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Combined effect of small- and large-angle scattering collisions on a spectral line shape

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

[a] V.E. Zuev Institute of Atmospheric Optics, Siberian Branch, Russian Academy of Sciences, 1 Academician Zuev Square, 634021 Tomsk, Russia
[b] Tomsk State University, Tomsk 634050 Russia

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ABSTRACT

Algebraic approximations for line profiles calculated on the basis of quantum-mechanical collision integral kernels for dipole–dipole, dipole–quadrupole, and quadrupole–quadrupole intermolecular interaction potentials were obtained. In derivation of the profiles velocity-changing collisions of molecules with scattering on small and large angles also with the speed-dependence of collision relaxation constants have been taken into account. It was shown that the relative contribution of small-angle collisions into the frequency of elastic velocity-changing collisions is much more pronounced for long-range potentials. A sensitive criterion for analysis of a line narrowing was proposed and tested.

1. Introduction

As is known, elastic velocity-changing collisions lead to Dicke's line narrowing [1,2] realizing at gas pressures low enough to provide noticeable Doppler line broadening. The physical mechanism of this phenomenon consists in compensation to some extent of the Doppler broadening due to random changes of the direction of a velocity of the absorbing molecule performing Brownian motion within the area whose size (the length of diffusion during light absorption) is restricted by a wavelength. In other words, standing molecule absorbs radiation in conditions when chaotic Doppler frequency shifts are minimized in average in the course of absorption. A spatial localization is needed for elimination of the phase modulation caused by translational motion of the absorbing molecule that gives rise to additional line broadening. If the interaction of molecule with light is long enough (i.e. the pressure broadening constant is small), then the line narrowing is pronounced. From here it is evident that the main contribution to this effect is caused by large-angle scattering collisions (LASC) with changes in velocity of the order of the most probable speed $\bar{v}$. Conventional hard collision model [3,4] describes this situation whereas hard collisions leading by definition to the establishing of equilibrium Maxwell distribution over velocities after each collision give considerable changes in velocity in average.

Collisions with a small-angle scattering (SASC) give much smaller changes in a velocity and much greater diffusion length that does not match the conditions for line narrowing. Therefore, in the case where such collisions prevail and the velocity-changing collisions with a large-angle scattering practically are absent, the narrowing must be negligible and hence the respective line profile will be flatter and closer to the Voigt one; scattering on zero angles gives the Voigt profile exactly.

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* Correspondence to: V.E. Zuev Institute of Atmospheric Optics, Siberian Branch, Russian Academy of Sciences, 1 Academician Zuev Square, 634021 Tomsk, Russia. Tel.: +7 3822491111, +7 3822491110; fax: +7 3822492086.

E-mail address: koch@iao.ru

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In this connection, it is significant to note that the widespread soft collision model [4–6] describes the line narrowing as well as the hard collision model does (e.g., see Ref. [7]), in spite of the given above qualitative argumentation of the absence of the collision line narrowing in the pure case of small-angle scattering. The reason for this lies in the fact that soft collision model [4–6] is based on the representation of the initial integral form of the collision integral in master equations for the density matrix as a right-hand part of the differential Fokker–Planck (diffusion) equation in the velocity space [4,6]. Though the supposition of light perturbing particles and hence small average changes in a velocity is exploited in this derivation (and the term “soft collisions” originates from here [4]), the obtained diffusion equation actually describes all sorts of collisions, SASC and LASC.[1] Moreover, namely the large-angle scattering collisions play the major role in forming the diffusion coefficient [8] and the line narrowing. Consequently, the term “soft” as regards the model [4–6] is not quite adequate since it implies LASC as well as SASC, and due to this circumstance, this model is merely an alternative variant of the hard collision model. Indeed, the line profiles from both the models are hardly distinguished [7] and attempts to combine them [9,10] in order to improve the physical meaning of the line shape models gave no any results on a relationship between SASC and LASC in forming a line shape, taking into account that true soft velocity-changing collisions can be attributed only to the small-angle scattering.

At the same time, the simultaneous account of soft and hard collisions (or SASC and LASC) in a spectral line profile is quite necessary because SASC make the line profile noticeably flatter as compared with the line profiles derived in the hard collision models. This action of SASC immediately follows from the above-considered mechanism of the collision narrowing and it was confirmed in Ref. [11] where a line profile was derived on the basis of the explicit introducing of SASC via a separate part of the collision integral additional to the common term representing hard collisions. In principal, this model allows determining the ratio of SASC and LASC frequencies by comparison of the line profile [11] with recorded line profiles.

For all types of intermolecular interaction, except for dipole–dipole one, a line profile is affected by the wind effect caused by translational motion of molecules, which creates the anisotropy of perturbation and implies the dependence of collision relaxation constants on the molecular speed [12–16]. As distinct from Dicke's line narrowing, the wind effect is not associated with the Doppler line broadening, but it also produces the line narrowing [17]. Both these mechanisms of narrowing superpose in most frequently used range of gas pressures where inhomogeneous line broadening takes place. The speed-dependent Nelkin – Ghatak line profile [15,18] describes this situation in the framework of the hard collision model. But, since Dicke's narrowing is rather reduced due to the action of SASC, the line profile [15,18] overestimates the actual line narrowing. In order to overcome this imperfection of the theory revealing in comparison of the latter with an experiment, often the parameters characterizing the speed-dependence[2] are treated as adjusting parameters in fitting of a model line profile to experimental ones (e.g., see Ref. [19]). Another approach, called “partially-correlated speed-dependent hard-collision model” (see Ref. [20] and references therein), consists in diminishing the speed dependence of the collision line broadening constant (and hence diminishing the line narrowing caused by the wind effect) by definition of the collision relaxation constant as a sum of speed-dependent and speed-independent parts, the ratio of which appears as an additional fitting parameter. The third manner to avoid disagreement between theory and experiment caused by disregard of SASC is ignoring Dicke's line narrowing and usage the speed-dependent Voigt line profile [12]. This may be justified in the case when SASC dominates LASC and gas pressures are sufficiently high. As is shown in Section 2, such situation is plausible for long-range intermolecular potentials. Finally, the model line profile [11] that explicitly takes into account the SASC is valid only for dipole–dipole intermolecular interaction when the wind effect is absent.

In the recent paper [17] numerical calculations of line profiles were performed that are based on the Rautian – - Shalagin quantum-mechanical kernel of the collision integral [21,22] with the use of the differential scattering cross section calculated for the isotropic dispersion intermolecular interaction potential. Thus, the joint action of Dicke's line narrowing including SASC and LASC and the wind effect have been simultaneously taken into account in a form excluding artificial assumptions. The parameterized line profile was developed on the base of the calculated profiles that contains a minimal number of adjusting parameters.

The goal of this paper is to carry out calculations of line profiles analogous to those of Ref. [17] for intermolecular interaction potentials proportional to r^{-n} with $n=3$, 4, and 5, where r is the distance between colliding molecules, and to develop respective analytical approximations for these line profiles suitable for experimental data processing. Also the questions on how the type of intermolecular potential affects the data processing and which are the indicators of line narrowing intrinsic to Dicke's and the wind effects in the presence of SASC are under consideration.

2. Line profiles for dipole–dipole, dipole–quadrupole, and quadrupole–quadrupole intermolecular interaction potentials

Numerical calculations of the line profiles for intermolecular interaction potentials $U(r)=-C_n/r^n$ with $n=3$, 4,

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[1] It seems astonishing that the supposition of small changes in a velocity gives the equation that well describes also the opposite case of large velocity's changes. But due to this fortunate accidental operation of mathematics, the effect of LASC on the line profile [4–6] remains hidden up to the present.

[2] Supposed to be fixed; there are the mass ratio of perturbing and absorbing molecules and the parameters characterizing the intermolecular interaction potential.