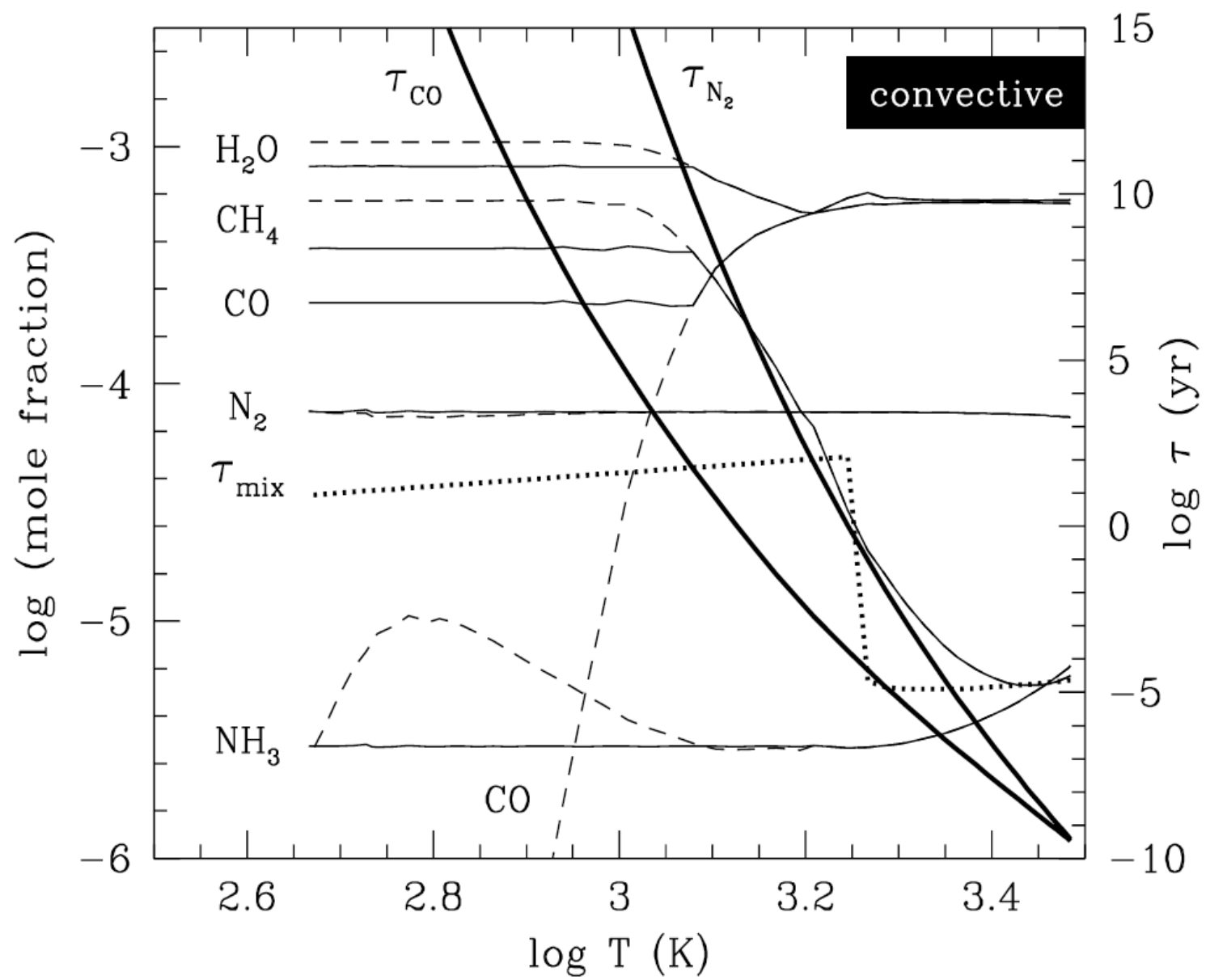


Non-equilibrium Chemistry

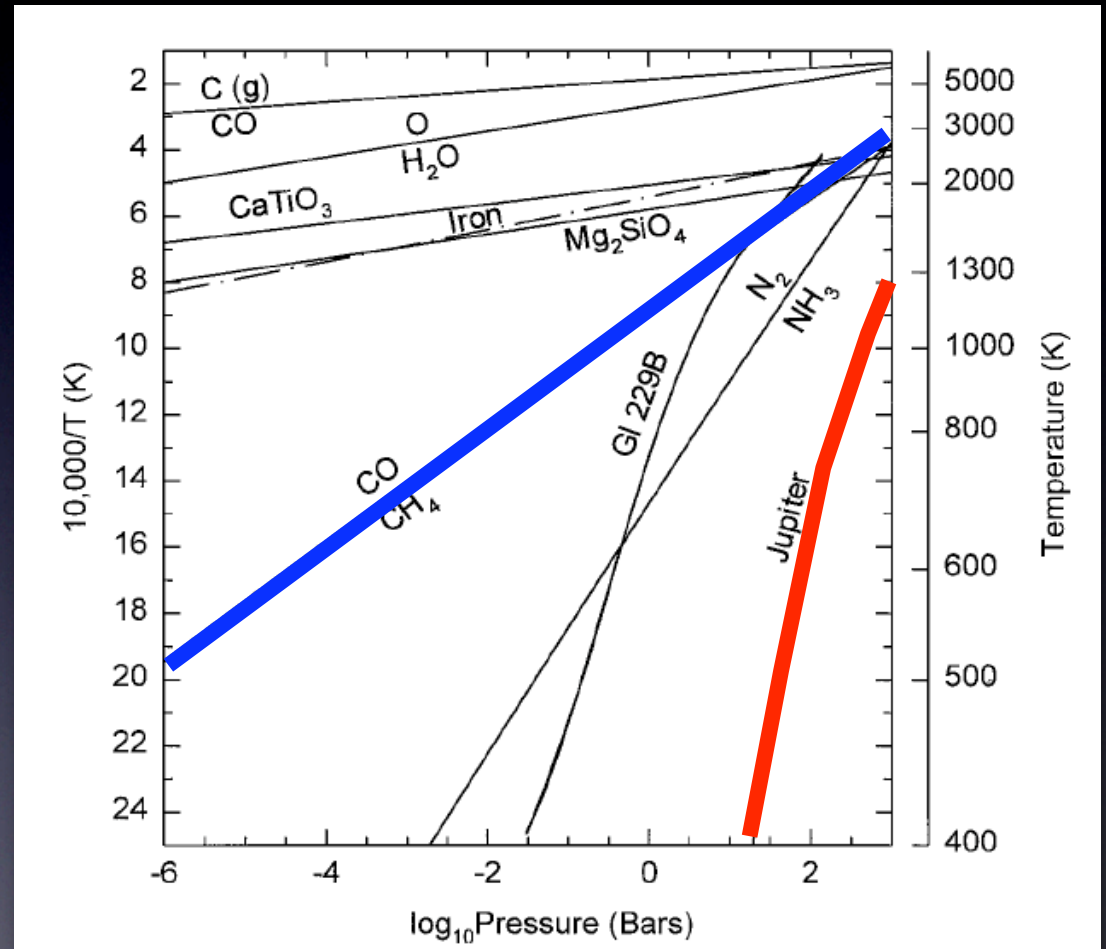
Mark Marley
NASA AMES

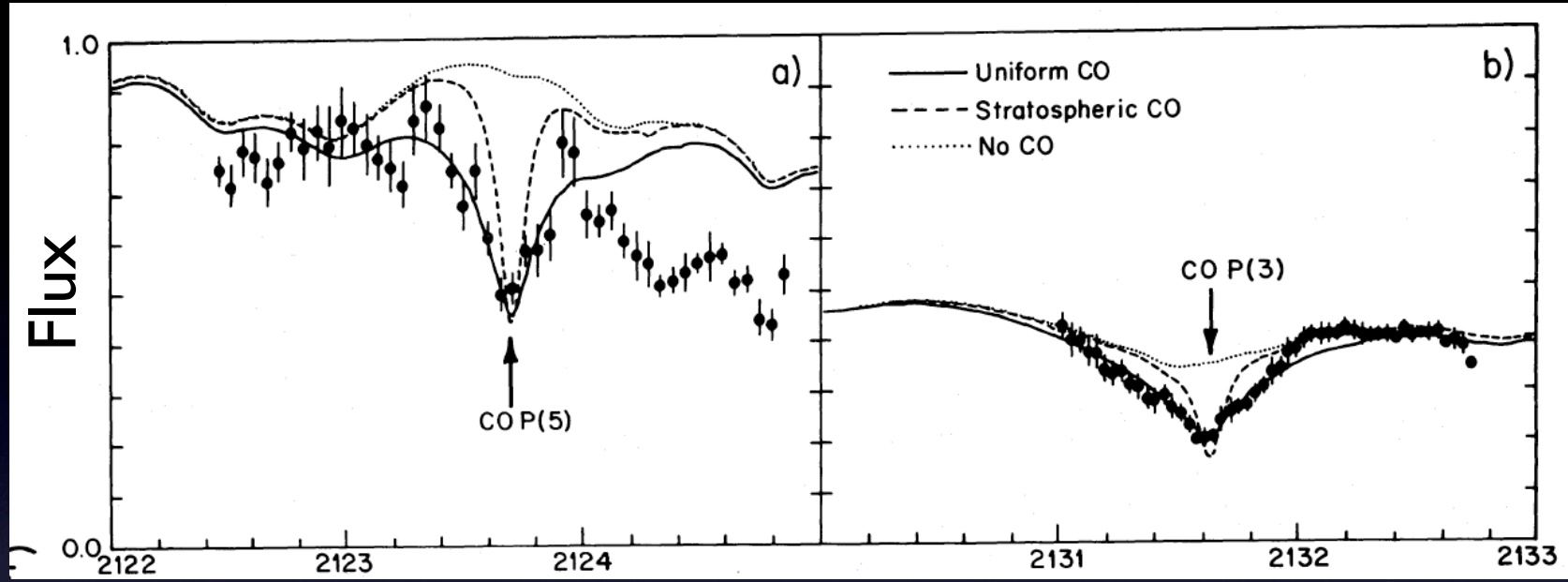
- Equilibrium Chemistry
 - specify abundance of elements
 - account for gravitational settling (rainout)
 - compute abundance of molecules at equilibrium (ignoring kinetics)
- Non-equilibrium chemistry
 - also account for kinetics
 - compare dynamical transport timescale to time to reach equilibrium



Example: CO on Jupiter

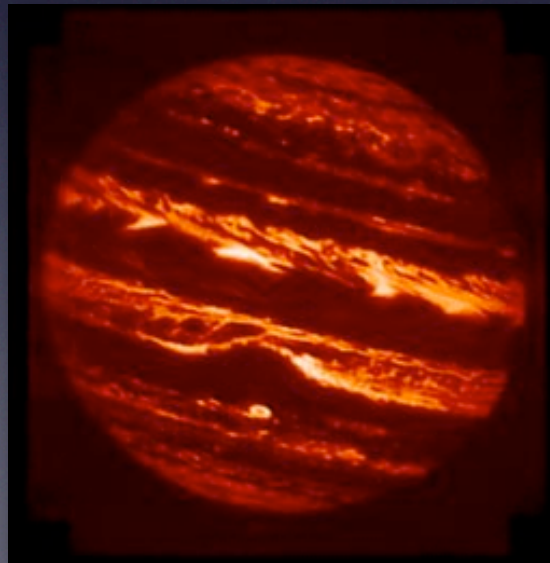
- Jupiter is well inside CH₄ stability regime
- Expect vanishingly small CO abundance





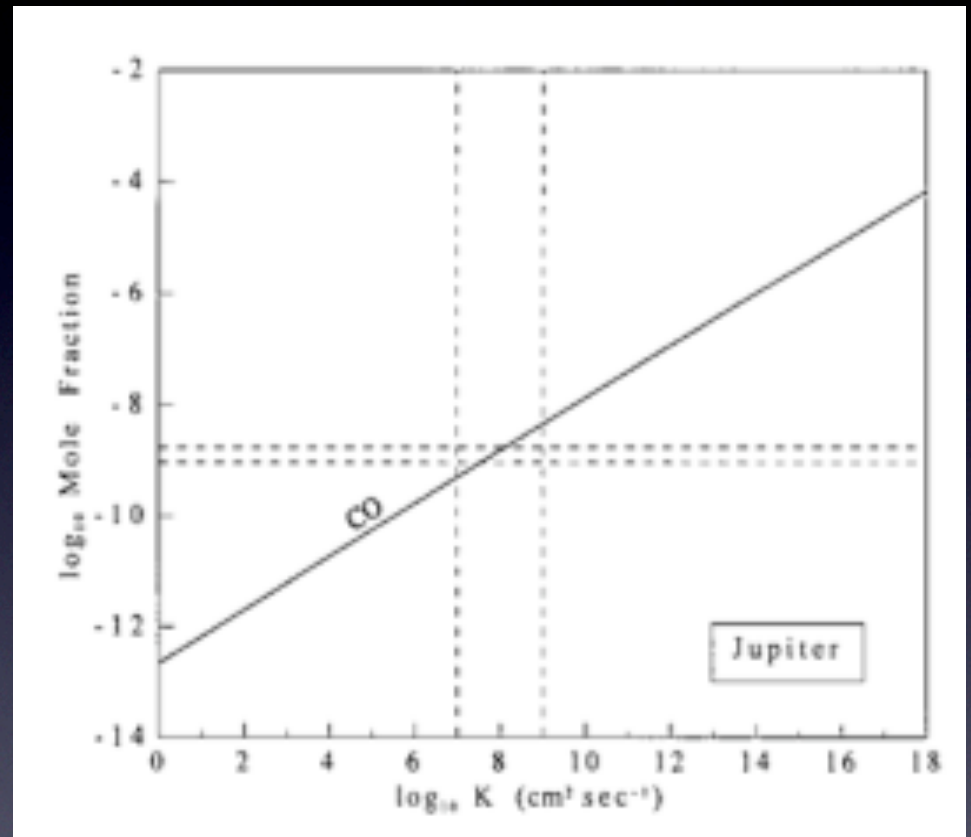
Wavenumber

Noll et al. 1988



Dynamical transport

- Strong CO bond allows dynamical $\tau \ll$ 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}



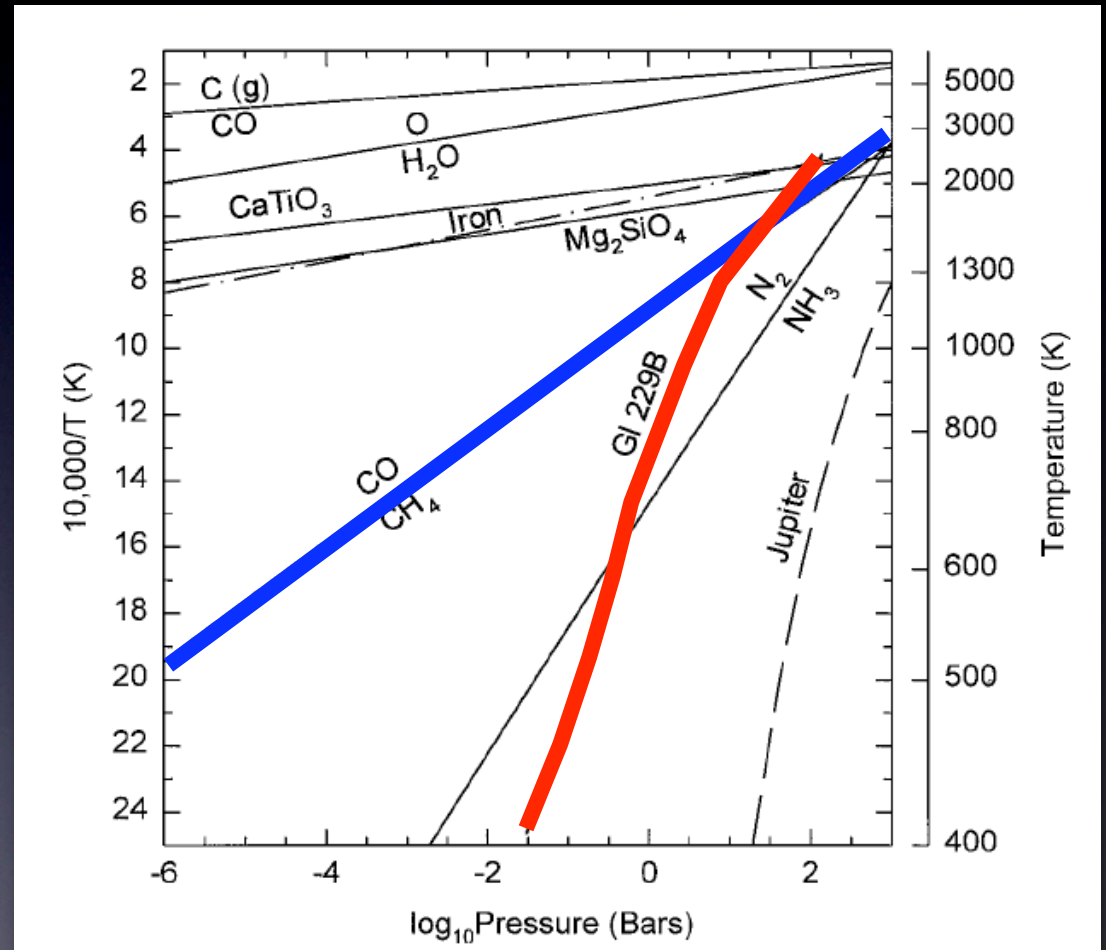
Fegley & Lodders (1994)

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 $\text{NH}_4\text{H}_2\text{PO}_4 \text{ (s)}$)
 - GeH_4 (instead of GeTe (s) and others)
- CO (instead of CH_4)
- All consistent with internal mixing by convection from deep interior
- $\text{Log } K_{zz} \text{ (cm}^2\text{/sec)} \sim 8$

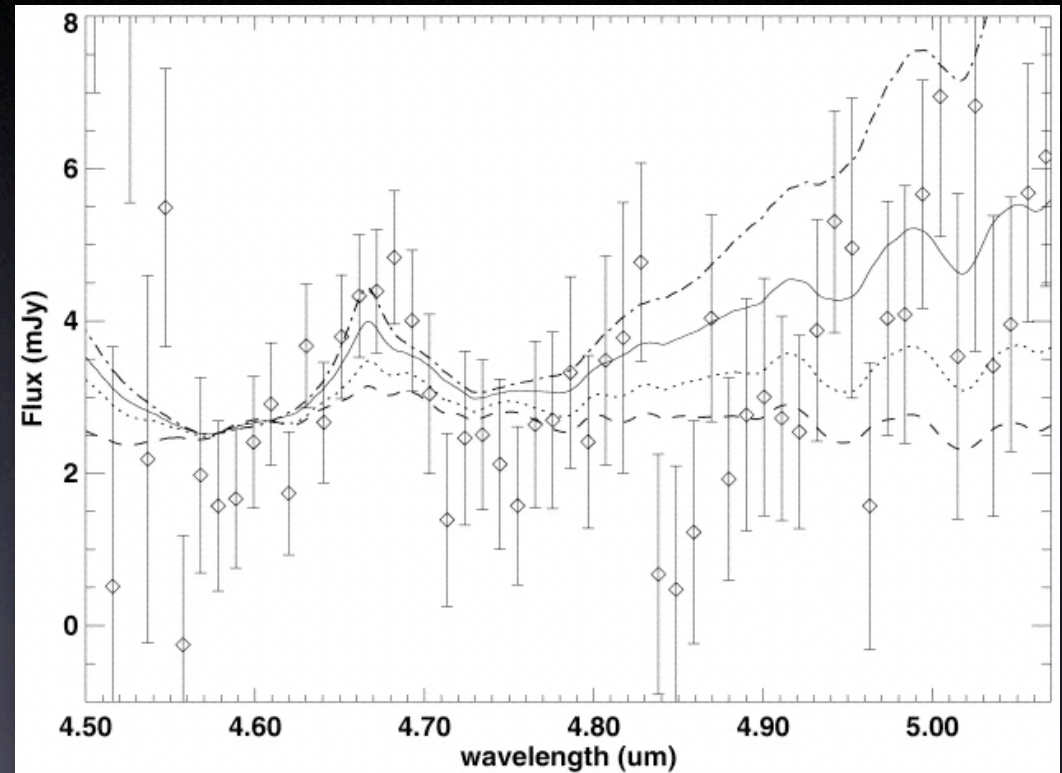
Example: CO on Gl229B

- Gl 229 B is also well inside CH₄ stability regime
- Expect vanishingly small CO abundance

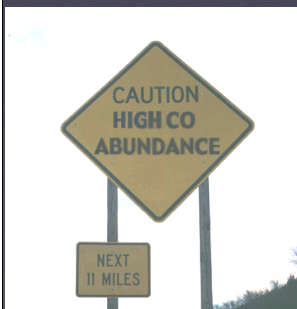


Non-equilibrium CO

- 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

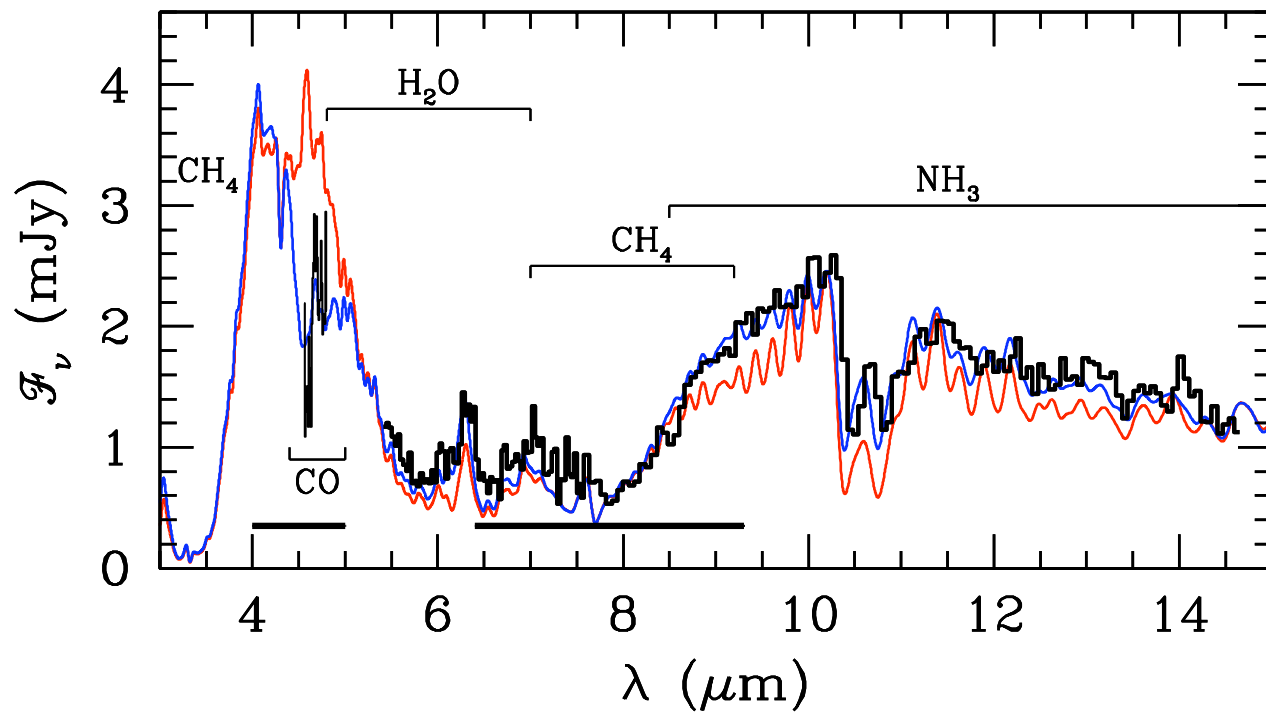
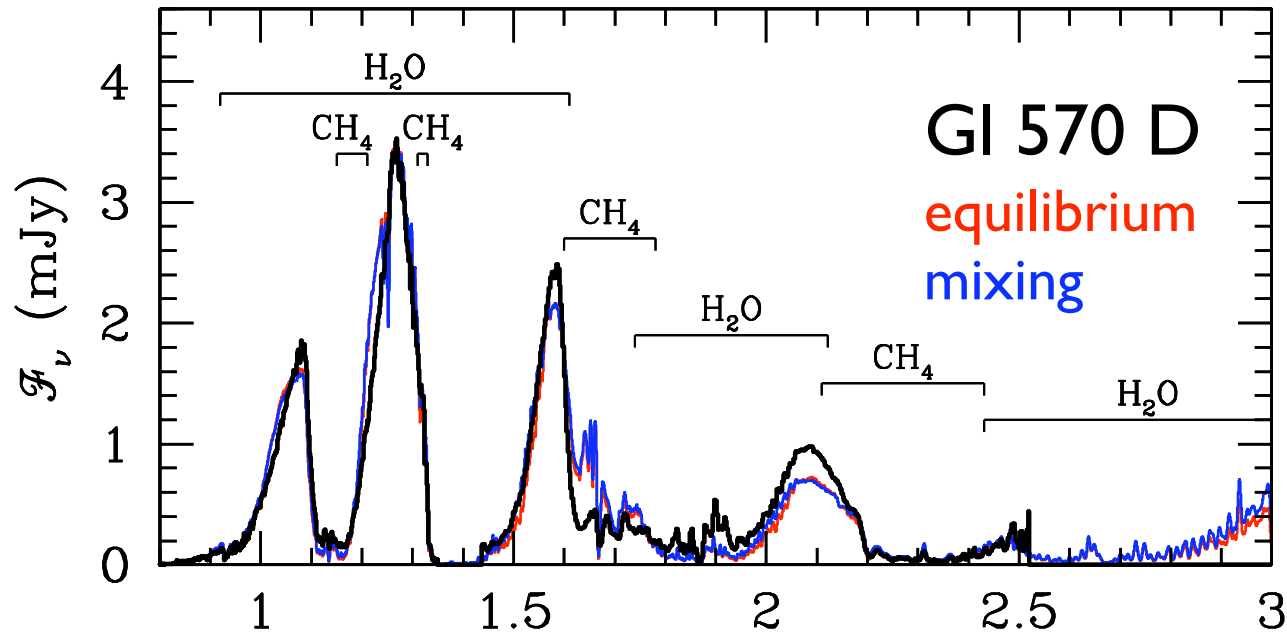


Noll et al. (1997)



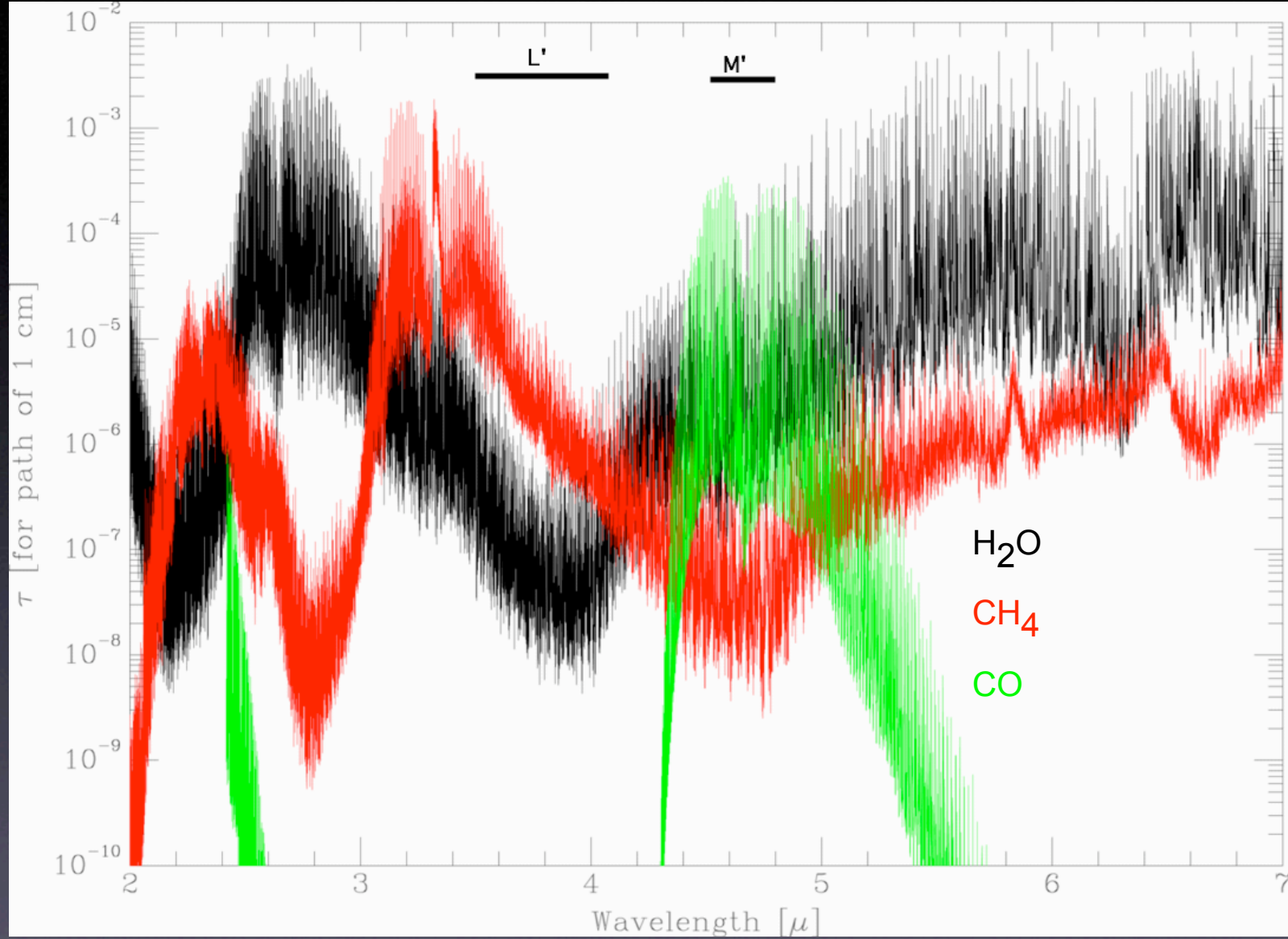
NH₃

- Ammonia works in the opposite sense as CO
- Invisible, stable N₂ is dredged up from deep atmosphere
- Decreases NH₃ abundance as seen by Spitzer IRS
- likely is postponing arrival of Y spectral type



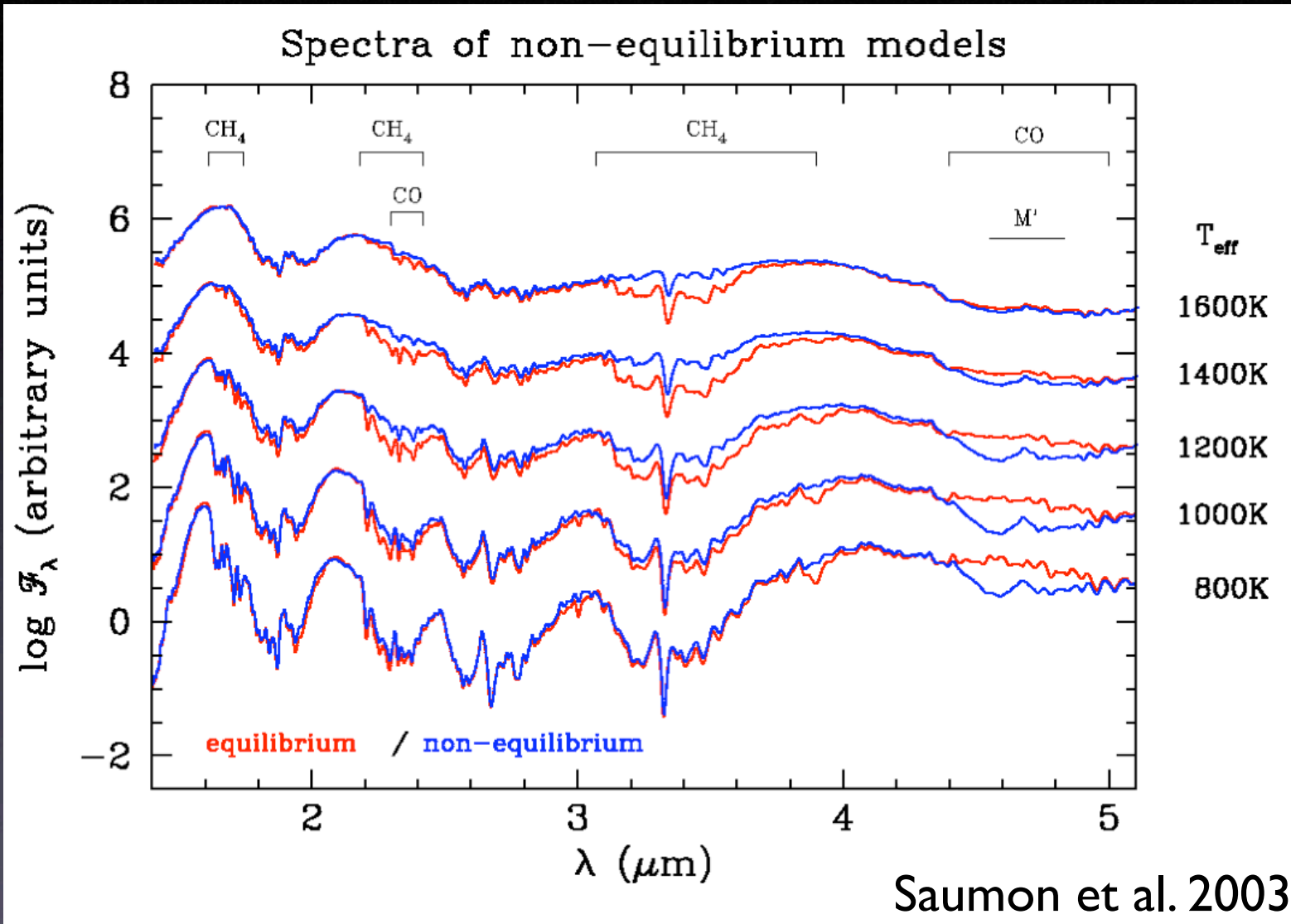
$T_{\text{eff}} \sim 800 \text{ K}$

must
 account for
 K_{zz} to fit
 spectrum



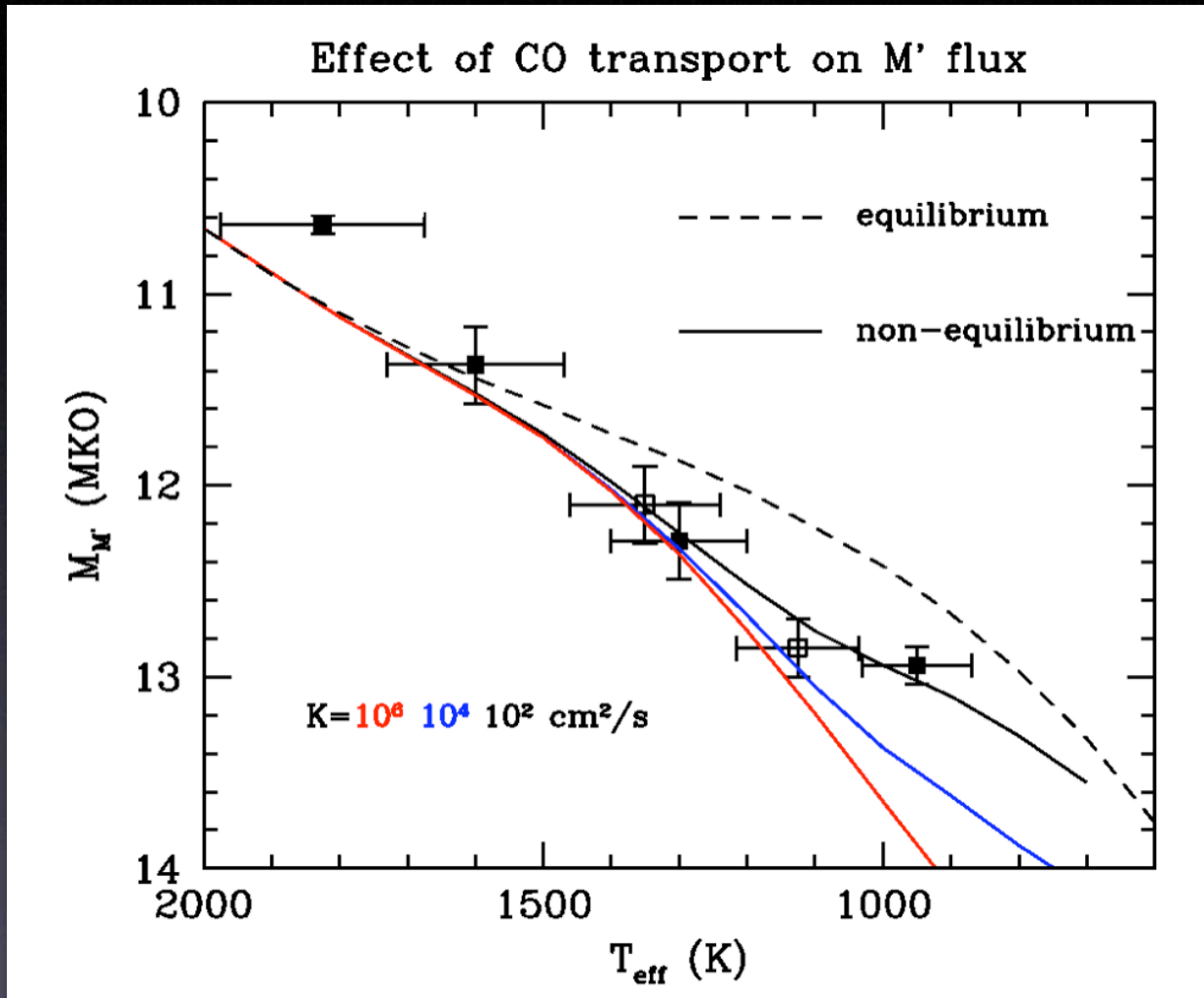
1000 K; 1 bar

Mixing Matters in Near- & Mid-IR



Methane arrives late at L, CO persists longer

Flux Suppression at M band?



- Hubeny & Burrows (2007) find maximum of 40% suppression 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 & CH₄)
- Log g, T_{eff}, [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)