The Journal of Chemical Physics

Theory of enantiomeric control in dimethylallene using achiral light

Cite as: J. Chem. Phys. **115**, 5349 (2001); https://doi.org/10.1063/1.1405116
Submitted: 20 March 2001 • Accepted: 01 August 2001 • Published Online: 12 September 2001

David Gerbasi, Moshe Shapiro and Paul Brumer

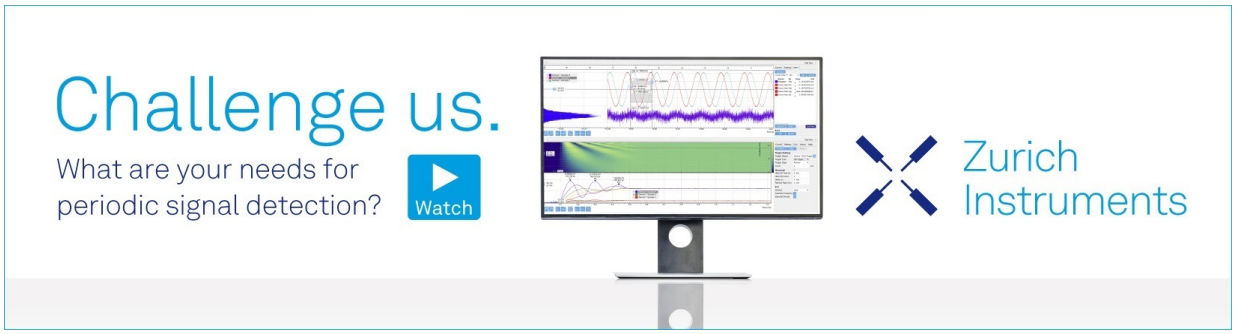
View Online Export Citation

ARTICLES YOU MAY BE INTERESTED IN

Enantiomeric purification of nonpolarized racemic mixtures using coherent light
The Journal of Chemical Physics **119**, 7237 (2003); https://doi.org/10.1063/1.1603732

Effect of molecular rotation on enantioseparation
The Journal of Chemical Physics **137**, 044313 (2012); https://doi.org/10.1063/1.4738753

Theory of the two step enantiomeric purification of 1,3 dimethylallene
The Journal of Chemical Physics **120**, 11557 (2004); https://doi.org/10.1063/1.1753552



AIP Publishing

© 2001 American Institute of Physics.

Theory of enantiomeric control in dimethylallene using achiral light

David Gerbasi, Moshe Shapiro,[a] and Paul Brumer
Chemical Physics Theory Group, The Department of Chemistry, University of Toronto, Toronto M5S 3H6, Canada

(Received 20 March 2001; accepted 1 August 2001)

Extensive control over enantiomer populations using achiral light is computationally demonstrated for J, M_J-selected 1,3 dimethylallene. In particular, by altering the detuning of one of three lasers incident on an J, M_J-polarized racemic mixture, one can alter the enantiomeric excess from ≈93% of the L enantiomer to ≈93% of the D enantiomer. © *2001 American Institute of Physics.* [DOI: 10.1063/1.1405116]

Considerable attention has recently been directed towards using lasers to alter the enantiomeric excess of an initially racemic mixture.[1–5] Traditionally, light-induced asymmetric synthesis scenarios have relied on the ability of left or right circularly polarized light[1] to differentiate between enantiomers via the (weak) magnetic dipole interaction. Recently[2,5] we demonstrated that it is possible to use linearly polarized light, and hence the strong dipole–electric field interaction, to control the interconversion of enantiomers if the molecules that are laser excited are M_j-selected, where M_j is the projection of the total angular momentum J along the direction of laser polarization.[6] Related arguments have been made by others about enantiomer control for oriented molecules,[3,4] with Ref. 4 relying upon the excitation of oriented molecules with shaped laser pulses. In both cases, specifying conditions on the molecules plus including laser phase introduces chirality into the total electric field-molecule system.

In our M_j-selected scenario a particular laser arrangement, discussed below, serves to excite more or less of the population of one enantiomer than the other. The excited molecules then collisionally relax and radiate back to the D and L ground state.[7] Laser pumping followed by relaxation in the ground and excited states is repeated again and again until convergence, leading to an excess of population of the desired enantiomer. This scenario, which we call laser distillation, is one example of a more general theorem[8] on possible scenarios for asymmetric synthesis based on the dipole–electric field interaction. It is of interest since neither the incident light nor the initial molecular system are chiral, but chiral discrimination and the enhancement of the population of one enantiomer over the other in a racemic mixture is nonetheless possible.

In this communication we demonstrate computationally that 1,3 dimethylallene provides an excellent candidate for this scenario, and that virtually total control over the enantiomeric excess resulting from irradiating a racemic mixture of 1,3 dimethylallene is possible. Specifically, we use our recently computed[9] potential energy surfaces and electric dipole moments for 1,3 dimethylallene in conjunction with a three-laser version of the laser distillation scenario, to demonstrate a vast range of control over the enantiomeric excess in an irradiated M_j polarized racemic mixture of D and L 1,3 dimethylallene.

Consider first the initial laser excitation scheme. Specifically, we examine a three-laser extension[10] of the scenario discussed in Ref. 2. Here, an electric field $\mathbf{E}(t)$ comprising three pulses is incident on a racemic mixture of chiral molecules in a fixed M_j state. The field $\mathbf{E}(t)$ is given by

$$\mathbf{E}(t)=\sum_{k=0,1,2}\mathbf{E}_k(t)\equiv\sum_{k=0,1,2}2\,\hat{\epsilon}_k\,\mathrm{Re}[\,\epsilon_k(t)\exp(i\omega_k(t))], \tag{1}$$

where $\epsilon_k(t)$ is the pulse envelope, ω_k is the central laser frequency, and $\hat{\epsilon}_k$ is the polarization direction. The central frequency of $\epsilon_1(t)$ is chosen to couple the ground vibrational states $|D\rangle$ and $|L\rangle$ of the right and left handed enantiomers with energies $E_D=E_L$ to eigenstate $|1\rangle$ of energy E_1, $\epsilon_2(t)$ to couple eigenstates $|D\rangle$ and $|L\rangle$ to state $|2\rangle$ of energy E_2, and $\epsilon_0(t)$ couples states $|1\rangle$ and $|2\rangle$ to one another. Here $|1\rangle$ and $|2\rangle$ are eigenstates of nuclear motion in the excited electronic state, and we choose $\hat{\epsilon}_0=\hat{\epsilon}_1=\hat{\epsilon}_2$ to define the z axis.

The molecule under consideration is assumed characterized by an achiral excited potential energy surface[11] so that $|1\rangle$ can be chosen to be symmetric with respect to inversion and $|2\rangle$ is antisymmetric with respect to inversion. By choosing ω_i near-resonant with $\omega_{iD}\equiv(E_i-E_D)/\hbar$, $(i=1,2)$ and $\omega_0\approx\omega_{21}\equiv(E_2-E_1)/\hbar$, and by making the pulse widths narrow, the system is well described as a laser coupled four level system. This being the case, we expand the total wave function $|\Psi\rangle$ as

$$\begin{aligned}|\Psi\rangle=&\,b_D(t)\exp(-iE_Dt/\hbar)|D\rangle+b_L(t)\\&\times\exp(-iE_Lt/\hbar)|L\rangle+b_1(t)\exp(-iE_1t/\hbar)|1\rangle\\&+b_2(t)\exp(-iE_2t/\hbar)|2\rangle.\end{aligned} \tag{2}$$

Substituting Eq. (2) into the time dependent Schrodinger equation gives the following set of coupled differential equations within the rotating wave approximation:

[a]Permanent address: Chemical Physics Department, The Weizmann Institute of Science, Rehovot, Israel 76100.

 © 2001 American Institute of Physics

$$\begin{aligned}
\dot{b}_1 &= i\exp(i\Delta_1 t)\Omega^*_{D,1}[b_D + b_L] + i\exp(i\Delta_0 t)\Omega^*_0 b_2 \\
\dot{b}_2 &= i\exp(i\Delta_2 t)\Omega^*_{D,2}[b_D - b_L] + i\exp(-i\Delta_0 t)\Omega_0 b_1 \\
\dot{b}_D &= i\exp(-i\Delta_1 t)\Omega_{D,1} b_1 + i\exp(-i\Delta_2 t)\Omega_{D,2} b_2 \\
\dot{b}_L &= i\exp(-i\Delta_l t)\Omega_{D,1} b_1 - i\exp(-i\Delta_2 t)\Omega_{D,2} b_2 .
\end{aligned} \tag{3}$$

Here $\Omega_{ij}(t) \equiv \mu_{ij}\epsilon_j(t)/\hbar$, $\Delta_j \equiv \omega_{j_D} - \omega_j$, $\mu_{ij} \equiv \langle i|\vec{\mu}_k \cdot \hat{\epsilon}_k|j\rangle$, with $i = D,L$, $k = 0,1,2$, $j = 1,2$, $\Delta_0 \equiv \omega_{21} - \omega_0$, and $\Omega_0(t) \equiv \mu_{12}\epsilon_0(t)/\hbar$. The quantity $\vec{\mu}_i$ is the electric dipole operator relevant to the particular transition. In obtaining Eq. (3) we have used the relations $\Omega_{D,1} = \Omega_{L,1}$, and $\Omega_{D,2} = -\Omega_{L,2}$, which are consequences[2] of the symmetric and antisymmetric nature of $|1\rangle$ and $|2\rangle$. The extent to which control can be achieved over enantiomer populations depends upon numerous system parameters, including the nature of the states $|1\rangle$, $|2\rangle$, the laser parameters, etc. Equation (3) can be solved numerically for various system parameters to display this dependence, as shown below. Specifically, we present results for the probabilities $|b_D|^2$ and $|b_L|^2$ at long times. Note that control arises, as in all coherent control scenarios, through quantum interference effects. Specifically, the presence of the three excitation frequencies in Eq. (1) allows for at least two interfering routes for excitation from states $|D\rangle$ and $|L\rangle$ to state $|1\rangle$ or $|2\rangle$.

To apply this approach to dimethylallene we require the Franck–Condon factors for excitation from the D and L eigenstates of the ground electronic state to the excited state levels. Essential input into this study are the results of our previous molecular structure computations.[9] Specifically, we constructed a cut through the full dimethylallene potential surface by computing ground and excited state energies as a function of the dihedral angle α between the H_3C—C═C and C═C—CH_3 planes and the C—C—C bending angle θ. Consideration of these cuts showed that dimethylallene, a chiral molecule by virtue of its overall molecular geometry, possesses two stable conformations in the ground state, corresponding to the right- and left-handed enantiomeric states, and does have an achiral first electronic state,[9] as required above. Further, we computed the electronic dipole moment[9] and the eigenstates of the potentials as a function of θ and α, the latter using the discrete variable representation with periodic boundary conditions[12] in α. Only high lying states were found to give significant Franck–Condon overlap with the ground state wave functions, hence the DVR computations required very large numbers of basis function (e.g., on the order of 25 000) for convergence. In addition, we approximate the rotational eigenfunctions of dimethylallene by those of a symmetric top with quantum numbers J, M_J, λ, where λ is the projection of J on a body fixed axis.

The reliability of our calculated eigenstates was verified by comparing computed absorption spectra to experimental data. Starting with Fermi's golden rule, the absorption cross section is given by $\sigma = D^2\omega L(\omega)/(6\epsilon_0\hbar c)$, where $D^2 = e^2|\mu|^2$ is the square of the transition dipole moment, ω is the transition frequency, and $L(\omega)$ is the lineshape function which includes both spontaneous emission and Doppler Broadening. The results are remarkably accurate when compared to experimental values.[13] That is, the computed extinction coefficient at the absorption maximum of 196.3 nm is 6601 ($cm^{-1}\,mol^{-1}\,L$) as compared to the experimental value of 6300, with the absorption maxima shifted by only 6 nm.

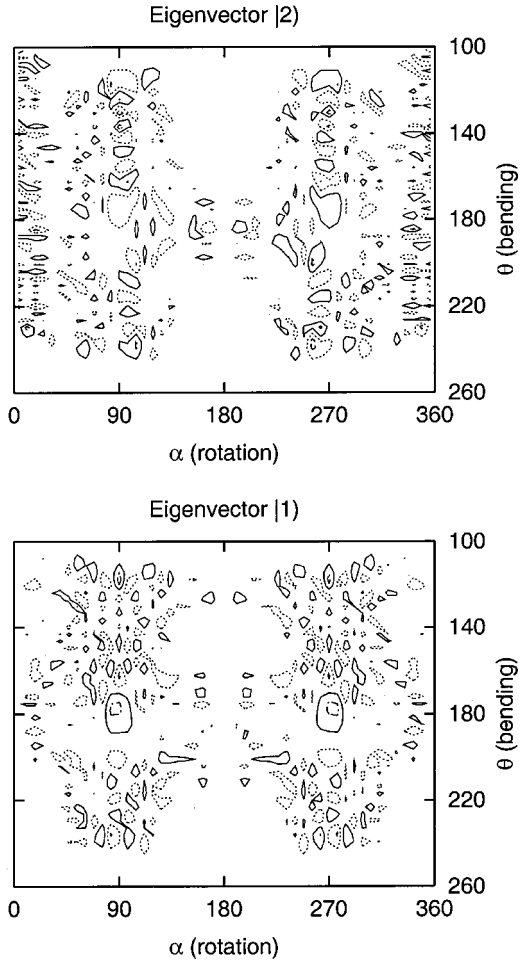


FIG. 1. Contour plots of $|1\rangle$ and $|2\rangle$ where dash–dash lines = 0.012 a.u., dot–dot lines = 0.004 a.u., solid lines = −0.004 a.u., and dot–dash lines = −0.012 a.u. Note that $|1\rangle$ is symmetric with respect to inversion and $|2\rangle$ is antisymmetric. Inversion here corresponds to changing $(\alpha - 180°)$ to $(\alpha + 180°)$.

Below we choose two eigenstates which have large Franck–Condon transition probabilities to demonstrate the extent of possible control. The α, θ dependence of the wave functions for these two states, shown in Fig. 1, make clear the symmetric and antisymmetric character of the states, as well as the very high level of excitation to which they correspond. Since we approximate dimethylallene by a symmetric top, we consider specific J, M_J, λ to J',M_J,λ' transitions. Our computations gave, for these wave functions and, for example, for rotational quantum numbers J, M_J,λ of 3, 2, 2 and 4, 2, 2 for the ground and excited electronic states: $\langle 1|\mu|D\rangle = \langle 1|\mu|L\rangle = 5.44\times10^{-3}$ a.u., $\langle 2|\mu|D\rangle = -\langle 2|\mu|L\rangle = 4.01\times10^{-3}$ a.u., $\langle 1|\mu|2\rangle = -8.17\times10^{-4}$ a.u., and $\omega_{21} = 261.78\,cm^{-1}$. Many other pairs of states defined by different vibrational or rotational quantum numbers show qualitatively similar control to the results for this case, discussed below.

We consider the extent of control achievable using Gaussian pulses of the form

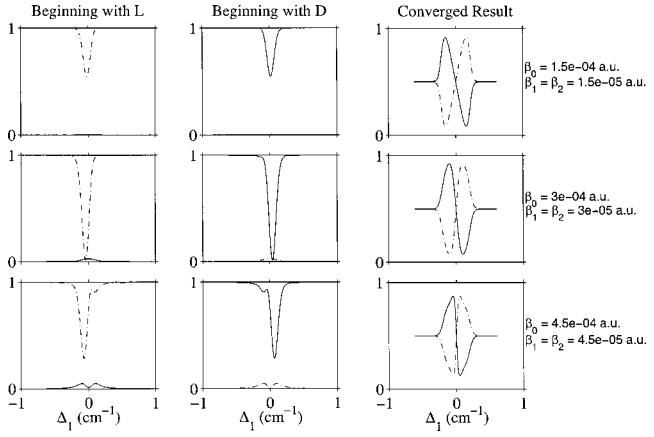


FIG. 2. Control over dimethylallene enantiomer populations as a function of the detuning Δ_1 for various laser powers. The first column corresponds to probabilities of L (dot–dash curves) and D (solid curves) after a single laser pulse, assuming that the initial state is all L, the second column are similar, but for an initial state which is all D. The right most column corresponds to the probabilities of L and D when one starts with a racemic mixture and carries out repeated excitations followed by spontaneous emission and collisional relaxation.

$$\epsilon_{\ell}(t)=\beta_{\ell}\exp\{-[(t-t_{\ell})/\alpha_{\ell}]^2\} \quad (l=0,1,2). \tag{4}$$

Results are presented for pulses with $\beta_0=10\beta_1$, $\beta_1=\beta_2$ and with all pulses of 100 ps duration full width at half maximum. These pulses are sufficiently narrow in frequency so that they excite only single levels in the excited state region, where the density of states for our 2-dimensional model is 0.34 states per wave number. Control results are shown in Fig. 2 as a function of the detuning Δ_1 of ω_1 from $(E_1-E_D)/\hbar$ and with $\Delta_2=\Delta_1$ for various laser powers. The other pulse, $\omega_0=261.78\,\mathrm{cm}^{-1}$, is resonant with the transition noted above. Three different sets of results are shown—those corresponding to a single pulse sequence starting with an initial state which is solely L (column 1), those corresponding to a single pulse sequence where the initial state is solely D (column 2), and the ''converged result'' which are composed of repeated steps of radiative excitation followed by relaxation until equilibrium has been established (column 3). In the latter case the initial state is taken as a racemic mixture. The results clearly show outstanding enantiomeric control over the dimethylallene enantiomers for a wide variety of powers. For example, the most impressive result is achieved for $\Delta_1=-0.0986\,\mathrm{cm}^{-1}$ and $\beta_0=3.0\times10^{-4}$ a.u., $\beta_1=\beta_2=3.0\times10^{-5}$ a.u., corresponding to laser powers of 3.16×10^9 W/cm^2 and 3.16×10^7 W/cm^2, respectively. Here a racemic mixture of dimethylallene can be converted, after a series of pulses, to a mixture of dimethylallene, containing 92.7% of the D-dimethylallene in this state. Similarly, detuning to $\Delta_1=0.0986\,\mathrm{cm}^{-1}$ results in a similar enhancement of L-dimethylallene. Slightly lower extremes of control are seen to be achievable for the two other laser powers shown. Further, control was achievable to field strengths down to 10^4 W/cm^2. Control can also be affected by varying other laser parameters such as the time ordering of the pulses, the relative laser powers, the remaining detunings, etc. For example, Fig. 3 shows control as a function of the field strength ratio β_0/β_1 for $\beta_1=\beta_2=3.0\times10^{-5}$ a.u. for various different time orderings $\Delta t=t_0-t_1$, with $t_1=t_2$. Control is clearly affected by a wide range of control parameters.

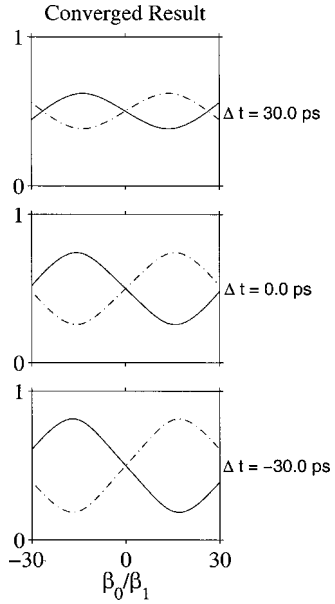


FIG. 3. Control over dimethylallene enantiomer probability as a function of the field ratio β_0/β_1 for $\beta_1=\beta_2=3.0\times10^{-5}$ a.u., $\Delta_1=0.09\,\mathrm{cm}^{-1}$ and various values of the time delay $\Delta t=t_1-t_0$ with $t_1=t_2$.

More detailed consideration of the results shown in Fig. 2 is enlightening. To do so, note that the probability $\mathcal{P}_D$ for forming the D enantiomer, after repeated iterations of laser excitation followed by collisional and radiative relaxation is given by[2]

$$\mathcal{P}_D=\frac{1+P_D'-P_L'}{2-P_D+P_L+P_D'-P_L'}, \tag{5}$$

where P_D and P_L denote the probabilities of $|D\rangle$ and $|L\rangle$ resulting from a single laser pulse sequence assuming that the system is initially solely in $|D\rangle$ (i.e. the results in column 2 of Fig. 2), and P_D' and P_L' denote results of a single laser pulse sequence exciting a system composed solely of $|L\rangle$ (i.e. the results shown in column 1 of Fig. 2). The probability of forming L in the specific J, M_J-state after the full iterative process is $\mathcal{P}_L=1-\mathcal{P}_D$. (Note that it is $\mathcal{P}_L$ and $\mathcal{P}_D$ that are shown as the ''converged results'' in Figs. 2 and 3.)

Given Eq. (5) we may extract trends that are responsible for increasingly good enantiomeric discrimination in the converged results. For example, results in Fig. 2 show that the enantiomeric discrimination is best for $|P_D-P_L|\approx1$ and $|P_D'-P_L'|\approx1$, but with $P_D\neq P_L'$ and $P_D'\neq P_L$. For example, at the maximal control point $\Delta_1=-0.153\,\mathrm{cm}^{-1}$ in the top row in Fig. 2 $P_D=0.998\,40$, $P_L'=0.975\,92$, and $P_D'\approx P_L\approx7.0\times10^{-3}$. In this instance the iterative laser distillation process gives an excellent result of $\mathcal{P}_D=0.915$. (Note that the small difference between P_D and P_L' and between P_D' and P_L is necessary for control; if these quantities are equal then enantiomeric control is lost.) Such large values of P_D and P_L' are, of course, not necessary for high quality control. For example, the maximum control in the middle row of Fig.

2 (at $\Delta_1 = -0.0986\,\mathrm{cm}^{-1}$, giving the results noted above, i.e., $\mathcal{P}_D = 0.927$) is obtained with $P'_L = 0.452\,99$, $P_D = 0.973\,50$, $P_L = P'_D = 0.017\,75$.

Finally, note that each Δ_1 point in the converged result column in Fig. 2 required a different number of iterations for convergence, although none required an excessive number of pulses. For example, the point of maximal control the top row of Fig. 2 required 852 pulses, the middle row required 42 pulses, and the bottom row required 29 pulses. In general, the number of pulses required is related to the difference between P_D and P'_L; the greater the difference, the less amount of pulses will be needed to reach equilibrium. These numbers constitute lower bounds to the real experiment which include other levels to which the system radiatively and collisionally relaxes.

To implement the above procedure experimentally one could impose an external magnetic field to split the M_J levels and excite the system on the required J, M_J to J',M_J transitions by appropriate laser tuning. Collisions and radiative relaxation re-equilibrate the J, M_J levels within each enantiomer. The laser pulses followed by re-equilibration is repeated many times. In this way we are able to affect the populations of all J, M_J levels of the system, converting them from L to D, even though we pump only on a particular J, M_J to J',M_J transition.

In summary, we have shown that dimethylallene is a strong candidate for laser control over the enantiomeric excess, which can be extensively enhanced using linearly polarized light from an initial racemic mixture. The method emphasizes the role of quantum interference in the symmetry-breaking control. Enantiomeric excesses of up to 92.7% can be achieved using very realistic pulse parameters. A full computation utilizing the asymmetric top levels of dimethylallene and including alternate pulse durations, collisional effects and competition due to internal conversion are underway.

The authors are grateful to Professor Malcolm Bersohn, University of Toronto, for suggesting that they consider dimethylallene as a candidate for the laser distillation scenario. Einat Frishman is acknowledged for helpful discussion and for computer programs. One of the authors (D.G.) holds a PGSA Fellowship from NSERC, Canada. M.S. acknowledges partial support for this work from the EU IHP Program (COCOMO Network) and the Minerva Foundation, Germany. This work was supported by the U.S. Office of Naval Research.

[1] A. Salam and W. J. Meath, Chem. Phys. **228**, 115 (1998); J. Chem. Phys. **106**, 7865 (1997).
[2] M. Shapiro, E. Frishman, and P. Brumer, Phys. Rev. Lett. **84**, 1669 (2000).
[3] Y. Fujimura, L. Gonalez, K. Hoki, J. Manz, and Y. Ohtsuki, Chem. Phys. Lett. **306**, 1 (1999); **310**, 578 (1999). Note, that this paper studies control starting with an initial superposition state, rather than with a racemic mixture.
[4] K. Hoki, Y. Ohtsuki, and Y. Fujimura, J. Chem. Phys. **114**, 1575 (2001). See also, Y. Fujimura, L. Gonzalez, K. Hoki, D. Kroner, J. Manz, and Y. Ohtsuki, Angew. Chem. Int. Ed. Engl. **39**, 4586 (2000); K. Hoki, D. Kroner, and J. Manz, Chem. Phys. **267**, 59 (2001).
[5] See also a related approach, M. Shapiro and P. Brumer, J. Chem. Phys. **95**, 8658 (1991).
[6] The restriction to a single M_j state is implicit, rather than explicit, in Ref. 2. If, in addition, the molecule is a symmetric top then one must consider inducing excitations between specific pairs of J,M_J, λ levels, where λ is the projection of J along a body fixed axis. A detailed discussion of angular momentum and associated selection rules is provided in M. Shapiro, E. Frishman, and P. Brumer (in preparation).
[7] In actuality, radiative emission occurs to all levels in the ground state. However, we assume rapid thermal equilibration of state populations so that the overall final control will be the same as if populations did radiate to the single ground state.
[8] P. Brumer and M. Shapiro, J. Chem. Phys. (submitted).
[9] E. Deretey, P. Brumer, and M. Shapiro, J. Phys. Chem. (submitted).
[10] In the previously considered scenario (Ref. 2) $\epsilon_1(t)$ and $\epsilon_2(t)$ were considered components of a single electric field.
[11] Systems with chiral electronic ground states and achiral excited electronic states are well established models in studies of chiral systems. See, for example, M. Quack, Angew. Chem. Int. Ed. Engl. **28**, 571 (1989); J. A. Cina and R. A. Harris, J. Chem. Phys. **100**, 2531 (1994); C. S. Maierle and R. A. Harris, *ibid.* **109**, 3713 (1998).
[12] D. T. Colbert and W. H. Miller, J. Chem. Phys. **96**, 1982 (1992).
[13] A. Rauk, A. F. Drake, and S. F. Mason, J. Am. Chem. Soc. **101**, 2284 (1979).