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Influence of Free Motion of Atoms on Atomic Density-Dependent Effects in Nonlinear Laser Spectroscopy of Resonant Gas Media

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We develop a nonlinear theory of propagation of a monochromatic light wave in a gas of two-level atoms under the condition of inhomogeneous Doppler lineshape broadening, while considering a self-consistent solution of the Maxwell–Bloch equations in the mean-field approximation using a single atom density matrix formalism. Our approach shows a significant deformation of the Doppler resonant lineshape (shift, asymmetry), which depends on the atomic density. These effects are a consequence of only the free motion of atoms in a gas and is not associated with interatomic interaction. In particular, the frequency shift of the field-linear contribution to the transmission signal is more than an order of magnitude greater than the shift due to the interatomic dipole–dipole interaction, and the first nonlinear correction has an even stronger deformation, which exceeds the effect of the interatomic interaction by three orders of magnitude. The found effects caused by the free motion of atoms require a significant revision of the existing picture of spectroscopic effects, which depend on the atomic density in a gas.

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Modern laser spectroscopy is a powerful research tool of great importance both for fundamental science and for numerous practical applications. The basic principles of this science were formulated several decades ago and are widely presented in scientific and educational literature [1–7]. A special role belongs to laser spectroscopy of atomic gases for quantum frequency and time standards (atomic clocks), which use the reference resonances excited at the frequency of atomic transitions. At the same time, the metrological characteristics of these devices are largely determined by the presence of frequency shifts of resonant transitions. These shifts can be divided into two main categories: field shifts, induced by external static and variable electromagnetic fields, and collisional shifts, due to interatomic interaction.

In the context of collisional shifts in one-component gas media, collective effects are of particular importance due to the interatomic dipole–dipole interaction, which affects the resonance lineshape (shift, asymmetry, broadening) [8–45]. As known [10], in the case of an ensemble of two-level atoms with an unperturbed frequency ω_0 for a closed optical transition $|g\rangle \leftrightarrow |e\rangle$ (see Fig. 1), the scale of the dipole–dipole interaction is determined by the Lorentz–Lorenz shift $\Delta_{\mathcal{LL}} = -\pi n k_0^{-3}\gamma_0$, where n is the atomic density (number of particles per unit volume), $k_0 = \omega_0/c$ (c is the speed of light in vacuum), γ_0 is the spontaneous decay rate of the upper level (see Fig. 1). In particular, for an ensemble of atoms confined within a layer of thickness L, the total negative shift due to dipole–dipole interaction is described by the formula [8]

$$\Delta_{dd} = \Delta_{\mathcal{LL}} - \frac{3}{4}\Delta_{\mathcal{LL}}\left(1 - \frac{\sin 2k_0L}{2k_0L}\right) < 0, \qquad (1)$$

where the second term is the collective Lamb shift. For a thick layer ($k_0L \gg 1$), from (1) we obtain

$$\Delta_{dd} \approx \frac{1}{4}\Delta_{\mathcal{LL}} = -0.79 n k_0^{-3}\gamma_0. \qquad (2)$$

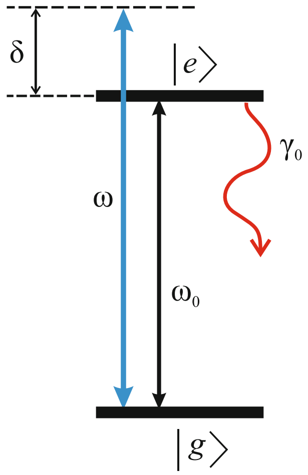

Fig. 1. Scheme of a two-level atom.

According to commonly accepted viewpoint, the interatomic dipole–dipole interaction is the main physical reason of the frequency shift, which is proportional to the atomic density in a gas (2). However, alternative effects caused by the free motion of atoms in a gas, which also depend on the atomic density and lead to the deformation (shift, asymmetry) of the field-linear Doppler lineshape, have been found recently [46]. In particular, the shift of the absorption resonance peak has a positive sign and exceeds (2) by more than an order of magnitude. These effects arise when the light wave propagation is described in the framework of a self-consistent solution of the Maxwell–Bloch equations in the single-atom approximation and, therefore, they are not related to the interatomic interaction.

In this paper, we develop an algorithm to construct a field-nonlinear theory of a running wave propagation in a gas of two-level atoms as a self-consistent solution of the Maxwell–Bloch equations. This allows us to obtain an analytical expression for a nonlinear signal of light transmission through a gas medium with an arbitrary optical thickness. It is found that the top of the resonance lineshape of the main field-nonlinear correction has a positive shift, which is proportional to the atomic density and exceeds the shift due to the interatomic dipole–dipole interaction (2) by more than three orders of magnitude. This huge effect can be used as an excellent object for experimental study of previously unexplored effects caused by the free motion of atoms in a gas. Experimental confirmation of the results obtained in this paper will be of fundamental importance for a substantial revision of the modern picture of spectroscopic effects that are depend on the atomic density in a gas.

Let us consider propagation along the z axis of a plane light wave with a real electric field $E = E(t,z)$ in a gas of free-moving two-level atoms (see Fig. 1). The interaction of atoms with the field is described by the electro–dipole interaction operator $-\hat{d}E$. Our analysis is carried out within the framework of a self-consistent solution of the Maxwell–Bloch equations, which includes the wave equation for the field (in the CGS system):

$$\left(\frac{\partial^2}{\partial z^2} - \frac{1}{c^2}\frac{\partial^2}{\partial t^2}\right)E(t,z) = \frac{4\pi}{c^2}\frac{\partial^2}{\partial t^2}P(t,z). \qquad (3)$$

The polarization of a gas medium in the single-atom approximation is defined as $P(t,z) = n\langle D\rangle$, where $\langle D\rangle$ is the average dipole moment of the atom. In the case of a monochromatic wave with frequency ω, the electric field $E(t,z)$ and the polarization of the medium $P(t,z)$ can be represented as follows:

$$\begin{aligned} E(t,z) &= e^{-i\omega t}E(z) + e^{i\omega t}E^*(z), \\ P(t,z) &= e^{-i\omega t}P(z) + e^{i\omega t}P^*(z). \end{aligned} \qquad (4)$$

Then, using (3), for the negative frequency components $E(z)$ and $P(z)$ we obtain the equation

$$\left(\frac{\partial^2}{\partial z^2} + k^2\right)E(z) = -4\pi k^2 P(z), \qquad (5)$$

where $k = \omega/c$ is the wavenumber in vacuum.

In our analysis, we use the single-atom density matrix $\hat{\rho}(v)$ (v is the atomic velocity), whose components $\rho_{mn}(v) = \langle m|\hat{\rho}(v)|n\rangle$ (where $m,n = e,g$) for a closed two-level system in the rotating-wave approximation are described by the equations

$$\begin{gathered} \left[v\frac{\partial}{\partial z} + \frac{\gamma_0}{2} - i\delta\right]\rho_{eg}(v) = \frac{id_{eg}E(z)}{\hbar}[\rho_{gg}(v) - \rho_{ee}(v)], \\ \left[v\frac{\partial}{\partial z} + \gamma_0\right]\rho_{ee}(v) \\ = \frac{i}{\hbar}[d_{eg}E(z)\rho_{ge}(v) - d_{ge}E^*(z)\rho_{eg}(v)], \qquad (6) \\ \rho_{ge}(v) = \rho^*_{eg}(v), \quad \rho_{gg}(v) + \rho_{ee}(v) = f(v), \\ \int_{-\infty}^{\infty} f(v)dv = 1, \end{gathered}$$

where $\delta = \omega - \omega_0$ is the frequency detuning of the laser field (4) in the laboratory reference frame, $d_{eg} = \langle e|\hat{d}|g\rangle = d^*_{ge}$ is the matrix element of the dipole moment operator. The diagonal elements of the density matrix $\rho_{gg}(v)$ and $\rho_{ee}(v)$ describe the populations in the ground and excited states, respectively, while the non-diagonal elements $\rho_{eg}(v)$ and $\rho_{ge}(v)$ correspond to optical coherence. The function $f(v)$ is the velocity distribution of atoms, which we assume to be Maxwellian:

$$f(v) = f_M(v) = \frac{e^{-(v/v_0)^2}}{v_0\sqrt{\pi}}, \quad v_0 = \sqrt{\frac{2k_BT}{m}},$$

where k_B is the Boltzmann constant, T is the temperature of the gas, m is the mass of the atom. The operator $v(\partial/\partial z)$ on the left-hand side of (6) is a one-dimensional version (for the plane wave case) of the scalar operator $(\mathbf{v}\cdot\nabla)$. The negative frequency component of the medium polarization in Eq. (5) is defined as:

$$P(z) = n\langle d_{ge}\rho_{eg}(v)\rangle_v, \tag{7}$$

where $\langle\ldots\rangle_v$ denotes integration over velocities, $\int_{-\infty}^{+\infty}\ldots dv$. Thus, Eqs. (5)–(7) constitute the Maxwell–Bloch system of equations in our case.

We will find a solution of Eqs. (5)–(7) using perturbation theory, based on the assumption that the following parameter is small (i.e., the saturation of the optical transition is small):

$$\frac{|d_{eg}E(z)|}{\hbar\gamma_0/2} \ll 1, \tag{8}$$

which is used as the decomposition parameter for the density matrix:

$$\hat\rho(v) = \hat\rho^{(0)}(v) + \hat\rho^{(1)}(v) + \hat\rho^{(2)}(v) + \hat\rho^{(3)}(v) + \ldots. \tag{9}$$

As the initial expansion term, we consider the density matrix for the gas of unperturbed atoms in the ground state:

$$\begin{gathered}\rho_{gg}^{(0)}(v) = f(v), \quad \rho_{ee}^{(0)}(v) = 0,\\ \rho_{eg}^{(0)}(v) = \rho_{ge}^{(0)}(v) = 0.\end{gathered} \tag{10}$$

In according with (9), for the electric field (4) and medium polarization (7) the following expansions take place:

$$\begin{aligned}E(z) &= E^{(1)}(z) + E^{(3)}(z) + E^{(5)}(z) + \ldots,\\ P(z) &= P^{(1)}(z) + P^{(3)}(z) + P^{(5)}(z) + \ldots.\end{aligned} \tag{11}$$

Using Eqs. (9)–(11) in Eqs. (5)–(7), at the first step of the iterative procedure, we obtain the system of equations

$$\left(\frac{\partial^2}{\partial z^2} + k^2\right)E^{(1)}(z) = -4\pi k^2 P^{(1)}(z), \tag{12}$$

$$\left(v\frac{\partial}{\partial z} + \frac{\gamma_0}{2} - i\delta\right)\rho_{eg}^{(1)}(v) = \frac{i}{\hbar}d_{eg}E^{(1)}(z)f(v),$$

$$P^{(1)}(z) = n\langle d_{ge}\rho_{eg}^{(1)}(v)\rangle_v,$$

the solution of which in the case of a running wave, as shown in [46], can be represented as follows:

$$\begin{gathered}E^{(1)}(z) = \mathcal{E}e^{\mathcal{K}kz},\\ \rho_{eg}^{(1)}(v) = \frac{id_{eg}f_M(v)}{\hbar(\gamma_0/2 - i\delta + \mathcal{K}kv)}\mathcal{E}e^{\mathcal{K}kz}.\end{gathered} \tag{13}$$

The complex dimensionless wavenumber $\mathcal{K}$ is determined from the equation

$$\mathcal{K}^2 + 1 = -\frac{i4\pi n|d_{eg}|^2}{\hbar}\left\langle\frac{f_M(v)}{\gamma_0/2 - i\delta + \mathcal{K}kv}\right\rangle_v. \tag{14}$$

Using the well-known expression

$$\gamma_0 = \frac{4k_0^3|d_{eg}|^2}{3\hbar},$$

for the spontaneous decay rate of the upper level $|e\rangle$, we rewrite (14) as:

$$\mathcal{K}^2 + 1 = -i\left\langle\frac{3\pi nk_0^{-3}\gamma_0 f_M(v)}{\gamma_0/2 - i\delta + \mathcal{K}kv}\right\rangle_v, \tag{15}$$

where the interatomic dipole–dipole interaction parameter $nk_0^{-3}\gamma_0$ appears explicitly, despite the single-atom density matrix approximation in our consideration. Assuming the wave propagation along the positive direction of the z axis, we impose the following conditions:

$$\operatorname{Im}\{\mathcal{K}\} > 0, \quad \operatorname{Re}\{\mathcal{K}\} < 0, \tag{16}$$

on the solution of Eq. (15).

The second iteration step is to determine the correction $\hat\rho^{(2)}(v)$ for the density matrix:

$$\begin{gathered}\left(v\frac{\partial}{\partial z} + \gamma_0\right)\rho_{ee}^{(2)}(v)\\ = \frac{i}{\hbar}\left[d_{eg}E^{(1)}(z)\rho_{ge}^{(1)}(v) - d_{ge}E^{(1)*}(z)\rho_{eg}^{(1)}(v)\right],\end{gathered} \tag{17}$$

$$\rho_{gg}^{(2)}(v) = -\rho_{ee}^{(2)}(v), \quad \rho_{eg}^{(2)}(v) = \rho_{ge}^{(2)}(v) = 0.$$

Substituting in (17) the expressions from (13), we obtain the equation

$$\begin{gathered}\left(v\frac{\partial}{\partial z} + \gamma_0\right)\rho_{ee}^{(2)}(v)\\ = \frac{|d_{eg}\mathcal{E}|^2}{\hbar^2}\frac{[\gamma_0 + (\mathcal{K} + \mathcal{K}^*)kv]f_M(v)e^{(\mathcal{K}+\mathcal{K}^*)kz}}{|\gamma_0/2 - i\delta + \mathcal{K}kv|^2},\end{gathered} \tag{18}$$

from which we find

$$\rho_{ee}^{(2)}(v) = -\rho_{gg}^{(2)}(v) = \frac{|d_{eg}\mathcal{E}|^2}{\hbar^2}\frac{f_M(v)e^{(\mathcal{K}+\mathcal{K}^*)kz}}{|\gamma_0/2 - i\delta + \mathcal{K}kv|^2}. \tag{19}$$

At the third step of the algorithm, we determine $\hat\rho^{(3)}(v)$, $E^{(3)}(z)$ and $P^{(3)}(z)$ from the equations

$$\left(\frac{\partial^2}{\partial z^2} + k^2\right)E^{(3)}(z) = -4\pi k^2 P^{(3)}(z),$$

$$\begin{gathered}\left[v\frac{\partial}{\partial z} + \frac{\gamma_0}{2} - i\delta\right]\rho_{eg}^{(3)}(v) = \frac{id_{eg}E^{(3)}(z)}{\hbar}[\rho_{gg}^{(0)}(v) - \rho_{ee}^{(0)}(v)]\\ + \frac{id_{eg}E^{(1)}(z)}{\hbar}[\rho_{gg}^{(2)}(v) - \rho_{ee}^{(2)}(v)],\end{gathered} \tag{20}$$

$$P^{(3)}(z) = n\langle d_{ge}\rho_{eg}^{(3)}(v)\rangle_v.$$

Using Eqs. (10), (13) and (19), we obtain the equation for $\rho_{eg}^{(3)}(v)$:

$$\begin{gathered}\left[v\frac{\partial}{\partial z}+\frac{\gamma_0}{2}-i\delta\right]\rho_{eg}^{(3)}(v)\\ =\frac{id_{eg}E^{(3)}(z)f_M(v)}{\hbar}-\frac{i2d_{eg}\mathcal{E}|d_{eg}\mathcal{E}|^2f_M(v)e^{(2\mathcal{K}+\mathcal{K}^*)kz}}{\hbar^3|\gamma_0/2-i\delta+\mathcal{K}kv|^2},\end{gathered} \tag{21}$$

which leads to the following spatial dependence for $E^{(3)}(z)$:

$$E^{(3)}(z)=\mathcal{A}e^{(2\mathcal{K}+\mathcal{K}^*)kz}. \tag{22}$$

This, in turn, allows us to write the solution for $\rho_{eg}^{(3)}(v)$:

$$\begin{gathered}\rho_{eg}^{(3)}(v)=\frac{id_{eg}f_M(v)\mathcal{A}e^{(2\mathcal{K}+\mathcal{K}^*)kz}}{\hbar[\gamma_0/2-i\delta+(2\mathcal{K}+\mathcal{K}^*)kv]}\\ -\frac{i2d_{eg}\mathcal{E}|d_{eg}\mathcal{E}|^2f_M(v)e^{(2\mathcal{K}+\mathcal{K}^*)kz}}{\hbar^3|\gamma_0/2-i\delta+\mathcal{K}kv|^2[\gamma_0/2-i\delta+(2\mathcal{K}+\mathcal{K}^*)kv]}.\end{gathered} \tag{23}$$

Substituting Eqs. (22) and (23) into the left and right parts of the wave equation (20), respectively, we find the expression for the amplitude $\mathcal{A}$:

$$\begin{gathered}\mathcal{A}=\frac{i6\pi nk_0^{-3}\gamma_0\mathcal{E}|d_{eg}\mathcal{E}|^2}{\hbar^2[(2\mathcal{K}+\mathcal{K}^*)^2+1+F(\delta)]}\\ \times\left\langle\frac{f_M(v)}{|\gamma_0/2-i\delta+\mathcal{K}kv|^2[\gamma_0/2-i\delta+(2\mathcal{K}+\mathcal{K}^*)kv]}\right\rangle_v,\end{gathered} \tag{24}$$

where

$$F(\delta)=i\left\langle\frac{3\pi nk_0^{-3}\gamma_0f_M(v)}{\gamma_0/2-i\delta+(2\mathcal{K}+\mathcal{K}^*)kv}\right\rangle_v. \tag{25}$$

Thus, the expression for the field can be written up to a cubic (in $\mathcal{E}$) term:

$$E(z)=E^{(1)}(z)+E^{(3)}(z)=\mathcal{E}e^{\mathcal{K}kz}+\mathcal{A}e^{(2\mathcal{K}+\mathcal{K}^*)kz}. \tag{26}$$

Let us consider an optical medium of length L ($0\le z\le L$) under the condition $kL\gg 1$ (in order to eliminate the influence of the Dicke effect [47] and other boundary effects [48]). We assume that at the entrance to the medium ($z=0$) the electric field is equal to E_0. In this case, from (26) we get

$$E(0)=E_0=\mathcal{E}+\mathcal{A}\Rightarrow\mathcal{E}=E_0-\mathcal{A}. \tag{27}$$

Our task is to calculate the spectroscopic signal at the exit from the medium ($z=L$), determined by the intensity $I(L)\propto|E(L)|^2$:

$$\begin{gathered}|E(L)|^2=\left|(E_0-\mathcal{A})e^{\mathcal{K}kL}+\mathcal{A}e^{(2\mathcal{K}+\mathcal{K}^*)kL}\right|^2\\ \approx|E_0|^2e^{2\operatorname{Re}\{\mathcal{K}\}kL}-2\operatorname{Re}\{\mathcal{A}E_0^*\}(e^{2\operatorname{Re}\{\mathcal{K}\}kL}-e^{4\operatorname{Re}\{\mathcal{K}\}kL}),\end{gathered} \tag{28}$$

where we have neglected small terms with $|\mathcal{A}|^2\propto|\mathcal{E}|^6$, since terms of this order will also appear from the contribution of $E^{(5)}$ [see (11)], which we do not take into account in this paper. Further, keeping the same accuracy, we can put $\mathcal{E}=E_0$ in the expression (24) for the amplitude $\mathcal{A}$. In this case, from (28) we obtain the final expression for the transmission signal:

$$\begin{gathered}I(L)\\ \approx I_0e^{2\operatorname{Re}\{\mathcal{K}\}kL}[1-3\pi nk_0^{-3}S_0(1-e^{2\operatorname{Re}\{\mathcal{K}\}kL})U(\delta)],\end{gathered} \tag{29}$$

where $I_0\propto|E_0|^2$ is the field intensity at the entrance to the medium, $S_0=4|d_{eg}E_0/\hbar\gamma_0|^2\ll 1$ is a small saturation parameter, and the function $U(\delta)$ is defined as:

$$\begin{gathered}U(\delta)\\ =\operatorname{Re}\left\langle\frac{if_M(v)[(2\mathcal{K}+\mathcal{K}^*)^2+1+F(\delta)]^{-1}\gamma_0^3}{|\gamma_0/2-i\delta+\mathcal{K}kv|^2[\gamma_0/2-i\delta+(2\mathcal{K}+\mathcal{K}^*)kv]}\right\rangle_v.\end{gathered} \tag{30}$$

Note that the analytical expression (29) was obtained in the framework of the self-consistent solution of the Maxwell–Bloch equations for any optical thickness of the medium, which was not previously presented in the scientific literature.

In the case of optically thin medium $|2\operatorname{Re}\{\mathcal{K}\}kL|\ll 1$, from (29) we get:

$$\begin{gathered}I(L)\\ \approx I_0[1+2\operatorname{Re}\{\mathcal{K}\}kL+6\pi nk_0^{-3}kLS_0\operatorname{Re}\{\mathcal{K}\}U(\delta)].\end{gathered} \tag{31}$$

For comparison, we consider a well-known expression for an optically thin medium:

$$I(L)\approx I_0[1+D(\delta)kL+6\pi nk_0^{-3}kLS_0B(\delta)], \tag{32}$$

where the function $D(\delta)$ (commonly referred to in the scientific literature as the Voigt profile) is defined as:

$$D(\delta)=-\frac{3}{2}\pi nk_0^{-3}\left\langle\frac{f_M(v)\gamma_0^2}{|\gamma_0/2-i\delta+ikv|^2}\right\rangle_v, \tag{33}$$

and the function $B(\delta)$ is:

$$B(\delta)=\frac{1}{8}\left\langle\frac{f_M(v)\gamma_0^4}{|\gamma_0/2-i\delta+ikv|^4}\right\rangle_v. \tag{34}$$

Note that the derivation of formulas (32)–(34) is based on an approximation when the expression for a running wave in vacuum:

$$E(z,t)=E_0e^{-i\omega t+ikz}+\text{c.c.}, \tag{35}$$

is used in the equation for the atomic density matrix. Moreover, the reduced Maxwell equation

$$\frac{\partial}{\partial z}\tilde{E}(z)=2i\pi k\tilde{P}(z), \tag{36}$$

is used instead of (5). Equation (36) is obtained from Eq. (5) by replacing:

$$E(z)=\tilde{E}(z)e^{ikz},\quad P(z)=\tilde{P}(z)e^{ikz}, \tag{37}$$

and neglecting the second derivative $\partial^2\tilde{E}(z)/\partial z^2$ in the left side of (36).

It should be noted that $D(\delta)$ and $B(\delta)$ are even functions on the detuning: $D(-\delta) = D(\delta)$ and $B(-\delta) = B(\delta)$. However, as shown in [46], the correct Doppler lineshape $\mathrm{Re}\{\mathcal{K}\}$ [see (31)] experiences significant deformation (asymmetry, shift), which is a consequence of the free motion of atoms in a self-consistent solution of the Maxwell–Bloch equations. In particular, the shift of the field-linear absorption signal is approximately equal to $19nk_0^{-3}\gamma_0$, which differs in sign and is more than an order of magnitude greater than the shift due to the interatomic dipole–dipole interaction (2). In this context, it is of particular interest to compare the lineshape of the field-nonlinear correction obtained in our consideration [see the expression $\mathrm{Re}\{\mathcal{K}\}U(\delta)$ in (31)] with the known expression (34). As seen in Fig. 2a, there is an asymmetry of the lineshape and a positive shift of the resonance peak, which is due to the free motion of atoms in a self-consistent description within the Maxwell–Bloch equations. Moreover, from numerical calculations, we have found that the shift for the nonlinear correction $\mathrm{Re}\{\mathcal{K}\}U(\delta)$ in the case of $k_0v_0/\gamma_0 \gg 1$ is proportional to the Doppler factor k_0v_0 and is approximately equal to:

$$25nk_0^{-3}(k_0v_0) = 25nk_0^{-2}v_0, \tag{38}$$

which is more than three orders of magnitude greater (at room temperature for the vast majority of atomic optical transitions) than the effect of interatomic dipole–dipole interaction (2). Note that we intentionally used a relatively large atomic density ($nk_0^{-3} = 0.01$) in the calculations of dependences in Fig. 2 in order to noticeably visualize the asymmetry and shift, caused by the free motion of atoms, on the scale of the entire lineshape.

In the case of an arbitrary optical thickness of the medium, the lineshape of the nonlinear correction, as follows from (29), is described by the general expression:

$$-3\pi nk_0^{-3}e^{2\mathrm{Re}\{\mathcal{K}\}kL}(1-e^{2\mathrm{Re}\{\mathcal{K}\}kL})U(\delta). \tag{39}$$

In Fig. 2b, it is shown an example of the frequency dependence (39) when the total absorption level at the center of the line is about 50%. As it is seen, there is an additional deformation with respect to an optically thin medium [see Fig. 2a], and the positive shift of the resonance top increased even more at the same atomic density.

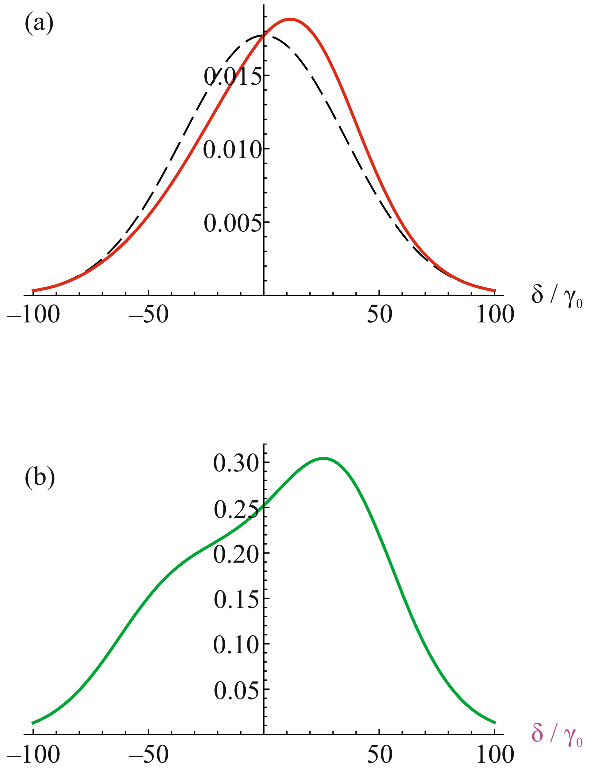

Fig. 2. Lineshape of the nonlinear correction in the transmission signal calculated with the parameters $nk_0^{-3} = 0.01$ and $k_0v_0/\gamma_0 = 50$. (a) Frequency dependences of (red solid line) $\mathrm{Re}\{\mathcal{K}\}U(\delta)$ and (black dashed line) $B(\delta)$ for an optically thin medium. (b) Frequency dependence of Eq. (39) for an optically thick medium ($kL = 2\pi \times 35$).

Thus, both contributions in the transmission signal (29) have a positive frequency shift: the field-linear contribution proportional to $\exp(2\mathrm{Re}\{\mathcal{K}\}kL)$ (see Fig. 3a) and the nonlinear contribution proportional to the expression (39) (see Fig. 2b). However, as shown in Fig. 3b, the top of the total dependence (29) maybe shifted to the left. This “graphical” effect depends on the value of the saturation parameter S_0 and arises due to the opposite direction of the resonant lineshapes in Figs. 2b and 3a. Therefore, it is of great importance to experimentally study only the lineshape of the nonlinear correction (39), for which the positive shift of the resonance peak (38) is more than three orders of magnitude exceeds the shift due to the interatomic dipole–dipole interaction (2). For experimental implementation, we propose to apply the well-known method using relatively slow harmonic modulation of the input intensity I_0 at the frequency f ($f \ll \gamma_0$), which leads to the following replacement in the formula (29):

$$I_0 \to I_0[1 + a\sin(ft)], \quad S_0 \to S_0[1 + a\sin(ft)], \tag{40}$$

where a is the modulation depth. As a result, the spectral dependence of the transmission signal at the second harmonic ($2f$) will be determined only by the contribution that is of interest to us (i.e., nonlinear in the light intensity), which is proportional to the expression (39).

Note that we have considered the case of a plane monochromatic running wave in an infinite flat layer

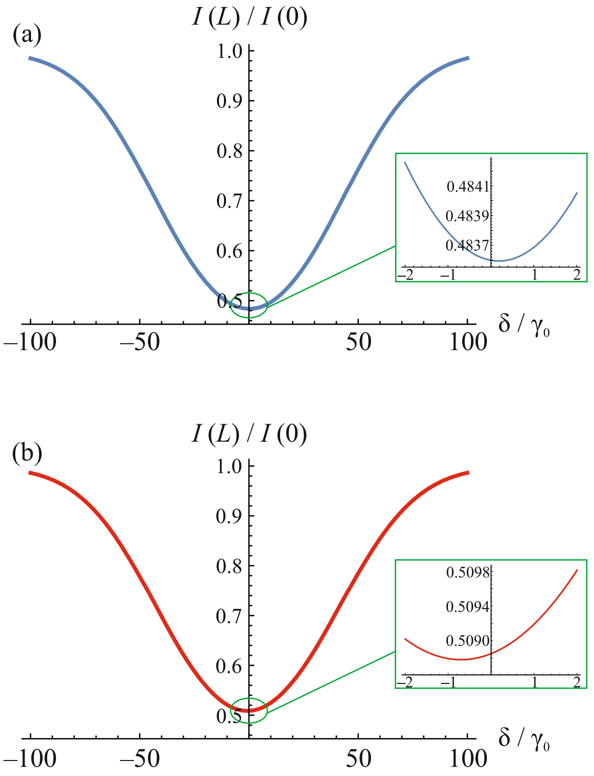

Fig. 3. Lineshape of the transmission signal calculated with the parameters $nk_0^{-3} = 0.01$, $S_0 = 0.1$, $k_0v_0/\gamma_0 = 50$, and $kL = 2\pi \times 35$. (a) Field-linear contribution $\exp(2\mathrm{Re}\{\mathcal{K}\}kL)$, where the inset shows in detail the central part of the resonance shifted to the right. (b) Full transmission signal (29), where the inset shows in detail the central part of the resonance shifted to the left.

of thickness L, when atoms are described by a stationary density matrix $\hat{\rho}(v)$, for which the time derivative $(\partial/\partial t)$ is missing from the left side of Eqs. (6). For the limited light beam with a transverse dimension r, the applicability of our approach is determined by the condition:

$$(r/v_0) \gg \gamma_0^{-1}, \tag{41}$$

where the quantity r/v_0 corresponds to the mean flight-time of atoms through the light beam, and γ_0^{-1} is the time for reaching the steady state of atoms, which is described by Eqs. (6). Usually, for dipole optical transitions $\gamma_0/2\pi > 1$ MHz takes place, and the most probable atomic velocity v_0 at room temperature (~300 K) is on the order of ~100 m/s. In this case, the inequality (41) is satisfied with a very large margin for $r \gtrsim 1$ mm and fully corresponds to typical experimental conditions ($r \sim 1$–10 mm) both for atomic vapor cells and for atomic beams. As for the degree of the light field non-monochromaticity, our analysis is applicable when the spectral distribution width is less than γ_0, which is quite common for modern lasers used in precision laser spectroscopy.

It should also be noted that the presented results were obtained for a closed two-level model, which strictly corresponds only to the real atomic transition $J_g = 0 \to J_e = 1$, where J_g and J_e are the angular momenta of the ground and excited states, respectively. Therefore, an additional problem is how to choose a suitable atom with such a transition. The even isotopes (with zero nuclear spin) of alkaline earth atoms (e.g., Mg, Ca, Sr, Yb, Hg) with closed optical transitions ${}^1S_0 \to {}^1P_1$ and ${}^1S_0 \to {}^3P_1$ seem to be the most appropriate. However, the melting temperature for almost all of these elements is very high (~1000 K), which makes it extremely difficult to experiment with vapor cells. The only exception is the even isotopes ${}^{196-204}$Hg of the mercury atom (melting point 234 K) with the ${}^1S_0 \to {}^3P_1$ intercombination transition convenient for our purposes ($\lambda = 253.7$ nm, $\gamma_0/2\pi = 1.3$ MHz) [49, 50]. However, when using atomic beams, it is possible to use any atoms of this specified group.

In conclusion, we have developed a consistent field-nonlinear theory of the Doppler lineshape for a running monochromatic wave in a gas of two-level atoms, based on a self-consistent solution of the Maxwell–Bloch equations in the mean-field approximation with the use of the single-atom density matrix formalism. In this approach, analytical expressions for the transmission signal in a gas with arbitrary optical thickness are obtained. It was found that the positive frequency shift of the nonlinear contribution to the spectroscopic signal exceeds the well-known negative shift due to the interatomic dipole–dipole interaction by more than three orders of magnitude. Despite the fact that the detected shift depends on the density of atoms, this huge effect is caused by only free motion of atoms in a self-consistent description within the Maxwell–Bloch equations and is not related to interatomic interaction. Note also that this shift is proportional to the Doppler linewidth, which is very unusual and has not been previously considered in the scientific literature. An experimental scheme, which allows to separately study the lineshape of only the field-nonlinear contribution, is proposed. In addition to the fundamental aspect, the obtained results are important for precision laser spectroscopy and optical atomic clocks.

We also note that in many modern theoretical calculations (e.g., see [24, 31, 32]), inhomogeneous Doppler broadening is described within the mathematical model of motionless atoms, where the resonance frequency of each atom in an ensemble is shifted by a Gaussian-distributed random variable with zero mean and the rms value k_0v_0. However, it should be emphasized that in this stochastic approach, the effects of the free motion of atoms, which we found, cannot be taken into account. Indeed, these effects are rigorously based on the presence of the differential operator $(\mathbf{v}\cdot\nabla)$ in the Bloch equations for the density matrix of moving atoms in combination with the complex-valued wave vector (due to the light absorption in a medium), which cannot be reduced only to the Doppler frequency shift for moving atoms.

As a further development of our approach, we can note the light propagation in a gas of atoms with Zeeman and hyperfine structure of energy levels. In this case, when constructing a field-nonlinear theory, it is necessary to take into account the redistribution of populations over the Zeeman sublevels in the ground state (due to spontaneous relaxation of the excited state), which is absent in the ideal two-level model considered by us. In addition, our approach can be generalized to describe a nonlinear sub-Doppler spectroscopy in the case of counterpropagating light waves.

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CONFLICT OF INTEREST

The authors declare that they have no conflicts of interest.

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