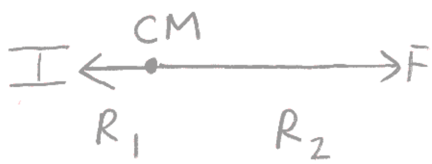
Chem 312
PS 5
p. 1

1. (4 pts total)



$$-R_1 + R_2 = 1.908\,\text{Å}$$

$$R_2 = \frac{m_I}{m_I + m_F} R = \frac{126.9045\,\cancel{u}}{(126.9045 + 18.9984)\,\cancel{u}} (1.908\,\text{Å})$$ 1 pt

$$R_2 = 1.660\,\text{Å}$$

$\boxed{\text{i.e. the CM is } 1.660\,\text{Å away from the F atom}}$ 1 pt

$$R_1 = R_2 - 1.908\,\text{Å} = (1.660 - 1.908)\,\text{Å} = -0.248\,\text{Å}$$ 1 pt

$\boxed{\text{i.e. the CM is } 0.248\,\text{Å away from the I atom}}$ 1 pt

2. Atkins Exer. 9.7b (8 pts total)

For a particle in a cube,

$$E = \frac{(n_x^2 + n_y^2 + n_z^2)h^2}{8mL^2}$$

Here, we define $n^2 \equiv n_x^2 + n_y^2 + n_z^2$

and note $E = \frac{3}{2}kT$

so, $\frac{3}{\cancel{2}_{\,1}}kT = \frac{n^2h^2}{\cancel{8}_{\,4}mL^2} \Rightarrow n = \sqrt{\frac{12kTmL^2}{h^2}} = \sqrt{12kTm}\,\frac{L}{h}$

2 pts

and $L^3 = 1.00\,m^3 \Rightarrow L = 1.00\,m$ and $m = 2m_N = 2(14.01u)$

So $n = \sqrt{12\left(1.381\times10^{-23}\frac{\cancel{J}}{\cancel{K}}\right)(300.\,\cancel{K})(2)(14.01\cancel{u})\left(\frac{1.661\times10^{-27}\cancel{kg}}{\cancel{u}}\right)\left(\frac{\cancel{kg}\,\cancel{m^2}\,\cancel{s^{-2}}}{\cancel{J}}\right)}$ 1 pt

$\times\left(\frac{1.00\,\cancel{m}}{6.626\times10^{-34}\,\cancel{J}\,\cancel{s}}\right)\left(\frac{\cancel{J}}{\cancel{kg}\,\cancel{m^2}\,\cancel{s^{-2}}}\right)$

$\boxed{n = 7.26\times10^{10}}$ 1 pt

$$\Delta E = E(n+1) - E(n) = [(n+1)^2 - n^2]\frac{h^2}{8mL^2}$$

$$= [n^2 + 2n + 1 - n^2]\frac{h^2}{8mL^2}$$

$$\Delta E = (2n+1)\frac{h^2}{8mL^2}$$

2 pts

$$\Delta E = \left[2(7.26\times10^{10})+1\right]\frac{(6.626\times10^{-34})^2 J^2 \cancel{s^2}}{8(2)(14.01\cancel{u})(1.00)^2 \cancel{m^2}}\left(\frac{\cancel{u}}{1.661\times10^{-27}\cancel{kg}}\right)$$ 1pt

$$\times\left(\frac{\cancel{kg}\,\cancel{m^2}\,\cancel{s^{-2}}}{\cancel{J}}\right)$$

$$\boxed{\Delta E = 1.71\times10^{-31}\ J}$$ 1pt

Chem312
PS5
p.4

3. Atkins Exer. 13.5b (5 pts total)

For a linear molecule, rotational $E = J(J+1)\frac{\hbar^2}{2I}$

so $\Delta E = E(J') - E(J'') = [J'(J'+1) - J''(J''+1)]\frac{\hbar^2}{2I} = h\nu$

J': final value; J'': initial value; ν: freq of photon absorbed in transition

and (for a diatomic molecule) $I = \mu R^2 = \left(\frac{m_C m_O}{m_C + m_O}\right) R^2$

$\therefore \nu = [J'(J'+1) - J''(J''+1)]\frac{\hbar^2}{2h}\left(\frac{m_C + m_O}{m_C m_O}\right)\left(\frac{1}{R^2}\right)$

2 pts for some kind of justification

2 pts

$$= [3(4) - 2(3)]\frac{(1.05457\times10^{-34})^2 \cancel{J^2}\cancel{s^2}}{2(6.62608\times10^{-34})\cancel{J}\cdot\cancel{s}}\left[\frac{(\overset{\text{exact}}{12} + 15.9949)\cancel{u}}{(12)(15.9949)\cancel{u^2}}\right]$$

$$\times\left(\frac{\cancel{u}}{1.66054\times10^{-27}\cancel{kg}}\right)\left[\frac{1}{(112.81)^2\,\cancel{pm^2}}\right]\left(\frac{\cancel{pm^2}}{10^{-24}\cancel{m^2}}\right)\left(\frac{\cancel{kg}\,\cancel{m^2}\,\cancel{s^{-2}}}{\cancel{J}}\right)\left(\frac{GHz}{10^9\cancel{s^{-1}}}\right)$$

$\boxed{\nu = 347.53\ GHz}$ 1 pt

4. Atkins Exer. 13.7b (6 pts total)

We showed in class that the spacing btwn adjacent lines in a pure rotational spectrum is $\Delta\Delta F = 2B$

and $B = \frac{\hbar}{4\pi c I}$ (for either a spherical or linear rotor)

$$\Rightarrow \Delta\Delta F = \cancel{2}\left(\frac{\hbar}{\cancel{4}_2 \pi c I}\right) \Rightarrow I = \frac{\hbar}{2\pi c (\Delta\Delta F)}$$ 1pt

$$I = \frac{1.0546 \times 10^{-34}\ \cancel{J}\cdot\cancel{s}}{2\pi(2.9979\times10^{10}\ \cancel{cm}\ \cancel{s^{-1}})(1.033\ \cancel{cm^{-1}})}\left(\frac{kg\ m^2\ \cancel{s^{-2}}}{\cancel{J}}\right)$$ 1pt

$$\boxed{I = 5.419_9 \times 10^{-46}\ kg\,m^2}$$ 1pt

and for a linear rotor, $I = \mu R^2 = \frac{m_{Cl} m_F}{m_{Cl} + m_F} R^2$

$$\Rightarrow R = \sqrt{I\left(\frac{m_{Cl} + m_F}{m_{Cl}\, m_F}\right)}$$ 1pt

$$= \sqrt{(5.419_9 \times 10^{-46}\ \cancel{kg}\, \cancel{m^2})\left[\frac{(34.9688 + 18.9984)\cancel{u}}{(34.9688)(18.9984)\cancel{u^2}}\right]\left(\frac{\cancel{u}}{1.6605\times10^{-27}\ \cancel{kg}}\right)} \times \left(\frac{Å}{10^{-10}\ \cancel{m}}\right)$$ 1pt

$$\boxed{R = 1.628\ Å}$$ 1pt

5. Atkins Exer 13.19b (6 pts total)

In general, $G(v) = (v+\frac{1}{2})\tilde{\nu} - (v+\frac{1}{2})^2 x_e\tilde{\nu} + (v+\frac{1}{2})^3 y_e\tilde{\nu}$

Here, we are told to assume $y_e = 0$

Write equations for the three transitions:

$$\Delta G(1\leftarrow 0) = G(1) - G(0) = \frac{3}{2}\tilde{\nu} - \frac{9}{4}x_e\tilde{\nu} - \left[\frac{1}{2}\tilde{\nu} - \frac{1}{4}x_e\tilde{\nu}\right]$$

Only 2 equations required for full credit; 1 pt per eqn

$$\boxed{2345.15\ \text{cm}^{-1} = \tilde{\nu} - 2x_e\tilde{\nu}} \quad [1]$$

$$\Delta G(2\leftarrow 0) = G(2) - G(0) = \frac{5}{2}\tilde{\nu} - \frac{25}{4}x_e\tilde{\nu} - \left(\frac{1}{2}\tilde{\nu} - \frac{1}{4}x_e\tilde{\nu}\right)$$

$$\boxed{4661.40\ \text{cm}^{-1} = 2\tilde{\nu} - 6x_e\tilde{\nu}} \quad [2]$$

$$\Delta G(3\leftarrow 0) = G(3) - G(0) = \frac{7}{2}\tilde{\nu} - \frac{49}{4}x_e\tilde{\nu} - \left[\frac{1}{2}\tilde{\nu} - \frac{1}{4}x_e\tilde{\nu}\right]$$

$$\boxed{6983.73\ \text{cm}^{-1} = 3\tilde{\nu} - 12x_e\tilde{\nu}} \quad [3]$$

Use [1] and [2] to solve for $\tilde{\nu}$ and x_e:

$-3*[1]$: $-7035.45\ \text{cm}^{-1} = -3\tilde{\nu} + 6x_e\tilde{\nu}$

$[2]$: $4661.40\ \text{cm}^{-1} = 2\tilde{\nu} - 6x_e\tilde{\nu}$ 1 pt

$-2374.05\ \text{cm}^{-1} = -\tilde{\nu} \Rightarrow \boxed{\tilde{\nu} = 2374.05\ \text{cm}^{-1}}$ 1 pt

and $[1] \Rightarrow 2x_e\tilde{\nu} = \tilde{\nu} - 2345.15\ \text{cm}^{-1}$

$$x_e = \frac{1}{2} - \frac{2345.15\ \text{cm}^{-1}}{2\tilde{\nu}} = \frac{1}{2} - \frac{2345.15\ \text{cm}^{-1}}{2(2374.05\ \text{cm}^{-1})}$$ 1 pt

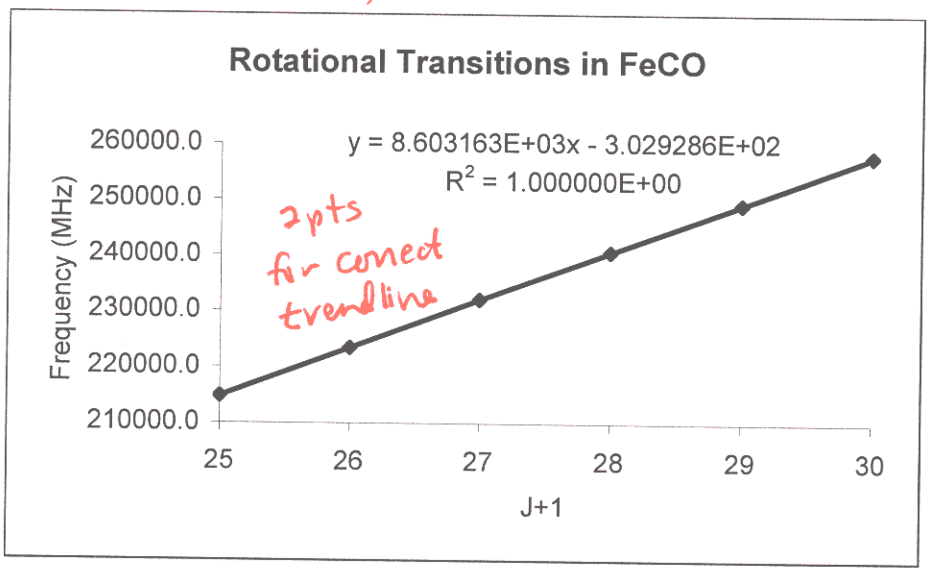
$= \frac{1}{2} - 0.493913$ (6th decimal place is the last sig fig)

1 pt $\boxed{x_e = 0.006087}$

Chem 312
PS 5
p. 7

6. Atkins and de Paula Problem 13.11 (8 pts total)

J+1	ΔF (MHz)
25	214777.7
26	223379.0
27	231981.2
28	240584.4
29	249188.5
30	257793.5



2 pts for spreadsheet and plot

$F = BJ(J+1)$

$\Delta F = F(J+1) - F(J) = B[(J+1)(J+2) - J(J+1)]$

$\Delta F = B[\cancel{J^2} + 3J + 2 - \cancel{J^2} - J] = B[2J+2] = 2B(J+1)$

so a plot of ΔF vs. $(J+1)$ will have a slope of $2B$

2 pts

slope = $2B = 8603.163$ MHz

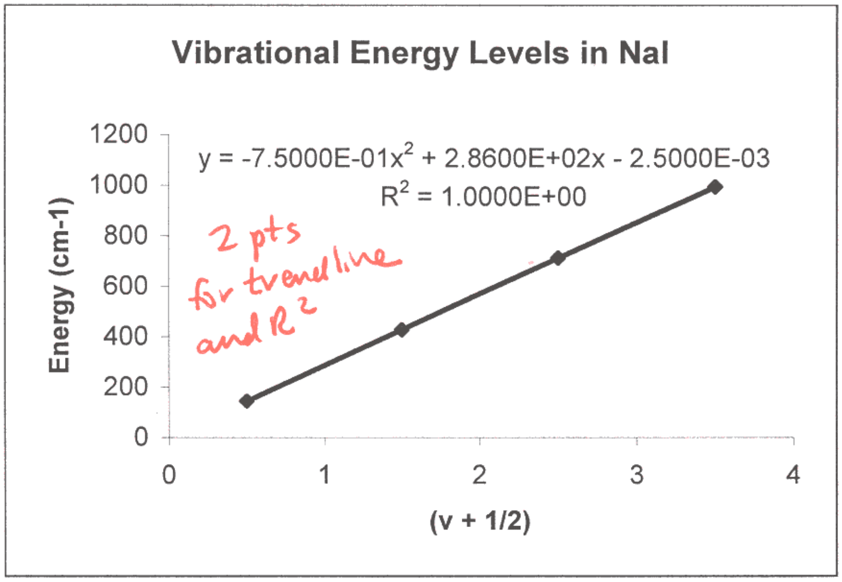
so $B = \frac{1}{2}(8603.163\,\cancel{\text{MHz}})\left(\frac{10^6\,\cancel{s^{-1}}}{\cancel{\text{MHz}}}\right)\left(\frac{\cancel{s}}{2.9979246\times10^{10}\,\text{cm}}\right)$ 1 pt

$\boxed{B = 0.1434853\,\text{cm}^{-1}}$ 1 pt

Chem 312
PS5
p. 8

7. Atkins and de Paula Problem 13.12 (12 pts total)

v+1/2	G(v) (cm-1)
0.5	142.81
1.5	427.31
2.5	710.31
3.5	991.81



2pts for spreadsheet and plot

The trendline (and the great R^2 value) indicate that the vibrational E levels are well fit by the expression

$G(v) = (v+\frac{1}{2})\tilde{\nu} - (v+\frac{1}{2})^2 x\tilde{\nu}$, where $\tilde{\nu} = 286.00\ \mathrm{cm}^{-1}$

and $x\tilde{\nu} = +0.75000\ \mathrm{cm}^{-1}$

$$\tilde{\nu} = \frac{1}{2\pi c}\sqrt{\frac{k}{\mu}} \Rightarrow k = 4\pi^2 c^2 \tilde{\nu}^2 \mu; \quad \mu = \frac{m_{Na} m_I}{m_{Na} + m_I}$$ 1pt

so $k = 4\pi^2 (2.99793\times10^{10})^2 \cancel{\mathrm{cm}^2}\, \mathrm{s}^{-2} (286.00)^2 \cancel{\mathrm{cm}^{-2}} \left[\frac{(22.9898)(126.9045)\cancel{u^2}}{(22.9898 + 126.9045)\cancel{u}}\right]$ 1pt

$* \left(\frac{1.66054\times10^{-27}\,\mathrm{kg}}{\cancel{u}}\right)$

↑ CRC ↑ p. 991 Atkins

$\boxed{k = 93.802\ \mathrm{kg\,s^{-2}}}$ 1pt

By definition, the zero-point E (ZPE) $= G(0) = \boxed{142.81\ \mathrm{cm}^{-1}}$ 1pt

For a Morse oscillator, $x_e = \frac{\tilde{\nu}}{4D_e} \Rightarrow D_e = \frac{\tilde{\nu}}{4x_e} = \frac{\tilde{\nu}^2}{4x_e\tilde{\nu}}$ 1pt

so $D_e = \frac{(286.00\ cm^{-1})^2}{4(0.75000\ cm^{-1})} = 27265._{33}\ \cancel{cm^{-1}}\left(\frac{eV}{8065.5\ \cancel{cm^{-1}}}\right)$ 1pt

$= \boxed{3.3805\ eV}$ 1pt

and $D_0 = D_e - ZPE = (27265._{33} - 142.81)\ cm^{-1}$

$= 27122._{52}\ \cancel{cm^{-1}}\left(\frac{eV}{8065.5\ \cancel{cm^{-1}}}\right)$ 1pt

$= \boxed{3.3628\ eV}$ (no pts)

7. Atkins Prob 13.24 [linear rotor only] (10 pts total)

Boltzmann distribution: $N_J = (\text{constant})\, g_J\, e^{-E_J/kT}$

For a linear rotor, $g_J = 2J+1$ and $E_J = hcBJ(J+1)$

So $N_J = (\text{constant})(2J+1)e^{-hcBJ(J+1)/kT}$

$$N_J = \text{constant}\,(2J+1)\exp\left[-\frac{hcB}{kT}J^2 - \frac{hcB}{kT}J\right]$$ 1 pt

Find the value of J that maximizes N_J, i.e. solve

$$\frac{dN_J}{dJ} = 0$$

$$\frac{dN_J}{dJ} = \text{constant}\left[(2J+1)\left(-\frac{2hcB}{kT}J - \frac{hcB}{kT}\right) + 2\right] \times \exp\left[-\frac{hcB}{kT}J^2 - \frac{hcB}{kT}J\right] = 0$$ 2 pts

$$\Rightarrow (2J+1)\left(-\frac{2hcB}{kT}J - \frac{hcB}{kT}\right) + 2 = 0$$ 1 pt

$$-\frac{4hcB}{kT}J^2 - \frac{2hcB}{kT}J - \frac{2hcB}{kT}J - \frac{hcB}{kT} + 2 = 0$$

$$-\frac{kT}{4hcB}\left[-\frac{4hcB}{kT}J^2 - \frac{4hcB}{kT}J - \frac{hcB}{kT} + 2 = 0\right]$$

$$J^2 + J + \left(\frac{1}{4} - \frac{kT}{2hcB}\right) = 0$$ 1 pt

Chem 312
PS 5
p. 11

Using quadratic formula

$$J = \frac{-1 \pm \sqrt{1^2 - 4(1)\left(\frac{1}{4} - \frac{kT}{2hcB}\right)}}{2(1)}$$

$$= -\frac{1}{2} \pm \frac{1}{2}\sqrt{1 - 1 + \frac{2kT}{hcB}}$$

$$J = -\frac{1}{2} \pm \sqrt{\frac{kT}{2hcB}}$$

2 pts

Since J must be ≥ 0, we reject the negative root.

$$\therefore \boxed{J_{max} = \sqrt{\frac{kT}{2hcB}} - \frac{1}{2}}$$

1 pt

For ICl at 25°C = 298.15 K

1 pt

$$J_{max} = \left[\frac{(1.381 \times 10^{-23} \cancel{J}\,\cancel{K^{-1}})(298.15\,\cancel{K})}{2(6.626 \times 10^{-34} \cancel{J \cdot s})(2.998 \times 10^{10} \cancel{cm}\,\cancel{s^{-1}})(0.1142\,\cancel{cm^{-1}})}\right]^{1/2} - \frac{1}{2}$$

1 pt

$$J_{max} = 29.6 \approx \boxed{30}$$