High-resolution studies on the influence of velocity-changing collisions on atomic and molecular line shapes.

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Abstract. Starting with the transport/relaxation equation in the impact limit we have developed some new analytical and numerical approaches for modelling pressure-broadened spectral profiles of isolated atomic or molecular lines. Particular attention is paid to the influence of velocity-changing collisions on the line shape described by the speed-dependent broadening and shifting rates. These new models are compared to existing high-resolution experimental spectra.

LINE SHAPE AND TRANSPORT/RELAXATION EQUATION

The shape of a spectral line broadened due to atomic collisions and thermal motion effects can be written as real part of the velocity integral [1]–[5]

$$I(\omega) = \frac{1}{\pi}\mathrm{Re} \int d^3\vec{v}\rho(\omega,\vec{v}). \tag{1}$$

where $\rho(\omega,\vec{v})$ describes the profile of the line corresponding to each velocity of absorber or emitter. For linear spectroscopy, the isolated line in the impact approximation $\rho(\omega,\vec{v})$ satisfies the following transport/relaxation equation

$$\rho_0(\vec{v}) = -i(\omega - \omega_0 - \vec{k}\cdot\vec{v})\rho(\omega,\vec{v}) - \widehat{S}\rho(\omega,\vec{v}), \tag{2}$$

where the ω_0 is the resonant frequency and $\rho_0(\vec{v})$ describes the initial velocity distribution of the absorbers or emitters in the initial state given by the Maxwellian velocity distribution $f_m(\vec{v}) = (\pi v_m^2)^{-3/2}\exp(-v^2/v_m^2)$. Here $v_m = \sqrt{2k_BT/m_A}$ is the most probable speed of the absorber or emitter of mass m_A, k_B is Boltzmann's constant and, T is the gas temperature. The collision operator $\widehat{S}$ describes the influence of the perturbers on the absorber or emitter interacting with the light. Equivalent approaches to this problem are also formulated in the framework of the correlation function formalism [1, 2, 6, 7].

The general expressions given above include all interesting effects such as velocity-changing collisions, speed-dependent broadening and shifting, and correlation between

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the velocity-changing and dephasing collisions. In the case where velocity-changing and dephasing collisions are uncorrelated the collision operator is expressed as the sum

$$\widehat{S} = \widehat{S}_D + \widehat{S}_{VC}, \tag{3}$$

of the dephasing collision operator $\widehat{S}_D$ and the velocity-changing collision operator $\widehat{S}_{VC}$. The operator $\widehat{S}_D$ is generally written as

$$\widehat{S}_D \rho(\omega, \vec{v}) = -\left[\Gamma(v) + i\Delta(v)\right] \rho(\omega, \vec{v}), \tag{4}$$

where $\Gamma(v)$ and $\Delta(v)$ are the speed-dependent collisional width (HWHM) and shift, respectively [6, 8]. The velocity-changing collisions are very often described using one of two models proposed a long time ago and known as the "soft collision" [9, 10] and "hard collision" [1, 11] models. In the soft collision model the velocity-changing collision operator $\widehat{S}_{VC}$ has the form [1]

$$\widehat{S}_{VC} \rho(\omega, \vec{v}) = \nu_{\text{diff}} \left(\frac{v_m^2}{2} \Delta_v + \vec{\nabla}_v \cdot \vec{v} \right) \rho(\omega, \vec{v}). \tag{5}$$

When velocity-changing collisions are described by the "hard" collision model the corresponding operator is written as follows [1]:

$$\widehat{S}_{VC} \rho(\omega, \vec{v}) = -\nu_{\text{diff}} \rho(\omega, \vec{v}) + \nu_{\text{diff}} f_m(\vec{v}) \int d^3\vec{v}' \, \rho(\omega, \vec{v}'). \tag{6}$$

The "soft" collision model was explored by Galatry [10] to obtain the first analytical expression describing the shape of Dicke narrowed [12] lines assuming that the collisional width and shift are independent of the absorber or emitter speed. Unfortunately, when the collisional width and shift are dependent on the absorber or emiter speed there is no general analytical expression for the line shape and only some approximate formulas can be given [13]-[15]. However, when the speed-dependence of the collisional width and shift is assumed to be a quadratic function, the analytical expression can be derived [16]. On the other hand, the mathematical simplicity of the "hard" collision model leads to an analytical expression for the shape of the line for any speed-dependent width and shift [1, 17].

Very flexible analytical expressions for the line shape were obtained using an idea due to Rautian and Sobelman that velocity-changing collisions in one part can be described by the "soft" collision model and in another part by the "hard" collision model. In such a case an additional parameter (a "hardness" factor) is introduced. As was shown in Ref. [18] the Rautian-Sobelman model can lead to profiles which are very close to the line shapes [19, 20] obtained using the Kielson-Storer model [21]. It was also assumed that the speed derivatives of the collisional width and shift can be neglected. These analytical expressions were independently derived by Robert and Lance [22, 23] and by the authors of this work [24, 25]. In the so-called "correlated speed-dependent asymmetric Rautian-Sobelman profile" (CSDARSP) the dispersion asymmetry (caused by the finite duration of collisions and/or the line mixing) and the correlation between velocity-changing and dephasing collisions were taken into account as well [25]. The dispersive asymmetry can be incorporated in the profile by replacing of $\rho(\omega,\vec{v})$ in Eq. (1) by $(1-i\chi)\rho(\omega,\vec{v})$ where χ is the asymmetry parameter. The correlation between velocity-changing and dephasing collisions [1] can be considered in a phenomenological way by replacing of the original frequency of the velocity-changing collisions $\nu_{\text{diff}} = k_B T/(m_A D)$ (D is the diffusion coefficient) by the quantity $\nu_{diff} - \eta(\Gamma + i\Delta)$ in which η is the correlation parameter. Chaussard *et al.* [26, 27] have demonstrated that this new analytical profile can fit experimental data over a wide range of physical condition.

The analytical expressions describing the spectral line shape are important for analysis and interpretation of experimental data. However, when deriving such expressions we always pay a price: making simplifications and introducing phenomenological quantities which can affect our interpretation of the physical effects. To be free from some of these limitations we are forced to make numerical line shape calculations which allow us to describe collisional processes affecting the shape of spectral lines in a more realistic way. The numerical method described in the following section is in fact a simpler version of the approach presented by Blackmore [3].

MATRIX APPROACH TO LINE SHAPE CALCULATIONS

To solve Eq. (2) numerically we represent the function $\rho(\omega,\vec{v})$ using an infinite set of orthonormal functions $\varphi_s(\vec{v})$ where $s = 0, 1, 2, \ldots$, in which $\int d^3\vec{v} f_m(\vec{v})\varphi_s^*(\vec{v})\varphi_{s'}(\vec{v}) = \delta_{s,s'}$ and $\varphi_0(\vec{v}) = 1$ (c.f. Ref. [5]). Then we can write the function $\rho(\omega,\vec{v})$ as

$$\rho(\omega,\vec{v}) = f_m(\vec{v}) \sum_{s=0}^{\infty} c_s(\omega)\varphi_s(\vec{v}), \tag{7}$$

where the coefficients $c_s(\omega)$ depend only on the frequency ω. Inserting Eq. (7) into the transport/relaxation equation, Eq. (2), we obtain an infinite system of complex simultaneous linear equations which can be written in the matrix form as [5, 19]

$$\underline{\mathbf{b}} = \mathbf{L}(\omega)\underline{\mathbf{c}}(\omega), \tag{8}$$

where the column vector $\underline{\mathbf{b}}$, contains elements $[\underline{\mathbf{b}}]_s = \delta_{s,0}$. The column vector $\underline{\mathbf{c}}(\omega)$ consists of the elements $[\underline{\mathbf{c}}(\omega)]_s = c_s(\omega)$. The matrix $\mathbf{L}(\omega)$ can be given in the following form

$$\mathbf{L}(\omega) = -i(\omega-\omega_0)\mathbf{1} + i\mathbf{K} - \mathbf{S}^f, \tag{9}$$

where $\mathbf{1}$ is the unit matrix, i.e. $[\mathbf{1}]_{s,s'} = \delta_{s,s'}$. $\mathbf{K}$ is the matrix which represents the Doppler shift, i.e. $[\mathbf{K}]_{s,s'} = \int d^3\vec{v} f_m(\vec{v})(\vec{k}\cdot\vec{v})\varphi_s^*(\vec{v})\varphi_{s'}(\vec{v})$, and $\mathbf{S}^f$ is the matrix which represents the collision operator, i.e. $[\mathbf{S}^f]_{s,s'} = \int d^3\vec{v}\varphi_s^*(\vec{v})\hat{S} f_m(\vec{v})\varphi_{s'}(\vec{v})$. In terms of coefficients $c_s(\omega)$ the line shape can be written in the following form [5, 19, 28]

$$I(\omega) = \frac{1}{\pi}\text{Re}\, c_0(\omega). \tag{10}$$

To calculate the line shape Eq. (8) should be solved at each frequency. In some cases it is more convenient to use a diagonalization technique (c.f. [19, 29, 30]). To do it in this way we need to find the full set of eigenvectors $\underline{\mathbf{e}}_j$ and corresponding eigenvalues ε_j which fulfil the following equation

$$(i\mathbf{K}-\mathbf{S}^f)\underline{\mathbf{e}}_j = \varepsilon_j \underline{\mathbf{e}}_j. \tag{11}$$

Once the eigenvectors and eigenvalues are known the coefficient $c_0(\omega)$ can be computed from the following expression

$$c_0(\omega) = \sum_{j=0}^{\infty} \frac{\beta_j [\underline{\mathbf{e}}_j]_0}{\varepsilon_j - i(\omega-\omega_0)}, \tag{12}$$

where the coefficients fulfil the relation $\underline{\mathbf{b}} = \sum_{j=0}^{\infty} \beta_j \underline{\mathbf{e}}_j$. In this case the time consuming diagonalization can be carried out once to calculate shape of a line for different frequencies.

In practice, the calculations are carried out using a finite set of basis functions what lead to approximate results. However, in cases where collisional processes have comparable or greater influence on the line shape than the Doppler broadening the computation can be done with sufficient accuracy using a small number of basis functions.

Using the approach presented above we are able to calculate the line shape in the case when velocity-changing collisions are described by the billiard-ball model (BB) [3, 28, 31]. In this model the velocity changing collisions are treated as collisions of rigid spheres. This model allows us to capture the dependence of velocity-changing collisions on the mass ratio α of the active atom or molecule and perturber. By changing the mass of the pertuber we can modify the nature of the collisions from mostly direction-changing collisions in the case of very heavy perturbers (corresponding in limit $\alpha = \infty$ to the Lorentz gas model) to collisions significantly changing speed in the case of very light perturbers (corresponding in limit $\alpha = 0$ to the soft collision model). Calculating the correlated speed-dependent asymmetric billiard-ball profile (CSDABBP) we also take into account the dispersion asymmetry and correlation between velocity-changing and dephasing collisions in the phenomenological way described above. In this case the matrix elements of the velocity-changing collision operator can be given by the analytical formula derived by Lindenfeld and Shizgal [28, 32].

In the following section both analytical and numerical approaches are applied to the analysis of experimental data.

APPLICATION

First, we present an example of the R(6) line from the fundamental band of HF perturbed by argon recorded with a linear-scan-controlled difference-frequency laser spectrometer [33]. The speed dependence of the broadening and shifting is computed from the realistic quantum close-coupling collision cross sections calculated by Green and Hutson [34] using an accurate HF-Ar van der Waals molecule potential. In Fig. 1, we compare several profiles to the 100 Torr trace fit simultaneously with the 200 and 500 Torr scans [35]. This multifitting procedure provides a test of the consistency of the lineshape model and parameters over the range of measured pressures [35, 36]. We obtain the best

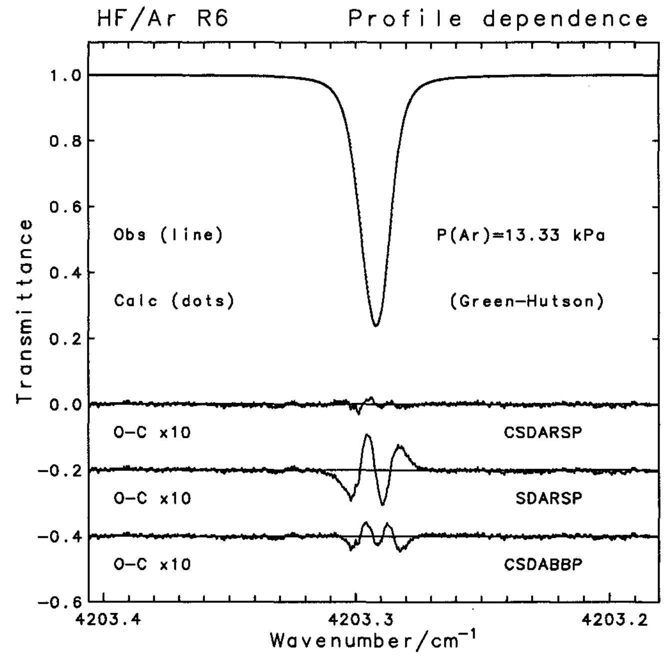

FIGURE 1. The measured shape of the R6 line of HF perturbed by argon compared to the correlated speed-dependent asymmetric Rautian-Sobelman profile (CSDARSP), the speed-dependent asymmetric Rautian-Sobelman profile (SDARSP) and the correlated speed-dependent asymmetric billiard-ball profile (SDABBP).

fit for the analytical CSDARSP, incorporating a linear combination of hard and soft collision models with a "hardness" fraction of 0.72. Correlation between the velocity-changing and dephasing collisions is crucial for explaining the observed asymmetry for these strongly shifted lines ($\Delta/\Gamma \simeq 2.6$) [33, 35]. If we neglect correlation, as seen for the SDARSP fit, we obtain large systematic residuals indicating that neither the speed dependence of the shift nor the collision duration effects have sufficient magnitude or the correct pressure dependence to account for this asymmetry. The residuals for CSDABBP are also worse than for the CSDARSP, though the latter does have one more parameter. This indicates that the billiard ball profile with a fixed mass ratio does not accurately interpolate between soft and hard collision models the way it does between the soft and the Lorentz gas models. In fact, the CSDABBP residuals are very similar to the pure soft collision profile for HF/Ar shown previously [35]. Generally though, billiard ball profiles are intermediate between hard and soft collision lineshapes and, when multifit over a range of pressures, exhibit discrepancies that could easily be distinguished experimentally. Because of convergence difficulties with the large number of basis functions needed for the CSDABBP in the Doppler regime, we have not included lower pressure traces [33, 35] in our fits here. Presented results demonstrate that we need to construct a realistic collision operator starting only from the intermolecular interaction

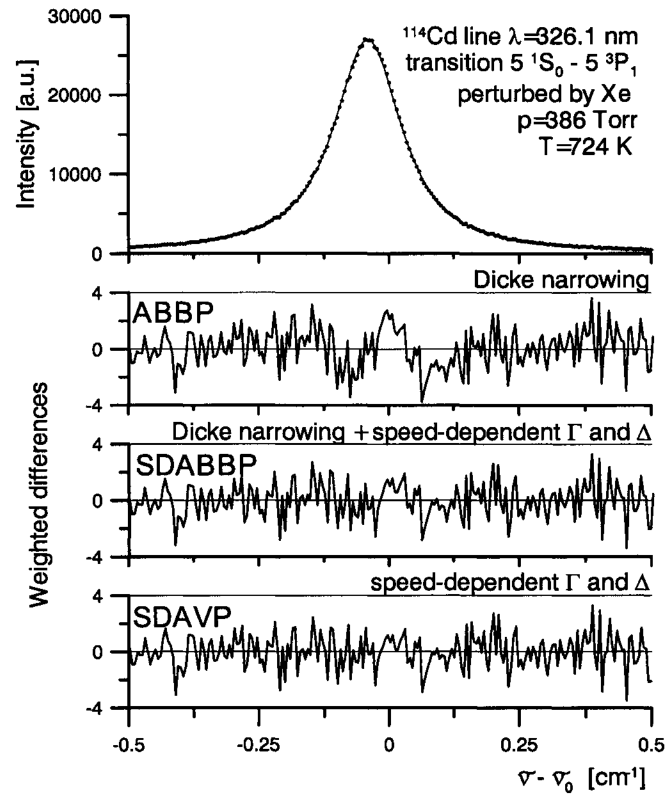

FIGURE 2. The measured shape of the Cd 326.1-nm line perturbed by xenon compared to the asymmetric billiard-ball profile (ABBP), the speed-dependent asymmetric billiard-ball profile (SDABBP) and the speed-dependent asymmetric Voigt profile (SDAVP). The weighted difference is defined as a difference of the measured and fitted intensity divided by the standard deviation of the measured intensity.

able to reach good description of measured profiles of HF perturbed by argon.

Now we turn to the intercombination line of ^{114}Cd perturbed by 386 Torr of xenon. Bielski *et al.* [37] observed that the Doppler width of this line obtained from the fit of the measured profile to the ordinary Voigt profile is significantly smaller than the value corresponding to the cell temperature. To verify the reason for this narrowing we have fitted the asymmetric billiard-ball profile (ABBP) in which the Dicke narrowing is taken into account using the billiard-ball model. As can be seen from Fig. 2 the Dicke narrowing itself cannot completely eliminate departures between the fitted and experimental profiles. Therefore, we have also fitted the data to the speed-dependent asymmetric Voigt profile (SDAVP) [38] which takes into account the speed dependence of collisional broadening and shifting but neglects the Dicke narrowing. We have used analytical speed dependence of collisional broadening and shifting given by the confluent hypergeometric function corresponding to the van der Waals potential [37, 6] which gives results close to those obtained using the potentials calculated by Czuchaj and Stoll [39]. As

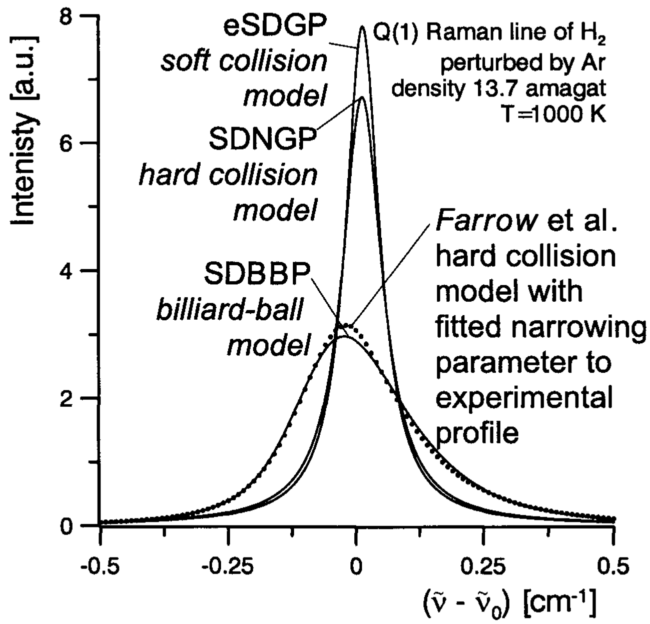

FIGURE 3. Comparison of the speed-dependent billiard ball profile (SDBBP), the speed-dependent Nelkin-Ghatak profile (SDNGP) and the "exact" speed-dependent Galatry profile (eSDGP) (solid lines) simulated for the Q(1) Raman line of H_2 perturbed by Ar and the profile fitted by Farrow *et al.* [48] (dotted) to their experimental data.

can be seen from Fig. 2 the differences are spread uniformly about zero which confirms the good quality of the SDAVP fit. We have also fitted the speed-dependent asymmetric billiard-ball profile (SDABBP) in which both the speed dependence of the collisional width and shift and the Dicke narrowing are taken into account. The quality of the fit is slightly worse than that for the SDAVP if the frequency of velocity changing collisions is fixed at the value expected for the Cd-Xe system based on the potentials calculated by Czuchaj and Stoll [39]. It would be necessary to improve the signal to noise ratio to conclude whether the Dicke narrowing is smaller than expected in the Cd-Xe system. However it also should be noted that Lewis and his coworkers [40] did not report any signs of the Dicke narrowing in their experiment with calcium perturbed by rare gases. Moreover, there is a increasing number of evidence for molecular systems for which narrowing of the line is caused by the speed dependence of collisional broadening rather than by Dicke narrowing [41]-[44]. Wehr *et al.* [45] discuss this problem for the P2 line of CO perturbed by argon [46].

Finally we show the results of simulations of the Q(1) Raman line of H_2 perturbed by argon at temperature 1000 K and the density 13.7 amagat which corresponds to the experiment of Farrow *et al.* [48]. We have calculated the speed-dependent billiard-ball profile (SDBBP) [3, 31, 47] taking into account the strong speed dependence of the shift of this line and the velocity-changing collisions described by the BB model. As can be seen from Fig. 3 the SDBBP appears much different than the speed-dependent Nelkin-Ghatak profile (SDNGP) [1, 17] and the exact speed-dependent Galatry profile (eSDGP) [16, 31] where velocity-changing collisions are described by the "hard" and "soft" collision models, respectively. Collisions of light hydrogen molecules with the much heavier argon atom change mostly the direction of the H_2 velocity. The speed is only slightly changed. On the other hand the "hard" and "soft" collision model describes collisions which significantly change the speed of colliding atoms or molecules. The difference between the SDBBP, SDNGP and eSDGP is caused only by different treatment of speed-changing collisions in these models. It should be noted that all three profiles were calculated with exactly the same value of parameters, assuming speed-independent collisional broadening and using a function describing speed dependence of the collisional shifting given by Farrow *et al.* [48]. Similar variations of the shape of line were also modelled by Lance and Robert [22] who changed the phenomenological "hardness" parameter in the CSDARSP. When we fit the SDNGP to the simulated SDBBP the fitted frequency of velocity-changing collisions will be more than 10 times smaller than the value used in the simulation. This can explain the results reported by Farrow *et al.* [48]. They fitted a profile based on the hard collision model to their experimental profiles of H_2 perturbed by argon and obtained a narrowing parameter more than 10 times smaller than expected. Recently, Hoang *et al.* [49] modelled such behavior for a wider range of perturbers using the molecular dynamic simulation (MDS) technique. We believe that the billiard-ball model is a promising tool to analyze the experimental line shape of H_2 perturbed by foreign gases.

CONCLUSIONS

Concluding we would like to point out that the flexible analytical expression describing the line shape in the form of the correlated speed-dependent asymmetric Rautian-Sobelman profile was derived. This expression with parameters having reasonable physical interpretation alow us to analyse experimental data for different systems and in wide range of conditions. We have demonstrated that the fast numerical line shape calculation for any kind of the collision operator are possible. It opens the way to the line shape calculations which are *ab initio* in spirit and are able to reach agreement with experimental results. Introducing the billiard-ball model to the treatment of the line shape allows us to describe the velocity-changing collisions in a way more realistic than other standard models used before. Especially, the variation between the direction- and speed-changing collisions caused by the change of the perturber-absorber mass ratio can be obtained as a natural consequence of application of the BB model.

The additional effort is necessary to reach a full agreement between theoretical and experimental results for the isolated lines. We need to have the realistic collision operators calculated starting from the intermolecular interaction and taking into account the speed dependence of collisional broadening and shifting, velocity-changing collisions and the correlations between them, in a unified way. In the case of the low density regime when the Doppler effect has dominant influence on the line shape the numerical method described above fails and another effective numerical approach should be developed. Further experimental investigations of the Dicke narrowing in atomic and molecular systems should lead to better understanding of the correlation between dephasing and velocity-changing collisions and their impact on the line shape.

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