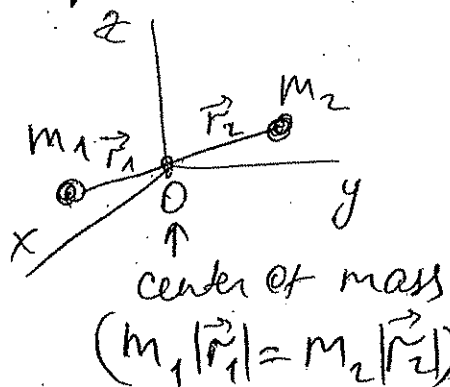


Rotation of diatomic molecules

Consider two atoms of masses m_1 and m_2 , separated by a fixed distance $r_e = |\vec{r}_1 + \vec{r}_2|$



rigid rotator equilibrium

The moment of inertia:

$$I = m_1 r_1^2 + m_2 r_2^2 = \mu r_e^2$$

$$r_e = |\vec{r}_1 - \vec{r}_2|, \quad \mu = \frac{m_1 m_2}{m_1 + m_2} \text{ - reduced mass}$$

The total angular momentum:

$$|\vec{L}| = (m_1 r_1^2 + m_2 r_2^2) \omega_R = \mu r_e^2 \omega_R$$

"
I

angular velocity

Hamiltonian $H = \frac{\vec{L}^2}{2I} = \frac{I \omega_R^2}{2}$

"
I

Energy levels can be found from $H |l, m\rangle = E |l, m\rangle$

Wave $\frac{\vec{L}^2}{2\mu r_e^2} |l, m\rangle = \frac{\hbar^2}{2\mu r_e^2} l(l+1) |l, m\rangle$

So, $E_l = \frac{\hbar^2}{2\mu r_e^2} l(l+1)$ ← energy levels of QM rigid rotator (energy is quantised!) (2)

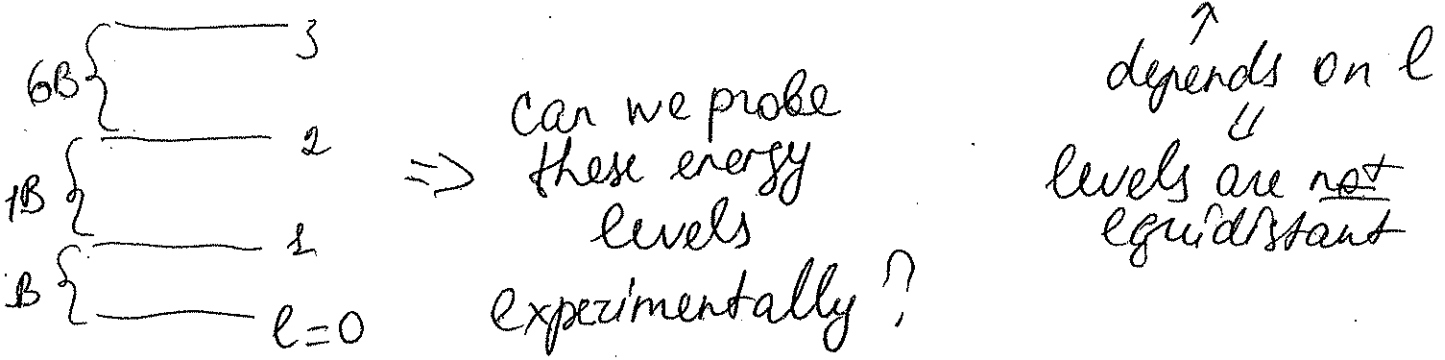
Introduce a rotational constant \Rightarrow

$B = \frac{\hbar^2}{2\mu r_e^2}$, then $\Rightarrow E_l = B l(l+1)$

Since E_l does not depend on $m \Rightarrow$ each E_l is $(2l+1)$ -degenerate (since $-l \leq m \leq l$).

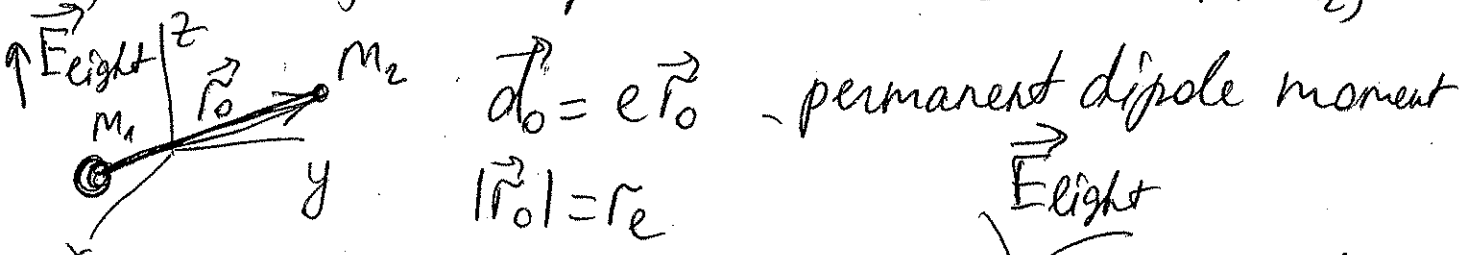
Separation between the adjacent energy levels:

$E_l - E_{l-1} = B [l(l+1) - (l-1)l] = 2Bl$



yes! \Rightarrow e.g. by having the molecule interact with light!

(a) Case of heteropolar molecules ($m_1 \neq m_2$)



Excite the molecule with light polarized along z

The energy of the light-molecule interaction (3)

$$H_{\text{interaction}} = -\vec{d}_0 \cdot \vec{E}_{\text{light}} = -eZ \cdot E_{\text{light}}$$

Experimentally observe absorption of light by the molecule (more on this in Phys 653) if $\langle H_{\text{interaction}} \rangle \neq 0$
 i.e. $\langle Z \rangle \neq 0$.

$$\langle Z \rangle = \langle r_e \cos\theta \rangle = r_e \langle l', m' | \cos\theta | l, m \rangle$$

Recall that $|l, m\rangle \Leftrightarrow Y_l^m(\theta, \varphi)$

Recursion relation for $Y_l^m(\theta, \varphi)$:

$$\cos\theta Y_l^m(\theta, \varphi) = \sqrt{\frac{l^2 - m^2}{4l^2 - 1}} Y_{l-1}^m(\theta, \varphi) + \sqrt{\frac{(l+1)^2 - m^2}{4(l+1)^2 - 1}} Y_{l+1}^m(\theta, \varphi)$$

\updownarrow \updownarrow \updownarrow
 $|l, m\rangle$ $|l-1, m\rangle$ $|l+1, m\rangle$

Then, $\langle Z \rangle = r_e \delta_{m', m} \left[\delta_{l', l-1} \sqrt{\frac{l^2 - m^2}{4l^2 - 1}} + \delta_{l', l+1} \sqrt{\frac{(l+1)^2 - m^2}{4(l+1)^2 - 1}} \right]$

\Rightarrow clearly, $\langle Z \rangle \neq 0$ only if $l' = l \pm 1 \Rightarrow$

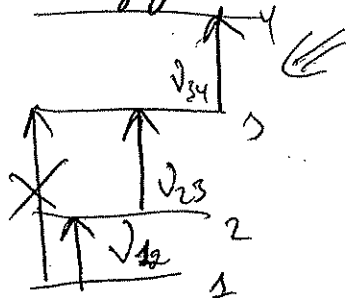
i.e. in this case the light-matter interaction can be observed only if $\Delta l = \pm 1, \Delta m = 0$ ← selection rules

If we choose X- or Y-polarised light \Rightarrow arrive at

$$\Delta l = \pm 1, \Delta m = \pm 1$$

(4)

In any case, we can probe only the adjacent energy levels E_l : $1 \rightarrow 2, 2 \rightarrow 3, 3 \rightarrow 4$ trans. $2 \rightarrow 1, \dots$ are allowed and others disallowed



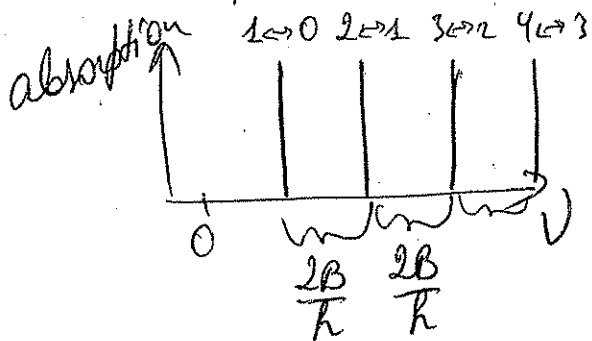
Introduce

$$\text{Bohr frequency } \nu_{l, l-1} = \frac{E_l - E_{l-1}}{h} = \frac{2B}{h} l$$

Then the difference between the adjacent frequencies observed in the spectrum \Rightarrow

$$\nu_{l+1, l} - \nu_{l, l-1} = \frac{2B}{h} (l+1 - l) = \frac{2B}{h} \leftarrow \text{does not depend on } l$$

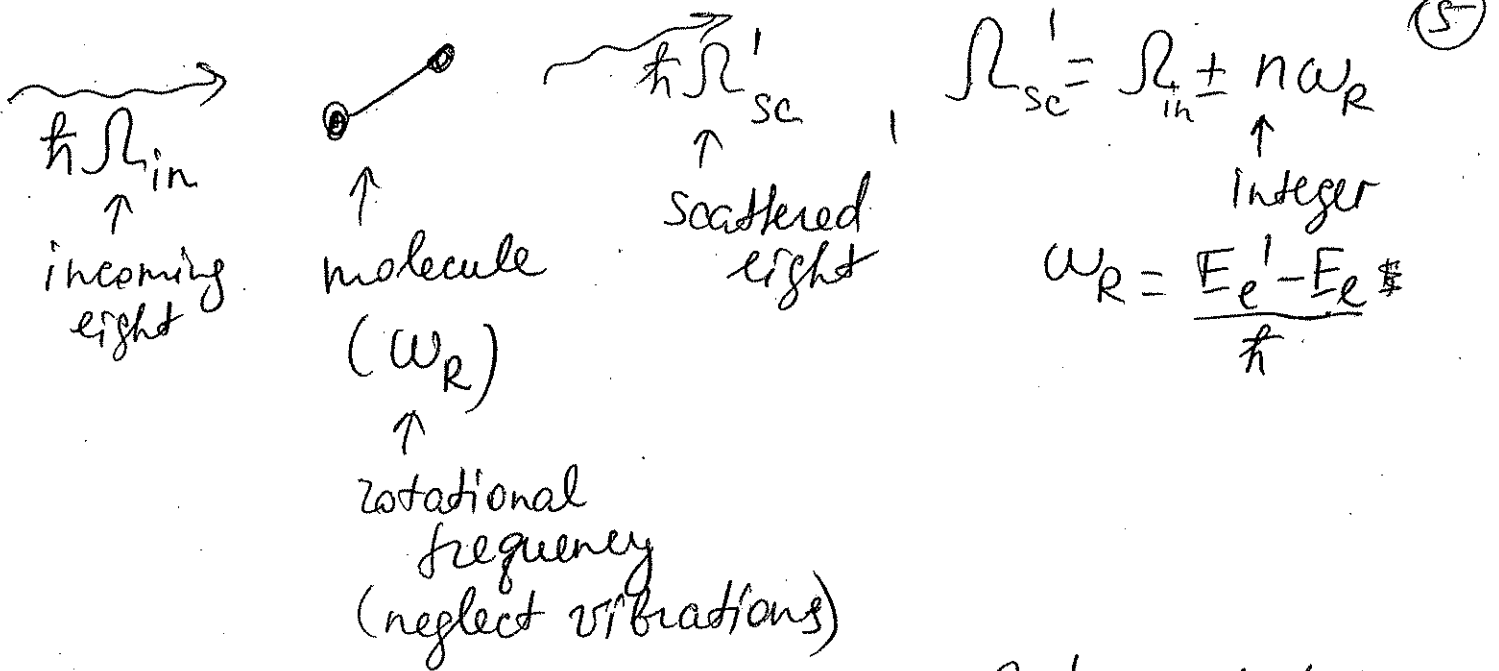
\Leftarrow equidistant \Rightarrow



\rightarrow pure rotational spectrum

(b) Case of homopolar molecules
no permanent dipole moment ($\vec{d}_0 = 0$) \Rightarrow $H_{\text{interact}} = \vec{d}_0 \cdot \vec{E}_{\text{light}} = 0$
no linear coupling with light

But the rotation of molecules can be observed by inelastic scattering of light (the Raman effect)



In this process either measure Ω_{sc} and determine ω_R , since it contains info about a molecule or use the scattering process to generate different frequencies of light and use as light sources (Raman shifters)

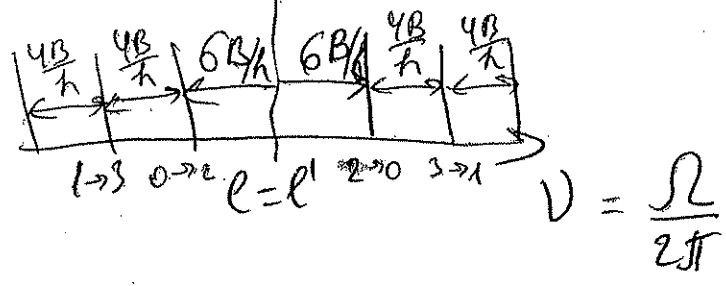
The efficiency of scattering is $\sim \langle z^2 \rangle$, as opposed to absorption ($\sim \langle z \rangle$) \Rightarrow need to evaluate $\langle \cos^2 \theta \rangle \Rightarrow$ once again, use properties of spherical harmonics and arrive at the selection rule $\Delta l = \pm 2, 0$

$$\begin{aligned}
 \Delta l = 0 &\Rightarrow l' = l \Rightarrow \text{Rayleigh line (elastic scattering)} \\
 &\quad (\Omega_{sc} = \Omega_{in}) \\
 \Delta l = l' - l = -2 &\Rightarrow \frac{\Omega_{sc}}{2\pi} = \frac{\Omega_{in}}{2\pi} + \frac{E_{l'+2} - E_{l'}}{2\pi\hbar} = \frac{\Omega_{in}}{2\pi} + \\
 &\quad + \frac{B}{2\pi\hbar} ((l'+2)(l'+3) - l'(l'+1)) = \\
 &\quad \text{with } l' = 0, 1, 2, \dots \\
 &= \frac{\Omega_{in}}{2\pi} + \frac{B}{\hbar} \cdot 4(l' + \frac{3}{2}) \Leftarrow \text{Raman anti-Stokes lines}
 \end{aligned}$$

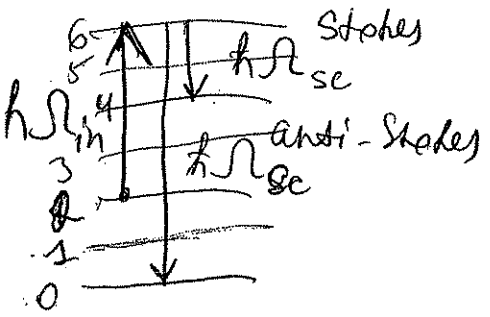
$$\Delta l = l' - l = 2 \Rightarrow \frac{\Omega_{sc}'}{2\pi} = \frac{\Omega_{in}}{2\pi} + \frac{E_l - E_{l-2}}{h} =$$

$$= \frac{B}{h} (l(l+1) - (l+2)(l+3)) = \frac{\Omega_{in}}{2\pi} - \frac{4B}{h} (l + \frac{3}{2})$$

Rayleigh line ($\Omega_{sc}' = \Omega_{in}$)
 Raman-anti-Stokes lines
 Raman-Stokes lines
 $l = 0, 1, 2, \dots$



Note: 1) In Raman rotational spectra, the Stokes and anti-Stokes lines appear with comparable intensities, since levels with various l 's are populated because $B \ll kT$



This is necessary for the observation of anti-Stokes lines for which the initial state must be 'at least $l=2$

2) The Raman rotational effect also exists for heteropolar molecules