

Coherent control of chirality flips in HCOOH(A'')ChunMei Liu,¹ Dongming Jia,^{1,*} Yuan Man^{2,†} and Yonggang Yang^{3,4}¹*Jiangsu Key Laboratory of Quantum Computing Science and Devices, College of Science, Nanjing University of Posts and Telecommunications, Nanjing 210023, China*²*Institut für Chemie und Biochemie, Freie Universität Berlin, 14195 Berlin, Germany*³*State Key Laboratory of Quantum Optics Technologies and Devices, Institute of Laser Spectroscopy, Shanxi University, Taiyuan 030006, China*⁴*Collaborative Innovation Center of Extreme Optics, Shanxi University, Taiyuan 030006, China*

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We design laser pulses to transform the oriented model formic acid (HCOOH) from its achiral ground state (A') to chiral configurations in the first excited state (A''). Optimal control of the production of the target enantiomer followed by enantiomer flips with highest enantiomeric excess is achieved by means of a linearly polarized laser pulse with optimal duration, field strength, frequency, and direction of polarization. The approach is motivated by effects of directionality of x-ray or laser pulses on different aspects of chirality of HCOOH discovered by the team of Dörner using cold target recoil ion momentum spectroscopy.

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I. INTRODUCTION

This work presents quantum model simulations of the coherent control of the selective production of enantiomers followed by chirality flips which proceed in the first excited state (A'') of formic acid (HCOOH). It is motivated by three discoveries of different aspects of the chirality of HCOOH by the joint experimental and theoretical team of experts coordinated by Dörner [1–3] (in brief the “Dörner-group”). First, since the equilibrium structure of HCOOH in the electronic ground state (A') is planar, it is achiral, with C_s symmetry; nevertheless, experimental investigations demonstrate that the individual molecules are chiral, allowing enantio-selective fragmentations [3]. This is a quantum effect due to out-of-plane delocalization of the nuclei in the vibronic ground state, cf. Ref. [4]. Second, one can use short (duration $\tau \approx 40$ fs) very strong (maximum intensity $I_{\max} \approx 1.3 \times 10^{15} \text{ W/cm}^2$) left or right circularly polarized laser pulses for enantio-selective multiphoton (wavelengths = 800 nm, photon energy $\hbar\omega = 1.55$ eV) multiple ionizations of the achiral molecule, followed by enantio-selective Coulomb explosion [1]. Third, multiple ionization followed by enantio-selective fragmentation can also be achieved by atomic core selective single-photon excitations (e.g., $C\ 1s \rightarrow \Pi^*$, $\hbar\omega = 288.2$ eV) by means of circularly or linearly polarized x-ray pulses, followed by Auger-Meitner decay

cascades [2]. The enantio-selectivity in Refs. [1–3] depends on the direction of the circularly polarized pulses, or on the direction of the linear polarization with respect to the molecule.

The experimental results in Refs. [1–3] were obtained by means of incoherent applications of cold target recoil ion momentum spectroscopy (COLTRIMS [5]) to myriads of single molecules. An advantage of COLTRIMS is that, upon measurement of the momenta of the fragments, one can reconstruct the geometry and the orientation of the multiple ionized single molecules with respect to the directions of the propagation or polarization of the laser or x-ray pulses. This way, the Dörner group discovered the important impact of these directions [1–3], stimulating the present search for directionality effects on coherent laser control. A disadvantage of COLTRIMS is that it does not reveal the individual processes which lead to enantiomer-selectivity, e.g., whether they proceed in the neutral or sequentially in the singly, doubly, and so on ionized target. Another disadvantage is that COLTRIMS destroys the object. Consequently, one cannot use COLTRIMS to observe any sequel processes triggered by the enantio-selective preparation of the target. Such processes are expected as a consequence of the fact that quantum mechanically, the selected enantiomers are not in an eigenstate, i.e., they can flip to the opposite enantiomers.

The challenge of the present work, stimulated by the results of the Dörner group [1–3], is to predict the effects of directionality of laser pulses for coherent control of enantiomer flips in the example of oriented HCOOH, specifically in its first excited state (A''), by means of quantum dynamics simulations. For this purpose, we adapt the simple one-dimensional (1D) model of the Dörner group [1–3], which accounts for the laser-induced dynamics of the most important degree of freedom of HCOOH, namely, its dihedral angle HCOO, called

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“ φ .” After all, torsional motions along φ lead from the planar molecular ground state (A') to the nonplanar configurations of the enantiomers in the excited state (A''); moreover, chirality flips from one enantiomer to the opposite enantiomer proceed along φ . By extrapolation, the success documented in Refs. [1–3] suggests that the 1D model can serve as proofs of principle, and it may even predict semi-quantitative (but of course not quantitative) results. Details of our implementation of the model are in Sec. II A below and in Sec. S1 of the Supplemental Material (SM) [6]. The present application to the model HCOOH, a molecule which is well characterized spectroscopically [7–9], serves as an example for other molecules which are achiral in the ground state but allow preparations of chiral excited states.

The literature already provides two scenarios for enantiomer-selective excitations of achiral molecules, followed by chirality flips. A prototype application is for the excitation of randomly oriented formamide molecules (CHONH_2) from the electronic ground state (A') to the first excited state (A''). The ground state has a single well potential with planar, achiral configuration at the potential minimum. The excited state has a symmetric double well potential with two minima supporting opposite enantiomers. Rouxel *et al.* suggested enantiomer-selective excitations by means of left or right circularly polarized short ($\tau = 30$ fs) laser pulses with photon energy ($\hbar\omega = 5.55$ eV) slightly below the ground to first valence excited state transitions (5.85 eV) [10]. The enantiomer-selectivity is achieved by interactions of the electric and magnetic fields of the laser pulses with the electric and magnetic transition dipoles of CHONH_2 . These localize the nuclear wavepacket in one or the other well of the double well potential of the excited electronic state, followed by transitions to the opposite potential well. The laser-driven nuclear wavepacket represents selective preparation of an enantiomer in the A'' state, followed by enantiomer flips. The mechanism of the wavepacket dynamics is, however, not revealed in Ref. [10]. In contrast, we shall present quantum simulations of the wavepacket dynamics of oriented HCOOH driven not only by circularly polarized, but also by elliptically polarized, and most importantly, by linearly polarized laser pulses with selective directionality, with photon energy above the ground to first valence excited state transitions, with laser-electric but without laser-magnetic dipole interactions, and with a detailed explanation of the resulting enantiomer selectivity and the subsequent enantiomer flips. The authors of Ref. [10] also suggested a method for probing the photoinduced molecular chirality by ultrafast x-ray spectroscopy; this may also be applied to the present chirality flips, but here we do not focus on methods for monitoring.

An alternative approach to light-induced temporary chirality in achiral molecules was developed by Leibscher *et al.* [11,12]. Essentially, they considered planar molecules, specifically COFCl, and suggested the preparation of the chiral superposition of the vibronic ground plus the first out-of-plane vibrational excited states, with subsequent chirality flips. This approach can be achieved by Raman excitation of oriented molecules [11] or by a combination of either microwave and IR pulses or a static field and a sequence of IR pulses applied to randomly oriented molecules [12].

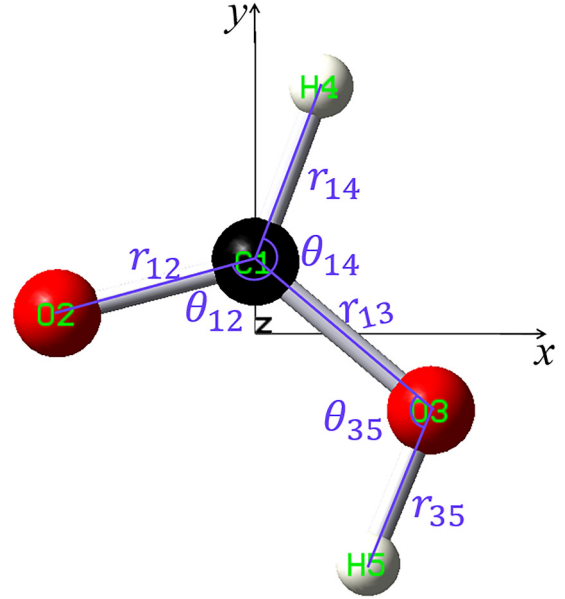


FIG. 1. Global minimum structure of HCOOH(A') in syn-conformation oriented in the laboratory xy plane. For convenience, the atoms are labeled H4-C1-O2-O3-H5. The C1-O3 bond serves as torsional axis for the torsion of the planar fragments H4-C1-O3-H5 versus O2-C1-O3. The values of the bond lengths and angles are listed in Table S1 of Sec. S1 of the SM [6].

II. RESULTS AND DISCUSSIONS

A. Model and techniques

Our implementation of the model of Refs. [1–3] aims at coherent control of enantiomer flips in oriented HCOOH (A''). The goal is the preferential preparation of either S- or R-enantiomers, followed by flips $S \rightarrow R \rightarrow S \rightarrow \dots$ or $R \rightarrow S \rightarrow R \rightarrow \dots$ with highest enantiomeric excess. For this purpose, we design optimally directed transform-limited laser pulses, preferably with linear polarization (Sec. II B) or alternatively with elliptical or circular polarizations (Sec. II C). The laser pulses excite formic acid from its electronic ground (g, A') state to the lowest excited (e, A'') state, starting from the vibronic ground state $\psi_{g,v=0}$. They are designed to transfer about 10% population from A' to A'' . In contrast with the effects of the intense pulses used in Refs. [1–3], the present pulses are so weak and the population transfer is so small that multiphoton excitations of higher states, or ionizations, are negligible. Accordingly, our implementation of the model of Refs. [1–3] accounts for the laser driven dynamics of just two nuclear wave functions $\psi_g(t) \equiv \psi_g(t; \text{par})$ and $\psi_e(t) \equiv \psi_e(t; \text{par})$ in electronic states (g, A') and (e, A''). Here the full notation “; par” emphasizes that the results depend on the parameters of the laser pulse; the condition “; par” may be dropped to simplify the notation. Moreover, our scenario assumes preorientation of HCOOH ($A', v = 0$) in the laboratory xy plane, with its center of mass at the origin and with its principal axes of inertia oriented along the laboratory x, y, z coordinates, as shown in Fig. 1. This type of preorientation may be achieved, e.g., by THz-assisted femtosecond-laser schemes or by all-optical field-free orientation techniques [13–15]. The preorientation remains

approximately valid because the characteristic value of $21 \text{ u}\text{\AA}^2$ of HCOOH's moment of inertia implies rotational timescales of around 20 ps, two orders of magnitude longer than the time for the selective preparation of enantiomers and subsequent chirality flips. The scenario of preoriented molecules is essential for the present approach because it relies on the optimal direction of polarization of the laser pulses with respect to the molecule.

The laser-driven nuclear wavepacket dynamics is described by means of the time-dependent Schrödinger equation (TDSE) in the frame of the Born-Huang expansion [16], neglecting diabatic couplings

$$i\hbar \frac{d}{dt} \begin{pmatrix} \psi_g(t) \\ \psi_e(t) \end{pmatrix} = \begin{pmatrix} H_g & V_{ge}(t) \\ V_{eg}(t) & H_e \end{pmatrix} \begin{pmatrix} \psi_g(t) \\ \psi_e(t) \end{pmatrix}, \quad (1)$$

with initial condition

$$\begin{pmatrix} \psi_g(t=0) \\ \psi_e(t=0) \end{pmatrix} = \begin{pmatrix} \psi_{g,v=0} \\ 0 \end{pmatrix}. \quad (2)$$

In Eq. (1), H_g and H_e are the molecular Hamiltonians of HCOOH in states g and e , coupled by the electric transition dipole $\mathbf{d} = \mathbf{d}_{ge} = \mathbf{d}_{eg} = (d_x, d_y, d_z)^T$ to the directed electric field $\boldsymbol{\epsilon}(t) = [\epsilon_x(t), \epsilon_y(t), \epsilon_z(t)]^T$ of the laser pulse

$$V_{ge}(t) = V_{eg}(t) = -\mathbf{d} \cdot \boldsymbol{\epsilon}(t) = -d_x \epsilon_x(t) - d_y \epsilon_y(t) - d_z \epsilon_z(t). \quad (3)$$

The electric-field components $\epsilon_x(t)$, $\epsilon_y(t)$, $\epsilon_z(t)$ of the laser pulse have amplitudes ϵ_x , ϵ_y , ϵ_z like an electric field with field strength ϵ directed along the polarization vector $\mathbf{e} = (\sin \theta \cos \phi, \sin \theta \sin \phi, \cos \theta)^T$, respectively. The pulse has a Gaussian envelope centered at t_m with parameter τ for duration. It oscillates with carrier frequency ω and with phases δ_x , δ_y , δ_z . Explicitly,

$$\begin{aligned} \epsilon_x(t) &= \epsilon_x e^{-(t-t_m)^2/\tau^2} \sin[\omega(t-t_m) + \delta_x], \quad \epsilon_x = \epsilon \sin \theta \cos \phi, \\ \epsilon_y(t) &= \epsilon_y e^{-(t-t_m)^2/\tau^2} \sin[\omega(t-t_m) + \delta_y], \quad \epsilon_y = \epsilon \sin \theta \sin \phi, \\ \epsilon_z(t) &= \epsilon_z e^{-(t-t_m)^2/\tau^2} \sin[\omega(t-t_m) + \delta_z], \quad \epsilon_z = \epsilon \cos \theta. \end{aligned} \quad (4)$$

Its mean temporal and spectral widths are

$$\Delta t = \tau/2, \quad \Delta E = \hbar/\tau, \quad (5)$$

in accord with the uncertainty relation $\Delta E \Delta t = \hbar/2$.

Optimal values of the parameters of the laser pulse $\text{par} = \{\tau, \epsilon, \omega, \phi, \theta\}$ yield coherent control of the preparation of enantiomers and subsequent enantiomer flips with the highest enantiomeric excess in HCOOH (A''), represented by $\psi_e(t)$. The phases allow applications of various types of electric fields. Our most important example, $(\delta_x, \delta_y, \delta_z) = (0, 0, 0)$, corresponds to a linearly polarized laser pulse, with the polarization directed along the vector $\mathbf{e}$, cf. Sec. II B. As an alternative, $(\delta_x, \delta_y, \delta_z) = (\pi/2, 0, 0)$ corresponds to the superposition of an elliptically polarized pulse propagating along z , plus a linearly z -polarized pulse. For the special case $\phi = \pi/2$, the elliptically polarized pulse degenerates to a circularly polarized pulse, cf. Sec. II C.

The molecular model Hamiltonians H_g and H_e account for the torsional motion which leads from the achiral planar initial state $\psi_{g,v=0}$ along φ to the chiral excited state represented

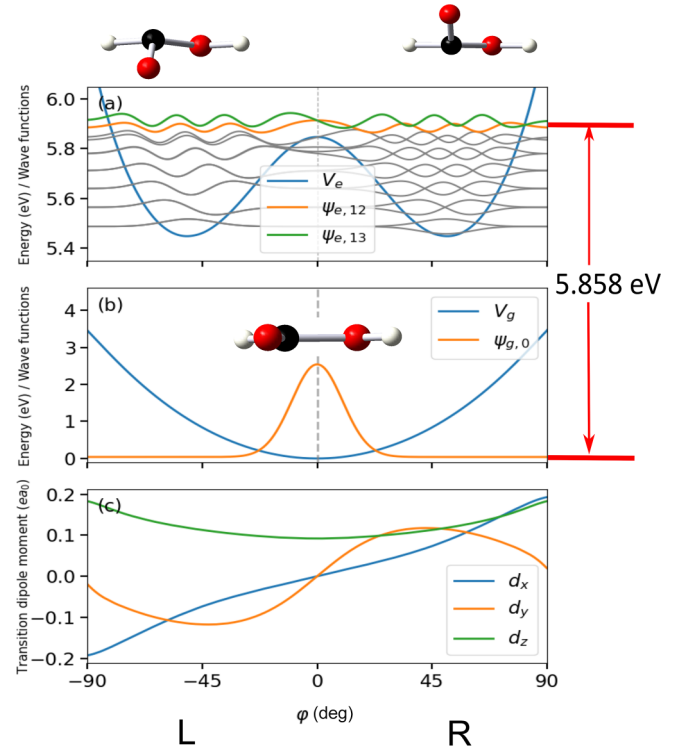


FIG. 2. Potential energy curves (a) $V_e(\varphi)$ and (b) $V_g(\varphi)$ of the excited (e, A'') and ground (g, A') states of the model HCOOH. The domains $-90^\circ < \varphi < 0^\circ$ (left, L) and $0^\circ < \varphi < 90^\circ$ (right, R) are assigned to S- and R-enantiomers, respectively. The inserts in panels (a) and (b) show the syn-conformations of the S- and R-enantiomers at the local minima ($\varphi = \pm 51^\circ$) of the double well potential $V_e(\varphi)$, and of the global minimum structure ($\varphi = 0$), respectively. Structural and energetic details are listed in Table S1 of Sec. S1.A in the SM [6]. Also shown in panels (a) and (b) are the wave functions $\psi_{e,v}(\varphi)$ and $\psi_{g,v=0}(\varphi)$ of the torsional eigenstates with quantum numbers $v = 0, 1, 2, \dots$, in the electronic states e and g ; their base lines indicate the values of the eigenenergies E_{ev} and $E_{g,v=0}$, respectively. The excitation energies $E_{ev} - E_{g0}$ are listed in Table S2 of Sec. S1.D in the SM [6]. For comparison, the photon energy (here $\hbar\omega = 5.858 \text{ eV}$) is indicated by the vertical arrow. The target doublet of excited states $\{v = 12, v + 1 = 13\}$ is highlighted by colors. Panel (c) shows the components $d_x(\varphi)$, $d_y(\varphi)$, $d_z(\varphi)$ of the $g \rightarrow e$ transition dipoles.

by $\psi_e(t)$. The corresponding reduced torsional moment of inertia is called “ $I(\varphi)$ ”; for the details, see Sec. S1.B of the SM [6]. Planar ($\varphi = 0$) and nonplanar ($\varphi = \pm 51^\circ$) molecular configurations in the ground (A') and excited (A'') states are illustrated in Figs. 1 and 2. The Hamiltonians include terms for the kinetic plus potential energies

$$\begin{aligned} H_j(\varphi) &= T(\varphi) + V_j(\varphi) \\ &= -\frac{\hbar^2}{2} \frac{\partial}{\partial \varphi} \frac{1}{I(\varphi)} \frac{\partial}{\partial \varphi} + V_j(\varphi), \quad j = g, e. \end{aligned} \quad (6)$$

The potential energy curves $V_g(\varphi)$ and $V_e(\varphi)$ and the components of the transition dipole $d_x(\varphi)$, $d_y(\varphi)$, $d_z(\varphi)$ in the domain $-90^\circ < \varphi < +90^\circ$ of the syn-conformation of HCOOH are shown in Fig. 2. The “left” (L) and “right” (R) subdomains $-90^\circ < \varphi < 0^\circ$ and $0^\circ < \varphi < +90^\circ$ are assigned to S- and R-enantiomers, respectively. The potential curves,

the transition dipoles as well as the results shown in Fig. 2 and listed in Table S1 of the SM, are calculated by means of the quantum chemical time dependent density functional theory with B3LYP functional and basis set with triple-zeta valence double polarization method (TD-DFT B3LYP/TZVPP [17–19]) as implemented in Gaussian 16 [20]; for details, see Sec. S1.C of the SM [6]. Apparently, $V_g(\varphi)$ is a symmetric single well potential, supporting the achiral ground state. The global minimum value is set to zero, $V_g(\varphi = 0) \equiv 0$. In contrast, $V_e(\varphi)$ is a symmetric double-well potential with a barrier at $\varphi = 0$, and with two “left, L ” ($\varphi < 0$) and “right, R ” ($\varphi > 0$) potential wells supporting the S- and R-enantiomers. For details and a comparison with previous experimental [8] and theoretical [9] results, see SM Table S1 in Sec. S1.A.

Figures 2(b) and 2(a) also show the torsional eigenfunctions $\psi_{g,v=0}(\varphi)$ and $\psi_{e,v}(\varphi)$, $v = 0, 1, 2, \dots, 13$ of the model HCOOH. They are labeled by electronic and torsional quantum numbers g or e and v . For even and odd values of v , they have even and odd symmetries. Their base lines indicate the values of the torsional eigenenergies $E_{g,v=0}$ and $E_{e,v}$. The torsional eigenfunctions and eigenenergies are obtained as solutions of the time-independent Schrödinger equations (TISE)

$$H_j \psi_{j,v}(\varphi) = E_{j,v} \psi_{j,v}(\varphi), \quad j = g, e \quad (7)$$

by means of the method developed in Ref. [21]. Details are in SM Sec. S1.D.

The x , y , and z components of the transition dipole moments for transitions between the electronic ground ($1^1A'$) and first excited ($1^1A''$) states of HCOOH are shown in Fig. 2(c), depending on the torsional angle φ . Integrating these transition dipoles with the nuclear wave functions for the ground state [cf. Fig. 2(b)] and the excited states [cf. Fig. 2(a)] yields the corresponding vibronic coupling matrix elements for transitions between the torsional states. Figure 2(c) reveals different even and odd symmetries of the components of the transition dipoles

$$\begin{aligned} d_x(-\varphi) &= -d_x(\varphi), \\ d_y(-\varphi) &= -d_y(\varphi), \\ d_z(-\varphi) &= +d_z(\varphi). \end{aligned} \quad (8)$$

Moreover, in the domain of the ground-state wave function $\psi_{g0}(\varphi)$,

$$|d_x(\varphi)| < |d_y(\varphi)| \ll |d_z(\varphi)| \quad \text{for } -30^\circ \leq \varphi \leq 30^\circ. \quad (9)$$

The TDSE (1) is solved by means of the method developed in Refs. [22,23]. Details are in the SM Sec. S2.A. The resulting time evolutions of the populations of the electronic excited state, of the probabilities of occupying the L and R domains of the S- and R-enantiomers in electronic state e and of the torsional eigenstates $\psi_{e,v}(\varphi)$ are calculated as

$$\begin{aligned} P_e(t; \text{par}) &\equiv P_e(t) = \int_{-90^\circ}^{+90^\circ} d\varphi |\psi_e(\varphi, t)|^2, \\ P_L(t; \text{par}) &\equiv P_L(t) = \int_{-90^\circ}^0 d\varphi |\psi_e(\varphi, t)|^2, \\ P_R(t; \text{par}) &\equiv P_R(t) = \int_0^{+90^\circ} d\varphi |\psi_e(\varphi, t)|^2, \end{aligned}$$

$$P_{e,v}(t; \text{par}) \equiv P_{e,v}(t) = \int_{-90^\circ}^{+90^\circ} d\varphi |\psi_e(\varphi, t) \psi_{e,v}(\varphi)|^2, \quad \text{par} = \{\tau, \epsilon, \omega, \phi, \theta\}. \quad (10)$$

The resulting enantiomeric excess is

$$ee(t; \text{par}) \equiv ee(t) = \frac{P_R(t) - P_L(t)}{P_R(t) + P_L(t)}. \quad (11)$$

B. Coherent control of the preparation of enantiomers and subsequent enantiomer flips in HCOOH(A') by an optimally directed linearly polarized laser pulse

Our primary goal is to design a linearly polarized well-directed transform-limited laser pulse, cf. Eq. (4), which excites the achiral HCOOH (A') to selective S- or R-enantiomers of HCOOH (A''), followed by enantiomer flips with highest enantiomer excess. The laser excitation is subject to a secondary condition, namely, to avoid competing multiphoton processes, the $A' \rightarrow A''$ population transfer probability should not exceed $P_e(t) \approx 0.1$.

To reach this goal, we suggest a strategy which calls for laser preparation of a superposition of a target doublet $v, v+1$ of the torsional states in HCOOH (A'') with even ($v = 2m$) and odd ($v+1 = 2m+1$) quantum numbers and symmetries. The states should have well-balanced, i.e., nearly equal populations, energies slightly above the potential barrier of HCOOH (A''), and the superpositions should be centered in the left (L) or right (R) domains [cf. Eq. (10)] depending on the target S- or R-enantiomers. Below, we apply this approach to the target doublet of states $\{v, v+1\} = \{12, 13\}$, cf. Fig. 2. The strategy is motivated by two reasons. First, it is well known that + or – superpositions of neighboring states with opposite symmetries undergo enantiomer flips in double-well potentials [24,25]. Second, eigenstates with energy slightly above the barrier of double-well potentials belong to transition state species which can be excited much more easily than eigenstates below or highly above the barrier [26,27].

The strategy is implemented by an approach to optimal parameters of the laser pulse $\text{par} = \{\tau, \epsilon, \omega, \phi, \theta\}$, which consists of three steps. Step (i) fixes the values of the parameters τ and ϵ for its duration and field strength to achieve rather simple mechanisms for preparing the target enantiomer, and for the subsequent enantiomer flips. To apply these mechanisms with efficient enantiomeric excess, step (ii) provides reasonable estimates of the other parameters ω, ϕ, θ for the laser frequency and for the direction of its polarization. These preliminary parameters serve as initial values for iterative optimization in step (iii). For the present goal, preparation of the target enantiomer and subsequent enantiomer flip with maximum absolute values of the enantiomeric excess, it suffices to determine the optimal laser parameters $\{\tau, \epsilon, \omega, \phi, \theta\}$ with 1, 1, 5, 3, and 3 significant decimals, respectively.

The search for optimal direction of the laser polarization is motivated as follows.

For symmetry reasons, excitation of the model HCOOH from its vibronic ground state $\psi_{g,v=0}(\varphi)$ to the doublet $v, v+1$ of excited states with even and odd symmetries must be mediated by molecular transition dipole elements with even and odd symmetries, that means by $d_z(\varphi)$ (even), and

at the same time, by $d_x(\varphi)$ and/or $d_y(\varphi)$ (odd), respectively, cf. Fig. 2(c) and Eq. (8). Consequently, the interaction of the transition dipole elements with the laser pulse Eq. (3) calls for electric-field components $\epsilon_z(t)$ as well as $\epsilon_x(t)$ and/or $\epsilon_y(t)$. According to Eq. (4), this condition can be satisfied by proper orientation of the polarization vector $\mathbf{e}$. Specifically, Eq. (9) suggests that the orientation angle θ should be chosen such that the larger values of $d_z(\varphi)$ compared to $|d_x(\varphi)|$ and/or $|d_y(\varphi)|$ are compensated for by smaller values of $|\epsilon_z|$ compared to $|\epsilon_x|$ and/or $|\epsilon_y|$. This means that the value of θ must be sufficiently close to 90° so that $|\cos \theta| \ll \sin \theta$, cf. Eq. (4).

Step (i). The parameter τ for the duration of the pulse is chosen such that the spectral width is slightly smaller than the energy gap of $\{v, v+1\}$,

$$\Delta E = \hbar/\tau \leq E_{e,v+1} - E_{e,v}, \quad (12)$$

cf. Eq. (5).

In practice, we set $\tau = 50$ fs, corresponding to $\Delta E = 0.013$ eV. This constrains the preparation of the target enantiomer, and the subsequent enantiomer flips to mechanisms which can be described by a wave function $\psi_e(\phi, t)$ of the excited state which consists of a superposition of just the two torsional eigenstates $\psi_{e,v}(\phi)$ and $\psi_{e,v+1}(\phi)$ of the target doublet $v, v+1 = 12, 13$. Details are in Sec. S2 of SM [6]. Together with the value $\tau = 50$ fs, we also set the time of the maximum of the laser intensity to $t_m = 150$ fs in Eq. (4). This ensures that the electric field is negligible at and before the initial time $t_i = 0$ fs of the laser propagation. Likewise, we shall analyze the results of the laser pulse at the time $t_f = 218$ fs when it achieves maximum population of the excited state [i.e., $\max P_e(t) = P_e(t_f)$]; the subsequent effects of the exponentially decaying laser pulse are negligible.

The field strength ϵ of the laser pulse is constrained to yield the target population

$$\begin{aligned} P_e(t \rightarrow \infty; \text{par}) \\ \approx P_{e,v=12}(t \rightarrow \infty; \text{par}) + P_{e,v=13}(t \rightarrow \infty; \text{par}) \leq 0.1. \end{aligned} \quad (13)$$

In practice, we set $\epsilon = 5$ GV/m, corresponding to maximum intensity $I_{\max} = 6.6$ TW/cm². This is much weaker than

the typical intensities of 1000 TW/cm² which are applied in COLTRIMS experiments [1–3]. Consequently, it simplifies the mechanism further since it excludes ladder climbing to more excited states by multiphoton excitations or ionizations. In other words, the quantum dynamics of the preparation of the target enantiomer, and of the subsequent enantiomer flips can be described in terms of just two wave functions which describe the quantum dynamics of the laser driven HCOOH in its ground and first-excited electronic states, $\psi_g(\varphi, t)$ and $\psi_e(\varphi, t)$. In fact, the constraint of Eq. (13) allows useful approximations of $\psi_g(\varphi, t)$ and $\psi_e(\varphi, t)$ in terms of time-dependent perturbation theory (TDPT). Details are in Sec. S2 of SM [6].

Step (ii). Reasonable (actually very good) estimates of the remaining laser parameters ω, ϕ, θ are obtained as follows: the carrier frequency ω is chosen such that the photon energy is halfway between the excitation energies of the target doublet $\{v, v+1\}$,

$$\hbar\omega = 0.5[(E_{e,v+1} - E_{g0}) + (E_{ev} - E_{g0})]. \quad (14)$$

The corresponding values of the laser frequency, wavelength, and photon energy are $\omega = 8.8999$ fs⁻¹, $\lambda = 211.8$ nm and $\hbar\omega = 5.858$ eV (cf. Fig. 2 and Table S2), respectively.

For an estimate of the angle ϕ of the optimal orientation of the laser polarization, we make use of a result of TDPT, namely, the enantiomeric excess is equal to zero at $\phi_0 = -16.4^\circ$ and at $\phi'_0 = \phi_0 + 180^\circ = 166.6^\circ$, cf. Eq. (S33) of Sec. S2 of SM [6]. Since our coherent control heads for maximum absolute values of the enantiomeric excess, it is reasonable to assume that this maximum is attained halfway between ϕ_0 and ϕ'_0 , that means at $\phi_0 + 90^\circ$. Hence, our initial estimate is $\phi = 73.6^\circ$.

Another result of TDPT is Eq. (S52) of Sec. S2 of SM [6]. This provides an approximation of the value of the angle θ of the optimal orientation of the laser polarization, for given values of the orientation angle ϕ (here $\phi = 73.6^\circ$) and of the laser frequency ω (here $\omega = 8.8999$ fs⁻¹). Using Eq. (S52), we set $\theta = 70.0^\circ$.

To summarize, steps (i) and (ii) yield preliminary parameters of the laser pulse

$$\text{par}[\text{for S(preliminary)}] = \{\tau = 50 \text{ fs}, \epsilon = 5 \text{ GV/m}, \omega = 8.8999 \text{ fs}^{-1}, \phi = 73.6^\circ, \theta = 70^\circ\}. \quad (15)$$

The electric field of this laser pulse, which is a preliminary “interim” result on the way to optimal control, is illustrated in the SM Fig. S2 in Sec. S2.B, together with the populations $P_e(t), P_L(t), P_R(t)$ of the excited (e, A'') state and of the left (L) and right (R) domains for the S- and R-enantiomers of the model HCOOH. Suffice it here to state that the “preliminary” pulse already achieves one of the goals of our strategy, namely, almost perfect preparation of the target doublet $v = 12, v+1 = 13$ with well-balanced populations $P_{e,v=12}(t \rightarrow \infty) = 0.0457, P_{e,v+1=13}(t \rightarrow \infty) = 0.0442$ summing up to $P_e(t \rightarrow \infty) = 0.0899$; the populations of all other excited states are less than 0.0001. Close to the end, specifically at $t = 218$ fs, the laser pulse prepares preferentially the target S-enantiomer, followed by enantiomer flips

$S \rightarrow R \rightarrow S \rightarrow \dots$ with period

$$T = \hbar/(E_{e,v=13} - E_{e,v=12}) = 142.6 \text{ fs}. \quad (16)$$

Accordingly, the preliminary set of parameters is denoted as “par [for S (preliminary)]” in Eq. (15). The “learned guess” of the “preliminary parameters,” Eq. (15), is already so good that the enantiomeric excess

$$\begin{aligned} ee[t = 218; \text{par for S(preliminary)}] \\ = \frac{0.00942 - 0.08164}{0.00942 + 0.08164} = -0.79302 \end{aligned} \quad (17)$$

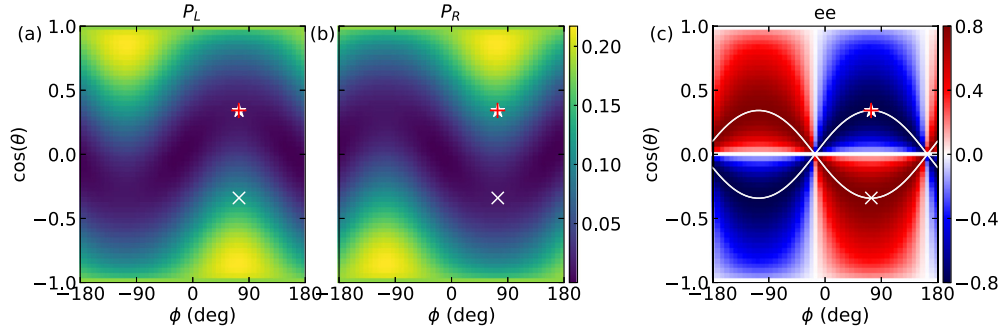


FIG. 3. Production of S- and R-enantiomers of the model $\text{HCOOH}(A'')$ depending on the angles θ, ϕ of the direction of the linear polarization of the transform-limited laser pulse, cf. Eq. (4). The results for S-enantiomers at $t = 218$ fs using the preliminary [Eq. (15)] and the optimal [Eq. (18)] laser parameters are marked by symbols “+” and “star,” respectively. Results for R-enantiomers using optimal parameters [Eq. (20)] are marked by symbol “x.” For each case, symmetry rules (see Sec. S2.C of the SM [6]) yield equivalent results for different sets of directional angles θ, ϕ . Left and middle panels: Populations $P_L(t = 218$ fs) and $P_R(t = 218$ fs) of the “left, L ” and “right, R ” domains for S- and R-enantiomers. Right panel: Enantiomeric excess “ $ee(t = 218$ fs).” The white curve in the right panel shows the analytical result for the extrema of $|ee|$ derived in Sec. S2.C of the SM [6].

is close to the minimum value of ee , cf. Eq. (11) and Fig. S2 in Sec. S2 of SM [6].

Step (iii). To improve, i.e., to lower this value of ee , we keep the fixed values of the parameters $\tau = 50$ fs, $\epsilon = 5$ GV/m and optimize the others iteratively in the order ω, ϕ , and θ . First, we use the preliminary values $\phi = 73.6^\circ$, $\theta = 70^\circ$ and search for “better” values of ω which should yield enantiomeric excess below the preliminary value, Eq. (17). This search turns out to be fruitless, which means the preliminary value $\omega = 8.8999$ fs $^{-1}$ can already be considered as optimum. This conclusion is confirmed by the TDPT Eq. (S48) which

expresses ω as the initial guess plus a modification. The modification, however, turns out to be smaller than 0.0001 fs $^{-1}$, i.e., it is negligible.

Next, we use the optimal frequency, $\omega = 8.8999$ fs $^{-1}$ and search for “better” values of the angles ϕ and θ of the optimal orientation of the laser polarization. For this purpose, Fig. 3 shows contour plots of the populations $P_L(t = 218$ fs), $P_R(t = 218$ fs) and of the enantiomeric excess $ee(t = 218$ fs) depending on θ, ϕ . Apparently, the lowest value of ee , namely, $ee(t = 218$ fs) = -0.79306 , cf. Eq. (11), is obtained for laser parameters

$$\text{par}(\text{for S; optimal}) = \{\tau = 50 \text{ fs}, \epsilon = 5 \text{ GV/m}, \omega = 8.8999 \text{ fs}^{-1}, \phi = 74.0^\circ, \theta = 70.1^\circ\}. \quad (18)$$

Figure 3 reveals that for each set of directional angles θ, ϕ , there are additional sets of angles which yield the same values of $P_L(t)$, $P_R(t)$ and $ee(t)$. Moreover,

$$P_L(t; \{\tau, \epsilon, \omega, \phi, \theta\}) = P_R(t; \{\tau, \epsilon, \omega, \phi, 180^\circ - \theta\}). \quad (19)$$

This is a consequence of the symmetry rules which are explained in SM Sec. S2.C. For example, the result in Eq. (19) is obtained by reflection of the electric field at the molecular plane, which means by replacing the directional θ angle by $180^\circ - \theta$.

The optimal laser field with parameters listed in Eq. (18) is illustrated in Fig. 4(a), together with the resulting populations $P_e(t)$, $P_L(t)$, and $P_R(t)$ of the excited state of the model HCOOH and of its L and R domains for S- and R-enantiomers. Apparently, laser preparation of the target S-enantiomer with an optimal value of $ee(t = 218$ fs) = -0.79306 is followed by enantiomer flips $S \rightarrow R \rightarrow S \rightarrow \dots$. This is also confirmed by the contour plot of the density $\rho_e(t) = |\psi_e(t)|^2$ shown in Fig. 4(b). The excited wavepacket is dominated by vibrational states $v = 12$ and 13 , and the alternating lobes arise from the time-dependent density of their coherent superposition.

Analogous optimal preparation of the R-enantiomer with subsequent enantiomer flips $R \rightarrow S \rightarrow R \rightarrow \dots$ is achieved by reflection of the electric field at the molecular plane, cf. Eq. (19). The corresponding laser parameters are

$$\text{par}(\text{for R; optimal}) = \{\tau = 50 \text{ fs}, \epsilon = 5 \text{ GV/m}, \omega = 8.8999 \text{ fs}^{-1}, \phi = 74.0^\circ, \theta = 180^\circ - 70.1^\circ\}. \quad (20)$$

The electric field of the pulse, the populations $P_e(t)$, $P_L(t)$, $P_R(t)$, and the density $\rho_e(t) = |\psi_e(t)|^2$ are documented in Fig. 5, entirely analogous to the results shown in Fig. 4. The enantiomeric excess is $ee(t = 218$ fs) = 0.79306 .

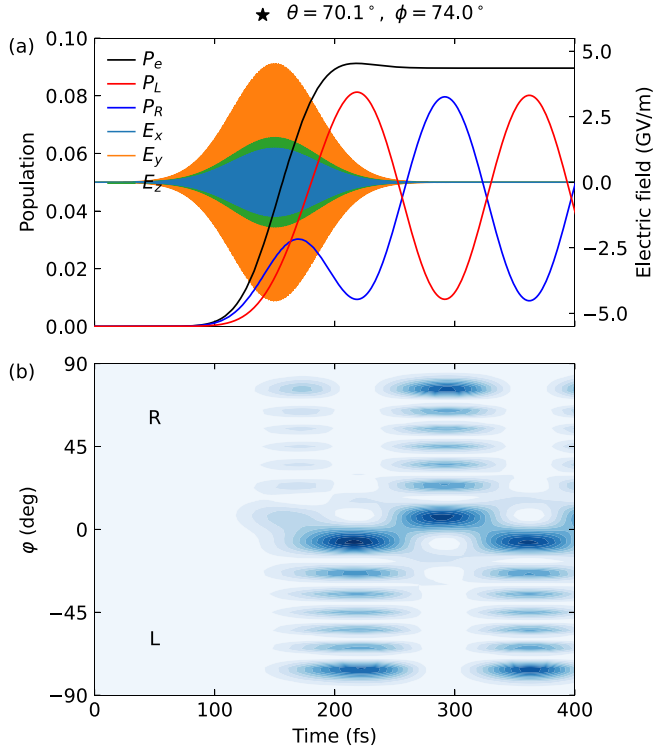


FIG. 4. Optimal laser pulse for preferential preparation of the S-enantiomer of the model HCOOH(A'') with enantiomeric excess $ee(t = 218 \text{ fs}) = -0.79306$, with subsequent enantiomer flips $S \rightarrow R \rightarrow S \rightarrow \dots$. (a) Electric field with parameters listed in Eq. (18), and the resulting populations $P_e(t)$, $P_L(t)$, $P_R(t)$ of the excited (e, A'') state and of the L and R domains of the S- and R-enantiomers of the model HCOOH. (b) Contour plot of the density $\rho_e(t) = |\psi_e(t)|^2$.

C. Coherent control of the preparation of enantiomers and subsequent enantiomer flips in HCOOH (A'') by superpositions of a linearly plus an elliptically or circularly polarized laser pulses

As a secondary result, we shall now show that the optimally directed linearly polarized laser pulses for coherent control of enantiomer flips in oriented HCOOH (A'') (Sec. II B) can be replaced by a superposition of an elliptically polarized pulse propagating along z plus a linearly z -polarized pulse. As an example, this is demonstrated for optimal preparation of the S-enantiomers, followed by flips $S \rightarrow R \rightarrow S \rightarrow \dots$ with highest enantiomeric excess.

As outlined already in Sec. II A, specifically in the discussion of Eq. (4) for the laser pulses, to reach this secondary goal, all we have to do is to adapt the optimal laser pulse of Sec. II B with the same optimal parameters, Eq. (18), but with phases $(\delta_x, \delta_y, \delta_z) = (\frac{\pi}{2}, 0, 0)$ instead of $(0, 0, 0)$.

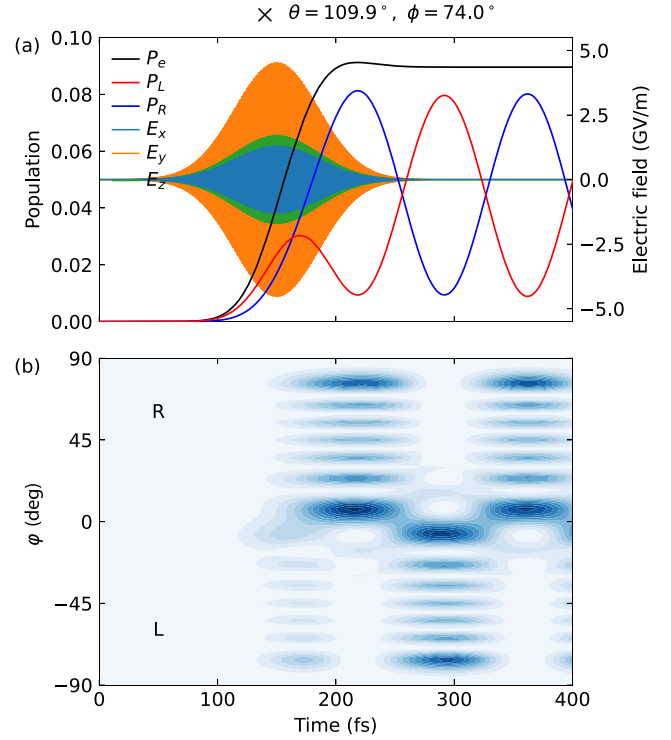


FIG. 5. Same as Fig. 4, but for optimal preparation of the R-enantiomer and subsequent enantiomer flips $R \rightarrow S \rightarrow R \rightarrow \dots$ of HCOOH(A''). The laser parameters are listed in Eq. (20).

Consequently, the electric-field components of the superimposed laser pulses are

$$\begin{aligned} \epsilon_x(t) &= \epsilon_x e^{-(t-t_m)^2/\tau^2} \sin\left[\omega(t-t_m) + \frac{\pi}{2}\right], \\ \epsilon_x &= \epsilon \sin \theta \cos \phi, \\ \epsilon_y(t) &= \epsilon_y e^{-(t-t_m)^2/\tau^2} \sin[\omega(t-t_m)], \quad \epsilon_y = \epsilon \sin \theta \sin \phi, \\ \epsilon_z(t) &= \epsilon_z e^{-(t-t_m)^2/\tau^2} \sin[\omega(t-t_m)], \quad \epsilon_z = \epsilon \cos \theta. \end{aligned} \quad (21)$$

As before, the optimal parameters θ, ϕ determine the amplitudes of the superimposed laser fields, cf. Eq. (4), but without the previous physical meaning of directionality. The laser field, Eq. (21) with optimal parameters, Eq. (18), is shown in Fig. 6, together with the populations $P_e(t)$, $P_L(t)$, $P_R(t)$. The results agree with those shown in Fig. 4, within graphical resolution. The enantiomeric excess is again optimal, $ee(t = 218 \text{ fs}; \text{optimal par for S}) = -0.78910$. This confirms the equivalence of the two approaches of Secs. II B and II C.

Finally, Fig. 7 shows the results for the superposition of a circularly polarized pulse propagating along z plus a linearly z -polarized pulse, with laser parameters

$$\text{par(for S; circular plus linear)} = \{\tau = 50 \text{ fs}, \epsilon = 6 \text{ GV/m}, \omega = 8.8999 \text{ fs}^{-1}, \phi = 45.0^\circ, \theta = 70.1^\circ\}. \quad (22)$$

A comparison of Fig. 7 with Fig. 6 shows that the constraint, i.e., the replacement of the optimal parameter, $\phi = 74.0^\circ$ for the elliptical pulse by $\phi = 45.0^\circ$ for the circularly polarized pulse reduces the enantiomeric excess from the optimal value -0.78910 to -0.72198 .

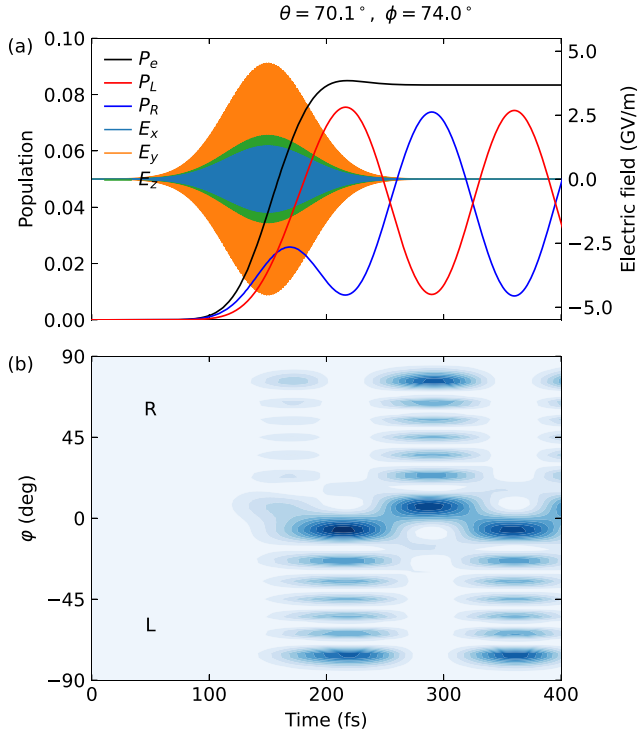


FIG. 6. Same as Fig. 4 for optimal preparation of the S-enantiomer and subsequent enantiomer flips $S \rightarrow R \rightarrow S \rightarrow \dots$ of $\text{HCOOH}(A'')$, but for the superposition of an elliptically polarized laser pulse propagating along z plus a linearly z -polarized laser pulse, cf. Eq. (21). The laser parameters are the same as listed in Eq. (18).

III. CONCLUSION

This investigation was motivated by the discovery of the Dörner group, namely, enantio-selectivity of Coulomb explosions of formic acid depending on the direction of propagation of the applied circularly polarized x-ray or laser pulses, or on the direction of polarization of linearly polarized laser pulses [1–3]. Here we discover corresponding effects of the directionality of linearly polarized laser pulses on coherent control of the formation of S- versus R-enantiomers of $\text{HCOOH}(A'')$, followed by enantiomer flips with highest enantiomeric excess. The results of Refs. [1–3] are obtained by means of COLTRIMS [5] which destroys the molecule by multiple ionization followed by enantio-selective fragmentation. In contrast, the present approach avoids competing multiple ionization or other multiphoton processes because it uses optimal laser pulses with rather weak intensities. Consequently, the present coherent control maintains the molecule during and after optimal preparation of the target enantiomer, say the S-enantiomer, and predicts sequel enantiomer flips such as $S \rightarrow R \rightarrow S \rightarrow \dots$ with highest enantiomeric excess. We are not aware of any other systematic investigation of the effect of the directionality of laser pulses on coherent control of enantiomer flips or other isomerizations.

Moreover, we showed that optimal control of enantiomer selectivity and subsequent enantiomer flips can also be achieved by means of a combination of two laser pulses, one of them elliptically polarized propagating along z , the other one linearly z polarized. Replacing the elliptically polarized

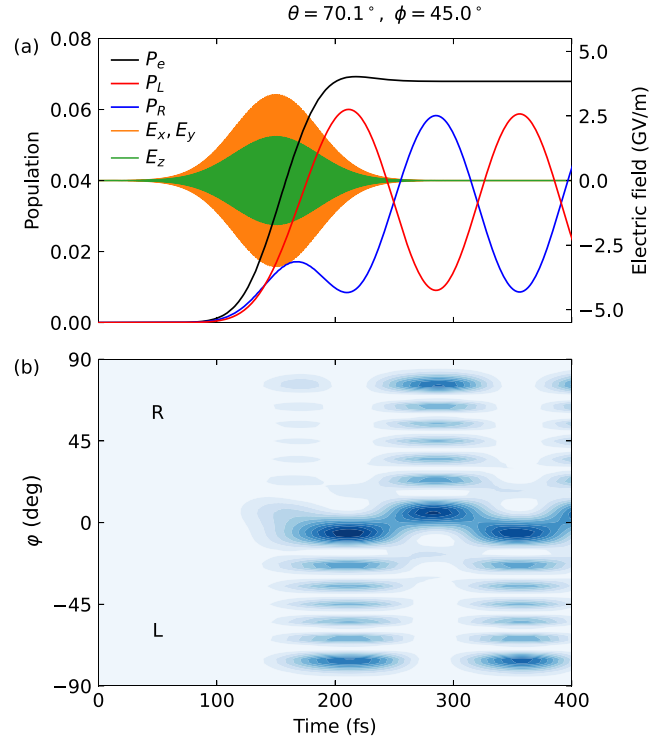


FIG. 7. Same as Fig. 6, but for the parameters for the superposition of the circularly polarized pulse propagating along z plus the linearly z -polarized pulse, listed in Eq. (22).

pulse by a circularly polarized laser pulse reduces the enantiomeric excess but still allows preferential production of the target enantiomer followed by enantiomer flips. The equivalence or near-equivalence of these three scenarios provides flexibility for experimental implementations. The laser parameters adopted in this work, including the pulse duration, field strength, and photon energy, are within the range of current femtosecond laser technology, as demonstrated in previous experimental studies [28–30]. Furthermore, the optimization procedure employed here does not require an exact reproduction of a unique theoretical optimum; rather, it provides a systematic strategy to identify suitable control parameters, which can also guide experimental optimization of the laser pulses.

The present study adapts the simple 1D model of Refs. [1–3], focusing on the laser-driven torsion from the achiral reactant $\text{HCOOH}(A')$ to the chiral S- or R-enantiomers of the excited $\text{HCOOH}(A'')$ with subsequent enantiomer flips. Extended investigations should employ multidimensional models to explore competing effects of intramolecular vibrational redistribution (IVR) [31]. As working hypothesis, IVR will damp the present periodic enantiomer flips.

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DATA AVAILABILITY

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

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