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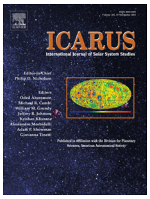

CO concentration in the upper stratosphere and mesosphere of Titan from VIMS dayside limb observations at 4.7 μm

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ABSTRACT

During the last 30 years, many works have focused on the determination of the CO abundance in Titan's atmosphere, but no measurement above 300 km has been done yet due to the faint signal of CO. Nevertheless, such measurements are particularly awaited as a confirmation of photochemical models predictions that CO is uniformly mixed in the whole atmosphere. Moreover, since CO is the main atmospheric reservoir of oxygen, its actual abundance has implications on the origins of Titan's atmosphere. In this work, we analyse a set of Cassini VIMS daytime limb observations of Titan at 4.7 μm, which is dominated by solar-pumped non-LTE (non-local thermodynamic equilibrium) emission of CO ro-vibrational bands. In order to retrieve the CO abundance from these observations, we developed a non-LTE model for the CO vibrational levels. The retrieval of the CO concentration is performed following a bayesian approach and using the calculated non-LTE populations. The data set analysed consists of 47 limb scanning sequences -about 1500 spectra- acquired by VIMS in 2006 and 2007. CO relative abundance profiles from 200 to 500 km are obtained, for each set analysed. The mean result shows no significant variations with altitude and is consistent with the prediction of a well-mixed vertical profile. However, if compared with Earth-based mm measurements, a small vertical gradient is plausible.

1. Introduction

Since the discovery of carbon monoxide in Titan's atmosphere (Lutz et al., 1983), the determination of its abundance has been the focus of many investigations and has stimulated an intense scientific debate. To date, only three molecules carrying oxygen have been detected in the atmosphere of Titan: CO_2, CO and H_2O. Among them CO is by far the most abundant, with a relative abundance of about 5×10^{-5}, compared with about 1.5×10^{-9} for CO_2 and 4×10^{-10} for H_2O.

The presence of CO in Titan's atmosphere has been a mystery for many years. CO molecule is substantially inert in Titan's environment, with an estimated chemical lifetime of the order of 10 kyr, and it does not condense even at tropospheric temperatures (Wilson and Atreya, 2004). Its extremely large bond energy of 10.7 eV makes CO difficult to be photolized by radiation, since hard UV photons are absorbed by the much more abundant N_2. Therefore, photodissociation is negligible with respect to other loss processes (Hörst et al., 2008; Wilson and Atreya, 2004). The main loss process of CO is the production of CO_2 through the reaction:

$$CO + OH \rightarrow CO_2 + H. \quad (1)$$

Most of the CO_2 produced is then photodissociated and essentially recycled back to CO (Wilson and Atreya, 2004). According to models, a minor part of CO_2 condenses at the cold Titan's tropopause and its deposition on the surface represents a sink for atmospheric oxygen, which is not at equilibrium on Titan. The overall net losses in the atmosphere for CO are due almost exclusively to CO_2 condensation and account for 1.8×10^{6} cm^{-2} s^{-1} (Hörst et al., 2008). This loss rate has to be compared with a total CO column of about 1.4×10^{22} cm^{-2}, corresponding to a uniform 50 ppmv CO fraction.

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This small net loss of oxygen means that either CO is not in a steady state in the atmosphere and is the remnant of a larger primordial concentration (Wong et al., 2002), or there is some active oxygen source in Titan's atmosphere. This 30-years-old question has been finally addressed by Hörst et al. (2008), who proposed that the observed CO abundance could be explained by the O^+ influx from Saturn's magnetosphere, measured by CAPS (Hartle et al., 2006). Following Hörst et al., many photochemical models assume now that CO is produced in the upper atmosphere around 1000 km through the reaction of O atoms with CH_3 (Krasnopolsky, 2009; Lara et al., 2014; Dobrijevic et al., 2014):

$$O + CH_3 \rightarrow CO + H_2 + H \tag{2}$$

However, since the photochemical production and losses of CO are extremely slow and its molecular mass is equal to that of N_2, CO is efficiently diffused throughout the atmosphere by eddy processes. Therefore, photochemical models predict a uniform CO volume mixing ratio (VMR) profile with no significant latitudinal and seasonal variations.

While there is now quite a good agreement on a 50 ppmv CO VMR, at least in the lower stratosphere, some previous Earth-based measurements have led to contradictory results. Observing the absorption of solar reflected radiation in the 4.7 µm region, Noll et al. (1996) concluded that tropospheric CO VMR was about 10 ppmv. More recently, the same absorption has been re-analysed by Lellouch et al. (2003) and López-Valverde et al. (2005), leading to a tropospheric relative abundance of 32 ± 10 ppmv; in the latter a non-LTE model of CO excited states was developed and the result suggested a larger abundance in the stratosphere, about 60 ppmv.

Rotational transitions of CO on Titan have been observed from Earth by many authors in the past 30 years (Muhleman et al., 1984; Gurwell and Muhleman, 1995; Hidayat et al., 1998; Gurwell and Muhleman, 2000; Gurwell, 2004), and most of these works agree very well with a 50 ppmv value for CO VMR. More recently, Serigano et al. (2016) have analysed ALMA observations of CO rotational lines and confirm the value of 49.6 ± 1.8 ppmv with a low uncertainty. These works were mostly sensitive to the lower stratosphere, between 100 and 300 km, and assumed a uniform CO VMR profile. Some of them, however, also attempted to derive the vertical distribution of CO, even with a low resolution. Hidayat et al. (1998) found a profile varying from 27 ppmv in the lower stratosphere to 5 ppmv at 300 km, while Gurwell and Muhleman (2000), using interferometric observations of the CO 2–1 rotational line, obtained an uniform 52 ± 2 ppmv profile as the best fit. However, their measurements were also compatible with a CO profile ranging from 48 ppmv in the lower stratosphere to 60 ppmv in the upper stratosphere at 300 km.

The beginning of the Cassini era has shed new light on many aspects of Titan's atmosphere and new analysis on CO are now available. The Composite Infrared Spectrometer (CIRS) and the Visual and Infrared Mapping Spectrometer (VIMS) aboard Cassini have both allowed new studies on CO. The former, by observing CO rotational lines in the far infrared 0.1 – 0.5 mm region and, the latter, by observing IR vibrational emission bands near 4.7 µm. Three results based on limb and nadir observations by CIRS have been reported to date, with CO abundances in the lower stratosphere of 45 ± 15 ppmv, 47 ± 8 ppmv and 55 ± 6 ppmv, respectively (Flasar et al., 2005; De Kok et al., 2007; Teanby et al., 2010); all assuming that the CO VMR is constant with altitude and with a significant contribution function between about 60 and 140 km.

The 4.7 µm band of CO is situated at the longest wavelength edge of VIMS spectral range, where the noise level and the background produced by the instrument's thermal radiation are larger. Nevertheless, to date, three works have been published based on VIMS measurements, either on the CO extinction during solar occultations (Bellucci et al., 2009; Maltagliati et al., 2015) or on thermal emission in the night side (Baines et al., 2006). They report a CO abundance in the lower stratosphere of 33 ± 10 ppmv (at 100 ± 30 km), 46 ± 16 ppmv (60-180 km) and 32 ± 15 ppmv (below ∼ 200 km), respectively.

Although most recent works do agree on a CO VMR of about 50 ppmv in the lower stratosphere (Gurwell and Muhleman, 2000; De Kok et al., 2007; Maltagliati et al., 2015; Serigano et al., 2016), the observational confirmation of the predicted well-mixed vertical profile is still awaited, because of contradictory results (Hidayat et al., 1998; López-Valverde et al., 2005).

The aim of this work is to retrieve the vertical distribution of CO from VIMS daytime measurements. The strong non-LTE solar pumping of the CO vibrational levels near 4.7 µm during daytime produces a strong limb radiance at these wavelengths that allows to retrieve CO up to high altitudes. Thus, we aim at measuring CO in the altitude range between 200 and 500 km, where it has not been measured yet, and hence to shed some light on the CO origin in Titan's atmosphere.

In Section 2 we describe the selection and calibration of the analysed data; in Section 4 we describe the non-LTE model for CO; in Sections. 5 and 7 we describe the analysis method and results; and, finally, in Section 8 we draw our conclusions.

2. VIMS observations of CO 4.7 µm emission

VIMS is an imaging spectrometer aboard Cassini working at visible and near-infrared wavelengths from 0.3 to 5.1 µm. The spectral resolution in the infrared region ranges between 15 and 20 nm, depending on the band considered. The instrumental line shape (ILS) is gaussian, with a slight deviation consisting in two small lobes beside the gaussian, accounting for less than 2% of the main window (Brown et al., 2004). VIMS takes hyper-spectral images, organised in cubes with two spatial and one spectral dimension: each cube contains a maximum of 64 × 64 pixels with 256 spectral bands; each pixel has a field of view of 0.5 by 0.5 mrad, in the nominal mode.

2.1. Data overview

In this work we analyse VIMS observations above Titan's limb, focusing on the long wavelength part of VIMS spectral range, from 4.2 µm to 5 µm. Various examples of average spectra are shown in Fig. 1 where we can see that the signal depends strongly on both the tangent altitude and the solar zenith angle (SZA) at the tangent point. Two main molecular emissions contribute to the spectrum: the peak at 4.55 µm is clearly a signature of the Q branch of CH_3D ν_2 band (the $2\nu_6$ band contributes as well), while the emission between 4.6 and 4.9 µm is mainly due to the fundamental, first hot and isotopic bands of CO. The shape of the CO signature changes with the tangent altitude: the hot band (centred at 4.72 µm) is the main responsible of the signal at low altitudes, whereas the fundamental band (centred at 4.67 µm) dominates the spectra above 400 km. We discuss this issue in more detail in Section 5.1. The continuum-like signal, which is due to the scattering of the solar radiation by Titan's aerosols, gives a non-negligible contribution at tangent altitudes lower than 300 km, thus constituting a major complication in the data analysis.

The vibrational excited states of the CO molecule are strongly out of LTE in Titan's middle atmosphere during daytime. The lower panel of Fig. 1 shows the average of a large set of VIMS spectra at 350 ± 25 km tangent altitude, for different SZAs. At smaller SZAs the continuum due to scattering increases and, at the same time, the intensity ratio between the CO and CH_3D bands changes. The CO emission is stronger with the sun higher above the horizon, when the solar radiation produces a larger pumping of the excited levels. This can be better appreciated in Fig. 2, where we show the