Journal of Quantitative Spectroscopy & Radiative Transfer 189 (2017) 18–23

Contents lists available at ScienceDirect

Journal of Quantitative Spectroscopy & Radiative Transfer

journal homepage: www.elsevier.com/locate/jqsrt

On parameterization of spectral line profiles including the speed-dependence in the case of gas mixtures

V.P. Kochanov [a,b,*]

[a] Laboratory of Theoretical Spectroscopy, V.E. Zuev Institute of Atmospheric Optics SB RAS 1, Akademician Zuev Square, 634021 Tomsk, Russia
[b] Physical Department of Tomsk State University, 36, Lenin Ave., 634050 Tomsk, Russia

ARTICLE INFO

Article history:
Received 10 November 2016
Accepted 11 November 2016
Available online 16 November 2016

Keywords:
Line profile parameters
Speed-dependence
Gas mixture

ABSTRACT

The physically grounded parameterization of a line profile including the speed-dependence was performed. It was shown that two actual parameters of the quadratic speed-dependence appear in gas mixtures instead of a single parameter in a pure gas. One of the parameters is associated with hard elastic velocity-changing collisions; the second is connected with the other sorts of collisions. For comparable concentrations of gas species, they may differ by 50% and depend nonlinearly on partial gas pressures. The dimensionless line narrowing parameter also reveals nonlinear pressure-dependence. The computational expressions for the line profile including all main physical mechanisms of its forming in conditions of gas mixtures are derived.

1. Introduction

The dependence of collision relaxation constants on the speed of an absorbing molecule [1–3] (so called wind effect [4]) noticeably affects a line shape. This physical mechanism of forming the latter is taken into account in majority of recent models for line profiles (e.g. see Refs. [5–9]). The detailed discussion of this and other mechanisms of a spectral shape forming (not being the task of this paper) can be found, for example, in Refs. [5–14]. Here we only note that namely the wind effect leads to specific features of parameterization of the profile applied to processing the absorption spectra recorded in the presence of one or more buffer gases.

The fact of the matter is that the speed-dependence is a characteristic of binary collisions of an absorbing molecule with perturbing particles. Thus, it is determined only by the parameters of the intermolecular interaction potential and the mass ratio of perturbing to absorbing molecules. Due to this circumstance, the parameters of the speed-dependence often are treated as pressure-independent ones. But this is valid in the cases of: a) the self-broadening; b) the line broadening of a small fraction of an absorbing gas by a homogeneous buffer gas; and c) when the ratios of concentrations of perturbing and absorbing gases are kept constant. Evidently, if concentrations of absorbing and perturbing gases are comparable and one of them is fixed, then the parameters of the speed-dependence will depend on the variable gas pressure when processing recorded line profiles with model profiles that contain adjustable parameters of the speed-dependence. This may lead to systematic errors in pressure broadening constants and other line parameters retrieved from such processing. Line broadening and shifting by a foreign gas or mixtures of buffer gases are typical in spectroscopic measurements, and there are examples of nonlinear pressure dependencies of a total line width caused by simultaneous action of the Dicke line narrowing [15,16] and the effect of the speed-dependence [17–21] Thereby, an account of combined physical mechanisms of line broadening in conditions of gas mixtures requires a special thorough consideration.

As far as the number of adjustable line parameters increases when broadening by several gases, it is desirable to reduce it with the aid of preliminary quantitative estimation of some parameters. In particular, it is possible to calculate the parameters of the speed-dependence for each pair of different colliding molecules of a gas mixture [1–5,10,14] as functions of the mass ratio of perturbing to absorbing molecules and to use them in fitting as fixed ones after a proper parameterization of a line profile. Moreover, calculations of a line profile based on the quantum-mechanical collision integral kernel [22] and inverse-power intermolecular interaction potential allow finding out the ratio of soft to hard collision frequencies also with the mean angle of scattering molecules on small angles [11,12,14]. These parameters also can be fixed. In order to use fixed pressure-independent parameters calculated for individual pairs of molecules, the line profile must be properly specified. Namely, all the parameters of pressure broadening, narrowing, and speed-dependence attributed to each species of a gas mixture must be included in the line profile explicitly. At the present, such

---

[*] Corresponding address: Laboratory of Theoretical Spectroscopy, V.E. Zuev Institute of Atmospheric Optics SB RAS 1, Akademician Zuev square, 634021 Tomsk, Russia.
E-mail address: koch@iao.ru

http://dx.doi.org/10.1016/j.jqsrt.2016.11.007
0022-4073/

specification is performed in respect to the hard collision model (e.g. see Ref. [9] and references therein), which it is not sufficient in a more general case of the combined action of hard and soft collisions.

The goal of this paper is to construct a model line profile that accounts for all essential underlying physical mechanisms discussed in Ref. [10–12,14] in conditions of combined line broadening by different gases. Specifically, the line profile derived lately in Ref. [14] is generalized to the case of gas mixtures.

2. The line profile

In order to derive the line profile, we use the master equation for the normalized constant part of the molecular polarization R (Eq. (5) in Ref. [14]) where the collision integral is partly reduced to a differential form and the speed-dependence in the right-hand part is omitted due to the smallness of the terms containing derivatives of R with respect to the velocity:

$$\left[\frac{1+\eta t^2}{1+\eta/2}(\nu-\nu_s)-i(\Omega-k\bar{v}\,t)\right]R(t)-\frac{1+\eta t^2}{1+\eta/2}\nu_h\frac{e^{-t^2}}{\sqrt{\pi}}\int_{-\infty}^{\infty}R(t_1)dt_1$$
$$=\frac{S}{\pi^{3/2}}e^{-t^2}+\nu_s\left[\theta^2\frac{d^2}{dt^2}R(t)-\xi t\frac{d}{dt}R(t)\right],\quad t\equiv\frac{v_z}{\bar{v}},\quad \bar{v}=\sqrt{2k_BT/m}\,. \tag{1}$$

Here t is the dimensionless projection of the active molecule's velocity on the wave vector, $\bar{v}$is the most probable thermal velocity, k_B is the Boltzmann constant, T is the gas temperature, and m is the mass of an absorbing molecule. The quantities ν_h and ν_s are input frequencies of the collision integral averaged over 3D-velocity. They describe the action of hard and soft velocity-changing collisions,[1] respectively. The parameter ν is the average output frequency of the collision integral diminished by the frequency of collisions with scattering on diffraction angles [11–14]. Ω is the frequency detuning, k is the wave number, S is the line intensity. θ is the ratio of mean velocity changes at classical small-angle scattering to the thermal velocity $\bar{v}$. The dimensionless parameter ξ is responsible for the asymmetry of the collision integral kernel caused by soft collisions. The parameter η describes the speed-dependence taken in the simplest quadratic form. The analytical expression for η is derived in Appendix for arbitrary mass ratios of perturbing to absorbing molecules.

Eq. (1) contains the parameters that are related to collisions of small amount of absorbing gas molecules with buffer gas molecules of one sort or to collisions between the same molecules in the case of self-broadening. Since line broadenings by different perturbing particles are statistically-independent processes, the immediate generalization of Eq. (1) to the case of a gas mixture reads:

$$\left[\sum_j\frac{1+\eta_j t^2}{1+\eta_j/2}(\nu_j-\nu_{sj})-i(\Omega-k\bar{v}\,t)\right]R(t)$$
$$-\sum_j\frac{1+\eta_j t^2}{1+\eta_j/2}\nu_{hj}\frac{e^{-t^2}}{\sqrt{\pi}}\int_{-\infty}^{\infty}R(t_1)\,dt_1=$$
$$\frac{S}{\pi^{3/2}}e^{-t^2}+\sum_j\nu_{sj}\theta_j^2\,\frac{d^2}{dt^2}R(t)$$
$$-\sum_j\nu_{sj}\xi_j\;t\frac{d}{dt}R(t), \tag{2}$$

where index j denotes collisions of an absorbing molecule with a buffer gas molecule of j-th sort, and the summation is carried out over all species of a gas mixture.

The evident parameterization of Eq. (2) leads to

$$\left[\frac{1+\eta_c t^2}{1+\eta_c/2}(\nu-\nu_s)-i(\Omega-k\bar{v}\,t)\right]R(t)$$
$$-\frac{1+\eta_h t^2}{1+\eta_h/2}\nu_h\frac{e^{-t^2}}{\sqrt{\pi}}\int_{-\infty}^{\infty}R(t_1)dt_1$$
$$=\frac{S}{\pi^{3/2}}e^{-t^2}+\nu_s\left[\theta^2\frac{d^2}{dt^2}R(t)-\xi t\frac{d}{dt}R(t)\right], \tag{3}$$

where new parameters are defined as follows:

$$\nu=\sum_j\nu_j,\qquad \nu_h=\sum_j\nu_{hj},\qquad \nu_s=\sum_j\nu_{sj},$$
$$\nu_j=\nu_j^{(p)}p_j,\quad \nu_{hj}=\nu_{hj}^{(p)}p_j,\quad \nu_{sj}=\nu_{sj}^{(p)}p_j,$$
$$\eta_h=\sum_j\frac{\nu_{hj}\,\eta_j}{1+\eta_j/2}\Big/\sum_j\frac{\nu_{hj}}{1+\eta_j/2},\qquad \eta_c=\sum_j\frac{(\nu_j-\nu_{sj})\eta_j}{1+\eta_j/2}\Big/\sum_j\frac{\nu_j-\nu_{sj}}{1+\eta_j/2},$$
$$\theta^2=\sum_j\nu_{sj}\theta_j^2\Big/\sum_j\nu_{sj},\qquad \xi=\sum_j\nu_{sj}\xi_j\Big/\sum_j\nu_{sj}. \tag{4}$$

Here p_j are the partial gas pressures, ${}_j^{\nu(p)}$, ${\nu_{hj}}^{(p)}$, and ${\nu_{sj}}^{(p)}$ are respective pressure broadening coefficients.

As is seen from the comparison of Eq. (1) with Eq. (3), they coincide except for the appearance of two parameters of speed-dependence, η_c and η_h, in Eq. (3) instead of the single parameter η presented in Eq. (1) and prescribed by the theory [10,14] for a homogeneous gas. As it follows from Eq. (4), in the cases of self-broadening or negligible concentration of an absorbing gas the coefficients of the speed-dependence are equal: $\eta_c=\eta_h$. The behavior of the parameters η_c and η_h and their ratio as functions of partial gas pressures is illustrated on the example of the mixture of two gases, e.g. the water vapor and the nitrogen (Fig. 1). The calculations presented in Fig. 1 show that when partial pressures are comparable, the relative difference between η_c and η_h reaches tens of percent. The parameter η_c exceeds η_h in the entire region of gas pressures.

The line profile derived on the basis of Eq. (3) and the scheme of calculations of Ref. [14] is

$$K_{sh}(\Omega)=K_h(\Omega)+K_s(\Omega);$$
$$K_h(\Omega)=\frac{S}{\sqrt{\pi}k\bar{v}}\,\mathrm{Re}\left[U_h(\Omega,\nu,\nu_h,\nu_s,\eta_c,\eta_h,k\bar{v})\right];$$
$$K_s(\Omega)=\frac{S}{\sqrt{\pi}k\bar{v}}\,\mathrm{Re}\left[U_s(\Omega,\nu,\nu_h,\nu_s,k\bar{v})\right]; \tag{5}$$

$$U_h(\Omega,\nu,\nu_h,\nu_s,\eta_c,\eta_h,k\bar{v})=\frac{w(T_1)+w(-T_2)}{(1-J)\,Q},\qquad w(z)=e^{-z^2}\mathrm{erfc}(-iz),$$

$$J=\frac{\eta_h}{\eta_c}\frac{1+\eta_c/2}{1+\eta_h/2}\frac{\nu_h}{\nu-\nu_s}+\frac{\sqrt{\pi}\,\nu_h}{(1+\eta_h/2)k\bar{v}Q}\left[\left(1+\eta_h{T_1}^2\right)w(T_1)+\left(1+\eta_h{T_2}^2\right)w(-T_2)\right],$$

$$T_1=-i\frac{1+\eta_c/2}{2\eta_c}\frac{k\bar{v}}{\nu-\nu_s}(1-Q),\qquad T_2=-i\frac{1+\eta_c/2}{2\eta_c}\frac{k\bar{v}}{\nu-\nu_s}(1+Q),$$
$$Q=\sqrt{1-\frac{4i\eta_c}{1+\eta_c/2}\frac{\nu-\nu_s}{k\bar{v}}\Omega_1},\qquad \Omega_1=\frac{\Omega+i(\nu-\nu_s)/(1+\eta_c/2)}{k\bar{v}};$$

$$U_s(\Omega,\nu,\nu_h,\nu_s,k\bar{v})=$$
$$-\frac{\nu_s}{3\sqrt{\pi}\,k\bar{v}}\left\{8\theta^2+\Omega_2\left[\begin{array}{l}-2\Omega_2\left(4\theta^2+5\xi-2\xi\,\Omega_2^2\right)+\\ i\sqrt{\pi}\left(3\left(4\theta^2+\xi\right)-4\left(2\theta^2+3\xi\right)\Omega_2^2+4\xi\,\Omega_2^4\right)w(\Omega_2)\end{array}\right]\right\},$$
$$\Omega_2=\frac{\Omega+i(\nu-\nu_h-\nu_s)}{k\bar{v}}.$$

Here erfc (z) is the complimentary complex error function [23]. The algebraic approximation for $w(z)\approx w_a(z)$ is given by Eq. (12) in

---

[1] Detailed description of the terms is given in Refs. [11–14].