



RESEARCH ARTICLE

# The Problem of CO<sub>2</sub> Reabsorption in Emission Spectra

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## ABSTRACT

The authors present a detailed explanation for selective reabsorption by the CO<sub>2</sub> ν<sub>3</sub>-band when passing its optical emission through an atmospheric-pressure air column (60 cm long, 410 ppm CO<sub>2</sub>) connecting a microwave-discharge cell and the entrance window of a high-resolution Fourier Transform spectrometer. The CO<sub>2</sub> band shapes are explained with a two-temperature model of emission and foreground absorption. Selective CO<sub>2</sub> atmospheric reabsorption is a common effect in optical emission measurements. It primarily affects the fundamental infrared bands, which comprise the main part of the missing laboratory emission and must be taken into account in (exo)planetary atmospheric models.

## 1. Introduction

Reabsorption (or even self-absorption, when mentioning the reabsorption of radiation by the emitter) is practically omnipresent in emission light sources, where reabsorption of a portion of the emitted light causes a light flux deficit. This deficit disrupts the linear dependence of signal and on analyte concentration that is stated

for any spectroscopic or spectrochemical measurement. For example, self-absorption by the emitter plays a major role in laser-induced breakdown spectroscopy (LIBS). In LIBS, self-absorption is a huge drawback because the nonlinear signal dependence can lead to false information on the quantity of an analysed sample. Many studies have been written on the problem of reabsorption in LIBS, e.g. Rezaei et al.<sup>[1]</sup> being among the most recent. Generally,

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self-absorption depends on the density of the analyte, the size of the emitter and the population of the lower energy level of a specific transition.

Raman emission spectroscopy is another optical emission method and also struggles with signal nonlinearity caused by reabsorption in quantitative measurements. According to Wu et al. [2], it is possible to control and restrict reabsorption by proper experimental methods, like the use of external and internal standards. Reabsorption was also studied in near-infrared (NIR) Fourier-transform (FT) Raman measurements of tetrahydrofuran by Petty [3], and by Agarwal et al. [4] in cellulosic materials.

Recently we studied the intensity ratio of the D<sub>1</sub> and D<sub>2</sub> sodium-doublet emission lines, which varies in spectra of astronomical sources and laboratory plasma [5]. This work probes the behaviour of this ratio under controlled laboratory conditions and shows the relative intensities of the Na doublet are determined by self-absorption dependent on the nitrogen buffer-gas pressure and discharge power. The emission-intensity ratio and individual line shapes were explained by a two-temperature model of sodium emission and foreground absorption.

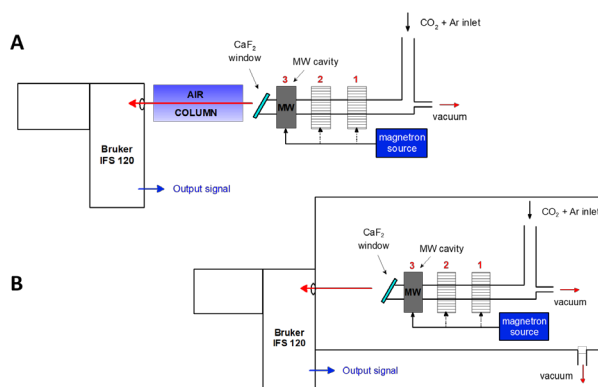
Reabsorption is also extensively studied in X-ray absorption spectroscopy. Trevorah et al. [6] presented a software approach accounting for potential self-absorption of secondary inelastically scattered fluorescence photons. Furthermore, publications from Nassar et al. [7] and Hargreaves et al. [8] have to be mentioned because of reabsorption present in experimental spectra.

CO<sub>2</sub> lasers are an emitting source that also suffers from self-absorption. The output power deficit of CO<sub>2</sub> lasers due to self-absorption was demonstrated in 1981 by Hishii et al. [9]. This effect was also noticed for low pressure of CO<sub>2</sub> active gas by Kaye et al. [10] in 1983.

Here, we find that the reabsorption of CO<sub>2</sub> emission spectra must always be taken into account during optical measurements. Especially if carbon dioxide is present in the laboratory system outside the emission region, because of its exceptional absorbing abilities.

## 2. Experimental Setup

The emission beam was created in a microwave discharge realized in a quartz tube of 12 mm external diameter and 150 mm total length. The front window of the tube was made from CaF<sub>2</sub> and the tube was constantly evacuated by a rotary vacuum pump to ensure a flowing regime of gases. The discharge tube was inserted into a microwave cavity connected to a magnetron microwave source (2.45 GHz). The experimental scheme is depicted in Figure 1.



**Figure 1.** A—Scheme of the microwave discharge in the air; B—Scheme of the microwave discharge in vacuum.

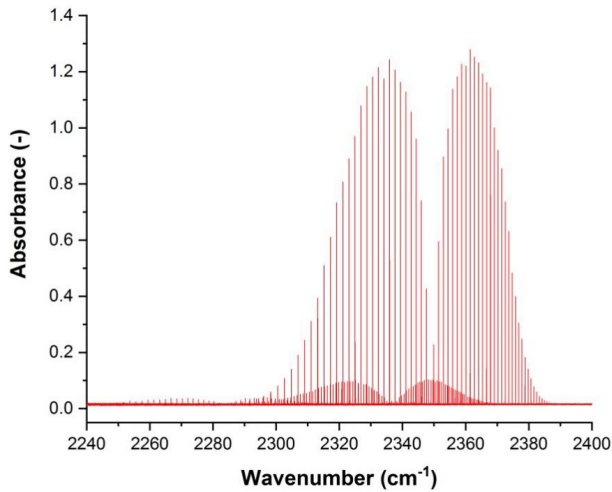
The discharge was made in CO<sub>2</sub> mixed with an argon buffer gas. The partial gas pressures were 0.1 Torr of CO<sub>2</sub> and 1 Torr of Ar. The output power of the magnetron was 30 W. The spectra were recorded with a Bruker 120 HR FTIR spectrometer. The spectrometer was equipped with a CaF<sub>2</sub> beam splitter and CaF<sub>2</sub> entry window. The aperture was set to 4 mm and a liquid-nitrogen-cooled InSb detector was used. The recorded spectral range was 1800 to 3500 cm<sup>-1</sup>, limited by an interference optical filter. The unapodized spectral resolution was 0.02 cm<sup>-1</sup> and 20 scans were accumulated to obtain a reasonable signal-to-noise ratio. The experimental arrangement used in this work is similar to our paper on sodium self-absorption [5].

As depicted in Figure 1, the experimental arrangement was performed in two setups. Panel A of Figure 1 shows the arrangement of discharge performed in air, where the emission optical beam passes through 60 cm of atmospheric air before entering the entry aperture of the spectrometer, undergoing reabsorption along its path. The second setup (panel B of Figure 1) shows the implementation of a vacuum chamber that housed the whole microwave cavity tube system. In this system, no external air column was present and therefore no reabsorption occurred. Also, it must be noted that significant effort was made to ensure there was no cold gas in between the microwave cavity and the CaF<sub>2</sub> window of the emission system tube. This fact is depicted in Figure 1 as shaded rectangles presenting MW cavity position. By varying the position of the cavity (numbers 1 to 3), an optimal position of the cavity was achieved.

## 3. Results and Discussion

Firstly, a pure absorption arrangement measurement of CO<sub>2</sub> was performed. This measurement was conducted in order to obtain a comparative spectrum of a fundamental band of CO<sub>2</sub>. This measurement was performed with pure CO<sub>2</sub> (Linde gas > 99.9%) of a pressure of 0.5 Torr, placed

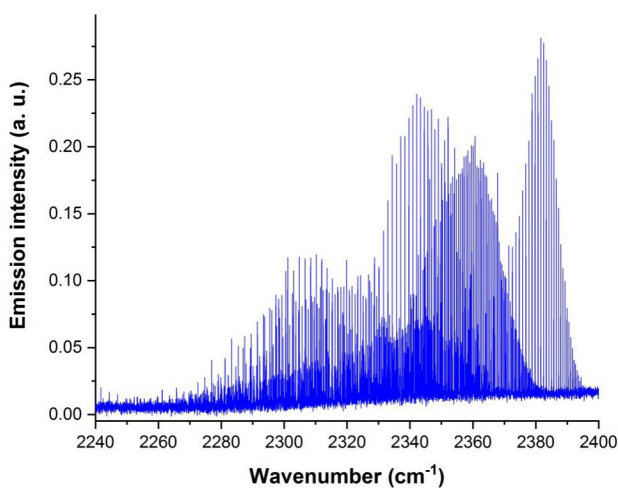
in a cell of 30 cm length at a temperature of 298 K. Other parameters were the same as described in experimental setup section. An absorbance spectrum depicted in Figure 2 was obtained.



**Figure 2.** CO<sub>2</sub> spectrum measured in absorption arrangement.

The spectrum of fundamental CO<sub>2</sub> band ( $\nu_3$ ) resembles itself in a well-defined two-branch shape. This is a shape of  $\nu_3$  band common for absorption measurements since CO<sub>2</sub> only absorbs a part of referential light and the population of energy levels is hence typical. Since a standard CO<sub>2</sub> gas was used, both the most common isotopes of <sup>12</sup>CO<sub>2</sub> and <sup>13</sup>CO<sub>2</sub> are present in the spectrum.

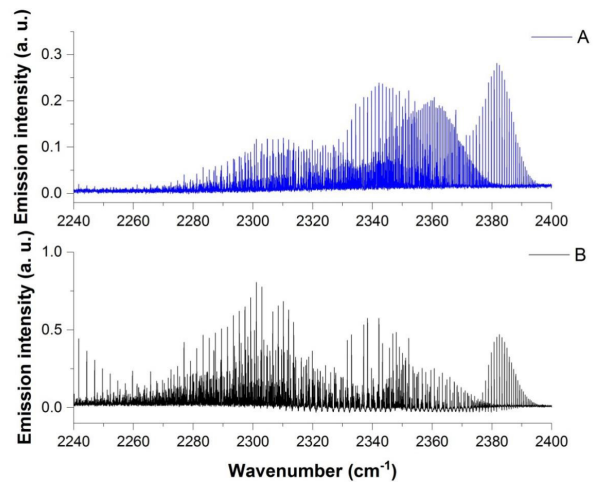
In an ideal case, the emission spectrum is a combination of fundamental  $\nu_3$  band together with additional several rovibrational excited states of CO<sub>2</sub> (Figure 3).



**Figure 3.** CO<sub>2</sub> fundamental band in emission arrangement (in vacuum).

Spectrum depicted in Figure 3 was obtained by emission measurement of CO<sub>2</sub> mixed with Ar of total pressure

of 1.1 Torr (0.1 Torr of CO<sub>2</sub> and 1 Torr of Ar). The whole apparatus was located in an evacuated vacuum chamber directly connected to the spectrometer. Emission light beam thus did not encounter any air during its path. Nevertheless, when the emission experiment is carried out in the standard laboratory environment and the emission light beam passes a column of atmospheric air before it enters the evacuated measuring device, the air containing CO<sub>2</sub> reabsorbs the emitted light and the resulting spectrum then looks different. The comparison of such spectrum with the previous one measured in vacuum (Figure 3) can be seen in Figure 4.



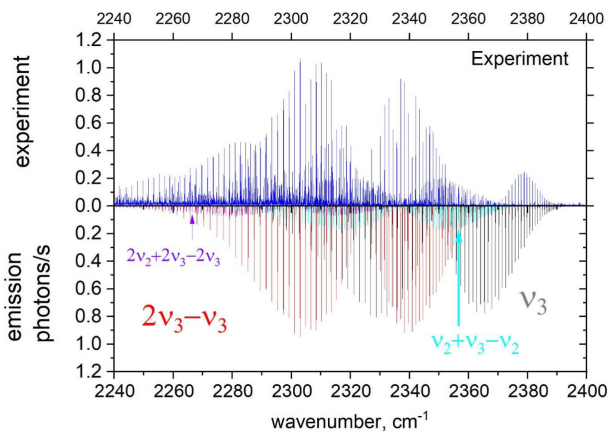
**Figure 4.** A comparison of vacuum-measured CO<sub>2</sub> emission spectrum (no reabsorption effect) (panel A) together with the reabsorbed CO<sub>2</sub> emission (60 cm long air column, atmospheric pressure, 410 ppm CO<sub>2</sub>) (panel B).

The spectrum depicted in panel B of Figure 4 was obtained in emission arrangement when creating a glow discharge of CO<sub>2</sub> mixed with argon as buffer gas of total pressure of 1.1 Torr (0.1 Torr of CO<sub>2</sub> and 1 Torr of Ar). The emission light beam passed 60 cm of air at atmospheric pressure and a standard laboratory temperature of 298 K before entering the spectrometer. Weak absorption features of CO<sub>2</sub> ( $\nu_3$  fundamental band) can be recognized below the horizontal background level as well as the line broadening caused by atmospheric CO<sub>2</sub> absorption. Due to atmospheric absorption a large part of the  $\nu_3$  emission spectrum is eliminated.

A theoretical spectrum has been modelled in collaboration with University College London that matches our experimental emission spectrum measured in air. A comparison of such a model and experimental emission spectrum is depicted in Figure 5.

Microwave discharge emission spectrum is shown in Figure 5 together with a theoretically modelled CO<sub>2</sub> emission. For the calculated spectrum we used a two-tempera-

ture (555 K and 700 K) non-LTE model from Pastorek et al. <sup>[11]</sup> where the  $2\nu_3 - \nu_3$  band was multiplied by a factor of 23 to match the experimental intensity. The theoretical model was constructed from the UCL-4000 line list <sup>[12]</sup> with the resolution =  $0.01 \text{ cm}^{-1}$ , Lorentzian line profile, a HWHM =  $0.017 \text{ cm}^{-1}$  and the rotational temperature set to  $T_R = 555 \text{ K}$ , corresponding to the experimental conditions. The effect of self-absorption is not included in the model. The shape of the experimental  $\nu_3$  emission band does not correspond well to the theoretical model due to elimination of the  $\nu_3$  atmospheric absorption in a spectral range of  $2300\text{-}2380 \text{ cm}^{-1}$  in the model. Only a few lines between  $2370$  and  $2390 \text{ cm}^{-1}$  are strong enough to match this part of the theoretical  $\nu_3$  band.



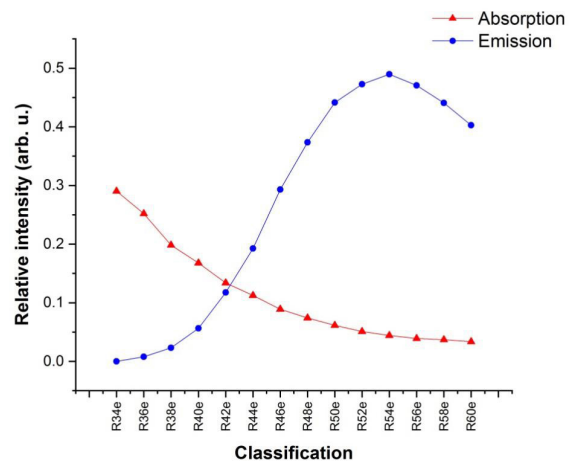
**Figure 5.** Experimental emission of the reabsorbed  $\text{CO}_2$  emission (60 cm long air column) (top) and theoretical (bottom) non-LTE emission spectrum of  $\text{CO}_2$ .

The experimental spectrum in Figure 5 can be matched to the hot  $\nu_2 + \nu_3 - \nu_2$  (01111-01101) and  $2\nu_3 - \nu_3$  (00021-00011) bands of  $\text{CO}_2$ , as well as to the  $2\nu_2 + \nu_3 - 2\nu_2$  (10012-02201) (lower display, plotted in green, blue and pink) spectrum. In the non-LTE model <sup>[13]</sup>, the vibrational temperature of the hot bands  $2\nu_3 - \nu_3$  and  $2\nu_2 + \nu_3 - 2\nu_2$  was set to 700 K, while other bands were modelled using  $T = 555 \text{ K}$ . The  $2\nu_3 - \nu_3$  band is an especially important feature of non-LTE  $\text{CO}_2$  within the Martian atmosphere <sup>[13]</sup> where the overpopulation of the upper state is caused by solar radiation pumping at  $2.7 \mu\text{m}$ . The fundamental band of  $\text{CO}_2$  around  $2300 \text{ cm}^{-1}$  was also detected in non-LTE emission via fluorescence of solar radiation in Venus's atmosphere by VIRTIS spectrometer <sup>[14]</sup>.

The hot bands ( $2\nu_2 + \nu_3 - 2\nu_2$ ,  $2\nu_3 - \nu_3$ , or  $\nu_2 + \nu_3 - \nu_2$ ) depicted in Figure 5 are unaffected by reabsorption in the atmospheric section of the measured optical path. Only the part of the most intense atmospheric infrared fundamental band ( $\nu_3$ ), (room temperature, relatively low  $J$  rotational excitation) has a high influence on the reabsorption

effect (see Figures 4 and 5).

The distribution of spectral intensity in absorption on rotational quantum number (room temperature, 0.5 Torr pressure and 30 cm optical path) and of  $\text{CO}_2$   $\nu_3$ -band  $R$ -branch emission (See Figure 4, panel B) can be seen in Figure 6. Comparison of spectra showing  $\text{CO}_2$  absorption spectrum (red) and emission (blue). Most lines appearing in the absorption spectrum are missing from the laboratory emission. The absorption spectrum intensities in Figure 6 have been obtained by measurement of 0.5 Torr of pure  $\text{CO}_2$  at room temperature (298 K) in a 30 cm long absorption cell (Figure 2). The unapodized spectral resolution was  $0.05 \text{ cm}^{-1}$  and other parameters were the same as for the emission experiments. Figure 6 clearly demonstrates differences in the  $\nu_3$  band rotation intensities of  $J$  when measured in absorption and emission. Rotational lines of the  $\text{CO}_2$   $\nu_3$ -band with  $J = 0$  to 34 are completely in the emission spectrum missing. The higher  $J$  vibrational transitions are starting to appear in the spectrum at frequencies higher than approximately  $2375 \text{ cm}^{-1}$  (see Figures 5 and 6).



**Figure 6.** Intensity distribution of  $\text{CO}_2$   $\nu_3$  lines in absorption and emission.

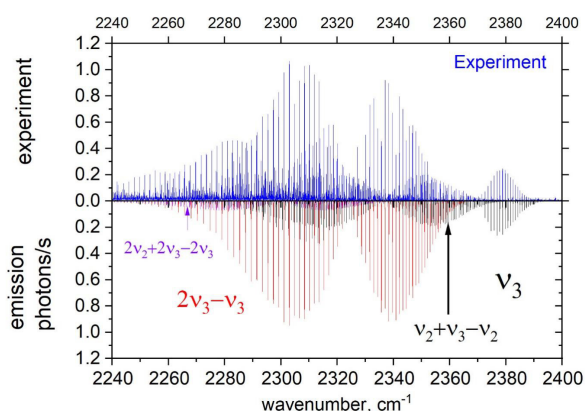
Around the line R42e, the emission intensity becomes almost as intense as selective reabsorption of  $\text{CO}_2$  (equilibrium). For higher  $J$ -values, emission prevails in the spectrum (the atmospheric room temperature absorption of high- $J$  transitions is weak, on the contrary the rotational excitation in the microwave discharge is high) which allows for the intense blue tail of the  $\nu_3$  band observed between  $2380$  and  $2400 \text{ cm}^{-1}$ , as depicted in Figures 5 and 6.

In order to get an exact model of our  $\text{CO}_2$  discharge emission through the atmospheric air column ( $I_{\text{tot}}$ ), one must include an absorption part of our simulation. The infrared  $\nu_3$  absorption band (Figure 2) was subtracted from

the simulated non-LTE emission spectrum shown in Figure 5. For the absorption spectrum we used  $T = 296$  K and the Lorentzian line profile of  $\text{HWHM} = 0.017 \text{ cm}^{-1}$ . The emission spectrum was modelled using a two-temperature non-LTE model. The total spectrum of  $\text{CO}_2$  was constructed as:

$$I_{\text{tot}} = I_{\text{vacuum emission}} - A \times I_{\text{absorb}},$$

where  $A$  was adjusted for the closest reproduction of the experimental spectrum and  $I_{\text{absorb}}$  is as in our paper<sup>[11]</sup> with the fundamental 00011 and hot bands 01111-01101 affected. The underlying line list is UCL-4000. A comparison of the experimental reabsorbed  $\text{CO}_2$  emission spectrum (60 cm long air column) (top) and theoretical (bottom) corrected ( $I_{\text{tot}}$ ) spectrum of  $\text{CO}_2$  is depicted in Figure 7.



**Figure 7.** Experimental emission of the reabsorbed  $\text{CO}_2$  emission (60 cm long air column) (top) and theoretical  $I_{\text{tot}}$  (bottom) reabsorption model of the non-LTE emission spectrum of  $\text{CO}_2$ .

## 4. Conclusions

This short letter points out the reabsorption effect in  $\text{CO}_2$  when its emission passes through a volume of atmosphere containing trace  $\text{CO}_2$  (410 ppm). The effect of reabsorption is most prominent for the fundamental transitions of the  $\nu_3$  band, especially for lower  $J$ -values.

The experimental results demonstrate the dominating absorption properties of the fundamental infrared carbon dioxide rovibrational bands. This must be taken into account in all cases of planetary atmospheric models that are based on measured emission data, including in models of exoplanetary atmospheres containing high  $\text{CO}_2$  concentrations.

## Author Contributions

SC invented the research, conducted the experiments, edited the manuscript, and provided funding. AP conducted the experiments, wrote the original manuscript, and

edited the manuscript. SNY performed theoretical calculations and modelling and provided funding.

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## Data Availability Statement

The data presented in this study are available on request from the corresponding author.

## Conflicts of Interest

Authors declare no conflicts of interest.

## References

- [1] Rezaei, F., Cristoforetti, G., Tognoni, E., et al., 2020. A review of the current analytical approaches for evaluating, compensating and exploiting self-absorption in Laser Induced Breakdown Spectroscopy. *Spectrochimica Acta Part B: Atomic Spectroscopy*. 169, 105878.
- [2] Wu, Z., Zhang, C., Stair, P.C., 2006. Influence of absorption on quantitative analysis in Raman spectroscopy. *Catalysis Today*. 113(1-2), 40-47.
- [3] Petty, C.J., 1991. Self-absorption in near-infrared Fourier transform Raman spectrometry. *Vibrational Spectroscopy*. 2(4), 263-268.
- [4] Agarwal, U.P., Kawai, N., 2005. “Self-Absorption” phenomenon in near-infrared fourier transform raman spectroscopy of cellulosic and lignocellulosic materials. *Applied Spectroscopy*. 59(3), 385-388.
- [5] Civiš, S., Heays, A.N., Knížek, A., et al., 2021. High resolution emission FT spectra of sodium in a microwave discharge: Intensity variation of the D1/D2 lines in exoplanetary atmospheres. *Journal of Quantitative Spectroscopy and Radiative Transfer*. 270,

- 107689.
- [6] Trevorah, R.M., Chantler, C.T., Schalken, M.J., 2019. Solving self-absorption in fluorescence. *IUCrJ*. 6(4), 586-602.
- [7] Nassar, R., Bernath, P., 2003. Hot methane spectra for astrophysical applications. *Journal of Quantitative Spectroscopy and Radiative Transfer*. 82(1-4), 279-292.
- [8] Hargreaves, R.J., Li, G., Bernath, P.F., 2011. Hot NH<sub>3</sub> spectra for astrophysical applications. *The Astrophysical Journal*. 735(2), 111.
- [9] Hishii, M., Nagai, H., Nagai, A., et al., 1981. Influence of self-absorption on output power characteristics of a high-pressure cw CO<sub>2</sub> laser. *Journal of Applied Physics*. 52(8), 4953-4958.
- [10] Kaye, A.S., Naylor, D.L., 1983. Runaway self-absorption in multikilowatt CO<sub>2</sub> lasers. *Applied Physics Letters*. 42(8), 641-642.
- [11] Pastorek, A., Clark, V.H., Yurchenko, S.N., et al., 2022. New physical insights: Formamide discharge decomposition and the role of fragments in the formation of large biomolecules. *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy*. 278, 121322.
- [12] Yurchenko, S.N., Mellor, T.M., Freedman, R.S., et al., 2020. ExoMol line lists—XXXIX. Ro-vibrational molecular line list for CO<sub>2</sub>. *Monthly Notices of the Royal Astronomical Society*. 496(4), 5282-5291.
- [13] Kutepov, A.A., Rezac, L., Feofilov, A.G., 2017. Evidence of a significant rotational non-LTE effect in the CO<sub>2</sub> 4.3 μm PFS-MEX limb spectra. *Atmospheric Measurement Techniques*. 10(1), 265-271.
- [14] Gilli, G., López-Valverde, M.A., Drossart, P., et al., 2009. Limb observations of CO<sub>2</sub> and CO non-LTE emissions in the Venus atmosphere by VIRTIS/Venus Express. *Journal of Geophysical Research: Planets*. 114(E5), 1-19.