# Raman Spectra

## pure rotational Raman spectra of Diatomic molecules

The selection rule for pure rotational raman spectra of a diatomic molecules are

$$\Delta J = 0, \pm 2$$

when $\Delta J = 0$, the scattered light has the same frequency as the incident radiation resulting Rayleigh scattering.

The rotational energy expression of a rigid rotator in terms of rotational term is given by

$$F(J) = BJ(J+1)$$

The difference of terms (or wave numbers) between two levels is

[J → Rotational quantum Numbe

$$\bar{\nu}_{J' \to J} = F(J') - F(J) = BJ'(J+1) - BJ(J+1)$$

$$= B[J'(J'+1) - J(J+1)]$$

when $\Delta J = +2$, $J' - J = 2$ or $J' = J+2$, the Raman shifts are given by

$$\bar{\nu}_{J+2 \to J} = B[(J+2)(J+3) - J(J+1)]$$

$$= (4J+6)B; \quad J = 0, 1, 2$$

Similarly when $\Delta J = -2$, $J' - J = -2$, $J' = J-2$, the Raman shifts are given by

$$\bar{\nu}_{J \to J-2} = B[(J-2)(J-1) - J(J+1)]; \quad J = 2, 3, 4$$

$$= -B(4J-2)$$

Readjusting the values of J we have

$$\bar{\nu}_{J \to J-2} = -B[4(J+2)-2]; \quad J = 0, 1, 2$$

$$= -B(4J+6)$$

Combining $\Delta J = \pm 2$, we have the Raman shift

$$\Delta\bar{\nu}_R = \pm B(4J+6)$$

Since the wavenumber of the Raman lines $= \bar{\omega}_{ex} \pm \Delta\bar{\nu}_R$, the Raman lines will appear at wavenumber given by the expression

$$\boxed{\bar{\nu} = \bar{\omega}_{ex} \pm B(4J+6)}$$

$\bar{\omega}_{ex}$ → wavenumber of incident radiation (Rayleigh lines)

(−) negative sign → stokes line. ($\bar{\nu} < \bar{\omega}_{ex}$)

(+) positive sign → antistokes line ($\bar{\nu} > \bar{\omega}_{ex}$)

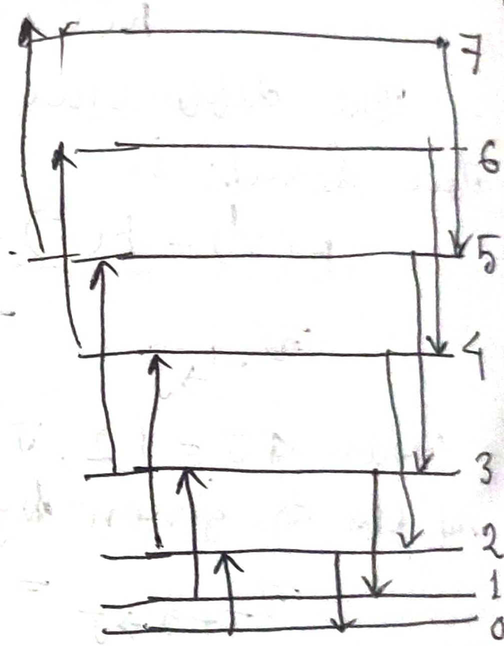
The expected pure rotational raman spectrum

when $J=0$ $\quad \bar{\nu} = \bar{\omega}_{ex} \pm 6B$

$=1$ $\quad \bar{\nu} = \bar{\omega}_{ex} \pm 10B$

$=2$ $\quad \bar{\nu} = \bar{\omega}_{ex} \pm 14B$

$=3$ $\quad \bar{\nu} = \bar{\omega}_{ex} \pm 18B$



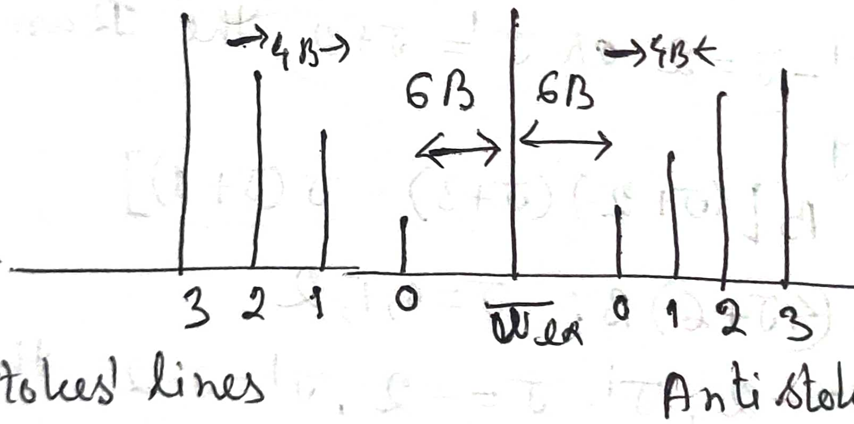


Fig: The Rotational energy level of a diatomic molecule

Q. Which of the following molecules will show pure rotational Raman spectrum: $H_2$, $HCl$, $CO$, $CH_4$, $CH_3Cl$, $H_2O$, $N_2O$, $C_2H_6$, $SF_6$

⇒ $H_2$, $CH_4$, $SF_6$ doesnot show rotational raman spectra ∵ because there is no change in polarizability in these molecules.

# Vibrational Raman spectra of Diatomic Molecules

The selection rules for the Vibrational Raman spectra are the same as those for pure vibrational spectra i.e

$$\Delta v = \pm 1, \pm 2 \ldots$$

The energy levels of the anharmonic vibrating diatomic molecules in terms of wavenumber are

$$G(v) = (v + \tfrac{1}{2})\overline{\omega_e} - (v + \tfrac{1}{2})^2 \overline{\omega_e} x_e$$

Considering, only $v=0$ to $v=1$ transition, the energy change in fundamental vibration band is given by

$$\overline{\nu}_{0 \to 1} = \overline{\omega_e}(1 - 2x_e)$$

The Raman lines observed corresponding to the fundamental vibration are —

$$\overline{\nu} = \overline{\omega_{ex}} \pm \overline{\omega_e}(1 - 2x_e)$$

$\overline{\omega_{ex}}$ ⟶ frequency (in $cm^{-1}$) of the excitation radiation

(+) ⟶ antistokes lines

(−) ⟶ Stokes lines

$v=0$ level is maximum and the transition from $v=0$ to a higher level results in Stokes lines, the intensities of stokes lines are more than tha of the antistokes lines. Similarly the intensit of overtone bands are also weak.