conditions for the validity of this assumptions have not been made clear.

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Effect of geometry and field intensity on the profiles of saturated-absorption resonances in low-pressure molecular gases

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It is shown theoretically that a unique interaction between the impact and field or transit broadening mechanisms makes the collision line shift dependent on the intensity and the geometry of the field. It is found in the particular case of the $\lambda = 3.39$ μm methane transition that the mechanism affects appreciably the reproducibility of the frequency. The joint influence of recoil and field and transit broadenings on the line shift is also considered. It is shown that allowance for transit effects alters the dependence of the line shift on the field intensity because of the recoil effect.

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1. INTRODUCTION

Modern nonlinear-spectroscopy methods can attain a very accurate agreement between the frequency of a laser and the frequency of the molecular transition. The experiments that have demonstrated the possibility of developing a high-grade unified laser frequency and length standard by this method[1] initiated an intense study of the causes that restrict the accuracy of the reproducibility of the molecular-transition frequency by such a standard. A rather large number of papers have been devoted to a theoretical investigation of the influence of collisions under specific conditions of very low absorbing-gas pressures,[2] saturation-field geometry,[3] quadratic Doppler effect,[4,5] and a number of other factors on the profile of the saturated-absorption resonance. Particular attention was paid to an improvement of the influence of the magnetic hyperfine structure of

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the $F_2^{(2)}$ component of the vibrational-rotational transition $P(7)$ of the ν_3 band of the methane molecule, whose frequency seems at present to be reproducible with the highest accuracy.[4-7] It can be regarded as universally accepted that it is precisely the effects connected with the presence of a magnetic hyperfine structure which make the principal contribution to the inaccuracy of the frequency of the indicated transition. Attempts were therefore made to tie-in the laser frequency with another methane-molecule transition[8,9] that has no hyperfine structure, but has a number of shortcomings in other respects.

The present paper is devoted to an investigation of the joint influence of the electromagnetic-field parameters, collisions with change of velocity, and the recoil effect on the reproducibility of the frequency of an isolated molecular transition when the line has either no hyperfine structure at all or a substantially resolved one. To describe the interaction of the molecular transition with the field of the electromagnetic wave we use for the molecule density matrix an equation in which, within the framework of a unified quantum-mechanical approach, are described both the internal degrees of freedom and the motion of its mass center. This approach is particularly convenient for the description of the recoil effect.

In Secs. 3 and 4 we investigate the influence exerted on the molecular-resonance shift by the specific interaction of the collision broadening of the line with the broadening due to transit effects and saturation. In the pressure region of interest to frequency stabilization, the resultant line shift is of the same order as the shift due to the influence of the magnetic hyperfine structure. The results obtained in these two sections have been briefly reported in Ref. 10.

The influence of the recoil effect on the molecular-resonance line shift following a change of the intensity of the saturating field was investigated in Ref. 11. In Sec. 5 we investigate the change produced in the line shift by the recoil effect under the influence of the joint action of two factors—the change of the intensity and geometry of the field in the resonator (transit effects). It turns out that allowance for transit effects changes considerably the relation obtained in Ref. 11 between the line shift and the saturation parameter.

2. EQUATION FOR THE DENSITY MATRIX

We consider the interaction of an atomic or molecular gas with an electric field $E(R, t)$ having the form of two opposing monochromatic Gaussian beams propagating along the z axis:

$$\mathbf{E}(\mathbf{R}, t)=\int \mathbf{E}(\mathbf{p})\exp(i\mathbf{pR}+i\omega t)\,d\mathbf{p}+\text{c.c.},$$
$$\mathbf{E}(\mathbf{p})=\frac{a_+^2}{8\pi}\mathbf{E}_+\exp\left(-ip_z z_+-\frac{1}{4}a_+^2\mathbf{p}_\perp^2\right)\delta\left[p_z-p_0\left(1-\frac{\mathbf{p}_\perp^2}{2p_0^2}\right)\right]$$
$$+\frac{a_-^2}{8\pi}\mathbf{E}_-\exp\left(-ip_z z_--\frac{1}{4}a_-^2\mathbf{p}_\perp^2\right)\delta\left[p_z+p_0\left(1-\frac{\mathbf{p}_\perp^2}{2p_0^2}\right)\right]. \quad (1)$$

The minimum radius of the caustic of such beams is reached in the planes $z=z_\pm$ and is equal to $a_\pm$; $p_0=\omega/c$, $\mathbf{p}_\perp^2=p_x^2+p_y^2$. We use the following equation for the density matrix

$$\frac{d\rho}{dt}=-\frac{i}{\hbar}[H_0,\rho]+\frac{i}{\hbar}[\mathbf{E}(\mathbf{R}_m,t)\mathbf{d},\rho]+\hat{L}\rho. \quad (2)$$

Here H_0 is the Hamiltonian of the free molecule and includes the kinetic energy of the motion of the molecule as a whole, $\mathbf{d}$ is the molecule dipole-moment operator, $\mathbf{R}_m$ is the coordinate of the molecule mass center, and the term $\hat{L}\rho$ describes the influence of the collisions between the investigated molecule and the perturbing particles. The power absorbed at the point R is given by

$$P(\mathbf{R}, t)=\mathrm{Sp}[\dot{\mathbf{d}}\delta(\mathbf{R}-\mathbf{R}_m)\mathbf{E}(\mathbf{R}, t)\rho]. \quad (3)$$

We consider next the spectral characteristics of the medium near the frequency ω_0 corresponding to the transition $1\to 2$ between nondegenerate states. It is known that in problems of this type we can confine ourselves to the two-level approximation and neglect the oscillations of the density-matrix elements at double the frequency. Substitution of (1) in (3) and subsequent averaging over the time yield

$$P(\mathbf{R})=2\hbar\omega_0\,\mathrm{Re}\int d\mathbf{k}\,d\mathbf{p}\frac{d\mathbf{q}}{(2\pi)^3}\lambda^*(\mathbf{p})e^{i\mathbf{qR}}\rho_{12}(\mathbf{k},\mathbf{k}-\mathbf{p}-\mathbf{q}). \quad (4)$$

Here $\lambda(\mathbf{p})=i\mathbf{d}_{12}\mathbf{E}(\mathbf{p})/\hbar$, $\rho_{12}(\mathbf{k},\mathbf{k}')\equiv\rho_{1\mathbf{k},2\mathbf{k}'}(t)e^{-i\omega t}$, $\rho_{1\mathbf{k},2\mathbf{k}'}(t)$ is the density matrix element in a representation in which the motion of the molecules as a whole is described quantum-mechanically, $\mathbf{k}$ is the wave vector of the motion of the molecule mass center; when the doubled frequencies are neglected, the values of $\rho_{12}(\mathbf{k},\mathbf{k}')$ in the stationary regime are independent of time. Under the experimental conditions, as a rule, the transverse dimension of the cell with the gas greatly exceeds the size of the caustic. Interest attaches therefore to the absorbed power integrating over the transverse coordinates; at the same time it is advantageous to retain the dependence of the absorbed power on the longitudinal coordinate, since this dependence reflects the position of the cell relative to the neck of the caustic. Integrating (4) with respect to x and y we get

$$P(z)=2\hbar\omega_0\,\mathrm{Re}\int d\mathbf{k}\,d\mathbf{p}\int_{-\infty}^{\infty}\frac{dq}{2\pi}e^{iqz}\lambda^*(\mathbf{p})\rho_{12}(\mathbf{k},\mathbf{k}-\mathbf{p}-q\mathbf{n}), \quad (5)$$

where $\mathbf{n}$ is a unit vector along the z axis.

For the time-independent quantities $\rho_{12}(\mathbf{k},\mathbf{k}')$ we get from (2), taking (1) into account, the system of equations

$$i\left(\Delta\omega+\frac{\hbar}{M}\mathbf{kp}-\frac{\hbar}{2M}\mathbf{p}^2\right)\rho_{12}(\mathbf{k},\mathbf{k}-\mathbf{p})=Z_0W(\mathbf{k})\lambda(\mathbf{p})$$
$$+(\hat{L}\rho)_{12}(\mathbf{k},\mathbf{k}-\mathbf{p})+\int d\mathbf{p}'\lambda(\mathbf{p}')[\rho_{22}(\mathbf{k}-\mathbf{p}',\mathbf{k}-\mathbf{p})-\rho_{11}(\mathbf{k},\mathbf{k}-\mathbf{p}+\mathbf{p}')], \quad (6)$$

$$i\left(\frac{\hbar}{M}\mathbf{kp}-\frac{\hbar}{2M}\mathbf{p}^2\right)\rho_{11}(\mathbf{k},\mathbf{k}-\mathbf{p})=(\hat{L}\rho)_{11}(\mathbf{k},\mathbf{k}-\mathbf{p})$$
$$+\int d\mathbf{p}'[\lambda(\mathbf{p}')\rho_{21}(\mathbf{k}-\mathbf{p}',\mathbf{k}-\mathbf{p})+\lambda^*(\mathbf{p}')\rho_{12}(\mathbf{k},\mathbf{k}-\mathbf{p}-\mathbf{p}')], \quad (7)$$

$$i\left(\frac{\hbar}{M}\mathbf{kp}-\frac{\hbar}{2M}\mathbf{p}^2\right)\rho_{22}(\mathbf{k},\mathbf{k}-\mathbf{p})=(\hat{L}\rho)_{22}(\mathbf{k},\mathbf{k}-\mathbf{p})$$
$$-\int d\mathbf{p}'[\lambda(\mathbf{p}')\rho_{21}(\mathbf{k}-\mathbf{p}+\mathbf{p}',\mathbf{k}-\mathbf{p})+\lambda^*(\mathbf{p}')\rho_{12}(\mathbf{k}+\mathbf{p}',\mathbf{k}-\mathbf{p})]. \quad (8)$$

Here $\rho_{ii}(\mathbf{k},\mathbf{k}')=\rho_{i\mathbf{k},i\mathbf{k}'}-\rho^{(0)}_{i\mathbf{k},i\mathbf{k}'}$, $i=1,2$, $\rho^{(0)}_{i\mathbf{k},i\mathbf{k}'}$ is the density matrix element diagonal in the internal quantum numbers in the absence of a field; in the case of the spatially homogeneous problem $\rho^{(0)}_{i\mathbf{k},i\mathbf{k}'}=(2\pi)^3Z_iW(\mathbf{k})\delta(\mathbf{k}-\mathbf{k}')$, where Z_i is the total population of

the level i, $W(\mathbf{k})$ is the Maxwellian distribution function of the molecules in the wave vectors; $Z_0 = Z_2 - Z_1$; $\Delta\omega = \omega = \omega_0$; M is the molecule mass. We represent the collision term in the form

$$(\hat{L}\rho)_{ij}(\mathbf{k}, \mathbf{k}-\mathbf{p}) = -(\Gamma_{ij}+\nu_{ij})\rho_{ij}(\mathbf{k}, \mathbf{k}-\mathbf{p}) + \int A_{ij}(\mathbf{k}, \mathbf{k}')\rho_{ij}(\mathbf{k}', \mathbf{k}'-\mathbf{p})\,d\mathbf{k}'. \quad (9)$$

The quantities Γ_{ij} play the role of the ordinary relaxation parameters in the equations for the density matrix, when no account is taken of the change of the molecule velocity in the collisions. The complex quantity $\Gamma_{12} = \Gamma + i\Delta$ determines the width and the shift of the line in the usual impact broadening collision, while Γ_{11} and Γ_{22} are the reciprocal lifetimes of the molecule on levels 1 and 2. The parameters ν_{11}, ν_{22}, $\nu_{12} = \nu'_{12} + i\nu''_{12}$, and the integral term in (9) with the kernel $A_{ij}(\mathbf{k}, \mathbf{k}')$ reflect the role of collisions with change of velocity, with

$$\nu_{ij}(\mathbf{k}') = \int A_{ij}(\mathbf{k}, \mathbf{k}')\,d\mathbf{k}. \quad (10)$$

The quantities Γ, ν, and A are proportional to the density. They can be connected with the exact values of the amplitudes of the scattering of the molecules in states 1 and 2.[12]

The equations (6)–(8) for the density matrix with the collision term (9) allow us to investigate the shapes of the nonlinear power resonances with allowance for the joint action of the transit effect, the recoil effect, the field broadening, and the collisions. The terms $\hbar\mathbf{p}^2/2M$ in the left-hand sides of (6)–(8) describe the recoil effect. If we neglect these terms, Eqs. (6)–(8) coincide with the equations for the space-time Fourier components of the density matrix elements $\rho_{ij}(\mathbf{R}, \mathbf{v}, t)$, in which the motion of the molecule mass center is described classically.

In nonlinear spectroscopy, use is made of several different methods for the registration of resonances of the saturated absorption of molecules. A cell with the tested gas is placed in the resonator of a linear or ring laser; alternately, the absorption of a cell taken outside the resonator is registered (out of the resonator spectroscopy). In the case of a cell placed in the resonator of the linear laser, it is always necessary to deal with saturation of the molecular transition by the standing-wave field. In the cases of a ring laser and spectroscopy outside the resonator one investigates the absorption of a weak wave in the presence of the strong opposing wave, or else the absorption of two opposing waves with comparable but not exactly equal amplitudes. We shall therefore study hereafter the absorption of opposing waves with arbitrary intensities, so as to make the results equally applicable for all the indicated cases.

3. JOINT ACTION OF TRANSIT EFFECTS AND VELOCITY-CHANGING COLLISIONS

The difficulties encountered in the solution of Eqs. (6)–(8) with the general-form collision integral (9) cannot be overcome. When considering concrete problems it becomes necessary therefore to use a model collision integral. It has become traditional recently to break up the collision integral (more accurately, the arrival term) into two terms:

$$\int A(\mathbf{k}, \mathbf{k}')\rho(\mathbf{k}', \mathbf{k}'+\mathbf{p})\,d\mathbf{k}' = \beta W(\mathbf{k})\int \rho(\mathbf{k}', \mathbf{k}'+\mathbf{p})\,d\mathbf{k}' + \int B(\mathbf{k}, \mathbf{k}')\rho(\mathbf{k}', \mathbf{k}'+\mathbf{p})\,d\mathbf{k}'. \quad (11)$$

The first term reflects the influence of the so called strong collisions, when the collision process is accompanied by large-angle scattering, and it can be assumed approximately that after the collision the scattering matrix, regardless of its form prior to the collision, is a Maxwellian distribution function in the wave vectors. When describing narrow absorption resonances with width much less than the Doppler line width, the role of the first term in (11) is small enough to be neglected, and only the contribution of the strong collisions to the departure term need be retained.

The second term of (11) describes the influence of weak collisions accompanied by scattering through small angles $\tilde{\theta} \ll 1$. We shall assume hereafter that the function $B(\mathbf{k}, \mathbf{k}')$ depends only on the difference of the arguments: $B(\mathbf{k}, \mathbf{k}') = B(\mathbf{k} - \mathbf{k}')$. This calls for the following comments.

As already mentioned, we are interested in a description of narrow absorption resonances near the center of the molecular transition. In this case the density-matrix elements $\rho(\mathbf{k}, \mathbf{k}+\mathbf{p})$ have sharp maxima at very small values k_z, $k_z \ll k_0$, where k_z is a projection of the wave vector on the z axis and k_0 is the mean thermal value of k. At the same time, $\rho(\mathbf{k}, \mathbf{k}+\mathbf{p})$ are smooth functions of the wave-vector components $\mathbf{k}_\perp$ perpendicular to the z direction. On the other hand, the function $B(\mathbf{k}, \mathbf{k}')$ which describes the contribution of the collisions accompanied by scattering through small angles $\tilde{\theta}$, have a sharp maximum at $\mathbf{k} = \mathbf{k}'$. Therefore the arguments $\mathbf{k}_\perp$ and $\mathbf{k}'_\perp$ of the function $B(\mathbf{k}, \mathbf{k}')$ under the integral sign in (11) can be regarded as equal: $B(\mathbf{k}_\perp, k_z; \mathbf{k}'_\perp, k'_z) \approx B(\mathbf{k}_\perp, k_z; \mathbf{k}_\perp, k'_z)$. Next, using the explicit form of the integral term, we can show that at small values of the arguments k_z and k'_z, which are the only ones of importance for our problem, the function B depends actually only on their difference $B(\mathbf{k}, \mathbf{k}') = B(\mathbf{k}_\perp, k_z - k'_z)$. Finally, the remaining slow dependence of B on $\mathbf{k}_\perp$ has the same meaning as the dependence of the relaxation coefficients Γ and ν in (9) on k. Usually this dependence is neglected and k is replaced by the mean value k_0. It is consistent to proceed in the same manner also with the function B, and to set it equal to $B = B(k_0, k_z - k'_z)$. The last equation is equivalent to the assumption made above, that the function B depends only on the difference between the arguments $\mathbf{k}$ and $\mathbf{k}'$.

Thus, the kernel of the collision integral in Eqs. (6)–(8) will be regarded as a difference kernel. We can then obtain the solution of these equations in third-order perturbation theory in the field, For the beam absorption coefficient $\alpha_\pm$, defined as the ratio of the total power absorbed from the beam per unit length in a given section z to the total energy flux of the same beam through this section, we obtain in the Doppler limit

$$\alpha_\pm = \alpha_0 + \alpha_\pm^{(3)},$$

$$\alpha_\pm^{(3)} = -\frac{1}{4}\alpha_0\tau_\pm^2|\varkappa_\pm|^2\int_0^\infty\int_0^\infty d\xi\,d\eta\,F_\pm^{(1)}(\xi, \eta)\,[\exp\{-[\Gamma_{11}+\nu_{11}-B_{11}(\xi)]\eta\} + \exp\{-[\Gamma_{22}+\nu_{22}-B_{22}(\xi)]\eta\}]\exp\{-2[\Gamma+\nu_{12}'-\varphi'(\xi)]\xi\}$$
$$-\frac{1}{4}\alpha_0\tau_\mp^2|\varkappa_\pm|^2\mathrm{Re}\int_0^\infty\int_0^\infty d\xi\,d\eta\,F_\pm^{(2)}(\xi, \eta)\,[\exp\{-[\Gamma_{11}+\nu_{11}-B_{11}(\xi)]\eta - 2[\Gamma_{12}+\nu_{12}+i(\Delta\omega-\delta)-\varphi(\xi)]\xi\} + \exp\{-[\Gamma_{22}+\nu_{22}-B_{22}(\xi)]\eta - 2[\Gamma_{12}+\nu_{12}+i(\Delta\omega+\delta)-\varphi(\xi)]\xi\}]. \quad (12)$$

Here α_0 is the linear coefficient of absorption, $\varkappa_\pm = \mathbf{d}_{12}\mathbf{E}_\pm/\hbar$, $\tau_\pm = \alpha_\pm/\nu_0$ is the time of flight of the molecule through the light beam, v_0 is the mean thermal velocity of the molecule, and $\delta = (\hbar/2M)\omega^2/c^2$ is the splitting due to the recoil effect. The role of the velocity-changing collisions is demonstrated by the functions

$$\varphi(\zeta) = \varphi'(\zeta) + i\varphi''(\zeta) = \int d(\Delta k_z) \frac{\sin(\Delta\omega_D \zeta k_0^{-1} \Delta k_z)}{\Delta\omega_D \zeta k_0^{-1} \Delta k_z} \bar{B}_{12}(\Delta k_z), \tag{13a}$$

$$B_{ii}(\zeta) = \int_{-\infty}^{\infty} d(\Delta k_z) \exp\left(i\Delta\omega_D \zeta \frac{\Delta k_z}{k_0} \right) \bar{B}_{ii}(\Delta k_z), \tag{13b}$$

$$\bar{B}(\Delta k_z) = \bar{B}(k_z - k_z') = \int d\mathbf{k}_\perp B(\mathbf{k} - \mathbf{k}'), \tag{13c}$$

where $\Delta\omega_D = p_0 v_0$ is the Doppler line width. The influence of the field geometry is described by the functions

$$F_\pm^{(1)} = \mathrm{Re}\{[|l_\pm|^2\tau_\pm^2 + |l_\pm|^2(1+l_\pm^2)\zeta^2 + 2l_\pm\zeta\eta + \eta^2]^{-1}\}, \tag{14a}$$

$$F_\pm^{(2)} = \frac{a_\pm^4}{a_\mp^4}\left\{ \frac{1}{2}(\tau_+^2|l_+|^2 + \tau_-^2|l_-|^2) + \frac{1}{4}\left[(\tau_+^2|l_+|^2 + \tau_-^2|l_-|^2) \frac{\tau_+^2 + \tau_-^2}{\tau_+^2\tau_-^2} + (l_\mp^* + l_\pm)^2 \right] \zeta^2 + (l_\mp^* + l_\pm)\zeta\eta + \eta^2 \right\}^{-1}, \tag{14b}$$

where $l_\pm = 1 \pm 2i(z - z_\pm)/p_0 a_\pm^2$. Neglecting the change of the atom velocity in the collisions ($B = 0$, $\varphi = 0$) we obtain from (12) the result of Ref. 3; if in addition we neglect the curvature of the wave fronts of the opposing beams, $l_\pm = 1$, then (12) coincides with the expression obtained in Ref. 13.

Equation (12) contains the three possible causes of the absorption-resonance shift. The first is the result of the joint action of the transit effects and the recoil effect and was investigated in detail in Ref. 14. The second cause of the shift is allowance for the curvature of the wave fronts $l_\pm \neq 1$, which is made in Ref. 3. In the present article we investigate the third cause, which is a result of the interaction of the velocity-changing collisions and the transit effects. We therefore neglect in the present section and in the next section the recoil effect and the curvature of the wavefront $l_\pm = 1$, and assume that $a_+ = a_-$, $\tau_+ = \tau_- = \tau_0$. Here $F_\pm^{(1)} = F_\pm^{(2)} = F = (\tau_0^2 + 2\zeta^2 + 2\zeta\eta + \eta^2)^{-1}$. After these simplifications Eq. (12) is still quite complicated, so that the shift of the resonance maximum can be investigated only numerically. In the case of particular applied interest, however, that of vibrational-rotational transitions of molecules such as CH_4, OsO_4, SF_6, further simplification is possible. In this case the collision line shift is much less than the width: $\Delta \ll \Gamma$, $\nu_{12}'' \ll \nu_{12}'$, $\varphi'' \ll \varphi'$, and consequently $\Gamma \approx \Gamma_{11} \approx \Gamma_{22}$, $\bar{B}_{11} \approx \bar{B}_{22} \approx B_{12}'$, $\nu_{11} \approx \nu_{22} \approx \nu_{12}' = \nu$, $\beta_{12}' \approx \beta_{11} \approx \beta_{22} = \beta$. Therefore in the vicinity of the maximum of the resonance the integrand in (12) can be expanded in terms of the small parameters $\Gamma^{-1}\Delta\omega$, $\Gamma^{-1}\Delta$, ν_{12}''/Γ, φ''/Γ Differentiating the result with respect to ω, we obtain for the position of the maximum with the resonance

$$\Delta\omega_M = -\Delta - \nu_{12}'' + I_1/I_2, \tag{15}$$

$$I_1 = \int_0^\infty\int_0^\infty d\zeta\, d\eta\, \zeta^2 F(\zeta,\eta)\varphi''(\zeta)\exp[-\chi(\zeta,\eta)], \tag{16a}$$

$$I_2 = \int_0^\infty\int_0^\infty d\zeta\, d\eta\, \zeta^2 F(\zeta,\eta)\exp[-\chi(\zeta,\eta)], \tag{16b}$$

$$\chi(\zeta,\eta) = 2(\Gamma+\nu)\zeta + (\Gamma+\nu)\eta - B_{11}(\zeta)\eta - 2\varphi'(\zeta)\zeta. \tag{16c}$$

The integrals I_1 and I_2 depend on the relation between the line impact-broadening parameters and the transit time τ_0. It is seen therefore from (15) that the collision shift of the resonance depends on the transit width. We investigate first this dependence at large and small values of the density of the perturbing gas.

We recall that the kernels of the collision integral $\bar{B}_{12}(\Delta k_z)$ and $\bar{B}_{ii}(\Delta k_z)$ describe the influence of collisions accompanied by a small change of velocity, and the difference from zero in the region $\Delta k_z \lesssim k_0\bar{\theta}$. Therefore, as seen from (13), the functions $\varphi(\zeta)$ and $B(\zeta)$ differ from zero in the region $\zeta \lesssim 1/\bar{\theta}\Delta\omega_D$, with $\varphi(\zeta = 0) = \nu_{12} - B_{12}$ and $B(\zeta = 0) = \nu - \beta$. At large values of $\zeta \gg 1/\bar{\theta}\Delta\omega_D$, the function $\varphi(\zeta)$ takes the form

$$\varphi(\zeta) = \frac{\pi}{\zeta}\frac{\bar{B}_{12}(0)k_0}{\Delta\omega_D} = \frac{\pi}{\zeta}\frac{\nu_{12} - \beta_{12}}{\bar{\theta}\Delta\omega_D}, \tag{17}$$

and the rate at which the function $B(\zeta)$ tends to zero depends on the concrete form of the kernel.

At large densities, when the parameters Γ and ν are large, $\Gamma, \nu \gg \bar{\theta}\Delta\omega_D$, the main contribution to the integrals in (16) is made by the region of small values of $\zeta \ll 1/\bar{\theta}\Delta\omega_D$. We must therefore put under the integral sign $\varphi(\zeta) = \nu_{12} - \beta_{12}$, $B(\zeta) = \nu - \beta$. The shift of the line maximum is then $\Delta\omega_M = -\Delta - \beta_{12}$ and does not depend on the transit width.

At lower densities, when the parameters Γ and ν are small, $\Gamma, \nu \ll \bar{\theta}\Delta\omega_D$, the main contribution to the integral in (16) is made by the region of large values $\zeta \gg 1/\bar{\theta}\Delta\omega_D$. Putting in this case $B = \varphi' = 0$ and using for φ'' expression (17), we get

$$\Delta\omega_M = -\Delta - \nu_{12}'' + (\nu_{12}'' - \beta_{12}'')\frac{\Gamma+\nu}{\bar{\theta}\Delta\omega_D} g_1([\Gamma+\nu]\tau_0), \tag{18}$$

$$g_1(x) = \int_0^\infty\int_0^\infty du\, dv \frac{2u\exp[-(u+v)]}{2x^2 + u^2 + 2uv + 2v^2}\left(\int_0^\infty\int_0^\infty du\, dv \frac{u^2\exp[-(u+v)]}{2x^2 + u^2 + 2uv + 2v^2} \right)^{-1}.$$

A plot of the function $g_1(x)$ is shown in Fig. 1. Thus, in first order in the small parameter $(\Gamma+\nu)/\bar{\theta}\Delta\omega_D$ the impact line shift becomes dependent on the transit time.

In the intermediate pressure region, to find the shift it is necessary to know the explicit form of the kernel of the collisions integral and the relation between the parameters $\Gamma + \beta$ and $\nu + \Gamma$, $\nu_{12}'' + \Delta$ and $\beta_{12}'' + \Delta$, which are determined by the specifics of the investigated transition. By way of example, Fig. 2 shows the dependence of the shift of the line maximum, referred to the quantity $-\Delta - \beta_{12}''$, on the density of the absorbing gas at different values of the transit time τ_0. The calculations were made for the broadening-constant ratios characteristic of the broadening of the $F_2^{(2)}$ component of the vibrational-rotational line $P(7)$ of the ν_3 band of methane

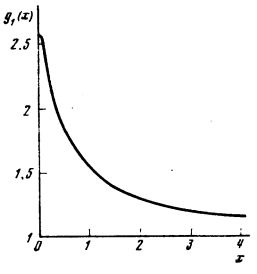

FIG. 1.

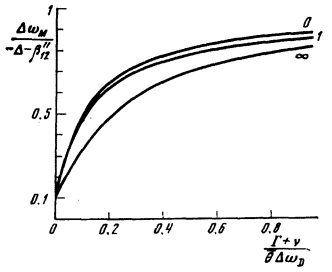

FIG. 2.

($\lambda = 3.39$ μm), namely $(\Gamma+\nu)/(\Gamma+\beta) = 3$,[15] $(\Delta+\beta_{12}'')/(\Delta+\nu_{12}'') = 10$.[16] The collision-integral kernel was approximated, following Ref. 17, by

$$B(\Delta k_z) = \frac{\nu-\beta}{k_0\bar{\theta}} \exp\left(-\frac{2|\Delta k_z|}{k_0\bar{\theta}}\right).$$

The numbers near the curves of Fig. 2 indicate the values of the ratio $\tau_0/(\Gamma+\nu)$.

The dependence of the impact line shift on the transit time τ_0 can be illustratively interpreted. It is known that the overwhelming contribution to saturated-absorption resonance is made by a small group of molecules whose wave-vector projections on the direction of propagation of the field are concentrated in a narrow region near the zero values of k_z determined from the condition $\hbar p_0 |\Delta k_z|/M \lesssim \gamma$, where γ is the homogeneous line width. If the resonance width γ is so small, $\gamma \ll \hbar p_0 k_0 \bar{\theta}/M \equiv \bar{\theta}\Delta\omega_D$, that scattering through an angle $\bar{\theta} \ll 1$ takes the molecule out of this region, then the change of the molecule velocity by the collisions leads to an additional shift of the broadening and shift of the resonance, so that

$$\gamma = 1/\tau_0 + \Gamma + \nu, \quad \Delta\omega_M = -\Delta - \nu_{12}'', \quad \gamma \ll \bar{\theta}\Delta\omega_D, \tag{19}$$

where $1/\tau_0$ reflects phenomenologically the contribution made to the broadening by the transit of the molecule through the light beam. In the other limiting case, $\gamma \gg \bar{\theta}\Delta\omega_D$, the change of the molecule velocity in the collisions does not take the molecule outside the region of resonant interaction with the field, and elastic scattering ceases to contribute to the width and shift of the resonance:

$$\gamma = 1/\tau_0 + \Gamma + \beta, \quad \Delta\omega_M = -\Delta - \beta_{12}'', \quad \gamma \gg \bar{\theta}\Delta\omega_D. \tag{20}$$

When the transit time τ_0 changes and the gas density is constant, a gradual transition takes place from (19) to (20), meaning a change of the line shift with changing τ_0 at constant density.

It is of interest to note that the foregoing reasoning indicates that at sufficiently strong broadening the transit effects, when $1/\tau_0 \gg \bar{\theta}\Delta\omega_D$, so that the condition $\gamma \gg \bar{\theta}\Delta\omega_D$ is always satisfied, should cause the shift to be described, as it were, by Eq. (20) and to be a linear function of the gas density in the entire pressure region. It is seen from Fig. 2, however, that this conclusion is wrong. The function $\Delta\omega_M$ differs from a linear one at all values of the transit time τ_0. This is due to the increase of the contribution made to the resonance by the slow molecules when τ_0 decreases, a fact that cannot be reflected, naturally, by the phenomenologically introduced relaxation constant $1/\tau_0$.

4. JOINT ACTION OF FIELD BROADENING AND VELOCITY-CHANGING COLLISIONS

The qualitative explanation of the dependence of the impact line broadening on the transit width can be used without modification to explain the line shift that results from field broadening. However, a quantitative investigation of this effect entails a number of difficulties. It is known that the field-broadening effect is not contained in the solutions of Eqs. (6)–(8), which are obtained in third-order perturbation theory in the field. The most direct way of jointly taking into account the field broadening and the collisions is to continue the successive-approximation procedure to include the fifth order. Apart from the fact that the equations obtained in this manner are very cumbersone, their applicability is limited since the perturbation-theory series begins to diverge already at sufficiently small values of the saturation parameter $(|\varkappa|/\gamma)^2 < 0.25$, whereas a typical experimental value of this parameter is $(|\varkappa|/\gamma)^2 \sim 1$. The possibility of obtaining a more exact solution of Eqs. (6)–(8), without resorting to expansion in a perturbation-theory series, and with a collision integral of the form (11), is practically nonexistent even in the case of the difference kernel. We therefore confine ourselves primarily to the case when the transit times are long enough, $1/\tau_0 \ll \gamma$, so that the transit broadening can be neglected; this reduces formally to neglect of the terms $\mathbf{k}_\perp \cdot \mathbf{p}_\perp$ in the scalar product $\mathbf{k}\cdot\mathbf{p}$ in the left sides of (6)–(8). In addition, we neglect the recoil effect [the term $\hbar\mathbf{p}^2/2M$ in Eqs. (6)–(8)] and the curvature of the wave front [the term $\mathbf{p}_\perp^2/2p_0^2$ in the argument of the delta function in (1)]. Next, taking the Fourier transforms of the functions $\rho_{ij}(\mathbf{k}, \mathbf{k}-\mathbf{p})$ with respect to the argument $\mathbf{p}_\perp$ and assuming that the $W(\mathbf{k})$ is a sufficiently smooth function of the argument $\mathbf{k}$, so that $\rho_{ij}(\mathbf{k}-\mathbf{p}', \mathbf{k}-\mathbf{p}) = \rho_{ij}(\mathbf{k}, \mathbf{k}-\mathbf{p}+\mathbf{p}')$, we obtain in place of (6)

$$\begin{aligned} i\left(\Delta\omega + \frac{\hbar}{M}k_z p_z\right)\tilde{\rho}_{12}(\mathbf{k}, p_z, \mathbf{r}_\perp) = Z_0 W(\mathbf{k}) \Big[&\varkappa_+ \exp\left(-\frac{\mathbf{r}_\perp^2}{a_+^2}\right)\delta(p_z - p_0) \\ &+ \varkappa_- \exp\left(-\frac{\mathbf{r}_\perp^2}{a_-^2}\right)\delta(p_z + p_0)\Big] \\ + \varkappa_+ \exp\left(-\frac{\mathbf{r}_\perp^2}{a_+^2}\right)&[\tilde{\rho}_{22}(\mathbf{k}, p_z - p_0, \mathbf{r}_\perp) - \tilde{\rho}_{11}(\mathbf{k}, p_z - p_0, \mathbf{r}_\perp)] \\ + \varkappa_- \exp\left(-\frac{\mathbf{r}_\perp^2}{a_-^2}\right)&[\tilde{\rho}_{22}(\mathbf{k}, p_0 + p_z, \mathbf{r}_\perp) - \tilde{\rho}_{11}(\mathbf{k}, p_z + p_0, \mathbf{r}_\perp)] \\ - (\Gamma_{12} + \nu_{12})\tilde{\rho}_{12}(\mathbf{k}, p_z, \mathbf{r}_\perp) &+ \int B_{12}(\mathbf{k}-\mathbf{k}')\tilde{\rho}_{12}(\mathbf{k}', p_z, \mathbf{r}_\perp)\, d\mathbf{k}', \end{aligned} \tag{21}$$

$$\tilde{\rho}_{ij}(\mathbf{k}, p_z, \mathbf{r}_\perp) = \int d\mathbf{p}_\perp \exp(i\mathbf{p}_\perp \mathbf{r}_\perp)\rho_{ij}(\mathbf{k}, \mathbf{k}-\mathbf{p})\, d\mathbf{p}_\perp. \tag{22}$$

Equations (7) and (8) are transformed similarly. We note that if we seek $\tilde{\rho}_{12}$ in the form $\tilde{\rho}_{12} = \tilde{\rho}_{12}^{(+)}\delta(p_z - p_0) + \tilde{\rho}_{12}^{(-)}\delta(p_z + p_0)$, then we obtain for $\tilde{\rho}_{12}^{(+)}$ and $\tilde{\rho}_{12}^{(-)}$ equations that agree with those used in Ref. 2, except that the dependence of the field on the coordinate $\mathbf{r}_\perp$ is retained in (21). Just as in Ref. 2, we seek the solution in the form

$$\tilde{\rho}_{ij}(\mathbf{k}, p_z, \mathbf{r}_\perp) = \psi_{ij}(k_z, p_z, r_\perp) W_\perp(\mathbf{k}_\perp), \tag{23}$$

where $W_\perp(\mathbf{k}_\perp)$ is the Maxwellian distribution function with respect to the perpendicular components of the vector $\mathbf{k}$. Substituting (23) in the integral term of (21), we can take the smooth function $W_\perp(\mathbf{k}_\perp)$ outside the integral sign at the point of the maximum of the kernel at

$\mathbf{k}=\mathbf{k}'$:

$$\int B_{ij}(\mathbf{k}-\mathbf{k}')W_{\perp}(\mathbf{k}_{\perp}')\psi_{ij}(k_z', p_z, \mathbf{r}_{\perp})d\mathbf{k}' = W_{\perp}(\mathbf{k}_{\perp})\int B_{ij}(k_z-k_z')\psi_{ij}(k_z', p_z, \mathbf{r}_{\perp})dk_z'. \quad (24)$$

The function $W_{\perp}(\mathbf{k}_{\perp})$ is then cancelled from the right- and left-sides of the equations.

Owing to the presence of the integral collision term, the system of equations for ψ can be solved as before only by expansion in a perturbation-theory series in the field. We confine ourselves therefore to the case of low densities of the perturbing gas $\Gamma+\nu \ll \bar{\theta}\Delta\omega_D$ and sufficiently small intensities of the saturating field $|\varkappa| \ll \bar{\theta}\Delta\omega_D$. These conditions limit the resonance width γ, which remains smaller than $\bar{\theta}\Delta\omega_D$; at the same time, the saturation parameter $|\varkappa/(\Gamma+\nu)|^2$ remains arbitrary, so that the relative contribution of the field broadening to the resonance width can be large.

The inequality $\gamma \ll \bar{\theta}\Delta\omega_D$ means that the function ψ is a steeper function of k_z than the kernel $\tilde{B}(k_z-k_z')$. The function B in the integral (24) can therefore be taken outside the integral sign at the point of the maximum of ψ at $k_z=0$:

$$\int \tilde{B}_{ij}(k_z-k_z')\psi_{ij}(k_z', p_z, \mathbf{r}_{\perp})dk_z' = B_{ij}(0)\int \psi_{ij}(k_z', p_z, \mathbf{r}_{\perp})dk_z' \equiv \frac{\nu_{ij}-\beta_{ij}}{\bar{\theta}\Delta\omega_D}\int \psi_{ij}(k_z', p_z, \mathbf{r}_{\perp})dk_z'.$$

Once these simplifications are made, only the spatial burnout, reflected in (21) by the presence of the terms $\rho_{ii}(\mathbf{k}, 2p_0, \mathbf{r}_{\perp})$ in the right-hand side of (21), prevents us from obtaining the exact solutions. Only in the case of absorption of a weak wave in the presence of a strong opposing wave ($|\varkappa_-| \ll |\varkappa_+|$, $|\varkappa_-|^2/(\Gamma+\nu)^2 \ll 1$) can be effects of spatial burnout be taken into account exactly. The absorption coefficient of the weak wave is then equal to

$$\frac{\alpha_-}{\alpha_0} = \frac{2}{\pi a_-^2}\mathrm{Re}\int d\mathbf{r}_{\perp}\exp\left(-\frac{2\mathbf{r}_{\perp}^2}{a_-^2}\right)\left\{1+\pi\frac{\nu-\beta}{\bar{\theta}\Delta\omega_D}\left(1-\frac{\Gamma+\nu}{\Gamma}\frac{I}{(1+I)^{1/2}}\right) - \frac{I}{(1+I)^{1/2}(1+(1+I)^{1/2}+2i\Omega)}\left[1-\frac{I}{1+(1+I)^{1/2}}f(i(1+I)^{1/2}-\Omega)\right]\cdot\left[1+\pi\frac{\nu-\beta}{\bar{\theta}\Delta\omega_D}\left(\frac{1+(1+I)^{1/2}}{(1+I)^{1/2}}-\frac{I}{(1+I)^{1/2}}\frac{\Gamma+\nu}{\Gamma}\right)+2\pi i\frac{\nu_{12}''-\beta_{12}''}{\bar{\theta}\Delta\omega_D}\right]\right\}, \quad (25)$$

$$I = \frac{|\varkappa_+|^2}{(\Gamma+\nu)^2}\exp\left(-\frac{2\mathbf{r}_{\perp}^2}{a_+^2}\right), \quad f(x) = \frac{(1-ix)(1-i\Omega-3ix)}{(1-2ix)[(1+i\Omega-ix)(1-i\Omega-3ix)+I]}, \quad \Omega=(\Delta\omega+\Delta)/(\Gamma+\nu).$$

In the derivation of (25) we have assumed, as before, that

$$\Gamma=\Gamma_{11}=\Gamma_{22}, \qquad \nu_{12}'=\nu_{11}=\nu_{22}=\nu, \qquad \beta_{12}'=\beta_{11}=\beta_{22}=\beta.$$

To calculate the line shift we can expand (25) in powers of the small parameter Ω, equate the derivative $d\alpha_-/d(\Delta\omega)=0$ to zero, and integrate. As a result we get

$$\Delta\omega_M = -\Delta-\nu_{12}''+(\nu_{12}''-\beta_{12}'')\frac{\pi(\Gamma+\nu)}{\bar{\theta}\Delta\omega_D}g_2(I_0). \quad (26)$$

where $I_0=|\varkappa_+|^2/(\Gamma+\nu)^2$. The analytic expression for the function $g_2(x)$ is quite unwieldy, and we confine ourselves only to its plots in Fig. 3. Curve 1 shows the function $g_2(x)$ at $a_-=a_+$, curve 2 shows the function $g_2(x)$ at $a_+=a_-$ but without allowance for the spatial

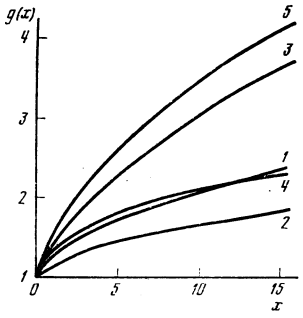

FIG. 3.

burnout, and curve 3 shows the function $g_2(x)$ at $a_- \ll a_+$. In the last case $a_- \ll a_+$ the distribution of the fields along the coordinate perpendicular to the resonator axis is of no importance whatever, since this result corresponds to the approximation of opposing plane waves. Comparison of curves 1 and 2 shows that the spatial burnout does not influence strongly the result (26).

A result similar to (26) can be obtained also in the case of the interaction of two strong waves of equal intensity (the Lamb dip). In this case, however, to obtain the result it is necessary to neglect the spatial burnout and to assume $a_+=a_-$. For the shift of the maximum we get

$$\Delta\omega_M = -\Delta-\nu_{12}''+(\nu_{12}''-\beta_{12}'')\frac{\pi(\Gamma+\nu)}{\bar{\theta}\Delta\omega_D}g_3(I_0). \quad (27)$$

In the case when the transverse dimension of the absorbing cell is much larger than the dimension of the caustic of the Gaussian beam, the function $g_3(x)$ takes the form

$$g_3(x)=(1+(1+2x)^{1/2})^{-1}x^{-2}(1+2x)^{1/2}\ln[1+x^{-2}(1+(1+2x)^{1/2})^{-2}(1+2x)^{-1/2}].$$

The plot of $g_3(x)$ is in this case the curve 4 of Fig. 3. In the opposite case, when the transverse dimension of the cell is much smaller than the dimension of the caustic we have $g_3(x)=(1+2x)^{1/2}(2+2(1+2x)^{1/2})\times(1+3(1+2x)^{1/2})^{-1}$ (curve 5 of Fig. 3).

5. JOINT ACTION OF TRANSIT EFFECTS, RECOIL EFFECTS, AND SATURATION

An obvious method of decreasing the role of the collisions that lead to a shift of the resonance is to decrease the pressure of the absorbing gas. At very low pressures, however, a new effect comes into play and leads to a shift of the resonance, namely the splitting of the resonance into two components as a result of the recoil effect. As can be seen from (14) (see also Ref. 13), at unequal lifetimes of the levels of the working transition the components of the doublet have different intensities. Under typical experimental conditions the doublet is not resolved, and the vertex of the resultant line contour is shifted relative to the central frequency of the transition. The magnitude of the shift depends on the ratio of the intensities of the components and on their widths, and as a result also on the transit time τ_0 and on the intensity of the field in the resonator.

In the case of weak saturation, the field broadening can be neglected, and the influence of the transit time τ_0 can be taken into account within the framework of

third-order perturbation theory by using Eq. (14). A detailed analysis of the shift in this approximation was presented in Ref. 14. To investigate the influence of the field broadening, the third-order approximation is insufficient. The corresponding calculations in fifth-order perturbation theory was carried out in Ref. 11, but without allowance for the transit time.

Equations (6)–(8) make it possible to calculate the absorption coefficient α and take simultaneously into account the recoil effect and the transit broadening. As will be shown below, allowance for the transit effects can alter substantially the result obtained in Ref. 11. The calculation was performed for a standing wave, neglecting the wave-front curvature and the velocity-change in collisions, in fifth-order perturbation theory in the field:

$$\alpha=\alpha_0+\alpha^{(3)}+\alpha^{(5)}.$$

The result $\alpha^{(3)}$ of third-order perturbation theory can be obtained from Eq. (12), in which we must put $B=0$, $\varphi=0$, $l_\pm=1$, $a_+=a_-$, $\varkappa_+=\varkappa_-=\varkappa$. The fifth-order perturbation-theory correction is given by

$$\alpha^{(5)}=\alpha_0\frac{|\varkappa|^4}{3}\int_0^\infty\int\int\int d\zeta_1\,d\zeta_2\,d\eta_1\,d\eta_2\exp[-2\gamma_{12}(\zeta_1+\zeta_2)]\cdot$$

$$\cdot\sum_{i,j=1}^{2}\exp[-\Gamma_i\eta_1-\Gamma_j\eta_2](G_{ij}^{\mathrm{I}}+G_{ij}^{\mathrm{II}}\exp[-2\gamma_{12}\eta_2]). \qquad (28)$$

The function G_{ij}^{I} describes the joint action of the population burnout and the recoil effect, and is equal to

$$G_{ij}^{\mathrm{I}}=K\{f_1(\Omega_i\zeta_1+2[j-i][\zeta_1+\zeta_2]\delta,\ \Omega_j\zeta_2)$$
$$+f_1(\Omega_j\zeta_1-2[j-i][\zeta_1+\zeta_2]\delta,\ \Omega_j\zeta_2)\}+Nf_1(\Omega_i\zeta_1,\ \Omega_j\zeta_2),$$

where $\Gamma_i=\Gamma_{ii}+\nu_{ii}$, $\gamma_{12}=\Gamma+\nu'_{12}$, $\Omega_1=\Delta\omega-\delta$, $\Omega_2=\Delta\omega+\delta$, $f_1(x,y)=4\cos x\cos y\times\cos(x+y)$. The function G_{ij}^{II} appears as a result of allowance for spatial burnout effects:

$$G_{ij}^{\mathrm{II}}=2Lf_2(\Omega_i\zeta_1+[(-1)^i+(-1)^j](2\eta_2+\zeta_2)\delta,\ \Omega_i\zeta_2,\ \Omega_i(2\eta_2+\zeta_1+\zeta_2)),$$
$$f_2(x,\ y,\ z)=4\cos x\cos y\cos z.$$

In the absence of transit effects $\tau_0\to\infty$ the coefficients K, N, and L are equal to unity. Allowance for the finite transit time leads to the expressions

$$K=\left[1+\frac{2}{3\tau_0^2}D\right]^{-1},\quad N=\left[1+\frac{2}{3\tau_0^2}(D+\zeta_2(2\zeta_2+2\zeta_1+2\eta_2+\eta_1))\right]^{-1},$$

$$L=\left\{1+\frac{2}{3\tau_0^2}[D+\eta_2(6\zeta_2+8\zeta_1+7\eta_2+4\eta_1)]\right\}^{-1},$$

$$D=2\eta_1^2+2\eta_2^2+5\zeta_1^2+3\zeta_2^2+2\eta_1\eta_2+5\eta_1\zeta_1+3\eta_1\zeta_2+4\eta_2\zeta_1+3\eta_2\zeta_2+6\zeta_1\zeta_2.$$

Neglecting the recoil effects, $\delta=0$, Eq. (28) differs only in form from the expression given in Ref. 18. The disparity between (28) at $\tau_0\to\infty$ and the result of Ref. 11 is apparently due to a misprint in this reference.

To calculate the line shift we proceed in the following manner. We assume that the splitting due to the recoil effect is much less than the width of the doublet components, and expand $\alpha^{(3)}$ and $\alpha^{(5)}$ in the small parameters $\Delta\omega/\gamma_{12}$ and δ/γ_{12}. After differentiating we obtain for the maximum of the line a rather cumbersome expression that contains quadruple integrals. In the limiting case $\tau_0\to\infty$ the result can be obtained in analytic form:

$$\Delta\omega_{\varkappa}=\delta\frac{\Gamma_2-\Gamma_1}{\Gamma_2+\Gamma_1}\left[1-\frac{|\varkappa|^2}{3}\frac{1}{\gamma_{12}(\Gamma_2-\Gamma_1)}\left(\frac{(2\gamma_{12}-\Gamma_1)\Gamma_2}{(2\gamma_{12}+\Gamma_1)^2}-\frac{(2\gamma_{12}-\Gamma_2)\Gamma_1}{(2\gamma_{12}+\Gamma_2)^2}\right)\right]. \qquad (29)$$

Equation (29), apart from the substitution $|\varkappa|^2\to\frac{3}{2}|\varkappa|^2$ agrees with the expression given in Ref. 11. The difference between the coefficients of $|\varkappa|^2$ is due to allowance for the Gaussian field distributions. At $\Gamma_1=\Gamma_2$ there is no line shift. It is interesting to note that the dependence of the line shift on the field intensity as $\tau_0\to\infty$ is due entirely to allowance for the effects of spatial burnout. If we put in (28) G_{ij}^{II}, then the coefficient of $|\varkappa|^2$ in (29) vanishes, i.e., this dependence disappears. At finite values of τ_0 the situation changes; in this case both the spatial burnout and the population burnout (the function G_{ij}^{I}) make, generally speaking, comparable contributions to the line shift.

When account is taken of the transit time, the resonance shift can be investigated only numerically. As a measure of the dependence of the line shift on the saturation parameter

$$I_0=\frac{2|\varkappa|^2}{\gamma_{12}}\left(\frac{1}{\Gamma_1}+\frac{1}{\Gamma_2}\right)$$

it is convenient to use the derivative $d(\Delta\omega_{\mathrm{M}})/dI_0$ at $I_0=0$. This quantity, in units of δ, is shown in Fig. 4 as a function of the ratio Γ_2/Γ_1 for different values of the parameter $\Gamma_1\tau_0$. We have assumed here that the relation $\gamma_{12}=(\Gamma_1+\Gamma_2)/2$ is satisfied. For radiative broadening this equality is satisfied exactly; for impact broadening of vibrational–rotational transitions of the molecules at low pressures $\gamma_{12}\ll\bar{\theta}\Delta\omega_D$ it is satisfied approximately but with a high degree of accuracy, since the scattering amplitudes in the upper and lower states are practically the same in this case. The dashed curve in Fig. 4 corresponds to the case $\tau_0\to\infty$ and is a plot of Eq. (29). It is seen from Fig. 4 that allowance for the finite transit time leads in general to a reversal of the sign of the derivative $d(\Delta\omega_{\mathrm{M}})/dI_0$, so that for any ratio of the values of Γ_1 and Γ_2 it is possible to choose a transit time τ_0 such that the dependence of the line shift on the saturating power is practically nonexistent.

6. CONCLUSION

For a quantitative estimate of the resonance shift due to the effects considered in the article, it is necessary to have complete information on the broadening constants of the corresponding transition. By now, the most detailed investigations were made of the broadening of the $F_2^{(2)}$ component of the vibrational–rotational transition $P(7)$ of the ν_3 band of methane ($\lambda=3.39\ \mu$m),

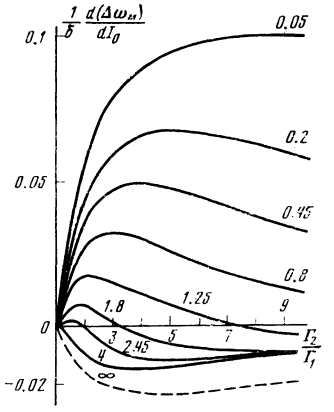

FIG. 4.

which is of particular interest for frequency stabilization. The width of the saturated-absorption resonance on this transition at various methane pressures p was experimentally measured in Ref. 15, from which it follows that $d(\Gamma+\beta)/dp \approx 5\times10^6$ Hz/Torr, $d(\nu+\Gamma)/dp \approx 20\times10^6$ Hz/Torr, and $\bar{\theta}\Delta\omega_D \approx 5\times10^5$ Hz. The line-shift parameters are given in Ref. 16, namely $d(\Delta+\nu_{12}'')/dp \approx -10^4$ and $d(\Delta+\beta_{12}'')/dp \approx -10^5$ Hz/Torr.

We estimate now the line shift due to the change of the transit time at a pressure typical of experiment, $p=4$ mTorr. At this pressure, the impact resonance width is $\Gamma+\nu \approx 8\times10^4$ Hz. Since this width is much less than the value $\bar{\theta}\Delta\omega_D$, we can estimate the line shift due to the joint action of the impact and transit broadenings by using Eq. (18). When τ_0 changes by a factor of 2, so that the parameter $(\Gamma+\nu)\tau_0$ changes from 1 to 2, the resonance shifts by approximately 40 Hz. The value of shift due to the quadratic Doppler effect and to the magnetic hyperfine structure of the line can be estimated by using the results of Ref. 6. The shift under approximately the same conditions is −20 and 10 Hz, respectively. Thus, at $p=4$ mTorr the dominant contribution to the resultant resonance shift, when the transit time is varied, is made by the collisions. When the pressure is decreased, as is seen from Eq. (18), the contribution of the collisions decreases in proportion to the square of the pressure, so that in the pressure region $p \lesssim 1$ mTorr the main contribution to the change of the position of the vertex of the resonance is made by the quadratic Doppler effect and by the magnetic hyperfine structure.

We estimate now the resonance shift when the saturation parameter I_0 changes from zero to unity at the same pressure $p=4$ mTorr. For a standing wave [Eq. (27)] we find that the resonance shifts by approximately 70 Hz. The shift due to the hyperfine structure is in this case approximately equal to −400 Hz,[7] and the shift due to the quadratic Doppler effect is - 30 Hz. Thus, for the $F_2^{(2)}$ component the main contribution to the dependence of the position of the maximum of the resonance on the saturation parameter is made by the magnetic structure of the line. Therefore in Refs. 8 and 9 they used for frequency stabilization the E component of the very same vibrational-rotational methane transition that has no magnetic hyperfine structure. The shift of the resonance maximum with changing saturation power, measured in Ref. 9, turned out to be smaller by only a factor of 4 than the shift of the $F_2^{(2)}$ component at the same pressure. So large a shift cannot be attributed to the quadratic Doppler effect. It appears that this shift is caused by the effect discussed in Sec. 4. A detailed calculation of the shift is difficult, since there is no information on the line-broadening parameters.

The influence of the recoil effect on the resonance shift in methane in the pressure region $p \gtrsim 1$ mTorr is negligibly small, since the scattering amplitudes in collisions in the upper and lower states are practically equal. However, at lower pressures, when the impact width of the resonance becomes commensurate with the radiative width, the recoil effect may exert a discernible influence on the shift. For example, at $p=0.1$ mTorr, $(\Gamma+\nu)\tau_0=1$, we obtain a value +10 Hz for the shift of the maximum of the resonance when the saturation parameter changes from $I_0=0$ to $I_0=1$.

We are grateful to I. I. Sobel'man for helpful discussions.

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