① For $^1H^{35}Cl$, the $R(0)$ line occurs at 2905.8 cm^{-1}.

To calculate the $R(0)$ line for $^1H^{37}Cl$:

$$\nu_{^1H^{35}Cl} = \frac{1}{2\pi}\sqrt{\frac{k}{\mu_{^1H^{35}Cl}}}$$

$$\nu_{^1H^{37}Cl} = \frac{1}{2\pi}\sqrt{\frac{k}{\mu_{^1H^{37}Cl}}}$$

since k is the same for both $^1H^{35}Cl$ & $^1H^{37}Cl$.

$$\frac{\nu_{^1H^{35}Cl}}{\nu_{^1H^{37}Cl}} = \sqrt{\frac{\mu_{^1H^{37}Cl}}{\mu_{^1H^{35}Cl}}} \quad - ①'$$

$$\mu_{^1H^{35}Cl} = \left(\frac{35\times1}{35+1}\right)\frac{10^{-3}}{N} \text{ kg.}$$

$$\mu_{^1H^{37}Cl} = \left(\frac{37\times1}{37+1}\right)\frac{10^{-3}}{N} \text{ kg.}$$

$$\frac{\mu_{^1H^{35}Cl}}{\mu_{^1H^{37}Cl}} = \frac{35}{36}\times\frac{38}{37} = 0.9985 \quad \text{(keep 4 digits).}$$

Eq^n ① ⟹ $\nu_{^1H^{37}Cl} = \nu_{^1H^{35}Cl} \times \sqrt{\frac{\mu_{^1H^{35}Cl}}{\mu_{^1H^{37}Cl}}} = 2905.8\times\sqrt{.9985}$

$$= 2903.5 \text{ cm}^{-1}$$

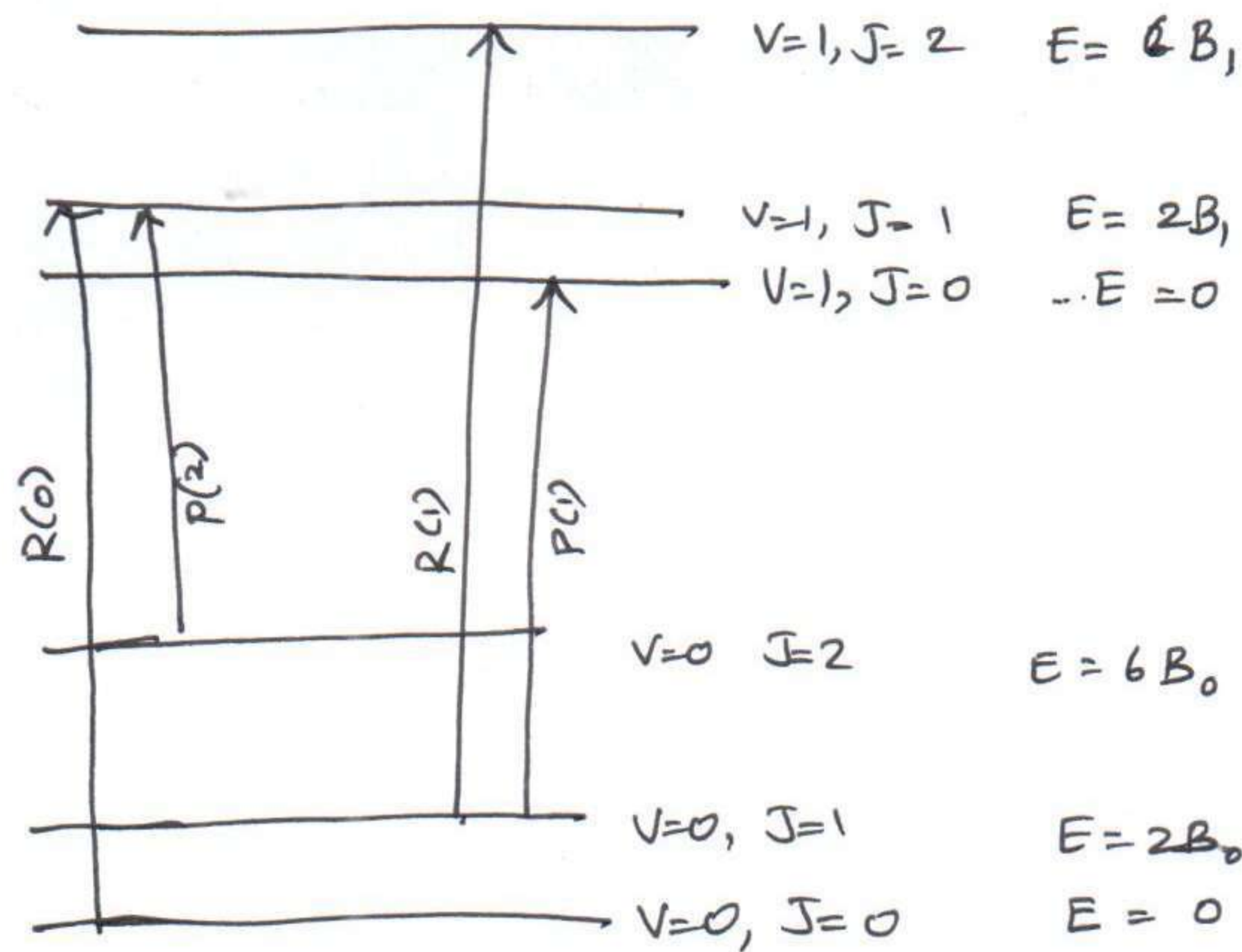Isotopic shift: $\Delta\nu = \nu_{^1H^{35}Cl} - \nu_{^1H^{37}Cl} = 2905.8 - 2903.5 = 2.3 \text{ cm}^{-1}$

Similarly for $\nu_{^2H^{35}Cl}$ is given by

$$\nu_{^2H^{35}Cl} = \nu_{^1H^{35}Cl} \cdot \sqrt{\frac{M_{^2H^{35}Cl}}{M_{^1H^{35}Cl}}} = \cancel{2905} \; 2905.8 \times \sqrt{\left(\frac{35}{36}\right)\left(\frac{37}{70}\right)}$$

$$= 2905.8 \times \sqrt{0.5139}$$

$$= 2083.1 \; cm^{-1}$$

Isotopic shift $\quad \nu_{^1H^{35}Cl} - \nu_{^2H^{35}Cl} = 2905.8 - 2083.1$

$$= 822.7 \; cm^{-1} \; !!$$

Isotopic substitution in the lighter species (i.e. D for H) causes a larger shift in the frequency that substitution in the heavier species (i.e. ^{37}Cl for ^{35}Cl).

(2)

Energy level diagram with transitions R(0), P(2), R(1), P(1):

- $v=1, J=2$ $E= 6B_1$
- $v=1, J=1$ $E= 2B_1$
- $v=1, J=0$ $E=0$
- $v=0, J=2$ $E= 6B_0$
- $v=0, J=1$ $E=2B_0$
- $v=0, J=0$ $E=0$

$$R(0) - P(2) = 6B_0 \qquad \text{(Transitions involve a common upper level)}$$

$$2905.8 - 2843.3 = 6B_0$$
$$\Rightarrow B_0 = 10.42 \text{ cm}^{-1}$$

$$R(1) - P(1) = 6B_1 \qquad \text{(Transitions involve a common lower level)}$$

$$2925.7 - 2865.2 = 6B_1$$
$$\Rightarrow B_1 = 10.08 \text{ cm}^{-1}.$$

$$\mu_{HCl} = \frac{35}{36} \times \frac{10^{-3}}{N} = 1.614 \times 10^{-27} \text{ kg}.$$

$$B_0 = \frac{h}{8\pi^2 \mu r_0^2 c} = \frac{6.626 \times 10^{-34}}{8 \times \pi^2 \times 1.614 \times 10^{-27} \times r_0^2 \times 3 \times 10^{10}} = 10.42$$

$$r_0^2 = 1.6633 \times 10^{-20} \text{ m}^2 \qquad r = 1.2897 \times 10^{-10} \text{ m} = 1.2897 \text{ Å}$$

$$\frac{B_1}{B_0} = \frac{r_0^2}{r_1^2} \quad :\Rightarrow r_1^2 = r_0^2 \left(\frac{B_0}{B_1}\right) = 1.6633 \times 10^{-20} \left(\frac{10.42}{10.08}\right)$$

$$= 1.7194 \times 10^{-20} \text{ m}^2$$

$$r_1 = 1.3113 \times 10^{-10} \text{ m} = 1.3113 \text{ Å}$$

$$\Delta r = .02 \text{ Å}$$

3) $B_0 = 10.42$ cm⁻¹ $B_0 + B_1 = 20.5$ cm⁻¹

   $B_1 = 10.08$ cm⁻¹ $B_1 - B_0 = -0.34$ cm⁻¹.

Since $B_1 < B_0$, 'R' branch will form the head. Value of J where head form is
given by :

$$m_H = -\frac{(B_1 + B_2)}{2(B_1 - B_2)} = -\frac{(10.42 + 10.08)}{2(10.08 - 10.42)} = -\frac{20.5}{(-.68)}$$

$$\approx 30$$

For the R branch $m = J'' + 1$ ∴   Hence

$$J'' + 1 = 30 \qquad \text{or} \qquad \underline{J'' = 29} \quad \text{is where} \quad \text{the}$$

turn around will occur to form the head. At this J'' value
the population will be negligible. Hence the head cannot be
observed .

4) If the difference between B_1 & B_0 were ten times larger, then

$$B_1 - B_0 = -3.4 \text{ cm}⁻¹.$$

If $B_0 = 10.42$ cm⁻¹ $B_1 = 7.02$ cm⁻¹.

$$m_H = \qquad - \frac{10.42 + 7.02}{2(-3.4)} = 2.56 \approx 3.$$

i.e. $J'' + 1 = 3$ or $J'' = 2$ is where the head

forms. This problem has used an exaggerated value for the
difference between B_0 & B_1. But this gives you an idea of
what happens when the difference is large.

_____

5. The ground state is labelled "X". It has a vibrational frequency of 212 cm^{-1} and an R_e of 2.66 Å. An excited electronic state labelled "B" has a vibrational frequency of 125 cm^{-1} and an R_e of 3.03 Å. Another excited electronic state labelled "a" has a vibrational frequency of 205 cm^{-1} and an R_e of 2.75 Å.

State	Vibrational Freq	R_e
X	212 cm^{-1}	2.66 Å
B	125 cm^{-1}	3.03 Å
a	205 cm^{-1}	2.75 Å

Usually, larger the difference in the internuclear distances between the initial and final states, longer the progression one sees. Hence the transition X→B is likely to show a longe progression than X→a.

6. In both transitions, the R_e in the upper state is larger than the ground state R_e. Hence one can expect to see red degraded band heads, where the "R" branch will show the head.

As we have already seen in an earlier problem, larger the difference in R_e (and hence larger the difference in the B values) quicker is the turn around of the branch to form the head. Since the X→B transition has the larger difference in the R_e values, one can expect to see a band head formation at lower J values in this transition relative to what one would observe in the X→a transition.

7. Na has the ground state electronic configuration $1s^2 2s^2 2p^6 3s^1$. Since the $1s^2\ 2s^2$ and $2p^6$ have completely filled shells, they will not contribute to the angular momentum and only the $3s^1$ needs to be considered. Since we have only electron to consider,
For the 's' electron, $l = 0$ and hence L = 0, implying we have an S state.
For the one electron, spin $s = ½$ and hence S=1/2. We have therefore a ^{2}S state. (Remember the superscript is the value for the degeneracy (2S+1).) Coupling the L and S, we get J, which is given by: J = (L+S), (L+S-1),…., |(L-S)|
Hence in this case the term state is ^{2}S$_{1/2}$

For the P state, in which the lone electron is excited to a 'p' orbital, we have again, L=1 (i.e. a P state) and since $s = ½$, S=1/2. We have therefore a ^{2}P state. The J values will be 3/2 and ½ and we therefore have ^{2}P$_{1/2}$ and ^{2}P$_{3/2}$ states.

 Hence the transitions from the ground state to the excited state will actually be
^{2}S$_{1/2}$ → ^{2}P$_{1/2}$ and ^{2}S$_{1/2}$ → ^{2}P$_{3/2}$. Hence one sees a doublet in this transition.

8. Please see Fig. 5.11 (Pg.147) in Banwell.

Problem set 5B

a. $1s^2 2p^1$

Completely closed shell configurations do not count towards angular momentum coupling. That they will no contribution towards L and S. In other words for closed shell configurations, L=0 and S=0. Hence $1s^2$ need not be considered. Only the $2p^1$ part of the electron configuration will count. For $2p^1$, l=1. Since it is the only electron present, L=l. Hence L=1, which is a P state. For the single electron, s=1/2. Hence S=1/2 or (2S+1) = 2. Hence the term state is ^2P, for which L=1 and S=1/2. Hence J will L+S, L+S-1, …..|(L-S)|, which will work out to 3/2 and ½.

Hence the term states will $^2P_{3/2}$ and $^2P_{1/2}$.

b. $1s^1 2p^1$

In this case, the 1s orbital is not completely filled and hence will contribute to the angular moment. There are two electrons, one in 1s and the other in 2p. Hence, l_1 =0 and l_2 =1. Hence L = (l_1+l_2), (l_1+l_2-1),…..| (l_1-l_2)|. This works out to L=1, which is a P state. Similarly, s_1 =1/2 and s_2 =1/2. Hence S = (s_1+s_2), (s_1+s_2-1),…..| (s_1-s_2)|. This works out to S=0 and 1. Hence you will get ^1P and ^3P states.

For the ^1P state, L= 1 and S=0 and the J state will be J=1 and hence the term state will be $^1P_1$

For the ^3P state, L=1 and S=1, and the J states will be J=2,1,0 and hence the term states will be $^3P_0$, $3P_1$, $3P_2$

c. $2p^1 3p^1$. l_1 =1 and l_2 =1; Hence L= 2, 1, 0. s_1 =1/2 and s_2 =1/2. S=0 and 1. Hence states are ^3D, ^1D, ^3P, ^1P , ^3S, ^1S, Inclusion of J, will yield,
$^3D_3$, $^3D_2 {}^3D_1$; $^1D_2$, $^3P_2$, $^3P_1$, $^3P_0$, $^1P_1$, $^3S_1$, $^1S_0$

d. $2p^1 3d^1$: States are: ^3F, ^1F, ^3D, ^1D , ^3P, ^1P, Inclusion of J, will yield
$^3F_4$, $^3F_3$, $^3F_2$; $^1F_3$, $^3D_3$, $^3D_2$, $^3D_1$, $^1D_2$, $^3P_2$, $^3P_1$, $^3P_0$, $^1P_1$

e. $1s^2 2s^2 2p^6 3s^1 3p^1$.   The initial part of the configuration $1s^2 2s^2 2p^6$ is closed shell and hence need not be considered. The rest is $3s^1 3p^1$, which is like problem 'b' $(s^1 p^1)$ and hence the states will be: ^1P and ^3P

f. $1s^2 2s^2 2p^6$. This is a closed shell configuration and hence the term state will be $^1S_0$.