Selective photodestruction of chiral molecules of a specified configuration by coherent laser radiation

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ABSTRACT

The method of selective destruction of small chiral molecules of a specified configuration, which is based on coherent action of the intense multicomponent ps and fs laser pulses, is suggested. Computer simulation results show its efficiency for the laser distillation of a racemic mixture of randomly oriented molecules in a gas phase at room temperature.

Keywords: chiral molecules, absolute asymmetric synthesis, laser coherent control

1. INTRODUCTION

The “chirality” is a symmetry property of an object, which does not coincide with its mirror image. Man’s hand and a screw are the typical examples of chiral objects. Correspondingly, any asymmetric molecule without inversion center is also a chiral object. Such chiral molecules can exist in two conformations, called left- (L) and right-handed (D) enantiomers, which are the mirror images of each other. One of the striking enigmas of Nature is that living nature prefers one type of enantiomers with respect to another one, so that only one type of enantiomers of each chiral molecule does exist in living nature. Therefore, the preferential synthesis of a required type of enantiomers which is called the absolute asymmetric synthesis (AAS) is a crucial problem, solution of which would open new horizons for a number of applications in chemistry, medicine, and pharmacy.

Realization of AAS is often difficult problem for chemicists, because chemical methods typically result in a racemic mixture, which consists of equal number of L- and D-enantiomers. Key difficulty in realization of the AAS is that all scalar properties of both enantiomers, such as energy levels, rotational constants etc., are almost identical and only tensor ones are different. At the same time, chemical synthesis of a racemic mixture of chiral molecules is in some cases a routine task. Therefore, the AAS of a required enantiomer from a racemic mixture is a challenging problem.

In the last decade, it has been demonstrated that methods of laser physics and specifically methods of coherent control are the universal and extremely effective tools for controlling molecular dynamics.[1] One can suppose then that they can also be effectively applied for the solution of the problem of AAS from racemic mixture.[2] Theoretically, laser-assisted AAS has been intensively studied in the literature where various ways of laser field–molecule interactions were analyzed: electric quadrupole and magnitochiral (see[3,4] and references therein), joint electro- and magnetodipole,[5–7] and pure electrodipole interactions.[8–32] However, despite all these theoretical studies and variety of developed scenarios, experimentally have been demonstrated only enantiomeric enrichment of a racemic mixture of rather large organic molecules due to the electroquarupole interaction with circularly polarized light[33–36] and due to the interaction with the laser field in the presence of strong dc magnetic filed (magneto-chiral effect).[37] Unfortunately, such interactions, as well as the magnetodipole interactions, are ineffective for small chiral molecules because electroquadrupole, magnetochiral, and magnetodipole effects in such molecules are very weak and, as a rule, are suppressed by the dominated electrodipole interaction. Therefore, the latter is widely analyzed in the bulk of available literature.

The question arises then, why none of the laser-assisted AAS scenarios suggested in Refs. 8–32 has not been realized experimentally? Surely, one of the obstacle for this is that it is difficult to detect the results of the AAS as in most papers the authors selected as the model molecules those showing dynamical chirality, when enantiomers are not stable and spontaneously interconverted at the time of about 10^{-9}–10^{-11} s.

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Even more essential difficulty for experimental realization of the scenarios suggested in Refs. 8–21 is that the chiral molecules must be preliminary oriented in space and that at least one of their molecular fixed axes must be codirected with space-fixed direction. Unfortunately, for small molecules such orientation is a separate, extremely interesting and difficult problem, which is not solved to the end so far. While the laser techniques for molecular arrangement, which simply leads to the collinear (but not necessarily parallel) arrangement of the molecule-fixed axes, are rather well-developed (see, for example, reviews[38, 39]), an effective and universal technique for orientation of molecules, which would lead to the parallel ordering of the molecular axes, is not developed yet. There are just a few experiments on orientation of small molecules and best results are achieved so far in experiments with molecules cooled in a supersonic jet up to a few Kelvins at the joint action of laser and electrostatic fields.[40] Therefore, preparation of an ensemble of well-oriented molecules, which can be used further for the purpose of the AAS, for instance, is a separate very difficult experimental problem.

That is why most attention nowadays is paid to the development of the AAS scenarios based exclusively on the use of electrodipole interaction of chiral molecules with the multicomponent laser field, which does not require preliminary orientation of the molecules.[25–32] First step in this direction has been made in Ref. 25, where authors derived a general condition for the AAS scenarios of such kind. Soon after that, a few more specific laser-assisted AAS scenarios were proposed.[26–32] Their experimental realization seems, unfortunately, also difficult and no one of them has been realized so far for the following reasons.

First of all, to be effective, all these scenarios require working temperatures of a few Kelvin. Second, the detection of the results of the AAS scenarios described in Refs. 27,29–32 remains a problem because the molecules used in these scenarios are chiral molecules having no stable enantiomers (the case of dynamical chirality). Third, AAS scenarios developed in Refs. 26–31 can be in fact experimentally applied only to the single spatially-localized molecules. This is due to fact that the direction of the AAS in this scenarios strongly depends on the position of the enantiomers, so that delocalization of the molecule in a spatial area of size comparable with the laser wavelengths leads to complete loss of control on the AAS reaction. Finally, applications of methods suggested in Refs. 25, 27, 28 are limited only by molecules with achiral excited electronic states.

Taking into account all listed above disadvantages of the available AAS scenarios, we suggest here a novel AAS scenario based on the electrodipole interaction of the incident laser field with chiral molecules, which can be applied to a non-oriented molecules having stable chiral configurations. This scenario does not require rigid spatial localization of the molecules and their preliminary cooling. In Sec. 2, we consider the basic component of the novel AAS scenario—exclusive excitation of preselected enantiomers from a racemic mixture based on the concept of the laser orientation-dependent selection of molecules proposed by us recently.[41] Also, qualitative description of the suggested AAS scenario is given. The numerical analysis of this scenario on example of SiHNaClF chiral molecules is given in Sec. 3. In conclusion, we summarize key results of this paper.

2. THE IDEA OF METHOD OF ASUMMETRIC SYNTHESIS

Let us consider a mixture of free gaseous chiral molecules. We assume that molecules in the mixture do not interact with each other and that they are initially in a thermodynamic equilibrium state with the density matrix $\hat{\rho}_0$. The important feature of absolute asymmetric synthesis of enantiomers for a such initial conditions is that it is an example of the process for which symmetry towards spatial inversion operation $\widehat{E^*}$ is violated. Operation $\widehat{E^*}$ does not change the state of a racemic mixture of randomly oriented chiral molecules:

$$\widehat{E^*}\hat{\rho}_0\widehat{E^*}^{-1} = \hat{\rho}_0. \tag{1}$$

Our aim is to elaborate rather universal scenario of AAS from racemic mixtures, which is based on the electrodipole interaction of molecules with an intense pulsed laser radiation. For such a scenario the photoinduced dynamics of chiral molecules in the mixture is described by the transformation $U\hat{\rho}_0U^{-1}$ with the evolution operator U of the form:

$$U(\vec{\mathcal{E}}) = \mathcal{T}\exp\left[-\frac{i}{\hbar}\int_{-\infty}^{t}\hat{H}(\vec{\mathcal{E}})dt\right], \tag{2}$$

where $\mathcal{T}$ is the time ordering operator and the hamiltonian $\hat{H}(\vec{\mathcal{E}}) = \hat{H}_0 + \hat{H}_I(\vec{\mathcal{E}})$ is the sum of the eigen hamiltonian of the molecule $\hat{H}_0$ and the hamiltonian $\hat{H}_I(\vec{\mathcal{E}})$ describing electrodipole interaction with the incident laser field. At the same time, the density matrices $\hat{\rho}_L$ and $\hat{\rho}_D$, which describe similar ensembles of nonoriented L- and D-enantiomers, respectively, are not invariant in respect to $\widehat{E^*}$ and connected to each other as $\hat{\rho}_{l(d)} = \widehat{E^*}\hat{\rho}_{d(l)}\widehat{E^*}^{-1}$. This relation illustrates that under inversion the left-handed enantiomers $|l\rangle$ are transferred into the right-handed $|d\rangle$ and vice versa:

$$\widehat{E^*}\,|l(d)\rangle = |d(l)\rangle\,. \tag{3}$$

We will limit our consideration by the case of molecules having stable chiral configurations and will consider the most rough strategy of laser distillation of a racemic mixture when an excess of the enantiomers of a given configuration is achieved by selective photo-destruction of the enantiomers of the opposite handiness. The photo-destruction of the molecules is due to their photoinduced transfer to the anti-bonded vibrational states of the excited electronic states.

The suggested AAS scenario is based on combination of the methods of coherent control in oriented chiral molecules[8–21, 25–32] and the concept of laser orientation-dependent selection of molecules developed by us earlier.[41]

To clarify the idea of the method, let us consider the dynamics of the AAS on example of an abstract stable chiral molecule. For a qualitative analysis of the AAS mechanism it is not necessary to specify the vibrational dynamics of the molecule, also we suppose that its rotational dynamics can be treated in the model of frozen molecules. In this model the photoinduced dynamics of a single molecule depends parametrically on a set of fixed variables ϑ characterizing its orientation. Action on the ensemble of molecules, as a whole, is determined then via a plain statistical averaging over ϑ. Conditions at which such simplified description is valid are fulfilled in an important from practical point of view case when the AAS from a racemic mixture is arranged at the normal conditions with the help of strong femtosecond pulses. In this case, the typical rotational energy significantly exceeds the value of rotational quanta and the duration of the laser pulses τ_{las} is significantly shorter than a typical period of molecular rotation.

We will show first how the AAS can be realized for oriented molecules. Let us assume that the molecules have three electronic levels g, e_{int}, and e^* that correspond to the ground and two excited states of the molecule for which transitions $g{\leftrightarrow}e_{\text{int}}$ and $e_{\text{int}}{\leftrightarrow}e^*$ are allowed and that the molecules in the excited state e^* dissociate with high probability. Let us denote as $\vec{\mathrm{d}}^{l}_{g,e_{\text{int}}}$ and $\vec{\mathrm{d}}^{l}_{e_{\text{int}},e^*}$ matrix elements of dipole moment, which describe transitions $g{\leftrightarrow}e_{int}$ and $g{\leftrightarrow}e^*$ in the L-enantiomers. Also we denote as $\vec{\xi}_l$ the molecular fixed axis in L-enantiomers, which is orthogonal to $\vec{\mathrm{d}}^{l}_{g,e_{\text{int}}}$ and $\vec{\mathrm{d}}^{l}_{e_{\text{int}},e^*}$. Taking in mind that L- and D-enantiomers are mirror images of each other it is obvious that configuration formed by these three vectors and configuration of the corresponding vectors $\vec{\xi}_d$, $\vec{\mathrm{d}}^{d}_{g,e_{\text{int}}}$, and $\vec{\mathrm{d}}^{d}_{e_{\text{int}},e^*}$ in D-enantiomers should be mirror images of each other. Let us also assume that we somehow oriented the molecules in a racemic mixture in a way that axes $\vec{\xi}_l$ and $\vec{\xi}_d$ are coincided with the spatially-fixed axes $\vec{z}$ (molecules can still freely rotate around $\vec{z}$- axis).

Let us show that if the angle between directions of the matrix elements of the dipole moments of the transitions $g{\leftrightarrow}e_{\text{int}}$ and $e_{\text{int}}{\leftrightarrow}e^*$ is different from zero and π, then the action of the two-component laser field $\vec{\mathcal{E}}_0 + \vec{\mathcal{E}}_1$ with the corresponding frequencies ω_0 and ω_1 tuned into the resonance with the two-photon transition $g{\rightarrow}e^*$ via the intermediate level e_{int}, can excite the L- and D-enentiomers with different efficacy. To prove this, let us assume that the field components are linearly polarized in the plane perpendicular to $\vec{z}$, so that the angle between directions of their polarizations is equal to Φ. Assuming probabilities P^{l}_{diss} and P^{d}_{diss} of photodissociation of L- and D-enantiomenrs proportional to the probability of two-photon transition to the state e^*, we have:

$$\frac{P^{l}_{\text{diss}}}{P^{d}_{\text{diss}}} = \frac{\left\langle \left| (\vec{\mathcal{E}}_1\vec{\mathrm{d}}^{l}_{g,e_{\text{int}}}(\theta))(\vec{\mathcal{E}}_0\vec{\mathrm{d}}^{l}_{e_{\text{int}},e^*}(\theta)) \right| \right\rangle_\theta}{\left\langle \left| (\vec{\mathcal{E}}_1\vec{\mathrm{d}}^{d}_{g,e_{\text{int}}}(\theta))(\vec{\mathcal{E}}_0\vec{\mathrm{d}}^{d}_{e_{\text{int}},e^*}(\theta)) \right| \right\rangle_\theta}, \tag{4}$$

where averaging is taken across all possible values of angle θ describing rotations of molecules around axis $\vec{z}$.

After averaging over θ, Eqs. (4) take the form:

$$\frac{P^l_{\rm diss}}{P^d_{\rm diss}}=\frac{-\pi\cos(\phi-\Phi)+4\arccos\left(\left|\sin\left(\frac{\phi-\Phi}{2}\right)\right|\right)\cos(\phi-\Phi)+2|\sin(\phi-\Phi)|}{-\pi\cos(\phi+\Phi)+4\arccos\left(\left|\sin\left(\frac{\phi+\Phi}{2}\right)\right|\right)\cos(\phi+\Phi)+2|\sin(\phi+\Phi)|}. \tag{5}$$

From this equation it follows that the photoinduced decay rates of L- and D-enantiomers are different, generally speaking. One can easily show that the major difference is realized at the values $\phi, \Phi = \pm\pi/4$, $\pm 3\pi/4$, when the ratio of the decay rates reaches the value of $\pi/2$. Due to this difference in the decay rates an excess of enantiomers, for which the decay rate is less than for another type of enantiomers, will be formed in a racemic mixture.

Therefore, for building up the AAS method, which will work at the room temperatures, we should first eliminate in the described scheme the requirement for the orientation of the axes $\vec{\xi}_l$ and $\vec{\xi}_d$ of the molecules parallel to $\vec{z}$ that is impossible to realize in experiment nowadays (see Introduction). In order to solve this problem, we will modify properly a method of laser orientation-dependent selection of molecules.[41] This method allows us to make selective manipulations (even at the room temperatures) with molecules of the required orientation in an ensemble of randomly oriented molecules. It is based on the transfer of molecules having reqired spatial orientation in a separate sub-ensemble in which molecules are distinguishable from other molecules by the specific internal state, which allows us to work with these molecules independently from the rest of the ensemble. In general case, such sub-ensemble must be dynamically refreshed as the molecules change their orientation during free thermal motion.

Key disadvantages of the selection scheme proposed in Ref. 41 are the necessity of using electrostatic field with amplitude close to the molecular ionization threshold and the specific requirements to molecular permanent dipole moment behavior under the laser excitation, which significantly narrows the types of molecules for which this scheme could be applied.

In this work, a novel variant of the laser scheme of orientation-dependent selection of molecules is proposed, which does not require electrostatic field. In this variant, selection of molecules is arranged by the final state of the photoinduced process, which we have to make orientation-dependent. In other words, we produce such photoinduced changes in the structure of the final state of the process, which we need to control, that its realization becomes possible only for the specifically oriented molecules. We will show that this modified selection scheme allows us to extend the ideas of the considered above scheme of the AAS in oriented molecules onto the case of randomly oriented chiral molecules. For this we need to organize the special orientation-dependent modification of the structure of the state e^*, so that the transition $e_{\rm int}\leftrightarrow e^*$ would be allowed only for molecules with directions of axis $\vec{\xi}_l$ or $\vec{\xi}_d$ close to the direction of axis $\vec{z}$; otherwise this transition is disabled.

Such dependence in our scheme results from the phase matched action of three additional intense laser fields $\vec{\mathcal{E}}_2$, $\vec{\mathcal{E}}_3$, and $\vec{\mathcal{E}}_4$ with frequencies satisfying the relation $\omega_4=\omega_2+\omega_3$ and chosen in a way that some three electronic states e_1, e_2, and e_3 of the molecule become coherently linked with each other via the electrodipole transitions ($\vec{\mathcal{E}}_2$ is near resonant to e_{12} transition, $\vec{\mathcal{E}}_2$ to $e_2\leftrightarrow e_3$ and $\vec{\mathcal{E}}_4$ to $e_1\leftrightarrow e_3$). Let us also require that the parameters of the state e_2 and of the laser fields $\vec{\mathcal{E}}_1$ and $\vec{\mathcal{E}}_0$ satisfy all the conditions for selective two-photon excitation of oriented enantiomers to the electronic state e_2, except for the large frequency detuning δ_2 from the two-photon resonance for the transition $g\leftrightarrow e_2$. The latter prevents the molecule's excitation into the state e_2 in the absence of additional field components $\vec{\mathcal{E}}_2$, $\vec{\mathcal{E}}_3$, and $\vec{\mathcal{E}}_4$. However, the presence of these additional components leads to modification of the eigen electronic states e_1, e_2, and e_3 of the molecule and, as a result, the fields $\vec{\mathcal{E}}_0$ and $\vec{\mathcal{E}}_1$ interact now with the dressed states, which structure and effective energies are determined by the amplitudes and polarizations of the fields $\vec{\mathcal{E}}_2$, $\vec{\mathcal{E}}_3$, and $\vec{\mathcal{E}}_4$, as well as by the configuration of the matrix elements of the transitions between levels e_1, e_2, and e_3, and, therefore, depend on the molecule's orientation. This dependency is in the core of the scheme for laser selection of molecules in accordance with their orientation.

In order to select the molecules accordingly to their orientation, one should choose levels e_1 and e_3 in a way that the matrix elements $\vec{\rm d}^{l(d)}_{e_1,e_2}$, $\vec{\rm d}^{l(d)}_{e_2,e_3}$, and $\vec{\rm d}^{l(d)}_{e_1,e_3}$ of dipole transitions $e_1\leftrightarrow e_2$, $e_2\leftrightarrow e_3$ and $e_1\leftrightarrow e_3$ for L-(D-)enantiomers were parallel to $\vec{\xi}_l$ ($\vec{\xi}_d$) and the direction of the polarization of the additional field components should be collinear to the axis $\vec{z}$.

Dynamics of the laser action on the molecules is characterized by the hamiltonian $\hat{\mathrm{H}} = \hat{\mathrm{H}}_{\mathrm{dressed}} - \hat{\vec{\mathrm{d}}}(\vec{\mathcal{E}}_0 + \vec{\mathcal{E}}_1)$, where $\hat{\mathrm{H}}_{\mathrm{dressed}} = \hat{\mathrm{H}}_0 - \hat{\vec{\mathrm{d}}}(\vec{\mathcal{E}}_2 + \vec{\mathcal{E}}_3 + \vec{\mathcal{E}}_4)$ describes free molecule's dynamics taking into account additional laser field components. In the RWA and with the help of representation (**??**), $\hat{\mathrm{H}}_{\mathrm{dressed}}$ reads as

$$\begin{aligned}\hat{\mathrm{H}}^{l}_{\mathrm{dressed,RWA}}(\varphi) = \hbar \Bigg(0 \left| l_g \right\rangle \left\langle l_g \right| + \delta_{e_{\mathrm{int}}} \left| l_g \right\rangle \left\langle l_g \right| + \textstyle\sum_{k=1}^{3} \delta_{e_k} \left| l_{e_k} \right\rangle \left\langle l_{e_k} \right| \Bigg) - \\ - \Bigg[\mathrm{d}_{e_1,e_2} A_2 \cos(\varphi) e^{-i\varphi_2} \left| l_{e_1} \right\rangle \left\langle l_{e_2} \right| + \mathrm{d}_{e_2,e_3} A_3 \cos(\varphi) e^{-i\varphi_3} \left| l_{e_2} \right\rangle \left\langle l_{e_3} \right| + \\ + \mathrm{d}_{e_1,e_3} A_4 \cos(\varphi) e^{-i\varphi_4} \left| l_{e_1} \right\rangle \left\langle l_{e_3} \right| + h.c. \Bigg]\end{aligned} \tag{6}$$

for the L-enantiometrs and is given by almost identical expression for D-enantiomers (except swapping the indices $l \leftrightarrow d$). Here $\mathrm{d}_{k,l} = \mathrm{d}^{l}_{k,l} = \mathrm{d}^{d}_{k,l}$, values of δ_j are determined by the frequency detunings of the laser field components from the resonance, and angle $\varphi = \widehat{\vec{\xi}_{l(d)}, \vec{z}}$ characterizes the orientation of the molecule with respect to the polarization direction of the additional field components. The possibility of orientation-dependent selection is based on the parametric dependency of eigen energies and eigen vectors of the dressed states, corresponding to the hamiltonian (6), on φ. Let us denote one of these dressed states as e^*, i.e., identify it with the state e^* in the considered above laser AAS scenario. Its structure is described with the linear combination of the form:

$$\left| l_{e^*} \right\rangle = C_1(\varphi) \left| l_{e_1} \right\rangle + C_2(\varphi) \left| l_{e_2} \right\rangle + C_3(\varphi) \left| l_{e_3} \right\rangle, \tag{7}$$

where coefficients C_k depend parametrically on the angle φ, as well as on the phases and amplitudes of the additional fields components.

In the following, we will assume that the parameters of the field are set to guarantee that for all values of φ the eigenvector (7) corresponds to the eigenvalue $\hbar\delta_{e^*}$ of the hamiltonian (6) (which is an effective energy of the state e^*), which is significantly different from the effective energies of two other eigenstates e' and e'' so that one can neglect the transitions $g \rightarrow e_{\mathrm{int}} \rightarrow e'$ and $g \rightarrow e_{\mathrm{int}} \rightarrow e''$ due to the large frequency detunings from the resonance. In this case, the problem of laser orientation-dependent selection of molecules is reduced to the problem of finding such parameters of laser pulses at which the two-photon transition $g \rightarrow e_{\mathrm{int}} \rightarrow e^*$ at large values of φ becomes ineffective either due to the small value of the matrix element $|\vec{\mathrm{d}}_{e_{\mathrm{int}},e^*}|$ or due to the large frequency detuning δ_{e^*} from the resonance for the two-photon transition $g \rightarrow e_{\mathrm{int}} \rightarrow e^*$. As the modulus of the matrix element $\vec{\mathrm{d}}_{e_{\mathrm{int}},e^*}$ can be written as the product $|\vec{\mathrm{d}}_{e_{\mathrm{int}},e^*}| = |C_2||\vec{\mathrm{d}}_{e_{\mathrm{int}},e_2}|$, the condition of its small value can be rewritten as $C_2 \rightarrow 0$.

Let us now find the parameters of the laser action at which the coefficient C_2 goes to zero for the molecules, which orientations are orthogonal ($\varphi = \pi/2$) and opposite ($\varphi = \pi$) to the required orientation. For $\varphi = \pi/2$ all non-diagonal elements of the hamiltonian (6) are equal to zero and, therefore, its eigenfunctions coincide with the eigenfunctions $\hat{\mathrm{H}}_0$. Therefore, for zeroing C_2 it is necessary that the dressed state $\left| l_{e^*} \right\rangle$ at $\varphi = \pi/2$ is transferred either into the state $\left| l_{e_1} \right\rangle$ or to $\left| l_{e_3} \right\rangle$. For $\varphi = \pi$, substituting $C_2 = 0$ in equation $\hat{\mathrm{H}}^{l}_{\mathrm{dressed,RWA}} \left| l_{e^*} \right\rangle = \hbar\delta_{e^*} \left| l_{e^*} \right\rangle$, we receive the following relationship between the amplitude components $\vec{\mathcal{E}}_2$, $\vec{\mathcal{E}}_3$, and $\vec{\mathcal{E}}_4$ and the optimal frequency detuning of the component $\vec{\mathcal{E}}_4$ from the resonance, as well as the relationship between the phases of the additional field components:

$$A_4 = \frac{\hbar\left(\delta_{e_1} - \delta_{e_3}\right) d_{e_1,e_2} d_{e_2,e_3}}{d_{e_1,e_3}\left(\frac{A_3}{A_2} d^2_{e_1,e_2} - \frac{A_2}{A_3} d^2_{e_2,e_3}\right)}, \quad \varphi_4 = \varphi_2 + \varphi_3. \tag{8}$$

At last, the optimal value of the frequency detuning δ_{e_2} is determined from the condition $\delta_{e^*}(\varphi = 0) = 0$.

For completing the analysis of the AAS scheme it is necessary to determine the directions of the laser field components propagation. It seems to be most optimal to use multicomponent laser field impact, which is composed of two laser pulses: first pulse, less intensive and longer than the second one, contains component $\vec{\mathcal{E}}_1$ and has a longitudinal profile closed to the rectangular shape. Its propagation direction $\vec{\kappa}_1$ lies in the plane xy and sets with axis $\vec{y}$ an angle Φ. Direction $\vec{\kappa}_2$ of propagation of the second laser pulse, shorter than the first one and more intensive, is parallel to the axis $\vec{y}$. This pulse consists of four frequency components $\vec{\mathcal{E}}_0$, $\vec{\mathcal{E}}_2$, $\vec{\mathcal{E}}_3$, and $\vec{\mathcal{E}}_4$. Time profiles of each of these four components can be Gaussian:

$$A_j = a_1 \exp(-2(t-t_0)^2/\tau_j^2), \tag{9}$$

where the relationship $\tau_0 < \tau_2, \tau_3, \tau_4$ is important.

For this configuration of the laser fields both the number of laser pulses and the angle between directions of their propagation achieve their minimum. Therefore, the region of overlapping between laser pulses in which the AAS takes place is maximal for such configuration. Space dimensions of the area in which the AAS is initiated are determined also by the duration and space profiles of the laser pulses. Increasing the duration of the pulses, however, leads simultaneously with enlarging the AAS area to enlarging the areas through which laser pulses propagate without overlapping and therefore to increase of various parasitic nonresonant processes caused by each of the pulses separately, which also could significantly reduce the quality of the AAS. Thus the value τ_1 for the duration of the 1st pulse of about few ps and the values τ_2, τ_3, and τ_4 on the order of 10^2 fs seem to be optimal for the majority of cases. Also, the frequency detuning $\delta_{e_{\mathrm{int}}}$ of the first pulse from the resonance must be chosen essentially large in order to suppress the unwanted excitation of the molecules into the state e_{int}. In this case, propagation of the 1st pulse will not significantly affect the vibronic dynamics of molecules. When the 1st and 2nd pulses are overlapped, first of all action of the field components $\vec{\mathcal{E}}_2$, $\vec{\mathcal{E}}_3$, and $\vec{\mathcal{E}}_4$, results in formation of the dressed states e^*, e' and e''. Then, the component $\vec{\mathcal{E}}_0$, having shorter duration, overlaps with the pulse $\vec{\mathcal{E}}_1$ and produces the selective two-photon excitation $g \rightarrow e^*$. By and large, the whole duration of the AAS process is determined by the duration of the 2nd pulse, and, therefore, is on the order of $\sim 10^2$ fs. As a rule, this time is significantly smaller than the characteristic period of molecular rotations, which confirms the validity of describing the AAS process with the help of the frozen molecule model.

In order to fulfil the second relationship (8) a phase matching of the components $\vec{\mathcal{E}}_2$, $\vec{\mathcal{E}}_3$, and $\vec{\mathcal{E}}_4$ is required. It is important to stress, that $\vec{\mathcal{E}}_2$, $\vec{\mathcal{E}}_3$, and $\vec{\mathcal{E}}_4$ are components of single pulse. Therefore phase matching condition (8 in case when dispersion is absent can be fulfilled in the region of space with dimensions sufficiently large then typical laser wavelength. Because the phase matching of the components $\vec{\mathcal{E}}_0$ and $\vec{\mathcal{E}}_1$ between each other and with the components $\vec{\mathcal{E}}_2$, $\vec{\mathcal{E}}_3$, and $\vec{\mathcal{E}}_4$ does not required, it is possible realize the AAS in a volume with dimensions essentially larger the wavelength of the laser radiation.

The considered above variant of the AAS scheme cannot be always applied to a specific molecule. For instance, in SiHNaClF molecule it is impossible to choose the levels e_1, e_2, and e_3 in a way that the matrix elements of the dipole transitions between them are parallel.

In this case, one can use an alternative variant of the AAS scheme, in which matrix elements of the dipole moments $\vec{\mathrm{d}}^{l(d)}_{e_1,e_2}$ and $\vec{\mathrm{d}}^{l(d)}_{e_2,e_3}$ are orthogonal to $\vec{\mathrm{d}}^{l(d)}_{e_1,e_3}$ (and correspondingly to $\vec{\xi}_l(d)$) and are parallel to each other. For selection of orientation now it is necessary set the polarizations of the components $\vec{\mathcal{E}}_2$ and $\vec{\mathcal{E}}_3$ lying in $\vec{x}$ direction i.e. orthogonally to polarization of $\vec{\mathcal{E}}_4$ component (which is still parallel to $\vec{z}$ axis).

This change also leads to the qualitative difference in the character of orientation-dependent selection of molecules. Namely, the condition of selection now not only that the vector $\vec{\xi}_l$ or $\vec{\xi}_d$ is parallel to axis $\vec{z}$, but also that the directions of the matrix elements $\vec{\mathrm{d}}^{l(d)}_{e_1,e_2}$ and $\vec{\mathrm{d}}^{l(d)}_{e_2,e_3}$ are collinear to the polarization direction of the components $\vec{\mathcal{E}}_2$ and $\vec{\mathcal{E}}_3$, i.e., to axis $\vec{x}$. This condition is, obviously, more restrictive and, therefore, we can simplify the AAS scheme for selected molecules using for excitation of the molecules in the state e^* only a single component $\vec{\mathcal{E}}_1$ (instead biharmonic pumping using two fields $\vec{\mathcal{E}}_1$ and $\vec{\mathcal{E}}_0$). Correspondingly, the frequency of $\vec{\mathcal{E}}_1$ now should be chosen near resonant to $g \leftrightarrow e*$, transition. Of course, polarization of $\vec{\mathcal{E}}_1$ component still should be orthogonal to $\vec{\xi}_{l(d)}$ and should set nonzero angle Ψ with the polarization directions of the components $\vec{\mathcal{E}}_2$ and $\vec{\mathcal{E}}_3$ i.e. with $\vec{x}$ axis. At that transition dipole moment $\vec{\mathrm{d}}^{l(d)}_{g,e_2}$ should be orthogonal to $\vec{\xi}_{l(d)}$ and should set nonzero angle ψ with the polarization directions of the components $\vec{\mathrm{d}}^{l(d)}_{e_1,e_2}$.

Analogously to preceding consideration it can be shown, that the optimal values of angles Φ and ϕ remains the same ($\pm\pi/4$ or $\pm 3\pi/4$). Also, the same are the conditions for choosing the amplitudes and frequencies of the components $\vec{\mathcal{E}}_2$, $\vec{\mathcal{E}}_3$, and $\vec{\mathcal{E}}_4$, specifically, the formula (8) remains valid. As a result, besides absence of the component $\vec{\mathcal{E}}_0$ and change of the polarization of the components $\vec{\mathcal{E}}_2$ and $\vec{\mathcal{E}}_3$, the structure and optimal directions of propagation of the respective laser pulses do not undergo any significant change: optimal laser impact, as before, consists of two laser pulses, first of which includes the component $\vec{\mathcal{E}}_1$ and propagates in the plane xy at the angle 45° towards axis $\vec{y}$, whereas the second pulse setting of the components $\vec{\mathcal{E}}_2$, $\vec{\mathcal{E}}_3$, and $\vec{\mathcal{E}}_4$ propagates along the axis $\vec{y}$.

We will show below that this last scenario can be used for the AAS of enantiomers of the SiHNaClF molecule from a racemic mixture. On example of this molecule we will also make quantitative estimates of the efficiency of the proposed AAS scenario.

3. NUMERICAL MODELING OF THE AAS SCENARIO FOR AN INITIALLY RACEMIC MIXTURE ON EXAMPLE OF SIHNACLF MOLECULES

Molecule SiHNaClF has been chosen by us for further theoretical analysis for several reasons.

First, among molecules having stable chirality this molecule is one of the simplest and, therefore, this circumstance significantly simplifies quantum-mechanical computations of the relevant molecular parameters (equilibrium configuration, electronic terms, transition dipole moments, etc.).

Second, the dominating process in the dynamics of nuclear subsystem in the relevant for our consideration excited electronic states, just after the excitation, is increasing of the bondlength Na–Si. As it will be clear from the further analysis, the AAS process is determined significantly by the dynamics of the excited vibronic wavepackets at the times about few dozens of fs. Thus, one can use a reduced one-dimensional description of the vibrational dynamics of the nuclear subsystem in which the bondlength Na–Si serves as the generalized vibrational coordinate q. This significantly reduces the computational time during the computer modeling.

Third, the characteristic angular velocity of rotations of SiHNaClF molecule at the temperature $T = 300$K is about 3.3×10^{11} Hz and thus the typical rotational time scale (~ 3 ps) is at the order of magnitude longer than the characteristic time of the photoinduced AAS process (~ 100 fs). Therefore, we can describe dynamics of the AAS process using the frozen molecule model.

Finally, an important circumstance from experimental realization point of view is that the lowest excited electronic states of the molecule are well-separated (energy gaps are larger than > 0.35 eV) and weekly bound. The equilibrium value of the coordinate q for these states significantly differs from the equilibrium value q_0 in the ground electronic state g. Therefore, transfer of molecule into these excited electronic states with the help of short laser pulses is accompanied by its strong vibrational excitation energy of which is comparable with energies of the respective vibrational potential barriers. As a result, one could expect that such excitation will lead with high probability to the dissociation of the molecules, which allows to use the low-lying electronic states as the states e_1, e_2, and e_3 in the scheme of laser orientation-dependent selection. Significant energy gaps between these states make also possible using of the strong laser fields without essential excitation of the parasitic nonresonant transitions. At the same time, the frequencies of the selecting laser field components are rather high, being in the near IR-range. The latter can significantly simplify generation of the respective pulses.

We model the laser-induced vibronic dynamics of the molecules using the Born-Oppenheimer approximation in the frame of the one-dimensional model of the vibrational dynamics with single generalized coordinate q. Information on the equilibrium molecular configuration and on the coordinate dependencies of the electronic energy and matrix elements of the dipole moment of the electronic transitions have been calculated using quantum-mechanical calculations software package “Gaussian 03”.[42,43]

From the analysis of calculated data we found that the parameters of the 2nd, 5th, and 7th excited electronic states correspond by and large to the requirements to the states e_1, e_2, and e_3, respectively, in the second variant of AAS scheme discussed in Sec. 2. However, the detailed inspection of the parameters of the optimal laser action based on the results of Sec. 2 shows that in the case of the equilibrium molecular configuration the frequencies of the components $\vec{\mathcal{E}}_2$, $\vec{\mathcal{E}}_3$, and $\vec{\mathcal{E}}_4$ become close to the resonance frequencies of about dozen of additional transitions between the excited electronic states. Therefore, we used in the calculations an extended basis, which includes besides the ground electronic state g also 11 lower excited electronic states (from 2nd to 12th). Dynamics of the nuclear subsystem of each electronic state was described using grid-representation of the wavefunctions (grid step is about 10^{-2} Å). Temporal dynamics of the molecule was calculated using standard symmetric split-operator method.[44, 45]

Significant difference in the equilibrium bondlengths Na–Si for the ground and most excited electronic states greatly affects the dynamics of the photoinduced excitation of the molecules. In the ground state, the vibrational wavefunction is localized in the vicinity of $q = q_0$ with the characteristic size of $\sim$0.13 Å. After the laser excitation, excited vibrational wavepacket quickly leaves the vicinity of q_0 at the characteristic time τ_{out}, which is about few dozens of fs for the working terms 2 and 7, for instance. Vibronic states of the ground electronic state g are almost not involved into the photoinduced dynamics of the molecule at $q \gg q_0$ because the corresponding wavepackets do not overlap and the resonance conditions are significantly violated. Therefore, the total number of excited molecules is determined mostly by the dynamics of the vibronic interaction in the vicinity of $q = q_0$. Respectively, the characteristic time τ_{out} serves here as an effective longitudinal relaxation time.

This circumstance implies essential limitations on the parameters of laser action: as soon as the required condition for the orientation-dependent laser selection of molecules is the creation and maintaining the coherent superposition of electronic states 2, 5, and 7, then the effective Rabi frequencies of the transitions between these states and controlling detunings $\frac{1}{\hbar}\delta_{e_1}$, $\frac{1}{\hbar}\delta_{e_2}$, and $\frac{1}{\hbar}\delta_{e_3}$, as well as $\frac{1}{\hbar}\delta_{e^*}$, should be greater or equal to the value of $1/\tau_{\text{out}}$. In order to fulfil this condition, the intensity of each selective components of the laser field $\vec{\mathcal{E}}_2$, $\vec{\mathcal{E}}_3$, and $\vec{\mathcal{E}}_4$ is to be greater than 10^{11} W/cm^2. On the other hand, it is well-known that the intensity of 10^{12} W/cm^2 is the typical threshold value above which the parasitic for our purpose ionization processes start to play significant role in the photoinduced dynamics. Respectively, the optimal values of the intensities of the selective components should lie in the interval 10^{11}–10^{12} W/cm^2, and the controlling detunings should be on the order of 10^3 cm^{-1}. An important requirement while choosing the frequencies of the laser components is also absence of significant resonances with the electronic states (in the vicinity of $q \sim q_0$), which are not involved in the AAS scheme.

Taking all these limitations into account, the following frequencies have been chosen for further calculations: $\omega_1 = 1.391 \times 10^{15}$ Hz ($\lambda_1 = 215.6$ nm), $\omega_2 = 3.297 \times 10^{14}$ Hz ($\lambda_2 = 909.3$ nm), $\omega_3 = 1.282 \times 10^{14}$ Hz ($\lambda_3 = 2339.1$ nm), and $\omega_4 = 4.579 \times 10^{14}$ Hz ($\lambda_4 = 654.8$ nm). The temporal profile of the components $\vec{\mathcal{E}}_2$, $\vec{\mathcal{E}}_3$, and $\vec{\mathcal{E}}_4$ we assume Gaussian, given by Eq. (9), where $\tau_2 = \tau_3 = \tau_4 = 141$ fs. As the peak intensities for the fields components we took I_1^0=2.62×10^9 W/cm^2, I_2^0=I_3^0=$1{,}17\times10^{11}$ W/cm^2 I_4^0=$4{,}28\times10^{11}$ W/cm^2, which in accordance with Sec. 2 should be optimal for the chosen frequencies. However, it is clear that these values are lower than the real optimal values because they were estimated without taking into account spreading of the vibronic wavepackets and without parasitic influence of the transitions to electronic states, which were not included into the respective analysis in Sec. 2. Therefore, we analyzed various sets of the maximal intensities of the form $I_j = \mu I_j^0$ ($j = 2, 3, 4$) and the optimal value of the coefficient μ was elaborated based on the computer modeling results.

The component $\vec{\mathcal{E}}_1$ is assumed of the rectangular pulse shape with the front and rear sloping:

$$A_1 = a_1 \times \begin{cases} \frac{1}{2}\left[1 - \cos(\pi \frac{t+\frac{\tau_1}{2}}{\delta\tau_1})\right], & -\frac{\tau_1}{2} < t < -\frac{\tau_1}{2} + \delta\tau_1 \\ 1, & -\frac{\tau_1}{2} + \delta\tau_1 < t < \frac{\tau_1}{2} - \delta\tau_1 \\ \frac{1}{2}\left[1 + \cos(\pi \frac{t-\frac{\tau_1}{2}}{\delta\tau_1})\right], & \frac{\tau_1}{2} - \delta\tau_1 < t < \frac{\tau_1}{2} \end{cases} . \qquad (10)$$

The duration of the sloping and amplitude intensity of this pulse have been chosen from conditions $\delta\tau_1 \gg 1/\delta_{e_2}$ and $d_{g,e_2} A_1 \ll \hbar\delta_{e_2}$. At these conditions, the action of the only component $\vec{\mathcal{E}}_1$ leads to insignificant nonresonant adiabatic population of the 5th excited electronic state, which in our AAS scheme is the state e_2. For computer modeling we used the following values: $\delta\tau_1 = 120$ fs, $I_1 < 6\times10^9$ W/cm^2, and $\tau_1 = 1$–5 ps. Calculations for the action of only $\vec{\mathcal{E}}_1$ component confirm that at the chosen parameters a small population of the 5th excited electronic state during the excitation practically does not depend on the pulse duration. After ending the laser action, the majority of excited molecules adiabatically return into the ground state so that the remaining ratio of excited molecules does not exceed 10^{-5}.

Dynamical picture of the photoexcitation qualitatively changes when both 1st and 2nd laser pulses act simultaneously, because the frequency of the component $\vec{\mathcal{E}}_1$ becomes resonant (for the molecules with a specific orientation) for the excitation of molecules into the dressed state e^*. As a result, during short time a fast nonadiabatic transfer and population redistribution across various excited electronic states take place. Vibronic wavepackets corresponding to the majority of these states rapidly move into the region of $q \gg q_0$. In this region new resonances arise due to the essential change of the electronic terms energy, which lead to the complex processes of population redistribution and to the involvement into dynamics of the high-lying electronic states that are not included into the AAS calculation scheme. In addition, at the time scale necessary for population transfer into the region of the large values of q the one-dimensional approximation for vibrational dynamics of the molecule is not valid. With this, the calculation scheme we use cannot guarantee the correct description of the population dynamics of the excited states and the dynamics of the dissociation of photoexcited molecules. Therefore, our estimations for the AAS efficiency have been made in a rough assumption that the dissociation probability of molecules is proportional to the total population of all excited electronic states after laser impact. With this assumption, one can introduce $\mathcal{R} = P_l/P_d$ as the AAS efficiency measure, where P_l and P_d are averaged over all possible molecular orientations excitation probabilities for the left- and right-handed enantiomers.

Also as a quantitative measure of the AAS we can use so called degree of chirality, $\chi = \frac{\mathcal{N}_L - \mathcal{N}_D}{\mathcal{N}_L + \mathcal{N}_D}$, which characterizes the relative excess of left-handed ($\mathcal{N}_L$) to right-handed ($\mathcal{N}_D$) enantiomers in the mixture of chiral molecules. For a racemic mixture it is equal to zero, whereas $\chi = +1$ ($\chi = -1$) corresponds to the pure ensemble of L(D)-enantiomers.

We have calculated dependencies of P_l, P_d, and $\mathcal{R}$ on the intensity of the component of the 2nd laser pulse for two different intensity values of the 1st laser pulse. From numerical results it follows that despite of the monotonic growth of the excitation probability for both enantiomers increasing intensity of the 1st laser pulse practically does not change the ratio of these probabilities and, respectively, the AAS efficiency remains almost the same for the whole range of intensities of the 2nd pulse. We also have found, that optimal intensities of the components of the 2nd laser pulse, corresponding to the amplitude value $\mathcal{R} \sim 1.38$, approximately two times differ from those predicted from the analysis of the results of Sec. 2.

Analysis of the laser action dynamics shows that this essential difference is mainly due to the parasitic quasiresonant interaction between several electronic states. Additional calculations show that if we can potentially exclude possibility of photoinduced excitation of these states, then the optimal value of μ would be reduced to 1.3 and, therefore, becomes close to 1. At the same time, the value of $\mathcal{R}$ would be raised up to 1.85, which means that additional resonances greatly affect the efficacy of the AAS, significantly reducing it.

Even at optimal intensities of components of 1-st pulse and peak intensity of second pulse of order 10^9 W/cm^2 the effect of a single action of a pair of laser pulses even of high intensity is rather small: the probability of excitation is of order 0.1%. Therefore, let us now consider a question which value of the degree of chirality χ in the mixture of chiral molecules can be achieved as a result of numerously repeated action of the pair of laser pulses in the AAS scheme. As soon as the AAS process is accompanied by destruction of a fraction of molecules, then improving the quality of the AAS should lead to decreasing the useful output. Let us introduce $\eta = N_f/N_0$, which characterizes the ratio of the number of molecules N_f after ending the AAS towards their initial number N_0. A simple analysis shows that the values η, χ, and $\mathcal{R}_s$ are related to each other through the following relationship:

$$\eta = \left[(1-\chi)(1+\chi)^{-\mathcal{R}_s}\right]^{\frac{1}{\mathcal{R}_s - 1}} . \tag{11}$$

Assuming that for the case of SiHNaClF molecules the value $\mathcal{R}_s$ is about 1.38, from 11 one can easily obtain that for achieving a noticeable nonracemity in the mixture of chiral molecules, which is characterized by $\chi \sim 0.2$, we need to destroy about 3/10 of the initial number of the molecules. At the same time, for achieving the same values of χ at $\mathcal{R}_s \sim 2$ (we have seen that such values of $\mathcal{R}_s$ could be achieved at the suppression of the interaction with additional electronic states) we should destroy less than half of the molecules. Therefore, one could expect that the more detailed calculations of the interaction parameters, which includes an additional optimization of the methods for choosing the frequencies of the laser pulses components and the relationship between the intensities of the components of the 2nd pulse will give us a possibility to significantly increase the AAS efficacy.

4. CONCLUSION

For using in the AAS scenarios, we essentially improved the scheme of laser orientation-dependent selection. In the novel scheme, the molecules are selected through modification of the final state of the controlled process with the help of the adiabatic interaction with the three-component coherent laser field and has a number of advantages (elimination of the necessity of using strong electrostatic fields, minimal requirements to molecular properties) by contrast with the suggested by us earlier scheme,[41] which make it essentially more universal and effective.

Novel method for laser-assisted AAS from a racemic mixture of noninteractive SiHNaClF molecules has been suggested. Our calculations show that application of the suggested AAS scheme at the room temperature can give the degree of chirality ~ 0.2 after the photodissociation of the 3/10 of the initial number of molecules. Furthermore, one can expect that the efficiency of the AAS can also be sufficiently improved after additional optimization of the parameters of the laser action. Key destructive contribution to the AAS gives a parasitic quasiresonant interaction with the few electronic states of the molecules. We also have shown, that our scheme in principle can applied to macroscopic volume of chiral reagents.

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