PHASE-MEMORY EFFECTS IN THE THEORY OF SPECTRAL LINE BROADENING IN GASES *

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It is found that the maintenance of phase memory in nonadiabatic collisions results in correlated broadening of various spectral components. This is manifested in a number of effects such as an additional line shift that is quadratic in the density, the allowing of forbidden transitions, and the merging or narrowing of some spectral components. The last two effects can be observed when the splitting of components is commensurable with their broadening, whereas the quadratic shift remains of considerable magnitude even in the case of very much greater splitting.

INTRODUCTION

THE effects of the phase coherence of different stationary atomic states represent a qualitatively new factor in the nonadiabatic theory of spectral line broadening as compared with the adiabatic theory. It is well known that adiabatic collisions alter only the phases of atomic states without mixing them. Therefore only the diagonal elements S_{ii} of the scattering matrix, which determine the widths and shifts of the corresponding i-th levels, are nonvanishing. All levels therefore are broadened independently, and the width of a spectral line is composed simply of the widths of the levels involved in the corresponding radiative transition.

Nonadiabatic collisions present an entirely different situation. Here not so much the phases as the amplitudes of stationary states are changed, thus inducing transitions between energy levels. This is a qualitative change, because nonadiabatic collisions affect not only $|S_{ii}|$, that is state populations, but also lead to the appearance of nonvanishing off-diagonal elements S_{ik}. The presence of the latter indicate that stationary states interfere and therefore cannot be changed independently of each other. Following a collision a system is no longer a simple statistical mixture of stationary states, so that the reaction of the system to a particular collision depends greatly on the result of the preceding collision.

The theoretical possibility of phase coherence between states in the nonadiabatic theory of line broadening is realized only when averaging over all possible impact parameters does not cause the vanishing of all terms containing off-diagonal elements of the scattering matrix. In this case we can affirm that the system maintains the phase memory of the state arising from a collision.

The most important consequence of the conservation of phase memory is obviously the fact that the broadenings of individual spectral components, as well as of different energy levels, can no longer be regarded as mutually independent. We therefore find a number of phase effects that establish a correlation between the widths, shifts, and intensities of different components in a complex spectrum.

In the present work we investigate these effects in the simplest quantum systems, determining their magnitudes and the conditions of their realization.

1. GENERAL THEORY OF THE LINE SHAPE

We know that the spectral composition of radiation absorbed by an atomic system is the Fourier transform of the correlation function

$$K(t) = \mathrm{Sp}\,\overline{\hat{F}(t)\hat{F}(0)} = \overline{F_{ik}(t)}F_{ki}(0) \qquad (1.1)$$

of the operator F that induces radiative transitions.[1] Averaging, denoted by a bar, is performed over the random realizations of thermal disturbance V(t) of the system. In a gas this disturbance consists in a sequence of collisions interspersed with periods of free flight.

The overall analysis of the spectrum can be performed conveniently in the impact approximation when the collision time is much shorter than the time of free flight. In this case we do not des-

*Translator's note: Regarding phase memory see E. L. Hahn, Phys. Rev. 80, 580 (1950).

cribe correctly the outlying statistical wings of the lines, but achieve our purpose most quickly by utilizing the available results obtained in the impact theory of relaxation.

It has been shown recently[2] that the behavior of a system having the Hamiltonian $\hat{H} = H_0 + \hat{V}(t)$ can be represented in the impact approximation by the relaxation equation (with $\hbar = 1$)

$$\dot{\bar{\rho}} = -i[\hat{H}_0, \bar{\rho}] - \hat{G}\bar{\rho}, \tag{1.2}$$

where all necessary averagings over V(t) have already been performed. A similar equation is obtained for the average operator $\hat{F}(t)$ in (1.1):

$$\dot{\bar{F}}_{ik} = (i\omega_{ik,\,lm} - G^{*}_{lm,ik})\bar{F}_{lm},$$
$$\omega_{ik,lm} \equiv \omega_{lm}\delta_{il}\delta_{km}, \quad \omega_{lm} = H_{ll}^{0} - H_{mm}^{0}. \tag{1.3}$$

In both instances the time-independent relaxation matrix $G_{ik,\,lm}$, that contains all relaxation times and frequency shifts resulting from collisions is represented by

$$G_{ik,\,lm} = \langle \delta_{il}\delta_{km} - S_{il}S_{km}^{*} \rangle. \tag{1.4}$$

The change in the atomic state that results from an individual collision is indicated in this equation by the S matrix, which in the interaction representation couples the wave functions existing before and after a collision as follows: $\psi_i(+\infty) = S_{ik}\psi_k(-\infty)$. The angular brackets denote averaging over all impact parameters of an individual collision.

The general solution of (1.3) is

$$\bar{F}_a(t) = [\exp(i\hat{\omega} - \hat{G}^{*})t]_{ba}F_b(0), \tag{1.5}$$

where a and b are collective indices that provide a successive enumeration of all permutations within (ik) and (lm). Inserting this solution into the correlation function (1.1) and performing a Fourier transformation, we finally obtain a formula for the frequency spectrum of the system:

$$I(\omega) = \mathrm{Re}\{[\hat{A}^{-1}]_{ab}F_a^{*}(0)F_b(0)\}, \tag{1.6}$$

where

$$A_{ba} = i(\omega - \omega_a)\delta_{ab} + G_{ab}^{*}. \tag{1.7}$$

This result contains in the most general form all information about the structure and shape of the spectrum in the impact approximation. The spectrum represented by (1.6) is a set of lines corresponding to transitions between all pairs of levels together with a series of lines grouped about the center frequency and corresponding to the relaxation of the populations at each level.

In the special case when we must consider light absorption by two degenerate or almost degenerate multiplet terms, as in[3-5], the general equation (1.6) can be simplified by assuming that there are no radiative transitions among components of a single term, but that collisions, on the other hand, induce transitions only within a multiplet group of levels. The only nonvanishing matrix elements $F_{\alpha'\beta'}$ and S-matrix components $S_{\alpha'\alpha''}$ and $S_{\beta'\beta''}$ are then those for which α numbers the states of the upper multiplet term and β those of the lower multiplet. We introduce the collective indices $a = \alpha'\alpha''$, $b = \alpha'\beta'$, $c = \beta'\alpha'$, and $d = \beta'\beta''$. We easily find that the matrix $\hat{A}$ can be divided into four submatrices:

$$\hat{A} = \begin{pmatrix} A_{a'a''} & & & 0 \\ & A_{b'b''} & & \\ & & A_{c'c''} & \\ 0 & & & A_{d'd''} \end{pmatrix}, \tag{1.8}$$

with radiative transitions corresponding only to the matrices $A_{b'b''}$ and $A_{c'c''}$, which alone are multiplied in (1.6) by nonvanishing elements of the operator $\hat{F}$ ($F_a = F_d = 0$). Moreover, the matrix $A_{c'c''}$ differs from $A_{b'b''}$ only in a sign reversal of the frequency and through complex conjugation, i.e., these matrices are essentially identical spectra that are mutual mirror images with respect to the center frequency. Since the line widths are usually small relative to the frequencies, the contribution of the spectrum on the negative half-axis of the frequencies can be neglected; the general equation (1.6) then becomes

$$I(\omega) = \mathrm{Re}\{[\hat{A}^{-1}]_{\alpha'\beta',\,\alpha''\beta''}F^{*}_{\alpha'\beta'}(0)F_{\alpha''\beta''}(0)\}. \tag{1.9}$$

This formula, derived within the framework of the correlation theory in[3-5], has provided a reference point for investigating the structures of multiplet spectra.

Because of the formulation of the problem whereby the structure of this formula is defined, together with a number of assumptions made by the authors for concrete systems, the phase terms appearing formally in (1.9) disappeared upon averaging. When any one of these assumptions is dropped the phase memory is manifested by several effects that will be described here.

On the basis of the general formula (1.6) and its simplified version (1.9) wherever possible, we shall study, in order of complexity, systems of two, three, and four levels.

2. TWO LEVEL-SYSTEMS

The two-level model is the simplest quantum system that is able to absorb radiation. This idealization is seldom applicable to real optical prob-

lems, although it is customary in magnetic and radio spectroscopy. Since only two states are involved, we cannot exclude from consideration the relaxation between the levels involved in radiative transitions. Thus the basic simplification of multiplet theory is unsuitable here and we must consider the general equation (1.6) directly.

We must first remember that because of normalization only three of the four density-matrix components ρ_{12}, ρ_{21}, ρ_{11}, and ρ_{22} are independent. It is therefore sufficient to retain the three components ρ_{12}, ρ_{21}, and $n = \rho_{11} - \rho_{22}$ in (1.2), denoted by the collective indices 1, 2, and 3; we thus reduce the fourth-order matrix $\hat{G}$ to the third order, and obtain ($\omega_0 \equiv \omega_{21}$)

$$A_{ab} = \begin{pmatrix} i(\omega+\omega_0) + \langle 1 - S_{11}^{*2}\rangle & \langle S_{12}^{*2}\rangle & \langle S_{11}^{*}S_{12}^{*}\rangle \\ \langle S_{12}{}^2\rangle & i(\omega-\omega_0) + \langle 1 - S_{11}{}^2\rangle & \langle S_{11}S_{12}\rangle \\ -2\langle S_{11}S_{12}{}^{*}\rangle & -2\langle S_{11}{}^{*}S_{12}\rangle & i\omega + 2\langle 1 - |S_{11}|^2\rangle \end{pmatrix}. \tag{2.1}$$

The assumption $\langle V(t)\rangle = 0$ leads to considerable simplification. This occurs, for example, for a vector interaction between colliding particles (interaction between a charge and a dipole, between two dipoles etc.), which vanishes as a result of averaging over the angle variables. In[3-5] such averaging led to complete disappearance of the phase memory. In the present problem however, averaging does not produce such extreme results even for a vector type of interaction. Angular averaging causes vanishing of only those elements of the matrix (2.1) that are linear in S_{12} (since S_{11} is an even function of V(t) and S_{12} is odd). At the same time the matrix is not diagonalized, because the elements A_{12} and A_{21}, which are bilinear in S_{12}, are retained. These elements represent the phase memory, which does not vanish as a result of averaging.

After inserting the averaged matrix (2.1) into (1.6) we obtain the spectrum

$$I(\omega) = \mathrm{Re}\left\{\frac{|F_{12}|^2 + iR}{i(\omega-\Omega_1)+\Gamma_1} + \frac{|F_{12}|^2 - iR}{i(\omega-\Omega_2)+\Gamma_2} + \frac{|F_{11}|^2 + |F_{22}|^2 - 2\,\mathrm{Re}(F_{11}F_{22}^{*})}{i\omega + 2\langle 1 - |S_{11}|^2\rangle}\right\}, \tag{2.2}$$

where

$$\Omega_{1,2} = \pm\,\mathrm{Re}\sqrt{\alpha^2 - |\beta|^2},$$

$$\Gamma_{1,2} = \mathrm{Re}\langle 1 - S_{11}{}^2\rangle \pm \mathrm{Im}\sqrt{\alpha^2 - |\beta|^2},$$

$$R = \mathrm{Re}(\beta F_{12}{}^2)\,/\sqrt{\alpha^2 - |\beta|^2},$$

$$\alpha = \omega_0 - \mathrm{Im}\langle 1 - S_{11}{}^2\rangle, \qquad \beta = \langle S_{12}{}^2\rangle. \tag{2.2a}$$

When the frequency exceeds the line width, resonance absorption can be described by the first term alone. For $\beta = 0$ we then obtain the ordinary Lorentz line of width $\Gamma = \mathrm{Re}\langle 1 - S_{11}^2\rangle$ with a shift $\Delta_0 = -\mathrm{Im}\langle 1 - S_{11}^2\rangle$.

The foregoing equations show that the maintenance of phase memory does not affect the width of the Lorentz line but leads to an additional shift $-|\langle S_{12}^2\rangle|^2/2\omega_0$, which unlike the ordinary quadratic shift depends on the gas density. To evaluate the contribution of this new term to the total shift we consider the potential $V(t) = C/R^2$ corresponding to broadening induced by charged particles. From perturbation theory, using rigid spheres of diameter ρ_0,[6] we then obtain the shift

$$\Delta = \Delta_0 - \frac{\Gamma^2}{2\omega_0} = \Delta_0\left(1 - \frac{2\pi^2 NC^2}{v\omega_0}\ln^2\frac{v}{2\omega_0\rho_0}\right). \tag{2.3}$$

With values of the parameters that are typical for broadening induced by plasma electrons: $v = 10^8$, $\omega_0 = 10^{14}$, and $C = 1$ cm^2/sec, it then follows that the additional phase shift equals the usual shift at the density $N \approx 10^{20}$ cm^{-3}.

The phase memory also induces some asymmetry of the line shape resulting from the term $(\omega - \Omega_1)/[(\omega - \Omega_1)^2 + \Gamma_1^2]$, which is odd in $(\omega - \Omega_1)$. Its amplitude $\langle S_{12}^2\rangle/\omega_0 = \Gamma/\omega_0$ equals the amplitude of the Lorentz line under about the same conditions as for a fairly large quadratic shift.

In addition to the resonant absorption represented by the first term in (2.2), with a relatively insignificant second term describing a line shift into the negative frequency region, a "loss term" also appears. The latter, which describes absorption near the center frequency and results from population relaxation, is observed, for example, when paramagnetic relaxation in longitudinal fields is investigated (F_{11}, $F_{22} \neq 0$, $F_{12} = 0$).[7]

We note that a contribution to this last-mentioned effect could also come from transverse fields if the interaction should be such (scalar, quadrupole etc.) that all matrix elements (2.1) remained nonvanishing following angular averaging. The spectrum would be influenced very much more by the phase memory if these matrix elements were retained. In that event the problem would, of course, be more complicated, and it would be necessary to solve a characteristic third-order

equation for the purpose of determining the spectrum.

3. THREE-LEVEL SYSTEMS

This problem is the simplest example that permits application of the simplified formula (1.9) of multiplet theory. Indeed, in correspondence with a situation often encountered in optical theory, relaxational transitions between ground and excited states can be neglected by comparison with relaxation within a nearly degenerate doublet term (Fig. 1). Making this assumption, we have a much simpler problem than in the preceding case. The matrix $\hat{A}$ is now given by

$$\begin{pmatrix} A_{12,12} & A_{12,13} \\ A_{13,12} & A_{13,13} \end{pmatrix} = \begin{pmatrix} i(\omega-\omega_0)+\langle 1-S_{22}^*\rangle & -\langle S_{23}^*\rangle \\ \langle S_{23}\rangle & i(\omega-\omega_0-\Delta\omega)+\langle 1-S_{22}\rangle \end{pmatrix} \tag{3.1}$$

and the corresponding spectrum consists of two lines with completely identical structures representing the transitions $1 \to 2$ and $1 \to 3$. We shall write out only the formulas for the $1 \to 2$ transition:

$$I(\omega) = I_0 \frac{\Gamma}{(\omega-\omega_0-\Delta)^2+\Gamma^2},$$

$$I_0 = \frac{1}{2}\left(1+\frac{\alpha}{\sqrt{\alpha^2+|\beta|^2}}\right)|F_{12}|^2 + \frac{1}{2}\left(1-\frac{\alpha}{\sqrt{\alpha^2+|\beta|^2}}\right)|F_{13}|^2 + \frac{i(\beta^* F_{21}^* F_{31} - \beta F_{31}^* F_{21})}{\sqrt{\alpha^2+|\beta|^2}} \tag{3.2}$$

where

$$\Gamma = \mathrm{Re}\langle 1-S_{22}\rangle, \quad \Delta = \Delta\omega/2 - \sqrt{\alpha^2+|\beta|^2}, \quad \alpha = \Delta\omega/2 - \mathrm{Im}\langle 1-S_{22}\rangle, \quad \beta = \langle S_{23}\rangle. \tag{3.2a}$$

It is noteworthy that in the present problem, unlike the preceding one, when angular averaging causes vanishing of the interaction all phase effects are completely eliminated. Of course, averaging never actually causes an interaction to vanish. If the dipole terms vanish higher order terms, especially the quadrupole terms, must be taken into account. It can be shown that the phase memory resulting from quadrupole interactions makes an appreciable contribution to line shifts under actual experimental conditions.

We shall now evaluate the magnitude of phase memory effects for a low-temperature neutral plasma. Here the dipole shift results from adiabatic collisions with ions and from nonadiabatic collisions with electrons. The quadrupole shift vanishes because the ionic and electronic contributions cancel each other.[8] Therefore the ordinary line shift Δ_0 (neglecting phase memory effects) depends only on the dipole interactions between atoms and charged particles:

$$\Delta_0 = -10C^{4/3}\left(\frac{v_i}{\Delta\omega^2}\right)^{1/3}N - \frac{\pi^4 C^2 N}{2v_e}, \tag{3.3}$$

where v_i and v_e are the mean velocities of the ions and electrons.

Collisions with ions make no contribution to the atomic phase memory because, as was indicated in our Introduction, the latter does not appear in an adiabatic interaction. The phase memory is thus generated only in collisions with electrons, and averaging of the dipole terms leaves only the contribution $\tilde{C}/R^3$ caused by dipole interactions. It is easy to perform a perturbation calculation based on the rigid sphere model:[6]

$$\beta = \langle S_{23}\rangle = -4\pi i N\tilde{C}\ln v_e/\rho_0\Delta\omega. \tag{3.4}$$

From (3.2) we find the total line shift when $|\beta| \ll \Delta\omega/2$:

$$\Delta = \Delta_0\left(1+\frac{|\beta|^2}{|\Delta_0|\Delta\omega}\right). \tag{3.5}$$

Calculations of β and Δ_0 using typical values of the parameters: $C = 1$ cm^2/sec, $\tilde{C} = 10^{-7}$ cm^3/sec, $v_e = 10^8$, $v_i = 6\times 10^5$, $\Delta\omega = 10^{14}$, and $\rho_0 = 10^{-8}$, show that the correction term in (3.5) is $\sim 4 \times 10^{-19}$ N and thus approaches unity for entirely feasible densities. The added shift resulting from the phase memory is easily distinguished from the normal shift because the latter is characterized by quadratic pressure dependence.

In addition to its influence on line shifts, the phase memory causes one additional effect. Let us assume that the $1 \to 2$ transition is forbidden ($F_{12} = 0$). Then if the phase memory is maintained the corresponding line still appears in the spectrum with the intensity $|\beta|^2|F_{13}|^2/\Delta\omega^2$. If the memory results from a quadrupole interaction the foregoing values of the parameters yield the ratio 10^{-40} N^2 between the line and its allowed component. With

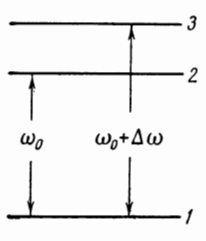

FIG. 1

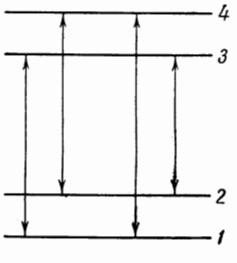

FIG. 2

$N = 10^{19}$ this constitutes 1% of the allowed line intensity, thus supplying evidence that it is actually possible to observe this phase effect.

4. FOUR-LEVEL SYSTEMS

This model (Fig. 2) is especially interesting because it enables us to investigate the correlated effects of collisions on different multiplet terms. For this purpose we must take into account the relaxational transitions within both doublet levels with no limitations on their relative magnitude.

Considering only vector interactions, in the interest of simplicity, we obtain the angle-averaged matrix $\hat{A}$:

$$\begin{pmatrix} i(\omega-\omega_{31})+\gamma_1 & -\beta_1 & 0 & 0 \\ -\beta_1^* & i(\omega-\omega_{42})+\gamma_1^* & 0 & 0 \\ 0 & 0 & i(\omega-\omega_{32})+\gamma_2^* & \beta_2^* \\ 0 & 0 & \beta_2 & i(\omega-\omega_{41})+\gamma_2 \end{pmatrix}, \tag{4.1}$$

where

$$\gamma_1 = 1 - \langle S_{11}S_{33}^* \rangle, \quad \gamma_2 = 1 - \langle S_{11}S_{33} \rangle,$$

$$\beta_1 = \langle S_{12}S_{34}^* \rangle, \quad \beta_2 = \langle S_{12}S_{34} \rangle. \tag{4.1a}$$

The phase memory, which, as always, is represented by the off-diagonal elements of this matrix, is maintained despite the averaging procedure, because these elements are bilinear in the interaction. The phase memory vanishes in this case only if there are no transitions in one of the doublet terms (when either $S_{12} = 0$ or $S_{34} = 0$). The presence of paired phase terms relates the transitions $1 \to 3$, $2 \to 4$ and $2 \to 3$, $1 \to 4$. Both pairs of lines are described similarly but independently, so that it is sufficient to present only the result for the first one:

$$I(\omega) = \operatorname{Re}\frac{1}{2}\left\{\frac{(1+\Lambda)|F_{31}|^2+(1-\Lambda)|F_{42}|^2+2i\Phi}{i(\omega-\Omega_-)+\Gamma_-} + \frac{(1+\Lambda)|F_{42}|^2+(1-\Lambda)|F_{31}|^2-2i\Phi}{i(\omega-\Omega_+)+\Gamma_+}\right\};$$

$$\Omega_\mp = \bar{\omega} \mp \operatorname{Re}\sqrt{\alpha_1^2-|\beta_1|^2}, \quad \Gamma_\mp = \operatorname{Re}\gamma_1 \mp \operatorname{Im}\sqrt{\alpha_1^2-|\beta_1|^2},$$

$$\Phi = \frac{\beta_1 F_{31}^* F_{42} + \beta_1^* F_{42}^* F_{31}}{\sqrt{\alpha_1^2-|\beta_1|^2}} \qquad \Lambda = \frac{\alpha_1}{\sqrt{\alpha_1^2-|\beta_1|^2}}$$

$$\alpha_1 = \Delta\omega + \operatorname{Im}\gamma_1, \quad 2\bar{\omega} = \omega_{31}+\omega_{42}, \quad 2\Delta\omega = \omega_{42}-\omega_{31}. \tag{4.2}$$

The result for the second pair of lines is obtained herefrom by permuting the indices 1 and 2.

As in the preceding case, a forbidden line can become allowed because the phase memory is maintained. If the $1 \to 3$ transition is forbidden, it follows from (4.2) that the intensity of the corresponding line is given by

$$I_{13} = |F_{42}|^2\left(1 - \frac{\Delta\omega + \operatorname{Im}\gamma_1}{[(\Delta\omega+\operatorname{Im}\gamma_1)^2-|\beta_1|^2]^{1/2}}\right). \tag{4.3}$$

The difference from the preceding case consists in the fact that the line is allowed despite angular averaging, i.e., even for dipole interactions between colliding particles.

The existence of relaxational transitions within both pairs of levels results in an entirely new effect, which is manifested most clearly when these transitions occur in an entirely identical manner: $S_{11} = S_{33}$ and $S_{12} = S_{34}$. In this situation we have $\operatorname{Im}\gamma_1 = 0$, $\beta_1 = \gamma_1 = \langle|S_{12}|^2\rangle$, and (4.2) is somewhat simplified, easily yielding two limiting cases. At low densities [β_1 is small and the radical in (4.2) is real] we have two lines with the frequencies $\Omega_\pm = \bar{\omega} \pm \sqrt{\Delta\omega^2-\beta_1^2}$ and width β_1; the latter increases with the density of the gas. However, if these line widths are comparable with the splitting ($\beta_1 = \Delta\omega$) and the lines merge, broadening of the spectrum terminates. With further increase of density ($\beta_1 > \Delta\omega$, and the radical is purely imaginary) the spectrum centered at the mean frequency $\bar{\omega}$ is of width $\Delta\omega^2/2\beta_1$; it thus narrows with increasing pressure (Fig. 3b).

The narrowing arises because of a special phase correlation of quantum states that is maintained despite relaxation. Since the relaxational transitions $1 \to 2$ and $3 \to 4$ are completely identical with respect to both their transitions probabilities ($|S_{11}| = |S_{33}|$) and phases ($\arg S_{11} = \arg S_{33}$), they only transform the two-level system 1—3 into the system 2—4 without affecting the phase state of the former. Thus the system as a whole resembles a harmonic oscillator that occasionally undergoes a change of frequency unaccompanied by a phase change. Such systems are often encountered in the investigation of magnetic resonance. The equations describing the narrowing of their spectra that were previously proposed with β introduced phenomenologically[9,10] are completely identical with those obtained from (4.2) when $S_{12} = S_{34}$ and $F_{13} = F_{24}$.

It is somewhat surprising that narrowing is maintained even if one of the investigated lines is forbidden (for example, $F_{13} = 0$, $F_{24} \neq 0$). In this case, as can be seen from the general equations

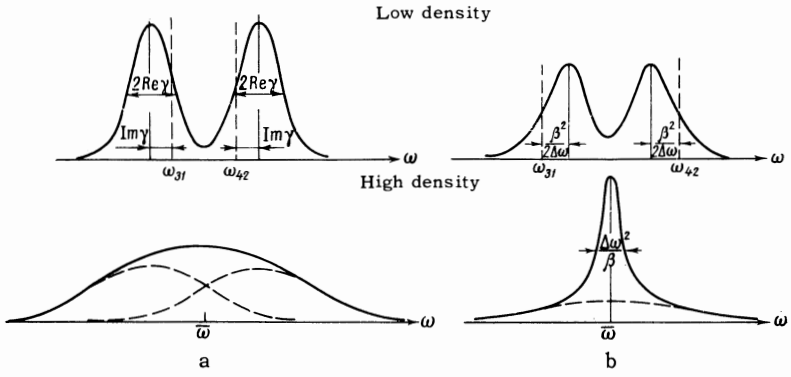

FIG. 3. Transformation of the spectrum with changing gas density. (a) $S_{12} \neq 0$, $S_{34} = 0$; (b) $S_{12} = S_{34} \neq 0$

(4.2), the narrowing effect consists in a displacement of the allowed component towards the spectral center of gravity followed by narrowing.

When $S_{12} \neq S_{34}$ narrowing may become impossible. In the case of maximum multiplet nonequivalence, i.e., in the complete absence of transitions in one of them ($S_{12} \neq 0$, $S_{34} = 0$), the phase memory for a vector interaction is averaged ($\beta_1 = 0$) and the broadening becomes normal. The spectrum consists of two lines with the frequencies $\Omega_1 = \omega_{31} - \operatorname{Im}\gamma_1$ and $\Omega_2 = \omega_{42} + \operatorname{Im}\gamma_1$ of width $\operatorname{Re}\gamma_1$ that increases continuously with the gas density. After the lines merge ($\operatorname{Re}\gamma_1 > \Delta\omega + \operatorname{Im}\gamma_1$) the overall width of the spectrum continues to increase (Fig. 3a).

The general equations in (4.2) describe all situations that lie between the already considered limiting cases and in which the phase memory is either maintained entirely or is completely absent. We derive herefrom the general conditions for the occurrence of narrowing when relaxation proceeds differently in the two multiplets. First of all, the term β_1 representing the phase memory must be sufficiently large:

$$|\beta_1| \gg \Delta\omega + \operatorname{Im}\gamma_1. \qquad (4.4)$$

The spectral width is then

$$\operatorname{Re}\gamma_1 - |\beta_1| + {}^1/_2(\Delta\omega + \operatorname{Im}\gamma_1)^2/|\beta_1|. \qquad (4.4a)$$

If the first two terms in this expression cancel, i.e.,

$$\operatorname{Re}\gamma_1 - |\beta_1| \ll {}^1/_2(\Delta\omega + \operatorname{Im}\gamma_1)^2/|\beta_1|, \qquad (4.5)$$

the remaining last term describing narrowing. The conditions (4.4) and (4.5) are necessary and sufficient for determining narrowing in gas spectroscopy. Narrowing can be observed both through density increase and temperature reduction, since $\beta \sim N/\bar{v}$.

It must be kept in mind that the two other lines corresponding to the transitions $1 \rightarrow 4$ and $2 \rightarrow 3$ behave somewhat differently than the already considered lines. These differences are associated with the fact that the parameters γ and β for these lines are defined differently. Specifically, in the limiting case of identical relaxational transitions ($S_{12} = S_{34}$) γ_2 and β_2 are complex and unequal to each other; therefore narrowing of these lines requires the condition (4.5), which is trivially fulfilled for the pair 1—3, 2—4, because $\beta_1 = \gamma_1$. A physical explanation of the difference in broadening of the two line pairs can be found in the fact that even when $S_{12} = S_{34}$ the frequency change from ω_{41} to ω_{32} during relaxation is linked to the interruption of the phase memory, which does not occur for the transformation $\omega_{31} \rightarrow \omega_{42}$.

The conditions required for narrowing $S_{12} \approx S_{34}$ of an arbitrary multiplet spectrum can be fulfilled only accidentally. However, it is easy to indicate the real physical situations when identity of the relaxational transitions is a direct consequence of the spectral structure. For example, in the Zeeman effect the hyperfine structure is involved, because magnetic relaxation between Zeeman sublevels having identical spin projections does not depend on the other quantum numbers. Therefore the π

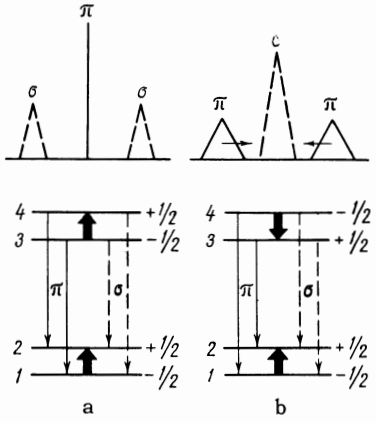

FIG. 4. Narrowing in the Zeeman hyperfine structure. a) Identical order of the levels, $S_{12} = S_{34}$; b) inverted order of the levels, $S_{12} = S_{34}$.

components are narrowed, while the σ components are broadened normally. Since the Zeeman splitting of both terms is identical, one of the two pairs of lines merges. For the same sequence of quantum numbers, in both multiplet terms the π components merge ($\Delta\omega = 0$); their relaxational width ($\frac{1}{2}\Delta\omega^2/\beta$) vanishes because of the narrowing effect (Fig. 4a). When the levels of one term are inverted (Fig. 4b) the σ components merge, while the π transitions are represented by two outer lines, which are narrowed. The afore-described effects permit direct experimental observation when collisional broadening is dominant over Doppler and spontaneous broadening.

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