Shapes of pressure- and Doppler-broadened spectral lines in the core and near wings

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The Rautian-Sobelman approach describing the collision-Doppler shape of spectral line that takes into account both soft and hard velocity-changing collisions is extended to the case when correlation between Doppler and collision broadening as well as the dispersion line asymmetry should be considered. Numerical calculations show that speed-dependent effects can produce the additional line narrowing as well as broadening and also the line asymmetry. It is shown that speed-dependent profiles based on the soft and hard collision models differ much more one from another than those which omit the speed-dependent effects.
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I. INTRODUCTION

Spectral line shapes emitted or absorbed by atoms (or molecules) in a gas phase are determined by two main factors: (i) collisions between the emitting or absorbing atoms (emitters) and perturbing particles (perturbers), and (ii) the thermal motion of emitters.

It is well established that the collisionally broadened and shifted line shape in the impact approximation can be described by a Lorentzian profile in the center and near wings of the line [1,2]. More detailed investigation shows, however, that the finite time of the collision duration may cause the so-called collision-time asymmetry of the line that is described by a dispersion distribution [3–9]. The dispersion asymmetry of the line can also be caused by other effects such as the mixing of overlapping lines [10] and collision-induced transitions [11]. In the first approximation the width, shift, and asymmetry of a collision-broadened line are linearly dependent on the perturber density. As was indicated by Berman [12] and other authors [13–15] the collision parameters of the line profiles such as their Lorentzian width and shift are, in the general case, dependent on the emitter velocity.

The Doppler broadening of a line can be treated separately from the collisional effects in such cases only when the collisions that change the velocity of the emitter can be neglected, i.e., for the free motion of emitter. Then the emitter velocity distribution can be described by the Maxwellian distribution giving rise to a Gaussian profile of the line with the width dependent on the temperature and independent of the perturber density. Dicke [16] has shown that if the motion of the emitter cannot be considered as a free motion so that collisions may induce velocity changes then the resulting width of the line may become smaller than the ordinary Doppler width at the same temperature (Dicke narrowing).

For example, when velocity-changing collisions occur, and frequency of such collisions is large enough, the emitter motion has the diffusion character and the shape of the Doppler broadened line is given by a Lorentzian profile whose width is inversely proportional to pertuber density [17]. To describe the Doppler shape of a broadened line due to velocity-changing collisions two models are used that correspond to so-called soft and hard collisions [18,19].

In many cases collision broadening and Doppler broadening occur simultaneously. The simplest expression describing the line shape in such a case and very often used in analysis of experimental data, is the Voigt profile (VP), which is a convolution of the Lorentzian and the Gaussian profiles. When velocity-changing collisions occur the Galatry profile (GP) and Nelkin-Ghatak profile (NGP) obtained using soft and hard collision models, respectively, are used [18–21]. On the other hand, when velocity-changing collisions can be neglected but correlation between collision and Doppler broadening occurs and dependence of collision parameters of the line on the emitter speed should be taken into account, the shape of the line is described by speed-dependent Voigt profile (SDVP) [12,13]. Experimental and theoretical investigations of spectral line shapes performed in recent years have indicated that in some cases it is necessary to take into account both the correlation between collision and Doppler broadening as well as the Dicke narrowing [22–28].

In this paper a uniform formula describing the shape in the core and near wings of a spectral line is proposed. It takes into account all of the above-mentioned effects such as the pressure broadening and shift, Doppler broadening, and collision narrowing, which are described using soft and hard collision models, correlation between pressure and Doppler broadening, and dispersion asymmetry of the line. To obtain such an expression one can use an approach similar to that used Ref. [28]. The intensity distribution $I(\omega)$ describing the shape of a broadened line can be generally written as a real part

$$I(\omega)=\mathrm{Re}\mathcal{I}(\omega) \tag{1}$$

of the complex line-shape function

$$\mathcal{I}(\omega)=\int d^3\vec{v}_E\mathcal{F}(\omega;\vec{v}_E). \tag{2}$$

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The complex profile $\mathcal{I}(\omega)$ is a sum of complex profiles $\mathcal{F}(\omega;\vec{v}_E)$ corresponding to emitters that have different velocities $\vec{v}_E$. These profiles can be evaluated using the following relation:

$$\mathcal{F}(\omega;\vec{v}_E)=\frac{1}{\pi}\int_0^{+\infty}dt\int d^3\vec{r}f(\vec{r},\vec{v}_E,t)\times\exp[i(\omega-\omega_0)t-i\vec{k}\cdot\vec{r}-Ng(t)], \quad (3)$$

where ω_0 is the unperturbed frequency of the emitted radiation, N is the perturber density, $\vec{k}$ is the wave vector of the emitted radiation ($k=\omega_0/c$, c is the speed of light), $g(t)$ is a function described by changes of the phase of the emitted radiation in the time t during collisions between emitter and perturber. The function $f(\vec{r},\vec{v}_E,t)$ is the probability density that the emitter, which has velocity $\vec{v}_E$ and is in the point 0 at time 0, will be at the position $\vec{r}$ at time t.

In this approach the spectral line shape is determined by choice of the form of functions $g(t)$ and $f(\vec{r},\vec{v}_E,t)$.

II. COLLISION BROADENING, SHIFT, AND ASYMMETRY

In order to describe the core and near wings of a spectral line emitted or absorbed by a gas at low pressure, it is often sufficient to use only a linear approximation to the function $g(t)$, which fulfills the following relation [1,3,4,7,9]:

$$Ng(t)=\xi+i\beta+(\Gamma+i\Delta)t, \quad (4)$$

where Γ and Δ are collisional width (half width at half maximum) and shift of the line. The parameters ξ and β dependent on the time of collision describe a collision decrease of the line intensity and the magnitude of the collision-time asymmetry, respectively. In general, collision parameters of the line are dependent on the emitter velocity. Following Baranger [10] and carrying out averaging over relative perturber-emitter velocities $\vec{v}_{EP}$ as in Ref. [13], the width and shift of the line can be written in the form

$$\Gamma(v_E)+i\Delta(v_E)=2\pi N\int d^3\vec{v}_{EP}f_{m_P}(\vec{v}_E+\vec{v}_{EP})v_{EP}\times\int_0^{+\infty}d\rho\,\rho\langle 1-S_{ii}S_{ff}^{-1}\rangle_{\text{ang.av.}}. \quad (5)$$

Velocities $\vec{v}_E$, $\vec{v}_{EP}$ occurring in the above expression are connected with perturber velocity $\vec{v}_P$ by the relation $\vec{v}_P=\vec{v}_E+\vec{v}_{EP}$. Here

$$f_{m_P}(\vec{v}_P)=\left(\frac{m_P}{2\pi k_B T}\right)^{3/2}\exp\left(-\frac{m_P v_P^2}{2k_B T}\right) \quad (6)$$

is the Maxwellian distribution of the perturber velocity, m_P is the perturber mass, T is gas temperature, and k_B is the Boltzmann constant. Similarly using results obtained in Ref. [9], the expression for ξ and β can be written in the form

$$\xi(v_E)+i\beta(v_E)=2\pi N\int d^3\vec{v}_{EP}f_{m_P}(\vec{v}_E+\vec{v}_{EP})v_{EP}\int_0^{+\infty}d\rho\,\rho\int_{-\infty}^{+\infty}dt_0\times\langle 1+S_{ii}S_{ff}^{-1}-U_{ii}(t_0,-\infty)U_{ff}^{-1}(t_0,-\infty)-U_{ii}(+\infty,t_0)U_{ff}^{-1}(+\infty,t_0)\rangle_{\text{ang.av.}}. \quad (7)$$

These results can be obtained using semiclassical theory, in which the motion of emitters and perturbers is described in a classical way and the evolution of emitter states is described using quantum mechanics. The time-evolution operator $\hat{U}(t_2,t_1)$ describes the evolution of emitter states during the emitter-perturber collision from time t_1 to t_2. The well-known scattering operator is $\hat{S}=\hat{U}(+\infty,-\infty)$. The symbol $\langle\cdots\rangle_{\text{ang.av.}}$ denotes angular averaging over all orientations of the collisions and subscripts ii and ff identify the elements of the time-evolution operator in initial and final states, respectively.

Collision line-shape parameters (5) and (7) averaged over distribution of emitter velocities $f_{m_E}(\vec{v}_E)$ are given by following relations:

$$\Gamma=\int d^3\vec{v}_E f_{m_E}(\vec{v}_E)\Gamma(v_E), \quad (8)$$

$$\Delta=\int d^3\vec{v}_E f_{m_E}(\vec{v}_E)\Delta(v_E), \quad (9)$$

$$\xi=\int d^3\vec{v}_E f_{m_E}(\vec{v}_E)\xi(v_E), \quad (10)$$

$$\beta=\int d^3\vec{v}_E f_{m_E}(\vec{v}_E)\beta(v_E). \quad (11)$$

It appears that the dependence of these parameters on the emitter velocity is particularly important when the perturber mass m_P is greater than that of the emitter m_E. This dependence can be neglected in the case, when $m_P \ll m_E$ and then the parameters Γ, Δ, ξ, and β may be often treated as independent of the emitter velocity.

The validity of Eq. (4) is limited to the cases when $|\xi+i\beta|\ll 1$, therefore $e^{-\xi-i\beta}$ in Eq. (3) can be substituted by $1-i\beta$ (in the first approximation $\text{Re}(e^{-\xi-i\beta})\approx 1$ and $\text{Im}(e^{-\xi-i\beta})\approx-\beta$). The assumption that $Ng(t)$ is a linear function of time leads to the conclusion that the collisional line shape is a sum of Lorentzian and dispersion distributions [1,3,4,7,9]. Other approaches to the collision effects lead also to the asymmetric line profile [2,5,6,8]. Asymmetry of a spectral line caused by other effects such as line mixing or collision-induced transition [10,11] may be described by an analogous dispersion function but the nature of its parameters may be quite different.

Although all calculations in this paper are performed taking into account collision-time asymmetry as a main reason of the dispersion asymmetry of the spectral line shape, the general conclusions and expressions for line profiles obtained in the following sections can be also applied in cases when this asymmetry is due to other effects.

III. EMITTER MOTION

In this approach, the emitter motion is described by the function $f(\vec{r},\vec{v},t)$, which in a great part determines a final form of the line profile. The choice of the expression for this function is dependent on the condition in which the line is analyzed. How long is the mean free path of the emitter between emitter-perturber velocity-changing collisions? Of what kind are these velocity-changing collisions, mainly soft or hard?

A. Free motion

The simplest model describing the influence of the emitter motion on the shape of emitted or absorbed spectral lines is based on the assumption that the motion of emitters can be treated as a free motion on straight-line trajectories. Velocity-changing collisions of emitters and perturbers are neglected in this case. Then the kinetic equation for the function $f(\vec{r},\vec{v},t)$ has the following form:

$$\frac{\partial f(\vec{r},\vec{v},t)}{\partial t}=-\vec{v}\cdot\vec{\nabla}_r f(\vec{r},\vec{v},t), \tag{12}$$

where $\vec{\nabla}_r$ is a gradient operator in $\vec{r}$ variables. Looking for a solution of this equation, one assumes that the emitter at time $t=0$ is in the position $\vec{r}=0$ and the probability that the emitter has velocity $\vec{v}$ is given by a Maxwellian distribution, which means

$$f(\vec{r},\vec{v},0)=\delta^3(\vec{r})f_{m_E}(\vec{v}), \tag{13}$$

where $\delta^3(\vec{r})$ is the three-dimensional δ Dirac function. The solution of Eq. (12) for any time t, obtained with this initial condition, can be written in the following form:

$$f_F(\vec{r},\vec{v},t)=\delta^3(\vec{r}-\vec{v}t)f_{m_E}(\vec{v}). \tag{14}$$

The subscript F means that the distribution $f_F(\vec{r},\vec{v},t)$ was obtained for the free motion case.

Substituting Eq. (14) in Eq. (3) and assuming that collisional line shape parameters are independent of the emitter velocity, the complex line profile, Eq. (2), can be written as

$$\mathcal{I}_{\mathrm{AVP}}(\omega)=\frac{e^{-\xi-i\beta}}{\pi}\int d^3\vec{v}_E f_{m_E}(\vec{v}_E)\frac{1}{\Gamma-i(\omega-\omega_0-\Delta-\vec{k}\cdot\vec{v}_E)}. \tag{15}$$

The real part of this profile is identical to the asymmetric Voigt profile (AVP). This profile is often used to analyze the measured line shapes including collision-time asymmetry [29] or line-mixing asymmetry. For $\xi+i\beta=0$, the well-known Voigt profile (VP) is obtained from Eq. (15). This is the simplest profile that is most frequently used in analysis of experimental data taking into account Doppler and pressure broadening and shift of the line. The Voigt profile is a convolution of Lorentzian and Gaussian distribution for which the half widths (full width at half maximum) are $\gamma_L=2\Gamma$ and $\gamma_D=\omega_D 2\sqrt{\ln 2}$, respectively, where $\omega_D=kv_{m_E}$ and $v_{m_E}=\sqrt{2k_BT/m_E}$ is the most probable emitter speed.

In general, collision parameters of the line are dependent on the emitter velocity, and the pressure and Doppler broadening cannot be treated as statistically independent effects. Taking into the account the dependence of collision parameters of the line profile on the emitter velocity and using Eqs. (2) and (3), the complex speed-dependent asymmetric Voigt profile (SDAVP) can be written in the form

$$\mathcal{I}_{\mathrm{SDAVP}}(\omega)=\frac{1}{\pi}\int d^3\vec{v}_E f_{m_E}(\vec{v}_E)\times\frac{\exp[-\xi(v_E)-i\beta(v_E)]}{\Gamma(v_E)-i[\omega-\omega_0-\Delta(v_E)-\vec{k}\cdot\vec{v}_E]}. \tag{16}$$

This profile was used in an analysis of their experimental data for the calcium resonance line by Lewis and his coworkers who have taken into account the collision-time asymmetry and the correlation between the pressure and Doppler broadening [30–33]. The speed-dependent asymmetric Voigt profile is a simple generalization of the speed-dependent Voigt profile (SDVP) given by Berman [12] and analyzed by Ward *et al.* [13]. In these papers the dispersion asymmetry was neglected. It should be noted that in general SDVP is not symmetric and can be narrower than the ordinary Voigt profile. This narrowing was first observed by McCartan and Lwin [34] for the Li-Xe system. The SDVP was recently used to describe the shape of the Cd-intercombination line perturbed by the Xe [35] (for the Cd-Xe system the perturber-emitter mass ratio α is close to one).

When the Doppler width is negligible in comparison to the collision width, the SDAVP can be transformed to the asymmetric weighted sum of Lorentz profiles (AWSLP) of the form

$$\mathcal{I}_{\mathrm{AWSLP}}(\omega)=\frac{1}{\pi}\int d^3\vec{v}_E f_{m_E}(\vec{v}_E)\frac{\exp[-\xi(v_E)-i\beta(v_E)]}{\Gamma(v_E)-i[\omega-\omega_0-\Delta(v_E)]}. \tag{17}$$

Such a profile was given by Pickett [14] who neglected the collision-time asymmetry. In general the weighted sum of Lorentz profiles (WSLP) given by him is also not symmetric. This is caused by dependence of the collision shift on the emitter velocity. This profile was used by Farrow *et al.* [15] to describe asymmetric line shapes obtained in their experiment.

B. Soft collisions

The soft collision model was the first theoretical model that made it possible to describe the shape of the spectral line taking into account velocity changing collisions for their low as well as high frequency. In this approach, one assumes that individually velocity-changing collisions are negligible but collectively are significant and the emitter motion can be described in terms of the theory of Brownian motion as a stochastic process. Assuming that the emitter motion is a diffusion motion, then following Chandresekhar [36] the kinetic equation for the function $f(\vec{r},\vec{v},t)$ can be written as

$$\frac{\partial f(\vec{r},\vec{v},t)}{\partial t} = -\vec{v}\cdot\vec{\nabla}_r f(\vec{r},\vec{v},t) + \hat{D}f(\vec{r},\vec{v},t), \tag{18}$$

where

$$\hat{D}f(\vec{r},\vec{v},t) = \nu_S \vec{\nabla}_v \cdot [\vec{v} f(\vec{r},\vec{v},t)] + \frac{v_{m_E}^2 \nu_S}{2}\Delta_v f(\vec{r},\vec{v},t), \tag{19}$$

and ν_S is the coefficient of the dynamical friction undergone by the moving emitters (or the effective velocity-changing collision rate), $\vec{\nabla}_v$ and Δ_v are a gradient and Laplacian operators in $\vec{v}$ variables, respectively.

As in the free motion case one assumes that the distribution function for $t=0$ is given by the relation

$$f(\vec{r},\vec{v},0) = \delta^3(\vec{r}) f_{m_E}(\vec{v}). \tag{20}$$

Inserting the solution of Eq. (18) with the initial condition (20) to Eq. (3) and assuming that collision parameters are independent of the emitter velocity, the complex line shape can be obtained. This complex line shape is identical with that which can be obtained using the function given by the following expression:

$$f_S(\vec{r},\vec{v},t) = W_{\nu_S}(\vec{r},t;\vec{v}) f_{m_E}(\vec{v}). \tag{21}$$

The subscript S means that this distribution function was obtained in the soft collision approach. In Eq. (21) the probability $W_{\nu_S}(\vec{r},t;\vec{v})$ of finding a particle after the time t at the position $\vec{r}$, if their initial position was 0 and initial velocity was $\vec{v}$, is given by [36]

$$W_{\nu_S}(\vec{r},t;\vec{v}) = \left(\frac{A}{\pi}\right)^{3/2} \exp\{-A[\vec{r}-\vec{v}(1-e^{-\nu_S t})/\nu_S]^2\}, \tag{22}$$

where

$$A = \frac{m_E \nu_S^2/(2k_B T)}{2\nu_S t - 3 + 4e^{-\nu_S t} - e^{-2\nu_S t}}. \tag{23}$$

Using Eq. (21) and assuming that collisional line-shape parameters are independent of the emitter velocity, the complex line shape, Eq. (2), can be written in the form

$$\mathcal{I}_{\mathrm{AGP}}(\omega) = \frac{1}{\pi}\int_0^{+\infty} dt \int d^3\vec{v}_E \int d^3\vec{r}\, W_{\nu_S}(\vec{r},t;\vec{v}_E) f_{m_E}(\vec{v}_E) \times \exp\{-\xi - i\beta - \Gamma t + i(\omega-\omega_0-\Delta)t - i\vec{k}\cdot\vec{r}\}. \tag{24}$$

The real part of this expression is identical with asymmetric Galatry profile (AGP). The Galatry profile (GP), which is a symmetric version of this profile, was first derived by Galatry in 1961 [18]. The soft collision approach and application of the kinetic equation (18) in the line shape theory was also investigated by Rautian and Sobelman [20]. In general, the Galatry profile is used in analysis of molecular line shapes in which the Dicke narrowing effect occurs.

In the case, when collision parameters are dependent on the emitter velocity, the complex line profile, Eq. (2), should be written in the following form:

$$\mathcal{I}_{\mathrm{SDAGP}}(\omega) = \frac{1}{\pi}\int_0^{+\infty} dt \int d^3\vec{v}_E \int d^3\vec{r}\, W_{\nu_S}(\vec{r},t;\vec{v}_E) f_{m_E}(\vec{v}_E) \times \exp\{-\xi(v_E) - i\beta(v_E) - \Gamma(v_E)t + i[\omega-\omega_0-\Delta(v_E)]t - i\vec{k}\cdot\vec{r}\}. \tag{25}$$

Hereafter this formula will be referred to as the speed-dependent asymmetric Galatry profile (SDAGP). It should be noted that the expression given by Eq. (25) can be different from the expression that can be obtained using the exact solution of Eq. (18). A general formula for the speed-dependent line profile in the soft collision approximation was obtained in Ref. [28]. The speed-dependent asymmetric Galatry profile is a simplification of the general expression obtained in [28] for the core and near wings of a spectral line. In [28] the speed-dependent Galatry profile (SDGP) was also derived and their properties were investigated in detail. Experimental investigation of simultaneous occurrence of speed-dependent effects and velocity changing collisions was done by Duggan *et al.* [37,23]. In particular, Duggan *et al.* [23] have used the soft collision model and included speed-dependent effects to interpret their earlier experimental data [37] on the broadening of CO lines. It should be noted that the speed-dependent Galatry profile was used to analyze experimental data and to find the magnitude of the systematic errors of measured broadening and shift coefficients caused by neglecting the speed-dependent effects [38,39]. The problem of applicability of the SDGP for the CO-He and CO-Ar systems was experimentally tested and thoroughly discussed by Duggan *et al.* [27] (in their paper the SDGP was termed as the correleted speed-dependent Galatry profile).

In the limit of high frequency of velocity-changing collisions the distribution (22) can be transformed to the δ Dirac function form

$$\lim_{\nu_S\to\infty} W_{\nu_S}(\vec{r},t;\vec{v}) = \delta^3(\vec{r}). \tag{26}$$

In such a case, the profiles SDAGP and SDGP can be transformed to the AWSLP, Eq. (17), and WSLP, respectively.

C. Hard collisions

The other way of taking into account the velocity-changing collision is the hard collision approach. In this approach the emitter velocity after collision with the pertuber is determined only by this collision and is independent of the velocity that the emitter had before collision. In this case the kinetic equation for the function $f(\vec{r},\vec{v},t)$ can be written in the following form [19]:

$$\frac{\partial f(\vec{r},\vec{v},t)}{\partial t} = -\vec{v}\cdot\vec{\nabla}_r f(\vec{r},\vec{v},t) - \nu_H f(\vec{r},\vec{v},t) + f_{m_E}(\vec{v})\nu_H \int d^3\vec{v}\,' f(\vec{r},\vec{v}\,',t), \tag{27}$$

where ν_H is the frequency of the velocity changing collisions in the hard collisions approach. To obtain the expression for the shape of the spectral line in the hard collisions approach, both sides of this equation should be multiplied by $\exp[i(\omega-\omega_0-\Delta+i\Gamma)t-i\vec{k}\cdot\vec{r}-\xi-i\beta]/\pi$ and integrated by parts over t and $\vec{r}$. As the result the equation for the function $\mathcal{F}(\omega,\vec{v})$ becomes

$$\frac{1}{\pi}e^{-\xi-i\beta}f_{m_E}(\vec{v}) + f_{m_E}(\vec{v})\nu_H\int d^3\vec{v}\,'\mathcal{F}(\omega,\vec{v}\,') = -i(\omega-\omega_0-\Delta-\vec{k}\cdot\vec{v}+i\Gamma+i\nu_H)\mathcal{F}(\omega,\vec{v}). \tag{28}$$

After some manipulation, which includes integration of both sides of this equation over $\vec{v}$ and using the definition of the AVP (15) and the definition of the complex line profile (2), the following equation is obtained:

$$\mathcal{I}_{\mathrm{AVP}*}(\omega) + \pi\nu_H\mathcal{I}_{VP*}(\omega)\mathcal{I}(\omega) = \mathcal{I}(\omega). \tag{29}$$

Here the profiles marked as AVP* and VP* are the AVP and the VP, respectively, in which the width Γ is replaced by the sum $\Gamma+\nu_H$ (this change is designated by an asterisk).

The solution of Eq. (29) is given in the following form:

$$\mathcal{I}_{\mathrm{ANGP}}(\omega) = \frac{\mathcal{I}_{\mathrm{AVP}*}(\omega)}{1-\pi\nu_H\mathcal{I}_{\mathrm{VP}*}(\omega)}. \tag{30}$$

Hereafter this profile will be referred to as the asymmetric Nelkin-Ghatak profile (ANGP). Such a line profile was used by Berman *et al.* [40] in studies of line mixing asymmetry in which also the Dicke narrowing effect was taken into account in the hard collision model. The symmetric version of this profile, which means Nelkin-Ghatak profile (NGP), was originally derived in order to describe the shape of Doppler broadened Mössbauer lines [19]. Rautian and Sobelman [20] have used the NGP to describe the line profiles for cases when the Doppler and pressure broadening as well as Dicke narrowing effect occur. They also discussed the problem of the correlation between phase-changing and velocity-changing collisions (different in origin from the speed-dependent correlation between the collision and Doppler broadening). The profile given by Rautian and Sobelman [20] for that case is the NGP with ν_H replaced by $\nu_H-\Gamma-i\Delta$ and hereafter will be referred as correleted Nelkin-Ghatak profile (CNGP).

Profiles AVP* and VP* in Eq. (30) should be replaced by speed-dependent profiles SDAVP* and SDVP*, respectively, when the dependence of the collision line profile parameters on the emitter velocity should be taken into account. In this case, speed-dependent asymmetric Nelkin-Ghatak profile (SDANGP) can be written in the form

$$\mathcal{I}_{\mathrm{SDANGP}}(\omega) = \frac{\mathcal{I}_{\mathrm{SDAVP}*}(\omega)}{1-\pi\nu_H\mathcal{I}_{\mathrm{SDVP}*}(\omega)}. \tag{31}$$

The speed-dependent Nelkin–Ghatak profile (SDNGP) in which the dispersion asymmetry of the line was neglected has been used by Lance *et al.* [26] to analyze line shapes of the C_2H_2 perturbed by the Xe. However, an extended version of the SDNGP was given for the first time by Robert *et al.* [22] to interpret the non-Lorentzian features in the profiles of Q-branch line of H_2 broadened by heavy perturbers. This profile will be referred to here as the correlated speed-dependent Nelkin–Ghatak profile (CSDNGP) because it takes into account correlation between phase-changing and velocity-changing collisions. Neither SDNGP nor SDANGP can be explicitly obtained using the approach presented here but this is possible starting from the equation for the time-dependent classical dipole, as was done in the more complicated case of the CSDNGP by Robert *et al.* [22].

D. Hard and soft collisions

The soft and hard collision models give different descriptions of the Doppler broadened line shape affected by the velocity changing collisions. For high frequency of velocity-changing collisions ν both models give rise to a Lorenzian profile for the Doppler broadened line in their core and near wing. The width (FWHM) of this profile is equal to ω_D^2/ν. For the case in which velocity changing collision can be omitted, which means when $\nu=0$, both models give the standard Gaussian distribution with the Doppler width γ_D. Contrary to the fact that these two models yield different results in the intermediate frequency range. In real experiments, the assumptions required by those models are not fulfilled completely so that there are both soft and hard collisions. To describe the influence of the soft and hard velocity-changing collisions occurring simultaneously, the kinetic equation should be taken in the form proposed by Rautian and Sobelman [20]

$$\frac{\partial f(\vec{r},\vec{v},t)}{\partial t} = -\vec{v}\cdot\vec{\nabla}_r f(\vec{r},\vec{v},t) + \hat{D}f(\vec{r},\vec{v},t) - \nu_H f(\vec{r},\vec{v},t) + f_{m_E}(\vec{v})\nu_H\int d^3\vec{v}\,' f(\vec{r},\vec{v}\,',t). \tag{32}$$

The effective frequency of velocity changing collisions ν, which can be written as the sum of the frequency of the soft and hard collisions, is connected with diffusion coefficient D for emitter in perturber gas by the following relation:

$$\nu = \nu_H + \nu_S = \frac{k_B T}{m_E D}. \tag{33}$$

To solve the problem formulated as outlined above we should note that the modified distribution function obtained in the frame of the soft collision model, labeled by the index $S*$ and given by the relation

$$f_{S*}(\vec{r},\vec{v},t)=e^{-\nu_H t}f_S(\vec{r},\vec{v},t) \tag{34}$$

fulfills the simpler differential equation

$$\frac{\partial f(\vec{r},\vec{v},t)}{\partial t}=-\vec{v}\cdot\vec{\nabla}_r f(\vec{r},\vec{v},t)+\hat{D}f(\vec{r},\vec{v},t)-\nu_H f(\vec{r},\vec{v},t). \tag{35}$$

Inserting the distribution function (34) into (3) the expression for $\mathcal{F}_{\mathrm{AGP}*}(\omega,v)$ can be obtained. On the other hand multiplying both sides of this equation by $\exp[i(\omega-\omega_0-\Delta+i\Gamma)t-i\vec{k}\cdot\vec{r}-\xi-i\beta]/\pi$ and integrating by parts over t and $\vec{r}$, one gets

$$\hat{G}\mathcal{F}_{\mathrm{AGP}*}(\omega,\vec{v})=\frac{1}{\pi}e^{-\xi-i\beta}f_{m_E}(\vec{v}). \tag{36}$$

Here the operator $\hat{G}$ is defined as

$$\hat{G}=-i(\omega-\omega_0-\Delta-\vec{k}\cdot\vec{v}+i\Gamma+i\nu_H-i\hat{D}). \tag{37}$$

To obtain the complex line profile for the soft and hard collisions case, both sides of the full kinetic equation (32) should be multiplied by $\exp[i(\omega-\omega_0-\Delta+i\Gamma)t-i\vec{k}\cdot\vec{r}-\xi-i\beta]/\pi$ and integrated by parts over t and $\vec{r}$. As a result the following equation is obtained:

$$\hat{G}\mathcal{F}(\omega,\vec{v})=\frac{1}{\pi}e^{-\xi-i\beta}f_{m_E}(\vec{v})+f_{m_E}(\vec{v})\nu_H\int d^3\vec{v}\,'\mathcal{F}(\omega,\vec{v}\,'). \tag{38}$$

Using relation (36) one can show that Eq. (38) is fulfilled by the function $\mathcal{F}(\omega,\vec{v})$, which fulfills the following equation:

$$\mathcal{F}(\omega,\vec{v})=\mathcal{F}_{\mathrm{AGP}*}(\omega,\vec{v})+\pi\nu_H e^{\xi+i\beta}\mathcal{F}_{\mathrm{AGP}*}(\omega,\vec{v})\int d^3\vec{v}\,'\mathcal{F}(\omega,\vec{v}\,'). \tag{39}$$

Integrating both sides of this equation by $\vec{v}$, one obtains the equation that should be fulfilled by the complex line profile

$$\mathcal{I}(\omega)=\mathcal{I}_{\mathrm{AGP}*}(\omega)+\pi\nu_H\mathcal{I}_{\mathrm{GP}*}(\omega)\mathcal{I}(\omega). \tag{40}$$

The solution of Eq. (40) is the asymmetric Rautian-Sobelman profile (ARSP)

$$\mathcal{I}_{\mathrm{ARSP}}(\omega)=\frac{\mathcal{I}_{\mathrm{AGP}*}(\omega)}{1-\pi\nu_H\mathcal{I}_{\mathrm{GP}*}(\omega)}. \tag{41}$$

The symmetric version of this profile is identical with the Rautian-Sobelman profile (RSP) [20]. A detailed analysis of the influence of velocity changing collisions on the shape of spectral lines was thoroughly studied in their pioneering work by Rautian and Sobelman [20].

The ARSP was obtained here in a formal way. In the approach presented here, when collision parameters of the line are dependent on the emitter velocity, the similar calculation cannot be carried out. To obtain the line shape taking into account the speed-dependent effects in expression (41) profiles AGP* and GP* should be replaced by speed-dependent profiles SDAGP* and SDGP*. The proposed result is

$$\mathcal{I}_{\mathrm{SDARSP}}(\omega)=\frac{\mathcal{I}_{\mathrm{SDAGP}*}(\omega)}{1-\pi\nu_H\mathcal{I}_{\mathrm{SDGP}*}(\omega)}. \tag{42}$$

It should be emphasized that the profile given by Eq. (42) is not derived but only proposed as a useful expression from which other profiles presented above can be obtained. Such a speed-dependent asymmetric Rautian-Sobelman profile (SDARSP) can be used to describe the shape of a spectral line taking into account the Doppler and pressure broadening and shift, the correlation between the Doppler and pressure broadening and shift, the dispersion asymmetry and the collisional narrowing caused by the soft and hard collisions. The speed-dependent Rautian-Sobelman profile (SDRSP) can be obtained assuming that $\xi+i\beta=0$, which means, omitting the dispersion asymmetry of the line.

IV. LINE PROFILES IN STANDARDIZED FORM

It is very useful to rewrite the profiles given above using reduced variables such as those introduced by Herbert [41]: $\tau=\omega_D t$, $u=(\omega-\omega_0)/\omega_D$, $g=\Gamma/\omega_D$, $d=\Delta/\omega_D$, $z=\nu/\omega_D$. Following Ward *et al.* [13] we also introduce the velocity-dependent dimensionless function:

$$B_W(x;\alpha)=\frac{\Gamma(xv_{m_E})}{\Gamma}, \tag{43}$$

$$B_S(x;\alpha)=\frac{\Delta(xv_{m_E})}{\Delta}, \tag{44}$$

$$B_D(x;\alpha)=\frac{\xi(xv_{m_E})}{\xi}, \tag{45}$$

$$B_A(x;\alpha)=\frac{\beta(xv_{m_E})}{\beta}. \tag{46}$$

These functions, which depend on the reduced emitter velocity $x=v_E/v_{m_E}$, the perturber-emitter mass ratio $\alpha=m_P/m_E$, and first of all on the emitter-pertuber interaction, generally differ from each other. When the emitter-perturber interaction potential can be written in the inverse-power form C_q/r^q, then as was shown Eqs. (43)–(46) can be written as [13]

$$B_W(x;\alpha)=B_S(x;\alpha)=(1+\alpha)^{-(q-3)/(2q-2)}M\left(-\frac{q-3}{2q-2},\frac{3}{2},-\alpha x^2\right), \tag{47}$$

and [42]

$$B_D(x;\alpha)=B_A(x;\alpha)=(1+\alpha)^{3/(2q-2)}M\left(\frac{3}{2q-2},\frac{3}{2},-\alpha x^2\right), \tag{48}$$

where $M(a,b,z)$ is the confluent hypergeometric function.

Using the above reduced variables and dimensionless functions the asymmetric Voigt profile (AVP), Eq. (15), can be given in one of the equivalent forms:

$$\mathcal{I}_{\mathrm{AVP}}(u)=\frac{1}{\pi}\int_{0}^{+\infty}d\tau\exp\left\{-\xi-i\beta+iu\tau-id\tau-g\tau-\frac{\tau^{2}}{4}\right\},\tag{49}$$

or

$$\mathcal{I}_{\mathrm{AVP}}(u)=\frac{e^{-\xi-i\beta}}{\pi^{3/2}}\int_{-\infty}^{+\infty}dx\,\frac{e^{-x^{2}}}{g-i(u-d-x)}.\tag{50}$$

Also the speed-dependent asymmetric Voigt profile (SDAVP), Eq. (16), can be written in two alternative forms

$$\mathcal{I}_{\mathrm{SDAVP}}(u)=\frac{4}{\pi^{3/2}}\int_{0}^{+\infty}d\tau\int_{0}^{+\infty}dx\,x^{2}e^{-x^{2}}\mathrm{sinc}(x\tau)\times\exp[-\xi B_{D}(x;\alpha)-i\beta B_{A}(x;\alpha)+iu\tau-idB_{S}(x;\alpha)\tau-gB_{W}(x;\alpha)\tau],\tag{51}$$

or

$$\mathcal{I}_{\mathrm{SDAVP}}(u)=\frac{2}{\pi^{3/2}}\int_{-\infty}^{+\infty}dx\,e^{-x^{2}}x\exp[-\xi B_{D}(x;\alpha)-i\beta B_{A}(x;\alpha)]\times\left\{\arctan\left[\frac{u-dB_{S}(x;\alpha)+x}{gB_{W}(x;\alpha)}\right]+\frac{i}{2}\ln\left[1+\left(\frac{u-dB_{S}(x;\alpha)+x}{gB_{W}(x;\alpha)}\right)^{2}\right]\right\},\tag{52}$$

where $\mathrm{sinc}(y)=\sin(y)/y$. Equation (52) is more convenient from the numerical point of view. The standardized asymmetric Galatry profile (AGP), Eq. (24), may be written in the following form:

$$\mathcal{I}_{\mathrm{AGP}}(u)=\frac{1}{\pi}\int_{0}^{+\infty}d\tau\exp\left\{-\xi-i\beta+iu\tau-id\tau-g\tau-\frac{1}{2z_{S}^{2}}(z_{S}\tau-1+e^{-z_{S}\tau})\right\}.\tag{53}$$

The standardized form of the speed-dependent asymmetric Galatry profile (SDAGP), Eq. (25), is given by

$$\mathcal{I}_{\mathrm{SDAGP}}(u)=\frac{4}{\pi^{3/2}}\int_{0}^{+\infty}d\tau\exp\left\{-\frac{1}{4z_{S}^{2}}(2z_{S}\tau-3+4e^{-z_{S}\tau}-e^{-2z_{S}\tau})\right\}\times\int_{0}^{+\infty}dx\,x^{2}e^{-x^{2}}\mathrm{sinc}[x(1-e^{-z_{S}\tau})/z_{S}]\times\exp[-\xi B_{D}(x;\alpha)-i\beta B_{A}(x;\alpha)+iu\tau-idB_{S}(x;\alpha)\tau-gB_{W}(x;\alpha)\tau].\tag{54}$$

And finally the speed-dependent asymmetric Rautian-Sobelman profile (SDARSP), Eq. (42), can be written as

$$\mathcal{I}_{\mathrm{SDARSP}}(u)=\frac{\mathcal{I}_{\mathrm{SDAGP}*}(u)}{1-\pi z_{H}\mathcal{I}_{\mathrm{SDGP}*}(u)},\tag{55}$$

where SDAGP* is given by

$$\mathcal{I}_{\mathrm{SDAGP}*}(u)=\frac{4}{\pi^{3/2}}\int_{0}^{+\infty}d\tau\exp\left\{-\frac{1}{4z_{S}^{2}}(2z_{S}\tau-3+4e^{-z_{S}\tau}-e^{-2z_{S}\tau})\right\}\times\int_{0}^{+\infty}dx x^{2}e^{-x^{2}}\mathrm{sinc}[x(1-e^{-z_{S}\tau})/z_{S}]\times\exp[-\xi B_{D}(x;\alpha)-i\beta B_{A}(x;\alpha)+iu\tau-idB_{S}(x;\alpha)\tau-z_{H}\tau-gB_{W}(x;\alpha)\tau].\tag{56}$$

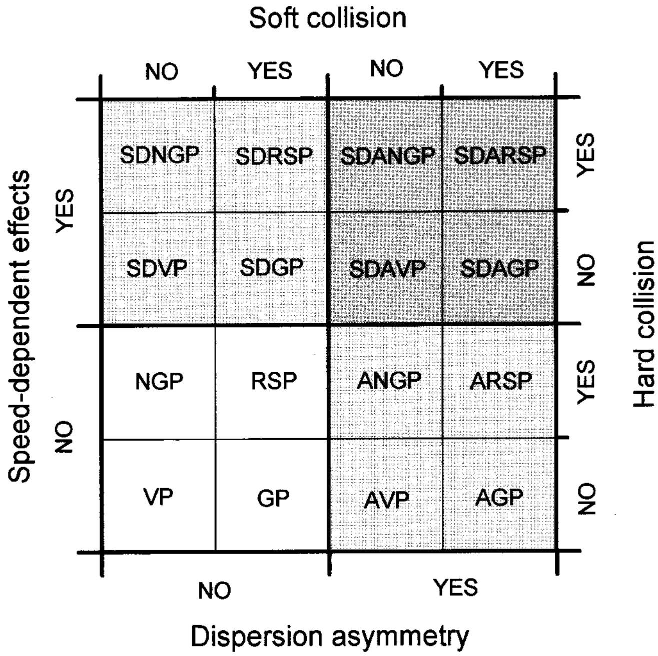

FIG. 1. Diagram of line profiles.

All standardized profiles presented here are normalized to unity if $\xi=0$, which means $\int_{-\infty}^{+\infty} du\, I(u)=1$. It should be noted that in many papers the other conventional normalization is often used: $\int_{-\infty}^{+\infty} du\, I(u)=\sqrt{\pi}$.

To describe the Doppler and pressure broadened line shape, one can use four ''elementary'' line profiles: Voigt (VP), Galatry (GP), Nelkin-Ghatak (NGP), and Rautian-Sobelman (RSP). The last three profiles permit one to describe the collision narrowing of the line. All those profiles are symmetric. To analyze the data, in which the collision-time asymmetry, line-mixing asymmetry, or collision-induced asymmetry occur, the asymmetric profiles, AVP, AGP, ANGP, and ARSP, should be used. In the case, when correlation between pressure and Doppler broadening is important, speed-dependent profiles, SDVP, SDGP, SDNGP, and SDRSP, will be helpful. The speed-dependent asymmetric profiles, SDAVP, SDAGP, SDANGP, and SDARSP, take into account those two effects: the dispersion asymmetry of the line and the correlation between Doppler and pressure broadening and shift of the line.

Figure 1 shows the diagram in which all sixteen profiles described above are placed. The place of each profile is determined by effects that this profile takes into account. All these profiles can be obtained from the speed-dependent asymmetric Rautian-Sobelman profile (SDARSP) making suitable simplifications. If the Doppler broadening of the line can be omitted the SDARSP also can be transformed to the asymmetric weighted sum of Lorentz profiles (AWSLP) or weighted sum of Lorentz profiles (WSLP).

In order to take into account the speed dependence of the collision parameters of the line and the collision narrowing, the convolution of the WSLP with the GP or NGP in the form that describes only the pure Doppler line shape is often used [23,25]. In the present work a profile proposed by Duggan *et al.* [23], which is a convolution of the WSLP and GP, will be marked as GP⊗WSLP, where the symbol ''⊗'' denotes a convolution. This idea was extended on the hard collisions case by Henry *et al.* [25] who used a convolution of the WSLP and NGP, which will be marked here as NGP ⊗WSLP. Such profiles were used by several authors [23,25–27] to describe experimental data in cases when the SDGP or SDNGP can be applied. As was shown [28], this approach gives quite good results for higher values of collision narrowing parameter z, but worse for small z. It was shown by Duggan *et al.* [27] that the values of the collision narrowing parameter of CO lines perturbed by He and Ar, obtained from the fit of GP⊗WSLP to the experimental data, can be unreasonable. Moreover Lance *et al.* [26] have shown that values of the collision narrowing parameter of C_2H_2 lines perturbed by Xe, obtained using NGP⊗WSLP, are not linearly dependent on the perturber pressure. These convolutions have also unsuitable asymptotic behavior for $z=0$. They cannot be transformed to SDVP. Calculations of profiles that are the simple convolution GP⊗WSLP or NGP ⊗WSLP require a similar or much longer computing time than direct calculations of the SDGP or SDNGP, respectively.

In general, the correlation between pressure broadening and shift and velocity-changing collisions should also be taken into account. In the approach presented in this paper it was not done. Rautian and Sobelman first considered such a correlation in Ref. [20]. As a result of inclusion of this correlation is the fact that the parameters ν_S and ν_H occurring in expressions (24) and (30) are in general complex. As was shown in this case, even for $\beta=0$ those profiles can be asymmetric [20]. Pine [43] has used the correlated profiles, correlated Galatry profile (CGP) and correlated Nelkin-Ghatak profile (CNGP), with the complex narrowing parameters to describe the asymmetric line shapes of the HF lines observed in his experiment. A more general description of the influence of these correlations on the shape of the line (CSDNGP), when the speed-dependent effects occur, was given by Robert *et al.* [22] in a hard collision approach and it was used to a very accurate analysis of the experimental data [24]. The analysis of experimental data carried out by Duggan *et al.* [27], who used SDGP, shows that such a correlation is very important also in other cases and so it seems that the correlated speed-dependent Galatry profile (CSDGP) would be useful. Unfortunately it is difficult to say how to evaluate the CSDGP and the correlated speed-dependent Rautian-Sobelman profile (CSDRSP), obviously. Results obtained by Duggan *et al.* [27] for CO lines perturbed by Ar show that their interpretation would be clear if ν_S in the SDGP is replaced by $\nu_S[1-(\Gamma+i\Delta)/\nu_T]$, where ν_T is the total collision rate. Such a change was first proposed by Rautian and Sobelman [20] for GP to take into account correlation between phase-changing and velocity-changing collisions.

The correlated speed-dependent asymmetric Rautian-Sobelman profile (CSDARSP) can be given only in a phenomenological way using in Eq. (42) for the SDARSP, following Pine [43], complex ν_H and ν_S. Some interpretation of these parameters can be done using relation $\nu_H+\nu_S=\nu[1-(\Gamma+i\Delta)/\nu_T]$ where $\nu=k_BT/(m_E D)$ is the effective frequency of velocity-changing collisions, which is conected with diffusion coefficient D, obviously, the assumption that ν_H and ν_S are speed independent is an approximation.

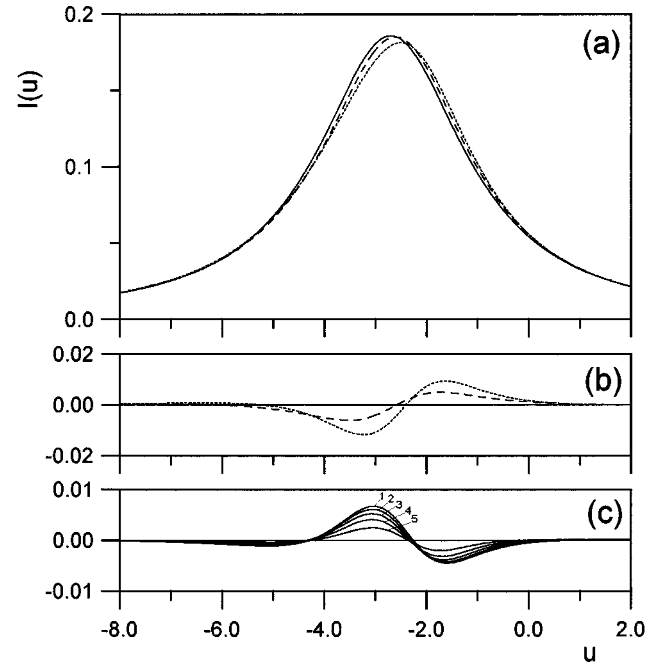

FIG. 2. Comparison of line shapes obtained for $g=1.6$, $d=-2.7$, $z=2.7$, $\alpha=2$. (a) The GP and NGP (full line), the SDNGP (dashed line), and the SDGP (dotted line). (b) Differences: SDNGP-GP (dashed line) and SDGP-GP (dotted line). (c) Differences: SDRSP-SDGP (see in the text).

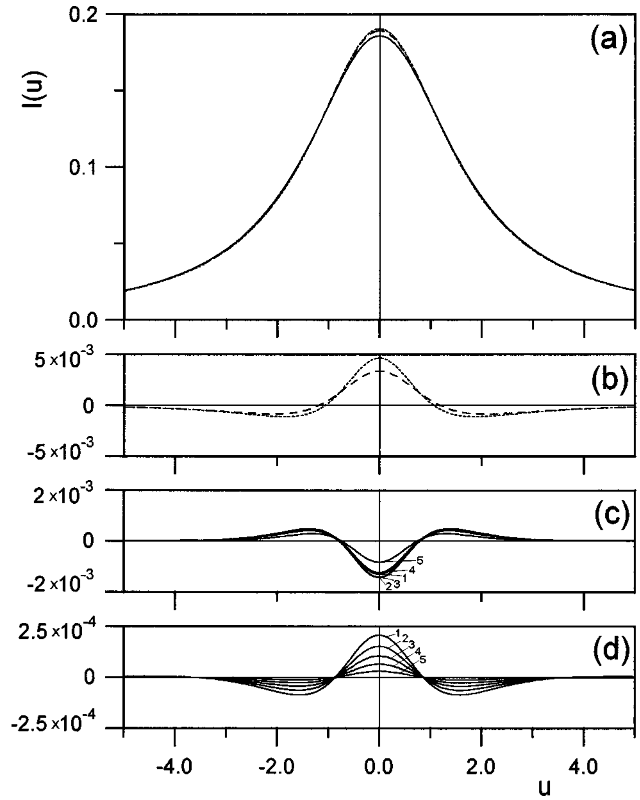

FIG. 3. Comparison of line shapes obtained for $g=1.6$, $d=0.0$, $z=2.7$, $\alpha=2$. (a) The GP and NGP (full line), the SDNGP (dashed line), and the SDGP (dotted line). (b) Differences: SDNGP-GP (dashed line) and SDGP-GP (dotted line). (c) Differences: SDRSP-SDGP (see in the text). (d) Differences: RSP-GP (see in the text).

V. RESULTS

In order to compare theoretical profiles resulting from various models discussed above we have performed numerical calculations for different line profiles and the same physical conditions corresponding to those in an experiment of Pine [43] on pressure broadening of the $P(5)$ line of HF $(v=1-0)$ perturbed by argon at a pressure of 500 Torr. The values of reduced parameters in this case are close to $g=1.6$, $d=-2.7$, and $z=2.7$. In these calculations it was assumed that $\xi=0$ and $\beta=0$ and that the dependence of the collision width and shift on the emitter velocity can be described by Eq. (47) with $q=6$ (for the van der Waals interaction) and $\alpha=2$ (for the HF-Ar system).

The comparison of four profiles GP, NGP, SDGP, and SDNGP is shown in Fig. 2(a). It can be seen that GP and NGP are very close to each other. On the other hand they differ markedly from the speed-dependent profiles SDGP and SDNGP. It is surprising that the widths of speed-dependent profiles, in particular SDGP, are larger than those of the GP and NGP. In this case, speed-dependent effects, in particular speed-dependent collision line shift, cause the additional broadening, not narrowing, as might be expected. Contrary to the GP and NGP, the difference between the SDGP and SDNGP is much more significant. Figure 2(b) shows differences between the speed-dependent profiles and the GP. As can be seen, the SDGP is more asymmetric than the SDNGP. This asymmetry is generated only by speed-dependent effects. The fluent transition from the SDGP to SDNGP can be achieved using the SDRSP. In Fig. 2(c) differences between the SDRSP and the SDGP are shown. The SDRSP was evaluated for a few combinations of values of z_S and z_H parameters ($z_H=1.0z$, $z_S=0.0z$; $z_H=0.8z$, $z_S=0.2z$; $z_H=0.6z$, $z_S=0.4z$; $z_H=0.4z$, $z_S=0.6z$; $z_H=0.2z$, $z_S=0.8z$ marked by numbers 1, 2, 3, 4, 5, respectively).

Calculations in which $d=0$ were carried out to show the role of the collision shift on the final line shape. All other parameters are the same as in the previous case. In Fig. 3(a) the profiles GP, NGP, SDGP, and SDNGP are compared. Speed-dependent profiles are narrower than the GP and NGP. The difference between the SDGP and SDNGP is much smaller than that obtained in the case for the nonzero collision shift $(d\neq 0)$. The differences between the speed-dependent profiles (SDGP and SDNGP) and GP are shown in Fig. 3(b). Figure 3(c) shows differences between the SDRSP and SDGP obtained for z_S and z_H that are the same as in Fig. 2. It is interesting to note that the largest difference is obtained for $z_H=0.8z$ and $z_S=0.2z$, which means the case that is not the pure hard collision one. In Fig. 3(d) the analogous plot of the differences between the RSP and the GP is presented.

As was shown, differences between the SDNGP and SDGP in both cases under investigation are much greater than those for the NGP and GP. Particularly, it occurs in the case when the collision shift is large enough. The SDGP and SDNGP can be asymmetric. The asymmetry observed by Pine [43] can also be caused by speed-dependent effects. The magnitude of this asymmetry is connected with the collision line shift and its dependence on the emitter velocity. It was shown that speed-dependent effects may cause the additional narrowing or broadening of the line. This can be manifested by a too high or too low magnitude of the collision narrowing parameter compared to its real value. The narrowing occurs for small collision line shifts and the broadening appears for large collision line shifts. This is in good agreement with experimental observations [37,43,23].

In the present calculations the dispersion asymmetry was omitted. The influence of the dispersion and speed-dependent asymmetry on the resulting spectral line shape was experimentally and theoretically investigated in Refs. [30–33] and [42].

VI. CONCLUSION

The speed-dependent asymmetric Rautian-Sobelman profile proposed in this paper is a uniform formula that yields in corresponding limits results of various theoretical profiles collected in a diagram in Fig. 1. This profile takes into account the correlation between the collision broadening and shift of the emitted or absorbed line and the thermal motion of the radiating particle as well as the change of velocity of this particle during its collision with the perturber and also the dispersion asymmetry of the line caused by different effects. Using this expression one can perform calculations that include the soft as well as the hard velocity-changing collisions.

The hard collision model is valid for the perturbers much heavier than the emitters. In this case also speed-dependent effects play a great role and the description of the line profile proposed by Robert *et al.* [22] should be used. The soft collision model is valid for the emitters much heavier than perturbers. In this case speed-dependent effects can be omitted and the approach proposed by Galatry [18] and developed by Rautian and Sobelman [20] should be used. On the other hand in a real situation there are many systems with intermediate mass ratio $0.5<\alpha<2.0$, for which the assumptions of either pure soft or pure hard collision models are not fulfilled completely and the speed-dependent effects should be taken into account. As shown by Henry *et al.* [25], diffusion coefficients obtained in such a case using profiles based only on the pure soft or pure hard collisions model, can be different from their real value. The SDRSP or SDARSP give the possibility to carry out calculations of line profiles in these intermediate cases. It may be that the use of the SDARSP will help to reduce divergences between results of the analysis of experimental data and their expected results in the case of CO lines perturbed by Ar [27] caused by the fact that such a system cannot be described by the pure soft or hard collision model.

It was shown, that the experimentally observed additional narrowing and broadening [37,43,23] can be caused by speed-dependent effects. It seems that the asymmetry of the line reported in [43] may be also caused by speed-dependent effects. As was shown, this is possible. Speed-dependent collisionally narrowed profiles can be also used to analyze of the experimental results obtained by Rohart *et al.* [44,45].

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