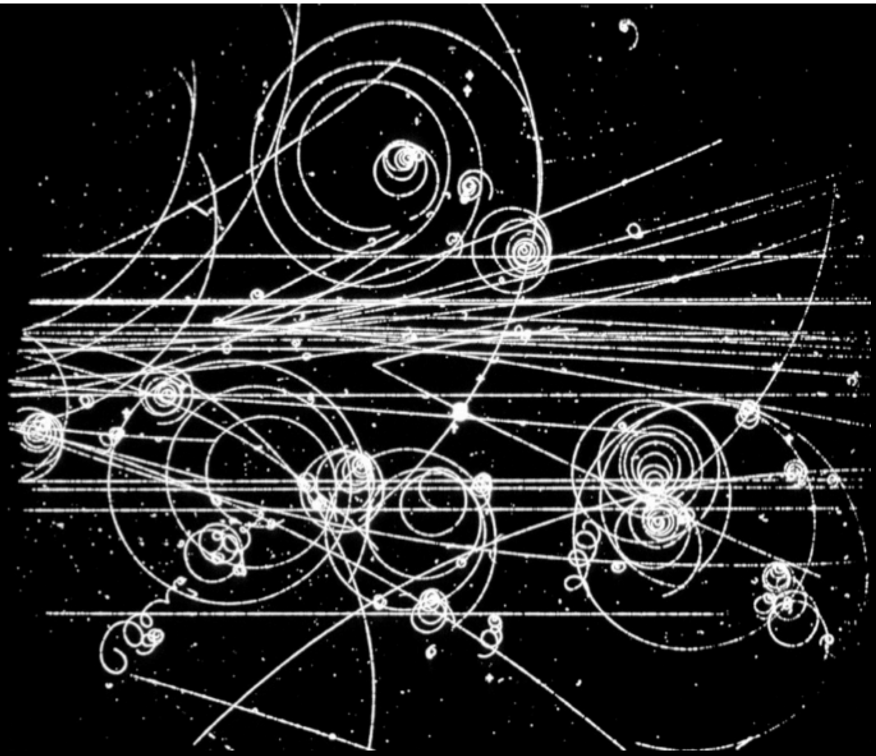
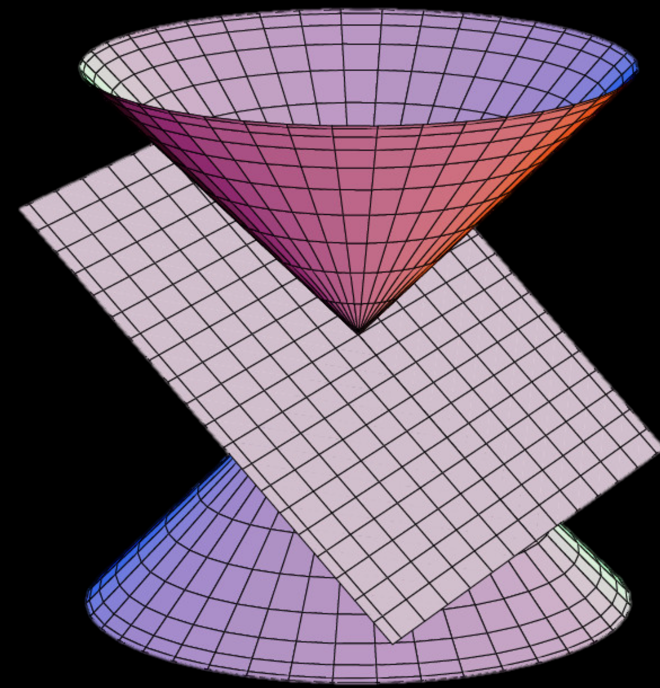




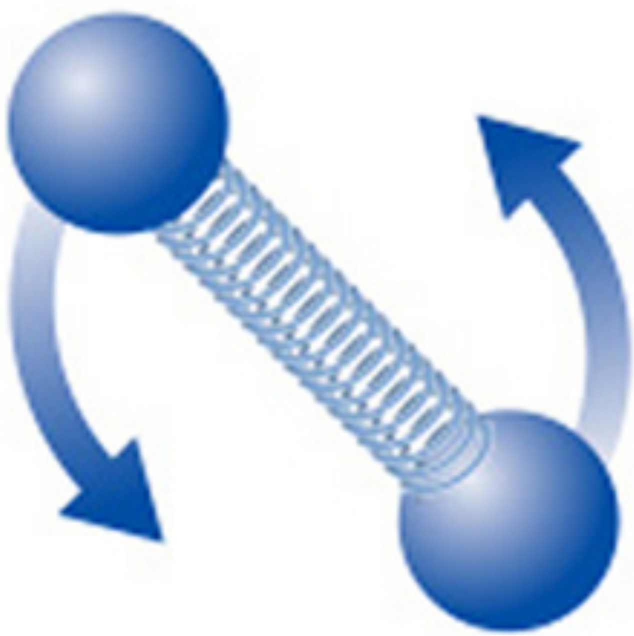
Modern Physics (Phys. IV): 2704

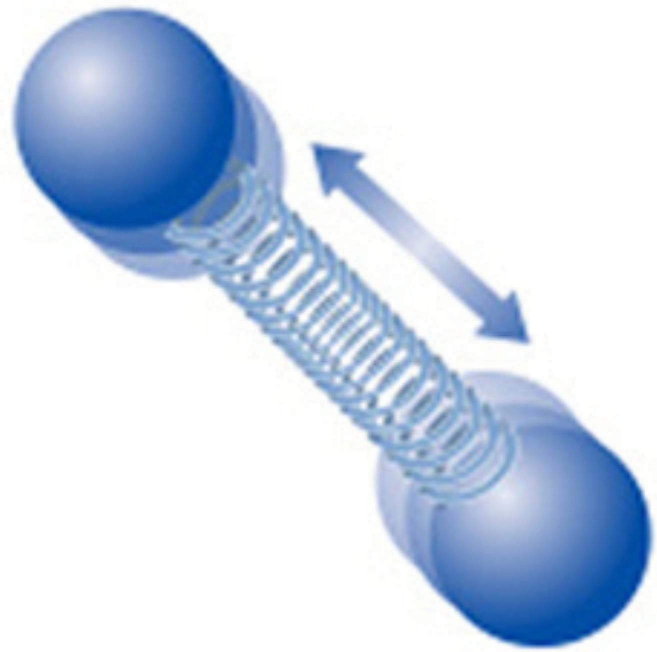
Professor Jasper Halekas
Van Allen 70
MWF 12:30-1:20 Lecture

Molecular Rotation/Vibration

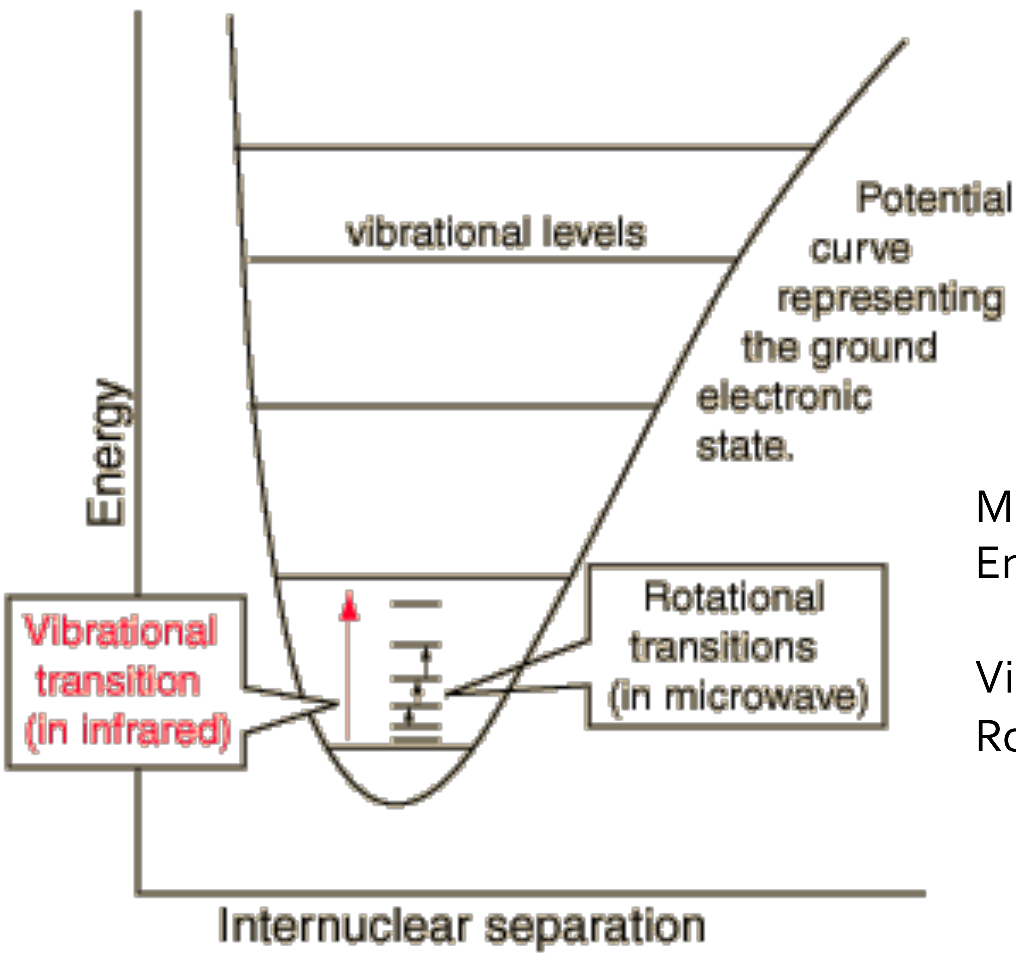
$E_L = L(L+1)\,\hbar^2/(2\mu R^2)$
$\quad = B\,L(L+1)$

$E_N = (N+1/2)\,\hbar\omega$
$\omega = \sqrt{(k/\mu)}$





Molecular Rotational/Vibrational Energy Levels



Molecular Hydrogen Energy Spacing:

Vibrational ~0.54 eV
Rotational ~0.014 eV

Concept Check

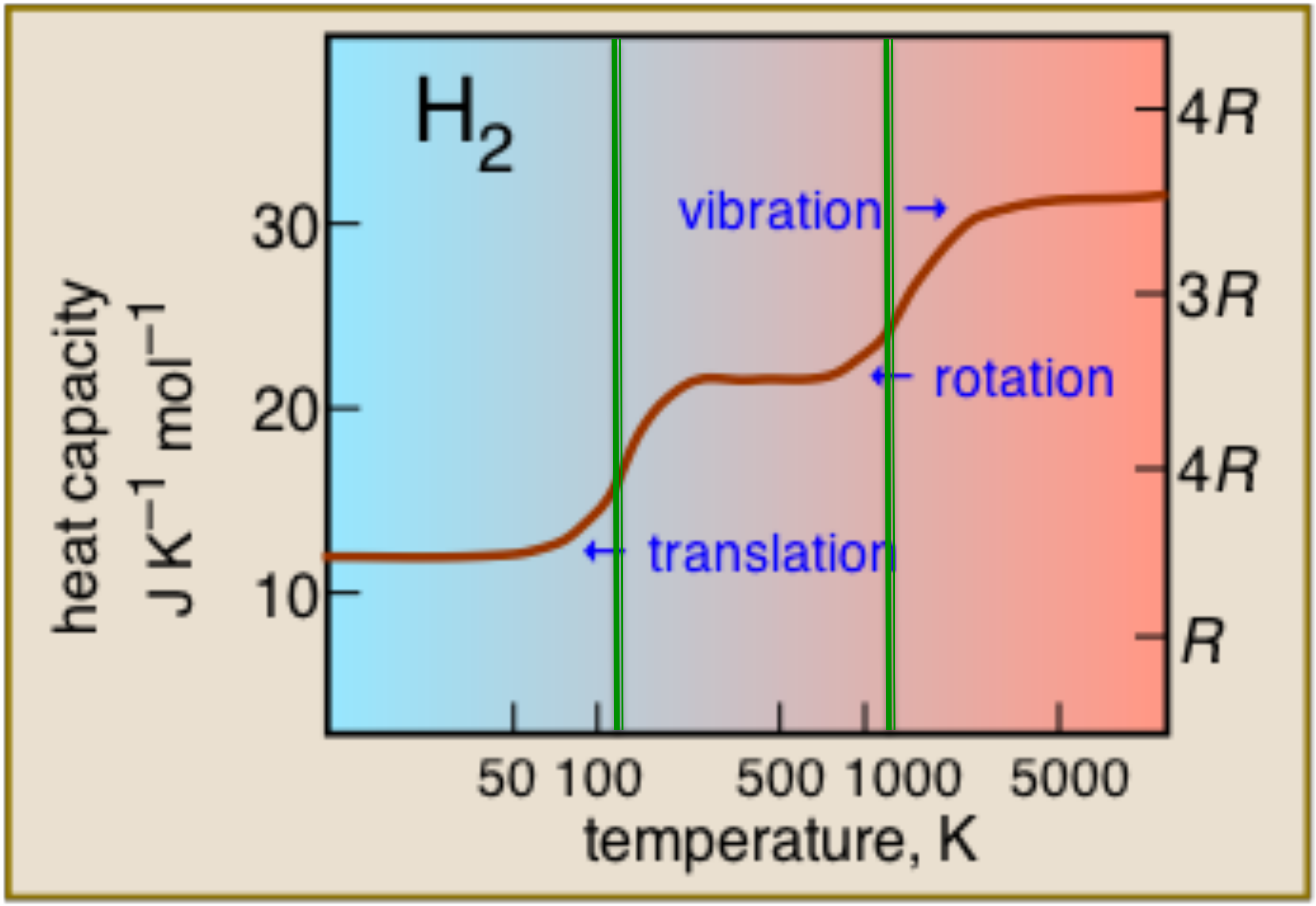
- A typical molecular translational kinetic energy at room temperature is ~0.03 eV. Which H_2 vibrational/rotational states would you expect to be excited by collisions?
- $N = 0, L \geq 0$
- $N \geq 0, L \geq 0$
- $N \geq 0, L = 0$
- Only $N = 0, L = 0$

Concept Check

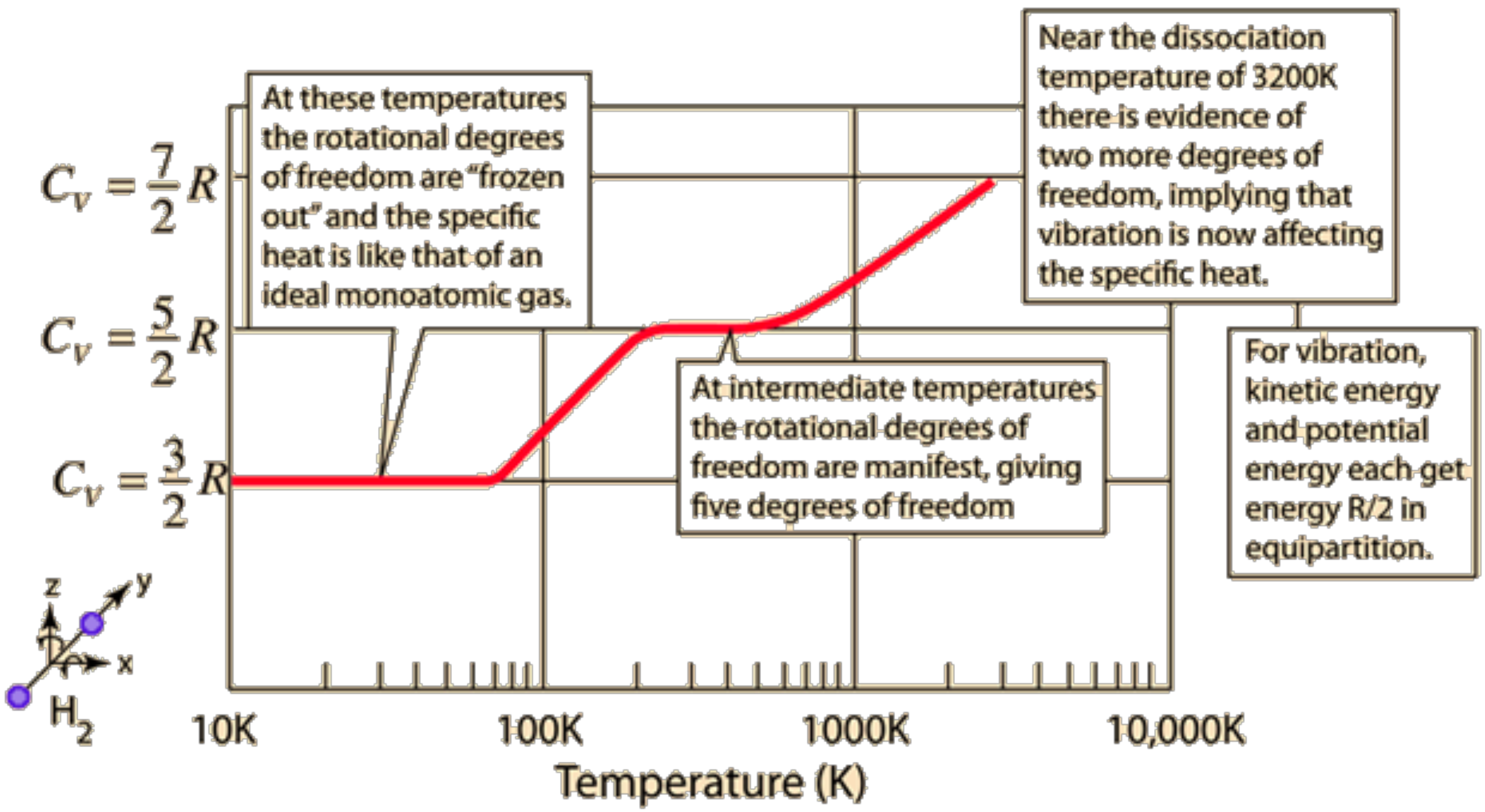
- A typical molecular translational kinetic energy at room temperature is ~0.03 eV. Which H_2 vibrational/rotational states would you expect to be excited by collisions?
- N = 0, L ≥ 0
- N ≥ 0, L ≥ 0
- N ≥ 0, L = 0
- Only N =0, L = 0

Vibration, Rotation, Heat Capacity

kT = 0.01 eV kT = 0.1 eV



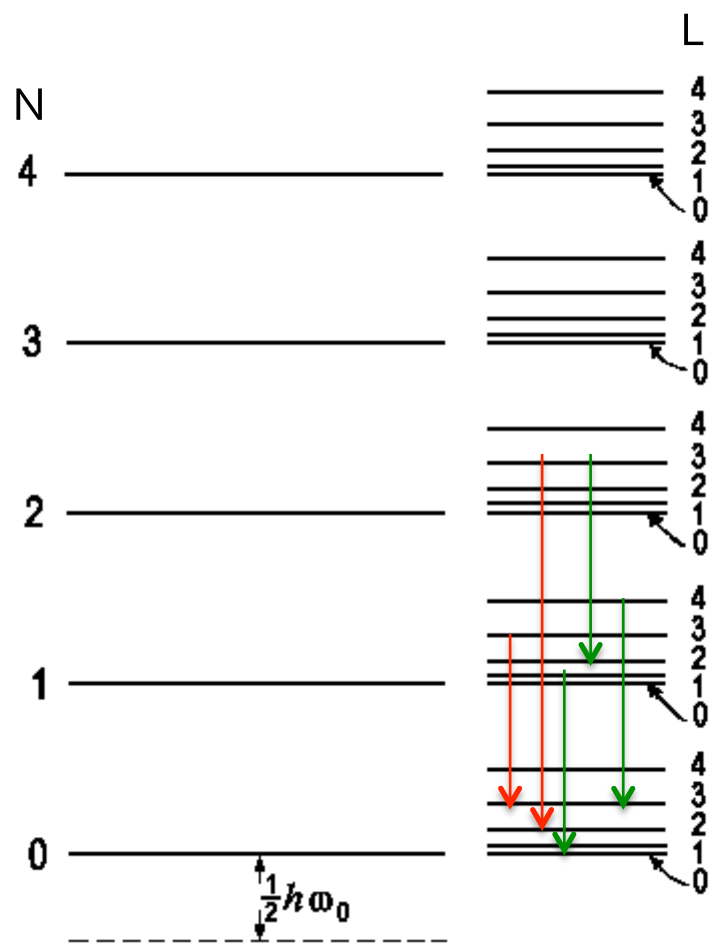
Vibration, Rotation, Heat Capacity



Heat Capacity – Solved!

- Quantization of rotational and vibrational energy levels solves a major problem in classical physics
- When a gas is too cold, collisions can't impart the minimum energy needed to induce a transition, so all energy goes into translational motion
- When a gas is hotter, collisions can excite higher rotational/vibrational states, which increases the amount of energy needed to change the temperature of the gas (and so increases its heat capacity)

Molecular Rotational/Vibrational Energy Levels



$\Delta L = \pm 1$

$\Delta N = \pm 1$

Allowed

Forbidden

Vibrational Spacing

$$E_N = (N + 1/2)\hbar\omega$$

$$\Delta E_N = \hbar\omega = h\nu = \hbar\sqrt{K/\mu}$$

Rotational Spacing

$$E_L = \frac{\hbar^2}{2\mu R^2} L(L+1)$$

$$= B L (L+1)$$

$$\Delta E_L = B(L+1)(L+2) - BL(L+1)$$

$$= B(L^2 + 3L + 2) - B(L^2 + L)$$

$$= B(2L + 2)$$

$$= 2B(L+1)$$

$$= 2B, 4B, 6B, \ldots$$

Concept Check

- The rotational energy levels are $E_L = BL(L+1)$. What would be the energy of a photon absorbed during a transition from L = 1 to L = 2?

A. $h\nu = 6B$
B. $h\nu = B$
C. $h\nu = 2B$
D. $h\nu = 4B$

Concept Check

- The rotational energy levels are $E_L = BL(L+1)$. What would be the energy of a photon absorbed during a transition from L = 1 to L = 2?

A. $h\nu = 6B$
B. $h\nu = B$
C. $h\nu = 2B$
D. $h\nu = 4B$

Population of Excited States

For given L, $2L+1$ possible states
$M_L = -L, \ldots, L$

$$P(E_{NL}) \propto (2L+1)\, e^{-E_{NL}/kT}$$

$$= (2L+1)\, e^{-[(N+\frac{1}{2})\hbar\omega + BL(L+1)]/kT}$$

@ room temperature, most molecules in $N=0$ state

$$P(E_{NL}) \propto (2L+1)\, e^{-BL(L+1)/kT}$$

Max $P(E_{NL})$ for $dP/dL = 0$

$$\Rightarrow \frac{d}{dL}\left[(2L+1)\, e^{-BL(L+1)/kT}\right] = 0$$

or $$2e^{-BL(L+1)/kT} + (2L+1)\cdot -\frac{B}{kT}\cdot(2L+1) \cdot e^{-BL(L+1)/kT} = 0$$

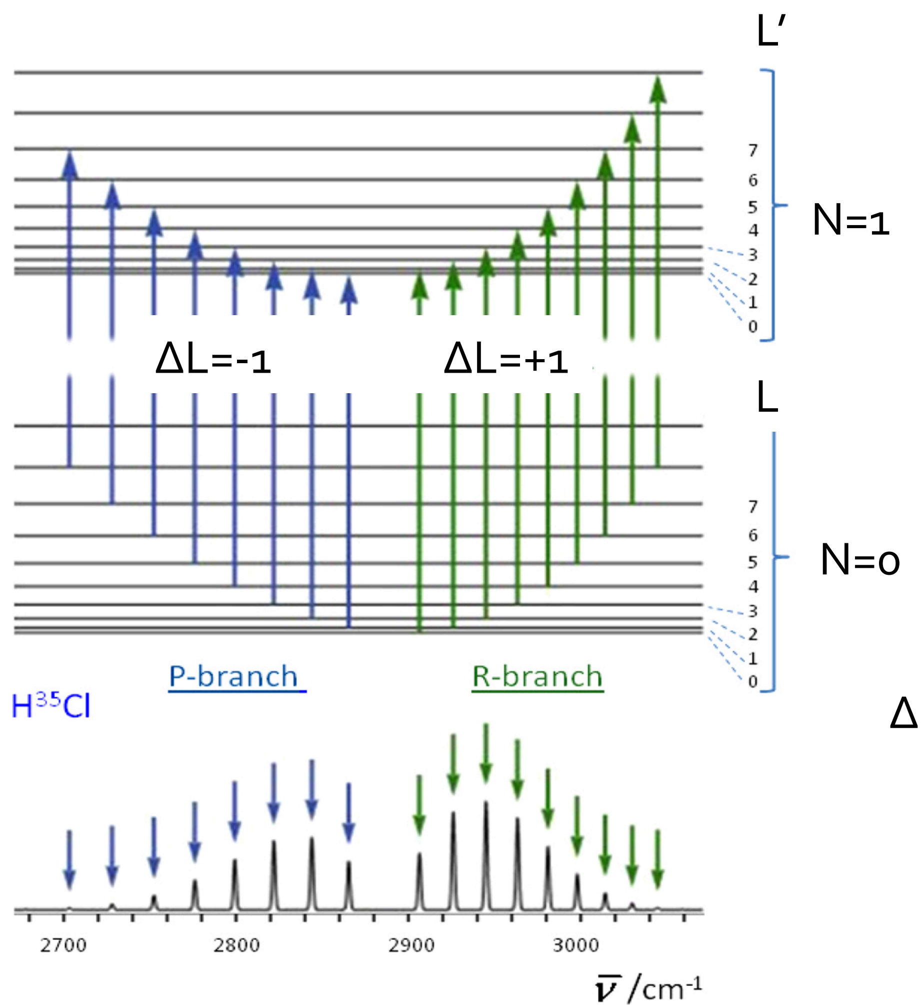
$$\Rightarrow 2 - (2L+1)^2\, B/kT = 0$$

$$\Rightarrow (2L+1)^2 = 2kT/B$$

$$\Rightarrow 2L+1 = \sqrt{2kT/B}$$

$\Rightarrow$ most probable $L = \left(\sqrt{\frac{2kT}{B}} - 1\right)/2$

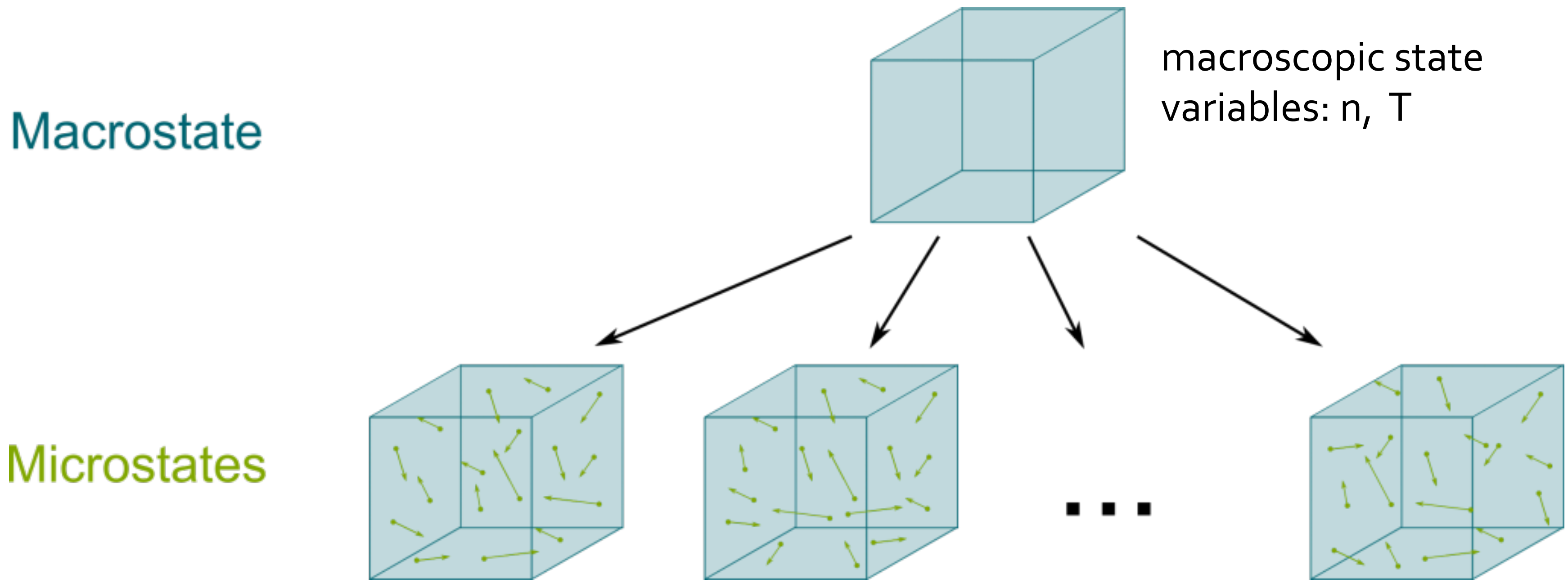
Molecular Absorption Spectra



$\Delta E = \hbar\omega - 2B$
$\hbar\omega - 4B$
$\hbar\omega - 6B$
....

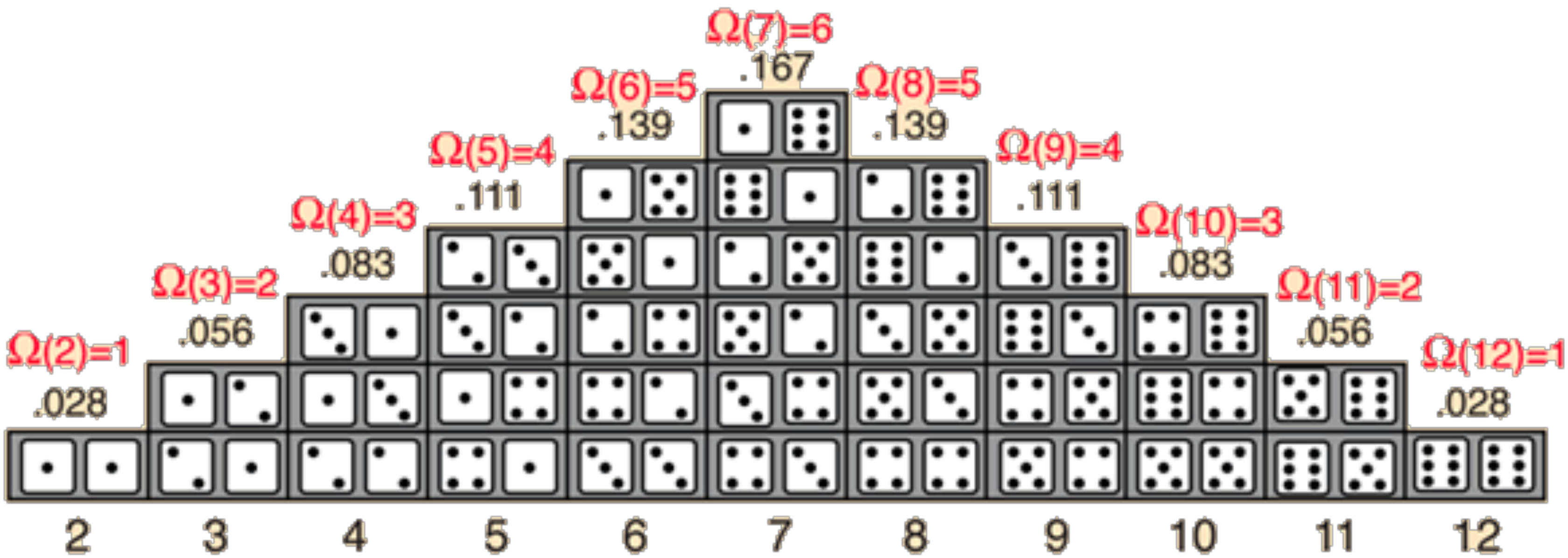
$\Delta E = \hbar\omega + 2B$
$\hbar\omega + 4B$
$\hbar\omega + 6B$
....

Macrostates/Microstates



Microscopic state variables: x_i, y_i, z_i, v_{xi}, v_{yi}, v_{zi}

Counting Macrostates/Microstates



Total number of microstates: 36

Total number of macrostates: 11