Resonant structure of the nonlinear polarization and the nonlinear spectrum of a gas near a surface

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(Submitted 3 May 1995)
Zh. Éksp. Teor. Fiz. **108**, 1614–1624 (November 1995)

This paper solves the problem of the interaction of laser light with a resonant gas near a solid surface using an approximation of two levels, flat surface, and weak saturation. It analyzes the resonant structure of polarization and the formation of new types of intra-Doppler resonances emerging in the spectrum of the gas in the surface region.

The problem of the resonant structure of the nonlinear polarization and the nonlinear spectrum of a gas near a surface that limits the volume occupied by the gas, i.e., the walls of a cell, arises in many areas of laser physics of gaseous media, such as in studies of optical resonances in low-pressure gas-discharge cells,[1–3] in the laser spectroscopy of selective mirror reflection,[4–7] in evanescent-wave spectroscopy,[8,9] and in diagnosis of the scattering of atomic particles by a solid surface.[10,11] In all such and similar situations the idea is actually to calculate the spectral characteristics of a gas at fairly small distances l from the surface, in the surface layer $0 \leqslant z \lesssim l$, with l the mean free path of a particle in relation to interparticle collisions in the gas.

Clearly, in this range of distances the one fact that the gaseous medium is restricted to a volume is enough for the spectral properties of the gas to differ drastically from those of an "unbounded" gas, i.e., far from the surface ($z \gg l$). The situation is well-known in relation to the linear (without allowing for saturation effects) spectral line profile of a gas[4]: near the surface the gas's spectral line profile is clearly asymmetric and resembles a "semi-Doppler" curve if the homogeneous linewidth Γ is small compared to the Doppler linewidth $k\bar{v}$ and the radiation propagates in a direction normal to the surface. The linear refractive index of the medium acquires a small "logarithmic peak" with a width of $\delta \sim \sqrt{\Gamma(k\bar{v})}$.

From the viewpoint of nonlinear (laser) spectroscopy and the problem of extending the existing methods to studies of the properties of a gas in the surface layer, the most interesting questions are the structure of polarization (and spectrum) of the gas near the surface, the types of emerging nonlinear spectral resonances, the formation mechanisms, and the qualitative difference between these resonances and the well-known intra-Doppler resonance in the nonlinear spectroscopy of gases.[12–15] At present there is no clear physical understanding of these matters, and the problem of nonlinear spectral characteristics of the surface layer of gas has never been discussed from this angle in the literature.

This paper solves the problem by using the simple model of a gas of two-level particles interacting with resonant radiation near an infinite flat surface. The main assumption is, as usual, that the surface has a perfectly sharp boundary in gas with fixed scattering properties. This means that the specified parameters of the problem are the kernels $\mu_{jk}(\mathbf{v}|\mathbf{v}')$ describing the scattering of particles by a surface along various elastic and inelastic channels $k \rightarrow j$ with changes in velocity, $\mathbf{v}' \rightarrow \mathbf{v}$ (Ref. 16). The supposition, therefore, is that laser radiation has no effect on the particle–surface interaction. In spectroscopy problems where the light intensity is moderate such a description is often justified. This is corroborated by numerical estimates done in a way similar to that followed by Namiot and Khokhlov.[17]

We examine a gas of two-level particles filling the entire half-space $z \geqslant 0$ to the right of an infinite flat surface. The particles are scattered by the surface and interact with the resonant radiation

$$\mathbf{E}(\mathbf{r},t) = \mathrm{Re} \sum_{\lambda} \mathbf{E}_{\lambda} \exp(-i\omega_{\lambda} t + i\mathbf{k}_{\lambda}\mathbf{r}), \tag{1}$$

which is an arbitrary set of traveling monochromatic plane waves with frequencies ω_{λ}, wave vector $\mathbf{k}_{\lambda}$, and amplitudes $\mathbf{E}_{\lambda} = \mathbf{e}_{\lambda} E_{\lambda}$, with $\mathbf{e}_{\lambda}$ the unit polarization vector of a wave. The energy levels of the particles are nondegenerate. The upper level m has a finite lifetime $\tau_m = 1/\Gamma_m$ determined by its spontaneous decay to the lower level n, which is assumed to be the ground level ($\tau_n = \infty$).

The state of the gas within the volume is described by a density matrix with elements $\rho_{ij}(x) \equiv \rho_{ij}(\mathbf{r},\mathbf{v},t)$, where $i,j = n,m$. We confine ourselves to the following range of distances to the surface: $0 \leqslant z \lesssim l$. Within this range, interparticle collisions in the gas are unimportant, and the equations for ρ_{ij} have the standard form[12,13]

$$\left(\frac{\partial}{\partial t} + \mathbf{v}\nabla + \Gamma_m\right)\rho_m = 2\mathrm{Re}\ iV^{*}_{mn}\rho_{mn},$$

$$\left(\frac{\partial}{\partial t} + \mathbf{v}\nabla\right)\rho_n = \Gamma_m\rho_m - 2\mathrm{Re}\ iV^{*}_{mn}\rho_{mn}, \tag{2}$$

$$\left(\frac{\partial}{\partial t} + \mathbf{v}\nabla + \Gamma\right)\rho_{mn} = iV_{mn}(\rho_m - \rho_n),$$

where $\rho_j \equiv \rho_{jj}$, and

$$V_{mn} = -\sum_{\lambda} G_{\lambda} \exp(-i\Omega_{\lambda} t + i\mathbf{k}_{\lambda}\mathbf{r}) \equiv \sum_{\lambda} V_{\lambda}(x), \tag{3}$$

$$\Omega_\lambda=\omega_\lambda-\omega_{mn}, \quad G_\lambda=\mathbf{d}_{mn}\mathbf{E}_\lambda/2\hbar,$$

is the matrix element of the operator of the particle–radiation dipole interaction, with $\mathbf{d}_{mn}$ and ω_{mn} the dipole moment and the center frequency of the transition, respectively.

The scattering of particles at the surface is described by the following boundary conditions:

$$\bar{\rho}_j^{(+)}(\mathbf{v})=\sum_k \int \mu_k(\mathbf{v}|\mathbf{v}')\frac{|\mathbf{nv}'|}{|\mathbf{nv}|}\bar{\rho}_k^{(-)}(\mathbf{v}')d^3v',$$

$$\bar{\rho}_{mn}^{(+)}(\mathbf{v})=\int \mu(\mathbf{v}|\mathbf{v}')\frac{|\mathbf{nv}'|}{|\mathbf{nv}|}\bar{\rho}_{mn}^{(-)}(\mathbf{v}')d^3v', \tag{4}$$

$$\bar{\rho}_{ij}^{(\pm)}=\theta(\pm\mathbf{nv})\rho_{ij}(x)|_{z=0}, \quad \theta(x)=\begin{Bmatrix}1, & \text{if } x\geq 0,\\ 0, & \text{if } x<0\end{Bmatrix}.$$

Here $\mu_{jk}(\mathbf{v}|\mathbf{v}')$ and $\mu(\mathbf{v}|\mathbf{v}')$ are the scattering kernels for, respectively, the diagonal and off-diagonal elements of density matrix ρ, and $\mathbf{n}$ is the unit vector normal to the surface and pointing in the direction of the gas (along the z axis). The boundary conditions (4) subsume both direct-scattering processes $(k,\mathbf{v}')\to(j,\mathbf{v})$ and processes of the desorption–adsorption type (the approximation of a stationary adsorption layer).

We will assume that in the absence of radiation ($\mathbf{E}=0$) the gas and the surface are in thermodynamic equilibrium, and the complete distribution function of the particles impinging on the surface remains at equilibrium even when $\mathbf{E}\neq 0$:

$$\rho^{(-)}(x)=\sum_j \rho_j^{(-)}(x)=\theta(-\mathbf{nv})\rho^{(0)}(\mathbf{v})\equiv NW^{(-)}(\mathbf{v}),$$

$$W^{(\pm)}(v)=\theta(\pm\mathbf{nv})W(v),$$

$$W(v)=(\sqrt{\pi}\bar{v})^3\exp[-(v/\bar{v})^2], \tag{5}$$

$$\rho^{(0)}(\mathbf{v})=NW(v), \quad N=N_m+N_n.$$

The particle concentration (or number density) N_j is assumed to be z-independent.

The condition (5) does not contradict Eqs. (2) and is equivalent to choosing the initial conditions in the form

$$\rho_n^{(-)}(t_0)=\theta(-\mathbf{nv})\rho^{(0)}(\mathbf{v}),$$

$$\rho_n^{(+)}(t_0)=\rho_m^{(\pm)}(t_0)=0, \quad \rho_{mn}(t_0)=0, \tag{6}$$

where t_0 is the time at which the field is "turned on."

Note that conditions (5) and (6) are approximate. Actually, even when $\mathbf{E}=0$ there is a transition region near the surface where the N_j are z-dependent. However, here this circumstance is not of great significance.

Now we proceed as follows. The boundary and initial conditions (4) and (6) are incorporated directly into Eqs. (2) by introducing into the respective right-hand sides the following fictitious sources:

$$q_{ij}(x)=\delta(t-t_0)\rho_{ij}(t_0)+|\mathbf{nv}|\delta(z)\bar{\rho}_{ij}^{(+)}(x). \tag{7}$$

After this we can treat the equations in the same way as we would in the case of an unbounded medium. Using the Green's functions of the left-hand sides of (2),

$$f_m(x|x')=f(x|x')\exp[-\Gamma_m(t-t')],$$

$$f_n(x|x')=f(x|x')\equiv\theta(t-t')\delta(\mathbf{v}-\mathbf{v}')\times\delta(\mathbf{r}-\mathbf{r}'-\mathbf{v}(t-t')), \tag{8}$$

$$f_{mn}(x|x')=f(x|x')\exp[-\Gamma(t-t')],$$

we can rewrite the equations in integral form and by substitutions reduce them to equations for $\rho^{(\pm)}$ and $F^{(\pm)}$, where

$$\rho^{(\pm)}=\rho_n^{(\pm)}+\rho_m^{(\pm)}, \quad F^{(\pm)}=\rho_n^{(\pm)}-\rho_m^{(\pm)}. \tag{9}$$

We now go to the limit $t_0\to-\infty$, allow for (5), and solve the equation for $\rho^{(+)}$. As a result instead of Eqs. (2) we have a system of integral equations for $F^{(\pm)}(x)$:

$$F^{(\pm)}(x)=\tilde{F}^{(\pm)}(x)-\int \mathscr{K}(x|x')F^{(\pm)}(x')dx' \tag{10}$$

with the kernel

$$\mathscr{K}(x|x')=4\ \mathrm{Re}\sum_{\lambda\mu} V_\lambda^* V_\mu \hat{f}_m(\lambda\mu)\hat{f}_{mn}(\mu)$$

$$\equiv 4\ \mathrm{Re}\int f_m(x|y)V_{mn}^*(y)f_{mn}(y|x')V_{mn}(x')dy \tag{11}$$

and the absolute terms

$$\tilde{F}^{(-)}(x)=\theta(-\mathbf{nv})\rho^{(0)}(\mathbf{v}),$$

$$\tilde{F}^{(+)}(x)=\hat{f}_m q_F+\Gamma_m\hat{f}_m\hat{f}q-4\ \mathrm{Re}\,\hat{f}_m V_{mn}^*\hat{f}_{mn}q_{mn}. \tag{12}$$

Here

$$q=q_n+q_m, \quad q_F=q_n-q_m,$$

$$q_j=\delta(z)|\mathbf{n}\cdot\mathbf{v}|\sum_k \hat{\mu}_{jk}\rho_k^{(-)}, \tag{13}$$

$$q_{mn}=\delta(z)|\mathbf{n}\cdot\mathbf{v}|\hat{\mu}\rho_{mn}^{(-)},$$

and the following notation has been introduced:

$$f_m(\lambda\mu\cdots)=f(x|x')\exp[-\Gamma_m(\lambda\mu\cdots)(t-t')],$$

$$f_{mn}(\lambda\mu\nu\cdots)=f(x|x')\exp[-\Gamma(\lambda\mu\nu\cdots)(t-t')],$$

$$\Gamma_m(\lambda\mu\cdots)=\Gamma_m+i\bar{\omega}_{\lambda\mu\cdots}, \tag{14}$$

$$\Gamma(\lambda\mu\nu\cdots)=\Gamma-i\bar{\omega}_{\lambda\mu\nu\cdots},$$

$$\bar{\omega}_{\lambda\mu\nu\cdots}=\bar{\omega}_\lambda-\bar{\omega}_\mu+\bar{\omega}_\nu-\cdots, \quad \bar{\omega}_\lambda=\Omega_\lambda-\mathbf{k}_\lambda\mathbf{v}.$$

Above and in what follows we use the following symbolic notation:

$$\hat{f}\varphi\equiv\int f(x|x')\varphi(x')dx',$$

$$\hat{\mu}\varphi\equiv\int \mu(\mathbf{v}|\mathbf{v}')\frac{|\mathbf{nv}'|}{|\mathbf{nv}|}\varphi(\mathbf{v}')d^3v'. \tag{15}$$

The integral sign stands for integration within infinite limits in all the variables $x\equiv(\mathbf{r},\mathbf{v},t)$.

If the solutions of Eqs. (10) have been found, the ρ_{ij} can be calculated using the following formulas:

$$\rho_{ij}=\rho_{ij}^{(+)}+\rho_{ij}^{(-)},\ \ \rho_j=\rho/2-b_jF,\ \ b_m=-b_n=1/2,$$

$$\rho^{(-)}=NW^{(-)},\ \ \rho^{(+)}=\hat{f}q, \tag{16}$$

$$\rho_{mn}^{(-)}=-i\hat{f}_{mn}V_{mn}F^{(-)},\ \ \rho_{mn}^{(+)}=\hat{f}_{mn}q_{mn}-i\hat{f}_{mn}V_{mn}F^{(+)}.$$

Equations (10) and formulas (16) provide a solution to the problem in the steady state ($t\to\infty$).

The above procedure (which is known as the Green's function method[12] simplifies the solution of such problems considerably. It can easily be generalized to the case of multilevel particles, the presence of collisions in the gas, and more general initial and boundary conditions. All modifications in this case are reduced to the emergence of functions more complicated than those specified in (8). If we were to proceed in the usual way, i.e., by solving the boundary value problem for system (2) directly, the exceptionally cumbersome intermediate expressions would make it practically impossible to arrive at a solution without simplifying assumptions.

For an arbitrary field, the solution of Eqs. (10) can be obtained only by successive approximations. Here we limit ourselves to the first iteration and retain in $F^{(\pm)}$ only the corrections for saturation that are quadratic in field strength, $\sim V_\lambda^* V_\mu$. As a result, for $F=F^{(+)}+F^{(-)}$ we obtain

$$F=F_0-\frac{4N}{\Gamma\Gamma_m}\mathrm{Re}\sum_{\lambda\mu} V_\lambda^* V_\mu F_{\lambda\mu},$$

$$F_0=NW-2N_mW^{(+)}\exp(-\tau\Gamma_m),\quad \tau=z/|\mathbf{nv}|, \tag{17}$$

$$F_{\lambda\mu}=\bar{F}_{\lambda\mu}-\tilde{F}_{\lambda\mu}\ \exp(-i\bar{\omega}_{\lambda\mu}\tau)+\sum_{s=1}^{3} F_{\lambda\mu}^{(s)}$$

$$\times\exp[-\gamma_s(\lambda\mu)\tau].$$

Here

$$\bar{F}_{\lambda\mu}=W\mathscr{L}_m(\lambda\mu)\mathscr{L}(\mu),$$

$$\tilde{F}_{\lambda\mu}=\sum_{jk} Y_{jk}(\lambda\mu)b_k, \tag{18}$$

$$Y_{jk}(\lambda\mu)=\hat{\mu}_{jk}\mathscr{L}_m(\lambda\mu)\mathscr{L}(\mu)W^{(-)}.$$

In (17) and (18) we have assumed that

$$\sum_k \hat{\mu}_{jk}\rho^{(0)}a_k\simeq N_jW^{(+)},\quad a_m=0,\quad a_n=1, \tag{19}$$

and introduced the following notation:

$$\mathscr{L}_m(\lambda\mu\cdots)=\frac{\Gamma_m}{\Gamma_m(\lambda\mu\cdots)},$$

$$\mathscr{L}(\lambda\mu\nu\cdots)=\frac{\Gamma}{\Gamma(\lambda\mu\nu\cdots)}. \tag{20}$$

Correspondingly, according to (16), for ρ and ρ_j we have

$$\rho=NW+\frac{4N}{\Gamma\Gamma_m}\mathrm{Re}\sum_{\lambda\mu} V_\lambda^* V_\mu \rho_{\lambda\mu},$$

$$\rho_j=\rho_{j0}+\frac{2N}{\Gamma\Gamma_m}\mathrm{Re}\sum_{\lambda\mu} V_\lambda^* V_\mu(\rho_{\lambda\mu}+c_jF_{\lambda\mu}),$$

$$\rho_{n0}=NW-\rho_{m0},\quad \rho_{m0}=N_mW^{(+)}\exp(-\tau\Gamma_m), \tag{21}$$

$$\rho_{\lambda\mu}=\tilde{F}_{\lambda\mu}\exp(-i\bar{\omega}_{\lambda\mu}\tau),\quad c_m=-c_n=1.$$

Finally, for ρ_{mn} we obtain

$$\rho_{mn}=-i\frac{N}{\Gamma}\sum_\lambda V_\lambda\left\{r_\lambda-\frac{2}{\Gamma\Gamma_m}\sum_{\mu,\nu} V_\mu^* V_\nu r_{\lambda\mu\nu}\right\},$$

$$r_\lambda=\bar{r}_\lambda+\sum_{s=1}^{2} r_\lambda^{(s)}\exp[-\gamma_s(\lambda)\tau], \tag{22}$$

$$r_{\lambda\mu\nu}=\bar{r}_{\lambda\mu\nu}-\tilde{r}_{\lambda\mu\nu}\exp(-i\bar{\omega}_{\mu\nu}\tau)+\sum_{s=1}^{5} r_{\lambda\mu\nu}^{(s)}\exp$$

$$[-\gamma_s(\lambda\mu\nu)\tau],$$

where

$$\bar{r}_\lambda=W\mathscr{L}(\lambda),$$

$$\bar{r}_{\lambda\mu\nu}=W\mathscr{L}(\lambda\mu\nu)\mathscr{L}_m(\mu\nu)[\mathscr{L}(\nu)+\mathscr{L}^*(\mu)], \tag{23}$$

$$\tilde{r}_{\lambda\mu\nu}=\mathscr{L}(\lambda)\sum_{jk}[Y_{jk}(\mu\nu)+Y_{jk}^*(\nu\mu)]b_k.$$

The explicit form of the resonance terms $F_{\lambda\mu}^{(s)}$, $r_\lambda^{(s)}$, and $r_{\lambda\mu\nu}^{(s)}$, with the corresponding exponents $\gamma_s(\lambda\mu)$, $\gamma_s(\lambda)$, and $\gamma_s(\lambda\mu\nu)$ in (17) and (22) are given in the Appendix.

The macroscopic polarization vector of the medium, $\mathbf{P}=\langle\mathrm{Tr}(\hat{d}\hat{\rho})\rangle$, is

$$\mathbf{P}(\mathbf{r},t)=\frac{2}{\Gamma}\ N\mathrm{Re}\ \sum_\lambda i\mathbf{d}_{mn}G_\lambda\mathscr{P}_\lambda\exp(-i\omega_\lambda t+i\mathbf{k}_\lambda\mathbf{r}). \tag{24}$$

Here

$$\mathscr{P}_\lambda=p_\lambda-\frac{2}{\Gamma\Gamma_m}\sum_{\mu\nu} V_\mu^* V_\nu\ p_{\lambda\mu\nu},$$

$$p_\lambda=\bar{p}_\lambda+\sum_{s=1}^{2} p_\lambda^{(s)},p_{\lambda\mu\nu}=\bar{p}_{\lambda\mu\nu}-\tilde{p}_{\lambda\mu\nu}+\sum_{s=1}^{5} p_{\lambda\mu\nu}^{(s)},$$

$$\bar{p}_\lambda=\langle\bar{r}_\lambda\rangle,\quad p_\lambda^{(s)}=\langle r_\lambda^{(s)}\exp[-\gamma_s(\lambda)\tau]\rangle, \tag{25}$$

$$\bar{p}_{\lambda\mu\nu}=\langle\bar{r}_{\lambda\mu\nu}\rangle,\quad \tilde{p}_{\lambda\mu\nu}=\langle\tilde{r}_{\lambda\mu\nu}\ \exp[-i\bar{\omega}_{\mu\nu}\tau]\rangle,$$

$$p_{\lambda\mu\nu}^{(s)}=\langle r_{\lambda\mu\nu}^{(s)}\ \exp[-\gamma_s(\lambda\mu\nu)\tau]\rangle.$$

The quantity $\mathscr{P}_\lambda$ describes the spectral and temporal properties of the medium at the frequency of the λ-component of the field. The angular brackets stand for integration over velocities.

To within a constant factor, the quantity Re $\mathscr{P}_\lambda$ averaged over rapid oscillations is the absorption coefficient of the gas at the frequency ω_λ and describes, as a function of $\Omega_\lambda=\omega_\lambda-\omega_{mn}$, the spectral absorption profile at this frequency at a distance z from the surface. Correspondingly, Im $\mathscr{P}_\lambda$ is a correction to the profile of the refractive index of the medium. Theoretically, these quantities and their values averaged over the measurement range (i.e., over z) can be evaluated experimentally.

Now let us discuss the results. If in (25) we retain only the terms $\bar{p}_\lambda$ and $\bar{p}_{\lambda\mu\nu}$, we arrive at the solution of the "bulk" problem (unbounded gas):

$$\bar{\mathscr{P}}_\lambda=\bar{p}_\lambda-\frac{2}{\Gamma\Gamma_m}\sum_{\mu\nu} V_\mu^* V_\nu \bar{p}_{\lambda\mu\nu},$$

$$\bar{p}_\lambda=\langle\mathscr{L}(\lambda)W\rangle, \tag{26}$$

$$\bar{p}_{\lambda\mu\nu}=\langle\mathscr{L}(\lambda\mu\nu)\mathscr{L}_m(\mu\nu)[\mathscr{L}(\nu)+\mathscr{L}^*(\mu)]W\rangle.$$

For $\Gamma\ll k\bar{v}$ the linear term Re $\bar{p}_\lambda$ describes a Doppler profile with a width $k\bar{v}$, and the nonlinear terms $\bar{p}_{\lambda\mu\nu}$ contain narrow intra-Doppler resonances (IDR) with widths Γ, Γ_m, and $|\Gamma\pm\Gamma_m|$.

The terms $p_\lambda^{(s)}$ and $p_{\lambda\mu\nu}^{(s)}$ in (25), which decay as z increases, describe the development of coherent polarization in a particle after the particle has collided with the surface. Terms of this type, as is known,[4–7] are responsible for the emergence of IDR in selective specular reflection spectra. For $z>l_p$ all terms of this type essentially vanish from (25). Here and in what follows $l_p\sim\bar{v}/\Gamma$ is the characteristic development time for ρ_{mn}.

The third group of terms in (25) are the undamped terms $\tilde{p}_{\lambda\mu\nu}$. Their appearance is caused by the scattering of particles at the surface, and their undamped nature is related to conservation of the number of particles in the system of levels n and m. Of course, if we allow for collisions in the gas, these terms decay as z increases with $z>l$. However, in the surface layer $0\leqslant z\lesssim l$ their amplitudes either remain constant or periodically change sign with variation of z. Spectral structures of this type were previously unknown.

When $z\gg l_p$, only the terms $\bar{\mathscr{P}}_\lambda$ and $\tilde{p}_{\lambda\mu\nu}$ remain in (25):

$$\mathscr{P}_\lambda=\bar{\mathscr{P}}_\lambda+\frac{2}{\Gamma\Gamma_m}\sum_{\mu\nu} V_\mu^* V_\nu \tilde{p}_{\lambda\mu\nu},$$

$$\tilde{p}_{\lambda\mu\nu}=\sum_j [\tilde{Y}_{jm}(\lambda\mu\nu)-\tilde{Y}_{jn}(\lambda\mu\nu)],$$

$$\tilde{Y}_{jk}(\lambda\mu\nu)=\langle\mathscr{L}(\lambda)\exp\{-i\tilde{\omega}_{\mu\nu}\tau\}\mathscr{L}(\lambda\mu\nu)\hat{\mu}_{jk}A_m(\mu\nu)\rangle,$$

$$A_m(\mu\nu)=\mathscr{L}_m(\mu\nu)[\mathscr{L}(\nu)+\mathscr{L}^*(\mu)]W^{(-)}. \tag{27}$$

Generally, the functions $\tilde{Y}_{jk}(\Omega_\lambda)$ contain IDR whose widths are determined by Γ and Γ_m and the widths of the kernels $\mu_{jk}(\mathbf{v}|\mathbf{v}')$.

When $z\ll l+p$ the resonance terms in (25) are combined and the expression for $\mathscr{P}_\lambda$ assumes a fairly simple form:

$$\mathscr{P}_\lambda\sim\langle(1+\hat{\mu})\mathscr{L}(\lambda)W^{(-)}\rangle-\frac{2}{\Gamma\Gamma_m}\sum_{\mu\nu} V_\mu^* V_\nu p_{\lambda\mu\nu},$$

$$p_{\lambda\mu\nu}=\langle(1+\hat{\mu})\mathscr{L}(\lambda\mu\nu)\mathscr{L}_m(\mu\nu)[\mathscr{L}(\nu)+\mathscr{L}^*(\mu)]W^{(-)}\rangle. \tag{28}$$

In structure this expression (at $\hat{\mu}=0$) is similar to (26). There is, however, an important difference: Eq. (26) contains "total" convolutions $\langle W\cdots\rangle$ over the entire velocity space, but (28) contains convolutions over the half-space $\mathbf{n}\cdot\mathbf{v}\leqslant 0$. The presence of "incoming" terms ($\hat{\mu}\neq 0$) in this respect changes nothing: in addition to $\langle W^{(-)}\cdots\rangle$ there appear convolutions $\langle W^{(+)}\cdots\rangle$. Generally, the sum of such "half-convolutions" is not equal to the "total" convolution, i.e., the terms of the type $\langle W^{(+)}\cdots\rangle$ and $\langle W^{(-)}\cdots\rangle$ enter into (28) in an essentially different manner.

A similar situation is observed in the entire region $z\lesssim l$. This reflects the fact that the distribution function $\rho_{ij}(\mathbf{v})$ exhibits a discontinuity in the surface region: it contains "steps" $\propto\theta(\pm\mathbf{n}\cdot\mathbf{v})$. This is especially evident from the general expressions (17)–(23) and (A1)–(A3). The result is formation of nonlinear resonances of a special type.

It appears that convolutions of the type $\langle(\mathscr{L})^{s+1}W^{(\pm)}\rangle$ ($s\geqslant 1$), which are nonlinear in the Lorentzians $\mathscr{L}$ and appear in $p_{\lambda\mu\nu}$, may contain, as functions of Ω_λ, narrow resonances with widths of order Γ. A characteristic feature of such resonances is that they may even appear when there is only one traveling monochromatic wave (the saturation "boundary effect," or SBE), which constitutes a nontrivial result from the standpoint of the traditional nonlinear spectroscopy of gases. According to the latter, at least two monochromatic fields are required to excite IDR in a gas with nondegenerate energy levels.[12–15]

Nonlinear resonances excited in spectra by a single monochromatic wave can exist in the entire surface region $0\leqslant z\lesssim l$. In addition to emerging by means of the SBE mechanism mentioned earlier, they also appear because the scattering of particles by a surface is different in different quantum states.

As an illustration of what has just been said, we discuss two examples for the case where there is only one wave $E(\mathbf{r},t)\propto\exp\{-i\omega t+i\mathbf{k}\cdot\mathbf{r}\}$ traveling through the gas at right angles to the surface.

In the near zone $z\ll l_p$, the expression for Re $\mathscr{P}(\Omega)$, calculated via (28) for the case where $\mu(\mathbf{v}|\mathbf{v}')=0$ and $\Gamma\ll k\bar{v}$ has the following form (we drop the subscript λ and put $\Omega=\omega-\omega_{mn}$):

$$\text{Re}\,\mathscr{P}(\Omega)\sim A'(\Omega)-\frac{\kappa}{2}\left[A'(\Omega)-\frac{\varepsilon}{\pi}\frac{\Gamma\Omega}{(\Gamma^2+\Omega^2)}\right]. \tag{29}$$

Here $\varepsilon=\text{sgn}(\mathbf{nk})$, and $A'(\Omega)$ is a "semi-Doppler" curve that has a width of approximately $\frac{1}{2}k\bar{v}$ and experiences a sharp drop with a slope $1/\Gamma$ in the region where $\Omega=0$. The last term in the square brackets on the right-hand side of (29) represents the nonlinear resonance caused by SBE. In the case at hand it is of the dispersion type. When $\mu(\mathbf{v}|\mathbf{v}')\neq 0$ the shape of the resonance may change, but the resonance itself will not disappear.

In the far zone $z\gg l_p$, from (27) in the same approximation we obtain ($l_p\ll l$)

$$\text{Re}\,\mathscr{P}(\Omega)\sim\left(1-\frac{\kappa}{2}\right)\exp\left[-\left(\frac{\Omega}{k\bar{v}}\right)^2\right]-\frac{\kappa}{2}\tilde{Y}(\Omega),$$

$$\tilde{Y}=\sum_{jk}\tilde{Y}_{jk}b_k,\quad \tilde{Y}_{jk}=\frac{k\bar{v}}{\sqrt{\pi}\Gamma}\langle L\hat{\mu}_{jk}LW^{(-)}\rangle, \tag{30}$$

$$L=\text{Re}\,\mathscr{L},\quad \mathscr{L}=\Gamma[\Gamma-i(\Omega-\mathbf{kv})]^{-1},$$

$$\kappa=4|G|^2\Gamma\Gamma_m.$$

The first term in (30) describes the ordinary Doppler profile of the gas in a single traveling wave. The function $\bar{Y}(\Omega)$ contains nonlinear resonances caused by scattering on the surface. It can be demonstrated that if all the kernels are velocity-dependent,

$$\mu_{jk}(\mathbf{v}|\mathbf{v}')=\bar{\mu}(\mathbf{v}|\mathbf{v}')\,\eta_{jk}(\mathbf{v}'), \tag{31}$$

then $\bar{Y}(\Omega)\equiv 0$. Such a situation, however, is not typical and therefore, generally, $\bar{Y}(\Omega)\neq 0$. If, for example, by the elastic channels, $n\to n$ and $m\to m$, the scattering is of the mirror type, by the quenching channel $m\to n$ the scattering is of the diffuse type, and the excitation channel $n\to m$ is inactive, then (30) acquires the form

$$\mathrm{Re}\,\mathscr{P}(\Omega)\left\{1-\frac{\kappa}{2}\left[1+\frac{\eta_{mn}}{4}\frac{\Gamma^2}{\Gamma^2+\Omega^2}\right]\right\}\exp\left\{-\left(\frac{\Omega}{k\bar{v}}\right)^2\right\}, \tag{32}$$

where η_{nm} is the quenching probability $(0\leqslant\eta_{nm}\leqslant 1)$.

In appearance (32) is similar to the known expression for the Doppler profile with a Lamb dip in the field of a standing wave (see, e.g., Ref. 15, p. 76). However, in the case at hand the nature of the narrow dip in (32) is different, and the dip manifests itself in a single traveling wave. Actually, the fact that the scattering kernels are not similar in the sense mentioned earlier is of secondary importance (the necessary condition). The physical reason for the appearance of such a resonance is the reversal of the sign of velocity when particles are reflected from the surface (the sign of the Doppler shift $\mathbf{k}\cdot\mathbf{v}$ changes). This is clear from the expression (30) for the function $\bar{Y}_{jk}(\Omega)$, which is the convolution of the Maxwellian distribution and the product of two Lorentzians with different signs of the Doppler shifts with respect to the projection of velocity on the direction of $\mathbf{n}$.

We have examined the problem with two levels, but similar results can be arrived at for the multilevel model of particles. If in the process the radiation involves only two levels, m and n, and the presence of a ground state is taken into account, then all the changes in (17)–(25) amount to an increase in the number of resonance terms and a redefinition of the coefficients b_j (their sum is zero).

Thus, even a brief analysis of the general results of the solution of a simple model problem points to a complex resonant structure of the nonlinear polarization and the nonlinear spectrum of a gas in the surface region. In fact, there emerges a new class of nonlinear spectroscopic resonances that have no analogs in the ordinary spectroscopy of gases: namely, nonlinear surface resonances, or NSR. The formation mechanisms for some types of NSR are quite unusual (NSR in a traveling wave or "undamped" NSR), while the known mechanisms of nonlinearity responsible for the formation of "bulk" NSR (the saturation effect, the nonlinear interference of states, and the like) manifest themselves in the spectra near the surface differently than inside the volume of the gas.

Financial support for this work was provided by the Russian Fund for Fundamental Research (Grant No. 93-02-03448).

APPENDIX: VALUES OF RESONANCE COEFFICIENTS AND EXPONENTS IN EQS. (17) AND (22)

The coefficients $\gamma_s(\lambda\mu)$ and $F^{(s)}_{\lambda\mu}$ in Eq. (17) are:

$$\begin{aligned}
&\gamma_1(\lambda\mu)=\Gamma_m,\quad \gamma_2(\lambda\mu)=\Gamma_m(\lambda\mu),\\
&\gamma_3(\lambda\mu)=\Gamma(\mu),\\
&F^{(1)}_{\lambda\mu}=2\varepsilon_m\Gamma\Gamma_m W^{(+)}[i\bar{\omega}_{\lambda\mu}(\Gamma-\Gamma_m+i\bar{\omega}_\mu)]^{-1}, \qquad \text{(A1)}\\
&F^{(2)}_{\lambda\mu}=(\Gamma_m-\Gamma+i\bar{\omega}_\lambda)^{-1}\left\{2\sum_k Y_{mk}(\lambda\mu)b_k\right.\\
&\quad-\hat{\mu}\mathscr{L}(\mu)W^{(-)}+\varepsilon_n\Gamma W^{(+)}/\Gamma_m(\lambda\mu)+i\varepsilon_m\Gamma[1\\
&\quad\left.+\mathscr{L}_m(\lambda\mu)]W^{(+)}/\bar{\omega}_{\lambda\mu}\right\},\\
&F^{(3)}_{\lambda\mu}=\Gamma_m(\Gamma_m-\Gamma_m+i\bar{\omega}_\lambda)^{-1}\{\varepsilon_n\mathscr{L}(\lambda)W^{(+)}\\
&\quad-\hat{\mu}\mathscr{L}(\mu)W^{(-)}+\varepsilon_m\Gamma W^{(+)}[1+\Gamma_m/\Gamma(\mu)](\Gamma_m\\
&\quad-\Gamma+i\bar{\omega}_\mu)^{-1}\}.
\end{aligned}$$

The coefficients $\gamma_s(\lambda)$ and $r^{(s)}_\lambda$ in Eq. (22) are:

$$\begin{aligned}
&\gamma_1(\lambda)=\Gamma_m,\quad \gamma_2(\lambda)=\Gamma(\lambda),\\
&r^{(1)}_\lambda=2\varepsilon_m\Gamma W^{(+)}\Gamma_m-\Gamma+i\bar{\omega}_\lambda, \qquad \text{(A2)}\\
&r^{(2)}_\lambda=\hat{\mu}\mathscr{L}(\lambda)W^{(-)}-\varepsilon_n\mathscr{L}(\lambda)W^{(+)}+\varepsilon_m\Gamma W^{(+)}\Gamma-\Gamma_m\\
&\quad+i\bar{\omega}_\lambda[1+\Gamma_m\Gamma(\lambda)].
\end{aligned}$$

The coefficients $\gamma_s(\lambda\mu\nu)$ and $r^{(s)}_{\lambda\mu\nu}$ in Eq. (22) are:

$$\begin{aligned}
&\gamma_1(\lambda\mu\nu)=\Gamma_m,\quad \gamma_2(\lambda\mu\nu)=\Gamma_m(\mu\nu),\\
&\gamma_3(\lambda\mu\nu)=\Gamma(\nu),\quad \gamma_4(\lambda\mu\nu)=\Gamma^*(\mu),\\
&\gamma_5(\lambda\mu\nu)=\Gamma(\lambda\mu\nu),\\
&r^{(1)}_{\lambda\mu\nu}=\Gamma(F^{(1)}_{\mu\nu}+F^{(1)*}_{\nu\mu})\Gamma(\lambda\mu\nu)-\Gamma_m,\quad r^{(2)}_{\lambda\mu\nu}=\Gamma(F^{(2)}_{\mu\nu}\\
&\quad+F^{(2)*}_{\nu\mu})\Gamma(\lambda)-\Gamma_m, \qquad \text{(A3)}\\
&r^{(3)}_{\lambda\mu\nu}=i\Gamma F^{(3)}_{\mu\nu}/\bar{\omega}_{\lambda\mu},\quad r^{(4)}_{\lambda\mu\nu}=i\Gamma F^{(3)*}_{\nu\mu}/\bar{\omega}_\lambda+\bar{\omega}_\nu,\\
&r^{(5)}_{\lambda\mu\nu}=\hat{\mu}\bar{r}_{\lambda\mu\nu}-\bar{r}_{\lambda\mu\nu}+\tilde{r}_{\lambda\mu\nu}-\sum_{s=1}^{4}r^{(s)}_{\lambda\mu\nu}.
\end{aligned}$$

The notation in Eqs. (A1)–(A3) is the same as in the main text, and $\varepsilon_j=N_j/N$.

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Translated by Eugene Yankovsky