Specific features of propagation of femtosecond laser pulses through a molecular gaseous medium under conditions of efficient alignment of molecules

A.V. Gulyaev, O.V. Tikhonova

Abstract. The propagation of femtosecond laser pulses in a molecular gaseous medium is studied with the rotational dynamics of molecules under the action of these pulses taken into account. Based on the simultaneous numerical solution of the wave equation describing the laser pulse evolution and the Schrödinger equation that determines the quantum state evolution of the medium molecules, the rotational dynamics of molecules in the laser field and the laser pulse evolution are analysed with their mutual influence taken into account. Efficient dynamic alignment of molecules along the direction of laser radiation polarisation is observed, which causes variation in the spatiotemporal pulse profile, as well as significant broadening and deformation of its spectrum in the course of propagation through the medium. The physical mechanisms of the observed phenomena are analysed by using the approximate analytical solution of the problem, derived for the case of preliminary excitation of the medium by a pump pulse (the pump-probe scheme).

Keywords: ultrashort laser pulses, propagation of radiation, orientational nonlinearity.

1. Introduction

The progress of experimental technique that allowed generation of record-breaking short laser pulses offers wide possibilities for observation of novel physical phenomena in the interaction of laser radiation with matter. Recently, it has become clear that in contrast to the standard hierarchy of characteristic molecular energies [1], in strong fields the rotational dynamics of a molecule can be faster than the vibrational one at the expense of simultaneous population of a large number of excited rotational states [2, 3]. In this case the interaction of the molecule with the laser ultrashort pulse (USP) may induce efficient population of high-energy rotational states under the action of sharp non-adiabatic pulse fronts. In addition, for homonuclear molecules the population of vibration-rotational states within the initial term is possible only by means of lambda-type transition via the upper electronic state. Compared with the excitation of vibrational states, such transitions between the rotational states appear to be much more efficient due to the small difference

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between the energies of the initial and the final states. As a result, the efficient rotational dynamics of excited molecules arises under the action of the field, which leads to a specific evolution of the polarisation response and optical properties of such molecular media. The polarisation response of the medium in this case is characterised by the so-called orientational nonlinearity [4, 5], associated with the process of molecular alignment and its time lag.

In the course of laser pulse propagation through the molecular medium of such type, the nonlinear physical phenomena may arise due to the mutual influence of the pulse and the medium, such as self-action and self-focusing of the laser radiation, etc. [6]. It is important to note that in the case of strong laser fields, when the rotational degrees of freedom are efficiently excited, the field power expansion of the polarisation response [6, 7] and different perturbation approaches (see, e.g., [8]), traditionally used for weak fields, appear to be incorrect. In this case the rotational dynamics of the molecule should be considered beyond the framework of perturbation theory, with the strong filed effects taken into account, and the arising polarisation response should be determined directly from the solution to the time-dependent Schrodinger equation.

Efficient population of rotational states under the action of the laser field was studied many times both theoretically and experimentally [2, 9–15]. However, the theoretical analysis was usually carried out in the given-field regime, i.e., with no account for the medium-induced changes in the incident laser pulse.

Thus, the propagation of laser radiation in a molecular medium in the regime of efficient molecular alignment is an important and yet unsolved problem that require correct description of the interaction between the pulse and the medium beyond the framework of perturbation theory and with the mutual influence of the field and the medium properly taken into account.

In the present paper the self-consistent problem of femtosecond laser pulse propagation in a molecular gaseous medium with orientational nonlinearity and efficient rotational motion of molecules is solved and the mutual influence of the spatiotemporal evolution of the laser pulse and the dynamics of the polarisation response is analysed. The results are obtained by simultaneously solving numerically the wave equation, describing the evolution of the laser pulse, and the time-dependent Schrödinger equation that determines the quantum state evolution of the medium molecules at different spatial positions. The temporal dynamics of molecular alignment in the laser field is studied, as well as the dispersion of the laser pulse and the spatiotemporal evolution of its spectrum in the process of propagation. For the propagation of a

probe pulse through the medium, initially excited by a pump pulse (the pump–probe scheme) the analytical theory is developed, yielding an approximate solution that demonstrates good agreement with the data of direct numerical modelling (at moderate penetration depths) and explains the arising physical effects. The obtained results are compared with those of [16, 17], based on the concept of time-dependent refractive index, the introduction of which is phenomenologically postulated without any theoretical justification.

2. Mathematical setting of the problem

Consider the interaction of a gaseous medium, consisting of light diatomic homonuclear molecules analogous to H_2 in their properties, with the pulses of a Ti : sapphire laser having the duration of a few tens of femtoseconds. In papers [3, 18] it was shown that in the field of a low-frequency radiation of the Ti : sapphire laser ($\hbar\omega_{las} = 1.55$ eV) at moderate intensities (up to $I = 10^{14}$ W cm^{-2}) the degree of ionisation of the molecular hydrogen ion H_2^+ appears to be negligibly small, and the population of the first excited ('repulsive') term of the molecule occurs in the regime, corresponding to the perturbation theory. Similarly, in our case at moderate intensities (up to $I = 10^{14}$ W cm^{-2}) one can neglect ionisation and dissociation due to the transitions to the higher-energy terms of the molecule. Besides, the population of bound vibration–rotational states from the initial (ground) term occurs at the expense of lambda-type transitions via the upper electronic term. In this case the smallness of the rotational constant as compared to the vibrational quantum leads to much more efficient population of rotational states as compared to the vibrational ones under the action of laser field. Therefore, in our case for a selected frequency of the laser field a certain range of intensities exists, for which the rotational dynamics is determinative, while the evolution of other molecular degrees of freedom can be neglected.

Within the framework of the Born–Oppenheimer approximation, considering only one (ground) electronic term of the molecule and averaging over the electron coordinates, the time-dependent Schrödinger equation, describing the rotational dynamics of a homonuclear molecule with the possible repopulation of the states via the lambda-type transitions has the form

$$i\hbar\frac{\partial}{\partial t}\Phi_1 = \left(T_n - \frac{1}{2}E^2\Delta\alpha\cos^2\theta\right)\Phi_1, \qquad (1)$$

where $T_n = -B\Delta_{\theta\varphi}$ is the nuclei kinetic energy operator, related to rotations; $\Delta\alpha = \alpha_\parallel - \alpha_\perp$ is the difference between the longitudinal (along the molecular axis) and transverse polarisabilities of the molecule; $B = \hbar^2/(2\mu R_0^2)$ is the rotational constant; μ is the reduced mass of the molecule; R_0 is the internuclear equilibrium distance; and θ is the angle between the molecular axis and the electric field strength vector E. The second term in the right-hand side of Eqn (1) in fact is the effective energy of interaction between the field and the induced dipole and may be accurately derived from the set of equations for the wave functions of the nuclear subsystem under the conditions of small population of excited terms (the perturbation theory regime for the electronic subsystem), as it was done in [7] for the case of vibrational states of the molecule. The validity conditions for Eqn (1) include also the narrow localisation of the pulse spectrum, i.e., the smallness of the frequency spec-

trum width as compared to the energy separation between the electronic states, which in the present case is satisfied with good reserve of tolerance.

The characteristic relaxation times for a gaseous medium under the normal conditions lie in the nanosecond range [9]; therefore, up to the subnanosecond range the interaction of an individual molecule with the electric field of the laser pulse can be considered within the theory based on the time-dependent Schrödinger equation (1) without addressing to the density matrix formalism. At room and lower temperatures, the population of all rotational excited states can be neglected. Therefore, the initial condition for Eqn (1) corresponds to the ground rotational state with $J = 0$.

Equation (1) was solved together with the wave equation that characterises the propagation of the laser pulse in the molecular gaseous medium. The input pulse was linearly polarised and had a wide (planar) wave front, which excludes from consideration the processes of laser radiation focusing and defocusing that should be taken into account for narrow laser beams. In this case the wave equation can be written in the form

$$\frac{\partial^2 E(z,t)}{\partial z^2} - \frac{1}{c^2}\frac{\partial^2 E(z,t)}{\partial t^2} = \frac{4\pi}{c^2}\frac{\partial^2 P(z,t)}{\partial t^2},$$
$$\hspace{9cm} (2)$$
$$E(z=0,t) = E_0(t) = \varepsilon_0(t)\cos\omega_{las}t.$$

Here the function $E_0(t)$ determines the temporal profile of the laser pulse at the medium input; its envelope is expressed as $\varepsilon_0(t) = \sin^2[\omega_{las}t/(2q)]$; ω_{las} is the laser radiation frequency; and q is the number of optical cycles that determines the absolute duration of the laser pulse.

The polarisation of the molecular medium entering the right-hand side of Eqn (2) was calculated as the mean dipole moment of a medium volume unit. Within the framework of the single-term approximation its projection onto the field direction is

$$P_E = N\langle\Phi_1|\Delta\alpha\cos^2\theta|\Phi_1\rangle, \qquad (3)$$

where N is the concentration of molecules in the medium, and the time-dependent wave function Φ_1 is determined by Eqn (1). Thus, the polarisation of the medium $P(z,t)$ is calculated directly by averaging the operator $\cos^2\theta$ over the quantum state of the molecules. Note, that according to expression (3), the polarisation of the molecular medium has a nonzero value only when the electric field is nonzero. Therefore, the present approximation does not account for the effects caused by the residual polarisation signal, which may be important in the problem of propagation of extremely short laser pulses having the duration of one or two field cycles, as shown in [19]. The correct consideration of the effects, related to the residual polarisation, requires full account for at least two electronic terms of the molecule.

To get a rigorous solution of the problem of pulse propagation through the molecular medium under study, Eqn (1) was solved numerically at each point of the medium (along the z axis) together with the wave equation (2). In this case at each point with the coordinate z the value of the field at the moment of time t is determined by the time dependence of the medium polarisation at all preceding moments of time. Such a problem is extremely cumbersome and requires involvement of significant computer resources. Equation (1) was solved

using the expansion of the function Φ_1 over the rotational eigenstates (spherical harmonics $Y_J^{(0)}$):

$$\Phi_1(\theta, t) = \sum_{J=0} C_J(t)\, Y_J^{(0)}(\theta).$$

This expansion reduces Eqn (1) to an infinite set of ordinary differential equations for time-dependent amplitudes of probability to find the molecule in different rotational eigenstates:

$$i\hbar \frac{\partial}{\partial t} C_J = BJ(J+1)C_J - \frac{1}{2}E^2 \Delta\alpha(\beta_J^{(J+2)}C_{J+2}$$

$$+ \beta_J^{(J-2)}C_{J-2} + \beta_J^{(J)}C_J),\,\ldots, \qquad (4)$$

where the matrix elements $\beta_J^{(J')} = \langle Y_J^0 | \cos^2\theta | Y_{J'}^0 \rangle$ are defined by the expressions

$$\beta_J^{(J+2)} = \sqrt{\frac{(J+1)^2(J+2)^2}{(2J+1)(2J+3)^2(2J+5)}},$$

$$\beta_J^{(J)} = \frac{2J^2 + 2J - 1}{(2J+3)(2J-1)},$$

$$\beta_J^{(J-2)} = \sqrt{\frac{J^2(J-1)^2}{(2J-3)(2J-1)^2(2J+1)}}.$$

To solve Eqn (2) we used the finite-difference method with a nine-point pattern on the basis of and implicit–explicit scheme [20]. The parameters of the chosen grid corresponded to discretisation with the step 0.01 of the input radiation wavelength in space and 0.001 of the field period in time. To reduce to a reasonable level the time resources necessary for the solution of the considered self-consistent problem, we developed a special algorithm, allowing high-precision integration up to hundreds of initial radiation wavelengths in depth at the expense of dynamical adaptation of the computational domain to the spatio-temporal domain of the actual pulse motion. For the solution of the problem we used the following values of parameters: $N = 3\times10^{19}$ cm^{-3}, $B \simeq 0.015$ eV, $\Delta\alpha \simeq 5.3\times10^{-24}$ cm^3, which are close to the typical ones for the H_2 molecule.

3. Results and discussion

Let us study the behaviour of the polarisation response of the molecular medium. Expression (3) shows that it is proportional to the quantity $\langle \Phi_1 | \cos^2\theta | \Phi_1 \rangle$. This fact means that the polarisation response of such a medium includes a number of new frequencies (corresponding to the rotational spectrum of the molecules) as compared to the initial spectrum of the propagating laser pulse. Hence, in the process of propagation the laser pulse spectrum can broaden due to Raman scattering at the rotational sublevels. The process of the pulse evolution in the course of propagation will be directly dependent on the degree of molecular alignment in the laser field, which is characterised just by the quantity $\langle \cos^2\theta \rangle$ [2], the maximal alignment of the molecules along the field direction corresponding to $\langle \cos^2\theta \rangle = 1$.

Figures 1a and 1b present the temporal dynamics of the quantity $\langle \cos^2\theta \rangle$ under the excitation of rotational states of

the H_2 molecule in the field of Ti:sapphire laser pulses with the duration of 30 optical cycles at different peak intensities. It is seen that in the process of laser action, molecules are efficiently aligned along the direction of the field due to populating a large number of rotational states. The process of alignment depends on the intensity of the exciting laser field in a complex nonmonotonic way, which can lead to absolutely different character of the rotational dynamics in the post-pulse regime (the moment of the pulse end is labelled with an arrow in Fig. 1). During the laser pulse the quantity $\langle \cos^2\theta \rangle$ in the case of light molecules experiences a few oscillations, which means that the characteristic rotational dynamics time
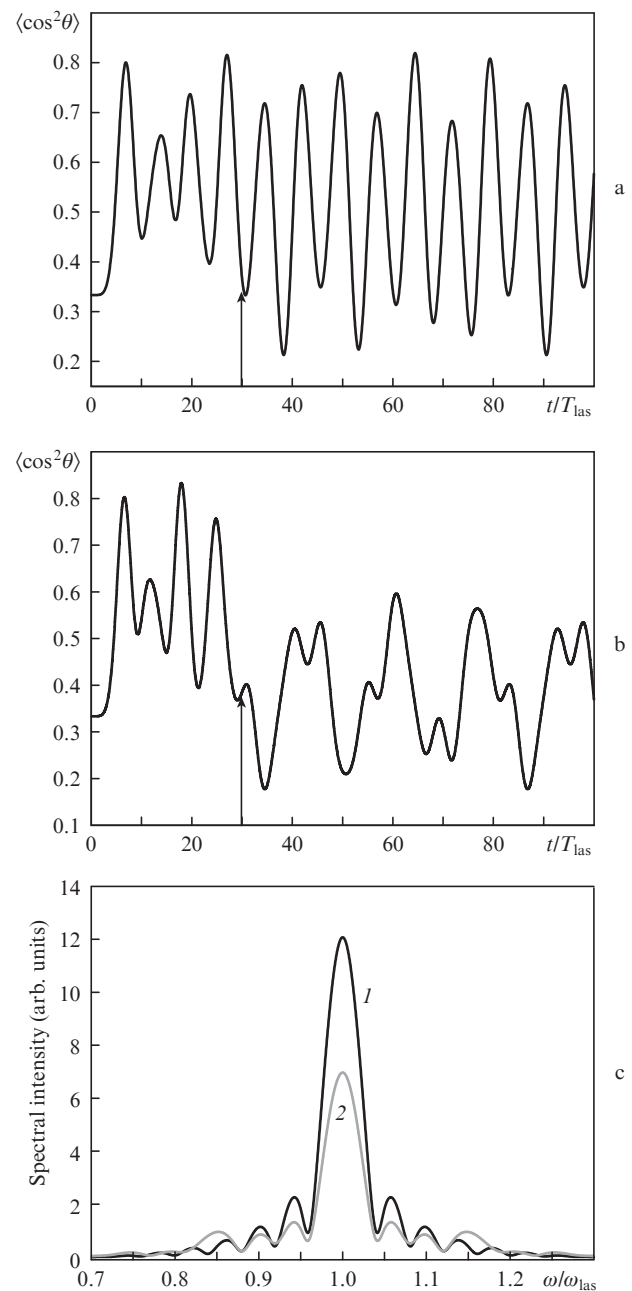

Figure 1. Dynamics of the alignment degree $\langle \cos^2\theta \rangle$ during the laser action and in the after-pulse regime for the pulse with peak intensity $I =$ (a) 6×10^{12} and (b) 7×10^{12} W cm^{-2}, and the spectral intensity of the pump pulse (1) and the polarisation signal (2) at (c) $I = 6\times10^{12}$ W cm^{-2}. The moment of the pulse end is marked by an arrow; $T_{\text{las}} = 2\pi/\omega_{\text{las}}$.

appears to be smaller than the duration of the laser pulse. But at the same time the central frequency of the laser field is several times larger than the frequency of the alignment parameter variation, so that even for light molecules one can consider the alignment dynamics to be slow in comparison with the period of optical oscillations. Hence, in the considered case a specific regime of interaction between the molecular medium and the laser pulse is implemented. Figure 1c presents the spectra of the exciting pulse and the polarisation response, excited by it. It is seen that new frequencies are present in the spectrum of the medium polarisation, which under the conditions of phase matching can provide the process of laser pulse spectrum broadening as the pulse propagates through the molecular medium.

When a high-power femtosecond laser pulse propagates through a medium the regimes are possible, in which due to the inertia of the molecular alignment process the propagating laser pulse itself has no time to 'feel' the influence of the thus polarisation response. In these regimes, in spite of the medium nonlinearity, the process of spectral broadening, induced by self-action, may appear to be suppressed. In this connection the problem of sequential propagation of two pulses (the pump–probe scheme) is of special interest. In such a scheme the second pulse will pass through a preliminary excited medium, the molecules of which may be characterised by a high degree of alignment, independent of the parameters of the propagating probing pulse, which may result in larger broadening of the spectrum.

In this case, if the second (probe) pulse is significantly weaker than the pump pulse, it is possible to assume that it practically does not affect the quantum state of the medium and propagates through a medium with the polarisation, the variation of which in time is determined by the first pulse, so that it is possible to provide a specific temporal profile of the polarisation response by varying the characteristics of the pump pulse. Then the problem of describing the propagation process is essentially simplified, since the Schrödinger equation and the wave equation are separated and solving a self-consistent problem is no more necessary. The polarisation response can be presented in the form $P(z,t) = A(z,t)E(z,t)$, where A(z,t) is a given function of coordinates and time that includes $\langle \cos^2\theta \rangle$ and does not depend directly on the field strength of the probe pulse. In this sense the polarisation may be referred to as 'quasi-linear', because it linearly increases with increasing field strength. At the same time the considered case is essentially different from the linear one. As already mentioned, in the spectrum of the polarisation response the amplitudes of frequency components are distributed in a way, different from that of the laser pulse, namely, the spectrum of polarisation is a convolution of the electric field spectrum and the function $\langle \cos^2\theta \rangle$. As a result, in spite of the linear relation of the spectra, an important role in the propagation may be played by nonlinear effects related to the frequency change.

The similarity between this case and the linear one makes it possible to expect the presence of analogous physical mechanisms, responsible for propagation of pulses in linear media and in the medium under study. In particular, if the function $A(z, t)$ slowly varies in time and space (as compared to the pulse duration), then one can say that the polarisation response is practically linear. Such an analogy allows the introduction of the quantity $n(z,t) = \sqrt{1 + 4\pi A(z,t)}$, analogous to the refractive index of the medium and varying in time at each point of the space. However, there are no reasons to

expect that the effect of such a 'refractive index' on the propagation process will be the change in the group velocity of the pulse as a whole and the spatiotemporal modulation of the phase velocities of different spectral components that determine the pulse shape {such an assumption was made in [16] without taking the spatial variation of $n(z, t)$ into account}. Such problems as the physical meaning of the introduced quantity and its role in the observed evolution of the pulse during its propagation require a separate study.

To solve these problems let us seek for an approximate solution of Eqn (4) describing the propagation of the probe pulse through the medium, whose rotational dynamics is determined by the effect of the given pump pulse. Neglecting the transverse effects in propagation and considering linearly polarised laser pulses, let us make use of the slow-varying amplitude equation [6] analogue, namely, let us seek for the solution of the wave equation in the form $E(z,t) = \varepsilon(z,t) \times \exp\{i[k(z,t)z - \omega t]\}$, where the wavenumber $k(z, t)$ can depend both on the coordinate along the propagation axis, and on the time, while the envelope $\varepsilon(z,t)$ varies slowly in comparison with the optical cycle corresponding to the pulse central frequency.

The substitution of this expansion into the wave equation (2) makes it possible to neglect some of the arising terms. First, the selection of fast-oscillating part in the expression for the laser pulse electric field strength assures the smallness of the second derivatives of the envelope both in time and the spatial coordinate. Second, in the equation the terms are present having the order of magnitude, determined directly by the function $A(z,t) = N\Delta\alpha \langle \Phi_1 | \cos^2\theta | \Phi_1 \rangle$. Indeed, at the concentrations and characteristics of the H_2^+ molecule, typical for gaseous media, the order of magnitude of $A(z, t)$ may be estimated as $10^{-4} - 10^{-5} \ll 1$. As a result, the expression for the 'refractive index' can be also approximately written in the form $n(z,t) \simeq 1 + 2\pi A(z,t)$, which illustrates the smallness of its variation. Third, as already mentioned, the change of $A(z, t)$ in time is described by the temporal dependence of the function $\langle \Phi_1 | \cos^2\theta | \Phi_1 \rangle$, and the maximal frequency of its variation is directly related to the number of rotational states, excited by the pulse. With the difference between the characteristic rotational energy and the energy of a quantum at the central frequency of radiation from the Ti : sapphire laser $(B/(\hbar\omega_{las}) \propto 10^{-2})$ taken into account, it is possible to assume that the function $A(z, t)$ is also slightly varying during one cycle of the laser field, if the maximal number of a populated rotational state does not exceed ten. For heavy molecules this limitation is much more liberal than in the case considered. These facts allow simplification of the wave equation by omitting the terms, proportional to A^2, to higher orders of partial derivatives of the slowly varying functions, as well as to their products (taking the fact that $\partial A/\partial t > \partial\varepsilon_0/\partial t$ into account).

It is natural to write the equation for slowly varying amplitudes in the accompanying coordinate frame and assume that $k(z,t) = \omega n(z,t)/c$, which should hold under a continuous transition from the case of weak dependence of $A(z,t)$ on the coordinate and time to the case of linear medium. Then the accompanying coordinates will be defined by the expressions

$$\xi = z, \quad \tau = t - zn/c. \tag{5}$$

Up to now we did not discuss the dependence of the function $A(z, t)$ on the spatial coordinate. Consider the situation

when a femtosecond pump pulse propagates through an unexcited molecular medium, which due to the inertia of the molecular alignment process has no time to essentially change its initial structure. In this case one can assume that all the influence of the medium on the pump pulse is reduced to affecting the velocity of its propagation. For the pump pulse the medium appears to be linear, and the refractive index n_0 can be found from the expression for $n(z,t)$ by replacing the mean value of the squared cosine of the alignment angle θ with the value 1/3, which corresponds to the unaligned state of the molecular medium. At different points of the medium such a pump pulse will provide similar time dependences of the function A, and the spatial dependence will be reduced to the effect of delay, i.e., $A(z,t) = A(t - zn_0/c)$. In this case up to the terms of the order A^2 one can write $A(z,t) \simeq A(t - zn/c)$, i.e., $n - n_0 \simeq 2\pi A - \text{const} \sim A$.

Let us rewrite the wave equation using the accompanying coordinates, taking the described smallness parameters into account and omitting the higher-order terms. Then the wave equation takes the form

$$2\mathrm{i}k(\tau)\frac{\partial \varepsilon}{\partial \xi} = \left(-2\mathrm{i}\frac{k}{c}\frac{\partial n}{\partial \tau} + \frac{4\pi}{c^2}\frac{\partial^2 A}{\partial \tau^2}\right)\varepsilon. \quad (6)$$

Equation (6), in which $A(\tau)$ and $n(\tau)$ are functions of the only variable τ, has a limited domain of applicability with respect to the laser pulse propagation depth, since in the process of its derivation among the omitted terms there were those that grow proportionally to different powers of z. The last term, proportional to the second derivative of $A(\tau)$, was intentionally left in the equation, because, on the one hand, it is the largest among the terms that determine the real part of the equation at small depths of penetration into the medium, and, on the other hand, this term can be significant in the case of populating a large number of rotational states in light molecules, when the dynamics of the quantity $\langle \Phi_1 | \cos^2\theta | \Phi_1 \rangle$ is fast.

The right-hand side of Eqn (6) does not depend on the variable ξ, so that it is not difficult to write its solution, which is an approximate solution of the initial problem:

$$E(z,t) = \varepsilon_0(\tau)\exp(-\mathrm{i}\omega\tau)\exp\left[-\xi\frac{1}{c}\frac{\partial n(\tau)}{\partial \tau} - \mathrm{i}\frac{2\pi}{kc^2}\frac{\partial^2 A}{\partial \tau^2}\right], \quad (7)$$

where $\varepsilon_0(\tau)$ is the initial envelope of the laser pulse. To obtain the electric filed strength one has to take the real part of solution (7). This solution describes several effects related to the influence of the spatiotemporal dynamics of the medium 'refractive index' on the process of laser beam propagation. First, the solution predicts deceleration of the entire pulse in the medium related to the motion of the pulse envelope $\varepsilon_0(\tau)$ with a certain 'group velocity'. The 'group velocity' can be defined as the velocity of the front edge or maximum of the pulse. Second, solution (7) characterises the phase velocity $v_{\mathrm{ph}} = c/n(\tau)$ [the second factor in (7)] and its dependence on the spatial and temporal coordinates via the dependence on τ. The stronger the molecular alignment, the larger the deceleration of the appropriate parts of the laser pulse, and vice versa – the alignment of molecules 'against' the field leads to acceleration of the spectral components. The modulation of the phase velocity causes generation of higher and lower frequencies at the expense of the relation $\partial v_{\mathrm{ph}}/\partial \tau \propto -\partial n/\partial \tau$, the sign of $\partial n/\partial \tau$ being determined by the temporal dependence of the

quantity $\langle \cos^2\theta \rangle$ (particularly, its time derivative) during the action of the laser pulse.

Third, the analytical solution predicts the existence of one more important phenomenon, affecting the laser pulse evolution, namely, the process of modulated absorption of the pulse energy by the medium, which gives rise to redistribution of the contributions from different frequency components and determines the shape of the laser pulse spatiotemporal profile. When a large number of rotational states are excited, one should also account for the fast dynamics of the quantity $\langle \cos^2\theta \rangle$, which can in this case yield a correction to the value of $n(\tau)$ at the moments of efficient molecular alignment. Hence, the evolution of the pulse in the medium is mainly determined by the dependence $n(\tau)$, and by choosing the delay of the probe pulse it appears possible to create a specific regime of the probe pulse propagation, the energy and spectrum of which will vary in a controllable way.

Figure 2 represents the results of numerical calculation of the variation in the temporal profile and the spectrum of a probe pulse having the duration of 30 optical cycles with the peak intensity $I = 10^{10}$ W cm^{-2}, propagating through the molecular medium, excited by the pulse with $I = 6\times 10^{12}$ W cm^{-2} (the evolution of molecular alignment being presented in Fig. 1a), as well as the analytical solution (7). At relatively small duration of the probe pulse ($\sim$75 fs) the present case is the case of a 'long' pulse, in the sense that during the action of the laser pulse the molecules have time to reorient several times. As a result, different parts of the pulse 'feel' different values of the 'refractive index', which leads to strong modulation of the pulse structure. Figure 2a shows the time dependences of the laser pulse electric field strength (rigorous numerical and analytical approximate solutions) for the penetration depth $150\lambda_{\mathrm{las}}$ ($\lambda_{\mathrm{las}} = 2\pi c/\omega_{\mathrm{las}}$), as well as the profile of the quantity $\langle \cos^2\theta \rangle$, characterising the dynamics of molecular alignment, induced by the pump pulse. The obtained results demonstrate perfect agreement (practically exact coincidence) of the analytical approximation (7) with the rigorous direct solution of the problem. Hence, at the considered penetration depths the analytical solution correctly describes the basic mechanisms responsible for the laser pulse propagation.

The major contribution to the change in the laser radiation frequency in the course of its propagation comes from the quantity

$$\frac{\partial(\omega\tau)}{\partial t} - \omega = -z\frac{\partial k(z,t)}{\partial t} \propto -\frac{\partial n(z,t)}{\partial t},$$

characterising the time derivative of the pulse phase [the second factor in the solution (7)]. In this case, as mentioned above, the direction of the spectrum broadening depends on the sign of the derivative $\partial n(z,t)/\partial t$: the higher frequencies arise during the time intervals when the derivative $\partial \langle \cos^2\theta \rangle/\partial t < 0$ and vice versa. One can see from Fig. 2a the correlations between the sign of the derivative of the mean value of squared cosine of the molecular alignment angle and the increase/decrease in the laser radiation frequency, which corresponds to the analytical solution.

In addition, in spite of its apparent smallness, the factor $\exp[-\xi c^{-1}\partial n(\tau)/\partial \tau]$ also contributes considerably to the variation of the laser pulse profile, describing the redistribution of energy within the pulse and determining the additional temporal modulation. The analytical solution obtained by omitting the mentioned exponential factor, is presented in Fig. 2b and demonstrates its insufficiency as compared to the rigorous solution. Therefore, the influence of the time-dependent
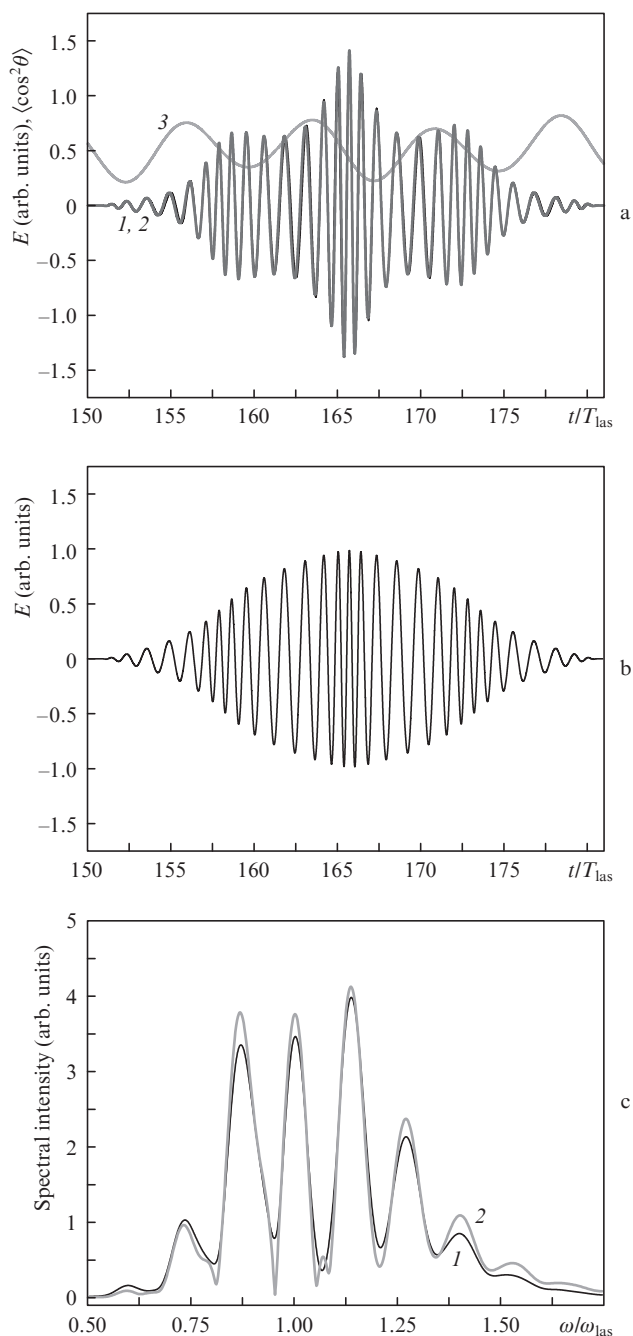
Figure 2. (a) Temporal profiles of the probe laser pulse with the duration of 30 optical cycles at the penetration depth $150\lambda_{las}$, obtained by (*1*) rigorous numerical solution and (*2*) approximate analytical solution of Eqn (7), and (*3*) the profile of the quantity $\langle \cos^2\theta \rangle$; (b) the analytical solution with no absorption taken into account, and (c) the laser pulse spectra at the same penetration depth, obtained by rigorous (*1*) numerical and (*2*) analytical solution.

occurs towards both lower and higher frequencies. The specific shape of the resulting spectrum is determined by the fact that similar frequencies are generated in different part of the laser pulse (see Fig. 2a), as a result of which the interference irregularity of the spectrum is observed. The neglect of absorption in the consideration of the spectrum evolution results in underestimation of the spectrum in the high-frequency region due to the neglected interrelation between the absorption and the frequency change. In this case the spectrum broadening weakly depends on the delay between the probe pulse and the pump pulse, because 'long' pulses experience several oscillations of the quantity $\langle \cos^2\theta \rangle$, and the summary effect is practically independent of the initial phase. However, the presence of modulated absorption can give rise to considerable difference in the temporal profile of such pulses.

More interesting is the case of 'short' pulses, when it is possible to implement the situation of only one chosen maximum of the quantity $\langle \cos^2\theta \rangle$, affecting the pulse evolution. In this case at definite values of the delay the sign of the derivative of the function $n(z, t)$ may remain unchanged during the entire pulse, thus providing one-side broadening of the spectrum (towards either high or low frequencies). The phase velocity will change monotonically during the pulse, providing a monotonically chirped pulse (a similar effect was described in [16, 17] for pulses of large (picosecond) duration in the case of slow molecular dynamics of heavy molecules).

Due to such broadening of the spectrum, the presence of the chirp in the laser pulse allows simple implementation of its further compression procedure. Figure 3 illustrates the results of numerical calculations for the case of propagation of a short pulse with the duration of five optical cycles under the same conditions of the molecular medium excitation, and at different delays of the probe pulse with respect to the pump pulse. The results of rigorous numerical calculation confirm the above considerations. Thus, at the delay $\delta t = 6.5T_{las}$ ($T_{las} = 2\pi/\omega_{las}$) (Figs 3a, c) the probe pulse presumably falls on region of the increasing quantity $n(z, t)$, which corresponds to phase velocity decreasing towards the pulse tail. Due to this fact the descending part of the pulse expands, thus increasing the pulse duration, and the spectrum broadens mainly towards lower frequencies. When the delay corresponds to the opposite phase of the quantity $\langle \cos^2\theta \rangle$, the opposite effect is observed (Figs 3b, d, delay $\delta t = 32.5T_{las}$): the frequency of the pulse increases towards the tail and the spectrum is shifted to the blue. Hence, choosing the delay between the pump and probe pulses one can control the direction of spectrum broadening of the probe pulse, as well as the chirp sign. Moreover, the quantity $\langle \cos^2\theta \rangle$ is itself of importance. In the case of large values of the molecular alignment parameter during the probe pulse, the 'group velocity' of the pulse appears to be smaller. As a result in Fig. 3b one can see noticeable retardation of the pulse with respect to the one propagating through a non-oriented medium, in contrast to Fig. 3a, in which no retardation is observed. Note also that the analytical solution in the case of 'short' pulses correctly predicts their evolution; however, the exact coincidence with the numerical solution (at the propagation depths considered) takes place only for $\delta t = 6.5T_{las}$. The reasons for that are discussed below.

Of special interest is the optimisation of the spectrum broadening procedure at the expense of a special choice of the delay between the pump pulse and the probe one. The idea is reasonable only for the case of 'short' pulses with the duration that allows experiencing the effect of a single oscillation
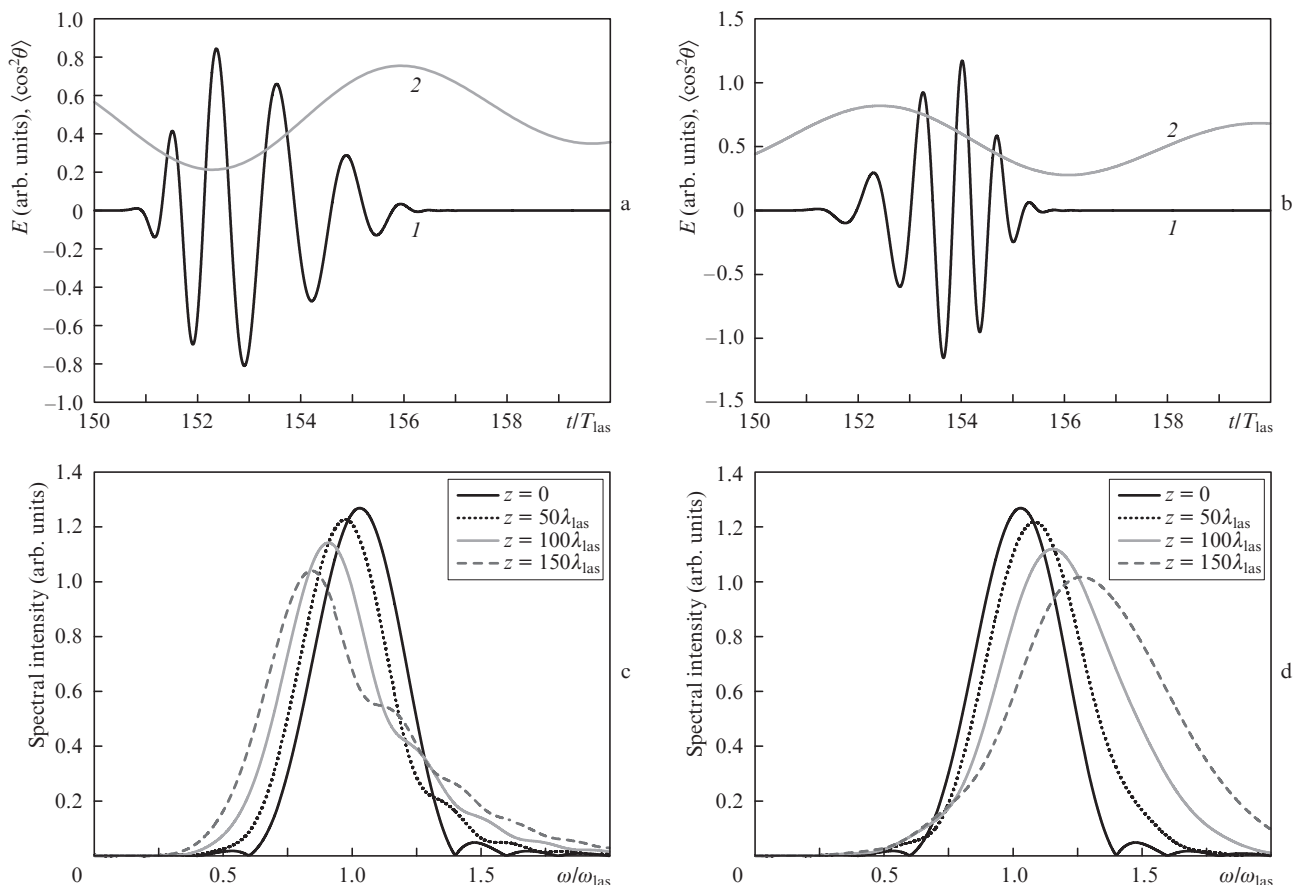
'refractive index' on the probe pulse propagation process is not reduced to the change of the phase velocity of frequency components. An effect that appears to be essential here is also the modulated absorption, the relation of which to the derivative of the 'refractive index' also clearly manifests itself in the pulse envelope shape, presented in Fig. 2a. As a result, the factor $n(z, t)$ has a wider physical meaning than merely a refractive index of the medium in its traditional understanding.

The analytical solution also correctly describes the dynamics of the pulse spectrum (Fig. 2c); the broadening in this case

Figure 3. (*1*) Temporal profiles of the probe laser pulse five optical cycles long at the penetration depth of $150\lambda_{las}$ and (*2*) the profile of the quantity $\langle \cos^2\theta \rangle$ (a, b), as well as the evolution of the pulse spectrum (c, d) with the growth of propagation depth z for the probe pulse delays with respect to the pump pulse $\delta t = 6.5 T_{las}$ (a, c) and $32.5 T_{las}$ (b, d).

of the $\langle \cos^2\theta \rangle$ profile. The analytical solution (7) predicts that the maximal broadening of the spectrum can be achieved if the probe pulse is situated in the region of monotonicity of the function $n(z, t)$. In this case the shift of the pulse spectrum will occur towards one side. Hence, for the exciting pulse considered, increasing the delay of the probe pulse five cycles long up to $\delta t = 34.4 T_{las}$ one can expect the efficiency growth in generating high-frequency components at the output of the medium.

The above considerations are illustrated in Fig. 4: when the delay between the pulses is increased up to $\delta t = 34.4 T_{las}$, the laser pulse completely covers the region in which the derivative of $n(z, t)$ is negative, the pulse maximum corresponding to lager value of the derivative than for the delay $\delta t = 32.5 T_{las}$. Figure 4b presents the spectra of the probe pulse calculated using the analytical formula at the penetration depth of $150\lambda_{las}$ for two values of the probe pulse delay mentioned above. In this case the rigorous solution essentially differs from the result of calculation using the analytical formula. From the rigorous solution (Fig. 4c) it is seen that the resulting spectra in the two cases differ insignificantly. Thus, there is a disagreement between the results of the rigorous solution and the analytical one for $\delta t = 32.5 T_{las}$.

This is due to the fact that the approximate analytical equation (6) was derived assuming that at all points of the medium the probe pulse experiences the influence of the same function $A(\tau)$ (the right-hand side of the equation does not depend on the variable ξ). Really the applicability of such an

assumption is limited. As we have seen above, the propagation of a laser pulse can be characterised by a considerable decrease in the group velocity as compared to the velocity of the pump pulse at the expense of coincidence of the probe pulse with the maximum of the 'refractive index' (see Fig. 3b). As a result, with increasing penetration depth the probe pulse 'drifts' with respect to the temporal profile $n(\tau)$, and just the spatiotemporal dependence $n(z, t)$ becomes essential, because at different points of the medium the pulse 'meets' different phases of the 'refractive index'. The capture of the laser pulse and its locking to the temporal dependence $n(\tau)$ are, therefore, possible only near its minimum (this case is illustrated in Fig. 3a), which corresponds to the motion of the probe signal with the velocity of the pump pulse. The derived analytical expression correctly describes the deceleration of the pulse front edge, but cannot describe the effect related to the 'drift' of the pulse to the minimum of the quantity $\langle \cos^2\theta \rangle$, characterised by a low degree of molecular alignment. This effect manifests itself in the broadening of the spectrum towards the short-wavelength region and demonstrates the necessity of the rigorous numerical solution of the problem in the case of 'short' laser pulses.

The use of a rigorous solution is also necessary when considering the problem of the pulse self-action in the process of its propagation. In the study of self-action one cannot separate the spatiotemporal evolution of the laser pulse profile and the medium dynamics, so that the derivation of an analytical approximation is hardly possible. Figure 5 presents the
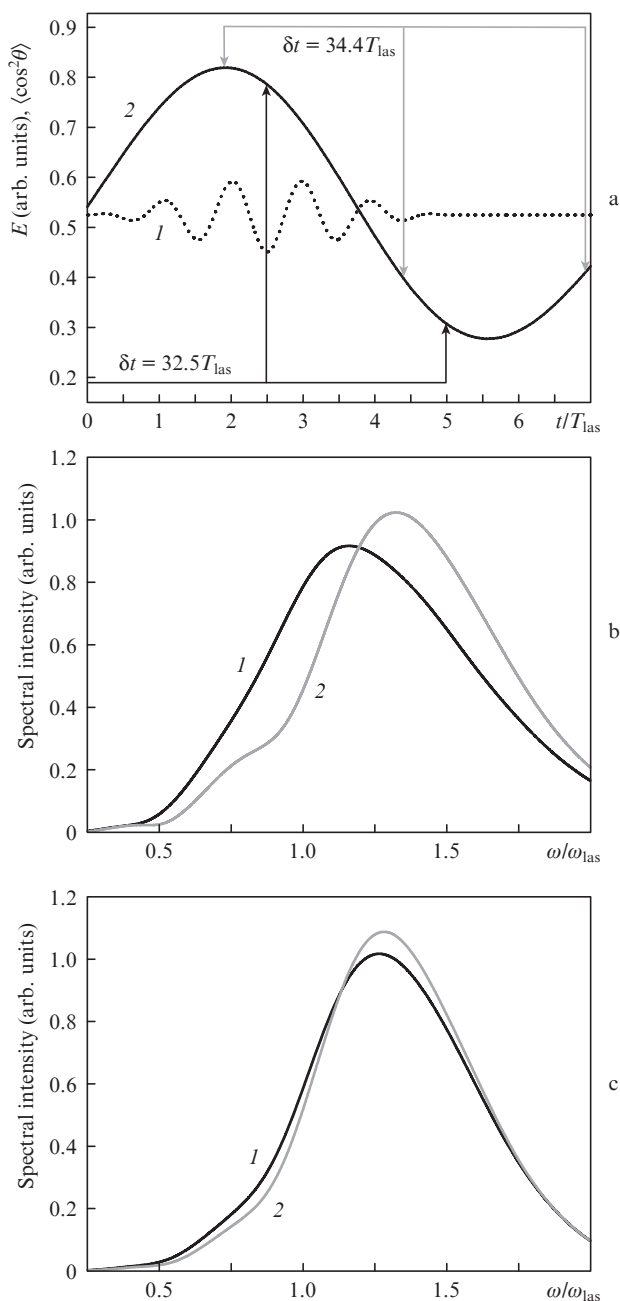
Figure 5. (a) Temporal profile of the laser pulse 50 optical cycles long with the peak intensity $I = 3 \times 10^{12}$ W cm^{-2} and (b) the spectra of this pulse at its propagation through the molecular medium at the penetration depth $z = 150\lambda_{las}$ and at the medium input ($z = 0$).

Figure 4. Illustration of the pulse (*1*) position with respect to the temporal profile of $\langle \cos^2\theta \rangle$ (*2*) at two delays of the probe pulse with respect to the pump pulse (the arrows show the position of the beginning, the maximum, and the end of the pulse) (a) and the spectra of the probe laser pulse five optical cycles long at the penetration depth $150T_{las}$ for $\delta t = 32.5T_{las}$ (*1*) and $34.4T_{las}$ (*2*), obtained by analytical (b) and rigorous numerical (c) solution.

strong modulation of the resulting spectrum, giving rise to a large set of new dominating frequencies.

4. Conclusions

In the present paper the process of propagation of short laser pulses through the molecular medium, characterised by orientational nonlinearity, is studied in detail. A numerical solution of the self-consistent system, consisting of the wave equation that characterises the spatiotemporal evolution of the pulse, and the Schrödinger equation, describing the dynamics of the rotational state of the medium molecules, was obtained. The developed approach allows a correct description of the quantum state of the medium molecules and an *ab initio* calculation of polarisation response, beyond the frameworks of approximate phenomenological concepts.

The evolution of the temporal profile and the spectrum of the probe pulse, propagating through the molecular medium, preliminarily excited by a pump pulse, are analysed. The scheme is promising from the point of view of controllable broadening of the probe pulse spectrum and wide possibilities for optimisation of this process. An approximate analytical solution of the present problem is found that correctly describes the basic features of the probe pulse propagation, allows understanding of physical mechanisms of the observed effects, and demonstrates the limited nature of their description using phenomenologically introduced refractive index of the medium. For 'short' probing pulses the rigorous solution

results of the rigorous numerical solution of the self-consistent problem for the pulse having the peak intensity $I = 3 \times 10^{12}$ W cm^{-2}. The wave equation, describing the transformation of the laser pulse, and the set of Schrödinger equations that determine the quantum state dynamics of the medium molecules were solved together. It is seen that in the process of self-action the effects that have been already discussed manifest themselves. The temporal profile of the pulse experiences strong deformations (Fig. 5a) and its spectrum essentially broadens (Fig. 5b). This is accompanied with
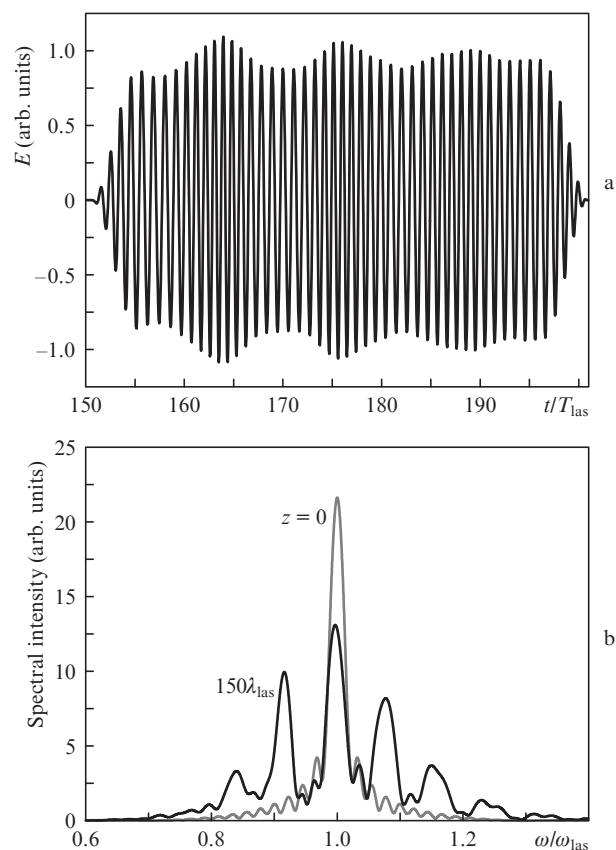
reveals the possibility of controllable directed broadening of the pulse spectrum, accompanied by the definite pulse chirping, which is of great interest from the point of view of obtaining self-compressing pulses. In addition, the effect of laser pulse 'drift' with respect to the profile of time-dependent refractive index of the medium towards the region with smaller degree of molecular alignment was found, which can give rise to a tendency of pulse self-splitting for pulses having large duration. All the effects manifest themselves even stronger in the process of single pulse propagation under the conditions of mutual influence of the pulse and the medium.

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