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Measurements of the CO_2 line parameters in the 10000–10300 cm^{-1} region

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ABSTRACT

The absorption spectra of carbon dioxide have been recorded in the near infrared region from 10,000 to 10,300 cm^{-1}, using the Bruker IFS 125 HR Fourier transform spectrometer and a 30 m multipass cell with the White type optical system. The spectra were recorded at a spectral resolution of 0.03 cm^{-1}, room temperature, a path length of 953.6 m and at two pressures of 294 and 523 mbar. The achieved sensitivity (noise equivalent absorption) at the level of $k_\nu = 1.38 \times 10^{-10}$ cm^{-1} allowed detection of a number of new transitions with the intensity values down to 10^{-29} cm/molecule at 296 K. Two bands 60014-00001 and 60015-00001 of $^{12}C^{16}O_2$ were detected for the first time. The line positions and intensities of these bands were determined using the Voigt profile as a line shape. The uncertainty of the line position determination was estimated to be about 0.003 cm^{-1} for the unblended lines with a high value of the signal-to-noise ratio. The uncertainty of the line intensity determination varies from 4% to 40% depending on the strength of the line and the extent of the line overlapping. The measured line intensities of the 60014-00001 and 60015-00001 bands together with those published earlier for the $\Delta P = 15$ series of transitions were used to fit the effective dipole moment parameters of this series. Here $P = 2V_1 + V_2 + 3V_3$ is the polyad number (V_i ($i = 1,2,3$) are the harmonic oscillators quantum numbers). The fitted parameters reproduce the measured line intensities within their experimental uncertainties. Using the effective Hamiltonian parameters published earlier and the fitted effective dipole moment parameters the line positions and intensities of the 6001i-00001 ($i = 1,2,3,4,5,6,7$) bands have been calculated. A comparison of the measured line positions and intensities to those contained in the new version (huang.seti.org) AMES line list as well as in the High-T line list are given.

1. Introduction

The Venus nightside transparency window at 1 μm could be used for the studies of the composition and physical properties of the atmosphere below the Venus clouds (25–45 km) [1,2]. This region could also be used for the study of the Martian atmosphere. There are two spectrometers operating in the 1 μm region on board ExoMars Trace Gas Orbiter [3]. The first one is a Fourier transform spectrometer situated in the NOMAD site [4]. The second one is an echelle spectrometer situated in the ACS site [5]. These spectrometers are aimed at measurements of the H_2O, O_2, OH and NO atmospheric constituents [6]. For the above mentioned investigations it is necessary to know the laboratory absorption spectrum of carbon dioxide in this region. To our knowledge there is no laboratory measurement of the carbon dioxide spectrum at 1 μm published in the literature. The HITRAN2012 [7], HITEMP [8], GEISA [9] and CDSD [10–12] databases do not contain the spectral line parameters in the 9718–11156 cm^{-1} region. Only the calculated line parameters of CO_2 can be found for this region in the "High-T" database [13] and in the AMES line list [14]. The aim of this paper is to measure the carbon dioxide line parameters at 1 μm for the extension of the CDSD database and for the validation of the "High-T" database [13] and of the AMES line list [14].

This paper is organized as follows. After description of the experimental details (Section 2), the rovibrational assignment, retrieval of the spectral line parameters and the comparison with the effective Hamiltonian (EH) predictions are presented in Section 3. Section 4 is devoted to the line intensity fit of the line intensities measured in this paper together with those published earlier for the $\Delta P = 15$ series of transitions. In Section 5, we compare our results with the variational calculations [13,14].

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2. Experimental details

The absorption spectra of the natural carbon dioxide have been recorded using the spectrophotometric complex based on a Bruker IFS 125 HR Fourier transform spectrometer and a 30 m base length multipass cell of the V.E. Zuev Institute of Atmospheric Optics (Tomsk). The cell is equipped with the modified White type three mirrors optical system. In comparison to our previous measurements [15] in this study we used mirrors covered with silver which have the value of the reflectance coefficient of approximately 98% in the visible and near IR regions. The constructed system of matching the Fourier spectrometer and the cell allowed us to effectuate 34 passes of a ray inside the cell, which gives a path length of 952.1 m at a basic distance between the mirrors of 28.005 m and an additional path of 1.56 m between the front mirror of the cell and the input/output cell windows. This path length was gained with utilization of a halogen lamp of 50 W as a light source and a diaphragm of 1.5 mm. A more detailed description of the spectrophotometric complex is given in Ref.[16].

Before the measurements the cell was pumped out to a pressure of 80 mbar using a rotary water ring pump, and then with three vacuum pumps it was pumped out to a pressure of 5×10^{-3} mbar. To avoid the pressure and temperature instability inside the large volume of the cell we filled it with CO_2 slowly for 2 hours and experiments were conducted 3 hours after the filling. The spectra were recorded in the spectral region from 10,000 to 10,300 cm^{-1} with an unapodized resolution 0.03 cm^{-1} at room temperature (during the measurements the temperature varied from 294 K to 295 K) using CO_2 natural sample of 99.9% purity. The Si detector was used to record the absorption spectra in this spectral region. The pressure of CO_2 was measured with a DVR-5 capacitance manometer (1100 mbar full scale), which has a stated uncertainty of ± 1 mbar according to the manufacturer. The absorption spectra of CO_2 have been recorded at 294 and 523 mbar. The temperature was measured by three thermocouples installed on the body of the cell. The minimal detectable absorption coefficient K_ν was 1.38×10^{-10} cm^{-1} as it is illustrated in Fig. 1. It was achieved by coaddition of 5000 interferograms and using a filter during the measurements.

For the spectra calibration we used the lines of the water vapor present in the cell as an impurity. The estimated values of the partial pressures of the water vapor were 0.2 and 0.4 mbar in the cases of the total pressures of 254 and 523 mbar, respectively. The positions of seven isolated lines of the $\nu_1+2\nu_2+\nu_3$ water band were taken from HITRAN2012 database [7]. The centers of these lines were determined for both pressures of 254 and 523 mbar. Then using the pressure shift coefficients determined in Ref.[17] we have found the positions of these lines corresponding to zero pressure. Comparing the determined positions to those published [7] we found the average calibration shift. The estimated accuracy of the calibration was about 0.002 cm^{-1}.

3. Rovibrational assignment and retrieval of the spectral line parameters

The assignment of the CO_2 lines was straightforward on the basis of the prediction with the effective Hamiltonian published in Ref.[18]. The spectral line parameters of the 60015-00001 band covering the 10012–10081 cm^{-1} spectral region were retrieved using the multispectrum fitting procedure [19], in which a nonlinear least-squares method is applied simultaneously to the spectra recorded at two pressures of 294 and 523 mbar. Within this procedure the computer code determines the line parameters by adjustment of the synthetic spectra to the observed ones. The adjustable parameters included the position, intensity, self-broadening and self pressure induced shift coefficients of each line and the background which was assumed to be constant. The 10171–10213 cm^{-1} spectral region is crowded by the lines of the water vapor which is present in the gas sample as an impurity. We managed to assign only 12 lines of the 60014-00001 band in this region. Two of them are presented in the insert of Fig. 2. Because of the blending of these lines with the considerably stronger lines of the water vapor (whose partial pressure was unknown) the multispectrum fit in this case was impossible. The line parameters (except the self pressure induced shift coefficients) were retrieved for each pressure independently. As a result, we present the mean values of the spectral line parameters for the 60014-00001 band. The spectral line shape was modeled with the Voigt profile in which the calculated value for the Doppler line width was used. The apparatus function was modeled by the sinc function with the iris radius of 0.75 mm. No adjustment of the iris radius was done. In Fig. 3, as an example we present the observed and simulated profiles of the R12 line of the 60014-00001 band. The residuals are also presented in this figure.

The uncertainty of the determined positions of the unblended lines with rather large values of the signal-to-noise ratio is estimated to be about 0.003 cm^{-1}. The uncertainty of the line intensity determination for the 60015-00001 band varies from 4% for the strong unblended lines to 11% for the very weak or blended lines. For the 60014-00001 band the uncertainties of the line intensity determination are larger. Their values are between 5% and 40%. The principal contribution to the line intensity uncertainties

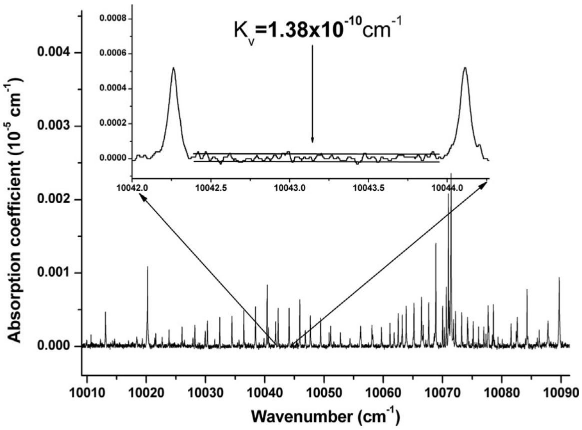

Fig. 1. Survey spectrum of CO_2 in the 10010–10090 cm^{-1} region: P=294 mbar, L=953.6 m, T=294 K. The insert demonstrates the sensitivity of the setup.

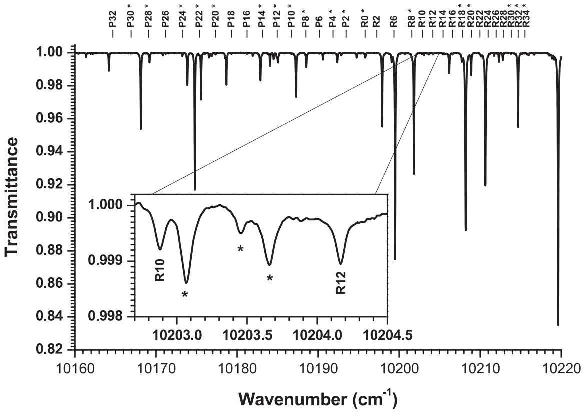

Fig. 2. Fourier transform spectrum of the carbon dioxide sample in the 10160–10220 cm^{-1} region (P= 294 mbar, L=953.6 m, T=294 K). All strong lines belong to the water vapor. The insert shows R10 and R12 lines of the 60014-00001 band of $^{12}C^{16}O_2$. The water lines in the insert are marked with the asterisks.

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