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Speed-dependent effects and Dicke narrowing in nitrogen-broadened oxygen

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ABSTRACT

We present the line-shape analysis of the nitrogen-broadened P9 P9 oxygen *B*-band transition measured by the optical frequency comb-assisted Pound–Drever–Hall-locked frequency-stabilized cavity ring-down spectrometer. Perturbation by both oxygen and nitrogen molecules is taken into account simultaneously in the line-shape analysis. Several line-shape models describing physical effects such as Dicke narrowing, the speed dependence of collisional broadening and shifting, and the correlation between velocity- and phase-changing collisions were used in the analysis. The comparison between the hypergeometric and quadratic approximations of the speed-dependent effects is presented. Observed line narrowing is mostly determined by the speed dependence of the collisional broadening.

1. Introduction

The oxygen *B* band [$b^1\Sigma_g^+(v=1) \leftarrow X^3\Sigma_g^-(v=0)$] occurring near 689 nm is nowadays very important in the atmospheric research [1]. Due to uniform and relatively constant mixing ratio of O_2 in the atmosphere the *B*-band lines are used to reduce errors due to air-mass uncertainties in simultaneous measurements of oxygen and other gases of scientific interest, particularly green house gases. The determination of pressure and temperature profiles of atmosphere based on the data from ACE-MAESTRO instrument on SCISAT satellite also uses the *B*-band lines [2]. The chlorophyll fluorescence emission peaks near 683 nm, very close to the O_2 *B* band. Therefore, satellite measurements of the fluorescence induced by sunlight provide important information about the vegetation status [3]. Another application of the oxygen *B* band is determination of cloud-top height and cloud coverage [4,5].

The experimental investigations of the O_2 *B*-band lines were performed by only a few groups [6–14]. The spectral line shapes obtained by them were mostly analyzed with the use of the Voigt profile and their results differed by even a few tens of percent. This implies a need for systematic high-resolution, high-accuracy measurements of line positions and pressure shifts [1] as well as intensities and widths [15] of the oxygen *B*-band lines. In a series of our earlier papers [16–22] the precise line-shape study of the self-broadened *B*-band transitions was presented. However, there is still a need for precise data for the oxygen *B*-band lines perturbed by foreign gases such as nitrogen and argon, other main constituents of air. In this paper we present the line-shape analysis of one of the oxygen *B*-band transitions perturbed by N_2.

The experimental setup dedicated to such study requires high sensitivity and high spectral resolution, as well as the absence of the instrumental errors. Here we use the optical

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frequency comb-assisted Pound–Drever–Hall-locked frequency-stabilized cavity ring-down spectrometer [23]. High sensitivity is a key feature of the cavity ring-down spectroscopy (CRDS) technique which was considered as an ideal tool to provide reference data for the satellite based monitoring systems [24]. Moreover, in our case the spectrometer sensitivity is increased by the use of the Pound–Drever–Hall (PDH) laser frequency stabilization technique [25,26]. High precision of the frequency axis is possible thanks to an active cavity length stabilization to the reference laser [27–29] and link to the optical frequency comb provides the absolute frequency axis of the recorded spectra [19–22]. Moreover, this system is practically free from the detection system nonlinearity [17].

The retrieval of the precise line-shape data requires also the knowledge of the proper line-shape profile. Commonly used Voigt profile is not sufficient to describe measured line shapes. Other effects such as Dicke narrowing [30], the speed dependence of collisional broadening and shifting [31], and the correlation between the velocity- and phase-changing collisions [32] should be taken into account. All of these effects are included in the partially correlated speed-dependent asymmetric Rautian–Sobelman profile (pCSDARSP) [33–36] in which the velocity changing collisions can be described within soft- [37] and hard-collision [38] model. This profile has several useful properties: analytical form, flexibility, simplification to many used models, availability of experimental data analyzed with this profile, and its applicability with the multispectrum fitting technique [39,40]. Therefore, pCSDARSP was proposed as a good candidate for implementation in future spectroscopic databases [23,41]. Its simplification limited to the hard-collision model, the partially correlated speed-dependent Nelkin–Ghatak profile (pCSDNGP) [42], with the quadratic speed dependence [43] was recently proposed [44] to use in the new generation of spectroscopic databases instead of the Voigt profile, and was recommended by IUPAC [45]. The main advantage of the quadratic pCSDNGP, called in Ref. [45] as Hartmann–Tran profile (HTP), is an efficient algorithm of its evaluation by calculation of simple combination of ordinary Voigt profiles [44].

In case of the quadratic speed dependence model a mixture of various perturbing gases can be treated as a single perturbing gas and its effective line-shape parameters can be calculated from parameters of its components [44,46]. However, in general case the speed-dependent collisional broadening and shifting must be treated separately for each perturber. In the present study such individual treatment of perturbers is applied for line profiles using the hypergeometric speed dependence model [47].

2. Experimental setup

The spectra were acquired using the optical frequency comb-assisted Pound–Drever–Hall-locked frequency-stabilized cavity ring-down spectrometer (OFC-assisted PDH-locked FS-CRDS) [23]. The detailed description of an active cavity length stabilization to the reference HeNe laser used in the FS-CRDS spectrometer can be found in Refs. [27–29]. Implementation of the PDH laser frequency stabilization technique to the FS-CRDS setup was presented in Refs. [23,26,48]. The absolute frequency of the probe laser (ECDL, external cavity diode laser) is measured at each point of the spectrum by the use of the optical frequency comb [20,23]. Recent developments in the OFC-assisted part of the system were described in Ref. [21]. The preparation of a sample of O_2–N_2 gas mixture was made in a vacuum chamber equipped with a fan to assure uniform mixing. We used high-purity oxygen (purity of 99.999%) and nitrogen (99.9996%) with natural isotopic abundance.

3. Line-shape models

In our analysis we used several line-shape profiles being limiting cases of pCSDARSP. The simplest one was the commonly used Voigt profile (VP) which takes into account the Doppler broadening and the collisional broadening and shifting. However, it is well known that the VP cannot reproduce the experimental spectra with the precision better than a few percent. Therefore, other physical effects affecting the line shape have to be taken into account.

It was shown by Dicke [30] that the velocity-changing collisions lead to the collisional (Dicke) narrowing of the line. The description of this effect usually uses two simplest models. The soft-collision approximation is included in the Galatry profile (GP) [37], while the hard-collision approximation is taken into account in the Nelkin–Ghatak profile (NGP) [38,32], which is also called the Rautian profile or simply hard-collision profile.

Another effect, elaborated by Berman [31], is the speed dependence of collisional broadening and shifting which is taken into account in the speed-dependent Voigt profile (SDVP). In order to describe the speed-dependent effects it is useful to introduce the reduced collisional width and shift functions $B_W(x)$ and $B_S(x)$ [47,33] dependent on the reduced absorber velocity $x = v_A/v_{m_A}$:

$$B_W(x) = \frac{\gamma_L(xv_{m_A})}{\gamma_L}, \tag{1}$$

$$B_S(x) = \frac{\delta(xv_{m_A})}{\delta}. \tag{2}$$

Here $\gamma_L(v_A)$ is the speed-dependent full width at half maximum (FWHM) collisional width and $\delta(v_A)$ is the speed-dependent collisional shift, while $\gamma_L = \int \mathrm{d}^3 v_A f_{m_A}(\vec{v}_A)\gamma_L(v_A)$ and $\delta = \int \mathrm{d}^3 v_A f_{m_A}(\vec{v}_A)\delta(v_A)$ are the collisional width and shift, respectively, thermally averaged over the Maxwellian distribution of the absorber velocity $\vec{v}_A$:

$$f_{m_A}(\vec{v}_A) = \left(\frac{1}{\pi v_{m_A}}\right)^{3/2} \exp\left(-\frac{v_A^2}{v_{m_A}^2}\right). \tag{3}$$

Here $v_{m_A} = \sqrt{2k_BT/m_A}$ is the most probable absorber speed, m_A is the absorber mass, T is the gas temperature, and k_B is the Boltzmann constant. In case when the absorber–perturber interaction at distance r is described by inverse-power potential $V(r) \sim r^{-q}$ the speed dependence of collisional broadening and shifting can be described by the hypergeometric function [47]. However, in molecular systems the speed-dependent functions $B_W(x)$ and $B_S(x)$ should be different as was shown by