

*Your lowest Chem 331 assignment mark will not be used to calculate your average assignment mark. So if you've handed in all the mandatory assignments (#1,2,3,4,5) and are happy with the results, a zero mark for this assignment will not affect your course mark.

- Q1.** High-resolution microwave spectroscopy is used for the most precise measurements of chemical bond lengths. For example, spectroscopic data give 10.5912 cm^{-1} for the rotational constant

$$\tilde{B} = \frac{h}{8\pi^2 c I}$$

- [3] of H^{35}Cl molecules. Calculate a precise bond length of the molecule. *Hint: $I = \mu r^2$ Data:*

$$h = 6.626070 \times 10^{-34} \text{ J s} \quad m_{\text{H}} = 1.673534 \times 10^{-27} \text{ kg} \quad m_{^{35}\text{Cl}} = 5.806719 \times 10^{-26} \text{ kg}$$

$$c = 2.997924 \times 10^{10} \text{ cm s}^{-1}$$

- Q2.** Calculate $|\vec{L}|$ and L_z for a H^{35}Cl molecule with $l = 3$ and $m = -2$. [2]

- Q3.** How rapidly are the nuclei moving in a rotating molecule? Calculate the speed of the H nucleus and the speed of the ^{35}Cl nucleus in a rotating H^{35}Cl molecule with $l = 1$ and $m = 0$. [4]

- Q4.** The energy levels of a diatomic molecule rotating in 3 dimensions are

$$E_l = l(l+1)B \quad l = 0, 1, 2, 3, \dots$$

$$B \text{ is the rotational constant} \quad B = \frac{h^2}{8\pi^2 I} = hc\tilde{B}$$

- a) Calculate the energies of the first five 3-dimensional rotational levels for H^{35}Cl ($l = 0, 1, 2, 3, 4$). Use the data given in Question 1.
- [5] b) Calculate the absorption frequencies for transitions between these levels assuming the changes in quantum number l are unrestricted.
- c) To illustrate how selection rules can simplify spectra, recalculate the absorption frequencies in **b** using the rigid rotor selection rule $\Delta l = 1$.

Q5. The transition dipole moment for a rigid rotor is proportional to

$$\mu \int_{-1}^1 P_{l'|m'}(u) \left[\frac{l-|m|+1}{2l+1} P_{l+1|m|}(u) + \frac{l+|m|}{2l+1} P_{l-1|m|}(u) \right] du$$

[3] μ is the electric dipole moment of the rotor and $P_{lm}(u)$ is the Legendre polynomial for quantum numbers l and m . Use this result to derive three selection rules for microwave spectroscopy. *Hint:* the Legendre polynomials are orthogonal.

Q6. The following frequencies are measured in the microwave absorption spectrum of $^{12}\text{C}^{16}\text{O}$:

[2]	3.84540 cm^{-1}	($l=0$ to $l=1$)
	7.69060 cm^{-1}	($l=1$ to $l=2$)
	11.53550 cm^{-1}	($l=2$ to $l=3$)
	15.37990 cm^{-1}	($l=3$ to $l=4$)
	19.22380 cm^{-1}	($l=4$ to $l=5$)
	23.06685 cm^{-1}	($l=5$ to $l=6$)
	<i>etc.</i>	

Use these data to show the $^{12}\text{C}^{16}\text{O}$ bond length increases very slightly as the rotational energy increases.

Q7. The selection rule $\Delta m = 0$ has no effect on the frequencies observed for rotational transitions.

[1] Why?

(Q1) High-resolution spectroscopy for H^{35}Cl gives

$$\tilde{B} = 10.5912 \text{ cm}^{-1} = \frac{h}{8\pi^2 I c} = \frac{h}{8\pi^2 \mu r^2 c} \quad \left(\begin{array}{l} \text{rotational} \\ B \\ \text{constant} \end{array} \right)$$

$$\text{reduced mass } \mu = \frac{m_{\text{H}} m_{^{35}\text{Cl}}}{m_{\text{H}} + m_{^{35}\text{Cl}}} = \frac{(1.673534) 58.06719}{1.673534 + 58.06719} \times 10^{-27} \text{ kg}$$

$$\mu = 1.6266528 \times 10^{-27} \text{ kg}$$

H^{35}Cl
bond length

$$r = \sqrt{\frac{h}{8\pi^2 c \mu \tilde{B}}}$$

$$r = \sqrt{\frac{6.626070 \times 10^{-34} \text{ J s}}{8\pi^2 (2.997924 \times 10^{10} \text{ cm s}^{-1}) (1.6266528 \times 10^{-27} \text{ kg}) 10.5912 \text{ cm}^{-1}}}$$

$$= \sqrt{1.624821 \times 10^{-20} \text{ m}^2}$$

$$= 1.27468 \times 10^{-10} \text{ m}$$

$$= 0.127468 \text{ nm}$$

$H^{35}Cl$ molecule with $l=3, m=-2$

Q2

magnitude of the total angular momentum:

$$|\vec{L}| = \sqrt{|\vec{L}|^2} = \sqrt{l(l+1)\hbar^2} = \sqrt{l(l+1)} \hbar$$

$$= \sqrt{l(l+1)} \frac{h}{2\pi} = \sqrt{12} \hbar$$

$$= \sqrt{3(3+1)} \frac{6.626070 \times 10^{-34}}{2\pi} \text{ J s}$$

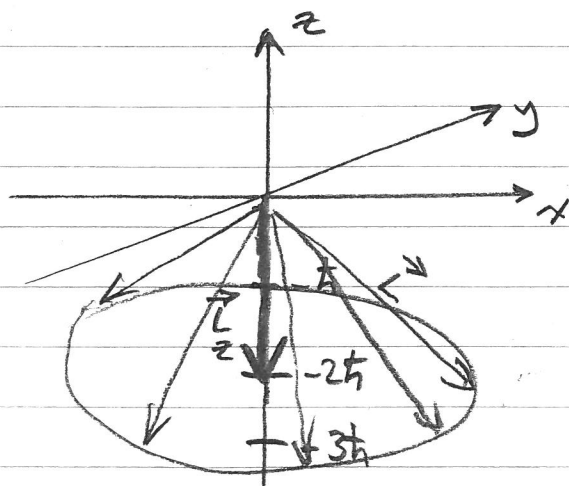
$$|\vec{L}| = 3.653144 \times 10^{-34}$$

z-component of the angular momentum:

$$L_z = m\hbar$$

$$= -2\hbar$$

$$L_z = -2.109144 \times 10^{-34} \text{ J}$$



magnitude of \vec{L}
is $\sqrt{12} \hbar$

z-component of \vec{L}
is $-2\hbar$

direction of \vec{L}
is unknown

Uncertainty Principle \implies (\vec{L}_x, \vec{L}_y are unknown)

Q3 How fast are rotating nuclei moving?

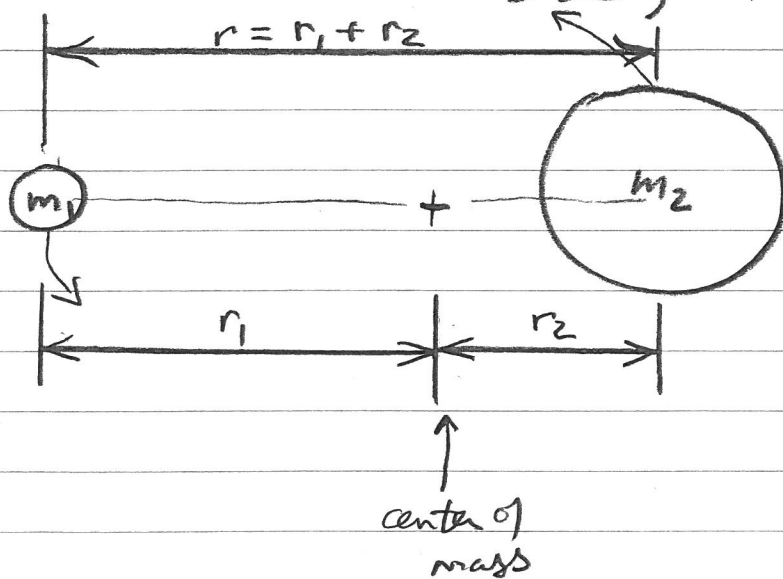
Consider a $H^{35}Cl$ molecule with $l=1, m=0$.

$$\text{total kinetic energy} = E_l = \frac{l(l+1)\hbar^2}{2I} = l(l+1)B$$

$$E_l = l(l+1)hc\tilde{B}$$

$$E_l = 1(1+1)(6.626 \times 10^{-34} \text{ Js}) \left(2.99792 \times 10^{10} \frac{\text{cm}}{\text{s}}\right) 10.5912 \text{ cm}^{-1}$$

$$E_l = 4.208 \times 10^{-22} \text{ J} \quad (\text{all kinetic, no potential energy})$$



$$r_1 m_1 = r_2 m_2$$

nuclear mass m_1 rotates at distance r_1 from the center of mass, nuclear mass 2 rotates at distance r_2

$$\frac{\text{nuclear speed } v_1}{\text{nuclear speed } v_2} = \frac{r_1}{r_2} = \frac{m_2}{m_1} \quad v_1 m_1 = v_2 m_2$$

(Q3 cont.)

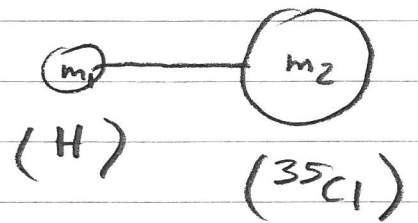
$$E_{\text{total}} = \text{total kinetic energy} = \frac{1}{2} m_1 v_1^2 + \frac{1}{2} m_2 v_2^2$$

fraction of the total kinetic due to the motion of nucleus 1:

$$\frac{E_1}{E_{\text{total}}} = \frac{\frac{1}{2} m_1 v_1^2}{\frac{1}{2} m_1 v_1^2 + \frac{1}{2} m_2 v_2^2} = \frac{m_1 v_1^2}{m_1 v_1^2 + m_2 \frac{m_1^2 v_1^2}{m_2^2}}$$

$$= \frac{1}{1 + \frac{m_1}{m_2}} = \frac{m_2}{m_1 + m_2}$$

$$\frac{1}{2} m_1 v_1^2 = \frac{m_2}{m_1 + m_2} E_{\text{total}}$$



$$v_1 = v_H = \sqrt{\frac{2}{m_1} \frac{m_2}{m_1 + m_2} E_{\text{total}}} = \sqrt{\frac{2}{m_H} \frac{m_{35Cl}}{m_H + m_{35Cl}} E_{\text{total}}}$$
$$= \sqrt{\frac{2}{1.6735 \times 10^{-27} \text{ kg}} \frac{58.067}{1.6735 + 58.067} 4.208 \times 10^{-22} \text{ J}}$$

$$v_H = 699.1 \text{ m s}^{-1}$$

$$v_2 = v_{35Cl} = \sqrt{\frac{2}{m_{35Cl}} \frac{m_H}{m_H + m_{35Cl}} 4.208 \times 10^{-22} \text{ J}}$$

$$v_{35Cl} = 20.1 \text{ m s}^{-1}$$

(Q3 cont.)

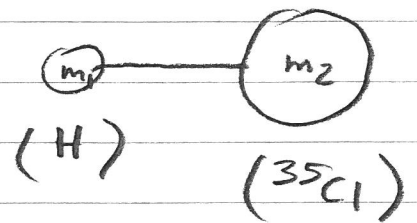
$$E_{\text{total}} = \text{total kinetic energy} = \frac{1}{2} m_1 v_1^2 + \frac{1}{2} m_2 v_2^2$$

fraction of the total kinetic due to the motion of nucleus 1:

$$\frac{E_1}{E_{\text{total}}} = \frac{\frac{1}{2} m_1 v_1^2}{\frac{1}{2} m_1 v_1^2 + \frac{1}{2} m_2 v_2^2} = \frac{m_1 v_1^2}{m_1 v_1^2 + m_2 \frac{m_1^2 v_1^2}{m_2^2}}$$

$$= \frac{1}{1 + \frac{m_1}{m_2}} = \frac{m_2}{m_1 + m_2}$$

$$\frac{1}{2} m_1 v_1^2 = \frac{m_2}{m_1 + m_2} E_{\text{total}}$$



$$v_1 = v_H = \sqrt{\frac{2}{m_1} \frac{m_2}{m_1 + m_2} E_{\text{total}}} = \sqrt{\frac{2}{m_H} \frac{m_{35\text{Cl}}}{m_H + m_{35\text{Cl}}} E_{\text{total}}}$$
$$= \sqrt{\frac{2}{1.6735 \times 10^{-27} \text{ kg}} \frac{58.067}{1.6735 + 58.067} 4.208 \times 10^{-22} \text{ J}}$$

$$v_H = 699.1 \text{ m s}^{-1}$$

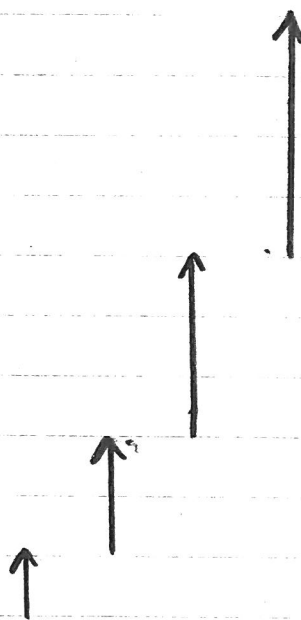
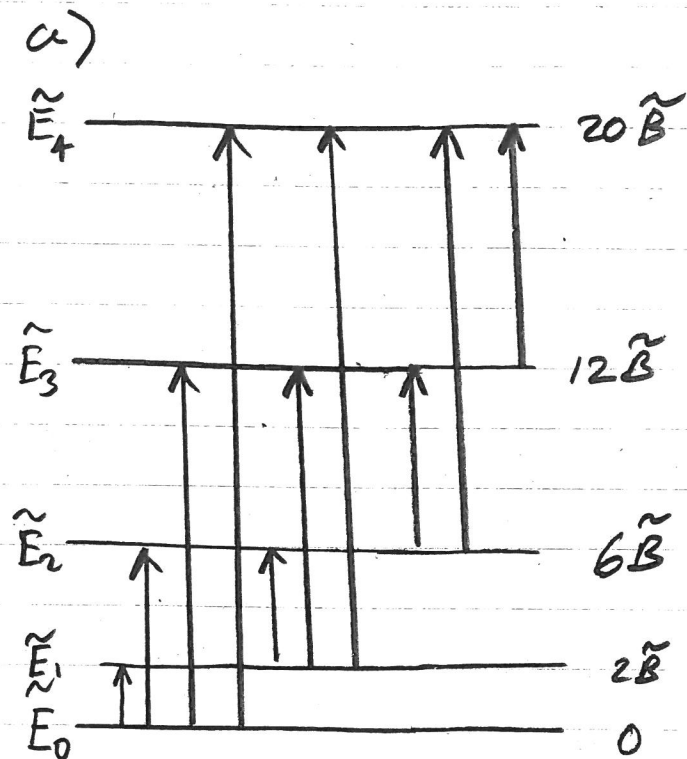
$$v_2 = v_{35\text{Cl}} = \sqrt{\frac{2}{m_{35\text{Cl}}} \frac{m_H}{m_H + m_{35\text{Cl}}} 4.208 \times 10^{-22} \text{ J}}$$

$$v_{35\text{Cl}} = 20.1 \text{ m s}^{-1}$$

Q4) $\tilde{E}_l = l(l+1)\tilde{B}$ $l = 0, 1, 2, 3, 4, \dots$

$\tilde{E}_0 = 0$ $\tilde{E}_1 = 1(2) = 2\tilde{B}$ $\tilde{E}_2 = 2(3)\tilde{B} = 6\tilde{B}$

$\tilde{E}_3 = 3(4)\tilde{B} = 12\tilde{B}$ $\tilde{E}_4 = 4(5)\tilde{B} = 20\tilde{B}$



b) absorption transitions
 Δl unrestricted
 $\Delta l = 1, 2, 3, 4$

frequencies:

$2\tilde{B}, 4\tilde{B}, 6\tilde{B}, 8\tilde{B}, 10\tilde{B}, 12\tilde{B}, 20\tilde{B}$

c) absorption transitions
 $\Delta l = +1$ selection rule

frequencies

$2\tilde{B}, 4\tilde{B}, 6\tilde{B}, 8\tilde{B}$

evenly spaced

simpler!

Q5

selection rules for rotational spectroscopy
(aka microwave spectroscopy)

transition intensity proportional to:

$$\mu \int P_{l',m'}(\mu) \left[\frac{l-|m|+1}{2l+1} P_{l+1,m'}(\mu) + \frac{l+|m|}{2l+1} P_{l-1,m'}(\mu) \right] d\mu$$

$l, m \rightarrow l', m'$ transition occurs if

$\mu \neq 0$ (molecule must have a permanent electric dipole moment)

Because the Legendre polynomials are orthogonal,

$l' = l+1$ or $l' = l-1$ to have a transition with non-zero intensity

\Rightarrow selection rule $\Delta l = \pm 1$

(+1 for absorption, -1 for emission)

also $m' = m$ $\Delta m = 0$

(Q6) A rigid diatomic molecule has energy levels

$$\tilde{E}_l = l(l+1)\tilde{B} = l(l+1) \frac{h}{8\pi^2 c \mu r^2}$$

with bond length r a constant.

For microwave absorption spectroscopy ($\Delta l = +1$), the transition frequencies are

$$\begin{aligned} \tilde{E}_{l+1} - E_l &= (l+1)(l+2)\tilde{B} - l(l+1)\tilde{B} \quad l=0,1,2,\dots \\ &= (l+1)(l+2-l)\tilde{B} = 2(l+1)\tilde{B} \\ &= 2\tilde{B}, 4\tilde{B}, 6\tilde{B}, 8\tilde{B}, \dots \end{aligned}$$

equally spaced transitions, spacing $2\tilde{B} = 2 \frac{h}{8\pi^2 \mu r^2}$
for $^{12}\text{C}^{16}\text{O}$:

