

STATISTICAL MECHANICS OF DIATOMIC GASES

$$u = \frac{3}{2}RT,$$

$$c_V = \left(\frac{\partial u}{\partial T} \right)_V = \frac{3}{2}R$$

	The translation kinetic energy	-1
E_{trans}		
E_{excit}	Excitation energy	-2
E_{vib}	Vibrational energy	-3
E_{rot}	Rotational energy	-4

$$E_{total} = E_{trans} + E_{excit} + E_{rot} + E_{vib}$$

$$Z_{sp} = \sum e^{-\beta E_{Total}} = \left(\sum e^{-\beta E_{trans}} \right) \left(\sum e^{-\beta E_{excit}} \right) \left(\sum e^{-\beta E_{rot}} \right) \left(\sum e^{-\beta E_{vib}} \right)$$

$$= z_{trans} z_{excit} z_{rot} z_{vib}$$

:

() -1

-2

-3

$$\Delta E_{excit} \approx 1 \text{ eV} \approx 10^4 \text{ K}$$

-4

$$\Delta E_{rot} \approx 10^{-4}, \quad \Delta E_{vib} \approx 10^{-3} \text{ eV to } 10^{-1} \text{ eV}$$

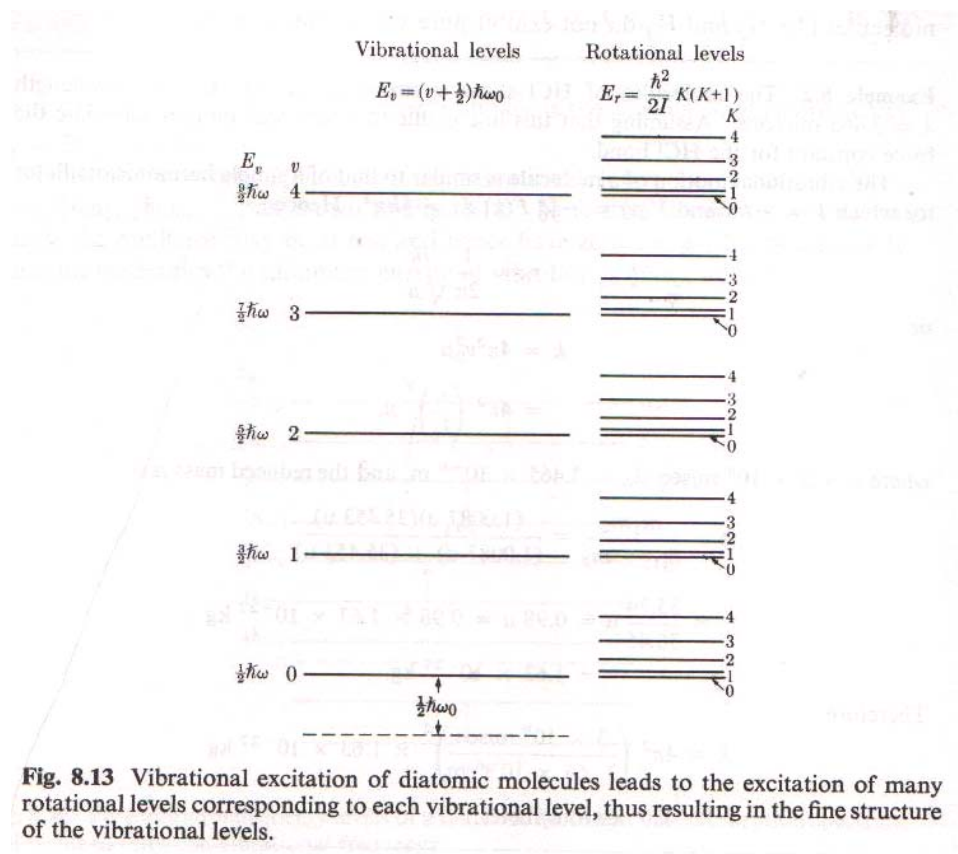


Fig. 8.13 Vibrational excitation of diatomic molecules leads to the excitation of many rotational levels corresponding to each vibrational level, thus resulting in the fine structure of the vibrational levels.

Vibrational mode

$$: \quad \omega = 2\pi f \quad m$$

$$H(p_x, q_x) = \frac{p_x^2}{2m} + \frac{1}{2}m\omega^2 q_x^2$$

:

$$\varepsilon_j = (j + \frac{1}{2})\hbar\omega, \quad j = 0, 1, 2, \dots$$

:

$$\varepsilon_{j\pm 1} - \varepsilon_j = \pm \hbar\omega \quad -1$$

$$. \hbar\omega / 2 \quad -2$$

$$. i \quad g_i = 1 \quad -3$$

$$: \quad -4$$

$$z_{vib} = \sum_v e^{-\beta \varepsilon_v} = \frac{e^{-a}}{1 - e^{-2a}} = \frac{1}{e^a - e^{-a}} = (2 \sinh a)^{-1}, \quad a = \frac{\theta_{vib}}{2T},$$

$$. (\sum_{n=0}^{\infty} e^{-nx} = \frac{1}{1 - e^{-x}}) \quad \theta_{vib} = \frac{\hbar\omega}{k_B}$$

-5

$$U_{vib} = - \left(\frac{\partial \ln Z_{vib}}{\partial \beta} \right)_{V,N} = N \hbar\omega \left[\frac{1}{2} + \frac{1}{e^{2a} - 1} \right]$$

: -6

$$C_{vib} = \left(\frac{\partial U_{vib}}{\partial T} \right)_{V,N} = N k_B \left(\frac{\theta_{vib}}{T} \right)^2 \frac{e^{\theta_{vib}/T}}{(e^{\theta_{vib}/T} - 1)^2}$$

This heat capacity decays exponentially as $T \ll \theta_{vib}$ and tends to zero as $T \rightarrow 0$, and tends to R per mole as $T \gg \theta_{vib}$,

z_{vib} :

Quantity	Formula	$T \rightarrow \infty$
Partition function	$Z_{vib} = (z_{vib})^N = (2 \sinh a)^{-N}$	$\left(\frac{k_B T}{\hbar \omega}\right)^N$
Helmholtz free energy	$F = -k_B T \ln Z_{vib} = Nk_B T \ln(2 \sinh a)$	$F = Nk_B T \ln(\beta \hbar \omega)$
Entropy	$S = -\left(\frac{\partial F}{\partial T}\right)_{V,N} = Nk_B [a \coth a - \ln(a \sinh a)]$	$S = Nk_B [1 - \ln(\beta \hbar \omega)]$
Internal energy	$U_{vib} = N \hbar \omega \left[\frac{1}{2} + \frac{1}{e^{2a} - 1} \right]$	$Nk_B T = nRT$
Vibrational capacity heat	$C_{vib} = Nk_B \left(\frac{\theta_{vib}}{T}\right)^2 \frac{e^{\theta_{vib}/T}}{(e^{\theta_{vib}/T} - 1)^2}$	$Nk_B = nR$

N_2 :
 $\hbar \omega = 0.3 \text{ eV}$ 1000 K

1000 K θ_{vib} :

$$\theta_{vib} = \frac{\hbar \omega}{k_B} = \frac{0.3 \times 1.9 \times 10^{-19} \text{ J}}{1.38 \times 10^{-23} \frac{\text{J}}{\text{K}}} = 3478 \text{ K}$$

: 3478 K 1000 K

$$c_{vib} = R \left(\frac{\theta_{vib}}{T}\right)^2 \frac{e^{\theta_{vib}/T}}{(e^{\theta_{vib}/T} - 1)^2}$$

$$= 8.31 \left(\frac{3478}{1000}\right)^2 \frac{e^{3478/1000}}{(e^{3478/1000} - 1)^2} = 3.31 \frac{\text{J}}{\text{mole K}}$$

$$c_{vib} = \frac{3}{2} R = 12.471 \frac{\text{J}}{\text{mole K}}$$

Rotational mode

:

$$\text{K.E.} = \frac{1}{2} I \omega^2 = \frac{(I \omega)^2}{2I} = \frac{L^2}{2I}$$

I

L

$$m_1 r_1 = m_2 r_2, \quad r_o = r_1 + r_2$$

:

$$I = m_1 r_1^2 + m_2 r_2^2 = \mu r_o^2, \quad \mu = \frac{m_1 m_2}{m_1 + m_2}$$

.

μ

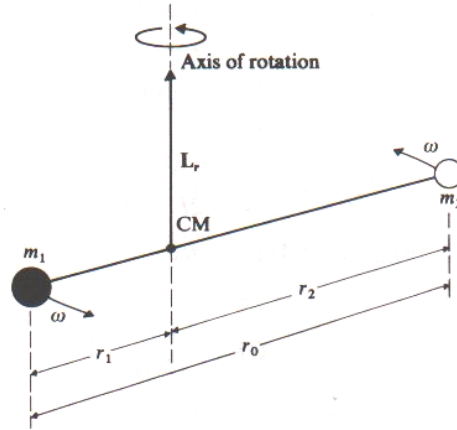


Fig. 8.8 Rotational motion of a diatomic molecule about an axis through the center of mass.

:

$$\epsilon_r = \frac{L^2}{2I} = \frac{l(l+1)}{2I} \hbar^2, \quad l = 0, 1, 2, \dots$$

$$g_l = (2l + 1)$$

l

:

$$z_{rot} = \sum_l g_l e^{-\beta \epsilon_l} = \sum_l (2l + 1) e^{-\beta \epsilon_l} = \sum_l (2l + 1) e^{-l(l+1) \theta_{rot} / T},$$

$$\theta_{rot} = \frac{\hbar^2}{2Ik_B}$$

Substance	$\theta_{vib} = \frac{\hbar \omega}{k} \text{ (K)}$	$\theta_{rot} = \frac{\hbar^2}{2Ik} \text{ (K)}$
H ₂	6140	85.4
O ₂	2260	2.1
N ₂	3352	2.9
Cl ₂	810	0.0347

$$T \ll \theta_{rot}$$

$z_{rot,q}$

$$z_{rot,q} = \sum_l (2l+1) e^{-\beta \varepsilon_l} = 1 + 3e^{-2\theta_{rot}/T},$$

$$U_{rot,q} = 6Nk_B \theta_{rot} e^{-2\theta_{rot}/T},$$

$$C_{V,rot,q} = 3Nk_B \left(\frac{2\theta_{rot}}{T} \right)^2 e^{-2\theta_{rot}/T}$$

$$T \gg \theta_{rot}$$

$z_{rot,c}$

$$z_{rot,c} = \int_0^{\infty} (2l+1) e^{-l(l+1)\theta_{rot}/T} dl \approx \int_0^{\infty} (2l) e^{-l^2\theta_{rot}/T} dl = \frac{T}{\theta_{rot}}$$

$$U_{rot,q} = Nk_B T,$$

$$C_{V,rot,q} = Nk_B = nR$$

Q₂, H₂, N₂, ... (Homonuclear) .σ
 .σ = 1 HCl, ... σ = 1
 :

$$z_{rot} = \frac{z_{rot,c}}{\sigma},$$

$$z_{rot} = \frac{z_{rot,q}}{\sigma},$$

. r_o = 1.0976 × 10⁻¹⁰ m N₂ θ_{rot} :
 : N₂ :

$$m = \frac{14.008}{6.023 \times 10^{26}} = 2.325 \times 10^{-26} \text{ kg},$$

$$\mu = m/2 = 1.163 \times 10^{-26} \text{ kg},$$

$$I = \mu r_o^2 = 1.163 \times 10^{-26} \text{ kg} \times (1.0976 \times 10^{-10} \text{ m})^2 = 14 \times 10^{-47} \text{ kg.m}^2.$$

:

$$\theta_{rot} = \frac{h^2}{8\pi^2 I k_B} = \frac{(6.625 \times 10^{-36})^2 \text{ J}^2 \text{ s}^2}{8\pi^2 \times 14 \times 10^{-47} \text{ kg.m}^2 \times 1.38 \times 10^{-23} \frac{\text{J}}{\text{molecule.K}}} = 2.88 \text{ K}$$

300 K H₂ :

$$. I = 6.29 \times 10^{-48} \text{ kg.m}^2$$

θ_{rot} :

:()

$$\theta_{rot} = \frac{h^2}{8\pi^2 I k_B} = \frac{(6.625 \times 10^{-36})^2 \text{ J}^2 \text{ s}^2}{8\pi^2 \times 6.29 \times 10^{-48} \text{ kg.m}^2 \times 1.38 \times 10^{-23} \frac{\text{J}}{\text{molecule.K}}} = 64.03 \text{ K}$$

:

$$z_{rot,c} = \frac{T}{\theta_{rot}} = \frac{300}{\theta_{rot}} = \frac{300}{64.03} = 4.69$$

:

$$\begin{aligned} z_{rot,q} &= \sum_{l=0}^{\infty} (2l+1)e^{-l(l+1)\theta_{rot}/T} = 1.000 + 3e^{-2 \times 64.03/300} + 5e^{-6 \times 64.03/300} + \dots \\ &= 1.000 + 1.958 + 1.389 + 0.540 + 0.126 + \dots \\ &= 5.001 \end{aligned}$$

:

$$l=1 \qquad \qquad \qquad l \qquad \qquad \qquad -1$$

.l

$$.(\quad) \qquad -l(l+1) \qquad \qquad \qquad -2$$

-3

$$\frac{64.03}{300}$$

$$Z_{sp} = z_{trans} z_{rot} z_{vib} = V \left(\frac{2\pi m}{\beta h^2} \right)^{3/2} \times z_{rot} \times z_{vib}$$

$$C_V = C_{V,trans} + C_{V,rot} + C_{V,vib}$$

$$= \frac{3}{2} Nk_B + Nk_B + Nk_B \left(\frac{\theta_{vib}}{T} \right)^2 \frac{e^{\theta_{vib}/T}}{(e^{\theta_{vib}/T} - 1)^2}$$

k_B

For most diatomic molecules the separation between the rotational energy levels is much less than kT_{room} , but the separation between vibrational levels is much greater than kT_{room} . This means that the heat capacity at room temperature is typically $5R/2$ per mole: with $3R/2$ coming from the translational heat capacity and the other R from the rotations. At room temperature the vibrational contributions is small, only coming into play at higher temperature.

