Absorption of an intense surface electromagnetic wave in a system consisting of a solid and a resonant gas

V. G. Bordo

Institute of General Physics, Academy of Sciences of the USSR

(Submitted 8 March 1988)
Zh. Eksp. Teor. Fiz. **95**, 594–600 (February 1989)

The propagation of an intense surface electromagnetic wave (SEW) along the interface between a solid and a low-density gas is analyzed for the case in which the wave is in resonance with the gas molecules. A dispersion relation for the SEW is derived to first order in the gas density. Analytic expressions are derived for the SEW absorption coefficient in the case in which the saturation is determined primarily by molecular collisions and in the case in which diffusion of excited molecules dominates. With increasing SEW intensity, the absorption coefficient tends toward the value found for a solid-vacuum interface.

1. The propagation of intense surface electromagnetic waves (SEWs) has recently been attracting increasing research interest, both theoretical and experimental.[1–6] The SEWs at the interface with a nonlinear medium whose dielectric-tensor components are proportional to the wave intensity were first studied in Refs. 1 and 2. The possibility of self-induced transparency for ultrashort light pulses propagating along a surface coated with a thin film of resonant material was predicted in Ref. 3. A dispersion relation for SEWs at an interface with a medium consisting of two-level atoms was derived in Ref. 4; the effect of saturation was taken into account. In those papers the nonlinear medium was assumed to be an optically uniaxial medium with a dielectric tensor component ε_{zz} which does not depend on the wave field. Experiments were carried out in Refs. 5 and 6 on SEWs in a metal-gas system under conditions for which the wave is in resonance with gas molecules. The wave intensity reached values comparable to the saturation intensity of molecular transitions. There is accordingly interest in the saturation of the SEW absorption at an interface with a gaseous medium.

In the present paper we consider an intense SEW which is propagating along an interface between a solid and a resonant gas. We assume that the wave is propagating incoherently, i.e., that the duration of the effect of the light is significantly longer than the relaxation times of the gas molecules. We seek a solution of Maxwell's equations by perturbation theory in which the small parameter is the number density of molecules in the gas. We derive analytic expressions for the SEW absorption coefficient in two limiting cases: that in which the saturation is determined primarily by collisions of molecules with each other and that in which a diffusion of excited molecules dominates.

2. We assume that a SEW is propagating along the interface between a solid, which occupies the half-space $z<0$ (medium 1), and a gas, which occupies the half-space $z>0$ (medium 2). We assume that medium 1 is linear and isotropic and has a dielectric constant

$$\varepsilon_1(\omega)=\varepsilon_1'(\omega)+i\varepsilon_1''(\omega).$$

We find a solution of Maxwell's equations which corresponds to a TM surface wave which is propagating along the x axis. We seek the components of the fields and the polarization of the gas in the form

$$\mathcal{F}={}^1/_2F(z)\exp(-i\omega t+ikx)+\text{c.c.},\tag{1}$$

where the amplitudes $H_{iy},E_{ix},E_{iz}P_x,P_z\,(i=1,2)$ are nonvanishing. Here k is the SEW wave number, and 2 Im k is the SEW absorption coefficient. Substituting expressions (1) into Maxwell's equations, we find the equations

$$\frac{dH_{iy}}{dz}=i\frac{\omega}{c}D_{ix},\qquad kH_{iy}=-\frac{\omega}{c}D_{iz},$$

$$\frac{dE_{ix}}{dz}-ikE_{iz}=i\frac{\omega}{c}H_{iy},\tag{2}$$

where $\mathbf{D}_1=\varepsilon_1\mathbf{E}_1$ and $\mathbf{D}_2=\mathbf{E}_2+4\pi\mathbf{P}$.

Let us assume that the SEW frequency ω is approximately equal to the frequency ω_{21} of transitions between molecular levels $|1\rangle$ and $|2\rangle$ and that we can ignore the interaction of the wave field with the other levels. The polarization can then be expressed in terms of the density matrix element

$$\tilde{\rho}_{12}=\rho_{12}\exp(-i\omega t+ikx)$$

in the following way:

$${}^1/_2P_\alpha(z)=N\langle\rho_{12}d_{21}{}^\alpha\rangle,\tag{3}$$

where $\mathbf{d}_{21}$ is the transition dipole moment; N is the molecular density; $\alpha=x,z$; and the angle brackets mean an average over the velocities and the orientations of the molecules. In the resonant approximation, the density matrix elements satisfy the following equations in the Wigner picture (Ref. 7, for example):

$$\frac{\partial\rho_{11}}{\partial t}=-\mathbf{v}\nabla\rho_{11}+\gamma_\parallel(n_1{}^e\rho_{22}-n_2{}^e\rho_{11})+{}^1/_2i\Omega(\rho_{21}-\rho_{12})+\mathrm{St}_1\,\rho_{11},$$

$$\frac{\partial\rho_{22}}{\partial t}=-\mathbf{v}\nabla\rho_{22}-\gamma_\parallel(n_1{}^e\rho_{22}-n_2{}^e\rho_{11})+{}^1/_2i\Omega(\rho_{12}-\rho_{21})+\mathrm{St}_2\,\rho_{22},$$

$$\frac{\partial\rho_{12}}{\partial t}=-\mathbf{v}\nabla\rho_{12}-[\gamma_\perp+i(\Delta+kv_x)]\rho_{12}+{}^1/_2i\Omega(\rho_{22}-\rho_{11}),$$

$$\rho_{21}=\rho_{12}{}^*,\qquad\int d\mathbf{v}\,\mathrm{Sp}\,\rho(\mathbf{v})=1,\tag{4}$$

where $\mathbf{v}$ is the velocity of a molecule, $\gamma_\parallel$ and $\gamma_\perp$ are the longitudinal and transverse relaxation rates, n_1^e and n_2^e are the equilibrium level populations, $\Delta=\omega_{21}-\omega$ is the deviation from the resonant frequency, St_1 and St_2 are collision operators, and $\Omega(z)=\mathbf{d}_{12}\mathbf{E}_2(z)/\hbar$ is the Rabi frequency. In writ-

0038-5646/89/020334-04$04.00

ing (4) we assumed that the absorption of the SEW along its propagation path can be ignored; i.e.,

$$\exp(ik^{*}x)\approx\exp(ikx).$$

Simultaneous solution of Eqs. (2)–(4) with the boundary conditions

$$H_{1y}(0)=H_{2y}(0),\quad E_{1x}(0)=E_{2x}(0)$$

reveals the fields in the two media. In its general formulation, however, this is a complicated problem, so we will restrict the analysis to a SEW at interface with a low-density gas. In this case the terms containing the polarization in Eqs. (2) can be treated as small perturbations, and in first order we can substitute the value of the density matrix determined by the SEW field in vacuum into expression (3).

3. Let us find a dispersion relation for the SEW to first order in the small parameter N. Eliminating the components H_{iy} and E_{ix} from the system (2), we find

$$\frac{d^2E_{1z}}{dz^2}-\left(k^2-\frac{\omega^2}{c^2}\varepsilon_1\right)E_{1z}=0, \tag{5}$$

$$\frac{d^2E_{2z}}{dz^2}-\left(k^2-\frac{\omega^2}{c^2}\right)E_{2z}=-4\pi\left(\frac{d^2P_z}{dz^2}+ik\frac{dP_x}{dz}+\frac{\omega^2}{c^2}P_z\right). \tag{6}$$

Equation (5) has a solution which decays with distance into medium 1:

$$E_{1z}(z)=E_{1z}(0)\exp(\varkappa_1 z), \tag{7}$$

where $\varkappa_1=(k^2-\omega^2\varepsilon_1/c^2)^{1/2}$, and $\mathrm{Re}\,\varkappa_1>0$. We solve Eq. (6) by perturbation theory. For this purpose, we construct the series

$$E_{2z}=E_{2z}^{(0)}+E_{2z}^{(1)}+\ldots,\qquad k=k^{(0)}+k^{(1)}+\ldots,$$

$$P_\alpha=P_\alpha^{(1)}+\ldots,\qquad {}^1/_2P_\alpha^{(n)}=N\langle\rho_{12}^{(n-1)}d_{21}{}^\alpha\rangle$$

in (6), and we equate terms with identical powers of the small parameter. The zeroth-order equation

$$\frac{d^2E_{2z}^{(0)}}{dz^2}-\left(k^{(0)2}-\frac{\omega^2}{c^2}\right)E_{2z}^{(0)}=0$$

has a solution which decays with distance into medium 2:

$$E_{2z}^{(0)}(z)=E_{2z}^{(0)}(0)\exp(-\varkappa_2^{(0)}z),$$

where $\varkappa_2^{(0)}=(k^{(0)2}-\omega^2/c^2)^{1/2}$ and $\mathrm{Re}\,\varkappa_2^{(0)}>0$. Writing (7) in the form

$$E_{1z}(z)=(E_{1z}^{(0)}(0)+E_{1z}^{(1)}(0)+\ldots)\exp[(\varkappa_1^{(0)}+\varkappa_1^{(1)}+\ldots)z],$$

and using the boundary conditions

$$H_{1y}^{(0)}(0)=H_{2y}^{(0)}(0),\quad E_{1x}^{(0)}(0)=E_{2x}^{(0)}(0),$$

we find the familiar dispersion law for SEWs at an interface between a linear medium and a vacuum[8]:

$$k^{(0)}=\frac{\omega}{c}\left(\frac{\varepsilon_1}{\varepsilon_1+1}\right)^{1/2}.$$

We write a solution of the second-order equation,

$$\frac{d^2E_{2z}^{(1)}}{dz^2}-\left(k^{(0)2}-\frac{\omega^2}{c^2}\right)E_{2z}^{(1)}-2k^{(0)}k^{(1)}E_{2z}^{(0)}$$
$$=-4\pi\left(\frac{d^2P_z^{(1)}}{dz^2}+ik^{(0)}\frac{dP_x^{(1)}}{dz}+\frac{\omega^2}{c^2}P_z^{(1)}\right), \tag{8}$$

in the form

$$E_{2z}^{(1)}(z)=\frac{1}{2\varkappa_2{}^{(0)}}\Big[\int^{z}\{\exp[\varkappa_2^{(0)}(z-\zeta)]$$
$$-\exp[-\varkappa_2^{(0)}(z-\zeta)]\}F(\zeta)\,d\zeta$$
$$-E_{2z}^{(0)}(z)\,k^{(0)}k^{(1)}(\varkappa_2^{(0)-1}+2z)\Big]$$
$$+C_1\exp(-\varkappa_2^{(0)}z)+C_2\exp(\varkappa_2^{(0)}z),$$

where $F(z)$ is the right side of (8). From the condition that the solution decay in the limit $z\to\infty$, we find

$$C_2=-\frac{1}{2\varkappa_2{}^{(0)}}\int^{\infty}\exp(-\varkappa_2{}^{(0)}\zeta)F(\zeta)\,d\zeta,$$

while the constants C_1 and $k^{(1)}$ are found from the boundary conditions

$$H_{1y}^{(1)}(0)=H_{2y}^{(1)}(0),\quad E_{1x}^{(1)}(0)=E_{2x}^{(1)}(0).$$

After some straightforward calculations, we find the dispersion relation in which we are interested:

$$k^{(1)}=4\pi k^{(0)}\varkappa_2{}^{(0)}\frac{\varepsilon_1}{\varepsilon_1+1}[E_{2z}^{(0)}(0)]^{-1}\int_0^\infty\exp(-\varkappa_2^{(0)}z)P_z^{(1)}\,dz. \tag{9}$$

4. The components of the polarization vector which appear in the expression for $k^{(1)}$ are determined by the zeroth-order perturbation-theory density matrix $\rho^{(0)}$. The matrix elements $\rho^{(0)}ij(i,j=1,2)$ in turn satisfy Eqs. (4) with

$$\Omega(z)=\Omega^{(0)}(z)\equiv\mathbf{d}_{12}\mathbf{E}_2{}^{(0)}(z)/\hbar,\quad k=k^{(0)}. \tag{10}$$

System (4) gives a microscopic description of the evolution of the state of the gas in the field of the SEW. If the macroscopic characteristics of the gas vary sufficiently slowly through the volume of the gas, a less detailed macroscopic description of this evolution is possible.[9] In this case we can assume in a first approximation that thermal equilibrium is established in each separate part of the gas, while the gas as a whole is not in equilibrium. We assume the inequalities

$$\varkappa_2{}^{(0)}v_T,\ \gamma_\parallel,\ \Omega^{(0)}\ll\gamma_\perp,\ \tau^{-1}, \tag{11}$$

where τ is the collision time, and v_T is the thermal velocity of a molecule. We wish to find an equation for the difference between the level populations. For this purpose, we rewrite (4), using the substitution (10), in the form

$$\partial\rho/\partial t=(L_0+L_1)\rho, \tag{12}$$

where we are including in the operator L_0 the collision operators and also the terms which describe the transverse relaxation, while the operator L_1 contains the other terms which appear on the right sides of Eqs. (4). In accordance with (11), the operator L_0 describes the rapid relaxation to a local equilibrium, while L_1 describes the relaxation to an equilibrium state of the gas as a whole. Since the field is slightly nonuniform ($1/\varkappa_2^{(0)} \gg v_T\tau$), and since the transitions between the levels of the molecule are slow ($\gamma_{\parallel}, \Omega_0 \ll \tau^{-1}$), the macroscopic evolution equations must take the form of diffusion equations for the excited and unexcited molecules, and they must include terms which incorporate the change in the state of the molecule. A diffusion equation can be constructed formally by treating the operator L_1 as a perturbation. Omitting the details of the derivation (see the Appendix), we write the result:

$$\partial w/\partial t = D\nabla^2 w - \gamma_{\parallel}(w-w_e) - a_\omega \Omega_0^2 \exp(-2\varkappa_2^{(0)} z) w, \quad (13)$$

where

$$w = \int d\mathbf{v}[\rho_{11}^{(0)}(\mathbf{v}) - \rho_{22}^{(0)}(\mathbf{v})], \qquad \Omega_0 \equiv \Omega^{(0)}(0),$$

w_e is the equilibrium difference between the populations, D is the self-diffusion coefficient,

$$a_\omega = \int d\mathbf{v} f(\mathbf{v}) \frac{\gamma_\perp}{\gamma_\perp^2 + (\omega_{21} - \omega + k^{(0)} v_x)^2}$$

is the shape of the absorption line of the molecule, and

$$f(\mathbf{v}) = \pi^{-3/2} v_T^{-3} \exp(-v^2/v_T^2)$$

is a Maxwellian velocity distribution.

We are interested in a steady-state solution of Eq. (13), so we equate the right side of this equation to zero. The substitution

$$y = \frac{\delta\Omega_0}{\chi_2^{(0)}} \left(\frac{a_\omega}{D}\right)^{1/2} \exp(-\varkappa_2^{(0)} z)$$

reduces the equation to an inhomogeneous modified Bessel equation. In this case, the solution of the equation is expressed in terms of Lommel's function,[10] but we will restrict the discussion to some limiting situations in order to find some final results in analytic form.

a. We assume $l \ll (D/\gamma_{\parallel})^{1/2} \ll \delta$, where l is the mean free path of a molecule, and $\delta \equiv 1/\varkappa_2^{(0)}$ is the depth to which the SEW penetrates into the gas. These inequalities are seen to have a simple physical meaning when we note that $(D/\gamma_{\parallel})^{1/2}$ is the average displacement of a molecule from its original position over the lifetime of the excited state. In this case the change in the difference between the level populations is determined primarily by longitudinal relaxation, and the diffusion of molecules can be ignored. Equation (13) contains a singular perturbation.[11] Its solution contains, in addition to a regular part which can be written as a series in the small parameter $\nu = \delta^{-1}(D/\gamma_{\parallel})^{1/2}$, so-called boundary terms, which decay rapidly in a boundary layer $0 < z \lesssim (D/\gamma_{\parallel})^{1/2}$. By virtue of the inequality $\nu \ll 1$, however, the molecules in the boundary layer contribute negligibly to the SEW absorption coefficient which we calculate below. We accordingly restrict the analysis to the regular part of the solution. To lowest order in ν, Eq. (13) has the steady-state solution

$$w_0(z) = \frac{w_e}{1 + G\exp(-2\varkappa_2^{(0)} z)}, \qquad (14)$$

where $G = a_\omega \Omega_0^0/\gamma_{\parallel}$ is the saturation parameter at $z = 0$.

b. We now assume $(D/\gamma_{\parallel})^{1/2} \gg \delta$. We assume that a molecule near the surface of the solid is in theromodynamic equilibrium with it. Equation (13) with the boundary conditions

$$w(0) = w(\infty) = w_e$$

has the steady-state solution

$$w_0(z) = w_e I_0(g\exp(-\varkappa_2^{(0)} z))\{1 + [I_0^{-1}(g) - 1]$$
$$\times \exp(-\varkappa_2^{(0)} \nu^{-1} z)\}, \qquad (15)$$

where I_n is the modified Bessel function of the first kind, of order n, and the dimensionless parameter

$$g = \delta\Omega_0 (a_\omega/D)^{1/2}$$

is a measure of the saturation.

The steady-state value of the matrix element ρ_{12}, which determines that polarization of the gas in the steady state, is found from the last two equations in the system (10). In the approximation under consideration here, we find

$$\rho_{12}^{(0)} = -\frac{i}{2} \frac{\Omega^{(0)}}{\gamma_\perp + i(\Delta + k^{(0)} v_x)} f(\mathbf{v}) w_0. \qquad (16)$$

5. We can find dispersion relations for the SEWs in the limiting cases discussed above. Calculating the components of the polarization vector with the help of (14) and (16), and substituting them into (9), we find, for case **a**, the relation

$$k^{(1)} = 2\pi\chi(\omega) k^{(0)} \frac{\varepsilon_1}{\varepsilon_1 + 1} \frac{\ln(1+G)}{G}, \qquad (17)$$

where

$$\chi(\omega) = -\frac{i}{\hbar} w_e N \int \frac{f(\mathbf{v})\, d\mathbf{v}}{\gamma_\perp + i(\omega_{21} - \omega + k^{(0)} v_x)} \langle d_{21}^z d_{12}^z \rangle$$

is the linear susceptibility of the gaseous medium. The imaginary part of relation (17) gives us the SEW absorption coefficient α in the gas:

$$\alpha = \alpha_0 \frac{\ln(1+G)}{G}$$

where α_0 is the absorption coefficient for a weak SEW in the gas.

Correspondingly, in case **b**, we find the dispersion relation

$$k^{(1)} = 4\pi\chi(\omega) k^{(0)} \frac{\varepsilon_1}{\varepsilon_1 + 1} \frac{I_1(g)}{g I_0(g)}$$

and the following expression for the SEW absorption coefficient:

$$\alpha = \alpha_0 \frac{2 I_1(g)}{g I_0(g)}.$$

Figure 1 shows plots of α versus the saturation parameter. For $G \gg 1$ ($g \gg 1$) we have $\alpha \sim 0$, and the SEW absorption is caused entirely by absorption in the solid. This result is a manifestation of bleaching of the gaseous medium.

The real part of $k^{(1)}$ determines the dispersion $\omega(\mathrm{Re}\, k)$ for a nonlinear surface polariton and thus the dependence of the phase and group velocities of the SEW on its intensity.

We wish to emphasize that the results derived above are valid under inequalities (11) and under the condition for the applicability of perturbation theory:

$$2\pi N |\chi(\omega)| \left|\frac{\varepsilon_1}{\varepsilon_1 + 1}\right| \ll 1.$$

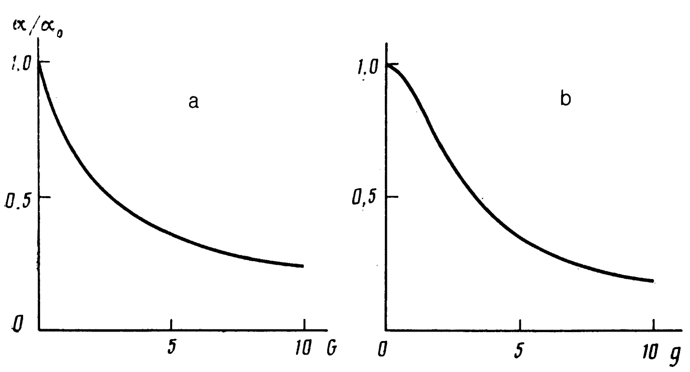

FIG. 1. The SEW absorption coefficient corresponding to absorption in a gas versus the saturation parameter. a—$(D/\gamma_{\parallel})^{1/2} \ll \delta$; b—$(D/\gamma_{\parallel})^{1/2} \gg \delta$.

These conditions can be satisfied, for example, during propagation of a SEW of moderate intensity which is resonant with a molecular vibrational transition at a gas pressure of tens of torr.

I wish to thank Yu. N. Petrov for suggesting this topic.

APPENDIX

We introduce a projection operator P such that $P\rho$ is proportional to the steady-state solution of the equation

$$\partial\rho/\partial t = L_0\rho.$$

Specifically,

$$P\rho(\mathrm{v}) = f(\mathrm{v})\,n,$$

where $f(v)$ is a Maxwellian velocity distribution, and

$$n = \begin{pmatrix} n_1 & 0 \\ 0 & n_2 \end{pmatrix}.$$

From (12), and using $PL_0 = 0$ and $L_0P = 0$, we find the equations

$$\frac{\partial}{\partial t} P\rho = PL_1P\rho + PL_1Q\rho, \qquad \text{(A1)}$$

$$\frac{\partial}{\partial t} Q\rho = QL_1P\rho + Q(L_0 + L_1)Q\rho, \qquad \text{(A2)}$$

where $Q = 1 - P$. A closed equation for $P\rho$, which is valid to second order in L_1 inclusively, is found after we solve (A2) for $Q\rho$ to first order in L_1 and substitute the result into the second term on the right side of (A1):

$$\frac{\partial}{\partial t} P\rho(t) = PL_1P\rho(t) + \int_0^\infty d\tau\, PL_1 e^{L_0\tau} QL_1P\rho(t). \qquad \text{(A3)}$$

Using the explicit expression for the matrix of operator L_1, and integrating (A3) over velocity, we find equations for n_1 ad n_2. From these equations we find Eq. (13) for $w = n_1 - n_2$. (A similar method was used in Ref. 7 to derive equations for a photoinduced drift.)

[1] V. M. Agranovich, V. S. Babichenko, and V. Ya. Chernyak, Pis'ma Zh. Eksp. Teor. Fiz. **32**, 532 (1980) [JETP Lett. **32**, 512 (1980).

[2] A. A. Maradudin, Z. Phys. **B41**, 341 (1981).

[3] V. M. Agranovich, V. I. Rupasov, and V. Ya. Chernyak, Pis'ma Zh. Eksp. Teor. Fiz. **33**, 196 (1981) [JETP Lett. **33**, 185 (1981)].

[4] P. I. Khadzhi and E. S. Kiseleva, Zh. Tekh. Fiz. **57**, 395 (1987) [Sov. Phys. Tech. Phys. 32, 242 (1987)].

[5] V. A. Kravchenko, Yu. N. Petrov, S. P. Surov, and V. A. Sychugov, Vysokochistye veschestva **3**, 94 (1987).

[6] V. G. Bordo, V. A. Kravchenko, Yu. N. Petrov, *et al.*, Preprint, Institute of General Physics, Academy of Sciences of the USSR, No. 11, 1988.

[7] G. Nienhuis and S. Kryszewski, Phys. Rev. **A36**, 1305 (1987).

[8] D. N. Mirlin, in: *Poverkhnostnye polyaritony* (V. M. Agranovich and D. L. Mills, editors), Nauka, Moscow, 1985, p. 29 (Earlier edition translated as *Surface Polaritons*, Elsevier, New York, 1982).

[9] E. M. Lifshits and L. P. Pitaevskiĭ, *Fizicheskaya kinetika*, Nauka, Moscow, 1979, p. 30 (*Physical Kinetics*, Pergamon, Oxford, 1981).

[10] G. N. Watson, *A Treatise on the Theory of Bessel Functions*, Cambridge Univ. Press, New York, 1952 (Russ. Transl., Part 1, IIL, Moscow, 1949.

[11] A. B. Vasileva and V. F. Butuzov, *Asimptoticheskie razlozheniya resheniĭ singulyarno-vozmushchennykh uraveneniĭ* (*Asymptotic Expansions of the Solutions of Singularly Perturbed Equations*), Nauka, Moscow, 1973.

Translated by Dave Parsons