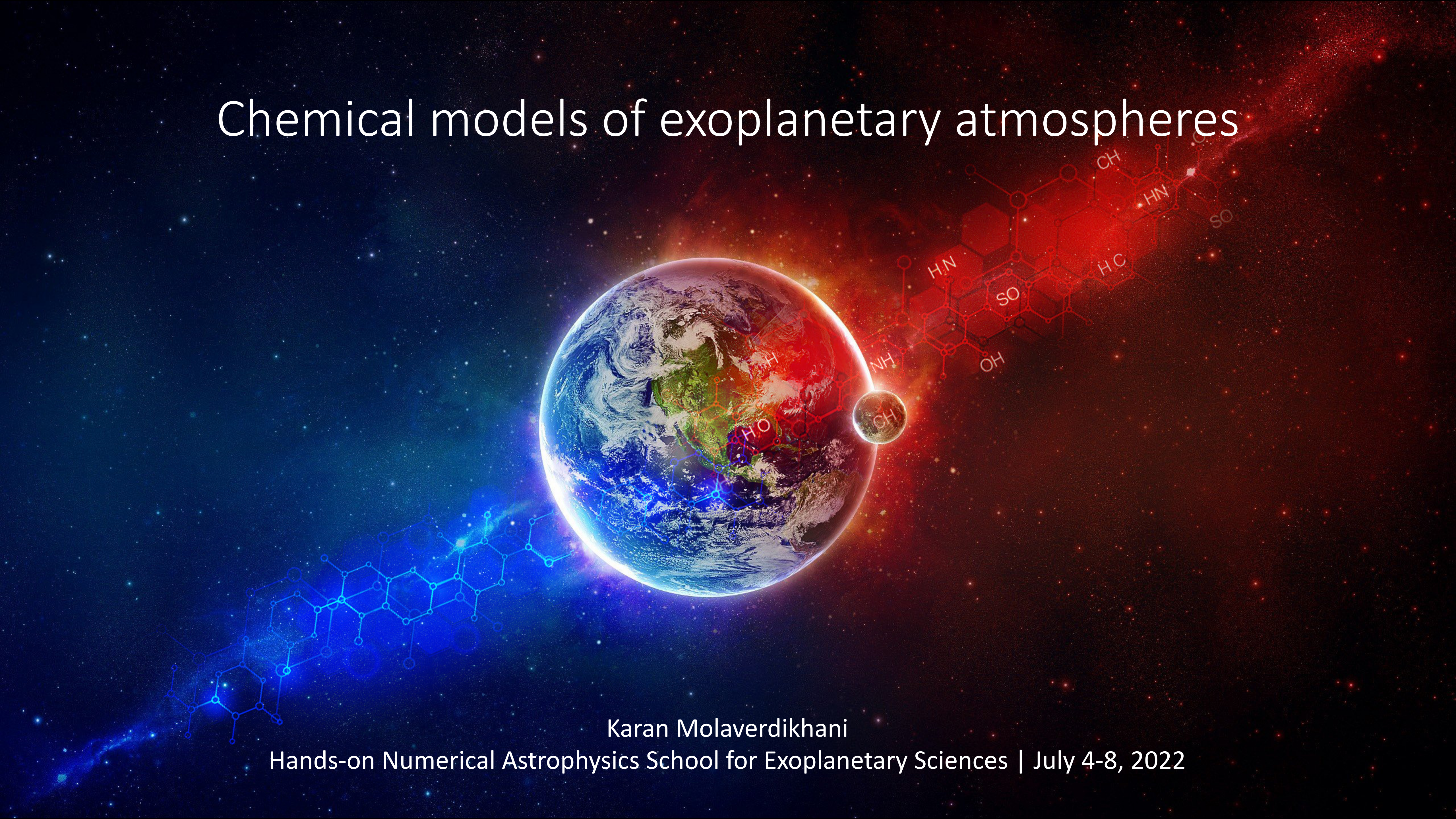
Chemical models of exoplanetary atmospheres



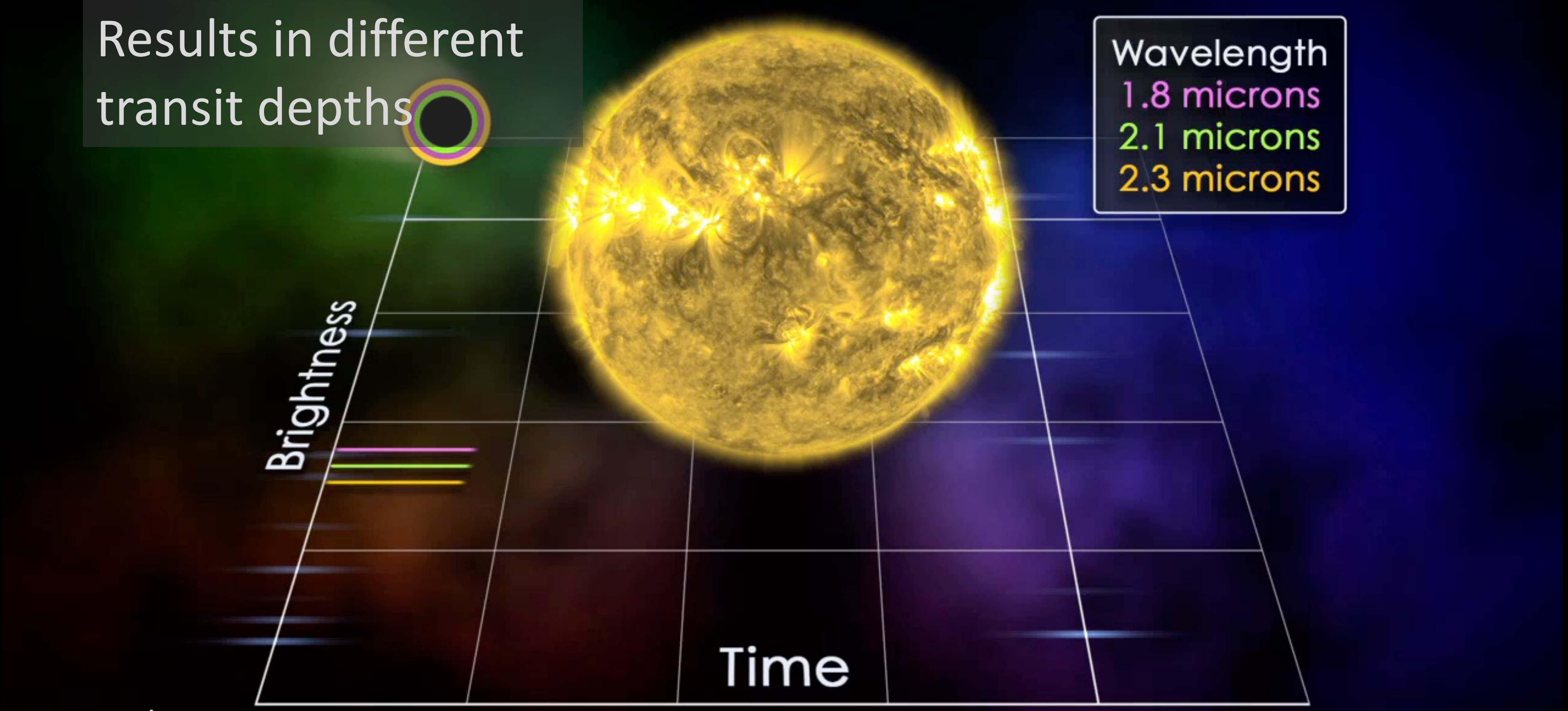
Karan Molaverdikhani

Hands-on Numerical Astrophysics School for Exoplanetary Sciences | July 4-8, 2022

Some refreshener!

Atoms/Molecules in a planet's atmosphere absorb certain wavelengths of a star's flux

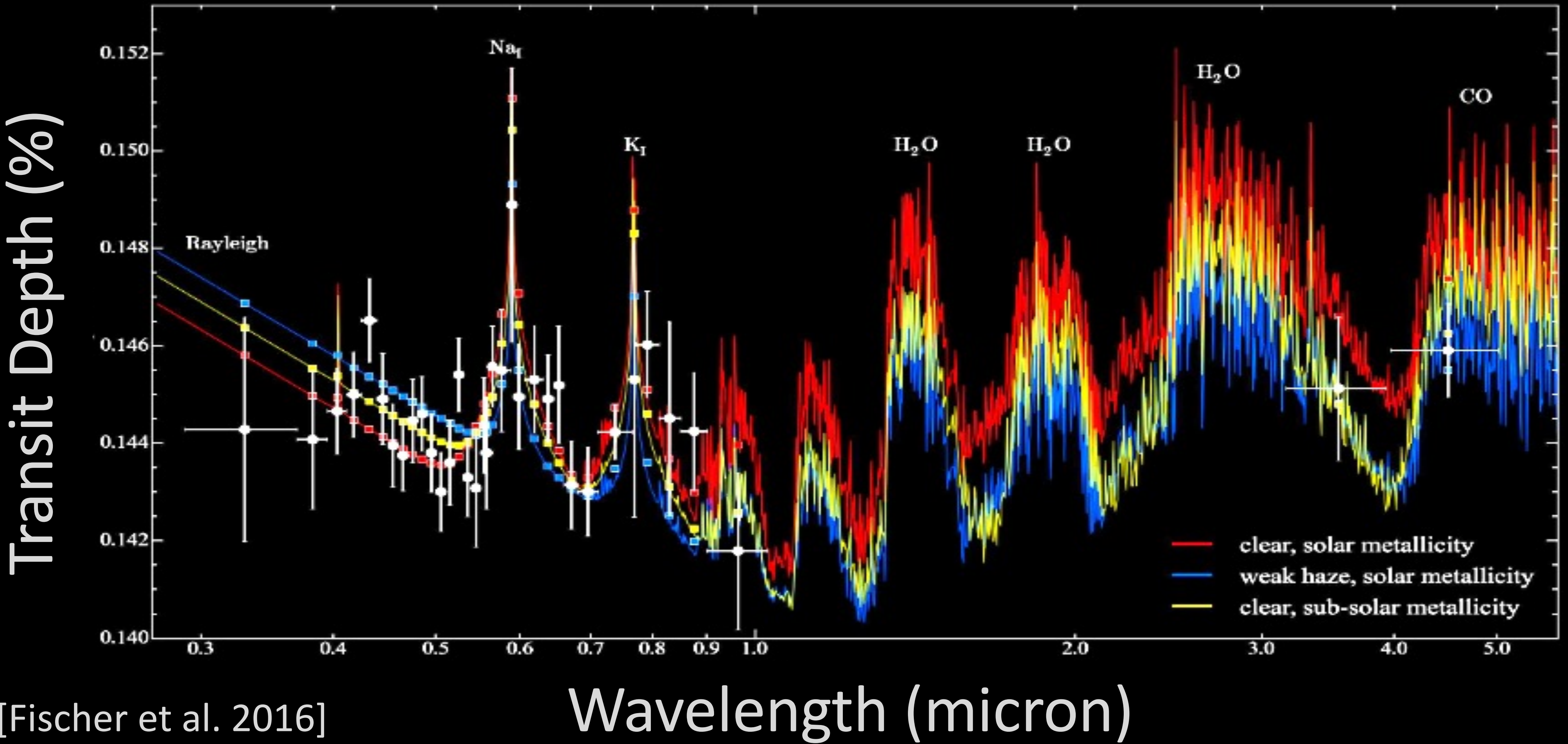
Results in different transit depths



[NASA/Goddard]

Transmission Spectroscopy

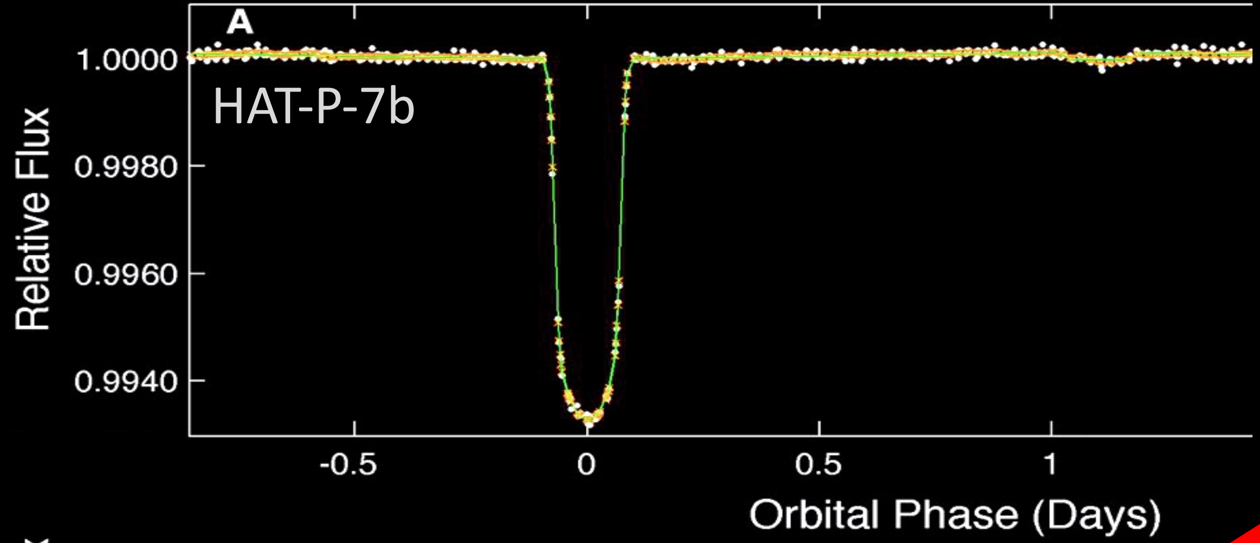
Transit Depth Curve

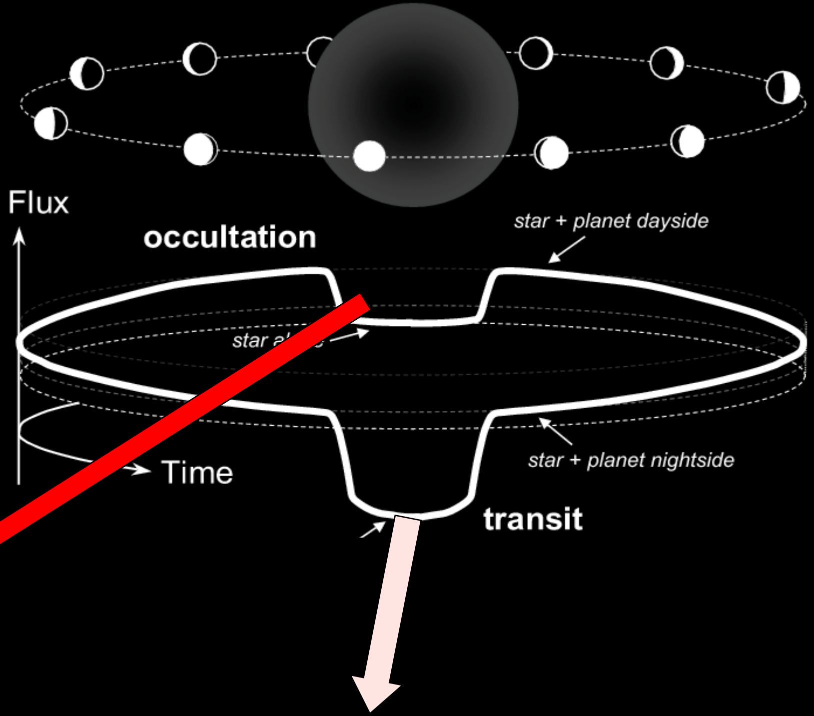


[Fischer et al. 2016]

Emission & Reflectance Spectroscopy

Secondary Eclipse



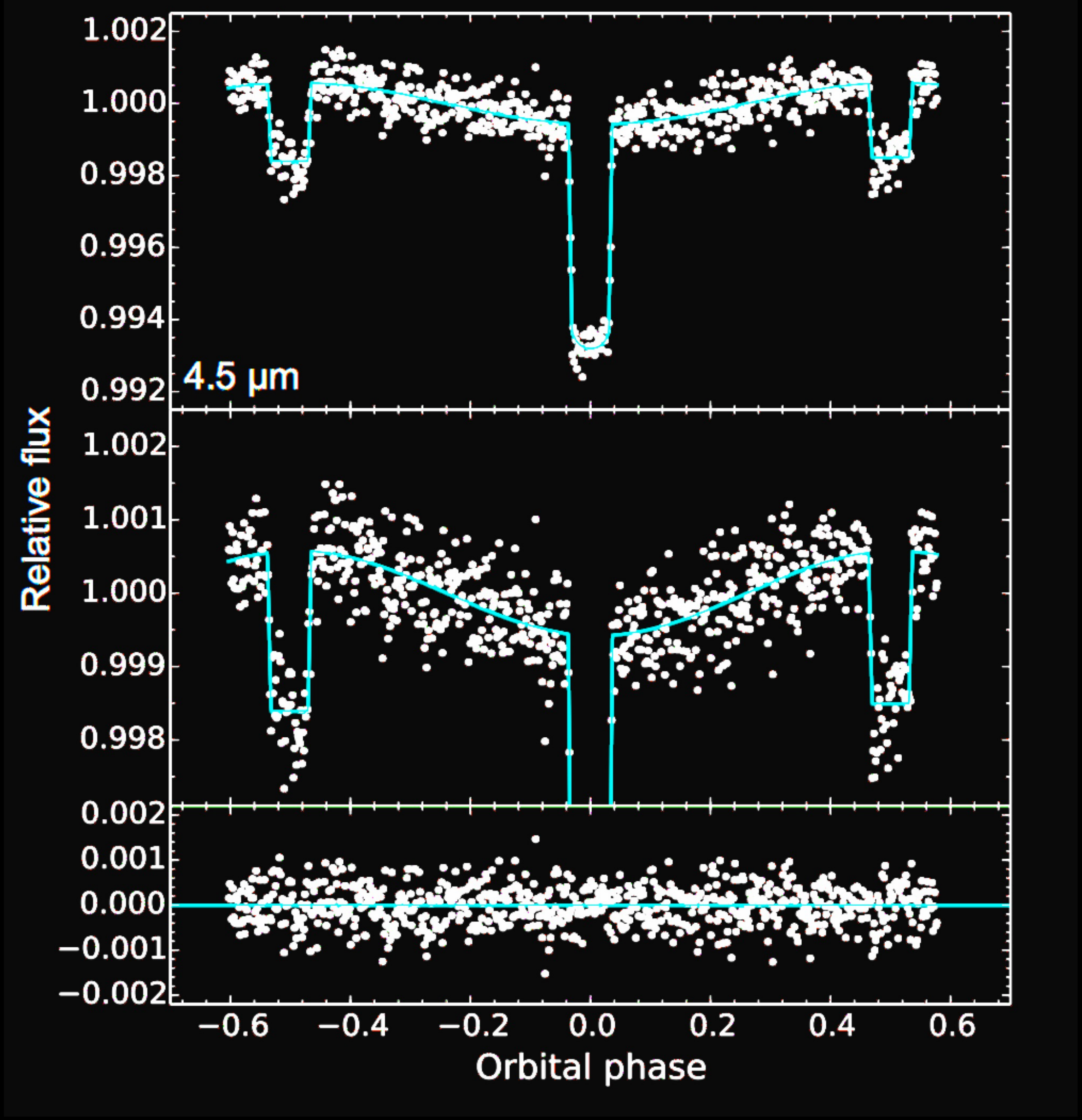


Relative Flux

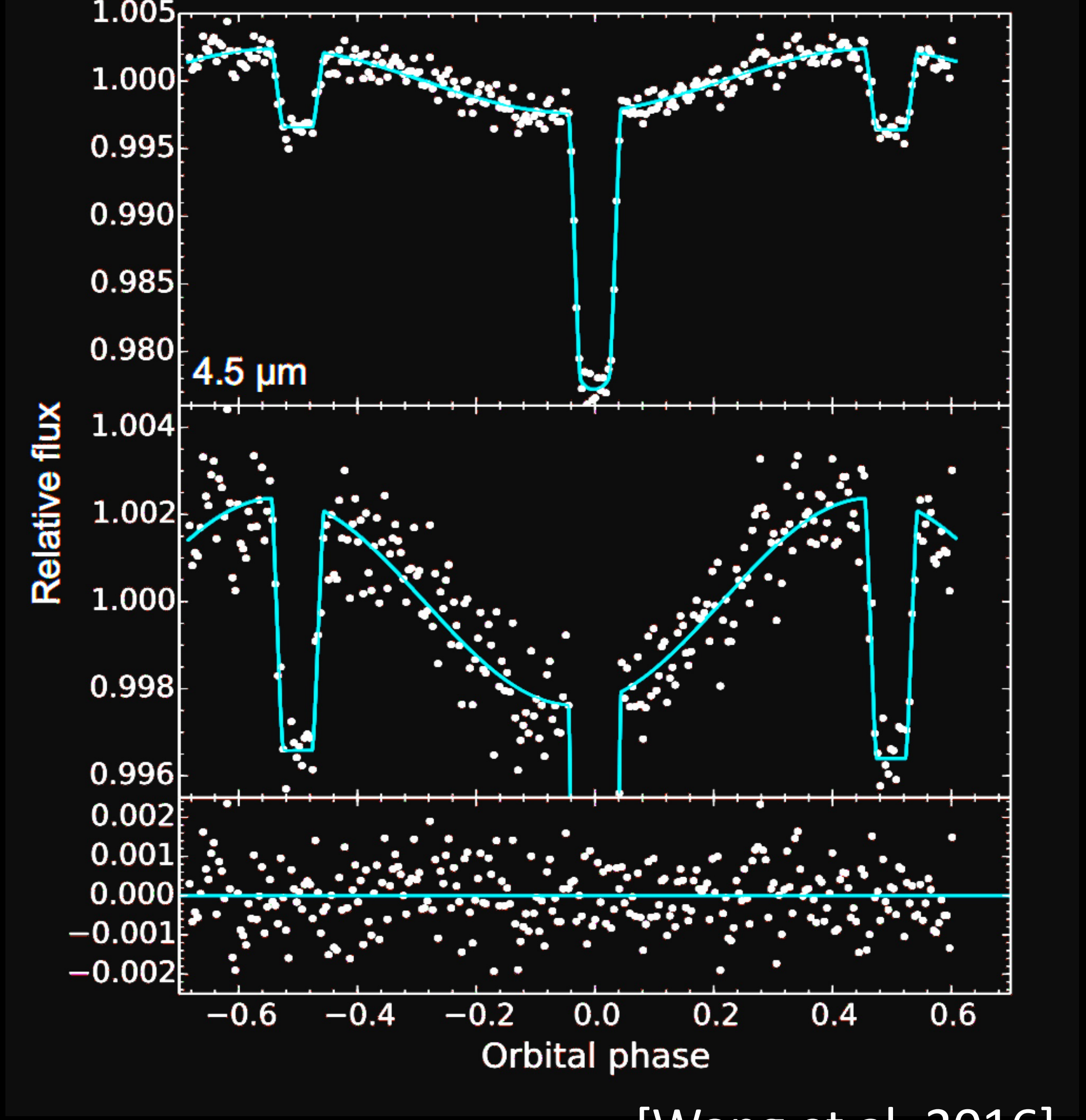
[Borucki et al. 2009]

Phase Curves: Longitudinal Mapping

HAT-P-7b

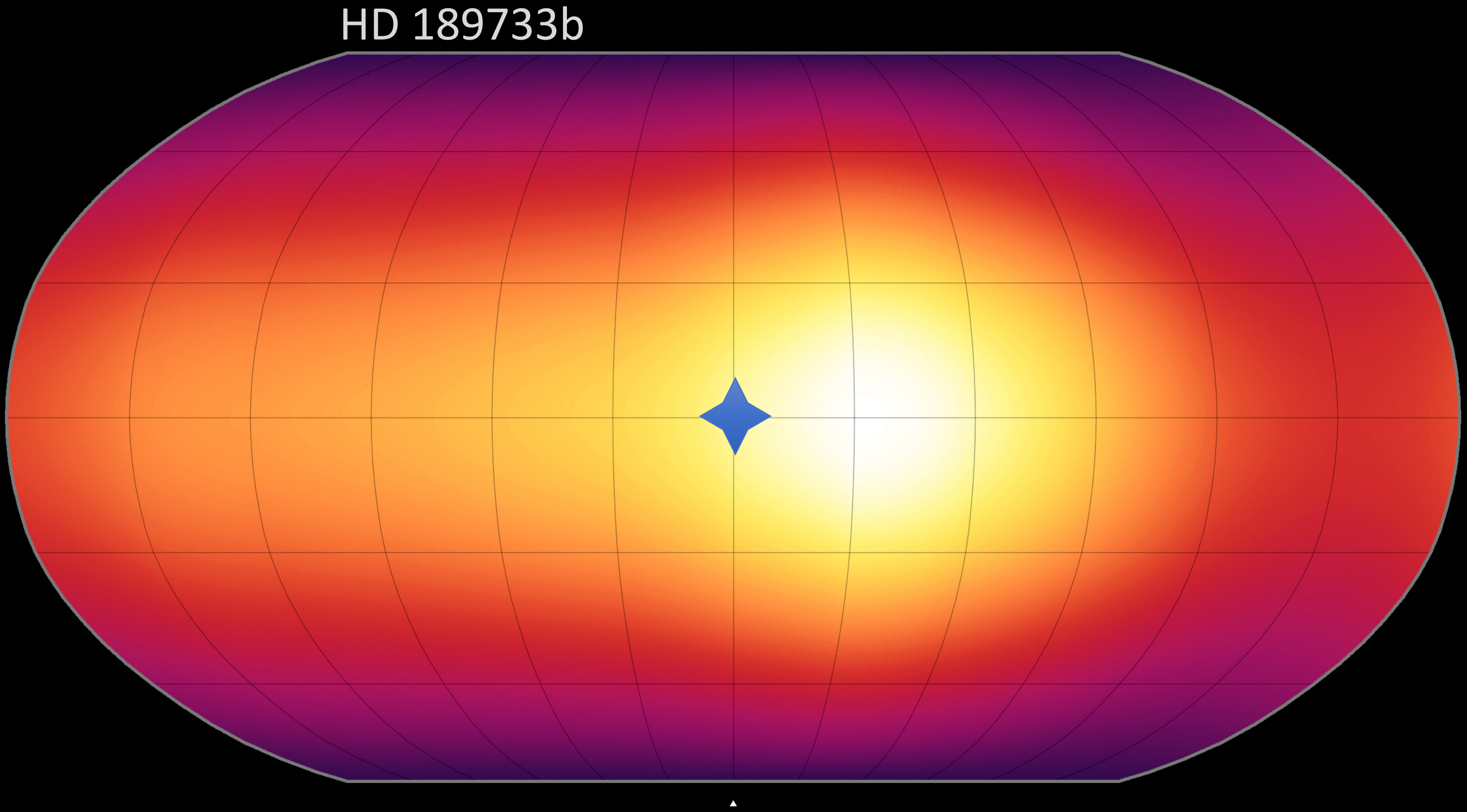


WASP-19b



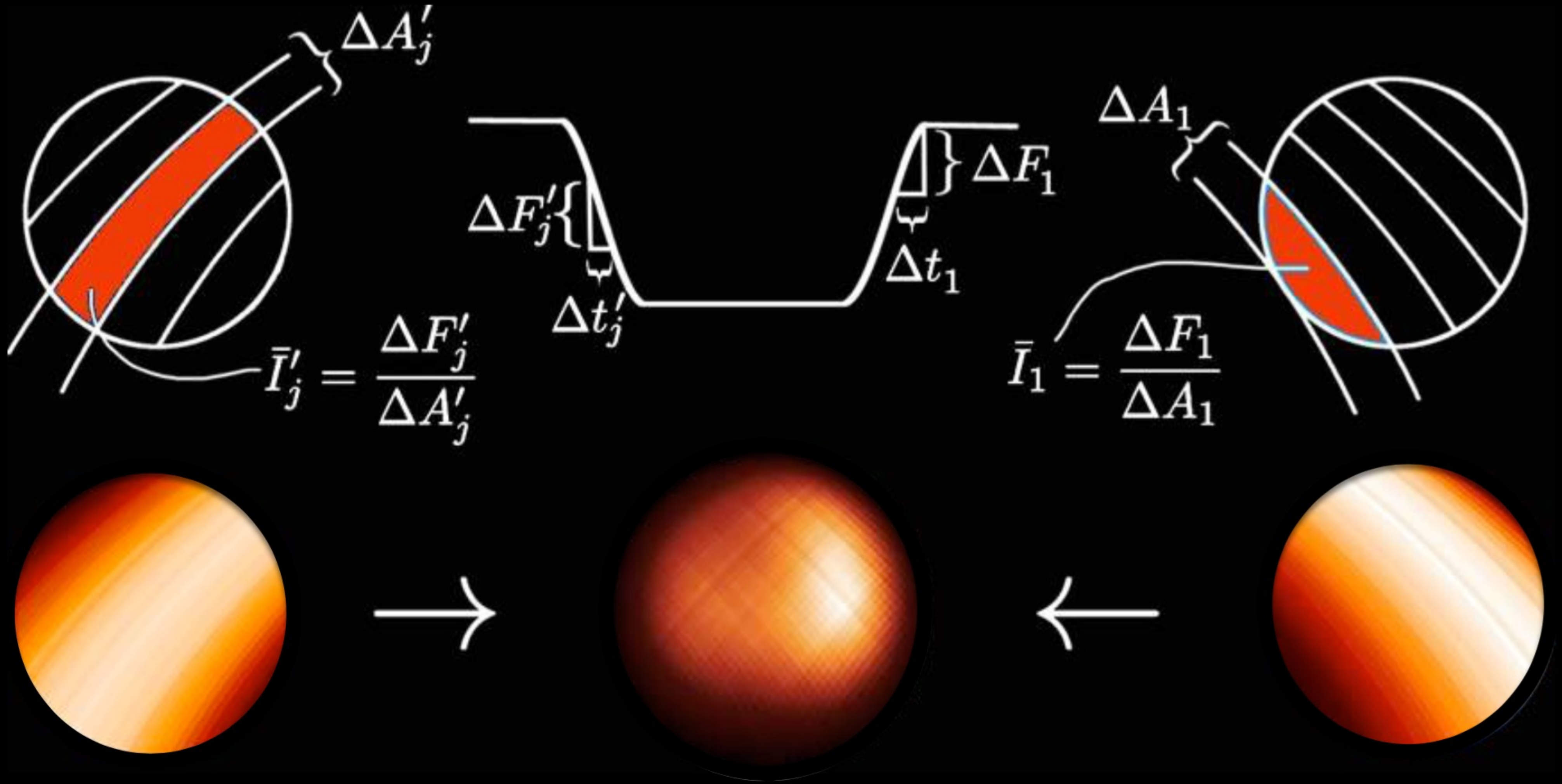
[Wong et al. 2016]

Phase Curves: Longitudinal Mapping

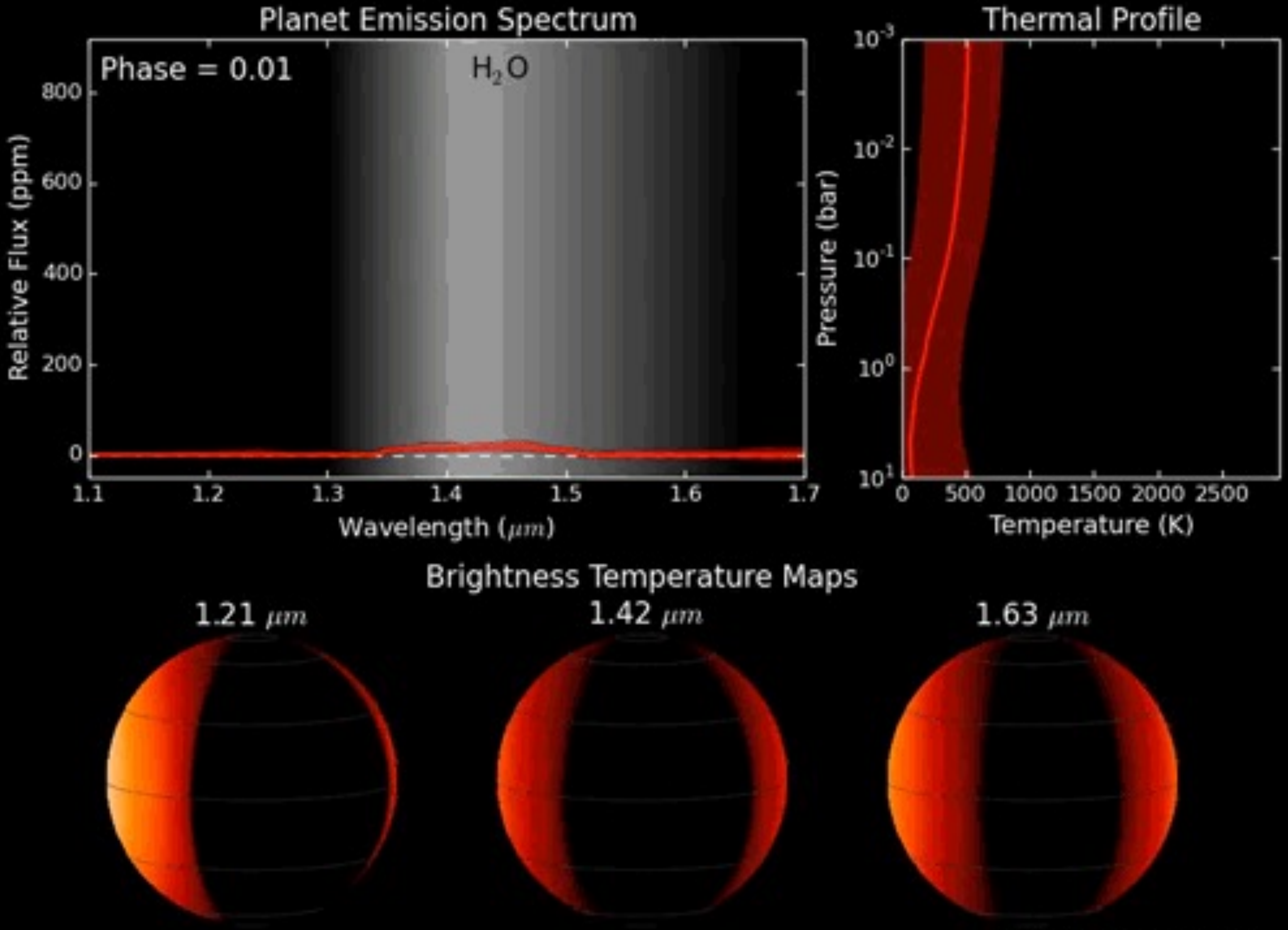


[Knuston et al. 2007]

Spatial Mapping

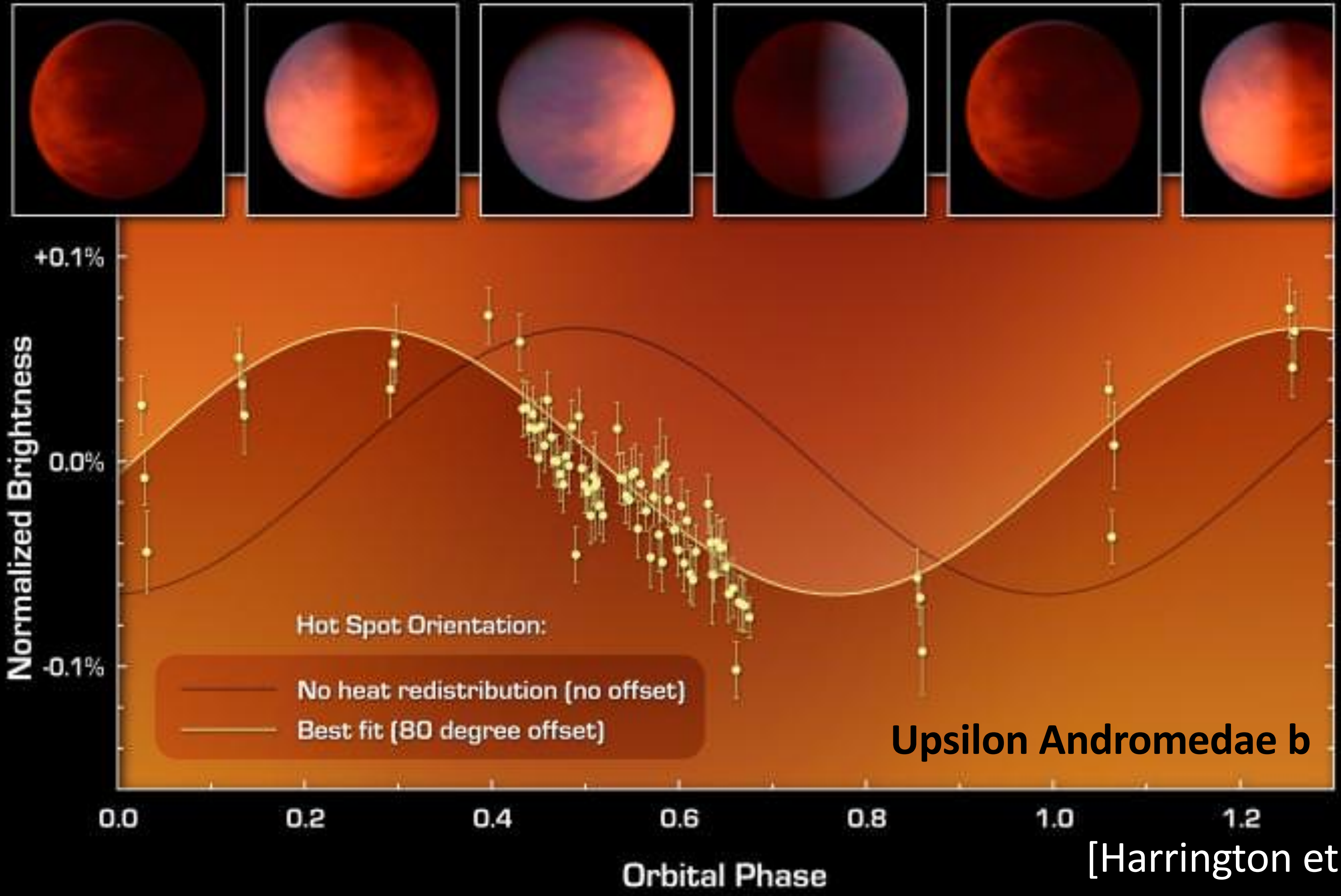


[Majeau et al. 2012]



K. B. Stevenson (2014)

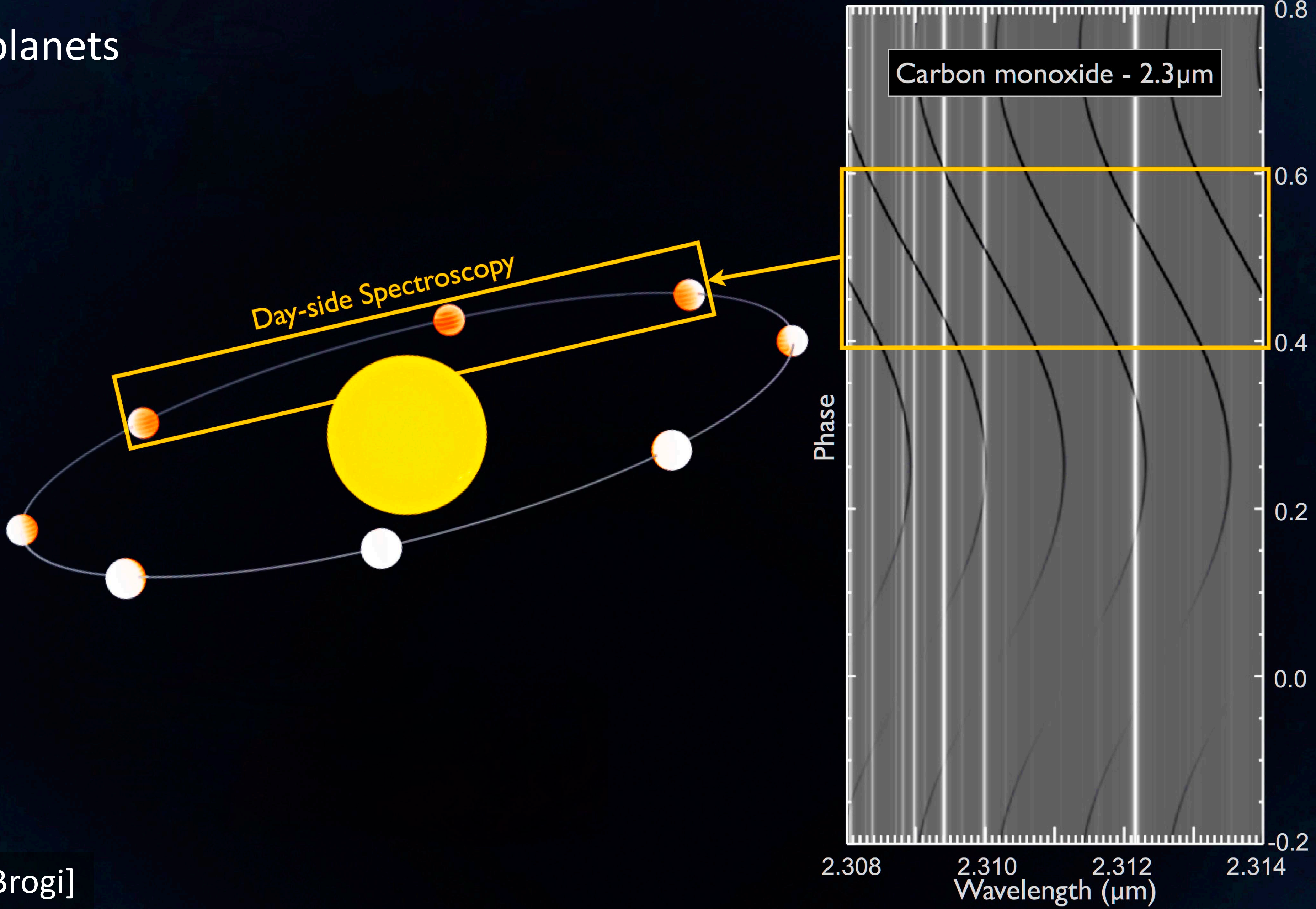
Phase Curves: Non-transiting planets



[Harrington et al. 2006]

High-resolution Spectroscopy

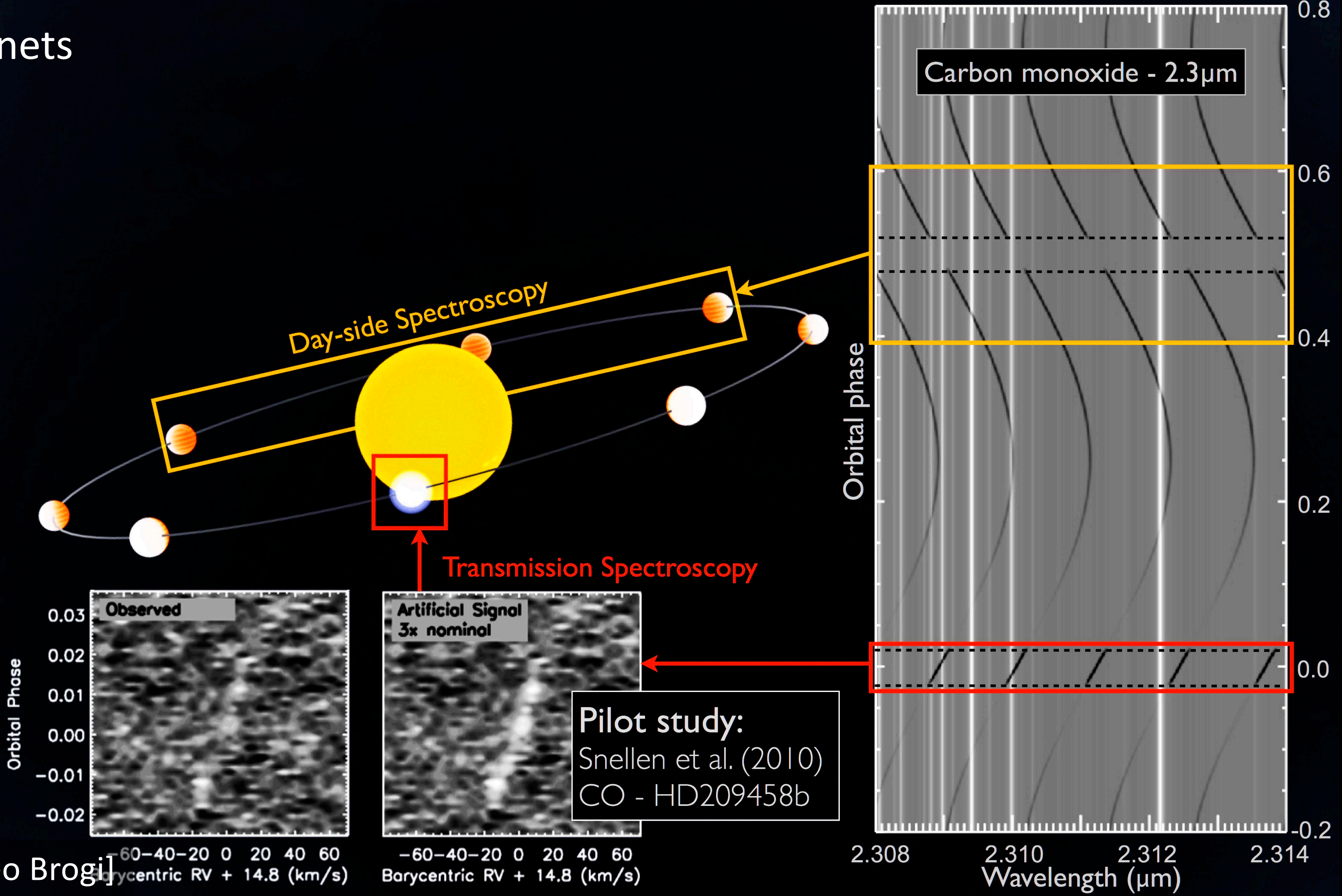
Non-transiting planets



[Courtesy of Matteo Brogi]

High-resolution Spectroscopy

Transiting planets

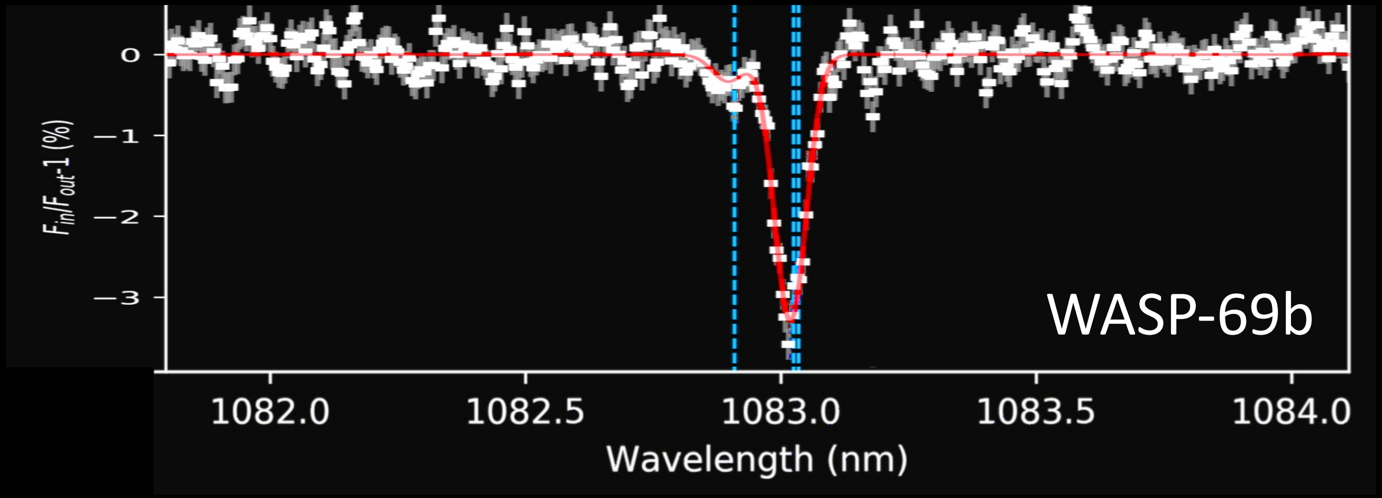


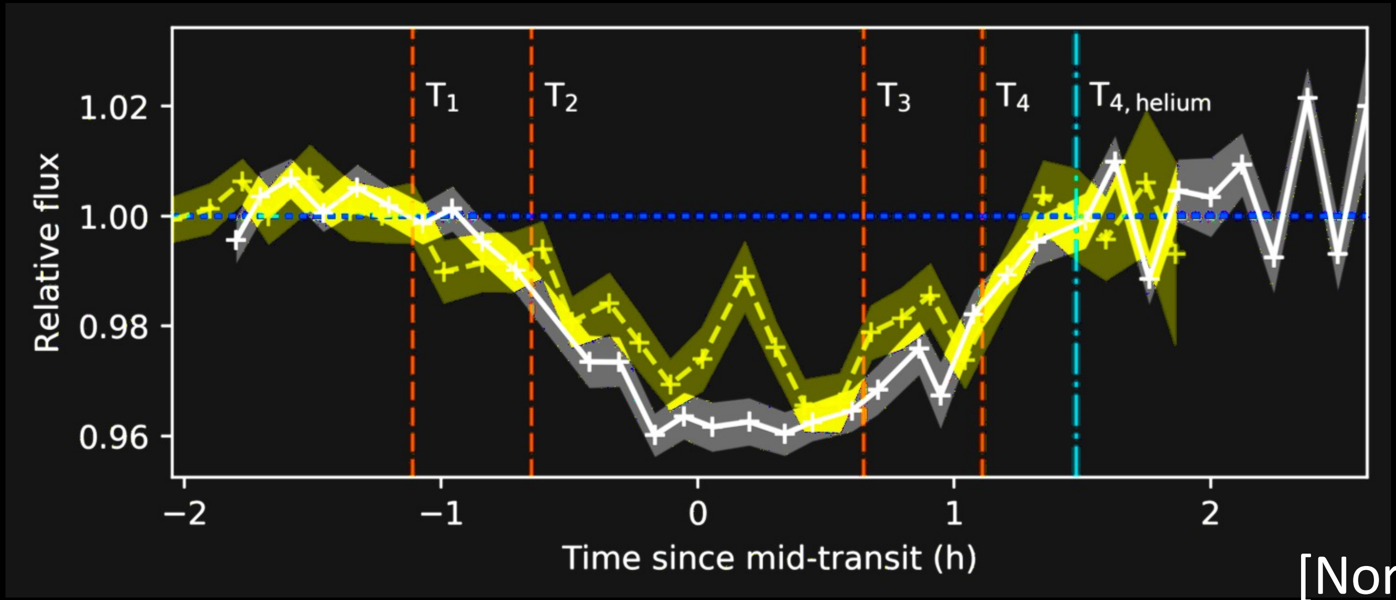
Pilot study:
Snellen et al. (2010)
CO - HD209458b

[Courtesy of Matteo Brogi]

High-resolution Spectroscopy

Resolved lines

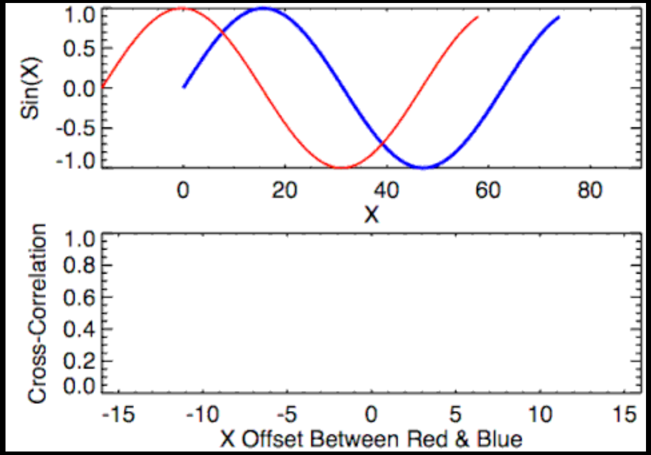




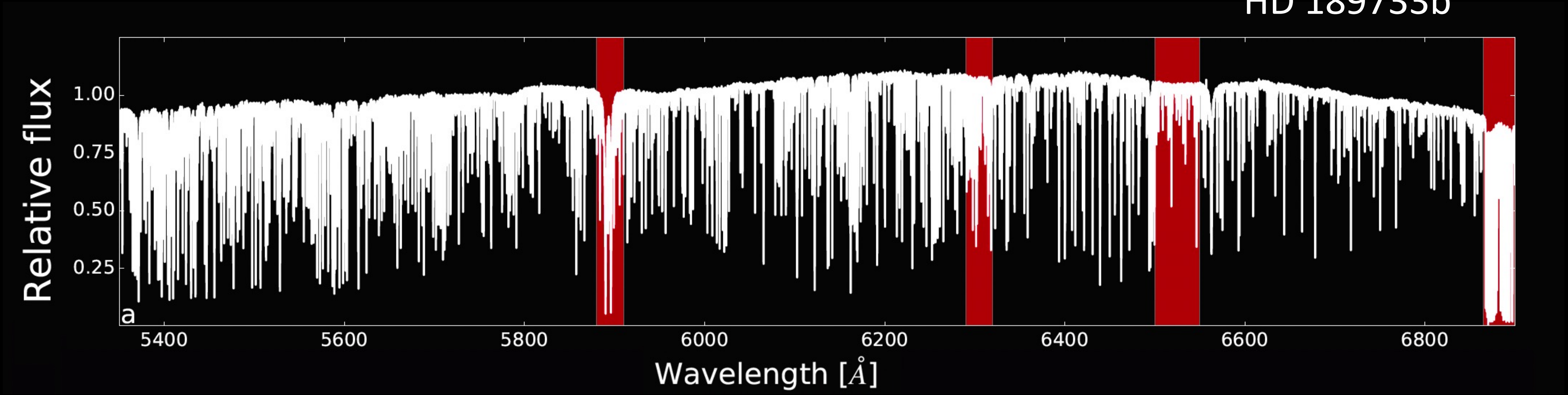
[Nortmann et al. 2018]

High-resolution Spectroscopy

Cross-Correlation Function (CCF)

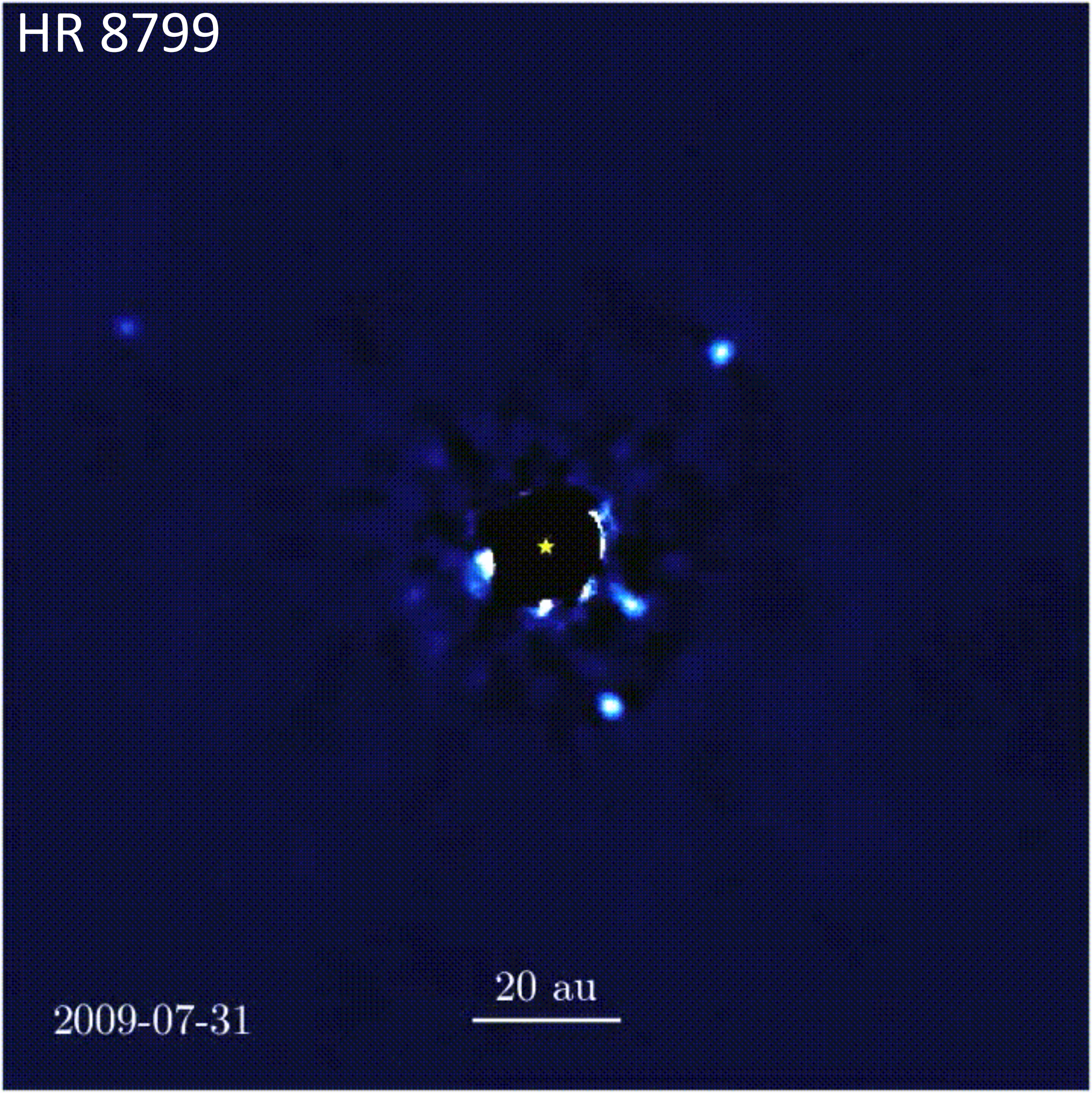


HD 189733b



[Allart et al. 2017]

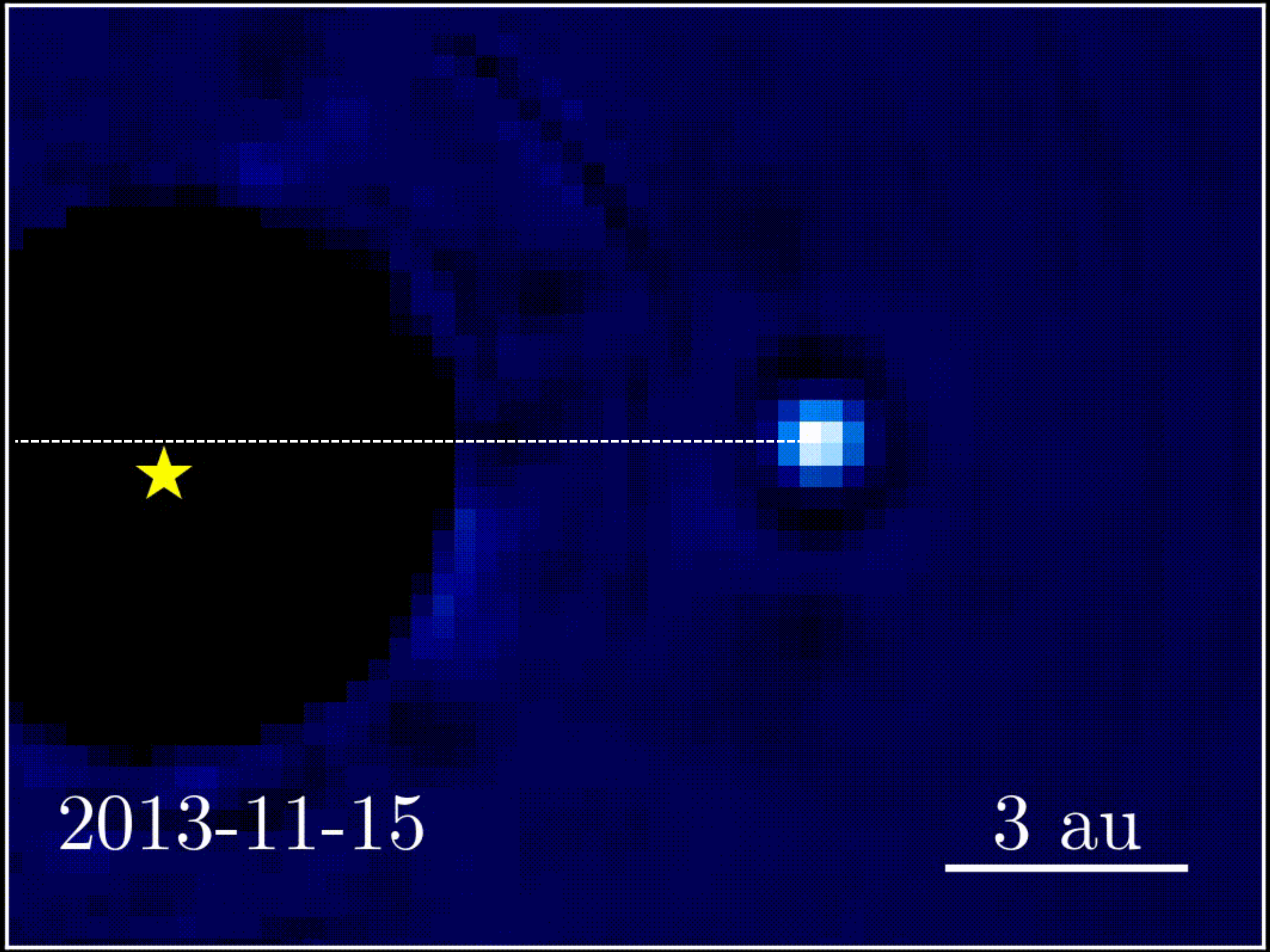
Directly Imaged



[Jason Wang of UC Berkeley/Christian Marois of NRC Herzberg]

Directly Imaged

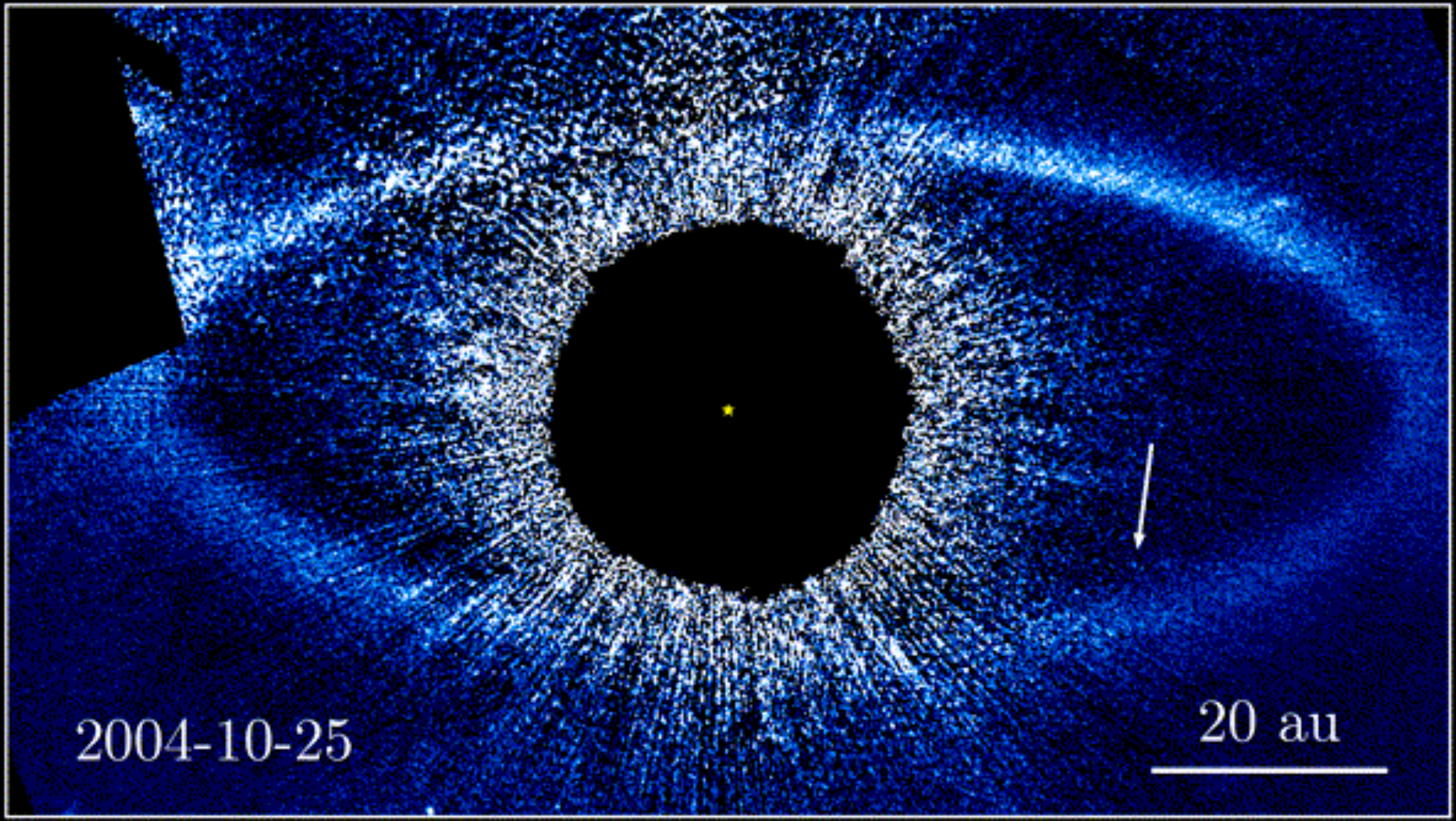
Beta Pictoris



[Jason Wang; UC Berkeley, Gemini Planet Imager Exoplanet Survey]

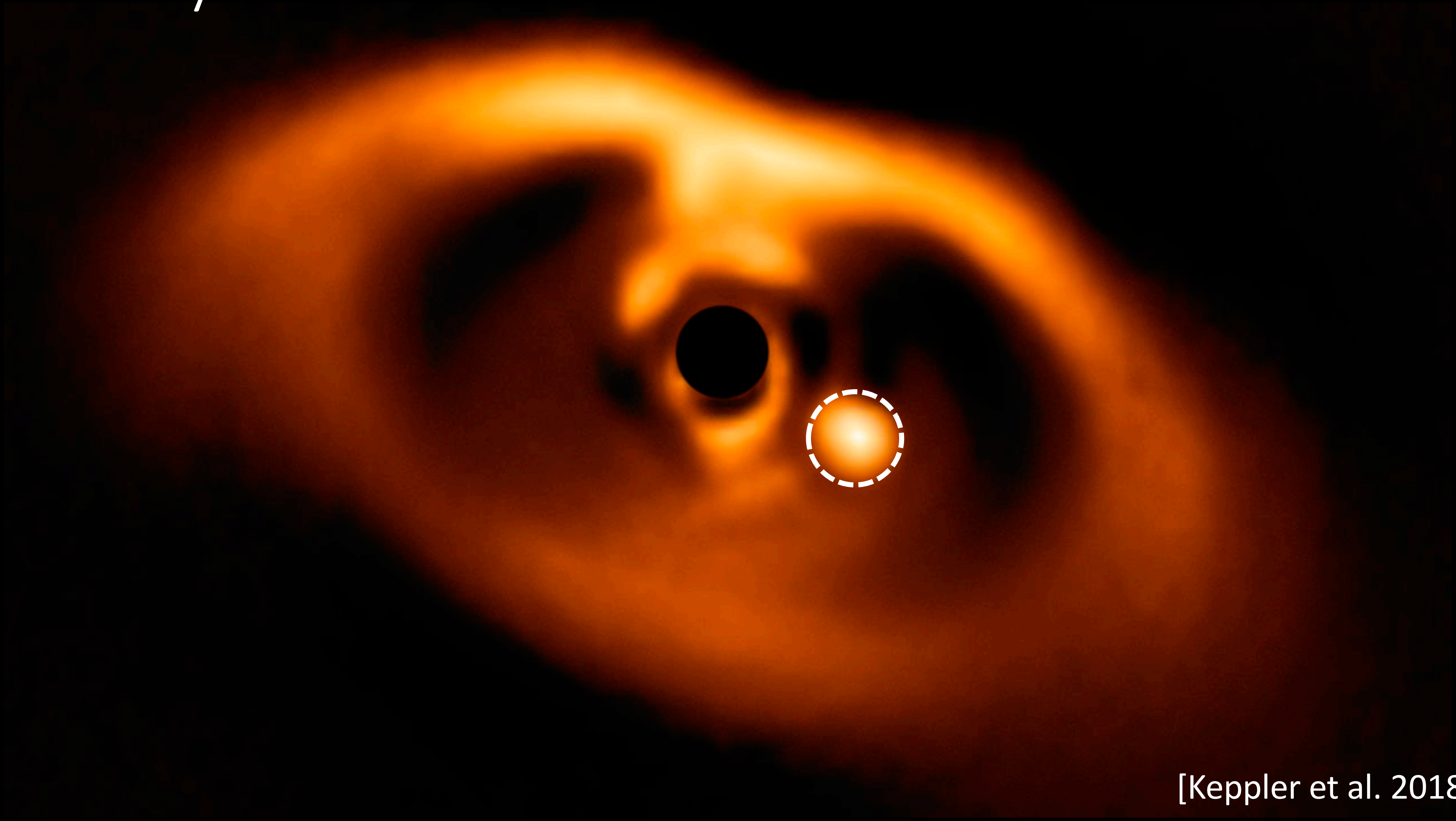
Directly Imaged

Fomalhaut b



[Jason Wang/Paul Kalas; UC Berkeley]

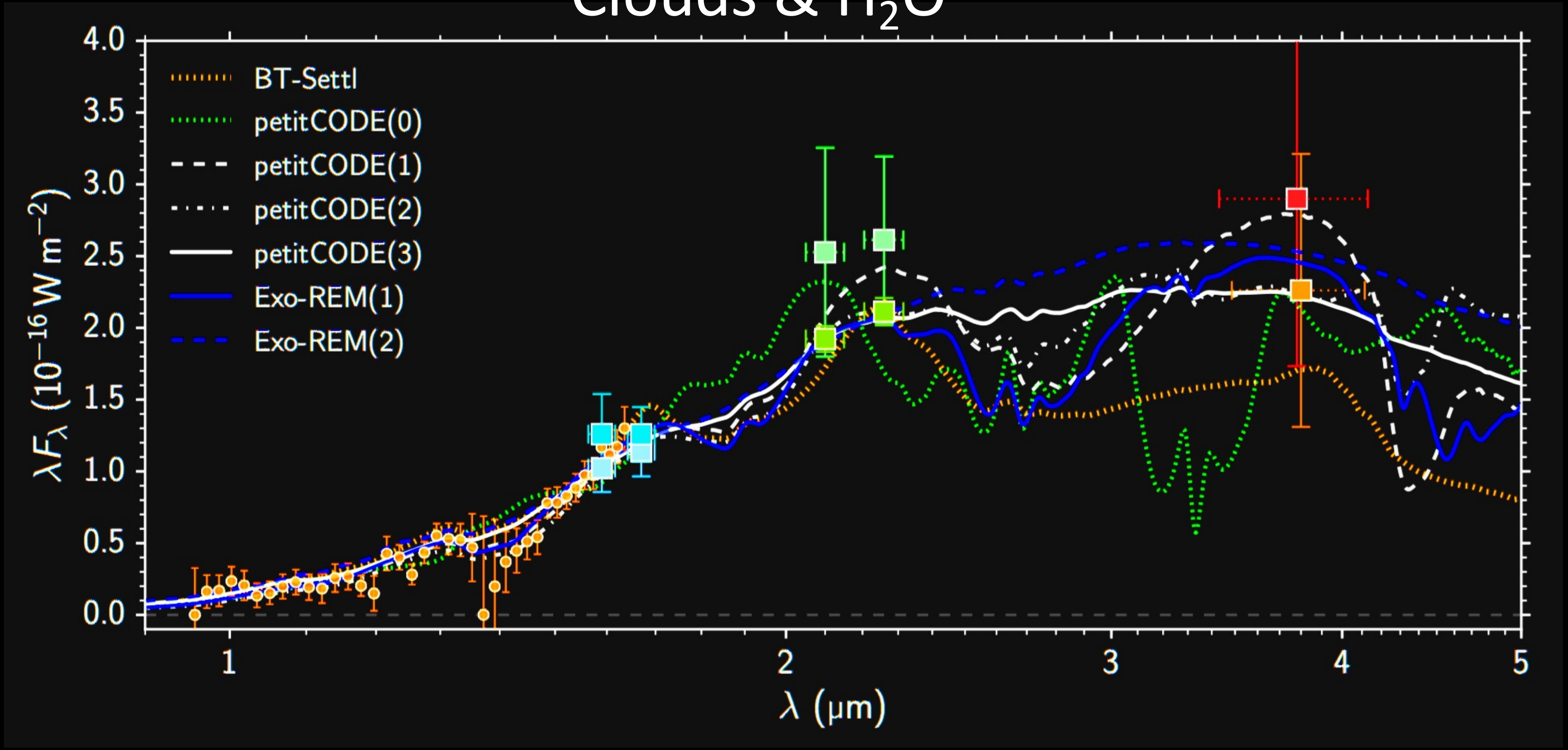
Newly Born PDS 70 b



[Keppler et al. 2018]

Newly Born PDS 70 b

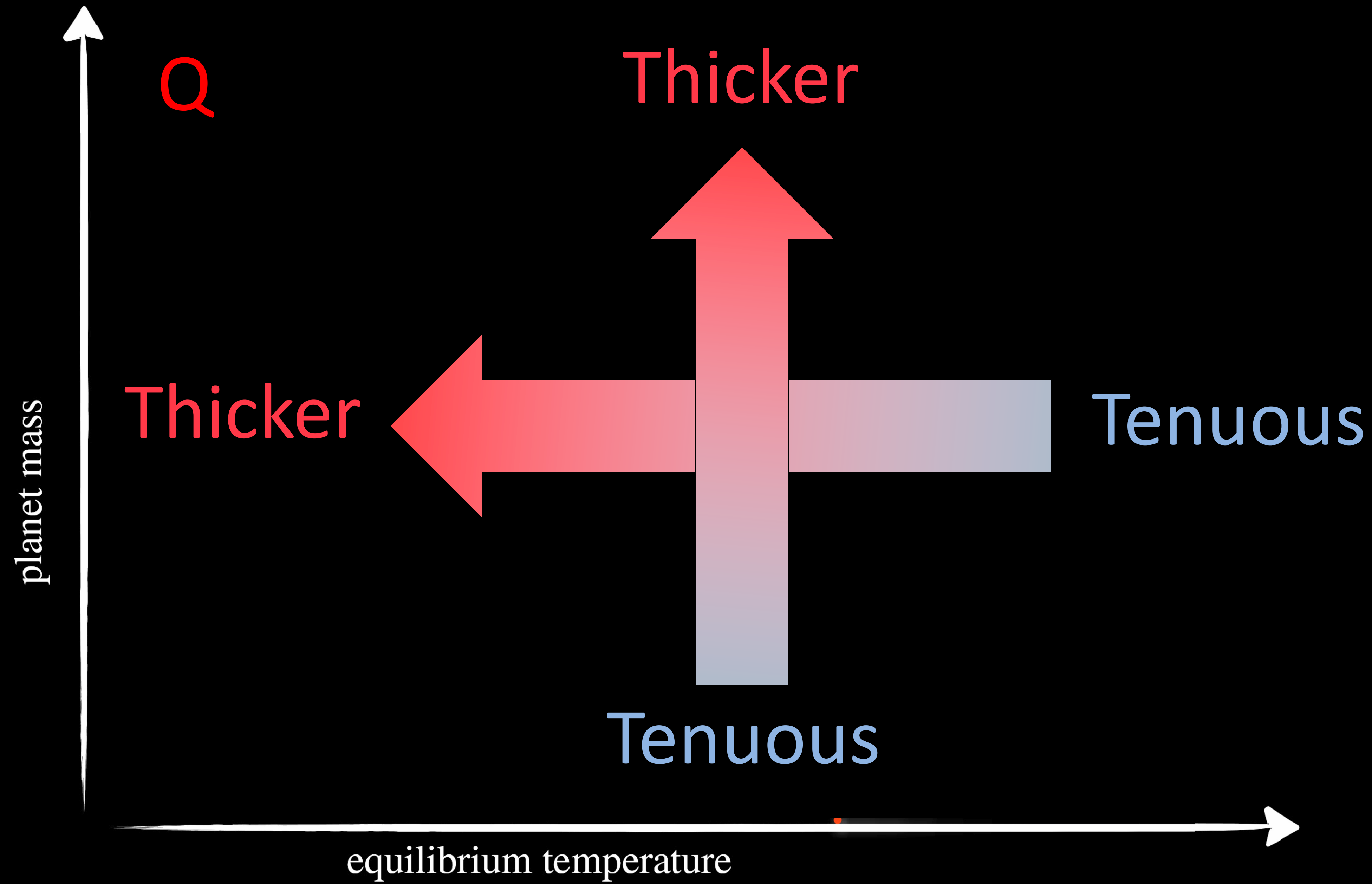
Clouds & H_2O



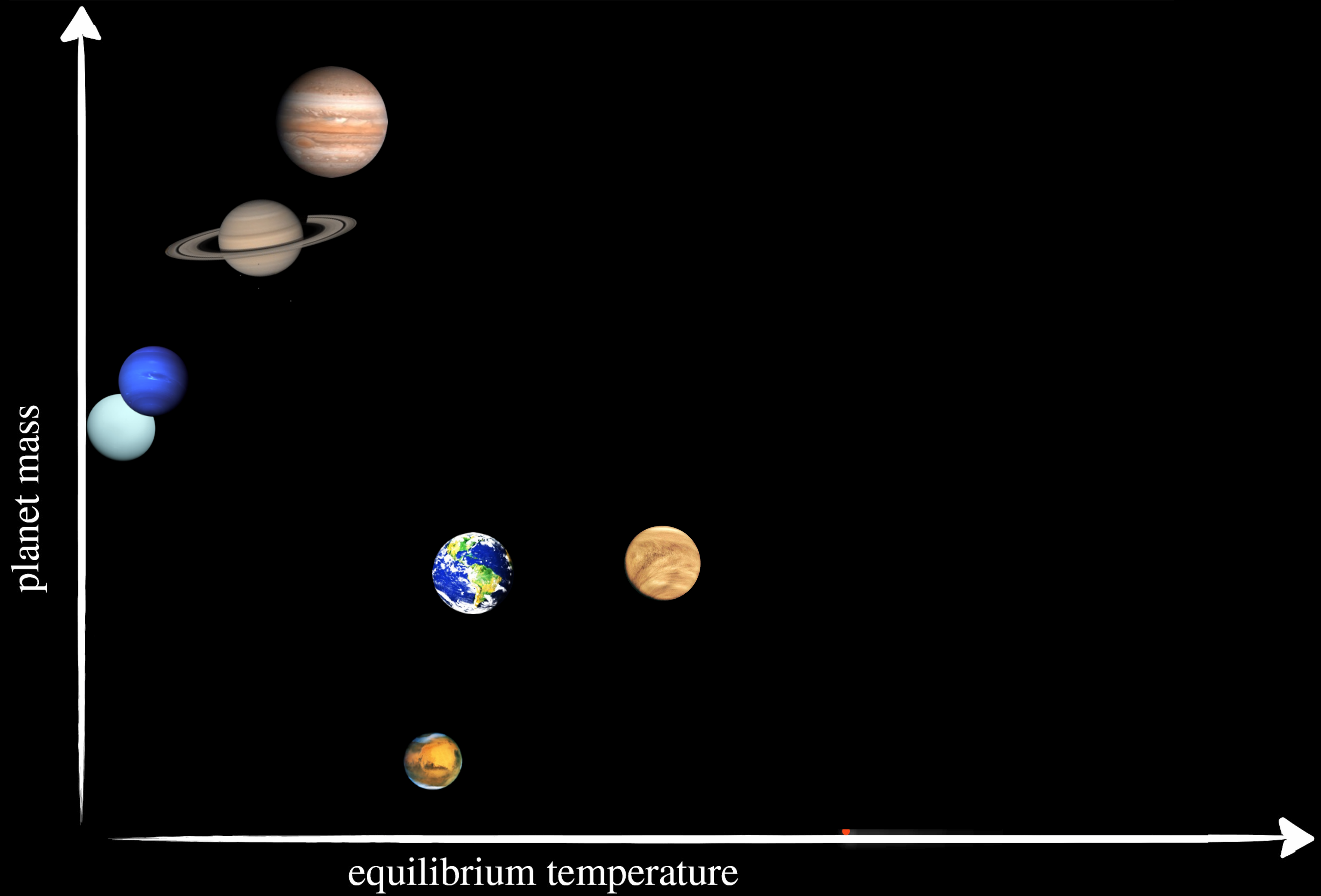
[Muller et al. 2018]

Let’s continue!

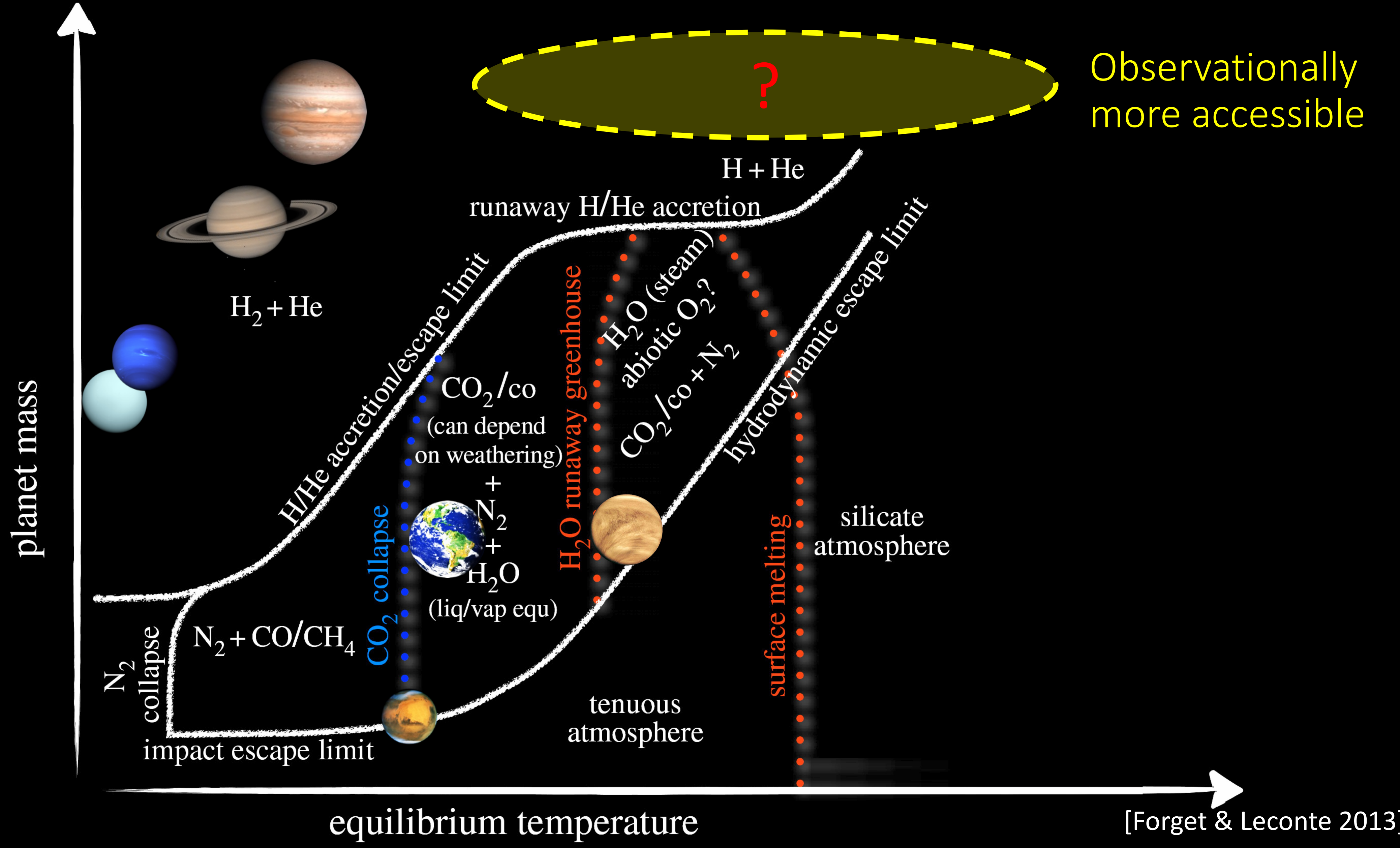
Possible atmospheric scenarios



Possible atmospheric scenarios



Possible atmospheric scenarios



[Forget & Leconte 2013]

Atmospheric composition: Solar system*

Giant Planets
Titan
Early earth
Early Mars?

- Two types:
  - Reducing: Carbon is in CH_4
  - Oxidizing: Carbon is in CO

Q

Venus (high altitude)
Mars
Modern Earth

[David Catling lecture 2016]

*Cold or temperate

Atmospheric composition: Solar system*

- Such classification would also allow Haze/cloud prediction
  - Reducing: Hydrocarbons (e.g. C_6H_6, Polycyclic aromatic hydrocarbon)
  - Oxidizing: e.g. SO_2, H_2SO_4, H_2O

- Haze
  - Meteorologist: Partile size: tiny
  - Planetary: Photochemicaly produced: Titan-Venus / condensation: earth

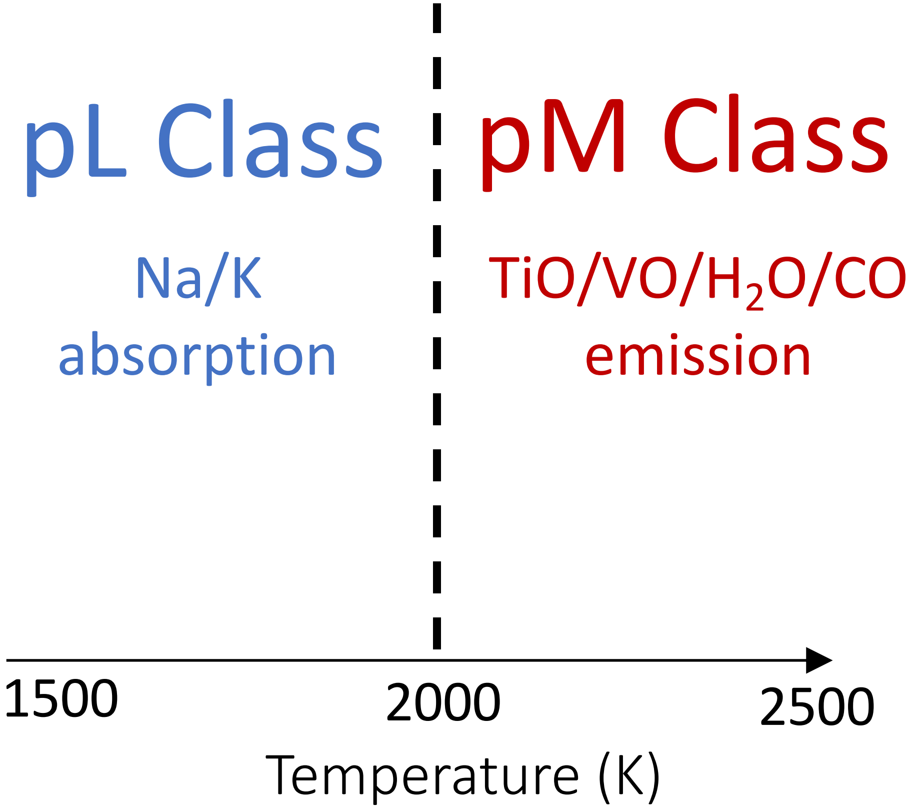
[David Catling lecture 2016]

*Cold or temperate

Atmospheric composition: Exoplanets

“A classification based on incident flux, equilibrium temperature, or other attributes …”

Q



pL Class

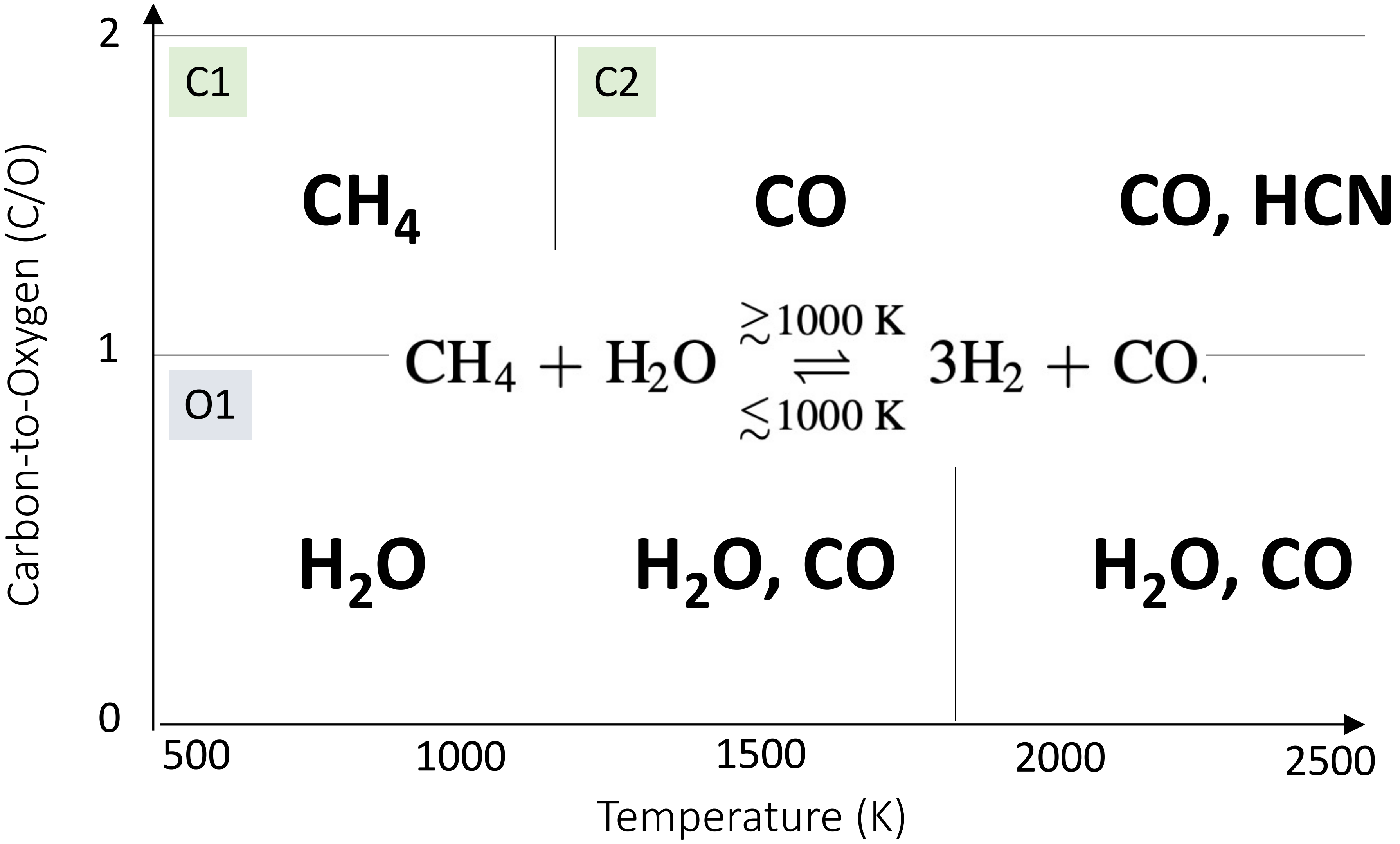
Na/K absorption

pM Class

TiO/VO/H_2O/CO emission

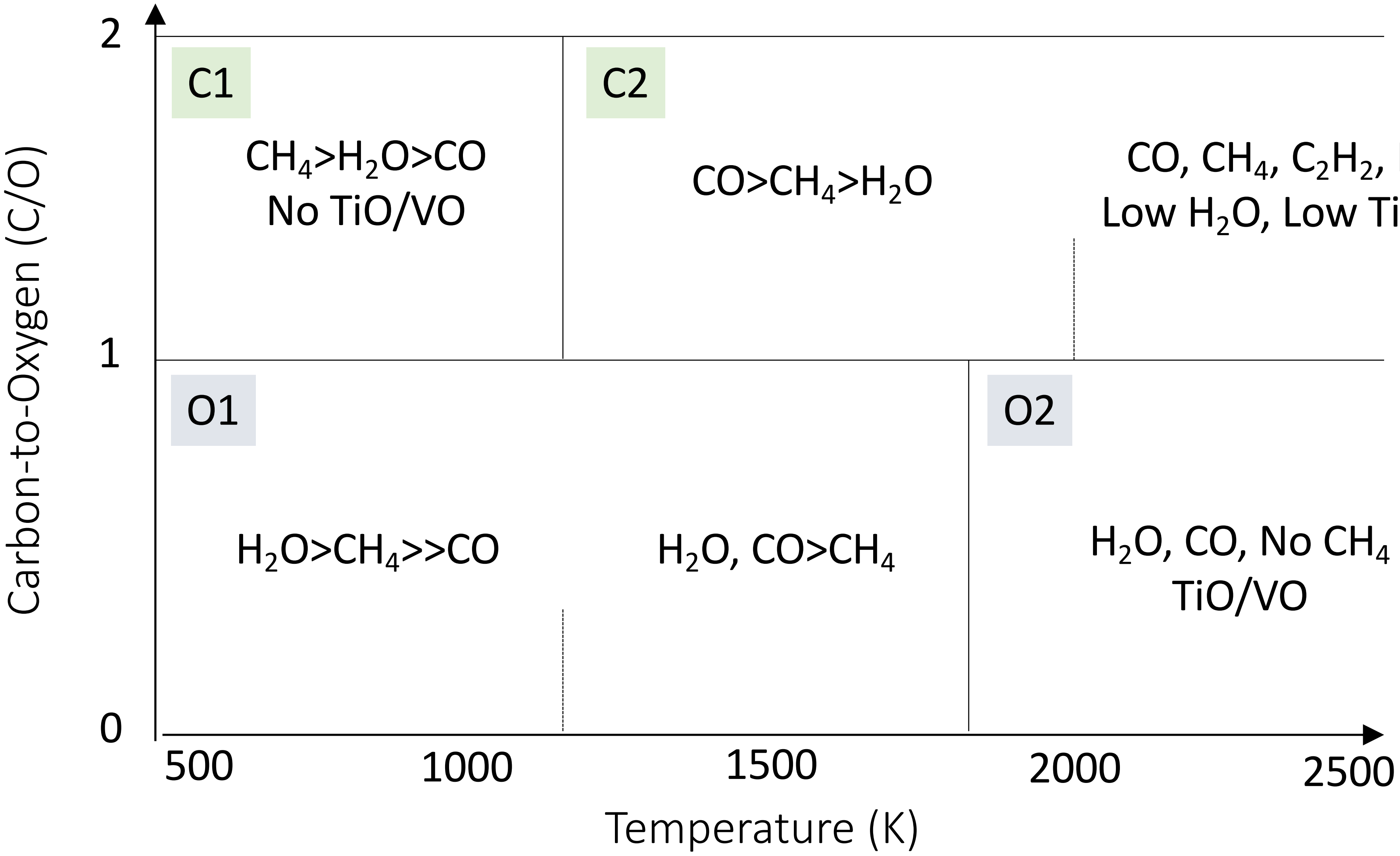
[Fortney et al. 2008]

C/O as a new dimension



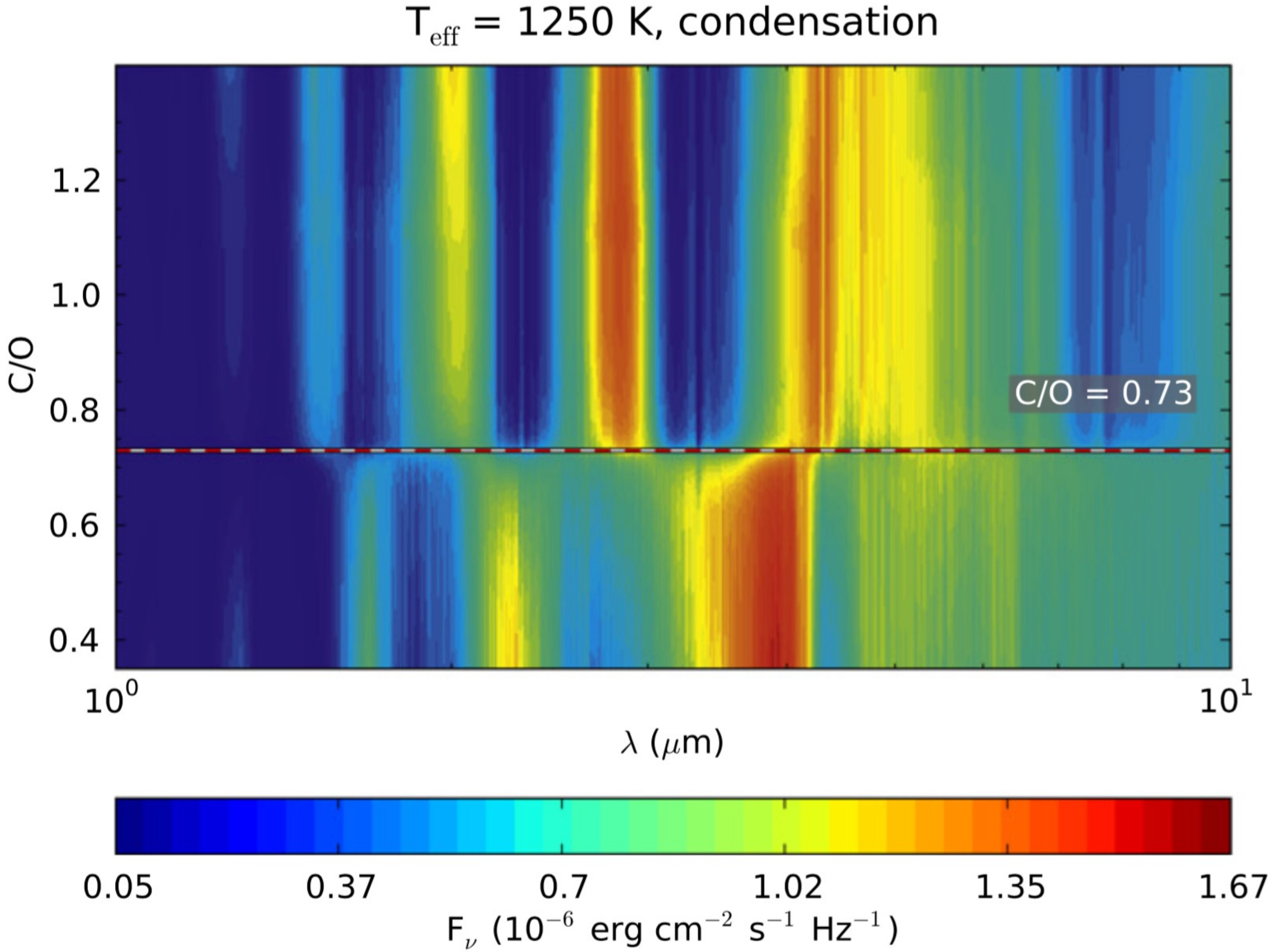
[Madhusudhan 2012]

Chemical Classification



[Madhusudhan 2012]

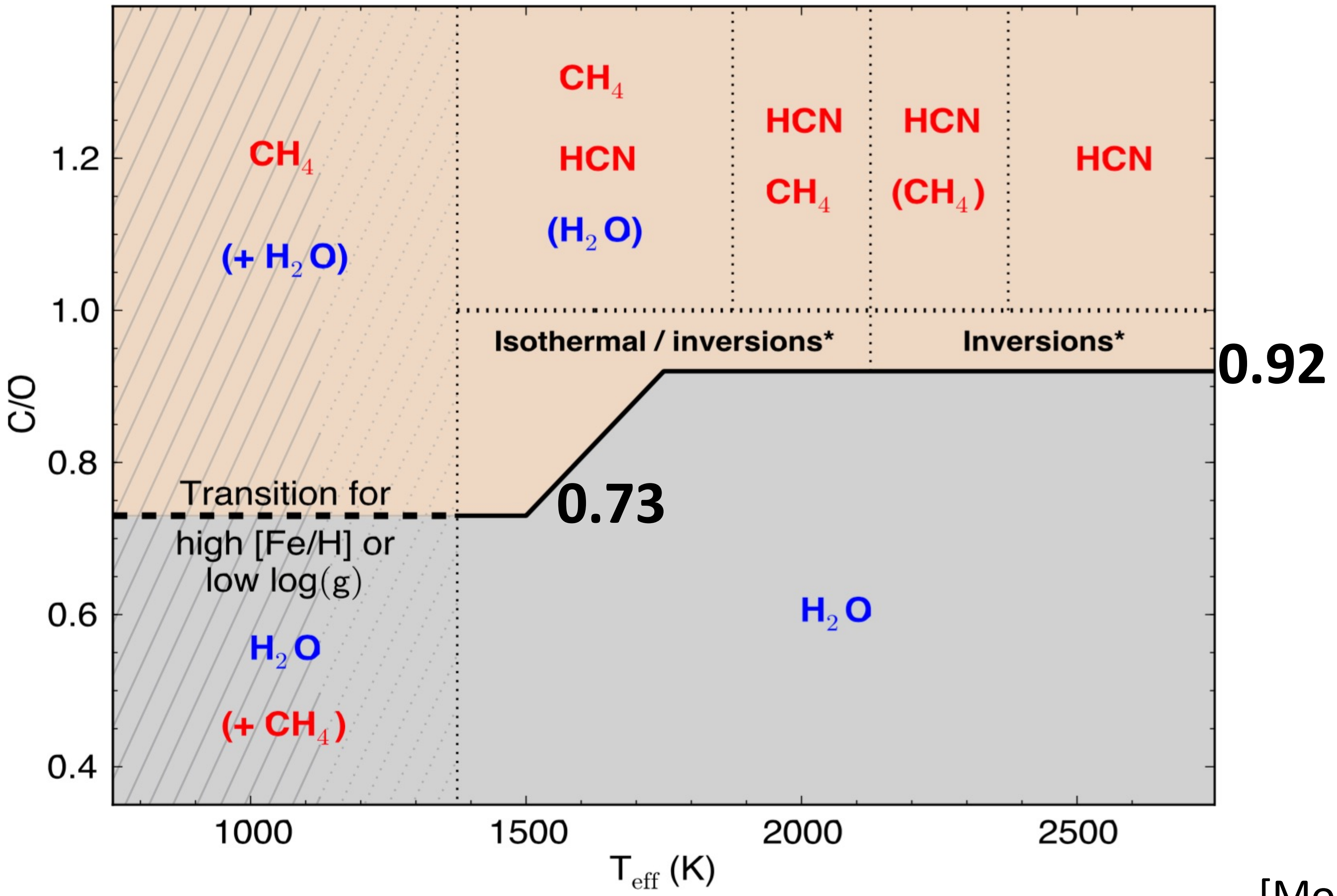
Synthetic emission spectra by petitCODE



[Mollière et al. 2015]

Chemo-Spectral Classification

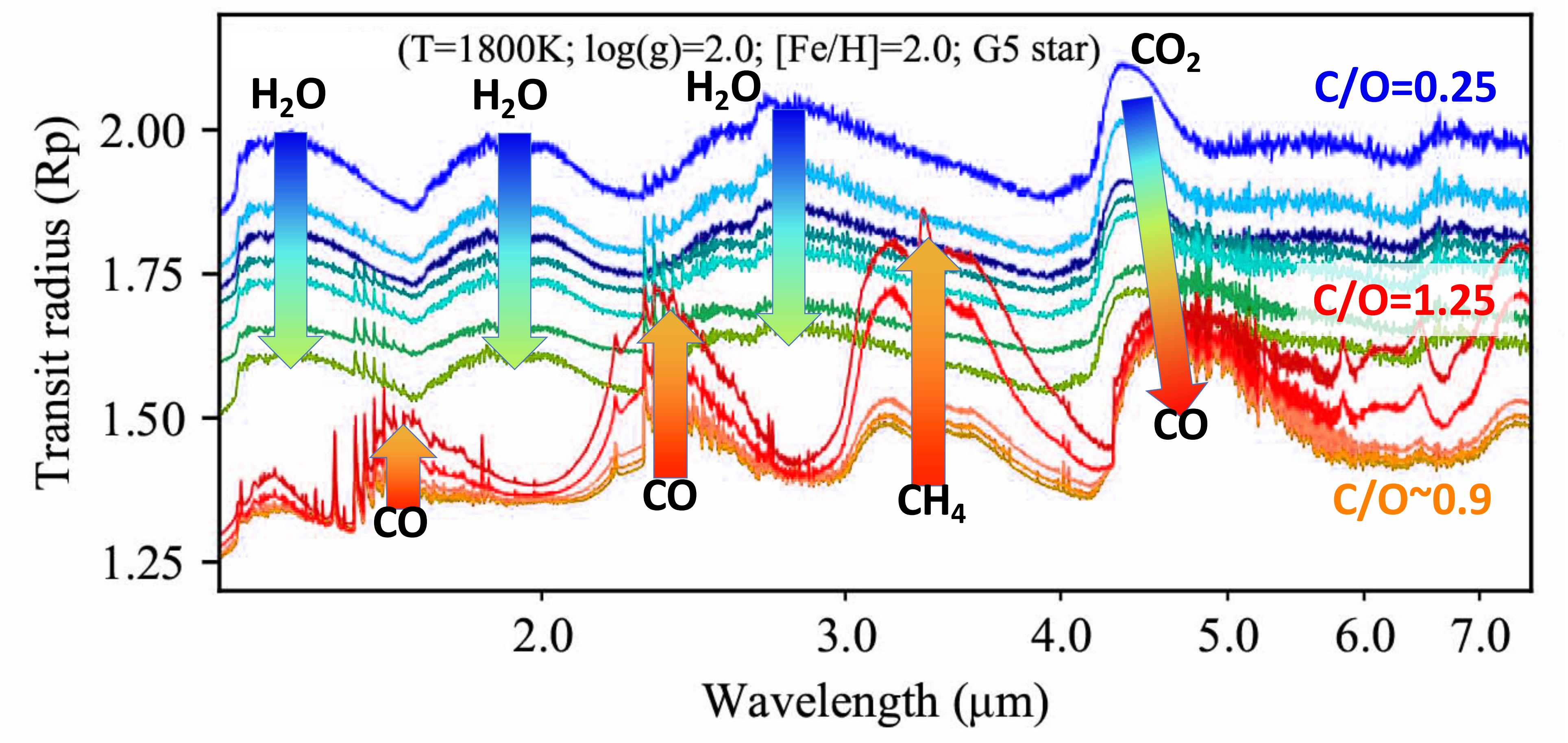
C/O provides a natural Chemo-spectral boundary; although not at 1



[Mollière et al. 2015]

Ch.-Sp. Classification: a quantitative approach

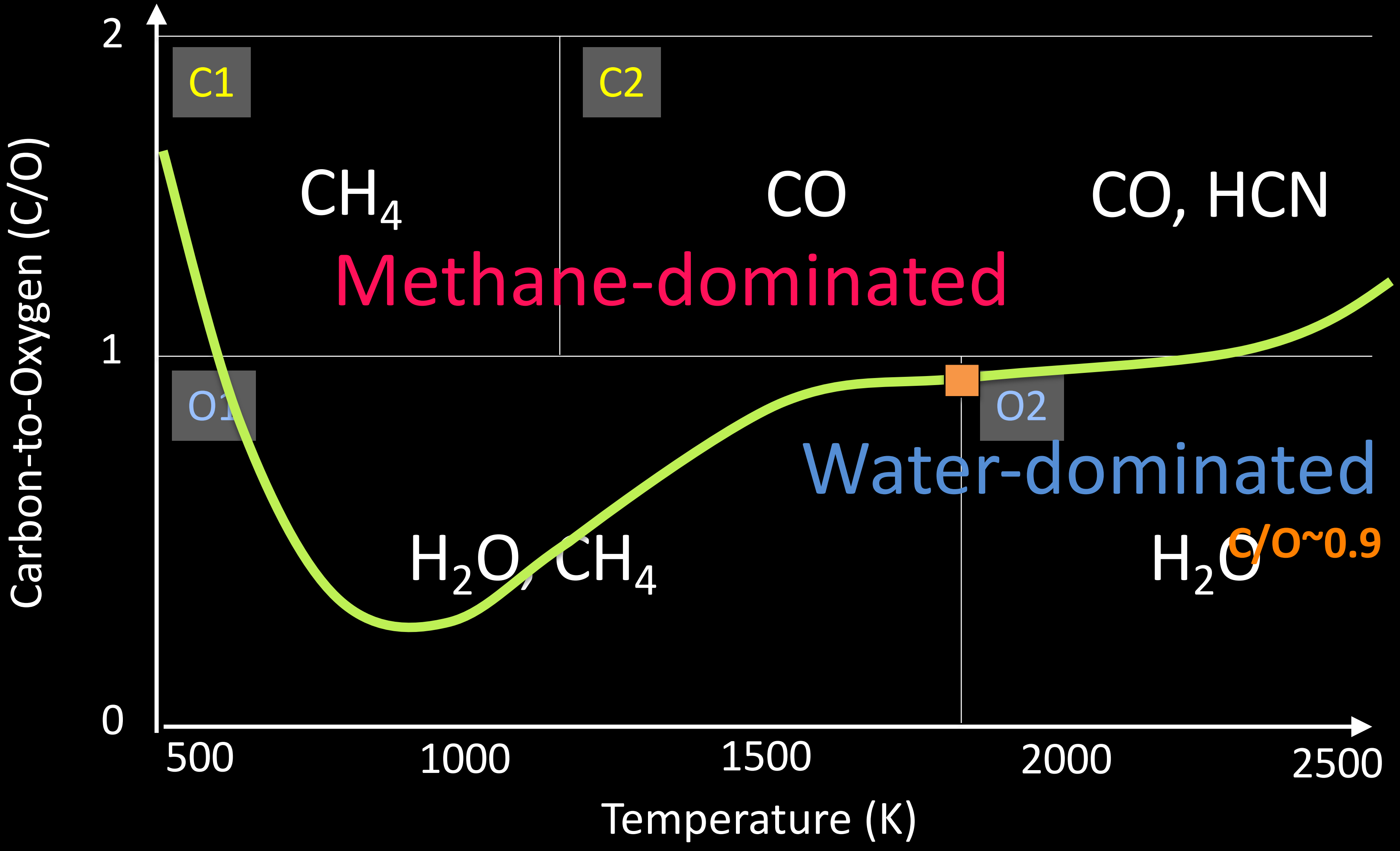
An example:



[Molaverdikhani et al. 2019a]

Dominant Sources in Photosphere

Water- to Methane-dominated spectra



[Molaverdikhani et al 2019a]

Transitional C/O ratios: “four classes”

Complete condensation

Oxygen removal by CO_2/CO as temperature increases

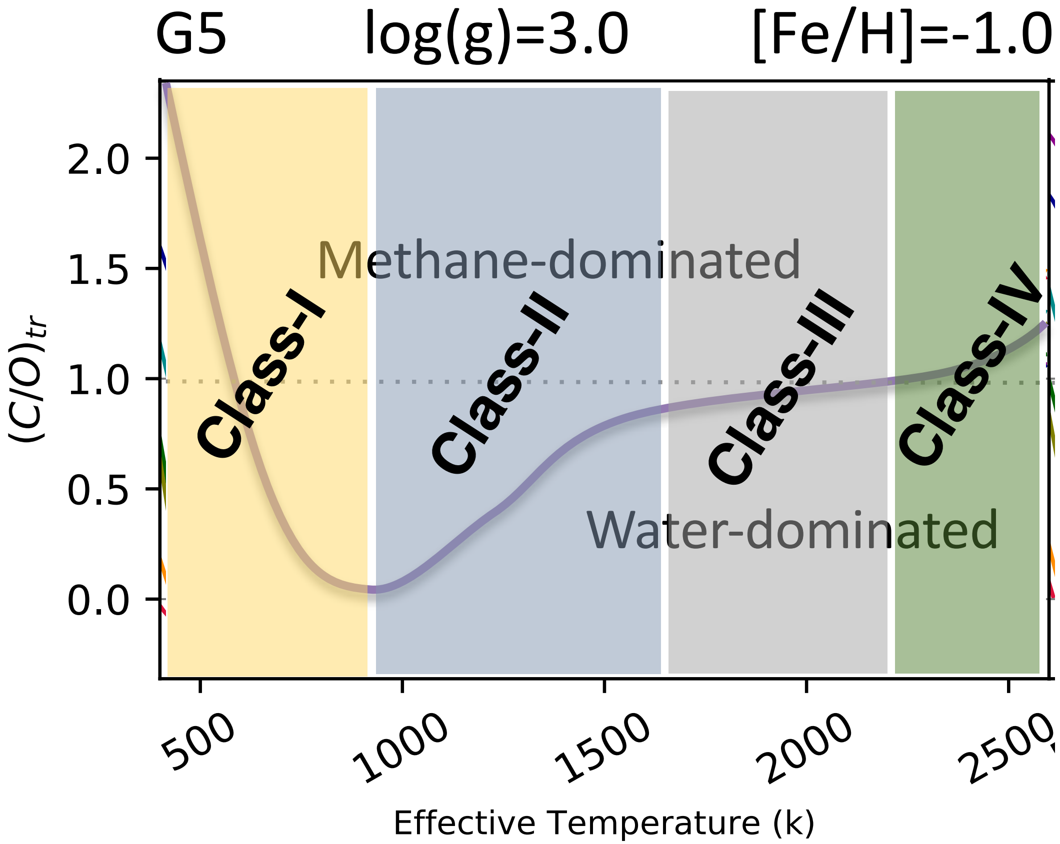
Partial evaporation

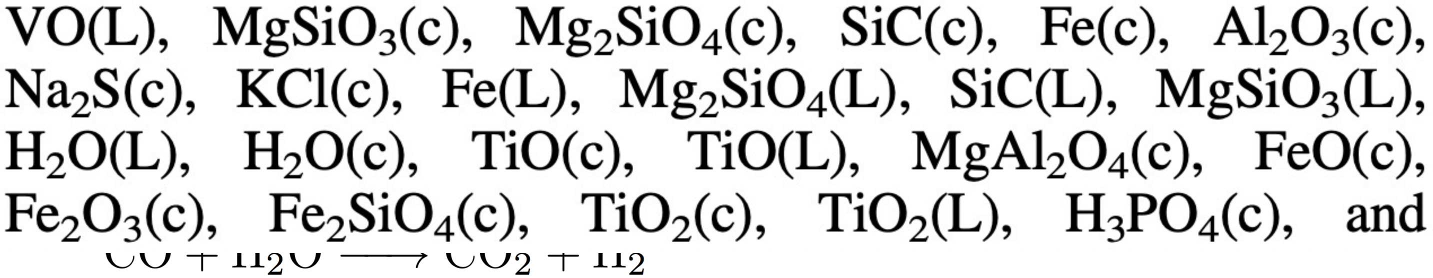
Oxygen abundance increases with temperature

Full evaporation

Oxygen content remains constant

CH_4 destruction by HCN production and water dissociation




$VO(L)$, $MgSiO_3(c)$, $Mg_2SiO_4(c)$, $SiC(c)$, $Fe(c)$, $Al_2O_3(c)$, $Na_2S(c)$, $KCl(c)$, $Fe(L)$, $Mg_2SiO_4(L)$, $SiC(L)$, $MgSiO_3(L)$, $H_2O(L)$, $H_2O(c)$, $TiO(c)$, $TiO(L)$, $MgAl_2O_4(c)$, $FeO(c)$, $Fe_2O_3(c)$, $Fe_2SiO_4(c)$, $TiO_2(c)$, $TiO_2(L)$, $H_3PO_4(c)$, and

$$CO + H_2O \longrightarrow CO_2 + H_2$$

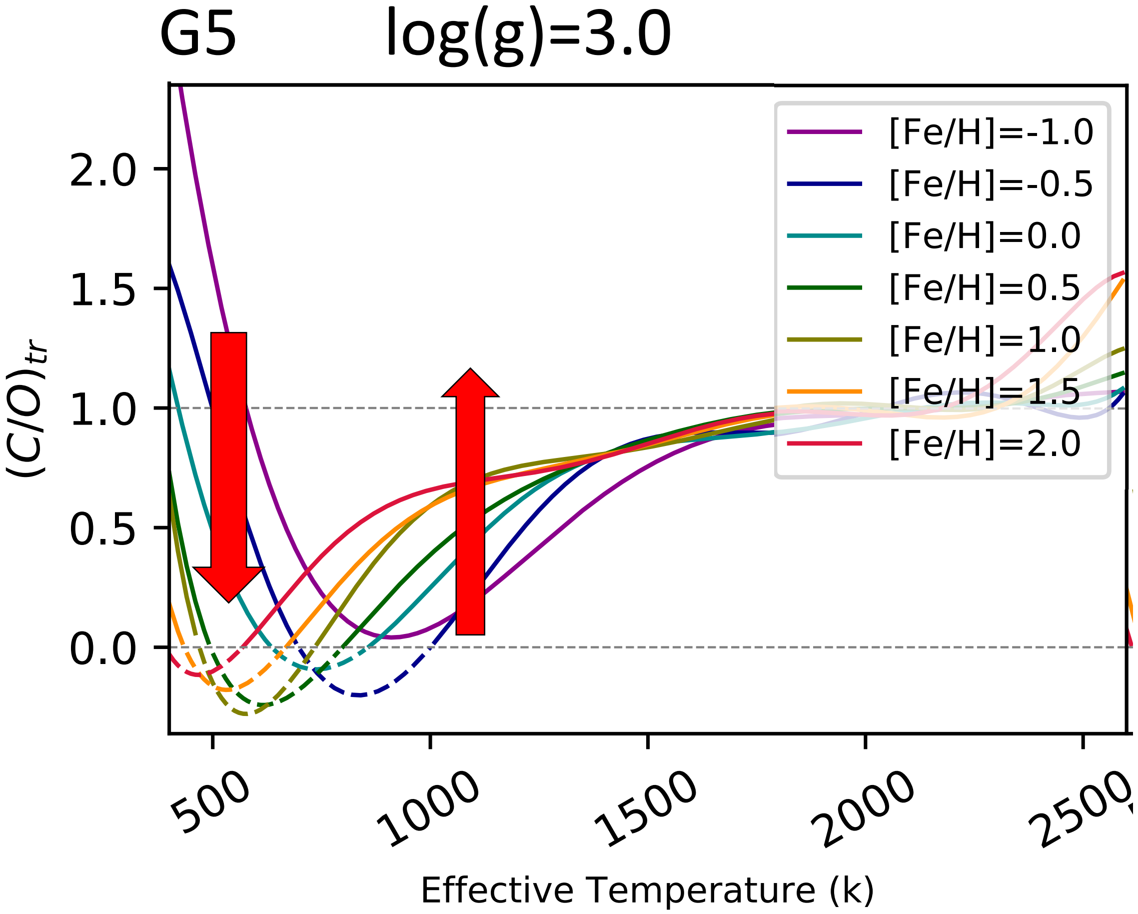
[Molaverdikhani et al. 2019a]

Impact of Metallicity

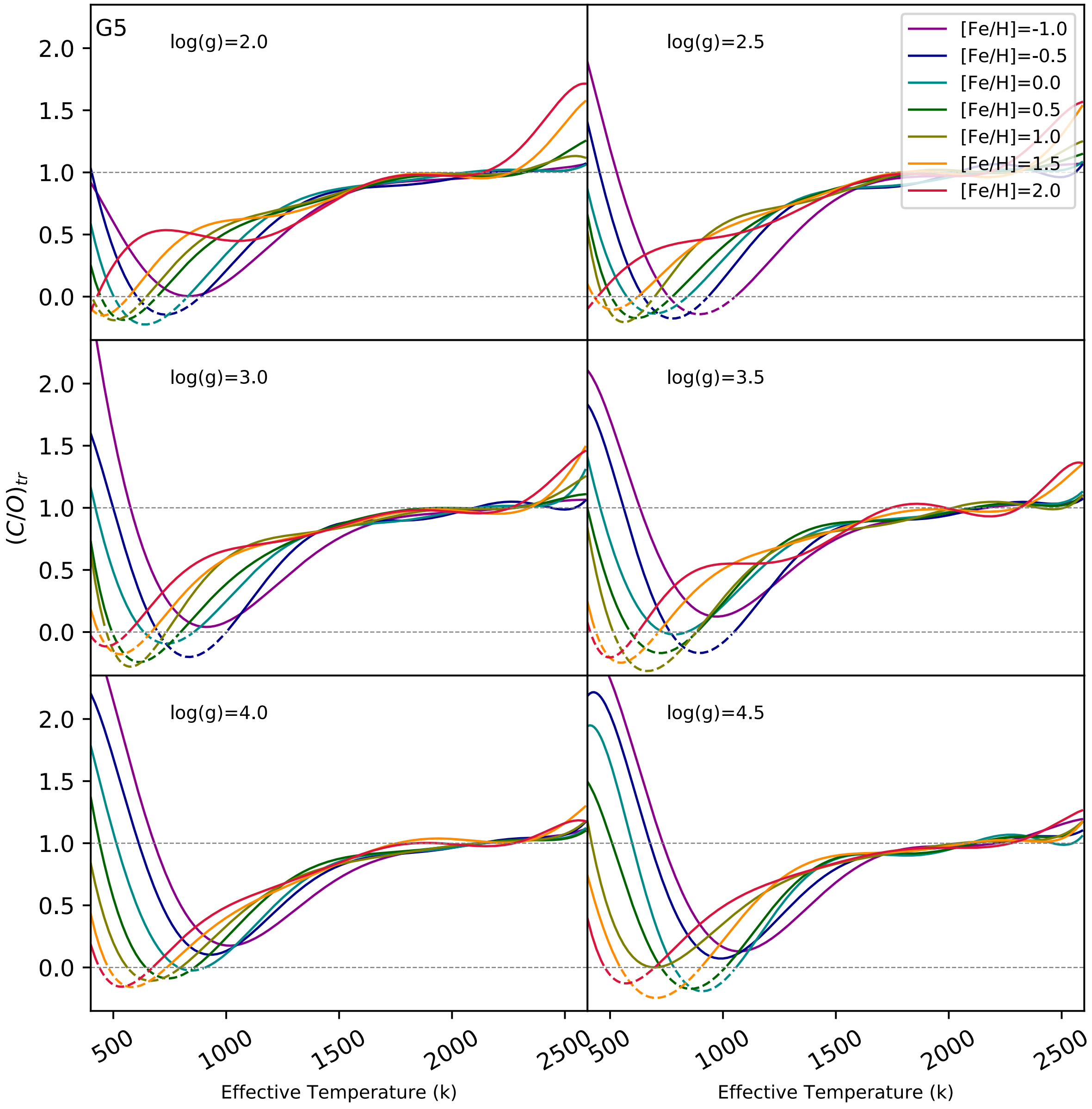
Class-I) At higher metallicity more Oxygen bound in CO_2

$$\mathrm{CO} + \mathrm{H_2O} \longrightarrow \mathrm{CO_2} + \mathrm{H_2}$$

Class-II) At higher metallicity more Oxygen is released by partial evaporation of condensates



Impact of Surface gravity



Lower metallicity

&

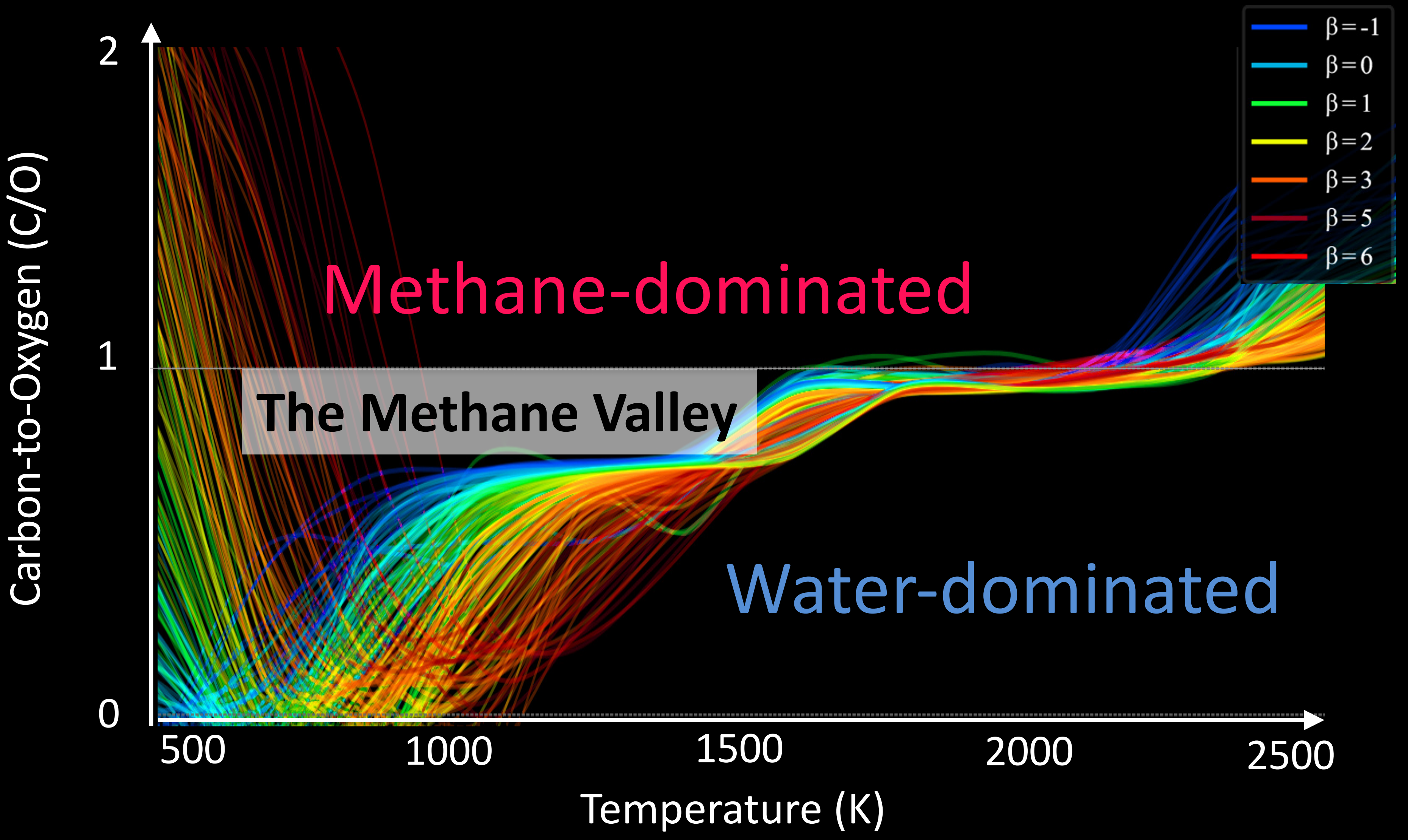
Higher log(g)

result in similar trends

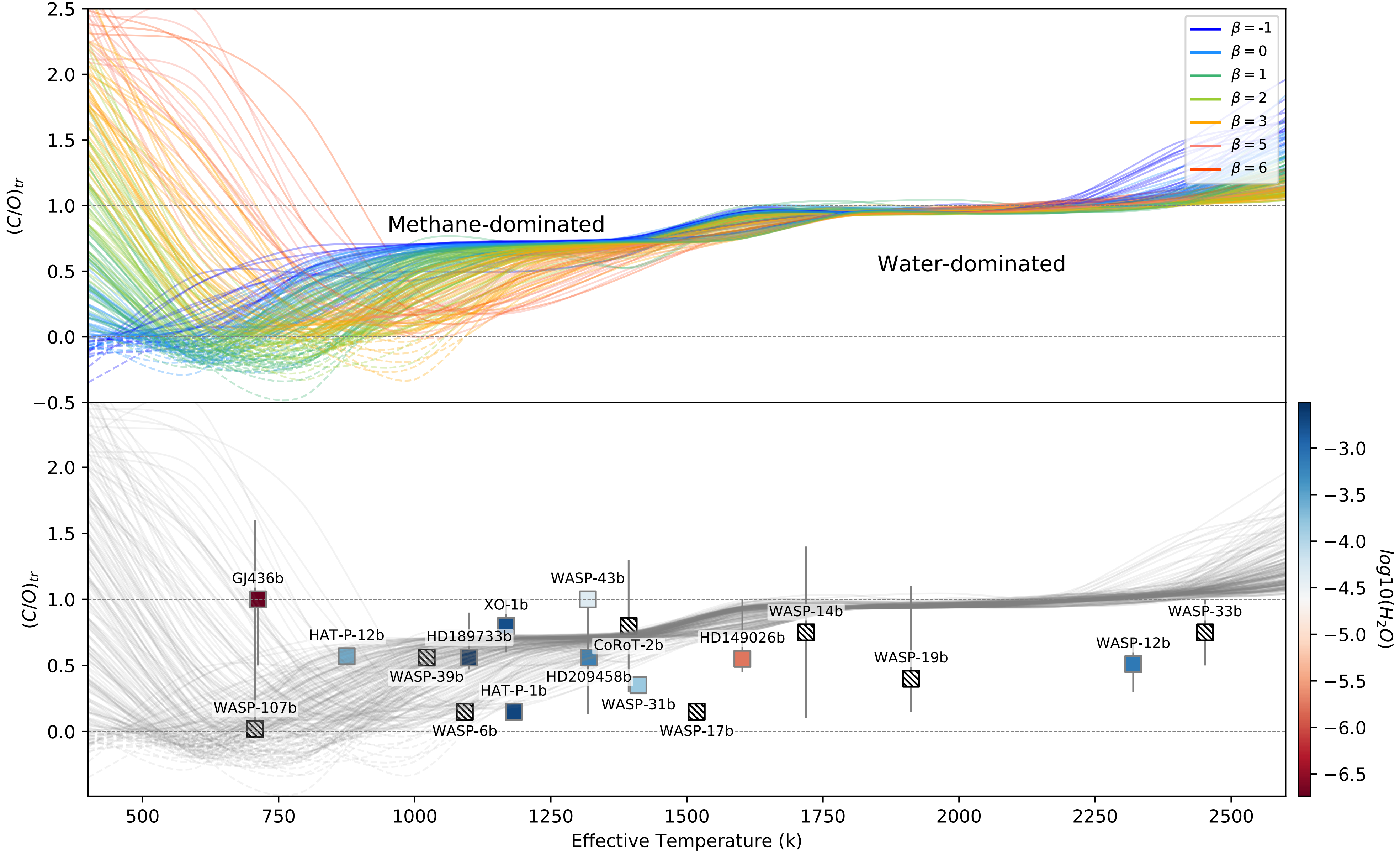
The beta factor:

$$\beta = log(g) - c_\beta[Fe/H]$$

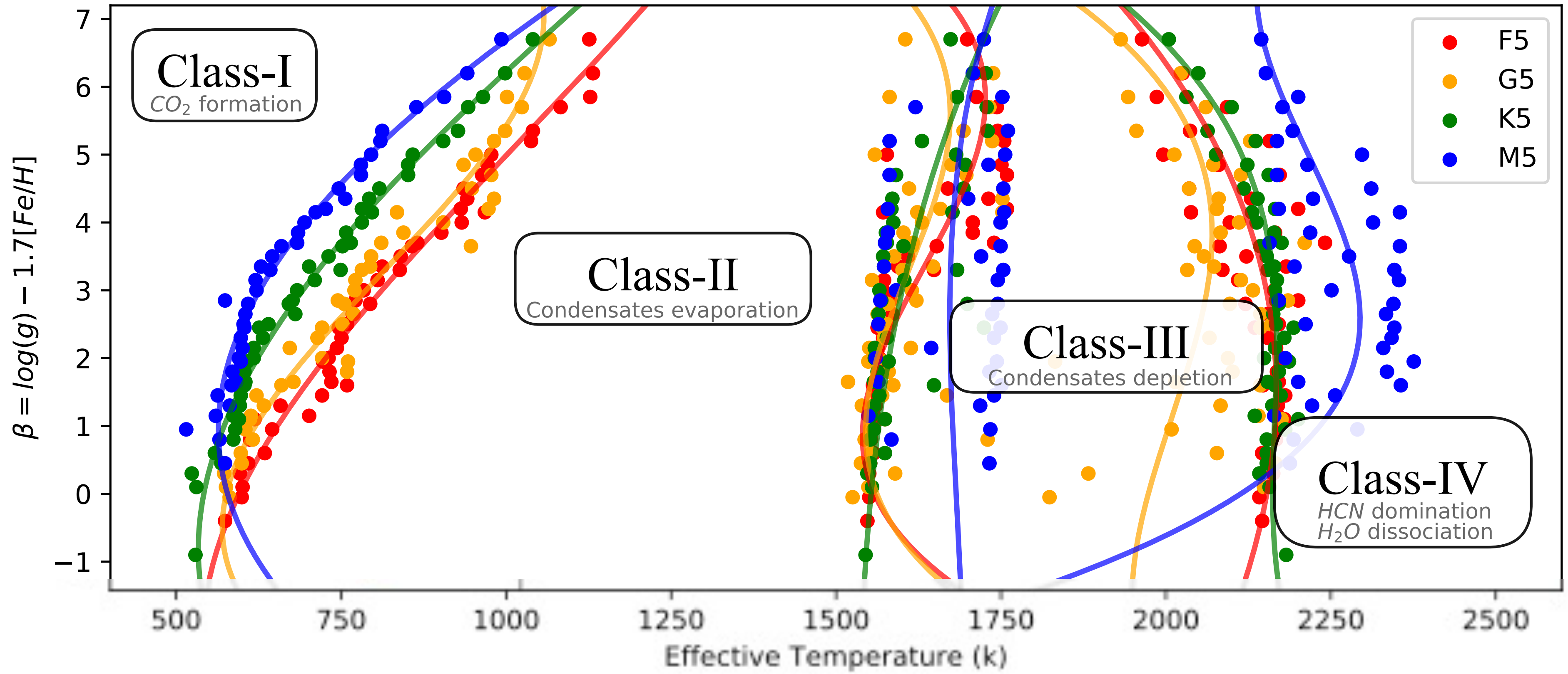
Dominant Sources in Photosphere



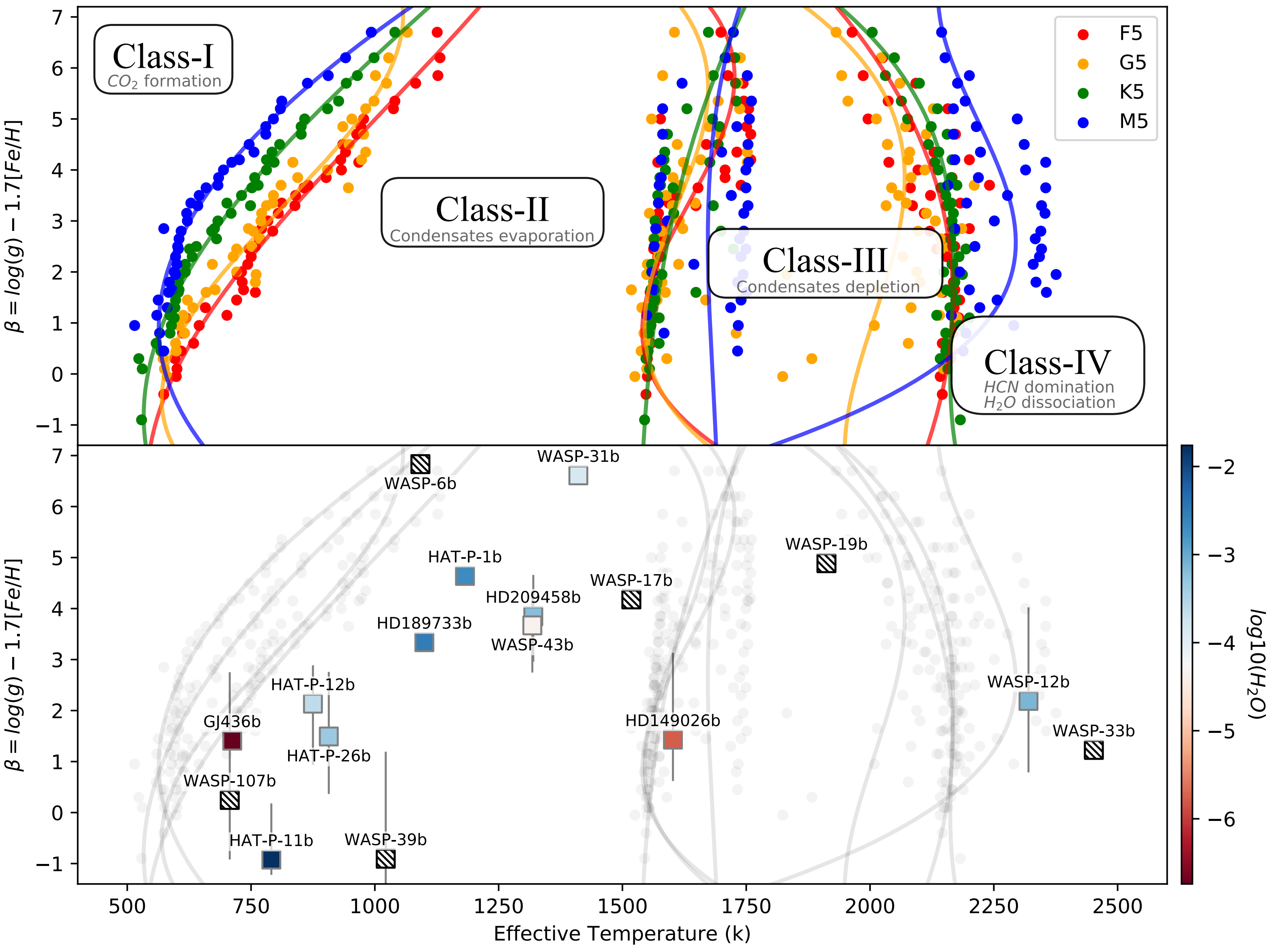
The Methane Valley: Observations



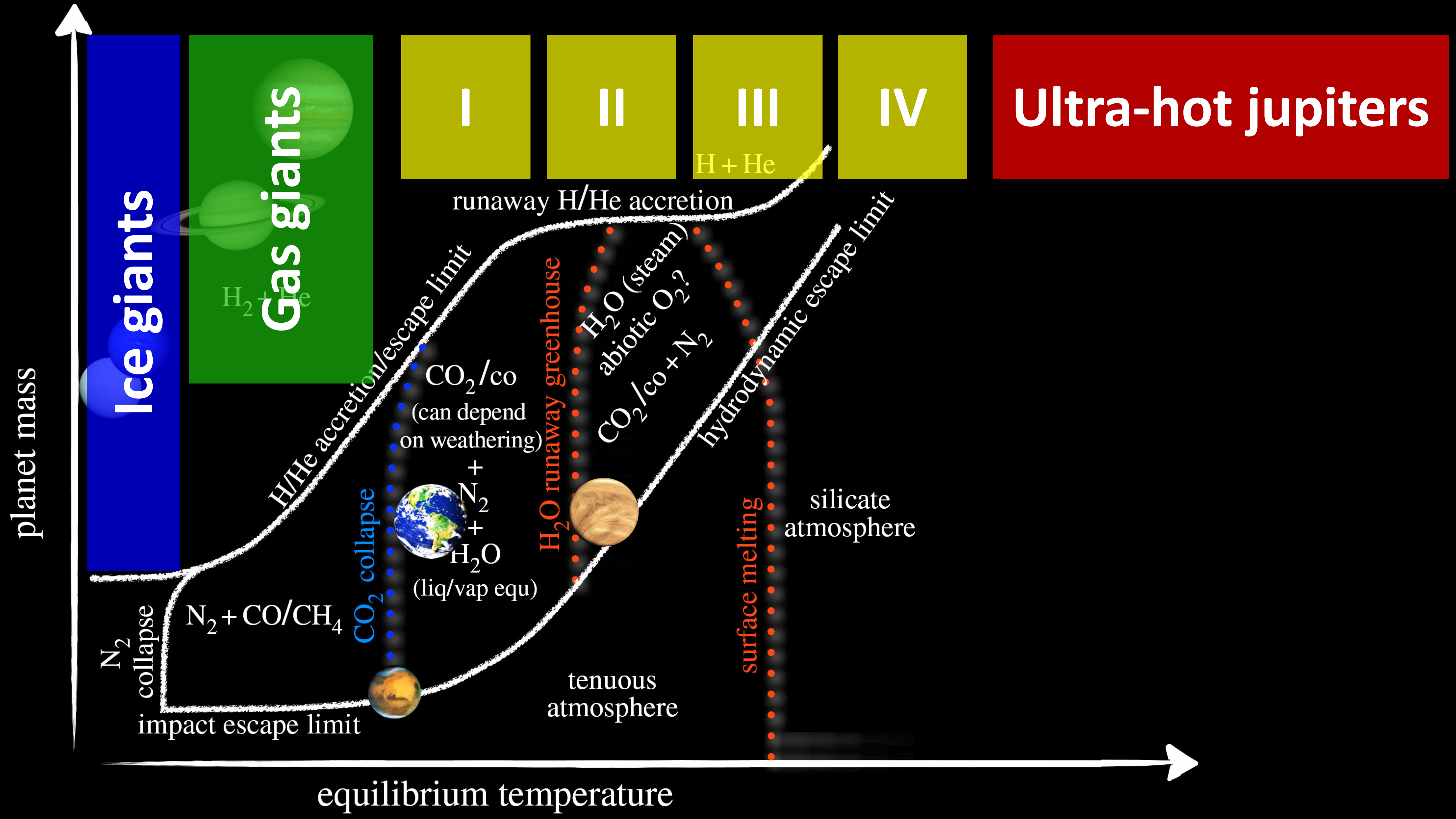
Beta-T_{eff} diagram



Beta-T_{eff} diagram: Observations

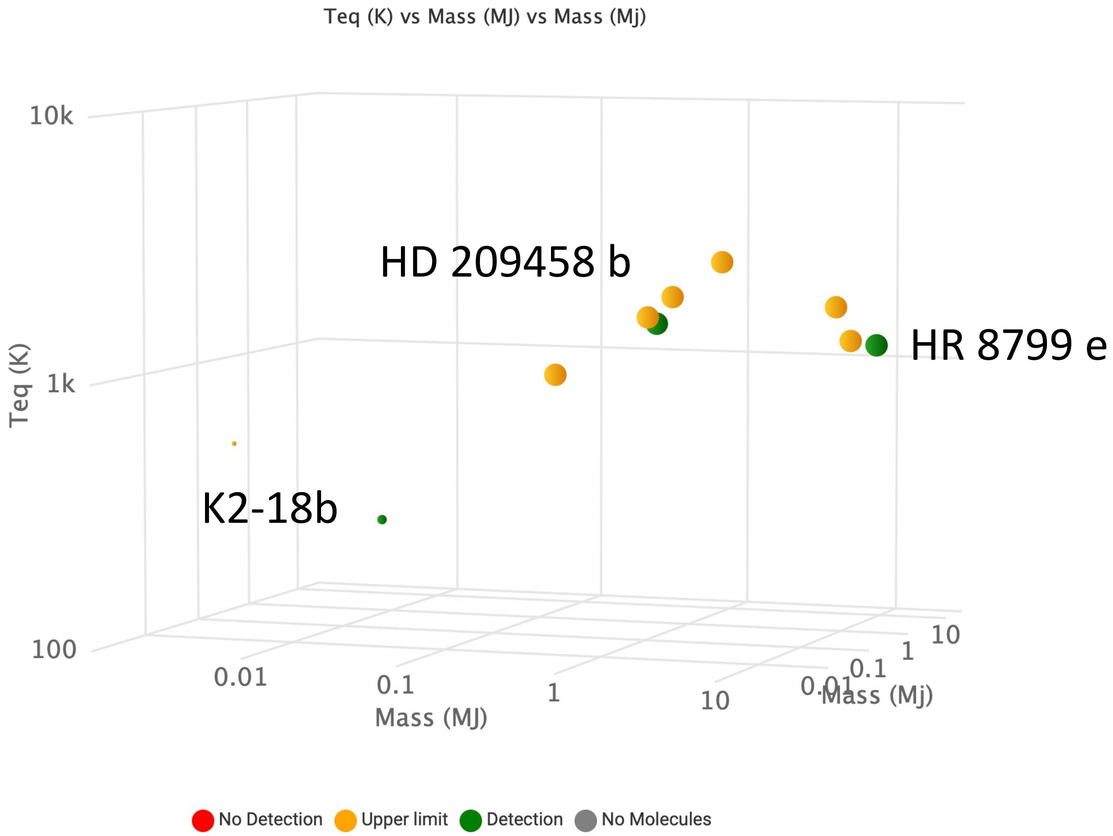


Planetary Periodic Table



Then we should see abundant of CH_4 on exoplanets!

But observations don’t agree with such a prediction!


Teq (K) vs Mass (MJ) vs Mass (Mj)

HD 209458 b

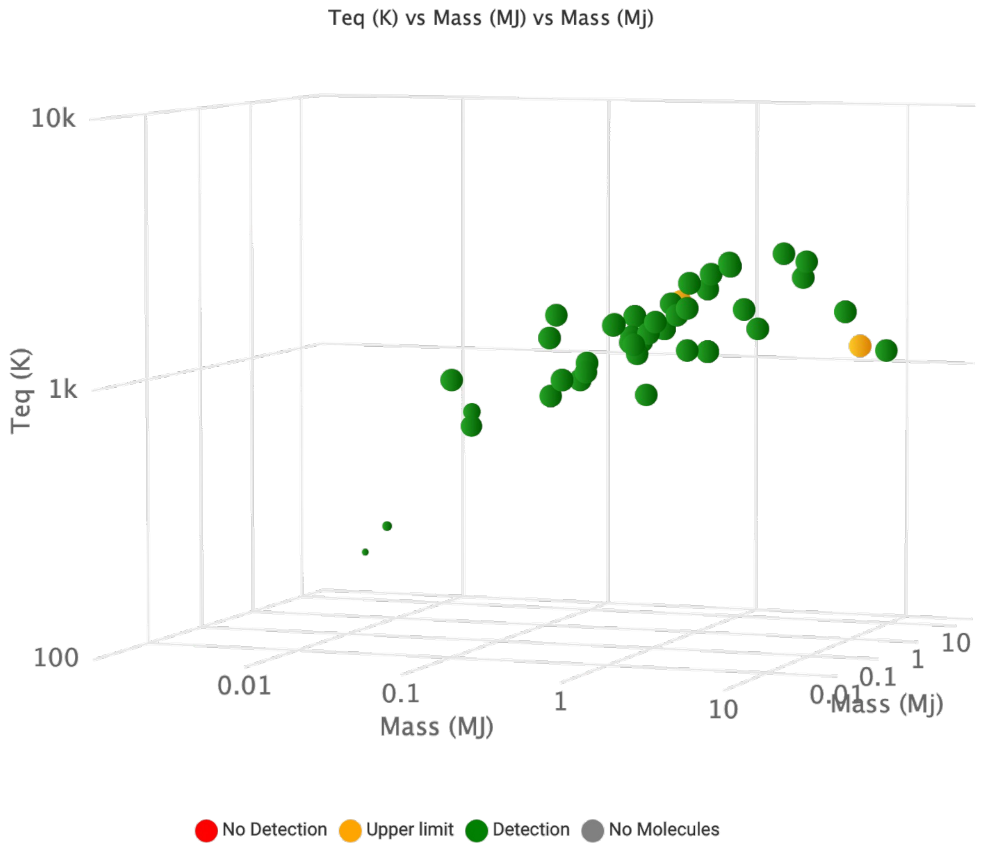
HR 8799 e

K2-18b

http://research.iac.es/proyecto/exoatmospheres/plot.php

Then we should see abundant of CH_4 on exoplanets!

Let’s compare that with **H_2O** detections:



http://research.iac.es/proyecto/exoatmospheres/plot.php

Q

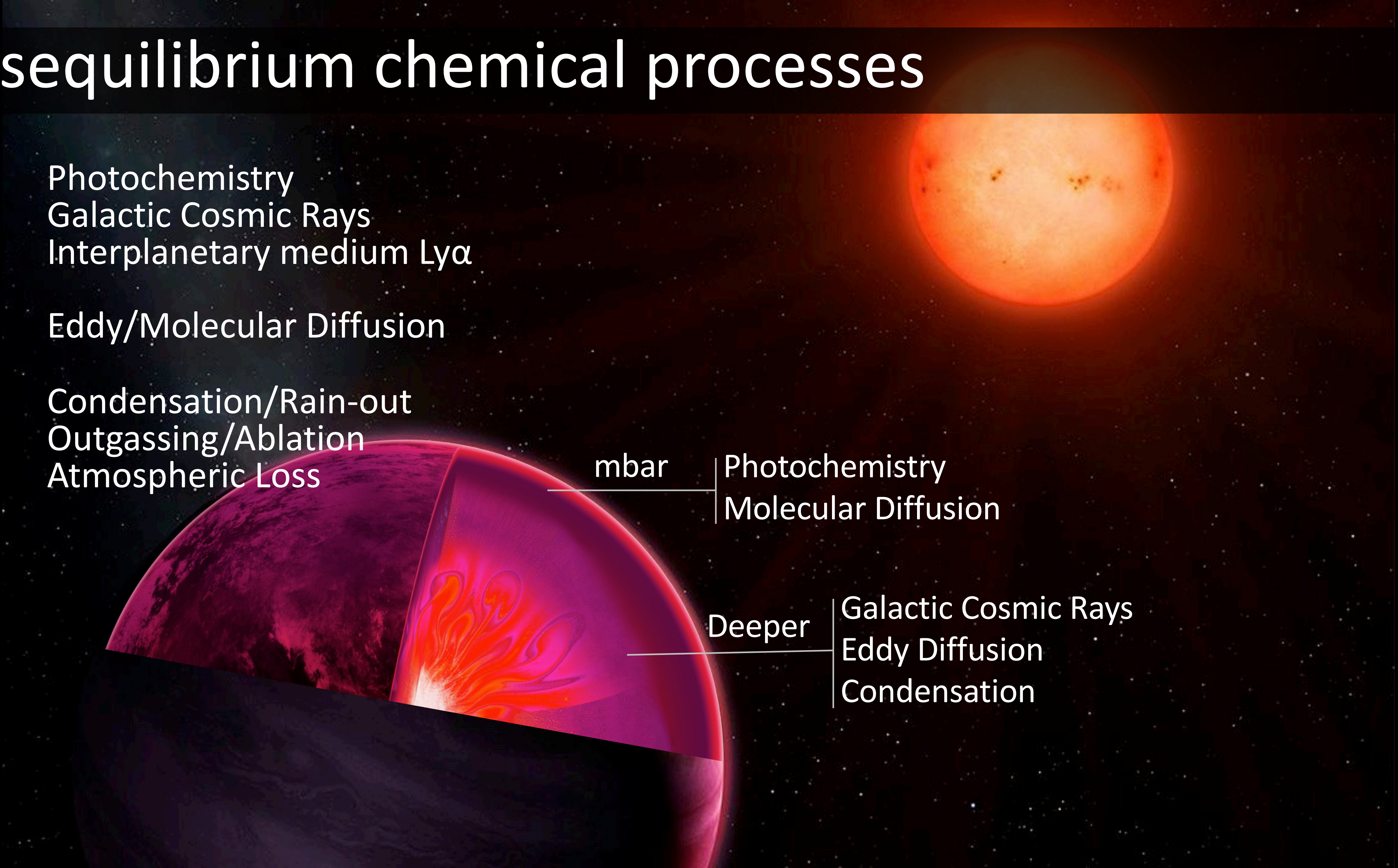
Missing atmospheric processes in our models?

Disequilibrium chemical processes

Photochemistry
Galactic Cosmic Rays
Interplanetary medium Lyα

Eddy/Molecular Diffusion

Condensation/Rain-out
Outgassing/Ablation
Atmospheric Loss



mbar

Photochemistry
Molecular Diffusion

Deeper

Galactic Cosmic Rays
Eddy Diffusion
Condensation

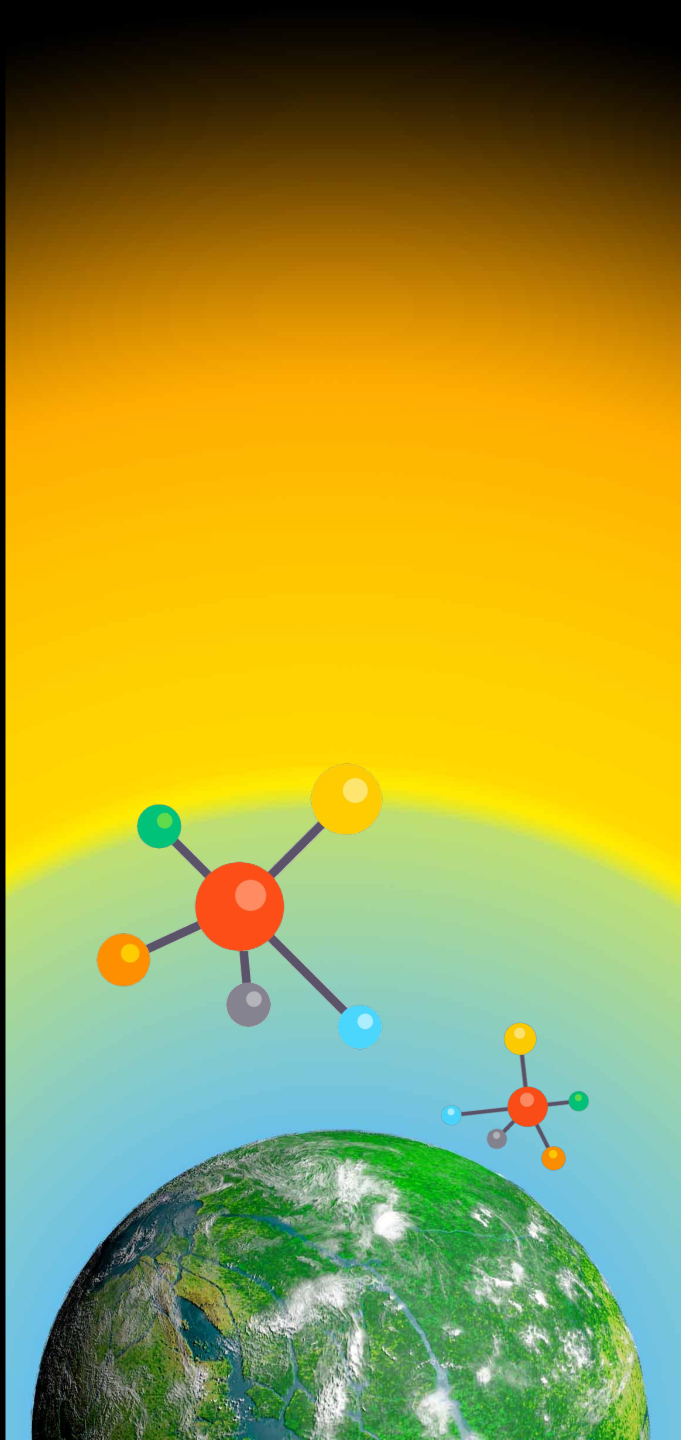
ChemKM

Chemical
Kinetic
Model

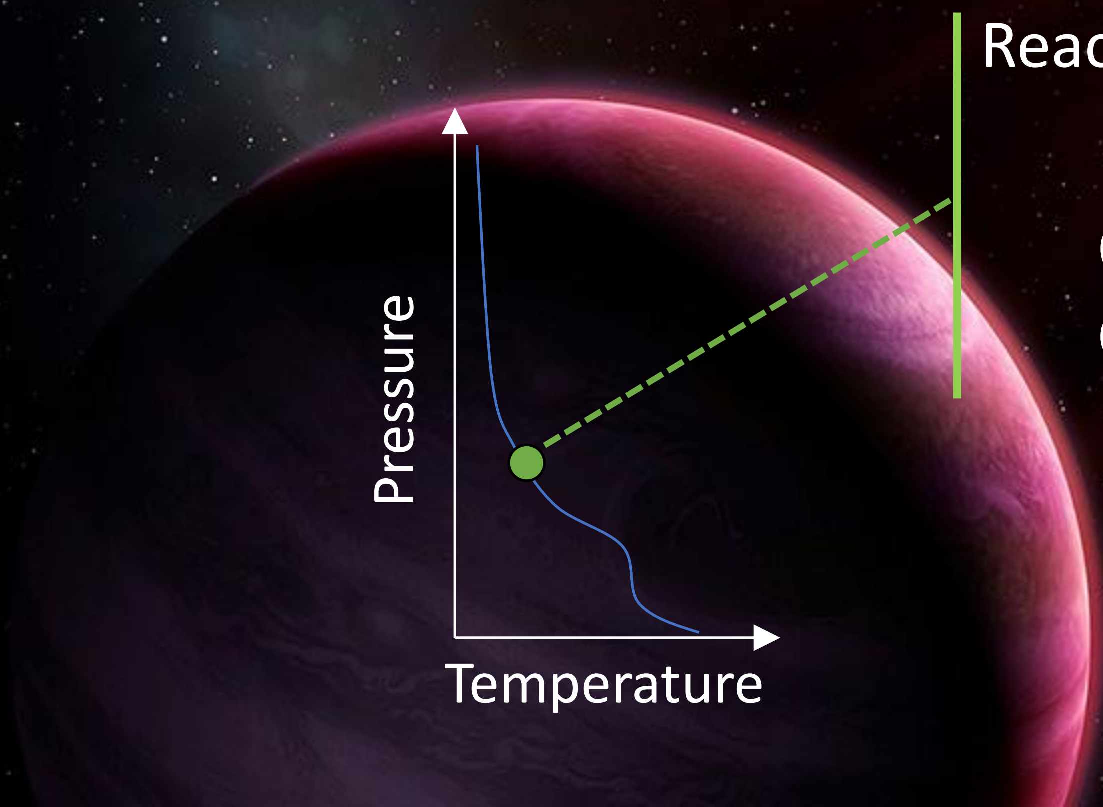
Ten Chemical Networks
Thousands of Reactions
Hundreds of Species

*Not so well documented yet! 🙈

[Molaverdikhani et al. 2019b]



Equilibrium Chemistry: Recall



Reactants

H
O
C

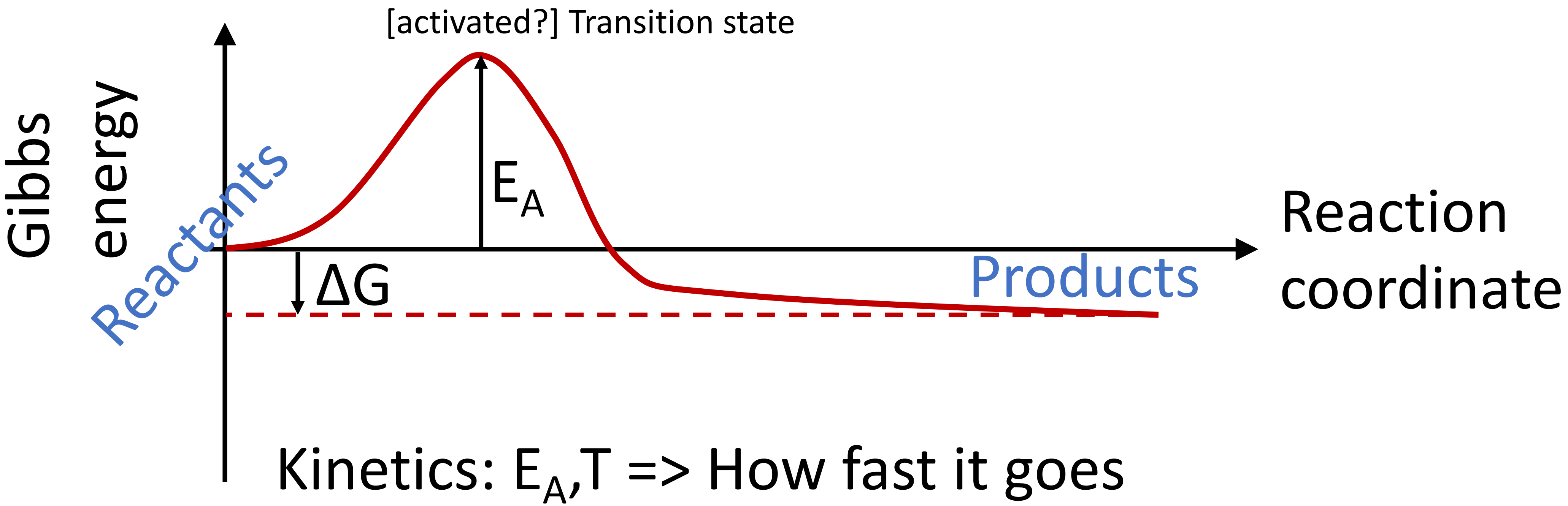
Gibb's Free Energy
$\longrightarrow$
Minimization

Products

H_2O
CH_4
CO
CO_2

Gibb's Free Energy: useful energy for work

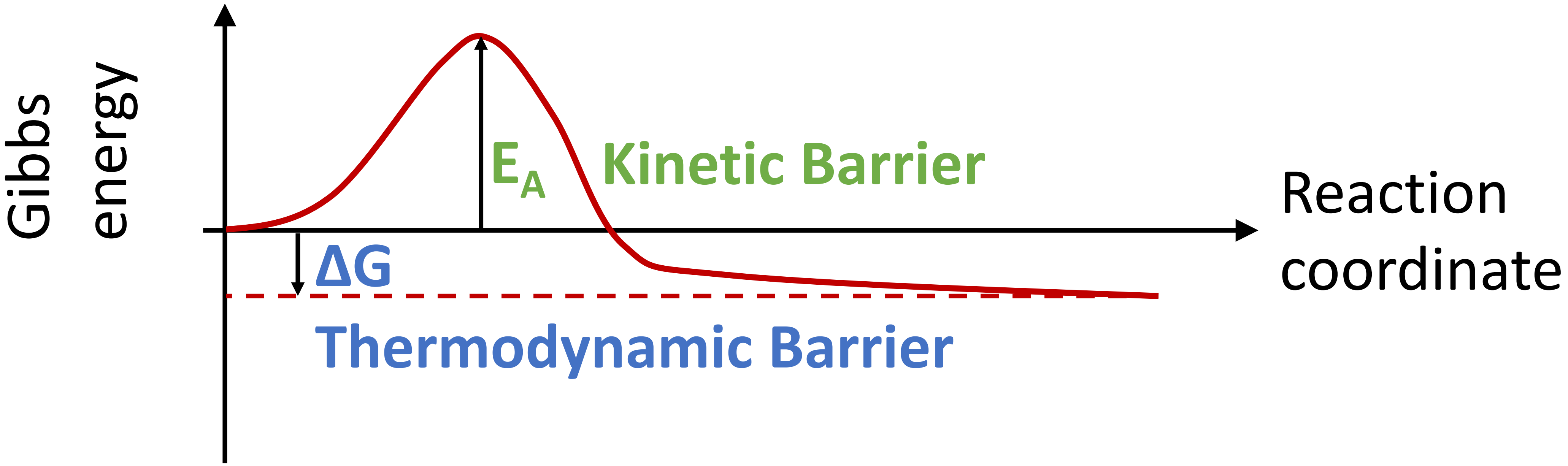
Equilibrium Chemistry: What actually happens[*]?



Kinetics: E_A,T => How fast it goes

*Transition state theory

Equilibrium Chemistry: What actually happens?



Thermodynamics: ΔG<0 => Should happen!

But it may not (and frequently doesn't) happen because of the **activation energy** (which depends on T)

Kinetic Reactions

2 reactants:

$$A + B \longrightarrow AB^{*} \longrightarrow C + D$$

Rate:

- **collision frequency:** ~ [A]·[B]
- Number of reactions per unit volume and unit time =

$$R_r = k_r n_A^{m} n_B^{n}$$

Rate coefficient
or rate constant

From lab measurements or
computational quantum chemistry

The Arrhenius equation

Gives the dependence of the rate constant of a chemical reaction on the absolute temperature as

$$k = Ae^{\frac{-E_a}{RT}}$$

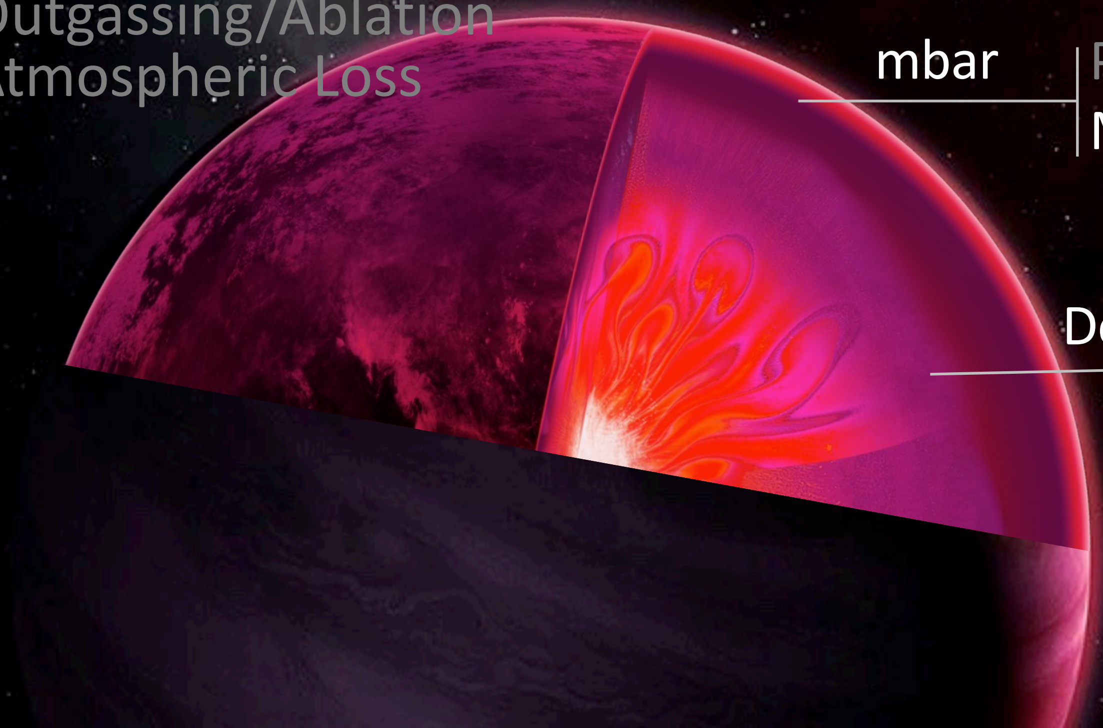
- k is the rate constant (frequency of collisions resulting in a reaction),
- T is the absolute temperature (in degrees Kelvin or Rankine),
- A is the pre-exponential factor. Arrhenius originally considered A to be a temperature-independent constant for each chemical reaction. However more recent treatments include some temperature dependence (Modified Arrhenius equation).
- Ea is the activation energy for the reaction (in the same units as RT),
- R is the universal gas constant

Disequilibrium chemical processes

Photochemistry
Galactic Cosmic Rays
Interplanetary medium Lyα

Eddy/Molecular Diffusion

Condensation/Rain-out
Outgassing/Ablation
Atmospheric Loss



mbar
- Photochemistry
- Molecular Diffusion

Deeper
- Galactic Cosmic Rays
- Eddy Diffusion
- Condensation

The equation of chemical kinetics

$$\frac{\partial n_i}{\partial t} = P_i - n_i L_i - \frac{\partial \Phi_i}{\partial z},$$

- n_i is the number density (cm^{-3})
- P_i is the total production rate (cm^{-3} s^{-1})
- L_i is the total loss rate (s^{-1}),
- ϕ_i is the net vertical flux (cm^{-2} s^{-1}) of species i at altitude z
    - (with respect to a reference level; usually 1 bar for gaseous giants)

The diffusion term

$$\Phi_{i,mol} = -n_T D_i \left(\frac{\partial f_i}{\partial z} - \frac{f_i}{H_a} + \frac{f_i}{H_i} + \frac{\alpha_i f_i}{T} \frac{dT}{dz} \right)$$

$$\Phi_{i,eddy} = -n_T K_{zz} \left(\frac{\partial f_i}{\partial z} \right),$$

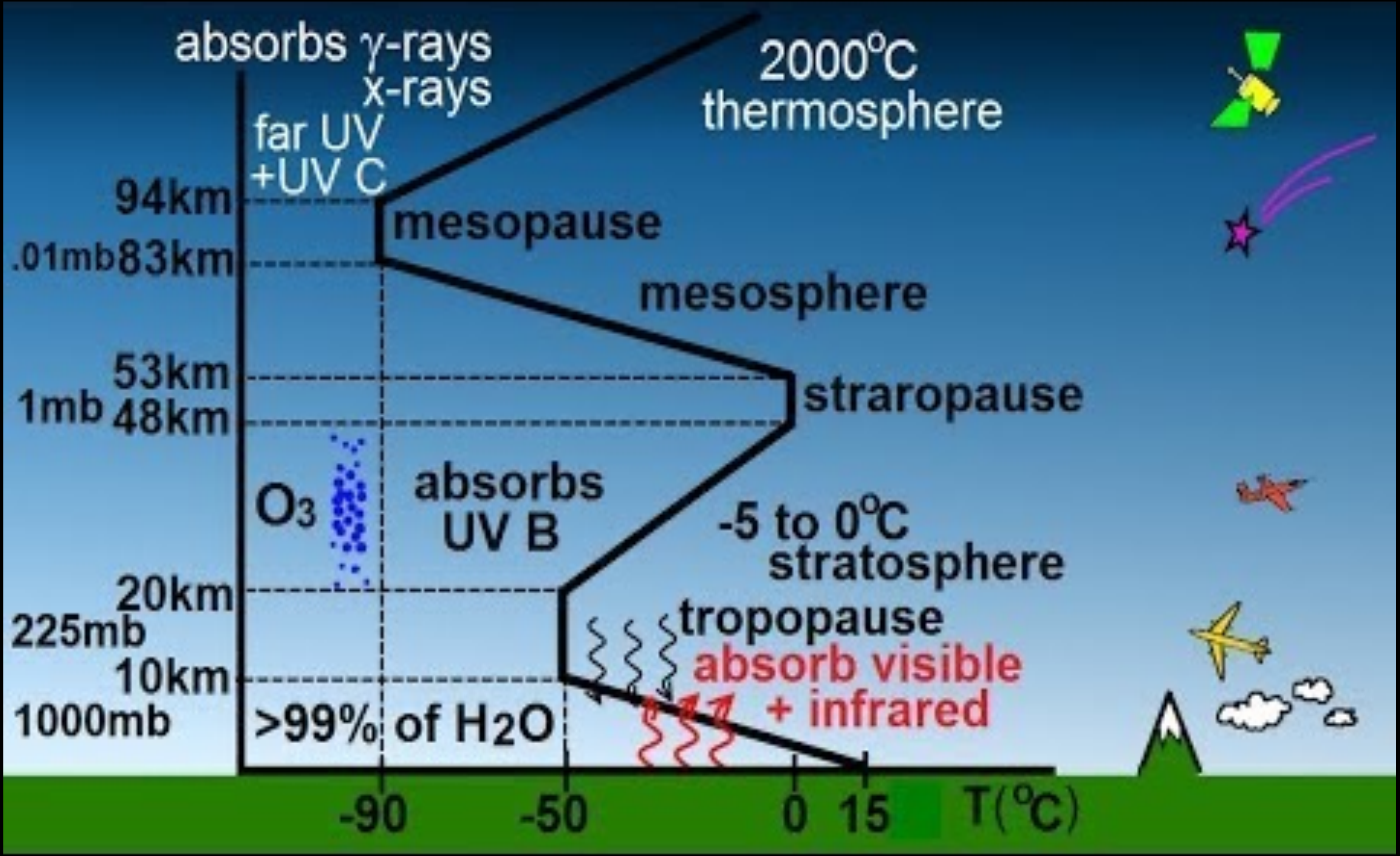
Atmospheric structure plays a key role

$f_i = n_i / n_T$

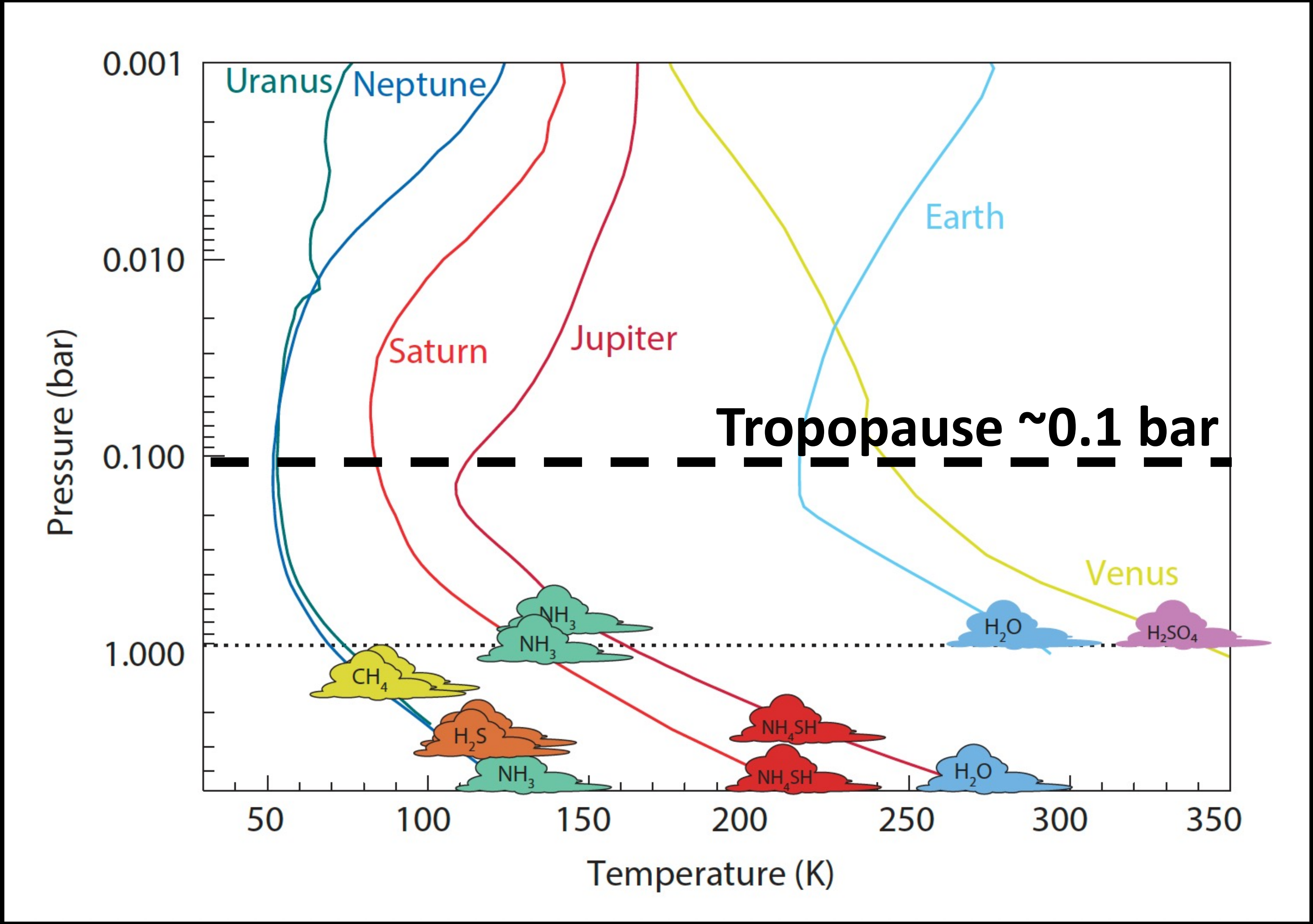
- K_{zz} is the eddy diffusion coefficient ($cm^2\ s^{-1}$),
- D_i is the molecular diffusion coefficient ($cm^2\ s^{-1}$),
- H_a is the mean scale height of the atmosphere,
- H_i is the scale height of species i,
- T is the gas kinetic temperature (K),
- and α_i is the thermal diffusion factor of species i.

Atmospheric structure: Earth

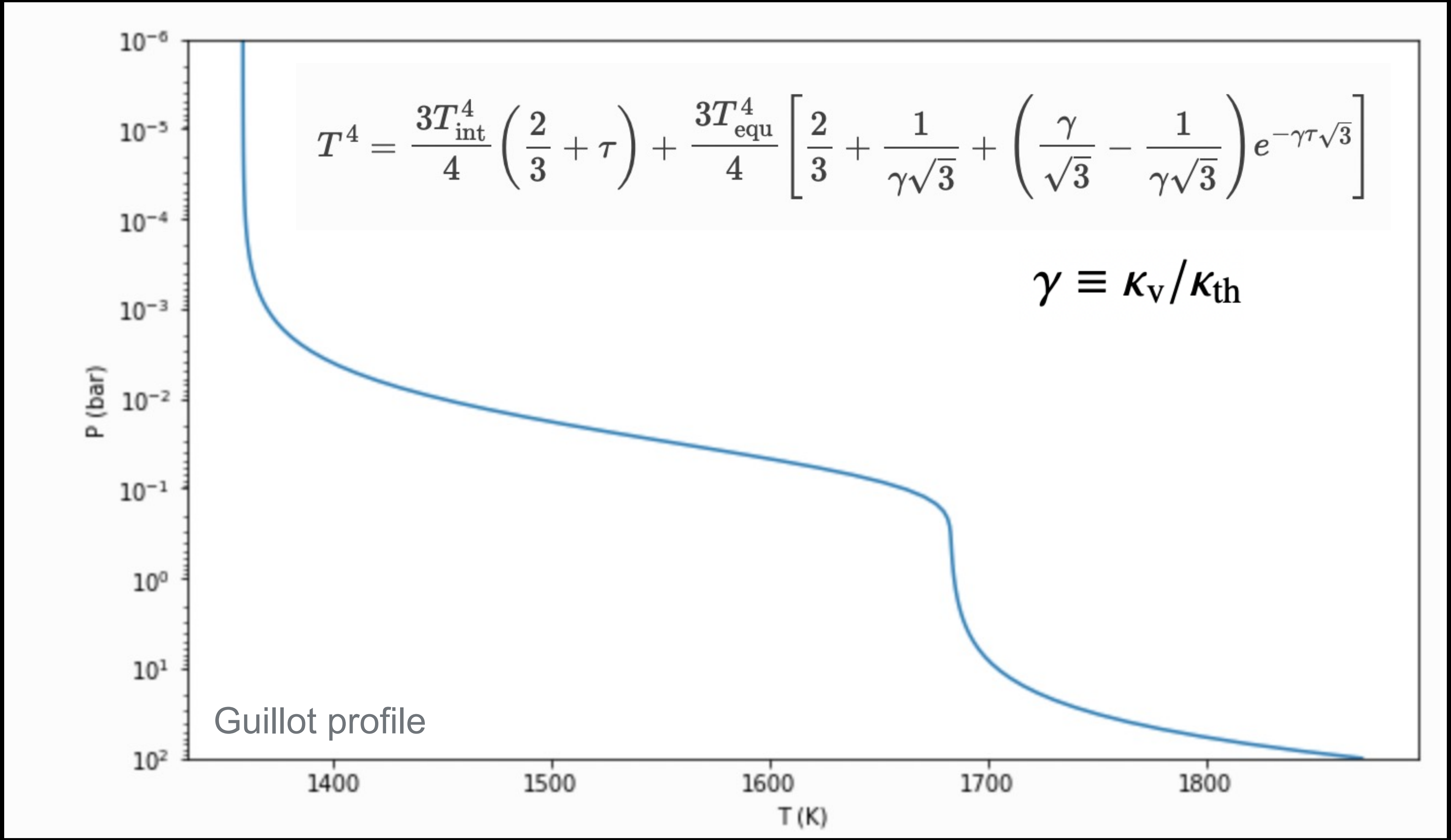
Q



Atmospheric structure: Solar system



Atmospheric structure: Exoplanets



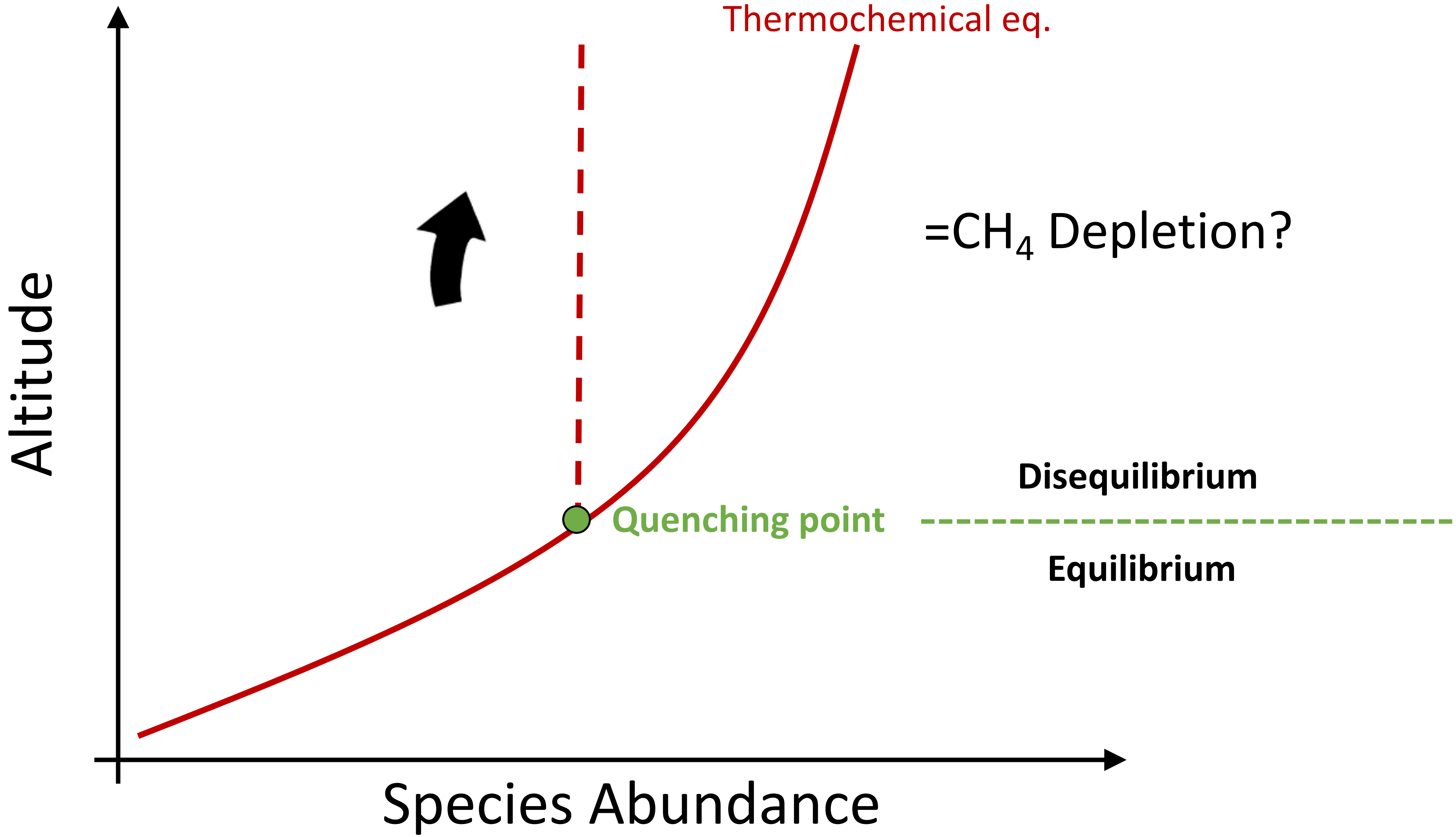
$$T^4 = \frac{3T_{\mathrm{int}}^4}{4}\left(\frac{2}{3}+\tau\right) + \frac{3T_{\mathrm{equ}}^4}{4}\left[\frac{2}{3}+\frac{1}{\gamma\sqrt{3}}+\left(\frac{\gamma}{\sqrt{3}}-\frac{1}{\gamma\sqrt{3}}\right)e^{-\gamma\tau\sqrt{3}}\right]$$

$$\gamma \equiv \kappa_{\mathrm{v}}/\kappa_{\mathrm{th}}$$

https://petitradtrans.readthedocs.io

Eddy Diffusion (Vertical mixing in 1D)

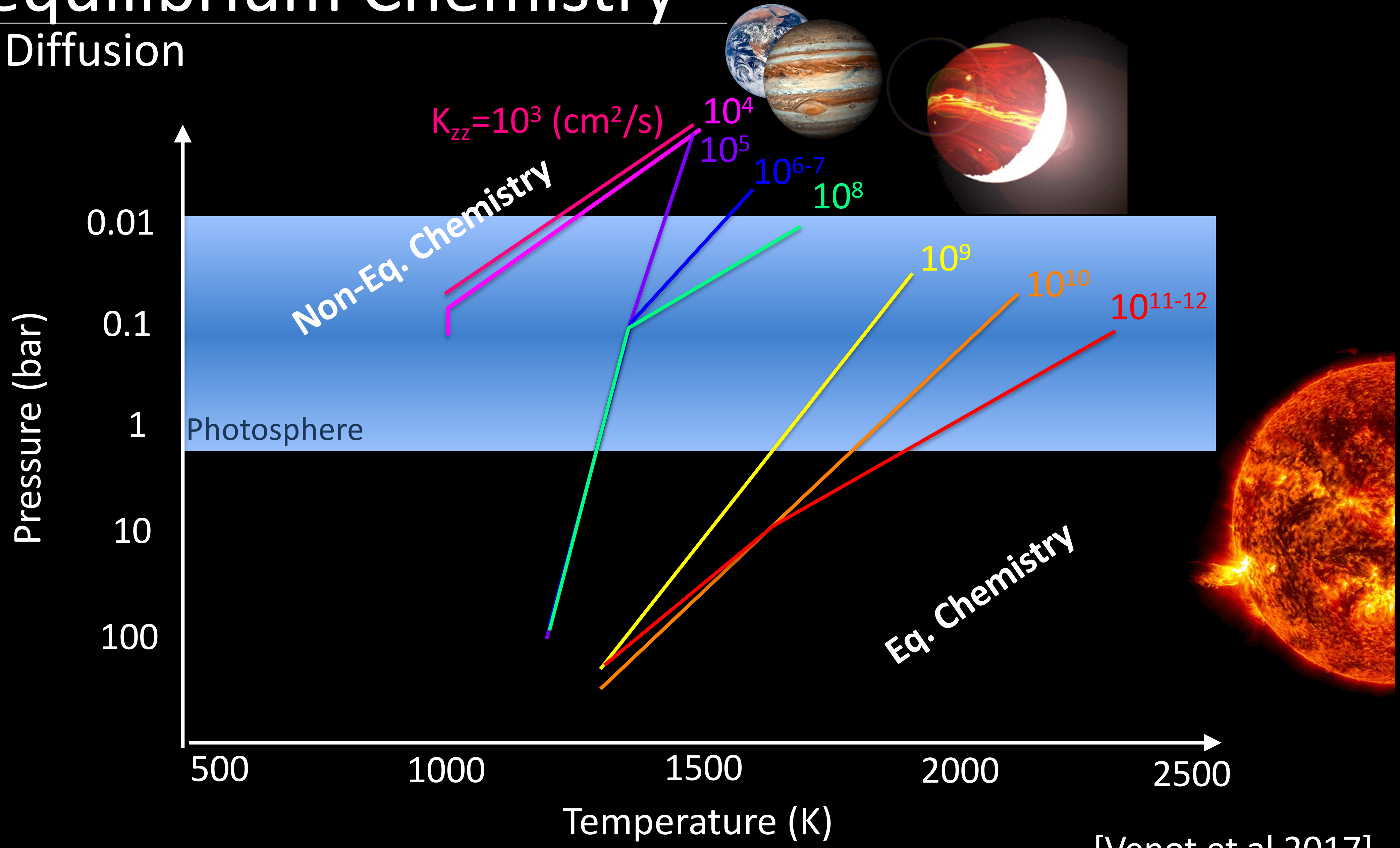
Q



$=CH_4$ Depletion?

Disequilibrium Chemistry

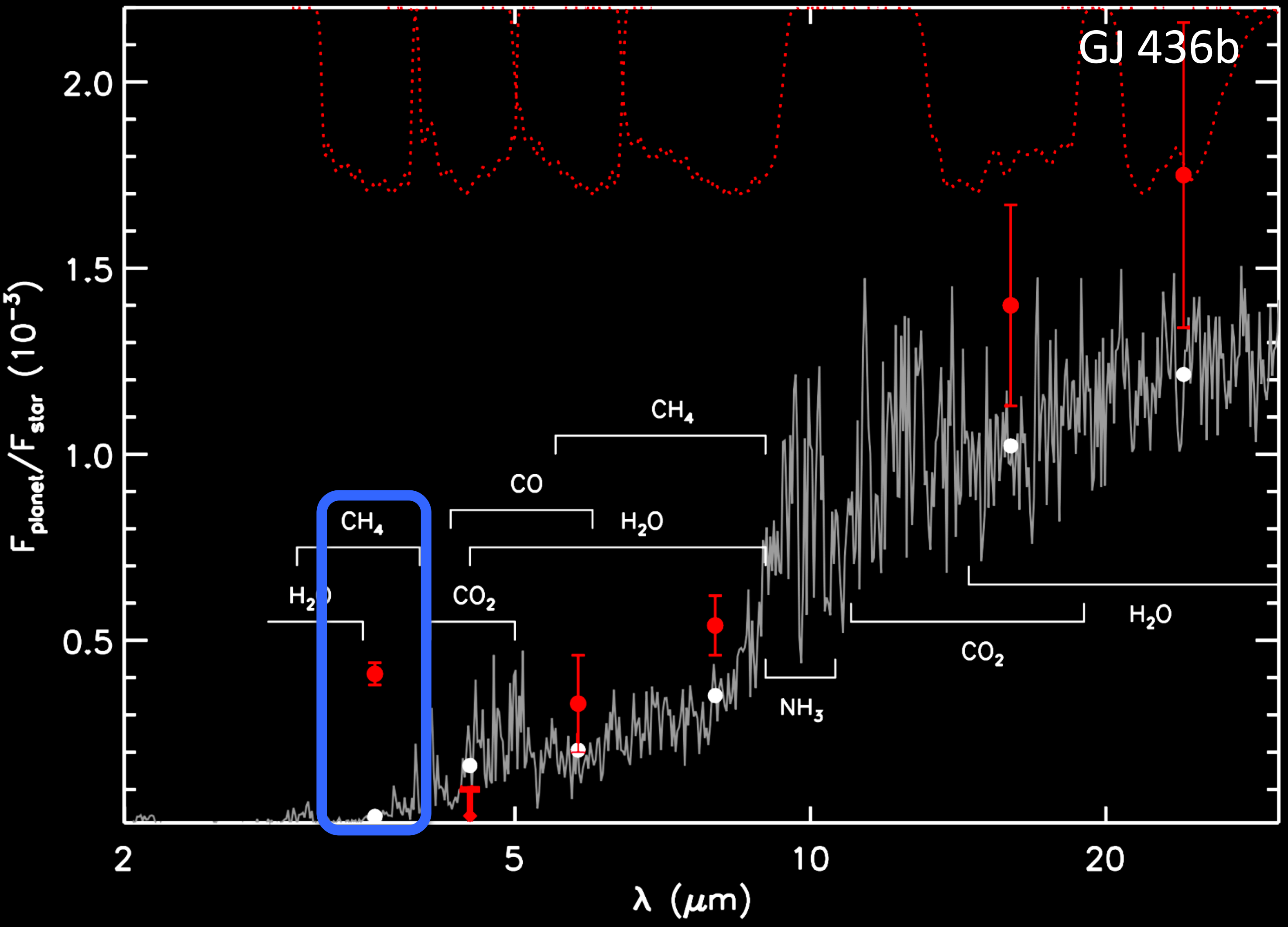
Eddy Diffusion



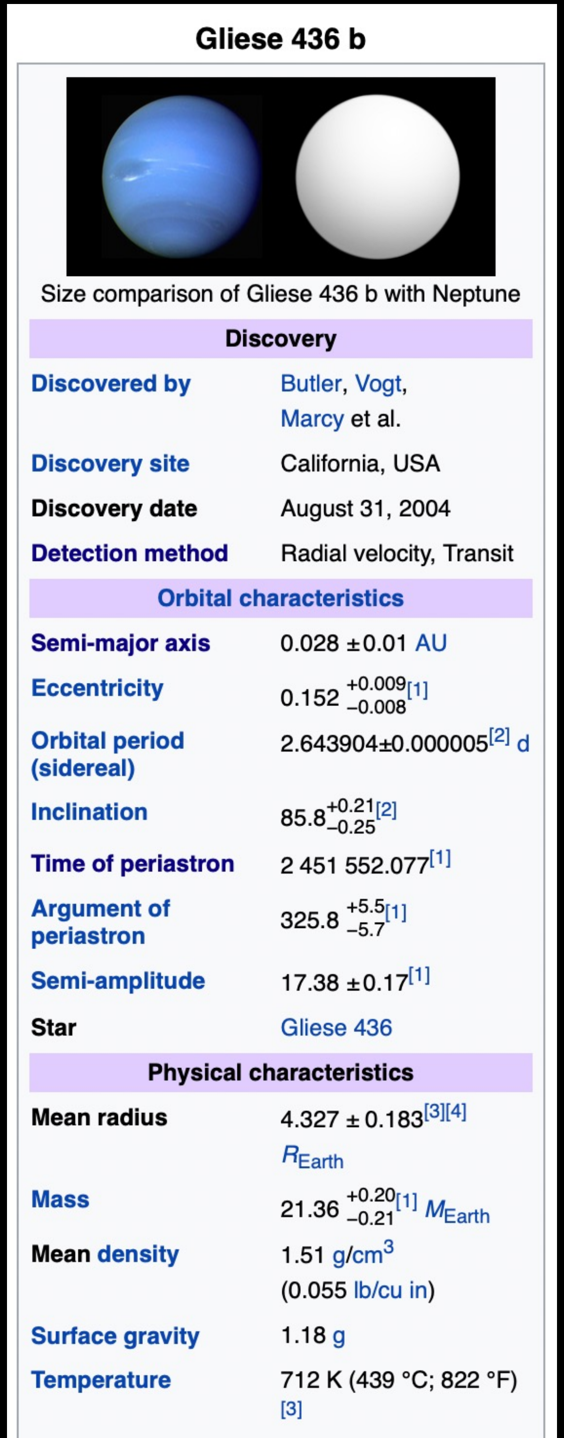
[Venot et al 2017]

Disequilibrium Chemistry

Observational indication?



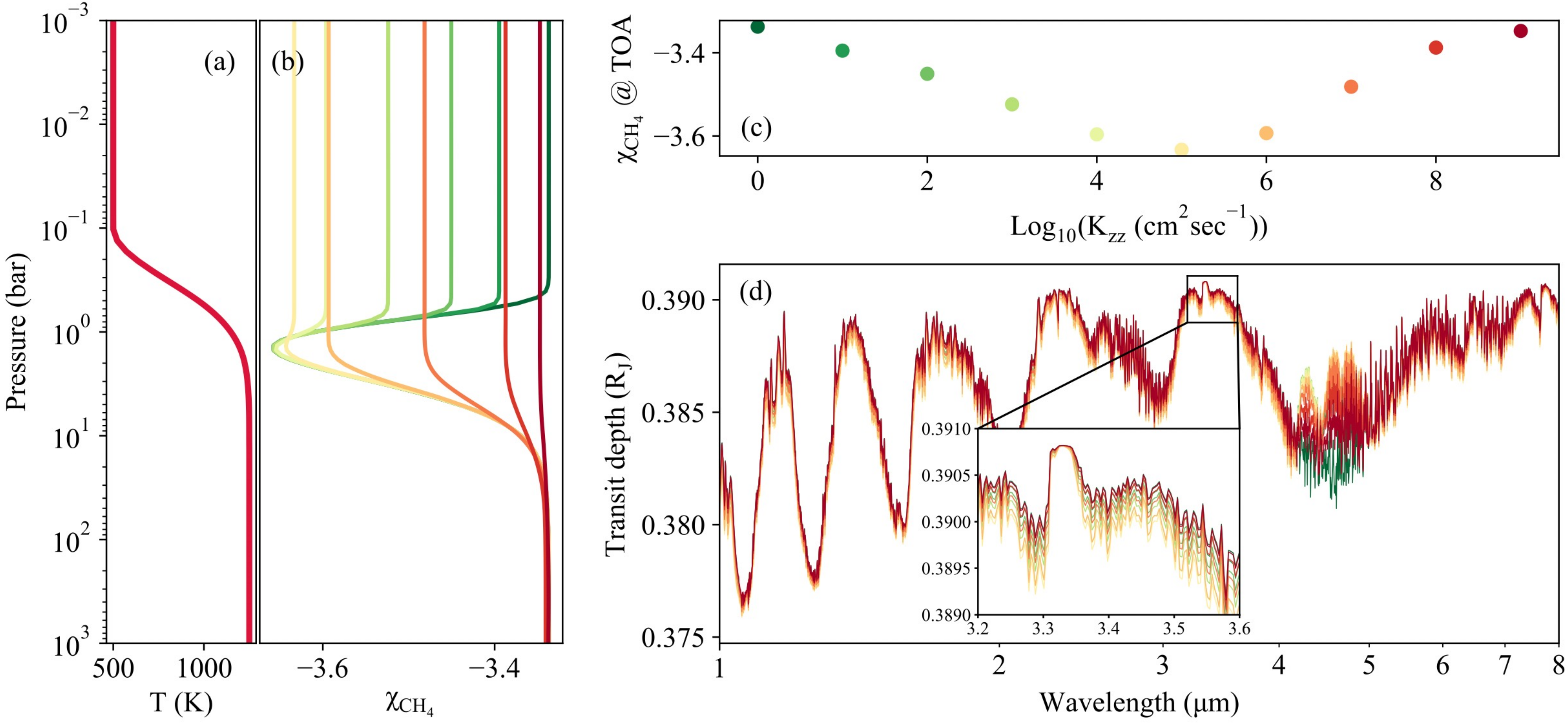
[Stevenson et al. 2010; Madhusudhan & Seager 2011]



Gliese 436 b

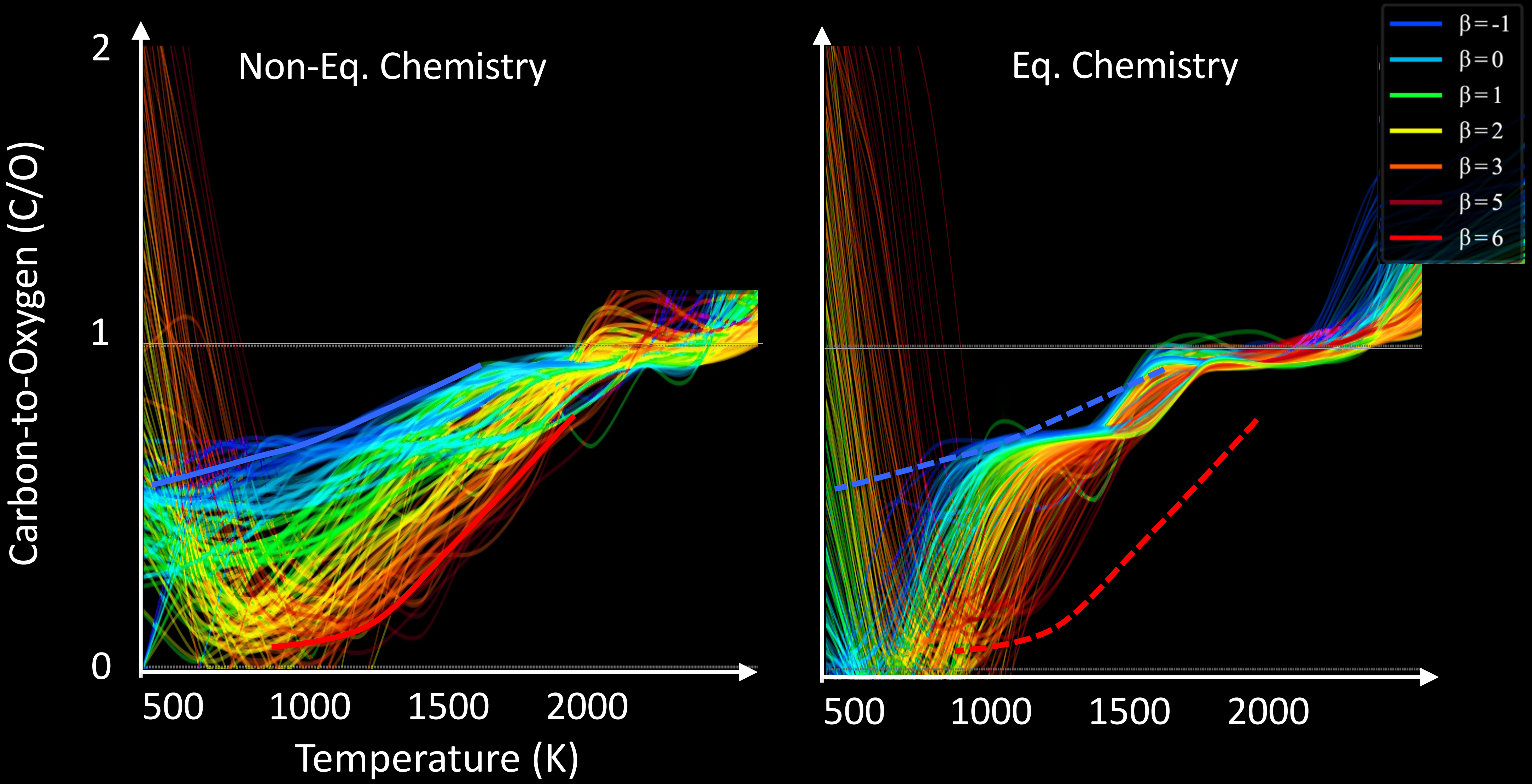
Size comparison of Gliese 436 b with Neptune

Discovery	
Discovered by	Butler, Vogt, Marcy et al.
Discovery site	California, USA
Discovery date	August 31, 2004
Detection method	Radial velocity, Transit
Orbital characteristics	
Semi-major axis	0.028 ±0.01 AU
Eccentricity	0.152 $^{+0.009}_{-0.008}$[1]
Orbital period (sidereal)	2.643904±0.000005[2] d
Inclination	85.8$^{+0.21}_{-0.25}$[2]
Time of periastron	2 451 552.077[1]
Argument of periastron	325.8 $^{+5.5}_{-5.7}$[1]
Semi-amplitude	17.38 ±0.17[1]
Star	Gliese 436
Physical characteristics	
Mean radius	4.327 ± 0.183[3][4] R_{Earth}
Mass	21.36 $^{+0.20}_{-0.21}$[1] M_{Earth}
Mean density	1.51 g/cm^3 (0.055 lb/cu in)
Surface gravity	1.18 g
Temperature	712 K (439 °C; 822 °F) [3]



(a) Simple parametric GJ 436b–like TP structure adapted from Madhusudhan & Seager (2011). (b) CH$_4$ abundance profiles caused by different K_{zz} values. Stronger mixing causes a deeper quenching level but does not guarantee a monotonic abundance variation. (c) CH$_4$ abundance at the TOA as a function of K_{zz} in this particular case. (d) Variation of the transmission spectrum as a function of K_{zz}. In this example, variation of the CH$_4$ abundance at the TOA appears as a slight shift in the transmission spectrum. The CO$_2$ and CO spectral features between 4 and 5 μm vary as well, resulting in higher CO$_2$ and CO molar fractions at the TOA when the mixing is in action.

The Effects of Eddy Diffusion

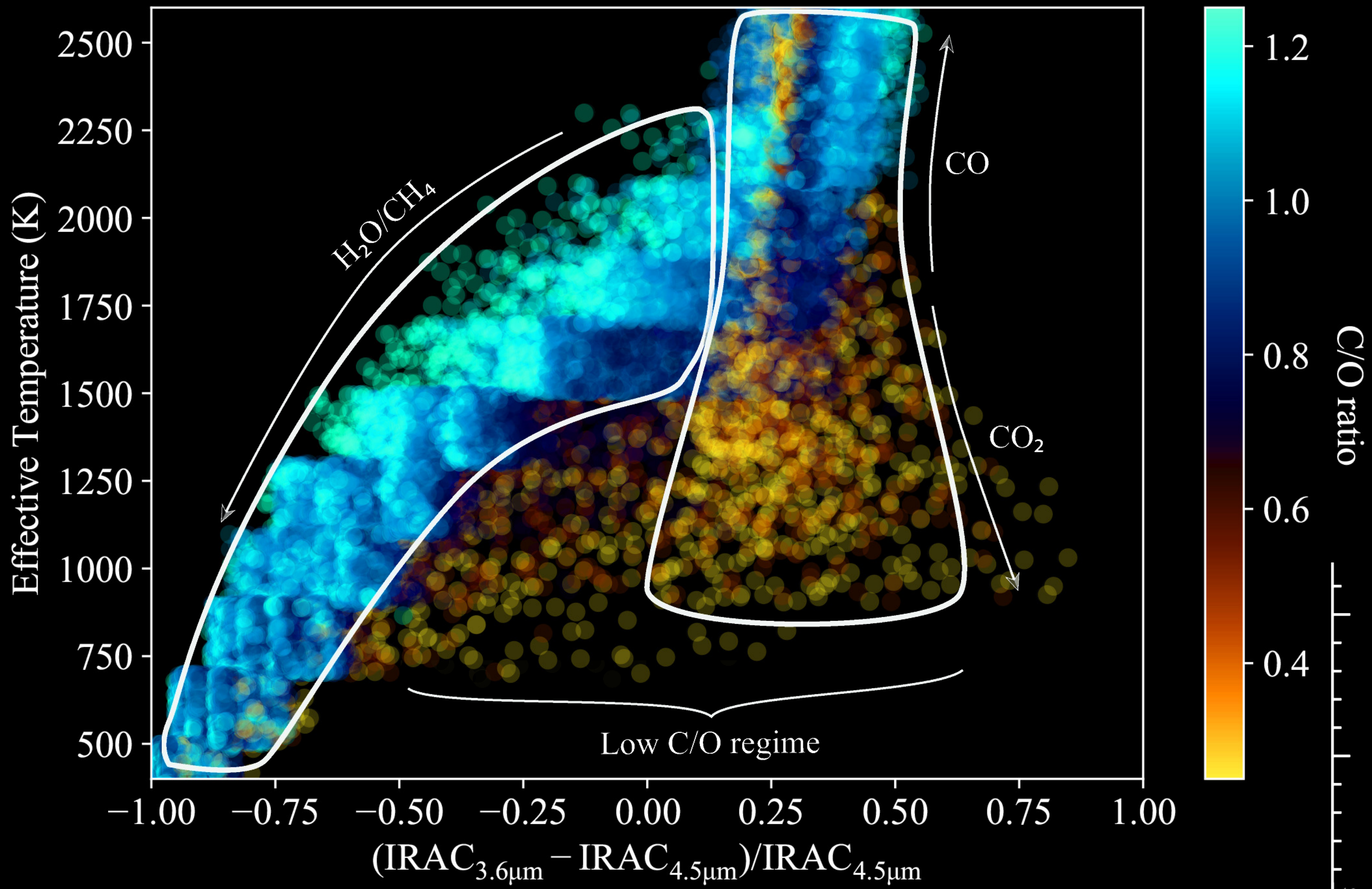


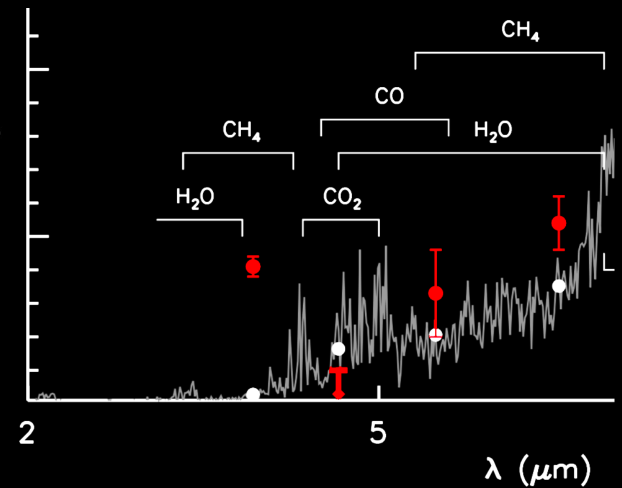
[Molaverdikhani et al 2018, in perp.]

Color Diagram

IRAC – Emission (Eq. Chemistry)

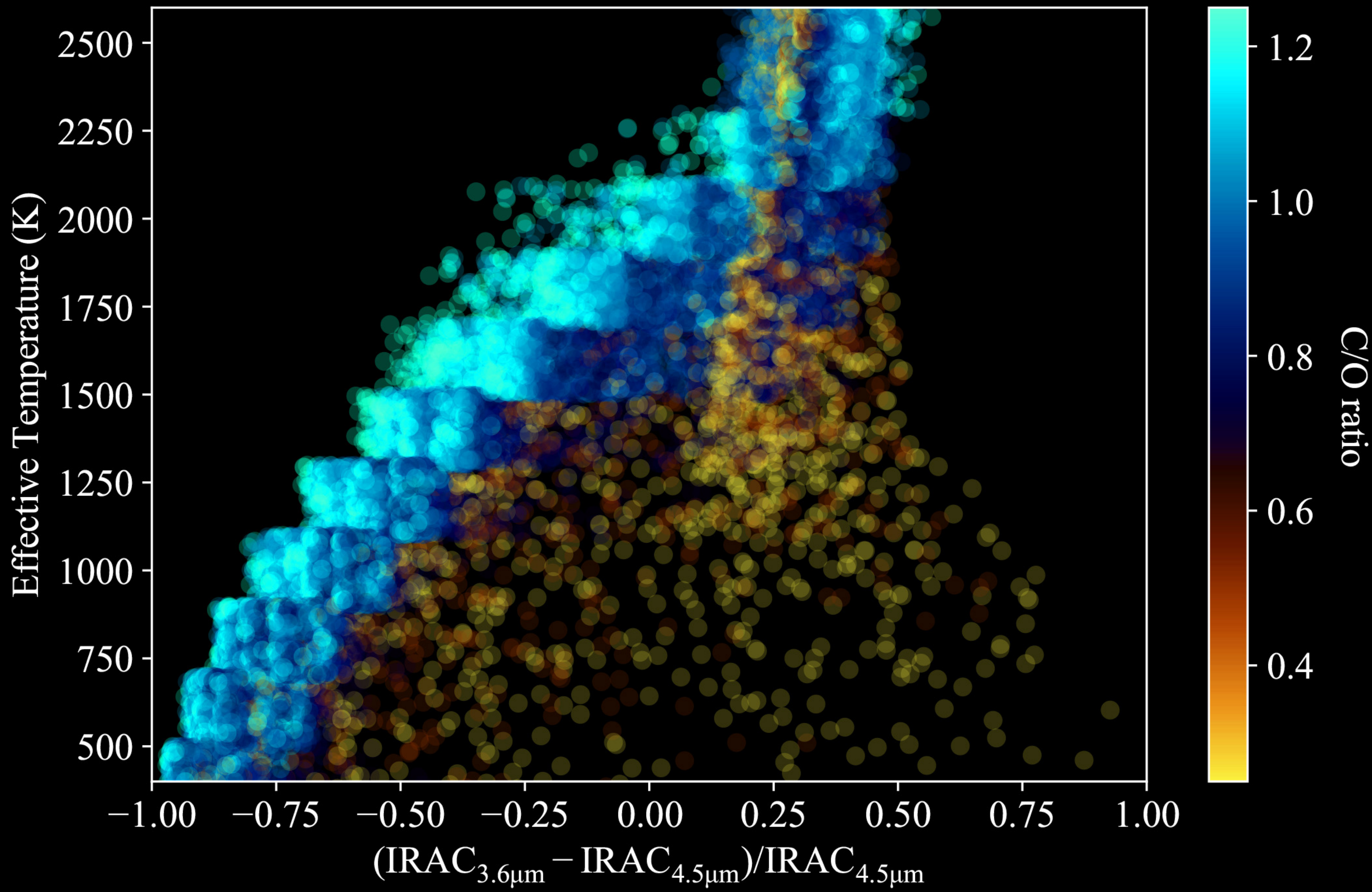
$$\mathrm{CH_4 + H_2O} \underset{\lesssim 1000\ \mathrm{K}}{\overset{\gtrsim 1000\ \mathrm{K}}{\rightleftharpoons}} \mathrm{3H_2 + CO}$$





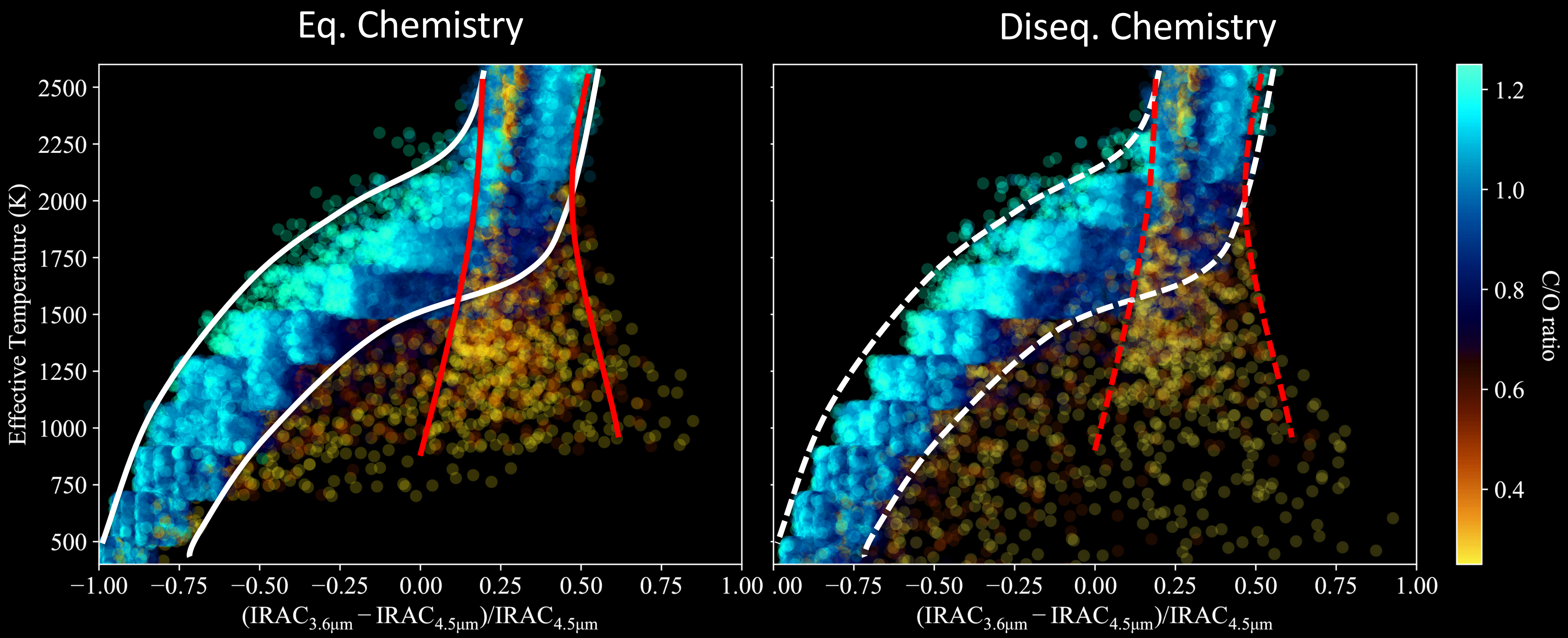
Color Diagram

IRAC – Emission (Diseq. Chemistry/$k_{zz}=10^{12}$)



Color Diagram

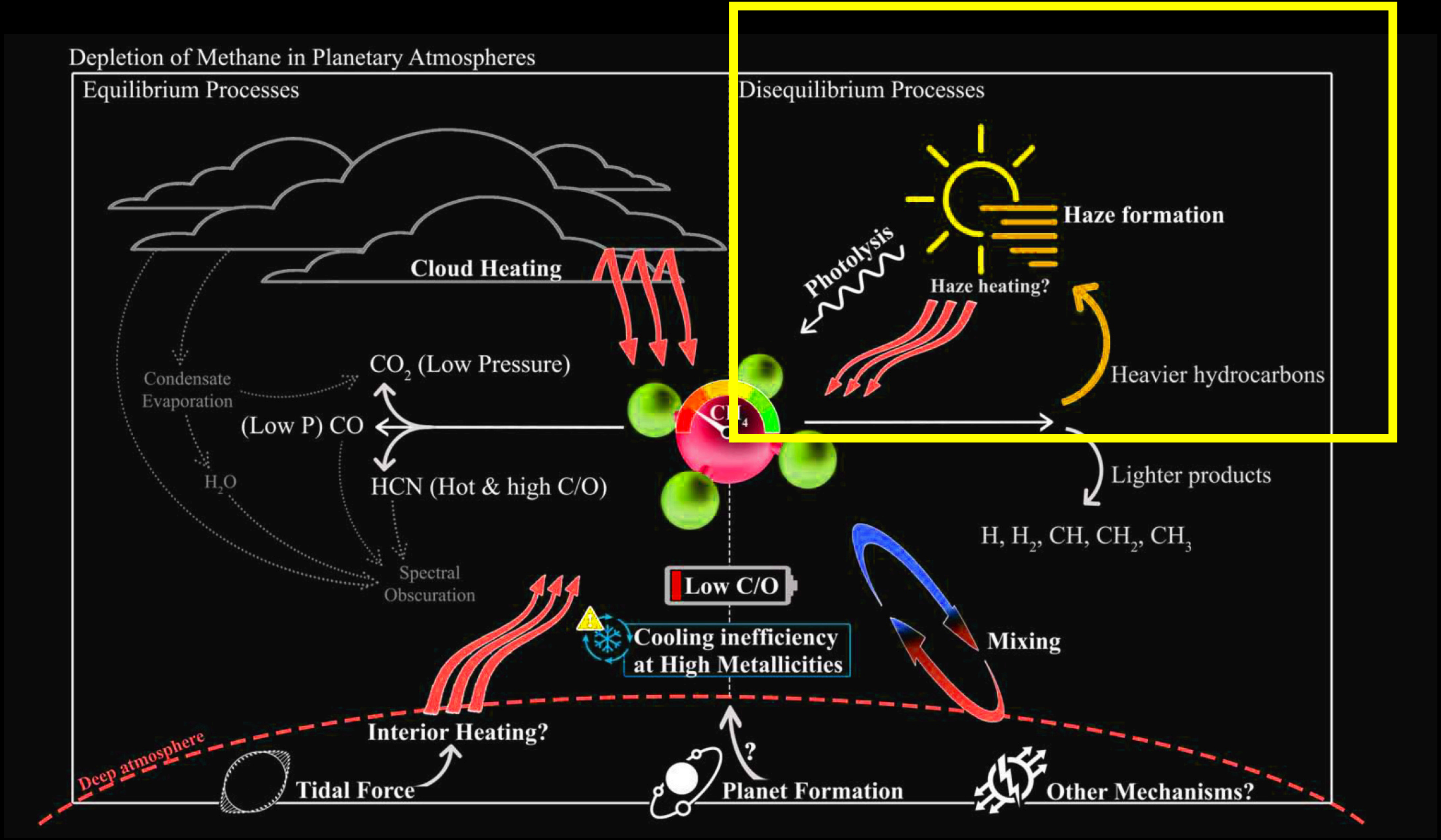
IRAC – Emission (Comparison)



Still abundant of CH_4 expected!?

Where is methane?

Photochemical processes



[Molaverdikhani et al. 2020b]

Disequilibrium chemical processes

Photochemistry
Galactic Cosmic Rays
Interplanetary medium Lyα

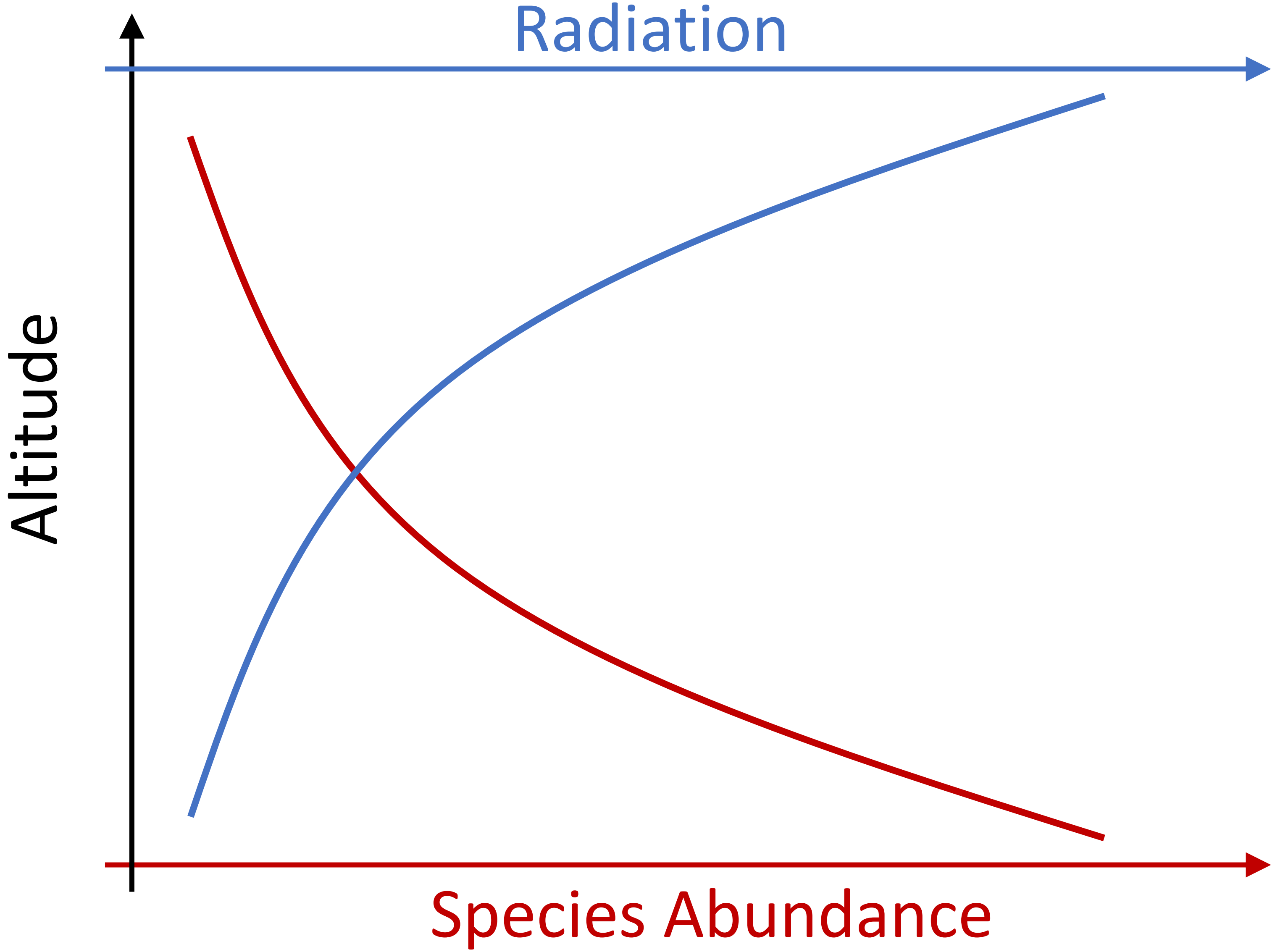
Eddy/Molecular Diffusion

Condensation/Rain-out
Outgassing/Ablation
Atmospheric Loss

mbar
Photochemistry
Molecular Diffusion

Deeper
Galactic Cosmic Rays
Eddy Diffusion
Condensation

How photochemistry works?

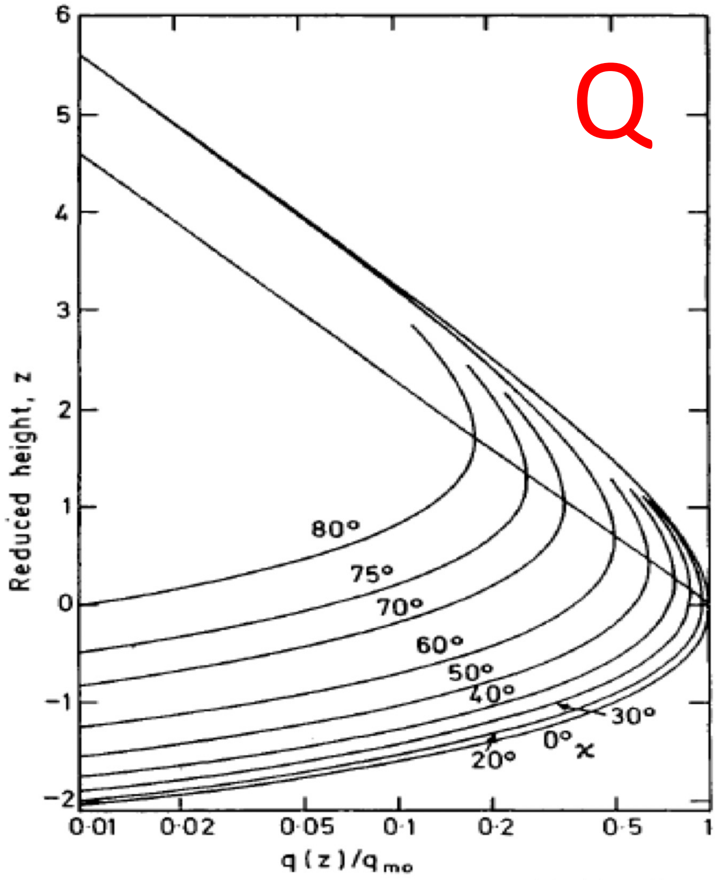


Radiation

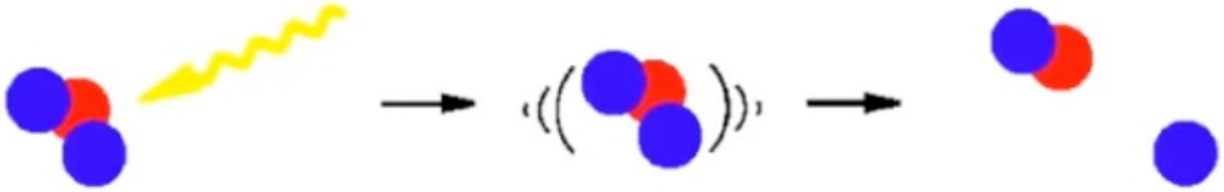
Altitude

Species Abundance

Chapman production function



How photochemistry works? Photolysis.



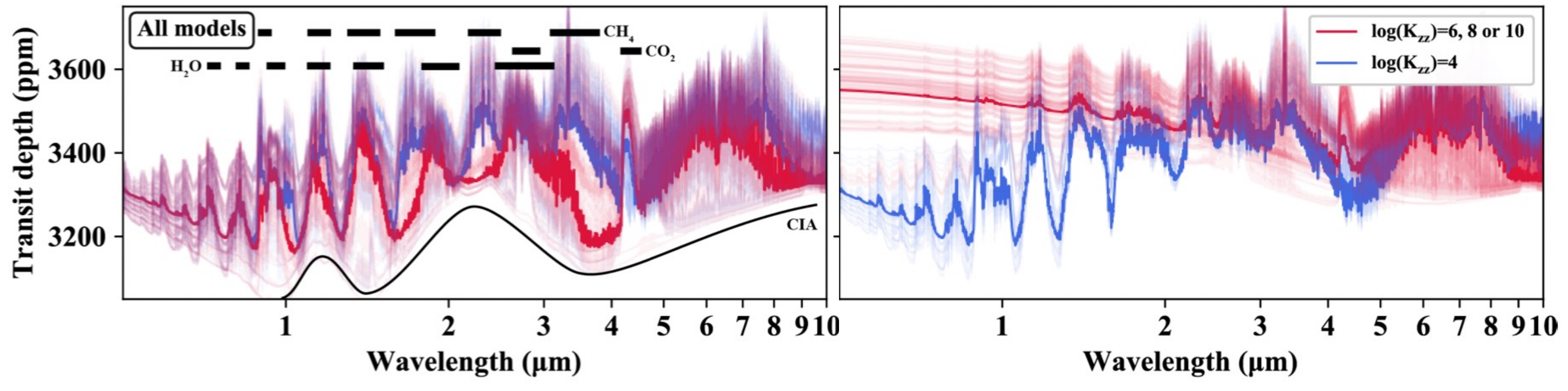
$$A + h\nu \rightarrow \text{products},$$

$$\text{rate} = \frac{\partial n_A}{\partial t} = -j_A n_A$$

Photochemical Haze: Kzz

Without haze opacity

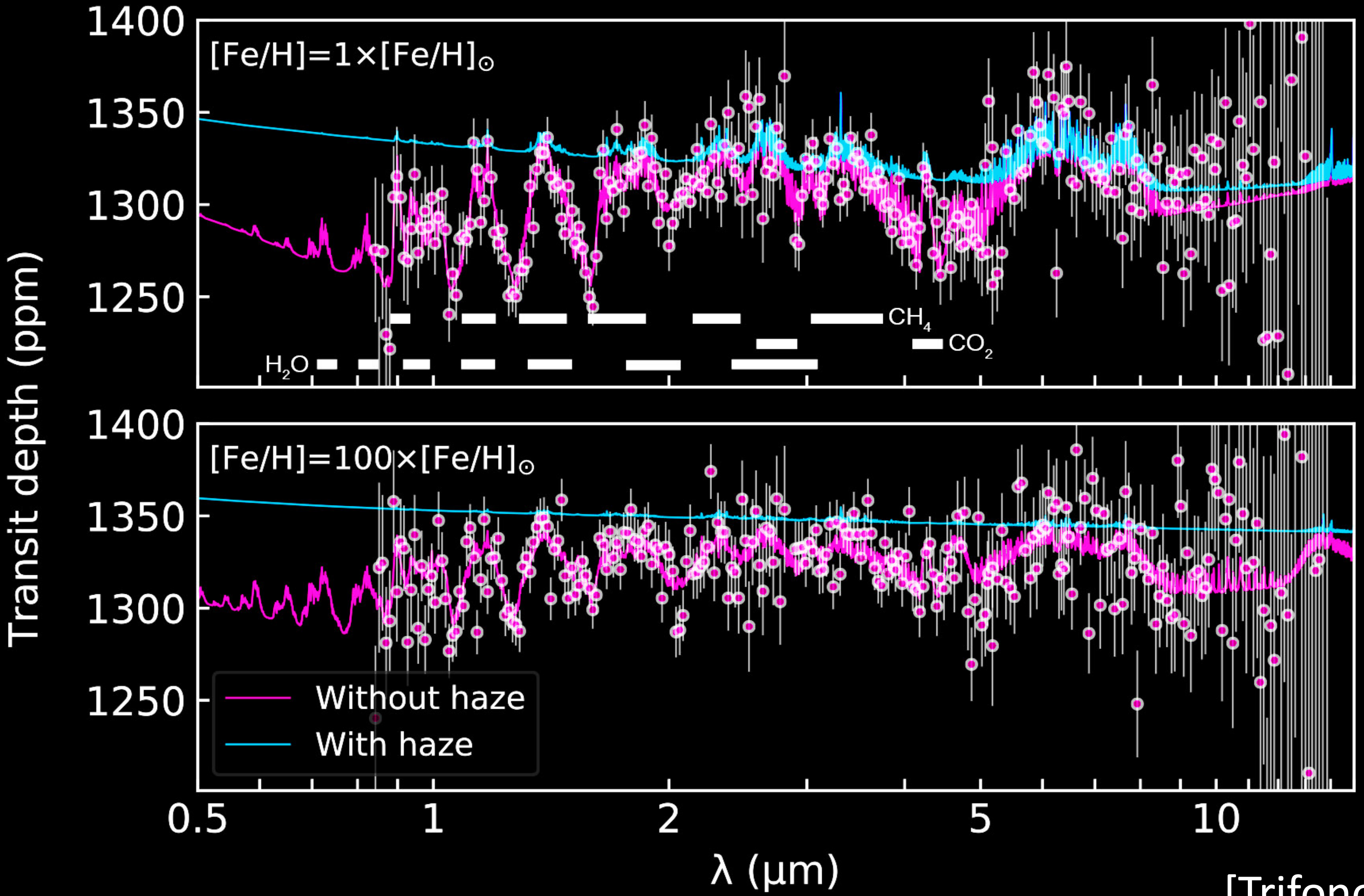
With haze opacity



Based on LTT 3780 c: 400 K

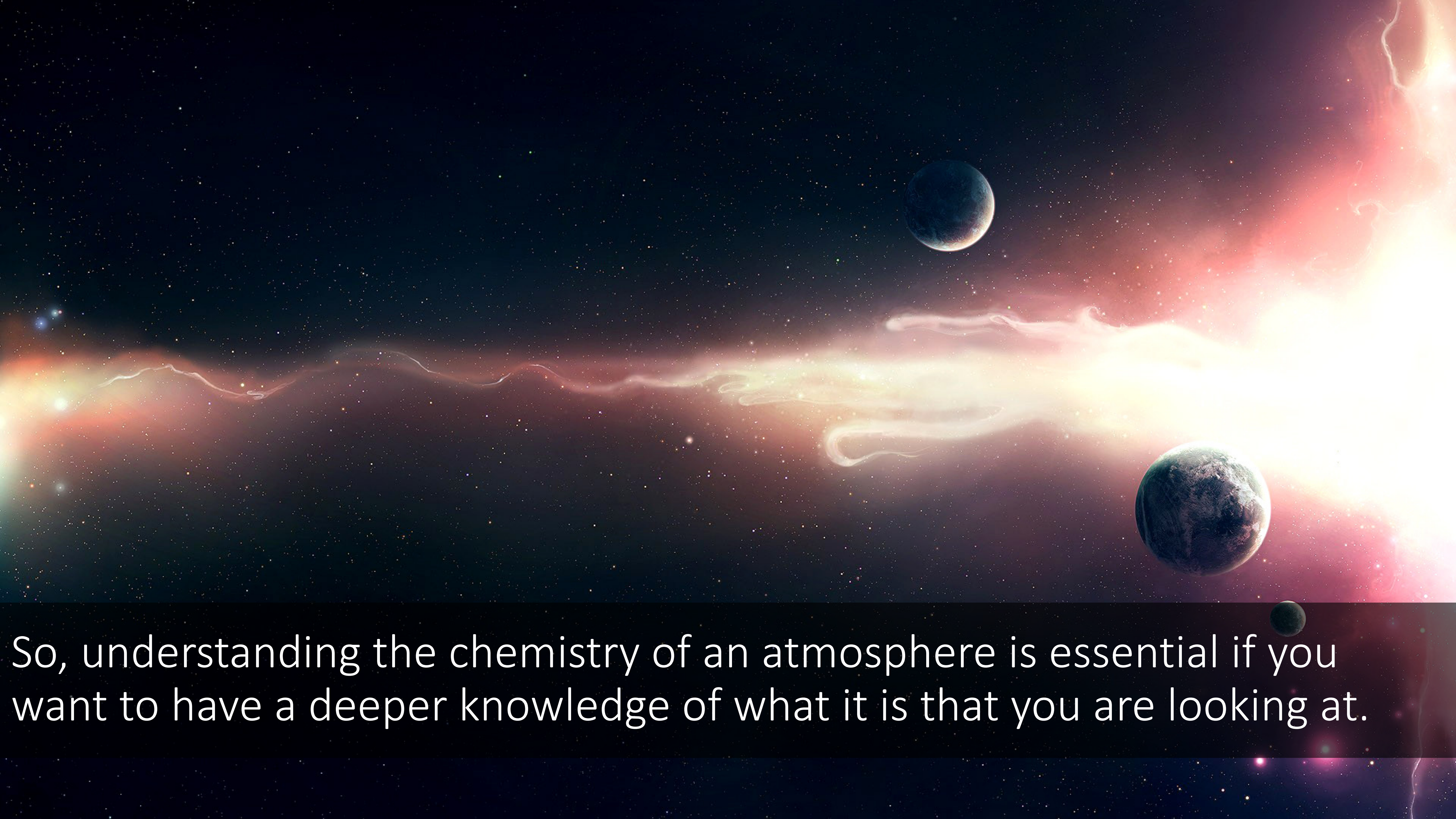
[Nowak et al. 2020; ***A&A***]

Photochemical Haze: [Fe/H]



GJ 486b

[Trifonov et al. 2021; *Science*]



So, understanding the chemistry of an atmosphere is essential if you want to have a deeper knowledge of what it is that you are looking at.

Let’s get started!

Make groups of two!

Pair up with someone whom you haven’t talked to yet!

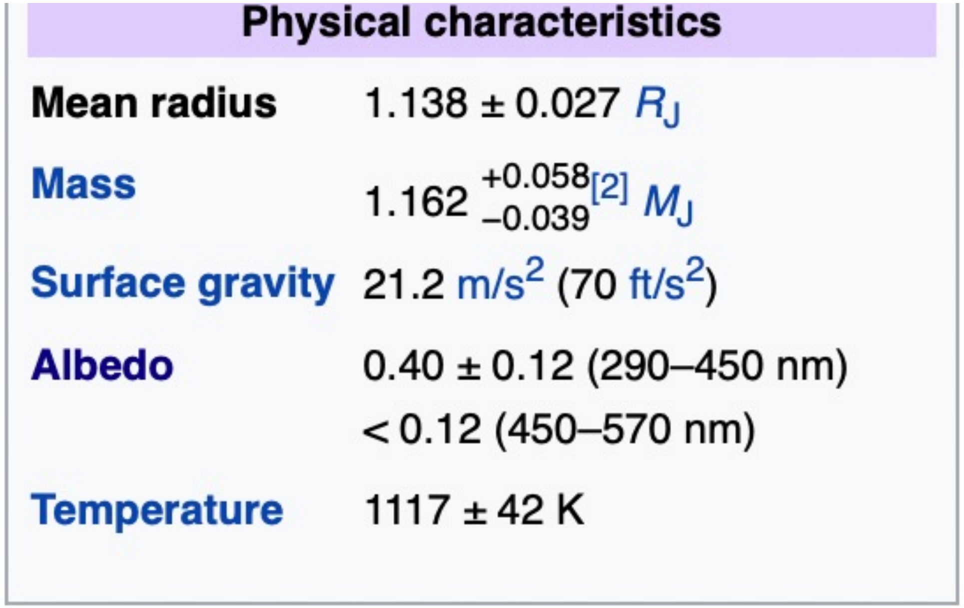
A few exercises:

1. Walk through VULCAN: HD 189733b
2. Quest to find Quenching points!
3. Thermochemical Equilibrium Test: Consistency & Convergence

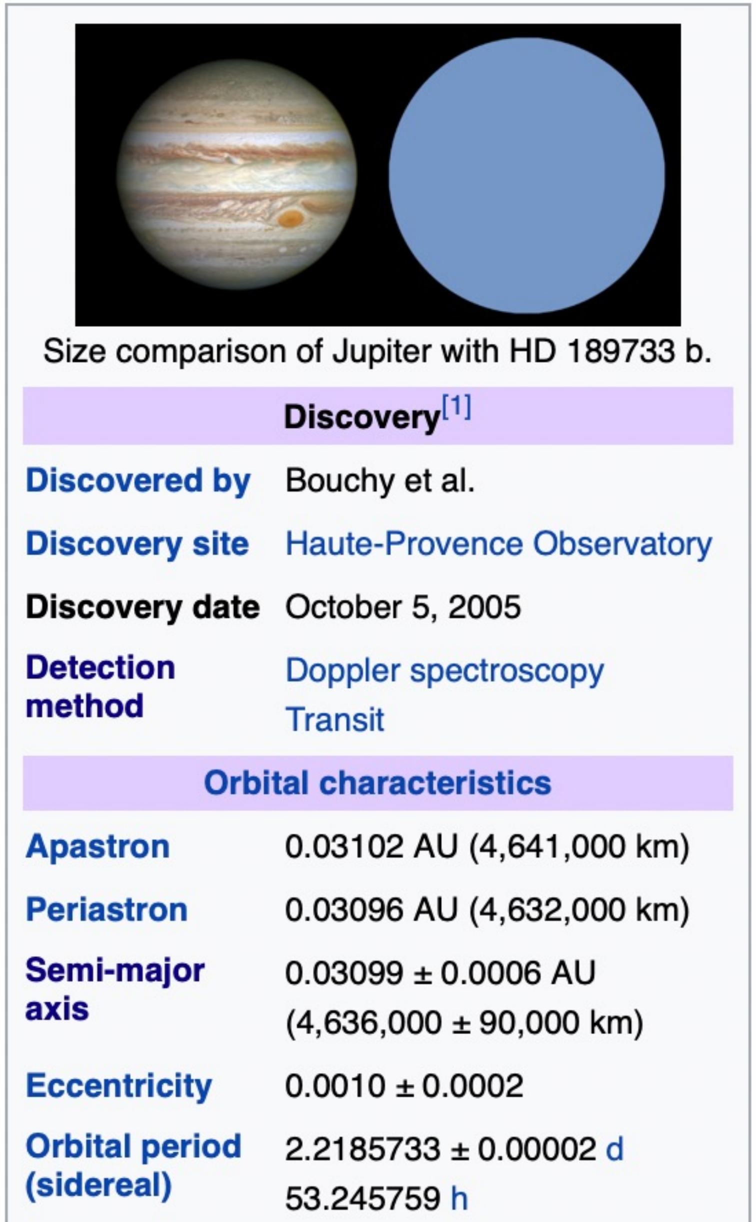
- A few Homeworks
  - Read & plot the output in petitRADTRANS
  - Run a model for JWST ERS targets

1. Walk through VULCAN: HD 189733b

- Directories & their content
  - Plot TP (compare w/ Teq) & Kzz



Physical characteristics	
Mean radius	1.138 ± 0.027 R_J
Mass	$1.162^{+0.058}_{-0.039}$[2] M_J
Surface gravity	21.2 m/s^2 (70 ft/s^2)
Albedo	0.40 ± 0.12 (290–450 nm) < 0.12 (450–570 nm)
Temperature	1117 ± 42 K



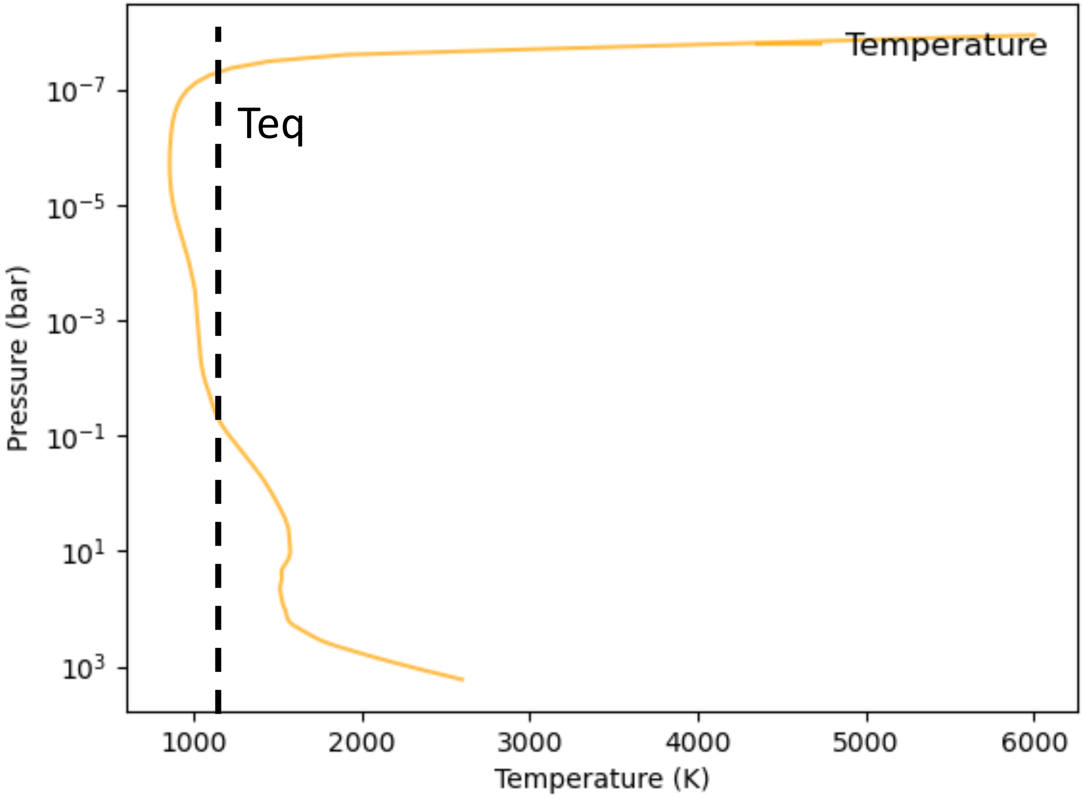
Size comparison of Jupiter with HD 189733 b.

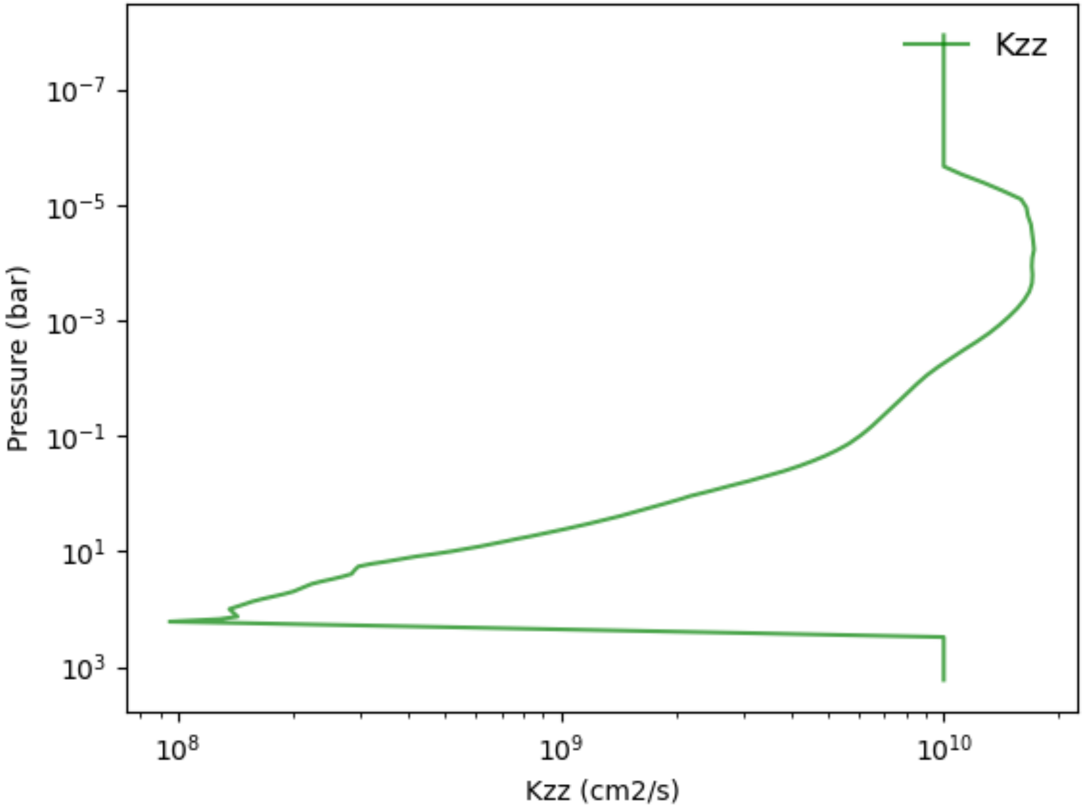
Discovery[1]	
Discovered by	Bouchy et al.
Discovery site	Haute-Provence Observatory
Discovery date	October 5, 2005
Detection method	Doppler spectroscopy Transit

Orbital characteristics	
Apastron	0.03102 AU (4,641,000 km)
Periastron	0.03096 AU (4,632,000 km)
Semi-major axis	0.03099 ± 0.0006 AU (4,636,000 ± 90,000 km)
Eccentricity	0.0010 ± 0.0002
Orbital period (sidereal)	2.2185733 ± 0.00002 d 53.245759 h

1. Walk through VULCAN: HD 189733b

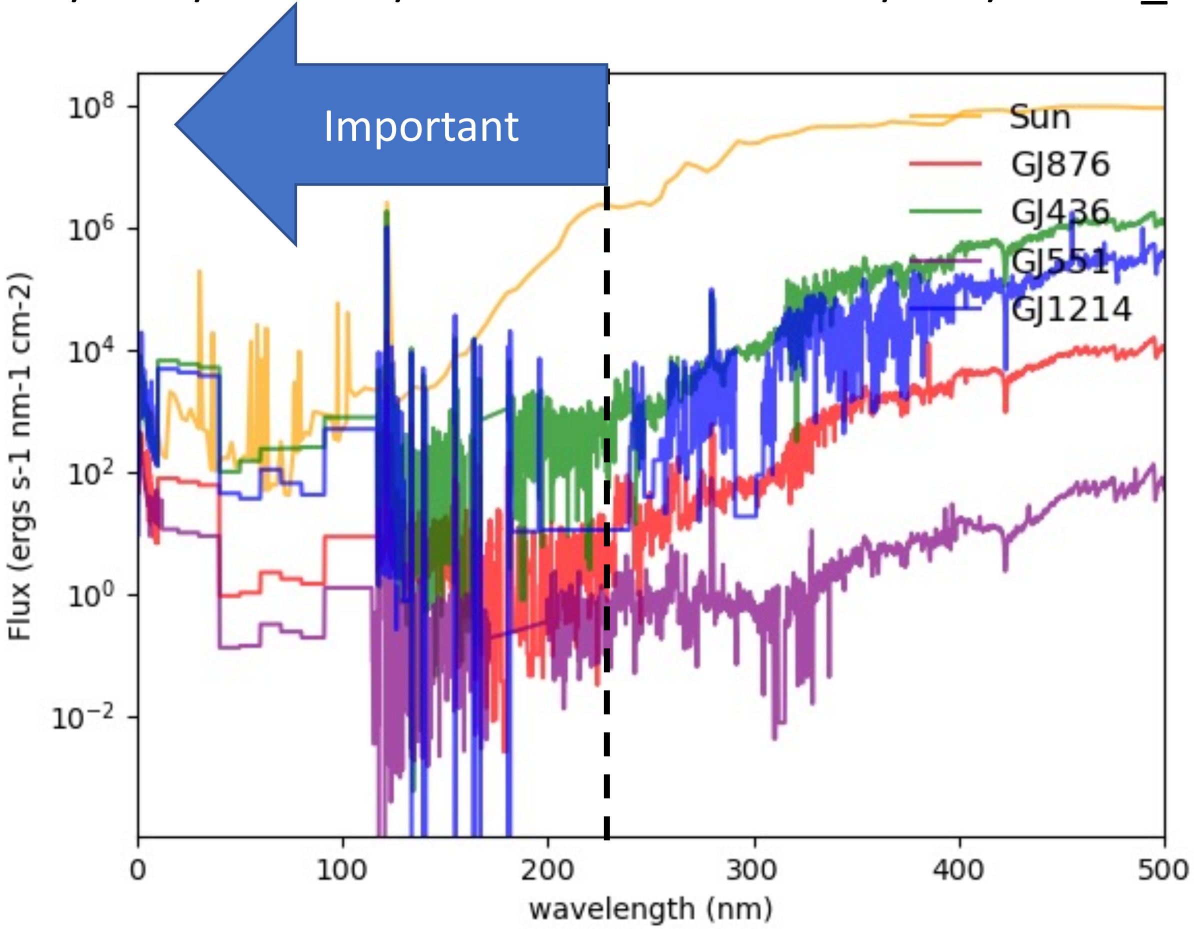
- Directories & their content
  - Plot TP (compare w/ Teq) & Kzz
    - /Users/karan/LMU/VULCAN/VULCAN-master-tests/atm/atm_HD189_Kzz.txt





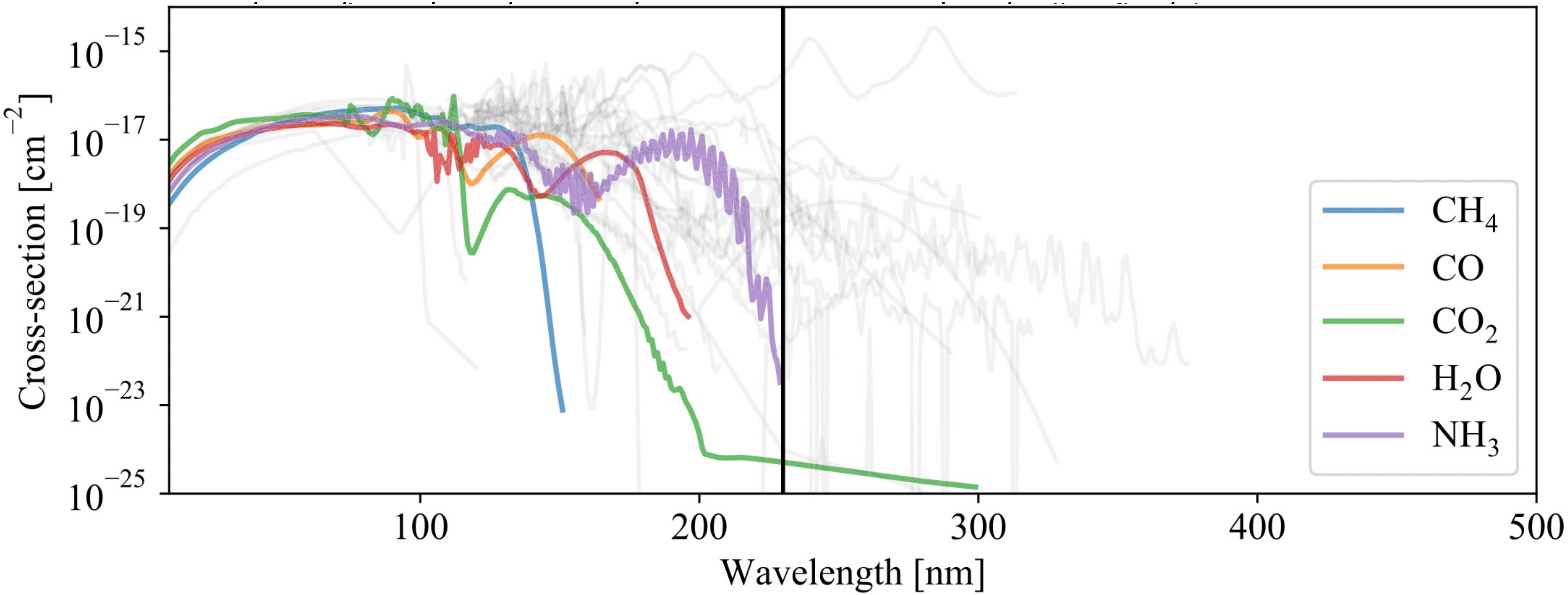
1. Walk through VULCAN: HD 189733b

- Directories & their content
  - Plot stellar spectra
    - /Users/karan/LMU/VULCAN/VULCAN-master-tests/atm/stellar_flux/plot_spectra.py



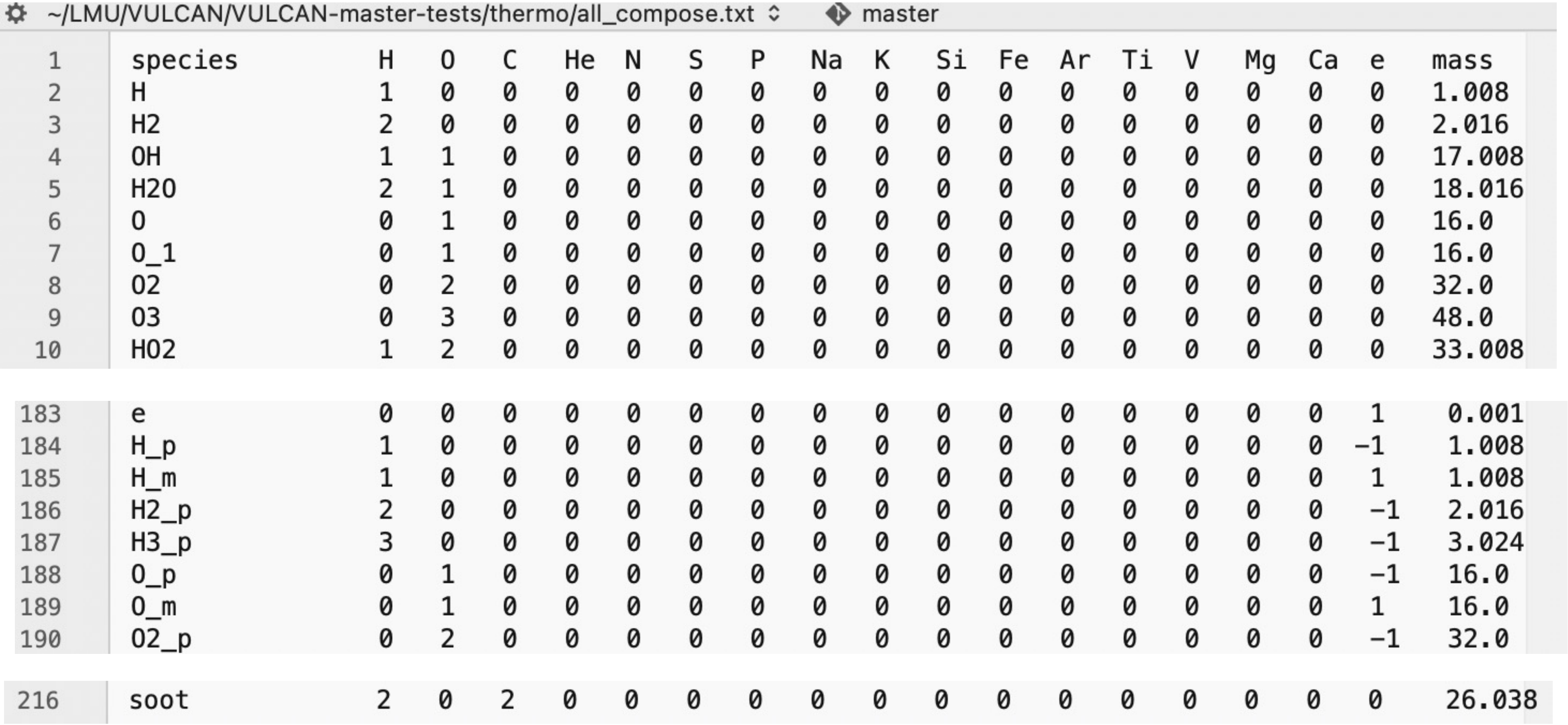
1. Walk through VULCAN: HD 189733b

- Directories & their content
  - Plot stellar spectra



1. Walk through VULCAN: HD 189733b

- **Thermo** files
  - /Users/karan/LMU/VULCAN/VULCAN-master-tests/thermo



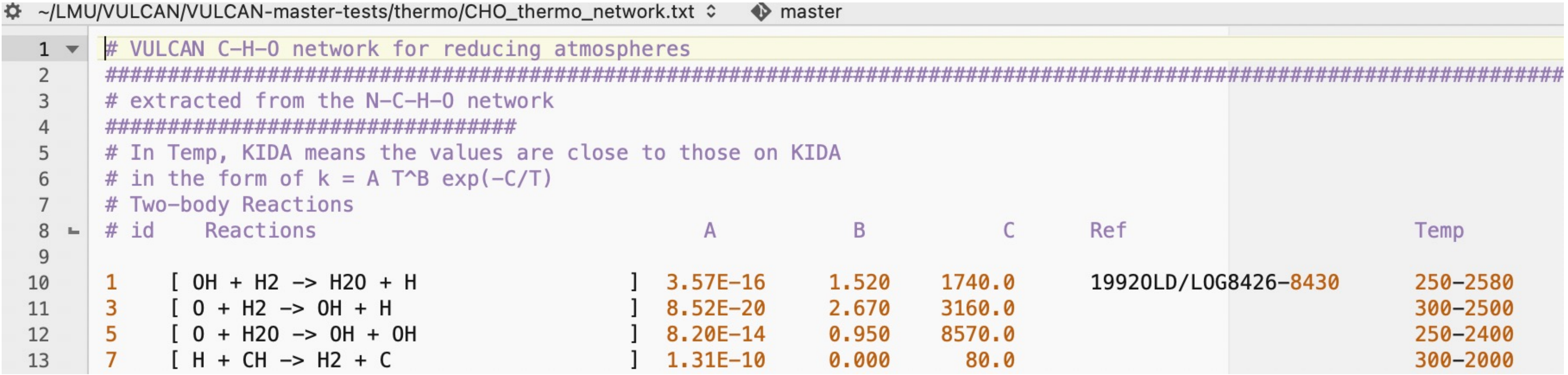
```
species         H   O   C   He  N   S   P   Na  K   Si  Fe  Ar  Ti  V   Mg  Ca  e   mass
H               1   0   0   0   0   0   0   0   0   0   0   0   0   0   0   0   0   1.008
H2              2   0   0   0   0   0   0   0   0   0   0   0   0   0   0   0   0   2.016
OH              1   1   0   0   0   0   0   0   0   0   0   0   0   0   0   0   0   17.008
H2O             2   1   0   0   0   0   0   0   0   0   0   0   0   0   0   0   0   18.016
O               0   1   0   0   0   0   0   0   0   0   0   0   0   0   0   0   0   16.0
O_1             0   1   0   0   0   0   0   0   0   0   0   0   0   0   0   0   0   16.0
O2              0   2   0   0   0   0   0   0   0   0   0   0   0   0   0   0   0   32.0
O3              0   3   0   0   0   0   0   0   0   0   0   0   0   0   0   0   0   48.0
HO2             1   2   0   0   0   0   0   0   0   0   0   0   0   0   0   0   0   33.008

e               0   0   0   0   0   0   0   0   0   0   0   0   0   0   0   0   1    0.001
H_p             1   0   0   0   0   0   0   0   0   0   0   0   0   0   0   0  -1    1.008
H_m             1   0   0   0   0   0   0   0   0   0   0   0   0   0   0   0   1    1.008
H2_p            2   0   0   0   0   0   0   0   0   0   0   0   0   0   0   0   -1   2.016
H3_p            3   0   0   0   0   0   0   0   0   0   0   0   0   0   0   0   -1   3.024
O_p             0   1   0   0   0   0   0   0   0   0   0   0   0   0   0   0   -1   16.0
O_m             0   1   0   0   0   0   0   0   0   0   0   0   0   0   0   0   1    16.0
O2_p            0   2   0   0   0   0   0   0   0   0   0   0   0   0   0   0   -1   32.0

soot            2   0   2   0   0   0   0   0   0   0   0   0   0   0   0   0   0    26.038
```

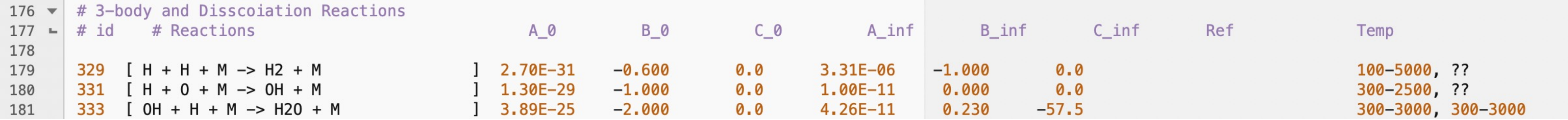
1. Walk through VULCAN: HD 189733b

- **Thermo** files
  - /Users/karan/LMU/VULCAN/VULCAN-master-tests/thermo



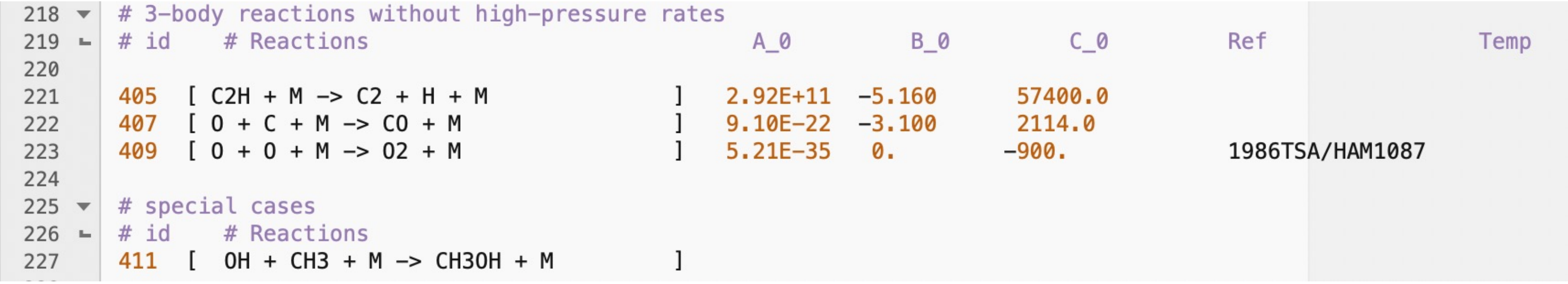
```
# VULCAN C-H-O network for reducing atmospheres
####################################################################################################################
# extracted from the N-C-H-O network
#################################
# In Temp, KIDA means the values are close to those on KIDA
# in the form of k = A T^B exp(-C/T)
# Two-body Reactions
# id     Reactions                                   A           B           C         Ref                        Temp

1     [ OH + H2 -> H2O + H                     ]  3.57E-16     1.520     1740.0       1992OLD/LOG8426-8430        250-2580
3     [ O + H2 -> OH + H                       ]  8.52E-20     2.670     3160.0                                   300-2500
5     [ O + H2O -> OH + OH                     ]  8.20E-14     0.950     8570.0                                   250-2400
7     [ H + CH -> H2 + C                       ]  1.31E-10     0.000       80.0                                   300-2000
```



```
# 3-body and Disscoiation Reactions
# id    # Reactions                              A_0        B_0        C_0        A_inf       B_inf      C_inf      Ref           Temp

329  [ H + H + M -> H2 + M                 ]  2.70E-31    -0.600      0.0      3.31E-06    -1.000       0.0                     100-5000, ??
331  [ H + O + M -> OH + M                 ]  1.30E-29    -1.000      0.0      1.00E-11     0.000       0.0                     300-2500, ??
333  [ OH + H + M -> H2O + M               ]  3.89E-25    -2.000      0.0      4.26E-11     0.230     -57.5                     300-3000, 300-3000
```

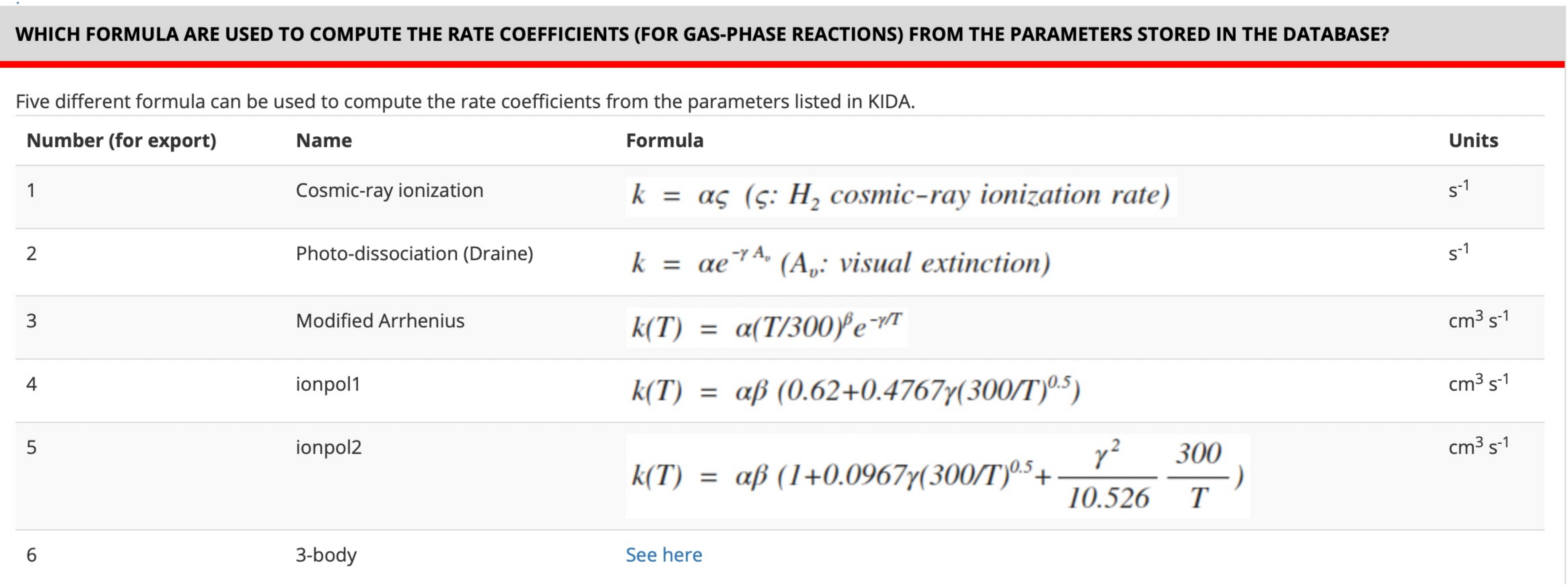


```
# 3-body reactions without high-pressure rates
# id     # Reactions                                A_0          B_0          C_0         Ref                   Temp

405   [ C2H + M -> C2 + H + M                 ]   2.92E+11   -5.160       57400.0
407   [ O + C + M -> CO + M                   ]   9.10E-22   -3.100       2114.0
409   [ O + O + M -> O2 + M                   ]   5.21E-35    0.         -900.            1986TSA/HAM1087

# special cases
# id     # Reactions
411   [  OH + CH3 + M -> CH3OH + M            ]
```

1. KIDA: https://kida.astrochem-tools.org



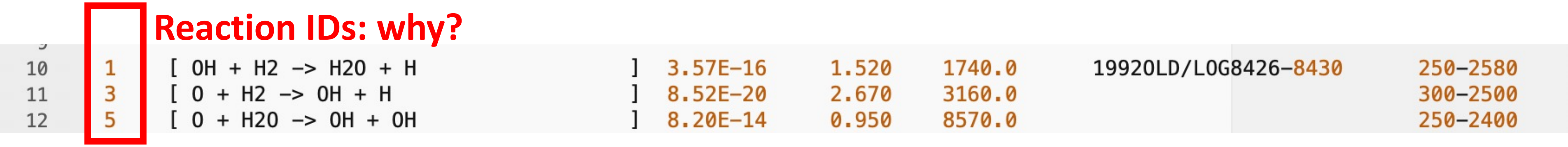
WHICH FORMULA ARE USED TO COMPUTE THE RATE COEFFICIENTS (FOR GAS-PHASE REACTIONS) FROM THE PARAMETERS STORED IN THE DATABASE?

Five different formula can be used to compute the rate coefficients from the parameters listed in KIDA.

Number (for export)	Name	Formula	Units
1	Cosmic-ray ionization	$k = \alpha\varsigma$ (ς: H_2 cosmic-ray ionization rate)	s^{-1}
2	Photo-dissociation (Draine)	$k = \alpha e^{-\gamma A_v}$ (A_v: visual extinction)	s^{-1}
3	Modified Arrhenius	$k(T) = \alpha(T/300)^{\beta} e^{-\gamma/T}$	$cm^3\ s^{-1}$
4	ionpol1	$k(T) = \alpha\beta\ (0.62+0.4767\gamma(300/T)^{0.5})$	$cm^3\ s^{-1}$
5	ionpol2	$k(T) = \alpha\beta\ (1+0.0967\gamma(300/T)^{0.5}+\frac{\gamma^2}{10.526}\frac{300}{T})$	$cm^3\ s^{-1}$
6	3-body	See here	

1. Walk through VULCAN: HD 189733b

- **Thermo** files
  - /Users/karan/LMU/VULCAN/VULCAN-master-tests/thermo



Reaction IDs: why?

```
1   [ OH + H2 -> H2O + H                     ]  3.57E-16    1.520    1740.0       1992OLD/LOG8426-8430       250-2580
3   [ O + H2 -> OH + H                       ]  8.52E-20    2.670    3160.0                                  300-2500
5   [ O + H2O -> OH + OH                     ]  8.20E-14    0.950    8570.0                                  250-2400
```

$$aA + bB \xrightleftharpoons[\text{reverse reactions}]{\text{Forward reactions}} cC + bB$$

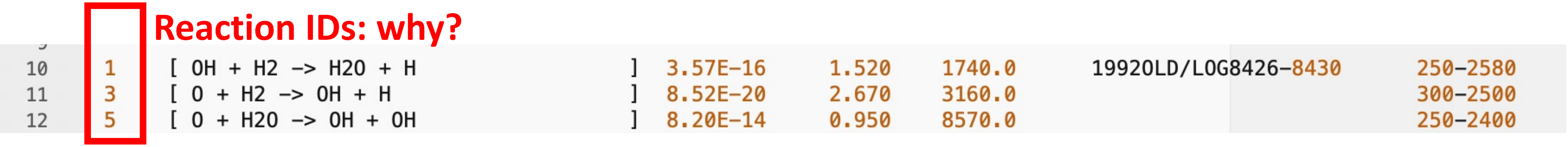
(Assuming it's reversable!)

$$K = \frac{k_f}{k_r}$$

The equilibrium constant is **equal to the rate constant for the forward reaction divided by the rate constant for the reverse reaction**

1. Walk through VULCAN: HD 189733b

- **Thermo** files
  - /Users/karan/LMU/VULCAN/VULCAN-master-tests/thermo



Reaction IDs: why?

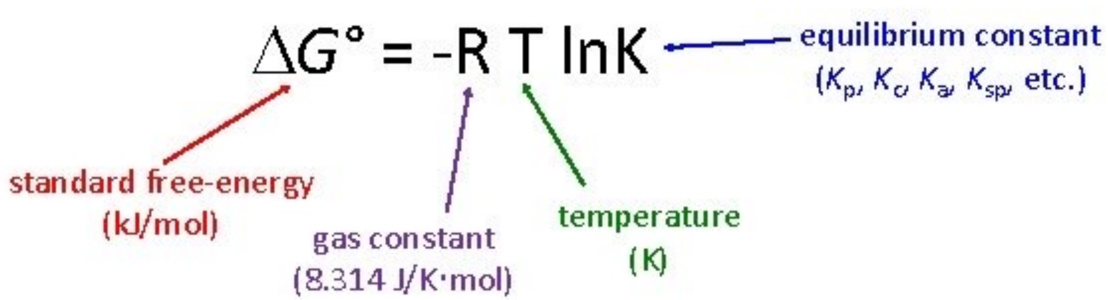
```
1  [ OH + H2 -> H2O + H            ]  3.57E-16   1.520   1740.0     1992OLD/LOG8426-8430     250-2580
3  [ O + H2 -> OH + H              ]  8.52E-20   2.670   3160.0                              300-2500
5  [ O + H2O -> OH + OH            ]  8.20E-14   0.950   8570.0                              250-2400
```

Forward reactions

$$aA + bB \rightleftharpoons cC + bB$$

reverse reactions

(Assuming it's reversable!)



$$\Delta G^\circ = -R\,T\,\ln K$$

$$K_c = \frac{[C]^c_{eq}\,[D]^d_{eq}}{[A]^a_{eq}\,[B]^b_{eq}}$$

(Equilibrium Constant)

$$\Delta G = \Delta H - T\Delta S$$

ΔH- *Enthalpy change*

T- *Temperature in Kelvin*

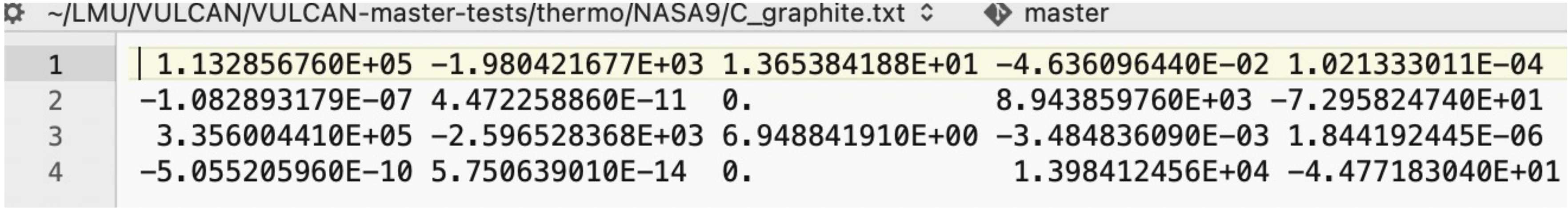
ΔS- *Entropy change*

$K_c >> 1$: Mixture contains mostly products

$K_c << 1$: Mixture contains mostly reactants

1. Walk through VULCAN: HD 189733b

- **Thermo** files
    - /Users/karan/LMU/VULCAN/VULCAN-master-tests/thermos/NASA9



```
 1.132856760E+05 -1.980421677E+03 1.365384188E+01 -4.636096440E-02 1.021333011E-04
-1.082893179E-07 4.472258860E-11  0.               8.943859760E+03 -7.295824740E+01
 3.356004410E+05 -2.596528368E+03 6.948841910E+00 -3.484836090E-03 1.844192445E-06
-5.055205960E-10 5.750639010E-14  0.                1.398412456E+04 -4.477183040E+01
```

$$\frac{C_p^0(T)}{R} = a_0 T^{-2} + a_1 T^{-1} + a_2 + a_3 T + a_4 T^2 + a_5 T^3 + a_6 T^4$$

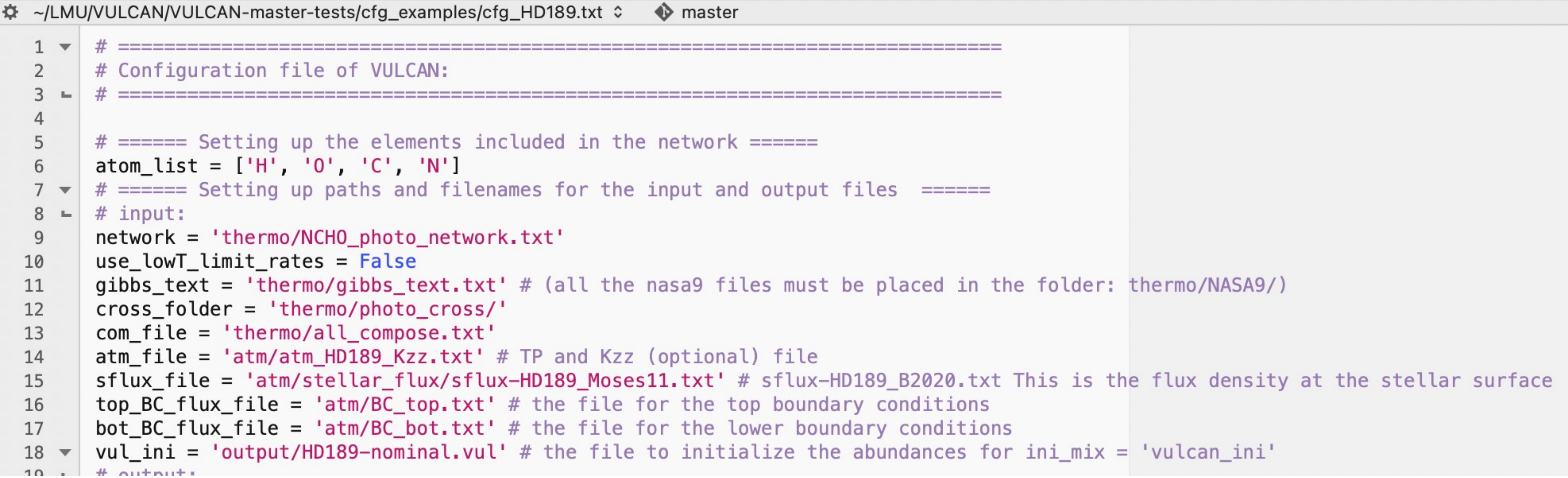
$$\frac{H^0(T)}{RT} = -a_0 T^{-2} + a_1 \frac{\ln T}{T} + a_2 + \frac{a_3}{2} T + \frac{a_4}{3} T^2 + \frac{a_5}{4} T^3 + \frac{a_6}{5} T^4 + \frac{a_7}{T}$$

$$\frac{s^0(T)}{R} = -\frac{a_0}{2} T^{-2} - a_1 T^{-1} + a_2 \ln T + a_3 T + \frac{a_4}{2} T^2 + \frac{a_5}{3} T^3 + \frac{a_6}{4} T^4 + a_8$$

/Users/karan/LMU/VULCAN/VULCAN-master-tests/thermo/make_compose.py

1. Walk through VULCAN: HD 189733b

- **vulcan_cfg.py** file
  - /Users/karan/LMU/VULCAN/VULCAN-master-tests/cfg_examples/cfg_HD189.txt
  - **Let’s open it!**

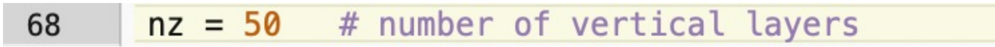


```
# ======================================
# Configuration file of VULCAN:
# ======================================

# ====== Setting up the elements included in the network ======
atom_list = ['H', 'O', 'C', 'N']
# ====== Setting up paths and filenames for the input and output files  ======
# input:
network = 'thermo/NCHO_photo_network.txt'
use_lowT_limit_rates = False
gibbs_text = 'thermo/gibbs_text.txt' # (all the nasa9 files must be placed in the folder: thermo/NASA9/)
cross_folder = 'thermo/photo_cross/'
com_file = 'thermo/all_compose.txt'
atm_file = 'atm/atm_HD189_Kzz.txt' # TP and Kzz (optional) file
sflux_file = 'atm/stellar_flux/sflux-HD189_Moses11.txt' # sflux-HD189_B2020.txt This is the flux density at the stellar surface
top_BC_flux_file = 'atm/BC_top.txt' # the file for the top boundary conditions
bot_BC_flux_file = 'atm/BC_bot.txt' # the file for the lower boundary conditions
vul_ini = 'output/HD189-nominal.vul' # the file to initialize the abundances for ini_mix = 'vulcan_ini'
# output:
```

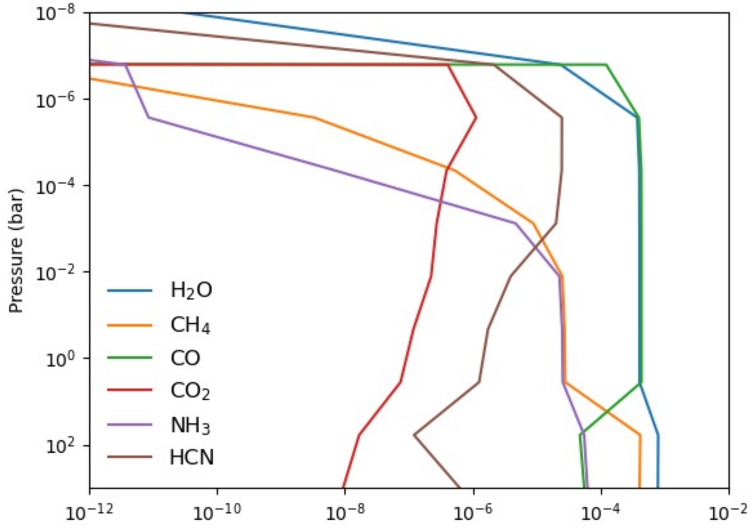
1. Walk through VULCAN: HD 189733b

- Let’s run HD 189733b model **fast**! Any suggestion?
  - Turn off plotting!
  - Solver parameters: atol, rtol, mtol (might work but dangerous!)
  - Atmospheric structure: nz (try 150; 50; 20; 10)
    - The resolution should depend on the purpose of your investigation and how important are your atmospheric fine structures

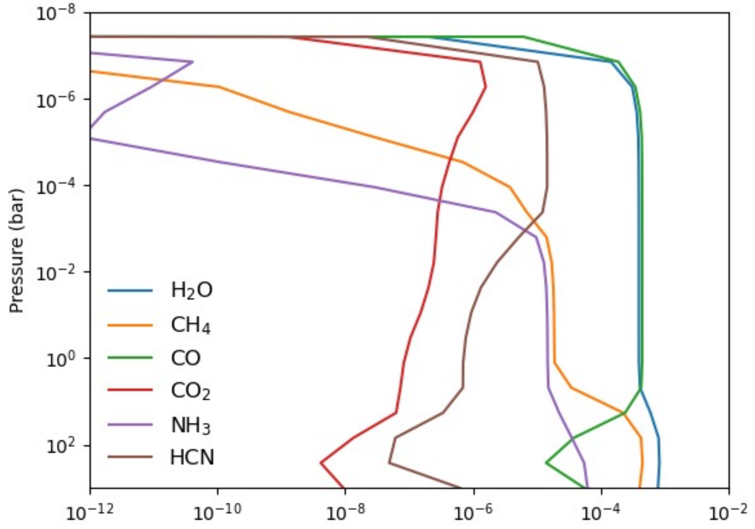


```
nz = 50    # number of vertical layers
```

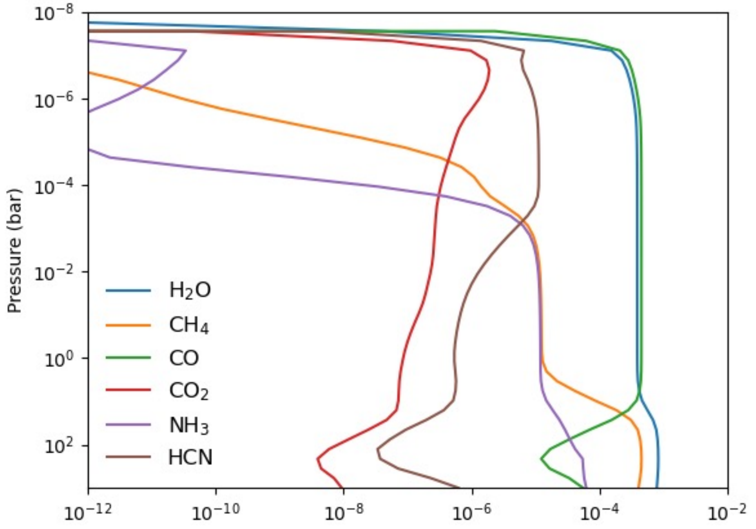
nz=10



nz=20



nz=50



1. Walk through VULCAN: HD 189733b

- Let’s run HD 189733b model **fast**! Any suggestion?
  - Turn off plotting!
  - Solver parameters: atol, rtol, mtol (might work but dangerous!)
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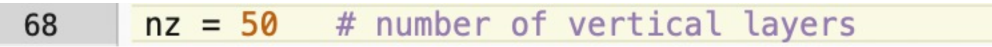


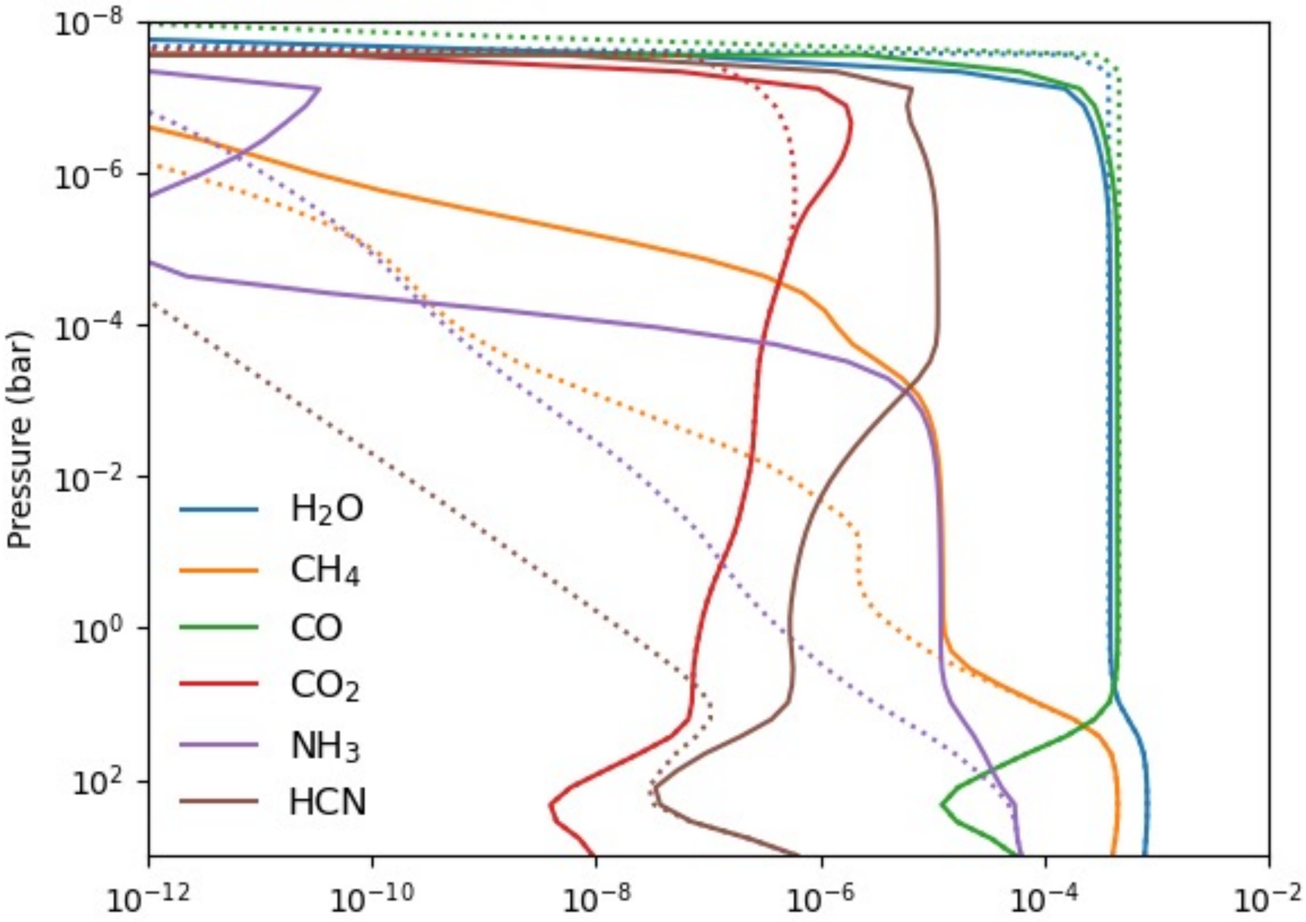
```
nz = 50    # number of vertical layers
```

    - The resolution should depend on the purpose of your investigation and how important are your atmospheric fine structures
- Plot the initial and final abundances for nz=50
  - plot_vulcan.py
- Plot abundances variation in time for nz=50
  - plot_evolution.py

1. Walk through VULCAN: HD 189733b

- Plot the initial and final abundances for nz=50
  - plot_vulcan.py

```
            #plt.plot(data['variable']['y_ini'][:,vulcan
```



1. Walk through VULCAN: HD 189733b

- Plot abundances variation in time for nz=50
  - Did you turn on in the config file:

```
save_evolution = True    # save the evolution of chemistry (y_time
save_evo_frq = 10
```

  - plot_evolution.py

```
vul_data = '../output/HD189.vul'
```

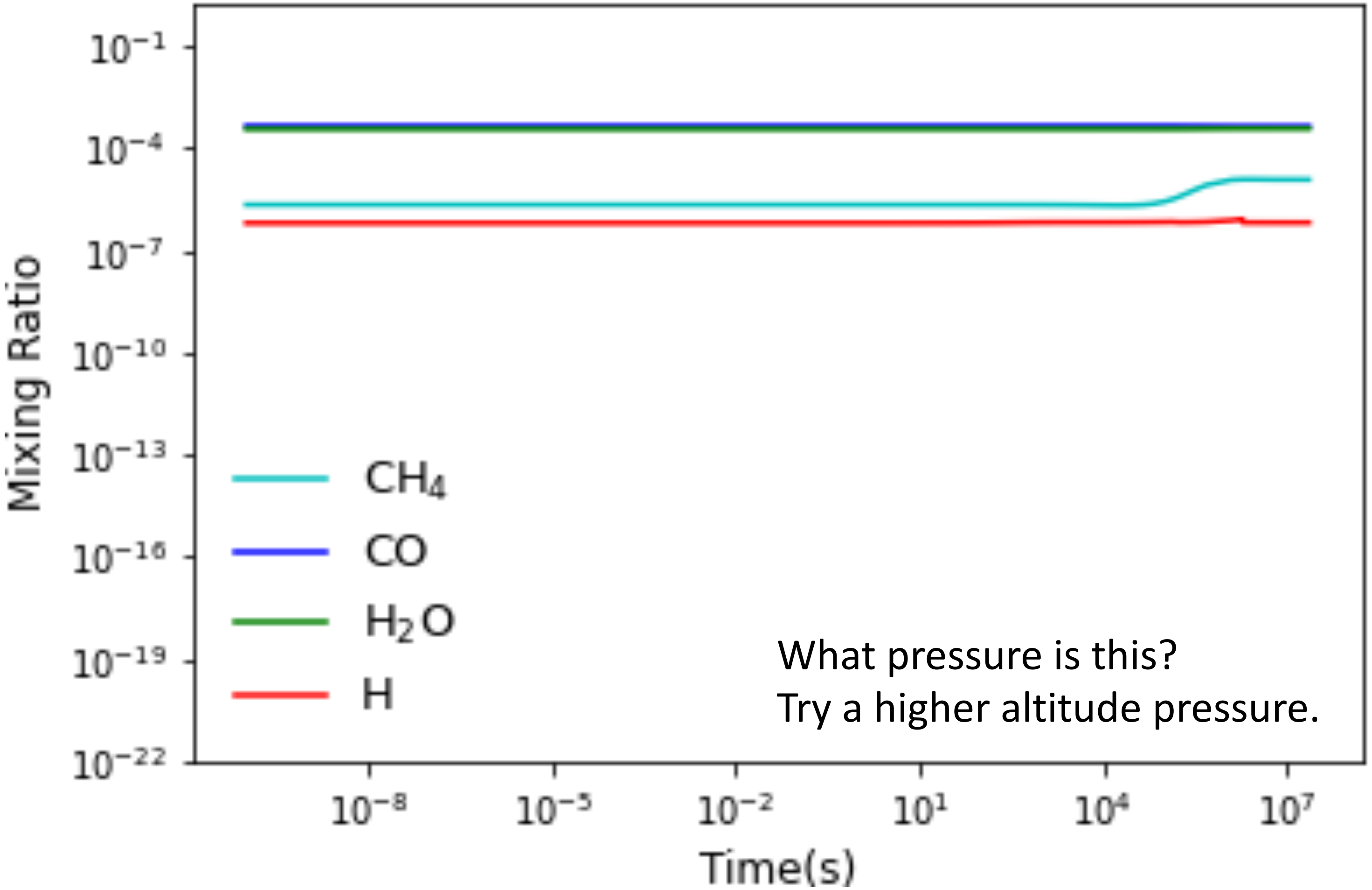
  - A few more tips …

```
plot_spec = ['CH4', 'CO', 'H2O', 'H']
# plot_spec = ['CH4','H2O', 'OH', 'O2', 'O3']
```

```
plt.figure()
```

1. Walk through VULCAN: HD 189733b

- Plot abundances variation in time for nz=50



What pressure is this?
Try a higher altitude pressure.

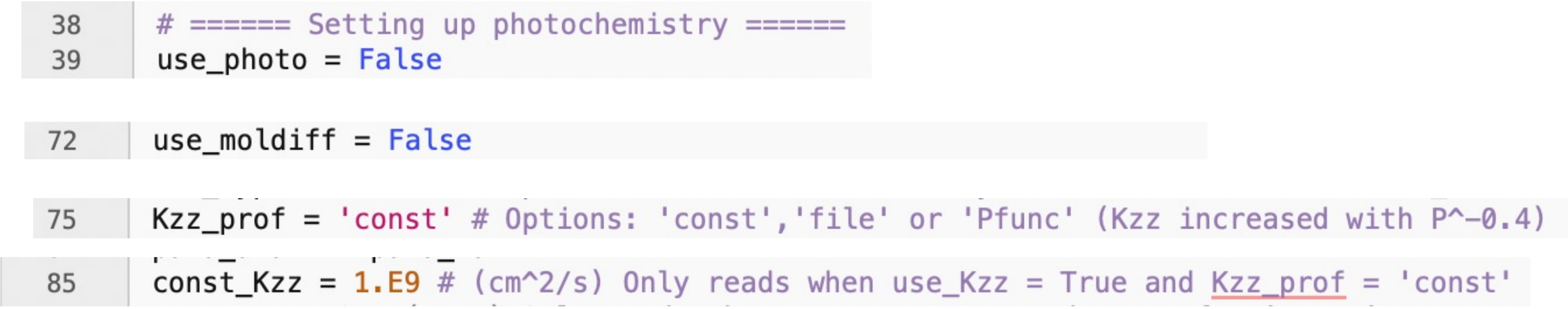
2. Quest to find Quenching point!

- Run HD189
  - nz=50
  - No photochemistry
  - No BC
  - No Molecular Diffusion
  - Turn on and off Eddy Diffusion
    - Assume constant Kzz=1e9 & 1e12 (cm^2/s) cases

- Compare the quenching points of major species

2. Quest to find Quenching point!

- Run HD189
  - nz=50, No photochemistry, No BC, No Molecular Diffusion, Turn on and off Eddy Diffusion
    - Assume constant Kzz=1e9 & 1e12 (cm^2/s) cases



```
# ====== Setting up photochemistry ======
use_photo = False
```

```
use_moldiff = False
```

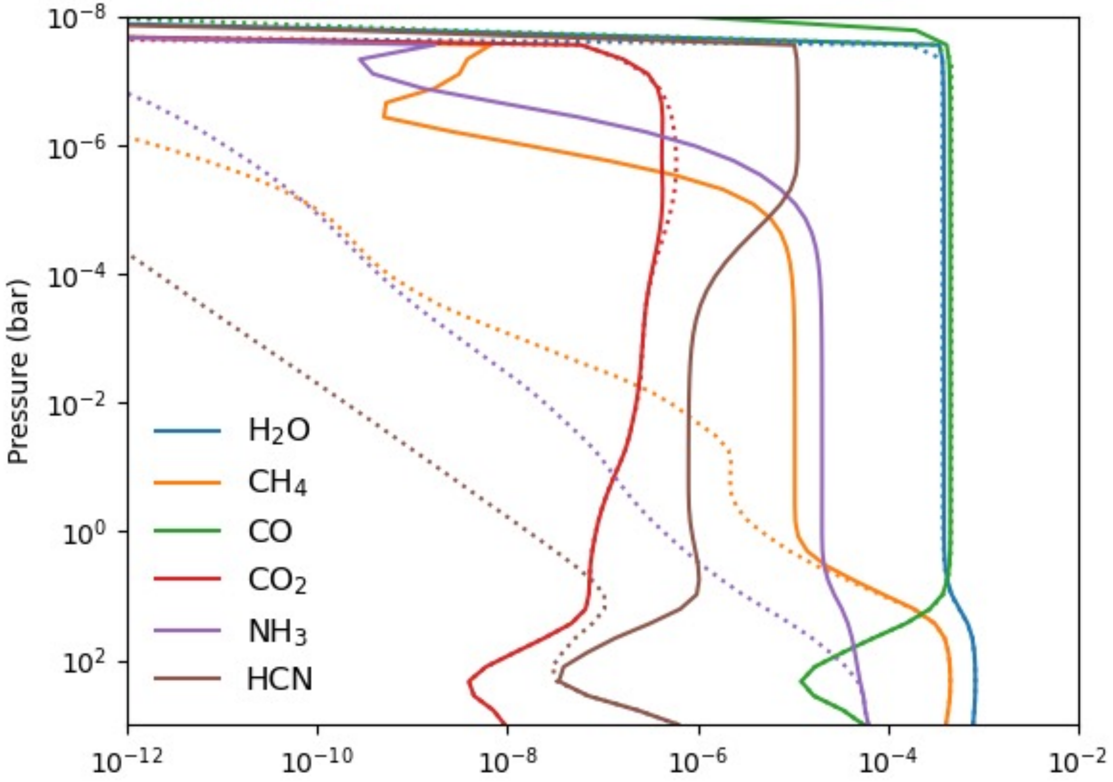
```
Kzz_prof = 'const' # Options: 'const','file' or 'Pfunc' (Kzz increased with P^-0.4)
```

```
const_Kzz = 1.E9 # (cm^2/s) Only reads when use_Kzz = True and Kzz_prof = 'const'
```

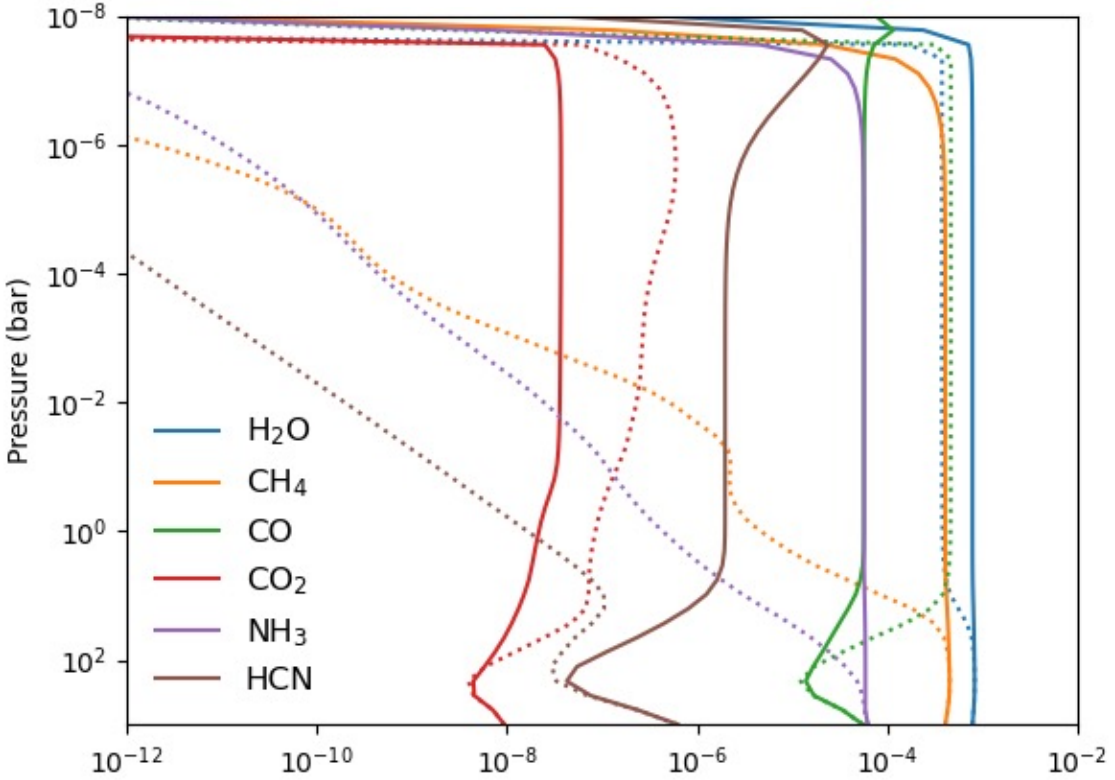
2. Quest to find Quenching point!

- Compare the quenching points of major species

Kzz=1e9



Kzz=1e12



3. Thermochemical Equilibrium: Consistency & Convergence

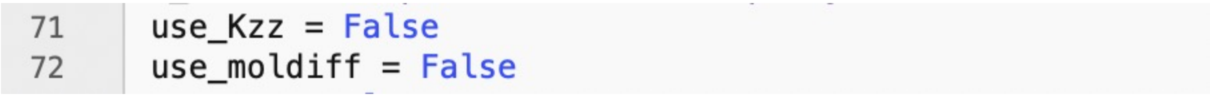
- Assume
  - TP as in HD 189
  - Elemental abundance initialization
    - Use the **customized elemental abundances**
  - No diffusion, photochemistry, or BC flux

- Calculate the abundances
  - With Gibbs initialization:
    - What is your expectation in terms of abundance evolution (plot it) and computational time?
  - Without Gibbs initialization:
    - What is your expectation in terms of convergence?
    - Are your results consistent with the previous part?

3. Thermochemical Equilibrium: Consistency & Convergence

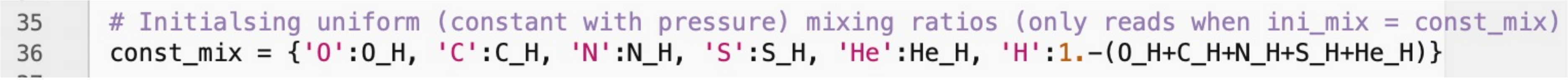
- Assume
  - TP as in HD 189
  - Elemental abundance initialization
    - Use the **customized elemental abundances**
  - No diffusion, No photochemistry, No BC flux

```
# ====== Setting up photochemistry ======
use_photo = False
```



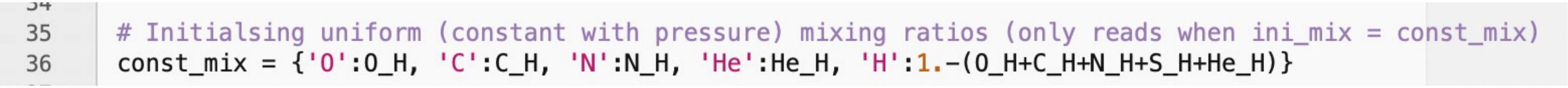
```
use_Kzz = False
use_moldiff = False
```

Kinda like this:



```
# Initialsing uniform (constant with pressure) mixing ratios (only reads when ini_mix = const_mix)
const_mix = {'O':O_H, 'C':C_H, 'N':N_H, 'S':S_H, 'He':He_H, 'H':1.-(O_H+C_H+N_H+S_H+He_H)}
```

But …



```
# Initialsing uniform (constant with pressure) mixing ratios (only reads when ini_mix = const_mix)
const_mix = {'O':O_H, 'C':C_H, 'N':N_H, 'He':He_H, 'H':1.-(O_H+C_H+N_H+S_H+He_H)}
```

3. Thermochemical Equilibrium: Consistency & Convergence

- Calculate the abundances with
  - With Gibbs initialization (**ini_mix = 'EQ'**):
    - What is your expectation in terms of abundance evolution (plot it) and computational time?

3. Thermochemical Equilibrium: Consistency & Convergence

- Calculate the abundances
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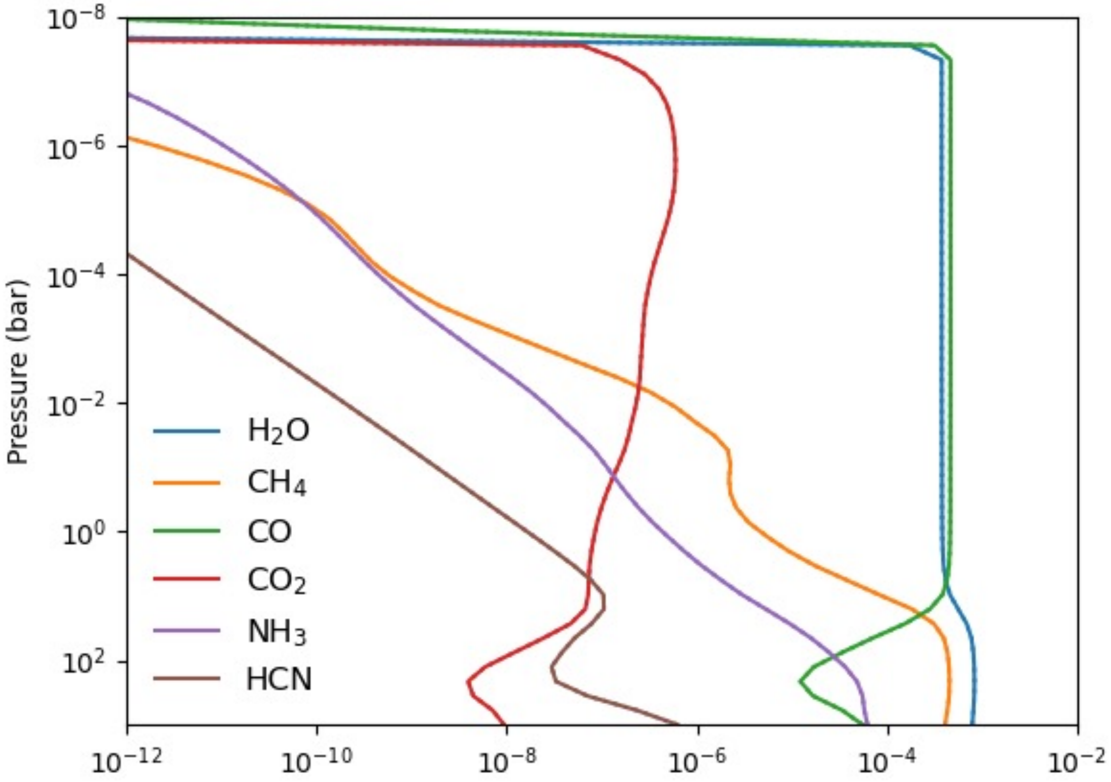
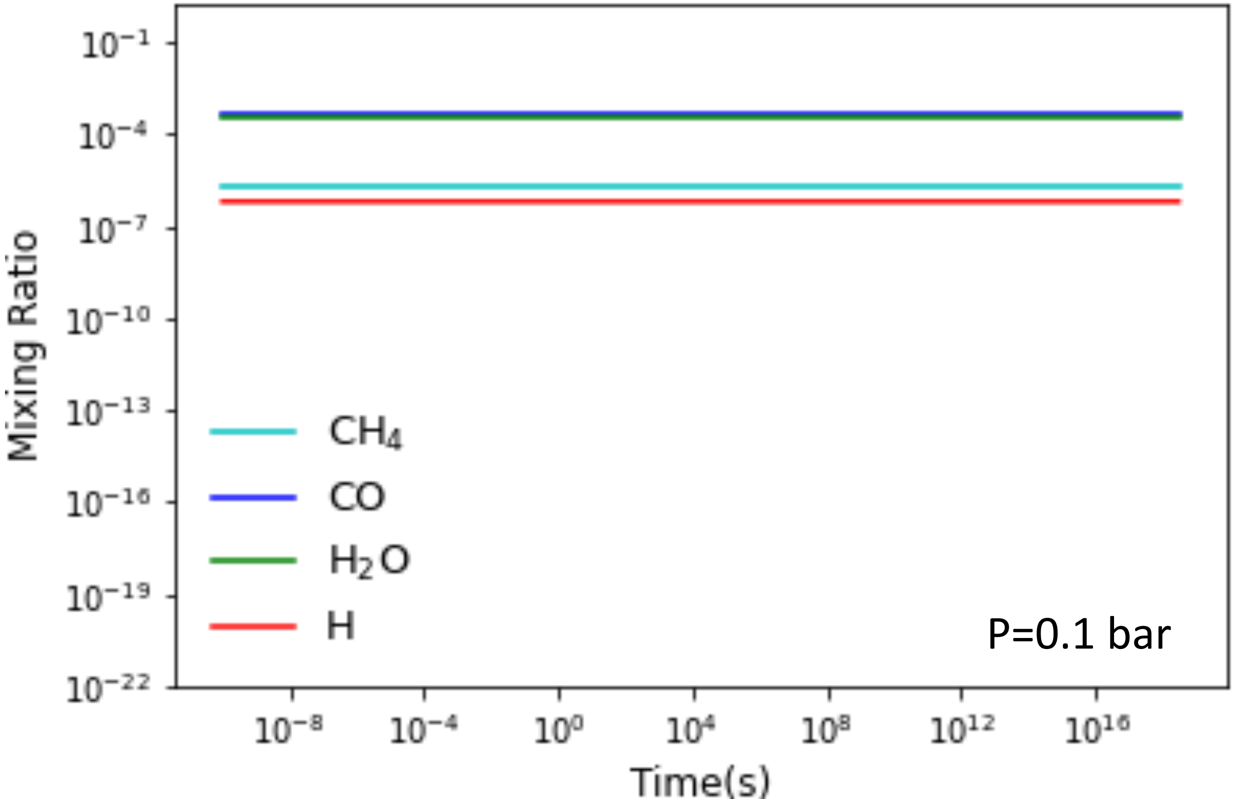
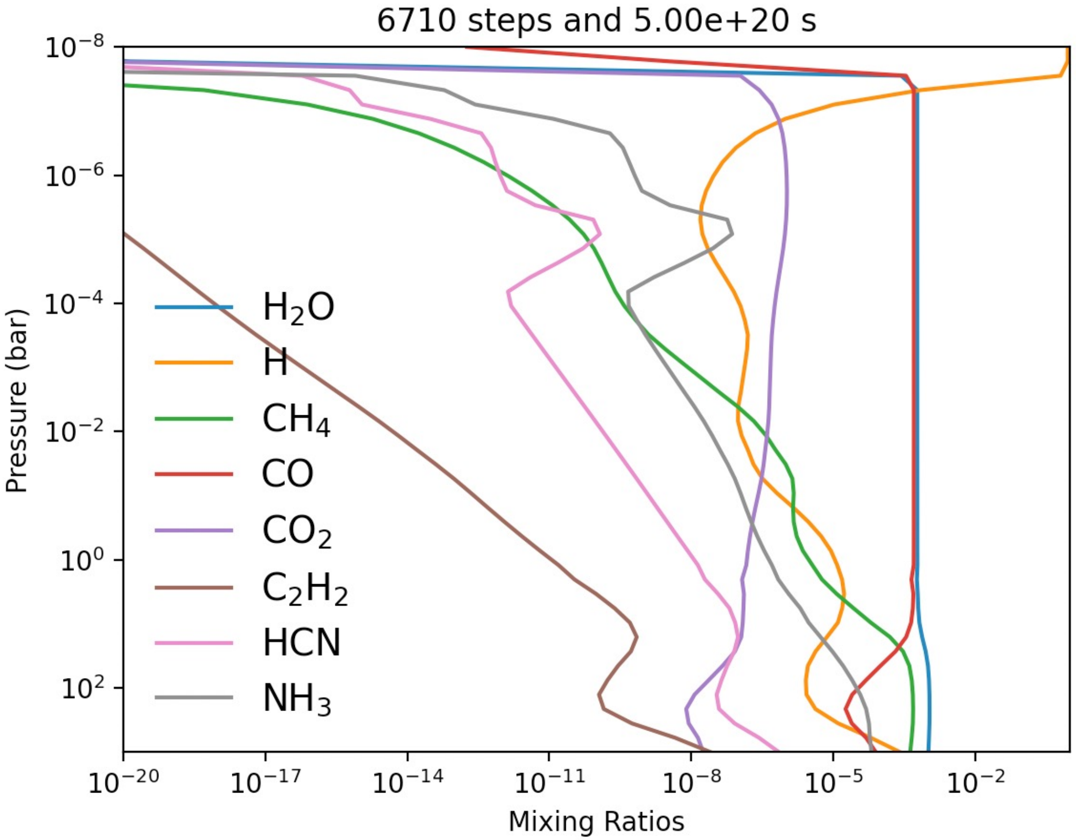




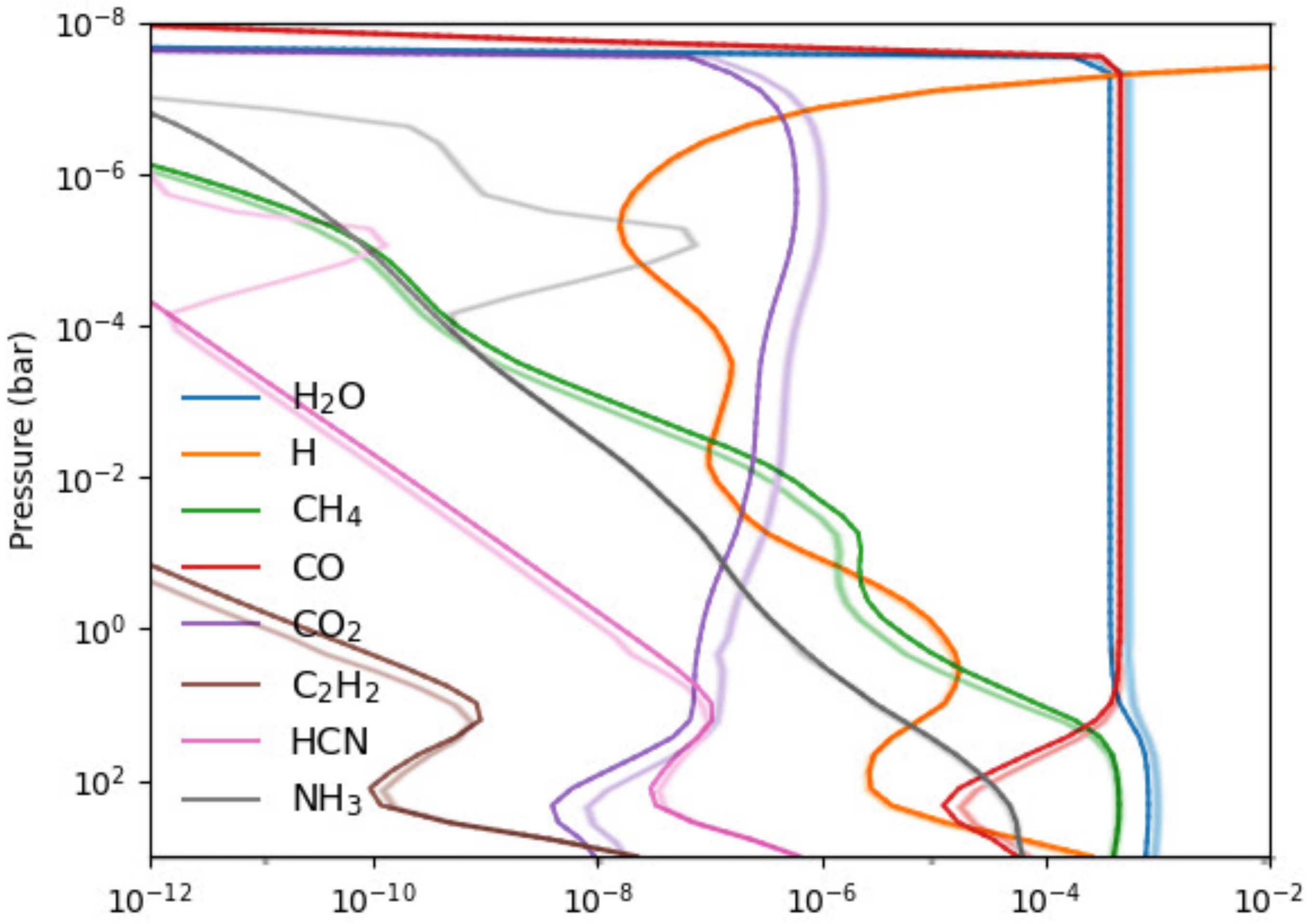
3. Thermochemical Equilibrium: Consistency & Convergence

- Calculate the abundances
  - Without Gibbs initialization (**ini_mix = 'const_mix'**):
    - What is your expectation in terms of convergence?
    - Are your results consistent with the previous part?



3. Thermochemical Equilibrium: Consistency & Convergence

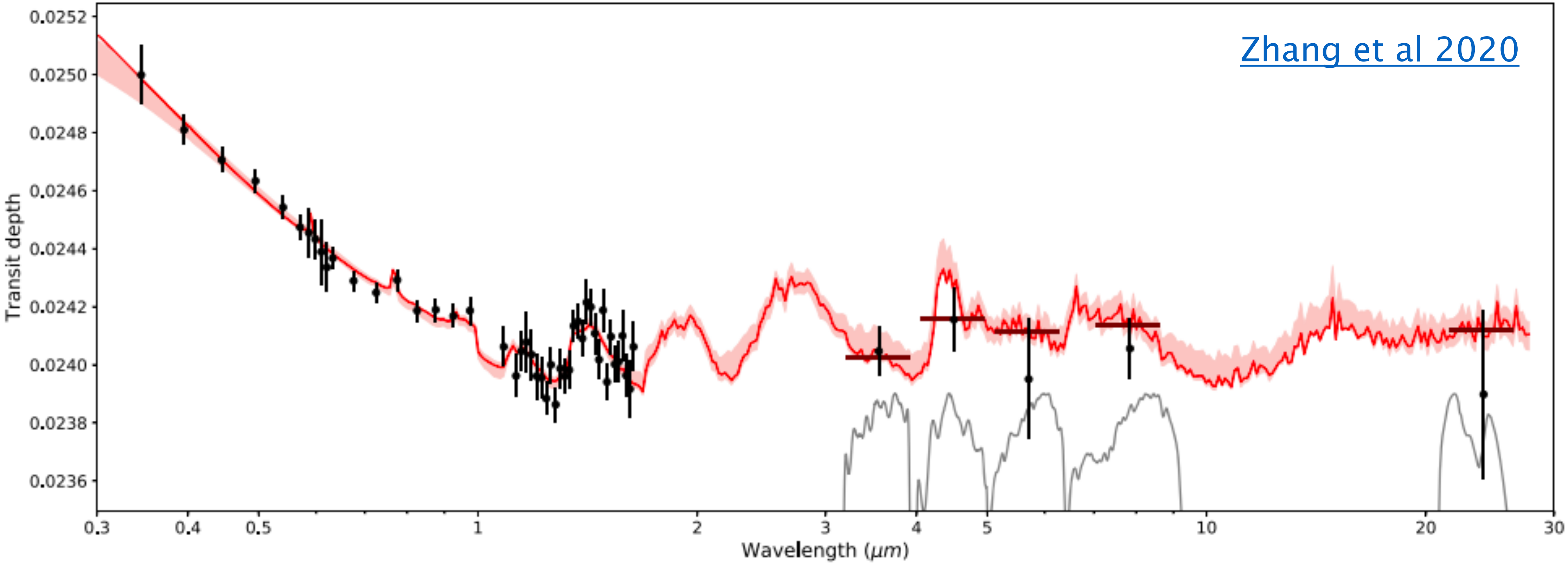
- Calculate the abundances (**ini_mix = 'EQ'**: **bold lines**)
  - Without Gibbs initialization (**ini_mix = 'const_mix': transparent lines**):



Some Homeworks!

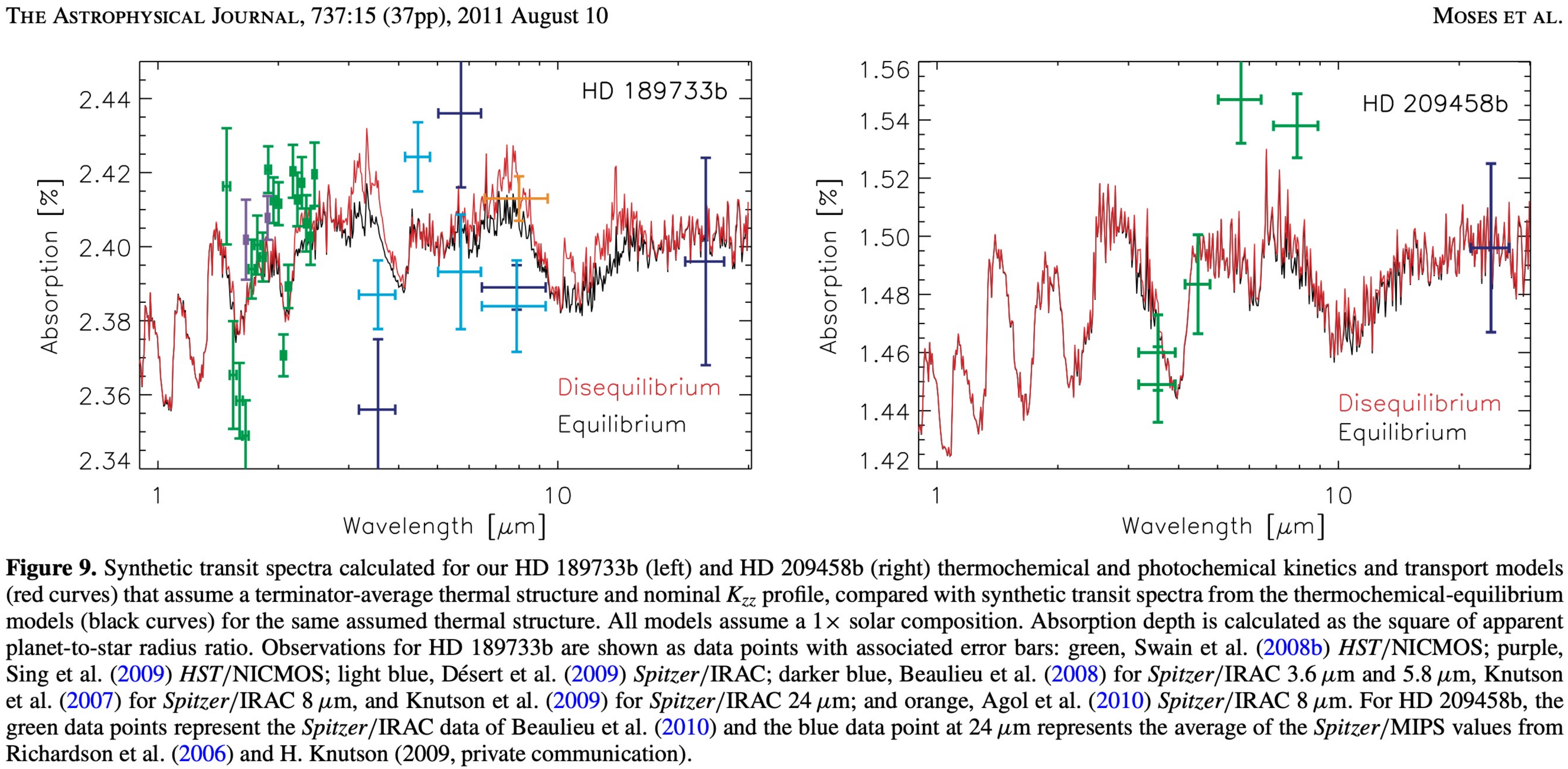
HW1: Read & plot the output in petitRADTRANS

- Use the results of your nominal HD189 model
- Check the units
- Read TP and abundances in pRT and plot a transmission spectrum for it.
- Is it consistent with what has been observed? If not, why?



HW2: Fingerprint of disequilibrium chemistry

- Calculate how much disequilibrium chemistry is important for JWST's ERS observations

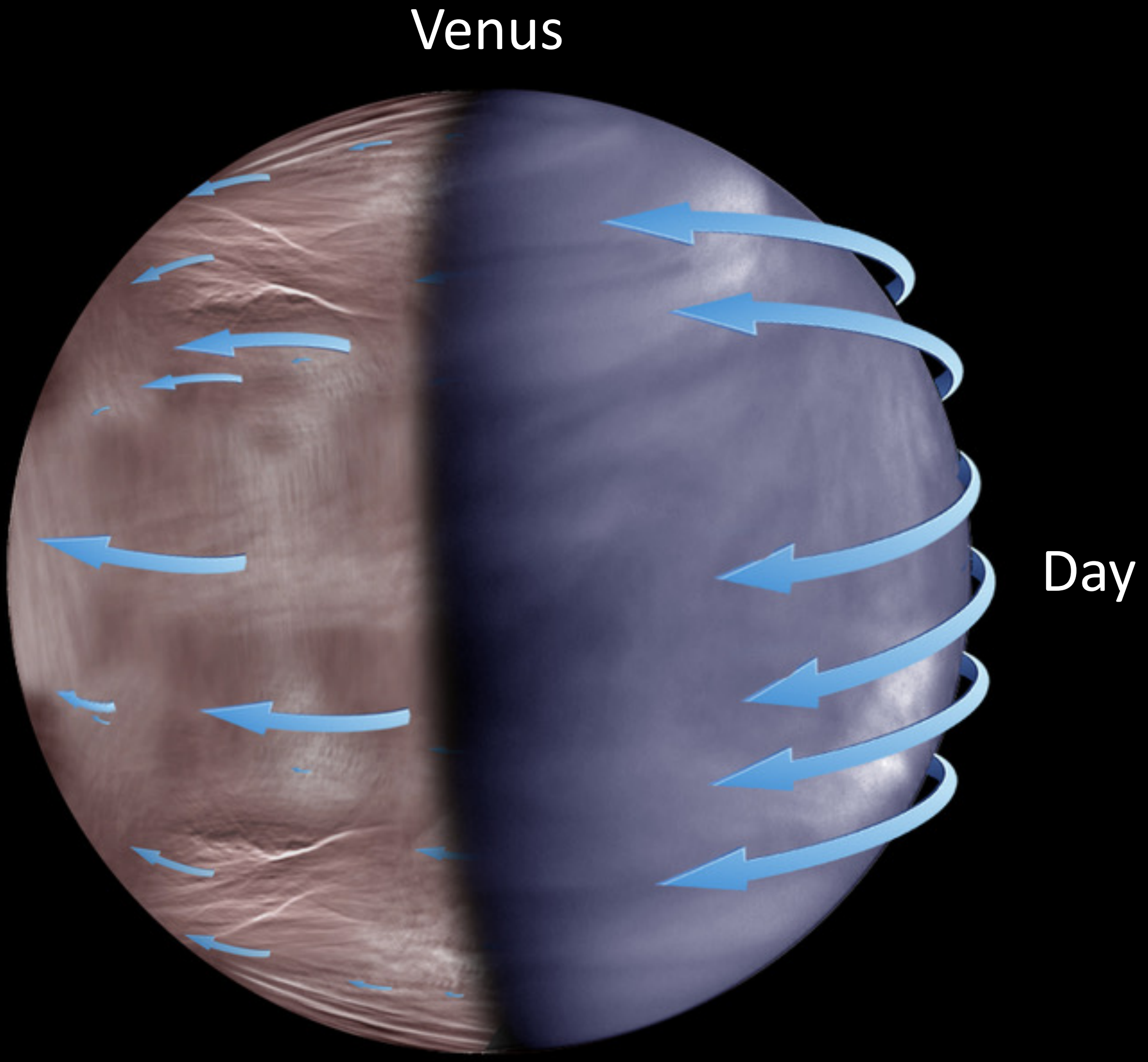


THE ASTROPHYSICAL JOURNAL, 737:15 (37pp), 2011 August 10 — MOSES ET AL.

Figure 9. Synthetic transit spectra calculated for our HD 189733b (left) and HD 209458b (right) thermochemical and photochemical kinetics and transport models (red curves) that assume a terminator-average thermal structure and nominal K_{zz} profile, compared with synthetic transit spectra from the thermochemical-equilibrium models (black curves) for the same assumed thermal structure. All models assume a 1× solar composition. Absorption depth is calculated as the square of apparent planet-to-star radius ratio. Observations for HD 189733b are shown as data points with associated error bars: green, Swain et al. (2008b) *HST*/NICMOS; purple, Sing et al. (2009) *HST*/NICMOS; light blue, Désert et al. (2009) *Spitzer*/IRAC; darker blue, Beaulieu et al. (2008) for *Spitzer*/IRAC 3.6 μm and 5.8 μm, Knutson et al. (2007) for *Spitzer*/IRAC 8 μm, and Knutson et al. (2009) for *Spitzer*/IRAC 24 μm; and orange, Agol et al. (2010) *Spitzer*/IRAC 8 μm. For HD 209458b, the green data points represent the *Spitzer*/IRAC data of Beaulieu et al. (2010) and the blue data point at 24 μm represents the average of the *Spitzer*/MIPS values from Richardson et al. (2006) and H. Knutson (2009, private communication).

Final words …

Planets are complex 3D objects!



More in Ludmila's talk!

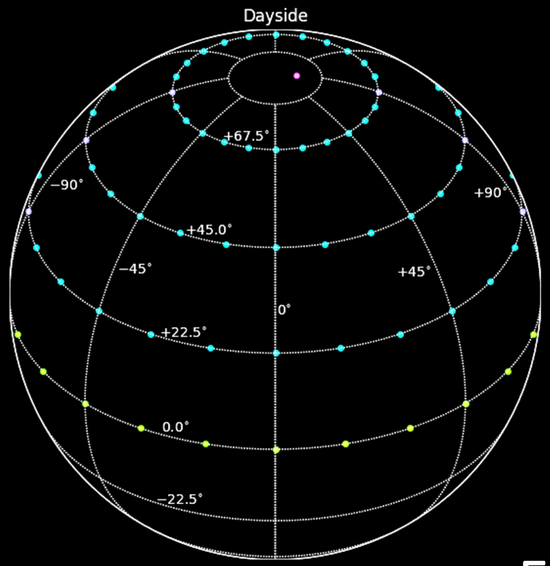
[ESA/Jaxa]

HAT-p-7b
T: 2700 K

DRIFT
(Clouds)

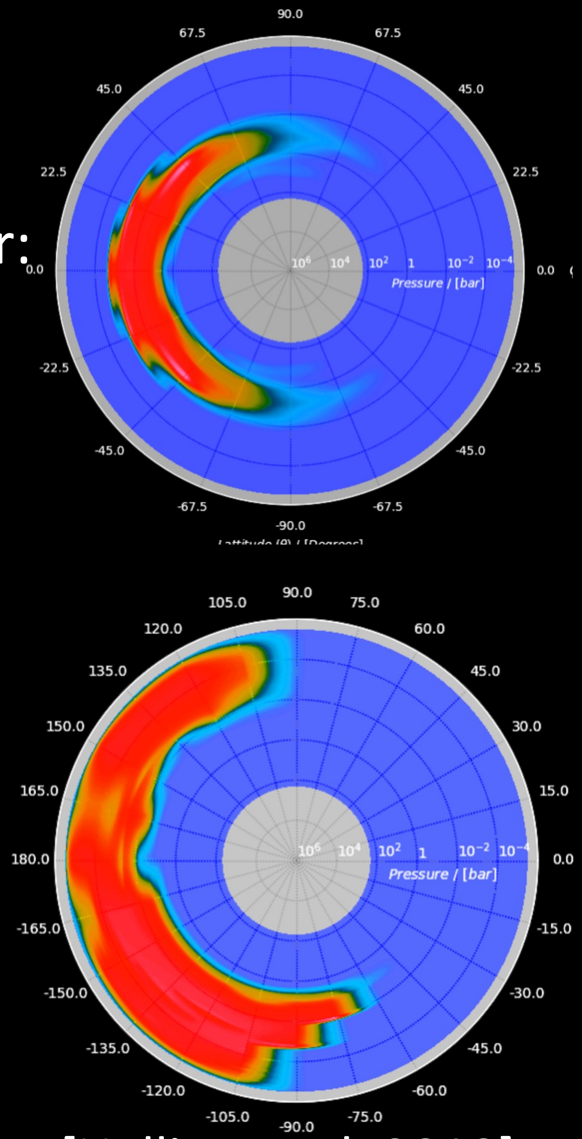
ChemKM
(Diseq. Chem)

GCM

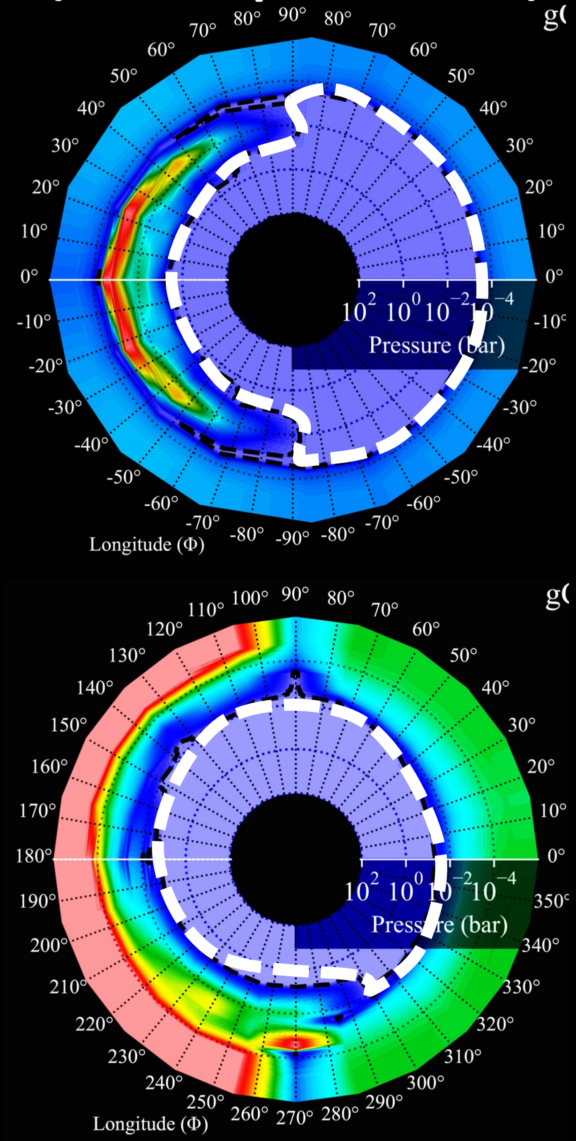


Terminator:

Equator:



[Helling et al. 2019]



[Molaverdikhani et al. 2020a]

More in Ludmila's talk!

Now planets are in your hand!

Let's be in touch!

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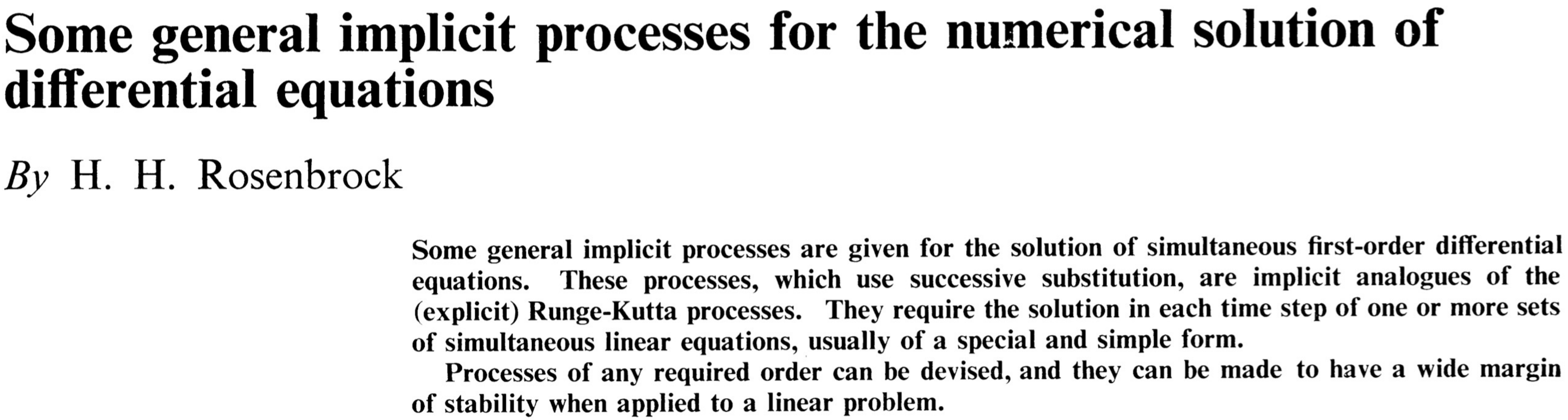
Karan.Molaverdikhani@lmu.de
Karan@lsw.uni-heidelberg.de
Karan@mpia.de

Or simply, google me.

Ros2

Rosenbrock methods for stiff differential equations are a family of single-step methods for solving ordinary differential equations. They are related to the implicit Runge–Kutta methods and are also known as Kaps–Rentrop methods.



Some general implicit processes for the numerical solution of differential equations

By H. H. Rosenbrock

Some general implicit processes are given for the solution of simultaneous first-order differential equations. These processes, which use successive substitution, are implicit analogues of the (explicit) Runge-Kutta processes. They require the solution in each time step of one or more sets of simultaneous linear equations, usually of a special and simple form.

Processes of any required order can be devised, and they can be made to have a wide margin of stability when applied to a linear problem.

The Computer Journal, Volume 5, Issue 4, 1963, Pages 329–330, https://doi.org/10.1093/comjnl/5.4.329