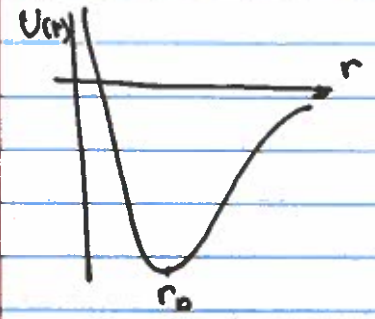
Vibrations of molecules



near equilibrium

$$U(r) \approx U(r_0) + \frac{1}{2}\frac{d^2U}{dr^2}(r-r_0)^2 + \dots$$

$$= U(r_0) + \underbrace{\frac{1}{2}\mu\omega_0^2(r-r_0)^2}_{\text{simple harmonic oscillator}}$$

$$E_{n_\nu} = \hbar\omega_0\left(n_\nu + \frac{1}{2}\right)$$

Rotovibrational spectrum (rotation + vibrations)

$$E_{n_\nu,\ell} = \hbar\omega_0\left(n_\nu+\frac{1}{2}\right) + \frac{\hbar^2\ell(\ell+1)}{2I}$$

Hierarchy of energe scales $\hbar\omega$ vs $\frac{\hbar^2}{2I}$

vibrations: $M\omega^2 \sim \frac{d^2U}{dr^2} \sim \frac{U}{a^2} \sim \frac{ke^2/a}{a^2} \sim \frac{ke^2}{a^3} \sim m_e E_R^2$

E_R - Rydberg energy $E_R = 13.6\,eV$

$$\hbar\omega_0 \sim \hbar\sqrt{\frac{m_e}{M}}\,E_R \lesssim 10^{-2}\cdot E_R \sim 0.1\,eV$$

rotations $I \sim Ma^2$

$$\frac{\hbar^2}{Ma^2} \sim \frac{m_e}{M_R}E_R \sim 10^{-4}E_R \sim 1\,meV$$

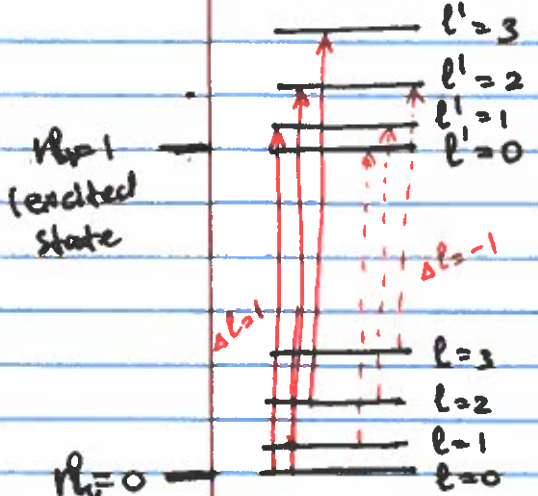
Average thermal energy at 300k $E_{th} \sim 0.03\,eV$

$\hbar\omega_0 > E_{th}$, not enough to excite vibrations

but

$E_{th} > \hbar^2/I$, rotational motion is possible

Transitions



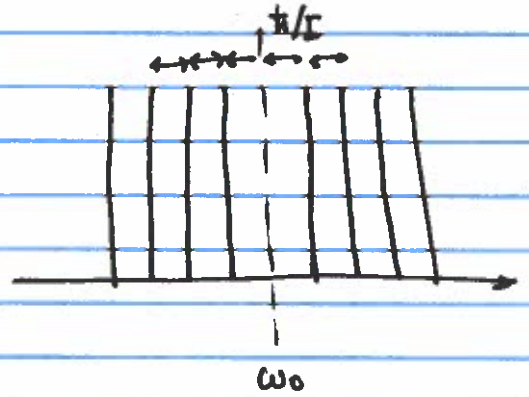
Selection rules

$\Delta l = 1$ or -1

$\Delta n = 1$ or -1

$\Delta l = 1$ branch $\quad \hbar\omega_{+l} = \hbar\omega_0 + \frac{\hbar^2 l(l+1)}{I} \qquad l = 0, 1, \ldots$

$\Delta l = -1$ branch $\quad \hbar\omega_{-l} = \hbar\omega_0 - \frac{\hbar^2 l}{I} \qquad l = 1, 2, \ldots$



The transition with $\omega = \omega_0$ is missing, since $l=0 \rightarrow l'=0$ transition is impossible

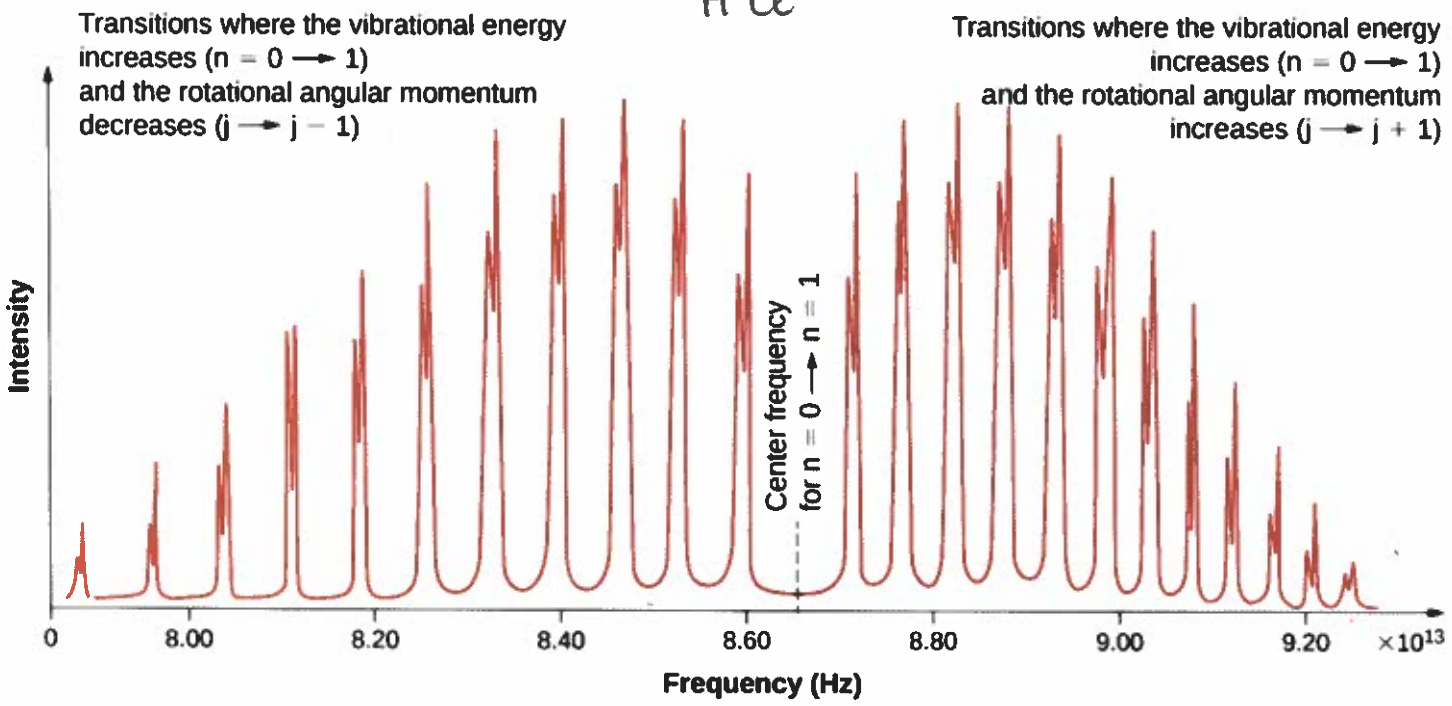
More accurate molecular potential

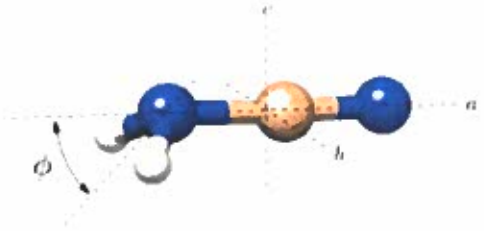
Morse potential

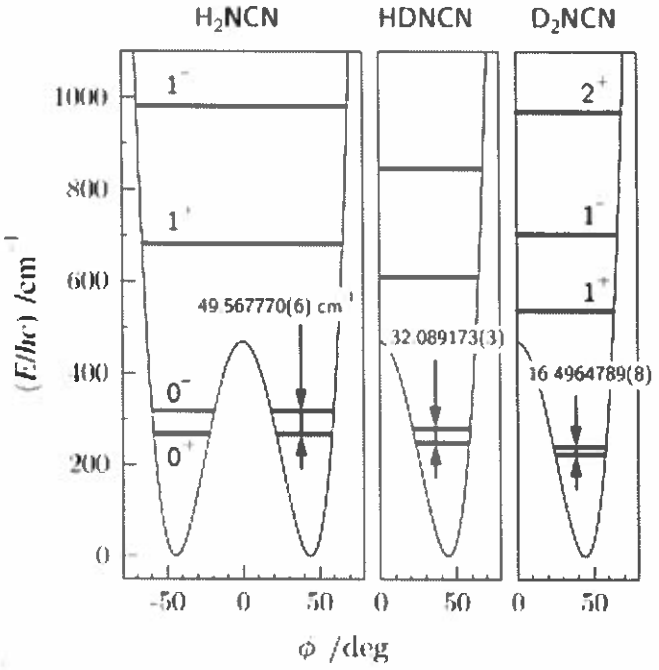
$$U_{Morse} = D_e \left(1 - e^{-a(r-r_e)}\right)^2$$

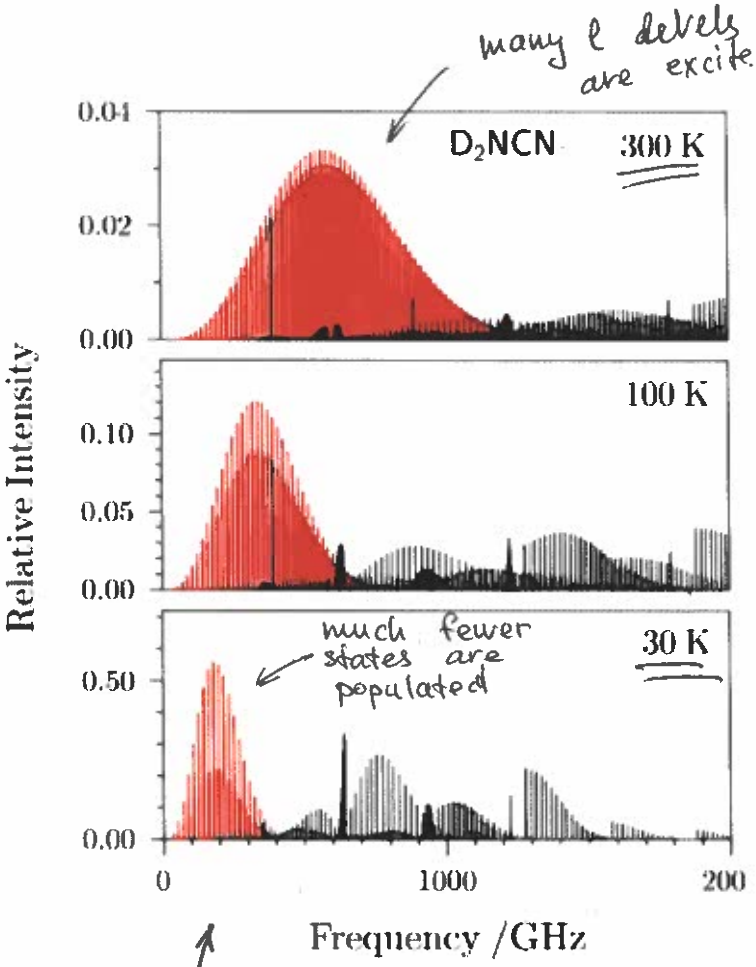
$$E_n = \hbar\omega_e\left(n+\tfrac{1}{2}\right) - \frac{\left[\hbar\omega_0\left(n+\tfrac{1}{2}\right)\right]^2}{4D_e}$$

H Cl


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)
Intensity
Center frequency for n = 0 → n = 1
0
8.00
8.20
8.40
8.60
8.80
9.00
9.20
×10^13
Frequency (Hz)







For an individual line

Absorption $\propto$ population of a bottom level

population $\propto e^{-E\ell/k_BT}$

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