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Isotopic effects on the control of molecular handedness of H_2POSH by ultrashort laser pulses

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Abstract. The selective preparation of an enantiomer starting from a pure state of H_2POSH representing a 50%:50% mixture of two enantiomers with opposite chiralities is extended to its deuterated counterpart, H_2POSD. A one-dimensional model involving the torsional angle of S–H/D around a pre-oriented P–S axis is used. The design of an appropriate sequence of ultrashort infrared laser pulses to achieve molecular handedness for H_2POSH/D is based on the characteristic level splitting and tunneling times of both molecules. A simple scheme of two linearly polarized laser pulses involving a three level system serves to convert the different isotopomers to opposite enantiomers, for any given mixture of H_2POSH and H_2POSD molecules.

PACS. 11.30.Rd Chiral symmetries – 33.15.Hp Barrier heights (internal rotation, inversion, rotational isomerism, conformational dynamics) – 42.50.Ct Quantum description of interaction of light and matter; related experiments

1 Introduction

The use of external fields to induce molecular handedness is becoming a hot topic inside the general field of laser pulse control of reactions in femtosecond chemistry [1,2]. The first suggestion to laser controlled symmetry breaking was made in the early nineties by Shapiro and Brumer [3]. In their work, linearly polarized lasers are applied to convert a prochiral molecule ABA′ into a coherent superposition of states, followed by asymmetric photodissociation, either A+BA′ or AB+A′. In the last few years, new scenarios of symmetry breaking based on coherent control [4–6] or optimal control [7] are starting to proliferate.

In a previous study [8], our group reported the selective preparation of enantiomers by means of local optimal control [9–11] applied to the phosphinothioic acid, H_2POSH, at a limit of low temperature. H_2POSH shows a double well potential energy curve, which supports two enantiomers (left, L and right, R) separated by a barrier. The molecule is assumed to be pre-oriented and initially in its torsional ground state, which corresponds to a coherent 50%:50% superposition of left and right atropisomers [12]. An optimal, elliptical polarized laser pulse in the time scale of ps drives the system into a coherent, almost 50%:50%, superposition of the two lowest torsional states, which yields a localized non symmetric state representing the pure enantiomer [13]. This study was based on the quantum simulation of wavepacket dynamics for the laser driven torsional motion of the model system in the electronic ground state. In a subsequent paper [14], we analysed the complicated optimal pulse, its resulting population dynamics and the symmetry selection rules, to find that the underlying mechanism can be translated into a simple pump-dump scheme *via* a doublet of excited torsional states with opposite symmetries. Thus, the particular transitions could be modeled by a simple series of sequential laser pulses with analytical shapes following the same kind of scheme undergone in the optimal pulses without any loss of selectivity. Furthermore, the decomposition of the complex optimal pulse into analytical ones allowed us to develop even simpler mechanisms and new scenarios for the selective preparation of enantiomers using linear polarized pulses instead of elliptically polarized ones. In reference [14] it was also shown that the selection of the left or right enantiomer can be controlled in two basic ways. One possibility consists on changing the corresponding left or right polarizations of the elliptical pump and/or dump pulse; the other introduces a delay time between the pump and dump pulses equivalent to the real tunneling time of the corresponding doublet, *i.e.* half of the full L → R → L oscillation period.

It is important to emphasize that the previous type of studies [3,8,14] consider as initial states molecular eigenstates and therefore, the time evolution of the laser driven coherent wavepacket is evaluated as solution of the time dependent Schrödinger equation. This situation is

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different from taking an incoherent superposition of states as an initial state, representing a racemic mixture, which must be described by density matrices obtained as solutions of the Liouville-Neumann equation. These scenarios have been addressed in references [15,16].

Other approaches to asymmetric synthesis by means of external fields have been reviewed in the literature [17,18]. An alternative suggestion is the use of the parity-violating weak neutral current interaction, which lifts the degeneracy of the different chiral molecules, so that one enantiomer may be excited selectively [19]. Also important are the complementary works intended to the stabilization of enantiomers [20] or the selective transformation into the opposite one [21], as well as into a superposition of chiral wavefunctions [22], which can be designed as sequential steps after converting a racemate into a pure enantiomer [15,16].

In this paper we will explore the effect of isotopic substitution of the hydrogen bonded to the sulfur in H_2POSH, giving H_2POSD. The heavier system should have lower energy eigenstates, allowing a larger number of excited doublets below the barrier, in comparison with the lighter isotopomer. Besides, the tunneling times of the lower doublets of H_2POSD should be longer in comparison with those of H_2POSH. These facts will influence the parameters of the ultrashort laser pulses used to achieve selectivity as well as the mechanisms employed. In principle, it is also possible to conceive a situation in which we have a mixture of H_2POSH and H_2POSD molecules. Then, with a certain sequence of laser pulses the H_2POSH set of molecules can be selectively converted to, for instance, the left enantiomer, while its deuterated counterpart, H_2POSD, is transformed to the right enantiomer using a different laser sequence. In that way we can control the desired target state exploiting the differences between the hydrogen and its heavier isotope. It is our purpose to show how to apply the mechanisms that have been found selective in the case of H_2POSH, to the deuterated counterpart. Moreover, we will demonstrate an even simpler scenario to prepare enantiomers for both H_2POSH and H_2POSD.

This paper will present the model and techniques in Section 2, the results and discussion in Section 3 and the conclusions in Section 4.

2 Model and techniques

As in our previous work [8,14,15], we adopt a one-dimensional potential energy curve as a function of the OPSH torsional angle ϕ, which describes the rotation of the S–H bond around the P–S molecular axis. H_2POSH forms left or right atropisomers depending on the negative or positive value of ϕ, respectively. For simplicity, we assume our model system, H_2POSH, to be preoriented with its P–S axis in the z-direction of the laser pulse, and the dihedral angle ϕ decoupled from others degrees of freedom. The potential energy curve calculated at the MP2/6-311G$(2p,d)$ level of theory (see details in Ref. [8]) is depicted in Figure 1 together with the energy levels $E_{v\pm}$ of the torsional eigenstates $\Phi_{v\pm}(\phi)$ for H_2POSH and H_2POSD. The corresponding dipole moment components, calculated at the same level of theory, have different symmetries along ϕ; μ_x is symmetric with respect to the mirror plane, whereas μ_y is antisymmetric with respect to the same plane [8].

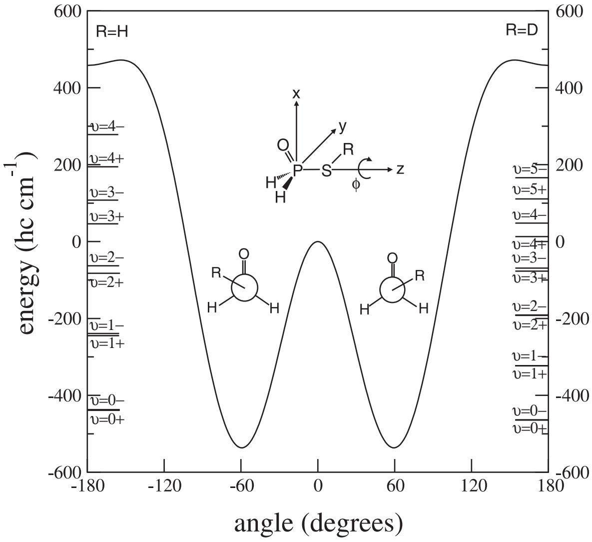


Fig. 1. The model system H_2POSR (R = H or D) with its double well potential and the torsional levels of H_2POSH (right) and H_2POSD (left).

The laser pulse preparation of enantiomers is simulated by means of representative molecular wavepacket propagations and the symmetry breaking is achieved due to the interaction of the laser field with the two components of the dipole moment which have different symmetries. The time evolution of the laser driven wavefunction $\Psi(t,\phi)$ is described by the time-dependent Schrödinger equation,

$$\mathrm{i}\hbar\frac{\partial}{\partial t}\Psi(t,\phi) = H(t)\Psi(t,\phi). \qquad (1)$$

The Hamiltonian in the semiclassical dipole approximation is given by

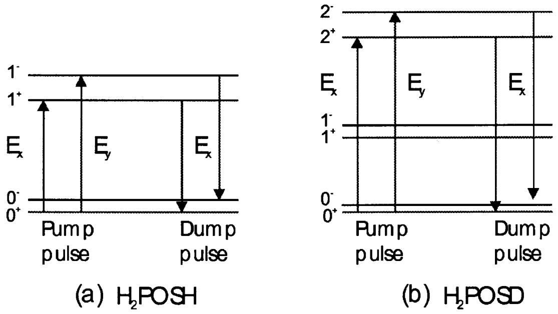
$$H(t) = -\frac{\hbar^2}{2I}\frac{\partial^2}{\partial\phi^2} + V(\phi) - \boldsymbol{\mu}(\phi)\cdot\mathbf{E}(t), \qquad (2)$$

which describes the kinetic and potential energies, together with the dipole couplings, $\mu_x(\phi)$ and $\mu_y(\phi)$, to the laser field, $E_x(t)$ and $E_y(t)$. I is the moment of inertia of the rotating hydrogen or deuterium, respectively.

The torsional eigenstates, $\Phi_{v\pm}(\phi)$, of the double well potential are calculated using the Fourier grid Hamiltonian technique [23]. For energies $E_{v\pm}$ below the potential barrier at $\phi = 0$, the localized eigenfunctions $\Phi_{v\pm}(\phi)$ occur as doublets of torsional states labeled with $v = 0, 1, 2, 3, ...$ and with + or − depending on the symmetry of the corresponding eigenfunction. As seen in Table 1, the number of localized doublets for H_2POSH and H_2POSD are different, they have different energy splittings, $\Delta E = (E_{v-} - E_{v+})$ and, therefore, the corresponding tunneling times, which are half of the full L → R → L

Table 1. Comparison of the energy splitting, ΔE_v (in cm^{-1}), and tunneling times, defined as half of the full L → R → L oscillation period τ_v (in ps), of the localized doublets comprised below the barrier for H_2POSH and H_2POSD, respectively.

v		H_2POSH	H_2POSD
0	ΔE_v	0.053	0.0007
	τ_v	630	47600
1	ΔE_v	1.6	0.036
	τ_v	20.9	927
2	ΔE_v	17.8	0.743
	τ_v	1.88	44.9
3	ΔE_v	-	8.087
	τ_v	-	4.12



(a) H_2POSH (b) H_2POSD

Fig. 2. Selective transitions for H_2POSH (a) *vs.* H_2POSD (b) between torsional states induced by an elliptically polarized pump pulse and a linearly polarized dump pulse.

oscillation period τ_v, defined as $\tau_v \Delta E_v = h$, are also different. Taking + or − superposition of these eigenstates, $\Phi_{v\pm}(\phi)$, we can obtain the corresponding left (L) or right (R) pure enantiomers, respectively [13]:

$$\Psi_{v\mathrm{L/R}}(\phi) = \frac{1}{\sqrt{2}}(\Phi_{v+} \pm \Phi_{v-}). \tag{3}$$

Torsional eigenstates for higher v above the barrier are delocalized and they are not shown in Table 1.

As initial condition, we choose our system to be in the lowest torsional state,

$$\Psi_v(t = 0, \phi) = \Phi_{0+}, \tag{4}$$

which corresponds to a 50%:50% coherent superposition of L and R enantiomers. The final goal after a sequence of adequate laser pulses is to populate either the left or the right state, $\Psi_{0\mathrm{L}}$ or $\Psi_{0\mathrm{R}}$, described by equation (3). For this purpose we will employ a sequence of laser pulses designed as:

$$\begin{aligned} E_x(t) &= E_x^0 \cos(\omega_x(t - t_\mathrm{d}) + \eta_x)s(t - t_\mathrm{d}) \\ E_y(t) &= E_y^0 \sin(\omega_y(t - t_\mathrm{d}) + \eta_y)s(t - t_\mathrm{d}) \end{aligned} \tag{5}$$

with amplitudes E_x^0, E_y^0, carrier frequencies ω_x, ω_y, time delays t_d, phases η_x, η_y, and shape functions $s(t)$. For convenience, we choose $\sin^2$ shape functions [24] of the form

$$\begin{aligned} s(t) &= \sin^2\left(\frac{\pi t}{t_\mathrm{p}}\right) \qquad \text{for} \quad 0 \le t \le t_\mathrm{p}, \\ s(t) &= 0 \qquad\qquad\quad \text{else} \end{aligned} \tag{6}$$

with pulse duration t_p. According to the symmetry of the dipole moment components, the interaction of the system with a x-linearly polarized laser pulse will only induce transitions between eigenstates of the same symmetry. Likewise, a y-linearly polarized pulse will only induce transitions between states of opposite symmetries. These symmetry selection rules will help us to design an appropriate sequence of laser pulses that forms a coherent superposition of the Φ_{0+} and Φ_{0-} eigenstates, and therefore creates a pure enantiomer (*cf.* Eq. (3)). In order to monitor the laser driven population dynamics of the molecular eigenstates $\Phi_{v\pm}(\phi)$, they are projected on $\Psi(t, \phi)$,

$$P_{v\pm}(t) = |\langle \Phi_{v\pm}(\phi) | \Psi(t, \phi) \rangle|^2. \tag{7}$$

In the same way, the preparation of the left or right enantiomer can be followed with the corresponding localization function defined as

$$P_{v\mathrm{L/R}}(t) = |\langle \Psi_{v\mathrm{L/R}}(\phi) | \Psi(t, \phi) \rangle|^2. \tag{8}$$

3 Results and discussion

In reference [14] we showed that it is possible to use not only elliptically polarized laser pulses in order to separate a 50%:50% coherent L/R mixture, but also linearly polarized light. One simple scheme involving both types of pulses was derived combining an elliptically polarized pump pulse with a linearly polarized dump one [14]. The efficacy of these pulses is based on the symmetry selection rules. As shown in Figure 2a, the $E_x(t)$ component of the elliptical pump pulse induces a transition of 50% of the population from the ground state Φ_{0+} to the symmetric first excited doublet component, Φ_{1+}, while the $E_y(t)$ part transfers the rest of the population from Φ_{0+} to the asymmetric component Φ_{1-}. This 50%:50% superposition of torsional excited states is dumped to the first doublet with one linearly polarized pulse that is short enough and, therefore, broad enough to induce transitions to both eigenstates, Φ_{0+} and Φ_{0-}, thus creating the pure left enantiomer of H_2POSH, according to equation (3).

For H_2POSD we can apply a similar type of mechanism, by going *via* the second excited doublet of eigenstates, $v = 2$. The corresponding selective transitions induced by the pump and dump pulses are shown in Figure 2b. The sequence of pulses of the type equation (5), together with the resulting population dynamics and the localization are illustrated in Figure 3. The parameters of the elliptically polarized pump pulse are $E_x^0 = 1.9$ GV/m, $E_y^0 = 1.3$ GV/m, $\omega_x = \omega_y = 273.00\ \mathrm{cm}^{-1}$, $\eta_x = \eta_y = 0°$, $t_\mathrm{d} = 0$ ps and $t_\mathrm{p} = 6$ ps. Likewise, the parameters of the linearly polarized dump pulse are $E_x^0 = 3.1$ GV/m, $\omega_x = 273.00\ \mathrm{cm}^{-1}$, $\eta_x = \eta_y = 0°$, $t_\mathrm{d} = 12$ ps and $t_\mathrm{p} = 6$ ps. It is interesting to note that we need a time gap of 6 ps between the pump and dump pulses in order to form $\Psi_{0\mathrm{R}}$,

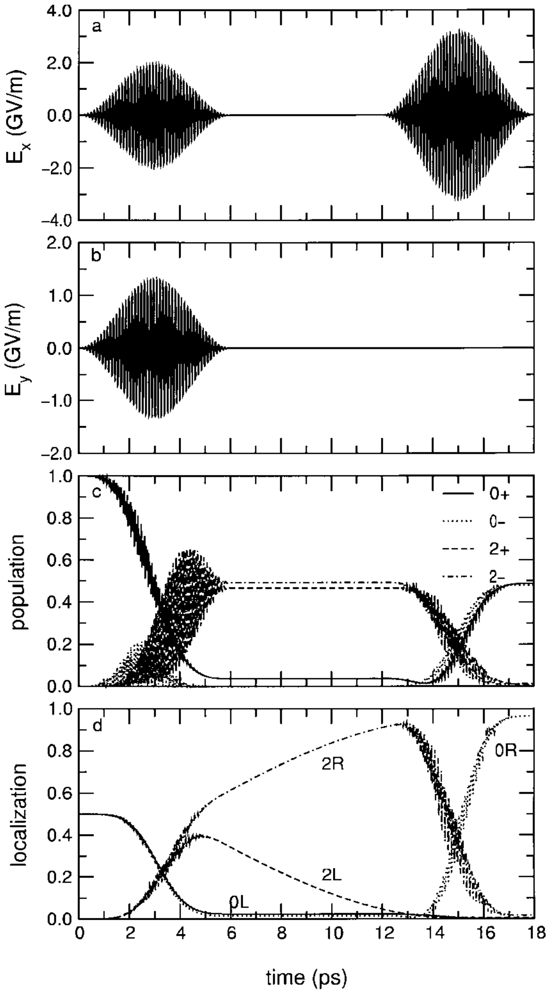


Fig. 3. Selective preparation of the right enantiomer of H$_2$POSD by an elliptical polarized pump pulse and a linear polarized dump pulse. Panels (a) and (b) show the electric field components E_x and E_y *versus* time, respectively. Panel (c) depicts the time-evolution of the population dynamics of the different eigenstates involved in the mechanism, as defined in equation (7). Panel (d) shows the time-evolution of the localization as defined in equation (8).

which was not necessary in the case of H$_2$POSH. The total time delay for the second pulse, t_d, of 12 ps is the time the wavepacket employs to accumulate the appropriate phase before it is dumped down. One sees from the localization in Figure 3d that, $\Psi_{2\mathrm{R}}$ is still not predominantly formed after the pump pulse, as it could be expected after forming a coherent 50%:50% superposition of the states Φ_{2+} and Φ_{2-}. Only after additional 6 ps, tunneling in the excited doublet Φ_{2+}, Φ_{2-}, supports the formation of more than 95% of $\Psi_{2\mathrm{R}}$, and only then it should be dumped to the doublet $v = 0$ to form $\Psi_{2\mathrm{R}}$. In the case of H$_2$POSH the time duration of the pulse is already sufficient to create the proper phase in the first excited doublet before dumping, because the tunneling time $\tau_1/2$ is much shorter than for H$_2$POSD (*cf.* Tab. 1). One can also use the first excited doublet, $v = 1$, in H$_2$POSD, using the above discussed mechanism, but all our attempts to achieve selectivity on a similar time-scale failed, due to the exceedingly long tunneling time, $\tau_1 \approx 1$ ns. Only after introducing a time delay of about 200 ps localization on the $\Psi_{1\mathrm{L}}$ state of H$_2$POSD is achieved by more than 90%, and it can be accordingly dumped to $\Psi_{0\mathrm{L}}$.

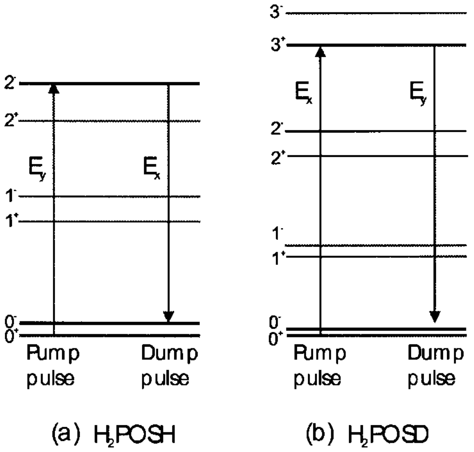


Fig. 4. Selective transitions for H$_2$POSH (a) *vs.* H$_2$POSD (b) between torsional states induced by linearly polarized pump and dump pulses.

These results point to the fact that, in principle, the wavepacket always needs a certain time to accumulate the proper phase, which creates localization in the right or left potential well in the intermediate excited doublet, before the dump process takes place. This time depends on the phase created in the excited doublet after the pump pulse. In the most unfavorable case, localization on the excited eigenstates is still close to 50%:50% after the pump pulse and a maximal time delay of a half of the tunneling time of the excited doublet (including the duration of the pump pulse) is needed to reach almost 100% localization of one enantiomer in the intermediate states.

As mentioned at the beginning of this section, it has been previously demonstrated that it is possible to use a sequence of exclusively linearly polarized laser pulses, each of them performing one of the transitions shown in the Figure 2, *i.e.* using four linearly polarized pulses [14]. Here we will show that there is a different and even simpler way to convert a coherent superposition of L/R into its pure enantiomers using linearly polarized laser pulses, which will be used to enantio-differentiate a given mixture of H$_2$POSH and H$_2$POSD molecules. The mechanism proposed is depicted in Figure 4. Two linear pulses involving three levels suffice for achieving selectivity, provided the pump and dump frequencies are different enough to avoid interference between them. Let us start with the case of H$_2$POSH. The sequence of laser pulses, the resulting population of the states and localization are shown in Figure 5. The underlying mechanism is illustrated in Figure 4a. The first linear pulse, $E_y(t)$, transfers close to 50% of the initial population from Φ_{0+} to Φ_{2-} whereas the second pulse, $E_x(t)$, returns it to Φ_{0-}, thus forming the target state $\Psi_{0\mathrm{L}}$. The optimum laser parameters are

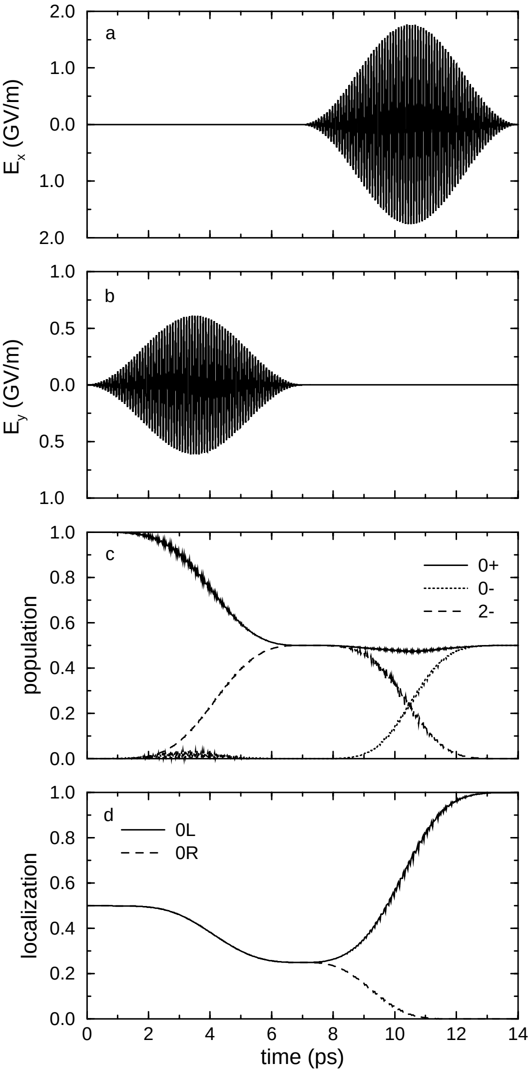


Fig. 5. Selective preparation of the left enantiomer of H_2POSH by two linearly polarized laser pulses. The notations are as in Figure 3.

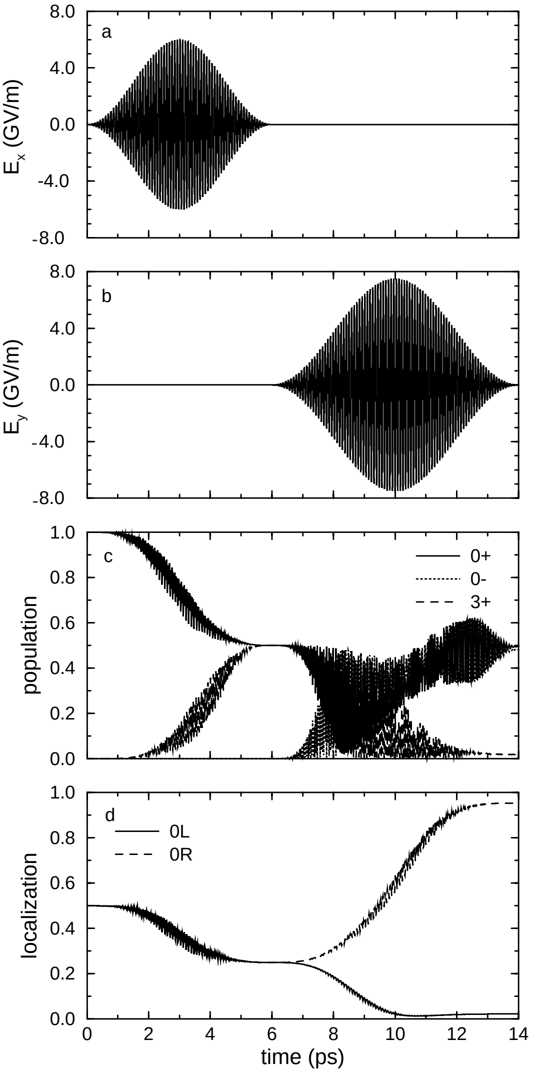


Fig. 6. Selective preparation of the right enantiomer of H_2POSD by two linearly polarized laser pulses. The notations are as in Figure 3.

$E_y^0 = 0.61$ GV/m, $E_x^0 = 1.76$ GV/m, $\omega_y = 373.36$ cm^{-1}, $\omega_x = 372.70$ cm^{-1}, $\eta_y = 0°$, $\eta_x = 25°$, and time duration, $t_\mathrm{p} = 7$ ps for both, the x- and y-polarized pulses.

The choice of Φ_{2-} as an intermediate eigenstate is not accidental. Firstly, the level splitting, $\Delta E_{v\pm}$, of the pair Φ_{v+} and Φ_{v-} ($v \neq 0$) has to be large enough to prevent that the x-polarized dump pulse also pumps the remaining 50% population from Φ_{0+} to Φ_{v+}. Within the duration of the ultrashort pulses we are using this is only achieved for $v \geq 2$. Secondly, one has to avoid carrier frequencies close to other resonant frequencies, which would produce undesired transitions destroying the enantiomer selectivity. This criterion excludes the alternative choice of Φ_{2+} as intermediate state since the $\Phi_{2+} \to \Phi_{0-}$ transition is near resonant with $\Phi_{2+} \to \Phi_{4-}$, and a hypothetical pulse designed to dump population from Φ_{2+} to Φ_{0-} would also pump it to the state Φ_{4-}.

The successful preparation of $\Psi_{0\mathrm{L}}$ for H_2POSH challenges us to prepare $\Psi_{0\mathrm{R}}$ for H_2POSD. In this case, the level splitting, $\Delta E_{v\pm}$, for $v = 2$ is not large enough to avoid pump and dump interference, therefore $v = 3$ is to be used (*cf.* Tab. 1). The corresponding series of selective transitions are summarized in Figure 4b. As intermediate state, Φ_{3+} is used. Therefore, we need a x-polarized pump laser pulse, $E_x(t)$, which transfers 50% of the initial population from Φ_{0+} to Φ_{3+}, and a y-polarized laser pulse to dump it from Φ_{3+} to Φ_{0-}. The corresponding optimized laser parameters are $E_x^0 = 6.0$ GV/m, $E_y^0 = 7.5$ GV/m, $\omega_x = 386.50$ cm^{-1}, $\omega_y = 390.00$ cm^{-1}, $\eta_x = \eta_y = 0°$, and time duration, $t_\mathrm{p} = 6$ and 8 ps, for the x-polarized and y-polarized pulses, respectively. These parameters yield the target state $\Psi_{0\mathrm{L}}$. If we use a 180°-phase shift, $\eta_y = 180°$, that is to say, we invert the polarization of the dump pulse, the pure right enantiomer of H_2POSD, $\Psi_{0\mathrm{R}}$, is obtained. The results can be seen in Figure 6. The intensities for the case of H_2POSD are higher than for H_2POSH since the transition is *via* a more excited doublet, $v = 3$ instead of $v = 2$, implying smaller transition dipole moments. The mechanism is, however, equivalent. The sequence of laser pulses for obtaining the left enantiomer of H_2POSH does not affect the deuterated counterpart, in the same way the laser pulses designed for obtaining the right enantiomer of H_2POSD also leave H_2POSH unaffected.

4 Conclusions

The purpose of this work was two-fold. First we wanted to extend our control of molecular handedness to a different molecule than H_2POSH, namely the deuterated counterpart, H_2POSD. We have shown that similar mechanisms allow us to selectively prepare a pure enantiomer starting from a coherent superposition of 50%:50% left and right enantiomers by means of an appropriate sequence of ultrashort infrared laser pulses. The differences between the laser pulses designed for H_2POSH and H_2POSD are governed by the intrinsic differences in the level splitting and tunneling times of each molecule. In particular, the tunneling times determine whether a time delay is necessary between pump and dump pulses in order to achieve selectivity. We have shown that, in the case of H_2POSD a time delay is needed due to the long tunneling times in the excited doublets of eigenstates used as intermediate states. On the contrary, for H_2POSH no delay is necessary, since the time duration of the pump pulse, of the same order of magnitude as a half of the tunneling time, is enough to achieve 100% localization on the intermediate doublet of eigenstates.

In addition, we have presented a different and simpler scenario to control molecular handedness in H_2POSH, using two linearly polarized pulses. On this basis, we could also accomplish the second goal of this work: given any mixture of H_2POSH and H_2POSD molecules we can apply two sequences of laser pulses which achieve independent selective preparations of left or right enantiomers, respectively.

After the end of the pulses, the pure enantiomers will start to tunnel towards the opposite enantiomer, destroying the achieved selectivity. The tunneling times, however, are long enough (630 ps and 47 600 ps, see Tab. 1) to subsequently stabilize the target state. In passing we note that the ns time scale of the tunneling time of H_2POSD, makes it a better candidate for the selective preparation of enantiomers and for subsequent stabilization.

Extensions of this work include taking into account the rotation of the phosphino group around the P–S axis [25], as well as other degrees of freedom in order to investigate the effects of intramolecular vibrational redistribution IVR. These models can also replace the initial state by a racemate at low temperature. Work along these lines is in progress.

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