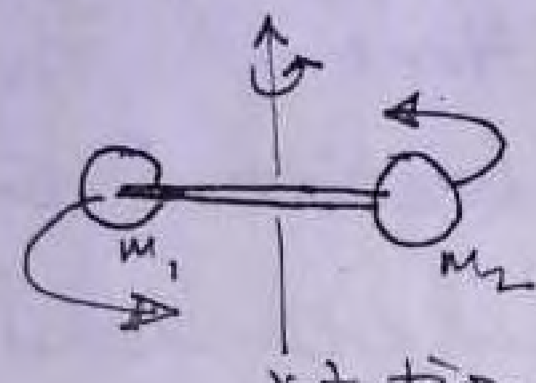
LINE SPLITTING DUE TO A SIMPLE, RIGID ROTATOR...

(This is a naive analysis)

A "simple, rigid rotator" has only one nonzero value for the moment of inertia, I, and the value along one axis vanishes. An example is a "dumbell"



rotation axis, through center of mass.

The kinetic energy due to rotation is then:

$$E_{rot} = \frac{L^2}{2I}$$

where L is the angular momentum.

Angular momentum is quantized (total angular momentum) as:

$$L_J^2 = \hbar^2 J(J+1) \quad , \text{ where } J = 0, 1, 2, \ldots$$

$\therefore$ The energy of the J^{th} rotational state is:

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

Dipole emission selection rules allow for only $\Delta J = \pm 1$ transitions, so:

$$|E_J - E_{J-1}| = \frac{\hbar^2}{2I}\left[J(J+1) - J(J-1)\right] = \frac{\hbar^2}{I} J \equiv \Delta E_J \qquad (2)$$

So a simple, rigid rotator has a rotational spectrum consisting of equally-spaced lines with spacing of $\Delta E = \hbar^2/I$.

In the case of an ~~atomic~~ electron transition, in a simple diatomic molecule, the line will be split because of these molecular rotational transitions. A further splitting is caused by vibrational energy transitions of the molecular bond.

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Let's ignore all these complications and assume that an electronic transition gives rise to a visible emission line at energy E_0, but this line is split into many individual lines due to the various rotational energies & transitions among the different molecules emitting the line.

In this case, $E_J = E_0 \pm \Delta E_J = E_0 \pm \frac{\hbar^2}{I} J$

Since $E = h\nu$, and $\nu = \frac{c}{\lambda}$

$$\frac{h}{\lambda_J} = \frac{h}{\lambda_0} \pm \frac{\hbar^2}{cI} J \rightarrow \frac{1}{\lambda_J} = \frac{1}{\lambda_0} \pm \frac{\hbar}{2\pi c I} J$$

Two adjacent lines in the spectrum would be separated by:

$$\boxed{\frac{1}{\lambda_J} - \frac{1}{\lambda_{J-1}} = \frac{\hbar}{2\pi c I}} \qquad (3)$$

Let's use the above equation to estimate the bond length of a diatomic molecule.

For a molecule with atoms m_1 & m_2 and bond length r, the moment of inertia about the center of mass is given by:

$$I = \mu r^2 \,, \quad \mu = \frac{m_1 m_2}{m_1 + m_2} \qquad (4)$$

μ is the reduced mass. If we measure the mass using energy units $(E = mc^2)$

Then $c^2 I = \mu r^2$ (μ in energy units)

Substituting in (3):

$$\boxed{\frac{1}{\lambda_J} - \frac{1}{\lambda_{J-1}} = \frac{\hbar c}{2\pi \mu r^2}} \quad (\mu \text{ in energy units}) \quad (5)$$

Measuring λ & r in Angstroms, with $\hbar c = 1970$ eVÅ, and measuring μ in proton masses, we get:

$$\left(\text{since } \frac{1}{\lambda_J} - \frac{1}{\lambda_{J-1}} = \frac{\lambda_{J-1} - \lambda_J}{\lambda_J \lambda_{J-1}} \right)$$

$$\left(\frac{r}{\text{Å}}\right) \simeq \sqrt{\frac{(\lambda_J/\text{Å})(\lambda_{J-1}/\text{Å})}{(3.0\times10^6)\left(\frac{\mu}{m_p}\right)(\lambda_{J-1}/\text{Å} - \lambda_J/\text{Å})}}$$

Question: for OH, $\mu \simeq m_p$. with

$\lambda_J \simeq \lambda_{J-1} \simeq 3080\,\text{Å}$

and $\lambda_{J-1} - \lambda_J \simeq 1.8\,\text{Å}$

what would r be?