Controlling electron quantum paths for generation of circularly polarized high-order harmonics by $\text{H}_2^+$ subject to tailored $(\omega, 2\omega)$ counter-rotating laser fields

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Recently, studies of high-order harmonics (HHG) from atoms driven by bichromatic counter-rotating circularly polarized laser fields as a source of coherent circularly polarized extreme ultraviolet (XUV) and soft-x-ray beams in a tabletop-scale setup have received considerable attention. Here, we demonstrate the ability to control the electron recollisions giving three returns per one cycle of the fundamental frequency $\omega$ by using tailored bichromatic ($\omega, 2\omega$) counter-rotating circularly polarized laser fields with a molecular target. The full control of the electronic pathway is first analyzed by a classical trajectory analysis and then extended to a detailed quantum study of $\text{H}_2^+$ molecules in bichromatic ($\omega, 2\omega$) counter-rotating circularly polarized laser fields. The radiation spectrum contains doublets of left- and right-circularly polarized harmonics in the XUV ranges. We study in detail the below-, near-, and above-threshold harmonic regions and describe how excited-state resonances alter the ellipticity and phase of the generated harmonic peaks.

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I. INTRODUCTION

High-order-harmonic generation (HHG) is an attractive table-top source of coherent, bright, and tunable extreme ultraviolet (XUV) and soft-x-ray radiation with applications in coherent diffractive imaging, ultrafast holography, and time resolved measurements [1–6]. Moreover, circularly polarized HHG may find additional applications in nanolithography, ultrafast spin dynamics, and magnetic circular dichroism [1,7–13].

A direct approach for generating circularly polarized HHG was suggested 22 years ago [14,15] and was recently measured by Fleischer et al. [7]. In this scheme, circularly polarized HHG is driven by copropagating circularly polarized bichromatic fields that rotate in opposite directions (counter-rotating) and interact with argon gas. This experiment [7] opened up the possibility and motivation of generating bright circularly polarized HHG comparable to the flux efficiency of linearly polarized HHG. Recently, Fan et al. [1] did just that: they generated bright circularly polarized soft-x-ray HHG beams with photon energies greater than 160 eV and flux comparable to the HHG flux obtained using linearly polarized 800 nm driving lasers. These bright circularly polarized high-order-harmonic beams in the soft-x-ray region were generated from He, Ne, and Ar atoms, and used to implement x-ray magnetic circular dichroism measurements in a tabletop-scale setup [1]. Previously, such radiation has only been available at large-scale x-ray facilities such as synchrotrons.

The primary characteristics of the bichromatic circularly polarized HHG spectra can be described in terms of energy and angular-momentum conservation, which gives rise to a doublet structure of the HHG spectrum. The right peak in the doublet has a circular polarization with the same helicity as the driving field with the higher frequency, and the left peak has a circular polarization with the same helicity as the driving field with the lower frequency [1,7–13,16,17]. The driving laser field parameters determine the spectral, temporal, and polarization properties of the circularly polarized HHG, enabling the creation of tailored circularly polarized HHG waveforms [16]. For instance, the frequencies of the bichromatic laser field can be chosen to tune the photon energy and bandwidth of the emitted harmonics from the XUV to the soft-x-ray region [1,16]. Also, in the same respect the relative intensity ratio of the bichromatic laser field can be adjusted to preferentially select either the right- or left-circularly polarized harmonics [16]. In the frequency domain, this enhances the harmonic orders that rotate in the same direction as the higher-intensity driving laser.

While impressive progress has been achieved in the generation of bright circularly polarized radiation by atomic targets, this area remains largely unexplored for molecular systems. In this work, we address the problem with the $\text{H}_2^+$ molecule subject to bichromatic counter-rotating circularly polarized intense laser fields and adopt the wavelengths (790 and 395 nm) reported in a recent experiment [16]. We show through the use of a tailored relative intensity ratio of the bichromatic laser field that we can generate radiation with circular polarization and have control over the electronic recollisions in the time domain for the $\text{H}_2^+$ molecule. We control the period of the recollisions with help from classical trajectory analysis and apply it to a nonperturbative quantum investigation to produce a recollision event that features three returns for any 790 nm cycle during the...
laser pulse. We also find that excited-state resonances can alter neighboring doublet structures in the HHG spectrum, and can also deviate the phase and ellipticity of neighboring doublets breaking down their perfect circular polarization.

The organization of this paper is as follows: In Sec. II we briefly discuss our theoretical and computational approach for the general treatment of the multiphoton dynamics of diatomic molecular systems subject to bichromatic counter-rotating circularly polarized intense laser fields. In Sec. III we explore the control of the electronic pathway with use of the standard classical approach. In Sec. IV we study HHG of H$_2^+$ molecules driven by bichromatic counter-rotating circularly polarized laser pulses. The HHG spectra exhibit a distinct doublet structure, and the harmonics within each doublet possess circular polarizations with opposite handedness. In Sec. V we employ the synchrosqueezing transform (SST) to analyze the time-frequency spectra of the below-, near-, and above-threshold HHG of H$_2^+$. We show that the electron returns are controlled with the intensity parameters used, and three dominant returns are seen within one cycle of the 790 nm field. In Sec. VI we provide a proof of perfect circular polarization and opposite handedness of the harmonics within the doublets by calculating their ellipticity and phase parameters from the dipole acceleration data for below-, near-, and above-threshold HHG regions. We also show that excited-state resonances have effects on neighboring harmonics altering their perfect circular polarization. Section VII contains concluding remarks.

II. THEORY AND NUMERICAL TECHNIQUES

To calculate the HHG spectra, we solve the time-dependent Schrödinger equation for the H$_2^+$ molecule in the bichromatic counter-rotating circularly polarized laser fields. The initial wave function is an unperturbed eigenfunction of H$_2^+$. For our calculations, we select the ground (1σ_g) electronic state. The nuclei are fixed at their positions, and the nuclear motion is not taken into account. To describe the diatomic molecular ion H$_2^+$, we make use of the prolate spheroidal coordinates $\xi$, $\eta$, and $\varphi$ which are related to the Cartesian coordinates $x$, $y$, and $z$ as follows [18]:

$$
\begin{align*}
x &= a \sqrt{(\xi^2 - 1)(1 - \eta^2)} \cos \varphi, \\
y &= a \sqrt{(\xi^2 - 1)(1 - \eta^2)} \sin \varphi, \\
z &= a \xi \eta (1 \leq \xi < \infty, -1 \leq \eta \leq 1).
\end{align*}
$$

In Eq. (1) we assume that the molecular axis is directed along the $z$ axis, and the nuclei are located on this axis at the positions $-a$ and $a$, so the internuclear separation $R = 2a$. The internuclear distance for the H$_2^+$ ($R_c = 2.00a_0$) molecule is fixed at its equilibrium distance $R_c$.

A. Generalized pseudospectral method and solution of time-independent eigenvalue problem

First, we solve the unperturbed eigenvalue problem and obtain the eigenvalues and eigenfunctions:

$$
\left(-\frac{1}{2} \nabla^2 + U(\xi, \eta)\right)\Psi(\xi, \eta, \varphi) = E \Psi(\xi, \eta, \varphi).
$$

Here the kinetic-energy operator in the prolate spheroidal coordinates reads

$$
-\frac{1}{2} \nabla^2 = -\frac{1}{2a^2} \left(\xi^2 - \eta^2\right) \left[\frac{\partial}{\partial \xi} \left(\xi^2 - 1\right) \frac{\partial}{\partial \xi} + \frac{\partial}{\partial \eta} \left(1 - \eta^2\right) \frac{\partial}{\partial \eta}\right] \\
\quad + \frac{\xi^2 - \eta^2}{(\xi^2 - 1)(1 - \eta^2)} \frac{\partial^2}{\partial \varphi^2},
$$

(3)

and the Coulomb interaction with the nuclei is as follows (the charge of each center is unity):

$$
U(\xi, \eta) = -\frac{2e}{a(\xi^2 - \eta^2)}.
$$

(4)

For the unperturbed molecule, the projection $m$ of the angular momentum onto the molecular axis is conserved. Thus the wave function $\Psi(\xi, \eta, \varphi)$ can be represented in a separable form,

$$
\Psi(\xi, \eta, \varphi) = \psi_m(\xi, \eta) \exp(i m \varphi),
$$

(5)

and separate eigenvalues problems for different $|m|$ are obtained,

$$
-\frac{1}{2a^2} \left(\xi^2 - \eta^2\right) \left[\frac{\partial}{\partial \xi} \left(\xi^2 - 1\right) \frac{\partial}{\partial \xi} + \frac{\partial}{\partial \eta} \left(1 - \eta^2\right) \frac{\partial}{\partial \eta}\right] \\
- \frac{m^2}{\xi^2 - 1 - \eta^2} \psi_m = E \psi_m.
$$

(6)

To solve Eq. (6), we use the generalized pseudospectral (GPS) method. Note that the exact eigenfunction $\psi_m$ behaves as $(\xi^2 - 1)^{|m|/2}(1 - \eta^2)^{|m|/2}$ in the vicinity of the nuclei; for odd $|m|$, this is a nonanalytical function of the coordinates. Straightforward numerical differentiation of such a function could result in significant loss of accuracy. We circumvent this difficulty by choosing a special mapping transformation within the GPS method [19]. Other details of the GPS method in prolate spheroidal coordinates can be found in Refs. [20–24].

Solving the eigenvalue problem (6) for different even and odd $m$, we obtain unperturbed energy values and eigenstates of H$_2^+$, which are used as initial states for time propagation as well as for construction of propagation matrices.

B. Solution of time-dependent Schrödinger equation in bichromatic circularly polarized laser pulses

The time-dependent Schrödinger equation in the bichromatic circularly polarized laser pulses is solved by means of the split-operator method in the energy representation [20–25]. We employ the following split-operator, second-order short-time propagation formula:

$$
\Psi(t + \Delta t) = \exp \left(-i \frac{1}{2} \Delta t H_0\right) \\
\times \exp \left[-i \Delta t V_{\text{ext}}(r, t + \frac{1}{2} \Delta t)\right] \\
\times \exp \left(-i \frac{1}{2} \Delta t H_0\right) + O((\Delta t)^3).
$$

(7)

Here $\Delta t$ is the time propagation step, $H_0$ is the unperturbed electronic Hamiltonian which includes the kinetic energy and interaction with the nuclei, $V_{\text{ext}}(r, t)$ is the term due to the
coupling to the bichromatic circularly polarized external fields in the following form:

$$V_{ext}(r,t) = \{E_1(t) + E_2(t)\} \cdot \mathbf{r}.$$  

(8)

The laser electric-field strengths $E_1(t)$ and $E_2(t)$ refer to the two frequency components of the bichromatic field.

In what follows, we assume that the laser fields $E_1(t)$ and $E_2(t)$ propagate along the $z$ axis and have circular polarizations on the $x$-$y$ plane. The counter-rotating fields $E_1(t)$ and $E_2(t)$ are expressed as follows:

$$E_1(t) = \frac{1}{\sqrt{2}} F_1(t)[\hat{e}_x \cos(\omega_1 t) + \hat{e}_y \sin(\omega_1 t)],$$  

(9)

$$E_2(t) = \frac{1}{\sqrt{2}} F_2(t)[\hat{e}_x \cos(\omega_2 t) - \hat{e}_y \sin(\omega_2 t)].$$  

(10)

Since the dipole approximation is well justified in the near-infrared and visible wavelength region, the fields are assumed uniform in space. In Eqs. (9) and (10), $\omega_1$ and $\omega_2$ denote the carrier frequencies while $F_1(t)$ and $F_2(t)$ represent the temporal pulse envelopes. We use the sinesquared pulse shape:

$$F_1(t) = F_1 \sin^2 \frac{\pi t}{N_1 T_1},$$  

(11)

$$F_2(t) = F_2 \sin^2 \frac{\pi t}{N_2 T_2},$$  

(12)

where $F_1$ and $F_2$ are the peak electric-field strengths, $T_1$ and $T_2$ are the optical cycle durations for each field ($T_1 = 2\pi/\omega_1$ and $T_2 = 2\pi/\omega_2$), and the integers $N_1$ and $N_2$ are the total pulse durations measured in optical cycles.

The dipole interaction potentials in the length gauge have the following expressions in prolate spheroidal coordinates:

$$E_1(t) \cdot \mathbf{r} = \frac{a}{\sqrt{2}} F_1(t) \sqrt{(\xi^2 - 1)(1 - \eta^2)} \times \cos(\phi - \omega_1 t),$$  

(13)

$$E_2(t) \cdot \mathbf{r} = \frac{a}{\sqrt{2}} F_2(t) \sqrt{(\xi^2 - 1)(1 - \eta^2)} \times \cos(\phi + \omega_2 t).$$  

(14)

In our calculations, we use the carrier wavelengths 395 nm for the field $E_1(t)$ ($\omega_1 = 0.1153$ a.u. = 3.14 eV) and 790 nm for the field $E_2(t)$ ($\omega_2 = 0.0576$ a.u. = 1.57 eV), respectively. One cycle of the $\omega_1$ and $\omega_2$ fields are 1.32 and 2.64 fs, respectively. The peak field strengths $F_1$ and $F_2$ correspond to the intensities $I_1 = 2 \times 10^{13}$ W/cm$^2$ and $I_2 = 1.25 \times 10^{13}$ W/cm$^2$, respectively. The pulse durations are chosen as $N_1 = 34$ and $N_2 = 17$. The total pulse duration for both fields is 45 fs. To obtain converged HHG spectra for the laser field parameters used in the calculations, we set the grid size (for $\xi$, $\eta$, and $\phi$ coordinates, respectively) to $160 \times 48 \times 48$ and use 4096 time steps per one 395 nm ($\omega_1$) optical cycle in the time propagation process. The spatial and temporal grid parameters have been varied to make sure all the results are fully converged. The linear dimension of the box where the time-dependent equations are solved is chosen as 50 a.u. to ensure accurate description of all important physics for the laser field parameters used in the calculations; between 30 and 50 a.u. we apply an absorber which smoothly brings down the propagated wave functions without spurious reflections from the boundary.

The HHG power spectra can be investigated accurately once the time-dependent wave function $\Psi(\xi,\eta,\phi,t)$ is available. We calculate the expectation values of the induced dipole acceleration in the $x$, $y$, and $z$ directions:

$$a_x(t) = \left\langle \frac{\partial^2 U(\xi,\eta,\phi)}{\partial x^2} \right\rangle \Psi(\xi,\eta,\phi,t)$$  

$$+ E_{1x}(t) + E_{2x}(t),$$  

(15)

$$a_y(t) = \left\langle \frac{\partial^2 U(\xi,\eta,\phi)}{\partial y^2} \right\rangle \Psi(\xi,\eta,\phi,t)$$  

$$+ E_{1y}(t) + E_{2y}(t),$$  

(16)

$$a_z(t) = \left\langle \frac{\partial^2 U(\xi,\eta,\phi)}{\partial z^2} \right\rangle \Psi(\xi,\eta,\phi,t).$$  

(17)

Then the power spectrum $S(\omega)$ (spectral density of the radiation energy) can be obtained by the Fourier transformation of the time-dependent dipole accelerations,

$$S_x(\omega) = \frac{2}{3\pi c^3} \left| \int_{-\infty}^{\infty} a_x(t) \exp(i\omega t) dt \right|^2,$$  

(18)

$$S_y(\omega) = \frac{2}{3\pi c^3} \left| \int_{-\infty}^{\infty} a_y(t) \exp(i\omega t) dt \right|^2,$$  

(19)

$$S_z(\omega) = \frac{2}{3\pi c^3} \left| \int_{-\infty}^{\infty} a_z(t) \exp(i\omega t) dt \right|^2,$$  

(20)

$$S_{\text{tot}}(\omega) = S_x(\omega) + S_y(\omega) + S_z(\omega).$$  

(21)

We note that, for the homonuclear diatomic molecule H$_2^+$ initially in the state with the definite parity and laser fields polarized in the plane perpendicular to the molecular ($z$) axis, the contribution $S_z(\omega)$ vanishes.

### III. Controlling Classical Return Times for Molecules in Bichromatic Counter-Rotating Circularly Polarized Laser Fields

The classical trajectory of the electron subject to bichromatic counter-rotating circularly polarized laser fields in the $x$-$y$ plane is given by the equations

$$x = \frac{1}{\sqrt{2}} \left[ \frac{F_1}{\omega_1^2} \cos \omega_1 t + \frac{F_2}{\omega_2^2} \cos \omega_2 t \right]$$  

$$+ \frac{1}{\sqrt{2}} \left[ \frac{F_1}{\omega_1^2} \sin \omega_1 t + \frac{F_2}{\omega_2^2} \sin \omega_2 t \right] (t - t_0)$$  

$$- \frac{1}{\sqrt{2}} \left[ \frac{F_1}{\omega_1^2} \cos \omega_1 t_0 + \frac{F_2}{\omega_2^2} \cos \omega_2 t_0 \right].$$  

(22)

$$y = \frac{1}{\sqrt{2}} \left[ \frac{F_1}{\omega_1^2} \sin \omega_1 t - \frac{F_2}{\omega_2^2} \sin \omega_2 t \right]$$  

$$- \frac{1}{\sqrt{2}} \left[ \frac{F_1}{\omega_1^2} \cos \omega_1 t_0 - \frac{F_2}{\omega_2^2} \cos \omega_2 t_0 \right].$$  

(23)
Here $F_1$ and $F_2$ are constants, so the pulse envelope is not taken into account. This approximation is reasonable in the vicinity of the envelope maximum where the HHG mostly takes place. Equations (22) and (23) correspond to the zero position and zero velocity at $t = t_0$ and generally describe an infinite motion of the electron. A closed periodic trajectory is obtained with the zero drift velocity. In this case one has instead of Eqs. (22) and (23):

$$
x = \frac{1}{\sqrt{2}} \frac{F_1}{\omega_1} \left[ \cos \omega_1 t - \cos \omega_1 t_0 \right],
$$

$$\quad + \frac{1}{\sqrt{2}} \frac{F_2}{\omega_2} \left[ \cos \omega_2 t - \cos \omega_2 t_0 \right],
$$

$$
y = \frac{1}{\sqrt{2}} \frac{F_1}{\omega_1} \left[ \sin \omega_1 t - \sin \omega_1 t_0 \right],
$$

$$\quad - \frac{1}{\sqrt{2}} \frac{F_2}{\omega_2} \left[ \sin \omega_2 t - \sin \omega_2 t_0 \right].
$$

(24)

The period of this trajectory is equal to the largest of the two optical cycles ($T_2$), thus in the general case it returns to the origin once per every $T_2$ time interval. However, if the field strengths $F_1$ and $F_2$ satisfy the condition

$$
\frac{F_2}{F_1} = \frac{\omega_1^2}{\omega_2^2},
$$

(26)

the trajectory may manifest three returns per $T_2$ optical cycle (2.64 fs) if a specific release time $t_0$ is chosen. The analytic expression of this trajectory for constant $F_1$ and $F_2$ is as follows ($\omega_2 t_0 = \pm \pi / 3$):

$$
x = \frac{F_1 \sqrt{2}}{\omega_1^2} \cos \left( \frac{1}{2} \omega_2 t \right) \cos \left( \frac{3}{2} \omega_2 t \right).
$$

(27)

$$
y = \frac{F_1 \sqrt{2}}{\omega_1^2} \sin \left( \frac{1}{2} \omega_2 t \right) \cos \left( \frac{3}{2} \omega_2 t \right).
$$

(28)

This property (three returns per $T_2$ optical cycle) is also preserved for the pulse envelope functions defined in Eqs. (11) and (12). The distance from the origin in the $x$-$y$ plane is calculated as

$$
r = \sqrt{x^2 + y^2}.
$$

(29)

A recollision event is detected when $r$ approaches zero.  

Figure 1(a) shows $x(t)$, $y(t)$, and $r(t)$ for the envelope functions (11) and (12) and peak field strengths $F_1$ and $F_2$ corresponding to the intensities $I_1 = 2 \times 10^{14}$ W/cm$^2$ and $I_2 = 1.25 \times 10^{13}$ W/cm$^2$, respectively. The gray filled box shows three returns per $T_2$ optical cycle (2.64 fs) in the central part of the pulse (22.0–27.3 fs). In Fig. 1(b) we show the classical electron trajectory that features three returns (threefold rosette shape) for any $T_2$ cycle during the laser pulse.

The circularly polarized laser pulses in the $x$ and $y$ domain ($E_x$ and $E_y$) using the controlled laser peak intensities $I_1$ and $I_2$ are shown in Figs. 2(a) and 2(b). Figure 2(a) shows the time-dependent electric field of the driving laser pulse for peak laser intensities of $I_1 = 2 \times 10^{14}$ W/cm$^2$ and $I_2 = 1.25 \times 10^{13}$ W/cm$^2$ for the total time duration of 45 fs. In Fig. 2(b) we show the counter-rotating laser fields in the $x$-$y$ polarization plane for the 45 fs time duration.

IV. CIRCULARLY POLARIZED HIGH-ORDER HARMONICS IN $H_2^+$ MOLECULES

The structure of the HHG spectra can be described in terms of the energy and angular-momentum conservation in the process of absorption of the driving fields photons and emission of the harmonic photon [1,6,7,13,14,16,17,21,25]. Energy conservation gives $\omega = n_1 \omega_1 + n_2 \omega_2$ for the frequency $\omega$ of the emitted photon after absorption of $n_1$ photons of frequency $\omega_1$ and $n_2$ photons of frequency $\omega_2$. Angular-momentum conservation requires $n_2 = n_1 \pm 1$ or $n_2 = n_1$ for the circularly polarized counter-rotating driving fields $E_1$ and $E_2$. However, for the quantum systems with inversion symmetry such as atoms and homonuclear diatomic molecules, emission of dipole radiation is forbidden in the case $n_2 = n_1$ due to parity restrictions. Then the emitted photon frequency can be represented as $\omega = (2n + 1)(\omega_1 + \omega_2)/2 \pm (\omega_1 - \omega_2)/2$, $n$ being a positive integer. This gives rise to a doublet structure of the HHG spectrum, with the frequency differences $\omega_1 + \omega_2$ between the
adjacent doublets and ω₁ − ω₂ between the photon emission peaks within the same doublet. The right peak in the doublet has a circular polarization with the same helicity as the driving field with the higher frequency (ω₂), whereas the left peak has a circular polarization opposite to each other. This rule is true except for higher-order below-threshold harmonics (H10–H20). In this region, excitation of the bound states and subsequent near-resonant emission alters the shape of the neighboring doublets in the HHG spectrum. In Fig. 3(b) two resonant peaks (marked A and B) are comparable in their height with the nearby regular harmonic peaks. The resonances A and B correspond to the transitions 1σ₂⁻1π₁ (H11.7) and 1σ₂⁻2π₂ (H15.6), respectively. Figures 3(c) and 3(d) show the above-threshold circularly polarized harmonics up to H74.

V. SYNCHROSQUEEZING TRANSFORM TIME-FREQUENCY SPECTRA

To analyze the underlying mechanism from the ab initio simulation, we perform the SST time-frequency analysis of the dipole acceleration for H₂⁺ interacting with the applied laser fields. In previous studies [27], several representative time-frequency methods have been compared for the atomic hydrogen system, including short-time Fourier transforms, such as the Gabor transform, the Wigner–Ville transform [28], and the SST [29,30], as well as the continuous wavelet transform, the bilinear time-frequency transform and the reallocation method, respectively. They found that both the Gabor and the Morlet transforms are subject to some obscure spectral features arising from a window and that the Wigner–Ville transform is accompanied by interference artifacts, resulting in incomprehensible analysis. Among these methods, only the SST can resolve the intrinsic blurring in the Gabor and the Morlet transforms [31]. Apart from the applications in atomic, molecular, and optical physics, the SST was successfully used for analysis of chronotaxic systems [32] and cardiovascular systems [33].

Here we perform the time-frequency SST analysis of the induced dipole accelerations \( a_x(t), a_y(t), \) and \( a_z(t) \) in the H₂⁺ diatomic molecule interacting with the applied laser fields [21,27,31,34]. The synchrosqueezing transforms \( \tilde{S}_x, \tilde{S}_y, \) and \( \tilde{S}_z \) of the corresponding dipole accelerations are defined as follows:

\[
\tilde{S}_{x,y,z}(t, \omega) = \int \frac{1}{\sqrt{\omega}} V_{x,y,z}(t, \omega) \frac{1}{\alpha \sqrt{\pi}} \times \exp \left( -\frac{\omega - \Omega^{I}_{x,y,z}(t, \omega)}{\alpha} \right) d\omega,
\]

where \( V_{x,y,z}(t, \omega) \) is the Morlet wavelet transform, \( \Omega^{I}_{x,y,z}(t, \omega) \) is the reallocation rule function, and \( \alpha \) is a smoothing parameter. In this study, \( \alpha = 2.6 \). The Morlet wavelet transform is given as

\[
V_{x,y,z}(t, \omega) = \int a_{x,y,z}(t') \sqrt{\omega} W(\omega(t' - t)) dt',
\]
where

$$W(\beta) = \frac{1}{\sqrt{\tau}} \exp(i\beta) \exp\left(-\frac{\beta^2}{2\tau^2}\right)$$

(32)
is the mother wavelet. The reallocation rule function is defined as

$$\Omega^\ell_{s,y,z}(t,\omega) = \begin{cases} 
-i\partial_t V_{s,y,z}(t,\omega) / V_{s,y,z}(t,\omega) & \text{for } V_{s,y,z}(t,\omega) \neq 0 \\
0 & \text{for } V_{s,y,z}(t,\omega) = 0
\end{cases}$$

(33)

where $\partial_t$ denotes the partial derivative in the temporal axis. In Fig. 4 we show the total absolute value of the SST spectrum $|\tilde{S}_{\text{tot}}(t,\tilde{\omega})|$ calculated as

$$|\tilde{S}_{\text{tot}}(t,\tilde{\omega})| = |\tilde{S}_s(t,\tilde{\omega})| + |\tilde{S}_y(t,\tilde{\omega})| + |\tilde{S}_z(t,\tilde{\omega})|.$$ 

(34)
The time-frequency spectrum $|\tilde{S}_{\text{tot}}|$ shows a periodic repetition of arches in the above-threshold region ($>H_{19.13}$) spanning to the 65th harmonic order ($H_{65}$). These periodic repetition of arches ($>H_{19.13}$) are comprised of three returns per $T_2$ optical cycle (2.64 fs). The quantum SST time-frequency analysis shows the same phenomena (three returns per $T_2$ optical cycle) as proposed by the controlled classical electron trajectories in Figs. 1(a) and 1(b).

VI. ELLIPTICITY AND RELATIVE PHASE SHIFT OF HARMONIC RADIATION

According to the discussion in Sec. IV, generation of high-order harmonics by bichromatic counter-rotating circularly

FIG. 4. SST time-frequency analysis $|\tilde{S}_{\text{tot}}|$ of the HHG spectra of $\text{H}_2^+$. The horizontal yellow solid line indicates the ionization potential $I_p$ at $\sim H_{19}$. The vertical white dashed lines indicates one cycle ($T_2$) of the $\omega_2$ field (2.64 fs). Three returns per $T_2$ optical cycle are observed, as proposed by the controlled classical electron trajectories in Figs. 1(a) and 1(b). The laser parameters used are the same as those in Fig. 3. The color scale is logarithmic.
polarized laser fields results in harmonic doublets, where in each doublet the harmonics are circularly polarized with opposite handedness. However, this argument assumes that the driving-field frequency components are perfectly monochromatic. In reality, the laser pulse has a finite duration, hence the harmonic peaks have a finite width, and polarization may vary even on the frequency range corresponding to the same harmonic peak. Near-resonant radiation from the excited states may also alter the polarization properties of the HHG spectrum in the below-threshold region. Here, we calculate the polarization properties of the harmonic radiation explicitly from the dipole acceleration data and show to what extent the harmonic peaks within the same doublet possess circular polarizations with left and right handedness.

Suppose we have a monochromatic field with the components along \( x \) and \( y \):

\[
F_x = a \cos(\omega t), \\
F_y = b \cos(\omega t + \beta).
\]

Generally, the field amplitudes along \( x \) and \( y \) are different (with their ratio \( r_{xy} = b/a \)), and there is a phase shift \( \beta \) between the field oscillations in the \( x \) and \( y \) directions. Actually, Eq. (35) represents an elliptically polarized field; the orientation of the ellipse in the \( x-y \) plane depends on the parameters \( r_{xy} \) and \( \beta \). The angle \( \alpha \) which determines the orientation of one of the ellipse axes with respect to the \( x \) axis is calculated as

\[
\alpha = -\frac{1}{2} \arctan \left(\frac{r_{xy}^2 \sin(2\beta)}{1 + r_{xy}^2 \cos(2\beta)}\right).
\]

The second axis has the orientation angle \( \alpha + \pi/2 \). Assuming the first axis to be the major axis of the ellipse, the ellipticity parameter is calculated as follows:

\[
\epsilon = \sqrt{\frac{\sin^2 \alpha + r_{xy}^2 \sin^2(\alpha + \beta)}{\cos^2 \alpha + r_{xy}^2 \cos^2(\alpha + \beta)}}.
\]

If the calculated ellipticity parameter \( \epsilon \) appears greater than unity, then the first axis is actually the minor axis, and the ellipticity parameter is given by \( 1/\epsilon \). From the Fourier transform of the induced dipole acceleration (which represents the harmonic field), one can obtain the parameters \( r_{xy} \) and \( \beta \) and calculate the ellipticity for the specific frequency \( \omega \). The circular polarization \( (\epsilon = 1) \) is only possible if \( \beta = \pm \pi/2 \) and \( r_{xy} = 1 \).

In Figs. 5–7, the filled maroon circles and filled teal squares indicate the positions of harmonic peaks within each doublet. The circular polarization of the harmonics marked with the teal squares has the same handedness (left helicity) as that of the driving field \( E_1(t) \), and the harmonics marked with the maroon circles are polarized with the same handedness (right helicity) as the driving field \( E_2(t) \).

Figure 5 shows the phase and ellipticity of the below-threshold harmonics in the HHG spectrum of the \( \text{H}_2^+ \) molecule (Fig. 3). As one can see in Fig. 5, the ellipticity of the below-threshold harmonics is near unity and the phases are very close to \( \pm \pi/2 \), indicating circular polarizations with left and right handedness. The phase and ellipticity of the harmonics are altered in the region where the excited-state resonances start to appear, hence, \( 1\sigma_g^{-1}\pi_u \) (H11.7) and \( 1\sigma_g^{-2}\pi_u \) (H15.6) excited-state resonance peaks shown in Fig. 3(b).

In the above-threshold plateau region (Figs. 6 and 7), the harmonics within the doublets still do not show perfect circular polarizations with their ellipticities and phases deviating from unity and \( \pm \pi/2 \), respectively. In the lower-energy part of this region (H19–H38; Fig. 6), right subpeaks in the doublets (teal squares) exhibit better circular polarization than the left subpeaks (maroon circles). In the higher-energy part (H54–H65, Fig. 7), the pattern is reversed; here more perfect circular polarization is observed for the left subpeaks (maroon circles). Generally, perfect circular polarization can be expected when the harmonic signals polarized in the \( x \) and \( y \) directions have equal strengths. The \( x \) and \( y \) components of the harmonic radiation, in turn, are induced by the \( x \) and \( y \) components of the driving field. Averaged over the total pulse duration, the intensities of the \( x \) and \( y \) components of the driving field are the same, but they may differ significantly on shorter (subcycle) time intervals (see Fig. 2). Since the high-order harmonics are predominantly generated during short recollision events in the central part of the laser pulse, they may be affected by the asymmetry between the \( x \) and \( y \) components of the driving field. In our previous work [17], we showed that for small frequency difference \( \omega_1 - \omega_2 \) this asymmetry can lead to
disappearance of the doublet structure and circular polarization of the harmonics in the HHG spectrum. In the present case $\omega_1 = 2\omega_2$, the doublet structure remains distinct but polarizations of the subpeaks may have significantly altered. As one can see from Fig. 3(c), the $x$ and $y$ contributions to the harmonic signal are very close to each other for the right subpeaks (teal squares) while considerable difference between these contributions is observed for the left subpeaks (maroon circles). Consequently, perfect circular polarization cannot be expected for the left subpeaks, in accordance with the results presented in Fig. 6. The pattern is changed for the higher-order harmonics, H54–H65. In this part of the spectrum [Fig. 3(d)], the $x$ and $y$ contributions to the harmonic signal are closer to each other for the left subpeaks (maroon circles), and their ellipticity is closer to unity than that of the right subpeaks (teal squares), as seen in Fig. 7. In the cutoff region, H67–74, both left and right subpeaks exhibit again almost perfect circular polarization. The transformations of the polarization properties of the above-threshold harmonics with their order could reflect the shifts of their emission times within the same optical cycle. With increasing harmonic order, the emission time of the harmonic is shifted backwards, as seen in the time-frequency spectrum (Fig. 4). Detailed analysis of this phenomenon could be a subject of a separate study.

VII. CONCLUSION

In this paper, we present a detailed investigation and analysis of $\text{H}_2^+$ diatomic molecules subject to bichromatic ($\omega$, $2\omega$) tailored counter-rotating circularly polarized intense laser fields. The intensities used in the calculations have been tailored through the use of classical trajectory analysis to produce three returns per $T_2$ optical cycle. The generated high-order harmonics exhibit circular polarization up to harmonic orders of H81. The HHG spectrum has a doublet structure where the harmonics within the same doublet have opposite (left and right) circular polarizations. The quantum SST analysis of the dipole accelerations shows distinctly three returns per $T_2$ optical cycle, agreeing with the proposed controlled classical trajectories analysis. In particular, we reveal that electron recollisions in molecular systems can be controlled through tailored bichromatic counter-rotating circularly polarized intense laser fields.

Furthermore, we find that excited-state resonances in the HHG spectrum can have effects on neighboring harmonics causing the phase and ellipticity to be altered from perfect circular polarization. Our study provides informative findings on the delicate electron dynamics in the below-, near-, and above-threshold harmonic regimes for diatomic molecules. Our findings can also be extended to facilitate the user-defined control of the electron quantum paths for experimental implementation of ultrashort and intense coherent light sources and frequency comb source, both in the VUV and soft-x-ray regimes, in the future.

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