

# First observation of 628 CO<sub>2</sub> isotopologue band at 3.3 μm in the atmosphere of Venus by solar occultation from Venus Express

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## Abstract

The new ESA Venus Express orbiter is the first mission applying the probing technique of solar and stellar occultation to the atmosphere of Venus, with the SPICAV/SOIR instrument. SOIR is a new type of spectrometer used for solar occultations in the range 2.2–4.3 μm. Thanks to a high spectral resolving power  $R \sim 15,000$ – $20,000$  (unprecedented in planetary space exploration), a new gaseous absorption band was soon detected in the atmospheric transmission spectra around  $2982 \text{ cm}^{-1}$ , showing a structure resembling an unresolved Q branch and a number of isolated lines with a regular wave number pattern. This absorption could not be matched to any species contained in HITRAN or GEISA databases, but was found very similar to an absorption pattern observed by a US team in the spectrum of solar light reflected by the ground of Mars [Villanueva, G.L., Mumma, M.J., Novak, R.E., Hewagama, T., 2008. *Icarus* 195 (1), 34–44]. This team then suggested to us that the absorption was due to an uncatalogued transition of the  $^{16}\text{O}^{12}\text{C}^{18}\text{O}$  molecule. The possible existence of this band was soon confirmed from theoretical considerations by Perevalov and Tashkun. Some SOIR observations of the atmospheric transmission are presented around  $2982 \text{ cm}^{-1}$ , and rough calculations of line strengths of the Q branch are produced, based on the isotopic ratio measured earlier in the lower atmosphere of Venus. This discovery emphasizes the role of isotopologues of CO<sub>2</sub> (as well as H<sub>2</sub>O and HDO) as important greenhouse gases in the atmosphere of Venus.

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## 1. Introduction

The investigation of planetary atmospheres by the technique of solar and stellar occultations has been exercised with great success on Earth, and more recently on Mars with the SPICAM instrument on board Mars Express orbiter (Bertaux et al., 2006; Quémerais et al., 2006). The new ESA Venus Express orbiter (VEX) is the first mission applying this technique to the study

of the atmosphere of Venus, with the SPICAV/SOIR instrument.

Launched on November 9, 2005, from Baïkonour, the ESA space probe Venus Express was placed into orbit around Venus on April 11, 2006. After some maneuvers to decrease the apocenter altitude, Venus Express (VEX) was put in a 24 h orbit with a pericenter at 200–300 km of altitude, near the North Pole. On board, the SPICAV instrument consists of a suite of three spectrometers with various scientific objectives (Bertaux et al., 2007a). One of them is SOIR (Solar Occultation in the Infra-Red), a high resolution spectrometer with a new optical design, which allows it to reach a resolving power  $\lambda/\Delta\lambda = 15,000$ – $20,000$  within a quite reasonable volume and mass

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(6 kg), working in the range 2.2–4.3 μm. To our knowledge, this is the highest resolution achieved up to now in planetary space exploration. The optical design includes a high dispersion grating working in high orders, and an Acousto-Optic Tunable filter (AOTF) to sort out one order at a time. A detailed description of SOIR may be found in Nevejans et al. (2006), while the in-flight performances are described in Mahieux et al. (2008). The main objective assigned to SOIR was to determine the vertical distribution of HDO and H<sub>2</sub>O, as high as possible in the atmosphere, to see if there was some fractionation mechanism (like condensation) that would modify the D/H ratio in the upper atmosphere, and possibly prevent D atoms from escaping Venus. In fact, as reported recently (Bertaux et al., 2007b), the HDO/H<sub>2</sub>O ratio does not vary very much with altitude up to 90 km.

Other objectives included the measurement of other known minor constituents (HCl, HF, CO), CO<sub>2</sub> isotopologues, and the search for new species in the atmosphere of Venus. The solar occultation technique from orbit, though restricted to the atmosphere region above the clouds (~60 km), is very sensitive since long path lengths are probed, and we were hoping to discover new gaseous (or aerosols) compounds revealed by their absorption of solar radiation.

Here we report the discovery of a new absorption band detected by SOIR in solar occultation in the very early days of the ESA Venus Express mission. The wavelengths and pattern did not correspond to any gas included in the HITRAN nor the GEISA databases (which are primarily built for the Earth's atmosphere). For several months this finding was kept confidential, while searching for other databases. The main absorption looked like a Q branch, and was located at 2982 cm<sup>-1</sup>. Scientific literature tells that an absorption around 2982 cm<sup>-1</sup> is typical of an asymmetric C–H bond, and we began to search other data bases, mainly of organic materials. Of the absorption features found near 2982 cm<sup>-1</sup>, none matched our observed signature.

Then on December 22, 2006 one of us (Bertaux) received a message from Mike Mumma, asking what SOIR was seeing on Venus around 2982 cm<sup>-1</sup>, and willing to compare to a new absorption feature that his group had detected in the solar spectrum scattered by Mars, as observed from the Earth's ground. When we compared the signatures, they were identical (within error bars). It should have rang a bell in our mind: what is most common to Venus and Mars atmosphere? CO<sub>2</sub>! In spite of this hint, we continued to search for organic material signature, until the group of Mumma and colleagues proposed to us in April 2007 that the absorption signature common to Mars and Venus was due to an uncatalogued band of 628 CO<sub>2</sub> isotope (628 CO<sub>2</sub> standing by convention for <sup>16</sup>O<sup>12</sup>C<sup>18</sup>O, dropping the 1 in front of 16, 12, 18). This identification was soon after confirmed by Perevalov and Tashkun (personal communication) on theoretical grounds. It is the rotation–vibration transition  $\nu_2 + \nu_3$ . Its existence in this spectrum region could have been predicted from the study of 628 CO<sub>2</sub> molecule observed transitions, either in gas phase or in argon and krypton matrices, giving the energy levels of the  $\nu_2$  (656.09 cm<sup>-1</sup>) and  $\nu_3$  (2323.91 cm<sup>-1</sup>) transitions (Dahoo et al., 2006), with  $\nu_2 + \nu_3 = 2980.0$  cm<sup>-1</sup>. This

transition does not exist for the main isotopologue 626 CO<sub>2</sub>, because it is forbidden by the symmetry of the molecule, which is linear. Replacing one atom of <sup>16</sup>O by one atom of <sup>18</sup>O breaks the symmetry, allowing the transition for 628 CO<sub>2</sub>. The selection rules then allows transitions with  $\Delta\ell = 1$  where  $\ell$  is the internal rotation quantum number for the degenerate mode  $\nu_2$ . One then observes 2982.0 cm<sup>-1</sup> since 2980.0 cm<sup>-1</sup> corresponds to  $\Delta\ell = 0$ . Let us note that for a symmetric molecule (626 or 636), besides  $\Delta\ell = 1$ , transitions are allowed only if at the same time  $\Delta V_2 + \Delta V_3$  is odd where  $V_2$  and  $V_3$  are quantum numbers of modes  $\nu_2$  and  $\nu_3$ , respectively.

A detailed spectroscopic study of our Venus SOIR observations will be presented in Wilquet et al. (2008) and is not repeated here. The purpose of this paper is to show some of the discovery observations of this new absorption feature in the atmosphere of Venus. The detection of the same signature in the atmosphere of Mars by the team of Mumma is reported and discussed in details in Villanueva et al. (2008).

## 2. Observations

The elongated orbit of Venus Express is in a plane which is almost inertially fixed, with the pericenter not far from the pole of Venus (and hence the ecliptic pole). In the course of Venus around the Sun, the orbit may either be totally out of the cylinder of shadow, or may cross this cylinder, providing the opportunity for a solar occultation as seen from the spacecraft. The occultation seasons occur twice every 225 days (the orbital period of Venus) and last for 45 or 60 days. Occultations occurring near the pericenter are preferred, because then the limb is at a smaller distance from the spacecraft, and the spatial (vertical) resolution, defined by the FOV projected at the limb, is greater. Since the pericenter is near the North Pole, the latitude of the region probed by the occultation is at high latitude for these near-limb occultations.

To perform an occultation, the whole spacecraft is oriented in such a way that the FOV of SOIR is directed to the Sun. This FOV is fixed at 90° from the FOV of the other optical instruments of VEX (PFS, the VMC camera and VIRTIS) to avoid damage from direct view of the Sun. When a solar occultation is performed, no other instrument is normally operated near the pericenter, which result in a sharing of the pericenter passes between SPICAV/SOIR and the other instruments.

As seen from Venus, the solar diameter is 44 arcmin. The entrance optics of SOIR makes an image of the Sun on the entrance slit of the spectrometer, which has a size of 2 × 30'. The slit is put parallel to the limb by orienting the spacecraft around the SOIR FOV axis. A specific tangent altitude where it is parallel to the limb must be specified (here 65 km) since the angle of the slit projected FOV to the limb is changing during the occultation. Atmospheric refraction is also taken into account, since the solar disc is moving away from the limb (w.r.t. its inertial direction) as seen from the spacecraft.

The image of the slit through the grating spectrometer is formed on a cryo-cooled HgCdTe 2D detector (from Sofradir company), with one pixel corresponding to 1' along the slit, and about 0.05 cm<sup>-1</sup> in the spectral direction. For the observa-

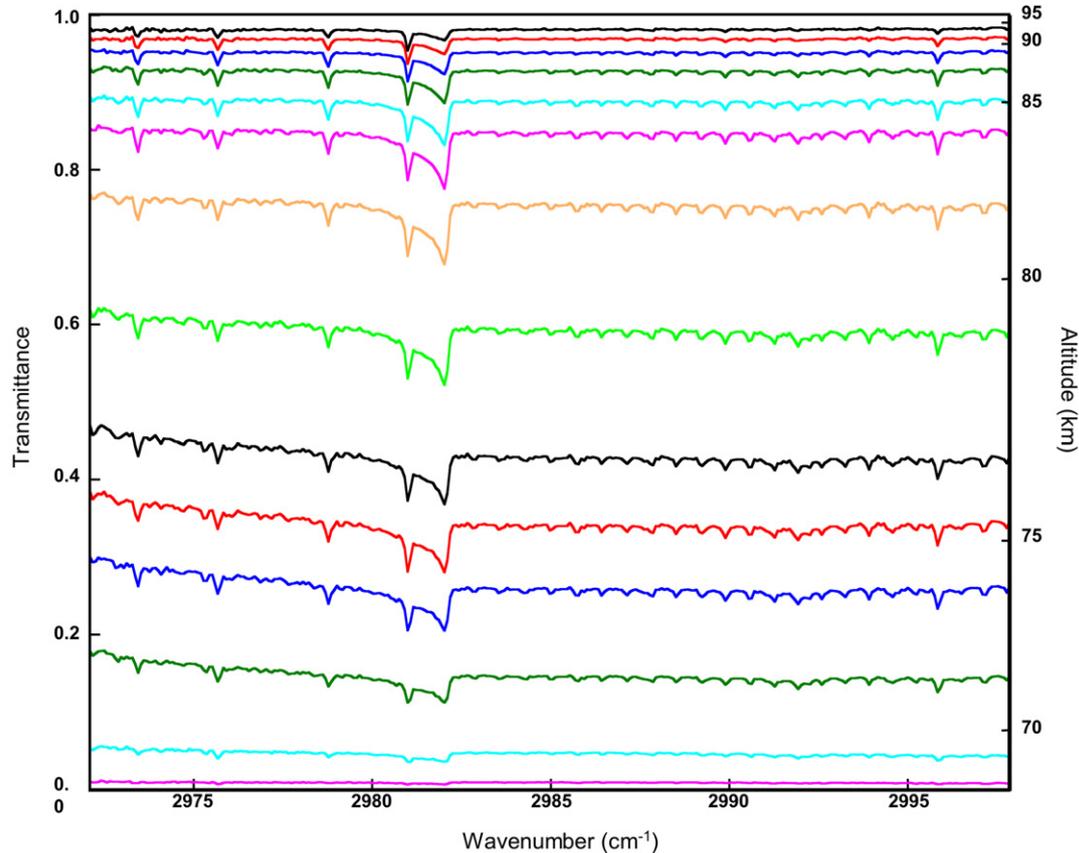


Fig. 1. Atmospheric transmission measured by SOIR during one single occultation. There is one different curve acquired each second, and the corresponding tangent altitude is indicated on the right scale (non-linear, not regular). Each transmission spectrum is obtained by ratioing the solar spectrum seen through the atmosphere to a reference spectrum obtained outside the atmosphere. The overall transmission is decreasing with altitude, owing to the continuous absorption by aerosols above the main cloud deck (the so-called haze). The main spectral feature at  $2980\text{--}2982\text{ cm}^{-1}$  looks like an unresolved Q branch. The depths of all lines (relative to the continuum) are increasing with decreasing altitudes and increase of the slant optical path.

tions reported here, 16 lines of the detector are binned together, forming two spectra probing the same altitude when the slit is parallel to the limb. The AOTF band pass is commanded electrically to let through one grating order. However, its bandpass is such that adjacent orders contribute also a little. During one second of observation, 4 wavelength positions of the AOTF are sequentially activated and repeated all along the occultation. A much more detailed description of SOIR may be found in Nevejans et al. (2006), while the in-flight performances are described in Mahieux et al. (2008).

One of the prime targets of SOIR was HCl, which was discovered in 1967 by FT high resolution spectroscopy (Connes et al., 1967), in the region of  $1.7\text{ }\mu\text{m}$ . Other transitions falling in the range of SOIR were selected to be observed by SOIR, namely around  $3.3\text{ }\mu\text{m}$ . HCl was indeed detected, and the first vertical profile of HCl in the atmosphere of Venus was obtained (Bertaux et al., 2007b). The order No. 133 (range  $2973\text{--}2997\text{ cm}^{-1}$ ) was selected by a proper command of the AOTF, together with selection of adjacent orders. To our surprise, in addition to the clear signature of HCl at several positions, a series of absorption lines was also always present during the occultations. In Fig. 1 are represented the atmospheric transmissions measured by SOIR during the occultation acquired on September 11, 2006. They are the ratio of the solar spec-

trum measured through the atmosphere at various altitudes (one per second) to the reference solar spectrum acquired outside the atmosphere (just before the occultation). Detector flat field features and solar small spectral features are eliminated by the ratio, leaving only the spectral structure of the transmission. The overall signal is decreasing because of the absorption by the aerosols of the haze (above the main cloud deck), beginning at  $\sim 100\text{ km}$ , and becoming completely opaque around  $\sim 68\text{ km}$ .

In Fig. 2, a theoretical absorption spectrum for HCl is compared to one of the typical transmission derived from Fig. 1. It shows that indeed the HCl lines are present in the observed spectrum (main lines at  $2978.7$  and  $2981\text{ cm}^{-1}$ , with 5 smaller lines at higher wavenumbers) in addition to a series of small lines, and a broader absorption showing a sharp edge at  $2982\text{ cm}^{-1}$ , after a progressive increase of the depth of absorption. This behavior is typical of a Q branch, where the many lines would be unresolved at the spectral resolution of the instrument (about  $0.15\text{ cm}^{-1}$  at this wavelength). The other small lines which are not from HCl are seen to vary in depth (relative to the continuum) with the main Q-branch type feature, all increasing with decreasing altitude of the tangent height, suggesting that they belong to the same species, apparently well mixed with the bulk atmosphere of  $\text{CO}_2$ . As discussed in Wilquet et al. (2008), their accurate wavenumbers are perfectly

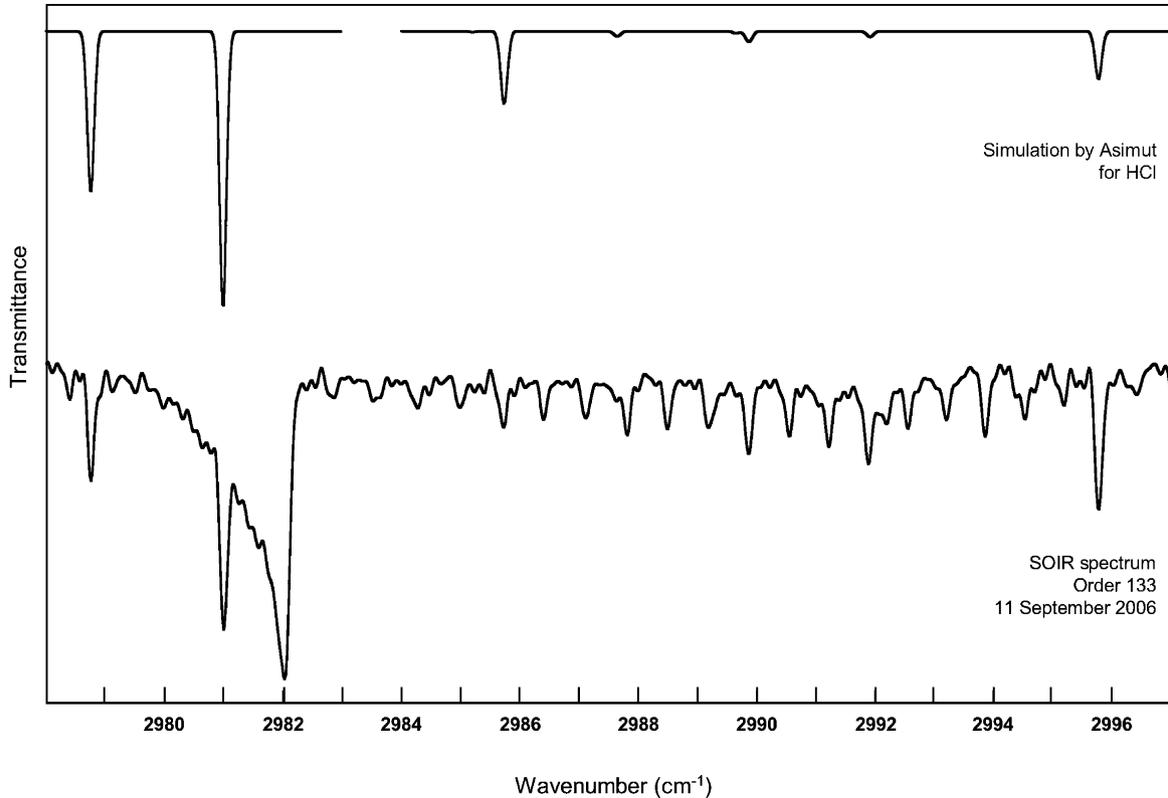


Fig. 2. One observed transmission spectrum taken around 83 km (lower curve) is compared to a synthetic spectrum of the absorption of HCl (upper curve). The main HCl absorption lines (including contributions from adjacent orders) are clearly identified in the observed spectrum. When corrected from these HCl absorptions, the main feature in the observed spectrum is even more resembling a Q branch, identified as the 628 isotopologue of CO<sub>2</sub>.

matched by the theoretical prediction of 628 CO<sub>2</sub>. This fully confirms the identification of this system by Villanueva et al. (2008) detected on Mars from ground based measurements. The transmission spectra collected by SOIR, though with a spectral resolution coarser than Mars spectra, are obtained with practically no correction, while the Mars absorption spectra had to be corrected for a rather large contribution due to telluric absorption (mainly by water bands).

### 3. Determining the line strengths

The suggestion of our US colleagues was confirmed by Valery Perevalov and Sergei Tashkun. Given the known energy levels of the ro-vibrational systems of  $\nu_2$  and  $\nu_3$  it is possible to predict the line positions of the whole system  $\nu_2 + \nu_3$ . The line strengths cannot be computed a priori so simply. However, we may derive them, using the atmosphere of Venus as a gigantic absorption cell. From the transmission spectra, the equivalent width  $W$  of a single line or a group of line may be estimated:

$$W = \int \frac{T(\nu) - T_c}{T_c} d\nu, \quad (1)$$

where the integral is made over a wave number interval encompassing the line or the group of lines,  $T_c$  is the transmission in the continuum near the line and  $T(\nu)$  is the transmission in the lines. The convolution of the spectrum with the instrumental resolution does not change the equivalent width  $W$ , even though the lines are not resolved, as is the case for the Q branch

at 2982 cm<sup>-1</sup>. In the following a crude estimate of the line strength  $S_Q$  is made, using this Q branch, in order to estimate its effect in laboratory spectra and in the Earth's atmosphere.

Integrating this observed Q branch over 2 cm<sup>-1</sup>, we find an equivalent width  $W$  of 0.14 cm<sup>-1</sup>, at an altitude of 77.5 km. At this altitude, the VIRA empirical model (Venus International Reference atmosphere; Keating et al., 1985) predicts a horizontal slant line density  $N$  of  $9.6 \times 10^{24}$  molec/cm<sup>2</sup> of CO<sub>2</sub> (the main isotopologue is by far dominating).

The strength of the absorption feature is by definition  $S_Q = W/N$ , if the individual (unresolved) lines are not saturated (otherwise, in case of saturation the line strength is underestimated). In the case of an isotopologue, there is a convention adopted by HITRAN (Rothman et al., 2005), which specifies the line strength of an isotopic line by using the  $N$  value, not of the isotopologue considered, but of the main isotopologue, and assuming the Earth's atmosphere isotopic ratio. This has been the source of much confusion for planetary scientists using blindly the HITRAN data base.

With this HITRAN convention, the derived value of  $S_Q$  comes to

$$\begin{aligned} S_Q(\text{HITRAN}) &= 0.14/9.6 \times 10^{24} \\ &= 1.46 \times 10^{-26} \text{ cm}^{-1}/(\text{molec}/\text{cm}^2). \end{aligned} \quad (2)$$

In order to have the true value (which could be measured in a cell with pure 628 CO<sub>2</sub> isotopologue, for instance), one has to know the true value of the  $N$  slant density of 628 CO<sub>2</sub> in our

observations. The  $^{16}\text{O}/^{18}\text{O}$  ratio was measured by mass spectrometry of  $\text{CO}_2$  in the lower atmosphere of Venus, and found to be  $2.0 \pm 0.1 \times 10^{-3}$ , close to the terrestrial value  $2.04 \times 10^{-3}$  (Hoffman et al., 1980). Assuming that the same ratio holds higher in the atmosphere of Venus (78 km), the true value of the line strength is (taking into account the two O atoms in the  $\text{CO}_2$  molecule):

$$S_{\text{Q}}(\text{true}) = 3.65 \times 10^{-24} \text{ cm}^{-1}/(\text{molec}/\text{cm}^2). \quad (3)$$

As said above, this is only a crude estimate, and the major source of uncertainty (a factor of 2) is the lack of  $\text{CO}_2$  main isotopologue simultaneous measurements. These measurements will be planned specially for this purpose in the future.

When 628  $\text{CO}_2$  was suggested to us, we were surprised to see that in a recent paper of Toth et al. (2007), investigating the absorption properties (line positions and strengths) of 628  $\text{CO}_2$  between 2200 and 7000  $\text{cm}^{-1}$ , there was no mention of our observed feature at 2982  $\text{cm}^{-1}$ . Looking carefully at their experimental conditions (their Table 2), their most sensitive runs for the detection of this band were their runs 155.9 and 155.12, enriched with 46% of pure 628  $\text{CO}_2$ , with a pressure of 0.56 Torr and path length of 385 m, temperature 296 K. This corresponds to a slant value of  $N(628)$  of  $3.3 \times 10^{20}$  molec/ $\text{cm}^2$ , and according to our value  $S_{\text{Q}}(\text{true})$  it would have given rise to an absorption of  $1.2 \times 10^{-3}$ , averaged over 2  $\text{cm}^{-1}$ . However, given their much higher resolution (than SOIR) of 0.01  $\text{cm}^{-1}$ , deeper absorption features could have been present in their spectra. Their  $S/N$  was 200–250 for these runs, and probably the absorption was marginally detectable and went unnoticed.

#### 4. Conclusions

The above calculation was performed with the assumption that the isotopic ratio is the same at high altitude in the atmosphere of Venus as measured in the lower atmosphere. This may not be the case, since SOIR was probing north high latitude regions, where we suspect a return flow of the Hadley's cell (rising at the sub-solar point) from the lower thermosphere. There, the photo-dissociation of  $\text{CO}_2$  by solar UV flux may present some differences between isotopologues, and subsequent recombination may reflect a differentiation process. In order to better measure the isotopic ratio, SOIR will need to be activated in such a mode where some AOTF orders are dedicated to a precise measurement of 626  $\text{CO}_2$ , and others are dedicated to 628  $\text{CO}_2$ , during the same occultation.

At the ground level of Venus, the vertical column is about  $1.33 \times 10^{27}$   $\text{CO}_2$  molec/ $\text{cm}^2$ , which, when applying  $W = S_{\text{Q}}N$ , yields  $W = 19 \text{ cm}^{-1}$ . This is of course impossible, since the integral of  $W$  is made over 2  $\text{cm}^{-1}$ . It just means that the Q branch is optically thick and opaque at ground level, and the formula  $W = S_{\text{Q}}N$  does not hold in these conditions. The accurate computation of the Venus greenhouse will certainly need to take into account this newly discovered  $\text{CO}_2$  absorption band, given the large amount of  $\text{CO}_2$ . This is true also of the already known HDO bands in the same spectral region, which (to our knowledge) has not been taken into account

in detailed Venus greenhouse calculations. Also, the molecule  $\text{D}_2\text{O}$  should be taken into account (about 1/1600 of  $\text{H}_2\text{O}$  molecules).

In the field of Earth observations, there have been considerable efforts to model the infrared radiation at top of the atmosphere, both from thermal and solar back-scattered radiation. Discrepancies between most accurate measurements (at high spectral resolution) and most sophisticated models often amount to 1%, depending on the spectral region. Given the above determined line strength, the equivalent width of the Q branch would amount to  $1.1 \times 10^{-4} \text{ cm}^{-1}$  for a one-way nadir looking instrument, averaged over 2  $\text{cm}^{-1}$ . This absorption is probably not detectable in the atmosphere of the Earth, unless a high resolution is used, with a high  $S/N$  ratio. Looking at the Sun at low elevation with a Michelson interferometer would give the best chances to detect the absorption band of 628 isotopologue in the atmosphere of the Earth.

As noted by Villanueva et al. (2008), this newly discovered band of 628  $\text{CO}_2$  lies in a spectral region where there are also a number of gaseous organic signatures (as possible biomarkers), like methane and ethane. The Q branch of 628  $\text{CO}_2$  is at 2982  $\text{cm}^{-1}$ , which is also the signature of a C–H bond. This is a source of possible confusion, and indeed we have been first searching spectral data bases of organic materials for sometime. In particular, we found  $\text{CHCl}_3$ ,  $\text{CH}_3\text{CN}$ ,  $\text{C}_4\text{H}_8$ ,  $\text{C}_2\text{H}_6$ ,  $\text{C}_6\text{H}_{12}$ , having strong spectral signature near 2982  $\text{cm}^{-1}$ . Fortunately, with the high resolution of SOIR, the mismatch of all these organic signatures and the one observed in the atmosphere of Venus was obvious.

The study of the atmospheres of Mars and Venus has led to the discovery of this new absorption band of 628  $\text{CO}_2$  isotopologue. It is useful to recall here that the very existence of  $^{18}\text{O}$  and  $^{17}\text{O}$  oxygen isotopes was first discovered by the observations of terrestrial atmospheric absorption bands in 1929 (Giauque and Johnston, 1929a, 1929b).

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