A search for predicted trace species in Titan’s Stratosphere using Cassini CIRS

Fifth NSF Workshop on Titan Chemistry
Poipu Koloa, Kauai, Hawaii, April 11-14th 2011

C. A. Nixon, R. K. Achterberg, D. E. Jennings, P. N. Romani,
N. A. Teanby, P. G. J. Irwin, J.-M. Flaud, L. R. Brown,
A. Coustenis, S. Vinatier, B. Bézard
Objectives

• The objectives and purpose of this study were:

1. To search for expected new trace stratospheric gas species in the Cassini CIRS infrared spectra of Titan.
2. Place upper limits on non-detections.
3. To compare to predictions from photochemical models and results from other Cassini instruments and draw conclusions.
Overview Of Talk

- Background: previous detections
- Observations: instrument and data.
- Analysis method
- Results
- Comparison to chemical models
- Conclusions
Molecular species in Titan’s atmosphere: a brief history through time …

• 1940s – CH$_4$ (Kuiper)
• 1970s - ground-based detections: C$_2$H$_2$, C$_2$H$_6$?
• Voyager era:
  - IRIS: HCN, C$_2$H$_2$, C$_2$H$_6$, HC$_3$N, C$_2$N$_2$, C$_4$H$_2$, C$_3$H$_4$, C$_3$H$_8$, CO$_2$, H$_2$
  - UVS: N$_2$
• 1980s-1990s ground-based: CO and CH$_3$CN
• 1990s-2000s, ISO: C$_6$H$_6$ and H$_2$O
• 2004+ Cassini: Ar (GCMS); many in ionosphere (INMS).
OBSERVATIONS
Cassini Composite Infrared Spectrometer (CIRS)
CIRS Focal Plane Locations

10-600 cm\(^{-1}\)

1100-1500 cm\(^{-1}\)

600-1100 cm\(^{-1}\)

Fig. 1
Example CIRS Titan Low Latitude Spectrum
DATA ANALYSIS

METHOD
Temperatures derived by iterative fitting of the \( \text{CH}_4 \nu_4 \) band (assuming Huygens VMR profile). Provides \( T \) at limb tangent point and above.

- Subsequently, these temperatures are fixed, and the spectral model is used to fit other known gases (mainly \( \text{C}_2\text{H}_4 \) at \( 949 \, \text{cm}^{-1} \)).
- The residual (data-model) is then searched for the signature of possible new species.
CIRS Search For Trace Species

• Initial visual search made for possible new gases (by subtracting data-model to get residual). No strong signals.

• Then proceeded to make calculation of upper limits for several species, chosen by combination of:
  • ‘Clean spectral range’ – mainly 9-11 microns
  • Model predictions for Titan’s stratosphere
  • Availability of spectral line data

<table>
<thead>
<tr>
<th>Species</th>
<th>Molecular Formula</th>
<th>Vibration</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ammonia</td>
<td>NH$_3$</td>
<td>$v_2$ at 950 cm$^{-1}$</td>
</tr>
<tr>
<td>Methanol</td>
<td>CH$_3$OH</td>
<td>$v_8$ at 1033 cm$^{-1}$</td>
</tr>
<tr>
<td>Acetonitrile</td>
<td>CH$_3$CN</td>
<td>$v_7$ at 1041 cm$^{-1}$</td>
</tr>
<tr>
<td>Formaldehyde</td>
<td>H$_2$CO</td>
<td>$v_6$ at 1167 cm$^{-1}$</td>
</tr>
<tr>
<td>Allene</td>
<td>CH$_2$CCH$_2$</td>
<td>$v_{10}$ at 841 cm$^{-1}$</td>
</tr>
</tbody>
</table>
Upper limits: method

• Upper limits derived by calculating $\chi^2$ figure of merit for a variety of trial abundances.

• Define:

$$\chi_j^2 = \sum_{i=1}^{M} \frac{(I_{data}(v_i) - I_{calc}(v_i,q_j))^2}{\sigma_i^2}$$

$$\Delta \chi_j^2 = \chi_0^2 - \chi_j^2$$

• Detections of 1σ, 2σ, 3σ when $\Delta \chi^2=-1, -4, -9$ respectively.

• Upper limits on non-detections of 1σ, 2σ, 3σ when $\Delta \chi^2=+1, +4, +9$ respectively.
T55 Flyby: 25°S

- Left-hand column shows residual after base model (black) and exaggerated trial-gas model (color)
- Right-hand column shows growth curve for $\chi^2$ (no detections...
**T64 Flyby: 76°N**

- Left-hand column shows residual after base model (black) and exaggerated trial-gas model (color)
- Right-hand column shows growth curve for $\chi^2$ (no detections...)

![Graphs showing T64 data and various models](image)
# Results for Upper Limits

**Table**: Calculated upper limits on abundances of undetected trace gases in Titan’s stratosphere.

<table>
<thead>
<tr>
<th>Gas</th>
<th>Latitude</th>
<th>Pressure (mbar)</th>
<th>Band</th>
<th>Wavenumber Range For Calculation</th>
<th>$1\sigma$ NESR (nW cm$^2$ sr$^{-1}$/cm$^1$)</th>
<th>Abundance Upper Limits (ppb$^a$)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Start (cm$^{-1}$)</td>
<td>End (cm$^{-1}$)</td>
<td>1σ</td>
</tr>
<tr>
<td>CH$_3$CCH$_2$</td>
<td>25°S</td>
<td>6.50</td>
<td>$\nu_{10}$</td>
<td>845</td>
<td>880</td>
<td>3.46</td>
</tr>
<tr>
<td>NH$_3$</td>
<td>25°S</td>
<td>7.60</td>
<td>$\nu_2$</td>
<td>960</td>
<td>1000</td>
<td>2.40</td>
</tr>
<tr>
<td>CH$_3$OH</td>
<td>25°S</td>
<td>0.27</td>
<td>$\nu_8$</td>
<td>1030</td>
<td>1050</td>
<td>1.74</td>
</tr>
<tr>
<td>CH$_3$CN</td>
<td>25°S</td>
<td>0.27</td>
<td>$\nu_7$</td>
<td>1030</td>
<td>1050</td>
<td>1.74</td>
</tr>
<tr>
<td>H$_2$CO</td>
<td>25°S</td>
<td>0.27</td>
<td>$\nu_6$</td>
<td>1070</td>
<td>1130</td>
<td>0.46</td>
</tr>
<tr>
<td>CH$_3$CCH$_2$</td>
<td>76°N</td>
<td>0.24</td>
<td>$\nu_{10}$</td>
<td>845</td>
<td>880</td>
<td>2.85</td>
</tr>
<tr>
<td>NH$_3$</td>
<td>76°N</td>
<td>0.26</td>
<td>$\nu_2$</td>
<td>960</td>
<td>1000</td>
<td>3.58</td>
</tr>
<tr>
<td>CH$_3$OH</td>
<td>76°N</td>
<td>0.018</td>
<td>$\nu_8$</td>
<td>1030</td>
<td>1050</td>
<td>0.96</td>
</tr>
<tr>
<td>CH$_3$CN</td>
<td>76°N</td>
<td>0.018</td>
<td>$\nu_7$</td>
<td>1030</td>
<td>1050</td>
<td>0.96</td>
</tr>
<tr>
<td>H$_2$CO</td>
<td>76°N</td>
<td>0.018</td>
<td>$\nu_6$</td>
<td>1070</td>
<td>1130</td>
<td>0.32</td>
</tr>
<tr>
<td>CH$_3$OH</td>
<td>76°N</td>
<td>0.30</td>
<td>$\nu_8$</td>
<td>1027</td>
<td>1052</td>
<td>0.35</td>
</tr>
<tr>
<td>CH$_3$CN</td>
<td>76°N</td>
<td>0.30</td>
<td>$\nu_7$</td>
<td>1029</td>
<td>1075</td>
<td>0.42</td>
</tr>
<tr>
<td>H$_2$CO</td>
<td>76°N</td>
<td>0.30</td>
<td>$\nu_6$</td>
<td>1080</td>
<td>1130</td>
<td>0.19</td>
</tr>
</tbody>
</table>

$^a$ Parts per billion.
IMPLICATIONS FOR CHEMICAL MODELS
Comparison to photochemical models (I): CH₂CCH₂ (allene)


- CIRS limits of 0.2 ppb (2 σ) at 107 km (25°S) and 1 ppb at 225 km (76°N) are pushing limits of W&A model (especially if expected winter polar enhancement in North).
- Lavvas model (mid-latitudes) appears consistent.
Comparison to photochemical models (II): CH$_3$CN (acetonitrile)

CIRS limits of ~80 ppb (2 $\sigma$) at 250 km (25°S) and 800 ppb at 350 km (76°N) are not strong constraints on W&A model.

Lavvas model (mid-latitudes) has much more CH$_3$CN than W&A; already inconsistent with mm observations of Marten et al. (low lat bias).
CIRS limits of ~0.9 ppb (2 σ) at 107 km (25°S) and 6 ppb at 225 km (76°N) are much higher than predicted abundances by 3 orders of magnitude (W&A, upper) … and 2 orders of magnitude (Lavvas, lower).
CIRS limits of ~16 ppb (2 σ) at 250 km (25°S) and 130 ppb at 350 km (76°N) are around 1 order of magnitude above W&A at 250 km.

CIRS limits of ~3 ppb (2 σ) at 250 km (25°S) and 70 ppb at 350 km (76°N) are >3 orders of magnitude larger than W&A.
CONCLUSIONS AND FURTHER WORK
Summary

• No evidence for five gases (allene, acetonitrile, formaldehyde, methanol, ammonia) after rigorous search of CIRS data.

• Allene and acetonitrile upper limits are testing, or close to testing the predictions of some models.

• NH$_3$, H$_2$CO and CH$_3$OH species are typically at ppt levels in models and CIRS will very likely not detect or constrain.

• Quantitative search must continue for other gas species (e.g. C$_3$H$_6$, C$_2$H$_3$CN).

• However, remains surprising that CIRS has not detected any new stratospheric gases despite intense 7-year search (Voyager IRIS found 9, ISO 2).
Why hasn’t CIRS detected any new trace gases in stratosphere?

1. IRIS and ISO have found all the species that exist in the stratosphere down to our detection limit of $\sim 1 \times 10^{-10}$.

2. It’s the wrong time of year –
   • abundances still increasing in the North?

3. Confusion with other species –
   • molecules such as CH$_4$, C$_2$H$_2$, C$_2$H$_6$ and C$_3$H$_8$ cover huge regions of the spectrum, meaning we have to model them very well to search in these regions – or search elsewhere.
Future Work Areas

• Focus on more likely species, even if line atlas not available, by ratioing band strengths.

• Work on subtracting propane bands (912, 1053, 1158 cm\(^{-1}\)) that may be hampering detections.

• Further data taking planned, focused on placing most sensitive array (FP4) at lower altitudes to increase S/N.

• Further stratospheric detections may require new generation of instruments, especially with much higher spectral resolution (SOFIA, JWST)
Additional Material
SPECTRAL COVERAGE

ULTRAVIOLET IMAGING SPECTROGRAPH

WIDE ANGLE

IMAGING

NARROW ANGLE

VISIBLE AND INFRARED MAPPING SPECTROMETER

COMPOSITE INFRARED SPECTROMETER

SPECTRAL RANGE (μm)

Fig. 3
CIRS Titan Timeline

Mid-IR Nadir Integ (composition—0.5 cm⁻¹)
Mid-IR Temp. map (3 cm⁻¹)
Far-IR Nadir Integ. (composition—0.5 cm⁻¹)

Mid-IR Temperature Limb Map (15.5 cm⁻¹)
Mid-IR Limb Integration (comp. — 0.5 cm⁻¹)
Far-IR Nadir Map (temperatures, aerosols, tropospheric CH₄—15.5 cm⁻¹)
Far-IR Limb Integ. (composition—0.5 cm⁻¹)

Far-IR Limb Scans (aerosols & clouds—15.5 cm⁻¹)
Far-IR Temperature Limb Scans (15.5 cm⁻¹)
High-res. nadir map (temp. & aerosols—15.5 cm⁻¹)
Detailed predictions for ISO & CIRS

Table II: Detectability Limits of Some Undetected Minor Species in Titan

<table>
<thead>
<tr>
<th>Molecule</th>
<th>Waven. (cm(^{-1}))</th>
<th>Band strength (cm(^{-2}) cm(^{-1}))</th>
<th>Mixing ratio</th>
<th>Predictions(^a)</th>
<th>BB((\nu))(^3)</th>
<th>Detectability limits (^4)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water H(_2)O</td>
<td>150.5</td>
<td>63.7(^a)</td>
<td>≤ 5 \times 10^{-7}(^a)</td>
<td>1.0 \times 10^{-9}(^a)</td>
<td>9.4 \times 10^{-7}</td>
<td>7.5 \times 10^{-10}</td>
</tr>
<tr>
<td>Allene CH(_2)=C=CH(_2)</td>
<td>356</td>
<td>65(^a)</td>
<td>≤ 6 \times 10^{-9}(^a)</td>
<td>1.8 \times 10^{-9}(^a)</td>
<td>7.4 \times 10^{-8}</td>
<td>1.3 \times 10^{-9}</td>
</tr>
<tr>
<td>Benzene C(_6)H(_6)</td>
<td>673.5</td>
<td>352(^b)</td>
<td>≤ 2 \times 10^{-7}(^c)</td>
<td>3.2 \times 10^{-9}(^c)</td>
<td>1.2 \times 10^{-6}</td>
<td>1.0 \times 10^{-7}</td>
</tr>
<tr>
<td>Acetonitrile CH(_3)=C≡N</td>
<td>363</td>
<td>4.5(^c)</td>
<td>≤ 2 \times 10^{-7}(^c)</td>
<td>3.2 \times 10^{-9}(^c)</td>
<td>1.2 \times 10^{-6}</td>
<td>1.0 \times 10^{-7}</td>
</tr>
<tr>
<td>Acrylonitrile CH(_2)=CH=C≡N</td>
<td>241(R)</td>
<td>7.5(^c)</td>
<td>&lt; 2 \times 10^{-7}(^c)</td>
<td>3.2 \times 10^{-9}(^c)</td>
<td>1.2 \times 10^{-6}</td>
<td>1.0 \times 10^{-7}</td>
</tr>
<tr>
<td>Propionitrile CH(_3)CH(_2)=C≡N</td>
<td>211(R)</td>
<td>7.5(^c)</td>
<td>&lt; 2 \times 10^{-7}(^c)</td>
<td>3.2 \times 10^{-9}(^c)</td>
<td>1.2 \times 10^{-6}</td>
<td>1.0 \times 10^{-7}</td>
</tr>
<tr>
<td>Cyanopropane CH(_2)=C≡C≡N</td>
<td>338</td>
<td>100(^c)</td>
<td>≤ 1 \times 10^{-7}(^c)</td>
<td>&lt; 1 \times 10^{-9}(^c)</td>
<td>1.1 \times 10^{-6}</td>
<td>1.0 \times 10^{-7}</td>
</tr>
<tr>
<td>Crotonitrile CH(_3)CH=CH=C≡N</td>
<td>148(P)</td>
<td>9(^c)</td>
<td>&lt; 2 \times 10^{-7}(^c)</td>
<td>&lt; 1 \times 10^{-9}(^c)</td>
<td>9.3 \times 10^{-7}</td>
<td>7.5 \times 10^{-10}</td>
</tr>
<tr>
<td>Butanenitrile CH(_3)(CH(_2)=C≡N</td>
<td>728</td>
<td>3.5(^d)</td>
<td>≤ 5 \times 10^{-7}(^d)</td>
<td>1.0 \times 10^{-9}(^d)</td>
<td>1.6 \times 10^{-7}</td>
<td>1.0 \times 10^{-9}</td>
</tr>
<tr>
<td>Isobutyronitrile (CH(_3)(_2)=CHC≡N</td>
<td>538</td>
<td>3.3(^d)</td>
<td>≤ 2 \times 10^{-7}(^d)</td>
<td>7.5 \times 10^{-11}(^d)</td>
<td>4.9 \times 10^{-7}</td>
<td>4.0 \times 10^{-9}</td>
</tr>
<tr>
<td>Cyclopropane-carbonitride Δ-C≡N</td>
<td>928</td>
<td>5.9(^d)</td>
<td>≤ 1.5 \times 10^{-7}(^d)</td>
<td>&lt; 1 \times 10^{-9}(^d)</td>
<td>3.3 \times 10^{-8}</td>
<td>1.5 \times 10^{-9}</td>
</tr>
</tbody>
</table>

\(^a\) Upper limit determined by V1 IRIS

\(^b\) Value determined by CIRS

\(^c\) Value determined by ISO

\(^d\) Value determined by CIRS

\(^e\) Value determined by ISO

\(^f\) Value determined by CIRS

\(^g\) Value determined by ISO

This set of forecasts has proved very accurate! Only the first three species were predicted to be detected by CIRS: two of them have.
## Observation Details

### Table 1 Cassini CIRS observations analysed in this report.

<table>
<thead>
<tr>
<th>Flyby #</th>
<th>Observation Name</th>
<th>Start Date and Time</th>
<th>Duration</th>
<th>CIRS Focal Plane</th>
<th>Latitude Range (mean)</th>
<th>Altitude Range (mean)</th>
<th>Pressure Range of Sensitivity</th>
<th>Number of Spectra</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Temperature Retrievals</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>T55</td>
<td>MIDIRTMAP002</td>
<td>22-MAY-2009 11:26:41</td>
<td>8 hrs</td>
<td>4</td>
<td>90°S-40°N</td>
<td>120-220 km</td>
<td>5.0-0.5 mbar</td>
<td>6263</td>
</tr>
<tr>
<td>T64</td>
<td>MIRLMBINT002</td>
<td>28-DEC-2009 05:16:59</td>
<td>4 hrs</td>
<td>4</td>
<td>75°N-76°N (75.5°N)</td>
<td>100-500 km (50 km bins)</td>
<td>3.8-0.0014 mbar</td>
<td>86, 126, 131, 141, 57, 67, 78, 61</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Upper Limits Calculations</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>T55</td>
<td>MIRLMPAIR002</td>
<td>22-MAY-2009 02:26:41</td>
<td>4 hrs</td>
<td>3</td>
<td>25±2°S (25.5°S)</td>
<td>97-122 km (107 km)</td>
<td>7.6 mbar</td>
<td>1213</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>4</td>
<td>25±2°S (25.5°S)</td>
<td>225-275 km (247 km)</td>
<td>0.27 mbar</td>
<td>941</td>
</tr>
<tr>
<td>T64</td>
<td>MIRLMPAIR001</td>
<td>27-DEC-2009 15:16:59</td>
<td>4 hrs</td>
<td>3</td>
<td>75.8±2.0°N (76.0°N)</td>
<td>204-254 km (224 km)</td>
<td>0.26 mbar</td>
<td>517</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>4</td>
<td>75.8±2.0°N (75.7°N)</td>
<td>325-375 km (348 km)</td>
<td>0.018 mbar</td>
<td>491</td>
</tr>
</tbody>
</table>
FP3 at 107 km, 25°S. Range 109 to 178 Kkm. FP4 altitude increasing from 230 to 290 km.
FP3 at 225 km, 76°N. Range 178 to 97 Kkm. FP4 altitude decreasing from XX to YY km.
• FP4 at 225 km, 62°N. Range 179 to 99 Kkm. FP3 altitude decreasing from XX to YY km.
Further Candidate Gases

- **Aliphatic hydrocarbons**: \( \text{C}_3\text{H}_6, \text{C}_4\text{H}_4, \text{C}_4\text{H}_6, \text{C}_4\text{H}_8 \ldots \) (various structural isomers available)
- **Cyanides**: \( \text{C}_2\text{H}_3\text{CN}, \text{C}_2\text{H}_5\text{CN}, \text{C}_3\text{H}_5\text{CN}, \text{C}_6\text{H}_5\text{CN} \ldots \)
- **Amines and imines**: \( \text{N}_2\text{H}_2, \text{N}_2\text{H}_4, \text{CH}_3\text{NH}_2, \text{CH}_2\text{NH} \ldots \)
- **Cyclics**: cyclopropane, cyclobutane, cyclopentane, cyclohexane …
- **Aromatics**: pyridine, pyrimidine, aniline, toluene …
- **PAHs**: naphthalene, anthracene, phenanthracene, pyrene, chrysene, perylene …