

## Photoinduced chirality of hydrogen peroxide molecules

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The feasibility of using nonlinear optical techniques to control the chiral states of molecules is examined with the hydrogen peroxide molecule as an example. Raman excitation of optical activity owing to a transition among states with different chiral symmetries is proposed, along with an experimental scheme for detecting the corresponding photoinduced optical rotation in hydrogen peroxide vapor. © 1999 American Institute of Physics.  
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### 1. INTRODUCTION

One of the most intriguing mysteries of nature is the chiral purity of the biological world. For example, with enviable consistency, nature chooses levorotatory helical DNA molecules and dextrorotatory sugar molecules, although the levo- and dextro-configurations are energetically equivalent.<sup>1</sup> Research on the chiral purity of the biological world and, as a whole, on the nature of the chiral symmetry of molecules, the construction of chiral properties and their experimental study, and attempts at controlling chirality are currently among the most pressing areas of modern physics.<sup>2–4</sup> In particular, the physical consequences of the existence of a universal mechanism for breaking of chiral symmetry<sup>5,6</sup> owing to the failure of reflection symmetry as the result of a weak interaction through neutral currents<sup>7,8</sup> are the subject of ongoing discussion. Besides the spontaneous breakdown of chiral symmetry, there is practical interest in research on the feasibility of deliberately controlling changes in the chiral symmetry, induced, for example, by light. If this is possible, then in optics we have at our disposal a powerful arsenal of experimental methods, both for exciting and for probing molecular systems,<sup>9</sup> which may be used in setting up an experiment on photoinduced chirality.

In this paper we study the feasibility of exciting chirally asymmetric states of the hydrogen peroxide molecule ( $\text{H}_2\text{O}_2$ ) by means of a laser pulse with specially selected parameters. The hydrogen peroxide molecule (Fig. 1a) is the simplest chiral molecule whose geometry is not invariant under the spatial inversion  $(x, y, z) \rightarrow (x, y, -z)$ . After this transformation, the initial position of the atoms of the molecule cannot be recovered by a rotational transition, since the torsional angles  $\pm \theta_{1,2}$  are inequivalent. The choice of direction of the vector  $\mathbf{n}_0$  from one oxygen atom of the molecule to the other makes it possible to assign a definite sign to the torsion angle  $\angle \text{HOOH}$  after choosing between the right- and left-handed coordinate systems. According to theoretical calculations and experiment,<sup>10–13</sup> the equilibrium torsion angle in the gaseous phase is  $\theta \approx \pm 120^\circ$ , where a positive sign corresponds to the so-called *d*-state (“dextro” or right-

handed) indicated in Fig. 1a and a negative sign, to the so-called *l*-state (“levo” or left-handed).

Let us examine qualitatively what happens when a chiral  $\text{H}_2\text{O}_2$  molecule interacts with an electromagnetic field. The existence of reflection symmetry between the minima of the torsional potential means that the eigenstates of the torsional Hamiltonian are split as a result of tunneling through the lower barrier and are described by even and odd wave functions  $\psi_S$ ,  $\psi_A$  (tunneling through the upper barrier and the additional splitting owing to it are negligible<sup>13</sup>). The relatively large splitting  $\Delta E_0 = 11.4 \text{ cm}^{-1}$  corresponds to a lack of stationary chirally asymmetric states, which, prior to the establishment of equilibrium, oscillate at the tunneling frequency relative to the stationary states  $\psi_S$  and  $\psi_A$ . Thus, in the  $\text{H}_2\text{O}_2$  molecule, in principle it is possible only to obtain an oscillatory optical rotation effect, as opposed to heavy molecules, for which the period of these oscillations can correspond to arbitrarily long times and the initial chirally asymmetric state is stable.

The Hamiltonians for the interaction of the molecule with an electromagnetic field

$$\hat{H}_I = - \sum \mathbf{d}_k \mathbf{E}(\mathbf{r}_k)$$

in the dipole ( $H_D$ ) and quadrupole ( $H_Q$ ) approximations have a qualitative difference owing to the fact that in the dipole approximation [for  $\mathbf{E}(\mathbf{r}_k) \rightarrow \mathbf{E}(\mathbf{r}_0)$ ] the contributions of the protons add, while in the quadrupole approximation [ $\mathbf{E}(\mathbf{r}_k) \rightarrow (\mathbf{r}_k - \mathbf{r}_0) \nabla \mathbf{E}(\mathbf{r}_0)$ ] they subtract, so that  $H_D$  is an even function, while  $H_Q$  is odd. For the corresponding off-diagonal matrix elements  $H_D^{12}$  and  $H_Q^{12}$  of the  $S \rightarrow A$  transition for the dipole and quadrupole Hamiltonians, we obtain

$$H_D^{12} = 0, \quad H_Q^{12} \neq 0. \quad (1)$$

This implies that the quadrupole interaction excites precession between states of a chiral molecule that are split owing to the  $d \leftrightarrow l$  tunneling transition between the right- and left-handed chiral configurations, while the dipole interaction only produces a modulation in the energy of the eigenstates, which therefore oscillates at the frequency of the exciting field. The existence of the quadrupole contribution offers the

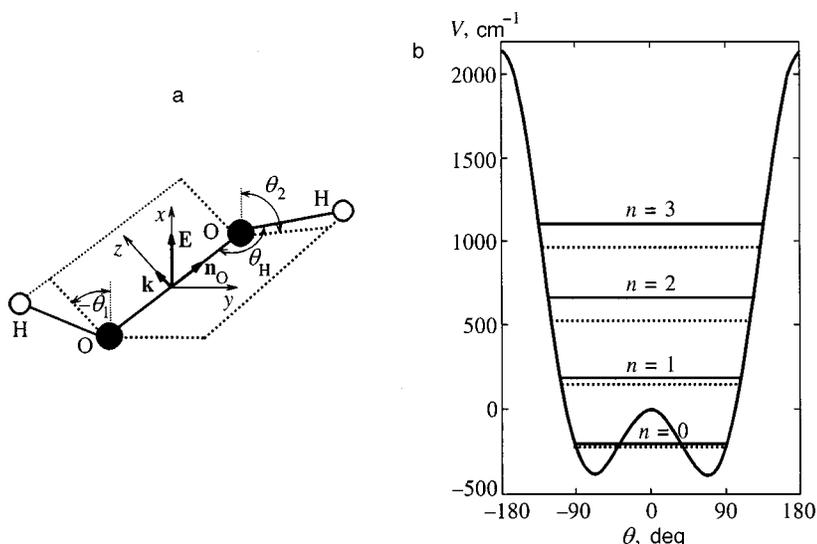


FIG. 1. (a) Geometry of an  $\text{H}_2\text{O}_2$  molecule in the  $d$ -configuration. The wave vector  $\mathbf{k}$  of the laser field  $\mathbf{E}$  is directed along the  $z$  axis,  $\mathbf{n}_O$  is a vector in the direction of the O–O bond,  $\theta_{1,2}$  are the torsion angles relative to the  $x\mathbf{n}_O$  plane, the equilibrium valence angles are  $\theta_H \approx 100^\circ$ , and  $a_O \approx 1.461 \text{ \AA}$  and  $a_H = 0.964 \text{ \AA}$  are the lengths of the O–O and O–H bonds, respectively. (b) Model function for the torsional potential  $V$  as a function of the torsion angle  $\theta$  and the position of the lowest energy levels for the symmetric (dots) and antisymmetric (continuous line) states.

opportunity, in principle, to selectively excite the  $d$ - or  $l$ -enantiomers using a fundamental quantum optical effect—the coherent precession of a two-level system driven by a coherent electromagnetic field pulse.

In this paper we discuss the conditions under which this photoinduced chirality effect (optical activity) can be detected experimentally. The excitation mechanism is first discussed using a single-photon model, and then a more realistic scheme of two-photon excitation using two lasers with orthogonal polarizations is proposed. As the following analysis shows, if a molecule is initially oriented along the  $z$  axis, then in principle a laser pulse of some duration can be used to bring it from an initial  $S$ - or  $A$ -state uniformly distributed across the  $d$ - and  $l$ -configurations, and which has no optical activity, into a state with a definite configuration and a sign corresponding to rotation of the plane of polarization of the incident field. This photoinduced chirality effect can be observed experimentally in its purest form in hydrogen peroxide vapor, since the interpretation of data for the liquid phase is made more complicated by the strong intermolecular interaction.

Let us estimate the order of magnitude of the effect in a single-photon excitation scheme. The condition for complete orientation of the dipole moment of the molecules along the  $z$  axis under the influence of a field of strength  $E$  is  $Eea_H \gg kT$ , which corresponds to  $E \gg 10^6 \text{ V/cm}$  at room temperature. If we do not require 100% orientation of the molecules, then much lower fields can be used to obtain a substantially lower degree of orientation,  $\kappa = Eea_H/kT$ , which can nevertheless be used to establish experimentally the presence of one or the other chiral configuration of the molecules by measuring the optical activity of the medium. In the frequency range of the electronic susceptibility, it can be estimated to lowest order by assuming that  $\kappa$  describes the fraction of the molecules strictly oriented in a given direction, while the remainder of the molecules is not oriented along the field. Then, for an upper bound estimate, on multiplying this small factor  $\kappa$  by the characteristic magnitude of the specific rotation  $[\alpha] \sim 10^2 \text{ deg}\cdot\text{cm}^3/\text{g}\cdot\text{dm}$  for materials with the most distinct optical activity, we obtain  $\sim 10^{-1}$

$\text{deg}\cdot\text{cm}^3/\text{g}\cdot\text{dm}$  for resonant excitation of optical activity at  $E \approx 10^3 \text{ V/cm}$ . A 1-mm thick layer of the vapor at standard temperature and pressure yields a rotation angle of the order of  $10^{-1}$  sec. This value is at the limit of sensitivity for linear polarization spectroscopic techniques. Thus, even neglecting the other complicating factors in a single-photon excitation scheme with initial orientation of the molecules by a constant electric field, observing the laser induced optical rotation will be difficult.

Another important point is the finite lifetime  $\tau_r$  of the chiral state owing to intermolecular collisions. It should at least be longer than the time the field propagates in the active region,  $\tau_c = L/c \geq 10^{-10} \text{ s}^{-1}$ , and a lower bound estimate is  $\tau_r = (\mathcal{N}v\sigma)^{-1}$ , where  $\mathcal{N}$  is the concentration of the molecules,  $v$  is the thermal speed, and  $\sigma$  is the collision cross section. For atmospheric pressure and room temperature we obtain  $\tau_r \sim 10^{-9} \text{ s}^{-1} > \tau_c$ .

The biharmonic excitation scheme using two laser pulses proposed here satisfies this restriction, and furthermore can be used to efficiently induce a given chiral state in the excited molecules.

## 2. THEORETICAL MODEL FOR PHOTOINDUCED CHIRALITY OF $\text{H}_2\text{O}_2$ MOLECULES

### 2.1. Reduced model for the dynamics of a free molecule

For an approximate description of the dynamics of molecules in a laser radiation field, it is appropriate to simplify the complete Hamiltonian by taking advantage of the small ratio of the masses of the protons and oxygen atoms. Then the dynamics of the protons can be treated in the adiabatic approximation with respect to the coordinates of the oxygen atom, and the dynamics of the latter reduces, in the simplest case, to averaging over the direction of the unit vector  $\mathbf{n}_O = (\sin \vartheta \cos \varphi, \sin \vartheta \sin \varphi, \cos \vartheta)$ , which specifies the orientation of the O–O-bond. Here the average over the  $z$ -direction (Fig. 1a) can be taken considering only the rotational dynamics of the protons relative to the O–O bond, given that the potential of the proton bond depends only on the torsion angle  $\theta = \theta_2 - \theta_1$ .

Given these considerations, the characteristic Hamiltonian in the reduced model, which accounts for the rotation of a molecule relative to the O–O bond as a whole and the torsional vibrations, has the form

$$\hat{H} = \hat{H}_H + \hat{H}_\theta, \quad (2)$$

where

$$\hat{H}_H = -\frac{\hbar^2}{4m_H r_H^2} \frac{\partial^2}{\partial \tilde{\theta}^2}, \quad (3)$$

$$\hat{H}_\theta = -\frac{\hbar^2}{m_H r_H^2} \frac{\partial^2}{\partial \theta^2} + V(\theta), \quad (4)$$

where  $\tilde{\theta} = (\theta_1 + \theta_2)/2$ ,  $m_H$  is the proton mass, and  $V(\theta)$  is the torsional potential. The vibrations of the valence angles  $\angle\text{HOO}$  are neglected here for simplicity.

Besides the uncertainty in the direction of  $\mathbf{n}_O$  mentioned above, the initial state of the molecule with respect to the average angle  $\tilde{\theta}$  includes an uncertainty associated with the rotation of the molecule relative to that direction, which corresponds to the third rotational degree of freedom of the molecule and supplements the two angles that specify the direction of  $\mathbf{n}_O$ . Here the corresponding frequencies of the transitions between the levels for free rotation about the O–O axis are

$$\omega_{n \rightarrow n+1} = 7.84 \cdot (n + 1/2) \text{ cm}^{-1},$$

and are a factor of four less than the corresponding frequencies of free internal rotation in view of Eqs. (3) and (4), which largely determines the form of the torsional potential  $U(\theta)$ .

## 2.2. Photoexcitation of rotational degrees of freedom of the molecule

In a field

$$\mathbf{E}(t) = \mathbf{E}_1 u_1(t) \cos(\omega_1 t + \varphi_1)$$

with envelope  $u_1(t)$  and frequency  $\omega_1 \gg \omega_{n \rightarrow n+1}$ , the quantum features of the resulting excitation are unimportant and the response is described by the classical equation

$$J \frac{d^2 \tilde{\theta}}{dt^2} = \frac{\partial}{\partial \tilde{\theta}} \mathbf{E}(t) \mathbf{d},$$

where  $J$  is the moment of inertia of the molecule. To zeroth order in the deviation, in the expression for the force on the right-hand side of the equation and for pulses that are not too short, with durations  $\tau_1 \gg 1/\omega_1$ , the response in the form of the change in the angle  $\tilde{\theta}$  at frequency  $\omega_1$  is given by

$$\Delta \tilde{\theta} \approx -\frac{\partial}{\partial \tilde{\theta}} \frac{\mathbf{E}_1(t) \mathbf{d}}{J \omega_1^2}. \quad (5)$$

This change leads to a modulation at frequency  $\omega_1$  in the quadrupole Hamiltonian acting on the internal rotation, and therefore to partial orientation of the molecule, which shows up as a loss of symmetry in the quadrupole Hamiltonian. In particular, when the O–O axis of a molecule is oriented

along the  $z$  axis, i.e.,  $\vartheta = 0$ , and the field  $\mathbf{E}_1$  is oriented along the  $y$  axis, the rotational symmetry reduces to a uniform distribution over the angle  $\tilde{\theta}$ ; the quadrupole moment has a dependence of the form  $\sin \tilde{\theta}$ . Here the orientation shows up in Eq. (5), which takes the form

$$\Delta \tilde{\theta} \approx \frac{E_1 d}{2J \omega_1^2} u_1(t) \cos \tilde{\theta} \cos \frac{\theta}{2} \cos(\omega_1 t + \varphi_1), \quad (6)$$

with  $\cos \tilde{\theta}$  having the same angular dependence as the derivative of the quadrupole Hamiltonian for the field  $\mathbf{E}_2 \parallel x$ , so that

$$\Delta \hat{H}_Q = (\partial \hat{H}_Q / \partial \tilde{\theta}) \Delta \tilde{\theta} \propto \cos^2 \tilde{\theta}.$$

An order of magnitude estimate in the visible range is

$$\Delta \tilde{\theta} \sim 10^{-10} \sqrt{I_1}, \quad (7)$$

where  $I_1$  is the intensity of the field  $\mathbf{E}_1$  in  $\text{W}/\text{cm}^2$  and the angle is in radians. This estimate reaches order unity only in fields stronger than the intra-atomic fields.

The dynamics of the torsional vibrations corresponding to the Hamiltonian  $\hat{H}_\theta$  are largely quantum mechanical owing to the relatively small mass of the proton compared to the heavier atoms. This shows up in the tunneling between the  $d$ - and  $l$ -states of the local potential minima (Fig. 1b), which leads to the formation of superposition eigenstates  $\psi_S$  and  $\psi_A$  that are split in energy and have equally represented  $d$ - and  $l$ -configurations, as well as to a nonrigidity of the molecular configuration owing to the quantum mechanical indeterminacy of the wave functions with respect to the torsion angle.

The form of the torsional potential of the  $\text{H}_2\text{O}_2$  molecule and the eigenenergies of the torsional potential have been studied both by *ab initio* computational techniques and by analyzing experimental spectroscopic data. Figure 1b shows the potential function and structure of the eigenlevels.<sup>14</sup> An estimate of the uncertainty in the local states with respect to the torsion angle using the formula for position fluctuations in the ground state of a harmonic oscillator yields

$$\sigma_\theta \approx [\hbar / (m_H r_H^2 \omega_0)]^{1/2} \approx 20^\circ.$$

The Hamiltonian  $\hat{\mathcal{H}}_I$  for interaction with a laser field in the dipole approximation, allowing only for the displacement of the proton charges, is

$$\hat{H}_D = -E_L e a_H \text{Re} \mathbf{e} (\mathbf{e}_1 + \mathbf{e}_2), \quad (8)$$

where  $a_H$  is the H–O distance,  $\mathbf{e}_{1,2}$  are the corresponding unit vectors for the directions of the proton bonds,  $\mathbf{e}$  is the polarization vector of the laser field, and  $e$  is the proton charge. The quadrupole component of the interaction Hamiltonian depends on the choice of the coordinate center. The displacement of the center leads to an additional dipole term which, however, is small and can be discarded, since it describes the same qualitative features of the interaction as the main dipole contribution. Thus, the coordinate center must be chosen as in Fig. 1 in order to obtain the simplest form of the Hamiltonian. The corresponding expression is

$$\hat{H}_Q = -\mathbf{E}_L \mathbf{d}_Q = -\frac{\mathbf{k} \mathbf{n}_O a_O}{2} E_L e a_H \operatorname{Re}[i \mathbf{e}(\mathbf{e}_2 - \mathbf{e}_1)], \quad (9)$$

where  $a_O$  is the O–O distance. This choice of the coordinate center on the O–O line for light propagating along that line (i.e.,  $\mathbf{k} \parallel \mathbf{n}_O$ ) means that the dependence of the quadrupole Hamiltonian  $H_Q$  on the torsion angle is determined solely by the odd function  $\sin(\theta/2)$ .

To calculate Eqs. (8) and (9), one must represent the polarization vector of the field in the form  $\mathbf{e} = (e_x, e_y, 0)$ , where the coefficients  $e_x$  and  $e_y$  are, in general, complex numbers, and calculate the corresponding coefficients,

$$C_{H_k} = (\mathbf{n}_x \mathbf{n}_{H_k}), \quad S_{H_k} = (\mathbf{n}_y \mathbf{n}_{H_k}),$$

where  $\mathbf{n}_x$  and  $\mathbf{n}_y$  are the unit vectors along the  $x$  and  $y$  axes and  $\mathbf{n}_{H_k}$  are the unit vectors along the O– $H_k$  bonds ( $k = 1, 2$ ). In this notation, the Hamiltonians (8) and (9) take the form

$$\begin{aligned} \hat{H}_D &= -E_L e a_H \operatorname{Re} e^{-i\varphi_L} [e_x (C_{H_1} + C_{H_2}) \\ &\quad + e_y (S_{H_1} + S_{H_2})], \\ \hat{H}_Q &= -\frac{k_L a_O}{2} E_L e a_H \operatorname{Re} i e^{-i\varphi_L} [e_x (C_{H_2} - C_{H_1}) \\ &\quad + e_y (S_{H_2} - S_{H_1})], \end{aligned} \quad (10)$$

where  $k_L$  is the modulus of the wave vector of the laser field,  $\varphi_L$  is the phase of the laser field, and the rotation angles  $\theta_{1,2}$

of the hydrogen bonds serve as coordinate operators. The projection coefficients of the proton dipole moments in the  $x$  or  $y$  directions of the laser polarization vector  $\mathbf{e}$  are calculated according to the formulas

$$\begin{aligned} C_{H_k} &= \mathbf{n}_x O(\mathbf{n}_{OOH_k}^\perp, \delta_H) O(\mathbf{n}_O, \theta_k) O(\mathbf{n}_{\mathbf{n}_x \mathbf{n}_O}^\perp, \pi/2 \\ &\quad - \angle \mathbf{n}_x \mathbf{n}_O) \mathbf{n}_x, \\ S_{H_k} &= \mathbf{n}_y O(\mathbf{n}_{OOH_k}^\perp, \delta_H) O(\mathbf{n}_O, \theta_k) O(\mathbf{n}_{\mathbf{n}_x \mathbf{n}_O}^\perp, \pi/2 \\ &\quad - \angle \mathbf{n}_x \mathbf{n}_O) \mathbf{n}_x \end{aligned}$$

as the scalar product of the vectors  $\mathbf{n}_{x,y}$  and the vectors obtained (a) by rotating the vector  $\mathbf{n}_x$  initially by an angle  $\pi/2 - \angle \mathbf{n}_x \mathbf{n}_O$  in the plane of  $\mathbf{n}_x \mathbf{n}_O$  until reaching a perpendicular to the  $\mathbf{n}_O$  axis, which is used as a basis axis for reading the torsion angles, (b) by rotating  $\mathbf{n}_x$  around the O–O axis by the torsion angle  $\theta_k$ , and (c) by a subsequent rotation of  $\mathbf{n}_x$  in the  $OOH_k$  plane by an angle  $\delta_H = \theta_H - \pi/2$  until the unit vector along  $\mathbf{n}_{H_k}$  is obtained.

Given the nonzero value of  $\delta_H$ , the analytic expressions for these coefficients end up being very cumbersome, so here we give them only for the approximation  $\delta_H = 0$ , i.e., for directions of the hydrogen bonds orthogonal to the O–O axis.<sup>1)</sup> The resulting relative error is less than  $\sim 10\%$  because  $\delta_H \approx 10^\circ$  is small. The three-dimensional rotation matrix for a rotation  $\alpha$  about the  $\mathbf{n}$  axis is

$$O(\mathbf{n}, \alpha) = \begin{pmatrix} n_x^2 + n_y^2 \cos \alpha + n_z^2 \cos \alpha & n_x n_y - n_x n_y \cos \alpha - n_z \sin \alpha & n_x n_z - n_x n_z \cos \alpha + n_y \sin \alpha \\ n_x n_y - n_x n_y \cos \alpha + n_z \sin \alpha & n_y^2 + n_x^2 \cos \alpha + n_z^2 \cos \alpha & n_y n_z - n_y n_z \cos \alpha - n_x \sin \alpha \\ n_x n_z - n_x n_z \cos \alpha - n_y \sin \alpha & n_y n_z - n_y n_z \cos \alpha + n_x \sin \alpha & n_z^2 + n_x^2 \cos \alpha + n_y^2 \cos \alpha \end{pmatrix}.$$

Hence, the coefficients can finally be written in the form

$$\begin{aligned} C_{H_1} &= \sqrt{1 - \sin^2 \vartheta \cos^2 \varphi} \cos \theta_1, \\ C_{H_2} &= \sqrt{1 - \sin^2 \vartheta \cos^2 \varphi} \cos \theta_2, \\ S_{H_1} &= (16 \sqrt{\cos^2 \vartheta + \sin^2 \varphi \sin^2 \vartheta})^{-1} [-2 \sin(2\varphi - \theta_1) \\ &\quad + \sin(2\varphi - 2\vartheta - \theta_1) - 8 \sin(\vartheta - \theta_1) + \sin(2\varphi \\ &\quad + 2\vartheta - \theta_1) - 2 \sin(2\varphi + \theta_1) + \sin(2\varphi - 2\vartheta + \theta_1) \\ &\quad + 8 \sin(\vartheta + \theta_1) + \sin(2\varphi + 2\vartheta + \theta_1)], \\ S_{H_2} &= (16 \sqrt{\cos^2 \vartheta + \sin^2 \varphi \sin^2 \vartheta})^{-1} [-2 \sin(2\varphi - \theta_2) \\ &\quad + \sin(2\varphi - 2\vartheta - \theta_2) - 8 \sin(\vartheta - \theta_2) + \sin(2\varphi \\ &\quad + 2\vartheta - \theta_2) - 2 \sin(2\varphi + \theta_2) + \sin(2\varphi - 2\vartheta + \theta_2) \\ &\quad + 8 \sin(\vartheta + \theta_2) + \sin(2\varphi + 2\vartheta + \theta_2)]. \end{aligned} \quad (11)$$

For the sum of the coefficients that determine the dipole potential we obtain

$$C_{H_1} + C_{H_2} = C_+ \cos(\theta/2), \quad S_{H_1} + S_{H_2} = S_+ \cos(\theta/2), \quad (12)$$

$$C_+ = 2 \sqrt{1 - \sin^2 \vartheta \cos^2 \varphi} \cos \bar{\theta},$$

$$\begin{aligned} S_+ &= 2(16 \sqrt{\cos^2 \vartheta + 2 \sin^2 \varphi \sin^2 \vartheta})^{-1} [-2 \sin(2\varphi - \bar{\theta}) \\ &\quad - 2 \sin(2\varphi + \bar{\theta}) + \sin(2\varphi - \bar{\theta} - 2\vartheta) + \sin(2\varphi + \bar{\theta} \\ &\quad - 2\vartheta) + 8 \sin(\bar{\theta} - \vartheta) + 8 \sin(\bar{\theta} + \vartheta) + \sin(2\varphi - \bar{\theta} \\ &\quad + 2\vartheta) + \sin(2\varphi + \bar{\theta} + 2\vartheta)], \end{aligned}$$

which depend on the torsional angle via the even function  $\cos(\theta/2)$ . Here  $\bar{\theta} = (\theta_1 + \theta_2)/2$  is the average rotation angle of the hydrogen bonds. For the differences of the coefficients determining the quadrupole potential, we obtain an expression that depends on the torsion angle in terms of the odd function  $\sin(\theta/2)$ :

$$C_{H_2} - C_{H_1} = C_- \sin \frac{\theta}{2}, \quad S_{H_2} - S_{H_1} = S_- \sin \frac{\theta}{2},$$

$$\begin{aligned}
 C_- &= -2\sqrt{1 - \sin^2 \vartheta \cos^2 \varphi} \sin \tilde{\theta}, \\
 S_- &= (16\sqrt{\cos^2 \vartheta + 2 \sin^2 \varphi \sin^2 \vartheta})^{-1} [(2 \cos(2\varphi - \tilde{\theta}) \\
 &\quad - 2 \cos(2\varphi + \tilde{\theta}) - \cos(2\varphi - \tilde{\theta} - 2\vartheta) + \cos(2\varphi + \tilde{\theta} \\
 &\quad - 2\vartheta) + 8 \cos(\tilde{\theta} - \vartheta) + 8 \cos(\tilde{\theta} + \vartheta) - \cos(2\varphi - \tilde{\theta} \\
 &\quad + 2\vartheta) + \cos(2\varphi + \tilde{\theta} + 2\vartheta)]. \quad (13)
 \end{aligned}$$

For a simplified analysis of the interaction of the rotational motion of a molecule about the O–O axis and the torsional vibrations, the numerical parameters of the torsional potential  $U(\theta)$  are important. The corresponding values of the frequency splitting of the levels,<sup>14</sup>  $\Delta E_0 = 11.44 \text{ cm}^{-1}$ ,  $\Delta E_1 = 116.34 \text{ cm}^{-1}$ , and  $\Delta E_2 = 206.57 \text{ cm}^{-1}$ , exceed the characteristic free rotation frequencies of the molecule as a whole for  $n \geq 1$ ; this means that it is possible to study transitions between the eigenstates of the torsional Hamiltonian  $\hat{H}_\theta$  directly in terms of the classical rotational coordinate  $\tilde{\theta}$ .

### 3. PHOTOEXCITATION DYNAMICS IN A TWO-LEVEL MODEL

If it is assumed that the frequencies of the transition between the eigenstates of the torsional Hamiltonian  $\hat{H}_\theta$  greatly exceed the rotation frequency of the proton bonds, then laser excitation is possible for a negligibly small deviation of the orientation angles  $\vartheta$  and  $\varphi$  of the molecule and a small deviation of the rotational angle  $\tilde{\theta}$ . Here it is possible to excite the symmetric/antisymmetric states  $\psi_S$  and  $\psi_A$  into a coherent superposition  $C_A \psi_A + C_S \psi_S$ . For  $S$ – $A$ -transitions with high enough transition energy  $\Delta E_n$ , which is nonzero because of tunneling between the  $d$ - and  $l$ -states, it can be estimated as

$$\Delta E \propto \exp(-2\sqrt{m_{\text{H}} a_{\text{H}}^2 \Delta V \Delta \theta / \hbar}),$$

where  $\Delta V$  and  $\Delta \theta$  are the characteristic height and width of the potential barrier. When the excitation frequency is chosen to be the resonant transition frequency  $\omega_0 = \Delta E_n / \hbar$ , only the resonant matrix elements will be significant in the Hamiltonians (10) and the torsional dynamics of the molecule can be examined in a two-level approximation.

Given the form (10) for the Hamiltonian, we have

$$\hat{H}_D \propto \cos \theta, \quad \hat{H}_Q \propto \sin \theta.$$

We show the form of the  $2 \times 2$  matrix for the single-photon interaction Hamiltonian  $\hat{H}_L$  for the total Hamiltonian  $\hat{H}_I = \hat{H}_D + \hat{H}_Q$  for the case of linear polarization  $e_x = 1, e_y = 0$ . (Here there is no advantage in using circular polarization in the quadrupole approximation, because the polarization does not appear in the dependence of the quadrupole moment on the coordinate  $\theta$  for this transition.) Given the representation of the interaction Hamiltonian in terms of the Pauli matrices for this transition, we obtain

$$\begin{aligned}
 \hat{H}_I &\rightarrow V_{12} \hat{\sigma}^+ + V_{21} \hat{\sigma}^- = V_{12}(t) \hat{\sigma}_1(t) \\
 &= V_{12}(0) \cos(\omega_L t + \tilde{\varphi}_L) (\cos(\omega_L t \hat{\sigma}_1) + \sin(\omega_L t \hat{\sigma}_2)),
 \end{aligned}$$

where  $V_{12} = V_{21}$  because the eigenfunctions  $\psi_k$  are real. After averaging over the oscillations in the field and the atomic polarization of the components at frequencies  $2\omega_L$  in the rotating wave approximation,<sup>15</sup> we obtain

$$\hat{H}_L = \begin{pmatrix} 0 & \frac{1}{2} Q S_{AS} e^{-i\tilde{\varphi}_L} \\ \frac{1}{2} Q S_{AS} e^{i\tilde{\varphi}_L} & 0 \end{pmatrix}, \quad (14)$$

where, with Eqs. (10), (12), and (13), we obtain

$$Q = k_L a_O E_L e a_H \sqrt{1 - \sin^2 \vartheta \cos^2 \varphi} \sin \tilde{\theta}, \quad (15)$$

where  $\tilde{\varphi}_L$  is the initial phase of the laser field, which also includes a phase contribution, determined by Eq. (10), to the polarization of the field and the orientation of the molecule, and

$$S_{AS} = \int_{-\pi}^{\pi} \psi_A(\theta) \sin \frac{\theta}{2} \psi_S(\theta) d\theta \quad (16)$$

is a dimensionless matrix element describing the tunneling effect.

As a result, the Hamiltonian (14) is described by the matrix

$$\hat{H}_\Omega = \begin{pmatrix} -\frac{\hbar \delta}{2} & \frac{Q}{2} S_{AS} e^{-i\tilde{\varphi}_L} \\ \frac{Q}{2} S_{AS} e^{i\tilde{\varphi}_L} & \frac{\hbar \delta}{2} \end{pmatrix}, \quad (17)$$

where  $\delta = \omega_L - \omega_{12}$  is the detuning of the laser field. This operator can be expressed in terms of the Pauli matrices:

$$\hat{H}_\Omega = \frac{\hbar}{2} (\mathbf{\Omega} \hat{\sigma}), \quad \mathbf{\Omega} = (-\delta, Q S_{AS} \cos \tilde{\varphi}_L, \sin \tilde{\varphi}_L). \quad (18)$$

The temporal evolution operator corresponding to the operator (17),

$$U(t) = \text{T exp} \left[ (-i/\hbar) \int \hat{H}_\Omega dt \right]$$

can be calculated analytically for (a) a rectangular pulse  $E_L = \text{const}$ , or (b) zero offset  $\delta = 0$ , using the equations

$$\begin{aligned}
 \text{a) } U(t) &= \cos\left(\frac{\Omega}{2} t\right) \hat{I} - i \sin\left(\frac{\Omega}{2} t\right) \left[ -\frac{\delta}{\Omega} \hat{\sigma}_3 \right. \\
 &\quad \left. + \frac{Q S_{AS}}{\Omega} (\hat{\sigma}_1 \cos \tilde{\varphi}_L + \hat{\sigma}_2 \sin \tilde{\varphi}_L) \right], \quad (19a)
 \end{aligned}$$

$$\text{b) } U(t) = \cos\left(\frac{\Phi}{2}\right) \hat{I} - i \sin\left(\frac{\Phi}{2}\right) (\hat{\sigma}_1 \cos \tilde{\varphi}_L + \hat{\sigma}_2 \sin \tilde{\varphi}_L), \quad (19b)$$

where  $\Omega = \sqrt{\Omega_0^2 + \delta^2}$  is the total Rabi frequency,  $\Omega_0 = Q S_{AS}$  is the Rabi frequency, and  $\Phi = \int \Omega(t) dt$  is the angle of the laser pulse.

For  $\delta = 0$ , in accordance with Eq. (19b), the initial incoherent states, represented in the form

$$\hat{\rho}_0 = \hat{I}/2 + w \hat{\sigma}_3/2 \quad (-1 \leq w \leq 1),$$

transform into the states

$$\hat{\rho}_t = \frac{1}{2} [\hat{I} + w(\hat{\sigma}_3 \cos \Phi - \hat{\sigma}_1 \sin \Phi \sin(\omega_L t + \tilde{\varphi}_L) - \hat{\sigma}_2 \sin \Phi \cos(\omega_L t + \tilde{\varphi}_L))], \quad (20)$$

where, besides the transformation (19), we have included free precession at the laser frequency, which is applicable in the standard form for the theory of the interaction<sup>16</sup> and the rotating wave approximation to the operators for the physical quantities. The components with  $\hat{\sigma}_1$  and  $\hat{\sigma}_2$  describe the contribution of the coherent superposition of the states  $\psi_S$  and  $\psi_A$ . In particular, for the lower initial state, which corresponds to  $w=1$  for  $\omega_L t + \tilde{\varphi}_L = \pi/2$ , a  $\pi/2$ -pulse, for which  $\Phi = \pm \pi/2$  and  $\cos \Phi = \pm 1$  in Eq. (20) and  $\Phi/2 = \pm \pi/4$  and  $\cos(\Phi/2) = \pm 1/\sqrt{2}$  in Eq. (19b), produces a jump from the initial  $\psi_S$  state into the chiral states  $\psi_{1,2} = (\psi_S \pm \psi_A)/\sqrt{2}$ , which correspond to the density matrices  $(\hat{I} \mp \hat{\sigma}_1)/2$ . Thus, for fixed angles

$$\Theta = (\vartheta, \varphi, \tilde{\theta})$$

it is possible to bring a molecule into a  $d$ - or  $l$ -state with 100% probability by an appropriate choice of parameters. In general, however, the resulting transformation of the state must be averaged over the angles  $\Theta$ .

This averaging can be accomplished using a standard superoperator technique.<sup>17</sup> For the result (20) of the excitation of an incoherent initial state, upon averaging only over the sign of the parameter  $Q$ , which depends on the orientation angle  $\tilde{\theta}$  of the hydrogen bonds along the  $x$  axis, which enters into the factor  $\sin \Phi$  in Eq. (20), we obtain the following structure for the density matrix:

$$\hat{\rho}_t = (\hat{I} - w \hat{\sigma}_3 \cos \Phi)/2.$$

This means that when there is no preferred orientation of the molecules in  $\tilde{\theta}$ , the density matrix transforms incoherently, i.e., diagonal density matrices transform into diagonal matrices. As a result of this transformation, the symmetry of the state,  $S$  or  $A$ , does not change, but the squared modulus of the wave function preserves reflection symmetry under the transformation  $\theta \rightarrow -\theta$ . Therefore, in order for reflection symmetry to be disrupted, the molecules must be oriented beforehand.

### 3.1. Excitation of initially oriented molecules

If there is an inhomogeneity in the distribution of the angles  $\tilde{\theta}$  owing to the existence of a preferred orientation of the molecules, then the excitation of incoherent states can contain a coherent component associated with the excitation of chiral states that differ from  $\psi_A$  and  $\psi_S$ . The scalar characteristic of the degree of chirality is the average

$$\chi = 2 \left( \langle \psi_l | \hat{\rho} | \psi_l \rangle - \frac{1}{2} \right) = -2 \left( \langle \psi_d | \hat{\rho} | \psi_d \rangle - \frac{1}{2} \right), \quad (21)$$

where

$$\psi_{l,d} = \frac{1}{2} [\psi_S \pm \psi_A]$$

describe, respectively, left- and right-handed chiral states, which correspond to degrees of chirality  $\chi = \pm 1$  for  $\hat{\rho} = |\psi_{l,d}\rangle\langle\psi_{l,d}|$ . For a state  $\hat{\rho}(t)$  excited by a rectangular laser pulse of duration  $\tau_p$  with phase  $\Phi = \Omega \tau_p$ , the corresponding dependence of the degree of chirality of the excited state on the detuning  $\delta$  and phases  $\Phi$ ,  $\tilde{\varphi}_L$  can be calculated analytically.

For zero frequency offset, the analytic dependence of the degree of chirality on the angle and phase of the laser pulse has the form

$$\chi = -\sin \Phi \sin \tilde{\varphi}_L.$$

The qualitative dependence for nonzero offset is shown in Fig. 2a. The important point is the dependence of the effect on the phase of the laser field.

## 4. EXPERIMENTAL SCHEME FOR OBSERVING PHOTOINDUCED CHIRALITY IN H<sub>2</sub>O<sub>2</sub>

Given the features of the hydrogen peroxide molecule analyzed above, we propose the following experiment for observing photoexcited optical activity as an indicator of the breakdown of reflection symmetry.

As a working two-level system, the most appropriate is the  $S-A$ -transition with  $n=1$ , which corresponds to a wavelength  $\lambda \approx 86 \mu\text{m}$  and frequency  $\omega_{12} = 116.34 \text{ cm}^{-1}$ , which is substantially greater than the corresponding frequency for  $n=0$  ( $11.44 \text{ cm}^{-1}$ ). To create a population in this transition it is easiest to use Raman excitation by two lasers tuned to the frequency of the  $S-S$ -transition  $n=0 \rightarrow n=1$ . Since only dipole-active transitions are used here, we can obtain an essentially complete saturation regime in the active volume of the medium, so that in this stage there are no important limitations and we can start with  $n_S \sim 1$  for estimating the initial population on this transition.

In view of the oscillations in the degree of chirality excited in this scheme, it seems appropriate to use a laser with frequency  $\omega_1$  for probing and another frequency  $\omega_2$ , which differs by the frequency  $\omega_1 - \omega_2 = \omega_{12}$  of the precession in the degree of chirality, for detection. This can be done efficiently using two crossed polarizers. Detection of nonzero polarization of the output field perpendicular to the probe field corresponds to detection of the rotation effect. Here the probe field can be simultaneously employed to create an effect analogous to the orientation by an electrostatic field described in Sec. 1. According to Eq. (6), it leads to an angular displacement by this frequency. Therefore, the quadrupole Hamiltonian corresponding to excitation by the other laser field at frequency  $\omega_2$  and with a polarization direction along the  $x$  axis receives a correction at the resonant frequency  $\omega_{12}$ ,

$$\Delta Q = \frac{E_1 E_2 e^2 a_H^2}{8J\omega_1^2} k_L a_O \sqrt{1 - \sin^2 \vartheta \cos^2 \varphi} \times \cos^2 \tilde{\theta} u_1(t) u_2(t). \quad (22)$$

Here an additional dependence on the torsional angle of the form  $\cos(\theta/2)$  should be included in the matrix element (16),

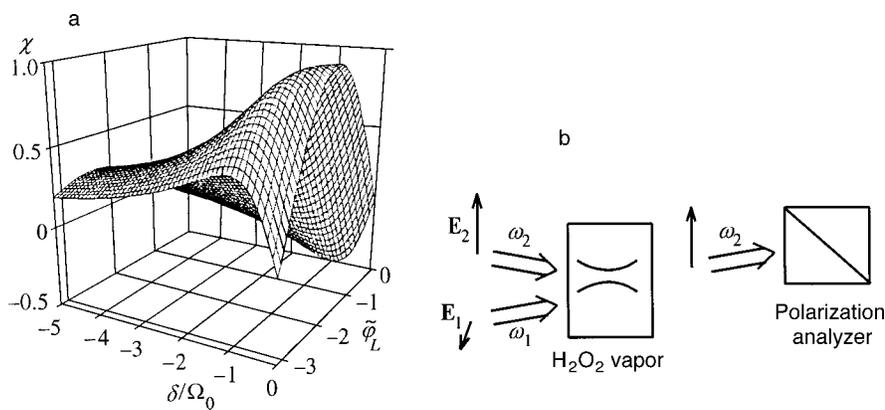


FIG. 2. (a) Degree of chirality  $\chi$  of the excited state as a function of the relative detuning  $\delta/\Omega_0$  and phase  $\tilde{\varphi}_L$  of the laser field. (b) Layout of an experiment with two-frequency excitation. Radiation from one of the lasers is also used as the probe radiation.

which reduces to the substitution  $\sin(\theta/2) \rightarrow (\sin \theta)/2$ ; this matrix element is also nonzero, while the additional time dependence of the form  $\cos(\omega_1 t + \varphi_1)$  reduces to replacing the laser frequency,  $\omega_L \rightarrow \omega_1 - \omega_2$ , and the phase,  $\tilde{\varphi}_L \rightarrow \varphi_1 - \varphi_2$ . Equation (22) yields the order of magnitude estimate

$$\Delta Q \tau_p / \hbar \sim 10^{-4} \sqrt{I_1 I_2} \tau_p,$$

where the pulse duration  $\tau_p$  is in seconds and the intensities  $I_1$  and  $I_2$  are in  $W/cm^2$ . Thus, in order to obtain the effect of a  $\pi/2$ -pulse for pulse lengths  $\sim 1$  ns, the average geometric intensities of the pulses employed must be of order  $I_0 = 10^4 / \tau_p \sim 10^{13} W/cm^2$ . This quantity only yields an upper bound on the laser power to be used, which may actually be bounded by the substantially lower intensities corresponding to small  $\Delta Q \tau_p / \hbar$ .

The minimum measured rotation angle  $\varphi_{\min}$ , in conjunction with the expected angular rotation  $\alpha = \Delta\varphi / \Delta L$ , determines the length  $L$  of the active region. For  $\alpha$ , we can proceed from the estimate  $\alpha = k_L^2 a_O (\varepsilon - 1)$ , where  $\varepsilon - 1 \sim 10^{-4}$  is the characteristic dispersion in the visible for  $H_2O_2$  vapor at atmospheric pressure produced by suitable heating of the cell. This estimate is based on the assumption that for the chiral state of the molecule, the order of the specific rotation compared to the linear polarization effect contains a small parameter  $k_L a_O \sim 10^{-3}$ . The corresponding minimum length of the active region is  $L = \varphi_{\min} / \alpha$ , which for  $\varphi_{\min}$  of order 1 arcsec yields  $L \sim 10^{-2}$  cm. It is important to note that this is precisely of the same order as the wavelength corresponding to free precession at this transition. In this way, propagation effects on the frequency of the transition are relatively unimportant. The corresponding minimum laser beam waist in the active region<sup>18</sup>  $w_0^2 = \lambda_L L / \pi$  corresponds to pulsed laser powers

$$W_L = I_0 w_0^2,$$

which for these parameters is of order  $10^7$  W.

The geometry of a two-frequency experimental layout is shown in Fig. 2b. Light at either of the two frequencies  $\omega_{1,2}$  can be used to detect the optical rotation effect. In this scheme, averaging over orientation shows up only as uncertainty in the Rabi frequency owing to the  $\cos^2 \tilde{\theta}$  dependence, which, as opposed to the electrostatic orientation method, does not lead to a drop in the response of the same order of magnitude as the effect itself. In order for the exciting field at

frequency  $\omega_2$  not to interfere with detection of the effect at the same frequency, the beams must be slightly skewed so that this does not have a significant effect on the field distribution in the active region.

### 5. CONCLUSION

The above analysis indicates the feasibility of controlled excitation and detection of molecular states with disrupted reflection symmetry by optical methods. Introducing the techniques of nonlinear optics into the study of chiral states would signify the emergence of an efficient source of new information on the dynamic parameters of molecules which determine the conformational properties of chiral states.

This work was initiated by Prof. N. I. Koroteev, who devoted the last years of his short life to studying the puzzle of chiral purity in nature. One of his major ideas was to apply the methods of nonlinear optics to research on this problem. He hoped that in this way, not only could new highly sensitive methods for nonlinear optical diagnostics of media with chiral symmetry be developed, but also the mechanisms for controlled regulation of chirality might be understood. His untimely passing precluded his doing so, but his ideas continue to live on in the work of his successors and students. We respectfully dedicate this paper to the memory of N. I. Koroteev.

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<sup>1)</sup>As necessary, the numerical calculations can be carried out using exact formulas.

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