

2F4Y: Molecular Structure & Energy Levels

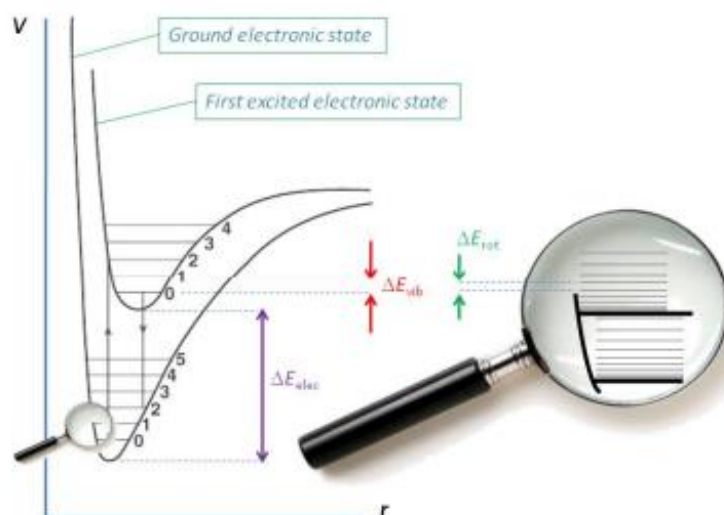
Fundamentals of Rotational & Vibrational Spectroscopy

Revision Helpsheet

Introduction to Molecular Spectroscopy

$$\Delta E = h\nu$$

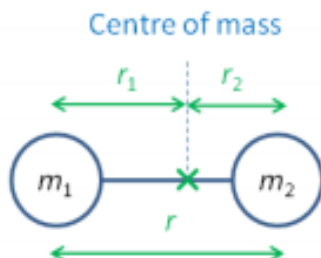
$$E = E_{elec} + E_{vib} + E_{rot}$$



Rotational Spectroscopy

Diatomic and Linear Polyatomic Molecules

$$m_1 r_1 = m_2 r_2$$

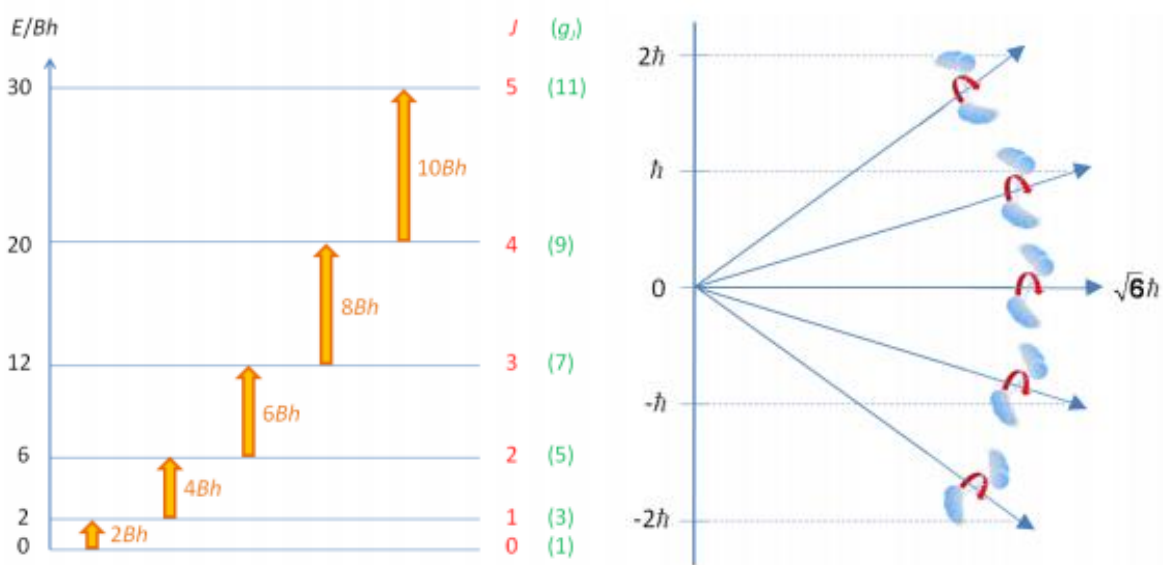


$$I = m_r r^2$$

$$m_r = \frac{m_1 m_2}{m_1 + m_2}$$

$$E = BhJ(J + 1)$$

$$B = \frac{h}{8\pi^2 I}$$

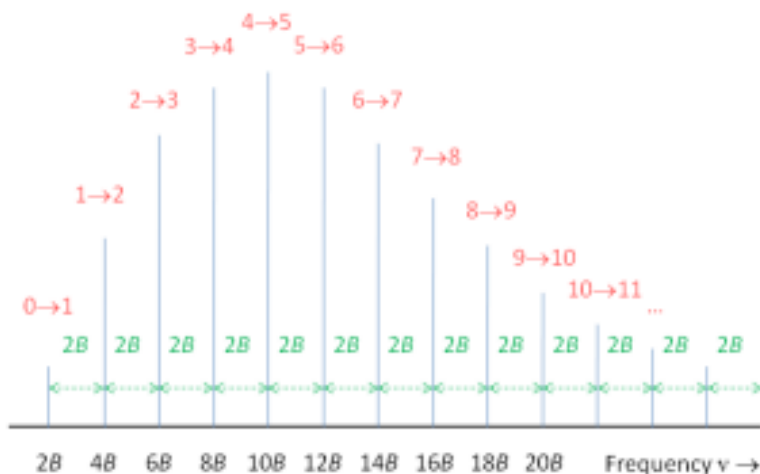


$$g_J = (2J+1)$$

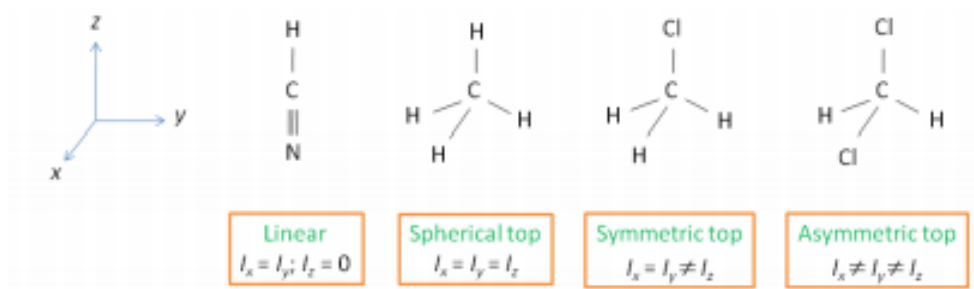
Rotational spectrum requires permanent dipole moment

$$\Delta J = \pm 1$$

The spacing between absorption lines in rotational spectra = 2B



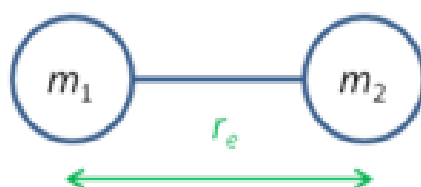
Non-Linear polyatomic molecules



Vibrational Spectroscopy

Diatomic Molecules

Simple harmonic oscillator



$$f = -k(r - r_e)$$

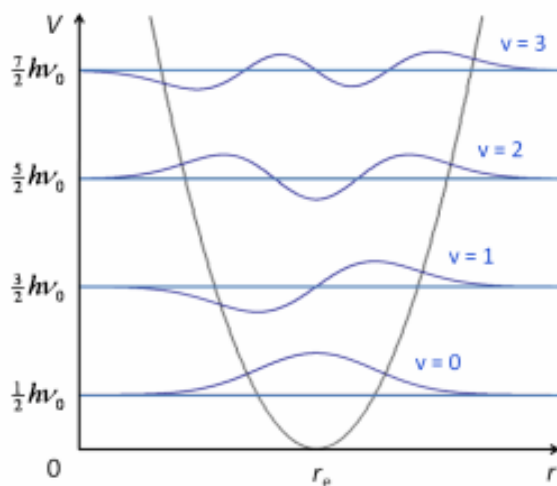
Classical frequency of vibration

$$\nu_0 = \frac{1}{2\pi} \sqrt{\frac{k}{m_r}}$$

$$E = \left(\nu + \frac{1}{2} \right) h\nu_0$$

$$\Delta\nu = \pm 1$$

For the transition to be allowed, the dipole moment of the molecule must change during the vibration

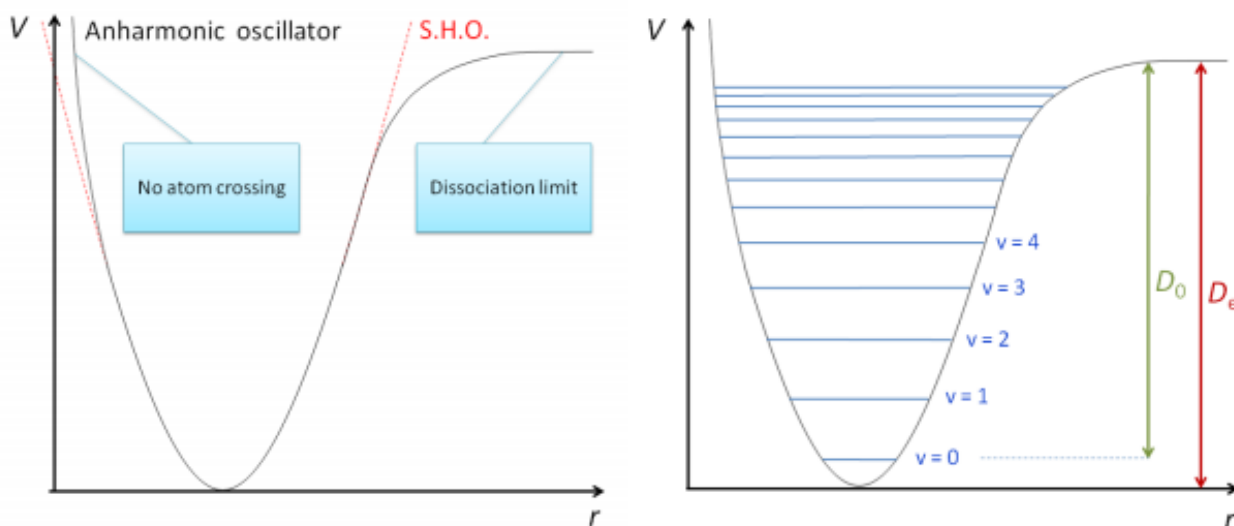


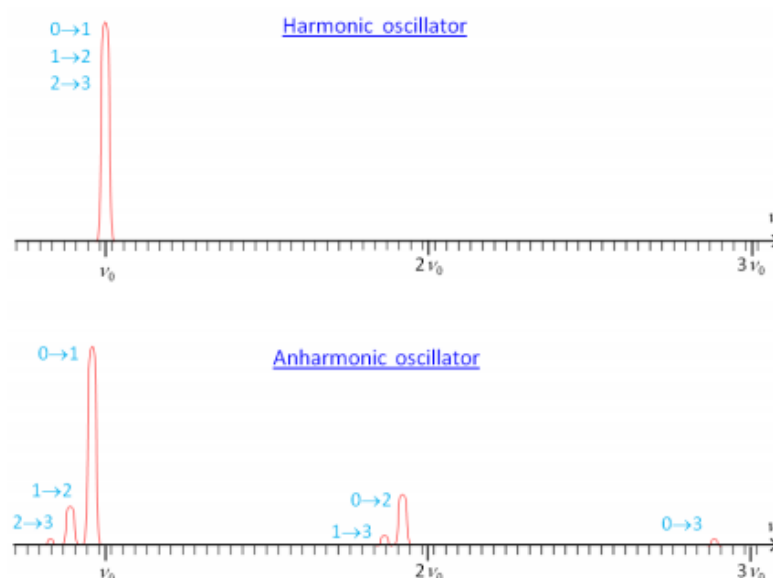
For the $v = 0 \rightarrow 1$ transition

$$\nu = \nu_0$$

The absorbed frequency of light equals the classical frequency of molecular vibration

Anharmonic Oscillator





0 → 1

Fundamental

1 → 3, 0 → 2, 0 → 3

Overtones

1 → 2, 2 → 3

Hotbands

$$E = \left[\left(v + \frac{1}{2} \right) - x_e \left(v + \frac{1}{2} \right)^2 \right] h\nu_0$$

x_e is the anharmonicity constant

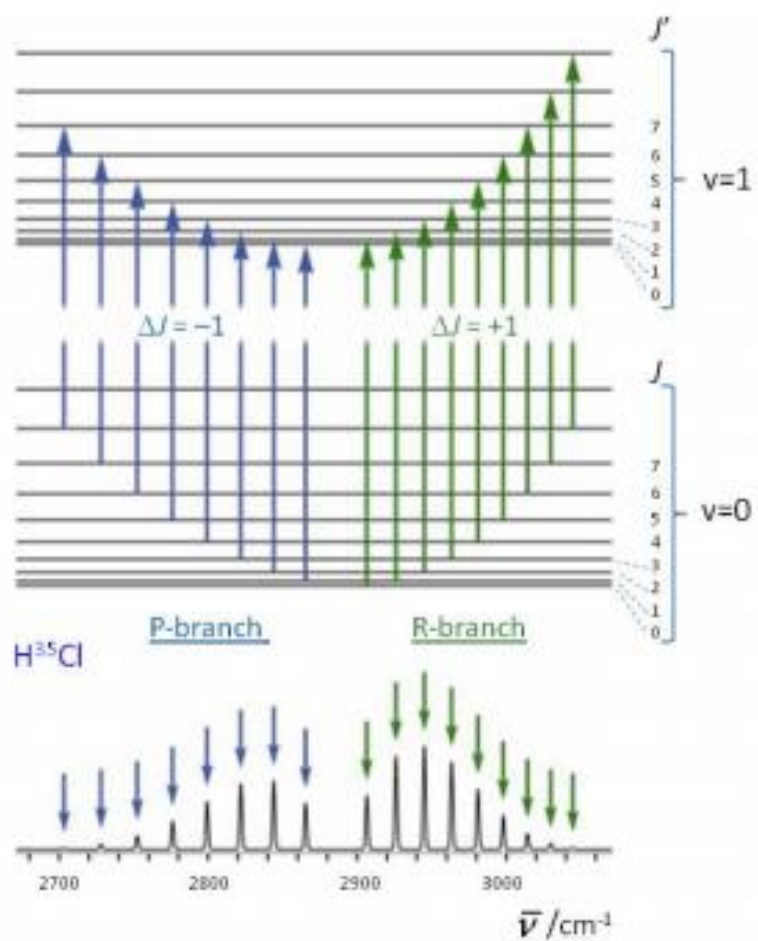
How to use this equation to calculate frequencies of transitions (ie $\nu_{0 \rightarrow 1}$):

- To simplify, divide both sides of the equation by h . Then you can express a vibrational energy level as a frequency

$$v = \left[\left(v + \frac{1}{2} \right) - x_e \left(v + \frac{1}{2} \right)^2 \right] \nu_0$$

- Calculate v for the higher energy state (E.g. $v=1$) and then subtract v for the lower energy state (E.g. $v=0$)

$$\nu_{0 \rightarrow 1} = \left\{ \left[\frac{3}{2} - \left(\frac{3}{2} \right)^2 x_e \right] - \left[\frac{1}{2} - \left(\frac{1}{2} \right)^2 x_e \right] \right\} \nu_0 = \nu_0 (1 - 2x_e)$$

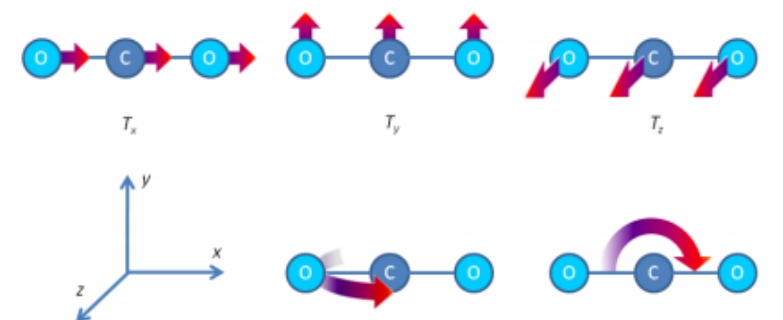


Polyatomic Molecules

Any polyatomic has $3N$ (n =co-ordinates) degrees of freedom

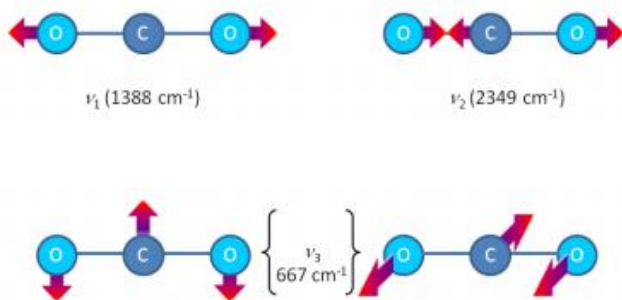
For a **linear** molecule

- 3 translational degrees of freedom
- 2 rotational degrees of freedom



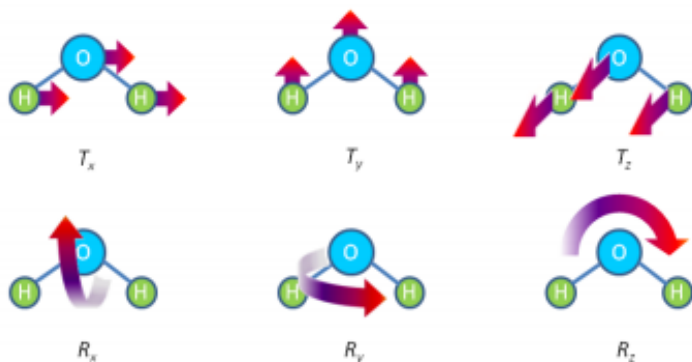
Therefore **$3N-5$** vibrational degrees of freedom remaining

$(3 \times 3) - 5 = 4$ vibrations remaining



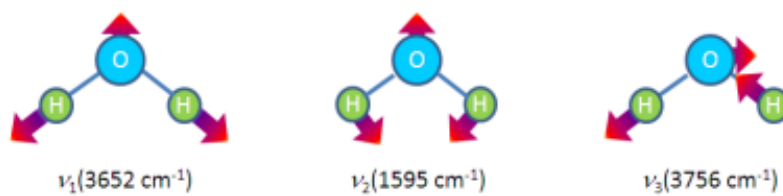
For a **non-linear** molecule

- 3 translational degrees of freedom
- 3 rotational degrees of freedom



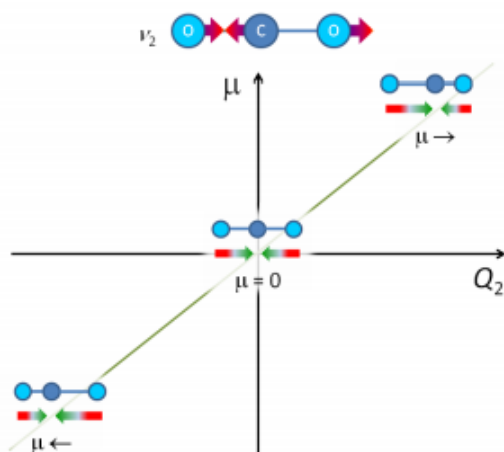
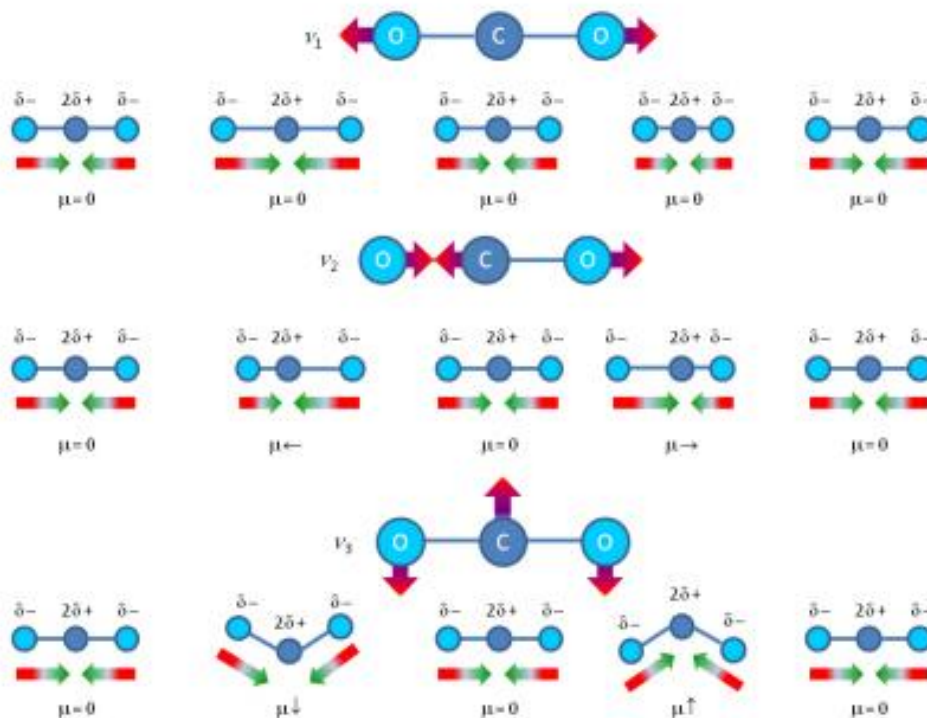
Therefore **3N-6** vibrational degrees of freedom remaining

$(3 \times 3) - 6 = 3$ vibrations remaining



$$E_i = \left(v_i + \frac{1}{2} \right) h\nu_i$$

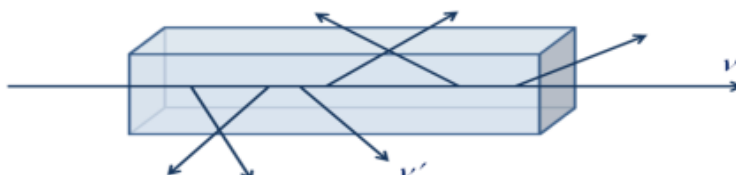
If the dipole moment changes in the course of a given vibration, as the molecule passes through its equilibrium configuration, that vibration will be active in the infra-red spectrum



Raman Spectroscopy

Result of scattering rather than absorption

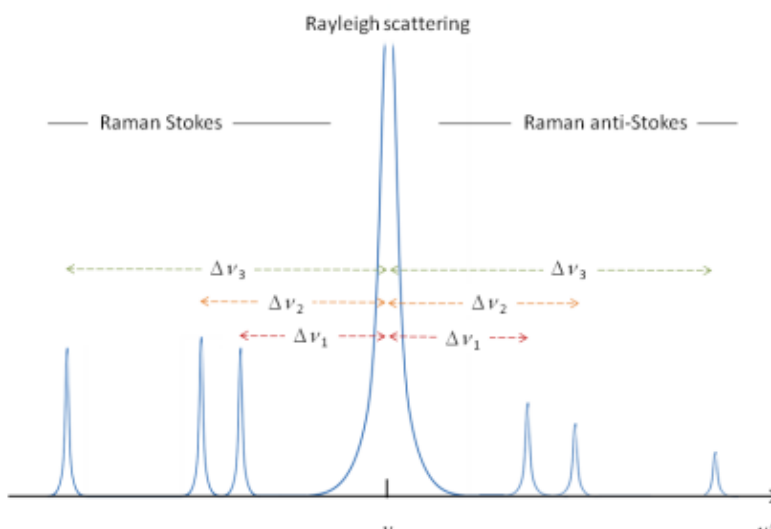
Most of scattered light has the same frequency ν' as the incident light ν : **Rayleigh Scattering**: $\nu' = \nu$.



Rayleigh Scattering responsible for blue sky and redness of the sun at dawn and sunset – light at blue end of spectra more effectively scattered than red



$$\mu_{induced} = \alpha E$$

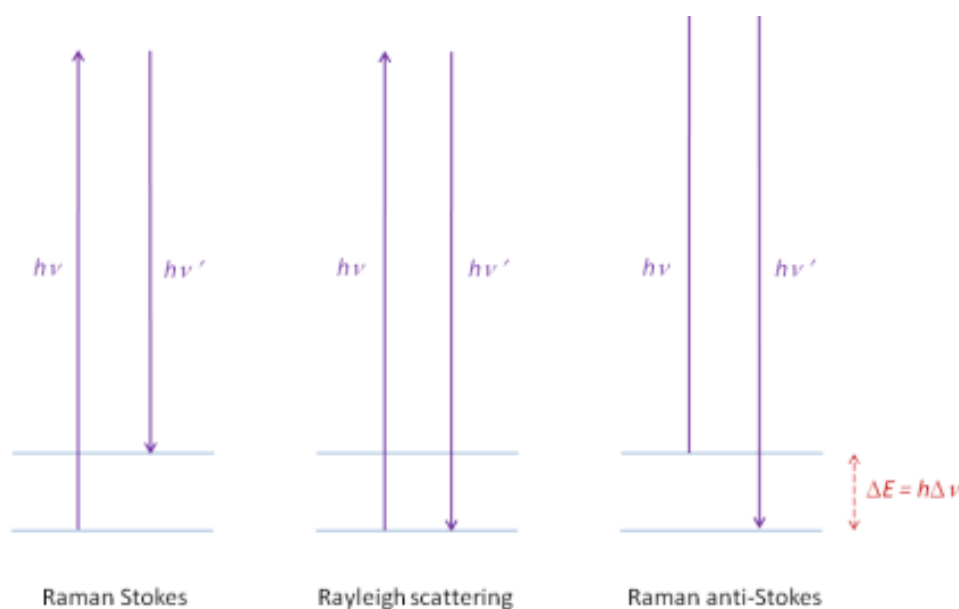


Raman Stokes:

$$\nu' = \nu - \Delta\nu$$

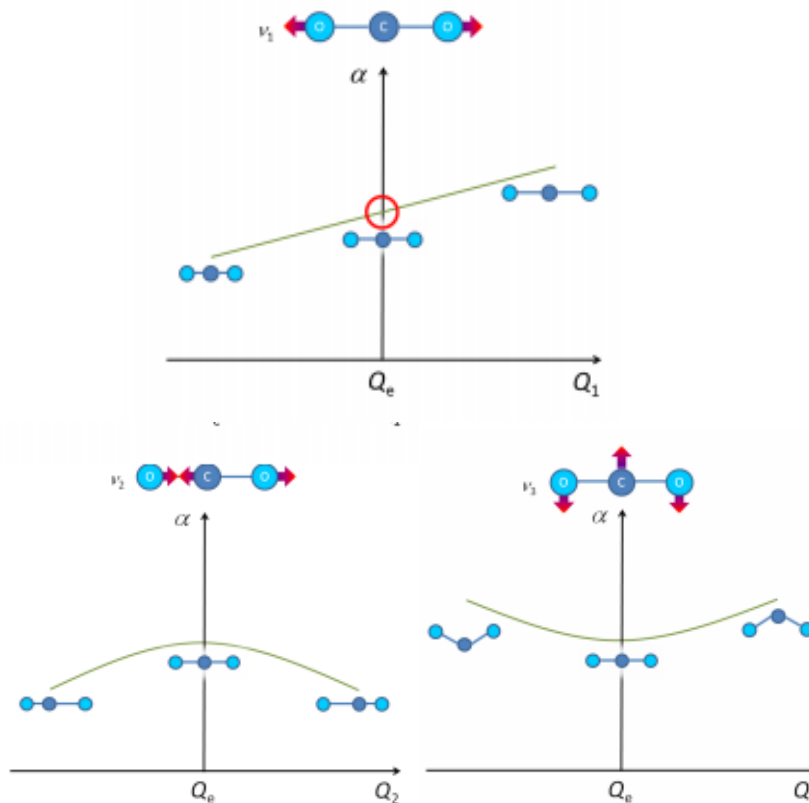
Raman Anti-Stokes:

$$\nu' = \nu + \Delta\nu$$



$$M_{\nu\nu} \propto \left(\frac{da}{dQ} \right) \Big|_{Q_e}$$

If the polarizability changes in the course of a given vibration, as the molecule passes through its equilibrium configuration, that vibration will be active in the Raman spectrum



Mutual exclusion rule for centrosymmetric molecules

Vibrations allowed in the spectrum are Raman-forbidden and vice versa

IR → ~~RAMAN~~

RAMAN → ~~IR~~

Raman-active modes must be of gerade (g) character

IR-active modes must be of ungerade (u) character

