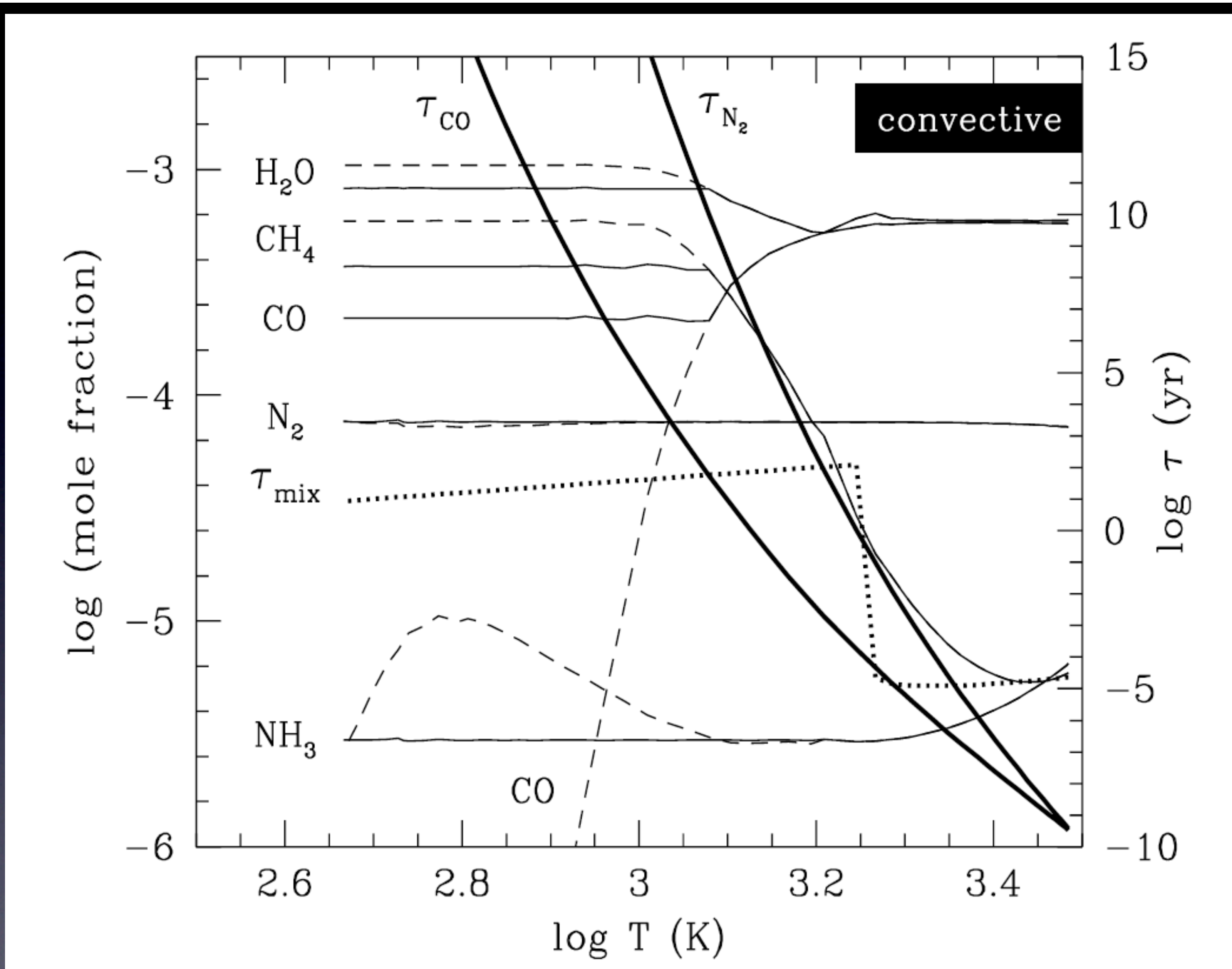
Non-equilibrium Chemistry

Mark Marley
NASA AMES

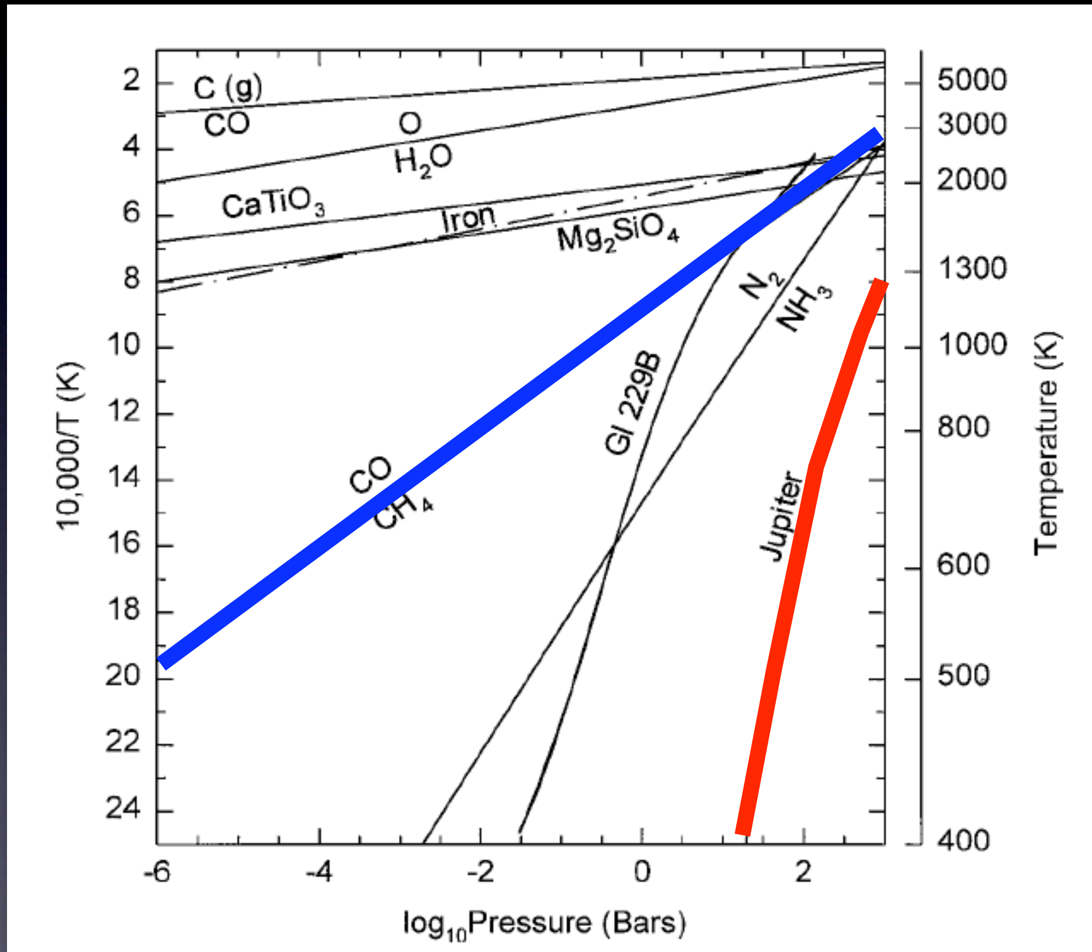
- Equilibrium Chemistry
  - specify abundance of elements
  - account for gravitational settling (rainout)
  - compute abundance of molecules at equilibrium (ignoring kinetics)
- Non-equilibrium chemistry
  - also account for kinetics
  - compare dynamical transport timescale to time to reach equilibrium

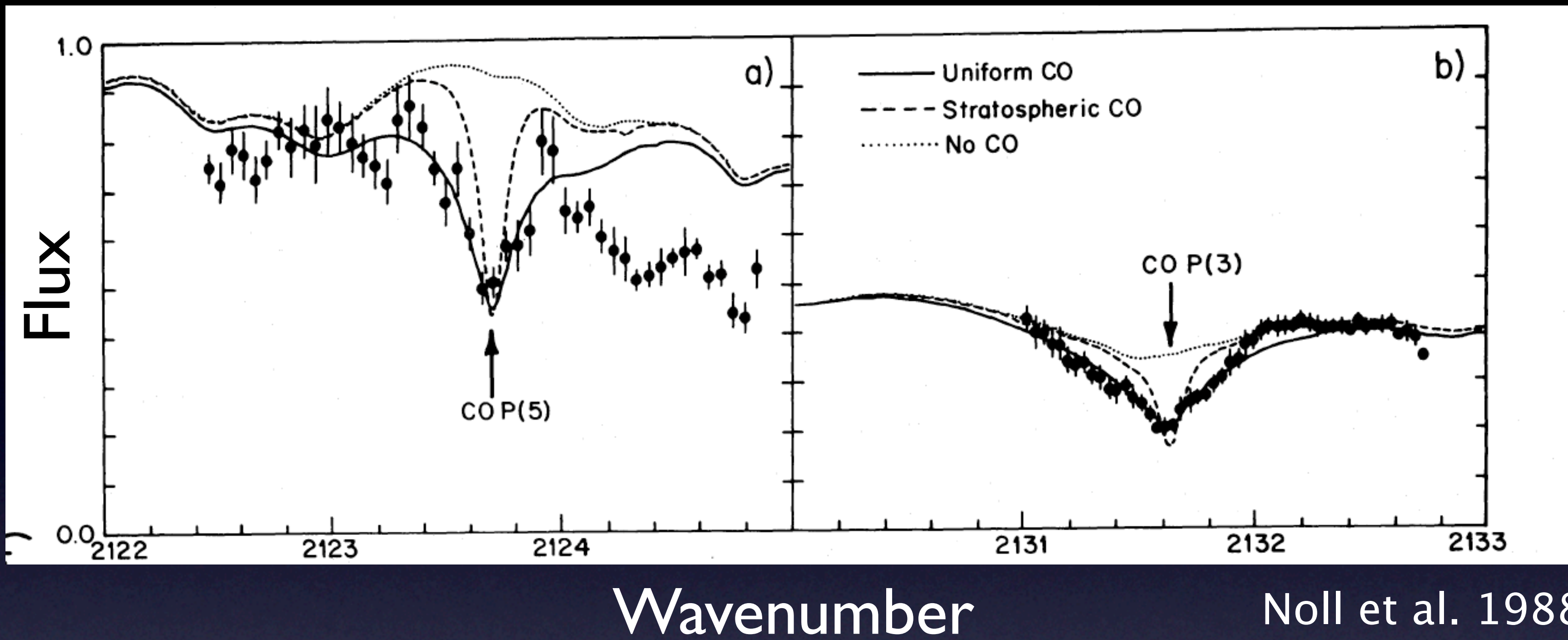


convective
τ_{CO}
τ_{N_2}
H_2O
CH_4
CO
N_2
τ_{mix}
NH_3
CO
log (mole fraction)
−3
−4
−5
−6
log τ (yr)
15
10
5
0
−5
−10
2.6
2.8
3
3.2
3.4
log T (K)

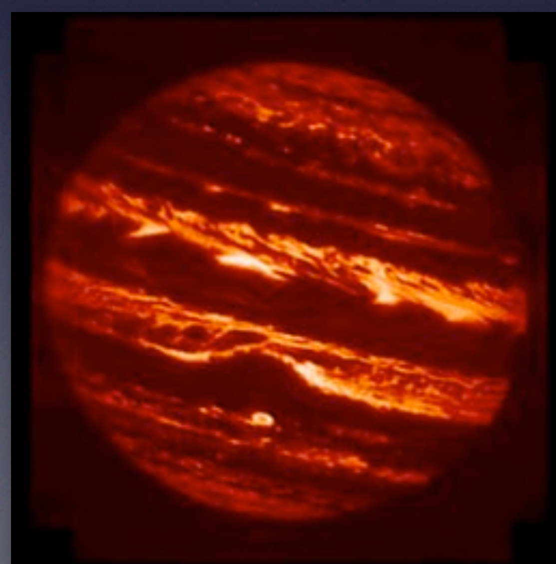
Example: CO on Jupiter

- Jupiter is well inside CH_4 stability regime
- Expect vanishingly small CO abundance



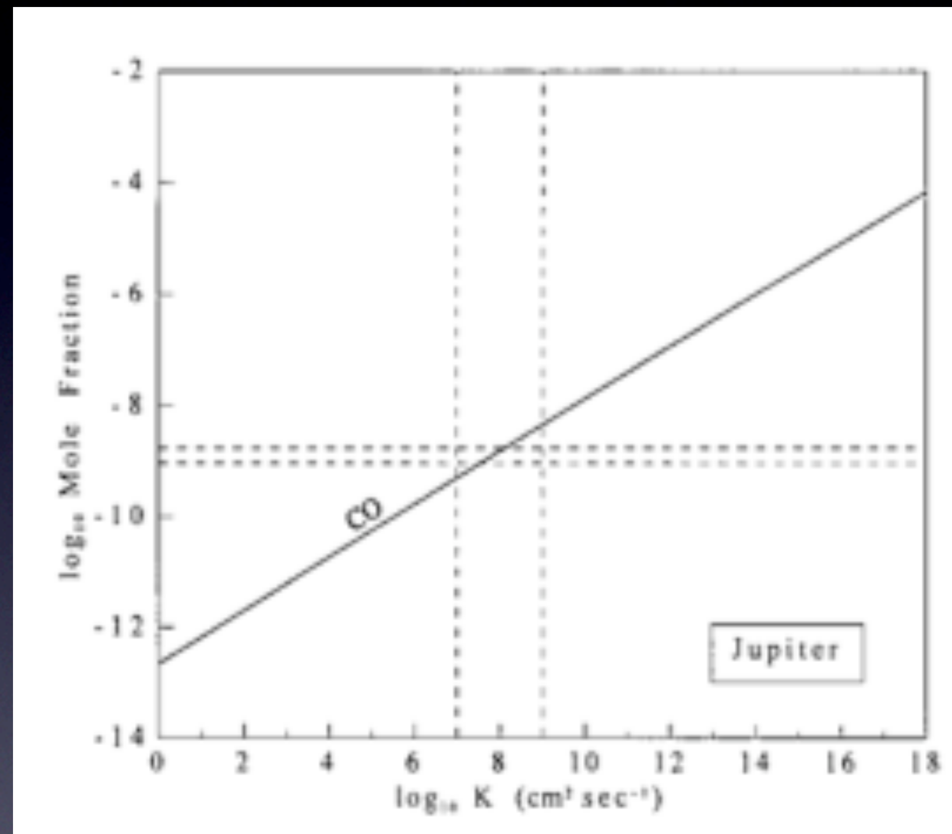


Noll et al. 1988



Dynamical transport

- Strong CO bond allows dynamical τ << chemical equilibrium τ
- CO abundant at depth
- Convection transports CO upwards to observable atmosphere
- abundance constrains vigor of mixing characterized as "eddy diffusivity" K_{zz}



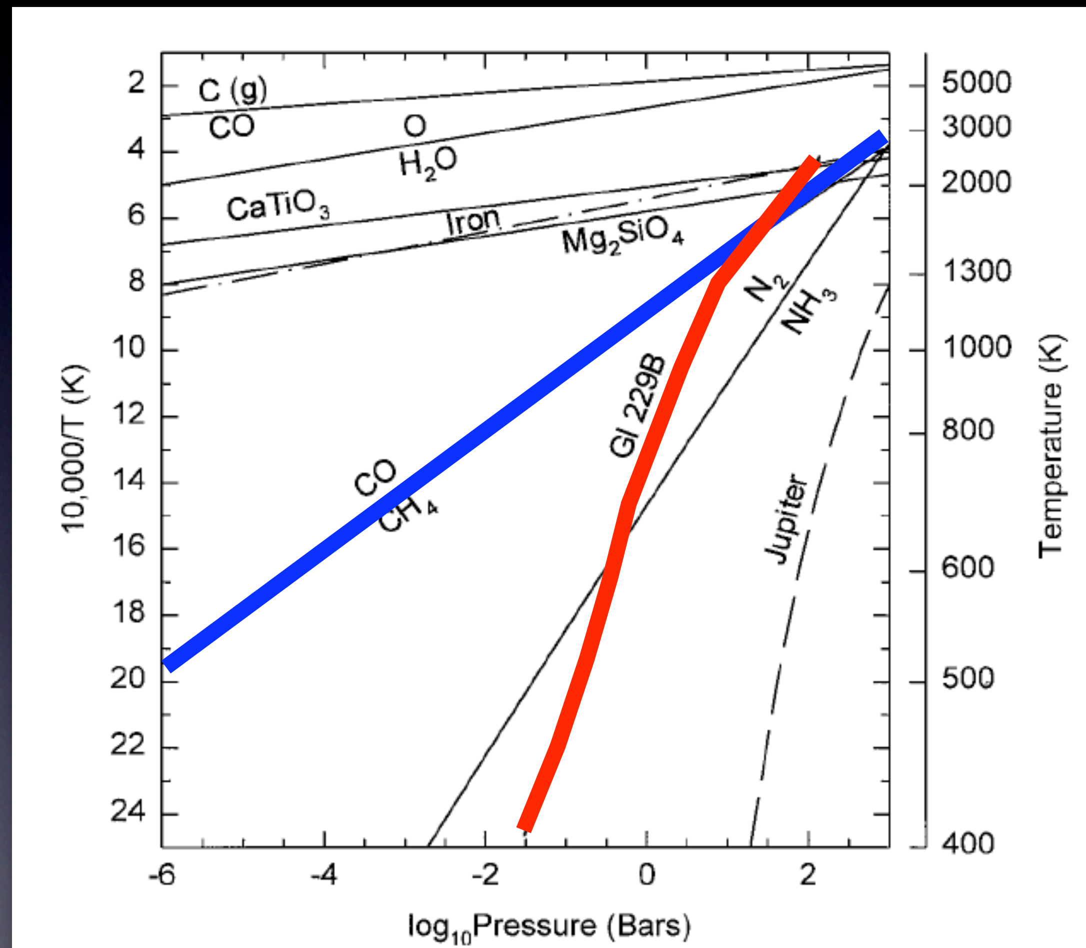
Fegley & Lodders (1994)

Non-equilibrium species in Jupiter & Saturn

- In equilibrium expect to have “rained out” at depth:
  - AsH_3 (instead of As (s))
  - PH_3 (instead of $NH_4H_2PO_4$ (s))
  - GeH_4 (instead of GeTe (s) and others)
- CO (instead of CH_4)
- All consistent with internal mixing by convection from deep interior
- Log K_{zz} (cm^2/sec) ~ 8

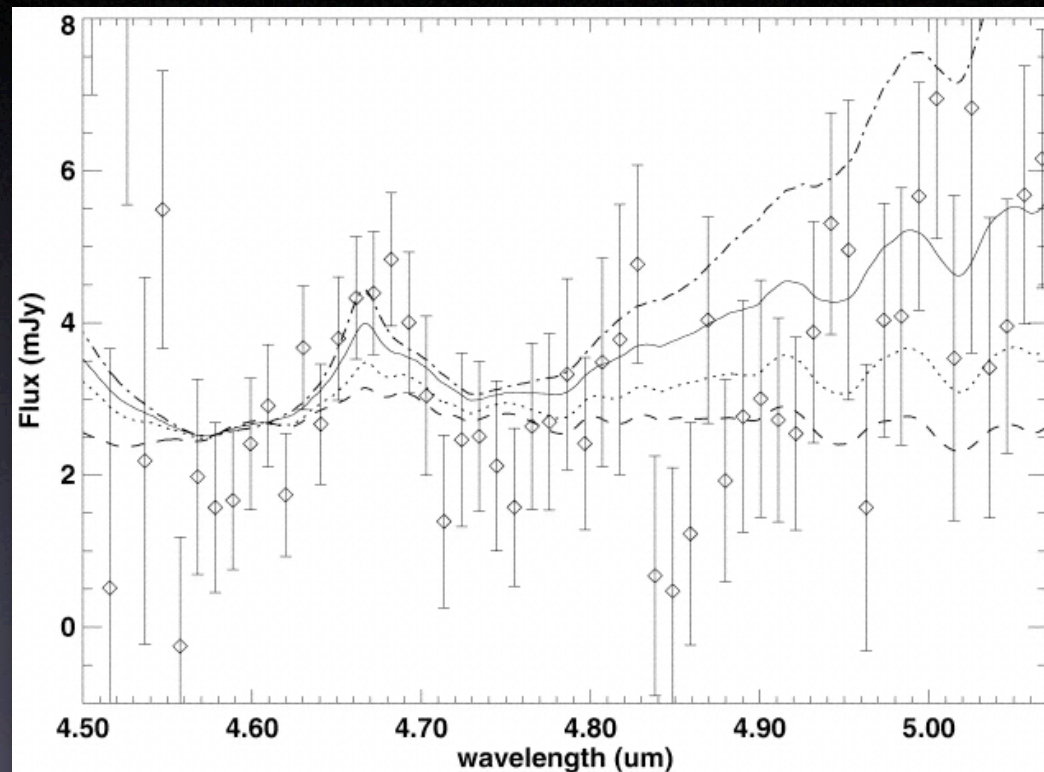
Example: CO on Gl229B

- Gl 229 B is also well inside CH_4 stability regime
- Expect vanishingly small CO abundance

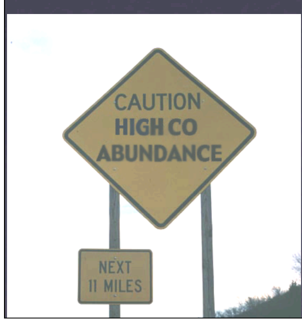


Non-equilibrium CO

- Predicted (Fegley & Lodders 1996) and observed (Noll et al. 1997) in Gl229B
- Can CO attenuate EGP 5-μm excess? Relevant for JWST planet search
- Strength of mixing provides input to cloud models

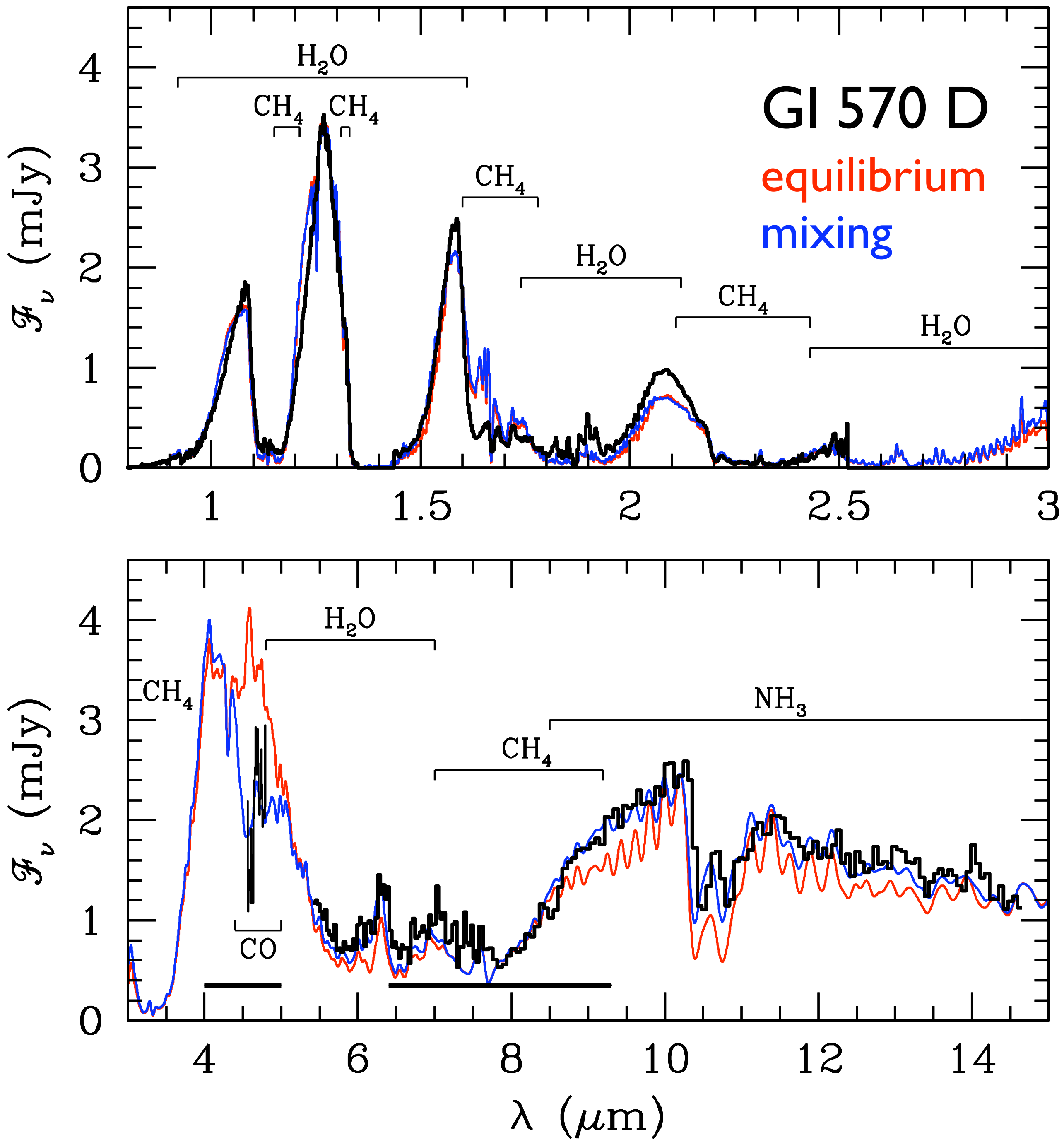


Noll et al. (1997)



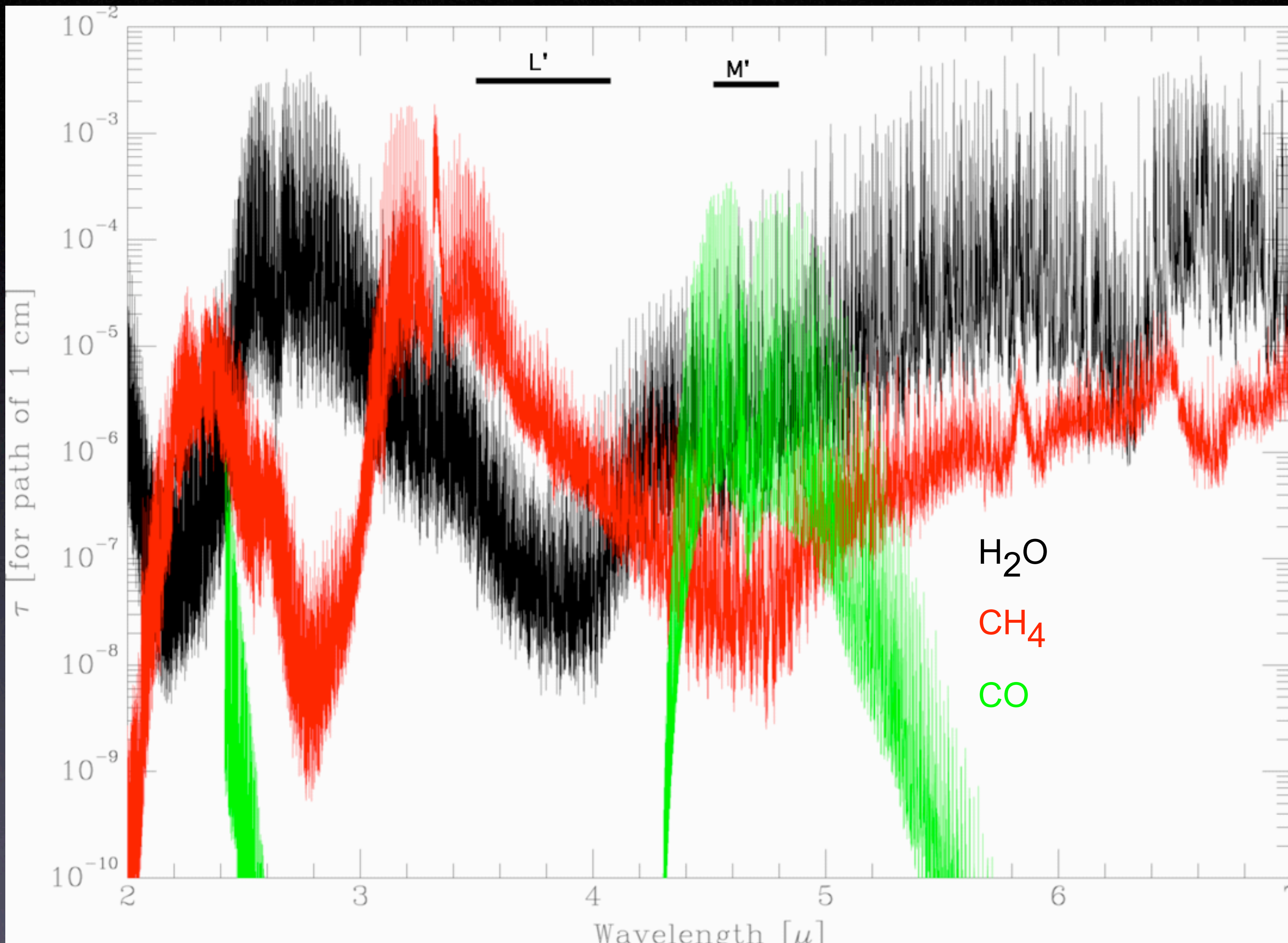
NH_3

- Ammonia works in the opposite sense as CO
- Invisible, stable N_2 is dredged up from deep atmosphere
- Decreases NH_3 abundance as seen by Spitzer IRS
- likely is postponing arrival of Y spectral type



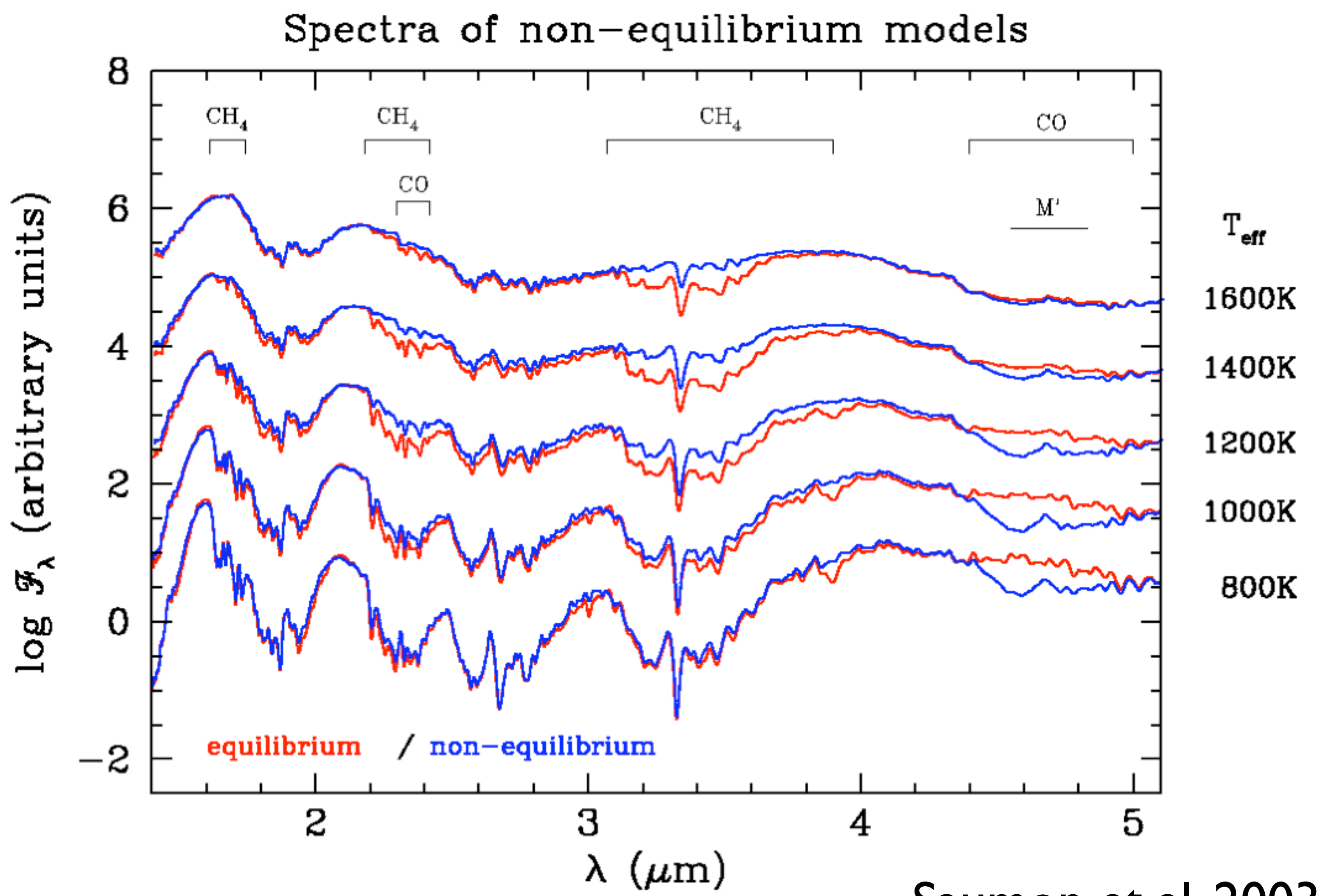
T_{eff} ~ 800 K

must account for K_{zz} to fit spectrum



1000 K; 1 bar

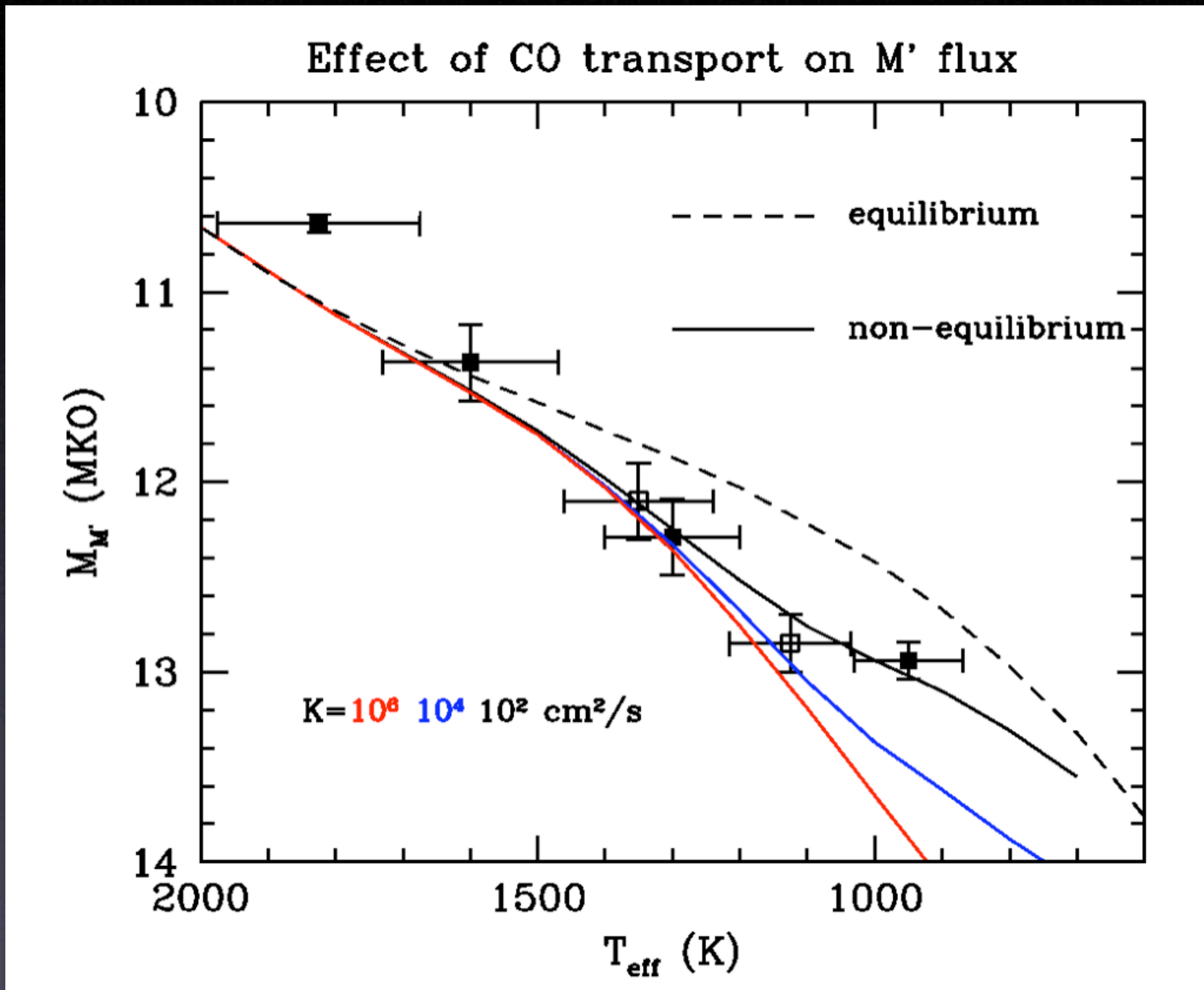
Mixing Matters in Near- & Mid-IR



Saumon et al. 2003

Methane arrives late at L, CO persists longer

Flux Supression at M band?



- Hubeny & Burrows (2007) find maximum of 40% supression around 1100 K, greatest at low g, negligible below 500 K

Saumon et al. (2003)

- Mixing is fundamental process in gas giants and brown dwarfs and must be considered in exoplanets (particularly impact on CO & CH_4)
- Log g, Teff, [M/H], K_{zz}, clouds all influence spectra
- Mixing can be in troposphere or stratosphere (eddy diffusion from breaking waves?)
- Test with HR 8799 planets and Fomalhaut b
- Opportunity to trace 3D winds on hot Jupiters, day-night instead of vertical T gradient (Showman)