

## McQuarrie – Chapter 8 – Extensions to polyatomics

$$H = H_{trans} + H_{int}$$

$$\varepsilon = \varepsilon_{trans} + \varepsilon_{int}$$

$$q = q_{trans} q_{int}$$

int = internal = vibrations and rotations

$$q_{tr} = \left( \frac{2\pi mkT}{h^2} \right)^{3/2} V$$

$$Q = \frac{(q_{tr} q_{int})^N}{N!}$$

### Degrees of freedom

Molecule with $n$ atoms	3 tr	
	3 rot (non linear)	2 rot (linear)
	(3n – 6) vibr.	(3n-5) vibr.

assume rigid rotor, harmonic oscillator

$$q = \frac{(q_{tr} q_{rot} q_{vibr} q_{el} q_{nuc})^N}{N!}$$

Allowing also for el. states and nuclear spin effects

$$q_{el} = \omega_{el} e^{D_e/kT} + \dots$$

take  $q_{nuc} = 1$  for now

vibr problem – normal coordinates  
different vibrations decouple

$\alpha = (3n-6)$  [(3n-5)] vibrations

$$\varepsilon = \sum_{j=1}^{\alpha} \left( n_j + \frac{1}{2} \right) h \nu_j, \quad n_j = 0, 1, 2, \dots$$

$$\nu_j = \frac{1}{2\pi} \sqrt{\frac{k_j}{\mu}}$$

$$q_{vib} = \prod \frac{e^{-\theta_{vj}/2T}}{(1 - e^{-\theta_{vj}/T})}$$

$E_{vib}$ ,  $C_{v, vib}$ : sums over contributions from all normal modes

Rotation is a bit more involved:

Linear molecules  $q_{rot} = \frac{8\pi^2 IkT}{\sigma h^2} = \frac{T}{\sigma \theta_r}$

$I = \sum_{j=1}^n m_j d_j^2$ , where  $d_j$  is measured from the center of mass.

$$x_{cm} = \frac{1}{M} \sum_{j=1}^n m_j x_j \quad \text{etc.}, \quad M = \sum m_i$$

In general

$$I_{xx} = \sum m_j \left[ (y_j - y_{cm})^2 + (z_j - z_{cm})^2 \right]$$

$$I_{yy} = \sum m_j \left[ (x_j - x_{cm})^2 + (z_j - z_{cm})^2 \right]$$

$$I_{zz} = \sum m_j \left[ (x_j - x_{cm})^2 + (y_j - y_{cm})^2 \right]$$

$$I_{xy} = \sum m_j (x_j - x_{cm})(y_j - y_{cm}), \text{ etc.}$$

Principle axes: X, Y, Z diagonalize  $I$

If a molecule has symmetry, easy to find X, Y, Z

$$\bar{A} = \frac{h}{8\pi I_A c}, \quad \bar{B} = \frac{h}{8\pi I_B c}, \quad \bar{C} = \frac{h}{8\pi I_C c} \quad (\text{in cm}^{-1})$$

↓  
 $\theta_A$

↓  
 $\theta_B$

↓  
 $\theta_C$

From rotational constants can calculate corresponding  $\theta$  values

$\theta_A = \theta_B = \theta_C$  spherical top

$\theta_A = \theta_B \neq \theta_C$  symm top

$\theta_A \neq \theta_B \neq \theta_C$  asymm top ← difficult

spherical tops  $\varepsilon_j = \frac{J(J+1)}{2} \hbar^2, \quad J = 0, 1, 2, \dots$

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

degeneracy  
factor

high  $T$

$$q_{rot} = \frac{1}{\sigma} \int_0^\infty (2J+1)^2 e^{-J(J+1)\hbar^2/2IkT} dJ$$

↑  
can ignore the "1"

$$= \frac{\sqrt{\pi}}{\sigma} \left( \frac{8\pi^2 IkT}{h^2} \right)^{3/2}$$

$I_A = I_B \neq I_C$  also solvable  
in closed form

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

Asymm. top

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

$$q_{rot} = \frac{\sqrt{\pi}}{\sigma} \sqrt{\frac{T^3}{\theta_A \theta_B \theta_C}}$$

So in the “high”  $T$  limit

$$E_{rot} = \frac{3}{2} NkT \quad \text{for non-linear molecules}$$

$$S_{rot} = Nk \ln \left[ \frac{\pi^{1/2}}{\sigma} \left( \frac{T^3 e^3}{\theta_A \theta_B \theta_C} \right)^{1/2} \right]$$

Although expressions for total  $E$  and  $S$  are rather involved,  $pV = NkT$

## Hindered rotation

e.g., ethane

- Minima at torsion angles 0, 120, 240, 360°
- Maxima ( $v_0$ ) at torsion angles = 60, 180, 300°

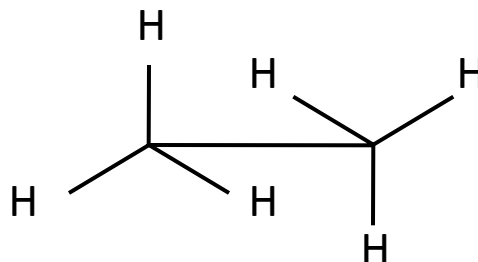
In general, have to solve the Schrödinger equation for the energy levels of the rigid rotor degree of freedom and use these in evaluating the partition function.

## Symmetry numbers for various point groups

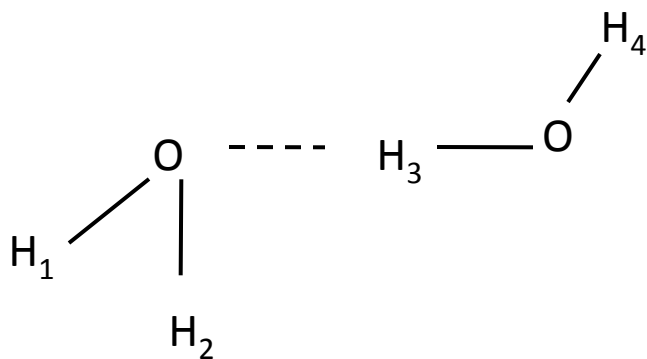
$C_1, C_{\infty v}, C_s, C_i$	1	
$C_2, C_{2v}, C_{2h}, D_{\infty h}$	2	
$C_3, C_{3v}, C_{3h}, S_6$	3	
$C_4, C_{4v}, C_{4h}$	4	
$C_5, C_{5v}, C_{5h}$	5	$\langle C_{70} \rangle$
$C_6, C_{6v}, C_{6h}$	6	
$D_2, D_{2d}, D_{2h}$	4	
$D_3, D_{3d}, D_{3h}$	6	
$D_4, D_{4d}, D_{4h}$	8	
$D_6, D_{6d}, D_{6h}$	12	
$T_d$	12	
$O_h$	24	
$I_h$	60	$\langle C_{60} \rangle$



Non-rigidity complicates the situation



Ethane -  
if freely rotating  
sym # = 18 rather  
than 6



expect  $\sigma = 1$ , but if ( $H_1$  and  $H_2$ ) and ( $H_3$  and  $H_4$ ) can exchange,  $\sigma = 4$ . What if the two water molecules can exchange?