Journal of Quantitative Spectroscopy & Radiative Transfer 219 (2018) 379–382

Contents lists available at ScienceDirect

Journal of Quantitative Spectroscopy & Radiative Transfer

journal homepage: www.elsevier.com/locate/jqsrt

Measurements of the broadening and shift parameters of the carbon monoxide spectral lines in the 1–0 band induced by pressure of carbon dioxide

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ARTICLE INFO

Article history:
Received 25 June 2018
Revised 30 August 2018
Accepted 30 August 2018
Available online 31 August 2018

Keywords:
Fourier spectroscopy
Carbon monoxide
CO_2 pressure broadening
Non-Voigt profile

ABSTRACT

The absorption spectra of a mixture of CO with CO_2 at different partial pressures of CO_2 have been recorded at room temperature in the 2000–2300 cm^{-1} region using a Bruker IFS 125 HR FTIR spectrometer. To obtain the spectral line parameters for the fundamental band of CO molecule, the quadratic speed-dependent Voigt profile was used for the first time. The CO_2 pressure induced broadening and shift coefficients for 49 spectral lines have been measured. A comparison with the published data is discussed.

1. Introduction

Discovery of carbon monoxide in Martian and Venusians atmospheres is dated to 1968–1969 [1,2]. To date, numerous measurements of CO concentration have been carried out on Mars (Ref. [3] and references therein) and Venus (Ref. [4] and references therein). However, there are significant quantitative differences in the data from different teams and instruments. At the same time, there still exist a problem of consistency between the observed concentrations of carbon monoxide and the concentrations predicted by photochemical models [5,6]. To determine the concentration profiles of CO in Martian and Venusians atmospheres, the accurate values of the CO line parameters including the CO_2 broadening and shift coefficients are needed. Moreover, the Voigt profile is no longer sufficient and more accurate models of the line profiles are required to fit the spectrum down to the noise level.

Experimental laboratory studies of the CO_2-broadening and shift coefficients of CO molecule were carried out both for the fundamental band and for the overtones [7–14]. While a sufficient accuracy was attained for the first overtone taking into account the Dicke narrowing or speed dependence [14], the line shape for the fundamental band was modeled with simple Voigt profile. It should be noted that in the most recent paper devoted to the fundamental band [13] the signal-to-noise ratio was only 150 that did not allow achieving high accuracy of the line parameters measurements.

The present paper is just devoted to the experimental determination of CO_2-broadening and shift line parameters in the fundamental band of the CO molecule. In total, the parameters of 49 lines were measured up to $J''_{max} = 26$ for the quadratic speed-dependent Voigt (hereinafter qSDV) profile [15].

2. Experiment

The measurements of the CO absorption spectra in the presence of CO_2 as a buffer gas were performed using high-resolution Fourier transform Bruker IFS 125 HR spectrometer (V.E. Zuev Institute of Atmospheric Optics SB RAS) in the 2000–2300 cm^{-1} spectral region. The experimental setup was described in detail in Ref [16]. and only a brief summary is given here. The spectrometer was equipped with a CaF_2 beam splitter, an InSb detector, and a globar as a light source. The absorption cell (7 cm length) with BaF_2 windows was used for the measurements. The temperatures, $CO–CO_2$ mixture and CO pressures are listed in Table 1. A sam-

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https://doi.org/10.1016/j.jqsrt.2018.08.031
0022-4073/

Table 1
Experimental conditions.

Spectrum number	Resolution (cm^{-1})	Partial pressure of CO (mbar)	Partial pressure of CO_2 (mbar)	Temperature °C
1	0.007	0.97	156	25.1
2	0.01	2.01	295	25.3
3	0.01	3.05	461	25.0
4	0.01	4.04	605	25.3

ple of natural carbon monoxide with a stated purity of 99.9% was used without further purification. The pressure of carbon monoxide ranged from 0.97 mbar to 4.04 mbar was measured with a Baratron gauge (100 mbar full scale) with an estimated uncertainty of 0.25%. The pressure of the CO–CO_2 mixture ranged from 156 mbar to 605 mbar was measured with a DVR-5 capacitance manometer (1100 mbar full scale) with an estimated uncertainty of 0.5%. In this pressure range, four absorption spectra of the CO–CO_2 mixture were measured. All absorption spectra were recorded at the near-room temperature. The unapodized spectral resolution R ($R = 0.9/L_{max}$, L_{max} – maximum optical path difference) varied from 0.007 to 0.01 cm^{-1}. The signal-to-noise ratio (expressed as the maximum signal amplitude divided by the RMS noise amplitude) was calculated using the standard procedure of the OPUS 6.5 software. The average value of the RMS noise amplitude in the spectral region under study was about 0.00015, giving a signal-to-noise ratio (SNR) of 6000 at absorbance of around 1. It was achieved by co-addition of 1500 interferograms.

2.1. Retrieval of the spectral line parameters

In the present work, the spectral line parameters were retrieved using the quadratic speed-dependent Voigt profile. For these purposes, the nonlinear least-squares method was applied to each spectrum recorded under different experimental conditions to retrieve line positions and line broadening parameters. This procedure was implemented in the computer code that determined the line parameters by adjustment of the synthetic spectra to the observed ones [17]. It was impossible to use multi-spectrum functionality in the code because of very weak and narrow lines with Doppler line width of CO and H_2O molecules presented in the volume of the interferometer. A subroutine to compute the complex normalized spectral shape of an isolated line by the qSDV model was taken from Ref. [18]. The calculated value for the Doppler line width was used. The adjustable parameters for each spectra included the position, intensity, CO_2- and self- broadening coefficients for each line. The line width was calculated using the following equations:

$$\gamma = \gamma^{CO} * P_{CO} + \gamma^{CO2} * P_{CO2}, \quad (1)$$

$$\gamma_2 = \gamma_2{}^{CO} * P_{CO} + \gamma_2{}^{CO2} * P_{CO2}, \quad (2)$$

where γ, γ_2 are the half-width of the line and the speed-dependence parameter of the half-width in cm^{-1}; γ^{CO}, $\gamma_2{}^{CO}$ are, respectively, the self-broadening coefficient and the speed-dependence parameter of the self-broadening coefficients in cm^{-1} atm^{-1}; γ^{CO2}, $\gamma_2{}^{CO2}$ are, respectively, the CO_2 pressure broadening coefficient and the speed-dependence parameter of the CO_2 pressure broadening coefficient in cm^{-1} atm^{-1}; P_{CO} and P_{CO2} are the partial pressures of carbon monoxide and CO_2 in atm. As pressures of CO for all four spectra were about ~0.5% of the total pressure, the effect of self-broadening on the line width and the effect of self-shift on the line shift were small. That is why we fixed the values of the self-broadening coefficients γ^{CO} for all lines to the HITRAN-2004 [19] values. These values were not changed in all newer versions of the HITRAN database. The values of $\gamma_2{}^{CO}$ were fixed to zero. Further, the line shift coefficients δ^{CO2} were determined by linear approximation of the pressure dependence of the line positions ν under the assumption that the line shift caused by the self-pressure of CO was negligibly small:

$$\nu = \nu_0 + \delta^{CO2} * P_{CO2}, \quad (3)$$

where ν_0 are vacuum wavenumbers. The values of the broadening coefficient were calculated as a mean value of the four quantities.

A comparison of the experimental and calculated line profiles for the R9 line of the 1–0 band of the CO molecule is shown in Fig. 1. The lower panel shows the residuals between the experimental and calculated spectra for the qSDV profile. One can see that the use of the speed-dependent Voigt profile has made possible the simultaneous simulation of the four experimental spectra

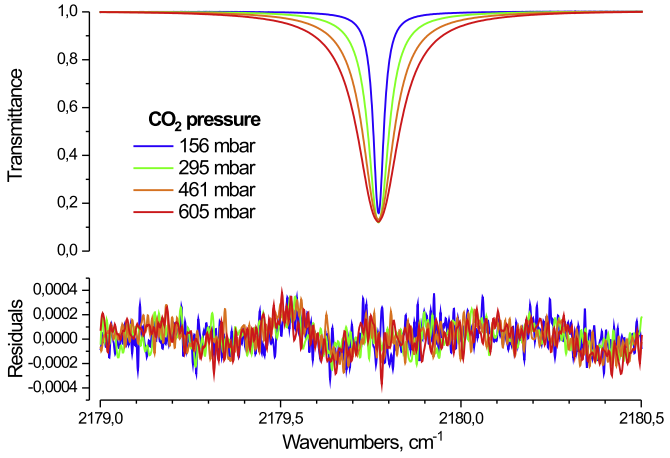

Fig. 1. Example of the experimental spectra (upper panel) and the residuals between the experimental and calculated spectra for the qSDV profile (lower panels) for the R9 line of the 1–0 band of CO molecule.

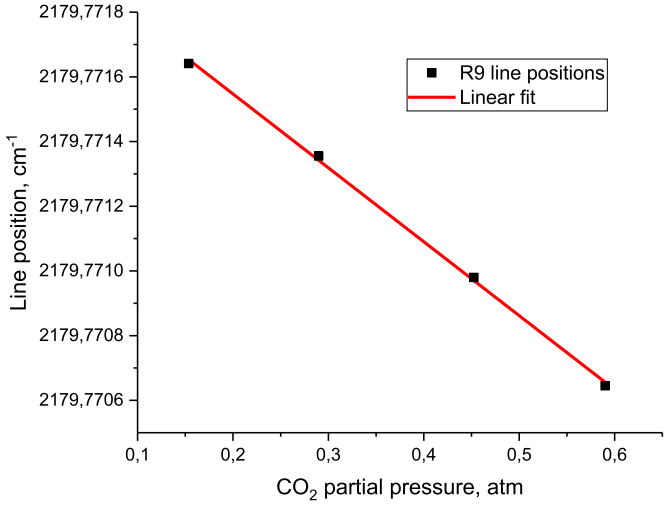

Fig. 2. Dependence of the R9 line position on the partial pressure of CO_2 in the 1–0 band of the CO molecule.