

Attosecond photoelectron interferometry of resonant structures between the Ar spin-orbit-split thresholds

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Resolving the ultrafast decay of metastable electronic states into channels associated with spin-orbit-split ionization thresholds is a long-standing goal of attosecond photoelectron spectroscopy. Here, we use a variant of the rainbow reconstruction of attosecond beating by interference of two-photon transitions technique to study, experimentally and theoretically, the ultrafast dynamics, resolved in photoelectron energy and emission angle, of the autoionizing states comprised in the narrow 177 meV energy gap between the $3p^{-1} \ ^2P_{3/2}$ and $^2P_{1/2}$ thresholds in argon. The scheme employs three pulses: an XUV attosecond pulse train (pump), generated as odd harmonics of a fundamental IR frequency ω ; a weak replica of the IR field (driver) that copropagates phase-locked with the pump; and a second IR pulse (probe) with controllable delay τ with respect to the pump. Two harmonics excite bound states below the $^2P_{3/2}$ threshold and the continuum above the $^2P_{1/2}$ threshold, and their overlapping sideband populates even-parity resonant states between the two thresholds, giving rise to resonant signals beating at both ω and 2ω . From the photoemission cross section and the β_2 and β_4 asymmetry parameters, we resolve both the nf and the np resonant series. In both theory and experiment, the relative weight of the ω and 2ω beatings changes significantly across the interthreshold gap, an evolution that we trace back to higher-order probe-photon processes. The resonant photoelectron emission is found to be strongly localized in small spots within the (β_2, β_4) region admissible for two-photon transitions.

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I. INTRODUCTION

Photoelectron interferometry has emerged as a powerful diagnostic of electron dynamics in atoms [1–4] and molecules [5–7]. These measurements temporally resolve the quantum beats associated with electronic wave packets through interferences between transitions to the continuum. By spectrally resolving the quantum beats in the photoelectron yield, one can characterize the complex amplitude and relative phases of the various ionization pathways [8–14]. In particular, attosecond-resolved interferometric techniques, such as reconstruction of attosecond beating by interference of two-photon transitions (RABBITT) [15], have yielded unprecedented insights into multicolor ionization pathways [16–21], strong-field modification of the electronic structures [11], correlated electron dynamics [22–25], and photoionization time delays [26–28]. This technique employs an XUV attosecond pulse train (APT), composed of odd

harmonics of a fundamental IR frequency ω , to ionize the system, together with a time-delayed weak replica of the IR pulse used to generate the APT. Two-photon pathways involving the absorption of photons from adjacent harmonics and the absorption or emission of a probe IR photon can lead to the same sideband. The interference of these pathways gives rise to oscillations in the photoelectron yield whose phase provides access to photoemission time delays.

A spectrally resolved extension of RABBITT, i.e., the rainbow RABBITT, has enabled precise characterization of autoionizing states excited by the pump pulse [12,29–31]. The energies, widths, and angular couplings of the transitions can be extracted from the corresponding RABBITT interferogram [18,32–35]. Parallel to these developments, the underthreshold RABBITT (uRABBITT) has been employed to probe the properties of discrete bound states. In this approach, one of the two-photon XUV + IR pathways proceeds through bound intermediate states. Recently, a uRABBITT scheme has been used to control the Fano interference between resonant and nonresonant ionization pathways and to image the dynamics of the associated bound electron wave packet [36]. Both RABBITT and uRABBITT methods exhibit an angular dependence, giving access to interference between different angular momentum channels, which adds another investigative dimension to the photoelectron interferometry [37–39].

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In this joint theoretical and experimental study, we employ a three-pulse rainbow-RABITT scheme, in which one of the two interfering arms proceeds resonantly through bound intermediate states, as in uRABITT, for a high-energy-resolution study of the $[3p^{-1}(^2P_{1/2}^o)np_{1/2}]_0^e$, $[3p^{-1}(^2P_{1/2}^o)np_{3/2}]_2^e$, and $[3p^{-1}(^2P_{1/2}^o)nf_{5/2}]_2^e$ autoionizing-state (AIS) series in the 177 meV energy gap between the narrow $3p^{-1}$ spin-orbit-split thresholds of Ar. Due to the low energy of the harmonics involved, the IR pulse copropagating with the harmonics cannot be filtered out without significantly depleting the harmonic intensity. Rather than a limitation, this circumstance provides an additional observable: The resonant sideband signal beats not only at 2ω , as in conventional RABITT, but also at the fundamental frequency ω .

The present approach differs from previous rainbow-RABITT and uRABITT studies in three respects. First, the three-pulse configuration, with a weak IR driver phase-locked to the pump, gives simultaneous access to the ω and 2ω beatings of each resonant feature; we show that the ratio of the two is a sensitive probe of the ionization dynamics, and that its evolution across the Rydberg series reflects processes beyond lowest-order perturbation theory. Second, the method operates within the 177 meV gap between the spin-orbit-split thresholds, a spectral region hosting overlapping nf and np autoionizing series that is inaccessible to conventional RABITT filtering schemes. Third, by combining the energy-resolved photoemission yield with the photoelectron anisotropy parameters β_2 and β_4 , we can separate resonant series that overlap in the angle-integrated spectrum.

Utilizing a velocity-map-imaging (VMI) spectrometer and the three-pulse pump-probe configuration described above, we record the interference between a bound-continuum pathway and a continuum-continuum pathway. The relative amplitude and phase of the ω and 2ω beatings are found to vary significantly with the principal quantum number n of the Rydberg series. We resolve the anisotropy parameters $\beta_2(E; \tau)$ and $\beta_4(E; \tau)$ as functions of the photoelectron energy E and of the probe time delay τ across this narrow spectral region. We distinguish between the $nf_{5/2}$ and $np_{1/2}$ series by analyzing the photoemission cross section alongside the β_2 and β_4 parameters [40]. Additionally, we measure the bounds of β_2 and β_4 for autoionizing electrons and observe a high degree of localization in the space of possible (β_2, β_4) parameters. These quantities are reproduced using an extension of the NewStock *ab initio* atomic ionization code that accounts semiempirically for threshold spin-orbit splitting [30]. Core features of the experimental and theoretical time-, energy-, and angularly resolved resonant spectra are in good agreement, confirming the validity of the present approach. Our work demonstrates how combining spectral- and angle-resolved photoelectron interferometry allows for a precise interrogation of electron correlation and spin-orbit effects in metastable atomic states, and it shows that the measurement of relative angularly resolved resonant photoemission delays is within reach.

The paper is organized as follows. Section II describes the experiment: the optical setup and pulse parameters (Sec. II A), the three-pulse interferometric scheme (Sec. II B), and the detection and data-processing procedures (Sec. II C). Sec-

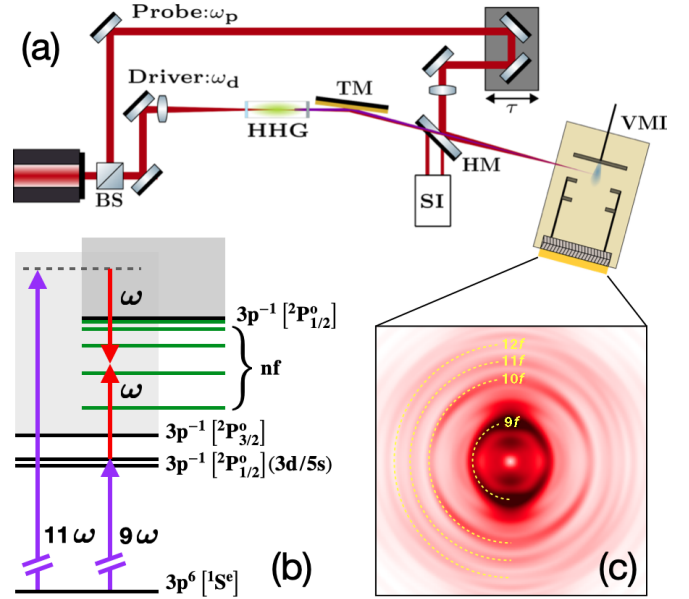


FIG. 1. (a) Diagram of the apparatus showing the probe and driver arms. BS: beam splitter, HHG: high harmonic generation waveguide, HM: holey mirror for recombination, TM: toroidal mirror, SI: stabilization interferometer, and VMI: velocity map imaging instrument. (b) Energy levels and excitation scheme: The ninth harmonic (H_9) of the APT is resonant with the $3p^{-1}(^2P_{1/2}^o)3d/5s$ Rydberg states. Absorption of an additional IR photon populates several autoionizing states between the $^2P_{3/2}^o$ and $^2P_{1/2}^o$ spin-orbit-split thresholds. The same region is also reached through the absorption of an XUV photon from the 11th harmonic (H_{11}), followed by the emission of an IR photon. The harmonic bandwidth is sufficiently wide to span the entire region between the thresholds. (c) The angularly and energy-resolved photoelectron spectrum between the two thresholds is recorded with a VMI detector; the dashed rings mark the 9–12f resonances, and the laser polarization axis is vertical.

tion III summarizes the theoretical model, with the technical details of the close-coupling basis, of the numerical time propagation, and of the two-photon asymmetry parameters deferred to Appendixes A–C, respectively. Section IV presents the results: the resonant ω and 2ω beatings of the nf series (Sec. IV A), their interpretation in terms of interfering multiphoton pathways (Sec. IV B), the angle-resolved spectra (Sec. IV C), the joint (β_2, β_4) distributions (Sec. IV D), and the Fourier analysis of the delay-dependent observables (Sec. IV E). Section V summarizes our conclusions and perspectives.

II. EXPERIMENTAL METHOD

A. Optical setup and pulse parameters

Figure 1 illustrates the experimental layout, the dominant excitation paths, and the observables recorded in this work. The pump-probe experiment employs a 1 mJ, 40 fs pulse with a central wavelength of 785 nm ($\hbar\omega = 1.579$ eV), emerging from a KM Labs Ti:Sapphire Dragon amplifier at 1 kHz. This beam is split equally into two paths using an ultrafast antireflection (AR)-coated dielectric beam splitter. One path (henceforth termed the *driver*) is routed and then focused,

using a 75 cm AR-coated thin lens, into an ~ 37 mm long hollow-core waveguide (inner diameter 0.2 mm, outer diameter 1.2 mm) made of borosilicate glass. The volume behind the waveguide is filled with Xe gas, forming a semi-infinite-like gas cell arrangement. The driver induces high harmonic generation (HHG), resulting in an XUV attosecond pulse train phase matched to yield primarily odd harmonics 9–19 of the fundamental. We do not use an Al filter to block the copropagating driver, as it would significantly reduce the intensity of the 9th and 11th harmonics that are employed in this study. As a result, a weak residual driver pulse, collinear with and phase-locked to the APT, also reaches the interaction chamber. The residual driver is much weaker than the probe pulse because (1) it rapidly diverges after the HHG waveguide and the toroidal mirror only captures a narrow ~ 25 mrad angular spread; (2) it is attenuated to 1/3 intensity due to the reflectivity of the toroidal mirror; and (3) it is clipped to 1/6 of its diameter by the holey(recombination) mirror. The second path from the beam splitter, henceforth termed the *probe*, is aligned into a SmarAct delay stage and then recombined collinear with the driver + APT on a holey mirror. Immediately before recombination, both paths are independently focused to the same focal position inside the VMI chamber. The driver + APT reflects off a grazing-incidence toroidal mirror, while the probe arm passes through a thin 1 m lens positioned so that the focal planes of the two arms overlap in the VMI chamber.

The APT pump pulse had an ~ 5 fs FWHM envelope and contained the odd harmonics 9–19 of the fundamental. Collinear and at a fixed phase delay with respect to the APT is the residual driver pulse at the fundamental frequency, with an ~ 40 fs FWHM and an estimated intensity at the focus of ~ 0.01 TW/cm². The probe pulse, also with ~ 40 fs FWHM, is delayed by τ relative to the pump, with an intensity at the focus of ~ 0.5 TW/cm². The experiment scans the probe delay over the range $\tau = [-5, 5]$ fs in steps of 0.2 fs, as measured by the pump-probe stability interferometer described in Sec. II C. Significant temporal overlap between the driver and the probe pulse is maintained throughout the entire delay range.

B. Three-pulse interferometric scheme

To study photoionization in the region between the spin-orbit-split thresholds of Ar, we use a RABBITT-like interferometric scheme, illustrated in Fig. 1(b). Two distinct XUV + IR two-photon paths contribute to the photoelectron signal in this region. The first path consists of excitation by the ninth harmonic (H_9), followed by the absorption of an IR photon, and is resonantly enhanced by the intermediate $3p^{-1}[^2P_{1/2}^o]3d$ and $3p^{-1}[^2P_{1/2}^o]5s$ bound states. The second path, in which the absorption of an XUV photon from the 11th harmonic (H_{11}) is followed by the stimulated emission of an IR photon, does not involve intermediate resonant states, but it does transit through the continuum that opens at the $3p^{-1}[^2P_{3/2}^o]$ threshold. Both paths terminate in the same sideband, located in the gap between the two thresholds, where they populate the even-parity autoionizing states of the $[^2P_{1/2}^o n\ell]$ series.

In either path, the IR photon can be exchanged with the probe or with the driver; we denote by ω_p (ω_d) an IR

photon exchanged with the probe (driver) pulse. Since the driver is phase-locked to the APT, only interference between pathways of which at least one involves the probe produces a delay-dependent signal. Pairs of interfering amplitudes in which one probe photon is absorbed and one is emitted give rise to the $\cos(2\omega\tau)$ beating characteristic of the RABBITT scheme. The driver alone is too weak to produce an appreciable two-photon signal. However, the interference between an amplitude involving a probe photon and one involving a driver photon is readily observable, and it gives rise to a $\cos(\omega\tau)$ oscillation. Three-pulse configurations of this kind have been employed in previous studies by us [11] and by other groups [41], and the multiphoton pathways contributing to the ω beating are well understood; their role in shaping the energy-resolved sideband profile is analyzed in Sec. IV B.

C. Delay stabilization, detection, and data processing

If left alone, air currents, vibrations, and thermal changes lead, over several-minute time scales, to a drift of the relative delay between the pump and probe arms. To keep the pump-probe delay stable at each set point of the scan, we pick off a small portion of both the probe and the weak copropagating driver beams and interfere them on a complementary metal-oxide semiconductor camera. The interference fringes are continuously monitored throughout the experiment. Changes in the pump-probe delay τ manifest as fringe motion on the camera. An active stabilization loop monitors the fringe position and applies corrective movements to the probe delay stage to keep the fringes stationary; the delay scan proceeds by stepping the stabilized set point.

Both pump and probe are focused into an effusive jet of Ar gas inside a single-ion-lens VMI spectrometer whose design follows Ref. [42]. Since low-kinetic-energy photoelectrons are of interest, a low voltage (300 V) was applied to the repeller electrode to increase the energy resolution. Photoelectron momenta are mapped onto a microchannel-plate (MCP)-phosphor detector whose fluorescence is imaged using a camera. Directly after the VMI chamber, a concave grating and charged-coupled device monitor the yield of the APT harmonics above the ninth harmonic.

From the VMI image, we estimate that each laser pulse produces on the order of 10 counts on the detector. The laser operates at 1 kHz, and each frame is acquired using a 10 s exposure time, corresponding to $\sim 10^5$ hits per image. To convert raw images into a photoelectron momentum map, each image undergoes a thresholding procedure to eliminate spurious hot pixels, a spatial convolution with a 3×3 pixel Gaussian kernel and, finally, an inverse Abel transformation using the Cartesian Pixel BASEX (CPBASEX) algorithm [43], which is based on the well-known Polar Basis Set Expansion (pBASEX) procedure [44]. The radial coordinate of the resulting distribution is proportional to the square root of the photoelectron kinetic energy. The linear polarization axis of both pump and probe pulses lies in the vertical plane, parallel to the MCP plate and orthogonal to the spectrometer axis. In the image shown in Fig. 1(c), the polarization axis corresponds to the vertical axis. The key observables for this study are

the photoelectron energy spectrum and angular distribution as functions of the probe delay τ .

III. THEORETICAL MODEL

To simulate the photoionization of argon in the energy region between the $^2P_{3/2}^o$ and $^2P_{1/2}^o$ ionization thresholds, we employed the NewStock atomic photoionization code [45], extended to semiempirically account for the 177 meV spin-orbit splitting of the ionization threshold. The main consequence of the spin-orbit splitting is that the high-lying members ($n > 8$) of the Rydberg series converging to the $^2P_{1/2}^o$ threshold become embedded in the $^2P_{3/2}^o \varepsilon_\ell$ continuum channels, into which they autoionize, releasing electrons with extremely small asymptotic kinetic energies, smaller than the 177 meV splitting itself, and of the order of a few tens of meV for the states studied here [cf. the energy scale in Fig. 1(b)]. In this regime, therefore, threshold effects are expected to play a disproportionate role across the $^2P_{1/2}^o n\ell$ Rydberg series.

To reproduce these effects, we first construct nonrelativistic close-coupling (CC) states $|\psi_{\alpha\nu}^\Gamma\rangle$ by coupling an ionic state $|\Phi_a\rangle$, where the index a labels the state of the parent ion, to a one-electron spin-orbital $|\phi_{\nu\ell m\sigma}\rangle$ with orbital angular momentum ℓ and radial index ν . The radial index ν enumerates the radial functions of the quantization-box basis and should not be confused with the principal quantum number n of the physical Rydberg states. The one-electron states form an effectively complete basis within a spherical quantization box with radius R_{BOX} as large as a few hundred Bohr radii. The CC states, computed in the electrostatic approximation, are subsequently recoupled to well-defined total angular momenta J , J_a , and j , associated with the neutral system, the residual ion, and the photoelectron, respectively; the explicit recoupling transformation is given in Eq. (A1). In the following, $\alpha = (a, J_a, \ell, j)$ is a collective index identifying the ionization channel, and $\Gamma = (J, M_J, \pi)$, where π is the total parity, identifies the global symmetry of the neutral system.

To evaluate the matrix elements of the field-free Hamiltonian $\hat{H}_0$, given by the nonrelativistic electrostatic Hamiltonian plus the spin-orbit correction, $\hat{H}_0 = \hat{H}_{\text{nr}} + \hat{H}_{\text{so}}$, we shift the diagonal nonrelativistic energy of all the close-coupling states associated with the $^2P_{1/2}^o$ threshold by an amount equal to the spin-orbit splitting $\Delta_a^{\text{so}} = 177$ meV,

$$\langle\psi_{\alpha\nu}^\Gamma|\hat{H}_0|\psi_{\beta\nu'}^\Gamma\rangle \simeq \langle\psi_{\alpha\nu}^\Gamma|\hat{H}_{\text{nr}}|\psi_{\beta\nu'}^\Gamma\rangle + \delta_{\alpha\beta}\delta_{\nu\nu'}\Delta_a^{\text{so}}. \quad (1)$$

Although this semiempirical procedure does not provide a rigorous short-range description of the spin-orbit interaction, the dominant spin-orbit effect for the highest members of the autoionizing series considered here is expected to arise from the threshold splitting itself. Furthermore, our approach has been successfully tested in the simulation of spin-orbit-resolved resonant RABBITT spectra in argon, in the energy region below the $3s^{-1}$ threshold [30], which yielded results similar to those of an independent R -matrix implementation that includes an explicit *ab initio* description of the spin-orbit interaction [46].

The remaining components of the close-coupling model are treated fully *ab initio*. Since the spectral region of interest lies between the $^2P_{3/2}^o$ and $^2P_{1/2}^o$ ionic states, the LS -coupled CC space in the structural calculations can be restricted to

the channels originating from the $^2P^o$ ion only. This choice greatly reduces the configuration space without appreciably affecting convergence. Indeed, the next ion-excitation threshold, corresponding to the $\text{Ar}(3s^{-1})$ state, is about 13.5 eV above the energy region of interest. We computed the ionic state at the multiconfiguration Hartree-Fock level [47], with configurations of the form $[\text{Ne}]3s^23p^{n_p}3d^{n_d}$, with $n_p + n_d = 5$ and $n_p \geq 2$. The neutral Ar states are computed in a configuration space that includes a localized channel, obtained by adding an electron to any of the active orbitals in any of the configurations of the ion, as well as the partial-wave channels (PWC) obtained by augmenting the $3p^{-1}^2P^o$ ion with a large set of one-electron spin-orbitals with angular momentum $\ell \leq 3$, whose radial parts are represented in a B -spline basis (see Appendix B).

To simulate one-photon and two-photon transitions from the ground state of argon, the only required symmetries J^π are 0^e , 1^o , and 2^e , where J is the total angular momentum and π is the parity (even or odd). The LS symmetries and PWC channels used in the generation of the J^π CC spaces are listed in Table I.

In this model space, the ground-state energy of the neutral argon atom is 15.512 eV below the $\text{Ar}^+ 3p^{-1} (^2P_{3/2}^o)$ threshold, to be compared with the National Institute of Standards and Technology (NIST) values for the ionization potential to the $^2P_{3/2}^o$ level, 15.760 eV, and to the $^2P_{1/2}^o$ level, 15.937 eV [48]. The $^2P_{1/2}^o$ threshold is raised with respect to the $^2P_{3/2}^o$ threshold by the full experimental spin-orbit splitting, as prescribed by Eq. (1), while the $^2P_{3/2}^o$ threshold is left unchanged, thus preserving the consistency in the representation of the lowest members of the $^2P_{3/2}^o n\ell$ Rydberg series.

To determine the evolution of the argon atom driven by the pump-probe pulse sequence, we numerically integrate the time-dependent Schrödinger equation (TDSE) in the configuration space spanned by the recoupled CC basis, using a second-order split-exponential propagator in the velocity gauge. The Hamiltonian is complemented by a complex absorbing potential (CAP), which prevents unphysical reflections at the quantization-box boundary, and the long IR pulses are handled with a wave-function partitioning technique [49] that periodically transfers the outgoing part of the wave packet to an analytical field-free propagation, thereby drastically reducing the required box size. The propagator, the CAP, the partitioning procedure, and the corresponding numerical parameters are detailed in Appendix B.

The pulses in the simulations are chosen to reproduce the same ionization paths as in the experiment. In the experiment, H_9 has a central frequency $\omega_0 = 14.31$ eV and a finite bandwidth (~ 150 meV FWHM) which comfortably spans both the $[^2P_{1/2}^o \otimes 5s]_1^o$ and $[^2P_{1/2}^o \otimes 3d]_1^o$ intermediate states, located at 14.255 and 14.304 eV, respectively, i.e., only 49 meV apart. Since the theoretical Rydberg energies are slightly shifted with respect to the experimental values, we employed an H_9 with the same bandwidth but $\omega_0 = 14.10$ eV, which makes it resonant with the numerical $[^2P_{1/2}^o \otimes 5s]_1^o$ (14.086 eV) and $[^2P_{1/2}^o \otimes 3d]_1^o$ (14.141 eV) states, 55 meV apart, and at the same time supports the presence of a sideband between the $^2P_{3/2}^o$ and $^2P_{1/2}^o$ ionization thresholds. The H_{11} in the simulations has, therefore, a central frequency of 17.28 eV, which is

TABLE I. Channels included in the J^π states expansion.

J^π	LS symmetries	PWC channels
0^e	$^1S^e, ^3P^e$	$^2P_{3/2}^o \otimes \epsilon p_{3/2}, ^2P_{1/2}^o \otimes \epsilon p_{1/2}$
1^o	$^1P^o, ^3P^o, ^3D^o$	$^2P_{3/2}^o \otimes \epsilon s_{1/2}, ^2P_{3/2}^o \otimes \epsilon d_{3/2}, ^2P_{3/2}^o \otimes \epsilon d_{5/2}, ^2P_{1/2}^o \otimes \epsilon s_{1/2}, ^2P_{1/2}^o \otimes \epsilon d_{3/2}$
2^e	$^1D^e, ^3P^e, ^3D^e, ^3F^e$	$^2P_{3/2}^o \otimes \epsilon p_{1/2}, ^2P_{3/2}^o \otimes \epsilon p_{3/2}, ^2P_{3/2}^o \otimes \epsilon f_{5/2}, ^2P_{3/2}^o \otimes \epsilon f_{7/2}, ^2P_{1/2}^o \otimes \epsilon p_{3/2}, ^2P_{1/2}^o \otimes \epsilon f_{5/2}$

twice the IR photon energy ($\omega_{\text{IR}} = 1.59$ eV) above H_9 . The harmonic intensity was 10 GW/cm^2 , while the intensities of the copropagating IR driver and of the probe pulse were 50 and 500 GW/cm^2 , respectively; the duration of both IR pulses was 40 fs. The driver intensity in the simulations is larger than the experimental estimate of Sec. II A ($\sim 10 \text{ GW/cm}^2$), which has significant uncertainty. The impact of the pulse parameters on the comparison between theory and experiment is discussed in Sec. IV A.

The channel-resolved final photoelectron amplitudes are then used to compute the angle-integrated photoelectron distribution, $dP(E; \tau)/dE$, and the angularly resolved photoelectron distribution, $dP(E, \hat{\Omega}; \tau)/dE d\Omega$. These quantities are related through the following parametrization [40]:

$$\frac{dP(E, \hat{\Omega}; \tau)}{dE d\Omega} = \frac{1}{4\pi} \frac{dP(E; \tau)}{dE} [1 + \beta_2(E; \tau) P_2(\cos \theta) + \beta_4(E; \tau) P_4(\cos \theta)], \quad (2)$$

where $P_\ell(x)$ are Legendre polynomials and β_2 and β_4 are the photoemission asymmetry parameters characteristic of two-photon single-ionization processes with linearly polarized light [40]. The β_k asymmetry parameters are given by

$$\beta_k(E; \tau) = \alpha_k(E; \tau)/\alpha_0(E; \tau), \quad (3)$$

where the coefficients α_k are bilinear forms of the channel-resolved ionization amplitudes; their explicit expression is given in Eq. (C1).

In particular, we examine the correlation between β_2 and β_4 through their unweighted and weighted joint distributions in the energy region from the $3p_{J=3/2}^{-1}$ threshold up to the $12f$ autoionizing state, which is well resolved in both the experiment and the simulation, over a delay range matching the experimental conditions,

$$P(\beta'_2, \beta'_4) = \frac{1}{T} \int_{E_{3/2}}^{E_{3/2} + \Delta E} dE \int_{\tau_{\min}}^{\tau_{\max}} d\tau \times \delta[\beta_2(E; \tau) - \beta'_2] \delta[\beta_4(E; \tau) - \beta'_4], \quad (4)$$

$$\bar{P}(\beta'_2, \beta'_4) = \frac{1}{T} \int_{E_{3/2}}^{E_{3/2} + \Delta E} dE \int_{\tau_{\min}}^{\tau_{\max}} d\tau \frac{dP(E; \tau)}{dE} \times \delta[\beta_2(E; \tau) - \beta'_2] \delta[\beta_4(E; \tau) - \beta'_4], \quad (5)$$

where $\Delta E = 93$ meV and $T = \tau_{\max} - \tau_{\min}$. In this representation, the $[3p_{J=1/2}^{-1} n\ell]_{J=0,2}$ autoionizing states give rise to a signature clearly distinguishable from that of the nonresonant background, as shown in Sec. IV D.

IV. RESULTS

A. Resonant ω and 2ω beatings of the nf series

Figure 2 shows the comparison between the experimental (a) and theoretical (b) angle-integrated XUV-pump IR-probe photoelectron spectra, as functions of the pump-probe delay, in the energy region between the $^2P_{3/2}^o$ and the $^2P_{1/2}^o$ thresholds, extending up to 93 meV above the $^2P_{3/2}^o$ threshold. This energy region encompasses the resonant features corresponding to three AIS series: $[^2P_{1/2}^o \otimes nf_{5/2}]_2^e$, $[^2P_{1/2}^o \otimes np_{3/2}]_2^e$, and $[^2P_{1/2}^o \otimes np_{1/2}]_0^e$. Since these are the only AIS series of interest in the present work, we use the following simplified notation to label them from this point on, in the same order: nf , $np_{3/2}$, and $np_{1/2}$. To isolate the dominant ω and 2ω modulations, both the experimental and theoretical photoelectron spectra have been filtered to remove time-delay oscillation modes with angular frequencies above $4 \text{ eV}/\hbar$. A quadratic background $S_{\text{bg}}(E, \tau) = A(E) + B(E)\tau + C(E)\tau^2$ was subtracted from the spectra before Fourier filtering, and subsequently added back to preserve the overall spectral profile. The theoretical spectrum was further convoluted in energy with a Gaussian of width $\sigma = 3$ meV to resemble the experimental resolution.

Before analyzing the resonant dynamics, it is useful to summarize the main differences between the experimental and theoretical spectra, which are apparent in Fig. 2 and persist in the figures that follow. First, the experimental features are broadened by the finite spectrometer resolution: The sharp theoretical resonance profiles are recovered only after convolution with a $\sigma \approx 3$ meV Gaussian, and the weaker np resonances, well separated in theory, are not resolved in the angle-integrated experimental spectrum. Second, the experimental maps carry noise from counting statistics and from the inverse Abel transformation, which affects most strongly the weakest features and, as discussed in Sec. IV E, the higher-order anisotropy parameter β_4 . Third, the absolute resonance positions differ slightly: The measured nf peaks lie approximately 1 meV above the values of Ref. [50], while the theoretical positions agree with the experimental ones within 1–2 meV (see below). Finally, the experimental pulse parameters, most notably the driver intensity, which is known only within a factor of a few, and the harmonic chirp, are imperfectly characterized, which affects the relative contrast of the ω and 2ω beatings (cf. the $9f$ panel of Fig. 3) and, in the simulations, motivated the choice of pulse parameters described in Sec. III. None of these differences affect the identification of the resonances or the trends discussed below; where they play a role, we point it out explicitly.

The central insets of both panels show the delay-integrated photoelectron spectra. The most prominent peaks correspond to the 9–12 f AIS. In the experimental data, the peaks for

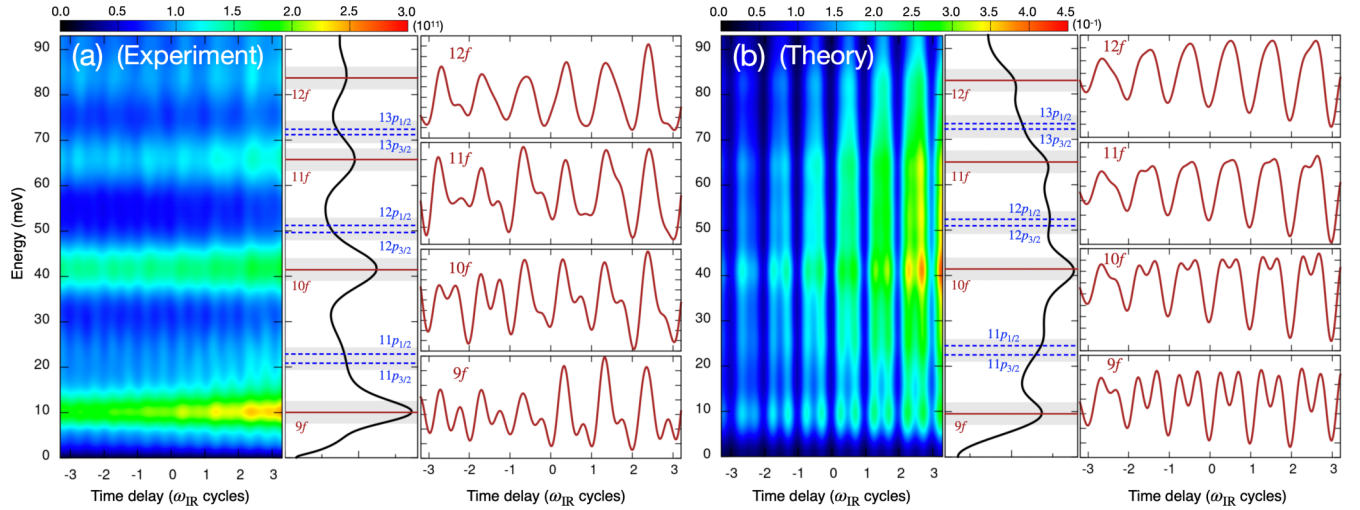


FIG. 2. (a) Left panel: Experimental photoelectron spectrum in the energy region between the $^2P_{3/2}^o$ and $^2P_{1/2}^o$ ionization thresholds, shown as a function of the pump-probe delay (horizontal axis), measured in units of IR optical cycles. Photoelectron energies (vertical axis) are measured from the $^2P_{3/2}^o$ threshold; the spectrum extends up to a maximum photoelectron energy of 93 meV. Central panel: Pump-probe-delay integrated photoelectron spectrum, with the positions of the $nf_{5/2}$ (solid horizontal lines) and $np_{1/2}$, $np_{3/2}$ (dashed horizontal lines) autoionizing states located in this energy interval indicated. Right panel: Photoelectron signals at the energies of the nf resonances as a function of the pump-probe delay, after removing frequency components above $4 \text{ eV}/\hbar$. (b) Same as panel (a), but for the theoretical simulations. To reproduce the experimental resolution, the theoretical spectra were convoluted with a Gaussian of width $\sigma = 3 \text{ meV}$ (see main text for more details).

the $11\text{--}13p_{3/2}$ and $11\text{--}13p_{1/2}$ AIS are not resolved within the current energy resolution. Their expected positions are indicated by dashed lines, based on independent measurements [50]. The positions of the observed nf states, indicated by solid lines centered at the peak maxima, are approximately 1 meV above the values reported in Ref. [50]. The theoretical positions of the AIS, highlighted in the time-delay integrated signal in panel (b), agree with the experimental values within $<1 \text{ meV}$ for the $9\text{--}12f$ AIS and within $<2 \text{ meV}$ for the $11\text{--}13p_{3/2}$ and $11\text{--}13p_{1/2}$ AIS.

To analyze the temporal behavior of the four nf AIS signals of interest, the photoelectron yields at each nf resonance were extracted by averaging the spectrum over a 5 meV energy interval centered on the corresponding spectral peak and removing the quadratic background. The resulting delay-

dependent line outs are shown in the two rightmost insets in Fig. 2. The amplitudes of the ω and 2ω modulations, obtained from the Fourier analysis of the nf AIS line outs, are shown in Fig. 3. Both experiment and theory reveal a pronounced increase of the $\omega/2\omega$ amplitude ratio in the oscillations of the nf signals with increasing principal quantum number: The $9f$ resonance exhibits comparable ω and 2ω amplitudes, whereas for the $12f$ resonance the ω component dominates.

B. Origin of the evolution of the $\omega/2\omega$ ratio

The agreement between experiment and theory in reproducing the n -dependent evolution of the $\omega/2\omega$ amplitude ratio is remarkable, considering the limited knowledge of the experimental pulse characteristics. At first sight, this evolution may itself seem surprising. In the simulations, the driver and probe pulses have identical frequencies and durations, and therefore produce identical two-photon absorption and emission amplitudes; one might then expect the spectral dependence of the ω and 2ω oscillations to be similar. The two modulations, however, collect contributions from different sets of interfering pathway pairs, listed in Table II.

The 2ω RABBITT modulation arises from a single interference term between the amplitude associated with probe-photon absorption and the amplitude associated with probe-photon emission, $H_9 + \omega_p$ and $H_{11} - \omega_p$. The ω modulation, instead, only requires that one of the two interfering amplitudes involves the absorption or emission of a probe photon, while the other involves the absorption or emission of a driver photon, which does not depend on the pump-probe delay. As a consequence, the ω beating results from the contribution of four distinct interference terms, (i)–(iv) in Table II. Terms (i) and (ii) involve one-photon absorption and one-photon emission and therefore lead to the same symmetric spectral profile of the sideband as the 2ω beating. Term (iii),

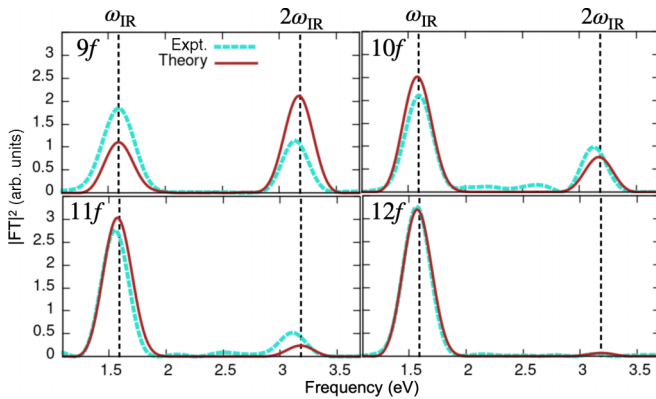


FIG. 3. Squared modulus of the Fourier transform of the experimental (dashed) and simulated (solid) delay-dependent $9\text{--}12f$ line outs of Fig. 2. The distributions have been normalized within the frequency interval shown to facilitate the comparison. The dashed vertical lines mark the ω_{IR} and $2\omega_{\text{IR}}$ frequencies.

TABLE II. Pairs of interfering two-photon pathways contributing to the delay-dependent beatings of the sideband signal. ω_p (ω_d) denotes an IR photon exchanged with the probe (driver) pulse. The last column indicates the spectral profile associated with each interference term (see text).

Beating	Interfering amplitudes	Spectral profile
2ω	$H_9 + \omega_p \leftrightarrow H_{11} - \omega_p$	Symmetric
ω (i)	$H_9 + \omega_d \leftrightarrow H_{11} - \omega_p$	Symmetric
ω (ii)	$H_9 + \omega_p \leftrightarrow H_{11} - \omega_d$	Symmetric
ω (iii)	$H_9 + \omega_p \leftrightarrow H_9 + \omega_d$	Tilted toward H_9
ω (iv)	$H_{11} - \omega_p \leftrightarrow H_{11} - \omega_d$	Tilted toward H_{11}

in contrast, has the same profile as the upper sideband of H_9 in the absence of H_{11} , and term (iv) the same profile as the lower sideband of H_{11} in the absence of H_9 ; both of these profiles are known to be tilted toward the originating harmonic, due to finite-pulse effects [51]. The 2ω component, therefore, exhibits a narrower photoelectron distribution, whereas the ω component is broader. Ultimately, this behavior reflects the markedly different energy dependence of the XUV + IR absorption pathways, mediated by intermediate bound states, and of the XUV-absorption/IR-emission pathways, involving continuum intermediate states and quasibound final states. In the threshold gap examined here, the broader profile of the ω beating favors higher photoelectron energies and could therefore plausibly account for the observed increase of the $\omega/2\omega$ ratio with increasing principal quantum number (see Fig. 3).

To verify this hypothesis, we computed the $\omega/2\omega$ ratio within lowest-order perturbation theory (LOPT), where only one IR photon is exchanged in either ionization path. While the ratio decreases significantly for the nonresonant background signal, it remains remarkably stable precisely at the energies of the nf resonances. This result shows that the mechanism described above does not, in fact, explain the observed drift of the $\omega/2\omega$ ratio in the resonance line-outs. Instead, the evolution of the $\omega/2\omega$ ratio in the resonant line outs arises entirely from higher-order contributions, involving the exchange of two or more probe photons in at least one of the interfering pathways, which are all accounted for in the TDSE simulations at intensities matching those in the experiment.

It is natural to ask under which conditions such higher-order processes become important. Two factors conspire to enhance them in the present measurement: The comparatively high probe intensity ($\sim 0.5 \text{ TW/cm}^2$), which is needed to obtain a measurable two-photon signal from the weak near-threshold harmonics, and the character of the final states, since slow photoelectrons and high-lying Rydberg resonances are associated with large radiative couplings, so that the exchange of additional IR photons is far more efficient than for the faster electrons detected in conventional RABBITT sidebands. We therefore expect similar higher-order signatures to be a general feature of RABBITT-type measurements performed close to an ionization threshold, or across high-lying resonances, at comparable probe intensities, whereas they should be suppressed at the lower probe intensities and

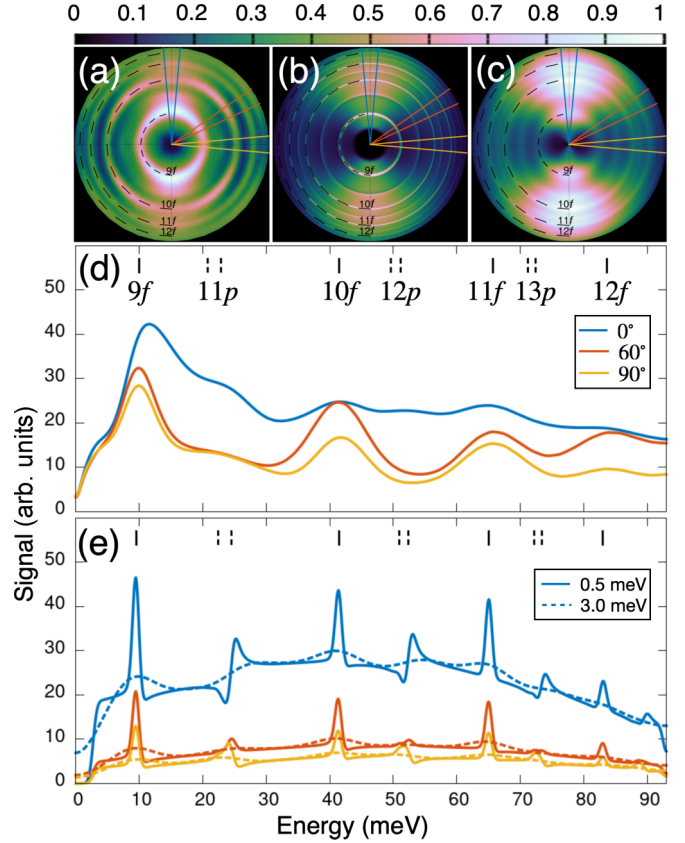


FIG. 4. Time-delay integrated photoelectron angular distributions [see Eq. (2)]. Panels (a)–(c) show the rescaled PADs as polar plots in momentum space: (a) experiment, (b) and (c) simulation with Gaussian convolution widths of 0.5 and 3.0 meV, respectively. The rings associated with the nf resonances are highlighted by black dashed lines. The radial lines indicate the three angular sectors around $\theta = 0^\circ$ (blue), 60° (red), and 90° (yellow), from which selected experimental [panel (d)] and theoretical [panel (e)] angle-resolved photoelectron yields are extracted. Theoretical results are shown for both convolution widths. Photoelectron energies in panels (d) and (e) are measured from the $^2P_{3/2}^o$ threshold. The experimental and theoretical positions of the nf and np resonances are indicated by vertical markers at the top of panels (d) and (e).

higher photoelectron energies of most published RABBITT experiments. Conversely, an LOPT-level interpretation of resonant beatings in this spectral region requires either weaker probe pulses or independent verification, such as the TDSE simulations employed here.

C. Angle-resolved photoelectron spectra

Photoelectron yields into particular solid angles, measured relative to the probe polarization, offer an additional point of comparison between theory and experiment. Figure 4 shows delay-integrated photoelectron yields within selected angular wedges, here chosen at 0° , 60° , and 90° relative to the probe polarization axis, for both experiment and theory. The insets display the corresponding full photoelectron angular distribution (PAD) from which the angularly resolved spectra are extracted. For linearly polarized pump and probe pulses, the PAD is fully characterized by the anisotropy

parameters $\beta_2(E; \tau)$ and $\beta_4(E; \tau)$, as described in Eq. (2). The PAD reflects the interference between two-photon pathways populating photoelectron partial waves with different orbital angular momenta, as expected in the presence of multiple resonant multiphoton pathways: direct ionization to the continuum through the 11th harmonic followed by probe-photon emission, and excitation through the ninth harmonic followed by probe-photon absorption into the same spectral region containing the nf autoionizing series.

A notable feature of the angularly resolved spectra is the enhanced visibility of the np resonances, particularly in the theoretical results shown in Fig. 4(e). Evidence of both the $11p$ and $12p$ states can also be seen in the experimental spectrum at 0° , whereas the $12p$ resonances are not discernible in the corresponding angle-integrated spectrum shown in the left inset of Fig. 2(a). This behavior indicates that angular resolution can bring to the fore the spectral signature of resonances that are partially or completely invisible in the angle-integrated spectrum at the same energy resolution. The theoretical calculations further predict that the Fano asymmetry parameter q [52] associated with the np resonances changes from positive along the laser polarization axis to negative for photoelectron emission perpendicular to it. Although the effect is not resolved experimentally with the current energy resolution, such a variation suggests that the anisotropy parameters $\beta_k(E; \tau)$ can be used to isolate the temporal behavior of different resonance series.

D. Joint distributions of the anisotropy parameters

As discussed in Refs. [40,53], the requirement that the PAD remain positive for all emission angles imposes nontrivial constraints on the allowed values of the anisotropy parameters (β_2, β_4) . The corresponding physically accessible region is shown in Fig. 5(a), together with representative PAD profiles associated with different sectors of the parameter space. We populate this region with the joint distributions of (β_2, β_4) obtained from photoelectrons in the energy region between the spin-orbit-split thresholds, using Eqs. (4) and (5). The points originating from the spectrum near the 9–12 f resonance energies are highlighted by yellow ellipses. For both experiment and theory, the distributions are concentrated in comparatively small patches of the (β_2, β_4) allowed region. In the experiment [Figs. 5(c) and 5(f)], the resonant contributions cluster into two distinct regions close to the origin, corresponding to nearly isotropic emission, whereas the nonresonant background is scattered toward positive values of both β_2 and β_4 , within region I, which is associated with a prolate photoelectron angular distribution, preferentially aligned to the laser polarization. The theoretical distributions [Figs. 5(d) and 5(g)] similarly exhibit two distinct resonant clusters, although shifted toward larger positive values of β_2 , straddling region VI, which corresponds to a butterflylike angular profile. Convolution of the theoretical spectra with a Gaussian kernel, introduced to reproduce the finite experimental energy resolution, substantially reduces the spread in β_4 and causes the two theoretical clusters to merge into a single elongated structure, as shown in Figs. 5(e) and 5(h). Although quantitative differences remain between experiment and theory, it is noteworthy that all distributions remain confined within the physically

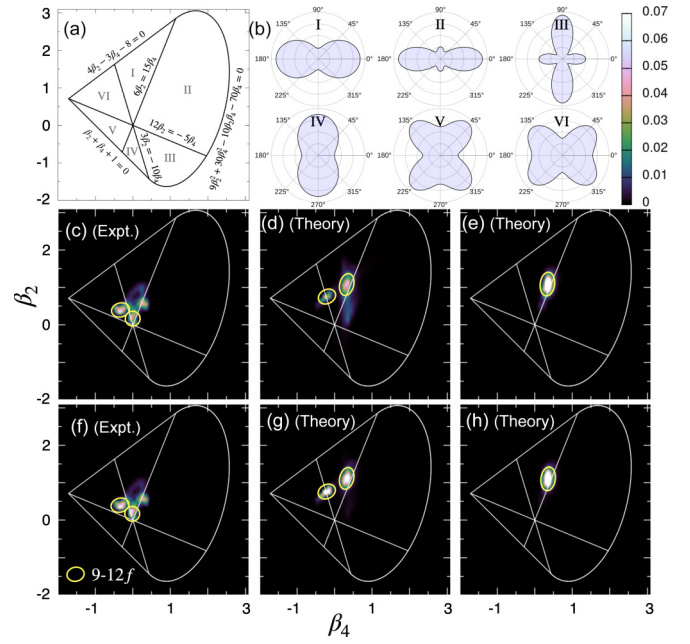


FIG. 5. Joint distributions of the anisotropy parameters (β_2, β_4) for photoelectrons with $E < 93$ meV and pump-probe delays in the range $[-10, 10]$ fs. Panel (a) shows the physically allowed region in (β_2, β_4) space, together with representative PAD distributions illustrated in panel (b) [40]. Panels (c)–(e) show unweighted distributions [Eq. (4)] obtained from experiment [panel (c)] and theory [panels (d) and (e)], where all events contribute equally. Panels (f)–(h) show the corresponding intensity-weighted distributions [Eq. (5)]. No energy convolution is applied in panels (d) and (g), whereas panels (e) and (h) are obtained by convolving the spectra with $\sigma = 3.0$ meV to reproduce the experimental resolution. The yellow contours highlight the region populated by the 9–12 f resonances.

allowed domain for two-photon ionization processes, despite the presence of the higher-order effects discussed in Sec. IV B.

E. Fourier analysis of the delay-dependent observables

To investigate the frequency content of the angular distributions, we Fourier transform the delay-dependent observables $\sigma(E, \tau)$, $\beta_2(E, \tau)$, and $\beta_4(E, \tau)$ with respect to the pump-probe delay τ . Figure 6 shows the corresponding Fourier amplitudes and phases in the vicinity of the ω and 2ω frequencies, for both experiment and theory. The ω beating amplitude of the total photoelectron yield σ exhibits a similar peak structure in experiment and theory, with pronounced peaks at the energies of the nf resonances, although broadened in the experiment. The experimental 2ω beating amplitude seems to enhance the np resonances, but the consistency of these data and their correspondence with theory is less clear. The $\beta_2(2\omega)$ beating amplitude is distinctly sensitive to the np resonances, which appear as pronounced peaks, whereas the nf states appear as window resonances. In this case, the experiment exhibits consistent strong peaks at the energies of the $11p$, $12p$, and $13p$ resonances, further confirming that angular resolution gives access to states not easily identifiable in the total photoelectron signal. In both theory and experiment, the np resonances have strongly asymmetric

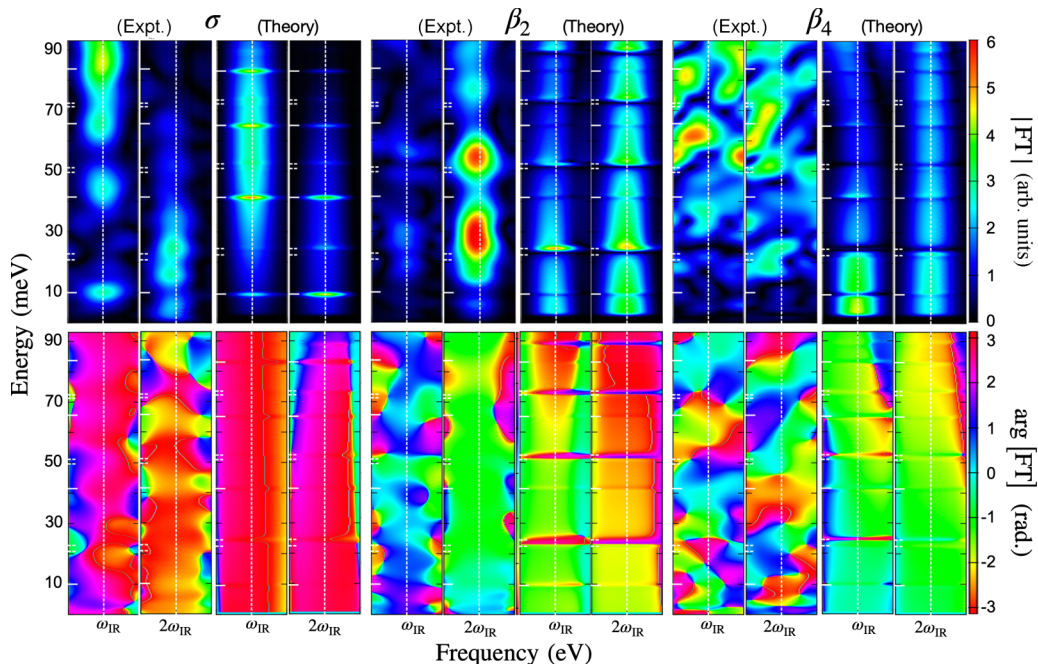


FIG. 6. Fourier amplitudes ($|FT|$) and phases ($\arg[FT]$) of the angle-integrated photoelectron yield σ and of the anisotropy parameters β_2 and β_4 , obtained from the delay-dependent observables over the spectral range $E < 93$ meV (measured from the $^2P_{3/2}^o$ threshold) and pump-probe delays $|\tau| < 10$ fs. For each observable, the left and right subpanels correspond to experiment and theory, respectively, where the latter includes an energy convolution with a Gaussian of width $\sigma = 0.5$ meV. Dashed vertical lines indicate the ω_{IR} and $2\omega_{IR}$ components within an interval of 0.8 eV, while white horizontal markers show the energies of the 9–12 f (solid) and 11–13 p (dashed) resonances. The $|FT|$ panels are independently rescaled to share a common color scale. The phase maps are shown in radians, using a cyclic color scale that preserves continuity at $\arg[FT] = \pm\pi$.

profiles. The finer energy resolution of the theoretical calculations reveals that this asymmetry arises because the $np_{3/2}$ series gives rise to local minima in β_2 , whereas the $np_{1/2}$ series produces local maxima. The experimental β_4 spectrum does not have a sufficient signal-to-noise ratio to provide a reliable measurement of this parameter at either ω or 2ω . Both its amplitude and phase are dominated by fluctuations with no evident counterpart in theory. This suggests that, within the present experimental conditions, β_4 is less informative than σ and β_2 .

The Fourier phase is a useful index of the robustness of each observable. The experimental phase of $\sigma(\omega)$ remains comparatively stable across the energy interval and is in broad agreement with theory. In the case of β_2 , the phase of the 2ω beating is once again the most indicative, undergoing an overall positive excursion across the energy interval in both theory and, more weakly, in the experiment. The present scheme is thus a significant step toward a full energy- and angle-resolved interferometric measurement in this challenging energy region. As the line outs for the 9 f and 10 f AIS in Fig. 2 suggest, there is some similarity between the relative phase of the ω and 2ω oscillations at some negative delays. However, a definitive comparison is not possible with the current experimental data, since the phase of the two beatings drifts with the pump-probe delay. These results suggest that the measurement of angularly resolved photoemission delays in such an extremely narrow energy region featuring multiple resonances is within reach, although the current data do not yet allow their quantitative extraction.

V. CONCLUSIONS AND PERSPECTIVES

We have combined an energy- and angle-resolved three-pulse variant of the rainbow-RABBITT technique, in which one interferometric arm proceeds resonantly through bound intermediate states, as in underthreshold RABBITT, with *ab initio* TDSE simulations, to perform a systematic study of the autoionizing series located between the two spin-orbit-split ionization thresholds of Ar. Both the ω and 2ω beating amplitudes and phases are found to depend on the principal quantum number n of the Rydberg-series members, an evolution that lowest-order perturbation theory cannot reproduce and that we trace back to higher-order probe-photon processes. The angle-resolved analysis yields the anisotropy parameters β_2 and β_4 , which reveal the signatures of the weaker np autoionizing series that are obscured in the angle-integrated analysis. In addition, we find that the anisotropy parameters of photoemission from these autoionizing series occupy a small, localized region within the (β_2, β_4) space allowed for two-photon transitions. These results illustrate the power of attosecond electron interferometry in deducing the detailed electronic structure and properties of overlapping series.

The extension of this approach to molecules will allow a differential analysis of the complex dynamics associated with metastable states that exhibit competing autoionization and dissociation channels. Such an extension will have to confront several challenges: The rotational averaging of the laboratory-frame photoelectron angular distributions, which

dilutes the anisotropy information unless it is circumvented by impulsive alignment or by recoil-frame coincidence detection; the increased spectral congestion of overlapping vibronic resonance series; and the fast dissociation of many molecular metastable states, which redistributes the oscillator strength among nuclear channels. The series-separating power of the angle-resolved observables demonstrated here is, however, may be precisely the kind of tool needed to disentangle such congested spectra.

ACKNOWLEDGMENTS

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DATA AVAILABILITY

There are no publicly available research data or software supporting this manuscript. Requests for further information or data should be sent to the authors.

APPENDIX A: RECOUPLING OF THE CLOSE-COUPPLING BASIS

The nonrelativistic close-coupling states are built by coupling the ionic states $|\Phi_a\rangle$ to one-electron spin-orbitals $|^2\phi_{\nu\ell m\sigma}\rangle$, where ν is the radial index introduced in Sec. III. The close-coupling states computed in the electrostatic approximation are recoupled to well-defined total angular momenta J , J_a , and j , associated with the neutral system, the residual ion, and the photoelectron, respectively,

$$|\psi_{\alpha\nu}^\Gamma\rangle = \sum_{S\Sigma LM} \Pi_{J_a j L S} C_{LM, S\Sigma}^{JM_j} \begin{Bmatrix} L & J & S \\ \ell & j & \frac{1}{2} \\ L_a & J_a & S_a \end{Bmatrix} \times \sum_{M_a m \Sigma_a \sigma} C_{L_a M_a, \ell m}^{LM} C_{S_a \Sigma_a, \frac{1}{2} \sigma}^{S\Sigma} |\Phi_a\rangle \wedge |^2\phi_{\nu\ell m\sigma}\rangle, \quad (\text{A1})$$

where $\Pi_{ab\dots} = \sqrt{(2a+1)(2b+1)\dots}$, the C 's are Clebsch-Gordan coefficients, $\alpha = (a, J_a, \ell, j)$ is the collective index identifying the ionization channel, i.e., the state a of the parent ion, its total angular momentum J_a , as well as the orbital angular momentum ℓ and total angular momentum j of the photoelectron, and $\Gamma = (J, M_j, \pi)$ identifies the global symmetry of the neutral system, with π the total parity. The symbol $\wedge$ indicates the antisymmetrized tensor product, and the quantity in curly brackets is a 9-j symbol [54].

APPENDIX B: NUMERICAL DETAILS OF THE TIME PROPAGATION

The reduced radial parts of the one-electron spin-orbitals that build the partial-wave channels consist of B -splines [55,56] of order 7, defined in a quantization box of $R_{\text{BOX}} = 500$ a.u., with an initial node spacing of $\Delta r = 0.25$ a.u. near the origin that gradually increases up to an asymptotic value of $\Delta r = 0.4$ a.u.

The TDSE,

$$i\partial_t |\Psi(t)\rangle = [\hat{H}_0 + \hat{H}'(t) + \hat{V}_{\text{CAP}}] |\Psi(t)\rangle, \quad (\text{B1})$$

is integrated in the configuration space spanned by the $|\psi_{\alpha\nu}^\Gamma\rangle$ basis functions, using a second-order split-exponential propagator,

$$|\Psi(t+dt)\rangle = \hat{U}(t+dt, t) |\Psi(t)\rangle, \quad (\text{B2})$$

$$\hat{U}(t+dt, t) = e^{-i\hat{V}_{\text{CAP}} dt} e^{-i\hat{H}_0 \frac{dt}{2}} e^{-i\alpha\vec{A}(t+\frac{dt}{2})\cdot\vec{P} dt} e^{-i\hat{H}_0 \frac{dt}{2}}, \quad (\text{B3})$$

where $\hat{H}_0$ is the field-free Hamiltonian, $\hat{H}'(t) = \alpha\vec{A}(t) \cdot \hat{\vec{P}}$ is the laser-matter interaction in the dipole approximation and velocity gauge, α is the fine-structure constant, $\vec{A}(t)$ is the radiation vector potential, and $\hat{\vec{P}}$ is the total canonical electronic momentum. Atomic units are used throughout, unless otherwise stated. To prevent unphysical reflections at the quantization-box boundary, the Hamiltonian includes a CAP [57], defined as

$$V_{\text{CAP}} = -iB_{\text{CAP}} \sum_{i=1}^{N_e} \theta(r_i - R_{\text{CAP}})(r_i - R_{\text{CAP}})^2, \quad (\text{B4})$$

where B_{CAP} and R_{CAP} are the CAP strength and starting radius, respectively, while $\theta(x)$ is the Heaviside step function. In our simulations, the CAP support, $[R_{\text{CAP}}, R_{\text{BOX}}]$, extends over an interval of about 100 Bohr radii.

The size of R_{CAP} imposes an upper limit on the maximum photoelectron momentum (k_{max}) that can be represented in the time-dependent wave packet, $k_{\text{max}} \approx R_{\text{CAP}}/\Delta T$, where ΔT is the total simulation time. Conversely, the calculation of the photoelectron spectrum over a prescribed spectral interval imposes lower bounds on the value of R_{CAP} and, consequently, of R_{BOX} . For example, predicting the photoelectron spectrum up to 1 eV from a pump-probe scheme with $\Delta T > 100$ fs would require a quantization box as large as 1200 a.u., which would render the present simulations prohibitively expensive. To circumvent this limitation, we employ a partitioning procedure described in detail in Ref. [49], which we briefly summarize below. At regularly spaced times $\{t_k\}$, the wave function is split into an inner and an outer component,

$$|\psi_{\text{in}}(t_k)\rangle = (1 - \hat{M})|\psi(t_k)\rangle, \quad |\psi_{\text{out}}^{(k)}(t_k)\rangle = \hat{M}|\psi(t_k)\rangle, \quad (\text{B5})$$

where $\hat{M}$ is a mask operator defined as

$$\hat{M} = \sum_{i=1}^{N_e} \Phi\left(\frac{r_i - R_M}{\sigma_M}\right), \quad \Phi(x) = \frac{1}{2} + \frac{1}{2}\text{erf}\left(\frac{x}{\sqrt{2}}\right), \quad (\text{B6})$$

and $\Phi(x)$ is the normal cumulative distribution function [58]. The smooth transition between the inner and outer components is centered at a mask radius R_M , intermediate between R_{CAP} and the spatial extent of the ionic states, which is of the order of a few tens of Bohr radii. The inner component continues to be evolved with the time-step propagator (B3), whereas the outer component is propagated to the final time t_f in a single step,

$$|\psi_{\text{out}}^{(k)}(t_f)\rangle = e^{-i\hat{H}_0(t_f-t_k)} |\psi_{\text{out}}^{(k)}(t_k)\rangle. \quad (\text{B7})$$

Finally, the spectral amplitude in channel (Γ, α) is given by

$$\mathcal{A}_{\alpha E}^\Gamma = \langle \psi_{\alpha E}^{\Gamma-} | \psi_{\text{in}}(t) \rangle + \sum_k e^{-iE(t_f-t_k)} \langle \psi_{\alpha E}^{\Gamma-} | \psi_{\text{out}}^{(k)}(t_k) \rangle, \quad (\text{B8})$$

where $|\psi_{\alpha E}^{\Gamma-}\rangle$ are channel-resolved scattering states satisfying incoming boundary conditions. This approach accurately reconstructs the final amplitude regardless of the duration of the infrared pulse, even when the simulation is conducted in a comparatively small box, provided that (1) the times t_k are chosen such that $\int_{t_k}^{\infty} \vec{A}(t) dt = 0$; and (2) R_M is sufficiently large for the commutator $[\hat{H}_0, \vec{A}(t) \cdot \hat{P}]$ to be negligible compared to $\hat{H}_0$ when acting on the outer states. In the present case, we find this latter condition to be met with $I_{\text{ir}} < 10 \text{ TW/cm}^2$ and $R_M = 125 \text{ a.u.}$ The masking operator greatly relaxes the constraint on the position of the absorber, and hence on the box size. Indeed, $R_{\text{CAP}} \geq R_M + k_{\text{max}} \Delta T_M$, where ΔT_M is the maximum time interval between two consecutive time values in $\{t_k\}$. In other words, the quantization box does not need to accommodate the expansion of the full wave packet across the whole duration of the pump-probe experiment, but only across a time interval commensurate with half a period of the IR probe, which is drastically shorter. Summarizing, the characteristic radii of the simulation are ordered as r_{ion} (few tens of a.u.) $< R_M$ (125 a.u.) $< R_{\text{CAP}}$ ($\simeq 400 \text{ a.u.}$) $< R_{\text{BOX}}$ (500 a.u.).

APPENDIX C: TWO-PHOTON ASYMMETRY PARAMETERS

The coefficients $\alpha_k(E; \tau)$ that determine the asymmetry parameters through Eq. (3) are given by

$$\begin{aligned} \alpha_k(E; \tau) = & \sum_{jj'} \sum_{JJ'} \sum_{\ell\ell'} \frac{\Pi_{jj'JJ'\ell\ell'}}{\sqrt{4\pi}} C_{\ell'0,\ell 0}^{k0} C_{J'0,J0}^{k0} \\ & \times (-1)^{1+\ell'+2J_a} \begin{Bmatrix} j' & k & j \\ J & J_a & J' \end{Bmatrix} \begin{Bmatrix} j' & k & j \\ \ell & \frac{1}{2} & \ell' \end{Bmatrix} \\ & \times i^{\ell'-\ell} e^{i(\sigma_\ell(E-E_a)-\sigma_{\ell'}(E-E_a))} \\ & \times \langle \Psi_{[(\ell, \frac{1}{2}), j, J_a], E}^- | \Psi(t_f; \tau) \rangle \\ & \times \langle \Psi(t_f; \tau) | \Psi_{[(\ell', \frac{1}{2}), j', J_a], E}^- \rangle, \end{aligned} \quad (\text{C1})$$

where $\Pi_{ab\dots} = \sqrt{(2a+1)(2b+1)\dots}$, σ_ℓ is the Coulomb phase shift, $|\Psi(t_f; \tau)\rangle$ is the total wave function from a simulation with time delay τ , evaluated at a time t_f after the end of the external pulses, and the $|\Psi_{\alpha E}^- \rangle$ are channel-resolved scattering states satisfying incoming boundary conditions.

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