain scarce, both in atoms [17,18] and in molecules [19]. In addition to the high demands in terms of energy resolution, such spin-orbit delays are often on the order of few tens of attoseconds or less, requiring very high fidelity and temporal resolution.

Here, we introduce an approach that combines a continuous tunability of the photon energy with the highest spectral resolution in any attosecond time-resolved experiment to date (50–73 meV) (cf. Refs. [2,20]). This is achieved by introducing a second-harmonic bandwidth compressor (SHBC) before high-harmonic generation (HHG). In addition to the recently demonstrated advantages of attosecond interferometry with visible (400 nm) driving and dressing pulses, which already features a narrow spectral bandwidth [16], the SHBC further narrows the second-harmonic spectral bandwidth to below 1 nm, while simultaneously introducing a continuous wavelength tuning over 11 nm without the need to adjust the input laser pulse spectrum. This narrow-band radiation is used, both for HHG and as a dressing field in our measurements.

We demonstrate the scientific potential of this approach by measuring the delays between photoelectron wave packets associated with the $^2P_{1/2}$ and $^2P_{3/2}$ spin-orbit components of the Ar^+ ground state. By tuning the central wavelength of the 400 nm light, the ninth harmonic (H9) is scanned across the $3s^2 3p^6 \rightarrow 3s^1 3p^6 5p$ autoionizing resonance of Ar at 27.99 eV, revealing its effect on the spin-orbit delay.

This experiment addresses the subtle effects of spin-orbit interaction and electron correlation on photoionization delays. Resonances can act as switches that funnel electrons from one channel to another. In a seminal study by Cheng and Johnson [21], it was shown how this mechanism, mediated by resonances that cannot be photoexcited within LS coupling,

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could explain strong variations in the ratio of the $4d_j$ partial photoionization cross sections in xenon. In Ref. [22], it was discussed how this channel switching results also in a pronounced difference between the photoionization delay of two channels in the same energy region.

In this work, we study how spin-orbit coupling and electron correlation modulate the coupling between dipole-allowed and dipole-forbidden channels in the vicinity of resonances. We show that spin-orbit interaction leads to a mixing between the dipole-accessible ^1P resonances and the dipole-forbidden ^3P resonances. This manifests itself as a rapid variation in the photoionization delays across the resonances. Whereas the resonances of ^1P symmetry are well studied with respect to photoionization cross sections [23–25] and delays [14,26], only the lowest-energy resonance of the corresponding ^3P series has been seen. This was done in an electron-impact experiment [27], where resonances of different symmetries were further heavily overlapping. The present study focuses on the second resonance in each of the $^{1,3}P$ series, dominated by the $[\text{Ne}]3s3p^65p$ configuration. We find that the spin-orbit-induced delay is small and constant in the nonresonant region, but grows significantly in the vicinity of the resonances. Of particular interest is the effect of the LS -forbidden ^3P resonance on the photoionization delays, which is of similar importance as the ^1P one, despite being undetectable in cross-section measurements. This underlines the resonance's ability to expose effects of spin-orbit coupling. Our calculations additionally show that electron correlation between singly and multiply excited configurations has an influence on the photoionization delays.

II. RESULTS

Figure 1 illustrates the approach and typical data obtained in this study. Tuning the central wavelength of the second harmonic scans the photon energy of H9 across the $3s^2 3p^6 \rightarrow 3s^1 3p^6 5p$ transition at 27.99 eV, corresponding to 398.6 nm. Attosecond interferometry was performed at sideband 9 (SB8) using harmonics 7 and 9 (H7, H9) and the extreme-ultraviolet-to-visible (XUV-VIS) delay was scanned over a range of 16 fs, corresponding to approximately 24 periods in the 2ω oscillation. Fundamental wavelengths were selected such that H9 spanned the energy range of the $3s^2 3p^6 \rightarrow 3s^1 3p^6 5p$ Rydberg transition of Ar.

For each measurement, a fast Fourier transform (FFT) along the XUV-VIS delay axis was performed and the 2ω component isolated [Fig. 1(b)]. The delay was determined from the phase of the 2ω oscillation by calculating a weighted average of the 2ω phase, using the 2ω amplitude as weights. The averaging was restricted to the full width at half maximum (FWHM) of each spin-orbit component. The resulting averaged phase was subsequently converted into a temporal delay.

Five consecutive measurements were performed for each fundamental wavelength. Photon-energy-dependent delays reported in this work correspond to the average over each set of five measurements at the respective fundamental wavelength, with uncertainties given by the corresponding standard deviations. Reported values and uncertainties were rounded according to the one- or two-significant-digit convention for experimental uncertainties.

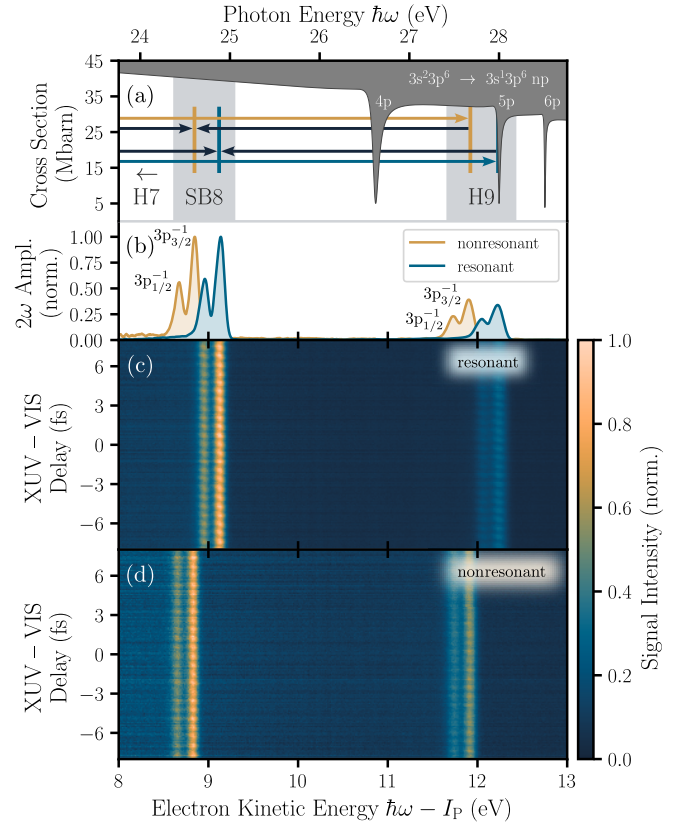


FIG. 1. Principle of high-resolution attosecond interferometry. Panel (a) shows the frequency-domain absorption spectrum of argon in the vicinity of the $3s^1 3p^6 np$ resonances. Harmonic and sideband energies are shown for differently tuned fundamental wavelengths. Panel (b) shows the Fourier magnitude spectrum at the 2ω frequency of the measured attosecond interferograms shown in panels (c) and (d). While panel (c) was recorded with the spectrum of H9 overlapping with the $n = 5$ resonance, panel (d) was recorded under nonresonant conditions.

The primary light source in this experiment was an amplified titanium:sapphire laser system providing pulses centered at 800 nm with energies of up to 2.4 mJ and a spectral bandwidth of 31 nm, supporting a transform-limited pulse duration of approximately 31 fs. Narrow-band second-harmonic radiation was generated using an SHBC [28], consisting of a UV-grade fused-silica prism with an apex angle of 69° , a cylindrical lens with a focal length of 400 mm, and a 500 μm thick β -barium borate (BBO) crystal, yielding second-harmonic pulses with a measured bandwidth of 0.93 nm (7.2 meV).

The working principle of the SHBC is illustrated in Fig. 2. A prism introduces a spectral dispersion in the horizontal plane. A 50/50 beam splitter creates two replica beams with opposite spatial chirps that are horizontally focused into the BBO crystal by a cylindrical lens. The second-harmonic signal arises from sum-frequency generation (SFG) between the two beams. Owing to the inverted spatial chirps, frequency components are symmetric with respect to the central fundamental frequency and overlap at each horizontal position in the focus. Consequently, SFG at each position involves only a narrow spectral slice of focal spot size σ_C , with all slices

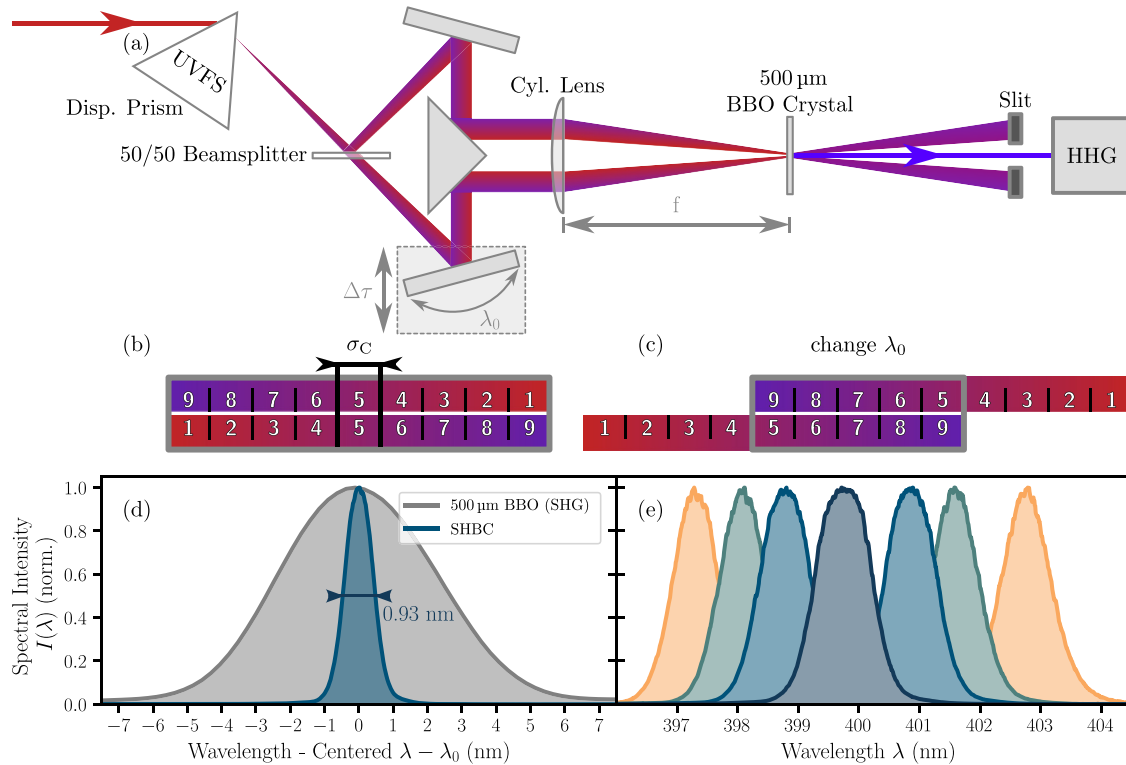


FIG. 2. Second-harmonic bandwidth compressor: (a) Schematic of the optical layout, (b) principle of bandwidth narrowing arising from the final spot size σ_C of each spectral component, and (c) principle of the tunability for the fundamental wavelength λ_0 by changing the horizontal overlap. (d) Experimental results demonstrating the bandwidth narrowing of the SHBC compared to those using the same BBO crystal in conventional SHG and (e) the spectral tunability.

generating the same second-harmonic frequency [Figs. 2(b) and 2(d)], resulting in efficient and narrow band SFG.

Tuning of the generated second-harmonic wavelength is achieved by laterally shifting the horizontal overlap of the two beams [Figs. 2(c) and 2(e)]. This breaks the symmetry of the overlapping frequency components with respect to the central frequency, resulting in a controlled shift of the generated second-harmonic wavelength while maintaining its narrow bandwidth. The output is then reshaped horizontally to symmetrize the beam profile using a Galilean telescope composed of cylindrical lenses and finally focused into the high-harmonic generation target filled with ~ 80 mbar of argon.

At an input pulse energy of 1.6 mJ (800 nm), the SHBC produced 0.32 mJ of second-harmonic radiation, which was used to drive HHG. The resulting attosecond pulse train (APT) was spectrally filtered to isolate H7 and H9 using a combination of an Al foil and a multilayer (Mo/Si) mirror (AXO Dresden). The APT and residual visible radiation were reflected off a two-component mirror, the inner part of which had the multilayer coating and the outer part a protected aluminum coating. Translation of the inner component was used to vary the delay between the XUV and VIS pulses, which were both refocused into the interaction region of a time-of-flight spectrometer. Additional details of the experimental setup are given in Refs. [16,29].

The fundamental spectrum was measured using an Ocean Optics HR4000 optical spectrometer, calibrated using atomic emission lines of He, Na, Cd, Hg, and Tl. The central wavelength was tuned using the SHBC. Resulting XUV photon

energies were calculated from the calibrated fundamental photon energy and the corresponding harmonic order. The fundamental bandwidth was measured using an additional high-resolution optical spectrometer with a resolution of $\Delta\lambda \sim 0.3$ nm at 400 nm. The XUV bandwidth was determined from photoelectron spectra via successive application of increasing retardation potentials, reducing electron kinetic energies to ≈ 1.7 eV. Extrapolating the width-kinetic energy trend to 0 eV yielded an asymptotic value of 50 and 73 meV in the cases of H7 and H9, respectively, which represent upper bounds on their spectral bandwidths.

Below, the experimentally measured delays are compared with calculated Wigner and atomic delays. These were, respectively, obtained from one- and two-photon matrix elements calculated using the relativistic random-phase approximation with exchange (RPAE) method [30]. The difference between the two corresponds to an effective continuum-continuum (CC) delay, which is also calculated.

The ninth harmonic covers the autoionizing [Ne]3s $3p^6 5p \ ^{1,3}P_{J=1}$ resonances. The dominating configuration is abbreviated as $3s^{-1}5p$ below. The pure ^3P component is not coupled to the ground state through dipole interactions. However, since the $J = 1$ resonances are mixtures of the two spin components, they both have a finite admixture of singlet character. This results in one ^1P -dominated and one ^3P -dominated resonance, both with a nonzero dipole coupling to the ground state. From hereon, the resonances are referred to as $3s^{-1}5p \ ^1P$ and $3s^{-1}5p \ ^3P$, according to their dominant configuration.

The relativistic RPAE calculation does not explicitly include the $3p^4(^1D)nd(^2S)n/\varepsilon p(^1P)$ and shakeup (SU) channels, which significantly affects the widths and cross-section profiles of all $3s^{-1}np$ autoionizing resonances [31], and has been shown to drastically affect the photoionization delay above the argon $3s$ ionization threshold [20]. Instead, the effect of the shakeup channels on the transition $3s^2 3p^6 \rightarrow 3s^1 3p^6 5p^1 P$ between the ground state and the pure ^1P autoionizing resonances was calculated nonrelativistically both when excluding ($\mathcal{M}_{3s \rightarrow 5p}^{\text{RPAE};\text{nr}}$) and when including ($\mathcal{M}_{3s \rightarrow 5p}^{\text{RPAE}+\text{SU};\text{nr}}$) shakeup effects. The ratio $\mathcal{M}_{3s \rightarrow 5p}^{\text{RPAE}+\text{SU};\text{nr}}/\mathcal{M}_{3s \rightarrow 5p}^{\text{RPAE};\text{nr}}$ between these was then used to rescale the corresponding relativistic matrix elements $\mathcal{M}_{3s \rightarrow 5p}^{\text{RPAE}}$ from the ground state. In this way, also the coupling with the $3p$ channels is affected. The effect of the shakeup on the coupling of the two components to the continua, not readily available nonrelativistically, was not accounted for. Further, the theoretical results below have been shifted down by 34 meV to align the $3s^{-1}5p^1 P$ energy with the experimentally measured literature data [23–25].

Figure 3(a) shows the theoretically calculated Wigner (one-photon), CC, and atomic (two-photon) delays for both $3p_j^{-1}\varepsilon l$ channels. A prominent deviation from the slowly varying background can be seen near the $3s^{-1}5p^1 P$ resonance. When the attention is turned to the difference between the two channels [Fig. 3(b)], the additional presence of the $3s^{-1}5p^3 P$ resonance can be seen as shoulder in the Wigner delay, and as a result also in the atomic delay.

Figure 4 shows the experimentally measured atomic delay $\tau_{1/2} - \tau_{3/2}$ between the $3p_j$ ionization channels, along with comparable theoretical data. In the theory, the finite pulse length was accounted for by convolution of intermediate energies. With the calculated resonance width (4 meV) significantly more narrow than the experimental (28.5(8) meV [25]) one, the convolution was done using a Gaussian distribution with an FWHM of 10.3 meV to preserve the same ratio between the spectral bandwidth of H9 and the resonance width as in the experiment.

III. DISCUSSION

The experimental data show a maximum of around 10 as near the $3s^{-1}5p^1 P$ resonance at $\hbar\omega_{\text{H9}} = 28$ eV. Far from the resonance, this delay approaches zero. A significant shoulder of a few attoseconds can be seen stretching toward lower energies. These phenomena are qualitatively replicated by the theoretical (RPAE + SU) data. There is both a peak at $\hbar\omega_{\text{H9}} = 28$ eV and a shoulder at lower energies. When artificially removing the $3s^{-1}5p^1 P$ resonance (dashed line), the shoulder remains while the maximum disappears. Likewise, performing calculations without the $3s^{-1}5p^3 P$ resonance (dotted line) removes most of the shoulder while keeping the maximum. The maximum can thus be linked to the $3s^{-1}5p^1 P$ resonance, while the $3s^{-1}5p^3 P$ one mainly contributes to the shoulder.

The theoretical delay maximum is, however, notably smaller than the experimental one. This might be traced back to missing shakeup configurations. Pure RPAE theory is known to underestimate the width and to fail to predict the small Fano q value that gives the window character of the resonance. This is illustrated in Fig. 4(c), where the photoabsorption cross-section contribution from the $3s^{-1}5p^1 P$

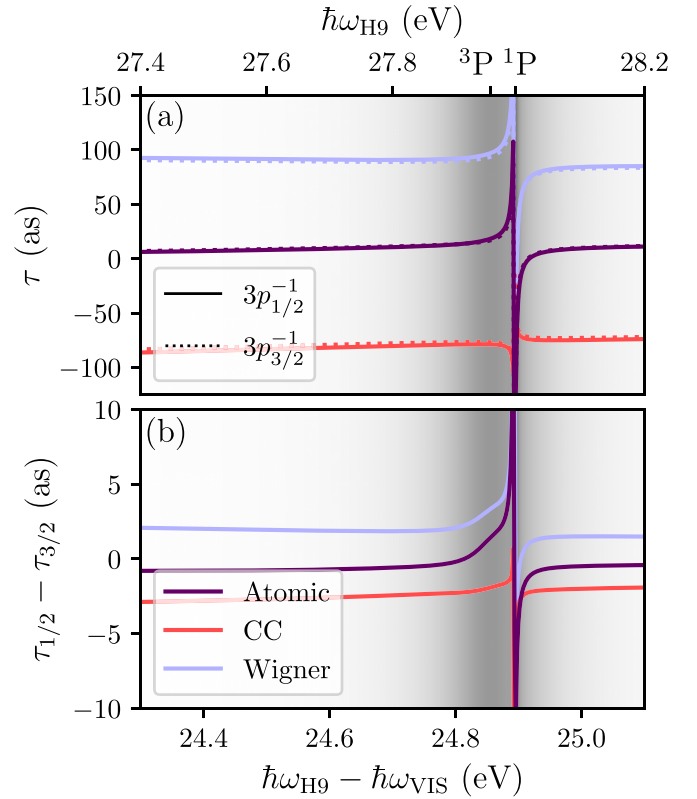


FIG. 3. In panel (a), the theoretically calculated delays τ corresponding to ionization from both the $3p_{1/2}$ (solid lines) and the $3p_{3/2}$ (dashed lines) orbital are shown. In panel (b), the corresponding differences $\tau_{1/2} - \tau_{3/2}$ in delay between the two are shown. Both panels show the results for the Wigner delay in blue, the CC delay in red, and the atomic delay in purple. The ordinates show the upper (ninth) harmonic excitation energy $\hbar\omega_{\text{H9}}$ (top) and the corresponding sideband energy $\hbar\omega_{\text{H9}} - \hbar\omega_{\text{VIS}}$ (bottom). The $3s^{-1}5p^1 P$ and $3s^{-1}5p^3 P$ energy positions have been marked, with the shaded area indicating their distributions. The calculations include effects from shakeup channels as indicated in the text.

resonance as calculated with (nonrelativistic) RPAE is compared with the results from Ref. [31]. The latter includes a range of higher-order correlation effects, e.g., the important shakeup configurations, and gives a width of 29.3 meV (experiment 28.5(8) meV [25]) and $q = -0.299$ (experiment $q = -0.177(3)$ [25]), while RPAE produces a width less than half of that, and a q value corresponding to a very asymmetric line profile, as seen from the beige line in Fig. 4(c), where the RPAE resonance position is shifted to agree with experiment. The scaling of the relativistic matrix elements to qualitatively account for these effects, as described above, is not enough to capture their contributions completely. Still the comparison in Fig. 4 with pure RPAE, i.e., where shakeup effects are completely absent, demonstrates their importance. Although the shoulder persists even without them, the maximum caused by the $3s^{-1}5p^1 P$ is reduced and shifted downward in energy.

IV. CONCLUSIONS

In conclusion, we have introduced an experimental technique that facilitates continuous photon-energy tunability and an unprecedented spectral resolution in an attosecond

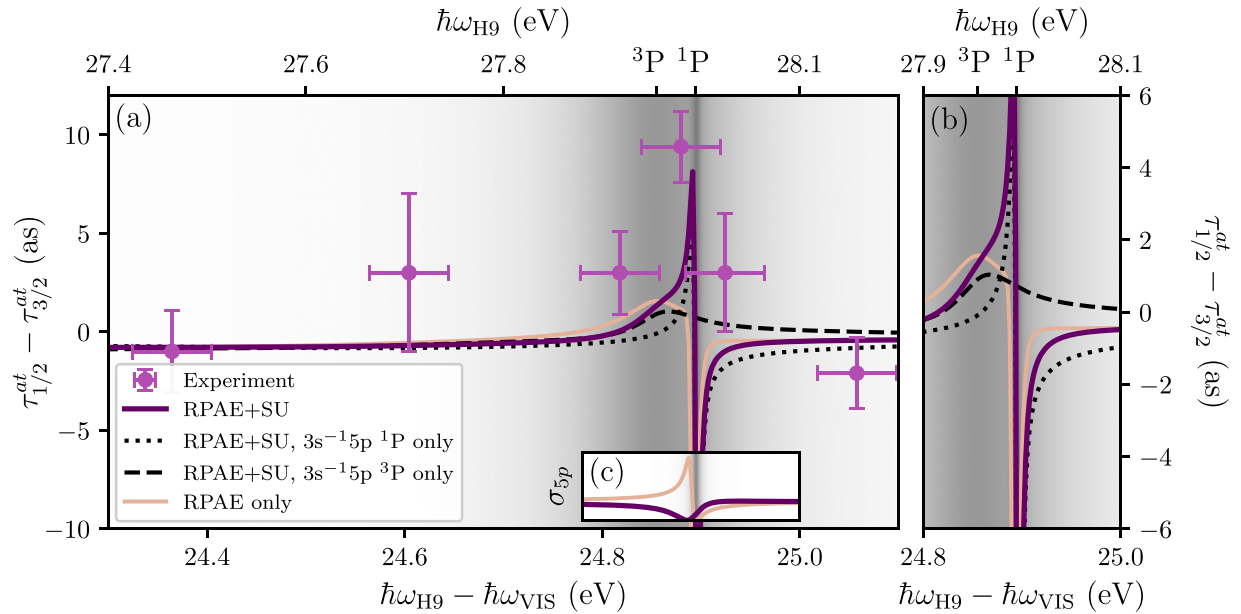


FIG. 4. The atomic delay difference $\tau_{1/2}^{at} - \tau_{3/2}^{at}$ between ionization from the $3p_{1/2}$ and the $3p_{3/2}$ orbital. In panel (a), the experimental and theoretical results are shown for a wider range of energies, while panel (b) shows a cutout of the theoretical results near the $3s^{-1}5p$ resonances, and the overlaid panel (c) shows the $3s^{-1}5p$ ^1P contribution to the photoabsorption cross section (see text for details). The experimental data, with error bars, are shown as purple points. The dark purple lines show the theoretical RPAE values with shakeup corrections included, convoluted with a 10.3 meV FWHM Gaussian, as elaborated on in the main text. In dotted (dashed) black, similar data are shown, but including only the $3s^{-1}5p$ ^1P ($3s^{-1}5p$ ^3P) resonance. In beige, theoretical RPAE data without shakeup corrections are shown. The ordinates show the sideband energy, harmonic energy, and $3s^{-1}5p$ ^{2S+1}P resonances analogously to Fig. 3.

time-resolved experiment. We have applied this new technique to study how spin-orbit interaction affects the photoionization delays in the vicinity of resonances by coupling continua of different spin multiplicities (singlet and triplet). Comparison of measurements and calculations has revealed the importance of including electron-correlation effects, specifically through the description of shakeup channels. Although the qualitative inclusion of the shakeup configurations improves the agreement between theory and experiment, it is not sufficient to quantitatively reproduce the measured photoionization delays. This is not completely unexpected because the q factor and width of the resonance are also not quantitatively reproduced, but it reveals the exceptional sensitivity of photoionization delays to subtle interactions.

These results demonstrate that measurements of photoionization delays with high spectral resolution offer a very stringent test of theory, capable of challenging state-of-the-art methods for the calculation of atomic photoionization delays. The high spectral resolution of the present technique will enable its extension to measure overlapping resonances in atoms and molecules. In the case of molecules, the high spectral resolution will be crucial for disentangling resonances

converging to different electronic and vibrational levels of the molecular cations, which will offer very detailed information on electron correlation and electron-nuclear coupling in molecules on attosecond timescales. Applying this method to “complex resonances” in molecules, i.e., resonances in which molecular autoionization and predissociation coexist, will enable the effects of interfering decay pathways to be studied through the sensitive lens of attosecond photoionization delays [32,33].

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DATA AVAILABILITY

All raw data shown in the figures of this article will be published upon acceptance of the manuscript.

- [1] A. Marian, M. C. Stowe, J. R. Lawall, D. Felinto, and J. Ye, United time-frequency spectroscopy for dynamics and global structure, *Science* **306**, 2063 (2004).
- [2] M. Isinger, R. J. Squibb, D. Busto, S. Zhong, A. Harth, D. Kroon, S. Nandi, C. L. Arnold, M. Miranda, J. M. Dahlström, E. Lindroth, R. Feifel, M. Gisselbrecht, and A. L’Huillier, Photoionization in the time and frequency domain, *Science* **358**, 893 (2017).
- [3] P. Kukura, D. W. McCamant, and R. A. Mathies, Femtosecond stimulated Raman spectroscopy, *Annu. Rev. Phys. Chem.* **58**, 461 (2007).
- [4] M. Schultze *et al.*, Delay in photoemission, *Science* **328**, 1658 (2010).
- [5] K. Klünder, J. M. Dahlström, M. Gisselbrecht, T. Fordell, M. Swoboda, D. Guénot, P. Johnsson, J. Caillat, J. Mauritsson, A. Maquet, R. Taïeb, and A. L’Huillier, Probing single-photon

- ionization on the attosecond time scale, *Phys. Rev. Lett.* **106**, 143002 (2011).
- [6] M. Huppert, I. Jordan, D. Baykusheva, A. von Conta, and H. J. Wörner, Attosecond delays in molecular photoionization, *Phys. Rev. Lett.* **117**, 093001 (2016).
- [7] T. Driver *et al.*, Attosecond delays in X-ray molecular ionization, *Nature (London)* **632**, 762 (2024).
- [8] J.-B. Ji *et al.*, Attosecond X-ray core-level chronoscopy of aromatic molecules, *Phys. Rev. X* **15**, 041031 (2025).
- [9] S. Heck, D. Baykusheva, M. Han, J.-B. Ji, C. Perry, X. Gong, and H. J. Wörner, Attosecond interferometry of shape resonances in the recoil frame of CF₄, *Sci. Adv.* **7**, eabj8121 (2021).
- [10] D. Guénot, D. Kroon, E. Balogh, E. W. Larsen, M. Kotur, M. Miranda, T. Fordell, P. Johnsson, J. Mauritsson, M. Gisselbrecht, K. Varjú, C. L. Arnold, T. Carette, A. S. Kheifets, E. Lindroth, A. L'Huillier, and J. M. Dahlström, Measurements of relative photoemission time delays in noble gas atoms, *J. Phys. B: At. Mol. Opt. Phys.* **47**, 245602 (2014).
- [11] S. Biswas, B. Förg, L. Ortmann, J. Schötz, W. Schweinberger, T. Zimmermann, L. Pi, D. Baykusheva, H. A. Masood, I. Lontos, A. M. Kamal, N. G. Kling, A. F. Alharbi, M. Alharbi, A. M. Azzeer, G. Hartmann, H. J. Wörner, A. S. Landsman, and M. F. Kling, Probing molecular environment through photoemission delays, *Nat. Phys.* **16**, 778 (2020).
- [12] X. Gong, S. Heck, D. Jelovina, C. Perry, K. Zinchenko, R. Lucchese, and H. J. Wörner, Attosecond spectroscopy of size-resolved water clusters, *Nature (London)* **609**, 507 (2022).
- [13] V. Gruson, L. Barreau, Á. Jiménez-Galan, F. Risoud, J. Caillat, A. Maquet, B. Carré, F. Lepetit, J.-F. Hergott, T. Ruchon, L. Argenti, R. Taïeb, F. Martín, and P. Salières, Attosecond dynamics through a Fano resonance: Monitoring the birth of a photoelectron, *Science* **354**, 734 (2016).
- [14] M. Kotur, D. Guénot, Á. Jiménez-Galán, D. Kroon, E. W. Larsen, M. Louisy, S. Bengtsson, M. Miranda, J. Mauritsson, C. L. Arnold, S. E. Canton, M. Gisselbrecht, T. Carette, J. M. Dahlström, E. Lindroth, A. Maquet, L. Argenti, F. Martín, and A. L'Huillier, Spectral phase measurement of a Fano resonance using tunable attosecond pulses, *Nat. Commun.* **7**, 10566 (2016).
- [15] S. Nandi, E. Plésiat, S. Zhong, A. Palacios, D. Busto, M. Isinger, L. Neoričić, C. L. Arnold, R. J. Squibb, R. Feifel, P. Decleva, A. L'Huillier, F. Martín, and M. Gisselbrecht, Attosecond timing of electron emission from a molecular shape resonance, *Sci. Adv.* **6**, eaba7762 (2020).
- [16] D. Hammerland, T. Berglitsch, P. Zhang, T. T. Luu, K. Ueda, R. R. Lucchese, and H. J. Wörner, Bond-length dependence of attosecond ionization delays in O₂ arising from electron correlation to a shape resonance, *Sci. Adv.* **10**, eadl3810 (2024).
- [17] I. Jordan, M. Huppert, S. Pabst, A. S. Kheifets, D. Baykusheva, and H. J. Wörner, Spin-orbit delays in photoemission, *Phys. Rev. A* **95**, 013404 (2017).
- [18] A. Jain, T. Gaumnitz, A. Bray, A. Kheifets, and H. J. Wörner, Photoionization delays in xenon using single-shot referencing in the collinear back-focusing geometry, *Opt. Lett.* **43**, 4510 (2018).
- [19] B. Grafstrom, A. Wang-Holtzen, J. Wang, P. H. Bucksbaum, J. P. Cryan, and A. S. Landsman, Relativistic effects in molecular photoemission delays, *Phys. Rev. A* **110**, L061101 (2024).
- [20] M. Li, H. Wang, R. Tahouri, R. Weissenbilder, J. Li, W. Wang, J. Cai, X. Hong, X. Shi, L.-W. Pi, D. Busto, M. Gisselbrecht, K. Ueda, P. V. Demekhin, A. L'Huillier, J. M. Dahlström, E. Lindroth, D. Ding, and S. Luo, Photoionization time delays probe electron correlations, *Phys. Rev. Lett.* **135**, 183202 (2025).
- [21] K. T. Cheng and W. R. Johnson, Orbital collapse and the photoionization of the inner 4*d* shells for Xe-like ions, *Phys. Rev. A* **28**, 2820 (1983).
- [22] S. Zhong, J. Vinbladh, D. Busto, R. J. Squibb, M. Isinger, L. Neoričić, H. Laurell, R. Weissenbilder, C. L. Arnold, R. Feifel, J. M. Dahlström, G. Wendin, M. Gisselbrecht, E. Lindroth, and A. L'Huillier, Attosecond electron–spin dynamics in Xe 4*d* photoionization, *Nat. Commun.* **11**, 5042 (2020).
- [23] R. P. Madden, D. L. Ederer, and K. Codling, Resonances in the photo-ionization continuum of Ar I (20–150 eV), *Phys. Rev.* **177**, 136 (1969).
- [24] S. L. Sorensen, T. Åberg, J. Tulkki, E. Rachlew-Källne, G. Sundström, and M. Kirm, Argon 3*s* autoionization resonances, *Phys. Rev. A* **50**, 1218 (1994).
- [25] N. Berrah, B. Langer, J. Bozek, T. W. Gorczyca, O. Hemmers, D. W. Lindle, and O. Toader, Angular-distribution parameters and *R*-matrix calculations of Ar resonances, *J. Phys. B: At. Mol. Opt. Phys.* **29**, 5351 (1996).
- [26] S. Luo, R. Weissenbilder, H. Laurell, R. Y. Bello, C. Marante, M. Ammitzböll, L. Neoričić, A. Ljungdahl, R. J. Squibb, R. Feifel, M. Gisselbrecht, C. L. Arnold, F. Martín, E. Lindroth, L. Argenti, D. Busto, and A. L'Huillier, Influence of final state interactions in attosecond photoelectron interferometry, *Phys. Rev. Res.* **6**, 043271 (2024).
- [27] P. Mitchell, J. A. Baxter, J. Comer, and P. J. Hicks, The excitation of autoionisation states of argon by electron impact, *J. Phys. B* **13**, 4481 (1980).
- [28] K. E. Thorn, N. R. Monahan, S. K. K. Prasad, K. Chen, and J. M. Hodgkiss, Efficient and tunable spectral compression using frequency-domain nonlinear optics, *Opt. Express* **26**, 28140 (2018).
- [29] A. Jain, T. Gaumnitz, A. Kheifets, and H. J. Wörner, Using a passively stable attosecond beamline for relative photoemission time delays at high XUV photon energies, *Opt. Express* **26**, 28604 (2018).
- [30] J. Vinbladh, J. M. Dahlström, and E. Lindroth, Relativistic two-photon matrix elements for attosecond delays, *Atoms* **10**, 80 (2022).
- [31] T. Carette, J. M. Dahlström, L. Argenti, and E. Lindroth, Multiconfigurational Hartree-Fock close-coupling ansatz: Application to the argon photoionization cross section and delays, *Phys. Rev. A* **87**, 023420 (2013).
- [32] N. Moiseyev, Quantum theory of resonances: Calculating energies, widths and cross-sections by complex scaling, *Phys. Rep.* **302**, 212 (1998).
- [33] M. Sommovilla, F. Merkt, J. Z. Mezei, and C. Jungen, Absorption, autoionization, and predissociation in molecular hydrogen: High-resolution spectroscopy and multichannel quantum defect theory, *J. Chem. Phys.* **144**, 084303 (2016).