SPECTRAL MANIFESTATIONS OF COLLISIONAL AND FIELD INTERFERENCE OF LINES IN A THREE–LEVEL SYSTEM WITH SPLIT GROUND STATE

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Received, September 27, 1994

Simultaneous action of collisional and field spectral exchanges on the absorption line profile and on the fluorescence excitation spectrum is considered for the case of a three–level Λ–system with split ground state. It is shown by means of numerical simulations, that the account for collisional spectral exchange in addition to the field one does not change the main qualitative features of the latter.

INTRODUCTION

It is known that ground states of the majority of atoms and molecules have fine and hyperfine structure due to nonzero nuclear spin and weak intramolecular interactions of different kinds. Moreover with nonzero total angular momentum in ground state the additional splitting with respect to the momentum projections is observed under influence of external constant electric and/or magnetic field. In solving problems of laser spectroscopy, laser remote sensing of the atmosphere, and so on, the ground state is conventionally considered to be nondegenerate since the value of splitting is lower than the intrinsic line width. However, as was shown in Refs. 1–4, in the case of sublevel superposition typical for ground state, in the absence of collisions, or at low buffer gas pressure the nonlinear interference effects (NIE)[5] come into force. Such effects were studied earlier mainly with respect to the excited atomic states.[6–12]

Under conditions of ground state sublevel superposition NIE manifests itself as polarization, induced by quasimonochromatic field of laser radiation, on two or more allowed optical transitions of a multilevel system. The polarization is induced effectively since the field is resonant to several transitions due to small value of splitting. At the same time the laser field induces polarizations on forbidden low–frequency transitions between ground state sublevels. Light–induced polarizations on low–frequency transitions couple polarizations on allowed optical transitions and in such a way the collisionally induced field interference of lines (spectral exchange, crossrelaxation) occurs.[13–16] The polarization coupling and, therefore, effects of field interference are more pronounced for smaller splitting and stronger electric field of light.

Formation of giant interference shift and broadening of lines in stationary absorption spectrum and spectrum of fluorescence excitation that can reach thousands of line widths of optical transitions[1] is one of the most appreciable manifestation of NIE in a three–level Λ–system under study. In a system with multiple–split ground state the effect of interference quenching of absorption with an increase in radiation intensity is more pronounced.[4] When the splitting vanishes, the interference coupling of optical polarizations and the manifestation of these effects are limited by natural physical factors. Among these are collisions that destroy the field–induced coherence between sublevels, finiteness of interaction between field and atoms due to finite laser pulse duration and finite travel time of atoms through the light beam, and also nonmonochromacity of laser radiation discussed in Ref. 2.

Collisions of an atom or a molecule, interacting with radiation, with particles of a buffer gas not only quench NIE taking place at high gas pressures but also strongly affect the field interference of lines at lower gas pressures. Indeed, the polarization coupling factor of the optical transitions explicitly depends on the longitudinal constant of collisional relaxation of a forbidden low–frequency transition.[1] In particular, the calculations performed in Ref. 1 demonstrate that the line can narrow with an increase in gas pressure if the constants of radiative relaxation of optical transitions are different. However, the model presented in Ref. 1 does not take into account the collisional interference of lines.[13–16] Following the analysis of general expressions for collisional integral in terms of scattering amplitudes[5] the collisional interference can occur in Λ–system discussed here in the case of small splitting of the ground state.

The aim of this paper is to develop a model allowing for collisional interference on the basis of conventional approach of collisional spectral exchange, and further consideration of joint influence of the field and collisional interference on stationary absorption spectra and spectra of fluorescence excitation in a three–level Λ–system with split ground state.

FORMULATION OF THE PROBLEM AND ITS ALGEBRAIC SOLUTION

Let the quantum system have the ground level (0), upper excited level (1), and metastable level (2) close to the ground one. Similarly to Refs. 1–4, we will describe this system using standard equations for medium density matrix in models of relaxation constants and uniform broadening in approximation of a rotating wave. Consider that the system is influenced by a monochromatic radiation with the electric field amplitude E and frequency ω which is close to ω_{10} and ω_{12} for allowed optical transitions 0–1 and 2–1. The collisional spectral exchange will be taken into account according to the conventional procedure[13–16] by introduction of constants proportional to pressure (crossrelaxation parameters) into equations for nondiagonal elements of the density matrix corresponding to polarizations of allowed optical transitions. As a result, the kinetic equations for stationary case and in the interaction representation take the form:

0235-6880/95/04 296-05 $02.00

$$[\Gamma_1 - i(\Omega - \delta_1)]\, R_1 = i\, V_1\, (\rho_0 - \rho_1) + i\, V_2\, r + \zeta_1\, R_2;$$

$$[\Gamma_2 - i(\Omega + \Delta - \delta_2)]\, R_2 = i\, V_2\, (\rho_2 - \rho_1) + i\, V_1\, r^* + \zeta_2\, R_1;$$

$$[\Gamma_3 + i(\Delta + \delta_3)]\, r = i\, V_2\, R_1 - i\, V_1\, R_2^*;$$

$$A_1\, \rho_1 - \gamma\, (\rho_0 - \rho_2) = 2\, V_1\, R_1''; \quad A_2\, \rho_1 + \gamma\, (\rho_0 - \rho_2) = 2\, V_2\, R_2'';$$
(1)

$$\rho_0 + \rho_1 + \rho_2 = 1.$$

Here ρ_i $(i = 0,\ 1,\ 2)$ are the level populations; $R_i = R_i' + iR_i''$ $(i = 1,\ 2)$ are parts of the complex nondiagonal elements of density matrix independent of time for optical transitions 0–1 and 2–1, respectively; r is polarization of the forbidden low–frequency transition 0–2; $V_i = V_i^* = d_i E/2\hbar$ $(i = 1,\ 2)$ are Raby frequencies for 0–1 and 1–2 transitions; d_i, A_i $(i = 1,\ 2)$ are matrix elements of the dipole moment and first Einstein coefficients for allowed optical transitions; $\Omega = \omega - \omega_{10}$ is the mismatch between the frequency of laser radiation and that of the transition 0–1; $\Delta = \omega_{20}$ is the frequency of the forbidden transition 0–2 or value of the ground state splitting; Γ_i, δ_i $(i = 1,\ 2,\ 3)$ are broadening and shift constants for 0–1, 2–1, and 0–2 transitions, respectively; γ is the rate of collisional population redistribution between 0 and 1 levels; $\zeta_i = \zeta_i' + i\zeta_i''$ $(i = 1,\ 2)$ are complex cross relaxation parameters for transitions 0–1 and 2–1 responsible for collisional interference of lines.

The principle difference between the field and collisional interference of lines may be illustrated by expressing r in terms of R_1 and R_2^* using the third equation of the system (1) and then substituting it into the first and the second equations of this system:

$$\left[\Gamma_1 \,\$\, i(\Omega \,\$\, \delta_1) + \frac{V_2^2}{\Gamma_3 + i(\Delta + \delta_3)}\right] R_1 - \frac{V_1\, V_2}{\Gamma_3 + i(\Delta + \delta_3)}\, R_2^* -$$
$$- \zeta_1\, R_2 = i\, V_1\, (\rho_0 - \rho_1);$$

$$\left[\Gamma_2 \,\$\, i(\Omega + \Delta \,\$\, \delta_2) + \frac{V_1^2}{\Gamma_3 \,\$\, i(\Delta + \delta_3)}\right] R_2 - \frac{V_1\, V_2}{\Gamma_3 \,\$\, i(\Delta + \delta_3)}\, R_1^* -$$
$$- \zeta_2\, R_1 = i\, V_2\, (\rho_2 - \rho_1). \qquad (2)$$

The second and third terms in the left–hand sides of equations (2) describe the field and collisional interference of lines, respectively. As comes out from Eqs. (2), for the field interference unlike to the collisional interference, the coupling of complex–conjugated polarizations R_1 and R_2^* takes place. The coupling parameters ζ_1 and ζ_2 responsible for collisional interference are proportional to gas pressure p and vanish when $p \to 0$. On the contrary, coupling parameters for field interference $V_1 V_2/[\Gamma_3 \pm i(\Delta + \delta_3)]$ reach their maximum values in the absence of collisions ($\Gamma_3 = 0$, $\delta_3 = 0$) and infinitely increase if $\Delta \to 0$. The third terms in brackets in equations (2) exhibit the same regularities. These specific features of NIE in the system considered cause the appearance of nontrivial effects of giant shift and broadening of lines[1] and interference quenching of the absorption[4] discussed above in the introduction.

Within the limits of low radiation intensity $V_1 V_2 \to 0$, the level populations can be considered to be constant. In this case, equations (2) involve only terms corresponding to the collisional spectral exchange and their right–hand sides become constant. By integrating Eqs. (2) over frequency Ω it can be readily shown that under these conditions R_1 and R_2 values as well as total intensity of line are independent of collisional relaxation constants. In other words, under weak field and in the absence of NIE the collisional interference, as would be expected, does not change total intensity of a line.

Consider now the upper level population ρ_1 to be the quantity sought in solution of the system (1). As a function of frequency Ω, ρ_1 presents the spectrum of fluorescence excitation for the transitions 1–0 and 1–2. It is also easy to show from Eqs. (1) that ρ_1 value is proportional to the field work under stationary conditions:

$$P = 2\, V_1\, \mathrm{Re}\, iR_1 + 2\, V_2\, \mathrm{Re}\, iR_2 = -\, \gamma_1\, \rho_1 \qquad (3)$$

and, correspondingly, to the absorption coefficient. In Eq. (3) the value $\gamma_1 = A_1 + A_2$ is the rate of radiative decay of the upper level. Hereinafter, by the term "line profile" we imply functions $\rho_1(\Omega)$ or $P(\Omega)$.

The exact solution of the system (1) can be written as:

$$\rho_1(\Omega) = \{2\, V_1^2\, V_2^2 + \gamma\, [V_2^2\, (G_1 - V_1^2\, Q_1) +$$
$$+ V_1^2\, (G_2 - V_2^2\, Q_2)]\}\{6\, V_1^2\, V_2^2 + (A_1 + 3\,\gamma)\, V_2^2\, G_1 +$$
$$+ (A_2 + 3\,\gamma)\, V_1^2\, G_2 + V_1^2\, V_2^2\, [(A_2 - 3\,\gamma)\, Q_1 +$$
$$+ (A_1 - 3\,\gamma)\, Q_2 + \gamma\,\gamma_1\, (G_1\, G_2 - V_1^2\, V_2^2\, Q_1\, Q_2)]\}^{-1}, \qquad (4)$$

where

$$G_{1,2} = \tilde{\Gamma}_{1,2} + \{\Omega_{1,2}\, [\tilde{\Gamma}_{2,1}\, \Omega_{1,2} \mp (V_1\, V_2\, D' + \zeta_{1,2}') \times$$
$$\times (\, V_1\, V_2\, D'' \mp \zeta_{2,1}'')] + (\, V_1\, V_2\, D'' \mp \zeta_{1,2}'') \times$$
$$\times [\tilde{\Gamma}_{1,2}\, (\, V_1\, V_2\, D'' \mp \zeta_{2,1}'') \mp \Omega_{1,2}\, (V_1\, V_2\, D' + \zeta_{2,1}')]\}/\mathrm{Det};$$

$$Q_{1,2} = D' - \zeta_{1,2}'/(V_1\, V_2) \pm \{\Omega_{1,2}\, [\tilde{\Gamma}_{2,1}\, (V_1\, V_2\, D'' \pm \zeta_{1,2}') \pm$$
$$\pm \Omega_{2,1}\, (\, V_1\, V_2\, D' + \zeta_{1,2}')] - (V_1\, V_2\, D'' \mp \zeta_{1,2}'') \times$$
$$\times [\tilde{\Gamma}_{1,2} \Omega_{2,1} \pm (V_1 V_2 D' + \zeta_{2,1}')\, (V_1\, V_2\, D'' \pm \zeta_{1,2}'')]\}/(V_1\, V_2\, \mathrm{Det});$$

$$\mathrm{Det} = \tilde{\Gamma}_1\, \tilde{\Gamma}_2 - (\, V_1\, V_2\, D' + \zeta_1')\, (\, V_1\, V_2\, D' + \zeta_2');$$

$$\tilde{\Gamma}_{1,2} = \Gamma_{1,2} + V_{2,1}^2\, D';\ \Omega_1 = \Omega + V_2^2\, D'' - \delta_1;$$

$$\Omega_2 = \Omega + \Delta - V_1^2\, D'' - \delta_2;$$

$$D' + i\, D'' = 1\, /\, [\Gamma_3 - i\, (\Delta + \delta_3)]. \qquad (5)$$

When considering interaction of a gas with radiation the expression (4) for $\rho_1(\Omega)$ should be modified by redefining Ω as $\Omega - k\nu$ (k is the wave number, and ν is the projection of atomic velocity vector onto the wave vector). Then, integration of Eq. (4) over velocity with Maxwell distribution should be carried out.

NUMERICAL CALCULATIONS OF THE LINE PROFILE AND DISCUSSION

Let us express parameters, entering into Eq. (4), as functions of gas pressure as follows

$$\gamma = \gamma_0\, p;$$
$$\Gamma_1 = 0.5\,\gamma_1 + \Gamma_{10}\,\gamma;\ \Gamma_2 = 0.5\,\gamma_1 + \Gamma_{20}\,\gamma;\ \Gamma_3 = \Gamma_{30}\,\gamma;$$
$$\delta_1 = \delta_{10}\,\gamma;\ \delta_2 = \delta_{20}\,\gamma;\ \delta_3 = \delta_{30}\,\gamma;$$
$$\zeta'_1 = \zeta'_{10}\,\gamma; \qquad \zeta''_1 = \zeta''_{10}\,\gamma; \qquad \zeta'_2 = \zeta'_{20}\,\gamma; \qquad \zeta''_2 = \zeta''_{20}\,\gamma. \qquad (6)$$

The relaxation constant for the forbidden transition Γ_3, Eq. (6), is proportional to the gas pressure since the radiative decay of the metastable level 2 to the ground level 0 is negligible.[17] This means that it governs the NIE manifestation in the scheme of level superposition discussed here[1].

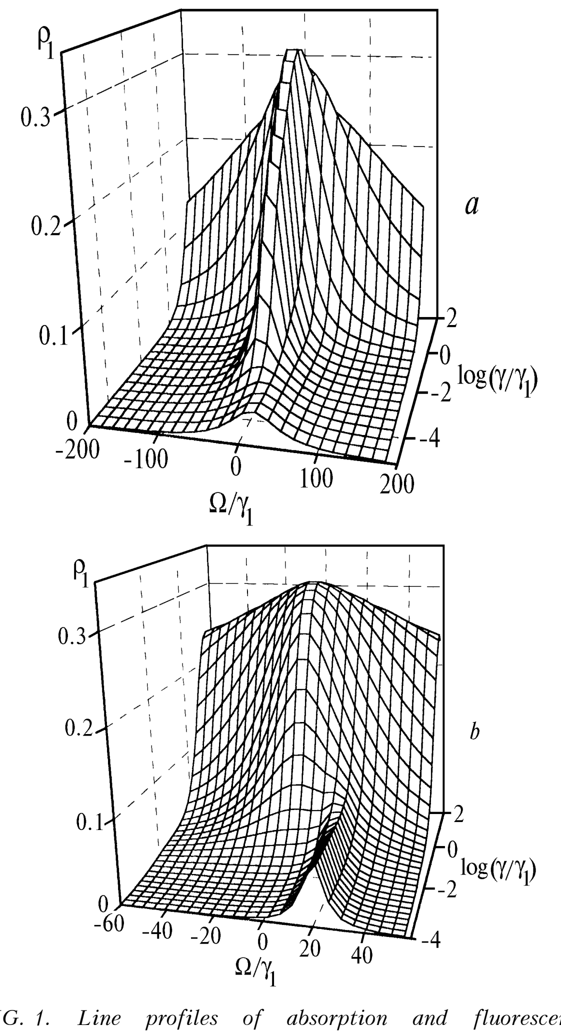

FIG. 1. Line profiles of absorption and fluorescence excitation spectrum with regard to NIE versus buffer gas pressure: $A_1 = 0.99\,\gamma_1$, $A_2 = 0.01\,\gamma_1$, $\Delta = 2.34\,\gamma_1$ *(a)*, $A_1 = A_2 = 0.5\,\gamma_1$, $\Delta = 4.11\,\gamma$ *(b)*, $V_1 = 10\,\gamma_1$, $V_2 = \gamma_1$, $\Gamma_{10} = \Gamma_{20} = \Gamma_{30} = 1.5$, $\zeta'_1 = \zeta'_2 = \zeta''_1 = \zeta''_2 = 0$. *Collisional spectral exchange is ignored.*

Figures 1*a* and *b* show line profile $\rho_1(\Omega)$ versus gas pressure P (γ value) taking into account NIE but in the absence of collisional interference ($\zeta_1 = \zeta_2 = 0$). It is calculated for the same values of parameters that were used for data plotted in Fig. 5 of Ref. 1 except for Γ_{30}. The cases $A_1 \neq A_2$ (*a*) and $A_1 = A_2$ (*b*) present two important situations when NIE manifestations are appreciably different including various pressure dependence of the line profile.[1–4]

The specific features of line profiles presented in Figs. 1*a* and *b* have been discussed in detail in Ref. 1. In particular, large interference shift at low gas pressure as well as complicated line profile structure that varies with pressure has been observed. In this paper, we use Fig. 1 as the reference for illustration of joint influence of collisional and field interference.

Figures 2*a* and *b* present the additions $\Delta\rho_1(\Omega)$ to $\rho_1(\Omega)$ profiles shown in Figs. 1*a* and *b*. These additions are caused by the influence of collisional interference in the case when ζ_1, $\zeta_2 \neq 0$:

$$\Delta\rho_1(\Omega) \equiv \rho_1(\Omega,\, \zeta_1 \neq 0,\, \zeta_2 \neq 0) - \rho_1(\Omega,\, \zeta_1 = 0,\, \zeta_2 = 0). \qquad (7)$$

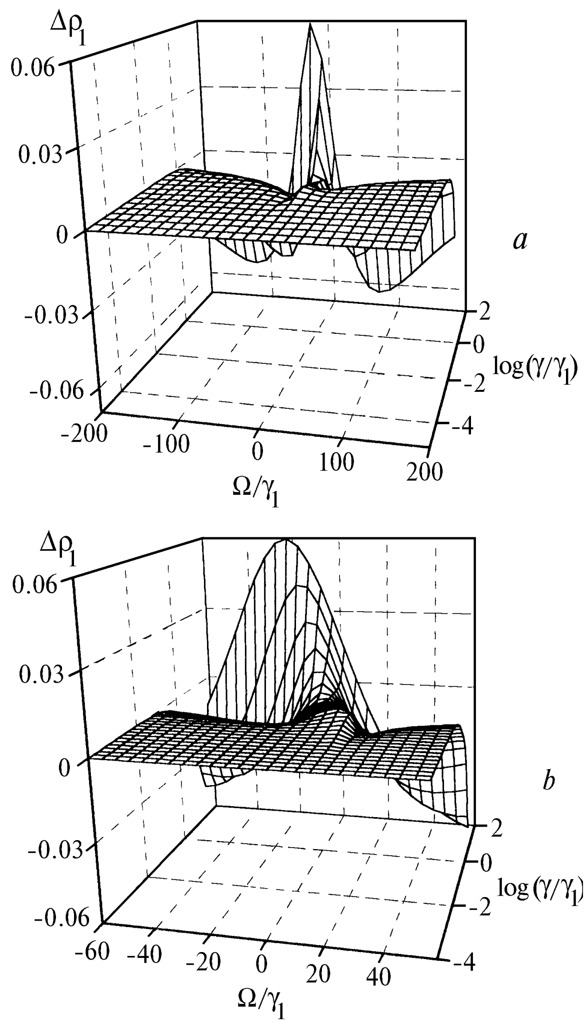

FIG. 2. Addition $\Delta\rho_1(\Omega)$ *to the profiles presented in Figs. 1a and b caused by collisional interference of lines. The values of parameters are the same as in Fig. 1 except for* $\zeta'_{10} = \zeta'_{20} = 1.3$, $\zeta''_{10} = \zeta''_{20} = 0.3$.

As is seen from Figs. 2*a* and *b*, the additions $\Delta\rho_1(\Omega)$ to $\rho_1(\Omega, \zeta_1 = 0, \zeta_2 = 0)$ profile have the shape characteristic of collisional spectral exchange being positive in the line center and negative in the near wings.

The specific feature of collisional interference in the presence of NIE and sufficiently intense field is nonzero value of the integral of $\Delta\rho_1(\Omega)$ over Ω at high gas pressure that can be estimated from Figs. 2*a* and *b*, in contrast to the case of a weak field and the absence of field interference, i.e., in accordance with the above discussion.

Noticeable asymmetry of $\Delta\rho_1(\Omega)$ function about the line center, which is more pronounced in the case shown in Fig. 2*b*, is mainly caused by the fact that signs of imaginary parts of collisional crossrelaxation parameters ζ_1'' and ζ_2'' are the same. This conclusion is confirmed by the data presented in Figs. 3*a* and *b*. Indeed, $\Delta\rho_1(\Omega)$ profiles are entirely symmetric when they are calculated with the same values of parameters that were used in Figs. 2*a* and *b* except for change of sign of the ζ_2'' parameter.

As it comes out from Figs. 1–3, the maximum relative addition $\Delta\rho_1$ to $\rho_1(\Omega, \zeta_1 = 0, \zeta_2 = 0)$ profile is 24% in the case (*a*) and 21% in the case (*b*).

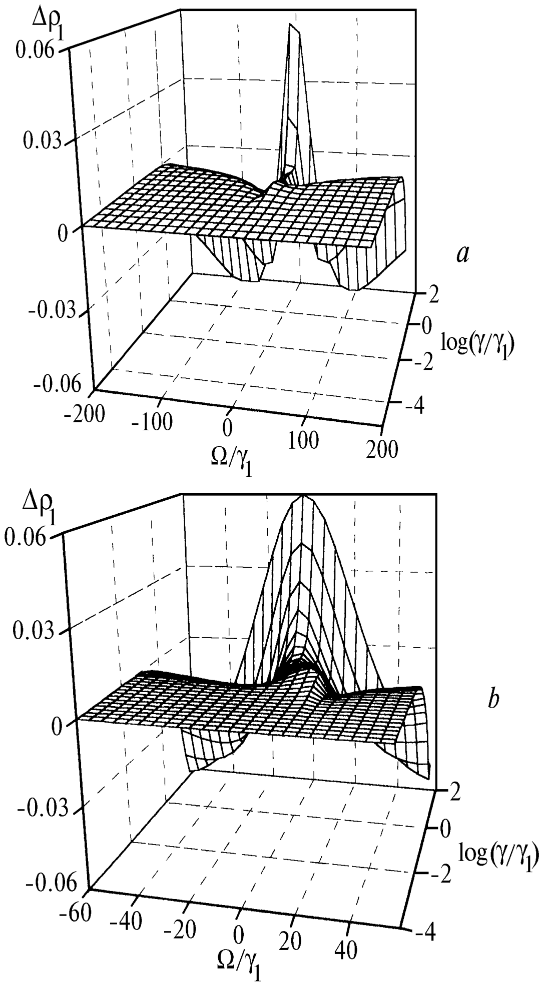

FIG. 3. The same as in Fig. 2 but $\zeta_{20}'' = -0.3$.

The case of weak field presented in Figs. 4*a* and *b* is of great interest too. Figure 4*a* demonstrates that, when the radiation intensity is reduced by four orders of magnitude from its value corresponding to Figs. 1*a* and 2*a*, the positive interference shift caused by NIE at low gas pressures disappears. This is in both qualitative and quantitative agreement with the analytical description of the line profile in the absence of collisions.[1] At the same time, the field interference in the medium range of gas pressure is even more pronounced. Indeed, the peak value of $\rho_1(\Omega)$ profile is higher at medium pressure than that at higher pressure. The amplitude ratio of $\rho_1(\Omega)$ peak values for medium and high gas pressure is appreciably lower in the case of an intense field than in the case of a weak field. This fact is the manifestation of "jump" character of NIE, which is described by introducing additional equation for polarization of forbidden transitions *r* in the system of equations for density matrix. This results in "field collapse" or formation of joint profile of two optical lines separated by the splitting value Δ. Such an effect can occur due to NIE even in a very weak field. Since the time of establishing stationary absorption becomes infinitely large if the intensity approaches zero[1] these conditions are very difficult to be realized in real experiments.

Figure 4*b* illustrates joint influence of the field and collisional interference at low intensity of radiation. As compared to the case of high intensity (Fig. 2*a*), several local peaks of $\Delta\rho_1(\Omega)$ function are observed. These peaks occur at a medium gas pressure. The initial $\rho_1(\Omega)$ profile is presented in Fig. 4*a*.

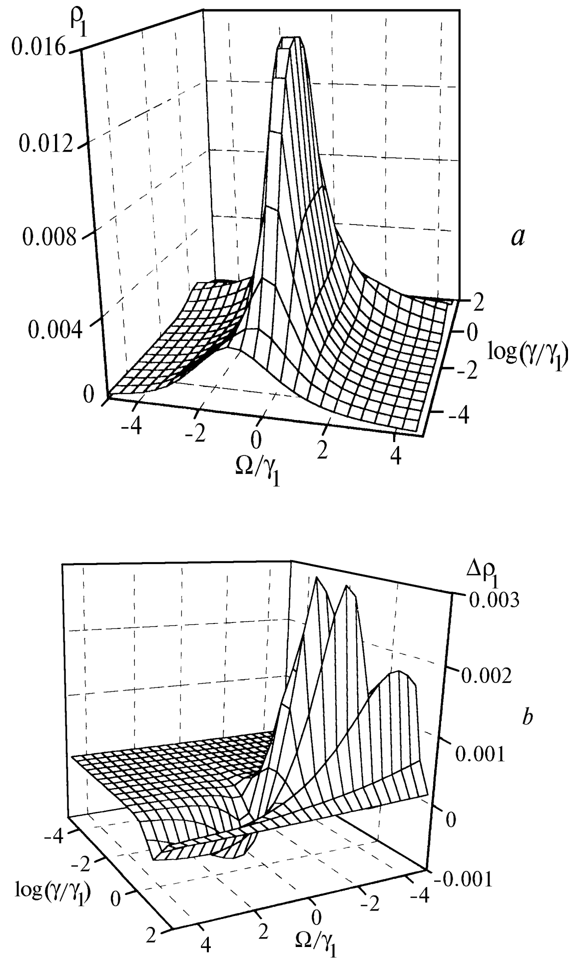

FIG. 4. Line profile $\rho_1(\Omega)$ *(a) and addition* $\Delta\rho_1(\Omega)$ *(b) for the same values of the parameters as in Figs. 1a and b except for* $V_1 = 0.1\gamma_1$ *and* $V_2 = 0.01\gamma_1$.

The relative value of addition $\Delta\rho_1$ to ρ_1 reaches 18%. This maximum is lower by a factor of 1.5 than that in the case of high intensity. The occurrence of local extrema of $\Delta\rho_1(\Omega = 0, \gamma)$ function is accounted for by the fact that in the case of ζ_1, $\zeta_2(\gamma)$ depending on gas pressure and for low V_1, V_2 values both numerator and denominator in the expression for $\rho_1(\Omega = 0, \gamma)$ are the second– and third–power polynomials of γ. This leads to the nonmonotonic behavior of $\Delta\rho_1(\gamma)$. The stronger is the field and the higher are V_1 and V_2 values the smoother is the dependence $\Delta\rho_1(\Omega)$ until it totally disappears.

CONCLUSION

Taking into account the collisional interference of lines in the case of ground state splitting with sublevel superposition we have found that despite of the fact that collisional crossrelaxation parameters were chosen to be rather high ($\zeta'_{i0}/\Gamma_{i0} \approx 87\%$, $i = 1$, 2) the collisional interference leads to additional line narrowing at medium gas pressure but does not change the qualitative manifestations of the field interference (NIE) discussed in detail in Ref. 1. Relative value of the addition to the line profile caused by collisional exchange does not exceed 25% and slightly decreases with decreasing radiation intensity. Under conditions of the strongest influence of interference the line amplitude, as a function of pressure, exhibits several local maxima and minima. In the general case of nonlinear absorption, the integral of the profile difference over frequency calculated with and without regard to collisional interference is nonzero in the presence of NIE.

The numerical estimations made show that NIE should be taken into account in the problems of high altitude laser remote sensing of the atmosphere, in particular, of sodium layers and layers of other atoms and ions of meteorite and artificial origin. Laser pulse energy ≥ 10 mJ, at a pulse duration ≥ 1–10 μs, and sounding altitude ≥ 70 km are required for this effect to occur. Magnetic field of the Earth induces sodium ground state splitting sufficient for NIE manifestation.

Nonlinear interference effects should be taken into account in the following problems:

1) exact *a priori* tuning of laser frequency at a resonance absorption line,

2) determination of reliable values of atomic concentrations from laser–induced fluorescence signals,

3) more reliable determination of temperature of the layer sounded from a fluorescence line width observed.

Another important and interesting application of NIE is measurement of magnetic and electric fields in the mesosphere and lower thermosphere using data on interference shifts and broadening of fluorescence lines. These parameters depend strongly and directly on the ground state splitting under the action of constant external fields.

REFERENCES

1.M.S. Zubova and V.P. Kochanov, Zh. Eksp. Teor. Fiz. **100**, No. 6, 1772–1786 (1992).

2. V.P. Kochanov, Atmos. Oceanic Opt. **5**, No. 11, 787–793 (1992).

3.V.P. Kochanov, Proc. SPIE **2205**, 28–48 (1993).

4. V.P. Kochanov and M.S. Zubova, Zh. Eksp. Teor. Fiz. **105**, No. 3, 499–514 (1994).

5. S.G. Rautian, G.I. Smirnov, and A.M. Shalagin, *Nonlinear Resonances in Atomic and Molecular Spectra* (Nauka, Novosibirsk, 1979), 312 pp.

6. G.E. Notkin, S.G. Rautian, and A.A. Feoktistov, Zh. Eksp. Teor. Fiz. **52**, No. 6, 1673–1687 (1967).

7. R.I. Sokolovskii, Opt. Spekstrosk. **27**, 1017–1020 (1969).

8. Im Tkhek–de, S.G. Rautian, E.G. Saprykin, et al., Zh. Eksp. Teor. Fiz. **62**, No. 5, 1661–1665 (1972).

9. S.G. Rautian and Ya.S. Bobovich, Opt. Spekstrosk. **34**, No. 3, 617–619 (1973).

10. G. Alzetta, A. Gozzini, and G. Orriols, Nuovo Cimento **36B**, 5 (1976).

11. G. Alzetta, L. Moi, and G. Orriols, *ibid*. **52B**, No. 2, 209–218 (1979).

12. G. Orriols, *ibid*. **53B**, No. 1, 1–24 (1979).

13. M. Baranger, Phys. Rev. **112**, No. 3, 855–865 (1958).

14. A.C. Kolb and H. Grim, *ibid* **111**, No. 2, 514–521.

15. V. Fano, *ibid* **131**, No. 1, 259–268 (1963).

16. A.I. Burshtein, *Lectures on Quantum Kinetics* (State University, Novosibirsk, 1968), V. 2, 265 pp.

17. G. Bete and E. Solpeter, *Quantum Mechanics of Atoms with One or Two Electrons* (Fizmatgiz, Moscow, 1960), 562 pp.