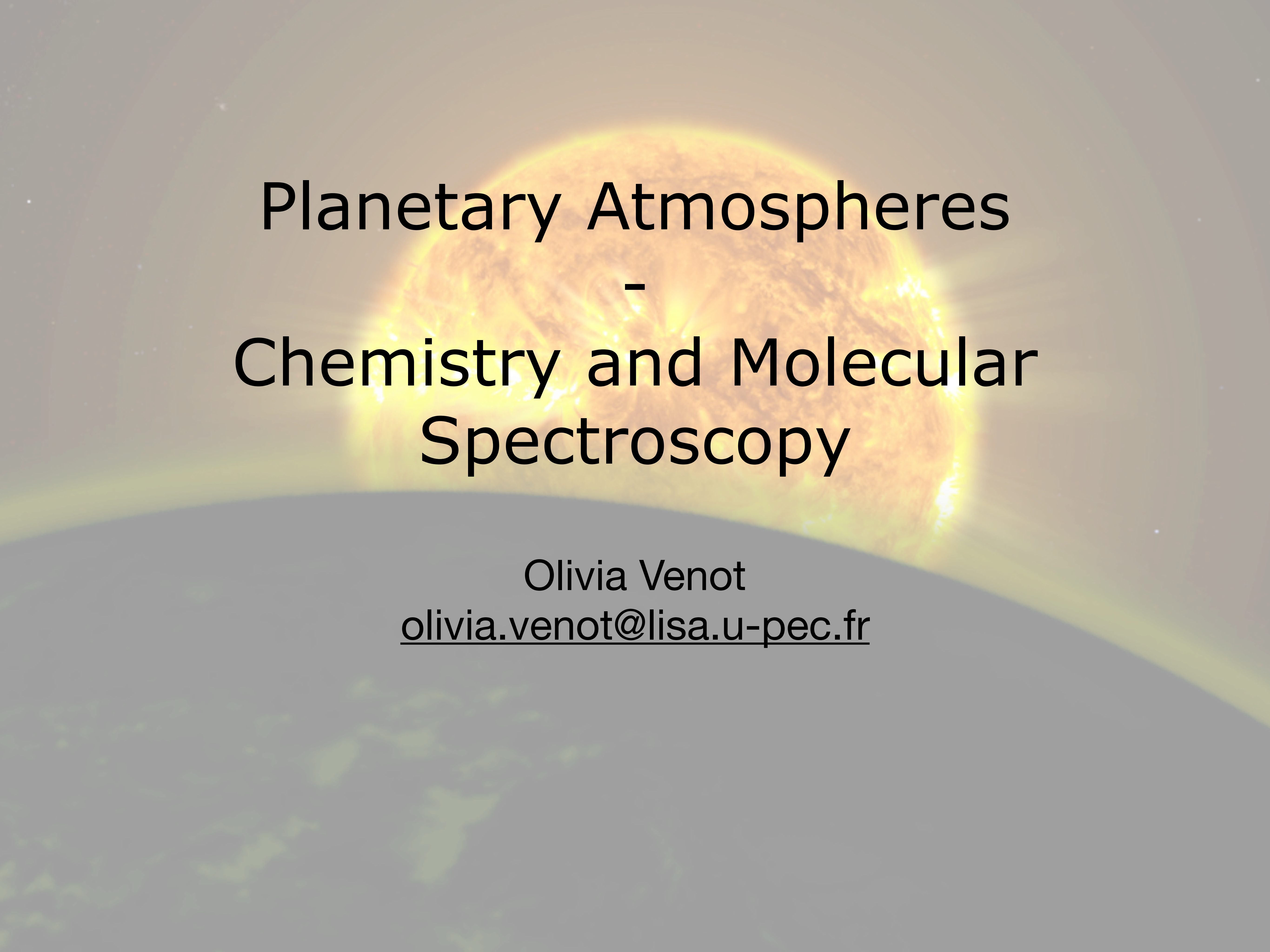
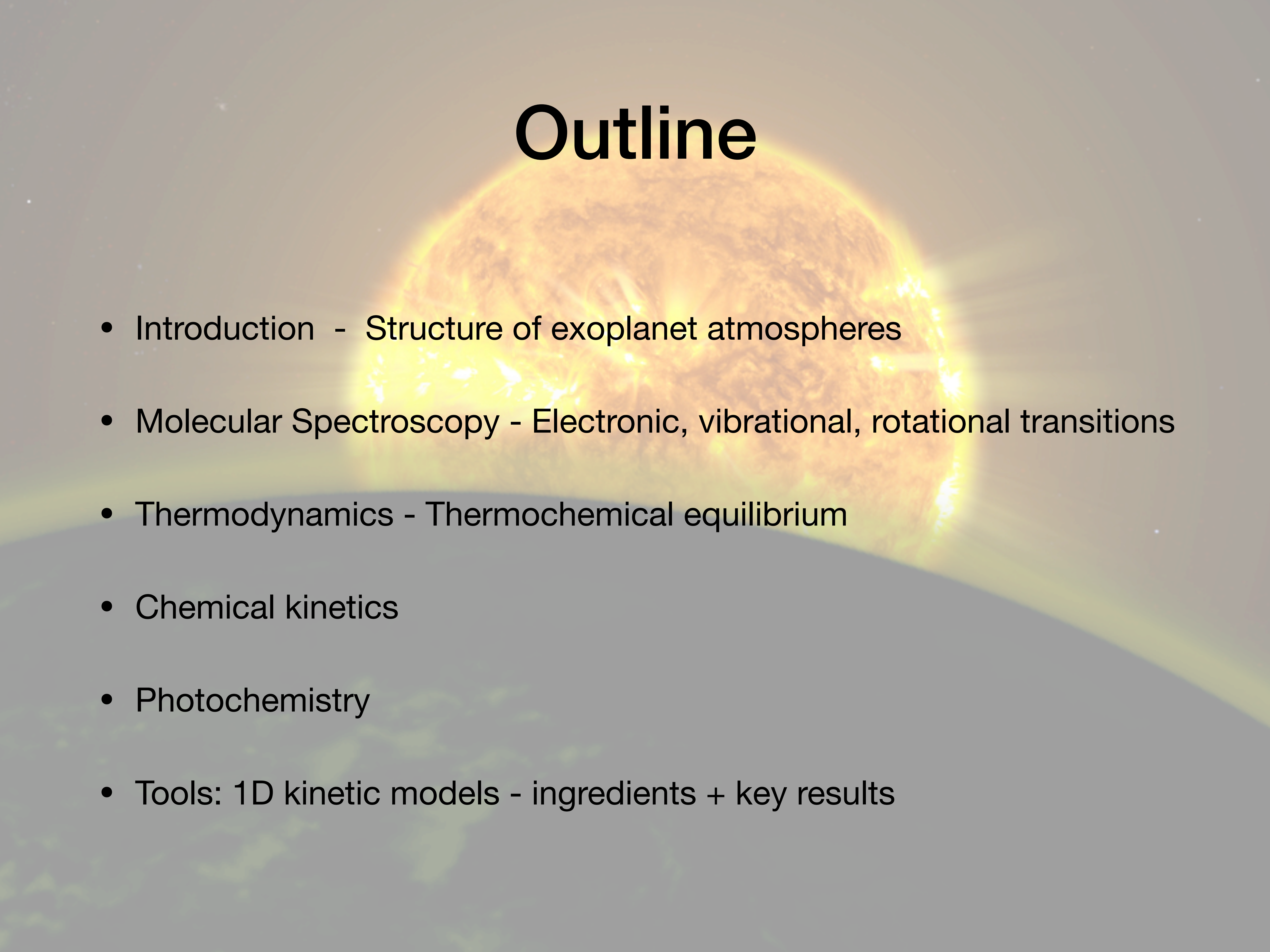


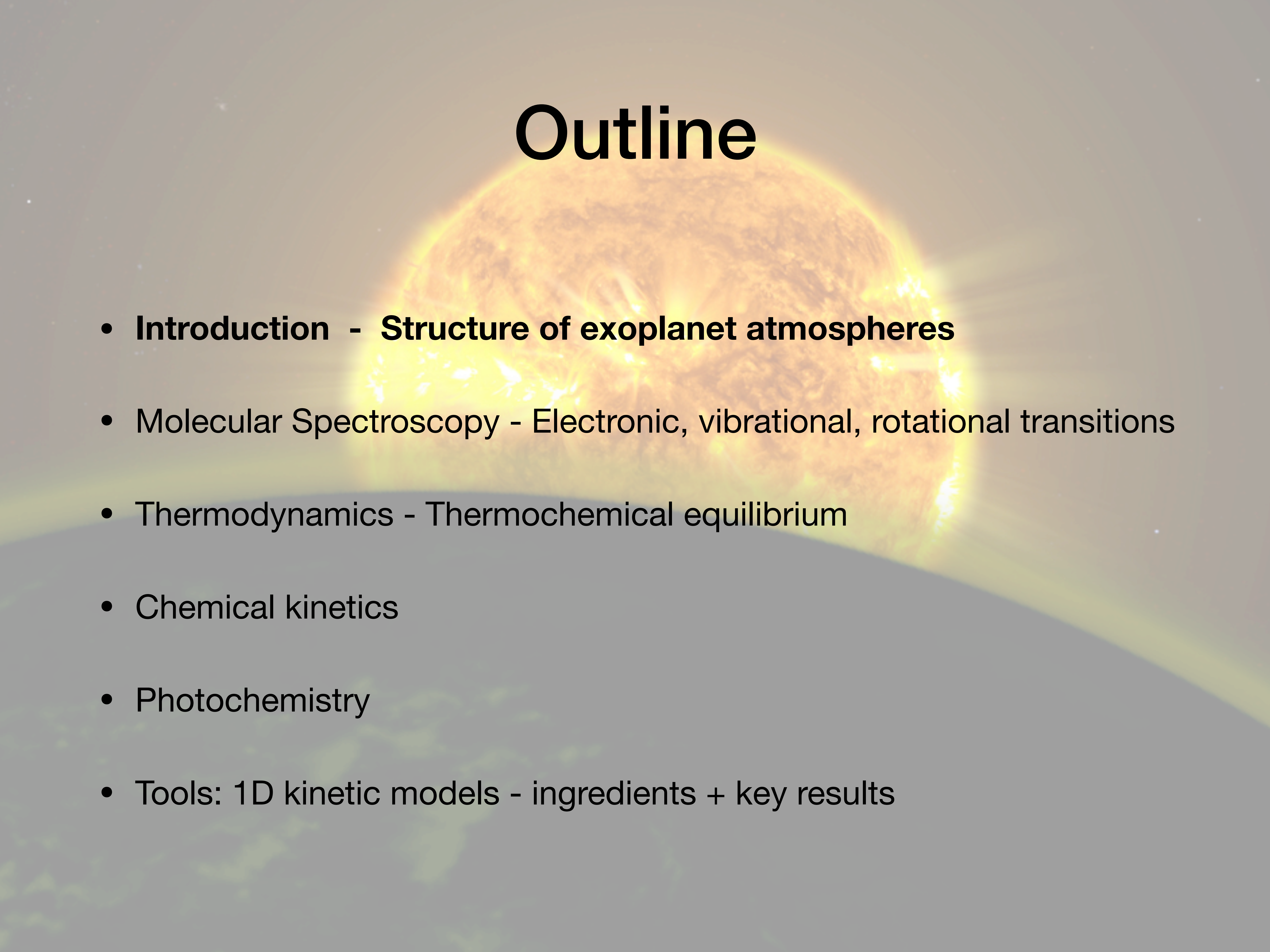
Planetary Atmospheres
-
Chemistry and Molecular Spectroscopy

Olivia Venot
olivia.venot@lisa.u-pec.fr



Outline

- Introduction - Structure of exoplanet atmospheres
- Molecular Spectroscopy - Electronic, vibrational, rotational transitions
- Thermodynamics - Thermochemical equilibrium
- Chemical kinetics
- Photochemistry
- Tools: 1D kinetic models - ingredients + key results



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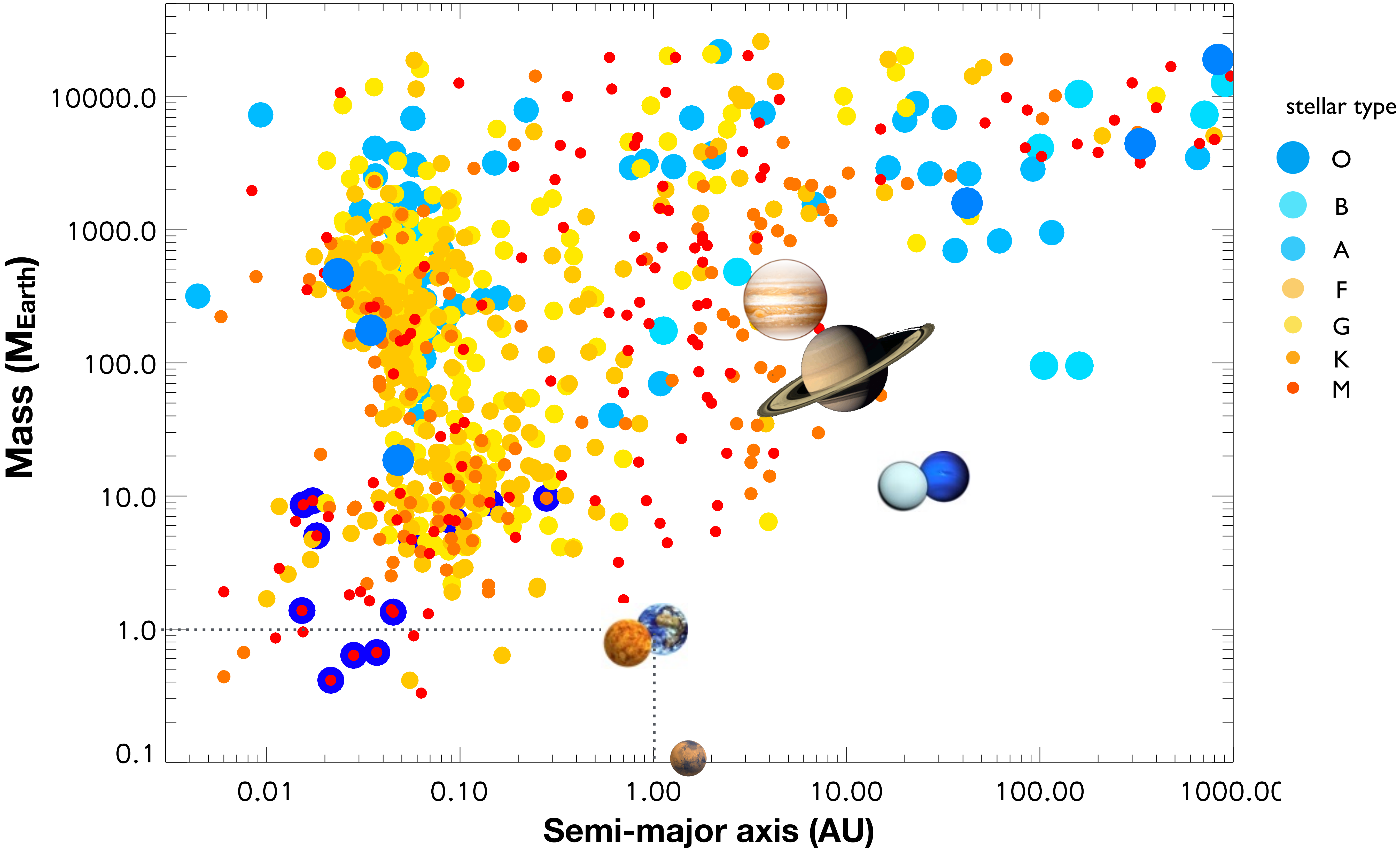
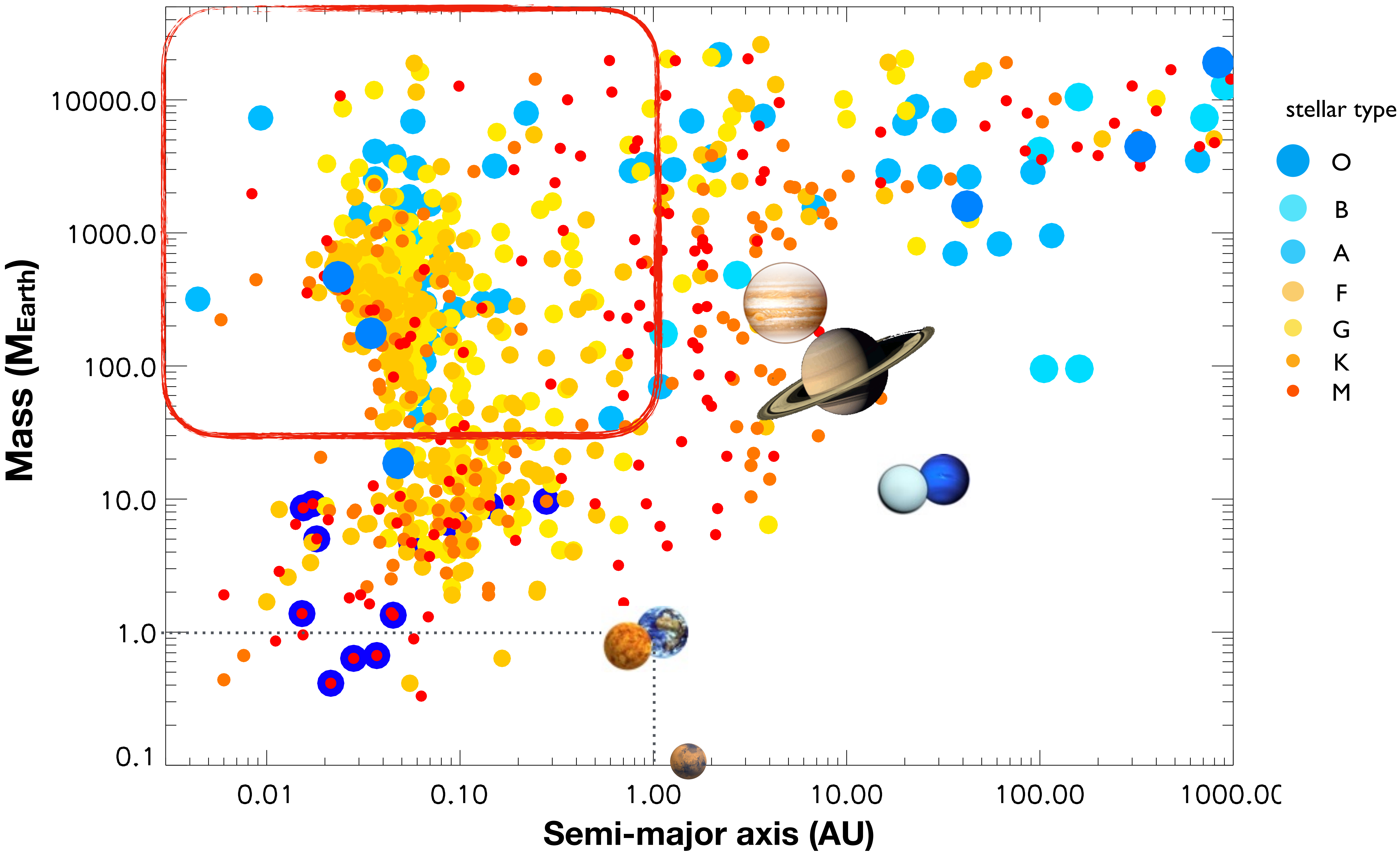
Diversity of planetary worlds



source: exoplanet.eu (september, 25st 2019)

4115 exoplanets + 8 solar system planets

Diversity of planetary worlds



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4115 exoplanets + 8 solar system planets

Some scientific questions

- What is the history of these planets ?

- How did they form ?

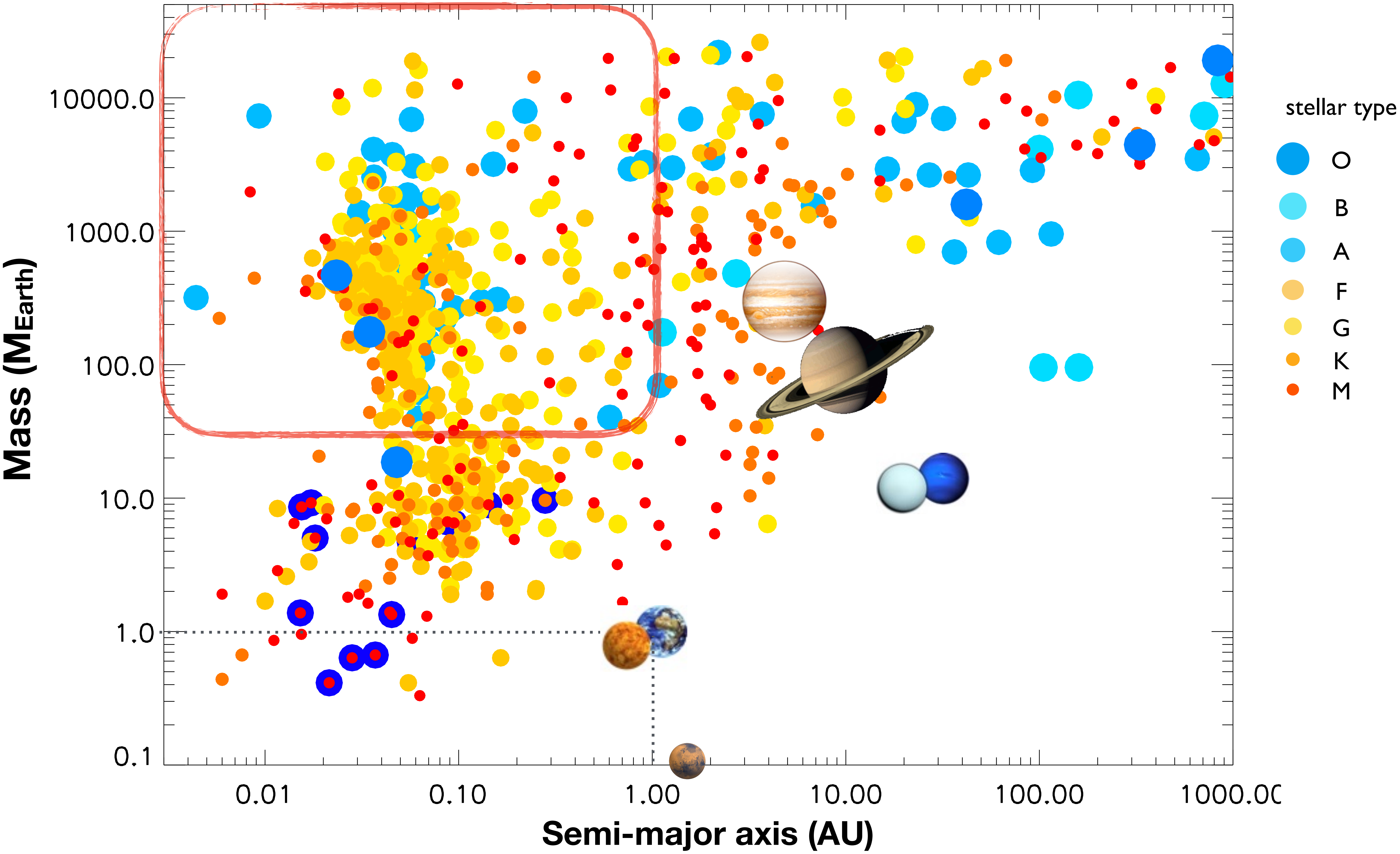
➡ What is the chemical composition of their atmosphere ?

➡ What are the elemental ratios ?

➡ Are they the same than their host star ? or are they enriched ?

➡ **Determine one or several scenarios of planetary formation, common with the Solar System (if possible)**

Diversity of planetary worlds



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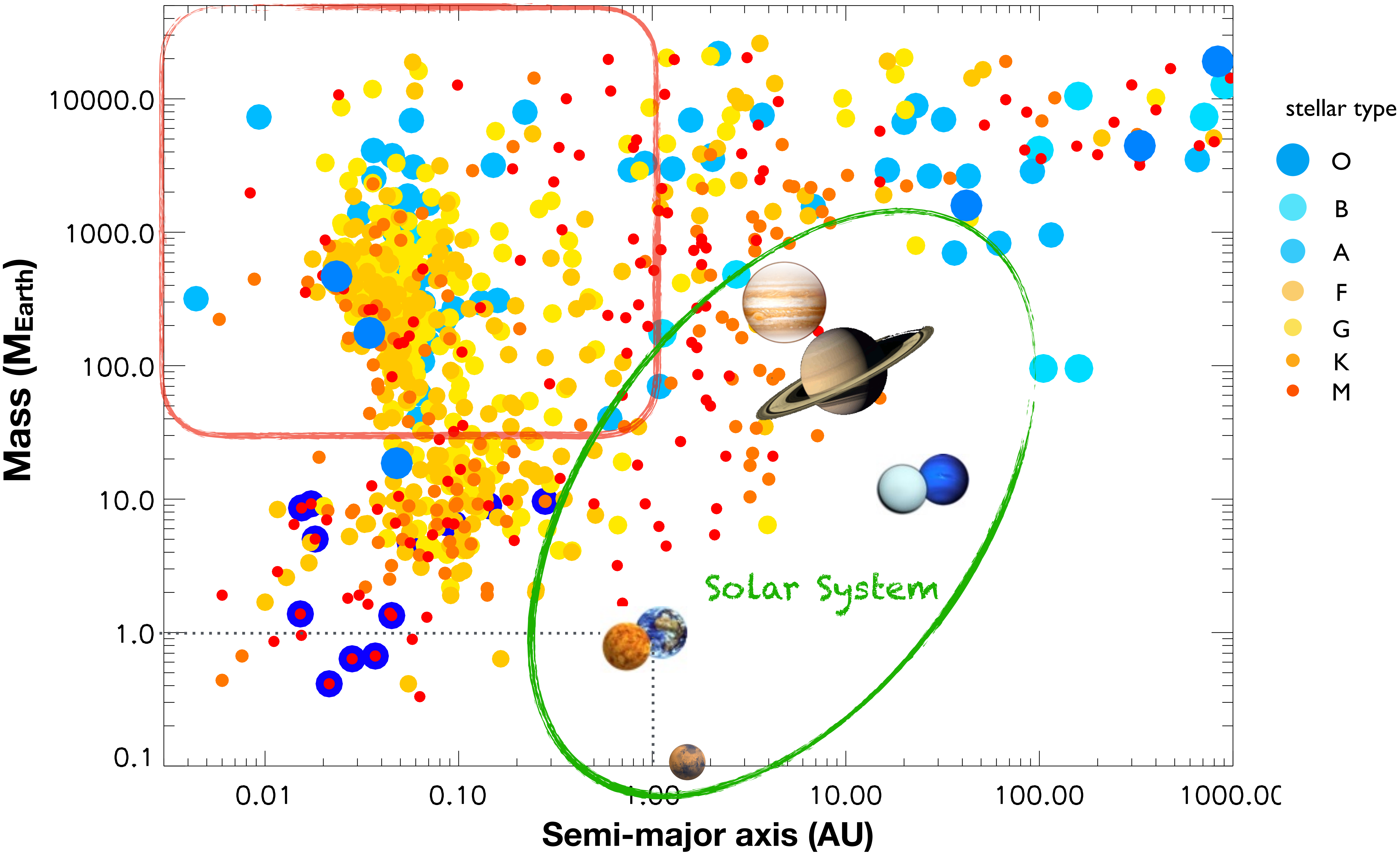

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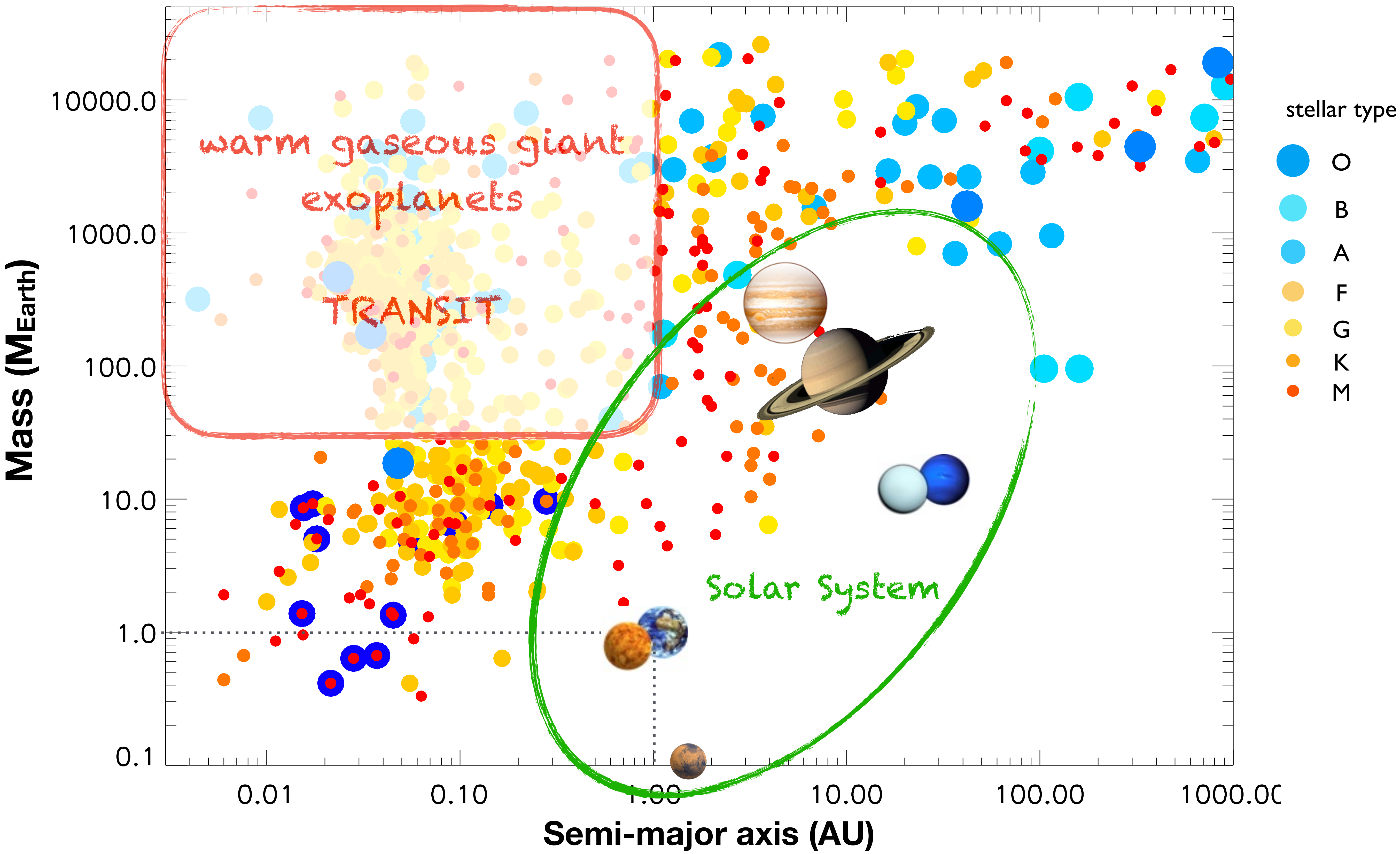

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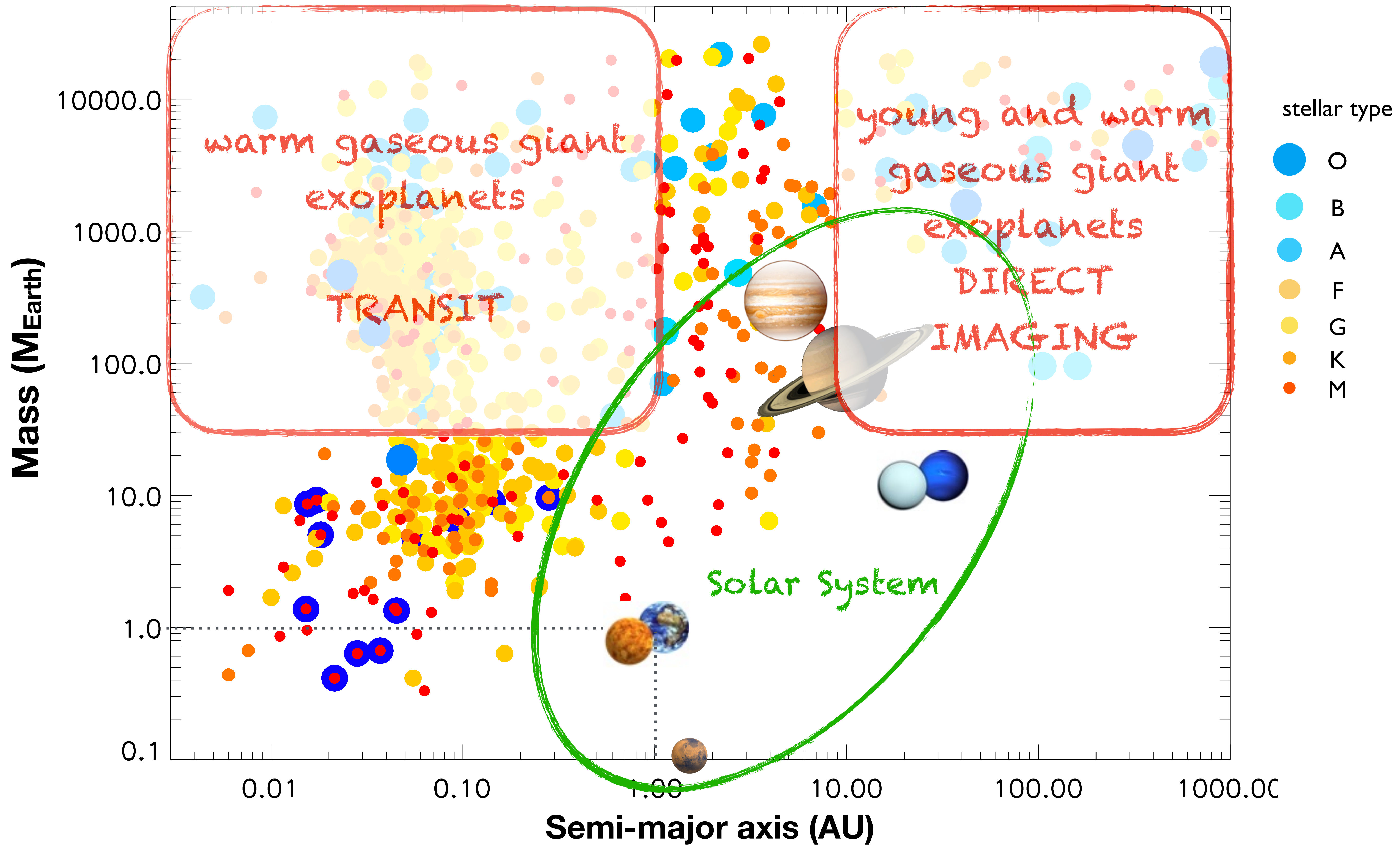

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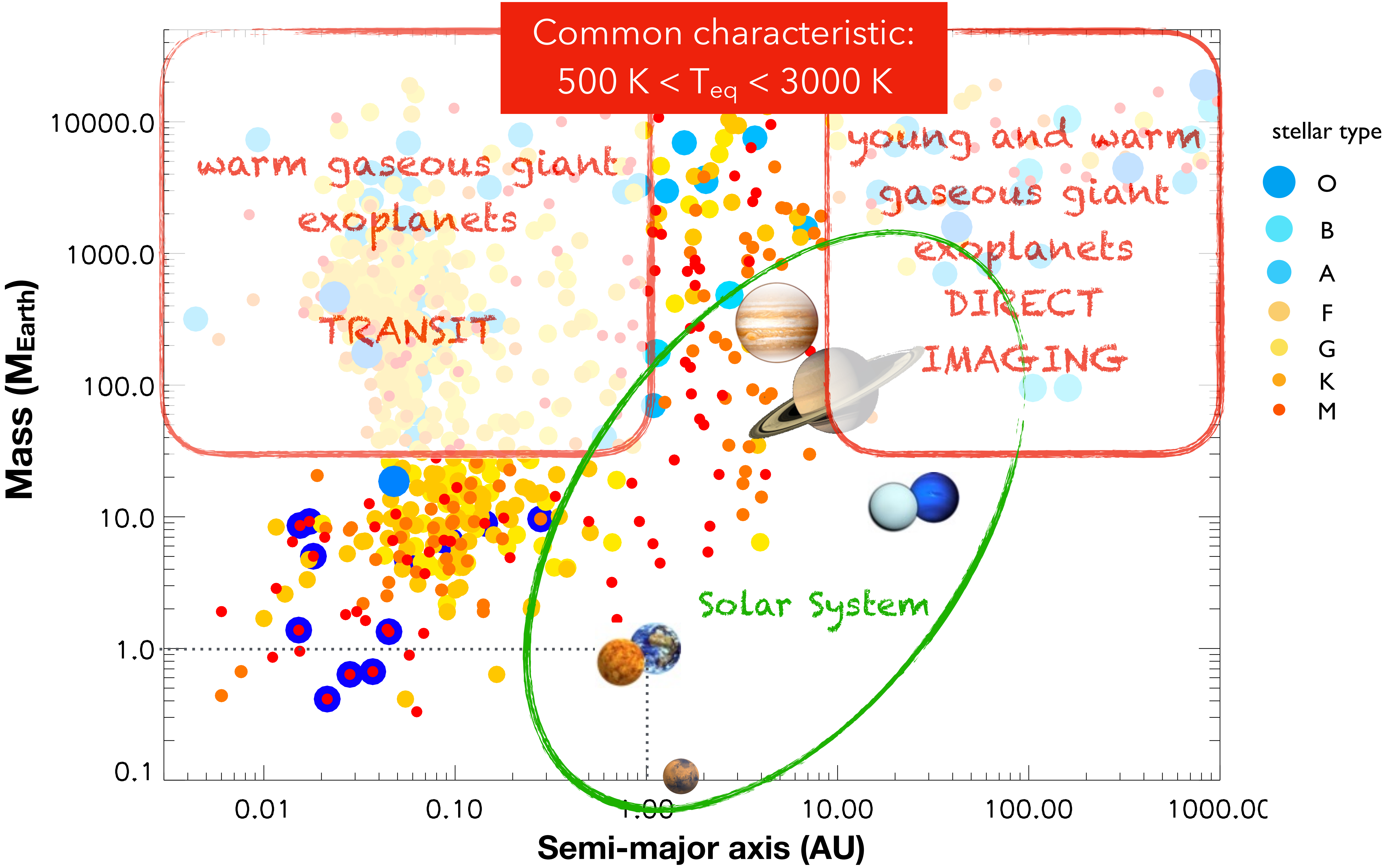

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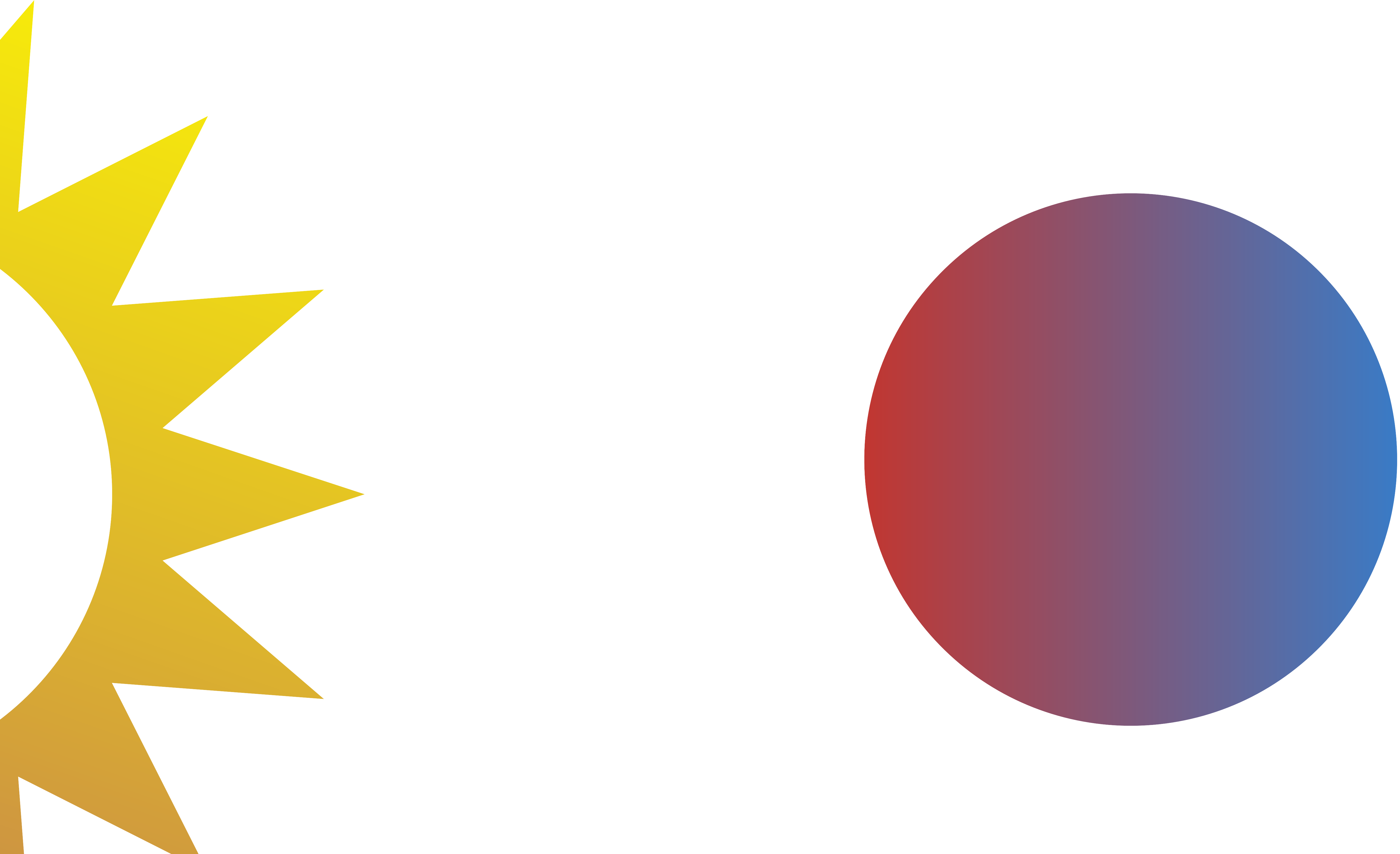
4115 exoplanets + 8 solar system planets

Out of equilibrium processes

Thermochemical Equilibrium: depends only of P, T, elementary abundances



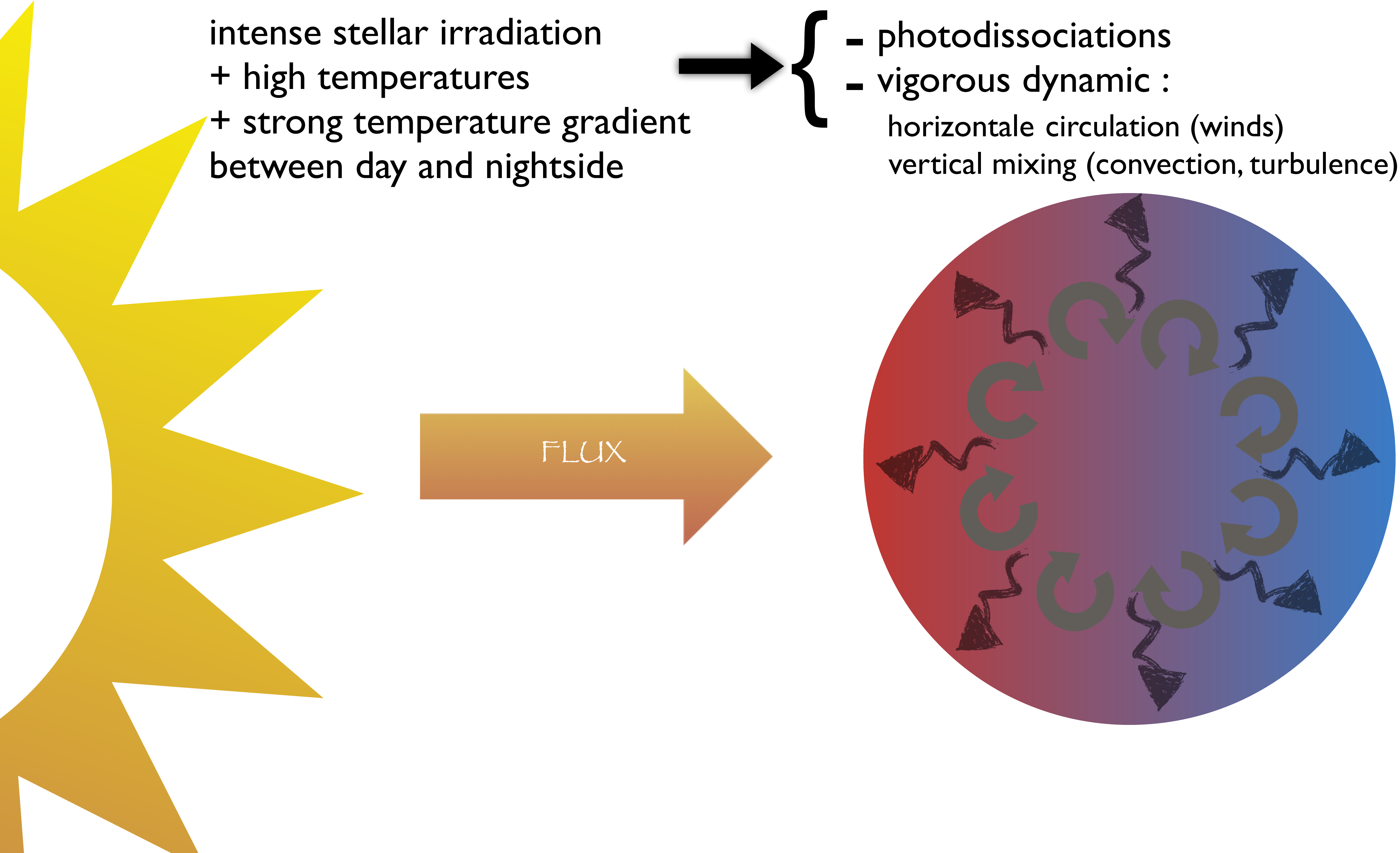
Out of equilibrium processes

Thermochemical Equilibrium: depends only of P, T, elementary abundances

intense stellar irradiation
+ high temperatures
+ strong temperature gradient
between day and nightside

→

- photodissociations
- vigorous dynamic :
  horizontale circulation (winds)
  vertical mixing (convection, turbulence)



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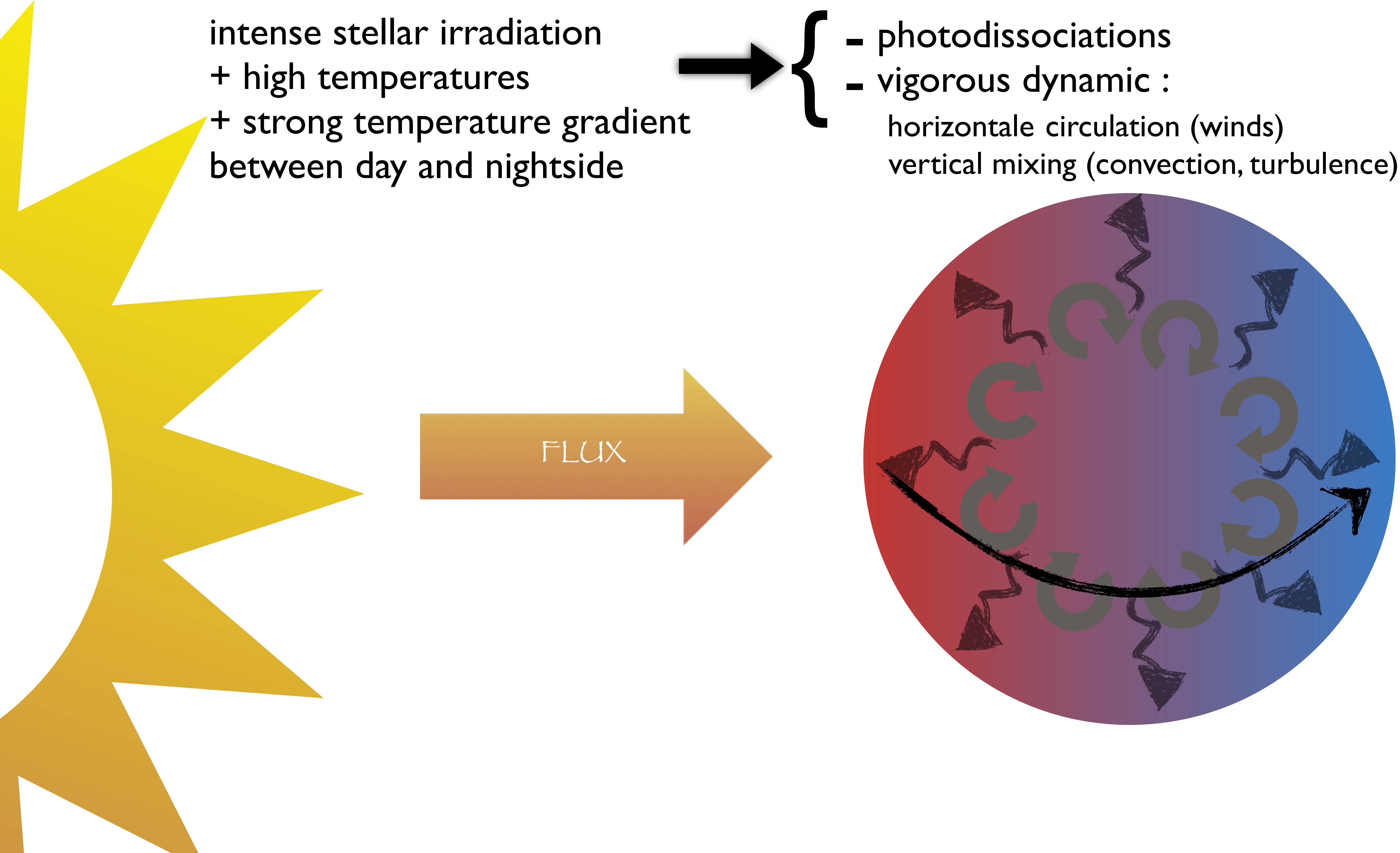

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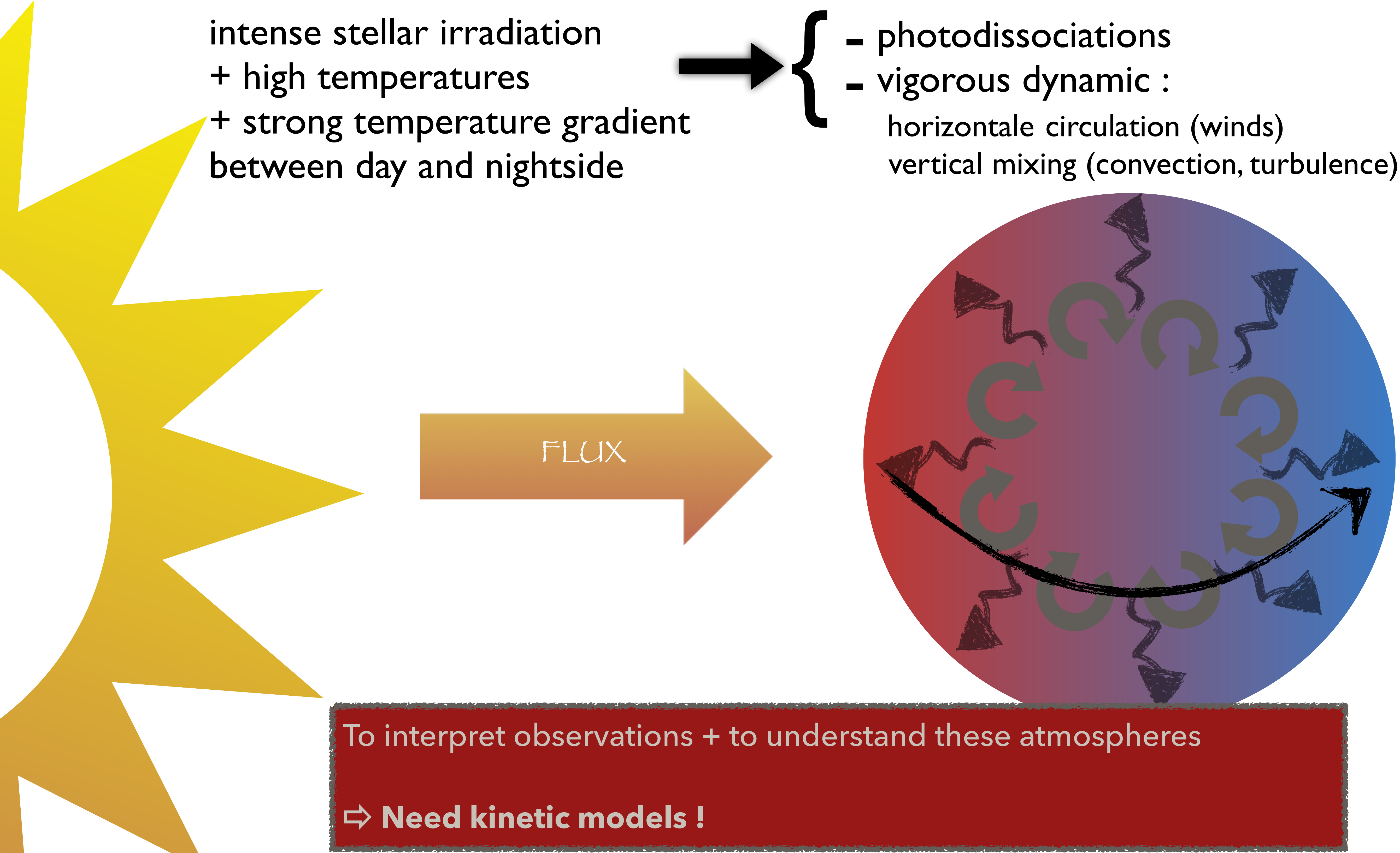
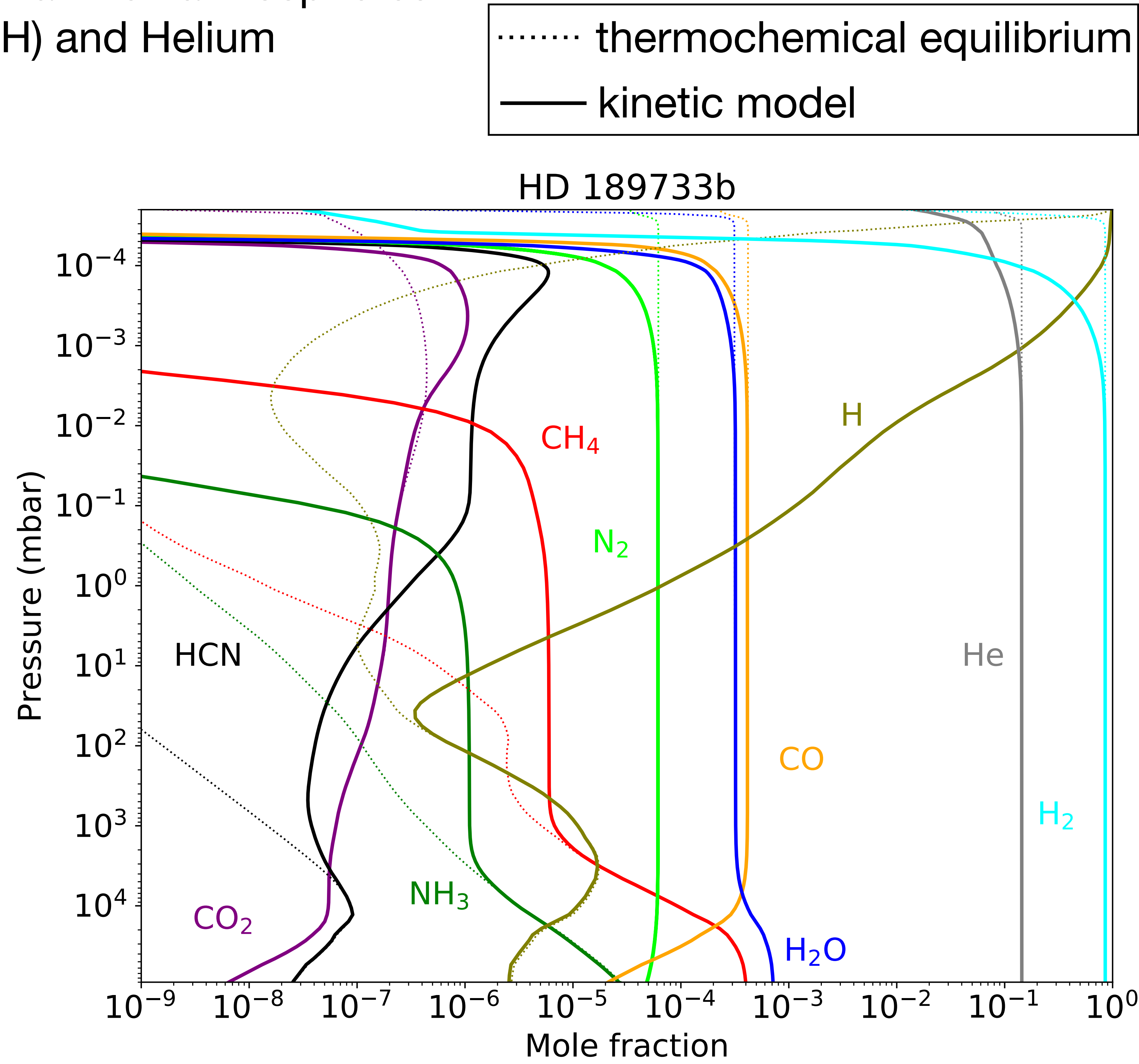


To interpret observations + to understand these atmospheres

⇨ **Need kinetic models !**

Structure of giant gaseous exoplanets

- From their small density, we know that their atmospheres are dominated by Hydrogen (H_2 or H) and Helium



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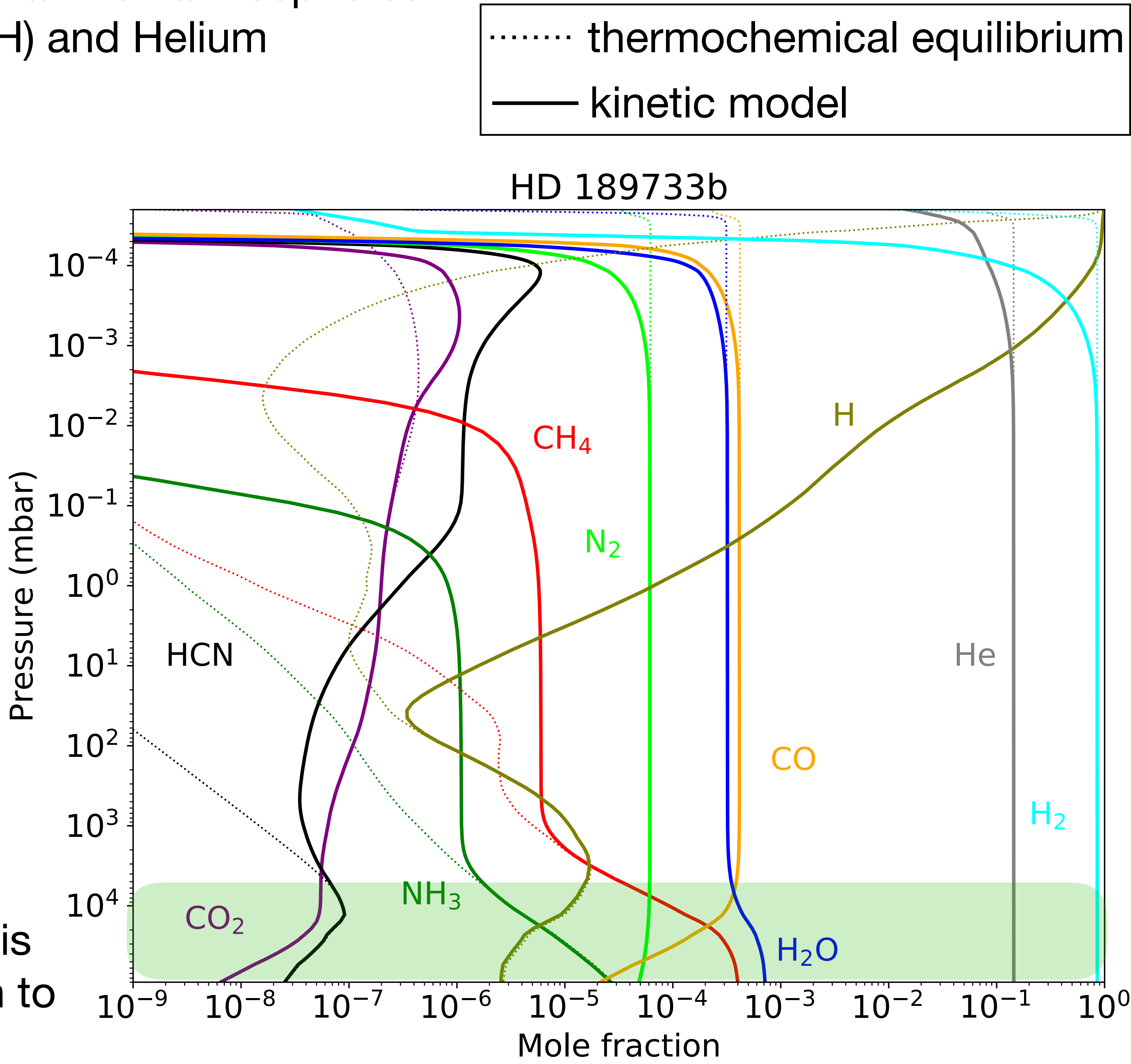

- **Thermo equilibrium:** temperature is very high so kinetics is fast enough to reproduce thermo equilibrium

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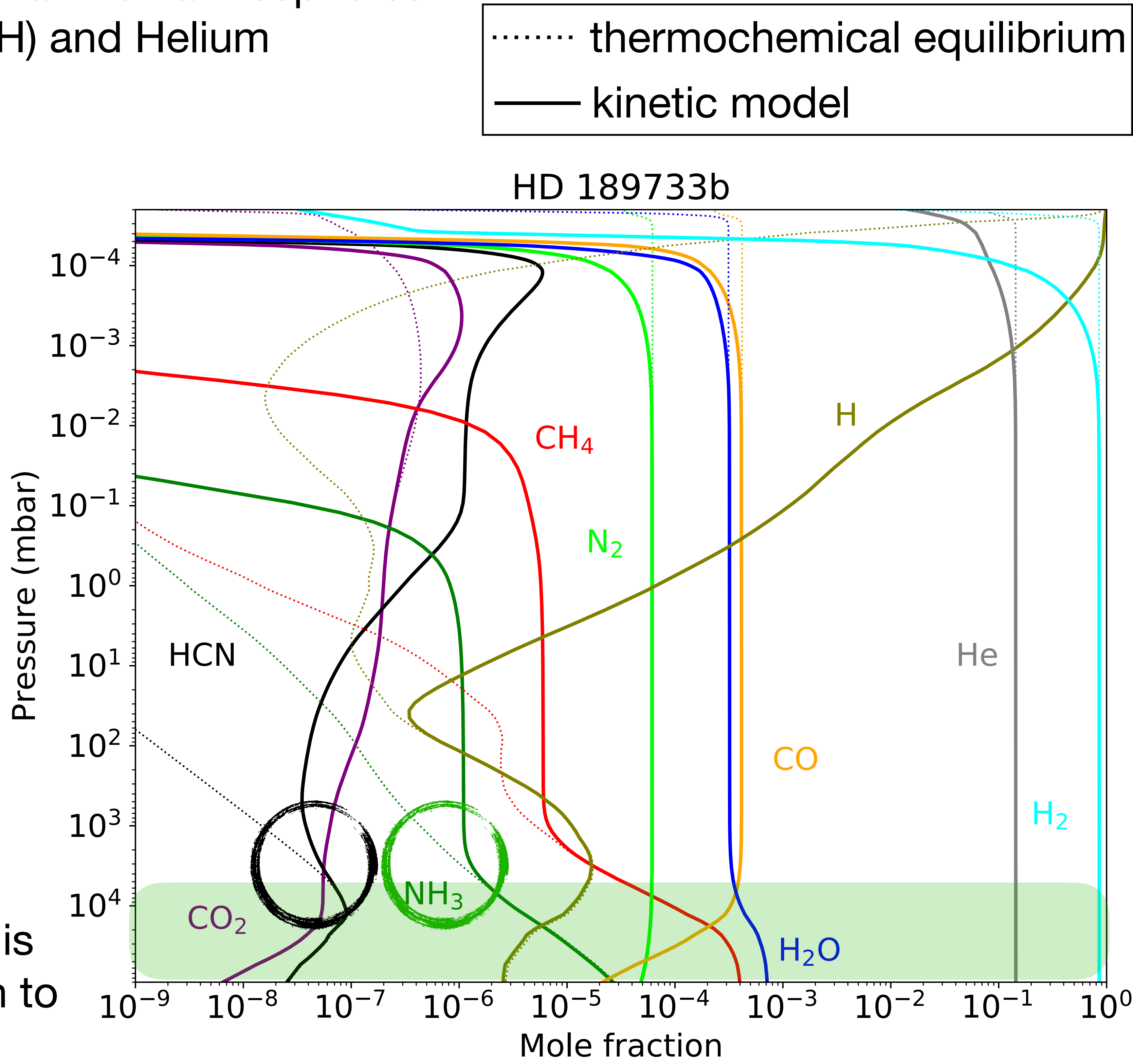

- **Quenching:** abundances depart from thermo equilibrium. They are frozen when

$$\tau_{chemical} > \tau_{dynamical}$$

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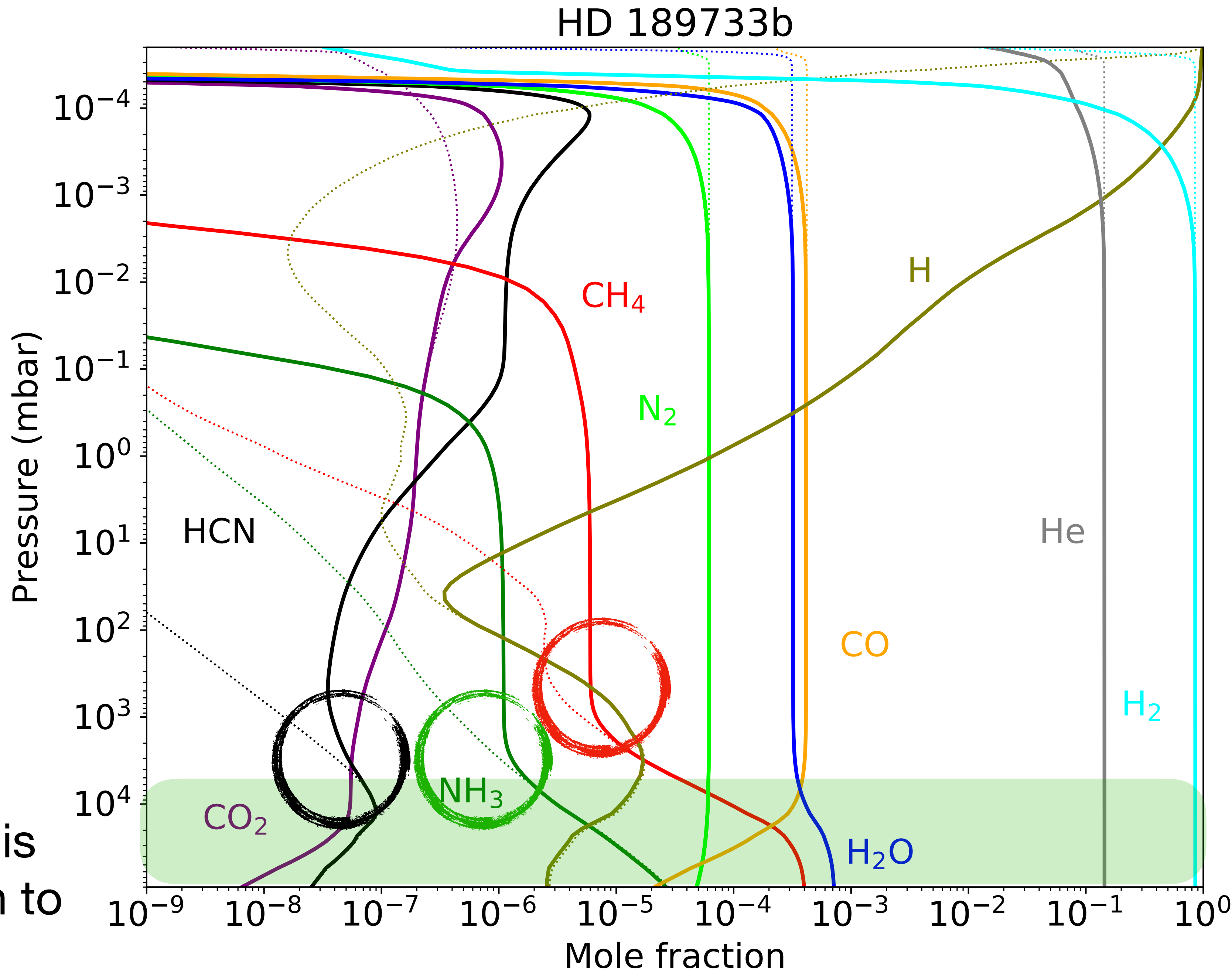

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  This level depends on $\tau_{chemical}$ so is proper to each species

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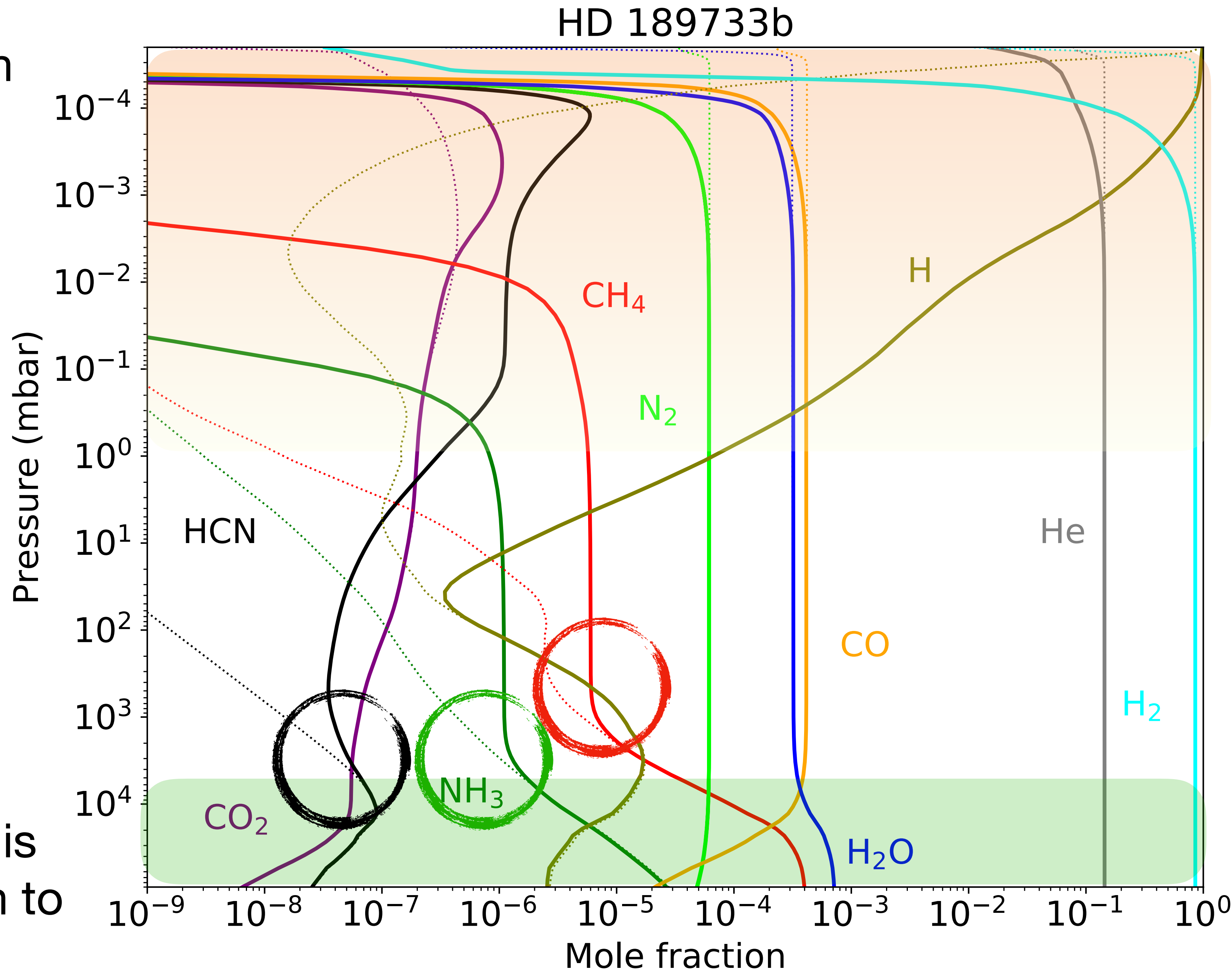
······· thermochemical equilibrium

—— kinetic model



- **Photodissociations:** UV irradiation from the star destroys or produces molecules.

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········ thermochemical equilibrium

—— kinetic model

- **Photodissociations:** UV irradiation from the star destroys or produces molecules.

  Effect can be seen as deep as 10/100 mbar

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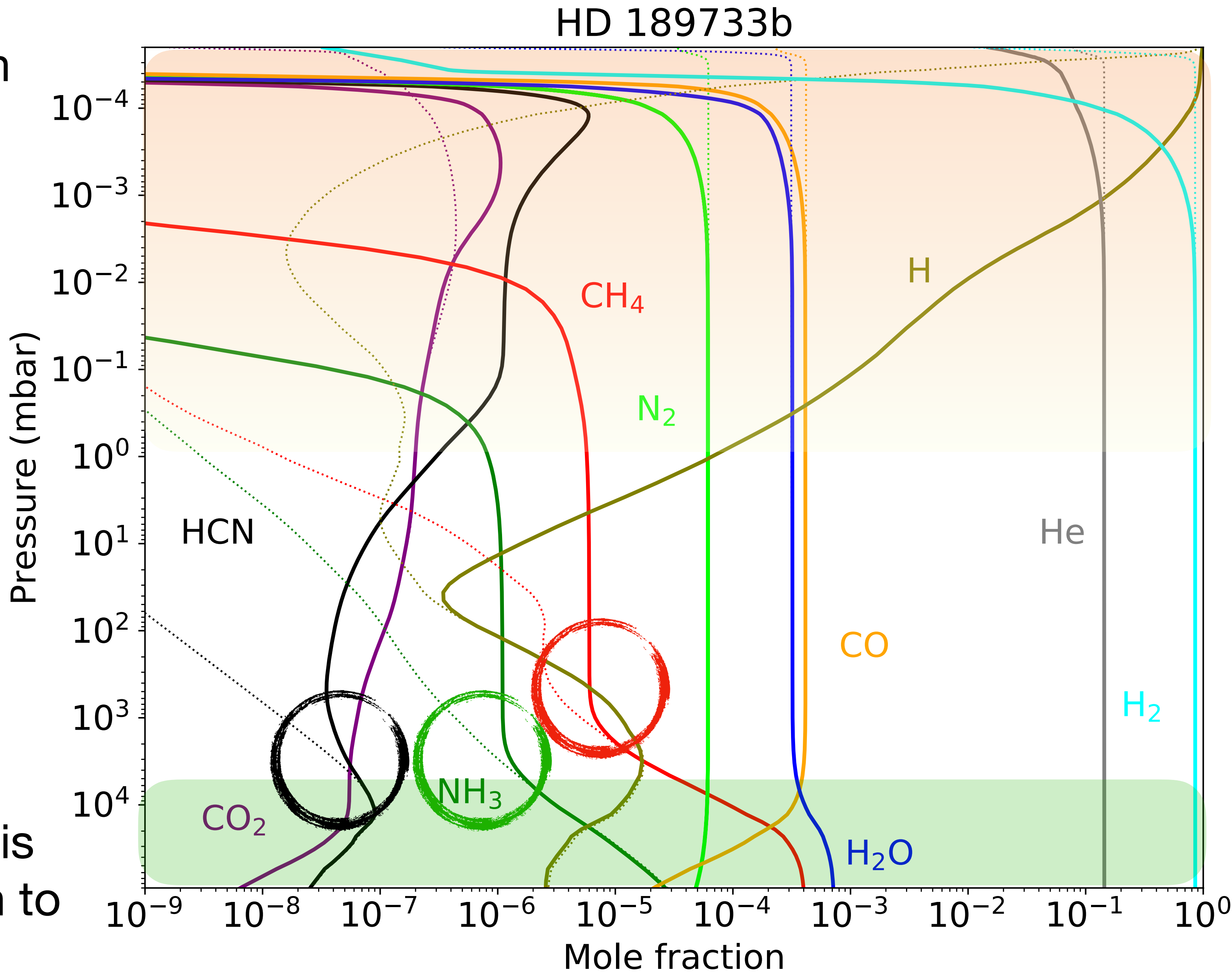
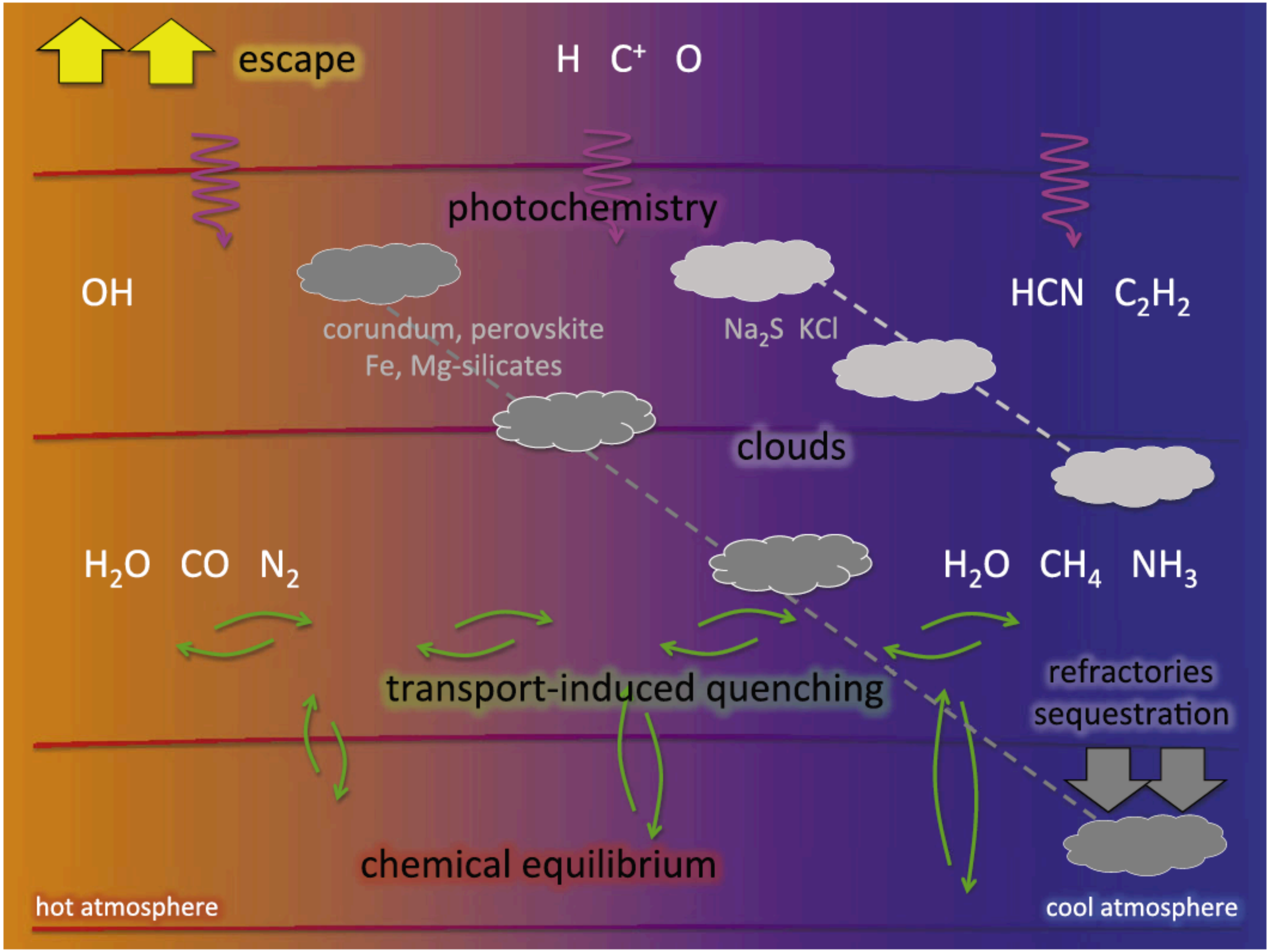
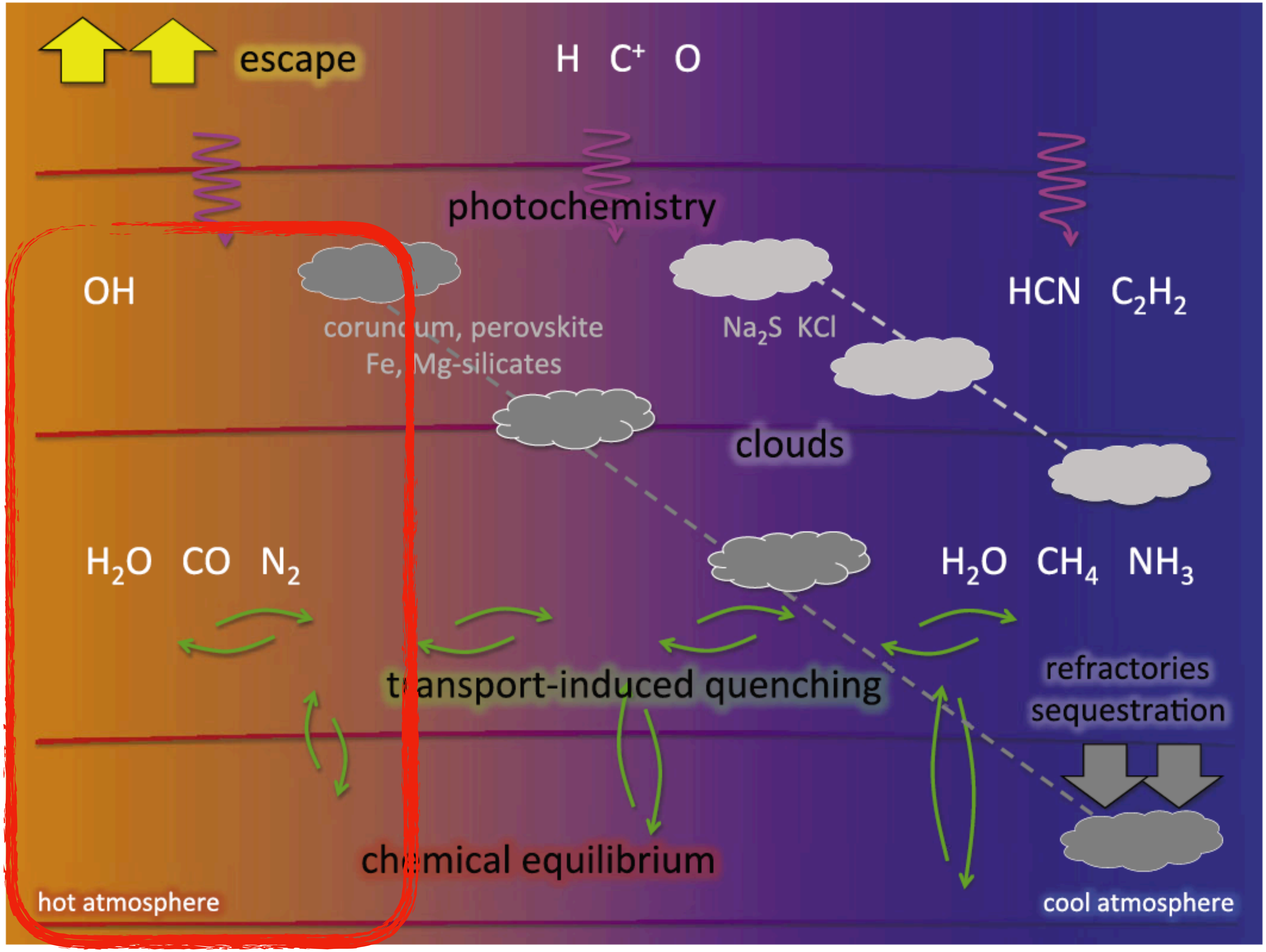


Structure of giant gaseous exoplanets



Madhusudhan et al. 2016

Structure of giant gaseous exoplanets



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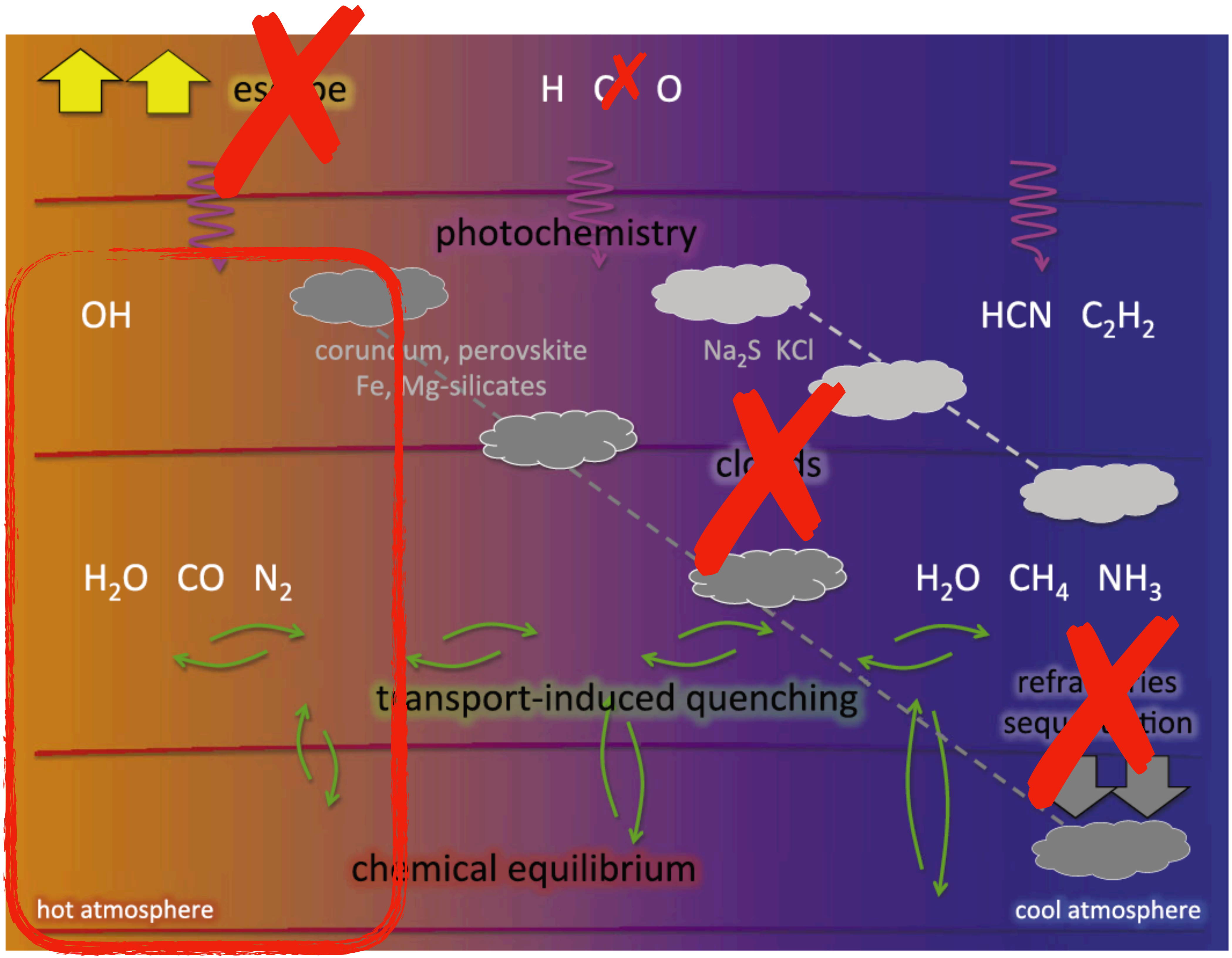

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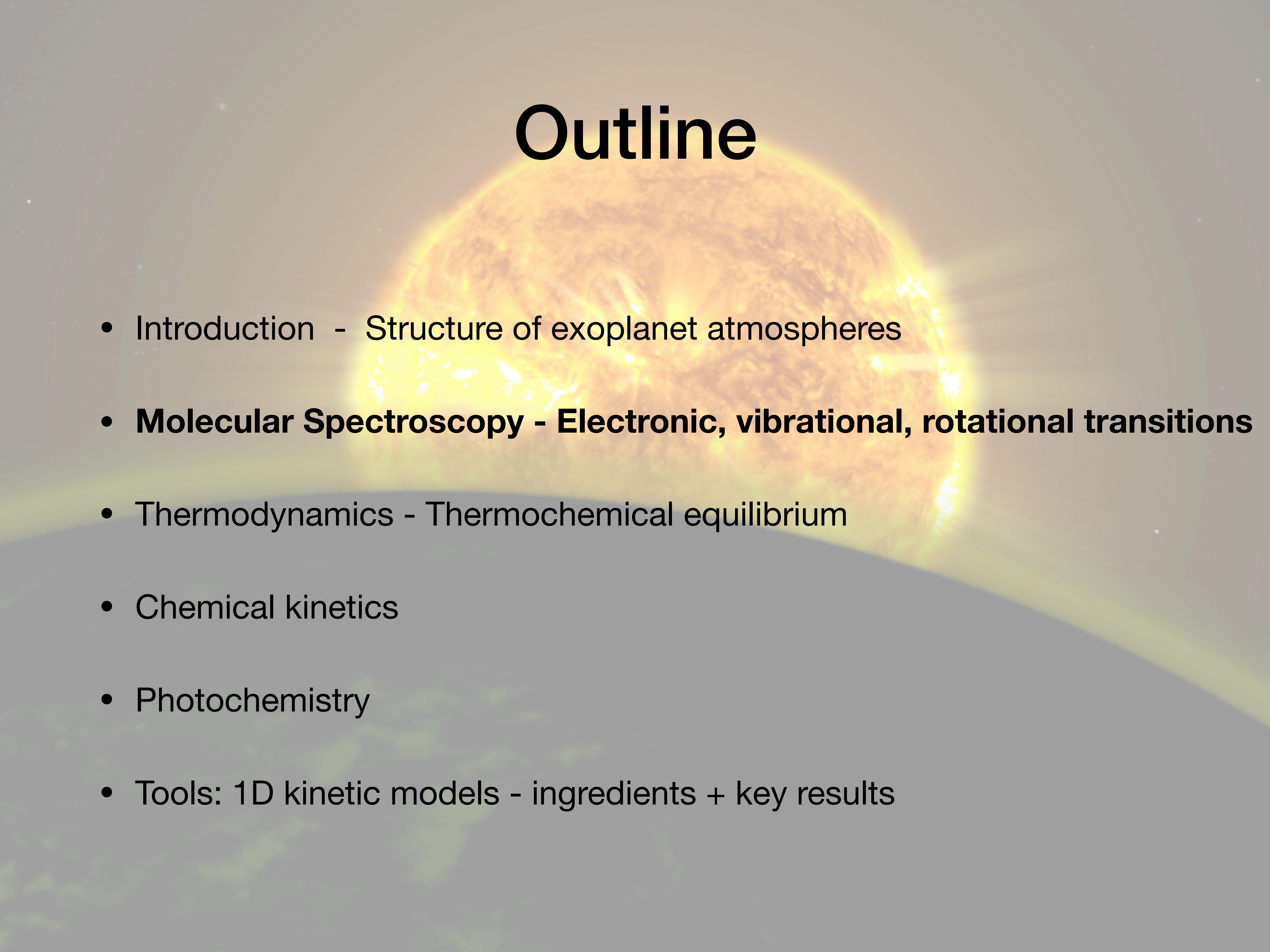

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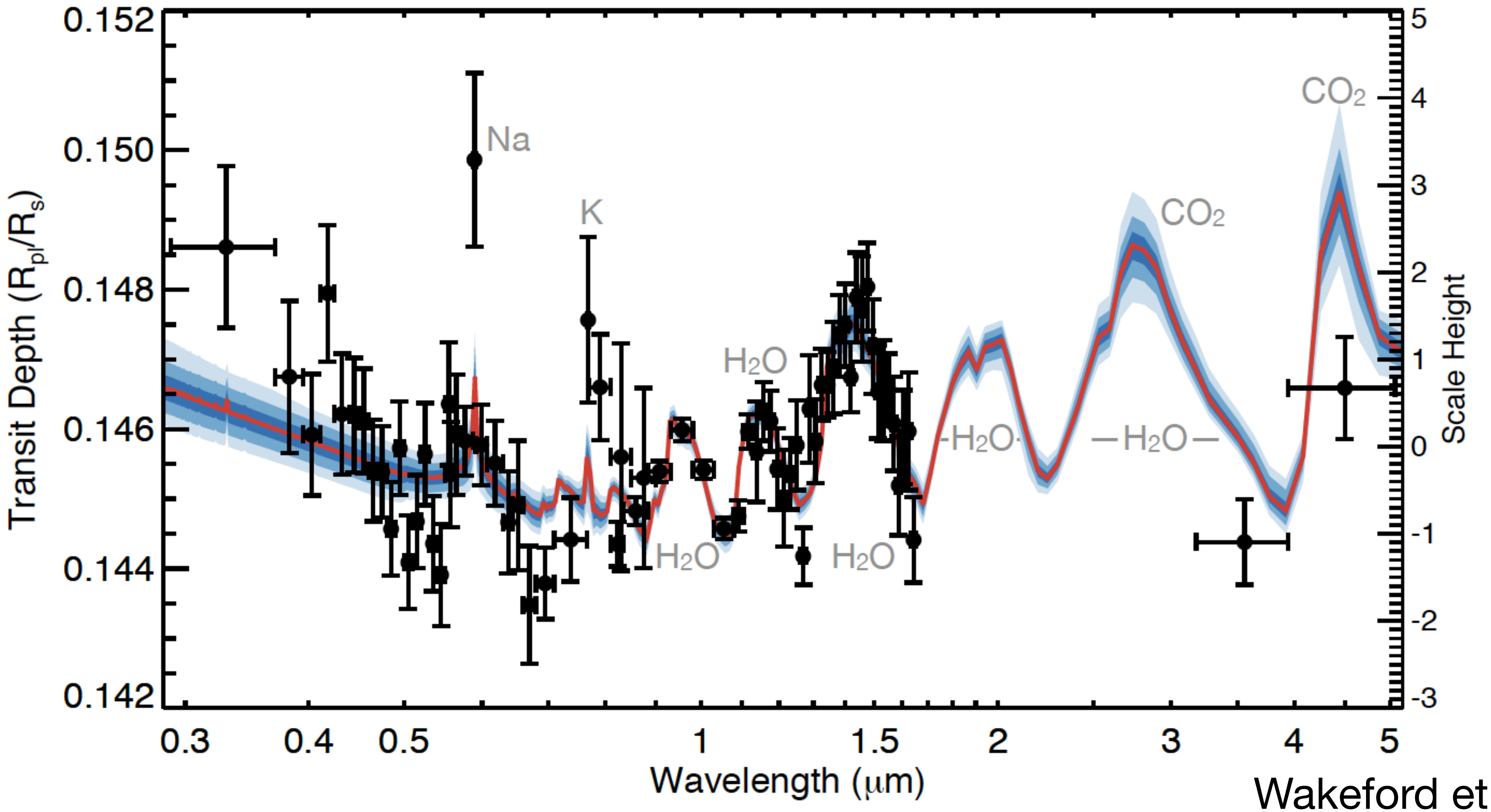
Spectroscopy



Wakeford et al. 2017

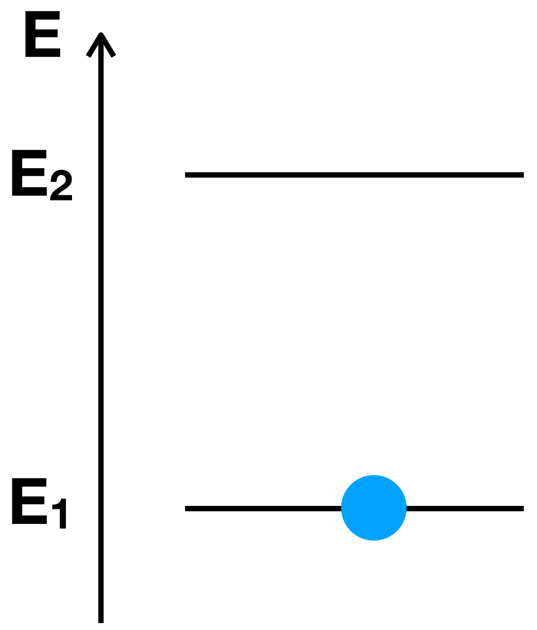
Fig. 6.— The complete transmission spectrum of WASP-39b (black points). This transmission spectrum incorporates data from HST STIS and WFC3, *Spitzer* IRAC, and VLT FORS2 completing the spectrum from 0.3–5.0 μm with currently available instruments. Using the ATMO retrieval code, which implements an isothermal profile and equilibrium chemistry, we determine the best fit atmospheric model (red) and show the 1, 2, and 3σ confidence regions (dark to light blue) based on the retrieved parameters.

Why are we able to say that H_2O, CO_2,… are in the atmosphere ?

➡ thanks to molecular spectroscopy !

Spectroscopy

- Molecules have discrete energy states



Spectroscopy

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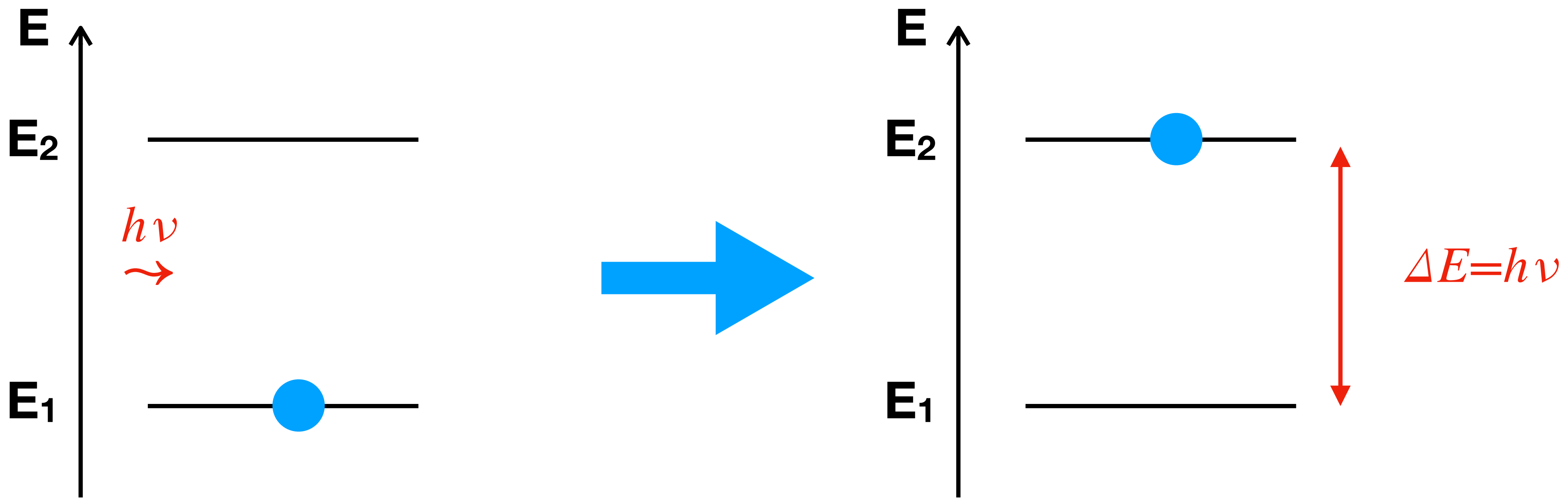
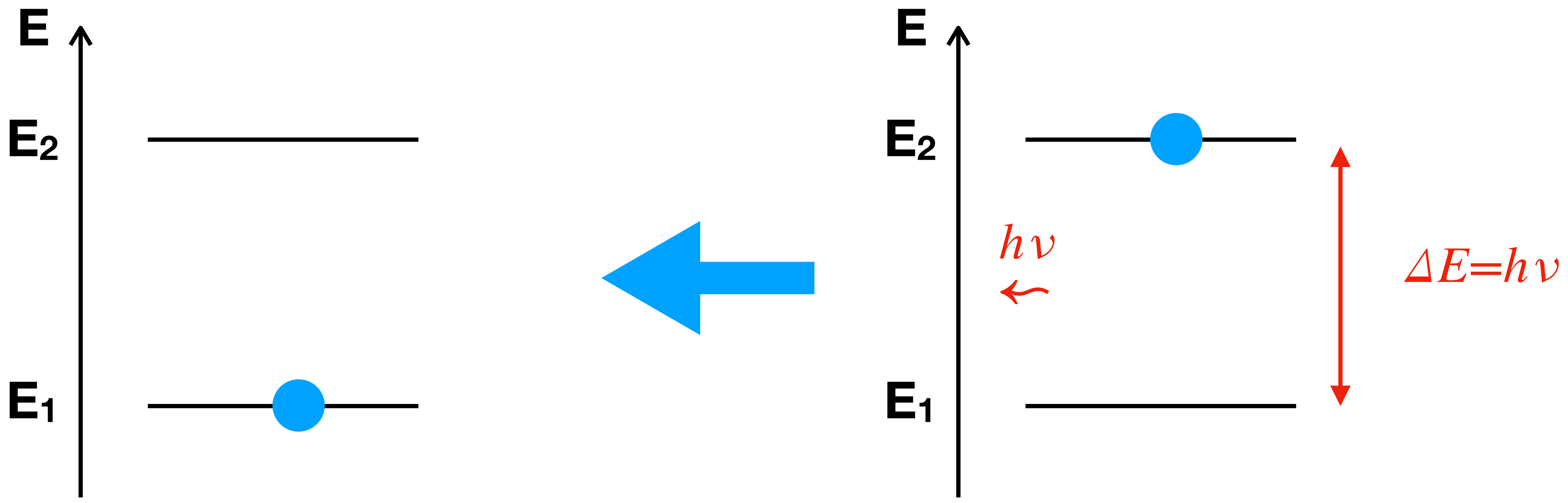


- An electromagnetic wave (a photon) induces transition between energy levels of a molecule

Spectroscopy

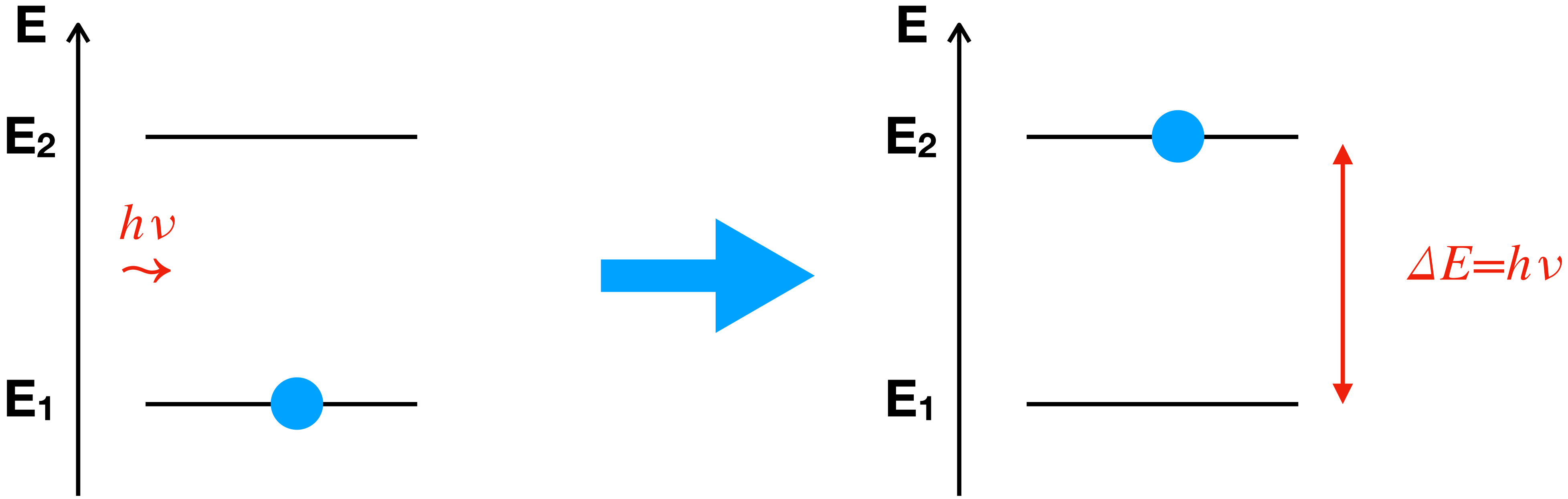
- Molecules have discrete energy states



- A downward transition can also happen and involves the emission of a photon

Spectroscopy

- Molecules have discrete energy states

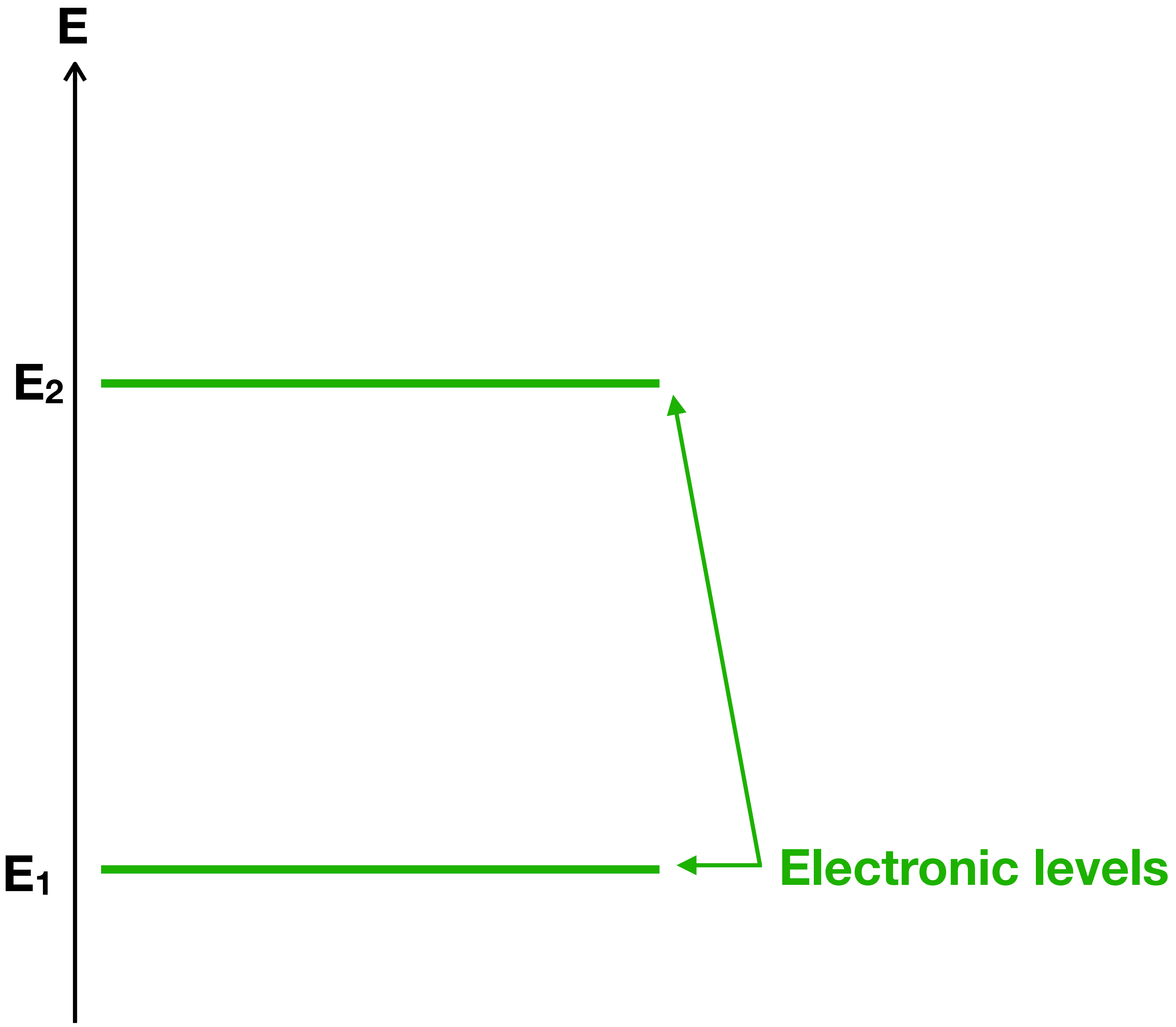


- An electromagnetic wave (a photon) induces transition between energy levels of a molecule

- The total energy of a molecule is the sum of its translation, vibration, rotation and electronic energies: $E_{tot} = E_{trans} + E_{rot} + E_{vib} + E_{elec}$

- Only E_{rot}, E_{vib}, and E_{elec} can be modified with a photon

Energy levels

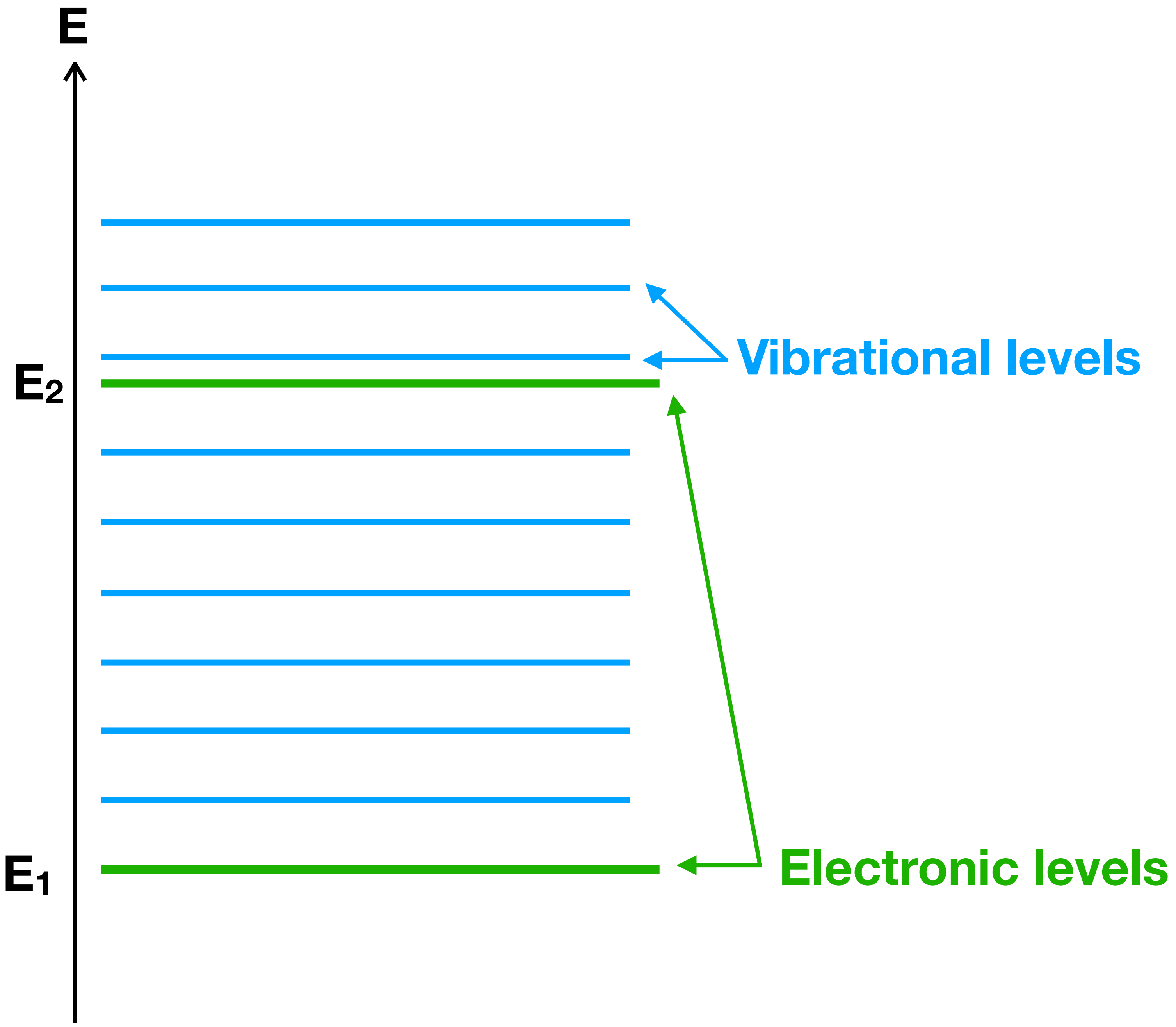


Transitions are induced by photons of different energies:

- V-UV (λ=1-700 nm): electronic

→ can break bonds in molecules (photodissociation)

Energy levels



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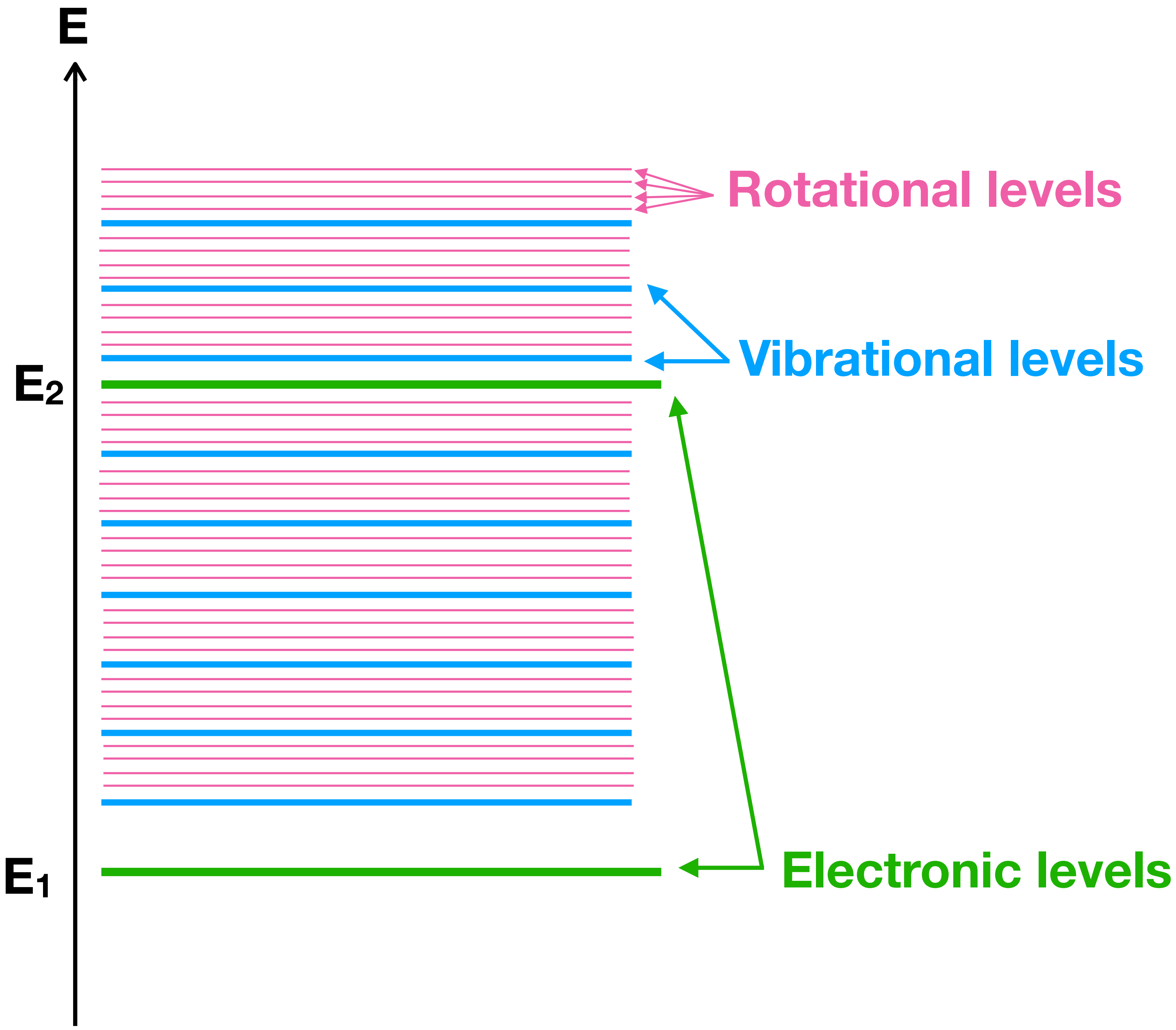
Energy levels



Transitions are induced by photons of different energies:

- V-UV (λ=1-700 nm): electronic
→ can break bonds in molecules (photodissociation)

- IR (λ=0.7-1000 μm) : vibrational

- μwave (λ=1-300 mm): rotational

Structure of molecules

- Internal structure of molecules is very complexe to describe because electrons behave <u>both like particles and waves</u>

- Classical physics is not sufficient and quantum mechanics must be used

- Impossible to know precisely where the electrons are: *Heisenberg Uncertainty Principle*

- Instead, only probabilities of finding an electron in a particular region around the atom can be calculated

- However, for simple molecules, classical physics can give correct results

Electronic energy levels

- For Hydrogen and hydrogen-like atoms, the Bohr model is accurate to determine the electronic energy levels:

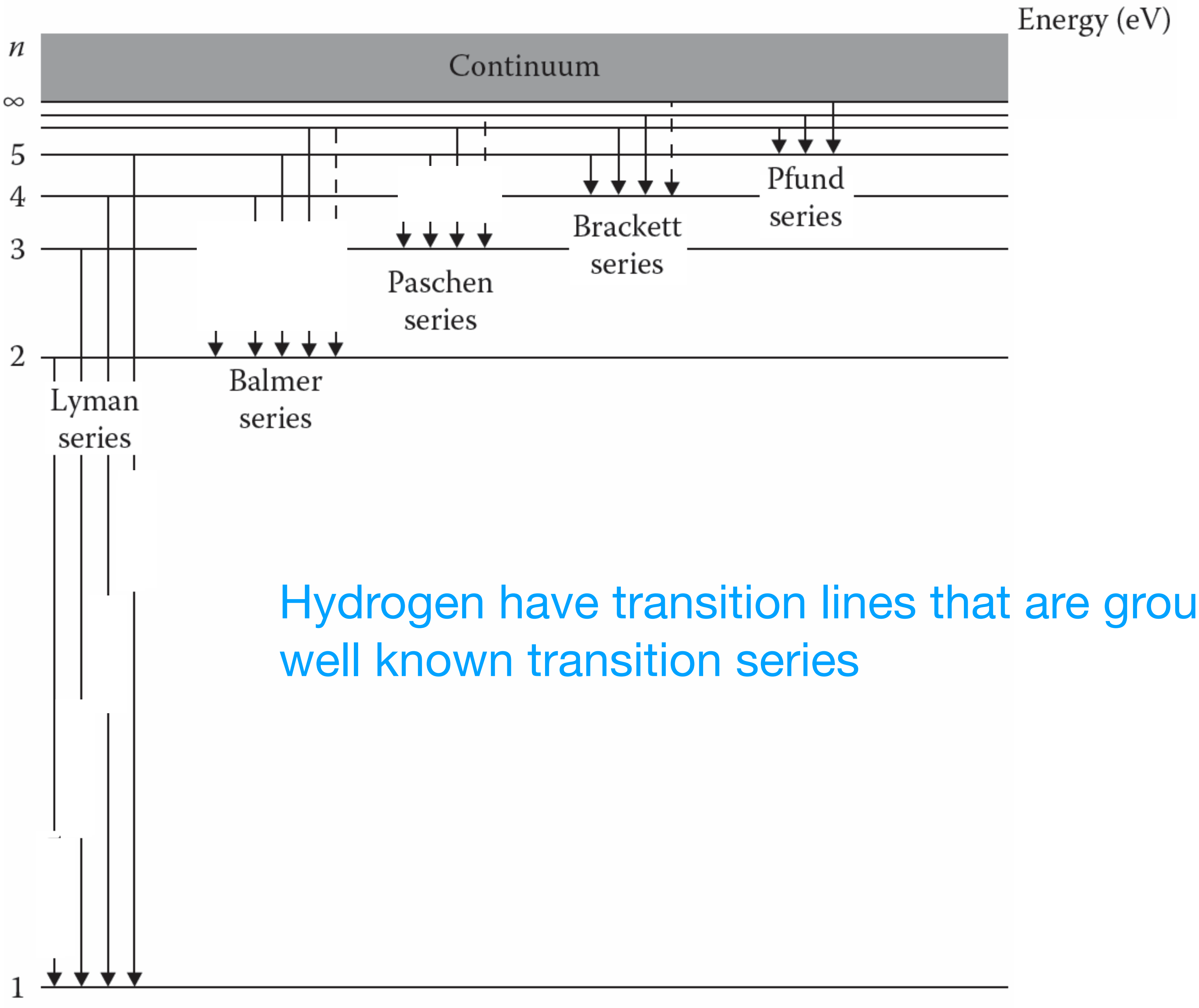
$$E_n = -\frac{Z^2 m e^2}{8 n^2 h^2 \epsilon_0^2} = \frac{-13.6 Z^2}{n^2}\ eV$$

- Transition between two electronic levels implies the absorption or emission of a photon with

$$\Delta E = -13.6 Z^2 \left[\frac{1}{n_1^2} - \frac{1}{n_2^2}\right]\ eV \text{ with } n_1 > n_2$$

⇒ *Only photons with these energies can be absorbed or emitted*

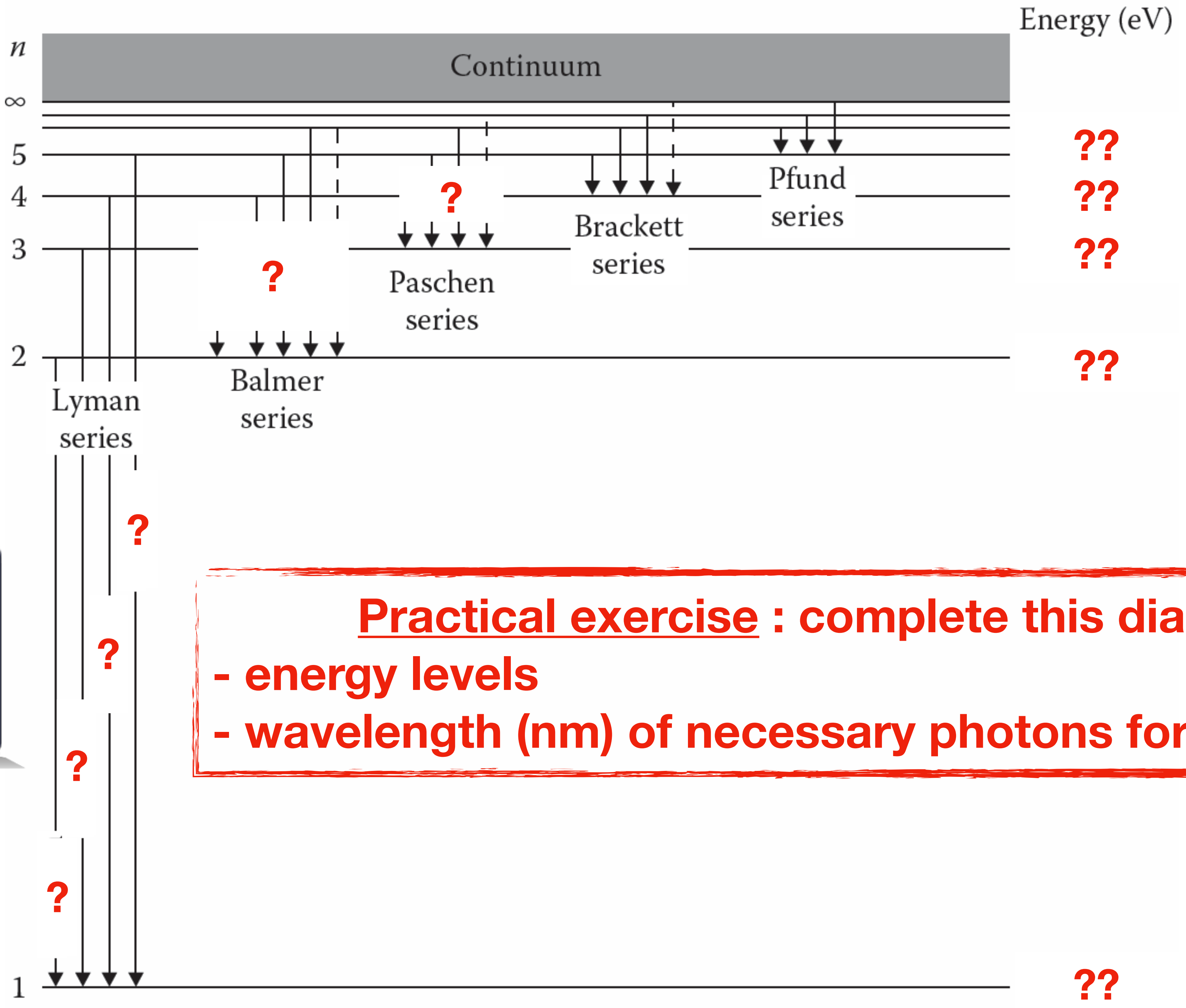
Electronic energy levels



Radiative transition series for the hydrogen atom H

Hydrogen have transition lines that are grouped in very well known transition series

Electronic energy levels

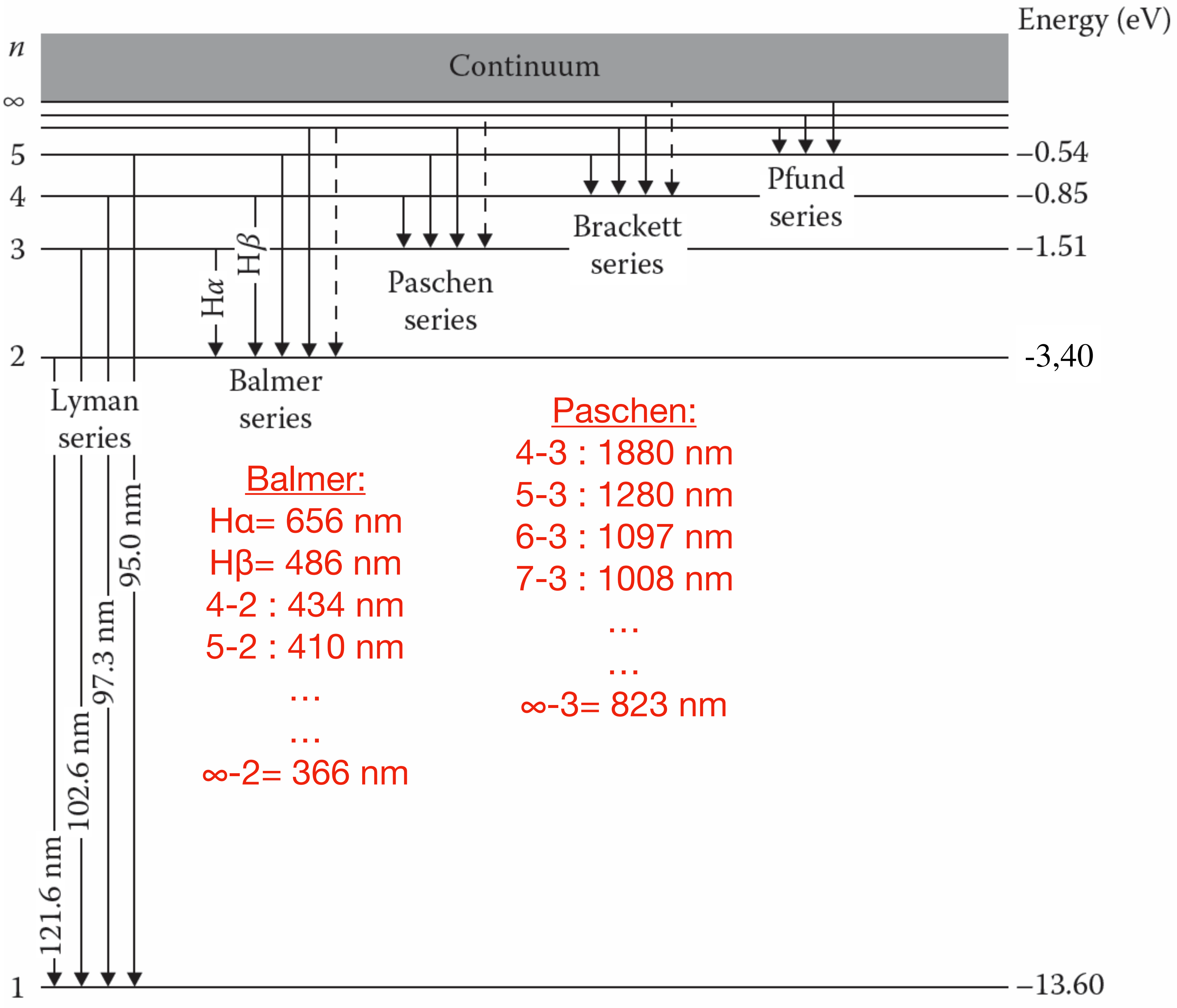


Radiative transition series for the hydrogen atom H

Practical exercise : complete this diagram

- **energy levels**
- **wavelength (nm) of necessary photons for transitions**

Electronic energy levels



Radiative transition series for the hydrogen atom H

Lyman:
Lyα= 121.6 nm
3-1= 102.6 nm
4-1 : 97.3 nm
5-1 : 95.0 nm
…
…
∞-1= 91.4 nm

Balmer:
Hα= 656 nm
Hβ= 486 nm
4-2 : 434 nm
5-2 : 410 nm
…
…
∞-2= 366 nm

Paschen:
4-3 : 1880 nm
5-3 : 1280 nm
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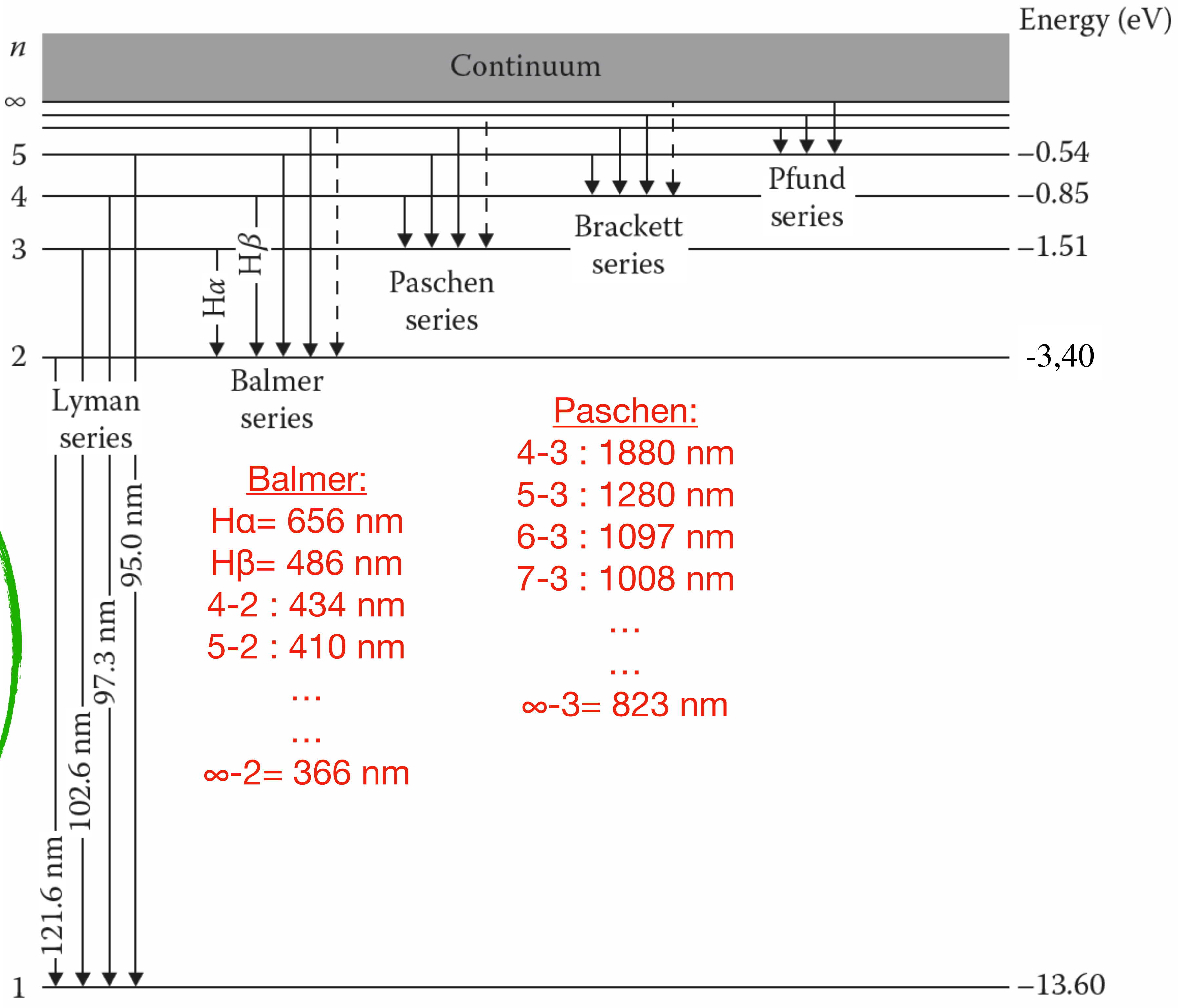
7-3 : 1008 nm
…
…
∞-3= 823 nm

Electronic energy levels



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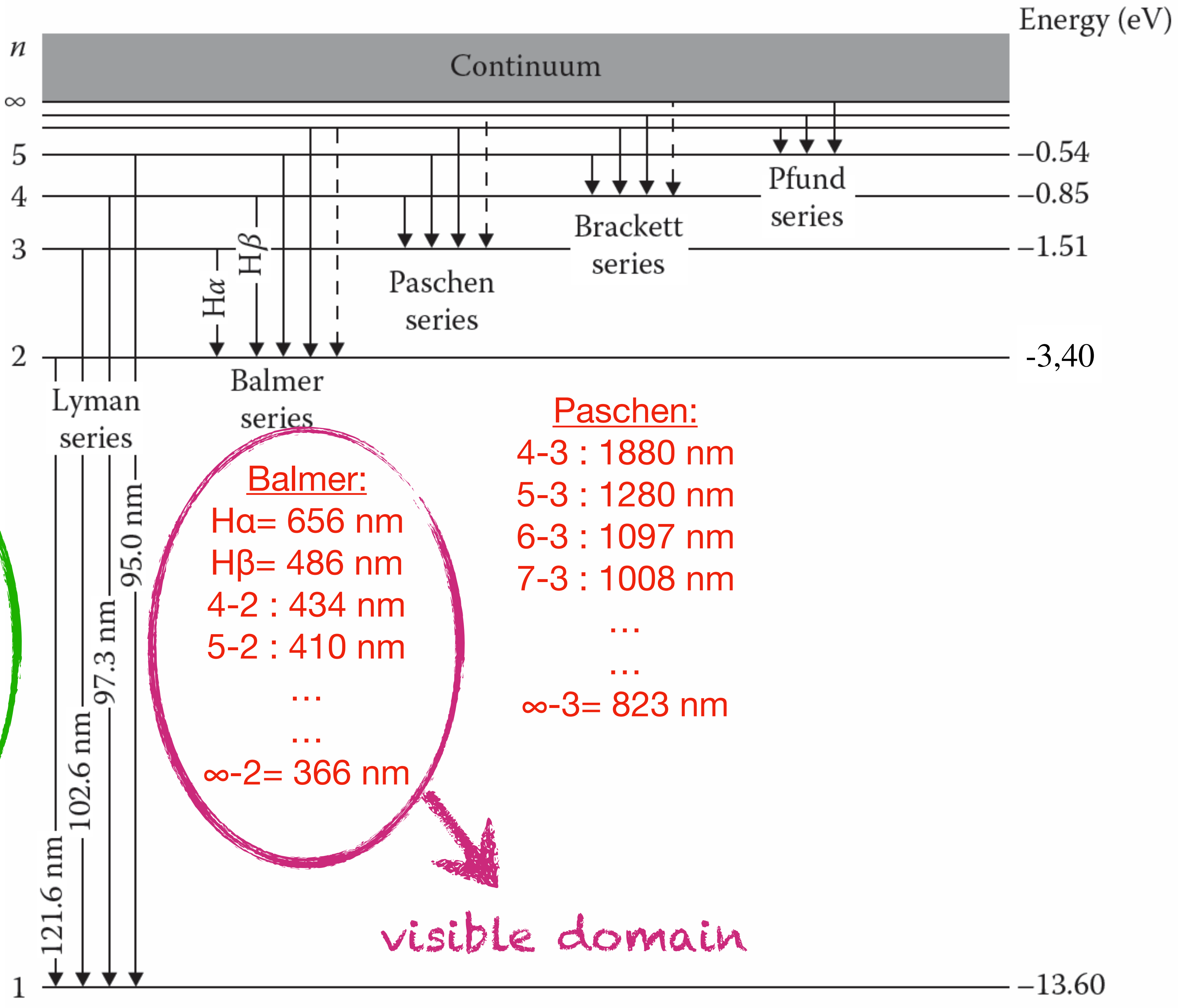

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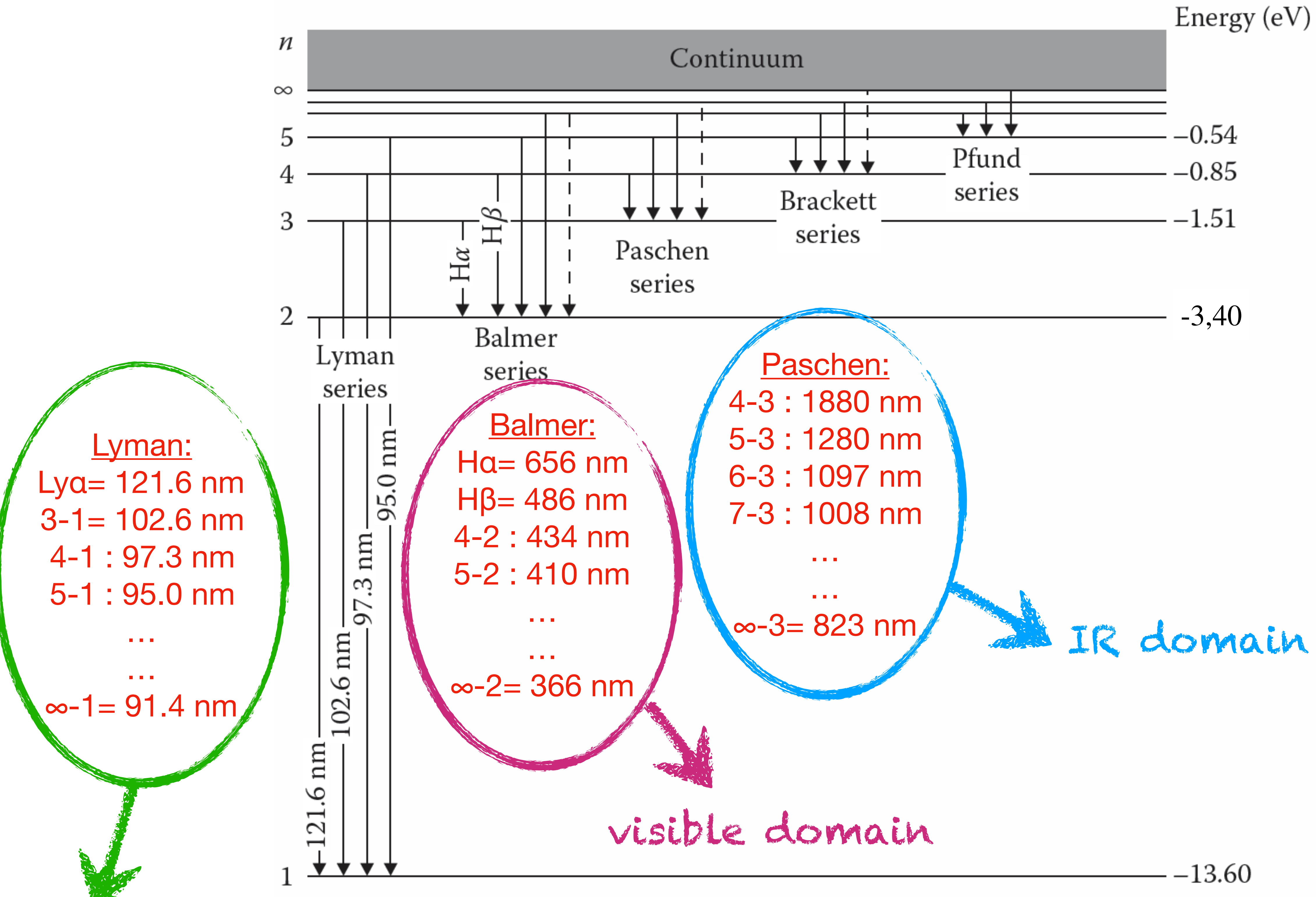
visible domain

UV domain

Electronic energy levels



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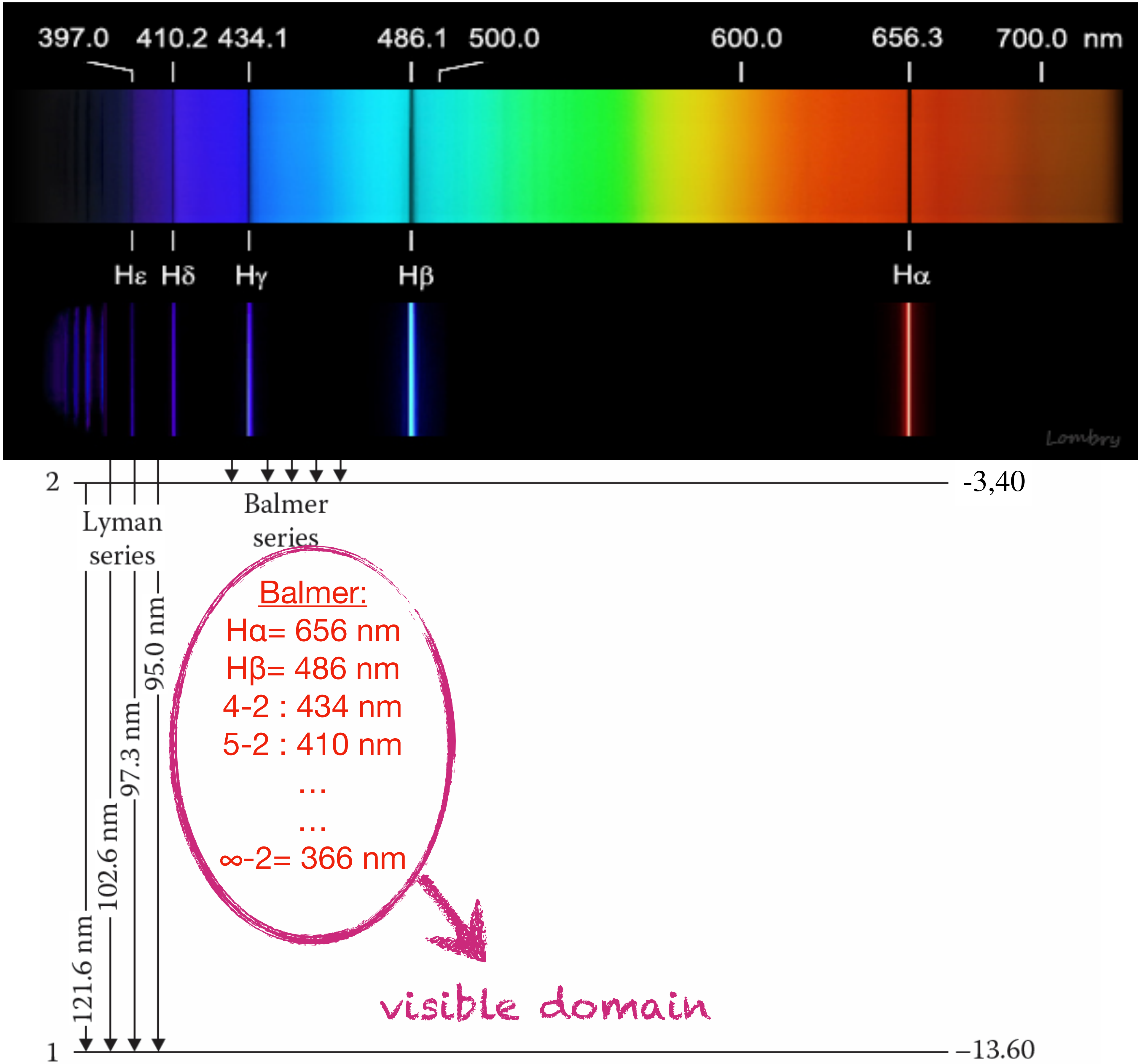
IR domain

visible domain

UV domain

Radiative transition series for the hydrogen atom H



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visible domain

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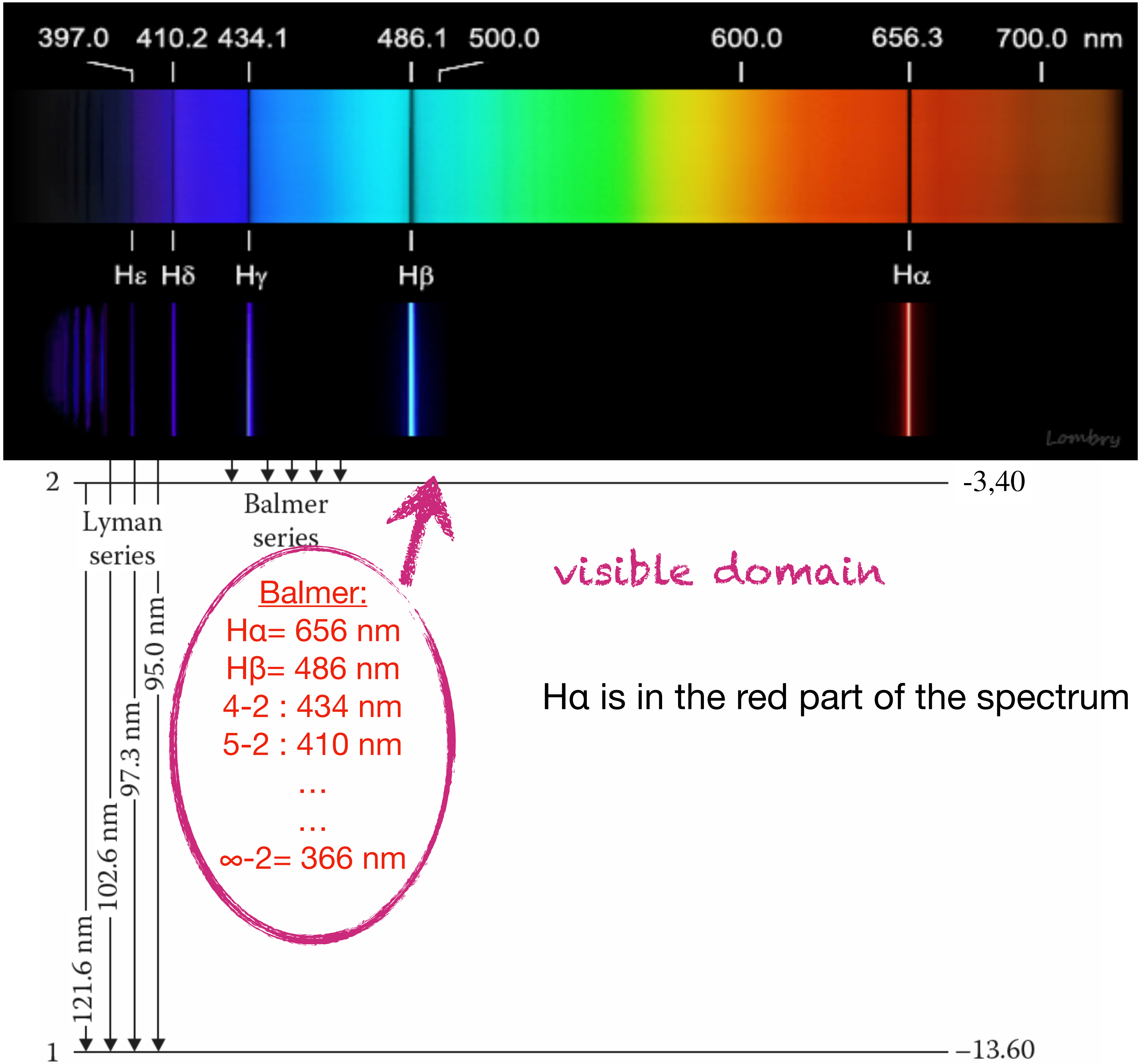

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<u>Balmer:</u>
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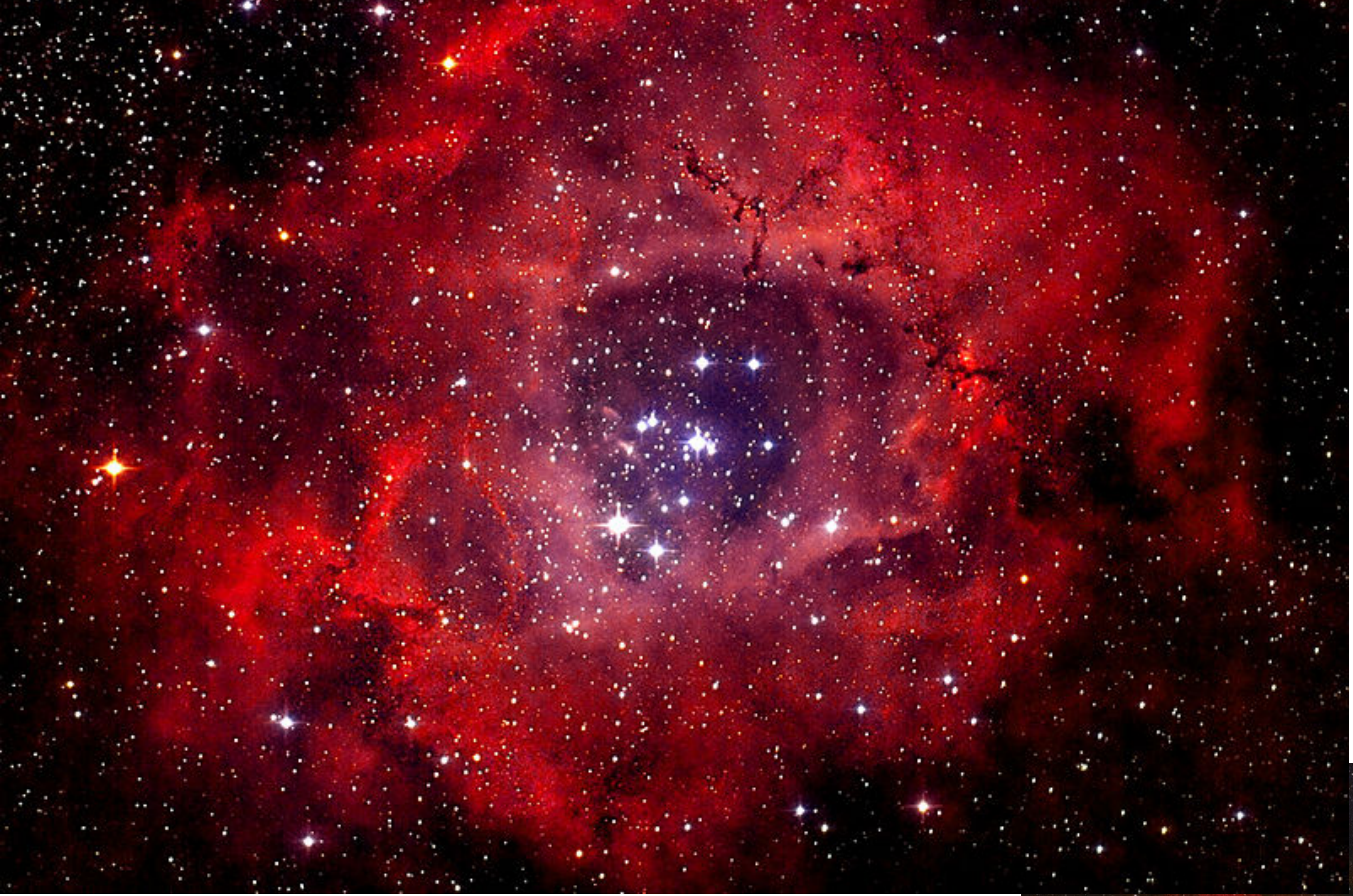
visible domain

Hα is in the red part of the spectrum



© Roberto Colombari

Hα is used to observed nebula, which contain mainly hydrogen

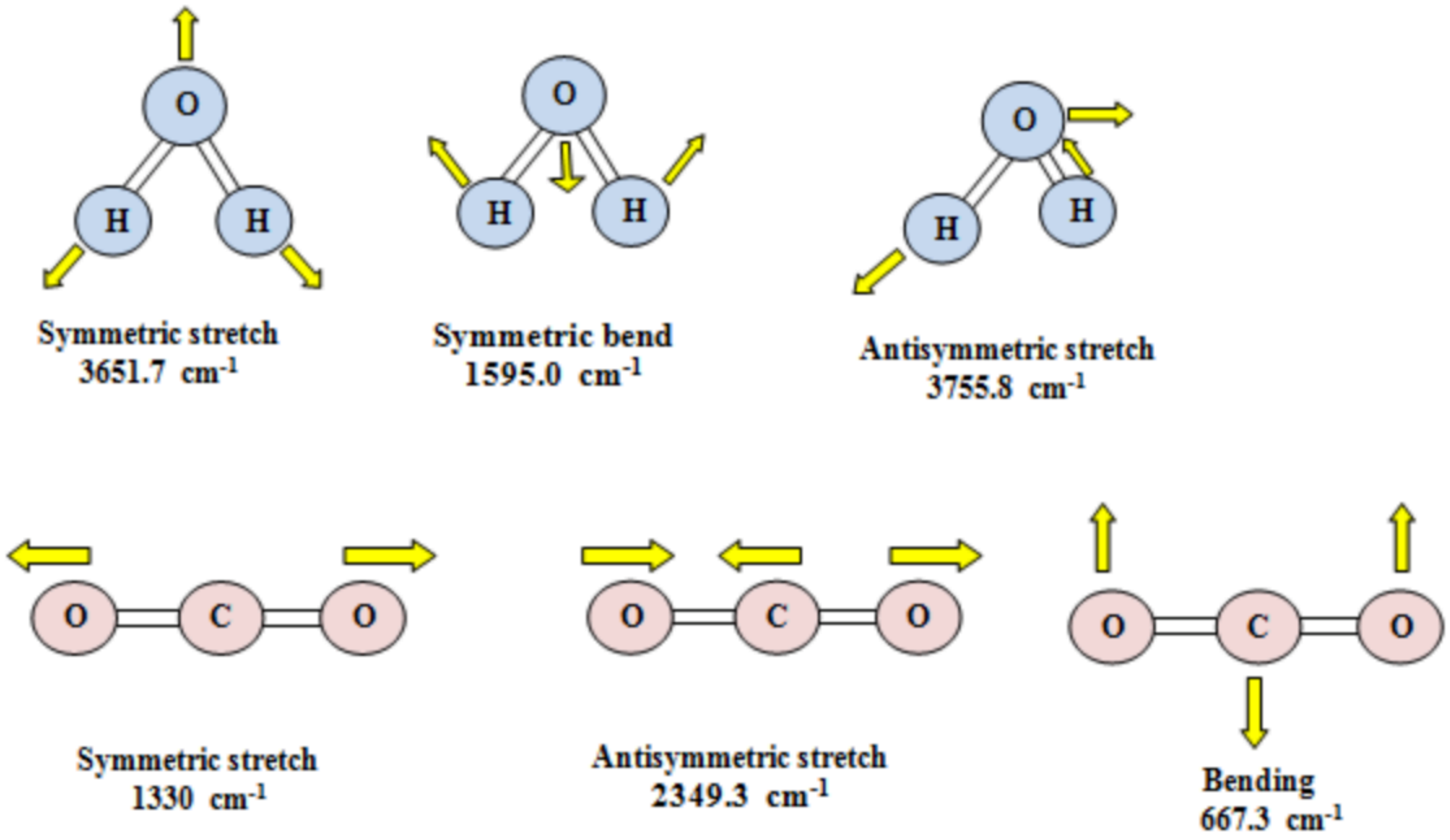
Not as simple to calculate the energy levels of more complex molecules, but they all have discrete electronic energy levels, with specific transition lines

Vibration energy levels

- In addition to electronic levels, a molecule with several atoms has vibrational energy levels.
- Each molecule has a defined number of vibration modes and each mode has its own frequency.

H_2O

CO_2



Vibration energy levels

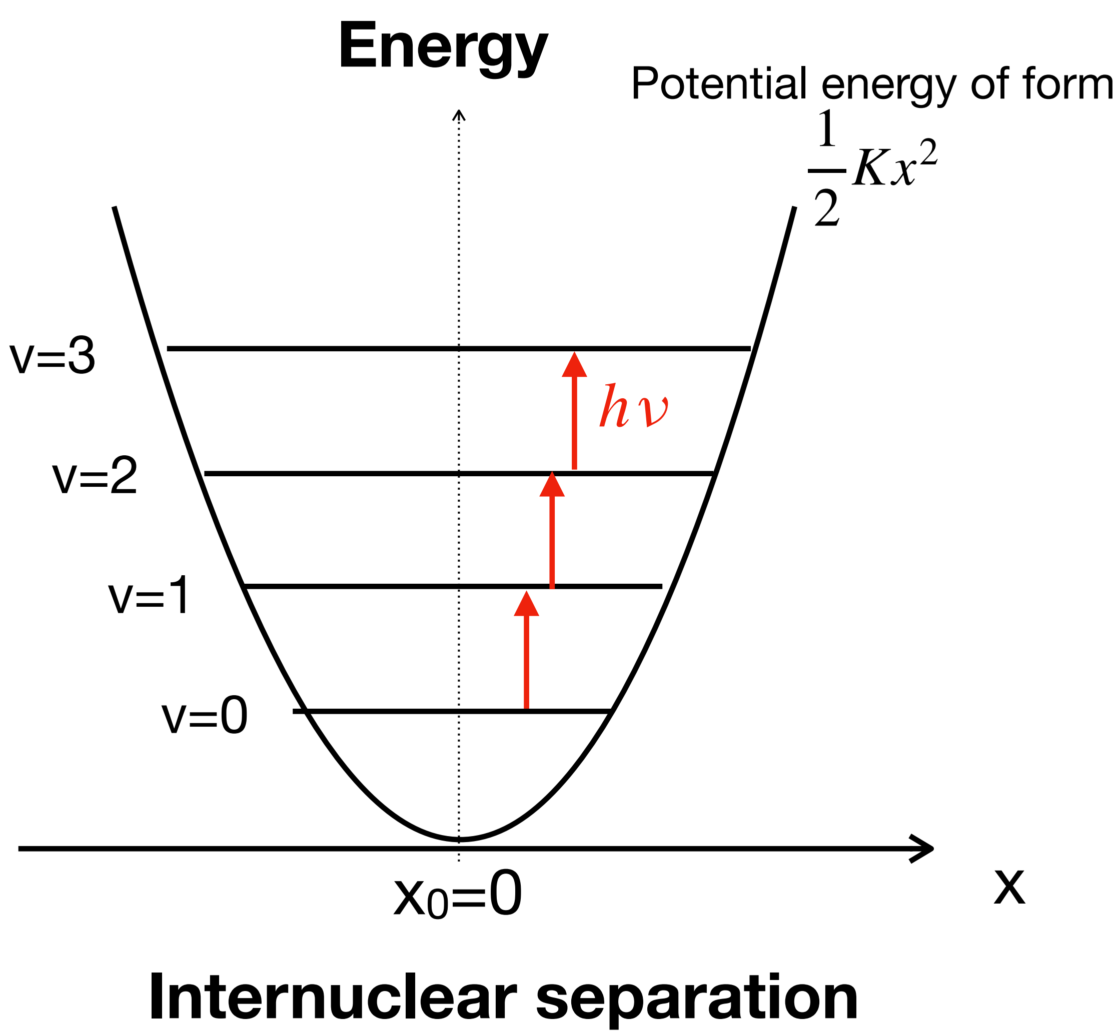
- A diatomic molecule can be treated as a harmonic oscillator: 2 masses on a spring with a potential energy that depends upon the square of the displacement from equilibrium position: $E_p(x) = \frac{1}{2}K(x - x_0)^2$

- The vibrational frequency is $\nu_{osc} = \frac{1}{2\pi}\sqrt{\frac{k}{\mu_r}}$

  where the reduced mass $\mu_r = \frac{m_1 m_2}{m_1 + m_2}$

- The energy levels are $E_\mathrm{v} = (\mathrm{v} + \frac{1}{2})h\nu_{osc}$ with v an integer value

- Only transitions with Δv = ±1 are allowed by quantum mechanics.



With a finer treatment (anharmonic oscillator), we find that transitions with Δv = ±2, ±3 exist but with a low intensity

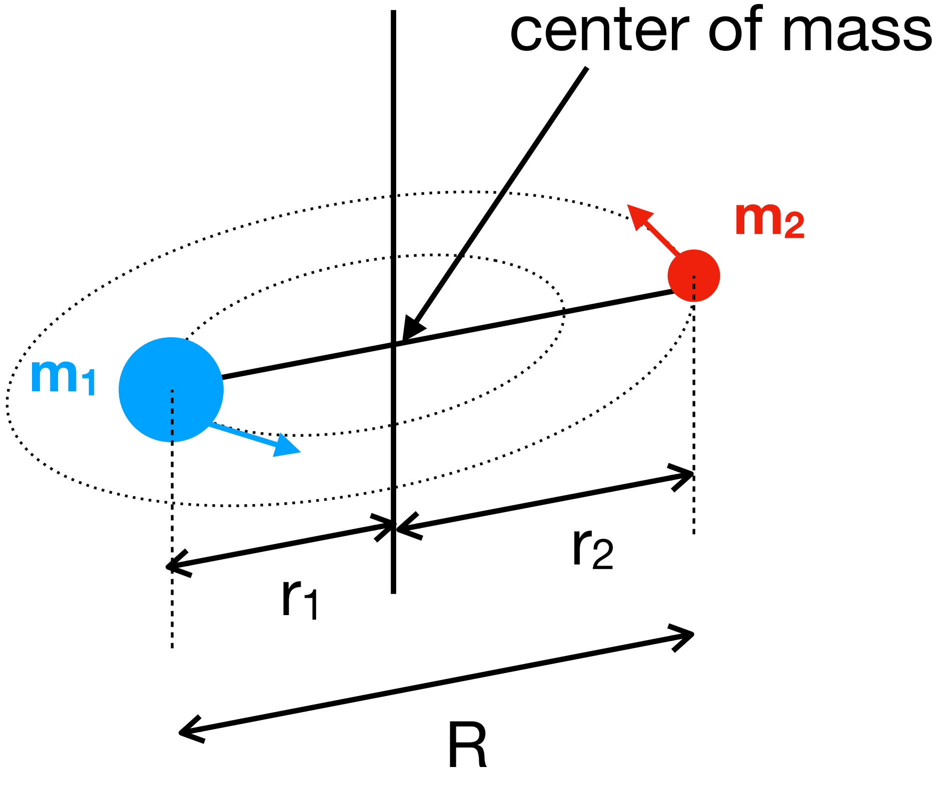
Rotation energy levels

- Finally, a diatomic molecule can rotate as a whole around an axis passing through the center of mass and perpendicular to the internuclear axis

- Treating the molecule as a rigid rotator and solving Schrödinger equation, we find that the possible energy levels are $E_{rot} = \dfrac{h^2 J(J+1)}{8\pi^2 I}$, with <u>J an integer value</u>, the moment of inertia $I = \mu_r R^2$, and the reduced mass $\mu_r = \dfrac{m_1 m_2}{m_1 + m_2}$

- The rotational frequency is $\nu_{rot} = \dfrac{h}{4\pi^2}\sqrt{J(J+1)}$

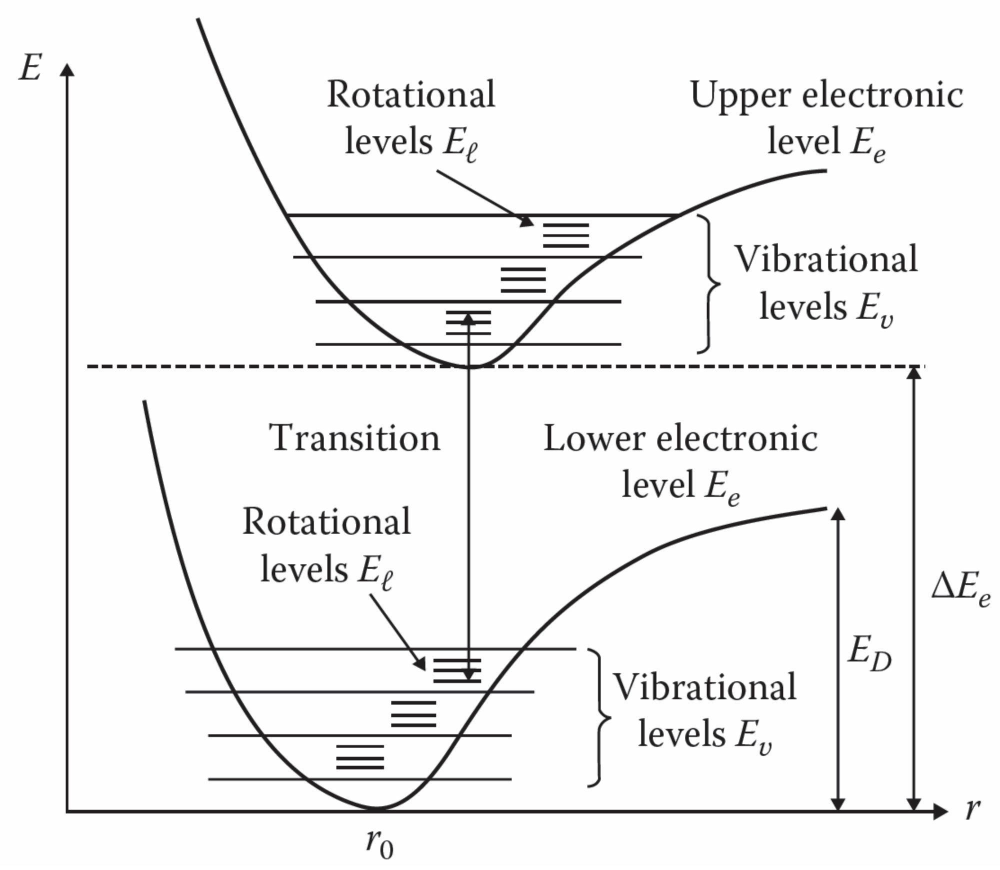
- Only transitions with ΔJ = ±1 are allowed by quantum mechanics.



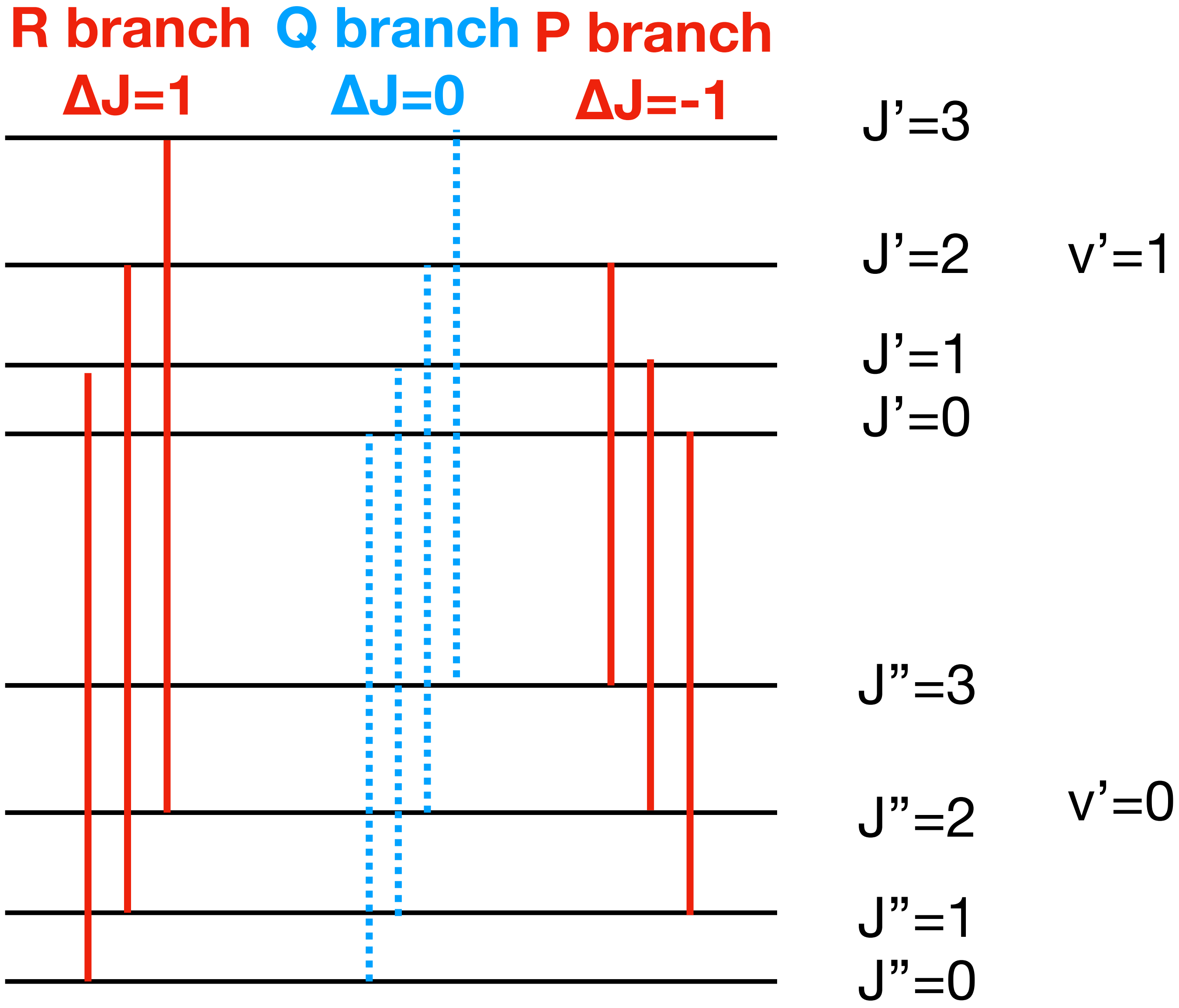
To rotate, the molecule must have a dipolar moment non-null (O_2, N_2 don't have)

Vibration-Rotation energy levels

- In reality, movements of rotation and vibration happen simultaneously.
- Rules of selection are the same Δv=±1, ΔJ=1 (*R branch*) and ΔJ=-1 (*P branch*)
- The transition with ΔJ=0 is called *Q branch* but is « forbidden » (in practise, happens but with a very low probability)



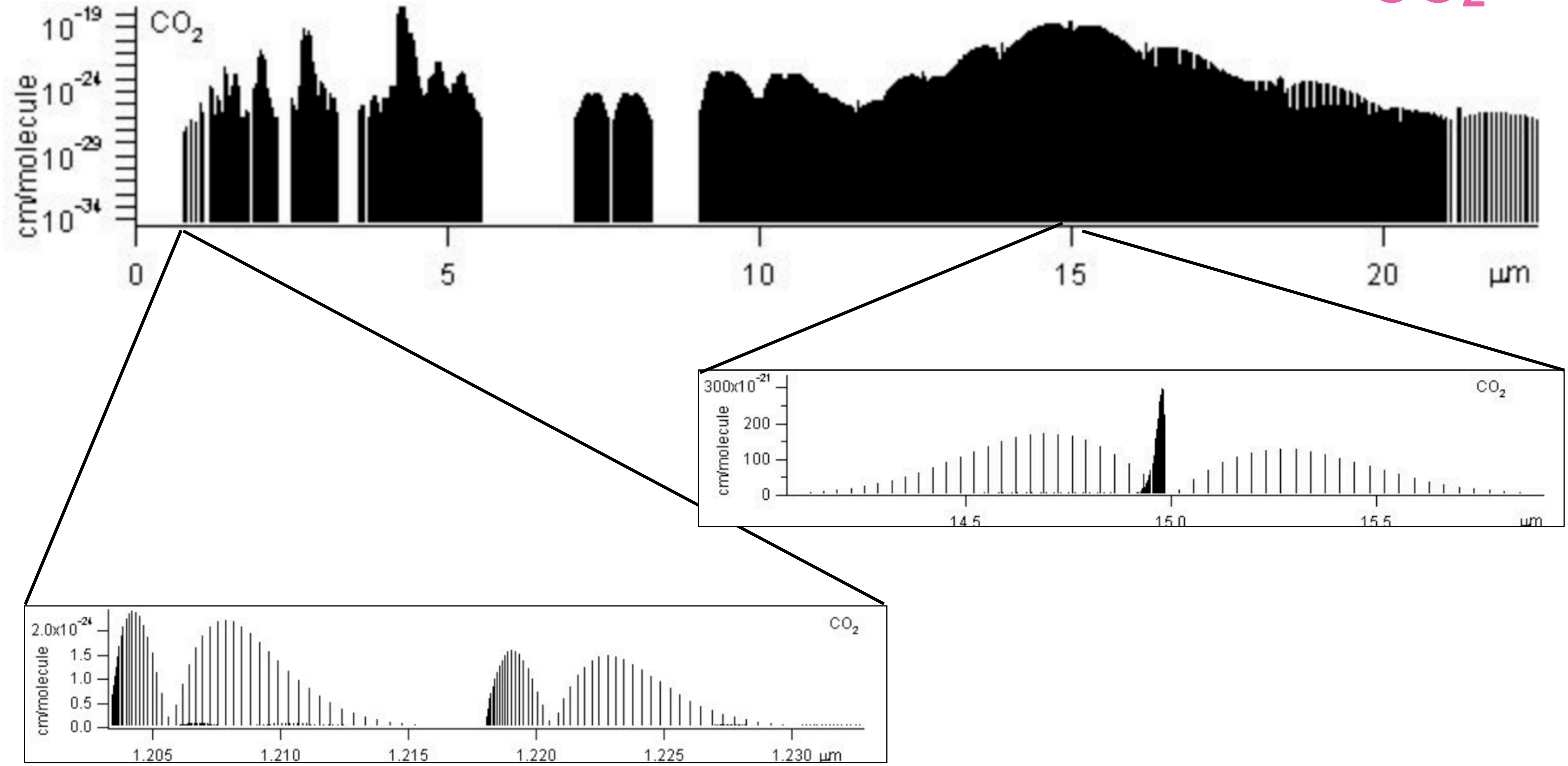
Courtesy of E. Hébrard , University of Exeter



Molecular spectra

- Each atom or molecule has its own unique set of energy transitions, with different intensities.

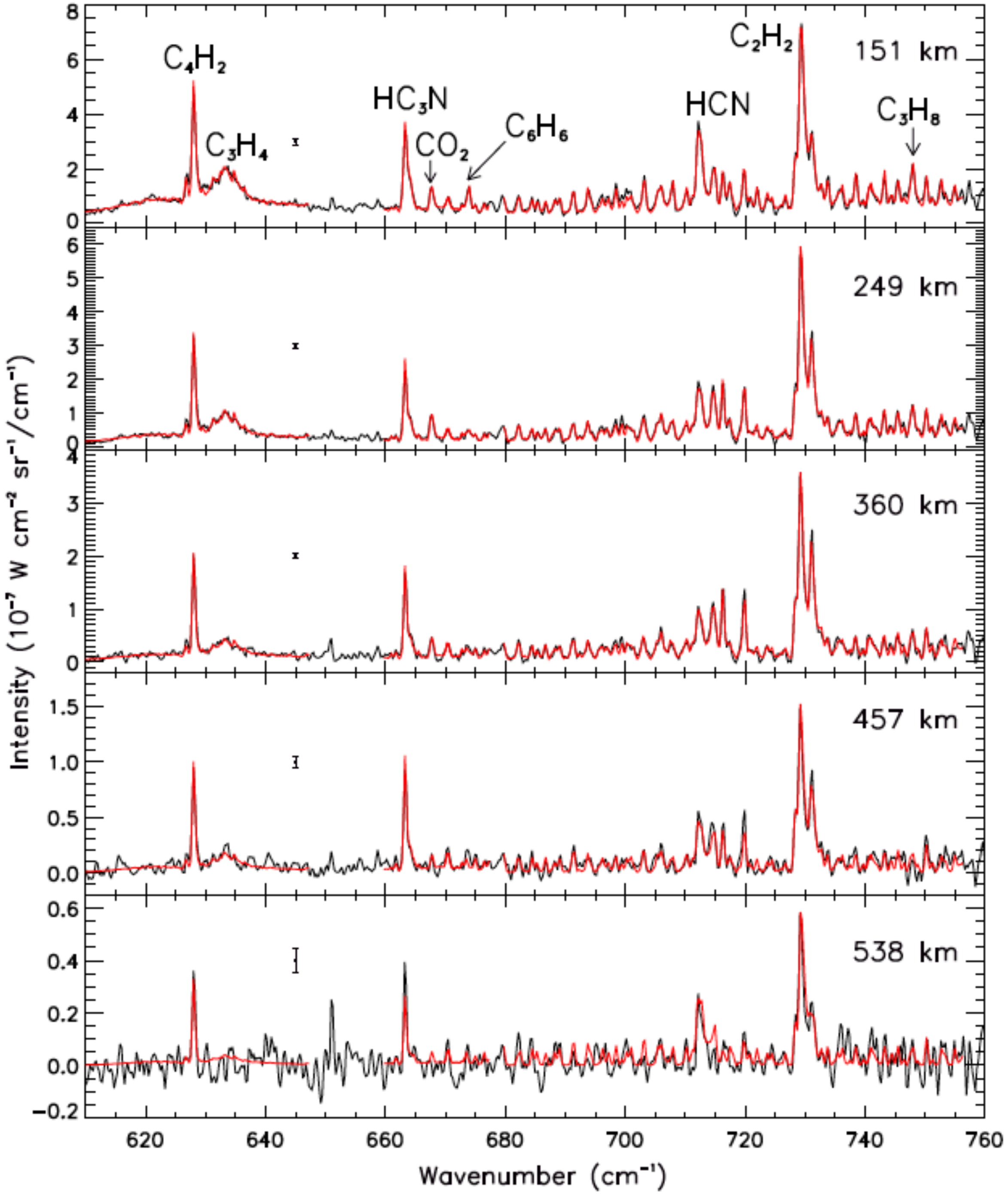
CO$_2$



Planetary Spectra

- Identification of individual molecular bands in planetary spectra permit to determine the composition of atmospheres.

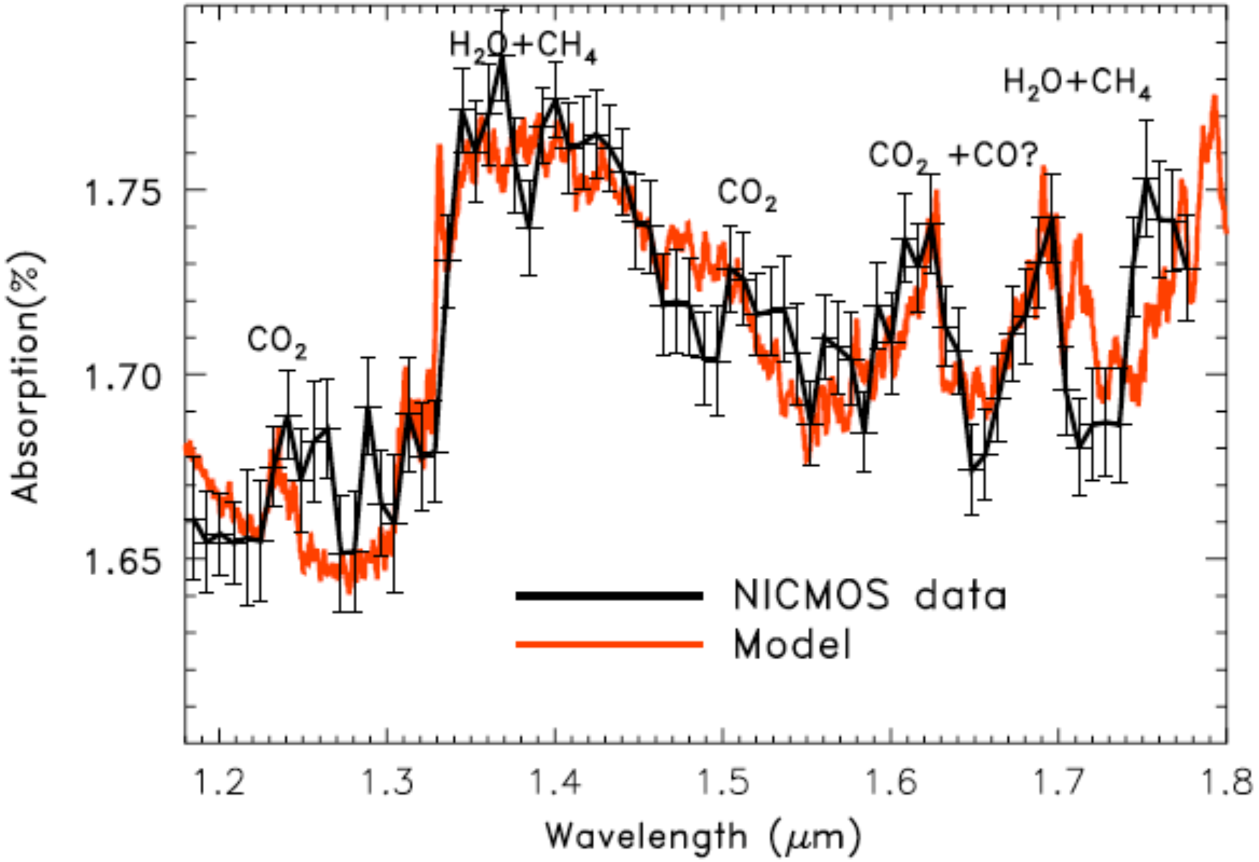
Titan atmosphere Vinatier et al. 2010



- Comparison between synthetic spectra and observations

- Much better resolution for Solar System bodies than for exoplanets…

XO-1b atmosphere Tinetti et al. 2010



Outline

- Introduction - Structure of exoplanet atmospheres
- Molecular Spectroscopy - Electronic, vibrational, rotational transitions
- **Thermodynamics - Thermochemical equilibrium**
- Chemical kinetics
- Photochemistry
- Tools: 1D kinetic models - ingredients + key results

Thermodynamic

- In the deep region of hot/warm gaseous giant exoplanets atmospheres, because P and T are high, chemical composition corresponds to thermochemical equilibrium.

- The chemical composition in these regions can be calculated using the laws of thermodynamics, considering this region as a closed system.

- The Gibbs free Energy (G) is the thermodynamic quantity the most appropriate to study and calculate this chemical equilibrium.

- The Gibbs free Energy is given by : $G = H - TS$

enthalpy

temperature

entropy

Thermodynamic

- Consider one reaction occurring in a mixture of gases with constant *P* and *T*.

- The 2nd law of thermodynamics states that the total entropy of an isolated system can never decrease over time:
  $\Delta S_{tot} \geq 0$ with $\Delta S_{tot} = \Delta S_{sys} + \Delta S_{ext}$ ← *mixture of gases*

  chemical reaction ↗

- The variation of enthalpy of the system corresponds to the heat exchanged during the reaction: $Q_P = \Delta H_{sys}$

  and this variation of enthalpy is received by the exterior => $\Delta S_{ext} = -\dfrac{Q_P}{T} = -\dfrac{\Delta H_{sys}}{T}$

- $\Delta S_{sys} - \dfrac{\Delta H_{sys}}{T} \geq 0$ => $\Delta H_{sys} - T\Delta S_{sys} \leq 0$ => $\boxed{\Delta G_{sys} \leq 0}$

- The reaction can occur <u>only if the Gibbs Energy of the system decreases</u> and the equilibrium state will be reached for the minimum of G_{sys}.

Thermodynamic

- In a system composed of L species, the Gibbs Energy of the system can be expressed as a function of the partial Gibbs Energy (=*chemical potential*) of each species l: $G_{sys} = \sum_{l=1}^{L} \mu_l N_l$

  with $\mu_l = g_l(T,P) + RT \ln N_l$ and N_l the number of moles of species l

- The Gibbs Energy of species l is : $g_l(T,P) = h_l(T) - Ts_l(T)$.

- Let express $h_l(T)$ and $s_l(T)$ with the values at Normal conditions of Pressure ($P^0 = 1.01325$ bar)

  $h_l(T)$ does not depend on P => $h_l(T) = h_l^0(T)$ (at P^0)

  $s_l(T)$ does depend on P => a term depending on pressure must be added:

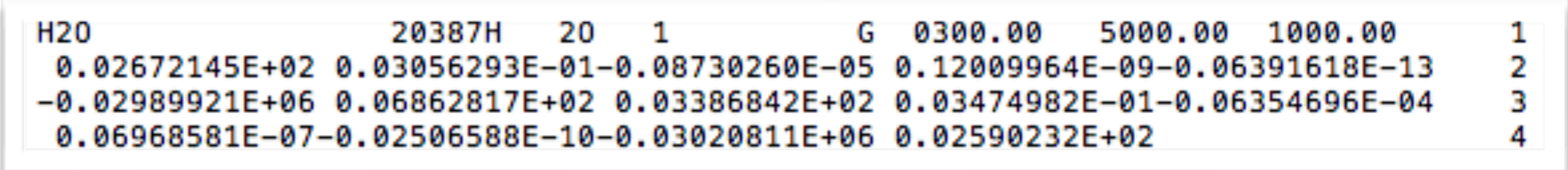
  $$g_l(T,P) = h_l^0(T) - Ts_l^0(T) + RT \ln \frac{P}{P^0}$$

- Finally, the total Gibbs Energy of the system is given by:

$$\boxed{G_{sys} = \sum_{l=1}^{L} \left(h_l^0(T) - Ts_l^0(T) + RT \ln \frac{P}{P^0} + RT \ln N_l \right) \times N_l}$$

NASA coefficients

- The thermodynamic properties of species $h_l^0(T)$ and $s_l^0(T)$ can be computed numerically thanks to NASA polynomials.



```
H2O                 20387H   2O   1           G  0300.00   5000.00  1000.00      1
 0.02672145E+02 0.03056293E-01-0.08730260E-05 0.12009964E-09-0.06391618E-13    2
-0.02989921E+06 0.06862817E+02 0.03386842E+02 0.03474982E-01-0.06354696E-04    3
 0.06968581E-07-0.02506588E-10-0.03020811E+06 0.02590232E+02                   4
```

- For each species, two sets of coefficients exist, corresponding to two ranges of temperature. In the format found in the literature, the first set of coefficients corresponds to the high temperature range (1000-6000 K), the second set to the low temperature range (300-1000 K)

- Originally, the format of these polynomials used 7 coefficients, but the update NASA polynomial format is using 9 coefficients. However, both format are still regularly used.

- 7-coefficients format :

$$\frac{h_l^0(T)}{RT} = a_{1l} + \frac{a_{2l}T}{2} + \frac{a_{3l}T^2}{3} + \frac{a_{4l}T^3}{4} + \frac{a_{5l}T^4}{5} + \frac{a_{6l}}{T}$$

$$\frac{s_l^0(T)}{R} = a_{1l}\ln T + a_{2l}T + \frac{a_{3l}T^2}{2} + \frac{a_{4l}T^3}{3} + \frac{a_{5l}T^4}{4} + a_{7l}$$

- 9-coefficients format :

$$\frac{h_l^0(T)}{RT} = -\frac{a_{1l}}{T^2} + \frac{a_{2l}\ln T}{T} + a_{3l} + \frac{a_{4l}T}{2} + \frac{a_{5l}T^2}{3} + \frac{a_{6l}T^3}{4} + \frac{a_{7l}T^4}{5} + \frac{a_{8l}}{T}$$

$$\frac{s_l^0(T)}{R} = -\frac{a_{1l}}{2T^2} - \frac{a_{2l}}{T} + a_{3l}\ln T + a_{4l}T + \frac{a_{5l}T^2}{2} + \frac{a_{6l}T^3}{3} + \frac{a_7lT^4}{4} + a_9l$$

Equilibrium composition

- Reminder: the Gibbs free Energy of the system is :

$$G_{sys} = \sum_{l=1}^{L} (h_l^0(T) - Ts_l^0(T) + RT\ln\frac{P}{P^0} + RT\ln N_l) \times N_l$$

- With NASA coefficients, we are able to calculate each term of this formula.

- For an initial molecular composition (or initial elemental abundances), the set of N_l that permits to have the lower G_{sys} will correspond to the thermochemical equilibrium composition.

- This composition is found numerically, with a Newton-Raphson method for instance.

Repartition of chemical elements

Application : Study the molecular composition of a mixture of gases as a function of T (between 200 and 2000K)

- P = 0.001 bar (2 groups)
- P = 1 bar (2 groups)
- P = 100 bar (2 groups)

- go on http://navier.engr.colostate.edu/code/code-4/index.html
- elements: C, H, O, N, He
- initial: $y_{H2} = 0.8317$, $y_{He}=0.1663$, $y_C=6.643 \times 10^{-4}$, $y_O=1.331 \times 10^{-3}$, $y_N=1.422 \times 10^{-4}$
- additional species: H, CH_4, CO_2, CH_3, CO, H_2O, O_2, N_2, NH_3, HCN

➡ which are the dominant molecules as a function of T ?

➡ at which T does the transition for the main C-bearing species occur?

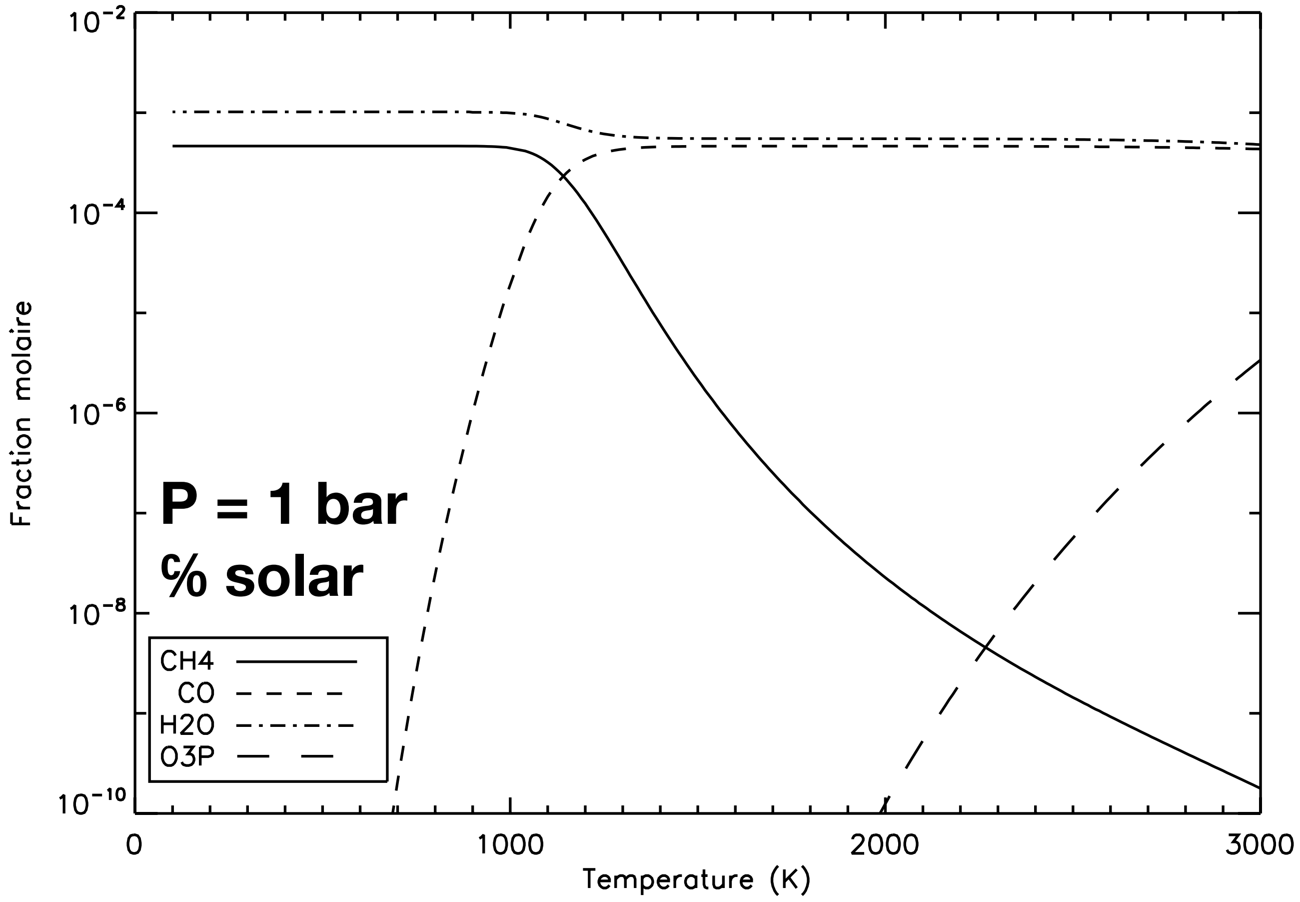
➡ same question for the main N-bearing species?

Repartition of chemical elements

- We can thus determined how the chemical elements are distributed among the different species as a function of T:

- For solar elemental abundances (% = 0.46), Carbon is mainly under the form of CH_4 at low T. At higher T, CO is the main C-bearing species. Transition occurs about **1100 K**.

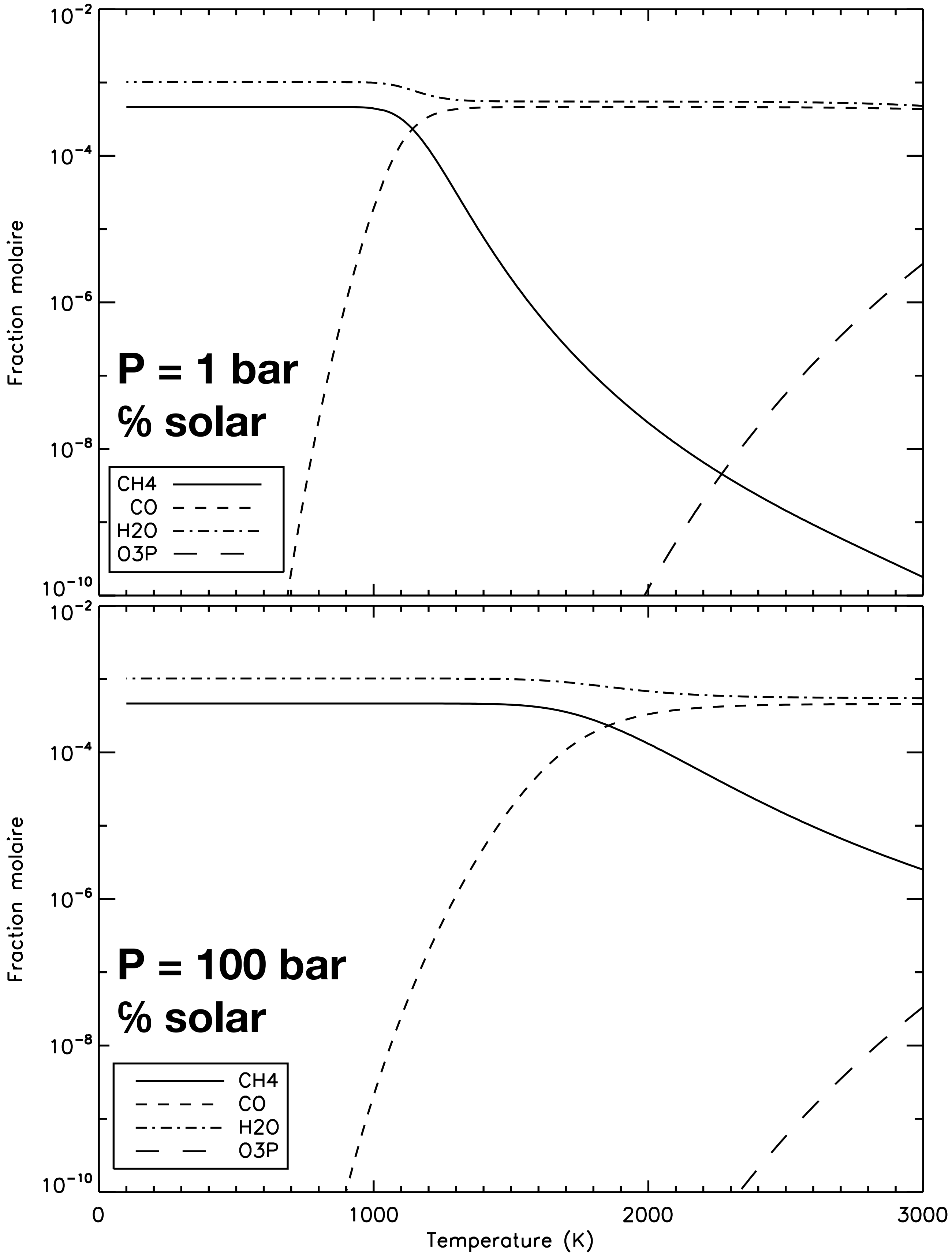
- H_2O is the main O-bearing species (up to 3000 K), but sees its abundance decreases when that of CO increases.



Repartition of chemical elements

- We can also see that P has an influence:

- At P = 100 bar, transition between CO/CH_4 occurs at higher T than at 1 bar: **~1800 K**.

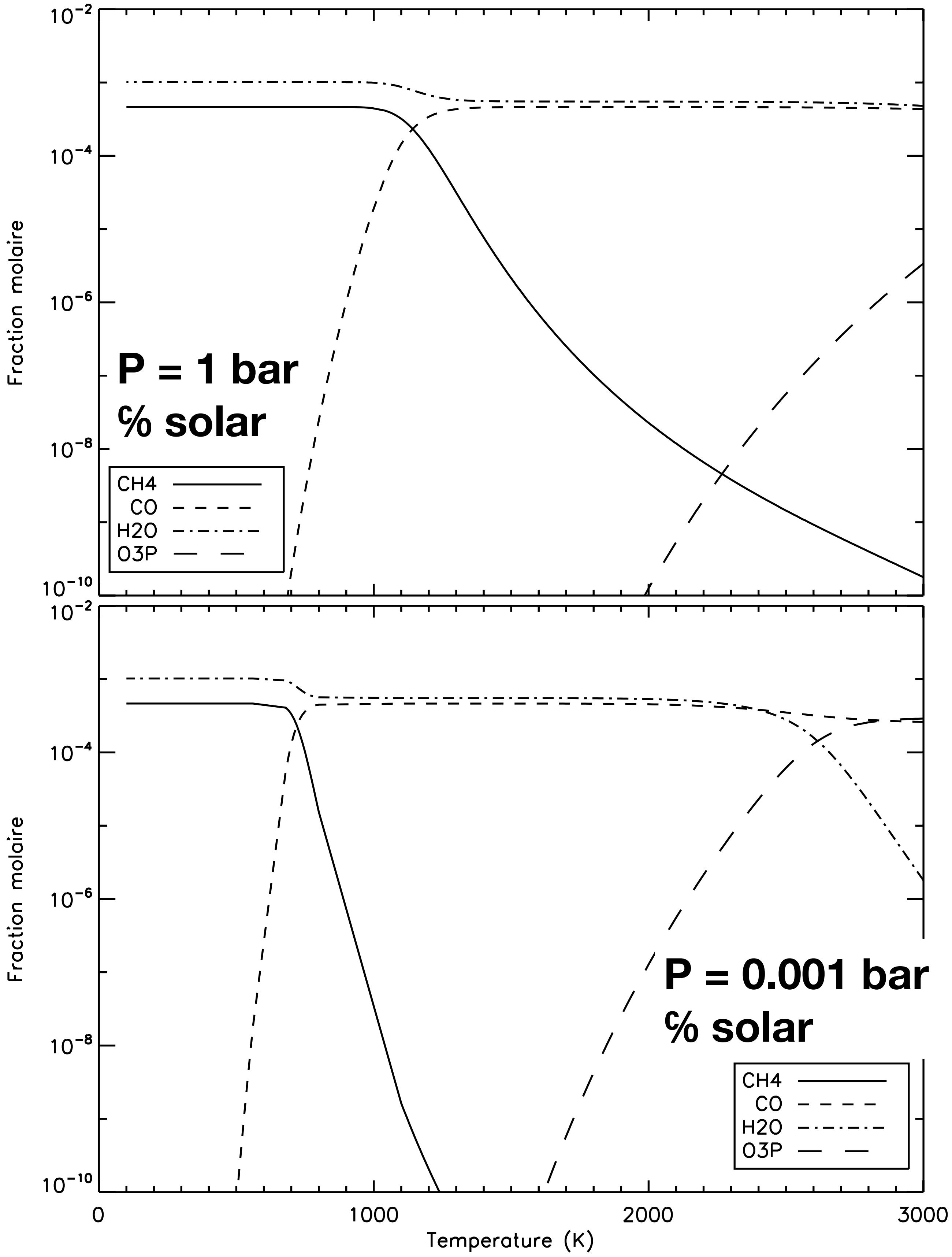


Repartition of chemical elements

- Conversely, when P decreases transition between CO/CH_4 occurs at lower T.
  At 0.001 bar, transition happens at **~700 K**.

- CO becomes more abundant than H_2O about 2500K.

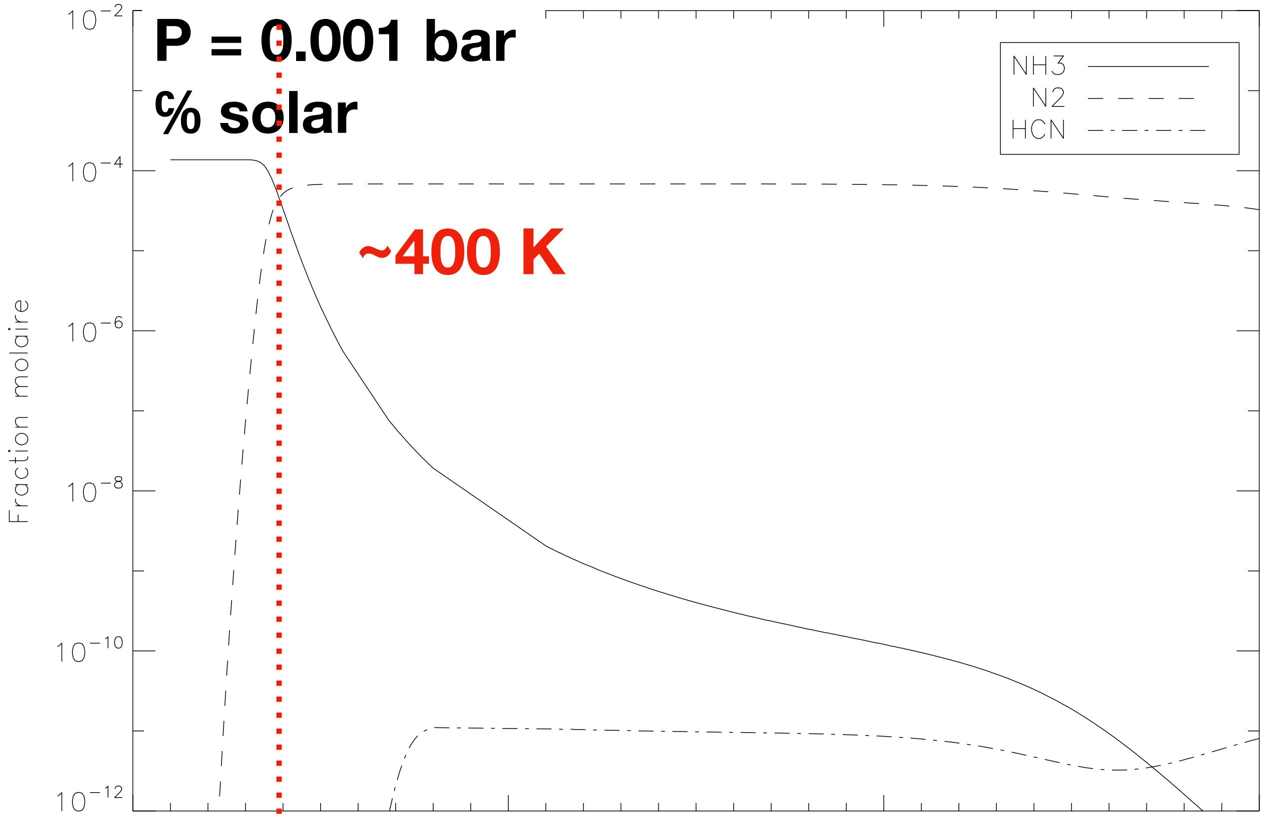
- We notice the increase of molecular oxygen, which becomes the reservoir of oxygen after 2900 K.



Repartition of chemical elements

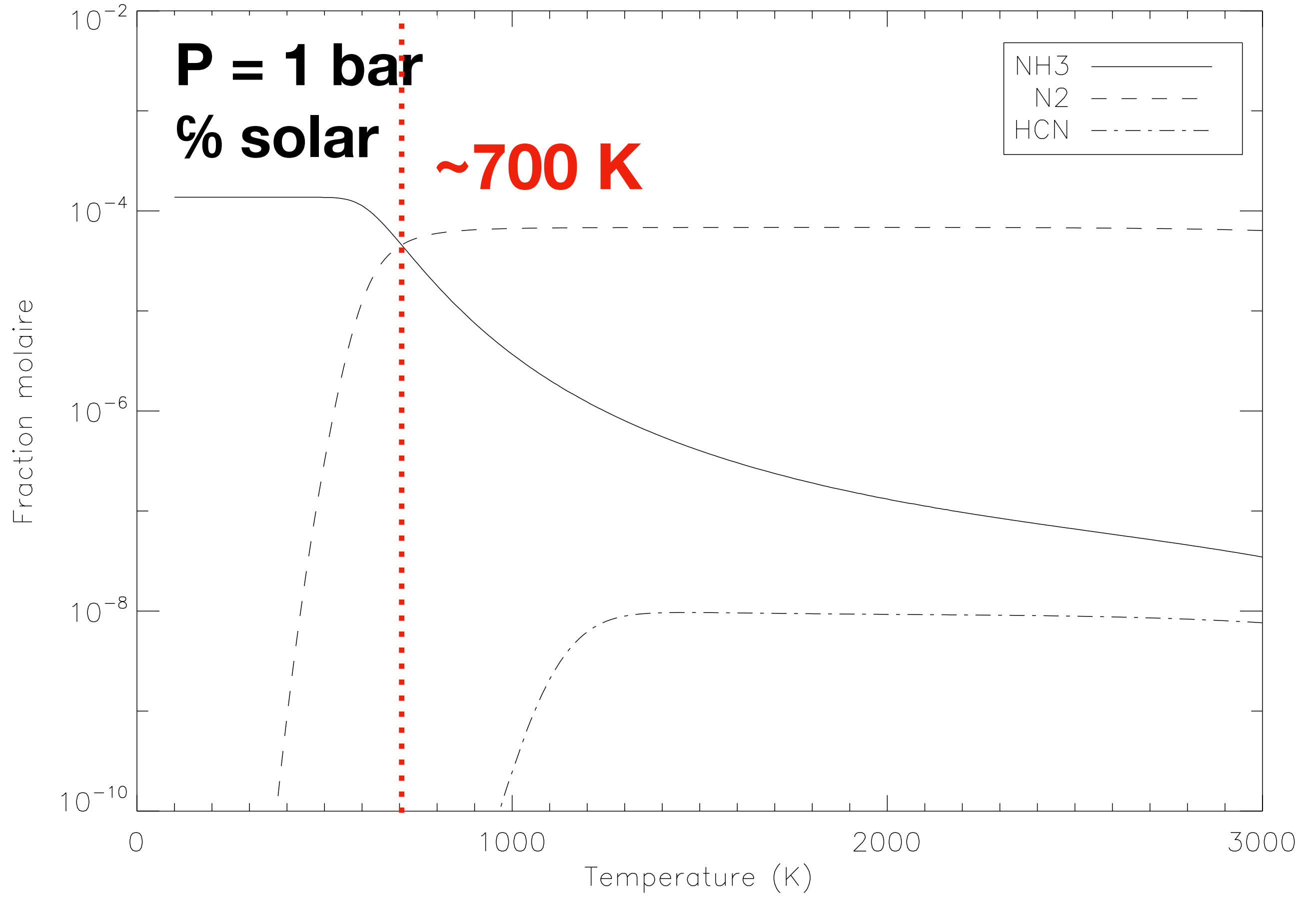
- The same behaviour is observed for Nitrogen species, NH_3 being the N-bearing species at low T, N_2 at high T.

- Temperature of transition increases together with P.



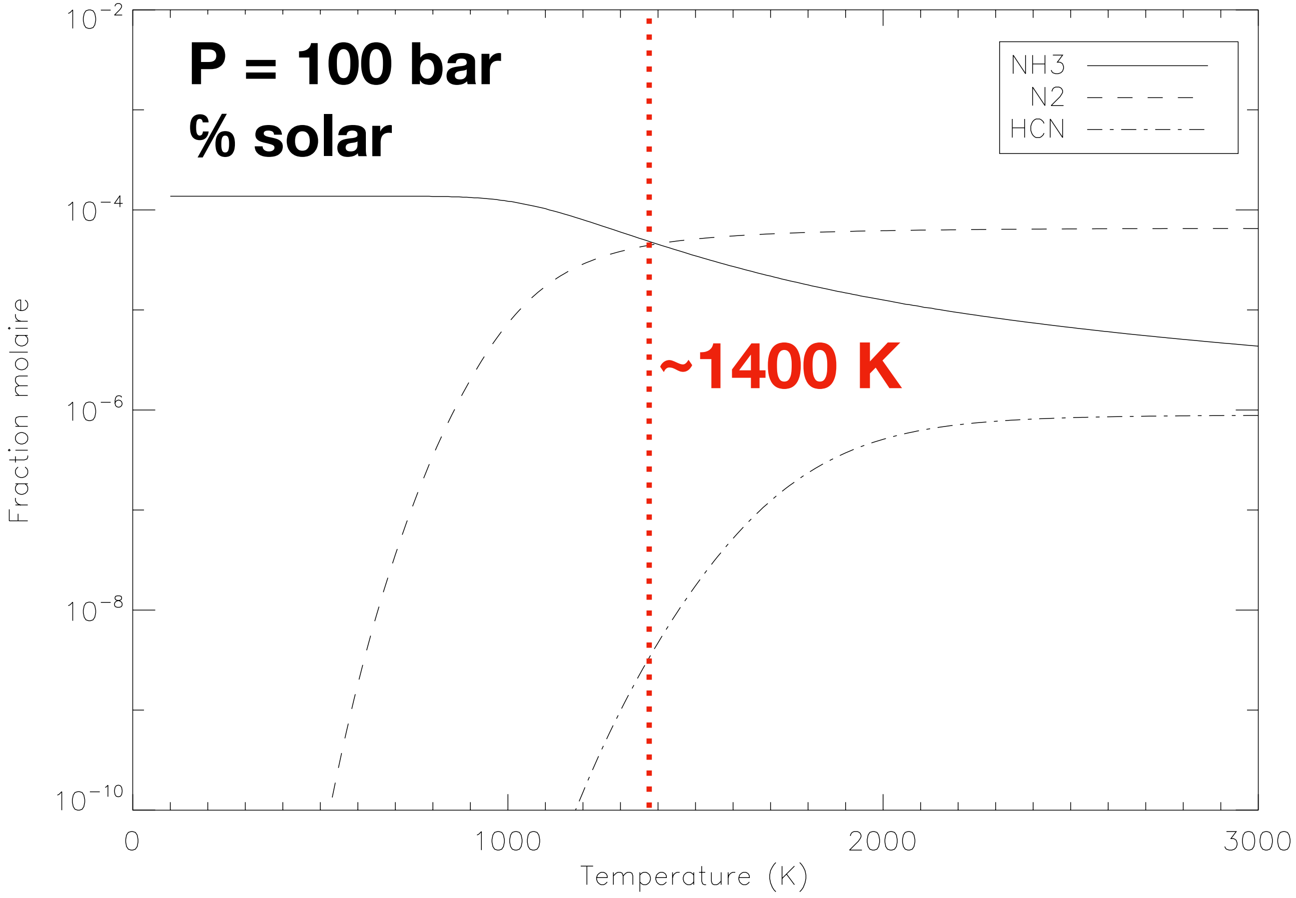
P = 0.001 bar
% solar

~400 K



P = 1 bar
% solar

~700 K



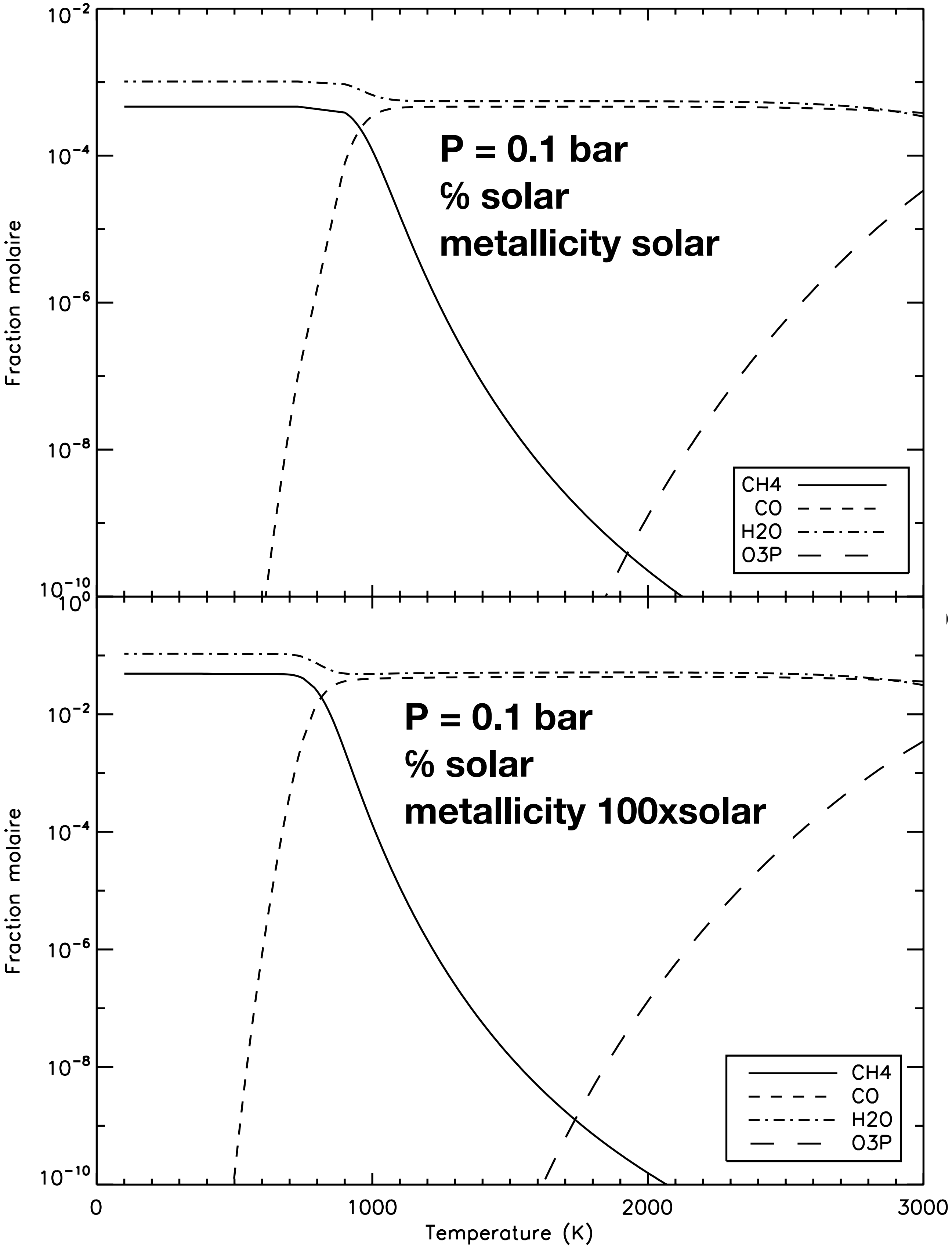
P = 100 bar
% solar

~1400 K

Repartition of chemical elements

- For a given elemental composition, P and T determine the molecular composition.

- The elemental composition influences also the molecular composition (i.e. C/H, O/H, N/H)



P = 0.1 bar
% solar
metallicity solar

P = 0.1 bar
% solar
metallicity 100xsolar

Repartition of chemical elements

- For a given elemental composition, P and T determine the molecular composition.

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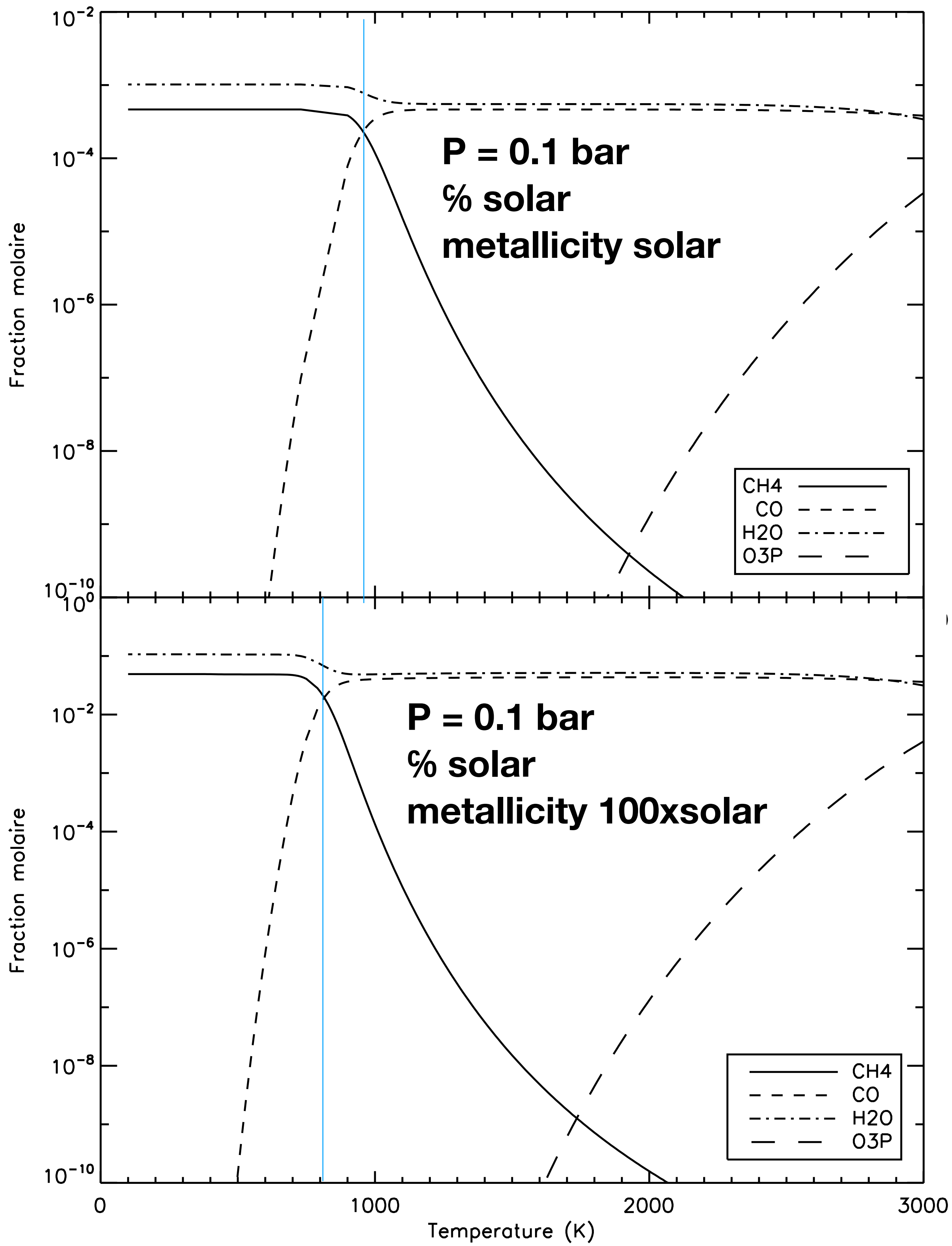
- An increase of the metallicity lowers the temperature of transition between CO / CH_4 (same for N_2/NH_3)



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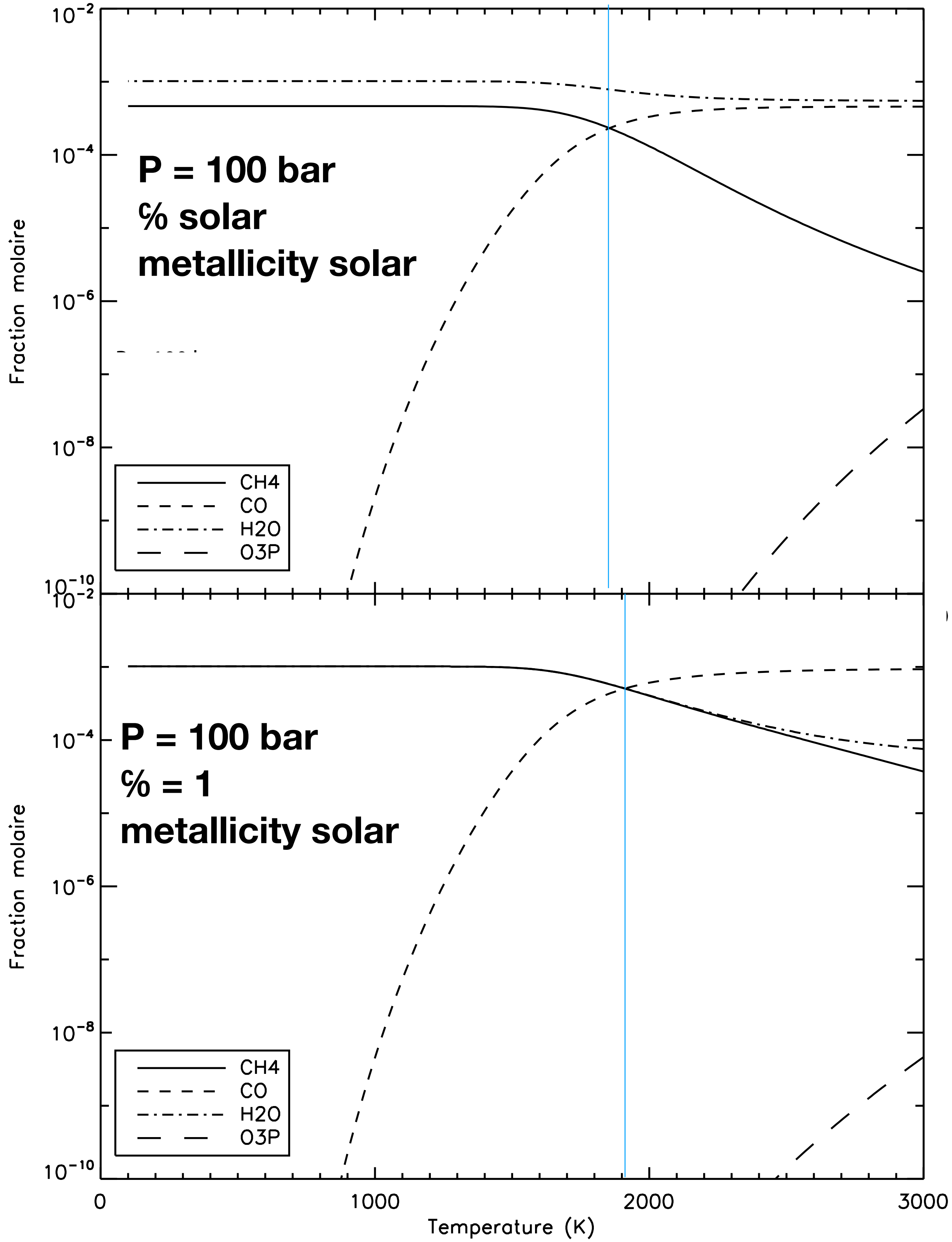
Repartition of chemical elements

- For a given elemental composition, P and T determine the molecular composition.
- The elemental composition influences also the molecular composition (i.e. C/H, O/H, N/H)
- An increase of the metallicity lowers the temperature of transition between CO / CH_4
  (same for N_2/NH_3)
- An increase of the ℅ ratio also slightly increases the temperature of transition.
- At high T and ℅=1, CO is the main C- and O-bearing species.



Reaction quotient

- Thermodynamic is useful but does not give information on the time required to reach equilibrium. In planetary atmospheres, disequilibrium processes compete with chemical reactions, so …

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*for non-ideal gas, one mu coefficient (0≤γ_l≤1)

** P^0, N^0, and Y^0 are the sta and 1

Reaction quotient

- Thermodynamic is useful but does not give information on the time required to reach equilibrium. In planetary atmospheres, disequilibrium processes compete with chemical reactions, so we need chemical kinetics….

- Let consider a reversible reaction involving L species of the general form $\sum_{l=1}^{L} \nu'_l \chi_l = \sum_{l=1}^{L} \nu''_l \chi_l$ with ν'_l and ν''_l the stoichiometric coefficients in the forward and reverse direction respectively.

- At any time t, the reaction is characterised by the reaction quotient (Q_R):

$$Q_R(t) = \prod_{l=1}^{L} a_l(t)^{\nu_l}$$ with $\nu_l = \nu''_l - \nu'_l$ and $a_l(t)$ the activity of species χ_l at instant t

- The activity of a species corresponds to its « effective concentration » in a mixture. Dimensionless quantity that can be expressed* as a function of its partial pressure ($a_l = p_l/P^0$), its molecular concentration ($a_l = n_l/N^0$), or its mixing ratio ($a_l = y_l/Y^0$) **

*for non-ideal gas, one must multiply p_l, n_l and y_l by the activity coefficient ($0 \leq \gamma_l \leq 1$)

** P^0, N^0, and Y^0 are the standard values : 1 bar, 1 molecule.cm^{-3}, and 1

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- Let consider a reversible reaction involving L species of the general form

$$\sum_{l=1}^{L} \nu_l' \chi_l = \sum_{l=1}^{L} \nu_l'' \chi_l$$

with ν'_l and ν''_l the stoichiometric coefficients in the forward and reverse direction respectively.

ex: A+B=C+2D $\Rightarrow Q_R(t) = \dfrac{a_C(t)a_D^2(t)}{a_A(t)a_B(t)}$

- At any time t, the reaction is characterised by the reaction quotient (Q_R):

$$Q_R(t) = \prod_{l=1}^{L} a_l(t)^{\nu_l}$$

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** P^0, N^0, and Y^0 are the standard values : 1 bar, 1 molecule.cm^{-3}, and 1

Equilibrium constant

- The reaction quotient with the activity expressed in pressure units (Q_p) is linked to Gibbs Energy through: $\Delta G = \Delta G^0 + RT \ln Q_p$

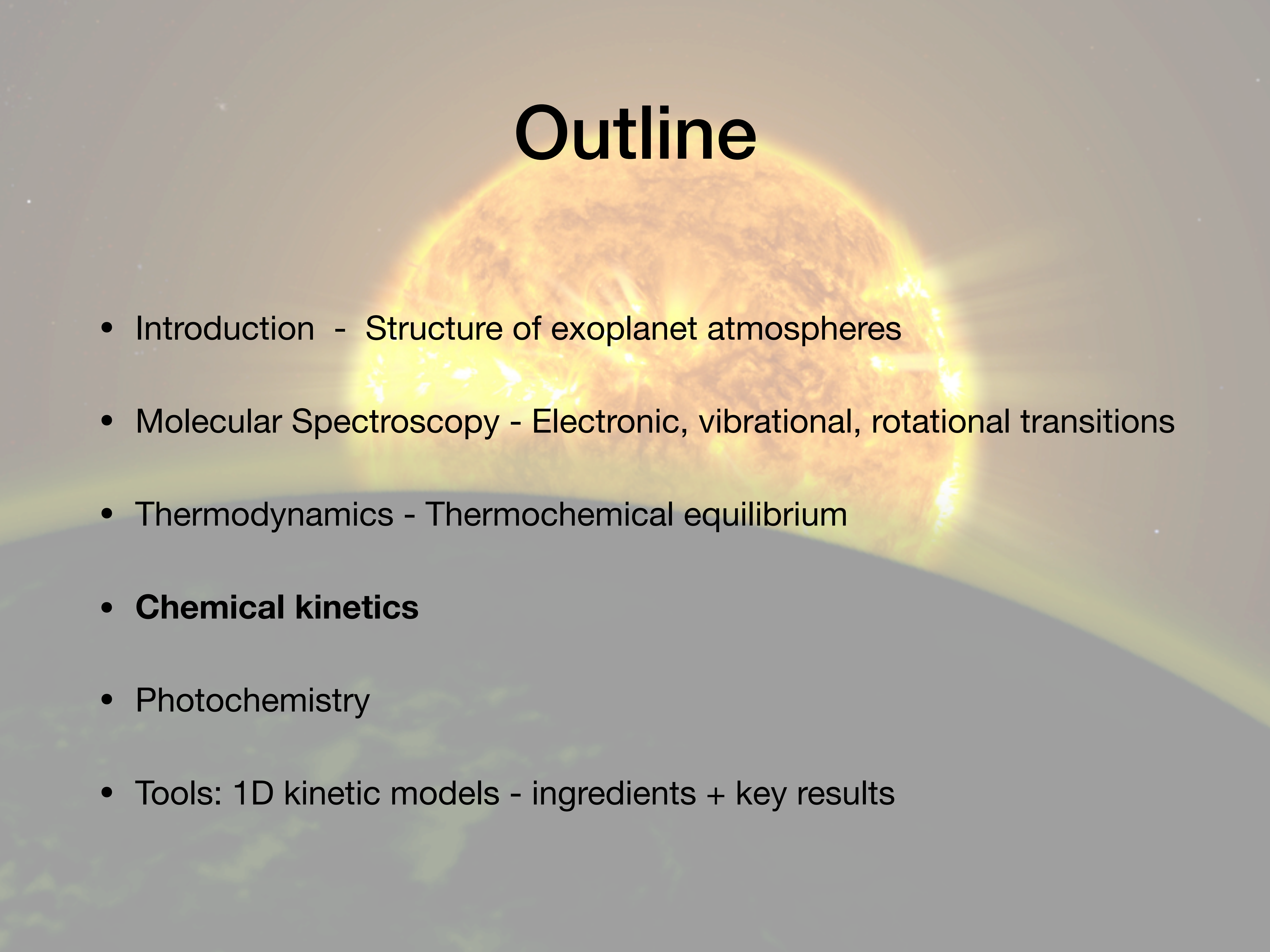
- When the reaction reached an equilibrium, and thus the system does not evolve anymore, Q_p is called equilibrium constant and is noted K_p and $\Delta G = 0$ => $\Delta G^0 = -RT \ln K_p$

- We obtain the expression of the equilibrium constant: $K_p = \exp(-\Delta G^0/RT)$

that can be also expressed : $K_p = \exp\left(\dfrac{\Delta S^0}{R} - \dfrac{\Delta H^0}{RT}\right)$

with $\dfrac{\Delta S^0}{R} = \displaystyle\sum_{l=1}^{L} \nu_l \dfrac{s_l^0(T)}{R}$ and $\dfrac{\Delta H^0}{RT} = \displaystyle\sum_{l=1}^{L} \nu_l \dfrac{h_l^0(T)}{RT}$

➡ The equilibrium constant of a reaction, K_p, can be calculated with NASA coefficients.



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Reaction rate

- We are still considering the reaction $\sum_{l=1}^{L} \nu'_l \chi_l = \sum_{l=1}^{L} \nu''_l \chi_l$

ex: A+B=C+2D

- Conservation of matter imposes: $-\frac{1}{\nu'_l}\frac{d[\chi_l]}{dt} = \frac{1}{\nu''_l}\frac{d[\chi_l]}{dt} = v$, where $[\chi_l]$ is the concentration of species χ_l (molecule.cm^{-3}) and v is the reaction rate (molecule.cm^{-3}.s^{-1})

ex: v=k(T)[A][B]

- The reaction rate, v, is proportional to the concentration of species. The general formula postulated by Van't Hoff is $v = k(T)\prod_l [\chi_l]^{\nu'_l}$ with $k(T)$ the rate coefficient.

- The production/loss rates of products/reactants are given by $\pm\frac{d[\chi_l]}{dt}$

P_C=d[C]/dt = k[A][B]
L_A=-d[A]/dt=k[A][B]

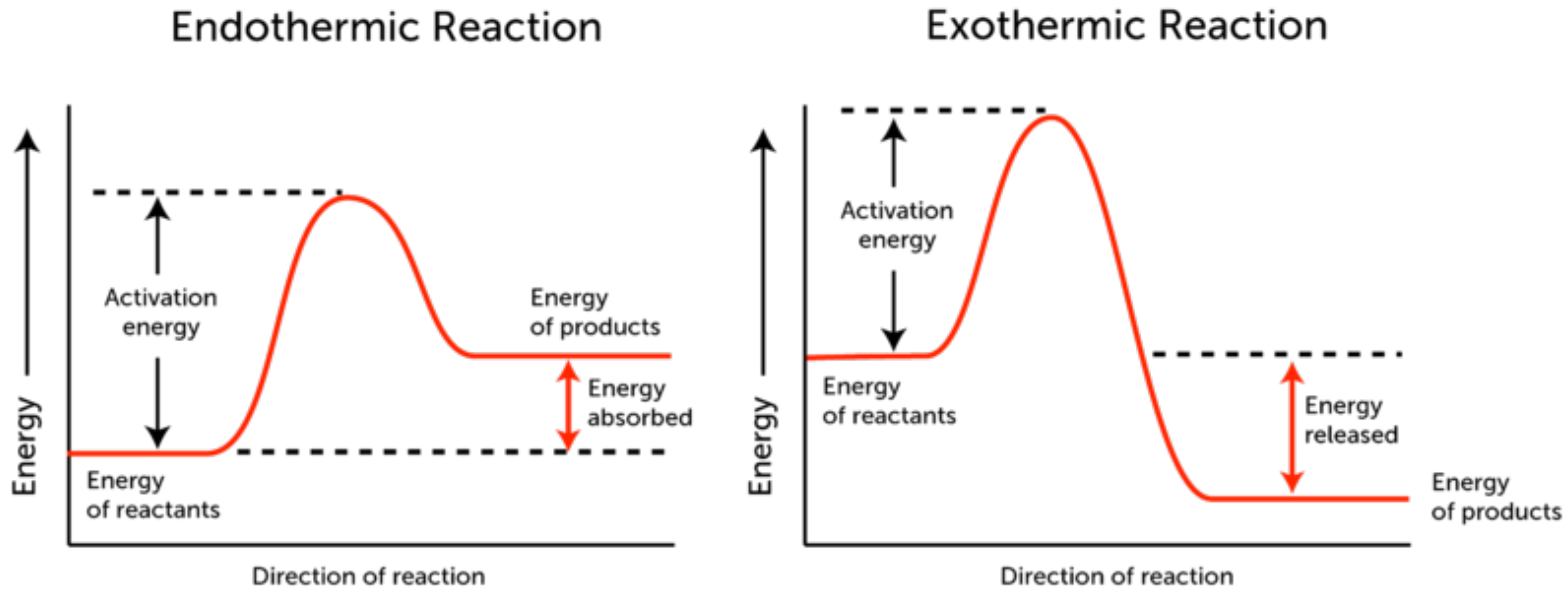
- The chemical lifetime of a species destroyed by this reaction is $\frac{[\chi_l]}{v}$

τ_A=1/k[B]

Rate coefficient

- The rate coefficient is expressed with an Arrhenius law, or, more commonly, with the modified Arrhenius law: $k(T) = AT^n \exp\left(-\frac{E_a}{RT}\right)$

Ea is the *activation energy* of the reaction.



Rate coefficient

- Units of $k(T)$ depends on the type of the reaction:
  - Unimolecular: **A⟶B+C**

    $v = k(T)[A] \Rightarrow$ $k(T)$ in s^{-1}

  - Bimolecular: **A+B⟶C+D**

    $v = k(T)[A][B] \Rightarrow$ $k(T)$ in $cm^3.molecule^{-1}.s^{-1}$

  - Termolecular: **A+B+M⟶AB+M**

    $v = k(T)[A][B][M] \Rightarrow$ $k(T)$ in $cm^6.molecule^{-2}.s^{-1}$

- A 3-bodies reaction is complex. It results from the association of 2 molecules:
  A+B⟶AB*
  followed by a deexcitation thanks to the collision with M (background gas):
  AB*+M⟶AB+M

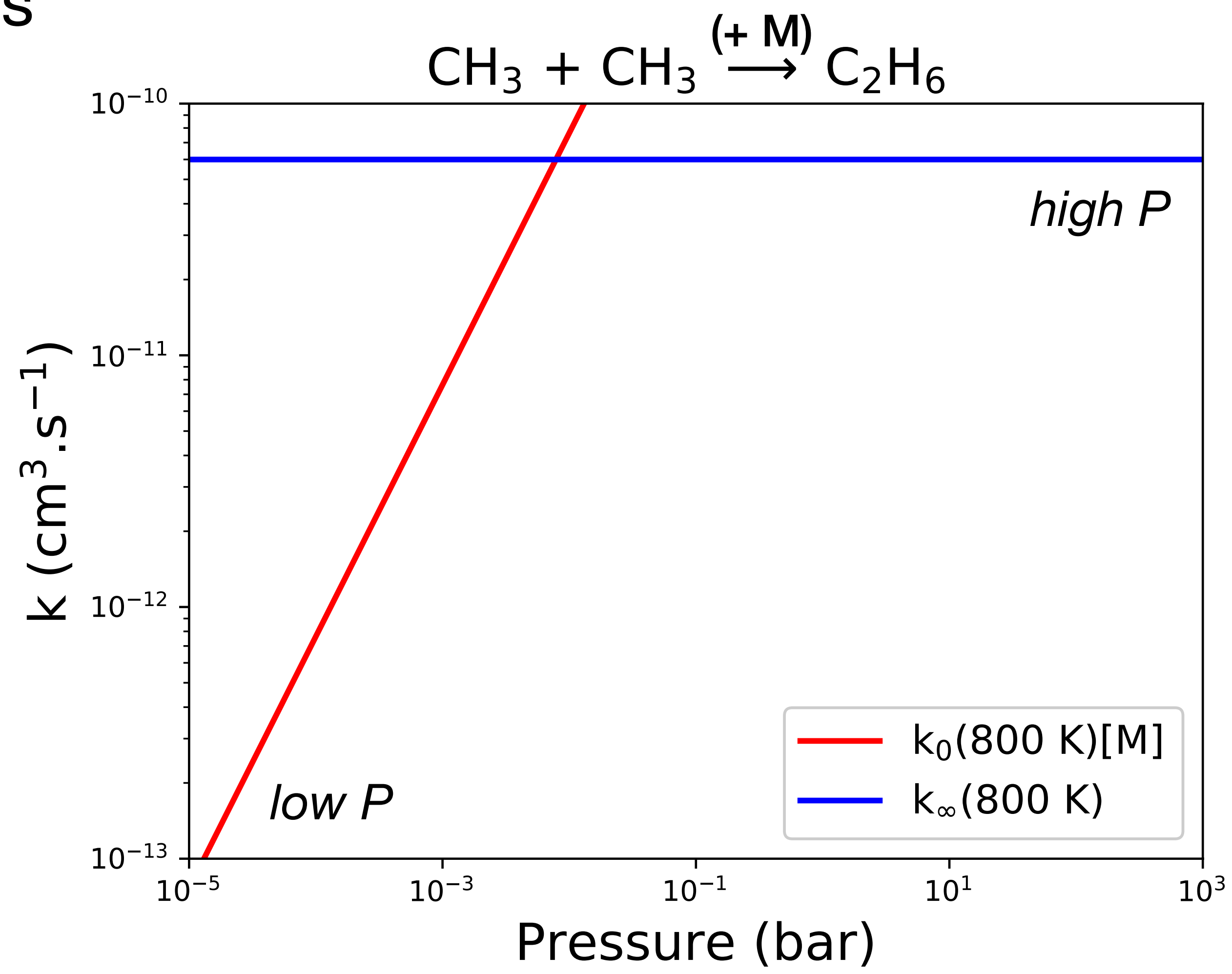
- **AB*** is not stable and will decay spontaneously if there is no collision with M:
  AB*⟶A+B

Three-bodies reactions

- The probability that **AB*** meets a **M** body is large at high P, because molecules are close to each other. In this case, the reaction rate does not depend on **[M]** and the reaction can be considered as bimolecular: **A+B⟶AB**
  ⇒ <u>In the high-pressure limit</u>: $v_\infty = k_\infty[A][B]$

- At low-pressure, the reaction rate is limited by the density of M.
  ⇒ <u>In the low-pressure limit</u>: $v_0 = k_0[A][B][M]$

- [M] is the sum of the density of each molecules (eventually weighted by their efficiencies)



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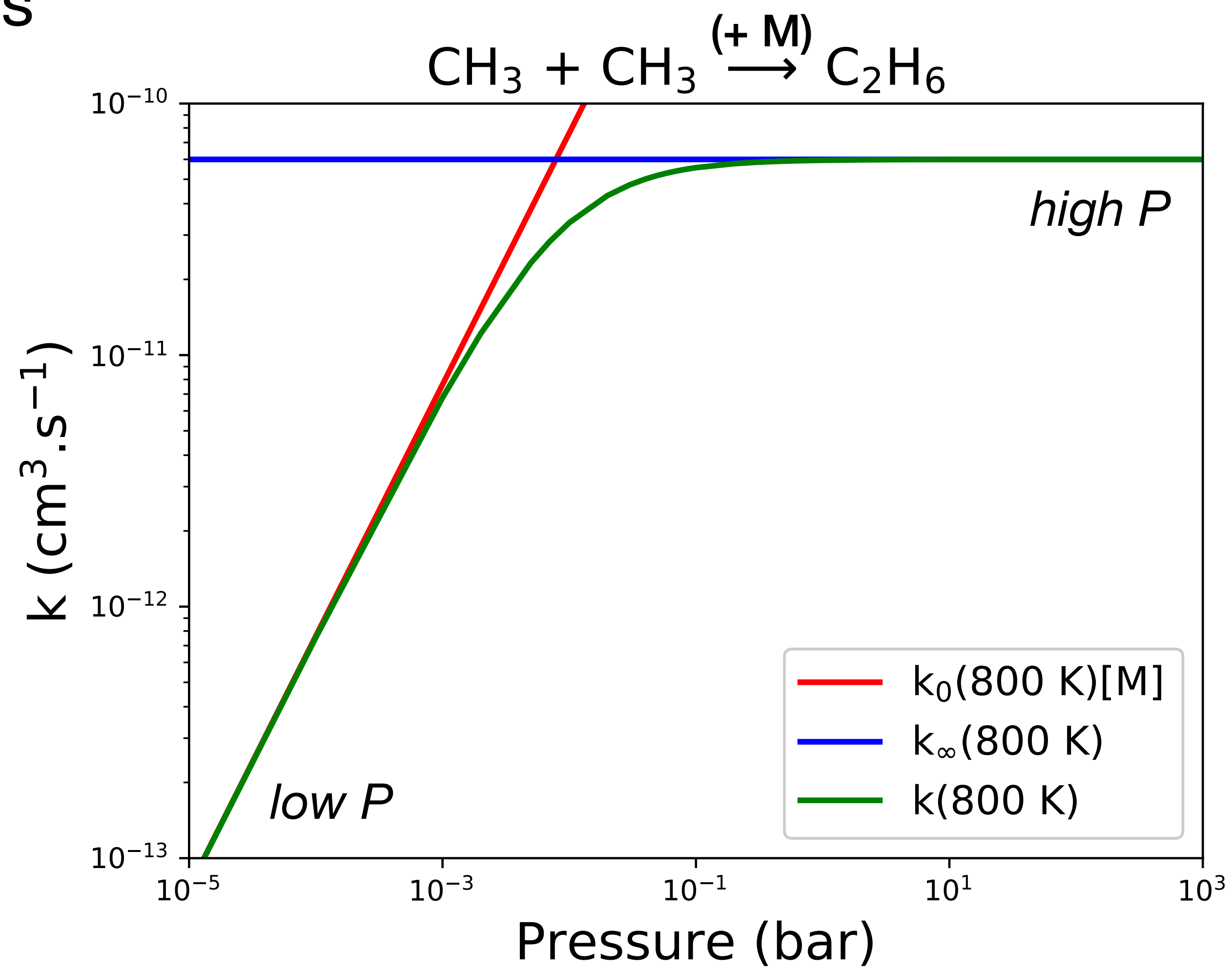
  ⇒ In the low-pressure limit: $v_0 = k_0[A][B][M]$

- [M] is the sum of the density of each molecules (eventually weighted by their efficiencies)

- The transition region between the low- and high-pressure regimes is called « fall-off » region. $k(T)$ is given by :

$$k(T) = k_\infty \left(\frac{P_r}{1+P_r} \right) F$$

with the reduced pressure $P_r = \frac{k_0[M]}{k_\infty}$



Three-bodies reactions

- The probability that **AB*** meets a **M** body is large at high P, because molecules are close to each other. In this case, the reaction rate does not depend on **[M]** and the reaction can be considered as bimolecular: **A+B⟶AB**
  ⇒ In the high-pressure limit: $v_\infty = k_\infty [A][B]$

- At low-pressure, the reaction rate is limited by the density of M.
  ⇒ In the low-pressure limit: $v_0 = k_0 [A][B][M]$

- [M] is the sum of the density of each molecules (eventually weighted by their efficiencies)

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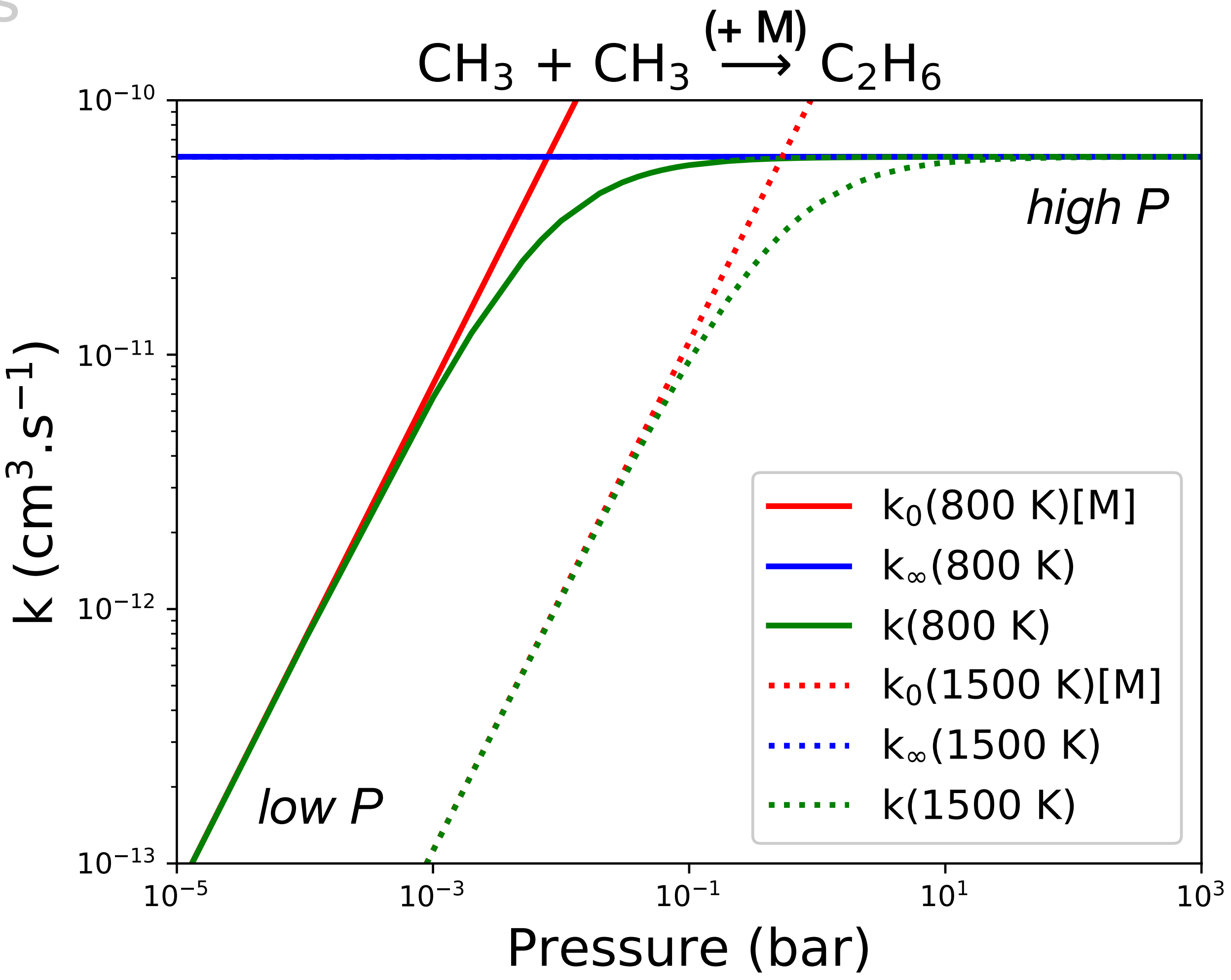
The notions of « low » and « high » pressure are temperature dependent !



Fall-off region

$$k(T) = k_\infty \left(\frac{P_r}{1+P_r} \right) F$$

- Several formulations for F exist:

- Lindemann: $F=1$

Lindemann et al. 1922

- Troe: $\log_{10} F = \dfrac{\log_{10}(F_{cent})}{1+\left[\dfrac{\log_{10}(P_r)+c}{N-d(\log_{10}(P_r)+c)}\right]^2}$ with

$$c = -0.4 - 0.67 \times \log_{10}(F_{cent})$$
$$N = 0.75 - 1.27 \times \log_{10}(F_{cent})$$
$$d = 0.14$$

Troe 1989, 1983
Gilbert et al. 1983

and $F_{cent} = (1-a)\exp\left(-\dfrac{T}{T^{***}}\right) + a\exp\left(-\dfrac{T}{T^{*}}\right) + \exp\left(-\dfrac{T^{**}}{T}\right)$

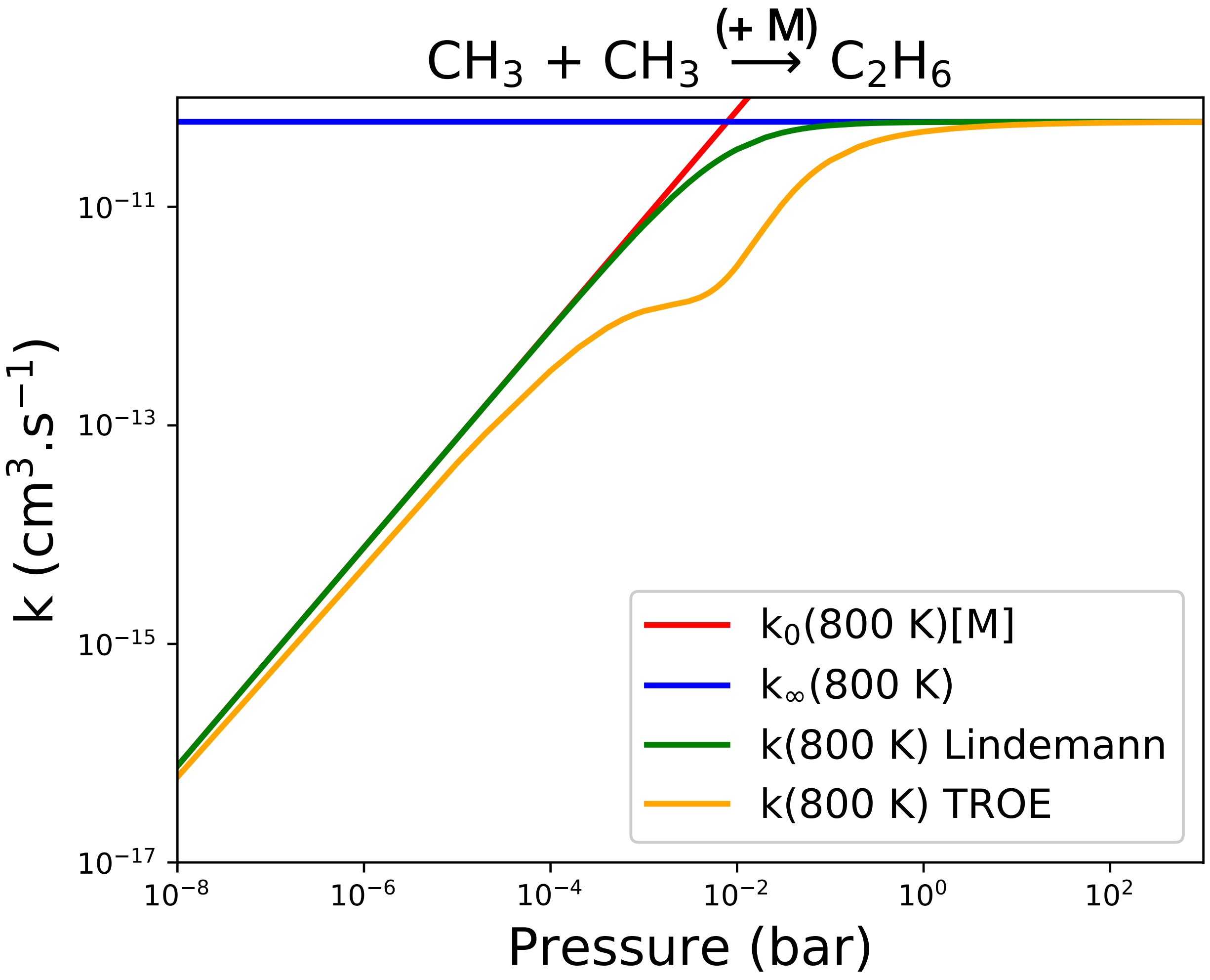
- SRI: $F = d\left[a\exp\dfrac{-b}{T} + \exp\dfrac{-T}{c}\right]^X T^e$ with $X = \dfrac{1}{1+(\log_{10} P_r)^2}$

Stewart et al. 1989
Kee et al. 1996

Three-bodies reactions

- The different expressions for F allow a better description of the fall-off region

- The more common expression used to study planetary atmospheres is « Troe »



- A new method is appearing and consists in a logarithmic interpolation of rates coefficients specified at individual pressures.

  The rate k at pressure P (with $P_1<P<P_2$) is given by :

$$\log k(P) = \log k(P_1) + (\log k(P_2) - \log k(P_1))\frac{\log P - \log P_1}{\log P_2 - \log P_1}$$

Reverse and forward rates

- The reaction $\sum_{l=1}^{L} \nu'_l \chi_l = \sum_{l=1}^{L} \nu''_l \chi_l$ can occur in both directions (forward and reverse)

$\boxed{\text{aA+bB = cC+dD}}$

- The associated rate coefficients are $k_f(T)$ and $k_r(T)$.
- The reaction rates are respectively $v_f = k_f(T) \prod_l [\chi'_l]^{\nu'_l}$ and $v_r = k_r(T) \prod_l [\chi''_l]^{\nu''_l}$

$\boxed{v_f = k_f(T)[A]^a[B]^b}$ $\boxed{v_r = k_r(T)[C]^c[D]^d}$

- When the reaction is at equilibrium $v_f = v_r$ and thus $\dfrac{k_f}{k_r} = \prod_l [\chi_l]^{\nu_l}$ $\boxed{\dfrac{k_f}{k_r} = \dfrac{[C]^c[D]^d}{[A]^a[B]^b}}$
- One can recognise the equilibrium constant, with the activity expressed in term of molecular concentration. Expressed in term of pressure, we obtain:

$$\frac{k_f}{k_r} = \left(\frac{P^0}{k_B T}\right)^{\sum_l \nu_l} K_p \quad \Rightarrow \boxed{\frac{k_f}{k_r} = \left(\frac{P^0}{k_B T}\right)^{\sum_l \nu_l} \exp(-\Delta G^0/RT)}$$

⇒ knowing k_f only, k_r is calculated with NASA coefficients …. !

Outline

- Introduction - Structure of exoplanet atmospheres
- Molecular Spectroscopy - Electronic, vibrational, rotational transitions
- Thermodynamics - Thermochemical equilibrium
- Chemical kinetics
- **Photochemistry**
- Tools: 1D kinetic models - ingredients + key results

Photolyses

- Photodissociations occur in the upper atmosphere of irradiated exoplanets

- After the absorption of a photon, the molecule A is excited: $\mathbf{A}+h\nu \longrightarrow \mathbf{A^*}$

- Depending on the energy of the absorbed photon, the molecule **A*** can dissociate and the photodissocation products can vary.

- The molecule **A** has N routes to photodissociate. At each wavelength, the probability that **A** dissociates through the route k is given by the branching ratio, $q_k(\lambda)$, verifying : $\sum_{k=1}^{N} q_k(\lambda) = 1.$

	Photodissociation route	*branching ratio [λ range]*
For instance:	$CH_4+h\nu \longrightarrow CH_3+H$	**1.0 [6-151] ; 0.42 [121.6]**
	$\longrightarrow {}^1CH_2+H_2$	**0.48 [121.6]**
Gans et al. 2011	$\longrightarrow {}^3CH_2+H+H$	**0.03 [121.6]**
	$\longrightarrow CH+H_2+H$	**0.07 [121.6]**

Photodissociation rate

- For these reactions, the rate coefficient is called the photodissociation rate and is noted J.

absorption cross section of species i (cm^2)

- For a molecule *i*, dissociating through the route k, $J_i^k(z) = \int_{\lambda_1}^{\lambda_2} \sigma_i^{abs}(\lambda) F(\lambda, z) q_k(\lambda) d\lambda$

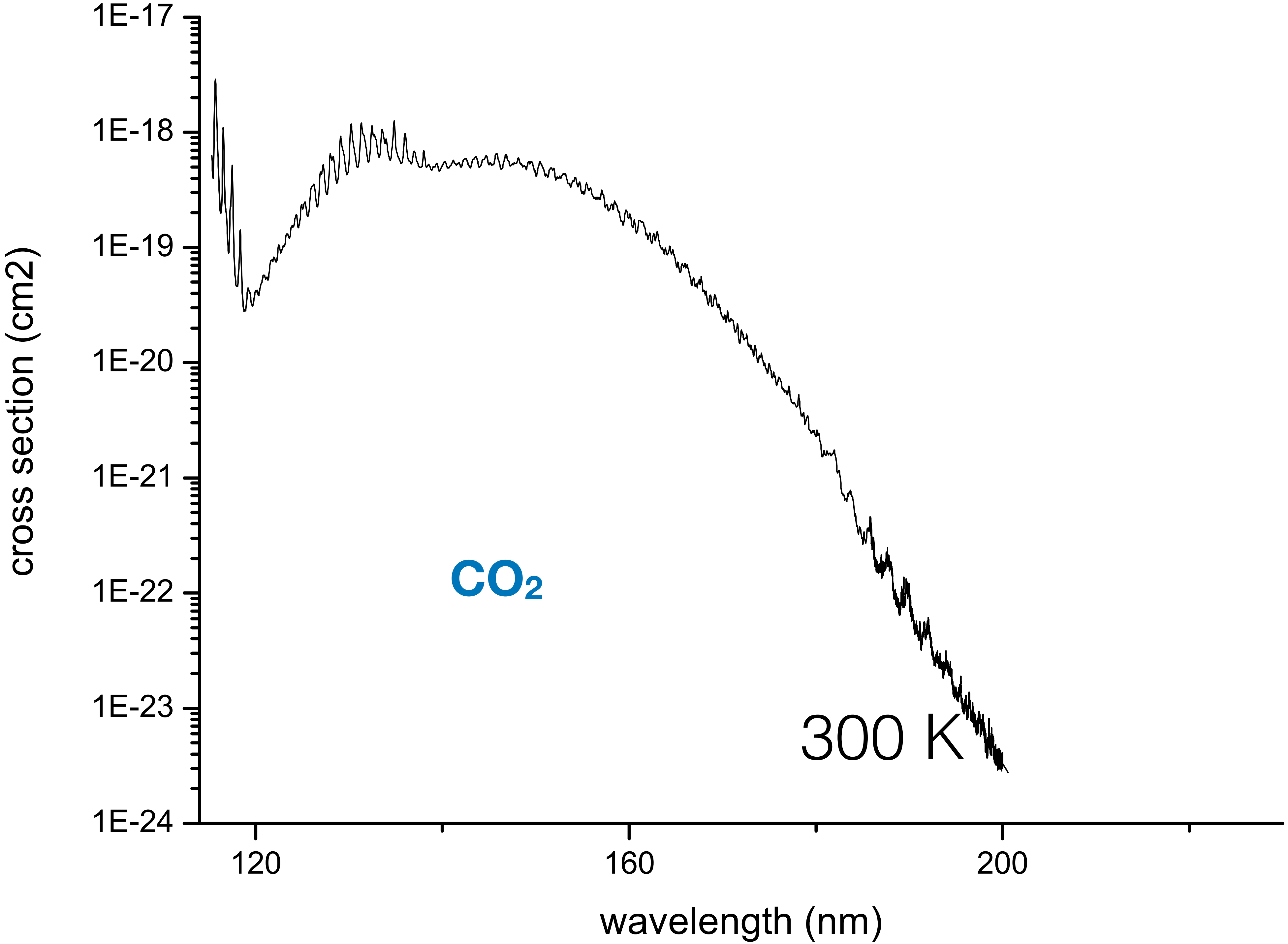
Actinic flux (cm^{-2}.s^{-1}.nm^{-1})

- The total photodissociation rate of the molecule *i* is the sum of the photodissociation rate in each route: $J_i(z) = \sum_{k=1}^{N} J_i^k(z)$

- Absorption cross sections and branching ratios are very important data to calculate the photodissociation rates. In reality these data depends on temperature, but their thermal dependency is badly quantified….

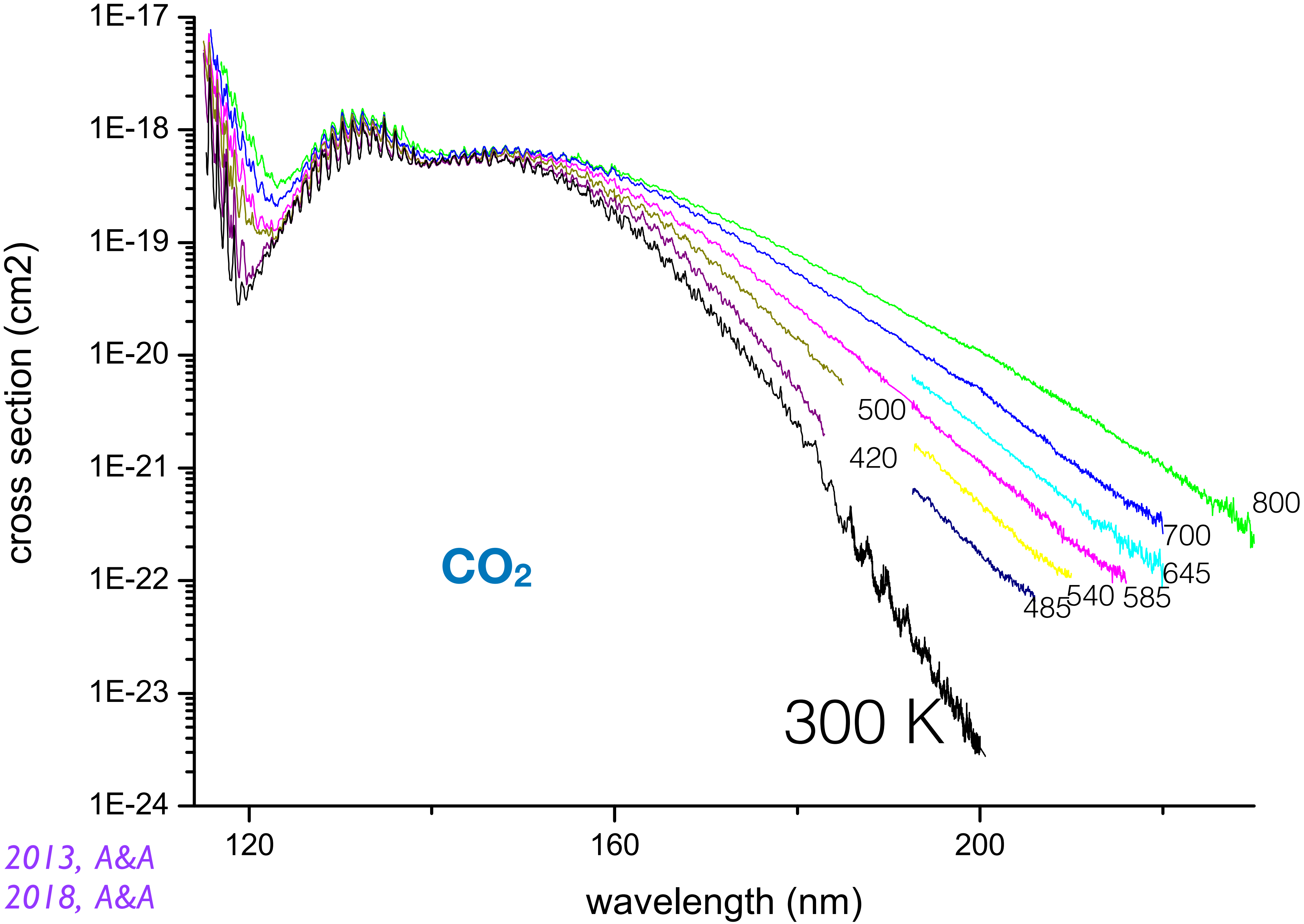
- Very few experimental measurement and not trivial to model theoretically

VUV Absorption cross section

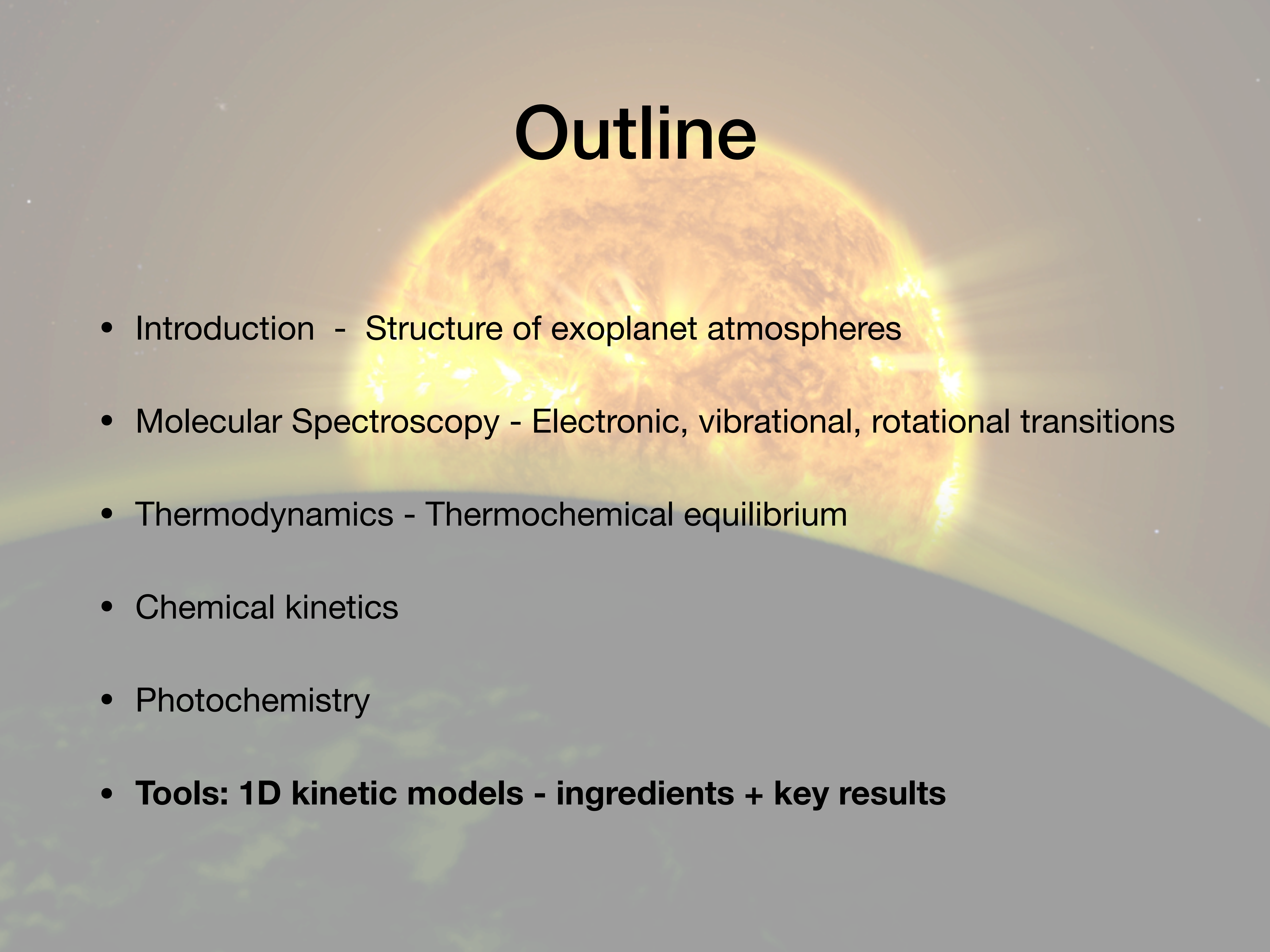


VUV Absorption cross section

- When temperature increases, electrons are excited and can move to rovibrational levels of higher energy. Thus, transition to a higher electronic level requires less energy, so the absorption of photons of less energy (longer wavelength) increases



Venot et al. 2013, A&A
Venot et al. 2018, A&A



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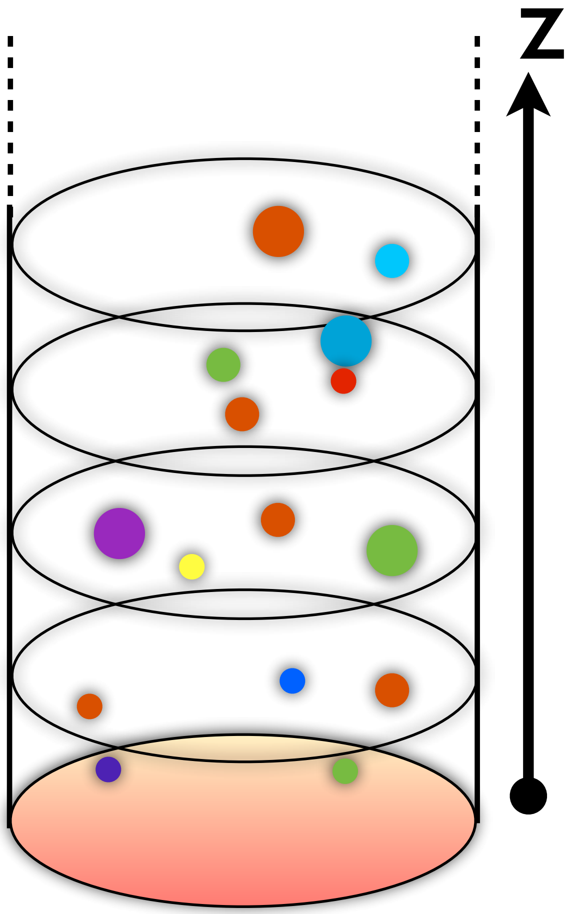
- Photochemistry
- **Tools: 1D kinetic models - ingredients + key results**

Thermo-photochemical model

- A thermo-photochemical model aims at reproducing all physical and chemical processes occurring in an atmosphere in order to study the evolution of its chemical compounds.

- Up to now, these models exist mainly in 1D.

- The atmosphere is represented by a column divided in several layers



- Each of these layers contains molecules that
  - photodissociate with UV radiation
  - react with each other
  - move from a layer to another thanks to mixing

- For each species and in each level, the thermo-photochemical model resolves the **continuity equation,** which describes the temporal evolution of the density of a species i at the altitude z

$$\frac{\partial n_i(z)}{\partial t} = P_i(z) - L_i(z) - div(\Phi_i(z)\overrightarrow{e_z})$$

with

$P_i(z)$ the production rate ($\mathrm{cm^{-3}s^{-1}}$)

$L_i(z)$ the loss rate ($\mathrm{cm^{-3}s^{-1}}$)

$n_i(z)$ the density ($\mathrm{cm^{-3}}$)

$\Phi_i(z)$ the flux ($\mathrm{cm^{-2}s^{-1}}$)

➡Large system of coupled differential equations

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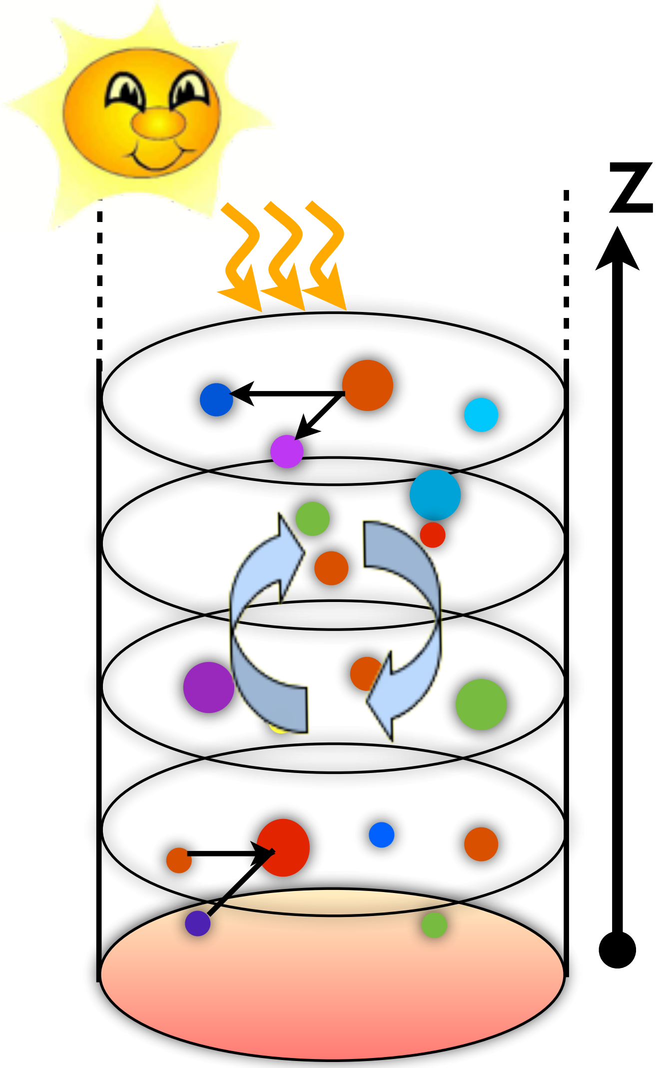

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with $D_i(z)$ the molecular diffusion coefficient ($\mathrm{cm^2 s^{-1}}$), $K(z)$ the eddy diffusion coefficient ($\mathrm{cm^2 s^{-1}}$), $\alpha_i(z)$ the thermal diffusion coefficient, and $H_i(z)$ the scale height (cm)

- Ingredients necessary to run such model are:
  - information/data for diffusion
  - a chemical scheme
  - a thermal profile
  - a stellar flux

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Molecular diffusion

- In planetary atmospheres, made of a major molecule, minor molecules undergo molecular diffusion when their density depart from hydrostatic equilibrium.

- The induced flux is proportional to the molecular diffusion coefficient D_i of the minor species i in the major molecule.

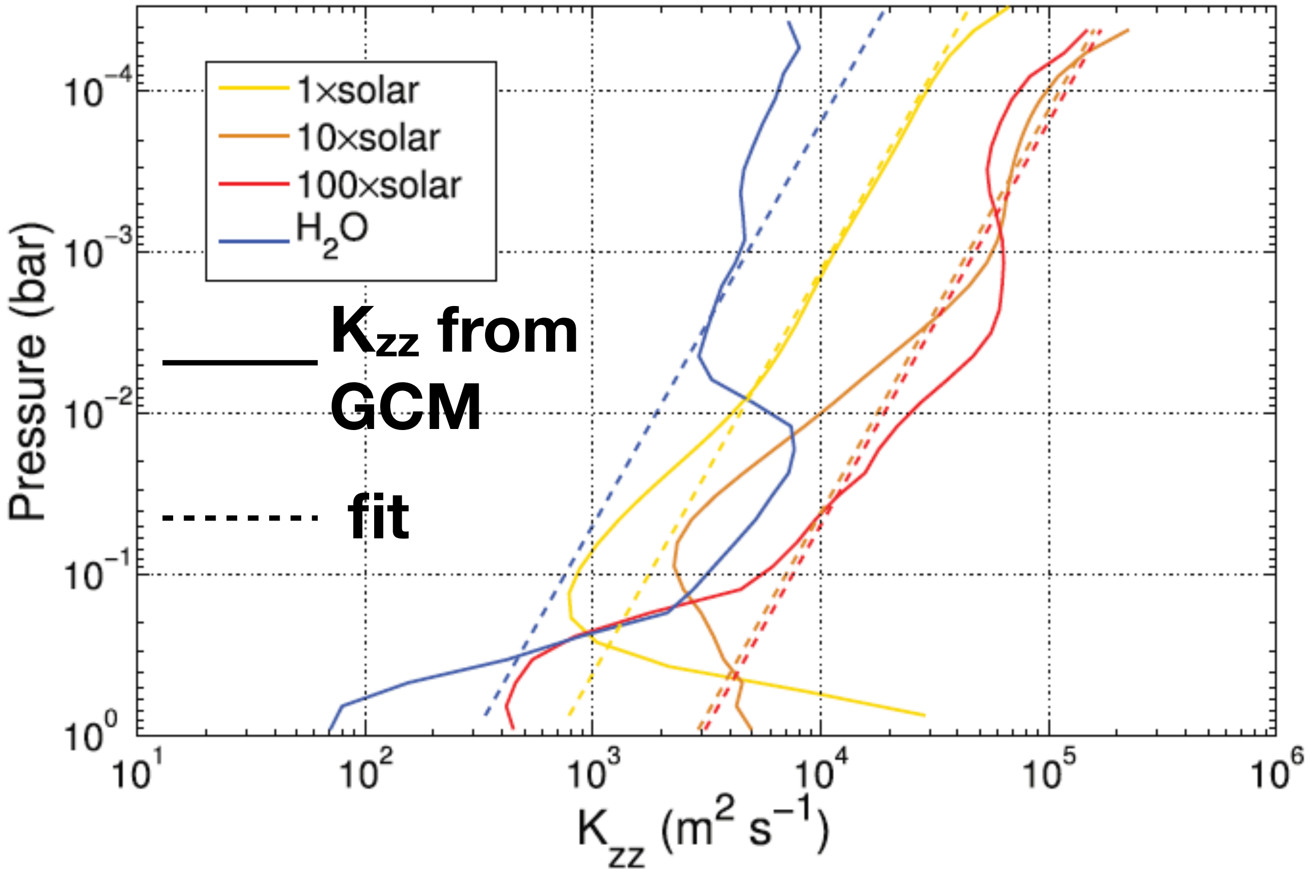
- In atmospheres in which the background is formed by 2 compounds A and B (like hot Jupiters atmospheres, made mainly of He and H_2), the minor species i diffuses in a binary mixing of gases with a coefficient D_{imix} given by:

$$D_{imix} = \left(\frac{y_A}{D_{iA}} + \frac{y_B}{D_{iB}} \right)^{-1} \qquad \text{with } D_{iX} = \frac{0.00143 T^{1.75}}{P M_{iX}^{1/2} [(\Sigma_v)_i^{1/3} + (\Sigma_v)_X^{1/3}]}$$

with P the pressure (bar), M_{iX} the reduced mass (kg), and Σ_v the sum of volumes of atomic diffusion of each atom of species *i* and *X*

Eddy diffusion

- The Eddy diffusion gathers all processes that tend to mix the atmosphere, wether at micro or macroscopic scale.
- For exoplanets, there is a very large uncertainty for this parameter.
- It can be set constant with altitude. In this case, *K(z)* is typically between 10^7-10^{12} cm^2s^{-1}
- It can be estimated from GCM, using tracers (*Parmentier et al. 2013, Charnay et al. 2015*)



warm Neptune GJ 1214b (Charnay et al. 2015)

$$K_{zz}(P) = K_{zz0} \times P_{\mathrm{bar}}^{-0.4}$$

$K_{zz0} = 7 \times 10^2\ \mathrm{m^2s^{-1}}$ for $1\times$ solar metallicity

$K_{zz0} = 2.8 \times 10^3\ \mathrm{m^2s^{-1}}$ for $10\times$ solar metallicity

$K_{zz0} = 3 \times 10^3\ \mathrm{m^2s^{-1}}$ for $100\times$ solar metallicity

$K_{zz0} = 3 \times 10^2\ \mathrm{m^2s^{-1}}$ for pure water case

Continuity equation

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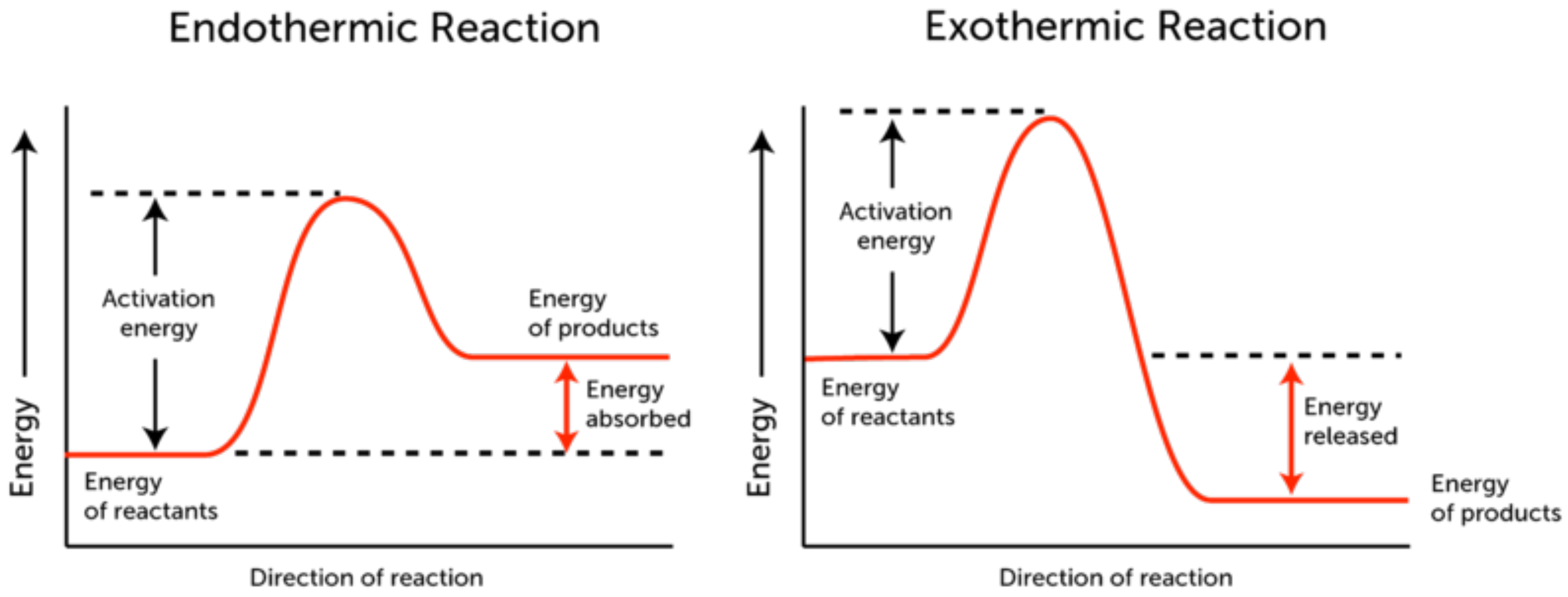
Chemical scheme

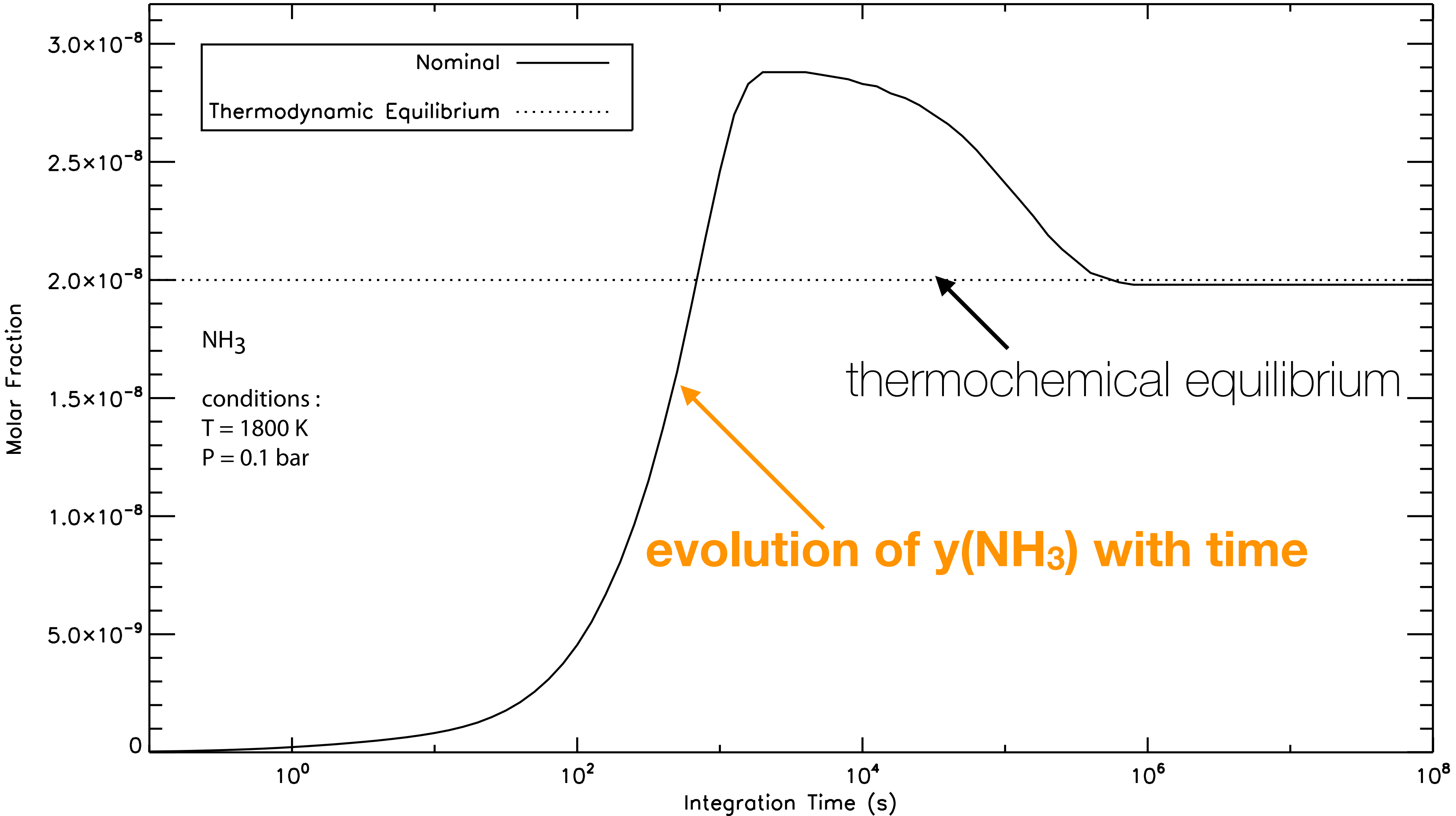
- To calculate the production and loss rates, the thermo-photochemical model needs a list of species and reactions, with the corresponding coefficients (Arrhenius, TROE,…)
  ➙ a chemical scheme/network
- The first chemical scheme used to study hot Jupiters atmosphere was one developed for Jupiter's atmosphere (applied to HD 209458b by Liang et al. 2003, 2004).
  ➙ scheme made for low temperature atmosphere
  ➙ lack of endothermic reactions that cannot be neglected at high temperature
  ➙ thermochemical equilibrium was not reproduce in the deep atmosphere
- For System solar planets (i.e. cold) endothermic reactions are not included because very slow. Lower boundaries conditions are set to fix mixing ratios.



Chemical scheme

- In hot exoplanet atmospheres, no need of boundaries conditions if thermochemical equilibrium is reproduced

- **All reactions must be reversed thanks to the equilibrium constant** (calculated with NASA coefficients): $\frac{k_f}{k_r} = \left(\frac{P^0}{k_B T}\right)^{\sum_l \nu_l} K_p$



thermochemical equilibrium

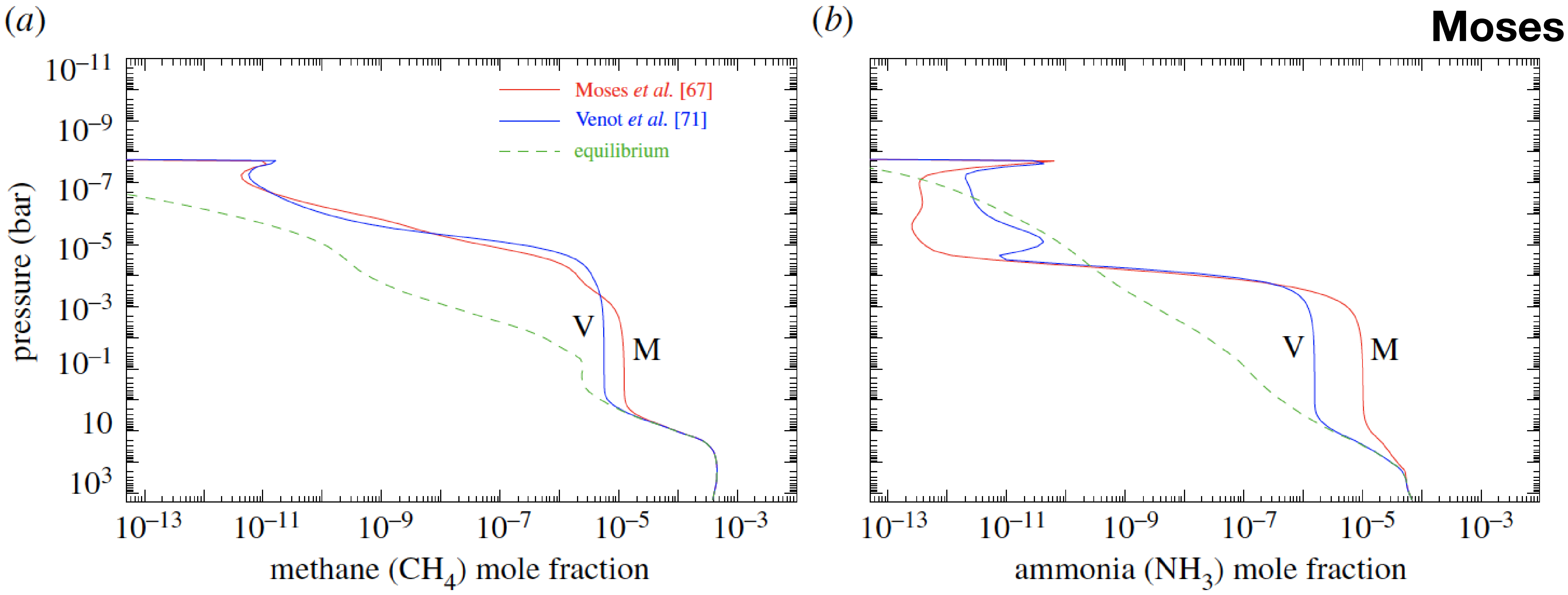
evolution of y(NH$_3$) with time

Chemical scheme

- To create the chemical scheme, no real rules:
  - usually/historically, made manually adding reactions found in literature to each others
  - developed from Jupiter's or Earth’s model (depending on kind of planets studied) (*Moses et al. 2011, Kopparapu et al. 2012, Hu et al. 2012,…*)
  ➝ uncertainty on the completeness of these schemes….

  - other approach: use chemical schemes validated experimentally in combustion field (*Venot et al. 2012, 2015*)

- Depending on the scheme used, differences in the predicted abundances can occur
  ➝ quenching does not occur at the same level



Moses et al. 2014

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- For models focusing on the deep/middle atmosphere ($P \gtrsim 10^{-8}$ bar), only neutral species need to be included in the chemical scheme

- Models for the upper atmosphere (thermosphere) need to include ions and electrons (*Yelle 2004, Garcia Munoz 2007, Koskinen et al. 2013*) and some models couple neutral and ions chemistry (*Lavvas et al. 2014, Rimmer et al. 2014, 2016*)

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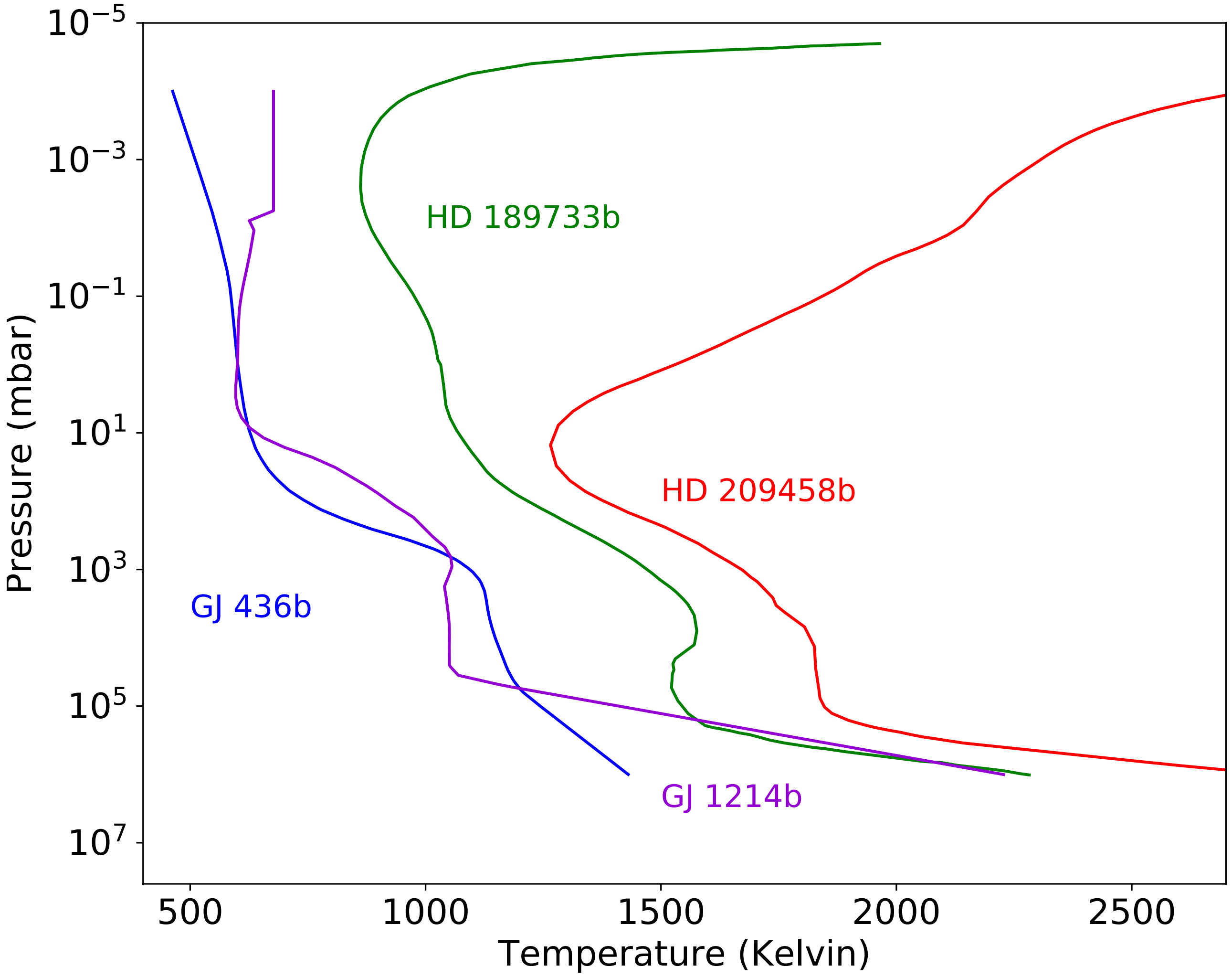
Thermal profile

- In most kinetic models, the thermal profile is a fix input parameter
- The PT profile comes from theoretical models (GCMs or 1D/2D radiative-convective models) or is derived from observations (with a retrieval code)
- Temperature between 500 and 3000 K for hot gaseous giant planets
- Temperature inversion are possible

<u>Case of HD 209458b</u>: first, thermal inversion was invoked to explain observations by Spitzer (e.g. Knutson+2008, Madhusudhan & Seager 2009, Line+2014) but Diamond-Lowe+2014 analysed the same data with a new method and found that thermal inversion was no longer necessary. Then the analyse of high-precision HST data (Line+2016) confirm that no thermal inversion exist in this planet…

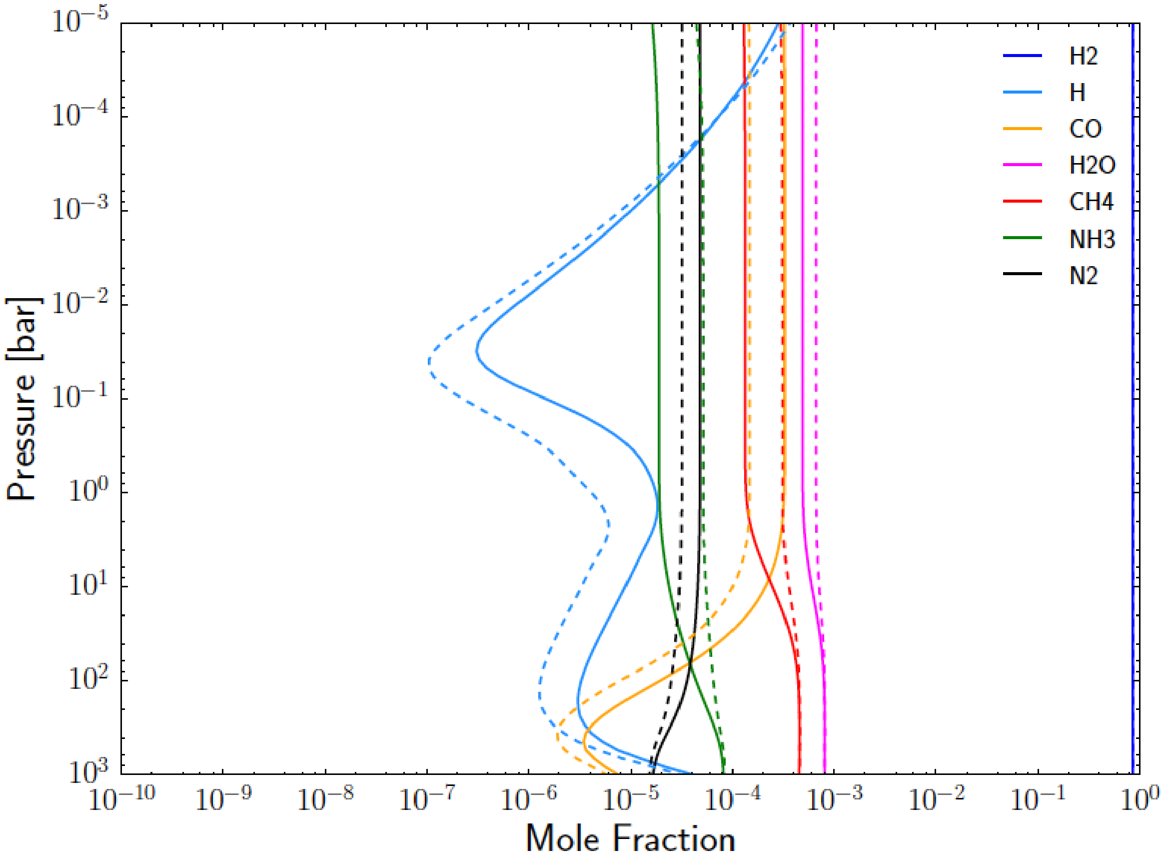


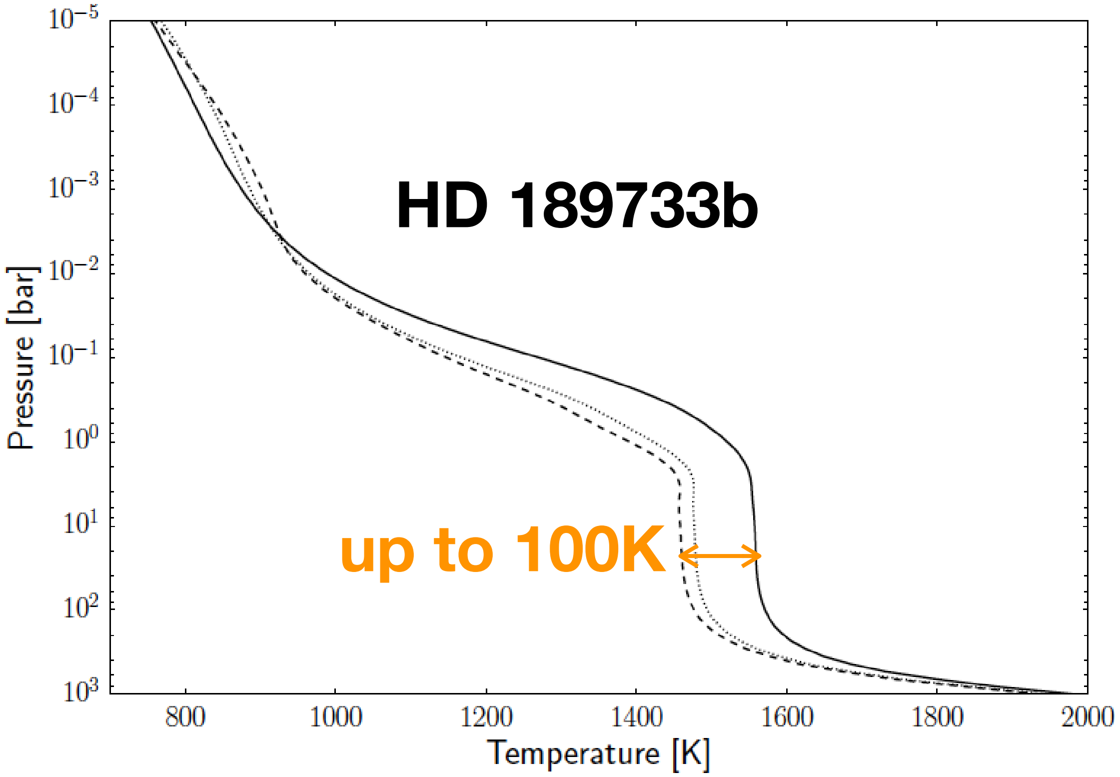
Thermal profile

- The limitation of using fix profiles is that the change of chemical composition (and thus opacity of the atmosphere) is not taken into account leading to a not-consistent result.

- Up to now, only one fully-consistent kinetic model has been developed (*Drummond et al. 2016*)

- Impact on the temperature (up to 100 K) and the chemical composition





——— initial PT (consistent with thermo equilibrium)

……… final PT (consistent with disequilibrium)

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with $D_i(z)$ the molecular diffusion coefficient ($\mathrm{cm^2 s^{-1}}$), $K(z)$ the eddy diffusion coefficient ($\mathrm{cm^2 s^{-1}}$), $\alpha_i(z)$ the thermal diffusion coefficient, and $H_i(z)$ the scale height (cm)

- Ingredients necessary to run such model are:
  - information/data for diffusion ➞ molecular and eddy
  - a chemical scheme
  - **a thermal profile**
  - a stellar flux

Continuity equation

$$\frac{\partial n_i(z)}{\partial t} = P_i(z) - L_i(z) - div(\Phi_i(z)\overrightarrow{e_z})$$

- Production (P_i) and loss (L_i) rates are calculated with formula of chemical kinetics (seen previously) and thanks to the chemical scheme.

- The flux (Φ_i) is calculated with the **diffusion equation**, taking into account molecular and eddy diffusions

$$\Phi_i(z) = -n_i(z)D_i(z)\left[\frac{1}{n_i(z)}\frac{\partial n_i(z)}{\partial z} + \frac{1}{H_i(z)} + \frac{(1+\alpha_i)}{T(z)}\frac{dT(z)}{dz}\right] - n_i(z)K(z)\left[\frac{1}{y_i(z)}\frac{\partial y_i(z)}{\partial z}\right]$$

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- Ingredients necessary to run such model are:
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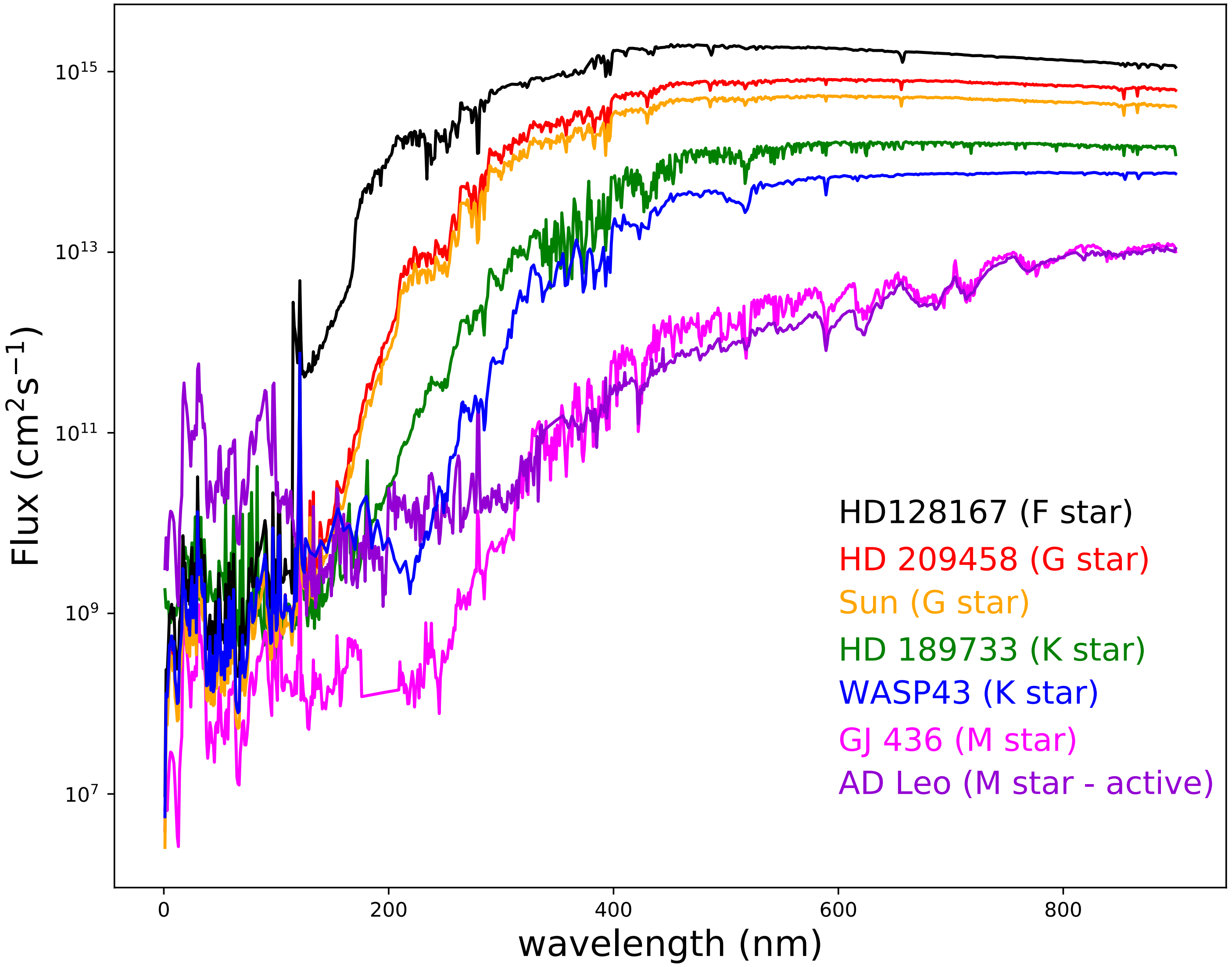
  - a chemical scheme
  - a thermal profile
  - **a stellar flux**

Stellar flux

- In thermo-photochemical model, the UV stellar flux is needed to calculate photodissociation rates
- Unlike the Sun, the stellar flux of other stars in this range is rarely known.
- Need to use proxy for which observations are available, eventually combined to theoretical models (e.g. X-exoplanets, Phoenix, Kurucz)

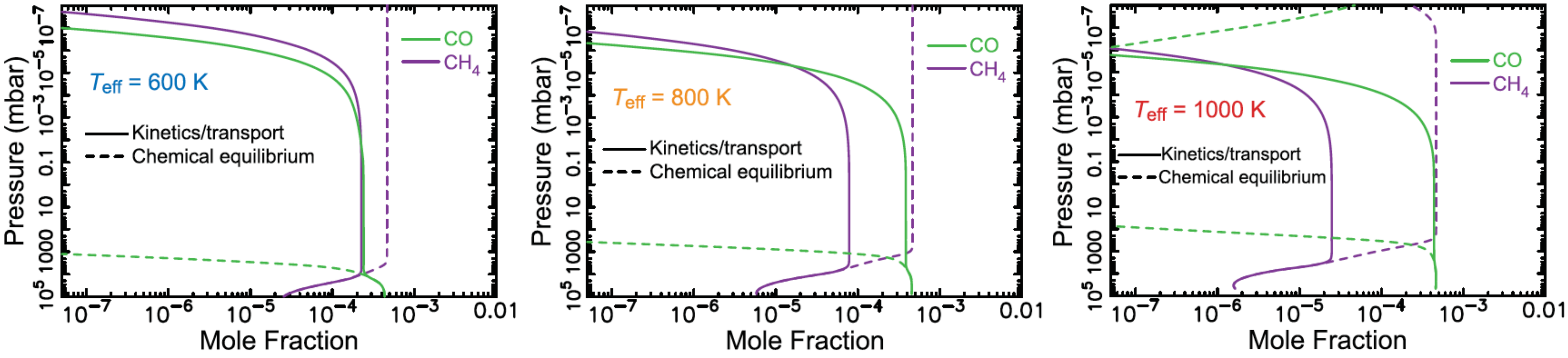


flux normalized at 1 AU

Some key results…

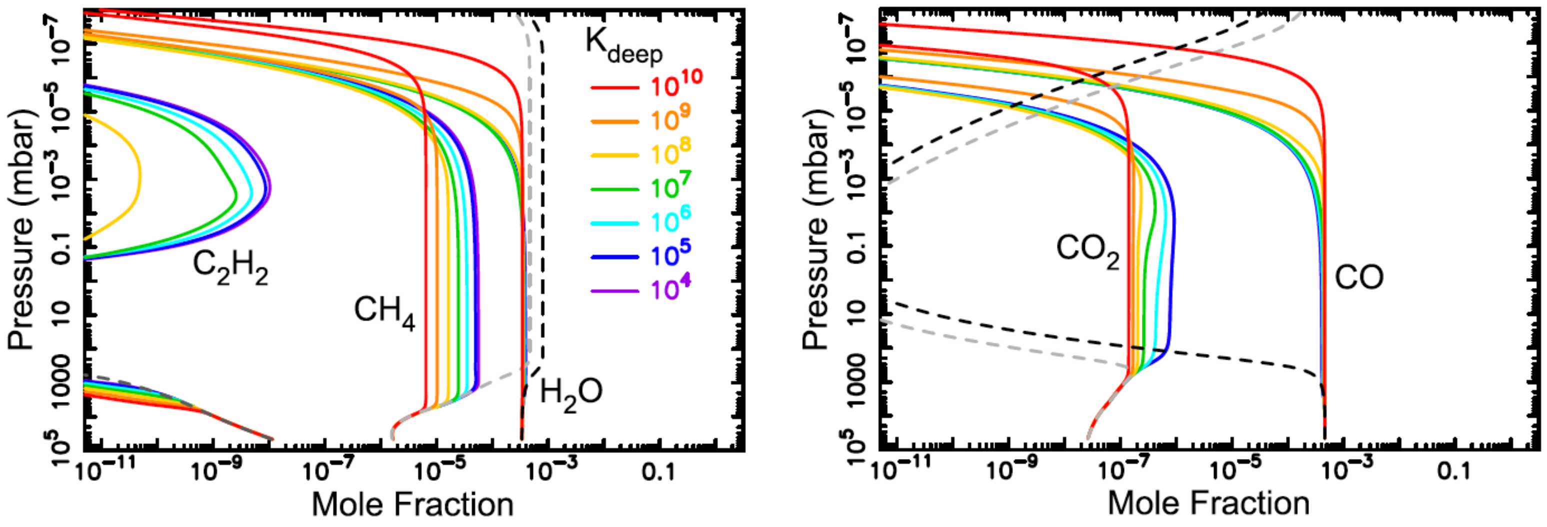
- In the deep atmosphere CO converted to CH_4 through the net reaction:
  $CO + 3H_2 \longrightarrow CH_4 + H_2O$ (detailed pathways vary depending on chemical schemes)

- The CO/CH_4 ratio is :
  - strongly modified by mixing compared to what is predicted by equilibrium
  - very dependent on effective temperature of the planet



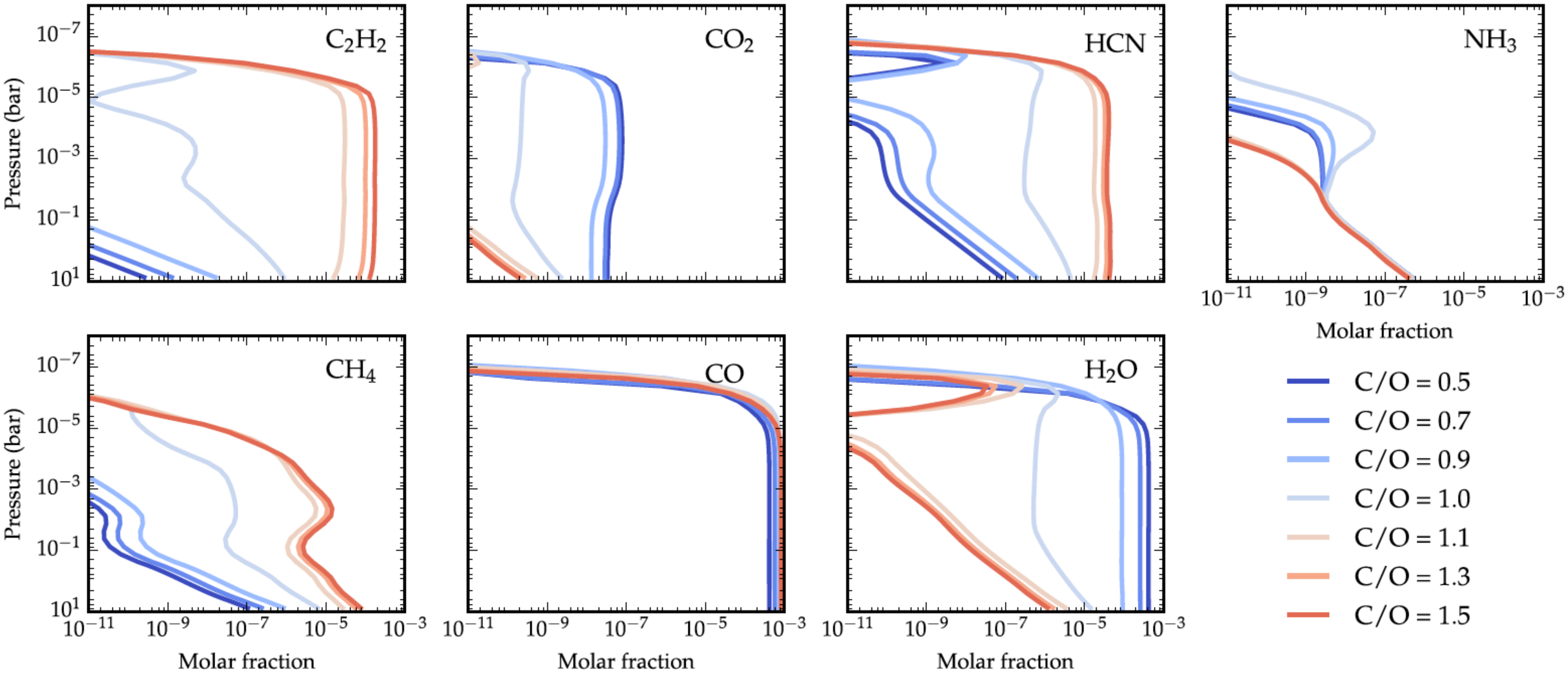
Young Giant Planets
Moses et al. 2016

- very dependent on Eddy diffusion coefficient



Carbon-Oxygen ratio

- in hot atmospheres ($T \gtrsim 800K$) molecular abundances are very dependent on the % ratio of the atmosphere

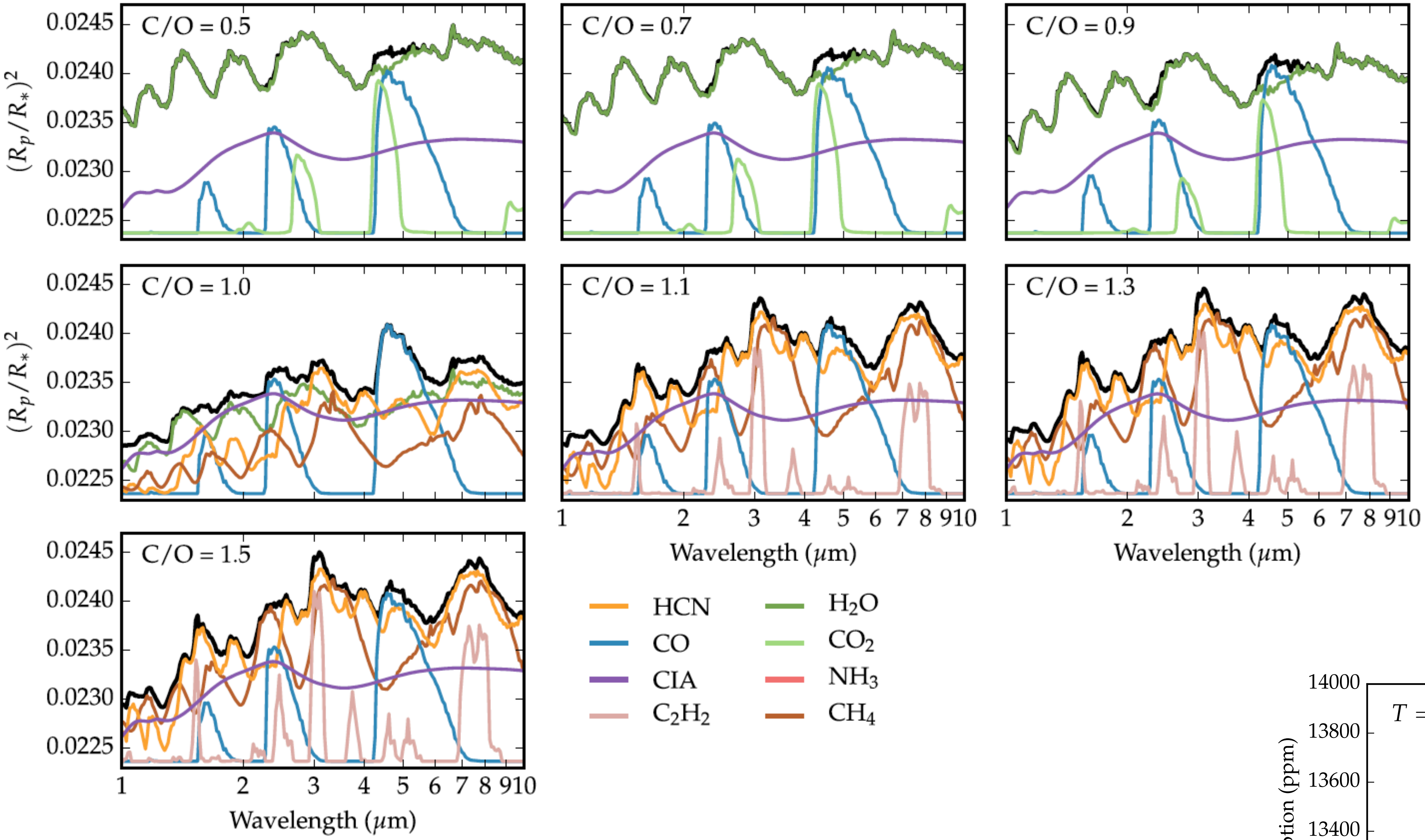


hot jupiter
Rocchetto et al. 2016

- low %: dominated by H_2O, CO, CO_2
  high %: dominated by CO, C_2H_2, HCN, CH_4

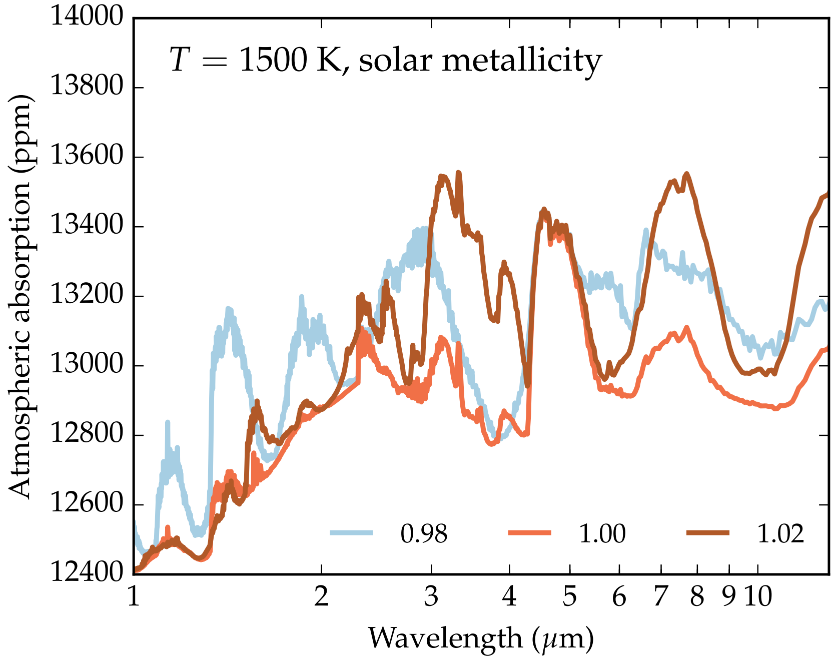
Carbon-Oxygen ratio

- The differences of composition are visible on spectra



hot jupiter

Rocchetto et al. 2016

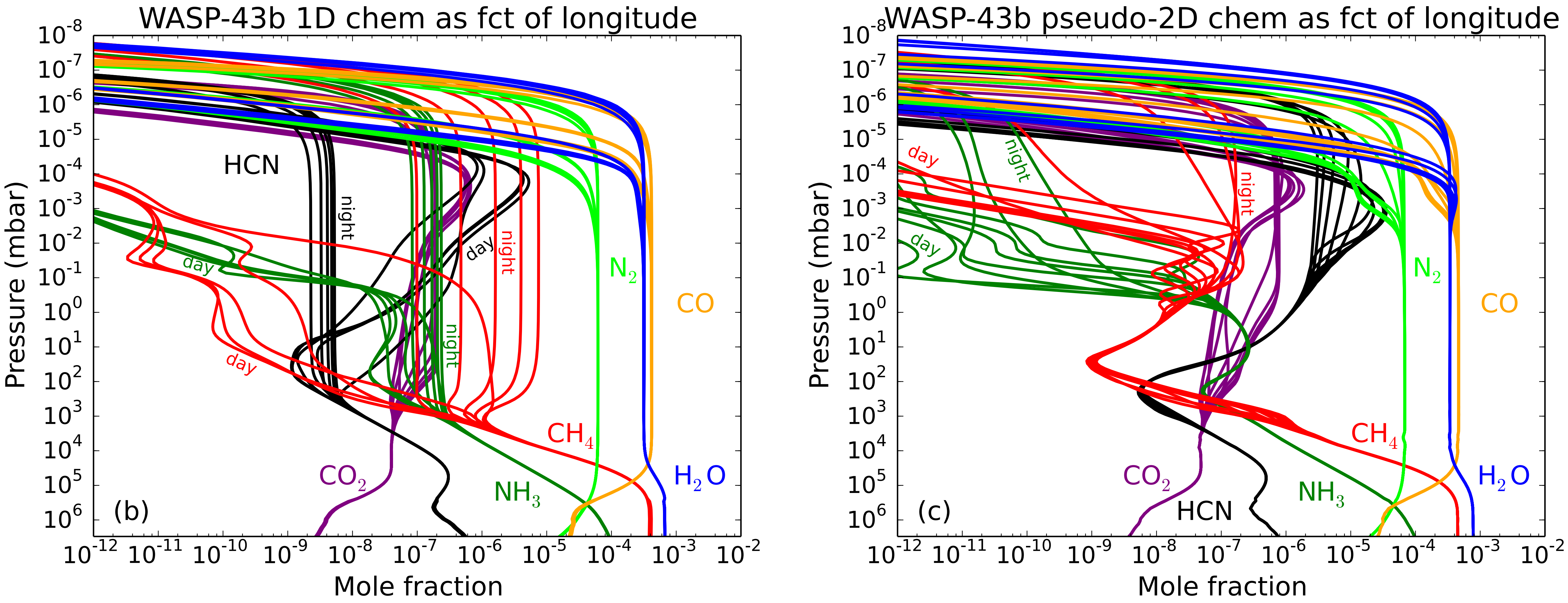


- Change of shape happens drastically around %=1

Towards 3D kinetic models

- Results presented are found with 1D models, taking into account vertical mixing only, but horizontal mixing has importance (Agúndez et al. 2012, 2014)

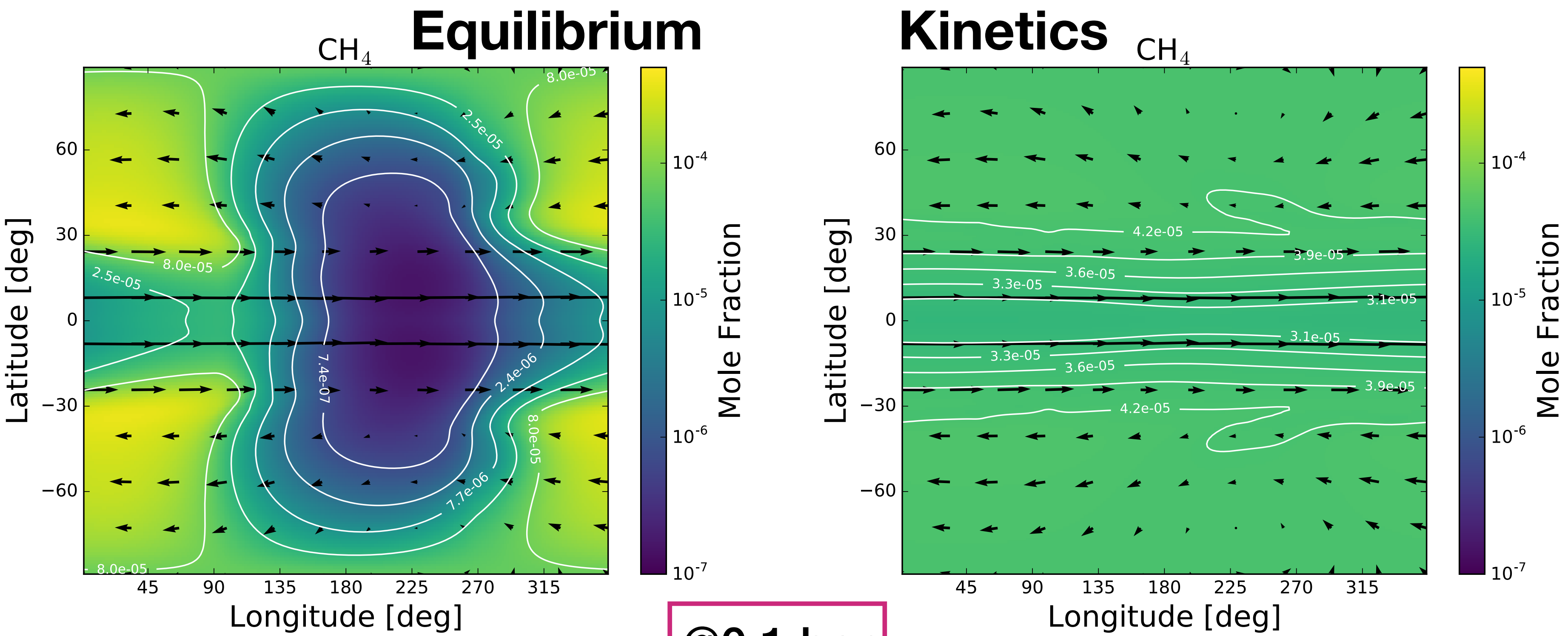
WASP43b Venot et al. in rev.



- With pseudo 2D model, we find that at equator, homogenisation of abundances, close to that of the dayside, or in-between day/night abundances, as for CH_4

Towards 3D kinetic models

- But what about other latitudes ?
- Need a real 3D kinetic model, but the major issue is the huge computational time required by a GCM included a set of 2000 reactions…
- solution: to use a reduced chemical scheme (less complete but enough to study major species - Venot et al. 2019)
- Very new model developed by B. Drummond at UNIVERSITY OF EXETER


Equilibrium **Kinetics**

@0.1 bar

Drummond et al. to be submitted

homogenisation of abundances for CH$_4$ and HCN

Towards 3D kinetic models

- But what about other latitudes ?
- Need a real 3D kinetic model, but the major issue is the huge computational time required by a GCM included a set of 2000 reactions…
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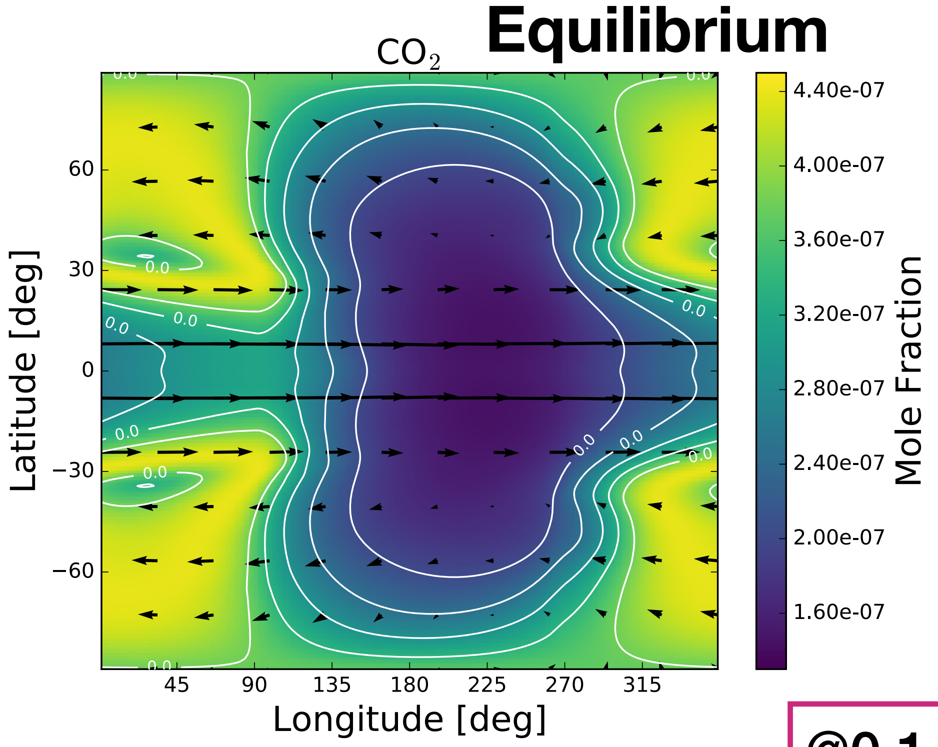
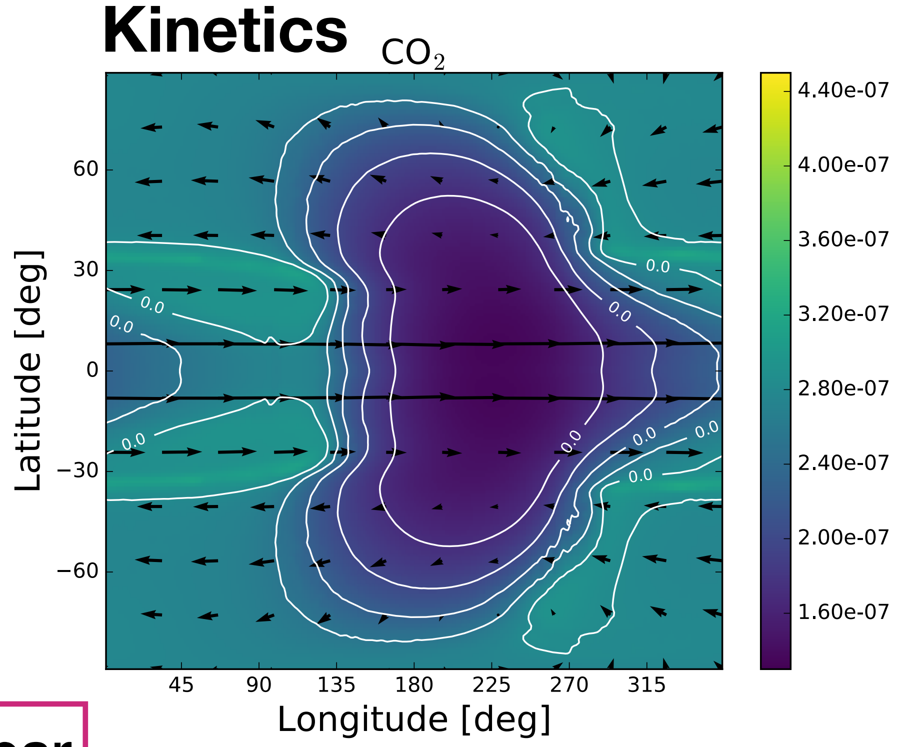
for CO_2, abundance at the nightside terminator decreases but there is still a significant horizontal gradient



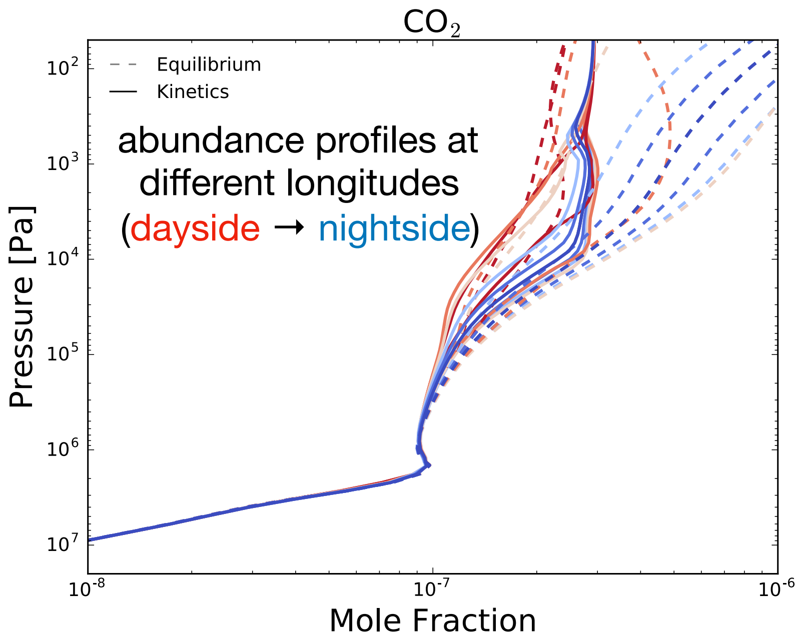
Equilibrium



Kinetics

@0.1 bar

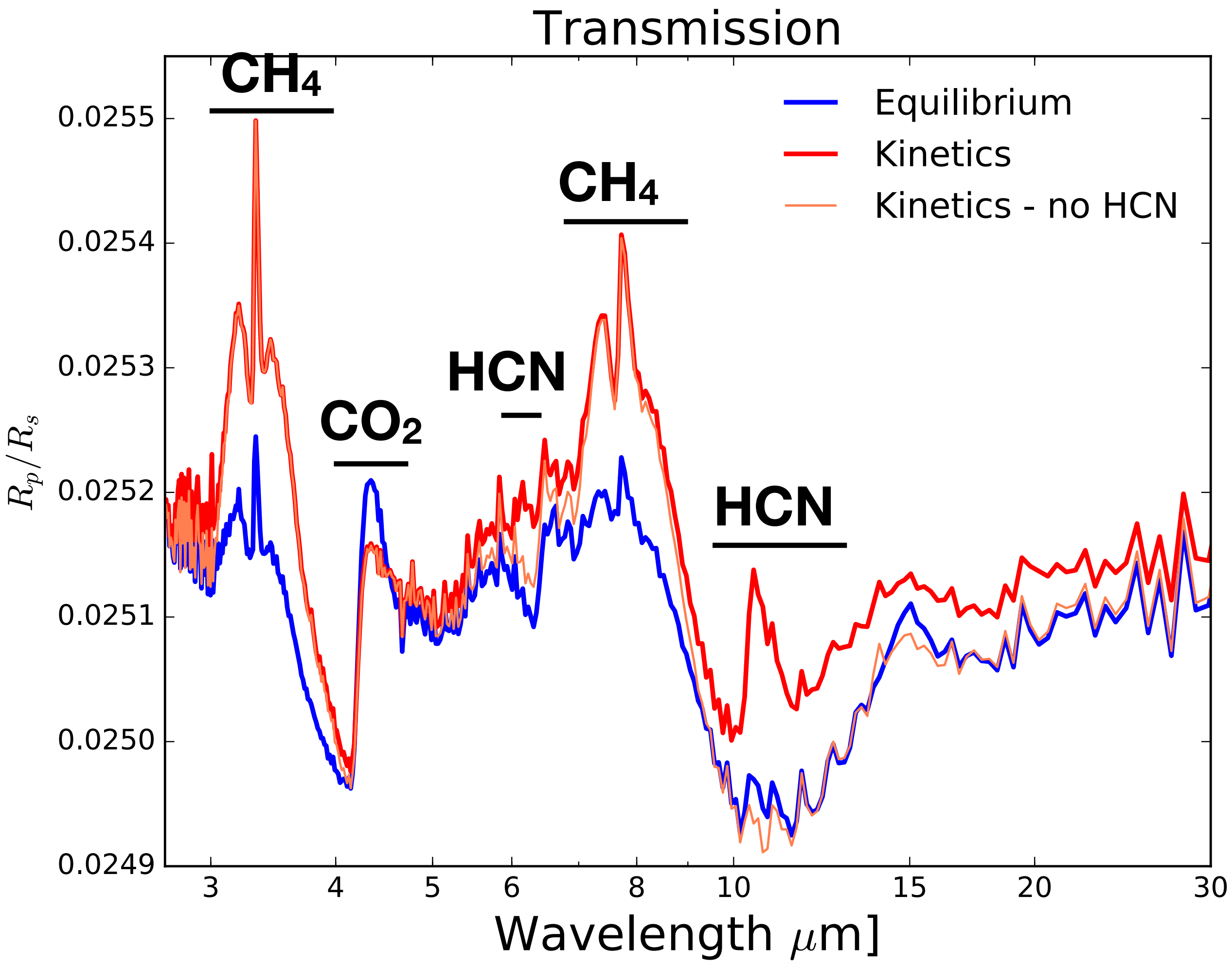
Drummond et al. to be submitted

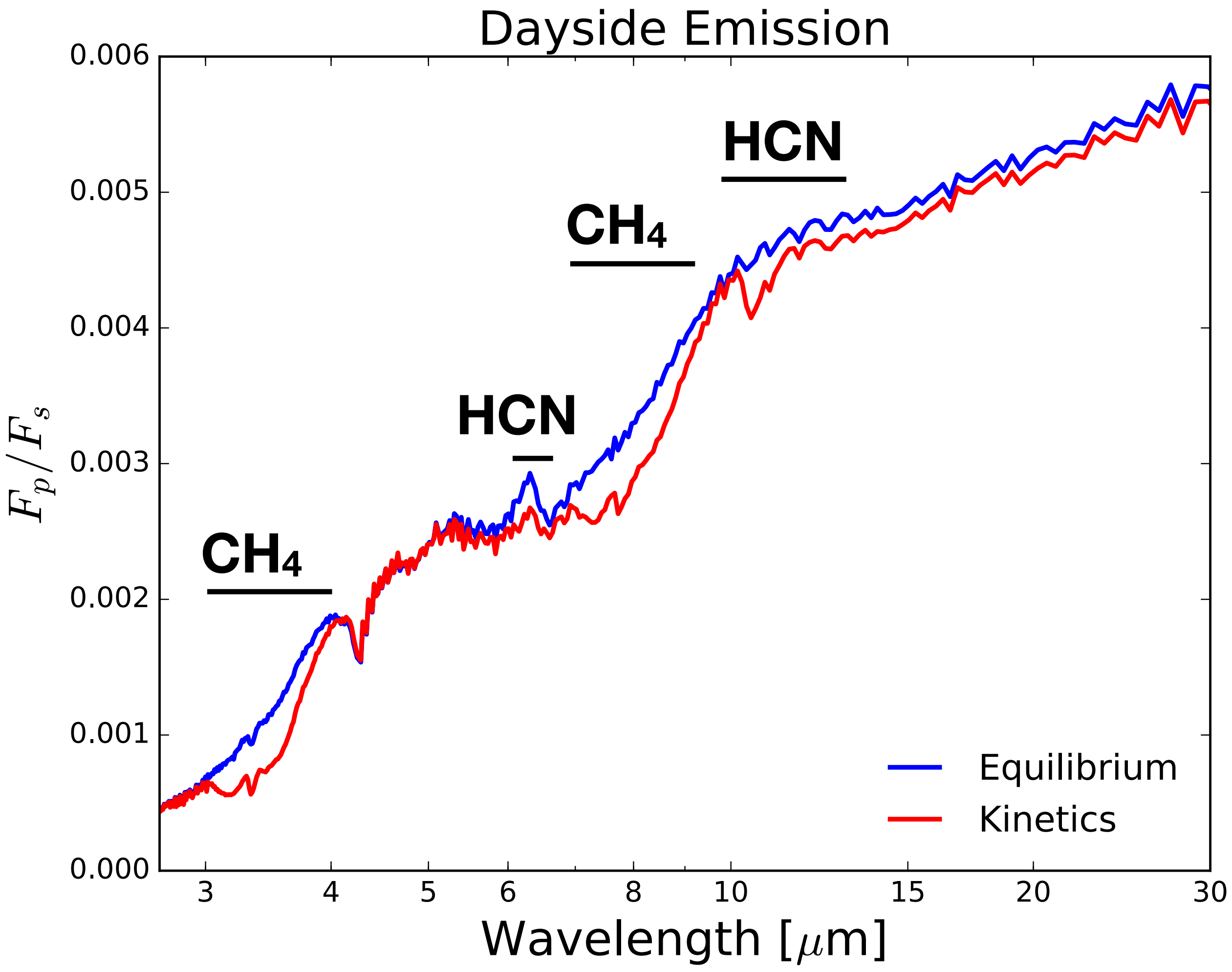


abundance profiles at different longitudes (dayside → nightside)

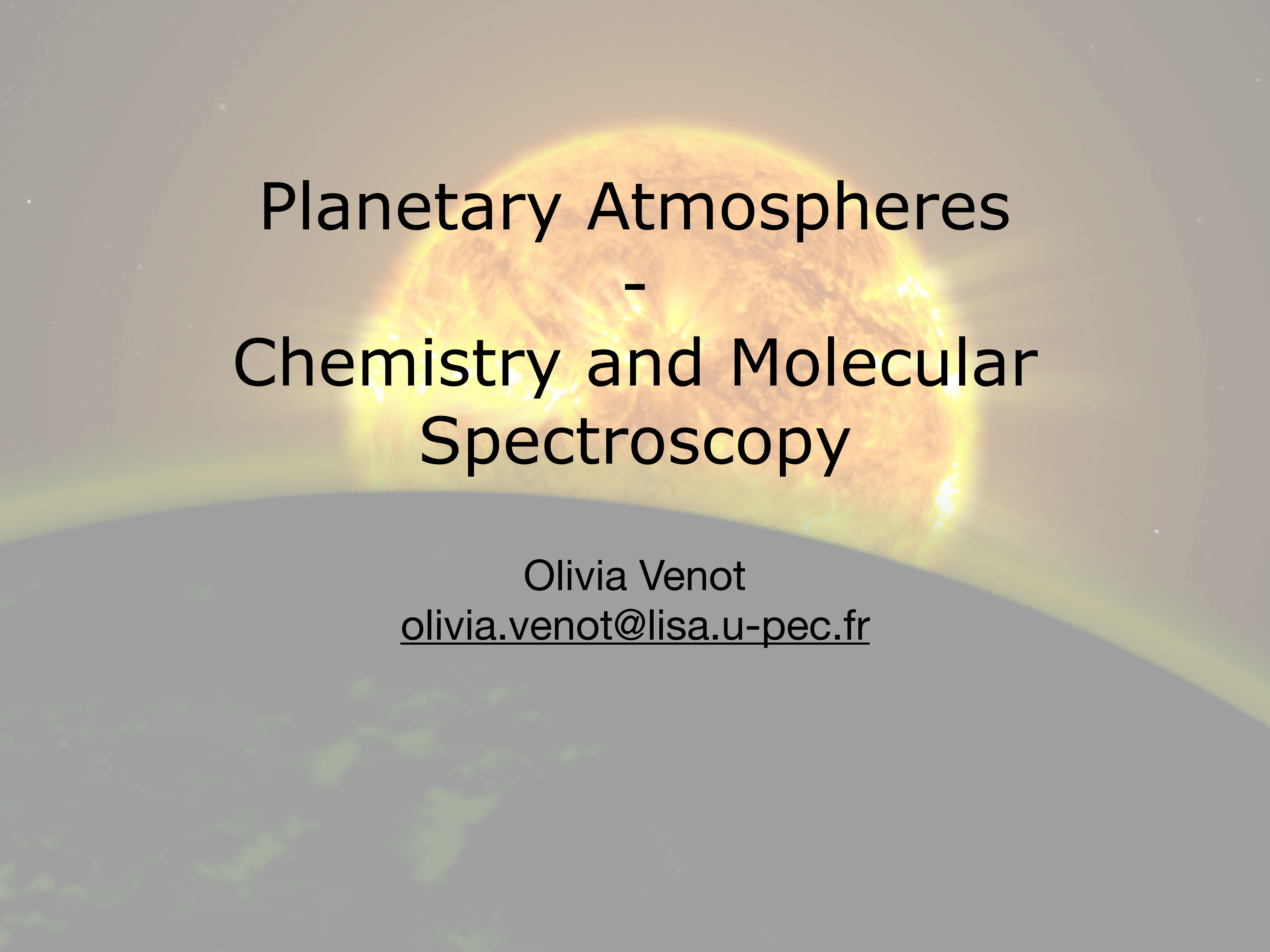
Towards 3D kinetic models

- The effects of 3D kinetics should be visible on the observations thanks to the spectral signature of CH_4, HCN and CO_2





Drummond et al. to be submitted



Planetary Atmospheres
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Chemistry and Molecular Spectroscopy

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