Enantioselective Topological Frequency Conversion

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Abstract

Two molecules are enantiomers if they are non-superimposable mirror images of each other. Electric dipole-allowed cyclic transitions $|1⟩ \rightarrow |2⟩ \rightarrow |3⟩ \rightarrow |1⟩$ obey the symmetry relation $O^R = -O^S$, where $O^{R,S} = (\mu_{R,S}^{21}E_{21})(\mu_{R,S}^{13}E_{13})(\mu_{R,S}^{32}E_{32})$, and $R, S$ label the two enantiomers. Here we generalize the concept of topological frequency conversion to an ensemble of enantiomers. We show that, within a rotating-frame, the pumping power between fields of frequency $\omega_1$ and $\omega_2$ is sensitive to enantiomeric excess, $\mathcal{P}_{2 \rightarrow 1} = \hbar \frac{\omega_1 \omega_2 C_L^R}{2\pi} (N_R - N_S)$, where $N_i$ is the number of enantiomers $i$ and $C_L^R$ is an enantiomer-dependent Chern number. Connections with chiroptical microwave spectroscopy are made. Our work provides an underexplored and fertile connection between topological physics and molecular chirality.

In the mid-nineteenth century, Louis Pasteur discovered that molecules can possess handedness, or chirality, an attribute that influences how they interact with their surroundings. More generally, the two species of a chiral molecule, referred to as enantiomers, are nonsuperimposable mirror images of each other and, while they feature many identical physicochemical
properties (up to very small parity violation corrections\textsuperscript{2}), they can also exhibit drastically
different behavior when exposed to chiral environments or stimuli. Thus, enantioselectivity
plays a crucial role in biological activity as well as in the synthesis, purification, and charac-
terization of pharmaceuticals\textsuperscript{3–5}. Traditionally, optical rotation and circular dichroism have
served as optical tools to obtain enantioselective information; however, these techniques rely
on the weak interaction between molecules and the magnetic component of the optical field.
A very active effort in chirality research consists of spatially shaping electromagnetic fields\textsuperscript{6–8}
to enhance these weak interactions. Other techniques that rely solely on electric dipole inter-
actions\textsuperscript{9} have been recently advocated. For instance, many efforts are currently invested in
photoelectron circular dichroism (PECD)\textsuperscript{10–13}. Yet, others focus on nonlinear optical signals
that depend on the sign of the electric fields with which the molecules interact\textsuperscript{14,15}, including
photoexcitation circular dichroism\textsuperscript{16}, the use of synthetic chiral fields\textsuperscript{17–20}, and microwave
three-wave mixing\textsuperscript{21–25}. More precisely, the latter technique can be understood through
cyclic three-level models\textsuperscript{26–32} where the product of three light-matter couplings [hereafter
referred to as the Král-Shapiro (KS) product] differs by a phase of $\pi$ between the two enan-
tiomers. This remarkable symmetry has been exploited to propose cyclic population transfer
schemes\textsuperscript{26,32} or the use of cross-polarized terahertz pulses\textsuperscript{33} to prepare the enantiomers in
different energy configurations or orientations for separation. This symmetry has also been
utilized to suggest an enantioselective generalization of the Stern-Gerlach\textsuperscript{34} or spin Hal\textsuperscript{35}
experiments, where spatial separation of enantiomers, rather than spins, is achieved using
artificial gauge fields\textsuperscript{36–38}. The analogy between enantiomer and spin labels is intriguing
and surprisingly underexplored, and serves as the motivation of our present work. More
specifically, we wish to demonstrate an enantioselective analogue to the Quantum Spin Hall
Effect (QSHE)\textsuperscript{39}.

On the other hand, since the pioneering work of Thouless, Kohmoto, Nightingale, and
den Nijs in relation to the Quantum Hall Effect (QHE)\textsuperscript{40}, notions of symmetry-protected
topological phases (SPTPs) have been at the heart of condensed matter research, and have
only been exacerbated in the past fifteen years with the discovery of topological insulatores. These notions guarantee that certain response properties of so-called topologically nontrivial systems are largely independent of material specification, instead depending only on products of universal constants and integer quantities known as topological invariants. The discrete nature of these properties implies that they are robust against material imperfections, thus making them attractive for metrology, among other applications. While topological protection was originally identified in translationally invariant 2D systems, its scope has been enlarged through the use of Floquet engineering in systems of different dimensionality and the consideration of the 2D phase space of 1D systems. Of particular interest is an elegant construction due to Martin, Refael, and Halperin called topological frequency conversion (TFC), where quantized "current" is observed. In this Letter, we design a novel spectroscopic scheme that generalizes TFC to the microwave spectroscopy of an ensemble of chiral molecules. The very first link between chiroptical spectroscopy and topology was suggested recently in work by Ordoñez and Smirnova within the context of PECD. These authors showed that the propensity field (a pseudoscalar) as a function of ejected photoelectron direction (Berry curvature) can be integrated over all solid angles to yield a quantized enantiosensitive flux which is proportional to a Chern number. Similarly, the authors showed that a microwave three-wave mixing signals can be interpreted in terms of an analogous quantity to the propensity field. However, it is not clear from that work if there exists a parameter space upon which integration of the signals lead to topological invariants, so geometric and topological consequences of these nonlinear spectroscopies were not explored. In this Letter, we use TFC to identify time as the missing parameter space and for simplicity, restrict our attention to frequency conversion rather than three-wave mixing. The result is a signal that is proportional to enantiomeric excess (EE), with a simple prefactor containing the sign of the KS product. Owing to the topological nature of the signal, it should also serve as a very sensitive detection of EE. As far as we are aware, our work provides the first connection between topological physics, chiroptical spectroscopy, and
nonlinear spectroscopy, and anticipates a fertile ground for further exploration.

\[
\begin{align*}
|1,3,-1,0\rangle & |1,3,0,0\rangle |1,3,+1,0\rangle \\
&-\mu_{R,3,0;1,0}\mathcal{E}_{31}(t) \\
&-\mu_{S,2,1;1,0}\mathcal{E}_{21}(t) \\
&-\mu_{S,2,-1;1,0}\mathcal{E}_{21}(t) \\
&-\mu_{R,3,0;2,1}\mathcal{E}_{32}(t) \\
&-\mu_{R,3,0;2,-1}\mathcal{E}_{32}(t)
\end{align*}
\]

\[2\delta \]

Figure 1: The model. (a) Cyclic three-level transitions for an asymmetric top, such as enantiomers. Three near-resonant, linear polarized lasers with modulated field amplitudes \( \mathcal{E}_{ij}(t) \) interact with these transitions. (b) The principal axes components of the dipole moments for the \( R \) and \( S \)-1,2-propanediol enantiomers. Note that
\[
(\mu_{R}^{a}\cdot \hat{a})(\mu_{R}^{b}\cdot \hat{b})(\mu_{S}^{c}\cdot \hat{c}) = -(\mu_{S}^{a}\cdot \hat{a})(\mu_{S}^{b}\cdot \hat{b})(\mu_{S}^{c}\cdot \hat{c})
\]

Following the principles of enantioselective microwave three wave-mixing\cite{50,51}, we treat the enantiomers as asymmetric tops whose Hamiltonian is

\[
H_0 = A J_a^2 + B J_b^2 + C J_c^2, \tag{1}
\]

where \( J_a, J_b, J_c \) are the angular momentum operators with respect to the principal axes \( \hat{a}, \hat{b}, \hat{c} \), and \( A > B > C \) are the corresponding rotational constants. The eigenstates are labeled as \( |J,\tau,M\rangle \), where \( J = 0,1,2... \) is the rotational quantum number, \( M = -J,-J+1, -J+2,..., J \) is the quantum number that characterize the projection of the total angular momentum along the \( z \)-laboratory-fixed axis, and \( \tau \) serves as the quantum number to differentiate between states with the same \( J \) and \( M \). We consider the the following low angular momentum
eigenstates of Eq. 1 with a rotational quantum number of $J = 0$ or $J = 1$

$$
|0, \tau = 1, 0\rangle,
|1, \tau = 2, M\rangle,
|1, \tau = 3, M\rangle,
$$

(2)

where $M = -1, 0, 1$ (see Supporting Information Section 1, SI-1). The ground state $|0, \tau = 1, 0\rangle$, with energy $\hbar \epsilon_1$, and the excited states $|1, \tau = 2, M\rangle$ and $|1, \tau = 3, M\rangle$, with energies $\hbar \epsilon_2, \hbar \epsilon_3$, respectively, are coupled to each other using a set of three orthogonally-polarized time-dependent electric fields

$$
\begin{align*}
\mathbb{E}_{21}(t) &= \mathcal{E}_{21}(t) \sin(\Omega_{21} t) \hat{y}, \\
\mathbb{E}_{32}(t) &= \mathcal{E}_{32}(t) \cos(\Omega_{32} t) \hat{x}, \\
\mathbb{E}_{31}(t) &= \mathcal{E}_{31}(t) \cos(\Omega_{31} t) \hat{z},
\end{align*}
$$

(3)

where $\hat{x}$, $\hat{y}$, $\hat{z}$ denote the three laboratory-fixed axes, the frequencies $\Omega_{21} = \epsilon_2 - \epsilon_1 - \delta$, $\Omega_{32} = \epsilon_3 - \epsilon_2 - \delta$, $\Omega_{31} = \epsilon_3 - \epsilon_1 - 2\delta$, are slightly detuned from the system's natural frequencies, and the field amplitudes $\mathcal{E}_{21}(t)$, $\mathcal{E}_{32}(t)$, $\mathcal{E}_{31}(t)$ are slowly modulated. Note from the selection rules for electric dipole interactions\textsuperscript{51}, that $\Delta M = 0$ for the $z$ polarized field and $\Delta M = \pm 1$ for the $x$ and $y$ polarized field (see Fig. 1). Ignoring all states that are not coupled through the driving electric fields, and assuming that $|\mu_{R,S}^{i,M;i',M;ij}(t)|/2 \ll \hbar \Omega_{ij}$, the Hamiltonian for the laser dressed $R$– and $S$–enantiomer, after making the rotating wave
approximation, is

\[
H^{R,S}(t) = \sum_{i=1,3} \hbar \epsilon_i |i,0\rangle \langle i,0| + \hbar \epsilon_2 \sum_{M=\pm 1} |2,M\rangle \langle 2,M|
- \mathcal{E}_{21}(t) \sum_{M=\pm 1} \left( \frac{i \mu_{2,M;1,0}^{R,S} e^{-i \Omega_{21}t}}{2} |2,M\rangle \langle 1,0| + \text{h.c.} \right)
- \mathcal{E}_{32}(t) \sum_{M=\pm 1} \left( \frac{\mu_{3,0,2,M}^{R,S} e^{-i \Omega_{32}t}}{2} |3,0\rangle \langle 2,M| + \text{h.c.} \right)
- \mathcal{E}_{31}(t) \left( \frac{\mu_{3,0,1,0}^{R,S} e^{-i \Omega_{31}t}}{2} |3,0\rangle \langle 1,0| + \text{h.c.} \right),
\]

where for simplicity we have introduced the notation $|1,0\rangle \equiv |0,\tau = 1,0\rangle$, $|2,M\rangle \equiv |1,\tau = 2,M\rangle$, $|3,0\rangle \equiv |1,\tau = 3,0\rangle$. In Eq. 4 $\mu_{i,M';j,M}^{R,S}$ is the component of the transition-dipole moment for the $|j,M\rangle \to |i,M'\rangle$ transition that is projected along the polarization axis of $\mathbb{E}_{ij}(t)$. Following the procedure of Refs. 50, 51, the values of $\mu_{i,M';j,M}^{R,S}$ are

\[
\mu_{2,\pm 1,1,0}^{R,S} = -\frac{i \mu_b^{R,S}}{\sqrt{6}},
\mu_{3,0,2,\pm 1}^{R,S} = \frac{\mu_a^{R,S}}{2\sqrt{2}},
\mu_{3,0,1,0}^{R,S} = -\frac{i \mu_c^{R,S}}{\sqrt{3}},
\]

where $\mu_a^{R,S}, \mu_b^{R,S}, \mu_c^{R,S}$ are the components of the dipole moment along the principal molecular axes. These components are real valued and $|\mu_a^{R}| = |\mu_b^{S}|$. Note that for the chosen polarizations for the three electric fields (see Eq. 3) and studied energy levels, $\mu_{i,M';j,M}^{R,S}$ does not depend on the quantum number $M$. The associated time-dependent wavefunction for the $R-$ and $S-$ enantiomer the system is $|\psi^{R,S}(t)\rangle$.

Next, we consider the rotating frame

\[
U(t) = e^{-i(\epsilon_2 - i \Omega_{21})t}|1,0\rangle \langle 1,0| + \sum_{M=\pm 1} e^{-i \epsilon_2 z t} |2,M\rangle \langle 2,M| + e^{-i(\epsilon_2 + i \Omega_{32})t} |3,0\rangle \langle 3,0|,
\]
such that $|\psi^{R,S}(t)\rangle = U(t)|\tilde{\psi}^{R,S}(t)\rangle$, in order to remove the central frequencies $\Omega_{ij}$. In this frame, $i\hbar \partial_t |\tilde{\psi}^{R,S}(t)\rangle = \mathcal{H}^{R,S}(t)|\tilde{\psi}^{R,S}(t)\rangle$, with the effective Hamiltonian:

$$
\mathcal{H}^{R,S}(t) = \frac{1}{2} \begin{pmatrix}
-2\hbar \delta & -\frac{\mu_b^{R,S}}{\sqrt{6}} \mathcal{E}_{21}(t) & -\frac{\mu_a^{R,S}}{\sqrt{6}} \mathcal{E}_{21}(t) & -\frac{i\mu_c^{R,S}}{\sqrt{3}} \mathcal{E}_{31}(t) \\
-\frac{\mu_b^{R,S}}{\sqrt{6}} \mathcal{E}_{21}(t) & 0 & 0 & -\frac{\mu_a^{R,S}}{2\sqrt{2}} \mathcal{E}_{32}(t) \\
-\frac{\mu_a^{R,S}}{\sqrt{6}} \mathcal{E}_{21}(t) & 0 & 0 & -\frac{\mu_a^{R,S}}{2\sqrt{2}} \mathcal{E}_{32}(t) \\
i\frac{\mu_c^{R,S}}{\sqrt{3}} \mathcal{E}_{31}(t) & -\frac{\mu_a^{R,S}}{2\sqrt{2}} \mathcal{E}_{32}(t) & -\frac{\mu_a^{R,S}}{2\sqrt{2}} \mathcal{E}_{32}(t) & 2\hbar \delta
\end{pmatrix}.
$$

(7)

After a change of basis (see SI-2), we arrive at the following effective Hamiltonian

$$
\mathcal{H}^{R,S}(t) = -\frac{\mu_b^{R,S}}{2\sqrt{3}\hbar} L_x - \frac{\mu_a^{R,S}}{4\hbar} L_y \\
+ \frac{\mu_c^{R,S}}{2\sqrt{3}\hbar} L_z - \frac{\delta}{2\hbar} (L_+^2 + L_-^2)
$$

(8)

where $L_x = \frac{\hbar}{\sqrt{2}} \begin{pmatrix} 0 & 1 & 0 \\ 1 & 0 & 1 \\ 0 & 1 & 0 \end{pmatrix}$, $L_y = \frac{\hbar}{\sqrt{2}} \begin{pmatrix} 0 & -i & 0 \\ i & 0 & -i \\ 0 & i & 0 \end{pmatrix}$, $L_z = \hbar \begin{pmatrix} 1 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & -1 \end{pmatrix}$ are the angular momentum operators for a spin-1 particle and $L_+ = \sqrt{2}\hbar \begin{pmatrix} 0 & 1 & 0 \\ 0 & 0 & 1 \\ 0 & 0 & 0 \end{pmatrix}$, $L_- = \sqrt{2}\hbar \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & 1 \\ 0 & 1 & 0 \end{pmatrix}$ are the corresponding ladder operators. We use the form of the effective Hamiltonian in Eq. 8 to calculate the topology of the system. Hereafter, we will assume that the slowly-modulated electric field amplitudes are

$$
\mathcal{E}_{21}(t) = E_{21} \sin(\omega_1 t), \\
\mathcal{E}_{32}(t) = E_{32} \sin(\omega_2 t), \\
\mathcal{E}_{31}(t) = E_{31} [m - \cos(\omega_1 t) - \cos(\omega_2 t)],
$$

(9)

where $\omega_1, \omega_2$ are two modulation frequencies, and $m$ is a scalar that characterizes a non-modulated component of the electric field. These functional forms are inspired from the
TFC scheme reported in Ref. 53.

**TFC.** —For completeness, we briefly rederive the TFC formalism using adiabatic perturbation theory (the original paper does so within Floquet theory\cite{53}). In the rotating frame, the rate of the system’s energy absorption for the enantiomers is given by $\partial_t E_{R,S}(t) = \langle \tilde{\psi}^{R,S}(t) | \partial_t \mathcal{H}^{R,S}(t) | \tilde{\psi}^{R,S}(t) \rangle$. In the long time limit, $t \to \infty$, the time-averaged energy-absorption rate, or average power, is

$$
P_{av}^{R,S} = \lim_{t \to \infty} \frac{1}{t} \int_0^t dt' \partial_t \mathcal{H}^{R,S}(t') = \sum_{\omega_i} P_{av}^{R,S}(\omega_i),
$$

(10a)

$$
P_{av}^{R,S}(\omega_i) = \lim_{t \to \infty} \frac{1}{t} \int_0^t dt' \omega_i \langle \partial_{\omega_i} \mathcal{H}^{R,S}(t') \rangle,
$$

(10b)

where $P_{av}^{R,S}(\omega_i)$ is the average power at the modulation frequency $\omega_i$.

Let $|\epsilon^{R,S}_i(t)\rangle$ denote the $i-$th adiabatic state of $\mathcal{H}^{R,S}(t)$, where $\mathcal{H}^{R,S}(t)|\epsilon^{R,S}_i(t)\rangle = \epsilon^{R,S}_i(t)|\epsilon^{R,S}_i(t)\rangle$ (Fig. 2). If $\omega_1, \omega_2$ are incommensurate, *i.e.*, $\omega_1/\omega_2$ is irrational, $\mathcal{H}^{R,S}(t)$ is not periodic. However, if we write $\mathcal{H}^{R,S}(t) = \mathcal{H}^{R,S}(\theta) = \mathcal{H}^{R,S}(\theta_1, \theta_2)$ with $\theta_i = \omega_i t \pmod{2\pi}$, we notice that $\mathcal{H}^{R,S}(\theta)$ is quasiperiodic, $\mathcal{H}^{R,S}(\theta_1 + 2\pi, \theta_2) = \mathcal{H}^{R,S}(\theta_1, \theta_2 + 2\pi) = \mathcal{H}^{R,S}(\theta_1, \theta_2)$, and the domain of $\mathcal{H}^{R,S}(\theta_1, \theta_2)$ is a two-dimensional torus $\mathbb{T} = [0, 2\pi) \otimes [0, 2\pi)$. Near the adiabatic limit where $\omega_1, \omega_2$ are much smaller than the instantaneous energy gap of $\mathcal{H}^{R,S}(t)$, and if the system is initiated in the $l-$th adiabatic state, *i.e.*, $|\tilde{\psi}^{R,S}(0)\rangle = |\epsilon^{R,S}_i(0)\rangle$, the expected quantities $\langle \partial_{\omega_1} \mathcal{H}^{R,S}(t) \rangle$ and $\langle \partial_{\omega_2} \mathcal{H}^{R,S}(t) \rangle$ for $|\tilde{\psi}^{R,S}(t)\rangle$, to first order in $\omega_1, \omega_2$ are

$$
\langle \partial_{\omega_1} \mathcal{H}^{R,S}(t) \rangle = \langle \partial_{\theta_1} \mathcal{H}^{R,S}(\theta) \rangle = \partial_{\theta_1} \epsilon^{R,S}_i(\theta) - i\omega_2 F^{R,S}_l(\theta)
$$

(11a)

$$
\langle \partial_{\omega_2} \mathcal{H}^{R,S}(t) \rangle = \langle \partial_{\theta_2} \mathcal{H}^{R,S}(\theta) \rangle = \partial_{\theta_2} \epsilon^{R,S}_i(\theta) + i\omega_1 F^{R,S}_l(\theta)
$$

(11b)

where $F^{R,S}_l(\theta) = i\langle \partial_{\theta_1} \epsilon^{R,S}_i(\theta) | \partial_{\theta_2} \epsilon^{R,S}_i(\theta) \rangle + \text{h.c.}$ is the Berry curvature of the $l-$th adiabatic band (see, SI-3).

According to the mean-value theorem for incommensurate $\omega_1, \omega_2$\cite{53}, the linear flow of $\theta$
covers the torus densely for long enough times. Thus, the time average of $F^R_S(t)$ is the same as the average of $F^R_S(\theta)$ over the entire torus $\mathbb{T}$:

$$\lim_{t \to \infty} \frac{1}{t} \int_0^t dt' F^R_S(t') = \frac{1}{4\pi^2} \int_{\mathbb{T}} d\theta F^R_S(\theta). \quad (12)$$

From a practical standpoint, $t \to \infty$ means $t > \frac{p}{\omega_1} = \frac{q}{\omega_2}$, where $\frac{\omega_1}{\omega_2} \approx \frac{p}{q}$ for $p, q \in \mathbb{Z}^+$. Substituting Eqs. 11a-11b into Eq. 10b gives rise to the average power lost by the fields at $\omega_1, \omega_2$ when the system is initiated in the $l$–th band, $P^R_S(\omega_1) = -P^R_S(\omega_2) = -\frac{\hbar \omega_1 \omega_2 C^R_S}{2\pi}$. Here the average of $\partial_t \epsilon^R_S(\theta)$ is zero since $\epsilon^R_S(\theta)$ is quasiperiodic in $\theta$, and $C^R_S = \frac{1}{2\pi} \int_{\mathbb{T}} d\theta F^R_S(\theta)$ is the Chern number of the $l$–th band for the corresponding enantiomer.

Thus, the enantiomer dependent average energy-pumping rate between the two modulation fields $P^R_S_{2 \to 1} = [P^R_S(\omega_2) - P^R_S(\omega_1)]/2$ is quantized,

$$P^R_S_{2 \to 1} = \frac{\hbar \omega_1 \omega_2 C^R_S}{2\pi}, \quad (13)$$

or in other words, after one period of the $\omega_2$ modulation, $C^R_S$ photons with frequency $\omega_1$ are produced. The photons produced are in the same spatial modes as the incoming electric fields. The very off-resonant nature of this process guarantees that the molecule does not retain energy and the energy transfer process occurs only between the fields.

For $\delta = 0$, $\mathcal{H}^{R,S}(\theta)$ (see Eq. 8), resembles half of the Bernevig-Hughes-Zhang Hamiltonian\textsuperscript{55}, except that the Pauli matrices are replaced with the spin-1 angular momentum operators. As expected, $\mathcal{H}^{R,S}(\theta)$ is topologically non-trivial for $|m| < 2$, where the Chern numbers for the upper ($U$) and lower ($L$) adiabatic bands remarkably acquire the value,

$$C^R_S_U = 2\text{sgn}(m)\text{sgn}(\mathcal{O}^R_S) = -C^R_S_L, \quad (14)$$

and that for the middle ($M$) band $C_M = 0$ (for an analytical proof, see SI-4). $\mathcal{O}^R_S = (\mu^R_a E_{12})(\mu^R_b E_{23})(\mu^R_c E_{31})$ is the KS product which obeys the enantioselective symmetry...
Figure 2: Example adiabatic bands giving rise to enantioselective TFC. The color gradient is a visual aid for the band dispersion.

relation $\mathcal{O}^R = -\mathcal{O}^S$, since $\mu_a^R \mu_b^R \mu_c^R = -\mu_a^S \mu_b^S \mu_c^S$, and we have assumed that $E_{ij} = E_{ji}$. Therefore $C_R^L = -C_L^S$, and the TFC for the two enantiomers initiated in the lower (upper) adiabatic band at $t = 0$ is expected to have the same magnitude but opposite sign, i.e., $\mathcal{P}_{2 \rightarrow 1}^R = -\mathcal{P}_{2 \rightarrow 1}^S$. This results begs us to consider the fruitful analogy between enantiomer label and spin degrees of freedom. Just like in the QSHE, where the transverse conductivity for opposite spins bears opposite signs, so does the TFC for opposite enantiomers. Eq. [14] is the central result of this letter and relates a fundamental topological invariant from chiroptical spectroscopy ($\text{sgn}\mathcal{O} = \pm 1$) with the notions of SPTPs. Fig. [3] shows the computed value of $C_R^L$ for different values of $m$ when $\delta \neq 0$.

By analogy with Eq. [10] we can compute the enantiomer dependent average power
Figure 3: Topological phase diagram. The value of $C_R^R$ is calculated taking the magnitudes of the light-matter couplings to be equal, i.e., $|\mu_{2,M'1,M}^R E_{21}| = |\mu_{3,M'2,M}^R E_{32}| = |\mu_{3,M'1,M}^R E_{31}| = \hbar D$, while the laser-driving parameters $m$ and $\delta$ are varied. We obtain $C_R^R = -2\text{sgn}(m)\text{sgn}(O^R)$ at the vicinity of $\delta = 0$, where $O^R = -O^S$ is the Král-Shapiro product, which is enantioselective.

absorbed in the original frame as $P_{av}^{R,S}(\Omega) = \lim_{t \to \infty} \frac{1}{t} \int_0^t dt' \Omega \langle \partial_{t'} H^{R,S}(t') \rangle$, obtaining:

\[
\frac{P_{av}^{R,S}(\omega_1)}{\hbar \omega_1} = \frac{P_{av}^{R,S}(\Omega_{21+1})}{\hbar \Omega_{21+1}} - \frac{P_{av}^{R,S}(\Omega_{21-1})}{\hbar \Omega_{21-1}} + \frac{P_{av}^{R,S}(\Omega_{31+1})}{\hbar \Omega_{31+1}} - \frac{P_{av}^{R,S}(\Omega_{31-1})}{\hbar \Omega_{31-1}},
\]

\[
\frac{P_{av}^{R,S}(\omega_2)}{\hbar \omega_1} = \frac{P_{av}^{R,S}(\Omega_{32+2})}{\hbar \Omega_{32+2}} - \frac{P_{av}^{R,S}(\Omega_{32-2})}{\hbar \Omega_{32-2}} + \frac{P_{av}^{R,S}(\Omega_{31+2})}{\hbar \Omega_{31+2}} - \frac{P_{av}^{R,S}(\Omega_{31-2})}{\hbar \Omega_{31-2}},
\]

where $\Omega_{ij \pm 1,2} = \Omega_{ij} \pm \omega_{1,2}$. Thus, the quantization due to the enantioselective TFC can be extracted from an experimentally detected difference power spectrum of the fields interacting with the molecule. Notice that the topology is preserved for $\delta \neq 0$ as long as $\hbar|\delta| < |\mu_{r,M'j,M}^{R,S} E_{ij}|/2$. In general, we expect our scheme to maintain the nontrivial topology with respect to changes in experimental conditions (such as laser spot size or collection efficiency) so long as adiabaticity still holds and the necessary peaks in the power spectrum can be resolved.

The dynamics of the system is calculated by numerically integrating the Schrödinger equation in the rotating frame (Eq. 7), and the power spectrum is obtained by returning to the original frame. In atomic units ($\hbar = 1$), the electric field amplitudes are taken to be $E_{21} = 5\sqrt{3} E_0$, $E_{32} = 6E$, $E_{31} = \sqrt{3} E_0$, where $E_0 = 4.0 \times 10^{-9} \text{ a.u.}$, the dipole
moment principal axes components are $\mu^R_a = \mu^S_a = 0.47$ a.u., $\mu^R_b = \mu^S_b = 0.75$ a.u., $\mu^R_c = -\mu^S_c = 0.14$ a.u., and the molecular transition energies are $\epsilon_2 - \epsilon_1 = 4.4 \times 10^{-8}$ a.u. and $\epsilon_3 - \epsilon_1 = 4.7 \times 10^{-8}$ a.u. The dipole moment components and molecular energies are extracted from a microwave three-wave-mixing model for $R$- and $S$-1,2-propanediol\textsuperscript{21}. Using these parameters, it is true that $|\mu^{R,S}_{i,M'};j,M \cdot E_{ij}(t)| / 2 \ll \hbar \Omega_{ij}$, so the rotating wave approximation holds. The slow incommensurate modulation frequencies and laser detuning are taken to be $\omega_1 = \frac{\omega_2}{\phi} = \delta = 1 \times 10^{-11}$ a.u., where we take $\phi = \frac{\sqrt{5}-1}{2}$ as in Ref. \textsuperscript{48} satisfying the perturbative condition $\hbar |\delta|, \hbar \omega_1, \hbar \omega_2 \ll |\mu^{R,S}_{i,M';j,M} \cdot E_{ij}| / 2$. Setting $m = 1.4$, the system is in the topologically nontrivial regime.

To obtain the desired enantioselective TFC, both enantiomers need to be prepared in the lowest adiabatic bands in the rotating frame at $t = 0$. Suppose that before fields are turned on ($\mu^{R,S}_{i,M';j,M} E_{ij}(t) \to 0$ as $t \to -\infty$), the molecules start in the ground state $|1, 0\rangle$. Under those circumstances, the eigenstates of Eq. \textsuperscript{7} are the states $|1, 0\rangle, |2, M\rangle, |3, 0\rangle$ with eigenenergies $\epsilon^{R,S}_{L,M,U}(-\infty) = -\delta, 0, \delta$, and the state of each molecule is $|\epsilon^{R,S}_L(-\infty)\rangle$. If the electric fields are slowly turned on at a rate $\omega_r$ that is much smaller than the instantaneous band gaps $|\epsilon^{R,S}_i(t) - \epsilon^{R,S}_j(t)|$, both enantiomers are prepared in the lower band, \textit{i.e.} $|\epsilon^{R,S}_L(0)\rangle$. Note that

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure4.png}
\caption{Adiabatic state preparation. Presented are the plots for the functions $\alpha(t)$ and $\beta(t)$. We also feature the populations $|\tilde{c}_R^2|, |\tilde{c}_L^2|$ (shifted vertically slightly to be visible) of the lower adiabatic state for each enantiomer. As shown, the system is effectively prepared in the lower adiabatic bands for both enantiomers.}
\end{figure}
the modulating frequencies $\omega_1, \omega_2$ must also be much smaller than $|\epsilon_{l}^{R,S}(t) - \epsilon_{r}^{R,S}(t)|$ at all times. Chirped microwave fields for $t < 0$ satisfy this constraint. The adiabatic protocol we choose is $E_{ij} \rightarrow E_{ij}\alpha(t)$ and $\omega_{1,2} \rightarrow \omega_{1,2}\beta(t)$, where the ramp-up functions slowly vary at the rate $\omega_r = 2 \times 10^{-13}$ a.u. (see Fig. 4),

$$\alpha(t) = \begin{cases} 0 & t < -\frac{2\pi}{\omega_r}, \\ \frac{1-\cos\omega_r t}{2} & -\frac{2\pi}{\omega_r} < t < -\frac{\pi}{\omega_r}, \\ 1 & -\frac{\pi}{\omega_r} < t, \end{cases}$$

(16a)

$$\beta(t) = \begin{cases} 0 & t < -\frac{\pi}{\omega_r}, \\ \frac{1+\cos\omega_r t}{2} & -\frac{\pi}{\omega_r} < t < 0, \\ 1 & 0 < t. \end{cases}$$

(16b)

After a sufficiently long time (we choose $t^* = 2000 \times 2\pi/\omega_2$), the frequency-resolved time-averaged power spectrum $P_{av}(\Omega)$ lost by the fields is numerically calculated considering only $t \geq 0$. This quantity is indeed enantioselective, and using Eqs. 15a and 15b, each enantiomer Chern number for the lower band $C_L^R = -2 = -C_L^S$ is extracted, revealing the topological nature of this nonlinear optical phenomenon (Fig. 5).

For an ensemble containing $N_R$ $R$–molecules and $N_S$ $S$–molecules, which are all prepared in the ground state $|1, 0\rangle$, the expected pumping rate is

$$\mathcal{P}_{2 \rightarrow 1} = \frac{\hbar \omega_1 \omega_2 C_L^R}{2\pi}(N_R - N_S).$$

(17)

which is zero for a racemic mixture, but otherwise, reveals the EE $|N_R - N_S|$ and chirality $\text{sgn}(N_R - N_S)$. Notice that in line with other nonlinear chiroptical signals that depend on electric but not magnetic dipole contributions, Eq. 17 contains no background achiral signal, unlike traditional circular dichroism, where both enantiomers have the same electric dipole and magnetic dipole absorption strengths for circularly polarized light.
Figure 5: Enantioselective TFC. Plotted is the difference power spectrum for the driving electric field when coupled to a single R− (red) and S− (cyan) 1,2-propanediol enantiomers. In terms of intensity, assuming the laser beam waist area is $\sim 1\text{ cm}^2$, the change observed is $\sim 10^{-15} \text{ W} \cdot \text{m}^{-2}$ per molecule. This spectrum is enantioselective, and using Eqs. 15a and 15b we can see that the frequency conversion in the rotating frame is topological, $\frac{2\pi P^R}{\hbar \omega_1 \omega_2} \rightarrow 1 = \frac{2\pi P^S}{\hbar \omega_1 \omega_2} \rightarrow 2 = -2$.

Let us briefly discuss the limits of enantioselective TFC. First, the linewidths of microwave transitions are on the order of 10-100 kHz\cite{57}, which are smaller than the adiabatic state preparation gap $\delta \approx 1\text{ MHz}$, as well as the light-matter interactions $|\mu_{ij} E_{ij}|/\hbar \approx 10\text{ MHz}$ inducing the topological gap, or even the smallest difference in energies in the power spectrum (see, Fig. 5, $\Omega_{31\pm 1} - \Omega_{31\pm 2} \approx 1\text{ MHz}$). Thus, the described protocol should be resilient to the finite linewidths of these transitions. Second, another source of imperfections stems from laser shot noise. Assuming that the laser beam waist area is $\sim 1\text{ cm}^2$ and considering the field strength above, the shot noise for a time interval $t^*$ is $\sqrt{N} \sim 10^9$ (where $N$ is the expected number of photons produced by the field, see SI-5). From the power spectrum (Fig. 5), we find that for the same time interval, that the minimal magnitude of the change in the photon number due to the TFC is $\min\left(\left|\frac{P_{av}(\Omega_{ij\pm 1,2})}{\hbar \omega_{ij\pm 1,2}}\right|\right) \approx 100 \times |N_R - N_S|$. Therefore, as long as the magnitude of the enantiomer excess $|N_R - N_S|$ is much larger than $\sim 10^7$ molecules, the signal should be detectable above the shot noise. In terms of percentage of the total molecule count $N_R+N_S$, the lower end of the EE detection limit for 1 mL of a 1 µM solution is $10^{-6}\%$. We conclude with a few comments on the observability of our predictions. First, this study has assumed the ideal limit that the molecules are at 0 K. Under typical experimental conditions for microwave-three wave mixing at 7 K\cite{21} all three rotational energy levels used in
our model are substantially thermally occupied. In this scenario, enantioselective frequency conversion still survives; however, the integer Chern number will be replaced by a thermal average of the Chern numbers $C^R_L, C^R_M, C^R_U$. Second, the excited-state thermal populations can be bypassed by working in a different energy range, such as the UV-visible one involving electronic transitions and the infrared one involving vibrations\cite{58,59}; the price to pay in the first case is the complication introduced by electron-vibration coupling. These complications will be addressed in future works.

In summary, we have presented an enantioselective TFC setup for an ensemble of chiral molecules. Owing to the dependence of the topological invariant on the sign of the KS product (Eq. 14), which differs by a phase of $\pi$ for the two enantiomers, the quantized time-averaged energy-pumping rate is of opposite sign for the $R$– and $S$– molecules, just like transverse conductivity is of opposite sign for up and down spins in the QSHE. We show that the computed signal is non-zero for any sample with EE and vanishes for a racemic mixture. An intriguing consequence of Eq. 13 is that as long as the timescale separations required by the model are fulfilled, the chemical identity of the probed molecules (e.g., through the strengths of the transition dipole moments) in the rotating frame is erased by the signal, leading to a universal nonlinear optical response which acknowledges the enantiomeric excess only. This characteristic is reminiscent to the very accurate determination of the quantum of conductance with a wide range of QHE systems. Thus, from a metrological standpoint, the generality of the enantioselective TFC can be exploited to accurately measure EE by running a linear fit of the pumping rate $P_{2 \rightarrow 1}$ for a series of experiments where $\omega_1$ (or $\omega_2$) is varied. Furthermore, if one is only concerned with $|EE|$, a practical asset of the presented methodology is that there is no need to calibrate the signal with an enantiopure sample beforehand. We believe that the removal of calibration counterbalances the complexity of the experimental setup proposed in this Letter.

While concepts of topology have been very productive in the exploration of new condensed matter physics phenomena, most of them are restricted to periodic solids (see Ref.
TFC is a powerful tool that opens doors to the application of those concepts to 0D systems such as finite molecular and non-periodic nanoscale systems. In particular, this work reveals that laser-dressed chiral molecules support SPTPs that are not adiabatically connected to their non-laser-dressed counterparts. It also provides a fruitful playground to explore further conceptual connections between topological physics and molecular chirality.

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Supporting Information Available:

Presentation of rotational eigenstates of an asymmetric top; discussion of the change of basis applied to obtain the necessary effective Hamiltonian, review of adiabatic perturbation theory; derivation of the expected laser power in the rotating frame; analytical evaluation of enantioselective Chern number for zero detuning; calculation of expected laser shot noise.

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