**Methane and Deuterium in Titan’s Atmosphere**

Jeremy Bailey

*School of Physics, University of New South Wales, NSW, 2052, Australia*

**Summary:** Observations of the near-infrared spectrum of Titan have been obtained with NIFS on the Gemini North 8m Telescope. The spectra have been modelled using a radiative transfer model based on the Huygens probe descent data on the structure of Titan’s atmosphere, and the latest laboratory data on the spectrum of methane. A detailed description of the model and the methane line data used was given in Ref. 1. Here that model is updated with new methane line data in the 1.55 μm window region, and a correction is made to the deuterium to hydrogen ratio (D/H) value derived in that paper. The new value is D/H = (1.43 ± 0.16) × 10⁻⁴. This agrees well with other recent determinations of Titan’s D/H and the significance of the results are discussed.

**Keywords:** Titan, methane, deuterium, planetary atmospheres, radiative transfer

**Introduction**

Saturn’s satellite Titan is the only satellite in the solar system to have a dense atmosphere. The atmosphere is composed mostly of nitrogen, but containing methane at an abundance of a few percent. This results in a methane “hydrological cycle” with methane condensing as clouds [2,3], falling as rain [4], and resulting in fluvial erosion features [5] and hydrocarbon lakes [6] on the surface.

Methane also dominates the spectrum, giving rise to a series of broad absorption features separated by window regions where the surface can be seen. Until recently the high resolution spectrum of Titan could not be modelled adequately at wavelengths shorter than about 2.1 μm due to the limitations of the available spectral line data. Recently new laboratory measurements of methane spectral lines, due largely to the work of the group at the University Joseph Fourier, Grenoble, have transformed the situation. The new measurements use direct absorption and cavity ring down spectroscopy (CRDS) [7] at both room temperature and cryogenic (~80 K) temperatures. By combining the measurements at two temperatures, the lower state energy of the transitions can be determined allowing the line intensity to be derived for any temperature, removing a key failing of previous lists that included only room temperature data at these wavelengths. The high sensitivity CRDS measurements also include very weak lines in the window regions that enable modelling of objects like Titan with long methane path lengths.

Analyses of Titan’s spectrum using the new line data are reported in Ref. 1 and Ref. 8. In both these studies once the methane lines were fitted it was possible to detect absorptions of other trace species such as CH,D and CO, allowing Titan’s CO abundance and D/H ratio to be determined. In this paper the analysis reported in Ref. 1 is updated by including the latest line measurements, and the determination of Titan’s D/H ratio in that paper is reconsidered.

**Observations**

The observations used here are the same as those described in Ref. 1. The Near-Infrared Integral Field Spectrograph (NIFS) [9] was used on the Gemini North 8m Telescope at Mauna
Kea, Hawaii in conjunction with the Altair adaptive optics system. Spatially resolved spectra were obtained in the near infrared J (1.15 – 1.36 µm), H (1.48 – 1.8 µm) and K (2.01 – 2.43 µm) bands at a spectral resolving power of $R = 5290$ in the H and K bands and 6040 in the J band.

Fig. 1. Images extracted from the NIFS spectral cube at three wavelengths The 2.03 µm image is in a methane transparency window and shows surface markings. The 2.12 µm image is sensitive to the troposphere, and the 2.30 µm image shows the stratosphere. The 3 by 3 pixel region extracted to give the spectra shown in the lower panels is indicated.

The data were reduced using the standard NIFS data reduction software to provide wavelength calibrated spectral cubes. The extracted spectra have been divided by NIFS spectra of G type stars to remove both telluric and solar features giving reflectance spectra (presented as radiance factor - I/F) which can be directly compared with models. Because of Doppler shifts in the stars, the cancellation of solar features is not perfect and leaves some residual features in the spectra.

Fig. 1 shows images extracted from the NIFS data at three wavelengths in the K band. These images show how Titan’s appearance changes at different wavelengths. The 2.03 µm image is in a methane “window” where absorption is at a minimum and surface markings can be seen. Similar windows occur at wavelengths of about 1.55 µm and 1.28 µm in the H and J bands. The 2.12 µm image is sensitive to the troposphere at about 10 km altitude. Methane clouds are sometimes seen as bright features at this wavelength, but no clouds are apparent at the time of these observations. The only structure seen is a limb brightening due to the aerosol haze. The 2.30 µm image is sensitive to the stratosphere (~50km altitude) which exhibits a seasonal north-south asymmetry in the limb brightening.
Fig. 1 also shows the spectra over a 3 x 3 pixel region in the centre of the disk in each of the three bands. These spectra were used for all of the analysis described here.

**Modelling of the Spectra**

The spectra were modelled using the VSTAR radiative transfer code [10]. VSTAR models a multi-layer atmosphere using a line-by-line treatment of molecular absorption, and a full multiple scattering approach to radiative transfer.

The model for Titan uses the Voyager Radio-Occultation pressure temperature profile [11], which agrees well with the profile determined by Huygens [12]. The methane volume mixing ratio as a function of altitude is from the Huygens GCMS measurements [13], and the aerosol properties and surface albedo are based on those determined from Huygens DISR observations [14, 15] with scaling factors (adjusted during model fitting) applied to the surface albedo and the aerosol optical depth at each of three altitude ranges (<30 km, 30 – 80 km, >80 km) to allow for differences from the conditions at the Huygens landing site. In addition to methane, absorption lines due to CO and collision-induced absorption due to an H₂-N₂ mixture are included in the model. Further details can be found in Ref. 1.

The methane spectral line list used in this work has been updated from that used in Ref. 1 by the inclusion of the most recent measurements by the Grenoble group described in Ref. 16 and 17.

<table>
<thead>
<tr>
<th>Wavenumber Range (cm⁻¹)</th>
<th>Wavelength Range (µm)</th>
<th>Source of line data</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>0 – 4800</td>
<td>&gt; 2.0833</td>
<td>HITRAN 2008 (Ref. 18)</td>
<td>Well modeled region</td>
</tr>
<tr>
<td>4700 – 5500</td>
<td>1.818 – 2.128</td>
<td>STDS (Ref. 19)</td>
<td>Preliminary model for Tetradecad</td>
</tr>
<tr>
<td>5500 – 5550</td>
<td>1.802 – 1.818</td>
<td>HITRAN 2008 (Ref. 18)</td>
<td>Includes empirical lower state energies from Ref. 20</td>
</tr>
<tr>
<td>5550 – 6165</td>
<td>1.622 – 1.802</td>
<td>GOSAT-2009 (Ref. 21)</td>
<td>Supplemented with low-temp line data from Ref. 22</td>
</tr>
<tr>
<td>6165 – 6750</td>
<td>1.481 – 1.622</td>
<td>CRDS (Ref. 16)</td>
<td></td>
</tr>
<tr>
<td>6750 – 7541</td>
<td>1.326 – 1.481</td>
<td>DAS (Ref. 23)</td>
<td></td>
</tr>
<tr>
<td>7541 – 7919</td>
<td>1.263 – 1.326</td>
<td>CRDS (Ref. 17)</td>
<td></td>
</tr>
<tr>
<td>7655 – 9200</td>
<td>1.087 – 1.263</td>
<td>HITRAN 2008 (Ref. 18)</td>
<td>Based on data from Ref. 24</td>
</tr>
</tbody>
</table>

*Table 1 – The Methane Line List (STDS: Spherical Top Data System; DAS: Direct Absorption Spectroscopy; CRDS: Cavity Ring Down Spectroscopy)*

The new laboratory data that covers the window regions at 1.55 µm and 1.28 µm is combined with other sources of line data [18–24] to give the full line list described in Table 1. The new spectral line data from Ref. 16 replaces data over a shorter range [25] used in the previous analysis and avoids the necessity to fill in gaps in wavelength coverage with estimated values of lower state energies as was done in Ref. 1.

Figure 2 shows the observed spectrum compared with the model spectrum obtained using the new line list. The model obtained using the HITRAN 2008 line list for methane, the best data available prior to the new laboratory data, is also shown for comparison, and clearly fails to fit the window region at 1.55 µm. The best fitting model parameters are listed in Table 2. The model is actually unchanged from that determined in Ref. 1. However, the fit to the spectrum
has significantly improved in the 1.55 µm window region with the addition of the new line data from Ref. 16.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
<th>Uncertainty</th>
</tr>
</thead>
<tbody>
<tr>
<td>Surface Albedo (at 1.6 µm)</td>
<td>0.108</td>
<td>0.009</td>
</tr>
<tr>
<td>Aerosol optical depth (&gt;80 km) at 1.5 µm</td>
<td>0.31</td>
<td>0.04</td>
</tr>
<tr>
<td>Aerosol optical depth (30–80 km) at 1.5 µm</td>
<td>0.34</td>
<td>0.07</td>
</tr>
<tr>
<td>Aerosol optical depth (&lt;30 km) at 1.5 µm</td>
<td>0.16</td>
<td>0.05</td>
</tr>
<tr>
<td>D/H</td>
<td>1.43 × 10⁻⁴</td>
<td>0.16 × 10⁻⁴</td>
</tr>
<tr>
<td>CO mixing ratio (ppmv)</td>
<td>50</td>
<td>11</td>
</tr>
</tbody>
</table>

**Table 2 — Parameters of best fitting model for Titan’s spectrum**

![Graph showing spectra of Titan](image)

**Figure 2 — Observed spectra of Titan (top panel) compared with predicted spectra using the VSTAR model and the new line list (middle panels), and the same model using the HITRAN 2008 line list (lower panels). The residuals (Data–Model) are shown beneath each model spectrum.**

Figure 3 shows an expanded view of the spectrum in the 1.53 – 1.59 µm wavelength region, a region that has particularly benefitted from the new line measurements. In this region the previous analysis of Ref. 1 showed two residual absorption features that remained after the model was fitted to the data. It was speculated that these were methane lines that were missing from the line list. This is confirmed by the new analysis as these features have disappeared with the model based on the new line data shown here.
The region shown in Figure 3 includes absorptions due to the $3\nu_2$ band (and other bands) of CH$_3$D as well as absorption in the CO 3-0 band. Both these absorptions are readily apparent in Figure 3 when the CH$_4$ lines only are fitted to the data. These absorptions can be used to determine the D/H ratio of Titan’s methane and the CO abundance in the lower atmosphere.

**Titan’s D/H Ratio**

In Ref. 1 it was determined that the best fitting D/H value for Titan’s spectrum in the 1.55 µm window region corresponded to a D/H of $1.147 \pm 0.13$ times the terrestrial value, and that this corresponded to a D/H of $(1.77 \pm 0.20) \times 10^{-4}$. That D/H ratio as a fraction of the terrestrial value is unchanged with the new analysis presented here. However, it has subsequently become apparent that the terrestrial D/H value we assumed in Ref. 1 is not the one that is appropriate in this case. In fact there is no single terrestrial value for D/H as different gas samples can have substantially different values depending on their source.

![Figure 3](image_url)

*Figure 3 — NIFS spectrum compared with model in the 1.53 to 1.59 µm wavelength region.*

*The upper panel shows the observed spectrum (shifted up by 0.06) compared with the modelled spectrum. The second panel shows the residuals of a model including only CH$_4$ lines. Absorption features due to the R and P branches of the CO 3-0 band, as well as absorptions due to CH$_3$D can be seen. The third panel adds CH$_3$D lines to the model based on our best fitting D/H ratio, and the fourth panel adds CO lines with a mixing ratio of 50 ppmv.*
In Ref 1. It was assumed that the appropriate terrestrial value of D/H was that adopted in the HITRAN spectral line database. Line intensities of isotopologue lines in that database are scaled for terrestrial isotopic composition based on a value of CH$_3$D/CH$_4$ of 6.1575 x 10$^{-4}$ (corresponding to a D/H of 1.54 x 10$^{-4}$). This is very close to the VSMOW (Vienna Standard Mean Ocean Water) value, which is the normal standard for D/H.

However, the line intensities used in our work were from the Grenoble group’s laboratory measurements of actual natural gas samples. Natural gas and other natural terrestrial sources of methane actually have D/H values that are substantially depleted compared with the VSMOW reference [16, 25]. The typical δD value for natural gas is −180±20‰ [26]. Therefore, as discussed in Refs 16 and 27 the line intensities actually correspond to a CH$_3$D/CH$_4$ value of 5 x 10$^{-4}$, about 18% lower than that adopted in HITRAN.

Our derived D/H value for Titan therefore needs correction compared with that published in Ref. 1 and the correct value is (1.43 ± 0.16) x 10$^{-4}$ as listed in Table 2.

Discussion and Conclusions

The new value of D/H derived here is in reasonable agreement with a number of other recent measurements. Abbas et al. [28] obtained (1.58 ± 0.16) x 10$^{-4}$ from Cassini CIRS measurements, and de Bergh et al. [8] obtained (1.13 ± 0.25) x 10$^{-4}$ using a different set of 1.55 µm spectroscopic observations and the same new spectral line data. The value of D/H is an important clue to the origin of the material, since ice formed at different locations in the solar system will have very different D/H values as a result of chemical fractionation in the early solar nebula [29,30]. In the case of Titan the observed value has been used to determine that Titan’s methane is probably of primordial origin, and not generated by serpentinization reactions in Titan’s interior [31].

The same techniques used here to study the D/H value in Titan’s atmosphere could also be applied to the four giant planets in the solar system all of which has a substantial methane content. Such observations could thus provide constraints on the formation location of their methane and potentially provide information on the migration of these planets during early solar system evolution.

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References


