4. Intramolecular Motions

4.1 Vibration

⟨Harmonic oscillator⟩

· Potential energy (V) and classical frequency (ν)

$$V(x) = \tfrac{1}{2} k_f x^2 \tag{4.1}$$

$$\nu = \frac{1}{2\pi} \sqrt{\frac{k_f}{\mu}} \tag{4.2}$$

   x: deviation ($= r - r_e$), k_f: force constant, μ: reduced mass

· Energy levels:

$$\varepsilon_\upsilon = h\nu\left(\upsilon + \tfrac{1}{2}\right) \tag{4.3}$$

$$\tilde{\varepsilon}_\upsilon = h\nu\upsilon \tag{4.3'}$$

· Density of states and partition function:

$$\rho_{vib}(\varepsilon) = \frac{d\upsilon}{d\varepsilon} = \frac{1}{h\nu} \tag{4.4}$$

$$q_{vib}(T) = \frac{\exp\left(-\dfrac{h\nu}{2k_BT}\right)}{1 - \exp\left(-\dfrac{h\nu}{k_BT}\right)} \tag{4.5}$$

$$\tilde{q}_{vib}(T) = \frac{1}{1 - \exp\left(-\dfrac{h\nu}{k_BT}\right)} \tag{4.5'}$$
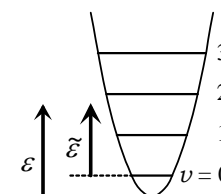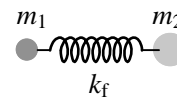
⟨Vibrational density of states⟩

· two vibrations: $\displaystyle \rho_{vib}^{(2)}(\varepsilon) = \int_0^\varepsilon \frac{1}{h\nu_1} \frac{1}{h\nu_2} d\varepsilon_2 = \frac{1}{h\nu_1} \frac{1}{h\nu_2} \varepsilon$

· three vibrations: $\displaystyle \rho_{vib}^{(3)}(\varepsilon) = \int_0^\varepsilon \int_0^{\varepsilon-\varepsilon_3} \frac{1}{h\nu_1} \frac{1}{h\nu_2} d\varepsilon_2 \frac{1}{h\nu_3} d\varepsilon_3 = \frac{1}{2} \frac{1}{h\nu_1} \frac{1}{h\nu_2} \frac{1}{h\nu_3} \varepsilon^2$

· → n_υ vibrations:

$$\rho_{vib}^{(n_\upsilon)}(\varepsilon) = \frac{1}{\Gamma(n_\upsilon) \prod h\nu_i} \varepsilon^{n_\upsilon - 1} \tag{4.6}$$

   $\Gamma(n) = (n-1)!, \; \Gamma(1) = \Gamma(2) = 1$

[example] vibrational density of states of CH_3OH at dissociation limit to $CH_3O + H$

   $n_\upsilon = 3\,n_{atom} - 6 = 3 \cdot 6 - 6 = 12$
   $D(CH_3O–H) = 436.8 \text{ kJ mol}^{-1} = 3.651 \times 10^4 \text{ cm}^{-1}$ (1 cm^{-1} = 11.963 J)
   ZPE: $(3681 + 3000 + 2844 + ...) / 2 = 1.085 \times 10^4 \text{ cm}^{-1}$
   $\Gamma(n_\upsilon) = 11! = 3.992 \times 10^7$
   $\Pi(h\nu_i) = 3681 \cdot 3000 \cdot 2844 \cdot ... = 1.013 \times 10^{38} \text{ cm}^{-12}$
   $\rho = [(3.651 + 1.085) \times 10^4]^{11} / (3.992 \times 10^7 \times 1.013 \times 10^{38}) = 6.65 \times 10^5 \text{ cm}$ (= 1 / cm^{-1} = states per cm^{-1})

[Exercise-4] Estimate the vibrational density of states of H_2O at dissociation limit to H + OH from Eq. (4.6)

D(H–OH) = 499.1 kJ mol^{-1}

vibrational frequencies (cm^{-1}): 3657, 1595, 3756

(answer) D(H–OH) = 499100 / 11.963 = 4.172×10^4 cm^{-1}, ZPE = (3657+1595+3756)/2 = 0.450×10^4 cm^{-1}

$\rho = [(4.172 + 0.450)×10^4]^2 / (2 × 3657·1595·3756) = 4.88×10^{-2}$ cm

Problem-4

Estimate the vibrational density of states for ethane [D(C-C) = 377 kJ mol^{-1}] at around dissociation threshold by eq. 4.6. Use the following vibrational frequencies in cm^{-1} (degeneracy).

2954, 1388, 995, 289, 2896, 1379, 2969(2), 1468(2), 1190(2), 2985(2), 1469(2), 822(2)

Note: ε in eq. 4.6 is the energy from classical origin.

4.2 Free rotor

⟨Free 1D rotation⟩

e.g.) dimethylacetylene

· Energy levels:

$$\varepsilon_j = Bj^2, \quad j = 0, \pm1, \pm2, ...$$
(4.7)

degeneracy: $g_j = 1$ or $g_{|j|} = 2$ (except for $j = 0$)

· Density of states and partition function:

$$\rho_{rot}^{(1D)}(\varepsilon) = \frac{g_{|j|}}{\sigma}\frac{d|j|}{d\varepsilon} = \frac{1}{\sigma B^{1/2}}\varepsilon^{-1/2}$$
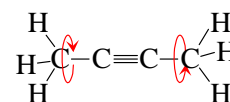(4.8)

$$q_{rot}^{(1D)}(T) = \frac{\sqrt{\pi}}{\sigma}\left(\frac{k_B T}{B}\right)^{1/2}$$
(4.9)

⟨Reduced moment of inertia⟩

· For symmetric coaxial rotors;
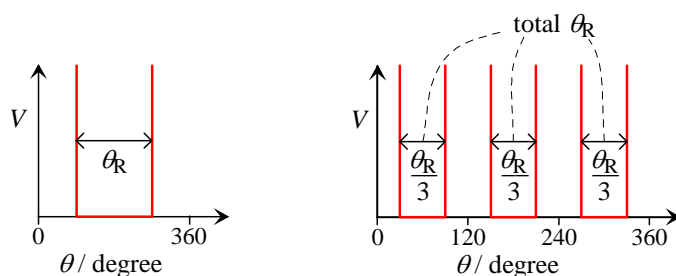
$$I_r = \frac{I_1 I_2}{I_1 + I_2}$$
(4.10)

· Other cases: see Pitzer, *J. Chem. Phys.* **14**, 239 (1946).

4.3 Hindered rotor

⟨Hard-sphere hindrance⟩

· $V(\theta) = 0$ for regions of total width θ_R (restriction angle), = ∞ for other.

(same as 1D translation with replacement: $m \rightarrow I$, $x \rightarrow \theta$, and $l \rightarrow \theta_R$)

$$\rho_{HS-HR}^{(1D)}(\varepsilon) = \frac{\theta_R}{2\pi}\rho_{rot}^{(1D)}(\varepsilon)$$
(4.11)

$$q_{\text{HS-HR}}^{(1D)}(T) = \frac{\theta_{\text{R}}}{2\pi} q_{\text{rot}}^{(1D)}(T) \tag{4.12}$$
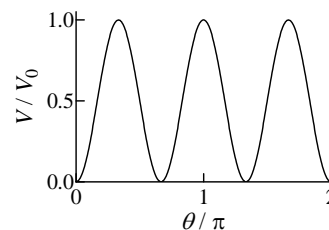
⟨Sinusoidal hindrance⟩

· Potential energy curve

$$V = \frac{V_0}{2}\left(1 - \cos n\theta\right) \tag{4.13}$$

· Pitzer-Gwinn approximation

$$q_{\text{SinHR}}(T) \cong q_{\text{SinHR}}^{\text{cl}}(T) \frac{q_{\text{vib}}(T)}{q_{\text{vib}}^{\text{cl}}(T)} \tag{4.14}$$

- classical partition function;

$$q_{\text{SinHR}}^{\text{cl}}(T) = q_{\text{rot}}^{(1D)}(T) \exp\left(-\frac{V_0}{2k_{\text{B}}T}\right) I_0\left(\frac{V_0}{2k_{\text{B}}T}\right) \tag{4.15}$$

- classical partition function for harmonic oscillator;

$$q_{\text{vib}}^{\text{cl}}(T) = \frac{k_{\text{B}}T}{h\nu} \tag{4.16}$$

$q_{\text{vib}}(T) \rightarrow$ (4.5), $q_{\text{rot}}^{(1D)}(T) \rightarrow$ (4.9). $I_0(x)$: zeroth-order modified Bessel function

$h\nu$ for (4.5) and (4.16) can be estimated by;

$$n^2 B V_0 = (h\nu)^2 \tag{4.17a}$$

or

$$n^2 \frac{B}{[\text{cm}^{-1}]} \frac{V_0}{[\text{cm}^{-1}]} = \left(\frac{\tilde{\nu}}{[\text{cm}^{-1}]}\right)^2 \tag{4.17b}$$

* Note : For many cases $\sigma = n$. But $\sigma \neq n$ may be used in 'approximation'.