Determination of atomic multiphoton ionization phases by trichromatic multichannel wave packet interferometry

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We present a multichannel photoelectron interferometry technique based on trichromatic pulse shaping for unambiguous determination of quantum phases in multiphoton ionization (MPI) of potassium atoms. The colors of the laser field are chosen to produce three energetically separated photoelectron interferograms in the continuum. While the red pulse is two-photon resonant with the 3d-state resulting in a (2+1) resonance-enhanced MPI (REMPI), a (1+2) REMPI occurs via the non-resonant intermediate 4p-state with an initial green or blue pulse. We show that ionization via a non-resonant intermediate state lifts the degeneracy of photoelectron interferograms from pathways consisting of permutations of the colors. The analysis of the interferograms reveals a phase shift of ±π/2 depending on the sign of the detunings in the (1+2) REMPI pathways. In addition, we demonstrate that the photoionization time delay in the resonant (2+1) REMPI pathway gives rise to a linear spectral phase in the photoelectron spectra. Insights into the underlying MPI processes are gained through an analytic perturbative description and numerical simulations of a trichromatic driven three level system coupled to the continuum.

I. INTRODUCTION

Being at the heart of atomic, molecular, and optical physics, photoionization has been studied for over a century, both experimentally and theoretically. Initially, Albert Einstein gave a theoretical interpretation of the photoelectric effect in his seminal 1905 publication [1], where he envisioned the possibility of processes in which an “energy quantum of emitted light can obtain its energy from multiple incident energy quanta”. Subsequently, a quantum mechanical description of two-photon transitions was given by Maria Göppert-Mayer in 1931 [2] paving the way to our modern understanding of multiphoton ionization (MPI). Sophisticated MPI schemes combined with highly differential detection techniques for the time-, energy- and angle-resolved measurements have established the field of nonlinear photoelectron spectroscopy yielding numerous applications in fundamental and applied physics, as described in monographs [3–11] and review articles [12–16]. Attosecond electron dynamics [17, 18], coherent control of atomic and molecular dynamics by shaped laser pulses [19–24] and the generation of free electron vortices [25–29] are examples for the wide variety of modern topics in atomic and molecular MPI. In addition to measuring the photoelectron probability density distribution the use of interferometric techniques [30] has made it possible to determine the phase of photoelectron wave packets. Quantum mechanical phases are key to coherent control [31, 32] and essential for the complete characterization of the wave function [33]. Knowledge about the phase of photoelectron wave functions from atomic [39, 41] and molecular [42–44] photoionization processes provides insights into the underlying dynamics [45] accompanied with photoemission phases and time delays [46–52]. In those measurements, the superposition of multiple partial waves gave rise to phase-sensitive interference patterns that allowed the quantum mechanical phase to be reconstructed. In general, the exact shape of an interferogram is determined by the ionizing radiation’s optical phase and the additional quantum phase due to the ionization dynamics. To distinguish between these two phases, in the following, the phase introduced by laser radiation will be referred to as optical phase, while the quantum mechanical phase resulting from ionization dynamics will be referred to as MPI-phase. Very recently, building on the results presented in [40], MPI-phases from multiple intermediate states were investigated in the photoionization of helium atoms [41].

In this paper, we demonstrate a trichromatic MPI scheme to decouple the MPI-phase measurement from the optical phase control for an unambiguous determination of the MPI-phase. We exemplify our scheme on the trichromatic three-photon ionization of potassium atoms to investigate the MPI-phases due to the intermediate resonances. It has been shown that interference patterns in photoelectron spectra from multichromatic MPI, such as bichromatic photoelectron vortices, are sensitive to the carrier-envelope phase (CEP) [28]. However, we have recently demonstrated a pulse-shaper-based trichromatic MPI scheme for quantum state holography [53] in which the photoelectron hologram is sensitive to the MPI-phases and the relative optical phases between the colors in the trichromatic pulse sequence but insensitive to the CEP. In this work, we use temporally overlapping trichromatic fields with the central frequencies of the red, green and blue spectral band chosen such that 2ωg = ωr + ωb. Due to this frequency condition, the laser...
pulses create free electron wave packets forming interferograms in three different photoelectron kinetic energy windows, referred to as interference channels. By design, the interferograms consist of wave packets from \((1+2)\) resonance enhanced MPI (REMPI) via the \(4p\)-state or \((2+1)\) REMPI via the \(3d\)-state. The observed interference patterns are sensitive to the MPI-phases as well as the relative optical phases. Motivated by the concerted generation of multiple interferograms in one photoelectron spectrum, the technique is termed trichromatic multichannel wave packet interferometry. Due to the temporal overlap of the fields, the observed interferograms also map the phases introduced by transiently populated bound atomic states. The MPI-phases are extracted from energy-resolved photoelectron spectra measured as a function of the relative optical phase of the green spectral component. In the resulting phase maps, the quantum phases manifest as relative phase shifts between the interferograms in the different channels. The interpretation of the experimental results is supported by the analysis of a model system consisting of a three-level atom coupled to the continuum. To simulate laser-induced bound and ionization dynamics we study both, the analytic perturbative description and the numeric solution of the time-dependent Schrödinger equation (TDSE).

II. PHYSICAL SYSTEM AND THEORY

In this section, we present the physical system studied by our shaper-based multichannel interferometry scheme. We provide a theoretical description of the measured photoelectron momentum distributions (PMDs) with emphasis on their dependence on the optical and MPI-phases. Based on the theoretical model, we analyze our experimental results in Sec. IV.

A. Physical system

The excitation scheme of potassium atoms interacting perturbatively with parallel linearly polarized (PLP) trichromatic fields is shown in Fig. 1(a). In the experiment, we use temporally overlapping trichromatic pulses to produce the interference of multiple MPI pathways from different combinations of red \((r)\), green \((g)\) and blue \((b)\) photons, i.e., single-color and frequency mixing contributions in the photoelectron spectrum. Usually, in multichromatic MPI, only permutations of a given color combination connect the same initial and final states. However, by appropriate choice of the field’s frequencies, even different color combinations give rise to interference in several energetically separated final states. In the experiment, the photon energies are chosen to ensure the same number of photons \((\text{three})\) not only in each frequency mixing pathway but also in the green single-color pathway. Consequently, the photoelectron interferograms are insensitive to CEP variations, but are controlled by the relative optical phases. To maximize the generation of the frequency mixing signals, all three colors overlap in time. The interference of frequency mixing pathways consisting of different photon combinations is observed when the central frequencies \(\omega_j\) and the time delays \(\tau_j\) of the trichromatic field are chosen such that

\[
2\omega_g = \omega_r + \omega_b < \omega_{\text{IP}}, \quad (1)
\]

where \(\omega_{\text{IP}} = \hbar \omega_{\text{IP}}\) describes the ionization potential. The spectral and temporal conditions \((1)\) and \((2)\) form the basic building block of the presented scheme which is visualized by the dashed box in the left inset of Fig. 1(a). When both conditions are met, the trichromatic field simultaneously generates three energetically separated photoelectron interferograms in the continuum. In the following, the corresponding energy windows centered around \(\varepsilon_1, \varepsilon_2\) and \(\varepsilon_3\) will be referred to as interference channels (cf. Fig. 1(a)). To study the MPI-phases induced by intermediate resonant states, the frequencies are further chosen to be either two-photon resonant with the 3d-state, i.e., \(\omega_2 = \omega_{3d}\), or one-photon near-resonant with the 4p-state, i.e., \(\omega_2 < \omega_{4p} < \omega_3\). Since the (near-)resonant excitation is more efficient, the 4p and 3d intermediate states select the resonance-enhanced pathways, listed in Tab. I.

For example, the interferogram in channel 1 is created by the interference of photoelectrons via the resonance-enhanced MPI pathways \(\mathcal{R}_1\) and \(\mathcal{R}_2\). The pathway \(\mathcal{R}_1\), denoted as \((ggr)\), describes the absorption of two green \((gg)\) photons and one red \((r)\) photon in this order. Similarly, the pathway \(\mathcal{R}_2\), denoted as \((rrb)\), describes the absorption of two red \((rr)\) photons and one blue \((b)\) photon. The other resonance-enhanced pathways leading to the channels 2 and 3 are labeled in the same way. Even though the color combinations of the individual MPI pathways are quite different, the total optical phase difference \(\Delta\varphi\) introduced by the respective laser pulses is the same for all interferograms. The perturbative description of the REMPI in Sec. III shows that this phase difference is \(\Delta\varphi = 2\varphi_g - \varphi_r - \varphi_b\), where \(\varphi_r, \varphi_g\) and \(\varphi_b\) are the relative optical phases of the red, green and blue pulse, respectively (cf. Eq. 5). Therefore, the variation of \(\Delta\varphi\) induces a uniform amplitude modulation of the interferograms in each channel. By scanning the relative optical phase \(\varphi_g\) and measuring energy-resolved photoelectron spectra we map out the amplitude modulation. In the following, these phase-resolved measurements are denoted as phase maps. Because the influence of the total optical phase difference \(\Delta\varphi\) and the CEP is the same in each interferogram, relative phase shifts between the recorded modulations in the phase maps are exclusively attributed to differences in the MPI-phases acquired in the corresponding pathways. Thus, in this trichromatic scheme the recorded phase maps provide direct access to the MPI-phases.
FIG. 1. (a) Excitation scheme of potassium atoms interacting perturbatively with a linearly polarized trichromatic field for multichannel interferometry together with the experimental multiphoton spectrum. We use temporally overlapping trichromatic pulses with frequencies $2\omega_3 = \omega_r + \omega_b$ (black dashed box in the left figure) to achieve interference of photoelectrons by MPI with different combinations of red, green and blue photons. The interference leads to three energetically separated photoelectron interferograms in the interference channels 1-3 (highlighted in orange, petrol and violet). The frequencies are spectrally confined to be either two-photon resonant with the $3d$-state, i.e. $2\omega_r \approx \omega_{3d}$, or one-photon near- but non-resonant with the $4p$-state, i.e., $\omega_g \ll \omega_{4p} < \omega_b$ (right bottom inset). The near-resonant excitation of the $4p$-state lifts the degeneracy of the frequency mixing pathways and causes the second channel to split into two bands ($\varepsilon_{\text{low}}^2$ and $\varepsilon_{\text{up}}^2$) around $\varepsilon_2$. (b) Measured and Abel-inverted photoelectron signals in polar coordinates. (c) Measured and tomographically reconstructed 3D PMD with color-coded interference channels at $\varepsilon_1$-$\varepsilon_3$.

via the observed phase shifts between the interferograms.

In the experiment we use temporally overlapping trichromatic PLP laser fields with central wavelengths of $\lambda_r = 925$ nm (red band), $\lambda_g = 797$ nm (green band) and $\lambda_b = 708$ nm (blue band). The corresponding frequencies $\omega_j$ meet the frequency condition in Eq. (1). To study the MPI-phase from resonant excitation, the red pulse is two-photon resonant with the $3d$-state $|3d\rangle$ with the very small detuning $\hbar\delta_{3d} = 2\hbar\omega_r - \hbar\omega_{3d} \approx 10$ meV (cf. left magnification in Fig. (1a)). The spectral full width at half maximum (FWHM) of the red pulse is $\hbar\Delta\omega_r \approx 30$ meV. In contrast, the MPI-phases due to the transient population dynamics in the non-resonant $4p$-state are studied with the green ($\hbar\Delta\omega_g \approx 60$ meV) and blue ($\hbar\Delta\omega_b \approx 70$ meV) pulses. To eliminate the spectral intensity of the pulse at the transition frequency $\omega_{4p}$, a mechanical blocker is inserted into the Fourier plane of our pulse shaper (cf. bottom right inset of Fig. (1a) and Fig. (3a)). This procedure guarantees non-resonant excitation of the $4p$-state despite the small detuning. As a consequence, the spectrum of the green pulse is slightly asymmetric. The detunings of the green and blue pulse are $\hbar\delta_{4p}^g = \hbar\omega_g - \hbar\omega_{4p} \approx -50$ meV and $\hbar\delta_{4p}^b = \hbar\omega_b - \hbar\omega_{4p} \approx 140$ meV, respectively (cf. right magnification in Fig. (1a)). Thus, our trichromatic scheme allows us to study MPI-phases from excitation of two different intermediate states either via resonant or via red- ($\delta_{4p}^g < 0$) and blue-detuned ($\delta_{4p}^b > 0$) near-resonant pathways simultaneously.

In our theoretical model, the atom is described by a three-level system coupled to the continuum. The bound part consists of the ground state $|g\rangle$ and the two (near-)resonant intermediate states $|a\rangle$ and $|b\rangle$. The final state $|f\rangle$ with variable energy describes the free electron in the continuum (for details see Sec. II B). Due to the
choice of the photon energies described above, the photoelectron interferograms in channels 1 and 3 are centered around the energies $\varepsilon_1 = 0.10 \text{ eV}$ and $\varepsilon_3 = 0.50 \text{ eV}$. Generally, pathways composed of the same color combinations are energetically degenerate since they differ only by permutations. However, the transient population of the near-resonant $4p$-state introduces a spectral shift. In particular, since the green pulse is slightly red-detuned ($\delta_{g}^{4p} < 0$) with respect to the $4s \rightarrow 4p$ transition, its transient population follows the laser field envelope with an additional temporal phase. As a consequence, the photoelectron signals mapping the $4p$-state are slightly shifted upwards in energy. For the same reason, wave packets created via pathways starting with a blue photon ($\delta_{b}^{4p} > 0$) are slightly shifted downwards in energy. Thus, near- but non-resonant excitation of the $4p$-state lifts the degeneracy of the involved frequency mixing contributions introducing an energetic splitting between the pathways with an initial green photon and those starting with a blue photon. In the interference channels 1 and 3 only the upper signals are observed since the multiplicity of the green-green-red and green-blue-red pathways favors the ones with a leading green photon. In channel 2 the red-green-blue pathway around $\varepsilon_2 = h(\omega_g + \omega_g + \omega_b) = 0.31 \text{ eV}$ exhibits both an up-shifted signal centered around $\varepsilon_{2u}$ and a down-shifted signal centered around $\varepsilon_{2l}$ from the pathways with an initial green photon and a down-shifted signal centered around $\varepsilon_{2l}$ from the pathways with an initial blue photon. Note that this energetic separation is not to be confused with the Stark shift or the Autler-Townes splitting. It is intensity-independent and fully consistent with the perturbative description of the excitation (see Sec. II B and Appendix B for more details). Indeed, the energetic separation permits us to investigate both, the red- and the blue-detuned near- but non-resonant excitation of the $4p$-state, independently in a single interference channel (cf. bottom right inset of Fig. [1](a)). In addition to the above mentioned interferograms, we observe photoelectron signals at $\varepsilon_4 = 0.73 \text{ eV}$ and $\varepsilon_5 = 0.93 \text{ eV}$. While the contribution at $\varepsilon_4$ originates from a frequency mixing pathway with two blue and one green photon, the one at $\varepsilon_5$ arises from the blue single-color pathway, depicted in Fig. [1](a). The former contribution is used for in-situ temporal pulse characterization in Sec. III B. Figure [1](b) depicts a section through the $y$-$z$-plane in polar representation and the energy-resolved spectrum obtained by integration over the angular coordinate of the measured PMD, highlighting the different contributions at $\varepsilon_1$-$\varepsilon_5$. Figure [1](c) shows the measured and Abel-inverted three dimensional PMDs of the three color-coded energetically nested $J(m = 0)$-type interferograms (details see Sec. III). In this figure, the 3D PMDs of the contributions around $\varepsilon_4$ and $\varepsilon_5$ are omitted for clarity.

B. Perturbative description

In this section, we provide a theoretical description of the photoelectron wave packets created in the multichannel interferometry scheme. We focus on the spectral phases in the different interference channels introduced by the (near-)resonant excitation in the MPI process. First, we introduce the trichromatic laser field in the temporal and spectral representation. Using perturbation theory, we derive a general expression for the photoelectron density, based on a multilevel model to calculate the MPI-phases in the relevant pathways.

The trichromatic PLP field is fully characterized by the scalar electric fields of each color. The total electric field (negative frequency analytic signal [55]) is therefore given by

$$E^-(t) = \sum_{j \in \{r,g,b\}} \mathcal{E}_j(t - \tau_j)e^{-i(\omega_j t - \varphi_j)}, \quad (3)$$

with the temporal pulse envelopes $\mathcal{E}_j(t)$ shifted in time by the delay $\tau_j$, the central frequency $\omega_j$ and the relative optical phase $\varphi_j$. In Eq. (3) the CEP of the field components is omitted because in our scheme the phase in the photoelectron spectrum introduced by the CEP is identical for all MPI pathways. The corresponding spectrum reads

$$\tilde{E}^-(\omega) = \sum_{j \in \{r,g,b\}} \tilde{\mathcal{E}}_j(\omega + \omega_j)e^{i(\varphi_j - (\omega + \omega_j)\tau_j)} \quad (4)$$

with the spectra of the envelopes $\tilde{\mathcal{E}}_j(\omega)$. Again, the three central frequencies $\omega_j$ are chosen such that the energy of two green photons equals the energy of one red plus one blue photon as described by Eq. (1). Simultaneous absorption of another red, green or blue photon in both processes provides the photon energy to overcome the ionization potential and gives rise to the interference channels $l = 1$, 2 and 3, respectively (cf. visualization of the basic building block in the left inset of Fig. [1](a)). Therefore, each interference channel $l$ consists of two pathways $\textbf{I}$ and $\textbf{II}$ either with at least two green photons ($\textbf{I}$) or with at least one red and one blue photon ($\textbf{II}$). Both pathways contain a photon of the additional color $x_l$ with $x = [r,g,b]$, e.g., $x_1 = r$ for the additional red photon in channel 1. Due to the temporal overlap of the three colors (cf. Eq. (2)), every permutation of the involved photons gives rise to another MPI pathway. We can write both pathways as a set containing all permutations of the involved colors, i.e., $\mathcal{Q}_4^{(l)} = \text{Sym}\{[g,g,x_l]\}$ and $\mathcal{Q}_4^{(l)} = \text{Sym}\{[r,b,x_l]\}$ where Sym denotes the symmetric group. In general the resulting photoelectron interferogram in channel $l$ is given by the superposition of all possible partial wave functions created via the pathways $\mathcal{Q}_4^{(l)}$ and $\mathcal{Q}_4^{(l)}$. However, as discussed in Sec. II A the intermediate resonances in the potassium atom select the relevant pathways. Therefore, the description focuses on
the superposition of relevant resonance-enhanced quantum pathways $I \in \Omega_{	ext{G}}^{(3)}$ and $I \in \Omega_{	ext{B}}^{(1)}$, where the ordering of the colors is fixed due to the resonances. As an example, we consider the superposition of the (ggb) and (brb) pathways in channel 3 (cf. Tab. I). Hence, we assume each interferogram $\Psi^{(l)}$ to be composed of two partial wave functions $\Psi^{(l)} = \Psi_{1/II}^{(l)} + \Psi_{II}^{(l)}$. In the momentum representation, with the photoelectron momentum $k = (k, \theta, \phi)$, these partial wave functions are written as

\[
\Psi_{1/II}^{(l)}(k) = c_{1/II}^{(l)}(k) e^{i\varphi_{1/II}^{(l)}} \psi_{3,0}(\theta, \phi) = |c_{1/II}^{(l)}(k)| e^{i(k_{1/II}^{(l)} + \varphi_{1/II}^{(l)})} \psi_{3,0}(\theta, \phi),
\]

where $\varphi_{1/II}^{(l)}$ represents the acquired optical phase and $c_{1/II}^{(l)}(k) = |c_{1/II}^{(l)}(k)| e^{i\varphi_{1/II}^{(l)}}$ denotes the photoelectron amplitude with the associated MPI-phase $\chi_{1/II}^{(l)}(k)$. Since the sum of the optical phases does not depend on the permutation of the colors, we find

\[
\varphi_1^{(l)} = 2\varphi_{g} + \varphi_{s} \quad \text{and} \quad \varphi_{II}^{(l)} = \varphi_{r} + \varphi_{b} + \varphi_{s},
\]

for all pathways to the states $\Psi_{1/II}^{(l)}$. Using Eq. (5), the resulting electron density of the photoelectron interferogram $\rho^{(l)} = |\Psi^{(l)}|^2$ is given by

\[
\rho^{(l)}(k) = \left[ O^{(l)}(k) + S^{(l)}(k) \cos \left( \gamma^{(l)}(k) + \Delta \varphi \right) \right] \times |\psi_{3,0}(\theta, \phi)|^2,
\]

with the signal offset $O^{(l)}(k) = |c_{1/II}^{(l)}(k)|^2 + |c_{II}^{(l)}(k)|^2$ and the signal amplitude $S^{(l)}(k) = 2|c_{1/II}^{(l)}(k)||c_{II}^{(l)}(k)|$. In Eq. (7) the MPI-phase difference in channel $I$ is denoted by $\gamma^{(l)}(k) = \chi_{1/II}^{(l)}(k) - \chi_{II}^{(l)}(k)$ and the optical phase difference by $\Delta \varphi = \varphi_{1}^{(l)} - \varphi_{II}^{(l)}$. Using Eq. (6), the optical phase difference reads

\[
\Delta \varphi = 2\varphi_{g} - \varphi_{r} - \varphi_{b}
\]

and is independent of the respective channel. Therefore, the phases between the interferograms are determined exclusively by the MPI-phase differences, which is the characteristic feature of our multichannel interferometry scheme. Equation (7) describes the photoelectron interferograms in each channel as $f(m = 0)$-type wave packets (cf. Fig. 1(c)), which are periodically intensity-modulated by variation of the relative optical phases $\varphi_j$.

The modulation frequency is determined by the number of involved photons of the respective color. The MPI-phase differences manifest in the phase shifts $\gamma^{(l)}(k) = \gamma_{\text{non}}^{(l)}(k)$ of the modulation, which sensitively depend on the intermediate resonances in the MPI pathways.

In the next step, we discuss the influence of the atomic structure on the phases $\chi_{1/II}^{(l)}(k)$ acquired in the MPI process by calculating the photoelectron amplitudes of the resonance-enhanced quantum pathways $\mathcal{R}_{1/II}$, $\mathcal{G}_{1/II}$ and $\mathcal{B}_{II}$ (see Tab. I) using perturbation theory. For simplicity, we reduce the atomic excitation scheme in Fig. 1(a) to the three most relevant states, i.e., the ground state $|g\rangle$ and the two (near-)resonant intermediate states $|a\rangle$, $|b\rangle$ coupled to a final state $|f\rangle$ with variable energy in the continuum. This model system is excited by a single-color laser pulse with central frequency $\omega_0$, as shown in Fig. 2(a). A detailed theoretical derivation of the population amplitudes is given in Appendix A. The generic scheme describes three-photon ionization similar to that in the experiment. The MPI process is subdivided into three steps. First, the state $|a\rangle$ (representing the $4p$-state) is non-resonantly excited from the ground state $|g\rangle$ (representing the $4s$-state). For a sufficiently large detuning of the laser central frequency $\omega_0$ with respect to the transition frequency $\omega_{a\gamma}$, i.e., $\delta_1 = \omega_0 - \omega_{a\gamma} \gg \Delta \omega$, implying $\tilde{E}(\delta_1) \approx 0$, the resulting time-dependent population amplitude of state $|a\rangle$ can be approximated by (cf. Eq. (B10))

\[
e^{a(t)} \propto \frac{e^{i\gamma_{\text{non}}^{(l)}(k)} \left( \delta_{1} \right) e^{-i\delta_{1} t \mathcal{E}(t)}},
\]

which explicitly depends on the detuning $\delta_1$. Consequently, the phase shift induced by the intermediate state $|a\rangle$, i.e. the $4p$-state, is different for the red-
and blue-detuned excitation and therefore responsible for the observed energy shift in channel 2. With the experimental parameters given in Sec. 1.1A the effective energy shift between \( \varepsilon_b^{2\text{up}} \) and \( \varepsilon_b^{2\text{low}} \) can be estimated to be about \( \hbar \Delta \zeta_{\text{theo}} = \hbar \Delta \zeta_b \approx 40\text{ meV} \).

Next, we consider the two-photon excitation of state \( |b\rangle \) (representing the 3d-state) via the transiently populated off-resonant state \( |a\rangle \) and distinguish between two limiting cases. In the two-photon resonant case, when \( \delta_2 = \delta_1 + \omega_0 - \omega_{\text{b}a} = 0 \), the population amplitude of \( |b\rangle \) is given by (cf. Eq. (B11))

\[
c_b^{\text{res}}(t) \propto e^{-i \hat{H}_b t / \hbar} \int_{-\infty}^{t} \mathcal{E}(t') \mathcal{E}^2(t') \mathrm{d}t'. \tag{11}
\]

In contrast, for non-resonant two-photon excitation, when \( \delta_2 \neq 0 \) and the two-photon resonance lies outside the bandwidth of the second order laser spectrum implying \( \mathcal{E}^{(2)}(\delta_2) \approx 0 \), the amplitude of the state \( |b\rangle \) reads (cf. Eq. (B15))

\[
c_b^{\text{non}}(t) \propto e^{-i \delta_2 t / \hbar} \mathcal{E}^2(t). \tag{12}
\]

The third photon maps the population amplitude of \( |b\rangle \) into the final continuum state \( |f\rangle \) with photoelectron kinetic energy \( \varepsilon = \hbar \omega_f - \hbar \omega_{\text{IP}} \). This photoionization step leads to the final state population amplitude of the free state \( |f\rangle \)

\[
c_f(t, \varepsilon) = -\frac{\mu_{\text{f}b}}{i\hbar} \int_{-\infty}^{t} c_b(t') \mathcal{E}(t') e^{-i\varepsilon(t') \varepsilon'} \mathrm{d}t', \tag{13}
\]

where \( \varepsilon(\varepsilon) = \omega_0 - \omega_{\text{f}b}(\varepsilon) = \omega_0 - \frac{\varepsilon}{\hbar} + \omega_b - \omega_{\text{IP}} \). Photoionization via the two-photon resonant pathway yields the final \( (t \to \infty) \) state amplitude (cf. Eq. (B18))

\[
c_f^{\infty, \text{res}}(\varepsilon) \propto \frac{1}{\delta_1} \left( \langle \mathcal{E}^{(2)}(0) \mathcal{E}(\varepsilon) \rangle - 2i \mathcal{E}^2(0) \frac{\partial \mathcal{E}}{\partial \omega}(\varepsilon) \right) = |c_f^{\infty, \text{res}}(\varepsilon)| e^{i \chi^{\infty, \text{res}}(\varepsilon)}. \tag{14}
\]

In contrast, the non-resonant pathway yields the amplitude of (cf. Eq. (B22))

\[
c_f^{\infty, \text{non}}(\varepsilon) \propto \frac{e^{i \varepsilon / \hbar}}{\delta_1 \delta_2} \mathcal{E}^{(3)}(\varepsilon + \delta_2) = |c_f^{\infty, \text{non}}(\varepsilon)| e^{i \chi^{\infty, \text{non}}}. \tag{15}
\]
Equations (14) and (15) show that for a positive detuning $\delta_2 > 0$, as in the experiment, and a symmetric and real-valued spectral envelope, the MPI-phases are determined by the sign of the detuning $\delta_1$, i.e.,

$$\chi^{\text{res}}(\varepsilon) = \begin{cases} \pi + \xi(\varepsilon) ; \delta_1 < 0 \\ \xi(\varepsilon) ; \delta_1 > 0 \end{cases}$$  \tag{16}

$$\chi^{\text{non}} = \begin{cases} 3\pi/2 ; \delta_1 < 0 \\ \pi/2 ; \delta_1 > 0 \end{cases}$$  \tag{17}

In Eq. (16), $\xi(\varepsilon)$ represents the temporally accumulated phase due to the resonant excitation of the 3d-state which is discussed in the following. Since the population built-up in the resonant state occurs on the time scale of the pulse duration, the reference partial photoelectron wave packet, created by non-resonant ionization, accumulates its time-evolution phase in the continuum during the formation of the photoelectron interferogram. Thus, the time delay introduced by the population dynamics in the resonant 3d-state manifests in a linear spectral phase between the 3d-resonant pathway $R_{II}$ and the non-resonant pathway $R_1$. For a Gaussian-shaped pulse envelope the phase can be approximated by $\xi(\varepsilon) = \tau_{\text{res}} \varepsilon(\varepsilon)$ with (see Appendix A for details)

$$\tau_{\text{res}} \approx \sqrt{\frac{\ln(2)}{\pi}} \frac{4}{\Delta \omega} \frac{\Delta t}{\sqrt{\ln(2)\pi}}.$$  \tag{18}

To verify the MPI-phases predicted by the perturbation theory, we numerically solve the TDSE for the model system depicted in Fig. 2(a). The numerical implementation is described in previous work [15, 60] and the Appendix A. The results of the simulation for the system depicted in Fig. 2(a) are depicted in Fig. 2 (b) and (c), respectively. In the non-resonant case, the time-dependent photoelectron amplitudes represented in the complex plane, describe almost straight lines as shown in the upper frame of (b). Each line is rotated by $\pm \pi/2$ with respect to the real axis, where the lower sign corresponds to $\delta_1 < 0$ (red-detuned) and the upper sign to $\delta_1 > 0$ (blue-detuned), as predicted by Eq. (17). This observation agrees with the variation of the MPI-phase $\chi^{\text{non}}$ from $\chi^{\text{non}} = -\pi$ to $\pi$ as the detuning varies from $h\delta_1 = -0.15$ eV to 0.15 eV as shown in the middle frame of (b). The bottom frame depicts the final population $|c_{f,\text{res}}^{\infty}|^2$ as function of the detuning $\delta_1$, showing a bell-shaped profile centered around $\delta_1 \approx 0$. Note that $\delta_2$ is a function of $\delta_1$.

Next, we consider two-photon resonant excitation of the state $|b\rangle$, with $\delta_1 < 0$. Since resonant excitation leads to an energy-dependent MPI-phase $\chi^{\text{res}}_{\delta_1<0}(\varepsilon)$ according to Eq. (16), we investigate the final state amplitude $c_f^{\infty}$ as a function of the photoelectron kinetic energy. The upper frame of Fig. 2(c) shows the time evolution of $c_f^{\text{res}}(t; \varepsilon)$ in the complex plane for different energies in the photoelectron continuum, i.e., different values of $\varepsilon(\varepsilon)$ (red, blue and grey lines). The red and blue shaded curves illustrate the corresponding time-dependent amplitudes for different values of $\varepsilon \neq 0$. The nearly horizontal grey line is connected to the final phase value of $\chi^{\infty}(\varepsilon) = \pi$ (cf. Eq. (16)), since the phase introduced by the population dynamics $\xi(\varepsilon)$ vanishes. In contrast, for $\varepsilon \neq \varepsilon$, the time evolution of the energy-dependent amplitude describes a curve moving either upwards ($\varepsilon > 0$, red lines) or downwards ($\varepsilon < 0$, blue lines) on the imaginary axis. The middle frame of (c) depicts the energy-resolved photoelectron amplitude $|c_f^{\infty,\text{res}}|^2$ (blue) and phase $\chi_f^{\infty,\text{res}}(\varepsilon)$ (black). Here, the symbols (circle, square and triangle) indicate the endpoints of the final state populations shown in the upper frame. In the region of a non-vanishing photoelectron amplitude $|c_f^{\infty,\text{res}}|^2$, the phase exhibits a linear behavior, confirming the assumption of $\xi(\varepsilon) \approx \tau_{\text{res}} \varepsilon(\varepsilon)$. The bottom frame shows a physical picture of the resonance-induced ionization time delay due to the windowing of the Gaussian-shaped temporal field envelope $E(t)$ with the time-dependent population amplitude of the state $|b\rangle$. While non-resonant excitation and ionization follows the field envelope almost instantaneously (cf. Eq. (9)), resonant ionization introduces a temporal shift in the order of the pulse duration according to Eq. (18), corresponding to a linear spectral phase.

### III. Experimental setup

In this section we describe our experimental setup and strategy. The trichromatic fields are generated using white light polarization pulse shaping [53, 61, 62] combined with photoelectron velocity map imaging (VMI) [63] to measure energy- and angle-resolved photoelectron spectra.

#### A. Experimental setup

The trichromatic experimental scheme is based on our setup previously reported in [53]. Briefly, trichromatic pulse shaping is implemented using a home-built 4f polarization pulse shaper [61] employing a dual-layer liquid crystal spatial light modulator (LC-SLM). The shaper is specifically adapted to the white light supercontinuum (WLS) [62] generated by seeding a neon-filled hollow core fiber compressor with 20 fs pulses ($\lambda_c = 790$ nm) from an amplified laser system (FEMTOLASERS Femtopower HR 3 kHz). Employing a custom broadband $p$-polarizer (CodiXX colorPol®) in the Fourier plane of the shaper, we generate a PLP trichromatic field (cf. inset in Fig. 3(a)) by spectral amplitude and phase modulation. To individually advance or delay the pulses of different colors in time, we apply linear spectral phase functions to the LC-SLM. Owing to the common-path geometry of the shaper-based scheme, the generated trichromatic pulse sequences are inherently phase-locked allowing for high-precision time- and phase-resolved measurements.
FIG. 3. (a) Measured trichromatic spectrum together with the WLS. The inset shows a schematic of the pulse shaper setup with a broadband p-polarizer and the mechanical blocker in the Fourier-plane to eliminate resonant excitation of the 4p-state. (b) Energy sections of the time-resolved measurements on the green-red (left) and green-blue (right) frequency mixing signals from in-situ temporal pulse characterization (circles and squares) together with Gaussian fits (solid and dashed lines) and corresponding FWHMs.

The measured spectrum of the trichromatic field is shown in Fig. 3(a) along with the input WLS. The central wavelength of the red pulse is set to $\lambda_r = 925 \text{ nm}$ (red), i.e., tuned to the two-photon resonance of the 3d-state, indicated by the right vertical orange line. The central wavelengths of the green and blue pulses are set to $\lambda_g = 797 \text{ nm}$ and $\lambda_b = 708 \text{ nm}$, respectively. Spectral components resonant with the 4p-state are eliminated by employing a mechanical blocker (cf. inset in Fig. 3(a)) in the Fourier-plane between the blue and green component (see also left vertical orange line). The spectral bandwidths of the red, green and blue bands are set to $\Delta \omega_\text{r} = 50 \text{ mrad/fs}$, $\Delta \omega_\text{g} = 90 \text{ mrad/fs}$ and $\Delta \omega_\text{b} = 100 \text{ mrad/fs}$ (FWHM of the intensity), corresponding to bandwidth-limited pulse durations of $\Delta t_\text{r} \approx 55 \text{ fs}$, $\Delta t_\text{g} \approx 32 \text{ fs}$ and $\Delta t_\text{b} \approx 28 \text{ fs}$, respectively, assuming Gaussian-shaped envelopes. Using a spherical mirror, the trichromatic pulse is focused into the interaction region of a VMI spectrometer filled with potassium vapor from a dispenser source. The peak intensity of the temporally overlapping trichromatic field in the interaction region is estimated to be in the order of $I_0 \approx 5 \times 10^{12} \text{ W/cm}^2$. Abel inversion of the recorded 2D VMI images, using the rBASEX algorithm [57], yields the PMD of the created photoelectron wave packets. Angle-integration and energy calibration [55] of the PMD leads to the energy-resolved photoelectron spectra shown in Fig. 1(b).

B. Experimental preparation and characterization

In this section, we describe how we prepare and characterize the shaper-generated trichromatic field for the experiment. To maximize the interference contrast in all three interference channels $l$ (cf. Fig. 1(a)), we optimize the temporal overlap and the amplitudes of the three colors together with the spectral overlap of the partial photoelectron wave packets in each channel. First, to compress the WLS in time, we use a shaper-based evolutionary optimization procedure to maximize the second harmonic yield of the WLS from a thin $\beta$-barium borate crystal (EKSMA OPTICS, cutting angle $\theta = 29.2^\circ$, 5 $\mu$m thickness) [60, 67]. Subsequently, an initial trichromatic spectrum is sculpted from the compressed WLS by spectral amplitude modulation. In the second step, the frequency mixing contributions in the second harmonic signal of the trichromatic field are maximized by shaper-based pairwise optimization of the second and third order dispersion. The refined and temporally compressed trichromatic field is then focused into the interaction region of the VMI spectrometer to perform an additional in-situ temporal characterization and an iterative spectral optimization of the sculpted field in the laser focus. To this end, we iteratively adjust the amplitude and central wavelength of the individual colors to maximize the contrast of the photoelectron interferograms in phase maps [53]. For the final characterization of the temporal overlap we perform bichromatic time-resolved measurements by varying the time delay $\tau_g$ of the green pulse with a stepsize of $\Delta \tau_g = 3.75 \text{ fs}$ and record the Green-Red and the Green-Blue photoelectron frequency mixing contributions. Figure 3(b) shows sections from these time-resolved measurements at kinetic energies $\varepsilon_1$ (left) as well as $\varepsilon_3$ and $\varepsilon_4$ (right) together with Gaussian fits (solid and dashed lines). The results show a maximal temporal overlap of the green and red pulse at $(1.7 \pm 0.8) \text{ fs}$ and of the green and blue pulse at $(-3.5 \pm 1.3) \text{ fs}$, i.e., within the temporal step size, ensuring efficient frequency mixing. By applying the procedure described in [53] we obtain pulse durations of $\Delta t_1 = (50 \pm 8) \text{ fs}$, $\Delta t_3 = (49 \pm 12) \text{ fs}$ and $\Delta t_4 = (29 \pm 12) \text{ fs}$ from the measured FWHMs shown in Fig. 3(b). The values for the red and blue pulse are in good agreement with the estimated bandwidth-limited pulse durations from Sec. IIIA. The retrieved pulse duration of the green component is slightly larger than the value obtained in Sec. IIIA which is attributed to the mechanically blocked edge of the green spectral component resulting in a non-Gaussian pulse shape. Overall, the results confirm a flat spectral phase of the trichromatic field.

C. Experimental strategy

To extract the MPI-phase differences from the measured photoelectron interferograms, the experiment consists of two parts. In Sec. IV A, we describe the energy- and phase-resolved measurements, i.e., phase maps. In the experiment, we vary the relative optical phase of the green pulse $\varphi_g$ and measure photoelectron spectra which
are energy-calibrated and angularly integrated
\[ \vartheta_{\text{int}}(\varepsilon) = \int_0^{2\pi} \vartheta(\varepsilon, \theta) \, d\theta, \] (19)
yielding the kinetic energy-resolved phase maps
\[ \vartheta_{\text{int}}(\varepsilon, \varphi_r; \varphi_r + \varphi_b), \]
with \( \varepsilon = \frac{(\hbar k)^2}{2m_e}. \) Changing the phase of the blue pulse by \( \pi \) inverts the measured phase maps. In Sec. IV B this inversion is used to remove the phase-insensitive background. To this end, we calculate the phase contrast map \( \varrho \)
\[ C(\varepsilon, \varphi_g) = \vartheta_{\text{int}}(\varepsilon, \varphi_g; 0) - \vartheta_{\text{int}}(\varepsilon, \varphi_g; \pi) \]
(20)
by subtracting two normalized measured phase maps with an effective phase difference of \( |\varphi_r + \varphi_b| = \pi. \)
The phase contrast map reveals even subtle imprints of the MPI-phases in the recorded photoelectron spectra. In particular, the splitting of channel 2 into an upper and a lower contribution corresponding to the red- and blue-detuned excitation of the 4p-state can be clearly seen. In addition, it directly maps the spectral phase due to the resonant excitation of the 3d-state in the interference channel 1.

IV. RESULTS AND DISCUSSION

In Sec. IV A we present the \( \varphi_g \)-resolved phase maps and demonstrate their inversion by changing optical phase of the blue pulse from \( \varphi_b = 0 \) to \( -\pi. \) In Sec. IV B we remove the phase-insensitive background by calculating the phase contrast map \( C(\varepsilon, \varphi_g) \) (cf. Eq. (20)) and retrieve the MPI-phases induced by the intermediate states 4p and 3d.

A. Phase control of the photoelectron interferograms

First, we investigate the phase control of the photoelectron interferograms in \( \varphi_g \)-resolved phase maps \( \vartheta_{\text{int}}(\varepsilon, \varphi_g; \varphi_r + \varphi_b). \) In Fig. 4 (a) and (b) the simulated and measured phase maps \( \vartheta_{\text{int}}(\varepsilon, \varphi_g; \pi) \) are compared. The observed phase dependence validates the scheme by showing that the same optical phase is imprinted in all interferograms (cf. Eq. (7)).

In the experiment, we vary \( \varphi_g \in [-\pi, \pi] \) with a step size of \( \delta \varphi_g = \frac{2\pi}{30} \) and set the phases of the red and blue pulse to \( \varphi_r = \pi \) and \( \varphi_b = 0, \) respectively. The upper frame of Fig. 4 b) depicts the measured phase map which shows the three energetically separated interference channels centered around \( \varepsilon_1, \varepsilon_2 \) and \( \varepsilon_3 \) in an energy-window of \( \varepsilon \in [0, 0.6] \text{ eV}. \) In accordance with the theoretical description in Sec. II B each channel is strongly amplitude modulated with a periodicity of \( \pi, \) however, each with an individual phase offsets due to MPI-phases. The \( \pi \)-periodicity is due to the fact, that effectively two green photons contribute to each interferogram, resulting in a modulation period of \( \frac{2\pi}{3} = \pi \) (cf. Eq. (8)). The results in channel 2 show small energetic oscillations of the signal attributed to the two slightly shifted contributions discussed in Sec. II A. These two contributions, which are hardly distinguishable at this point, are more clearly visible in the phase contrast map and, therefore, they will be discussed in detail in Sec. IV B. First, we analyze the modulations in channels 1 and 3 around \( \varepsilon_1 \) and \( \varepsilon_3. \)

To quantitatively evaluate the modulation of the photoelectrons in the channels 1 and 3, we take sections through the phase maps along the phase axis at \( \varepsilon_1 \) (orange squares) and \( \varepsilon_3 \) (violet circles). These sections are shown in the bottom frame of Fig. 4 b) together with cosine fits through the data (orange dashed and

FIG. 4. Simulated and measured phase maps of photoelectron interferograms from multichannel interferometry by varying the phase of the green pulse \( \varphi_g \in [-\pi, \pi]. \) (a) Simulated phase map obtained by numerical solution of the TDSE for the perturbative interaction of a three-level atom with the trichromatic field having optical phases of \( \varphi_r = \pi, \varphi_b = 0. \) (b) Measured phase map for \( \varphi_r = \pi, \varphi_b = 0 \) with a step size of \( \delta \varphi_g = \frac{2\pi}{3} \approx 0.16 \text{ rad}, \) showing the three energetically separated interference channels around \( \varepsilon_1=\varepsilon_3. \) Bottom frame: section through the phase maps along the phase axis at \( \varepsilon_1 \) (orange) and \( \varepsilon_3 \) (violet) to emphasize the modulation. (c) same as the bottom frame of (b) but for \( \varphi_r = \pi, \varphi_b = -\pi. \)
FIG. 5. Simulated (a) and measured (b) phase contrast maps $C(\varepsilon, \varphi_g)$ with $\varphi_r = \pi$ extracted from inverting the phase maps by changing the phase of the blue pulse from $\varphi_b = 0$ to $\varphi_b = -\pi$. (a) Simulated phase contrast map based on the numerical results described in Sec. IV A shown in Fig. 4(a). (b) Measured phase contrast map calculated from the results of Sec. IV A shown in Fig. 4(b). The different channels are indicated by horizontal lines. To emphasize the interference channels, we apply super-Gaussian filters to blank the space between the regions of interest. (c)-(e) Sections through the measured phase contrast map (circles) at the kinetic energies of $\varepsilon_3^c$ (c), $\varepsilon_2^{up}$ (d) and $\varepsilon_2^{low}$ (e) together with cosine fits through the data (lines). The MPI-phase differences $\Delta \gamma$ are highlighted by vertical dashed black lines through the frames (c)-(e).

Our interpretation of the experimental findings are confirmed by the simulated phase map in Fig. 4(a) for $\varphi_r = \pi$, $\varphi_b = 0$ which is in good agreement with the measured phase map in the upper frame of (b). In the simulation, we consider a three-level system consisting of the states $4s$, $4p$ and $3d$ (similar to Sec. II B and the Appendix A) which interacts with a sequence of three Gaussian-shaped pulses similar to those used in the experiment (see Sec. II B). By numerically solving the TDSE for the three-level system, we obtain the bound state population dynamics. Subsequently, we calculate the energy-resolved photoelectron spectra using time-dependent perturbation theory (see e.g. [70] for details).

B. MPI-phase retrieval

In this section, we study the phase shifts between the interferograms observed in the different interference channels. These phase shifts originate from the MPI-phases acquired in the corresponding photoionization processes. For the background-free determination of the phase shifts in Fig. 4, we calculate the phase contrast maps $C(\varepsilon, \varphi_g)$ according to Eq. (20) from the phase maps presented in Sec. IV A. The simulated and experimental phase contrast maps are depicted in Fig. 5(a) and (b), respectively. To highlight the measured interferograms in Fig. 5(b), we apply super-Gaussian filters to blank the space between the regions of interest. The phase shifts between the modulations in all channels will be discussed in Sec. IV B.
the Fourier-plane produces a strongly non-Gaussian optical spectrum with vanishing intensity at resonance, the assumption \( E(\delta_1) \approx 0 \) is still valid. Moreover, the choice of frequencies in the experiment leads to a slight energetic separation in the frequency-mixing and the green single-color signals of 20 meV. The results show that both contributions in channel 2 exhibit a \( \pi \)-periodic oscillation similar to those observed in channel 1 and 3 (see discussion in Sec. IV A). Again, for quantitative evaluation of the MPI-phases, we take energy sections through the phase contrast map along the \( \varphi_g \)-axis. The sections at \( \varepsilon_3 \) (violet circles), \( \varepsilon_2^{\text{up}} \) (petrol blue circles) and \( \varepsilon_2^{\text{low}} \) (green circles) are shown in Fig. 3(c)-(e) along with cosine fits through the data (lines). The phases \( \gamma(l) \) extracted from the channels \( l = 2(\text{up/low}) \), 3 provide the MPI-phase difference

\[
\Delta \gamma(l-l') = \gamma(l) - \gamma(l')
\]

(21)

between two channels \( l \) and \( l' \). To rationalize the extracted phase differences \( \Delta \gamma \), we discuss the values \( \Delta \gamma(3-2, \text{low}) \) and \( \Delta \gamma(2, \text{up}-2, \text{low}) \) by comparing them with the theoretical results, starting with \( \Delta \gamma(3-2, \text{low}) \). In both the channels 3 and (2, low), two ionization pathways interfere, one of which originates from a blue-detuned near-resonant transition, the other from a red-detuned near-resonant transition. Consequently, the MPI-phase difference between the interference channel 3 and the lower part of channel 2 is expected to vanish (cf. Tab. I), in good agreement with the measured phase difference of \( \Delta \gamma(3-2, \text{low}) = 0.0 \text{ rad} \).

In multichromatic photoionization, different final states are addressed with different combinations and permutations of the colors in the laser field. However, the pathways to create the photoelectrons in the interference channel 2, i.e., \( G_{\text{II}}^{\text{up}} \) at \( \varepsilon_2^{\text{up}} \) and \( G_{\text{II}}^{\text{low}} \) at \( \varepsilon_2^{\text{low}} \) differ only in the permutations of the photons – albeit with the common reference pathway \( G_1 \) (cf. Sec. II A and Fig. 1(a)). Therefore, the phase difference within the interference channel 2 is uniquely determined by the MPI-phases introduced by the red-detuned (upper signal) and blue-detuned (lower signal) \( (1+2) \) REMPI processes. To analyze the dynamics, we first note that the red/blue detuning of the field corresponds to an opposite sign of \( \delta_1 \). As a consequence, the two contributions in the interference channel 2 map the transient population dynamics of the 4p-state but with opposite signs in the amplitude \( 1/\delta_1 \) and in the time-dependent phase \( \delta_1 t \) as described by Eq. (9). While the sign change in the phase explains the previously described energetic splitting, the different signs of the amplitudes lead to a theoretical MPI-phase difference of \( \Delta \gamma_{\text{theo}}(2, \text{up}-2, \text{low}) = -\pi \) (cf. Fig. 2b) and Tab. I. The measured MPI-phase difference of \( \Delta \gamma(2, \text{up}-2, \text{low}) = -3.1 \text{ rad} \) confirms the above physical picture.

Finally, we discuss the interference pattern observed in channel 1 by analyzing the phase contrast map shown in Fig. 5. Both, the measured and the simulated phase contrast maps in frame (a) and (b) show a pronounced spectral shearing around \( \varepsilon_1 \) corresponding to an approximately linear spectral phase. Following the discussion in Sec. III B, we explain the linear spectral phase by identifying a time delay in the resonant photoionization. The \( (2+1) \) REMPI pathway \( R_{\text{II}} \) in channel 1 consists of the 2-photon resonant excitation of the 3d-state with the red pulse and the 1-photon ionization with the blue pulse. The physical picture to rationalize the time delay is illustrated in the bottom frame of Fig. 2(c). Due to the 2-photon resonance, the time evolution of the population amplitude of the 3d-state has a sigmoidal shape. Since the REMPI process is characterized by the ionization of the resonant 3d-state, the product of the temporal envelope of the ionizing pulse and the time-dependent population amplitude appear in the perturbative description of the photoionization in Eq. (13). Hence, the temporal envelope of the ionizing blue pulse \( E_\text{b}(t) \) is windowed by the sigmoidal-shaped population amplitude \( f_\text{II}^\text{\sigma}(t) \). The windowing results in a time delayed formation of the photoelectron wave packet from \( (2+1) \) REMPI with respect to the temporal pulse envelope. The interference of the time delayed wave packet from the resonant \( (2+1) \) REMPI pathway \( R_{\text{II}} \) with the wave packet from the near-resonant \( (1+2) \) REMPI pathway \( R_1 \) in channel 1 gives rise to the spectral shearing in the phase map [27, 53, 71]. Assuming a Gaussian-shaped temporal pulse envelope \( \tilde{E}(t) \), the associated linear spectral phase can be approximated around the center of the signal \( (\pi(\varepsilon) = 0) \) by \( \xi(\varepsilon) \approx -\frac{\omega_R}{\omega_b} \varepsilon + \xi_0 \) with the resonance-induced time delay \( \tau_{\text{res}} \) from Eq. (18) (see Appendix B 3 a for a detailed discussion). For the field parameters used in the experiment (Sec. III B), we calculate a delay of \( \tau_{\text{res}} \approx 19 \text{ fs} \) which corresponds to a slope of 37 meV/\( \text{rad} \). This slope derived from theory is indicated in Fig. 5(b) and in good agreement with the observed shearing in the phase contrast map of channel 1. Our results show that multichannel interferometry with temporally overlapping trichromatic fields allows to unambiguously determine the MPI-phases acquired in REMPI processes.

V. SUMMARY AND CONCLUSION

In this work, we presented a pulse shaper-based trichromatic multichannel wave packet interferometry scheme to study the quantum phases induced by multiphoton ionization (MPI) dynamics. We demonstrated the scheme on the MPI of potassium atoms with temporally overlapping parallel linearly polarized trichromatic fields. By appropriate choice of the optical frequencies so that \( 2\omega_b = \omega_1 + \omega_0 < \omega_\text{IP} \), the photoelectron wave packets overlap in different interference channels and create three energetically separated interferograms. These interferograms are sensitive to both the optical and the MPI-phases acquired along the different MPI pathways. Due to the design of the scheme, the optical
phase is identical in all interferograms. Therefore, the measured phase shifts directly revealed the MPI-phases introduced by the MPI dynamics in the different interference channels. Specifically, the red pulse was tuned to the two-photon 4s → 3d transition, opening a (2+1) REMPI pathway via ionization with the blue pulse. The green and the blue pulse were tuned close to the 4p-resonance with opposite detunings to implement two different (1+2) REMPI pathways via trichromatic frequency mixing. We observed high-contrast phase-shifted intensity modulations in the photoelectron interferograms by varying the green pulse’s relative phase. By introducing an optical phase of −π to the blue pulse, the interferograms were inverted and used to remove the phase-insensitive background. Analysis of the background-free interferograms unambiguously revealed the MPI-phases introduced by the intermediate resonances.

The measured interferograms showed that the MPI-phases in the photoelectron interferogram manifest in three different ways. First, we observed an energetic splitting of the photoelectron interferograms from red- and blue-detuned (1+2) REMPI. Although interferograms from frequency mixing pathways consisting of the permutations of different should be energetically degenerate, we demonstrated that the near- but non-resonant excitation of the intermediate 4p-state lifts this degeneracy. Second, we observed constant phase shifts of π both between the split interferograms within one interference channel and between interferograms of different interference channels. These phase shifts between the different (1+2) REMPI signals originate from population amplitudes with opposite signs. Finally, we demonstrated that the photoionization time delay through the resonant excitation of the 3d-state in the (2+1) REMPI pathway gives rise to a linear spectral phase in the photoelectron interferograms observed in the pronounced spectral shearing. All observations were analyzed using an analytic perturbative description and numerical simulations of a trichromatic driven three-level system coupled to the continuum.

In conclusion, we demonstrated that our shaper-based trichromatic multichannel interferometry scheme is a powerful tool to measure the phase of the ultrafast free electron wave packets. We showed that the resonance-induced photoionization time delay associated with a linear spectral phase is a general feature of processes involving a resonant intermediate state. For example, the structure of bichromatic photoelectron vortices as reported in 28–30 is affected by the intermediate resonances. Currently, we investigate further applications of multichromatic free electron vortex spectroscopy in our labs. In general, our results show that multicolor schemes open up entirely new perspectives for the measurement and coherent control of ultrafast quantum dynamics if we succeed in harnessing the great variety of interference pathways by a suitable design of the experiment.

VI. ACKNOWLEDGMENTS

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Appendix A: Generic three-level system

For the convenience of the reader and to introduce our notation, this appendix provides a detailed description of the multichannel interferometry scheme studied in the experiment. In this section, we describe the perturbative excitation of a generic three-level atom by a laser electric field \( E(t) = E(t)e^{-i\omega t} \), with the pulse envelope \( \tilde{E}(t) \) and the central frequency \( \omega_0 \). The three-level model system, as depicted in Fig. 2(a), consists of the states \( |g\rangle \), \( |a\rangle \) and \( |b\rangle \) with the corresponding transition frequencies \( \omega_{ag} \), \( \omega_{ab} \), and \( \omega_{ba} \). Expanding the system state into this basis, i.e. \( |\psi(t)\rangle = \sum_{n=a,b,g} c_n(t)|n\rangle \), the laser-atom interaction is described by the TDSE

\[
\frac{i\hbar}{\partial t} \begin{pmatrix} c_g(t) \\ c_a(t) \\ c_b(t) \end{pmatrix} = \mathcal{H}(t) \begin{pmatrix} c_g(t) \\ c_a(t) \\ c_b(t) \end{pmatrix} \tag{A1}
\]

for the population amplitudes \( c_n(t) \). The Hamiltonian is given in the dipole approximation by

\[
\mathcal{H}(t) = \begin{pmatrix} 0 & -\mu_{ag}E^*(t) & 0 \\ -\mu_{ag}E(t) & \hbar\omega_a & -\mu_{ab}E^*(t) \\ 0 & -\mu_{ab}E(t) & \hbar\omega_b \end{pmatrix} \tag{A2}
\]

The TDSE is solved iteratively on a discrete temporal grid with stepsize \( \delta t \) using the short-time propagator technique 74–76

\[
\begin{pmatrix} c_g(t+\delta t) \\ c_a(t+\delta t) \\ c_b(t+\delta t) \end{pmatrix} = e^{-i\mathcal{H}(t)\delta t} \begin{pmatrix} c_g(t) \\ c_a(t) \\ c_b(t) \end{pmatrix} \tag{A3}
\]

and assuming the atom to be initially in the ground state. The photoionization of the population in state \( |b\rangle \) is described by the excitation of a final free electron state \( |f\rangle \) with \( \omega_{bf}(\varepsilon) = \omega_f(\varepsilon) - \omega_b \) as shown in Fig. 2(a).

Appendix B: Perturbative description of MPI-phases

1. Excitation of the state \( |a\rangle \)

The population amplitude \( c_a(t) \) of the state \( |a\rangle \) is given by 1st order perturbation theory 77, 78

\[
c_a(t) = -\frac{\mu_{ag}}{i\hbar} \int_{-\infty}^{t} \mathcal{E}(t')e^{-i\delta t} dt', \tag{B1}
\]
with the detuning $\delta_1 = \omega_0 - \omega_{bg}$ and the transition dipole moment $\mu_{bg}$. For $t \to \infty$, Eq. [B1] leads to the well-known result $c_a(\infty) = -\frac{i\mu_{bg}}{\hbar}\hat{E}(\delta_1)$. Hence, the final population amplitude of state $|a\rangle$ is given by the spectral amplitude at the transition frequency. In general, by extending the integral in Eq. [B1] up to infinity, utilizing the Heaviside function $\theta(t)$, we obtain

$$c_a(t) = -\frac{\mu_{bg}}{2\pi\hbar} \int_{-\infty}^{\infty} \hat{E}(\omega)e^{-i\delta_1 t}\theta(t-t')dt'. \quad (B2)$$

Applying the Fourier transform in combination with the convolution theorem the amplitude can be written as

$$c_a(t) = -\frac{\mu_{bg}}{2\pi i\hbar} \left[ \pi \delta(\omega) + i\frac{\epsilon_{-i\omega}}{\omega} \right] \hat{E}(\omega)(\delta_1). \quad (B3)$$

Note that the convolution integral of the second term is only defined as its Cauchy principal value [79, 80], denoted as $\hat{f}$. Hence, the time-dependent population amplitude of $|a\rangle$ reads

$$c_a(t) = -\frac{\mu_{bg}}{2\pi i\hbar} \left( \pi \hat{E}(\delta_1) - i \int_{-\infty}^{\infty} \hat{E}(\omega)e^{i(\omega t - \delta_1 t)}d\omega \right). \quad \quad (B4)$$

$$\quad a. \text{Resonant excitation of the state } |a\rangle:\n$$

For resonant excitation of the state $|a\rangle$, i.e. $\delta_1 = 0$, the population amplitude is given by

$$c_a^{\text{res}}(t) = -\frac{\mu_{bg}}{2\pi i\hbar} \left( \pi \hat{E}(0) - i \int_{-\infty}^{\infty} \hat{E}(\omega)e^{i\omega t}d\omega \right). \quad (B5)$$

Since the spectrum $\hat{E}(\omega)$ is symmetric, the real part of the integral vanishes and we find

$$c_a^{\text{res}}(t) = -\frac{\mu_{bg}}{2\pi i\hbar} \left( \pi \hat{E}(0) + \int_{-\infty}^{\infty} \hat{E}(\omega)\sin(\omega t)d\omega \right). \quad (B6)$$

For $t \to \pm\infty$ the integral is identified with $\pm\pi\hat{E}(0)$ by using the definition of the $\delta$-distribution S1 S2. Hence, in the resonant case we obtain the known expressions

$$c_a^{\text{res}}(-\infty) = 0 \quad \text{and} \quad c_a^{\text{res}}(\infty) = -\frac{\mu_{bg}}{i\hbar} \hat{E}(0). \quad (B7)$$

In the following, we consider the non-resonant excitation of the state $|a\rangle$, since the equivalent 4p-state in the experiment is also excited only near- but non-resonantly (cf. mechanical blocker in Sec. [11]).

$$1 \text{ Here, we use } \mathcal{F}\{f\}(\omega) = \int_{-\infty}^{\infty} f(t)e^{-i\omega t}dt \text{ as the convention for the Fourier transform of the function } f \text{ and the convolution theorem } \mathcal{F}\{f \ast g\}(\omega) = \mathcal{F}\{f\}(\omega) \ast \mathcal{F}\{g\}(\omega).$$

$$\quad b. \text{Non-resonant excitation of the state } |a\rangle:\n$$

For the non-resonant excitation of $|a\rangle$, i.e. if the detuning $\delta_1$ exceeds the spectral width $\Delta \omega$, it follows $\hat{E}(\delta_1) \approx 0$ such that the population amplitude from Eq. [B4] reads

$$c_a^{\text{non}}(t) = -\frac{\mu_{bg}}{2\pi \hbar} e^{-i\delta_1 t} \int_{-\infty}^{\infty} \hat{E}(\omega)e^{i\omega t}d\omega. \quad (B8)$$

For such a large detuning $\delta_1$ we use a series expansion of the fraction in the integral as $rac{1}{\omega - i\delta_1} \approx -\frac{i}{\delta_1} - \frac{\omega}{\delta_1^2} + \mathcal{O}\left(\frac{\omega^2}{\delta_1^3}\right)$. Thus, the principal value can be approximated by

$$\int_{-\infty}^{\infty} \hat{E}(\omega)e^{i\omega t}d\omega \approx -2\pi \left( \frac{1}{\delta_1} \hat{E}(t) - i \frac{\partial \hat{E}(t)}{\partial t} \right), \quad \quad \quad \quad (B9)$$

with the linear temporal phase $\zeta = \frac{\delta_1^2 \hat{E}(0)}{i \delta_1 \hat{E}(0)}$, neglecting higher order phases and assuming a symmetric pulse envelope, i.e., $\delta_1 \hat{E}(0) = 0$. For a Gaussian-shaped envelope the phase $\zeta$ takes the form $\zeta = -\Delta \omega^2 \frac{t}{\sin^2(\delta_1 t)}$. Therefore the transient population amplitude of the state $|a\rangle$ for non-resonant excitation is given by

$$c_a^{\text{non}}(t) \approx -\frac{\mu_{bg}}{\delta_1 \hbar} e^{-i\delta_1 t} \hat{E}(t), \quad \quad \quad \quad \quad (B10)$$

with the reduced detuning $\hat{\delta}_1 = \delta_1 + \zeta$. Hence, for non-resonant excitation the population amplitude $c_a(t)$ of the state $|a\rangle$ follows the temporal field envelope $\hat{E}(t)$ and decreases with the detuning via $1/\hat{\delta}_1$ which also takes into account its sign.

2. Excitation of the state $|b\rangle$

For the excitation of the state $|b\rangle$ via a two-photon process we apply 2\textsuperscript{nd} order perturbation theory. Assuming a non-resonant excitation of state $|a\rangle$, we build on the results from Sec. B1 i.e., Eq. [B10]. The population amplitude of $|b\rangle$ then takes the form

$$c_b(t) = -\frac{\mu_{ba}}{i\hbar} \int_{-\infty}^{t} c_a^{\text{non}}(t')\hat{E}(t')e^{-i\omega_{ba}t'}e^{i\omega_{ba}t'}dt'$$

$$= \frac{\mu_{ba} \mu_{bg}}{i\delta_1 \hbar^2} \int_{-\infty}^{t} \hat{E}(t')e^{-i\delta_2 t'}dt', \quad \quad \quad \quad \quad (B11)$$

with $\delta_2 = \delta_1 + \omega_{ba} - \omega_{ba}$. Note that the energy conservation is incorporated by the phase $e^{-i\delta_1 t}$ from Eq. [B11], shifting the transition frequency in the 2\textsuperscript{nd} order about the detuning of the non-resonant excitation from 1\textsuperscript{st} order, i.e., $\omega_{ba} \to \delta_1 + \omega_{ba}$. Following an analogous procedure
as described in Sec. B 1 we find
\[
c_b(t) = \frac{\mu_b^{(2)}}{2\pi i\delta_1 \hbar^2} \left( \pi \tilde{E}(0) - i \int_{-\infty}^{\infty} \tilde{E}(\omega) e^{-i(\delta_2 - \omega)t} d\omega \right),
\]
with \(\mu_b^{(2)} = \mu_{ba}H_{ag}\) as the two photon transition dipole moment.

a. Resonant excitation of state \(|b\rangle\):

For two-photon resonant excitation of \(|b\rangle\) we assume \(\delta_2 = 0\), leading to
\[
c_b^{\text{res}}(t) = \frac{\mu_{bg}^{(2)}}{2\delta_1 \hbar^2} \left( \pi \tilde{E}(0) - i \int_{-\infty}^{\infty} \tilde{E}(\omega) e^{i\omega t} d\omega \right).
\]
For a symmetric temporal pulse envelope \(\tilde{E}(t)\) and the MPI process to take place in a narrow time window, we can apply a series expansion at \(t = 0\). In this way, we find the analytical description for the resonant two-photon probability amplitude
\[
c_b^{\text{res}}(t) = \frac{\mu_{bg}^{(2)}}{2\delta_1 \hbar^2} e^{-i\frac{t^2}{2}} \left( \tilde{E}(0) + 2t\tilde{E}^2(0) + O(t^3) \right).
\]
Note that the term in the order of \(t^2\) vanishes since \(\tilde{E}(t)\) is assumed to exhibit a maximum at \(t = 0\). The second term in Eq. (B14) represents the linearly time-increasing population amplitude due to laser excitation and is a sufficient approximation only for \(t \approx 0\).

b. Non-resonant excitation of state \(|b\rangle\):

For non-resonant excitation of the \(|b\rangle\) state we use \(\delta_2 \neq 0\) in Eq. (B12). Analogous to 1st order perturbation theory in Sec. B 1 we assume a sufficiently large detuning compared to the spectral width of the second order spectrum such that \(\tilde{E}(2)(\delta_2) \approx 0\), which leads to
\[
c_b^{\text{non}}(t) \approx \frac{\mu_{bg}^{(2)}}{\hbar^2 \delta_1 \delta_2} e^{-i\delta_2 t} \tilde{E}^2(t).
\]
Due to the large detuning \(\delta_2\) in the experiment, we neglect an additional resonance induced quantum phase at this point, i.e., \(\delta_2 \approx \delta_2\). Similar to Eq. (B10), the population amplitude \(c_b^{\text{non}}(t)\) follows the quadratic temporal field envelope and decreases with the detunings via \(1/(\delta_1 \delta_2)\) which also takes into account their signs.

3. Excitation of the state \(|f\rangle / photoionization

To describe the photoionization of the (non-)resonantly excited state \(|b\rangle\) into the final free electron state \(|f\rangle\) at energy \(\epsilon = \hbar\omega_f - \hbar\omega_{IP}\), we assume a perturbative one photon transition with \(t \rightarrow \infty\). Since we examine both resonant and non-resonant excitation of the state \(|b\rangle\) in the experiment (and in Sec. B 2), we distinguish between these two cases also for the photoionization step.

a. Photoionization of the resonantly excited state \(|b\rangle\)

To describe the photoionization of the resonantly excited state \(|b\rangle\), we build on Eq. (B14) which leads to
\[
c_f^{\text{res}}(\epsilon) \approx \frac{\mu_{fg}^{(3)}}{2\hbar^3 \delta_1} \int_{-\infty}^{\infty} \left( \tilde{E}^2(0) + 2t\tilde{E}^2(0) \right) \mathcal{E}(t') e^{-i\epsilon t'} dt',
\]
where \(\mu_{fg}^{(3)} = \mu_{fb} \mu_{bg} \mu_{gb}^{(2)}\) denotes the three-photon transition dipole moment and
\[
\mathcal{E}(\epsilon) = \omega_0 - \omega_f - \omega_b - \omega_{IP} \quad (B17)
\]
photoelectron detuning. Now, the linearly increasing population amplitude in the second term of Eq. (B16) windows the laser electric field of the probe pulse, ensuring the assumption of \(t \approx 0\) for the linear approximation in Sec. B 2. This windowing results in a time-shift between the probing electric field and the probed photoelectron distribution, resulting in a linear spectral phase (cf. bottom frame in Fig. 2(c)). Hence, the second term is equivalent to the first time-like moment of one part of the final population amplitude. Making use of the differentiation theorem for the Fourier transform [81, 82] we obtain the photoelectron amplitude
\[
c_f^{\text{res}}(\epsilon) \approx \frac{\mu_{fg}^{(3)}}{2\hbar^3 \delta_1} \tilde{E}^2(0) \tilde{E}(\varpi(\epsilon)) e^{-i\epsilon t},
\]
\[
\varpi(\epsilon) = \omega_0 - \omega_f - \omega_b = \frac{\epsilon}{\hbar} + \omega_b - \omega_{IP} \quad (B18)
\]
Around the center contribution of the photoelectron signal at \(\varpi(\epsilon) = 0\), the photoelectron amplitude can be approximated by
\[
c_f^{\text{res}}(\epsilon) \approx \frac{\mu_{fg}^{(3)}}{2\hbar^3 \delta_1} \tilde{E}^2(0) \tilde{E}(\varpi(\epsilon)) e^{i\xi(\epsilon)},
\]
with the additional resonance induced and energy-dependent quantum phase
\[
\xi(\epsilon) = -2 \tilde{E}^2(0) \frac{\partial \varpi}{\partial \epsilon} (\varpi(\epsilon)),
\]
Using again a Gaussian-shaped envelope we find
\[
\xi(\epsilon) = 4\sqrt{\ln(2)} \frac{\varpi(\epsilon)}{\Delta \omega} - \tau_{\text{res}} \frac{\epsilon}{\hbar} + \xi_0,
\]
with the resonance induced time delay $\tau_{\text{res}} = \sqrt{\frac{\ln(2)}{\Delta \nu}}$, and an offset $\xi_0 = 4\sqrt{\frac{\ln(2)}{\Delta \nu}} \omega_{\Delta \omega}^{-\omega_{\Delta \omega}}$.

\[ c_{f, \text{non}}^{\infty}(\varepsilon) = -\frac{\mu_{fg}^{(3)}}{i \hbar^3 \delta_1 \delta_2} \int_{-\infty}^{\infty} \mathcal{E}^3(t') e^{-i \delta_1 t'} e^{-i \omega \varepsilon(t') dt'} = i \frac{\mu_{fg}^{(3)}}{\hbar^3 \delta_1 \delta_2} \mathcal{E}^3(\varepsilon) (\pi(\varepsilon) + \delta_2), \quad (B22) \]

which agrees with the results from [77, 83] for fully non-resonant MPI processes.

\[ \text{b. Photoionization of the non-resonantly excited state} |b\rangle \]

Photoionization of the non-resonantly excited state $|b\rangle$ is based on Eq. (B15) and leads to a photoelectron am-

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