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著者	藤村 勇一
journal or publication title	Journal of Chemical Physics
volume	116
number	17
page range	7509-7517
year	2002
URL	http://hdl.handle.net/10097/46266

doi: 10.1063/1.1467054

Theory of stimulated Raman adiabatic passage in a degenerated reaction system: Application to control of molecular handedness

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(Received 3 January 2002; accepted 11 February 2002)

We have developed a new type of stimulated Raman adiabatic passage (STIRAP) that is applicable to a degenerated reaction system. The direction of the photon polarization vector is the adiabatic parameter in the STIRAP. The molecular handedness of H₂POSH, a preoriented phosphinotioic acid that has two stable configurations, *L* and *R* enantiomers, is used as a model system. The control of molecular handedness in both pure and mixed state cases are considered. In the case of a pure state, a STIRAP with a linearly polarized single laser allows an almost complete transfer from an *L* (*R*) enantiomer to the other by adiabatically changing its polarization direction. The adiabatic criterion for changing the polarization direction is clarified. In the case of a mixed state, a STIRAP with two linearly polarized laser pulses allows a selective preparation of pure enantiomers from its racemic mixture. In the low temperature limit, a five-level model reduces a three-level model by setting the direction of the polarization of the pump and Stokes pulses in such a way that only the forward transfer is allowed, while the reverse is forbidden. Furthermore, in the case of mixed state, relaxation effects originating from vibrational mode couplings are taken into account, and the influence of the population decay from intermediate states on the STIRAP is compared with that by a π -pulse approach. © 2002 American Institute of Physics. [DOI: 10.1063/1.1467054]

I. INTRODUCTION

Stimulated Raman adiabatic passage (STIRAP) is an effective method for complete population transfer.^{1–11} The main features of this method are that it is robust and that no sophisticated experimental setup is needed compared to other control methods such as pulse-shaping techniques.^{12–18} However, most STIRAPs have so far been applied to nondegenerated systems in which the pump and Stokes processes do not overlap each other in the frequency domain.

The STIRAP process is understood well in terms of a three-level system composed of $|1\rangle$, $|2\rangle$, and $|3\rangle$ that interact with partially overlapping pump and Stokes pulses. Here, the initial state $|1\rangle$ and the final state $|3\rangle$ are assumed to be nondegenerated, and the central frequencies of the two pulses are different. In order to obtain complete population transfer from $|1\rangle$ to $|3\rangle$, the pump laser should selectively couple $|1\rangle$ to $|2\rangle$ and the Stokes laser should selectively couple $|2\rangle$ to $|3\rangle$. The adiabatic rapid passage is carried out by applying the Stokes pulse before the pump pulse counterintuitively. On the other hand, if the initial and final states are degenerated, the simple, counterintuitive treatment breaks down because the pump and Stokes pulses cannot be distinguished. Therefore, it is difficult to select degenerated or quasidegenerated reaction channels by a conventional STIRAP. A typical example of such degenerated systems is a selective preparation of enantiomers.^{19–26} To the best of our knowledge, there has been no discussion on an application of STIRAP to such a reaction system.¹ In this paper, we propose a new STIRAP method that is applicable to a degenerated system. Here,

molecules are assumed to be oriented on a surface or preoriented in a gas phase by a static electric field²⁷ or by electromagnetic fields.^{28–31} In this method, the temporal behavior of the photon polarization is a factor controlling the adiabatic rapid passage of the system. As a model of degenerated systems, we treat a transfer of molecular handedness of preoriented enantiomers that have two stable configurations: *L* and *R*.

This paper is organized as follows. In Sec. II A, we show that in the case of a pure state a STIRAP, taking into account the polarization dependence of the linearly polarized laser field, brings about almost complete population transfer from one localized state to the other in a degenerated system. In Sec. II B, the STIRAP method described in Sec. II A is extended to a mixed state case in which selective preparation of pure enantiomers from a racemic mixture is treated. In Sec. III, both the pure state and mixed state treatments are applied to a control of molecular handedness of preoriented H₂POSH (a preoriented phosphinotioic acid). In the mixed state treatment, the influence of relaxations on the product yield is also examined. The results obtained are compared with those obtained by a π -pulse approach.

II. THEORY

Consider a molecule that has two degenerated configurations, *L* and *R* enantiomers, in the electronic ground state and an achiral excited state.^{32–35} Figure 1 shows a general scheme of a molecular handedness control. The two solid curves in the figure denote the electronic ground and excited states of the enantiomers. These states are connected by two laser pulses 1 and 2 with central frequencies ω_1 and ω_2 . The polarization directions of those pulses are specified by the

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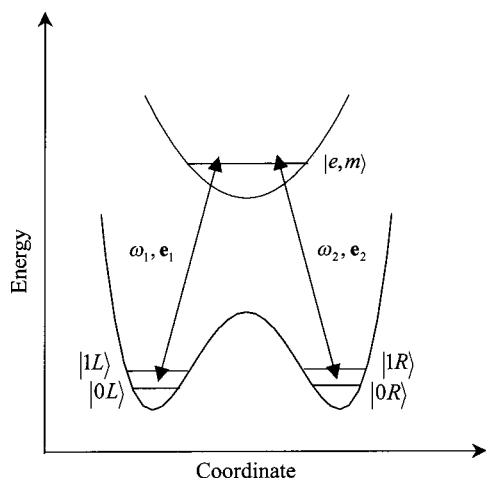


FIG. 1. A general scheme of enantiomer control by two laser pulses. The lower curve expresses the ground state potential energy along an enantiomer reaction coordinate in which $|nL\rangle$ and $|nR\rangle$ are localized states in the left and right wells, respectively. The upper potential curve expresses an achiral electronic excited state e , in which the molecular eigenstates are defined as $|e, n\rangle$ ($n=0,1,2,\dots$). In the figure, only an eigenstate $|e, m\rangle$ is denoted.

unit vectors \mathbf{e}_1 and \mathbf{e}_2 . The lower curve expresses the ground state potential energy along an enantiomer reaction coordinate in which the left and right wells correspond to the two stable configurations, that is, L and R enantiomers. $|nL\rangle$ and $|nR\rangle$ represent the localized states in left and right wells, respectively. Both wells are sufficiently separated by the potential barrier. The upper potential curve expresses an achiral electronic excited state e , in which the molecular eigenstates are defined as $|e, n\rangle$ ($n=0,1,2,\dots$). These molecular eigenstates are symmetric or antisymmetric with respect to the enantiomer plane. We neglect rotational effects of the molecule.³⁶

A. Transfer of molecular handedness from an L (R) enantiomer to an R (L) enantiomer

We first consider the population transfer of a pure state from the initial state $|0L\rangle$ to the final state $|0R\rangle$ by a new STIRAP method. The laser-driven dynamics is semiclassically described by the time-dependent Schrödinger equation

$$i\hbar \frac{d|\Psi(t)\rangle}{dt} = [H_0 - \boldsymbol{\mu} \cdot \mathbf{E}(t)] |\Psi(t)\rangle, \quad (1)$$

where H_0 is the molecular Hamiltonian, $\boldsymbol{\mu}$ is the dipole moment operator, and $\mathbf{E}(t)$ is the total electric field. STIRAP generally requires an intermediate state that can optically couple strongly to both an initial state and a final state. Therefore, an achiral state $|e, m\rangle$ is chosen as an intermediate state for a STIRAP, and we consider the dynamical behavior of the system by means of an effective three-level system consisting of $|0L\rangle$, $|e, m\rangle$, and $|0R\rangle$. This model is a prototype of selective population transfer in an equally separated three-level system.

We employ $\mathbf{E}(t)$ given as

$$\mathbf{E}(t) = \mathbf{e}_1 A_1(t) \cos \omega_1 t + \mathbf{e}_2 A_2(t) \cos \omega_2 t \quad (\omega_1 = \omega_2), \quad (2)$$

where $A_1(t)$ and $A_2(t)$ represent the envelopes of laser pulses 1 and 2, respectively. Both ω_1 and ω_2 are supposed to

be resonant to the transitions between $|0L\rangle$ ($|0R\rangle$) and $|e, m\rangle$, and we redenote these frequencies as $\omega_1 = \omega_2 = \omega$. Therefore, the form of $\mathbf{E}(t)$ can be simplified as

$$\begin{aligned} \mathbf{E}(t) &= (\mathbf{e}_1 A_1(t) + \mathbf{e}_2 A_2(t)) \cos \omega t \\ &= \frac{\mathbf{A}(t)}{|\mathbf{A}(t)|} |\mathbf{A}(t)| \cos \omega t = \boldsymbol{\eta}(t) A(t) \cos \omega t, \end{aligned} \quad (3)$$

where $\mathbf{A}(t) \equiv \mathbf{e}_1 A_1(t) + \mathbf{e}_2 A_2(t)$, $A(t) \equiv |\mathbf{A}(t)|$ ($\neq 0$), and $\boldsymbol{\eta}(t)$ is the time-dependent unit vector of the polarization direction, which is defined as

$$\boldsymbol{\eta}(t) \equiv \mathbf{A}(t) / |\mathbf{A}(t)|. \quad (4)$$

Equation (3) shows that two lasers with the same frequency ω and with two different linearly polarizations are equivalent to a single laser with a time-dependent polarization unit vector.

Using the rotating wave approximation (RWA) under the resonance condition, the Hamiltonian in the interaction picture can be written as

$$\begin{aligned} H_I(t) &= -\frac{\boldsymbol{\eta}(t) A(t)}{2} \cdot [\boldsymbol{\mu}_{0L,em} |0L\rangle \langle e, m| \\ &\quad + \boldsymbol{\mu}_{0R,em} |0R\rangle \langle e, m|] + \text{h.c.}, \end{aligned} \quad (5)$$

where $\boldsymbol{\mu}_{0L,em}$ and $\boldsymbol{\mu}_{0R,em}$ are the transition dipole moments in the L and R enantiomers, respectively. Defining the relative angle between $\boldsymbol{\eta}(t)$ and $\boldsymbol{\mu}_{0L,em}$ as $\eta_L(t)$ and that between $\boldsymbol{\eta}(t)$ and $\boldsymbol{\mu}_{0R,em}$ as $\eta_R(t)$, the Hamiltonian Eq. (5) can be rewritten as

$$\begin{aligned} H_I(t) &= -\frac{1}{2} A(t) \mu_{0,em} (\cos \eta_L(t) |0L\rangle \langle e, m| \\ &\quad + \cos \eta_R(t) |0R\rangle \langle e, m|) + \text{h.c.}, \end{aligned} \quad (6)$$

where the absolute values of $\boldsymbol{\mu}_{0L,em}$ and $\boldsymbol{\mu}_{0R,em}$ are the same and denoted by $\mu_{0,em}$. The eigenvalues and eigenvectors of the Hamiltonian are given by

$$\begin{aligned} E_- &= \frac{\hbar \sqrt{\Omega_1^2(t) + \Omega_2^2(t)}}{2}, \\ |u_-\rangle &= \frac{1}{\sqrt{2}} (\sin \Theta |0L\rangle - |e, m\rangle + \cos \Theta |0R\rangle), \end{aligned} \quad (7a)$$

$$\begin{aligned} E_0 &= 0, \\ |u_0\rangle &= \cos \Theta |0L\rangle - \sin \Theta |0R\rangle, \end{aligned} \quad (7b)$$

$$\begin{aligned} E_+ &= -\frac{\hbar \sqrt{\Omega_1^2(t) + \Omega_2^2(t)}}{2}, \\ |u_+\rangle &= \frac{1}{\sqrt{2}} (\sin \Theta |0L\rangle + |e, m\rangle + \cos \Theta |0R\rangle), \end{aligned} \quad (7c)$$

with

$$\Theta(t) = \tan^{-1} \frac{\Omega_1(t)}{\Omega_2(t)}, \quad (8)$$

where the time-dependent Rabi frequencies $\Omega_1(t)$ and $\Omega_2(t)$ are defined as

$$\Omega_1(t) = \frac{\mu_{0,em} \cos \eta_L(t) A(t)}{\hbar}, \tag{9}$$

and

$$\Omega_2(t) = \frac{\mu_{0,em} \cos \eta_R(t) A(t)}{\hbar},$$

respectively. As can be seen in Eqs. (7), these dressed states have familiar forms for analysis of a conventional STIRAP. The population transfer from $|0L\rangle$ to $|0R\rangle$ can be understood well by the adiabatic time evolution of $|u_0\rangle$ following the time variation of $\Omega_1(t)$ and $\Omega_2(t)$. Therefore, it can be seen from Eqs. (7b) and (8) that complete population transfer in a degenerated system can be achieved by taking into account only the adiabatic change in the polarization direction of the linearly polarized electric field. For the initial condition $|\Psi(0)\rangle = |0L\rangle$, the population of $|0R\rangle$, $P_{R0} = |\langle 0R | \Psi(t) \rangle|^2$ evolves as

$$P_{R0}(t) = \sin^2 \Theta(t),$$

with

$$\Theta(t) = \tan^{-1} \frac{\cos \eta_L(t)}{\cos \eta_R(t)} \tag{10}$$

by setting the following adiabatic changes in $\eta_L(t)$ and $\eta_R(t)$ from the initial state ($t=0$) to the final state ($t=t_f$):

$$\begin{aligned} \eta_L(0) &= \frac{\pi}{2}, & \eta_R(0) &\neq \frac{\pi}{2} \\ \rightarrow \eta_L(t_f) &\neq \frac{\pi}{2}, \end{aligned} \tag{11}$$

$$\eta_R(t_f) = \frac{\pi}{2}.$$

To avoid nonadiabatic couplings between the dressed states, the rate of change in the $\Theta(t)$ must be small compared to the frequency $\sqrt{\Omega_1^2(t) + \Omega_2^2(t)}/2$ that corresponds to the energy separation between the dressed states.³⁷ Therefore, the adiabatic criterion is given by

$$|\dot{\Theta}(t)| \ll \frac{\sqrt{\Omega_1^2(t) + \Omega_2^2(t)}}{2}, \tag{12}$$

where the dot represents the derivative with respect to time.

From Eq. (8), $\dot{\Theta}(t)$ is given by

$$\dot{\Theta}(t) = \frac{\dot{\Omega}_1(t)\Omega_2(t) - \Omega_1(t)\dot{\Omega}_2(t)}{\Omega_1^2(t) + \Omega_2^2(t)}. \tag{13}$$

Here, we define the relative angle between $\mu_{0L,em}$ and $\mu_{0R,em}$ as α ($0 \leq \alpha \leq \pi$). Assuming that the unit vector $\eta(t)$ evolves in the plane formed by the two vectors $\mu_{0L,em}$ and $\mu_{0R,em}$, we obtain the relation between α and $\eta_L(t)$ ($\eta_R(t)$) as

$$\alpha = \eta_L(t) - \eta_R(t). \tag{14}$$

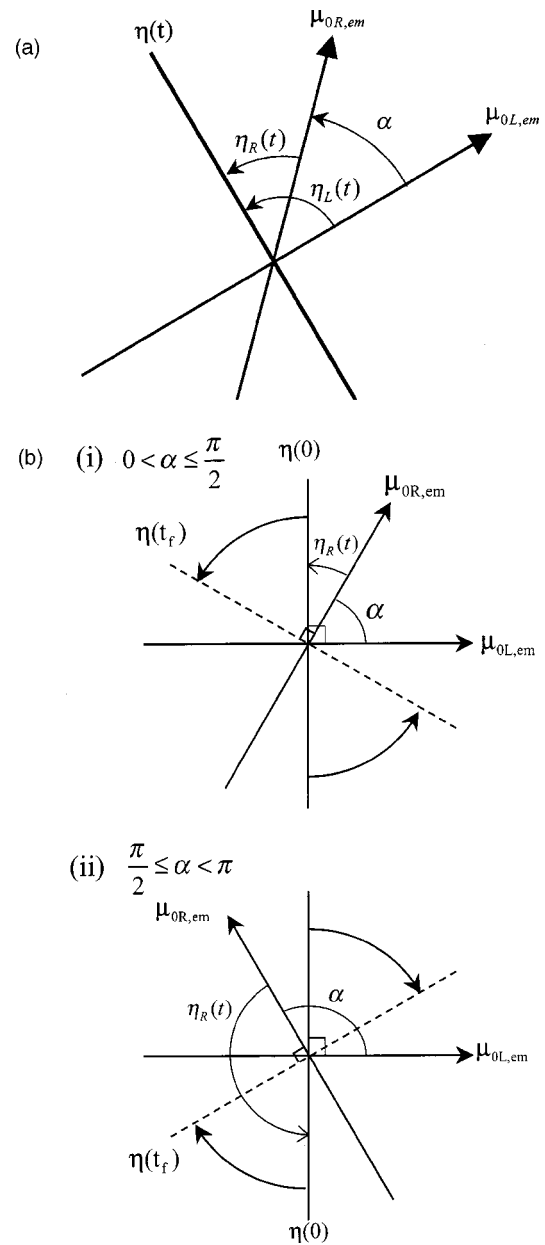


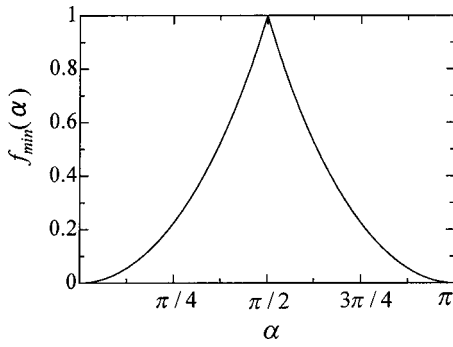
FIG. 2. (a) Two-dimensional geometrical structure of the time-dependent polarization vector $\eta(t)$, where $\alpha(0 \leq \alpha \leq \pi)$ is the relative angle between $\mu_{0L,em}$ and $\mu_{0R,em}$, $\eta_R(t)$ is the relative angle between $\eta(t)$ and $\mu_{0L,em}$, and $\eta_L(t)$ is that between $\eta(t)$ and $\mu_{0R,em}$. (b) The allowed direction of the photon polarization vector $\eta(t)$ for $|0L\rangle \rightarrow |0R\rangle$ transfer in the pure state case: (i) $0 < \alpha \leq \pi/2$ case and (ii) $\pi/2 \leq \alpha < \pi$ case.

Figure 2(a) shows a two-dimensional geometrical structure of the time-dependent $\eta(t)$. For a complete population transfer from $|0L\rangle$ to $|0R\rangle$, it follows from Eq. (11) that $\eta_R(t)$ is swept as

$$\eta_R(0) = \frac{\pi}{2} - \alpha \rightarrow \eta_R(t_f) = \frac{\pi}{2}, \tag{15}$$

for $0 < \alpha \leq \pi/2$, and

$$\eta_R(0) = \frac{3\pi}{2} - \alpha \rightarrow \eta_R(t_f) = \frac{\pi}{2}, \tag{16}$$

FIG. 3. Plot of $f_{\min}(\alpha)$ as a function of α .

for $\pi/2 < \alpha \leq \pi$. The allowed ranges in the direction of the photon polarization vector $\boldsymbol{\eta}(t)$ are shown in Fig. 2(b). Curled arrows connecting $\boldsymbol{\eta}(0)$ and $\boldsymbol{\eta}(t_f)$ indicate the range of $\boldsymbol{\eta}(t)$ from $t=0$ to $t=t_f$.

Substituting Eq. (9) with Eq. (14) into Eq. (12), we obtain the adiabatic criterion

$$\dot{\eta}_R(t) \leq \frac{\mu_{0,em} A(t)}{2\hbar} f_\alpha(\eta_R(t)) \quad (17)$$

with a function $f_\alpha(\eta_R(t))$ defined as

$$f_\alpha(\eta_R(t)) = \frac{[\cos^2 \eta_R(t) + \cos^2(\alpha - \eta_R(t))]^{3/2}}{\sin \alpha}, \quad (18)$$

where $\alpha \neq 0, \pi$. The function $f_\alpha(\eta_R(t))$ has a minimum at $\eta_R(t) = \pi/2 - \alpha/2$ for $0 < \alpha \leq \pi/2$ and a minimum at $\eta_R(t) = \pi - \alpha/2$ for $\pi/2 < \alpha \leq \pi$. Therefore, at these times, the effects of nonadiabatic couplings become maximum. We define $f_{\min}(\alpha)$ as

$$f_{\min}(\alpha) = \begin{cases} f_\alpha\left(\eta_R = \frac{\pi}{2} - \frac{\alpha}{2}\right) = \sqrt{2} \frac{\sin^2 \frac{\alpha}{2}}{\cos \frac{\alpha}{2}}, & \text{for } 0 < \alpha \leq \pi/2, \\ f_\alpha\left(\eta_R = \pi - \frac{\alpha}{2}\right) = \sqrt{2} \frac{\cos^2 \frac{\alpha}{2}}{\sin \frac{\alpha}{2}}, & \text{for } \pi/2 < \alpha \leq \pi. \end{cases} \quad (19)$$

Figure 3 shows $f_{\min}(\alpha)$ as a function of α . As can be seen from the figure, $f_{\min}(\alpha)$ becomes maximum at $\alpha = \pi/2$. In this case, the nonadiabatic coupling effects are minimized. The adiabatic condition breaks down when α approaches 0 or π . This is simply because the magnitudes of the component of $\boldsymbol{\eta}(t)$ projected to $\boldsymbol{\mu}_{0R,em}$ and that to $\boldsymbol{\mu}_{0L,em}$ are the same: $|\eta_R(t)| = |\eta_L(t)|$. This results in a constant Θ .

So far we have considered a population transfer from an L enantiomer to an R enantiomer. The reverse population transfer can be treated by exchanging $\boldsymbol{\eta}(t_f)$ with $\boldsymbol{\eta}(0)$ in Fig. 2(b).

B. Preparation of pure enantiomers from a racemic mixture

We now apply the technique described in the previous subsection to the preparation of pure R enantiomers from an equal mixture of preoriented L and R enantiomers (racemic mixture). For a statistical mixed state, the dynamical behavior of the system is described by the Liouville–von Neumann equation for the density matrix $\rho(t)$

$$i\hbar \frac{d\rho(t)}{dt} = [H_0 - \boldsymbol{\mu} \cdot \mathbf{E}(t), \rho(t)]. \quad (20)$$

For the initial state, we assume that only the two lowest localized states $|0L\rangle$ and $|0R\rangle$ are equally distributed at a low temperature:

$$\rho(t=0) = \frac{1}{2}(|0L\rangle\langle 0L| + |0R\rangle\langle 0R|). \quad (21)$$

Starting from the initial condition, we prepare pure R enantiomers with the following control scheme:

$$\rho(t=0) = \frac{1}{2}(|0L\rangle\langle 0L| + |0R\rangle\langle 0R|) \quad (22)$$

↓ STIRAP

$$\rho(t=t_f) = \frac{1}{2}(|1R\rangle\langle 1R| + |0R\rangle\langle 0R|). \quad (23)$$

Note that $\rho(t=t_f)$ is also a one-to-one statistical mixture of the lowest and first excited R enantiomers, because statistical probabilities or eigenvalues of $\rho(t)$ must be conserved for processes under a unitary condition.²³

For the above control scheme, we utilize two laser pulses

$$\mathbf{E}(t) = \mathbf{e}_1 A_1(t) \cos \omega_1 t + \mathbf{e}_2 A_2(t) \cos \omega_2 t, \quad (24)$$

where the central frequency of pump laser 1, ω_1 , is resonant to the transition between $|0L\rangle(|0R\rangle)$ and $|e,m\rangle$ and that of Stokes laser 2, ω_2 , is resonant to the transition between $|1R\rangle(|1L\rangle)$ and $|e,m\rangle$. To analyze the laser-driven dynamics of the system, we consider an effective five-level system consisting of $|0L\rangle$, $|1L\rangle$, $|0R\rangle$, $|1R\rangle$, and $|e,m\rangle$ that interact with the laser fields. Using the RWA with the resonance condition, the Hamiltonian in the interaction picture can be written as

$$H_I(t) = -\frac{1}{2} \mathbf{e}_1 A_1(t) \cdot [\boldsymbol{\mu}_{0L,em} |0L\rangle\langle e,m| + \boldsymbol{\mu}_{0R,em} |0R\rangle\langle e,m| + \text{h.c.}] - \frac{1}{2} \mathbf{e}_2 A_2(t) \cdot [\boldsymbol{\mu}_{1L,em} |1L\rangle\langle e,m| + \boldsymbol{\mu}_{1R,em} |1R\rangle\langle e,m| + \text{h.c.}] \quad (25)$$

Defining the relative angles between $\mathbf{e}_i (i=1,2)$ and $\boldsymbol{\mu}_{nM,em} (M=L,R; n=0,1)$ as η_{nM}^i , we rewrite Eq. (25) as

$$H_I(t) = -\frac{1}{2} A_1(t) [\mu_{0,em} \cos \eta_{0L}^1 |0L\rangle\langle e,m| + \mu_{0,em} \cos \eta_{0R}^1 |0R\rangle\langle e,m| + \text{h.c.}] - \frac{1}{2} A_2(t) [\mu_{1,em} \cos \eta_{1L}^2 |1L\rangle\langle e,m| + \mu_{1,em} \cos \eta_{1R}^2 |1R\rangle\langle e,m| + \text{h.c.}], \quad (26)$$

where $\mu_{n,em} (n=0,1)$ denotes the magnitude of $\boldsymbol{\mu}_{nL,em} (\boldsymbol{\mu}_{nR,em})$. The laser-driven dynamics of the system is obviously influenced by the choice of the relative angles.²⁶ In order to completely separate the pump and Stokes processes,

namely, the laser pulses 1 and 2 selectively induce forward transitions, $|0L\rangle \rightarrow |e,m\rangle$ and $|e,m\rangle \rightarrow |1R\rangle$, while they suppress backward transitions $|0R\rangle \rightarrow |e,m\rangle$ and $|e,m\rangle \rightarrow |1L\rangle$, respectively, we impose the following conditions for \mathbf{e}_1 and \mathbf{e}_2 :

$$\begin{aligned} \mathbf{e}_1 \cdot \boldsymbol{\mu}_{0L,em} &\neq 0, & \mathbf{e}_1 \cdot \boldsymbol{\mu}_{0R,em} &= 0, \\ \mathbf{e}_2 \cdot \boldsymbol{\mu}_{1R,em} &\neq 0, & \mathbf{e}_2 \cdot \boldsymbol{\mu}_{1L,em} &= 0. \end{aligned} \quad (27)$$

The above conditions are satisfied by choosing the relative angles as

$$\eta_{0L}^1 \neq \frac{\pi}{2}, \quad \eta_{0R}^1 = \frac{\pi}{2} \quad (28)$$

$$\eta_{1R}^2 \neq \frac{\pi}{2}, \quad \eta_{1L}^2 = \frac{\pi}{2}.$$

The choice of Eq. (28) reduces the five-level system to an effective three-level system whose interaction Hamiltonian is expressed as

$$\begin{aligned} H_I(t) &= -\frac{1}{2}A_1(t)\cos\eta_{0L}^1\boldsymbol{\mu}_{0,em}|0L\rangle\langle e,m| \\ &\quad -\frac{1}{2}A_2(t)\cos\eta_{1R}^2\boldsymbol{\mu}_{1,em}|1R\rangle\langle e,m| \\ &\quad + \text{h.c.} \end{aligned} \quad (29)$$

Therefore, the localized densities $|1L\rangle\langle 1L|$ and $|0R\rangle\langle 0R|$ do not contribute to the laser-driven dynamics, and the selective preparation of R enantiomers from the racemic mixture can be achieved by the STIRAP described above.

The localization densities $P_L(t)(P_R(t))$ defined as

$$P_L(t) \equiv \text{Tr}[(|0L\rangle\langle 0L| + |1L\rangle\langle 1L|) \rho(t)] \quad (30a)$$

and

$$P_R(t) \equiv \text{Tr}[(|0R\rangle\langle 0R| + |1R\rangle\langle 1R|) \rho(t)] \quad (30b)$$

are, respectively, given by

$$P_L(t) = \frac{1}{2} \cos^2 \Theta(t)$$

and

$$P_R(t) = \frac{1}{2} + \frac{1}{2} \sin^2 \Theta(t), \quad (31)$$

with

$$\Theta(t) = \tan^{-1} \frac{A_1(t)\cos\eta_{0L}^1\boldsymbol{\mu}_{0,em}}{A_2(t)\cos\eta_{1R}^2\boldsymbol{\mu}_{1,em}}. \quad (32)$$

Equations (31) and (32) show that a complete population transfer from the lowest state of L enantiomer to the first excited vibronic state of R enantiomer can be performed by applying the pump and Stokes pulses counterintuitively just as in the ordinary STIRAP method.²

III. RESULTS AND DISCUSSION

We apply the new STIRAP method proposed in Sec. II to a transfer of molecular handedness of a preoriented H₂POSH.²¹ As shown in Fig. 4, it is assumed that the P–S bond is oriented along the z axis and that the O=P–S groups are in the x – z plane. In this simplified model, the torsional motion of the hydrogen bonded to the sulfur, ϕ , is the reaction coordinate. Since we consider the electronic

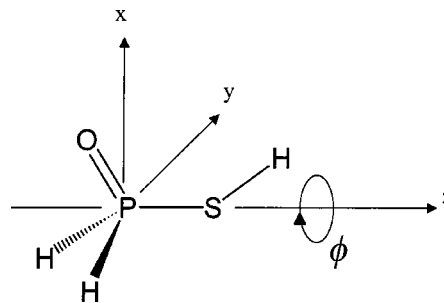


FIG. 4. A preoriented H₂POSH model, where ϕ is the torsional angle around the P–S axis.

ground state S_0 and the first excited singlet state S_1 in the Born–Oppenheimer approximation, the Hamiltonian of the system in an electric field is given as

$$H(t) = \begin{pmatrix} T + V_g(\phi) & -\boldsymbol{\mu}_{ge}(\phi) \cdot \mathbf{E}(t) \\ -\boldsymbol{\mu}_{eg}(\phi) \cdot \mathbf{E}(t) & T + V_e(\phi) \end{pmatrix}, \quad (33)$$

where T is the kinetic energy operator of the torsional motion

$$T = -\frac{\hbar^2}{2I} \frac{d^2}{d\phi^2}, \quad (34)$$

with I being the moment of inertia of the torsional hydrogen. The second terms of the diagonal elements $V_g(\phi)$ and $V_e(\phi)$ represent the potential energies along the reaction coordinate in which g and e denote the ground and the first electronic excited states, respectively. The interaction of the molecule with the electric field is semiclassically treated in the dipole approximation including the dipole operators $\boldsymbol{\mu}_{nm}(\phi)$ ($n, m = g, e$) and the electric field $\mathbf{E}(t)$. Since we employ ultraviolet laser fields, the electric dipole interactions $-\boldsymbol{\mu}_{ii}(\phi) \cdot \mathbf{E}(t)$ ($i = g, e$) were neglected. We made use of the known *ab initio* results for $V_g(\phi)$ and $V_e(\phi)$ and those for the transition dipole moment $\boldsymbol{\mu}_{ge}(\phi)$.²⁵

The eigenstates of each electronic state are obtained by solving the time-independent Schrödinger equations:

$$[T + V_g]|g, v \pm\rangle = E_{gv \pm}|g, v \pm\rangle, \quad v = 0, 1, 2, \dots, \quad (35a)$$

$$[T + V_e]|e, v'\rangle = E_{ev'}|e, v'\rangle, \quad v' = 0, 1, 2, \dots, \quad (35b)$$

where $|g, v \pm\rangle$ and $|e, v'\rangle$ represent torsional eigenstates of the electronic ground and excited states, and $E_{gv \pm}$ and $E_{ev'}$ are the associated eigenenergies, respectively. The signs $+$ and $-$ in $|g, v \pm\rangle$ mean that the corresponding eigenfunctions are symmetric and antisymmetric with respect to ϕ , respectively. The torsional eigenfunctions were calculated using the Fourier grid Hamiltonian method with 256 grid points.³⁸ The torsional states localized in the left and right wells are obtained from the superposition of the eigenstates below the barrier

$$|g, vL\rangle = \frac{1}{\sqrt{2}}(|g, v+\rangle + |g, v-\rangle), \quad (36a)$$

$$|g, vR\rangle = \frac{1}{\sqrt{2}}(|g, v+\rangle - |g, v-\rangle). \quad (36b)$$

It has been found that the angles between the projections of $\boldsymbol{\mu}_{0L,em}(\boldsymbol{\mu}_{0R,em})$ to the y - z plane and the z axis are nearly $-\pi/4(\pi/4)$,²⁵ where $\boldsymbol{\mu}_{0L,em} \equiv \langle g,0L | \boldsymbol{\mu}_{ge} | e,m \rangle$ and $\boldsymbol{\mu}_{0R,em} \equiv \langle g,0R | \boldsymbol{\mu}_{ge} | e,m \rangle$.

In the actual treatment, we employed a sufficient number of eigenstates to reach numerical convergency.

We first examined a pure state case in which the transfer of the molecular handedness from the initial state $|g,0L\rangle$ to the final state $|g,0R\rangle$ is induced by a laser polarized in the y - z plane. For simplicity, the laser field used takes the following form:

$$\mathbf{E}(t) = \boldsymbol{\eta}(t) A_0 \cos \omega t, \quad (37)$$

where A_0 is the amplitude and ω is laser frequency that is fixed to the energy separation between $|e,5\rangle$ and $|g,0L\rangle(|g,0R\rangle)$. The time dependence of the unit vector $\boldsymbol{\eta}(t)$ is specified by $\eta_L(t)(\eta_R(t))$ for which we employ the following function for the sake of convenience:

$$\eta_L(t) = \frac{\pi}{2} + \frac{\pi}{2} \sin^2\left(\frac{\pi}{2} \frac{t}{t_f}\right), \quad (38a)$$

with

$$\eta_R(t) = \eta_L(t) - \frac{\pi}{2}. \quad (38b)$$

Therefore, the direction of the unit vector evolves from that of $\boldsymbol{\mu}_{0R,em}$ to that of $\boldsymbol{\mu}_{0L,em}$ around the z axis in the y - z plane to satisfy Eq. (11). The derivatives of both $\eta_L(t)$ and $\eta_R(t)$ with respect to time take the same form as each other:

$$\dot{\eta}_L(t) = \dot{\eta}_R(t) = \frac{\pi^2}{4t_f} \sin\left(\frac{\pi t}{t_f}\right). \quad (39)$$

This function has a maximum at $t = t_f/2$.

The laser parameters were set to $A_0 = 2.2 \times 10^9$ V/m and $t_f = 6.0$ ps. The value of intensity is taken in order that the three-level picture is held in good approximation. In a region of stronger intensity, the efficiency of the population transfer becomes worse. This is due to the influence of competitive transitions. Given A_0 , t_f is estimated from Eq. (17). Since $\alpha \approx \pi/2$ in this model, it can be seen from Eq. (19) that the value of $f_\alpha(\eta_R(t))$ is always larger than 1 during the time evolution of the system. Substituting Eqs. (38b) and (39) into Eq. (17) at $t = t_f/2$ under the condition $\alpha \approx \pi/2$ and taking $A(t)$ in Eq. (17) as A_0 , we obtain

$$\frac{\pi^2}{2\mu_{0,em}A_0} \ll t_f. \quad (40)$$

In our simulation, the left-hand side of Eq. (40) is about 1.2 ps, and we set it five times, 6.0 ps as t_f .

Figure 5 shows temporal behaviors of the molecular handedness. We can see from Fig. 5 that the molecular handedness from $|g,0L\rangle$ to $|g,0R\rangle$ was nearly completely transferred within 6 ps. It is interesting to see in Fig. 5 that $d\eta_R(t)/dt$ is maximized at $t \sim 3$ ps when the population of L and R enantiomers are equal. At that time, the nonadiabatic effects become maximum [See Eqs. (17) and (18)]. We have confirmed the robustness of the solutions with respect to

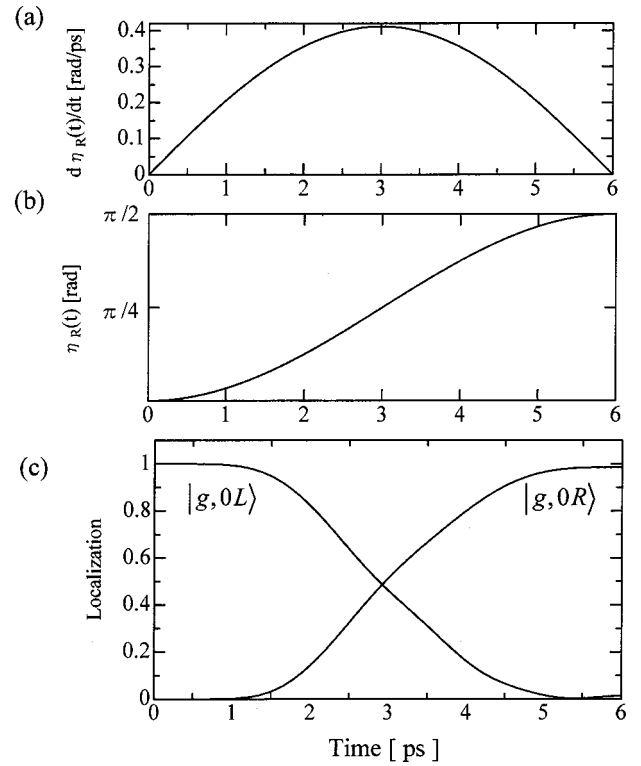


FIG. 5. Transfer of molecular handedness from $|g,0L\rangle$ to $|g,0R\rangle$ by a laser with time-dependent polarization: (a) $d\eta_R(t)/dt$ vs time, (b) $\eta_R(t)$ vs time, and (c) population vs time.

changes in A_0 and t_f , although the results are not shown. Other types of $\eta_R(t)$ such as a Gaussian form can be adopted as well.

We now present the results of a selective preparation of R enantiomers from a preoriented racemic mixture at a low temperature limit:

$$\rho(t=0) = \frac{1}{2}(|g,0L\rangle\langle g,0L| + |g,0R\rangle\langle g,0R|) \quad (41)$$

↓ STIRAP

$$\rho(t=t_f) = \frac{1}{2}(|g,1R\rangle\langle g,1R| + |g,0R\rangle\langle g,0R|). \quad (42)$$

That is, we consider a transfer of the molecular handedness from $|g,0L\rangle$ to $|g,1R\rangle$. The total electric field $\mathbf{E}(t)$ is composed of two components with Gaussian-type envelopes

$$\mathbf{E}(t) = \sum_{i=1}^2 \mathbf{e}_i A_i(t), \quad (43)$$

with

$$A_i(t) = A_i^0 g_i(t) \cos \omega_i t, \quad (44)$$

and

$$g_i(t) = \exp[-(t-t_i)^2/\sigma_i^2], \quad (45)$$

where A_1^0 and A_2^0 are the maximum amplitudes of the pump and Stokes pulses, respectively, and $g_i(t)$ is the Gaussian envelope function that is characterized by the center of time t_i and pulse width σ_i . The laser frequencies ω_1 and ω_2 were fixed to the transition frequencies $\omega_{e5,g0L} \equiv (E_{e5} - E_{g0L})/\hbar$ and $\omega_{e5,g0R} \equiv (E_{e5} - E_{g1R})/\hbar$, respectively.²⁵ The laser pa-

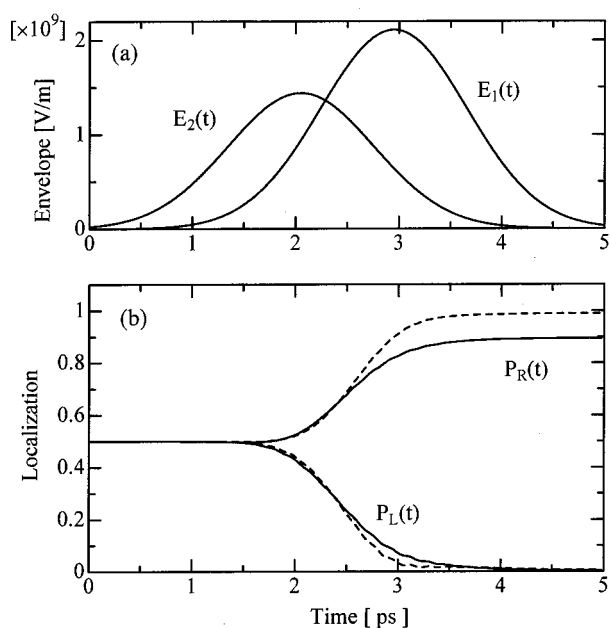


FIG. 6. Selective preparation of *R* enantiomers from a racemic mixture by STIRAP: (a) envelope of laser pulses vs time, and (b) time evolution of $P_L(t)$ and $P_R(t)$, which are defined in Eq. (46). Dashed lines and solid lines are the case for $\Gamma=0$ and $1/\Gamma=0.5$ ps, respectively.

rameters were set to $A_1^0=2.1\times 10^9$ V/m, $A_2^0=1.4\times 10^9$ V/m, $\sigma_1=\sigma_2=1.0$ ps, and $t_1-t_2=0.9$ ps. We have chosen the directions of \mathbf{e}_1 and \mathbf{e}_2 as $-\pi/4$ and $\pi/4$ from the z axis in the $y-z$ plane to satisfy Eq. (28). The time evolution of $\rho(t)$ is estimated by $P_L(t)$ and $P_R(t)$, which are defined as

$$P_L(t) = \text{Tr}[(|g,0L\rangle\langle g,0L| + |g,1L\rangle\langle g,1L|)\rho(t)] \quad (46a)$$

and

$$P_R(t) = \text{Tr}[(|g,0R\rangle\langle g,0R| + |g,1R\rangle\langle g,1R|)\rho(t)], \quad (46b)$$

respectively.

Figure 6 shows the enantiomer control of H_2POSH in the mixed case. Dashed lines denote the temporal behaviors in the absence of any damping effects. The final product yield is 98.9% by applying the pumping and Stokes pulses counterintuitively shown in Fig. 6(a). González *et al.*²⁵ have proposed an interesting strategy to separate enantiomers from a racemic mixture in a subpicosecond time scale using chirped laser pulses and a half STIRAP method. Their control field consists of a five step sequence of pulses that achieves 100% of racemate purification of H_2POSH in the low temperature limit. As shown in Fig. 6, in our new STIRAP method, only pump and Stokes pulses are counterintuitively applied in achieving almost complete purification within 5 ps.

So far, we used a simplified model of H_2POSH in which all vibrational modes except for the torsional mode are frozen. In fact, Manz's group recently found a significant coupling between the torsional motions of an S-H bond and the

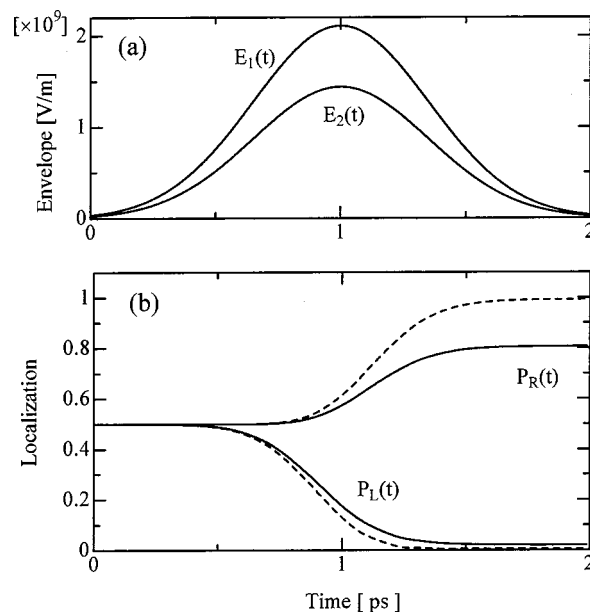


FIG. 7. Selective preparation of an *R* enantiomer by a π -pulse approach: (a) envelope of laser pulses vs time, and (b) time evolution of $P_L(t)$ and $P_R(t)$. Dashed line and solid line are the cases for $\Gamma=0$ and $1/\Gamma=0.5$ ps, respectively.

stretching vibrational mode of a P-S bond in the S_1 state. Therefore, it is necessary to incorporate such a mode coupling effect into a density matrix formalism for a realistic study of laser control. For a quick assessment of the mode coupling, we examined the efficiency of population transfer by the STIRAP by introducing a damping term Γ . This damping term originating from the mode coupling is derived using an effective Hamiltonian formalism. The resultant effective Hamiltonian matrix is expressed as a modification of Eq. (33), i.e., $i\Gamma/2$ is added in the diagonal matrix element H_{22} . Although the process becomes nonunitary due to $\Gamma \neq 0$, this treatment may be a good approximation for the description of a dissipative system since the population in the electronic excited state was small for the STIRAP and rapidly passes through for the π pulse approach described below.

We compared the results obtained by the STIRAP with those obtained by a π pulse-like approach that is effective for a fast population transfer in a three-level system based on a nonadiabatic process.³⁹ This approach requires the following conditions for two laser pulses with the Gaussian envelopes:

$$\mu_{0L,e5}A_1^0g_1(t) = \mu_{1R,e5}A_2^0g_2(t) = \Omega(t)\hbar, \quad (47)$$

$$\int \Omega(t)dt = \sqrt{2}\pi.$$

For convenience, we call this approach the π -pulse approach. In this method, there is no time delay between two pulses. This makes the population created in the electronic excited state pass rapidly.

The solid lines in Fig. 6(b) denote the temporal behaviors of the preparation of pure enantiomers with lifetime $1/\Gamma=0.5$ ps by the STIRAP. Figure 7 shows the population dynamics by the π -pulse approach. The dashed lines in Fig. 7(b) show the population dynamics with $\Gamma=0$, and the solid

lines show the results with the lifetime $1/\Gamma = 0.5$ ps. In Fig. 7(b), the maximum amplitudes were set to be the same as those in the STIRAP and $\sigma_1 = \sigma_2 = 0.6$ ps. The final localizations in the case of $\Gamma = 0$ were 99.2% and 98.9% for the π -pulse approach and the STIRAP, respectively. In the case of $1/\Gamma = 0.5$ ps, these values decreased to 80.7% and 89.4%, respectively. The population transfer by the STIRAP proceeds via a dark state consisting of $|g,0L\rangle$ and $|g,1R\rangle$, namely, without any appreciable population of intermediate states, and the efficiency of the process is therefore not greatly influenced by the decay from the intermediate states. The results indicate that the STIRAP is more efficient for population transfer than is the π -pulse approach. The value of the lifetime adopted here is tentative at present and seems to be the maximum. Therefore, the effects of Γ shown in Figs. 6 and 7 are qualitative, and a realistic value of Γ is needed to quantitatively discuss the effects of the mode couplings in the electronically excited state of H_2POSH .

The new method developed in this paper is based on a two-step optical process of a single STIRAP excitation. In many reaction systems involving polyatomic molecules of interest, the Franck-Condon factors for excitation to the upper electronic surface are usually very poor because of a change in their multidimensional potential energy surfaces. Therefore, the direct application of the single STIRAP excitation results in negligibly small population transfer. However, a method of sequential STIRAP excitations⁴⁰ is applicable to such reaction systems by introducing the concept of the time-dependent photon polarization vectors proposed in this paper.

IV. CONCLUSIONS

We have developed a new type of STIRAP method that is applicable to population transfer in a degenerated system. Two cases of statistical states, a pure state and a mixed state were taken into account. Preoriented H_2POSH was treated as a model for the molecular handedness.

For a pure state case, we showed an almost complete population transfer from an L (R) enantiomer to an R (L) enantiomer by a laser with a time-dependent polarization direction. We have clarified the adiabatic criterion as well.

For a mixed state case, we demonstrated the preparation of pure enantiomers from its racemic mixture. In the low temperature limit, a five-level model reduces a three-level model by setting the direction of polarizations of both pump and Stokes pulses in such a way that the forward process is optically allowed and backward is forbidden. We carried out simulations taking into account a relaxation of an electronic excited state. We compared the results obtained by the STIRAP with those obtained by a π -pulse approach under the conditions that the maximum intensities are the same and both pulses have Gaussian envelopes. The comparison showed that the STIRAP can maintain a higher product yield than can the π -pulse approach in spite of longer irradiation of the pulse in the STIRAP.

Experimentally, combined with a new technique of time-dependent polarization control,⁴¹ the STIRAP presented here is a promising method for selective population transfer in

other (pseudo) degenerated systems such as a hydrogen-bonded system.^{42,43}

ACKNOWLEDGMENTS

The authors thank Professor J. Manz and Dr. L. González for their critical comments and fruitful suggestions. This work was partly supported by a German-Japanese International Joint Research Project, Grants-in-Aid for Scientific Research from the Ministry of Education, Science, Sports, Culture and Technology, Japan (Nos. 10640480 and 13640497) and a Grant-in Aid for Scientific Research on Priority Areas (No. 11166205). One of the authors (K.H.) acknowledges support from the Research Fellowship of the Japan Society for the Promotion of Science (No. 6254).

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