

## Resonant Electromagnetic (EM) Interactions in Planetary atmospheres

There are three classes of energy states that interact with EM radiation that we are interested in to understand how light (EM radiation) interacts with the gaseous portion of the atmosphere.

Electronic: Electron transition between different electron orbits

Vibrational: Transitions between different vibrational modes of the molecule.

Rotational: Rotation of the molecule around different axes of rotation.

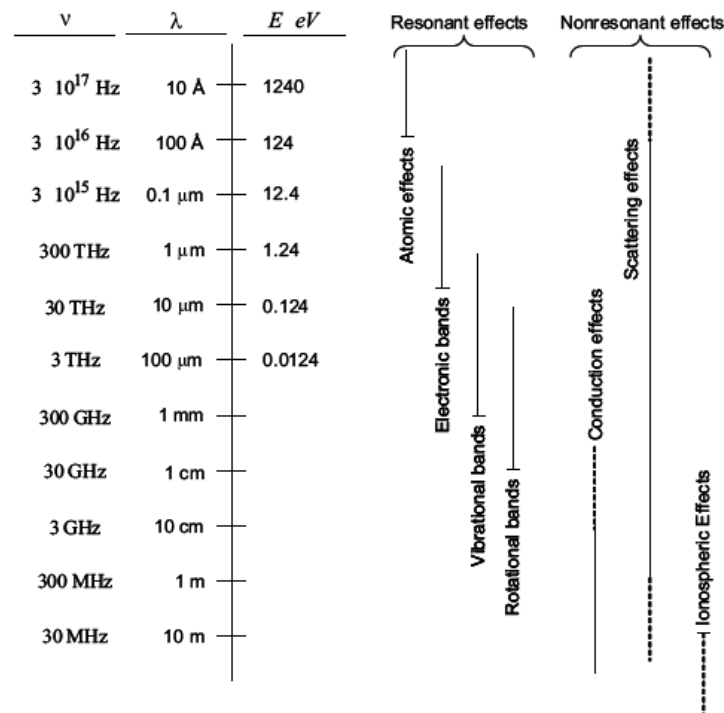


Figure 2-15. Correspondence of spectral bands, photon energy, and range of different wave-matter interaction mechanisms of importance in remote sensing. The photon energy in electron volts is given by  $E(\text{eV}) = 1.24/\lambda$ , where  $\lambda$  is in  $\mu\text{m}$ .

### Rotational Energy levels and spectra: The Electric Dipole

A molecule must have a permanent electric dipole moment to interact radiatively with pure rotational modes.

**What is an electric dipole? It refers to the situation when two equal and opposite charges are separated by some distance. See <http://hyperphysics.phy-astr.gsu.edu/hbase/electric/dipole.html>.** The electric dipole moment is a vector equal to the charge times the separation distance and is directed toward the positive charge.

To have a permanent electric dipole moment, the molecule must have some asymmetry in its geometry that results in a net offset between its electron cloud and the positive charge distribution. The water molecule has a large permanent electric dipole moment.  $\text{O}_2$ ,  $\text{N}_2$ ,  $\text{CO}_2$ ,  $\text{CH}_4$  do not and do not have pure rotational EM spectra associated with a permanent electric

dipole moment. The rotational lines are only apparent as part of the vibrational-rotational spectra of these molecules. So the vibrational line is actually a band of rotational lines centered on the vibrational line energy transition.

Note, O<sub>2</sub> has line spectra at microwave frequencies because of a *magnetic* dipole moment.

### Additional material on rotational energy transitions

Recall from our discussion and the notes on heat capacity of a diatomic molecule that we discussed the rotational energy levels as being associated with the moment of inertia. This same energy distribution is relevant to interactions with electromagnetic radiation. The moment of inertia,  $I$ , is given as

$$I = \int r^2 \rho dV \quad (1)$$

In the simple dumbbell molecule, the rotational energy levels are

$$E = \frac{h^2}{8\pi^2 I} j(j+1) \quad (2)$$

units check: J<sup>2</sup> s<sup>2</sup>/(kg m<sup>2</sup>) = J OK

Reminder: Planck's constant,  $h$ , is 6.6x10<sup>-34</sup> J s.

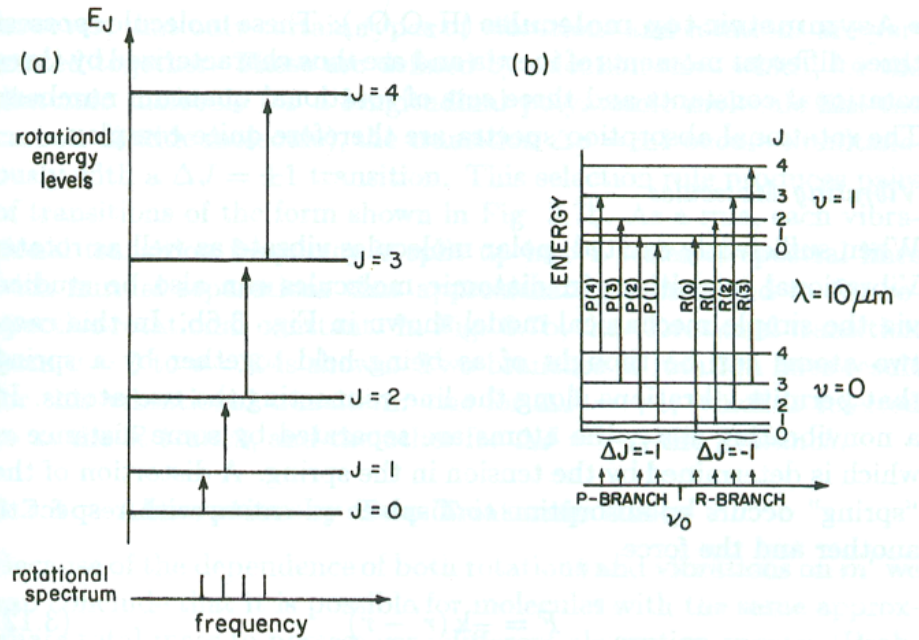
The absorption and emission lines associated with rotational energy levels are due to differences between these energy levels

$$\Delta E_{ji} = \frac{h^2}{8\pi^2 I} [j(j+1) - i(i+1)] = h\nu_{ji} \quad (3)$$

$$\nu_{ji} = \frac{h}{8\pi^2 I} [j(j+1) - i(i+1)] \quad (4)$$

Quantum selection rules require that  $j = i+1$ , then

$$\nu_{ji} = \frac{h}{8\pi^2 I} [(i+1)(i+2) - i(i+1)] = \frac{h}{8\pi^2 I} [(i+1)(i+2-i)] = \frac{h}{4\pi^2 I} (i+1) \quad (5)$$



**Figure 3.7** (a) Energy levels and the resulting spectrum of molecular rotation. (b) Vibrational-rotational transitions between the lowest vibrational and rotational levels.

*From Figure 3.7 of Graeme Stephens' textbook*

To get a feel for the spectral frequencies here, let's consider the water molecule. It consists of one oxygen atom and 2 hydrogen atoms. It's geometry is given in Elachi and van Zyl (EvZ) [Figures 8-4 and 8-5](#). The angle between the two O-H lines is  $104^\circ$ , a bit more than  $90^\circ$ . The length of each OH line is  $0.96 \text{ \AA} = 0.96 \times 10^{-10} \text{ m}$ .

Water has three different rotational modes plus all of the energy levels for each mode and the energy transitions between modes creating a rich and complex rotational spectrum.

To estimate  $I$ , assume the first rotational mode in EvZ, spinning around a line drawn through the oxygen atom and splitting the 2 hydrogen atoms. The center of mass is essentially in the oxygen atom. The distance of the each hydrogen atom to the spin axis is

$$r = 0.96 \times 10^{-10} \sin(52^\circ) \text{ m} = 0.76 \times 10^{-10} \text{ m}$$

The hydrogen atom mass is  $1.7 \times 10^{-27} \text{ kg}$ . So  $I_{H_2O} \sim 2 m r^2$  where  $m$  is the mass of each hydrogen atom

$$I = 2 \times 1.7 \times 10^{-27} \times 0.57 \times 10^{-20} = 1.9 \times 10^{-47} \text{ kg m}^2.$$

So

$$h/(4\pi^2 I) = 6.626068 \times 10^{-34} / 40 / 1.9 \times 10^{-47} = 8.6 \times 10^{11} \text{ Hz} = 860 \text{ GHz}.$$

The lowest transition is from  $j=0$  to  $j=1$  yielding a frequency of  $h/(4\pi^2 I) = 860 \text{ GHz}$ . The corresponding wavelength is  $0.35 \text{ mm}$ . This is an approximate estimate that gets us to the approximate frequency and wavelength regime of the strong water rotational lines.

Water's pure rotational lines are relatively high in frequency because of the low mass of the hydrogen atoms. The frequency is inversely proportional to  $I = mr^2$  so small mass mean high frequency.

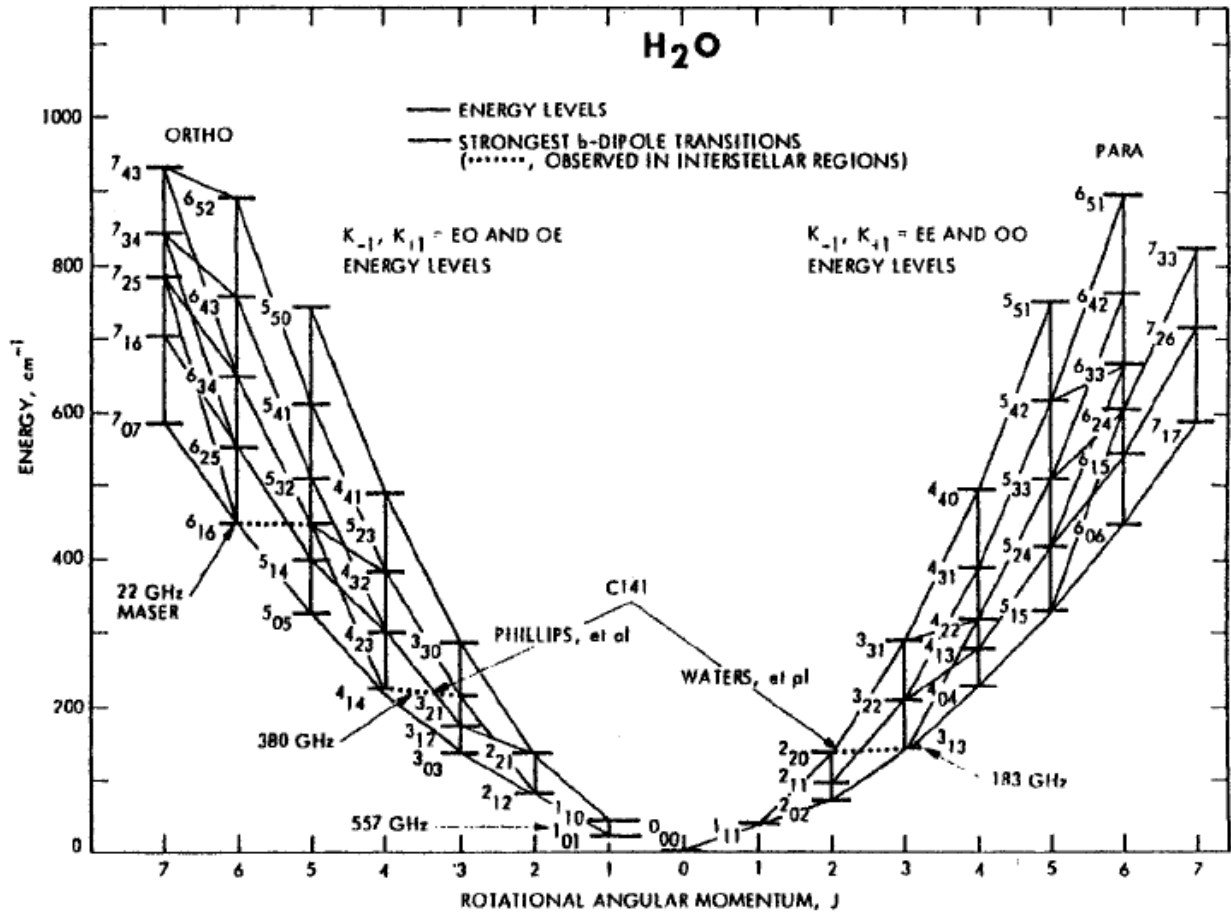
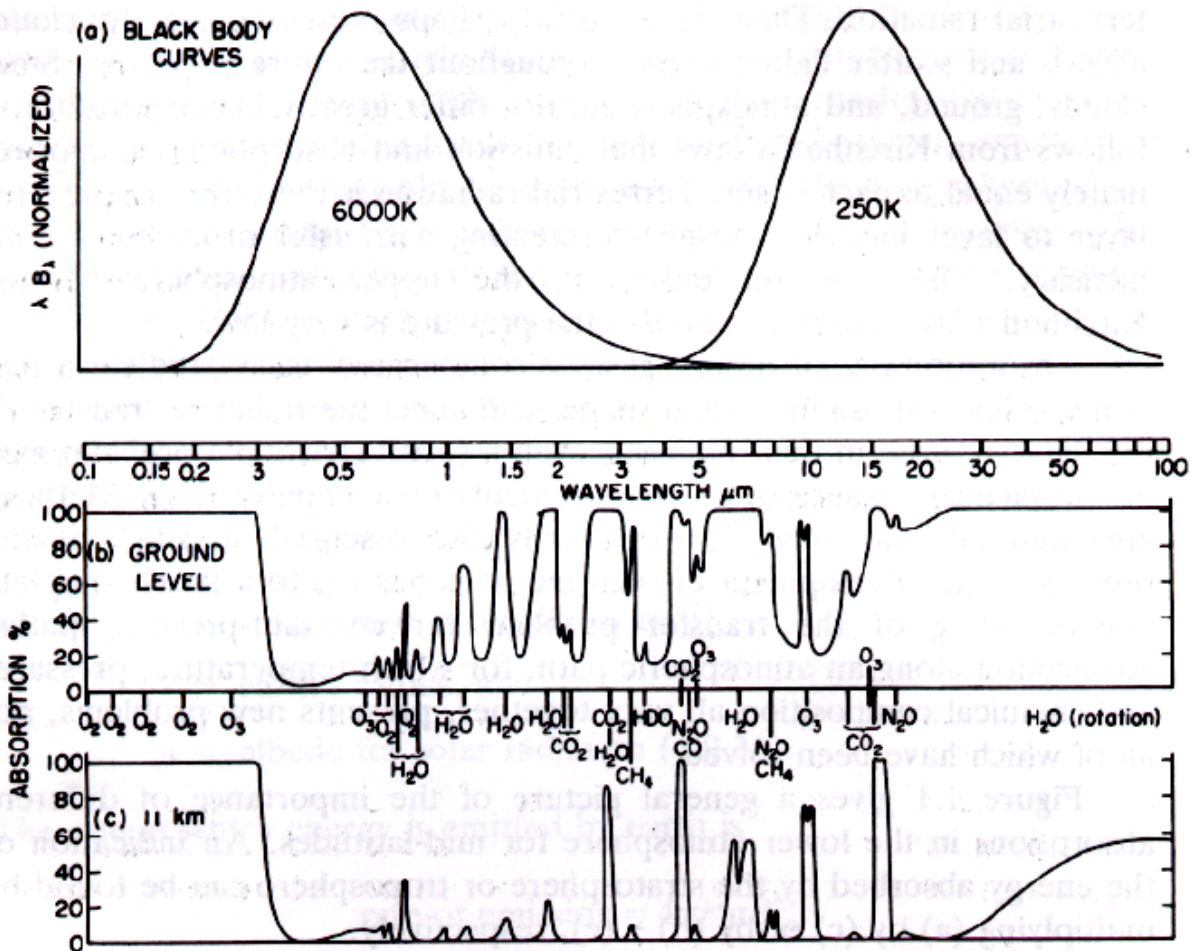


Figure 10-1 from EvZ. Rotational line spectrum of H<sub>2</sub>O. Scale: 100 cm<sup>-1</sup> = 3,000 GHz

Remembering from the Einstein coefficients, note that the line strengths are associated with the Boltzmann distribution of the energy levels and the energy separation between the lines which defines the net absorption resulting from the absorption minus the stimulated emission.

See water vapor spectrum EvZ figure 8-6

These transitions produce a near continuum in the far IR of Earth's emission and absorption spectrum.



**FIG. 1.1** Atmospheric absorptions. (a) Black-body curves for 6000 K and 250 K. (b) Atmospheric absorption spectrum for a solar beam reaching ground level. (c) The same for a beam reaching the temperate tropopause. The axes are chosen so that areas in (a) are proportional to radiant energy. Integrated over the earth's surface and over all solid angles, the solar and terrestrial fluxes are equal to each other; consequently, the two black-body curves are drawn with equal areas. Conditions are typical of mid-latitudes and for a solar elevation of 40° or for a diffuse stream of terrestrial radiation.

### CO:

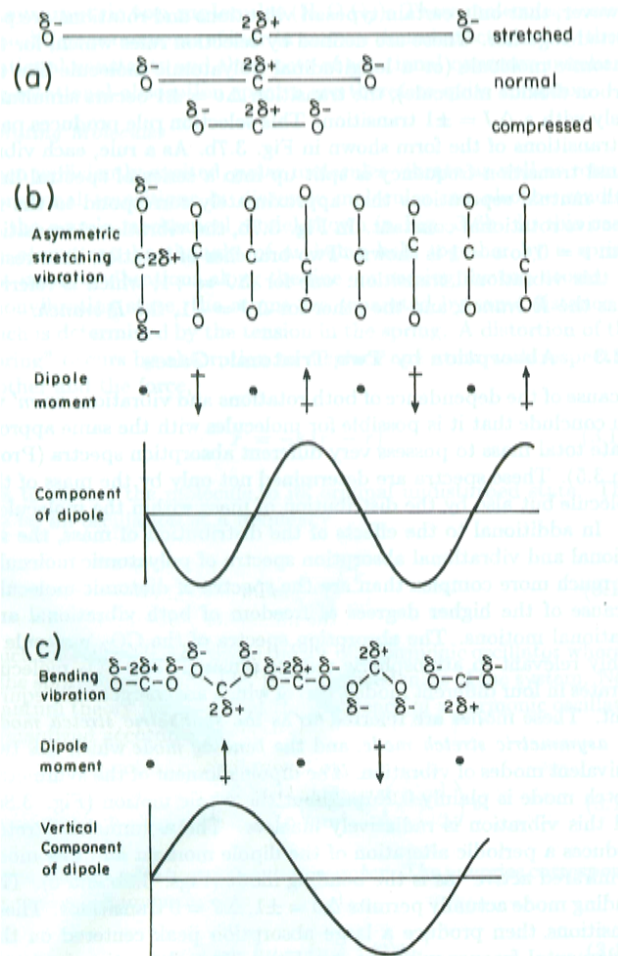
CO is a simple 2 atom molecule which is asymmetric so the dumbbell rotational model works. The rotational spectrum consists of approximately equally spaced rotational absorption lines spaced about 110 GHz apart. The isotopes like CO<sup>18</sup> have very similar spectra.

### CO<sub>2</sub>:

Fundamental rotational frequency is 72 GHz. The EM spectrum of rotational lines only exists as lines in a vibrational-rotational spectrum. CO<sub>2</sub> has no pure rotational EM spectrum. The pure rotational energy levels of the molecule exist but they don't interact with EM radiation. The rotational lines are only apparent as part of the vibrational-rotational spectra of these molecules. So the vibrational line is actually a band of rotational lines centered on the vibrational line energy transition.

**Vibrational energy levels and spectra**

Molecules vibrate when excited. An example of CO<sub>2</sub> vibrational modes is given below, Figure 3.8 from G. Stephens' textbook.



**Fig. 3.8** (a) The symmetric stretching of a vibrating CO<sub>2</sub> molecule. (b) The asymmetric stretching of the CO<sub>2</sub> molecule showing the fluctuating dipole moment. (c) The bending motion of the carbon dioxide molecule and its associated dipole fluctuation (Banwell, 1983).

The vibration can be thought of in terms of the simple harmonic oscillator (SHO) model where there is a restoring force that drives the oscillator back towards its nominal position or configuration

$$F = -kx' \tag{6}$$

where  $F$  is a force,  $x'$  is a displacement from a nominal position, in this case  $x'=0$  and  $k$  is a spring constant. The frequency of the oscillation that results from such a simple restoring force is

$$\nu' = \frac{1}{2\pi} \sqrt{\frac{k}{\mu}} \quad (7)$$

where  $\mu$  is the reduced mass for the system. In the case of a 2 atom molecule, the reduced mass is

$$\mu = \frac{M_1 M_2}{M_1 + M_2} \quad (8)$$

where  $M_1$  and  $M_2$  are the masses of the two atoms in the molecule. When we do the quantum mechanical version of a SHO, the energy levels and frequency of the SHO are quantized such that

$$\nu = \left(v + \frac{1}{2}\right) \frac{1}{2\pi} \sqrt{\frac{k}{\mu}} = \left(v + \frac{1}{2}\right) \nu' \quad (9)$$

where  $v$  is the vibrational quantum number, 0, 1, ...

### Estimating Vibrational Energy Levels

The vibrational frequency of the molecules of interest depends on each molecule's spring constants,  $k$ . There are multiple spring constants for each molecule because there are multiple vibrational modes for each molecule (see Figure above as example).

Textbooks say (correctly) that the vibrational energy spectrum is at higher frequencies than the rotational spectrum. So how can we estimate  $k$  to get a sense of what molecular vibrational energy levels look like and what frequencies and wavelengths are typical of vibrational EM spectrum.

Let's try water. We should be able to get a sense of the magnitude of the restoring force to the crystal lattice by looking at how much energy it takes to move a molecule of water out of the lattice (the latent heat). We can then set this equal to WORK required to move a molecule out of the lattice. WORK is force times distance. We know the separation distance between molecules so we can figure out the force. Knowing the force we can estimate the spring constant approximately.

As all atmospheric scientists should know, the binding energy of water is the latent heat of water, that is the amount of energy required to move water from a condensed state to the gas phase. The latent heat is about 2.5e6 J/kg at typical Earth temperatures. Strictly speaking this is the energy to move water from the liquid phase to the gas phase but the extra energy to go from solid to liquid is only about another 10% and we are only trying to get a crude estimate.

We convert J/kg to J/molecule using 0.018 kg/mole for water and 1 mole =  $6 \times 10^{23}$  molecules. So the energy to free 1 water molecule is 2.5e6 J/kg \* 0.018 kg/mole \* 1/6e23 mole/molecule  $2.5/6 \times 10^{(6-23)} = 4 \times 10^{-18}$  J/molecule = 25 eV/molecule where 1.6e-19 J/eV.

Now we set this energy equal to "WORK" =  $F_{avg} d$ . The distance to separate a water molecule from the other water molecules is approximately  $1 \text{ \AA} = 10^{-10}$  m which is the distance between water molecules. So

$$F_{avg} = 4 \times 10^{-18} / 10^{-10} = 4 \times 10^{-8} \text{ kg m/s}^2.$$

Now we set  $F_{avg}$  equal to  $-kx$  where we choose  $x$  to be about half of  $d$  to be crudely representative.

$$F_{avg} = kx \text{ for } x=0.5 \times 10^{-10}$$

So  $k = 4 \times 10^{-8} / 0.5 \times 10^{-10} = 8 \times 10^2 \text{ kg/s}^2$ .

As a crude estimate of the reduced mass of a water molecule, we approximate it as  $0.018 \text{ kg} / 6 \times 10^{13} \text{ molecules} / 3$  because there are 3 atoms in the water molecule.

Plugging this  $k$  into the vibrational frequency equation, we get

$$\nu' = 4.5 \times 10^{13} \text{ Hz}$$

Note that this frequency is quite a bit higher than the *rotational* constant frequency ( $9 \times 10^{11} \text{ Hz}$ ) we estimated previously for water. So indeed the *vibrational* spectrum is significantly higher in frequency and energy than the *rotational* spectrum.

This frequency corresponds to a wavelength of 6 microns which is indeed in the thermal IR band. The photon energy  $h\nu' = 6.6 \times 10^{-34} \text{ J sec} \times 4.5 \times 10^{13} \text{ Hz} = 3 \times 10^{-20} \text{ J}$ . We divide this by  $1.6 \times 10^{-19} \text{ J/eV}$  to get 0.2 eV which is indeed in the IR range

Another approach to estimating the spring constant is to use either the bulk modulus or Young's modulus. Young's modulus,  $E$ , is a property of the solid equal to the stress (force /area) divided by the strain, the fractional change in length. Consider a rod where we apply a compressional force,  $F$ , on each end and then measure how much the rod shortens,  $\Delta L/L$  where  $L$  is the original length of the rod.

$$E = \text{stress/strain} = F/A / (\Delta L/L) \quad (10)$$

$A$  is the surface area over which the force is applied. Solving for  $F$  we get  $F = EA \Delta L/L$ .

Assuming  $A \sim L^2$ , then  $F \sim EL \Delta L$ . Our spring constant is therefore  $k = EL$ .

We take  $E$  of steel to be representative,  $E_{steel} = 2 \times 10^{11} \text{ N/m}^2$ . For a molecule, we'll take  $L \sim 2 \text{ \AA}$ . So  $EL = k = 2 \times 10^{11} \text{ N/m}^2 \times 2 \times 10^{-10} \text{ m} = 40 \text{ N/m}$ .

Plugging this into the vibrational frequency equation,

$$\nu' = \frac{1}{2\pi} \sqrt{\frac{k}{\mu}} \quad (11)$$

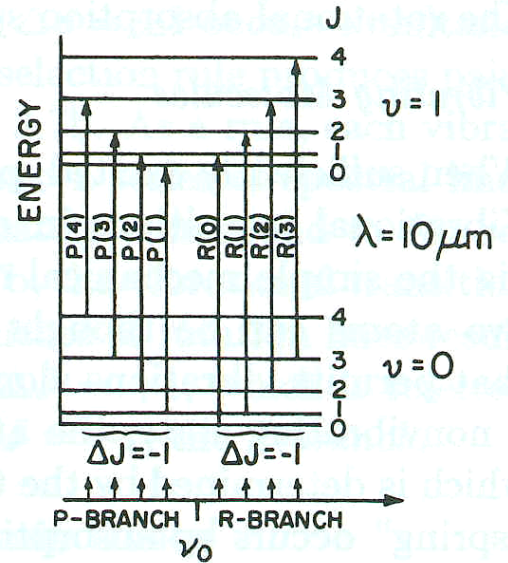
we get that for water, the frequency is  $10^{13} \text{ Hz}$ . This corresponds to a wavelength of 30 microns. The frequency is a bit too low and the wavelength a bit too long but it is in the right range approximately.

So these crude physical arguments have given us a simple understanding of the vibrational restoring force and why the vibrational frequencies and energies are typically in the thermal IR band.



### Vibrational-Rotational Spectrum

The vibrational ‘line’ is actually a band of rotational lines centered on the vibrational line energy transition. For molecules with no permanent dipole moment, the rotational lines are only apparent as part of the vibrational-rotational spectra of these molecules. The selection rules are  $\Delta J = \pm 1$  and  $\Delta v = \pm 1$ . The R and P branches in the figure are defined as follows. The R-branch is  $\Delta J = +1$ . The P-branch is  $\Delta J = -1$ .  $\nu_0$  is the frequency of the nominal vibrational line center.



### Crosssection associated with gas absorption & emission

Now, we return to an equation that we introduced briefly for  $\alpha (= k)$  that represents the absorption coefficient for gases

$$\alpha = k_{\nu,\nu} = S_{\nu,\nu} f(\nu - \nu_0) \tag{12}$$

where  $S$  is the line strength of the absorption line,  $f$  represents the shape of the absorption line,  $\nu$  is the frequency of the measurement and  $\nu_0$  is the line center of the absorption line. The line shape is due to a combination of Doppler and pressure broadening. The line strength is given as

$$S_{\nu,\nu} = n_m \frac{g_i \exp(-E_i/kT)}{Z} \frac{C_{ij}}{c} [1 - e^{-h\nu_{ij}/kT}] = n \frac{n_m}{n} \frac{g_i \exp(-E_i/kT)}{Z} \frac{C_{ij}}{c} [1 - e^{-h\nu_{ij}/kT}] \tag{13}$$

where  $n_m$  is the number density of molecule:  $m$ ,  $n$  is the total number density of the bulk gas =  $P/k_B T$  and  $n_m/n$  is the volume mixing ratio of constituent  $m$  of the gas,  $E_i$  is the energy of the lower energy level ( $i$  and  $j$ ) of the molecule,  $\nu_0 = \nu_{ij}$ ,  $g$  is the number of states that have this particular energy transition,  $Z$  is the partition function which is  $\sum_i g_i \exp(-E_i/k_B T)$  which is the sum of population of all of the available states at a particular temperature,  $T$ , and  $C_{ij}$  is an electromagnetic coupling factor for this particular energy transition. Remember that the distribution of the population of molecules is defined by the Boltzmann distribution

The  $[1 - e^{-h\nu_{ij}/kT}]$  term represents the absorption minus the stimulated emission term. The stimulated emission term is the term responsible for lasers.

We can write these equations in terms of crosssections by recognizing the following

$$k_{\nu,\nu} = S_{\nu,\nu} f(\nu - \nu_0) = n_m \frac{g_i \exp(-E_i/kT) C_{ij}}{Z} \frac{C_{ij}}{c} [1 - e^{-h\nu_{ij}/kT}] f(\nu - \nu_0) \quad (14)$$

but as we have discussed, the extinction, absorption or scattering coefficient can be thought of and written as a crosssection per particle or molecule times the number density of particles or molecules

$$k = \sigma n \quad (15)$$

So (14) and (15) imply that the absorption crosssection of a gas molecule at a particular frequency and pressure is given by

$$\sigma_{\nu,\nu} = \frac{g_i \exp(-E_i/kT) C_{ij}}{Z} \frac{C_{ij}}{c} [1 - e^{-h\nu_{ij}/kT}] f(\nu - \nu_0) \quad (16)$$

So even the absorption (and emission) by gases has an effective crosssection related to how it interacts with EM radiation.

Next we discuss the lineshape function,  $f(\nu - \nu_0)$ .