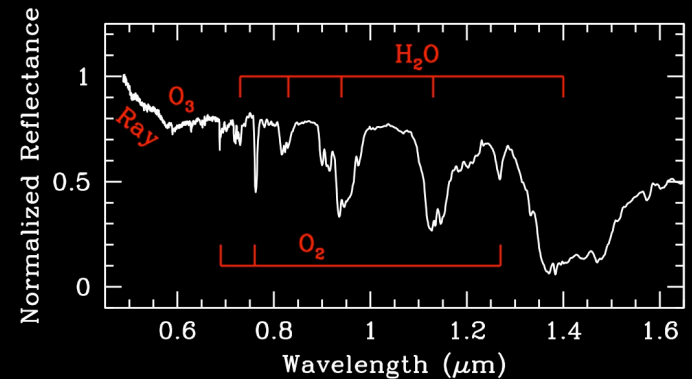


# Radiative Transfer and Molecular Lines

## Sagan Workshop 2009



Sara Seager

MIT

# Lecture Contents

- Overview of Equations for Planetary Atmospheres
- Radiative Transfer
- Thermal Inversions
- Molecular Line Primer

# Planet Atmosphere Equations

$$\frac{dI(s, \nu, \mu, t)}{ds} = \varepsilon(s, \nu, \mu, t) - \kappa(s, \nu, t)I(s, \nu, \mu, t)$$

Energy transport

$$E_{out} = E_{in,*} + E_{in,planet}$$

Consv. of Energy  
(in each layer)

$$\frac{dP(r)}{dr} = -\frac{Gm(r)\rho(r)}{r^2}$$

Hydrostatic Eq.

$$P = nkT$$

Ideal Gas Law

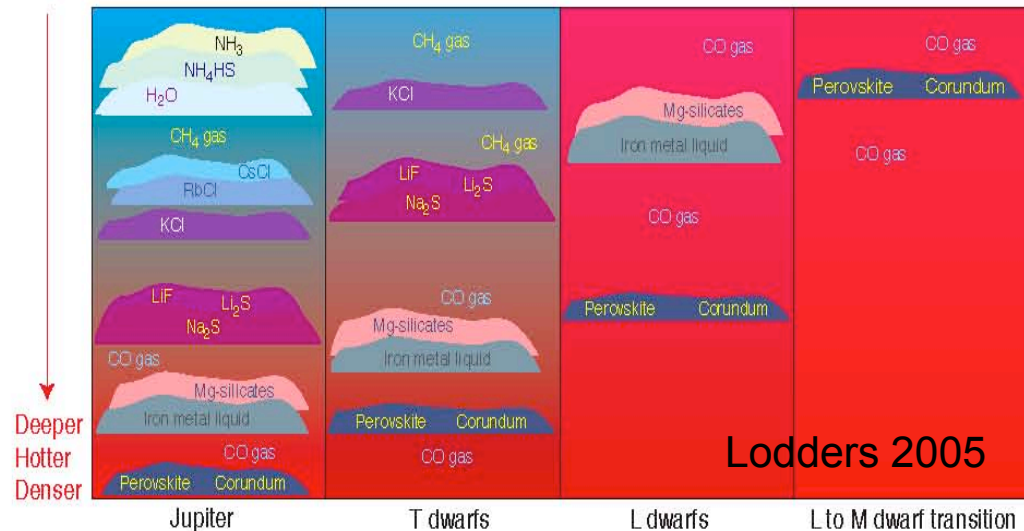
No simple equation

Chemical Equilibrium

Want to derive: Flux,  $T$ ,  $P$ ,  $\rho$ , chemical composition

# Atmosphere Model Uncertainties

- Only known inputs
  - Surface gravity
  - Radiation from star
- Unknowns:
- Atmospheric circulation
- Clouds
  - Particle size distribution, composition, and shape
  - Fraction of gas condensed
  - Vertical extent of cloud
- Chemistry
  - Elemental abundances
  - Nonequilibrium
  - Photochemistry
- Opacities
- Internal Luminosities



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# Definition of Intensity

Intensity is a ray of infinitesimally small area, frequency interval, solid angle, and time interval. The intensity is traveling in the direction of photon propagation.

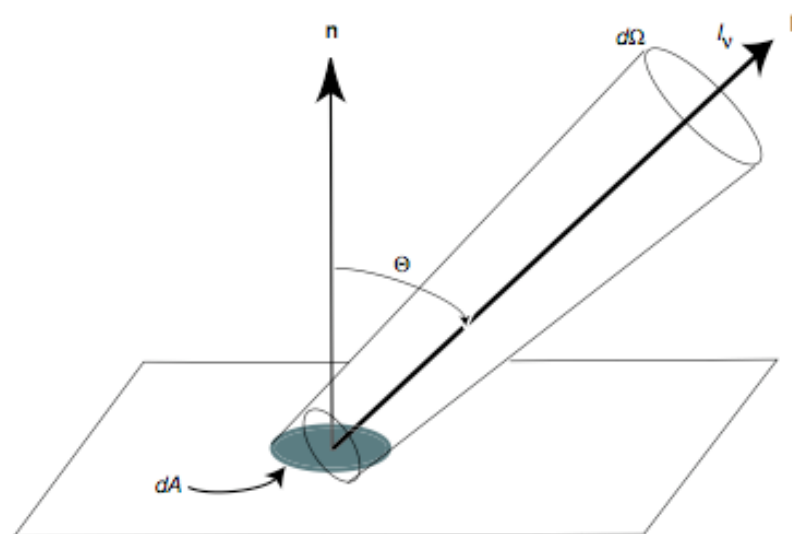


Figure 2.1 Definition of the specific intensity  $I(\mathbf{x}, \hat{\mathbf{k}}, \nu, t)$ .

$$dE(\nu, t) = I(\mathbf{x}, \hat{\mathbf{k}}, \nu, t) \hat{\mathbf{k}} \cdot \hat{\mathbf{n}} d\Omega dA d\nu dt.$$

# 1D Radiative Transfer Equation

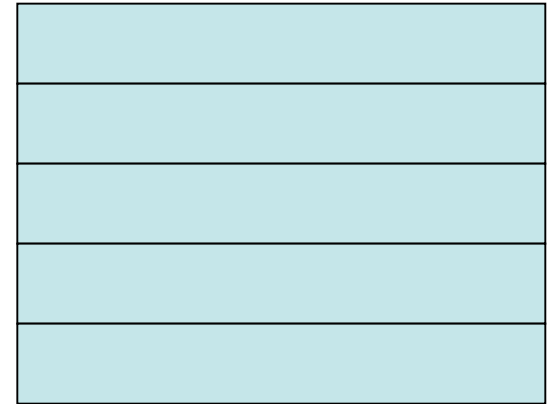
Change in Intensity = gains to the beam - losses from the beam

$$\frac{dI(s, \nu, t)}{ds} = \varepsilon(s, \nu, t) - \kappa(s, \nu, t)I(s, \nu, t)$$

*I = intensity,  $\varepsilon$  = emissivity,  $\kappa$  = absorption coefficient*

# Optical Depth $\tau$

$$d\tau = -\kappa ds$$



- A measure of transparency
- Think of an object in a fog
- When the object is immediately in front of you, the intervening fog has  $\tau = 0$
- As the object moves away,  $\tau$  increases
- $\tau$  is frequency-dependent
- We use  $\tau$  as a vertical distance scale



# 1D Radiative Transfer Equation

- Equation from before  $\frac{dI(z, \nu, t)}{dz} = \varepsilon(z, \nu, t) - \kappa(z, \nu, t)I(z, \nu, t)$

- Divide by  $\kappa$   $\frac{dI(z, \nu, t)}{\kappa(z, \nu, t)dz} = \frac{\varepsilon(z, \nu, t)}{\kappa(z, \nu, t)} - I(z, \nu, t)$

- Substitute  $\tau$  and use Kirchoff's Law  $-\frac{dI(\tau, \nu, t)}{d\tau} = B(\tau, \nu, t) - I(\tau, \nu, t)$

# 1D Radiative Transfer Solution

$$\frac{dI(\tau, \nu, t)e^{-\tau}}{d\tau} - I(\tau, \nu, t)e^{-\tau} = -B(\tau, \nu, t)e^{-\tau}$$

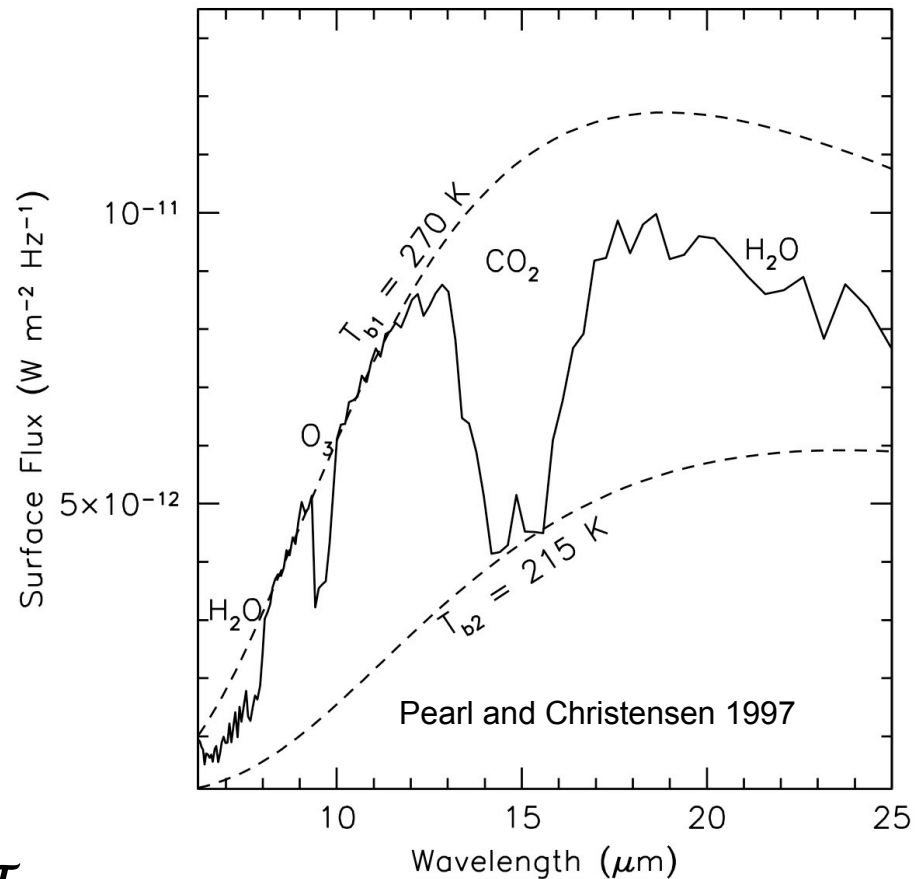
$$\int_0^{\infty} \left[ \frac{dI(\tau, \nu, t)e^{-\tau}}{d\tau} - I(\tau, \nu, t)e^{-\tau} \right] d\tau = \int_0^{\infty} -B(\tau, \nu, t)e^{-\tau} d\tau$$

$$I(\tau_{\infty}, \nu, t)e^{-\tau=-\infty} - I(\tau_0, \nu, t)e^{-\tau=0} = \int_0^{\infty} -B(\tau, \nu, t)e^{-\tau} d\tau$$

$$I(\tau_0, \nu, t) = \int_0^{\infty} B(\tau, \nu, t)e^{-\tau} d\tau$$

Emergent intensity is like a black body with “bites” taken out of it.

# Earth's Thermal Emission Spectrum



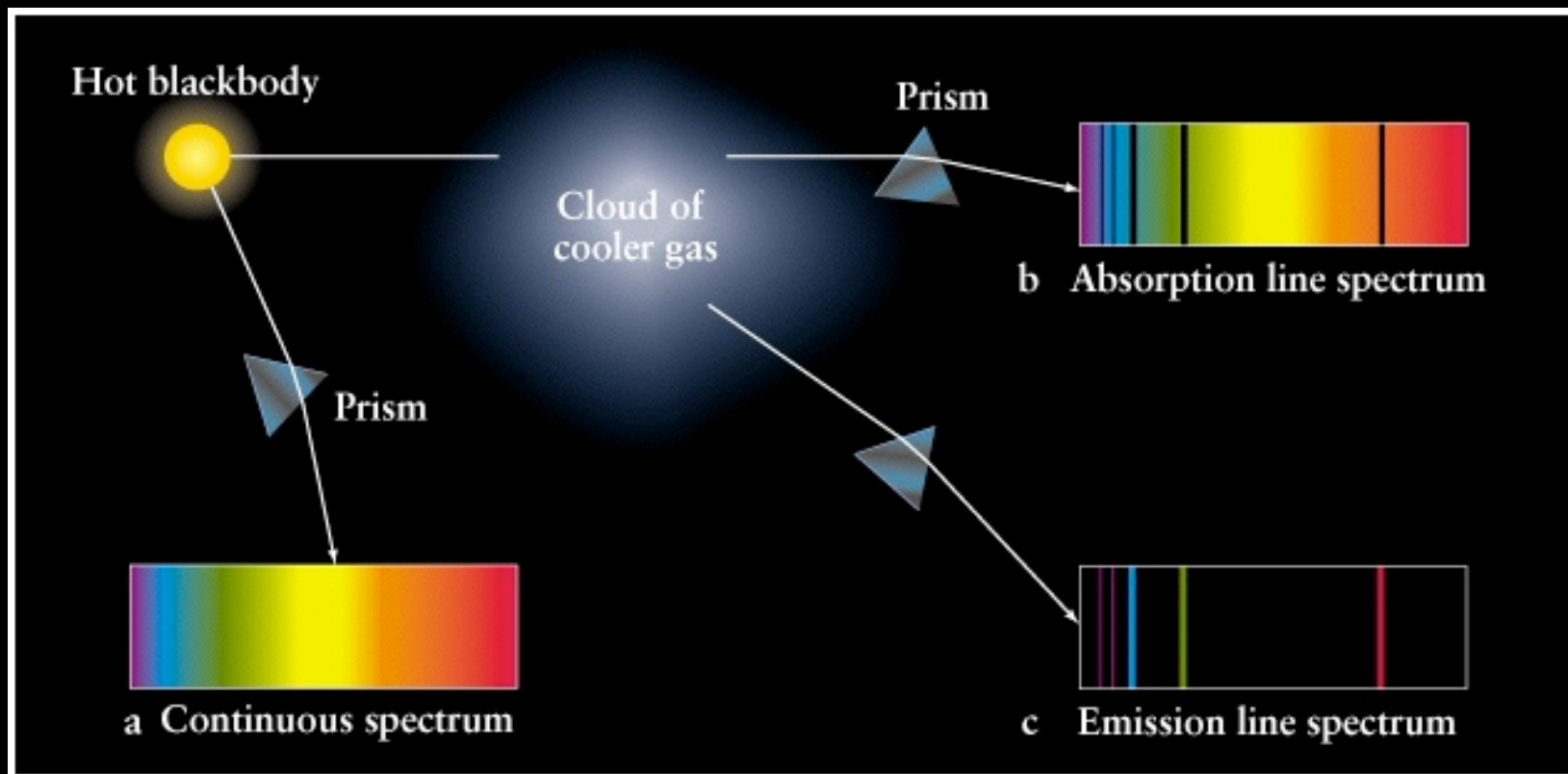
$$I(\tau_0, \nu, t) = \int_0^\infty B(\tau, \nu, t) e^{-\tau} d\tau$$

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- **Thermal Inversions**
- Molecular Line Primer

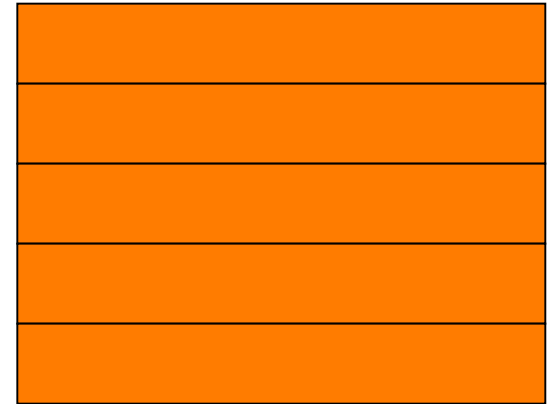
# Origin of Absorption and Emission Lines



# Constant Temperature

Assume that the deepest layer of a planetary atmosphere is a black body.

For an isothermal planet atmosphere, the spectrum emerging from the top of the atmosphere will also be a black body



# Constant Temperature

$$I(0, \nu, t) = B(T, \nu, t)$$

...

$$I_3(z, \nu, t) = B_5(z, \nu, t)$$

$$\frac{dI_3(z, \nu, t)}{dz} = 0$$

$$\frac{dI_3(z, \nu, t)}{dz} = \varepsilon_3(z, \nu, t) - \kappa_3(z, \nu, t)I_4(z, \nu, t)$$

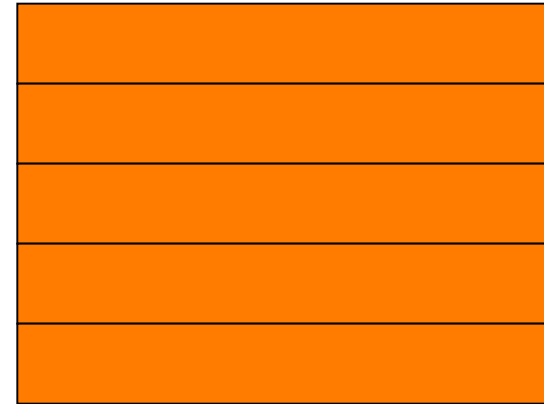
$$\frac{dI_4(z, \nu, t)}{dz} = 0, I_4(z, \nu, t) = B_5(z, \nu, t)$$

$$\varepsilon(z, \nu, t) = \kappa(z, \nu, t)B(z, \nu, t)$$

$$\frac{dI_4(z, \nu, t)}{dz} = \varepsilon_4(z, \nu, t) - \kappa_4(z, \nu, t)I_5(z, \nu, t)$$

$$I_5(z, \nu, t) = B_5(z, \nu, t)$$

Read going up



# Constant Temperature

$$I(\tau_0, \nu, t) = \int_0^{\infty} B(\tau, \nu, t) e^{-\tau} d\tau$$

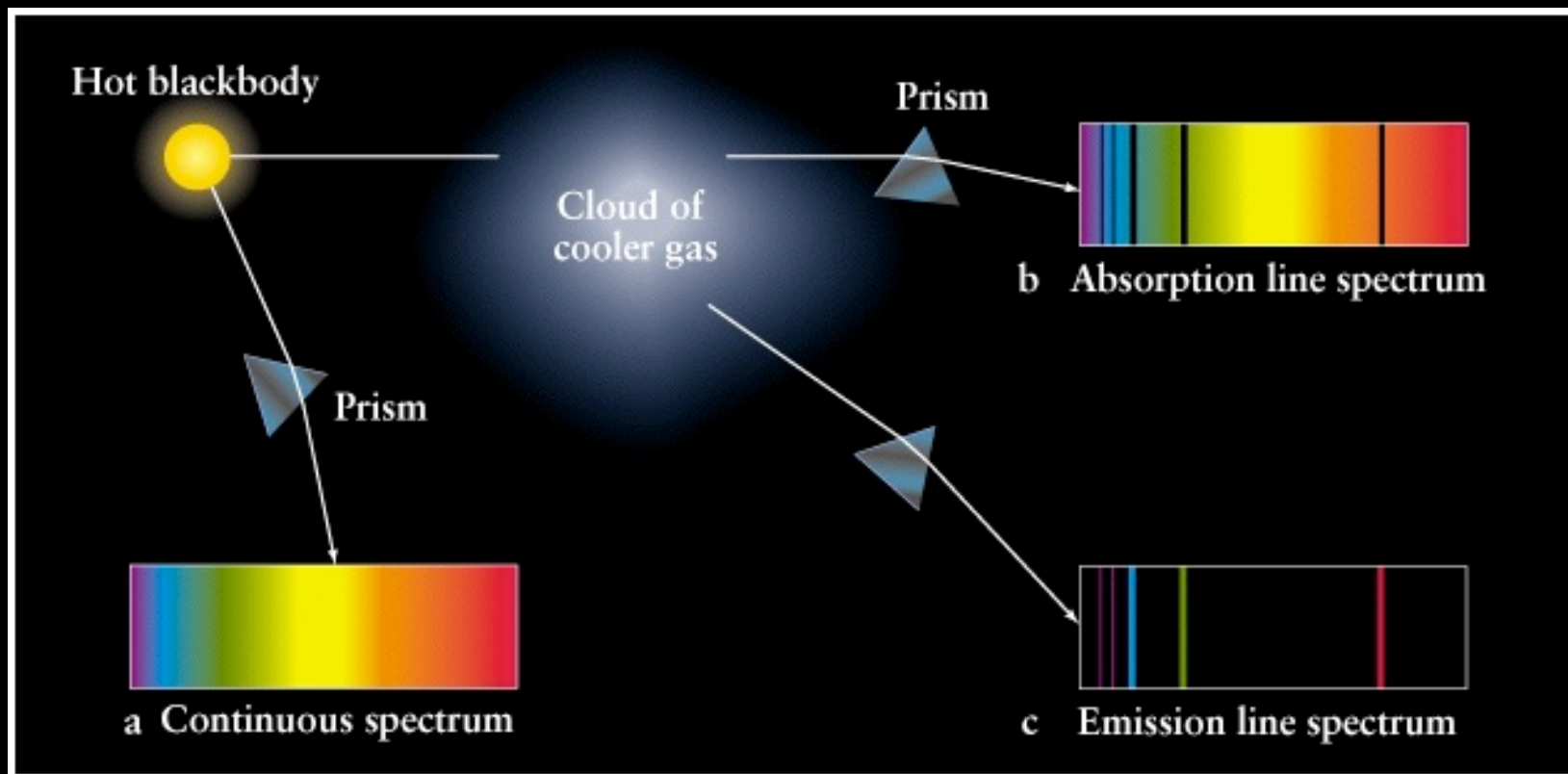
- No absorption or emission lines!
- Mathematically, constant  $T$  means  $B(\tau, \nu, t) = \text{constant}$  and can be removed from integrand

$$\int_0^{\infty} e^{-\tau} d\tau = 1$$

$$I(\tau_0, \nu, t) = B(T, \nu)$$



# Origin of Absorption and Emission Lines



# Decreasing T with Increasing Altitude

Think of this situation as cooler layers of gas overlying hotter layers. According to the conceptual picture law, an absorption spectrum will result.



# Decreasing T with Increasing

# Altitude

$$I(\tau_0, \nu, t) = \int_0^\infty B(\tau, \nu, t) e^{-\tau} d\tau$$

Take two values of  $\kappa$  at neighboring frequencies.

$\kappa_1$  is in the band center and

$\kappa_2$  is in the neighboring “continuum”;

$\kappa_1$  is  $\gg \kappa_2$ .

Consider an optical depth  $\tau$

From optical depth definition  $\tau = \kappa s$ ,

$s_1$  is shallower than  $s_2$ .

And  $T_1 < T_2$ , and  $B_1 < B_2$ .

Therefore,  $I_1 < I_2$  namely the intensity is lower in the band center than the continuum, generating an absorption line.



$$\varepsilon(z, \nu, t) = \kappa(z, \nu, t) B(z, \nu, t)$$

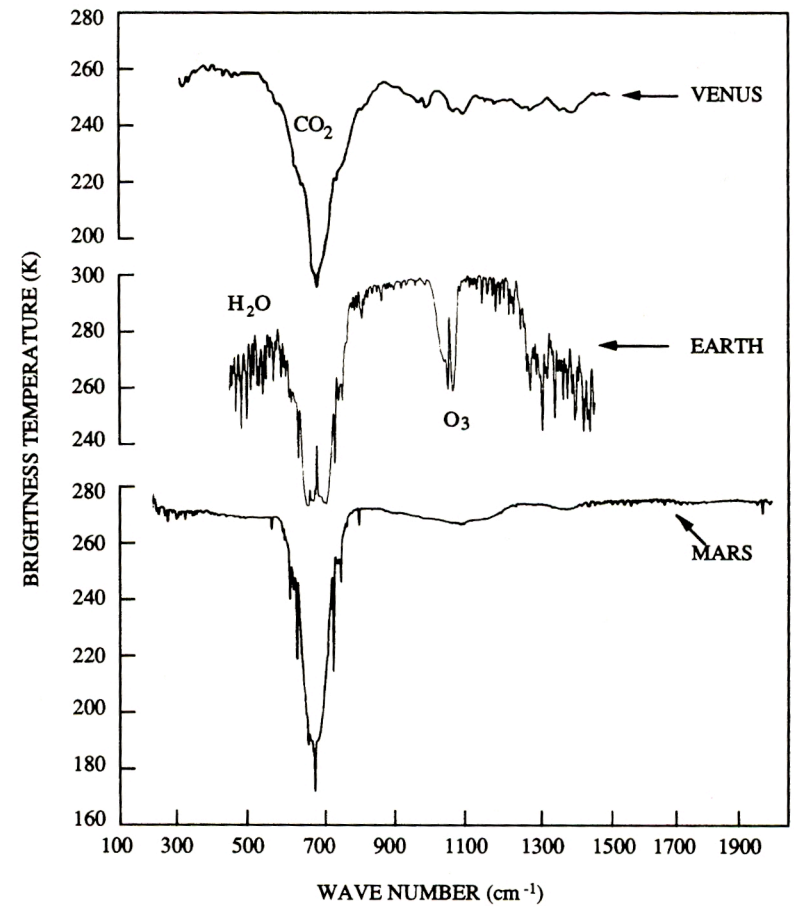
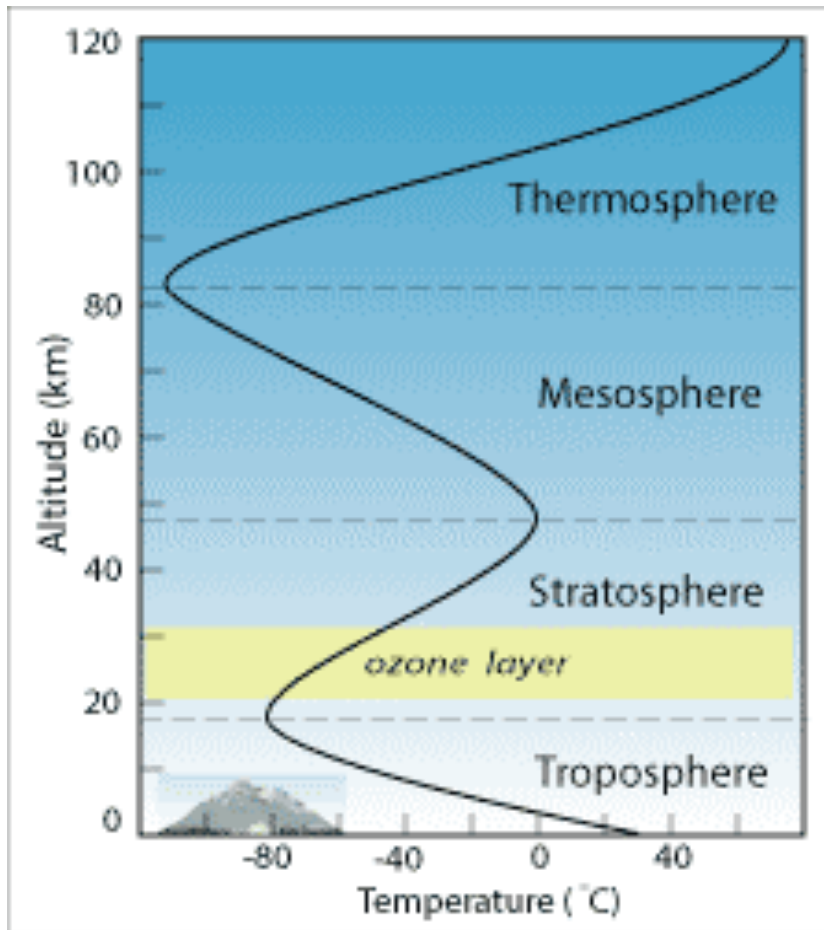
# Decreasing T with Increasing Altitude

Do you expect emission or absorption lines if the temperature is increasing with altitude?

Think of the simple conceptual picture of where emission lines come from.



# Earth

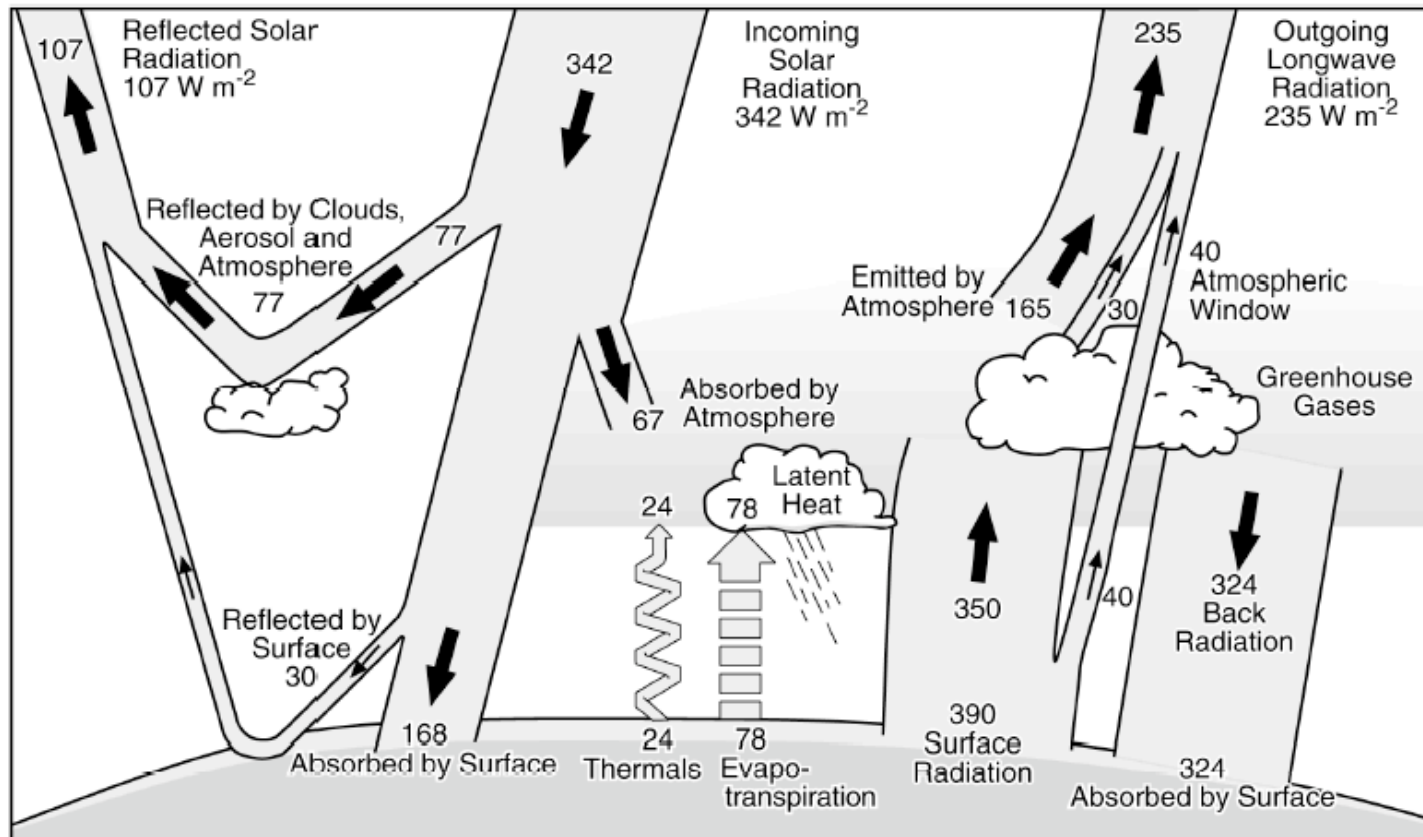


Hanel et al. 2003

# Lecture Contents

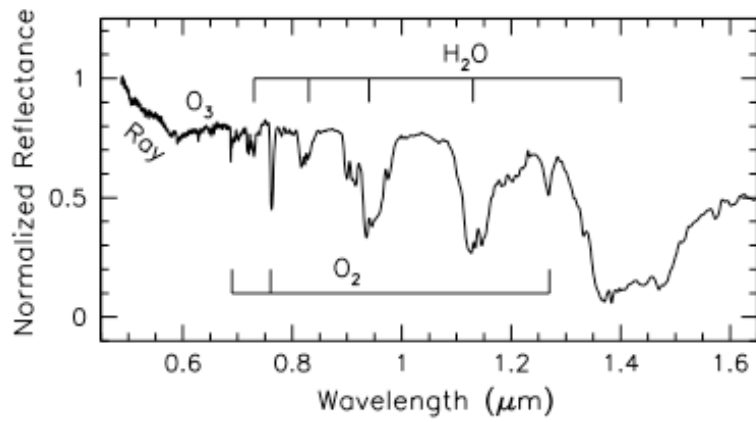
- Overview of Equations for Planetary Atmospheres
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# Atmosphere Processes

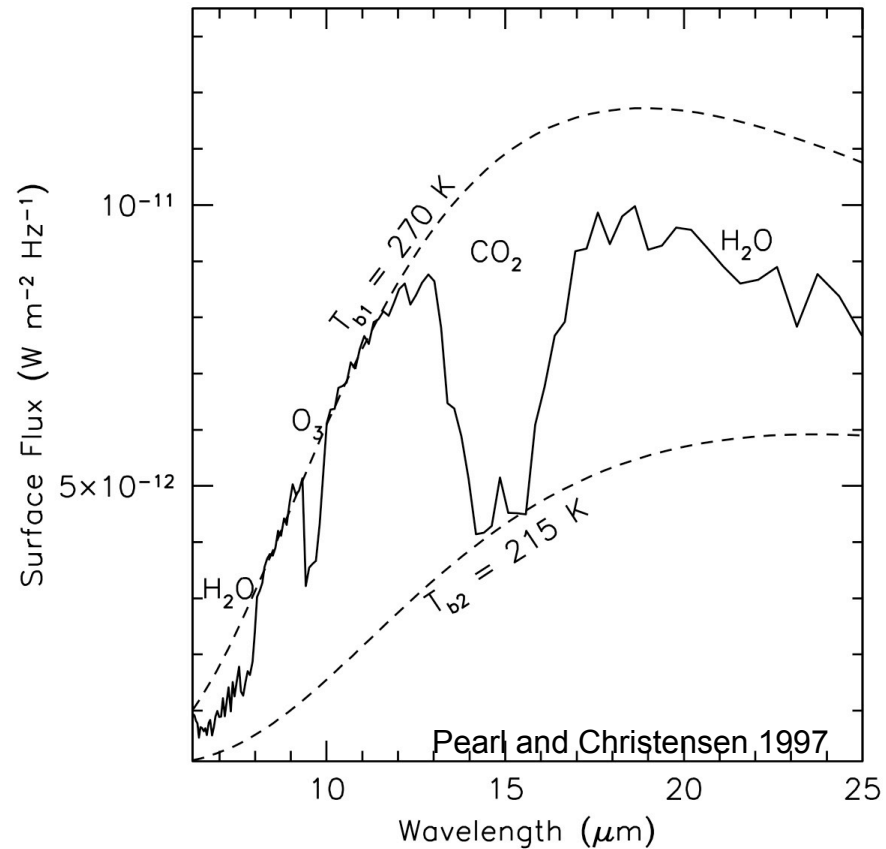


[Kiehl and Trenberth, 1997](#)

# Earth's Thermal Emission Spectrum



Turnbull et al. 2007



Pearl and Christensen, 1997

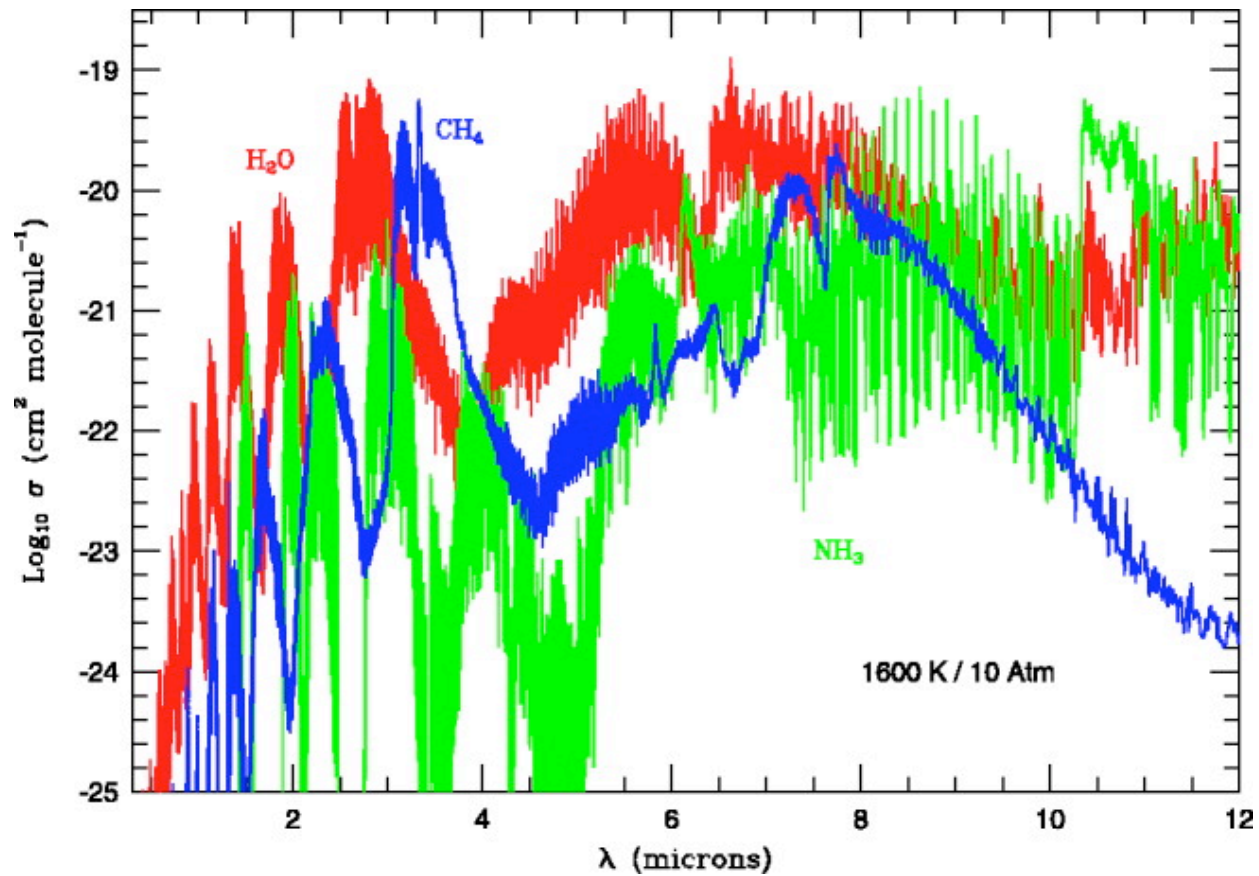
Molecular absorption controls energy balance.

Which molecule is Earth's strongest greenhouse gas?

CO<sub>2</sub>, N<sub>2</sub>, H<sub>2</sub>O, N<sub>2</sub>O, or CH<sub>4</sub>



# Line-By-Line Opacities



Burrows and Sharp 2007

# Absorption Coefficient

$$k_{\nu} = Sf(\nu - \nu_0)$$

For a given molecule at  
a given frequency

$k$  is in units of [m<sup>2</sup>/molecule]

$S$  is the line strength

$f$  is the (normalized) broadening function

$\nu_0$  is the wavenumber of an ideal,  
monochromatic line

$$\int_{-\infty}^{\infty} k_{\nu} d\nu = S$$

Normalized

\*Note:  $\kappa_{\nu} = nk_{\nu}$  in units of [m<sup>-1</sup>], where  $n$  is the number density for a given molecule

# Summary

We want to find the absorption coefficient for a given transition

$$k_\nu = S f(\nu - \nu_0)$$

$$\int_{-\infty}^{\infty} f(\nu - \nu_0) d\nu = 1$$

Line broadening includes Doppler broadening and collisional broadening.

$$S \sim |\mathbf{R}_{ij}|^2$$

Line strength is related to the square of transition probability, itself originating from quantum mechanics

$$B_{fi} = \frac{1}{4\pi} \frac{8\pi^3 \nu_{fi}}{3hc} \left| \int \Phi_f^* (\bar{\mu} \Phi_i) dV \right|^2 \left| \int \Sigma_f^* \Sigma_i d\sigma \right|^2$$

Selection rules for permitted lines

$$\frac{N_j}{N} = \frac{g_j e^{-E_j/KT}}{\sum_i g_i e^{-E_i/KT}}$$

The energy level population ratio in LTE is defined by Boltzmann statistics.  $g$  is the degeneracy.

$$\varepsilon_\nu = k_\nu B_\nu$$

Emission coefficient in LTE (Kirchoff's Law)

# Summary

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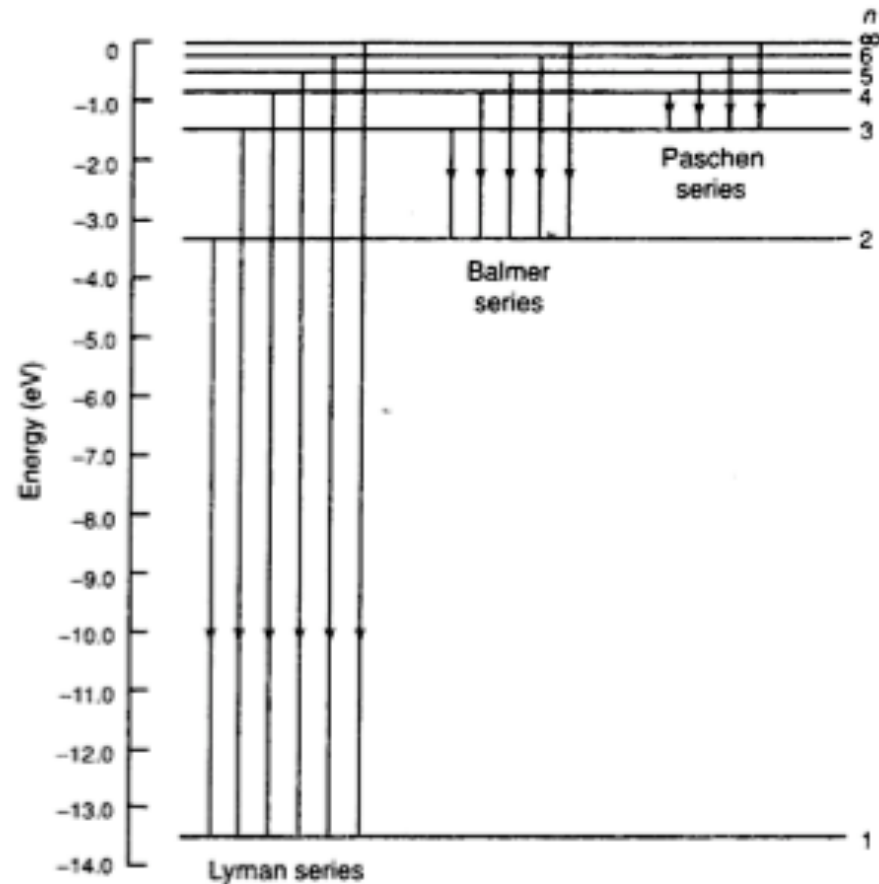
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Emission coefficient in LTE (Kirchoff's Law)

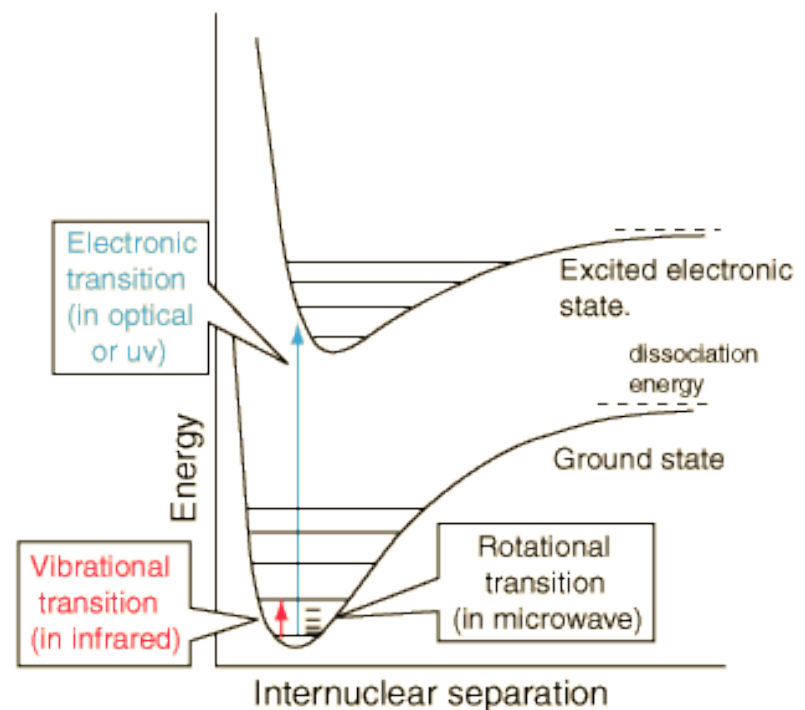
# H Atom Energy Levels



**Figure 1.9** Energy level diagram for a hydrogen atom showing the quantum number  $n$  for each level and some of the transitions that appear in the spectrum. An infinite number of levels is crowded in between the levels marked  $n = 6$  and  $n = \infty$ .

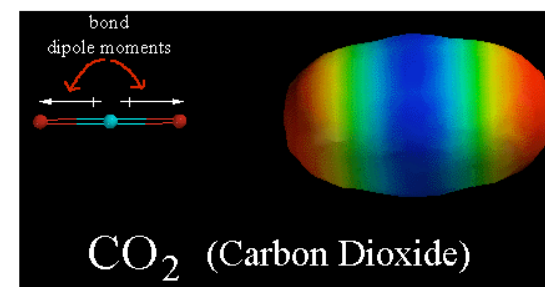
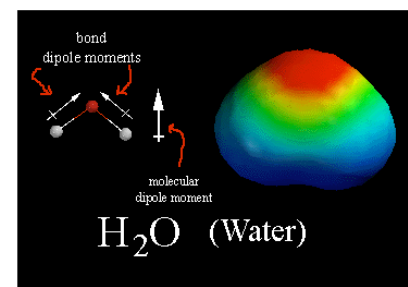
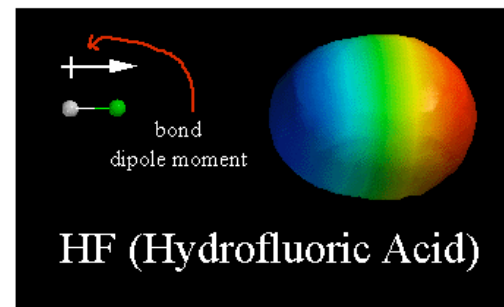
# Molecular Energy Levels

- Electrons travel much faster than nuclei
- We may assume that the electronic energy depends only on the positions of the nuclei and not on their own velocities
- The potential energy distribution is then a function of the internuclear distances alone
- The potential energy has a minimum at locations where the attractive binding forces balance repulsive internuclear forces.

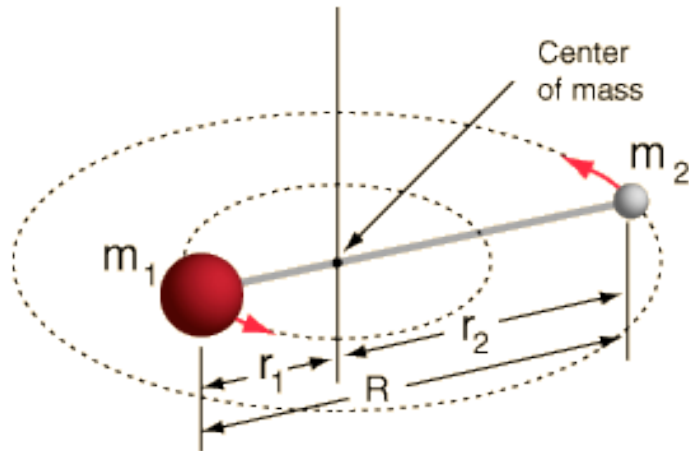


# Molecular Energy Levels

- Which molecules have rotational-vibrational transitions?
- Must have an electric dipole to interact with radiation
- Electric dipole: a difference between the center of charge and the center of mass
- Homonuclear molecules do not have a dipole moment



# Rotational Energy Levels



- Rotation of a diatomic molecule
- approximate the molecule as two masses  $m_1$  and  $m_2$  at a fixed separation  $r_1$  and  $r_2$
  - the molecule rotates about an axis perpendicular to the line joining the nuclei

Linear diatomic molecules can be approximated by a classical rigid rotor. The classical expression for energy is  
Total energy = Kinetic energy + Potential energy.  
A classical rigid rotor has no potential energy.

$$E = \frac{1}{2} \sum_i m_i v_i^2 = \frac{1}{2} I \omega^2 = \frac{L^2}{2I}$$

$\omega$  is the rotation frequency

$I$  is the moment of inertia  $= \sum_i m_i r_i^2$

$L$  is the angular momentum  $L = \sum_i m_i \omega r_i$



# Rotational Energy Levels

In classical theory  $E$  and  $\omega$  can assume any value  
In quantum mechanics, the rigid rotor can only exist in discrete energy states.

To find the energy states, we would use the time-independent Schrodinger equation (with the Hamiltonian expressed in terms of the angular momentum operator).

A pure rotational spectrum has energies at microwave frequencies.

$$H\Psi = \frac{L^2}{2I} \Psi = E\Psi$$

$$H\Psi = \frac{J(J+1)\hbar^2}{2I} \Psi$$

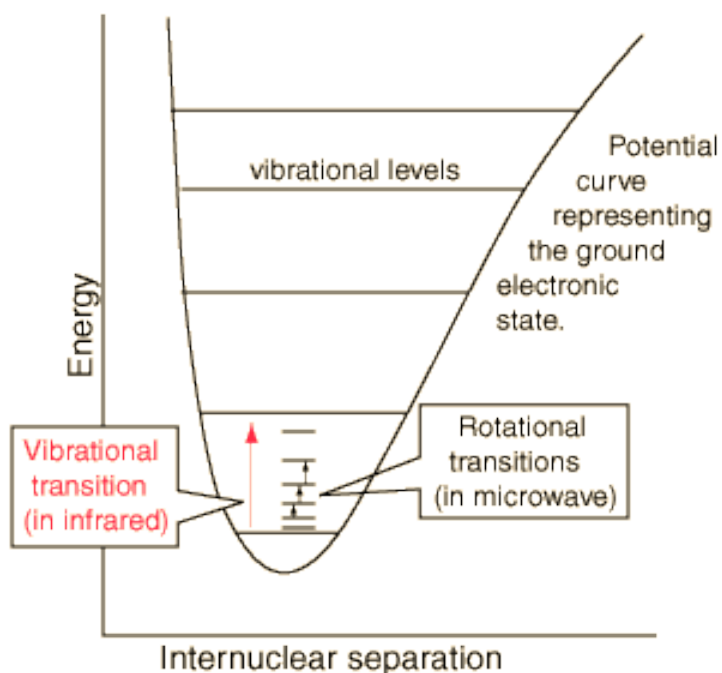
$$E_J = \frac{\hbar^2}{2I} J(J+1)$$

$$J = 0, 1, 2, \dots$$

$$B = \frac{\hbar^2}{2I}$$

$$\frac{N_J}{N_0} = (2J+1)e^{-BJ(J+1)/KT}$$

# Vibrational Energy Levels



The potential energy can be approximated by the parabolic form of the simple harmonic oscillator.

Similar to a simple harmonic oscillator but with quantized energy levels at equally spaced values.

- In a linear diatomic molecule all vibratory motion takes place along the line joining the atoms.
- Think of the atoms in periodic motion with respect to the center of mass.
- As the molecule vibrates, rotational modes are also excited. Vibration and rotation occur together.

# Vibrational Energy Levels

$$E = \frac{1}{2}m_1v_1^2 + \frac{1}{2}m_2v_2^2 + V(x)$$

$$V(x) = \frac{1}{2}Cx^2$$

$$E = \frac{p^2}{2\mu} + \frac{1}{2}Cx^2$$

...Associate with the QM operator ...

$$E_v = (v + 1/2)\hbar \left[ \frac{1}{2\pi} \sqrt{\frac{C}{\mu}} \right]$$

$$E_{v_k} = \hbar\omega_0(v_k + 1/2)$$

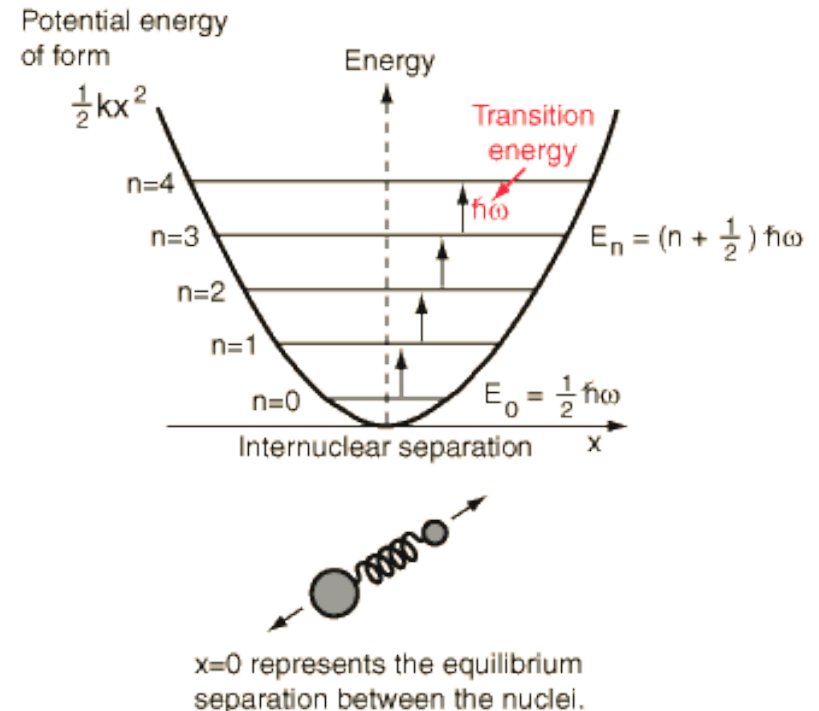
$$v_k = 0, 1, 2, \dots$$

$\mu$  is the reduced mass

$k$  denotes the normal modes

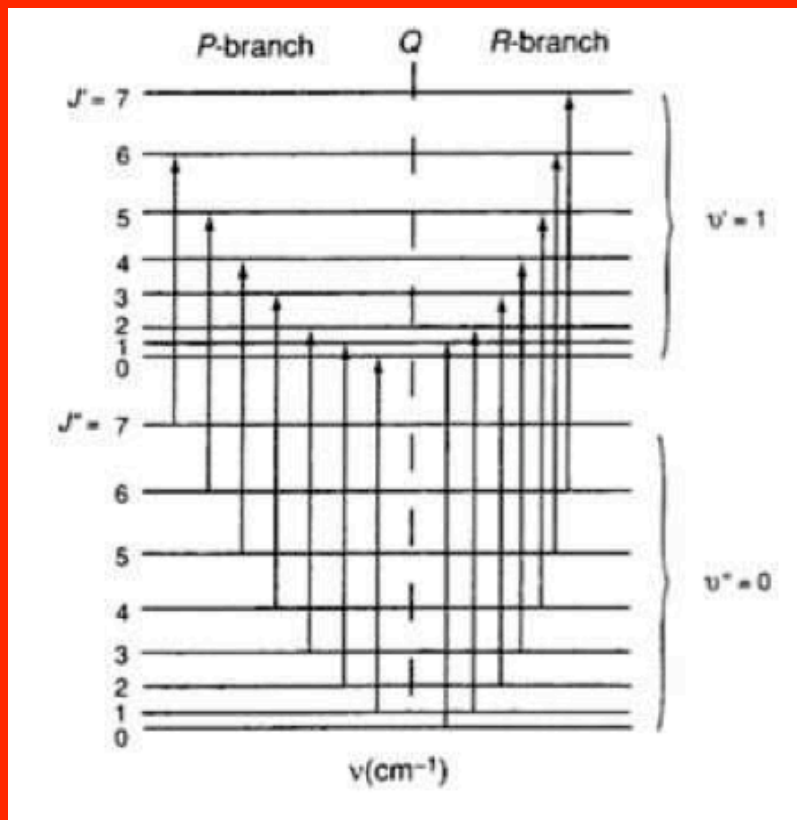
$C$  is the bond force constant

$$\omega_0 = \sqrt{\frac{C}{\mu}}$$



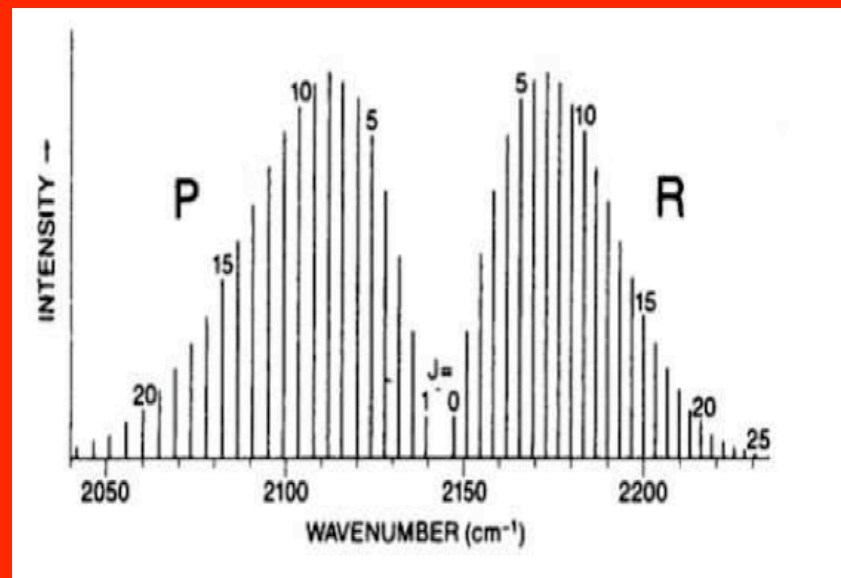
Energies ~ infrared

# Rotational Vibrational Transitions



$\Delta J = -1$  P branch

$\Delta J = 1$  R branch

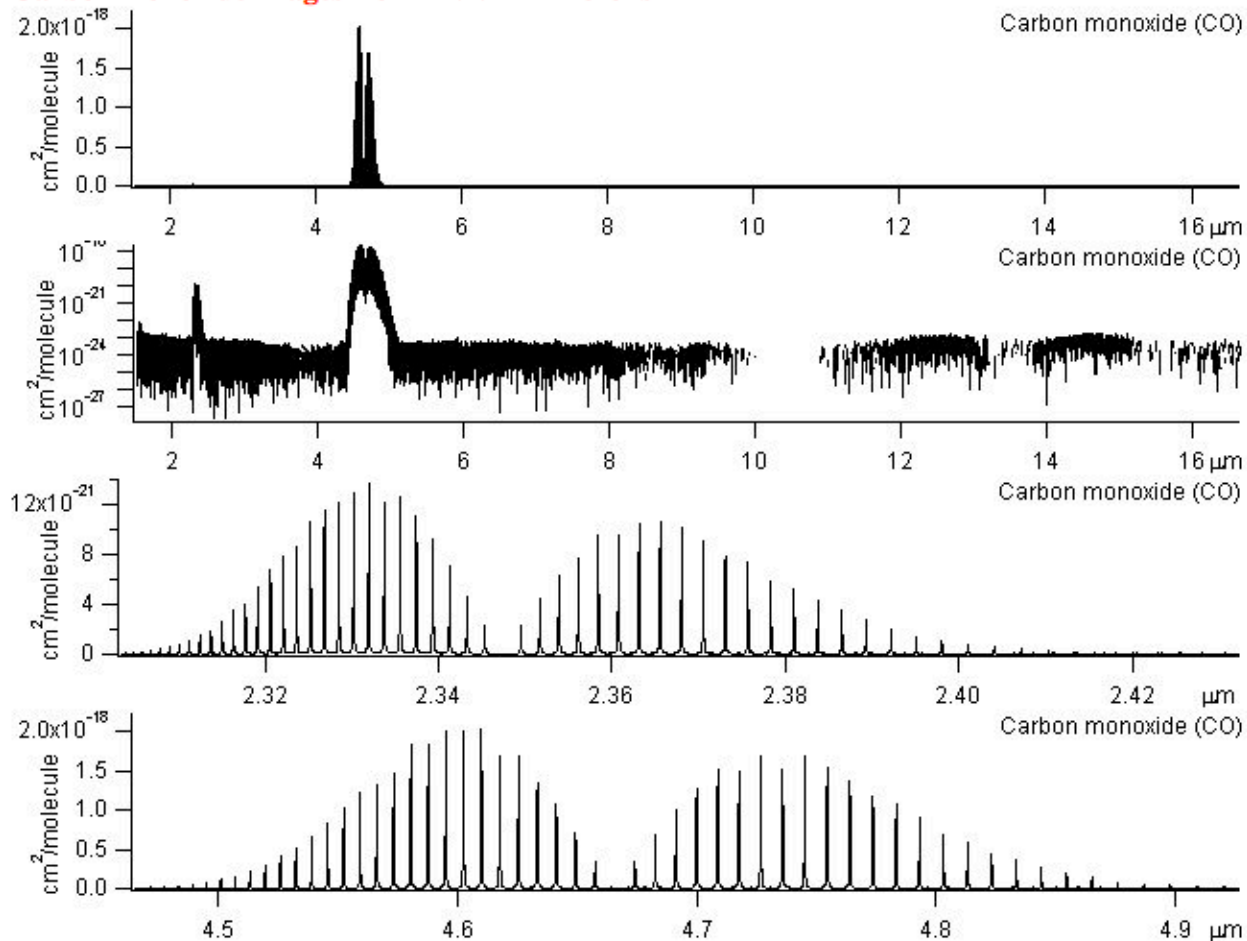


Simulated intensity of rotational-vibrational transitions of the CO molecule for the  $\nu = 1-0$  band.

The vibrational transitions are always accompanied by rotational transitions.

# Rotational Vibrational Cross-Sections for CO

Carbon monoxide images from PNNL in microns



From the VPL website

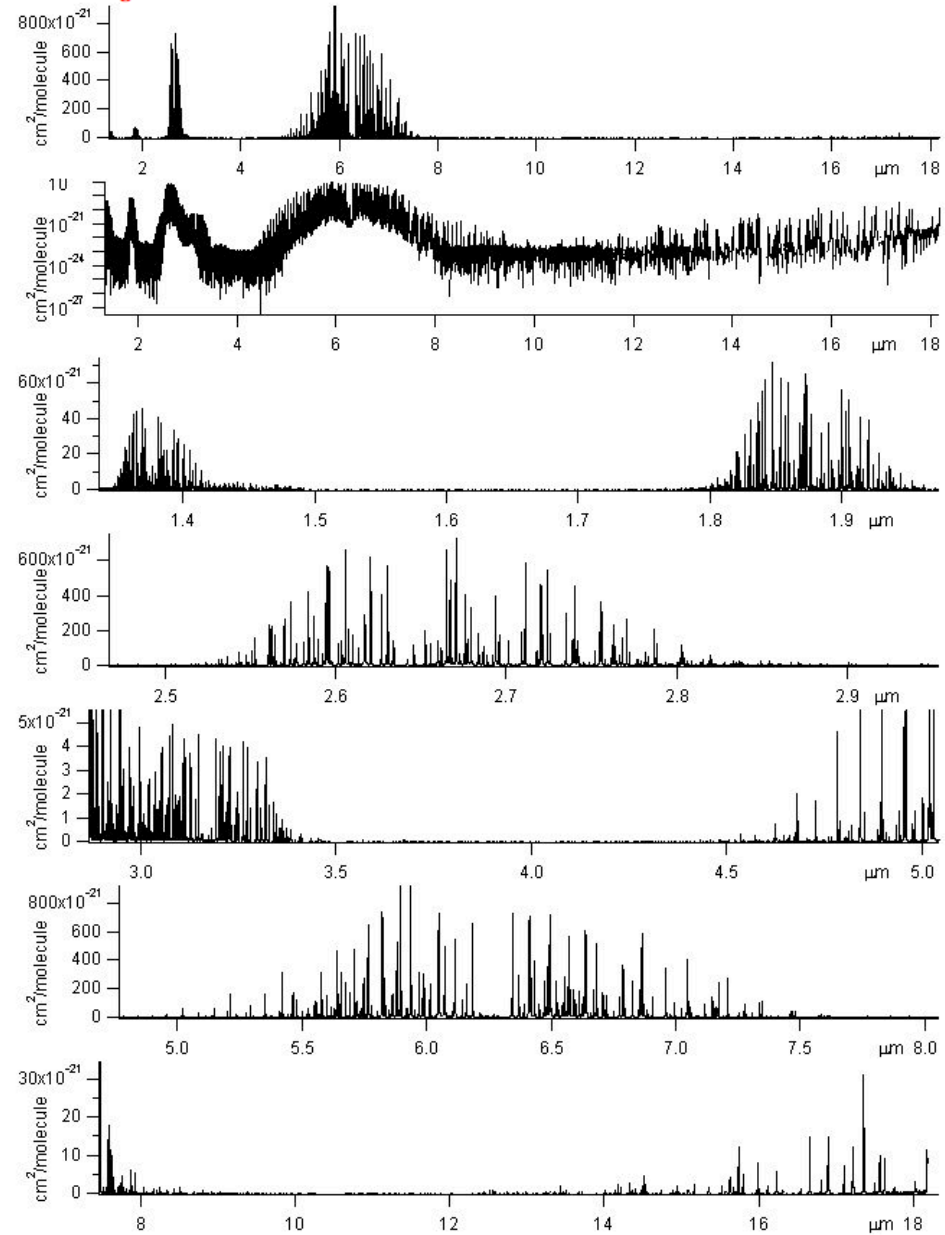
# Non-Linear Molecules

$3N-6$  vibrational modes, where  $N$  is the number of atoms

[http://en.wikipedia.org/wiki/Water\\_absorption](http://en.wikipedia.org/wiki/Water_absorption)

# Water Vapor Cross Sections

Water images from PNNL



From the VPL website

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- Radiative Transfer
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- Thermal Inversions
  - Absorption lines for no thermal inversion
  - Emission lines indicate thermal inversion
- Molecular Line Primer
  - Molecular vibrational and rotational lines (which appear in the IR spectrum) were outlined for a linear molecule



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No simple equation

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# A New Text Book

Exoplanet Atmospheres: Physical  
Processes

Sara Seager

Princeton University Press

Should appear by end of 2009