

Vibrational - Rotational Spectra

$$E_{n,l} \approx E_c + \left(n - \frac{1}{2}\right) h\nu + \frac{l(l+1)\hbar^2}{2I}$$

$$\Delta l = \pm 1$$

$$\Delta n = \pm 1$$

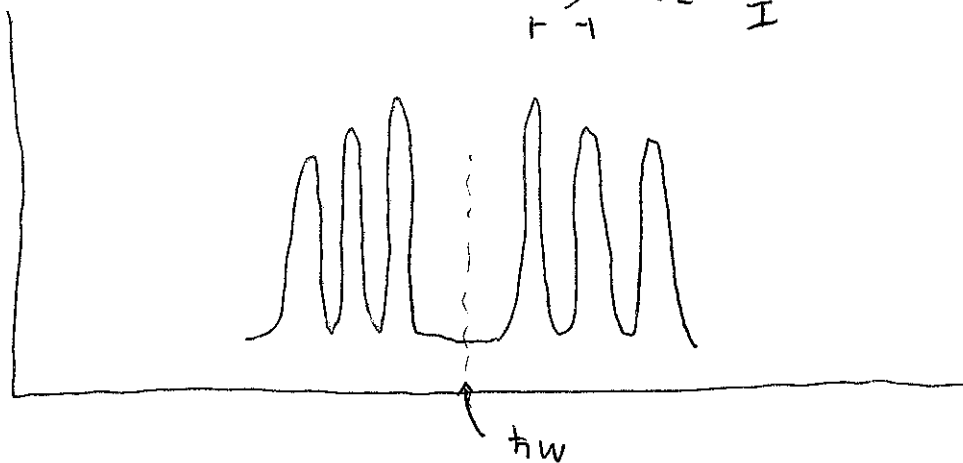
$$n=1 \rightarrow n=2$$

$$E_{\gamma} = E_{2,l+1} - E_{1,l} = E_c + \left(2 - \frac{1}{2}\right) h\nu + \frac{(l+1)(l+2)\hbar^2}{2I} - \left[E_c + \left(1 - \frac{1}{2}\right) h\nu + \frac{l(l+1)\hbar^2}{2I} \right] = h\nu + \frac{(l+1)\hbar^2}{I} \quad \left. \vphantom{E_{\gamma}} \right\} l \rightarrow l+1$$

$$E_{\gamma} = E_{2,l-1} - E_{1,l} = E_c + \left(2 - \frac{1}{2}\right) h\nu + \frac{(l-1)l\hbar^2}{2I} - \left[E_c + \left(1 - \frac{1}{2}\right) h\nu + \frac{l(l+1)\hbar^2}{2I} \right] = h\nu - \frac{l\hbar^2}{I} \quad \left. \vphantom{E_{\gamma}} \right\} l \rightarrow l-1$$

$$\Delta E = \frac{\hbar^2}{I}$$

Absorption



Electronic-Vibrational Spectra

\vec{J} - total angular momentum - electronic + rotational

$$E_{\text{tot}} \approx E_e + \left(n - \frac{1}{2}\right) \hbar \omega + \frac{j(j+1) \hbar^2}{2I} + \frac{m_j^2 \hbar^2}{2I_e}$$

$$\Delta m_j = \pm 1, 0$$

$$\Delta j = \pm 1, 0$$

$$\text{if } m_j = \Delta m_j = 0$$

$$\text{or } \Delta j = \pm 1$$

no restriction on n

Absorption from δ Ophiuchi



O
earth

gas containing
CN molecule

photons are absorbed by CN $j=0$, and $j=1$

$$\lambda_0 = 387.5 \text{ nm} \quad j=0$$

$$\lambda = \lambda_0 + 0.061 \text{ nm} \quad j=1$$

$$\frac{n_1}{n_0} = \frac{1}{4}$$

Some energy source must be populating $j=1$ state

Assume there is some temperature

$$\frac{n_1}{n_0} = \frac{(2j+1) e^{-E_1/KT}}{(2j+1) e^{-E_0/KT}} = 3 e^{-\Delta E/KT} = \frac{1}{4}$$

$$\Delta E = E_1 - E_0$$

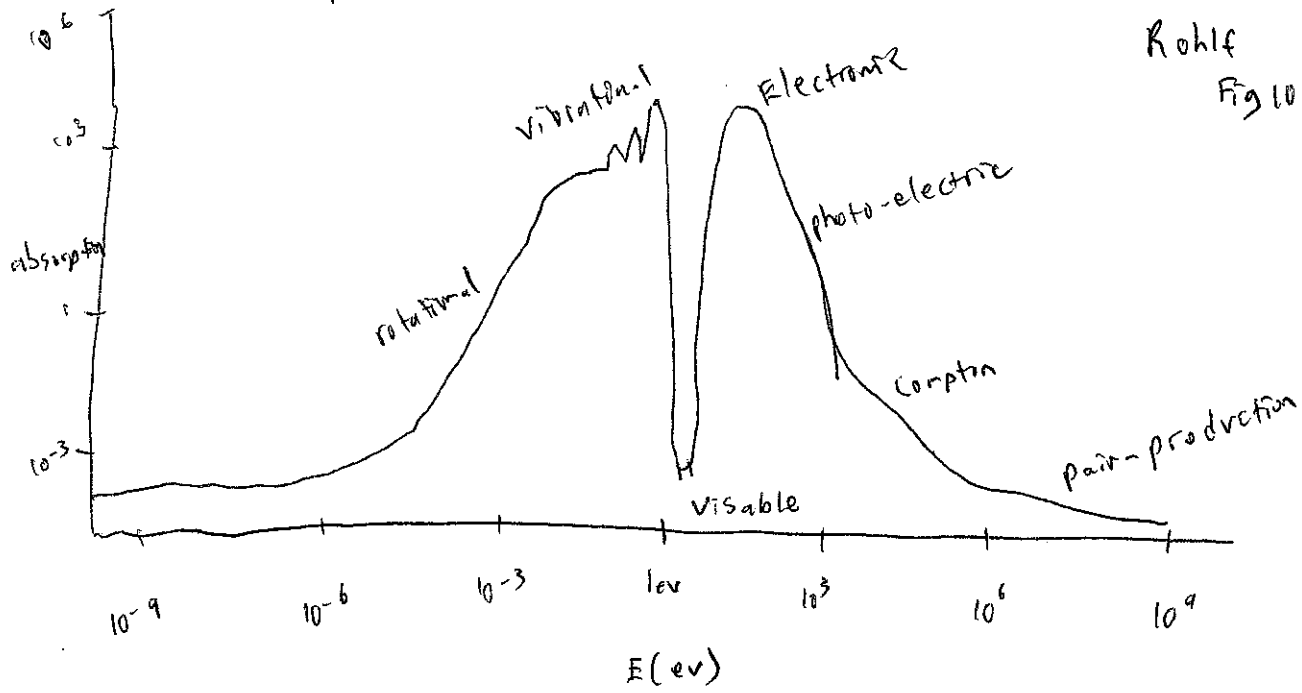
$$\frac{\Delta E}{KT} = \ln(12)$$

$T \approx 2.3 \text{ K}$ ← space has some background temperature!

Now know this is cosmic microwave background

Absorption spectrum of water

Rohlf
Fig 10-15



In class problem:

O_2 has $r = 0.12 \text{ nm}$

$$Z = 8$$

$$A = 16$$

$$f = 4.7 \times 10^{-13} \text{ Hz}$$

what are the vibrational and rotational energies in eV?

draw the $n=1 \rightarrow n=2$ absorption spectra