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# Exo-Atmospheres Summer School II



– VULCAN 1D photochemical kinetics

<https://github.com/exoclime/VULCAN>



Shang-Min (Shami), Tsai  
University of Oxford



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# Exo-Atmospheres Summer School II



– VULCAN 1D photochemical kinetics

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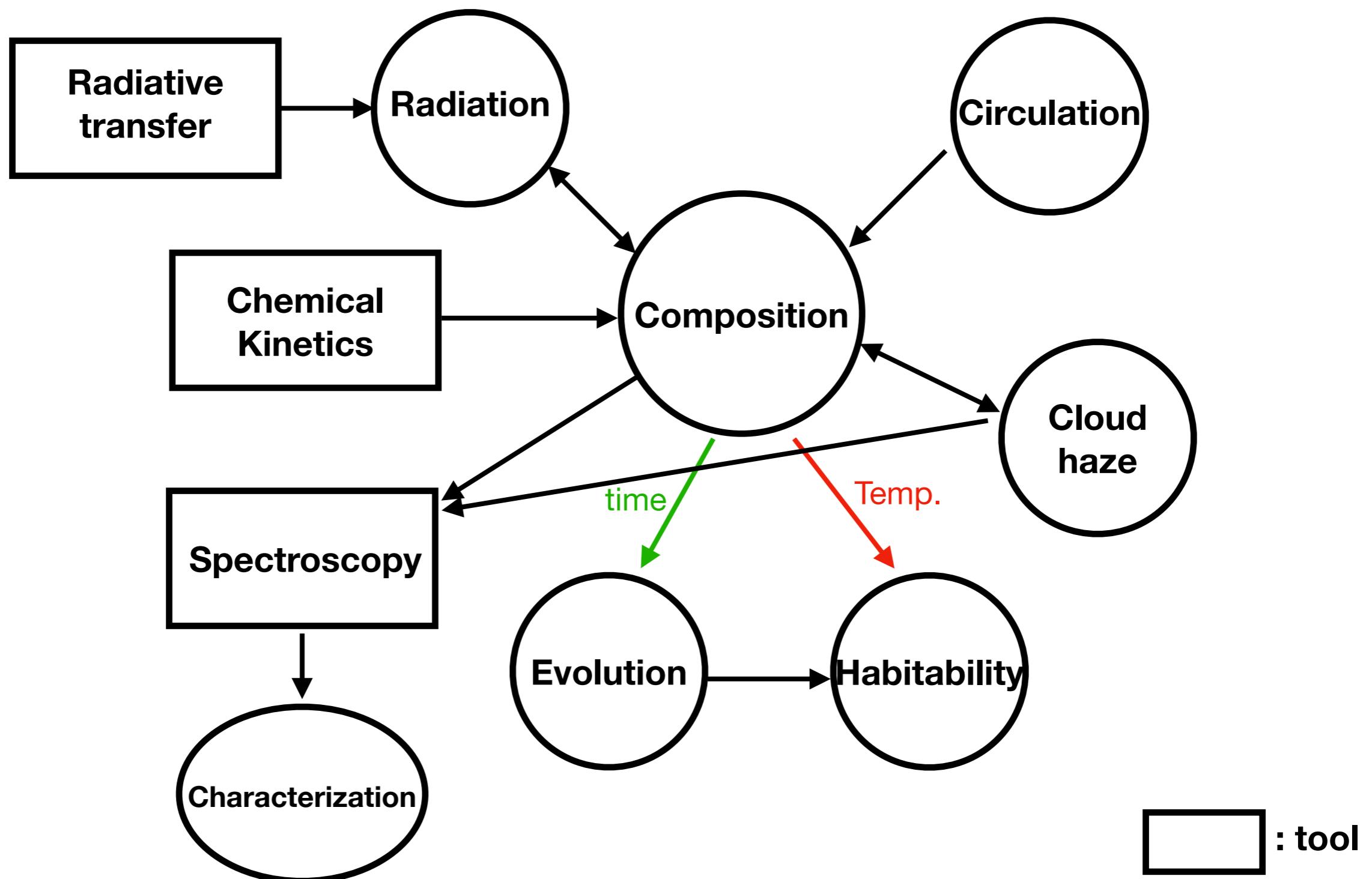


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# What is VULCAN

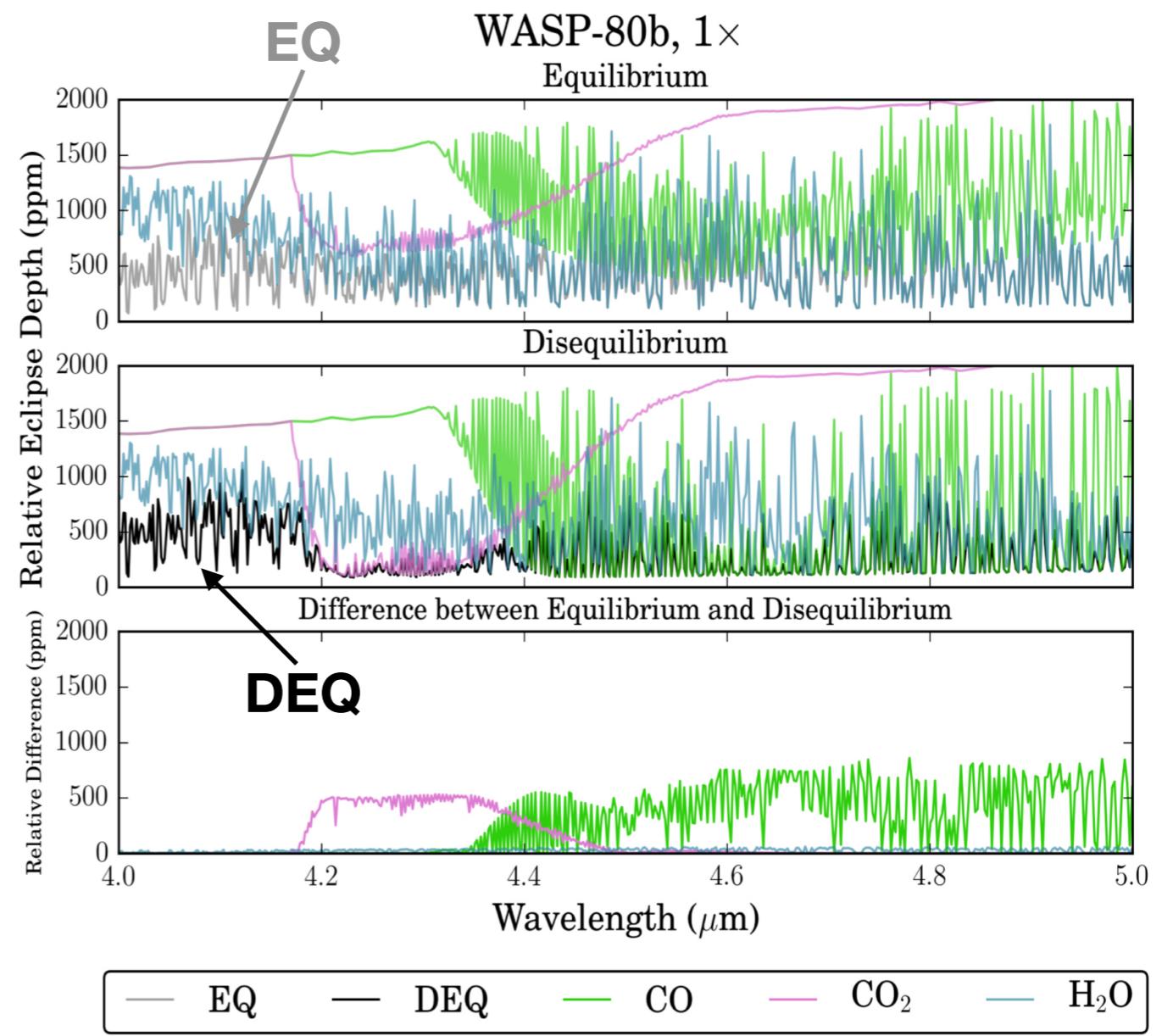
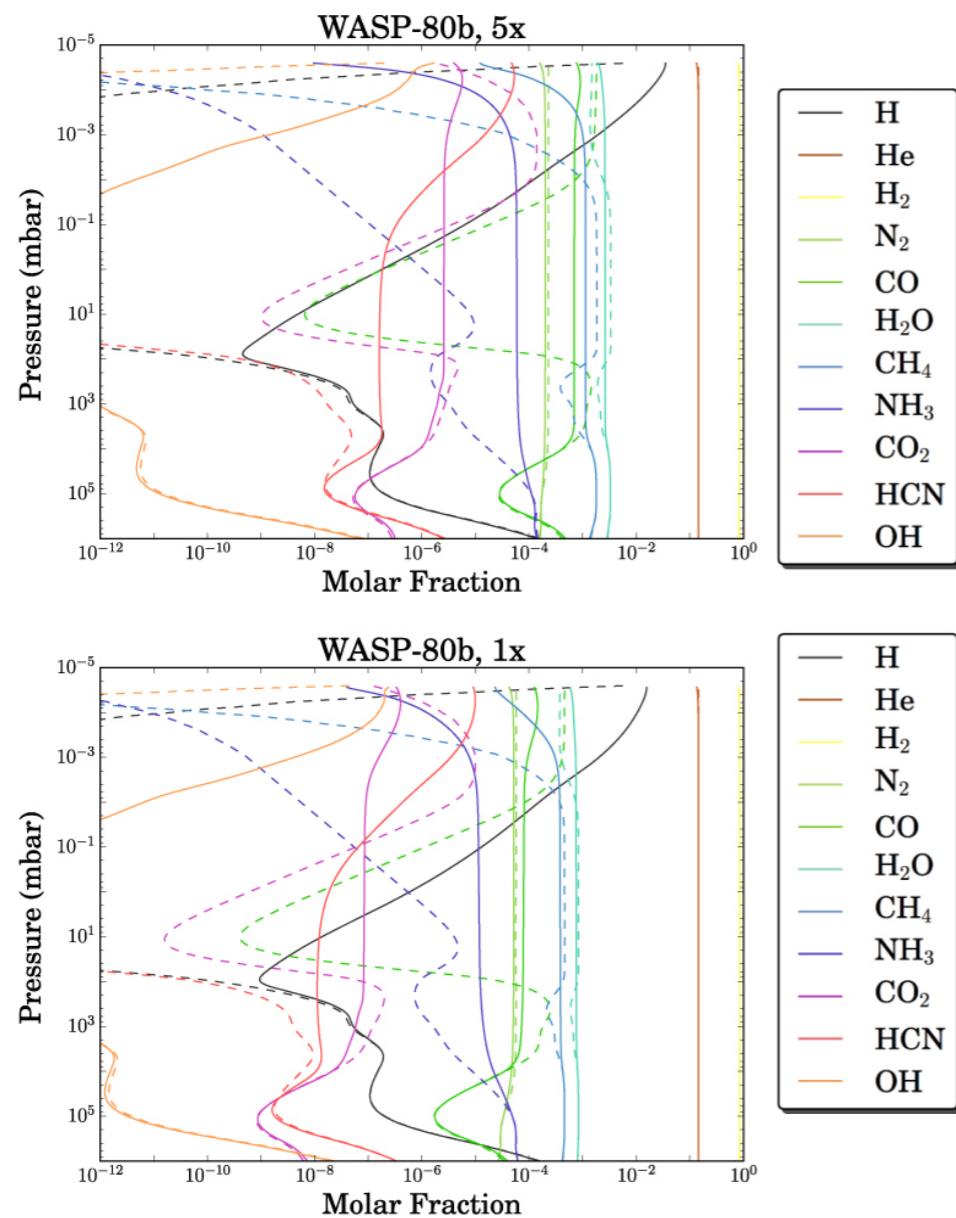
- Photochemical kinetics model for planetary atmospheres
- Computes the steady-state chemical composition with the given T-P, stellar flux, boundary conditions
- Includes thermochemistry, photochemistry, transport, condensation, surface emission and atmospheric escape

# Concepts & tools



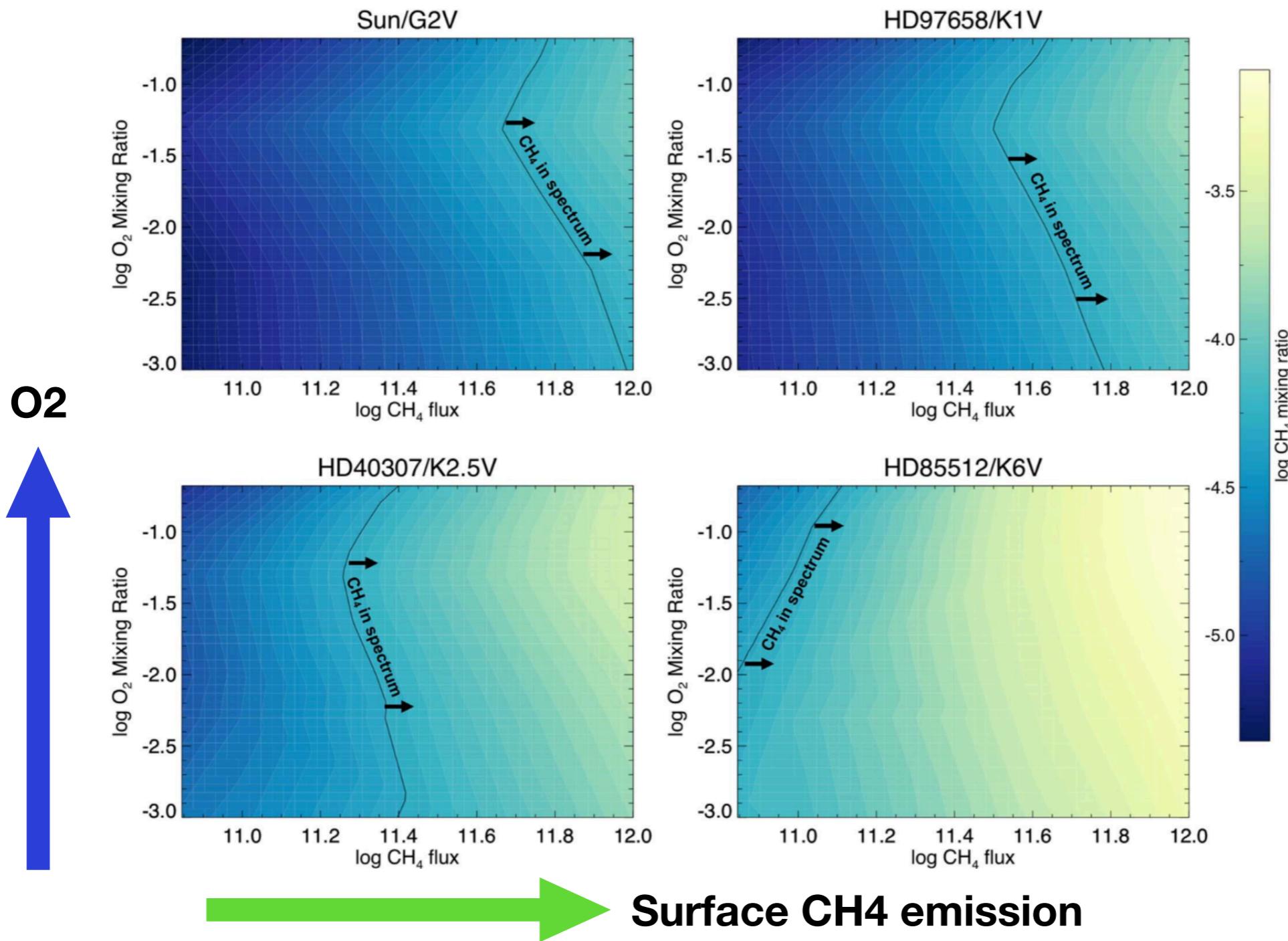
# Characterization of exoplanet atmospheres

Blumenthal et al. (2018) ApJ, 853, 2



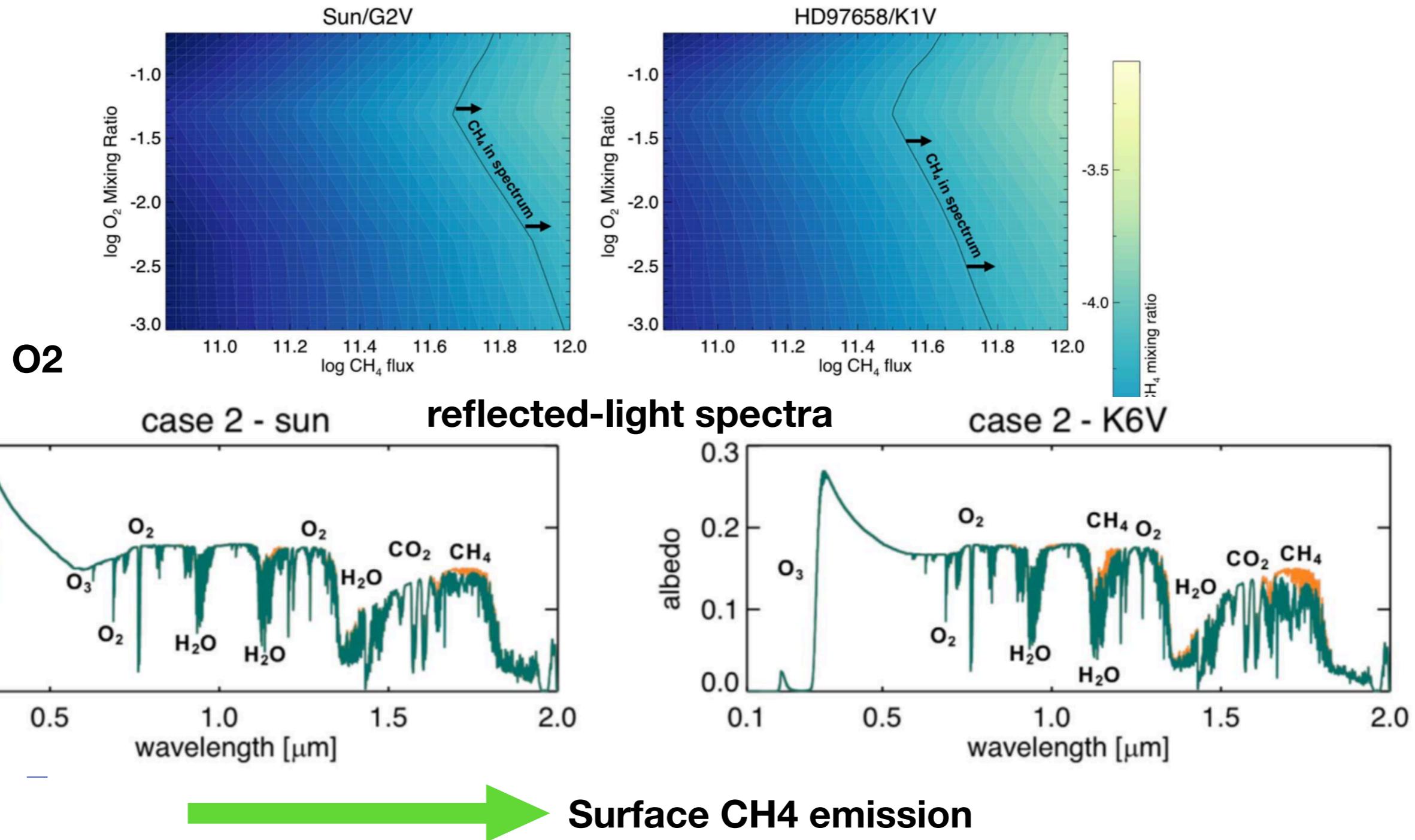
# Biosignatures

Arney 2019 ApJ

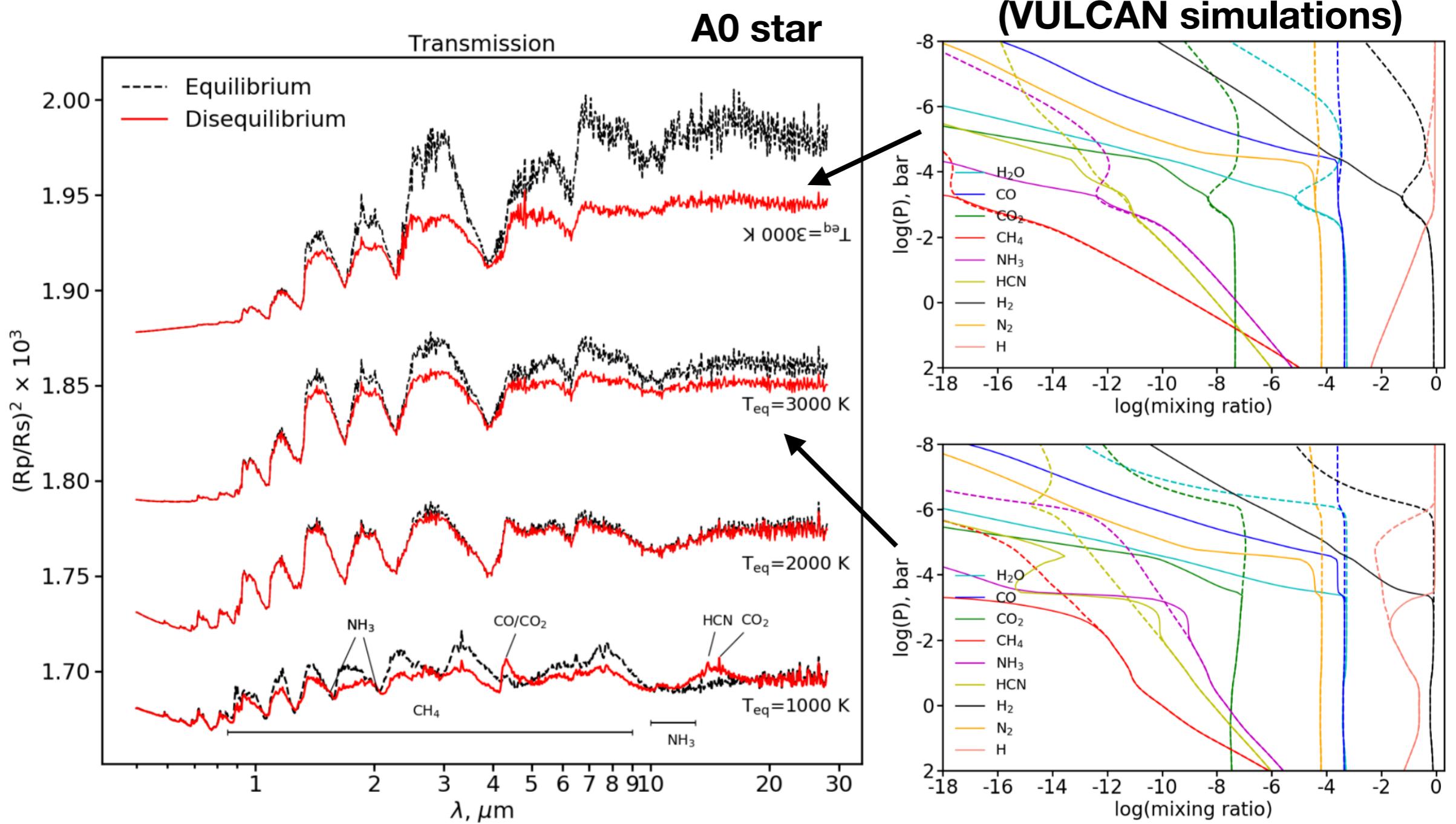


# Biosignatures

Arney 2019 ApJ

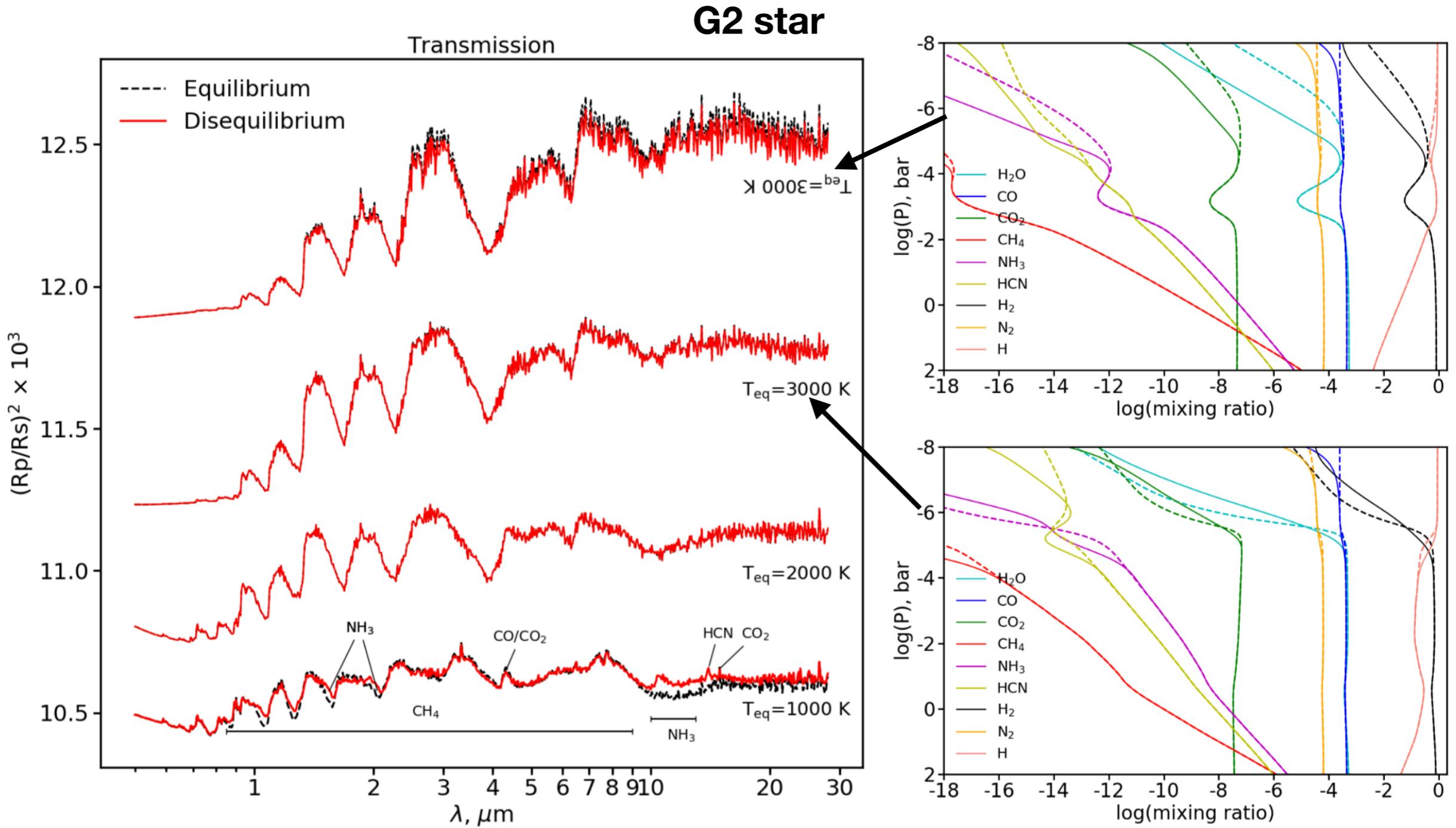


# Stellar impact



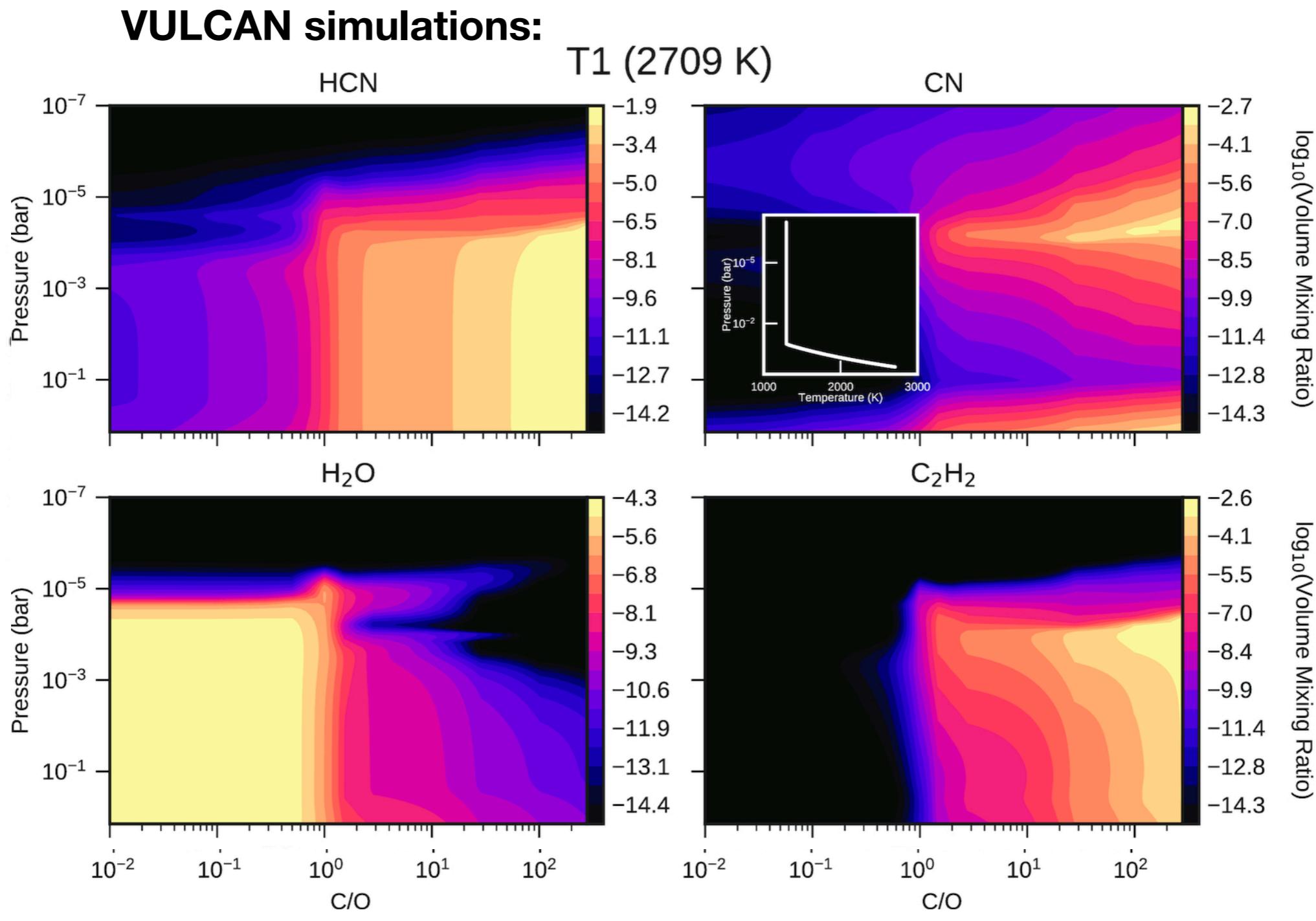
D. Shulyak et al. (2020)

# Stellar impact



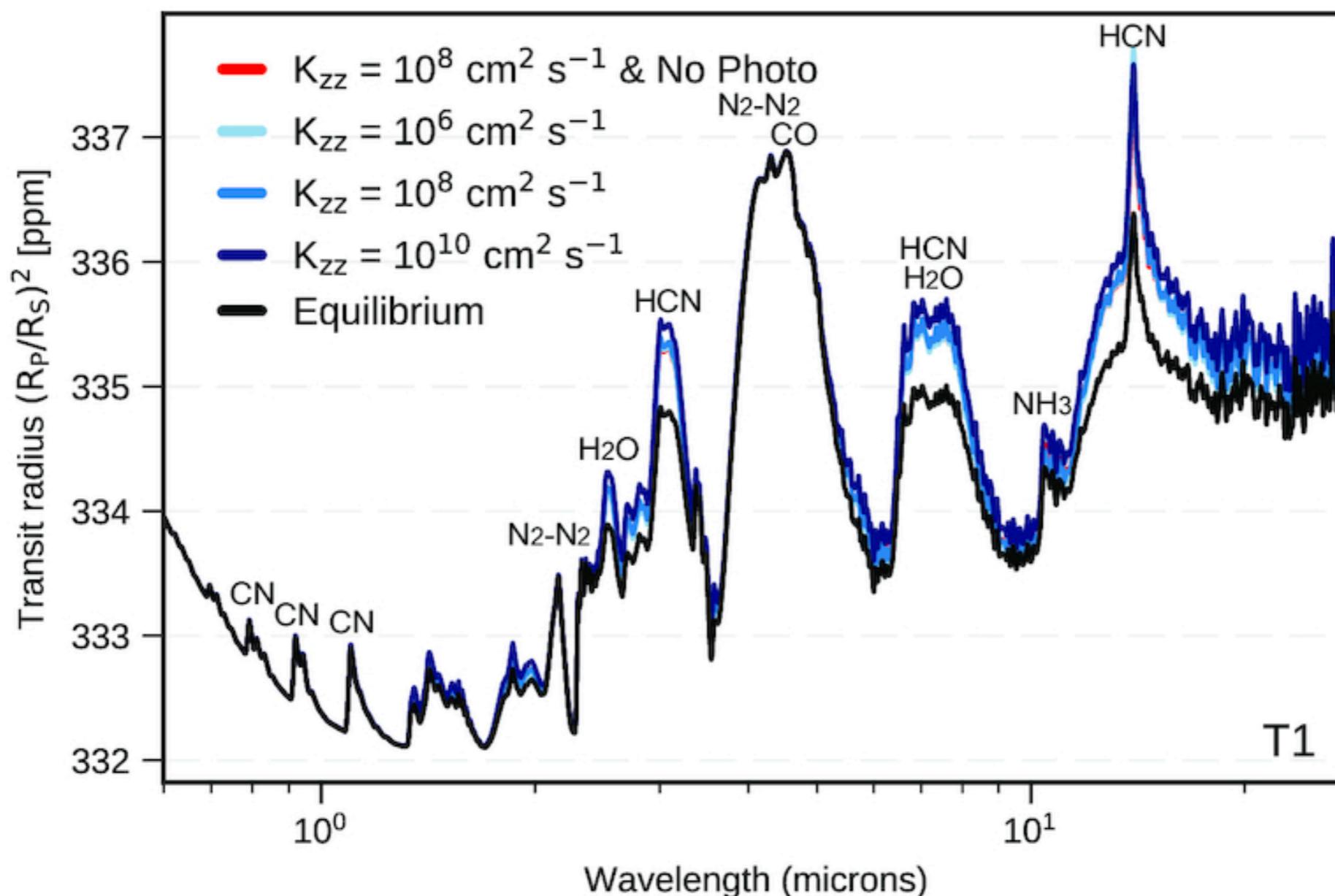
**D. Shulyak et al. (2020)**

# N<sub>2</sub> hot super-Earth



Zilinskas et al. 2020

# N<sub>2</sub> hot super-Earth



# Equilibrium chemistry

Reactions are spontaneous when the change in the Gibbs free energy is negative

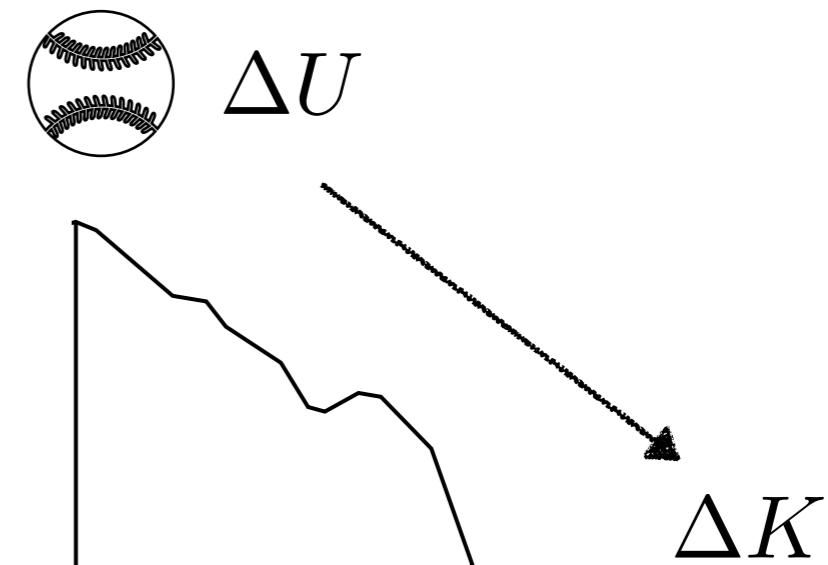
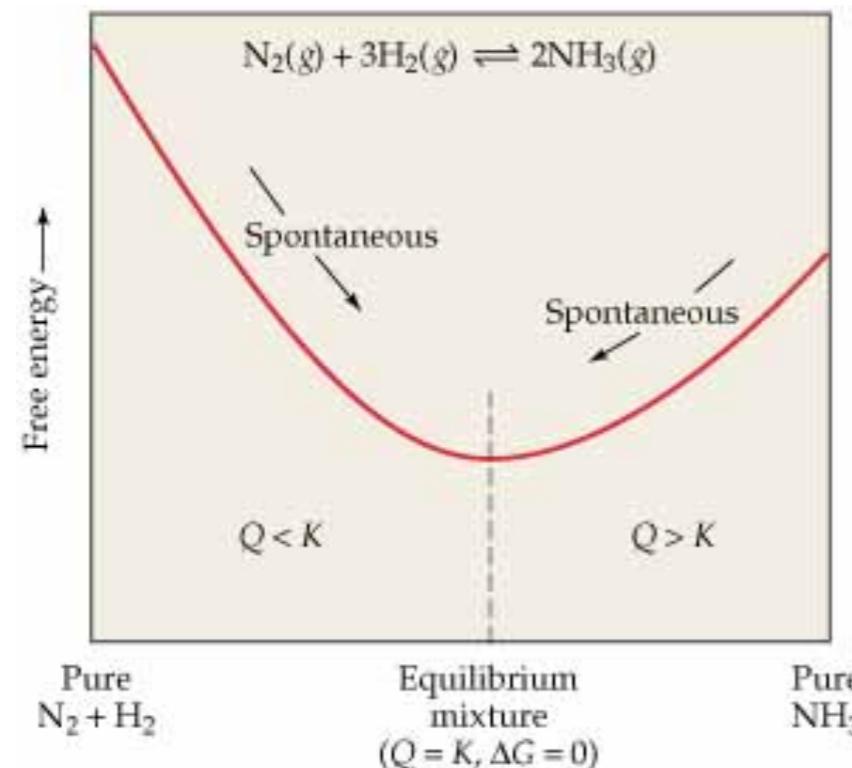
$$\Delta G = \Delta H - T\Delta S$$

G: Gibbs free energy H: enthalpy S: entropy

(Spontaneous reactions are not necessarily exothermic)



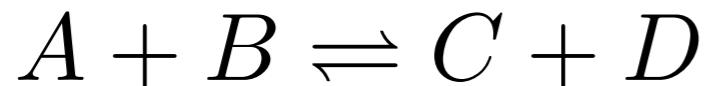
$$\Delta G = cG_C - (aG_A + bG_B)$$



**FastChem**

– minimising the Gibbs free energy  
<https://github.com/exoclime/FastChem>

# Thermochemical kinetics



Forward rate (molecule cm<sup>-3</sup>s<sup>-1</sup>):

$$-\frac{d[A]}{dt} = k_f[A][B]$$

T dependence of the rate constant:

$$k = AT^b \exp(-E_a/kT)$$

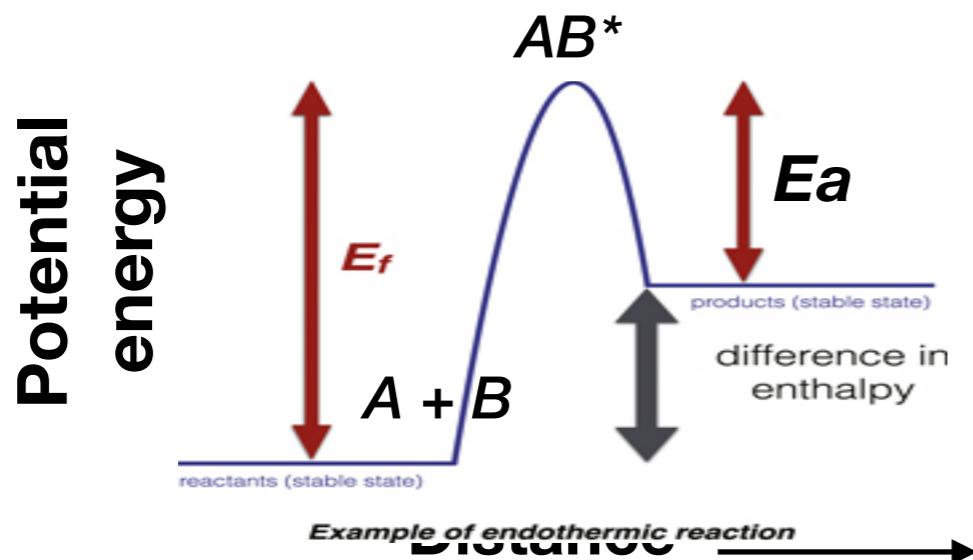
collision rate

activation energy

Chemical timescale:

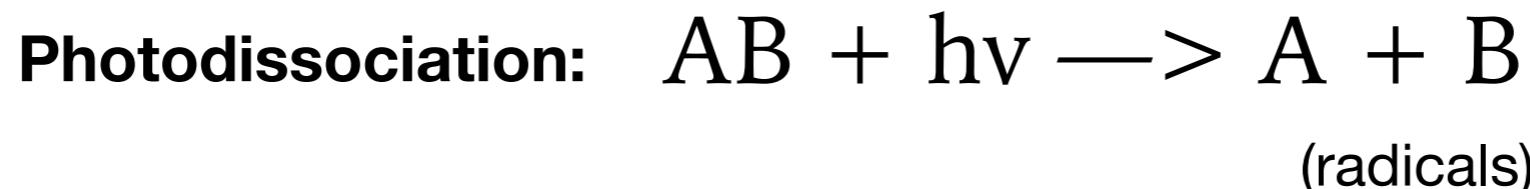
$$\tau_A = \frac{[A]}{\text{forward rate}} = \frac{1}{k_f[B]}$$

$$K_{eq} = \frac{[C][D]}{[A][B]} = \frac{k_f}{k_r} = \exp(G_f - G_r)/RT$$



**Thermodynamics** (i.e. the difference of the standard Gibbs free energy between reactants and products) can be used to “**reverse**” the forward rate, to ensure **equilibrium** is consistently achieved.

# Photochemistry



$$\frac{d[\text{AB}]}{dt} = -j[\text{AB}]$$

.....  
radical + nonradical  $\rightarrow$  radical + nonradical  
radical + radical  $\rightarrow$  nonradical + nonradical  
.....

$j$ : photodissociation coefficient ( $\text{s}^{-1}$ )

$$j = \int_{\lambda} q(\lambda) \sigma_d(\lambda) J(z, \lambda) d\lambda$$

$$J_0(z, \lambda) = F e^{-\frac{\tau}{\mu_0}} / (hc/\lambda)$$

$q$ : quantum yield (0-1)  
 $\sigma_d$ : absorption cross-section ( $\text{cm}^2$ )  
 $J$ : actinic flux (photons  $\text{cm}^{-1} \text{ s}^{-1}$ )

$$J_{diff}(z, \lambda) = \int_{4\pi} I(z, \lambda, \Omega) d\Omega$$

(mean intensity)

$$J(z, \lambda) = J_0(z, \lambda) + J_{diff}(z, \lambda)$$

direct beam    diffuse beam

— two-stream method (Malik et al. (2019); Heng et al. (2018))

# Model equations

$$\frac{\partial[n_i]}{\partial t} = P_i - L_i - \frac{\partial\phi_i}{\partial z}$$

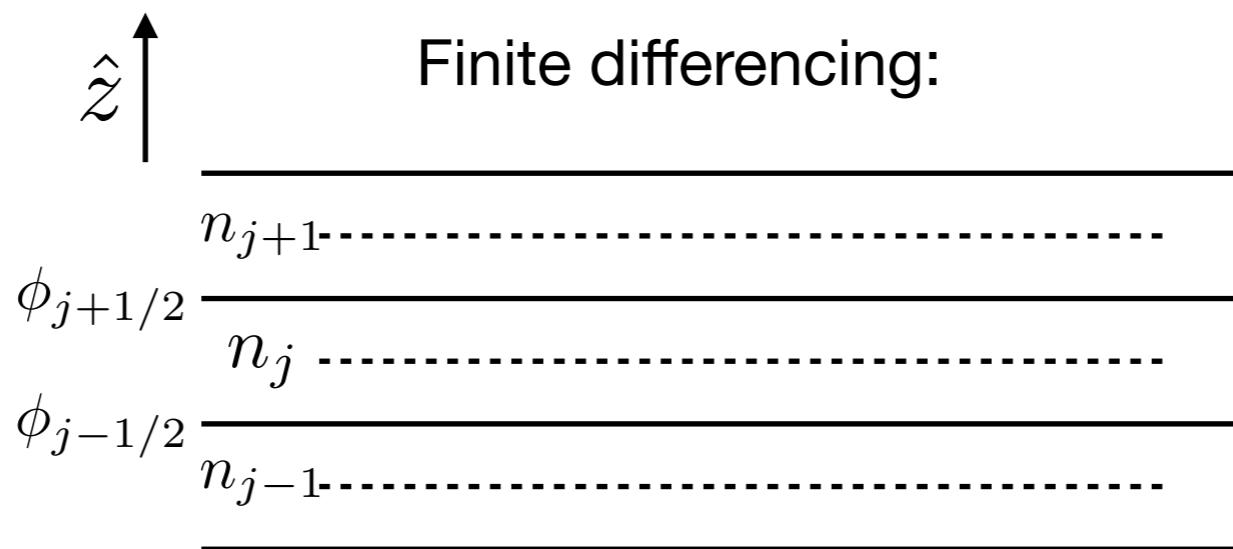
Size:  $N_{\text{species}} \times N_{\text{levels}}$  !

$[n_i]$ : number density of  $i$  species (molecules  $\text{cm}^{-3}$ )

$\Phi_i$ : transport flux (eddy diffusion + molecular diffusion)

$P_i$ : chemical production ( $\text{cm}^{-3}\text{s}^{-1}$ )

$L_i$ : chemical loss ( $\text{cm}^{-3}\text{s}^{-1}$ )

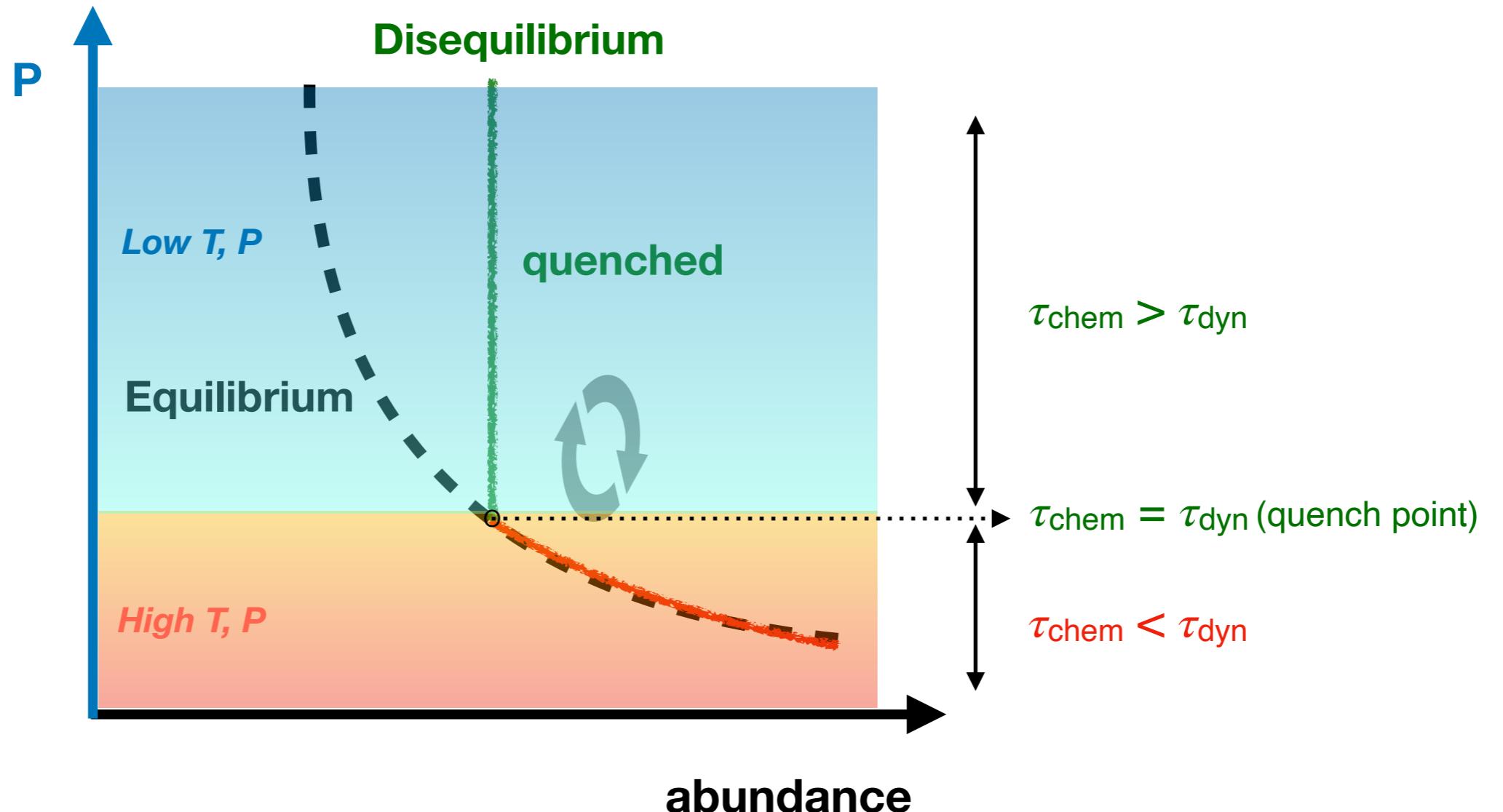


# Transport-induced quenching

$$\frac{\partial[n_i]}{\partial t} = P_i - L_i - \frac{\partial\phi_i}{\partial z}$$

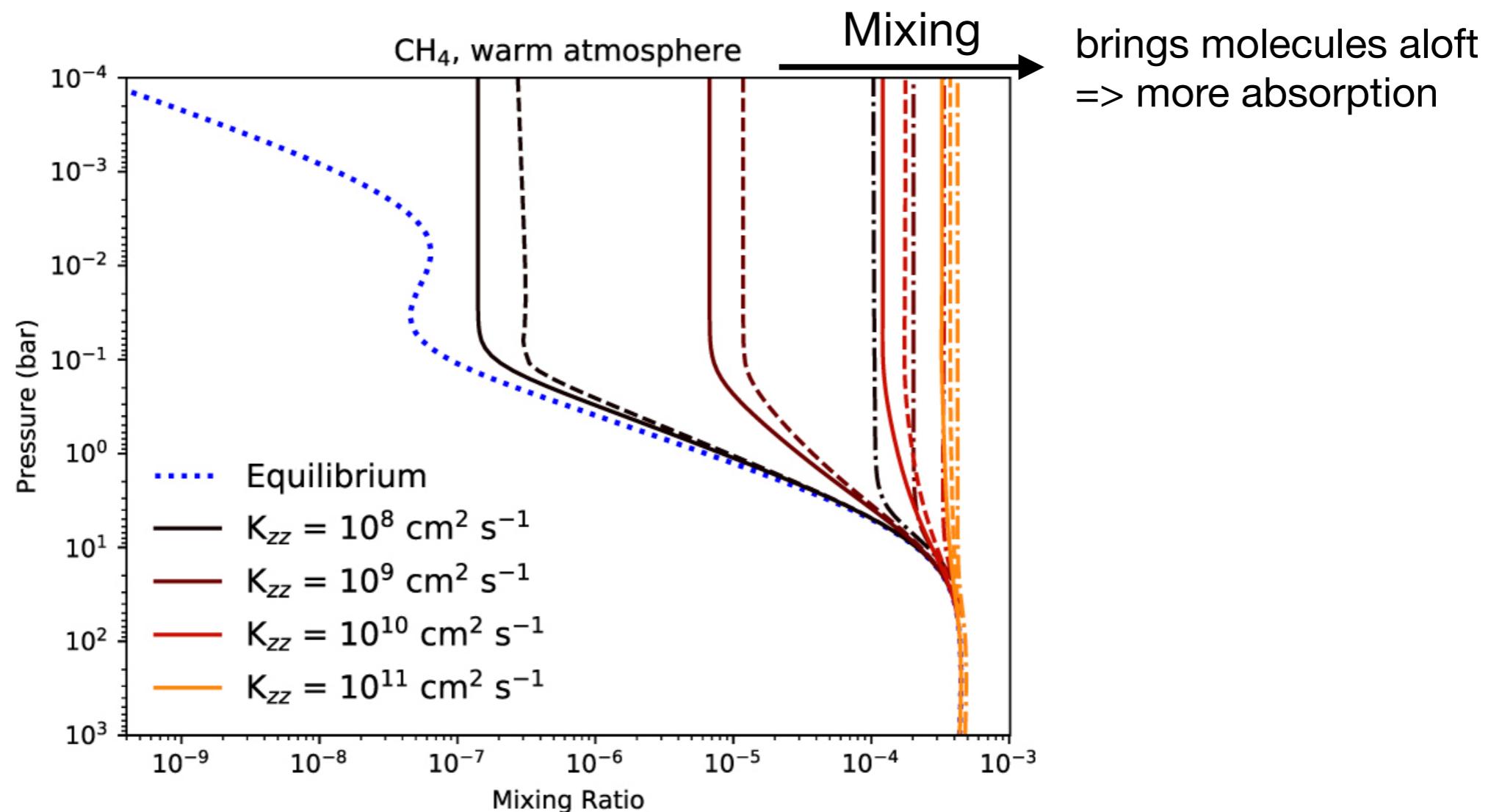
$$\phi_i = n_i v - K_{zz} n_{\text{tot}} \frac{\partial X_i}{\partial z} - D \left[ \frac{\partial n_i}{\partial z} + n_i \left( \frac{1}{H_i} + \frac{1 + \alpha_T}{T} \frac{dT}{dz} \right) \right]$$

advection      eddy diffusion      molecular and thermal diffusion



# Transport-induced quenching

$$\frac{\partial[n_i]}{\partial t} = P_i - L_i - \frac{\partial\phi_i}{\partial z}$$



# Chemical networks for reducing atmospheres

From Molaverdikhani et al. (2019)

Chemical Network	Elements	Species	Reactions	Reference
Moses Hot Jupiters	H-C-O-N	90	800	Moses et al. 2011
Venot 2012	H-C-O-N	103	963	Venot et al. 2012
Hébrard 2012	H-C-O-N	135	788	Hébrard et al. 2012
Hébrard 2013	H-C-O-N	90	941	Hébrard et al. 2013
Venot 2015	H-C-O-N	238	2011	Venot et al. 2015
VULCAN H-C-O	H-C-O	29	300	Tsai et al. 2017
Moses Ice-giants	H-C-O	69	385	Moses et al. 2018
Venot reduced	H-C-O-N	29	181	Venot et al. 2019
Pearce HCN	H-C-N	11	42	Pearce et al. 2019

VULCAN N-H-C-O

~55

~700

Tsai et al. (in prep.)

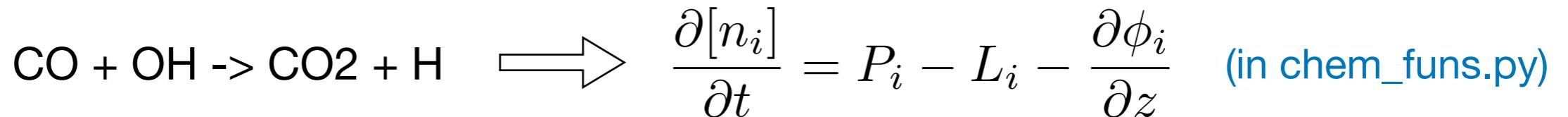
VULCAN S-N-H-C-O

~80

~900

# Code details

- Developed in python 3 (NumPy)
- ODE solver:
  - 2nd order Rosenbrock method for the “stiff” ODE system (Verwer 1998)
  - Using `scipy.linalg.solve_banded` for  $A X = B$
- Can call FastChem to initialise compositions from chemical equilibrium
- Flexible chemical networks



- Readme on [Github](#)
- `vulcan_cfg.py`: the configuration file  
`store.py`: defines all the classes and variables

# Kinetics resources

- Thermodynamics data: NASA polynomials (<http://garfield.chem.elte.hu/Burcat/burcat.html>)
- Reaction rates: NIST, KIDA, MPI-Mainz
- UV photo cross sections: Leiden database, PhiDRates

## Questions and feedbacks



<http://vulcan-kinetics.slack.com/>