

1. a) The rotational constant B of H^{35}Cl is 10.591 cm^{-1} . Calculate the moment of inertia of the molecule and the bond length. Use $m_{\text{H}} = 1.67265 \times 10^{-27} \text{ kg}$ and $m_{\text{Cl}} = 5.80672 \times 10^{-26} \text{ kg}$.
- b) Assuming that the rotation of H^{35}Cl is classical, calculate the number of revolutions per second the molecule makes in the $J = 10$ rotational state.
2. a) The results we derived for the rotation of diatomic molecules also apply to linear polyatomic molecules. The moment of inertia of the linear $\text{H}^{12}\text{C}^{14}\text{N}$ molecule is $1.89 \times 10^{-46} \text{ kg m}^2$. Use this information to predict the microwave ("pure rotational") absorption spectrum of $\text{H}^{12}\text{C}^{14}\text{N}$.
- b) The moment of inertia for a set of point masses rotating about an axis is defined as

$$I = \sum_i m_i r_i^2$$

r_i is the perpendicular distance of mass m_i from the axis of rotation. The moment of inertia of the $\text{H}^{12}\text{C}^{14}\text{N}$ molecule is therefore

$$I = m_{\text{H}} r_{\text{H}}^2 + m_{\text{C}} r_{\text{C}}^2 + m_{\text{N}} r_{\text{N}}^2$$

Show that the moment of inertia of $\text{H}^{12}\text{C}^{14}\text{N}$ can be written as

$$I = \frac{m_{\text{H}} m_{\text{C}} r_{\text{HC}}^2 + m_{\text{H}} m_{\text{N}} r_{\text{HN}}^2 + m_{\text{C}} m_{\text{N}} r_{\text{CN}}^2}{m_{\text{H}} + m_{\text{C}} + m_{\text{N}}}$$

where r_{HC} , r_{HN} , and r_{CN} are the bond lengths.

- c) Given the bond lengths $r_{\text{HC}} = 106.8 \text{ pm}$ and $r_{\text{CN}} = 115.6 \text{ pm}$, calculate the moment of inertia I and compare the result to the spectroscopic value $1.89 \times 10^{-46} \text{ kg m}^2$. Use $m_{\text{H}} = 1.67265 \times 10^{-27} \text{ kg}$, $m_{\text{C}} = 1.99265 \times 10^{-26} \text{ kg}$, $m_{\text{N}} = 2.32527 \times 10^{-26} \text{ kg}$.
3. In class, your instructor asked to accept (as his instructors asked him to accept), without proof, that the moment of inertia for a linear molecule rotating about the bond axis can be ignored because all of the nuclei are located on the axis of rotation and are therefore not moving.

Let's test this assumption for the H_2 molecule by comparing the moment of inertia of two spinning protons (rotating about their centers) with the moment of inertia of a hydrogen molecule rotating about an axis perpendicular to the bond axis.

- a) Using spherical coordinates, show that a solid spherical body of radius R , mass M , and uniform density ρ spinning about its center has the moment of inertia

$$I_{\text{sphere}} = \frac{8}{15} \pi \rho R^5 = \frac{2}{5} MR^2$$

Useful integral: $\int \sin^3 ax \, dx = -\frac{\cos ax}{3} [\sin^2 ax + 2]$

b) The radius of a proton is about 1.7×10^{-15} m. Calculate the moment of inertia of two protons spinning around their centers.

c) Compare the result from part b with the moment of inertia of a H_2 molecule (bond length 74.16×10^{-12} m) to show that the moment of inertia for the rotation of H_2 about the bond axis is negligible.

4. Using the table of data in your notes, calculate the rotational energy of ${}^7\text{Li}{}^7\text{Li}$ in the $J = 10$ rotational state. Also calculate the contribution to the energy of rotation from centrifugal distortion.

5. Calculate the fraction of the total vibrational energy due to anharmonic vibration for a H^{35}Cl molecule in the

a) $n = 0$ vibrational state

b) $n = 5$ vibrational state.

Use
$$E_n = v_e \left(n + \frac{1}{2}\right) - x_e v_e \left(n + \frac{1}{2}\right)^2$$

6. A simple function that gives a good representation of the potential energy of a diatomic molecule is the Morse potential

$$V(q) = D_e (1 - e^{-\beta q})^2$$

D_e is the bond dissociation energy and $q = R - R_0$ is the displacement of the internuclear distance from the equilibrium value R_0 .

a) Show that the force constant calculated from the Morse potential is $k = 2D_e\beta^2$.

b) For H^{35}Cl , given that $D_e = 7.31 \times 10^{-19}$ J and $\beta = 1.83 \times 10^{10} \text{ m}^{-1}$, calculate k .

7. Determine the number of translational, rotational, and vibrational degrees of freedom for the following molecules:

a) CH_3Cl

b) OCS

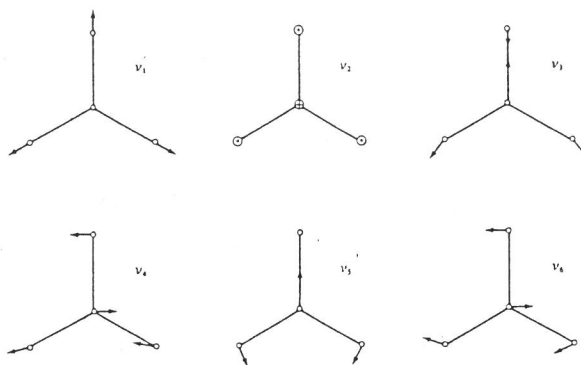
c) C_6H_6

d) HCCH

e) H_2CO

f) cyclopropane

8. The normal modes of vibration of the planar GaI_3 molecule are sketched below. Which modes are infrared-active?



9. Explain why the force constants and the equilibrium nuclear separations of H_2 , HD , and D_2 are the same under the Born-Oppenheimer approximation. Are the fundamental vibrational frequencies the same? Are the rotational constants the same?

10. A sample cell contains a gas mixture of two diatomic molecules from the table below. A Raman spectrum of the mixture shows the vibrational-rotational lines whose Raman shifts, in cm^{-1} , are:

3300.64, 3543.88, 3761.62, 3787.11, 3845.38, 3929.13
 4012.89, 4030.35, 4138.52, 4264.15, 4347.91, 4395.20
 4431.67, 4515.42, 4760.05, 5003.29, 5246.53, 5489.76

- Identify the two molecules in the mixture.
- Identify the S branch and O branch lines for each molecule.
- Which Raman lines correspond to the Q branch for each molecule?

molecule	$\tilde{\nu}_0/\text{cm}^{-1}$	\tilde{B}/cm^{-1}
$^{12}\text{C}^{16}\text{O}$	2861.8	14.457
$^{35}\text{Cl}^{35}\text{Cl}$	564.9	0.2438
$^{35}\text{Cl}^{19}\text{F}$	793.2	0.51651
$^{12}\text{C}^{16}\text{O}$	2170.21	1.9313
H_2	4395.2	60.809
H^{35}Cl	2989.74	10.5909
H^{19}F	4138.52	20.939
$^{127}\text{I}^{127}\text{I}$	214.57	0.03735
$^7\text{Li}^7\text{Li}$	351.43	0.6727
^7LiH	1405.1	7.5131
$^{14}\text{N}^{14}\text{N}$	2359.61	2.010
$^{14}\text{N}^{16}\text{O}$	1904.03	1.7046
$^{16}\text{O}^{16}\text{O}$	1580.36	1.44566
^{16}OH	3735.21	18.871

- (1.) a) Ignoring small centrifugal stretching effects, the rotational energy levels of a diatomic molecule are

$$E_J = \frac{\hbar^2}{2I} J(J+1)$$

In wavenumbers, $\tilde{E}_J = \frac{E_J}{hc} = \tilde{B} J(J+1) = \frac{\hbar^2}{2Ihc} J(J+1)$

for H^{35}Cl :

$$\tilde{B} = 10.591 \text{ cm}^{-1} = 10.395 \text{ cm}^{-1} \frac{100 \text{ cm}}{\text{m}} = 1039.5 \text{ m}^{-1}$$

(rot SI) (SI)

$$\tilde{B} = \frac{\hbar^2}{2Ihc} \quad I = \frac{\hbar^2}{2hc\tilde{B}} = \frac{(1.05459 \times 10^{-34})^2}{2(6.62618 \times 10^{-34})(2.99792 \times 10^8)1039.5}$$

$$I = 2.69296 \times 10^{-47} \text{ kg m}^2 = \mu r^2$$

$$\mu = \frac{m_{\text{H}} m_{\text{Cl}}}{m_{\text{H}} + m_{\text{Cl}}} \quad (\text{reduced mass}) \quad r = \text{bond length}$$

$$\mu = \frac{1.67265 \times 10^{-27} \cdot 5.80672 \times 10^{-26}}{1.67265 \times 10^{-27} + 5.80672 \times 10^{-26}} = 1.62582 \times 10^{-27} \text{ kg}$$

$$r = \sqrt{\frac{I}{\mu}} = 0.12870 \text{ nm} = 128.70 \text{ pm}$$

b) $E_{10} = \frac{(1.05459 \times 10^{-34})^2}{2(2.69296 \times 10^{-47})} (10)(11) = 2.2714 \times 10^{-20} \text{ J}$

$$E_{10} = \frac{1}{2} I \omega^2 \quad \text{angular velocity} \quad \omega = \sqrt{\frac{2E_{10}}{I}} = 4.1072 \times 10^{13} \text{ s}^{-1}$$

(microwaves)

(1.5 cont.)

$$\left(\begin{array}{l} 1 \text{ revolution} \\ \text{per second} \end{array} \right) = \left(\begin{array}{l} 2\pi \text{ radians} \\ \text{per second} \end{array} \right)$$

number of rotations per second = $\frac{\omega}{2\pi} = \frac{4.1072 \times 10^{13} \text{ s}^{-1}}{2\pi} = 6.5368 \times 10^{12}$

angular speed (radians per second)

② a) $\tilde{B} = \frac{h^2}{2Ihc} = \frac{h^2}{(2\pi)^2 2Ihc} = \frac{h}{8\pi^2 Ic}$

$$\tilde{B} = \frac{6.62618 \times 10^{-34}}{8\pi^2 (1.89 \times 10^{-46}) 2.99792 \times 10^8} = 148.112 \text{ m}^{-1}$$

$$\tilde{B} = 1.481 \text{ cm}^{-1}$$

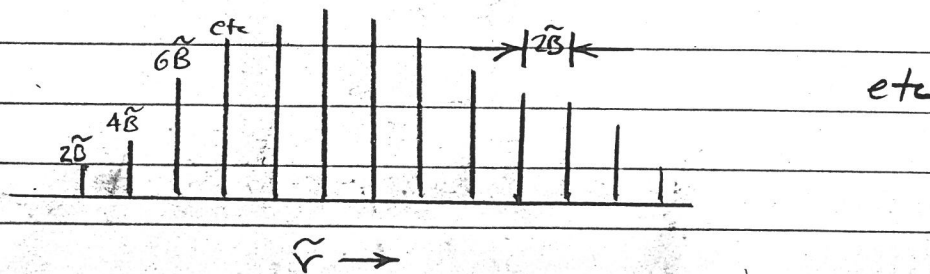
assuming $\tilde{E}_J = \tilde{B} J(J+1)$

absorption $J \rightarrow J+1$
($\Delta J = +1$)

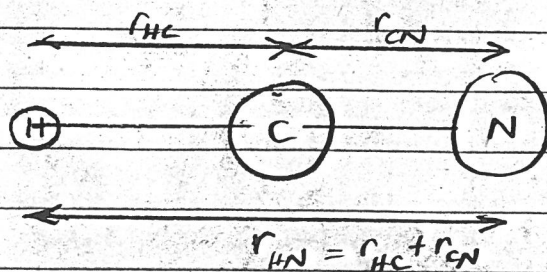
$$0 \rightarrow 1 \quad \tilde{\nu}_{01} = \tilde{E}_1 - \tilde{E}_0 = \tilde{B}(1)(2) - 0 = 2\tilde{B} = 2.962 \text{ cm}^{-1}$$

$$1 \rightarrow 2 \quad \tilde{\nu}_{12} = \tilde{E}_2 - \tilde{E}_1 = \tilde{B}6 - \tilde{B}2 = 4\tilde{B} = 5.924 \text{ cm}^{-1}$$

$$2 \rightarrow 3 \quad \tilde{\nu}_{23} = \tilde{E}_3 - \tilde{E}_2 = \tilde{B}12 - \tilde{B}6 = 6\tilde{B} = 8.886 \text{ cm}^{-1}$$



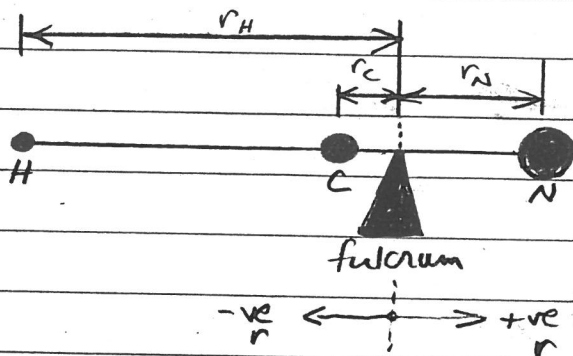
b)



(25 cont.)

The HCN molecule rotates about its center of mass

defined as:



$$m_H r_H + m_C r_C + m_N r_N = 0$$

$$r_{HC} = r_C - r_H$$

$$r_{HN} = r_N - r_H$$

$$r_{CN} = r_N - r_C$$

$$I = \frac{m_H m_C r_{HC}^2 + m_H m_N r_{HN}^2 + m_C m_N r_{CN}^2}{m_H + m_C + m_N}$$

(start with this equation and work backwards)

$$(m_H + m_C + m_N) I = m_H m_C (r_C - r_H)^2 + m_H m_N (r_N - r_H)^2 + m_C m_N (r_N - r_C)^2$$

$$= m_H m_C r_C^2 - 2m_H m_C r_C r_H + m_H m_C r_H^2 + m_H m_N r_N^2 - 2m_H m_N r_N r_H + m_H m_N r_H^2 + m_C m_N r_N^2 - 2m_C m_N r_N r_C + m_C m_N r_C^2$$

$$= m_H (m_C + m_N) r_H^2 + m_C (m_H + m_N) r_C^2 + m_N (m_H + m_C) r_N^2$$

$$- 2m_H m_C r_C r_H - 2m_H m_N r_N r_H - 2m_C m_N r_N r_C$$

add and subtract $m_H r_H^2 + m_C r_C^2 + m_N r_N^2$:

$$(m_H + m_C + m_N) I = m_H (m_C + m_N) r_H^2 + m_C (m_H + m_N) r_C^2 + m_N (m_H + m_C) r_N^2 + m_H^2 r_H^2 + m_C^2 r_C^2 + m_N^2 r_N^2$$

$$- m_H^2 r_H^2 - m_C^2 r_C^2 - m_N^2 r_N^2$$

$$- 2m_H m_C r_C r_H - 2m_H m_N r_N r_H - 2m_C m_N r_N r_C$$

$$= m_H (m_H + m_C + m_N) r_H^2 + m_C (m_H + m_C + m_N) r_C^2 + m_N (m_H + m_C + m_N) r_N^2 - (r_H m_H + r_C m_C + r_N m_N)^2$$

from definition of center of mass = 0

(2 b cont.)

$$I = m_H r_H^2 + m_C r_C^2 + m_N r_N^2 \quad \checkmark$$

$$c) \quad r_{HC} = 106.8 \text{ pm} \quad r_{CN} = 115.6 \text{ pm}$$

$$\therefore r_{HN} = 106.8 + 115.6 = 222.4 \text{ pm}$$

$$m_H = 1.67265 \times 10^{-27} \text{ kg}$$

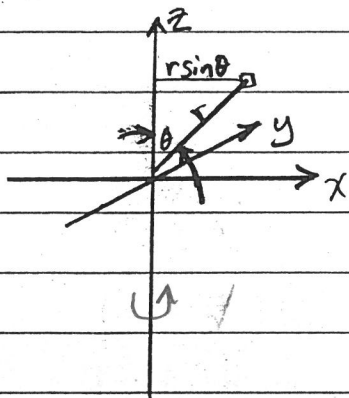
$$m_C = 1.99265 \times 10^{-26} \text{ kg}$$

$$m_N = 2.32527 \times 10^{-26} \text{ kg}$$

$$I = \frac{(10^{-24})(10^{-26})}{0.167265 + 1.99265 + 2.32527} \left(0.167265(1.99265)(106.8)^2 + 0.167265(2.32527)(222.4)^2 + 1.99265(2.32527)(115.6)^2 \right)$$

$$= 1.8942 \times 10^{-46} \text{ kg m}^2 \quad \checkmark$$

- ③ a) volume element $dr = r^2 \sin \theta dr d\theta d\phi$
with mass ρdr is a distance $r \sin \theta$ from
the axis of rotation (the z axis)



$$I = \sum_i r_i^2 m_i$$

$$= \int (r \sin \theta)^2 \rho dr$$

$$= \rho \int_0^{2\pi} \int_0^{\pi} \int_0^R r^4 \sin^3 \theta dr d\theta d\phi$$

$$I = \rho \int_0^{2\pi} d\phi \int_0^R r^4 dr \int_0^{\pi} \sin^3 \theta d\theta = \rho \frac{2\pi R^5}{5} \int_0^{\pi} \sin^3 \theta d\theta$$

$$I = \frac{2\pi \rho R^5}{5} \left[\frac{1}{3} \cos \theta (\sin^2 \theta + 2) \right] \Big|_0^{\pi} = \frac{2\pi \rho R^5}{5} \left[\frac{1}{3} (-1)(2) - \left(\frac{1}{3} \right) (1)(2) \right]$$

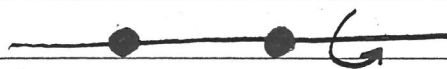
(3a cont.)

$$I = \frac{8\pi}{15} \rho R^3 = \frac{4}{3} \pi R^3 \frac{2}{5} R^2 = \frac{2MR^2}{5}$$

b) moment of inertia of two spinning protons:

$$= 2 \left(\frac{2}{5} m_p R_p^2 \right) = 2 \frac{2}{5} (1.67265 \times 10^{-27}) (1.7 \times 10^{-15})^2$$

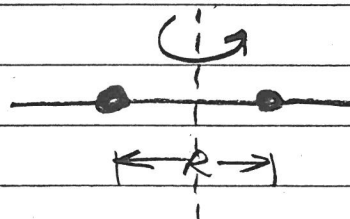
$$= 3.87 \times 10^{-57} \text{ kg m}^2$$



moment of inertia of rotating H_2 molecule:

c) $I = \mu R^2$

$$= \frac{m_p m_p}{m_p + m_p} R^2$$



$$= \frac{m_p}{2} R^2 = \frac{1.67265 \times 10^{-27}}{2} (74.16 \times 10^{-12})^2$$

$$= 4.599 \times 10^{-48} \text{ kg m}^2 \quad (\text{larger than } I \text{ in b) by a factor of } 1.2 \times 10^9)$$

④ $\tilde{E}_J = \tilde{B} J(J+1) - \tilde{D} J^2(J+1)^2$
centrifugal distortion term

$$\tilde{E}_{10} = 0.673 (10)11 - 0.0009 \cdot 10^2 (11)^2$$

$$= 74.03 \text{ cm}^{-1} - 10.89 \text{ cm}^{-1}$$

$$= 63.14 \text{ cm}^{-1} = 6314 \text{ m}^{-1}$$

(SI)

(4 cont.)

$$\begin{aligned} \text{rotational energy} &= \tilde{E}_{10} hc = (63.14) (6.62618 \times 10^{-34}) (2.997925 \times 10^8) \\ &= 1.254 \times 10^{-21} \text{ J} \end{aligned}$$

$$\begin{aligned} \text{contribution from centrifugal distortion} &= - \frac{10.89}{63.14} 1.254 \times 10^{-21} = -2.163 \times 10^{-22} \text{ J} \\ &\text{(significant, -17\% of total } \tilde{E}_{rot}) \end{aligned}$$

⑤ $\text{H}^{35}\text{Cl} \quad \tilde{\nu}_e \ 2989.7 \text{ cm}^{-1} \quad \chi_e \tilde{\nu}_e \ 52.05 \text{ cm}^{-1}$

$$\underline{n=0} \quad \tilde{F}_0 = \nu_e \left(0 + \frac{1}{2}\right) - \chi_e \tilde{\nu}_e \left(0 + \frac{1}{2}\right)^2$$

$$= \frac{2989.7}{2} - \frac{52.05}{4} = 1494.85 - 13.01$$

$$= 1481.84$$

anharmonic contribution
(-0.88%)
↓

$$\underline{n=5} \quad \tilde{F}_0 = \nu_e (5.5) - \chi_e \tilde{\nu}_e (5.5)^2$$

$$= 16443.35 - 1574.51$$

$$= 14868.8 \text{ cm}^{-1}$$

(-10.6%)

anharmonic contribution significant
(increases with n)

⑥ a) $V(q) = D_e (1 - e^{-\beta q})^2 \quad q = R - R_0 \quad \text{so } dq = dR$

$$\frac{dV}{dR} = \frac{dV}{dq} = 2D_e (1 - e^{-\beta q}) (-e^{-\beta q}) (-\beta)$$

$$\frac{dV}{dR} = 0 \text{ at } q = 0$$

(6a cont.)

$$\frac{dV}{dq} = \frac{dV}{dR} = 2\beta A_e (-e^{-\beta q} + e^{-2\beta q})$$

$$\frac{d^2V}{dq^2} = \frac{d^2V}{dR^2} = 2\beta A_e (\beta e^{-\beta q} - 2\beta e^{-2\beta q})$$

$$\left. \frac{d^2V}{dR^2} \right|_{q=0} = 2\beta A_e (\beta - 2\beta) = -2\beta^2 A_e$$

Hooke's Law:

$$\text{Force} = -kq = -\frac{dV}{dq}$$

force constant

$$k = \frac{d^2V}{dq^2}$$

b) $k = 2\beta^2 A_e$

$$= 2(1.83 \times 10^{10} \text{ m}^{-2})^2 (7.31 \times 10^{-19} \text{ J})$$
$$k = 489.6 \text{ N m}^{-1}$$

(7.) molecule	N no. nuclei	translational d.f.	rotational d.f.	vibration d.f.
CH ₃ Cl	5	3	3	3N-6=9
C ₆ H ₆	12	3	3	3N-6=30
H ₂ CO	4	3	3	3N-6=6
OCS (linear)	3	3	2	3N-5=4
HCCl (linear)	4	3	2	3N-5=7
cyclopropane (C ₃ H ₆)	9	3	3	3N-6=21

- ⑧ The dipole moments must change with the vibration if it is IR active.

So, all modes are IR active except for ν_1 (symmetric stretch)

- ⑨ According to the Born-Oppenheimer approximation, the potential energies $V_{H-H}(R)$, $V_{H-D}(R)$, $V_{D-D}(R)$ are

identical for H_2 , HD , and D_2 molecules as a function of the nucleus-nucleus distance R . Why? Because the nuclear charges and electronic wave functions are assumed to be identical.

The bond lengths, $\frac{dV}{dR}$, $\frac{d^2V}{dR^2}$ and therefore the force constant k are identical:

$$k_{H_2} = k_{HD} = k_{D_2}$$

The fundamental frequencies (ν_e) and the rotational constants (B) , however, are different because they depend on the reduced mass

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

$$B = \frac{h}{8\pi^2 \mu R^2}$$

$$\mu_{HH} = \frac{m_H m_H}{m_H + m_H}$$

$$\mu_{DD} = \frac{m_D m_D}{m_D + m_D}$$

$$\mu_{HD} = \frac{m_H m_D}{m_H + m_D}$$

$$= \frac{m_H}{2}$$

$$= \frac{m_D}{2}$$

10) a) the measured Raman shifts are $> 3300 \text{ cm}^{-1}$.

Only 3 of the molecules have $\tilde{\nu}_0$ values $> 3300 \text{ cm}^{-1}$, so the two molecules in the sample must be H_2 ($\tilde{\nu}_0 = 4395.2 \text{ cm}^{-1}$), H^{19}F ($\tilde{\nu}_0 = 4138.52 \text{ cm}^{-1}$) or ^{16}OH ($\tilde{\nu}_0 = 3735.21 \text{ cm}^{-1}$)

As shown in the notes, the Raman lines in the O and S branches are separated by $4\tilde{B}$:

$$\text{H}^{19}\text{F}: 4\tilde{B} = 83.756 \text{ cm}^{-1}$$

$$\text{H}_2: 4\tilde{B} = 243.236 \text{ cm}^{-1}$$

$$^{16}\text{OH}: 4\tilde{B} = 75.484 \text{ cm}^{-1}$$

suggestion: plot the data!

for the lowest frequency line (3300.64 cm^{-1}), notice

$$3300.64 + 243.236 = 3543.876 \text{ cm}^{-1} \text{ in agreement}$$

a) with the next line 3543.88

$\therefore \text{H}_2$ is one of the molecules with Stokes (S branch lines)

$$3300.64, 3543.88, 3787.12, 4030.35, \cancel{4273.59} \text{ (not observed)}$$

so the Q branch for H_2 must be the next H_2 line after 4030.35 cm^{-1}

starting at the highest frequency line, $5489.76 - 243.236 = 5246.524$ in agreement with the observed 5246.53 line,

so the Anti-Stokes (O Branch) lines for H_2 are:

$$5489.76, 5246.52, 5003.28, 4760.05, \cancel{4516.81} \text{ (not observed)}$$

The lowest frequency line not assigned to H_2 is 3761.62 ,

and notice $3761.62 + 83.756 = 3845.38$, which is observed,

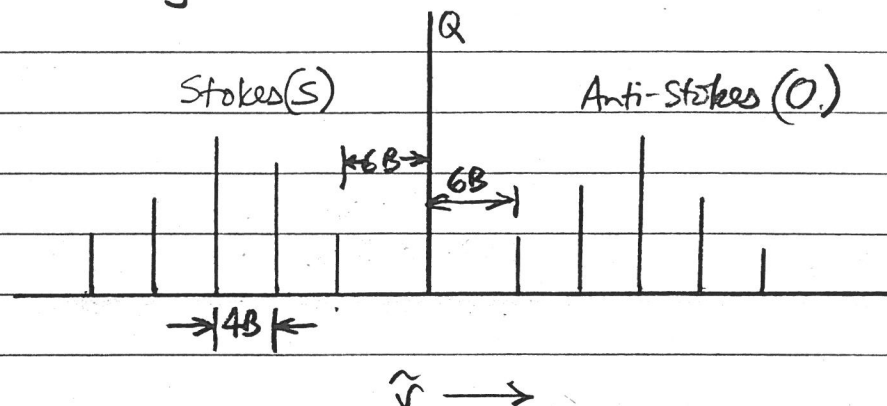
so the other molecule must be H^{19}F with S Branch

$$\text{lines } 3761.62, \cancel{3845.38}, 3929.13, 4012.89, \cancel{4096.64} \text{ (not observed)}$$

The highest frequency line not assigned to H_2 is 4515.42 cm^{-1} , so the Anti-Stokes lines (O Branch) for H^{19}F are:

$$4515.42, 4431.67, 4347.91, 4264.15, \cancel{4180.40} \text{ not observed}$$

b) The first lines of the O and S branches are offset from the Q line by $6\tilde{B}$ =



The lines at 4138.52 cm^{-1} and 4395.20 cm^{-1} are unidentified.

$$\begin{aligned} \text{But notice } 4030.35 + 6\tilde{B}_{\text{H}_2} &= 4030.35 + 6(60.809) \\ &= 4030.35 + 364.854 \\ &= 4395.204 \text{ cm}^{-1} \quad \checkmark \text{ observed} \end{aligned}$$

$$\begin{aligned} \text{check: the lowest frequency O line} - 6\tilde{B}_{\text{H}_2} \\ = 4760.05 - 364.854 = 4395.196 \quad \checkmark \end{aligned}$$

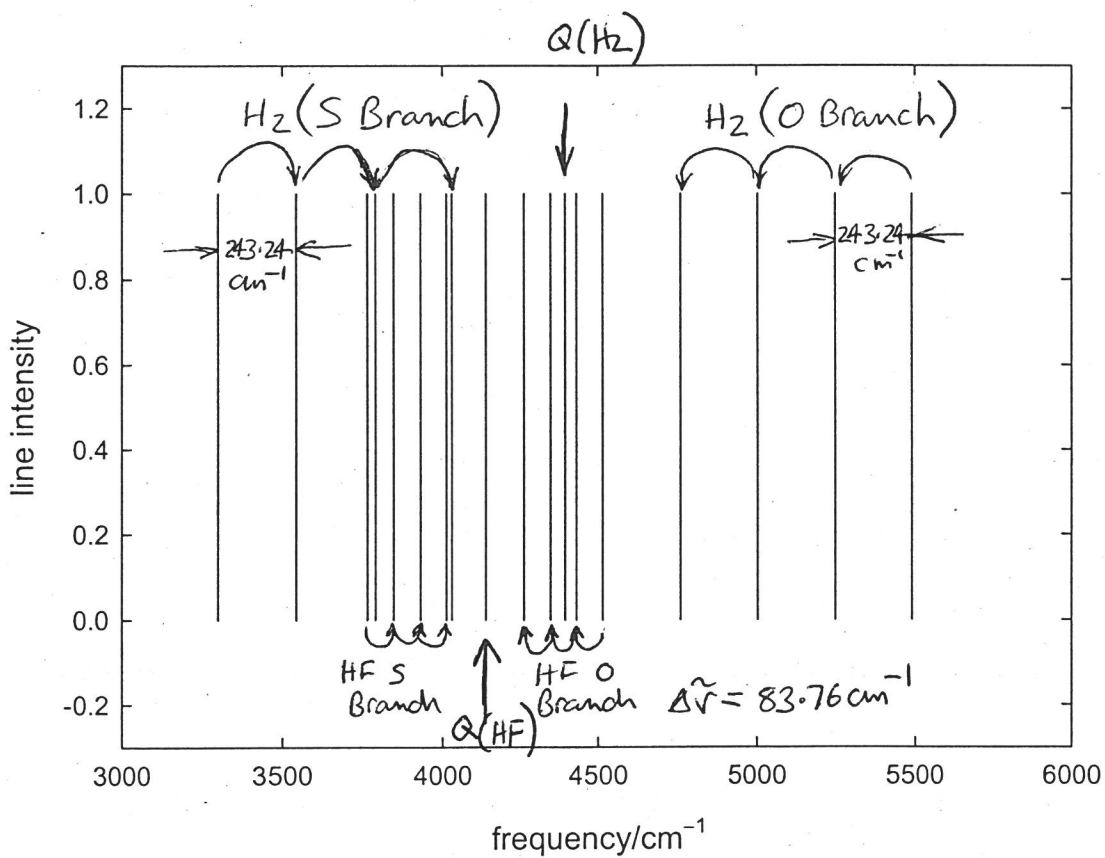
O₂ // average the 4030.35 and 4760.05 lines =

$$\text{H}_2 \text{ Q branch} = \frac{4030.35 + 4760.05}{2} = 4395.2 \text{ cm}^{-1}$$

for H¹⁹F:

$$\text{Q branch} = \frac{4012.81 + 4264.15}{2} = 4138.52 \text{ cm}^{-1} \quad \checkmark \text{ observed}$$

(10 cont.)



(10 cont.)

