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## The methane mole fraction in Titan's stratosphere from DISR measurements during the Huygens probe's descent

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#### ABSTRACT

We present a determination of the methane mole fraction in Titan's stratosphere using spectral measurements by the Upward Looking Infrared Spectrometer (ULIS) of the Descent Imager/Spectral Radiometer (DISR) aboard the Huygens probe. We analyzed the 1.4-µm band of methane for which a complete linelist, down to very low intensities, was recently made available. The DISR/ULIS measurements were used to derive the methane transmittance along the path from the probe to the Sun during the descent from 135 to 29 km. Fitting the transmittance ratios to remove residual instrumental effects, we derived a stratospheric methane mole fraction of 1.44 (+0.27/-0.11)%, taking into account random errors and uncertainties in the spectroscopic parameters. This value is fully consistent with the simultaneous measurement of the methane profile by the Huygens Gas Chromatograph/Mass Spectrometer (GCMS). It disagrees with the  $\sim$ 1% mixing ratio recently inferred from Cassini/CIRS spectra at low latitudes near 85 km. Possible reasons for the discrepancy and uncertainties in the methane spectroscopic parameters are discussed. © 2014 Elsevier Inc. All rights reserved.

#### 1. Introduction

Methane (CH<sub>4</sub>) is a key compound of Titan's atmosphere. In the troposphere, it is responsible for a methane cycle, which presents many similarities with the hydrological cycle on Earth with surface reservoirs, clouds and channels likely carved by methane rain. In the upper atmosphere, the dissociation of methane and dinitrogen gives rise to a wealth of photochemical compounds through neutral and ion chemistry. This complex chemistry eventually produces organic aerosols that fill Titan's atmosphere down to the surface and are important in the stratospheric energy balance. Characterizing the vertical and horizontal distribution of methane on Titan is thus important to understand Titan's global system with its complex interactions between chemistry, dynamics and meteorology.

There is only a limited number of measurements of the methane abundance in Titan's stratosphere. On 14 January 2005, the Gas Chromatograph Mass Spectrometer (GCMS) on the Cassini-Huygens probe determined the vertical profile of methane from 140 km altitude to the surface (Niemann et al., 2005, 2010). The CH<sub>4</sub> mole fraction was constant from the surface  $(5.65 \pm 0.18) \times 10^{-2}$  up to approximately 7 km. Above 7 km, the CH<sub>4</sub> mole fraction was found to decrease with altitude up to  $\sim$ 45 km and was constant in the stratosphere. The stratospheric

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140 km, is  $(1.48 \pm 0.09) \times 10^{-2}$ . This value is consistent with saturation above CH<sub>4</sub> ice near the temperature minimum. More recently, Lellouch et al. (2014) used spectra recorded by the Cassini Composite InfraRed Spectrometer (CIRS) to determine the methane abundance near ~85 km (15 mbar) and investigate its variation with latitude. This analysis is based on the combined analysis of nadir and limb spectra of the methane  $v_4$  band at 7.7  $\mu$ m and rotational lines beyond 65 µm, which allows us to disentangle methane abundance and temperature profile. A mole fraction as low as  $(0.95 \pm 0.08) \times 10^{-2}$  was derived for a spectral selection recorded in September-October 2006 at latitudes 13-17°S, close to the latitude of the Huygens landing site (10.3°S). This result seems inconsistent with the Huygens/GCMS value and reconciling the two would require that the absolute line strengths of the rotational lines are 20% weaker than measured by Boudon et al. (2010). Lellouch et al.'s analysis also shows evidence for significant variations of the  $CH_4$  mole fraction with latitude: from ~1.0% at low latitudes and near  $\pm 50-55^{\circ}$  to  $\sim 1.5\%$  at  $\pm 30-35^{\circ}$  and polar latitudes. A previous and preliminary analysis of a large average of CIRS spectra centered at 15°S and recorded on July 2, 2004, led to a 1.6 ± 0.5% CH<sub>4</sub> mole fraction (Flasar et al., 2005). This determination however bears large uncertainties due to the preliminary status of the data calibration and the large footprint of the field of view, which was encompassing a large range of latitudes and emission angles.

value, derived from an average of data recorded between 75 and









Information on the methane profile in the stratosphere and mesosphere is also available from solar occultations observed with the Cassini Visual and Infrared Mapping Spectrometer (VIMS). Analyzing of a solar occultation on 15 January 2006 at a latitude of 71°S, Bellucci et al. (2009) found that the absorption in the 2.3- $\mu m$  methane band was well fitted above 230 km with a constant mole fraction between 1.4 and  $1.7 \times 10^{-2}$ . However, the VIMS data below this altitude could not be reproduced with this mole fraction for reasons that are not really understood. More recently, Maltagliati et al. (2014) analyzed a set of Cassini/VIMS solar occultations recorded at 70°S (January 2006), 1°N (April 2009), 27°N (September 2011) and 40°N (September 2011). Fitting the 1.4and 1.7-µm methane bands between altitudes of 500 and 150 km. Maltagliati et al. derived a methane mole fraction of  $1.28 \pm 0.06 \times 10^{-2}$ , with no significant variation between the different occultations. The 2.3-µm band, used by Bellucci et al. (2009), leads to CH<sub>4</sub> mole fractions larger than derived from the 1.4- and 1.7-µm bands, which is attributed to an additional absorption by ethane, not included in the retrievals.

The Descent Imager/Spectral Radiometer (DISR) aboard the Huygens probe recorded upward-looking and downward-looking spectra of the ambient radiation at visible (0.48-0.96 µm) and infrared ( $0.85-1.7 \mu m$ ) wavelengths (Tomasko et al., 2005) during all the descent. The upward-looking spectra show several methane bands whose depth increases during the descent with decreasing altitude, due to increasing atmospheric path (Tomasko et al., 2008). In principle, these data can be used to derive the methane profile as they essentially measure the absorption of solar radiation by atmospheric methane above the probe. However this was not possible until now due to the lack of reliable spectroscopic data for methane shortward of 2 µm. Tomasko et al. (2008) actually took an inverse approach and used the methane profile measured by the GCMS (Niemann et al., 2005) to determine CH<sub>4</sub> absorption coefficients along the path from the probe to the Sun for the whole range 830-1620 nm.

The situation has vastly improved over the past years with the advent of a linelist of methane covering the range  $5852-7919 \text{ cm}^{-1}$  (1.263–1.709 µm) (Campargue et al., 2012, 2013). Positions and intensities were derived from spectra recorded at 80 K and at room temperature by Differential Absorption Spectroscopy (DAS) in the strong absorption regions and high-sensitivity Cavity Ring Down Spectroscopy (CRDS) in the more transparent regions. The spectral range covered by this list includes the 1.4-µm methane band observed by DISR.

In this paper, we present an analysis of the 1.4- $\mu$ m methane band observed by the Upward-Looking Infrared Spectrometer (ULIS) of DISR during its descent to the surface. We used the empirical linelist produced by Campargue et al. (2012, 2013) to model the methane absorption in this band during the descent and determine the methane mole fraction in the stratosphere. Section 2 describes the DISR/ULIS observations used in this study. In Section 3, we present the radiative transfer modeling and the spectroscopic parameters that are used to model the DISR/ULIS spectra. In Section 4, we derive the best fitting CH<sub>4</sub> mole fraction in the stratosphere and associated error bars. We discuss these results in Section 5 and present conclusions in Section 6.

#### 2. Observations

The DISR instrument included an Upward-Looking Infrared Spectrometer (ULIS) that covered the spectral range from 830 to 1620 nm during the descent through Titan's atmosphere (Tomasko et al., 2002). The ULIS was fed by fibers leading from the fore optics, that looked upward, to the slit plane of the spectrometer. A diffusing plate and external baffles limited the field of view (FOV) to 170° in azimuth and from 5° to 88° in zenith angle. The relative response of the ULIS is shown in Fig. 1 of Tomasko et al. (2008). A linear array of 150 detector elements was used, with 136 active elements measuring the radiation from 822.7 to 1717.6 nm and a wavelength step (i.e. interval between elements) decreasing from 7.3 to 6.0 nm. The spectral resolution of ULIS (Full Width at Half Maximum,  $\Delta\lambda$ ) varied slightly with the optics temperature and also over the spectral range. Above 90 km, the optics temperature was ~264 K, which yields  $\Delta\lambda$  ~16 nm between 1300 and 1500 nm, according to pre-launch calibration measurements. At 55 km, the optics temperature had dropped to 257 K and the spectral resolution increased to ~18.3 nm in this same spectral region. Details on the ULIS observations and calibration can be found in Tomasko et al. (2008).

ULIS collected data from an altitude of 141 km down to the surface (and after landing). Most spectra were obtained by integrating over several rotations of the probe. Data collection was managed by the Sun sensor system of DISR. However, due to the unexpected rotation direction of the probe, data were collected at random azimuth angles relative to the Sun rather at specified azimuths as planned. Following Tomasko et al. (2008, Section 5), we define f as the response of the FOV at the zenith angle of the Sun (0 if the Sun is not in the FOV) averaged over the azimuth angles of the integration sequence and normalized such that f=1 when the spectrum is collected with a uniform azimuth distribution from  $0^{\circ}$  to 360°. We selected the spectra for which f > 0.8, and thus had the Sun in the FOV for a significant fraction of the integration time. To increase the S/N ratio, we binned the spectra into eight altitude bins between 141 and 27 km. The bins vary from 126-141 km at the beginning of the measurements to 27-30 km at the bottom of our selection and contain 4-10 spectra each (Table 1). All bins except the lowest one are above the methane cold trap (near 40 km), above which the CH<sub>4</sub> mole fraction is expected to be constant. We averaged the spectra in each bin with a weight proportional to f and obtained the eight spectral averages shown in Fig. 1a.

The relative *I/F* intensity of the spectra does not only reflect the extinction of solar radiation during the descent. Differences between the spectra also arise from different values of  $\langle f \rangle$ , e.g. the spectrum with the highest I/F corresponds to the largest  $\langle f \rangle$ (1.418) as expected (Table 1). But this is not always the case. For example, the spectra at 77.4 and 64.9 km have similar  $\langle f \rangle$  but, near 1280 and 1580 nm (outside of the methane band), the I/F at 64.9 km is 15% larger than that at 77.4 km whereas the atmospheric extinction can only be larger. As discussed in Tomasko et al. (2008), we believe that this is due to the tips in attitude during descent, not taken into account here, and possibly inaccuracies in the azimuth information, which both affect the *f* parameter. To eliminate these geometry effects and extract the information on the methane absorption alone, it is thus required to work on the band depths themselves by ratioing the spectra to the continuum values derived from the I/F in the two nearby methane windows. This also allows us to remove the aerosol extinction, assuming that it varies smoothly over the spectral range of interest.

We proceeded essentially as in Tomasko et al. (2008, Section 5). For each spectrum, we defined two continuum values  $I_{1,c}$  and  $I_{2,c}$  at  $\lambda_1 = 1282$  and  $\lambda_2 = 1584$  nm respectively, by averaging the I/F intensity at 3 wavelengths around  $\lambda_1$  and around  $\lambda_2$ . We interpolated between the two values  $I_{1,c}$  and  $I_{2,c}$  to get a reference value  $I_c(\lambda)$  using Eq. (6) of Tomasko et al. (2008). We then divided the I/F intensities, noted  $I(\lambda)$ , by  $I_c(\lambda)$ . The residual methane absorption at the window wavelengths  $\lambda_1$  and  $\lambda_2$  was estimated by Tomasko et al. (2005), they derived linear absorption coefficients in the windows that yield averages of 0.009 and 0.039 km<sup>-1</sup> amagat<sup>-1</sup> over the 3 wavelengths centered at  $\lambda_1$  and  $\lambda_2$ . Following Campargue et al.

Table 1DISR/ULIS spectral selections.

| Altitude<br>range (km)                             | Number of<br>spectra   | Mean<br>value of <i>f</i> ª                  | Mean<br>altitude (km)                        | Solar zenith<br>angle (°)                    |
|--|------------------------|--|--|--|
| 126-141  | 5                      | 1.06   | 134.8  | 38.9   |
| 105-113  | 4                      | 1.42   | 109.5  | 37.6   |
| 87-94  | 5                      | 1.12   | 90.3   | 37.3   |
| 73-83  | 7                      | 0.95   | 77.4   | 37.1   |
| 63-67  | 7                      | 0.95   | 64.9   | 36.9   |
| 50-54  | 8                      | 1.04   | 52.1   | 36.4   |
| 38-42  | 8                      | 1.00   | 40.0   | 35.9   |
| 27-30  | 10                     | 1.22   | 28.5   | 35.3   |
| 87-94<br>73-83<br>63-67<br>50-54<br>38-42<br>27-30 | 7<br>7<br>8<br>8<br>10 | 1.12<br>0.95<br>0.95<br>1.04<br>1.00<br>1.22 | 90.3<br>77.4<br>64.9<br>52.1<br>40.0<br>28.5 | 37.5<br>37.1<br>36.9<br>36.4<br>35.9<br>35.3 |

<sup>a</sup> See text for definition of *f*.



**Fig. 1.** Averages of DISR/ULIS spectra recorded in various altitude ranges during the Huygens descent. a: Raw spectra expressed in *I/F* units; b: Spectra rescaled to represent the atmospheric transmittance toward the Sun due to methane only.

(2012), we added 0.024 km<sup>-1</sup> amagat<sup>-1</sup> to these values and calculated the corresponding absorption of the direct solar radiation for each ULIS spectrum. At 28.5 km, it amounts to only ~1% at 1282 nm and ~2% at 1584 nm. We multiplied  $I(\lambda)/I_c(\lambda)$  by a methane transmittance interpolated between those at  $\lambda_1$  and  $\lambda_2$  to correct the ratios for this residual methane opacity in the windows as in Tomasko et al. (2008, Section 5). The ratios  $S_i$  (i = 1, 8) are shown in Fig. 1b. Tomasko et al. (2008) showed that these intensity ratios in the methane bands do not depend on the *f* factor or on the mean azimuth of the Sun provided that *f* is larger than typically 0.5. This means that scattering effects are minimized, the direct flux being dominant over the scattered radiation, so that the ratios in Fig. 1b represent the direct atmospheric transmittance from the Sun to the probe due to methane only.

Note that, to produce these ratios, we made two additional corrections. We interpolated the intensities at 1496 and 1571 nm in the spectra at 40 and 52 km from those at adjacent wavelengths



**Fig. 2.** Ratios of DISR/ULIS methane transmittance spectra at different altitudes (lines with squares) are compared with calculations for a stratospheric CH<sub>4</sub> mole fraction of 1.48% and the E1500 methane linelist (solid lines). a: Observed and synthetic spectra are ratioed to a reference spectrum at  $z_1 = 134.8$  km; b: Observed and synthetic spectra at altitude  $z_i$  are ratioed to those at altitude  $z_{i-1}$ , where the  $(z_i)$  are the mean altitudes of DISR/ULIS spectra (Table 1). The  $z_2/z_1$  ratio, plotted in a is not plotted again in b for clarity.

as they show excess noise in the altitude range 35-60 km. We also subtracted 0.004 from all I/F (before ratioing) to correct for a bias in subtracting shutter open and closed sequences (see Tomasko et al., 2008).

The spectra in Fig. 1 look rather noisy but actually many features appear consistently in several spectra, such as an odd-even pixel variation below 1300 nm, a  ${\sim}5\%$  dip around 1500 nm, and a  $\sim$ 10% slope between  $\sim$ 1480 and  $\sim$ 1580 nm in high-altitude spectra. All these features are not expected from methane absorption and likely result from imperfect calibration. We then decided to work on ratios of spectra taken at different altitudes to remove systematic calibration errors. We considered two possible ratios:  $S_i/S_1$ (i = 2, 8) and  $S_i/S_{i-1}$  (i = 2, 8). The two data sets are shown in Fig. 2. In the first case, the methane band depths are more pronounced than in the second case, which is favorable in terms of S/N ratio, but they rely on the accuracy of a single reference spectrum (at 135 km). Any error or noise on the 135-km spectrum is propagated to all ratioed spectra. In the second case, the band depths are weaker but one can expect that a possible variation of the detector response during the descent is better accounted for.

#### 3. Radiative transfer model

Synthetic transmittance spectra were generated using a line-by-line radiative transfer model. The atmospheric grid consists of 96 levels equally spaced in log(p) between 1457 and

 $0.5 \times 10^{-2}$  mbar. The transmittance to the Sun was calculated as a function of altitude (*z*), between *z* and the top of our grid, considering spherical shells and taking into account the variation of the solar zenith angle with the altitude of the probe during the descent (Table 1). Spectra were calculated with a step of approximately  $3 \times 10^{-3}$  cm<sup>-1</sup>, less than half of the CH<sub>4</sub> Doppler width, and convolved with a Gaussian function of Full Width at Half Maximum (FWHM) of 85 cm<sup>-1</sup>, which corresponds to the DISR/ULIS resolution around 1.4 µm.

The temperature profile is that retrieved by Lellouch et al. (2014) from a selection of Cassini/CIRS spectra recorded near the latitude of the Huygens site during Flyby Tb (red line profile in their Fig. 11), assuming a methane mole fraction of 1%. This profile is fully consistent with the HASI thermal profile (Fulchignoni et al., 2005) below 150 km within error bars. Above 160 km, our profile is essentially constrained by the CIRS limb measurements and disagree somewhat with the HASI profile, which was derived from accelerometric measurements and is thus model-dependent and less reliable. The altitude profile is determined from the *T*(*p*) profile using the equation of hydrostatic equilibrium with a surface gravity of 135.4 cm s<sup>-2</sup>, mole fractions of 0.9425 (N<sub>2</sub>), 0.0565 (CH<sub>4</sub>) and 0.001 (H<sub>2</sub>) in the near-surface atmosphere, the CH<sub>4</sub> profile of Niemann et al. (2010), and taking into account the non-ideal behavior of N<sub>2</sub> gas, significant only in the lower troposphere.

The only significant molecular absorbers in the range 1250-1600 nm are CH<sub>4</sub>, CH<sub>3</sub>D and marginally CO. We extracted the CO line parameters from the GEISA-09 database (Jacquinet-Husson et al., 2011). Our linelists for CH<sub>4</sub> and CH<sub>3</sub>D are based on the work by Campargue et al. (2012, 2013). These authors recorded laboratory methane spectra at 80 K and 296 K between 5852 and 7919  $cm^{-1}$  (1.263–1.709  $\mu m)$  using Differential Absorption Spectroscopy (DAS) and Cavity Ring Down Spectroscopy (CRDS) at sub-Doppler resolution. From these spectra, they extracted line sets (positions and intensities) at both temperatures, which are complete down to very low line strengths (Fig. 3 of Campargue et al., 2012). The 296- and 80-K line sets include 55,262 and 42,943 lines respectively. Lower energy levels (E) could be determined for transitions observed both at 80 and 296 K. However, 55% of the 296-K line list are lines that were observed only at this temperature, due to a high lower energy level. To add these lines to the 80-K list, two approaches are possible. Campargue et al. (2013) assigned them lower energy levels such that their intensities are just below the detectivity limit at 80 K. This choice yields an upper limit for methane absorption at temperatures intermediate between 80 and 296 K, as found in Titan's stratosphere above 60 km. Hereafter, this linelist is noted C2013. An alternate choice is to assume that these lines have very high energy levels so that their intensity is negligible at all levels in Titan's stratosphere, i.e. below 185 K. To incorporate the Campargue et al. measurements in the HITRAN2012 database, Brown et al. (2013) attached an artificial (default) value  $E = 999.999 \text{ cm}^{-1}$  to such lines. Here, we set  $E = 1500 \text{ cm}^{-1}$  for these lines to produce a linelist hereafter noted E1500. This linelist yields a lower limit for methane absorption in Titan's stratosphere. There are also 16,478 lines that were observed only at 80 K, being masked by stronger lines in the 296-K spectra. These lines have low energy levels and we attached a value of  $E = 100 \text{ cm}^{-1}$  to these single lines (Campargue et al. (2013) and Brown et al. (2013) chose an artificial value of -1 cm<sup>-1</sup> to identify them in their linelists). In this paper, we used these two linelists, C2013 and E1500, to model the DISR observations and we consider that they provide lower and upper limits to the actual methane transmittance in Titan's stratosphere.

We assigned broadening parameters to  $CH_4$  and  $CH_3D$  lines according the lower energy level of the transition as in Campargue et al. (2012), using a formulation based on measurements by Lyulin et al. (2009) in the range 5550–6236 cm<sup>-1</sup> (1.60–1.80 µm). While the so-calculated halfwidths are close to the values recommended by Brown et al. (2003, Table 11) at room temperature, our temperature exponents *n* are larger: 0.80–0.86 vs. 0.65–0.73 in Brown et al. for J'' = 0-9. Brown et al.'s recommendations are based on measurements in the strongest octad bands near 2.3 µm (Brown et al., 2003) while Lyulin et al.'s measurements pertain to tetradecad bands, around 1.7 µm. We tested the effect of such a change of *n* on the retrieved methane mole fraction (Section 4). We used a sub-Lorentzian line shape by multiplying the Voigt profile by a  $\chi$  factor that departs from unity beyond 25.6 cm<sup>-1</sup> from line center (Eq. (6) of Campargue et al., 2012). The choice of the  $\chi$  factor does not affect the calculated methane transmittance in the altitude range we investigate (*z* > 28 km).

We made calculations for different values of the stratospheric methane mole fraction ( $q_s$ , constant with altitude). In the troposphere, the methane vertical profile is fixed to that determined by Niemann et al. (2010) up to 34.4 km (214 mbar) and joins  $q_s$  at 39.6 km (155 mbar). The CH<sub>3</sub>D/CH<sub>4</sub> ratio is set to a constant value of  $\frac{1}{4}$  D/H with D/H =  $1.32 \times 10^{-4}$  (Bézard et al., 2007). For CO, we used a constant mole fraction of 45 ppmv, in agreement with de Kok et al. (2007).

#### 4. Retrieval of stratospheric methane mole fraction

Fig. 2 shows ratios of methane transmittance at different altitudes calculated from the probe to the Sun for a stratospheric CH<sub>4</sub> mole fraction of 1.48% (Niemann et al., 2010). In this calculation, the E1500 linelist, providing a lower limit to methane absorption in Titan's stratosphere, was used. Clearly, the shape of the methane band is overall correctly reproduced by the model at the different altitudes. A few hot pixels are still visible at some altitudes. We also note that the model tends to underestimate the methane absorption in the low-wavelength wing of the band and overestimate it in the high-wavelength wing. This slight mismatch can be corrected by assuming a small calibration error in the ULIS wavelengths amounting to  $\sim$ 1.5 nm, i.e. about a fourth of the pixel size. We hereafter include this correction in our analysis. It can be noted that a  $\sim 0.15$  pixel spectral shift with respect to laboratory calibration was also suggested for the Upward-Looking Visible Spectrometer (ULVS) of DISR by Karkoschka and Tomasko (2010) from the slope of methane band wings.

Fig. 3 shows the sensitivity of the calculated transmittance ratios to the methane mole fraction. Two values were used: 1.48% as derived from Huygens/GCMS measurements (Niemann et al., 2010) and 1.0% as obtained by Lellouch et al. (2014) from Cassini/CIRS measurements at low latitudes. In both cases, the E1500 linelist was used. A comparison with the ULIS measurements clearly shows that the GCMS value better reproduces the data when the E1500 linelist is used. Fig. 4 compares calculations with the E1500 and with the C2013 CH<sub>4</sub> linelists, assuming the same 1.48% methane mole fraction in the stratosphere. As expected, the C2013 linelist yields more methane absorption in Titan's upper stratosphere. The effect is significant in the ratios of the transmittances at altitudes above 65 km to that at 134.8 km (Fig. 4a). On the other hand, the ratios between successive altitudes below 70 km are essentially insensitive to the choice of the CH<sub>4</sub> linelist (Fig. 4b). At such levels, the temperature is below 100 K and the effect of the lines observed in the 296-K laboratory spectra but not in the 80-K spectra becomes negligible.

To determine the best fitting methane mole fraction, we performed a lest-squares fit analysis on either the whole band from 1297 to 1573 nm or only over the core of the band 1356– 1402 nm, which is not affected by uncertainties on the ULIS wavelength shift and less sensitive to uncertainties in the continuum around the band. We calculated synthetic transmittance spectra



Fig. 3. Ratios of DISR/ULIS methane transmittance spectra at different altitudes (lines with squares) are compared with calculations for stratospheric CH<sub>4</sub> mole fractions of 1.48% (solid lines) and 1.0% (dashed lines) using the E1500 methane linelist. DISR/ULIS spectra have been shifted by +1.5 nm. See Fig. 2 for definitions of Panels a and b.



Fig. 4. Transmittance spectral ratios at different altitudes calculated with the E1500 (solid lines) and the C2013 (dashed lines) CH<sub>4</sub> linelists. A 1.48% CH<sub>4</sub> mole fraction is assumed in both cases. See Fig. 2 for the characteristics of the ratios in Panels a and b.

for CH<sub>4</sub> mole fractions of 0.76%, 1.00%, 1.24%, 1.48%, 1.72%, 1.96% and 2.20% and, in each case, calculated the residuals of the fits with the DISR data for the two types of ratios  $S_i/S_1$  (i = 2, 8) and  $S_i/S_{i-1}$ (i = 2, 7). In the second case, the noise for the calculation of the residuals was assumed to vary as  $1/S_{i-1}$ . We did not consider the ratio  $S_8/S_7$  because it is almost insensitive to the stratospheric methane. For a given ratio, the rms residuals of the fit were fitted as a function of methane mole fraction using a spline interpolation and the best-fitting methane abundance was taken as the one that minimizes this function. We consider that this minimum rms value provides an estimate of the noise level ( $\sigma_i$ ) and we derived the 1-SD random error bars on the methane mole fraction as those yielding a rms residuals  $\sigma_i \times \sqrt{n/(n-1)}$ , where *n* is the number of spectral points used in the fit (8 for the band center and 44 for the whole band).

The mean value of the rms residuals  $\sigma = \langle \sigma_i \rangle$  of the transmittance ratios is 0.0122, which corresponds to an error on the transmittance of 0.0122/ $\sqrt{2} = 0.0086$  per point. The 1-SD error on the continuum reference around 1282 or 1584 nm, based on three data points, is thus  $0.0086/\sqrt{3} = 0.0050$ . We calculated that the corresponding uncertainty on the averaged continuum level is ±0.0036 when fitting the band center (1355–1400 nm) and ±0.0040 when fitting the whole band (1295–1571 nm). To evaluate the propagation of this continuum uncertainty in the retrieved CH<sub>4</sub> mole fraction, we successively multiplied the eight  $S_i$  by 1.0036 or 0.9964 when fitting the band center (1.004 or 0.996 when fitting the whole band) and derived the change in the best fitting CH<sub>4</sub> for each ratio  $S_i/S_1$  or  $S_i/S_{i-1}$ . Doing so, we obtained error bars due to uncertainties in the continuum of the numerator and of the denominator of the transmittance ratio.

The results of the retrievals are given in Tables 2 and 3 for the  $S_i$  $S_1$  (*i* = 2, 8) and  $S_i/S_{i-1}$  (*i* = 2, 7) ratios respectively. They are also plotted in Fig. 5 in blue (C2013 linelist) and red (E1500 linelist). The error bars that are indicated are the guadratic sum of the three uncertainties discussed above: random noise, continuum level of the numerator, and continuum level of the denominator of the ratios. The last lines of the tables indicate the best fitting CH4 mole fraction averaged over all altitudes and the associated  $\chi^2$ . Lower values of  $\chi^2$  are obtained using the E1500 methane linelist with respect to the C2013 one; they are still somewhat larger than the expected value, which is the number of independent determinations minus 1, i.e. 6 for Table 1, and 5 for Table 2. The transmittance ratios below  $\sim$ 60–70 km are not very sensitive to the assumed CH<sub>4</sub> linelist (Fig. 4) and point to a methane mole fraction of 1.4-1.5% (Fig. 5). At higher altitudes, the C2013 linelist yields significantly lower CH<sub>4</sub> mole fractions, typically 1.2%, which explains the unacceptably large values of  $\chi^2$  in these cases (up to 30, Table 1). The E1500 linelist does a better job at high altitudes but still tends to vield larger CH₄ mole fractions than below 60–70 km.

To try to make the fits more consistent in terms of  $CH_4$  mole fraction at all altitudes, we constructed a  $CH_4$  linelist in which the lower energy levels of the "single" transitions observed at 296 K but not at 80 K by Campargue et al. (2013) are intermediate between those in the E1500 and C2013 linelists. To do so, we added 250 cm<sup>-1</sup> to the energy levels assigned by Campargue et al. to such "single" lines to make their intensities at 80 K just below the detec-

| Table 2                |                |           |               |         |
|------------------------|----------------|-----------|---------------|---------|
| Methane mole fractions | retrieved from | DISR/ULIS | transmittance | ratios. |

| Transmittance ratio   | Methane mole fraction $(q_{CH4})$ and associated errors |  |                                       |                                       |  |                                       |  |
|---|---|--|---------------------------------------|---------------------------------------|--|---------------------------------------|--|
|   | Center of band (1356-1402 nm)                           |  |                                       | Whole band (1297–1573 nm)             |  |                                       |  |
|   | E1500 linelist  | C2013 linelist                         | Intermediate<br>(E+250)               | E1500 linelist                        | C2013 linelist                         | Intermediate<br>(E+250)               |  |
| 109.5/134.8 km  | 1.80 + 0.23/-0.17                                       | 1.23 + 0.085/-0.10                     | 1.53 + 0.20/-0.12                     | 1.88 + 0.30/-0.28                     | 1.34 + 0.19/-0.17                      | $1.70 \pm 0.25$                       |  |
| 90.3/134.8 km   | $1.49 \pm 0.08$   | 1.075 + 0.085/<br>-0.07                | 1.33 + 0.10/-0.09                     | $1.50 \pm 0.12$                       | $1.15 \pm 0.09$                        | $1.40 \pm 0.11$                       |  |
| 77.4/134.8 km   | 1.46 ± 0.055  | 1.11 ± 0.07                            | $1.32 \pm 0.07$                       | $1.485 \pm 0.06$                      | 1.20 + 0.05/-0.06                      | 1.41 + 0.07/-0.08                     |  |
| 64.9/134.8 km   | $1.40 \pm 0.055$  | $1.205 \pm 0.04$                       | $1.30 \pm 0.05$                       | 1.415 ± 0.045                         | $1.23 \pm 0.03$                        | 1.36 ± 0.055                          |  |
| 52.1/134.8 km   | 1.37 ± 0.055  | 1.26 ± 0.03                            | 1.33 ± 0.05                           | $1.46 \pm 0.04$                       | 1.37 ± 0.05                            | $1.45 \pm 0.04$                       |  |
| 40.0/134.8 km   | $1.47 \pm 0.05$   | 1.42 ± 0.06                            | $1.46 \pm 0.05$                       | 1.53 ± 0.04                           | 1.49 ± 0.035                           | $1.53 \pm 0.04$                       |  |
| 28.5/134.8 km   | 1.14 + 0.37/-0.23                                       | 1.10 + 0.33/-0.22                      | 1.13 + 0.36/-0.23                     | $1.49 \pm 0.10$                       | $1.46 \pm 0.09$                        | $1.49 \pm 0.10$                       |  |
| Average mole fraction (and associated $\chi^2$ ) <sup>a</sup> | $1.44 \pm 0.025$<br>( $\chi^2 = 8.1$ )                  | $1.24 \pm 0.02$<br>( $\chi^2 = 18.5$ ) | $1.36 \pm 0.03$<br>( $\chi^2 = 8.3$ ) | $1.48 \pm 0.02$<br>( $\chi^2 = 5.6$ ) | $1.31 \pm 0.02$<br>( $\chi^2 = 46.5$ ) | $1.46 \pm 0.02$<br>( $\chi^2 = 7.4$ ) |  |

<sup>a</sup> Values in bold correspond to the lowest  $\chi^2$  among the different CH<sub>4</sub> linelists.

#### Table 3

Methane mole fractions retrieved from DISR/ULIS transmittance ratios.

| Transmittance ratio   | Methane mole fraction $(q_{CH4})$ and associated errors |  |                                       |                                       |  |  |  |
|---|---|--|---------------------------------------|---------------------------------------|--|--|--|
|   | Center of band (1356–1402 nm)                           |  |                                       | Whole band (1297–1573 nm)             |  |  |  |
|   | E1500 linelist  | C2013 linelist                         | Intermediate<br>(E+250)               | E1500 linelist                        | C2013 linelist                         | Intermediate<br>(E+250)                |  |
| 109.5/134.8 km  | 1.80 + 0.23/-0.17                                       | 1.23 + 0.085/-0.10                     | 1.53 + 0.19/-0.13                     | 1.88 + 0.39/-0.32                     | 1.37 + 0.21/-0.20                      | 1.73 ± 0.29                            |  |
| 90.3/109.5 km   | 1.30 + 0.16/-0.13                                       | $1.00 \pm 0.09$                        | 1.20 + 0.13/-0.14                     | 1.25 + 0.22 / -0.24                   | 1.03 + 0.14/-0.13                      | 1.18 + 0.23/-0.18                      |  |
| 77.4/90.3 km  | 1.39 + 0.11/-0.14                                       | 1.18 + 0.07/-0.11                      | 1.30 + 0.13/-0.08                     | 1.46 + 0.185/<br>-0.18                | 1.255 ± 0.15                           | 1.42 + 0.18/-0.17                      |  |
| 64.9/77.4 km  | 1.31 + 0.075/<br>0.065                                  | 1.255 ± 0.05                           | 1.30 + 0.07/-0.06                     | 1.285 + 0.095/<br>-0.05               | 1.24 + 0.07/-0.08                      | 1.28 + 0.10/-0.075                     |  |
| 52.1/64.9 km  | $1.34 \pm 0.07$   | $1.35 \pm 0.07$                        | $1.35 \pm 0.07$                       | $1.52 \pm 0.08$                       | 1.54 + 0.10/-0.09                      | 1.53 + 0.10/-0.09                      |  |
| 40.0/52.1 km  | 1.53 ± 0.08   | $1.535 \pm 0.07$                       | 1.53 + 0.08/-0.07                     | $1.545 \pm 0.06$                      | 1.545 + 0.075/<br>-0.065               | 1.55 + 0.075/-0.07                     |  |
| Average mole fraction (and associated $\chi^2$ ) <sup>a</sup> | $1.41 \pm 0.04$<br>( $\chi^2 = 11.4$ )                  | $1.28 \pm 0.03$<br>( $\chi^2 = 26.7$ ) | $1.38 \pm 0.04$<br>( $\chi^2 = 9.7$ ) | $1.49 \pm 0.04$<br>( $\chi^2 = 8.4$ ) | $1.39 \pm 0.04$<br>( $\chi^2 = 20.6$ ) | $1.47 \pm 0.045$<br>( $\chi^2 = 7.5$ ) |  |

<sup>a</sup> Values in bold correspond to the lowest  $\chi^2$  among the different CH<sub>4</sub> linelists.

tivity limit. We made this adjustment for the "single" lines between 1348 and 1408 nm, i.e. near the band center. Outside of this range, we set an energy level of  $1500 \text{ cm}^{-1}$  as for the E1500 linelist. We name this "intermediate" linelist E+250.

The results on the methane retrievals using E+250 are given in Tables 2 and 3 and shown in Fig. 5 (green line). The  $\chi^2$  associated with the best fit CH<sub>4</sub> value for the  $S_i/S_1$  ratios are a bit larger than those based on the E1500 linelist (Table 2) while they are a bit lower when fitting the  $S_i/S_{i-1}$  ratios (Table 3). Whether we choose the E + 250 or E1500 linelist, the  $\chi^2$  associated with the CH<sub>4</sub> retrievals are in some cases as high as 10-11, about twice the expected value (fitting of the band center in Table 3). This suggests that the error bars may be underestimated by some 30-40%. On the other hand, fitting of the  $S_i/S_{i-1}$  ratios for the whole band (Table 2) leads to  $\chi^2$  of 6–7, which is close to the expected value (~6). We also note that the CH<sub>4</sub> values derived from fitting of the whole band are 6-7% larger than those derived from the band center alone. We have no strong opinion on which one is more reliable and we retain both determinations as acceptable. Overall, all the best fit CH<sub>4</sub> mole fractions derived from either the band center or the whole band and using either E1500 or E+250 are in the interval 1.33-1.54%. This interval includes increased error bars in cases where  $\chi^2$  is significantly larger than the degrees of freedom (6 or 5). We retain 1.44% as the central value.

In Fig. 6, we also show the individual ULIS data as a function of altitude for two spectral ranges: the band center 1362–1402 nm (red symbols) and an average of the two line wings near half maximum in the intervals 1323–1337 nm and 1440–1453 nm (blue

symbols). The data are plotted as the ratio of methane transmittance at altitude z and altitude 134.8 km. The data points are compared with calculations using either the E1500 linelist (Panel *a*) or the C2013 line list (Panel b) and CH<sub>4</sub> mole fractions of 1.00%, 1.48% and 1.96%. Fig. 7a clearly confirms that, using the E1500 spectroscopic parameters, the GCMS abundance (1.48%) correctly reproduces the methane absorption observed by DISR/ULIS both in the core and in the wings of the methane band. Clearly a value as low as 1% is excluded. When the Campargue et al. (2013) energy levels are used (C2013 linelist), a single CH<sub>4</sub> abundance does not allow us to reproduce the whole absorption vertical profile in the band center: above  $\sim$ 70 km, the data suggest a mole fraction around 1.1% increasing to  $\sim$ 1.4% below 45 km. Also the methane mole fraction best fitting the band wings seems to be lower by  $\sim$ 0.2–0.3% than that best fitting the band core. So, again, this suggests that the Campargue et al. (2013) linelist (C2013) is not adequate to reproduce the observed methane absorption profile in Titan's stratosphere.

We tested the influence of the broadening parameters on the methane retrievals by decreasing the temperature exponents n by 15%, which corresponds to the difference between those we used following Campargue et al. (2012) and those recommended by Brown et al. (2003) based on measurements near 2.3 µm. The calculations based on these two sets of n coefficients are shown in Fig. 7. In both cases, the E1500 linelist was used. Lower values of n (dashed lines) yield less absorption because the lines are narrower at Titan's temperatures and thus provide less absorption in the line wings, the cores being saturated. The differences with



**Fig. 5.** CH<sub>4</sub> mole fraction retrieved from the transmittance ratios at altitudes  $z_i$  and  $z_1$  (Panels a and b) and transmittance ratios at altitudes  $z_i$  and  $z_{i-1}$  (Panels c and d) as a function of altitude  $z_i$ . The best fit values are derived either from the band core 1356–1402 nm (Panels a and c) or from the whole band 1297–1573 nm (Panels b and d). Results in blue derive from the C2013 methane linelist, those in red from the E1500 linelist, and those in green from the A+250 "intermediate" linelist. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

the nominal n values (solid lines) increase with depth because temperature decreases with depth along with the difference in line widths. The best fitting CH<sub>4</sub> mixing ratios, shown in Fig. 8 at the different altitudes, are larger for smaller n coefficients than in our nominal case. Averaged over all altitudes, the best fitting mixing ratios are larger than in our nominal case by 0.13-0.17%, using either the band core or the whole band and either the  $S_i/S_{i-1}$  or  $S_i/S_1$ transmittance ratios. However the  $\chi^2$  associated with these retrievals are significantly larger, between 10 and 14, than in our nominal case. This is also seen in Fig. 8: the inferred mole fractions below 55 km are significantly larger than at 65-90 km for the lower *n* case (blue line), which does not happen in the nominal case (red line). We consider that these lower *n* coefficients, similar to those recommended by Brown et al. (2003), yield an upper limit on the methane mole fraction and we conclude that  $q_{CH4} = 1.44$ (+0.27/-0.11)%, taking into account all uncertainties.

#### 5. Discussion

Our analysis of the 1.4- $\mu$ m methane band observed by the DISR/ ULIS during the Huygens descent indicates a stratospheric mole fraction of 1.44 (+0.27/-0.11)%. This is fully consistent with the simultaneous *in situ* measurement by the Huygens/GCMS (Niemann et al., 2010), which yields 1.48 ± 0.09%.

On the other hand, it is inconsistent with the recent determination based on Cassini/CIRS spectra, which yields  $q_{CH4} = 0.95 \pm 0.08\%$ in the 70–180 km altitude range near 15°S (Lellouch et al., 2014). This value was derived from both limb spectra recorded in September 2006 (T17 flyby) at 14.7–15.3°S around 121 km altitude and nadir spectra recorded in October 2006 (T20 flyby). The projected field of view of the CIRS nadir spectra covers about 250 km. It is worth noting that CIRS selections centered at 0° and 15°N (limb and nadir) also yield low CH<sub>4</sub> abundances: 0.96 ± 0.08% and



**Fig. 6.** Observed (symbols) and synthetic (lines) transmittance ratio of methane, T(z)/T(134.8 km), as a function of altitude *z*. Calculations include either the E1500 methane linelist (Panel a) or the Campargue et al. (2013) linelist (Panel b). Spectral ranges corresponding to the band core (red) and to an average of the line wings on both sides near half maximum (blue) were considered. Calculations were performed for three different stratospheric CH<sub>4</sub> mole fractions showing increasing absorption: 1.00% (dashed lines), 1.48 (solid lines) and 1.96% (dotted lines). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

 $1.0 \pm 0.10\%$  respectively. Such low values are clearly excluded by the DISR/ULIS data, which yield a lower limit of 1.33%. We see possible reasons for this surprising discrepancy. First, the difference could be real and point to horizontal or temporal variations. The



**Fig. 7.** Comparison of synthetic transmittance ratio spectra calculated with the E1500 methane linelist using different temperature exponents n for the Lorentz halfwidths. *Solid lines*: nominal n (Campargue et al., 2012); *dashed lines*: nominal n were multiplied by 0.85 to be similar to those recommended by Brown et al. (2003).



**Fig. 8.** CH<sub>4</sub> mole fraction retrieved from the transmittance ratios at altitudes  $z_i$  and  $z_1$  over the whole band for two sets of different temperature exponents n of the Lorentz halfwidths: nominal (red) and 0.85 time the nominal ones (blue). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

CIRS spectra were recorded 1.5 year after the Huygens descent and pertain, at least for the nadir selections, to a relatively large area ( $\sim$ 250 km). A local or temporal variation in the stratospheric methane would imply local sources, which could be injection of methane ice particles in the lower stratosphere by convective events as proposed by Lellouch et al. (2014). However, the fact that methane was uniformly mixed within error bars over several scale heights in the stratosphere during the Huygens descent, as attested by the GCMS and DISR data, suggests that it should also have spread horizontally over a large area as a result of eddy mixing. With a dynamical time constant of approximately 15 years at 85 km (Lellouch et al., 2014), it is difficult to understand how the methane mole fraction could have decreased from 1.48% to less than 1% in only 1.5 year. Another possibility is that the Lellouch et al. abundances are incorrect. To fit the low-latitude CIRS spectra with the GCMS methane abundance would require an error of 20% in the methane line strengths reported by Boudon et al. (2010). This possibility is rejected by Boudon et al. who claim an uncertainty lower than 1% and it is also at odds with ab initio calculations of the rotational spectrum by Cassam-Chenaï and Liévin (2012) who reproduce Boudon et al.'s line strengths within 6%. There is some uncertainty in the Lorentz halfwidths of the rotational lines used by Lellouch et al., which come from the HITRAN 2008 database (Rothman et al., 2009). Subsequent room-temperature measurements of several rotational lines by Sanzharov et al. (2012) yield values that generally agree with those found in HITRAN 2008 which are based on an average for vibrational bands. However, there are no measurements of the temperature dependence of these halfwidths and the values used for the temperature exponent n are again based on those from vibrational bands. If the ncoefficients for the rotational lines were significantly smaller (by maybe 30%) than set in the HITRAN database, the CIRS-derived methane mole fraction at low latitudes could possibly increase up to the GCMS value. We may finally note that, while the Lellouch et al. (2014) retrievals at 15°S are inconsistent with the

present analysis, some of the mole fractions they derived at other latitudes (80°S, 35°S, 30°N, 62°N) agree with the present result.

Maltagliati et al. (2014) recently analyzed a set of VIMS solar occultations. They focused on the 1.4- and 1.7-µm bands of methane to retrieve the CH<sub>4</sub> vertical profile in the upper stratosphere. The 2.3-µm band was previously used by Bellucci et al. (2009) to analyze a VIMS solar occultation at 71°S but Maltagliati et al. (2014) showed that this band includes some additional absorption by ethane. The egress occultation data at 1°N, recorded during Flyby T53 in April 2009, yield a methane mole fraction of 1.28 ± 0.02%, averaged over the 150-500 km range. This value corresponds to a directly retrieved mole fraction of 1.14% that is multiplied by 1.1 to account for the neglect of scattering in the radiative transfer. The methane mole fractions derived at other latitudes (27°N, 40°N, 70°S) are similar within error bars. This is significantly less than the Huygens/GCMS value and also less than the value we derive here from DISR data. One could again invoke local/ temporal variations between the Huygens in situ measurements at 10°S in January 2005 and the VIMS occultation data at 1°N in April 2009 but this possibility would need to be quantitatively assessed in terms of localized sources of stratospheric methane and transport by dynamics.

The DISR/ULIS spectra recorded in the stratosphere during the descent can be fitted with a single methane mole fraction using the E1500 linelist. In this list, the lines observed by Campargue et al. (2013) at 296 K but not at 80 K were assigned a lower energy level  $E = 1500 \text{ cm}^{-1}$  and do not contribute to the absorption at Titan's temperatures. This approach is similar to that used to generate the HITRAN 2012 linelist ( $E = 999.99 \text{ cm}^{-1}$  was assigned to these lines). On the other hand, the energy levels of these same lines in the C2013 linelist are lower and were set by Campargue et al. (2013) to yield intensities at 80 K just below the sensitivity limit of the experiment. Above  $\sim$ 70 km, these lines bring a nonnegligible absorption that increases with temperature (and thus altitude). As a result, the CH<sub>4</sub> mole fraction inferred in the upper stratosphere is smaller than at lower levels (Fig. 5) and a single mole fraction cannot reproduce all spectra within error bars. Adding some 250  $\text{cm}^{-1}$  to the energy levels of Campargue et al. (2013) allows us to restore an acceptable fit of the spectra throughout the descent with a uniform methane mole fraction. We conclude that the energy levels set by Campargue et al. (2013) for the lines only observed at 296 K in their experiments are too low and we recommend either to add at least  $250 \text{ cm}^{-1}$  to these energy levels or to set them to 1500 cm<sup>-1</sup> or to use directly the HITRAN 2012 line parameters when modeling Titan's atmosphere.

A large fraction of the uncertainty attached to the derived methane mole fraction originates from uncertainties on the collisional halfwidths in the 1.4-µm band at Titan's low temperatures. As a nominal case, we followed the procedure described in Campargue et al. (2012). We used the dependence of the N<sub>2</sub>-broadening coefficients and temperature exponent *n* on the lower energy level (or quantum number *J*) of the transitions derived by Lyulin et al. (2009) from tetradecad bands in the range 1.60-1.80 µm  $(5550-6236 \text{ cm}^{-1})$ . As noted by Lyulin et al., while the broadening coefficients agree with those set in HITRAN, the exponents n differ considerably and are typically 15% larger. The HITRAN coefficients are based on measurements in the strongest octad bands near 2.3 µm (Brown et al., 2003, 2013). Decreasing our nominal n coefficients by 15% to agree with those of HITRAN makes our best fitting CH<sub>4</sub> mole fraction increase from 1.44% to 1.61%. However, the  $\chi^2$  associated with these retrievals get worse and we consider that the *n* coefficients from HITRAN yield an upper limit on the CH<sub>4</sub> mole fraction and that the Lyulin et al. higher temperature exponents are a better choice to model the region of the icosad, possibly because they correspond to the closest polyad.

#### 6. Conclusions

We have modeled the 1.4- $\mu$ m band of methane observed by DISR/ULIS during its descent in Titan's stratosphere. We took advantage of recent laboratory measurements of CH<sub>4</sub> lines in the range 1263–1709 nm described in Campargue et al. (2012, 2013), which provided a complete list of CH<sub>4</sub> and CH<sub>3</sub>D lines down to very low intensities. We used measurements between 28 and 135 km and chose to work on transmittance ratios at different altitudes to minimize instrumental effects that are not precisely characterized.

We infer a methane mole fraction in the stratosphere of 1.44 (+0.27/-0.11)%, taking into account random errors and uncertainties in the spectroscopic parameters. This determination agrees quite well with the in situ measurement by the Huygens/GCMS,  $1.48 \pm 0.09\%$  (Niemann et al., 2010). On the other hand, it is not consistent with the surprising low mixing ratio of 0.95 ± 0.08% inferred by Lellouch et al. (2014) in the 70–180 km altitude range from Cassini/CIRS spectra at 10°S. Temporal or horizontal variations between the Huygens and CIRS measurements do not appear very likely, considering the long dynamical timescale on Titan's atmosphere, but need to be quantified by numerical simulations involving local convective injection of methane in the lower stratosphere and vertical and horizontal diffusion by eddies and advection. Another possibility is a systematic error in the line parameters of the CH<sub>4</sub> rotational lines used by Lellouch et al. (2014), either in the line strengths or in the collisional halfwidths at low temperatures. We note however that the 20% change in the rotational line intensities that would be needed to reconcile the CIRS and GCMS measurements is well beyond the quoted uncertainties on the laboratory measurements (Boudon et al., 2010) or ab initio calculations (Cassam-Chenaï and Liévin, 2012). Independent laboratory measurements to confirm or not the Boudon et al. (2010) intensities would still be valuable. Also, laboratory measurements of the Lorentz halfwidths of these rotational lines at low temperatures are clearly needed. Finally, we note that our determination is also larger than the recent analysis of a set of VIMS solar occultations which yields 1.28 ± 0.02% at 1°N in April 2009 (Maltagliati et al., 2014).

Our analysis of the DISR data in the 1.4-µm methane band still suffers from uncertainties in the spectroscopic parameters despite the huge improvement brought by the advent of a complete linelist in this region (Campargue et al., 2012, 2013 and references herein). The first difficulty is the lack of defined lower energy levels for lines that were observed at 296 K but not at 80 K in the laboratory setup. Our analysis suggests that overall the energy levels of such "single" lines are large so that they do not significantly affect the calculated absorption in Titan's stratosphere. We thus recommend assigning them a lower energy level of at least  $1000 \text{ cm}^{-1}$  (as in HITRAN 2012 or in our E1500 linelist). In contrast, Campargue et al. (2013) chose to assign them an energy level such that their intensities are just below the detectivity level at 80 K, but this choice causes too much absorption in the upper stratosphere compared to that in the lower stratosphere, assuming a uniform profile for methane abundance. A possibility that we tried is to add some  $250 \text{ cm}^{-1}$  to the energy levels set by Campargue et al. (2013) to such single lines in the core of the band; this procedure also yields acceptable fits to the methane band throughout the descent. To improve the situation, new Differential Absorption Spectroscopy (DAS) and Cavity Ring Down Spectroscopy (CRDS) measurements at temperatures intermediate between 80 and 296 K would allow us to constrain the energy levels of these "single" lines. Theoretical analysis of some methane bands of the icosad would also provide spectroscopic identification, and thus energy levels, of lines observed by Campargue et al. The second problem with the methane spectroscopic parameters is the lack of measurements of methane line widths in the 1.4- $\mu$ m region. While room-temperature N<sub>2</sub>-broadened halfwidths do not seem to strongly vary from one band to another, this is not the case for the exponent of their temperature dependence. In the region of the tetradecad (1.7  $\mu$ m), closest to the region we analyzed here, Lyulin et al. (2009) derived values significantly larger than in the dyad (v<sub>4</sub>) or octad bands near 2.3  $\mu$ m (Brown et al., 2003). The choice of these temperature exponents significantly affects the calculated methane absorption, especially in the lower stratosphere at very low temperatures (70–100 K). Laboratory measurements of line width parameters at low temperatures in the icosad bands, around 1.4  $\mu$ m, are definitely needed to reduce the uncertainty in modeling the absorption in Titan's low atmosphere.

Finally, it would be interesting to extend our modeling to bands at lower wavelengths, starting with the triacontad around  $1.16 \mu m$ . However, this would first require a huge experimental effort to produce a full linelist of CH<sub>4</sub> and CH<sub>3</sub>D lines down to low enough intensities by means of Differential Absorption Spectroscopy (DAS) and Cavity Ring Down Spectroscopy (CRDS).

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