

Multiphoton ionization with three-dimensional light fields

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We employ, for the first time, bichromatic three-dimensional (3D) polarization-shaped ultrashort laser fields in atomic multiphoton ionization to create previously inaccessible free-electron angular momentum wave packets. The 3D fields are created by the noncollinear superposition of two polarization-shaped pulses of different colors from a supercontinuum polarization pulse shaper and provide electric-field components along all spatial directions. The resulting photoelectron momentum distributions, recorded via velocity map imaging, demonstrate full 3D quantum control of electronic superposition states extending beyond the constraints of planar polarization fields by unlocking all dipole selection rules $\Delta m = 0, \pm 1$. As an application, 3D pump-probe fields are used to map spin-orbit dynamics of the potassium *3d* fine structure doublet. Our shaper-based approach establishes a route to fully controllable 3D light fields for chiral-sensitive light-matter interactions and ultrafast spectroscopy.

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I. INTRODUCTION

The recognition of light as a purely transverse wave, first established by Fresnel through his studies of polarization and soon after confirmed by Maxwell's electromagnetic theory, forms a cornerstone of modern optics. Today, light fields can be structured almost at will, enabling diverse applications across optical technologies, from superresolution microscopy and optical tweezers to materials processing, as well as in quantum technologies for metrology, information processing, and the coherent control of quantum phenomena [1–4] (see Ref. [5] for a review).

The generation of structured light generally involves either tailoring its spatial properties, including the generation of optical vortex beams [6,7], or controlling the spectrotemporal characteristics of ultrashort laser pulses [8–10]. Ultrafast pulse shaping has advanced substantially since the advent of scalar pulse shaping [11], which allowed temporal control of the amplitude and spectral phase of linearly polarized pulses. Subsequent developments introduced polarization shaping [12,13], vector field synthesis [14], and supercontinuum pulse shaping [15], permitting subcycle control of the vectorial electric field [16]. A common feature of these techniques is that the resulting light fields are planar, with the local polarization vector confined to the transverse plane normal to the propagation direction.

In contrast, three-dimensional (3D) light fields, featuring an additional longitudinal electric-field component, are generated, for example, by tight focusing [17,18] or the

noncollinear superposition of laser beams. The latter approach is widely used in nonlinear optics, including ultrashort pulse characterization [9], coherent anti-Stokes Raman scattering [19], and noncollinear optical parametric amplification [20]. In the extreme nonlinear optical regime, Hickstein *et al.* demonstrated control over the polarization state of XUV pulses by driving the high-harmonic generation (HHG) with two noncollinearly overlapping counterrotating circularly polarized (CRCP) infrared pulses [21]. Recently, 3D fields generated by the noncollinear superposition of two pulsed beams with variable polarization and spectrum were proposed as efficient enantiosensitive probes [22,23] of chiral light-matter interactions [24–27]. Theoretical work has shown that such light fields are locally chiral, offering enhanced sensitivity in interactions with chiral matter, such as chiral molecules. The exceptionally strong chiroptical responses predicted for these 3D fields have attracted significant interest, positioning them as promising candidates for chiral recognition applications [28,29]. It has also been proposed that locally chiral light fields could imprint chirality on atomic systems by exciting unusual electronic superposition states [30,31] and create chiral photoelectron wave packets [32,33].

Here, we report the first experimental realization of atomic multiphoton ionization (MPI) with polarization-shaped bichromatic 3D femtosecond (fs) laser fields. While planar fields [two-dimensional (2D)] enable excitation along multiphoton pathways composed of either $\sigma^\pm$ or π transitions, 3D fields unlock all dipole selection rules $\Delta m = 0, \pm 1$ simultaneously, owing to their three independent field components. Thus, 3D fields open up excitation pathways to target channels that are inaccessible to planar laser fields. Shaping of the 3D field allows us to control the quantum interference of these pathways, leading to the generation of photoelectron superposition states spanning all magnetic quantum numbers. Using the 3D fields, we create free-electron angular momentum superposition states via atomic resonance-enhanced multiphoton ionization (REMPI), yielding photoelectron wave packets that have not been observed previously.

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In our experiment, the 3D fields are generated by the noncollinear superposition of two polarization-shaped fs-laser pulses of different colors, provided by a supercontinuum polarization-pulse shaper [15,34]. The resulting photoelectron wave packets, created through the interaction of the 3D fields with potassium atoms, are detected with energy and angular resolution using velocity-map imaging (VMI) [35]. Analysis of the measured photoelectron momentum distributions (PMDs), by comparison with simulations, confirms that they arise from a coherent superposition of partial waves encompassing all magnetic quantum numbers. Furthermore, we demonstrate the suitability of the noncollinear ionization scheme for time-resolved pump-probe studies by imaging ultrafast spin-orbit wave packet (SOWP) dynamics in the potassium 3*d* fine structure doublet. The observed PMDs highlight the potential of the 3D fields for time-resolved investigations of ultrafast dynamics with unprecedented directional sensitivity. Specifically, our shaper-based approach provides a direct route to the generation of fully controlled 3D fields and paves the way for experimental realization of the chiroptical schemes proposed by Smirnova and co-workers [22], including the creation of chiral electron wave packets in atoms [31] and molecules [36], and the efficient enantiosensitive discrimination of chiral molecules [26,37] using locally chiral light fields.

II. PHYSICAL SYSTEM AND EXPERIMENTAL SETUP

We consider the interaction of a potassium atom with a bichromatic 3D laser field. The 3D field is generated by the noncollinear superposition of two pulses of different colors, referred to as red and blue pulses. The pulses propagate in the *y*-*z* plane along the wave vectors $\mathbf{k}_r$ and $\mathbf{k}_b$, oriented at $\pm 22.5^\circ$ relative to the *z* axis. At the intersection region, the resulting temporal 3D field is the sum of the individual fields $\mathbf{E}_{k_r}(t)$ and $\mathbf{E}_{k_b}(t)$ as

$$\mathbf{E}(t) = \mathbf{E}_{k_r}(t) + \mathbf{E}_{k_b}(t), \quad (1)$$

which oscillates locally in all three spatial dimensions.

The central wavelengths of the red and blue pulses are $\lambda_r = 929$ nm and $\lambda_b = 720$ nm, respectively. The resulting field ionizes the potassium atom through multiple ionization pathways, as illustrated in Fig. 1(a). Individually, the red and blue pulses induce four- and three-photon ionization. The corresponding single-color photoelectron wave packets are centered at $\varepsilon_r = 1.0$ eV and $\varepsilon_b = 0.8$ eV, defining a broad energy window for background-free detection [34,38] of the two-color signals. Here, “background-free” refers to the energetic separation of the two-color signal from the single-color signals. Photoelectron wave packets created by the interplay of the two pulses are released along different three-photon two-color pathways [see right-hand side of Fig. 1(a)]. The central wavelength of the red pulse is chosen such that the pathway involving two red photons is resonantly enhanced by the potassium 3*d* state, while the central wavelength of the blue pulse is chosen such that the two-color signal from the (2 + 1) REMPI pathways is observed close to the ionization threshold. The corresponding photoelectron wave packet from (2 + 1) REMPI is centered at $\varepsilon_{3D} = 0.05$ eV, well separated from the two single-color signals.

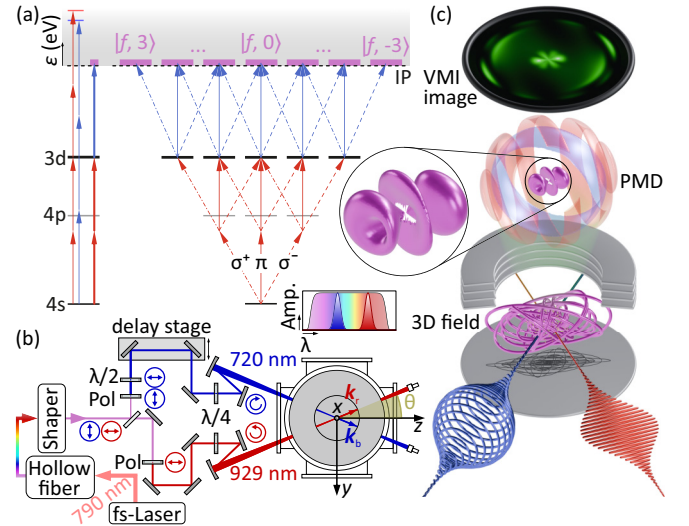


FIG. 1. (a) Simplified (left) and detailed (right) bichromatic excitation scheme for the potassium atom interacting with a 3D laser field. (b) Schematic of the experimental setup including the pulse shaper, the noncollinear interferometer, and the VMI spectrometer. (c) Illustration of the experiment.

The 3D field is described in terms of the spherical basis set consisting of two CRCP transverse components in the *x*-*y* plane and one linearly polarized longitudinal component along the *z* axis. Within the dipole approximation, the transverse components drive $\sigma^\pm$ transitions, while the longitudinal component drives π transitions. Figure 1(a) (right) illustrates the manifold of ionization pathways for the (2 + 1) REMPI process, including all dipole-allowed transitions between the magnetic sublevels governed by the selection rules $\Delta m = 0, \pm 1$. Unlike planar fields, the 3D configuration provides access to all seven angular momentum continua $|f, m\rangle$ ($m = -3, \dots, +3$), where *f* refers to the spectroscopic notation of the orbital angular momentum $l = 3$. According to Fano’s propensity rule [39], the total photoelectron wave function for *N*-photon ionization from the $l = 0$ ground state is expressed as a superposition of angular momentum partial waves:

$$\psi^{(N)}(\varepsilon, \mathbf{\Omega}) = \sum_{m=-N}^N a_{N,m}(\varepsilon) Y_{N,m}(\mathbf{\Omega}). \quad (2)$$

Here, the amplitudes $a_{N,m}(\varepsilon)$ define the kinetic energy spectrum of the partial waves and their angular part is given by the spherical harmonics $Y_{N,m}(\mathbf{\Omega})$.

In our experiment, 20 fs, 790 nm pulses with energies of 0.9 mJ from an amplified fs-laser system are coupled into a neon-filled hollow-core fiber to generate a white-light supercontinuum (WLS), as illustrated in Fig. 1(b). Using a home-built polarization pulse shaper [15,34], the WLS is compressed and a red and a blue spectral band, orthogonal linearly polarized and centered at $\lambda_r = 929$ nm and $\lambda_b = 720$ nm, respectively, is extracted from the WLS by spectral amplitude modulation [15,40]. A noncollinear interferometer separates the red and the blue pulse via orthogonal polarizers. Additional $\lambda/2$ and $\lambda/4$ wave plates in each arm enable the generation of bichromatic pulses with

parallel linear (PLP), corotating circular (COCP), CRCP, red-circular/blue-linear (RCBL), or red-linear/blue-circular (RLBC) polarization. Two spherical mirrors ($f = 250$ mm) focus the beams into the interaction region of a VMI spectrometer, where they intersect at an angle of $2\theta = 45^\circ$. The temporal overlap between the two pulses is adjusted by delaying one arm of the interferometer with a precision translation stage (PHYSIK INSTRUMENTE M-511.HD1) and is determined *in situ* using a two-step procedure. First, a coarse estimate of the temporal overlap is obtained by spectral interferometry using the white-light pulse in both arms. For this purpose, a thin fused-silica plate oriented along the z direction is inserted into the interaction region. A spectrometer is used to record the spectral interference fringes of the reflected and transmitted beams, thus providing an estimate of the stage position at which the pulses overlap temporally. In a second step, the temporal overlap is refined for the two-color field by using a β -barium borate crystal (29.2° , $5\ \mu\text{m}$) and maximizing the sum-frequency generation yield. Initial pulse compression of the white-light pulses is performed using our established routine based on the evolutionary optimization of second-harmonic generation in the said crystal [15]. In addition, the individual second-harmonic signals generated in the interaction region are used to fine-tune the temporal compression of both laser pulses using the pulse shaper. By this means, we ensure transform-limited pulses in the interaction region of the VMI. The complete photoelectron imaging setup is shown in Fig. 1(c). An einzel lens in the VMI setup enables operation in either momentum- or spatial-imaging mode. Further details of the setup are provided in Ref. [40].

III. RESULTS

Figure 2 shows representative results. Panel (a) shows measured power spectral densities of the red and blue pulses. The corresponding transform-limited pulse durations are about 30 fs, respectively. The peak laser intensity of the resulting 3D field is about $10^{12}\ \text{W}/\text{cm}^2$. The resulting Keldysh parameter is $\gamma \approx 6$, confirming that the experiment was performed in the MPI regime [41]. Panel (b) displays spatial images of the individual beams and their intersection. The $(2 + 1)$ REMPI signal appears as a bright spot at the beam intersection. By shifting the pulses, we confirm the spatio-temporal overlap established using the procedure described in Sec. II. Specifically, the two-color signal disappears when the blue pulse is shifted to arrive slightly before the red pulse, as expected for a $(2 + 1)$ REMPI scheme. Panels (c) and (d) present the corresponding PMDs for the PLP and COCP polarization configurations, respectively. The observed f - and g -type wave packets created by the individual blue or red pulses agree with the expected three- and four-photon ionization pathways. Their (rotational) symmetry axes are aligned perpendicular (in the PLP case) and parallel (in the COCP case) to the respective propagation directions. By design, the single-color contributions are well separated from the two-color signal near the ionization threshold, enabling background-free detection of photoelectron wave packets. In the following, we focus on this region of interest (ROI), marked by the purple circle, and analyze the PMDs created by different 3D field configurations.

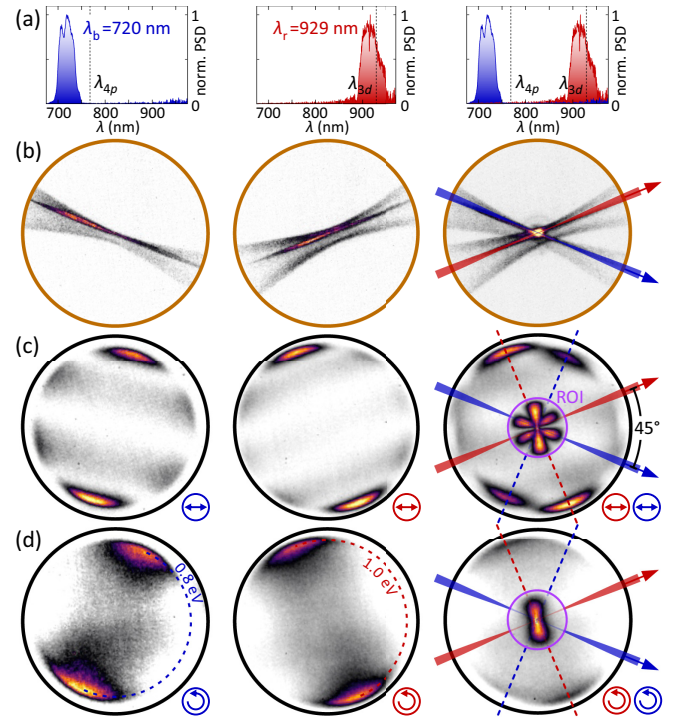


FIG. 2. (a) Measured optical spectra. (b) VMI images recorded in spatial imaging mode for the colors individually and combined. VMI images recorded in momentum imaging mode for the (c) PLP and (d) COCP configurations for blue pulse (left), red pulse (center), and both pulses combined (right). The two-color signal created by the 3D fields is indicated by purple circles marking the ROI.

Our key results are presented in Fig. 3. The top row shows the 3D laser fields (purple) along with their Cartesian projections (gray) with red and blue arrows indicating the corresponding propagation directions. The second row shows the measured VMI images within the ROI, which are compared to simulated photoelectron projections (third row) and the corresponding 3D PMDs (fourth row) obtained from Eq. (2). A quantitative comparison is provided by the photoelectron angular distributions of the simulated (gray) and measured (purple) photoelectron projections depicted in the insets between the second and third rows. The general description of our simulation model is provided in Refs. [42–44]. The extension to the 3D scheme is detailed in the Appendix. The close agreement across all five configurations validates our model and provides the basis for a more detailed analysis. The bar plot insets next to the 3D PMDs display the m -partial wave amplitudes [cf. Eq. (2)] in the common reference frame defined by the z axis oriented along the bisector of the two propagation axes. The m decompositions demonstrate that all target states are accessed via $\sigma^\pm$ and π transitions. In the following, we examine the five polarization configurations column by column.

In the PLP configuration, the field oscillates within the y - z plane and is therefore equivalent to a collinear bichromatic field with tilted linear polarizations propagating along the x direction. Its projections along the x axis form a Lissajous-type curve. The PMD resembles a deformed $|f, 0\rangle$ -type wave

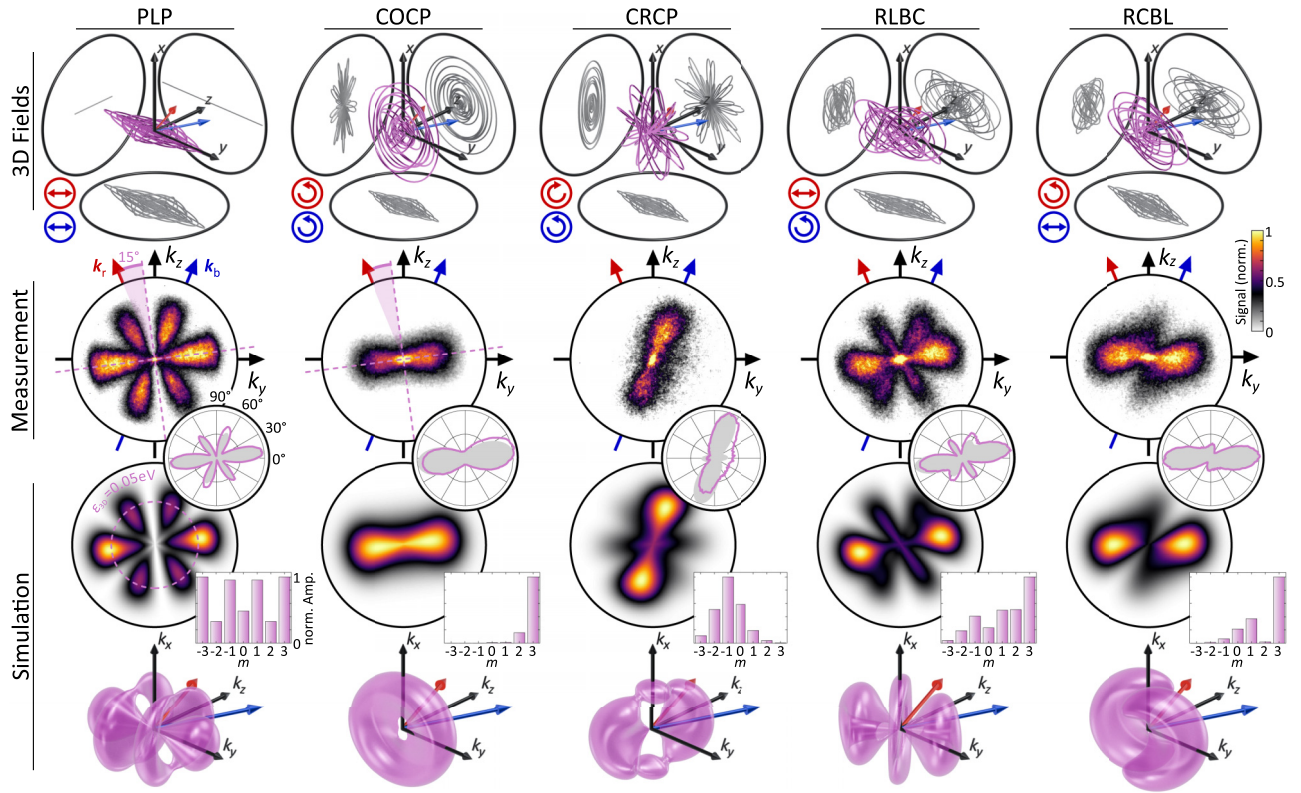


FIG. 3. First row: 3D fields for the PLP, COCP, CRCP, RLBC, and RCBL configurations. Second row: Measured VMI images within the ROI. Third and forth rows: Simulated 2D projections and 3D densities of the PMDs. The top insets show the photoelectron angular distributions of the measured (purple) and simulated (gray) PMDs for a quantitative comparison. The bottom insets show the decomposition of the wave packets into angular momentum partial waves.

packet rotated by approximately 15° toward the red propagation axis.

The PMD for the COCP configuration shows a predominantly $|f, 3\rangle$ -type wave packet and is aligned in the same direction. In addition to the prominent $m = 3$ component, it contains smaller adjacent m contributions. The toroidal photoelectron emission mirrors the structure of the 3D field: The field vector traces a circular trajectory around z , while gradually tilting around y , giving rise to the characteristic petaloid (y) and helical (z) projections.

Switching the handedness of the red pulse yields the CRCP pulse configuration (third column) where the characteristic projection exchange roles: Rather than rotating around the z axis, the field now circles predominantly around the y axis while tilting around the z axis. As a result, the photoelectron emission is directed mainly along z in the CRCP configuration. The m decomposition reveals a broader distribution of partial waves, with its maximum centered around $m = -1$.

For the discussion of the RLBC and RCBL configurations, we adopt a different reference frame aligned with the red pulse propagation direction. In our $(2 + 1)$ REMPI scheme, a single ionization pathway is strongly enhanced, allowing us to choose a suitable reference frame such that a single $|3d, m\rangle$ state is excited by the red pulse, either by two $\sigma^\pm$ or two π transitions. The noncollinear ionizing blue pulse drives one-photon ionization from the excited state to three different target continua $|f, m\rangle$, with $\Delta m = 0, \pm 1$. The bound-state excitations in the RLBC and RCBL

configurations are identical to the PLP and COCP cases, respectively: In the reference frame defined by the red pulse, the two-photon excitation populates selectively either the $|3d, 0\rangle$ (RLBC) or the $|3d, 2\rangle$ (RCBL) state. The pronounced differences in the PMD structures originate from the ionization step, where the noncollinear blue pulse drives transitions into a set of adjacent m continua with $m = -1, 0, 1$ (RLBC) and $m = 1, 2, 3$ (RCBL).

The previously unobserved PMD structures provide a glimpse into the capabilities of advanced quantum control unlocked by full vectorial 3D fields, which enables simultaneous access to all Δm selection rules. The resulting m distributions in the common reference frame reflect this capability through their richer and more intricate structure. Our results show that full experimental access to these unusually structured 3D PMDs will require the use of emerging 3D reconstruction approaches that combine VMI with high-resolution time-of-flight detection [45].

Finally, we apply our 3D noncollinear scheme in a pump-probe setting to demonstrate its capabilities for the imaging of ultrafast electron dynamics. As a specific example, we excite a coherent superposition of the $3d_{3/2}$ and $3d_{5/2}$ states, and map the resulting SOWP dynamics into the continuum. While SOWP dynamics in atomic fine structure doublets are well studied [38], the bichromatic 3D fields employed here unlock additional ionization pathways and generate photoelectron wave packets that could not be observed so far. In our noncollinear $(2 + 1)$ REMPI scheme, the red pulse launches the

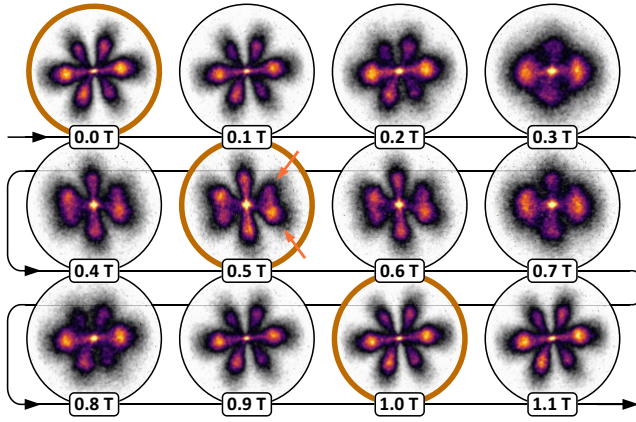


FIG. 4. Time series of VMI images from the noncollinear bichromatic pump-probe study of the SOWP in the $3d$ fine structure doublet mapped into the continuum by the time-delayed blue pulse in the PLP configuration.

SOWP, while the delayed blue pulse probes its time evolution. The SOWP period is determined by the $3d$ fine structure splitting of $\Delta\epsilon_{3d} \approx 0.2862$ meV, yielding $T = \frac{h}{\Delta\epsilon_{3d}} \approx 14.45$ ps. By varying the time delay in increments of $0.1 T$, we recorded ten PMDs per SOWP period.

Figure 4 shows the PLP results. At the beginning of each period ($0.0 T$), the PMD corresponds to the rotated $|f, 0\rangle$ -type wave packet discussed above (cf. Fig. 3). As the delay increases, the photoelectron distribution changes, mapping the precession of the coupled electron spin and orbital alignment about the total angular momentum [46,47]. After half a period ($0.5 T$), the PMD has evolved into the characteristic shape of a rotated $|f, \pm 1\rangle$ -type photoelectron wave packet, indicating the transition $|3d, 0\rangle \rightarrow |3d, \pm 1\rangle$ in the bound system. This change in the angular part of the wavefunction is a hallmark for SOWP dynamics and reflects the accompanying flip of the electron spin induced by the spin-orbit interaction [47]. The subsequent return to the original $|f, 0\rangle$ -type distribution at $1.0 T$ completes the spin-orbit cycle.

Notably, the PMDs exhibit a pronounced asymmetry in their lobes (orange arrows), reflecting directional sensitivity enabled by the noncollinear scheme. By incorporating dynamics as an additional degree of freedom, our 3D noncollinear scheme enables the creation of more intricate PMDs and establishes the potential of 3D vectorial laser field control for time-resolved studies.

IV. CONCLUSION

In conclusion, we have experimentally demonstrated a versatile noncollinear bichromatic framework that enables quantum control of MPI through full vectorial control of 3D light fields. By noncollinearly superimposing two polarization-shaped pulses, we created 3D fields with both transverse and longitudinal components, which unlock all dipole selection rules in the $(2+1)$ REMPI scheme. Our results reveal previously unobserved PMDs, which arise from the coherent superposition of photoelectron angular momentum partial waves encompassing all magnetic quantum numbers—MPI channels that are fundamentally inaccessible

to planar laser fields. The conceptual clarity of our experimental approach, combined with reference measurements using single-color ionization and fully differential energy- and angle-resolved photoelectron detection, allowed us to unambiguously identify the contributing ionization pathways. The excellent agreement between experimental data and simulations provides evidence for quantum control of MPI using 3D light fields. We further extended the approach to a non-collinear pump-probe experiment, mapping the evolution of an ultrafast SOWP in the potassium $3d$ fine structure doublet, highlighting the potential of the 3D fields for time-resolved investigations of ultrafast dynamics with unprecedented directional sensitivity. While 3D light fields have been the subject of extensive theoretical investigations, their experimental realization has been lacking. This work provides the first experimental demonstration of MPI driven by fully controllable 3D light fields.

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DATA AVAILABILITY

The data that support the findings of this article are not publicly available upon publication because it is not technically feasible and/or the cost of preparing, depositing, and hosting the data would be prohibitive within the terms of this research project. The data are available from the authors upon reasonable request.

APPENDIX: NUMERICAL MODEL

In this Appendix, we introduce the simulation model for atomic MPI dynamics driven by a bichromatic 3D laser field. We compute the bound-state dynamics by solving the time-dependent Schrödinger equation (TDSE) and evaluate the photoelectron amplitudes using time-dependent perturbation theory. A detailed description of the simulation model is given in Refs. [42,44] and in the review [43]. The electric fields of the red (r) and blue (b) pulse are described by the negative frequency analytical signals as

$$E_p^-(t) = [\mathcal{E}_{+1,p}^-(t)\mathbf{e}_{+1} + \mathcal{E}_{-1,p}^-(t)\mathbf{e}_{-1}]e^{-i\omega_p t}, \quad (\text{A1})$$

with $p = r, b$. The total 3D field is described by the superposition of the red and the blue pulse, each rotated around the x axis by $\pm\theta$, respectively:

$$\begin{aligned} E_\theta^-(t) &= \mathcal{R}_x(\theta) \cdot E_r^-(t) + \mathcal{R}_x(-\theta) \cdot E_b^-(t) \\ &= E_{+1}^-(t, \theta)\mathbf{e}_{+1} + E_0^-(t, \theta)\mathbf{e}_0 + E_{-1}^-(t, \theta)\mathbf{e}_{-1}. \end{aligned} \quad (\text{A2})$$

Here, $\mathcal{R}_x(\theta)$ denotes the rotation matrix and $E_\pm^-(t, \theta)$ represent the circularly polarized transversal components of the local bichromatic 3D field, which drive atomic $\Delta m = \pm 1$ transitions, whereas $E_0^-(t, \theta)$ is the linearly polarized

longitudinal field component, which unlocks additional $\Delta m = 0$ transitions—inaccessible with planar fields.

The (2 + 1) REMPI of potassium atoms by the 3D field is decomposed into the two-photon excitation of the 3d states and the one-photon ionization from the 3d manifold into an f -type continuum. The neutral excitation dynamics are obtained by solving the TDSE for the nine-state atomic system, as depicted in Fig. 1(a), comprising the ground state 4s, the three 4p states ($m = 0, \pm 1$), and the five 3d states ($m = 0, \pm 1, \pm 2$), within the dipole approximation. In the interaction picture and rotating wave approximation, the TDSE reads

$$\frac{d}{dt} \begin{pmatrix} c_1 \\ c_2 \\ \vdots \\ c_9 \end{pmatrix} = i \begin{pmatrix} 0 & \Omega_{21}^*(t) & \dots & \Omega_{91}^*(t) \\ \Omega_{21}(t) & 0 & & \Omega_{92}^*(t) \\ \vdots & & \ddots & \vdots \\ \Omega_{91}(t) & \Omega_{92}(t) & \dots & 0 \end{pmatrix} \begin{pmatrix} c_1 \\ c_2 \\ \vdots \\ c_9 \end{pmatrix},$$

with the Rabi frequencies

$$\Omega_{n'n}(t) = \frac{1}{\hbar} \langle n' | \boldsymbol{\mu} \cdot \mathbf{E}_\theta^-(t) | n \rangle e^{i\omega_{n'n}t}, \quad (\text{A3})$$

where $\boldsymbol{\mu}$ is the dipole operator and $\omega_{n'n} = \omega_{n'} - \omega_n$ are the transition frequencies. For planar fields, the Rabi frequency is only nonzero for transitions with $\Delta m = m' - m = \pm 1$. In contrast, the 3D field enables additional $\Delta m = 0$ transitions. The TDSE is solved numerically on a discrete temporal grid using the short-time propagator technique [4,48]. The solution yields the amplitudes $c_n(t)$ of the 3d states ($n = 5, \dots, 9$), from which the continuum amplitudes $a_{f,m}(\varepsilon)$ [cf. Eq. (2)] are calculated as a function of the photoelectron kinetic energy via first-order time-dependent perturbation theory:

$$a_{f,m}(\varepsilon) \propto \sum_{n=5}^9 \int_{-\infty}^{\infty} c_n(t) \langle f, m | \boldsymbol{\mu} \cdot \mathbf{E}_\theta^-(t) | n \rangle e^{i\frac{1}{\hbar}(\varepsilon - \varepsilon_0)t} dt.$$

The central photoelectron energy is $\varepsilon_0 = \hbar\omega_{3d} - \varepsilon_{\text{IP}}$, where $\varepsilon_{\text{IP}} = 4.34$ eV denotes the potassium ionization potential. With all three Δm selection rules available, all seven f continua ($m = 0, \pm 1, \pm 2, \pm 3$) are accessible by the 3D laser field (compare bar plots in Fig. 3). The total wave function describing the 3D PMD is given by Eq. (2). For the simulations presented in Fig. 3, Gaussian-shaped pulses with the same amplitude and a pulse duration of 25 fs are used.

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- [1] S. A. Rice and M. Zhao, *Optical Control of Molecular Dynamics* (Wiley, New York, 2000).
 - [2] M. Shapiro and P. Brumer, *Principles of the Quantum Control of Molecular Processes* (John Wiley and Sons, Hoboken, NJ, 2003), Vol. 1.
 - [3] D. Goswami, Optical pulse shaping approaches to coherent control, *Phys. Rep.* **374**, 385 (2003).
 - [4] D. Tannor, *Introduction to Quantum Mechanics: A Time-Dependent Perspective* (University Science Books, Sausalito, CA, 2007).
 - [5] H. Rubinsztein-Dunlop, A. Forbes, M. V. Berry, M. R. Dennis, D. L. Andrews, M. Mansuripur, C. Denz, C. Alpmann, P. Banzer, and T. Bauer, Roadmap on structured light, *J. Opt.* **19**, 013001 (2017).
 - [6] Y. Shen, X. Wang, Z. Xie, C. Min, X. Fu, Q. Liu, M. Gong, and X. Yuan, Optical vortices 30 years on: OAM manipulation from topological charge to multiple singularities, *Light Sci. Appl.* **8**, 90 (2019).
 - [7] A. Forbes, M. de Oliveira, and M. R. Dennis, Structured light, *Nat. Photon.* **15**, 253 (2021).
 - [8] A. M. Weiner, Ultrafast optical pulse shaping: A tutorial review, *Opt. Commun.* **284**, 3669 (2011).
 - [9] A. Monmayrant, S. Weber, and B. Chatel, A newcomer's guide to ultrashort pulse shaping and characterization, *J. Phys. B* **43**, 103001 (2010).
 - [10] J. Köhler, M. Wollenhaupt, T. Bayer, C. Sarpe, and T. Baumert, Zeptosecond precision pulse shaping, *Opt. Express* **19**, 11638 (2011).
 - [11] A. M. Weiner, Femtosecond pulse shaping using spatial light modulators, *Rev. Sci. Instrum.* **71**, 1929 (2000).
 - [12] T. Brixner, G. Krampert, T. Pfeifer, R. Selle, G. Gerber, M. Wollenhaupt, O. Graefe, C. Horn, D. Liese, and T. Baumert, Quantum control by ultrafast polarization shaping, *Phys. Rev. Lett.* **92**, 208301 (2004).
 - [13] N. Dudovich, D. Oron, and Y. Silberberg, Quantum control of the angular momentum distribution in multiphoton absorption processes, *Phys. Rev. Lett.* **92**, 103003 (2004).
 - [14] C. Manzoni, O. D. Mücke, G. Cirimi, S. Fang, J. Moses, S.-W. Huang, K.-H. Hong, G. Cerullo, and F. X. Kärtner, Coherent pulse synthesis: Towards sub-cycle optical waveforms, *Laser Photonics Rev.* **9**, 129 (2015).
 - [15] S. Kerbstadt, D. Timmer, L. Englert, T. Bayer, and M. Wollenhaupt, Ultrashort polarization-tailored bichromatic fields from a CEP-stable white light supercontinuum, *Opt. Express* **25**, 12518 (2017).
 - [16] M. Ivanov and E. Pisanty, High-harmonic generation: Taking control of polarization, *Nat. Photon.* **8**, 501 (2014).
 - [17] T. Bauer, P. Banzer, E. Karimi, S. Orlov, A. Rubano, L. Marrucci, E. Santamato, R. W. Boyd, and G. Leuchs, Observation of optical polarization Möbius strips, *Science* **347**, 964 (2015).
 - [18] D. Ayuso, A. F. Ordonez, M. Ivanov, and O. Smirnova, Ultrafast optical rotation in chiral molecules with ultrashort and tightly focused beams, *Optica* **8**, 1243 (2021).
 - [19] S. A. J. Druet and J.-P. E. Taran, CARS spectroscopy, *Prog. Quantum Electron.* **7**, 1 (1981).
 - [20] G. Cerullo, A. Baltuska, O. D. Mücke, and C. Vozzi, Few-optical-cycle light pulses with passive carrier-envelope phase stabilization, *Laser Photonics Rev.* **5**, 323 (2011).
 - [21] D. D. Hickstein, F. J. Dollar, P. Grychtol, J. L. Ellis, R. Knut, C. Hernandez-Garcia, D. Zusin, C. Gentry, J. M. Shaw, T. T. Fan, K. M. Dorney, A. Becker, A. Jaron-Becker, H. C. Kapteyn, M. M. Murnane, and C. G. Durfee, Non-collinear generation of angularly isolated circularly polarized high harmonics, *Nat. Photon.* **9**, 743 (2015).
 - [22] D. Ayuso, O. Neufeld, A. F. Ordonez, P. Decleva, G. Lerner, O. Cohen, M. Ivanov, and O. Smirnova, Synthetic chiral light for

- efficient control of chiral light-matter interaction, *Nat. Photon.* **13**, 866 (2019).
- [23] O. Neufeld, D. Ayuso, P. Decleva, M. Y. Ivanov, O. Smirnova, and O. Cohen, Ultrasensitive chiral spectroscopy by dynamical symmetry breaking in high harmonic generation, *Phys. Rev. X* **9**, 031002 (2019).
- [24] V. Wanie, E. Bloch, E. P. Månsson, L. Colaizzi, S. Ryabchuk, K. Saraswathula, A. F. Ordóñez, D. Ayuso, O. Smirnova, A. Trabattoni, V. Blanchet, N. Ben Amor, M.-C. Heitz, Y. Mairesse, B. Pons, and F. Calegari, Capturing electron-driven chiral dynamics in UV-excited molecules, *Nature (London)* **630**, 109 (2024).
- [25] C. Sparling and D. Townsend, Two decades of imaging photoelectron circular dichroism: From first principles to future perspectives, *Phys. Chem. Chem. Phys.* **27**, 2888 (2025).
- [26] D. Ayuso, A. F. Ordóñez, and O. Smirnova, Ultrafast chirality: The road to efficient chiral measurements, *Phys. Chem. Chem. Phys.* **24**, 26962 (2022).
- [27] C. Lux, M. Wollenhaupt, T. Bolze, Q. Liang, J. Köhler, C. Sarpe, and T. Baumert, Circular dichroism in the photoelectron angular distributions of camphor and fenchone from multiphoton ionization with femtosecond laser pulses, *Angew. Chem. Int. Ed.* **51**, 5001 (2012).
- [28] O. Neufeld, H. Hübener, A. Rubio, and U. De Giovannini, Strong chiral dichroism and enantiopurification in above-threshold ionization with locally chiral light, *Phys. Rev. Res.* **3**, L032006 (2021).
- [29] D. Habibović, K. R. Hamilton, O. Neufeld, and L. Rego, Emerging tailored light sources for studying chirality and symmetry, *Nat. Rev. Phys.* **6**, 663 (2024).
- [30] A. F. Ordóñez and O. Smirnova, Propensity rules in photoelectron circular dichroism in chiral molecules. I. Chiral hydrogen, *Phys. Rev. A* **99**, 043416 (2019).
- [31] N. Mayer, S. Patchkovskii, F. Morales, M. Ivanov, and O. Smirnova, Imprinting chirality on atoms using synthetic chiral light fields, *Phys. Rev. Lett.* **129**, 243201 (2022).
- [32] G. P. Katsoulis, Z. Dube, P. B. Corkum, A. Staudte, and A. Emmanouilidou, Momentum scalar triple product as a measure of chirality in electron ionization dynamics of strongly driven atoms, *Phys. Rev. A* **106**, 043109 (2022).
- [33] A. Geyer, J. Stindl, I. Dwojak, M. Hofmann, N. Anders, P. Roth, P. Daum, J. Kruse, S. Jacob, S. Gurevich, N. Wong, M. S. Schöffler, L. P. H. Schmidt, T. Jahnke, M. Kunitski, R. Dörner, and S. Eckart, Chiral electron momentum distribution upon strong-field ionization of atoms, *Phys. Rev. Res.* **7**, L032061 (2025).
- [34] D. Köhnke, K. Eickhoff, T. Bayer, and M. Wollenhaupt, Multichromatic supercontinuum polarization shaping applied to photoelectron holography, *New J. Phys.* **25**, 123025 (2023).
- [35] A. T. J. B. Eppink and D. H. Parker, Velocity map imaging of ions and electrons using electrostatic lenses: Application in photoelectron and photofragment ion imaging of molecular oxygen, *Rev. Sci. Instrum.* **68**, 3477 (1997).
- [36] Y. Chen, D. Haase, J. Manz, H. Wang, and Y. Yang, From chiral laser pulses to femto- and attosecond electronic chirality flips in achiral molecules, *Nat. Commun.* **15**, 565 (2024).
- [37] M. Davino, E. McManus, P.-H. Tran, V.-H. Hoang, A. F. Ordóñez, G. Gibson, T. Saule, A.-T. Le, and C. A. Trallero-Herrero, Symmetries in three-dimensional photoelectron momentum spectroscopy as precursory methods for dichroic and enantiosensitive measurements, *Phys. Rev. Appl.* **23**, 014022 (2025).
- [38] S. Kerbstadt, D. Pengel, D. Johannmeyer, L. Englert, T. Bayer, and M. Wollenhaupt, Control of photoelectron momentum distributions by bichromatic polarization-shaped laser fields, *New J. Phys.* **19**, 103017 (2017).
- [39] U. Fano, Propensity rules—An analytical approach, *Phys. Rev. A* **32**, 617 (1985).
- [40] S. Kerbstadt, K. Eickhoff, T. Bayer, and M. Wollenhaupt, Odd electron wave packets from cycloidal ultrashort laser fields, *Nat. Commun.* **10**, 658 (2019).
- [41] L. V. Keldysh, Ionization in the field of a strong electromagnetic wave, *J. Exptl. Theoret. Phys. (U.S.S.R.)* **47**, 1945 (1964) [*Sov. Phys. JETP* **20**, 1307 (1965)].
- [42] P. Hockett, M. Wollenhaupt, C. Lux, and T. Baumert, Complete photoionization experiments via ultrafast coherent control with polarization multiplexing. II. Numerics and analysis methodologies, *Phys. Rev. A* **92**, 013411 (2015).
- [43] M. Wollenhaupt, V. Engel, and T. Baumert, Femtosecond laser photoelectron spectroscopy on atoms and small molecules: Prototype studies in quantum control, *Annu. Rev. Phys. Chem.* **56**, 25 (2005).
- [44] M. Wollenhaupt, M. Krug, J. Köhler, T. Bayer, C. Sarpe-Tudoran, and T. Baumert, Photoelectron angular distributions from strong-field coherent electronic excitation, *Appl. Phys. B* **95**, 245 (2009).
- [45] M. Davino, E. McManus, N. G. Helming, C. Cheng, G. Moğol, Z. Rodnova, G. Harrison, K. Watson, T. Weinacht, G. N. Gibson, T. Saule, and C. A. Trallero-Herrero, A plano-convex thick-lens velocity map imaging apparatus for direct, high resolution 3D momentum measurements of photoelectrons with ion time-of-flight coincidence, *Rev. Sci. Instrum.* **94**, 013303 (2023).
- [46] S. Zamith, M. A. Bouchene, E. Sokell, C. Nicole, V. Blanchet, and B. Girard, Observation of the oscillation of an angular wavepacket, *Eur. Phys. J. D* **12**, 255 (2000).
- [47] T. Bayer, D. Gräfin, S. Kerbstadt, D. Pengel, K. Eickhoff, L. Englert, and M. Wollenhaupt, Time-resolved 3D imaging of ultrafast spin-orbit wave packet dynamics, *New J. Phys.* **21**, 033001 (2019).
- [48] D. Bauer, *Computational Strong-Field Quantum Dynamics. Intense Light-Matter Interactions* (De Gruyter, Berlin, 2017), Vol. 1.