Rotational energy $E_\ell = \frac{\hbar^2}{2\mu r_0^2}\ell(\ell+1)$

$$\Delta E_\ell = E_\ell - E_{\ell-1} = \frac{\hbar^2}{2\mu r_0^2}\ell \approx \frac{m_e}{M}\underbrace{\frac{\hbar^2}{2\mu_e r_0^2}}_{E_R} = \frac{m_e}{M}E_R$$

Hierarchy of energies

Electron excitation $\Delta E \sim E_R$ (a few - tens of eV)

Vibrational excitation $\hbar\omega_0 \sim \sqrt{\frac{m_e}{M}}E_R$

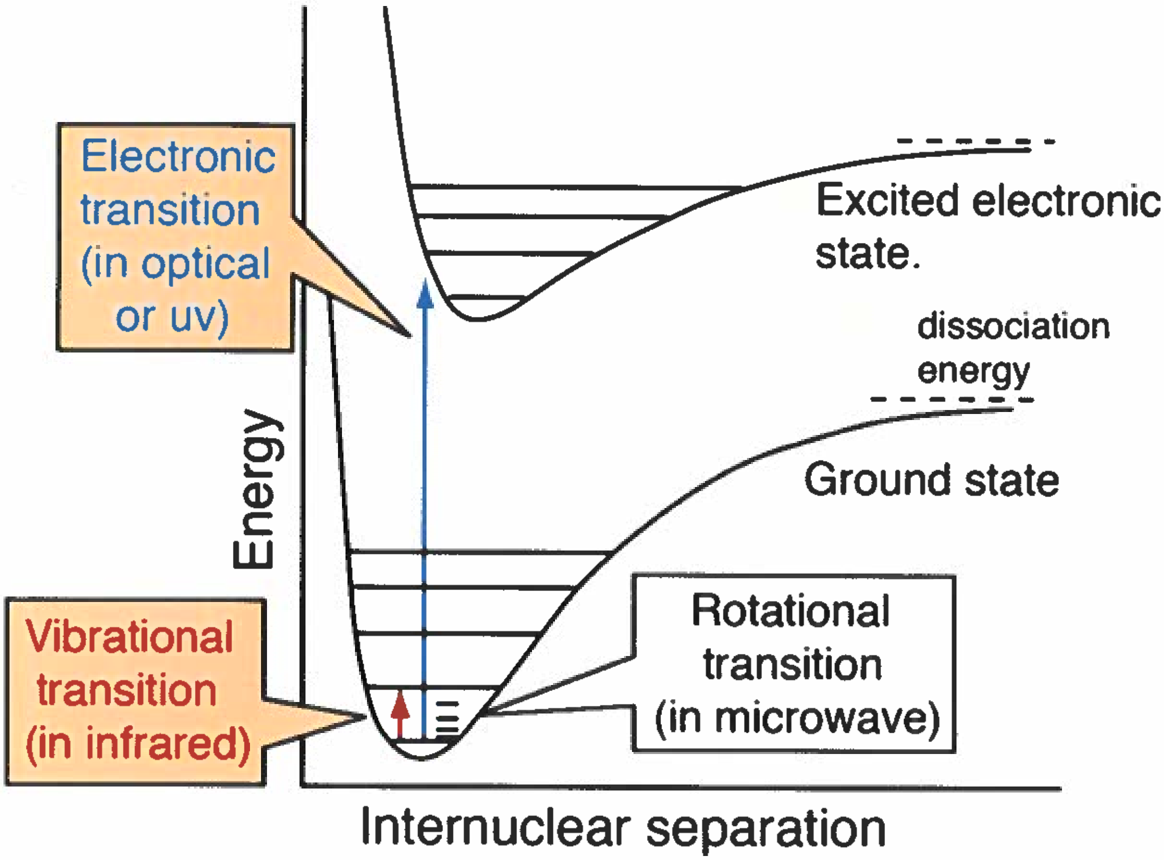
$$m_e = 9.1 \cdot 10^{-31}\ \text{kg} \qquad \frac{m_e}{M} \lesssim 10^{-4}$$

$$M \sim m_{Na} = 3.8 \cdot 10^{-26}\ \text{kg}$$

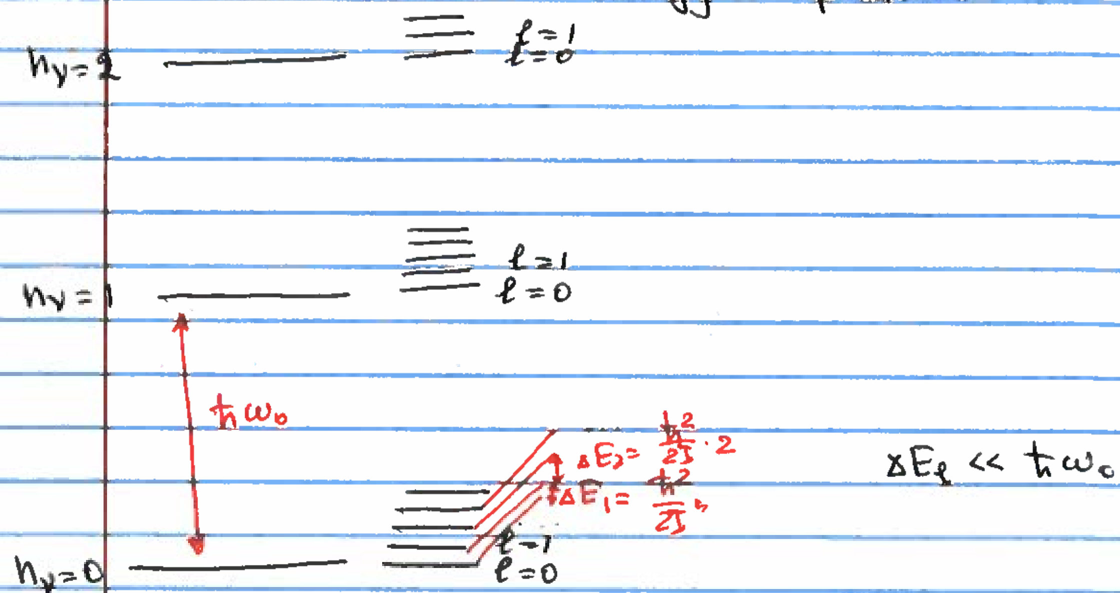
$$\hbar\omega_0 \sim 10^{-2}E_R \sim 0.1\ \text{eV}$$

Rotational excitation $\Delta E_\ell \approx \ell \cdot \frac{m_e}{M}E_R \sim 10^{-4}E_R$

$$\Delta E_\ell \sim 10^{-4}E_R = 0.001\ \text{eV} \sim 1\ \text{meV}$$


Electronic transition (in optical or uv)
Excited electronic state.
dissociation energy
Ground state
Energy
Vibrational transition (in infrared)
Rotational transition (in microwave)
Internuclear separation

Rotovibrational energy spectrum



What are possible state for an ~~atom~~ molecule at the room temperature?

Level population (i.e. the probability of an atom / molecule to occupy the particular state) is given by the Boltzmann law

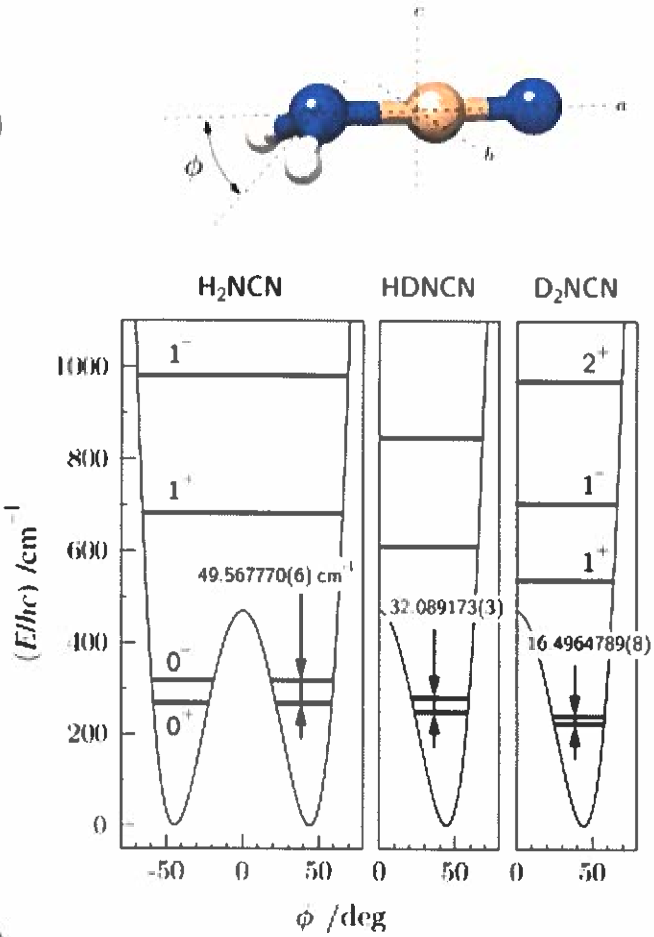
$$n(E) = \text{degeneracy}(E) \cdot e^{-E/k_B T}$$

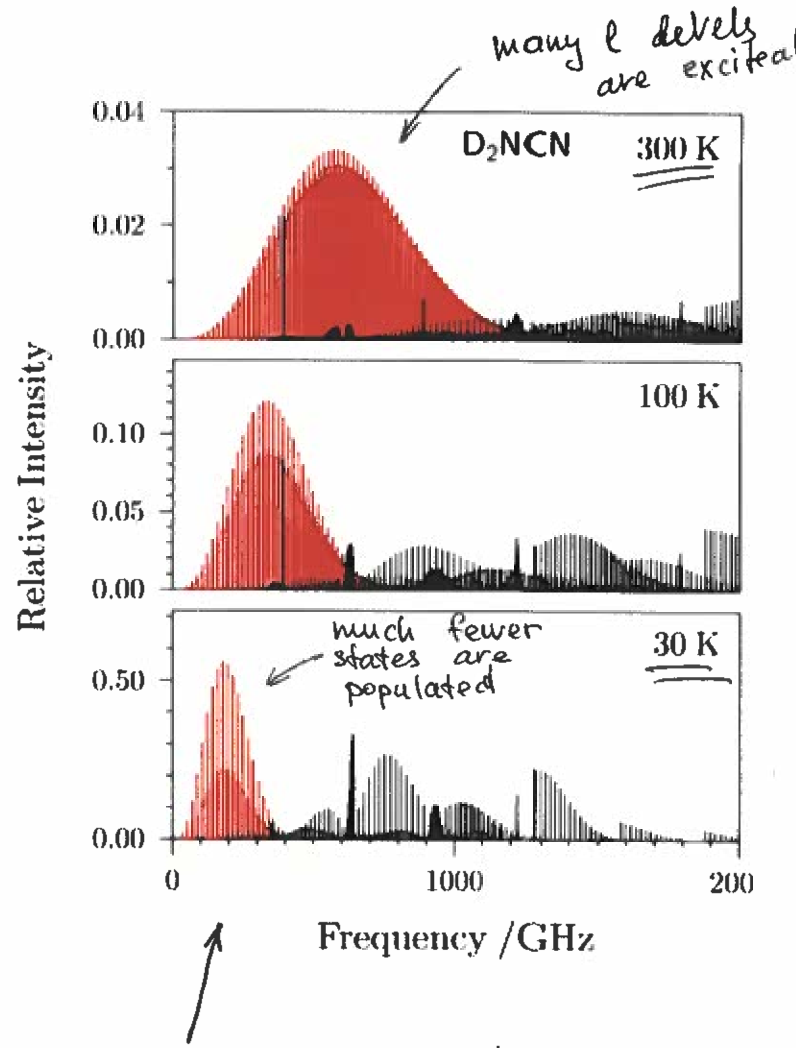
Room temperature $k_B T \sim 0.03$ eV

electron excitation	vibration exitation	rotation exitation
10 eV	0.1 eV	0.001 eV

Thermal energy $k_B T = 0.03$ eV

Excited electronic and vibrational states are <u>empty</u>, but rotational states are occupied.





For an individual line

Absorption $\propto$ population of a bottom level

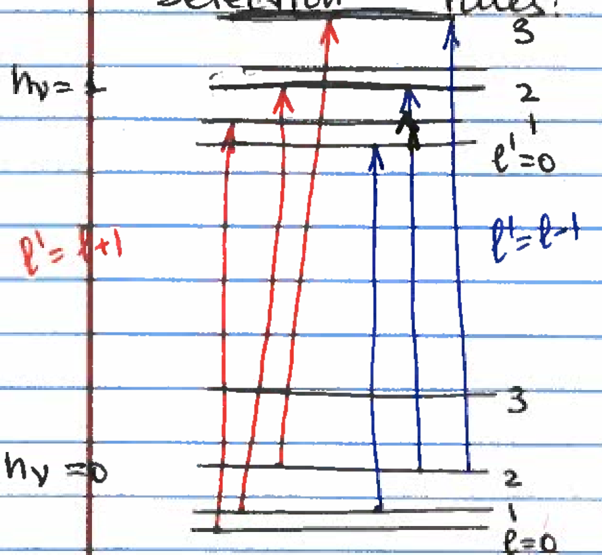
Population $\propto e^{-E_l/k_BT}$

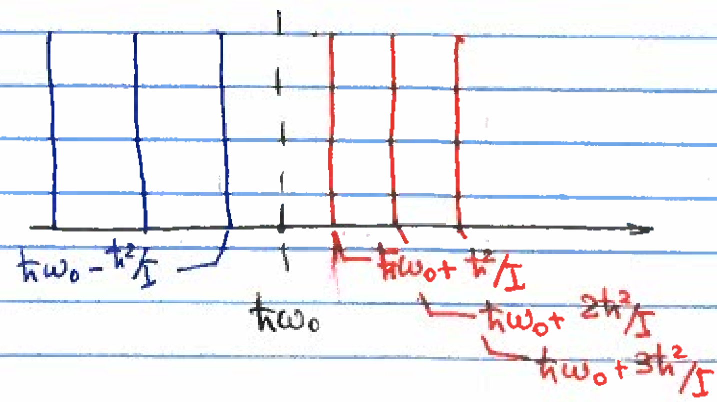
The lower the temperature the less molecules are in the state with higher l

Molecular spectroscopy → transitions b/w various rotational and vibrational levels

Selection rules: $\Delta n_v = \pm 1$

$\Delta \ell = \pm 1$





$\Delta \ell = +1$

Transition frequency: $E_{ground, \, n_v=0, \ell} = \frac{1}{2}\hbar\omega_0 + \frac{\hbar^2}{2I}\ell(\ell+1)$

$E_{excited, \, n_v=1, \ell'=\ell+1} = \frac{3}{2}\hbar\omega_0 + \frac{\hbar^2}{2I}(\ell+1)(\ell+2)$

$$\Delta E_{\ell\to\ell+1} = \hbar\omega_0 + \frac{\hbar^2}{I}(\ell+1) \qquad \ell = 0, 1, \ldots$$

$\Delta \ell = -1$

Transition frequency: $E_{excited, \, n_v=1, \ell'=\ell-1} = \frac{3}{2}\hbar\omega_0 + \frac{\hbar^2}{2I}(\ell-1)\ell$

$$\Delta E_{\ell\to\ell-1} = \hbar\omega_0 - \frac{\hbar^2}{I}\cdot\ell \qquad \ell = 1, 2 \ldots$$

The absorption spectrum consists of an equidistant set of lines separated by $\Delta E = \hbar^2/I$ around frequency ω_0

However the line at exactly ω_0 is missing!

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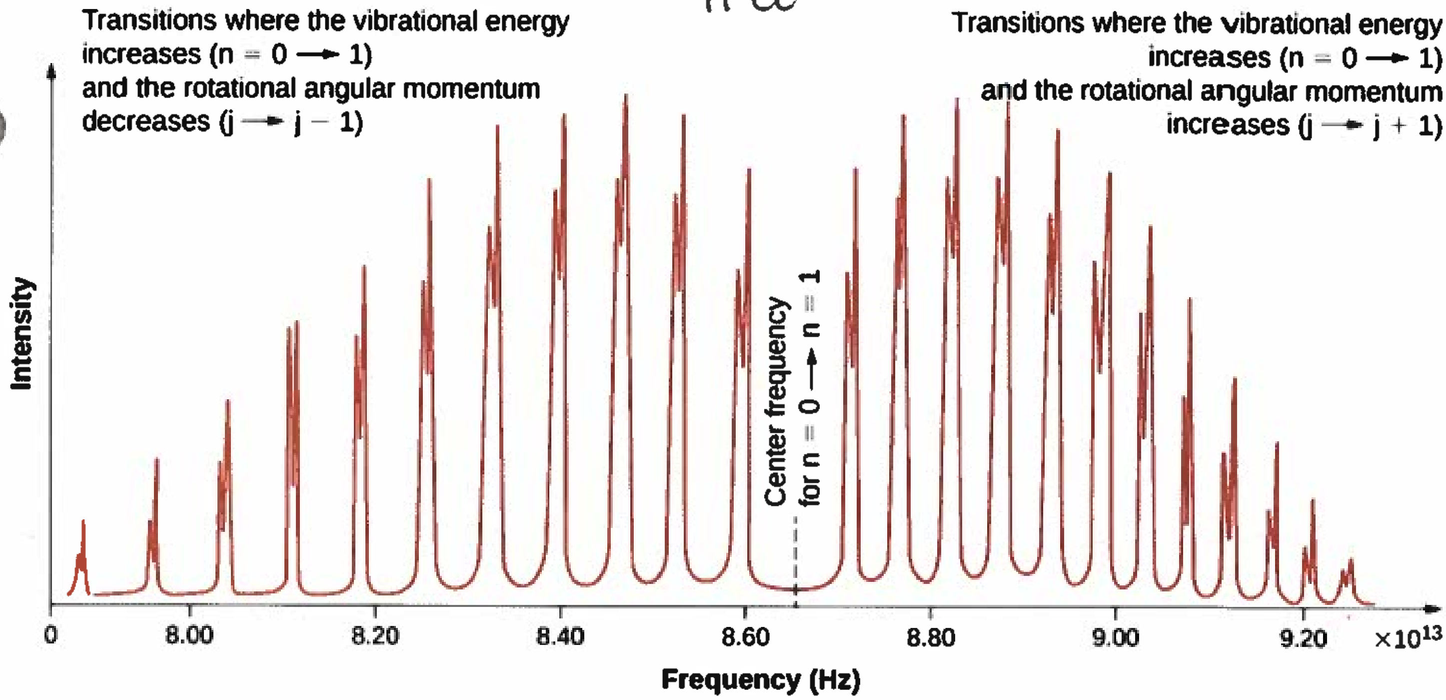
Transitions where the vibrational energy increases (n = 0 → 1) and the rotational angular momentum decreases (j → j − 1)
Transitions where the vibrational energy increases (n = 0 → 1) and the rotational angular momentum increases (j → j + 1)
Center frequency for n = 0 → n = 1
Intensity
0
8.00
8.20
8.40
8.60
8.80
9.00
9.20
×10¹³
Frequency (Hz)