

HITRAN Conference
Cambridge, 16-18 June 2010

Titan's neutral atmospheric chemistry from the astronomical point of view

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LESIA, Observ. de Paris-Meudon, Meudon



Titan, the largest kronian satellite...

Physical parameters:

$$R = 2\,575 \text{ km}$$

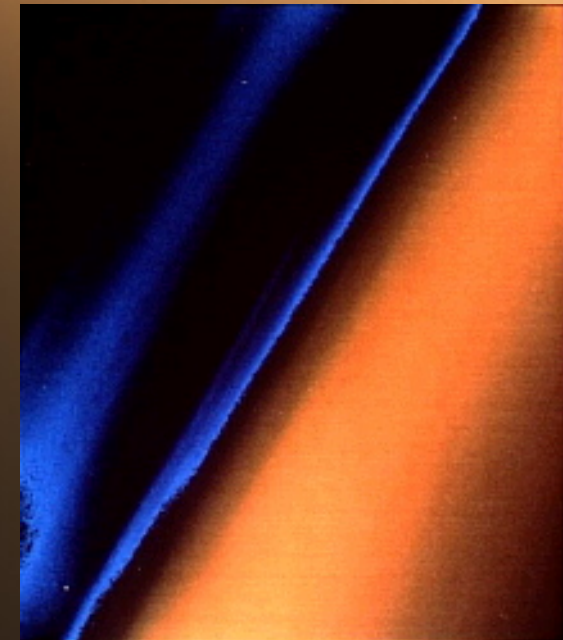
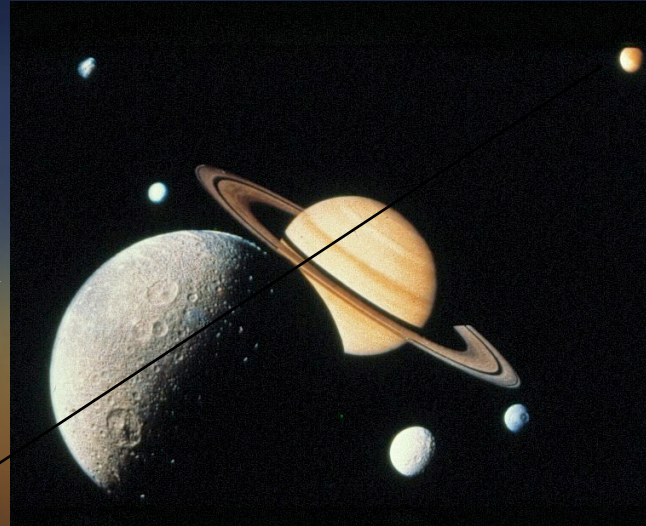
$$m = 1,831 M_{\text{Moon}}$$

Orbital parameters:

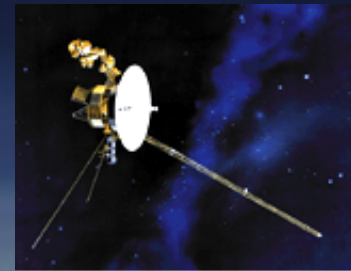
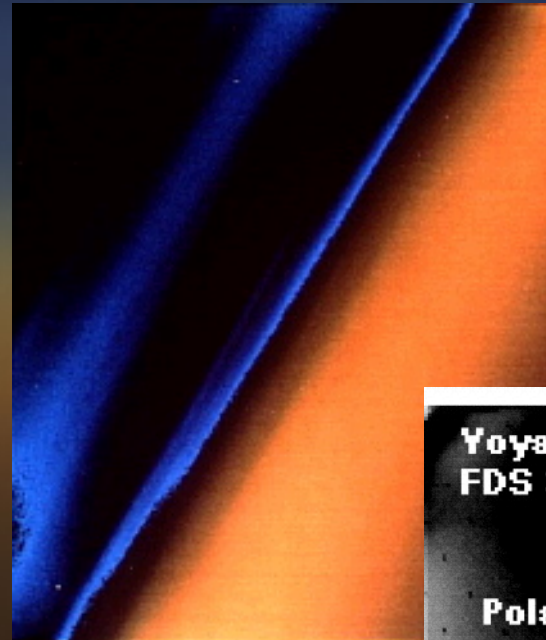
$$a = 1\,221\,830 \text{ km} \sim 20 R_{\text{Saturn}}$$

$$P = 15,95 \text{ j}$$

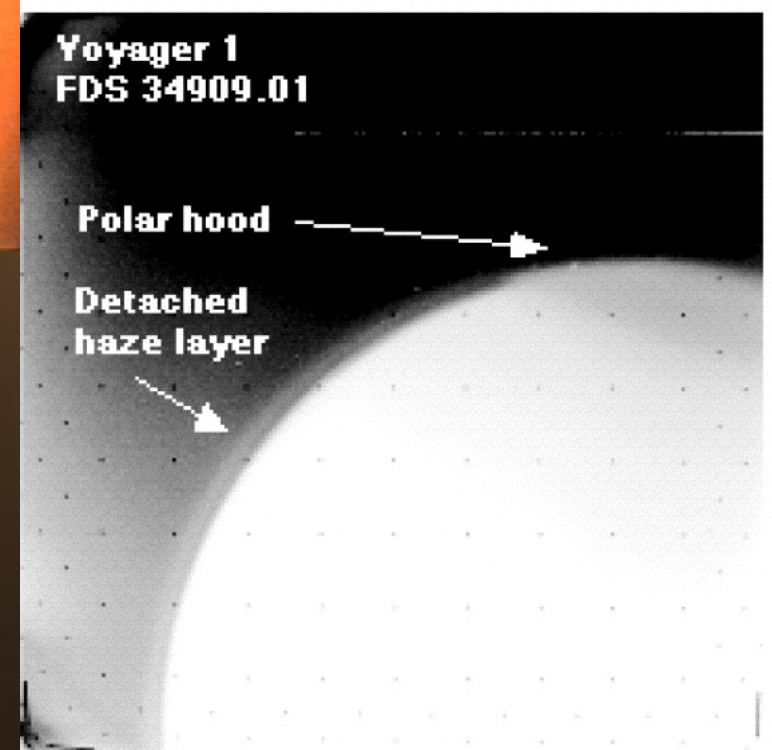
$$e = 0,0292$$



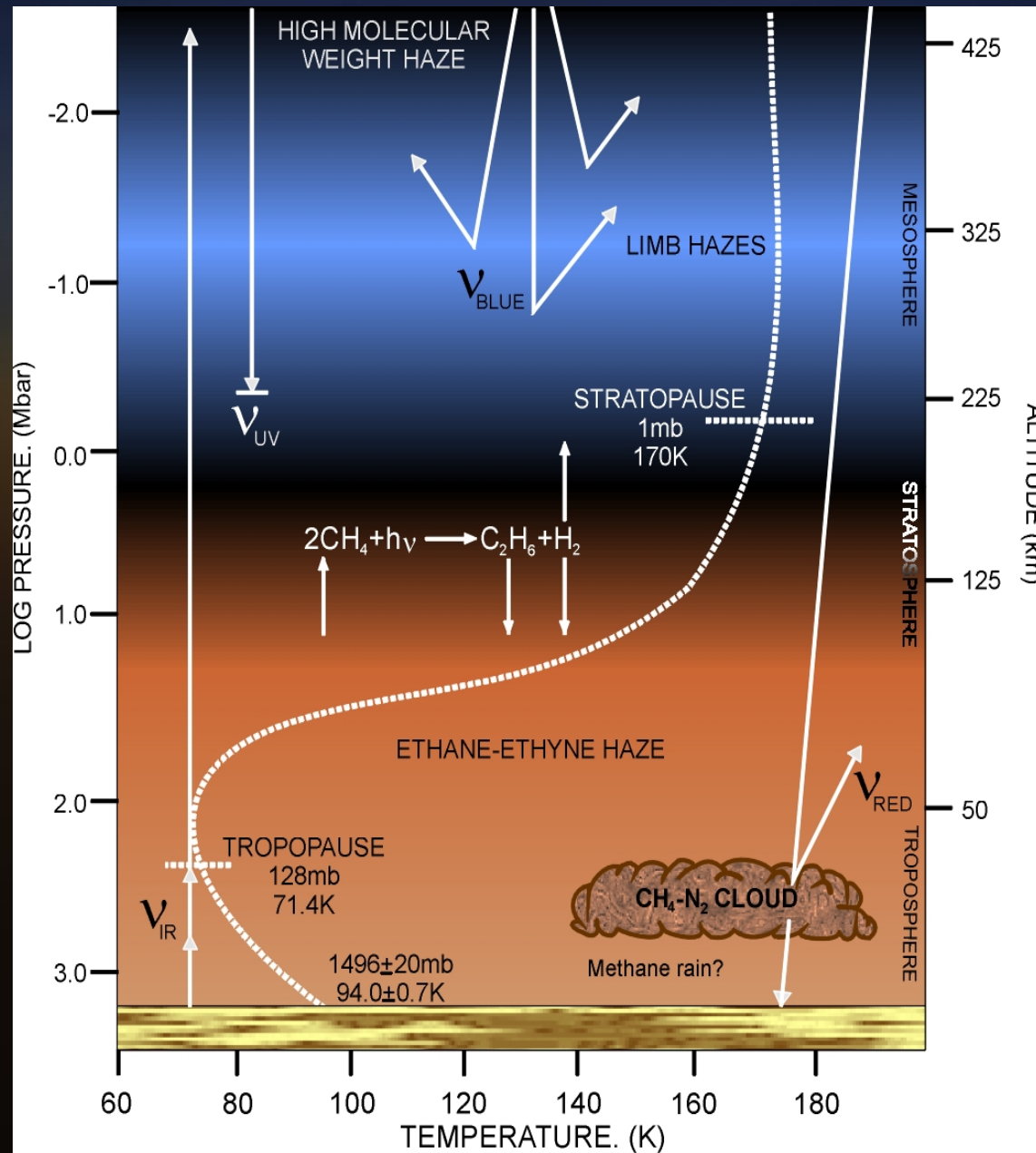
Titan's atmosphere seen by Voyager



Voyager 1 Launch to Jupiter/Saturn
Sept. 5, 1977



Titan



Temperature inversion

By greenhouse effect below 40 km in altitude

Composition of the atmosphere :

- * N₂ is the major component (~97%)

- * CH₄ & other hydrocarbons

- * H₂

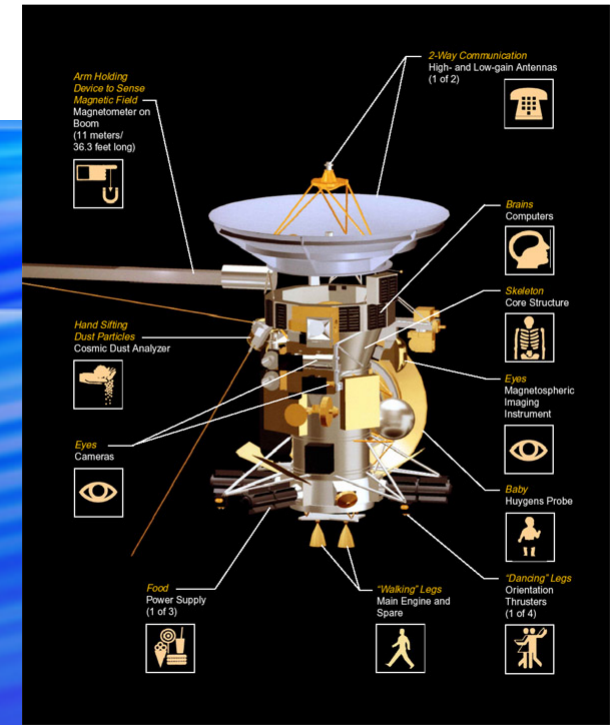
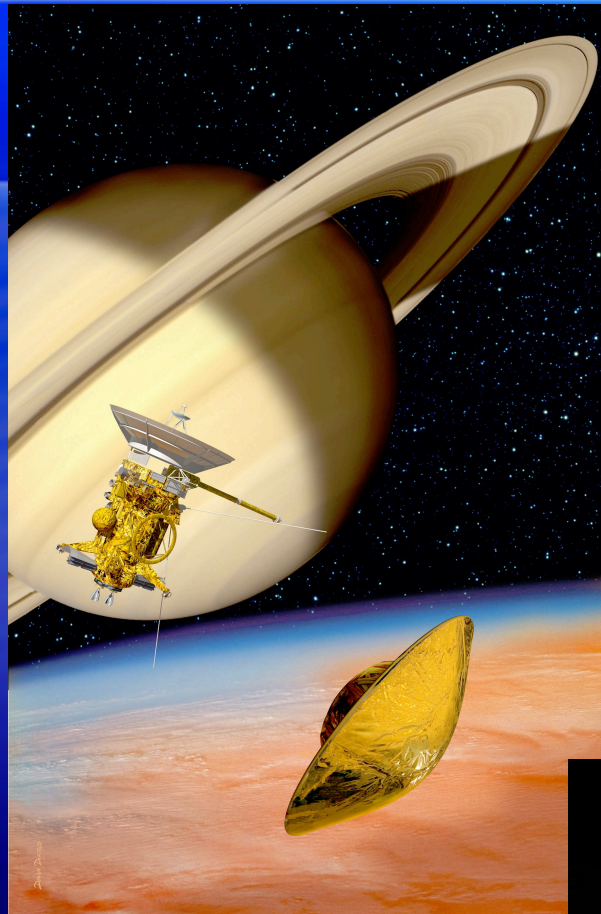
- * nitriles

- Little oxygen:

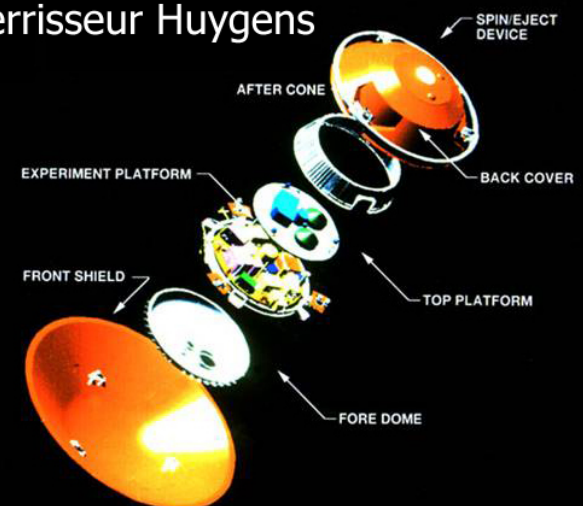
H₂O, CO, CO₂

Huygens et Cassini

- *Thermal and chemical structure in the stratosphere of Titan from IR spectra of **CIRS** on the orbiter.*
- **HASI** determined temperature, pressure and density in the whole atmosphere during the Huygens descent.
- Spectra and images taken by **DISR**, give information on the composition of the surface and constrain the distribution of the aerosols on Titan.

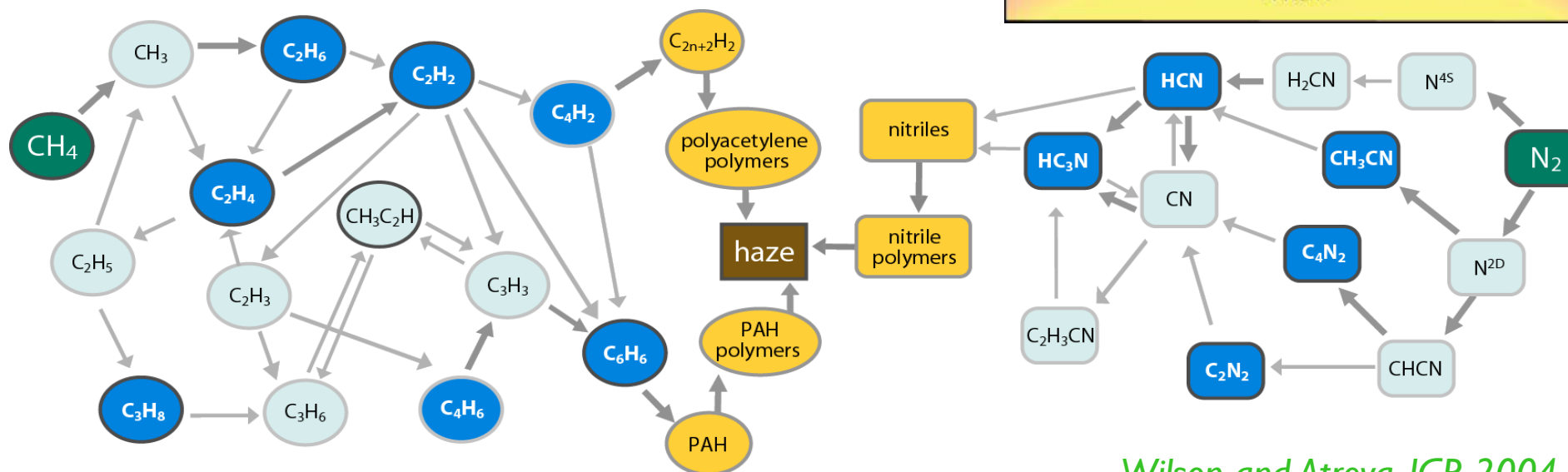
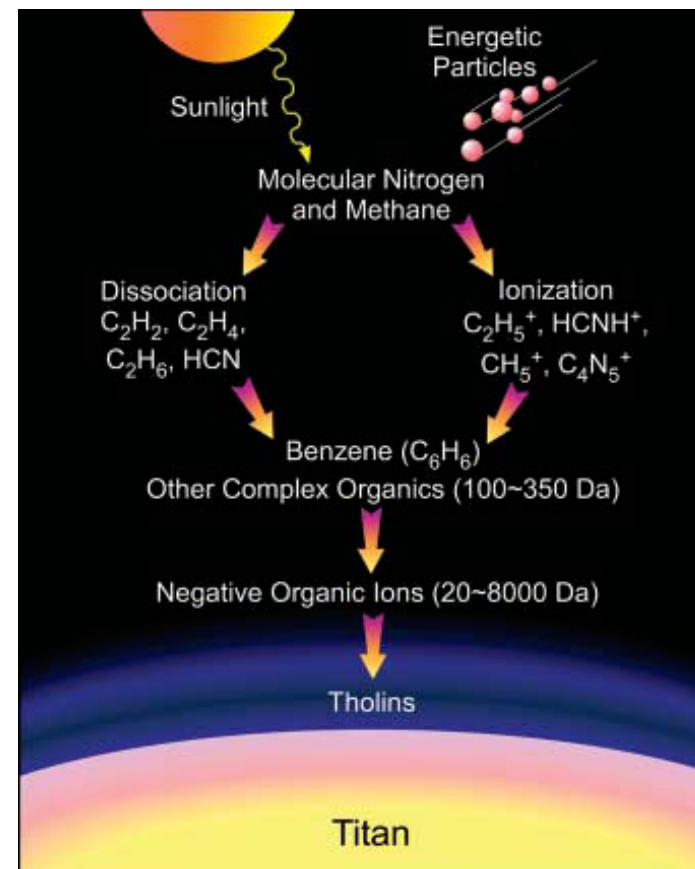


Atterrisseur Huygens



Organic chemistry on Titan

*Cassini/INMS on Titan:
Waite et al (2006)*



Wilson and Atreya, JGR 2004

Gas		Mole fraction		Comments-Ref.
<i>Major components</i>				
Nitrogen	N ₂	0.97		Inferred indirectly
Methane	CH ₄	1.4-1.8×10 ⁻²		Stratosphere (1,2)
		4.9 ×10 ⁻²		Surface (2,3)
Monodeuterated methane	CH ₃ D	8×10 ⁻⁶		(4)
Hydrogen	H ₂	0.0011		(5)
Argon	³⁶ Ar	2.8×10 ⁻⁷		(2)
	⁴⁰ Ar	4.32×10 ⁻⁵		(2)
		<i>Equator</i>	<i>North Pole</i>	
<i>Hydrocarbons</i>				
Ethane	C ₂ H ₆	1.3×10 ⁻⁵	1.7×10 ⁻⁵	(4)
Acetylene	C ₂ H ₂	3.7×10 ⁻⁶	4.0×10 ⁻⁶	(4)
Monodeuterated acetylene	C ₂ HD	2×10 ⁻⁹		
Propane	C ₃ H ₈	6.0×10 ⁻⁷	8.0×10 ⁻⁷	(4)
Ethylene	C ₂ H ₄	1.6×10 ⁻⁷	1.1×10 ⁻⁷	(4)
Methylacetylene	C ₃ H ₄	6.4×10 ⁻⁹	1.2×10 ⁻⁸	(4)
Diacetylene	C ₄ H ₂	1.3×10 ⁻⁹	4.2×10 ⁻⁹	(4)
Benzene	C ₆ H ₆	3.0×10 ⁻¹⁰	1.1×10 ⁻⁹	(4)
<i>Nitriles</i>				
Hydrogen cyanide	HCN	1.3×10 ⁻⁷	5.5×10 ⁻⁷	(4,6)
Cyanoacetylene	HC ₃ N	3.0×10 ⁻¹⁰	2.2×10 ⁻⁹	(4)
Cyanogen	C ₂ N ₂	5×10 ⁻¹⁰	9×10 ⁻¹⁰	(6)
Dicyanogen	C ₄ N ₂			Solid form only (7)
Acetonitrile	CH ₃ CN	1.5×10 ⁻⁹		(8)
<i>Oxygen compounds</i>				
Water vapor	H ₂ O	8×10 ⁻⁹		(9) at 400 km
Carbon dioxide	CO ₂	1.5×10 ⁻⁸	1.9×10 ⁻⁸	(4)
Carbon monoxide	CO	(2-4) ×10 ⁻⁵		Troposphere (10,11)
		(3-6)×10 ⁻⁵		Stratosphere (1,12)
<i>Isotopic ratios</i>				
¹³ C/ ¹⁴ C		82.3±1		(2)
¹⁴ N/ ¹⁵ N in HCN		67		(11)
In N ₂		183±5		(2)
D/H in CH ₃ D		1.3×10 ⁻⁴		(4)
in HD		2.3×10 ⁻⁴		(2)
in C ₂ HD		1.7×10 ⁻⁴		(4)

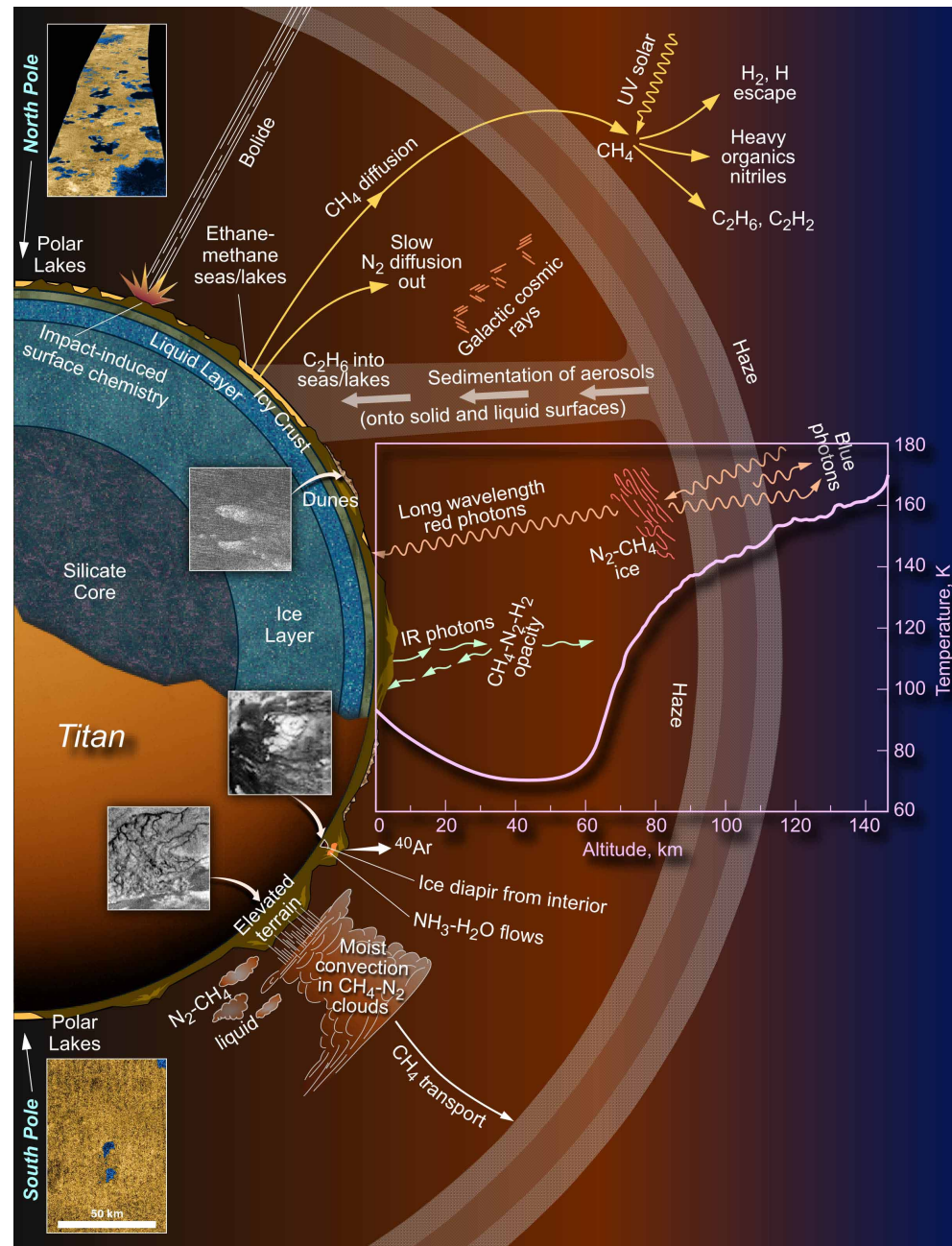
1. Flasar *et al.* (2005) from Cassini/CIRS data
2. Niemann *et al.* 2005 from Huygens/GCMS data
3. Tomasko *et al.* (2005) from Huygens/DISR data
4. Coustenis *et al.* (2007) from Cassini/CIRS data
5. Samuelson *et al.* (1997a) from V1/IRIS data
6. Teanby *et al.* (2006) from Cassini/CIRS data
7. Samuelson *et al.* (1997b) from V1/IRIS data
8. Bézard *et al.* (1993) from disk-averaged ground-based heterodyne mm observations
9. Coustenis *et al.* (1998) from ISO/SWS data
10. Lellouch *et al.* (2003) from ground-based VLT data at 5 micron
11. Marten *et al.* (2002) from disk-averaged ground-based heterodyne mm observations
12. Gurwell and Muhleman (2000) from disk-averaged mm heterodyne data

From Vuitton, Waite, et al. INMS

Ionospheric species detected by INMS	Neutral mole fractions
H ₂	4 × 10 ⁻³
CH ₄	3 × 10 ⁻²
C ₂ H ₂	3 × 10 ⁻⁴
C ₂ H ₄	6 × 10 ⁻³
C ₂ H ₆	1 × 10 ⁻⁴
C ₄ H ₂	6 × 10 ⁻⁵
HCN	2 × 10 ⁻⁴
HC ₃ N	2 × 10 ⁻⁵
CH ₃ CN	1 × 10 ⁻⁵
C ₂ H ₃ CN	1 × 10 ⁻⁵
C ₂ H ₅ CN	5 × 10 ⁻⁷
NH ₃	7 × 10 ⁻⁶
CH ₂ NH	< 1 × 10 ⁻⁵

*Coustenis & Taylor
2008 (WSP)*

Titan: a world of high interest for planetology and astrobiology studies



Context

Dense planetary atmospheres:

Observations : Voyager, ground-based, ISO and Cassini-Huygens

Titan (N_2 , CH_4), 1,5 bar, 94 K on the surface

Long atmospheric paths

scale heights of a few tens of km

Temperatures difficult to achieve in a laboratory

Titan : 70-94 K in troposphere; <200 K in stratosphere

Space exploration and instrumentation:

Observations : Cassini-Huygens : 2004-2017

Thermal IR :

Cassini/CIRS : $7\mu\text{m}$ -1mm (resolution up to 0.5 cm^{-1})

Near-IR:

Cassini/VIMS : $0,35$ - $5,2\ \mu\text{m}$ (resolution 7-16 nm)

Huygens/DISR : $0,48$ - $1,7\ \mu\text{m}$ (resolution: 5-17 nm)

Context

Goals:

Cartography of the chemical composition with high precision

Detect new components with low abundance levels (including isotopes)

Determine the origin and evolution of the planetary bodies

Need for spectroscopic measurements at the right p , T conditions to be able to perform the spectroscopic analysis

We study the physical properties in the atmosphere of the giant planets and Titan with radiative transfer calculations

- **Using a line-by-line code**

solving for

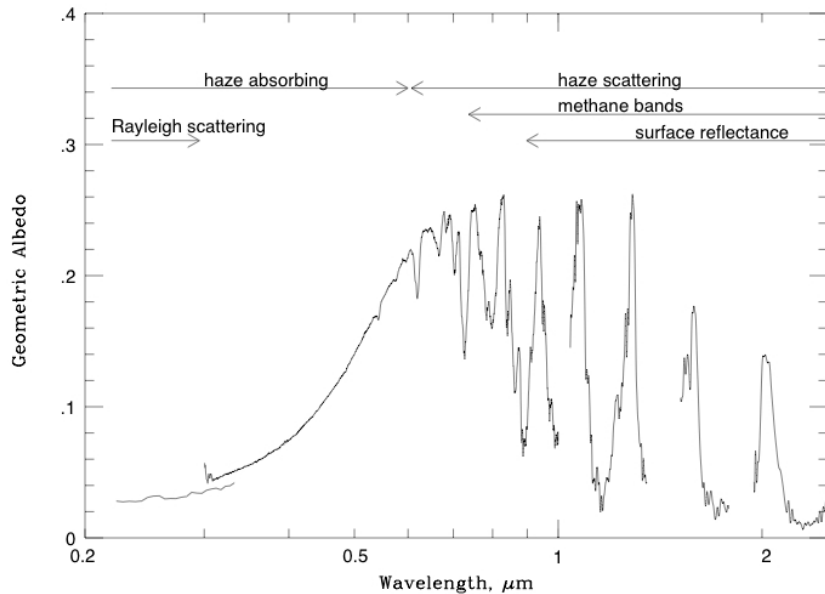
- **Opacity sources**

- Chemical abundances (gas and solid)

- Haze/aerosols

- clouds

- **Temperature structure**



Titan's UV and near-IR spectrum mainly through ground-based measurements (CFHT, UKIRT, IRTF, Keck, VLT, etc), with the exception of HST and ISO from space.

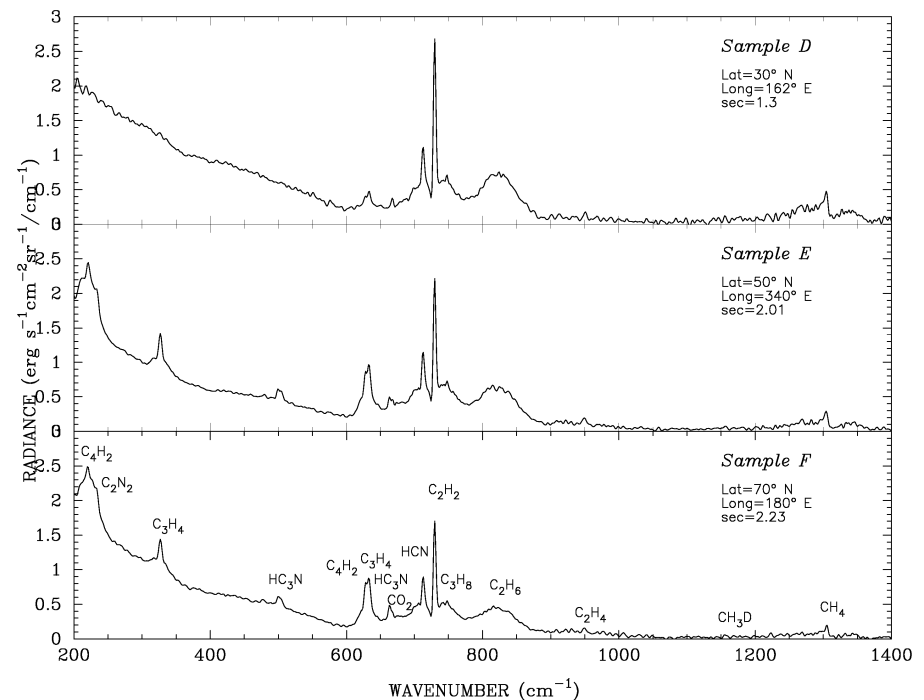
7

→

50 μm

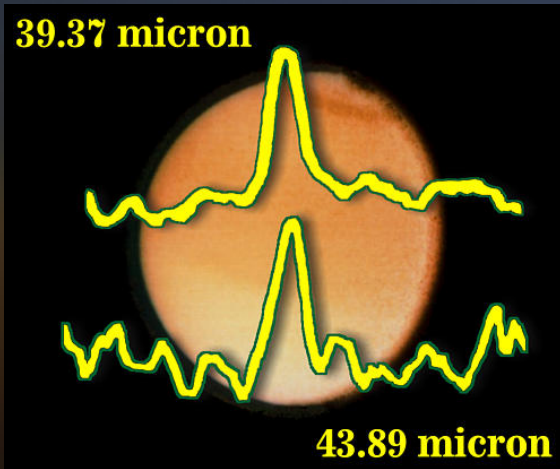
Titan's far-IR spectrum mainly through space observations since 1980: Voyager, ISO and Cassini in the future. (Parts thereof were observed from the ground e.g. by Gillett long before that and also since then).

→ 5 μm



Discoveries on Titan by Infrared Space Observatory (ISO)

A. Coustenis, A. Salama, B. Schulz, E. Lellouch, Th. Encrenaz, S. Ott, M. Kessler, Th. De Graauw, the ISO Titan Team

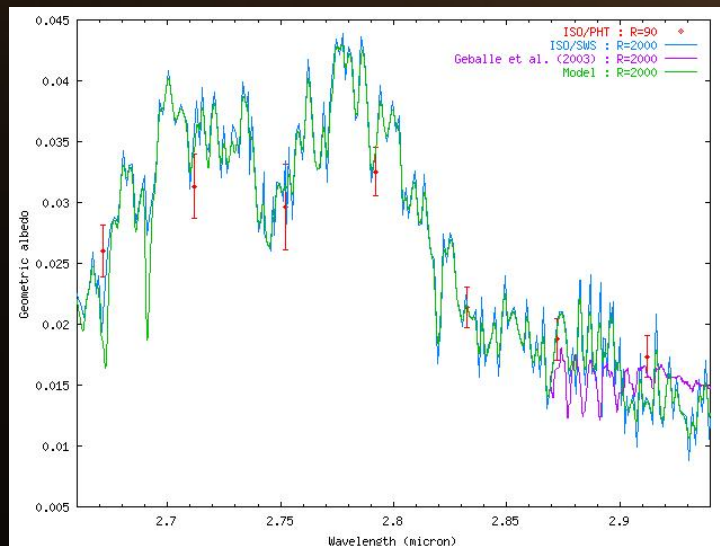
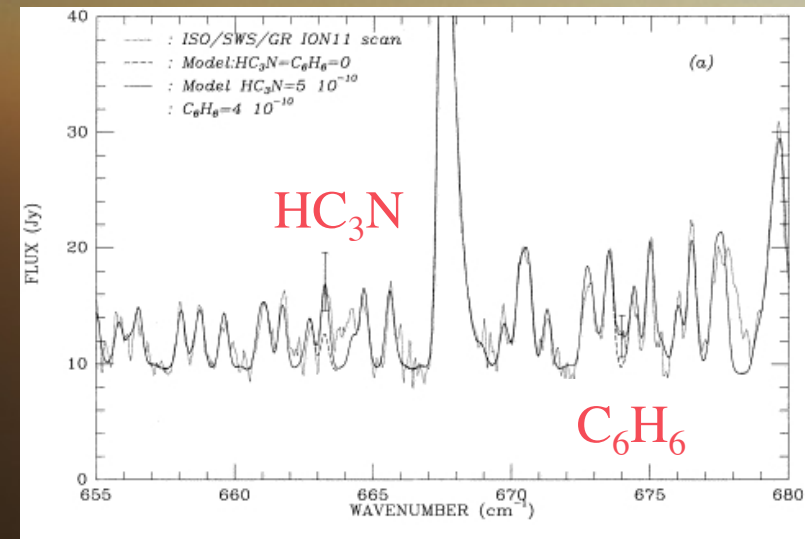


Water vapour

(Coustenis et al., 1998)

Benzene (C₆H₆)

(Coustenis et al., 2003)

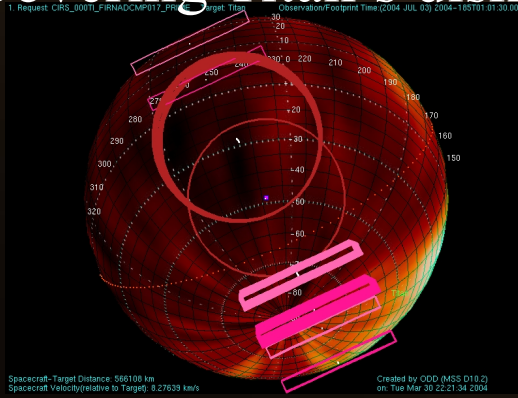


First surface albedo spectrum in the 3 micron methane window

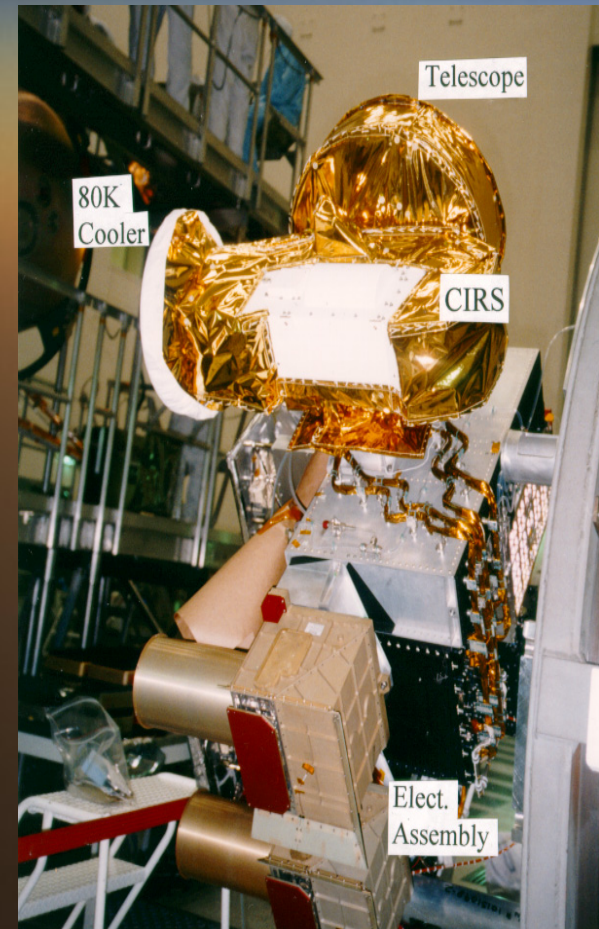
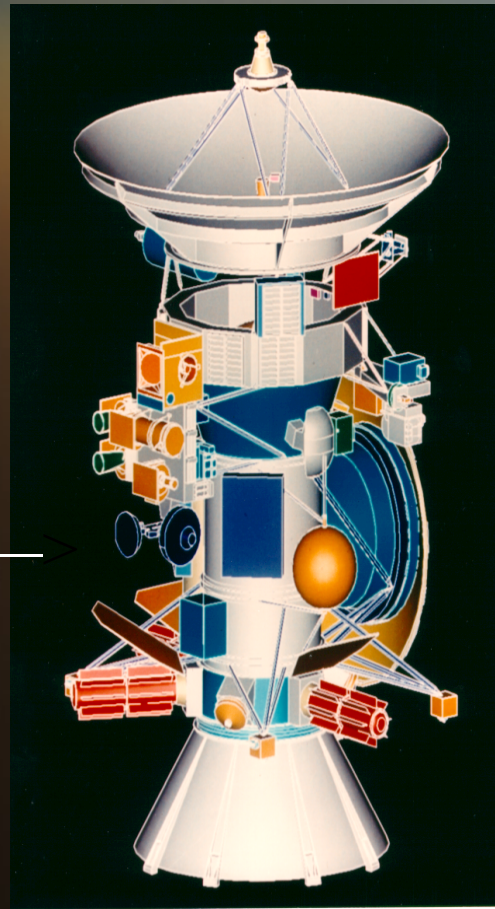
(Coustenis et al., 2004-2005)

*We have analyzed CIRS observations
(nadir and limb) covering the
thermal infrared region (10-1500 cm^{-1})*

Since July 2, 2004 : TB-
T62 flybys
FP3 and FP4 spectra
high resolution apodized
(0.53 cm^{-1}) or medium
resolution (2.5 cm^{-1})
Covering Titan's disk

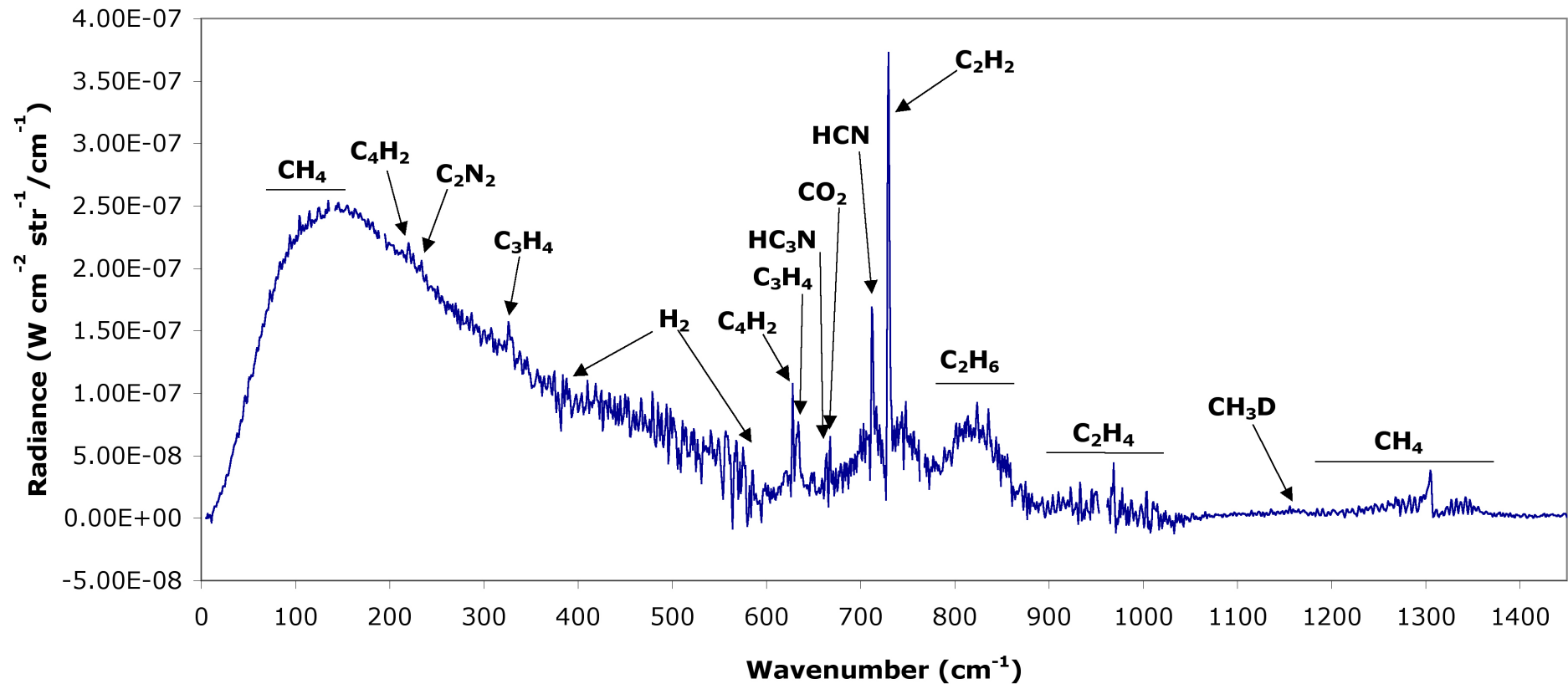


CIRS →

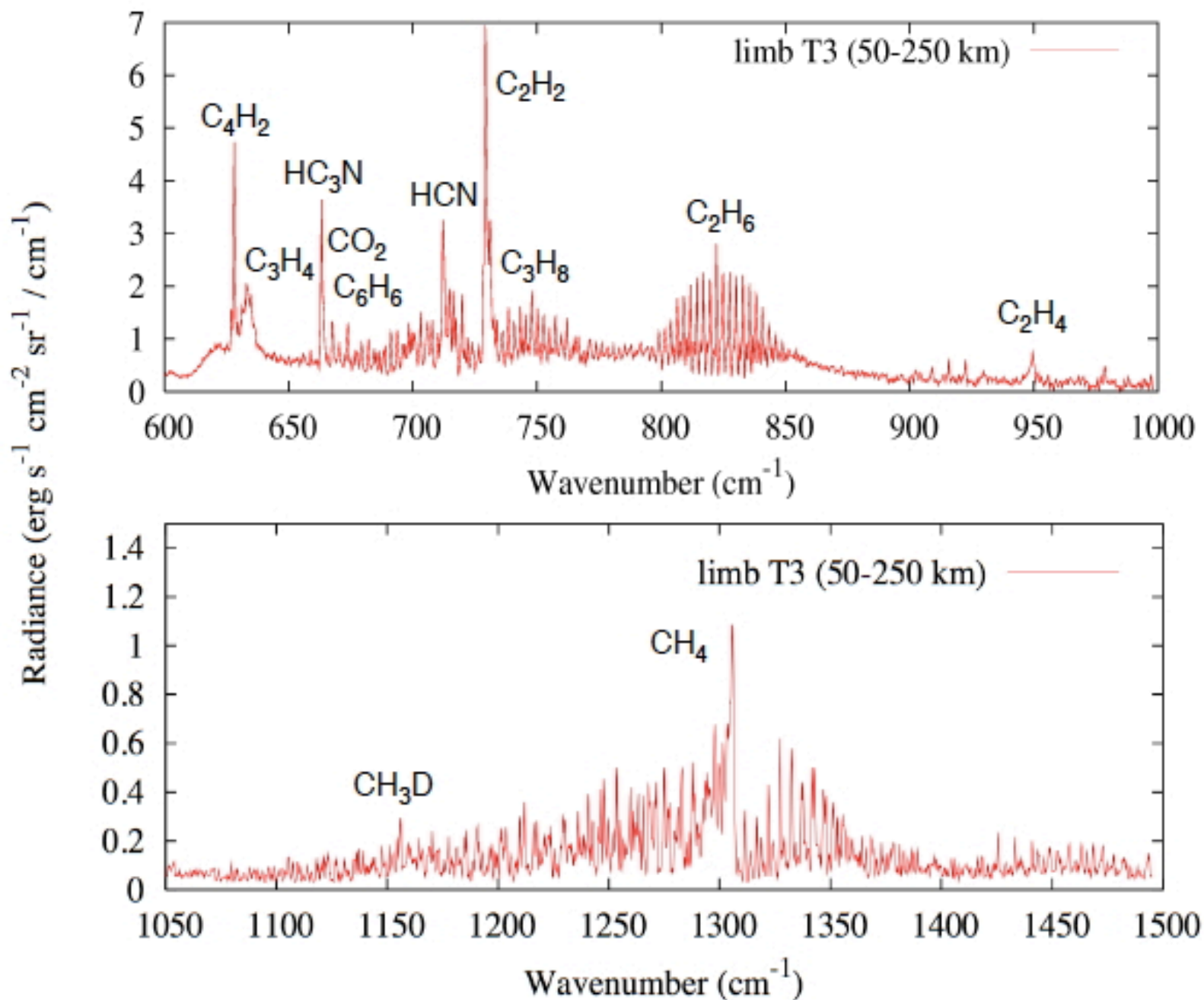


Cassini-CIRS Ta at Titan

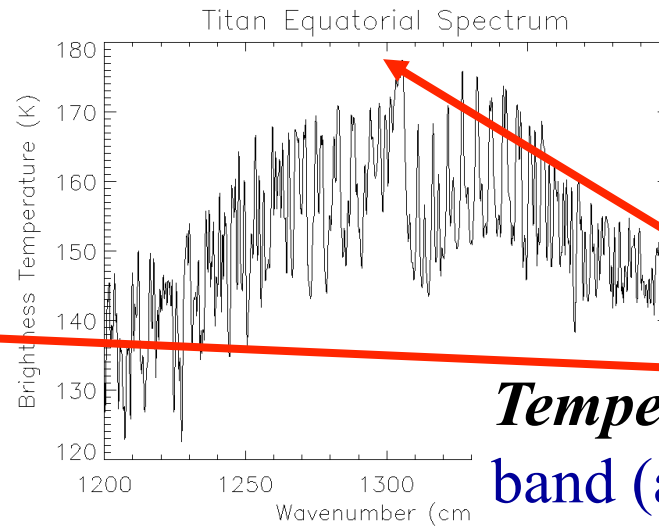
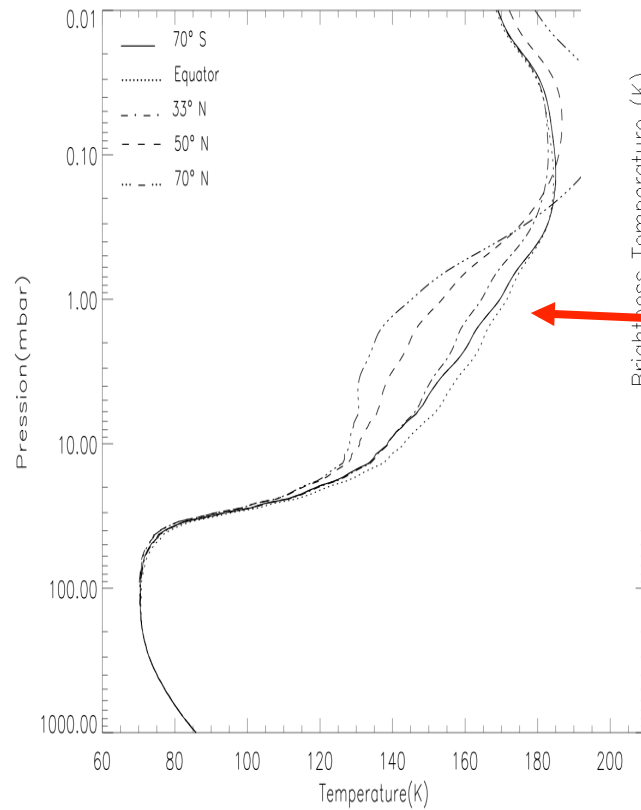
Titan North from Ta Flyby Resolution 1.7 cm^{-1}



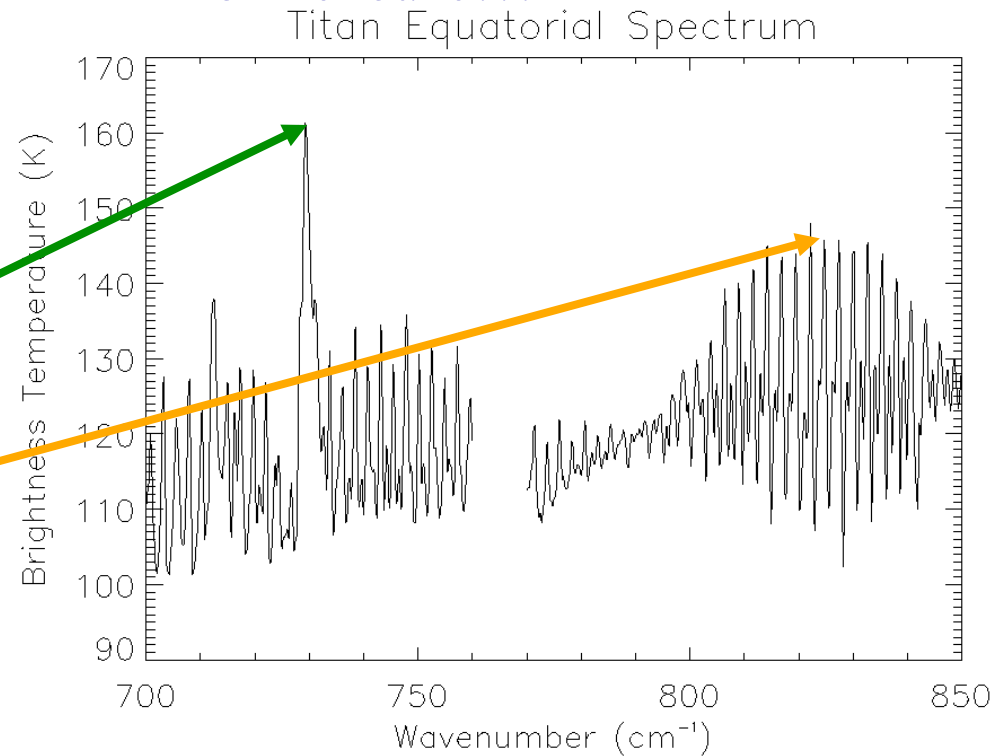
Titan



Spectral Modelling

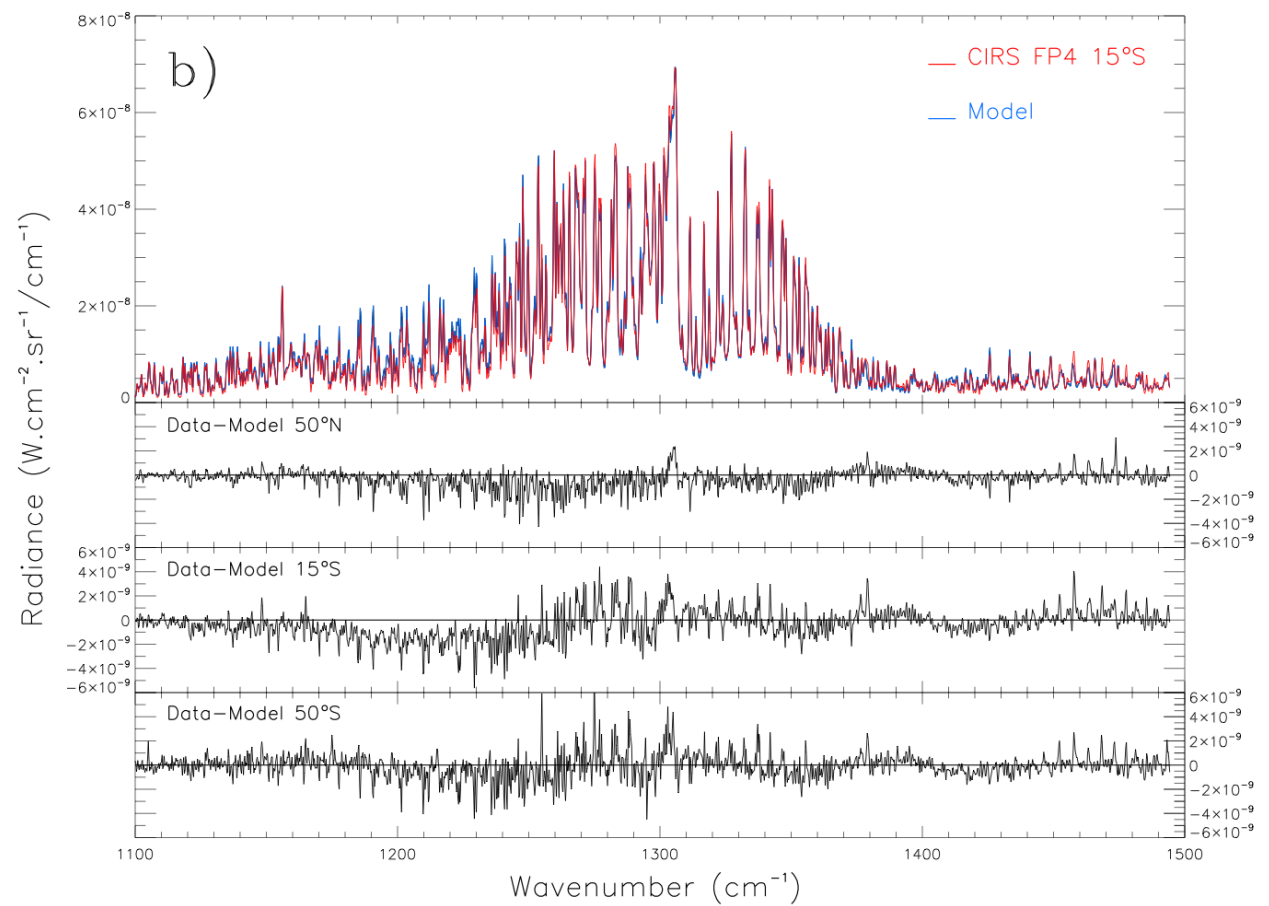
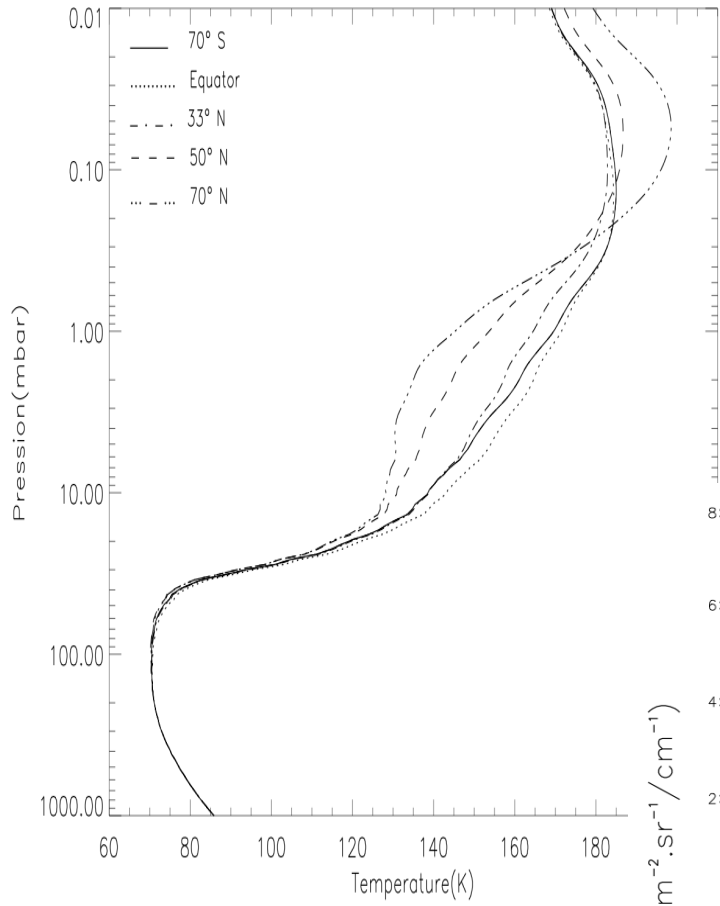


Temperatures from CH₄ ν₄ band (assuming Huygens VMR profile). Can use these to measure...



Abundances from emission bands of ¹³CH₄, C₂H₂, ¹³C¹²CH₂, C₂H₆, ¹³C¹²CH₆
- allows calculation of isotopic ratios.

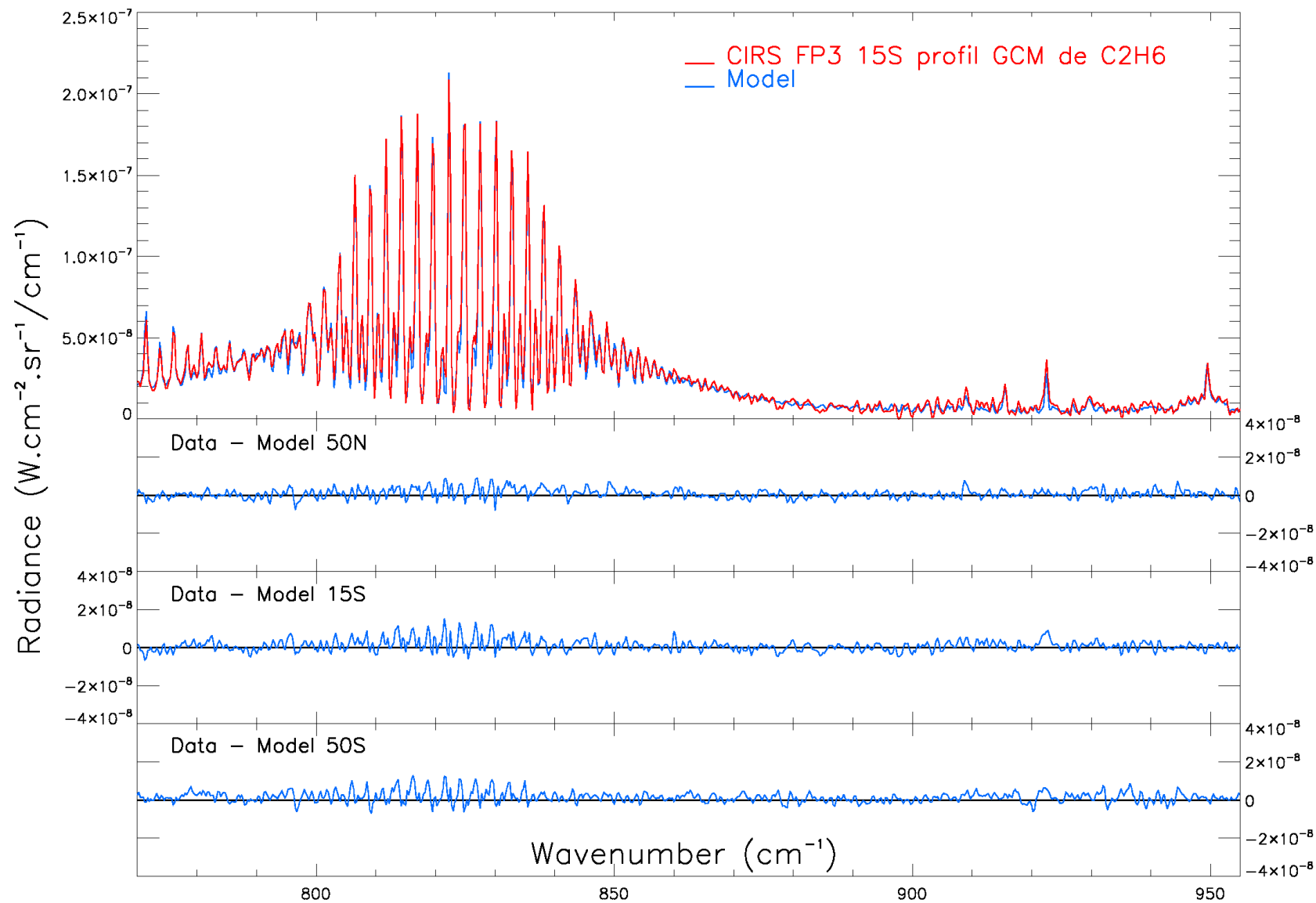
Titan ν_4 CH₄ band with CIRS Gives access to thermal profile



Achterberg et al., 2008

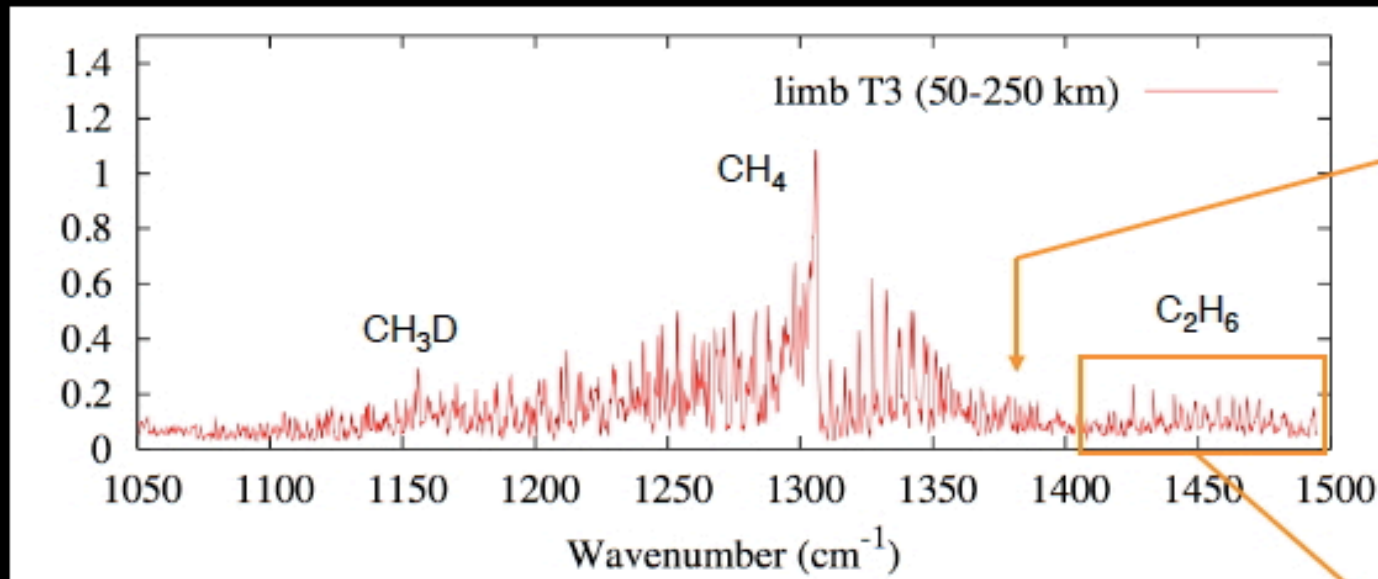
Coustenis et al., 2010

The ν_9 C_2H_6 band at 821 cm^{-1}

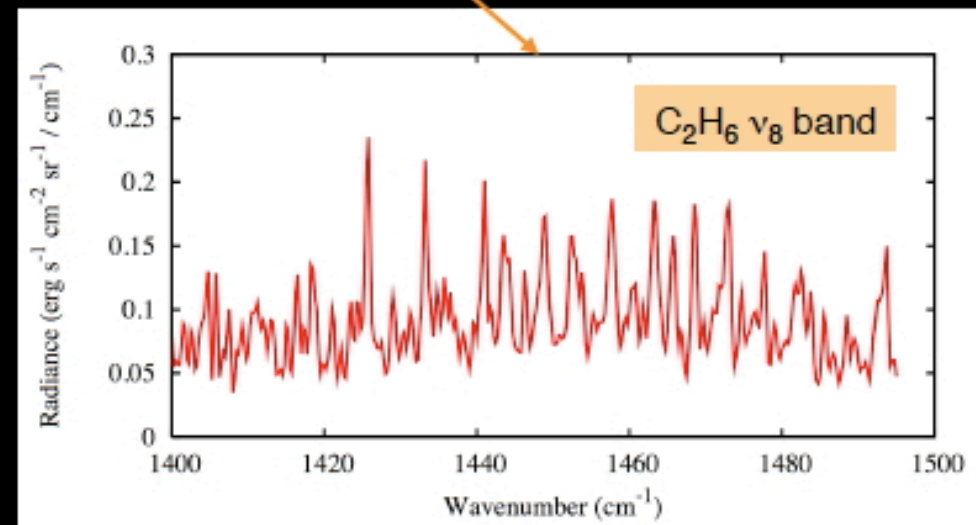


Coustenis et al., 2010 with new spectro data by Jean Vander Auwera

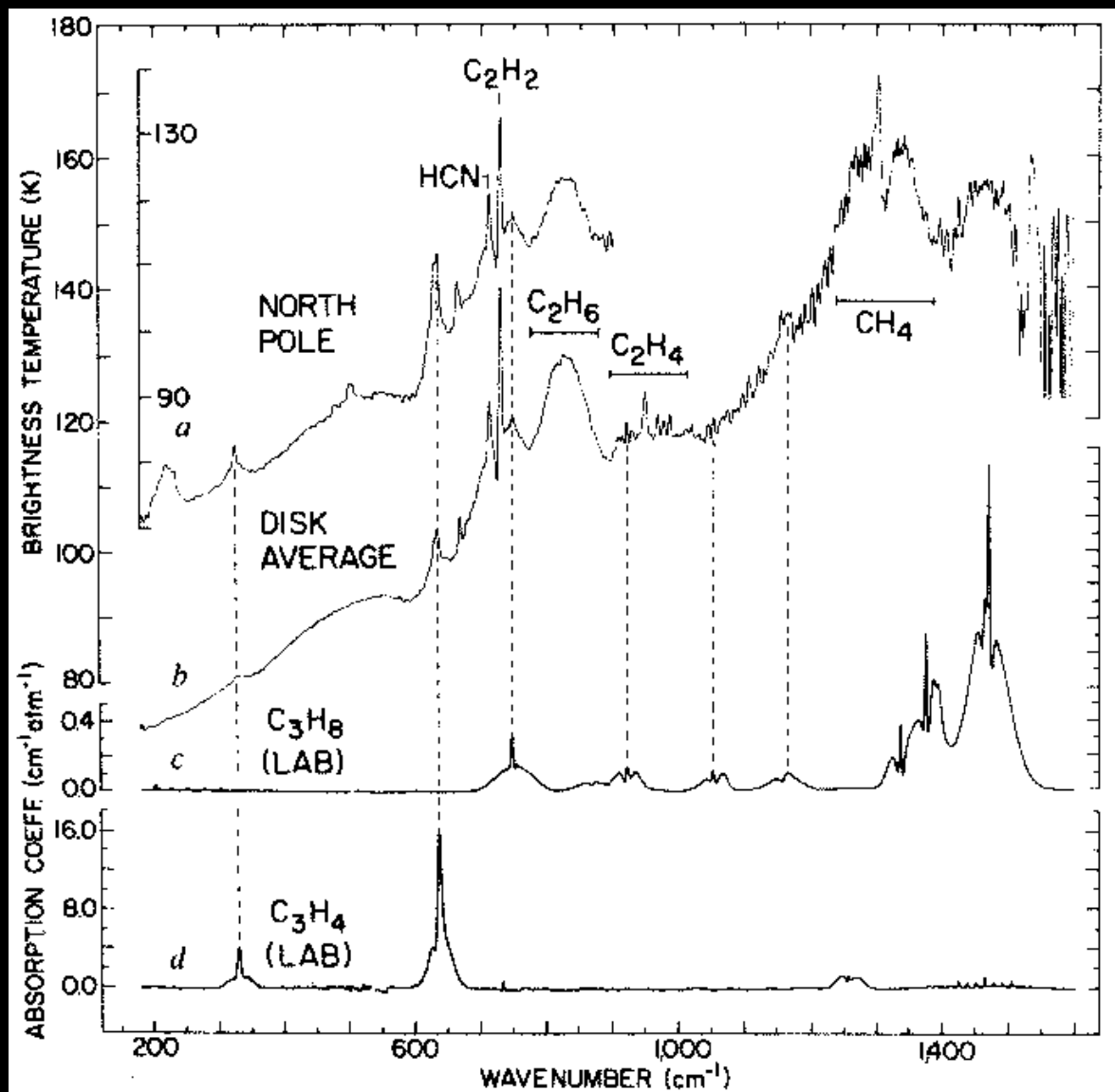
Ethane band



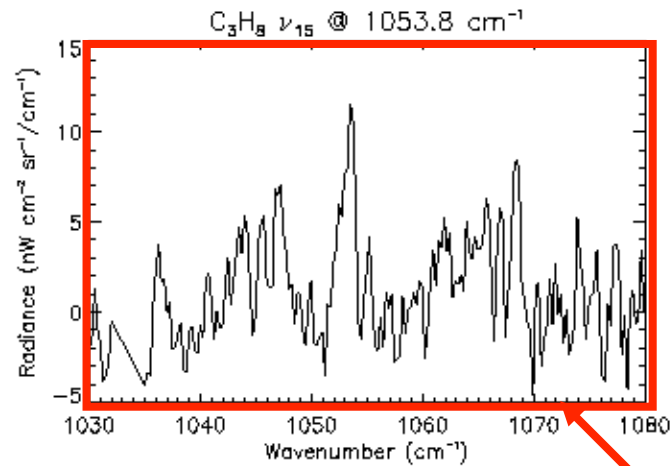
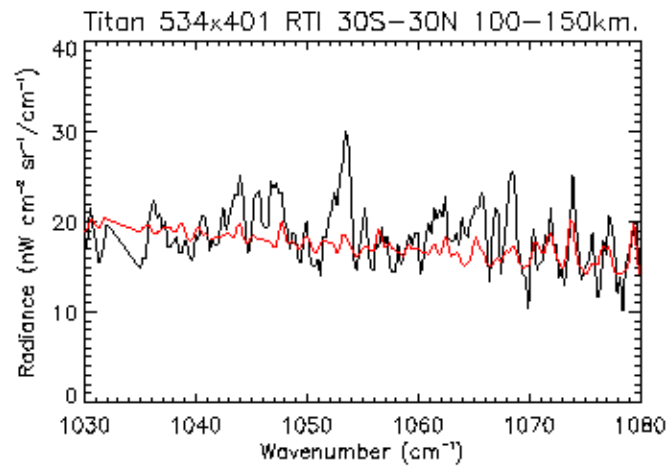
C₂H₆ v₆ band



Propane - Historical Perspective

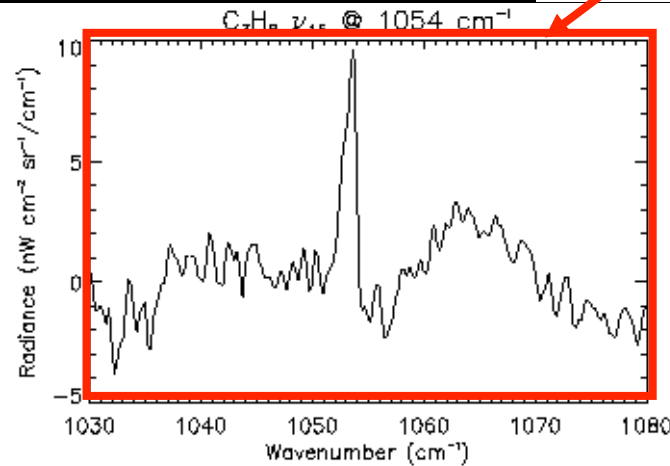
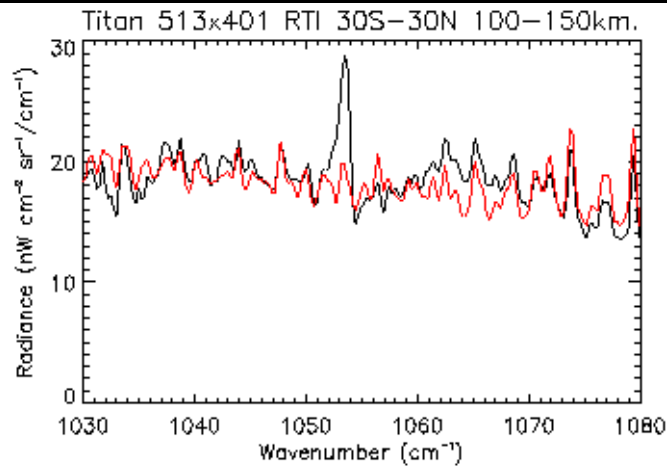
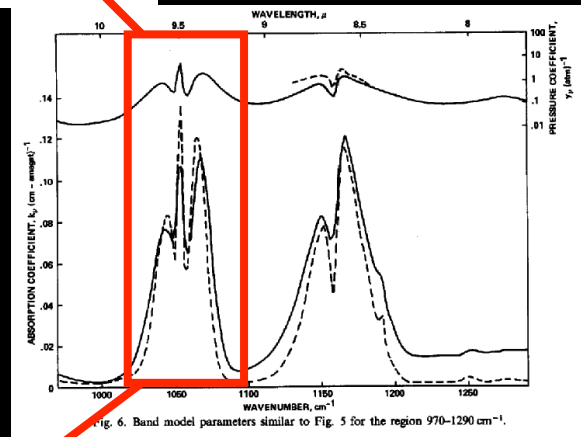


- First identification of C₃H₈ on Titan came from Voyager IRIS (Maguire *et al. Nature, 1981*)
- Although multiple bands were identified, the S/N was poor,
- Only the ν_{21} band at 748 cm⁻¹ was ever used for VMR determination (papers by Coustenis *et al.*)



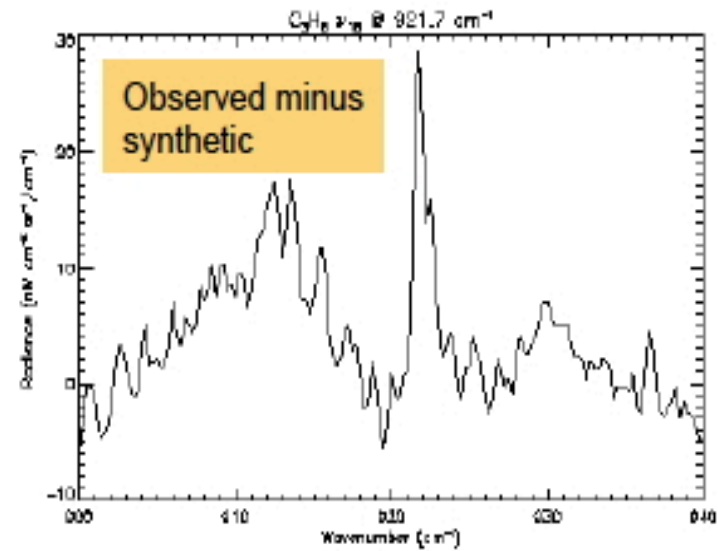
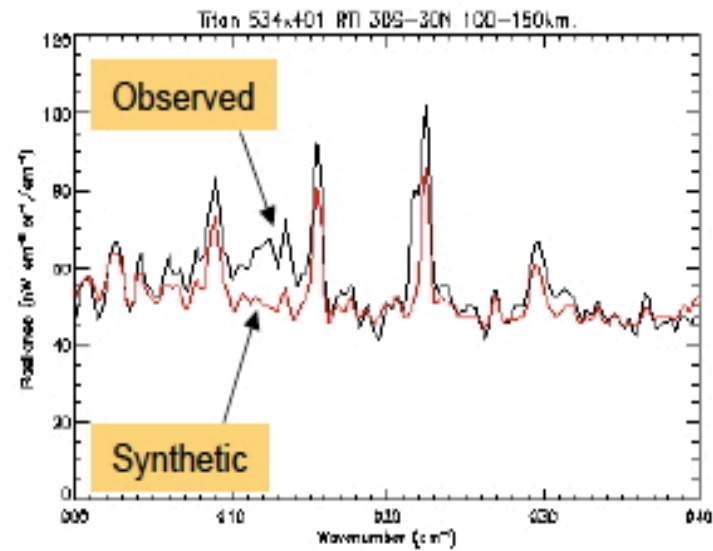
**CIRS
FP3**

ν_{15} band @ 1054 cm^{-1}

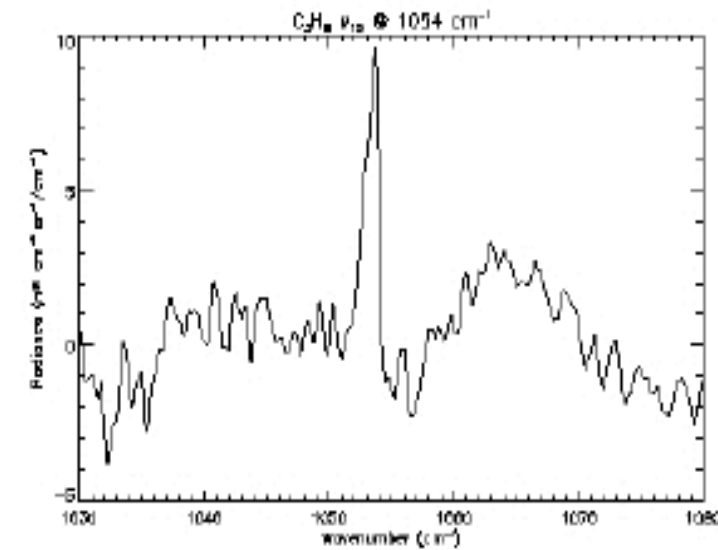
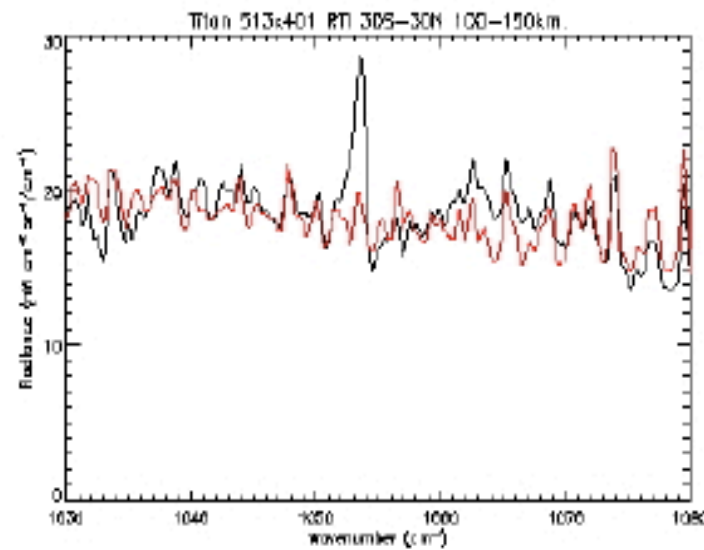


**CIRS
FP4**

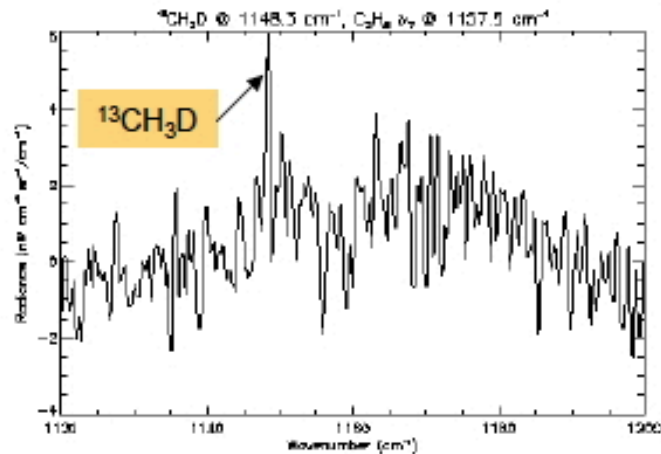
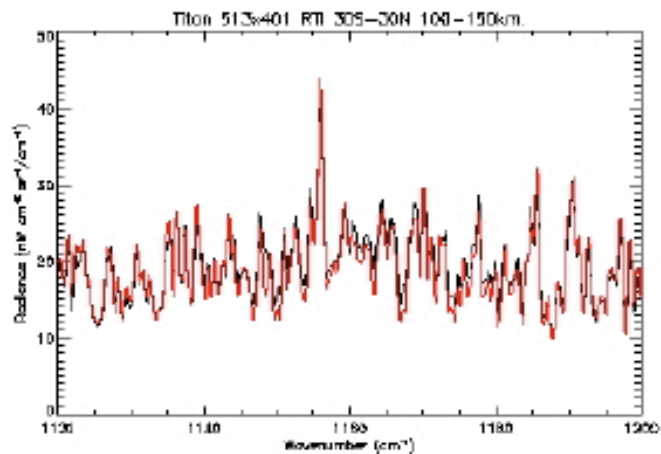
Propane



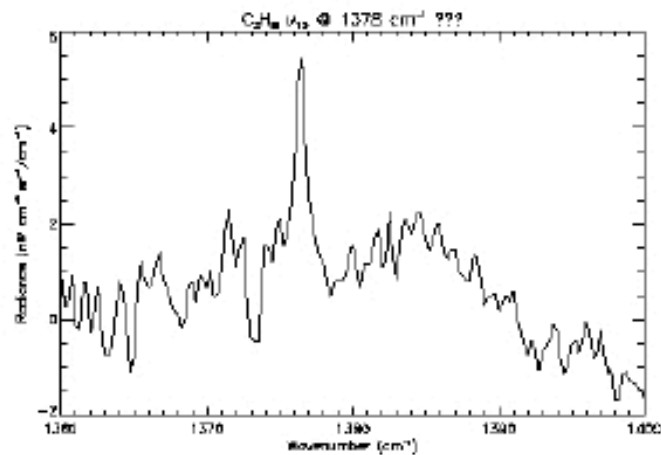
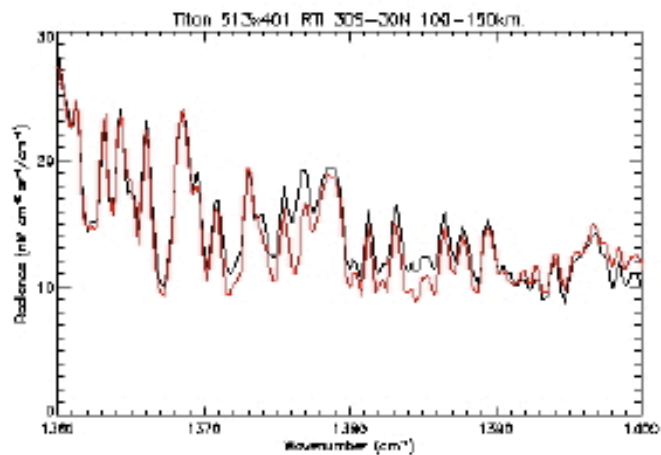
922 cm^{-1}



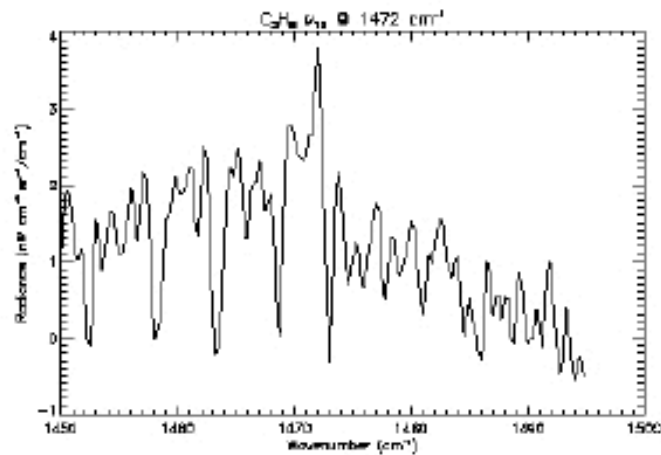
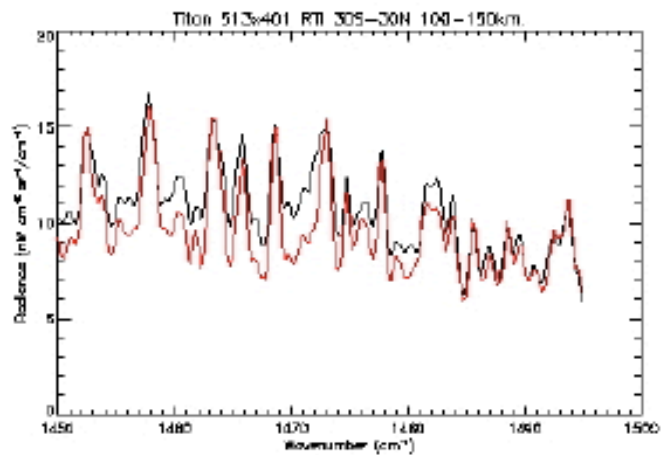
1054 cm^{-1}



1158 cm⁻¹



1377 cm⁻¹

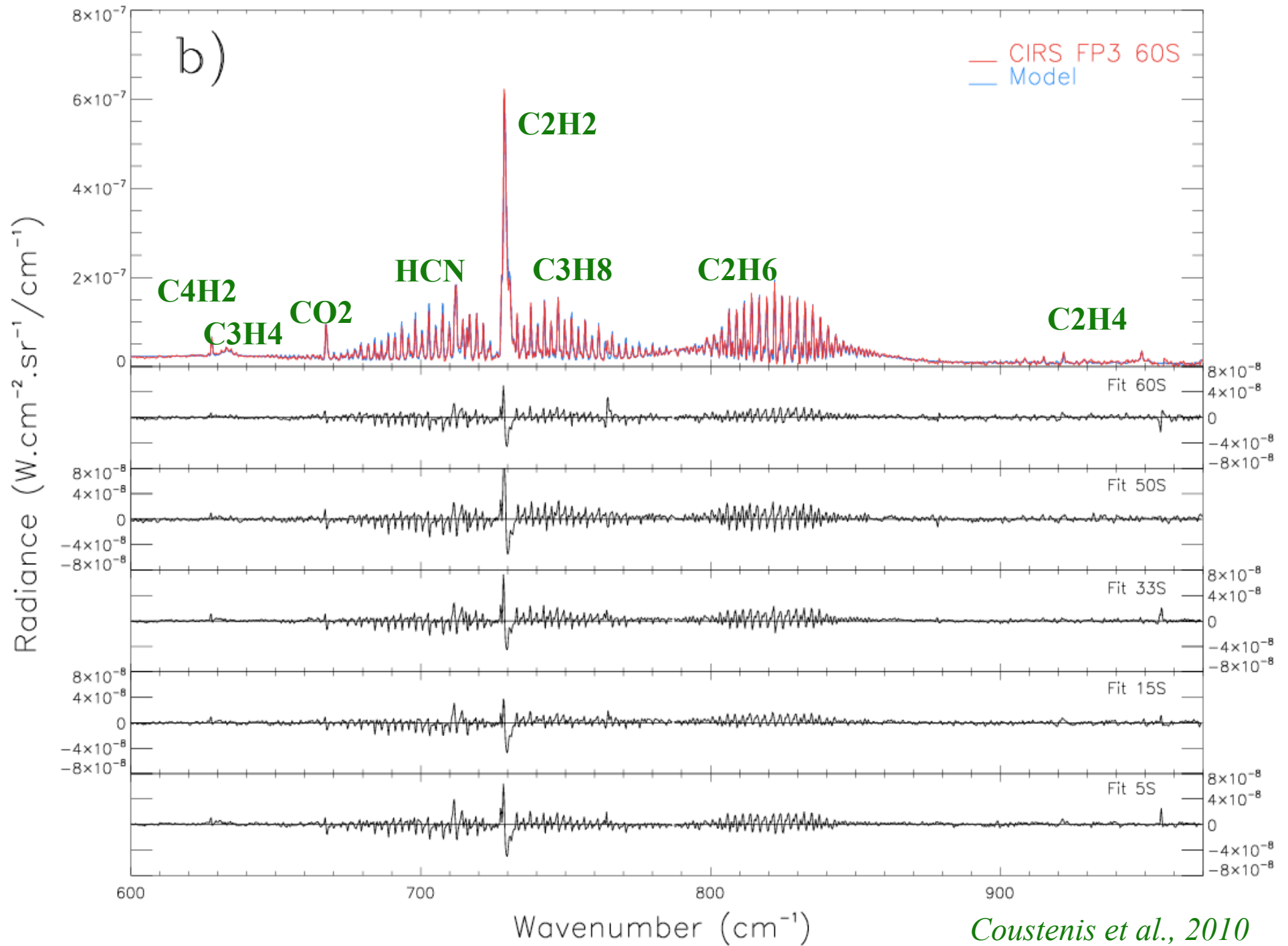


1472 cm⁻¹

Propane - Summary

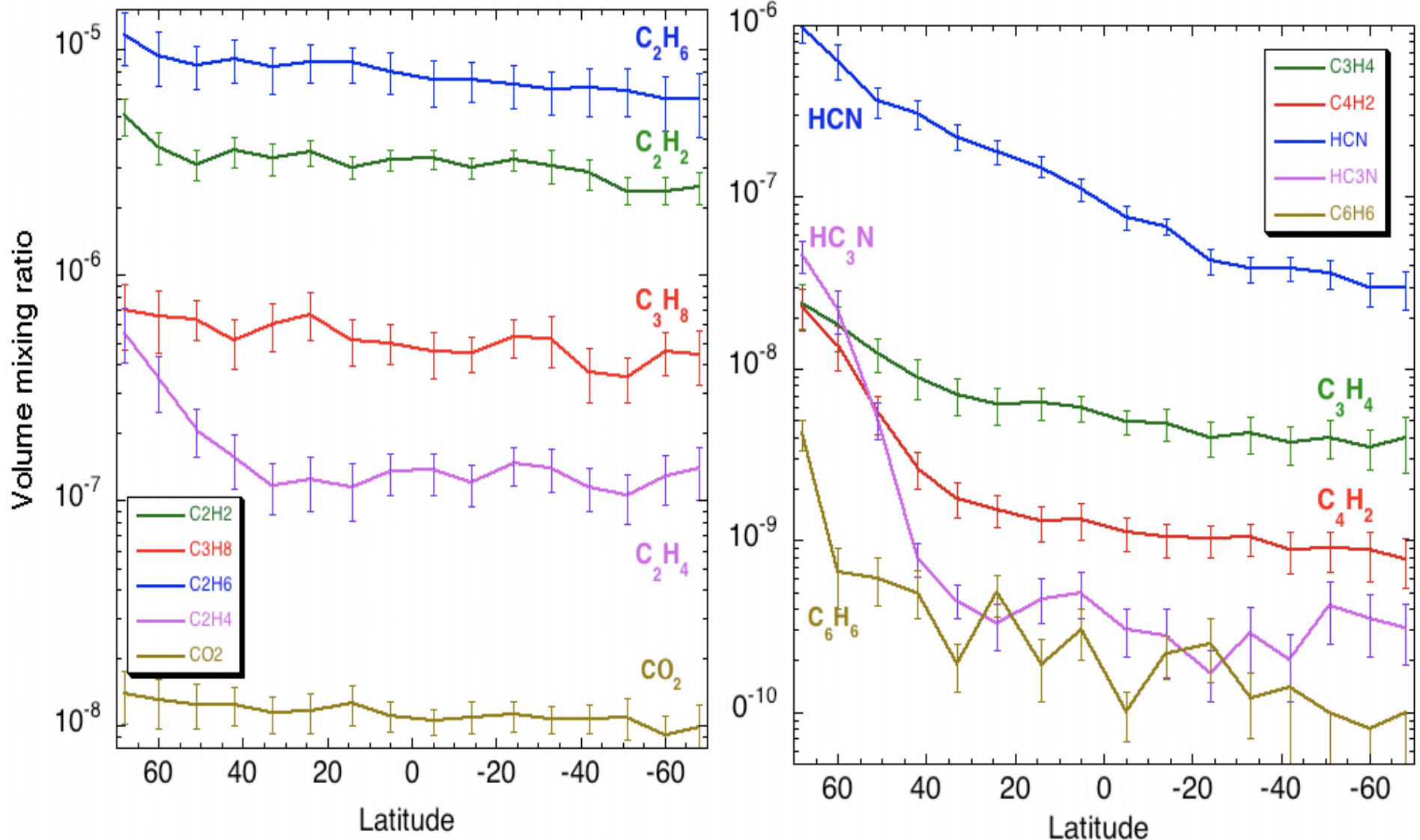
- All four bands of propane tentatively identified by IRIS are now clearly seen by CIRS at much higher S/N.
- In addition 2-3 further bands have now been identified on CIRS residuals, enabled by modeling and subtraction of stronger species (CH_4 , C_2H_6).

PROPANE BANDS ON TITAN			
Wavenumber	Band	IRIS	CIRS
748	v21	Y	Y
860	v8	N	MAYBE
922	v16	Y	Y
1054	v15	Y	Y
1157	v7	Y	Y
1338	v14	N	N
1376	v13	N	Y
1472	v19	N	Y

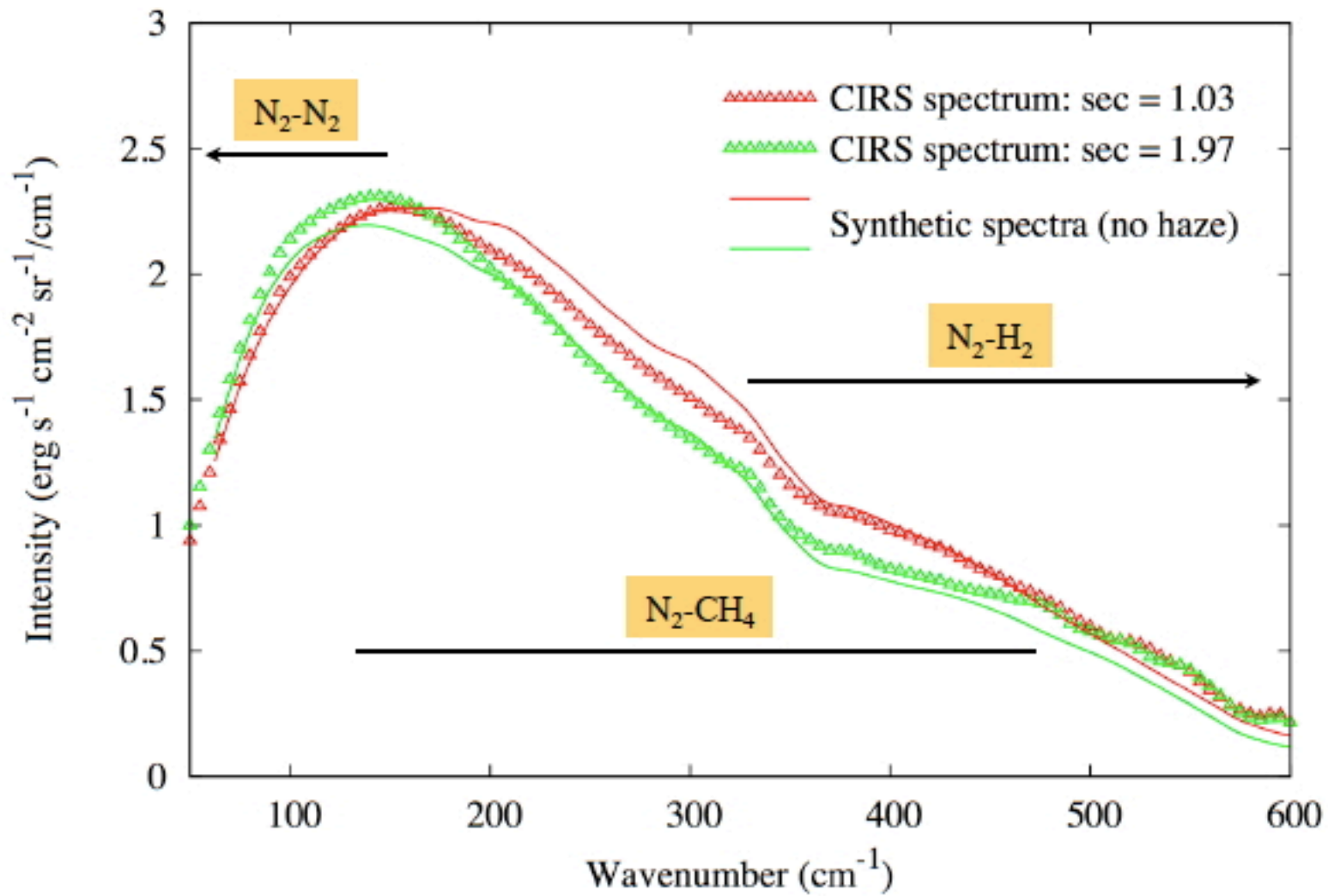


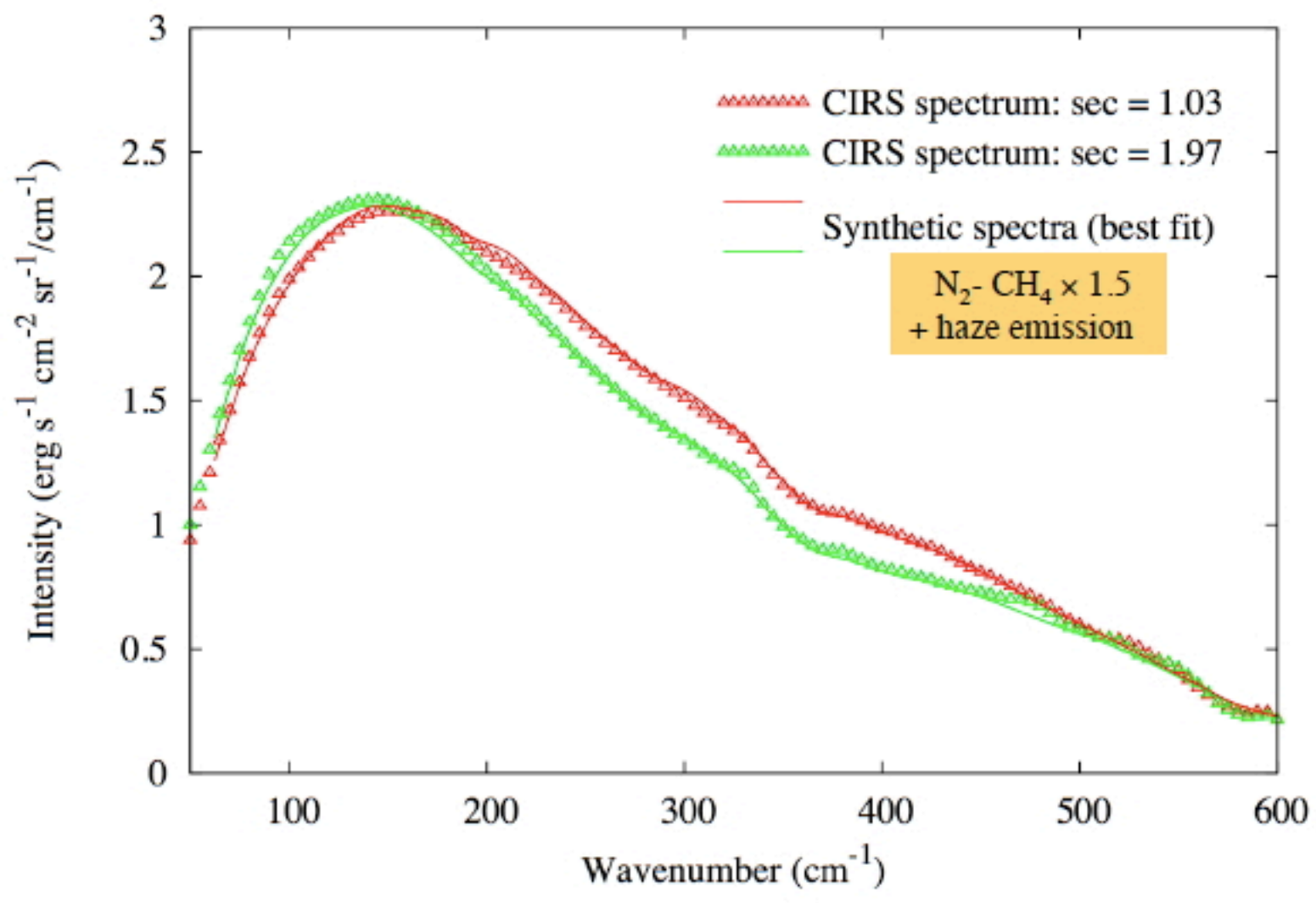
Coustenis et al., 2010

Meridional variations



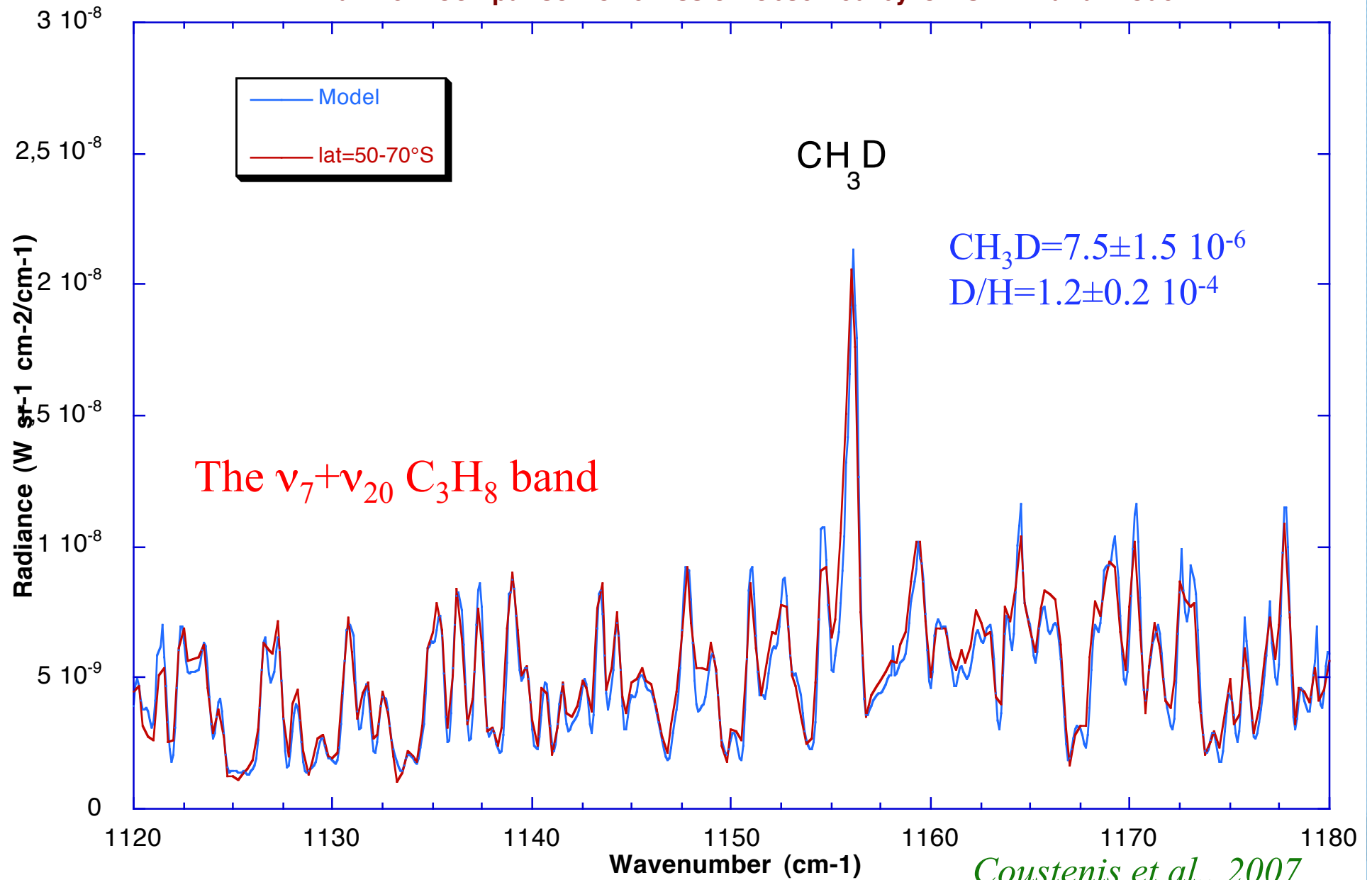
Strong increase in the North : HCN, HC3N, C3H4, C4H2, C2H4, C6H6
Small increase for: C2H2, C2H6





**New detections
- Isotopic Ratios**

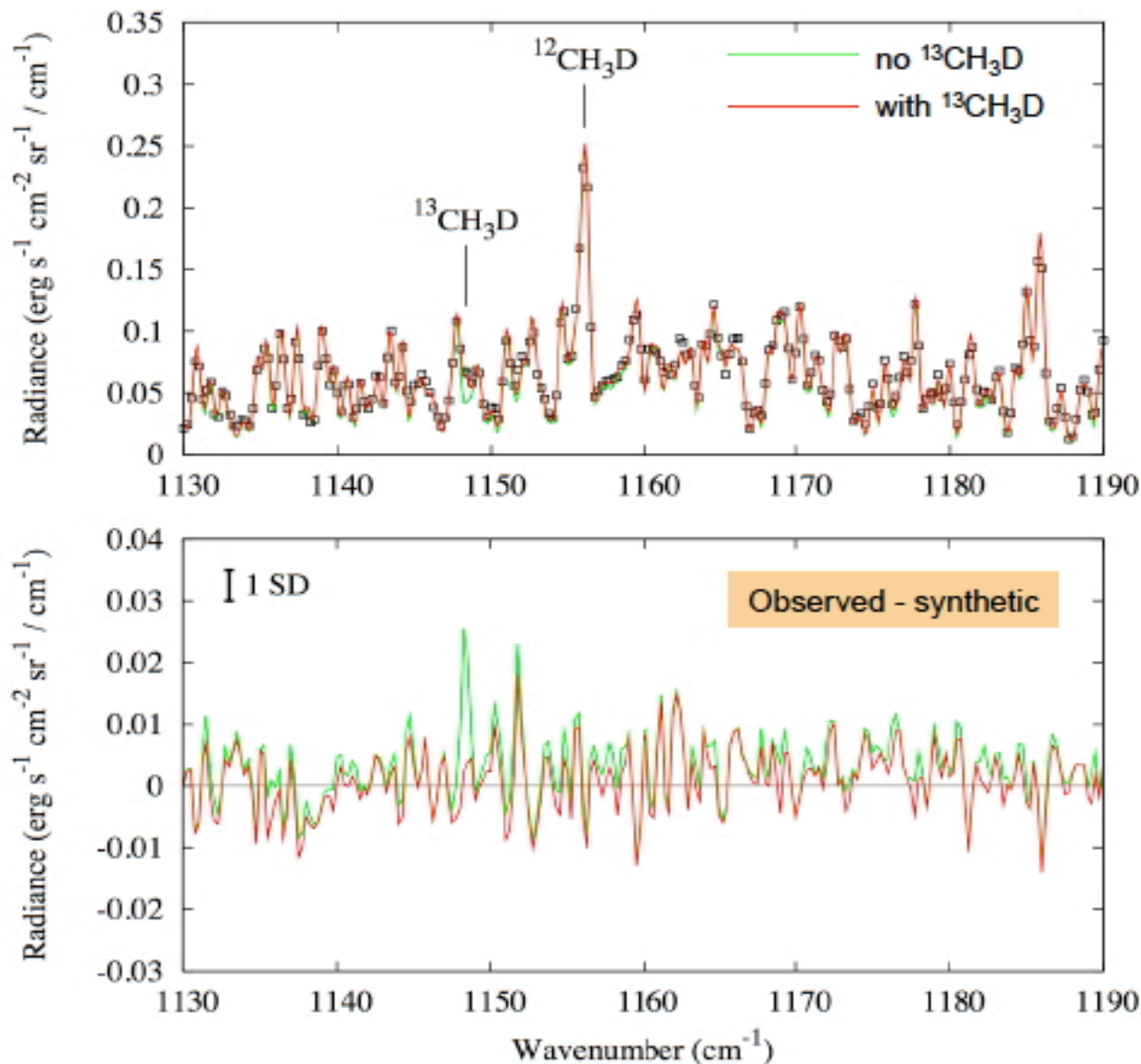
Titan/T0 : Comparison of emission observed by CIRS FP4 and model



Coustenis et al., 2007

Bézard et al., 2007

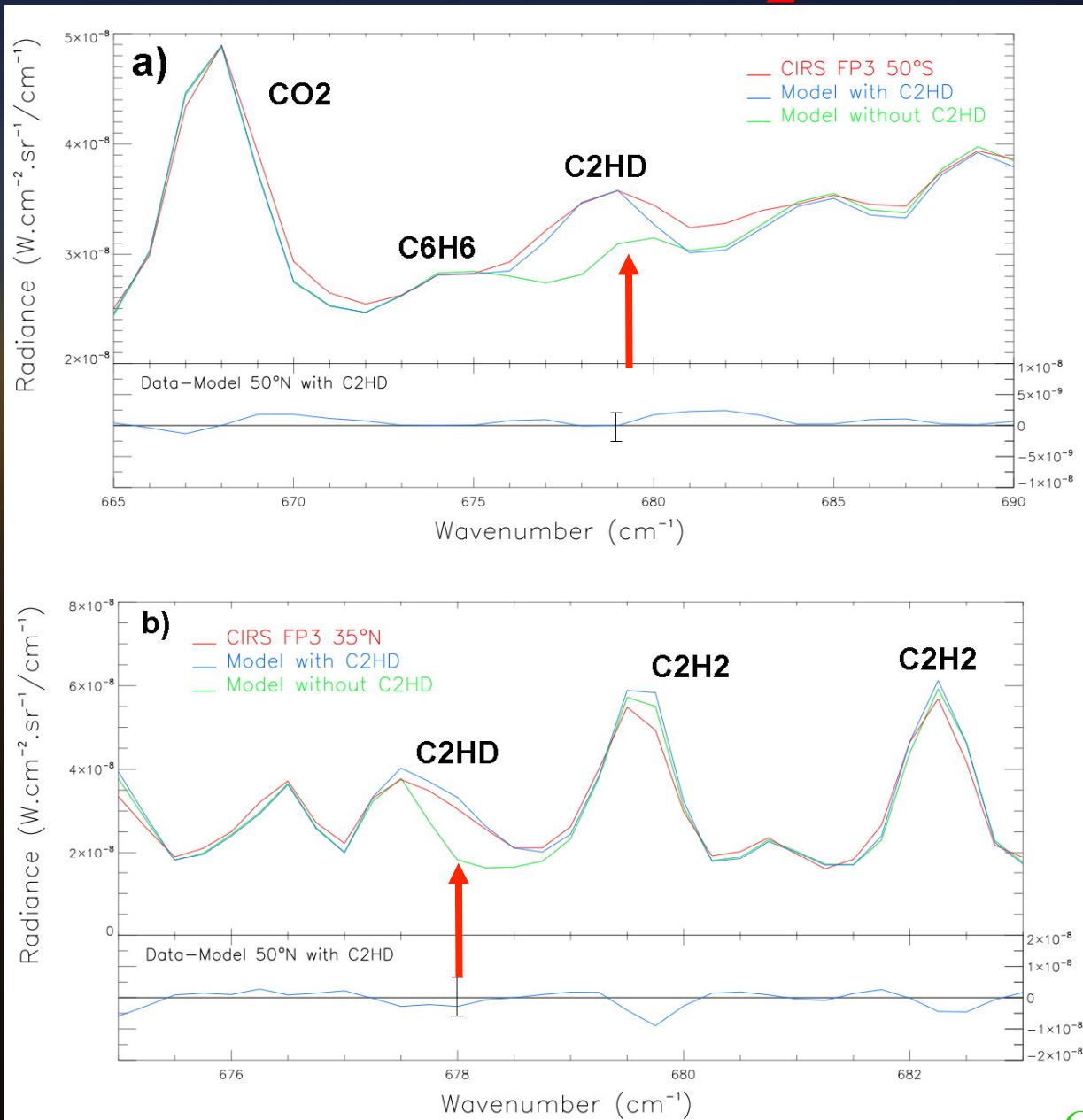
Detection of $^{13}\text{CH}_3\text{D}$ (ν_6) on Titan



The intensity of the ν_6 band of $^{13}\text{CH}_3\text{D}$ was not measured

The ν_7 and ν_{20} propane bands exist in this region but are not analyzed due to lack of a line-by-line database only band model

Detection of C₂H₂D

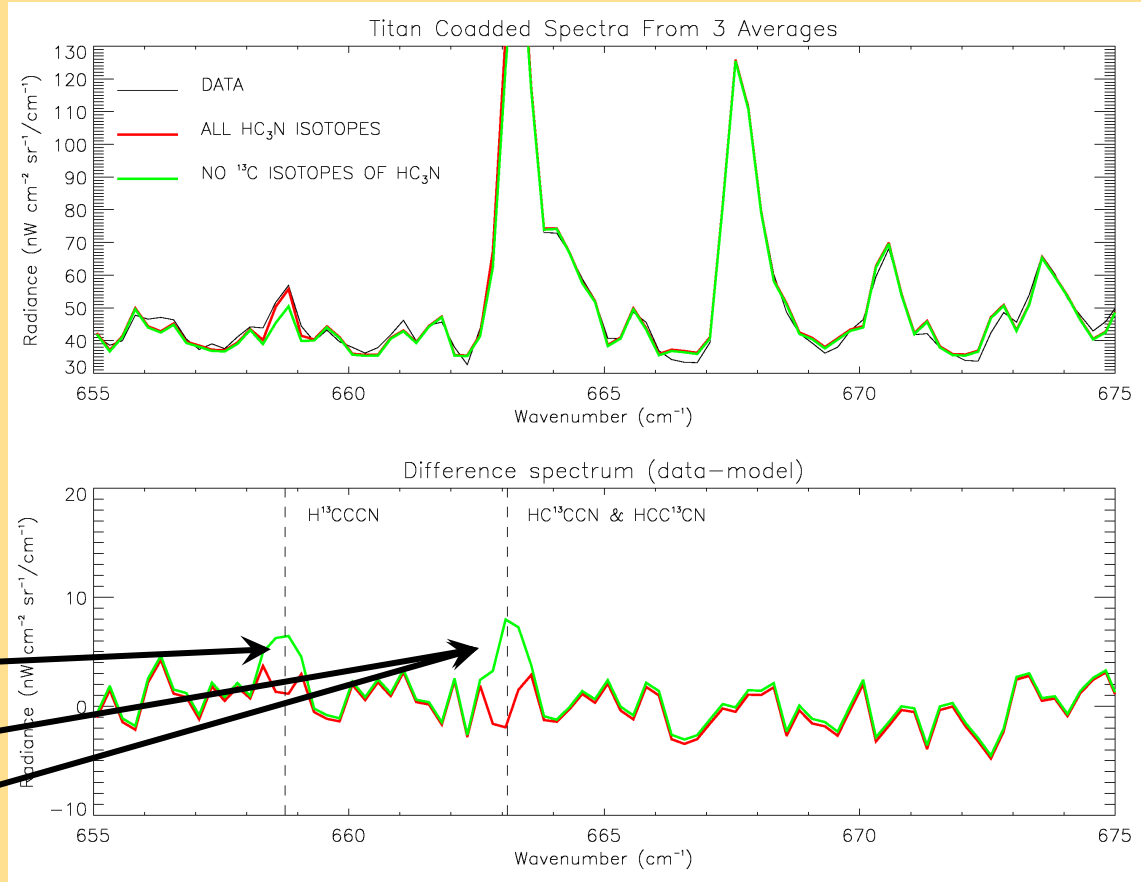




^{13}C in HC_3N : $\text{H}-\text{C}\equiv\text{C}-\text{C}\equiv\text{N}$

- Cyanoacetylene formed by substitution of $-\text{CN}$ (from HCN) into C_2H_2 and C_2H_4 .
- HC_3N has a strong ν_5 band @ 663.4 cm^{-1} due to bending of CH .
- Replace $^{12}\text{C} \rightarrow ^{13}\text{C}$ changes frequency:
 - $\text{H}^{13}\text{CCCN} = 658.7\text{ cm}^{-1}$
 - $\text{HC}^{13}\text{CCN} = 663.1\text{ cm}^{-1}$
 - $\text{HCC}^{13}\text{CN} = 663.1\text{ cm}^{-1}$

(Jolly et al. JMS, 242, 46-54, 2007)

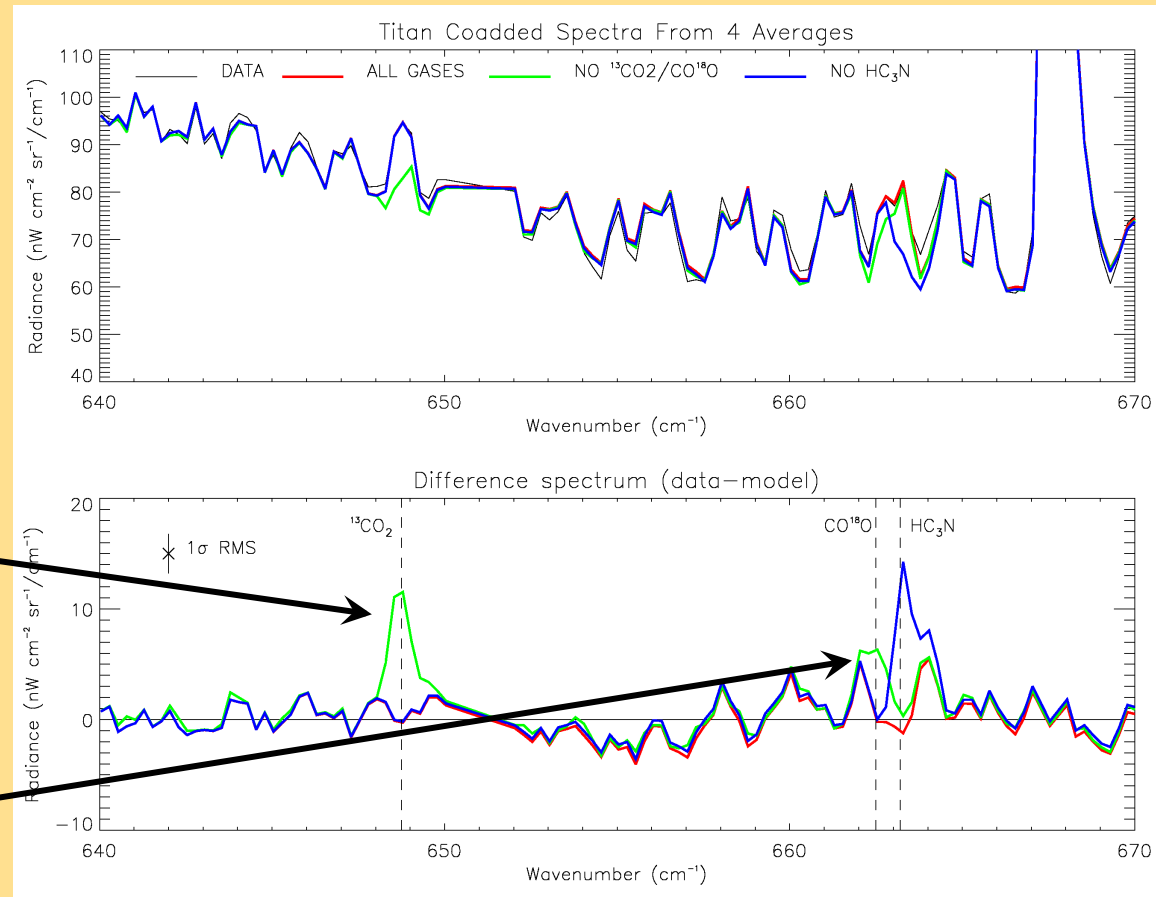


Modeling implies $^{12}\text{C}/^{13}\text{C} \sim 78 \pm 12$, in line with Huygens GCMS (82.3 ± 1). Potential to discriminate between C from HCN and C_2H_2 .



Isotopes of CO₂

- CO₂ has been mapped via ν_2 band @ 667 cm⁻¹.
- Stratospheric abundance $\sim 10^{-8}$.
- Recently we have detected the isotopic emission of ¹³CO₂ @ 648.5 cm⁻¹ (6- σ detection).
- ... and *probably* the C¹⁸O¹⁶O emission at 662.5 cm⁻¹ (3- σ detection, σ = NESR only).



Retrieved isotopic ratios are $^{12}\text{C}/^{13}\text{C} \sim 84 \pm 17$, in line with Huygens GCMS (82.3 ± 1), and $^{16}\text{O}/^{18}\text{O} \sim 346 \pm 110$, perhaps 1.5x enriched versus terra.

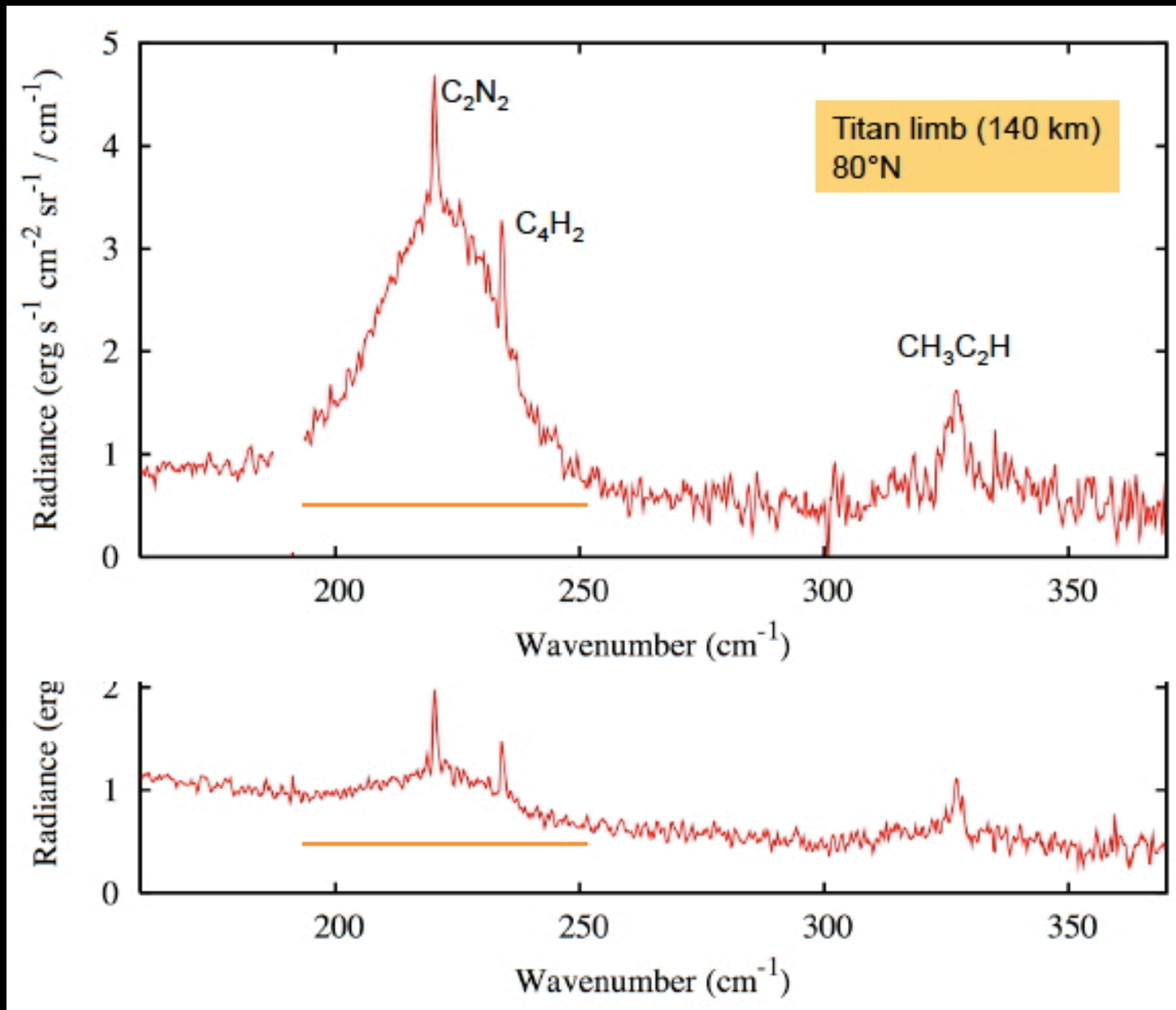


Summary of CIRS isotopic detections

	SINGLE ISOTOPES				DOUBLE ISOTOPES	
	D	¹³ C	¹⁵ N	¹⁸ O	¹³ C ²	D ¹³ C
Hydrocarbons						
CH ₄	D/H ~ 1.2E-4 (Coustenis 07)	¹² C/ ¹³ C ~ 77 (Nixon 08)				D/H ~ 1.3E-4 ¹² C/ ¹³ C ~ 82 (Bezard 07)
C ₂ H ₂	D/H ~ 1.8E-4 (Coustenis 08)	¹² C/ ¹³ C ~ 85 (Nixon 08)			POSSIBLE	
C ₂ H ₄		POSSIBLE				
C ₂ H ₆	POSSIBLE	¹² C/ ¹³ C ~ 90 (Nixon 08)				
C ₃ H ₄ , C ₄ H ₂		POSSIBLE				
Nitriles						
HCN		¹² C/ ¹³ C ~ 75 (Vinatier 07)	¹⁴ N/ ¹⁵ N ~ 56 (Vinatier 07)			
HC ₃ N		Y- H ¹³ CCCN Y- HC ¹³ CCN Y- HCC ¹³ CN (Jennings in	UNLIKELY DUE TO SPECTRAL RESOLUTION			
Other						
CO ₂		¹² C/ ¹³ C ~ 84 (Nixon subm)		¹⁶ O/ ¹⁸ O ~ 346* (Nixon subm)		

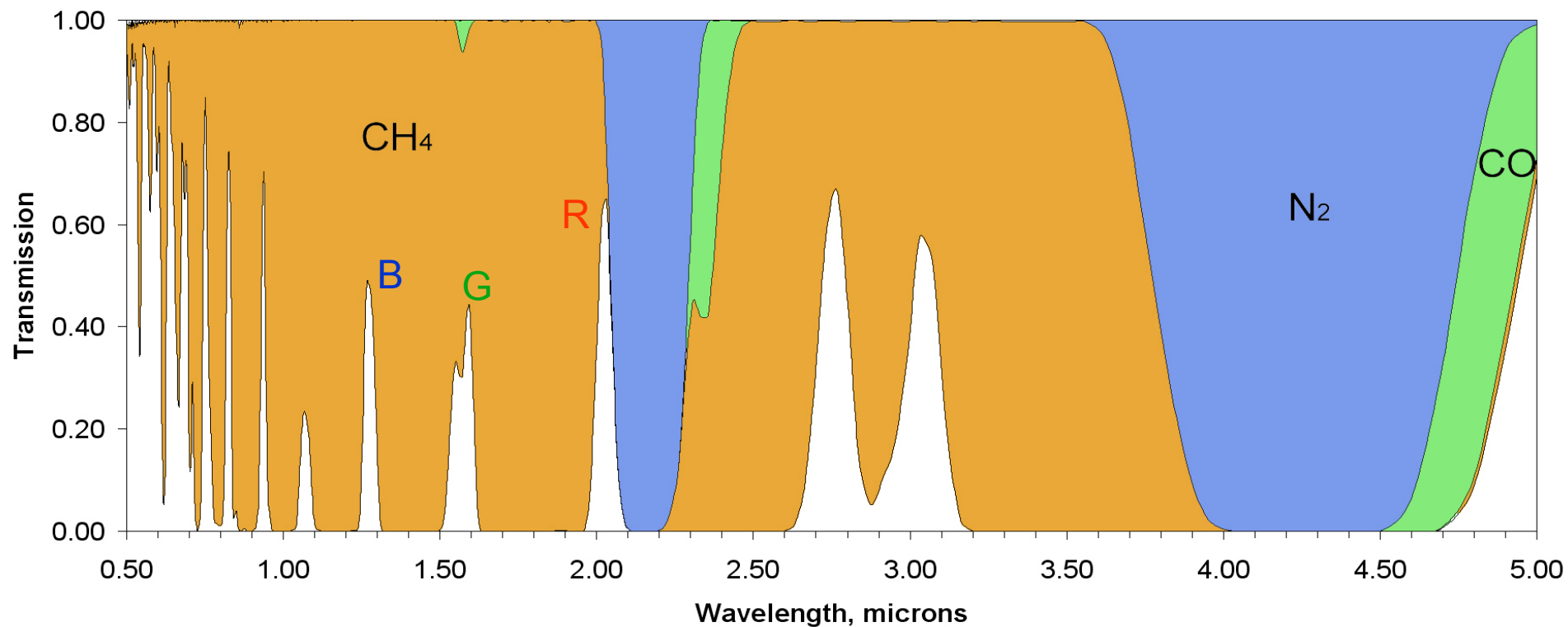
*Tentative

Unidentified features



The near IR spectrum of Titan

Principal Absorbing Gases in Titan's Atmosphere



Detected and searched-for molecules on Titan

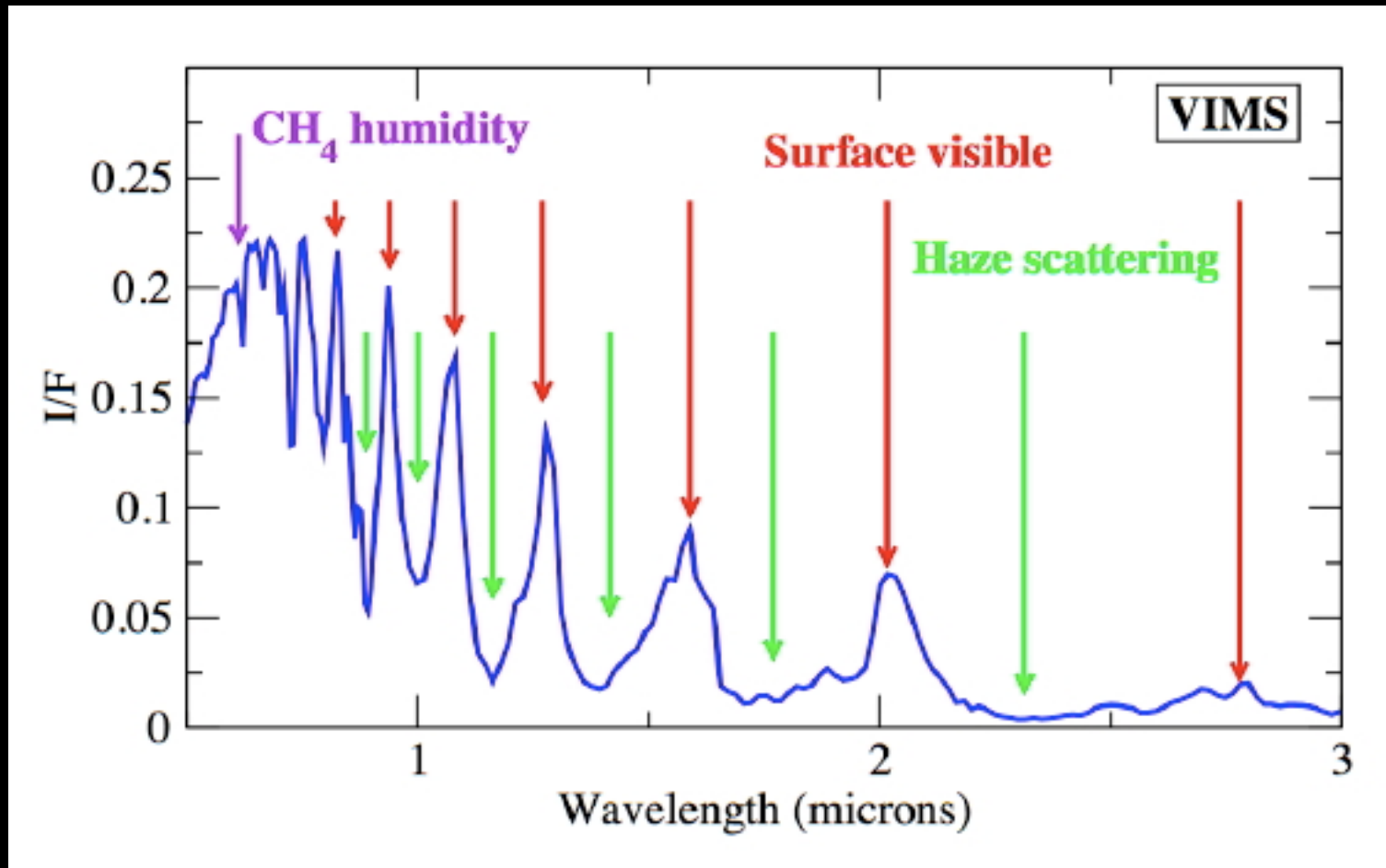
Species	IUPAC name	Common name	Molar mass (g mol ⁻¹) ^b
C ₂ H ₄	ethene	ethylene	28.0532
C ₂ H ₂	ethyne	acetylene	26.0373
CH ₃ C ₂ H	propyne	methyl-acetylene	40.0639
C ₄ H ₂	1,3-butadiyne	diacetylene	50.0587
C ₆ H ₆	cyclohexatriene	benzene	78.1118
HCN	formonitrile	cyanide	27.0254
CH ₂ NH	methyleneimine	-	29.0413
CH ₃ CN	ethanenitrile	acetonitrile	41.0520
C ₂ H ₃ CN	2-propenenitrile	acrylonitrile	53.0627
HC ₃ N	2-propynenitrile	cyanoacetylene	51.0468
C ₂ N ₂	ethanedinitrile	cyanogen	52.0349
C ₄ N ₂	2-butyndinitrile	dicyanoacetylene	76.0563

Constituent	First detection/ range/Means	Ref. of first detection
<i>Major</i>		
Molecular nitrogen, N ₂	Voyager Radio occultation; UV	1,2
Nitrogen, N	Voyager, 1134 Å multiplet	2
Methane, CH ₄	Ground-based, UV and IR : 6190&7250 Å, 1.1&7.7 μm	3,4,5
Monodeuterated methane, CH ₃ D	Ionosphere with Cassini/INMS	6
Hydrogen, H	Ground-based at 1.65 and 8.6 μm	7,8
Hydrogen, H ₂	V1, 1216 Å	2
Hydrogen, H ₂	Ground-based, 3-0 S(1)	4
Argon, (Ar ³⁶ , Ar ⁴⁰)	Ionosphere, Cassini/INMS	6
	Cassini-Huygens/GCMS	9
<i>Minor</i>		
Ethane, C ₂ H ₆	Ground-based, 822 cm ⁻¹	10,11
Acetylene, C ₂ H ₂	Ground-based, 729 cm ⁻¹	7,12
	Ionosphere, Cassini/INMS	6
Monodeuterated acetylene, C ₂ HD	Cassini/CIRS, 678 cm ⁻¹	13
Propane, C ₃ H ₈	V1/IRIS, 748 cm ⁻¹	5,14
Ethylene, C ₂ H ₄	Ground-based, 950 cm ⁻¹	7
Methylacetylene, CH ₃ C ₂ H	V1/IRIS, 328, 633 cm ⁻¹	5,14
Diacetylene, C ₄ H ₂	V1/IRIS, 220, 628 cm ⁻¹	15
Benzene, C ₆ H ₆	ISO and Cassini/CIRS, 674 cm ⁻¹	9,13,16
	Huygens/GCMS	
Hydrogen cyanide, HCN	V1/IRIS, 712 cm ⁻¹	5
Cyanoacetylene, HC ₃ N	V1/IRIS, 500, 663 cm ⁻¹	15
Cyanogen, C ₂ N ₂	V1/IRIS, 233 cm ⁻¹	15
Dicyanogen, C ₄ N ₂	V1/IRIS, solid form at 474 cm ⁻¹	17
Acetonitrile, CH ₃ CN	220.7 GHz multiplet	18
Carbon monoxide, CO	Ground-based, mm, submm, microwave, infrared	19
Carbon dioxide, CO ₂	V1, 667 cm ⁻¹	20
Water, H ₂ O	ISO/SWS, 237, 243 cm ⁻¹	21
Ammonia, NH ₃ , C ₂ H ₃ CN, C ₂ H ₅ CN, CH ₂ NH	Suggested indirectly by modelling	22
	Cassini/INMS ionospheric data	

¹Lindal et al. (1983); ²Broadfoot et al. (1981a); ³Kuiper (1944); ⁴Trafton (1972); ⁵Hanel et al. (1981); ⁶Waite et al. (2005); ⁷Gillett (1975); ⁸Lutz et al. (1981); ⁹Niemann et al. (2005); ¹⁰Gillett et al. (1973); ¹¹Danielson et al. (1973); ¹²Caldwell et al. (1977); ¹³Cousten et al. (2007); ¹⁴Maguire et al. (1981); ¹⁵Kunde et al. (1981); ¹⁶Cousten et al. (2003); ¹⁷Samuelson et al. (1997); ¹⁸Bézar et al. (1993); ¹⁹Lutz et al. (1983); ²⁰Samuelson et al. (1983); ²¹Cousten et al. (1998); ²²Vuitton et al. (2006).

Table from Coustenis & Taylor 2008, WSP.

Titan: near-IR bands of methane



* About 3 km-amagat of CH₄ in the atmosphere

* Inhomogeneous path

- T= 94 K; p= 1,5 bar at the surface

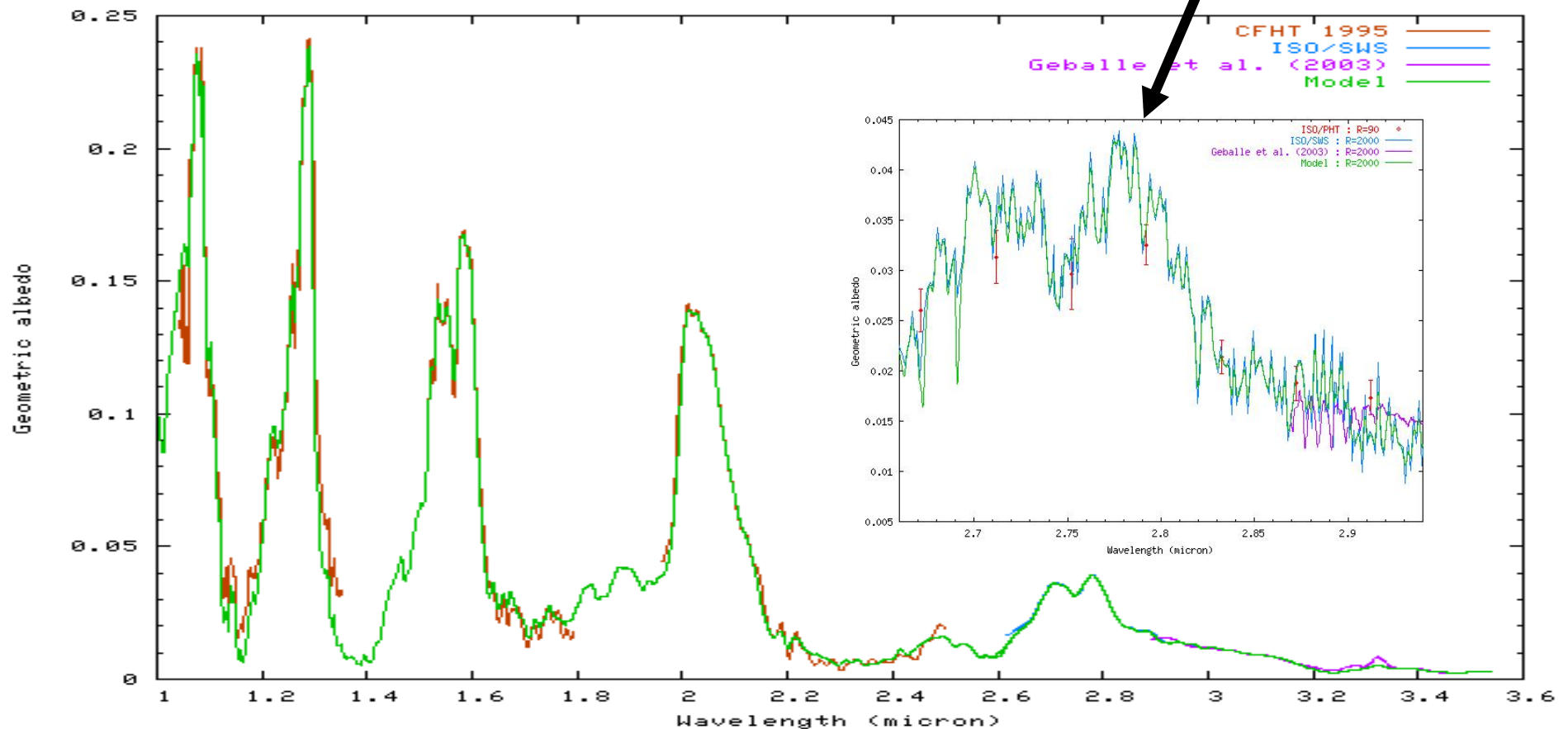
- T = 70-180 K; p= 100-0,1 mbar in the stratosphere

Brown et al. (2005)

Full spectrum of Titan in the near-IR: 1-5 μm : Modelling for the surface composition

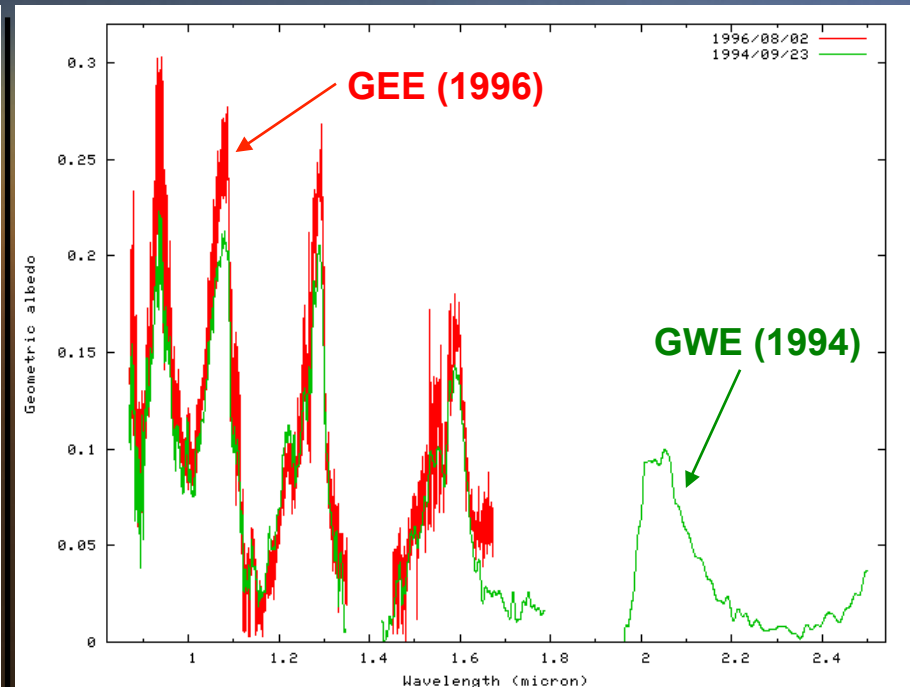
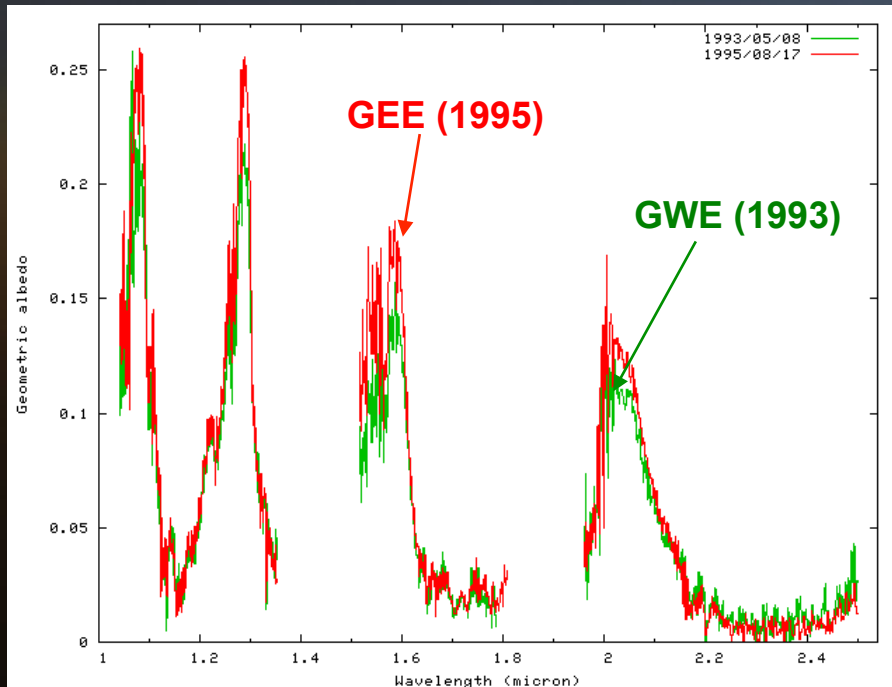
CFHT/FTS, VLT/ISAAC et ISO:
(Coustenis et al., 1995; Negrao, Coustenis et al., 2006, 2007)

First spectrum of Titan in the
3-micron region
(Coustenis et al., 2006)



CFHT/FTS data

We have observed Titan in a series of campaigns from 1991 to 1996 with the Fourier Transform Spectrometer on the CFH Telescope. The 1991-1993 data were previously analyzed in Coustenis et al. (1995). We present here also three new datasets from the 1994, 1995 and 1996 observations, with additional information from the 0.94 micron methane window on Titan.



Date: 1993/08/05
LCM: 253° (GWE)
Range: 1 to 2.5 μm
Resolution: 5-8.5 cm^{-1}
CH₄ windows: 1.08, 1.28,
1.58, 2.0 μm

Date: 1995/08/17
LCM: 67° (GEE)
Range: 1 to 2.5 μm
Resolution: 5-8.5 cm^{-1}
CH₄ windows: 1.08, 1.28,
1.58, 2.0 μm

Date: 1994/09/23
LCM: 233° (GWE)
Range: 0.9 to 2.5 μm
Resolution: 25 cm^{-1}
CH₄ windows: 0.94, 1.08,
1.28, 1.58,
2.0 μm

Date: 1996/08/02
LCM: 60° (GEE)
Range: 0.9 to 1.7 μm
Resolution: 3 cm^{-1}
CH₄ windows: 0.94, 1.08,
1.28, 1.58 μm

The atmospheric model

We used in this work the Rannou et al. (2003) radiative and transfer code to analyse this data. This is an updated version of McKay et al. (1989) code. The update concerns mainly the fractal description of the aerosols.

It is a 1D plane parallel model with 70 atmospheric layers, from 0 to 700 km, with a length of about 9.4 km. The model considers inputs on

- the aerosol formation

- the haze production rate ($0.805 \times 10^{-13} \text{ Kg m}^{-2} \text{ s}^{-1}$)

- the haze production pressure (1.5 Pa)

- the aerosol charging rate ($20 \text{ e}^- \mu\text{m}^{-1}$)

- the eddy diffusion coefficient (0)

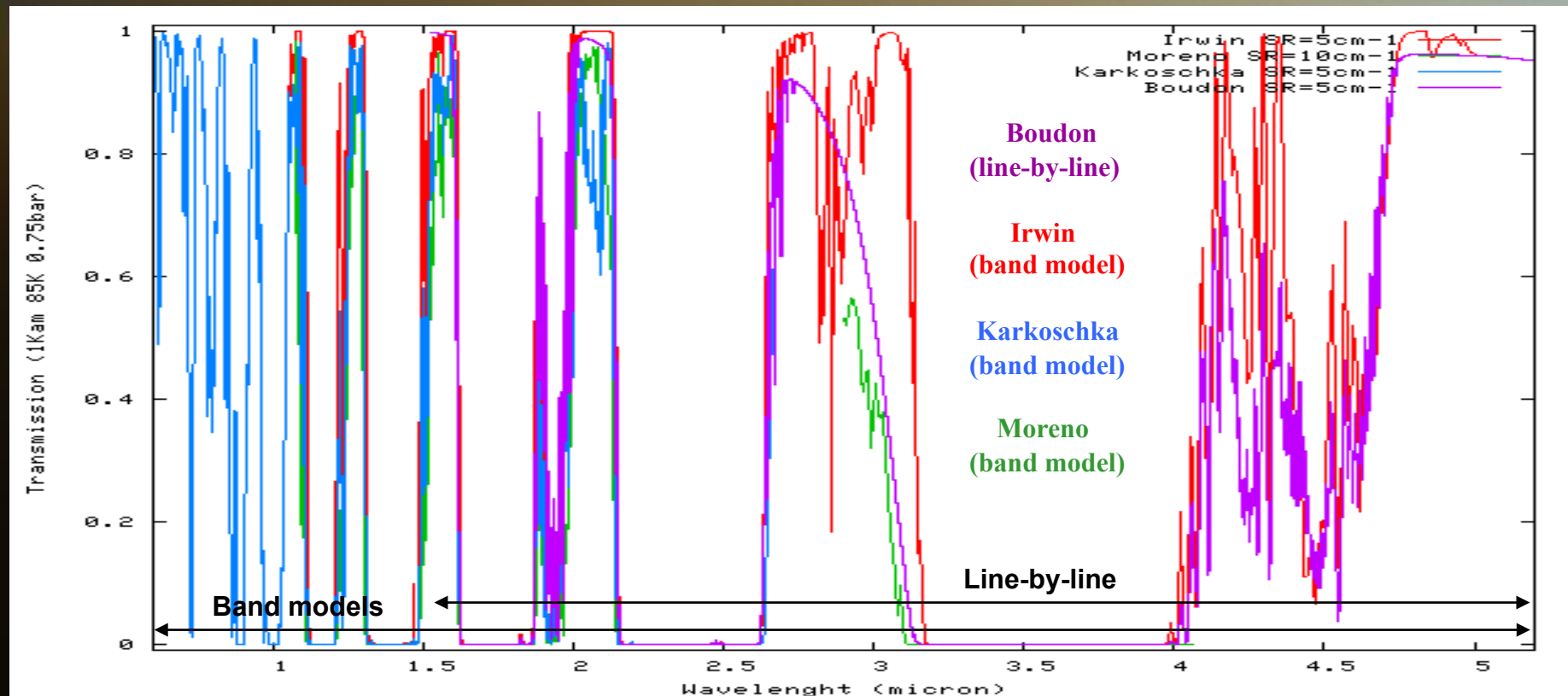
For the radiative transfer calculation inputs also include the aerosol imaginary refractive index, the methane vertical profile, the methane absorption coefficients and the ground reflectivity.

The methane mixing ratio (as a function of altitude) is defined first at the surface. It remains constant up to the saturation point, then following the saturation curve until the tropopause and remains constant above that level.

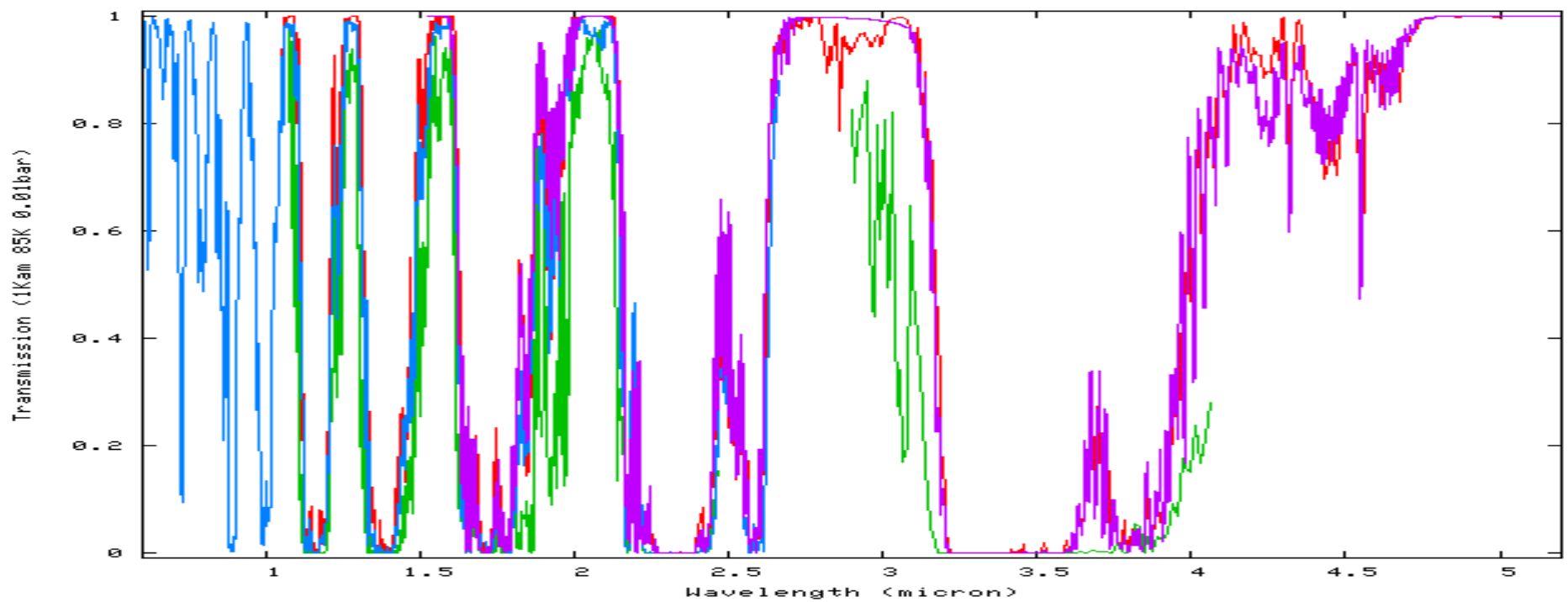
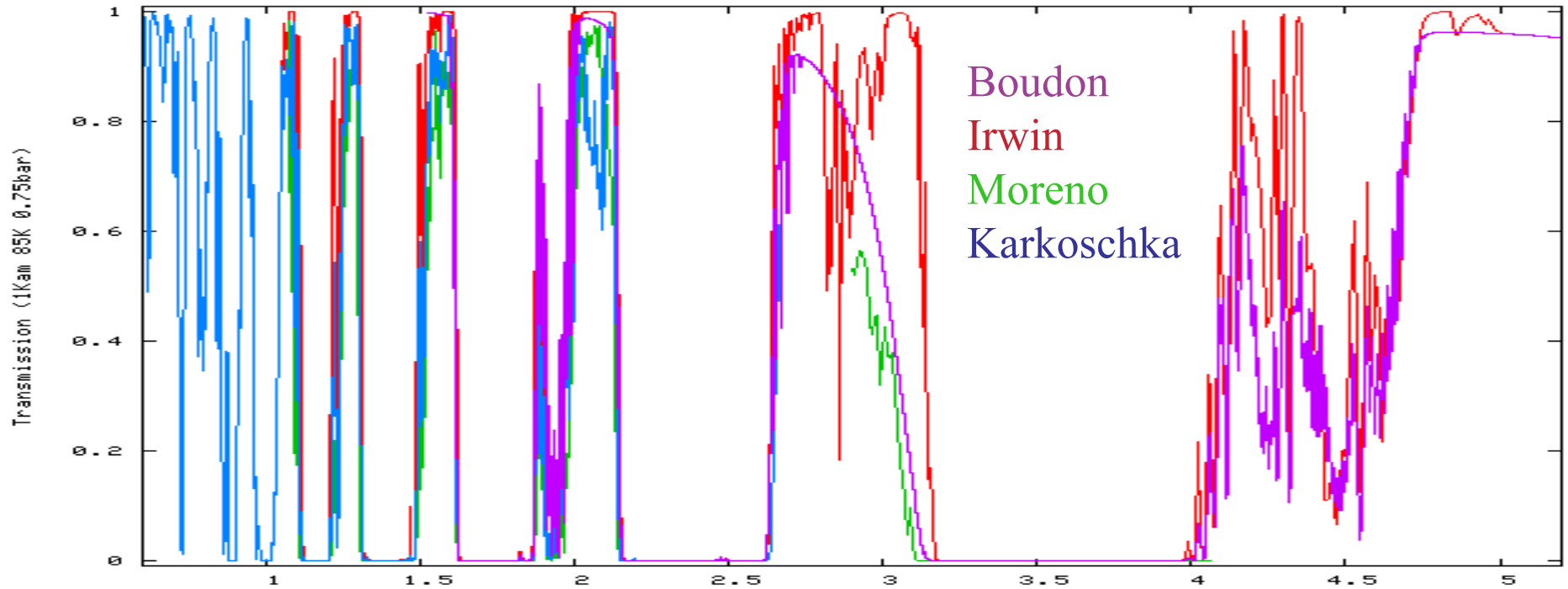
We fixed the surface methane mixing ratio at 5%, according to recent results from the DISR experiment onboard the Huygens probe (Tomasko et al., 2005), yielding a stratospheric mixing ratio of 1.78% which, although higher than the CIRS results, is still within the error bars presented in Flasar et al. (2005).

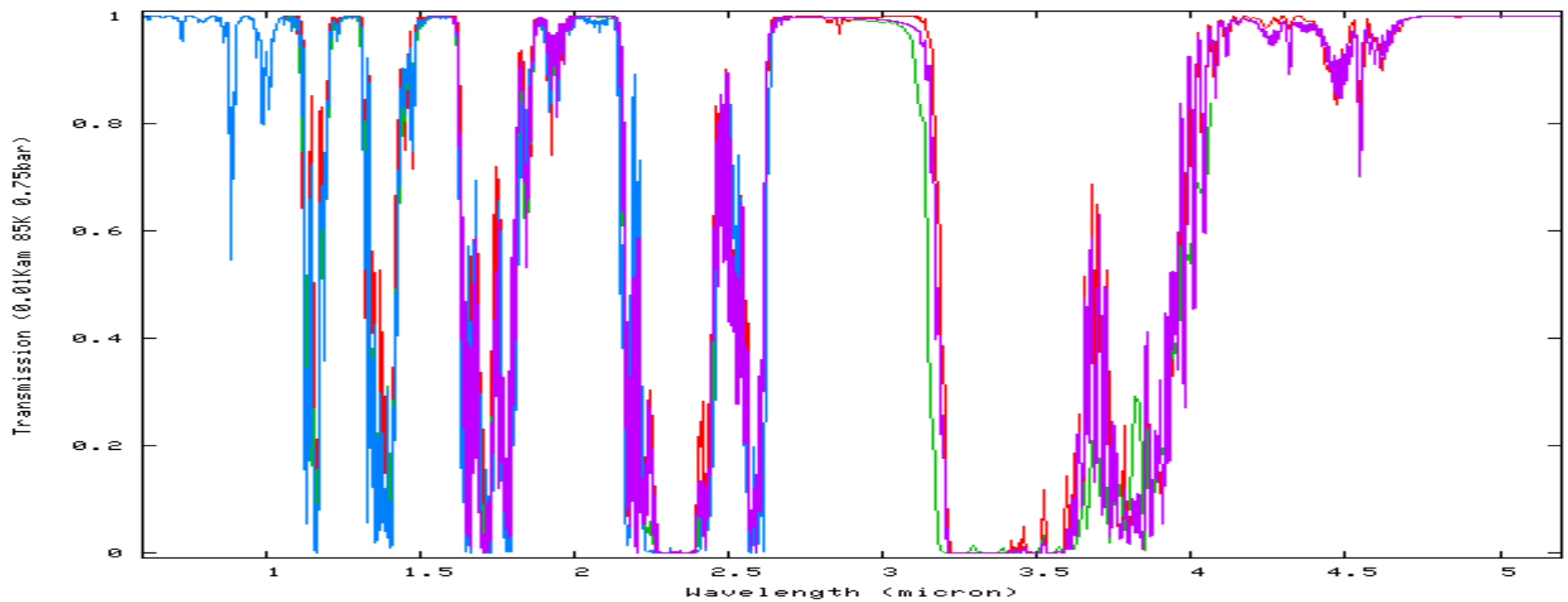
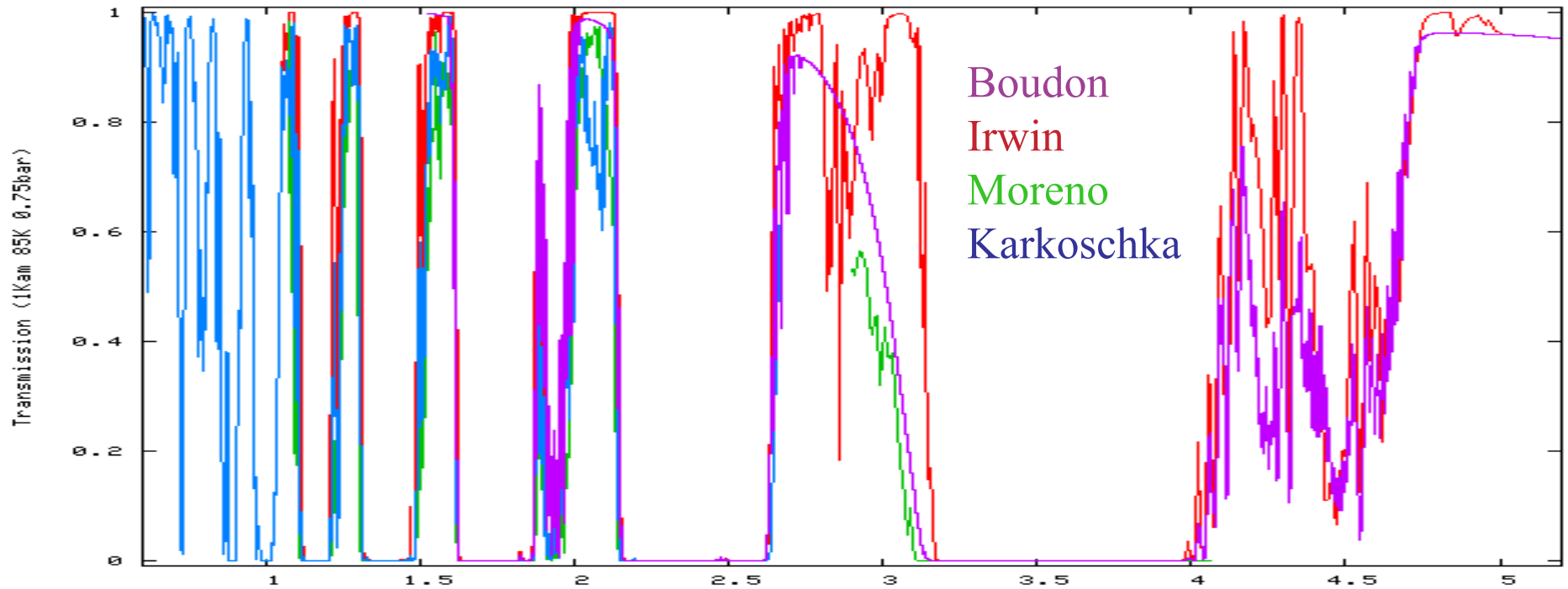
Methane absorption coefficients

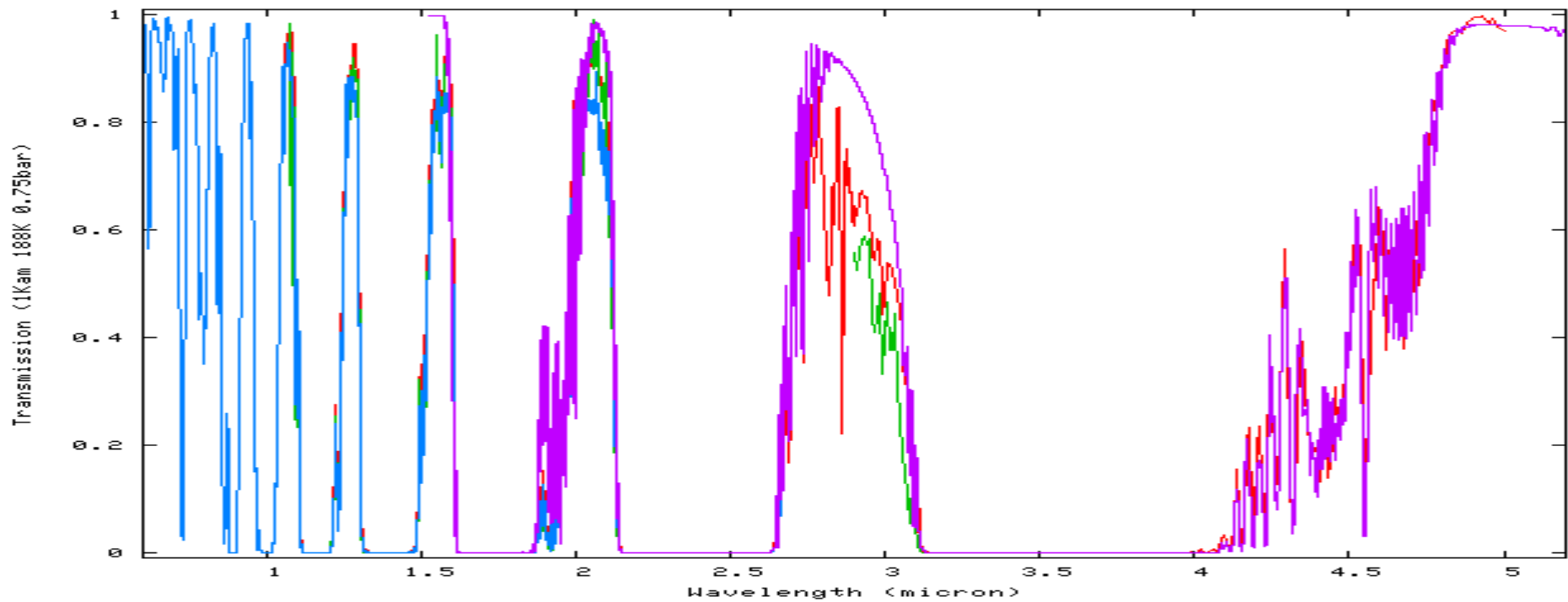
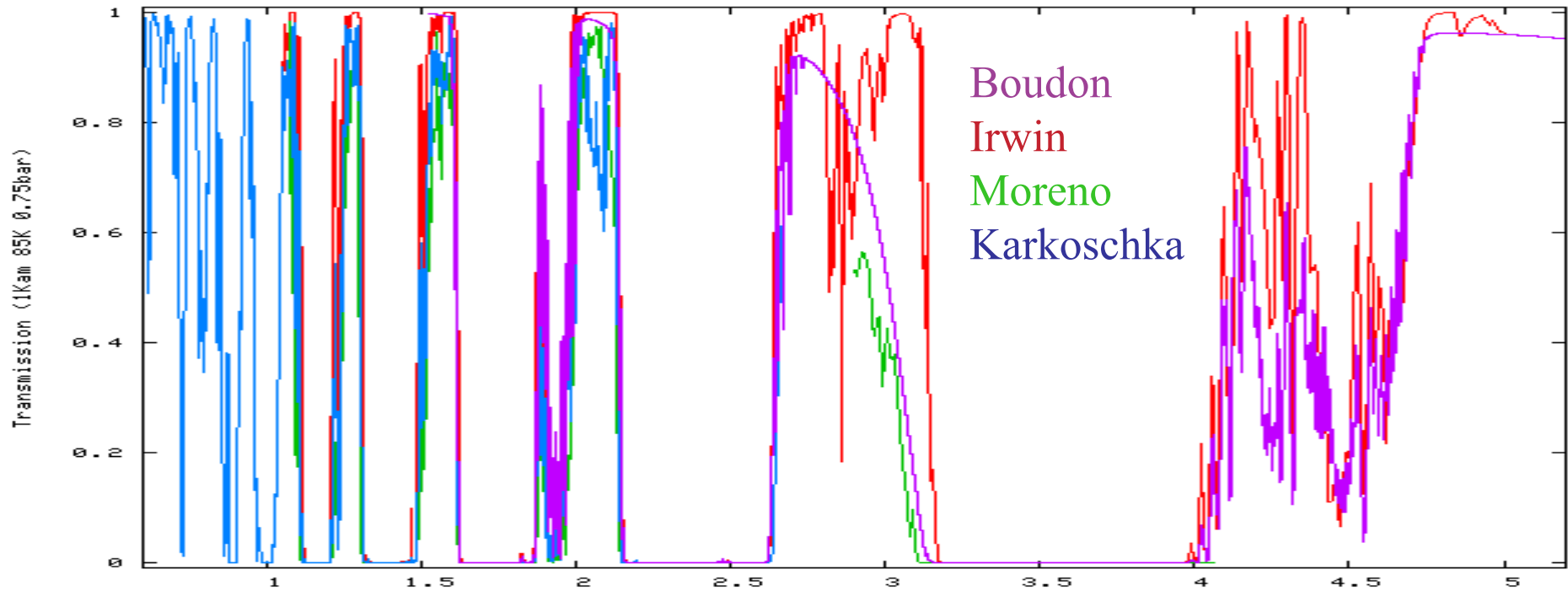
In this work we compare methane absorption coefficients from line-by-line calculations by Boudon et al. (2006) with coefficients from band models by Irwin et al. (2006), E. Karkoschka (private communication for $\lambda < 1.05$ micron and Karkoschka (1998) for $\lambda > 1.05$ micron) and R. Moreno (updated from Coustenis et al. (1995)). These coefficients are plotted below, calculated for one condition of pressure and temperature.



Path-length: 1 km.am ; Temperature: 85 K ; Pressure: 750 mbar

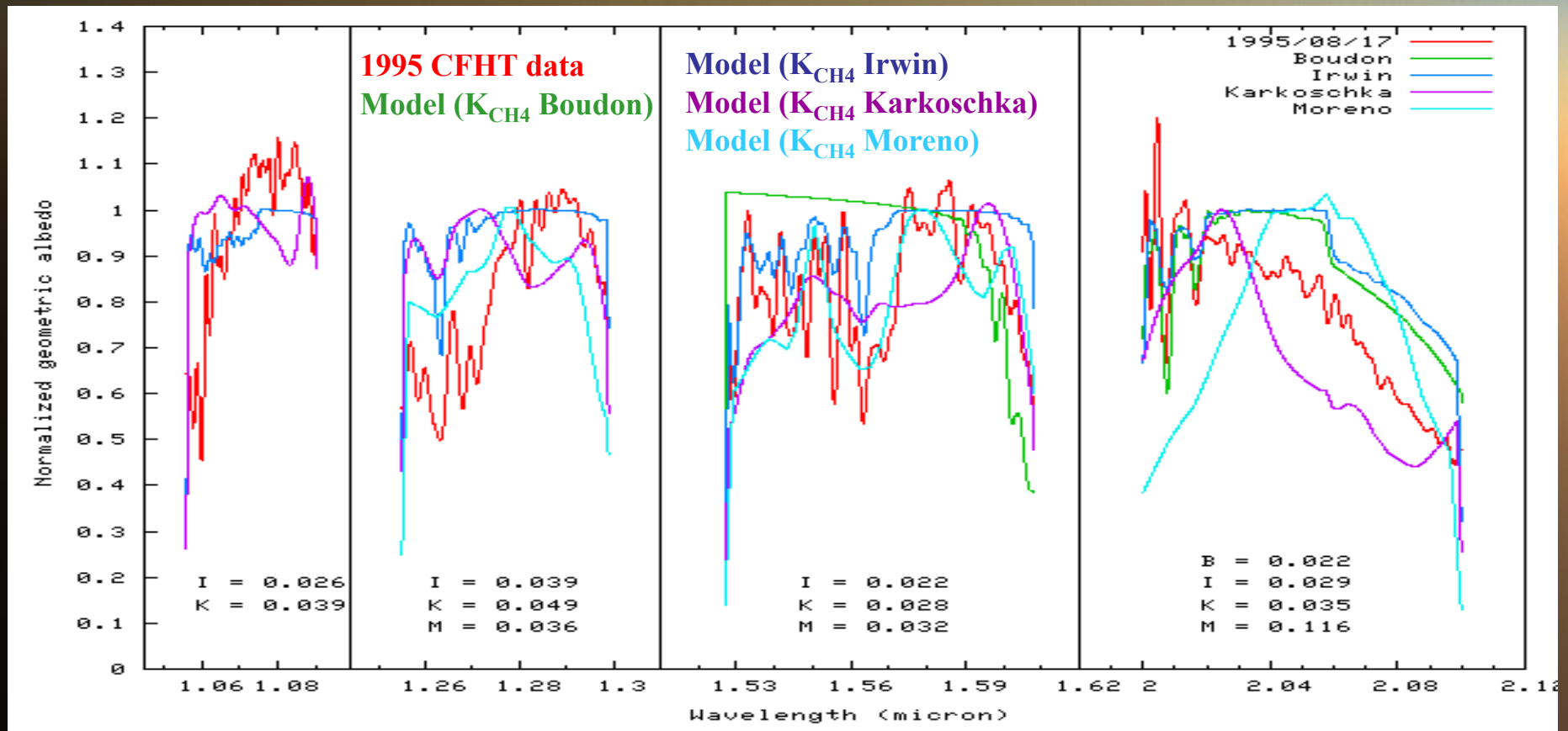






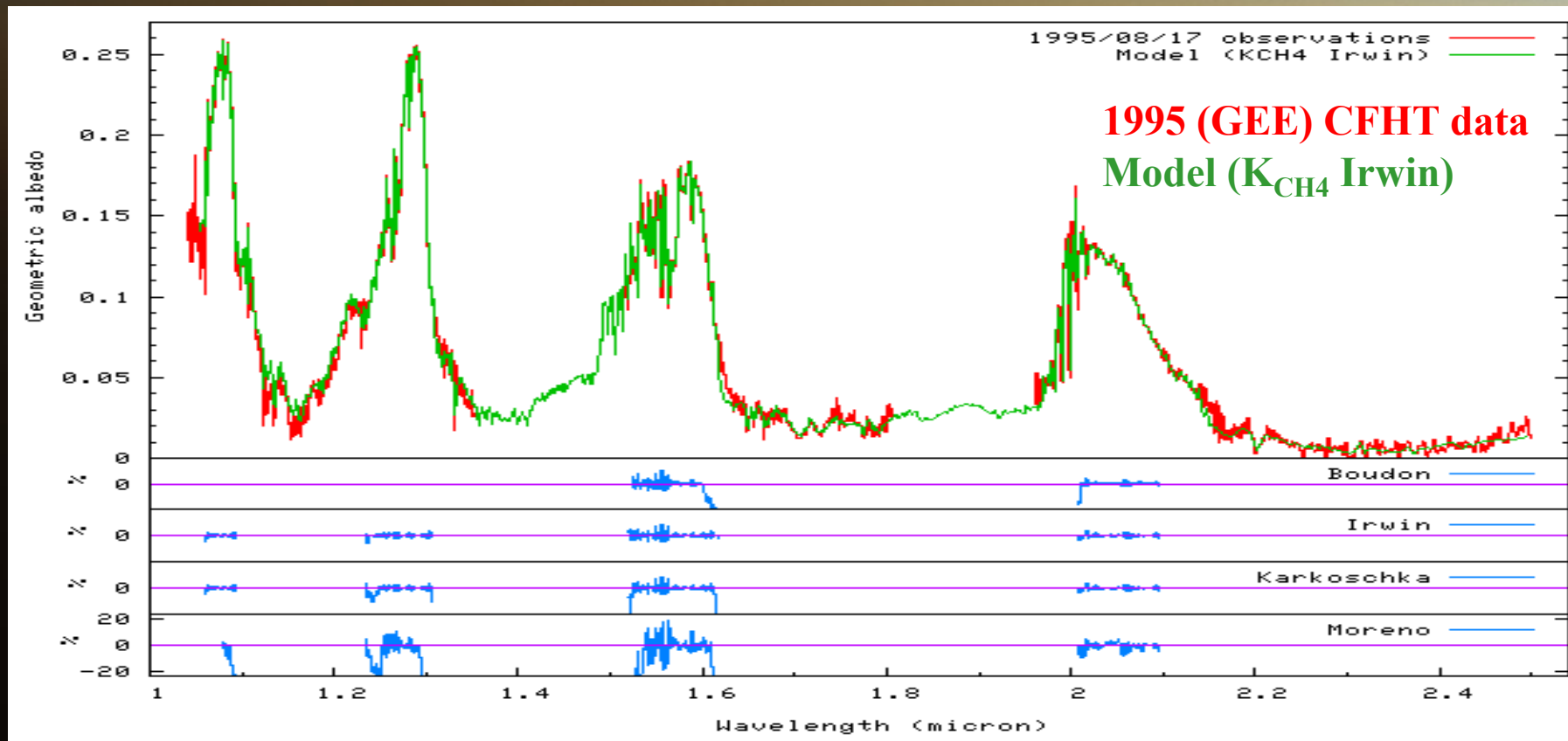
Fit of the CFHT data (with a constant surface albedo)

We calculated the geometric albedo (using a constant surface albedo) in the different methane windows, and then normalized the geometric albedo value at the center of each methane window. This was done both for the observations (the figure below shows the 1995 data as an example) and for the model, for each set of methane coefficients. The χ^2 factor was calculated for each set of coefficients. Line-by-line calculations by Boudon et al. (2006) and Irwin et al. (2006) band model seem to yield the best results.



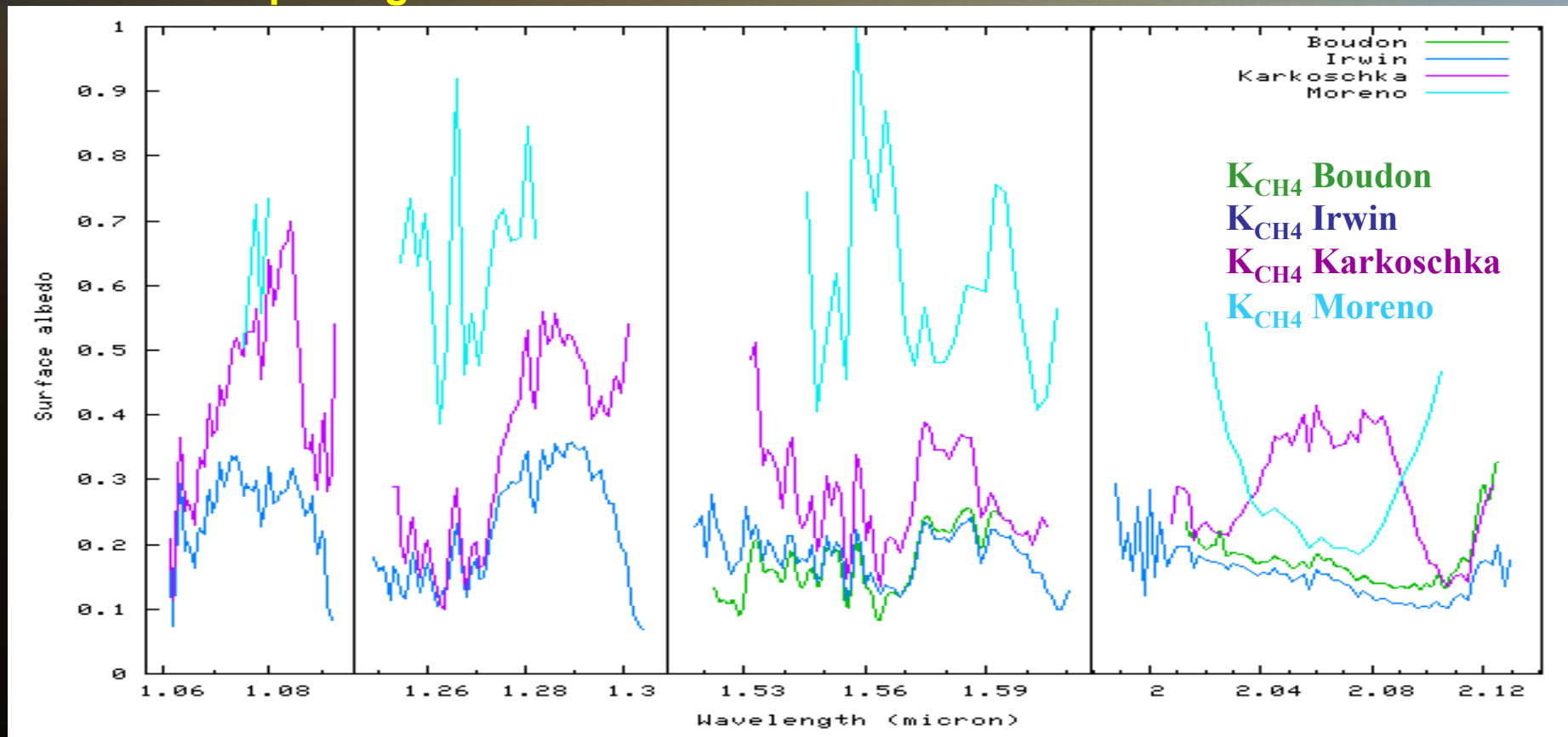
Fit of the CFHT data (with a variable surface albedo)

The next step in the comparison of the methane coefficient datasets is the study of their influence on the retrieved surface albedo. For this a fit of each dataset from 1993 to 1996 was performed, using the four sets of methane coefficients at our disposal. The figure below shows an example for the 1995 observations using the Irwin et al. (2006) coefficients. We furthermore show in the same figure four panels indicating the remaining differences between the model and the data in the methane windows.

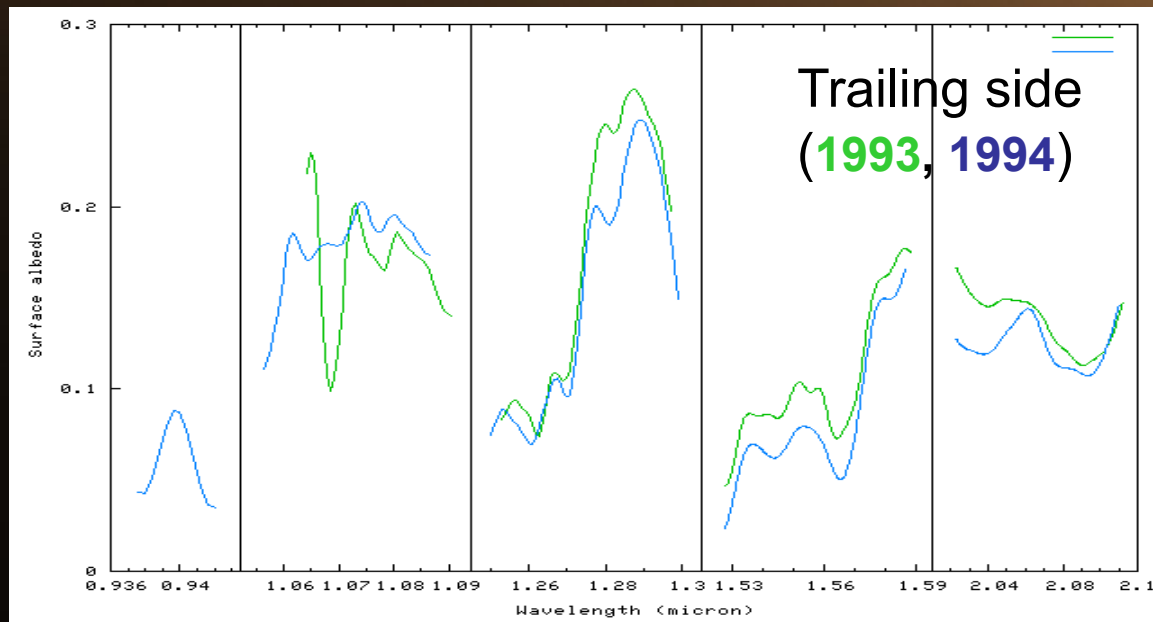
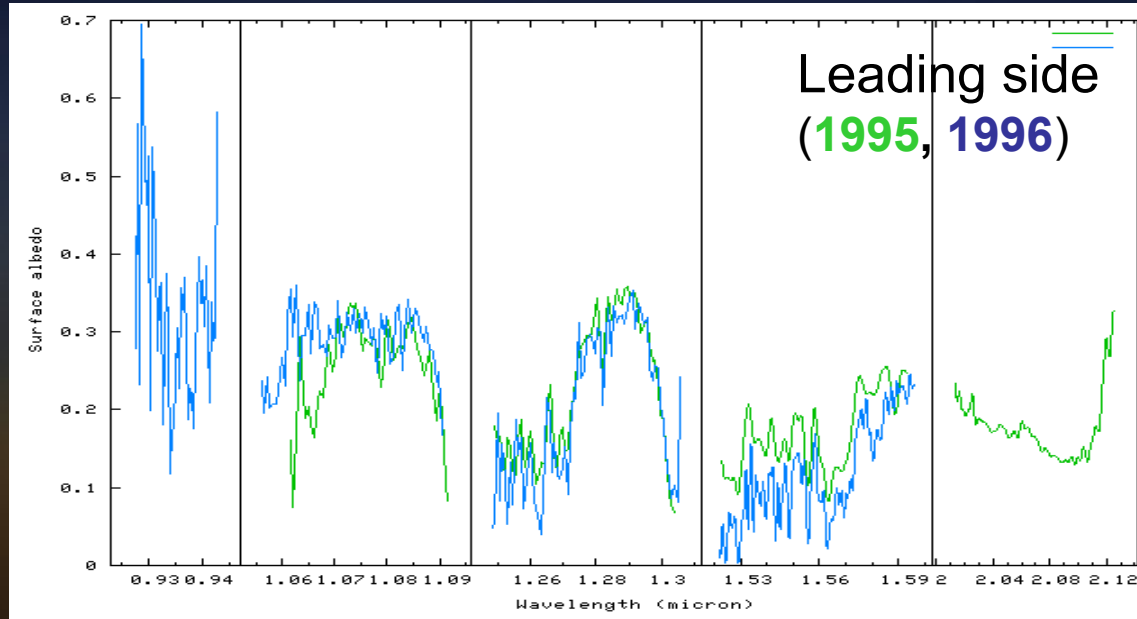


Surface albedo (1995, GEE)

The figure below serves the purpose of showing the large influence of the methane absorption coefficients in the retrieval of the surface albedo. The Karkoschka and Moreno datasets produce the highest surface albedos. Boudon and Irwin coefficients yield quite similar surface albedos for both the dark and the bright sides of Titan at 1.6 and 2.0 micron. These dramatic differences explain, at least in part, the reasons why various investigators have been reporting such different surface albedo values.

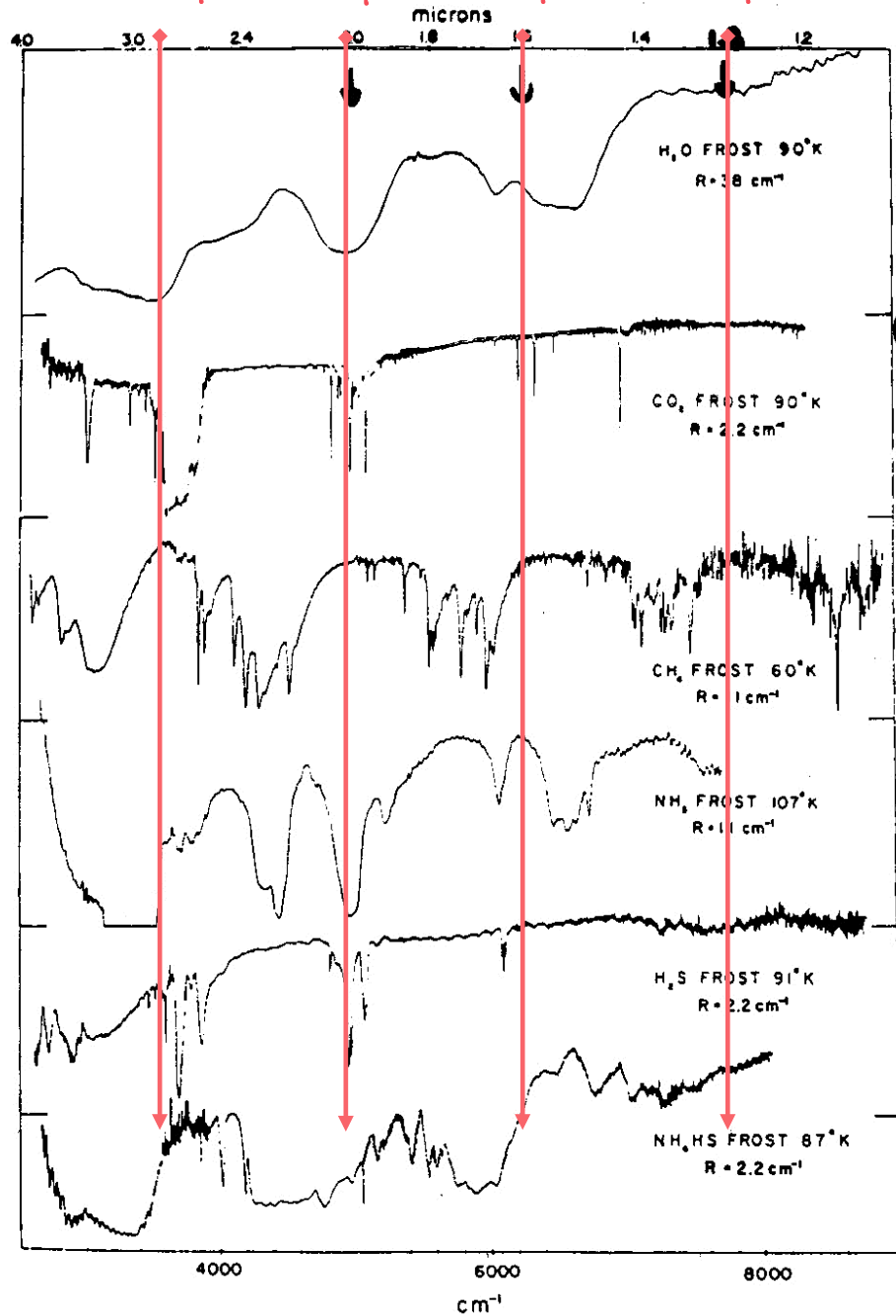


Surface albedo



Surface albedos derived for Titan's bright and dark side. The values from the Aug. 17, 1995 dataset are quite compatible with those from the Aug. 2, 1996 observations. Similarly, for the trailing side: the Aug. 5, 1993 data are quite compatible with those inferred from the Sept. 23, 1994 dataset. Given the uncertainties, the leading hemisphere appears significantly brighter than the trailing hemisphere. The differences of the extreme surface albedo from 233 LCM to 67 LCM are : 340%, 57%, 40%, 44% and 50% at 0.94, 1.08, 1.28, 1.6 and 2.0 microns.

2.75 μm 2.0 μm 1.6 μm 1.3 μm



H2O ←

CO2 ←

CH4 ←

NH3 ←

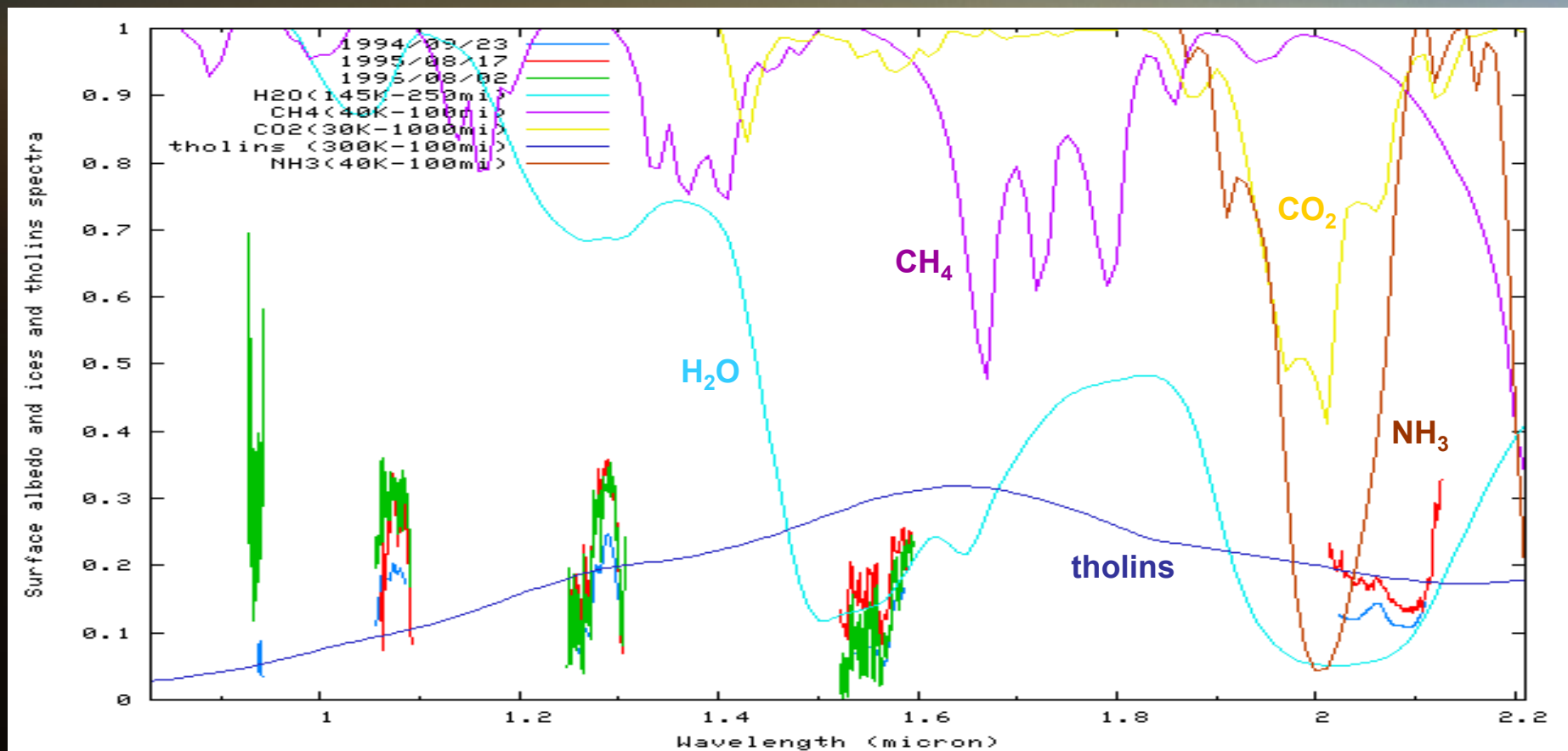
?

?

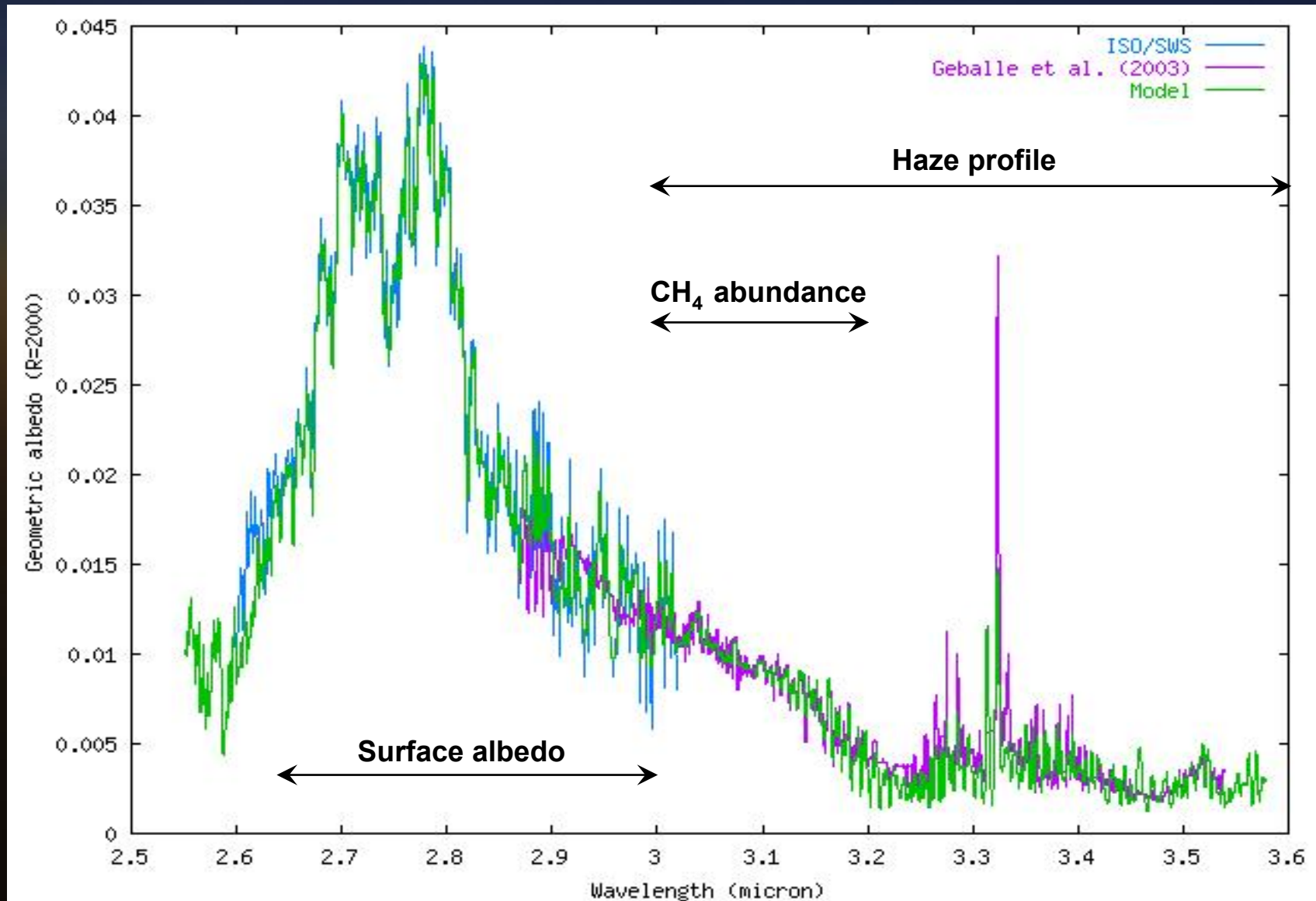
?

Comparison with the ices

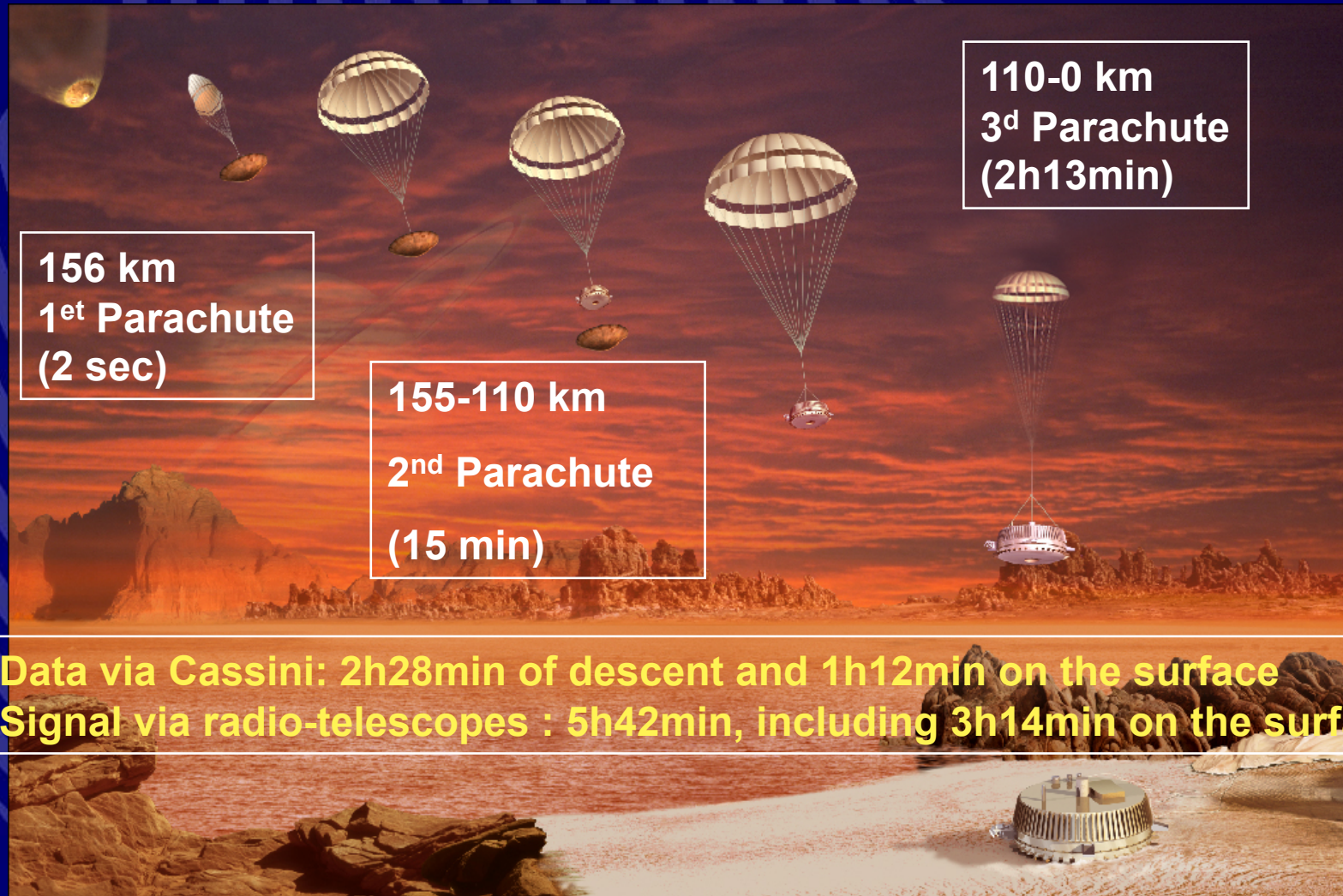
This figure shows the comparison between the retrieved surface albedo, for both the dark and bright side, and the spectra of tholins (Coll et al., 1999), H₂O ice (Grundy and Schmitt, 1998), CH₄ ice (Grundy et al., 2002), CO₂ ice (Quirico and Schmitt, 1997) and NH₃ ice (Schmitt et al., 1998). Water ice could explain the form of the surface albedo at longer wavelengths but a darker component (tholins?) is necessary to fit the albedo at shorter wavelengths.



⇒ ISO/SWS and Keck II fit



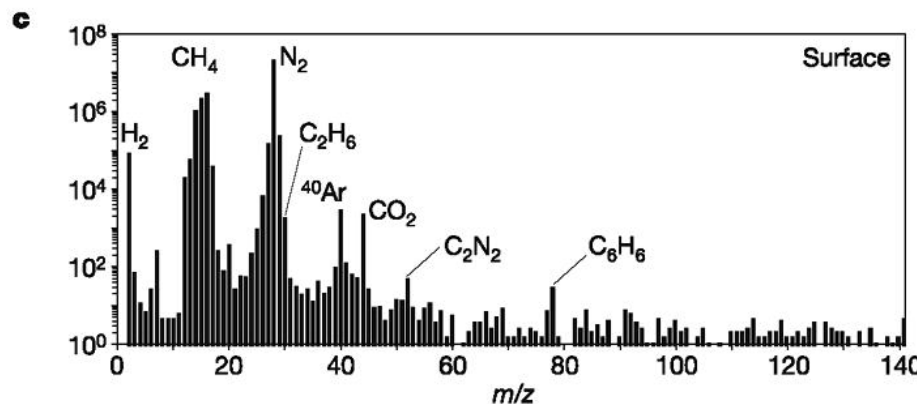
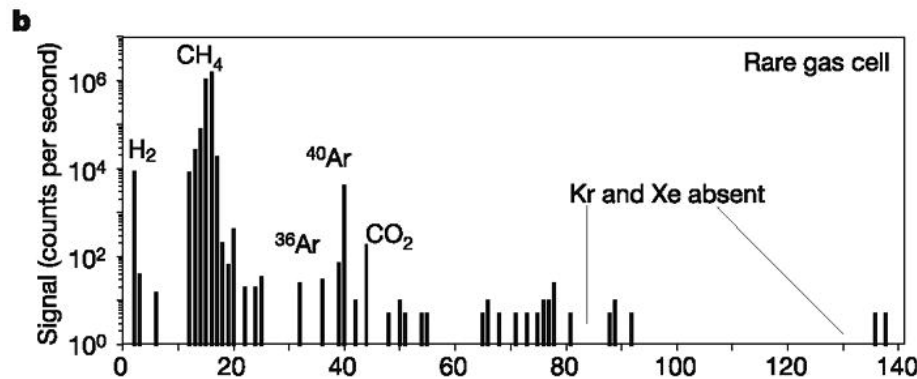
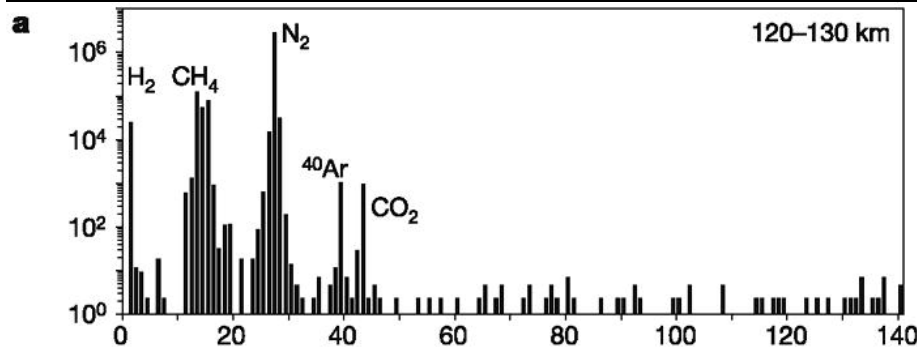
Huygens Descent and Landing Overview





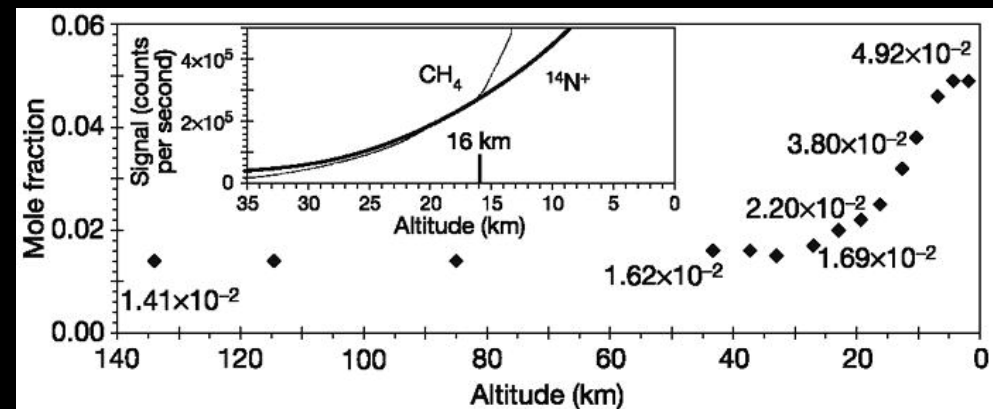
Observations with Huygens GCMS

(Niemann et al., Nature, 438, 779-784, 2005)



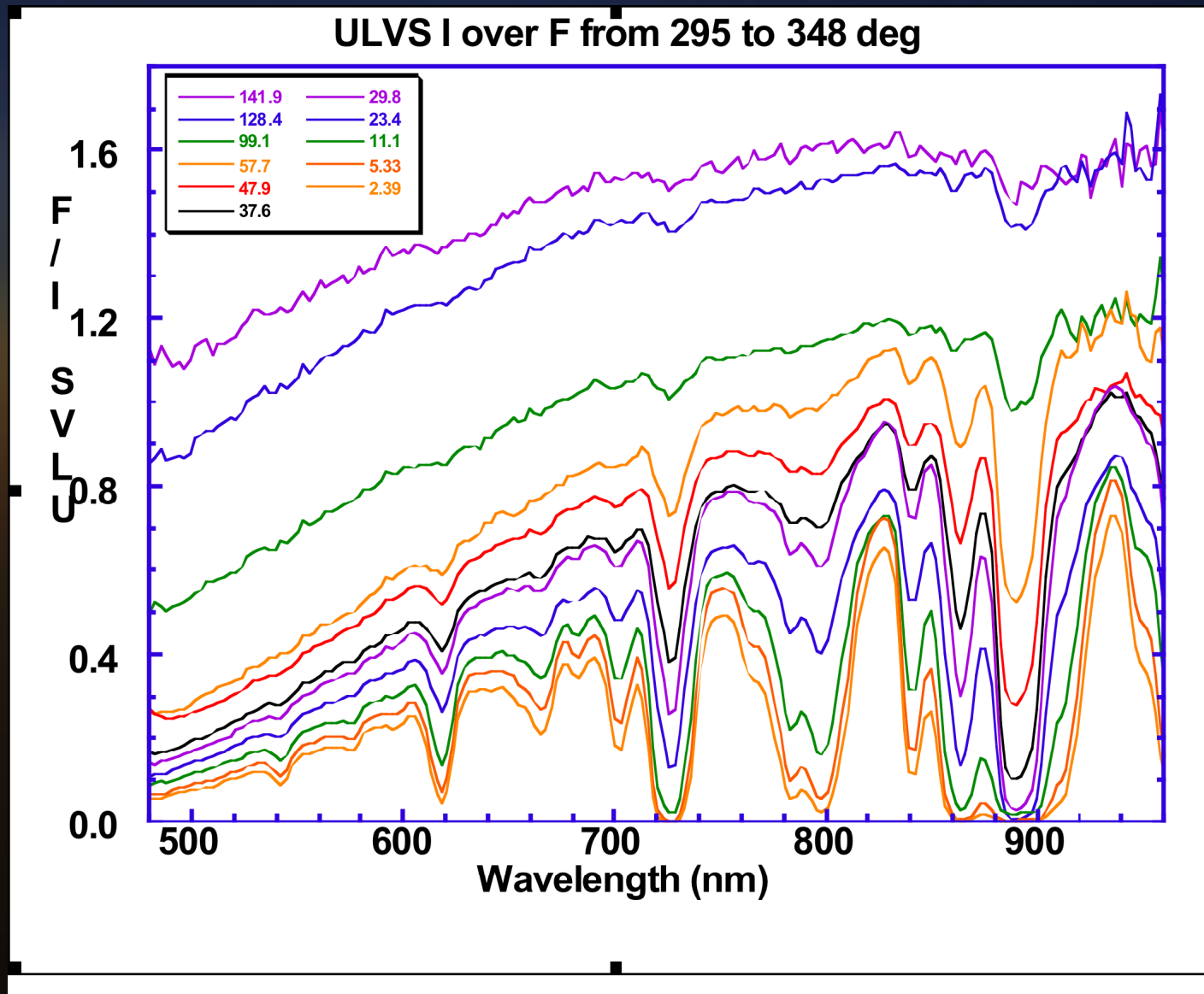
Detection of various organic compounds in the atmosphere and on the surface:

Ethane, acetylene, cyanogen, benzene, carbon dioxide, Argon.

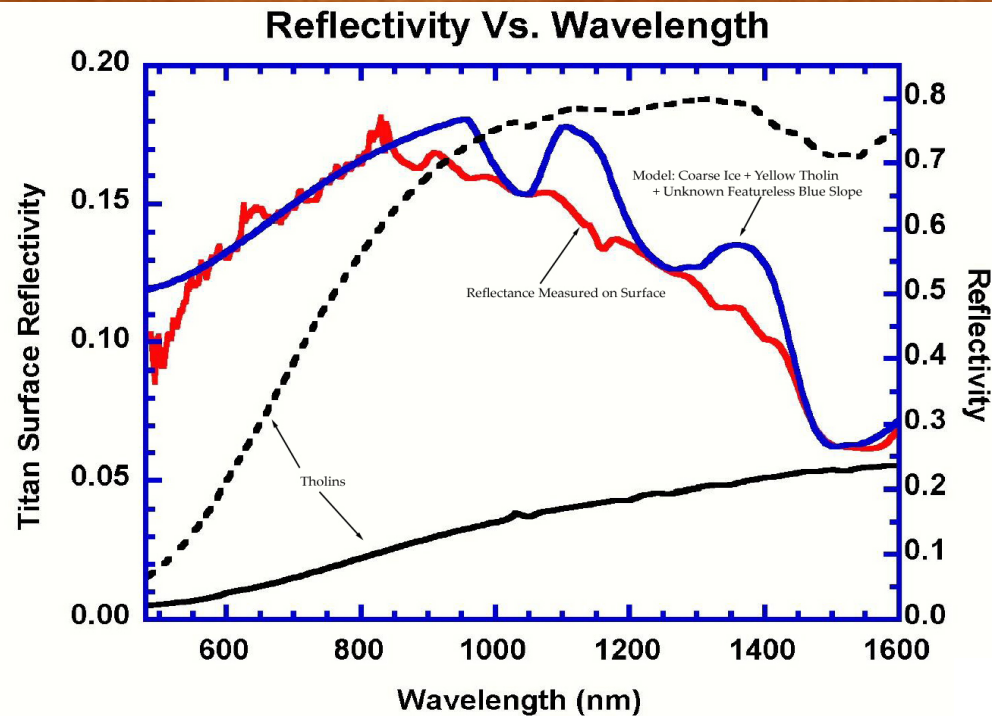


Vertical profile of methane in Titan's lower atmosphere

Aerosols and methane bands on Titan from Huygens DISR



➤ Fit of the DISR data: 0.8–1.6 micron

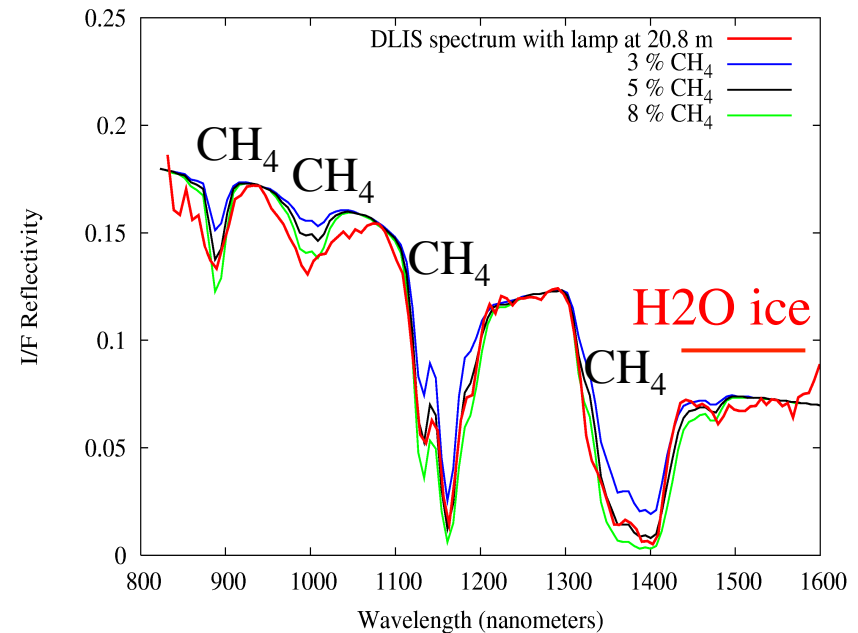


Surface reflectivity measured by DISR (in red)
(Tomasko et al., 2005)

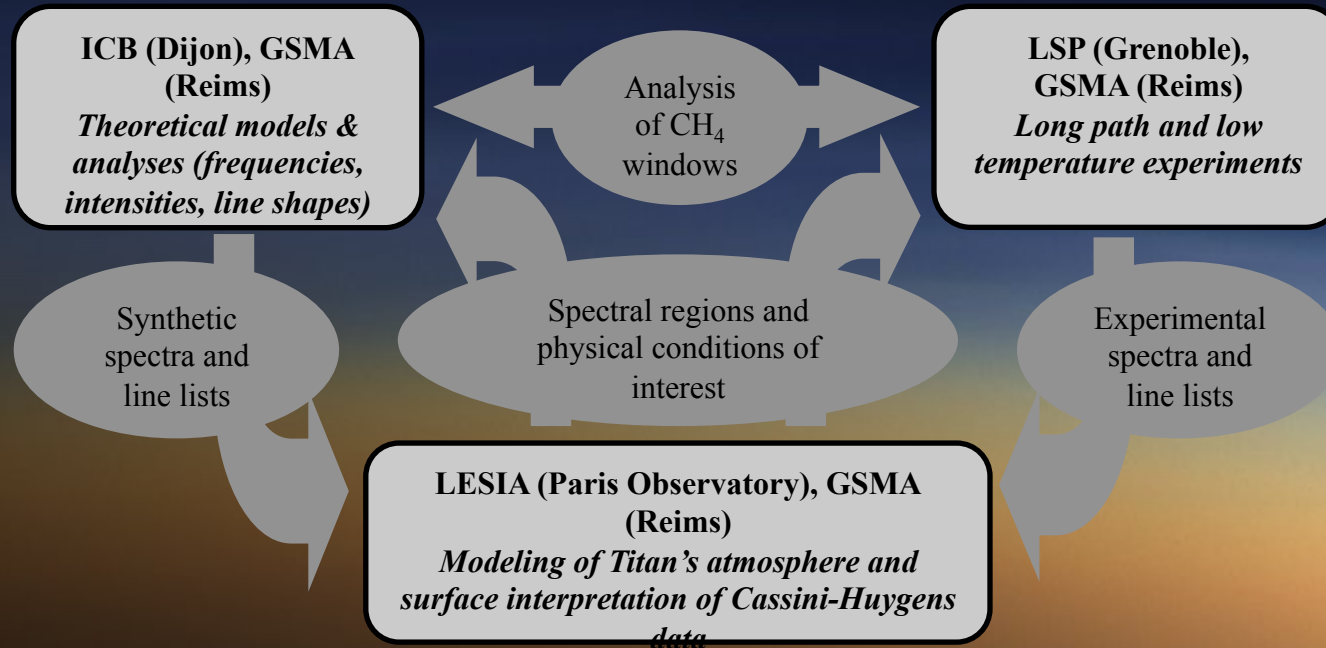
- **Methane** : about 5% at the surface
- **Surface** :
 - Dark material
 - absorption by water ice + ?

No data available for the CH₄ absorption at $\lambda < 1.6$ micron (theoretical or experimental)

Jacquemart et al., 2008



ANR CH4@Titan : Coustenis et al. 01/01/2009-31/12/2012



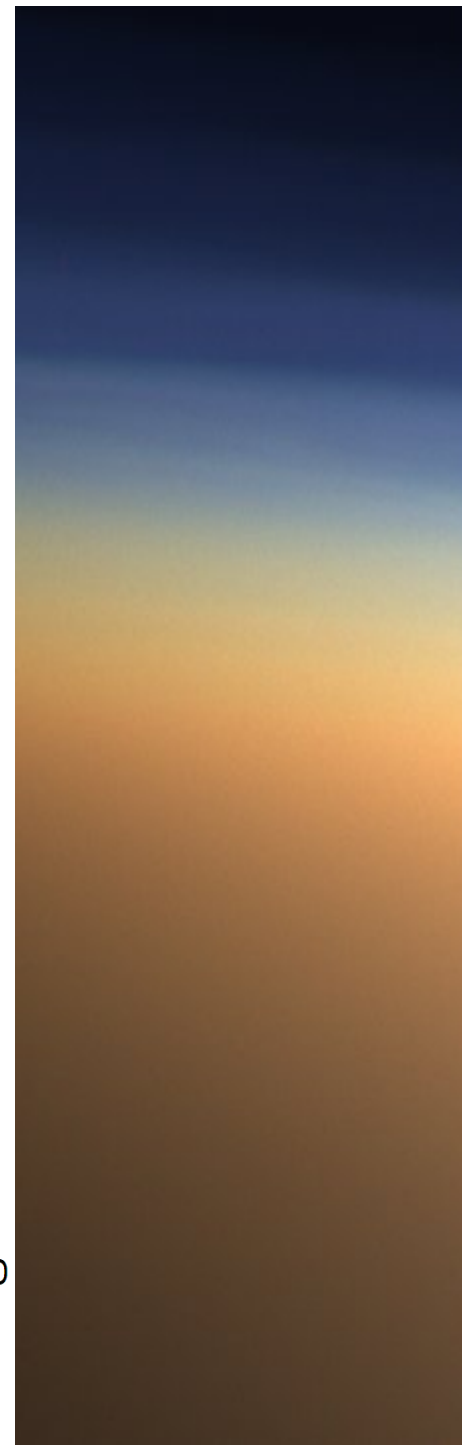
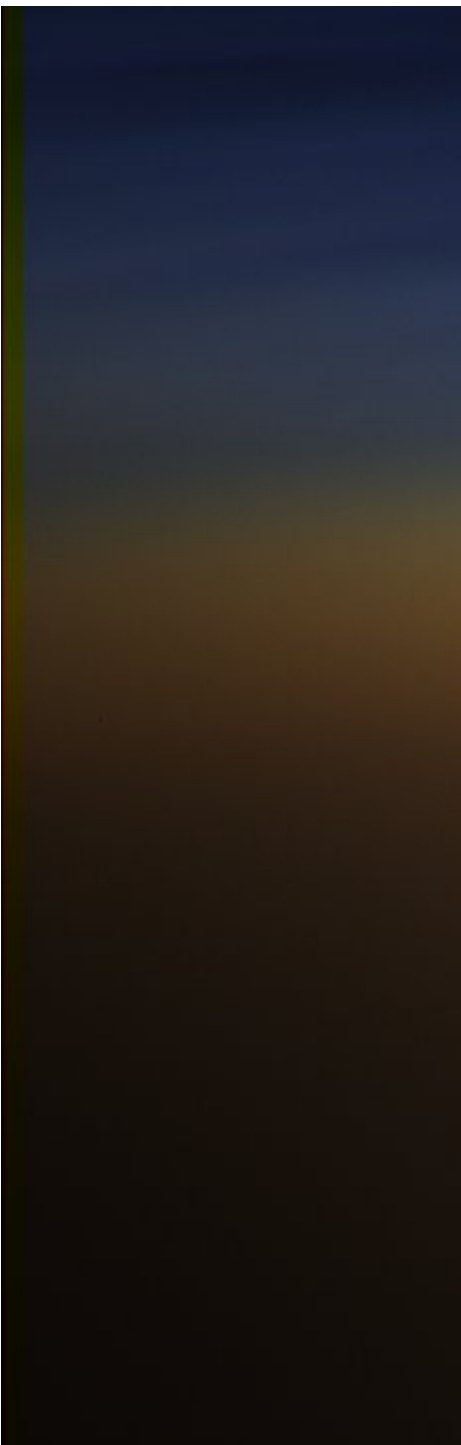
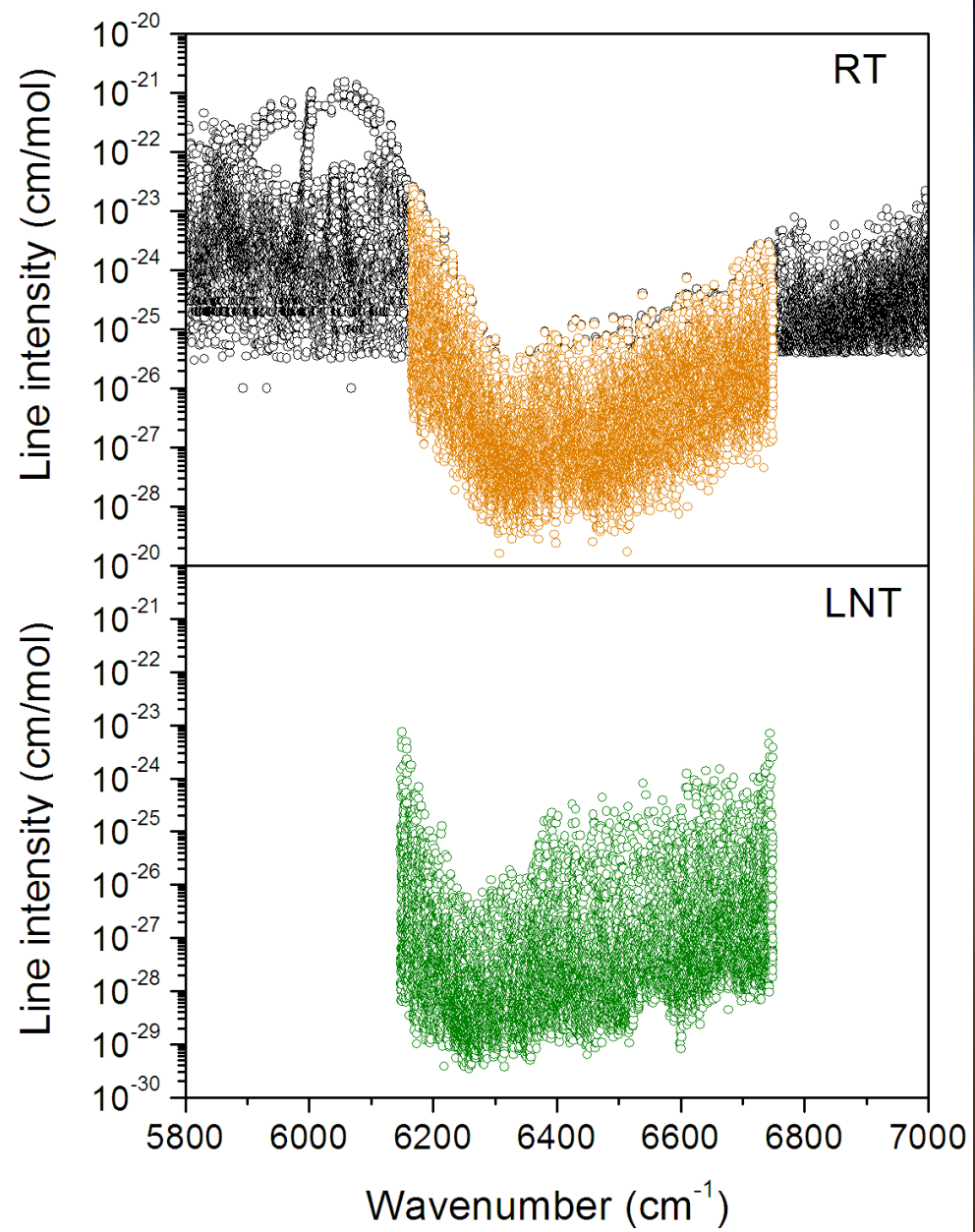
Partenaire	Organisme gestionnaire des crédits	Responsable scientifique
Partenaire 1	CNRS DELEGATION REGIONALE ILE DE FRANCE OUEST ET NORD	Mme Coustenis Athéna
Partenaire 2	CNRS DELEGATION REGIONALE CENTRE EST	M. Boudon Vincent
Partenaire 3	CNRS DELEGATION REGIONALE ALPES	M. Campargue Alain
Partenaire 4	UNIVERSITE CHAMPAGNE-ARDENNE REIMS	M. Tyuterev Vladimir
TOTAL		

Obs Paris-Meudon

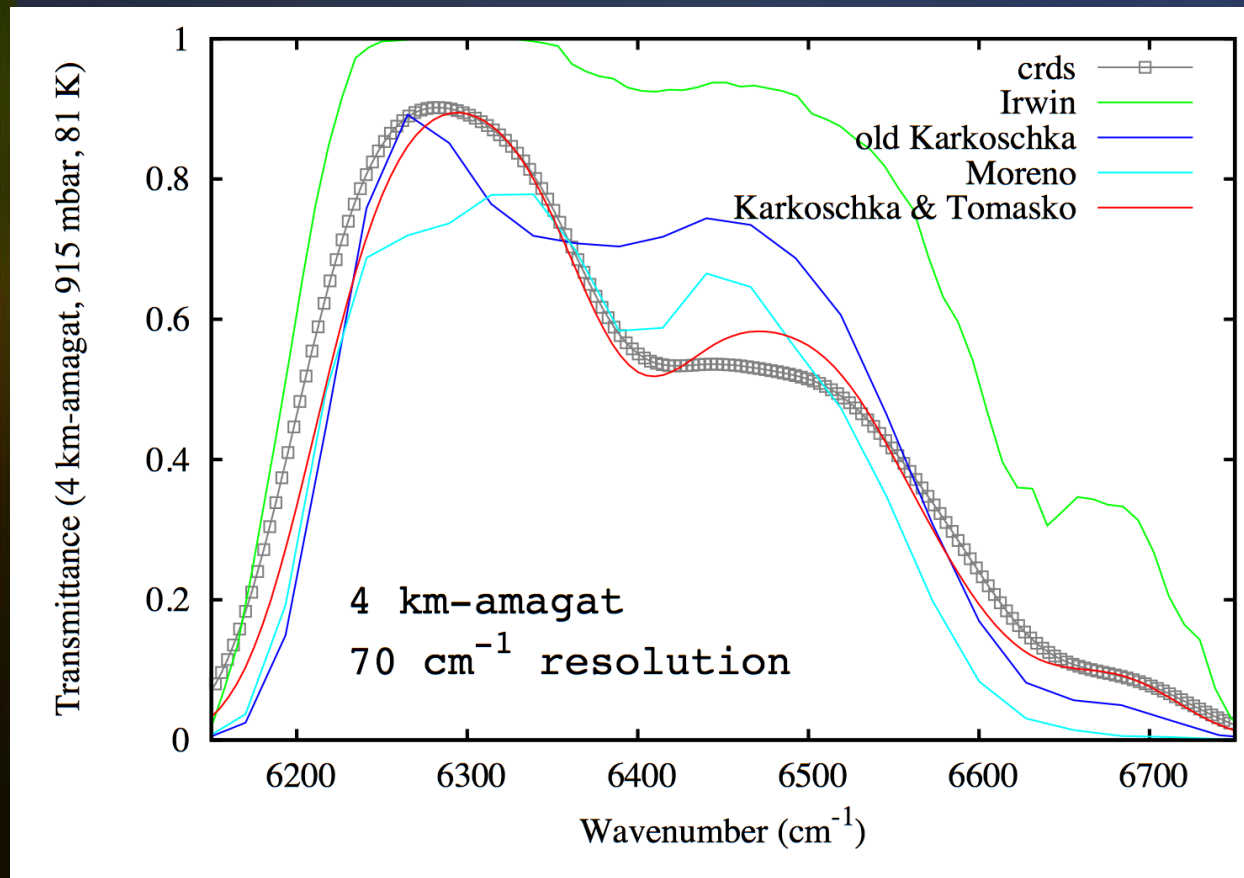
Univ. Bourgogne, Dijon

LSP, Grenoble

GSMA, Univ. Reims



Comparison with band models and DISR data inferences

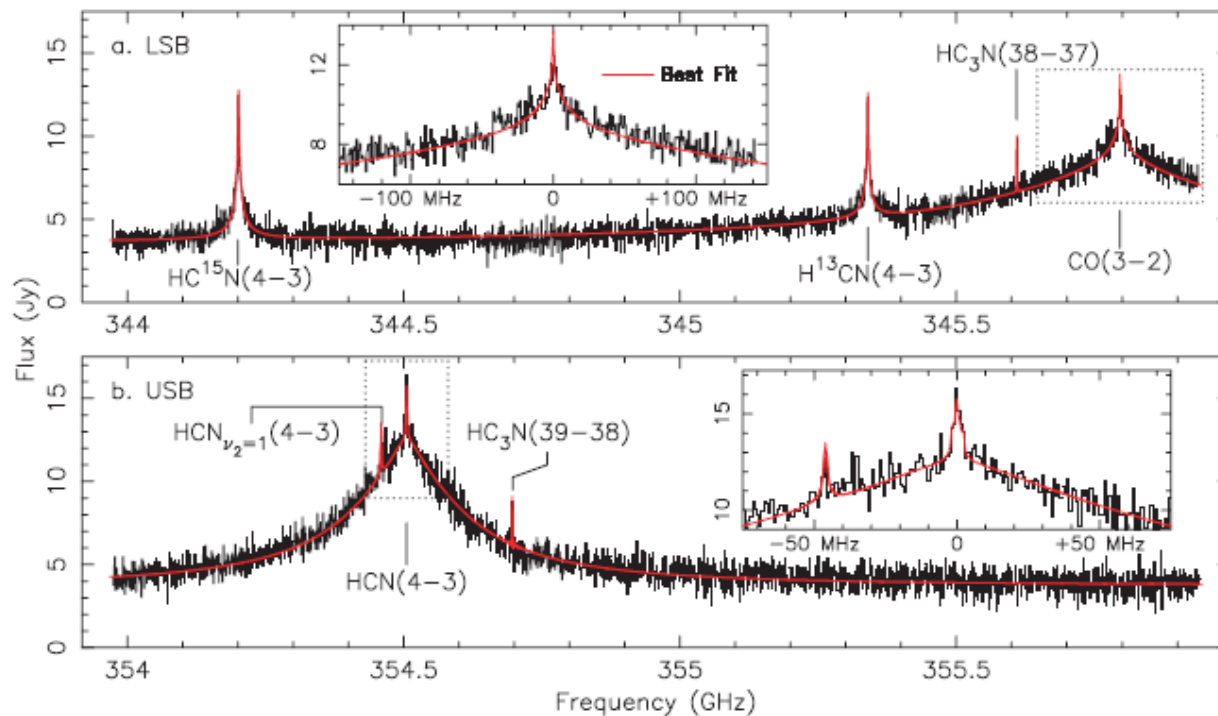
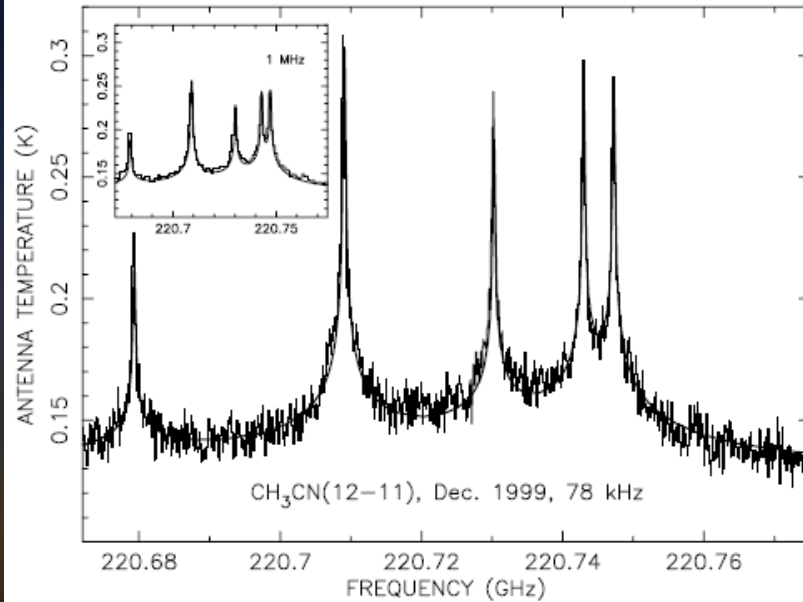


- Comparison with different band models used in analysis of Titan spectra (VIMS, DISR)

- Irwin et al. (2006): not enough absorption
- Good agreement with Karkoschka & Tomasko's (2009) model based on lab and DISR data

Nitriles on Titan at (sub)mm wavelengths

IRAM, Marten et al. 2002



*SMA (8 x 6m diameter
interferometer, located
near summit of Mauna
Kea, HI),
Gurwell 2004*

TSSM

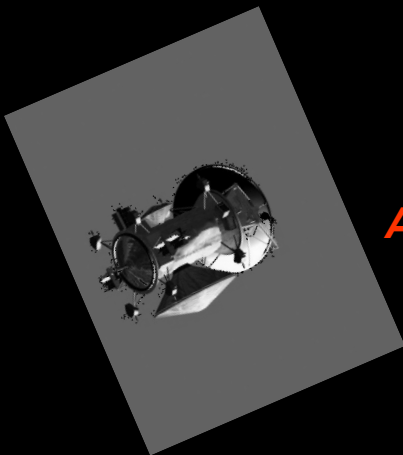
Titan Saturn System Mission



"...oh brave new world..."

A 2008 TSSM ESA-NASA-JPL study

***A. Coustenis, J. Lunine, D. Matson, J-P. Lebreton, K. Reh, Ch. Erd
and the Joint Science Definition Team***



TSSM ^{Science} mission architecture

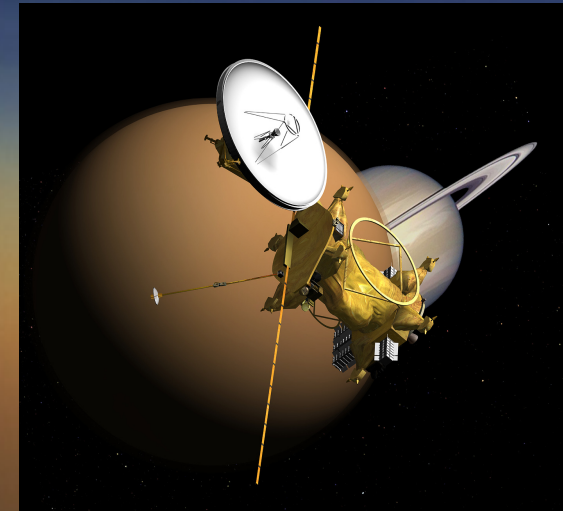
Combining

- the orbiter (first of Saturn, with Enceladus flybys, then dedicated to Titan), with
- a hot-air balloon/montgolfière, and
- a North-pole lake-landing probe



A hot-air balloon (Titan montgolfière) will float at 10 km above the surface around the equator for at least 6 months (T=83K, wind speed=1-2 m/s) with altitude control

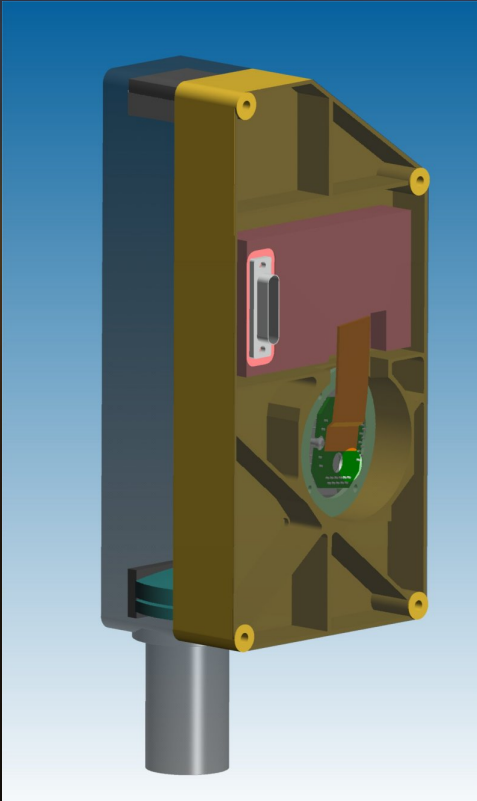
Dedicated Titan orbiter will also be used for relay



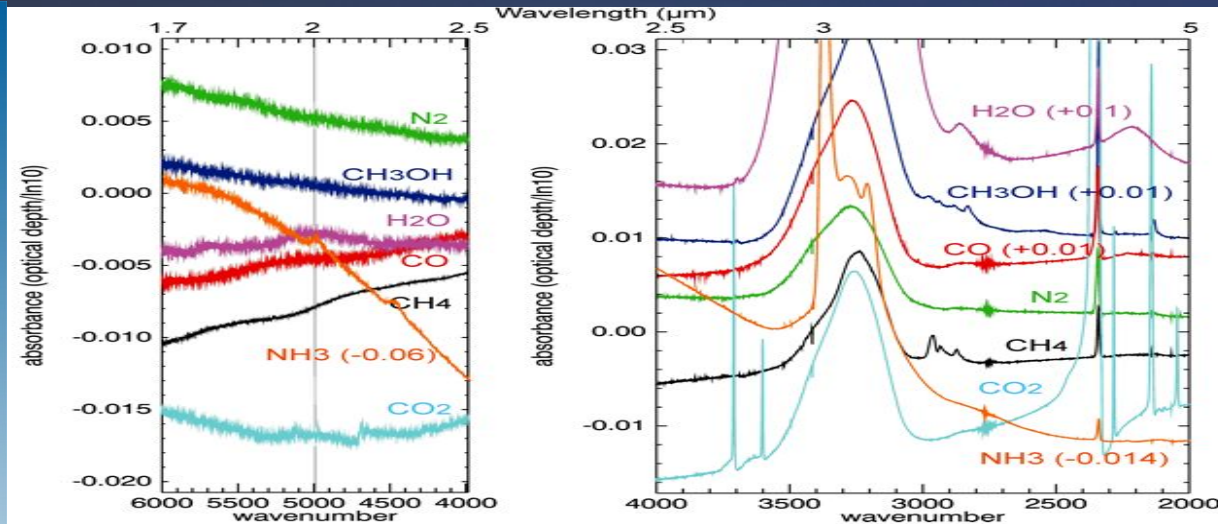
A short-lived (9 hrs) probe/lander with chemical analysis package will land in a northern lake (Kraken Mare)



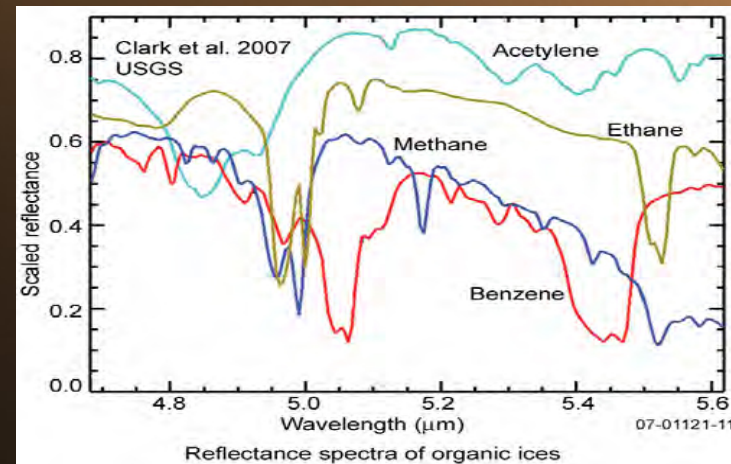
Instrument requirement for composition



BIS will inherit from VIHI (Visible and IR Hyperspectral Imager) on BepiColombo



Near-IR-spectrometer (BIS)
Wavelength range:
near-IR (1-5.6 μ)



Reflectance spectra of organic ices

Future investigations in the thermal IR with TSSM

- TSSM/ Thermal IR spectrometer (TIRS): will work in 7-333 micron ($30\text{-}1500\text{ cm}^{-1}$)
 - Try to ascertain whether interspecies variations in $^{12}\text{C}/^{13}\text{C}$ are real.
 - Search for new species (CH_3CN , C_3H_6 , $\text{CH}_2\text{CHCH}_2\dots$) & isotopes (HC_3^{15}N , $^{13}\text{C}_2\text{H}_2\dots$)
- Community:
 - Need line data for many bands of propane.
 - Need more accurate line data for most isotopic species.

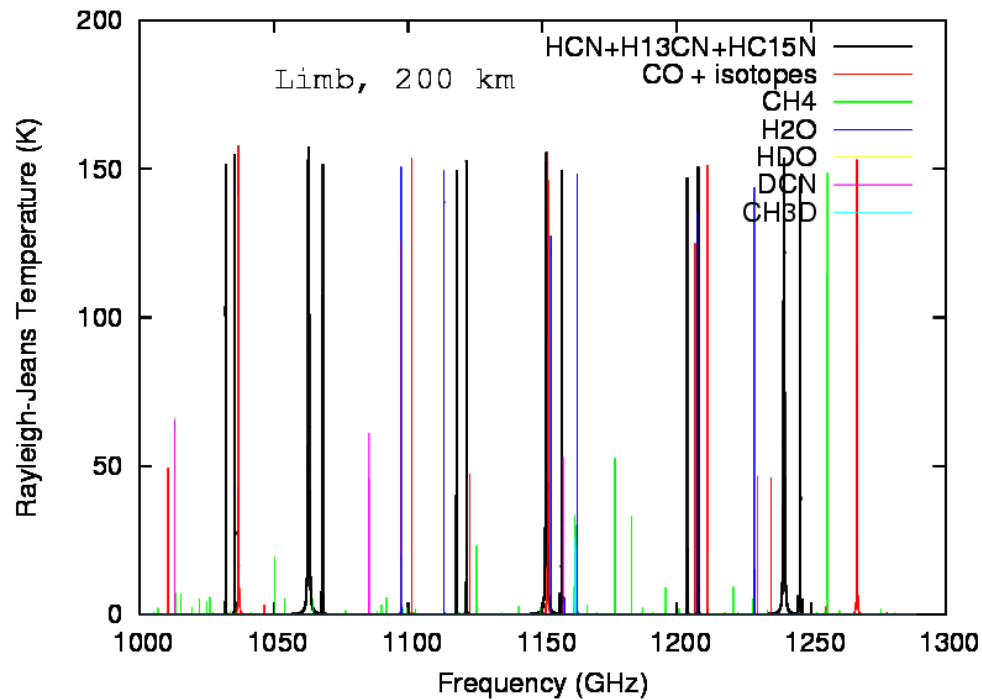
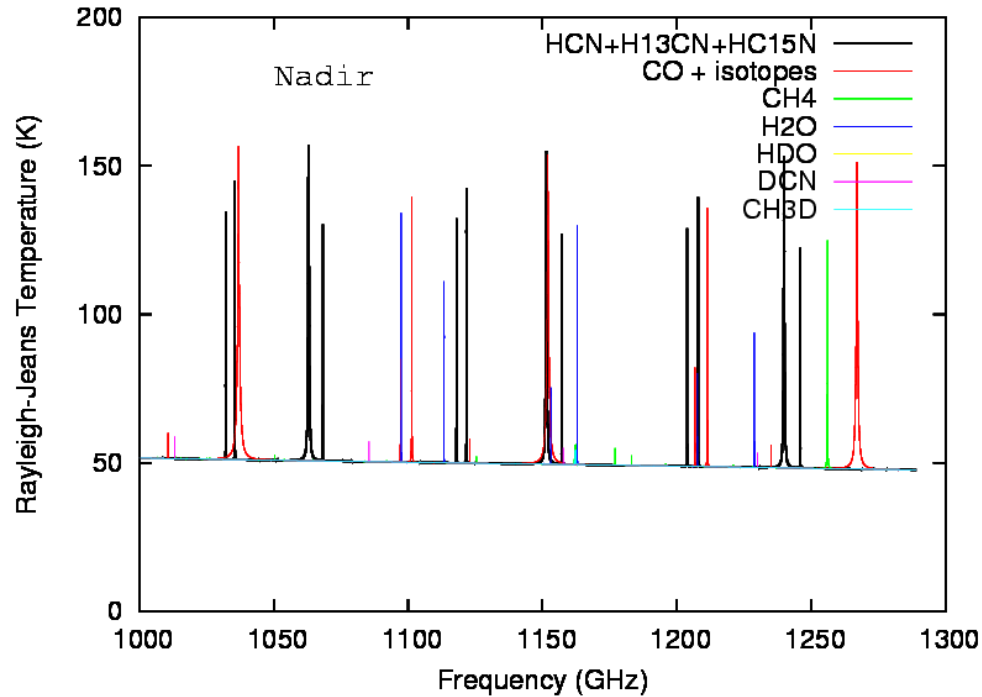
The case for a submillimeter sounder (SMS)

on the TSSM Titan Orbiter

E. Lellouch, S. Vinatier, P. Hartogh,
G. Beaudin, R. Moreno, A. Coustenis et al.

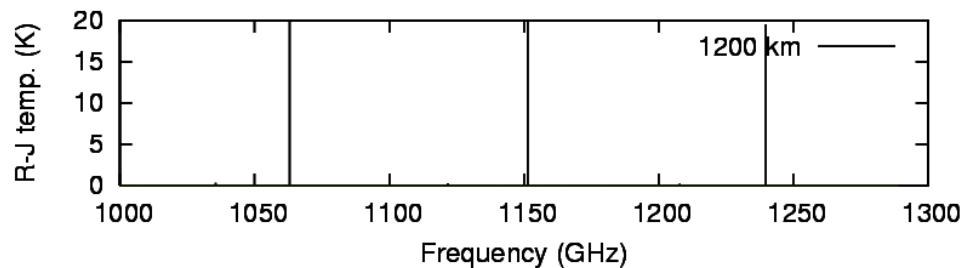
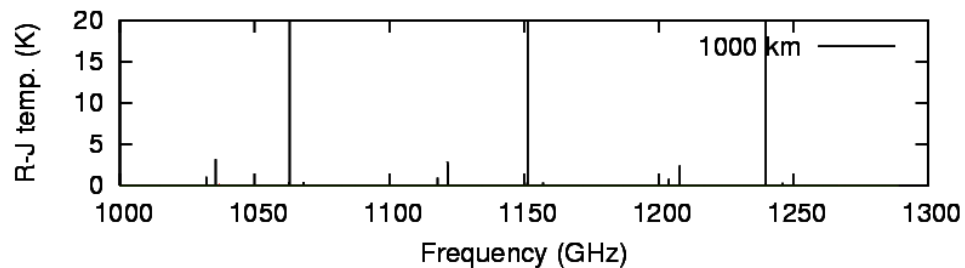
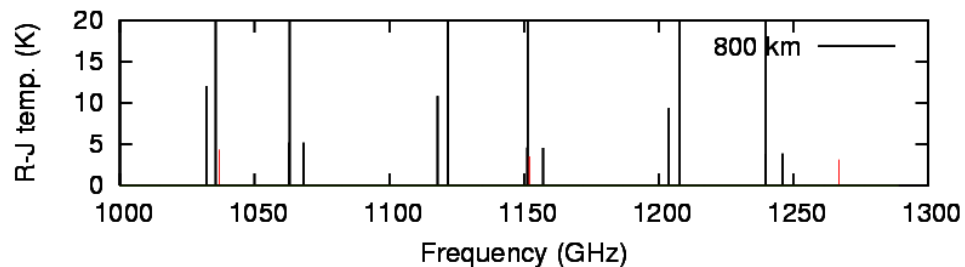
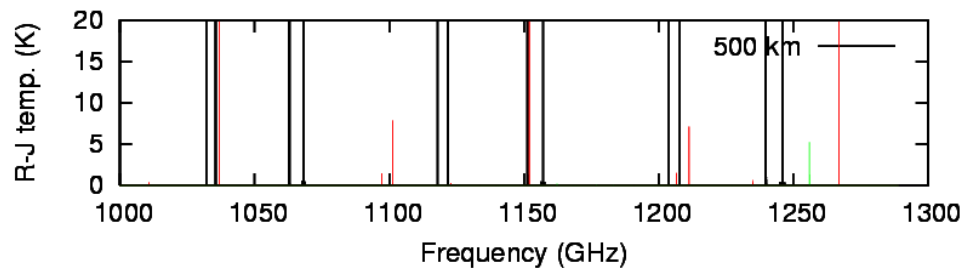
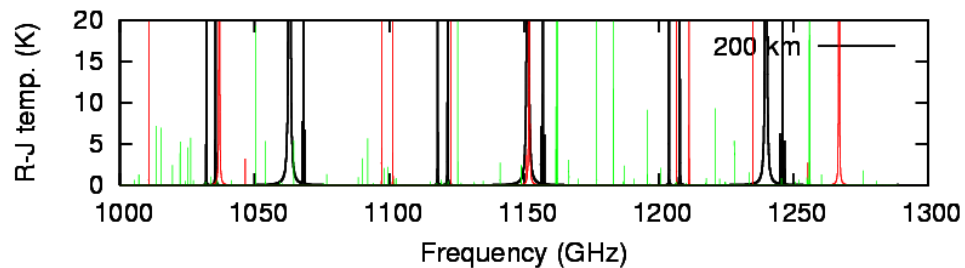
Main science goals

- Determine the 3-D field of temperature, wind, and composition in the stratosphere, mesosphere and lower thermosphere of Titan
- (Enceladus science goals: composition, density, temperature and dynamics of gas plume, but models need to be done)



Titan's expected spectrum at 1.0-1.3 THz

Detection limit :
 Typically 1.5 K in 1 mn
 0.2 K in 1 hr



Titan's expected spectrum at 1.0-1.3 THz

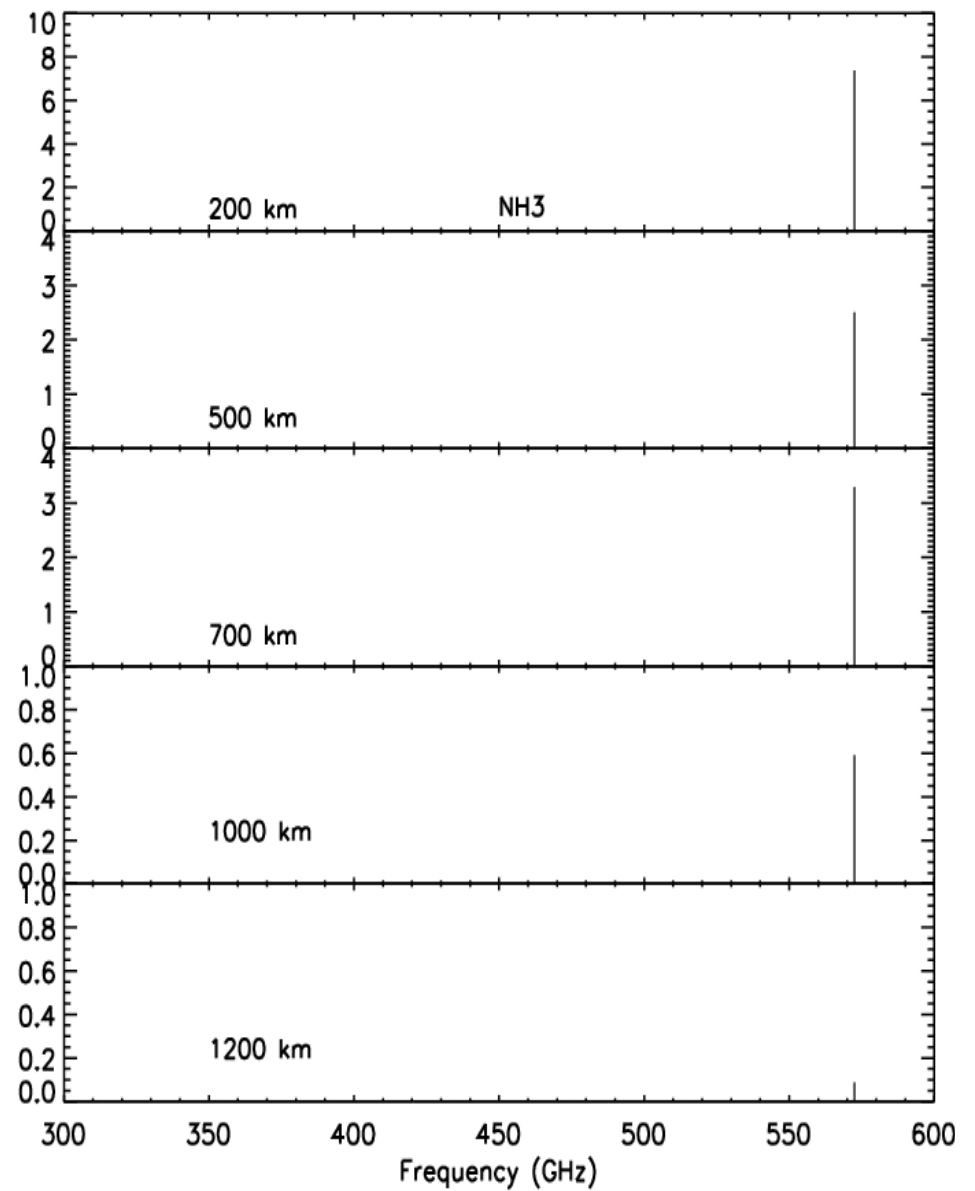
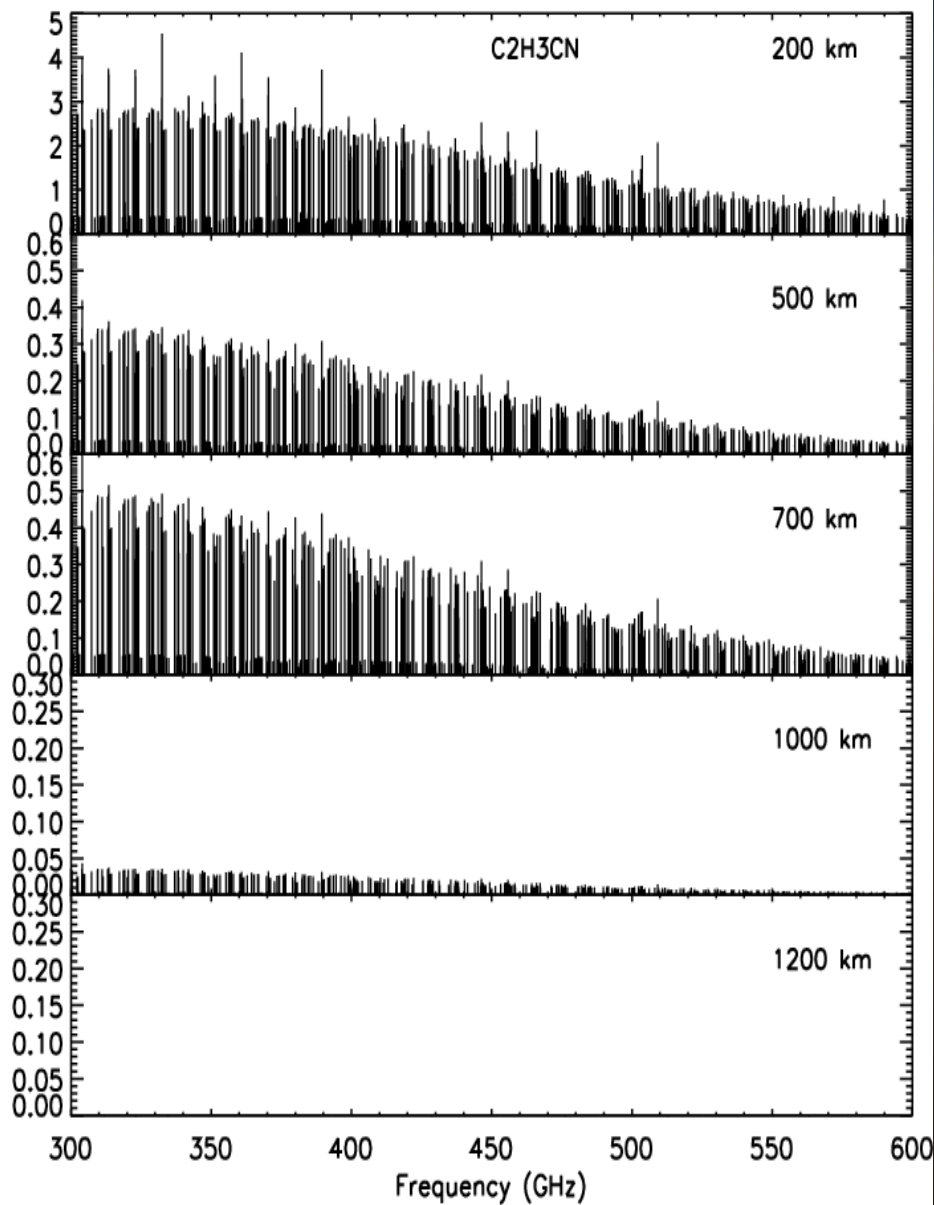
HCN CO CH₄

THERMAL SOUNDING:

- From CH₄ (uniform) : up to ~500 km
- From CO (almost certainly uniform) ; no homopause uncertainty problem: up to ~800 km
- From HCN (not uniform vertically nor spatially, but feasible through multiple lines incl. isotopes, cf. CO on Venus) : up to ~1200 km

Advantage: *LTE is not a major issue like in IR*

Detectability of C₂H₃CN and NH₃ (models P. Lavvas)



Agnostospheric chemistry

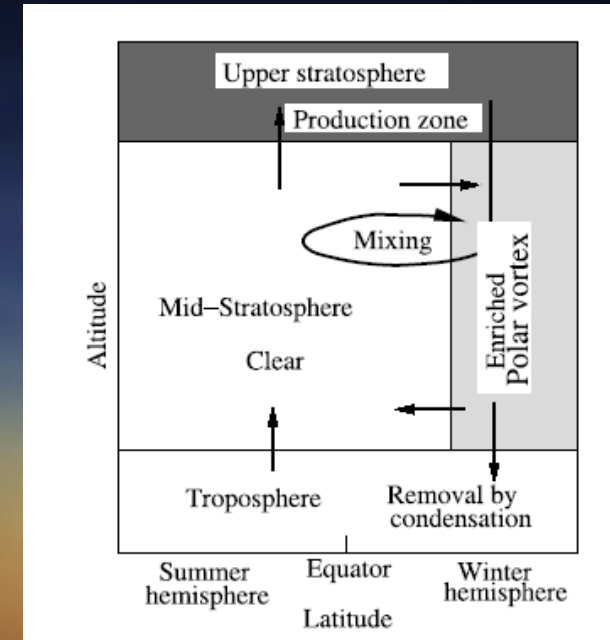
- *Study chemistry-dynamics couplings:*
Obtain 3-D (i.e. altitude-latitude-local time) distribution of known minor stratospheric species and relation to wind field

- *Study chemical complexity:*

Search for and map « INMS species » at deeper (<900 km) levels: heavy nitriles (HC₅N, C₂H₃CN..., NH₃, CH₂NH, CH₃CCH...): calculations show that many species can be detected. More species (HC₅N, etc...) TBD

→ **Make the link between thermospheric and stratospheric chemistry**

- *Study some specific problems:*
 - Origin of oxygen (H₂O, CO)
 - Isotope ratios
 - D/H in HCN and H₂O vs. in CH₄



Titan chemistry from synergy of submm with thermal IR

	Thermal IR	Submm
Temperature sounding	CH ₄ and N ₂ 0-550 km	CH ₄ , CO, HCN ~100 – 1200 km
Winds	Thermal winds (zonal)	Direct winds (zonal +meridional) (and thermal winds)
Composition	Hydrocarbons Nitriles (light) CO ₂ Condensates, isotopes	Nitriles, some hydrocarbons (CH ₃ CCH, CH ₂ NH...) CO, H ₂ O, NH ₃ Rare isotopic species



**Some conclusions and thoughts
for further developments**

Titan

organics that
remain to be seen

Some organics, as yet unobserved on Titan in the thermal IR, but potentially observable with CIRS and their deduced upper limits in Titan's atmosphere from previous observations.

Studied compounds	Strongest signatures		Upper limit of mean mixing ratio in Titan's stratosphere	
	Frequency (cm ⁻¹)	Band strength at 300 K (cm ⁻² atm ⁻¹)	using Voyager IRIS spectra	using ISO disk-average data
Hydrocarbons				
CH ₂ CCH ₂	356	65	5 × 10 ^{-9a}	2 × 10 ^{-9b}
	845	407		
C ₄ H ₄	629	288	7 × 10 ^{-10c}	
C ₆ H ₂	622	428	4.4 × 10 ^{-10d}	
C ₈ H ₂	621.5	496	4 × 10 ^{-10e}	
Nitriles				
CH ₃ CN	362 ^l	4.4		
CH ₂ CHCN	230	10	8.4 × 10 ^{-8g}	<5 × 10 ^{-10b}
	954	100		
CH ₃ CH ₂ CN	207	15	2.5 × 10 ^{-7a}	< 1 × 10 ^{-10b}
	1075	37		
CH ₃ CH ₂ CH ₂ CN	728/742	3.5	5 × 10 ^{-7a}	
(CH ₃) ₂ CHCN	538	3.3	2 × 10 ^{-7a}	
ΔCN	726	19	1.5 × 10 ^{-7a}	
	818	34		
CH ₃ CCCN	338	100	1.0 × 10 ^{-8a}	
	499	91		
CH ₃ CHCHCN	728	230	2.5 × 10 ^{-7a}	< 5 × 10 ^{-10b}
CH ₂ CHCH ₂ CN	557	64	4 × 10 ^{-8h}	< 5 × 10 ^{-10b}
	942	110		
CH ₂ C(CH ₃)CN	535	33	7.5 × 10 ^{-8h}	<5 × 10 ^{-10b}
	928	130		
C ₄ N ₂	614	34.4	5.6 × 10 ⁻⁹ⁱ	
NCCHCHCN (trans)	947	178	1 × 10 ^{-8j}	
Other N organics				
CH ₃ NC	526	8.8	1.3 × 10 ^{-9k}	
CH ₂ N ₂	419	144	5.0 × 10 ^{-9k}	
CH ₃ N ₃	250	9	5.4 × 10 ^{-9k}	

Flasar et al., 2004

What do we need to interpret our observations

For molecules known to be present

- Line positions for all bands, including hot bands
 - Absolute band strength
 - Data for most abundant isotopes
- Then data for molecules to be searched
- All this in the right conditions of p, T and in N_2 and H_2 -He

Spectroscopic needs

Laboratory measurements

- Long pathlength (e.g. CRDS)
- p-T range covering Titan's atmosphere

Spectroscopic analyses

- Tetradecade (1,6-1,9 μm) : still incomplete
- Isodecade (1,3-1,5 μm) : almost no analysis
- Higher polyades (<1,28 μm) : no analysis

Studies of far wings of CH_4 broadened in N_2

- Laboratory measurements and modeling
- The far wing of ν_3 could be a significant source of opacity in the 2.75 μm window
- Only available measurements are for CH_4 broadened by H_2 (Hartmann et al. 2000)

