E. Statistical Physics of Rotational and Vibrational Motions in a gas of diatomic molecules

Phenomena : Three pieces of physics

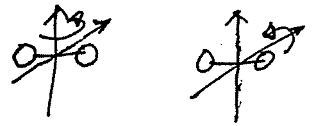
(a) Maxwell (~1870): $\frac{1}{2}kT$ contribution to average energy per (quadratic) degree of freedom

Diatomic molecules

Heat Capacity: $\underbrace{\frac{3}{2}Nk} + \underbrace{Nk} + \underbrace{Nk}$

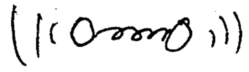
translational motion of molecules (Center of Mass motion as if molecule is a point particle)

$\frac{1}{2}Nk + \frac{1}{2}Nk$



rotational motion (internal, i.e. within molecule)

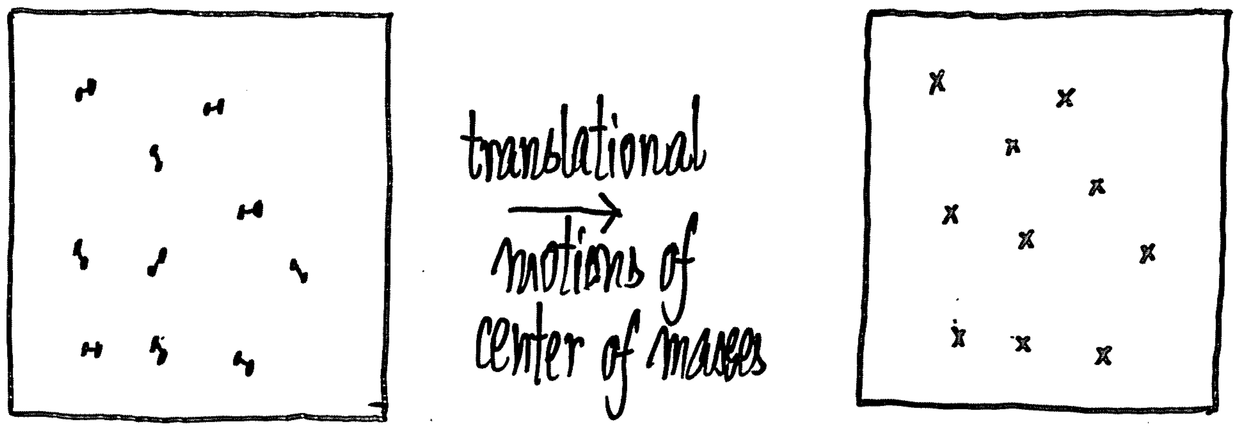
oscillator



vibrational motion (internal, i.e. within molecule)

∴ Expected to see $\frac{7}{2}Nk$ or $\frac{7}{2}R$ per mole

- But the "last" Nk (due to vibrational motion) is there for some molecules (e.g. Br_2, I_2) but not there for other molecules (e.g. H_2, O_2) at "ordinary" temperatures (300-400K).
- Only at high temperatures, see $\frac{7}{2}Nk$.

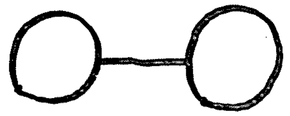


A jar of diatomic molecules

x ≡ CM of molecules

The statistical mechanics of the CM motions⁺ of molecules is the same problem as a monatomic gas!

But, zooming into a molecule:



In additional to CM translational motion, there are also:

Internal degrees of freedom
- Vibrational motion (in x-direction, 1 degree of freedom)
- Rotational motion (about y-axis and z-axis, 2 degrees of freedom) (or needs 2 angles for its orientation)

⁺ We did the problem of ideal monatomic gas within microcanonical ensemble. We will treat this translational part within canonical ensemble later.

Historically, this expectation was often written as

$$E = \frac{7}{2}kTN = \frac{7}{2}pV$$

$$\Rightarrow pV = \frac{2}{7}E \equiv (\gamma-1)E$$

$$\text{with } \gamma = \frac{9}{7} \quad (\underline{\text{expected}}) = 1.286$$

$$\text{Data:}\quad \left.\begin{array}{lll} O_2\ (T=100^\circ C) & \gamma = 1.399 & \times \\ H_2\ (T=100^\circ C) & \gamma = 1.404 & \times \\ I_2\ (T=185^\circ C) & \gamma = 1.30 & \checkmark \end{array}\right\} \text{observed}$$

The physics is ...

$$Z = \underbrace{\frac{(z_{\text{trans}})^N}{N!}}_{\substack{\uparrow \\ \text{translational} \\ \text{motion}}} \cdot \underset{\substack{\uparrow \\ \text{rotational} \\ \text{partition} \\ \text{function}}}{(z_{\text{rot}})^N} \cdot \underset{\substack{\uparrow \\ \text{vibrational} \\ \text{partition} \\ \text{function}}}{(z_{\text{vib}})^N}$$

Non-interacting molecules

z_{trans} is related to $\frac{p^2}{2M}$ (kinetic energy of CM motion of molecule)

z_{rot} is related to $\frac{J(J+1)\hbar^2}{2I}$ (rotational energy)

$$z_{\text{vib}} = \frac{e^{-\beta\frac{\hbar\omega}{2}}}{1-e^{-\beta\hbar\omega}} \quad (\text{oscillator})$$

↑ related to $(n+\frac{1}{2})\hbar\omega$ (vibrational energy)

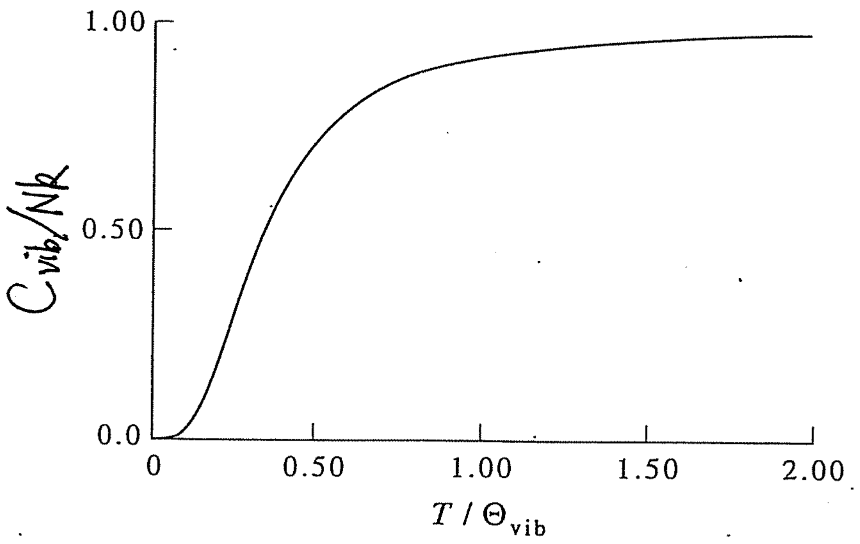
<u>Recall</u>: N oscillators of angular frequency ω (same ω)

$$C_{\text{vib.}} = Nk\left(\frac{\hbar\omega}{kT}\right)^2 \frac{e^{\frac{\hbar\omega}{kT}}}{\left(e^{\frac{\hbar\omega}{kT}}-1\right)^2}$$

$$\text{Define: } \frac{\hbar\omega}{k} \equiv \underset{\substack{\uparrow \\ \text{molecule's} \\ \text{property}}}{\Theta_{vib}} \qquad \Big(\underset{\substack{\uparrow \\ \text{molecule's} \\ \text{property}}}{\omega} \sim \sqrt{\frac{K \leftarrow \text{bonding}}{\mu \leftarrow \text{reduced mass}}} \Big)$$

$$C_{\text{vib.}} = Nk\left(\frac{\Theta_{vib}}{T}\right)^2 \frac{e^{-\frac{\Theta_{vib}}{T}}}{\left(e^{\frac{\Theta_{vib}}{T}}-1\right)^2}$$

"Universal behavior"



	Θ_{vib}
H_2	6215K
HCl	4227K
N_2	3374K
O_2	~2230K
I_2	308K
CO	~3080K

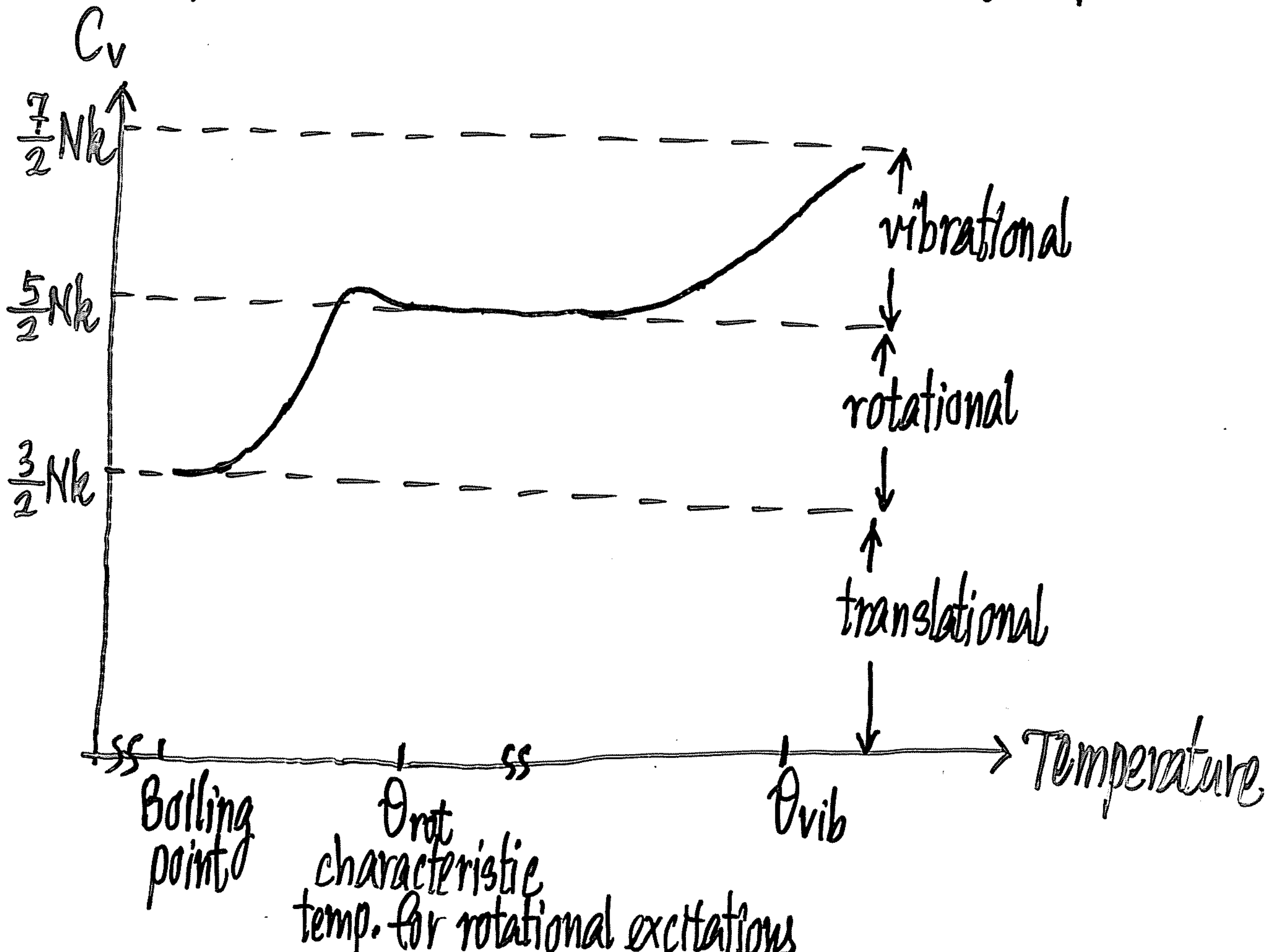
So, for T=300K,

$$\left\{\begin{array}{ll} \frac{T}{\Theta_{vib}} = 0.048 \text{ for } H_2 & (\text{no contribution to } C_{vib}) \\ \frac{T}{\Theta_{vib}} = 0.974 \text{ for } I_2 & (\sim\text{full contribution to } C_{vib}) \end{array}\right.$$

- For not-too-heavy molecules, only n=0 vibrational ground state is significantly occupied and contribution to C_{vib} is tiny for $T \ll \Theta_{vib}$.

Schematic features of $C_V(T)$ for a Diatomic Gas

- Above Boiling point, the translational motions of the molecules contribute to C_V as an ideal gas, i.e. $C_{V,\text{trans}} = \frac{3}{2}Nk$
- At higher temperatures, rotational levels can be excited $\Rightarrow$ $C_{V,\text{rot}}$ contributes to C_V
- At even higher temperatures, vibrational levels can be excited $\Rightarrow$ $C_{V,\text{vib}}$ contributes to C_V



(b) Vibrational States are not (much) excited at room temperature

$$Z_{vib} = e^{-\frac{\beta\hbar\omega}{2}} \sum_{n=0}^{\infty} e^{-\beta\hbar\omega n} = e^{-\frac{\beta\hbar\omega}{2}}\Big[\overset{\text{ground state}}{1} + e^{-\beta\hbar\omega} + \cdots\Big] = \frac{e^{-\frac{\beta\hbar\omega}{2}}}{1-e^{-\beta\hbar\omega}}$$

∴ By definition,

$$\text{Prob. of oscillator in ground state} = \frac{1}{\frac{1}{1-e^{-\beta\hbar\omega}}} = 1-e^{-\beta\hbar\omega} = 1-e^{-\frac{\theta_{vib}}{T}}$$

e.g. Take <u>HCl</u>, $\theta_{vib} = 4227K$, $T = 300K$, $\frac{\theta_{vib}}{T} \sim 14$

$$\text{Prob. of oscillator in ground state} = 1 - e^{-14} \approx 1$$

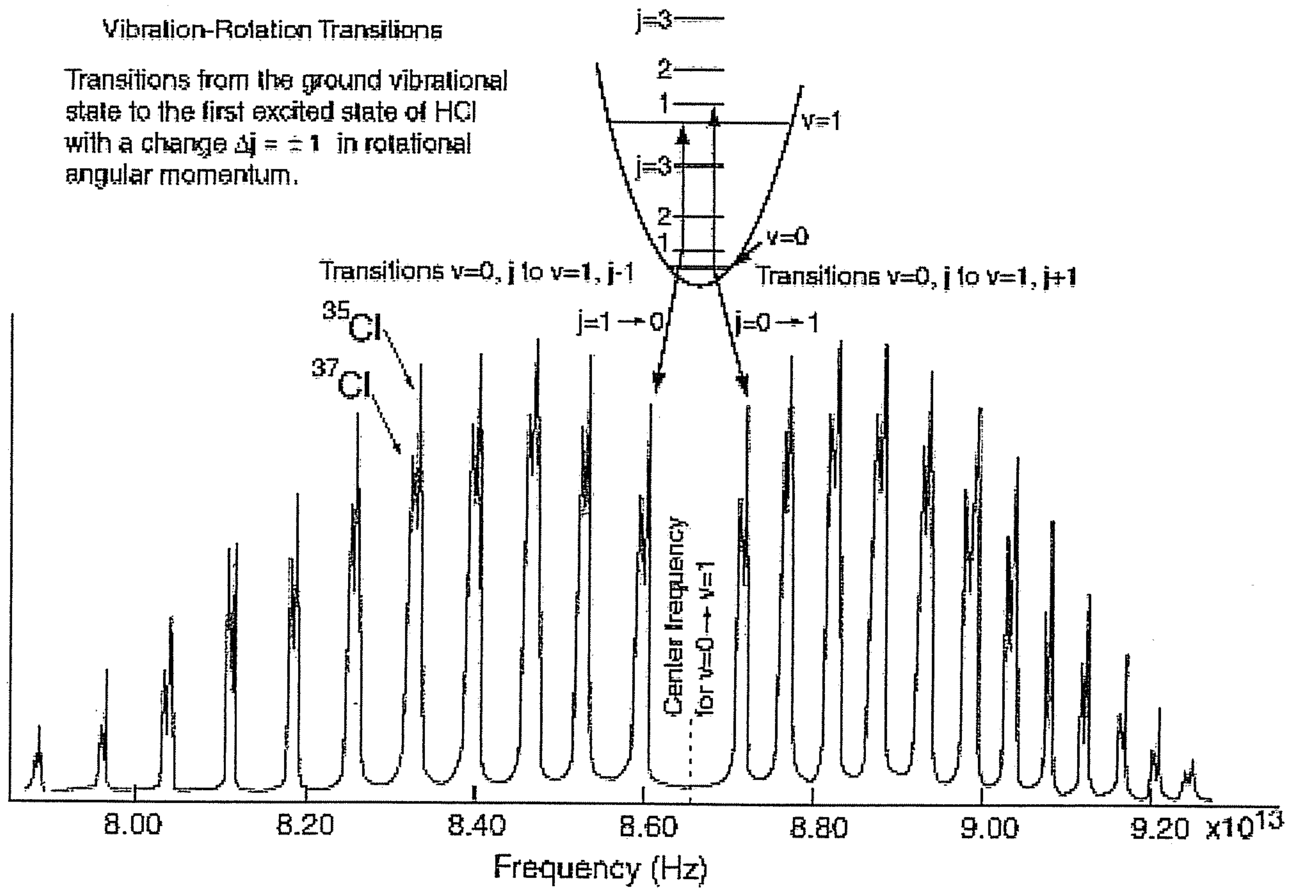
$$\boxed{\text{∴ Most molecules are in the vibrational ground state at room temperature!}}$$

"Most" means molecules with light atoms.

By product,

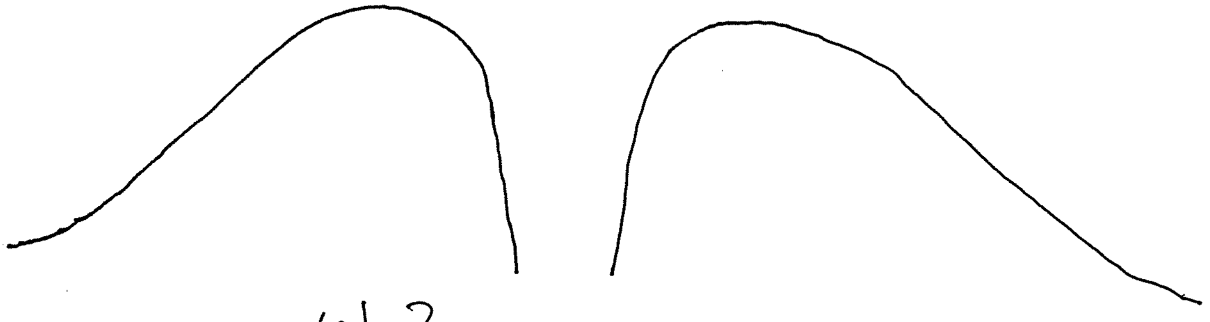
$$\text{Prob. of oscillator in any excited state} = e^{-\frac{\theta_{vib}}{T}}$$

(c) Shape of envelope in vibrational-rotational spectrum



- (See Applied QM)
  - location of mid-gap ⇒ Spring constant (bond strength)
  - spacing between lines ⇒ Moment of Inerta (bond length)

How about the "envelope"?



Why?

The physics is . . .

$\Delta E_{el} \sim 1eV$
$\Delta E_{vib} \sim 0.1 eV$
$\Delta E_{rot} \sim 0.001 eV$

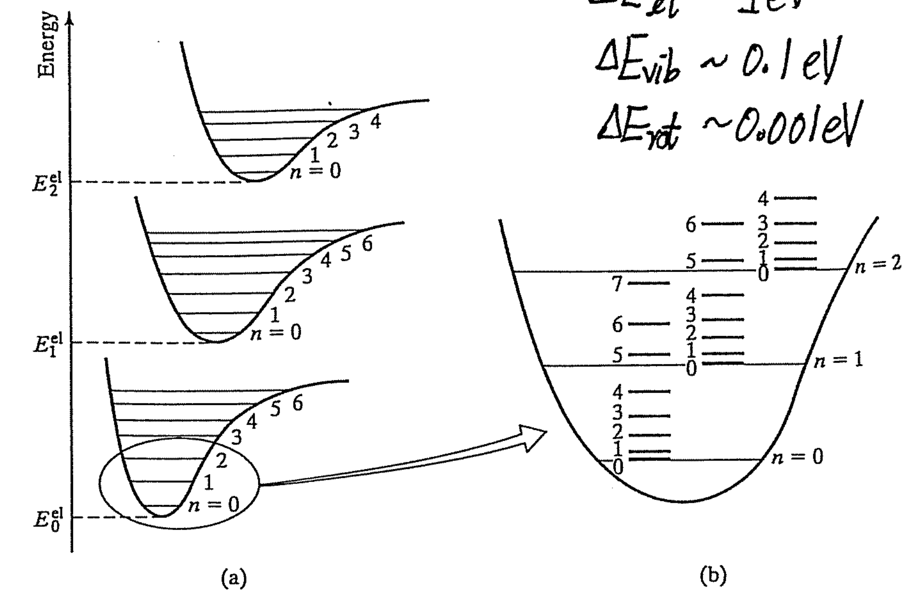


FIGURE 12.28
Energy levels of a diatomic molecule have the form $E_i^{el} + E_n^{vib} + E_l^{rot}$. **(a)** For each electronic level, there is a ladder of vibrational levels, labeled $n = 0, 1, \cdots$. (On the scale of this picture the rotational levels are too closely spaced to be shown.) **(b)** Above each vibrational level is a "subladder" of very closely spaced rotational levels, as illustrated by this enlargement of the three lowest vibrational levels. The rotational levels are labeled by the quantum number $l = 0, 1, 2, \cdots$, shown on their left. Note that in most molecules the rotational levels are much more closely spaced than shown here.

[Figures taken from Taylor, Zafiratos, Dubson "Modern Physics for Scientists and Engineers"]

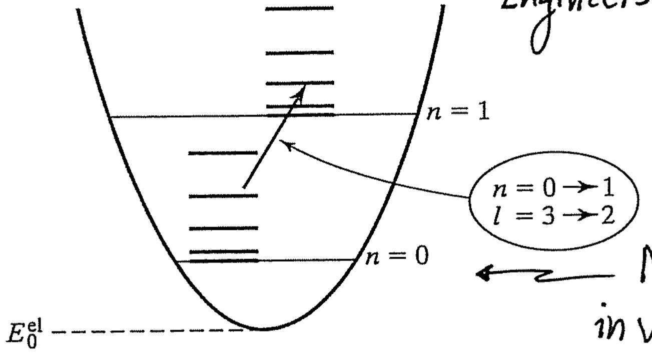
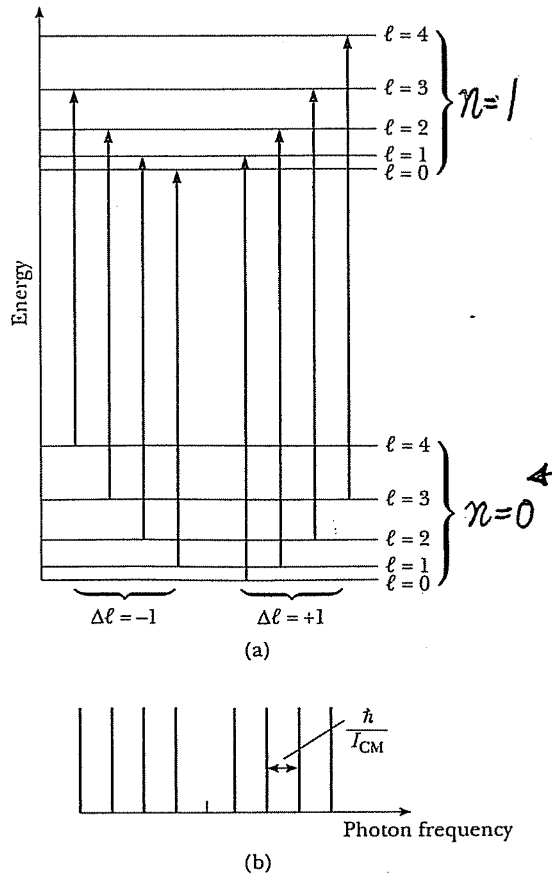


FIGURE 12.30
In a vibrational–rotational transition the electronic state is unchanged, but both n and l change by one unit. In the transition shown, n increases ($n = 0 \to 1$) and l decreases ($l = 3 \to 2$). Since the total energy increases, this transition entails the absorption of a photon. (Spacing of the rotational levels is greatly exaggerated.)

Most molecules in vibrational ground state

Absorption Transitions (selection rules)

[Figure taken from Serway, Moses, Moyer, "Modern Physics"]



Distribution of molecules in rotational levels belonging to n=0 vibrational state matters!

How do molecules occupy rotational levels?

z_{rot} = rotational partition function of a molecule

$$= \underbrace{\sum_{l=0}^{\infty}\sum_{m_l=-l}^{+l}}_{\text{sum all rotational states}} e^{-\frac{l(l+1)\hbar^2}{2IkT}}$$

$$= \sum_{l=0}^{\infty} \underbrace{(2l+1)}_{\text{given } l,\ (2l+1) \text{ terms from } m_l} e^{-\frac{l(l+1)\hbar^2}{2IkT}}$$

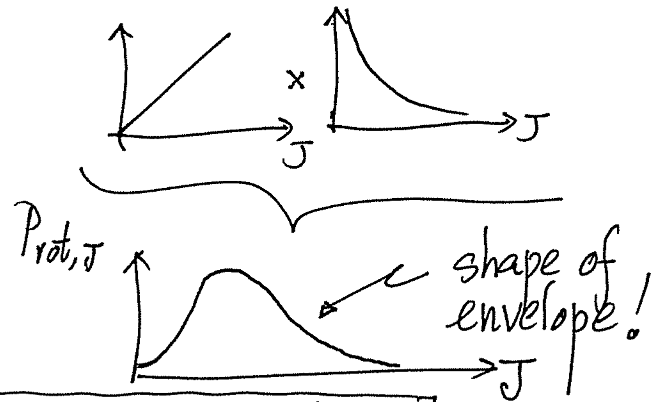
$\because$ rotational energy $\frac{l(l+1)\hbar^2}{2I}$ does not depend on m_l

$$= \sum_{J=0}^{\infty}(2J+1)\, e^{-\frac{J(J+1)\hbar^2}{2IkT}}$$

(chemists call "l" as "J")

$\therefore$ Prob. of molecule in rotational level J (or l)

$$P_{rot,J} = \frac{(2J+1)\, e^{-\frac{J(J+1)\hbar^2}{2IkT}}}{z_{rot.}} \propto \underbrace{(2J+1)}_{\text{increases with } J}\ \underbrace{e^{-\frac{J(J+1)\hbar^2}{2IkT}}}_{\text{drops rapidly with } J}$$



Meaning: Most molecules are in excited rotational states at room temperature!

$$P_{rot,J} \propto (2J+1)\, e^{-\frac{J(J+1)\hbar^2}{2IkT}}$$

- See a rotational energy scale $\frac{\hbar^2}{2I}$ ← moment of inertia $\sim \mu R_0^2$

$\Rightarrow$ a rotational temperature scale $\theta_{rot} \equiv \frac{\hbar^2}{2Ik}$

$$= \frac{h^2}{8\pi^2 Ik} = \frac{hB}{k}$$

where $B = \frac{h}{8\pi^2 I}$ is a molecule parameter

[not to confuse it with magnetic field]

Data

	$\theta_{rot.}$
H_2	85.3K
I_2	0.0537K
O_2	2.07K
N_2	2.88K
HCl	15.02K
Br_2	0.116K

At T=300K, rotational levels (for n=0 vibrational state) are excited!

Example: CO $\theta_{rot} = 2.77K$ $\frac{\theta_{rot}}{T} = 0.00923$ for T=300K

$$P_{rot,J} = \frac{(2J+1)\, e^{-J(J+1)\frac{\theta_{rot}}{T}}}{z_{rot}}$$ has a peak at J=7

Refs: For Sec. E, see D. McQuarrie "Physical Chemistry: A molecular approach" and "Statistical Mechanics".