

Laser-assisted orientation-dependent selection of molecules as a tool of symmetry breaking in isotropic molecular ensembles

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A method for coherent laser control of randomly oriented molecules at high temperatures (up to room temperature) is suggested, which rests on the technique proposed by us earlier of laser-assisted orientation-dependent selection (ODS) [Phys. Rev. A 77, 011401R (2008)]. It is shown that the ODS is of practical importance for the problem of field-free orientation of molecules. The efficacy of the method is justified by simulations of the photoinduced dynamics of BF molecules via direct numerical solution of the nonstationary Schrödinger equation.

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I. INTRODUCTION

Control of molecular orientation is among the rapidly developing areas of modern laser physics over the last two decades [1–6]. Such stable interest in the problem is due to the intensive development of the experimental tools of laser physics, which offers now a wide spectrum of techniques for studying molecular structure and for coherent control of molecular dynamics. For applications, as a rule, it is more interesting to control the dynamics of macroscopic molecular ensembles in the gas phase than the dynamics of single molecules. However, the random spatial arrangement and, especially, the isotropic orientation of the molecules in such ensembles leads to dissimilarities in their response to the laser impact. This obstacle not only can result in the essential decrease of the coherent control efficacy, but, in some cases, makes it impossible due to symmetry considerations. A widely used approach to cope with this problem is to first break the initial orientational symmetry of the ensemble, i.e., to order the molecules, before proceeding with the necessary manipulations on the ensemble. Then all the specifics of coherent control in isotropic media are reduced to finding an effective way of ordering the molecules.

As a matter of fact, two types of molecular ordering are of practical importance: the *molecular alignment*, when molecules are confined collinear to the laboratory frame axes, and *molecular orientation*, which in addition implies codirectional ordering of molecules with respect to the directions of the laboratory axes. Over the last decade, the technique of molecular alignment made its way from laboratory experiments to technology, which has been developed in detail and offers a wide spectrum of perspective applications, including the generation of short pulses [7,8], the study of ionization processes and generation of high harmonics [9–16], analysis of molecular orbital structure [17] and their tomography [18], study of various collisional and relaxation processes [19,20], nanolithography [21], isotope separation [22,23], control of chemical reactions and rovibronic dynamics [24–26] and some other stereochemistry problems, construction of quantum gates [27], etc.

At the same time, the laser-assisted orientation of molecules is a problem that is far from a solution. Presently, it is

mostly at the level of theoretical studies and does not have practical applications, where “traditional” methods of molecular orientation, such as the application of strong electrostatic fields [28–34] or hexapole focusing [35–37], still appear to be more convenient. Among possible mechanisms of orientation, the combined action of a strong electrostatic field with a laser alignment field [38–40], usage of short, shaped IR pulses [41–46], and the action of multifrequency laser pulses with specially selected phase matching between their components [47–52] are being considered. Unfortunately, application of these methods is so far limited to the case of low temperatures (about a few kelvin), while the energies of random thermal rotations and laser electro-dipole interaction are comparable. An open question still is the dynamical orientation of nonpolar molecules.

It has been discovered that, along with the regular orientation (typically referenced as *dynamical*), there exists also so-called *geometrical* molecular orientation, which has been shown in orientation-dependent selective ionization of molecules [53–55]. In this work, we discuss the feasibility of using a similar effect as an alternative mechanism of field-free molecular orientation at high temperatures.

A problem for existing laser-based orientational scenarios is the impossibility of coping with molecular free rotations at high temperatures with the use of sub-breakdown laser intensities. The method of orientation-dependent selection (ODS), suggested by us, was designed to overcome this difficulty. Instead of forced reorientation of the molecules, it is based on the selective excitation of the properly oriented part of the molecules into an excited vibronic state, which can serve then as a “label” that allows further separate addressing of these labeled molecules without disturbing the others. Thus, the ODS is targeted at splitting an initially isotropic molecular ensemble into two subensembles of labeled (i.e., excited) properly oriented molecules and all other (unexcited) molecules.

In our recent work [57,58], we have outlined several methods of realization of ODS and analyzed the feasibility of employing this approach for the absolute asymmetric synthesis of enantiomers from a racemic mixture of chiral molecules, as well as for molecular orientation. In this work, we will study in further detail the mechanism of ODS. In Sec. II, we present the fundamentals of the proposed ODS scheme. Then, in Sec. III, we quantify ODS efficacy on the example

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of a field-free orientation of an isotropic ensemble of BF molecules at room temperature. The emphasis is on those peculiarities of the molecular dynamics that were not yet considered in our previous work [57]. In the Conclusion, we summarize key results of this work.

II. PRINCIPAL SCHEME OF LASER-ASSISTED ODS

In this section, we will consider the laser-assisted ODS of molecules in an isotropic ensemble when the selection criterion for molecules is a small angle θ between the fixed molecular direction $\vec{\zeta}$ and the spatially fixed axis \vec{z} . We will assume that initially all molecules in the ensemble are in the ground vibronic state $|0\rangle$. Also, we will consider for simplicity the whole molecular ensemble as an ideal gas (noninteracting molecules) at temperature T . Our task is to develop a method for selective transfer of molecules, satisfying the selection criterion (small angle θ), into a specific excited vibronic state $|1\rangle$. Obviously, the excitation time τ for the molecules must be much smaller than their characteristic rotational time τ_{rot} :

$$\tau \ll \tau_{\text{rot}}. \quad (1)$$

The suggested solution of this task is based on the electro-dipole interaction of molecules with a short multicomponent laser pulse $\vec{\mathcal{E}} = \sum_j \vec{\mathcal{E}}_j$ with

$$\vec{\mathcal{E}}_j = 2\vec{\epsilon}_j A_j(t) \cos(\omega_j t + \varphi_j), \quad (2)$$

where $A_j(t)$, ω_j , and φ_j are the slowly varying amplitudes, carrying frequencies, and initial phases of the respective components and $\vec{\epsilon}_j$ are the unit vectors characterizing their polarization.

We can split the components $\vec{\mathcal{E}}_j$ into two groups in accordance with their functions. The components of the first group are responsible for the laser-induced modification of the eigenstates of the molecule during pulse propagation, in particular, for the *adiabatic* dressing of the vibronic eigenstate $|1\rangle$ into the specially designed state $|\tilde{1}(\theta)\rangle$. The orientational angle θ in parentheses indicates that both the structure and the effective energy of this dressed state depend on the orientation of the molecules.¹

The components of the second group, *nonadiabatically* interacting with the molecules, are responsible for the resonant transfer of molecules from the ground vibronic state $|0\rangle$ into a subspace of excited vibronic states. The crucial point here is that the excitation efficacy depends not only on the intensity and polarization properties of the field components of this second group, but also on the orientation-dependent properties of the target state $|\tilde{1}(\theta)\rangle$. Therefore, by changing the parameters of the field components of the first group, we can adjust the orientational dependence of the efficacy of excitation by field components of the second group.

¹When analyzing the ODS using relation (1), this dependence can be considered as parametric because one can neglect its quantum peculiarities and the dynamics of rotations during the short laser impact.

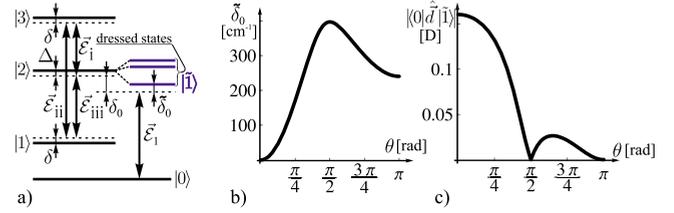


FIG. 1. (Color online) Mechanism of laser ODS. (a) Scheme of laser-induced transitions employed; (b) detuning $\tilde{\delta}_0$ vs orientational angle θ of the molecule; (c) similar dependence for the absolute value of the dipole transition moment $|\langle 0|\hat{d}|\tilde{1}\rangle|$. Dependencies (b) and (c) represent the case of BF molecules at the optimal laser field parameters given in the next section.

For clarity, we will use roman numbers ($j=i, ii, iii, \dots$) for enumerating the field components belonging to the first group. The rest of the components belonging to the second group we will enumerate with arabic numbers ($j=1, 2, 3, \dots$).

For further analysis, let us consider the simplest case when the population transfer between the states $|0\rangle$ and $|\tilde{1}\rangle$ is due to the one-photon transition and, therefore, the second group of field components is presented by the single component $\vec{\mathcal{E}}_1$. Denote the detuning of its frequency ω_1 from the resonant transition between the states $|0\rangle$ and $|\tilde{1}\rangle$ as $\tilde{\delta}_0(\theta, t)$. Note that this detuning depends on both the orientation of the molecule and the time. To set up orientation-selective excitation by the component $\vec{\mathcal{E}}_1$, one should establish a set of components of the first group that provide the following excitation conditions:

- (1) The detuning $\tilde{\delta}_0(\theta)$ is reduced to zero whereas the amplitude of the matrix element of the dipole moment $\langle 0|\hat{d}|\tilde{1}\rangle$ reaches its maximal value at $\theta \rightarrow 0$.
- (2) For any θ except values in the vicinity of zero the detuning $\tilde{\delta}_0(\theta)$ is large and/or value $|\langle 0|\hat{d}|\tilde{1}\rangle|$ is negligibly small. (3)

The major difficulty in satisfying the above conditions, as in the case of the problem of orientation of molecules, arises from the necessity to distinctly affect the molecules with parallel and antiparallel orientational geometry relative to spatially fixed axes. It was shown both theoretically [49–52,56] and experimentally [53–55] that this kind of symmetry breaking can be achieved via specific coherent superposition of quasimonochromatic harmonics of a simple form.

Improving this approach for the needs of our ODS problem, we obtained the following scenario based on the excitation scheme shown in Fig. 1. In addition to levels $|0\rangle$ and $|1\rangle$, the laser excitation process affects also two auxiliary levels $|2\rangle$ and $|3\rangle$. The laser radiation consists of four com-

ponents $\vec{\mathcal{E}}_1$, $\vec{\mathcal{E}}_i$, $\vec{\mathcal{E}}_{ii}$, and $\vec{\mathcal{E}}_{iii}$. The latter three belong to the first group in the above classification and link pairwise the levels $|2\rangle$ and $|3\rangle$, $|1\rangle$ and $|3\rangle$, and $|1\rangle$ and $|2\rangle$, respectively, via the quasiresonance transitions whose frequencies satisfy the condition $\omega_{ii} = \omega_i + \omega_{iii}$.² The detunings δ and Δ (Fig. 1) serve as important parameters for tuning the scheme. The frequency ω_1 of the component $\vec{\mathcal{E}}_1$ is chosen in the vicinity of the frequency of the transition $|0\rangle \rightarrow |2\rangle$ with detuning δ_0 . The value of δ_0 must be taken large enough to prevent excitation of molecules by the component $\vec{\mathcal{E}}_1$ without the field components of the first group.

Let us assume for simplicity that all the field components have the same Gaussian temporal profile

$$A_j(t) = A_j \exp(-2t^2/\tau^2), \quad (4)$$

and restrict ourselves to analysis of the most vivid example of the ODS process, when the polarizations $\vec{\mathcal{E}}_j$ of all the components are parallel to the axis \vec{z} and the dipole moments of all working transitions are collinear with $\vec{\zeta}$.

Let us write the Hamiltonian $\hat{H} = \hat{H}_0 - \hat{d} \cdot \vec{\mathcal{E}}$ of the molecules interacting with the laser field in a four-level approximation in the basis $\{|0\rangle, |1\rangle, |2\rangle, |3\rangle\}$ of eigenstates of the eigen-Hamiltonian \hat{H}_0 of the molecules. In the interaction representation and in the frame of the rotating wave approximation, the effective Hamiltonian \hat{H} takes the form

$$\hat{H}(\theta) = \hbar \begin{pmatrix} \delta_0 & 0 & \Omega_{0,2}^{(1)} & 0 \\ 0 & \delta & \Omega_{1,2}^{(iii)} & \Omega_{1,3}^{(ii)} \\ \Omega_{0,2}^{(1)*} & \Omega_{1,2}^{(iii)*} & \Delta & \Omega_{2,3}^{(i)} \\ 0 & \Omega_{1,3}^{(ii)*} & \Omega_{2,3}^{(i)*} & -\delta \end{pmatrix}, \quad (5)$$

where

$$\Omega_{m,n}^{(j)}(t, \theta) = (\vec{\zeta} \cdot \langle m | \hat{d} | n \rangle) e^{i(E_n - E_m)t/\hbar} A_j \cos(\theta) e^{i\varphi_j}. \quad (6)$$

It is convenient to consider the photoinduced process as interaction of the field component $\vec{\mathcal{E}}_1$ with the dressed states $|\tilde{k}\rangle = \sum_{l=1}^3 C_{k,l}(t, \theta) |l\rangle$ ($k=1, 2, 3$) that are produced by the field components of the first group, and reduced to eigenstates $|k\rangle$ in the field-free regime (i.e., $C_{k,l} \rightarrow 0$ at $l \neq k$ and $C_{k,l} \rightarrow 1$ at $l=k$ in the limit of $\vec{\mathcal{E}} \rightarrow 0$). By definition, such states are eigenstates of the Hamiltonian \hat{H}_d , which can be derived from Eq. (5) by excluding all field components of the second group (i.e., as a result of artificial replacement of $\Omega_{0,2}^{(1)}$ with zero). The expansion coefficients of the dressed states $C_{k,l}$ parametrically depend on the intensities of the field components of the first group, and the corresponding eigenvalues \tilde{E}_k characterize their effective energies.

A key peculiarity of the dressed states is that, under specific conditions of *adiabatic* photoinduced dynamics (while the field components of the second group are absent), the

dressed states almost do not interact with each other. In other words, if a molecule is initially in the state $|k\rangle$, then the evolution of its state will be described by the wave vector $|\tilde{k}(t)\rangle$ and the states $|\tilde{l}\rangle$ with $l \neq k$ will remain almost unpopulated. This obstacle allows us to exclude states $|\tilde{l}\rangle$ from consideration and thus sufficiently simplify the description of the photoinduced dynamics.

Necessary conditions for the adiabatic evolution of the quantum states have been studied in detail both in the frame of the formal adiabatic perturbation theory [62] and in application to the specific case of pulsed laser action on the molecules [59–61]. In general form, the adiabatic condition can be written as the following inequality:

$$\left| \langle \tilde{l} | \frac{d}{dt} | \tilde{k} \rangle \right|^2 \ll \frac{1}{\hbar^2} (\tilde{E}_l - \tilde{E}_k)^2. \quad (7)$$

One of the distinctive features of the proposed ODS scheme is the quasiresonant character of interaction between the laser field and the molecules when the detunings Δ and δ are smaller than or of the order of the peak values of $\Omega_{m,n}^{(j)}$ ($m, n \neq 0$). In the literature, the formation and evolution of the dressed states in such a regime is designated resonant adiabatic passage (RAP) [51]. The feature of RAP attractive for our purposes is the extremely strong dependence of the structure and the effective energies of the dressed states versus molecular orientation. This feature has been studied in detail in Ref. [51], where the possibility of orientation of the molecules at the adiabatic transformation of the initial vibronic state into one of the dressed states has been demonstrated. In the ODS method, in contrast with Ref. [51], we assume that none of the dressed states is initially populated (see Fig. 1) and the orientational dependence of their characteristics is used for creation of a kind of “plug,” which controls the process of photoexcitation of molecules from the ground state by the field components of the second group.

Note that, in order to satisfy simultaneously the adiabaticity condition (7) and the condition (1) of the pulsed ODS regime, it is necessary to use rather intense laser radiation. Simple speculations by analogy with Ref. [60] show that at RAP the inequality (7) can be satisfied if

$$\min(\Omega_{m,n}^{(j)}) \tau \gg 2\pi. \quad (8)$$

[Computer simulation results presented below show that the sign \gg in Eq. (8) can be replaced with \geq .] In the case of light diatomic molecules, the inequality (1) requires the use of laser pulses with duration of about $\tau \lesssim 100$ fs. Assuming that the matrix elements of the dipole moment are of the order of 1 D, we have from Eq. (7) that the peak intensity of the laser field components of the first group must be not less than 10^{11} W/cm².

Let us take a closer look into parameters of the laser action, which satisfy the ODS conditions (3). For simplicity, we will demand secure satisfaction of these conditions only in the vicinity of $t=0$, where the excitation is most powerful. Taking into account the resonant character of the interaction, one can write $\langle 0 | \hat{d} | \tilde{1} \rangle = C_{1,2} \langle 0 | \hat{d} | 2 \rangle \propto C_{1,2}(t, \theta)$. Thus, the mag-

²Let us note that the cycle of transitions induced by these components in accordance with [56] satisfies minimum requirements for the laser-induced spatial symmetry breaking.

nitude of the matrix element $\langle 0|\hat{d}|\tilde{1}\rangle$ is determined by the value of the coefficient $C_{1,2}$ in expansion of the dressed state $|\tilde{1}\rangle$ over the basis of eigen molecular states.

Then, let us first require the equality $C_{1,2}=0$ to be exactly satisfied for the two limiting cases when molecules are oriented orthogonal ($\theta=\pi/2$) and opposite ($\theta=\pi$) to the desired direction. At $\theta=\pi/2$ all the off-diagonal elements $\Omega_{m,n}^{(j)}(t, \theta)$ of the Hamiltonian (5), being proportional to $\cos(\theta)$, become equal to zero. Therefore, the eigenfunctions (5) coincide with the eigenfunctions of the unperturbed molecular Hamiltonian \hat{H}_0 and, in particular, $|\tilde{1}\rangle=|1\rangle$, i.e., the equality $C_{1,2}|_{\theta=\pi/2}=0$ is always satisfied. Thus, additional analysis is required only for the case of $\theta=\pi$. The required relationships between the molecular and field parameters can be easily derived by substituting $C_{1,2}=0$ into the equation $(\hat{H}_d|_{\theta=\pi}|\tilde{1}\rangle=\tilde{E}_1|\tilde{1}\rangle)$. As a result, we have

$$A_{ii} = |\tilde{\alpha}|, \quad \varphi_{ii} = \varphi_i + \varphi_{iii} + [1 - \text{sgn}(\tilde{\alpha})] \frac{\pi}{2}, \quad (9)$$

where

$$\tilde{\alpha} = \delta \frac{2\hbar(\vec{\zeta} \cdot \vec{d}_{1,2})(\vec{\zeta} \cdot \vec{d}_{2,3})}{(\vec{\zeta} \cdot \vec{d}_{1,3}) \left(\frac{A_i}{A_{iii}} \vec{d}_{2,3}^2 - \frac{A_{iii}}{A_i} \vec{d}_{1,2}^2 \right)}. \quad (10)$$

Second, let us determine the detuning δ_0 from the following condition: $\tilde{\delta}_0|_{\theta=0}=0$. Typical dependencies $|\langle 0|\hat{d}|\tilde{1}\rangle|(\theta)$ and $\tilde{\delta}_0(\theta)$ on the parameters of the laser action determined from the above conditions are shown in Figs. 1(b) and 1(c). From this figure one can see that in the range of angles $0 < \theta < \pi/4$ the detunings from the resonance are small and the value of $|\langle 0|\hat{d}|\tilde{1}\rangle|$ reaches its maximum, i.e., the most favorable conditions for the excitation of the transition $|0\rangle \rightarrow |\tilde{1}\rangle$ are satisfied. Increasing the angle θ leads to a fast increase of the detuning $\tilde{\delta}_0$ and fast decrease of the value $|C_{1,2}|$, so that in the range of angles $\pi/4 < \theta < \pi/2$ the transition becomes blocked. Further increase of the angle θ up to the value of π is accompanied by a significant decrease of the detuning from the two-photon resonance, but the value of $|C_{1,2}|$ in all this interval remains small, so that the transition probability $|0\rangle \rightarrow |\tilde{1}\rangle$ is still low. Thus, after the laser pulse is off, i.e., after finishing the adiabatic transformation $|\tilde{1}\rangle \rightarrow |1\rangle$, the excited state $|1\rangle$ is primarily populated by those molecules whose orientation is characterized by small values of the angle θ .

It is worth noting here that although the speculations given above provide a rather clear qualitative outline of the idea of the suggested ODS method, they do not give a reliable and complete description of the real dynamical picture and cannot be used to make a conclusion about the efficacy of the ODS method. Instead, our speculations allow us to make a rough estimate of the optimal parameters for the laser action. With this, Eqs. (9) and (10) give a patently understated estimate for the amplitudes of the field components

because the excitation of the molecules takes place during the whole time of the laser action, but not only at the peak laser field intensities.

In the next section of the paper, our qualitative speculations given above will be corroborated with the help of a more quantitative model.

III. NUMERICAL ANALYSIS OF THE LASER-BASED ODS AND ITS APPLICATION TO THE MOLECULAR ORIENTATION PROBLEM: THE BF MOLECULE

We choose the BF molecule for further quantitative consideration for several reasons. First, this molecule is a typical one from a large class of light diatomic heteroatomic molecules whose orientation is hard to control because of fast rotations at high temperatures. One more argument arises from the specific parameters of its electronic terms, which are not only rather friendly for calculation but also very convenient for realization of the ODS scenario. Namely, they allow us to simplify the general ODS scheme [Fig. 1(a)], and to perform ODS using laser fields from an experimentally available range of frequencies. The latter makes the BF molecule an attractive candidate for an experimental test of our theoretical proposals.

For the following, let us choose a molecule-fixed unit vector directed from the B to the F atom as the molecular direction $\vec{\zeta}$ under control. The first moment $\cos(\theta)$, where $\theta=(\vec{\zeta}, \vec{z})$, will be used as a quantitative characteristic of the degree of molecular orientation.

In the previous section, we introduced the ODS method as an auxiliary tool for preparation of energetically separated anisotropic ensembles of the molecules that can be used for further processing. However, there exists at least one burning issue, which can be directly solved within the ODS scheme considered in Sec. II (Fig. 1). This is the laser-induced field-free dynamical orientation of linear molecules.

Let us first clarify why the energetic separation in the molecular ensemble can lead by itself to the dynamical orientation of the molecules. For this we will consider an ensemble of noninteracting BF molecules, which is in thermodynamic equilibrium with the temperature $T \sim 300$ K; then almost all molecules (more than 99.9%) are in the ground vibronic state $|0\rangle$ of symmetry $^1\Sigma$.

Suppose that just before $t=0$ we have performed the ODS, so that at $t=0$ we have the n th part of the molecules from the ensemble instantly excited to some vibronic state $|1\rangle$ where the orientation of these excited molecules corresponds to angles $\theta|_{t=0}$ close to zero. By introducing the notations $\langle \cos \theta \rangle_0$ and $\langle \cos \theta \rangle_1$ for the degrees of orientation of the vibronically unexcited and excited molecules, respectively, we can present the ensemble-averaged degree of orientation in the form $\langle \cos \theta \rangle = (1-n)\langle \cos \theta \rangle_0 + n\langle \cos \theta \rangle_1$. Note that, according to the definition of the ODS, at time $t=0$ we have $\langle \cos \theta \rangle = 0$, whereas each of the above subensembles is anisotropic: $\langle \cos \theta \rangle_1|_{t=0} = \xi > 0$ and $\langle \cos \theta \rangle_0|_{t=0} = -[n/(1-n)]\xi < 0$.

All key peculiarities of the post-ODS free rotational dynamics of the molecules can be understood in the frame of so-called rotational revivals. The essence of this effect is that

an arbitrary rotational state of any free linear rigid quantum rotor with moment of inertia I at any initial time instant will be exactly restored later within subsequent free evolution at integer multiples of the revival time $\tau_{\text{rev}} = \pi\hbar/B$, where $B = 2\pi^2\hbar^2/I$ is the rotational constant of the rotor. This means that, once the anisotropic state has been constructed by laser means, it can be revived and utilized much later in the field-free regime.

That is why the rotational revivals are at the heart of various scenarios of field-free molecular ordering (see the reviews [1–6]). The ODS-based orientation is not an exception. Its underlying mechanism can be qualitatively clarified if we envisage molecules in the employed vibronic states $|0\rangle$ and $|1\rangle$ as rigid rotors with slightly different rotational constants B_0 and B_1 . Nevertheless, the corresponding tiny difference between revival times $\tau_{\text{rev},0}$ and $\tau_{\text{rev},1}$ may be comparable with the typical classical rotational period of molecules, especially at high temperatures. If the latter is true, the state of excited molecules at $t = \tau_{\text{rev},1}$ will be nearly the same as just after the ODS, so that $\langle \cos \theta \rangle_{t=\tau_{\text{rev},1}} = \xi$, but unexcited molecules will yet remain to be distributed almost isotropically. This results in a short-term spike in the total ensemble-averaged degree of orientation: $\langle \cos \theta \rangle_{t=\tau_{\text{rev},1}} = n\xi$. A similar picture occurs near any integer multiples of $\tau_{\text{rev},1}$. Similar spikes but of opposite sign would also arise near integer multiples of $\tau_{\text{rev},0}$ (except $t = k\tau_{\text{rev},0} = l\tau_{\text{rev},1}$, where k and l are integers).

The conceptual correctness of the picture described above of the photoinduced molecular dynamics has been confirmed by the results of numerical simulations on the example of BF molecules. As the working levels $|1\rangle$, $|2\rangle$, and $|3\rangle$ in the ODS scheme [Fig. 1(a)] we choose the ground vibrational states of the second, fourth, and sixth excited electronic states of symmetry $^1\Sigma$ (third, seventh, and tenth excited electronic levels, respectively). The calculated energies of these states (at $J=0$) with respect to the ground vibronic state are 68 300, 87 112, and 104 415 cm^{-1} , respectively.³ Such a specific choice of levels is advantageous as it allows us to simplify the ODS scheme shown in Fig. 1(a). That is, the relatively small ($2\Delta \sim 1508 \text{ cm}^{-1}$) difference between the energies of the transitions $|1\rangle \leftrightarrow |2\rangle$ and $|2\rangle \leftrightarrow |3\rangle$ allows simultaneous quasisonant excitation of both transitions by the frequency component $\vec{\mathcal{E}}_i$. Therefore, the number of field components of different frequencies can be reduced by removing $\vec{\mathcal{E}}_{\text{iii}}$. *Inter alia*, this drastically simplifies the generation of the required laser pulse in experiment: instead of using three phase-matched components $\vec{\mathcal{E}}_i$, $\vec{\mathcal{E}}_{\text{ii}}$, and $\vec{\mathcal{E}}_{\text{iii}}$ generated by means of parametric generation, it is enough now to phase-match only two components $\vec{\mathcal{E}}_i$ and $\vec{\mathcal{E}}_{\text{ii}}$ with the frequencies $\omega_{\text{ii}} = 2\omega_i$, which can be done using second harmonic generation, for instance.

To simulate realistic experimental conditions, we assume that each of the components $\vec{\mathcal{E}}_1$, $\vec{\mathcal{E}}_i$, and $\vec{\mathcal{E}}_{\text{iii}}$ has a Gaussian profile described by Eq. (4), where $\tau \approx 70$ fs. This value of τ

assures a reliable pulsed ODS regime [Eq. (1)] even at room temperature (at $T=300$ K the characteristic value of τ_{rot} is about 20 times larger than τ).

We define the rest of the laser action parameters via the following procedure. At the first step, the initial peak intensity values I_j for each of the components $\vec{\mathcal{E}}_j$ were chosen. For the components of the first group (i.e., $\vec{\mathcal{E}}_i$ and $\vec{\mathcal{E}}_{\text{ii}}$) an arbitrary choice of values has been practically bounded by the range $10^{11} - 10^{12} \text{ W/cm}^2$. The lower bound here originates from conditions for the quasisonant character of interaction $\Delta \lesssim \Omega_{1,3}^{(\text{ii})}, \Omega_{1,2}^{(\text{i})}, \Omega_{2,3}^{(\text{i})}$, where $\Omega_{m,n}^{(j)}$ is determined by Eq. (6), and the presence of the upper bound is due to the necessity of operating below the tunnel ionization threshold. Therefore, we choose the following values as initial ones: 1.17×10^{11} and $1.05 \times 10^{12} \text{ W/cm}^2$, respectively. We also were compelled to restrict the initial peak intensity of the $\vec{\mathcal{E}}_1$ component to $4.67 \times 10^{11} \text{ W/cm}^2$ to provide selective interaction with only one of the dressed states (specifically with the state $|\tilde{1}\rangle$).

At the second step, with the help of Eqs. (9) and (10) (where one has to set $A_{\text{iii}}=A_i$ and $\varphi_{\text{iii}}=\varphi_i$), we found the respective detunings from the resonance and then calculated the laser frequencies. These frequencies were used in all our calculations without further optimization.

Finally, we simulated laser-assisted ODS of the molecule itself to correct the peak intensities of each of the components, as well as the phase matching between the components of the first group. Maximization of the value of $\cos \theta$ served as the optimization criterion.

Calculations of the photoinduced dynamics of molecules have been done in the short-pulse approximation [63]. We began by treating the vibronic dynamical problem of interaction of the molecule with the laser pulse for various fixed orientations of the molecules (namely, $\theta = 0^\circ, 6^\circ, 12^\circ, \dots, 180^\circ$) by solving the corresponding non-stationary Schrödinger equation using the split-operator technique [64,65]. The basis for our calculations was composed of 11 electronic terms. Additional levels were included to allow for possible impact of parasitic nonresonant transitions. The results of these calculations served then as the starting point for subsequent simulations of free postpulse rotational dynamics for each vibronic state of the molecule. Specifically, we analyze independently the photoinduced changes and postpulse dynamics of all rotational states with $J \leq 39$ in initial incoherent thermal superposition. Here, the effect of the centrifugal stretching of the molecules in first order has been taken into account. The rotational basis for each occupied vibronic state consisted of all eigenstates with $J \leq 56$. Note that the rotational energy of the highest included rotational state is an order of magnitude higher than the initial rotational temperature and thus the rotational dynamics was calculated excessively accurately.

For the thermodynamically equilibrium initial state of the molecules with $T=300$ K, the following optimal parameters of the laser pulse have been found: $\omega_1 = 2.577 \times 10^{15} \text{ Hz}$

³All calculations of the parameters of the molecular terms were made *ab initio* with the software package GAUSSIAN 03 and the basis sets 6-311+G(3df,3pd) and AUG-cc-pVQZ.

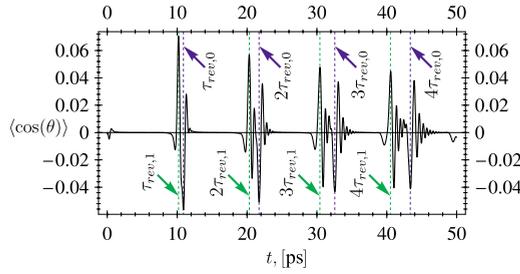


FIG. 2. (Color online) Degree of orientation $\langle \cos \theta \rangle$ as a function of time.

(116.3 nm),⁴ $I_1 = 4.67 \times 10^{11}$ W/cm²; $\omega_i = 5.384 \times 10^{14}$ Hz (556.8 nm), $I_i = 1.82 \times 10^{11}$ W/cm²; $\omega_{ii} = 1.076 \times 10^{15}$ Hz (278.4 nm), $I_{ii} = 1.64 \times 10^{12}$ W/cm².⁵ With this, the components $\vec{\mathcal{E}}_i$ and $\vec{\mathcal{E}}_{ii}$ must be phase matched so that $\varphi_{ii} = 2\varphi_i + 2.9$.

The corresponding temporal dependence of the degree of orientation of the molecules is shown in Fig. 2. Note that, just after the ending of the laser pulse (i.e., at the time moment $t=0$) about 97% of the molecules are in the states $|0\rangle$ ($\sim 88.7\%$) and $|1\rangle$ ($\sim 8.3\%$), and the remaining 3% are almost entirely localized in the states $|2\rangle$ and $|3\rangle$, so that the population of the rest of the vibronic states is negligibly small. These data testify to the high degree of the adiabaticity of the process of formation and evolution of the dressed states. They also mean that the dependence shown in Fig. 2 should basically be a sum of two series of rotational revivals, produced, respectively, by molecules in the vibronic state $|1\rangle$ (with the corresponding revival period $\tau_{\text{rev},1} \simeq 10.1$ ps) and in the state $|0\rangle$ ($\tau_{\text{rev},0} \simeq 10.8$ ps). Both series of revival spikes are clearly seen in Fig. 2 (see the arrows), although subsequent revivals become less pronounced and are gradually washed out. The latter is a signature of sufficient deviations from the rigid rotor approximation on a long-time scale due to the Coriolis distortions.

Figure 3 provides complementary information about the angular distributions of the molecules near the first positive and negative revival spikes. In agreement with the previous discussion, one can see that the positive orientational spike at $t=10.2$ ps is produced by strongly asymmetrical distribution of the excited molecules: more than 83% of these molecules have a positive projection of their molecular axes $\vec{\zeta}$ on the laboratory axis \vec{z} , whereas the molecules in the ground vibronic state are almost isotropically distributed. At $t=10.8$ ps a reversed picture is observed: the molecules in the excited state are distributed near symmetrically with respect to the upward-backward direction of the axis \vec{z} , but the analogous distribution of the unexcited molecules is notably asymmetrical.

A remarkable feature of the dependencies in Figs. 2 and 3 is the extraordinary high peak values for the degree of ori-

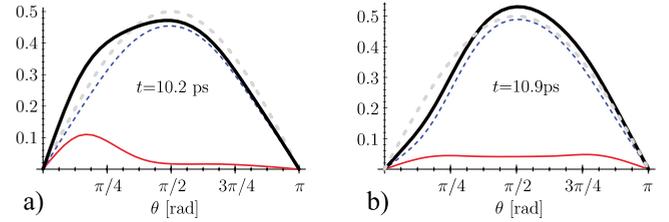


FIG. 3. (Color online) Angular distributions of the molecules at $t=10.2$ (a) and 10.9 ps (b). On both plots the total distribution is shown by thick continuous lines. Thin continuous and dashed lines display the partial angular distributions of the molecules in the excited vibronic state $|1\rangle$, and in the ground vibronic state $|0\rangle$, respectively. For comparison, the initial isotropic distribution (thick dashed line) is also shown.

entation of the molecules of up to 0.071. To our knowledge, up to now there is no other alternative laser method giving such high degrees of orientation at room temperature. The analysis of the ODS quality, however, gives even more exciting results. The orientational distribution in the subensemble of excited molecules in the state $|1\rangle$ at $t=10.2$ ps (see the thin continuous line in Fig. 3) corresponds to $\langle \cos(\theta) \rangle_1 = 0.70$, which is to our knowledge a record degree of orientation for room temperature.

From this one can conclude that the suggested ODS-based mechanism of molecular orientation is much more effective (by an order of magnitude) than the “kick” mechanism widely discussed in the literature. A detailed comparison of these two methods was given in our recent work [57]. Therefore, we will clarify here only the question about the stability of the photoinduced dynamics of the molecules with respect to the parameters of the laser impact. For this, we will use Fig. 4(a), which shows the dependence of the amplitude value of $|\langle \cos(\theta) \rangle|$ on the peak intensities I_i and I_{ii} . One can see that in the region of optimal intensities found above there is a well-pronounced maximum. However, one can also see that an essential increase of the amplitude of $|\langle \cos(\theta) \rangle|$ happens also with increase of the peak intensity of the component $\vec{\mathcal{E}}_i$ up to the value of $\sim 5 \times 10^{11}$ W/cm². The existence of this second area of peak values of $|\langle \cos(\theta) \rangle|$ is caused by resonance interaction with another, higher-lying dressed state $|\tilde{3}\rangle$. In this area of pulse parameters, not the state $|1\rangle$ but the state $|\tilde{3}\rangle$ becomes the most populated among the excited vibronic states when the laser pulse is off. Thus, exactly this state along with the ground state $|0\rangle$ determine the general characters of the registered rotational structure. Therefore, increase of intensity of the component $\vec{\mathcal{E}}_i$ will result in disappearance of the orientational spikes in the vicinity of multiples of $\tau_{\text{rev},1}$ with simultaneous rise of another set of spikes near multiples of $\tau_{\text{rev},3}$ [see Fig. 4(b)].

It is important to note that a switch to this second area of intensities with the same phase matching between field components will invert the laser excitation preferences from molecules with θ close to zero to those with θ close to π . Therefore, the molecules in the first and second regions of intensities will bring in opposite contributions to the mean value of $\langle \cos(\theta) \rangle$ [Fig. 4(c)]. In a real experiment, the spatial distribution of the laser field is almost always essentially

⁴Laser radiation with such a wavelength can be obtained as a result of laser generation in the Laiman series of molecular hydrogen with the use of Ti:sapphire laser pumping [66].

⁵In agreement with the note in the bottom of Sec. II, the optimal intensities are approximately 1.5 times higher than those obtained with Eqs. (9) and (10).

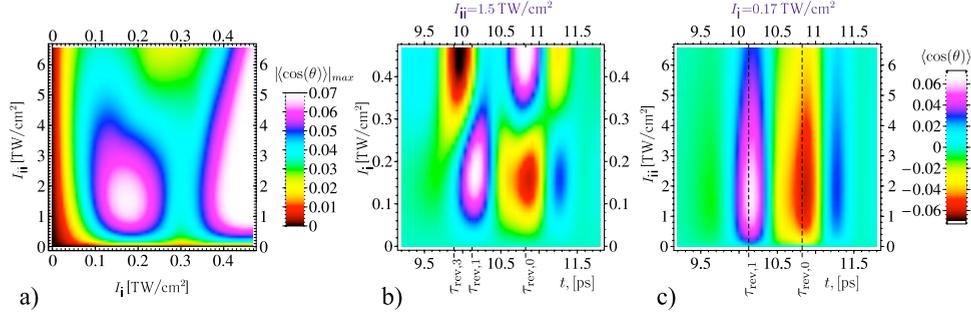


FIG. 4. (Color online) (a) Dependence of the maximal degree of orientation $|\langle \cos(\theta) \rangle|_{\max}$ vs the peak intensities of the components $\vec{\mathcal{E}}_i$ and $\vec{\mathcal{E}}_{ii}$. (b), (c) Temporal dependence of $\langle \cos(\theta) \rangle$ in the vicinity of $t = \tau_{\text{rev},0}$ for the different peak intensities I_i and I_{ii} . Here, the components $\vec{\mathcal{E}}_i$ and $\vec{\mathcal{E}}_{ii}$ have been chosen matched in such a way that $\varphi_{ii} = 2\varphi_i + \pi$. The correspondence between the numerical values and their color codes is shown in the insets.

heterogeneous. Therefore, from the experimental point of view, it seems preferable to use the laser component $\vec{\mathcal{E}}_i$ with the peak intensity $I_i \lesssim 2.5 \times 10^{11} \text{ W}/\text{cm}^2$. Under this choice, the only intensity-dependent parameter will be the amplitude of spikes of $\langle \cos(\theta) \rangle_{\max}$, determining the efficacy of orientation, but not the shape of the dependence $\langle \cos[\theta(t)] \rangle$ [Figs. 4(b) and 4(c)].

Thus, based on the data plotted in Fig. 4, we can conclude that the effect of orientation is rather stable toward variations of the peak intensities of the laser field components. For instance, a decrease by a factor of 2 of the orientation efficacy is achieved only after approximately doubling in the intensities of the components $\vec{\mathcal{E}}_i$, $\vec{\mathcal{E}}_{ii}$, or $\vec{\mathcal{E}}_1$.

Finally, let us analyze how the deviations in phase matching between the components $\vec{\mathcal{E}}_i$ and $\vec{\mathcal{E}}_{ii}$, i.e., imperfect satisfaction of the second relation in Eq. (9), affects the orientation efficacy. For this, we made a series of simulations of the photoinduced orientational dynamics for various values of the phase-locking parameter $\phi = \varphi_{ii} - 2\varphi_i$ at the optimal values of the intensities of the laser field components. Note that, due to the relation $\langle \cos \theta \rangle|_{\phi=\phi_0} = -\langle \cos \theta \rangle|_{\phi=\phi_0+\pi}$, which is satisfied for all values of ϕ_0 , it is only necessary to track the changes in the photoinduced dynamics in the range of values $0 \leq \phi < \pi$. The results describing the vicinity of the first rotational revival are shown in Fig. 5. From Fig. 5(a) one can see that the value of the parameter ϕ determines both the temporal dynamics and the amplitude of the laser-assisted

orientation. The peak values of $\langle \cos(\theta) \rangle$ are achieved in the vicinities of $\phi=0$ and $\phi=\pi$, which is in agreement with the results of the above analysis. It is interesting to note that the effect of the laser-assisted orientation of the molecules will arise at all values of ϕ [Fig. 5(b)]. However, the amplitude of the orientational spikes at the values $\phi \sim \pm \pi/2, \pm 3\pi/2$ will be approximately one order of magnitude lower than the peak amplitude.

IV. CONCLUSION

In conclusion, the ODS-based method of isotropy breaking by a single multifrequency femtosecond laser pulse has been shown numerically to be one of the most effective proposals for the case of high-temperature molecular ensembles. On the example of the BF gas at room temperature, we demonstrated that, in addition to the possibility of preparation of well-oriented subensembles of vibronically excited molecules with the degree of orientation up to 0.7, it also allows one to achieve extremely high degrees of orientation (up to 0.07) for the molecular ensemble as a whole. It is worth stressing that we do not employ the interaction of the laser field with the molecular permanent dipole moment for the orientation of the molecules. This means that the suggested ODS method can be applied to any molecule regardless of the value of its permanent dipole moment, except for those molecules for which the orientation concept cannot be applied (for example, homoatomic molecules). At the same time, the ODS-based orientation of molecules with a large permanent dipole moment (like BF molecules) has a number of interesting applications such as retrieving information about the molecular structure, and generation of few-cycle tetrahertz pulses, which will be analyzed in a forthcoming presentation.

Our simulations confirmed the stability of the proposed ODS-based scheme with respect to variations of the parameters of the laser pulse. From the experimental point of view, however, a key disadvantage of the suggested method is the

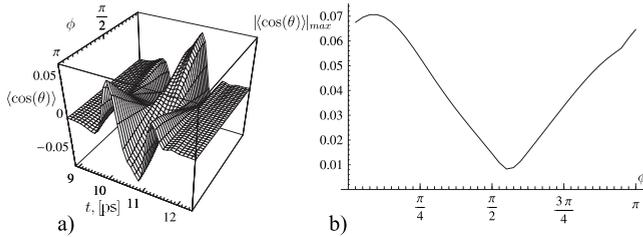


FIG. 5. (a) Time dependence of the degree of orientation $\langle \cos(\theta) \rangle$ in the vicinity of $t = \tau_{\text{rev},1}$ as a function of the phase-locking parameter ϕ . Only the interval $0 < \phi < \pi$ is plotted, taking into account the relation $\langle \cos \theta \rangle|_{\phi=\phi_0} = -\langle \cos \theta \rangle|_{\phi=\phi_0+\pi}$. (b) Dependence of the maximal absolute value of the degree of orientation $|\langle \cos(\theta) \rangle|_{\max}$ vs ϕ .

obligatory phase matching of some of the components of the laser field, although, the formation of anisotropy in the orientational distribution of the molecules will occur for any phase relation between the field components (see Fig. 5).

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