ELECTRICAL PROPERTIES OF RESONANT GASEOUS MEDIA

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The basic properties of the static polarization of a gas in the field of resonant laser radiation were studied. The computation of spectral behavior of the induced polarization for two-level freely oriented molecules was performed. Spectroscopic applications of this effect were discussed.

INTRODUCTION

The propagation of powerful resonant radiation in absorbing media is accompanied by different nonlinear effects. They affect the change in characteristics of the powerful radiation, probing radiation, and absorbing medium in a beam channel.[1] The propagation of the pulse of resonant radiation in the medium causes changes in the electrical characteristics of the medium itself that can be useful in spectroscopy. Thus, in Refs. 2 and 3 a laser beam was transmitted through the gas enclosed in an inductance coil connected to a high-sensitivity oscillograph. The light-induced emf was recorded, with the signal amplitude being a function of detuning between the laser radiation frequency and the frequency of the absorption line. In Ref. 4 the effect of resonant radiation of a CO_2 laser on the electrical characteristics of OsO_4 gas was studied theoretically and experimentally. Laser radiation propagated in the gas, enclosed in a capacitor with a constant voltage applied to its plates. The radiation amplitude was modulated with a frequency of 300 Hz, and the electrical signal of the same frequency was recorded on the plate§ of this condenser. The amplitude of the signal was proportional to the pressure of the gas and the intensity of laser radiation and it amounted to $\sim 10^5$ V/cm provided that resonance exists between the radiation frequency and the absorption frequency of the gas.

These experiments show that recording the changes in the electrical characteristics of an absorbing gaseous medium due to the effect of optical radiation with tunable frequency can be applied in investigations without the spectral instruments required in traditiond methods.

The improvement of this technique for measuring quasistatic characteristics of the medium due to the effect of laser radiation, from our point of view, makes it possible to develop quite simple spectral devices like the opto-acoustic and opto-thermal spectrometers which are widely used now.

In this work the main features in the behavior of static polarization of a gas in the field of resonant radiation are studied in the model of two-level freely oriented particles suspended in gaseous medium, and different spectroscopic applications of the effect are discussed.

RELAXATION MODEL AND FORMULATION OF THE BASIC EQUATIONS

Let us examine the semiclassical two-level system for which the change in the molecule orientation is described by classical methods. In order to describe the relaxation process in such a model, the following relaxation parameters are introduced: $W_{i\Omega,i\Omega'}$ is the relaxatin rate of the i-th level with the change in the angle Ω Ω' and $W_{i\Omega,j\Omega'}$ is the rate of nonradiative transition between the levels with a possible change in orientation.

We will assume that transitions without the change in the angle are most probable. In this case

$$W_{i\Omega,j\Omega'} = W_{ij}(\Omega)\delta(\Omega - \Omega'). \tag{1}$$

If a constant electric field with the intensity E is applied between the plates of the condenser, the molecules of the gas under equilibrium conditions have the following distribution of orientation angles

$$\rho_{ii}^{(e)}(\Omega) = C_i e^{a_i\cos\Theta}, \quad a_i = p_i E/kT. \tag{2}$$

The system of molecules will tend toward this distribution only if the principle of detailed equilibrium holds, including the statistical field for the fixed level i

$$e^{a_i\cos\Theta} W_{i\Omega,i\Omega'} = e^{a_i\cos\Theta'} W_{i\Omega',i\Omega} \tag{3}$$

and for the transition between the levels i j

$$W_{ij} e^{a_i\cos\Theta} = W_{ij} e^{(a_j\cos\Theta + \hbar\omega_i j/kT)} \tag{4}$$

Here p_1 is the dipole moment of the i-th excitation state and Θ is the angle between the vector

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E of the constant field intensity and the axis of the molecule.

In the simplest case, (3) and (4) are valid when

$$\left.\begin{aligned} W_{1\Omega,\, j\Omega'} &= W_1 e^{a_1/2\cdot(\cos\Theta' - \cos\Theta)} \\ W_{1j}(\Omega) &= W_{1j} e^{-a_1 \cos\Theta} \end{aligned}\right\}, \tag{5}$$

where W_i and W_{ij} are independent of orientation.

We shall analyze the absorption of radiation in the medium based on the balance equations, the applicability criteria for which are well-known[1]

$$\dot\rho_{11} = -(W_{1j}/l_1 + W_E + W_1 I_1/l_1)\rho_{11} + W_1 R_1/l_1 + (W_{1j}/l_j^2 + W_E)\rho_{jj}, \tag{6}$$

where i, $j = 1, 2$, $i \neq j$;

$$l_1 = \exp(a_1/2\cdot\cos\Theta); \tag{7}$$

$$I_1 = \int l_1 d\Omega; \tag{8}$$

$$R_1 = \int \rho_{11}(\Omega)\, l_1^{-1}\, d\Omega \tag{9}$$

In Eqs. (8) and (9) the integral is taken over the total solid angle.

$$W_E = \frac{\sigma_0 \cos^2\Theta_\omega I_\omega}{(\omega - \omega_{0E})^2 + \Gamma^2}, \tag{10}$$

where W_E is the probability of the absorption of radiation with the intensity I_ω at the frequency ω in the presence of the static field E, σ_0 is the absorption cross-section in the region of the maximum of the absorption line, Θ_ω is the angle between the axis of the molecule and the vector of the intensity E_ω of the light field, Γ is the half-width of the absorption line, and ω_{0E} is the frequency of the molecular transition, which is a function of the intensity E of the static field

$$\omega_{0E} = \omega_{21} - \frac{\Delta p E}{h}\cos\Theta, \quad \Delta p = p_2 - p_1.$$

The system (6) is solved with the normalization condition

$$\int [\rho_{11}(\Omega) + \rho_{22}(\Omega)]\, d\Omega = 1. \tag{11}$$

taken into account.

It is a system of integro-different ial equations, whose complete analysis is difficult. However. solving this system of algebraic equations for ρ_{ii} under stationary conditions ($\dot\rho_{ii} = 0$), we obtain

$$\rho_{11} = \Delta_1/\Delta, \tag{12}$$

where

$$\Delta = W_1 W_2 I_1 I_2 + (W_{12}/l_1^2 + W_E) W_2 I_2/l_2 + (W_{21}/l_2^2 + W_E) W_1 I_1/l_1. \tag{13}$$

$$\Delta_1 = (W_{1j}/l_j^2 + W_E + W_j I_j/l_j) W_1 R_1 l_1 + (W_{j1}/l_j^2 + W_E) W_j R_j l_j, \quad j \neq i. \tag{14}$$

Multiplying Eq. (12) by l_1^{-1} and integrating over the solid angle, we obtain the system for R_1

$$R_1 = \left[W_{j1} W_1 \int \frac{d\Omega}{l_j^2 \Delta} + W_1 \int \frac{W_E d\Omega}{\Delta} + W_1 W_j I_j \int \frac{d\Omega}{l_j \Delta}\right] R_1 + \left[W_{j1} W_j \int \frac{d\Omega}{l_1 l_j \Delta} + W_j \int \frac{W_E l_j d\Omega}{l_1 \Delta}\right] R_j, \tag{15}$$

$$i,\ j = 1,\ 2,\ i \neq j.$$

All integrals in Eq. (15) are known functions of the dipole moments p_1, temperature T, relaxation parameters, detuning $\delta = \omega - \omega_0$ (in zero static field). Intensity I of radiation, and the angle Θ_0 between the vectors of the intensity **E** of the static field and the field $\mathbf{E}_\omega$ of the light wave.

It is possible to find ρ_{ii} by finding R_1 from Eq. (15) and substituting it into Eq. (12). One can check that this solution satisfies the normalization condition (11) for the selected integration procedure.

STATIC POLARIZATION OF MEDIUM INDUCED BY LASER RADIATION

Let us examine the parallel and perpendicular components of induced polarization when the vector **E** of the static field is directed along the r-axis (Fig. 1). For the i-th polarization component ($i = z, x$) we have

$$P_1 = \frac{p_1 + p_2}{2} \langle \cos\Theta_1 (\rho_{11} + \rho_{22}) \rangle_{\Theta,\varphi} + \frac{p_1 - p_2}{2} \langle \cos\Theta_1 (\rho_{11} - \rho_{22}) \rangle_{\Theta,\varphi}. \tag{16}$$

where $\langle\ldots\rangle_{\Theta,\varphi}$ denotes an averaging over the orientations, $\cos\Theta_z = \cos\Theta$ for the parallel component, and $\cos\Theta_x = \sin\Theta\cos\varphi$ for the perpendicular component.

If quasimonochromatic optical radiation with an intensity less than 10^6–10^7 W/cm^2 interacts with the vibrational-rotational transitions of small molecules, the case of weak saturation effect is realized. It is possible to analyze different polarization mechanisms in this case.

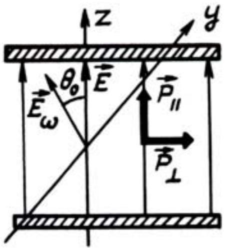

FIG. 1. Diagram of propagation of radiation in a gas enclosed in a condenser.

Corresponding expressions for P_1 can be derived directly from Eqs. (13)–(16) with the help of an expansion in terms of powers of W_E. The same result can be obtained by assuming that

$$\rho_{11} = \rho_{11}^{(e)} + \delta\rho_{11}, \tag{17}$$

where $\rho_{ii}^{(e)}$ is the equilibrium population in the presence of a static electrical field defined by (2). Substituting Eq. (17) into Eq. (6) and linearizing the system (6), we obtain the system

$$\left.\begin{aligned}&(W_{12}/l_1^2 + W_1 I_1/l_1)\delta\rho_{11} - (W_{12}/l_2^2)\delta\rho_{22} = -W_E d_0 + W_1 \delta R_1 l_1\\ &-(W_{12}/l_1^2)/\delta\rho_{11} + (W_{21}/l_1^2 + W_2 I_2/l_2)\delta\rho_{22} = W_E d_0 + W_2 \delta R_2 l_2\end{aligned}\right\} \tag{18}$$

Here, analogous to Eq. (9)

$$\delta R_1 = \int \delta\rho_{11}(\Omega) l_1^{-1} d\Omega. \tag{19}$$

By integrating Eq. (18), we obtain the system for

$$\delta R_1 \text{ and } \delta N_1 = \int \delta\rho_{11}(\Omega) d\Omega.$$

Employing the relationship $\delta N_1 = \delta N_2$. which follows from the normalization condition, we find δR_1 and δR_2 from obtained system, and then we find $\delta\rho_{11}$ and $\delta\rho_{22}$ from Eq. (18). By substituting the results into Eq. (16) and taking into consideration the relations

$$a_1 \ll 1, \quad \left|\frac{p_2 - p_1}{p_2 + p_1}\right| \ll 1 \quad a_1 \approx a_2, \quad l_1 \approx 1 + \frac{a_1}{2}\cos\theta,$$

which are usually valid, we obtain for P_i the following expressions for the polarization components:

a) parallel to the static field

$$\langle\delta P_{\parallel}\rangle = \frac{d_0(p_1 - p_2)}{2B}\left\{-(W_1 + W_2)\left[C_1 + \frac{a}{2}C_2 \times \left[4 - \frac{W_1 W_2}{B}\right]\right] + \frac{a C_0}{3(W_{21} + W_{12})}\left[V\left(1 - \frac{W_1 W_2}{2B}\right) + W_1 W_2 \times \left(\frac{W_1 W_2}{B} - 3\right)\right]\right] + \frac{d_0(p_1 + p_2)}{2B}(W_1 - W_2)\left\{C_1 + \frac{a}{2} \times \left[4 - \frac{W_1 W_2}{2}\right]C_2 + \frac{a C_0}{3}\left[1 - \frac{W_1 W_2}{2B}\right]\right\}, \tag{20}$$

where

$$B = W_1 W_2 + W_2 W_{12} + W_1 W_{21},$$

$$V = (W_1 - W_2)(W_{12} - W_{21}), \quad d_0 = (W_{21} - W_{12})/(W_{21} + W_{12}),$$

$$C_n = \int \cos^n\theta\, W_E d\Omega,$$

b) perpendicular to the static field

$$\langle\delta P_{\perp}\rangle = \frac{d_0(p_1 - p_2)}{2B}\left\{-S_0(W_1 + W_2) + \frac{a}{2}(W_1 + W_2)S_1 V_1\right\} + \frac{d_0(p_1 + p_2)}{2B}\left\{(W_1 - W_2)\left[S_0 - \frac{a}{2}S_1 W_1\right]\right\} \tag{21}$$

where $V_1 = \dfrac{W_1 W_2}{B} - 4$,

and $S_n = \int \cos^n\Theta \sin\Theta \cos\varphi W_e d\Omega$.

Note that the Integrals C_n and S_n are functions of the Stark shift parameter $b = \dfrac{(p_1 - p_2)E}{h\Gamma}$. If b is small, C_0 and S_0 0 and C_1 and $S_1 \neq 0$.

Expressions (20) and (21) make it possible to select the following mechanisms for how the resonant optical radiation affects the static polarizabi1lty of the absorbing gas:

1) The change in polarizability under conditions of excitation caused by the difference in dipole moments of the ground and excited states with the characteristic parameter $(p_1 - p_2)/(p_1 + p_2)$. This parameter can be 5–6% in magnitude for vibrational-rotational transitions In an H_2O molecule.

2) Burning out the "hole" in orientations because of the dependence of the transition frequency on the orientation, b is the parameter characterizing the Stark shift in the field E.

3) Different contribution of these effects because of the different orientational relaxation of low and upper states, the parameter is

$$W = (W_1 - W_2)/(W_1 + W_2)$$

The computation of the varying component of the intensity, appearing on the condenser plates when modulated resonant radiation propagates in the absorbing gas enclosed in the condenser was performed for the following parameters: $\Theta_0 = 45°$, $W_1 = 10^8$ sec^{-1}, $W_2 = (1.02\text{–}1.06) \cdot 10^8$ sec^{-1}, $\Gamma = (3.2 \div 0.8) \cdot 10^9$ sec^{-1}, $p_1 = 1.0$ D, $p_2 = 1.05$ D, $W_{21} \simeq 10^7$ sec^{-1}, $W_{12} = 0$, $E = 3 \cdot 10^3$ V/cm, $I = 0.1\, I_s$, and the density of absorbing molecules $N \sim 10^{19}$ cm^{-3}.The amplitude of the voltage on the plates of condenser is defined by the expression

$$U_{(\parallel,\perp)} = -4\pi N \langle P_{=,\perp} \rangle h, \tag{22}$$

where h is the distance between the plates of the condenser. In computations we used $h = 1$ cm.

The plots of $U_{\parallel,\perp}$ as a function of b, W, and δ (where δ is the detuning of the laser frequency from resonance) are given in Figs. 2 and 3. If δ is replaced by $-\delta$, all dependences are characterized by nearly exact asymmetry. This indicates that the Stark mechanism accompanied by burning up the "hole" in orientations predominates. As seen from Fig. 2, the amplitude of the effect of polarization of the gas is proportional to b, and changes in the parameters p_1, p_2, E, and Γ for fixed b affect the behavior of $U_{\parallel,\perp}$ insignificantly.

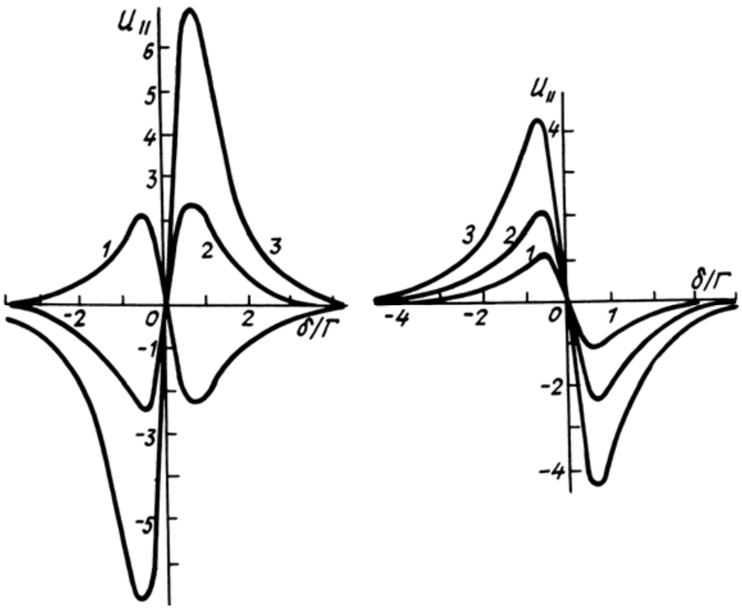

FIG. 2. Spectral behavior of the amplitudes of the signal $U_{\parallel}$
a) vs the orientation W: 1) $W = -0.0991$, *2)* $W = -0.0196$, *and 3)* $W = -0.0291$ *at* $\Gamma = 1.6 \cdot 10^{-9}$ sec^{-1};
b) vs the line width Γ*: 1)* $\Gamma = 3.2 \cdot 10^{9}$ *sec*$^{-1}$ *(b = 0.14). 2)* $\Gamma = 1.6 \cdot 10^{9}$ *sec*$^{-1}$ *(b = 0.28). and 3)* $\Gamma = 0.8 \cdot 10^{9}$ *sec*$^{-1}$*(b = 0.66).*

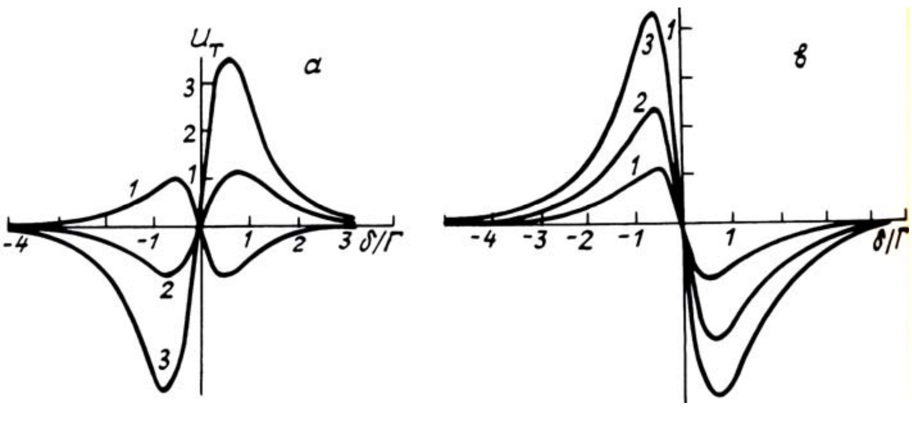

FIG. 3. Spectral behavior of the amplitudes of signal $U_{\perp}$*: for a and b notations see the caption to FIG. 2.*

Figure 3 shows that the amplitude and even the sign of this effect are very sensitive to the change in orientational relaxation of ground and excited states. Therefore, experimental observations of this effect make it possible to study the orientational relaxation of molecules in a laser radiation field.

As is seen from Figs. 2 and 3, $U_{\perp}$ is nearly 2 times as large as $U_{\parallel}$ under the same experimental conditions. But $U_{\perp}$ is more convenient for recording since almost complete discrimination is performed when applying power to the condenser in which the static field is formed.

Thus, the suggested simple experimental technique together with opto-acoustic detection can be used for recording the changes in the optical characteristics of the medium enclosed in the localized volume as a function of changes in the optical characteristics of the laser radiation itself.

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