

Q1) NO, as benzene is a symmetric molecule and its for uniform expansion the dipole moment of benzene would always remain 0.

Therefore the ~~transition dipole integral~~ would $\frac{d\mu}{dt} \neq 0$ and the first selection rule gets violated (as $\Delta v \neq \pm 1$ from second rule)

Q2) for a diatomic molecule (assuming rigid)

$$E_J = \frac{h^2 J(J+1)}{8\pi^2 I}$$

where J is the rotational quantum number
taking values $0, 1, 2, \dots$

$$E_2 = \frac{h^2 (2)(3)}{8\pi^2 I} = \frac{6h^2}{8\pi^2 I}$$

$$E_3 = \frac{h^2 (3)(4)}{8\pi^2 I} = \frac{12h^2}{8\pi^2 I}$$

now we know $h\nu = \Delta E$

$$\therefore h\nu = \frac{h^2}{8\pi^2 I} (12 - 6)$$

$$\nu = \frac{3h}{4\pi^2 I}$$

$$\boxed{\nu = \frac{3h}{4\pi^2 I}}$$

Yes, moment of inertia $\boxed{I = \frac{3h}{4\pi^2 \nu}}$

given we know the mass of the 2 atoms (m_1, m_2) we can compute bond length (r_0) as

$$I = \mu r_0^2 \quad \text{reduced mass} = \frac{m_1 m_2}{m_1 + m_2}$$
$$\therefore r_0 = \sqrt{\frac{I}{\mu}} = \sqrt{\frac{I(m_1 + m_2)}{m_1 m_2}}$$

Q3) Given $T = 300\text{ K}$

from Boltzmann distribution we know

$$N \propto e^{-\frac{E}{k_B T}}$$

$$\therefore N_0 \propto e^{-\frac{E_0}{k_B T}} \quad \& \quad N_1 \propto e^{-\frac{E_1}{k_B T}}$$

$$\therefore \frac{N_1}{N_0} = e^{-\frac{(E_1 - E_0)}{k_B T}}$$

now for a single diatomic molecule we can

substitute $E_1 - E_0 = h\nu$ frequency
planck's constant

i) vibration harmonically

$$\text{using } \nu = 1000\text{ cm}^{-1} = 10^5\text{ m}^{-1}$$

$$\text{we get } \frac{N_1}{N_0} = e^{-\frac{6.626 \times 10^{-34} \times 10^5}{1.38 \times 10^{-23} \times 300}}$$

$$\boxed{\frac{N_1}{N_0} = e^{-1.60 \times 10^{-8}}}$$

ii) for rotation

$$\text{using } \nu = 10\text{ cm}^{-1} = 10^3\text{ m}^{-1}$$

$$\boxed{\frac{N_1}{N_0} = e^{-1.6 \times 10^{-10}}}$$

$$\text{Comparing ratios} = \frac{e^{-1.6 \times 10^{-8}}}{e^{-1.6 \times 10^{-10}}} = e^{-1.6(10^{-8} - 10^{-10})}$$

$$= \frac{e^{-1.6(10^{-8})(1 - 1/100)}}{e^{-1.6(10^{-8})(1 - 1/100)}}$$

≈ 1 and that was expected

as energy diff b/w vibrational states is greater than that in rotational states.

Q4) For a polyatomic molecule with N atoms, we first define the coordinates of each atom $(\vec{r}_1, \vec{r}_2, \vec{r}_3 \dots \vec{r}_N)$

we also define their equilibrium configurations $(\vec{r}_{0,1}, \vec{r}_{0,2}, \vec{r}_{0,3}, \dots, \vec{r}_{0,N})$

now the potential energy of the system

$$U(\vec{r}_1, \vec{r}_2 \dots \vec{r}_N) = U(\vec{r}_{0,1}, \vec{r}_{0,2} \dots \vec{r}_{0,N}) + \nabla_{3N} U \Big|_0 \cdot \Delta \vec{r}_{3N} + \frac{1}{2} \nabla_{3N}^2 U \Big|_0 \cdot \Delta \vec{r}_{3N} \Delta \vec{r}_{3N} + \dots$$

Using Taylor series expansion

$$\nabla_{3N} U = \left(\frac{\partial U}{\partial \vec{r}_1}, \frac{\partial U}{\partial \vec{r}_2}, \dots, \frac{\partial U}{\partial \vec{r}_N} \right)$$

each \vec{r}_i is 3 dimensional

$$\Delta \vec{r}_{3N} = (\vec{r}_1 - \vec{r}_{0,1}, \vec{r}_2 - \vec{r}_{0,2}, \dots, \vec{r}_N - \vec{r}_{0,N})$$

now for small $\Delta \vec{r}$ $\nabla_{3N} U = 0$

also we ignore higher order terms.

we also assume $U(\vec{r}_{0,1}, \vec{r}_{0,2} \dots \vec{r}_{0,N}) = 0$

$$U(\vec{r}_1, \vec{r}_2 \dots \vec{r}_N) = \frac{1}{2} \nabla_{3N}^2 U \Big|_0 \Delta \vec{r} \Delta \vec{r}$$

→ this quantity is our Hessian matrix

$$H = \begin{pmatrix} \frac{\partial^2 U}{\partial x_1^2} & \frac{\partial^2 U}{\partial x_1 \partial y_1} & \frac{\partial^2 U}{\partial x_1 \partial z_1} & \dots \\ \frac{\partial^2 U}{\partial y_1 \partial x_1} & \frac{\partial^2 U}{\partial y_1^2} & \dots & \dots \\ \vdots & \vdots & \ddots & \ddots \end{pmatrix}$$

(3N x 3N)

in the hessian matrix $H_{ij} = \frac{\partial^2 U}{\partial \vec{r}_i \partial \vec{r}_j}$

But this hessian matrix will be non diagonal for a coupled system

we diagonalize the Hessian matrix
to convert this coupled

system to an uncoupled system
which allows easy computation as we
can now consider it as a problem with N
independent systems.

To diagonalize our Hessian matrix we use
eigen decomposition.

$$X^{-1} H X = \begin{pmatrix} \lambda_1 & & 0 \\ & \lambda_2 & \\ 0 & & \ddots \\ & & & \lambda_{3N} \end{pmatrix}$$
$$\Rightarrow H X = X \begin{pmatrix} \lambda_1 & & 0 \\ & \lambda_2 & \\ 0 & & \ddots \\ & & & \lambda_{3N} \end{pmatrix}$$

~~eigenvectors~~ \searrow \swarrow eigenvalue

$$\text{or } H X_i = \lambda_i X_i$$

\searrow eigenvector

these X_i 's are our normal modes and
 λ_i 's are the corresponding frequencies.

vibrational density of the states is

$$\rho(\omega) = \sum_{i=1}^A \delta(\omega - \omega_i)$$

where $A = 3N - 6$ for non linear molecules
and $3N - 5$ for linear molecules.

$$Q3) U(x_1, x_2) = \frac{1}{2} k_1 x_1^2 + \frac{1}{2} k_2 x_2^2 + \frac{1}{2} k_{12} (x_1 - x_2)^2$$

$$U(x_1, x_2) = \frac{1}{2} k_1 x_1^2 + \frac{1}{2} k_2 x_2^2 + \frac{1}{2} k_{12} x_1^2 + \frac{1}{2} k_{12} x_2^2 - k_{12} x_1 x_2$$

for a 2D problem of 2 particles
Hessian matrix would be (2×2)

$$\begin{bmatrix} \frac{\partial^2 U}{\partial x_1^2} & \frac{\partial^2 U}{\partial x_1 \partial x_2} \\ \frac{\partial^2 U}{\partial x_1 \partial x_2} & \frac{\partial^2 U}{\partial x_2^2} \end{bmatrix}$$

$$\frac{\partial^2 U}{\partial x_1^2} = \frac{\partial}{\partial x_1} (k_1 x_1 + 0 + k_{12} x_1 - k_{12} x_2)$$

$$= (k_1 + k_{12})$$

similarly $\frac{\partial^2 U}{\partial x_2^2} = k_2 + k_{12}$

$$\frac{\partial^2 U}{\partial x_1 \partial x_2} = \frac{\partial}{\partial x_2} (k_1 x_1 + k_{12} x_1 - k_{12} x_2)$$

$$= (-k_{12})$$

$$\frac{\partial^2 U}{\partial x_1 \partial x_2} = -k_{12}$$

$$H = \begin{bmatrix} k_1 + k_{12} & -k_{12} \\ -k_{12} & k_2 + k_{12} \end{bmatrix}$$

eigenvectors of $H = \begin{bmatrix} a \\ b \end{bmatrix}$

so $H \begin{bmatrix} a \\ b \end{bmatrix} = \lambda \begin{bmatrix} a \\ b \end{bmatrix}$ or $(H - \lambda I) = 0$

$$\begin{bmatrix} k_1 + k_{12} - \lambda & -k_{12} \\ -k_{12} & k_2 + k_{12} - \lambda \end{bmatrix} \begin{bmatrix} a \\ b \end{bmatrix} = 0$$

$$(k_1 + k_{12} - \lambda)(k_2 + k_{12} - \lambda) - k_{12}^2 = 0$$

$$k_1 k_2 + k_{12} k_2 - \lambda k_2 + k_1 k_{12} + k_{12}^2 - \lambda k_{12} - \lambda k_1 - \lambda k_{12} + \lambda^2 - k_{12}^2 = 0$$

$$\lambda^2 - \lambda(k_1 + k_2 + 2k_{12}) + (k_1 k_2 + k_1 k_{12} + k_2 k_{12}) = 0.$$

2 solns of this are

$$\lambda = (k_1 + k_2 + 2k_{12}) \pm \sqrt{k_1^2 + k_2^2 + 4k_{12}^2 + 2k_1 k_2 + 4k_1 k_{12} + 4k_2 k_{12} - 4k_1 k_2}$$

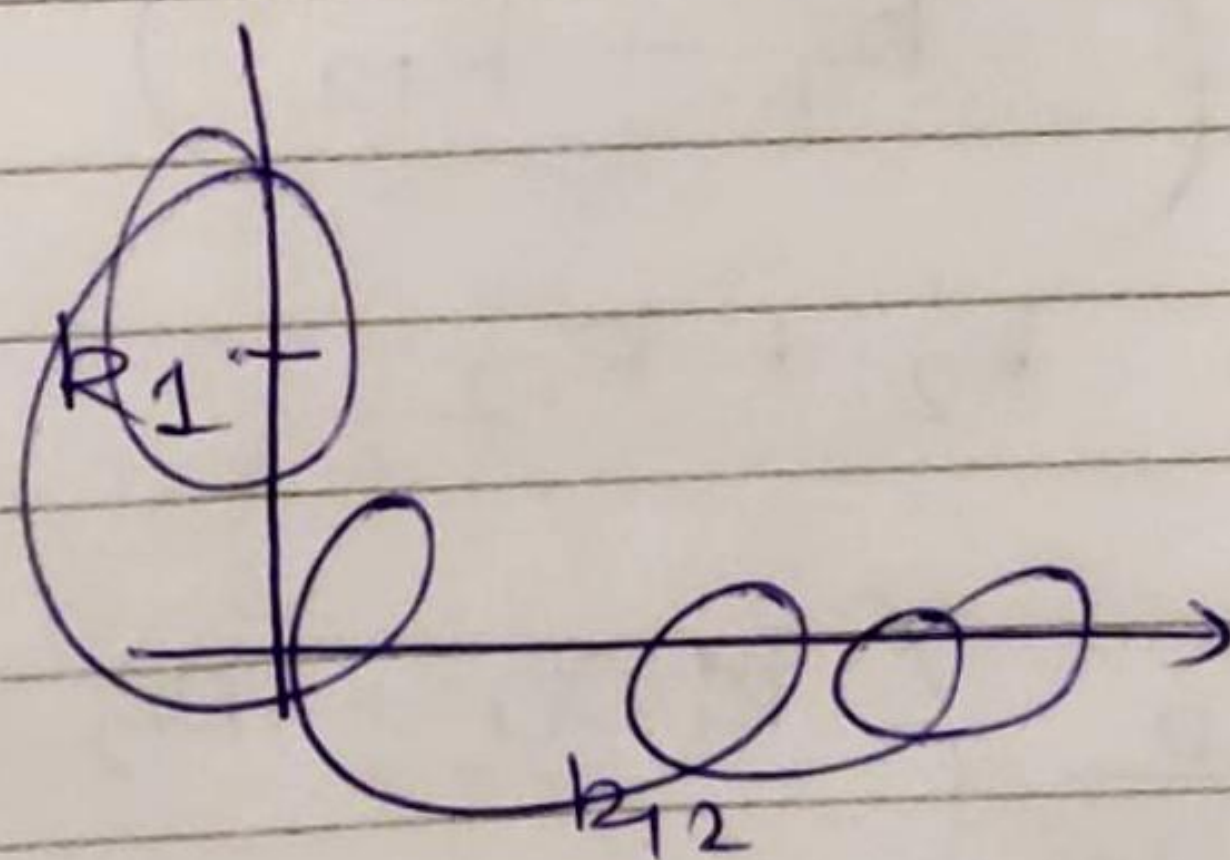
frequencies

$$\lambda = \frac{k_1 + k_2 + 2k_{12} \pm \sqrt{k_1^2 + k_2^2 + 4k_{12}^2 - 2k_1 k_2}}{2}$$

if $k_{12} = 0$ then $\lambda = \frac{k_1 + k_2 \pm (k_1 - k_2)}{2}$

$$\lambda = k_1 / \infty / k_2$$

~~as k_1, k_2~~



as k_1, k_2 are constants

$$\lambda = \frac{C + 2k_{12} \pm \sqrt{d + 4k_{12}^2}}{2}$$

Q6) $\hat{H} \psi_M(\vec{r}) = E_M \psi_M(\vec{r})$
 $\hat{H} (C_A \psi_A(\vec{r}) + C_B \psi_B(\vec{r})) = E_M (\psi_M(\vec{r}))$

multiply $\psi_A^*(\vec{r})$ & integrate on both sides

assume i) $\int \psi_A^* \hat{H} \psi_A(\vec{r}) d\vec{r} = E_{Is, A}$

ii) $\int \psi_A^* \hat{H} \psi_B(\vec{r}) d\vec{r} = -V$

& multiplying ψ_A^* & integrating,

$$[C_A E_{Is, A} + C_B (-V) = E_M C_A]$$

similarly for ψ_B^* & integrate

$$[-C_A (V) + E_{Is, B} C_B = E_M C_B]$$

$$(E_{Is, A} - E_M) C_A - V C_B = 0$$

$$-V C_A + (E_{Is, B} - E_M) C_B = 0$$

$$\begin{vmatrix} E_{Is, A} - E_M & -V \\ -V & E_{Is, B} - E_M \end{vmatrix} = 0$$

note $E_{Is, A} = E_{Is, B}$

$$\therefore (E_{Is} - E_M)^2 = V^2 \quad (\text{antibonding})$$

$$\text{or } [E_M = E_{Is} \pm V]$$

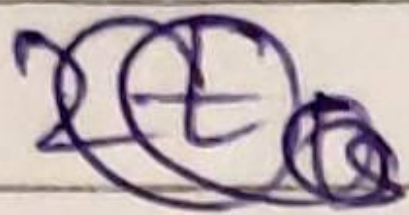
$$E_M = E_{Is} + V$$

$$E_M = E_{Is} - V$$

(bonding)

(antibonding) $\begin{pmatrix} C_A \\ C_B \end{pmatrix} = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ -1 \end{pmatrix} \rightarrow \frac{\psi_A}{\sqrt{2}} - \frac{\psi_B}{\sqrt{2}}$

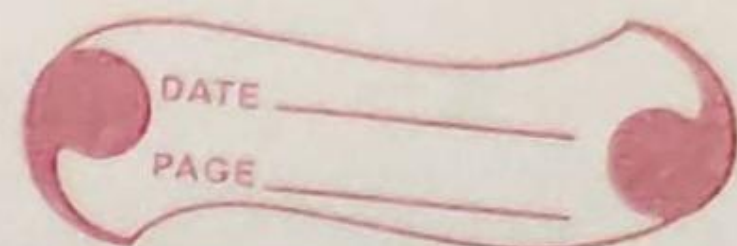
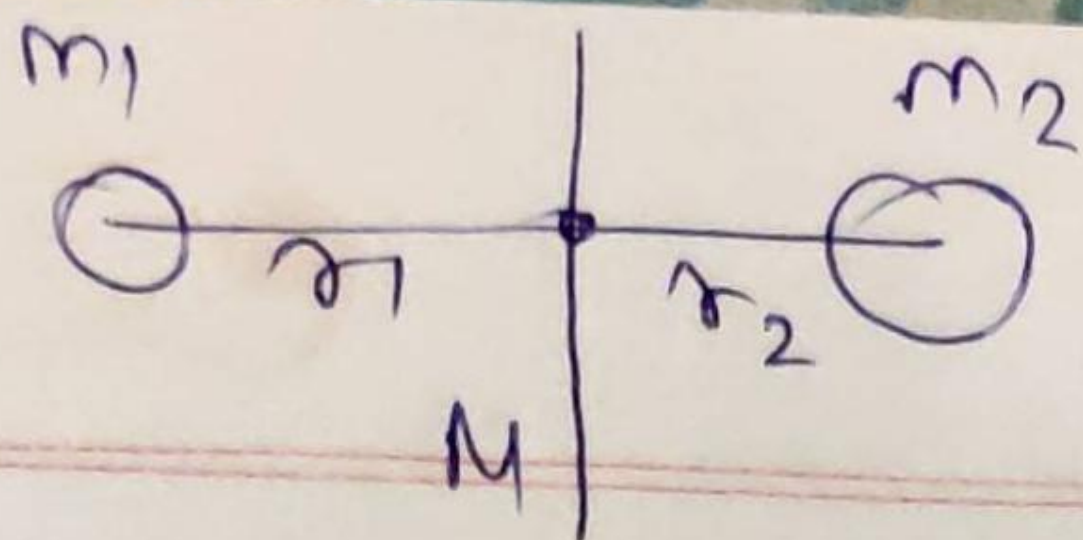
(bonding) $\begin{pmatrix} C_A \\ C_B \end{pmatrix} = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ 1 \end{pmatrix} \rightarrow \frac{\psi_A}{\sqrt{2}} + \frac{\psi_B}{\sqrt{2}}$

so we get diff between both levels
of  $2V$.

They physically represent diff in energies
of bonding/antibonding orbitals.

The reason is that it takes a lot of
energy to move a electron from one
orbital to other but not so much to
unbreak or rotate it.

Q7)



by rotating along like M, there are centrifugal forces acting on the atoms of the molecule.

for atom 1 force = $m_1 \omega^2 r_1^2$

for atom 2 force = $m_2 \omega^2 r_2^2$

total force pulling atoms away

$$= \omega^2 (m_1 r_1^2 + m_2 r_2^2) = \omega^2 (I)$$

Rotational energy for a molecule

$$= \frac{h^2}{8\pi^2 I} l(l+1)$$

∴ In theory we can break a diatomic bond by rotating it through COA as they