

RESEARCH ARTICLE

Polarization Control in High Harmonic Generation Using Molecular Structures in Nonaligned Molecules

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The symmetry of the target system plays a decisive role in the polarization of high harmonic generation (HHG). Molecules breaking the isotropic symmetry can be utilized to manipulate HHG polarization, but it has long been believed that prealignment is necessary to manifest the microscopic molecular structural effect within the macroscopic ensemble. In this work, we show that the molecular structural effect can be exploited in nonaligned molecular ensembles with appropriate 2-dimensional driving fields, despite the ensembles exhibiting isotropic macroscopic symmetry. The feasibility of this scheme is comprehensively elaborated with a multiscale theory from the perspective of symmetry breaking and is experimentally validated employing bichromatic counterrotating circularly polarized driving fields as an example. By varying the intensity ratio of the bichromatic components, substantially chiral high harmonics are generated from nonaligned molecules associated with the highest HHG efficiency, where, by contrast, the spectral chirality is nearly zero from the reference atom. Remarkably, we observe a simultaneous enhancement of both the chirality and yield of the harmonics from CO₂, overcoming a commonly observed trade-off of the HHG efficiency for higher spectral chirality. Our findings hold the potential for a straightforward and robust pathway toward attosecond light sources with high brightness and large ellipticity.

Introduction

High harmonic generation (HHG) is an extremely nonlinear optical phenomenon that arises from the interaction of intense laser fields with matter. This process can be well understood with the semiclassical 3-step model, involving ionization, propagation, and recombination of an active electron in the strong driving field [1,2]. The unique and ideal characteristics of HHG render it an exceptional source for generating extreme ultraviolet attosecond pulses [3–6], which have extensive application in atomic, molecular, and solid-state time-resolved spectroscopy [7–10]. Nevertheless, the majority of efforts have primarily resulted in the generation of linearly polarized attosecond pulses, with linearly polarized driving lasers. The availability of bright circularly polarized (CP) and elliptically polarized (EP) attosecond pulses has been a long-standing request for probing the structures and ultrafast dynamics of matter, from chiral species [11,12] to ferromagnetic materials [13,14], with exceptional temporal resolutions.

To date, several schemes have been proposed to obtain CP or EP high harmonics and attosecond pulses. For example, one can convert linearly polarized harmonics to circular polarization through multiple reflections on surfaces [15]. This approach

leads to a drastic decrease in photon flux by 2 orders of magnitude. Given the limited availability of transmissive components in the extreme ultraviolet realm, the most widely considered strategy is in situ manipulation. Namely, the high harmonic polarization is manipulated at the generation site by controlling the HHG process, which is mostly realized by optimizing the driving laser [16–25]. One common way involves using a 2-dimensional (2D) driving field synthesized by 2 collinearly propagating lasers with different frequencies [16–22], particularly the versatile bichromatic counterrotating circularly polarized (BCCP) field [18–22,26,27]. It is worth noting that, although individual harmonics can exhibit circular or elliptical polarization due to the selection rule of HHG [28–30], this does not guarantee the generation of CP or EP attosecond pulses as neighboring harmonics possess opposite helicities. To obtain CP or EP attosecond pulses, it is necessary to ensure that one helicity component dominates over the other within a specific spectral range, corresponding to a high chirality of HHG in this range. One can further optimize the waveform of the 2D driving fields, manipulating the electron propagation trajectories in the microscopic HHG process, so as to increase the spectral chirality. However, an accompanying decrease in HHG efficiency is commonly observed in both theoretical simulations and experiments

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[22,31–33]. Alternatively, CP or EP attosecond pulses can be produced using noncollinearly propagating driving lasers [23–25]. This approach is more intricate in experimental implementation, demanding precise attosecond accuracy and sophisticated techniques. Furthermore, the noncollinear geometry limits the interaction volume available for HHG. Thus, employing either a collinear or a noncollinear setup, a trade-off typically emerges between the HHG efficiency and spectral chirality when modifying the HHG process by optimizing the driving laser.

To avoid sacrificing the HHG efficiency, an alternative strategy involves optimizing the target itself [34–39], which is generally based on preparing a symmetry-broken target system. For example, it has been proposed that EP attosecond pulses can be generated through highly prealigned molecules [34,35] or current-carrying states with nonzero angular momentum [36,37], even using a linearly polarized driving field. Unlike atoms, the molecular structure breaks the isotropic symmetry, which modifies the harmonic polarization. It has been conventionally believed that a prealignment is necessary to exploit the structural effect, attributed to the averaging out of the microscopic structure in nonaligned ensembles that results in isotropic symmetry at the macroscopic scale. Despite these proposals, achieving high-degree molecular alignment or orientation as well as preparing current-carrying states remains challenging in experiments. It was also proposed that EP attosecond pulses can be obtained by driving Ne with BCCP fields based on the asymmetric dynamics of the degenerate current-carrying states [21,40]. Nevertheless, the scheme may not be favorable for low-frequency drivers, which are needed to generate ultrashort attosecond pulses (see the discussions in Sec. 3 of Supplement 1). Therefore, there are still obstacles persisting in the efficient production of CP and EP attosecond pulses.

In this paper, we challenge the seemingly natural and widely prevailing consensus, showing that the molecular structural effect can be exploited in HHG polarization control from non-aligned molecular gases. Firstly, we explore the origin of this possibility by establishing a multiscale theory associating the microscopic molecular structure with the symmetry breaking for the macroscopic ensemble. The theoretical analysis sheds light on the basis of the polarization control and provides guidance for efficiently generating high harmonics with high spectral chirality. Subsequently, we present illustrative numerical results to more visually demonstrate the picture of the underlying

physics. Lastly, we validate our theory with experimental evidence by employing nonaligned N_2 and CO_2 molecules and BCCP driving fields as illustrative examples. The results show that the polarization property of HHG exhibits exceptional sensitivity to the molecular structures, even in the absence of alignment. By varying the intensity ratio of the bichromatic components of the BCCP fields, substantially chiral high harmonics are generated from both N_2 and CO_2 associated with the highest HHG efficiency, where, by contrast, the spectral chirality is nearly zero from the reference atom Ar. Remarkably, we observe a simultaneous enhancement in both spectral chirality and HHG efficiency for CO_2 , overcoming the conventional trade-off between them. Our findings hold the potential to produce bright and highly EP attosecond pulses.

Theory

To elaborate on the feasibility of exploiting the microscopic structural effects from nonaligned ensembles, we resort to the 3-step picture of HHG in multicycle driving lasers. We first analyze the dipole moment, responsible for the harmonic radiation, corresponding to one trajectory by reformulating it directly in relation to the ensemble. Then, we consider the interference of the radiations contributed by different trajectories, which leads to the finally observed harmonic spectrum. Lastly, we present illustrative numerical results to provide a more intuitive visualization of the symmetry analysis.

Analysis for one trajectory

Within the nonaligned molecular ensemble, where molecules are evenly distributed across all directions, ionized electrons with identical initial conditions trace the same propagation trajectory and generate harmonic radiation with equal photon energy upon recombination, as shown in Fig. 1. We consider a specific propagation trajectory characterized by ionization time t_i and recombination time t . The electrons recombine with momentum $\mathbf{k}$. To analyze the polarization of the harmonic radiation from the ensemble, we need to consider not only the ensemble's symmetry but also the symmetry of the single molecule with respect to the ionization and recombination directions. Thus, 2 coordinate systems determined by the trajectory ($S:xyz$ and $S':x'y'z'$) are established for each molecule, with the x axis antiparallel to the recombination direction and the

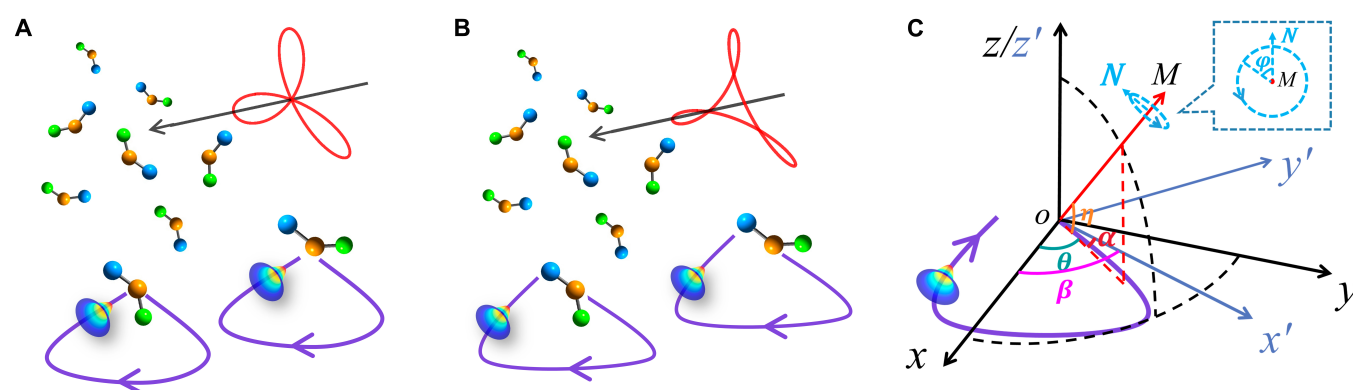


Fig. 1. Schematic of the high harmonic generation (HHG) process in non-aligned molecules for (A) head-on and (B) non-head-on recombinations. Illustrative trajectories are depicted by the purple curves. The cones represent the continuum wave packet. The red curves show typical Lissajous figures of the example bichromatic counterrotating circularly polarized (BCCP) fields. The intensity ratios $I_{\omega}/I_{2\omega}$ for the example BCCP fields in (A) and (B) are 1:1 and 2:1, respectively. (C) Illustration of the coordinate systems and angles for each molecule used in the theoretical analysis.

x' axis parallel to the ionization direction, as illustrated in Fig. 1C. The angle between the x and x' axes is denoted as β . z/z' is the laser propagation direction. The origins of the coordinate systems are located at the center of the molecules. Herein, we explore thin gas mediums generated from a supersonic gas jet under low-ionization conditions, where the phase matching effects are minimized [22,41–43]. Upon the recombination at t , the harmonic radiation from the macroscopic ensemble is determined by the coherent superposition of the microscopic dipole moments from individual molecules oriented at all possible angles (atomic units are used throughout unless stated otherwise):

$$\mathbf{D}_k(t; t_i) = \sum_{\theta, \eta, \varphi} \mathbf{d}_{\theta, \eta, \varphi, k}(t; t_i) = \sum_{\theta, \eta, \varphi} \langle \phi_{\theta, \eta, \varphi} | \hat{\mathbf{r}} | f[\alpha(\theta), \eta, \varphi] \phi_k \rangle. \quad (1)$$

We refer to $\mathbf{D}_k$ as the total dipole moment of the ensemble. $|\phi_{\theta, \eta, \varphi}\rangle$ is the ground state of the molecule with orientation denoted by 3 angles $\{\theta, \eta, \varphi\}$, and $\mathbf{d}_{\theta, \eta, \varphi, k}$ symbolizes the microscopic dipole moment for $|\phi_{\theta, \eta, \varphi}\rangle$. As depicted in Fig. 1C, the orientation angles are described associated with a given axis fixed in the molecular frame (labeled the M axis): θ is the angle between the x axis and the projection of the M axis on the polarization plane (xoy), η is the elevation angle of the M axis out of the xoy plane, and φ denotes the rotation of the molecular orbital around the M axis. To clearly define the orientation of $\varphi = 0$, another axis in the molecular frame (the N axis) orthogonal to the M axis is chosen. We denote $\varphi = 0$ when the N axis lies in the Moz plane. $|\phi_k\rangle$ is the continuum state of the recombining electron. Notably, in the ket, $|\phi_k\rangle$ is multiplied by an amplitude f for each orientation $\{\theta, \eta, \varphi\}$. This amplitude accounts for the fact that the continuum wave packets are born in different ionization directions with respect to the molecular orbital, denoted by the angles $\{\alpha, \eta, \varphi\}$ as illustrated in Fig. 1. α is the angle between the x' axis and the projection of the M axis on the polarization plane, with the relation $\alpha(\theta) = \beta - \theta$. Given the nonspherical structure of molecules, the ionization rate $f(\alpha, \eta, \varphi)$ is nonisotropic too. The angular dependence of f is a direct manifestation of the microscopic molecular structural effect.

According to Eq. 1, understanding the harmonic radiation of the ensemble roots on first studying the microscopic response of individual molecules. However, this poses a challenge for theoretical analysis. For a more straightforward analysis, it is advantageous to directly relate the total dipole moment to the ensemble. To this end, we equivalently reformulate Eq. 1 as

$$\mathbf{D}_k(t; t_i) = \left\langle \sum_{\theta, \eta, \varphi} f[\alpha(\theta), \eta, \varphi] \phi_{\theta, \eta, \varphi} | \hat{\mathbf{r}} | \phi_k \right\rangle = \Phi \hat{\mathbf{r}} \phi_k. \quad (2)$$

Here, we represent $|\Phi\rangle = \left| \sum_{\theta, \eta, \varphi} f[\alpha(\theta), \eta, \varphi] \phi_{\theta, \eta, \varphi} \right\rangle$. Equation 2 has the same mathematical form as the microscopic dipole moment, although their underlying physics are entirely different. The polarization of the radiation will be closely related to the symmetry of the term $|\Phi\rangle$. By construction, the symmetry of $|\Phi\rangle$ is dependent on $f(\alpha, \eta, \varphi)$, which associates the molecular structure effect with the behavior of the ensemble at different scales. With Eq. 2, the challenge of analyzing the structural effect of each molecule at the microscopic scale is transferred to directly analyzing the symmetry breaking for the ensemble at the macroscopic scale.

Specifically, the perpendicular component of $\mathbf{D}_k$ is calculated in the coordinate representation as $D_{y,k} = \int_{x=-\infty}^{\infty} \int_{y=0}^{\infty} \int_{z=-\infty}^{\infty} \Phi^*(x, y, z) y \phi_k(x, y, z) dx dy dz$. To facilitate the symmetry analysis, we explicitly establish the relationship between the total dipole moment and the symmetries by reformulating the equation as

$$D_{y,k} = \int_{x=-\infty}^{\infty} \int_{y=0}^{\infty} \int_{z=-\infty}^{\infty} y (1 - \hat{\sigma}_{xz}) [\Phi^*(x, y, z) \phi_k(x, y, z)] dx dy dz, \quad (3a)$$

$$D_{y,k} = \int_{x=-\infty}^{\infty} \int_{y=0}^{\infty} \int_{z=-\infty}^{\infty} y (1 - \hat{\mathcal{R}}_{\pi}^x) [\Phi^*(x, y, z) \phi_k(x, y, z)] dx dy dz, \quad (3b)$$

where $\hat{\sigma}_{xz}$ denotes the mirror reflection about the xz plane and $\hat{\mathcal{R}}_{\pi}^x$ denotes the rotation of π about the x axis. Equations 3a and 3b indicate that the perpendicular component can appear if the wave functions do not satisfy the mirror symmetry and the π rotation symmetry. There are 3 cases for symmetry breaking: (a) the symmetry of $|\phi_k\rangle$ is (approximately) preserved, while that of $|\Phi\rangle$ is broken; (b) the symmetry of $|\Phi\rangle$ is preserved, while that of $|\phi_k\rangle$ is broken; and (c) the symmetries of both $|\Phi\rangle$ and $|\phi_k\rangle$ are broken. Indeed, we will show below that breaking the symmetry of $|\Phi\rangle$ or $|\phi_k\rangle$ corresponds to the 2 collinear strategies: optimizing the target or the laser field waveform, respectively. For brevity, we will discuss the 2 typical scenarios corresponding to (a) and (b), while the scenarios for (c) can be addressed by integrating the discussions on (a) and (b).

(a) Head-on recombination: We first discuss the former scenario in which the laser field drives the continuum electrons to recollide with the parent ion directly, instead of missing the parent ion. This is the most prevalent case in general HHG experiments since the HHG radiation upon the head-on recombination is the highest. For small molecules, the recombining wave packet approximately possesses the mirror and rotation symmetry $(1 - \hat{\sigma}_{xz})\phi_k = 0$ and $(1 - \hat{\mathcal{R}}_{\pi}^x)\phi_k = 0$. In this case, Eqs. 3a and 3b become

$$D_{y,k} = \int_{x=-\infty}^{\infty} \int_{y=0}^{\infty} \int_{z=-\infty}^{\infty} y \phi_k(x, y, z) (1 - \hat{\sigma}_{xz}) \Phi^*(x, y, z) dx dy dz, \quad (4a)$$

$$D_{y,k} = \int_{x=-\infty}^{\infty} \int_{y=0}^{\infty} \int_{z=-\infty}^{\infty} y \phi_k(x, y, z) (1 - \hat{\mathcal{R}}_{\pi}^x) \Phi^*(x, y, z) dx dy dz. \quad (4b)$$

Thus, the key question is whether $\Phi(x, y, z)$ breaks the $\hat{\sigma}_{xz}$ and $\hat{\mathcal{R}}_{\pi}^x$ symmetries. $D_{y,k} = 0$ if either of the symmetries is satisfied.

Firstly, we examine the mirror symmetry of $\Phi(x, y, z)$. For nonchiral molecules, $\hat{\sigma}_{xz}\phi_{\theta, \eta, \varphi}(x, y, z) = \phi_{-\theta, \eta, -\varphi}(x, y, z)$ and the ionization rate satisfies $f(\alpha, \eta, \varphi) = f(-\alpha, \eta, -\varphi)$, which can be understood from the picture that 2 orbitals mirror symmetric about the $x'oz'$ plane have the same ionization rate. Considering these relations, one gets (see Supplement 1 for details)

$$\hat{\sigma}_{xz}\Phi(x, y, z) = \sum_{\theta, \eta, \varphi} f[-\alpha(-\theta), \eta, \varphi] \phi_{\theta, \eta, \varphi}(x, y, z). \quad (5)$$

Thus, the mirror symmetry $(1 - \hat{\sigma}_{xz})\Phi^* = 0$ requires $f[-\alpha(-\theta), \eta, \varphi] = f[\alpha(\theta), \eta, \varphi]$. Namely,

$$f(-\beta - \theta, \eta, \varphi) = f(\beta - \theta, \eta, \varphi) \quad (6)$$

as $\alpha(\theta) = \beta - \theta$. Similarly, one will find that the rotation symmetry $(1 - \hat{\mathcal{R}}_\pi^x)\Phi^* = 0$ requires the same condition Eq. 6 (see Supplement 1 for details). For chiral molecules, the $\hat{\sigma}_{xz}$ symmetry is intrinsically broken [44]. The above discussion is reduced to whether $\Phi(x, y, z)$ breaks the $\hat{\mathcal{R}}_\pi^x$ symmetry, again resulting in the condition Eq. 6.

If Eq. 6 holds, only harmonics parallel to the recombination direction are generated, while the perpendicular component is suppressed. For molecules, the condition is guaranteed when linearly polarized driving fields are employed. In this case, the ionization and recombination occur in the same direction so that $\beta = 0$, and thus, Eq. 6 holds for any system. As a result, only linearly polarized harmonics can be generated with a linearly polarized driver. However, when 2D fields are employed, the ionization and recombination directions are misaligned, i.e., $\beta \neq 0$. For molecules, $f(-\beta - \theta, \eta, \varphi) \neq f(\beta - \theta, \eta, \varphi)$ and the symmetries of $|\Phi\rangle$ are broken. Consequently, the perpendicular component emerges upon recombination, predominantly giving rise to EP harmonic radiation. Note that, the elliptical polarization obtained here emerges due to the effect of the nonisotropic molecular structure, as manifested by $f(\alpha, \eta, \varphi)$, instead of through laser optimization. The same conclusion is applicable to all trajectories that recombine at different times t .

(b) Non-head-on recombination: The second scenario for symmetry breaking in Eqs. 3a and 3b corresponds to the experimental efforts to achieve nonzero spectral chirality from atomic gases by optimizing the waveform of the driving laser. Considering $(1 - \hat{\sigma}_{xz})\Phi^* = 0$ and $(1 - \hat{\mathcal{R}}_\pi^x)\Phi^* = 0$ for atoms due to their isotropic microscopic structure, Eqs. 3a and 3b become

$$D_{y,k} = \int_{x=-\infty}^{\infty} \int_{y=0}^{\infty} \int_{z=-\infty}^{\infty} y \Phi^*(x, y, z) (1 - \hat{\sigma}_{xz}) \phi_k(x, y, z) dx dy dz, \quad (7a)$$

$$D_{y,k} = \int_{x=-\infty}^{\infty} \int_{y=0}^{\infty} \int_{z=-\infty}^{\infty} y \Phi^*(x, y, z) (1 - \hat{\mathcal{R}}_\pi^x) \phi_k(x, y, z) dx dy dz. \quad (7b)$$

Changing the driving field waveform deflects the electron trajectory. As a result, the center of the recombining wave packet misses the center of the parent ion, i.e., the origin of the xyz coordinate. For these recombining wave packets, $(1 - \hat{\sigma}_{xz})\phi_k \neq 0$ and $(1 - \hat{\mathcal{R}}_\pi^x)\phi_k \neq 0$ and nonlinearly polarized radiation can be obtained upon the recombination. However, HHG based on non-head-on recombination will dramatically sacrifice efficiency [31]. This is one major problem we aim to avoid in this work.

In the following, we will focus on the first scenario using nonaligned molecules. In light of the preceding discussion, we can define $(1 - \hat{\mathcal{R}}_\pi^x)\Phi^*(x, y, z) = \Lambda \Phi^*(x, y, z)$, with Λ reflecting the symmetry breaking closely associated with the generation of the perpendicular components. Note that the symmetry breaking originates from the nonisotropic microscopic molecular structure: $\Lambda = 0$ for $f(\beta - \theta, \eta, \varphi) = f(-\beta - \theta, \eta, \varphi)$. The ellipticity of the obtained harmonic radiation upon the single

recombination ϵ is positively correlated with $D_{y,k}$ [37] and thus Λ , denoted as $\epsilon \sim \Lambda$. Incidentally, this theoretical framework can be generally used to help understand the polarization control in other works, such as utilizing the asymmetric responses of degenerate current-carrying states to the BCCP fields (see Sec. 3 of Supplement 1 for details).

HHG considering interference for different trajectories

In the experiment, the observed high harmonics result from the interference of radiation upon recombinations of different trajectories. The result of the interference is closely related to the symmetry of the target and the driving laser, thereby leading to the selection rule of HHG. To make our discussion concise, we take the BCCP field as an example. The BCCP field possesses a C_3 symmetry, which is invariant under a time translation of $T/3$ (T is the optical period of the fundamental laser) and a rotation of $2\pi/3$; see Fig. 1. There are 3 shortest trajectories per cycle with a recombination momentum magnitude k , which contribute to harmonics with an angular frequency $\omega_h = N\omega = k^2/2 + I_p$. $\omega = 2\pi/T$ is the angular frequency of the fundamental component of the BCCP field, and I_p is the ionization potential of the target.

We define the harmonic radiation of the ensemble contributed by the first trajectory as $\mathbf{E}_{1,\omega_h} = E_0[1 + \epsilon, 1 - \epsilon]^T e^{iN\omega t}$, corresponding to the ellipticity of ϵ upon the single recombination. The 2 elements of the vector represent the right- and left-rotating components. E_0 represents the magnitude of the radiation. Then, the interference of the 3 contributions in one cycle is (see Supplement 1 for details)

$$\mathbf{E}_{\text{cycle},\omega_h} = E_0 \begin{bmatrix} (1 + \epsilon) \left\{ 1 + 2\cos\left[(N-1)\frac{2}{3}\pi\right] \right\} \\ (1 - \epsilon) \left\{ 1 + 2\cos\left[(N+1)\frac{2}{3}\pi\right] \right\} \end{bmatrix} e^{iN\omega t}. \quad (8)$$

For a multicycle driving pulse, N is an integer corresponding to the harmonic order. Equation 8 indicates the selection rule of HHG from the nonaligned molecules in the BCCP field: $3n$ -order (n is an integer) harmonics are suppressed, only the right-rotating component is allowed for $3n + 1$ orders, and only the left-rotating component is allowed for $3n - 1$ orders. More importantly, the analysis above shows that the amplitudes of adjacent left- and right-rotating harmonics are unequal for nonzero ϵ , leading to nonzero spectral chirality of HHG. Specifically, the spectral chirality can be quantified as $\chi = [(1 + \epsilon)^2 - (1 - \epsilon)^2] / [(1 + \epsilon)^2 + (1 - \epsilon)^2] = 2\epsilon / (1 + \epsilon^2) \sim \Lambda$ [22,32,45], positively correlated with ϵ ($-1 \leq \epsilon \leq 1$) and the symmetry breaking Λ . The nonzero spectral chirality for various orders allows for the opportunity to synthesize EP attosecond pulses in the temporal domain.

It is also worth noting that not all specific forms of 2D driving fields are appropriate choices. One should consider the selection rules and avoid the symmetry-based restrictions that hinder the generation of CP and EP harmonics. For instance, in the case of multicycle orthogonal 2-color fields, if the temporal periodicity of the HHG process is well maintained, the selection rule allows only the generation of linearly polarized harmonics with mutually perpendicular polarization directions [29,45]. This can be intuitively understood as follows: while individual recombination contributes to EP radiation as discussed in the ‘‘Analysis for one trajectory’’ section, interference

between radiations from 2 symmetric trajectories in adjacent half cycles results in the cancellation of one polarization component. In this case, the spectral chirality approaches zero.

Numerical demonstration for the symmetry analysis

To more intuitively elaborate the above symmetry analysis regarding the total dipole moment, we present illustrative numerical results as a visualization of the analytical discussion in the “Analysis for one trajectory” section taking N_2 and CO_2 as examples.

According to Eqs. 3a and 3b, whether the perpendicular harmonic component can be generated upon head-on electron recombination depends on the symmetry of $|\Phi\rangle$. Based on Eq. 2, $\Phi(x, y, z)$ is obtained by superposing various molecular orbitals $\phi_{\theta, \eta, \varphi}(x, y, z)$ of all different orientation angles, weighted by their ionization rates $f[\alpha(\theta), \eta, \varphi]$. In this subsection, for the sake of clarity and simplicity while not losing generality for the illustration, we consider only molecules orientated in the laser polarization plane (the $x - y$ plane). In Fig. 2A and D, we show the isosurface plot of $\Phi(x, y, z)$ for N_2 and CO_2 respectively “seen” by the recombining electron following the trajectory depicted in the insets (corresponding to the radiation of 13th harmonic). The trajectory is calculated by numerically solving the Newton equation with zero initial velocity. The driving field is composed of right-rotating circularly polarized light at 800 nm and left-rotating circularly polarized light at 400 nm, both with an intensity of $0.75 \times 10^{14} \text{ W/cm}^2$. The individual molecular orbitals are obtained with the Hartree–Fock method [46], and the ionization rate is evaluated by the Ammosov–Delone–Krainov theory [47].

As expected, the obtained $\Phi(x, y, z)$ possess a strongly isotropic structure and break the $\hat{\sigma}_{xz}$ and $\hat{R}_\pi^x$ symmetries, because of the orientation-dependent weights f for the molecular orbitals. Consequently, remarkable perpendicular components D_y were

generated, as shown in Fig. 2B and E. By contrast, if we eliminate the molecular structure effect by forcing $f = 1$, $\Phi(x, y, z)$ will possess an isotropic structure and no perpendicular components will be obtained. To intuitively examine the polarization state of the harmonic radiation upon the recombination, we project the total dipole momentum $\mathbf{D}_k$ on the right- and left-rotating components $D_{\pm, k} = (D_{x, k} \pm iD_{y, k}) / \sqrt{2}$ [48]. $|D_{+, k}| = |D_{-, k}|$ indicates that the harmonic radiation upon the recombination is linearly polarized. $|D_{+, k}| > |D_{-, k}|$ corresponds to the right-rotating elliptical or circular polarization, and vice versa. The ellipticity of the radiation can be evaluated according to the relation $2\epsilon / (1 + \epsilon^2) = (|D_{+, k}|^2 - |D_{-, k}|^2) / (|D_{+, k}|^2 + |D_{-, k}|^2)$ [49]. The ellipticity of the radiation for N_2 and CO_2 are presented in Fig. 2B and E, respectively. Likewise, substantial EP radiation can be obtained with nonisotropic f and Φ , while the radiation is linearly polarized when an isotropic f is imposed.

To gain a deeper insight, we decouple the total dipole moment (corresponding to the trajectory radiating the 13th harmonic) into the recombination dipole moment of individual molecular orbitals with the in-plane orientation angle θ as $\mathbf{d}_k(\theta) = \langle \phi_\theta | \hat{\mathbf{r}} | \phi_k \rangle$, where $\mathbf{D}_k = \sum_\theta f[\alpha(\theta)] \mathbf{d}_k(\theta)$. Herein, the individual molecular recombination dipole moment $\mathbf{d}_k(\theta)$ is obtained by quantitative rescattering theory [46, 50]. For both N_2 and CO_2 , the phase difference between $d_{y, k}(\theta)$ and $d_{y, k}(-\theta)$ is π , leading to $d_{\pm, k}(\theta) = d_{\mp, k}(-\theta)$. Thus, the harmonic radiation should be symmetric about $\theta = 0$ but with opposite ellipticities: $|d_{+, k}(\theta)|^2 - |d_{-, k}(\theta)|^2 = -(|d_{+, k}(-\theta)|^2 - |d_{-, k}(-\theta)|^2)$. The results are shown in Fig. 2C and F, where the red and blue areas indicate right-elliptical polarization ($|d_{+, k}(\theta)| > |d_{-, k}(\theta)|$) and left-elliptical polarization ($|d_{+, k}(\theta)| < |d_{-, k}(\theta)|$), respectively. Meanwhile, the ionization rate f , shown by the red

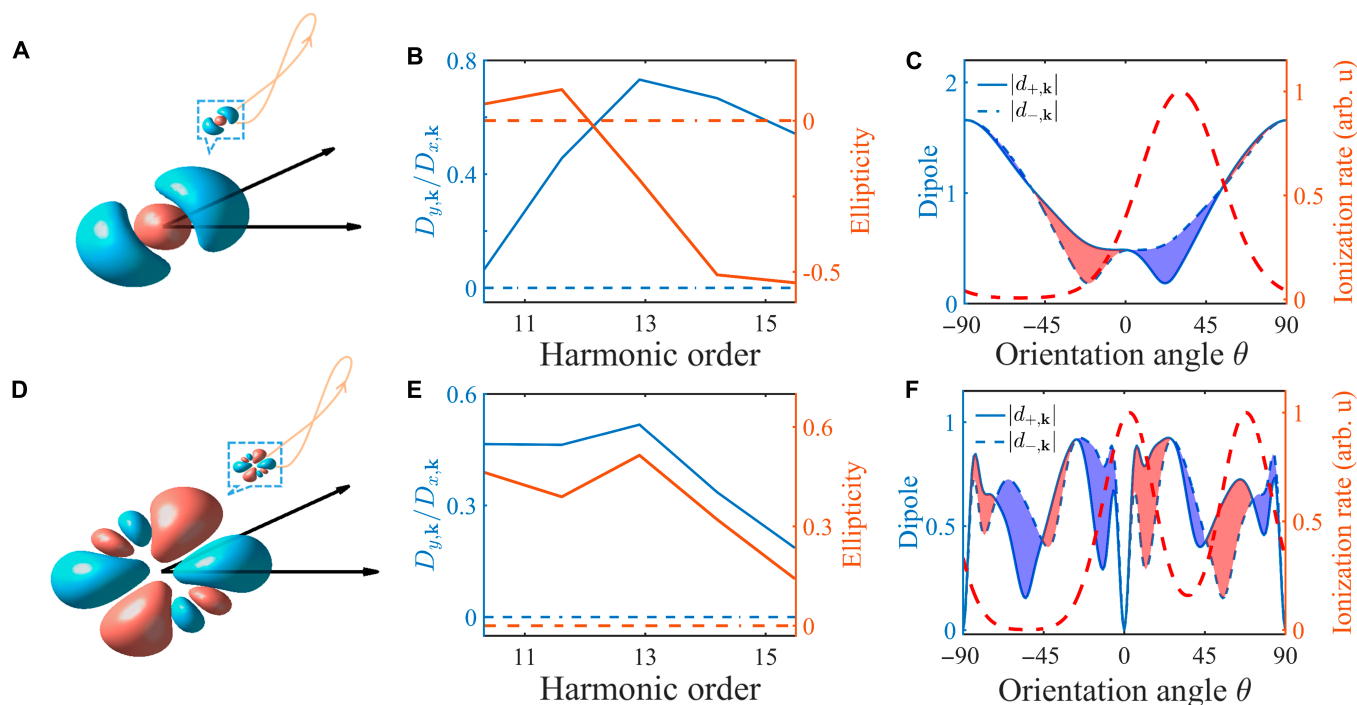


Fig. 2. The isosurface plot of $\Phi(x, y, z)$ for (A) N_2 and (D) CO_2 . The ratio of $D_{y,k}$ to $D_{x,k}$ and the harmonic radiation ellipticity for (B) N_2 and (E) CO_2 . The numerical $d_{+,k}$ and $d_{-,k}$ for (C) N_2 and (F) CO_2 as a function of orientation angle θ . The red dashed lines represent the ionization rate.

curves in Fig. 2C and F, serves as a filter for the individual recombination dipole moment as $\mathbf{D}_k = \sum_{\alpha} f[\alpha(\theta)] \mathbf{d}_k(\theta)$. If f is constant (isotropic atom) or symmetric about $\theta = 0$ (linearly polarized driving laser), the supposition of individual $\mathbf{d}_k(\theta)$ would lead to a total dipole moment for zero ellipticity, since $|D_{+,k}|^2 - |D_{-,k}|^2 = \left(\left| \sum_{\alpha} f[\alpha(\theta)] d_{+,k}(\theta) \right|^2 - \left| \sum_{\alpha} f[\alpha(\theta)] d_{-,k}(\theta) \right|^2 \right) = 0$. However, in the case of molecules (f is orientation dependent) driven by 2D driving fields ($\beta \neq 0$), the ionization serves as a filter that selects part of $\mathbf{d}_k(\theta)$ asymmetric about $\theta = 0$.

Specifically, N_2 has a σ_g highest occupied molecular orbital where ionization is maximized along the molecular axis. As a result, the ionization peaks at about $\theta = 35^\circ$ as shown in Fig. 2C, mainly selecting contributions for negative ellipticity. Thus, the total harmonic radiation upon the recombination is left-EP as shown in Fig. 2B. The orbital of CO_2 possesses the π_g symmetry, for which the ionization is suppressed along the molecular axis but maximized at about $\alpha = \pm 33^\circ$. Accordingly, the distribution of the ionization has 2 peaks at about $\theta = 2^\circ$ and $\theta = 68^\circ$ (see Fig. 2F), which mainly selects contributions for positive ellipticity, leading to right-EP radiation as shown in Fig. 2E.

One can see that the symmetry of the molecular orbital can affect the total result by determining the features of the weights. For example, if the ionization for CO_2 (in Fig. 2F) possessed a distribution similar to that of N_2 corresponding to the σ_g symmetry, more contributions with negative ellipticity around 35° will be selected and the sign of ellipticity of the harmonic radiation may be altered. However, the final result is still essentially dependent on the specific feature of the recombination dipole moment, namely, the specific structure of the orbital.

Methods

The theoretical discussion above has comprehensively elucidated the basis of the polarization control within the collinear strategies and offers guidelines for efficiently generating high harmonics with high spectral chirality: (a) A laser field capable of driving the electron for a (nearly) head-on recombination is favorable. (b) Meanwhile, the dynamical symmetry with the driving field should lead to selection rules allowing the generation of EP or CP harmonics. (c) The target system should possess a microscopic structure that substantially breaks the isotropic symmetry. Accordingly, we will demonstrate our scheme experimentally with nonaligned N_2 and CO_2 driven by the BCCP fields, in line with these guidelines. The choice of the BCCP field as a demonstrative example brings additional convenience to experiments: the left- and right-rotating harmonics are separated in frequency according to the selection rule, making it easier to evaluate spectral chirality without the need for a polarization analyzer in the ultraviolet range.

The schematic layout of the experimental apparatus is shown in Fig. 3. We perform the experiment by using a commercial Ti:sapphire-based laser system. It delivers 35-fs pulses with a central wavelength of 800 nm at a repetition of 1 kHz. The initial beam is divided into 2 separate beams with a 70/30 intensity ratio. The stronger one is frequency up-converted to the second harmonic at 400 nm by a β -phase barium borate crystal (300 μm thick, type I), and the weaker beam remains at the fundamental wavelength. Both the second harmonic and fundamental beams separately pass through half-wave plate and polarizer pairs to control the pulse energy (not displayed for conciseness) and half-wave plate and quarter-wave plate pairs

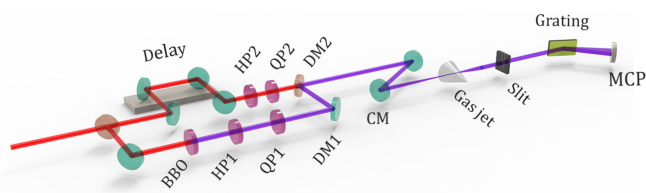


Fig. 3. Schematic layout of the experimental setup for the HHG of nonaligned gases driven by BCCP laser fields. HP1, half-wave plate 1; HP2, half-wave plate 2; QP1, quarter-wave plate 1; QP2, quarter-wave plate 2; DM1, dichroic mirror 1; DM2, dichroic mirror 2; BBO, β -phase barium borate; CM, concave mirror; MCP, microchannel plate.

to yield nearly circular polarization with right-rotating helicity for the fundamental beam and left-rotating helicity for the second harmonic beam, respectively. In the end, both beams are carefully combined in a collinear geometry by dichroic mirrors and focused onto a supersonic gas jet by a silver-coated concave mirror with a focal length of 250 mm. The ellipticities of the fundamental beam and the second harmonic beam are both measured via a wire grid polarizer after the concave mirror and have a value of approximately 0.98. The relative time delay between the 2 beams is precisely controlled by stepping the fundamental beam with a motorized stage. The intensities of both beams are tunable throughout the experiment. The generated harmonics are dispersed by a slit and a flat-field grating. Then, the frequency-resolved harmonics are imaged onto a microchannel plate with a phosphor screen, which exhibits a good spatial uniformity of gain (see Sec. 8 of Supplement 1 for details). Finally, the image of generated harmonics is read out by a charge-coupled device. The harmonic spectra are determined via integrating the microchannel plate image along the divergence angle.

Results and Discussion

Figure 4 shows the harmonic spectra of nonaligned N_2 and CO_2 molecules driven by the BCCP field. The result of an Ar atom is displayed for comparison as well. The same gas pressure (0.3 atm) and the same gas jet position are applied for different gases. For these spectra, the total intensity of the driving laser is estimated to be approximately $1.5 \times 10^{14} \text{ W/cm}^2$, and the intensity ratio $I_\omega / I_{2\omega} = 1$, where I_ω and $I_{2\omega}$ are the intensities of the fundamental and second harmonic components, respectively. Within the spectra, a pronounced suppression of $3n$ -order harmonics is observed for both the atom and nonaligned molecules. Although $3n$ -order harmonics can be generated from individual molecules, the observed high harmonics from the nonaligned ensemble are a coherent superposition of radiations contributed by the molecules oriented at various angles, which will lead to the cancellation of the $3n$ harmonics. The result of the coherent superposition can be understood by the selection rule, which is more explicitly explained by the analytical derivation in the “HHG considering interference for different trajectories” section of the main text and Sec. 2 of Supplement 1. This observation aligns with the selection rules as indicated in Eq. 8, confirming that the BCCP driving field has been well synthesized in our experiment. Accordingly, $3n \pm 1$ -order harmonics are right (RCP) and left circularly polarized (LCP), respectively. The spectral chirality χ can be readily calculated as $\chi = (I_{\text{RCP}} - I_{\text{LCP}}) / (I_{\text{RCP}} + I_{\text{LCP}})$ [22,32,45], where I_{RCP} and I_{LCP} represent the integrated signals for all of the observed RCP

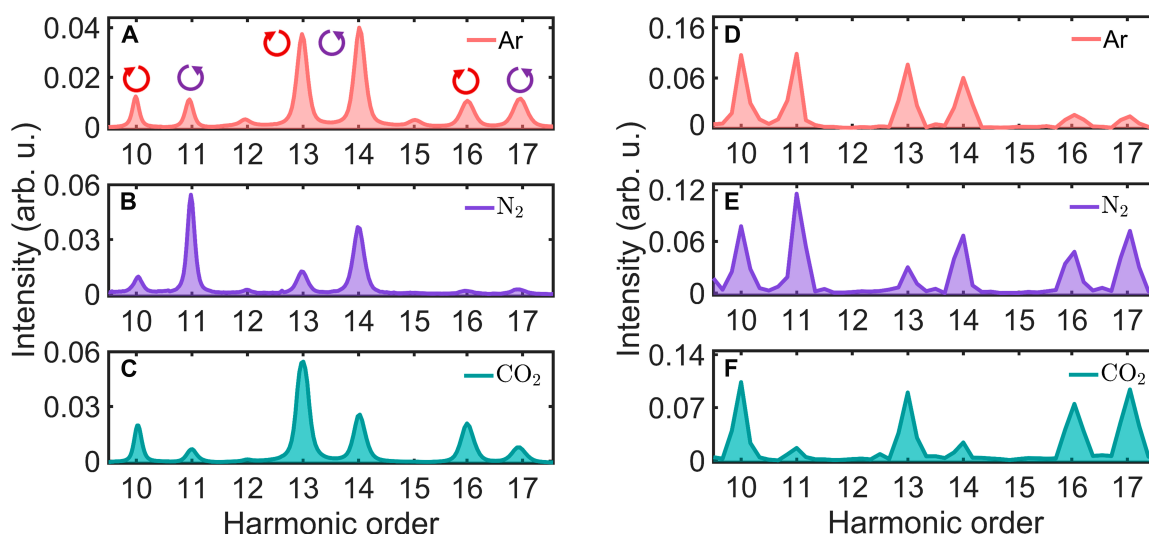


Fig. 4. The measured harmonic spectra of (A) Ar atoms, (B) nonaligned N_2 molecules, and (C) nonaligned CO_2 molecules driven by the BCCP field. The total intensity is $1.5 \times 10^{14} \text{ W/cm}^2$ with an intensity ratio $I_\omega / I_{2\omega} = 1$. The corresponding numerical harmonic spectra with the same laser conditions are presented in (D) to (F), respectively.

and LCP harmonics in the spectra, respectively. Note that some spectra still exhibit residual indications of the $3n$ -order harmonics, implying that a slight degeneration of the driving laser polarization may occur while performing some of the measurements. In fact, any laser fields that satisfy the conditions concluded from the above analysis work for our scheme, and a perfect BCCP field is not necessary. The imperfect polarization will not affect our conclusions; see Sec. 6 of Supplement 1 for detailed discussion.

For Ar, the intensities of adjacent harmonics are approximately equal, resulting in a small spectral chirality close to 0. This is consistent with earlier findings by Dorney et al. [22] regarding the phenomenon that the spectral chirality for Ar approaches zero with an intensity ratio close to 1:1, although the experimental conditions such as the total laser intensity are different. One can increase the spectral chirality by changing the intensity ratio $I_\omega / I_{2\omega}$. However, the modified laser field would drive the continuum electrons away from the parent core, leading to a substantial decrease in the HHG efficiency, as discussed in the “Analysis for one trajectory” section for Scenario (b). By contrast, substantially nonzero spectral chirality is obtained for nonaligned molecules, even in the case that the spectral chirality is close to zero for Ar and that the HHG efficiency is approximately maximized (also shown in the results of the scanning intensity ratio below), which implies nearly direct recombination of the continuum electrons. For nonaligned N_2 , the $3n - 1$ -order (LCP) harmonics prevail over the $3n + 1$ -order (RCP) harmonics, resulting in a negative spectral chirality of $\chi \approx -0.5$. Conversely, for nonaligned CO_2 , the $3n + 1$ -order (RCP) harmonics dominate the harmonic spectra, leading to a positive spectral chirality of $\chi \approx 0.4$. These observations confirm that the molecular structural effect can be utilized even in nonaligned ensembles to increase the spectral chirality of HHG. The intrinsic benefit of utilizing the structural effect is that it avoids the sacrifice of HHG efficiency by modifying the waveform of the driving field. The opposite sign of the spectral chirality observed for the 2 molecules suggests that the harmonic polarization of nonaligned molecules is highly sensitive to the microscopic molecular structure.

Meanwhile, our method can be combined with optimizing the driving field to control the harmonic polarization, for instance, by adjusting the intensity ratio $I_\omega / I_{2\omega}$ [22,40]. This corresponds to the third case (c) for symmetry breaking discussed with Eqs. 3a and 3b. By altering the driving field, both the propagation trajectories and $|\Phi\rangle$ can be manipulated. In Fig. 5, we present the results of nonaligned N_2 , where the intensity ratio is tuned under a total intensity of $1.5 \times 10^{14} \text{ W/cm}^2$. Specifically, the intensity ratios $I_\omega / I_{2\omega}$ from top to bottom rows are 1, 1.2, and 1.4, respectively. As $I_\omega / I_{2\omega}$ increases, the relative intensity of $3n + 1$ -order harmonics rises. Correspondingly, the spectral chiralities χ from the top to bottom rows are -0.5 , 0, and 0.35, respectively. Namely, in the temporal domain, the synthesized pulse reverses from left rotating to right rotating.

To delve deeper into the results, we summarize the obtained harmonic yield and spectral chirality as a function of $I_\omega / I_{2\omega}$ ranging from 0.85 to 4 in Fig. 6A and B, for nonaligned N_2 and CO_2 as well. The numerical yield of the n -order harmonic is obtained by summing the harmonic spectrum across $n\omega \pm 0.5\omega$. Then, the theoretical yield is the sum of yields for each-order harmonics above the ionization threshold. The numerical spectral chirality is computed over the same harmonic orders as the experiment. As expected, with $I_\omega / I_{2\omega}$ deviating from around 1, the harmonic yields for both N_2 and CO_2 decrease, in accordance with the result of the atom [22]. Nevertheless, since the molecular structural effect plays a pivotal role here, a modest adjustment in the intensity ratio is needed for efficient polarization control and the increase in the spectral chirality can be accompanied by less reduction in the HHG efficiency. For example, with the intensity ratio increasing to 4 for N_2 , the spectral chirality reaches as high as 0.7, while the harmonic yield is decreased by only one order of magnitude. The positive spectral chirality of nonaligned N_2 is also observed at an intensity ratio of $I_\omega / I_{2\omega} \approx 1.8$ in Barth and Smirnova [51].

Moreover, comparing the results of N_2 and CO_2 , an intriguing phenomenon emerges. For N_2 , one can see approximately opposite trends of the harmonic yield and the spectral chirality as a function of $I_\omega / I_{2\omega}$. This shows the trade-off of the 2 quantities commonly observed previously. However, for nonaligned

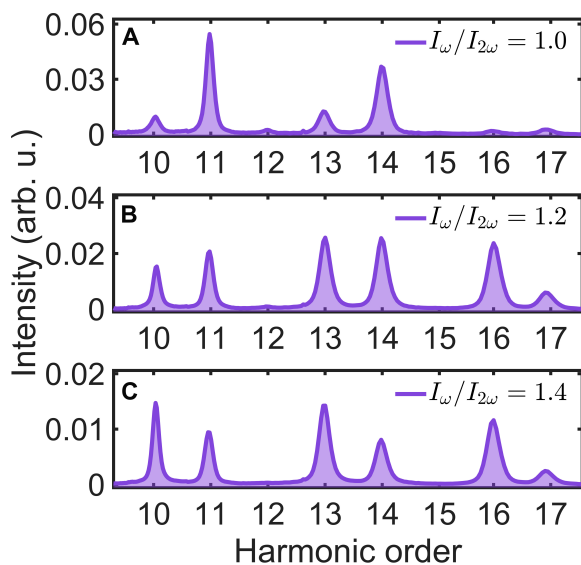


Fig. 5. The measured harmonic spectra of nonaligned N_2 molecules driven by the BCCP fields. The total intensity remains at $1.5 \times 10^{14} \text{ W/cm}^2$. The intensity ratios $I_\omega/I_{2\omega}$ for (A), (B), and (C) are 1, 1.2, and 1.4, respectively.

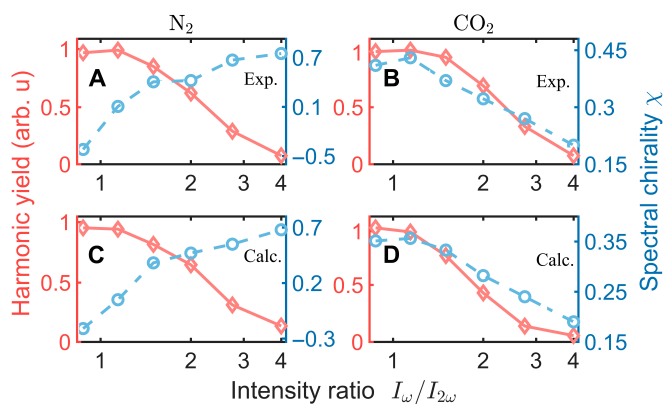


Fig. 6. The measured harmonic yield and spectral chirality χ of nonaligned (A) N_2 and (B) CO_2 molecules as a function of the intensity ratio $I_\omega/I_{2\omega}$. The total intensity of the driving laser remains at $1.5 \times 10^{14} \text{ W/cm}^2$. Results of numerical simulations based on the 2-dimensional time-dependent Schrödinger equation (2D-TDSE) with a total intensity of $1.5 \times 10^{14} \text{ W/cm}^2$ are present in the bottom row for (C) N_2 and (D) CO_2 as well. The harmonic yield is normalized to the case of $I_\omega/I_{2\omega} = 1$. Calc., calculated; Exp., experimental.

CO_2 , both the spectral chirality and the harmonic yield increase as the intensity ratio $I_\omega/I_{2\omega}$ decreases. The distinct behaviors between N_2 and CO_2 again reflect the high sensitivity of the harmonic polarization to the specific microscopic structure, even within nonaligned targets. The abnormal trend in the spectral chirality for CO_2 implies that the modulation of the harmonic polarization predominantly arises from molecular structural effects, namely, based on the manipulation of $|\Phi\rangle$ rather than the trajectories. More importantly, the findings from CO_2 indicate the possibility of simultaneously maximizing both the spectral chirality and HHG efficiency, which is critical to producing bright highly EP attosecond pulses.

Given the different orbital symmetries for N_2 and CO_2 (σ_g and π_g), respectively, it is interesting to ask whether the orbital symmetry determines their distinct behaviors. The opposite signs of spectral chirality can be understood according to the

discussions in the “Numerical demonstration for the symmetry analysis” section, which should be dependent on the specific feature of the dipole moment, namely, the specific structure of the molecular orbital. Likewise, the trend of the spectral chirality is not uniquely determined by the orbital symmetry either but depends on its specific structure. For example, Sec. 5 in Supplement 1 shows the experimental results of O_2 , whose molecule has the same π_g symmetry as CO_2 . The spectral chirality possesses a trend opposite to that of CO_2 . On the other hand, the abnormal trend is not restricted to π_g orbitals.

Figure 6 shows the summarized harmonic yield and spectral chirality obtained by numerically solving the 2D time-dependent Schrödinger equation. In these simulations, the target molecules are modeled by the soft-core potential $V(r) = -\sum_m \left[(Z_{mi} - Z_{mo}) e^{-[(r - \mathbf{R}_m)^2/\rho_m]} + Z_{mo} \right] / \sqrt{\xi_m^2 + (\mathbf{r} - \mathbf{R}_m)^2}$, where m labels the nuclei at fixed positions $\mathbf{R}_m$. For the N_2 molecule, Z_{Np} , Z_{No} , ρ_N , and ξ_N^2 are 0.5, 7, 0.7, and 1.2, respectively. For the CO_2 molecule, they are 0.173, 8, 0.577, and 1.3 for the oxygen atom and 0.654, 6, 0.75, and 1.05 for the carbon atom, respectively. We first calculate the harmonic radiation of the single molecule aligned at angles from 0° to 175° , with an interval of 5° . More details on the soft-core potential and the numerical calculation can be found in Sun et al. [52]. Then, the harmonic spectrum of the nonaligned ensemble is obtained by coherently superposing these individual harmonic radiations. The laser parameters utilized in the simulations are the same as those employed in the experiments. In this work, we focus on the generation of high harmonics with nonzero spectral chirality while not substantially sacrificing the harmonic yield compared to a head-on recollision (with an intensity ratio close to 1:1). Thus, we are focused on the spectral chirality and the HHG efficiency relative to that of a 1:1 intensity ratio. In this regard, the simulation results corroborate the same phenomena observed in the experiments, including the exhibition of nonzero spectral chirality at a 1:1 intensity ratio as well as the trends of the spectral chirality and HHG yield as a function of the intensity ratio. Note that this numerical simulation only takes into account the nonisotropic structure of molecules and a direct coherent superposition of the harmonic radiation from single molecules with various orientations as in Theory. The spectral chirality vanishes for a 1:1 intensity ratio if the molecular potentials are replaced by isotropic soft-core potentials (see Sec. 7 of Supplement 1 for details). Therefore, the agreement between the simulation and experiment further confirms that the observations are indeed due to the proposed effect instead of other effects, such as phase matching, not included in the simulation.

Considering the short cutoff due to the use of the 800-nm fundamental driving laser, a longer driving wavelength is favorable to extend the width of the EP spectrum. We present a simulation result involving nonaligned CO_2 driven by a BCCP field with a fundamental wavelength of 1,200 nm. Both the intensities of the fundamental field and its second harmonic are $1.2 \times 10^{14} \text{ W/cm}^2$. As illustrated in Fig. 7, within the range from the 30th to the 60th orders, the LCP $3n - 1$ -order harmonics dominate over the RCP $3n + 1$ -order harmonics. This signifies that the synthesis of harmonics within this range holds the potential for generating EP attosecond pulses with a substantial ellipticity. Here, the effect of depolarization is not taken into account and it may lead to an uncertainty in the effective ellipticity [53].

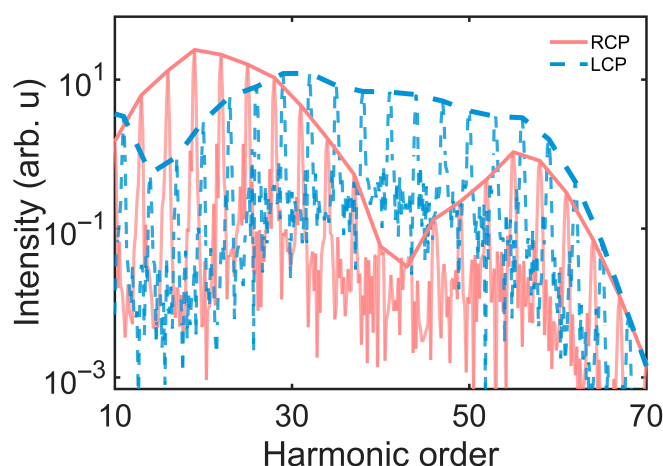


Fig. 7. Simulated high harmonic spectra of the left-rotating (left circularly polarized [LCP]) and right-rotating (right circularly polarized [RCP]) components for nonaligned CO_2 driven by the BCCP field with the fundamental wavelength of 1,200 nm. Both the intensities of the fundamental component and its second harmonic are $1.2 \times 10^{14} \text{ W/cm}^2$.

Looking forward, our multiscale analysis concerns the manifestation of the microscopic structural effect in the macroscopic nonaligned gas medium while not yet taking into account the effects of light propagation and spatial structure as in the paper by Lerner et al. [30], which are meanwhile insignificant in the present experiments. In other experimental conditions, the macroscopic effects may play an important role. Thus, in the future, our scheme can be combined with other techniques such as utilizing gas-filled waveguides [13,14,54,55] or applying structured light.

Conclusion

In conclusion, this study presents both theoretically and experimentally a novel scheme to control the polarization of HHG utilizing the microscopic molecular structural effect without the need for prealignment. We have comprehensively elucidated the basis of the polarization control with a multiscale symmetry analysis associating the microscopic molecular structure with the symmetry breaking for the macroscopic ensemble. The analysis unveils the benefit of our scheme in HHG efficiency and offers guidelines for efficiently generating CP or EP attosecond pulses. The experimental results confirm that the polarization properties of HHG exhibit exceptional sensitivity to the molecular structures, even in the absence of molecular alignment. By varying the intensity ratio, we find that substantially nonzero spectral chirality can be achieved associated with the highest HHG efficiency from both the nonaligned N_2 and CO_2 . Moreover, our study has showcased a simultaneous enhancement in both spectral chirality and HHG efficiency for CO_2 , overcoming the trade-off between them. These findings are expected to contribute substantially to the development of attosecond light sources with superior brightness and large ellipticity, thus advancing the field of ultrafast laser science and its applications.

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Author contributions: P. Lan and X.Z. conceived and designed the experiment. J.L., C.Z., and L.H. performed the experiments. X.Z. conducted the symmetry analysis. J.L. and X.Z. performed the simulations. W.L., W.H., and P. Lu participated in the discussions and analyses. J.L., X.Z., and P. Lan prepared the manuscript.

Competing interests: The authors declare that they have no competing interests.

Data Availability

The data that support the findings of this study are available within the article.

Supplementary Materials

Supplementary Text
Figs. S1 to S8

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