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Quadratic speed dependence of collisional broadening and shifting for atmospheric applications

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ABSTRACT

Precise analysis of spectroscopic data requires a proper handling of speed-dependent effects on molecular lines. Recently, new fast algorithms implementing a quadratic speed dependence of collisional width and shift were developed. In this report we show, how to evaluate the effective quadratic speed dependence in multi-component gases for atmospheric applications. Moreover, we derived relations between parameters describing quadratic speed dependence and temperature dependence of an averaged collisional width and shift. These relations can be directly applied in molecular spectra analysis and are useful for construction of new generation of spectroscopic databases.

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1. Introduction

It is well established now [1,2] that for analysis of molecular line shapes at atmospheric condition the speed dependence of collisional broadening and shifting [3,4] should be taken into account, especially if spectra needs to be analyzed or calculated with subpercent accuracy. One of the simplest descriptions of such speed dependence can be done with quadratic function of absorbing molecule speed [5–9]. For many investigated systems it was experimentally demonstrated that the use of quadratic speed dependence of collisional broadening and shifting considerably improves the quality of the line-shape analysis [10–40]. This kind of approach becomes more popular especially in case of investigation of molecular systems from Earth atmosphere, like greenhouse gases, for which quite often the perturber to absorber mass ratio is close to unity [41].

In most physical situations, however, quadratic speed dependence can be treated only as an approximation to the real one [9,19,42,43]. Moreover, it was shown that the use of more physically justified hypergeometric function

can give noticeable better description of measured line shapes than use of quadratic function, when spectra are obtained with a high signal to noise ratio [29]. Therefore, when quadratic speed dependence of collisional broadening and shifting is used one need to realize approximations and limitation of this approach.

Nevertheless, quadratic speed dependence of collisional broadening and shifting is a convenient tool in the line-shape analysis getting popularity around spectroscopists. It is caused mostly by its simplicity. Thanks to the use of quadratic speed dependence of collisional broadening and shifting simple expressions for Dicke narrowed line shapes were obtained [44,45] or integrals for matrix elements of dephasing collision operator can be evaluated analytically [46]. A new strong impulse for the interest in a such approach was given by the fast numerical algorithm for the quadratic speed-dependent Voigt profile (SD_qVP) proposed by Boone et al. [47]. Using this algorithm SD_qVP can be evaluated very efficiently as a sum of two ordinary Voigt profiles. Recently Ngo et al. [48–51] incorporated this kind of algorithm for calculation of a partially correlated speed-dependent Nelkin–Ghatak profile (pCSDNGP) proposed by Pine [11,43]. This profile becomes very attractive for construction of new databases, atmospheric research and other metrological applications, such as the Boltzmann constant

measurement [52,53], because of its flexibility and variety of physical effects which can be accounted for in this model. The quadratic partialy correlated speed-dependent Nelkin-Ghatak profile (pCSDqNGP) was used before to demonstrate importance of simultaneous inclusion of speed-dependent effects and velocity-changing collisions for Boltzmann constant determination [54]. Now as was demonstrated by Tran et al. [50,51] quadratic pCSDNGP (called here pCSD$_q$NGP) can be also calculated very quickly. Therefore pCSD$_q$NGP was proposed by Ngo et al. [48,49] as a basic line shape model to replace the Voigt profile in spectroscopic databases and radiative transfer codes. This profile was recently recommended by IUPAC for isolated molecular lines [55] and tested on some measured molecular spectra [33,40].

In this paper we discuss relation between temperature dependence of collisional broadening and the parameter describing its quadratic speed dependence. Also temperature dependence of this parameter is given. The validity of this approximation is briefly discussed by comparison with speed dependence of collisional width and shift for $1/r^q$−type of interaction potential [3,4]. Next, we show how to get values of parameters describing quadratic speed dependence for multi-component gas samples if values of such parameters are known for single-component case. The relations given in paper will be particularly useful for users of SD$_q$VP and pCSD$_q$NGP analyzing atmospheric data in which molecular transitions are perturbed by two or more perturbers in a range of temperatures.

2. Quadratic speed dependence

The speed-dependent collisional width $\Gamma(v; T)$ for given temperature T and absorber speed v can be written [3,4]

$$\Gamma(v;T) = \int d^3\vec{v}_P f_{m_P}(\vec{v}_P)\Gamma^{(r)}(|\vec{v}_P - \vec{v}|), \tag{1}$$

in terms of collisional width $\Gamma^{(r)}(v_r)$ dependent on the relative perturber–absorber speed $v_r = |\vec{v}_P - \vec{v}|$ averaged over Maxwellian distribution $f_{m_P}(\vec{v}_P) = (\pi v_{m_P}^2)^{-3/2}\exp(-v_P^2/v_{m_P}^2)$ of perturber velocity $\vec{v}_P$, where $v_{m_P} = \sqrt{2k_BT/m_P}$ is the most probable perturber speed, m_P is the perturber mass, and k_B is the Boltzmann constant. The well known speed-independent collisional width averaged over absorber and perturber velocities or just over relative velocity is given by the following relations:

$$\Gamma(T) = \int d^3\vec{v} f_{m_A}(\vec{v})\Gamma(v;T) = \int d^3\vec{v}_r f_\mu(\vec{v}_r)\Gamma^{(r)}(v_r). \tag{2}$$

Here $f_{m_A}(\vec{v}) = (\pi v_{m_A}^2)^{-3/2}\exp(-v^2/v_{m_A}^2)$ is the Maxwellian distribution of the absorber velocity $\vec{v}$, $v_{m_A} = \sqrt{2k_BT/m_A}$ is the most probable absorber speed, m_A is absorber mass, $f_\mu(\vec{v}_r) = (\pi v_\mu^2)^{-3/2}\exp(-v_r^2/v_\mu^2)$ is the Maxwellian distribution of the relative velocity $\vec{v}_r$, where $v_\mu = \sqrt{2k_BT/\mu}$ is the most probable relative speed, $\mu = m_A m_P/(m_A + m_P)$ is the reduced absorber–perturber mass.

The quadratic speed dependence of $\Gamma(v; T)$ on v at given temperature T can be obtained if the dependence of the collisional width $\Gamma^{(r)}(v_r)$ on the relative speed v_r is quadratic as well. We assume here that it is a case.

Following Berger at al. [56], see also [57–62] we take

$$\Gamma^{(r)}(v_r) = \mathcal{G}_0 + \mathcal{G}_2 v_r^2 \tag{3}$$

where $\mathcal{G}_0$ and $\mathcal{G}_2$ are constant coefficients. Inserting Eq. (3) into Eq. (1) the speed-dependent collisional width

$$\Gamma(v;T) = \Gamma(T)B_q\left(a(T); \frac{v}{v_{m_A}}\right) \tag{4}$$

can be then written in terms of the dimensionless quadratic speed-dependent function [6,9,44]:

$$B_q(a;x) = 1 + a\left(x^2 - \tfrac{3}{2}\right). \tag{5}$$

In Eq. (4) the averaged collisional width

$$\Gamma(T) = G_0 + G_2(T) \tag{6}$$

is calculated inserting Eq. (3) into Eq. (2). The temperature dependent coefficient $G_2(T)$ is proportional to temperature T and given by the following expressions:

$$G_2(T) = \frac{3}{2}\frac{1+\alpha}{\alpha}\mathcal{G}_2 v_{m_A}^2 = \frac{3}{2}\mathcal{G}_2 v_\mu^2, \tag{7}$$

where $\alpha = m_P/m_A$ is a perturber to absorber mass ratio. The parameter describing quadratic speed dependence is the following:

$$a(T) = \frac{2}{3}\frac{G_2(T)}{G_0 + G_2(T)}\frac{\alpha}{1+\alpha} = \frac{2}{3}\frac{g_2(T)}{1+g_2(T)}\frac{\alpha}{1+\alpha}. \tag{8}$$

It is convenient to express this quantity in terms of the dimensionless parameter

$$g_2(T) = \frac{G_2(T)}{G_0}. \tag{9}$$

Now we can express the temperature dependence of the averaged collisional width

$$\Gamma(T) = G_0 + G_2(T_{\text{ref}})\frac{T}{T_{\text{ref}}} = \Gamma(T_{\text{ref}})\frac{1 + g_2(T_{\text{ref}})\frac{T}{T_{\text{ref}}}}{1 + g_2(T_{\text{ref}})} \tag{10}$$

and quadratic speed dependence parameter

$$a(T) = a(T_{\text{ref}})\frac{1 + g_2(T_{\text{ref}})}{\frac{T_{\text{ref}}}{T} + g_2(T_{\text{ref}})} \tag{11}$$

in terms of $g_2(T_{\text{ref}})$ calculated in some reference temperature T_{ref}. It is worth to notice that relation between parameter $a(T)$ and temperature derivative of collisional width in case investigated here can be given in the following form:

$$a(T) = \frac{2}{3}\frac{\alpha}{1+\alpha}\frac{T}{\Gamma(T)}\frac{d\Gamma}{dT}\bigg|_T. \tag{12}$$

It is often convenient to operate with collisional or pressure broadening coefficients $(\Gamma/N)_T$ or $(\Gamma/p)_T$ at given temperature T. For ideal gas the number density N and pressure p are related by well known equation of state $p_T = Nk_BT$. The temperature dependence for coefficient $(\Gamma/N)_T$ is the same like in Eq. (10)

$$\left(\frac{\Gamma}{N}\right)_T = \left(\frac{\Gamma}{N}\right)_{T_{\text{ref}}}\frac{1 + g_2(T_{\text{ref}})\frac{T}{T_{\text{ref}}}}{1 + g_2(T_{\text{ref}})}. \tag{13}$$

However, in case of coefficient $(\Gamma/p)_T$ the temperature dependence has a different form

$$\left(\frac{\Gamma}{p}\right)_T = \left(\frac{\Gamma}{p}\right)_{T_{\text{ref}}}\frac{\frac{T_{\text{ref}}}{T} + g_2(T_{\text{ref}})}{1 + g_2(T_{\text{ref}})}. \tag{14}$$