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Laser coherent control of molecular chiral states via entanglement of the rotational and torsional degrees of freedom

Stanislav S. Bychkov,[1] Boris A. Grishanin,[1] Victor N. Zadkov[1]* and Hiroaki Takahashi[2]

[1] Faculty of Physics and International Laser Center, M. V. Lomonosov Moscow State University, Moscow 119899, Russia
[2] Department of Chemistry, Waseda University, Tokyo 169-8555, Japan

A new mechanism for controlling chiral states in simple chiral molecules with internal rotation, which employs the coherent quantum entanglement of the rotational–torsional states of the molecules, is proposed. It requires no preliminary spatial alignment of the molecules in a solution. A novel scenario for the preferential laser synthesis of enantiomers from a racemic solution of chiral molecules employing this new mechanism of inducing chirality is proposed and analyzed in detail and experimental scheme realizing this scenario is discussed. It is suggested that a non-linear optical activity coherent anti-Stokes Raman scattering (NOA-CARS) spectroscopic technique is used for both inducing the gyration wave in the medium (vapor) of chiral molecules and detecting this photoinduced gyration wave in the medium by registering the NOA-CARS signal. All numerical estimates are made for the hydrogen peroxide and deuterated hydrogen peroxide chiral molecules. Copyright © 2002 John Wiley & Sons, Ltd.

INTRODUCTION

Preliminary studies show that methods of laser physics can help in resolving one of the key issues of practical importance in the field of molecular chirality—whether laser physics and non-linear optics can be used for preferential synthesis of a required type of enantiomers from an initially racemic mixture of molecular enantiomers.[1-8] A positive answer to this crucial question would open new horizons for a number applications in chemistry, medicine and pharmacy.

A specific aspect of chiral molecule–laser field interaction lies in the fact that the electric field not only creates the responding rotation moment of the molecule, but also induces transitions between the chiral states, owing to the interaction potential dependence on both the rotational degrees of freedom of the molecule in free space and the internal rotation degree of freedom, chiral or reaction coordinate. Keeping this in mind, one can suggest two basically different schemes for preferential synthesis. One of

*Correspondence to: Victor N. Zadkov, Faculty of Physics and International Laser Center, M. V. Lomonosov Moscow State University, Moscow 119899, Russia.
E-mail: zadkov@comsim1.phys.msu.su

them is based on preferential *selection* of left- or right-handed enantiomers from a racemic mixture with no change in the nuclear configurations of the molecules. The other is based on a photoinduced synthesis of a required type of enantiomers from the others using methods of coherent control. Such synthesis is called *laser distillation* and, as was shown first in Ref. 7, may be efficient for practical applications it is worth noting also that methods of coherent control of chiral states allow one to prepare the chiral states (left- and right-handed) in a coherent superposition, which can be seen as an implementation of a quantum bit of information (qubit); therefore, molecular chiral states can be, in general, used for the purpose of quantum information processing,[9] in contrast with the preferential *selection* schemes that turned out to be inefficient.[1-6]

Although the methods of coherent control of molecular states have been known for a long time,[10-12] their applications for controlling molecular chiral states are just at the development stage. So far, only a few scenarios of laser distillation from a racemic mixture based on the coherent control of the corresponding ro-vibrational molecular states have been proposed[7,8,13-16] and none of them has been realized experimentally so far. This is partly due to the intrinsic nature of the chiral transitions—their phase sensitivity to the molecule rotations in free space averaging over which cancels the distillation effect.[14,16] In other words, it reveals in complete suppression of the chiral asymmetry of the field–molecule interaction in the case of rotationally

symmetric interaction, unless special efforts to break down this symmetry are undertaken (see the next section).

In this paper, we present a detailed analysis of coherent control methods for molecular chiral states and suggest a new laser distillation scenario for the preferential synthesis of enantiomers from a racemic solution. Most general features of a chiral molecule–laser field interaction and comparative analysis of possible laser distillation scenarios from a racemic solution are discussed in the next section. To elucidate key peculiarities of using coherent control for manipulating molecular chiral states, we start with the hydrogen peroxide molecule (H_2O_2) and its isotopomer (HOOD), the simplest chiral molecules. These molecules have, in addition to the internal rotational or chiral degree of freedom, rotational degrees of freedom corresponding to the molecule's rotation in free space. A new laser distillation scenario for H_2O_2 and HOOD employing quantum entanglement between rotational and chiral molecular degrees of freedom is proposed in the section Laser Preferential Synthesis of Enantiomers from a Racemic Vapor of Molecules. In the following sections of the paper we discuss in detail the feasibility of an experimental scheme for the proposed laser distillation scenario. It is shown that an experimental scheme employing a variance of coherent anti-Stokes Raman spectroscopy for registration of non-linear optical activity (NOA-CARS) can be effectively used for both laser distillation of a racemic solution and registration of the optical rotation in this solution. Polarization properties of the NOA-CARS signal produced by scattering of the probe pulse in the presence of gyration wave, due to the photoinduced non-racemicity in the solution, are analyzed and the intensity of the signal is estimated.

MECHANISMS OF LASER CONTROL OF MOLECULAR CHIRAL STATES

Possible scenarios for preferential laser synthesis of enantiomers from a racemic solution

There are two different approaches to construct scenarios of preferential laser synthesis of a required enantiomer from a racemic solution of chiral molecules. One of them employs an asymmetry of the non-local polarized laser field–molecule interaction. Quadrupole or magneto-dipole interaction with a chiral molecule results in breaking down the symmetry of the $D \leftrightarrows L$ transitions (throughout the paper we will use notations D and L to designate right- and left-handed molecular chiral states, respectively) and therefore an excess of a required enantiomer can be achieved. So far, only two scenarios employing this idea have been proposed—one on non-resonant interaction of continuous-wave (cw) circular-polarized light with the electronic subsystem of a chiral molecule[1] and the other based on resonant interaction of the pulsed circular-polarized light with the nuclear subsystem of a chiral molecule.[2] However, even a qualitative analysis shows that both scenarios based on the relatively weak quadrupole or magneto-dipole interaction cannot

be effectively used for applications in chemistry and pharmaceutics. The first scenario, for example, yields only an excess of about 10^{-6}% of a required type of enantiomers from a racemic solution. An experimental realization of the second scenario requires the use of laser intensities at least 10% higher than the allowable spectroscopic maximum of 10^{13} W cm^{-2}.

A different approach employs the dipole interaction, which, obviously, is much more intensive than quadrupole or magneto-dipole interactions used in the first approach. A few scenarios based on this approach have been proposed so far.[3–7] They all are based on the dependence of laser field interaction with chiral molecular states, L and D, on the coherent laser field phases, by varying which one can control the excess of the enantiomers of a required type from a racemic solution. This interaction also has a rotationally symmetric dependence on the molecules' orientation (and this obstacle has not been previously taken into account by other authors), which cancels the effect of laser distillation of enantiomers from a racemic solution due to the averaging over rotations of molecules. In order to cope with this obstacle, one should therefore either align preliminarily the molecules in a solution or use the chiral-asymmetric spatial structure of the applied laser field (see the next subsection).

For example, the scenario suggested in Ref. 7 uses the dynamics of a chiral molecule in the excited electronic state. The potential of the excited electronic state is suggested to be a quasi-harmonic function of the reaction coordinate θ, with the minimum at $\theta = 0$. Two of its first eigenstates $|1\rangle$, $|2\rangle$ are represented with symmetric and antisymmetric wavefunctions with respect to $\theta = 0$, respectively (the transition frequency between these states lies in the infrared region). Skipping averaging over the molecules' rotations, it can be shown that an appropriate scenario may be implemented with use of two subpicosecond pulses [Fig. 1(a)].[7] A laser
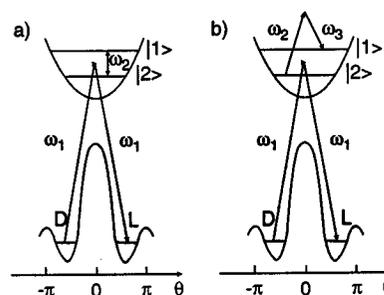
Figure 1. (a) Laser synthesis scenario from a racemic mixture of spatially aligned enantiomers with the use of two laser pulses with frequencies ω_1 and ω_2.[7] (b) Laser synthesis scenario from a racemic mixture of isotropically distributed enantiomers with use of three laser pulses with frequencies ω_1, ω_2 and ω_3 and non-coplanar polarization vectors.[16] Reaction coordinate θ is responsible for the chirality of the ground electronic state.

pulse $\vec{\mathcal{E}}_2$ with frequency ω_2 prepares the coherent superposition of the $|1\rangle$ and $|2\rangle$ states. Then, simultaneous action of two laser pulses $\vec{\mathcal{E}}_1$ and $\vec{\mathcal{E}}_2$ (the frequency ω_1 lies in the ultraviolet region) asymmetrically transfers population into L- and D-states owing to the coherent interference of the corresponding wavefunctions.

Symmetry analysis of laser field-chiral molecule interaction

Previously suggested scenarios for the preferential synthesis of enantiomers from a racemic solution[1-7] are all based on simple models of interaction of an optical field with a single molecular reaction coordinate, leaving out of the discussion questions of how other intramolecular coordinates and intermolecular interactions affect the molecule's dynamics along the reaction coordinate. At the same time, it is well known that molecular degrees of freedom are entangled and can essentially affect the molecule's dynamics along the selected reaction coordinate. Here we will clarify the role of molecular rotational degrees of freedom, which, as we will show later, essentially affect the molecule's dynamics. For simplicity, we will neglect the intermolecular interactions and intramolecular energy redistribution during the excitation.

We will start with introducing a quantitative characteristic of a chiral medium, the *degree of chirality* χ, which in terms of quantum mechanics can be written as an averaged *chirality operator*:

$$\hat{\chi} = |L\rangle\langle L| - |D\rangle\langle D| \qquad (1)$$

where $|L\rangle$ and $|D\rangle$ denote the ground electronic–vibrational states of the L- and D-enantiomers, respectively. This operator has only two non-zero eigenvalues $\chi = \pm 1$ with the corresponding eigenstates $|L\rangle$ and $|D\rangle$; all other eigenvalues are equal to zero in the residue subspace and therefore are not involved in the chiral properties of the final state. The corresponding non-zero submatrix is simply the Pauli matrix $\hat{\sigma}_3$.

The chirality operator as given in Eqn (1) is also a pseudo-scalar function of the nuclei coordinates of a chiral molecule[17,18] and therefore must satisfy the symmetry relation $\hat{R}^{-1}\hat{\chi}\hat{R} = -\hat{\chi}$, where $\hat{R}$ is the inversion operator performing inversion operation $\vec{r} \rightarrow -\vec{r}$ for the coordinates of all the nuclei and electrons with respect to the inversion center of the chiral configurations. For the simplest chiral molecules H_2O_2 and HOOD the chirality operator takes similarly to Ref. 17 the form $\hat{\chi} = \text{sign}(\hat{\vec{n}}_{OO} \cdot [\hat{\vec{n}}_{OD} \times \hat{\vec{n}}_{OH}])$, where vectors $\hat{\vec{n}}_{OO}$, $\hat{\vec{n}}_{OH}$, and $\hat{\vec{n}}_{OD}$ are the operators of the unit vectors along the corresponding bonds, which are chosen to be the right- and left-handed orthogonal bases for the $|D\rangle$- and $|L\rangle$-states, respectively. In terms of internal molecule coordinates, these vectors depend on the bond angles, but the chirality operator depends only on the torsional angle θ between two O—H (for the H_2O_2 molecule) or O—D and O—H (for the HOOD molecule) bonds.

As a next step, we will qualitatively analyze scenarios of the preferential synthesis of a required type of enantiomers from a racemic solution. To do this, we will start with analyzing the properties of a free molecule's dynamics, which is a sum of translational, rotational and internal electronic–vibrational dynamics. Translational dynamics are decoupled from rotation of the molecule as a whole and its internal rotation dynamics and results in optical spectroscopy only in the corresponding Doppler detunings. By contrast, rotation of the molecule as a whole is coupled with its internal rotation dynamics in a very complicated way. However, in the simplest models of a molecule's dynamics, one can neglect this coupling and the steady state of a free molecule can then be written as a tensor product of the corresponding Euler angles $\vec{O}$, which depend on the free rotations density matrix $\hat{\rho}_O^{(0)}$ and the chirality operator:

$$\hat{\rho}_0 = \hat{\rho}_O^{(0)} \otimes \left(n_L^{(0)} |L\rangle\langle L| + n_D^{(0)} |D\rangle\langle D| \right) \qquad (2)$$

where $n_L^{(0)}$ and $n_D^{(0)}$ are the initial populations of the L- and D-states, which are equal to each other for a racemic mixture, $n_L^{(0)} = n_D^{(0)} = 1/2$.

The degree of chirality is determined by the transformed density matrix:

$$\chi = \text{Tr} \left(\hat{\chi} \otimes \hat{I}_{rot} \right) S_I(\mathbf{E}) \hat{\rho}_0 \qquad (3)$$

where $S_I(\mathbf{E})$ is the transition or dynamics superoperator in the interaction representation, which depends on the Euler angles and applied optical fields, and $\hat{I}_{rot}$ is the unity operator in the quantum-mechanical representation of the rotational space. The resulting chirality depends on two probabilities $p(L|\mathbf{E})$ and $p(D|\mathbf{E})$ of photoinduced transitions to the $|L\rangle$- and $|D\rangle$-states, respectively:

$$\chi = p(L|\mathbf{E}) - p(D|\mathbf{E})$$
$$p(L|\mathbf{E}) = S_{LL}(\mathbf{E})n_L^{(0)} + S_{LD}(\mathbf{E})n_D^{(0)} \qquad (4)$$
$$p(D|\mathbf{E}) = S_{DD}(\mathbf{E})n_D^{(0)} + S_{DL}(\mathbf{E})n_L^{(0)}$$

Here matrix elements

$$S_{\alpha\beta} = \text{Tr}|\alpha\rangle\langle\alpha| \otimes \hat{I}(S_I(\mathbf{E})|\beta\rangle\langle\beta| \otimes \rho_O^{(0)}) \qquad (5)$$

with $\alpha, \beta = L, D$ and $0 \leq S_{\alpha\beta} \leq 1$ describe conditional probabilities of the resulted chiral states β for the fixed initial states α.

To proceed further and elucidate the general properties of $S_{\alpha\beta}$ versus the applied laser fields, we need to specify the dynamics superoperator $S_I(\mathbf{E})$ first. Taking into account dipole and quadrupole/magnetodipole terms in laser field–matter interaction and relaxation interactions, the transition superoperator takes the form

$$S_I(\mathbf{E}) = \text{T} \exp\left\{ -\frac{i}{\hbar} \int_0^t \left([\hat{U}_0^{-1}\hat{H}_I\hat{U}_0, \odot] + \mathcal{L}_r \right) d\tau \right\} \qquad (6)$$

where T is the time ordering operator, $\odot$ is the substitution symbol, which means that expression $[\hat{A}, \odot]$ represents a commutator with $\hat{A}$, $\hat{U}_0$ is the free evolution operator, $\hat{H}_I = \hat{H}_I^P + \hat{H}_I^Q$, $\hat{H}_I^P = -\mathbf{E} \cdot \vec{d} - \mathbf{E} \cdot \hat{\mu}$ is the dipole term of the Hamiltonian of the molecule interaction with the multi-component laser field $\mathbf{E} = \Re e \sum_k \vec{\mathcal{E}}_k(t) e^{-i\omega_k t}$, $\vec{d}$ is the nuclei dipole moment operator and $\hat{\mu}$ is the electronic one. $\hat{H}_I^Q = -\mathbf{H} \cdot \hat{\vec{m}} - e(\hat{r}_{k\alpha} \nabla_\alpha E_\beta) \hat{r}_{k\beta}$ is the magneto-dipole and quadrupole components of the interaction Hamiltonian, where H is the total strength of the magnetic field in the laser field, $\hat{\vec{m}}$ is the magnetic dipole moment of the electronic configuration, $\hat{\vec{r}}_k$ is the vector radius of the kth electron and e is the electron charge; $\mathcal{L}_r$ is the relaxation Liouvillian, which describes the relaxation processes.[19]

Using Eqn (6) for the dynamics superoperator, we will prove that any scenario for laser-assisted preferential synthesis of a required type of enantiomers from a racemic solution employing dipole interaction and achiral structure of the incident fields polarizations result in no change in $S_{\alpha\beta}$ after inversion $\mathcal{R}: L \leftrightarrows D$. Therefore, all such kinds of scenarios are useless for controlling chirality in a racemic solution.

The inversion superoperator $\mathcal{R}$ in terms of the operators $\hat{R}$ acting on the wavefunctions can be written in the Schrödinger picture as $\mathcal{R} = \hat{R} \odot \hat{R}^{-1}$ and in the Heisenberg picture it takes the form $\mathcal{R}^{-1} = \hat{R}^{-1} \odot \hat{R}$. In addition, any rotation $\hat{U}_\varphi$ at the arbitrary rotation angle φ leaves the initial symmetric density matrix unchanged, $\hat{U}_\varphi \rho_0^{(0)} \hat{U}_\varphi^{-1} = \rho_0^{(0)}$. Then, one can easily see from Eqn (6) that transition $L \leftrightarrows D$ is equivalent to the inversion of the superoperator $S(\mathbf{E})$. Taking also into account that the Hamiltonian of a free motion is a symmetric function with respect to inversion (we neglect here well-known weak interactions[20] because their contribution is much smaller than the considered effects), i.e., $\mathcal{R}^{-1} \hat{H}_0 = \hat{H}_0$, one can obtain after inversion the transformed dynamics superoperator in the form

$$\mathcal{R}S_I(\mathbf{E})\mathcal{R}^{-1} = \mathrm{T} \exp \left\{ -\frac{i}{\hbar} \int_0^t \left([\hat{U}_0^{-1}(\mathcal{R}^{-1}\hat{H}_I)\hat{U}_0, \odot] \right. \right.$$
$$\left. \left. + \mathcal{R}\mathcal{L}_r\mathcal{R}^{-1} \right) d\tau \right\} \qquad (7)$$

Here the transformation of the interaction Hamiltonian is equivalent to the inversion of the dipole moment $\mathcal{R}\vec{d} = -\vec{d}$, the latter being equivalent to inversion of the electric field strength E.

Inversion of the incident laser field in 3D space can be decoupled into a mirror reflection with respect to an arbitrary plane and a corresponding rotation. In the case of a coplanar polarization configuration of the incident laser fields, 3D inversion reduces to a simple rotation because coplanar polarization configuration is invariant with respect to reflection, if its polarization plane is used as a reflection plane. Then, keeping in mind that $S_{\alpha\beta}(\mathbf{E})$ are invariant with respect to any rotation and the relaxation Liouvillian $\mathcal{L}_r$ is

invariant with respect to inversion, one can readily get from Eqn (7) on account of Eqn (5) the transition probabilities to the chiral states:

$$S_{LD}(\mathbf{E}) = S_{DL}(\mathbf{E}), S_{DD}(\mathbf{E}) = S_{LL}(\mathbf{E}) \qquad (8)$$

The degree of chirality on account of Eqn (4) then takes the form

$$\chi = (n_L^{(0)} - n_D^{(0)})[S_{LL}(\mathbf{E}) - S_{LD}(\mathbf{E})] \qquad (9)$$

For an initially racemic mixture, $n_L^{(0)} = n_D^{(0)}$, Eqn (9) clearly shows that the initial racemicity of the mixture will be preserved in time. For quadrupole/magnetodipole interaction and coplanar configuration of the incident laser fields polarizations we will receive the same result—preserving racemicity of an initially racemic solution, whereas for the circularly polarized incident laser fields polarization structure the initial racemicity can break down. In other words, one of the conditions for laser-assisted control of chiral states of a chiral medium with rotational symmetry is a specific configuration of the polarizations of the incident laser fields, which encodes the helicity of the problem.

Such symmetry analysis applied to the scenarios in Refs 1–7 shows that the scenarios in Refs 3–7, employing dipole transitions, are more effective than those in Refs 1 and 2. All the described scenarios require for their successful implementation use of helical structure of the polarizations of the incident fields or, as will be shown, a preliminary alignment of the chiral molecules in a solution, which is a separate difficult problem. In our early work[15,16] we suggested as a solution to this problem using a non-coplanar configuration of the polarizations of the incident laser fields.

Summarizing this section of the paper, we have elucidated analyzing the symmetry properties of incident laser field–chiral matter interaction two key qualitative feasibility criteria for laser control of molecular chiral states. First, configuration of the polarizations of the incident laser fields must have a helical structure, otherwise a preliminary spatial alignment of chiral molecules in a racemic solution is required. Second, suggested scenarios will be effective only for the chiral molecules of which the dynamics along the reaction coordinate (internal rotation) are weakly coupled with the dynamics along other degrees of freedom.

LASER PREFERENTIAL SYNTHESIS OF ENANTIOMERS FROM A RACEMIC VAPOR OF H_2O_2 AND HOOD MOLECULES

To proceed further, we need at this point to specify a chiral molecule that we will apply to an analysis for laser preferential synthesis scenarios suggested in later sections. One of the simplest molecular chiral structures—the hydrogen peroxide molecule (H_2O_2) or its isotopomer (HOOD)—suits our purpose well, fits the feasibility criteria outlined earlier

and its vapor can be used in an experimental realization of the suggested scenarios.

As any chiral molecule, hydrogen peroxide has a double-well ground-state potential with the minima corresponding to the L- and D-chiral states. The potential barrier separating these two minima determines the tunnelling or transition time between L- and D-states. For such a small molecule as hydrogen peroxide, this time lies in the picosecond region and, therefore, the chiral transition dynamics are of oscillatory type. This is far from the case with stable enantiomers, largely polyatomic molecules, that attract most attention owing to their practical interest and for which the transition time could be many orders of magnitude higher than for small molecules because the potential barrier separating the minima for the chiral states is much higher (in the limit of organic or biomolecules, the transition time could be on the order of years to millions of years). Nevertheless, studying the hydrogen peroxide molecule can give us an insight into the fundamental mechanisms controlling molecular chiral states, both theoretically and in an experiment.

Moreover, the creation and control of dynamic chiral states are directly connected with the *quantum entanglement* of these states,[21] which plays a crucial role in speeding up the algorithms of quantum information processing.[22,23] Therefore, molecular chiral states could be considered, in principle, as an embodiment for the physical realization of a qubit (quantum bit of information).

Dynamics of free H_2O_2 and HOOD molecules

The hydrogen peroxide (H_2O_2) molecule or its isotopomer, the deuterated hydrogen peroxide molecule (HOOD), are the simplest molecules showing helicity of their structure—four nuclei, one of which located out-of-plane, result in a helical or chiral 3D non-coplanar structure as shown in Fig. 2. It can be described in terms of internal coordinates $(\theta, \theta_1, \theta_2, r_1, r_2, r_3)$ introduced in Fig. 2. The helicity of the molecule depends on the torsional angle θ. The complete set of angles, which are to be taken into account in describing the molecule's dynamics, include additionally Euler angles[24] $\vec{O} = (\vartheta, \varphi, \tilde{\theta})$ that describe the rotation of the molecule as a whole.[25]

The free dynamics of a such kinds of molecules have been investigated both experimentally, with the help of absorption spectroscopy,[26-28] and theoretically, performing *ab initio* calculations and applying empirical methods.[29-31] The theoretical results are in good agreement with experiment and show that coupling between the molecule's dynamics along the reaction (chiral) coordinate θ and along other coordinates can be neglected. Then, the number of essential coordinates of the molecules to be taken into account is reduced to just four: the torsional angle θ and three Euler angles $\vec{O}$.

The chiral dynamics of the H_2O_2 and HOOD molecules are therefore determined by motion of the light hydrogen (deuterium) nuclei around the O—O bond formed from
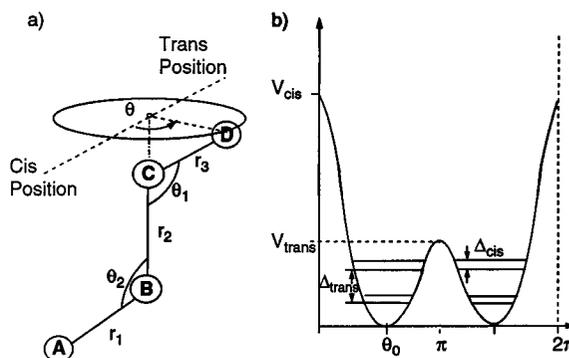
Figure 2. (a) Geometry of the hydrogen peroxide (H_2O_2) molecule with a helical structure and corresponding molecular degrees of freedom: r_1, r_2 and r_3 are the distances between nuclei, θ_1 and θ_2 are the bending angles and θ is the torsional angle (reaction coordinate). (b) Ground-state double-well potential for a molecule with helical structure similar to the hydrogen peroxide molecule versus torsional angle.

much heavier oxygen nuclei. For a free molecule, the dynamics of light nuclei decouples into internal rotation along torsional angle θ and their total rotation as a whole along the rotational angle $\tilde{\theta}$, which is taken between the angle separating two proton bonds.

For the scenarios employing Raman pumping schemes (see Fig. 1), the dynamics of the heavy oxygen nuclei forming an O—O bond may be considered in the zeroth approximation as classical and, therefore, coupling between rotation of the molecule as a whole and its internal rotation is negligible. Hence the only dynamic coordinates to be considered are the angles θ and $\tilde{\theta}$ that should be described as quantum-mechanical operators, whereas the two other angles determining the direction of the O—O bond can be treated in the zeroth approximation as classical values, which should be statistically distributed when an ensemble of molecules is considered. This approximation perfectly fits our purpose to demonstrate the feasibility of the laser preferential synthesis scenarios.

As a result, a simplest two-dimensional model Hamiltonian of the free molecule's dynamics takes the form

$$\hat{H} = \hat{H}_\theta + \hat{H}_{\tilde{\theta}}$$

$$\hat{H}_{\tilde{\theta}} = \frac{\mu_{zz}}{2}\hat{J}_{zz}^2, \quad \hat{J}_{zz} = -i\hbar\frac{\partial}{\partial\tilde{\theta}} \qquad (10)$$

$$\hat{H}_\theta = \frac{\mu_{\theta\theta}}{2}\hat{J}_{\theta\theta}^2 + V(\theta), \quad \hat{J}_{\theta\theta} = -i\hbar\frac{\partial}{\partial\theta}$$

where $\mu_{\theta\theta}$ and μ_{zz} are the components of the inverse tensor of inertia, corresponding to the internal rotation and rotation of the molecule as a whole along $\tilde{\theta}$ angle. They can be estimated as $\mu_{\theta\theta} \approx 4\mu_{zz} \approx 2/(m_H a_H^2)$ for H_2O_2 and $\mu_{\theta\theta} \sim 3/(2m_H a_H^2)$, $\mu_{zz} \sim 1/(3m_H a_H^2)$ for HOOD, where a_H is the length of
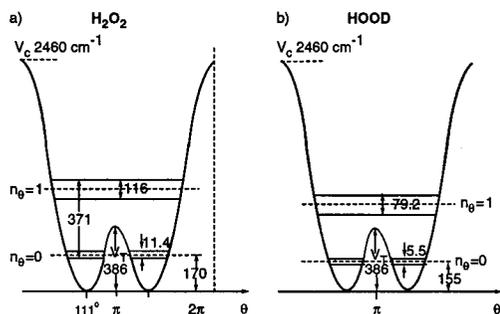
Figure 3. Ground-state double-well potentials for (a) H_2O_2 and (b) HOOD molecules.

the O—H bond. Parameters of the symmetric double-well potential are given in Fig. 3.

In accordance with Eq. (10), internal rotation of the molecule and its rotation as a whole are independent, so that eigenfunctions of the corresponding Hamiltonians are represented with the tensor products of their individual eigenfunctions, producing the separable states in the product space $\mathcal{H} = \mathcal{H}_{\text{tors}} \otimes \mathcal{H}_{\text{rot}}$ of the rotational $\mathcal{H}_{\text{rot}}$ and torsional $\mathcal{H}_{\text{tors}}$ spaces. The rotational eigenfunctions are represented with the twofold degenerate exponential or cosine–sine wavefunctions

$$|n_{\pm}\rangle = \frac{1}{\sqrt{2\pi}}e^{\pm in\tilde{\theta}}, \quad |n_{c,s}\rangle = \frac{1}{\sqrt{\pi}}\cos n\tilde{\theta}, \frac{1}{\sqrt{\pi}}\sin n\tilde{\theta} \quad (11)$$

Eigenfunctions of the torsional Hamiltonian $\hat{H}_{\theta}$ are the antisymmetric and symmetric couples, $\psi_A(\theta)$ and $\psi_S(\theta)$, if the torsional angle equal to zero is chosen at the torsional energy trans-barrier maximum $\theta = \pi$. It is worth noting that both the ψ_S and ψ_A energy levels possess an additional small splitting due to tunnelling through a sufficiently high but finite cis-barrier (Fig. 3). This cis-splitting is of the order of 10^{-4} cm^{-1}, which is small enough to be neglected. The eigenfunctions of the total free energy potential are combined as the tensor products of the form |chirality, rotation⟩ = |chirality⟩ ⊗ |rotation⟩, where the chirality basic states are denoted by indices A and S, which do not correspond to the L- and D-states, but to their antisymmetric and symmetric combinations, and the rotation basis states are denoted by integral indices n with the corresponding subscript c or s. Therefore, for the eigenstates we use the notation $|A, n_{c,s}\rangle$ or $|S, n_{c,s}\rangle$ with the parameters determining the chiral and rotation states, respectively.

Typical frequencies of the rotational motion for the H_2O_2 molecule are comparable to those for torsional dynamics, but they are much higher than the frequency of O—O bond rotation, which we skip in the discussion here. The O—O bond orientation angles then are treated here as non-dynamic classical variables revealing only at the averaging over the molecule's orientation angles. The characteristic frequencies of the coupled rotational–torsional dynamics are

still much smaller than those for the rest of the intramolecular degrees of freedom. This prevents the rotational–torsional excitation from rapid decay via the intramolecular energy redistribution mechanisms and preserves the coherence during the excitation of the molecule. Excitation schemes used for preferential laser synthesis from a racemic solution will be discussed in the following sections.

Quantum entanglement of the rotational–torsional states and photoinduced chirality

For an ensemble of spatially aligned H_2O_2 or HOOD molecules with defined orientation angles, one can easily create a coherent superposition of L- and D-states simply applying coherent Raman pumping to the corresponding $|S\rangle \rightarrow |A\rangle$ transition. By contrast, for an ensemble of randomly oriented molecules, the non-coplanarity criterion outlined earlier prevents this simple solution and one has to align the molecules first. Earlier we suggested a scheme with Raman pumping,[13,14] which employs rotational alignment of the molecules in a strong laser field due to the laser-induced rotation over the rotation angle $\tilde{\theta}$ with the frequency of one of the Raman components. However, using such a scheme requires, owing to the non-resonant character of interaction, intensities close to the ionization limit, which is difficult to realize in an experiment.

A preferential laser synthesis scenario from H_2O_2 or HOOD vapor proposed here employs a completely different idea of coherent control of the phases of rotational–torsional states phases via entanglement of the rotational and torsional subsystems in the process of pumping molecules by incident laser fields. In an attempt to elucidate this idea we should first discuss the properties of molecule's rotational–torsional dynamics under the resonant interaction, which involves only two torsional states $|S\rangle$, $|A\rangle$ and two rotational states $|0\rangle$, $|n\rangle$ (at this stage, we neglect for simplicity the rotational degeneration).

As a result of interaction dynamics, a molecule goes into the coherent state, which, in the general case, is an entangled (not separable in the form of the tensor product) rotational–torsional state:

$$|\psi_{\text{ent}}\rangle = c_1|\psi_1\rangle + c_2|\psi_2\rangle + c_3|\psi_3\rangle + c_4|\psi_4\rangle$$

$$|\psi_{1,2}\rangle = \frac{|L\rangle|+\rangle \pm |D\rangle|-\rangle}{\sqrt{2}}, \quad |\psi_{3,4}\rangle = \frac{|L\rangle|-\rangle \pm |D\rangle|+\rangle}{\sqrt{2}} \quad (12)$$

where $|+\rangle = \frac{|0\rangle + |n\rangle}{\sqrt{2}}$, $|-\rangle = \frac{|0\rangle - |n\rangle}{\sqrt{2}}$ and $|n\rangle$ is an eigenrotational state. The new rotational basis $|\pm\rangle$ is chosen here by analogy with the basis of symmetric and antisymmetric functions made of the chiral basis states $|L\rangle$ and $|D\rangle$.

If one considers two particles A and B as a material implementation of the rotational and torsional degrees of freedom, e.g. two polarization-entangled photons, the terminology of quantum information theory can be used by analogy. For example, states $|\psi_{1,2,3,4}\rangle$ are then the

well-known Bell states.[32] In particular, the state produced under biharmonic excitation of the transition $|S, 0\rangle \rightarrow |A, 2\rangle$ at some time instants coincides either with the $|\psi_1\rangle$ or the $|\psi_2\rangle$ state. This means that under coherent excitation the joint rotational–torsional symmetry is revealed in the form of quantum entanglement. Although this symmetry is preserved, it does not contradict unequal transition probabilities to the L- and D-states for a fixed rotational state, provided that it is restored in the form of the reverse asymmetry for the other corresponding rotational state.

Construction of a preferential laser synthesis scenario of required enantiomers from a racemic solution proposed here should include several steps: first, an excitation of the rotational–torsional dynamics, which should generate a properly entangled state; next, applying additional laser pulses to provide non-equal population of the rotational states $|+\rangle$ and $|-\rangle$, which initially have equal probabilities being incoherently and equally formed out of the basis states $|0\rangle$ and $|n\rangle$; then, applying a probe field to register the induced chirality. This probe field will scatter in accordance with its phase relations to the previous waves and, having some definite phase, scatter as in a chiral medium because the total rotational–chiral symmetry is revealed only at temporal oscillations, being broken at a single time instant.

The efficiency of an experimental scheme realizing the above- described abstract scheme is typically determined from the requirements of the specific registration scheme and system. We can, for example, consider registration of the polarization plane rotation, which reveals the chiral properties of the medium, as it becomes gyrotropic during the time of an experiment for the laser synthesis. Therefore, the choice of a specific working transition to be used in an experiment is directly determined by the aim of obtaining the maximum possible signal of the scattered polarization. The latter is determined by the gyration operator, which, in its turn, determines the optical activity in the medium.

To calculate the optical activity, we can use classical models adopted for quadrupole and magnetic dipole moments.[33,34] For the H_2O_2 and HOOD molecules the most appropriate model is the classical model of Kuhn,[35] treating the chiral molecule as a system of two coupled harmonic electronic oscillators moving at some distance from one another in orthogonal directions. In the case of H_2O_2 and HOOD they are evidently associated with the O—H and O—H or O—D bonds. The distance a_0 between the oscillators is equal to the length of the O—O bond. Then, the equations of the oscillators' motion can be written as

$$m_e \ddot{\xi} + \omega_0^2 \xi + K\eta = -ie(\vec{k} \cdot \vec{r}_1)(\vec{\mathcal{E}} \cdot \vec{n}_\xi)e^{-i\omega t}$$
$$m_e \ddot{\eta} + \omega_0^2 \eta + K\xi = -ie(\vec{k} \cdot \vec{r}_2)(\vec{\mathcal{E}} \cdot \vec{n}_\eta)e^{-i\omega t} \quad (13)$$

where m_e is the electron mass, ω_0 is the oscillator frequency, K is the coupling coefficient, $\vec{k}$ is the wavevector of the probe field, $\vec{n}_\xi$ and $\vec{n}_\eta$ are the unit vectors along the ξ and η

directions, $\vec{r}_1$ and $\vec{r}_2$ are the electrons' radius-vectors, $\vec{\mathcal{E}}$ is the field strength amplitude and ω is the probe field frequency.

The coupling coefficient K is responsible for the phase correlation of the electronic vibrations and, consequently, determines the unequal representation of the right- and left-handed configurations of the molecule, that is the responding electronic chirality. There exist several microscopic models to calculate K, depending on the specific type of a molecule. In the case of large molecules it has a non-zero value owing to the secondary re-emission (i.e. electron–electron interaction via the electromagnetic field) of the optically active electrons, which can be calculated using the Kirkwood model.[36] In the opposite case of small, simple molecules, the main mechanism is overlapping of the electron clouds. For H_2O_2 and HOOD molecules this latter mechanism is a prevailing one, but the overlapping is rather weak because the distance between the oscillators is relatively large, $a_0 \approx 1.5$ Å, and electron clouds are localized at the distance of a Bohr radius, $a_B \approx 0.5$ Å, which is much smaller than a_0. Hence, the gyration operator $\hat{d}$, which determines the polarization response

$$\hat{p}^Q = \frac{i}{2}[\hat{d} \times \vec{E}] \quad (14)$$

can be written as an expansion over the small parameter K/ω_0^2:

$$\hat{d} = \hat{d}^{(0)} + \hat{d}^{(1)}(K) + \cdots \quad (15)$$

where $\hat{d}^{(0)}$ depends only on the nuclei configuration chirality, whereas $\hat{d}^{(1)}(K)$ determines the chirality of the electronic component.

The gyrotropic polarization rotation effect is then determined by the quantum-mechanical average of the operator given in Eqn (15) with additional averaging over the O—O axis rotations. With the assumption that the exciting electromagnetic wave propagates along the z axis, it yields

$$\hat{d} = (0, 0, \hat{d}), \quad \hat{d}^{(0)} = \frac{2\pi}{\lambda} \frac{e^2 k a_0}{m_e} \frac{\cos^2 \vartheta}{(\omega_0^2 - \omega^2)} \cos 2\theta \sin \theta$$

$$\hat{d}^{(1)}(K) = \frac{2\pi}{\lambda} \frac{e^2 k a_0}{m_e} \frac{\cos^2 \vartheta}{(\omega_0^2 - \omega^2)} \frac{K}{(\omega_0^2 - \omega^2)} \sin \theta \quad (16)$$

where λ is the wavelength of the probe field. From Eqn (16), it follows that the gyration operator depends only on the dynamic rotational–torsional coordinates θ and $\bar{\theta}$. For the case of stable chirality when it is impossible to control any rotational angles, the term $\hat{d}^{(0)}$ would become zero after independent averaging over the rotational angle $\bar{\theta}$, so that the optical rotation is determined only with the second couple coefficient dependent term.

At this point it is worth stressing that the quantum entanglement described earlier leads to the fact that K-independent term $\hat{d}^{(0)}$ is not equal to zero after partial

averaging over the O—O bond rotation and goes to zero only after the last rotational averaging over $\tilde{\theta}$. This means that this term, although untypical for a general discussion of the gyrotropic properties, yields a new possibility of achieving optical rotation without breaking the total isotropic symmetry, when the correlations between the rotational and torsional states are present.

If the molecule reaches one of the Bell states $|\psi_i\rangle$, which are all maximally entangled states, then in accordance with Eqn (3) and (16) we obtain for the zeroth-order gyration $d^{(0)} \neq 0$, although for the degree of chirality we obtain zero, $\chi = 0$. This means that in H_2O_2- and HOOD-like molecules with coupled rotational–torsional dynamics, optical rotation may be present even in the absence of the average chirality. In other words, if the medium is racemic on average, it can undergo temporal dynamics, which shows temporal oscillations of optical rotation in the media. This situation seems paradoxical only at first sight, when one thinks of the chiral properties of the medium as something stable. However, the discussion above shows that there could be realized a so-called *conditional chirality* which is the property of the rotational states, whereas the definition of the degree of chirality has nothing to do with rotations.

For the case of H_2O_2 or HOOD molecules, the conditional chirality can be excited by the biharmonic pumping of the $|S, 0\rangle \rightarrow |A, 2_c\rangle$ transition. Our estimates show that for the vapor densities that can be used in an experiment the chirality determined by the K-dependent term yields a too weak signal-to-noise ratio to register. The question is therefore whether a much stronger effect due to the conditional chirality can be basically registered under the same conditions. The answer to this question can be given by an approximate evaluation of the average value of the dimensionless variance of the gyration and chirality operators

$$\hat{g} \propto \sin\theta\cos 2\tilde{\theta}, \quad \hat{\chi} \propto \sin\theta \tag{17}$$

These two operators, being dependent only on the rotational–torsional coordinates, commute with each other and therefore have the same eigenfunctions listed below:

$$|L\rangle|+\rangle, \quad |L\rangle|-\rangle, \quad |D\rangle|+\rangle, \quad |D\rangle|-\rangle,$$
$$|+\rangle = \frac{|0\rangle + |2_c\rangle}{\sqrt{2}} \quad |-\rangle = \frac{|0\rangle - |2_c\rangle}{\sqrt{2}} \tag{18}$$

Then, the operators of interest can be written in the form of spectral decomposition as

$$\hat{\chi} = (|L\rangle\langle L| - |D\rangle\langle L|) \otimes (|+\rangle\langle +|+|-\rangle\langle -|)$$
$$\hat{g} = (|L\rangle\langle L|-|D\rangle\langle L|) \otimes (|+\rangle\langle +|-|-\rangle\langle -|) \tag{19}$$

Their averaging gives the corresponding average values in terms of the joint probabilities $p(L, \pm)$ and $p(D, \pm)$ of finding

a molecule in the rotational state $|+\rangle$ or $|-\rangle$ and the chiral state $|L\rangle$ or $|D\rangle$:

$$\chi = \frac{1}{2}[p(L, +) - p(D, +)] + \frac{1}{2}[p(L, -) - p(D, -)]$$
$$g = \frac{1}{2}[p(L, +) - p(D, +)] - \frac{1}{2}[p(L, -) - p(D, -)] \tag{20}$$

For the quantum state determined with Eqn (12), Eqn (19), after averaging the projectors, yields the average values given in Eqn (20) in the form of

$$\chi = 2\Re e(c_1 c_2^* - c_3 c_4^*), \quad g = |c_1|^2 + |c_2|^2 - |c_3|^2 - |c_4|^2 \tag{21}$$

Preliminary analysis shows that an effective preferential laser synthesis scenario from an initially racemic vapor of H_2O_2 or HOOD molecules should use two pairs of Raman pumping fields, one of which excites the coupled transition $|S, 0\rangle \rightarrow |A, 2_c\rangle$ with the frequency $\omega_{20} + \omega_{AS}$ and the other excites the rotational $|0\rangle \rightarrow |2\rangle$ transition. Then, a probe field—one of the components of the biharmonic pumps—is scattered in the excited medium with a photoinduced gyration wave producing, as we will show in the next section, an NOA-CARS signal.

Scenario of preferential laser synthesis from a racemic solution

As was pointed out in the previous section, an effective scenario of preferential laser synthesis from a racemic solution should employ the Raman pumping scheme. We propose here to use resonant Raman pulses with a pulse duration much longer than the transition time between L- and D-states in order to benefit from the advantages of the resonant interaction. The phase of the induced rotational–torsional oscillation then depends on the difference in the phases of the pumping Raman pulses, i.e. the phases of pumping fields determine the controllable chiral state oscillation at each time instant. If we cannot control the phases of the laser pulses, the chiral state will be affected randomly. For an experimental demonstration of the effect, controlling phases of the Raman pulses is not so crucial because all the induced oscillations phases of different molecules are the same for all the molecules in a physically small volume of the medium. Keeping this notion in mind, we skip further detailed discussion of the impact of the random character of the laser phases on the induced chirality.

The excitation scheme discussed above is shown in Fig. 4. All further estimates will be made under the assumption that we are working with the vapor of H_2O_2 molecules at room temperature and normal pressure.

The excitation scheme employs three laser pulses with frequencies ω_1, ω_2 and ω_3 applied to the rotational–torsional subsystem, which satisfy the resonance conditions $\omega_{12} \sim \omega_{20} + \omega_{AS}$ and $\omega_{13} \sim \omega_{20}$.

The pulse duration for the pulsed biharmonic excitation with frequencies ω_1, ω_2 is determined by two key factors.
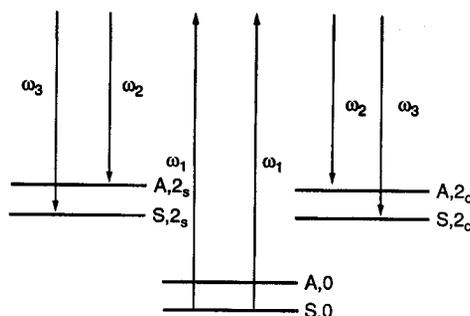
Figure 4. Excitation scheme for a non-racemic mixture of H_2O_2 or HOOD molecules (vapor) with the use of three picosecond laser pulses.

First, in order to employ methods of coherent control, the pulse duration should be less than the dephasing time Γ^{-1} of the working transition, which for a gas at normal temperature and atmospheric pressure is of the order of $\tau_p \ll \Gamma^{-1} \sim 10$ ns. Second, the pulse duration has a lower limit determined by the pulse spectral width, which should be less than the tunnelling frequency, $\delta \sim 10^{12}$ s^{-1}, to obtain a resonantly enhanced signal. Therefore, the pulse duration should obey the inequalities $\delta^{-1} \ll \tau_p \ll \Gamma^{-1}$ and its optimal value lies in the picosecond range, $\tau_p \sim 10^{-11}$ s. The lower the pressure, the longer is the pulse duration that may be chosen owing to the reduction in the collisional dephasing rate Γ.

The information on the chiral properties of the medium (solution, vapor) is encoded in the rotational–torsional dynamics, which is described in terms of the excited states $|S, 0\rangle$, $|A, 0\rangle$, $|S, 2_c\rangle$, $|A, 2_c\rangle$, $|S, 2_s\rangle$, $|A, 2_s\rangle$, where the degeneration of the excited rotational states is included. The complete dynamic analysis of the simplest system includes six states, but for a qualitative analysis the degeneration does not affect the chiral properties essentially, so that we can reduce the system to the four levels $|S, 0\rangle$, $|A, 0\rangle$, $|S, 2_c\rangle$, and $|A, 2_c\rangle$. These basis states, as was revealed in analysis of their linear combinations in the form of Eqn (19), are responsible for the gyrotropic properties of the media.

In terms of the rotational–torsional states [Eqn (11)], the interaction Hamiltonian in the rotating wave approximation (RWA) takes the form

$$\hat{H}_I = \hbar\Omega_r \hat{\sigma}_1^{(chir)} \otimes \hat{\sigma}_4^{(rot)} + \hbar\Omega_e(-\hat{\sigma}_3^{(chir)} \otimes \hat{\sigma}_3^{(rot)} + \hat{\sigma}_4^{(chir)} \otimes \hat{\sigma}_4^{(rot)}) \tag{22}$$

where

$$\hat{\sigma}_1^{(chir)} = \frac{1}{\sqrt{2}}(|L\rangle\langle L| + |D\rangle\langle D|), \quad \hat{\sigma}_1^{(rot)} = \frac{1}{\sqrt{2}}(|+\rangle\langle+| + |-\rangle\langle-|)$$

$$\hat{\sigma}_3^{(chir)} = \frac{i}{\sqrt{2}}(|L\rangle\langle D| - |D\rangle\langle L|), \quad \hat{\sigma}_3^{(rot)} = \frac{i}{\sqrt{2}}(|+\rangle\langle-| - |-\rangle\langle+|)$$

$$\hat{\sigma}_4^{(chir)} = \frac{1}{\sqrt{2}}(|L\rangle\langle L| - |D\rangle\langle D|), \quad \hat{\sigma}_4^{(rot)} = \frac{1}{\sqrt{2}}(|+\rangle\langle+| - |-\rangle\langle-|) \tag{23}$$

Ω_e and Ω_r are the Rabi frequencies for the biharmonic pumping of the rotational–torsional transition $|S, 0\rangle \rightarrow |A, 2_c\rangle$ by the fields with the frequencies ω_1, ω_2 and, simultaneously, biharmonic pumping of the rotational $|0\rangle \rightarrow |2\rangle$ transition by the fields with the frequencies ω_1, ω_3. Neglecting for simplicity the relaxation processes, the degree of chirality and gyration on the basis of Eqns (6), (19), and (22) take the form

$$\chi = 2\langle \text{Tr}\hat{U}_0^{-1}\hat{\sigma}_4^{(chir)} \otimes \hat{\sigma}_1^{(rot)}\hat{U}_0 S_I(\mathbf{E})\hat{\rho}_0 \rangle_{\hat{O}}$$
$$g = 2\langle \text{Tr}\hat{U}_0^{-1}\hat{\sigma}_4^{(chir)} \otimes \hat{\sigma}_4^{(rot)}\hat{U}_0 S_I(\mathbf{E})\hat{\rho}_0 \rangle_{\hat{O}} \tag{24}$$

where the transition superoperator for the rectangular shape pulses, expressed with the help of the time evolution operator, corresponding to the action of the multi-component field, is simply a unitary operator:

$$S_I(\mathbf{E}) = \hat{U}_I(\mathbf{E}) \odot \hat{U}_I^{-1}(\mathbf{E}), \quad \hat{U}_I(\mathbf{E}) = \exp\left(-\frac{i}{\hbar}\hat{H}_I t\right) \tag{25}$$

At room temperature and normal pressure, the equilibrium state corresponds to the density matrix of the form $\hat{\rho}_0 \sim (1/2)[\hat{\sigma}_1^{(chir)} \otimes \hat{\sigma}_1^{(rot)} + \hat{\sigma}_1^{(chir)} \otimes \hat{\sigma}_2^{(rot)}]$.

In the frame of the model of photoinduced rotational–torsional dynamics presented here, one can calculate the expressions as given in Eqn (24) with the help of computer algebra, which results in the following equations:

$$\chi = A_\chi(\tau_p)\sin\omega_{AS}t, \quad A_\chi(\tau_p) = \frac{2\Omega_e\Omega_r}{\Omega_e^2 + \Omega_r^2}\sin\Omega_e\tau_p\sin^2\frac{\Omega}{2}\tau_p$$

$$g = A_g^{(1)}(\tau_p)\sin(\omega_{20} + \omega_{AS})t + A_g^{(2)}(\tau_p)\sin(\omega_{20} - \omega_{AS})t \tag{26}$$

where $\Omega = \sqrt{\Omega_e^2 + \Omega_r^2}$ and $A_g^{(1,2)}$ are represented by equations similar to those for A_χ.

So far, we have been discussing the dynamics of hydrogen peroxide molecules. The photoinduced dynamics of HOOD molecules essentially differ from those of H_2O_2 molecules because all the transitions in the HOOD molecule are Raman-active, in contrast to H_2O_2, where these transitions are forbidden and allowed only in the quadrupole approximation. Also, the laser pulses intensities for the pulse duration of $\tau_p \sim 10^{-11}$ s should fit the condition $\Omega\tau_p \sim 1$, where Ω corresponds to the saturation regime, and for H_2O_2 approach the ionization threshold values, whereas they are much lower than the threshold intensity for the HOOD molecules.

Equations (26) correspond to the fixed orientation angles of the O—O bond and should be averaged over the corresponding orientation angles φ and ϑ, included in the Rabi frequencies as parameters. Analyzing these equations, one can show that for non-saturating intensities, $\Omega\tau_p \ll 1$, and the coplanar multi-component laser field configuration, the total effect of the photoinduced non-racemicity in the solution does not vanish. Moreover, the order of magnitude of the degree of chirality and the gyration remains at the same level as for the precisely spatially aligned O—O bonds of the molecules.

REGISTRATION OF PHOTOINDUCED CHIRALITY BY MEANS OF NOA-CARS

In accordance with Eqn (26), a photoinduced gyration wave is generated in the medium, which oscillates in time and space at a combined frequency $\omega_{20} + \omega_{AS} \sim \omega_{12}$. Scattering of one of the biharmonic pulsed fields at this photoinduced gyration wave gives rise to the NOA-CARS signal. In this section, we will discuss the registration scheme in detail and will assume for simplicity that an ensemble (vapor) of chiral molecules is excited by only two pumping fields (Fig. 4), which is enough to perform the preferential laser synthesis from a racemic solution at the low temperature limit $kT \ll \hbar\omega_{AS}$.

The photoinduced gyration wave in the medium is described by the gyration vector $\vec{d}^{(0)}$, which oscillates at the Raman frequency of the pumping field. Scattering of the probe field—one of the fields of the Raman pumping—gives a rise to the quadrupole polarization $P^{(3)Q}$, which oscillates at the anti-Stokes (Stokes) frequency. This polarization response, in turn, induces the NOA-CARS signal in which information on the chiral properties of the medium is encoded.[37] Feasibility studies of the NOA-CARS measurements for the problem of distinguishing non-racemity in the medium of chiral molecules have been reported[37] for a pure medium of organic molecules. The non-local response at the anti-Stokes frequency given by the quadrupole polarization $P^{(3)Q}$ and registered experimentally was assigned to the presence in the medium of the soluted mirror-asymmetric bioorganic molecules.

In our case, the gyration vector of the photoinduced gyration wave in the medium oscillates at a frequency $\omega_1 - \omega_2$ and one can readily obtain with the help of Eqns (15) and (16) a general expression for the quadrupole polarization at the anti-Stokes frequency due to the photoinduced gyration wave:

$$\vec{P}^{(3)Q}(\omega_a) = \frac{i}{2}N[\vec{d}(\omega_1 - \omega_2) \times \vec{E}(\omega_1)], \quad \omega_a = 2\omega_1 - \omega_2 \quad (27)$$

where N is the concentration of the vapor and $\vec{E}(\omega) = \vec{e}_{\omega_1}\mathcal{E}_{\omega_1}e^{i\omega_1 t}$. With the help of Eqn (27), one can calculate the scattered signal.

In the slowly varying amplitude approximation, Eqn (27) transforms into the wave equation for the amplitude $\mathcal{E}_a$ of the NOA-CARS signal, which for a collinearly propagating Raman pumping pulses takes the form

$$2ik_a \frac{\partial \mathcal{E}_a(\xi, z)}{\partial z} e^{i(\omega_a t - k_a z)} = \frac{4\pi}{c^2} \frac{\partial^2}{\partial t^2} P^{(3)Q}(\omega_a) \quad (28)$$

where k_a is the wavevector of the NOA-CARS field, $\xi = t - \frac{z}{c}$ is the running coordinate and c is the speed of light in the vapor.

For the collinear pumping scheme the phase-matching condition $\vec{k}_a \sim 2\vec{k}_1 - \vec{k}_2$ is obeyed with good accuracy and we

can readily obtain, with the help of Eqns (28), (26) and (27), an expression for the NOA-CARS signal amplitude $\mathcal{E}_a$ with polarization vector $\vec{e}_a = [\vec{k} \times \vec{e}_{\omega_1}]/k$ at the end of the medium:

$$\mathcal{E}_a = \frac{\omega_a^2}{2k_a c^2} \frac{\omega_p^2}{(\omega_0^2 - \omega^2)} ka_0 \langle \cos^2 \vartheta A_g(\tau_p) \rangle_{\varphi, \vartheta} \mathcal{E}_{\omega_1} L \quad (29)$$

where $\omega_p = \sqrt{4\pi Ne^2/m_e}$ is the plasma frequency, k is the wavevector of the probe pulse and L is the length of the active medium.

As follows from Eqn (29), the intensity $I_a = c|\mathcal{E}_a|^2/8\pi$ of the NOA-CARS signal depends not only on the intensities of the biharmonic pumping, but also on their polarization properties. The latter determines the gyration value g after its averaging over the isotropically oriented O—O bond. For example, for the counter-propagating circular polarizations of the pump pulses we have $g = 0$ and $I_a = 0$.

The choice of polarization schemes of the laser pump fields in an experiment is extremely important. One should keep in mind that in addition to the useful signal there exists a prevailing strong coherent background from the medium due to the anti-Stokes scattering on the vibration–rotational oscillations of the molecule. To cope with this coherent background, a discrimination of the useful signal is to be made with the use of one of the following configurations of the biharmonic pump field:[37]

(a) Polarization vectors of the pump fields are co-propagating; the polarization of the registered anti-Stokes signal is orthogonal to the polarization plane of the pump fields.

(b) Polarization vectors of the pump fields are orthogonal to each other; the polarization plane of the registered anti-Stokes signal is orthogonal to the polarization plane of the probe field.

(c) Pump fields are circularly polarized and counter-propagating, which leads to the complete suppression of the non-linear dipole polarization at the anti-Stokes frequency due to the photon's moment conservation.[38]

Brief analysis of these three choices shows that (a) is preferable from the experimental point of view; for (b) the useful NOA-CARS signal has a strong background from the pump field and for (c) we cannot control the molecular chirality. The corresponding experimental scheme is shown in Fig. 5. The polarization plane of the NOA-CARS signal when Raman pump pulses have collinear polarization vectors is in accordance with Eqn (27) orthogonal to the polarization plane of the probe pulse.

QUALITATIVE RESULTS AND NUMERICAL ESTIMATES

Calculation of the intensity I_a of the NOA-CARS signal was made with approximation of constant pump fields, i.e. $I_a \ll I_p$. We do not consider here the more general case of $I_p \sim I_a$ as it can hardly be used for preferential laser synthesis
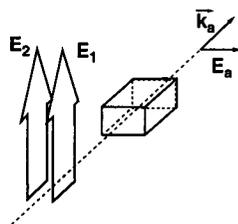
Figure 5. Excitation and detection of the conditional non-racemic state in H_2O_2 and HOOD vapors using NOA-CARS with suppression of the coherent background in the direction along the registered NOA-CARS signal polarization.

[such pump intensities lead to the number of non-linear processes via the non-resonant susceptibility tensor $\chi_{ijkl}^{(3)NR}$].

For the polarization scheme shown in Fig. 5, with the use of the maximum concentration of the vapor of chiral molecules, $N \sim 10^{19}$ cm^{-3}, and the cell length $L \sim 10$ cm, we obtain finally with the help of Eqn (29) the following numerical estimates. For the vapor of H_2O_2 molecules the gyration value reaches $g \sim 10^{-3}$ for the maximum allowed pump intensities $I_1, I_2 \sim 10^{11}$ W cm^{-2} for the pulse duration $\tau_p \sim 10^{-11}$ s. The corresponding NOA-CARS signal intensity is $I_a \sim 10^2$ W cm^{-2}. For the vapor of HOOD molecules, the figures are much better: $g \sim 0.25$ for the same pump intensities and the NOA-CARS signal intensity reaches the value of $\sim 10^8$ W cm^{-2}. Such a striking difference in numerical estimates for the H_2O_2 and HOOD molecules is due to the difference in the symmetrical properties of these molecules—in contrast to H_2O_2, the HOOD molecule is of C_2-asymmetric type.

For the vapor of HOOD molecules, in the case of saturating intensities giving a high gyration value $g \sim 0.25$, the quadrupole polarization $P^{(3)Q}(\omega_a)$ is of the same order of magnitude as the polarization $P^{(3)D}(\omega_a)$ of the coherent background, for which the corresponding non-linear susceptibility is $\chi^{(3)D} \sim 10^{-15}$ CGSE. This means that the NOA-CARS signal essentially prevails over the unavoidable noise effects, e.g. due to the photoinduced anisotropy at high intensities.

CONCLUSIONS

We have elucidated two key qualitative feasibility criteria for the preferential laser synthesis of enantiomers from a racemic solution. First, the configuration of the polarizations of the incident laser fields must have a helical structure, otherwise a preliminary spatial alignment of chiral molecules in a racemic solution is required. Second, suggested scenarios will be effective only for chiral molecules for which the dynamics along the reaction coordinate (internal rotation) are weakly coupled with the dynamics along other degrees of freedom.

A new mechanism for controlling chiral states in simple chiral molecules with internal rotation, which employs the coherent quantum entanglement of the rotational–torsional states of the molecules, has been proposed. It requires no preliminary spatial alignment of the molecules in a solution. Such a mechanism can also be applied to chiral molecules whose electronic structure shows no helical properties.

A novel scenario for the preferential laser synthesis of enantiomers from a racemic solution of simple chiral molecules employing the mechanism of inducing chirality via quantum entanglement was proposed and analyzed in detail. An experimental scheme realizing this scenario was discussed.

It is shown that NOA-CARS would be a suitable spectroscopic technique for both inducing the gyration wave in the medium (vapor) of chiral molecules and detecting this photoinduced gyration wave in the medium simply by registering the NOA-CARS signal. With the appropriate choice of polarizations of the pump laser fields, the NOA-CARS signal can be several orders of magnitude higher than coherent noise (background). Properties of two candidates for an experiment—H_2O_2 and HOOD molecules—have been analyzed in detail and preference was made in favor of HOOD molecules because of their symmetry advantages.

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