

Molecular Spectroscopy - Rotational Transitions

ASTR
300B

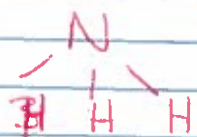
We define the principle axes of a molecule in the center of mass frame such that the moment of inertia tensor is diagonal:

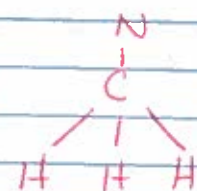
$$\mathbf{I} = \begin{bmatrix} I_{xx} & 0 \\ 0 & I_{yy} \\ 0 & 0 & I_{zz} \end{bmatrix}$$

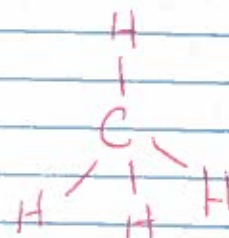
Label them as: $I_A \leq I_B \leq I_C$
 least \rightarrow greatest

4 Basic types of molecules:

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

Symmetric Top NH3  $I_A = I_B < I_C$ OBLATE

CH3CN  $I_A < I_B = I_C$ PROLATE

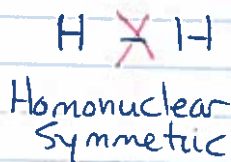
Spherical Top CH4  $I_A = I_B = I_C$

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 $\langle \psi_i | \hat{\mu}_e | \psi_f \rangle \neq 0$

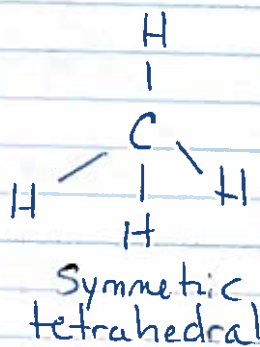
the molecule must possess a permanent electric dipole moment $\mu_e \neq 0$.

Examples:



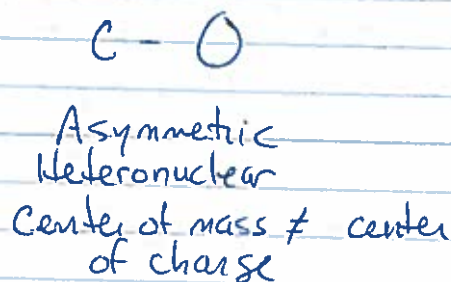
$\mu_e = 0$
↓

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)

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

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

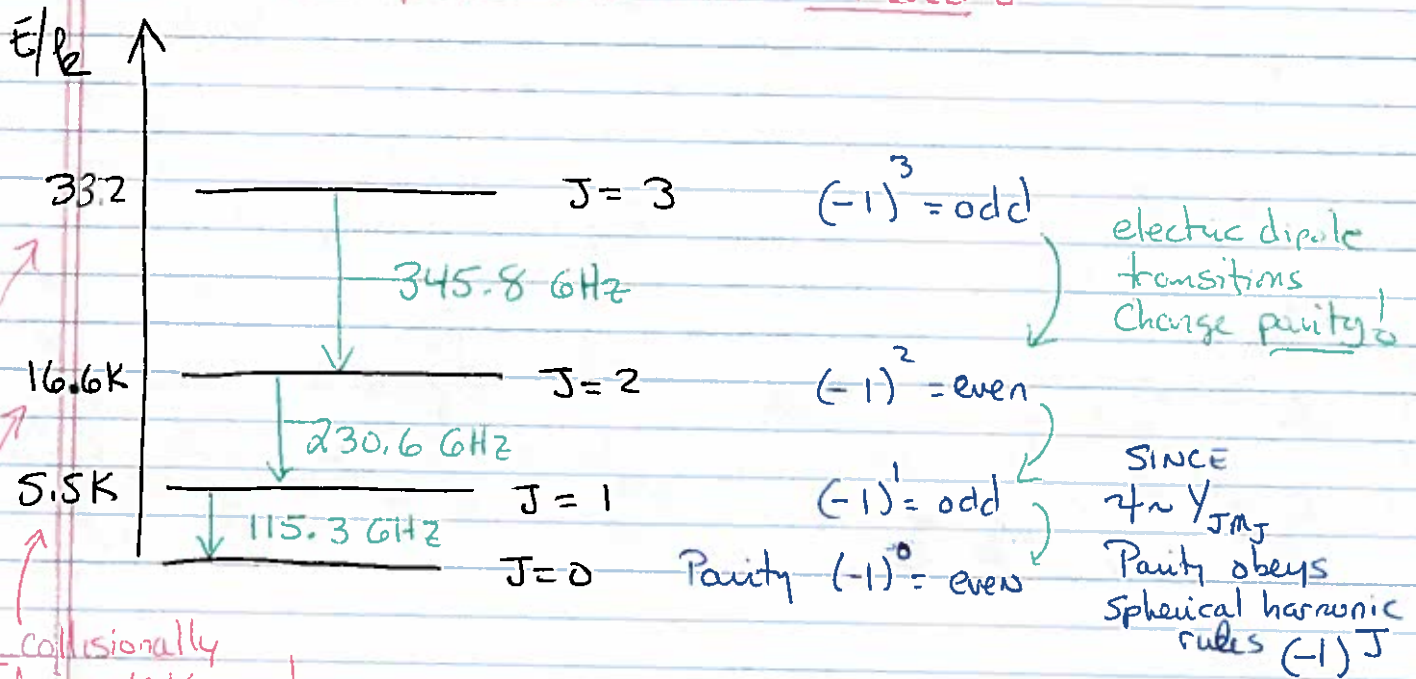
$$= 2B(J+1) \quad \text{LINEAR with } J!$$

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

Heteronuclear Example: CO

$$\mu_e = 0.11 \text{ D}$$

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 :

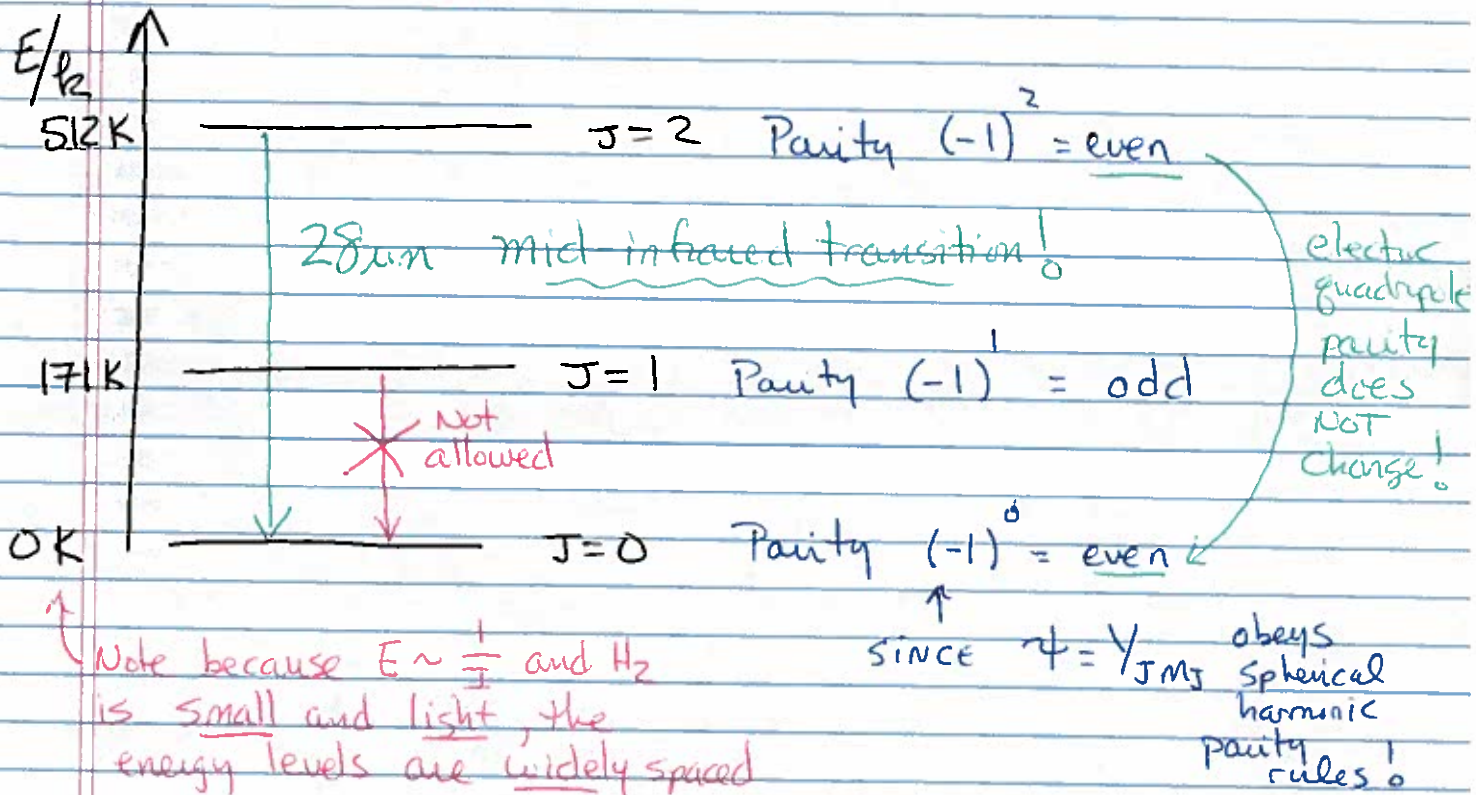
$A(01-0)$	$\sim 7.2 \times 10^{-8} \text{ s}^{-1}$	← low → in radio makes for "small" A values
$A(02-1)$	$\sim 6.9 \times 10^{-7} \text{ s}^{-1}$	
$A(03-2)$	$\sim 2.5 \times 10^{-6} \text{ s}^{-1}$	

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

Homonuclear Example : H_2 $\mu_e = 0$

No electric dipole $\Delta J = \pm 1$ transitions allowed!

But electric quadrupole $\Delta J = \pm 2$ are allowed



Note - a common misconception is that H_2 does not easily radiate in cold ($T_K \sim 10K$) molecular clouds because $\mu_e = 0$ and $\Delta J = -1$ is NOT allowed.

Not the case - CONSIDER Boltzmann! In $T_K = 10K$ gas, the first level that H_2 can radiate out of is $J=2$ 512 K above ground

$$\frac{n_{J=2}}{n_{J=0}} \sim e^{-512/10} \sim e^{-51} \quad \text{In } 10K \text{ gas, } H_2 \text{ } J=2 \text{ NOT collisionally excited!}$$

Note that electric quadrupole transitions have $A_{ue} \sim \nu^5$ so the high frequency (28 μm) makes this Einstein A comparable to electric dipole transitions of CO

$$A_{2-0}(H_2) \sim 2.94 \times 10^{-11} \text{ s}^{-1}$$