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Einat Frishman, Moshe Shapiro, David Gerbasi, et al.

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Einat Frishman and Moshe Shapiro
Chemical Physics Department, The Weizmann Institute of Science, Rehovot, Israel 76100
and Department of Chemistry, The University of British Columbia, Vancouver, Canada V6T 1Z1

David Gerbasi and Paul Brumer
Chemical Physics Theory Group, Department of Chemistry, University of Toronto, Toronto, Canada M5S 3H6

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Angular momentum constraints for coherently controlling chiral purification of racemic mixtures using the dipole-electric field interaction are examined in detail for two different scenarios. First shown is that achieving enantiomeric control in our earlier scheme [M. Shapiro, E. Frishman, and P. Brumer, Phys. Rev. Lett. **84**, 1669 (2000)], using parallel laser pulses, requires that the system be *M*-polarized, where *M* is the projection of the total angular momentum along the axis of laser polarization. An alternate scenario is then introduced that allows chiral control in an *unpolarized* racemic mixture by using three mutually perpendicular linearly polarized light fields. Analytic expressions for the enantiomeric excess in both cases are derived and computational results are presented. © *2003 American Institute of Physics.* [DOI: 10.1063/1.1603732]

I. INTRODUCTION

Enantio-selective processes,[1,2] i.e., the class of processes designed to preferentially increase the concentration of a selected enantiomer in a racemic mixture, is of great interest, both practically as well as theoretically. The possibility of achieving enantio-selectivity using optical methods has been the focus of recent attention.[3–12]

Earlier suggestions of optical methods designed to selectively enhance a desired enantiomer centered on the use of circularly polarized light,[2,3] relying upon the very weak magnetic-dipole interaction with the field. Recently, however, we[4–8] and others[9–11] have designed methods that utilize the far stronger electric electric dipole interaction with the field (i.e., $\boldsymbol{\mu}\cdot\mathsf{E}$) for achieving enantio-selectivity. We were also able to formulate a general theorem,[12] according to which enantio-selectivity can be achieved in a laser–molecule scenario that is reliant upon the $\boldsymbol{\mu}\cdot\mathsf{E}$ interaction only when the time evolution resulting from the laser–molecule interaction is dependent upon the sign of the electric field vector (i.e., the time evolution changes upon inversion of E).

A promising approach was introduced in Refs. 4 and 5 in which we examined control in a four level system coupled by linearly polarized light. Specifically, three parallel linearly polarized pulsed lasers were used to selectively excite a racemic mixture of two enantiomers, denoted *D* (dextrorotatory) and *L* (levorotatory). The chosen laser configuration (discussed below) allowed for preferential excitation of either *D* or *L*, hence discriminating between the enantiomers. Repeated application of this laser sequence, followed by relaxation, resulted in the selective enhancement of the concentration of either *D* or *L*. It turns out, as shown explicitly below, that since the three lasers are parallel and linearly polarized, this corresponds to control in a system of fixed *M*, where *M* is the projection of the total angular momentum *J* along the polarization direction of the incident light. This method was applied[5] to a realistic model[13] of dimethylallene, where we computationally demonstrated enantiomeric excesses of over 90%, using lasers of reasonable intensity.

Requiring *M*-selection adds an experimental complexity we would like to avoid. For this reason we consider here the effects of *M* averaging in two scenarios for optical enantiomeric purification using linearly polarized light. The first is that introduced above, and termed laser configuration **A**. In this case a racemic mixture is irradiated with three laser frequencies of the same linear polarization. In the second, denoted laser configuration **B**, the mixture is irradiated with three mutually perpendicular beams of linearly polarized light. Here, we focus on the case of the symmetric top; extensions to the asymmetric top are straightforward and will be briefly discussed. A more detailed consideration concerning the asymmetric top, with realistic applications, is found elsewhere.[14]

In both cases we first consider control for one value of *M*, limiting attention to the ladder of states accessed by weak to moderately strong laser fields. In the case of configuration **A** this corresponds to the eight level scheme in Fig. 1. For configuration **B**, ten levels are involved, as shown in Fig. 2. Subsequently, we consider averaging over *M*. In both configurations this can be done analytically to show that control is lost in configuration **A** upon *M*-averaging, but retained in configuration **B**. Extending configuration **B** beyond the ten level case, which would occur with higher fields, requires a numerical study, as provided in Sec. IV.

Results in this paper show that *M* averaging leads to the loss of control in configuration **A** since the enantiomeric excesses generated by states with quantum numbers *J*, *M* exactly cancels those with quantum numbers *J*, $-M$. However,

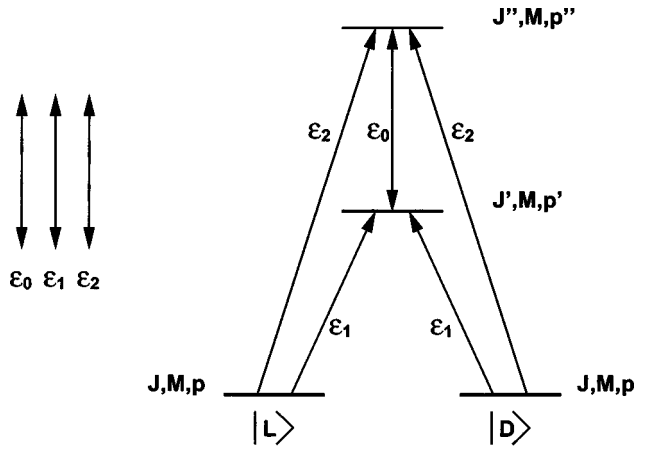

FIG. 1. Original scheme previously introduced in Ref. 4. For the symmetric top the p's assume values of ± 1 so that there are eight levels.

enantiomeric control survives M-averaging in configuration **B**, with the M and $-M$ terms contributing constructively. This then provides a general method for enantiomeric control, via the $\boldsymbol{\mu}\cdot\mathsf{E}$ interaction, in traditional racemic mixtures.[15] The mechanism, an implementation of coherent control,[16] is distinctly different from that recently proposed[11] for three laser chiral control, where one laser is specifically designed to orient the molecule.

In all cases considered below we assume the symmetry of the potential surfaces is that of Ref. 4, i.e., the ground state is assumed to possess a high barrier for enantio-conversion which is hence forbidden (a ''chiral'' situation), whereas enantio-conversion is assumed facile in the excited state (an ''achiral'' situation). A follow-up paper[14] considers control in a realistic model of dimethylallene.

II. LASER CONFIGURATION A: FOUR STATE MODEL

We consider first the simplified model in Ref. 4. In this case a racemic mixture of the two enantiomers, D and L, in the ground electronic state and in the ground vibrational eigenstates $|D\rangle$ and $|L\rangle$, of energy $E_D=E_L$. We choose the electric field so as to excite the system to two vib-rotational eigenstates $|1\rangle$ and $|2\rangle$, of energy E_1 and E_2, of the electronically excited state. Since the excited electronic state is achiral we can choose $|1\rangle$ to be symmetric with respect to inversion and $|2\rangle$ to be antisymmetric. The states $|1\rangle$ and $|2\rangle$ are coupled to one another by an additional laser field (see Fig. 1). Specifically, we choose $\mathsf{E}(t)$ to be composed of three parallel linearly polarized light pulses,

$$\mathsf{E}(t)=\sum_{k=0,1,2}\mathsf{E}_k(t)$$

$$=\sum_{k=0,1,2}[\boldsymbol{\epsilon}_k(t)\exp(i\nu_k t)+\boldsymbol{\epsilon}_k^*(t)\exp(-i\nu_k t)]\hat{\boldsymbol{\epsilon}}_k, \qquad (1)$$

where $\boldsymbol{\epsilon}_k$ is the pulse envelope, ν_k is the central laser frequency, and $\hat{\boldsymbol{\epsilon}}_k$ is the polarization direction. The frequency ν_0 is chosen in near-resonance with the transition frequency $\omega_{21}\equiv(E_2-E_1)/\hbar$, ν_1 is chosen near $\omega_{1\mathrm{D}}\equiv(E_1-E_D)/\hbar$ and ν_2 is chosen near $\omega_{2\mathrm{D}}\equiv(E_2-E_D)/\hbar$.

With the above configuration, the time dependent Schrödinger equation for the molecule in the presence of radiation assumes the form,

$$i\hbar\partial|\Psi\rangle/\partial t=H_{\mathrm{tot}}(t)|\Psi\rangle,$$
$$H_{\mathrm{tot}}(t)=H_M-\sum_k\boldsymbol{\mu}_k\cdot\mathsf{E}_k(t), \qquad (2)$$

where H_M is the molecular Hamiltonian and $\boldsymbol{\mu}_k$ is the transition-dipole moment for the electronic transition induced by $\mathsf{E}_k(t)$.

Equation (2) is converted to a set of differential equations by expanding $|\Psi\rangle$ in eigenstates $|j\rangle$ of the molecular Hamiltonian [i.e., $H_M|j\rangle=E_j|j\rangle$],

$$|\Psi\rangle=\sum_j b_j(t)\exp(-iE_j t/\hbar)|j\rangle \qquad (3)$$

and substituting Eq. (3) into Eq. (2) to give

$$\dot{b}_i=\frac{i}{\hbar}\sum_{jk}b_j\exp(-i\omega_{ji}t)\langle i|\boldsymbol{\mu}_k\cdot\mathsf{E}_k(t)|j\rangle, \qquad (4)$$

where $\omega_{ji}=(E_j-E_i)/\hbar$.

Considering the laser coupling, only four molecular states are relevant and Eq. (3) becomes

$$|\Psi\rangle=b_D(t)\exp(-iE_D t/\hbar)|D\rangle$$
$$+b_L(t)\exp(-iE_L t/\hbar)|L\rangle+b_1(t)\exp(-iE_1 t/\hbar)|1\rangle$$
$$+b_2(t)\exp(-iE_2 t/\hbar)|2\rangle. \qquad (5)$$

Equation (4), in the rotating wave approximation, is then given by

$$\dot{b}_1=i\exp(i\Delta_1 t)[\Omega_{D,1}^*b_D+\Omega_{L,1}^*b_L]+i\exp(-i\Delta_0 t)\Omega_0^*b_2,$$
$$\dot{b}_2=i\exp(i\Delta_2 t)[\Omega_{D,2}^*b_D+\Omega_{L,2}^*b_L]+i\exp(i\Delta_0 t)\Omega_0 b_1,$$
$$\dot{b}_D=i\exp(-i\Delta_1 t)\Omega_{D,1}b_1+i\exp(-i\Delta_2 t)\Omega_{D,2}b_2, \qquad (6)$$
$$\dot{b}_L=i\exp(-i\Delta_1 t)\Omega_{L,1}b_1+i\exp(-i\Delta_2 t)\Omega_{L,2}b_2,$$

where

$$\Omega_{kj}(t)\equiv\langle k|\mu_j|j\rangle\epsilon_j(t)/\hbar,\quad k=D,L;\quad j=1,2,$$

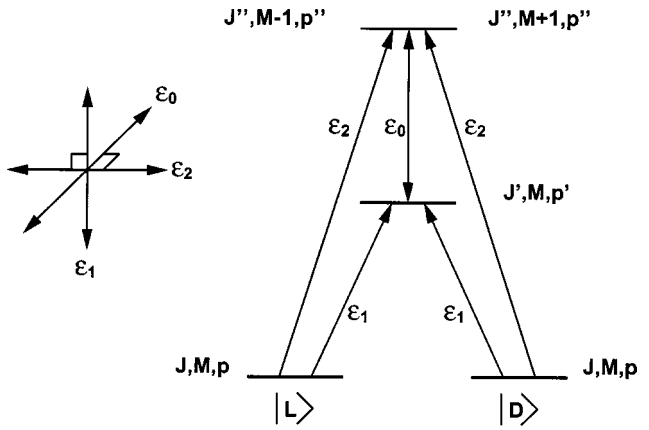

FIG. 2. Ten level scenario for symmetric top in configuration B. Note that the p's assume values of ± 1.

$$\Omega_0(t) \equiv \langle 2|\mu_0|1\rangle \epsilon_0(t)/\hbar, \tag{7}$$

$$\Delta_j \equiv \omega_{jD} - \nu_j, \quad \Delta_0 \equiv \omega_{21} - \nu_0,$$

with $\mu_i \equiv \boldsymbol{\mu}_i \cdot \hat{\boldsymbol{\epsilon}}_i$, $i=0, 1, 2$.

States $|D\rangle$ and $|L\rangle$ can be rewritten in terms of a symmetric state $|S\rangle$ and an antisymmetric state $|A\rangle$,

$$|D\rangle = |A\rangle + |S\rangle,$$
$$|L\rangle = |A\rangle - |S\rangle. \tag{8}$$

Using this relation, and the fact that $|1\rangle$ and $|2\rangle$ have opposite symmetry properties with respect to inversion, one can readily show[4] that

$$\Omega_{L,1} = \Omega_{D,1} = \Omega_{A,1}; \quad \Omega_{L,2} = -\Omega_{D,2} = \Omega_{S,2}. \tag{9}$$

Hence, we can write Eq. (6) as

$$\begin{aligned}
\dot{b}_1 &= i \exp(i\Delta_1 t)[\Omega^*_{D,1} b_D + \Omega^*_{D,1} b_L] + i \exp(-i\Delta_0 t)\Omega^*_0 b_2,\\
\dot{b}_2 &= i \exp(i\Delta_2 t)[\Omega^*_{D,2} b_D - \Omega^*_{D,2} b_L] + i \exp(i\Delta_0 t)\Omega_0 b_1,\\
\dot{b}_D &= i \exp(-i\Delta_1 t)\Omega_{D,1} b_1 + i \exp(-i\Delta_2 t)\Omega_{D,2} b_2,\\
\dot{b}_L &= i \exp(-i\Delta_1 t)\Omega_{D,1} b_1 - i \exp(-i\Delta_2 t)\Omega_{D,2} b_2.
\end{aligned} \tag{10}$$

A. Changing the sign of the fields

Equation (10) describes the time evolution of the amplitude in levels $|D\rangle$, $|L\rangle$, $|1\rangle$, and $|2\rangle$. As noted above, only if the dynamics depend on the sign of the overall electric field, then the scenario represented by these equations allows for enantiomeric control.[12] Consider then the effect of changing $\mathsf{E} \to -\mathsf{E}$, i.e., $\epsilon_0 \to -\epsilon_0$, $\epsilon_1 \to -\epsilon_1$, and $\epsilon_2 \to -\epsilon_2$. Under this transformation, Eq. (10) becomes

$$\begin{aligned}
\dot{b}_1 &= -i \exp(i\Delta_1 t)[\Omega^*_{D,1} b_D + \Omega^*_{D,1} b_L]\\
&\quad - i \exp(-i\Delta_0 t)\Omega^*_0 b_2,\\
\dot{b}_2 &= -i \exp(i\Delta_2 t)[\Omega^*_{D,2} b_D - \Omega^*_{D,2} b_L]\\
&\quad - i \exp(i\Delta_0 t)\Omega_0 b_1,\\
\dot{b}_D &= -i \exp(-i\Delta_1 t)\Omega_{D,1} b_1 - i \exp(-i\Delta_2 t)\Omega_{D,2} b_2,\\
\dot{b}_L &= -i \exp(-i\Delta_1 t)\Omega_{D,1} b_1 + i \exp(-i\Delta_2 t)\Omega_{D,2} b_2.
\end{aligned} \tag{11}$$

By defining $b'_1 = -b_1$, Eq. (11) can be rewritten as

$$\begin{aligned}
\dot{b}'_1 &= i \exp(i\Delta_1 t)[\Omega^*_{D,1} b_D + \Omega^*_{D,1} b_L] + i \exp(-i\Delta_0 t)\Omega^*_0 b_2,\\
\dot{b}_2 &= i \exp(i\Delta_2 t)[-\Omega^*_{D,2} b_D + \Omega^*_{D,2} b_L] + i \exp(i\Delta_0 t)\Omega_0 b'_1,\\
\dot{b}_D &= i \exp(-i\Delta_1 t)\Omega_{D,1} b'_1 - i \exp(-i\Delta_2 t)\Omega_{D,2} b_2,\\
\dot{b}_L &= i \exp(-i\Delta_1 t)\Omega_{D,1} b'_1 + i \exp(-i\Delta_2 t)\Omega_{D,2} b_2.
\end{aligned} \tag{12}$$

These equations are identical to those in Eq. (10) except that $b_D \to b_L$, and vice versa. Hence, $\mathsf{E} \to -\mathsf{E}$ affects the dynamics and enantiomeric control is possible, consistent with previous studies.[4] Of additional interest is that the effect is precisely that which one would expect from the inversion of the total system, i.e., of both the molecule and the electric field, in which the dynamics of the D enantiomer and the L enantiomer interchange with one another.

Note, for interest below, that in this scenario changing the sign of any one of the three electric field constituents ϵ_i has the same effect as changing the sign of total electric field insofar as it reverses the roles of enantiomeric selectivity. Specifically, $L \leftrightarrow D$ reversal occurs when we change the sign of either ϵ_1, ϵ_2 or ϵ_0. This can easily be verified by defining new (primed) probability amplitudes such as $b'_2 = -b_2$ for $\epsilon_0 \to -\epsilon_0$ and $b'_L = -b_D$ and $b'_L = -b_L$ for $\epsilon_1 \to -\epsilon_1$. Similarly, changing the sign of ϵ_2 in Eq. (10) directly gives Eq. (12) without further algebra. Note also that if we change the sign of any two electric fields constituents ϵ_i then the enantiomeric selectivity remains unchanged. For example, consider sign reversal of both ϵ_0 and ϵ_1. Then the original equations [Eq. (10)] are recovered by defining $b'_2 = -b_2$, $b'_L = -b_D$, and $b'_L = -b_L$.

B. Angular momentum considerations

The above discussion does not consider the role of angular momentum, shown here to be crucial to overall control. Specifically, to consider the effect of averaging over M, the situation that would exist in a nonpolarized medium, we associate with each of the $|D\rangle$, $|L\rangle$, $|1\rangle$, and $|2\rangle$ states, a parity-adapted symmetric-top wave function of the type,

$$\begin{aligned}
\mathcal{D}^{J,p}_{\lambda,M}(\phi,\theta,\chi) \equiv t_\lambda \left(\frac{2J+1}{8\pi^2}\right)^{1/2} &\{D^J_{\lambda,M}(\phi,\theta,\chi)\\
&+ p(-1)^\lambda D^J_{-\lambda,M}(\phi,\theta,\chi)\},
\end{aligned} \tag{13}$$

where (ϕ,θ,χ) are three Euler angles of rotation in a space-fixed coordinate system, $D^J_{\lambda,M}(\phi,\theta,\chi)$ are the rotational matrices in Edmonds' notation,[17] $p = \pm 1$, and $t_\lambda = 2^{-(1/2)}$ for $\lambda > 0$ and $t_\lambda = 1/2$ for $\lambda = 0$. Here J is the total angular momentum, M is its proportion of the space fixed z-axis and λ is its projection on the molecular axis. It is seen from Eq. (13) that every vib-rotational level is doubly degenerate in p, except for $\lambda = 0$. The extension to the asymmetric top is straightforward insofar as the p degeneracy is removed and the wave functions maintain the same M dependence as the symmetric top.

The $\mathcal{D}^{J,p}_{\lambda,M}(\phi,\theta,\chi)$ are eigenfunctions of the inversion operator $\mathcal{I}$,

$$\mathcal{I}\mathcal{D}^{J,p}_{\lambda,M}(\phi,\theta,\chi) = p(-1)^J \mathcal{D}^{J,p}_{\lambda,M}(\phi,\theta,\chi), \tag{14}$$

a property that follows from the basic relation,

$$\mathcal{I}D^J_{\lambda,M}(\phi,\theta,\chi) = (-1)^{J+\lambda} D^J_{-\lambda,M}(\phi,\theta,\chi).$$

Given the above rotational wave functions, the wave functions in the ground electronic state are written as

$$|L_p\rangle = |v_L\rangle \mathcal{D}^{J,p}_{\lambda,M}, \quad |D_p\rangle = |v_D\rangle \mathcal{D}^{J,p}_{\lambda,M}, \tag{15}$$

and the excited state wave functions are written (see Fig. 1) as,

$$|1_{p'}\rangle = |v_1\rangle \mathcal{D}^{J',p'}_{\lambda',M'}, \quad |2_{p''}\rangle = |v_2\rangle \mathcal{D}^{J'',p''}_{\lambda'',M''}, \tag{16}$$

where the $|v_i\rangle$ are the vibrational components of the wave function. Since the eigenvalues of the symmetric top Hamiltonian depend upon J and λ we can excite between selected levels J, λ, J', λ' and J'', λ'' by choosing the appropriate laser frequency. The energy does not, however, depend upon the values of p, p', p''. Hence, the system comprises eight levels, i.e., four energetically degenerate sets, as shown in Fig. 1(b).

We assume, with no loss of generality, that $|1_{p'}\rangle$ is symmetric with respect to inversion, and therefore that $|1_{-p'}\rangle$ is antisymmetric. Similarly, $|2_{p''}\rangle$ is assumed symmetric and hence $|2_{-p''}\rangle$ is antisymmetric. It is then notationally convenient to relabel the states as follows:

$$|1\rangle\equiv|1_{-p'}\rangle,\quad |2\rangle\equiv|1_{p'}\rangle,\quad |3\rangle\equiv|2_{-p''}\rangle,\quad |4\rangle\equiv|2_{p''}\rangle. \tag{17}$$

With this notation $|i\rangle$ with even values of i are symmetric with respect to inversion and $|i\rangle$ with odd values of i are antisymmetric with respect to inversion.

The state wave function can then be expanded in terms of the above set of vib-rotational wave functions as

$$\begin{aligned}|\Psi\rangle=&b_{D_p}\exp(-iE_Dt/\hbar)|D_p\rangle+b_{D_{-p}}\exp(-iE_Dt/\hbar)|D_{-p}\rangle\\&+b_{L_p}\exp(-iE_Lt/\hbar)|L_p\rangle+b_{L_{-p}}\exp(-iE_Lt/\hbar)|L_{-p}\rangle\\&+b_1\exp(-iE_1t/\hbar)|1\rangle+b_2\exp(-iE_2t/\hbar)|2\rangle\\&+b_3\exp(-iE_3t/\hbar)|3\rangle+b_4\exp(-iE_4t/\hbar)|4\rangle,\end{aligned} \tag{18}$$

giving the following set of coupled equations in the rotating wave approximation:

$$\begin{aligned}\dot b_{L_p}=&i\exp(-i\Delta_1t)(b_1\Omega^*_{1,L_p}+b_2\Omega^*_{2,L_p})\\&+i\exp(-i\Delta_2t)(b_3\Omega^*_{3,L_p}+b_4\Omega^*_{4,L_p}),\\\dot b_{L_{-p}}=&i\exp(-i\Delta_1t)(b_1\Omega^*_{1,L_{-p}}+b_2\Omega^*_{2,L_{-p}})\\&+i\exp(-i\Delta_2t)(b_3\Omega^*_{3,L_{-p}}+b_4\Omega^*_{4,L_{-p}}),\\\dot b_{D_p}=&i\exp(-i\Delta_1t)(b_1\Omega^*_{1,D_p}+b_2\Omega^*_{2,D_p})\\&+i\exp(-i\Delta_2t)(b_3\Omega^*_{3,D_p}+b_4\Omega^*_{4,D_p}),\\\dot b_{D_{-p}}=&i\exp(-i\Delta_1t)(b_1\Omega^*_{1,D_{-p}}+b_2\Omega^*_{2,D_{-p}})\\&+i\exp(-i\Delta_2t)(b_3\Omega^*_{3,D_{-p}}+b_4\Omega^*_{4,D_{-p}}),\\\dot b_1=&i\exp(i\Delta_1t)(b_{L_p}\Omega_{1,L_p}+b_{L_{-p}}\Omega_{1,L_{-p}}+b_{D_p}\Omega_{1,D_p}\\&+b_{D_{-p}}\Omega_{1,D_{-p}})+ib_4\exp(-i\Delta_0t)\Omega^*_{4,1},\\\dot b_2=&i\exp(i\Delta_1t)(b_{L_p}\Omega_{2,L_p}+b_{L_{-p}}\Omega_{2,L_{-p}}+b_{D_p}\Omega_{2,D_p}\\&+b_{D_{-p}}\Omega_{2,D_{-p}})+ib_3\exp(-i\Delta_0t)\Omega^*_{3,2},\\\dot b_3=&i\exp(i\Delta_2t)(b_{L_p}\Omega_{3,L_p}+b_{L_{-p}}\Omega_{3,L_{-p}}+b_{D_p}\Omega_{3,D_p}\\&+b_{D_{-p}}\Omega_{3,D_{-p}})+ib_2\exp(i\Delta_0t)\Omega_{3,2},\\\dot b_4=&i\exp(i\Delta_2t)(b_{L_p}\Omega_{4,L_p}+b_{L_{-p}}\Omega_{4,L_{-p}}+b_{D_p}\Omega_{4,D_p}\\&+b_{D_{-p}}\Omega_{4,D_{-p}})+ib_1\exp(i\Delta_0t)\Omega_{4,1}.\end{aligned} \tag{19}$$

Here $\Omega_{i,j}\equiv\langle i|\mu_k|j\rangle\epsilon_k/\hbar$, $\Delta_k\equiv\omega_{i,j}-\omega_k$, $i=1,2,3,4$, $j=L_p, L_{-p}, D_p, D_{-p}$, $k=0,1,2$. In a fashion similar to that of the four level scheme above [Eq. (8)], states $|L_p\rangle$ and $|D_p\rangle$ can be rewritten in terms of definite parity states $|S_p\rangle$ and $|A_p\rangle$, and again without loss of generality, we can assign states $|S_p\rangle$ and $|A_p\rangle$ to be overall symmetric and antisymmetric respectively. Their counterparts $|L_{-p}\rangle$ and $|D_{-p}\rangle$ obtained by changing p to $-p$, are of symmetry opposite to $|L_p\rangle$ and $|D_p\rangle$. Therefore, one can show that

$$\begin{aligned}&\Omega_{1,L_p}=-\Omega_{1,D_p}=\Omega_{1,S_p},\quad \Omega_{3,L_p}=-\Omega_{3,D_p}=\Omega_{3,S_p},\\&\Omega_{1,L_{-p}}=\Omega_{1,D_{-p}}=\Omega_{1,A_{-p}},\quad \Omega_{3,L_{-p}}=\Omega_{3,D_{-p}}=\Omega_{3,A_{-p}},\\&\Omega_{2,L_p}=\Omega_{2,D_p}=\Omega_{2,A_p},\quad \Omega_{4,L_p}=\Omega_{4,D_p}=\Omega_{4,A_p},\\&\Omega_{2,L_{-p}}=-\Omega_{2,D_{-p}}=\Omega_{2,S_{-p}},\\&\Omega_{4,L_{-p}}=-\Omega_{4,D_{-p}}=\Omega_{4,S_{-p}}.\end{aligned} \tag{20}$$

Hence, Eq. (19) can be rewritten as

$$\begin{aligned}\dot b_{L_p}=&i\exp(-i\Delta_1t)(b_2\Omega^*_{2,L_p}-b_1\Omega^*_{1,L_p})\\&+i\exp(-i\Delta_2t)(b_4\Omega^*_{4,L_p}-b_3\Omega^*_{3,L_p}),\\\dot b_{D_p}=&i\exp(-i\Delta_1t)(b_2\Omega^*_{2,L_p}+b_1\Omega^*_{1,L_p})\\&+i\exp(-i\Delta_2t)(b_4\Omega^*_{4,L_p}+b_3\Omega^*_{3,L_p}),\\\dot b_{L_{-p}}=&i\exp(-i\Delta_1t)(b_1\Omega^*_{1,L_{-p}}-b_2\Omega^*_{2,L_{-p}})\\&+i\exp(-i\Delta_2t)(b_3\Omega^*_{3,L_{-p}}-b_4\Omega^*_{4,L_{-p}}),\\\dot b_{D_{-p}}=&i\exp(-i\Delta_1t)(b_1\Omega^*_{1,L_{-p}}+b_2\Omega^*_{2,L_{-p}})\\&+i\exp(-i\Delta_2t)(b_3\Omega^*_{3,L_{-p}}+b_4\Omega^*_{4,L_{-p}}),\\\dot b_1=&i\exp(i\Delta_1t)[\Omega_{1,L_p}(b_{D_p}-b_{L_p})+\Omega_{1,L_{-p}}(b_{D_{-p}}+b_{L_{-p}})]\\&+ib_4\exp(-i\Delta_0t)\Omega^*_{4,1},\\\dot b_2=&i\exp(i\Delta_1t)[\Omega_{2,L_p}(b_{D_p}+b_{L_p})+\Omega_{2,L_{-p}}(b_{D_{-p}}-b_{L_{-p}})]\\&+ib_3\exp(-i\Delta_0t)\Omega^*_{3,2},\\\dot b_3=&i\exp(i\Delta_2t)[\Omega_{3,L_p}(b_{D_p}-b_{L_p})+\Omega_{3,L_{-p}}(b_{D_{-p}}+b_{L_{-p}})]\\&+ib_2\exp(i\Delta_0t)\Omega_{3,2},\\\dot b_4=&i\exp(i\Delta_2t)[\Omega_{4,L_p}(b_{D_p}+b_{L_p})+\Omega_{4,L_{-p}}(b_{D_{-p}}-b_{L_{-p}})]\\&+ib_1\exp(i\Delta_0t)\Omega_{4,1}.\end{aligned} \tag{21}$$

We can readily show that the dynamics in Eq. (21) is sensitive to the sign of the total electric field and hence[12] that

enantiomeric control is possible. Further, for use below, we note that changing the sign of any one component of the electric field, i.e., $\epsilon_0 \rightarrow -\epsilon_0$, or $\epsilon_1 \rightarrow -\epsilon_1$, or $\epsilon_2 \rightarrow -\epsilon_2$, results in a reversal of the role of the enantiomeric selectivity; specifically, $L_{-p} \leftrightarrow D_{-p}$ and $L_p \leftrightarrow D_p$. Similar conclusions as those reached following Eq. (12) can be made when only one or two electric fields change sign. That is, the roles of L and D are reversed when the sign of only one field component is changed but remain the same if two field components are changed. As an example, consider the change $\epsilon_0 \rightarrow -\epsilon_0$. By defining $b_1' = -b_1$, $b_3' = -b_3$, $b'_{L_{-p}} = -b_{L_{-p}}$ and $b'_{D_{-p}} = -b_{D_{-p}}$, it can be shown that the roles of enantiomeric selectivity are reversed.[18]

To see the effect of averaging over the M quantum number we examine the relationship between enantiomeric control with a given value of M and with the corresponding value of $-M$. Consider then the M dependence of the dipole transition matrix elements. The projection of the $\mu_l (l = 0,1,2)$ dipole operators on the polarization directions $\hat{\epsilon}_l$ can be related (see Ref. 19) to the (x,y,z) body-fixed components of the dipole operators as,

$$\mu_l \equiv \boldsymbol{\mu}_l \cdot \hat{\epsilon}_l = f_l t_{q_l} \sum_{K=-1}^{K=1} \mu_l^{(K)} \{ D^1_{K,q_l}(\phi,\theta,\chi) + p_l (-1)^{q_l} D^1_{K,-q_l}(\phi,\theta,\chi) \}, \tag{22}$$

where

$$\mu_l^{(0)} \equiv \mu_l^z, \quad \mu_l^{(-1)} \equiv (\mu_l^x - i\mu_l^y)/\sqrt{2},$$

$$\mu_l^{(1)} \equiv -(\mu_l^x + i\mu_l^y)/\sqrt{2}. \tag{23}$$

Here $f_l = 1$, $q_l = 0$, $p_l = 1$ for $\hat{\epsilon}_l$ along the Z axis, $f_l = -1$, $q_l = 1$, $p_l = 1$ for $\hat{\epsilon}_l$ along the X axis, and $f_l = i$, $q_l = 1$, $p_l = -1$ for $\hat{\epsilon}_l$ along the Y axis.

Given Eqs. (15), (16), and (22), consideration of dipole transition matrix elements requires the following integrals [Edmonds (Ref. 17), Eq. (4.6.2)]:

$$\begin{aligned}
&(\mathcal{D}^{J',p'}_{\lambda',M'} | D^1_{K,q} | \mathcal{D}^{J,p}_{\lambda,M}) \\
&\equiv \int_0^{2\pi} d\phi \int_0^{\pi} \sin\theta d\theta \int_0^{2\pi} d\chi \mathcal{D}^{J',p'*}_{\lambda',M'}(\phi,\theta,\chi) \\
&\quad \times D^1_{K,q}(\phi,\theta,\chi) \mathcal{D}^{J,p}_{\lambda,M}(\phi,\theta,\chi) \\
&= (-1)^{-M'} t_{\lambda'} t_{\lambda} [(2J'+1)(2J+1)]^{1/2} \\
&\quad \times \begin{pmatrix} J' & 1 & J \\ -M' & q & M \end{pmatrix} F(J',\lambda',p';J,\lambda,p;K) \\
&\equiv (-1)^{M'} \begin{pmatrix} J' & 1 & J \\ -M' & q & M \end{pmatrix} B(J',\lambda',p';j,\lambda,p;K),
\end{aligned} \tag{24}$$

where nonzero 3-j symbols require $M + q - M' = 0$ and where

$$\begin{aligned}
&F(J',\lambda',p';J,\lambda,p;K) \\
&= (-1)^{\lambda'} \begin{pmatrix} J' & 1 & J \\ -\lambda' & K & \lambda \end{pmatrix} \\
&\quad + p(-1)^{\lambda+\lambda'} \begin{pmatrix} J' & 1 & J \\ -\lambda' & K & -\lambda \end{pmatrix} \\
&\quad + p' \begin{pmatrix} J' & 1 & J \\ \lambda' & K & \lambda \end{pmatrix} + p'p(-1)^{\lambda} \begin{pmatrix} J' & 1 & J \\ \lambda' & K & -\lambda \end{pmatrix}.
\end{aligned} \tag{25}$$

$B(J',\lambda',p';j,\lambda,p;K)$ has been defined in Eq. (24) in order to expose the M and M' dependence of the matrix element.

C. *M*-averaging

Consider now the average over the M quantum number where all components ϵ_i are Z-polarized. The relevant integrals in Eq. (24) would then have $q = 0$. In accord with this equation the entire M dependence, within the transition dipole moments, is contained in a single 3-j symbol. The property of the 3-j coefficients with respect to $M \rightarrow -M$ transformation is given by[17]

$$\begin{pmatrix} J_2 & 1 & J_1 \\ M' & 0 & -M \end{pmatrix} = (-1)^{J_1+1+J_2} \begin{pmatrix} J_2 & 1 & J_1 \\ -M' & 0 & M \end{pmatrix}. \tag{26}$$

Here nonzero 3-j symbols require $M = M'$. As a consequence of Eq. (26) some or all of the transition matrix elements will change signs when $M \rightarrow -M$, depending on which J states are involved in the excitation scheme. Since these matrix elements enter into the dynamics via the Ω's, such a change in sign is equivalent to changing the sign of the associated electric field component.

The selection rule $\Delta J = 0, \pm 1$, and the requirement that dipole transitions induced by all of the ϵ_i are nonzero, allows for only two possible angular momentum scenarios. The first, where all J states have the same value, and the second where some states have the same J and other states have angular momentum $J \pm 1$. As an example, consider excitation from the ground $|L_p\rangle$ and $|D_p\rangle$ states with angular momentum J to excited state levels $|i\rangle$, $i = 1,...,4$, with angular momentum $J+1$. In this case, dipole coupling matrix elements associated with ϵ_1 and ϵ_2 are unaffected by $M \rightarrow -M$, however, couplings associated with ϵ_0 will change sign. Hence the $-M$ case behaves in the same way as that of M with field component $-\epsilon_0$. In accord with the discussion following Eq. (21), in this case the enhancement of D over L (or vice versa) resulting from the M case is countered by the enhancement of L over D from $-M$. Further, for $M = 0$, the coupling associated with at least one of the ϵ_i components will be zero. This is analogous to turning off the associated ϵ_i field component, so that the $M = 0$ case shows no enantiomeric control. Hence, control is lost upon M averaging.

In the other possible scenario, where all J quantum numbers are the same, all transition dipole moments change sign with $M \rightarrow -M$. The effect is similar to changing the sign of all three electric field components. As noted in the discussion following Eq. (21), this interchanges the role of D and L, hence ensuring loss of control upon M-averaging.

We note that this argument is independent of the p values of the energy levels. As such the arguments apply equally well to the asymmetric top where the p degeneracy does not exist.[14]

III. LASER CONFIGURATION B: MULTISTATE MODEL

Consider now laser configuration **B**, where the three field polarizations are mutually orthogonal. Here we show that it is possible to generate enantiomeric excess in a non-M-polarized media, i.e., enantiomeric control is not lost upon M-averaging. Specifically, consider the case where $\hat{\epsilon}_1$ lies along the Z direction, $\hat{\epsilon}_2$ lies along the X direction, and $\hat{\epsilon}_0$ lies along the Y direction. All fields are linearly polarized. The $|D\rangle$, $|L\rangle$, $|1\rangle$, and $|2\rangle$ states in this case are identical to those of configuration **A**. However, the selection rule for the coupling to levels $|3\rangle$ and $|4\rangle$ now allows for $\Delta M=\pm 1$, doubling the number of coupled excited states. To retain the previous notation we use $|3^+\rangle$ and $|4^+\rangle$ to designate $M+1$ and $|3^-\rangle$ and $|4^-\rangle$ to designate $M-1$ components of the indicated states. Note that the value of the M quantum number does not alter the parity of the states. Note also that additional M states, coupled in higher order, are not included in this section, but are treated computationally in Sec. IV.

In this case, ten molecular states are relevant in lowest order and Eq. (3) becomes,

$$\begin{aligned}|\Psi\rangle=&b_{D_p}\exp(-iE_Dt/\hbar)|D_p\rangle+b_{D_{-p}}\exp(-iE_Dt/\hbar)|D_{-p}\rangle\\&+b_{L_p}\exp(-iE_Lt/\hbar)|L_p\rangle+b_{L_{-p}}\exp(-iE_Lt/\hbar)|L_{-p}\rangle\\&+b_1\exp(-iE_1t/\hbar)|1\rangle+b_2\exp(-iE_2t/\hbar)|2\rangle\\&+\exp(-iE_3t/\hbar)(b_{3^+}|3^+\rangle+b_{3^-}|3^-\rangle)\\&+\exp(-iE_4t/\hbar)(b_{4^+}|4^+\rangle+b_{4^-}|4^-\rangle).\end{aligned}\tag{27}$$

Substituting into the Schrödinger equation gives, in the rotating wave approximation,

$$\begin{aligned}\dot{b}_{L_p}=&i\exp(-i\Delta_1t)(b_2\Omega^*_{2,L_p}-b_1\Omega^*_{1,L_p})\\&+i\exp(-i\Delta_2t)[(b_{4^+}\Omega^*_{4^+,L_p}+b_{4^-}\Omega^*_{4^-,L_p})\\&-(b_{3^+}\Omega^*_{3^+,L_p}+b_{3^-}\Omega^*_{3^-,L_p})],\\
\dot{b}_{D_p}=&i\exp(-i\Delta_1t)(b_2\Omega^*_{2,L_p}+b_1\Omega^*_{1,L_p})\\&+i\exp(-i\Delta_2t)[(b_{4^+}\Omega^*_{4^+,L_p}+b_{4^-}\Omega^*_{4^-,L_p})\\&+(b_{3^+}\Omega^*_{3^+,L_p}+b_{3^-}\Omega^*_{3^-,L_p})],\\
\dot{b}_{L_{-p}}=&i\exp(-i\Delta_1t)(b_1\Omega^*_{1,L_{-p}}-b_2\Omega^*_{2,L_{-p}})\\&+i\exp(-i\Delta_2t)[(b_{3^+}\Omega^*_{3^+,L_{-p}}+b_{3^-}\Omega^*_{3^-,L_{-p}})\\&-(b_{4^+}\Omega^*_{4^+,L_{-p}}+b_{4^-}\Omega^*_{4^-,L_{-p}})],\\
\dot{b}_{D_{-p}}=&i\exp(-i\Delta_1t)(b_1\Omega^*_{1,L_{-p}}+b_2\Omega^*_{2,L_{-p}})\\&+i\exp(-i\Delta_2t)[(b_{3^+}\Omega^*_{3^+,L_{-p}}+b_{3^-}\Omega^*_{3^-,L_{-p}})\\&+(b_{4^+}\Omega^*_{4^+,L_{-p}}+b_{4^-}\Omega^*_{4^-,L_{-p}})],\\
\dot{b}_1=&i\exp(i\Delta_1t)\Omega_{1,L_p}(b_{D_p}-b_{L_p})\\&+i\exp(i\Delta_1t)\Omega_{1,L_{-p}}(b_{D_{-p}}+b_{L_{-p}})\\&+i\exp(-i\Delta_0t)(b_{4^+}\Omega^*_{4^+,1}+b_{4^-}\Omega^*_{4^-,1}),\\
\dot{b}_2=&i\exp(i\Delta_1t)\Omega_{2,L_p}(b_{D_p}+b_{L_p})\\&+i\exp(i\Delta_1t)\Omega_{2,L_{-p}}(b_{D_{-p}}-b_{L_{-p}})\\&+i\exp(-i\Delta_0t)(b_{3^+}\Omega^*_{3^+,2}+b_{3^-}\Omega^*_{3^-,2}),\\
\dot{b}_{3^+}=&i\exp(i\Delta_2t)\Omega_{3^+,L_p}(b_{D_p}-b_{L_p})\\&+i\exp(i\Delta_2t)\Omega_{3^+,L_{-p}}(b_{D_{-p}}+b_{L_{-p}})\\&+i\exp(i\Delta_0t)b_2\Omega_{3^+,2},\\
\dot{b}_{3^-}=&i\exp(i\Delta_2t)\Omega_{3^-,L_p}(b_{D_p}-b_{L_p})\\&+i\exp(i\Delta_2t)\Omega_{3^-,L_{-p}}(b_{D_{-p}}+b_{L_{-p}})\\&+i\exp(i\Delta_0t)b_2\Omega_{3^-,2},\\
\dot{b}_{4^+}=&i\exp(i\Delta_2t)\Omega_{4^+,L_p}(b_{D_p}+b_{L_p})\\&+i\exp(i\Delta_2t)\Omega_{4^+,L_{-p}}(b_{D_{-p}}-b_{L_{-p}})\\&+i\exp(i\Delta_0t)b_1\Omega_{4^+,1},\\
\dot{b}_{4^-}=&i\exp(i\Delta_2t)\Omega_{4^-,L_p}(b_{D_p}+b_{L_p})\\&+i\exp(i\Delta_2t)\Omega_{4^-,L_{-p}}(b_{D_{-p}}-b_{L_{-p}})\\&+i\exp(i\Delta_0t)b_1\Omega_{4^-,1},\end{aligned}\tag{28}$$

where we have made use of Eq. (20) and the notation is a natural extension of that previously introduced [Eq. (19)].

Once again, changing the sign of the electric fields results in a change in dynamics. Hence,[12] this ten-level scheme allows for enantiomeric control. Further, as in configuration **A**, changing the sign of either one ϵ_i field component or of all three field components results in loss of control, whereas if two field components change sign then control is maintained. Qualitative motivation for this result resides in the fact that changing the sign of either one field or three results from reflecting the field through either one plane or three perpendicular planes, respectively. Since each reflection equals inversion followed by rotation, this corresponds to an overall operation with an odd number of inversion steps. This being the case, one expects that the effect of the inversions on the electric field would be similar to that of the inversions on the molecule, i.e., the interchange of L and D, which is indeed the case. By contrast, changing the sign of two fields components implies reflecting the field through perpendicular planes. This corresponds to two steps of rotation and inversion. However, since rotations and inversions

commute, the result of changing the sign of two field components is equivalent to a rotation of the electric field vector. Such a rotation cannot affect the role of L and D, and hence does not affect the enantiomeric selectivity.

M averaging

As in configuration **A**, an examination of the angular momentum attributes of these differential equations provide insight into the effects of averaging over M. In this case, however, we can show that in the ten level case **B** the M and $-M$ terms contribute equally, so that control is maintained after M averaging. To see this consider how each M dependent 3-j symbol changes when $M \rightarrow -M$. Given [Eqs. (22) and (24)] we have for the dipole transition matrix element associated with ϵ_1 that

$$\begin{pmatrix} J' & 1 & J \\ -M & 0 & M \end{pmatrix} \xrightarrow[M \rightarrow -M]{} (-1)^{J'+J+1} \begin{pmatrix} J' & 1 & J \\ -M & 0 & M \end{pmatrix}. \tag{29}$$

Similarly, for the term associated with ϵ_2,

$$\left[\begin{pmatrix} J' & 1 & J \\ -(M+1) & 1 & M \end{pmatrix} - \begin{pmatrix} J' & 1 & J \\ -(M-1) & -1 & M \end{pmatrix} \right] \xrightarrow[M \rightarrow -M]{} (-1)^{J'+J} \left[\begin{pmatrix} J' & 1 & J \\ -(M+1) & 1 & M \end{pmatrix} - \begin{pmatrix} J' & 1 & J \\ -(M-1) & -1 & M \end{pmatrix} \right], \tag{30}$$

and for the term associated with ϵ_0

$$\left[\begin{pmatrix} J' & 1 & J \\ -(M+1) & 1 & M \end{pmatrix} + \begin{pmatrix} J' & 1 & J \\ -(M-1) & -1 & M \end{pmatrix} \right] \xrightarrow[M \rightarrow -M]{} (-1)^{J'+J+1} \left[\begin{pmatrix} J' & 1 & J \\ -(M+1) & 1 & M \end{pmatrix} + \begin{pmatrix} J' & 1 & J \\ -(M-1) & -1 & M \end{pmatrix} \right]. \tag{31}$$

As in configuration **A**, depending on the values of J, some or all of the transition dipole moments may or may not change sign. Consider then the excitation scheme where all J quantum numbers are the same. It is easily seen from Eqs. (29), (30), and (31), that $M \rightarrow -M$ has the same effect as $\epsilon_1 \rightarrow -\epsilon_1$, $\epsilon_0 \rightarrow -\epsilon_0$, and $\epsilon_2 \rightarrow \epsilon_2$. Therefore, from previous discussions, both M and $-M$ contribute equally and control is maintained with M averaging. Similar results obtain for the case where two levels are of similar J and the third is of angular momentum $J \pm 1$. Hence enantiomeric control survives M averaging in configuration **B**. Note that the same M considerations are applicable to the asymmetric top.

IV. COMPUTATIONAL TESTS: LASER DISTILLATION

The results above indicate that M-averaged control is possible for configuration **B** assuming that the fields significantly couple only the ten indicated levels. A generalized, albeit computational, extension of these results to include all M levels is provided in this section. Specifically, we show that the full system of states that are coupled by three perpendicular linearly polarized lasers shows control, even upon M-averaging. Note, however, that numerical studies do show that the ten level approximation is, in most cases, an excellent approximation.

Further, we note that the results described above deal with the effect of a single set of laser pulses on a racemic mixture. To provide an effective method for purification of a racemic mixture we previously proposed[4,5] a systematic "laser distillation" scheme comprising two repeated steps. In step one the system is irradiated with the set of laser pulses as described above. In step two the system is allowed to collisionally and radiatively relax back to the ground state. This pair of steps is repeated until an equilibrium population is achieved. Below, we computationally consider the effectiveness of this laser distillation sequence in configuration **B**.

To outline the computation associated with laser distillation we describe, for notational simplicity, the case where there is no p degeneracy (e.g., the asymmetric top). Computations below are, however, for the symmetric top, where the p degeneracy is added as noted later below.

Consider the system initiated in a racemic mixture of $|L,M\rangle$'s and $|D,M\rangle$ of fixed J. Here we have explicitly indicated the M quantum number of the ground state. In the first step the system is excited with a laser pulse sequence as described above. In the second step, the system collisionally and radiatively relaxes so that all the population returns to the ground state to produce an incoherent mixture of $|L,M\rangle$'s and $|D,M\rangle$'s. This pair of steps is then repeated until the populations of $|L,M\rangle$ and $|D,M\rangle$ reach convergence.

To obtain the equilibrium result computationally note that the population after laser excitation, but before radiative relaxation, consists of the weighted sum of the results of $2*(2J+1)$ computations: $N_D/(2J+1)$ times the results of laser excitation starting solely with molecules in $|D,M\rangle$ for $M=-J,\ldots,J$, plus $N_L/(2J+1)$ times the results of laser excitation starting solely with molecules in $|L,M\rangle$ for $M=-J,\ldots,J$.

Let $P_{D,M}^{D,M_1}$ and $P_{L,M}^{D,M_1}$ denote the probabilities of $|D,M\rangle$ and $|L,M\rangle$ resulting from laser excitation assuming that the initial system is comprised solely of molecules in $|D,M_1\rangle$ and let $P_{D,M}^{L,M_1}$ and $P_{L,M}^{L,M_1}$ be the corresponding probabilities for excitation from an initial system composed solely of $|L,M_1\rangle$.

The populations of $|D,M\rangle$ and $|L,M\rangle$ after laser excitation of the mixture are

$$\frac{1}{2J+1}\sum_{M_1}\left[N_D P_{D,M}^{D,M_1}+N_L P_{D,M}^{L,M_1}\right] \tag{32}$$

and

$$\frac{1}{2J+1}\sum_{M_1}\left[N_D P_{L,M}^{D,M_1}+N_L P_{L,M}^{L,M_1}\right], \tag{33}$$

respectively. The total D and L populations are therefore, $N_D P_D+N_L P_D'$ and $N_D P_L+N_L P_L'$, respectively, where we have denoted

$$P_q\equiv\frac{1}{2J+1}\sum_{M_1,M}P_{q,M}^{D,M_1},\quad P_q'\equiv\frac{1}{2J+1}\sum_{M_1,M}P_{q,M}^{L,M_1} \tag{34}$$

for $q=D,L$. The remainder of the population,

$$\mathcal{N}^{\mathrm{ex}}=N_D[1-P_D-P_L]+N_L[1-P_D'-P_L'] \tag{35}$$

is in the upper levels $|1,M\rangle$ and $|2,M\rangle$, $M=-J-1,...,J+1$.

Radiative emission, or collision relaxation, from these excited levels then follows, with the excited population dividing itself equally between the $2*(2J+1)|D,M\rangle$ and $|L,M\rangle$ states.

The effect of collisions is also such as to equilibrate the population amongst the M states. The resultant populations $\mathcal{N}_D$ and $\mathcal{N}_L$ in ground states $|D\rangle$ and $|L\rangle$ are then

$$\mathcal{N}_D=0.5N_D[1+P_D-P_L]+0.5N_L[1+P_D'-P_L'] \tag{36}$$

and

$$\mathcal{N}_L=N_D+N_L-\mathcal{N}_D. \tag{37}$$

The sequence of laser excitation followed by collisional relaxation and radiative emission is then iterated until the system equilibrates. Clearly, equilibrium is obtained when the populations, postradiative emission, are the same as those prior to laser excitation, i.e., when $\mathcal{N}_D=N_D$ and $\mathcal{N}_L=N_L$. These conditions reduce to $N_D(1-P_D+P_L)=N_L(1+P_D'-P_L')$. If the total population is chosen to be normalized $(N_D+N_L=1)$, then the final probabilities $\mathcal{P}_D$, $\mathcal{P}_L$ of populating states $|D\rangle$ and $|L\rangle$ are

$$\mathcal{P}_D=\frac{1+P_D'-P_L'}{2-P_D+P_L+P_D'-P_L'} \tag{38}$$

and with $\mathcal{P}_L=1-\mathcal{P}_D$.

The excess of the probability ΔP of one enantiomer over another is given by

$$\Delta P=\mathcal{P}_D-\mathcal{P}_L=2\mathcal{P}_D-1=\frac{P_D-P_L+P_D'-P_L'}{2-P_D+P_L+P_D'-P_L'}. \tag{39}$$

Note that although we focus upon a single J level, the scenario extends to the entire set of equilibrated J levels. Specifically, as the laser targeted J level is enantiomerically enriched, the other J levels feed population into the depleted J level during the collisional relaxation step, so that the entire system ultimately becomes enantiomerically enriched.

In the case of the symmetric top, explicitly computed below, the above argument is extended by introducing the p degeneracy. Thus, for example, the system is initially comprised of a racemic mixture of states $|L,M,p\rangle$ and $|D,M,p\rangle$ with $M=-J,-J+1,...,J-1$, J, $p=1$ and $p=-1$. Independent computations are done starting with each of the $2\times2\times(2J+1)$ independent initial states, which serve as input into the total calculation.

We consider the following model for computational purposes: an initial state is composed of an unpolarized racemic mixture of states is irradiated with pulses having Gaussian envelopes,

$$\epsilon_l=\beta_l e^{i\theta_l}e^{-[(t-t_l)/\alpha_l]^2}. \tag{40}$$

The values of the vibrational part of the transition dipole (see Appendix) were taken as $\mu^x=0.9$, $\mu^y=1.0$, and $\mu^z=1.1$ for all transitions. We have chosen $J=1$ $\lambda=0$, $\lambda'=1$ and $\lambda''=1$. In this case the ground states only have $p=1$ allowed.

Results subsequent to laser excitation were obtained by numerically solving the full set of coupled levels for all relevant M and p states. The excess after a single pulse is given as the differences between the D and L populations in an initial racemic mixture where each of the allowed states is equally populated. The ''converged'' results pertain to the results after iteratively exciting and relaxing the system as described above. The particular results shown below were obtained by optimizing the converged excess using a simulated annealing routine[20] with respect to the following free parameters of the system: the field amplitudes β_l, phases θ_l, pulse peak times t_l, durations α_l, and detunings Δ_l.

Figures 3 and 4 below shows the populations of the D and L enantiomers after a single pulse (and before relaxation) and after a convergent sequence of pulse followed by relaxation for a number of different parameters. In the cases shown, all variables other than that explicitly varied along the abscissa are those for which the converged excess reached a maximal (or minimal) value. Note, that many such maxima and minima with values close to 1 (or -1) occur in this multidimensional parameter space.

In Fig. 3 the phase θ_0 of the field ϵ_0, is varied whereas in Fig. 4 the amplitude β_0 is varied. As can be seen, a large maximal converged excess can be attained, even though the single-pulse selectivity is very small. This is due to the fact

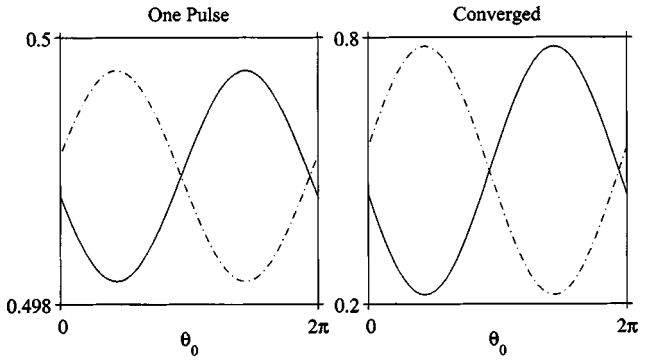

FIG. 3. Left: enantiomeric excess after one pulse (and before relaxation); right: the converged enantiomeric excess. Here we vary the phase θ_0. The values of the other parameters are $J=1$, $\lambda=0$, $\lambda'=1$, $\lambda''=1$, $\alpha_0=7.66$ ps, $\alpha_1=10.51$ ps, $\alpha_2=11.21$ ps, $\beta_1=3.98\times10^{-6}$ a.u., $\beta_2=5.00\times10^{-6}$ a.u., $t_0=0.0$ ps, $t_1=-23.24$ ps, $t_2=-2.06$ ps, $\theta_1=3.99$, $\theta_2=5.95$, $\Delta_1=1.43\ \mathrm{cm}^{-1}$, $\Delta_2=-2.11\ \mathrm{cm}^{-1}$, and $\beta_0=1.28\times10^{-6}$. Note the different ordinate scales.

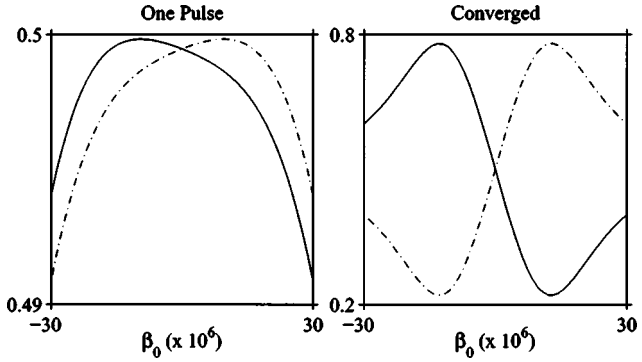

FIG. 4. As in Fig. 3 but varying the amplitude β_0, with $\theta_0=1.39$. Note the different ordinate scales.

that at the end of the pulse one of the enantiomers is almost unaffected, while the other enantiomer is somewhat depleted into the excited states.

V. DISCUSSION AND SUMMARY

We have considered angular momentum issues associated with two specific control schemes for enhancing the population of a desired enantiomer through the electric field–electric dipole interaction. Both of these scenarios invoke principles of coherent control,[16] i.e., the use of controllable quantum interference effects to affect the outcome of system dynamics. That is, in both cases the ground states $|D\rangle$ and $|L\rangle$ are excited to specific excited vib-rotational states by a scenario that implicitly involves at least two coherent routes that interfere with one another. For example, in laser configuration **A**, $|1\rangle$ can be reached from the ground state by one photon excitation with ϵ_1, or by ϵ_2 excitation from the ground state to state $|2\rangle$, followed by stimulated emission with ϵ_0 to $|1\rangle$. The interference term discriminates between enantiomers due to the sign of excitation amplitudes [i.e., see Eq. (9)], allowing for selective control over particular enantiomers. In accord with Ref. 4 cumulative enhancement of population in a desired enantiomer then results by sequentially irradiating the system with the three lasers, followed by spontaneous emission and collisional relaxation, processes that are repeated until the population of the L and D enantiomers converge.

Results of the angular momentum analysis showed that in irradiating a racemic mixture with laser configuration **A**, as previously proposed,[4] control is achieved only if the system is M-polarized. This led to the introduction of a second laser configuration, termed laser configuration **B**, that provides an effective means for controlling enantiomer populations in an ordinary nonpolarized racemic mixture. Studies on configuration **B** applied to realistic systems are currently ongoing.[14]

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APPENDIX: SELECTION RULES

Some features of the dipole matrix elements, and the associated selection rules are summarized in this Appendix.

By inserting Eq. (23) into Eq. (22) we have that μ_l is given by

$$\mu_l = f_l \Big\{ \mu_l^{(z)}[D^1_{0,q_l}(\phi,\theta,\chi) + p_l(-1)^{q_l} D^1_{0,-q_l}(\phi,\theta,\chi)] + \frac{1}{\sqrt{2}}[\mu_l^{(x)} - i\mu_l^{(y)}][D^1_{-1,q_l}(\phi,\theta,\chi) + p_l(-1)^{q_l} D^1_{-1,-q_l}(\phi,\theta,\chi)] - \frac{1}{\sqrt{2}}[\mu_l^{(x)} + i\mu_l^{(y)}] \times [D^1_{1,q_l}(\phi,\theta,\chi) + p_l(-1)^{q_l} D^1_{1,-q_l}(\phi,\theta,\chi)] \Big\}, \quad \text{(A1)}$$

where $f_X=-1$, $f_Y=i$, $f_Z=1$.

This can be rewritten in terms of the symmetry adapted $\mathcal{D}$ functions by using Eq. (13) in the form,

$$\mathcal{D}^{1,p}_{K,q_l}(\phi,\theta,\chi) \equiv t_K \left(\frac{3}{8\pi^2}\right)^{1/2} \{D^1_{K,q_l}(\phi,\theta,\chi) + p(-1)^K D^1_{-K,q_l}(\phi,\theta,\chi)\}. \quad \text{(A2)}$$

Inserting Eq. (A2) into Eq. (A1) gives

$$\mu_l = f_l \left(\frac{8\pi^2}{3}\right)^{1/2} \{\mu_l^{(z)}[\mathcal{D}^{11}_{0,q_l}(\phi,\theta,\chi) + p_l(-1)^{q_l}\mathcal{D}^{11}_{0,-q_l}(\phi,\theta,\chi)] - \mu_l^{(x)}[\mathcal{D}^{11}_{1,q_l}(\phi,\theta,\chi) + p_l(-1)^{q_l}\mathcal{D}^{11}_{1,-q_l}(\phi,\theta,\chi)] - i\mu_l^{(y)}[\mathcal{D}^{1-1}_{1,q_l}(\phi,\theta,\chi) + p_l(-1)^{q_l}\mathcal{D}^{1-1}_{1,-q_l}(\phi,\theta,\chi)]\}, \quad \text{(A3)}$$

where the $1/\sqrt{2}$ factors of the x, y components are canceled by $1/t_K$.

The total dipole moment, and hence each component, must be antisymmetric with respect to inversion. For the x and z components, $\mu^{(x)}$ and $\mu^{(z)}$ are symmetric, and the angular part is antisymmetric. For the y component, $\mu^{(y)}$ is antisymmetric, and the angular part is symmetric. Therefore, as required, the total dipole is antisymmetric.

We may obtain a useful set of expressions by using the relation,

$$\begin{pmatrix} j_1 & j_2 & j_3 \\ m_1 & m_2 & m_3 \end{pmatrix} = (-1)^{j_1+j_2+j_3} \begin{pmatrix} j_1 & j_2 & j_3 \\ -m_1 & -m+_2 & -m_3 \end{pmatrix}. \quad \text{(A4)}$$

Rearranging the elements we get

$$F(J',\lambda',p';J,\lambda,p;-K) = (-1)^{J'+1+J}(-1)^{\lambda+\lambda'} pp' F(J',\lambda',p';J,\lambda,p;K). \quad \text{(A5)}$$

Therefore,

$$\left(\frac{8\pi^2}{3}\right)^{1/2}(\mathcal{D}^{J',p'}_{\lambda',M'}|\mathcal{D}^{1p''}_{K,q}|\mathcal{D}^{J,p}_{\lambda,M})$$

$$\equiv(\mathcal{D}^{J',p'}_{\lambda',M'}|D^1_{K,q}+p''(-1)^K D^1_{-K,q}|\mathcal{D}^{J,p}_{\lambda,M})$$

$$\equiv(-1)^{-M'}t_{\lambda'}t_\lambda[(2J'+1)(2J+1)]^{1/2}\begin{pmatrix} J' & 1 & J \\ -M' & q & M\end{pmatrix}$$

$$\times[1+(-1)^{J'+1+J}pp'p'']F(J',\lambda',p';J,\lambda,p;K) \tag{A6}$$

since the relations of the $3j$ symbols ensure us that $(-1)^{\lambda+\lambda'+K}=1$. Therefore the required selection rules are obtained.

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