# Surface-polariton absorption and scattering spectra in a gas bounded by a solid

V. G. Bordo

*Institute of General Physics, Academy of Sciences of the USSR*

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Theoretical absorption and scattering spectra are derived for surface polaritons propagating along an interface between a solid and a gas. The polariton frequency is assumed to be close to the frequency of an atomic transition in the gas. It is assumed that the spatial dispersion resulting from the nonuniformity of the polariton field is important. There may be a scattering of the polariton by a gas atom, accompanied by the emission of a photon. The polariton absorption and scattering lines have a distinctive shape, which is determined by spatial dispersion and also by the scattering of the gas atoms by the solid surface.

## 1. INTRODUCTION

Surface polaritons are electromagnetic waves propagating along an interface between media.[1] The field of a surface polariton falls off rapidly with distance into either medium, so these waves are sensitive to the properties of the interface and to processes occurring near the interface.

If one of the media is a gas, one might expect to see consequences of collisions of gas atoms or molecules with the solid surface in the spectra of the surface polaritons. It was thus shown theoretically in Refs. 2 and 3 that the absorption coefficient for an intense surface wave at resonance with a molecular transition depends strongly on the probability for a vibrational relaxation of a molecule on the solid surface. It was assumed in those papers that the time $\tau$ taken by the atomic particles to cross the region in which the polariton field is localized is significantly longer than the transverse relaxation time $T_2$. On the other hand, it is easy to arrange the condition $\tau \lesssim T_2$. For example, the depth to which the field of a visible-range surface polariton propagating along an aluminum surface penetrates into vacuum is some tenths of a micron.[4] If the thermal velocity of the atoms is $V_T \sim 10^4$ cm/s, and if the relaxation time is $T_2 \sim 10^{-7}$ s, this condition holds by a wide margin. In this situation, the spatial dispersion which stems from the nonuniformity of the polariton field becomes important.

A corresponding situation prevails during the selective reflection of light from an interface between a transparent insulator and a gas. Several interesting effects occur as a result. In particular, when light is incident normally on the interface, the reflection spectrum exhibits a sub-Doppler structure, which is a consequence of collisions of gas atoms with the surface.[5-8] In the case of total internal reflection, the reflection coefficient becomes sensitive to the behavior of the atoms in a thin surface region.[9] Intense pump light saturates the atomic transitions in the gas, as can be seen from the reflection of a probe beam, in the case of either normal incidence[10] or total internal reflection.[11] The saturation effect is also seen in a spectral broadening of the selective reflection of intense light.[12] The width of the reflection line increases with increasing angle of incidence of the light.[13] A sub-Doppler structure is observed in the fluorescence spectrum detected on the side of the insulator at an angle above the critical angle.[14]

Underlying these effects is a nonlocal coupling of the polarization of the gas with the electromagnetic field. The nonlocal nature of this coupling is seen in the circumstance that the polarization of the atoms scattered by the solid surface is time-varying and is determined by the boundary conditions at the surface. In a crude approximation we could assume that some of the atoms are specularly scattered by the surface, without a change in polarization, while the other atoms are adsorbed on the surface and then escape from the surface with a completely quenched polarization.[15] The behavior of the polarization differs for these two types of scattering; the differences may be seen in optical spectra.

In this paper we derive a theory for the spectra of surface-polariton absorption and scattering in a gas bounding a solid. We assume that the polariton frequency is close to the frequency of a transition between the ground state and an excited state of the gas atom, and we assume that the polariton intensity is too low to saturate the transition. We investigate the consequences of the scattering of atoms by the solid surface in the spectra.

## 2. ABSORPTION COEFFICIENT FOR SURFACE POLARITONS

We consider an interface between a solid, which occupies the half-space $z<0$, and a gas, which occupies the half-space $z>0$. We assume that the solid is isotropic and has a dielectric constant $\varepsilon_1(\omega) = \varepsilon_1'(\omega) + i\varepsilon_1''(\omega)$. We assume that the relation $|\varepsilon_1'(\omega)| \gg \varepsilon_1''(\omega)$ holds in the frequency ($\omega$) range under consideration, and we assume that the optical density of the gas is small in comparison with unity. The condition for the existence of surface polaritons at the interface is the inequality $\varepsilon_1'(\omega) \leqslant -1$. Only $p$-polarized surface polaritons can exist.[1] If the solid is a metal, this inequality holds at all frequencies below $\omega_p/2^{1/2}$, where $\omega_p$ is the plasma frequency.

Under these assumptions, the absorption coefficient for surface polaritons can be written approximately as

$$\alpha = \alpha_0 + \alpha_1,$$

where $\alpha_0$ is the absorption coefficient for surface polaritons at the vacuum-solid interface, and $\alpha_1$ is the contribution of the gas to the absorption. In calculating $\alpha_1$ we can assume that $\varepsilon_1(\omega)$ is real. The coefficient $\alpha_1$ can in turn be defined as

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$$\alpha_1 = \frac{\int\limits_0^\infty \overline{Q(z)}\,dz}{\int\limits_{-\infty}^\infty \overline{S_x(z)}\,dz}, \tag{1}$$

where $Q = \vec{\mathscr{E}}\,\partial\vec{\mathscr{P}}/\partial t$ is the power dissipated by the polariton field on the periodic change in the gas polarization $\vec{\mathscr{P}}$,

$$S = \frac{c}{4\pi}[\vec{\mathscr{E}}/\vec{\mathscr{H}}]$$

is the Poynting vector, the superior bar means an average over the period of the field, and the $x$ axis is oriented along the polariton propagation direction. The electric and magnetic fields $\vec{\mathscr{E}}$ and $\vec{\mathscr{H}}$ in (1) correspond to a solid-vacuum interface and can be written in the form[4]

$$\vec{\mathscr{E}}_i(\mathbf{r}, t) = {}^1/_2[\mathbf{s}\mathbf{k}_i]\frac{c}{\omega}E_i \exp(i\mathbf{k}_i\mathbf{r} - i\omega t) + \text{c.c.}$$

$$\vec{\mathscr{H}}_i(\mathbf{r}, t) = {}^1/_2\mathbf{s}_i\varepsilon_i E_i \exp(i\mathbf{k}_i\mathbf{r} - i\omega t) + \text{c.c.},$$

where $i = 1$ for the solid, $i = 2$ for the gas, $\mathbf{k}_1 = (q, 0, -i\varkappa_1)$, $\mathbf{k}_2 = (q, 0, i\varkappa_2)$, $\varepsilon_2 = 1$, and $\mathbf{s}$ is a unit vector along the $y$ axis. The wave vector of the surface polariton, $q$, is related to the frequency $\omega$ by the dispersion relation

$$q = \frac{\omega}{c}\left[\frac{\varepsilon_1(\omega)}{\varepsilon_1(\omega)+1}\right]^{1/2}. \tag{2}$$

The depths to which the fields penetrate into the media making contact are given by

$$\varkappa_i = \left(q^2 - \frac{\omega^2}{c^2}\varepsilon_i\right)^{1/2}, \qquad \operatorname{Re}\varkappa_i > 0.$$

We assume that the polariton propagation distance

$$L = (2\operatorname{Im} q)^{-1}$$

is significantly larger than the distance traveled by an atom over the relaxation time, so the spatial dispersion along the $x$ direction is negligible. In this case the steady-state polarization can be written

$$\vec{\mathscr{P}}(\mathbf{r}, t) = {}^1/_2\mathbf{P}(z)\exp(i\mathbf{k}_2\mathbf{r} - i\omega t) + \text{c.c.} \tag{3}$$

Making the necessary substitutions in (1), and carrying out some straightforward manipulations, we find[16]

$$\alpha_1 = 8\pi q\varkappa_2\frac{\varepsilon_1}{\varepsilon_1+1}\frac{1}{E_{2z}}\int\limits_0^\infty \exp(-2\varkappa_2 z)\operatorname{Im}P_z(z)\,dz, \tag{4}$$

where $\mathbf{E}_2 = E_2(c/\omega)[\mathbf{s}\,\mathbf{k}_2]$. As in the case of total internal reflection from an interface between a transparent insulator and a gas,[13] the integral in (4) determines the contribution of the gas to the spectrum of frustrated total internal reflection in the Kretschmann geometry.

To express the polarization of the gas in terms of microscopic characteristics, we assume that the polariton frequency is close to the frequency ($\omega_0$) of the transition between the ground state $|1\rangle$ and the excited state $|2\rangle$ state of the atom, and we assume that the interaction of the field with other states can be ignored. By definition we have then

$$\vec{\mathscr{P}}(\mathbf{r}, t) = N\langle\rho_{21}(\mathbf{r}, t)\mathbf{d}_{12}\rangle + \text{c.c.} \tag{5}$$

where $N$ is the number density of atoms in the gas, $\rho$ is the density matrix of the atom, $\mathbf{d}$ is the dipole-moment operator, and the angle brackets mean an average over the ensemble of atoms.

## 3. SCATTERING OF SURFACE POLARITONS IN THE GAS

Surface polaritons are, as we know, nonradiating oscillation modes which are localized near the surface. The dispersion curve $\omega(q)$ for surface polaritons, determined by relation (2), lies to the right of the lightlike line $\nu = ck_x$, which corresponds to propagation of the light along the surface. It never intersects this line. Consequently, there is no point on the curve at which energy and momentum can be simultaneously conserved during the emission of a photon:

$$\hbar\omega = \hbar\nu, \quad q = k_x. \tag{6}$$

This restriction is lifted if, for example, the surface has irregularities,[17] if a periodic lattice is formed on the surface, or if the refractive index of the medium depends on the coordinates, as it does when fluctuations are taken into account.[18] In this case momentum is conserved in events in which surface polaritons are converted into photons, within a wave vector characterizing the irregularity or periodicity of the surface. If the solid is bordered by a gas, the conservation laws can be satisfied if a gas atom participates in the process by which a surface polariton is converted into a photon.

Let us examine the process by which a surface polariton is scattered by a moving gas atom, and a photon is created as a result. The conservation laws for the scattering event are

$$\hbar\mathbf{q} + m\mathbf{V} = \hbar\mathbf{k} + m\mathbf{V}', \tag{7}$$

$$\hbar\omega + {}^1/_2 mV^2 = \hbar\nu + {}^1/_2 mV'^2,$$

where $\mathbf{V}$ and $\mathbf{V}'$ are the velocities of the atom before and after the scattering, and $m$ is the mass of the atom. From (7) we find an expression for the frequency of the emitted photon:

$$\nu = \omega - (\mathbf{q} - \mathbf{k})\mathbf{V} - \frac{\hbar}{2m}(q^2 + k^2 - 2qk\cos\vartheta), \tag{8}$$

where $\vartheta$ is the angle between the vectors $\mathbf{q}$ and $\mathbf{k}$. The second term on the right side of (8) describes the frequency change due to the Doppler effect, and the third describes the photon-frequency decrease due to recoil. Estimates show that the recoil energy is negligible in comparison with the first two terms in (8).

To calculate the spectral power density of the scattered light, we note that in the classical description the scattering results from oscillations of the atomic dipole moment induced by the field of the surface polariton. In the wave zone the field of the scattered wave is

$$\vec{\mathscr{E}}_s(\mathbf{R}, t) = -\frac{\omega^2}{c^2R^3}[[\mathbf{d}(t)\mathbf{R}]\mathbf{R}]. \tag{9}$$

(Strictly speaking, the electromagnetic field reflected from the interface contributes to $\vec{\mathscr{E}}_s$ (Ref. 19). For simplicity, however, we will assume that the reflection can be ignored.) The field $\vec{\mathscr{E}}_s$ can be resolved into positive- and negative-frequency parts:

$$\vec{\mathscr{E}}_s = \vec{\mathscr{E}}_s^{(+)} + \vec{\mathscr{E}}_s^{(-)}, \tag{10}$$

where $\vec{\mathscr{E}}_s^{(+)} \sim \exp(-i\omega t)$. The power spectrum of the scattering light is expressed in terms of the correlation functions

$$G_{jk}(\mathbf{R}, t; \mathbf{R}', t') = \langle \mathscr{E}_{sj}^{(-)}(\mathbf{R}, t) \mathscr{E}_{sk}^{(+)}(\mathbf{R}', t') \rangle$$

in the following way:

$$I(\nu, \mathbf{R}) = \int_{-\infty}^{\infty} e^{-i\nu\tau} \sum_j G_{jj}(\mathbf{R}, t; \mathbf{R}, t+\tau)\, d\tau.$$

In a quantum-mechanical description of the scattering, the vector **d** is replaced by the dipole-moment operator of the atom in the Heisenberg representation, and the correlation functions are expressed in terms of the atomic density matrix $\rho$:

$$G_{jk}(\mathbf{R}, t; \mathbf{R}', t') = \mathrm{Sp}[\rho \hat{\mathscr{E}}_{sj}^{(-)}(\mathbf{R}, t) \hat{\mathscr{E}}_{sk}^{(+)}(\mathbf{R}', t')]. \tag{11}$$

We introduce raising and lowering operators:

$$a^+ \equiv |2\rangle\langle 1|, \quad a \equiv |1\rangle\langle 2|.$$

The operator **d** can then be written as

$$\mathbf{d} = \mathbf{d}^{(+)} + \mathbf{d}^{(-)}, \tag{12}$$

where $\mathbf{d}^{(+)} = \mathbf{d}_{21} a^+$, $\mathbf{d}^{(-)} = [\mathbf{d}^{(+)}]^+$ and the superscript plus sign means the Hermitian adjoint. Using (9), (10), and (12), we find then

$$\hat{\mathscr{E}}_s^{(+)}(\mathbf{R}, t) = \mathbf{\Phi}(\mathbf{R})\, a(t),$$

where

$$\mathbf{\Phi}(\mathbf{R}) = -\frac{\omega^2}{c^2 R^3}[[\mathbf{d}_{12}\mathbf{R}]\mathbf{R}],$$

and $a(t)$ is the operator $a$ in the Heisenberg representation. The correlation function in (11) can now be written in the form

$$G_{jk}(\mathbf{R}, t; \mathbf{R}', t') = \Phi_j^*(\mathbf{R}) \Phi_k(\mathbf{R}') g(t, t'),$$

where $g(t,t') \equiv \langle a^+(t) a(t') \rangle$. The Fourier transform of the function $g(t, t+\tau)$ determines the power spectrum of the scattered field:[20]

$$I(\nu, \mathbf{R}, t) = |\mathbf{\Phi}(\mathbf{R})|^2 \tilde{g}(\nu, t), \tag{13}$$

where

$$\tilde{g}(\nu, t) = \int_{-\infty}^{\infty} e^{-i\nu\tau} g(t, t+\tau)\, d\tau.$$

According to the quantum regression theorem,[21] the two-time correlation function $g(t,t')$ can be expressed in terms of the one-time correlation function:

$$g(t, t') = Q_{21,11}(t', t) \langle a^+(t) \rangle + Q_{21,21}(t', t) \langle a^+(t)\, a(t) \rangle, \tag{14}$$

where the functions $Q_{21,ij}$ are defined by the equation

$$\rho_{21}(t') = \sum_{ij} Q_{21,ij}(t', t) \rho_{ij}(t). \tag{15}$$

Using

$$\langle a^+(t) \rangle = \rho_{12}(t), \quad \langle a^+(t)\, a(t) \rangle = \rho_{22}(t),$$

we can put (14) in the form

$$g(t, t') = \sum_i Q_{21,i1}(t', t) \rho_{i2}(t). \tag{16}$$

## 4. DENSITY MATRIX OF AN ATOM IN THE FIELD OF A SURFACE POLARITON

In the resonant approximation, the steady-state value of the matrix element $\rho_{21}$ can be written

$$\rho_{21}(\mathbf{r}, t) = \sigma_{21}(z) \exp[i(\mathbf{k}_2\mathbf{r} - \omega t - \psi)], \tag{17}$$

where the matrix $\sigma$ satisfies the system of equations

$$\begin{gathered} V_z \frac{d\sigma_{21}}{dz} + [\gamma + i(\Delta + \mathbf{k}_2\mathbf{V})]\sigma_{21} = \frac{i}{2}\Omega w, \\ V_z \frac{dw}{dz} + 2\gamma(w - w_e) = i\Omega(\sigma_{21} - \sigma_{12}) e^{-2\varkappa_2 z}. \end{gathered} \tag{18}$$

Here **V** is the velocity of the atom; $\Delta = \omega_0 - \omega$ is the detuning from resonance, $\Omega e^{-i\psi} = \mathbf{d}_{21}\mathbf{E}_2/\hbar$; $w = \sigma_{11} - \sigma_{22}$ is the difference in populations, $w_e$ is the equilibrium value of this difference, and we are assuming that collisions of atoms with each other can be ignored and that the rate of radiative decay of the excited state is $2\gamma$. For simplicity we set $w_e = 1$ at this point.

We are interested in the case in which the intensity of the polariton field is too low to saturate the atomic transition. Using a perturbation theory in the parameter $\Omega$ to solve system (18), we find the following equations in first order ($\mu \equiv \sigma_{21}$):

$$\begin{gathered} V_z \frac{d\mu^{(1)}}{dz} + [\gamma + i(\Delta + \mathbf{k}_2\mathbf{V})]\mu^{(1)} = \frac{i}{2}\Omega, \\ V_z \frac{dw^{(1)}}{dz} + 2\gamma w^{(1)} = 0. \end{gathered} \tag{19}$$

These equations have the general solutions

$$\begin{gathered} \mu^{(1)}(z) = i\frac{\Omega}{2\Gamma} + A \exp\left(-\frac{\Gamma}{V_z} z\right), \\ w^{(1)}(z) = B \exp\left(-\frac{2\gamma}{V_z} z\right), \end{gathered}$$

where $\Gamma = \gamma + i(\Delta + \mathbf{k}_2\mathbf{V})$, and the constants $A$ and $B$ are found from the boundary conditions.

Separate boundary conditions should be imposed for the atoms which are moving toward the surface, with negative velocity components $V_z < 0$, and for the atoms which are moving away from the surface, with $V_z > 0$. We label the corresponding solutions with minus and plus subscript. For atoms with $V_z < 0$ the following conditions must hold:

$$\mu^{(1)}(z) \exp(-\varkappa_2 z) \to 0, \quad w^{(1)}(z) \to 0 \quad \text{as} \quad z \to \infty.$$

These conditions correspond to values $A = B = 0$. We thus have

$$\mu_-^{(1)}(z) = i\frac{\Omega}{2\Gamma}, \quad w_-^{(1)} = 0. \tag{20}$$

Boundary conditions for the atoms with $V_z > 0$ are imposed on $z = 0$ and depend on the nature of the scattering of the atoms by the surface. The following is the simplest assumption regarding the scattering process, and is at the same time fairly realistic: An atom approaching the surface has a certain probability $\eta$ to be scattered in the specular direction. In this case there is no change in the quantum state or polarization of the atom, but there generally is a change in the phase of its state.[15] On the other hand, there is a probability $(1-\eta)$ that the atom will be adsorbed on the surface. The desorbed atoms (the diffusely scattered atoms) are in the ground state and have a Maxwellian velocity distribution. Their polarization has been completely quenched. We accordingly write a solution of Eqs. (19) in the form

$$\mu_+^{(1)}(z)=i\frac{\Omega}{2\Gamma}+\left[\mu_+^{(1)}(0)-i\frac{\Omega}{2\Gamma}\right]\exp\left(-\frac{\Gamma}{V_z}z\right), \tag{21}$$

where

$$\mu_+^{(1)}(0)=\mu_-^{(1)}(0)\exp(i\Delta\Phi)=i\frac{\Omega}{2\tilde{\Gamma}}\exp(i\Delta\Phi),$$

$\tilde{\Gamma}=\gamma+i(\Delta+\mathbf{k}_2^*\mathbf{V})$ for specular reflection, $\mu_+^{(1)}(0)=0$ for diffuse reflection, and $\Delta\Phi=\Phi_2-\Phi_1$, where $\Phi_1$ and $\Phi_2$ are the scattering phase shifts for the atoms in the ground and excited states, respectively.

In second-order perturbation theory, we restrict the discussion to the population difference. The equation for $w^{(2)}$,

$$V_z\frac{dw^{(2)}}{dz}+2\gamma w^{(2)}=-2\Omega\,\mathrm{Im}\,\mu^{(1)}\exp(-2\varkappa_2 z)$$

has the solutions

$$w_\pm^{(2)}(z)=\exp\left(-\frac{2\gamma}{V_z}z\right)\Bigg\{w_\pm^{(2)}(z_\pm)-\frac{2\Omega}{V_z}\int_{z_\pm}^{z}\exp\left[2\left(\frac{\gamma}{V_z}-\varkappa_2\right)z'\right]\mathrm{Im}\,\mu_\pm^{(1)}(z')dz'\Bigg\},$$

where

$$z_-=\infty,\ z_+=0,\ w_-^{(2)}(\infty)=0,\ w_+^{(2)}(0)=w_-^{(2)}(0)$$

for specular scattering, and $w_+^{(2)}(0)=0$ for diffuse scattering.

Expressions (20) and (21) describe the response of atoms which are moving toward and away from the surface, respectively, to the field of the surface polariton. In the former case the polariton field increases adiabatically for the moving atom. This situation corresponds to a local coupling between the atomic dipole moment and the field. In the latter case the external field for the atom changes suddenly at the time at which it leaves the surface. The dipole moment of an atom moving away from the surface is not in a steady state, and it cannot be expressed in terms of the field of the surface polariton in a local fashion. The nonlocal response of the atom is described by the second and third terms in (21). In the case $\gamma/V_z\gg\varkappa_2$, i.e., in the case in which the transit time of the atom through the region in which the polariton field is localized is much longer than the relaxation time, the contribution of these terms of the polariton absorption coefficient can be ignored. In this case we have $\mu_-^{(1)}=\mu_+^{(1)}$, and the absorption coefficient contains no information about the scattering of atoms by the surface.

Let us find an explicit expression for the parameter $\Delta\Phi$. Estimates show that the duration of the interaction of the atom with the surface potential during the scattering is much longer than the reciprocal of the transition frequency $\omega_0$. In this case the change in the phase of the state $|i\rangle$ as the result of specular scattering is, in the adiabatic approximation,[22]

$$\Phi_i=-\frac{1}{\hbar}\int_{-\infty}^{\infty}U_i[\mathbf{r}(t)]dt,$$

where $U_i(\mathbf{r})$ is the adsorption potential for an atom in state $|i\rangle$. The potentials $U_i$ depend on the distance from the atom to the surface and also on the position of the atom along the surface. In several cases, however, the latter dependence can be ignored. We assume for simplicity that the adsorption potentials depend on only the coordinate $z$. We can write

$$\Delta\Phi=\frac{2}{\hbar V_z}\int_{z_1}^{\infty}[U_1(z)-U_2(z)]dz,$$

where $z_1$ is the turning point for motion in the potential $U_1$. The position of $z_1$ depends on the velocity of the atom, but if the repulsive part of the potential falls off sufficiently rapidly toward the surface this dependence can be ignored.

## 5. ABSORPTION AND SCATTERING SPECTRA OF SURFACE POLARITONS

Let us calculate the absorption coefficient for surface polaritons. From (3), (5), and (17) we have

$$^1/_2\mathbf{P}(z)=N\langle\sigma_{21}(z)\mathbf{d}_{12}\rangle e^{-i\psi}. \tag{22}$$

We substitute solutions (20) and (21) into (22), and we then substitute the result into (4). The angle brackets in this case mean an average over the orientations and velocities of the atoms, which have a Maxwellian distribution:

$$f(V)=\pi^{-3/2}V_T^{-3}\exp\left(-\frac{V^2}{V_T^2}\right),$$

where $V_T$ is the most probable velocity of the atoms. The final result can be written

$$\alpha_1=8\pi q\frac{\varepsilon_1}{\varepsilon_1+1}\frac{N\langle|d_{12}^z|^2\rangle}{\hbar\omega_D}\,\mathrm{Im}\,(R+i\eta\tilde{\varkappa}_2 S), \tag{23}$$

where

$$R=\frac{1}{\pi}\int_0^\infty\frac{x\exp(-x^2)}{(\xi^2+x^2)^{1/2}}\ln\frac{\tilde{\varkappa}_2x+i(\xi^2+x^2)^{1/2}}{\tilde{\varkappa}_2x-i(\xi^2+x^2)^{1/2}}dx,$$

$$S=\frac{1}{\pi}\int_{-\infty}^{\infty}\int_0^\infty\frac{z\exp(i\beta/z)\exp(-x^2-z^2)}{(\xi+i\tilde{q}x+\tilde{\varkappa}_2z)^2}dz\,dx$$

and where we have introduced

$$\omega_D=\frac{\omega}{c}V_T,\qquad \xi=\frac{\gamma+i\Delta}{\omega_D},$$

$$\tilde{q}=\frac{c}{\omega}q,\qquad \tilde{\varkappa}_2=\frac{c}{\omega}\varkappa_2,\qquad \beta=\frac{2}{\hbar V_T}\int_{z_1}^{\infty}[U_1(z)-U_2(z)]dz.$$

Note that Im$R$ is an even function of the detuning $\Delta$, while Re$S$ does not have a definite parity with respect to $\Delta$ in the case $\beta\neq0$. Consequently, when there are specularly scat-

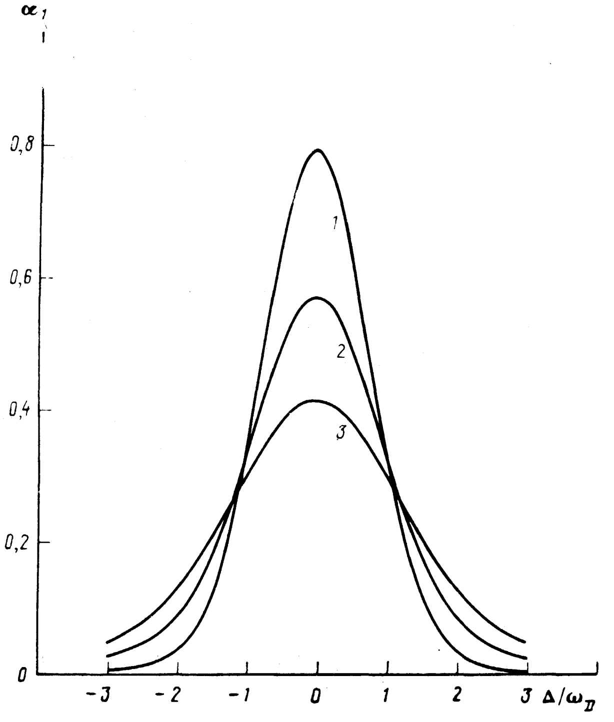

FIG. 1. The absorption coefficient $\alpha_1$ for $\eta = 0$ and $\beta = 0$. 1—$\tilde{\varkappa}_2 = 0$; 2—0.5; 3—1.

tered atoms ($\eta \neq 0$) the polariton absorption spectrum is asymmetric with respect to the frequency $\omega = \omega_0$. The asymmetry disappears from the spectrum both at $\beta \ll 1$ and at $\beta \gg 1$, because of the fast oscillations of the integrand which determines the function $S$.

In the limit in which the nonuniformity of the polariton field is slight, and the relation $\varkappa_2 \ll \omega/c$ holds, the function $R(\Delta)$ tends toward a Voigt shape:

$$R(\varkappa_2=0)=\frac{i}{2\pi^{1/2}}\int_{-\infty}^{\infty}\frac{\exp(-x^2)\,dx}{\xi+ix}\equiv\frac{1}{2}R_0(\xi).$$

The second term in (23) can be ignored in this case.

Figures 1–3 show polariton absorption spectra for $\gamma = 0.1\omega_D$ and for various values of the parameters $\varkappa_2$, $\eta$, and $\beta$. The absorption coefficient $\alpha_1$ is expressed in arbitrary units. Corresponding to a large value of $\varkappa_2$ (Fig. 1) is a large width of the absorption line. In other words, the spatial dispersion leads to an additional spectral broadening. The broadening is of two types. First, there is the time-of-flight broadening. Second, with increasing $\varkappa_2$ there is an increase in $q$ (without change $\omega/c$), which leads to a large Doppler broadening.

To estimate $\alpha_1$, we adopt the following parameter values: $q = 10^5$ cm$^{-1}$, $\omega_D = 10^9\,\mathrm{s}^{-1}$, $d_{12} = 10^{-18}$ esu, $N = 5\cdot 10^{14}$ cm$^{-3}$, $|\varepsilon_1| \gg 1$, and $\gamma \ll \omega_D$. Substituting into (23), we find $\alpha_1 \sim 400$ cm$^{-1}$. This result is comparable to the value of $\alpha_0$.

Let us calculate the spectral power density of the scattered light, using perturbation theory. In the first nonvanishing order in $\Omega$, we have the following expansion for the correlation function:

$$g^{(2)}(t,t')=Q^{(1)}_{21,11}(t',t)\rho^{(1)}_{12}(t)+Q^{(0)}_{21,21}(t',t)\rho^{(2)}_{22}(t), \qquad (24)$$

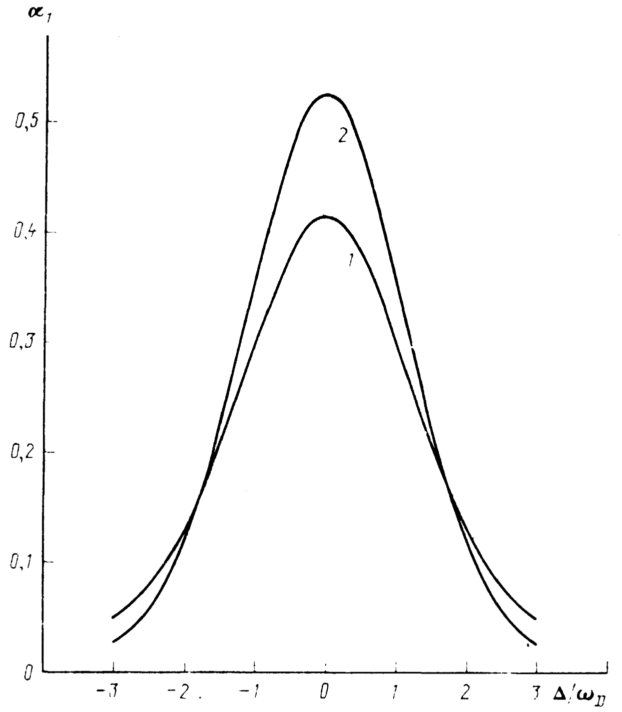

FIG. 2. The absorption coefficient $\tilde{\alpha}_1$ for $\beta = 0$ and $\tilde{\varkappa}_2 = 1$. 1—$\eta = 0$, 2—1.

where the functions $Q^{(1)}_{21,11}$ and $Q^{(0)}_{21,21}$ are found from

$$\rho^{(1)}_{21}(t')=Q^{(1)}_{21,11}(t',t)\rho^{(0)}_{11}(t)+Q^{(0)}_{21,21}(t',t)\rho^{(1)}_{21}(t).$$

To find $Q^{(1)}_{21,11}$ and $Q^{(0)}_{21,21}$, we go back to (17), (20), and (21). Using

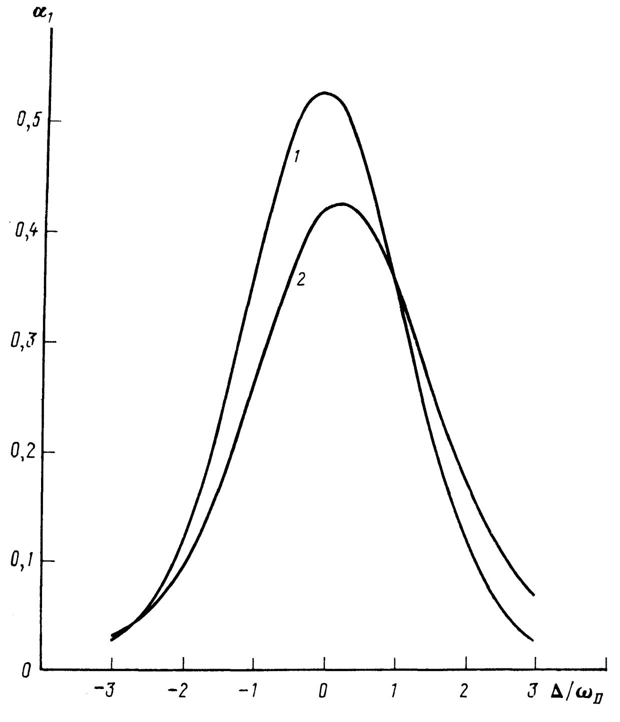

FIG. 3. The absorption coefficient $\alpha_1$ for $\tilde{\varkappa}_2 = 1$ and $\eta = 1$. 1—$\beta = 0$; 2—1.

$$\mathbf{r}(t+\tau)=\mathbf{r}(t)+\mathbf{V}\tau$$

and recognizing that $\rho_{11}^{(0)}=1$, we find

$$Q_{21,21}^{-(0)}(t+\tau,t)=0,$$

$$Q_{21,11}^{-(1)}(t+\tau,t)=i\frac{\Omega\exp(-i\psi)}{2\Gamma}\exp\{i[\mathbf{k}_2\mathbf{r}(t)-\omega t]\}\exp[i(\mathbf{k}_2\mathbf{V}-\omega)\tau], \tag{25}$$

$$Q_{21,21}^{+(0)}(t+\tau,t)=\exp[i(\mathbf{k}_2\mathbf{V}-\omega+i\Gamma)\tau],$$

$$Q_{21,11}^{+(1)}(t+\tau,t)=i\frac{\Omega\exp(-i\psi)}{2\Gamma}\exp\{i[\mathbf{k}_2\mathbf{r}(t)-\omega t]\}\times\exp[i(\mathbf{k}_2\mathbf{V}-\omega)\tau][1-\exp(-\Gamma\tau)].$$

The superscripts plus and minus of the functions $Q_{21,i1}$ correspond to values $V_z>0$ and $V_z<0$. Expressions (25) determine the correlation functions $g_-^{(2)}(t,t+\tau)$ and $g_+^{(2)}(t,t+\tau)$ at $\tau\leqslant 0$ and $\tau\geqslant 0$, respectively. The quantities $g_\pm^{(2)}(t,t+\tau)$ at the remaining values of $\tau$ are further defined as

$$g_\pm(t,t-\tau)=g_\pm^*(t,t+\tau).$$

In calculating the power spectrum of the scattered field, we bear in mind that (13) describes the emission spectrum of an immobile atom. To take the thermal motion of the atoms into account, we make the substitution $\nu\rightarrow\nu-\mathbf{kV}$ to account for the Doppler effect, and we average the result over velocity with a Maxwellian distribution function. In addition, to find the resultant contribution of atoms to the intensity of the scattered light, we multiply (13) by the number density of atoms in the gas, and we integrate over the volume occupied by the gas. As a result we find

$$I(\nu)=\frac{NLD}{\varkappa_2}|\Phi(\mathbf{R})|^2[\tilde{g}_-(\nu)+\tilde{g}_+(\nu)],$$

where

$$\tilde{g}_-(\nu)=\frac{\Omega^2}{8}\int\limits_{V_z<0}d\mathbf{V}\,f(V)\frac{1}{|\Gamma(\mathbf{V})|^2}\frac{(-\varkappa_2V_z)}{(\nu-\omega+\mathbf{pV})^2+(\varkappa_2V_z)^2},$$

$$\tilde{g}_+(\nu)=\tilde{g}_\omega(\nu)+\tilde{g}_{\omega_0}(\nu). \tag{26}$$

$$\tilde{g}_\omega(\nu)=\frac{\Omega^2}{8}\operatorname{Re}\left\{\int\limits_{V_z>0}d\mathbf{V}\,f(V)\frac{1}{\Gamma(\mathbf{V})\Gamma^*(\mathbf{V})}\times\left[1+\eta e^{-i\Delta\Phi}\frac{2\varkappa_2V_z}{\tilde\Gamma^*(\mathbf{V})}\right]\frac{1}{\varkappa_2V_z+i(\nu-\omega+\mathbf{pV})}\right\},$$

$$\tilde{g}_{\omega_0}(\nu)=-\frac{\Omega^2}{8\gamma}\operatorname{Re}\left\{\int\limits_{V_z>0}d\mathbf{V}\,f(V)\frac{\varkappa_2V_z}{\Gamma(\mathbf{V})\tilde\Gamma(\mathbf{V})}\times\left[1-\eta\left(\frac{\Gamma(\mathbf{V})}{\Gamma^*(\mathbf{V})}-e^{-i\Delta\Phi}\frac{\tilde\Gamma(\mathbf{V})}{\tilde\Gamma^*(\mathbf{V})}+e^{i\Delta\Phi}\frac{\Gamma(\mathbf{V})}{\tilde\Gamma(\mathbf{V})}\right)\right]\frac{1}{\gamma+i(\nu-\omega_0-\mathbf{kV})}\right\}.$$

The functions $\tilde{g}_-$ and $\tilde{g}_+$ determine the contribution to the scattering spectrum from the atoms with $V_z<0$ and $V_z>0$, respectively; $\mathbf{p}\equiv\mathbf{q}-\mathbf{k}$; $D$ is the width of the region in which the polaritons propagate. We see that the spectrum of the scattered light consists of two components: one at the polariton frequency $\omega$ and one at the frequency $\omega_0$ of the atomic transition. The first component corresponds to a resonant scattering of polaritons by the gas atoms. The second component results from the time-varying nature of the atomic dipole moment as the atom moves away from the surface. The shape of the spectral lines depends on the relative number of atoms which are specularly scattered, on the difference between the adsorption potentials in $\Delta\Phi$, and also on the direction along which the scattered light is observed.

If the nonuniformity of the polariton field is only slight, $\varkappa_2\ll\gamma/V_T$, we can write

$$\tilde{g}_{\omega_0}\ll\tilde{g}_\omega=\tilde{g}_-$$

and the scattering spectrum is independent of the parameters of the atom-surface interaction. In the case $\varkappa_2=0$ we can write

$$\tilde{g}_-+\tilde{g}_\omega=\frac{\pi}{8}\Omega^2\int d\mathbf{V}\,f(V)\frac{1}{\gamma^2+(\Delta+qV_x)^2}\delta(\nu-\omega+\mathbf{pV}).$$

In other words, we find the expression for the scattering spectrum of a bulk wave in a gas.

To illustrate Eqs. (26), we consider the case in which atoms are excited far in the wing of the absorption line, i.e., the case $|\Delta|\gg\gamma$, $qV_T$, $\varkappa_2V_T$. We assume for simplicity $k_y=k_z=0$. We can then write

$$\tilde{g}_-(\nu)+\tilde{g}_\omega(\nu)\approx\frac{\Omega^2}{4\Delta^2}\operatorname{Im}\frac{R(\nu)}{p_0V_T},$$

where the function $R$ is given in (23), and the parameters in terms of which this function are expressed have the values

$$\xi=i\frac{\nu-\omega}{p_0V_T},\qquad\tilde\varkappa_2=\frac{\varkappa_2}{p_0},\qquad p_0^2=2\frac{\omega^2}{c^2}\left(1\pm\frac{qc}{\omega}\right).$$

The minus sign here corresponds to forward scattering, and the plus sign to backscattering. The width of the scattering line is determined by the quantity $|p_0|V_T$. At the same time, for $k_z=0$, we have the following expression for $\tilde{g}_{\omega_0}$:

$$\tilde{g}_{\omega_0}(\nu)\approx\frac{\Omega^2}{8\pi\Delta^2}\frac{\varkappa_2}{\gamma k}\operatorname{Re}R_0\times\left[\frac{\gamma+i(\nu-\omega_0)}{kV_T}\right]\int\limits_0^\infty xe^{-x^2}\left(1-\eta+4\eta\sin^2\frac{\beta}{2x}\right)dx.$$

We see that the line has a Voigt shape and is determined by the magnitude of the photon wave vector. In other words, it does not depend on the observation direction. The contribution of the specularly scattered atoms vanishes in the case $\beta=0$. The reason is that in this case an atom moving away from the surface has a dipole moment which is the same as the steady-state value.

To estimate the scattering efficiency, we consider the average power of the light scattered into the half-space $z>0$:

$$W=\frac{c}{4\pi^2}\int\int\limits_{-\infty}^{\infty}I(\nu)d\nu\,dS,$$

where $dS$ is an area element of a spherical surface of radius $R$. The power of the surface polaritons, on the other hand, is

$$W_0 = \frac{c^2 q |E_2|^2 D}{16\pi\omega\varkappa_2}\left(1 - \frac{1}{\varepsilon_1^2}\right).$$

For the excitation of atoms far in the wing of the absorption line, with $|\varepsilon_1| \gg 1$, we have

$$\frac{W}{W_0} = \frac{2\pi}{3}\frac{\omega^4 d_{12}^4}{c^4 \hbar^2 \Delta^2} NL.$$

Using the parameter values $\omega/c = 10^5\ \mathrm{cm}^{-1}$, $d_{12} = 10^{-18}$ esu, $\Delta = 10^{10}\ \mathrm{s}^{-1}$, $N = 5\cdot 10^{14}\ \mathrm{cm}^{-3}$, and $L = 10^{-2}$ cm, we find the estimate $W/W_0 \sim 10^{-5}$.

## 6. CONCLUSION

We have studied the absorption and scattering spectra for surface polaritons propagating along an interface between a gas and a solid under conditions such that the polariton is at resonance with an atomic transition in the gas. An important aspect of this analysis is the nonuniformity of the polariton field. This nonuniformity gives rise to a spatial dispersion. The nonlocal nature of the response of the gas to the polariton field gives the spectral lines a specific shape and makes the spectra dependent on the parameters of the interaction of the gas atom with the solid surface. The spectrum of the scattered light contains, in addition to the component corresponding to resonant scattering, a component at the frequency of the atomic transition. This component is due entirely to the spatial dispersion. The numerical estimates above show that the effects discussed here could be seen experimentally.

The basic results of this paper also apply to the case in which waveguide polaritons are propagating through a plate bordered by a gas.

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