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Shape of collision-broadened lines of carbon monoxide

A.F. Seleznev [b], G.V. Fedoseev [a], M.A. Koshelev [a,b], M.Yu. Tretyakov [a,b,*]

[a] Institute of Applied Physics, Russian Academy of Sciences, 46 Ulyanov str., Nizhny Novgorod 603950, Russia
[b] Lobachevsky State University of Nizhni Novgorod, 23 Gagarina pr., Nizhny Novgorod 603950, Russia

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ABSTRACT

We consider lineshape of the rotational spectrum of a CO molecule under the conditions of prevailing collisional broadening. Several series of experimental data obtained at relatively high (up to 1000) signal-to-noise ratio of self-broadening and broadening by noble gases have been analyzed. We used for analysis several well known models beyond the Voigt profile. It is confirmed that the use of the Hartman–Tran profile needs certain requirements in order to obtain meaningful and unambiguous results. A simple numerical simulation is suggested to evaluate the result of the model usage for any particular set of experimental data. Parameters of the collisional line narrowing were obtained. It is shown that under the experimental conditions, deviations of the shape of the observed lines from the Voigt profile are solely due to the wind effect.

1. Introduction

The instruments used for remote sensing of the atmosphere in the millimeter and submillimeter wave range from ground stations, airplanes and satellites allow one to obtain substantial data for weather forecasts and prediction of climate changes. For example, oxygen lines can provide atmospheric temperature profiles. The distribution of air humidity is determined from the lines of water vapor. Observation of the lines of minor gas constituents permits finding, for example, distribution of greenhouse gases, which is an important issue in the context of global warming. Correct interpretation of atmospheric absorption profiles requires accurate laboratory measurements of the corresponding parameters of spectral lines [1].

It is known that in most cases the traditional Voigt model is unable to ensure sufficient accuracy of the description of the absorption lines recorded with high signal-to-noise ratios (several hundreds or more). The actual line is somewhat higher and narrower than the corresponding Voigt profile [2]. Two fundamentally different physical mechanisms affecting the line shape are known, namely, the velocity changing collisions, i.e., collisional narrowing of Doppler broadened lines (Dicke effect) [3] and the speed dependence of the collisional relaxation of absorbing molecules (the so-called “wind” effect) [4]. These two effects occur simultaneously and manifest themselves in very similar ways. Therefore, it is extremely difficult to estimate their individual contribution to the shape of the experimental line, even if the signal-to-noise ratio is high [2].

Corresponding models have been developed to allow for these “subtle” effects. These models were frequently used to approximate experimental lines (see, e.g., Ref. [5] and the references therein). It was stated in several papers (see, e.g., Ref. [6]) that under certain conditions, experimental data can be approximated with the same accuracy by models allowing either for the Dicke effect, or for the wind effect only. At the same time, it was noted that in the majority of cases the models allowing only for the Dicke

* Corresponding author at: Institute of Applied Physics, Russian Academy of Sciences, 46 Ulyanov str., Nizhny Novgorod 603950, Russia.
Tel.: +7 831 4164866; fax: +7 831 4363792.
E-mail address: trt@appl.sci-nnov.ru (M.Yu. Tretyakov).
URL: http://www.mwl.sci-nnov.ru/ (M.Yu. Tretyakov).

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effect fail to reproduce the experimental data corresponding to the prevailing collisional broadening conditions [6,7]. The study of these issues on an example of the OCS spectrum [5] showed that, at least for pure gases of polar molecules and in the pressure range where the collisional broadening is dominant, the observed line shape (excluding some specific cases) is governed by the wind effect.

This paper is aimed at further studying of the collisional narrowing effects. Herein, we discuss the results of fitting the known models (the Galatry profile [8], the quadratic speed-dependent Voigt profile [9], the partially-correlated quadratic-speed-dependent hard-collision profile, also known as the Hartman-Tran profile [10,11]) to the experimental recordings of the CO molecule rotational lines.

The dipole moment of about 0.1 debye, the absence of the superfine structure of the lines, and rather wide intervals between successive lines of the rotational spectrum make the main isotopologue of the carbon monoxide molecule (CO) extremely attractive for laboratory studies [12,13]. Due to the fact that CO is one of the major atmospheric pollutants, which is often related to large emissions of CO_2, its study is important from the viewpoint of the greenhouse effect and global climate issues [14,15]. Moreover, since it is the second most common molecule (after H_2) in the interstellar medium, CO plays an important role in the evolution of molecular gas clouds, where active star formation takes place; therefore, studies of its spectrum are of great importance for astrophysics [16].

The experimental details and features of the measurement method are described briefly in Section 2. In Section 3, the line-shape models are considered. Section 4 presents different aspects of analysis of the obtained data and their comparison with the results of earlier works. The main findings of the study are summarized in the Conclusion.

2. Details of the experiment

The CO spectrum rotational lines ($J=1\leftarrow0$ at 115,271.2018(5)[1] MHz, $2\leftarrow1$ at 230,538.0000(5) MHz, $3\leftarrow2$ at 345,795.9899(5) MHz, $4\leftarrow3$ at 461,040.7682(5) MHz, $5\leftarrow4$ at 576,267.9305(5) MHz and $7\leftarrow6$ at 806,651.806(5) MHz) were studied at room temperature (296–300 K) under self-pressure broadening conditions. Additionally, the $J=2\leftarrow1$ line was studied under the conditions of broadening by pressure of noble gases, specifically, xenon (Xe), krypton (Kr), and neon (Ne).

The experimental recordings of absorption lines were obtained by using a backward-wave oscillator (BWO) based spectrometer with radio acoustic detection of absorption (RAD spectrometer). The principle of the spectrometer operation and its features are described in detail in Refs. [18,19]. Continuous-wave coherent radiation is produced by a BWO. The BWO radiation frequency is stabilized and controlled by a phase-lock-loop system with reference to the harmonic of a microwave synthesizer. To increase the stability and accuracy of frequency setting, the synthesizer is synchronized with a rubidium clock. The use of a highly stable, digitally tunable radiation source, as well as synchronous detection of the amplitude-modulated absorption signal allows efficient averaging of the useful signal and recording of the absorption profiles with the signal-to-noise ratio sufficient for the precise line-shape analysis.

Details of spectra recordings, preparation of gas mixtures, and detailed description of the data processing method can be found in Ref. [5] and the references therein. The experimental conditions are specified in Table 1. The experimentally obtained profiles were analyzed by means of varying parameters of the model functions with the use of minimization methods and the discrete Fourier transform. Both common procedures, namely the one-by-one spectrum analysis and the multi-spectrum fitting were used to retrieve line-shape parameters. The maximum optical thickness of the sample was 0.041. Nevertheless, its influence on the line shape was noticeable, hence, the Beer–Lambert law was taken into account.

3. Line-shape models

It is well known that the Voigt profile (VP) is a convolution of the Lorentz profile (LP) related to collisions of molecules and the Gauss profile related to the Doppler effect which results from motion of molecules. The half-width of the Lorentz profile determines the rate Γ of collisional relaxation, which characterizes the coherence decay time $\tau=1/\Gamma$ in the considered ensemble of molecules. The wind effect is, basically, the dependence of the collisional relaxation on the absolute speed of the active (radiation-absorbing) molecule. Several models were proposed to allow for this fundamental effect, which received the common name of “the speed dependent Voigt model (SDV)”.

In this work, we used the quadratic Speed-Dependent Voigt Profile (qSDVP) model [9], where the dependence of the collisional relaxation on the velocity of the absorbing molecule is approximated by

$$\Gamma(V_a)=\Gamma_0+\Gamma_2\left[\left(\frac{V_a}{V_{a0}}\right)^2-\frac{3}{2}\right]. \quad (1)$$

Here V_{a0} is the most probable speed of the absorbing molecules, and Γ_2 is the parameter responsible for the speed dependence of the collisional relaxation. The shape of the line is calculated as the Fourier transform of the polarization correlation function, where Γ_0 and Γ_2 enter as adjustable parameters [5,9]. The qSDVP model can be used relatively easily for fitting to the experimental recordings of the lines. Moreover, the parameter Γ_2 should increase linearly with increasing gas pressure, which allows one to test the obtained values easily.

The Dicke effect is based on the fact that the intermolecular collisions, which do not affect the internal state of the active molecule, lead to velocity changes. The corresponding confinement of the diffusion process results in reduction of the Doppler width of the line. The effect is usually described by the Galatry profile [8] or by the Rautian profile [23].

[1] Measured line frequencies from Ref. [17] are given.