



Speed-dependent spectral line profile including line narrowing and mixing

Victor 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., 63405 Tomsk, Russia



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ABSTRACT

A line profile model was developed that accounts for all essential underlying physical mechanisms. The model is based on the quantum-mechanical collision integral kernel calculated for intermolecular interaction potentials $\propto r^{-n}$ with $n=3..6$ where r is the distance between colliding molecules. It was shown that collisions of molecules with scattering on classical small angles flatten the line profile. The relative flattening reaches 10% for $n=3$ and has a smaller value, $\sim 2\%$, for $n=6$ in conditions of inhomogeneous line broadening. An algebraic expression for the line profile was obtained, which allows processing recorded spectra with preliminary estimation and constraint of some of the profile's parameters.

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1. Introduction

Recently it was ascertained [1–4] that soft collisions of molecules with scattering on classical small angles $\sim 0.1..0.3$ rad noticeably diminish Dicke line narrowing [5,6]. This means that the spectral line profile accounting for soft collisions is flatter (and close to the Voigt profile) than the line profile in the hard collision model [7,8]. It is shown (see Ref. [2, Fig. 2]) that the frequency of small-angle scattering collisions can exceed the frequency of large-angle scattering collisions up to 10 times for long-range (dipole–dipole and dipole–quadrupole) intermolecular interactions and light perturbing molecules. Hence, the account of soft collisions is necessary for quantitative processing of the high quality data on spectral line shapes. The speed-dependent line

profiles [1,2] derived on the basis of the quantum-mechanical collision integral kernel [9] and the differential cross-sections calculated for intermolecular interaction potentials $\propto r^{-n}$ with $n=3..6$ make it possible to account for both small- and large-angle scattering collisions. Such profiles contain only physically meaningful adjustable parameters such as the frequencies of soft and hard collisions and the parameter of the collision line narrowing. These profiles can be used in data processing for different pairs of colliding molecules and certain types of simplest inverse-power interaction potentials.

The type of an intermolecular interaction potential determines the speed-dependence of collision relaxation constants, the relation of frequencies of small- and large-angle scattering collisions, and the angle characteristics of scattering. The actual interaction potentials are more complex than the inverse-power ones because of their combined type, the presence of a repulsive part (potential well), and their dependence on mutual orientation of colliding molecules. It can be expected that proper modeling and parameterization of the collision integral kernel

* Correspondence address: Laboratory of Theoretical Spectroscopy, V.E. Zuev Institute of Atmospheric Optics SB RAS 1, Akademician Zuev square, 634021 Tomsk, Russia.

Tel.: +7 3822491111 1110; fax: +7 3822492086.

E-mail address: koch@iao.ru

[9] will provide a more flexible and simple line profile appropriate for processing experimental line shapes. Such model profile must include all essential physical mechanisms of its forming: (1) the Doppler and the collision line broadening, (2) Dicke line narrowing reduced by the effect of small-angle scattering collisions, (3) wind effect leading to the speed-dependence of collision relaxation constants, (4) line mixing. As a result of the modeling, parameters additional to those presented in common profiles appear. Namely, the full set of parameters for a separate spectral line is the line intensity S , the line center Ω_0 , the output frequency of the collision integral ν , the input frequencies of soft and hard collisions ν_s and ν_h , respectively, the parameter η defining the speed-dependence of the above frequencies, the mean angle θ of scattering absorbing molecules on small angles, and the parameter ξ related to the asymmetry of the collision integral kernel caused by the wind effect (speed-dependence). In the case of interfering lines, the complementary cross-relaxation parameters ξ_m are introduced which describe the line mixing effect for m -th line. In general, the parameters ν , ν_s , ν_h , and ξ_m are complex, and thus they describe the line shifting and asymmetry as well as the line broadening [10,11].

The abundance of adjustable parameters allows one to explore the effect of various physical mechanisms accounted for the line profile by means of variation of the parameters and comparison of the corresponding calculated profiles. On the other hand, a lot of parameters make it difficult to fit the profile, because some of the parameters may strongly correlate.

The aim of this paper is to create such a line profile model, investigate an influence of soft collisions on its shape, and give the recommendations for its usage in spectral analysis.

2. Model collision integral kernel

The master equation for the normalized constant part of the light-induced molecular polarization R [1,2] in the 1D-velocity approach (see Ref. [12] and references therein) reads

$$\begin{aligned} & \left[\frac{1+\eta t^2}{1+\eta/2} \nu - i(\Omega - k\bar{v}t) \right] R(t) - \frac{1+\eta t^2}{1+\eta/2} \nu_h \frac{e^{-t^2}}{\sqrt{\pi}} \int_{-\infty}^{\infty} R(t_1) dt_1 - \\ & \frac{1+\eta t^2}{1+\eta/2} \nu_s \int_{-\infty}^{\infty} A(t, t_1) R(t+t_1) dt_1 = \frac{S}{\pi^{3/2} k\bar{v}} e^{-t^2}; \\ & t \equiv \frac{V_z}{\bar{v}}, \bar{v} = \sqrt{2k_B T/m}, \end{aligned} \quad (1)$$

where the collision integral is represented as a sum of the hard-collision part proportional to the frequency ν_h and the small-angle scattering part with the frequency ν_s . Here the speed-dependence is taken in a most simple quadratic form, the same for all the collision relaxation constants ν , ν_h , and ν_s [10,12], which are the quantities averaged over one-dimensional velocity. This form of the speed-dependence allows expressing the solution of Eq. (1) through the roots of a quadratic equation. More realistic approximation of the speed-dependence [12] leads to the analytical line profile expressed via the roots of a cubic

equation. The kernel $A(t, t_1)$ describes the action of soft collisions with the scattering on classical small angles. The diffraction-scattering part of the kernel is in order of magnitude more narrow than $A(t, t_1)$ and thus it works as the δ -function which leads to renormalization $\nu \rightarrow \nu - \nu_d$, where ν_d is the frequency of collisions with scattering on diffraction angles [1–3]. Ω in Eq. (1) is the frequency detuning, $k\bar{v}$ is the Doppler line half-width at the $1/e$ height, k is the wave number at the given transition, ν_z is the component of a molecular velocity parallel to the wave vector, S is the line intensity, k_B is the Boltzmann constant, T is the gas temperature, and m is the mass of an absorbing molecule.

On the basis of calculations performed for dispersion intermolecular interaction potential (see Fig. 2b in Ref. [1]), the following model kernel normalized by its square was chosen:

$$\begin{aligned} A(t, t_1) &= \frac{\theta^{-1} + a_2 |t|}{2 + (a_1 \theta^{-1} + a_2 \theta) |t| + a_1 a_2 t^2} \times \\ & \left\{ \Theta(t) \left[\Theta(-t_1) e^{t_1/(\theta + a_1 |t|)} + \Theta(t_1) e^{-t_1(\theta^{-1} + a_2 |t|)} \right] + \right. \\ & \left. \Theta(-t) \left[\Theta(-t_1) e^{t_1(\theta^{-1} + a_2 |t|)} + \Theta(t_1) e^{-t_1/(\theta + a_1 |t|)} \right] \right\}, \Theta(t) = \begin{cases} 1, & t \geq 0 \\ 0, & t < 0 \end{cases} \end{aligned} \quad (2)$$

Here θ is the ratio of mean velocity changes at classical small-angle scattering to the most probable thermal velocity \bar{v} and $\Theta(t)$ is the unit step function. It should be noted that the use of the function $A(t, t_1) \propto 1/\{\exp[-c_1(t-t_1)] + \exp[c_2(t-t_1)]\}$ with a smooth top gave worse results of its fitting to kernels calculated in Refs. [1,2].

Parameters a_1 , a_2 , and θ were obtained from fitting the model

$$A_{tot}(t, t_1) = a A(t, t_1) + b \exp[-(t+t_1)^2] \quad (3)$$

to the quantum-mechanical kernels calculated in Refs. [1,2] for intermolecular potentials $\propto r^{-n}$. This fit simultaneously included multiple kernels with $n=3\dots 6$ and $\beta=0\dots 10$, where $\beta \equiv m_b/m$ is the perturbing to absorbing molecular mass ratio. The second term in the right-hand part of Eq. (3) represents hard collisions where the coefficients a and b retrieved from the fitting determine the ratio $r \equiv \nu_s/\nu_h = a/(\pi^{1/2} b)$. The examples of the fitting are presented in Fig. 1. As is seen from the comparison of the squares under curve 2 and among curves 1 and 2, in the case of the dipole-dipole intermolecular interaction the scattering on classical small angles dominates the scattering attributed to hard collisions (Fig. 1a and b), while these types of scattering (“soft” and “hard”) are comparable for the shot-range Van der Waals interaction with $n=6$ (Fig. 1c and d).

The determined parameters a_1 and a_2 satisfy the conditions: $a_1 |t| \ll 1$ and $a_2 \theta^2 |t| \ll 1$ at $|t| < 3$. This allows expansion of the exponents in Eq. (2) up to the second order of magnitude for a_1 and a_2 . The value of the kernel at the $1/e$ maximum gives $A(t, t_1) \approx A(|t_1|) \equiv \theta$. Since $\theta \sim 0.15\dots 0.3 < 1$, the function $R(t+t_1)$ under the integral in Eq. (1) can also be expanded in the powers of t_1 :

$$R(t+t_1) \approx R(t) + t_1 \frac{d}{dt} R(t) + \frac{1}{2} t_1^2 \frac{d^2}{dt^2} R(t). \quad (4)$$

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