Profile of doublet lines subject to collisional narrowing and mixing

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Equations for the profiles of doublet and multiplet lines are obtained within the framework of the hard collision model. These equations take into account both the collisional narrowing and mixing of spectral lines.

1. Introduction

In recent years the quality of experimental data on spectral line profiles obtained in routine measurements by the methods of laser and Fourier transform spectroscopy has been significantly improved thus allowing more detailed consideration of collisional processes which influence a line shape. The direct effect of collisions of a molecule absorbing radiation with particles of a buffer gas on the width and shifting of homogeneously broadened spectral lines can now be measured accurate to $\sim 1\%$ (Refs. 1 and 2). For inhomogeneously broadened lines at the pressure about 100 to 200 Torr, the accuracy achieved in experiments requires more fine effects associated with translational motion of molecules to be taken into account. Such fine effects include the Dicke narrowing of lines,[3–5] wind effect[6] due to anisotropic perturbation of the moving absorbing molecule by atoms and molecules of the buffer gas, and mixing (spectral exchange, cross-relaxation) within a group of overlapping lines.[7–10] If the mass of the perturbing particles is less than or comparable with the mass of the absorbing molecule, manifestations of the wind effect, such as asymmetry and shift of the line shape, due to the speed dependence of the broadening and shift constants[11–13] and degeneration of energy levels by projections of the total angular momentum[14] are significantly less pronounced than the Dicke narrowing observed in many experiments. Therefore, when dealing with light perturbing gases, thereafter we consider the perturbation to be isotropic.

As known, molecules of various symmetry have the hyperfine cluster structure of energy levels. A rigid asymmetric top at large values of the rotational quantum numbers presents the examples of double degenerate clusters, whereas 4-, 6-, and 8-degenerate clusters are typical of spherical tops.[15] The distance between levels in a cluster can vary widely, but in most cases it does not exceed several hundredths or thousandths of reciprocal centimeter. As a result, multiplets arise in the IR and visible spectra unresolved within the Doppler line width. Because of large rotational moments, collisional widths for such multiplets are, as a rule, small, what leads to pronounced collisional narrowing of lines.

Generally accepted models of hard[5,16,17] and soft[4,5,17] collisions obviously cannot be applied to processing of the profiles of such lines, because these models are applicable only to description of isolated lines in the absence of mixing. The well-known equations for the shape of mixed doublet lines[7–9] can be applied only in the case of the Lorentz broadening, and they ignore the Dicke narrowing. In Ref. 2 the profile model taking into account both the collisional narrowing and mixing has been used for processing of experimental results on broadening of lines in the P- and R-branches of the ν_3 band of q m$_4$. However, this model is valid only for small cross-relaxation parameters, that is, for little pronounced mixing. The aim of this paper is a derivation of equations for profiles of close, overlapping, and unresolved doublet and multiplet lines subject to mixing and collisional narrowing. The equations to be derived must be applicable to arbitrary cross-relaxation parameters of lines.

2. Profile of a group of overlapping lines

In the model of hard collisions and non-degenerate states and in the approximation of a linear field, the equations for the off-diagonal elements of the density matrix or (accurate to a factor) polarizations of transitions with allowance for mixing and collisional narrowing of a group of M close or coincident lines have the following form[11]:

$$[\nu_m - i(\Omega_m - kv)]R_m - W(v)\left[\tilde{\nu}_m <R_m> + \sum_{\substack{k=1 \\ k \neq m}}^{M} \tilde{\nu}_{mk}<R_k>\right] =$$

$$= iV_m\, n_m^0\, W(v)\ , \tag{1}$$

$$m = 1, \ldots, M; \quad <R_m> \equiv \int_{-\infty}^{\infty} R_m(v)\mathrm{d}v;$$

$$W(v) = \exp\left[-(v/\overline{v})^2\right]/(\sqrt{\pi}\overline{v});$$

$$\overline{v} = \sqrt{2k_BT/m_a}; \quad V_m = d_m E/(2\hbar); \quad \Omega_m = \omega - \omega_{0m} ,$$

where ω and E are the frequency and electric field strength of the light wave; R_m and d_m are the polarization and matrix element of the dipole moment of the mth transition; V_m is the Rabi frequency; Ω_m is the detuning of the radiation frequency from the frequency ω_{0m} of the mth line center; $k = 2\pi/\lambda$ is the wave number; v is the projection of the absorbing molecule velocity onto the wave vector; k_B is the Boltzmann constant; T is the gas temperature; m_a is the mass of absorbing molecules; n_m^0 is the equilibrium population difference of the lower and upper levels combining with the field for the mth transition. Parameter ν_m is the sum of the radiative relaxation constant and the output frequency of the collision integral for the mth transition (in most cases the radiative relaxation constants of levels for rotational–vibrational molecular transitions are negligibly small). The constants $\tilde{\nu}_m$ and $\tilde{\nu}_{mk}$ are the elastic and inelastic input frequencies of the collision integral, respectively. The latter is also known as a cross-relaxation parameter. The ratio $\beta = \tilde{\nu}_m/(k\overline{v})$ determines the degree of collisional narrowing of lines, and along with the ratio $\alpha = \tilde{\nu}_m/\gamma_m$, where γ_m is the uniform line halfwidth in the absence of interference, it is called the narrowing parameter. The cross-relaxation parameter $\tilde{\nu}_{mk}$ is the probability of polarization transfer from the kth transition to mth transition in unit time as a result of inelastic collisions which redistribute populations within two groups of levels corresponding to the upper and lower levels of the optical transitions of the given multiplet; they are assumed rather close to each other.

The sought parameter proportional to the absorption coefficient is the field work, that is, the number of absorption events in unit time from the lower states of all the transitions interacting with radiation:

$$P = 2 \, \text{Re} \, i \sum_{m=1}^{M} V_m^* <R_m> . \qquad (2)$$

The frequencies of the collision integral ν_m, $\tilde{\nu}_m$, and $\tilde{\nu}_{mk}$ are complex parameters whose imaginary part determines the shifting and asymmetry of the line profile. Within the framework of the isotropic perturbation model, they can be considered independent of the absorbing molecules' speed.

In the case of identical scattering of a molecule being in the upper and lower states of the mth optical transition, it follows from the equations for the frequencies of the collision integral in terms of the scattering amplitude[11] and the optical theorem of scattering[18] that these frequencies are real and satisfy the following equations[11]:

$$\nu_m - \tilde{\nu}_m - \sum_{\substack{k=1 \\ k \neq m}}^{M} \tilde{\nu}_{mk} = \tilde{\nu}_{inel} > 0 ; \qquad (3)$$

$$\tilde{\nu}_{mk} = \tilde{\nu}_{km} \exp[(E_k - E_m)/(k_BT)] , \qquad (4)$$

where E_k and E_m are the energies of lower states of the kth and mth transitions, respectively, and $\tilde{\nu}_{inel}$ in the accepted model of non-degenerate states is the half-sum of speeds of the molecule inelastic transitions from the upper and lower states of the mth transition to all the states not entering into the multiplet under consideration, i.e., it is the result of significantly inelastic collisions. Actually, because of degeneration of the energy levels by projections of the total angular momentum (this degeneration is always present in the absence of continuous external fields), $\tilde{\nu}_{inel}$ contains, along with the contribution from inelastic collisions, the contribution from elastic collisions, which change an orientation of the molecule. It follows from Eq. (3) that in the absence of line mixing ($\tilde{\nu}_{mk} = 0$) for the mth isolated transition $\tilde{\nu}_{inel}$ is equal to the collisional halfwidth of the line $\gamma_m = \nu_m - \tilde{\nu}_m$. Below it is shown that even in the presence of mixing, under certain conditions, Eq. (3) gives the effective collisional halfwidth of the Lorentzian profile of an unresolved multiplet line at high pressure of the buffer gas.

For transitions in the visible and IR spectral regions the equilibrium population difference n_m^0 is equal, to a good approximation, to the lower level population of the considered transition N_m not perturbed by the radiation field:

$$N_m = ng_m(2J_m + 1) \exp [- \hbar c E_m/(k_BT)]/Q ; \quad (5)$$

$$Q = \sum_k g_k(2J_k + 1) \exp [- \hbar c E_k/(k_BT)] ,$$

where n is the density of absorbing molecules; E_m and J_m are the energy and the rotational quantum number of the lower level of the corresponding transition; g_m is its nuclear statistical weight; $\hbar$ is the Planck constant; c is the speed of light.

The analytical solution of Eq. (1) can be obtained in the general case at arbitrary relations between the parameters ν_m, $\tilde{\nu}_m$, and $\tilde{\nu}_{mk}$ by integration over speed and inversion of $M \times M$ matrices. However, at $M > 2$ this solution is too cumbersome. Therefore, let us restrict our consideration to searching for an exact solution of Eq. (1) for doublet lines ($M = 2$) without any restrictions on its parameters. For $M > 2$ let us construct the model analytical solution for the particular case of the input and output frequencies being the same for different multiplet components, while the output and elastic and inelastic input frequencies remain different.

3. Profile of a doublet line

For $M = 2$, using Eqs. (1) and (2) and substituting

$$V_i^2 n_1^0 \to - S_i/2\pi, \quad V_i V_j n_j^0 \to - G_{ij}\sqrt{S_i S_j}/2\pi,$$

$$V_i V_j n_i^0 \to - G_{ji}\sqrt{S_i S_j}/2\pi, \quad G_{ij} \equiv \sqrt{N_j/N_i} , \quad (6)$$

we derive the equation for the absorption coefficient of a doublet line

$$k_d(\omega) = \frac{1}{\pi} \operatorname{Re} \left\{ S_1 w_1 + S_2 w_2 - [S_1 \tilde{v}_2 + S_2 \tilde{v}_1 - \right.$$

$$\left. - \sqrt{S_1 S_2} (G_{12} \tilde{v}_{12} + G_{21} \tilde{v}_{21})] w_1 w_2 \right\} /$$

$$\left\{ 1 - \tilde{v}_1 w_1 - \tilde{v}_2 w_2 + (\tilde{v}_1 \tilde{v}_2 - \tilde{v}_{12} \tilde{v}_{21}) w_1 w_2 \right\} ; \quad (7)$$

$$w_i \equiv \frac{\sqrt{\pi}}{k\bar{v}} w \left(\frac{\Omega_i + i v_i}{k\bar{v}} \right),$$

where $w(z)$ is the complex probability function; S_i, $i = 1, 2$ are the intensities of the doublet components.

As a rule, for the doublets under discussion the energy difference between the upper and lower energy levels is far less than the thermal energy: $|E_1 - E_2| \ll k_B T$. Besides, the relaxation constants for the two combining transitions can be considered equal to a high degree of certainty:

$$v_1 = v_2 \equiv v , \quad \tilde{v}_1 = \tilde{v}_2 \equiv \tilde{v} ,$$

$$\tilde{v}_{12} = \tilde{v}_{21} \equiv \zeta ; \quad S_{1,2} \equiv g_{1,2} S . \quad (8)$$

As a result, Eq. (7) becomes somewhat simpler because the number of terms entering into it decreases:

$$k_d(\omega) = \frac{S}{\pi} \operatorname{Re} \frac{g_1 w_1 + g_2 w_2 - (g_1 + g_2)(\tilde{v} - \zeta) w_1 w_2}{1 - \tilde{v}(w_1 + w_2) + (\tilde{v}^2 - \zeta^2) w_1 w_2} . \quad (9)$$

The line shape (9) at different values of the parameters of narrowing $\alpha = \tilde{v} / \gamma$, $\gamma \equiv v - \tilde{v}$ and cross-relaxation $\xi \equiv \zeta / \gamma$ is shown in Fig. 1 as an example of the joint effect of collisional narrowing and mixing on the doublet line. Equation (9) was used for processing the experimental line profiles of resolved and unresolved doublets of the v_2 band of $m_2 n$ nearby 5 μm. The experimental data were recorded with the Fourier transform spectrometer.[19] In particular, the results of processing support the assumptions (8).

In the limiting case of homogeneous broadening or for far wings of a line, where

$$\sqrt{\Omega_{1,2}^2 + v^2} \ll k\bar{v} , \quad (10)$$

having used the asymptotic expansion[20]:

$$w \left(\frac{\Omega_{1,2} + i v}{k\bar{v}} \right) \cong \frac{k\bar{v}}{v - i\Omega_{1,2}} \Big/ \sqrt{\pi} , \quad (11)$$

we have from Eq. (9)

$$k_d(\Omega) =$$

$$= \frac{S}{\pi} \frac{(\gamma + \zeta)[\gamma^2 - \zeta^2 - \Omega(\Omega + \Delta)] + \gamma(2\Omega + \Delta)(\Omega + \Delta/4)}{[\gamma^2 - \zeta^2 - \Omega(\Omega + \Delta)]^2 + \gamma^2(2\Omega + \Delta)^2} = \quad (12)$$

$$= \frac{S(\gamma - \zeta)}{\pi} \frac{1 + \Delta \dfrac{(\gamma - 2\zeta)\,\Omega + \gamma\Delta/2}{2(\gamma - \zeta)\,[\Omega^2 + (\gamma + \zeta)^2]}}{\Omega^2 + (\gamma - \zeta)^2 + 2\Delta \dfrac{\Omega(\Omega^2 + \gamma^2 + \zeta^2) + \Delta(\gamma^2 + \Omega^2)/2}{\Omega^2 + (\gamma + \zeta)^2}} ; \quad (12a)$$

$$\Delta \equiv |\omega_{01} - \omega_{02}|, \quad \Omega \equiv \Omega_1, \quad \Omega_2 = \Omega - \Delta .$$
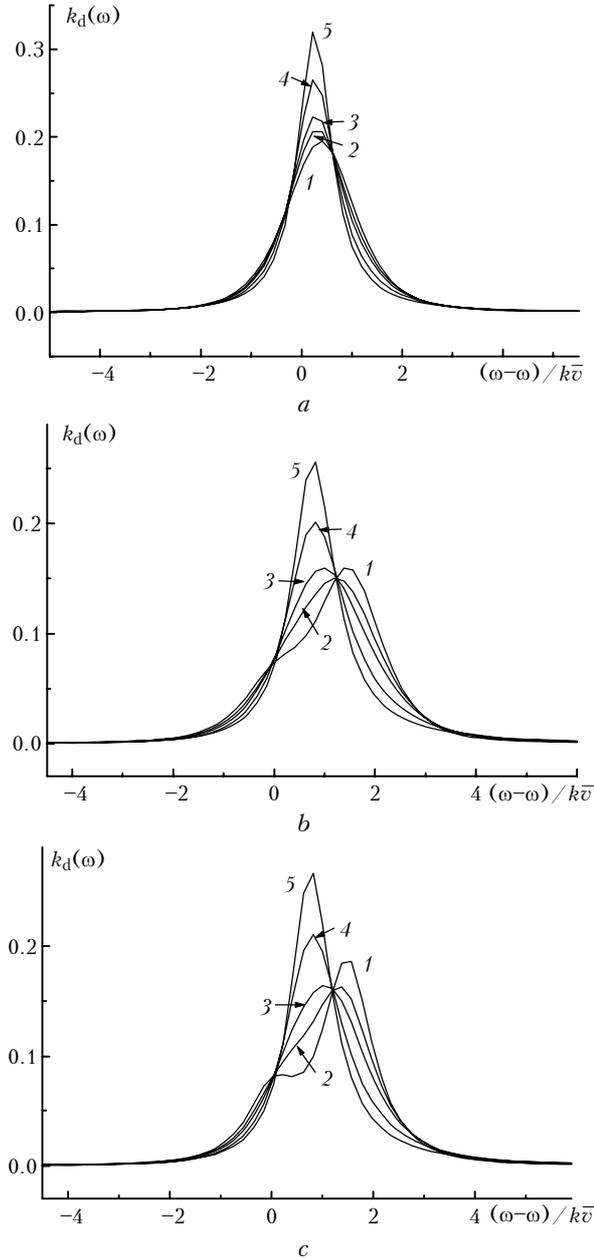

Fig. 1. Line shape $k_d(\omega)$ described by Eq. (9) for $\gamma / k\bar{v} = 0.2$; $\alpha = 2$ (a, b) and 5 (c) and $(\omega_{02} - \omega_{01})/k\bar{v} = 0.5$ (a) and 1.5 (b, c); $\zeta/\gamma = 0.1$ (curves 1), 1 (2), 2 (3), 5 (4), and 10 (5).

Equation (12) coincides with the well-known profile of a doublet line subject to the collisional exchange.[7–10] From Eq. (12a) it is seen that for the

unresolved doublets $(\Delta \to 0)$ $k_d(\Omega)$ is the Lorentz profile with the halfwidth $\tilde{\nu}_{inel} = \gamma - \zeta$ less than the collisional line halfwidth γ by the cross-relaxation parameter ζ.

4. Profile of a multiplet

Similarly to the case of the doublet line profile, under the assumption of equal relaxation constants for all transitions taking part in the absorption:

$$\nu_m = \nu \ , \quad \tilde{\nu}_m = \tilde{\nu} \ , \quad \tilde{\nu}_{mk} = \zeta, \tag{13}$$

for the profile of a multiplet consisting of M components we have

$$k_{mult}(\omega) = \frac{1}{\pi} \text{Re} \sum_{m=1}^{M_{LL}} \frac{w_m}{1 - (\tilde{\nu} - \zeta)w_m} \times$$

$$\times \left\{ S_m + \zeta \sum_{m=1}^{M} \frac{G_{mk}\sqrt{S_m S_k}w_k}{1-(\tilde{\nu}-\zeta)w_k} \middle/ \left[1 - \zeta \sum_{m=1}^{M} \frac{w_k}{1-(\tilde{\nu}-\zeta)w_k} \right] \right\}. \tag{14}$$

Assuming $S_m = g_m S$, Eq. (14) can be simplified:

$$k_{mult}(\omega) =$$

$$= \frac{S}{\pi} \text{Re} \left\{ \sum_{m=1}^{M} \frac{g_m w_m}{1-(\tilde{\nu}-\zeta)w_m} \middle/ \left[1 - \zeta \sum_{m=1}^{M} \frac{w_k}{1-(\tilde{\nu}-\zeta)w_k} \right] \right\}. \tag{15}$$

In the limiting case of high pressures Eq. (15) takes the form

$$k_{mult}(\omega) =$$

$$= \frac{S}{\pi} \text{Re} \left\{ \sum_{m=1}^{M} \frac{g_m}{\gamma + \zeta - i\,\Omega_m} \middle/ \left[1 - \zeta \sum_{m=1}^{M} \frac{1}{\gamma + \zeta - i\,\Omega_k} \right] \right\}. \tag{16}$$

Equations (15) and (16) form the model bounded, first of all, by the condition (13) which can be verified from comparison with the experiment. Correspondingly,

its terms ν, $\tilde{\nu}$, and ζ are the effective parameters averaged over all multiplet components.

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