Real single-loop cyclic three-level configuration of chiral molecules

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I. INTRODUCTION

Chiral molecule cannot be superimposed on its mirror image through pure translation and/or rotation. The handedness of the two mirror images (enantiomers) is fundamentally important for the enantiomer-selective of their pharmacological effects [1–4], biological processes [5], the homo-chirality of life [6], and even fundamental physics representing systems with broken parity states [7]. Despite this, enantio-separation is an important and challenging task in chemistry and medicine [8–12].

Soled optical enantio-separation methods have also been investigated theoretically [13–22]. One interesting kind of methods [18–22] among them is based on a system with a cyclic three-level (Δ-type) configuration [23, 24]. In general, such a system driven by electric-dipole transitions is forbidden in natural atoms, but can exist in chiral molecules and other symmetry-broken systems [25–31]. For chiral molecules, Kráľ et al. [18, 19] proposed a system with the Δ-type configuration to realize enantio-separation in the inner-state space via applying three optical (microwave) fields to invoke both one-photon and two-photon processes in the lowest three vibrational levels. The product of the three Rabi frequencies will change sign with enantiomer. This leads to the chirality-dependency of the system due to the interference of the one-photon and two-photon processes. After adiabatical (or diabatical) processes, molecules of different chirality which are initially in their respective ground states are transferred to final levels at different energies [18]. With the Δ-type configuration, the inner-state enantio-separation can also be realized by a purely dynamic transfer process via applying optical ultrashort $\pi/2$ and $\pi$ pulses [20]. Based on the Δ-type configuration, one can realize the spatial enantio-separation via a chirality-dependent generalized Stern-Gerlach effect [21, 22].

However, a real gas molecule should involve the subspace of rotational states and each rotational state may have degenerate magnetic sub-levels. Thus, the ideal single-loop Δ-type configuration [18–22, 32] would be replaced by a multiple-loop Δ-type configuration [33]. For the spatial enantio-separation [21, 22], this effect of the molecular rotation will give birth to the relevant reduction of the chirality-dependent generalized Stern-Gerlach effect [33]. Very recently, some experimental groups have utilized the multiple-loop Δ-type configuration to realize the inner-state enantio-separation [34] as well as enantio-discrimination [35–43] in gas phase samples. It was pointed out [34] that one of the reasons limiting the experimental efficiency is the appearance of multiple loops. With the multiple-loop Δ-type configuration, it is not possible to achieve perfect enantio-separation as theoretically proposed in Refs. [18–20]. Therefore, constructing a real single-loop Δ-type configuration, with no connections to other states, is strongly demanded for enantio-separation.

For chiral symmetric top molecules, it was theoretically pointed out in Ref. [33] that under the consideration of the molecular rotation the real single-loop Δ-type configuration is prohibited due to the selection rules. However, many kinds of chiral molecules are of asymmetric tops. The selection rules of asymmetric tops are different from those of symmetric tops. In this paper, we aim to present a scheme to construct the real single-loop Δ-type configuration for chiral asymmetric top molecules (instead of the symmetric top ones considered in Ref. [33]) under the consideration of molecular rotation. In order to elucidate our scheme, we assume all the states are in the vibrational ground state and choose the working states to be the rotational ground state and other two higher-energy rotational states. Three electromagnetic (optical, microwave, or radio frequency) fields are used to invoke three electric-dipole-allowed transitions among them. With the help of

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the electric-dipole selection rules, we can realize a real single-loop $\Delta$-type configuration of three single states by appropriately choosing the polarization vectors and the frequencies of the three electromagnetic fields. We also demonstrate that the product of the three corresponding Rabi frequencies will change sign with enantiomer, which guarantees the chirality-dependency of the configuration.

II. ELECTRIC-DIPOLE SELECTION RULES FOR ROTATIONAL TRANSITIONS OF ASYMMETRIC TOP

General chiral molecules such as 1,2—propanediol, 1,3—butanediol, carvone, and menthone are of asymmetric tops. For an asymmetric top molecule, the rotational eigenfunctions are $|J, \tau, M\rangle$ with the angular momentum quantum number $J$, the magnetic quantum number $M$, and $\tau$ running from $-J$ to $J$ in unit steps in the order of increasing energy [44]. They can be written as a linear combination of prolate symmetric top eigenfunctions $|J, K, M\rangle$ [44]:

$$|J, \tau, M\rangle = \sum_{K=-J}^{J} A_{K,\tau}^{J}|J, K, M\rangle. \tag{1}$$

The coefficients $A_{K,\tau}^{J}$ are given by solving the static Schrödinger equation of the asymmetric top in the basis of prolate symmetric top eigenfunctions [44]. The total wavefunction of the molecule can be described as $|\alpha\rangle = |v_{\alpha}\rangle|J_{\alpha}, \tau_{\alpha}, M_{\alpha}\rangle$ with the vibrational wavefunction $|v_{\alpha}\rangle$. For clarity, we have used |...⟩ and |...⟩ to distinguish the asymmetric top and symmetric top eigenfunctions.

We consider a linearly $Z$ polarized or a circularly polarized (in the $X$-$Y$ plane) electromagnetic field in the space-fixed frame

$$E_{\sigma}^{s} = \text{Re}\{e_{\sigma}^{s} E_{\alpha} e^{-i(2\pi v t + \varphi_{s})}\}. \tag{2}$$

Any electromagnetic field can be written as a linear combination of them. Here “$s$” indicates the space-fixed frame, and $e_{\sigma}^{s}$ ($\sigma = 0, \pm 1$) is the polarization vector of the electromagnetic field. $E_{\alpha}^{s}$, $\nu$, and $\varphi_{s}$ are, respectively, the field amplitude, the frequency, and the initial phase of the electromagnetic field. Specifically, $\sigma = 0$ corresponds to a linearly $Z$ polarized electromagnetic field with the polarization vector $e_{0}^{s} = e_{2}^{s}$; $\sigma = 1$ ($\sigma = -1$) corresponds to a circularly polarized electromagnetic field rotating about the $Z$-axis in the right-hand (left-hand) sense with the polarization vector $e_{1}^{s} = (e_{x}^{s} + ie_{y}^{s})/\sqrt{2}$ $[e_{-1}^{s} = -(e_{x}^{s} - ie_{y}^{s})/\sqrt{2}]$ [45].

Considering only the electric-dipole-allowed transition between an upper level $|\alpha\rangle$ and a lower level $|\beta\rangle$, the Hamiltonian $\hat{H}_{\sigma}^{s}$ in the interaction picture is given as

$$H_{\sigma}^{s} = \frac{1}{2} \Omega_{\alpha\beta}^{s} e^{i[2\pi(f_{\alpha\beta} - \nu)t]} |\alpha\rangle\langle \beta| + h.c., \tag{3}$$

where $f_{\alpha\beta} = f_{\alpha} - f_{\beta}$ ($> 0$) is the transition frequency with energies of the two states $h f_{\alpha}$ and $h f_{\beta}$ ($h$ is the Planck constant), and the Rabi frequency is

$$\Omega_{\alpha\beta}^{s} = E_{\alpha}^{s} e^{i\varphi_{s}} \langle \alpha|\hat{\mu} \cdot e_{\sigma}^{s} |\beta\rangle. \tag{4}$$

Here $\hat{\mu}$ is the electric dipole operator consisting of a sum over all the (nuclear and electronic) charges, weighted by their position vectors measured from a common origin [44]. We have assumed that $f_{\alpha\beta}$ is close to $\nu$. With this, the counter-rotating terms like $\Omega_{\alpha\beta}^{s} e^{i2\pi f_{\alpha\beta} t} |\alpha\rangle\langle \beta|$ and the permanent-dipole terms like $(\Omega_{\alpha\alpha}^{s} e^{i2\pi \nu t} + \Omega_{\alpha\alpha}^{s} e^{-i2\pi \nu t}) |\alpha\rangle\langle |\alpha|$ have been ignored in Eq. (3) since they oscillate rapidly and will affect little the dynamics of the system. Here we have defined $\Omega_{\alpha\beta}^{s} = E_{\alpha}^{s} e^{i\varphi_{s}} (j|\hat{\mu} \cdot e_{\sigma}^{s} |j)$ and $\Omega_{\alpha\beta}^{s} = E_{\alpha}^{s} e^{-i\varphi_{s}} (j|\hat{\mu} \cdot (e_{\sigma}^{s})^{*} |j')$ with $j, j' = \alpha, \beta$.

The components of the electric dipole in the space-fixed frame $\hat{\mu}_{\sigma}^{s} = |\hat{\mu} \cdot e_{\sigma}^{s}|$ can be obtained by a rotation from the molecular frame [33, 44]

$$\hat{\mu}_{\sigma}^{s} = \sum_{\sigma' = \pm 1, 0} [D_{\sigma\sigma'}^{1}(\psi, \theta, \phi)]^{*} \hat{\mu}_{\sigma'}^{m}. \tag{5}$$

The notation “$m$” indicates the molecular frame. $D_{\sigma\sigma'}^{1}$ is the rotation matrix in three dimensions. "$e_{\sigma}^{s}$" denotes taking conjugate complex. $\psi$, $\theta$, $\phi$ are the Euler angles connecting the molecular frame and the space-fixed frame. $\hat{\mu}_{\sigma}^{m}$ are the components of the electric dipole in the molecular frame with $\hat{\mu}_{\sigma}^{m} = \hat{\mu}_{\sigma}^{m}$ and $\hat{\mu}_{\sigma}^{m} = (\hat{\mu}_{\sigma}^{m} + i\hat{\mu}_{\sigma}^{m})/\sqrt{2}$. Here $x$, $y$, $z$ are the principal axes of the molecule in the molecular frame. We have used $(X, Y, Z)$ and $(x, y, z)$ to distinguish the coordinates in the space-fixed frame and that in the molecular frame. With Eq. (5), the Rabi frequency is

$$\Omega_{\alpha\beta}^{s} = (-1)^{M_{\beta}+\sigma} E_{\sigma}^{s} e^{i\varphi_{s}} W_{J, M_{\sigma}, J_{\beta}, M_{\beta}}^{s} \Gamma_{J_{\alpha}, J_{\beta}} \times \sum_{K_{\alpha} = -J_{\alpha}}^{J_{\alpha}} \sum_{K_{\beta} = -J_{\beta}}^{J_{\beta}} (-1)^{-K_{\beta}+\sigma'} (A_{K_{\alpha}, J_{\alpha}}^{J_{\beta}})^{*} A_{K_{\beta}, J_{\beta}}^{J_{\beta}} W_{J, M_{\sigma}, J_{\beta} K_{\beta}}^{s}. \tag{6}$$

where the reduced matrix element is

$$\Gamma_{J_{\alpha}, J_{\beta}} = \sqrt{(2J_{\alpha} + 1)(2J_{\beta} + 1)} \sum_{\sigma' = \pm 1, 0} \langle v_{\alpha} | \hat{\mu}_{\sigma'}^{m} | v_{\beta} \rangle \times \sum_{K_{\alpha} = -J_{\alpha}}^{J_{\alpha}} \sum_{K_{\beta} = -J_{\beta}}^{J_{\beta}} (-1)^{-K_{\beta}+\sigma'} (A_{K_{\alpha}, J_{\alpha}}^{J_{\beta}})^{*} A_{K_{\beta}, J_{\beta}}^{J_{\beta}} W_{J, M_{\sigma}, J_{\beta} K_{\beta}}^{s} \tag{7}$$

and $W_{J, M_{\sigma}, J_{\beta} M_{\beta}}^{s} = \left( \begin{array}{c} J \\ M_{\sigma} \end{array} \right) -1 ^{J+J'} -M' \rangle$ for $\sigma'' = 0, \pm 1$ are $3j$-symbols. We note that the process to achieve Eq. (6) is similar to that in Ref. [33] except that we consider the case of asymmetric tops instead of the case of symmetric tops in Ref. [33].

Obviously, $3j$-symbols play a central role in determining electric-dipole selection rules. For the selection rules of $J$, we have $\Delta J = J_{\alpha} - J_{\beta} = 0, \pm 1$ according to the $3j$-symbols in both Eq. (6) and Eq. (7). The selection rules of $M$ are directly related to the polarization vectors of the
electromagnetic field as demonstrated by the 3j-symbol in Eq. (6), which gives $\Delta M = M_a - M_\beta = \sigma$.

In principle, using the Wigner-Eckart theorem, one can write the Rabi frequency in the form of Eq. (6) and easily get the selection rules of $J$ and $M$. However, the reduced matrix element (7) is fundamentally important for constructing the real single-loop $\Delta$-type configuration. This will be seen distinctly when we simplify our discussion to the case of symmetric tops with reducing Eq. (7)

$$\Gamma_{J_a K_a, J_\beta K_\beta} = \sqrt{(2J_a + 1)(2J_\beta + 1)} \times \sum_{\sigma' = \pm 1} (-1)^{-K_\beta + \sigma'} \langle \sigma_a | \mu_{\sigma a}^m | \sigma_{\beta} \rangle W_{J_a K_a, J_\beta K_\beta}^{(\sigma')}. \tag{8}$$

The 3j-symbol $W_{J_a K_a, J_\beta K_\beta}$ here establishes the selection rules of $K$. This is one of the reasons for preventing the formation of the closed $\Delta$-type configuration for chiral symmetric top molecules. For the case of asymmetric tops, the sum over $K_a$ and $K_\beta$ in Eq. (7) releases the selection rules of $K$ and thus offers the possibility of forming the closed single-loop $\Delta$-type configuration for chiral asymmetric top molecules.

### III. REAL SINGLE-LOOP $\Delta$-TYPE CONFIGURATION

Our task is to establish a scheme to form the real chirality-dependent single-loop $\Delta$-type configuration with the help of discussions in Sec. II for chiral asymmetric top molecules. For simplicity, we assume all the states are in the vibrational ground state $|v_\beta\rangle$ (in fact the case of different vibrational states will bring the similar results). With this, we only take the rotational subspace into consideration and shorten $\langle v_\beta | \mu_{\sigma a}^m | v_\beta \rangle$ to $\mu_{\sigma}^m$ in further discussions.

#### A. General formula

A natural starting state of the single-loop $\Delta$-type configuration is the rotational ground state $|J_a, \tau_a\rangle \equiv |0, 0\rangle$ which has no magnetic degeneracy. We apply three electromagnetic fields to resonantly couple, respectively, with three cyclic transitions $|0, 0\rangle \rightarrow |J_a, \tau_a\rangle \rightarrow |J_\beta, \tau_\beta\rangle \rightarrow |0, 0\rangle$. They can be written as

$$E_1 \equiv \text{Re} \left\{ \sum_{\sigma = \pm 1} E_{1, \sigma} e^{i(2\sigma \nu a + \phi_{a, \sigma})} \right\},$$

$$E_2 \equiv \text{Re} \left\{ \sum_{\sigma = \pm 1} E_{2, \sigma} e^{-i(2\sigma \nu b + \phi_{b, \sigma})} \right\},$$

$$E_3 \equiv \text{Re} \left\{ \sum_{\sigma = \pm 1} E_{3, \sigma} e^{-i(2\sigma \nu c + \phi_{c, \sigma})} \right\}$$

with $\nu_1 = f_{b1}$, $\nu_2 = f_{c1}$, and $\nu_3 = f_{a1}$. According to the selection rules of $J$, we have $J_b = J_c = 1$. Ignoring all the transitions that are off-resonantly coupled with the three fields, the total Hamiltonian in the interaction picture in the rotating-wave approximation can be arranged as

$$H_{\text{total}} = \left( \frac{\Omega_1}{2} |b\rangle \langle a| + \frac{\Omega_2}{2} |c\rangle \langle b| + \frac{\Omega_3}{2} |c\rangle \langle a| + h.c. \right) + H',$$ \tag{9}

where $|a\rangle = |0, 0, 0\rangle$. $H'$ in Eq. (9) is uncoupled with $|a\rangle$, when we choose

$$|b\rangle = \sin \theta_1 \sin \phi_1 e^{i\varphi_{2,0} |1, \tau_a, 1\rangle + \sin \theta_1 \sin \phi_1 e^{i\varphi_{1,0} \times |1, \tau_b, 0\rangle + \cos \theta_1 e^{i\varphi_{1,-1} - |1, \tau_c, -1\rangle}, \tag{10}$$

and

$$|c\rangle = \sin \theta_3 \sin \phi_3 e^{i\varphi_{3,0} |1, \tau_c, 1\rangle + \sin \theta_3 \sin \phi_3 e^{i\varphi_{3,0} \times |1, \tau_c, 0\rangle + \cos \theta_3 e^{i\varphi_{3,-1} - |1, \tau_c, -1\rangle}. \tag{11}$$

Here $\sin \theta_\lambda \cos \phi_\lambda = \frac{E_{\lambda,1}}{E_{\lambda}}$, $\sin \theta_\lambda \sin \phi_\lambda = \frac{E_{\lambda,0}}{E_{\lambda}}$, and $\cos \theta_\lambda = \frac{E_{\lambda,1}}{E_{\lambda}}$ are satisfied, $H'$ is uncoupled to the Hilbert space $\{|a\rangle, |b\rangle, |c\rangle\}$, and the evolution of a system initially prepared in the Hilbert space will be governed by the single-loop $\Delta$-type configuration with Hamiltonian

$$H_{sl} = \frac{1}{2} \left( \Omega_1 |b\rangle \langle a| + \Omega_2 |c\rangle \langle b| + \Omega_3 |c\rangle \langle a| + h.c. \right). \tag{13}$$

The Rabi frequencies $\Omega_1 = -\Gamma_{17\tau_a,0} E_1 / \sqrt{3}$ and $\Omega_3 = -\Gamma_{17\tau_\beta,0} E_3 / \sqrt{3}$ are nonzero when $\Gamma_{17\tau_a,0} \neq 0$ and $\Gamma_{17\tau_\beta,0} \neq 0$. The Rabi frequency $\Omega_2$ is proportional to $\Gamma_{17\tau_\beta,1\tau_a}$ and the ratio between them is determined by the polarization vectors of the three fields. From the results in Sec. II, we know $\Gamma_{17\tau_\beta,0}, \Gamma_{17\tau_\beta,0}$, and $\Gamma_{17\tau_\beta,1\tau_a}$ are irrelevant to the polarization vectors of the three fields. In order to have a closed $\Delta$-type configuration, we will ensure $\Gamma_{17\tau_a,0}, \Gamma_{17\tau_\beta,0}$, and $\Gamma_{17\tau_\beta,1\tau_a}$ are nonzero first in the following.

#### B. $(J, \tau)$-level structure and chirality-dependency

As demonstrated previously, $J_b = J_c = 1$. In the $J = 1$ subspace, there are three rotational states $|J = 1, \tau = -1\rangle = |J = 1, \tau = 0\rangle, |1, 0\rangle = \{|1, 1\rangle - |1, -1\rangle\} / \sqrt{2}$, and $|1, 1\rangle = \{|1, 1\rangle + |1, -1\rangle\} / \sqrt{2}$ [44]. According to the rotational Hamiltonian $H_{\text{rot}} = \hbar (A J_a^2 + B J_b^2 + C J_c^2)$ (for the asymmetric top molecule with the rotational constants $A > B > C$) [44], we have the eigenvalues for the $J = 0$ and $J = 1$ rotational states as $h f_J = 0, -1 = h(B + C)$, $h f_{J,1} = h(A + C)$, and $h f_{J,-1} = h(A + B)$.

Three candidates of $(J, \tau)$-level structures for constructing the closed $\Delta$-type configuration are shown in Fig. 1. Take the first one [Fig. 1(a)] as an example. It is formed by three cyclic transitions $|0, 0\rangle \rightarrow |1, -1\rangle \rightarrow |1, 1\rangle \rightarrow |0, 0\rangle$. The $\Gamma_{17\tau_a,0}$, $\Gamma_{17\tau_\beta,0}$, and $\Gamma_{17\tau_\beta,1\tau_a}$ are nonzero first in the following.
\[[(\text{b}) \text{ and Fig. } 1] \]

\[\begin{align*}
(\Gamma_{1,0,0}^{\mu_x}W_{10,00}^{(1)}) & \propto \mu_x^m, \\
(\Gamma_{11,1-1}^{\mu_x}W_{11,10}^{(1)} + \mu_{-1}W_{11,10}^{(-1)}) & \propto \mu_x^m, \\
(\Gamma_{11,00}^{\mu_x}W_{11,10}^{(1)} + \mu_{-1}W_{11,10}^{(-1)}) & \propto \mu_x^m.
\end{align*}\]

Here \(\mu_x^m, \mu_y^m,\) and \(\mu_z^m\) are the nonzero components of the electric dipole in the molecule frame along the respective principal axes. Thus, the \((J, \tau)\)-level structure in Fig. 1 (a) is available to form the closed \(\Delta\)-type configuration.

Moreover, the chirality-dependency of the \(\Delta\)-type configuration is also reflected in the \((J, \tau)\)-level structure. It is known that the sign of \(\mu_x^m\mu_y^m\mu_z^m\) fully determines the chirality of an enantiomer [34–38, 40, 42]. The sign of any two of the three dipole moment components is arbitrary and changes with the choice of axes, whereas the sign of the combined quantity \(\mu_x^m\mu_y^m\mu_z^m\) is axis independent and changes sign with enantiomer. Combining this with Eq. (6), the product of the three reduced matrix elements in Eq. (14) as well as the product of the three Rabi frequencies in Eq. (13) will change sign with enantiomer. This guarantees the chirality-dependency of the \(\Delta\)-type configuration. Applying similar analyses on the other two candidates shown in Fig. 1 (b) and Fig. 1 (c), we find that they are also available to form the closed and chirality-dependent \(\Delta\)-type configuration.

C. \(M\)-level structure with \(Z\) and circularly polarized electromagnetic fields

Starting from the rotational ground state, so far we have given three kinds of \((J, \tau)\)-level structures for forming the closed and chirality-dependent \(\Delta\)-type configuration. However, due to the magnetic degeneracy of \(|J_b = 1, \tau_b\rangle\) and \(|J_c = 1, \tau_c\rangle\), generally such a \(\Delta\)-type configuration still has multiple loops when the polarizations of the electromagnetic fields are not appropriately chosen. In this subsection, we will turn to the conditions (12), which provide the selection of the appropriated polarization vectors of the three electromagnetic fields to achieve the single-loop \(\Delta\)-type configuration with the Hamiltonian (13).

We consider the situation where only the linearly \(Z\) \((\sigma = 0)\) or circularly polarized electromagnetic field \((\sigma = \pm 1)\) is applied to resonantly couple with each transition in the \(\Delta\)-type configuration. The three electromagnetic fields are \(E_1 = \text{Re} \{E_1, \sigma_1 \varepsilon_{\sigma_1} e^{-i(2\pi \nu_1 t + \varphi_{\sigma_1})}\}\), \(E_2 = \text{Re} \{E_2, \sigma_2 \varepsilon_{\sigma_2} e^{-i(2\pi \nu_2 t + \varphi_{\sigma_2})}\}\), and \(E_3 = \text{Re} \{E_3, \sigma_3 \varepsilon_{\sigma_3} e^{-i(2\pi \nu_3 t + \varphi_{\sigma_3})}\}\). Here, \(\sigma_1, \sigma_2,\) and \(\sigma_3\) stand for their polarization vectors.

In this case, according to the selection rules of \(M, E_1,\) and \(E_3\) only evoke transitions \(|0, 0, 0\rangle \rightarrow |1, \tau_b, M_b\rangle\) and \(|0, 0, 0\rangle \rightarrow |1, \tau_c, M_c\rangle\), respectively. Thus, we have \(|b\rangle = |J_b = 1, \tau_b, M_b\rangle\) and \(|c\rangle = |J_c = 1, \tau_c, M_c\rangle\). If \(E_2\) can evoke the transition \(|b\rangle \rightarrow |c\rangle\), the conditions (12) are satisfied according to the selection rules of \(M\) and we can form the real single-loop \(\Delta\)-type configuration with the Hamiltonian (13).

All possible \(M\)-level structures for constructing the single-loop \(\Delta\)-type configuration are listed in Table I. We would like to note that, according to the selection

\[\begin{array}{ccccccc}
M_b & M_b & M_c & \sigma_1 & \sigma_2 & \sigma_3 \\
0 & 1 & 0 & 1 & \text{−}1 & 0 \\
0 & \text{−}1 & 0 & \text{−}1 & 1 & 0 \\
0 & 0 & 1 & 0 & 1 & 1 \\
0 & 0 & \text{−}1 & 0 & \text{−}1 & \text{−}1 \\
0 & \text{−}1 & \text{−}1 & 0 & \text{−}1 & \text{−}1 \\
0 & 1 & 1 & 1 & 0 & 1 \\
\end{array}\]

Table I. \(M\)-level structure to form the real single-loop \(\Delta\)-type configuration starting from the rotational ground state. \(\sigma_1, \sigma_2,\) and \(\sigma_3\) label the polarization vectors of the electromagnetic fields \(E_1, E_2,\) and \(E_3\). Here we only choose the \(Z\) polarized \((\sigma = 0)\) electromagnetic field and circularly polarized \((\sigma = \pm 1)\) electromagnetic field rotating about the \(Z\)-axis. The \((J, \tau)\)-level structure of the configuration could be any one of the three cases in Fig. 1.

rules of \(J\) and \(M\), it seems the closed single-loop \(\Delta\)-type configuration among \(|0, 0, 0\rangle, |J_b = 1, \tau_b, M_b = 0\rangle,\) and \(|J_c = 1, \tau_c, M_c = 0\rangle\) can be constructed with three linearly \(Z\) polarized electromagnetic fields. However, such a configuration will fail since the transition \(|J_b = 1, \tau_b, M_b = 0\rangle \rightarrow |1, \tau_c, 0\rangle\) is forbidden by \(W_{1010}^{(1)} = 0\). So far, we can form a closed and chirality-dependent single-loop \(\Delta\)-type configuration described by the Hamiltonian (13) for chiral asymmetric top molecules. The \((J, \tau)\)-level and \(M\)-level structures for constructing the single-loop \(\Delta\)-type configuration (as well as the polarizations of the electromagnetic fields) are given by Fig. 1 and
Table I respectively. In addition, we note that changing the axis of quantization (i.e., change Z to X or Y) will give the equivalent configuration to what we form above.

D. M-level structure with linearly polarized electromagnetic fields

In the recent experiment [36] of enanto-separation based on the (multiple-loop) Δ-type configuration, the three electromagnetic fields are linearly polarized. In this subsection, we consider this situation of purely linearly polarized fields and will prove the single-loop configuration can be formed only when the polarization vectors of the three electromagnetic fields are mutually vertical to each other with the help of the conditions (12).

Without loss of generality, we can set $E_1$ as a linearly $Z$ polarized field. This gives $|b⟩ = |1, τ_0, 0⟩$ and

$$\sin θ_1 \sin φ_1 = ±1.$$  \hfill (15)

Combining this with the condition $⟨c'|H_{total}|b⟩ = 0$ and the condition $⟨c|H_{total}|b⟩ = 0$, we can prove that both $E_2$ and $E_3$ are in the $X - Y$ plane and vertical to $E_1$.

Generally, we can set $E_2$ as a linearly $X$ polarized field. This gives

$$E_{2,1} e^{iφ_{2,1}} = -E_{2,-1} e^{iφ_{2,-1}}.$$  \hfill (16)

With the condition $⟨c'|H_{total}|b⟩ = 0$, we can prove that $E_3$ is a linearly $Y$ polarized field and vertical to $E_2$.

Changing the definition of the coordinates in the space-fixed frame will not alter the physical properties. Thus, for a real single-loop configuration coupled with three linearly polarized fields, we have proven the polarization vectors of the fields must be mutually vertical to each other.

IV. EXPERIMENTAL REALIZATION FOR 1,2-PROPANEDIOL

Now we take 1,2-propanediol as an example to construct real single-loop Δ-type configurations. The rotational constants and the components of the electric dipole in the molecule frame for 1,2-propanediol are $A = 8,572.05$ MHz, $B = 3,640.10$ MHz, $C = 2,790.96$ MHz, $|μ_{1z}| = 1.916$ Debye, $|μ_{2z}| = 0.365$ Debye, and $|μ_{3z}| = 1.201$ Debye with 1 Debye $= 3.33564 \times 10^{-30}$ C $\cdot$ m [47]. The $(J, τ)$-level structure of the single-loop Δ-type configurations is formed by $|J_0, τ_0⟩ = |0, 0⟩$, $|J_1, τ_1⟩ = |1, -1⟩$, and $|J_1, τ_1⟩ = |1, 1⟩$ as shown in Fig. 1 (a). Three microwave fields are applied to couple resonantly with the transitions among them, respectively, with the corresponding frequencies $ν_1 = f_{ba} = 6,431.06$ MHz, $ν_2 = f_{cb} = 5,781.09$ MHz, and $ν_3 = f_{ca} = 12,212.15$ MHz. In the current related experiment [34], the coupling strengths (about 10 MHz) are much less than the detunings (about 1 GHz). All the other off-resonantly transitions are largely detuned coupled with these microwave fields and then can be ignored. Thus, one can form the chirality-dependent Δ-type configurations for 1,2-propanediol.

A. Single-loop Δ-type configuration with Z and circularly polarized electromagnetic fields

In this subsection, we show one of the single-loop Δ-type configurations with choosing the first case of the M-level structure in Table I. The working states are $|a⟩ = |J = 0, τ = 0, M = 0⟩$, $|b⟩ = |1, -1, 1⟩$, and $|c⟩ = |1, 1, 0⟩$. The polarization vectors of the three microwave fields are chosen according to Table I, labeled with $σ_1 = 1, σ_2 = -1$, and $σ_3 = 0$. Thus the three microwave fields are $E_1 = Re(e^{iπν_1 t} E_{1,1} e^{-i2πν_1 t})$, $E_2 = Re(e^{iπν_2 t} E_{2,-1} e^{-i2πν_2 t})$, and $E_3 = Re(e^{iπν_3 t} E_{3,0} e^{-i2πν_3 t})$ with $E_{1,1} > 0$, $E_{2,-1} > 0$, and $E_{3,0} > 0$. For simplicity, we have set the initial phase of them to be zero.

For clarity, we show in Fig. 2 all the magnetic sub-levels in the $\{ |J = 0, τ = 0⟩, |1, -1⟩, |1, 1⟩ \}$ subspace and all the electric-dipole-allowed transitions that are coupled resonantly with the three microwave fields. The rotation states $|1, 1, 1⟩$ and $|1, -1, -1⟩$ are decoupled with the chosen microwave fields. Note that the transition $|1, -1, 0⟩ → |1, 1, -1⟩$ (the dashed arrow in Fig. 2) is also coupled with the field $E_2$. However, it is not involved in the single-loop Δ-type configuration constructed by $|a⟩ = |0, 0, 0⟩$, $|b⟩ = |1, -1, 1⟩$, and $|c⟩ =$
|1, 1, 0⟩ in Fig. 2. The corresponding Rabi frequencies are Ω1 = −Γ11,1,00E1/√3, Ω2 = −Γ11,1,−1E2/√6, and Ω3 = −Γ11,00E3/√3, where E1 = E1,1, E2 = E2,−1, and E3 = E3,0 are the intensities of the three microwave fields.

B. Single-loop Δ-type configuration with linearly polarized electromagnetic fields

![Diagram of single-loop Δ-type configuration](image)

Figure 3. Real single-loop Δ-type configuration coupled with three linearly polarized electromagnetic fields for 1,2-propanediol. Their frequencies are ν1 = 5,781.09 MHz, ν2 = 6,431.06 MHz, ν3 = 12,212.15 MHz. Their polarizing vectors are Z, X, and Y respectively. They are resonantly coupled respectively with cyclic electric-dipole-allowed transitions |a⟩ → |b⟩ → |c⟩ → |a⟩. Here |a⟩ = |0, 0, 0⟩, |b⟩ = |1, −1, 0⟩, and |c⟩ = (|1, 1, 1⟩ + |1, 1, −1⟩)/√2. The dashed arrows denote for the transitions |b′⟩ → |c′⟩ and |b″⟩ → |c″⟩, which are coupled with the X polarized field, and, however, are not involved in the single-loop Δ-type configuration based on |a⟩, |b⟩, and |c⟩. Here |b′⟩ = |1, −1, 1⟩, |b″⟩ = |1, −1, −1⟩, |c′⟩ = |1, 1, 0⟩, and |c″⟩ = (|1, 1, 1⟩ + |1, 1, −1⟩)/√2.

In this subsection, we show an example of the real single-loop configurations resonantly coupled with three linearly polarized electromagnetic fields (as demonstrated in Fig. 3) according to the discussions in Sec. III D. Here, E1 = Re{ε30E1,0e^{−i2πν1t}} with E1,0 > 0, E2 = Re{(ε21E2,1 + ε2,−1E2,−1)e^{−i2πν2t}} with E2,1 = −E2,−1 > 0, and E3 = Re{(ε3,0E3,0 + ε3,−1E3,−1)e^{−i2πν3t}} with E3,1 = E3,−1 > 0 are linearly Z, X, and Y polarized electromagnetic fields, respectively. For simplicity, we have set the initial phase of them to be zero.

With Eq. (10) and Eq. (11), we have the three working states |a⟩ = |0, 0, 0⟩, |b⟩ = |1, −1, 0⟩, and |c⟩ = (|1, 1, 1⟩ + |1, 1, −1⟩)/√2. The corresponding Rabi frequencies are Ω1 = −Γ11,1,00E1/√3, Ω2 = −Γ11,1,−1E2/√6, and Ω3 = −Γ11,00E3/√3, where E1 = E1,1, E2 = √2E2,1, and E3 = √2E3,1 are the intensities of the three microwave fields. Generally to ensure that the dynamics of each transition can affect the global dynamics of the three-level process. In principle, this can be achieved by adjusting the intensities of the involved microwave fields and/or choosing the appropriate specific three levels. Here the absolute values of the three transition dipole moments are, respectively, given as |Γ11,1,00/√3| = |μν1/√3| ≃ 0.693 Debye, |Γ11,1,−1/√6| = |μν2/√6| ≃ 0.958 Debye, and |Γ11,00/√3| = |μν3/√3| ≃ 0.211 Debye. The three Rabi frequencies can be comparable under current experimental conditions [34], where the ratio of the intensities of the three microwave fields is 1 : 0.75 : 2.75 and correspondingly we can give comparable Rabi frequencies as |Ω1| : |Ω2| : |Ω3| ≃ 1 : 1.04 : 0.84. This argument is also suitable for the example in Sec. IV A, where the Rabi frequencies have the same forms as those of here.

We also give the four states |b′⟩ = |1, −1, 1⟩, |b″⟩ = −|1, −1, −1⟩, |c′⟩ = −|1, 1, 0⟩, and |c″⟩ = (|1, 1, 1⟩ − |1, 1, −1⟩)/√2. The transitions |b⟩ → |b′⟩ and |b⟩ → |b″⟩ are coupled with the X polarized field. However, they are not involved in the single-loop Δ-type configuration.

V. SUMMARY AND DISCUSSION

In conclusion, via appropriately choosing the frequencies and polarization vectors of three applied electromagnetic fields, we have established the scheme to form the closed and chirality-dependent real single-loop Δ-type configuration starting from the rotational ground state for chiral asymmetric top molecules with only electric-dipole-allowed rotational transitions under the consideration of molecular rotation.

With our scheme, we have overcome the impediment to enantio-separation due to the averaging over the degenerate magnetic sub-levels. With our scheme, an inner state will be only occupied by one of the enantiomers via applying previous theoretical proposals [18–20]. However, there are other impediments to enantio-separation in practice such as the temperature and the phase mismatching. At finite temperate, the system is initially in a thermal equilibrium state. The population in the upper states (|b⟩ and |c⟩) will execute the cycle “in reverse” [40]. Extending our results to the cases where different vibrational states are involved, we can achieve higher population difference between the states initially driven and thus enantio-separation will be increased. Since the wave-vectors (k1, k2, and k3) of the three electromagnetic fields cannot be parallel, there are inevitable phase mismatching in practice. It will impede the enantio-separation [40]. In our discussion, we have |k1| > |k2| > |k3|. In order to minimize the effect of the phase mismatching, we should take k1 and k2 to be parallel and k3 to be perpendicular to them [43].

In addition, systems with Δ-type configuration are also used in the enantio-discrimination experiments [35–42]. The Δ-type configuration used in the experiment [35] also starts from the rotational ground state and thus is similar to the case we consider here. However, such a configuration in this experiment [35] is not a single-loop Δ-type one. The upper two levels are off-resonantly coupled by
a time-varying electric field. Such an electric field will
couple other levels to the configuration. These couplings
can not be ignored. Using our scheme to form a real
single-loop $\Delta$-type configuration may help to improve the
enantio-discrimination efficiency in experiments.

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Appendix A: Calculation of $|b\rangle$ and $|c\rangle$

For the transition $|J_a, \tau_a\rangle \rightarrow |J_b, \tau_b\rangle$ coupled with $E_1$, we have

$$H_1 = \frac{1}{2} \Gamma_{\tau_a,00} \langle -E_{1,1} e^{i\varphi_{1,1}} W_{11,00}^{(1)} |J_b, \tau_b, 1\rangle \langle 0, 0, 0 |$$
$$+ E_{1,0} e^{i\varphi_{1,0}} W_{01,00}^{(1)} |J_b, \tau_b, 0\rangle \langle 0, 0, 0 | - E_{1,-1} e^{i\varphi_{1,-1}} W_{11,00}^{(-1)}$$
$$\times |J_b, \tau_b, -1\rangle \langle 0, 0, 0 | + h.c.$$

$$= \frac{1}{2} \Gamma_{\tau_a,00} \langle -E_{1,1} e^{i\varphi_{1,1}} |J_b, \tau_b, 1\rangle \langle a | + E_{1,0} e^{i\varphi_{1,0}} |J_b, \tau_b, 0\rangle \langle a | + E_{1,-1} e^{i\varphi_{1,-1}} |J_b, \tau_b, -1\rangle \langle a | + h.c.$$

$$= \frac{1}{2} \Omega_b |b\rangle \langle a | + h.c. \quad (A1)$$

Here $\Omega_b = -\frac{\Gamma_{\tau_a,00}}{\sqrt{3}} E_1$ and

$$|b\rangle = \frac{E_{1,1} e^{i\varphi_{1,1}}}{E_1} |J_b, \tau_b, 1\rangle + \frac{E_{1,0} e^{i\varphi_{1,0}}}{E_1} |J_b, \tau_b, 0\rangle$$
$$+ \frac{E_{1,-1} e^{i\varphi_{1,-1}}}{E_1} |J_b, \tau_b, -1\rangle. \quad (A2)$$

Making $\sin \theta_3 \cos \phi_3 = E_{3,1} / E_1$, $\sin \theta_3 \sin \phi_3 = E_{3,0} / E_1$, and $\cos \theta_3 = E_{3,-1} / E_1$, we have

$$|b\rangle = \sin \theta_3 \cos \phi_3 |J_b, \tau_b, 1\rangle + \sin \theta_3 \sin \phi_3 |J_b, \tau_b, 0\rangle$$
$$\times |J_b, \tau_b, 0\rangle + \cos \theta_3 e^{i\varphi_{1,-1}} |J_b, \tau_b, -1\rangle. \quad (A3)$$

$$|b\rangle = \sin \phi_3 e^{i\varphi_{1,1}} |J_b, \tau_b, 1\rangle - \cos \phi_3 e^{i\varphi_{1,0}} |J_b, \tau_b, 0\rangle. \quad (A4)$$

and

$$|b\rangle = \cos \theta_3 \cos \phi_3 |J_b, \tau_b, 1\rangle + \cos \theta_3 \sin \phi_3 e^{i\varphi_{1,0}}$$
$$\times |J_b, \tau_b, 0\rangle - \sin \theta_3 e^{i\varphi_{1,-1}} |J_b, \tau_b, -1\rangle. \quad (A5)$$

For the transition $|J_a, \tau_a\rangle \rightarrow |J_c, \tau_c\rangle$ coupled with $E_3$, we have

$$H_3 = \frac{1}{2} \Gamma_{\tau_c,00} \langle -E_{3,1} e^{i\varphi_{3,1}} W_{11,00}^{(1)} |J_c, \tau_c, 1\rangle \langle 0, 0, 0 |$$
$$+ E_{3,0} e^{i\varphi_{3,0}} W_{01,00}^{(1)} |J_c, \tau_c, 0\rangle \langle 0, 0, 0 |$$
$$- E_{3,-1} e^{i\varphi_{3,-1}} W_{11,00}^{(-1)} |J_c, \tau_c, -1\rangle \langle 0, 0, 0 | + h.c. \quad (A6)$$

This can be arranged as $H_3 = \frac{1}{2} \Omega_3 |c\rangle \langle a | + h.c.$ with $\Omega_3 = -\frac{\Gamma_{\tau_c,00}}{\sqrt{3}} E_3$ and

$$|c\rangle = E_{3,1} e^{i\varphi_{3,1}} |J_c, \tau_c, 1\rangle + E_{3,0} e^{i\varphi_{3,0}} |J_c, \tau_c, 0\rangle$$
$$+ E_{3,-1} e^{i\varphi_{3,-1}} |J_c, \tau_c, -1\rangle. \quad (A7)$$

Making $\sin \theta_3 \cos \phi_3 = E_{3,1} / E_3$, $\sin \theta_3 \sin \phi_3 = E_{3,0} / E_3$, and $\cos \theta_3 = E_{3,-1} / E_3$, we have

$$|c\rangle = \sin \theta_3 \cos \phi_3 |J_c, \tau_c, 1\rangle + \sin \theta_3 \sin \phi_3 e^{i\varphi_{3,0}}$$
$$\times |J_c, \tau_c, 0\rangle + \cos \theta_3 e^{i\varphi_{3,-1}} |J_c, \tau_c, -1\rangle. \quad (A8)$$

and

$$|c\rangle = \sin \phi_3 e^{i\varphi_{3,1}} |J_c, \tau_c, 1\rangle - \cos \phi_3 e^{i\varphi_{3,0}} |J_c, \tau_c, 0\rangle. \quad (A9)$$

Appendix B: Specific expression of $\langle c|H_{total}|b\rangle$ etc.

In order to calculate the specific expression of $\langle c|H_{total}|b\rangle$ etc., we first give the Hamiltonian for the transition $|J_b, \tau_b\rangle \rightarrow |J_c, \tau_c\rangle$ coupled with $E_2$. It can be expressed as

$$H_2 = \sum_{\sigma=0,\pm 1} H_{2,\sigma}. \quad (B1)$$

Here

$$H_{2,1} = \frac{1}{2} E_{2,1} e^{i\varphi_{2,1}} \Gamma_{\tau_c,1\tau_b}(W_{11,01}^{(1)} |J_c, \tau_c, 0\rangle \langle J_b, \tau_b, 0 |$$
$$- W_{11,01}^{(1)} |J_c, \tau_c, 1\rangle \langle J_b, \tau_b, 0 |) + h.c.$$}
$$= \frac{E_{2,1} e^{i\varphi_{2,1}} \Gamma_{\tau_c,1\tau_b}}{2 \sqrt{3}} (|J_c, \tau_c, 0\rangle \langle J_b, \tau_b, 1 |$$
$$+ |J_c, \tau_c, 1\rangle \langle J_b, \tau_b, 0 |) + h.c., \quad (B2)$$

$$H_{2,0} = \frac{1}{2} E_{2,0} e^{i\varphi_{2,0}} \Gamma_{\tau_c,1\tau_b}(W_{11,01}^{(1)} |J_c, \tau_c, 1\rangle \langle J_b, \tau_b, 1 |$$
$$+ W_{11,01}^{(1)} |J_c, \tau_c, 0\rangle \langle J_b, \tau_b, 1 |) + h.c.$$}
$$= \frac{E_{2,0} e^{i\varphi_{2,0}} \Gamma_{\tau_c,1\tau_b}}{2 \sqrt{3}} (|J_c, \tau_c, 0\rangle \langle J_b, \tau_b, 1 |$$
$$- |J_c, \tau_c, 1\rangle \langle J_b, \tau_b, 0 |) + h.c., \quad (B3)$$

and

$$H_{2,-1} = \frac{1}{2} E_{2,-1} e^{i\varphi_{2,-1}} \Gamma_{\tau_c,1\tau_b}(W_{11,01}^{(-1)} |J_c, \tau_c, 1\rangle \langle J_b, \tau_b, -1 |$$
$$+ W_{11,01}^{(-1)} |J_c, \tau_c, 0\rangle \langle J_b, \tau_b, -1 |) + h.c.$$}
$$= \frac{E_{2,-1} e^{i\varphi_{2,-1}} \Gamma_{\tau_c,1\tau_b}}{2 \sqrt{3}} (|J_c, \tau_c, -1\rangle \langle J_b, \tau_b, 0 |$$
$$+ |J_c, \tau_c, 0\rangle \langle J_b, \tau_b, 1 |) + h.c. \quad (B4)$$
Thus, we have

\[
H_2 = \frac{\Gamma_{1\tau,1\gamma}E_2}{2\sqrt{6}} \left( -\sin \theta_2 \cos \phi_2 e^{i\phi_2,1} |J_c, \tau_c, 0 \rangle |J_b, \tau_b, -1 \rangle - \sin \theta_2 \cos \phi_2 e^{i\phi_2,1} |J_c, \tau_c, 1 \rangle |J_b, \tau_b, 0 \rangle - \sin \theta_2 \sin \phi_2 e^{i\phi_2,0} |J_c, \tau_c, -1 \rangle |J_b, \tau_b, -1 \rangle + \sin \theta_2 \sin \phi_2 e^{i\phi_2,0} |J_c, \tau_c, 1 \rangle |J_b, \tau_b, 1 \rangle + \cos \theta_2 e^{i\phi_2,-1} |J_c, \tau_c, 1 \rangle |J_b, \tau_b, 0 \rangle + \cos \theta_2 e^{i\phi_2,-1} |J_c, \tau_c, 0 \rangle |J_b, \tau_b, 1 \rangle \right) + h.c. \quad (B5)
\]

Here, we use \( \sin \theta_2 \cos \phi_2 = E_{2,1}/E_2 \), \( \sin \theta_2 \sin \phi_2 = E_{2,0}/E_2 \), and \( \cos \theta_2 = E_{2,-1}/E_2 \). We have

\[
\langle c | H_{\text{total}} | b \rangle = \langle c | H_2 | b \rangle = \frac{\Gamma_{1\tau,1\gamma}E_2}{2\sqrt{6}} \times \\
- \cos \theta_1 \sin \theta_2 \cos \phi_2 \sin \phi_3 e^{i(\phi_1,1+\phi_2,1-\phi_3,0)} \\
- \cos \theta_1 \sin \theta_2 \sin \phi_2 \cos \phi_3 e^{i(\phi_1,1+\phi_2,0-\phi_3,1)} \\
- \sin \theta_1 \sin \phi_1 \sin \theta_2 \cos \phi_2 \sin \phi_3 e^{i(\phi_1,0+\phi_2,1-\phi_3,1)} \\
+ \sin \theta_1 \cos \phi_1 \sin \theta_2 \sin \phi_2 \cos \phi_3 e^{i(\phi_1,1+\phi_2,0-\phi_3,1)} \\
- \sin \theta_1 \cos \phi_1 \cos \theta_2 \sin \phi_3 e^{i(\phi_1,1+\phi_2,1-\phi_3,0)} \\
= \frac{1}{2} \Omega_2, \quad (B6)
\]

\[
\langle c' | H_{\text{total}} | b \rangle = \langle c' | H_2 | b \rangle = \frac{\Gamma_{1\tau,1\gamma}E_2}{2\sqrt{6}} \times \\
\cos \theta_1 \sin \theta_2 \cos \phi_2 \cos \phi_3 e^{i(\phi_1,1+\phi_2,1-\phi_3,0)} \\
- \sin \theta_1 \sin \phi_1 \sin \theta_2 \cos \phi_2 \sin \phi_3 e^{i(\phi_1,0+\phi_2,1-\phi_3,1)} \\
+ \sin \theta_1 \cos \phi_1 \sin \theta_2 \sin \phi_2 \cos \phi_3 e^{i(\phi_1,1+\phi_2,0-\phi_3,1)} \\
- \sin \theta_1 \cos \phi_1 \cos \theta_2 \cos \phi_3 e^{i(\phi_1,1+\phi_2,1-\phi_3,0)} \\
= 0, \quad (B7)
\]

\[
\langle c'' | H_{\text{total}} | b \rangle = \langle c'' | H_2 | b \rangle = \frac{\Gamma_{1\tau,1\gamma}E_2}{2\sqrt{6}} \times \\
- \cos \theta_1 \sin \theta_2 \cos \phi_2 \cos \theta_3 \sin \phi_3 e^{i(\phi_1,1+\phi_2,1-\phi_3,0)} \\
+ \cos \theta_1 \sin \theta_2 \sin \phi_2 \sin \theta_3 \cos \phi_3 e^{i(\phi_1,0+\phi_2,0-\phi_3,1)} \\
- \sin \theta_1 \sin \phi_1 \sin \theta_2 \cos \phi_2 \cos \theta_3 \cos \phi_3 e^{i(\phi_1,0+\phi_2,1-\phi_3,1)} \\
- \sin \theta_1 \cos \phi_1 \sin \theta_2 \sin \phi_2 \cos \theta_3 \cos \phi_3 e^{i(\phi_1,1+\phi_2,0-\phi_3,1)} \\
+ \sin \theta_1 \cos \phi_1 \cos \theta_2 \cos \theta_3 \sin \phi_3 e^{i(\phi_1,1+\phi_2,1-\phi_3,0)} \\
= 0, \quad (B8)
\]

\[
\langle c | H_{\text{total}} | b' \rangle = \langle c | H_2 | b' \rangle = \frac{\Gamma_{1\tau,1\gamma}E_2}{2\sqrt{6}} \times \\
\cos \phi_1 \sin \theta_2 \cos \phi_2 \sin \theta_3 \cos \phi_3 e^{i(\phi_1,0+\phi_2,1-\phi_3,1)} \\
- \cos \phi_1 \cos \theta_2 \cos \theta_3 \sin \phi_3 e^{i(\phi_1,0+\phi_2,-1-\phi_3,1)} \\
+ \sin \phi_1 \sin \theta_2 \sin \phi_2 \sin \theta_3 \cos \phi_3 e^{i(\phi_1,1+\phi_2,0-\phi_3,1)} \\
- \sin \phi_1 \cos \theta_2 \sin \theta_3 \sin \phi_3 e^{i(\phi_1,1+\phi_2,-1-\phi_3,0)} \\
= 0, \quad (B9)
\]

\[
\langle c | H_{\text{total}} | b'' \rangle = \langle c | H_2 | b'' \rangle = \frac{\Gamma_{1\tau,1\gamma}E_2}{2\sqrt{6}} \times \\
\sin \theta_1 \sin \theta_2 \cos \phi_2 \sin \theta_3 \sin \phi_3 e^{i(\phi_1,1+\phi_2,1-\phi_3,0)} \\
+ \sin \theta_1 \sin \theta_2 \sin \phi_2 \cos \theta_3 \sin \phi_3 e^{i(\phi_1,1+\phi_2,0-\phi_3,1)} \\
- \cos \theta_1 \sin \phi_1 \sin \theta_2 \cos \phi_2 \sin \phi_3 e^{i(\phi_1,0+\phi_2,-1-\phi_3,1)} \\
+ \cos \theta_1 \sin \phi_1 \cos \theta_2 \sin \phi_2 \cos \phi_3 e^{i(\phi_1,1+\phi_2,0-\phi_3,1)} \\
+ \cos \theta_1 \sin \phi_1 \cos \theta_2 \cos \phi_2 \cos \phi_3 e^{i(\phi_1,1+\phi_2,1-\phi_3,0)} \\
= 0. \quad (B10)
\]

Appendix C: M-level structure with linearly polarized electromagnetic fields

With \( \langle c' | H_{\text{total}} | b \rangle = 0 \), we have

\[
\sin \theta_2 \cos \phi_2 \sin \phi_3 = 0. \quad (C1)
\]

This gives \( E_{2,1} \propto \sin \theta_2 \cos \phi_2 = 0 \) or \( E_{3,0} \propto \sin \phi_3 = 0 \). If \( E_{2,1} = 0 \), \( E_{2,-1} \) should be equal to zero. Otherwise, \( E_2 \) will not be a linearly polarized field. In this case, we have \( |c \rangle = |1, \tau_c, 0 \rangle \). However, the transition \( |1, \tau_c, 0 \rangle \rightarrow |1, \tau_c, 0 \rangle \) is prohibited. Therefore, we have to choose

\[ E_{3,0} \propto \sin \phi_3 = 0, \quad E_{2,1} \propto \sin \theta_2 \cos \phi_2 \neq 0. \quad (C2) \]

That means \( E_3 \) should be in the \( X - Y \) plane.

With the above results and the condition \( \langle c | H_{\text{total}} | b' \rangle = 0 \) in Eq. (B9), we have

\[
\sin \theta_2 \sin \phi_2 \sin \theta_3 = 0. \quad (C3)
\]

If \( \sin \theta_3 = 0 \), we have \( E_{3,1} = 0 \). This conflicts with the fact that \( E_{3,0} = 0 \) [see Eq. (C1)] and \( E_3 \) is not a linearly polarized field. Thus we have to make

\[ E_{2,0} \propto \sin \theta_2 \sin \phi_2 = 0, \quad E_{3,1} \propto \sin \theta_3 \neq 0. \quad (C4) \]

That means \( E_2 \) is also in the \( X - Y \) plane. With \( \sin \phi_3 = 0 \) and \( \sin \theta_2 \sin \phi_2 = 0 \), the condition \( \langle c | H_{\text{total}} | b'' \rangle = 0 \) in Eq. (B10) is satisfied.

Now, we have proven \( E_2 \) and \( E_3 \) are in the \( X - Y \) plane. Thus they are vertical to \( E_1 \). Generally, we can set \( E_2 \) as a linearly \( X \) polarized field. This gives

\[ E_{2,1} e^{i\phi_2,1} = -E_{2,-1} e^{i\phi_2,-1}. \quad (C5) \]
With the above results and $\langle e''|H_{\text{total}}|b\rangle = 0$, we have

$$E_{3, -1} e^{i\varphi_{3, -1}} = E_{3, 1} e^{i\varphi_{3, 1}}.$$  \hspace{1cm} (C6)

Therefore, $E_3$ is a linearly $Y$ polarized field and vertical to $E_2$.  

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[46] \[ W_{10,00}^{(0)} = -1/\sqrt{3}, \ W_{11,00}^{(1)} = 1/\sqrt{3}, \ W_{-1,00}^{(-1)} = 1/\sqrt{3}, \ W_{10,10}^{(1)} = 1/\sqrt{6}, \ W_{11,01}^{(-1)} = -1/\sqrt{6}, \ W_{01,01}^{(-1)} = 1/\sqrt{6}, \ W_{11,11}^{(-1)} = -1/\sqrt{6}, \ W_{01,11}^{(0)} = 0, \ W_{11,11}^{(0)} = -1/\sqrt{6}, \ W_{11,11}^{(-1)} = 1/\sqrt{6}. \]