

# Abundances in the solar system: what we achieved and how much was it dependent on space probes?

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### Introduction: a typical planet radiation



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## Introduction: thermal IR emission

**Outgoing thermal emission of a planet** 



Pb: How to decouple temperature and composition contributions?

- Temperature:
  - fit of the observed I<sub>v</sub>
  - a gas uniformely mixed with known abundance
- Abundance:
  - fit of the observed  $I_v > \tau \Rightarrow q$
  - -T is known

## Introduction: radiative transfer



Absorption line

Width of the line depends on the gas density: the higher is the abundance, the larger is the line  $\Leftrightarrow$  pressure broadening

Absorption/emission depends on the temperature gradient in the region of the radiation emission (where  $\tau = 1$ ).

## Introduction: line opacity and level probed

### How to probe several levels?

For a given molecule, lines of different intensities originate from different levels



Line 1 has a small absorption coefficient => probe deeper in the atmosphere. Line 2 has a high absorption coefficient => probe higher in the atmosphere.

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## Introduction: line profile vs thermal profile



Region of positive thermal gradient => emission line Region of negative thermal gradient => absorption line If isothermal profile => no line

## Introduction: line profile vs thermal profile



## Titan

## Titan's composition: an historical overview

1925: Jeans studied the atmospheric escape process => Titan should have kept an atmosphere.

 $\rightarrow$  gas of molecular weight  $\geq$  16 : possibly Ar, Ne, N<sub>2</sub>, CH<sub>4</sub>, NH<sub>3</sub> from thermodynamical theory

 $\rightarrow$  no H<sub>2</sub> and He because they are too light and should have escaped

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1944 : first detection of CH<sub>4</sub> (Kuiper, 1944)



1961 – 1973 : UV ground-based observations (McCord et al. 1971) and space observations with the Orbiting Astronomical Observatory (Caldwell et al., 1973)



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Very similar spectra for Titan and Saturn except in UV => 2 different models for Titan
- low density atmosphere => Rayleigh scattering is not efficient.
- Rayleigh scattering exists but is masked by an UV absorber = haze.

If an UV absorber exists = > deposition of energy at high altitude => T  $\nearrow$  with height

### Possible detection of H<sub>2</sub>: unexpected from Jean's escape calculations



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Rmq: In 1981, Trafton et al. mentioned that their 1972 and 1975  $\rm H_2$  observations were mostly due to  $\rm CH_{4.}$ 

### Titan's photometry: thermal emission (12 - 20 µm)



Jupiter satellites (no atmosphere) temperatures : close to BB emission (Gillet et al., 1970).

Titan : farther from the Sun,  $A_b = 0.29$ => Titan's equilibrium temperature should be 82 K.

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**Titan at 12 µm** (Allen et al., 1971) : used O'Brien Observatory (76 cm)  $\rightarrow$  T<sub>b</sub> = 125 ± 5 K (hyp: R<sub>Titan</sub> = 2405 km) => Greenhouse effect in a thin atmosphere

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**Titan at 20 µm** (Morrison et al., 1972) : Mauna Kea observatory (2.24 m). interesting because = peak of the BB emission  $\rightarrow$  T<sub>b</sub> = 93 K, puzzling! (R<sub>Titan</sub> = 2550 km)

2 possibilities : - surface emissivity is very low

- opacity of the atmosphere very high at 20  $\mu$ m  $\rightarrow$  possibly H<sub>2</sub> (collision induced), then the surface pressure should be ~1 atm

### Titan's spectroscopy: thermal emission (8 - 13 µm)



Gillet et al., (1973) : observations at Mount Lemmon (152 cm)

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Gillet et al., (1973) : observations at Mount Lemmon (152 cm), assumed : R<sub>Titan</sub> = 2440 km.

2 possible interpretations : - If T  $\searrow$  with height => strong absorber around 10 µm : NH<sub>3</sub> (10.5 µm) ?

- If T  $\nearrow$  with height => strong emission features in the 8 µm and 12.5 µm regions : CH<sub>4</sub> (7.7 µm), C<sub>2</sub>H<sub>6</sub> (12.2 µm)

Need of a better spectral resolution

## Titan's atmosphere: the first models

- Greenhouse effect in a massive atmosphere (Pollack, 1973)
- Strong atmospheric inversion in a much less massive atmosphere (Danielson et al., 1973)
- Greenhouse effect + inversion (Low and Rieke, 1974)

- Photochemical models (Strobel, 1974)

## Titan: confirmation of a temperature inversion



Thermal emission of the UV-absorbing aerosols explain the observations at 10 and 20  $\mu$ m.

## Titan's thermal emission (8-13 µm): a better resolution



Gillett et al, 1975: observations at Kitt Peak (2.1 m and 4 m), assumed : R<sub>Titan</sub> = 2900 km.

They fitted the data with a model including a temperature inversion at 160 K (stratosphere) -  $q_{C2H6} = 0.5$  atm-cm

- $q_{C2H2} = 1.0 atm-cm$
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They derived :

-  $q_{C2H4} = 0.002$  atm-cm (in agreement with photochemical model)

-  $q_{CH3D} \sim 0.5$  atm-cm

## Titan's thermal emission (8-13 µm): a better resolution



### Titan's thermal profiles: models

- atmosphere of  $CH_4$  in equilibrium with a solid  $CH_4$  surface with  $T_{surf}$  = 86 K and

 $P_{surf} = 20 \text{ mbar} (Calwell, 1978).$ 

- atmosphere of N<sub>2</sub> (CH<sub>4</sub> = minor constituent) with  $T_{surf}$  = 200 K and P<sub>surf</sub> = 20 bars (Hunten, 1978) = greenhouse model due to pressure-induced absorption in N<sub>2</sub>.



### Atmosphere of N<sub>2</sub>, m=28



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Consensus: T inversion with ~160 K (from the thermal emission of  $CH_4$  at 7.7  $\mu$ m)

### Titan in far IR (0.3-6 cm): surface temperature

Radio wavelength -> no gas absorption in this spectral region, except NH<sub>3</sub>, but was not detected in Titan's atmosphere => should probe the surface temperature

- Jaffe et al., 1980 : observation with the VLA (interferometer) at 1.3, 2 and 6 cm. -> derived  $T_{h} = 87 \pm 9 \text{ K}$ 



## Knowledge on Titan's atmosphere before space probes

- Molecular gas detected : CH<sub>4</sub>, C<sub>2</sub>H<sub>6</sub>, C<sub>2</sub>H<sub>2</sub>, CH<sub>3</sub>D, C<sub>2</sub>H<sub>4</sub> and maybe H<sub>2</sub>
   -> poor constrains of their column densities.
- Aerosols absorbing in UV => heating of the stratosphere = temperature inversion.
- Thermal emission of  $CH_4$  at 7.7  $\mu$ m => stratosphere temperature = 160 K.
- Cold surface temperature < 100 K.

Uncertainty on the main composition:

- atmosphere of CH<sub>4</sub>
- atmosphere of  $N_2$  (CH<sub>4</sub> = minor constituent)

Some photochemical models => based on  $CH_4 + H_2$  photochemistry

### Thermal profile

Inferred from radio occultation measurements (Lindal et al., 1983)

- Radio occultation measurements => T/m profile

- Mid-IR spectrometry at 540 cm<sup>-1</sup> =>  $T_{surf}$  = 94-97 K



m ~ 28 amu => atmosphere

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The predicted surface and tropopause temperature were close to the Voyager observations. The tropopause was thought to be 150 km higher than observed. Stratospheric temperature were correct.

### **Composition**

UVS solar occultations and airglow measurements: emission lines of N and N<sub>2</sub>
 => N<sub>2</sub> is the major component (82-95 %)
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### Composition

As the thermal profile was known => constrains of the molecular abundances with radiative transfer models.

But nadir observations => no vertical resolution



1995 : first General Circulation Model of Titan's atmosphere => explanation of the spatial distribution of molecules

- Observation in near IR
- 1983: CO detection at 4.5  $\mu$ m, q<sub>co</sub> = 6 x 10<sup>-5</sup> (Lutz et al 1983)

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- Observations in mm/submm : very high resolution
- Detection of CH<sub>3</sub>CN
- Vertical profiles of nitriles outside the Voyager range (from the line profile)
- <sup>15</sup>N/<sup>14</sup>N in HCN, <sup>18</sup>O/<sup>16</sup>O in CO
- Wind speed from the Doppler shifts of the lines .



10<sup>-13</sup> 10<sup>-12</sup> 10<sup>-11</sup> 10<sup>-10</sup> 10<sup>-9</sup> 10<sup>-8</sup> 10<sup>-7</sup> 10<sup>-6</sup> 10<sup>-5</sup> MIXING RATIO

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- High resolution ground based observations:
- -> thermal profile from  $CH_4$  lines at 7.7  $\mu$ m in the 300-600 km range (higher than Voyager)

-> wind velocity from Doppler shift from  $C_2H_6$  lines at 12  $\mu$ m





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## Space observations (ISO) detection of H<sub>2</sub>O and C<sub>6</sub>H<sub>6</sub> (Coustenis et al., 1998, 2003).





## Titan's composition: before and after space probes

	Before Voyager	Voyager	Ground/satellites	Cassini
$\begin{array}{c} {\rm CH}_4 \\ {\rm H}_2 \\ {\rm C}_2 {\rm H}_2 \\ {\rm C}_2 {\rm H}_6 \\ {\rm C}_2 {\rm H}_4 \\ {\rm C}_3 {\rm H}_8 \\ {\rm CH}_3 {\rm C}_2 {\rm H} \\ {\rm HCN} \\ {\rm HCN} \\ {\rm HC}_3 {\rm N} \\ {\rm CH}_3 {\rm CN} \\ {\rm CO}_2 \\ {\rm CO} \\ {\rm H}_2 {\rm O} \\ {\rm C}_6 {\rm H}_6 \end{array}$	1 - 2 km. Am < 2 km.Am 1 cm. Am 0.5 cm. Am 2. 10 <sup>-3</sup> cm.Am	<ul> <li>the main com</li> <li>⇒ impossible to</li> <li>the level protocolumn density</li> </ul>	ponent was unknown to infer abundances oed for each molecule is u y ratio ≠ abundances ratio	nknown:

Before Voyager : only column densities inferred for  $CH_4$ ,  $H_2$ ,  $C_2H_2$ ,  $C_2H_6$  and  $C_2H_4$ . Coupling between T and composition -> importance of the thermal profile observed with Voyager

## Titan's composition: before and after space probes

	"Before" Voyager (a)	Voyager	Ground/satellites	Cassini
$CH_4$	1.3-2.6 %	6% (alt. var.)		4.9% surf, 1.48% atm.
$H_2$	< 2.6 %	0.2 %		0.1 %
$\overline{C_2H_2}$	1 x 10 <sup>-5</sup>	2.2 x 10 <sup>-6</sup>	5.5 x 10 <sup>-6</sup> (ISO)	2.0 x 10 <sup>-6</sup>
$\overline{C_2H_6}$	2 x 10 <sup>-6</sup>	1.3 x 10 <sup>-5</sup>	2.0 x 10 <sup>-5</sup> (ISO)	1.0 x 10 <sup>-5</sup>
$C_2H_4$	3 x 10 <sup>-10</sup>	9 ± 5 x 10 <sup>-8</sup>	1.2 x 10 <sup>-7</sup> (ISO)	1.0 x 10 <sup>-7</sup> (alt. var.)
$C_3H_8$				
CH <sub>3</sub> C <sub>2</sub> I	Н			
HCN				
HC <sub>3</sub> N				
CH <sub>3</sub> CN	l			
CO <sub>2</sub>				
CO				
H <sub>2</sub> O				
$C_6H_6$				
(a)Deri	ved from column densities and Vo	oyager results		

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After Voyager: very good constraints because the T profile was known from Voyager

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$C_2H_2$	1 x 10 <sup>-5</sup>	2.2 x 10 <sup>-6</sup>	5.5 x 10 <sup>-6</sup> (ISO)	2.0 x 10 <sup>-6</sup>
$C_2H_6$	2 x 10 <sup>-6</sup>	1.3 x 10 <sup>-5</sup>	2.0 x 10 <sup>-5</sup> (ISO)	1.0 x 10 <sup>-5</sup>
$C_2H_4$	3 x 10 <sup>-10</sup>	9 ± 5 x 10⁻ <sup>8</sup>	1.2 x 10 <sup>-7</sup> (ISO)	1.0 x 10 <sup>-7</sup> (alt. var.)
$C_3H_8$	-	7± 4 x 10 <sup>-7</sup>	2 x 10 <sup>-7</sup> (ISO)	1.0 x 10 <sup>-7</sup>
$CH_3C_2$	Н -	4 ± 2 x 10 <sup>-9</sup>	1.2 x 10 <sup>-8</sup> (ISO)	8 x 10 <sup>-9</sup>
HCN	-	1.6 x 10 <sup>-7</sup>	5 x 10 <sup>-7</sup> (alt. var.)	1 x 10 <sup>-7</sup>
$HC_3N$	-	< 1.5 x 10 <sup>-9</sup>	10 <sup>-12</sup> -10 <sup>-8</sup> (alt.var.)	1 x 10 <sup>-9</sup>
CH <sub>3</sub> CI	N -	-	1 x 10 <sup>-8</sup> (alt. var.)	-
$CO_2$	-	1.4 x 10 <sup>-8</sup>	2.0 x 10 <sup>-8</sup> (ISO)	1.6 x 10 <sup>-8</sup>
CO	-	-	6 x 10 <sup>-5</sup> (near IR)	4.7 x 10 <sup>-5</sup>
H <sub>2</sub> O	-	-	8 ± 5 x 10 <sup>-9</sup> (ISO)	4 x 10 <sup>-10</sup>
$C_6H_6$	-		4 x 10 <sup>-10</sup> (ISO)	4 x 10 <sup>-10</sup>

(a)Derived from column densities and Voyager results

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## Saturn

### Saturn's composition: before space probes flybys

- 1932: identification of CH<sub>4</sub> and NH<sub>3</sub>

- 1962: first observation of  $H_2$  from S(1) and S(0) lines in the (4-0) band (Spinrad et al., 1962)

From the line width:

a<sub>H2</sub>= 76±20 km.Am (encrenaz 1973)



H<sub>2</sub> detection by Encrenaz et al., 1973

## Saturn's thermal profile before space probes flybys



But the equilibrium temperature of Saturn should be 75 K (including ring shadowing)  $\Rightarrow$  Internal source of heating

### Saturn's temperature: comparison with probes results

Pioneer flyby (Sept. 1979)



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Pioneer flyby (Sept. 1979)



Good constraints on the deep thermal profile from H<sub>2</sub>-H<sub>2</sub> and H<sub>2</sub>-He collision-induced absorption spectrum

-> independent from the "insitu" spacecraft measurements

### Saturn's composition: constraints before the probes

**Case of CH<sub>4</sub> and H<sub>2</sub>** from the  $3v_3$  CH<sub>4</sub> band (0.83 - 1.67  $\mu$ m) -> many CH<sub>4</sub> lines over a continuum due to H<sub>2</sub> pressure-induced absorption



Buriez and deBergh (1981) =>  $CH_4/H_2 = (4 \pm 2).10^{-3}$ 

From Voyager: (2 - 4).10<sup>-3</sup> From Cassini: (4.7 ± 0.2).10<sup>-3</sup>

H<sub>2</sub> and CH<sub>4</sub>: Good constraints from ground-based observations

### Saturn's composition: constraints before the probes



From Voyager :  $(0.5 - 2) \times 10^{-4}$ , Courtin et al. (1984) From Cassini : 1 - 3 bar :  $q_{NH3} = (1.4 - 5).10^{-4}$  with latitudinal variations, Fletcher et al. (2011)

## Saturn's composition: constraints before the probes

### **Case of NH**<sub>3</sub>

Many other constrains from the ground and with ISO and Herschel satellites

Reference	q <sub>NH3</sub>	Method
Courtin et al. (1984)	$(0.5 - 2.0) \times 10^{-4}$	Voyager/IRIS 180–300 cm <sup>-1</sup>
de Pater and Massie (1985)	$5 \times 10^{-4}$ at <i>p</i> > 3 bar	Very Large Array (VLA)
	$3 \times 10^{-5}$ at <i>p</i> < 1.25 bar	
Briggs and Sackett (1989)	$0.7 - 1.1 \times 10^{-4}$ at <i>p</i> = 2 bar	Radio T <sub>B</sub>
Grossman et al. (1989)	$1.2 \times 10^{-4}$ around condensation level	VLA
Noll and Larson (1990)	Upper limit $3 \times 10^{-4}$	5 µm spectra
de Graauw et al. (1997)	$1.1 \times 10^{-4}$ at <i>p</i> = 1.2 bar	ISO/SWS
Kerola et al. (1997)	Less than $1 \times 10^{-9}$ at radiative-convective boundary	3 μm data
Orton et al. (2000)	$1 \times 10^{-4}$ with 3–4× uncertainty	Sub-mm PH <sub>3</sub> analysis
Burgdorf et al. (2004)	$1 \times 10^{-4}$	ISO/LWS 96-101 cm <sup>-1</sup>
Kim et al. (2006)	$6 \times 10^{-8}$ at 460 mbar	3 μm data
	$3 \times 10^{-8}$ at 390 mbar	-
Fletcher et al. (2009a)	$(3.3 \pm 0.3) \times 10^{-7}$ at 690 mbar	Cassini/CIRS far-IR

Vertical profile from the Herschel satellite : Fletcher et al., 2012

NH<sub>3</sub>: good constraints from the ground-based and Earth satellites, independently of Saturn's probes.



## Saturn's composition: hydrocarbons

### **C**<sub>2</sub>**H**<sub>6</sub>

- From ground or Earth satellites :

q<sub>C2H6</sub> = 1.8 x 10<sup>-6</sup>, 12.2 μm Tokunaga et al. (1975)
 (6±1) x 10<sup>-6</sup> < 20 mbar, IUE (UV satellite), Winkelstein et al. (1983)</li>
 (1.3 ±0.3) x 10<sup>-5</sup> at 0.5 mbar, ISO/SWS (infrared satellite), Moses et al. (2000)
 (1.5 ±0.5) x 10<sup>-5</sup> at 0.5 mbar, IRTF, Greathouse et al. (2005)

### - From spacecrafts:

Voyager:  $(3\pm1) \ge 10^{-6} < 20$  mbar, Voyager/IRIS, Courtin et al. (1984) Cassini:  $(1.4\pm0.2) \ge 10^{-5}$  at 1 mbar

C<sub>2</sub>H<sub>6</sub>: agreement between ground-based and spacecraft measurements

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### Other hydrocarbons:

- **C<sub>2</sub>H<sub>2</sub>:** many measurements with IUE, TEXES/IRTF, SWS/ISO, Celeste/IRTF
- $C_{3}H_{8}$ : (2.6 ±0.8) x 10<sup>-6</sup> with TEXES/IRTF while (0.9 1.5) x 10<sup>-7</sup> from Cassini/CIRS
- **CH<sub>3</sub>C<sub>2</sub>H**: 1 measurement with SWS/ISO , in agreement with Cassini/CIRS
- **C<sub>4</sub>H<sub>2</sub>:** 1 measurement with SWS/ISO , in agreement with Cassini/CIRS
  - **C**<sub>6</sub>**H**<sub>6</sub>: only detection with SWS/ISO, no detection from probes

## Saturn's composition

### Oxygen compounds

- CO: detection in submm but not with the probes
- CO<sub>2</sub>: 1 measurement from ISO/SWS (3.0 x 10<sup>-10</sup> at 0.3-10 mbar), agrees with Cassini/CIRS

### <mark>// H</mark>2O :

- $1.5 \times 10^{-7}$  at 2 mbar from IUE (UV)
- $6.0 \times 10^{-9}$  at 2 mbar from SWS/ISO (2.4 45  $\mu$ m)

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## **Jupiter**

1932: detection of  $CH_4$  and  $NH_3$  (Wildt, 1932) 1960: detection of  $H_2$  (Kiess et al.)

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### Thermal profile

constrained from  $H_2$ - $H_2$  and  $H_2$ -He collision induced absorptions (Houck et al., 1975)





1975 : Jupiter's infrared spectrum

1975 : Jupiter's infrared spectrum



Detection of CH<sub>4</sub>, NH<sub>3</sub>, H<sub>2</sub> from the IR spectrum.

1975 : Jupiter's infrared spectrum



Detection of CH<sub>4</sub>, NH<sub>3</sub>, H<sub>2</sub> from the IR spectrum.

## Jupiter composition before probes flybys

#### High spectral resolution observations in IR Tokunaga et al., 1979 2.0-INTENSITY ERGS/CM<sup>2</sup>- SEC - CM<sup>-1</sup>-STER 0 5 5 .5+ 145° K 15<sub>NH3</sub> 140° K ທີ sP(4,K) 134°K 120° K 0.0 850 870 **880** 890 900 820 830 840 860 810 800 WAVENUMBER (CM<sup>-1</sup>)

- line profile of NH<sub>3</sub> absorption lines => sensitivity to different levels , while continuum is sensitive to the NH<sub>3</sub> cloud deck
- $C_2H_6$  observed in emission => emission comes from a region where T / with height

### Jupiter thermal profile: comparison with probes



Good agreement from ground-based observations and Pioneer spacecraft

### Jupiter composition: comparison with probes

### Abundances, some examples

		Before spacecrafts	From spacecrafts
		(Ridgway, 1976)	(Taylor, 2004)
")	$H_{2}$	0.89	0.86
"	He	0.05 - 0.15	0.136
"	$CH_4$	7 x 10 <sup>-4</sup>	1.8 x 10 <sup>-3</sup>
"	NH <sub>3</sub>	2 x 10 <sup>-4</sup>	7.0 x 10 <sup>-4</sup>
	H <sub>2</sub> 0	1 x 10 <sup>-6</sup>	>5.0 x 10 <sup>-4</sup>
	Non eq	uilibrium gas	
"	CO	2 x 10 <sup>-9</sup>	1.5 x 10⁻ <sup>9</sup>
•	PH <sub>3</sub>	4 x 10 <sup>-7</sup>	5 x 10 <sup>-7</sup>
	Photoc	hemical products	
•••	C <sub>2</sub> H <sub>6</sub>	4 x 10 <sup>-4</sup>	3 x 10 <sup>-6</sup>

2 x 10<sup>-8</sup>

Disagreement mostly come from the thermal profiles

8 x 10<sup>-5</sup>

 $\mathbf{C}_{2}\mathbf{H}_{2}$ 

### Conclusions regarding the solar system observations

### Giant planets

Main composition =  $H_2$  (~ 90%) and He (~ 10 %).

T in the troposphere can be constrained by the absorption-induced bands of  $H_2$  = most reliable probe for temperature sounding for giant planets.

- $\Rightarrow$  Good estimation of the molecular abundances in the troposphere
- $\Rightarrow$  But for photochemical product emitting in the stratosphere, constrains are poorer
- -> need of high spectral resolution observations to probe higher.

### Conclusions regarding the solar system observations

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### Telluric planets

Very difficult ... because the main composition is a priori unknown. Large spectral coverage => constrains on the T at several level: e.g. surface temperature in radio and stratospheric temperature in mid-IR.

The knowledge of the T profile from Voyager observations was crucial in the knowledge of Titan's composition.

## Perspectives: 2 promising methods for hot Jupiters

### Use of primary transit and secondary transit spectra simultaneously (Griffith et al., 2014)

- Primary transit -> terminator, absorption of the stellar light => sensitive to the planet composition and not so much to the T profile
- Secondary transit -> day side, stellar light diffusion + thermal emission => sensitive to the composition and the T profile



Fit of the secondary transit + primary transit of XO-2b (include  $H_2O$ ,  $CH_4$ , CO,  $CO_2$ )

Need of large spectral range and high resolution to decouple T and composition.

### Perspectives: 2 promising methods for Hot Jupiters

### Detection of a molecule from high resolution spectra (Snellen et al. 2010)

High spectral resolution observation of exoplanets with VLT/CRIRES (R = 100 000)

Principle: molecular lines are Doppler shifted while the planet is moving on its orbit, whereas the stellar spectrum is not.



Detection of CO in transit: HD209 and HD189 outside transit: τ -Boo and 51 Peg