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## Oxygen compounds in Titan's stratosphere as observed by Cassini CIRS

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#### **Abstract**

We have investigated the abundances of Titan's stratospheric oxygen compounds using  $0.5~\rm cm^{-1}$  resolution spectra from the Composite Infrared Spectrometer on the Cassini orbiter. The CO abundance was derived for several observations of far-infrared nadir spectra, taken at a range of latitudes (75° S–35° N) and emission angles (0°–60°), using rotational lines that have not been analysed before the arrival of Cassini at Saturn. The derived volume mixing ratios for the different observations are mutually consistent regardless of latitude. The weighted mean CO volume mixing ratio is  $47 \pm 8~\rm ppm$  if CO is assumed to be uniform with latitude.  $H_2O$  could not be detected and an upper limit of 0.9 ppb was determined.  $CO_2$  abundances derived from mid-infrared nadir spectra show no significant latitudinal variations, with typical values of  $16 \pm 2~\rm ppb$ . Mid-infrared limb spectra at 55° S were used to constrain the vertical profile of  $CO_2$  for the first time. A vertical  $CO_2$  profile that is constant above the condensation level at a volume mixing ratio of 15 ppb reproduces the limb spectra very well below 200 km. This is consistent with the long chemical lifetime of  $CO_2$  in Titan's stratosphere. Above 200 km the  $CO_2$  volume mixing ratio is not well constrained and an increase with altitude cannot be ruled out there.

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#### 1. Introduction

Three oxygen compounds have previously been detected in Titan's stratosphere:  $CO_2$ ,  $H_2O$  and CO. Carbon dioxide in Titan's stratosphere was first detected by the Voyager IRIS instrument (Samuelson et al., 1983). More detailed analysis of Voyager data and analysis of data from the Infrared Space Observatory (ISO) and from Cassini Composite Infrared Spectrometer (CIRS) show a mixing ratio of 15–20 ppmv (Coustenis et al., 1989, 2003; Flasar et al., 2005). The temperature and pressure at Titan's tropopause are such that condensation occurs, providing a sink for  $CO_2$ . Therefore, the equilibrium stratospheric abundance of  $CO_2$  would be expected to be the same as the

saturation level at the tropopause if  $CO_2$  originates from below the tropopause. Instead, the observed values are at least a thousand times larger, indicating that  $CO_2$  is replenished in the stratosphere. The most effective way to produce  $CO_2$  is via the following chemical reaction:

$$CO + OH \rightarrow CO_2 + H. \tag{1}$$

This scheme requires (i) a sufficient abundance of CO, and (ii) a source of oxygen in the form of OH. The OH radical can be formed from photolysis of H<sub>2</sub>O, or from reactions involving CO and CH<sub>4</sub> (Samuelson et al., 1983). CO is one of the more abundant trace gases in Titan's atmosphere (see below), so the first condition is satisfied. Also, water ice is common in the Solar System and a continuous stream of icy dust particles falling into the atmosphere could provide the oxygen. This mechanism was previously suggested to explain the oxygen source for the giant planets (Feuchtgruber et al., 1997). These dust particles

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heat up in the atmosphere, leaving a trail of gas along their way. An attempt to model the effect of infalling dust particles is presented by English et al. (1996). They show that most of the resulting vapours are deposited high in Titan's atmosphere over a broad range of altitudes centred around 750 km. At these high altitudes H<sub>2</sub>O can be readily destroyed by ultraviolet radiation, creating the OH radical needed to produce CO<sub>2</sub>. CO<sub>2</sub> is only slowly destroyed in the stratosphere, with a chemical lifetime of several hundred years (Wilson and Atreya, 2004).

Not all water molecules are destroyed and converted to CO<sub>2</sub>. According to photochemical models (e.g., Lara et al., 1996; Wilson and Atreya, 2004) a significant amount of water should remain high in the atmosphere, with the abundance quickly dropping with decreasing altitude. A dedicated observation with the Earth-orbiting infrared telescope ISO, using its high spectral resolution and high sensitivity, confirmed the existence of water vapour in Titan's stratosphere at 0.4 ppb, assuming that H<sub>2</sub>O is constant above the saturation level (Coustenis et al., 1998). Like CO<sub>2</sub>, H<sub>2</sub>O also condenses at the tropopause. However, unlike CO<sub>2</sub>, H<sub>2</sub>O has a relatively short lifetime against photolysis (of the order of 5 years; Coustenis et al., 1998) and thus a continuous influx is needed to achieve a steady state abundance that is consistent with observations.

CO is very stable in Titan's atmosphere: it has a chemical lifetime of 500 Myr (Lellouch et al., 2003) and it does not condense at the tropopause. CO is thus expected to be uniformly mixed throughout the entire atmosphere in an equilibrium situation, since the timescale of mixing is much smaller than that of the destruction of CO. Previous observations of CO in Titan's atmosphere (summarised in Table 1) have not conclusively confirmed such a uniform profile. Despite the multitude of observations at various wavelengths, there is no consensus on the mixing ratio and vertical profile of the gas. Although most of the observations that probe the stratosphere show a volume mixing ratio (VMR) of at least 50 ppm, Hidayat et al. (1998) derived a vertical profile that decreases with altitude. However, this profile does not fit subsequent 5 µm data from Lopez-Valverde et al. (2005). It is also inconsistent with CO concentrations derived by Gurwell and Muhleman (1995, 2000) and Gurwell (2004), which use the same CO rotational lines. The most reliable tropospheric CO concentration is most likely given by Lellouch et al. (2003), since they use improved lineshapes and improved 5 µm observations compared to earlier tropospheric measurements, according to the authors. However, their tropospheric VMR of  $32 \pm 10$  ppm is lower than that derived for the stratosphere, which is unexpected given that CO should not condense in Titan's atmosphere. Lopez-Valverde et al. (2005) find that a higher stratospheric CO mixing ratio ( $\sim$ 60 ppm) is required to match CO fluorescence emission at 5 µm. Thus, a depletion of CO in the troposphere cannot be ruled out, based on observations made so far. However, a physical mechanism that would explain a decrease in the troposphere has not yet been put forward.

The Composite Infrared Spectrometer (CIRS) on board the Cassini orbiter has the capability to study all three of the previously detected oxygen compounds (Flasar et al., 2004).  $CO_2$  has its  $\nu_2$  band in the mid-infrared (at 667.75 cm<sup>-1</sup>),

Table 1
Previous determinations of CO abundances in Titan's atmosphere [extended from Table 1 in Gurwell and Muhleman (2000)]

Altitude	CO VMR	Wavelength	Reference
	(ppm)		
Troposphere	$48^{+100}_{-32}$	1.57 μm	Lutz et al. (1983)
Troposphere	$10^{+10}_{-5}$	4.8 μm	Noll et al. (1996)
Troposphere	$32^{+10}_{-10}$	4.8 μm	Lellouch et al. (2003)
Stratosphere	$60^{+40}_{-40}$	2.6 mm	Muhleman et al. (1984)
Stratosphere	$2^{+2}_{-1}$	2.6 mm	Marten et al. (1988)
Stratosphere	$50^{+10}_{-10}$	2.6 mm	Gurwell and Muhleman (1995)
Stratosphere	$27^{+5}_{-5}$	2.6, 1.3, 0.9 mm	Hidayat et al. (1998)
Stratosphere	$52^{+6}_{-6}$	1.3 mm	Gurwell and Muhleman (2000)
Stratosphere	$51_{-4}^{+4}$	0.9 mm	Gurwell (2004)
Stratosphere	60	4.8 µm	Lopez-Valverde et al. (2005)
Stratosphere	$45^{+15}_{-15}$	150–500 μm	Flasar et al. (2005)

*Note*. The table shows a wide range of CO VMR values, giving rise to debates about the CO abundance and vertical profile.

whereas CO and  $H_2O$  have rotational lines in the far-infrared (between 10 and 300 cm<sup>-1</sup>). CIRS has three separate focal planes that together measure the infrared spectrum between 10 and 1400 cm<sup>-1</sup>. FP1 covers the far-infrared (10–600 cm<sup>-1</sup>) and has a single circular field-of-view (FOV) with a full-width half-maximum of 2.5 mrad. The mid-infrared is covered by FP3 (600–1100 cm<sup>-1</sup>) and FP4 (1100–1400 cm<sup>-1</sup>), which each comprise of an array of 10 pixels, each having a  $0.27 \times 0.27$  mrad FOV.

In this paper we use CIRS data with an apodised resolution of 0.5 cm<sup>-1</sup>, which is the maximum resolution obtainable by CIRS. We use downward viewing (nadir) observations, taken on multiple close approaches of Cassini with Titan, to obtain abundances and distributions with latitude of Titan's stratospheric oxygen compounds. We also use a horizontal viewing (limb) observation to constrain the vertical profile of CO<sub>2</sub>. Analysis of Titan's oxygen compounds with both a high spectral resolution and a high spatial resolution was not presented before in literature. Such an analysis gives a better view of the three-dimensional distribution of oxygen compounds on Titan.

#### 2. Observations

The FP3 nadir data that were used to obtain the latitudinal  $CO_2$  distribution consist of sequences of maximum 5330 spectra taken from observations lasting less than 16 h. Table 2 summarises the data used from each Titan flyby. For each observation sequence, spectra were averaged in bins with a width of  $10^{\circ}$  latitude and a spacing of  $5^{\circ}$  latitude to achieve Nyquist sampling.

The FP1 sequences used for determining CO and H<sub>2</sub>O abundances are summarised in Table 3. These sequences last up to 4 h. Their observation numbers refer to the flybys listed in Table 2.

To obtain information about the vertical profile of CO<sub>2</sub>, limb observations from the T6 flyby on 28 August 2005 were used. Limb observations probe the atmosphere at different altitudes.

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