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Power-law temperature dependence of collision broadening and shift of atomic and molecular rovibronic lines

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ABSTRACT

The classical phase-shift theory of spectral line shapes is used to examine various aspects of the applicability of the power-law relations to the description of temperature variations of pressure broadening and shifting coefficients of the isolated atomic and rovibronic molecular lines in a wide temperature range. Model calculations performed for potentials of the Lennard-Jones type indicate that the temperature dependence exponents of the broadening and shifting can be related to the details of the intermolecular interactions. It is shown that they are sensitive to the range of temperatures assumed in the fit and therefore extreme care must be taken when the power-law temperature dependence is used as a scaling law. The problems of the failure of the power-law and of variations in the sign of pressure shift coefficients with increasing temperature are discussed. Very good fits of Frost's empirical formula for temperature dependence of pressure shift to the theoretical ones are obtained.

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1. Introduction

The temperature dependence of parameters describing profiles of pressure broadened lines in molecular spectra has been the topic of a great deal of study in the last decades. Most experiments were performed in the infrared and microwave regions for pure rotational lines and were stimulated by the use of the balloon-borne and ground-based spectrometers to study and monitor the Earth atmosphere [1–6]. The measured line profiles were analysed in terms of Lorentzian shapes characterized by their halfwidths (FWHM) Γ and shifts Δ which were found to be proportional to the gas pressure p, and then the collision broadening $\gamma = \Gamma/p$ and shift $\delta = \Delta/p$ coefficients (expressed in frequency/pressure unit) were determined as functions of temperature T: $\gamma = \gamma(T)$ and $\delta = \delta(T)$ [7,8]. The usual approach is to assume the temperature dependence of the collision broadening coefficient in the form of a power-law:

$$\gamma(T) = \gamma(T_0)\left[\frac{T}{T_0}\right]^n, \tag{1}$$

where T_0 is the reference (e.g. room) temperature. The exponent n is perturber specific and its values – usually determined by linear regression analysis of plots $\log\gamma$ versus $\log T$ – are reported in the literature and included in spectroscopic database (HITRAN'2004 [9], HITRAN'2008 [10]).

It was established long time ago [11–14] that the T^n temperature dependence of γ can be derived from the phase-shift theory of pressure broadening in the impact limit provided the interaction between the radiating and perturbing molecules at the distance R is governed by an inverse power potential $V(R) \propto R^{-m}$. Then one obtains $n = -(m+1)/2(m-1)$. In particular, $n = -7/10$ for $m = 6$ (van der Waals potential), $n = -6/8$ for $m = 5$ (electric quadrupole–electric quadrupole interaction), and $n = -5/6 \approx -0.83$ for $m = 4$ for (electric quadrupole–electric dipole interaction). In many cases, however,

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experimental values of temperature exponents n differ from these theoretical predictions. One of the reasons of these discrepancies may be caused by the fact that the phase shift theory cannot be applied to the case of broadening of pure rotational lines in the infrared or microwave regions, where – as Anderson [15] first showed – inelastic effects play a crucial role in the formation of pressure broadened profiles. To include such effects Robert and Bonamy [16] have developed a semi-classical theory of pressure broadening of molecular lines based on the resolvent operator formalism which in recent years was used as basis for several advanced theoretical studies of temperature dependences of the broadening and shifting of many rotational lines. In particular, Bonamy et al. [17] performed computations of the broadening coefficients for infrared lines of CO perturbed by Ar and discussed some aspects of the power-law dependence. In three very recent papers Gamache et al. [18] and Lamouroux et al. [19,20] reported results of their calculations of pressure broadening and shift coefficients of some rotational lines of CO_2 perturbed by N_2 [18], O_2 and air [20] as well as self-broadened lines of CO_2 [19]. From calculated values they determined on the basis of the power-law relation, Eq. (1), the temperature dependence exponents of the broadening coefficients in several temperature ranges corresponding either to Earth's atmosphere (200–350 K) or to the atmospheres of Mars (125–296 K) and Venus (296–700 K), where the self-broadening of CO_2 lines is important. These calculations and many earlier ones which are reviewed in the monograph by Hartmann et al. [7] show that inelastic effects must be taken into account to obtain reliable theoretical data on collisional broadening and shifting of rotational lines in the infrared and microwave ranges.

The situation looks different, however, in the case of rovibronic lines in the ultraviolet such as those corresponding to the $A \leftarrow X(0,0)$ band at 226 nm in the NO molecule perturbed by Ar and N_2 studied experimentally by Chang et al. [21], the $B \leftarrow X(0,0)$ band near 230 nm in the CO molecule perturbed by N_2, CO_2 and CO studied by Di Rosa and Farrow [22] as well as the $A^2\Sigma^+ \leftarrow X^2\Pi(0,0)$ band at 310 nm of the hydroxyl (OH) radical perturbed by Ar, N_2, H_2O and CO_2 investigated by Rea et al. [23,24] and Hwang et al. [25]. The main result of these studies was that both for the NO and CO as well as for the OH bands the experimental values of $\gamma(T)$ could be fitted well to the power-law, Eq. (1). The values of the temperature exponents n obtained by Chang et al. [21] from the best fits are equal to -0.65 for NO+Ar (in the temperature range between 295 and 2800 K) and -0.75 for NO+N_2 (for the range 295–2700 K). The best fits made for CO by Di Rosa and Farrow [22] yielded (for temperatures between 295 and 1000 K) the following values of n: -0.63 for CO+CO_2, -0.65 for CO+CO, and -0.77 for CO+N_2. For the hydroxyl radical band the experimental values of n reported by Rea et al. (for temperatures between 780 and 2440 K) are -0.92 for OH–Ar, -0.54 for OH–N_2 [23], and -0.66 for OH–H_2O [24], while the values determined by Hwang et al. [25] are -1.0 for OH–Ar, -0.75 for OH–N_2 and -0.87 for OH–H_2O.

A very important result of these experiments is that both for the NO 226 nm band and the CO 230 nm band the pressure broadening coefficients of rovibronic lines do not depend on the rotational quantum number J. These lines correspond to transitions between different electronic states in the molecule. The lack of an observable J-dependence of the pressure broadening coefficients seems to indicate that – in contrast with the infrared and microwave regions – for the ultraviolet bands inelastic events due to rotational energy transfer are of less importance and in the qualitative analysis may be omitted. So, many characteristics of the pressure broadening of rovibronic lines in the NO $A \leftarrow X$, CO $B \leftarrow X$ and OH $A\Sigma \leftarrow X\Pi$ bands bear striking similarities to those of atomic spectral lines for which the phase-shift theories of line broadening due to Lindholm and Foley were originally developed (*cf.* e.g. [12–14]). As noted by Di Rosa and Hanson [26] the fact that for rovibronic transitions the upper and lower states are generally very different causes that their broadening and shift are likely affected by only dispersion when the perturbing particles are neutral and non- or weakly polar. On the grounds of such arguments they and several other researchers [21,22] have adopted the Lindholm–Foley phase-shift theory to interpret the temperature exponents n in the power-law relation, Eq. (1). In their analysis an inverse-power (mostly van der Waals) potential was used, which is, however, completely inadequate for the description of the broadening and shift by perturbers of low polarizability. Such perturbers usually cause a blue line shift, indicating the predominance of a repulsive rather than an attractive part of the interaction potential.

The goal of the present paper is to perform tests of the utility and applicability of the power-law relation, Eq. (1), to the description of the temperature dependence of the pressure broadening coefficients for real physical situations in the framework of the phase-shift Lindholm–Foley theory assuming the difference $\Delta V(R)$ of interaction potentials in the upper and lower electronic states of the absorbing molecule in the form of a Lennard-Jones (12-m) model function:

$$\Delta V(R) = \Delta C_{12} R^{-12} - \Delta C_m R^{-m}, \tag{2}$$

where the term $\propto R^{-12}$ models the repulsion energy. Here ΔC_{12} and ΔC_m denote differences of the force constants for the repulsive and attractive branches of the interaction energy, respectively. Obviously, as an isotropic interaction the Lennard-Jones function cannot account for any orientational effects which may give rise to the dependence of line shape parameters on rotational quantum numbers. Although this function represents rather poor approximation to the real interaction its simplicity enables one to analyse various aspects of the power-law temperature dependence of γ, in particular the variation of the temperature exponent n with the variation of potential parameters as well as with temperature. We are concerned here with isolated spectral lines and transitions are assumed to occur between two adiabatic states and mixing among upper or lower states is ignored. Such an assumption is justified for many atomic lines as well as for some rovibronic lines in the UV region associated with electronic transitions in molecules, but it is not justified for rotational lines in the infrared and microwave regions.

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