

TL 9-49 (HCl Spectroscopy)

• Suppose HCl is illuminated with  $\lambda = 435.8 \text{ nm}$  light.

a) Find 4 absorption lines nearest to this.

• Looking at table 9-8, for  $\text{H}^{35}\text{Cl}$ ,  $E_{0r} = \frac{\hbar^2}{2I} = 1.32 \text{ meV}$

and the rotational frequency is  $f_0 = 8.97 \text{ e}13 \text{ Hz}$

• The incident frequency is  $f = \frac{c}{\lambda} = 6.879 \text{ e}14 \text{ Hz}$ ,

which is much higher than the frequency needed to

take the HCl from  $E_{n=0} = \frac{1}{2} h f_0$   
to  $E_{n=1} = \frac{3}{2} h f_0$  }  $\Delta E = h f_0$

• So to absorb this photon, we need to excite the HCl from, say  $n=0$  to  $n =$  much higher. How much higher?  $n \Delta E = h f$

$$n = \frac{h f}{h f_0} = \frac{f}{f_0} \stackrel{6.879}{=} \frac{6.879 \text{ e}14}{8.97 \text{ e}13}$$

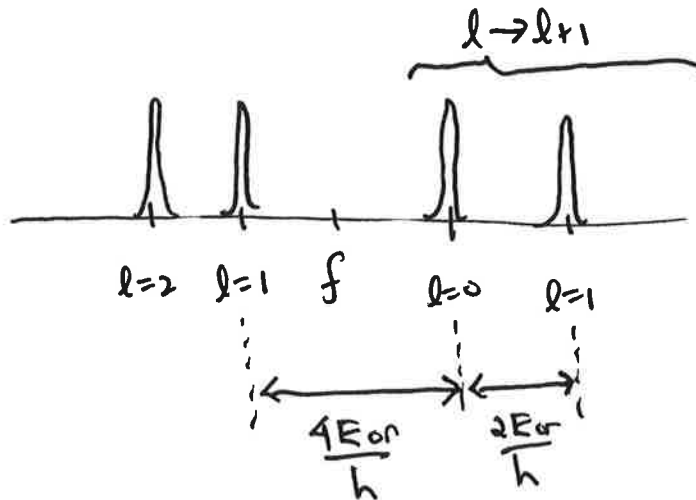
$$n = 7.67 \approx 8$$

• Let's take  $n=8$ . So the frequency associated with the transition from  $n=0$  to  $n=8$  is  $8 h f_0 =$

$$8 f_0 = 7.18 \times 10^{14} \text{ Hz}$$

- Now, what rotational states/transitions lie nearby?
- Since  $E_{0r} = 1.32 \text{ meV}$ , we can find the ~~lines~~ absorption lines that lie on either side of

$$f = 7.18 \times 10^{14} \text{ Hz}$$



$$\frac{2E_{0r}}{h} = 6.38 \text{ e}11 \text{ Hz}$$

- So the transition from  $(n=0, l=0)$   
to  $(n=8, l=1)$

$$\text{is at } f = 7.18 \text{ e}14 \text{ Hz} + 6.38 \text{ e}11 \text{ Hz}$$

$$f = 7.186 \text{ e}14 \text{ Hz}$$

and from  $(n=0, l=1)$  to  $(n=8, l=2)$  □

$$f = 7.18 \text{ e}14 \text{ Hz} + 2 \cdot 6.38 \text{ e}11 \text{ Hz}$$

$$f = 7.193 \text{ e}14 \text{ Hz}$$

- And on the other side, from  $(n=0, l=1)$  to  $(n=8, l=0)$

$$f = 7.171 \text{ e}14 \text{ Hz}$$

and from  $(n=0, l=2)$  to  $(n=8, l=1)$

$$f = 7.167 \text{ e}14 \text{ Hz}$$

b) The absorption lines in fig 9-30 correspond to a transition between two very nearby vibrational states ( $n=0$  to  $n=1$ ). This is in the microwave spectrum. Our light is in the visible. So we cannot compare. But we can compare the gaps. Our gaps are

$$\left. \begin{array}{l} \text{big gap: } \frac{4E_{\text{or}}}{h} = 12.76 \text{ e11 Hz} \\ \text{little gap: } \frac{2E_{\text{or}}}{h} = 6.38 \text{ e11 Hz} \end{array} \right\} \text{ Calculated}$$

$$\begin{array}{l} \text{Observed: } 8.72 \text{ e13} - 8.60 \text{ e13} = 0.12 \text{ e13} \\ \text{Big gap} \quad \quad \quad \approx 12 \text{ e11 Hz } \checkmark \\ \text{Little gap} \quad \quad \quad \approx 6 \text{ e11 Hz } \checkmark \end{array}$$