

Chapter 5

Molecular Vibrations and Time-Independent Perturbation Theory

Homework Solutions

1. $\frac{d^2 y}{dx^2} = -4y$ Form of solution: $y = \sum_{n=0}^{\infty} a_n x^n = a_0 + a_1 x + a_2 x^2 + a_3 x^3 + a_4 x^4 + \dots$

Specific Recursion Relations

$$\frac{dy}{dx} = a_1 + 2a_2 x + 3a_3 x^2 + 4a_4 x^3 + \dots$$

$$\frac{d^2 y}{dx^2} = 2a_2 + 6a_3 x + 12a_4 x^2 + \dots$$

$$\begin{aligned} \frac{d^2 y}{dx^2} = -4y \quad \rightarrow \quad \frac{d^2 y}{dx^2} &= 2a_2 + 6a_3 x + 12a_4 x^2 + \dots = -4[a_0 + a_1 x + a_2 x^2 + \dots] \\ &= -4a_0 - 4a_1 x - 4a_2 x^2 + \dots \end{aligned}$$

$$2a_2 = -4a_0 \quad \rightarrow \quad a_2 = -2a_0$$

Equate powers of x to get: $6a_3 = -4a_1 \quad \rightarrow \quad a_3 = -2a_1 / 3$

$$12a_4 = -4a_2 \quad \rightarrow \quad a_4 = -a_2 / 3$$

General Recursion Relations: FYI only (not requested in the problem)

$$y = \sum_{m=0}^{\infty} a_m x^m$$

$$\frac{dy}{dx} = \sum_{m=1}^{\infty} m a_m x^{m-1}$$

$$\frac{d^2 y}{dx^2} = \sum_{m=2}^{\infty} (m-1) m a_m x^{m-2}$$

Let's convert summation index to start at 0 by defining: $n = m-2 \rightarrow m = n+2$

$$\frac{d^2 y}{dx^2} = \sum_{n=0}^{\infty} (n+1)(n+2) a_{n+2} x^n$$

$$\frac{d^2 y}{dx^2} = -4y \quad \rightarrow \quad \sum_{n=0}^{\infty} (n+1)(n+2) a_{n+2} x^n = -4 \left(\sum_{n=0}^{\infty} a_n x^n \right) = \sum_{n=0}^{\infty} -4a_n x^n$$

Equate coefficients of equal exponent terms:

$$(n+1)(n+2) a_{n+2} = -4a_n \quad \rightarrow \quad a_{n+2} = -\frac{4}{(n+1)(n+2)} a_n$$

Note: You will find that this general recursion formula reduces to the specific relations above if you use it with $n=0, 1$ or 2

2. $\psi_1 = A_1 x e^{-\alpha x^2/2} \quad \alpha = \frac{\mu\omega}{\hbar} \quad \omega = \sqrt{\frac{k}{\mu}}$

(a) Normalization

$$\langle \psi | \psi \rangle = \int_{-\infty}^{\infty} \left[A_1 x e^{-\alpha x^2/2} \right]^2 dx = 1 = A_1^2 \int_{-\infty}^{\infty} x^2 e^{-\alpha x^2} dx = 2A_1^2 \int_0^{\infty} x^2 e^{-\alpha x^2} dx = 2A_1^2 \frac{1}{4\alpha} \sqrt{\frac{\pi}{\alpha}}$$

$$A_1^2 = 2\alpha \left(\frac{\alpha}{\pi} \right)^{1/2} \rightarrow A_1 = (2\alpha)^{1/2} \left(\frac{\alpha}{\pi} \right)^{1/4}$$

(b) $\langle x \rangle$

$$\langle x \rangle = \langle \psi_1 | x | \psi_1 \rangle = \int_{-\infty}^{\infty} x \left[A_1 x e^{-\alpha x^2/2} \right]^2 dx = A_1^2 \int_{-\infty}^{\infty} x^3 e^{-\alpha x^2} dx = 0 \quad \text{because integrand is odd}$$

(c) $\langle x^2 \rangle$

$$\langle x^2 \rangle = \langle \psi_1 | x^2 | \psi_1 \rangle = \int_{-\infty}^{\infty} x^2 \left[A_1 x e^{-\alpha x^2/2} \right]^2 dx = A_1^2 \int_{-\infty}^{\infty} x^4 e^{-\alpha x^2} dx = 2A_1^2 \int_0^{\infty} x^4 e^{-\alpha x^2} dx$$

$$= 2A_1^2 \left(\frac{3}{8\alpha^2} \right) \left(\frac{\pi}{\alpha} \right)^{1/2} = 2 \left[2\alpha \left(\frac{\alpha}{\pi} \right)^{1/2} \right] \left(\frac{3}{8\alpha^2} \right) \left(\frac{\pi}{\alpha} \right)^{1/2} = \frac{3}{2\alpha}$$

(d) $\langle p \rangle$

$$\frac{d\psi}{dx} = \frac{d}{dx} \left[A_1 x e^{-\alpha x^2/2} \right] = A_1 \left[x(-2\alpha x/2) e^{-\alpha x^2/2} + e^{-\alpha x^2/2} \right] = A_1 e^{-\alpha x^2/2} (1 - \alpha x^2)$$

$$\langle p \rangle = \langle \psi_1 | \hat{p} | \psi_1 \rangle = \int_{-\infty}^{\infty} \left[A_1 x e^{-\alpha x^2/2} \right] \left[\frac{\hbar}{i} \frac{d(A_1 x e^{-\alpha x^2/2})}{dx} \right] dx = \frac{\hbar}{i} A_1^2 \int_{-\infty}^{\infty} x e^{-\alpha x^2/2} [e^{-\alpha x^2/2} (1 - \alpha x^2)] dx$$

$$= \frac{\hbar}{i} A_1^2 \int_{-\infty}^{\infty} [e^{-\alpha x^2} (x - \alpha x^3)] dx = \frac{\hbar}{i} A_1^2 \left\{ \int_{-\infty}^{\infty} x e^{-\alpha x^2} dx - \alpha \int_{-\infty}^{\infty} x^3 e^{-\alpha x^2} dx \right\} = \frac{\hbar}{i} A_1^2 \{0 - 0\} = 0$$

$\langle p \rangle = 0$: Both integrals vanish because the integrands are odd functions of x

(e) $\langle p^2 \rangle$

$$\frac{d^2\psi}{dx^2} = \frac{d}{dx} \left[A_1 e^{-\alpha x^2/2} (1 - \alpha x^2) \right] x = A_1 \left\{ e^{-\alpha x^2/2} (-2\alpha x) + (1 - \alpha x^2) (-2\alpha x/2) e^{-\alpha x^2/2} \right\}$$

$$= A_1 \left[e^{-\alpha x^2/2} (\alpha^2 x^3 - 3\alpha x) \right]$$

$$\begin{aligned}
\langle p^2 \rangle &= \int_{-\infty}^{\infty} \psi_1 (-\hbar^2) \frac{d^2 \psi_1}{dx^2} dx = \int_{-\infty}^{\infty} A_1 x e^{-\alpha x^2/2} (-\hbar^2) A_1 \left[e^{-\alpha x^2/2} (\alpha^2 x^3 - 3\alpha x) \right] dx \\
&= A_1^2 (-\hbar^2) \int_{-\infty}^{\infty} e^{-\alpha x^2} (\alpha^2 x^4 - 3\alpha x^2) dx = A_1^2 (-\hbar^2) \left\{ \alpha^2 \int_{-\infty}^{\infty} x^4 e^{-\alpha x^2} dx - 3\alpha \int_{-\infty}^{\infty} x^2 e^{-\alpha x^2} dx \right\} \\
&= A_1^2 (-\hbar^2) \left\{ \alpha^2 \cdot 2 \cdot \frac{3}{8\alpha^2} \sqrt{\frac{\pi}{\alpha}} - 3\alpha \cdot 2 \cdot \frac{1}{4\alpha} \sqrt{\frac{\pi}{\alpha}} \right\} = A_1^2 (-\hbar^2) \left\{ \frac{3}{4} \sqrt{\frac{\pi}{\alpha}} - \frac{3}{2} \sqrt{\frac{\pi}{\alpha}} \right\} \\
&= A_1^2 (-\hbar^2) \left\{ -\frac{3}{4} \sqrt{\frac{\pi}{\alpha}} \right\} = \left(2\alpha \sqrt{\frac{\alpha}{\pi}} \right) \left(+\frac{3}{4} \hbar^2 \sqrt{\frac{\pi}{\alpha}} \right) = \frac{3}{2} \hbar^2 \alpha
\end{aligned}$$

$$(f) \langle T \rangle = \left\langle \frac{p^2}{2\mu} \right\rangle = \frac{1}{2\mu} \langle p^2 \rangle = \frac{1}{2\mu} \left(\frac{3}{2} \hbar^2 \alpha \right) = \frac{3}{4} \frac{\hbar^2}{\mu} \frac{\mu \omega}{\hbar} = \frac{3}{4} \hbar \omega$$

$$(g) \langle V \rangle = \left\langle \frac{kx^2}{2} \right\rangle = \frac{k}{2} \langle x^2 \rangle = \frac{k}{2} \left(\frac{3}{2\alpha} \right) = \frac{3}{4} \frac{k}{\left(\frac{\mu \omega}{\hbar} \right)} = \frac{3}{4} \hbar \frac{k}{\mu} \frac{1}{\omega} = \frac{3}{4} \hbar \omega^2 \frac{1}{\omega} = \frac{3}{4} \hbar \omega$$

$$3. \quad \omega_x = \sqrt{\frac{k_x}{\mu}} \quad \omega_y = \sqrt{\frac{k_y}{\mu}} = \sqrt{\frac{9k_x}{\mu}} = 3\sqrt{\frac{k_x}{\mu}} = 3\omega_x$$

$$\begin{aligned}
E = E_x + E_y &= \left(n_x + \frac{1}{2} \right) \hbar \omega_x + \left(n_y + \frac{1}{2} \right) \hbar \omega_y = \left(n_x + \frac{1}{2} \right) \hbar \omega_x + \left(n_y + \frac{1}{2} \right) \hbar (3\omega_x) \\
&= \left(n_x + \frac{1}{2} \right) \hbar \omega_x + \left(3n_y + \frac{3}{2} \right) \hbar \omega_x = (n_x + 3n_y + 2) \hbar \omega_x
\end{aligned}$$

n_x	n_y	E	g
0	0	2 ħω _x	1
1	0	3 ħω _x	1
2	0	4 ħω _x	1
3	0	5 ħω _x	2
0	1		
1	1	6 ħω _x	2
4	0		
2	1	7 ħω _x	2
5	0		
3	1	8 ħω _x	3
0	2		
6	0		

4. (a) Force Constant

$$\mu = \frac{m_C m_O}{m_C + m_O} = \frac{(12 \text{ amu})(16 \text{ amu})}{12 \text{ amu} + 16 \text{ amu}} = 6.86 \text{ amu} \cdot \frac{1.66 \times 10^{-27} \text{ kg}}{1 \text{ amu}} = 1.14 \times 10^{-26} \text{ kg}$$

$$\tilde{\nu} = \frac{1}{2\pi c} \sqrt{\frac{k}{\mu}}$$

$$k = [2\pi c \tilde{\nu}]^2 \mu = [2(3.14)(3.00 \times 10^{10} \text{ cm/s})(2170 \text{ cm}^{-1})]^2 (1.14 \times 10^{-26} \text{ kg})$$

$$= 1910 \text{ kg/s} = 1910 (\text{kg} \cdot \text{m/s}) / \text{m} = 1910 \text{ N/m}$$

(b) ZPE and Energy Spacing

$$\omega = 2\pi\nu = 2\pi c \tilde{\nu} = 2(3.14)(3.00 \times 10^{10} \text{ cm/s})(2170 \text{ cm}^{-1}) = 4.09 \times 10^{14} \text{ s}^{-1}$$

$$E_0 = \frac{1}{2} \hbar \omega = \frac{1}{2} (1.05 \times 10^{-34} \text{ J} \cdot \text{s}) (4.09 \times 10^{14} \text{ s}^{-1})$$

ZPE:

$$= 2.15 \times 10^{-20} \text{ J} \times 6.02 \times 10^{23} \text{ mol}^{-1} \times \frac{1 \text{ kJ}}{10^3 \text{ J}} = 12.9 \text{ kJ/mol}$$

$$\Delta E_0 = \hbar \omega = (1.05 \times 10^{-34} \text{ J} \cdot \text{s}) (4.09 \times 10^{14} \text{ s}^{-1})$$

ΔE:

$$= 4.29 \times 10^{-20} \text{ J} \times 6.02 \times 10^{23} \text{ mol}^{-1} \times \frac{1 \text{ kJ}}{10^3 \text{ J}} = 25.8 \text{ kJ/mol}$$

5. $k = 320 \text{ N/m} = 320 (\text{kg} \cdot \text{m/s}^2) / \text{m} = 320 \text{ kg/s}^2$

$$\mu = \frac{m_{Cl} \cdot m_{Cl}}{m_{Cl} + m_{Cl}} = \frac{m_{Cl}}{2} = \frac{35 \text{ amu}}{2} = 17.5 \text{ amu} \cdot \frac{1.66 \times 10^{-27} \text{ kg}}{1 \text{ amu}} = 2.91 \times 10^{-26} \text{ kg}$$

$$\tilde{\nu} = \frac{1}{2\pi c} \sqrt{\frac{k}{\mu}} = \frac{1}{2(3.14)(3.00 \times 10^{10} \text{ cm/s})} \sqrt{\frac{320 \text{ kg/s}^2}{2.91 \times 10^{-26} \text{ kg}}} = 556 \text{ cm}^{-1}$$

6. $\tilde{\nu}_1 = 2349 \text{ cm}^{-1}$, $\tilde{\nu}_2 = 1334 \text{ cm}^{-1}$, $\tilde{\nu}_3 = \tilde{\nu}_4 = 667 \text{ cm}^{-1}$

$$\frac{E(0,0,0,0)}{hc} = \frac{1}{2} \tilde{\nu}_1 + \frac{1}{2} \tilde{\nu}_2 + \frac{1}{2} \tilde{\nu}_3 + \frac{1}{2} \tilde{\nu}_4$$

$$(a) \quad = \frac{1}{2} (2349 \text{ cm}^{-1}) + \frac{1}{2} (1334 \text{ cm}^{-1}) + \frac{1}{2} (667 \text{ cm}^{-1}) + \frac{1}{2} (667 \text{ cm}^{-1})$$

$$= 2509 \text{ cm}^{-1}$$

$$E(0,0,0,0) = hc (2509 \text{ cm}^{-1}) = (6.63 \times 10^{-34} \text{ J} \cdot \text{s}) (3.00 \times 10^{10} \text{ cm/s}) (2509 \text{ cm}^{-1})$$

$$= 4.99 \times 10^{-20} \text{ J} \times 6.02 \times 10^{23} \text{ mol}^{-1} \times \frac{1 \text{ kJ}}{10^3 \text{ J}} = 30.0 \text{ kJ/mol}$$

$$\begin{aligned}
 \frac{E(0,2,1,0)}{hc} &= \frac{1}{2}\tilde{\nu}_1 + \frac{5}{2}\tilde{\nu}_2 + \frac{3}{2}\tilde{\nu}_3 + \frac{1}{2}\tilde{\nu}_4 \\
 (b) \quad &= \frac{1}{2}(2349\text{ cm}^{-1}) + \frac{5}{2}(1334\text{ cm}^{-1}) + \frac{3}{2}(667\text{ cm}^{-1}) + \frac{1}{2}(667\text{ cm}^{-1}) \\
 &= 5844\text{ cm}^{-1}
 \end{aligned}$$

$$\begin{aligned}
 E(0,2,1,0) &= hc(5844\text{ cm}^{-1}) = (6.63 \times 10^{-34}\text{ J} \cdot \text{s})(3.00 \times 10^{10}\text{ cm/s})(5844\text{ cm}^{-1}) \\
 &= 1.16 \times 10^{-19}\text{ J} \times 6.02 \times 10^{23}\text{ mol}^{-1} \times \frac{1\text{ kJ}}{10^3\text{ J}} = 70.0\text{ kJ/mol}
 \end{aligned}$$

$$\frac{\Delta E}{hc} = \frac{E(0,2,1,0)}{hc} - \frac{E(0,0,0,0)}{hc} = 5844\text{ cm}^{-1} - 2509\text{ cm}^{-1} = 3335\text{ cm}^{-1}$$

$$\begin{aligned}
 \Delta E &= hc(3335\text{ cm}^{-1}) = (6.63 \times 10^{-34}\text{ J} \cdot \text{s})(3.00 \times 10^{10}\text{ cm/s})(3335\text{ cm}^{-1}) \\
 &= 6.63 \times 10^{-20}\text{ J} \times 6.02 \times 10^{23}\text{ mol}^{-1} \times \frac{1\text{ kJ}}{10^3\text{ J}} = 40\text{ kJ/mol}
 \end{aligned}$$

7. $^{127}\text{I}_2 : \tilde{\nu} = 215\text{ cm}^{-1}$

$$(a) \quad \mu = \frac{m_I m_I}{m_I + m_I} = \frac{m_I}{2} = \frac{127\text{ amu}}{2} \cdot \frac{1.66 \times 10^{-27}\text{ kg}}{1\text{ amu}} = 1.05 \times 10^{-25}\text{ kg}$$

$$\tilde{\nu} = \frac{1}{2\pi c} \sqrt{\frac{k}{\mu}}$$

$$\begin{aligned}
 k &= [2\pi c \tilde{\nu}]^2 \mu = [2(3.14)(3.00 \times 10^{10}\text{ cm/s})(215\text{ cm}^{-1})]^2 (1.05 \times 10^{-25}\text{ kg}) \\
 &= 172\text{ kg/s}^2 = 172(\text{kg} \cdot \text{m/s}) / \text{m} = 172\text{ N/m}
 \end{aligned}$$

(b) Intensity Ratio: $T = 300\text{ }^\circ\text{C} = 573\text{ K}$

$$\frac{hc\tilde{\nu}}{kT} = \frac{(6.63 \times 10^{-34}\text{ J} \cdot \text{s})(3.00 \times 10^{10}\text{ cm/s})(215\text{ cm}^{-1})}{(1.38 \times 10^{-23}\text{ J/K})(573\text{ K})} = 0.54$$

$$\frac{I_{1 \rightarrow 2}}{I_{0 \rightarrow 1}} = \frac{N_1}{N_0} = \frac{e^{-E_1/kT}}{e^{-E_0/kT}} = \frac{e^{-(3/2)hc\tilde{\nu}/kT}}{e^{-(1/2)hc\tilde{\nu}/kT}} = e^{-hc\tilde{\nu}/kT} = e^{-0.54} = 0.58$$

8. The Spectroscopic Dissociation Energy (D_e) is the energy gap from the very bottom of the potential well to the separated atoms.

The Thermodynamic Dissociation Energy (D_0) is from the lowest vibrational energy level to the separated atoms.

The two Dissociation Energies are related by: $D_e = D_0 + E_0(\text{vib}) = D_0 + \frac{1}{2}hc\tilde{\nu}$

$$E_0(\text{vib}) = \frac{1}{2}hc\tilde{\nu} = \frac{1}{2}(6.63 \times 10^{-34} \text{ J} \cdot \text{s})(3.00 \times 10^{10} \text{ cm/s})(2990 \text{ cm}^{-1})$$

$$= 2.97 \times 10^{-20} \text{ J} \times 6.02 \times 10^{23} \text{ mol}^{-1} \times \frac{1 \text{ kJ}}{10^3 \text{ J}} = 17.9 \text{ kJ/mol}$$

$$D_e = D_0 + E_0(\text{vib}) = D_0 + \frac{1}{2}hc\tilde{\nu} = 428 \text{ kJ/mol} + 17.9 \text{ kJ/mol} \approx 446 \text{ kJ/mol}$$

9.
$$\Delta E = \int_{-\infty}^{\infty} \psi^{(0)*} H^{(1)} \psi^{(0)} dx = \int_0^{a/2} A \sin\left(\frac{\pi x}{a}\right) [B] A \sin\left(\frac{\pi x}{a}\right) dx + \int_{a/2}^a A \sin\left(\frac{\pi x}{a}\right) [2B] A \sin\left(\frac{\pi x}{a}\right) dx$$

$$\Delta E = A^2 B \int_0^{a/2} \sin^2(\alpha x) dx + 2A^2 B \int_{a/2}^a \sin^2(\alpha x) dx \quad \left(\alpha = \frac{\pi}{a} \right)$$

$$= A^2 B \left[\frac{1}{2}x - \frac{1}{4\alpha} \sin(2\alpha x) \right]_0^{a/2} + 2A^2 B \left[\frac{1}{2}x - \frac{1}{4\alpha} \sin(2\alpha x) \right]_{a/2}^a$$

$$= A^2 B \left[\left(\frac{a}{4} - \frac{1}{4\alpha} \sin(\alpha a) \right) - \left(0 - \frac{1}{4\alpha} 0 \right) \right] + 2A^2 B \left[\left(\frac{a}{2} - \frac{1}{4\alpha} \sin(2\alpha a) \right) - \left(\frac{a}{2} - \frac{1}{4\alpha} \sin(\alpha a) \right) \right]$$

Note: $\sin(\alpha a) = \sin\left(\frac{\pi a}{a}\right) = \sin(\pi) = 0$ and $\sin(2\alpha a) = \sin\left(2 \frac{\pi a}{a}\right) = \sin(2\pi) = 0$

$$\Delta E = A^2 B \left[\left(\frac{a}{4} - 0 \right) - \left(0 - \frac{1}{4\alpha} 0 \right) \right] + 2A^2 B \left[\left(\frac{a}{2} - 0 \right) - \left(\frac{a}{4} - 0 \right) \right]$$

$$= \frac{A^2 B a}{4} + \frac{A^2 B a}{2} = A^2 \frac{3Ba}{4} = \left(\sqrt{\frac{2}{a}} \right)^2 \frac{3Ba}{4} = \frac{2}{a} \cdot \frac{3Ba}{4} = \frac{3}{2} B$$

$$E = E^{(0)} + \Delta E = \frac{h^2}{8ma^2} + \frac{3}{2} B$$

10.
$$H = -\frac{\hbar^2}{2\mu} \frac{d^2}{dx^2} + \gamma x^4 = -\frac{\hbar^2}{2\mu} \frac{d^2}{dx^2} + \frac{1}{2} kx^2 + \left(\gamma x^4 - \frac{1}{2} kx^2 \right) = H^{(0)} + H^{(1)}$$

Thus the perturbation is:
$$H^{(1)} = \left(\gamma x^4 - \frac{1}{2} kx^2 \right)$$

$$\begin{aligned} \Delta E &= \int \psi_0^{(0)*} H^{(1)} \psi_0^{(h)} d\tau = \int_{-\infty}^{\infty} A e^{-\alpha x^2/2} \left(\gamma x^4 - \frac{1}{2} kx^2 \right) A e^{-\alpha x^2/2} dx = A^2 \int_{-\infty}^{\infty} e^{-\alpha x^2} \left(\gamma x^4 - \frac{1}{2} kx^2 \right) dx \\ &= A^2 \gamma \int_{-\infty}^{\infty} x^4 e^{-\alpha x^2} dx - \frac{k}{2} A^2 \int_{-\infty}^{\infty} x^2 e^{-\alpha x^2} dx = I_1 - I_2 \end{aligned}$$

$$I_1 = A^2 \gamma \int_{-\infty}^{\infty} x^4 e^{-\alpha x^2} dx = 2A^2 \gamma \int_0^{\infty} x^4 e^{-\alpha x^2} dx = 2A^2 \gamma \left[\frac{3}{8\alpha^2} \sqrt{\frac{\pi}{\alpha}} \right]$$

$$= 2\gamma \left(\frac{\alpha}{\pi} \right)^{1/2} \frac{3}{8\alpha^2} \left(\frac{\pi}{\alpha} \right)^{1/2} = \frac{3\gamma}{4\alpha^2} = \frac{3\gamma}{4} \frac{\hbar^2}{k\mu}$$

$$I_2 = \frac{k}{2} A^2 \int_{-\infty}^{\infty} x^2 e^{-\alpha x^2} dx = 2 \frac{k}{2} A^2 \int_0^{\infty} x^2 e^{-\alpha x^2} dx = A^2 k \left[\frac{1}{4\alpha} \sqrt{\frac{\pi}{\alpha}} \right]$$

$$= k \left(\frac{\alpha}{\pi} \right)^{1/2} \frac{1}{4\alpha} \left(\frac{\pi}{\alpha} \right)^{1/2} = \frac{k}{4\alpha} = \frac{k}{4} \frac{\hbar}{\sqrt{k\mu}} = \frac{1}{4} \hbar \sqrt{\frac{k}{\mu}} \left(= \frac{1}{4} \hbar \omega \right)$$

$$\Delta E = I_1 - I_2 = \frac{3\gamma}{4} \frac{\hbar^2}{k\mu} - \frac{1}{4} \hbar \omega$$

$$E = E^{(0)} + \Delta E = \frac{1}{2} \hbar \omega + \frac{3\gamma}{4} \frac{\hbar^2}{k\mu} - \frac{1}{4} \hbar \omega = \frac{1}{4} \hbar \omega + \frac{3\gamma}{4} \frac{\hbar}{k\mu}$$

Note: The simplification I've shown (putting I_2 in terms of $\hbar\omega$) isn't really necessary.

11. Experimental HCl Frequencies:

Fundamental: $\tilde{\nu}_{0 \rightarrow 1} = 2885 \text{ cm}^{-1}$

First Overtone: $\tilde{\nu}_{0 \rightarrow 2} = 5664 \text{ cm}^{-1}$

$$\frac{E_n}{hc} = \left(n + \frac{1}{2}\right) \tilde{\nu} - \left(n + \frac{1}{2}\right)^2 x_e \tilde{\nu}$$

$$(1) \tilde{\nu}_{0 \rightarrow 1} = \frac{E_1}{hc} - \frac{E_0}{hc} = 2885 \text{ cm}^{-1} = \left[\frac{3}{2} \tilde{\nu} - \frac{9}{4} x_e \tilde{\nu}\right] - \left[\frac{1}{2} \tilde{\nu} - \frac{1}{4} x_e \tilde{\nu}\right] = \tilde{\nu} - 2x_e \tilde{\nu}$$

$$(2) \tilde{\nu}_{0 \rightarrow 2} = \frac{E_2}{hc} - \frac{E_0}{hc} = 5664 \text{ cm}^{-1} = \left[\frac{5}{2} \tilde{\nu} - \frac{25}{4} x_e \tilde{\nu}\right] - \left[\frac{1}{2} \tilde{\nu} - \frac{1}{4} x_e \tilde{\nu}\right] = 2\tilde{\nu} - 6x_e \tilde{\nu}$$

Eliminate $x_e \tilde{\nu}$: $3 \cdot (1) - (2)$

$$3(2885) - 1(5664) = \tilde{\nu} = 2991 \text{ cm}^{-1}$$

Use (1)

$$x_e \tilde{\nu} = \frac{\tilde{\nu} - 2885}{2} = \frac{2991 - 2885}{2} = 53 \text{ cm}^{-1}$$

$$x_e = \frac{x_e \tilde{\nu}}{\tilde{\nu}} = \frac{53 \text{ cm}^{-1}}{2991 \text{ cm}^{-1}} = 0.018$$

12. Vibrational Contributions to Thermodynamic Properties

Preliminary Calculations: Partition Function and Derivative

$$T = 800^\circ \text{C} = 1073 \text{ K}$$

$$q^{vib} = \frac{e^{-\frac{\Theta_v}{2T}}}{1 - e^{-\frac{\Theta_v}{T}}}$$

$$\Theta_v = \frac{hc\tilde{\nu}}{k} = \frac{(6.63 \times 10^{-34} \text{ J} \cdot \text{s})(3.00 \times 10^{10} \text{ cm/s})(270 \text{ cm}^{-1})}{1.38 \times 10^{-23} \text{ J/K}} = 389 \text{ K}$$

$$\frac{\Theta_v}{T} = \frac{389 \text{ K}}{1073 \text{ K}} = 0.363$$

$$\ln Q^{vib} = \ln (q^{vib})^N = N \ln(q^{vib}) = N \ln \left(\frac{e^{-\frac{\Theta_v}{2T}}}{1 - e^{-\frac{\Theta_v}{T}}} \right) = -\frac{N\Theta_v}{2T} - N \ln \left(1 - e^{-\frac{\Theta_v}{T}} \right)$$

$$\begin{aligned}\left(\frac{\partial \ln Q^{vib}}{\partial T}\right)_{V,n} &= \frac{d \ln Q^{vib}}{dT} = +\frac{N\Theta_v}{2T^2} - N \frac{1}{1-e^{-\frac{\Theta_v}{T}}} \left(-1 \cdot e^{-\frac{\Theta_v}{T}}\right) \left(\frac{\Theta_v}{T^2}\right) \\ &= N \left[\frac{\Theta_v}{2T^2} + \frac{\Theta_v}{T^2} \cdot \frac{e^{-\frac{\Theta_v}{T}}}{1-e^{-\frac{\Theta_v}{T}}} \right]\end{aligned}$$

Enthalpy: H^{vib}

$$H^{vib} = kT^2 \left(\frac{\partial \ln Q^{vib}}{\partial T}\right)_{V,N} + kT \left(\frac{\partial \ln Q^{vib}}{\partial \ln V}\right)_{T,N} = kT^2 \left(\frac{\partial \ln Q^{vib}}{\partial T}\right)_{V,N} + 0 = U^{vib}$$

$$\begin{aligned}H^{vib} &= kT^2 \left(\frac{\partial \ln Q^{vib}}{\partial T}\right)_{V,n} = kT^2 N \left[\frac{\Theta_v}{2T^2} + \frac{\Theta_v}{T^2} \cdot \frac{e^{-\frac{\Theta_v}{T}}}{1-e^{-\frac{\Theta_v}{T}}} \right] = kT^2 (nN_A) \left[\frac{\Theta_v}{2T^2} + \frac{\Theta_v}{T^2} \cdot \frac{e^{-\frac{\Theta_v}{T}}}{1-e^{-\frac{\Theta_v}{T}}} \right] \\ &= nR \left[\frac{\Theta_v}{2} + \Theta_v \cdot \frac{e^{-\frac{\Theta_v}{T}}}{1-e^{-\frac{\Theta_v}{T}}} \right] = nR \frac{\Theta_v}{2} + nR\Theta_v \cdot \frac{e^{-\frac{\Theta_v}{T}}}{1-e^{-\frac{\Theta_v}{T}}} = H_{ZPE}^{vib} + H_{therm}^{vib}\end{aligned}$$

Alternate form for H^{vib} (to simplify taking next derivative)

$$H^{vib} = nR \frac{\Theta_v}{2} + nR\Theta_v \cdot \frac{e^{-\frac{\Theta_v}{T}}}{1-e^{-\frac{\Theta_v}{T}}} \cdot \frac{e^{+\frac{\Theta_v}{T}}}{e^{+\frac{\Theta_v}{T}}} = nR \frac{\Theta_v}{2} + nR\Theta_v \cdot \frac{1}{e^{+\frac{\Theta_v}{T}} - 1} = H_{ZPE}^{vib} + H_{therm}^{vib}$$

$$\begin{aligned}H^{vib} &= (2 \text{ mol})(8.31 \text{ J / mol}) \frac{389 \text{ K}}{2} + (2 \text{ mol})(8.31 \text{ J / mol} \cdot \text{K})(389 \text{ K}) \cdot \frac{1}{e^{0.363} - 1} \\ &= 3230 \text{ J} + 14770 \text{ J} = 18000 \text{ J} = 18.0 \text{ kJ}\end{aligned}$$

Note that the ZPE contribution to H^{vib} (and to U^{vib}) is independent of temperature, the thermal contribution varies with temperature.

For example, at $T = 2000^\circ\text{C} = 2273 \text{ K}$, the thermal contribution to $H^{vib} = 34,600 \text{ J}$

Constant Pressure Heat Capacity, C_p^{vib}

$$C_p^{vib} = \left(\frac{\partial H}{\partial T}\right)_{P,n} = \frac{dH}{dT} (= C_V^{vib})$$

$$\begin{aligned}
C_p^{vib} &= \frac{d}{dT} \left[nR \frac{\Theta_v}{2} + nR \Theta_v \cdot \frac{1}{e^{+\frac{\Theta_v}{T}} - 1} \right] = 0 + nR \Theta_v \frac{d}{dT} \left[e^{+\frac{\Theta_v}{T}} - 1 \right]^{-1} \\
&= nR \Theta_v (-1) \left[e^{+\frac{\Theta_v}{T}} - 1 \right]^{-2} \frac{d}{dT} \left[e^{+\frac{\Theta_v}{T}} - 1 \right] = nR \Theta_v (-1) \left[e^{+\frac{\Theta_v}{T}} - 1 \right]^{-2} e^{+\frac{\Theta_v}{T}} \left(-\frac{\Theta_v}{T^2} \right) \\
&= nR \left(\frac{\Theta_v}{T} \right)^2 \frac{e^{+\frac{\Theta_v}{T}}}{\left[e^{+\frac{\Theta_v}{T}} - 1 \right]^2} \\
&= (2 \text{ mol})(8.31 \text{ J} / \text{mol} \cdot \text{K})(0.363)^2 \cdot \frac{e^{0.363}}{\left[e^{0.363} - 1 \right]^2} = 16.4 \text{ J} / \text{K}
\end{aligned}$$

Note: Equipartition of Energy predicts that the contribution should be

$nR = 2(8.31) = 16.6 \text{ J/K}$. We are fairly close to the limit $S^{vib} = k \ln(Q^{vib}) + \frac{U^{vib}}{T}$ because of (a) the low frequency and (b) the high temperature.

Entropy: S^{vib}

Note: $U^{vib} = H^{vib} = 18000 \text{ J} = 18.0 \text{ kJ}$

$$\begin{aligned}
k \ln Q^{vib} &= -\frac{kN\Theta_v}{2T} - kN \ln \left(1 - e^{-\frac{\Theta_v}{T}} \right) = -knN_A \left(\frac{\Theta_v}{T} \right) - knN_A \ln \left(1 - e^{-\frac{\Theta_v}{T}} \right) \\
&= -nR \left(\frac{\Theta_v}{T} \right) - nR \ln \left(1 - e^{-\frac{\Theta_v}{T}} \right) \\
&= -(2 \text{ mol})(8.31 \text{ J} / \text{mol} \cdot \text{K})(0.363) - (2 \text{ mol})(8.31 \text{ J} / \text{mol} \cdot \text{K}) \ln(1 - e^{-0.363}) \\
&= +13.74 \text{ J} / \text{K}
\end{aligned}$$

$$S^{vib} = k \ln Q^{vib} + \frac{U^{vib}}{T} = 13.74 \text{ J} / \text{K} + \frac{18000 \text{ J}}{1073 \text{ K}} = 13.74 + 16.77 = 30.5 \text{ J} / \text{K}$$

Gibbs Energy: G^{vib}

$$G^{vib} = -kT \ln Q^{vib} + kT \left(\frac{\partial \ln Q^{vib}}{\partial \ln V} \right)_{T,N} = -kT \ln Q^{vib} + 0 = -kT \ln Q^{vib} = A^{vib}$$

$$G^{vib} = -T(k \ln Q) = -(1073 \text{ K})(+13.74 \text{ J} / \text{K}) = -14740 \text{ J} \approx -14.7 \text{ kJ}$$

13. $\Gamma(v_1) = a_2 \quad \Gamma(v_2) = b_1 \quad \Gamma(v_3) = b_2$

(a) Activity of Fundamental modes

We will use the "shortcut" shown in the lecture (and in many other courses)

IR Activity

$v_1(a_2)$ is **NOT** IR active because none of x, y, z belong to the a_2 representation

$v_2(b_1)$ **IS** IR active because x belongs to the b_1 representation

$v_3(b_2)$ **IS** IR active because y belongs to the b_2 representation

Raman Activity

All three vibrations **ARE** Raman active because every representation has one or more of quadratic functions (x^2 , y^2 , z^2 , xy , xz , yz).

(b) Activity of Combination modes

(b1) $v_1 + v_3 \quad |0,0,0\rangle \rightarrow |1,0,1\rangle$

$$\psi_{fin} = |1,0,1\rangle \quad \Gamma(\psi_{fin}) = a_2 \times a_1 \times b_2 = B_1$$

$$\psi_{init} = |0,0,0\rangle \quad \Gamma(\psi_{init}) = a_1 \times a_1 \times a_1 = A_1$$

IR Activity

$$M_{0i}^x = e \langle \psi_{fin} | x | \psi_{init} \rangle \quad \Gamma = B_1 \times B_1 \times A_1 = A_1$$

$$M_{0i}^y = e \langle \psi_{fin} | y | \psi_{init} \rangle \quad \Gamma = B_1 \times B_2 \times A_1 = A_2 \neq A_1$$

$$M_{0i}^z = e \langle \psi_{fin} | z | \psi_{init} \rangle \quad \Gamma = B_1 \times A_1 \times A_1 = B_1 \neq A_1$$

This mode **IS** IR active because M_{0i}^x transforms as A_1

Raman Activity

$$\langle \psi_{fin} | x^2 | \psi_{init} \rangle \quad \Gamma = B_1 \times A_1 \times A_1 = B_1 \neq A_1 \quad \text{Same for } y^2 \text{ and } z^2 \text{ integrals}$$

$$\langle \psi_{fin} | xy | \psi_{init} \rangle \quad \Gamma = B_1 \times A_2 \times A_1 = B_2 \neq A_1$$

$$\langle \psi_{fin} | xz | \psi_{init} \rangle \quad \Gamma = B_1 \times B_1 \times A_1 = A_1$$

$$\langle \psi_{fin} | yz | \psi_{init} \rangle \quad \Gamma = B_1 \times B_2 \times A_1 = A_2 \neq A_1$$

This mode **IS** Raman Active because the xz integral transforms as A_1

(b2) $v_2 - v_3 \quad |0,0,1\rangle \rightarrow |0,1,0\rangle$

$$\psi_{fin} = |0,1,0\rangle \quad \Gamma(\psi_{fin}) = a_1 \times b_1 \times a_1 = B_1$$

$$\psi_{init} = |0,0,1\rangle \quad \Gamma(\psi_{init}) = a_1 \times a_1 \times b_2 = B_2$$

IR Activity

$$M_{0i}^x = e \langle \psi_{fin} | x | \psi_{init} \rangle \quad \Gamma = B_1 \times B_1 \times B_2 = B_2 \neq A_1$$

$$M_{0i}^y = e \langle \psi_{fin} | y | \psi_{init} \rangle \quad \Gamma = B_1 \times B_2 \times B_2 = B_1 \neq A_1$$

$$M_{0i}^z = e \langle \psi_{fin} | z | \psi_{init} \rangle \quad \Gamma = B_1 \times A_1 \times B_2 = A_2 \neq A_1$$

This mode is **NOT** IR active because none of the three transition moments transform as A_1

Raman Activity

$$\langle \psi_{fin} | x^2 | \psi_{init} \rangle \quad \Gamma = B_1 \times A_1 \times B_2 = A_2 \neq A_1 \quad \text{Same for } y^2 \text{ and } z^2 \text{ integrals}$$

$$\langle \psi_{fin} | xy | \psi_{init} \rangle \quad \Gamma = B_1 \times A_2 \times B_2 = A_1$$

$$\langle \psi_{fin} | xz | \psi_{init} \rangle \quad \Gamma = B_1 \times B_1 \times B_2 = B_2 \neq A_1$$

$$\langle \psi_{fin} | yz | \psi_{init} \rangle \quad \Gamma = B_1 \times B_2 \times B_2 = B_1 \neq A_1$$

This mode **IS** Raman Active because the xy integral transforms as A_1