Laser Distillation of Enantiomers
from an Isotropic Racemic Mixture

S. S. Bychkov, B. A. Grishanin, and V. N. Zadkov

International Laser Center and Department of Physics, M. V. Lomonosov Moscow State University,
Vorob'evy gory, Moscow, 119899 Russia
e-mail: grishan@comsim1.phys.msu.su
Received April 10, 2001

1. INTRODUCTION

The problem of preferential synthesis with light from a racemic solution of enantiomers has been under discussion over last decades [1–8]. Two different solutions have been discussed so far.

One solution is based on preferable *selection* of left- or right-handed enantiomers from a racemic solution with no change in their nuclear configurations. We will call such a laser scenario *laser selection scenario*. One of the laser selection scenarios was discussed in [1], where the preferential synthesis from a racemic solution was demonstrated with the use of circularly polarized laser light with the inhomogeneous intensity distribution along the laser beam radius (though the yield of the scenario was quite small).

Another solution is based on a *photoinduced synthesis* of left-handed enantiomers from right-handed ones or vice-versa. We will call such a laser synthesis *laser distillation* of enantiomers. Obviously, laser distillation of enantiomers scenario works for a racemic solution only if the photoinduced dynamics of left-handed or *L*-enantiomers differs from the dynamics of right-handed or *D*-enantiomers. Several models for laser distillation scenarios for a preferential production of required enantiomers from a racemic solution were discussed in the literature over a few last years [2–5]. For example, it has been discussed an interaction of a circularly polarized light with a racemic solution [2, 4]. However, calculations give a negligible difference of about $10^{-6}\%$ in preferential synthesis of *L*- over *D*-enantiomers or vice-versa. Another scenario suggested by Shapiro *et al.* [5] seems to be more promising. It encodes the quantum coherences in the molecule to selectively enhance the production of either *L*- or *D*-enantiomers. However, as we show in this paper, Shapiro's scenario does not work for a racemic *isotropic* solution.

In this paper, we elucidate the role of the rotational degrees of freedom for the process of laser distillation of enantiomers from a racemic isotropic solution for any possible laser scenario (Section 2). It is shown that the laser distillation scenario suggested in [5], which is based on coherent control, does not work for the achiral synthesis from a racemic *isotropic* solution. This is due to the fact that rotational degrees of freedom of enantiomers constituting the solution are homogeneously distributed over the Euler angles and averaging over this distribution cancels the effect. A modified scenario is suggested (Sections 3 and 4), which works for the case of *isotropic* racemic solution. A detailed analysis of this scenario shows its efficacy for the preferable synthesis of enantiomers of required handedness. The results of this paper are summarized in the Conclusions (Section 5).

2. ROTATIONAL SYMMETRY ANALYSIS OF A LASER DISTILLATION SCENARIO FROM A RACEMIC SOLUTION

In the following we will suppose, for simplicity, that the nuclear configuration of a stable enantiomer in the ground electronic state depends only on a reaction coordinate θ and the Euler angles $\mathbf{O} = (\varphi, \vartheta, \tilde{\theta})$, which characterize the rotation of the enantiomer in free space. We suppose also that all other intramolecular degrees of freedom are fixed and are not changed during enantiomer's dynamics. For stable enantiomers, the double-well potential that is typical for chiral molecules, has a high barrier along the reaction coordinate. Therefore, the splitting of the rotational levels of the enantiomer due to switching between left- and right-handed configurations is negligible: the eigenstates of the Hamiltonian, $\psi_L(\theta)$ and $\psi_D(\theta)$, are equally possible in a racemic mixture of *L*- and *D*-enantiomers at thermodynamical equilibrium. For large molecules, most interesting for practical purposes, the high potential barrier is due to the essential mass of the enantiomer $M \gtrsim 10^3 m_H$, where m_H is the proton mass. In this case, rotations of the enantiomer in free space can be treated as classical because $\hbar\omega_{n, n+1} \ll kT$, where $\omega_{n, n+1}$ are the frequencies of rotational transitions. Rotational dynamics of such an enantiomer along the reaction coordinate θ is described in terms of the states $\psi_L(\theta)$ and $\psi_D(\theta)$ (in matrix representation, by $|L\rangle$ and $|D\rangle$, respectively) and dynamics along the Euler angles $\mathbf{O}$ can be counted on by simple classical averaging over an initial distribution, which is not changed during laser excitation.

This simple model of enantiomer dynamics in isotropic medium is sufficient to elucidate the fundamen-

tal role of rotational symmetry, which imposes restrictions on possible scenarios for the laser distillation of enantiomers from a racemic isotropic mixture. From the analysis below it follows that any laser distillation scenario that employs coplanar configuration of the laser fields polarizations does not work for an isotropic mixture.

Let us define the *degree of chirality* operator, which is the operator $\hat{\chi} = |L\rangle\langle L| - |D\rangle\langle D|$ that defines an excess of L-enantiomers in a racemic mixture (i.e., the nonracemicity of the mixture). Eigenstates of $\hat{\chi}$ are $|L\rangle$- and $|D\rangle$-states and the eigenvalues are equal to ± 1. In matrix representation the degree of chirality operator is simply the Pauli matrix $\hat{\sigma}_z$. Similar definitions of the degree of chirality operator one can find in [9, 10], where it is shown that $\hat{\chi}$ is a pseudoscalar, i.e., $\hat{R}\hat{\chi}\hat{R}^{-1} = -\hat{\chi}$, where $\hat{R}$ is the inversion operator that mirrors a radius vector as $\mathbf{r} \longrightarrow -\mathbf{r}$. Excess of L-enantiomers at the fixed Euler angles $\mathbf{O}$, or simply the degree of chirality χ, can be expressed through the degree of chirality operator $\hat{\chi}$ and the transition superoperator $\mathcal{S}_I(\mathbf{O})$, which describes the transformation of density matrix $\hat{\rho}_0 \longrightarrow \hat{\rho}_t$ over the time t. For an ensemble of molecules, the degree of chirality is to be averaged over the Euler angles:

$$\chi = \langle \mathrm{Tr}[\hat{\chi}\mathcal{S}_I(\mathbf{O})\hat{\rho}_0]\rangle_{\mathbf{O}}. \tag{1}$$

We will suppose in the following that molecules in a racemic mixture are homogeneously distributed over the Euler angles.

The transition superoperator, describing photoinduced dynamics of a chiral molecule along the reaction coordinate, can be written if we neglect rotations of the molecule in free space as

$$\mathcal{S}_I(\mathbf{O}) = T\exp\left\{-\frac{i}{\hbar}\int_0^t [\hat{U}_0^{-1}\hat{H}_I\hat{U}_0, \odot]d\tau\right\}, \tag{2}$$

$$\hat{U}_0 = e^{-\frac{i}{\hbar}\hat{H}_0\tau},$$

where T is the time ordering operator, expression $[\hat{A}, \odot]$ with the substitution symbol $\odot$ describes the superoperator for commuting the transformed density matrix with the operator $\hat{A}$, $\hat{H}_I = \mathbf{E} \cdot \hat{\mathbf{d}} - \mathbf{E} \cdot \hat{\boldsymbol{\mu}}$ is the interaction Hamiltonian of the molecule with incident laser field $\mathbf{E} = \Re\sum_k \mathcal{E}_k(t)e^{-i\omega_k t}$, $\hat{\mathbf{d}}$ is the dipole moment operator of the nuclear configuration of the molecule, and $\hat{\boldsymbol{\mu}}$ is the electron dipole moment operator.

For enantiomers homogeneously distributed along the Euler angles, we have $\mathcal{R}\hat{\rho}_0 = \hat{\rho}_0$, where $\mathcal{R} = \hat{R}\odot\hat{R}^{-1}$, and, therefore,

$$-\chi = \langle \mathrm{Tr}[\mathcal{R}\hat{\chi}\mathcal{S}_I\hat{\rho}_0]\rangle_{\mathbf{O}} = \langle \mathrm{Tr}[\hat{\chi}\mathcal{R}\mathcal{S}_I\mathcal{R}^{-1}\hat{\rho}_0]\rangle_{\mathbf{O}}. \tag{3}$$

Then, comparing Eq. (3) with Eq. (1) we immediately have $\chi = 0$ if

$$\langle \mathcal{S}_I(\mathbf{O}) - \mathcal{R}\mathcal{S}_I(\mathbf{O})\mathcal{R}^{-1}\rangle_{\mathbf{O}} = 0. \tag{4}$$

Let us prove that Eq. (4) is strictly fulfilled for a coplanar configuration of the laser fields polarizations and is valid in general case to the third order of the expansion of the transition superoperator (2) by the powers of $\hat{H}_I$.

To prove this, let us expand Eq. (4) in series taking into account the correct time ordering:

$$\langle \mathcal{S}_I - \mathcal{R}\mathcal{S}_I\mathcal{R}^{-1}\rangle_{\mathbf{O}} = \sum_{n=1}^{\infty} \langle \mathcal{S}_I^{(n)} - \mathcal{R}\mathcal{S}_I^{(n)}\mathcal{R}^{-1}\rangle_{\mathbf{O}}, \tag{5}$$

where

$$\mathcal{S}_I^{(n)} = \left(-\frac{i}{\hbar}\right)^n \int_0^t dt_n \int_0^{t_n} dt_{n-1}\ldots\int_0^{t_2} [\hat{H}_I(t_n)\ldots[\hat{H}_I(t_1), \odot]]dt_1,$$

$$\mathcal{R}\mathcal{S}_I^{(n)}\mathcal{R}^{-1}$$

$$= \left(-\frac{i}{\hbar}\right)^n \int_0^t dt_n \int_0^{t_n} dt_{n-1}\ldots\int_0^{t_2} [\mathcal{R}\hat{H}_I(t_n)\ldots[\mathcal{R}\hat{H}_I(t_1), \odot]]dt_1.$$

The inversion transformation of the interaction Hamiltonian in expansion (5) is equivalent to the inversion of the dipole moment operator $\mathcal{R}\hat{\mathbf{d}}_k = (-\hat{d}_{kx}, -\hat{d}_{ky}, -\hat{d}_{kz})$, which, in its turn, is equivalent to the inversion of the vector $\mathbf{E}$. From Eq. (1) and on account of Eq. (5) the degree of chirality takes the form

$$\chi = \sum_{n=1}^{\infty} \varepsilon_{\alpha_1\ldots\alpha_n}^{(n)} \int_0^t dt_n \int_0^{t_n} dt_{n-1}\ldots\int_0^{t_1} E_{\alpha_1}(t_1)\ldots E_{\alpha_n}(t_n)dt_1, \tag{6}$$

where

$$\varepsilon_\alpha^{(1)} \propto \frac{1}{\hbar}\sum_n \rho_{nn}^{(0)}\langle d_{nn, \alpha}\rangle_{\mathbf{O}},$$

$$\varepsilon_{\alpha, \beta}^{(2)} \propto \frac{1}{\hbar^2}\sum_{n, m} \rho_{nn}^{(0)}\langle d_{nm, \alpha}d_{mn, \beta}\rangle_{\mathbf{O}},$$

$$\varepsilon_{\alpha, \beta, \gamma}^{(3)} \propto \frac{1}{\hbar^3}\sum_{n, p, m} \rho_{nn}^{(0)}\langle d_{nm, \alpha}d_{mp, \beta}d_{pn, \gamma}\rangle_{\mathbf{O}},$$

$\alpha_n, \alpha, \beta, \gamma = x, y, z$ and n, p, m number the levels incident laser fields act on which.

Let us specify the tensors $\varepsilon^{(1)}$, $\varepsilon^{(2)}$, and $\varepsilon^{(3)}$ after averaging over the homogeneous distribution over the Euler angles **O**.

It follows from Eq. (6) that $\varepsilon^{(1)}$ being the first rank tensor (vector) corresponds up to the dimensional coefficients to the permanent dipole moment vector of the medium, all components of which are equal to zero for an isotropic medium. Second rank tensor $\varepsilon^{(2)}$ corresponds to the linear susceptibility tensor $\tilde{\chi}^{(1)}$, nondiagonal components of which are equal to zero for isotropic medium. Moreover, according to Eqs. (5) and (6) diagonal components of $\varepsilon^{(2)}$ are also equal to zero. Tensor $\varepsilon^{(3)}$ corresponds up to the dimensional coefficients to the nonlinear susceptibility tensor $\tilde{\chi}^{(2)}$ for an isotropic and gyrotropic medium [11] and, therefore, its coefficients satisfy the following relation: $\varepsilon^{(3)}_{\alpha,\beta,\gamma} \propto \epsilon_{\alpha,\beta,\gamma}$, where $\epsilon_{\alpha,\beta,\gamma}$ is the Levi–Civita tensor.

Let us now prove that in general case only those components of $\varepsilon^{(n)}$ are non-zero for which all three indices x, y, z are present and each index appears an odd number of times. First, from expansion (6) it follows immediately that those components of tensor $\varepsilon^{(n)}$ are non-zero, for which one index (or three different indices simultaneously) appears an odd number of times. Second, consider in the equation for the degree of chirality for a single molecule the term whose indices in the $\hat{\varepsilon}^{n}$, for instance x, y appear an even number of times and index z appears an odd number of times. This means that the x, z-projections of all dipole moments for the transitions in the conjugated molecule, which are obtained by rotating an original molecule around the OY-axis by π, change the sign. Then, summation of the degrees of chirality for original and conjugated molecules leads to the zeroing of the components of tensor $\varepsilon^{(n)}$ indices x and y of which appear an even number of times. As a result, the only nonzero components of tensor $\varepsilon^{(n)}$ are those in which all indices x, y, z are present and every index appears an odd number of times. For instance, for the fifth rank tensor $\hat{\varepsilon}^{(5)}$ the following tensor components are non-zero: $\varepsilon^{(5)}_{xxxyz}$, $\varepsilon^{(5)}_{xyyyz}$, $\varepsilon^{(5)}_{xyzzz}$, $\varepsilon^{(5)}_{yxxxz}$, etc.

Now we will apply this symmetry analysis to the laser distillation scenarios. For coplanar polarizations $\mathscr{E}_k(t)$ we can choose as OZ-axis an axis that is orthogonal to the plane formed by the vectors $\mathscr{E}_k(t)$. Then, the only nonzero components are the x, y-projections of the incident laser field **E**. From Eq. (6) it follows that in the expansion appear only zero components of the tensor $\varepsilon^{(n)}$ for which index z is absent and, therefore, $\chi = 0$. Thus, a laser distillation scenario from a racemic isotropic solution will be successful only if the configuration of the polarizations of the incident fields is non-coplanar or, in other words, shows helicity.

Presented above analysis shows that for coplanar polarizations of the incident laser fields the transitions $D \longrightarrow L$ and $L \longrightarrow D$ are jointly compensated in a racemic isotropic solution, where molecules are homogeneously distributed over the Euler angles, and the solution remains the racemic solution.

For a laser distillation scenario applied to a racemic isotropic solution of enantiomers, the symmetry of the $L \longrightarrow D$ and $D \longrightarrow L$ transitions, which is due to the homogeneous distribution of the enantiomers over the Euler angles, can be violated in two possible ways. First, we can align the enantiomers in a solution and therefore made the distribution over the Euler angles inhomogeneous. This can be done, for instance, with the help of strong laser field, which aligns the dipole moments of the enantiomers. Such a scheme was calculated in [6, 7] for a vapor of hydrogen peroxide molecules. The calculations show, however, that the laser field intensities necessary for aligning the enantiomers are close on the order of magnitude to the intraatomic field intensity. Second, we can use a non-coplanar configuration of incident laser field polarizations, which is considered below in Section 3. An extension of a laser distillation scenario [5], described in our paper, is based on the use of three linearly polarized pulsed (in subpicosecond time scale) laser fields with *non-coplanar* configuration of polarizations. Non-coplanarity of the polarization vectors is the necessary condition to form a chiral field configuration in 3D space. The chirality of such a field configuration is revealed in the process of enantiomer–laser field interaction in dipole approximation even locally, i.e., in a specific point of space. By contrast, the chiral properties of a circularly polarized light are not shown in dipole approximation for local interactions and became apparent only for non-local interactions.

3. LASER DISTILLATION SCENARIO OF CHIRAL ENANTIOMERS IN A RACEMIC SOLUTION WITH CHIRAL LIGHT

In the laser distillation scenario for achiral synthesis from a racemic solution suggested in [5] authors consider the following model for the molecule's dynamics in free space. Excited state potential of the molecule along the reaction coordinate θ is assumed to be a quasiharmonic one with the minimum located at $\theta = 0$. It is supposed also that there are two states, $|1\rangle$ and $|2\rangle$, in the excited state, which are described by symmetric and antisymmetric wave functions in respect to $\theta = 0$, respectively. The $|1\rangle \longrightarrow |2\rangle$ transition frequency lies in IR range. Neglecting consideration of Section 2 specific for isotropic media, the authors of [5] have shown that for the given model a laser distillation scenario for achiral synthesis from a racemic solution can be realized with the help of two pulsed laser fields (Fig. 1a). In this scenario a pulsed (subpicosecond) laser field $\mathbf{E}_2$ is used for forming a coherent superposition of states $|1\rangle$ and $|2\rangle$. Then, asymmetric transfer of population from

L- and *D*-states is achieved through the coherent superposition of states $|1\rangle$, $|2\rangle$ which is linked by the second laser pulsed field $\mathbf{E}_1$ with the ground states. In this scheme polarizations of the fields are always coplanar and, therefore, described laser distillation scenario does not work for a racemic *isotropic* solution (Section 2).

Let us now consider how one has to modify Shapiro's scenario [5] for the achiral synthesis with light from a racemic mixture of enantiomers. For this purpose, we will employ the same idea and model for the free molecule's dynamics, suggested in [5], but will use for generation the coherent superposition of states $|1\rangle$ and $|2\rangle$ pulsed Raman pumping laser fields with linear polarizations vectors of which form the plane different from the plane linear polarization of the laser field pumping the electronic transition lies in (Fig. 1b):

$$\mathbf{E}_2(t) = (0, E_2(t), 0),$$

$$\mathbf{E}_3(t) = (0, E_3(t)\cos\gamma, E_3(t)\sin\gamma),$$

where γ is the angle between *OXY*-plane and polarization vector of the field $\mathbf{E}_3(t)$. With this symmetry choice, pumping of the electronic transition with the laser field $\mathbf{E}_1(t)$ destroys symmetry in population transfer from *L*- and *D*-states via the states $|1\rangle$ and $|2\rangle$ in the excited electronic state. Polarization plane for the filed $\mathbf{E}_1(t)$ is to be chosen non-coplanar:

$$\mathbf{E}_1(t) = (E_1(t), 0, 0).$$

In rotating wave approximation (RWA), the interaction Hamiltonian $\hat{H}_I$ for the four-level system (Fig. 1b) has the form:

$$\hat{H}_I = \frac{\hbar}{2}\begin{pmatrix} 0 & 0 & \Omega_1 & -\Omega_1 \\ 0 & 0 & \Omega_1 & \Omega_1 \\ \Omega_1 & \Omega_1 & \Delta_1 & \Omega_2 \\ -\Omega_1 & \Omega_1 & \Omega_2 & -\Delta_2 \end{pmatrix}, \quad (7)$$

where

$$\Omega_1 \propto \frac{\mathbf{E}_1\langle 1|\hat{\boldsymbol{\mu}}|D\rangle_{\mathbf{0}}}{\hbar},$$

$$\Omega_2 \propto \frac{1}{\hbar^2}\sum_p \frac{(\mathbf{E}_2 \cdot \langle 1|\hat{\mathbf{d}}|p\rangle_{\mathbf{0}})(\langle p|\hat{\mathbf{d}}|2\rangle_{\mathbf{0}} \cdot \mathbf{E}_3)}{\omega_2 - \omega_{1,p}} \quad (8)$$

are the Rabi frequencies of one-photon electronic transition excited by the pulsed laser field $\mathbf{E}_1(t)$ and Raman transition $|1\rangle \longrightarrow |2\rangle$ pumped by the pulsed laser fields with frequencies ω_2 and ω_3, respectively, Δ_1 is the laser detuning at the $|L\rangle \longrightarrow |1\rangle$ transition.

For the following calculations we will assume that (i) $\Omega_2 \ll \omega_{1,2}, \Delta_1$ and (ii) that $\Omega_1 \sim \omega_{12}$, where ω_{12} is the
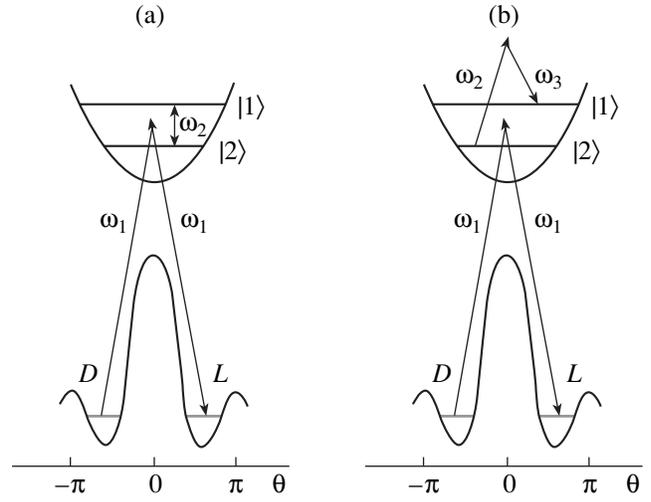
Fig. 1. (a) Shapiro's scheme for coherent laser distillation scenario from a racemic mixture of stable enantiomers with the help of two pulsed laser fields [5]. (b) Scheme for laser distillation from a racemic solution and homogeneous distribution of enantiomers over the Euler angles with the help of three pulsed laser fields with frequencies ω_1, ω_3, ω_3, linear polarizations of which are not coplanar. Here θ is the reaction coordinate.

$|1\rangle \longrightarrow |2\rangle$ transition frequency. The first assumption sets an upper limit on the laser fields intensities $\mathbf{E}_2$, $\mathbf{E}_3$ that can be used in the resonant approximation. The second assumption ensures the coherent control in the molecule that is determined by the laser field $\mathbf{E}_1$.

Let us decompose the interaction Hamiltonian $\hat{H}_I$ into sum of the Hamiltonian $\hat{H}_1$, which stays for the one-photon population transfer of *L*- and *D*-states via $|1\rangle$ and $|2\rangle$ states, and the Hamiltonian $\hat{H}_2$, which stays for the coherent superposition of $|1\rangle$ and $|2\rangle$ states. Then, taking into account that $\hat{H}_1 \gg \hat{H}_2$, the transition superoperator (2) in RWA takes the form

$$\mathcal{S}_I(\mathbf{O}) = (\hat{U}_1 \odot \hat{U}_1^{-1})\left(1 - \frac{i}{\hbar}\int_0^t [\hat{U}_1^{-1}\hat{H}_2\hat{U}_1, \odot]d\tau + \ldots\right), \quad (9)$$

$$\hat{U}_1 = e^{-\frac{i}{\hbar}\hat{H}_1 t},$$

where

$$\hat{H}_1 = \begin{pmatrix} 0 & 0 & \Omega_1 & -\Omega_1 \\ 0 & 0 & \Omega_1 & \Omega_1 \\ \Omega_1 & \Omega_1 & \Delta_1 & 0 \\ -\Omega_1 & \Omega_1 & 0 & -\Delta_2 \end{pmatrix}, \quad \hat{H}_2 = \begin{pmatrix} 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & \Omega_2 \\ 0 & 0 & \Omega_2 & 0 \end{pmatrix}. \quad (10)$$
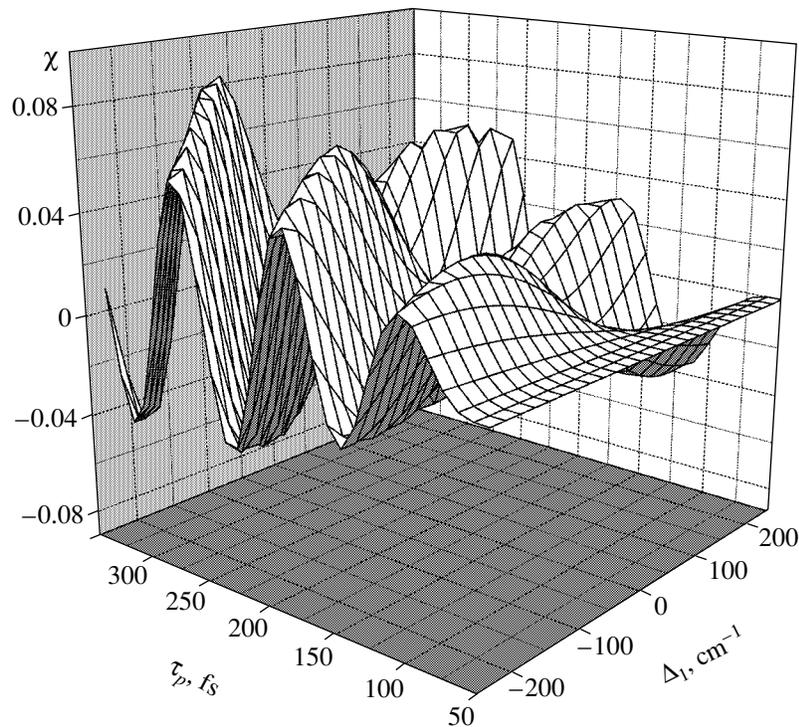
Fig. 2. The degree of chirality χ versus detuning Δ_1 and laser pulses duration τ_p calculated for the case of orthogonal linear polarizations of incident laser fields $\mathbf{E}_1(t)$, $\mathbf{E}_2(t)$, and $\mathbf{E}_3(t)$. The following parameters were used for calculation: Ω_1, $\omega_{1,2} = 100$ cm^{-1}, $\Omega_2 = 10$ cm^{-1}.

Finally, putting Eq. (9) in Eq. (1) for the degree of chirality χ, we get

$$\chi \sim -\frac{i}{\hbar}\left\langle \mathrm{Tr}\,\hat{\chi}\hat{U}_1 \odot \hat{U}_1^{-1}\int\limits_0^t[\hat{U}_1^{-1}\hat{H}_2\hat{U}_1, \hat{\rho}_0]d\tau\right\rangle_{\mathbf{O}}. \quad (11)$$

It is important to note that, as it follows from (11), the degree of chirality depends *linearly* on the parameters of Raman pumping of $|1\rangle \longrightarrow |2\rangle$ transition and, therefore, is equal to zero in the absence of coherent superposition of states $|1\rangle$ and $|2\rangle$, i.e., for $\hat{H}_2 \longrightarrow 0$. For our simple model of photoinduced dynamics, described by the unitary operator $\hat{U}_1$ and Hamiltonian $\hat{H}_2$, Eq. (11) can be calculated with the help of computer algebra analytically. Resulted formula is too bulky to be presented in the paper, but can be easily evaluated numerically. The degree of chirality χ versus the detuning Δ_1 and laser pulses duration τ_p is shown in Fig. 2.

4. DISCUSSION

Theoretical calculations for the laser distillation scenario for synthesis from a racemic isotropic mixture of enantiomers outlined in the previous section show that, according to Eq. (11), the degree of chirality χ with the use of three laser fields depends on the angle γ between the planes of the polarization vectors of the incident fields as $\chi \sim \sin\gamma$. Therefore, for $\gamma = 0$ the scenario does not work for the isotropic mixture of enantiomers which are homogeneously distributed over the Euler angles (Section 2). The maximum value of the degree of chirality is obviously achieved for the orthogonal polarizations of the incident fields, when $\gamma = \pi/2$.

Optimal for the laser distillation scenario pulse duration of linearly polarized pulsed fields is limited by the Rabi frequency Ω_1, $\tau_p < 2\pi/\Omega_1$, otherwise our theoretical analysis cannot be applied [12]. It follows from Eq. (11) that for $\tau_p < 2\pi/\Omega_1$ the degree of chirality $\chi \sim \Omega_2/\Omega_1$ and, therefore, do not exceed up to the order of magnitude $\sim 10\%$.

Analysis of Fig. 2 shows that the maximum value of the degree of chirality $\chi_{\mathrm{max}} \sim 8\%$ is achieved at $\Delta_1 \sim -150$ cm^{-1} and $\tau_p \sim 250$ fs. From the Rabi frequencies used in calculations and for the minimal estimates for $\mu_{1,D} \sim ea_B$ and $d \sim ea_B$, where a_B is the Bohr radius, we can also estimate the intensities of the incident fields. For the laser field pumping electronic transition we have $I_1 \sim 10^9$ W/cm^2. For the laser fields forming Raman pumping we have I_2, $I_3 \sim 10^{12}$ W/cm^2, if their frequencies are in the visible range, and I_2, $I_3 \sim 10^9$ W/cm^2, if their frequencies are in IR range.

5. CONCLUSIONS

In conclusion, it is shown that coherent synthesis with light from a racemic mixture of enantiomers with homogeneous distribution of enantiomers over rotational degrees of freedom is only possible when the incident laser field configuration is of chiral nature. This condition is fulfilled for nonlocal magneto-dipole [2] or quadrupole interaction of circular polarized light with enantiomers. In electro-dipole approximation, i.e., for local interactions, enantiomers do not distinguish between circular and linear polarizations and helicity of the incident field comes into play only for non-coplanar configurations of polarizations for the incident fields.

For stable enantiomers with the total mass of $M \geq 10^3 m_H$, we propose a laser distillation scenario for synthesis from a racemic isotropic solution. In contrast to the Shapiro's scenario [5] this scenario can be used for homogeneous distribution of enantiomers over the Euler angles. Its efficacy depends on the configuration of polarizations of the incident fields and their intensities. It is shown that it is feasible to achieve the maximum efficacy with the incident field intensities much smaller than the intraatomic ones.

REFERENCES

1. Kucirka, J. and Shekhtman, A., 1996, *Phys. Lett. A*, **221**, 273.
2. Shao, J. and Hangi, P., 1997, *J. Chem. Phys.*, **107**, 23.
3. Marquardt, R. and Quack, M., 1996, *Z. Phys. D*, **36**, 229.
4. Salam, A. and Meath, W., 1997, *J. Phys.*, **106**, 7865.
5. Shapiro, M., Frishman, E., and Brumer, P., 2000, *Phys. Rev. Lett.*, **84**, 1669.
6. Grishanin, B.A. and Zadkov, V.N., 1999, *JETP*, **89**, 669.
7. Grishanin, B.A. and Zadkov, V.N., 2000, *Nonlinear Opt.*, **23**, 285.
8. Grishanin, B.A., Zadkov, V.N., and Bychkov, S.S., 2000, *Technical Digest of XIX European CARS Workshop* (Moscow).
9. Harris, A., Kamien, R., and Lubensky, T., 1999, *Rev. Mod. Phys.*, **71**, 1745.
10. Osipov, M., Pickup, B., and Dunmur, D., 1995, *Mol. Phys.*, **84**, 1193.
11. Shen, Y.R., 1984, *The Principles of Nonlinear Optics* (New York: Wiley).
12. In this case, expansion of the transition superoperator (9) we used in the course of theoretical calculations is not valid and we have a complex dependence of χ on Δ_1 and τ_p, which hampers the coherent achiral synthesis from a racemic isotropic mixture of enantiomers.