Laser-assisted molecular orientation in gaseous media: new possibilities and applications

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Abstract. It was shown recently by us that an isotropic distribution of molecules in gaseous media can be drastically effected via their orientation-dependent selective excitation by a strong femtosecond multicomponent laser pulse. In the present paper, we analyze the specific effects accompanying the dynamical orientation of molecules driven this way. It is demonstrated that the peculiarities of the post-pulse transient angular distribution of molecules allow original proposals for the generation of pulsed terahertz radiation and also for the determination of the molecular rotational constants.

Contents

1. Introduction

Laser-assisted methods of angular ordering of molecules in the gas phase have nowadays become of major concern in a wide range of applications including the generation of short pulses [1, 2], studying ionization processes and the generation of high harmonics [3]–[10], analysis of molecular orbital structure [11]–[13], their tomography inclusive [14], studying

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various collisional and relaxation processes [15, 16], nanolithography [17], isotope separation [18, 19], the control of chemical reactions and of rovibronic dynamics [20]–[22], and some other stereochemistry problems, the construction of quantum gates [23], etc. In comparison with the 'classical' methods (based on the application of an electrostatic field [24]–[30] or hexapole focusing [31]–[33]), the variety of modern laser techniques of ordering [34]–[39] have benefits not only in the quality of ordering, but also in the unique ability to form controllable transient angular distributions in the field-free regime.

The present paper is targeted at an analysis of the side effects resulting from such time-dependent patterns for the case of the recently suggested by us method of controling the angular distribution of molecules via orientation-dependent selection (ODS) [40]–[42]. The ODS was proposed as an alternative to other laser-assisted mechanisms of coherent control of orientation, namely the combination of strong electrostatic and laser fields [43]–[48], and the action of short shaped infrared (IR) [49]–[54] of multifrequency laser pulses [55]–[61]. The laser-driven dynamics resulting from the latter mechanisms (in the nonadiabatic regime) can be satisfactorily reproduced within the famous model of kicked quantum rotor [49]–[54], where the external influence is simulated by the 'sudden' *strong* changes in angular momentum distribution. Contrariwise, the origin of the ODS-driven orientation is the 'sudden' *slight* changes in geometry of some molecules in the ensemble caused by their selective resonant excitation. This difference leads to crucial changes in all the specifics of post-excitation rotational dynamics and opens new possibilities in coherent control of molecular rotational dynamics, in particular, in resolution of the long-standing problems of orientation at room temperatures [40, 41] and absolute asymmetric synthesis of enantiomers from a racemic mixture of chiral molecules [42].

Here we will focus on the effects that accompany the media symmetry breaking, caused by the ODS-driven orientation of linear polar molecules. It will be shown that the laser-driven changes in angular distribution of the molecules result in such spatial-time-dependent macroscopic polarizations of the media, which provide conditions for the generation of few-cycle pulses of radiation in the terahertz (THz) domain. The timing, shape and spectrum of such pulses will be of special interest because they are found to be dependent on intramolecular properties rather than on the characteristics of the initiating laser action. Thus, a spectroscopic analysis of such pulses allows retrieval of information about the molecular rotational constants.

The paper is organized as follows. In section 2, we give a brief review of the principles of ODS-driven orientational symmetry breaking with the example of BF molecules. In section 3, the possibility of employing the ODS for generation of the THz radiation is discussed and simple estimates for the possible parameters of this effect are given. Section 4 contains a detailed analysis of the THz pulses spectrum and an explanation of its peculiarities. Also, a method for the determination of molecular rotational constants along with nonrigidity corrections to them of any order is suggested. In section 5, we summarize the key results of this work.

2. Basics of the ODS-driven orientation

In this section, we briefly outline with the example of BF molecules general ideas about the orientational isotropy breaking via the ODS, which were discussed in detail in our previous publications [40]–[42]. Let us first introduce the molecule-fixed unit vector $\vec{\zeta}$, directed from a boron atom to a fluorine one. As a measure of molecular distribution anisotropy relative to the spatially fixed z-axis in each spatial point $\vec{R}$ at any time instant t, it is convenient and sufficient

for our purposes to choose the ensemble-averaged value of the first moment $\cos(\theta)|_{\vec{R},t}$, where $\theta = \widehat{(\vec{\zeta}, \vec{z})}$ (we will skip an explicit indication of $\vec{R}$ dependence below). Then, the symmetry breaking of the media with preferential orientations of the molecules along (backward to) the z-axis can be identified by positive (negative) shifts of $\langle \cos(\theta) \rangle$ from its zero value, corresponding to the initial equilibrium isotropic distribution.

The key principle of the ODS-driven scenario tells us that macroscopic orientation can be produced by a sudden (with respect to the molecular rotations) *intramolecular* excitation of a portion of molecules with the well-defined orientation (i.e. with θ close to zero) at some time instant $t = t_0$. Let us denote by $|0\rangle$ an initial unexcited vibronic state and by $|1\rangle$ a vibronic state of the excited portion of molecules. Suppose also that excited molecules constitute the nth part of all the molecules in the vicinity of $\vec{R}$. Using notations $\langle \cos \theta \rangle_0$, $\langle \cos \theta \rangle_1$ for the degrees of orientation of vibronically unexcited and excited molecules, respectively, we can write an ensemble-averaged degree of orientation in the form $\langle \cos \theta \rangle = (1 - n)\langle \cos \theta \rangle_0 + n \langle \cos \theta \rangle_1$. Because of the supposed sudden and anisotropic regime of excitation, we obtain the following partial distributions just after the laser action:
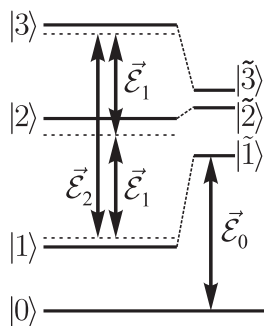
$$\langle \cos \theta \rangle_1 |_{t=t_0} = \xi > 0, \qquad \langle \cos \theta \rangle_0 |_{t=t_0} = -\frac{n}{1-n}\xi < 0,$$

but the total distribution still remains isotropic: $\langle \cos \theta \rangle |_{t=t_0} = 0$.

It is easy to show, however, that we need not exert any additional efforts to violate the last equality, because it will happen automatically as a result of the subsequent free rotations of the molecules. This effect originates from changes in the molecular geometry accompanying vibronic excitation. Specifically, the state $|1\rangle$ in our sample scenario for BF molecules will be the second electronic state of the $^1\Sigma$ symmetry (the third excited electronic level) with the excitation energy of $68\,300\,\text{cm}^{-1}$. The equilibrium bond length for rotationally cold molecules in this state is about $1.206\,\text{Å}$, whereas it is about $1.248\,\text{Å}$ in the ground state $|0\rangle$. Thus, the rotational dynamics of both unexcited ($i = 0$) and excited ($i = 1$) molecules at least at the early times after the excitation can be described in the frame of the model of rigid rotors (with rotational energy levels $E_{\text{rot},i} = B_i J(J + 1)$, where J is the quantum number of the angular momentum) with slightly different rotational constants $B_0 = 1.546\,\text{cm}^{-1}$ and $B_1 = 1.653\,\text{cm}^{-1}$.

From now on, we will assume that the initial state of the molecules is a thermodynamic equilibrium state corresponding to the temperature $T \sim 300\,\text{K}$; then the rotational energy distribution is rather accurately described by the classical Maxwell formula. The specifics of the ODS-driven excitation in this case is that the Maxwell-like partial energy distributions are preserved for both vibronically excited and unexcited molecules with the effective temperatures $T_0 \simeq T$ for unexcited molecules and $T_1|_{T \to \infty} = T \times B_1/B_0$ for the excited ones [40]. Thus, at the early times after the ODS, both partial angular distributions will demonstrate quasiclassical behavior, i.e. undergo fast (at a scale of $1\,\text{ps}$ for $T = 300\,\text{K}$) smearing of anisotropies in the corresponding degrees of orientation.

However, the further free rotational dynamics of linear rigid rotors shows an interesting phenomenon of the so-called rotational revivals, i.e. exact reconstructions of the rotor's state at integer multiples or revival times $\tau_{\text{rev},i} = \pi\hbar/B_i$ due to the commensurability of energetical separations between the rotational levels. Rotational revivals are of special importance for the laser coherent control of molecular dynamics, because they allow us to revive and utilize once constructed anisotropic state at a much latter time in the field-free regime [34]–[39].

Figure 1. Principal scheme of the laser-driven ODS.

Therefore, according to the rigid rotor model, averages $\langle\cos\theta\rangle_i$ will have almost zero value everywhere except for 1 ps vicinities of series of time instants $t = t_0 + lt_{\mathrm{rev},i}$, where sharp and pronounced spikes of orientational asymmetry should be observed. At $l = 0$, i.e. at $t = t_0$, the spike of $\langle\cos\theta\rangle_1$ is compensated by the spike of opposite sign of $\langle\cos\theta\rangle_0$, resulting in zero overall degree of orientation. For $l \neq 0$, however, positive and negative spikes become separated in time due to the difference in revival times ($\tau_{\mathrm{rev},0} \simeq 10.8$ ps and $\tau_{\mathrm{rev},1} \simeq 10.1$ ps) because of the slight inequality of rotational constants B_i. Even for $l = 1$, this difference (about 0.7 ps) is enough to clearly resolve both spikes and thus to result in pronounced time-varying asymmetry in orientational distribution of the molecules between $t_0 + 9$ ps and $t_0 + 12$ ps (see figure 2 in [41]).

Let us briefly describe the mechanism of the laser-assisted ODS employed in the strategy outlined above. To provide a 'sudden' regime of excitation, one needs to employ a pulsed irradiation with a duration at least one order of magnitude shorter than the typical period of molecular rotations at a given temperature (i.e. about 100 fs in our example). If the dipole moment of the transition $|0\rangle \to |1\rangle$ is directed along $\vec{\zeta}$, it is evident that the laser pulse tuned in resonance with this transition and linearly polarized along the z-axis is capable of only performing the preferential excitation of the molecules oriented collinear to the z-axis. However, it will equally act on the forward-directed ($\theta \sim 0$) and backward-directed ($\theta \sim \pi$) molecules. Thus, our main challenge is to manage a symmetry-breaking forward-direction-selective character of the excitation, which is insensitive enough to variations of the parameters of the laser pulse to guarantee that the effect is stable and is preserved across the laser pulse cross section. It is well known that such a stability is intrinsic to the adiabatic regime of the interaction with the laser radiation [62]–[65]. Therefore, our main idea is to realize the ODS with the help of a multicomponent laser pulse $\vec{\mathcal{E}} = \sum_{k=0}^{2} \vec{\mathcal{E}}_k$, where the component $\vec{\mathcal{E}}_0$ is used for the nonadiabatic excitation of the molecules from their ground vibronic state, whereas the rest of the components adiabatically interacting with the molecules are used to assure the necessary asymmetry of the excitation.

The resulting excitation scheme is shown in figure 1. Besides the levels $|0\rangle$ and $|1\rangle$, it includes also two additional levels $|2\rangle$ and $|3\rangle$, which correspond to the fourth and sixth excited electronic states of the symmetry $^1\Sigma$ (the seventh and tenth excited electronic levels, respectively) with the excitation energies of 87 112 and 104 415 cm^{-1} [40]. All employed levels are connected to each other by parallel transitions. The components of the laser pulse are linearly polarized along the z-axis and have Gaussian temporal profile $\exp\left[-2(t - t_0)^2/\tau^2\right]$ with $\tau \simeq 70$ fs. Other parameters (amplitudes, frequencies and relative phases) of the components
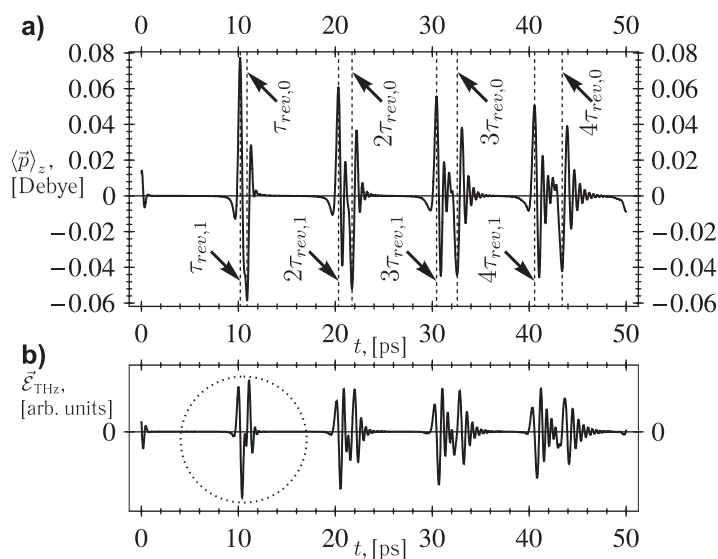
$\vec{\mathcal{E}}_1$ and $\vec{\mathcal{E}}_2$ with the frequencies $\omega_2 = 2\omega_1$ are set to provide the best conditions for the cyclic population transfer between levels $|1\rangle$, $|2\rangle$ and $|3\rangle$ in the regime of resonant adiabatic passage (RAP) [59]. It has been shown that the corresponding odd-length cyclic chain of transitions results in orientational symmetry breaking [66]. In particular, the effect of such a chain of transitions in the RAP regime is the adiabatic transformation of the eigen vibronic states $|1\rangle$, $|2\rangle$ and $|3\rangle$ into the effective dressed states $|\tilde{1}\rangle$, $|\tilde{2}\rangle$ and $|\tilde{3}\rangle$ with strongly asymmetrical dependence of their structure and effective energies relative to the forward–backward orientation of the molecules with respect to the z-axis [59]. These dressed states compose a natural basis for describing the 'pumping' caused by the component $\vec{\mathcal{E}}_0$. We chose the frequency ω_0 of this component in the vicinity of the frequency of the transition $|0\rangle \leftrightarrow |2\rangle$, but still essentially far from the resonances with both, this transition and the transitions $|0\rangle \leftrightarrow |1\rangle$, $|0\rangle \leftrightarrow |3\rangle$, $|0\rangle \leftrightarrow |\tilde{2}\rangle$ and $|0\rangle \leftrightarrow |\tilde{3}\rangle$ for all possible orientations of the molecules. The only resonance with the transition $|0\rangle \leftrightarrow |\tilde{1}\rangle$ is demanded to be held exactly for the molecules codirectional to the z-axis.

As a result, the interaction of a molecule with the laser pulse begins with the field-dressing of yet unpopulated excited molecular states without any population transfer. Near the peak of the pulse, the dressed state $|\tilde{1}\rangle$ becomes tuned in resonance with the exciting component $\vec{\mathcal{E}}_0$. However, the orientation-dependent properties of the state $|\tilde{1}\rangle$ result in its selective pumping only for the molecules with $\theta \sim 0$. Further evolution during the laser pulse turn-off leads, on the one hand, to the violation of the resonance conditions and termination of the population transfer. On the other hand, the corresponding gradual decrease in the dressing field leads to the adiabatical flow of the excited population in the frame of the transformation of the dressed state $|\tilde{1}\rangle$ back into the eigenstate $|1\rangle$, thus completing the ODS.

A thorough analysis of the discussed scheme and details of its possible realization for BF molecules are given in [40, 41], where the following optimal frequencies and the peak intensities I_k of the laser pulse components were found: $\omega_0 = 2.577 \times 10^{15}$ Hz (116.3 nm), $I_0 = 4.67 \times 10^{11}$ W cm^{-2}; $\omega_1 = 5.384 \times 10^{14}$ Hz (556.8 nm), $I_1 = 1.82 \times 10^{11}$ W cm^{-2}; $\omega_2 = 1.076 \times 10^{15}$ Hz (278.4 nm), $I_2 = 1.64 \times 10^{12}$ W cm^{-2}. In addition, the components $\vec{\mathcal{E}}_1$ and $\vec{\mathcal{E}}_2$ should be phase-matched, so that $\varphi_2 = 2\varphi_1 + 2.9$. Note that relative change of the phases of these components by π reverses the direction of the selection, and thus the ODS effect vanishes or becomes unpredictable without thorough phase control.

References [40, 41] also present the results of several numerical simulations of the ODS-driven symmetry breaking in a gas of BF molecules. They clearly reveal the main strength of the ODS—its high efficiency at high temperatures. Specifically, calculations show that the laser pulse with the above given parameters results in orientational asymmetry in a gas of BF molecules at room temperature with peak values of $\langle \cos \theta \rangle$ and $\langle \cos \theta \rangle_1$ of up to 0.071 and 0.7, respectively. Such a striking efficacy comes from a minor dependence of an attainable peak in the degree of orientation on the initial temperature of the molecules, which affects mainly the widths of spikes in orientational distribution—the higher the temperature, the sharper the spikes. This feature is in startling contrast with other techniques of symmetry breaking based on the strong rotational heating of the molecules by a 'kick', produced by the laser pulse. In the latter case, the preservation of the effect's quality at higher temperatures requires stronger heating of the molecules and thus the stronger kick, whereas in the ODS-driven scenario the rotational heating itself is only a slight side effect, as discussed above.

Therefore, the ODS-driven symmetry-breaking influence on the molecules is endowed with many features that are unique relative to the previously suggested laser-assisted scenarios of

Figure 2. (a) The calculated averaged value of the z-projection of the permanent dipole moment $\vec{p}$ of a BF molecule as a function of time after the laser pulse arrival. (b) The corresponding temporal profile of the generated THz radiation. The laser pulse is assumed to have the optimal parameters given in section 2, and the initial temperature of the molecules is 300 K.

such a kind. One could thus expect the reflection of these features in multifarious phenomena caused by the ODS. Specifically, in the following sections of the paper we will consider the effects that accompany the ODS of the molecules with a rather large permanent dipole moment. The BF molecule still remains a good object for our studies and hence will be further used for quantitative estimates.

3. Use of the laser-assisted ODS for generation of the THz radiation

The possibility of generation of the THz radiation follows from the fact that the simultaneous orientation of the polar molecules in some region of space leads to the creation of time-varying macroscopic polarization. To clarify this, let us consider a volume filled with a gas of BF molecules. The calculated permanent dipole moment $\vec{p}$ for a BF molecule is about one Debye (D) for all employed vibronic states: 0.95 D in the ground state, and 1.18, 1.23 and 1.25 D in the states $|1\rangle$, $|2\rangle$ and $|3\rangle$, correspondingly[2]. Thus, the ODS laser pulse produces temporal variations of the averaged value of the z-projection of the permanent molecular dipole (figure 2(a)).

Because of the approximate relation $\langle \cos(\theta) \rangle = \langle \vec{p} \rangle_z$ [Debye], the plot shown in figure 2(a) rather accurately reproduces, both qualitatively and quantitatively, the dependence $\langle \cos(\theta) \rangle(t)$ (compare with figure 1(b) in [41])[3]. From this figure, one can clearly see the pronounced spikes

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[2] All calculations of the BF molecule properties were made '*ab initio*' using the 'Gaussian 03' software package and the basis sets $6 - 311 + G(3df, 3pd)$ and AUG-cc-pVQZ.

[3] However, the differences between the permanent dipole moments in the ground and excited states cause some peculiarities in the dependence shown in figure 2(a), which are unexpected for the corresponding dependence $\langle \cos(\theta) \rangle(t)$: namely, the existence of the spike at $t = 0$ and sufficient asymmetry in the heights of positive and negative spikes.

of the macroscopic polarization, arising near the revival time instants $t = m\tau_{\text{rev},i}$ ($i = 1, 2$; $m = 1, 2, \ldots$). The oscillating 'tails' observed after the higher order spikes arise from smearing of rotation revivals due to deviations from the rigid rotor model and are a result of the accumulated effect of the Coriolis distortions of the higher J rotational states. Because of strict timing between the laser pulse arrival and each spike's occurrence, the propagation of the ODS laser pulse along the x-axis in the media will produce the series of pulsed polarization waves running with the group velocity $\vec{\upsilon}$ of the laser pulse. These waves in accordance with the Maxwell equations will result in generation of the short THz pulses.

In this work, we will restrict ourselves to the simplest estimates for the possible parameters of this effect. For this, let us consider a model situation when BF molecules fill the semispace with $x > 0$. Assume that this semispace is illuminated by a laser pulse constituting a plane wave polarized along the z-axis and propagating along the x-axis. Let us also assume that we can neglect any transformation of the laser pulse resulting from its interaction with the media (i.e. suppose that the given-field approximation is valid for a description of the action of the laser radiation). These assumptions allow us to write the induced polarization of the media in the form

$$\vec{P}(\vec{R}, t) = n\vec{p}(x - \upsilon t), \tag{1}$$

where $p(\xi)$ is the function plotted in figure 2(a) and n is the concentration of the molecules. Inserting equation (1) into the wave equation for generating the THz wave

$$\frac{\partial^2}{\partial x^2}\vec{\mathcal{E}}_{\text{THz}} - \frac{1}{c^2}\frac{\partial^2}{\partial t^2}\vec{\mathcal{E}}_{\text{THz}} = \frac{4\pi}{c^2}\frac{\partial^2}{\partial t^2}\vec{P},$$

one can calculate the gain of the THz pulse $\vec{\mathcal{E}}_{\text{THz}}$:

$$\frac{\partial}{\partial x}\vec{\mathcal{E}}_{\text{THz}}(\xi, x) = -\frac{2\pi n}{c}\frac{\partial}{\partial \xi}(\langle \vec{p} \rangle_z (\xi, x)), \tag{2}$$

where $\xi = t - x/c$ is the running time. Deriving equation (2), we neglected the dispersion of the group velocities of the laser and THz pulses. The validity of this approximation is warranted by the extremely small thickness of the gaining layer of the active media (see the discussion below). Let us assume that the molecular concentration is of the order of N_A/V_m, where N_A is the Avogadro constant and $V_m \simeq 22.4 \, \text{liter mol}^{-1}$ is the molar volume of the ideal gas in normal conditions. Then, for the optimal parameters of the laser action given in section 2, we obtain the peak gain $\frac{d}{dx}|\vec{\mathcal{E}}_{\text{THz}}|_{\max} \sim 2 \times 10^6 \, \text{V cm}^{-2}$.

In fact, the above estimate of the gain is correct only for the superficial layers of the media, where the given-field approximation is valid. Destruction of the laser pulse caused by its interaction with the molecules leads to the gradual vanishing of the gain in the bulk of the media and sets a limit on the accessible peak value for the output amplitude of the THz radiation. To roughly estimate it, we can introduce an effective depth L of the active layer of the media. The main mechanism for the vanishing the ODS abilities of the laser pulse in absorption and scattering is the loss of the phase-locking between the components $\vec{\mathcal{E}}_1$ and $\vec{\mathcal{E}}_2$. This mechanism seems to be the dominant one taking into account the fragility of the phase relations and stability of the laser-driven ODS with respect to the variations of the amplitudes of the pulse components [40, 41]. Moreover, changes in the phase relations can lead to switching of the amplification of the THz pulse to its attenuation due to reversal of the direction of the selection. Therefore, the effective depth L is also a good approximation for the optimal overall

thickness of the active media. In order to estimate L it should be noted that the effective areas of the components of the pulse (i.e. quantities such as $\frac{1}{\hbar}\int_{-\infty}^{+\infty}|\vec{\mathcal{E}}_2\langle 1|\hat{\vec{d}}|3\rangle|\,\mathrm{d}t$, etc) have their values at the order of magnitude or less than π. Therefore, for the rough upper estimate of L it is reasonable to assume that each molecule 'knocks-out' a photon from each component of the laser pulse during its propagation. It is important to stress that under the 'knocking-out' of the photons, we imply both reduction of the laser field intensity and the effective reduction of the amplitudes of the phase-locked part of radiation. Then it is natural to estimate the effective depth L at the order of magnitude equal to the length of 'knocking-out' of all photons from any of the pulse components. Specifically, for our model parameters we receive an estimate $L \sim 10^{-3}$–10^{-2} cm, which corresponds to the peak values $|\vec{\mathcal{E}}_{\mathrm{THz}}|_{\max} \sim 10^5$–$10^6$ V m^{-1}.[4] Therefore, with the help of the laser-assisted ODS one can receive rather powerful pulses of the THz radiation.

Note that the above estimate for L is at an order of magnitude lower than the central wavelength of the induced THz radiation. This substantiates neglecting the dispersion of the group velocities of the laser and the THz pulses used while deriving equation (2). Moreover, it means that along with the generation of the THz pulse, which propagates collinear to the pumping radiation, the pulse with the opposite propagation direction will also be gained with almost the same efficiency. Taking also into account that generation of the THz pulse itself goes with the time delay $\sim\tau_{\mathrm{rev},1}$ with respect to the pumping laser pulse, one can conclude that the ODS laser pulse and the output THz pulse are separable in both spatial and temporal domains. This circumstance could be one of the advantages of the proposed technique from the point of view of various possible applications.

It is essential to stress that the homogeneous spatial distribution of the laser field intensity generally cannot be realized in the experiment where the gain conditions for THz radiation will vary across the focal spot of the incident radiation. In [40], however, it was shown that with the use of a laser pulse whose components $\vec{\mathcal{E}}_k$ ($k = 0, 1, 2$) have peak intensities less than 2.5×10^{11} W cm^{-2}, the only intensity-dependent parameter will be the amplitude of spikes of $\langle\cos(\theta)\rangle_{\max}$, determining the efficacy of orientation of molecules, but not the shape of the dependencies $\langle\cos(\theta(t))\rangle$ (and thus $\langle\vec{p}\rangle_z(t)$). This will guarantee the coherent generation of THz radiation across the focal spot if the phase relations between components $\vec{\mathcal{E}}_k$ are preserved. From the results of [40] it also follows that the gain of THz pulse will slowly vary with the deviations of amplitudes of these components (this is the consequence of the adiabatic nature of ODS). Namely, the double decrease of the gain is expected only after approximately double upward or downward change in the intensity of any of the components $\vec{\mathcal{E}}_k$.

4. Determination of the molecular rotational constants

In this section, we will analyze the shape and the spectrum of THz radiation. We will also show that this spectrum can be used for determining the molecular rotational parameters.

Very important and interesting peculiarities of the ODS-driven generation come from the structural analysis of the THz radiation: unlike the intensity, the shape and spectrum of the generated pulses depend weakly on the laser pulse parameters; they are very sensitive to the

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[4] In the above speculations, we did not consider the decay and self-action effects along with the propagation of the THz pulse. However, our estimates show that these effects become essential only at the higher amplitudes of the THz radiation ($|\vec{\mathcal{E}}_{\mathrm{THz}}|_{\max} \sim 10^7$–$10^8$ V/m^{-1}).

properties of the molecules of the active media. Moreover, it is not the adsorbed laser radiation but a regular thermal energy stored in the rotational degrees of freedom of the molecules that serves as a source of the THz radiation gain. All these features are native for the ODS-driven rotational dynamics, where laser action serves just as a tool for the orientation-selective change of the rotational molecular constants to make molecular rotations correlated even without significant changes in its rotational energies, as discussed in section 2 and in [40, 41]. Thus, the absorbed laser energy is stored in the vibronic degrees of freedom and does not affect the generation.

The structure of the induced THz pulses can be easily determined from equation (2):

$$\vec{\mathcal{E}}_{\text{THz}}(\xi, x) \propto \frac{\partial}{\partial \xi} \langle \vec{p} \rangle (\xi, x). \tag{3}$$

Its temporal profile is shown in figure 2(b). Without loss of generality, we will analyze the spectrum of a single THz pulse, rounded by the dashed curve in figure 2(b), which goes nearly one revival period after the initiating laser pulse.

The total power spectrum of the radiation of the molecular ensemble is determined by the interference of the contributions from molecular subensembles, consisting of molecules in different vibronic states $|i\rangle$ ($i = 0, 1$). During the ODS, the laser pulse correlates rotations of the molecules irrelative to their rotational speeds or directions of rotations owing to the sudden character of the excitation. Thus, one can expect that the spectral density of the THz radiation at frequency ν should be proportional to the squared density of the molecules having the same rotational frequency. In section 2, it was mentioned that energy distributions over the rotational degrees of freedom for both excited and unexcited molecules after the ODS are still the Maxwell ones. Therefore, at the initial temperature $T \gg B_i$, one can expect the spectral distribution $W(\nu)$ of the THz pulse energy to be the sum of contributions $W_i(\nu)$ from each subensemble of the form
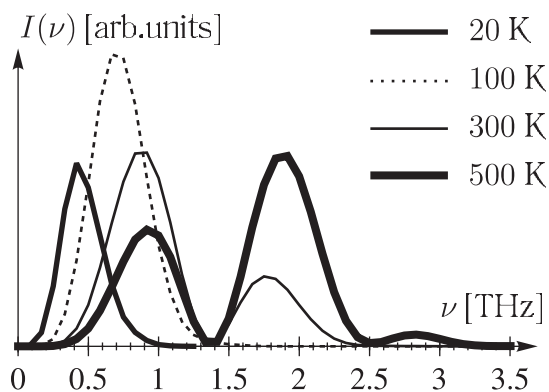
$$W_i(\nu) \propto \left(\frac{I_i}{T_i} \right)^3 \nu^4 \exp\left(-\frac{4\pi^2 I_i \nu^2}{kT_i} \right), \tag{4}$$

where I_i are the momenta of inertia of the molecules in the ith vibronic state, and T_i are the effective temperatures introduced in section 2. From equation (4), it follows that the spectrum of radiation emitted by each of the ith isolated subensembles is entirely determined by its rotational temperature T_i.

Calculations show that if one could somehow measure the 'partial' spectrum of the radiation emitted independently by vibronically unexcited or excited molecules, then one would see their excellent compliance with the predictions of equation (4). However, the real spectrum of the THz pulse described by equation (3) is qualitatively different from a simple sum of the contributions $W_i(\nu)$.

Figure 3 shows such spectra for four pulses originating from the ODS of BF molecules with different initial temperatures. One can see that the qualitative agreement with predictions of equation (4) holds on only for initial temperatures $T \lesssim 100\,\text{K}$. The spectra corresponding to the molecules with higher temperatures demonstrate the pronounced peculiarity—the series of gaps.

A very interesting property of these gaps is that their positions do not depend on the temperature and parameters of the laser action. Let us show that this feature is a consequence of the laser-induced correlations between rotations of the molecules in different vibronic states, namely the result of destructive interference of emission of vibronically excited and unexcited

Figure 3. Spectral distribution of the THz pulse energy for the fixed optimal parameters of the laser pulse given in section 2 and different initial molecular temperatures.

molecules or, in other words, the result of the mutual compensation of the macroscopic polarizations produced by the molecules rotating with the gap frequency. Such a compensation naturally arises for all the molecules just after the ODS pulse: the nonzero average dipole moment of the molecules in the ground state is almost entirely compensated by the excited molecules (up to the differences in their permanent dipole momenta). This compensation is generally violated during the subsequent rotational revivals due to the differences of rotational constants B_0 and B_1, except for the molecules rotating with the gap frequencies ν_n ($n = 1, 2, \ldots$ and $\nu_{n+1} > \nu_n$). Most of the unexcited molecules rotating with these frequencies have exactly oppositely oriented excited counterparts rotating with the same frequency. Thus the gap frequencies are mutual classical rotational frequencies for the molecules in states $|0\rangle$ and $|1\rangle$, i.e.

$$\nu_n = \frac{1}{2\pi\hbar} \frac{\partial E_{\text{rot},i}(J)}{\partial J}\Big|_{J=j_{i,n}} \quad (i = 0, 1), \tag{5}$$

where $j_{i,n}$ are the corresponding angular momentum quantum numbers. It is important to stress that inequality $E_{\text{rot},0}(J) \neq E_{\text{rot},1}(J)$ allows only solutions of equation (5) with $j_{0,n} \neq j_{1,n}$, i.e.

$$j_{0,n} - j_{1,n} = n. \tag{6}$$

In other words, the physical meaning of the ordinal number n is the difference between quantum numbers of the angular momentum of the molecules in the ground and excited states, having the same classical rotational frequency ν_n.

The set of equations (5) and (6) allows us to determine the frequency ν_n of the nth gap in the spectrum[5]. Note that while solving the system of these equations we should consider parameters $j_{0,n}$ and $j_{1,n}$ not as integers but as real numbers because of the semiclassical character of the equations.

From equations (5) and (6), it is evident that the gap frequencies exclusively depend on the parameters of the ground $|0\rangle$ and excited $|1\rangle$ vibronic states of the molecule. Note that for each n we have a system of three equations with only two patently unknown parameters $j_{0,n}$ and $j_{1,n}$. Therefore, from equations (5) and (6) we can determine the molecular parameters using the measured spectra.

[5] Certainly, equations (5) and (6) are valid only if $h\nu_n \gg B_0$, B_1, i.e. when the concept of the classical frequency is valid.

Specifically, the rotational energy of the molecule in ith vibronic state can be written in the form of a standard expansion:

$$E_{\text{rot},i}(J) = J(J+1)\,[B_i + J(J+1)(D_i + \cdots)]. \tag{7}$$

Let us assume, for example, that the values ν_1 and ν_2 have been retrieved from an experiment. Then, using known values of B_0 and D_0 we can find the parameters B_1 and D_1 of the excited electronic state or, alternatively, calculate the corrections D_0 and D_1 using known values of B_0 and B_1, etc. Analogously, the knowledge of the gap frequencies with higher ordinal numbers allows us to calculate the higher order nonrigidity corrections.

From the fact that the thermal rotational energy serves as an energy reservoir for the generation of the THz radiation, one can also expect that the process of generation of the THz radiation can lead to a reduction of the rotational molecular energy. Another consequence is a blue shift of the position of the maximum of the spectral density of the THz response (and corresponding shortening of the duration of the orientational peaks) accompanied by a slight increase of the gain coefficient with increasing the initial temperature of the molecules. For BF molecules the gain increase is about $\sim$20% when the temperature changed from 75 to 300 K.

Unfortunately, the feature considered above set essential limitations on the maximal possible efficacy of the laser impact energy's is transformation into the energy of the THz radiation. If we designate this efficacy as η, which is the ratio of the total THz radiation energy to the energy of the absorbed laser radiation, then it is obvious that η cannot exceed the ratio of the average rotational energy of the molecules to their vibronic excitation energy. Respectively, in the considered ODS-based scheme, $\eta \lesssim 0.3\%$ for the case of BF molecules at room temperature.

5. Conclusion

In conclusion, the laser-driven ODS of linear molecules has been numerically shown to be one of the most effective proposals for orientational symmetry breaking in molecular ensemble at high temperatures. It allows both to prepare the well-oriented subensembles of vibronically excited BF molecules with the degree of orientation up to 0.7 and to achieve extremely high degrees of orientation (up to 0.07) for the molecular ensemble as a whole. The latter directly opens the way for several intriguing applications. The suggested method of generation of the pulsed THz radiation allows us to produce few-cycle THz pulses, which are well separated from an initiating laser pulse in both spatial and time domains. The carrier frequency of such pulses is easily tunable by the temperature of the molecular ensemble. Although this method of generation has a rather low efficacy in terms of energetical outcome, it may be effectively applied to stereochemical studies of molecular rotational constants of different vibronic states and any corrections to them caused by molecular nonrigidity. One of the advantages of such studies is the possibility of performing measurements at arbitrary (except too low) temperatures.

From an experimental point of view, however, the key bottleneck for the considered applications of the ODS is the obligatory phase matching of some of the components of the laser field. However, the formation of the anisotropy in the orientational distribution of the molecules will take place for any phase relations between the field components (see figure 5 in [40]). Therefore, generation of the THz radiation (and thus the measurements of rotational constants) can be performed even without special phase matching of the field components.

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