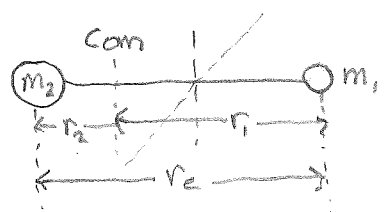


# Ideal Diatomic Molecule



com:  $m_1 r_1 = m_2 r_2$

$I_x = I_y, I_z = 0$  approx

$I_x = I_y = \mu r_e^2; \mu = \frac{m_1 m_2}{m_1 + m_2}$

For an ideal gas composed of diatomic molecules we have:

$\hat{H} = \sum_{i=1}^N \hat{H}_i$      $\hat{H}_i$  - Hamiltonian for the  $i^{th}$  molecule

## Translation

We can always separate translation from from the internal modes in a com coordinate system, ie

$\hat{H}(\text{molecule}) = \hat{H}_T + \hat{H}_{\text{internal}}$  And  $E_{\text{TOTAL}} = E_T + E_I$

Furthermore,

$E_T = \frac{n^2 h^2}{8mL^2}$  where  $m = m_1 + m_2$

## Internal Modes (arbitrary molecule)

$$\hat{H}_I = \underbrace{-\frac{\hbar^2}{2m} \sum_{\alpha} \frac{1}{m_{\alpha}} \nabla_{\alpha}^2}_{\text{KE of Nucleus}} \underbrace{-\frac{\hbar^2}{2m_e} \sum_i \nabla_i^2}_{\text{KE of } e^{-}'s} + \underbrace{\sum_{\beta > \alpha} \sum_{\alpha} \frac{z_{\alpha} z_{\beta} e^2}{r_{\alpha\beta}}}_{\text{Nuclear Repulsion}} + \underbrace{\sum_{i>j} \sum_j \frac{e^2}{r_{ij}}}_{e^{-} \text{ Repulsion}} - \underbrace{\sum_{\alpha} \sum_i \frac{z_{\alpha} e^2}{r_{i\alpha}}}_{e^{-} \text{ nucleus attraction}}$$

which leads to an insolvable problem in QM.

## Born Oppenheimer Approximation

Since the nuclear motions are much slower than  $e^{-}$  motions, then

$|KE \text{ of } e^- \text{ cloud}| \gg |KE \text{ of nucleus}|$



$|\frac{-\hbar^2}{2m_e} \nabla_i^2 \psi| \gg |\frac{-\hbar^2}{2m_\alpha} \nabla_\alpha^2 \psi|$  where  $m_\alpha = 1846 m_e$  and  $\nabla_i^2 \approx \nabla_\alpha^2$

electrons                      nuclei

Thus we can write:

$$\hat{A}_I \approx \underbrace{\frac{-\hbar^2}{2m_e} \nabla_i^2}_{KE \text{ of } e^-} - \underbrace{V_{e-n}(r_{ij})}_{\text{attraction}} + \underbrace{V_{e-e}(r_{ij})}_{\text{repulsion}} + \underbrace{V_{n-n}(r_{\alpha\beta})}_{\text{repulsion}}$$

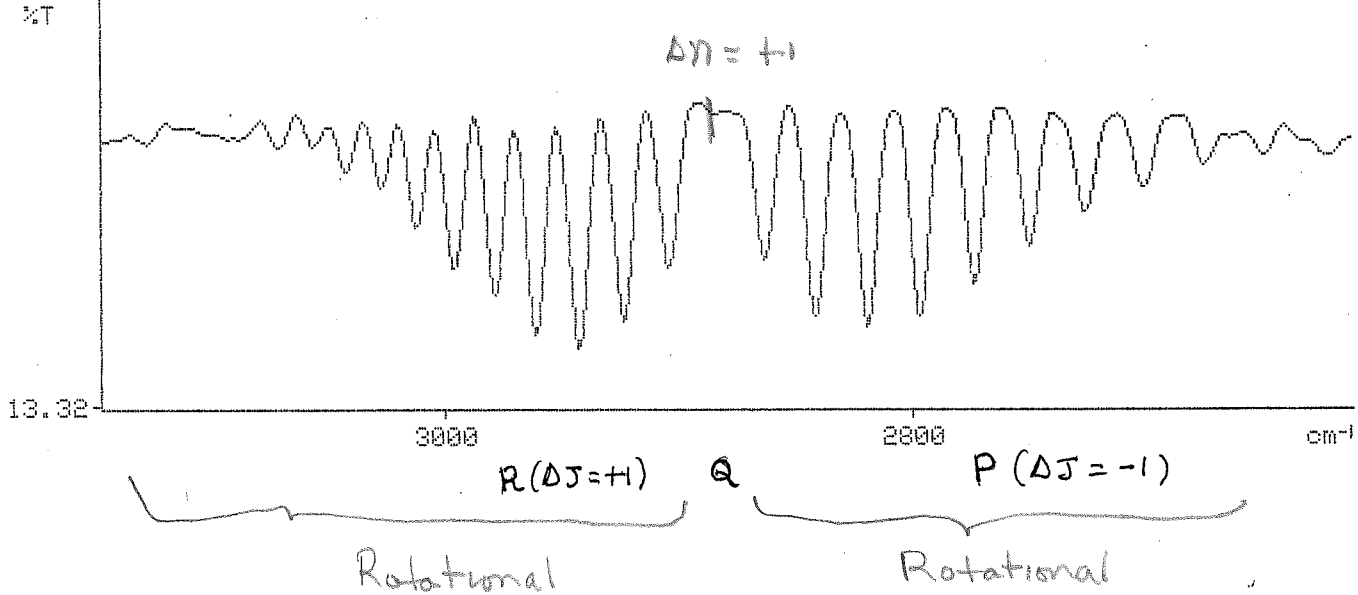
$$= \hat{H}_e + \underbrace{V_{n-n}(r_{\alpha\beta})}_{\substack{\text{Separate out and view as a fixed field} \\ \uparrow}}$$

Thus we have:

$\hat{H}_e \psi_e = E_e \psi_e$  w The repulsive term contributing an additive constant to  $E_{\text{total}}$

X: 1 scan, 8.0cm-1, flat

01:08



Hydrogen Chloride rotational line frequencies:

P branch

R branch

	$\underline{J}$		$\underline{J}$
		3071.4	10
		3056.5	9
2676.3	9	3042.5	8
2701.3	8	3028.6	7
2725.5	7	3012.8	6
2750.6	6	2996.1	5
2773.8	5	2979.3	4
2797.1	4	2961.6	3
2819.4	3	2943.1	2
2841.7	2	2923.5	1
2863.1	1	2904.0	0

# Spectroscopy

$$\bar{\nu} = \frac{1}{\lambda} = \frac{\nu}{c}$$

$$1 \text{ eV} \approx 8000 \text{ cm}^{-1}$$

Rotational transitions occur in the far IR & micro-wave ( $10^2$  to  $10^1 \text{ cm}^{-1}$ ) & vibrational transitions in the IR ( $10^4$  to  $10^2 \text{ cm}^{-1}$ ) roughly.

Rotational Transitions occur only if the molecule has a permanent dipole moment, i.e.  $\mu \neq 0$ . This excludes homonuclear diatomics & symmetrical molecules like  $\text{CH}_4$ . If a transition occurs then  $\Delta J = \pm 1$  or  $J \rightarrow J \pm 1$ .

Vibrational transitions occur together w/ rotational transitions if the molecule has either a permanent dipole or an induced dipole arising from asymmetric stretches. Again, the homonuclear diatomics are excluded. If a transition occurs the  $\Delta n_v = \pm 1$ . Consistency of a single line  $\approx 10^3 \text{ cm}^{-1}$ . Rotational lines are then embedded on either side of the vib. transition (& branch).

Electronic Transitions: In this case you get the electronic transition together w/ vib & rot. lines.

⊗  $\text{BCl}_3$  (planar),  $\text{H}_2$ ,  $\text{O}_2$ ,  $\text{N}_2$ ,  $\text{CO}_2$  etc.

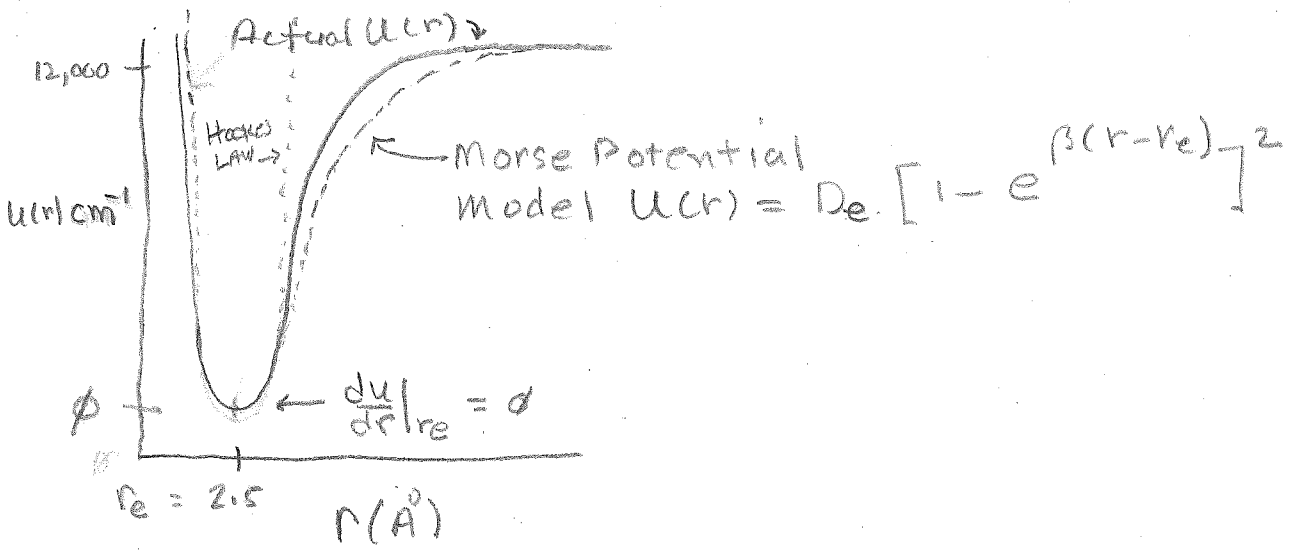
# Internal Modes

The internal modes now include: Vibration, Rotation and Electronic. Since the vibrational amplitude is quite small we will assume the molecule is a rigid dumbbell of fixed internuclear distance  $r_e$ . We now expand the internuclear potential about  $r_e$ , i.e.,

$$\begin{aligned}
 U(r) &= U(r_e) + (r-r_e) \left. \frac{dU}{dr} \right|_{r=r_e} + \frac{1}{2} (r-r_e)^2 \left. \frac{d^2U}{dr^2} \right|_{r=r_e} + \dots \\
 &= U(r_e) + \frac{1}{2} k (r-r_e)^2 + \underbrace{\frac{1}{6} \gamma (r-r_e)^3 + \dots}_{\text{anharmonic terms}} \\
 &\approx U(r_e) + \frac{1}{2} k (r-r_e)^2 \quad \text{since } \left. \frac{dU}{dr} \right|_{r=r_e} = 0 \text{ at } r_e
 \end{aligned}$$

$U(r)$  vs  $r$  minimum  $r_e$ ,  $U(r_e)$  determines our energy zero.  $k$  is the force const. Large  $k \Rightarrow$  stiff bonds and conversely, small  $k$ , weaker bonds.

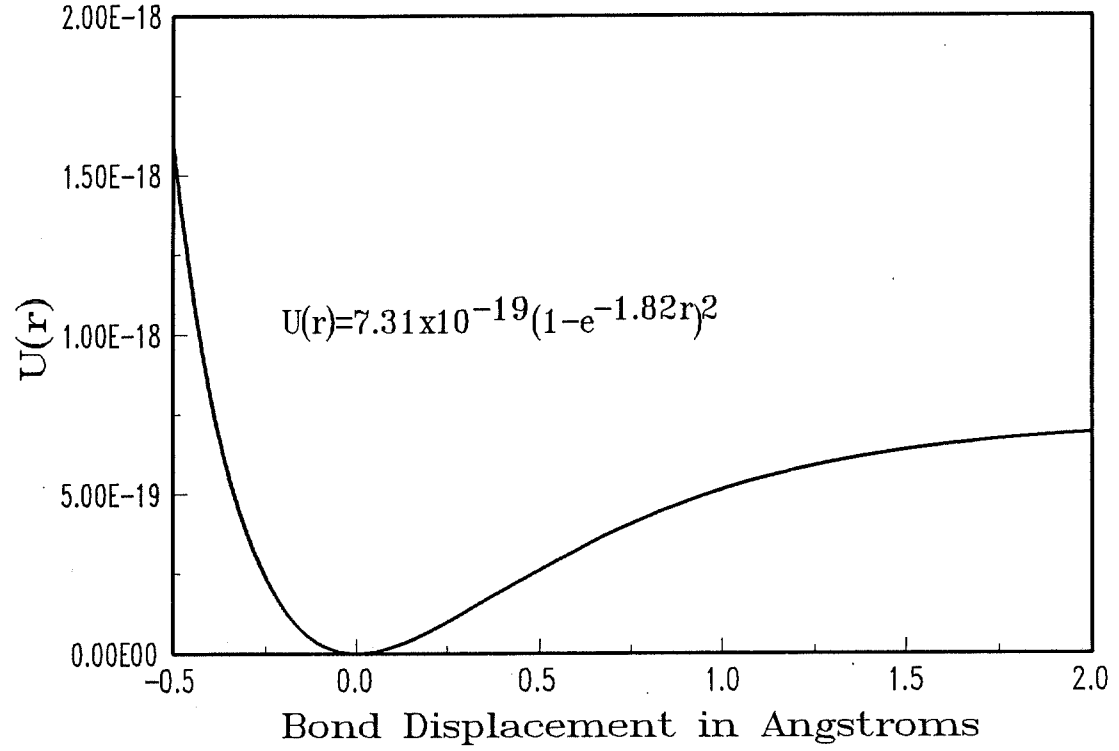
## Potential Energy, $U(r)$



### Approximations:

In addition to assuming the molecule has a fixed bond distance  $r = r_e$  (Rigid Rotor approx) which obviates centrifugal stretching due to rotation, we also assume Hooker's Law holds so that vibration is governed by the  $\frac{1}{2} k (r-r_e)^2$  term, i.e.,

### Morse Potential for HCL



$$U(r) \approx U(r_e) + \frac{1}{2}k(r-r_e)^2 = \frac{1}{2}k(r-r_e)^2 \text{ as } U(r_e) = 0$$

and which is called the harmonic oscillator approx.

With these approximations, the total energy is fully separable, so

$$E_{\text{TOTAL}} = E_T + E_r + E_v + E_e + E_{\text{nuclear}}$$

$\uparrow$  particle in a box       $\underbrace{\hspace{10em}}$  Internal modes       $\underbrace{\hspace{5em}}$  constant =

### Summary of Approximations

- 1) Born Oppenheimer - Ignore nuclear motion relative to elec.
- 2) Rigid Rotor - no centrifugal stretch
- 3) Harmonic Oscillator -  $U(r) \approx \frac{1}{2}kx^2$   $x = r - r_e$

Note - no higher order terms approx.  $k$  is the spring constant

### Partition Functions

With these approximations we have

$$Q = \frac{q^N}{N!} = \frac{(q_T q_r q_v q_e)^N}{N!}$$

where we have set  $q_n = 1$  as usual.

### Energy Level Expressions

#### Translation

$$E_n = \frac{n^2 h^2}{8m a^2} \quad n^2 = \frac{n_x^2}{a^2} + \frac{n_y^2}{b^2} + \frac{n_z^2}{c^2}$$

Vibration: HO Approximation, One Dimension

$$\hat{H} = -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} + \frac{1}{2} kx^2$$

$E_n = (n + \frac{1}{2}) h\nu$   $n = 0, 1, \dots$  and  $\omega_j = 1$  all  $n$ , ie non-deg.

where  $\nu = \frac{1}{2\pi} (k/m)^{1/2}$  &  $\mu = \frac{m_1 m_2}{m_1 + m_2}$

Rotation: Rigid Rotor (like a H atom w fixed radius)

$$\hat{H} = -\frac{\hbar^2}{2I} \left\{ \frac{1}{\sin\theta} \frac{\partial}{\partial\theta} \left( \sin\theta \frac{\partial}{\partial\theta} \right) + \frac{1}{\sin^2\theta} \frac{\partial^2}{\partial\phi^2} \right\}$$

$E_J = \frac{J(J+1)\hbar^2}{2I}$   $J = 0, 1, \dots$  and  $\omega_j = 2J+1$  degeneracy

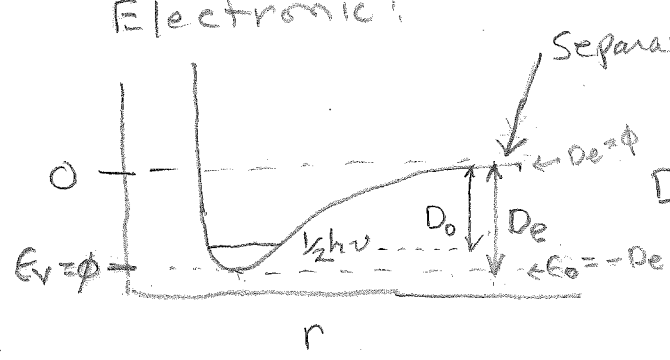
$I = \mu r_e$  where  $r_e = \frac{m_1 m_2}{m_1 + m_2} r_e$

Energy zeros

Vibration: Even though  $E_0 = \frac{1}{2} h\nu$  we take  $E_0$  to be the bottom of the potential well, ie  $E_0 = 0$  for vibration

Rotation: Choose  $E_0 = 0$  when  $J = 0$ , ie a stopped rotor.

Electronic:



$D_e$  - zero of energy which is the energy to take the atoms from the btm. of the well to separation at infinity. Thus the g.s. energy is  $E_0 = -D_e$  so  $\phi_{elec} = w_{elec} + \frac{D_e}{4\pi\epsilon_0 r}$

$D_0$  - dissociation energy which can be measured spectroscopically.



# Partition Functions

1) Translation - Point particle of mass  $m_1 + m_2$  located at the COM.

$$q_T = \left[ \frac{2\pi (m_1 + m_2) kT}{h^2} \right]^{3/2} V$$

2) Electronic

$$q_e = w_{e1} e^{+D_e/kT} + w_{e2} e^{-E_2/kT} + \dots$$

$$\approx w_{e1} e^{D_e/kT} \text{ usually}$$

3) Nuclear

$$q_n = w_{n,1} \equiv 1 \text{ by convention}$$

4) Vibrational (One dimension)

Here:

$$E_n = (n + \frac{1}{2}) h\nu \quad n = 0, 1, \dots$$

$$\nu = \frac{1}{2\pi} \sqrt{\frac{k}{\mu}} \quad \mu = \frac{m_1 m_2}{m_1 + m_2} \text{ red. mass, } k = \text{force const.}$$

So

$$q_{\text{vib}}(T) = \sum_{n=0}^{\infty} e^{-\beta E_n} = e^{-\beta h\nu/2} \sum_{n=0}^{\infty} e^{-\beta n h\nu}$$

which is a simple geometric series, i.e.

$$\sum_{n=0}^{\infty} a^n x^n = \frac{1}{1 - a x} \text{ for } a > 0, x < 0$$

So, since  $a \equiv e^{-\beta h\nu/2}$  we have

$$q_{\text{vib}}(T) = \frac{e^{-\beta h\nu/2}}{1 - e^{-\beta h\nu}} = \frac{e^{-\Theta_v/2T}}{1 - e^{-\Theta_v/T}} \quad \Theta_v = \frac{h\nu}{k_B} = \text{vib. temp.}$$

Table 6.1, p 95 gives a range of  $\Theta_v$  values for different molecules. Note that  $q_{\text{vib}}(T)$  is an exact expression.

### The Classical Limit

Provided  $\Delta E \ll kT$  or  $\Theta_v \ll T$  i.e., most states are populated,

The classical limit

$$q_{\text{vib}}(T) = e^{-\beta h\nu/2} \sum_{n=0}^{\infty} e^{-n h\nu/kT} \rightarrow e^{-\beta h\nu/2} \int_0^{\infty} e^{-nh\nu/kT} dn$$

$$= \frac{kT}{h\nu} \quad \text{classical limit; } \Theta_v \ll T$$

### Thermodynamic Functions FOR VIBRATION

Again

$$A = -kT \log Q = -kT \log \left[ \frac{q_T q_R q_V q_N}{N!} \right]^N$$

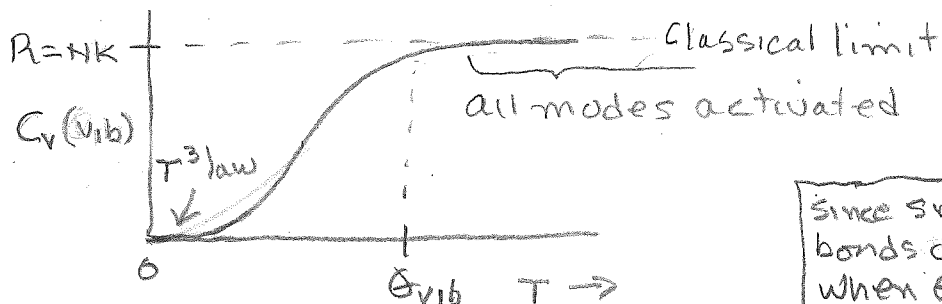
We can separate out the vib. contribution, i.e.

$$E_V = NkT^2 \frac{\partial \log q_V}{\partial T} = Nk \left[ \frac{\Theta_v}{2} + \frac{\Theta_v}{e^{\Theta_v/T} - 1} \right] \quad \Theta_v = \frac{h\nu}{k_B}$$

$$C_V = \left( \frac{\partial E}{\partial T} \right)_{V,N} = Nk \left( \frac{\Theta_v}{T} \right)^2 \frac{e^{\Theta_v/T}}{(e^{\Theta_v/T} - 1)^2}$$

## Comments:

- 1) Note that Limit  $E_v \rightarrow NkT$  so  $C_v \rightarrow Nk$  ie we get the Classical limit corresponding to  $q_{vib} \rightarrow \frac{kT}{h\nu}$



Note:  $\Theta_v = \frac{h\nu}{k_B} = \frac{h}{k_B} \cdot \frac{1}{2\pi} \sqrt{\frac{k_{fc}}{\mu}}$   
 $= \frac{h}{k_B} \left(\frac{k_{fc}}{\mu}\right)^{1/2}$  ie  $\Theta_v \propto k_{fc}^{1/2}$  so,

Since small force constants imply weaker bonds and a smaller  $\Theta_v$  value, so when  $\Theta_v$  is small we expect classical behavior for a molecule at lower temps than when  $\Theta_v$  is larger.

- a) At low temperatures,  $T \ll \Theta_v$ , vib. modes are not excited so there is little contribution to  $C_v$ ,  $E$  etc.
- b) If  $T \gg \Theta_v$  then all vib. modes are excited and  $C_v$  &  $E$  are constants. Classical behaviour.
- c) At intermediate temps,  $C_v$  is temp. dept.

This exponential behavior is characteristic of all modes, not just vibration,

This can be seen in table 6.2, p98 of the text where

$$f_{n>0} = 1 - f_0 = e^{-\Theta_v/T} = \text{frac. of molecules in all excited states}$$

gas	$\Theta_v$ °K	$f_n$	
		300°	1000°
H <sub>2</sub>	6215	@ 10 <sup>-9</sup>	@ 10 <sup>-3</sup>
N <sub>2</sub>	3374	" 10 <sup>-5</sup>	" 10 <sup>-2</sup>
I <sub>2</sub>	310	4 x 10 <sup>-1</sup>	7 x 10 <sup>-1</sup>

Again, we see that the table confirms that, for a given  $T$ , molecules w a small force constant & hence smaller  $\Theta_v$  values, since  $\Theta_v = \frac{h\nu}{k_B} = \frac{h}{k_B} \left(\frac{k_{fc}}{\mu}\right)^{1/2}$ , have weaker bonds & are more easily excited.

# Rotational P.F. for Heteronuclear Diatomics

We have:

$$\epsilon_J = \frac{J(J+1)\hbar^2}{2I}; \quad w_j = 2J+1, \quad I = \mu r_e^2$$

Case I: Classical (High-Temp) Limit;  $\Theta_r \ll T$

$$q_{rot}(T) = \sum w_j e^{-\epsilon_j/kT}$$

$$= \sum_{\text{levels, } J=0} (2J+1) e^{-\frac{J(J+1)\hbar^2}{2Ik_B T}} = \sum_{\text{levels, } J=0} (2J+1) e^{-J(J+1)\Theta_r/T}$$

where  $\bar{B} = \frac{\hbar^2}{8\pi^2 I}$  and  $\Theta_r = \frac{\bar{B}}{k_B} = \frac{\hbar^2}{2Ik_B}$

So, assuming  $\Theta_r \ll T$ , we can replace the  $\sum$  by an  $\int$ , or

$$q_{rot}(T) \approx \int_0^\infty e^{-J(J+1)\Theta_r/T} d[J(J+1)] = \frac{T}{\Theta_r} \text{ OR } \frac{2Ik_B T}{\hbar^2}$$

$$q_{rot}(T) = \frac{8\pi^2 I k_B T}{h^2} \text{ if } \Theta_r = \frac{\hbar^2}{2Ik_B} \ll T \text{ CLASSICAL LIMIT}$$

## Comments

1)  $\Theta_r$  is the rotational temp & is molecule dependant.

2)  $\Theta_r = \frac{\hbar^2}{2Ik_B}$  or  $\Theta_r \propto \frac{1}{I} = \frac{1}{\mu r_e^2} = \frac{m_1 + m_2}{m_1 m_2} r_e^2$  ie  $\Theta_r \propto \frac{1}{m_1 m_2}$

which suggests that the bigger, ie more massive molecules will behave classically at lower temperatures since  $\Theta_r \ll T$  is the criterion for classical behavior.

In fact, most molecules ( $H_2, D_2$  &  $HD$  are notable exceptions) behave classically at room temperatures.

Case II) Intermediate Temperatures:  $\Theta_r \lesssim T$  - Still Classical

Here we use the Euler MacLaurin Summation Formula

$$\sum_{x=a}^b f(x) = \int_a^b f(x) dx + \frac{1}{2} \{ f(b) - f(a) \} + \sum_{k=1}^{\infty} \frac{(-1)^k B_k}{(2k)!} * \left\{ f^{(2k-1)}(b) - f^{(2k-1)}(a) \right\}$$

where  $f^{(2k-1)}$  is the  $(2k-1)^{th}$  derivative of  $f$ . Note that  $2k-1$  skips the even exp's.

View this as replacing a sum by an integral + correction terms.

$B_k$  denotes the Bernoulli numbers which can be generated from the Bernoulli generating function.

Here  $B_1 = \frac{1}{6}$ ,  $B_2 = \frac{1}{30}$ ,  $B_3 = \frac{1}{42}$ , ...

Applying the summation formula to  $g_{rot}$  when  $\Theta_r \lesssim T$  gives

$$g_{rot}(T) = \frac{T}{\Theta_r} \left\{ 1 + \frac{1}{3} \left( \frac{\Theta_r}{T} \right) + \frac{1}{15} \left( \frac{\Theta_r}{T} \right)^2 + \frac{4}{315} \left( \frac{\Theta_r}{T} \right)^3 + \dots \right\}$$

which is considered good to within 1% for  $\Theta_r < T$ .

Case III) Low Temperature Limit:  $\Theta_r > T$

Here  $\Delta E > kT$  or  $\Theta_r > T$  so we use the sum directly i.e.

$$g_{rot}(T) = 1 + 3e^{-2\Theta_r/T} + 5e^{-6\Theta_r/T} + \dots$$

and is good to 0.1% for  $\Theta_r > 0.7T$

# Homonuclear Diatomics Rotational Partition Function

## Classical Limit

For the heteronuclear diatomic, we obtained for the classical limit the expression,

$$g_{\text{rot}}(T) = \frac{T}{\Theta_r} = \frac{8\pi^2 I k T}{h^2}$$

However this is wrong for the homonuclear molecule because we have overcounted the number of unique states by a factor of 2 due to symmetry. This is most easily seen when calculating  $g_{\text{rot}}$  (homonuclear) using classical stat. mech's. but the conclusion must also be true for the quantal treatment since the classical method is a limiting case.

Consequently we define a symmetry number,  $\sigma$  as follows for the classical limit:

$$\sigma = \begin{cases} 1 & \text{Heteronuclear} \\ 2 & \text{Homonuclear} \end{cases} \quad \text{so } g_r = \frac{T}{\sigma \Theta_r} = \frac{8\pi^2 I k T}{\sigma h^2}$$

## Comments

- 1) The classical limit or Euler-Maclaurin equivalent is always correct for homonuclear and heteronuclear diatomics when  $\Theta_r \ll T$ . As a rule of thumb, when  $\Theta_r < 0.2T$ , the molecule will behave classically.

For example, most gases when  $\Theta_r < 10$ , the classical limit above will hold when  $T > 50^\circ \text{K}$ , and the gas is homonuclear.

2)  $\sigma$  is called the 'symmetry number' & is a measure of how many indistinguishable orientations a molecule can have. For example:  $\sigma = 2$  (Homonuclear diatomics) but  $\sigma = 12$  ( $C_6H_6$  - Benzene).

3) For  $H_2$  &  $D_2$ ,  $\Theta_r$  values are unusually large, i.e.

$\Theta_r(H_2) = 85.3$  and  $\Theta_r(D_2) = 42.7$ . The 20% rule says that only above  $T > 426^\circ K$  ( $H_2$ ) and  $T > 200^\circ K$  ( $D_2$ ) will the classical treatment be okay. Otherwise a qm. mechanical approach is required.

3) In general, and provided  $\Theta_r/T < 0.2$ , we can write  $q_r$  to include  $\sigma$ , i.e.  $\rightarrow$  molecule

$$q_r = \frac{1}{\sigma} \sum_{J=0}^{\infty} (2J+1) e^{-\Theta_r J(J+1)/T}$$

Thus, we have a simple form for  $q_r$  that applies to both homo-nuclear and heteronuclear diatomics in the classical limit.

# Diatomic Thermodynamic Functions - Classical Limit. 67

1) Provided  $\Theta_r \ll T$  we can write  $q_r(T)$  as either

$$q_{rot}(T) = \frac{T}{\sigma \Theta_r} \left\{ 1 + \frac{1}{3} \left( \frac{\Theta_r}{T} \right) + \frac{1}{15} \left( \frac{\Theta_r}{T} \right)^2 + \dots \right\} \quad \text{or, if } \Theta_r \ll T$$

$$q_{rot}(T) = \frac{T}{\sigma \Theta_r} \quad \text{so } (m = m_1 + m_2) \quad \text{Classical Limit}$$

$$Q(N, T) = \left[ \frac{(2\pi m k T)^{3/2}}{h^3} V \right] \left[ \frac{8\pi^2 I k T}{\sigma h^2} \right] \left[ \frac{e^{-\Theta_v/2T}}{1 - e^{-\Theta_v/T}} \right] \left[ \omega_e e^{-D_e/kT} \right]$$

Trans.      Rot.      Vib.      Elec.  
 Classical    classical    Qtm. Mech    Grd. state

$$A(N, V, T) = -kT \log Q = -kT \log \frac{Q(N, T)^N}{N!}$$

So

$$\frac{E}{NkT} = \frac{5}{2} + \frac{h\nu}{2kT} + \frac{h\nu/kT}{(e^{h\nu/kT} - 1)} - \frac{D_e}{kT}$$

$$\frac{C_v}{Nk} = \frac{5}{2} + \left( \frac{h\nu}{kT} \right)^2 \frac{e^{h\nu/kT}}{(e^{h\nu/kT} - 1)^2}$$

$PV = NkT$  etc.

Approximations include

- 1)  $\bar{c}_v \ll 1$
- 2)  $RR \dot{=} HO \dot{=} BO$
- 3)  $\Theta_r \ll T$



# CLASSICAL STATISTICAL MECHANICS

Our motivation to invoke classical mechanics at this point is that the classical limit of high temp's and large qtm. numbers would seem to suggest a connection between the qtm. mech. p.f. and some kind of classical analog. So we ask, does such a relationship exist?

$$\sum e^{-\epsilon_i / kT} \leftrightarrow \int H(p, q) dp dq$$

at high temperatures or large quanta, i.e. large  $n$ ?

The above expression recognizes the relationship between the qtm. mechanical Hamiltonian  $\epsilon_i$ , the energy  $\epsilon_i$ , the equivalent classical Hamiltonian written in terms of  $p$  &  $q$ .

## Three Examples

a) One Dimensional Harmonic Oscillator:

Here:

$$E = (n + \frac{1}{2}) h\nu \quad n = 0, 1, \dots \quad \text{Q.M.}$$

$$E = H(p, q) = \frac{p^2}{2\mu} + \frac{kx^2}{2} \quad \mu = \frac{m_A m_B}{m_A + m_B} \quad \text{C.M.}$$

We now write tentatively,

$$g(\text{classical}) = C \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} e^{-H(p, q) / kT} dp dq$$

where  $C$  can be adjusted to force agreement between  $g(\text{qtm})$  &  $g(\text{classical})$ .

We have:

$$\begin{aligned}
 c \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} e^{-H(p,q)/kT} dp dq &= c \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} e^{-\left[\frac{p^2}{2m} + \frac{1}{2}kx^2\right]/kT} dp dq \\
 &= \int_{-\infty}^{\infty} e^{-a q^2/kT} dq \int_{-\infty}^{\infty} e^{-b^2 p^2/kT} dp \\
 &= c \frac{\sqrt{\pi}}{\left[\frac{2\pi^2 \mu v^2}{kT}\right]^{1/2}} \cdot \frac{\sqrt{\pi}}{\left[2\mu kT\right]^{-1/2}} \\
 &= \frac{c kT}{v} \frac{1}{1} \approx \frac{1}{2\pi} \sqrt{\frac{k}{\mu}}
 \end{aligned}$$

The qtm. mech. equivalent in the high temperature limit is:

$$\rho_{\text{vis}} (\text{1dim}) = \frac{kT}{h\nu}$$

which suggest  $c = \frac{1}{h}$  ie,

$$\sum_{\text{States}} e^{-\epsilon_j/kT} \rightarrow \frac{1}{h} \int \int_{p,q} e^{-H(p,q)/kT} dp dq$$

b) Rotational Partition Function for a Rigid Rotor - 2 Dimen.

For a heteronuclear diatomic molecule, we have

$$\omega_J = 2J + 1$$

$$q_{rot} = \sum w_j e^{-\epsilon_j/kT} = \sum_{J=0}^{\infty} (2J+1) e^{-\beta \bar{B} J(J+1)} \quad J=0, 1, 2, \dots$$

where  $\bar{B} = \frac{h}{8\pi^2 I c}$  and  $I = \mu r_e^2$

For high temperatures, we have, using the phase integral,

$$q_{rot} = \sum w_j e^{-\epsilon_j/kT} \approx \int_0^{\infty} (2J+1) e^{-\Theta_r J(J+1)} dJ \quad \text{and} \quad \Theta_r = \frac{\bar{B}}{k}$$

where  $\Theta_r \ll T \ll \Theta_v$  and  $\Theta_v = \frac{h\nu}{k}$

We find that, as we have already seen:

$$q_{rot}(T) = \frac{8\pi^2 I k T}{h^2} \quad \text{for } \Theta_r \ll T \text{ (classical limit)}$$

Classically, we would write, where  $H = \frac{1}{2I} (P_\theta^2 + \frac{P_\phi^2}{\sin^2 \theta})$

$$q_{rot}^{class} = \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} dP_\theta dP_\phi \int_0^{2\pi} d\phi \int_0^\pi d\theta e^{-\beta H} = 8\pi^2 I k T \cdot C$$

which agrees w the phase integral if

$C = \frac{1}{h^2}$  for two dimensions. We seem to have

a pattern, i.e.,  $C = \frac{1}{h^{\text{dimension}}}$

## c) Monoatomic Ideal Gas:

Classically

$$q_T = C \cdot \iiint_P \iiint_V e^{-H(p,q)/kT} dp_x dp_y dp_z dx dy dz$$

$$H(p,q) = \frac{\bar{p}^2}{2m} = \frac{1}{2} (p_x^2 + p_y^2 + p_z^2) \text{ as } U(x,y,z) = \emptyset \text{ ideal gas}$$

$$q_T = C \cdot (2\pi m kT)^{3/2} V$$

and again,

$$q_T (\text{qm. mech}) = \sum_{n_x, n_y, n_z} e^{-\frac{n^2 h^2}{8mL^2}} = \frac{(2\pi m kT)^{3/2}}{h^3} V$$

and which holds for virtually all temperatures since  $\Delta E \ll kT$  is nearly always true for translation.

Thus comparison shows:

$$C = \frac{1}{h^3} \text{ for a 3 dimensional ideal monoatomic gas.}$$

Conclusion

We conclude, at least provisionally, that we get a factor of  $\frac{1}{h}$  for each conjugate pair  $dp_j, dq_j$  in the Classical integral.

# Generalization for a Single Particle

For a single particle with  $s$  dimensions, we assume

$$q = \sum_i e^{-E_i/kT} \xrightarrow{\Delta E \ll kT} \frac{1}{h^s} \int_P \int_Q e^{-H(P, Q)/kT} \prod_{i=1}^s d\vec{p}_i d\vec{q}_i$$

where  $1 \leq s \leq 3$ .

## Comment on the Phase Integral

For vibration, translation & rotation, the qtm. sum  $\sum e^{-E_n/kT}$  was replaced by the phase integral when  $\Delta E \ll kT$ . But the use of classical stat. mech. is also valid when  $\Delta E \ll kT$  or better, when  $\bar{\epsilon}_j \ll 1$ . Hence the use of the classical phase integral or the classical expression above, are equivalent.

$$q = \sum_{\text{exact}} e^{-E_i/kT} \underset{\Delta E \ll kT}{\approx} \int_0^\infty e^{-E_n/kT} dn = \frac{1}{h^s} \int_{-10}^\infty \int e^{-H(P, Q)/kT} \prod_i^s d\vec{p}_i d\vec{q}_i$$

equivalent

## Mixed Modes

In the case where some mode are classical & the rest quantum mechanical, we have, since

$$H = H_{\text{class}} + H_{\text{qtm}} \quad \text{then}$$

$$q = q_{\text{class}} \cdot q_{\text{qtm}}$$

$$\text{where } q_{\text{class}} = \frac{1}{h^s} \int \int e^{-H(P, Q)/kT} \prod_{i=1}^s d\vec{p}_i d\vec{q}_i$$

$$\text{and } q_{\text{qtm}} = \sum_{\text{levels}} w_i e^{-E_i/kT}$$

Query

Which modes can be treated classically?

Again,

Translation - always

Rotation - usually

Vibration - occasionally

Electronic - never

Nuclear - never

Classical System Partition Function

We have for  $N$  particles which are independent:

$Q_{MB} = q^N$  distinguishable particles MB statistics

$Q_{CMB} = \frac{q^N}{N!}$   $\bar{q} \ll 1$  indist. " CMB "

So we have:

$$Q_{CMB} = \frac{q^N}{N!} = \frac{1}{N!} \prod_{s=1}^N \left\{ \frac{1}{h^3} \int \dots \int e^{-\beta H_s} \prod_{i=1}^3 dp_{si} dq_{si} \right\} \quad 1 \leq s \leq N$$

$$= \frac{1}{N!} \frac{1}{h^{3N}} \int \dots \int e^{-\beta H} \prod_{i=1}^{3N} dp_i dq_i$$

where  $H = \sum_{i=1}^N H_i(\bar{p}_i, \bar{q}_i)$

for a system of  $N$  independent indistinguishable particles  
 $H$  is the  $n$  body Hamiltonian.

# INTERACTING PARTICLES

68.6

So far, everything we have done assumes, consistent with our assumption that  $Q$  for a system could be written as a sum over particle states, i.e.

$$Q(N, V, T) = \sum_j e^{-E_j/kT} = \sum_{i, j, k, \dots} e^{-(E_i + E_j + E_k + \dots)/kT}$$
$$= \frac{q^N}{N!} \quad \text{Independent, indistinguishable particles}$$

$q \ll 1$

By 'independent' we mean at most weakly interacting so as to not influence each particles energy state spectrum. We now relax that assumption and conjecture that

$$Q = \frac{1}{N! h^{3N}} \int \dots \int e^{-\beta H(p, q)} \prod_{i=1}^{3N} dp_i dq_i$$

holds for interacting particles as well.

## Example monoatomic Gas

$$H(p, q) = \frac{1}{2m} \sum_{j=1}^N (p_{x_j}^2 + p_{y_j}^2 + p_{z_j}^2) + \underbrace{U(x_1, y_1, z_1, \dots, x_N, y_N, z_N)}_{U \approx \text{PE}}$$

Then, from  $Q$  above we have

$$Q_{\text{class}}(\text{monoatomic gas}) = \frac{1}{N!} \left( \frac{2\pi m kT}{h^2} \right)^{3N/2} Z_N$$

where  $3N$  integrals

$$Z_N = \int_V \dots \int_V e^{-U(\vec{r})/kT} \prod_{i=1}^N d\vec{r}_i \quad d\vec{r}_i = (dx_i, dy_i, dz_i)$$

and is known as the classical configurational integral and is responsible for much of the research in the field of statistics mech, esp, liquids,

For an ideal gas, where  $u(\vec{r}) = 0$

$$Z_N = \int e^{-u/kT} \prod_i d\vec{r}_i \rightarrow \int \dots \int \prod_i d\vec{r}_i \rightarrow V^N$$

So

$$Q_{\text{class}} (\text{monoatomic gas}) = \frac{1}{N!} \left( \frac{2\pi m kT}{h^2} \right)^{3N/2} V^N \text{ etc.}$$

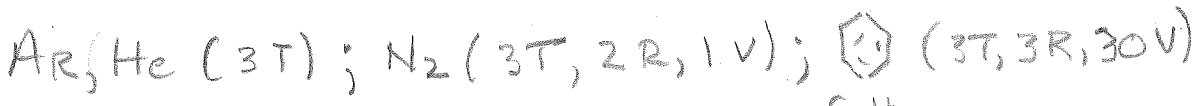
Which is exactly what we got for the translational p.f. for the ideal monoatomic gas previously where we used the classical phase integral.

### Equipartition of Energy

In the classical limit, each squared term in the Classical Hamiltonian contributes  $\frac{1}{2} kT$  / molecule / deg of freedom to the energy or  $\frac{1}{2} k$  to  $C_v$ .

In particular, for a molecule consisting of  $n$ -atoms we have  $3n$  degrees of freedom of which:

<u>MODE</u>	<u>DEG. OF Freedom</u>
Trans.	3
Vib -	$\left\{ \begin{array}{l} 3n - 5 \text{ linear} \\ 3n - 6 \text{ non-linear} \end{array} \right.$
Rot -	$\left\{ \begin{array}{l} 2 \text{ linear} \\ 3 \text{ non-linear} \end{array} \right.$



These modes are only fully activated when  $\Theta_v, \Theta_r \ll T$ . Translation is always activated as  $\Theta_t \ll T$ .



# Ideal Polyatomic Gas

## Degrees of Freedom

A molecule w/  $N$  atoms has  $3N$  degrees of freedom which include:

3 for the com translational coordinates

2 for a linear molecule } rotation  
3 " " non " " }

$3N - 5$  for a linear molecule } vibration

$3N - 6$  " " non " " }

### Example

Cholesterol  
 $C_{27}H_{45}OH$  w/  
 $3N = 222$  deg. of free.  
of which  
3T  
3R  
 $3N - 6 = 216$  Vib  
modes  $\equiv$  216  
normal modes.

## General Relationships AND Approximations

$$Q(N, V, T) = \frac{(q_T q_r q_v q_e q_n)^N}{N!}$$

where again, translation alone ensures that  $\bar{C}_v \ll 1$ , so MB statistics apply. In addition, we use the Canonical ensemble so

$$A = -kT \log Q(N, V, T)$$

Our approximations are the same as for the diatomic molecule, namely, we assume:

- 1) Born-Oppenheimer approximation for the nuclei
- 2) Rigid-Rotor approx. for each bond
- 3) Harmonic Oscillator approx which is now a complicated potential surface.

# Partition Functions

## Translational

In terms of the center of mass system:

$$q_{\text{trans}} = \left[ \frac{2\pi M kT}{h^2} \right]^{3/2} V \quad \text{where } M = \sum_{i=1}^N m_i$$

where  $m_i$  = mass of the  $i^{\text{th}}$  atom.

## Vibrational

The  $3N-5$  or  $3N-6$  vibrational modes are characterized by a set of 'normal vibrational' frequencies, one for each of the  $3N-5$  or  $3N-6$  vibrational modes.

This basis set of frequencies are the frequencies in which all vibrational motions, no matter how complicated, can be analyzed. Since these normal modes are independent we can view a polyatomic molecule as consisting of a sum of independent harmonic oscillators in which

Case:

$$E_{\text{vib}} = \sum_{j=1}^{3N-5/6} \left( n_j + \frac{1}{2} \right) h\nu_j \quad n_j = 0, 1, \dots$$

where

$$\nu_j = \frac{1}{2\pi} \left( \frac{k_j}{\mu_j} \right)^{1/2} \quad \text{where each mode has its own } k \text{ \& } \mu.$$

and

$\nu_j$  =  $j^{\text{th}}$  normal frequency,  $\mu_j$  the reduced mass.

# Examples of Normal Modes

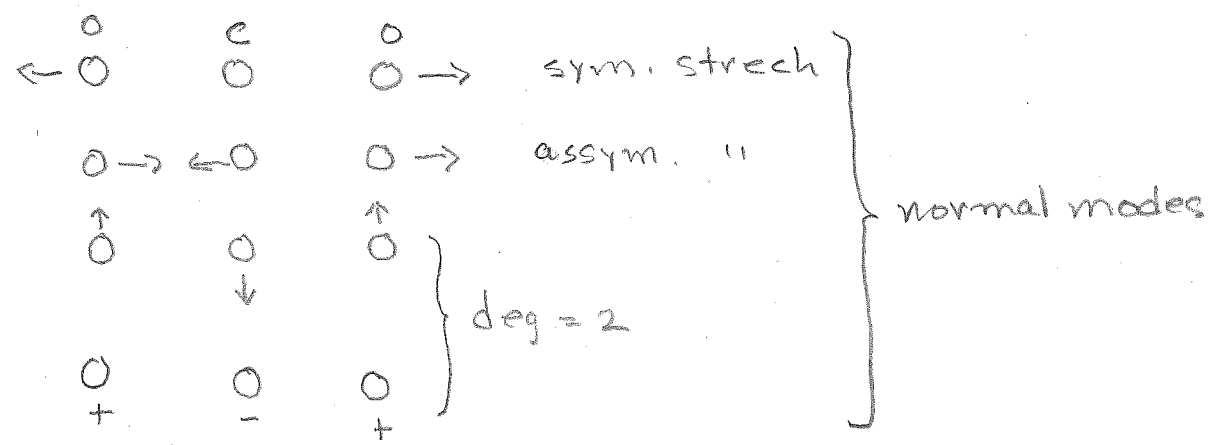
1)  $CO_2$  Linear  $N=3$

Deg. of freedom =  $3N = 9$

3 - Trans.

$3N - 5 = 4$  Vibrational

2 - Rotation

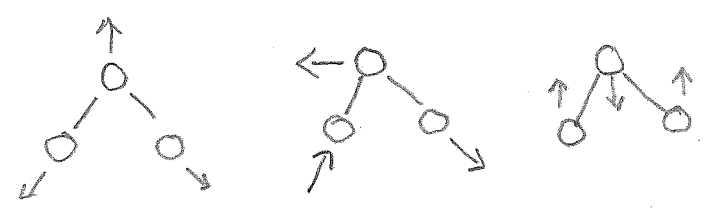


2)  $H_2O$  Planar,  $N=3$ , 9 Deg. of Freedom

3 - Trans

$3N - 6 = 3$  - Vib.

3 - Rot.



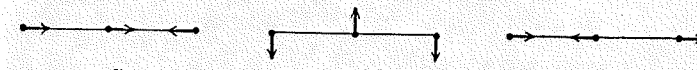
al vibrations invariably pro-  
ally sharp and intense, while  
ity of the triangular  $YX_2$   
 $\nu_2$  (1 and 7) are polarized and  
third frequency  $\nu_3$  gives rise  
ll be noted, incidentally, in  
ency is completely unsym-  
aman lines are thus seen to  
icular vibrations responsible

ormal modes of vibration of  
217 and 218; a dotted circle  
stricted to one direction, in the  
of the various vibrations in  
various characteristics of the  
be recalled that the letters  
 $E$  and  $F$  are used for doubly  
 $p$  and  $d$  refer to polarized

SPECTRA 7


ortant spectra of polyatomic  
-red region of the spectrum,  
As already seen, the elec-  
be of great value, and the  
of limited usefulness because  
mic molecules, the rotational  
give rise to the fine structure  
ility that a polyatomic mole-  
ia, rotational structure is  
va of these moments of  
les, the spacing between suc-  
complete resolution is not  
be obtained, as will be ex-  
of the band. In spite of its  
al structure of the vibration  
r it facilitates the often diffi-  
with the normal vibrational  
the influence of rotation on  
sued by classifying molecules  
ationships of the moments of  
ecules; these have two equal  
so they behave like diatomic  
st of molecules having either

$XYZ$  linear:



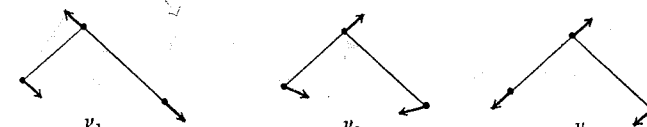
Symbol	$\nu_1$	$\nu_2(2)$	$\nu_3$
Class	$A_1$	$E_1$	$A_1$
Infra-Red	ac. ( $\pi$ )	ac. ( $\sigma$ )	ac. ( $\pi$ )
Raman	ac. ( $p$ )	ac. ( $d$ )	ac. ( $p$ )

$YX_2$  linear:



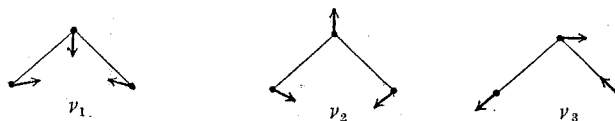
Symbol	$\nu_1$	$\nu_2(2)$	$\nu_3$
Class	$A_g$	$E_u$	$A_u$
I. R.	inac.	ac. ( $\sigma$ )	ac. ( $\pi$ )
Raman	ac. ( $p$ )	inac.	inac.

$XYZ$  angular:



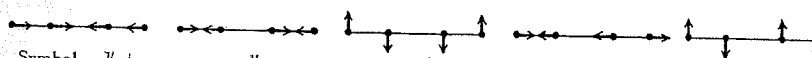
Symbol	$\nu_1$	$\nu_2$	$\nu_3$
Class	$A'$	$A'$	$A'$
I. R.	ac. ( $\pi$ )	ac. ( $\pi$ )	ac. ( $\sigma$ )
Raman	ac. ( $p$ )	ac. ( $p$ )	ac. ( $p$ )

$YX_2$  angular:



Symbol	$\nu_1$	$\nu_2$	$\nu_3$
Class	$A_1$	$A_1$	$B_1$
I. R.	ac. ( $\pi$ )	ac. ( $\pi$ )	ac. ( $\sigma$ )
Raman	ac. ( $p$ )	ac. ( $p$ )	ac. ( $d$ )

$X_2Y_2$  linear:



Symbol	$\nu_1'$	$\nu_2$	$\nu_3(2)$	$\nu_4$	$\nu_5(2)$
Class	$A_{1g}$	$A_{1g}$	$E_{1u}$	$A_{1u}$	$E_{1g}$
I. R.	inac.	inac.	ac. ( $\sigma$ )	ac. ( $\pi$ )	inac.
Raman	ac. ( $p$ )	ac. ( $p$ )	inac.	inac.	ac. ( $d$ )

We then have for vibration:

$$q_{\text{vib}} = \prod_{j=1}^{3N-5/6} \frac{e^{-\Theta_{v,j}/2T}}{(1 - e^{-\Theta_{v,j}/T})}$$

$$E_{\text{vib}} = NK \sum_{j=1}^{3N-5/6} \left( \frac{\Theta_{v,j}}{2} + \frac{\Theta_{v,j} e^{-\Theta_{v,j}/T}}{1 - e^{-\Theta_{v,j}/T}} \right)$$

$$C_{\text{vib}} = NK \sum_{j=1}^{3N-5/6} \left[ \left( \frac{\Theta_{v,j}}{T} \right)^2 \frac{e^{-\Theta_{v,j}/T}}{(1 - e^{-\Theta_{v,j}/T})^2} \right]$$

where  $\Theta_{v,j} = \frac{h\nu_j}{k_b}$  characteristic or vibrational temperature  
Get one  $\Theta_v$  value for each normal mode.

See Table 8-1, p 132 of McQuarrie for typical values of  $\Theta_v$  etc.

## Electronic

As before, we take the energy zero as the bottom of the well in which case

$$q_{\text{elec.}} = \omega_{\text{el}} e^{D_e/kT} + \dots \quad \text{This corresponds to the zero for all } n \text{ atoms at infinity.}$$

## Nuclear

Again,

$$q_{\text{nuc}} \approx 1$$

$$\textcircled{*} \hat{H}_{\text{vib}} = \sum_{j=1}^{3N-5/6} \frac{\hbar^2}{2\mu_j} \frac{\partial^2}{\partial Q_j^2} + \sum_{j=1}^{3N-5/6} \frac{k_j}{2} Q_j^2$$

where  $Q_j$  results from a judicious choice of coord's that eliminate all cross terms due to the relative coordinates.

CLASSIFICATION OF POLYATOMICS

These are very much more complicated and so are usually classified by their moments of inertia.

COM COORDINATES

These are given by:

$$x_{com} = \frac{1}{M} \sum_{j=1}^n m_j x_j \quad M = \sum_{i=1}^n m_i$$

$$y_{com} = \frac{1}{M} \sum m_j y_j$$

$$z_{com} = \frac{1}{M} \sum m_j z_j$$

where  $x_j$  etc. are the coord's of each nucleus in some suitable coord. system, and relative to the com.

Moments of Inertia (Principal)

$$I_A \equiv I_{xx} = \sum_{j=1}^n m_j [(y_j - y_{com})^2 + (z_j - z_{com})^2]$$

$$I_B \equiv I_{yy} = \sum_{j=1}^n m_j [(x_j - x_{com})^2 + (z_j - z_{com})^2]$$

$$I_C \equiv I_{zz} = \sum_{j=1}^n m_j [(x_j - x_{com})^2 + (y_j - y_{com})^2]$$

All cross terms have been eliminated by using the Principal axes.

Rotational Constants (cm<sup>-1</sup>)

$$\bar{A} = \frac{h}{8\pi^2 I_A} \quad \bar{B} = \frac{h}{8\pi^2 I_B} \quad \bar{C} = \frac{h}{8\pi^2 I_C}$$

One can also calc.  $\Theta$  values from  $\bar{A}$ ,  $\bar{B}$  &  $\bar{C}$ ,

from which  $I_A$  etc. can be calculated since there are extensive tables of the Rotational Constants.

In term of Moments of Inertia we have, 7/15  
 where  $q_{rot}$  is for the classical limit.

Linear molecules; HCN, CO<sub>2</sub> etc,

$$I_A = I_B = I; I_C = 0$$

$$E_J = \frac{h^2}{2I} J(J+1) \quad J = 0, 1, \dots; \quad I = \sum_{j=1}^n m_j d_j^2 \quad d_j = \text{dist from the com}$$

$$\omega_J = 2J+1$$

$$q_{rot} = \frac{8\pi^2 I k_B T}{\sigma h^2} = \frac{T}{\sigma \Theta_r} \quad \text{where } \begin{cases} \sigma = 1 & \text{unsymmetric linear} \\ \sigma = 2 & \text{symmetric "} \\ \Theta_r = \frac{h^2}{8\pi^2 I k_B} \end{cases}$$

Spherical Top; CH<sub>4</sub>, CCl<sub>4</sub> etc.

$$I_A = I_B = I_C$$

$$E_J = \frac{h^2}{2I} J(J+1) \quad J = 0, 1, \dots$$

$$\omega_J = (2J+1)^2$$

$$q_{rot} = \frac{1}{\sigma} \int_0^\infty (2J+1)^2 e^{-J(J+1) h^2 / 2I k_B T} dJ = \frac{\pi^{1/2}}{\sigma} \left( \frac{8\pi^2 I k_B T}{h^2} \right)^{3/2} = \frac{\pi^{1/2}}{\sigma} \left( \frac{T}{\Theta_r} \right)^{3/2}$$

Symmetric Top C<sub>6</sub>H<sub>6</sub>, CHCl<sub>3</sub>

$$I_A = I_B \neq I_C$$

$$E_{J,k} = \frac{h^2}{2} \left\{ \frac{J(J+1)}{I_A} + k^2 \left( \frac{1}{I_C} - \frac{1}{I_A} \right) \right\} \quad \begin{matrix} J = 0, 1, \dots \\ k = J, J-1, \dots, -J \end{matrix}$$

$$\omega_{J,k} = 2J+1$$

$$q_{rot} = \frac{1}{\sigma} \sum_{J=0}^{\infty} (2J+1) e^{-\alpha_A J(J+1)} \sum_{k=-J}^J e^{-(\alpha_C - \alpha_A) k^2}$$

$$\text{where } \alpha_j = \frac{h^2}{2I_j k_B T} \quad j = A \text{ or } C$$

$$\text{OR } q_{rot} = \frac{\pi^{1/2}}{\sigma} \left( \frac{8\pi^2 I_A k_B T}{h^2} \right) \left( \frac{8\pi^2 I_C k_B T}{h^2} \right)^{1/2} = \frac{\pi^{1/2}}{\sigma} \frac{T}{\Theta_A} \left( \frac{T}{\Theta_C} \right)^{1/2}$$

Note

J = total angular momentum qtm. number

k = component of angular mom. along the C axis.

A symmetric Top; Eg H<sub>2</sub>O etc

No closed form  $E_{rot}$  is possible unless  $I_A < I_B < I_C$ .  
 For this case however, (again 2 qm numbers)

$$E_{JK} = \frac{\hbar^2}{2I_B} J(J+1) + \frac{\hbar^2}{2} \left( \frac{1}{I_A} - \frac{1}{I_B} \right) K_b^2$$

with an equivalent expression for c & B,

The Classical P.f. is then:

$$q_{rot} = \frac{\sqrt{\pi}}{\sigma} \left( \frac{8\pi^2 I_A K T}{h^2} \right)^{1/2} \left( \frac{8\pi^2 I_B K T}{h^2} \right)^{1/2} \left( \frac{8\pi^2 I_C K T}{h^2} \right)^{1/2}$$

$$= \frac{\pi^{1/2}}{\sigma} \left( \frac{T^3}{\Theta_A \Theta_B \Theta_C} \right)^{1/2} \quad \text{where } \Theta_A = \frac{h^2}{8\pi^2 I_A K_B} \text{ etc.}$$

And:

$$E_{rot} = \frac{3}{2} N K T$$

$$C_{V,ROT} = \frac{3}{2} N K = \frac{3}{2} R$$

$$S_{rot} = N K \log \left[ \frac{\pi^{1/2}}{\sigma} \left( \frac{T^3 e^3}{\Theta_A \Theta_B \Theta_C} \right)^{1/2} \right]$$

Symmetry Number,  $\sigma$

$\sigma$  is defined as the number of ways the molecule can be rotated into a configuration identical to the original. Eg,

- 1) Homonuclear Diatomics:  $\sigma = 2$
- 2) Heteronuclear " "  $\sigma = 1$
- 3) Pyramidal molecules, CHCl<sub>3</sub>  $\sigma = 3$
- 4) Tetrahedral, CH<sub>4</sub>  $\sigma = 12$
- 5) Benzene, C<sub>6</sub>H<sub>6</sub>  $\sigma = 12$
- 6) C<sub>2</sub>H<sub>4</sub>  $\sigma = 4$



$$\Theta_{v,j} = \frac{h\nu_j}{k_B}; \quad \Theta_{r,I_j} = \frac{h^2}{8\pi^2 I_j k}$$

j = A, B, C

### 8-3 THERMODYNAMIC FUNCTIONS

We can now use the results of Sections 8-1 and 8-2 to construct  $q(V, T)$ . We get for linear polyatomic molecules

$$q = \left(\frac{2\pi M k T}{h^2}\right)^{3/2} V \cdot \frac{T}{\sigma \Theta_r} \cdot \left\{ \prod_{j=1}^{3n-5} \frac{e^{-\Theta_{vj}/2T}}{(1 - e^{-\Theta_{vj}/T})} \right\} \omega_{e1} e^{D_e/kT} \quad (8-23)$$

$$-\frac{A}{NkT} = \ln \left[ \left(\frac{2\pi M k T}{h^2}\right)^{3/2} \frac{V e}{N} \right] + \ln \left( \frac{T}{\sigma \Theta_r} \right) - \sum_{j=1}^{3n-5} \left[ \frac{\Theta_{vj}}{2T} + \ln(1 - e^{-\Theta_{vj}/T}) \right] + \frac{D_e}{kT} + \ln \omega_{e1} \quad (8-24)$$

$$\frac{E}{NkT} = \frac{3}{2} + \frac{2}{2} + \sum_{j=1}^{3n-5} \left[ \left( \frac{\Theta_{vj}}{2T} \right) + \frac{\Theta_{vj}/T}{(e^{\Theta_{vj}/T} - 1)} \right] - \frac{D_e}{kT} \quad (8-25)$$

$$\frac{C_V}{Nk} = \frac{3}{2} + \frac{2}{2} + \sum_{j=1}^{3n-5} \left( \frac{\Theta_{vj}}{T} \right)^2 \frac{e^{\Theta_{vj}/T}}{(e^{\Theta_{vj}/T} - 1)^2} \quad (8-26)$$

$$\frac{S}{Nk} = \ln \left[ \left(\frac{2\pi M k T}{h^2}\right)^{3/2} \frac{V e^{5/2}}{N} \right] + \ln \left( \frac{T e}{\sigma \Theta_r} \right) + \sum_{j=1}^{3n-5} \left[ \frac{\Theta_{vj}/T}{e^{\Theta_{vj}/T} - 1} - \ln(1 - e^{-\Theta_{vj}/T}) \right] + \ln \omega_{e1} \quad (8-27)$$

$$pV = NkT \quad (8-28)$$

and for nonlinear polyatomic molecules:

$$q = \left(\frac{2\pi M k T}{h^2}\right)^{3/2} V \cdot \frac{\pi^{1/2}}{\sigma} \left( \frac{T^3}{\Theta_A \Theta_B \Theta_C} \right)^{1/2} \cdot \left\{ \prod_{j=1}^{3n-6} \frac{e^{-\Theta_{vj}/2T}}{(1 - e^{-\Theta_{vj}/T})} \right\} \omega_{e1} e^{D_e/kT} \quad (8-29)$$

$$-\frac{A}{NkT} = \ln \left[ \left(\frac{2\pi M k T}{h^2}\right)^{3/2} \frac{V e}{N} \right] + \ln \frac{\pi^{1/2}}{\sigma} \left( \frac{T^3}{\Theta_A \Theta_B \Theta_C} \right)^{1/2} - \sum_{j=1}^{3n-6} \left[ \frac{\Theta_{vj}}{2T} + \ln(1 - e^{-\Theta_{vj}/T}) \right] + \frac{D_e}{kT} + \ln \omega_{e1} \quad (8-30)$$

$$\frac{E}{NkT} = \frac{3}{2} + \frac{3}{2} + \sum_{j=1}^{3n-6} \left( \frac{\Theta_{vj}}{2T} + \frac{\Theta_{vj}/T}{e^{\Theta_{vj}/T} - 1} \right) - \frac{D_e}{kT} \quad (8-31)$$

$$\frac{C_V}{Nk} = \frac{3}{2} + \frac{3}{2} + \sum_{j=1}^{3n-6} \left( \frac{\Theta_{vj}}{T} \right)^2 \frac{e^{\Theta_{vj}/T}}{(e^{\Theta_{vj}/T} - 1)^2} \quad (8-32)$$

$$\frac{S}{Nk} = \ln \left[ \left(\frac{2\pi M k T}{h^2}\right)^{3/2} \frac{V e^{5/2}}{N} \right] + \ln \frac{\pi^{1/2} e^{3/2}}{\sigma} \left( \frac{T^3}{\Theta_A \Theta_B \Theta_C} \right)^{1/2} + \sum_{j=1}^{3n-6} \left[ \frac{\Theta_{vj}/T}{e^{\Theta_{vj}/T} - 1} - \ln(1 - e^{-\Theta_{vj}/T}) \right] + \ln \omega_{e1} \quad (8-33)$$

$$pV = NkT \quad (8-34)$$

Table 8-1 contains the characteristic rotational temperatures, the characteristic vibrational temperatures, and

$$D_0 = D_e - \sum \frac{1}{2} h\nu_i$$

Query: Just how good are Polyatomic molecule calculations? 53

## Comparison w Experiment

<u>Polyatomic Gas</u> 298.15 K, 1 atm	<u>S<sub>spec.</sub></u> eu	<u>S<sub>exp</sub></u> eu	<u>Difference</u>	<u>Comment</u>
CO <sub>2</sub>	51.1	51.0	∅	} exp. error
NH <sub>3</sub>	46.1	46.0	0.11	
CH <sub>3</sub> Cl	55.8	56.0	0.2	
C <sub>6</sub> H <sub>6</sub>	64.5	64.4	∅	
CO	47.3	46.2	1.1	R log 2 = 1.4
H <sub>2</sub> O	45.1	44.3	0.8	R log 3/2 = 0.8
D <sub>2</sub> O	46.7	45.9	0.8	R log 3/2 = 0.8
NNO (184.6 K)	48.5	47.4	1.1	R log 2 = 1.4
CH <sub>3</sub> D (99.7 K)	39.5	36.7	2.8	R log 4 = 2.7

## Residual Entropy

For CO<sub>2</sub>, NH<sub>3</sub>, CH<sub>3</sub>Cl & C<sub>6</sub>H<sub>6</sub> the agreement is excellent but for CO, H<sub>2</sub>O etc., the discrepancies are too large to be explained by experimental error. In every case where this is found to be true,  $S_{spec} > S_{exp}$  & this is due to what is often called the 'Residual Entropy'.

The experimental entropy assumes that  $S(0) = k \log \Omega(0) = \emptyset$  as  $\Omega(g.s. at 0^{\circ}K) = 1$ , i.e. it assumes every Xal at 0°K is in its lowest energy state, i.e. a perfect Xal devoid of packing errors. However some molecules can have two or more energetically equivalent orientations in the solid state leading to a metastable state where the g.s. entropy in the Xal is given by  $S = k \log \Omega(0^{\circ}K) > 0$  since  $\Omega > 1$ . In CO,  $S(0) = 2^N$  since all N molecules can have 2 equivalent orientations.

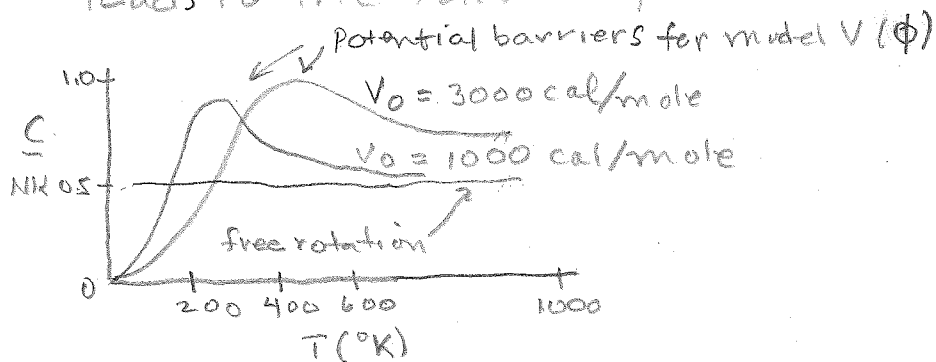
The correction terms in the previous table show that the  $k \log(\text{no. of configurations})^N$  gives excellent agreement with the spectroscopic values.

## Hindered Rotation

Prior to 1936 it was assumed that the terminal  $\text{CH}_3$  groups in an alkane could rotate freely. However a discrepancy of @ 1-2 e.u. was typical of  $C_v$  data at or near room temperature.  $\text{e.u.} \equiv 1 \text{ cal/mole deg}$



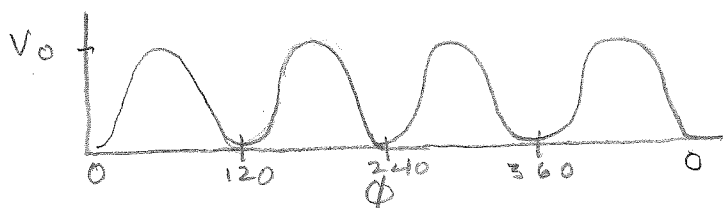
In ethane,  $N = 8$  so  $3N - 6 = 18$  normal modes, one of which is a torsional rotation. This rotation is inactive in both the IR & Raman so there is no information on the frequency available. However if one measures  $C_v$  in the gas phase & subtracts out all the various contributions, the difference will be  $C_v(\text{torsional})$ . This leads to the following curve:



where it is generally assumed that the potential energy of rotation is modelled by:

$$V = \frac{1}{2} V_0 (1 - \cos 3\phi)$$

and looks like:



$V_0 \approx 2.7 - 3.0 \text{ kcal/mole}$  for  $\text{C}_2\text{H}_6$   
The top of the pot. is when the  $\text{CH}_3$  groups are aligned,