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Influence of the interaction potential shape on the Dicke narrowed spectral line profiles affected by speed-dependent collisional broadening and shifting

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ABSTRACT

Variations of the Dicke narrowed spectral line profiles caused by change of the interaction potential shape are investigated. We propose line shape model, which incorporates the speed-dependent collisional broadening and shifting as well as the velocity-changing collisions, described by the class of $r^{-\nu}$-type repulsive potentials. Following Blackmore (1987) [55], calculations were carried out using the Liouville formalism. In contrast to previous analysis, we concluded that the pure Dicke narrowed profiles calculated for various potential types can differ by almost 20%. Assuming the same speed dependence of collisional broadening and changing the type of interaction potential responsible for velocity-changing collisions the subpercent variations of calculated line shapes were observed. It was shown that in the case when these both contributions, the collisional broadening and the velocity-changing collisions, are related to the $r^{-\nu}$-type interaction potential the variations of calculated line shapes are more than one order of magnitude bigger than in previous case and are dominated by speed-dependent collisional broadening. In the case of supersensitive spectroscopy, where accuracy of the line shapes measurements approaches 10^{-6}, the accuracy of the retrieved line shape parameters can be strongly affected by the assumed type of interaction potential related to velocity-changing collisions.

1. Introduction

It was shown experimentally [1–8] that – in order to perform an appropriate analysis of spectral line profiles – in many cases it is necessary to take into account speed dependence of dephasing collisions [9,10] as well as Dicke narrowing due to velocity-changing collisions [11,12]. In the last two decades several analytic or quasi-analytic expressions describing shapes of isolated spectral lines have been derived [13–22]. Moreover, it was demonstrated that the spectral lines which are coupled by collisions can also be treated in the similar way [23–25]. The comprehensive review of this subject can be found in [26].

Line shape models mentioned above have been successfully applied to describe experimental data in many cases [1–8]. However, rapid development of spectroscopic methods leads to a dramatic increase of signal to noise ratios (SNR) of measured spectra. At present, the SNR about 1000 or 2000 became almost a standard value for many experimental line shape studies. It was demonstrated that in some cases spectral line shapes can be measured with the SNR values higher than 10,000 for a single line measurement [27–29] or even higher than 200,000 as was very recently demonstrated for averaging about thousand of records [30]. Experimental investigation of spectral line shapes with accuracy at level 10^{-5} together with absolute measurement of light frequency by the optical frequency comb [31–35] opens new possibilities for study of physical effects leading to formation of spectral lines profiles such as relativistic effects [36–39]

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or manifestation of difference between realistic and model speed dependence of collisional broadening on measured line shape [40]. Work on optical determination of the Boltzmann constant [41–44] is a natural field which can benefit from measurements with so high accuracy. It was shown [45–47] that even at very low pressures when spectral line profile is dominated by Doppler broadening the collisional effects like Dicke narrowing or speed-dependent broadening and shifting can noticeably affect determination of Boltzmann constant on the level of required precision 10^{-6}. At this point it is not clear at which level of accuracy analytical or quasi-analytical line shape models can be applied. Therefore development of line shape calculation techniques starting from basic principles, *ab initio* in spirit, is strongly desired [48–50].

To handle the influence of perturber–absorber mass ratio within the velocity-changing contribution to the spectral line shape a speed-dependent billiard-balls profile (SDBBP) [51] was introduced. In this approach the perturber–absorber velocity-changing collisions are approximated with a hard spheres model and a formula for the profile was derived using formalism presented by Shapiro et al. [52] based on works by Lindenfeld and Shizgal [53,54] and similar to this developed earlier by Blackmore [55]. It should be emphasized that in contrast to soft- or hard-collisions models the SDBBP model is based on the Boltzmann collisional term for a finite mass ratio and hence more accurately coincides with a real physical systems. Within this approach the dephasing and velocity-changing contributions to the collisions were assumed to be statistically uncorrelated. The problem of statistical correlations between pressure broadening and Dicke narrowing was investigated in the past [21,56–63]. Recently, Ngo et al. [64] applied the classical molecular dynamics simulations to predict the influence of these correlations on spectral line profiles. Phenomenological way of applying the partial statistical correlations to the SDBBP model was presented by Lisak et al. [65]. Validity of the SDBBP model was verified experimentally for both uncorrelated and correlated cases [65–70].

In this work we investigate the influence of interaction potential shape on the Dicke narrowed spectral line profiles affected by speed-dependent collisional broadening and shifting. Natural extension of the SDBBP is to introduce more general potential describing velocity-changing collisions than the hard spheres one. We do this for the class of $r^{-\nu}$-type potentials in the similar way to Blackmore approach [55]. On the one hand, this paper constitutes an extension of Blackmore's results [55] since we carefully discussed speed-dependent collisions, but on the other hand it also expands the SDBBP model [51,52] by more general potentials describing velocity-changing collisions.

2. Theoretical description

2.1. Transport/relaxation equation

We consider here the gas mixture of absorber particles highly diluted in the perturber bath. The total pressure is assumed to be low enough to fulfil the impact approximation. Following [52,71] we are looking for the stationary solution of the transport/relaxation equation for the line shape distribution $f(\omega,\vec{v})$, which is proportional to the optical coherence velocity distribution

$$f_m(\vec{v}) = -i(\omega-\omega_0-\vec{k}\cdot\vec{v})f(\omega,\vec{v}) - \hat{S}f(\omega,\vec{v}), \tag{1}$$

where $\vec{v}$ is the absorber velocity, $\vec{k}$ is the wave vector, ω is the light frequency and the ω_0 is the frequency of the unperturbed isolated transition. The $f_m(\vec{v}) = (\sqrt{\pi}v_m)^{-3} e^{-(v/v_m)^2}$ function is the Maxwellian velocity distribution, where the most probable speed $v_m = \sqrt{2k_BT/m_1}$, and k_B, T, m_1 are the Boltzmann constant, the temperature and the absorber mass, respectively. The $\hat{S}$ operator describes the relaxations of optical coherence and its flows between various velocity classes. In the following considerations the dephasing collisions and the velocity-changing collisions are assumed to be statistically independent, what allows to write the $\hat{S}$ operator as a simple sum $\hat{S} = \hat{S}_{VC} + \hat{S}_D$, where the $\hat{S}_{VC}$ and $\hat{S}_D$ operators describe velocity-changing and dephasing collisions, respectively. The correlation between the velocity-changing and dephasing collisions can be easily included in this model in the phenomenological way proposed by Lisak et al. [65]. The line shape distribution function $f(\omega,\vec{v})$ allows to calculate the absorption line profile $I(\omega)$ as a following integral

$$I(\omega) = \frac{1}{\pi}\mathrm{Re}\int f(\omega,\vec{v})\, d^3\vec{v}. \tag{2}$$

It is convenient [52,54,55] to rewrite Eq. (1) in terms of $h(\omega,\vec{v})$ function given by relation $f(\omega,\vec{v}) = f_m(\vec{v})h(\omega,\vec{v})$. The solution of Eq. (1) can be found by decomposing operators and unknown function in orthonormal basis $\{\phi_s(\vec{v})\}$. Introducing a scalar product $\langle\phi_{s'}|\phi_s\rangle = \int d^3\vec{v} f_m(\vec{v})\phi_{s'}(\vec{v})\phi_s(\vec{v})$ and setting $\phi_0(\vec{v}) = 1$, we can reduce Eq. (1) to the set of linear coupled equations for $c_s(\omega)$ coefficients [52]

$$\underline{\mathbf{b}} = (-i(\omega-\omega_0)\mathbf{1} + i\mathbf{K} - \mathbf{S}^f)\underline{\mathbf{c}}(\omega), \tag{3}$$

where column $\underline{\mathbf{c}}(\omega)$ consists of $c_s(\omega) = \langle h(\omega,\vec{v})|\phi_s(\vec{v})\rangle$, matrix $\mathbf{K}$ is given by $[\mathbf{K}]_{s',s} = \langle\phi_{s'}|\vec{k}\,\vec{v}|\phi_s\rangle$, $\mathbf{1}$ is an identity matrix, $\underline{\mathbf{b}}$ is a column defined as $[\underline{\mathbf{b}}]_s = \delta_{s,0}$ ($\delta_{s',s}$ is the Kronecker delta) and the matrix $\mathbf{S}^f$ is given by $[\mathbf{S}^f]_{s',s} = \langle\phi_{s'}|\hat{S}^f|\phi_s\rangle$, where $\hat{S}^f$ is defined by the following equation:

$$\hat{S}f_m(\vec{v})h(\omega,\vec{v}) = f_m(\vec{v})\hat{S}^f h(\omega,\vec{v}). \tag{4}$$

In practice the infinite system of coupled linear equations (3) is reduced to the system of at most a few thousand equations. Finally, the spectral line shape function Eq. (2) can be written as [52]

$$I(\omega) = \frac{1}{\pi}\mathrm{Re}\langle\phi_0(\vec{v})|h(\omega,\vec{v})\rangle = \frac{1}{\pi}\mathrm{Re}[c_0(\omega)]. \tag{5}$$

2.2. Velocity-changing collisions

To perform an *ab initio*, in spirit, calculations the Boltzmann collision operator describing velocity-changing