



# Photochemistry in Laboratory

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# STRUCTURE OF GIANT GASEOUS EXOPLANETS

- From their small density, we know that their atmospheres are dominated by Hydrogen (H<sub>2</sub> or H) and Helium

..... thermochemical equilibrium  
— kinetic model

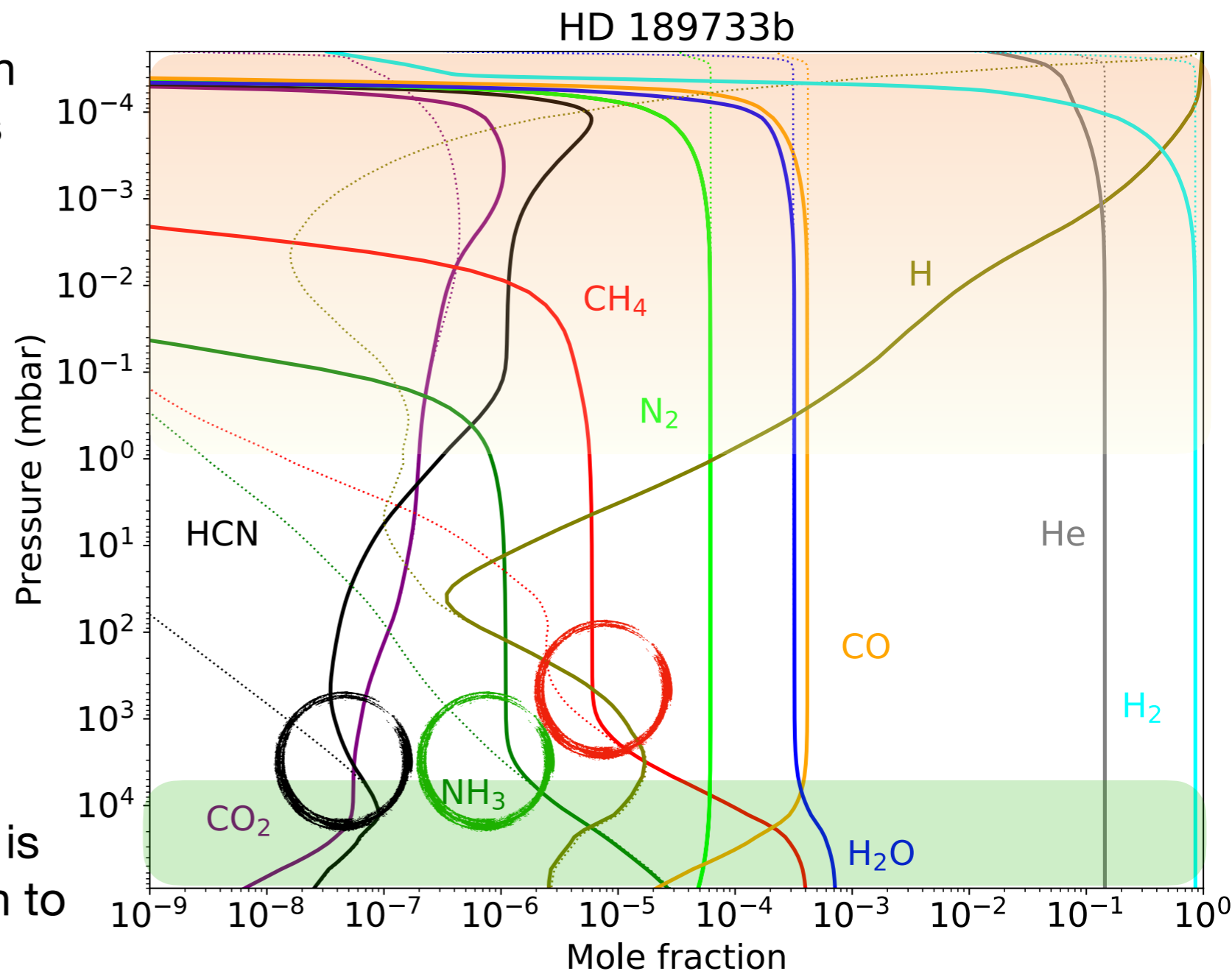
- Photodissociations:** UV irradiation from the star destroys or produces molecules. Effect can be seen as deep as 10/100 mbar

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

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

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

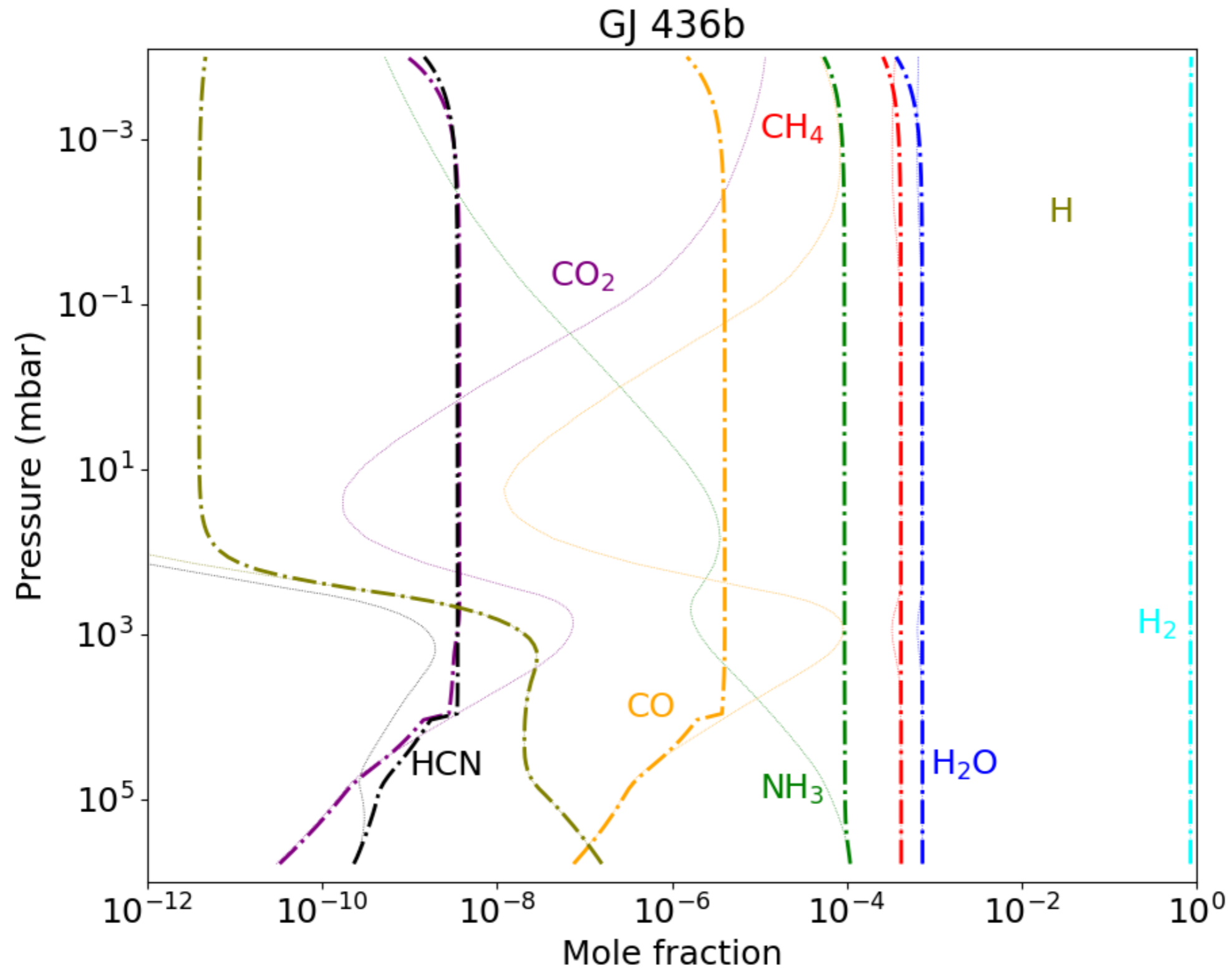
- Thermo equilibrium:** temperature is very high so kinetics is fast enough to reproduce thermo equilibrium



# PHOTOCHEMISTRY AT HIGH TEMPERATURE

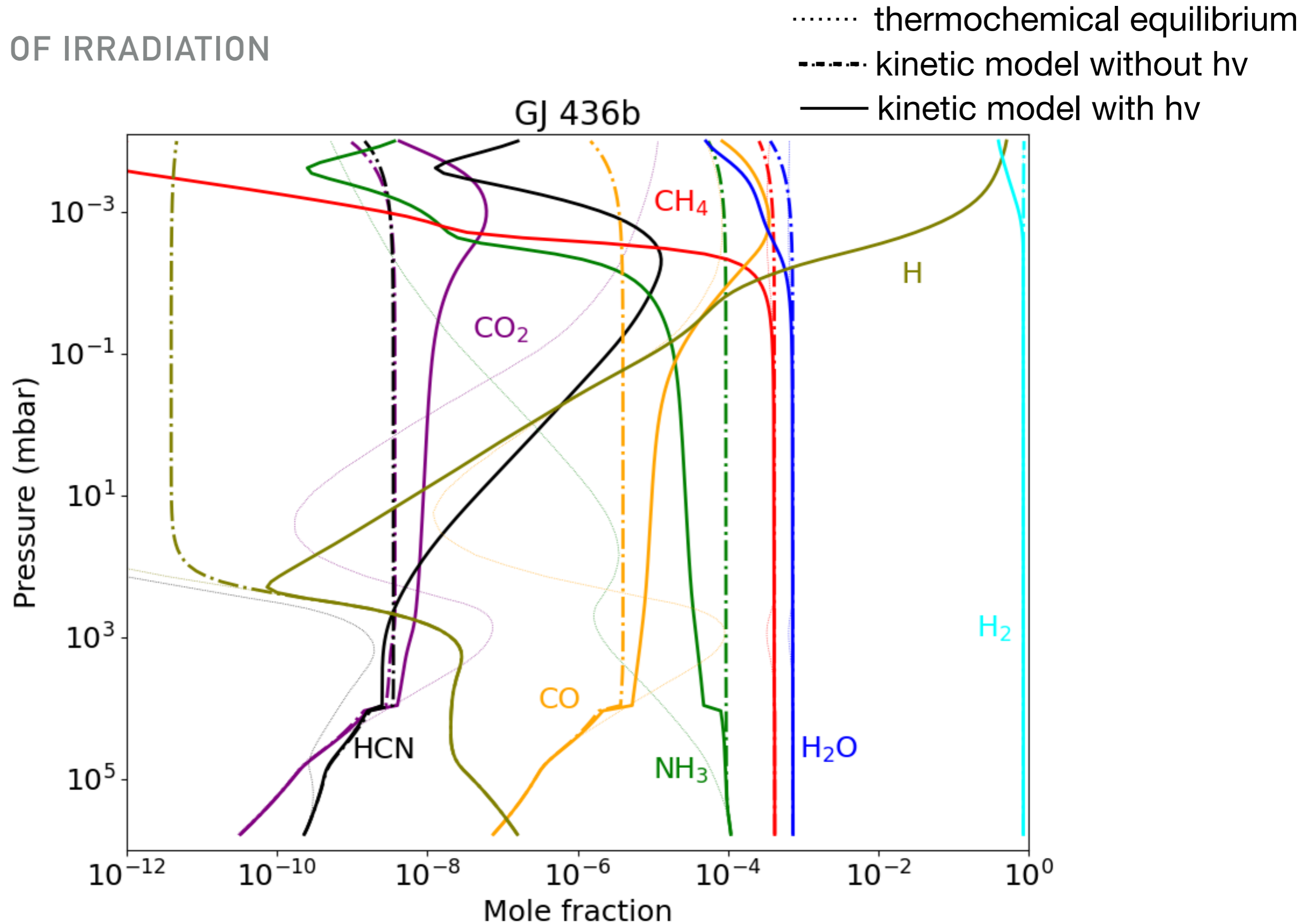
## EFFECT OF IRRADIATION

- ..... thermochemical equilibrium
- .-.- kinetic model without  $h\nu$



# PHOTOCHEMISTRY AT HIGH TEMPERATURE

## EFFECT OF IRRADIATION



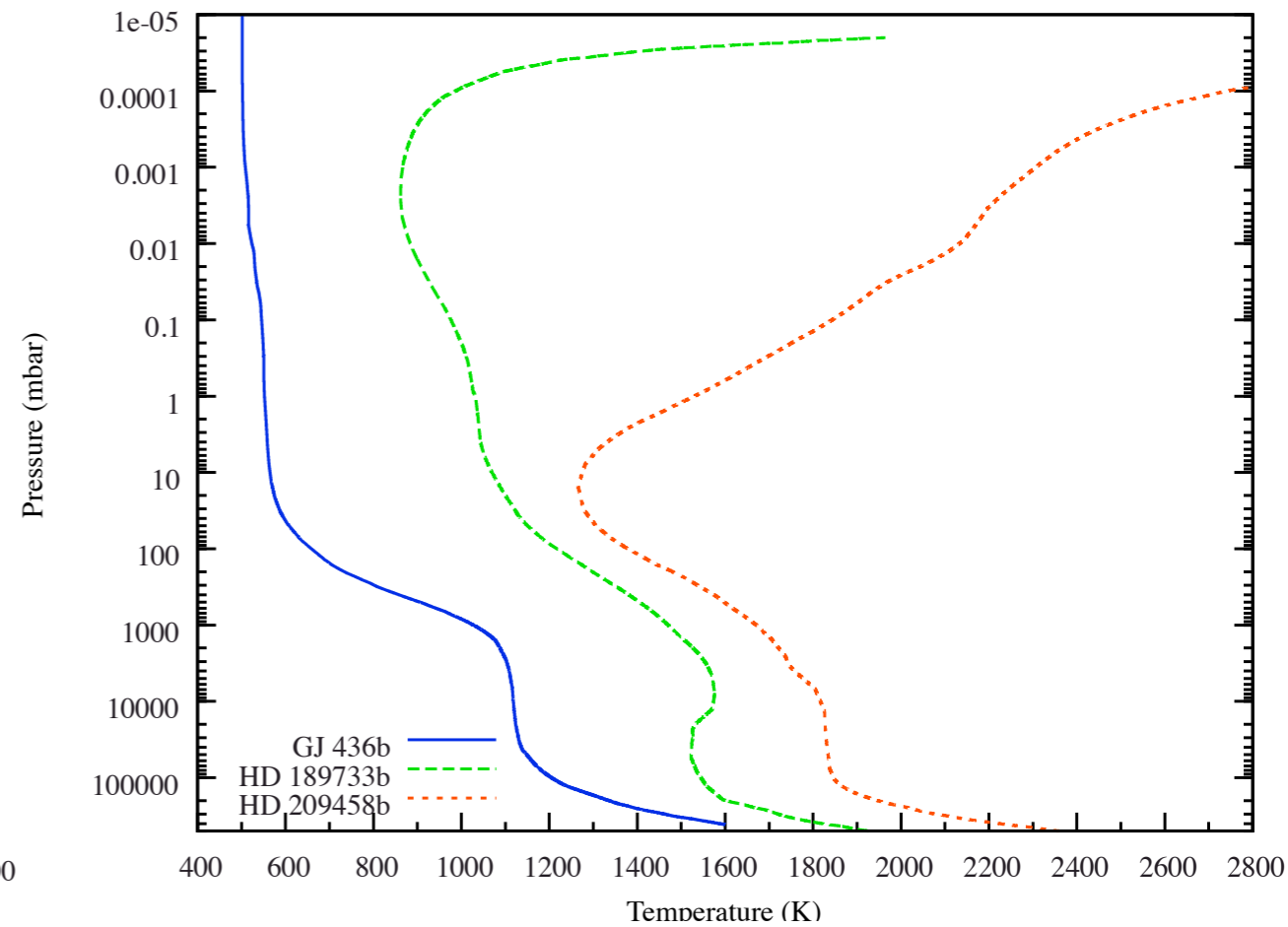
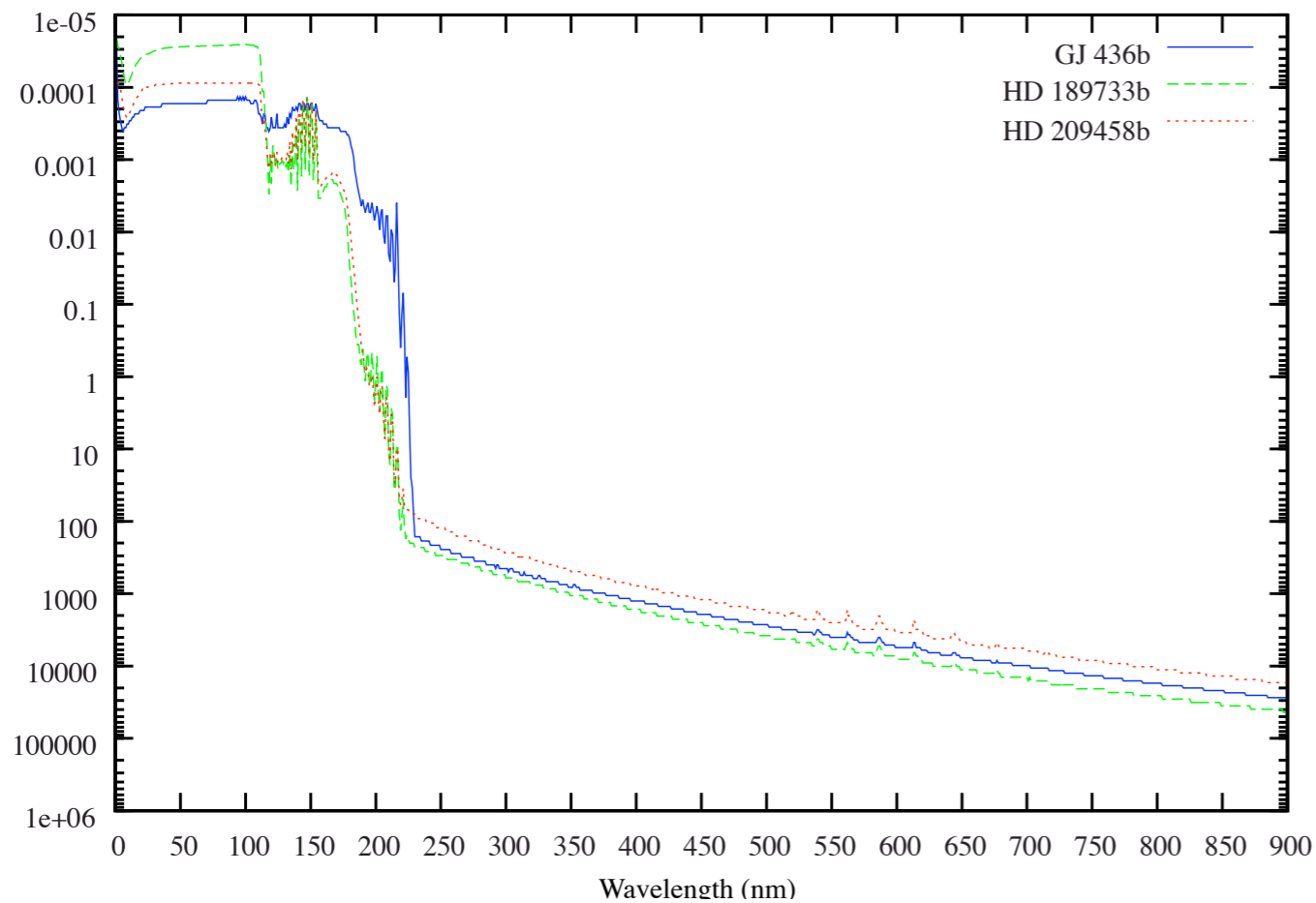
# PHOTOCHEMISTRY AT HIGH TEMPERATURE

## WHERE DO PHOTODISSOCIATIONS OCCUR ?

HD 189733b, HD 209458b (Hot Jupiters), and GJ 436b (Warm Neptune)

penetration of stellar flux (level  $\tau=1$ )

thermal profiles



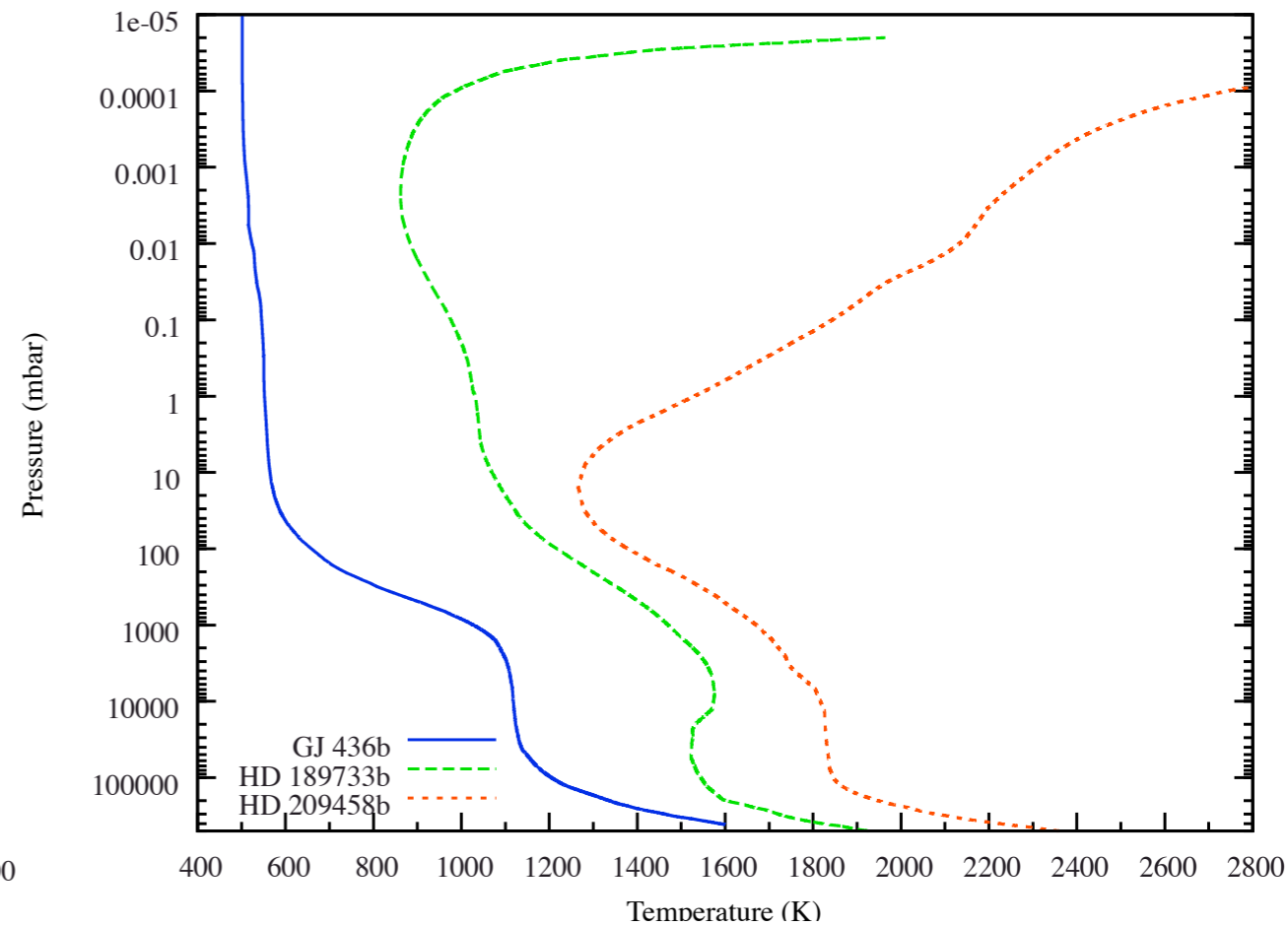
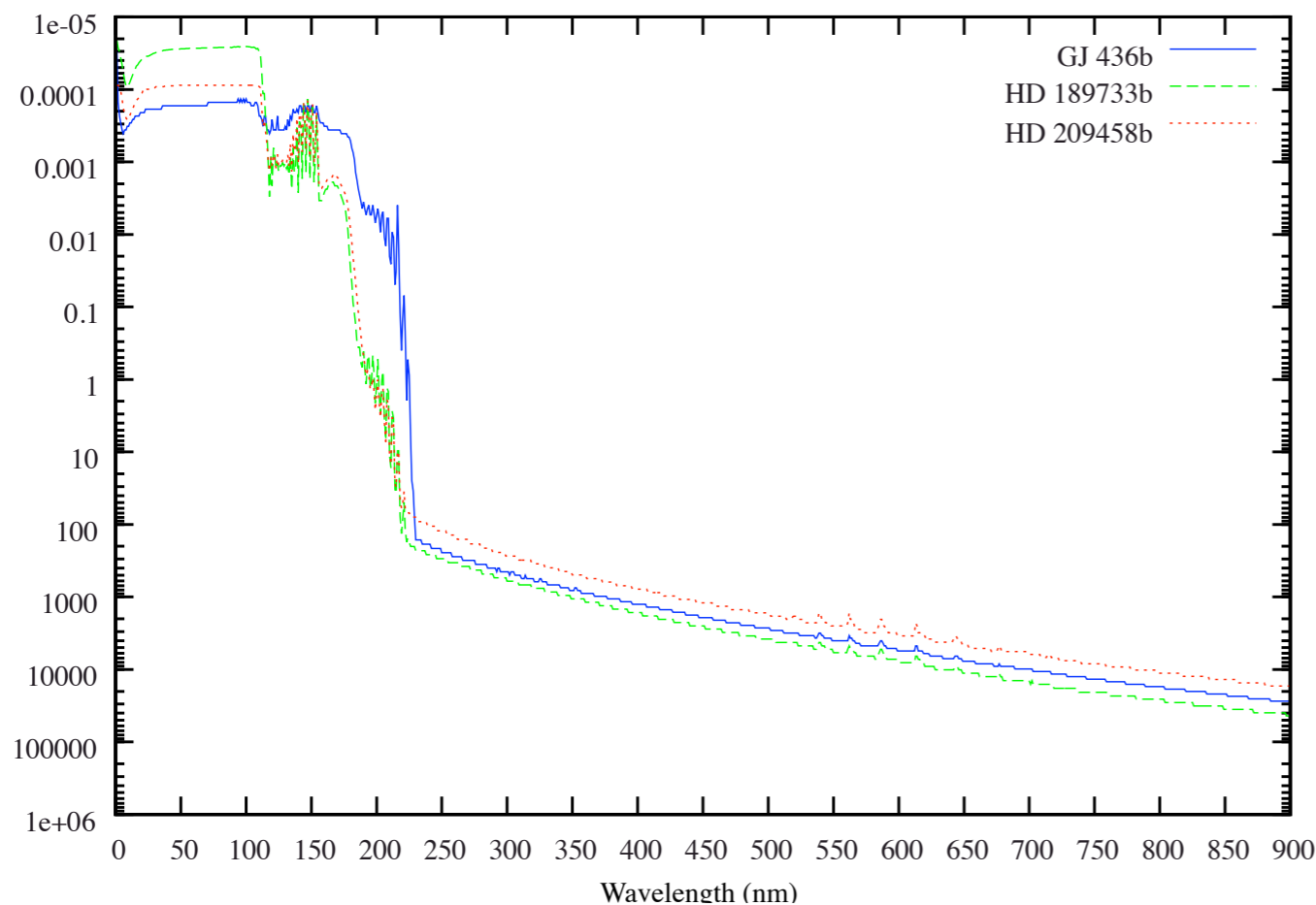
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$\lambda$  of interest for photochemistry:  $< 250$  nm

penetrate down to  $P = 100$  mbar

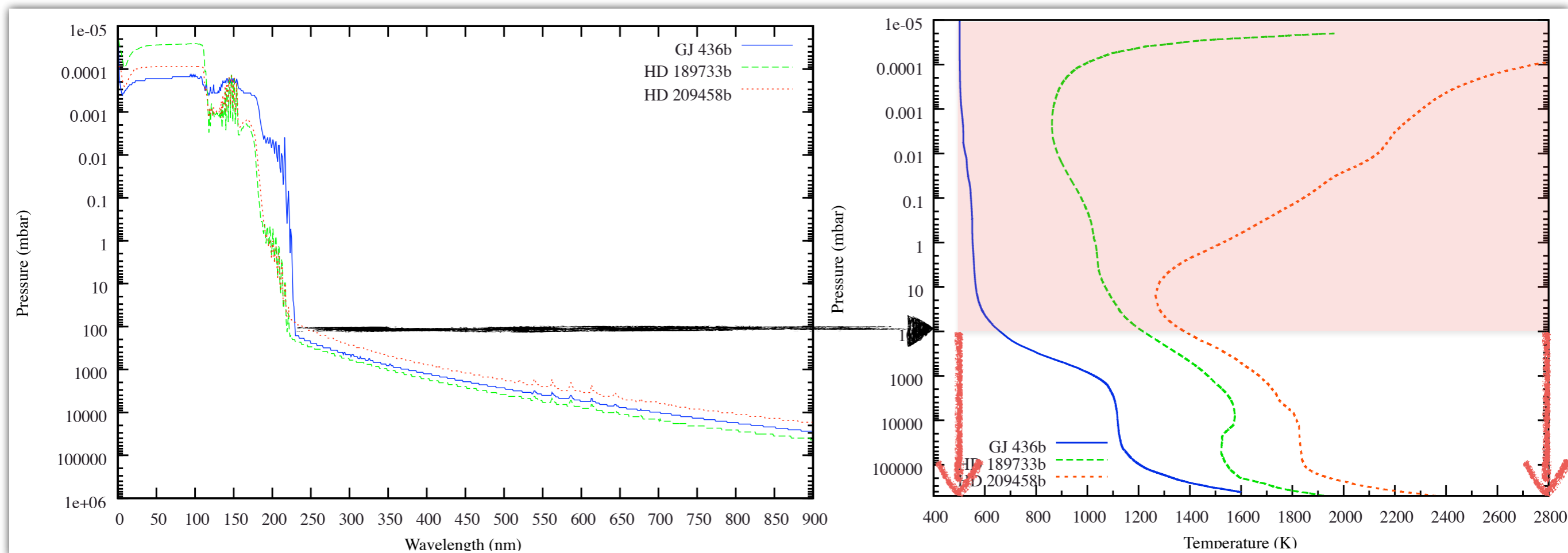
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500 - 2800 K !

penetrate down to  $P = 100$  mbar



# PHOTOCHEMISTRY AT HIGH TEMPERATURE

## VUV ABSORPTION CROSS-SECTIONS

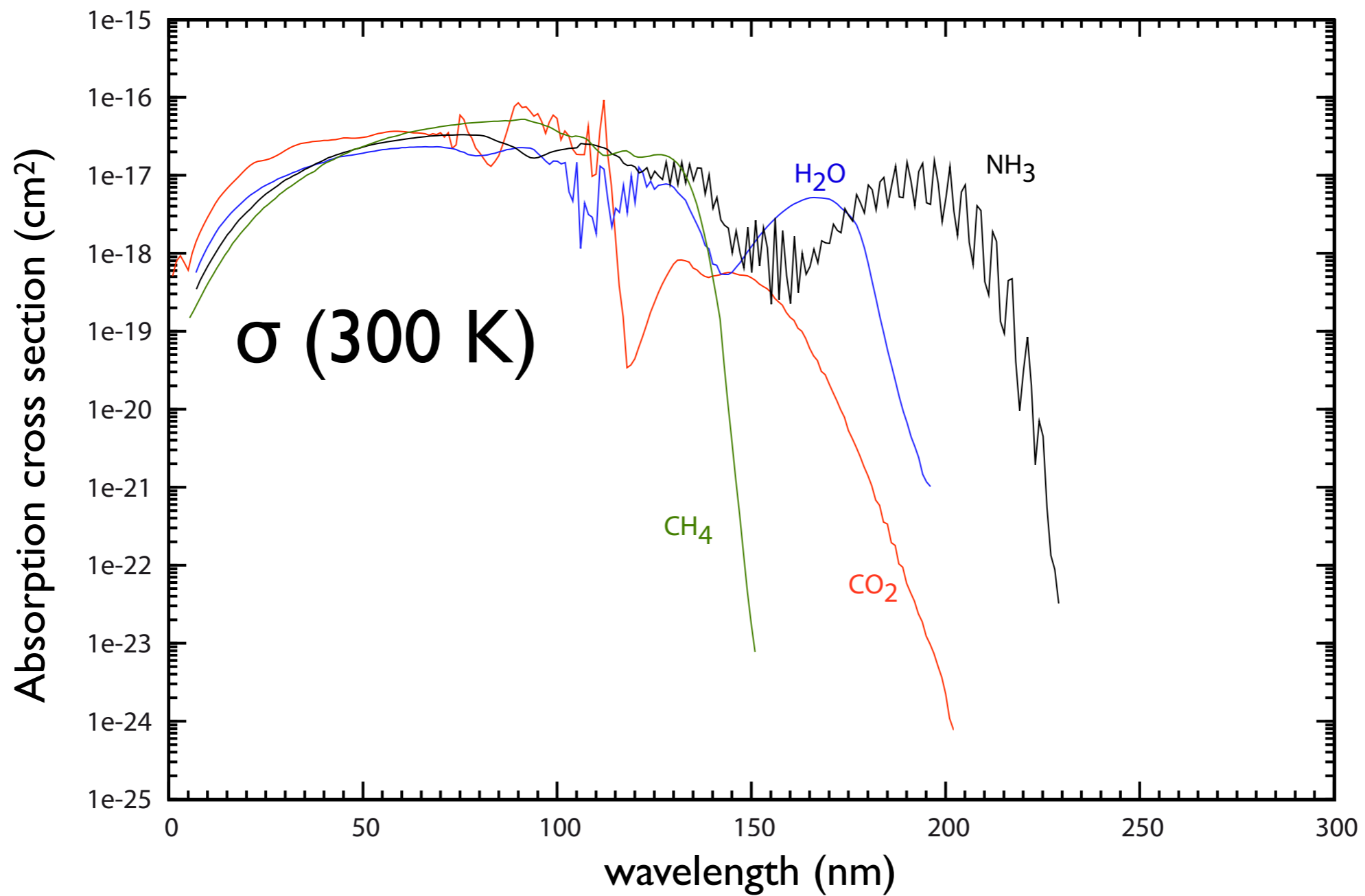
$\sigma(\lambda, T)$  are crucial data for atmospheric models

Photodissociations rate :

$$J^k(z) = \int_{\lambda_1}^{\lambda_2} \sigma(\lambda, T) F(\lambda, z) q_k(\lambda, T) d\lambda$$

Actinic flux :

$$F(\lambda, z) = F_0(\lambda) \exp\left(-\sigma(\lambda, T) \int_z^{\infty} n(h) dh\right)$$





# PHOTOCHEMISTRY AT HIGH TEMPERATURE

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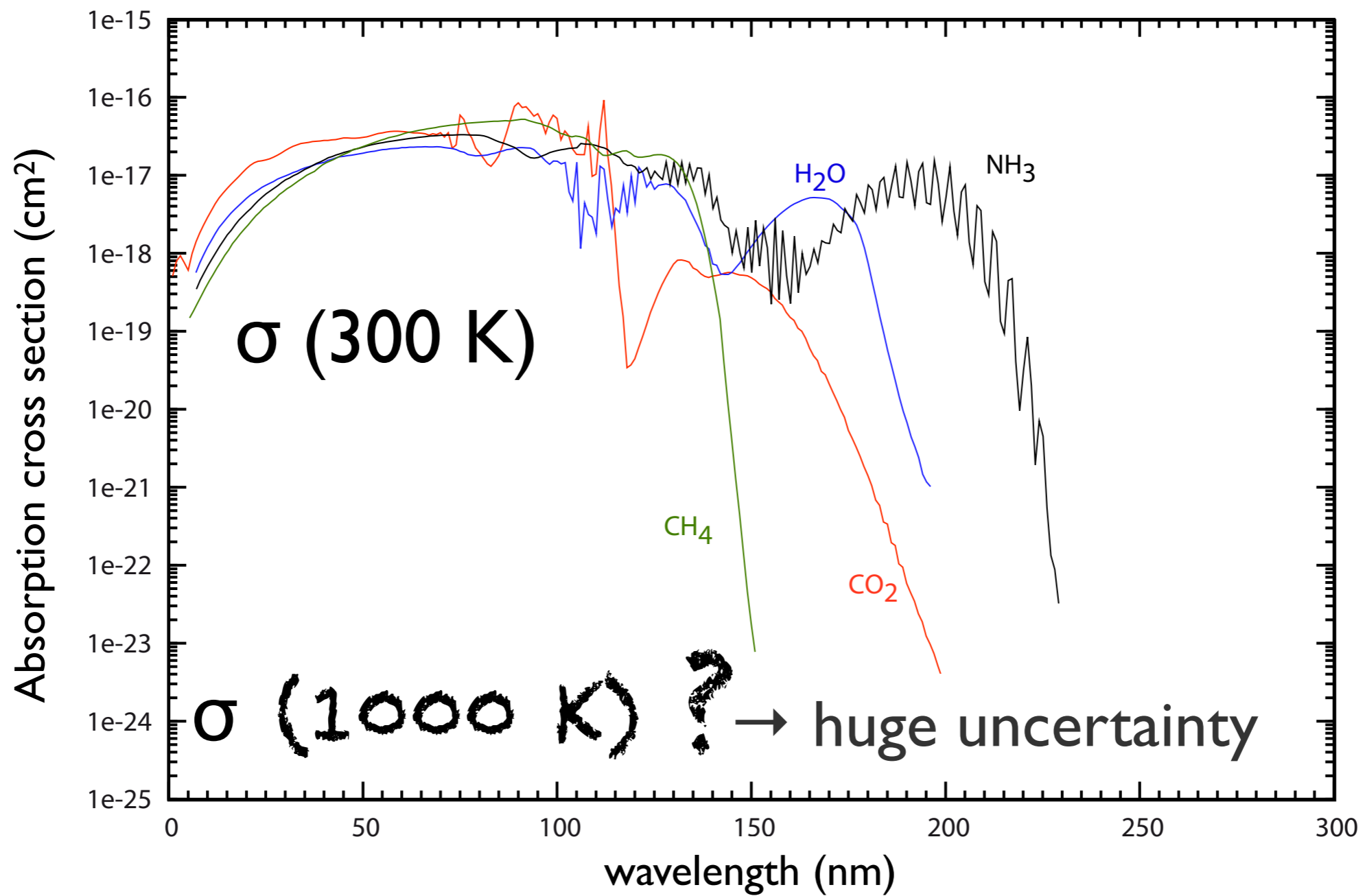
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# EXPERIMENTAL SETUP

T up to 1200K



synchrotron BESSY / SOLEIL  
 $115 < \lambda < 190 \text{ nm}$

UV lamp at LISA  
 $190 < \lambda < 230 \text{ nm}$

115-230 nm

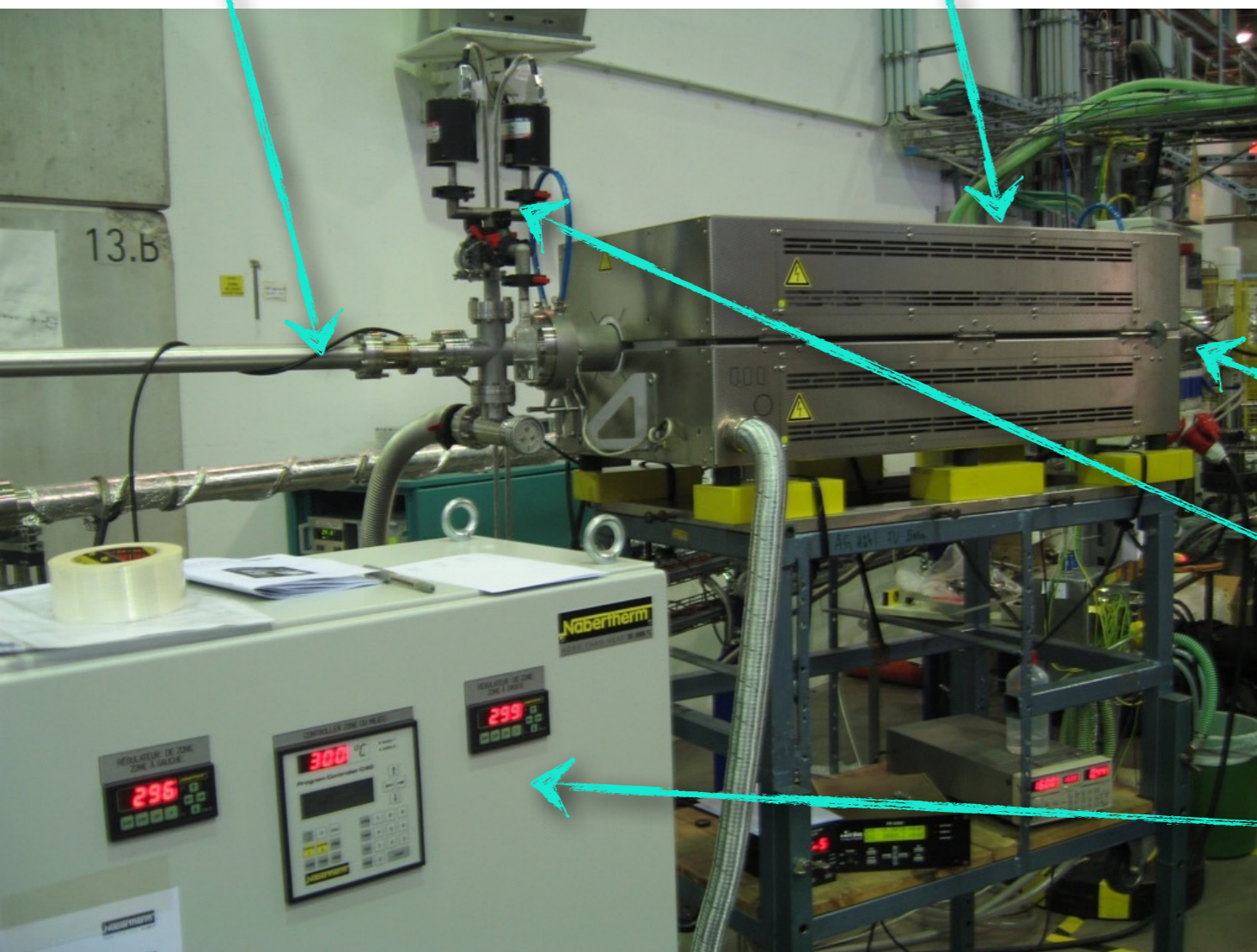
incident flux

oven + cell containing gas

photomultiplier

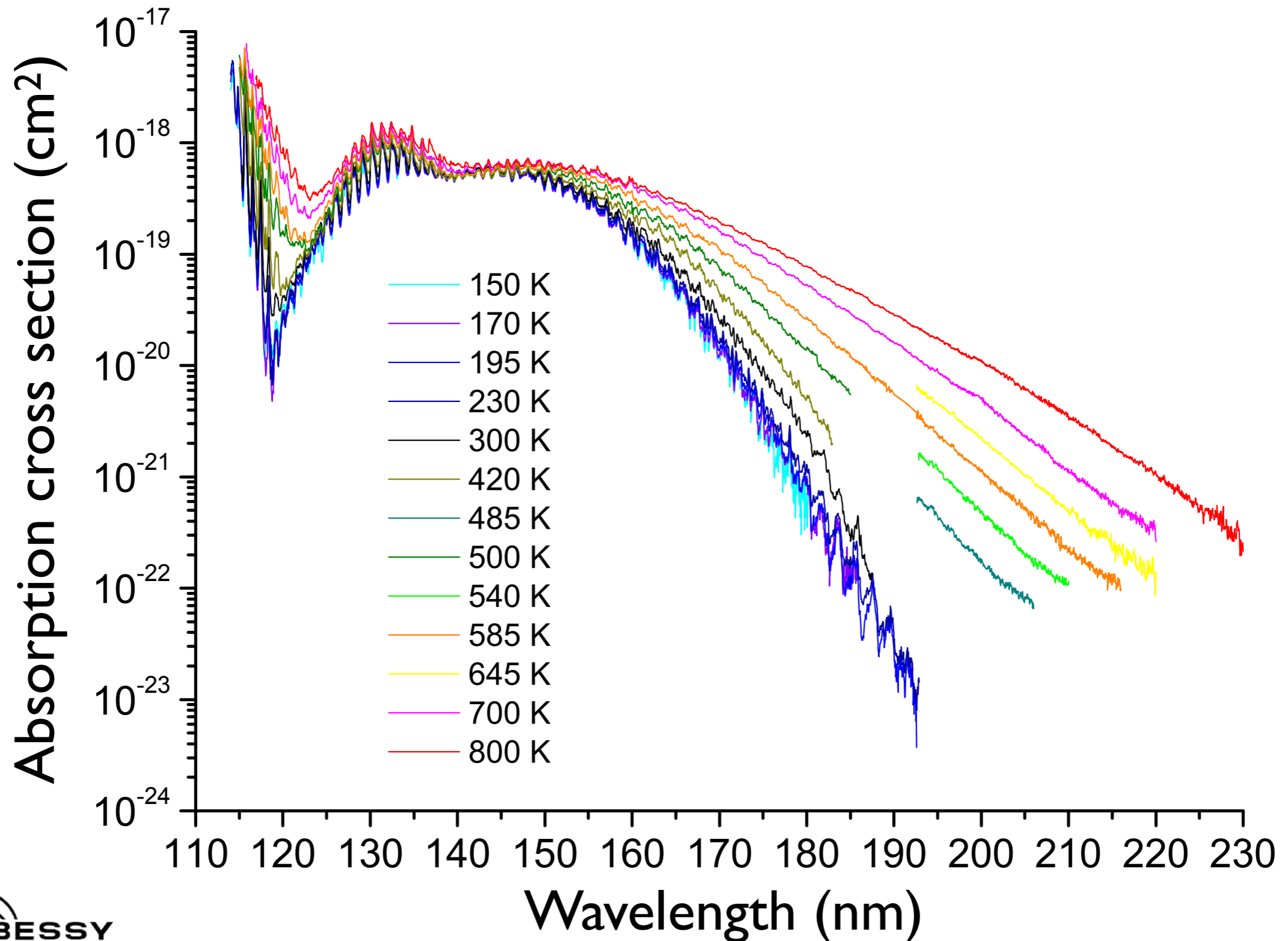
injection of gas

control of temperature



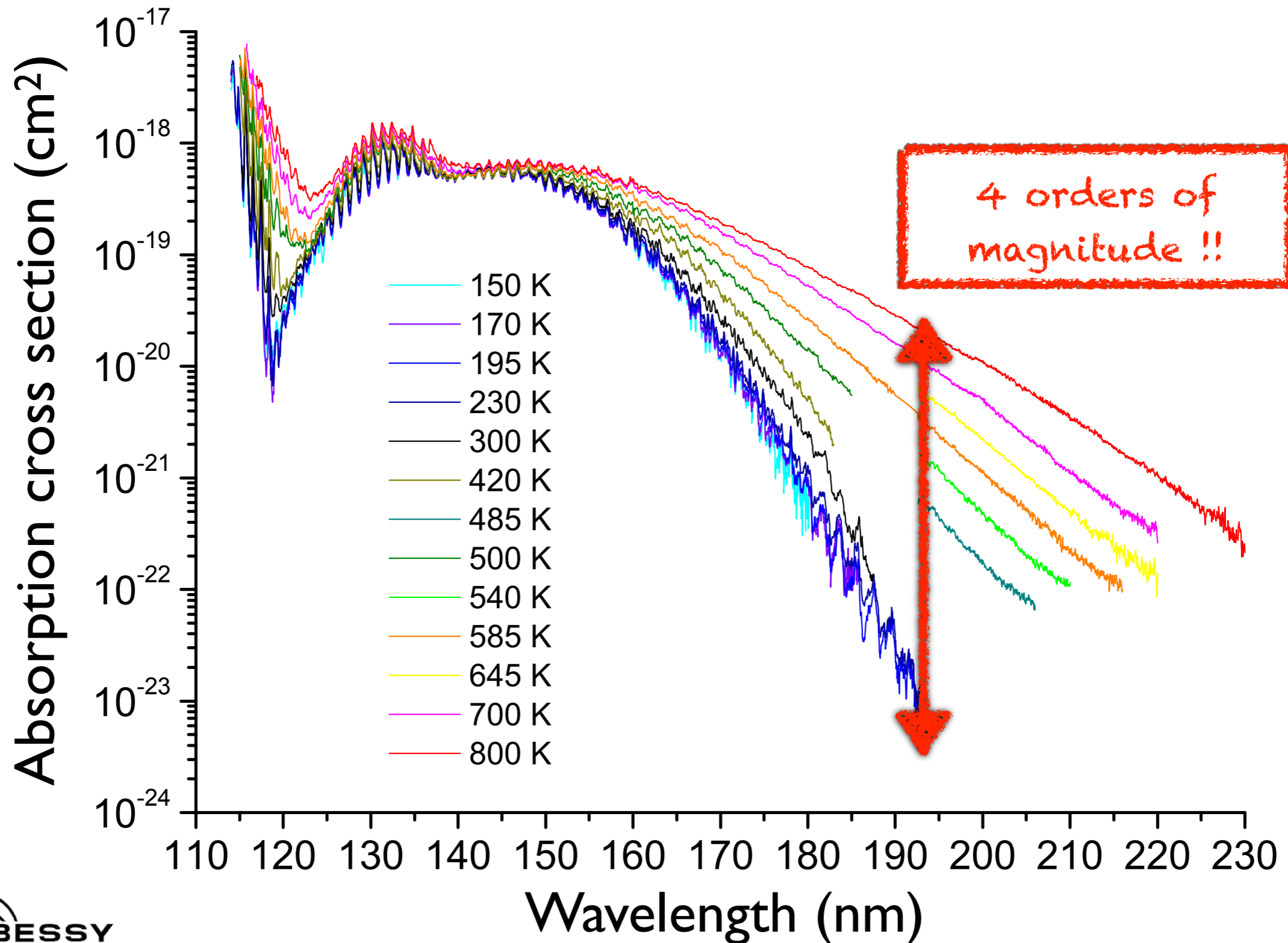
# CO<sub>2</sub> ABSORPTION CROSS-SECTION

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



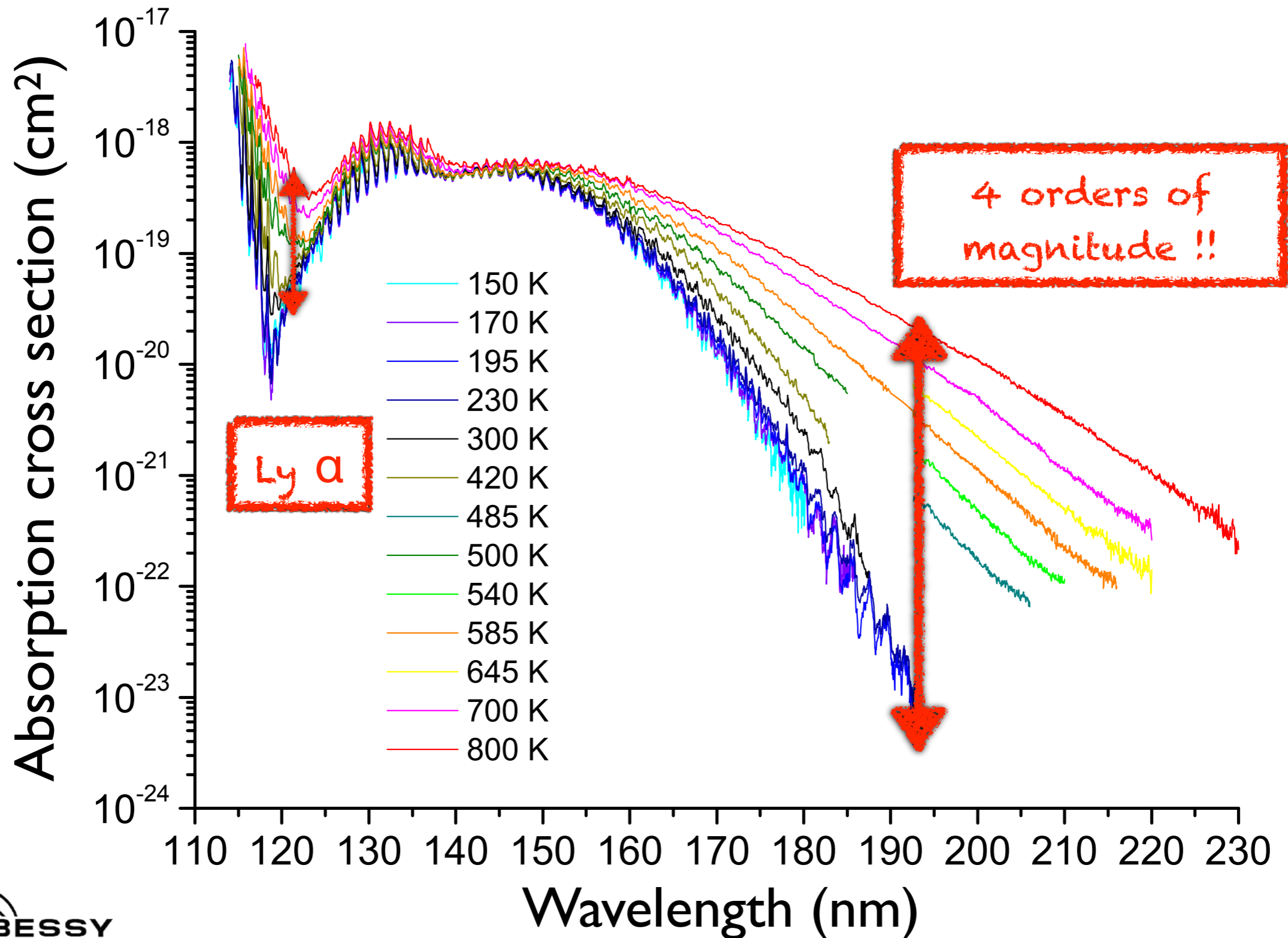
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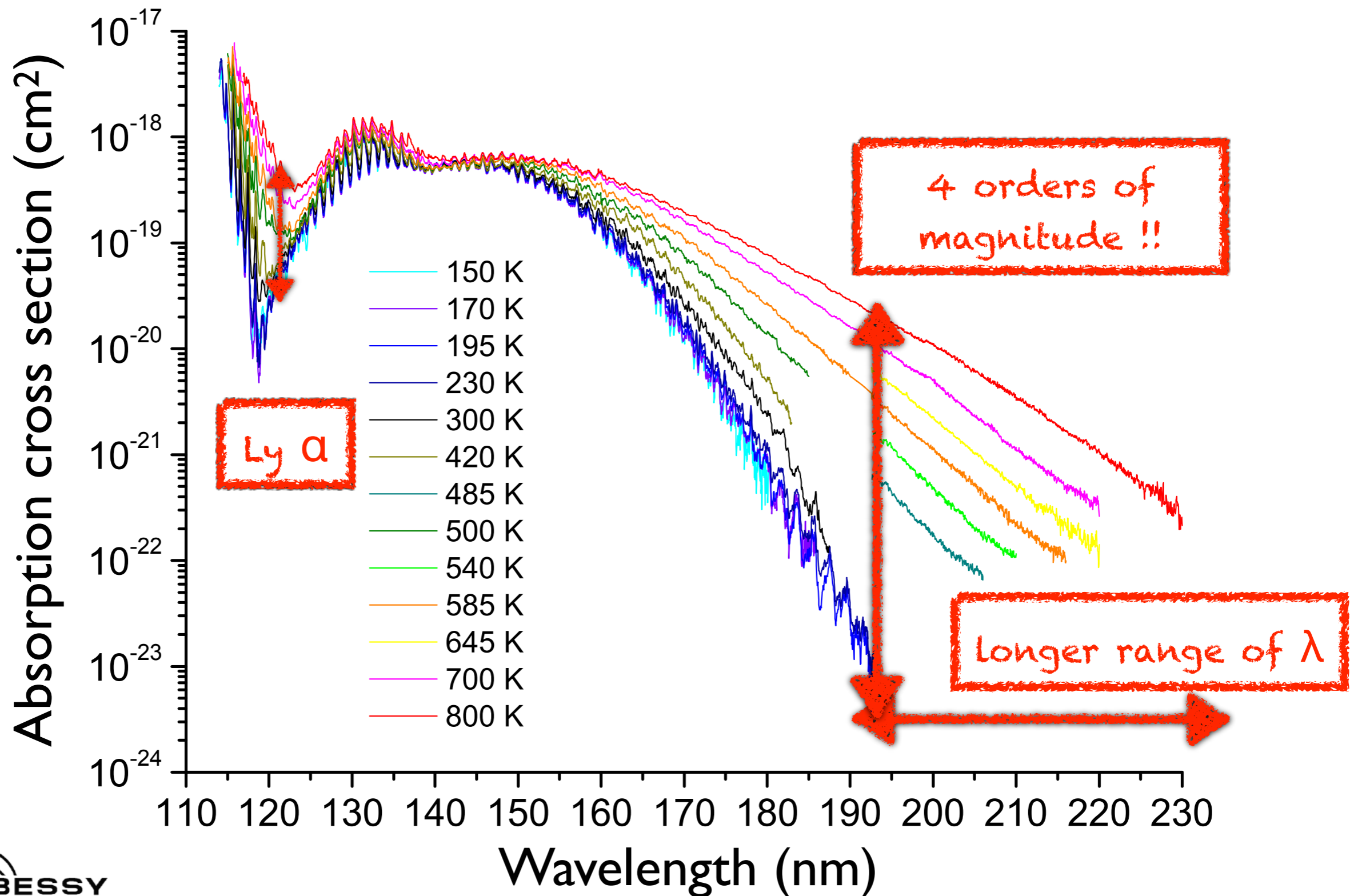
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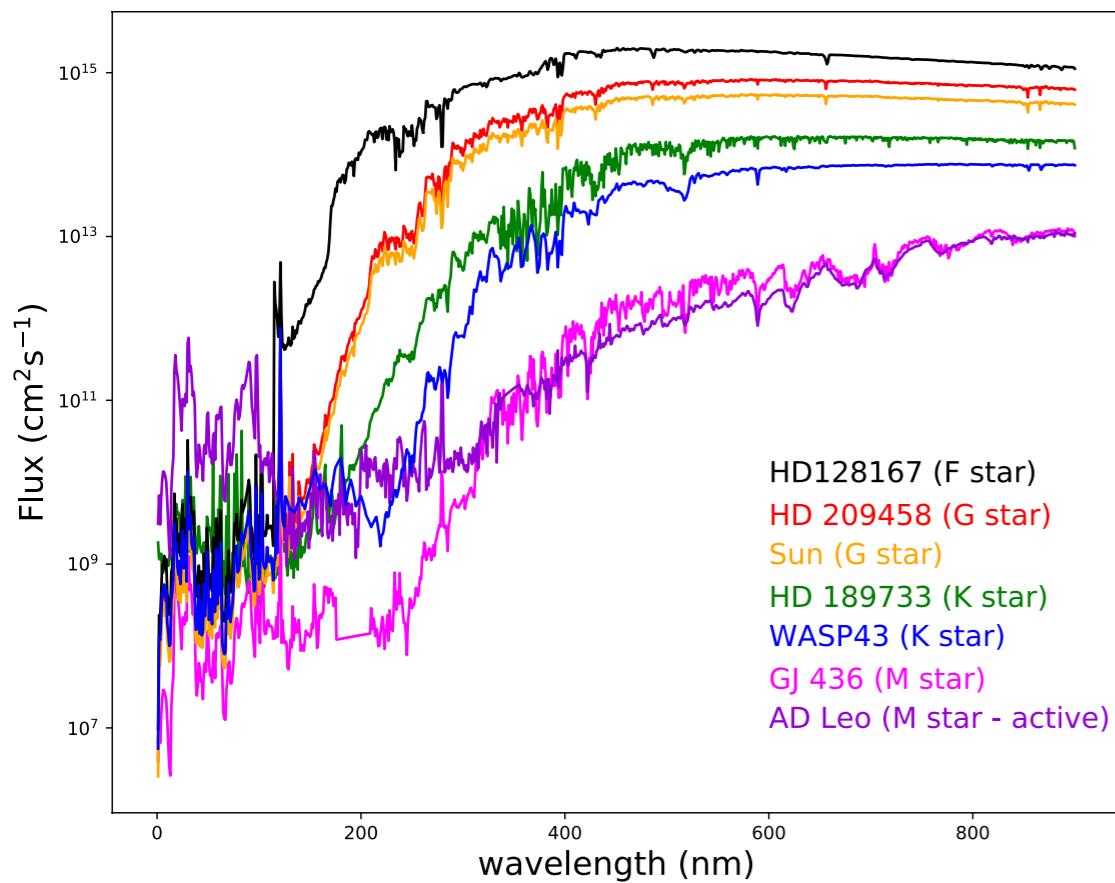
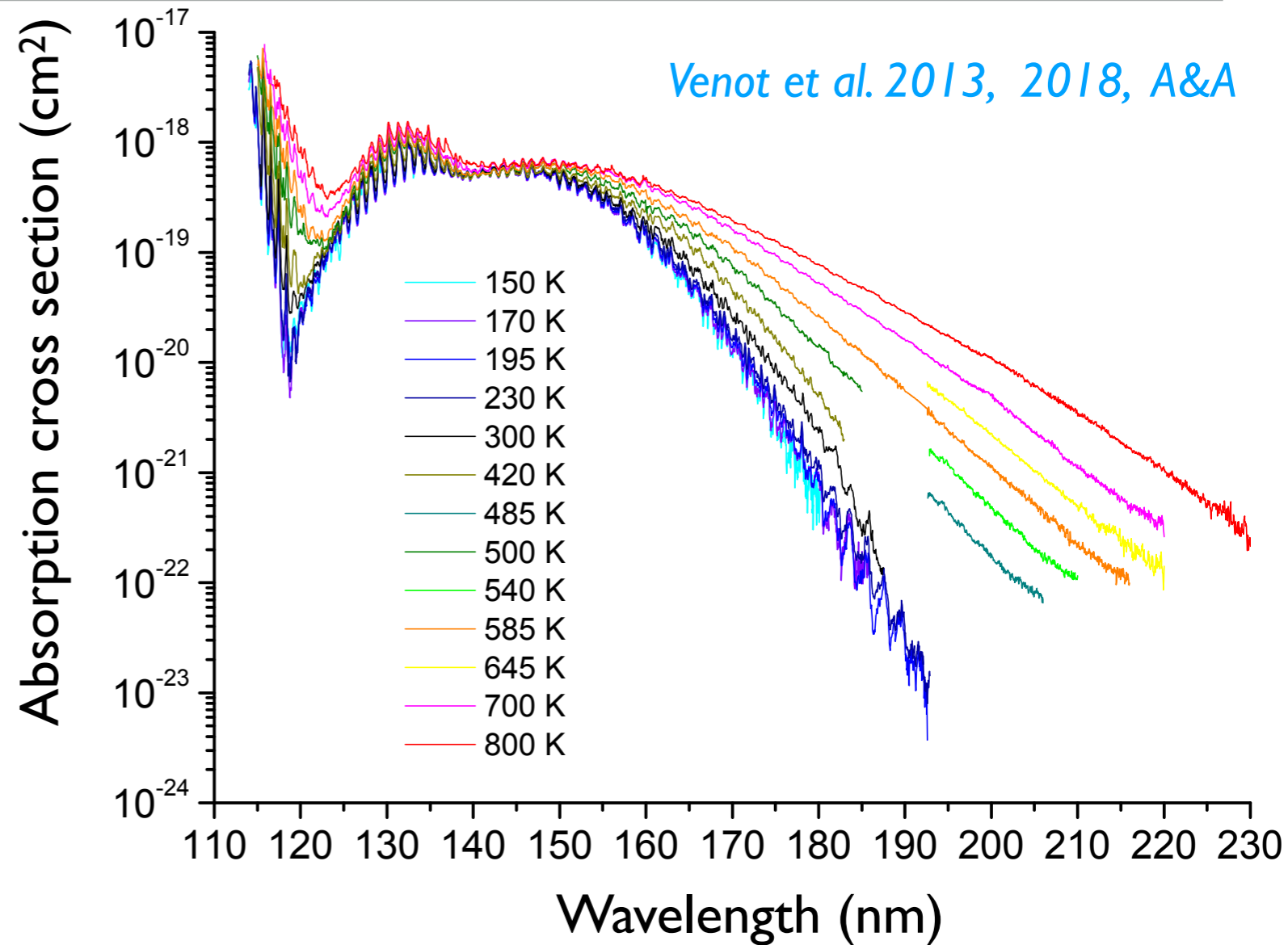


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between 150 and 230 nm a stellar flux generally increases by several orders of magnitude

→ photodissociations rate highly impacted !



Photodissociations rate :

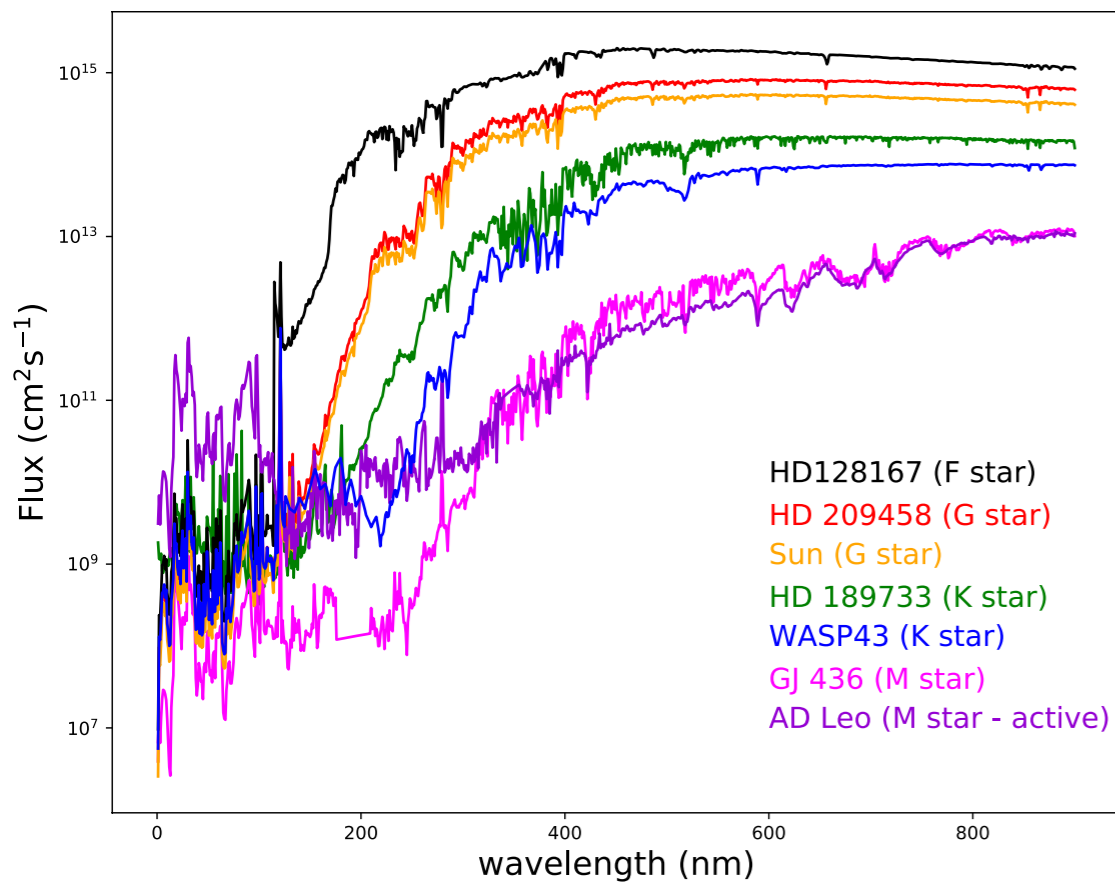
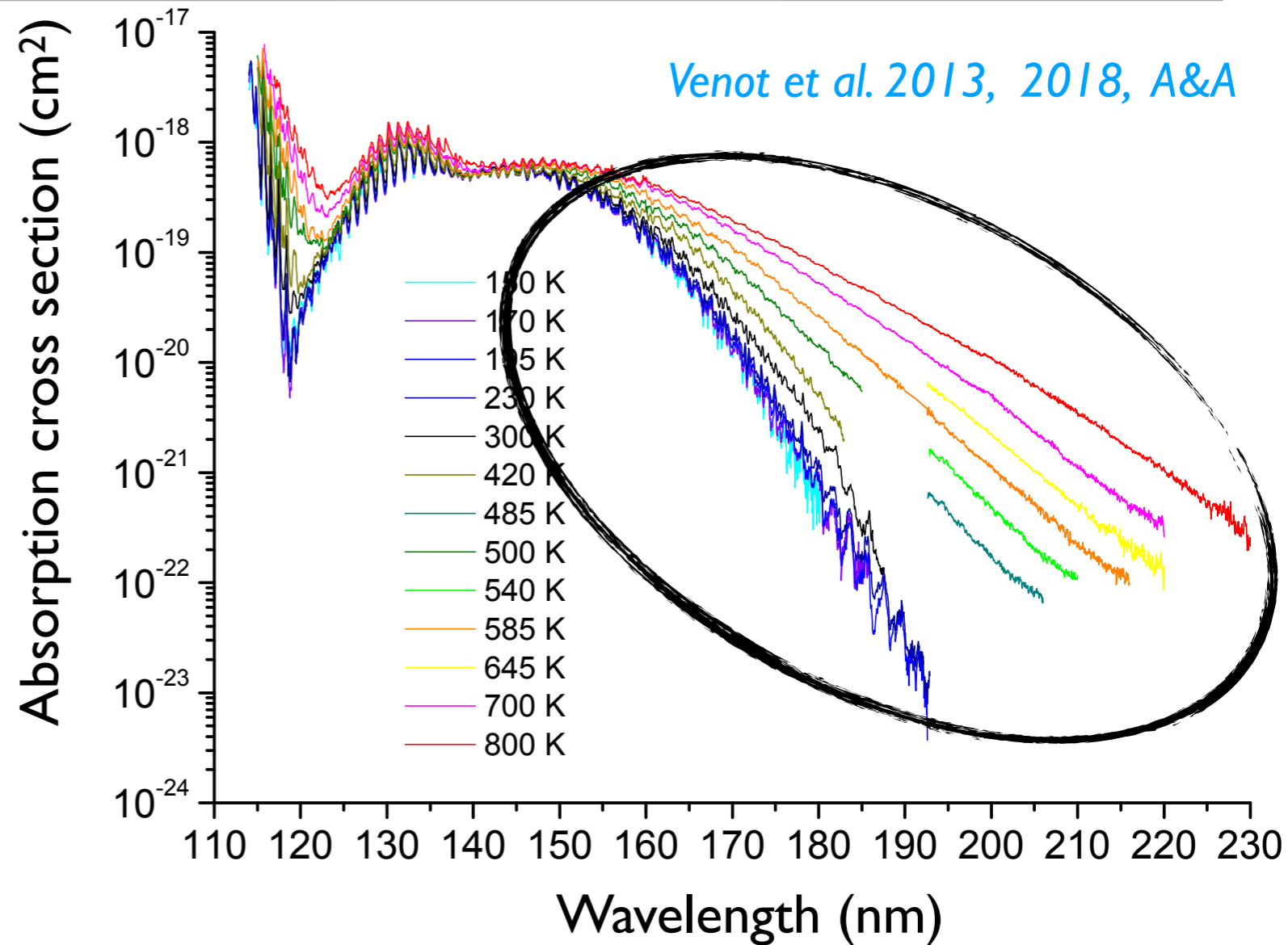
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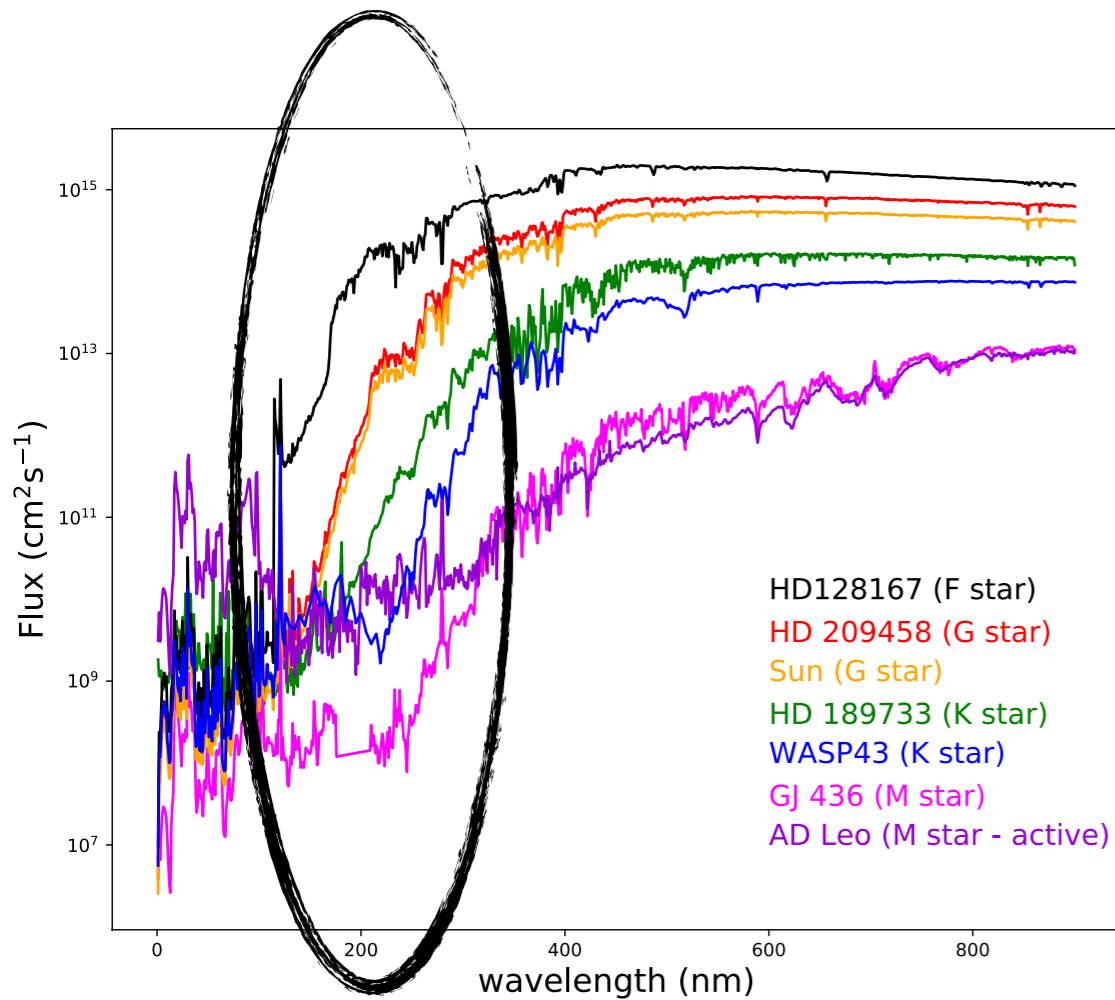
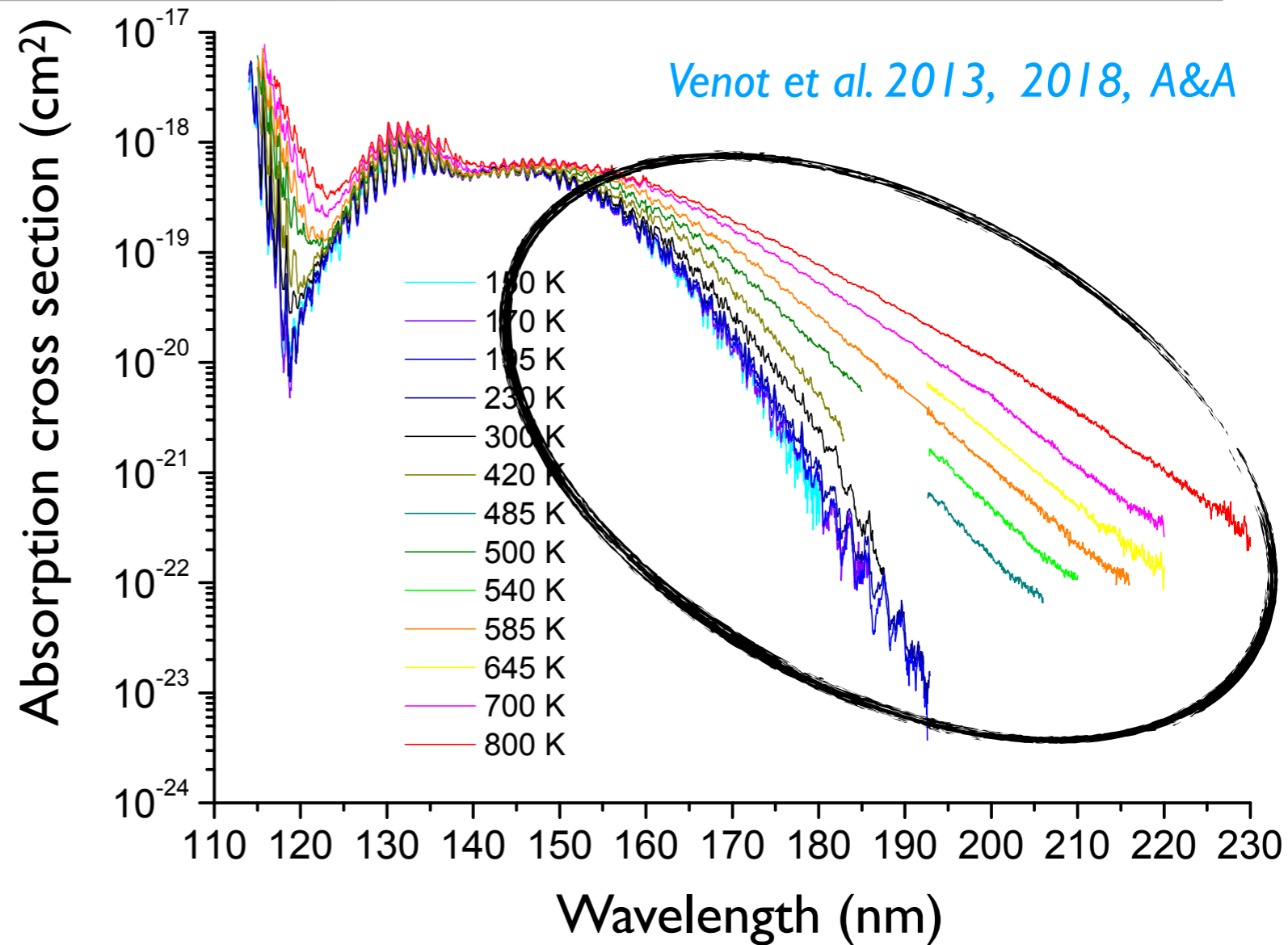


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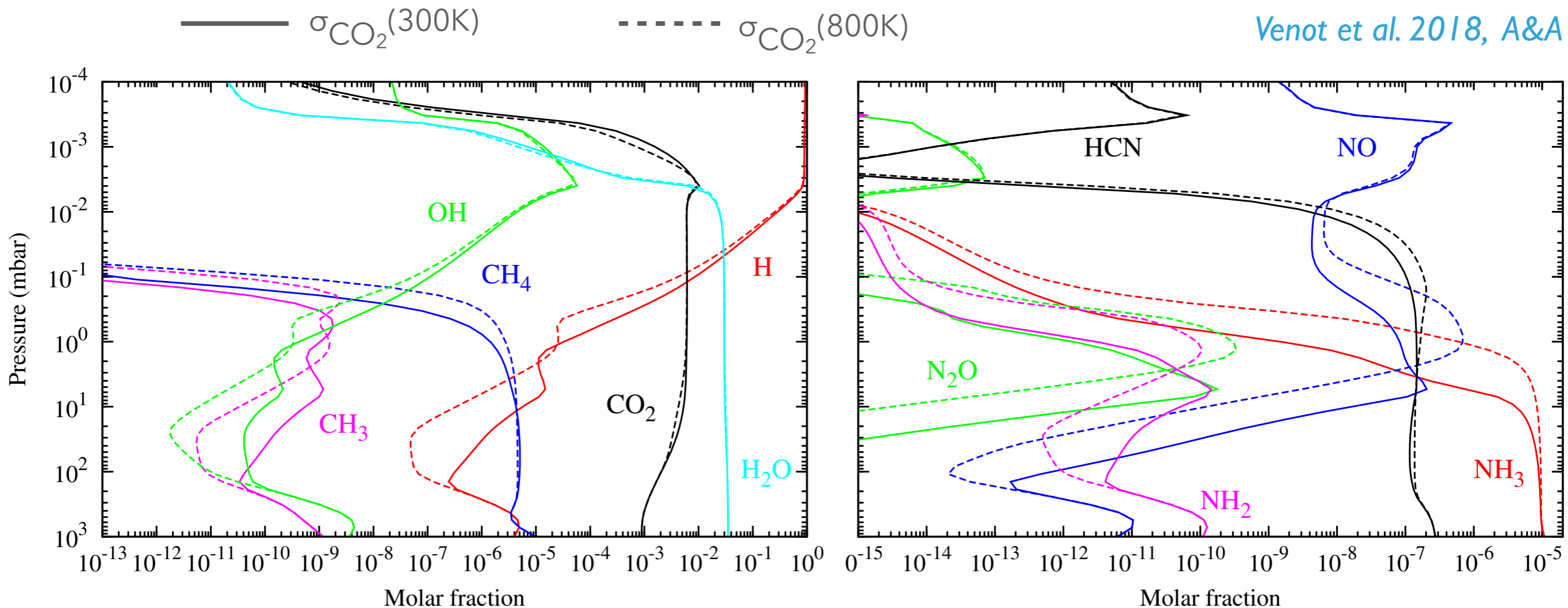
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# EFFECT ON THE ATMOSPHERIC COMPOSITION

- shielding + strong coupling between molecules through the continuity equation:

$$\frac{\partial n_i}{\partial t} = P_i - L_i - \text{div}(\Phi_i \vec{e}_z)$$

➔ change of  $\sigma_{\text{CO}_2}$  affects many species. Some species see their abundance more modified than that of  $\text{CO}_2$  !

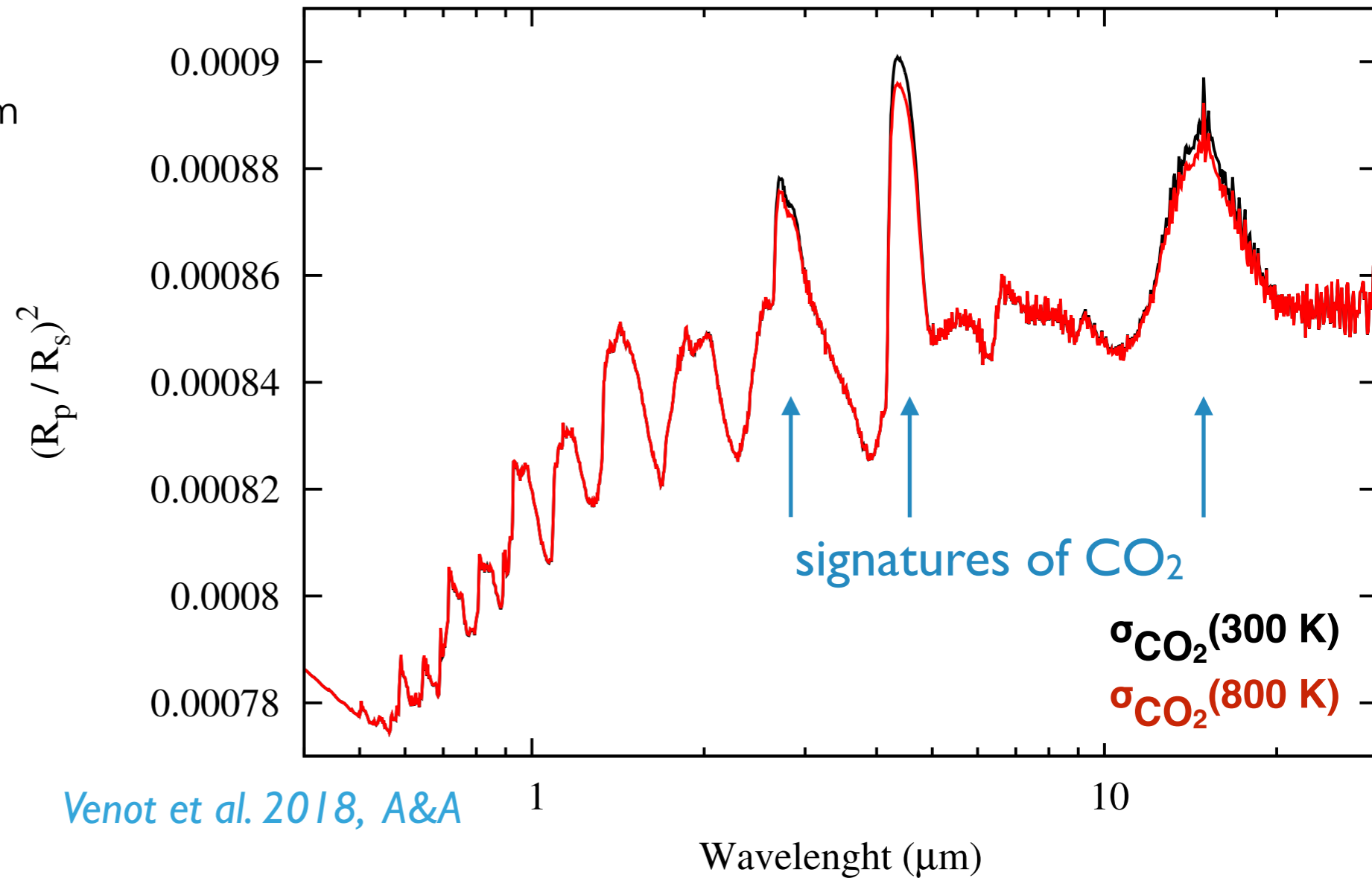


# EFFECT ON OBSERVATIONS

IR transmission synthetic spectrum  
calculated with Tau-REx  
(Waldmann et al. 2015a,b)

differences only in CO<sub>2</sub>  
absorption bands

small departures (< 5 ppm)  
→ not detectable !

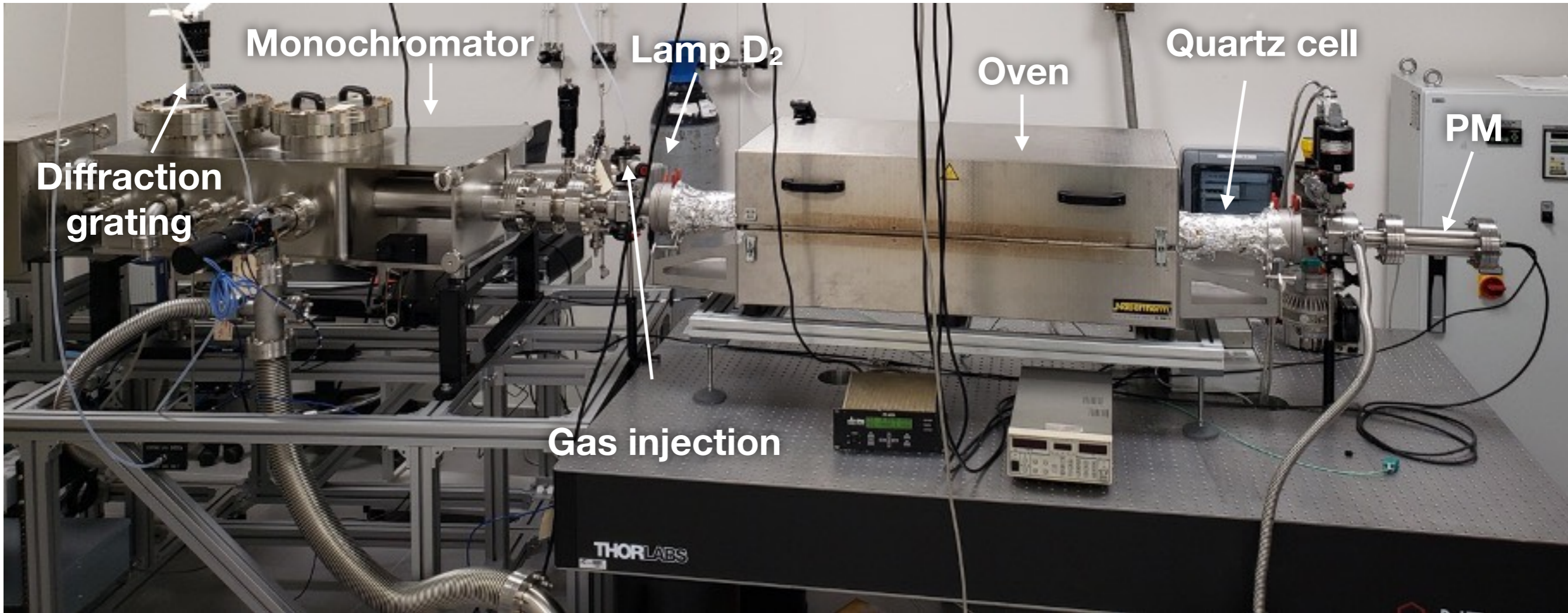


**don't conclude too fast ... only**  $\sigma_{\text{CO}_2}$  has been changed in this study ...

with the absorption cross section at high temperature of all species:

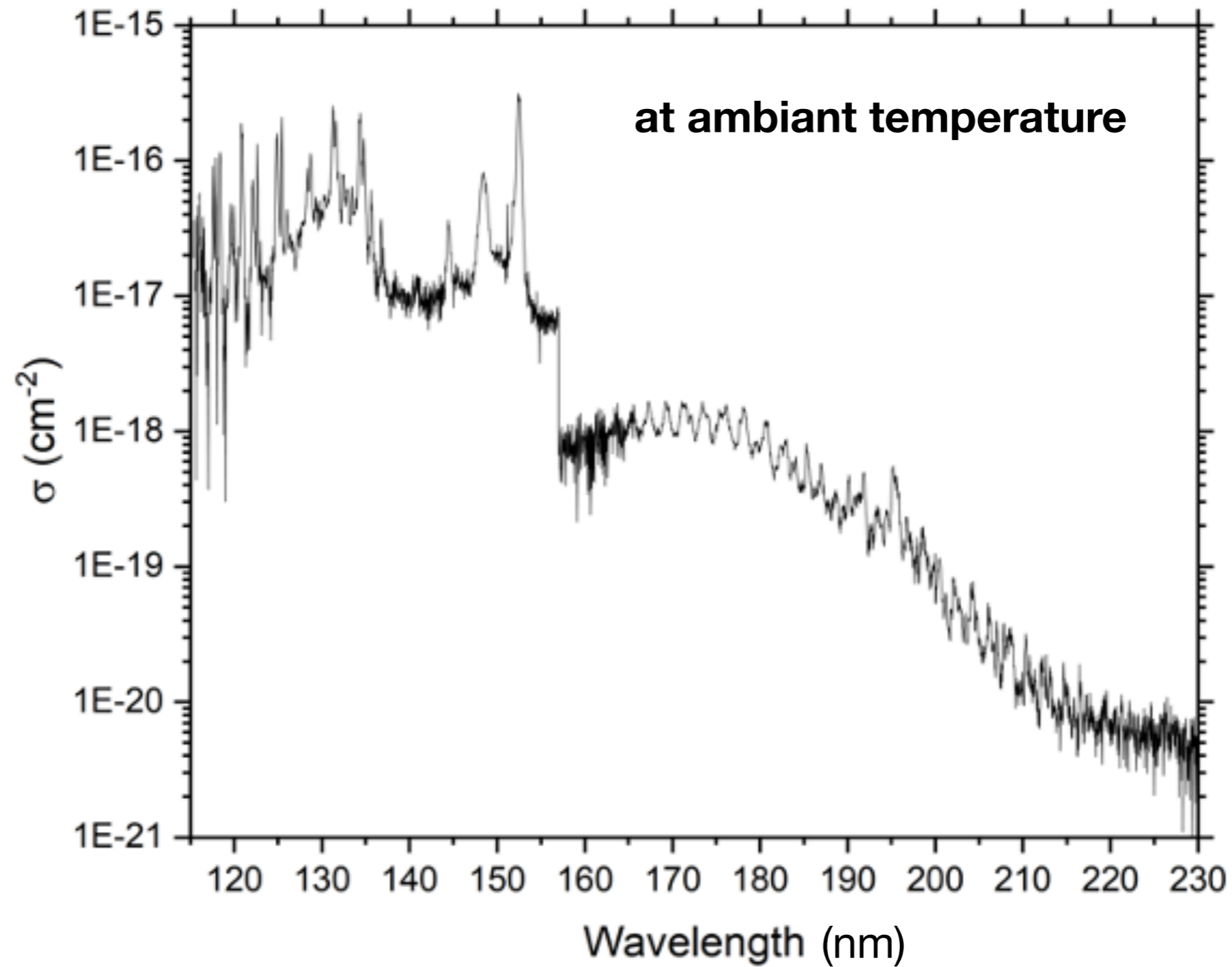
➔ more important changes of atmospheric composition

➔ more effect on the observables

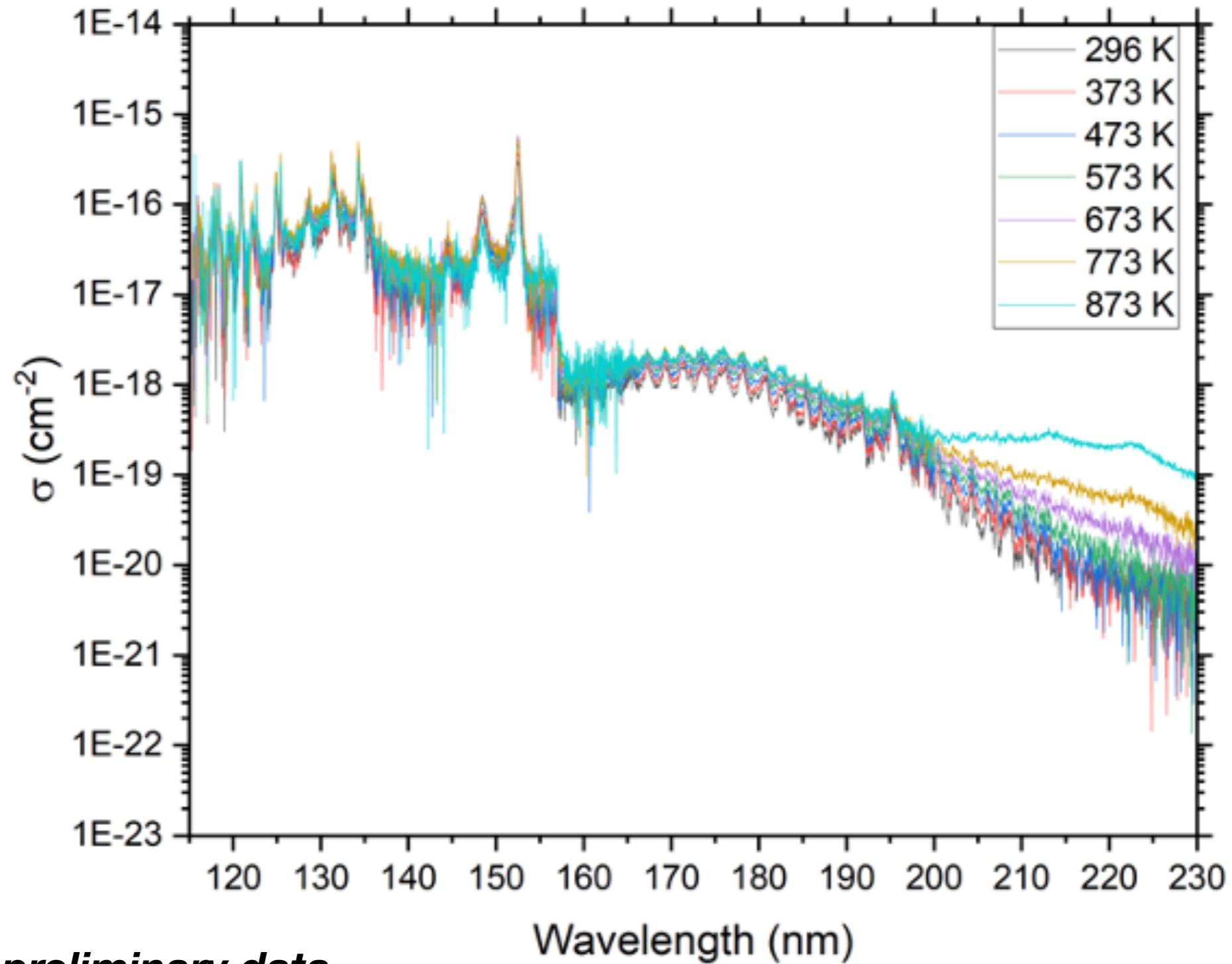


- ▶ future : study the thermal dependency of abs. cross section for all the molecules absorbing and abundant
- ▶ considerable increase of measurements in frequency and in quantity (limited currently by the short allocated time on synchrotron facilities)
- ▶ new VUV spectroscopy platform
  - ▶  $\lambda$  range = [50-300] nm
  - ▶ resolution = 0.01 nm
- ▶ next targets :  $\text{NH}_3$ ,  $\text{C}_2\text{H}_2$ ,  $\text{HCN}$ ....

# C<sub>2</sub>H<sub>2</sub> ABSORPTION CROSS-SECTION



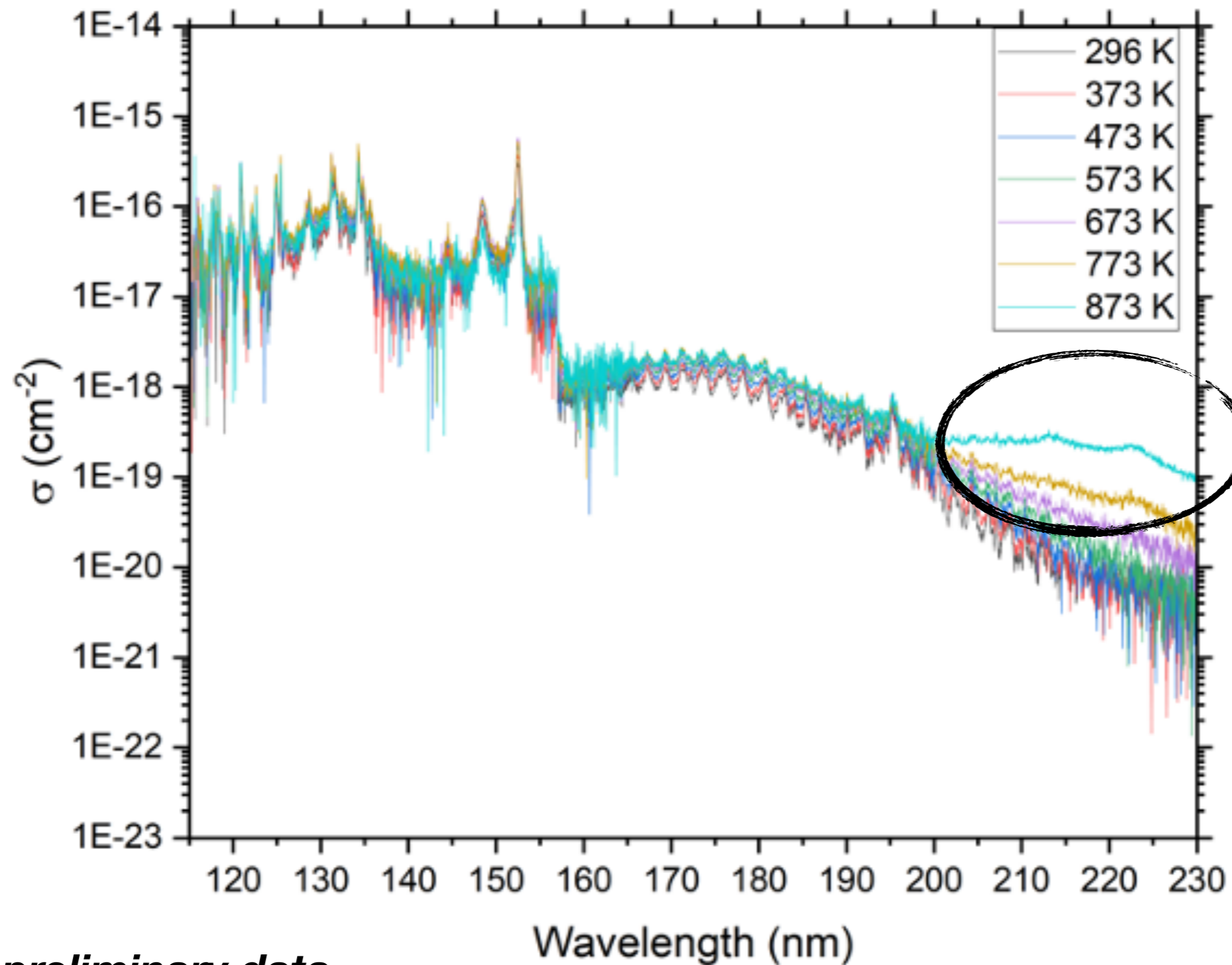
# C<sub>2</sub>H<sub>2</sub> ABSORPTION CROSS-SECTION



*preliminary data*

*Fleury, Poveda, Venot et al. in prep*

# C<sub>2</sub>H<sub>2</sub> ABSORPTION CROSS-SECTION



suspicious  
increase....  
thermal  
dissociation ?

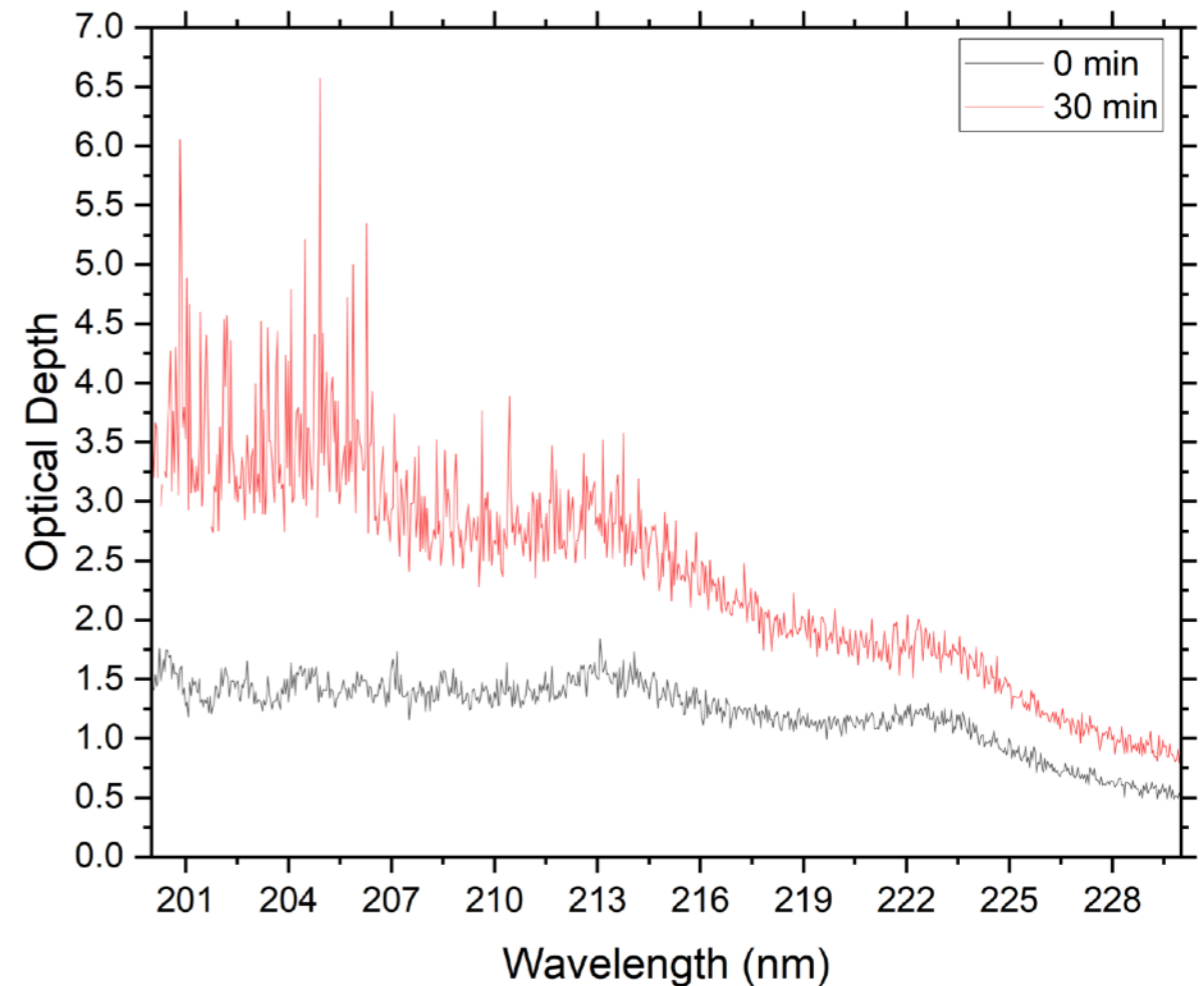
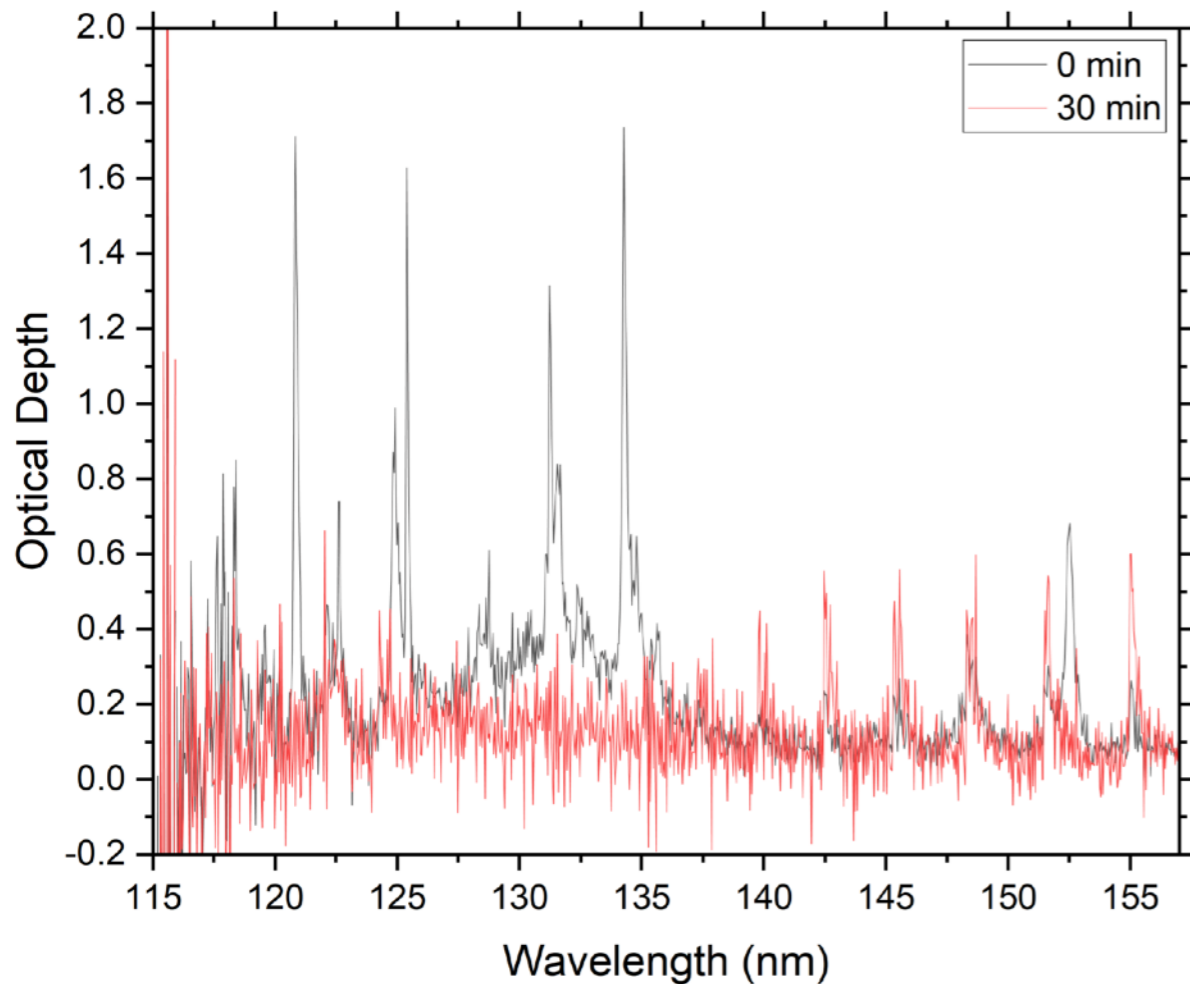
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# EXPERIMENTAL ISSUES

## THERMAL DISSOCIATION

- ▶ above  $\sim 700$  K : thermal dissociation of molecules
- ▶ Pressure in the cell increases,  $C_2H_2$  absorption features decrease, but new features...  
= new compound ?

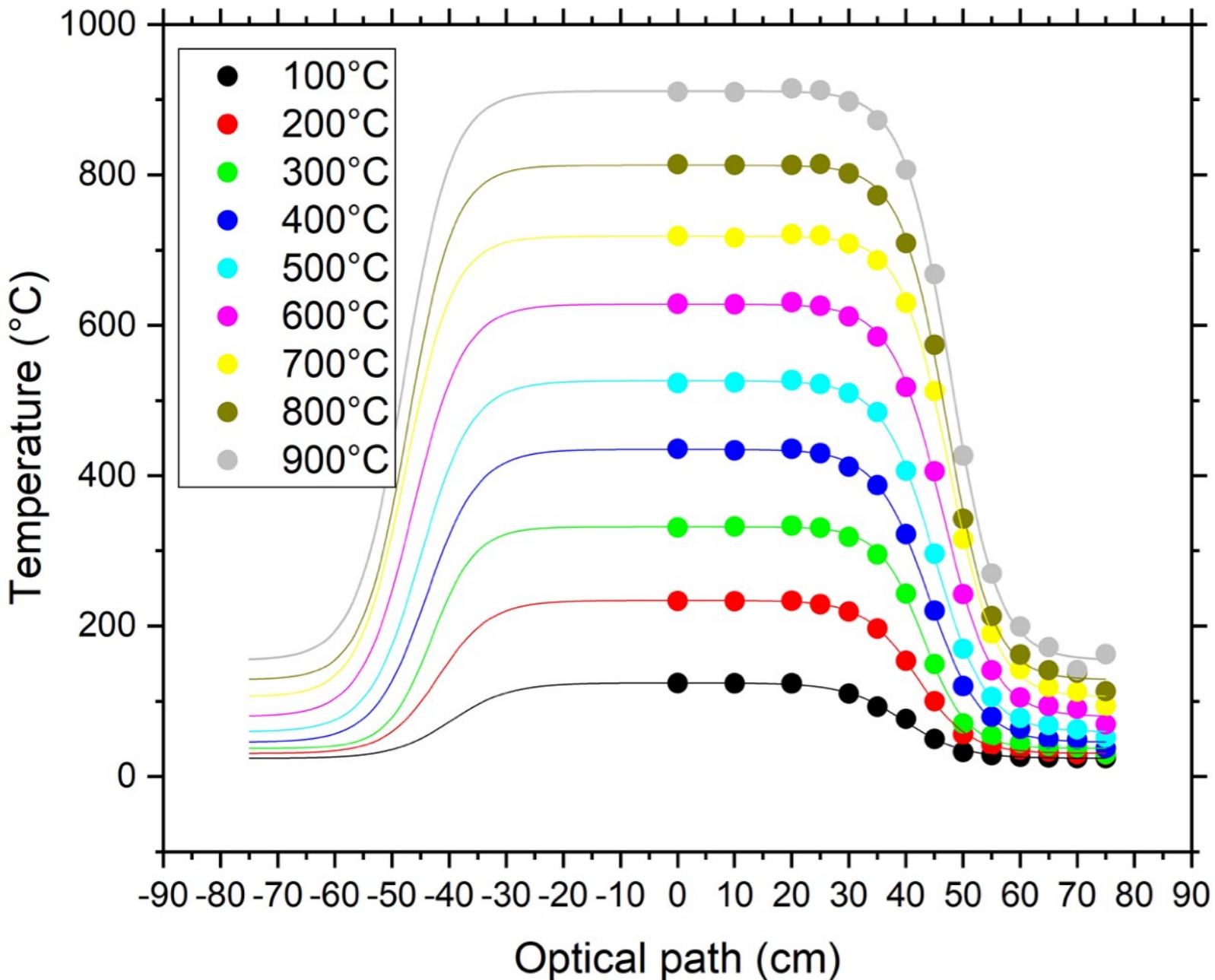


- ▶ difficult to monitor acquisition of 20 minutes...
- ▶ change from the previous Kantal cell to Quartz: reduces the issue but does not remove it



# EXPERIMENTAL ISSUES

## TEMPERATURE INSIDE THE CELL



cell

- ▶ thermal gradient: uncertainty on the T corresponding to the absorption measured (combination of parcels of gas at different T)
- ▶ data processing in Venot+2018: all the gas is at T<sub>max</sub>
- ▶ from now (data on new UV platform): modelling of the thermal gradient



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