

Molecular Spectroscopy - Rotational Transitions

ASTR
300B

We define the principle axes of a molecule in the center of mass frame such that the moment of inertia tensor is diagonal:

$$\mathbf{I} = \begin{bmatrix} I_{xx} & 0 \\ 0 & I_{yy} \\ 0 & 0 & I_{zz} \end{bmatrix}$$

Label them as:

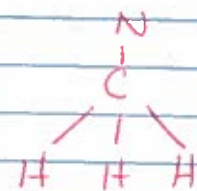
$$I_A \leq I_B \leq I_C$$

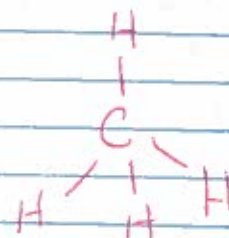
least \rightarrow greatest

4 Basic types of molecules:

LINEAR CO C=O $I_A = 0 \quad I_B = I_C$

Symmetric Top NH3  $I_A = I_B < I_C$ OBLATE

CH3CN  $I_A < I_B = I_C$ PROLATE

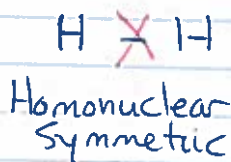
Spherical Top CH4  $I_A = I_B = I_C$

Asymmetric Top H2O  $I_A \neq I_B \neq I_C$

Most rotational transitions are via electric dipole transitions. For the matrix element to be non-zero $\langle \psi_i | \hat{\mu}_e | \psi_f \rangle \neq 0$

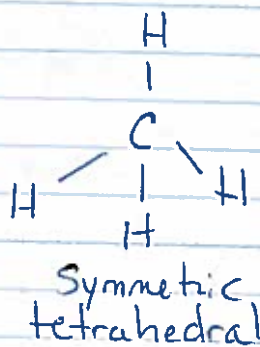
the molecule must possess a permanent electric dipole moment $\mu_e \neq 0$.

Examples:



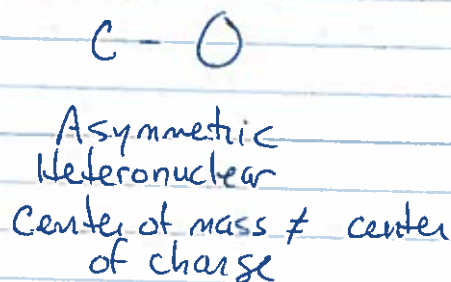
$\mu_e = 0$
↓

No electric dipole transitions!



$\mu_e = 0$

NO ED transitions!

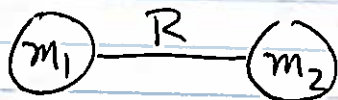


$\mu_e = 0.11 \text{ D}$

Typical value of $\mu_e \sim 1 \text{ Debye} \equiv 10^{-18} \text{ esu}\cdot\text{cm}$

Note $\vec{\mu}_e$ is a vector. For more complicated molecules (like asymmetric tops) we need to figure out along which axis $\vec{\mu}_e$ is oriented to determine selection rules for rotational transitions. (e.g. in H_2O $\vec{\mu}_e$ lies along b inertial axis)

The RIGID ROTOR



$$R = \text{CONST}$$

$$I = \frac{m_1 m_2}{m_1 + m_2} R^2 = \mu R^2$$

↑ reduced mass

Schrodinger's Equation: $\hat{H}\psi = E\psi$

$H = T + V$ ← set $V = 0$ for rigid rotor. (Real molecules have $V(r) \dots$)

Thinking classically $T = KE = \frac{1}{2} \frac{J^2}{I}$ ← angular momentum

$$\hat{H}\psi = \frac{1}{2I} \hat{J}^2 \psi = E\psi \quad \text{but} \quad \hat{J}^2 \psi = \hbar^2 J(J+1)\psi$$

$E = \frac{\hbar^2}{2I} J(J+1)$

 ← Note spacing of energy levels is quadratic in J !

Since $R = \text{const}$, the solutions $\psi = Y_{Jm_J}(\theta, \phi)$ just angular part
Spherical harmonics!

Traditionally, we define the "rotational constant" B such that

$E = hB J(J+1)$

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

Selection rules for electric dipole transitions dictate that for $\langle \psi_i | \hat{\mu}_e | \psi_f \rangle \neq 0 \Rightarrow \Delta J = \pm 1$ (pure rotational)

$$\nu_{J+1 \rightarrow J} = \frac{E_{J+1} - E_J}{h} = B \left[\frac{J^2 + 3J + 2}{(J+1)(J+2)} - \frac{J^2 + J}{J(J+1)} \right]$$

$$= B [2J + 2]$$

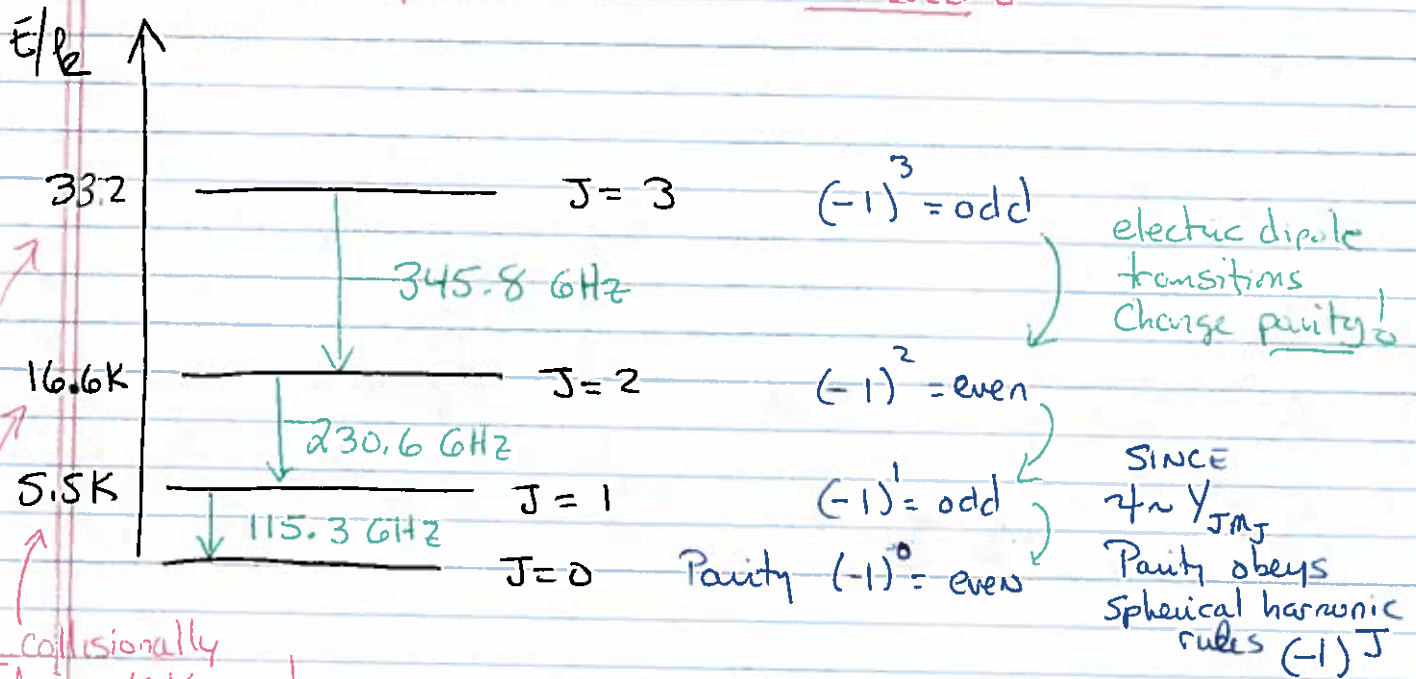
$$= 2B(J+1) \quad \text{LINEAR with } J!$$

Thus, the rotational spectrum is a simple linear "ladder" in frequency!

Heteronuclear Example: CO

$\mu_e = 0.11 D$

Electric dipole $\Delta J = \pm 1$ allowed!



easily collisionally excited in 10K gas!

Note the linear sequence 115, 230, 345, etc. GHz.
All observable from the ground with radio telescopes!

Einstein A_s : $A(01-0) \sim 7.2 \times 10^{-8} s^{-1}$
 $A(02-1) \sim 6.9 \times 10^{-7} s^{-1}$
 $A(03-2) \sim 2.5 \times 10^{-6} s^{-1}$

← low → in radio makes for "small" A values

$A \sim J^3$ for electric dipole, so rapid increase in A from 1-0 to 3-2, etc.