5.62 Physical Chemistry II
Spring 2008

<u>5.62 Lecture #15</u>: Polyatomic Molecules: Rotation and Vibration

Reading: Hill, pp. 151-153, 156-159
Maczek pp. 53, 58-63

<u>VIBRATIONAL CONTRIBUTIONS TO MACROSCOPIC PROPERTIES (CONT.)</u>

High Temperature or Classical Limit of $(E - E_0)_{vib}$: $T \gg \theta_{vib}$

$$\left(E - E_0\right)_{vib} = \frac{Nk\theta_{vib}}{e^{\theta_{vib}/T} - 1} \simeq \frac{Nk\theta_{vib}}{1 + \theta_{vib}/T + \dots - 1} = NkT$$

$$e^x \simeq 1 + x + \frac{x^2}{2!} + \frac{x^3}{3!} + \dots \text{ for } x < 1$$

This quantum result yields the same value for $(E–E_0)_{vib}$ as the classical approach when $T \gg \theta_{vib}$ or $\varepsilon_{vib} \ll kT$. Classical equipartition principle says that each vibrational degree of freedom contributes NkT to total average energy (but ony if $T \gg \theta_{vib}$). However, $T \gg \theta_{vib}$ is a condition that does not obtain very often.

Other Thermodynamic Functions:

*

$$A_{vib} = -kT \ln Q_{vib} = \frac{Nk}{2}\theta_{vib} - NkT \ln q_{vib}^*$$

$$= \frac{Nk}{2}\theta_{vib} - NkT \ln\left(\frac{1}{1 - e^{-\theta_v/T}}\right)$$

$$\left(A - E_0\right)_{vib} = NkT \ln\left(1 - e^{-\theta_v/T}\right)$$

$$\left(A - E_0\right)_{vib} = NkT \ln\left(1 - e^{-x}\right) \qquad\qquad x = \theta_{vib}/T, \; NkT = nRT$$

$$\frac{\left(A - E_0\right)_{vib}}{nRT} = \ln\left(1 - e^{-x}\right) \qquad\qquad \text{another Einstein function}$$

* S_{VIB}

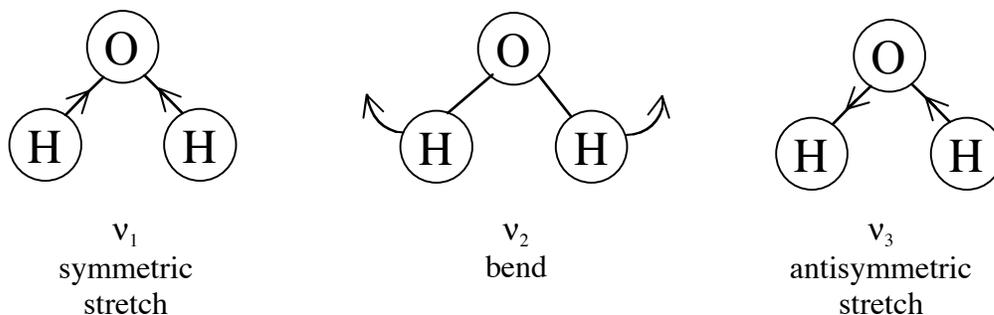$A = E - TS$

$$S = \frac{E - A}{T} = \frac{\left(E - E_0\right) - \left(A - E_0\right)}{T}$$

This expresses the fact that entropy cannot depend on an arbitrary choice for the zero of energy.

$$S = \frac{nRx}{e^x - 1} - nR\ln\left(1 - e^{-x}\right) \qquad , \qquad x = \frac{\theta_{VIB}}{T}$$

$$\boxed{\frac{S_{vib}}{R} = \frac{x}{e^x - 1} - \ln\left(1 - e^{-x}\right)}$$ Another Einstein function

$$C_V^{vib} = \left(\frac{\partial(E - E_0)_{vib}}{\partial T}\right)_{V,N}$$

$$* \quad C_V^{vib} = Nk\theta_{vib}\frac{\partial\left(e^{\theta_v/T} - 1\right)^{-1}}{\partial T}$$

$$C_V^{vib} = \frac{Nk\theta_{vib}^2}{T^2}\frac{e^{\theta_v/T}}{\left(e^{\theta_v/T} - 1\right)^2}$$

$$\boxed{\frac{C_V^{vib}}{nR} = \frac{x^2 e^x}{\left(e^x - 1\right)^2}}$$ another Einstein function, plotted

POLYATOMIC MOLECULES — INTERNAL DEGREES OF FREEDOM

3N degrees of freedom — 3N independent coordinates needed to specify positions of N atoms in a molecule

	diatomic or linear polyatomic	non-linear polyatomic
translation	3	3
rotation	2	3
vibration	3N–5	3N–6
	3N	3N

Example: Vibrations of CO_2

N = 3   3N = 9 total degrees of freedom

linear molecule $\Rightarrow$ 4 vibrational degrees of freedom
                                                       4 vibrational modes

symmetric
stretch
$\leftarrow$ (O) — (C) — (O) $\rightarrow$ frequency
ν_1

bend
(O) — (C) — (O)
ν_{2b}

bend
$(-)$ — $(+)$ — $(-)$
ν_{2a}
modes

$\left.\begin{array}{c}\ \\ \ \end{array}\right\}$ degenerate

antisymmetric
stretch
$\leftarrow$ (O) — (C) $\rightarrow\!\!\leftarrow$ (O)
ν_3

Example: Vibrations of H_2O $N = 3$ $3N = 9$ deg. of freedom

nonlinear molecule $\Rightarrow$ 3 vibrational degrees of freedom

(O)
(H)   (H)

(O)
(H)   (H)

(O)
(H)   (H)

ν_1
symmetric
stretch

ν_2
bend

ν_3
antisymmetric
stretch

POLYATOMIC MOLECULES — INTERNAL MOLECULAR PARTITION FUNCTION

$$q_{int} = g_0 e^{-\varepsilon_0/kT} q_{vib}^0 q_{rot}^0 + g_1 e^{-\varepsilon_1/kT} q_{vib}^1 q_{rot}^1 + \ldots$$

MOLECULAR ROTATIONAL PARTITION FUNCTION — LINEAR POLYATOMIC MOLECULE

2 rotational degrees of freedom

$$q_{rot} = \frac{kT}{\sigma hcB_e} = \frac{T}{\sigma\theta_{rot}} = \frac{8\pi^2 IkT}{\sigma h^2} \qquad \varepsilon_{rot} \ll kT$$
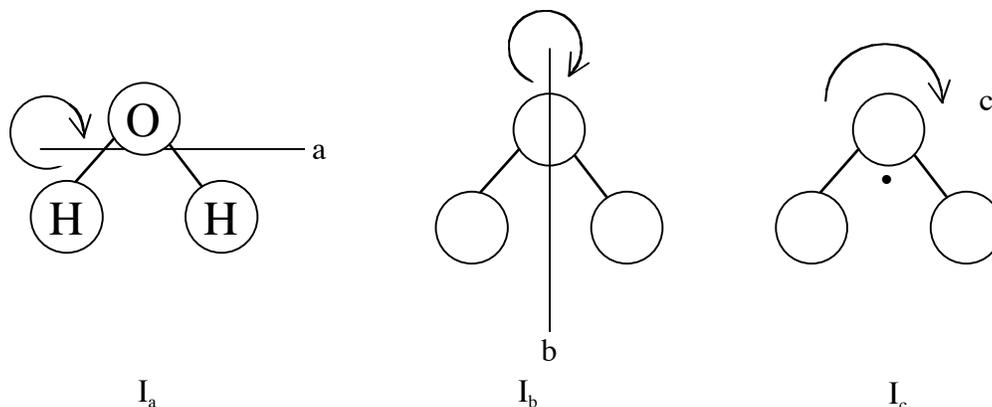
same form as for diatomic molecule

$\sigma = 1$ linear molecule with no symmetry HCN, NNO

$$\sigma = 2 \quad \text{linear molecule with a center of symmetry } CO_2, C_2H_2$$

MOLECULAR ROTATIONAL PARTITION FUNCTION—NON-LINEAR POLYATOMIC MOLECULE

3 rotational degrees of freedom - 3 princpal axes of rotation, each with a different I and each with different ε_{rot}.

$$I_a \qquad\qquad\qquad I_b \qquad\qquad\qquad I_c$$

Sum over all rotational states for each rotation (for $\theta_{rot} < T$):

$$q_{rot} = \frac{\pi^{1/2}}{\sigma}\left(\frac{8\pi^2 I_a kT}{h^2}\right)^{1/2}\left(\frac{8\pi^2 I_b kT}{h^2}\right)^{1/2}\left(\frac{8\pi^2 I_c kT}{h^2}\right)^{1/2}$$

rotational partition function for each axis

$$= \frac{8\pi^2 (2\pi kT)^{3/2}\left(I_a I_b I_c\right)^{1/2}}{\sigma h^3} = \frac{\pi^{1/2} T^{3/2}}{\sigma \theta_a^{1/2}\theta_b^{1/2}\theta_c^{1/2}}$$

where

$$\theta_a = \frac{hcA_e}{k} = \frac{h^2}{8\pi^2 I_a k} \qquad \text{and} \qquad A_e = \frac{h}{8\pi^2 I_a c}$$

$$\theta_b = \frac{hcB_e^a}{k} = \frac{h^2}{8\pi^2 I_b k} \qquad \text{and} \qquad B_e^a = \frac{h}{8\pi^2 I_b c}$$

[but, for prolate symmetric top

$$E_{rot} = AK^2 + \frac{B+C}{2}\left[J(J+1)-K^2\right] \qquad (B = C)$$

this makes the identical role played by a, b, and c axis rotations in q_{rot} seem surprising.]

$\sigma \equiv$ symmetry number = no. of different ways of achieving, exclusively, by rotation, a given spatial orientation that differs only in labels on identical nuclei (without breaking any bonds).

e.g. $HCCl_3$: $\sigma = 3$ C_2H_4: $\sigma = 4$ C_6H_6: $\sigma = 12$

Pictures?

For both linear and nonlinear polyatomic molecules, the high temperature limit or classical limit for q_{rot} is okay most of the time: $\varepsilon_{rot} \ll kT$.

MOLECULAR VIBRATIONAL PARTITION FUNCTION – POLYATOMIC MOLECULES

Each vibrational mode is treated separately. Energies of each vibrational mode add, so the partition function factors into a product of the sums over all vibrational energy levels for each vibrational mode. The sum over vibrational energy levels results in an analytical expression as for a diatomic. Energy levels are calculated within the harmonic oscillator model. Each mode i, with frequency ω_1, is assumed to be independent of excitation in the other modes. Two assumptions: harmonic and uncoupled.

$$q^*_{vib} = \prod_{i=1}^{n_v} \frac{1}{1-e^{-hc\omega_i/kT}} = \prod_{i=1}^{n_v} \frac{1}{1-e^{-\theta^i_{vib}/T}}$$

product is over all vibrational modes
where $i \equiv i^{th}$ vibrational mode n_v = # of vibrational modes

$$q_{vib} = \prod_{i=1}^{n_v} \frac{e^{-hc\omega_i/2kT}}{1-e^{-hc\omega_i/kT}} = \prod_{i=1}^{n_v} \frac{e^{-\theta^i_{vib}/2T}}{1-e^{-\theta^i_{vib}/T}}$$

FINISHED!   Now we can calculate all contributions, translational and internal, to macroscopic properties of all gas phase molecules.