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[26] For the specific case of singlet-excited azoalkanes, electron transfer from the exciplex cannot compete with the radiationless deactivation due to the endergonic energetics ($\Delta G_{et} = 20-40\,kJ\,mol^{-1}$, refs. [11, 12]). Similarly, hydrogen transfer within the exciplex, which has been postulated for other systems,[3, 7, 10] is unlikely to compete for azoalkanes as revealed by the small amount of product formation (<5%).

From a Racemate to a Pure Enantiomer by Laser Pulses: Quantum Model Simulations for H_2POSH**

Yuichi Fujimura, Leticia González, Kunihito Hoki, Dominik Kröner, Jörn Manz,* and Yukiyoshi Ohtsuki

Laser pulse control of chemical reactions is a hot topic in femtosecond chemistry.[1] After the theoretical design of various scenarios for laser pulse control,[2–7] experimental verifications have been demonstrated, initially for small molecules[8–10] but recently also for larger ones, for example selective laser pulse separation of different ligands from organometallic molecules.[11] A particular challenge in this field is the design of laser pulses for the selective preparation of enantiomers. The first suggestion was made by Shapiro and Brumer,[12] in which a laser pulse was used to convert a prochiral initial state of a symmetric precursor molecule ABA′ into a coherent superposition of two states with opposite symmetries, thus breaking the symmetry of the system. Subsequently, a second pulse should photodissociate the preexcited ABA′ system into selective enantiomers, either A + BA′ or AB + A′. A second scenario, presented for the model system H_2POSH assumed that the system is initially in its torsional ground state, which corresponds to a coherent 50%:50% superposition of left and right atropisomers.[13] An optimal laser pulse then drives the system to a coherent near 50%:50% superposition of the two lowest torsional states which have opposite symmetries, thus preparing a pure enantiomer. An alternative approach, introduced by Quack, suggests that it should be possible to selectively excite enantiomers, because they have slightly different energies due to interactions.[14, 15] Complementary to these proposals,[12–15] various methods have been developed for the subsequent laser pulse control of pure enantiomers, for example their stabilization[16] or the selective transformation of one enantiomer either into the opposite one[17] or into a superposition of chiral wavefunctions.[18]

Herein, we address the challenging problem of laser pulse preparation of a pure enantiomer from a racemate.[19] The corresponding initial state is an incoherent superposition of states representing enantiomers with opposite chiralities, in contrast to the previous papers[12, 13] which considered less demanding cases of pure initial states. Exemplarily, we shall simulate the laser pulse driven molecular dynamics from the racemate towards a pure enantiomer by using representative wavepackets for the torsional motion of the pre-oriented model system H_2POSH in the electronic ground state at low temperature.

H_2POSH forms a left and a right atropisomer depending on the negative or positive values of the P-O-S-H dihedral angle ϕ.[13] The corresponding double-well potential V along the torsional angle ϕ is shown in Figure 1 (adapted from reference [13]) together with the levels $E_{v\pm}$ of the torsional

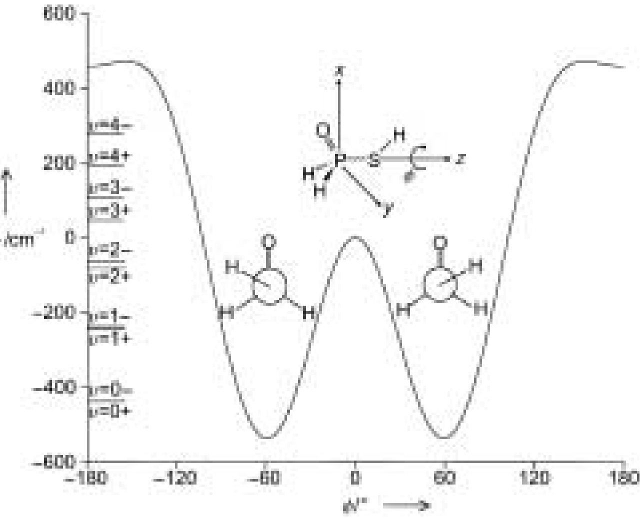

Figure 1. Double-well potential and torsional energy levels of the model H_2POSH (ab initio results adapted from ref. [13]).

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eigenfunctions $\Phi_{v\pm}(\phi)$. All other degrees of freedom are neglected. For energies $E_{v\pm}$ below the potential barrier at $\phi = 0$, the $\Phi_{v\pm}(\phi)$ eigenfunctions occur as doublets of vibrational states labeled $v = 0, 1, 2$ with + or − symmetries, with splittings corresponding to tunneling times τ_v of 630, 20.9, and 1.88 ps, respectively. The sums (+) or differences (−) of these eigenstates yield corresponding torsional states for the left and right enantiomers [Eq. (1a) and (1b), respectively],[20] approximately embedded in the left and right potential wells, respectively. Torsional eigenstates $\Phi_{v\pm}(\phi)$ with higher energies, $v = 3,4$, etc., are delocalized.

$$\Psi_{v\mathrm{L}} = \frac{1}{\sqrt{2}}(\Phi_{v+} + \Phi_{v-}) \tag{1a}$$

$$\Psi_{v\mathrm{R}} = \frac{1}{\sqrt{2}}(\Phi_{v+} - \Phi_{v-}) \tag{1b}$$

For a given temperature T, the system is assumed to be in thermal equilibrium, described by the density ρ, where Q is the partition function [Eq. (2)].

$$\rho_{\mathrm{eq}} = \sum_{v\pm} \Phi_{v\pm} \frac{\mathrm{e}^{(-E_{v\pm}/k_{\mathrm{B}}T)}}{Q} \Phi^{*}_{v\pm} \tag{2}$$

For simplicity, let us consider the particular case at low temperature ($T < 40$ K) where only the two torsional eigenstates of the lowest doublet are populated with nearly equal probabilities. Then, the initial thermal distribution [Eq. (2)] at $t = 0$ can be rewritten as approximately the sum of equal densities for the left and right enantiomers [Eq. (3)].

$$\rho_{\mathrm{eq}}(t=0) \approx \frac{1}{2}(\Phi_{0+}\Phi^{*}_{0+} + \Phi_{0-}\Phi^{*}_{0-}) = \frac{1}{2}(\Psi_{0\mathrm{L}}\Psi^{*}_{0\mathrm{L}} + \Psi_{0\mathrm{R}}\Psi^{*}_{0\mathrm{R}}) \tag{3}$$

Now the task is to design a laser pulse which drives the initial racemic state towards a final state which represents (nearly) a pure target enantiomer, for example the left enatiomer. The laser driven dynamics is simulated, in semiclassical dipole approximation, by solving the time-dependent Liouville–von Neumann equation [Eq. (4)].

$$i\hbar \frac{\partial}{\partial t}\rho = [\hat{H},\rho] \tag{4}$$

In this equation $\hat{H}$ is the Hamiltonian operator with contributions for the kinetic torsional energy, for the torsional potential, and for the interaction of the molecular dipole $\vec{\mu}$ with the electric field $\vec{\varepsilon}(t)$ of the laser pulse. We assume that $\vec{\varepsilon}(t)$ propagates along the z axis, that is parallel to the P–S bond of the preoriented molecule. The laser field $\vec{\varepsilon}(t)$ is then constructed by using the techniques given in reference [6] from five linearly x- or y-polarized subpulses which in accord with the symmetry selection rules induce nearly perfect state selective torsional transitions. Specifically, the dipole components μ_x and μ_y have + and − symmetry, respectively;[13] thus, the interacting linearly x- and y-polarized subpulses induce transitions only between states with identical or opposite symmetries, respectively. Projection of the resulting density $\rho(t)$ on the states $\Psi_{v\mathrm{L}}$ and $\Psi_{v\mathrm{R}}$, respectively, yields the populations $P_{v\mathrm{L}}$ and $P_{v\mathrm{R}}$, respectively.

The laser pulse which drives the initial racemate towards a (nearly) pure enantiomer is shown in Figure 2b. The corresponding five subpulses have amplitudes 1.446, 0.611, 1.76, 0.08, 0.17 GV m^{-1}, frequencies 352.75, 373.36, 372.7, 160.0, 161.0 cm^{-1}, phase shifts 0, 0, 25, 0, 180°, and durations of 7 ps. The resulting populations of the torsional states v of the left and right enantiomers are shown in Figure 2c. At the end of the laser pulse, the total population of the left enantiomer is close to 1, while the population of the right enantiomer is close to zero; the remaining small fraction is accounted for in the population of delocalized torsional states.

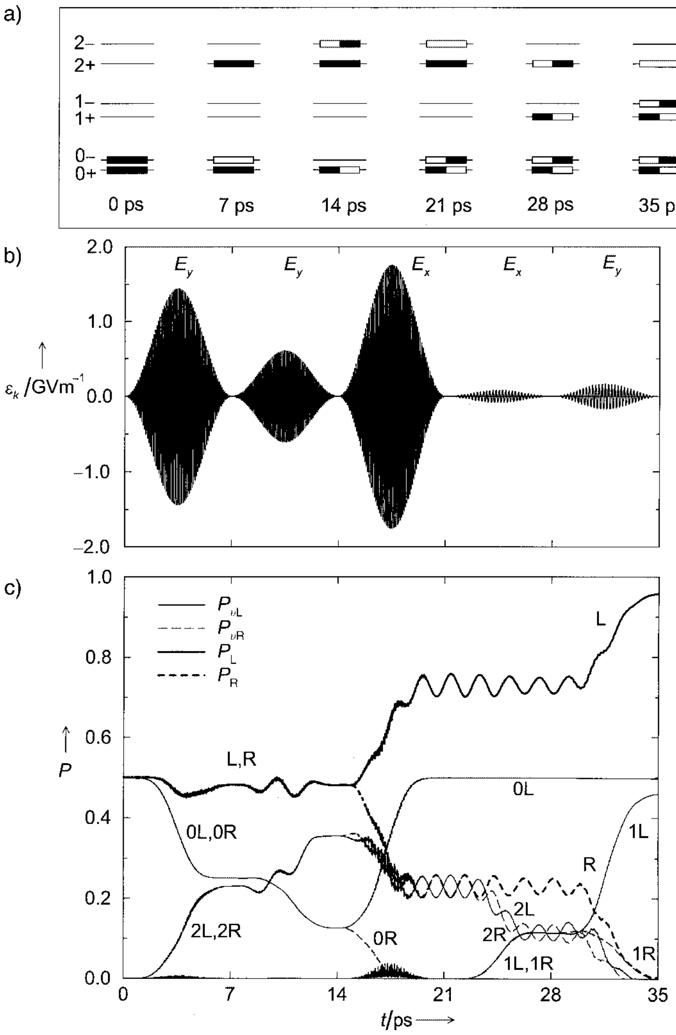

Figure 2. Selective preparation of the left enantiomer from a preoriented racemate of left and right atropisomers of the model H_2POSH, by means of a series of laser pulses. a) Selective transitions between the torsional states $\Phi_{v\pm}$, as induced by the subpulses (see b). b) Electrical fields of the linearly x- or y-polarized pulses. c) Resulting populations $P_{v\mathrm{L}}$ and $P_{v\mathrm{R}}$ of the torsional levels $v = 0, 1, 2$, and the total populations P_{L} and P_{R} of the left (L) and right (R) enantiomers; marginal populations of more excited delocalized levels are not shown.

The underlying mechanism for the preparation of the left enantiomer is illustrated by the selective transitions induced by the five sequential subpulses, as indicated in Figure 2a. The first, y-polarized subpulse almost completely transfers the population of the initial state Φ_{0-} into the excited state Φ_{2+}, without influencing the population of the other initial state Φ_{0+}. Next, the second and third y- and x-polarized subpulses transfer the initial population of the other initial state Φ_{0+} into the ground state of the left enantiomer, $\Psi_{0\mathrm{L}}$, while leaving the "parking" population of state Φ_{2+} unaffected. This is achieved by first transferring half of the initial population of Φ_{0+} into the excited state Φ_{2-} and subsequently to Φ_{0-}, which then interferes coherently with the remaining fraction of Φ_{0+} leading to the formation of the target state of the left enatiomer Ψ_{0L}. Finally, the "parking" population of Φ_{2+} is dumped into the excited ($v = 1$) state of the left enantiomer Ψ_{1L}, by means of the fourth and fifth subpulses which create the corresponding coherent superposition of states Φ_{1+} and Φ_{1-}, respectively, without influencing the population of Ψ_{0L}.

The net effect is conversion of the undesirable right portion of the racemate from its torsional ground state to the left enantiomer in its first torsional excited state, while keeping the initial fraction of the desired enantiomer in its torsional ground state. This is accomplished by transferring the incoherent population of two initial states (the racemate) into an incoherent superposition of two coherent states (the left enantiomer), where the coherences in each of the doublet states are introduced by the second to fifth subpulses. After the end of the laser pulses, the pure enantiomer tunnels back and forth towards the opposite enantiomer. Therefore, the resulting enantiomer selectivity remains, however, only for half of the tunneling time ($\tau_1/2$). This time is long enough, however, for subsequent laser control or reactions which may stabilize the target pure enantiomer.[16, 17]

Tunneling is also present during the laser pulse, but it does not impair the final localization, because it is exceedingly slow (630 ps) for Ψ_{0L} and, moreover, the more rapid tunneling of the intermediate excited states Ψ_{1L} and Ψ_{1R} or Ψ_{2L} and Ψ_{2R} compensate each other since their populations are designed to be nearly equal.

In conclusion, a preoriented racemate can be converted into a pure enantiomer by means of linearly polarized laser pulses. In our simulation the temperature is so low that only the lowest doublet of torsional states is populated. Extensions to higher temperatures are however straightforward, and involve transitions to other "parking" states followed by sequential transfers into appropriate excited states of the target enantiomer. Our approach can also be extended to rotating molecules, for example by means of alignment along the P–S axis but allowing free rotation around it.[21] The linear polarized laser pulses which define a left- or right-handed coordinate system in our model case, are then replaced by circular polarized laser pulses. Additional details of this extended general model will be published elsewhere. The present results should also serve as a reference for more complex situations such as the inclusion of the effects of intramolecular vibrational redistribution.

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Bis(pentafluorophenyl)xenon, $Xe(C_6F_5)_2$: A Homoleptic Diorganoxenon Derivative[**]

Nicola Maggiarosa, Dieter Naumann,[*] and Wieland Tyrra

Dedicated to Prof. Dr. Herbert Jacobs on the occasion of his 65th birthday

In 1989, pentafluorophenylxenon borates were synthesized as first examples of organoxenon derivatives.[1, 2] In the following years, numerous new Xe–C compounds with the structural element $[Xe{-}C]^+$ were synthesized and characterized.[3–8] The only $C_6F_5Xe^{II}$ compounds with two covalent bonds are C_6F_5XeCl, $[(C_6F_5Xe)_2Cl]^+[AsF_6]^-$,[9] and $C_6F_5XeOCOC_6F_5$.[10] The existence of a xenon derivative with two xenon–carbon bonds has not yet been confirmed. Already in 1979, $Xe(CF_3)_2$ was described;[11] however, these results could not be reproduced and are therefore the subject of controversy.

Investigations of the substitution reactions of XeF_2 suggested that the synthesis of a compound containing the fragment C-Xe-C and stable enough for spectroscopic detection should be possible by the reactions of XeF_2 and

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