Planetary and Space Science ∎ (∎∎∎∎) ∎∎∎–∎∎∎

Contents lists available at ScienceDirect

Planetary and Space Science

journal homepage: www.elsevier.com/locate/pss

Planetary Pioneers Series

Carbon dioxide opacity of the Venus' atmosphere

Marcel Snels [a,*], Stefania Stefani [b], Davide Grassi [b], Giuseppe Piccioni [b], Alberto Adriani [b]

[a] Istituto di Scienze dell'Atmosfera e del Clima (ISAC) - Consiglio Nazionale delle Ricerche (CNR), Rome, Italy
[b] Istituto di Astrofisica e Planetologia Spaziali (IAPS) - Istituto Nazionale di AstroFisica (INAF), Rome, Italy

ARTICLE INFO

Article history:
Received 22 March 2014
Received in revised form
29 July 2014
Accepted 2 August 2014

Keywords:
Carbon dioxide
Absorption
Collision induced
Continuum
Opacity

ABSTRACT

Venus' atmosphere consists of about 95% of carbon dioxide, which accounts for most of the absorption of the radiation emitted by its hot surface. The large densities and high temperatures of Venus' atmosphere make the absorption much more complex than for low density atmospheres such as Earth or Mars. Available experimental data are at present insufficient and theoretical models inadequate to describe complex absorption line shapes and collision-induced phenomena. Here we present a survey of all absorption and scattering processes which influence the transparency of Venus' atmosphere for what concerns carbon dioxide.

Contents

1. Introduction

Venus has often been considered a twin planet of the Earth, although many differences exist. Venus' atmosphere consists mainly of carbon dioxide, which causes a strong greenhouse effect, by capturing most of the radiation emitted by the planet. The temperature at the surface is about 730 K, and the pressure is about 90 atm. An important part of what we know at present about Venus is due to observation of radiation both from the Earth and from spacecraft. Carbon dioxide, being the major absorber, conditions the observation of minor gases, clouds and the surface, which are mainly observed in spectral windows being partially transparent to carbon dioxide absorption.

The opacity of Venus' atmosphere is mainly due to the absorption by its main constituent, carbon dioxide, and to a lesser extent to absorption by water vapor and other trace species (CO, SO_2 HF, HCl, HBr, HI, and others) and by the cloud opacity. A proper understanding of the carbon dioxide opacity is necessary in order to model radiative transfer through the atmosphere of Venus. The cloud opacity depends on wavelength and plays an important role at wavelengths greater than 2.5 μm (Pollack et al., 1993), while the near infrared region is relatively transparent. While carbon dioxide absorbs most of the radiation emitted by the surface for mid-infrared wavelengths, some spectral transparency windows occur at near infrared wavelengths (1.10, 1.18, 1.27, 1.31, 1.74 and 2.3 μm). The opacity of these windows can be divided into gaseous opacity, due to the absorption and scattering of gases, and cloud opacity. The gaseous opacity can be further divided into absorption by dipole allowed absorption bands and collision-induced or continuum opacity. The continuum opacity is caused by transitions which occur due to the interaction of the absorbing molecule with another molecule, and is thus proportional to the square of the density. In this definition not only collision-induced absorption

* Corresponding author.
E-mail address: m.snels@isac.cnr.it (M. Snels).

http://dx.doi.org/10.1016/j.pss.2014.08.002
0032-0633/

bands contribute to the continuum absorption, but also the dimer absorption and far wings of allowed bands do so.

The pioneering work of Pollack et al. (1993) describes the analysis of ground based Venus' nightside thermal emission in terms of carbon dioxide continuum opacity. The near-infrared windows of the nightside of Venus have also been exploited to determine the water content of the deep atmosphere. A detailed study of high resolution spectra recorded in the spectral transparency windows at 1.1, 1.18, 1.27, 1.31, 1.74 and 2.3 μm by using the Fourier Transform Spectrometer at the 3.6 m Canada–France–Hawaii telescope revealed H_2O mixing ratios of about 30 ppm in the 30–40 km altitude range. The analysis was based on a line-by-line radiative transfer model including permitted CO_2 bands, and an additional opacity assumed to be proportional to the square of the CO_2 density (de Bergh et al., 1995).

With the advent of spectral information from satellite-borne (Galileo, NIMS, Pioneer, Venera, Venus Express) instruments, a wealth of data has become available for analysis. Recently Bailey (2009) reported a review of water vapor mixing ratios in the Venus deep atmosphere, determined from nightside spectra in the 1.18, 1.27, 1.74 and 2.3 μm transparency windows recorded by different instruments. Very recently, Bézard and de Bergh (2007) and Bézard et al. (2009, 2011) analyzed the 1.10 and 1.18 nightside windows observed by SPICAV and VIRTIS in order to determine the water vapor mixing ratio. They determined a water vapor mixing ratio of 30 ppm continuum between 5 and 25 km while assuming a carbon dioxide binary absorption coefficient of $7(2)\times 10^{-10}$ cm^{-1} amagat^{-2} for both transparency windows.

Laboratory experiments at room temperature in the 1.18 μm window have been reported by Snels et al. (2014). They performed cavity ring down measurements on pure carbon dioxide and on mixtures of carbon dioxide with small water vapor mixing ratios (40 ppm) and determined a binary absorption coefficient of $5.47(28)\times 10^{-10}$ cm^{-1} amagat^{-2} at 1180.7 nm.

Dipole allowed absorption of carbon dioxide is well understood for what concerns the central part of the bands, including line mixing effects, but lineshapes at high pressure are difficult to model and are often treated in a semi-empirical way. Collision-induced bands have been observed in Venus' atmosphere and in laboratory, but a theoretical model to describe intensities, line shapes and temperature behavior is not yet available. As a result the so-called continuum absorption, including far wings and collision-induced absorption, becoming important at high densities, although in principle theory has been developed to deal with all collision-induced processes (Hartmann et al., 2008), is still difficult to simulate due to the lack of feasible calculations, except for the far infrared region. More experimental measurements are required in order to test model calculations and to fit empirical models. Here we will present a survey of the current state of spectroscopic knowledge concerning carbon dioxide absorption in dense and hot atmospheres, both from a theoretical and an experimental point of view. A concise introduction will be given for what concerns the effect of collisions on molecular spectra and the various theoretical efforts to deal with these, but for a more general background we refer to an excellent review by Hartmann et al. (2008), while the collision-induced absorption in gases has been extensively discussed in Frommhold (1993) and van Kranendonk (1957, 1958, 1974).

2. Absorption by carbon dioxide

2.1. Linear absorption by carbon dioxide

The absorption spectrum of carbon dioxide is well documented and is based on a wealth of spectroscopic data obtained with a variety of experimental techniques. Theoretical studies have been performed with the goal to model and predict line positions and intensities. An effective Hamiltonian has been developed, for a global fit of about 13,000 experimental line positions initially for the major isotopomer of carbon dioxide, $^{12}C^{16}O_2$ (Tashkun et al., 1998) but subsequently extended to other, also asymmetric isotopomers (Tashkun et al., 2000, 2001). The global treatment of vibrational–rotational states of a molecule allows us to calculate rovibrational levels which have not yet been explored by experiment and thus predict rovibrational transitions, which have not yet been measured. The effective Hamiltonian coupled with the effective dipole moment approach can be used to calculate line intensities with a good precision, up to within a few percent of the measured values (Perevalov et al., 1995; Tashkun et al., 1999). During the last few decades effective Hamiltonians have been developed to perform global fits of experimental lines for symmetric ($^{13}C^{16}O_2$, Tashkun et al., 2000) and non-symmetric carbon dioxide isotopomers ($^{16}O^{13}C^{18}O$, Ding et al., 2003; $^{16}O^{12}C^{17}O$ and $^{16}O^{12}C^{18}O$, Tashkun et al., 2001).

The availability of line positions and intensities is a necessary, but not sufficient ingredient for the simulation of absorption spectra in planetary atmospheres. Collisions between absorbing molecules with other molecules (which can be absorbers or not) are important for line shapes, line mixing, collision-induced absorption and dimer formation. Pioneering work has been done by Anderson (1949), Tsao and Curnutte (1962), Welsh et al. (1949), Welsh (1972), van Kranendonk (1952, 1957, 1958, 1974), van Kranendonk and Kiss (1959), Robert and Bonamy (1979) and many others to develop a theory which can account for line broadening, Dicke narrowing and collision-induced absorption.

Generally several assumptions are made such as limiting the problem to binary collisions involving non-reactive molecules in local thermal equilibrium conditions. Moreover most theories have been developed in the impact approximation, which means that the duration of the collision is short with respect to the time between successive strong collisions and small with respect to $1/(2\pi|\nu-\nu_0|)$, which implies that only wavelengths are considered relatively close to the center wavelength ν_0. Another approximation is that the velocities during the collisions are constant and that the collision parameters possess no velocity dependence. This allows us to treat the Doppler broadening and the pressure broadening independently and to obtain a Voigt line shape, which is a convolution of a Gaussian and a Lorentzian line shape. For low respectively high pressure the Voigt line shape becomes approximately a Gaussian respectively Lorentzian line shape. When one takes into account velocity changes due to the collisions and a velocity dependence of the broadening parameters, more complex line shapes have to be used, which present small, but significant deviations from the Voigt line shape, such as the Galatry line shape (soft collision) and the Nelkin–Ghatak and Rautian line shape (hard collision). An intercomparison of measured pressure broadening and pressure shifting parameters of carbon dioxide has been reported recently by Gamache et al. (2014). The authors discuss the effect of the line shape models used on the half widths obtained. The rotational and the vibrational dependence of the half widths have also been discussed by these authors. In conclusion they state that the temperature dependence of the broadening parameters is not well documented and that a great experimental effort is required to produce these data.

A very thorough review on the collisional effects on molecular spectra has been given by Boulet (2004) and Hartmann et al. (2008).

Up to so far isolated lines have been considered, but when broadened lines start to overlap one has to take line mixing into account. Line mixing occurs, due to transfer of vibrational and/or rotational energy within the absorber during the collision, thus transferring line intensity within the spectral manifold involved.

Please cite this article as: Snels, M., et al., Carbon dioxide opacity of the Venus' atmosphere. Planetary and Space Science (2014), http://dx.doi.org/10.1016/j.pss.2014.08.002