Nonlinear response of a molecular gas caused by orientation effects in the field of an intense femtosecond laser pulse

E.A. Volkova, A.M. Popov, O.V. Tikhonova

Abstract. **The orientation anisotropy of a molecular gas induced by a high-power femtosecond pulse is studied by the method of direct numerical integration of the nonstationary Schrödinger equation. The contribution of the anisotropy to the nonlinear polarisation of the gas is calculated. It is shown that the orientation nonlinearity caused by the efficient alignment of molecules along the laser field is accompanied by a considerable repopulation of the rotational levels of a molecule and cannot be described by the perturbation theory. It is found that the inertia of this nonlinearity depends on the laser-field strength.**

Keywords: *femtosecond pulses, rotational molecular dynamics, radiation self-focusing, orientation nonlinearity.*

1. Introduction

The advent of lasers generating terawatt femtosecond pulses has inspired a renewed interest in the study of various already known nonlinear-optical phenomena. Nonlinear-optical effects are usually quantitatively described by expanding various phenomenological characteristics of a medium, for example, polarisation P as a power series in the field amplitude E. The expansion of the functional $P(E)$ in a series contains, apart from the linear term, also terms that are quadratic and cubic in the field as well as higher-order terms, which are characterised by nonlinear suscepti-bilities of the corresponding orders [1, 2]. Note that this approach can be applied only in the case of moderate fields. However, the advent of high-power lasers requires the consideration of the influence of strong laser fields on various parameters of a medium. In this case, the per-turbation theory is no longer applicable and the expansion in a power series in the field becomes incorrect. The non-linear properties of the medium can be considered beyond the framework of the perturbation theory by calculating nonlinear polarisation quantum-mechanically using the numerical integration of the nonstationary Schrödinger equation. Then, the nonstationary Schröddinger equation

E.A. Volkova, A.M. Popov, O.V. Tikhonova D.V. Skobeltsyn Institute of Nuclear Physics, M.V. Lomonosov Moscow State University, Vorob'evy gory, 119992 Moscow, Russia

and Maxwell's equations describing the propagation of laser radiation in the medium are solved simultaneously.

One of the most interesting effects observed during the interaction of high-power short laser pulses with a molecular medium is the efficient rotational dynamics of molecules under the conditions when ionisation and dissociation are insignificant. Such a situation contradicts to the well-known accepted notion of the electron and vibrational–rotational dynamics of molecules, according to which the molecular rotations are the slowest process and can be observed only in the case of picosecond and nanosecond pulses [3]. The traditional time hierarchy of motions of various molecular subsystems corresponds to rather long picosecond or nano-second pulses with a long switching on duration. A specific feature of ultrashort laser pulses is their fast switching on, which leads to a significant population of many rotational sublevels and the efficient rotational dynamics of molecules resulting in the orientation of the molecular axis in a certain direction. Note that this problem was discussed in many papers and the alignment of molecules in a laser field was studied both experimentally and theoretically [4, 5].

If such a regime is realised when ionisation and dissociation are suppressed (for example, when the photon energy is properly chosen), then the nonlinear properties of the medium are determined not by the electron contribution to the high-frequency Kerr effect but the orientation anisotropy of molecules [6, 7]. It is known that the Kerr nonlinearity can cause the self-focusing effect [1, 2], which was studied in many papers (see reviews [8, 9] and references therein).

The orientation nonlinearity produced in a strong field cannot be treated within the framework of the perturbation theory. In addition, it is assumed usually that the Kerr nonlinearity is inertialess, whereas orientation effects are related to the inertia of the rotational degrees of freedom of molecules, which substantially depends on the laser field strength. Therefore, there appears the necessity to abondon the traditionally used model of the medium.

The orientation Kerr nonlinearity of a molecular medium can be described by analysing the quantum dynamics of molecules in an external laser field. In the general case, this analysis should be performed using the Neumann equation for the density matrix [10, 11]. However, the characteristic collision time of atoms and molecules in a gas at the atmospheric pressure irradiated by ultrashort laser pulses of duration $\tau_p \approx 10 - 100$ fs can be estimated as $T_c \approx 1/N\sigma v$, where $N \cong 10^{19}$ cm^{-3} is the concentration of particles, $\sigma \cong 10^{-15}$ cm^2 is the collision cross section, and

the velocity v of thermal motion does not exceed 3×10^5 cm s^{-1} even for light molecules. In this case, T_c is approximately equal to 10^{-9} s, which is many orders of magnitude greater than the laser pulse duration. Therefore, the collision relaxation can be neglected under these conditions. Note that relaxation processes related to the action of the vacuum electromagnetic field have the relaxation time of the same order of magnitude ($\sim 10^{-9}$ s), which suggests that the relaxation term in the Neumann equation can be neglected at all. This means in fact that the interaction of the molecular medium with laser radiation can be studied by solving the nonstationary Schrödinger equation for a molecule in the field of the electromagnetic wave. In this case, the 'mixed' state of a molecular ensemble is taken into account only by the choice of the initial condition corresponding to the incoherent superposition of different vibrational–rotational states with the population probabilities determined from the Gibbs distribution.

In this paper, we studied the orientation anisotropy of a molecular gas produced due to the dynamic alignment of molecules in a strong ultrashort laser field by the method of direct numerical integration of the nonstationary Schrödinger equation.

2. Numerical model

The interaction of a molecule with a laser radiation field is described quantum-mechanically by the nonstationary Schrödinger equation

$$i\hbar \frac{\partial \Psi}{\partial t} = \hat{H} \Psi \qquad (1)$$

with the Hamiltonian

$$\hat{H} = \hat{H}_e + \hat{T}_N + \frac{e^2}{R} - \boldsymbol{d}\boldsymbol{E},$$

where $\hat{H}_e$ is the Hamiltonian of the electron subsystem of the molecule; $\hat{T}_N$ is the kinetic energy operator of nuclei in the centre-of-mass system of the molecule; $\boldsymbol{d}$ is the dipole moment operator of the molecule in the centre-of-mass system, which is equal to the dipole moment of the electron subsystem for a homonuclear molecule; R is the internuclear distance in the molecule; and $\boldsymbol{E}$ is the laser field strength.

The solution of Eqn (1) can be expanded in the Born–Oppenheimer approximation as a series in the eigenfunctions of the stationary electron problem $\varphi_i(\boldsymbol{r}, \boldsymbol{R})$

$$\Psi(\boldsymbol{r}, \boldsymbol{R}, t) = \sum_i \Phi_i(\boldsymbol{R}, t) \varphi_i(\boldsymbol{r}, \boldsymbol{R}) \qquad (2)$$

with the expansion coefficients characterising the time-dependent nuclear parts of the wave function of various electron terms. Here, we use, as in Ref. [12], a two-dimensional (planar) molecule in the one-electron approximation as a model system. We used a planar molecular geometry because it was necessary to study separately the electron dynamics of the system to determine the range of laser parameters at which the ionisation and dissociation of molecules were insignificant. Our calculations of the probabilities of ionisation and excitation of various electronic states of the molecule by laser photons with

the energy $\hbar\omega = 1.55$ eV ($\lambda = 800$ nm) showed that it is sufficient to consider only two lower terms in expansion (2) up to the intensity 3×10^{14} W cm^{-2}. In this case, the system of equations characterising the nuclear parts $\Phi_{1,2}(R, \theta, t)$ of the wave functions of two lower terms have the form

$$i\hbar \frac{\partial \Phi_1(R, \theta, t)}{\partial t} = [\hat{T}_N + V_{eff}^{(1)}(R)]\Phi_1(R, \theta, t)$$

$$-eE(t)[x_{12}(R)\cos\theta + y_{12}(R)\sin\theta]\Phi_2(R, \theta, t),$$

$$i\hbar \frac{\partial \Phi_2(R, \theta, t)}{\partial t} = [\hat{T}_N + V_{eff}^{(2)}(R)]\Phi_2(R, \theta, t) \qquad (3)$$

$$-eE(t)[x_{12}(R)\cos\theta + y_{12}(R)\sin\theta]\Phi_1(R, \theta, t),$$

where $V_{eff}^{(1,2)}$ is the effective potential energy of interaction between nuclei, which takes the electronic energy of the corresponding term into account; θ is the angle between the electric-field direction and the molecular axis. The quantities ex_{12} and ey_{12} are the matrix elements of the projections of the electron transition dipole moment on the molecular axis and the direction perpendicular to the axis. Taking into account the symmetry of the wave functions of two lower electronic states of the model molecule under study, we have $y_{12} \equiv 0$.

Note that system (3), which characterises the vibrational–rotational dynamics of the molecule in the plane of the internuclear axis and field polarisation, will have a similar form in the three-dimensional case. The dynamics of the system in the three-dimensional and two-dimensional cases proves to be qualitatively similar if the initial state in the three-dimensional model is characterised by the isotropic distribution over the azimuthal angle ϕ.

We solved system (3) numerically by expanding the required nuclear functions $\Phi_{1,2}(R, \theta, t)$ in the eigenfunctions of the angular momentum operator:

$$\Phi_{1,2}(R, \theta, t) = \sum_{m=-\infty}^{\infty} \chi_{1,2}^{(m)}(R, t) \frac{\exp(im\theta)}{\sqrt{2\pi}}.$$

We assumed that the system is initially in a rotational state $|v = 0, m\rangle$ at the lower term in the lower vibrational state.

3. Results and discussion

3.1 Nonlinear polarisation of a quantum system

Taking (2) into account, the solution of system (3) allows us to obtain the total time-dependent wave function of the molecule. This function can be used to calculate various phenomenological parameters of the molecular medium. In particular, the average quantum value of polarisation of N identical molecules (in the absence of collisions between them) is the sum of N equal quantum averages of dipole moments calculated for a molecule

$$\langle \boldsymbol{P} \rangle = N \langle \boldsymbol{d} \rangle, \qquad (4)$$

where $\langle \boldsymbol{d} \rangle = \langle \Psi | \boldsymbol{d} | \Psi \rangle$ is calculated using the total wave function of system (2). Because the dipole moment of the

nuclear subsystem of a homonuclear molecule in the centre-of-mass system is zero, we have in the approximation of two terms for the projection of polarisation on the field direction

$$\langle P(t) \rangle_E = N \int |\Psi(\boldsymbol{r}, \boldsymbol{R}, t)|^2 er \cos(\boldsymbol{Er}) \mathrm{d}^2 r \mathrm{d}^2 R$$

$$= 2Ne\mathrm{Re}\langle \Phi_2(\boldsymbol{R}, t) | x_{12}(R) \cos \theta | \Phi_1(\boldsymbol{R}, t) \rangle. \quad (5)$$

Polarisation (5) contains the orientation nonlinear part appearing due to the dynamic alignment of molecules in the wave field [12]. The nonlinearity of the electron polarisability is ignored. We will show below that the orientation nonlinearity in the case of a multiphoton electronic transition between two lower terms of the molecule proves to be dominant and can be greater by a few orders of magnitude than the cubic inertialess nonlinearity determined by electronic transitions in the molecule.

By using (3) in the case when the upper-term population is small, we can show [2] that expression (5) takes the form

$$\langle P(t) \rangle_E = NE(t)\langle \Phi_1(\boldsymbol{R}, t) | \alpha_{\parallel}(R) \cos^2 \theta | \Phi_1(\boldsymbol{R}, t) \rangle, \quad (6)$$

where $\alpha_{\parallel}$ is the electronic polarisability of the molecule along the internuclear axis, which has the form

$$\alpha_{\parallel}(R) = e^2 |x_{12}(R)|^2 \frac{2[V_{\mathrm{eff}}^{(2)}(R) - V_{\mathrm{eff}}^{(1)}(R)]}{[V_{\mathrm{eff}}^{(2)}(R) - V_{\mathrm{eff}}^{(1)}(R)]^2 - (\hbar\omega)^2} \quad (7)$$

in the two-term model. The averaging in (6) is performed taking into account possible variations in the internuclear distance R and angle θ between the molecular axis and the direction of field polarisation. When a change in the internuclear distance is small, polarisability can be considered approximately constant and corresponding to the initial equilibrium value R_0. Then, polarisation proves to be proportional to the averaged value of $\cos^2 \theta$

$$\langle P(t) \rangle_E = NE(t)\alpha_{\parallel}(R_0)\langle \Phi_1(R, \theta, t) | \cos^2 \theta | \Phi_1(R, \theta, t) \rangle. \quad (8)$$

Note that expression (6) has the universal form and is valid both in the two-dimensional and three-dimensional cases. By separating the linear and nonlinear parts of polarisation in (6), we obtain

$$\langle P(t) \rangle_E = NE(t)\big(\langle \alpha_{\parallel} \cos^2 \theta \rangle|_{t=0} + \langle \alpha_{\parallel} \Delta \cos^2 \theta \rangle\big). \quad (9)$$

Here, the first term in parentheses is the quantum average of $\cos^2 \theta$ in the absence of the field and is equal to $1/2$ and $1/3$ for the equally probable distribution of molecules over all orientations in the two-dimensional and three-dimensional cases, respectively. The second term $\langle \alpha_{\parallel} \Delta \cos^2 \theta \rangle = \langle \alpha_{\parallel} \cos^2 \theta \rangle - \langle \alpha_{\parallel} \cos^2 \theta \rangle|_{t=0}$ describes the orientation effect. Therefore, nonlinear polarisation proves to be equal to the field and the $\eta(E, t) = \langle \alpha_{\parallel} \Delta \cos^2 \theta \rangle$ as the function of time and the wave-field amplitude.

3.2 Propagation of laser radiation in a nonlinear medium and self-focusing condition

The wave equation characterising the propagation of radiation in a medium has the form

$$\nabla^2 \boldsymbol{E} = \frac{1}{c^2}\frac{\partial^2 \boldsymbol{E}}{\partial t^2} + \frac{4\pi}{c^2}\frac{\partial^2 \langle \boldsymbol{P} \rangle}{\partial t^2}, \quad (10)$$

where $\boldsymbol{E}$ is the wave electric field strength and $\langle \boldsymbol{P} \rangle$ is polarisation appearing in the medium. By separating the linear $\langle \boldsymbol{P}_1 \rangle$ and nonlinear $\langle \boldsymbol{P}_2 \rangle$ parts of polarisation, we obtain for the solution of the form

$$\boldsymbol{E} = \boldsymbol{E}_0(\rho, z, t) \exp[\mathrm{i}(kz - \omega t)]$$

in the parabolic approximation that

$$\Delta_{\perp} \boldsymbol{E}_0 + 2\mathrm{i}k\left(\frac{\partial \boldsymbol{E}_0}{\partial z} + \frac{1}{c/n}\frac{\partial \boldsymbol{E}_0}{\partial t}\right)$$

$$= \frac{4\pi}{c^2}\exp[-\mathrm{i}(kz - \omega t)]\frac{\partial^2 \langle \boldsymbol{P}_{\mathrm{n}} \rangle}{\partial t^2}. \quad (11)$$

Here, $k = (\omega/c)\sqrt{\varepsilon}$; $n = \sqrt{\varepsilon}$ is the linear refractive index; and ε is the dielectric constant. Note that $n \approx 1$ in a gas at the atmospheric pressure. By separating from (9) the expression

$$\langle \boldsymbol{P}_{\mathrm{n}} \rangle_E = N\eta(E_0, t)\boldsymbol{E}(t) \quad (12)$$

for nonlinear polarisation and taking into account that the function $\eta(E_0, t)$ is smooth ($\partial \eta/\partial t \ll \omega\eta$), we rewrite (11) in the reference system coupled with a laser pulse in the form*

$$\mathrm{i}k\frac{\partial \boldsymbol{E}_0}{\partial z'} = -\frac{1}{2}\Delta_{\perp}\boldsymbol{E}_0 - \frac{2\pi\omega^2}{c^2}N\eta(E_0, t)\boldsymbol{E}_0. \quad (13)$$

This equation is similar to the nonstationary Schrödinger equation in which the field amplitude E_0 and the coordinate z' play the role of the wave function Ψ and time t, respectively. The first term in the right-hand side of (13) characterises the diffraction divergence of radiation, while the second term is analogous to the potential depending on the field E_0. When $\eta > 0$, the nonlinearity of the second term can cause radiation self-focusing. Obviously, self-focusing is observed if the focusing nonlinear properties of the medium dominate over the diffraction divergence, i.e., when the condition

$$\frac{1}{2}\Delta_{\perp}E_0 < \frac{2\pi k^2 N\eta(E_0, t)E_0}{n^2} \quad (14)$$

is fulfilled. One can easily see that the estimate of the self-focusing threshold depends on the form of the function $\eta(E_0, t)$. The most important is the time dependence of η, which is determined by the inertia of the orientation properties of the medium. In particular, when $\eta = 0$, Eqn (13) does not contain nonlinearities and describes the propagation of radiation in a linear medium.

3.3 Inertia of the orientation nonlinearity of a medium

As shown above, the nonlinear polarisation of a molecular medium caused by the dynamic alignment of molecules in the wave field is determined by the function $\eta(E_0, t) = \langle \alpha_{\parallel} \Delta \cos^2 \theta \rangle$ if the populations of all the electronic terms, except the initially populated term, are small. The

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*From the mathematical point of view, this corresponds to the change of variables $(z, t) \to (z' = z + (c/n)t, t)$.

calculations of the vibrational–rotational dynamics of the model molecule showed that the internuclear distance remains almost constant and equal to the equilibrium value R_0 up to laser radiation intensities $(1-2)\times 10^{14}$ W cm^{-2}, whereas rotational motion substantially affects the molecular dynamics [12]. In this case, polarisability takes the value $\alpha_{\parallel} = \alpha_{\parallel}(R_0)$ corresponding to the equilibrium internuclear distance, while nonlinear polarisation is proportional to the factor $\langle\Delta\cos^2\theta\rangle$: $\langle P_n\rangle \sim \eta \sim \langle\Delta\cos^2\theta\rangle$.

Figure 1 shows the time dependence of $\langle\cos^2\theta\rangle$ calculated numerically for a smoothed trapezoid pulse (pulse front and 'plateau' durations were 5 and 10 optical cycles, respectively) at two different intensities for the isotropic initial angular distribution of molecules. An increase in $\langle\cos^2\theta\rangle$ means that molecules are aligned along the field, which corresponds to the enhancement of the focusing properties of the medium. When the pulse intensity is low (curve *1*), the degree of alignment during the pulse is low. At high pulse intensities (curve *2*), the degree of alignment can achieve 0.8–0.9.
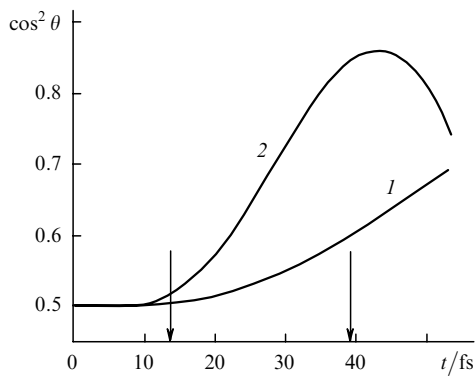

Figure 1. Time dependence of the quantum-mechanical average value of $\cos^2\theta$ for a laser pulse with the front and 'plateau' durations equal to 5 and 10 optical cycles, respectively, and the intensity $P = 2 \times 10^{13}$ (*1*) and 10^{14} W cm^{-2} (*2*). The molecule was initially in the lower vibrational–rotational state $|v = 0, m = 0\rangle$. The arrows show the beginning and end of the pulse plateau.

The physical mechanism of alignment can be qualitatively explained based on the classical expression for the effective potential energy characterising the rotation of a molecule in the laser field [13, 14]. The minima of this potential correspond to the angles 0 and π between the molecular axis and the laser field direction, while its depth is proportional to the laser radiation intensity. Note that the alignment shown in Fig. 1 occurs dynamically, i.e., the alignment of molecules along the field is changed to a partially perpendicular alignment, the time required for the maximum alignment along the field being dependent on the laser radiation intensity. This time is approximately 600 fs in weak fields and about of 40 fs for the field intensity equal to 10^{14} W cm^{-2}. The alignment time characterises the inertia of the orientation properties of a molecular medium and represents the 'response' time of orientation nonlinearity in Eqn (13), i.e., nonlinearity can be neglected at times that are noticeably shorter than the characteristic inertia time.

In this case, the self-focusing threshold (14) allows the estimate of the characteristic time after which the focusing

properties of the medium dominate over the diffraction divergence of the laser beam.

3.4 Focusing threshold in the case of adiabatic switching on a pulse

Consider the case of adiabatic switching on the field resulting in the established regime, when the factor η characterising the orientation nonlinearity takes a time-independent value. This value is determined by the field strength and also depends substantially on the laser radiation frequency. It can be shown that in the case of sufficiently low frequencies (in the case of multiphoton electronic transitions between two lower terms for the equilibrium internuclear distance), the orientation nonlinearity caused the alignment of molecules along the field can exceed considerably the cubic Kerr nonlinearity related to electronic transitions.

Indeed, because the orientation effects are caused by the efficient population of many rotational sublevels of the lower term, the energy defect does not exceed a few hundredths of electron volt in this process. At the same time, the cubic electronic Kerr nonlinearity resulting in self-focusing is caused by the transition between two electronic states. In the case of low frequencies, this process proves to be strongly non-resonant, with the energy defect of the order of the difference between the electronic levels ~ 10 eV.

The ratio of nonlinear contributions to the polarisation of these two processes is approximately equal to the ratio of energy defects, which results in the dominating role of rotational nonlinearity with the factor $\sim 10^2 - 10^3$. The consideration of the Raman repopulation of the rotational sublevels of the lower term within the framework of the perturbation theory gives the analytic expression for polarisation

$$\langle \boldsymbol{P}_n\rangle_E = \langle\cos^2\theta\rangle N\alpha_{\parallel}\boldsymbol{E}(t) = N\alpha_{\parallel}\boldsymbol{E}(t)\left(\frac{1}{2} + \frac{\alpha_{\parallel}E_0^2}{64B}\right), \quad (15)$$

where B is the rotational constant of the molecule.

Taking (15) into account, the threshold condition for self-focusing (14) yields the estimate of the threshold radiation power $W = (cE_0^2/8\pi)\pi r_0^2$ (where r_0 is the laser beam radius) in the form

$$W_{th} = \frac{Bcn^2}{k^2 N\alpha_{\parallel}^2}, \quad (16)$$

which amounts to 10^8 W for the density of the molecular medium $N = 10^{19}$ cm^{-3} and is independent of the laser beam radius. Note that these estimates are valid only for moderate laser fields, in which the alignment degree is small.

In the strong-field limit in the established regime, owing to the adiabatic switching on the laser field, molecules can be oriented along the field and efficiently maintained predominantly aligned (Fig. 2). A similar result was obtained analytically in Ref. [15]. The alignment efficiency is equal to unity in the strong-field limit, resulting in the doubling of the polarisation of a medium compared to the polarisation of molecules with the isotropic initial angular distribution. In this case, the threshold condition for focusing reduces to the restriction imposed on the minimum radius of the laser beam ($r \geqslant r_{min}$) at which the beam can be still held due to the focusing properties of the medium:
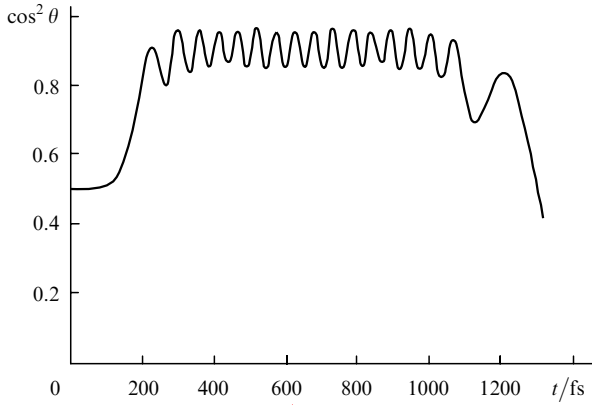
Figure 2. Same as in Fig. 1 for the pulse front and plateau durations equal to 150 and 200 optical cycles, respectively, and the pulse intensity $P = 10^{14}$ W cm^{-2}.

$$r_{min} \approx 10\lambda. \qquad (17)$$

Therefore, the avalanche process of self-focusing is saturated in strong fields. A higher degree of self-focusing cannot be achieved due to the increasing role of the diffraction divergence of the laser beam compared to the focusing properties of the 'potential'.

3.5 Consideration of the thermal molecular motion

As mentioned in Introduction, in the case of ultrashort laser pulses, collisions between molecules in a gas of density $N \sim 10^{19}$ cm^{-3} can be neglected, which allows one not to use the formalism of the density matrix. However, because the temperature of the medium is nonzero, it is necessary to specify the initial state of the system in the form of the incoherent superposition of different rotational states populated according to the Boltzmann distribution. This means that the problem of molecular dynamics in the laser field should be solved separately for each initially populated rotational level, and then the obtained probabilities and quantum averages should be summed with the corresponding weights. In a homonuclear molecule, due to the symmetry of its states with respect to the interchange of nuclei, only rotational states with even quantum numbers can be populated in the lower electronic term. The maximum number of the rotational sublevel, which will be still populated due to the thermal motion of molecules, was estimated to be $|m_{max}| = 6$ for room temperature. This means that the initial population of all higher-lying rotational sublevels is negligibly small and can be neglected in the averaging of results over an incoherent molecular ensemble.

Let us analyse the rotational dynamics of a molecule initially occupying the $m = 2$ level in the field. In the case of adiabatic switching on a pulse in the established regime, the estimate with the help of the perturbation theory for weak fields gives

$$\langle \cos^2 \theta \rangle = \frac{1}{2} - \frac{\alpha_{||} E_0^2}{192B}. \qquad (18)$$

The minus sign at the nonlinear part means, unlike (15), the alignment of molecules predominantly perpendicular to the laser radiation polarisation and, hence, defocusing of laser radiation. Therefore, the contribution of the $m = 2$ states to

the incoherent superposition reduces the effect of molecular orientation and can weaken self-focusing.

However, the analytic result obtained in the case of rectangular pulses by means of the perturbation theory for the same initial condition demonstrates a more complicated effect:

$$\langle \cos^2 \theta \rangle = \frac{1}{2} + \frac{\alpha_{||}}{32} \frac{E_0^2}{12B} \left(1 - \cos \frac{12B}{\hbar} t \right)$$

$$- \frac{\alpha_{||}}{32} \frac{E_0^2}{4B} \left(1 - \cos \frac{4B}{\hbar} t \right). \qquad (19)$$

Depending on the time instant, the nonlinear part can be either positive or negative. At short times, the right-hand side of (19) can be expanded into a series to obtain in the first order

$$\langle \cos^2 \theta \rangle = \frac{1}{2} + \frac{\alpha_{||} E_0^2}{8\hbar^2} B t^2 + \dots . \qquad (20)$$

Note that (20) coincides exactly with the expansion obtained for the $m = 0$ initial state in the case of instant switching on,

$$\langle \cos^2 \theta \rangle = \frac{1}{2} + \frac{\alpha_{||} E_0^2}{64B} \left(1 - \cos \frac{4B}{\hbar} t \right) \approx \frac{1}{2} + \frac{\alpha_{||} E_0^2}{8\hbar^2} B t^2, \quad (21)$$

and corresponds to the alignment of molecules along the field, resulting in self-focusing. Expansion (20) is valid only for $t \ll \hbar/12B \approx 30$ fs. For times ~ 30 fs, it is necessary to take the next expansion terms in (20), whereas (21) still remains valid under these conditions. This analysis is excellently confirmed by numerical calculations. Figure 3 shows the time dependences of $\langle \cos^2 \theta \rangle$ obtained for a rectangular pulse for two different initial conditions $m = 0$ and 2. One can easily see that the time dynamics at the initial time interval $t < 20$ fs virtually coincides for both cases.

Similar results can be also obtained for a smoothed trapezoid pulse. Figure 4 shows the dynamics of $\langle \cos^2 \theta \rangle$ during the pulse of intensity 10^{14} W cm^{-2} with the front and 'plateau' durations equal to 5 and 10 optical cycles, respectively, for different initial conditions ($m = 0, 2, 4, 6$). One can easily see that the medium has defocusing
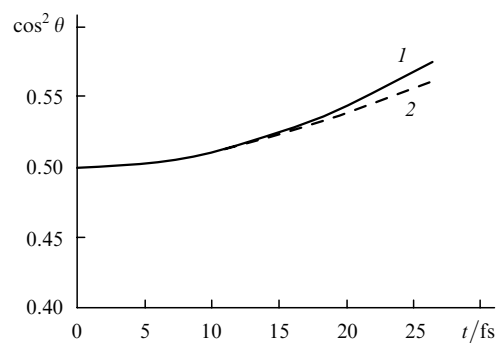

Figure 3. Time dependence of the quantum-mechanical average value of $\cos^2 \theta$ for a rectangular laser pulse of duration equal to 10 optical cycles and the intensity $P = 2 \times 10^{13}$ W cm^{-2}. The molecule was initially in the vibrational–rotational state with $|v = 0, m = 0\rangle$ (1) or with $|v = 0, m = 2\rangle$.

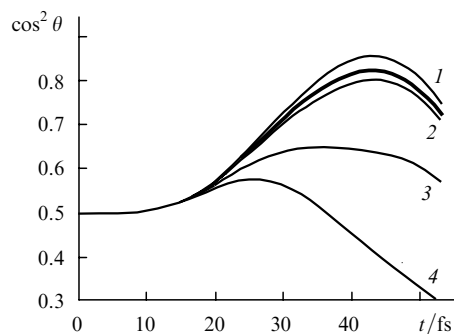**Figure 4.** Time dependence of the quantum-mechanical average value of $\cos^2\theta$ calculated for different initial rotational states of a molecule: $|m = 0\rangle$ (1), $|m = \pm 2\rangle$ (2), $|m = \pm 4\rangle$ (3), $|m = \pm 6\rangle$ (4), and the total value of $\langle\cos^2\theta\rangle$ obtained by the incoherent averaging of partial contributions with the weights corresponding to the Boltzmann distribution at the temperature $T = 300$ K (thick curve).

properties only in the initial state with $m = 6$. The total value of $\langle\cos^2\theta\rangle$ obtained by averaging partial contributions with the corresponding weights ($W_{m0} = 0.5033$, $W_{m=\pm2} = 0.4542$, $W_{m=\pm4} = 0.0417$, $W_{m=\pm6} = 8 \times 10^{-4}$) shown with the thick curve is close to the result for $m = 0$.

Therefore, the incoherent superposition of various rotational sublevels in the initial state in the case of short pulses results in the efficient alignment of molecules along the field, which corresponds to radiation self-focusing. Note that characteristic durations at which the dynamic disordering of molecules caused by the thermal incoherent population of different rotational states has no time to manifest itself are 50–100 fs. In addition, the orientation nonlinearity for all initial states with $m \neq 0$ leads to self-focusing only for pulses with a sufficiently fast non-adiabatic switching on. However, our calculations showed that only the pulses with the switching on time of ~ 1 ps can be considered adiabatic. Most of the pulses used at present for studying the dynamics of atomic and molecular systems in strong fields have duration no more than 100 fs. The switching on time and duration of such pulses are too short to cause self-focusing due to the alignment of molecules along the direction of the electric field of the wave.

4. Conclusions

Therefore, the analysis of the interaction of a molecule with an intense laser pulse has shown that there exists a range of sufficiently strong fields in which the efficient rotational dynamics of the molecule takes place, while the dissociation and ionisation of the system are negligibly small. We have revealed the effective dynamic alignment of nondissociated molecules, which can cause the orientation nonlinearity resulting in the self-focusing of radiation in the medium. A specific feature of the orientation anisotropy is a substantial redistribution of rotational sublevels during the interaction of the system with the pulse, which corresponds to the strong-field regime and cannot be described within the framework of the perturbation theory. We also found that this effect is inertial, the degree of inertia being substantially dependent on the laser field strength: the characteristic time of the appearance of a considerable anisotropy in a strong field can be only a few tens of femtoseconds. By solving the nonstationary Schrödinger equation for a molecule in the

intense laser pulse field, we calculated the contribution of dynamic alignment of molecules to the nonlinear polarisation of the medium and analysed the threshold self-focusing conditions. We have found the saturation of avalanche self-focusing in a strong field and have shown that in the case of ultrashort laser pulses, the defocusing effect caused by incoherent population of different rotational levels does not develop due to the short pulse duration.

Note that, although we have performed calculations for a planar molecule, all the effects discussed above will also take place qualitatively for three-dimensional molecules. Because the alignment of real molecules is in fact determined by the difference between the longitudinal and transverse components of polarisability, the use of the two-term approximation in calculations only introduces quantitative differences and does not reduce the generality of the conclusions obtained. Therefore, these results reflect qualitatively orientation effects and nonlinear response in the laser field for a broad class of molecular media. In the case of heavier molecules, the inertia of the orientation response of the medium increases and it is necessary to increase the laser-pulse duration to achieve self-focusing. For molecular hydrogen, the self-focusing effect can be expected for pulses no shorter than 60 fs with the intensity no more than 10^{14} W cm^{-2}. In the case of shorter pulses, which were obtained experimentally in Ref. [16], the orientation nonlinearity has no time to develop due to the inertia of the medium. The restriction imposed on the pulse intensity is related to the efficient ionisation of molecules and the formation of a plasma resulting in radiation defocusing. Note that the intensities $3 \times 10^{13} - 10^{14}$ W cm^{-2} correspond to a substantial repopulation of rotational states, which cannot be described by means of the perturbation theory. This specific feature of self-focusing can be observed experimentally.

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