Phase-matched locally chiral light for global control of chiral light-matter interaction

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Compiled October 4, 2023

Locally chiral light is an emerging tool for probing and controlling molecular chirality. It can generate large and freely adjustable enantioselectivities in purely electric-dipole effects, offering its major advantages over traditional chiral light. However, the existing types of locally chiral light are phase-mismatched, and thus the global efficiencies are greatly reduced compared with the maximum single-point efficiencies or even vanish. Here, we propose a scheme to generate phase-matched locally chiral light. To confirm this advantage, we numerically show the robust highly efficient global control of enantiospecific electronic state transfer of methyloxirane at nanoseconds. Our work potentially constitutes the starting point for developing more efficient chiroptical techniques for the studies of chiral molecules.

http://dx.doi.org/10.1364/ao.XXXXX

Molecular chirality plays a central role in chemical reactions, biological activities, drug industries, and life’s chemistry, which makes probing and controlling molecular chirality vitally important and challenging tasks across natural science. Using single circularly light (i.e., traditional chiral light) to probe [1–4] molecular chirality began with the first discovery of molecular chirality. It was also proposed to control enantiomeric excess in an inner state [5], i.e., enantiospecific state transfer. The enantioselectivities generated by the traditional chiral light come from the interference between electric- and magnetic-dipole light-matter interactions. The relative strength between them is almost a fixed parameter at a ratio of (≈ 1/137) [5], so the generated enantioselectivities are usually tiny and not freely adjustable.

Locally chiral light (LCL) [6–12] is an emerging chiral light source that can generate large and freely adjustable enantioselectivities in purely electric-dipole effects. LCLs are multichrome, composed of carrier waves with well-designed polarizations and frequencies. While the traditional chiral light’s degree of chirality (DOC) at a single point in space is determined by the electric and magnetic fields at that point and nearby [13], LCLs’ DOC at a single point only depends on the electric field at that point (or equivalently the local electric field). Specifically, at each fixed point in space, the tip of the electric field vector draws a chiral 3D Lissajous curve when it evolves in time. Beyond probing and controlling chiral molecules, the LCLs were also proposed to imprint chirality on achiral matter [14], offering new opportunities to realize laser-driven achiral–chiral phase transitions in matter [15–17].

With the benefit of hindsight, the studies of all-electric-dipole chiroptical techniques by using LCLs began almost two decades ago in the framework of the cyclic three-level model [18–21], where the driving electromagnetic fields are tricolor LCLs. The three carrier waves couple with chiral molecules in the one-photon (near-)resonance, and thus the dynamics of chiral molecules can be described by the cyclic three-level model [22–28]. Experimentally, the tricolor LCLs were used in the well-demonstrated microwave techniques of enantiodetection [29–34] and enantio-specific state transfer [35–37]. The equivalent chiroptical techniques in the UV-IR region [18] are long pursued but never realized. One key problem is that tricolor LCLs are phase-mismatched [38], such that their DOCs and the generated enantioselectivities change periodically in space and even vanish by integrating over the whole spatial period (or equivalently globally achiral). This problem becomes grave in the UV-IR region because of the short wavelengths [7].

To solve this problem, chirality polarized light (CPL) [11] and locally-and-globally chiral light (LGCL) [6] were proposed. CPL is globally achiral but has the polarization of chirality, just like the neutral and polarized one-dimensional medium of alternating negative and positive charges. This property makes the emission directions highly enantioselective for CPL. LGCL is more efficient because it is globally chiral. However, they are still phase-mismatched, such that the enantiospecific electronic state transfer in the UV-IR region is still out of reach. Moreover, CPL and LGCL worked in the strong-field region, which is usually accompanied by the destruction of the molecule or the change of the molecular conformer (not chirality).

In this Letter, we propose a scheme to generate a novel type of LCL without the phase-mismatch problem. Thus, we name it the phase-matched LCL. This feature offers our scheme advantages over existing LCLs in global control of chiral light-molecule interactions. To illustrate this, we use a four-color example of our scheme and numerically show its ability in the robust highly efficient global control of enantiospecific electronic state transfer of methyloxirane at nanoseconds in the UV-IR re-
The second sub-beam, labeled with \( (a) \), is monochrome and exhibits circular polarization. Such a condition is phase-matched. In contrast, the nonzero CCFs of the tricolor LCL and LGCL are functions of \( k_1 \cdot r \) (see Sec. 1C and Sec. 1D of Supplement), i.e., they are phase-mismatched. We note that Eq. (1) provides a general scheme to form phase-matched LCLs, including the two-color phase-matched LCL (see Sec. 1B of Supplement).

For the four-color example, we are interested in the case of the one-photon (near-)resonance. Because the residual electronic transitions are coupled with the overall field off-resonantly, they are negligible in the weak-field region, yielding the simplified working model as shown in Fig. 1 (d). The molecules also have vibrational and rotational degrees of freedom. We deal with them in the Born-Oppenheimer approximation. According to the Franck-Condon principle [39], which says that an electronic transition occurs within a stationary nuclear framework, the vibrational degrees of freedom can be assumed frozen, i.e., the electronic transitions are vertical transitions. In our discussions, we are interested in the gaseous phase chiral molecules. For them, the rotational degree of freedom is described by \( \hat{H}_{rot} = \hbar (A_{\sigma}^2 + B_{\sigma}^2 + C_{\sigma}^2) \) [40]. \( A_{\sigma}, B_{\sigma}, C_{\sigma} \) are angular momentum operators along the principal axes of the moment of inertia, respectively. \( A, B, C \) are the corresponding rotational constants. Because the nuclear locations are preserved in electronic vertical transitions, the rotational constants are preserved in our consideration.

In the rotating-wave approximation, the concrete Hamiltonian of the chiral light-molecule interaction is

\[
\hat{H} = \sum_{n=1}^{N} \left( \frac{1}{2} \Omega_{n}^{\sigma} \hat{s}_{n} + \sum_{i>j=1}^{3} \Omega_{ij}^{\sigma} \hat{s}_{ij} \hat{r}_{a\beta} + h.c. \right) + \sum_{i \neq 1} \Delta_{1} \hat{s}_{ii} + \hat{H}_{rot}.
\]

The detunings are \( \Delta_{1} = \omega_{0} - (v_{1} - v_{0}), \Delta_{21} = v_{2} - v_{1} - \omega_{1}, \Delta_{31} = v_{3} - v_{1} - \omega_{3}, \) and \( \Delta_{32} = v_{3} - v_{2} - \omega_{2}. \) \( \hat{r}_{a\beta} = \{ |a\rangle \langle b| \} \) are operators in the rotational degree of freedom with \( |a\rangle = |K_{a}^{\prime},L_{a}^{\prime},M_{a}^{\prime}\rangle \) being the asymmetric-top rotational eigenstates [40]. We note that \( \sum_{n} \) means that the summation is taken over all \( n \), \( K_{a}^{\prime}, L_{a}^{\prime}, M_{a}^{\prime} \). \( \hat{s}_{ij} \) are operators in the electronic degree of freedom. Because the transition electric dipoles change signs with enantiomers [see Fig. 1(a)], the interaction Hamiltonian (2) is enantioselective as indicated by \( \Omega_{ij}^{\sigma} = -i \Omega_{ji}^{\sigma} \) with the subscripts “L” and “R” denoting the chirality. We note that the operators \( \hat{s}_{ij} = i \hat{J}_{i} \hat{J}_{j} \) are defined in the new basis with \( |0\rangle = e^{-i \Delta_{1} t} |0\rangle \), \( |1\rangle = e^{-i \Delta_{21} t} |1\rangle \), \( |2\rangle = e^{-i \Delta_{31} t} |2\rangle \), and \( |3\rangle = e^{-i \Delta_{32} t} |3\rangle \). Then, the spatially and temporally oscillated phases \( k_{1} \cdot r - \omega_{l} t \) are

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**Fig. 1.** (a) Four-color phase-matched LCL: the \( c = 1 \) sub-beam is a \( z \)-polarized three-color field propagating in the \( x \)-direction, and the \( c = 2 \) sub-beam is a one-color circularly polarized field propagating in the \( z \)-direction. The carrier waves are Gaussian beams with waists of \( w_{0,0} = 10^{3} \lambda_{0} \) and \( w_{0,1} = w_{0,2} = w_{0,3} = 10^{3} \lambda_{1} \). The wavelengths \( \lambda_{0} \) and \( \lambda_{1} \) are chosen accordingly to the example of methyloxirane in Fig. 2. The lowest-order CCFs \( \{ h^{(2)}(\omega_{0},... \omega_{n-1}) \} \) are chosen according to the example of methyloxirane in Fig. 2.

Specifically, we show the amplitude [Fig. 1(b)] and phase [Fig. 1(c)] of lowest-order CCFs \( \{ h^{(3)} \} \) in the \( y-z \) plane at \( z = 0 \) for the four-color example. The results clearly show that the four-color example is phase-matched. In contrast, the nonzero CCFs of the tricolor LCL and LGCL are functions of \( k_{1} \cdot r \) (see Sec. 1C and Sec. 1D of Supplement), i.e., they are phase-mismatched. We note that Eq. (1) provides a general scheme to form phase-matched LCLs, including the two-color phase-matched LCL (see Sec. 1B of Supplement).
Global control of enantiospecific electronic state transfer of methyloxirane by using our four-color phase-matched LCL. (a) Temporal envelopes of the applied fields at \( r = 0 \). (b) Time evolution of the population in each working electronic state for molecules at \( r = 0 \), yielding the enantiomeric excess of \(-99.27\%\) at \( r = 0 \). (c-f) \( \log_{10}(P_3^2) \) and \( \log_{10}(P_3^3) \) after the four pulses in the \( y-z \) plane for \( x = 0 \) and \( x = 2\omega_{0,0} \approx 0.32\, \text{mm} \). (g) \( P_{2D}^0(x) \equiv \int dydzP_0^0(x) \) with \( Q(=L,R) \) denoting the handedness of the chiral molecules. The global enantiomeric excess is \( \epsilon_{\text{global}} \approx -93.74\% \).

Transferred to \( \Omega_{32}^{(3)}e^{i(\omega t-\delta k \cdot r)} \) with \( \delta \omega \equiv \omega_3 - \omega_2 - \omega_1 = 0 \) and \( \delta k \equiv k_3 - k_2 - k_1 = 0 \). This clearly indicates that the Hamiltonian (2) is phase-matched, such that the molecules at different positions evolve identically in the plane-wave limit.

To illustrate the advantages of our four-color phase-matched LCL, we use methyloxirane as an example, which is a typical chiral molecule [see Fig. 1(d)]. The working electronic states \( |0\rangle, |1\rangle, |2\rangle, \) and \( |3\rangle \) are chosen as the electronic ground state, the \( 3p_\pi \)-state, the \( 3p_\pi \)-state, and the \( 3d_\pi \)-state [12]. The carrier waves with angular frequencies \( \omega_0, \omega_1, \omega_2, \) and \( \omega_3 \) are chosen resonantly couple with transitions \( |0\rangle \leftrightarrow |1\rangle \leftrightarrow |2\rangle \leftrightarrow |3\rangle \leftrightarrow |0\rangle \) [see Fig. 1(d)]. The corresponding wavelengths are \( \lambda_0 \approx 162.2633\, \text{nm} \), \( \lambda_1 \approx 6241.4404\, \text{nm} \), \( \lambda_2 \approx 1541.6517\, \text{nm} \), and \( \lambda_3 \approx 2047.3531\, \text{nm} \) [12]. The spatial profiles of carrier waves are shown in Fig. 1(a).

To achieve enantiomeric excess in the state \( |3\rangle \), we take the temporally square pulses, whose amplitudes at \( r = 0 \) evolve as shown in Fig. 2(a). To justify the validity of using the classical description of light in our discussions, we give the average photon number of the pulses, which are about \( 6.2\times10^{13}, 7.7\times10^{13}, 8.7\times10^{17}, \) and \( 1.2\times10^{18} \). They are large enough to make the photon-number phase uncertainty negligible [41]. The two enantiomers are assumed initially in the state \( |0\rangle \leftrightarrow |1\rangle \leftrightarrow |2\rangle \leftrightarrow |0\rangle \). This is a good approximation at the rotational temperature \( T_{\text{rot}} \lesssim 10 \text{ mK} \) because the relative populations in the first excited rotational state with respect to the ground rotational state is \( \lesssim 7 \times 10^{-6} \).

The evolution of the population in each electronic state at \( r = 0 \) is shown in Fig. 2(b), which is given by summing over its rotational sub-states. We note that the light-molecule interactions in sufficiently high \( J \) are negligible because these transitions are off-resonantly coupled with light. That is to say, although the number of rotational levels is infinite, the calculations can be done in the subspace with \( J \leq J_o \). We numerically find that the calculations converge at \( J_o = 3 \) [see Sec. II A of Supplement]. We then use the results in Fig. 2(b) to illustrate the advantages of our four-color phase-matched LCL. When all pulses end, while almost all the population of the right-handed molecule is transferred to the electronic state \( |3\rangle \), most of the left-handed molecule’s population is transferred to the electronic state \( |2\rangle \). We focus on the enantiomeric excess in the electronic state \( |3\rangle \) defined as \( \epsilon \equiv (P_3^3 - P_3^1)/(P_3^3 + P_3^1) \), where \( P_3^1 \) and \( P_3^3 \) are the final populations in the electronic state \( |3\rangle \) for the two enantiomers. The achieved enantiomeric excess corresponding to Fig. 2(b) is about \( \epsilon \approx 99.27\% \).

Usually, the \( M \)-degeneracy problem and the broad frequency features of applied fields significantly reduce enantioselectivity. In our calculations, without their influences, the applied pulses will form perfect \( \pi-\pi/2-\pi-\pi/2 \) pulses, yielding the final enantiomeric excess of 100%. Here, we carefully design the polarization and the center frequency of each field, these problems are largely resolved at nanoseconds, and thus these pulses did not deviate too much from perfect \( \pi \) and \( \pi/2 \) pulses. Then, these final high enantiomeric excess is considerably high.

In Fig. 2(c-f), we give \( \log_{10}(P_3^1) \) and \( \log_{10}(P_3^3) \) in the \( y-z \) plane at \( x = 0 \) and \( x = 2\omega_{0,0} \). In the case of \( x = 0 \), \( \rho_3^1 \) [see Fig. 2(c)] are much smaller than \( \rho_3^3 \) [see Fig. 2(d)] near the origin of the plane. When the molecules are away from the origin of the plane, \( \rho_3^1 \) and \( \rho_3^3 \) decrease to zero. Because the waist of the \( \omega_0 \) field is much smaller than that of others, the decreasing rate in the \( y \)-direction is much larger than that in the \( z \)-direction. In the case of \( x = 2\omega_{0,0} \) [see Fig. 2(e) and Fig. 2(f)], similar phenomena happen in the \( y-z \) plane.

In the case of \( x = 0 \) in the \( x \)-direction. To evaluate global efficiency, we define the global enantiomeric excess

\[
\epsilon_{\text{global}} = \frac{P_3^3 - P_3^1}{P_3^3 + P_3^1}
\]

with \( P_3^0 \equiv \int d^2r \rho_3^0(t) \). The corresponding global enantiomeric excess is \( \epsilon_{\text{global}} \approx -93.74\% \). This shows considerably high efficiency in the global control of chiral light-molecule interactions. For the tricolor LCLs, \( \epsilon_{\text{global}} \) quickly decreases to zero when the size of the sample becomes comparable to the wavelengths (see Sec. II B of Supplement). Thus, our four-color LCLs show a considerable advantage in global control of chiral light-molecule interaction. At typical supersonic beam temperature \( T_{\text{rot}} = 1 \text{ K} \) [37] and with the same four-color LCLs, the enantiomeric excess at the origin is about 93% and the global enantiomeric excess is about 91% (see Sec. II A of Supplement).

We also explore the robustness against control errors at \( T_{\text{rot}} \leq 10 \text{ mK} \) (see Fig. 3). When the relative variations of \( \omega_{0,0} \) and \( \omega_{1,1} \) are limited to \( \pm 50\% \), the worst result is \( \epsilon_{\text{global}} \approx -87\% \) [see Fig. 3(a)]. That is to say, the high global efficiency is robust against the variations of the waists of the beams. As shown in Fig. 3(b), the variation of \( \delta \varphi \equiv \varphi_3 - \varphi_2 - \varphi_1 \) can affect the enantiomeric excess. The highly efficient global control \( (|\epsilon_{\text{global}}| \geq 90\%) \) can be achieved around \( \delta \varphi = 0 \) and \( \delta \varphi = \pi \). We note that the variation of \( \varphi_0 \) will not affect the
enantiomeric excess. As shown in Fig. 3 (c), the high global efficiency is robust against the relative variations of the pulses’ duration ($dt/1$). For $E_0, E_1, E_3$, and $E_2$ pulses, $|\epsilon_{\text{global}}| \geq 0.90$ can be obtained with the relative variations about $-50\% \sim 100\%$, $-15\% \sim 30\%$, $-25\% \sim 75\%$, and $-25\% \sim 15\%$, respectively. Each line in Fig. 3 (c) is obtained by changing the duration of the corresponding pulse around its value in Fig. 2 and fixing the other pulses’ duration to their values in Fig. 2. Correspondingly, the pulses’ duration for the four carrier waves can be tuned in the regions about $0.37 \sim 1.10$ ns, $1.35 \sim 2.06$ ns, $1.38 \sim 3.22$ ns, and $1.65 \sim 2.52$ ns, respectively. In Fig. 3 (d), we show $\epsilon_{\text{global}}$ as the function of the variation of each pulse’s amplitude around the corresponding value in Fig. 2, which also show considerable robustness.

We believe our scheme provides a promising chiral light source in the UV-IR region. It purely depends on strong electric-dipole effects and is phase-matched. Our results clearly show its advantage in global control of enantiospecific state transfer. It constitutes the starting point for the applications of other UV-IR spectroscopic techniques in the studies of chiral molecules.

We note that there are other factors that limit the enantiospecific state transfer in the UV-IR region, including the involvement of multiple rotational levels due to the broad-frequency features of the applied fields and the short lifetime of electronic excited states. These problems exist for all the chiral light source, and should be addressed in further research.

Acknowledgments. This work is supported by the National Natural Science Foundation of China (No. 12105011, No. 12234004, No. 12088101, No. U2330401, and No. 11904022).

Disclosures. The authors declare no conflicts of interest.

Data availability. No data were generated or analyzed in the presented research.

Supplemental document. See Supplement for supporting content.

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