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Study of the optical properties of CO_2 at high pressure and high temperature: comparison between measured and simulated spectra

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Abstract. Here we present a new experimental set up to characterize the optical properties of the CO_2, the main constituent of the venusian atmosphere, at extreme conditions. The gas optical transmittance has been recorded by a Fourier Transform InfraRed (FT-IT) interferometer able to work in a wide spectral range, from 350 to 25000 cm^{-1} (0.4 to 29 μm), with a relatively high spectral resolution, from 10 to 0.07 cm^{-1}. A special customized gas cell, designed to support pressure up to 350 bar and temperature up to 300° C, has been integrated inside the interferometer. We reproduced in our cell the Venusian deep atmospheric physical conditions for CO_2 according to a vertical profile, varying the CO_2 pressure from 1 to 30 bar and temperature from 298 to 600K. The measurements have been compared with synthetic spectra obtained using three different models: one implementing a line by line calculation; the second one takes into account the line mixing effect in the strong collision approximation and the last one is a different approach to the line mixing effect. The preliminary comparison leads us to conclude that for gases under extreme conditions it is necessary to take into account the line mixing effect.

Key words. Gas: C_2O – Conditions: high pressure high temperature – Experimental setup: FT-IR and gas cell – Atmosphere: Venus – Model: Line mixing and line shape – Bands: Collision Induced Absorption

1. Introduction

The conventional spectroscopic databases, like HITRAN (Rothmana et al. 2005), HITEMP (Rothmana et al. 2010), CDSD (Tashkun & Perevalov 2006), do not or contain very limited amount of information about optical properties of gases at extreme conditions, in the specific case at high pressure and high temperature. While extensive data set exist for

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radiative transfer calculations concerning the Earth's atmosphere, important information and a thorough understanding of the behavior of dense planetary atmospheres is still missing. For example, the most important difference between CO_2 absorption, the main constituent of the Venus' atmosphere, with respect to Earth, is the density of atmospheres. Spectroscopic absorption lines are broadened by collisions between molecules and a correct theoretical description of the energy transfer occurring during the collisions is essential for deriving theoretical line shapes which match the experimental data. This work is organized as following: in section 2, we present our experimental setup and the measurement procedure, in section 3 a brief description of the three models used to obtainer the synthetic spectra. Results and discussion about the preliminary comparison are reported in the section 4 and in the section 5 we gives some conclusions and future work.

2. Experimental Set up

In our laboratory we have assembled an experimental setup consisting of a Fourier Transform InfraRed (FT-IR) interferometer and a special customized high pressure-high temperature (HP-HT) gas cell. Thanks to four different detectors (InGaAs, MCT, Si and DTGS), two lamps Mid-InfraRed and Near-InfraRed and two beam splitters of KBr and CaF_2, we can work in a wide spectral range from 350 to 25000 cm^{-1} (0.4 to 29μm). Each spectrum can be acquired with a resolution from 10 to 0.07 cm^{-1}. The cell is about 2 cm of optical path and designed to support pressure up to 250 bar and temperature up to 650 K. The absorption cell consists of three parts, a central hot chamber which contains the gas to be measured and two lateral cold chambers filled with buffer. We recreate the same conditions found in the deep atmosphere of Venus as from the Venus International Reference Atmosphere (VIRA) (Moroz & Zasova 1997). We reproduced the real vertical profile by varying the pressure and temperature of the gas from 1 to 30 bar and from 294 to 650 K respectively. This corresponds to an altitude from 50 km down to 15 km. The procedure is as follows: the central box is heated up to the target of temperature, for example 373 K, while the lateral part is maintained cold. The three chambers are filled with Argon (Ar) at the preset pressure, and the background is recorded. Afterwards the Ar in the central section is substituted by CO_2 at the preset pressure and the absorption spectrum is recorded. The same procedure has been applied to all measurements.

3. Model description

The measurements have been compared with synthetic spectra obtained using three different models: ARS Code, software "Solution" and a "Line mixing" model.

3.1. ARS code

This model is based on the ARS Code, (Ignatiev 1990-2007). This software is a set of routines implementing line by line calculation of gases and aerosol opacity, transmittance, and atmospheric radiance spectra.
We must define values of pressure, temperature and optical path to be used as input for the model. It's necessary to define a wave number grid which is based on line positions, widths and strengths and this depends on the physical conditions. Subsequently, using the conventional spectroscopic data bases, HITRAN, CDSD or HITEMP, we extract optical information about spectral lines and we calculate monochromatic gaseous absorption coefficients. Finally, according to the p and T values, we obtain the CO_2 absorbance.

3.2. "Solution" Code

This code, is a line shape models valid at high pressure. This tools take into account two different mechanisms: "line mixing" and far wings. The first study the interference of rotational states whene individual rotational lines overlap. In this case the net absorption coefficient of a molecular gas is obtained by adding absorption values caused by all vibrational bands. The equation that describe this

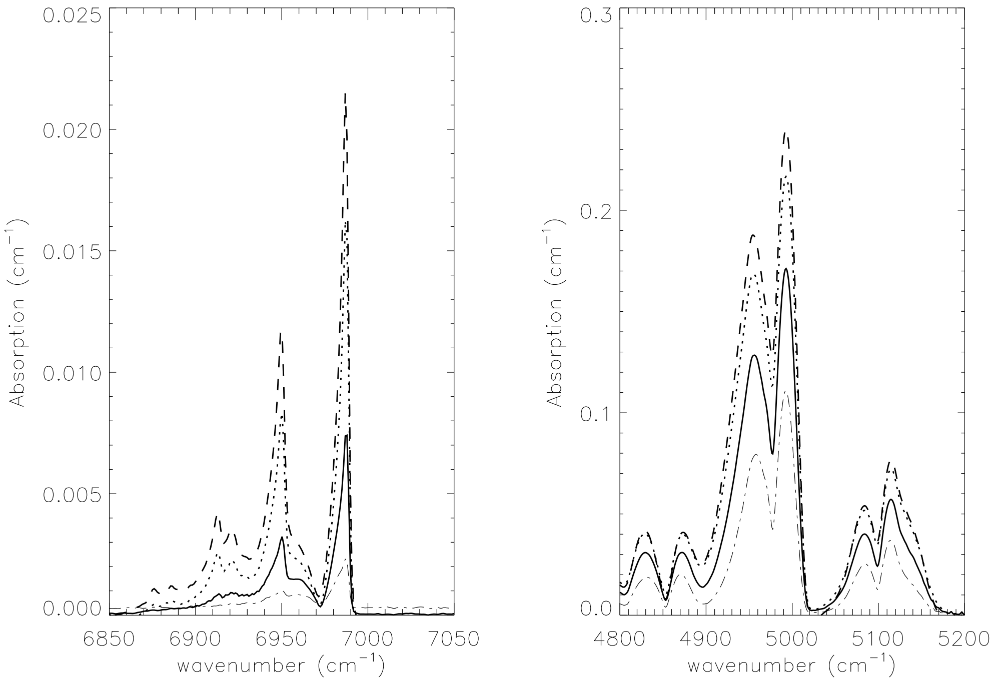

Fig. 1. CO_2 normalized absorption at different pressure and temperature. In the left the spectra at p≃1 bar and T≃349 K (dash dot), p≃5 bar and T≃429K (black curve), p≃15 bar and T≃544K (dotted) and p≃23 bar T≃583K (dashed). In the right the spectra at p≃9 bar and T≃502K (dash dot) p≃18 bar and T≃563K (black curve) p≃28 bar and T≃600k (dotted) and p≃32 bar T≃622K (dashed).Each spectrum is acquired with a resolution of 2 cm^{-1}

effect is reported in 2 (Afanasenko & Rodin 2007):

$$\kappa(\nu) = \sum_j F\left(\sum_i S_{i,j} f(\nu - \nu_i, \Delta_i^L, \Delta^D)\right) \qquad (1)$$

where i and j refer to the index bands and rotational transition respectively, S is the oscillator strength and Δ^L and Δ^D refer to the broadening factor due to the collisional and Doppler respectively. The second effect is a dense, short-pathlengths intermolecular collisions, which determine ”far wings” of spectral lines and are believed to reveal non-Poisson statistics. The far wing profile is formed in dense collision and is determined by the rapidly growing region of the potential intermolecular interaction, with different regions of the potential dominating at different offset frequencies (Afanasenko & Rodin 2005). The inner part of the line profile is drawn by a Lorentz shape and the outer part by the equation 2:

$$f = \frac{1}{R_s} \frac{D_s * \delta\omega}{(\omega - \omega_0)^{\left(1+\frac{3}{A_s}\right)}} \qquad (2)$$

$$\int \frac{exp\left(-\epsilon\left(\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right)\frac{hc}{KT}\right)}{\sqrt{R_s^2 - r^2}}$$

where

$$R_s = \frac{C_s}{(\omega - \omega_0)^{\frac{1}{A_s}}} \qquad (3)$$

and A_s, D_s C_s are constants and parameterize all quantum-mechanical effects and do not depend on the thermo dynamical conditions.
ϵ and σ are parameters which occur in the

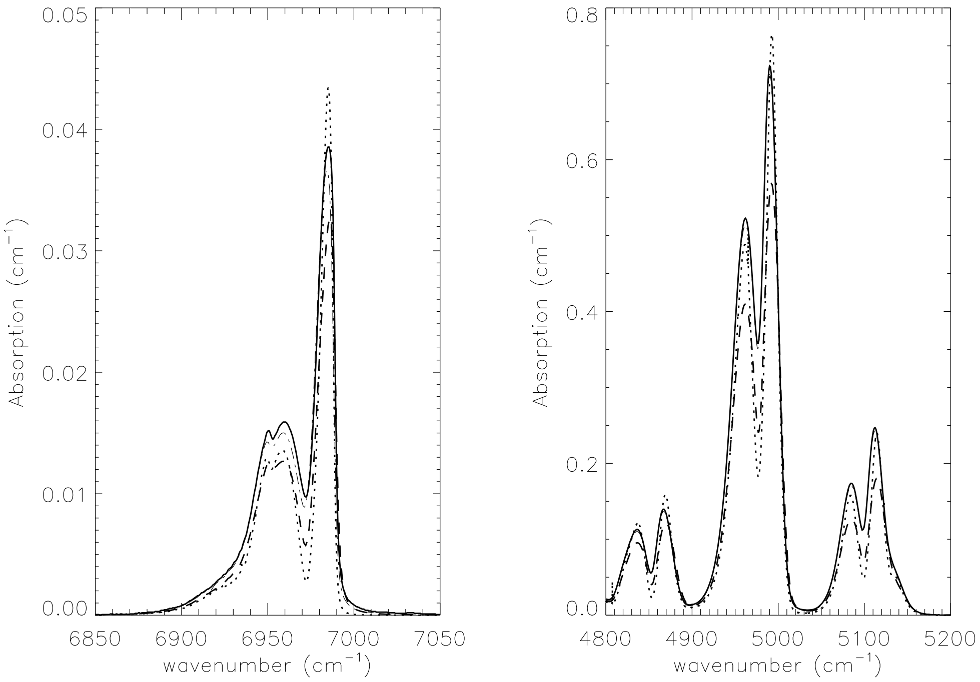

Fig. 2. Comparison between data(dashed curve) and synthetic spectra obtained by ARS CODE (dashed dot dot curve), Solution Code (dashed dot curve) and "Line mixing" model (dotted curve). In the left panel the CO_2 absorption at p≃20 bar and T≃294K, in the right at p≃40 bar and T≃373K.

expression for the Lennard-Jones potential (Byron Bird &, Warren 1979).

3.3. "Line mixing" model

The model accounts for the lines interferences due to inter-molecular collisions (or line-mixing), which have a very important influence on the spectral shape. Assuming the impact approximation, the absorption coefficient is a function of the wave number σ, of the CO_2 density N and of the temperature T. In this approach, we neglect Doppler effects and the influence of mean velocity and velocity changes induced by collisions. For a detailed description refer to (Tran et al. 2010).

4. Results

For each point of VIRA profile, representing a single thin layer of the Venus atmosphere, we measured the CO_2 absorbance. Some experimental spectra, acquired with a resolution of 2 cm^{-1}, are shown in Fig. 1. In this figure you can see the bands intensity increasing found to be with the pressure. This effect should be proportional with it. The width of the bands is weakly temperature dependent.

The measurements have been compared with synthetic spectra obtained from three different models, described in subsection 3.1, 3.2 and 3.3. Comparisons between experimental and simulated spectra are reported in Fig. 2. We calculated the integrated band area in different spectral range and evaluated the difference between data and synthetic spectra, in order to quantify the matching. Results are reported in Table 1. As you can see we have

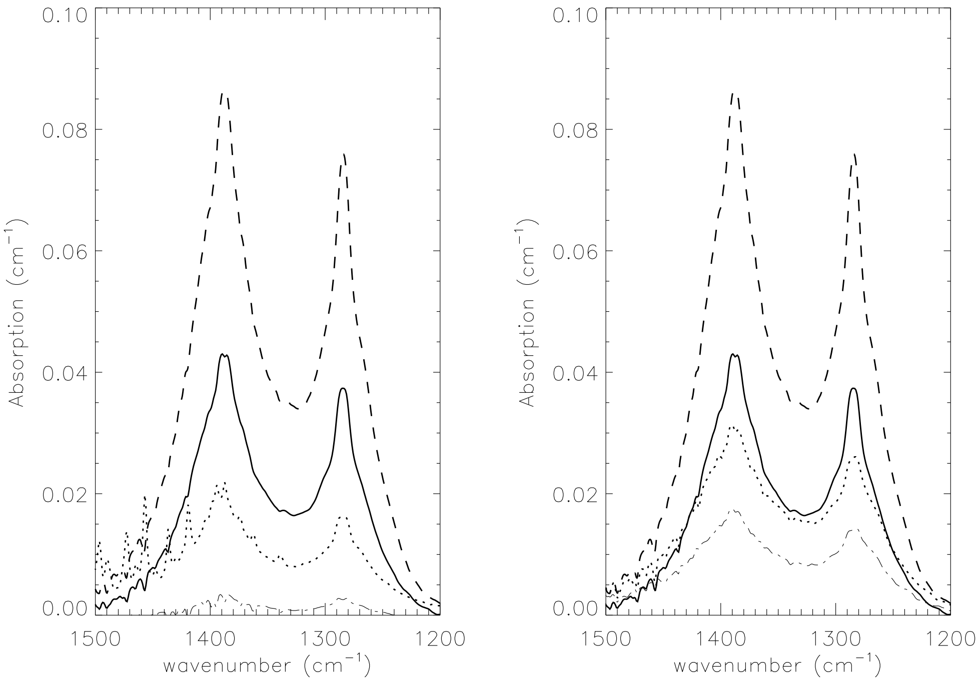

Fig. 3. Collision Induced Absorption (CIA) bands at different pressure and temperature. On left the spectra at p≃ 10, 20 30 and 40 bar and T≃ 294K. On right the spectra at p≃ 30 bar and T≃ 373K, p≃ 40 bar and T≃ 373K, p≃ 30 bar and T≃ 294K, p≃ 40 bar and T≃294 K

the best fit with the "Line mixing" model, in fact differences between our data and synthetic spectra are smaller respect to the other models. In some cases (see the 2^{nd} column of the 2^{nd} row in the Table 1) the difference is smaller than 0.003 %. This result leads us to conclude that for gases under extreme conditions, the shape of the spectral lines no longer follows the conventional Voigt form and that it is mandatory to take into account the line mixing effect to reduce the discrepancy.

During the campaign of measurements we observed several absorption bands which are strictly forbidden due to the symmetry of the CO_2 molecule. In low density conditions this molecule has not electrical transition dipole moment but, when we increase the pressure, we have strong collisions between CO_2-CO_2 atoms that induce a dipole. This phenomenon is called Collision Induced Absorption (CIA). We observed intense bands due to CIA, in different spectral range (see the Fig. 3). In principle, the CIA is found to be temperature dependent and the band integrated area shows a quadratic behavior versus density.

5. Conclusions

CO_2 spectra have been measured for a wide range of temperatures and pressures for a large spectral range. We were able to measure the optical properties of Venus atmosphere from an altitude of 50 km down to 15 km. Our results will be used to improve the radiative transfer modeling for remote sensing data analysis. Comparison of data and models led us to conclude that for gases at extreme conditions is necessary to consider the "line mixing" effect and intermolecular collisions for a better agreement. In this case the "Line mix-

Table 1. Integrated bands area. (LM), (SC) and (AC) refer to the "Line Mixing" model, Solution Code and Ars Code

Data (M) (cm^{-1})	Area (LM) (cm^{-1})	Area (SC) (cm^{-1})	Area (AC) (cm^{-1})	Spectral Range (cm^{-1})
1.605	1.559	2.573	1.4191	[2115-2025]
1.044	1.048	0.729	0.853	[7050-6880]
0.149	0.146	0.096	0.098	[8350-8150]
52.163	52.115	43.664	41.967	[4800-5200]
0.909	0.861	0.713	0.679	[6100-6500]
1.516	1.513	1.19	1.213	[6850-7050]
	$\Delta(M-LM)$ (%)	$\Delta(M-SC)$ (%)	$\Delta(M-AC)$ (%)	Spectral Range (cm^{-1})
	0.046	0.968	0.114	[2115-2025]
	0.004	0.245	0.191	[7050-6880]
	0.003	0.053	0.051	[8350-8150]
	0.048	8.499	10.196	[4800-5200]
	0.048	0.196	0.196	[6100-6500]
	0.003	0.326	0.285	[6850-7050]

ing" model show a best fit with data. In our measurements we identified absorption features due to CIA that will be better quantified once that the line mixing model is considered appropriate to interpret the data. This is especially important to support the data exploring the deep atmosphere of Venus, as for example the data from the Visible and infraRed Thermal Imaging Spectrometer (VIRTIS) the ESA Venus Express mission.

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