# The composition of Titan's atmosphere

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# Plan of chapter

- Introduction
  - Historical background
    - Voyager, ground-based, ISO and Cassini / Huygens
  - Current monitoring of Titan's atmospheric composition by Cassini

- Main compounds and noble gases
  - $CH_4$ vertical profile
  - Horizontal variations of tropospheric and stratospheric $CH_4$
  - $H_2$ mole fraction
  - Noble gases

- Photochemical products (hydrocarbons and nitriles)
  - Stratosphere / Lower mesosphere (up to ~500 km)
  - Upper mesosphere / Thermosphere

# Plan of chapter

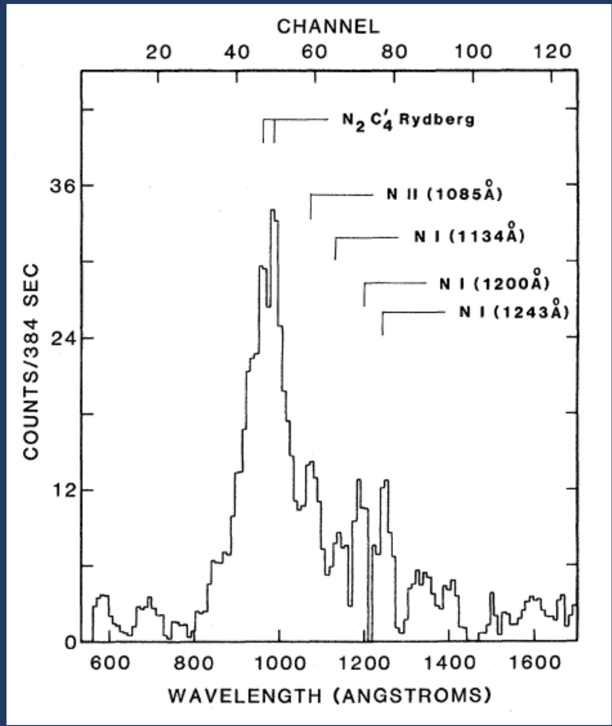
- Oxygen-bearing compounds
  - $H_2O$, CO and $CO_2$
  - Upper limits ($CH_3OH$, $H_2CO$, $CH_3C_2O$)
- Isotopic ratios
  - D/H (in $CH_4$ and $H_2$)
  - $^{12}C/^{13}C$ (in $CH_4$, other hydrocarbons, HCN and $CO_2$)
  - $^{14}N/^{15}N$ (in $N_2$ and HCN)
  - $^{16}O/^{18}O$ in CO and $CO_2$

Talk by C. Nixon

- Conclusions
  - What is missing?
    - Some in situ measurements, better sounding of the region 500-900 km, extended monitoring of seasonal variations
  - Future ground-based observations or space mission projects

# Introduction: Historical background

- Voyager 1 flyby in 1980
  - UVS detection of $N_2$ (Broadfoot et al. 1981)
  - IRIS: surface temperature of 94-97 K (Samuelson et al. 1981)
  - RSS: thick atmosphere, *T* / *m* profile (Lindal et al. 1983)
  - ⇒ m=28 amu
  - $N_2$ is dominant constituent
    - 6% upper limit on CO (Strobel and Shemansky 1982)

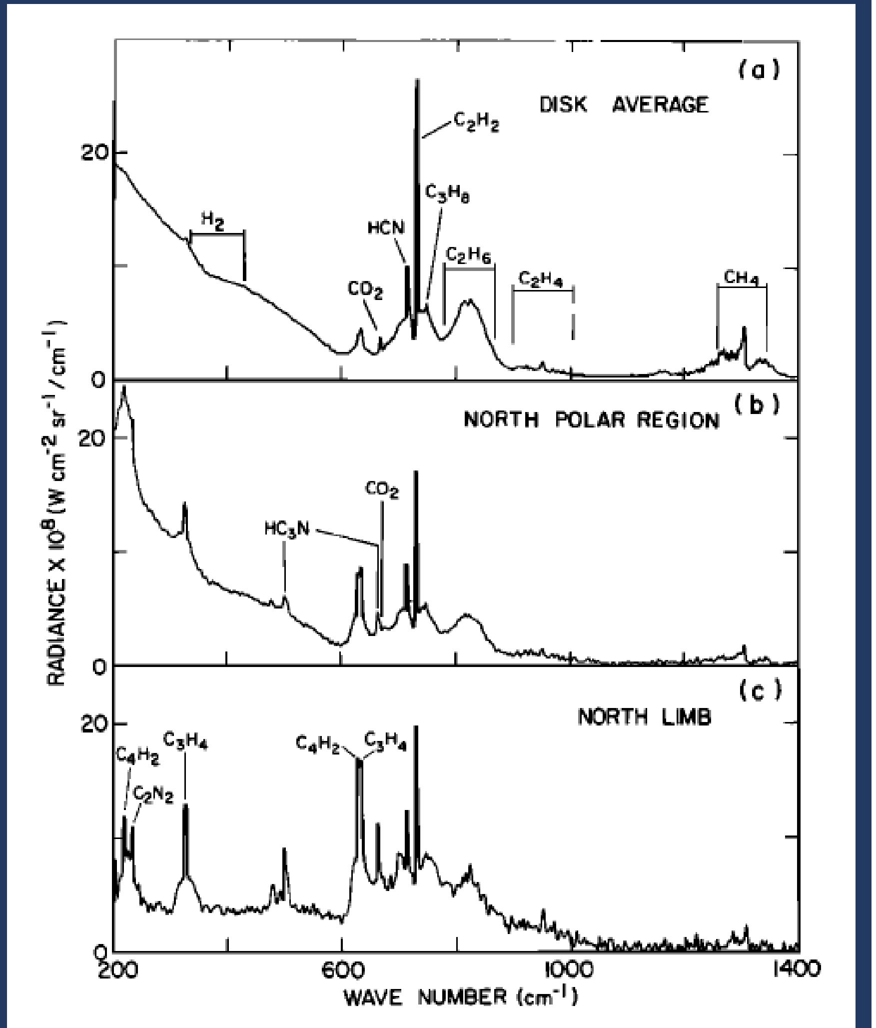



Broadfoot et al. 1981

# Introduction: Historical background

- IRIS: suite of hydrocarbons and nitriles (Hanel et al. 1981, Kunde et al. 1981) and detection of $CO_2$ (Samuelson et al. 1983)

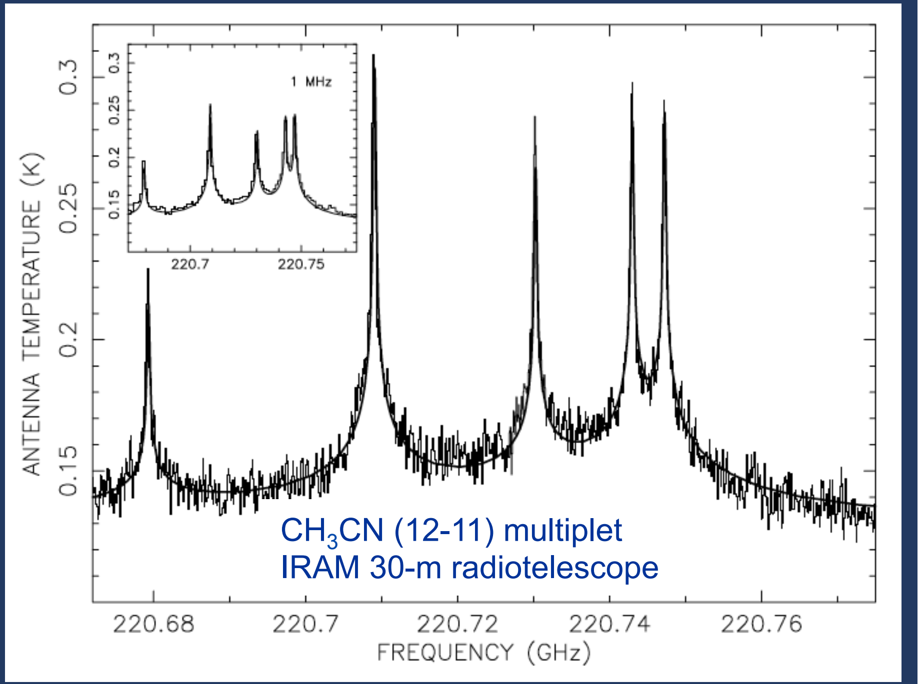
- Striking differences between equator and north pole




Kunde et al. 1981

# Introduction: Historical background

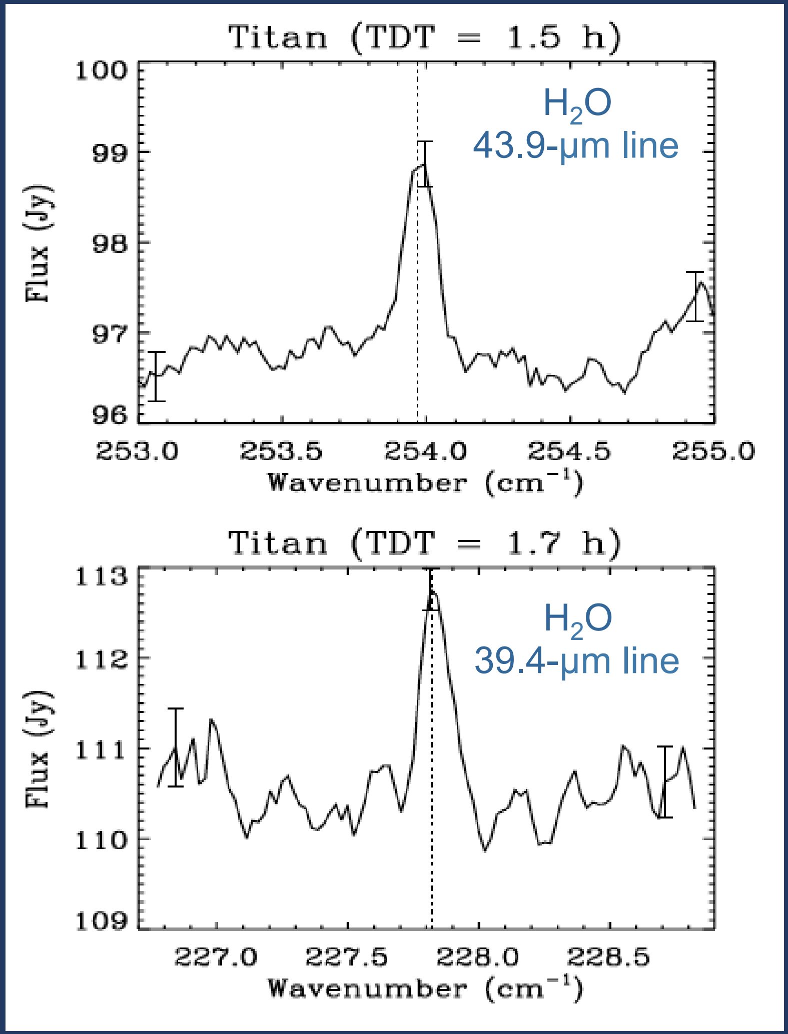
- Ground-based observations
  - Near-IR spectroscopy
    - Detection of CO (Lutz et al. 1983)
  - Thermal infrared spectroscopy
    - Detection of $CH_2CCH_2$ (Roe et al. 2004)
  - Millimeter heterodyne spectroscopy
    - Detection of $CH_3CN$ (Bézard et al. 1993, Marten et al. 2002) and of disk-average $HC_3N$
    - Disk-averaged vertical profiles of HCN and CO
    - Isotopic ratios in HCN and CO




Marten et al. 2002

# Introduction: Historical background

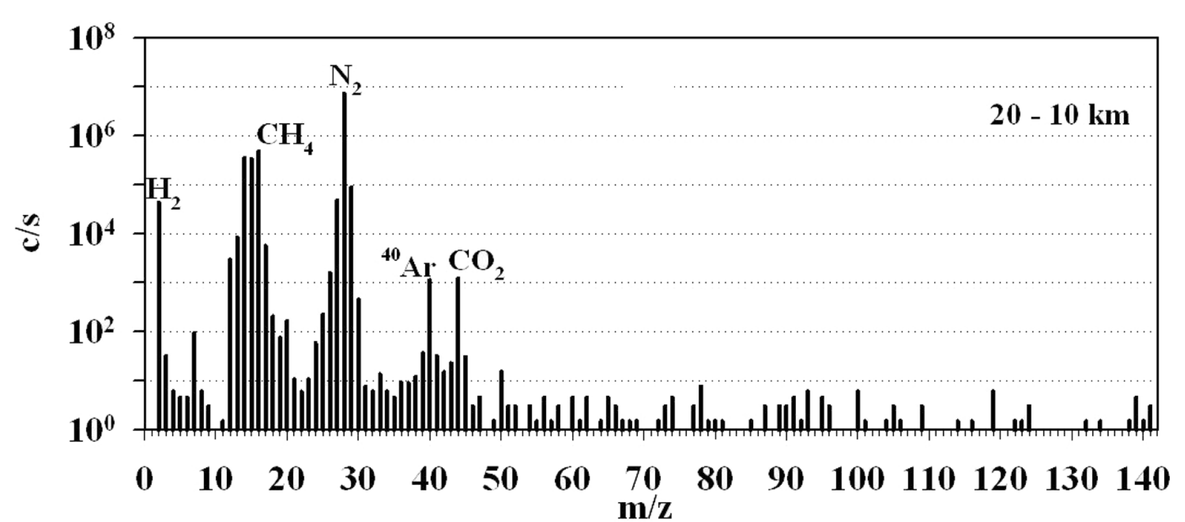
- ISO observations of Titan
  - Disk-averaged spectrum in the range 7-30 µm (345-1400 cm$^{-1}$) at resolution ~8 times better than IRIS
  - Detection of $H_2O$ (Coustenis et al. 1998)
  - Tentative detection of benzene ($C_6H_6$) (Coustenis et al. 2003)




Coustenis et al. 1998

# Introduction: Cassini / Huygens

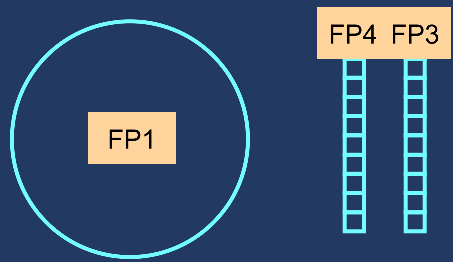
- Huygens / GCMS (Gas Chromatograph Mass Spectrometer)
  - Niemann et al. (2002)
  - Mass range (*m*/*Z*): 2 - 141
  - Measurement sequence
    - 146-65 km: Inlet leak L1
    - Samples for noble gas and enrichment cell collected at 75-77 km and analyzed from 65 to 56 km
    - 56-0 km: Inlet leak L2
    - Gases evaporating from the surface analyzed



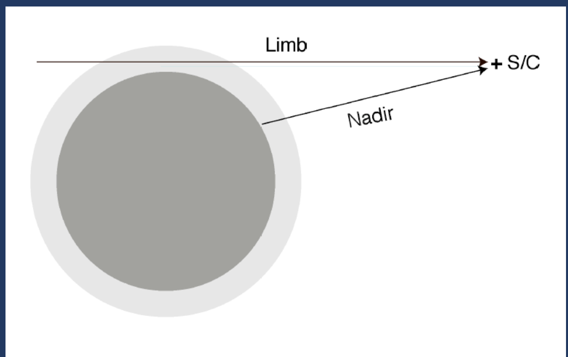

Niemann et al. 2010

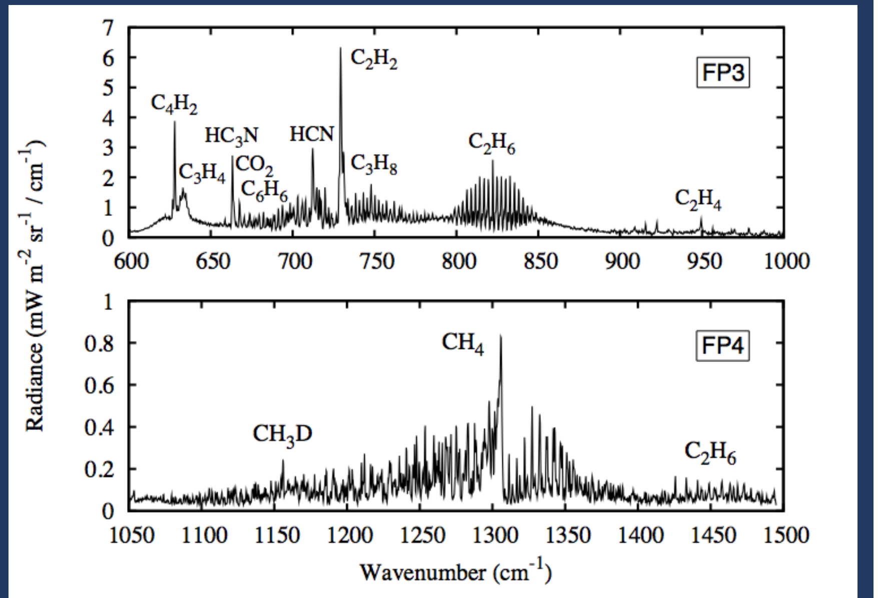
# Introduction: Cassini / Huygens

- Cassini / CIRS (Composite Infrared Spectrometer)
  - Flasar et al. (2004)
  - Three focal planes; Spectral range: 10 - 1500 $cm^{-1}$ (7 µm - 1 mm); resolution up to 0.5 $cm^{-1}$



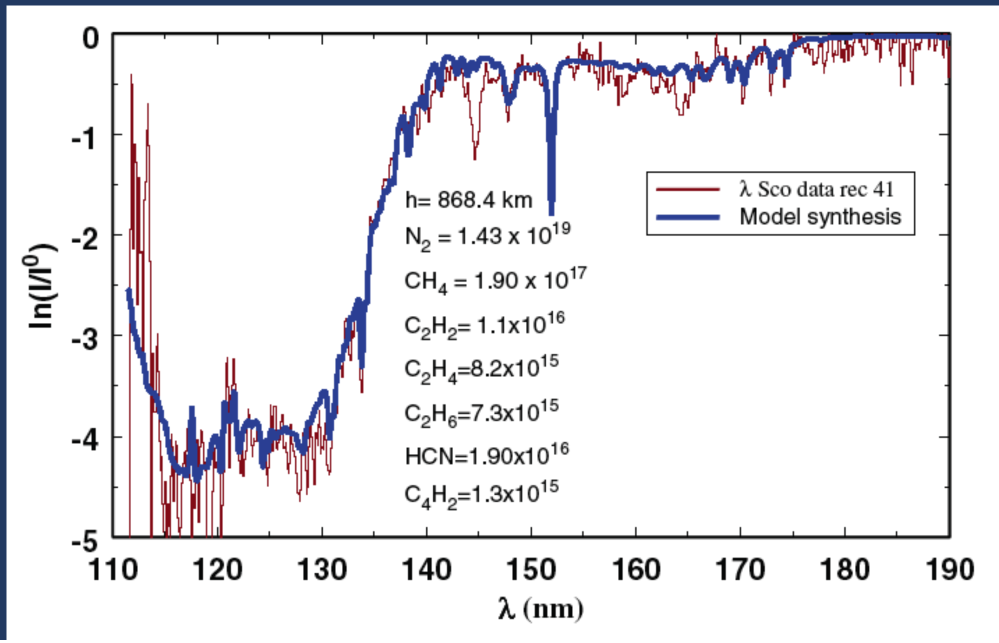

  - Observing modes
    - Nadir
      - T profile in the range 180-250 km
      - Gas abundances around 120 km
    - Limb
      - Vertically-resolved sounding up 500 km



# Introduction: Cassini / Huygens

- Cassini / UVIS (Ultraviolet Imaging Spectrometer)
  - Esposito et al. (2004)
  - Two channels: FUV (112-191 nm) and EUV (56-118 nm); resolution up to 0.275 nm
  - Solar and stellar occultation modes
    - FUV: Sounding of the atmosphere in the range ~400-1400 km
    - Vertical profiles of $CH_4$, other hydrocarbons, HCN and $HC_3N$

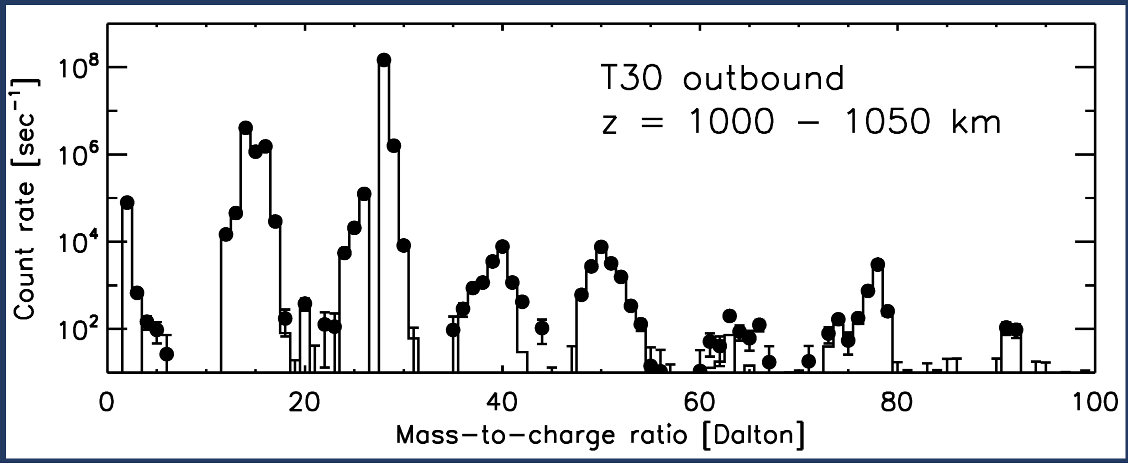



Shemansky et al. 2005

# Introduction: Cassini / Huygens

- Cassini / INMS (Ion and Neutral Mass Spectrometer)
  - Waite et al. (2004)
  - Mass range (*m*/*Z*) 1-99 amu and resolution $M/\Delta M$ ~100

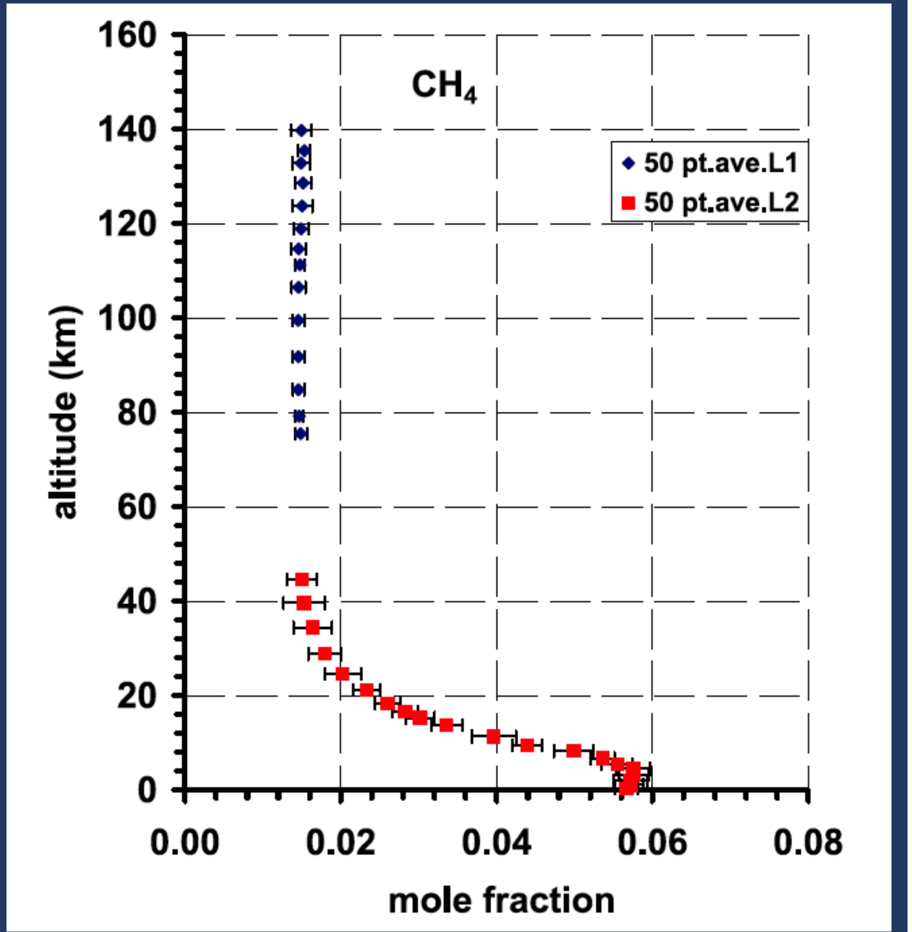
  - Operation modes
    - Close source neutral (for non-reactive neutrals)
      - Sensitivity of the order of $10^4$ $cm^{-3}$
    - Open source neutral mode (for reactive neutrals)
    - Open source ion mode (for positive ions)
  - Concentrations measured between C/A (950-1000 km) and ~ 1500 km ($N_2$, $CH_4$, $H_2$) and ~ 1200 km (minor species)




Cui et al. 2009

# Main compounds: $CH_4$

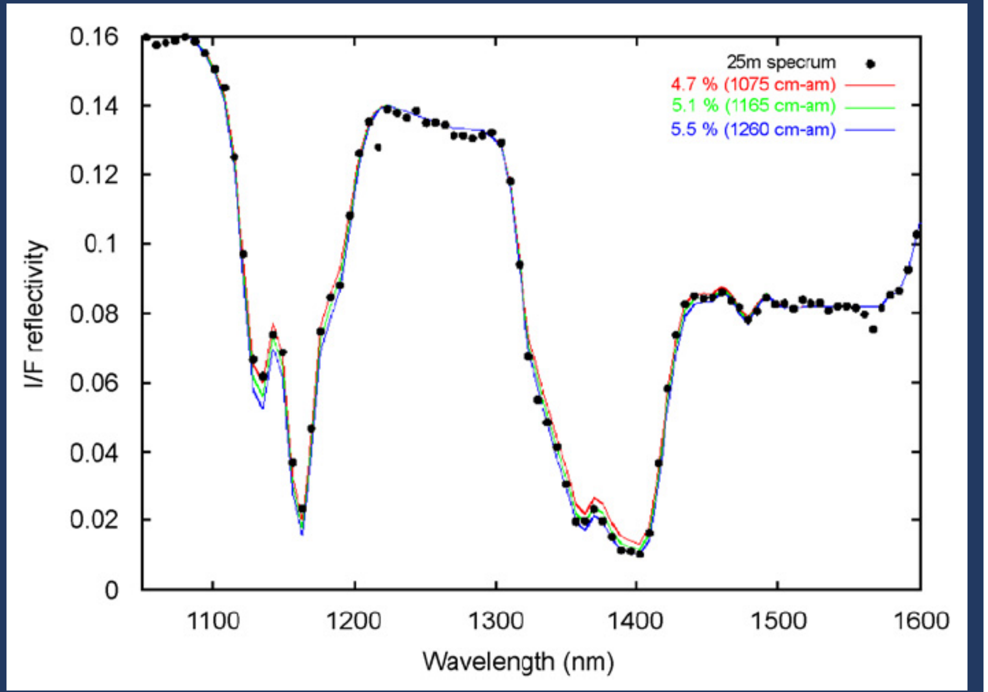
- $CH_4$ mole fraction profile from Huygens / GCMS
  - 0-7 km: 5.65 ± 0.09%
  - 7-45 km: decrease with height
    - 7-13 km: consistent with saturation above liquid $CH_4$ + dissolved $N_2$
  - Stratosphere: 1.48 ± 0.09%
    - Consistent with tropopause cold trap for saturation above $CH_4$ ice
    - Agrees with Cassini/CIRS preliminary determination (1.6 ± 0.5%, Flasar et al. 2005)




Niemann et al. 2010

# Main compounds: $CH_4$

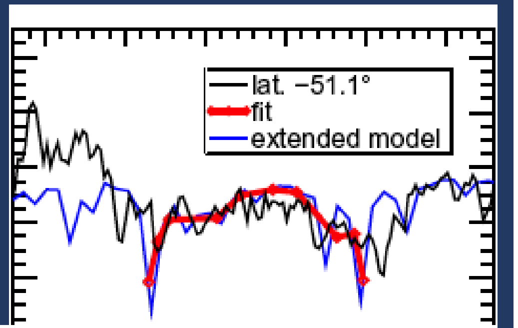
- $CH_4$ surface mole fraction from Huygens / DISR
  - Spectrum of Titan's surface illuminated by DISR lamp at 25 m altitude
  - 5.1 ± 0.8% (Jacquemart et al. 2008)
  - 4.5 ± 0.5% (Schröder and Keller 2008)

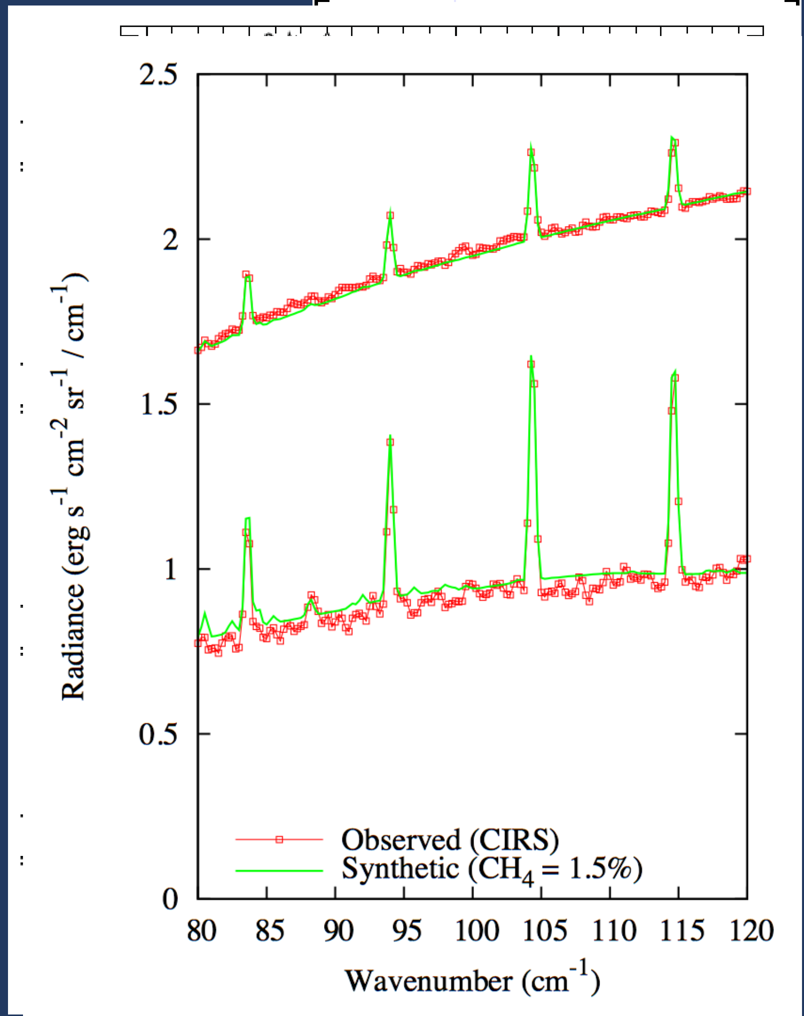



Jacquemart et al. 2010

# Main compounds: $CH_4$

- Methane horizontal variations?
  - Important for characterizing the methane cycle
  - Troposphere below 10 km:
    - NIRSPEC/Keck spectra: 1.56-µm $CH_3D$ band (Penteado and Griffith 2010)
    - Latitude range 32°S-18°N
    - No variation of $CH_4$ abundance below 10 km to within 20%
  - Troposphere: 20-50 km
    - VIMS spectra: 0.6-µm $CH_4$ band (Penteado et al. 2010)
    - No *evidence* for variation from 70°S to 45°N
    - Up to 60% decrease from 27°S to 19°N still allowed by data
  - Stratosphere: 70-130 km
    - CIRS spectra: $CH_4$ rotational lines (Lellouch et al. work in progress)
    - No variation in excess of 20% from 80°S to 70°N

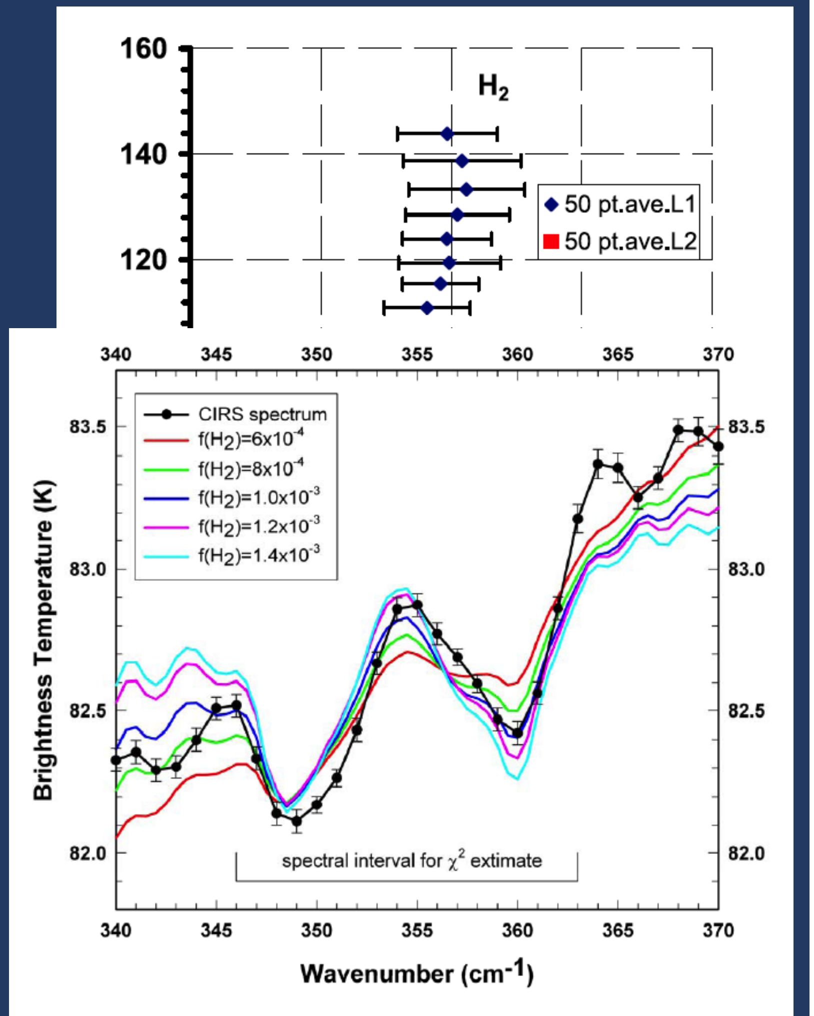


# Main compounds: $H_2$

- $H_2$ mole fraction from Huygens / GCMS
  - $1.01 \pm 0.16 \times 10^{-3}$ (0-140 km)

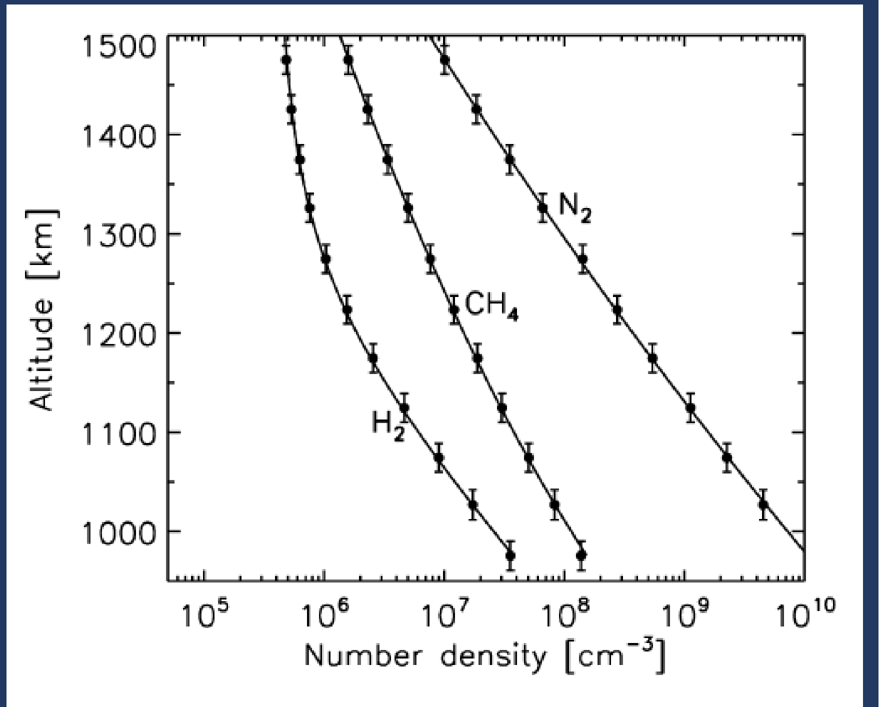
- $H_2$ mole fraction from Cassini / CIRS
  - S(0) line at 350 $cm^{-1}$ (troposphere): $0.96 \pm 0.24 \times 10^{-3}$ (Courtin et al. 2007)
  - Agrees with Voyager /IRIS (Samuelson et al. 1997, Courtin et al. 1995)
  - Possible enhancement > 40°N (by 30%) and > 60°N (by 70%) (Courtin et al. 2008)




Niemann et al. 2010
Courtin et al. 2007

# Main compounds: $H_2$

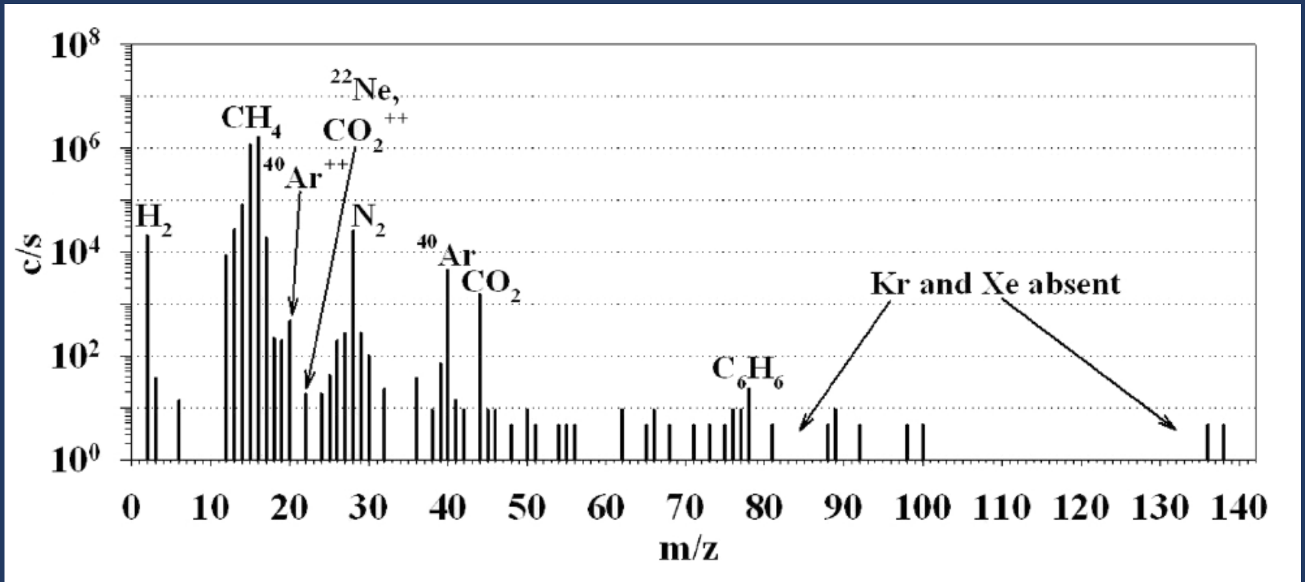
- $H_2$ mole fraction from Cassini / INMS
  - $3.3 \times 10^{-3}$ at 981 km
  - Increases with altitude due to diffusive separation
  - Factor of ~3 difference with value 800 km below not expected!
    - Long chemical lifetime
    - Large escape rate




Cui et al. 2009

# Noble gases

- $^{40}$Ar (radiogenic)
  - Huygens / GCMS
    - $3.39 \pm 0.12 \times 10^{-5}$ at 75-77 km
  - Cassini / INMS
    - $1.42 \pm 0.03 \times 10^{-5}$ at 981 km (Cui et al. 2009)
    - Decreases with altitude due to diffusive separation
  - Vertical profile used to derive eddy mixing profile (Yelle et al. 2008)




Niemann et al. 2010

# Noble gases

- $^{36}$Ar (primordial)
  - Huygens / GCMS
    - $2.1 \pm 0.8 \times 10^{-7}$ at 75-77 km

- $^{22}$Ne (primordial)
  - Huygens / GCMS: tentative detection
    - $2.8 \pm 2.1 \times 10^{-7}$ at 75-77 km

- Upper limits on Kr and Xe
  - $< 1 \times 10^{-8}$

# Main compounds and noble gases

| *Main compounds* | |
|---|---|
| surface | |
| $N_2$ | 94.3 % |
| $CH_4$ | 5.6% |
| $H_2$ | 0.1% |
| stratosphere | |
| $N_2$ | 98.4% |
| $CH_4$ | 1.5% |
| $H_2$ | 0.1% |

| *Noble gases* | |
|---|---|
| $^{40}Ar$ | 34 ppmv |
| $^{36}Ar$ | 0.1 - 0.3 ppmv |
| $^{22}Ne$ | 0.07 - 0.5 ppmv |

- Possible latitudinal variations of $H_2$
- No evidence for large $CH_4$ variations so far
- Sole gases (along with CO) detected in the troposphere
  - Photochemical compounds, produced at high altitudes, condense out in the lower stratosphere

# Photochemical compounds (hydrocarbons and nitriles)

- Products of $N_2$-$CH_4$ coupled photochemistry
- 2-D (altitude-latitude) mapping of the photochemical compounds:
  - Coupling of chemistry and dynamics
    - Chemical sources and sinks
    - General circulation
- Temporal variations of the photochemical compounds:
  - Seasonal variations
    - General circulation
  - Diurnal variations (high altitude)
    - Solar-driven and auroral-driven chemistry
- Altitude range
  - 120-500 km: thermal infrared spectroscopy (CIRS)
  - 400-1400 km: occultation ultraviolet spectroscopy (UVIS)
  - 950-1500 km: in situ mass spectroscopy (INMS)

# Photochemical compounds (hydrocarbons and nitriles)

- Mole fractions of species at mid-latitudes around 120 km (in 2005)

| *Hydrocarbons* | |
|---|---|
| $C_2H_6$ | 8 ppm |
| $C_2H_2$ | 3 ppm |
| $C_2H_4$ | 0.15 ppm |
| $C_3H_8$ | 0.5 ppm |
| $CH_3C_2H$ | 8 ppb |
| $C_4H_2$ | 1.5 ppb |
| $C_6H_6$ | 0.3 ppb |

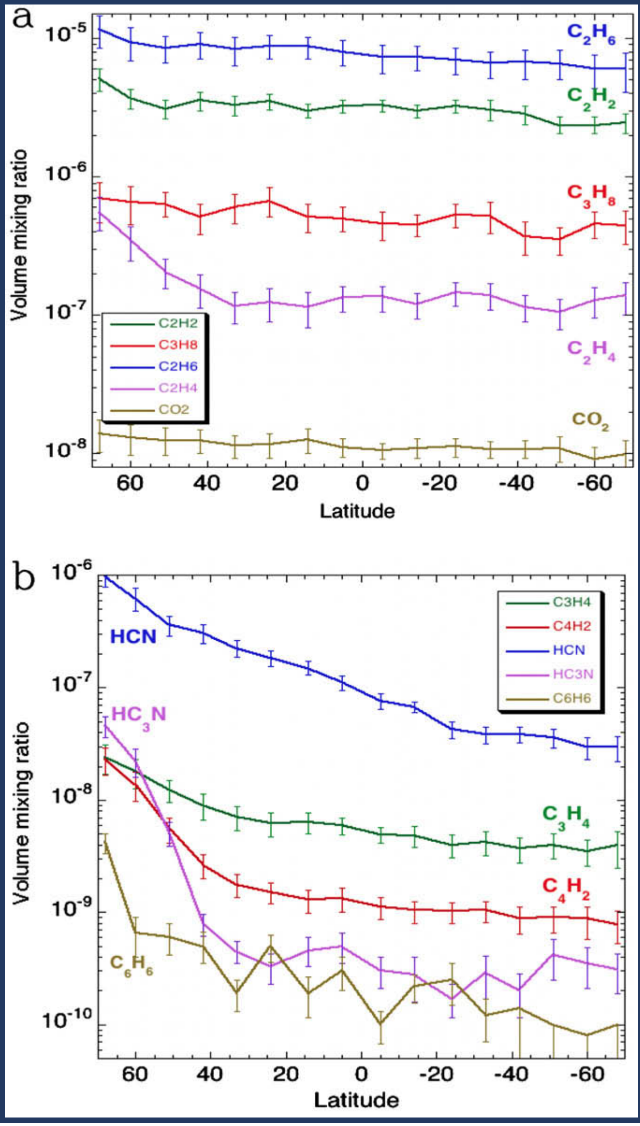
| *Nitriles* | |
|---|---|
| HCN | 100 ppb |
| $CH_3CN$ | 5 ppb* |
| $HC_3N$ | 0.3 ppb |
| $C_2N_2$ | 0.1 ppb |

*: (disk-averaged) (Marten et al. 2002)

Vinatier *et al.* (2010)
Coustenis *et al.* (2010)

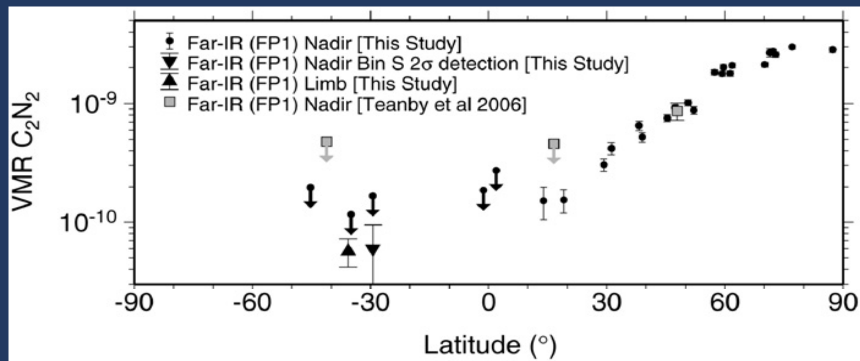
Teanby *et al.* (2006, 2009)

# Photochemical compounds (lower stratosphere)




Coustenis *et al.* (2010)

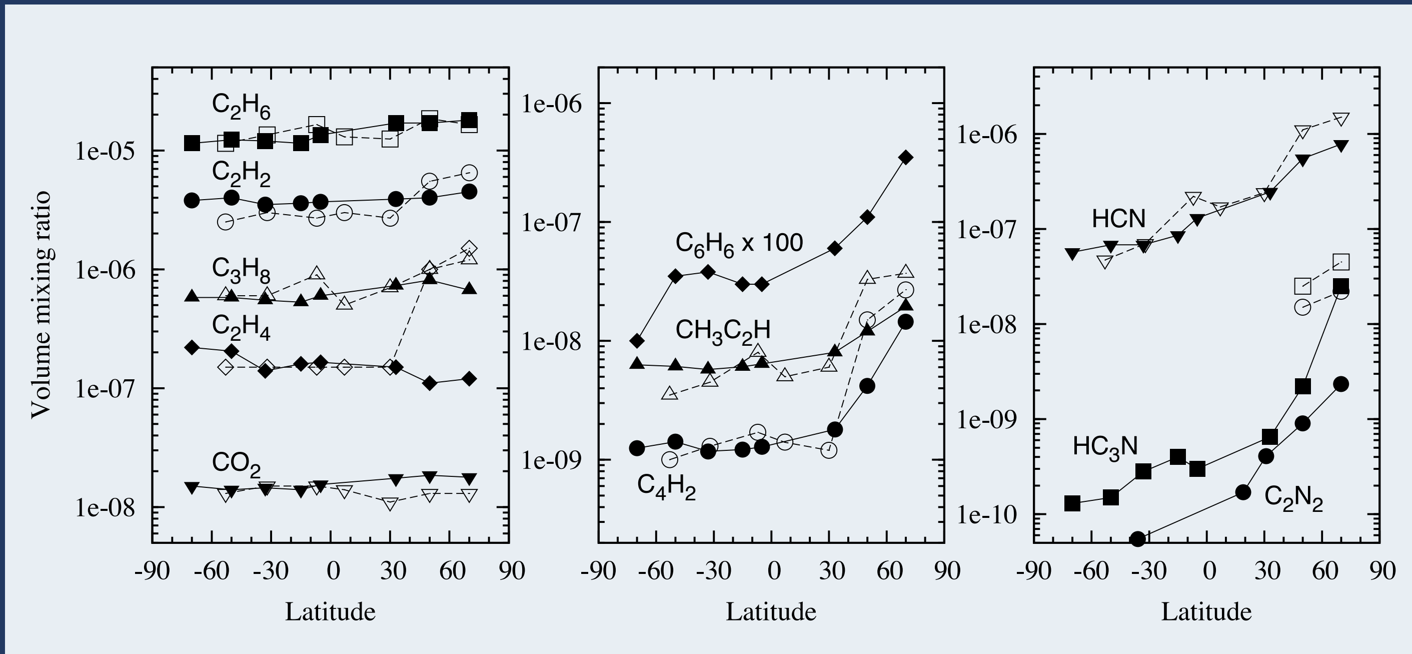
- Horizontal variations around 120 km (2004-2008)
  - All hydrocarbons and nitriles are more abundant > 45°N
  - Enrichment largest for minor hydrocarbons $CH_3C_2H$, $C_4H_2$, $C_6H_6$ and for nitriles
  - HCN north-to-south increase is more gradual




Teanby *et al.* (2009)

# Photochemical compounds (lower stratosphere)

- Comparison with Voyager observations (1980)
  – North polar enrichment was larger in 1980 (Spring equinox) than in 2005 (Winter solstice)

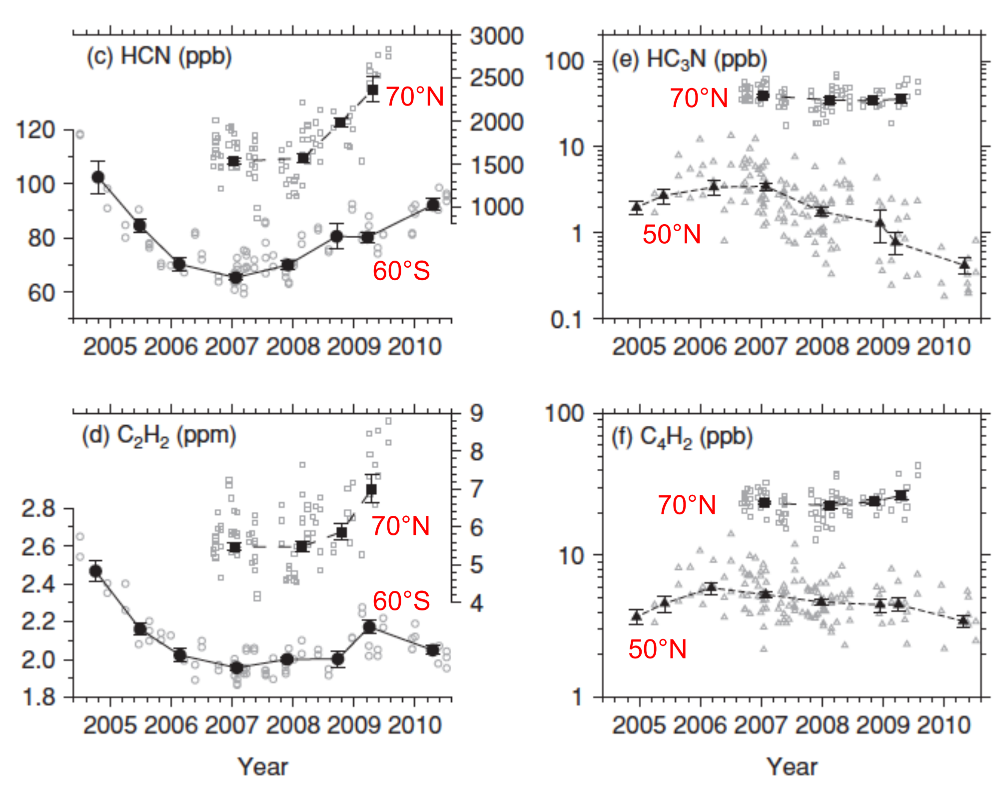



Filled symbols: Cassini
Empty symbols: Voyager

Bézard (2009): based on data from Coustenis & Bézard (1995) and Coustenis et al. (2007)

# Photochemical compounds (lower stratosphere)

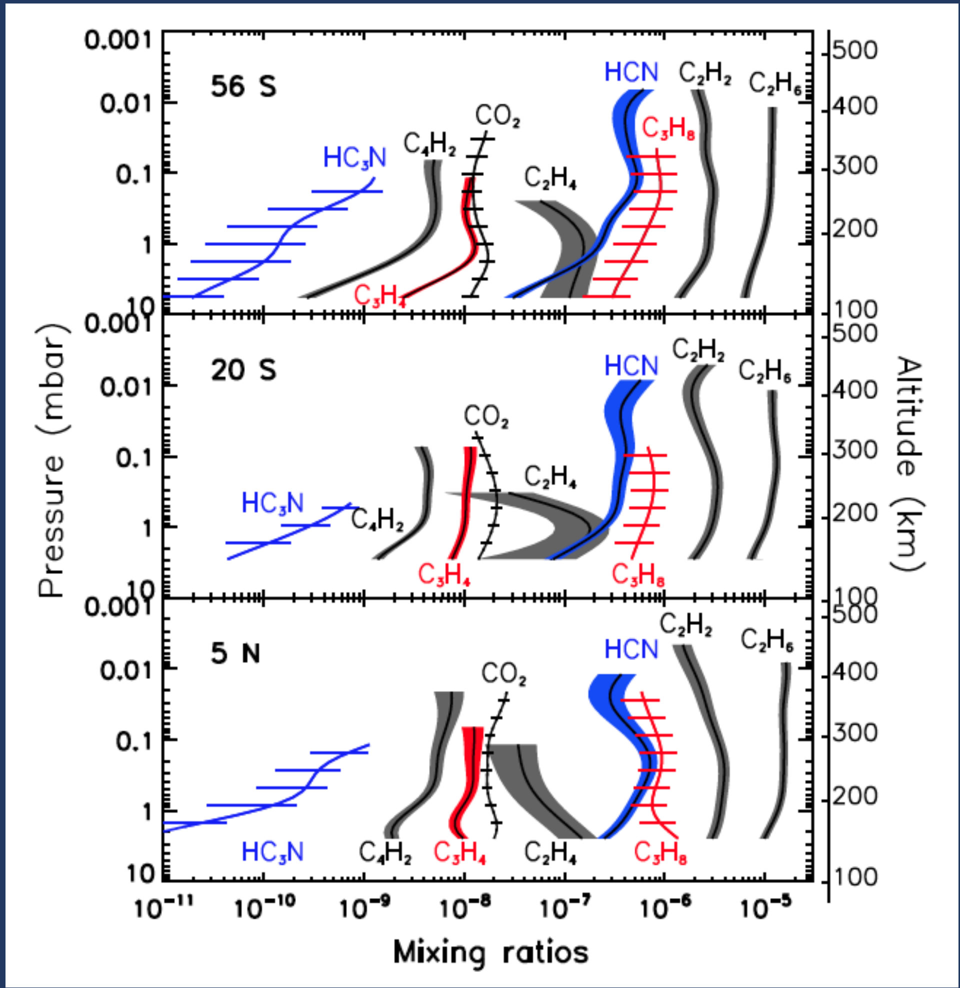
- Seasonal changes observed by Cassini (2004-2010)
  - HCN and $C_2H_2$: increase at high northern latitudes in 2008-2009
    increase at high southern latitudes in 2008-2009
    dissipation of enriched south polar cap till 2006
  - $HC_3N$ and $C_4H_2$
    - No change in northern polar vortex
    - Decrease at 50°N
  - North polar vortex:
    - Northward migration of the boundary
    - Reduction in lateral mixing across boundary
  - South polar region:
    - Weakening of the upwelling circulation




Teanby et al. (2010)

# Photochemical compounds (stratosphere - lower mesosphere)

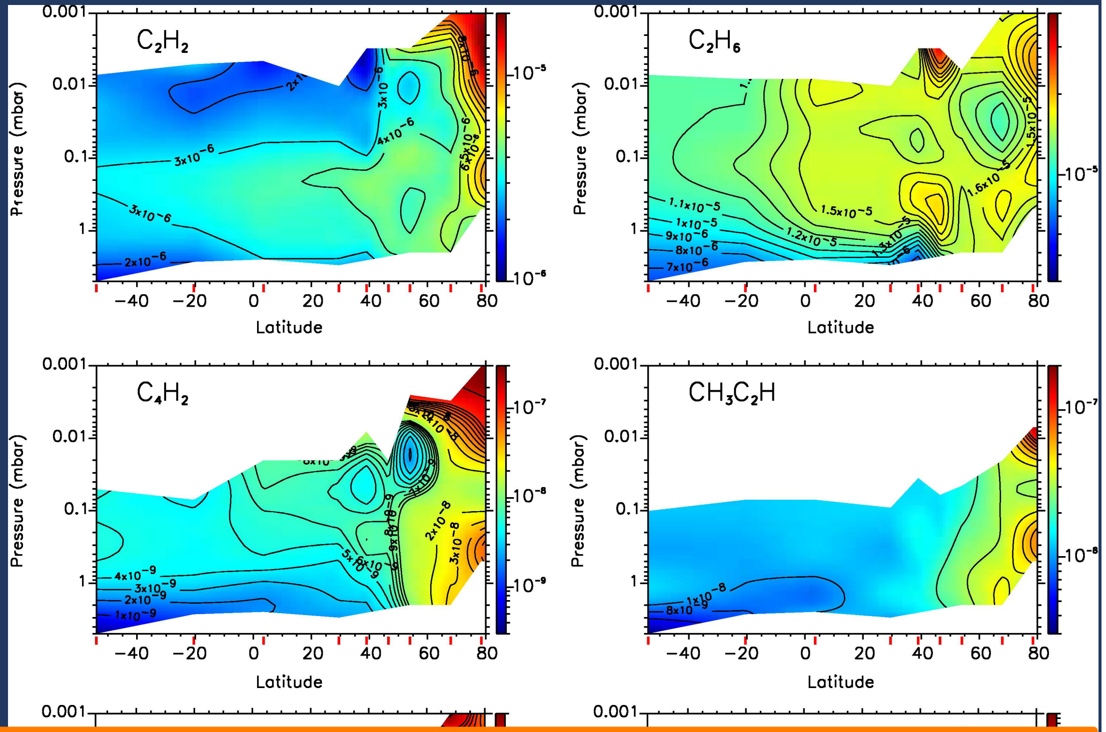
- Southern and mid-latitudes (< 30°N)
  - All mixing ratios, except for $C_2H_4$, increase with height in the stratosphere
  - Gradient is steepest for short-lived species $HC_3N$ and $C_4H_2$
  - Long-lived species $C_2H_6$ and $C_3H_8$ are quasi-uniform in altitude and latitude
  - $C_2H_4$ mixing ratio decreases with height




Vinatier et al. (2010)

# Photochemical compounds (stratosphere - lower mesosphere)

- North polar vortex
  - Significant enrichment poleward of 50°N (except for alkanes which are quasi-uniform)
  - At 80°N, marked minimum near 300 km (Vinatier et al. 2010)
  - Regions depleted in $C_2H_2$, HCN and $C_4H_2$ around 350-400 km and 55°N (Teanby et al. 2008, Vinatier et al. 2010)



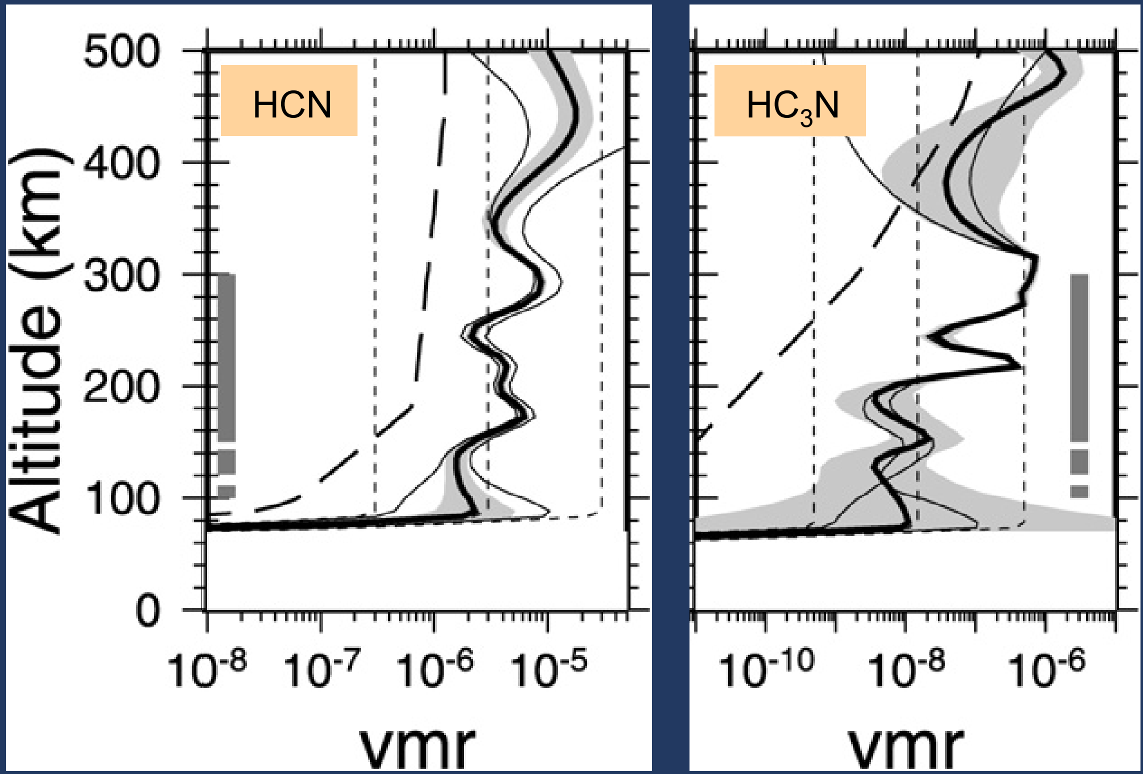

Vinatier et al. (2010)

- North polar vortex (2005-2008):
  - Descending branch of meridional Hadley cell
  - Complex structure (not reproduced by GCMs)
    - Regions depleted in photochemical compounds
    - Various mixing processes (Teanby et al. 2008)

# Photochemical compounds (stratosphere - lower mesosphere)

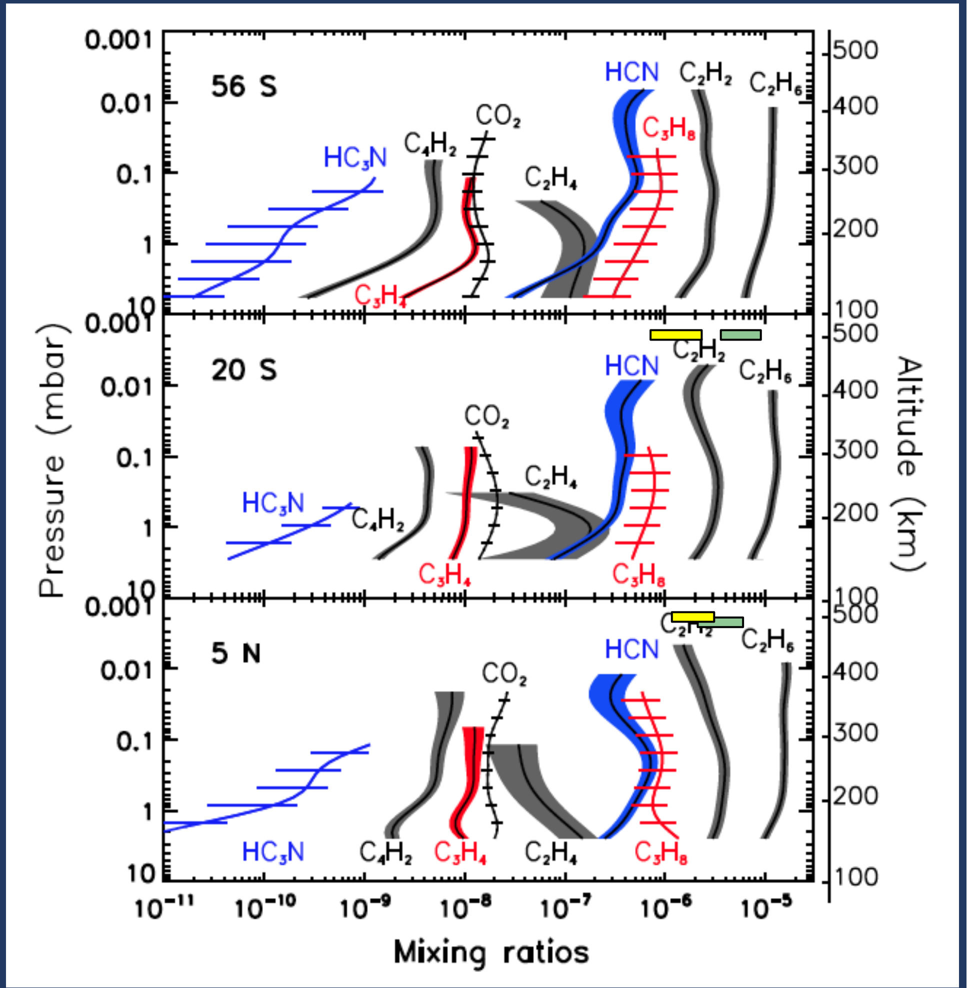
- Layered structure in the polar vortex (82°N, T4 flyby) (Teanby et al. 2007)
  - Seen for HCN and $HC_3N$ in 10-km height resolution data
  - Linked to discrete haze layers seen in ISS images?

Teanby et al. (2007)



# Photochemical compounds (upper mesosphere – lower thermosphere)

- Voyager 1 UVS solar occultation (Vervack et al. 2004)
  - 4°N (ingress) and 16°S (egress)
  - $C_2H_2$, $C_2H_4$ and $HCN/HC_3N$ profiles from 500 to 1100 km
    - $C_2H_2$ at 500 km agrees with CIRS
    - $C_2H_4$ at 500 km is 50 times larger than CIRS value at 250 km




Vinatier et al. (2010)

# Photochemical compounds (upper mesosphere – lower thermosphere)

- Mixing ratios of $C_2H_2$ and $C_2H_4$ increase with height (500-900 km)
- ⇒ source at higher altitudes

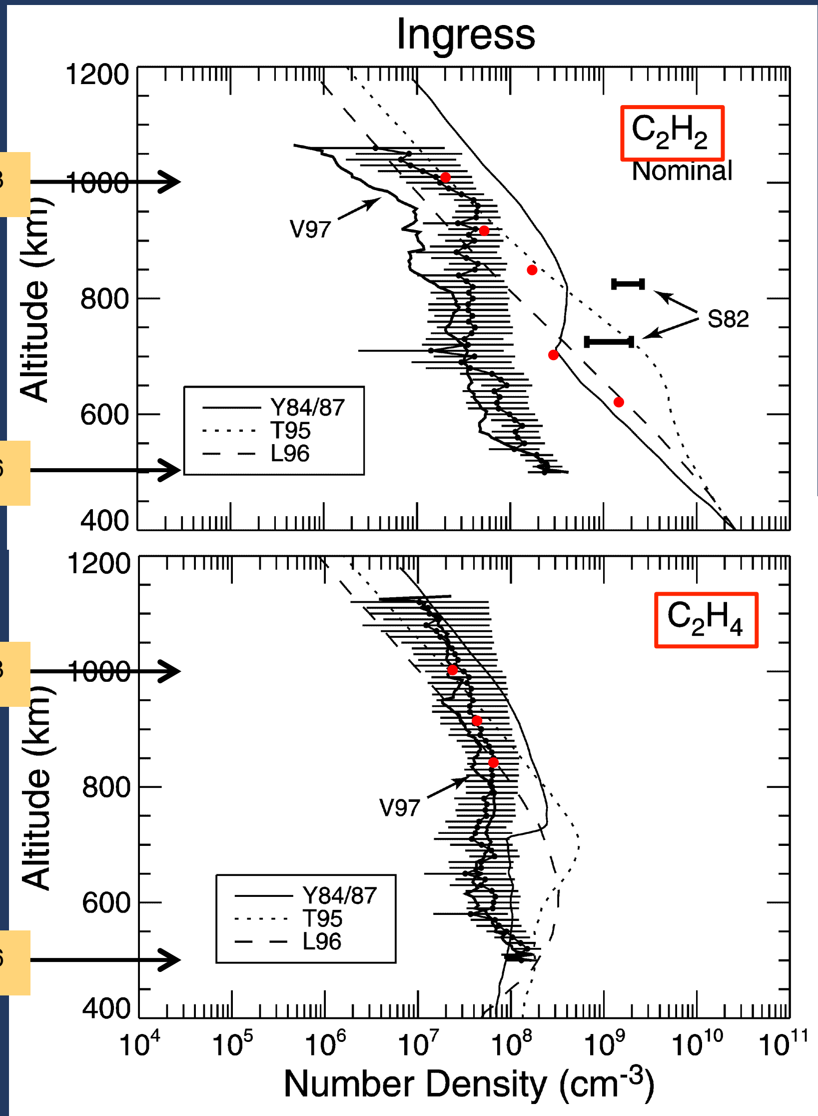
- Cassini UVIS stellar occultation (Shemansky et al. 2005)
  - 36°S
  - $C_2H_2$, $C_2H_4$, $C_2H_6$, $C_4H_2$ and HCN/$HC_3N$ profiles from 600-800 to 1000 km
    - $C_2H_4$ agrees with UVS
    - $C_2H_2$ at 615 km is 20 times larger than UVS and 50 times larger than CIRS value at 500 km ⇒ ?

q ~ 1×10$^{-3}$

q ~ 4×10$^{-6}$

q ~ 2×10$^{-3}$

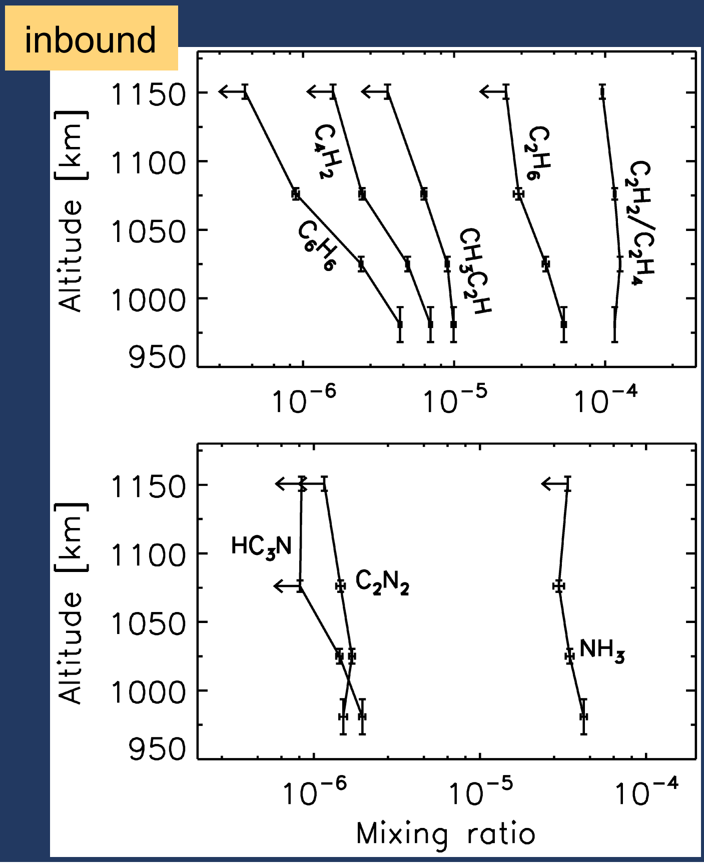
q ~ 2×10$^{-6}$

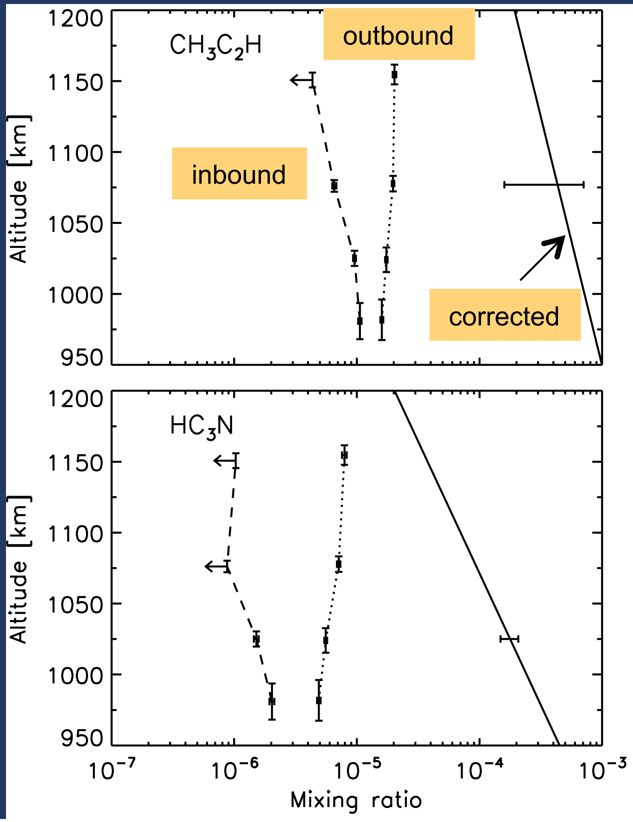



Vervack et al. (2004)

# Photochemical compounds (thermosphere)

- INMS: neutral species in the range 950-1200 km
  - Detection of $C_2H_2$, $C_2H_4$, $C_2H_6$, $CH_3C_2H$, $C_4H_2$, $C_6H_6$, $CH_3CN$, $HC_3N$, $C_2N_2$ and $NH_3$ (Cui et al. 2009)
  - Wall effects in the instrument

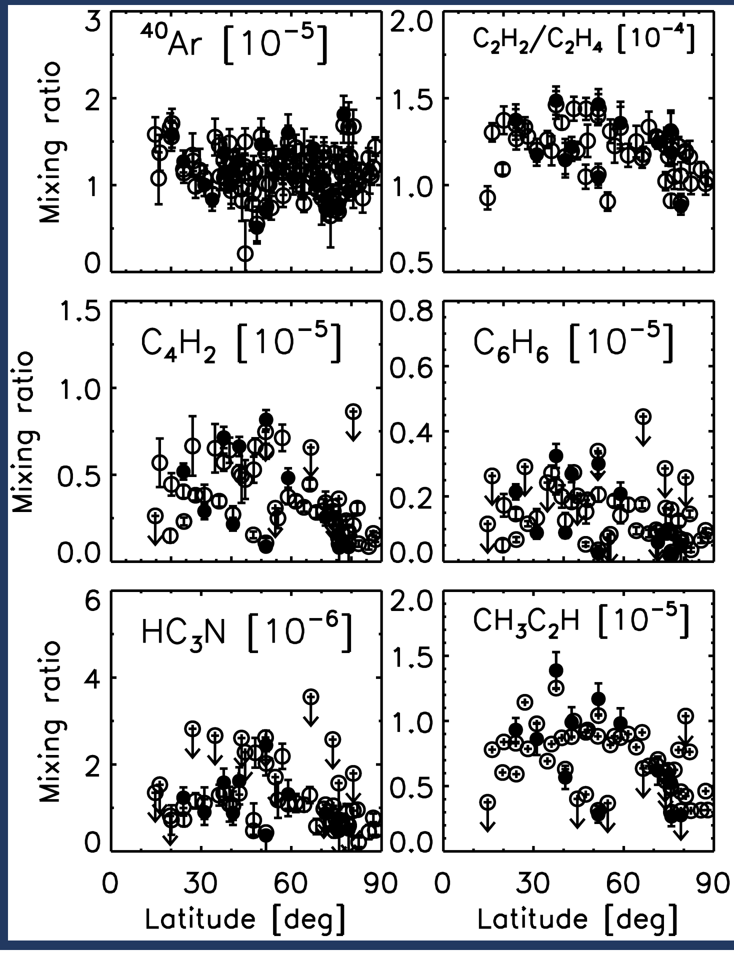



Cui et al. (2009)

# Photochemical compounds (thermosphere)

- Detection of benzene ($C_6H_6$) (Waite et al. 2005; Vuitton et al. 2006)
  - Mole fraction: ≈ 4 × $10^{-6}$ at 980 km
  - Precursor of more complex aromatic species…
- First detection of $NH_3$
  - Mole fraction: ≈ 3-4 × $10^{-5}$ below 1100 km (but some may be formed in the instrument…)
- Depletion of heavy photochemical species near north polar region




Cui et al. (2009)

# Photochemical compounds (thermosphere)

- INMS: ion species measurements at 1000-1200 km also probe the neutral composition (Vuitton et al. 2007)
  - Detection of polyynes ($C_4H_2$, $C_6H_2$, $C_8H_2$) and cyanopolyynes ($HC_3N$, $HC_5N$)
  - Probable detection of methylcyanopolyynes ($CH_3C_3N$, $CH_3C_5N$) and methylpolyynes ($CH_3C_4H$, $CH_3C_6H$)
  - And ammonia ($NH_3$), methanimine ($CH_2NH$), other nitriles…
- ⇒ Most complex molecules identified so far are produced by ion-molecule chemistry

| *Hydrocarbons* | |
|---|---|
| $C_2H_4$ | 1000 ppm |
| $C_4H_2$ | 10 ppm |
| $C_6H_2$ | 0.8 ppm |
| $C_6H_6$ | 3 ppm |
| $CH_3C_6H$ | 0.3 ppm |
| $C_7H_8$ | 0.2 ppm |
| $C_8H_2$ | 0.2 ppm |

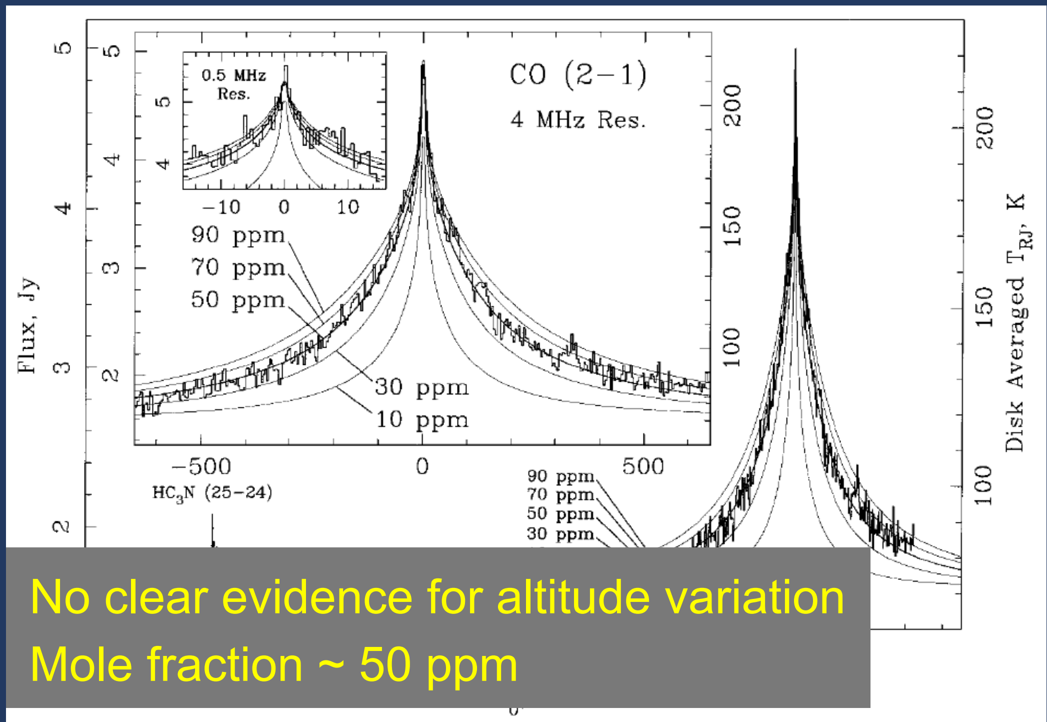
| *Nitriles* | |
|---|---|
| HCN | 2000 ppm |
| $CH_3CN$ | 3 ppm |
| $HC_3N$ | 40 ppm |
| $C_2H_3CN$ | 10 ppm |
| $C_2H_5CN$ | 0.5 ppm |
| $CH_3C_3N$ | 4 ppm |
| $HC_5N$ | 1 ppm |
| $C_5H_5N$ | 0.4 ppm |
| $CH_3C_5N$ | 0.3 ppm |
| $C_6H_7N$ | 0.1 ppm |
| $NH_3$ | 6.7 ppm |
| $CH_2NH$ | 10 ppm |

Vuitton et al. (2007)

# Oxygen-bearing compounds

- Carbon monoxide (CO)
  - Near-infrared spectroscopy
    - 1.6 µm spectroscopy (Lutz et al. 1983, de Bergh et al. 2011)
    - 4.8-µm spectroscopy (Noll et al. 1993, Lellouch et al. 2003, Baines et al. 2006)

troposphere




lower stratosphere 80 km

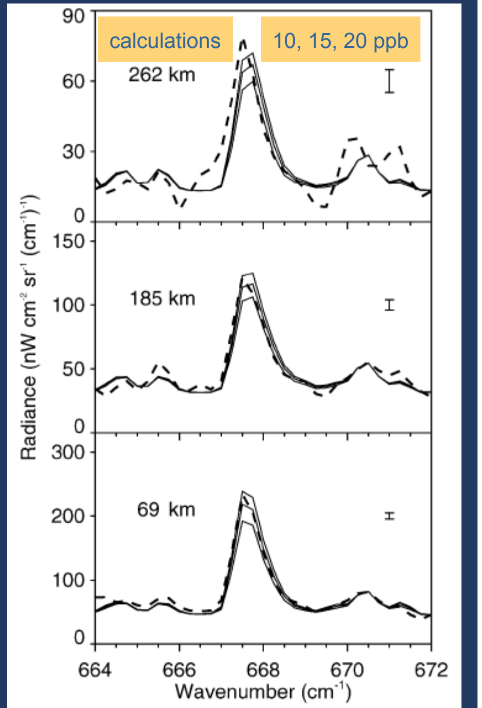
stratosphere 60-400 km

  - No clear evidence for altitude variation
  - Mole fraction ~ 50 ppm

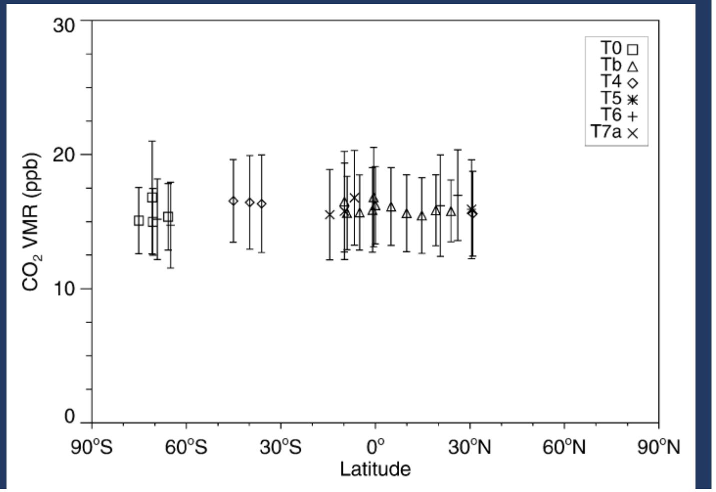
Gurwell and Muhleman 2000

# Oxygen-bearing compounds

- Water vapor ($H_2O$)
  - Detection by ISO (Coustenis et al. 1998)
    - Column density: $2.6^{+1.9}_{-1.6} \times 10^{14}$ molecule cm$^{-2}$
    - Mole fraction ~ 8 ppb at 400 km
  - Detected in Cassini / CIRS spectra




- Carbon dioxide ($CO_2$)
  - 15-µm band observed by Cassini / CIRS (de Kok et al. 2007, Teanby et al. 2009, Vinatier et al. 2010)
  - Mole fraction of 16 ± 2 ppb uniform in latitude and altitude (120-350 km)




de Kok et al. 2007

# Oxygen-bearing compounds

| *Oxygen compounds* | | |
|---|---|---|
| $H_2O$ | 8 ppb | ~ 400 km |
| CO | 50 ppm | 0 - 400 km |
| $CO_2$ | 16 ppb | 120-350 km |

- External flux of oxygen in Titan's atmosphere
  - Hörst et al. (2008)
  - Oxygen ions ($O^+$) from the magnetosphere (Enceladus?)
  - OH or $H_2O$ from meteoritical ablation

# Isotopic ratios

- D/H
  - In $H_2$: $(1.35 \pm 0.3) \times 10^{-4}$ (GCMS)
  - In $CH_4$: ~ $1.3 \times 10^{-4}$ (CIRS, ground-based IR)
  - ⇒Primordial icy material, fractionation processes (escape, $CH_4$ photochemistry)
- $^{12}C/^{13}C$
  - In $CH_4$: $91.1 \pm 1.4$ (GCMS), CIRS and INMS measurements
  - In $C_2H_6$, $C_2H_2$, $CH_3D$, HCN, $HC_3N$, $CO_2$: consistent with Earth value (89)(CIRS)
  - ⇒ fractionation processes ($CH_4$ photochemistry)?
- $^{14}N/^{15}N$
  - In $N_2$: $167.7 \pm 0.6$ (GCMS), INMS ⇒ 0.6 time Earth ratio
  - In HCN: ~ 60 (CIRS, ground-based mm)
  - ⇒ non-thermal escape of $N_2$?, fractionation in $N_2$ photolysis
- $^{16}O/^{18}O$
  - In CO: ~ 400 (ground-based mm – M. Gurwell) ⇒ 0.8 time Earth ratio
  - In $CO_2$: ~ 350 (CIRS)
  - ⇒ non-thermal escape of CO?

# Conclusions

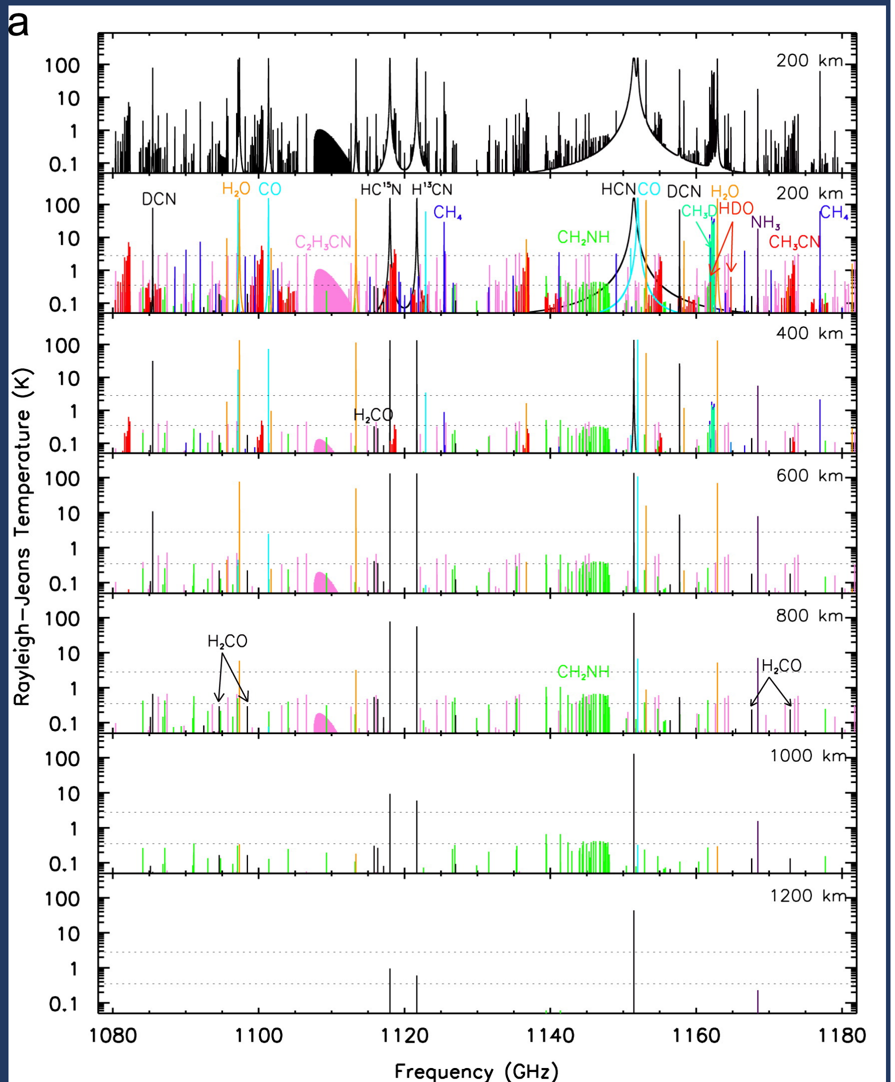
- What is presently missing?
  - Some in situ measurements
    - More sensitive measurements of noble gases: Ne, Kr, Xe with isotopic abundance ⇒ origin of the atmosphere
    - Ethane tropospheric abundance ⇒ methane cycle
  - Extended monitoring of seasonal variations
    - Will be provided by Cassini Solstice mission
  - More complete sounding of the region 500-900 km
    - Important region for UV-driven chemistry
    - Information from UVIS is limited

- Future observations
  - Ground-based facilities
    - ALMA (2013; Early Science in 2011): possible detection of new species, maps of nitrile profiles (HCN, $HC_3N$, $CH_3CN$) at high resolution
  - Space missions
    - Titan balloon or descent probe for in situ (GCMS) measurements

# Conclusions

- Titan orbiter for sounding of the region 500-900 km

- Submillimeter-wave heterodyne spectrometer (Lellouch et al. 2010)
  - Passive limb observations
  - Numerous species available (nitriles, $H_2O$, $NH_3$ etc.)




Lellouch et al. 2010