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Experimental setup for the optical characterisation of gases at typical planetary atmospheric conditions

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INTRODUCTION

The study of the optical properties of gases at planetary conditions are very important to interpret the remote sensing data, in particular those acquired by the VIRTIS instrument on board VENUS-EXPRESS [1]. For this purpose, we have built up an experimental apparatus employed to study the optical properties of gases, in particular CO_2, the principal absorber of the Venus atmosphere. The experimental data obtained are used to update the database for the radiative transfer calculations in order to improve the accuracy of the composition parameters retrieval from remote sensing data analysis. The system employed consist of two dedicated gas cells integrated with a Fourier Transform InfraRed (FT-IR) spectrometer. The first apparatus, a High Pressure High Temperature (HP-HT) gas cell, is designed to sustain a pressure up to 300 bar and a temperature up to 570 K with an optical path of about 2 cm. The second one, a Multi Pass (MP), is a cell with a variable optical path from 2.5 to 30 m, able to work with pressure up to 10 bar and temperature up to 473 K. These two apparatus have been used to study the optical properties of the carbon dioxide, at typical Venusian conditions. The last one, independent from the FT-IR, is designed to sustain a pressure up to 100 bar and makes use of the Cavity Ring Down (CRD) technique with a tunable laser. Thanks to the high reflectivity of the mirrors we able to mimic an optical path up to 5 km, thus suitable for weak absorptions in thin or dense atmosphere.

EXPERIMENTAL SETUP

HPHT GAS CELL

The HP-HT gas cell, shown in figure 1, allows us to simulate in the lab similar physical conditions found in the deep atmosphere of Venus below the clouds. In this way it is possible to measure the optical properties of CO_2 from 50 down 16 km of equivalent altitude above the Venus' surface.

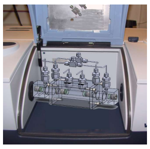

Figure 1: An image of the HP-HT gas cell

MP GAS CELL

The Multi Pass (MP), taking advantage of the multiple reflections, allows us to work with a variable optical path from 2.5 to 30 m. This cell is designed to work with gases at a pressure up to 10 bar and temperature up to 473 K (figure 2).

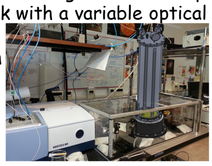

Figure 2: An image of the MP gas cell

CRD GAS CELL

The Cavity Ring Down (CRD) technique is used to record precisely the loss rate of the gas, the cell used for our purpose, is shown in figure 3. It is not coupled with the FT-IR but uses dedicated tunable lasers at different wavelengths, allowing to obtain very long absorption path lengths. Presently the cell works at room temperature and should sustain pressure up to 100 bar.

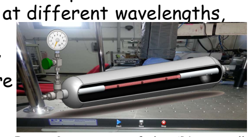

Figure 3: An image of the CRD gas cell

RESULTS AND DISCUSSIONS

RESULTS FROM HPHT AND MP GAS CELLS

We reproduced in our HP-HT gas cell the real Venusian physical conditions for the CO_2 in a grid from the VIRA profile [2]. For each point of the grid we have acquired the spectra of the carbon dioxide with a resolution of 2 cm^{-2} [3].Some results are shown in figure 4.

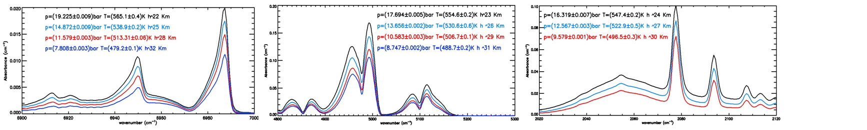

Figure 4: CO_2 absorption coefficients acquired with a resolution of 2 cm^{-2} according to the VIRA profile.

COLLISIONAL INDUCED ABSORPTION (CIA)

Using both the HP-HT and the MP gas cell we have performed the relevant measurements on the Collisional Induced Absorption (CIA) bands. The spectra measured between [1150-1550] and [2850-3150] cm^{-1} are presented in figure 5, where only some examples have been reported. According to the analysis performed in [4], we evaluated the Band Integrated Area (BIA) and the results are shown in figure 6. As can be seen, we obtained a quadratic behaviour versus density suggesting the formation by two bodies rather than by only one. The results of the quadratic fit and standard deviation, are summarized in table 1. An other interesting result is shown in figure 7 where we have compared our analysis (black stars) with that performed in [5] (black squares). As can be seen our data are in good agreement with the curve confirming the temperature dependency compared to the results obtained at lower temperatures. For what concerns the results on the band located at [2850-3150] cm^{-1}, we refer to the work [6], where an extensive study on the density dependence by the temperature is reported. As can be seen in figure 8, we have obtained the same quadratic behaviour with a difference between the two curves due to probably at a different way to evaluate the base line. In this spectral range, is very difficult to have a good method to calculate the base line because of the CIA band is between two strong CO_2 absorptions.

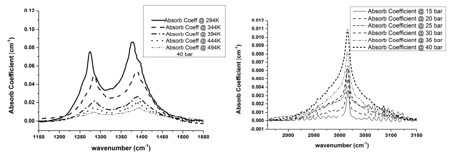

Figure 5: CO_2 collisional induced absorption bands acquired with a resolution of 2 cm^{-1}. On the left the spectra measured at different temperatures and 40 bar, on the right at room temperature and different pressures.

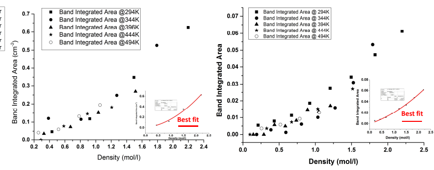

Figure 6: Band integrated area vs density calculated for the band observed @ 1300 cm^{-1} (on the left) and at 3100 cm^{-1} (on the right).

RESULTS FROM CRD APPARATUS

Using a DFB laser to illuminate the CDR gas cell, we measured the carbon dioxide loss rate in the spectral range from 1179 to 1182 nm, varying the CO_2 pressure from 1 up to 38 bar and maintaining the temperature constant at 294 K. As shown in figure 9, the attenuation due to carbon dioxide varies both linearly and quadratically with the density[7]. The first contribution being due to weak allowed bands and Rayleigh scattering and the second due to far wings of bands outside the spectral window and to the so-called continuum absorption, which includes contributions of very far bands (> 250 cm^{-1}) and Collisional Induced Absorption (CIA). The quadratic dependence on the density is 3.44×10^{-7} $cm^{-1}(mol/l)^{-2}$ = 6.85×10^{-10} cm^{-1} Am^{-2} . This value is in good agreement with what evaluated by Bézard and his coworks [8]. Small quantities of water vapor are present in the Venus atmosphere (about 30-40 ppm) and contribute significantly to the CO_2 spectrum[9].

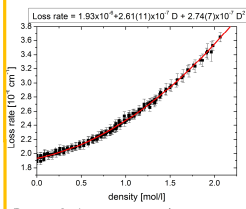

Figure 9. Loss rate vs density recorded at different pressure and room temperature in the 1.18 μm window. The black squares are the experimental data and the red curve is the best fit.

We've varied the pressure of the carbon dioxide from 5 to about 31 bar and recorded the loss rate in the tunable range of the laser, 1179-1183 nm. The results are shown in figure 10 where, as can be seen, an impurity of the water vapor is present. The estimated value is about 50-75 ppm

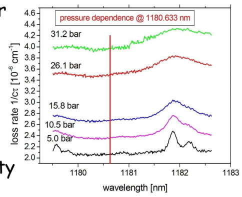

Figure 10. Loss rate vs wavelength acquired at different pressures in the tunable spectral range. The band observed at about 1182 is due to the water vapor

Spectral Range (cm^{-1})	
[1150-1500] cm^{-1}	[2850-3150] cm^{-2}
(Poly Fit ± STD)*10^{-4} Amagat^{-2}cm^{-2}	(Poly Fit ± STD)*10^{-5} Amagat^{-2}cm^{-2}
1.50 ± 0.14	1.19 0.14
4.26 ± 0.38	4.49 0.55
1.74 ± 0.65	1.38 0.76
1.44 ± 0.19	1.48 0.19
1.68 ± 0.79	1.46 0.30

Table 1: Results of the quadratic fit obtained using our experimental data

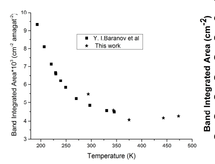

Figure 7: Comparison between our data (black stars) and these in [5].

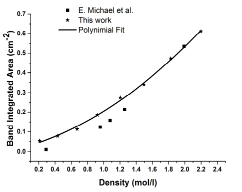

Figure 8: Comparison between our data (black stars and these in [6] (black squares), for the band between [2850-3100] cm-1

CONCLUSIONS

The CO_2 spectra have been measured for a wide range of temperatures, pressures and for a large spectral range. All data are now available and can been downloaded from: http://exact.iaps.inaf.it[3].A theoretical model including line mixing effects as well as far wings corrections for the strongest absorption bands reproduces satisfactory the laboratory spectra, for all pressures and temperatures explored so far [10]. First measurements obtained using the innovative design of the Cavity Rind Down technique, have been performed on carbon dioxide in the 1180 nm transparency window of Venus. The quadratic component measured varying the pressure from 38 down to 1 bar is in good agreement with analyses performed by [8] using the data acquired by VIRTIS at Venus on NADIR looking geometry. For what concerns the Collisional Induced Absorption (CIA) bands, we can confirm that the band located at [1150-1550] cm-1 is due to the strong Fermi-coupled doublet (ν1, 2ν2). The band integrated intensity, calculate for both bands, shows a quadratic dependence versus density in the spectral range of interest opposed to the absorption by isolated molecules, which follows Beer's law. This behaviour suggests an absorption by pairs rather than by individual molecules. For what concerns the temperature dependence of the BIA, more extensive studies are in progress.

WORK IN PROGRESS

In order to extend the pressure range, and to overcome some present limitations, we designed a new heatable\coolable cell placed inside a vacuum chamber as shown in figure 10. With the new cell we plan to develop a setup valid for both FT-IR and CRD techniques (represented in figure 11 and 12 respectively), allowing us to measure the optical properties of gases with pressure from 50 down to a few bars and a temperature from -200 up to 250°C.

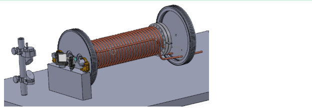

Figure 11: Design of the coolable/heatable cell

References :

[1]:Piccioni G. et al, VIRTIS: the Visible and Infrared Thermal Imaging Spectrometer. Eur. Space Agency Spec. Publ., ESA SP-1295, 2007.
[2]:Moroz V et al, Vira-2: a review of inputs for updating the Venus international Reference Atmosphere. Advances in Space Research, vol. 19, Issue8, pp 1191-1201, 1997.
[3]:Stefani S. et al, Experimental CO_2 absorption coefficients at high pressure and high temperature. JQSRT 2013, vol. 117, pp 21–28.
[4]:Vigasin A. et al, Temperature variations of the interaction induced absorption of fCO_2 in the ν1, 2ν2 region: FTIR measurements and dimer contribution. Journal of Molecular Spectroscopy 2002, vol. 213, pp 51
[5]: Yuri I. et al, Infrared spectrum of the continuum and dimer absorption in the vicinity of the O_2 vibrational fundamental in O_2/CO_2 mixtures. Journal of Molecular Spectroscopy 2004, Vol. 228, Issue 2, pp. 432–440,
[6]:Thomas M.E. et al, Integrated intensities of N2, CO2, and SF6 vibrational bands from 1800 to 5000 cm 1 as a function of density and temperature. JQSRT 1989, vol. 42, pp 465-476.
[7]:Snels M. et al, Carbon dioxide absorption at high densities in the nightside transparency window of Venus. JQRST 2014, vol. 133, pp. 464-471
[8]:Bèzard B. et al, The 1.10-and 1.18 μm nigthside windows of Venus observed by SPICAV-IR aboard Venus Express. Icarus 2011, vol. 216, pp 173–183
[9]:Bèzard B. et al, Water vapour abundance near the surface of Venus from Venus Express/VIRTIS observations. J Geophys Res Planets 2009, vol. 114
[10]:Tran H. et al, Measurements and modelling of high pressure pure CO_2 spectra from 750 to 8500 cm^{-1}. I- central and wing regions of the allowed vibrational bands. JQSR, 2011, vol. 112, pp 925 936.

Acknowledgements
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