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Assignment and rotational analysis of new absorption bands of carbon dioxide isotopologues in Venus spectra

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ABSTRACT

We present absorption bands of carbon dioxide isotopologues, detected by the Solar Occultation for the Infrared Range (SOIR) instrument on board the Venus Express Satellite. The SOIR instrument combines an echelle spectrometer and an Acousto-Optical Tunable Filter (AOTF) for order selection. It performs solar occultation measurements in the Venus atmosphere in the IR region (2.2–4.3 μm), at a resolution of 0.12–0.18 cm^{-1}. The wavelength range probed by SOIR allows a detailed chemical inventory of the Venus atmosphere above the cloud layer (65–150 km) to be made with emphasis on the vertical distributions of gases. Thanks to the SOIR spectral resolution, a new CO_2 absorption band was identified: the 21101–01101 band of $^{16}O^{12}C^{18}O$ with R branch up to $J=31$. Two other previously reported bands were observed dispelling any doubts about their identifications: the 20001–00001 band of $^{16}O^{13}C^{18}O$ [Villanueva G, et al. J Quant Spectrosc Radiat Transfer 2008;109:883–894] and the 01111–00001 band of $^{16}O^{12}C^{18}O$ [Villanueva G, et al. J Quant Spectrosc Radiat Transfer 2008;109:883–894 and Wilquet V, et al. J Quant Spectrosc Radiat Transfer 2008;109:895–905]. These bands were analyzed, and spectroscopic constants characterizing them were obtained. The rotational assignment of the 20001–00001 band was corrected. The present measurements are compared with data available in the HITRAN database.

1. Introduction

Interest in the composition of the Venus atmosphere began as early as Lomonosov's report [1], from the observations of the 1671 transit, that Venus had an atmosphere and the later discovery by Adams and Dunham [2] that its main constituent was carbon dioxide (CO_2). Venus has an atmosphere very different from that of the Earth: it is much denser, heavier, and extends to a much higher altitude. Despite the harsh conditions on Venus' surface, the atmospheric pressures and temperatures at ∼50–65 km levels in Earth and Venus are comparable. Measurements of the chemical and isotopic composition of the Venus atmosphere provide essential boundary conditions for theories and models describing the formation of the planet Venus and the origin and evolution of its atmosphere.

The SOIR (Solar Occultation in the IR) spectrometer is an extension mounted on top of the SPICAV instrument [3], one of the seven instruments on board Venus Express,

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a planetary mission of the European Space Agency (ESA) launched in November 2005 and inserted into orbit around Venus in April 2006 [4]. SOIR [5] was developed at IASB/BIRA, which is also responsible for planning its operations and for the scientific interpretation of its observations. It is designed to measure the atmospheric transmission in the IR (2.2–4.3 μm) at high resolution (around 0.15 cm^{-1}) using the solar occultation technique. This technique [6] allows the derivation of unique information about the vertical structure and composition of the Venus mesosphere to be made. SOIR is the first high-resolution mid-IR spectrometer onboard a spacecraft investigating the Venus atmosphere. The wavelength range probed by SOIR enables a sensitive search for any minor molecular species from the top of the clouds up to an altitude of about 175 km to be carried out, and leads to detailed information on the vertical composition and structure of the Venus atmosphere above the clouds.

As, for example, shown by the work of Mandin [7], special emphasis can be placed on the detection of new bands of CO_2 and its isotopologues which cannot be observed on Earth or in the laboratory because of their weak intensity, but are seen in Venus spectra because CO_2 is present in large quantities and because of the optical path length. Recently, a new band of isotopic CO_2 near 3.3 μm was identified from SOIR measurements of the Venus atmosphere [8] and Earth based measurements of Mars [9]. This raised the possibility to observe other new isotopic CO_2 bands in the wavelength range of the SOIR instrument and a systematic search for such bands was therefore initiated.

In this work (TW) we report the observation of a new band centered at 2791.53 cm^{-1}, assigned as the 21101–01101 band of $^{16}O^{12}C^{18}O$. Two other bands, namely, the 20001–00001 band of $^{16}O^{13}C^{18}O$ centered at 2701.95 cm^{-1} and the 01111 − 00001 band of $^{16}O^{12}C^{18}O$ centered at 2982.12 cm^{-1}, were already reported in [8] and [9], respectively. The rotational structure of the 20001–00001 band was observed by Villanueva et al. [10], who assigned the observed lines as P23–P3. In the CDSD-296 databank [11], these lines are assigned as R4–R24: this latter assignment is used in the present work. For the 01111–00001 band, we analyzed an extended set of observed line positions.

Note that the usual vibrational notation for carbon dioxide is used throughout the paper, namely v_1, v_2, l_2, v_3, r. v_1, v_2, v_3 are the quantum numbers associated with the three modes of vibration (v_1 is the symmetric stretch, v_2 is the bending mode and v_3 is the antisymmetric stretch mode), l_2 is the quantum number associated with the angular momentum induced by the doubly degenerate bending mode v_2, and can take the value v_2, v_2–2, v_2–4,… The last label, r, is a ranking index, which numbers the different states of a Fermi polyad $2v_1+v_2=const$ in descending energy order. The index r runs from 1 to v_1+1 [12].

2. Measurements

The instrument [3,5] and its in-flight performance [13], including data handling, onboard background subtraction, calibrations of the AOTF and the echelle spectrometer, have already been extensively described, whereas the retrieval technique and some results are discussed in the papers by Vandaele et al. [6] and Mahieux et al. [14,15]. SOIR is an echelle grating spectrometer operating in the IR, combined with an AOTF for the selection of the diffraction grating orders. The SOIR detector has 320 columns of pixels along the wavenumber axis and 256 rows along the spatial axis. To avoid saturation, short integration times are used (20–30 ms), depending on the wavelength at which the measurement is taken. The background signal is measured and subtracted onboard. In order to improve the signal-to-noise ratio (SNR), a number of measurements can be accumulated as long as the total measuring time remains below 250 ms. Due to telemetry limitations, only 8 spectra, each 320 pixels long, can be downloaded per second. During the observation periods (i.e. per orbit), these 8 spectra are taken in four different diffraction orders (4 different radio-frequencies applied to the AOTF), each corresponding to two large bins of 16 or 12 rows on the detector.

The instrument features lead to a division of the investigated spectral range (2256–4369 cm^{-1}) into 94 small wavenumber domains, called diffraction orders. The computed wavenumber interval (cm^{-1}) associated with the detector pixels 0 and 319 for echelle orders 101 to 194 can be found in the literature [5].

In solar occultation mode as performed by SOIR, transmittance spectra are obtained by division of all the spectra recorded during an occultation with a reference spectrum obtained when the light path does not intercept the atmosphere (beginning of sunset or end of sunrise observations). As the light beam probes deeper layers in the atmosphere, two processes reducing the transmittance take place: extinction by aerosols and absorption by trace gases. In general, spectra containing useful information on the Venus atmosphere correspond to tangent heights between 65 km (slightly above the top of the cloud layer) and 175 km.

The three bands analyzed in this paper are observed in the grating diffraction orders 120–121, 124–125 and 131–134. These grating orders correspond to the spectral ranges 2680–2725 cm^{-1}, 2770–2815 cm^{-1} and 2930–3015 cm^{-1}, respectively.

3. Spectral analysis

As the three regions of interest have been recorded many times since the instrument began operations around Venus, we selected a number of spectra for each order to determine the line positions. We chose spectra with good SNR, not affected by saturation and for which the calibration procedure was successful. The SNR has been calculated for all recorded spectra during in-flight calibrations, using the "full Sun spectra" [13].

Considering that the SOIR instrument scans the Venus atmosphere from its top to the top of the Venusian clouds, a selection has to be made in terms of altitudes as well. Specifically, the lower boundary of the considered altitude range was taken to be the altitude at which the atmospheric absorption lines had transmittances reaching zero at their center, before convolution with the instrument resolution function (saturation criterion [14]).