Assignment (22)

① Particle in a Box — D; Rigid Rotor — C
Harmonic Oscillator — B; One-electron Atom — A

② $^1H^{35}Cl \rightarrow 6.26\times10^{13}$ Hz

linear molecule, so $E = \frac{\hbar^2 J(J+1)}{2\mu r_e^2} \rightarrow \Delta E = E_f - E_i = \frac{\hbar^2}{2\mu r_e^2}\left(J_f(J_f+1) - J_i(J_i+1)\right)$

$J_f = J_i + 1$

$h\nu = \Delta E = \frac{h^2}{2\mu r_e^2}\left[(J_i+1)(J_i+2) - J_i(J_i+1)\right] = \frac{\hbar^2}{2\mu r_e^2}\left[J_i + 1 + J_i - J_i\right] = \frac{\hbar^2(J_i+1)}{\mu r_e^2}$

$h\nu = \frac{h^2(J_i+1)}{4\pi^2\mu r_e^2} \rightarrow r_e = \sqrt{\frac{h(J_i+1)}{4\pi^2\mu\nu}} \xrightarrow{J_i=0} r_e = \sqrt{\frac{h}{4\pi^2\mu\nu}} = \sqrt{\frac{h(M_H+M_{Cl})}{4\pi^2(M_H)(M_{Cl})\nu}}$

$r_e = \sqrt{\frac{(6.626\times10^{-34}\,J\cdot s)(1+35)}{4\pi^2(1)(35)(1.661\times10^{-27}\,kg)(6.26\times10^{13}\,Hz)}} = 1.29\times10^{-10}\,m = 129\,pm$

ⓐ $^{12}C^{14}N \rightarrow r_e = 119\,pm$

$k = 1630\,N/m$

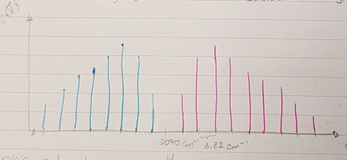
$\mu = \frac{(12\times14)(1.661\times10^{-27}\,kg)}{(12+14)} = 1.075\times10^{-26}\,kg$

$\Delta E_{vib} = h\nu_0 = \frac{h}{2\pi}\sqrt{\frac{k}{\mu}} = hc\tilde{\nu}_{vib}$

$\tilde{\nu}_0 = \frac{1}{2\pi c}\sqrt{\frac{k}{\mu}} = \frac{1}{2\pi(2.998\times10^8\,m/s)}\left[\frac{1630\,N/m}{1.07\times10^{-26}\,kg}\right]^{1/2} = 2.07\times10^5\,m^{-1} = 2070\,cm^{-1}$

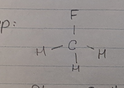
$\Delta E_{rot} = \frac{\hbar^2 J(J+1)}{4\pi^2\mu r_e^2} = hc\tilde{\nu}_{rot}$

$\tilde{\nu}_{rot} = \frac{h(J+1)}{4\pi^2 c\mu r_e^2} = \frac{(6.626\times10^{-34}\,J\cdot s)(J+1)}{4\pi^2(2.998\times10^8\,m/s)(1.075\times10^{-26}\,kg)(119\times10^{-12}\,m)^2} = (382\,m^{-1})(J+1) = (3.82\,cm^{-1})(J+1)$



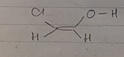
③ Spherical top:

prolate symm. top:

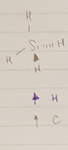


Oblate symm. top:

Asymetric



⑤ SiH_4



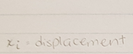
1 1 3P — 1L 1L 1L

it is really similar to CH_4

1L 3S — 1L

⑥ x_i - displacement of each atom

$O_1 - C_2 - O_3$



$m_1 = m_3$

$k_{ij} = \frac{\partial^2 V}{\partial x_i \partial x_j}$, $i,j = \{1,2,3\}$

$V = \frac{1}{2}k(x_2 - x_1)^2 + \frac{1}{2}k(x_3 - x_2)^2$

$V = \frac{1}{2}k(x_1^2 + 2x_2^2 + x_3^2 - 2x_1x_2 - 2x_2x_3)$

$\mathbb{K} = \begin{pmatrix} \frac{1}{2}k(2) & \frac{1}{2}k(-2) & \frac{1}{2}k(0) \\ \frac{1}{2}k(-2) & \frac{1}{2}k(2) & \frac{1}{2}k(-2) \\ \frac{1}{2}k(0) & \frac{1}{2}k(-2) & \frac{1}{2}k(2) \end{pmatrix} = \begin{pmatrix} k & -k & 0 \\ -k & 2k & -k \\ 0 & -k & k \end{pmatrix}$

$\sum F_i = \sum_{ij} -k_{ij}x_j = m_i a_i$

$m_1 a_1 = -kx_1 + kx_2$

$m_2 a_2 = kx_1 - 2kx_2 + kx_3$

$m_3 a_3 = kx_2 - kx_3$

* general solution of harmonic oscillator is: $x(t) = \alpha_1 e^{i(\omega t - \delta_1)} + \alpha_2 e^{i(\omega t - \delta_2)} = e^{i\omega t}\left[\alpha_1 e^{-i\delta_1} + \alpha_2 e^{-i\delta_2}\right] = e^{i\omega t}(C)$

$a_i = \frac{\partial^2 x_i(t)}{\partial t^2} = (i\omega)^2 x_i(t)$

$a_i = -\omega^2 x_i(t)$

$m_1(-\omega^2)e^{i\omega t}C_1 = -ke^{i\omega t}C_1 + ke^{i\omega t}C_2$

$m_2(-\omega^2)e^{i\omega t}C_2 = ke^{i\omega t}C_1 - 2ke^{i\omega t}C_2 + ke^{i\omega t}C_3$

$m_3(-\omega^2)e^{i\omega t}C_3 = ke^{i\omega t}C_2 - ke^{i\omega t}C_3$

$-\omega^2\underbrace{\begin{pmatrix} m_1 & 0 & 0 \\ 0 & m_2 & 0 \\ 0 & 0 & m_3 \end{pmatrix}}_{\mathbb{M}}\underbrace{\begin{pmatrix} C_1 \\ C_2 \\ C_3 \end{pmatrix}}_{\mathbb{C}} = \underbrace{\begin{pmatrix} -k & k & 0 \\ -k & 2k & -k \\ 0 & -k & k \end{pmatrix}}_{-\mathbb{K}}\begin{pmatrix} C_1 \\ C_2 \\ C_3 \end{pmatrix}$

$-\omega^2\mathbb{M}\mathbb{C} + \mathbb{K}\mathbb{C} = 0$

$(\mathbb{K} - \omega^2\mathbb{M})\mathbb{C} = 0$

$\det(\mathbb{K} - \omega^2\mathbb{M}) = 0$

solution is: $\omega_1 = 0 \rightarrow$ translational

$\omega_2 = \sqrt{\frac{k}{m_1}} \rightarrow$ sym

$\omega_3 = \sqrt{\frac{k}{m_1} + \frac{2k}{m_2}} \rightarrow$ assym.

* trivial solution: $C_1 = C_2 = C_3 = 0$.
* others: $C_1 \neq 0$, $C_2 \neq 0$, $C_3 \neq 0$

⑥

$\omega_2 = \sqrt{\frac{k_{sym}}{m_1}}$

$\omega_3 = \sqrt{\frac{k}{m_1} + \frac{2k}{m_2}}$

$k = m_1\omega_2^2$

$\frac{m_1 k + 2m_1 k}{m_1 m_2} = \omega_3^2 \rightarrow k = \frac{\omega_3^2 m_1 m_2}{m_2 + 2m_1}$

$\Delta E = E_f - E_i = h\nu = hc\tilde{\nu} = \frac{h}{2\pi}\omega$

$\omega = 2\pi c\tilde{\nu}$

$\omega_2 = \sqrt{\frac{k_{sym}}{m_1}} = 2\pi c\tilde{\nu}_{sym}$

$k_{sym} = 4\pi^2 c^2 \tilde{\nu}_{sym}^2 m_1 = 4\pi^2(2.998\times10^8\,m/s)^2(134000\,m^{-1})^2(16)(1.661\times10^{-27}\,kg)$

$k_{sym} = 1693.85\,N/m$

$k_{asym} = \frac{4\pi^2 c^2 \tilde{\nu}_{asym}^2 m_1 m_2}{m_1 + 2m_1} = \frac{4\pi^2(2.998\times10^8\,m/s)^2(234900\,m^{-1})^2(16)(12)(1.661\times10^{-27}\,kg)}{16(2) + 12}$

$k_{asym} = 1414.02\,N/m$

$k_{average} = 1556.17\,N/m$

⑦ $\rho_{\substack{bonding\\antibonding}}(\vec{r}) = \frac{|\psi_{\substack{bonding\\antibonding}}(\vec{r})|^2}{\int|\psi_{\substack{bonding\\antibonding}}(\vec{r})|^2 d\vec{r}} = \frac{|\phi_{1s}^A(\vec{r}) \pm \phi_{1s}^B(\vec{r})|^2}{\int|\phi_{1s}^A(\vec{r}) \pm \phi_{1s}^B(\vec{r})|^2 d\vec{r}}$

consider $\phi_{1s}^A(\vec{r})$ and $\phi_{1s}^B(\vec{r})$ real.

$= \frac{|\phi_{1s}^A(\vec{r})|^2 \pm 2\phi_{1s}^A(\vec{r})\phi_{1s}^B(\vec{r}) + |\phi_{1s}^B(\vec{r})|^2}{\int|\phi_{1s}^A(\vec{r})|^2 \pm 2\phi_{1s}^A(\vec{r})\phi_{1s}^B(\vec{r}) + |\phi_{1s}^B(\vec{r})|^2 d\vec{r}} = \frac{|\phi_{1s}^A(\vec{r})|^2 \pm 2\phi_{1s}^A(\vec{r})\phi_{1s}^B(\vec{r}) + |\phi_{1s}^B(\vec{r})|^2}{2 \pm 2\int\phi_{1s}^A(\vec{r})\phi_{1s}^B(\vec{r})d\vec{r}}$

$S = \int\phi_{1s}^A(\vec{r})\phi_{1s}^B(\vec{r})d\vec{r}$

$\rho_{nonbonding}(\vec{r}) = \left[|\phi_{1s}^A(\vec{r})|^2 + |\phi_{1s}^B(\vec{r})|^2\right] \Big/ \left[\int|\phi_{1s}^A(\vec{r})|^2 d\vec{r} + \int|\phi_{1s}^B(\vec{r})|^2 d\vec{r}\right]^{-1}$

$\rho_{\substack{bonding\\antibonding}}(\vec{r}) = \frac{\rho_{nonbonding}(\vec{r}) \pm 2\phi_{1s}^A(\vec{r})\phi_{1s}^B(\vec{r})}{2 \pm 2S} = \frac{\rho_{nonbonding}(\vec{r}) \pm \phi_{1s}^A(\vec{r})\phi_{1s}^B(\vec{r})}{1 \pm S}$

$\rho_{\substack{bonding\\antibonding}}(\vec{r}) - \rho_{nonbonding}(\vec{r}) = \frac{\rho_{non}(\vec{r}) \pm \phi_{1s}^A(\vec{r})\phi_{1s}^B(\vec{r})}{1 \pm S} - \rho_{non}(\vec{r})$ → taylor series.

$= \rho_{non}(\vec{r}) \pm \phi_{1s}^A(\vec{r})\phi_{1s}^B(\vec{r})\left[1 \mp S + S^2 \mp S^3 + S^4 \mp \cdots\right] - \rho_{non}(\vec{r})$

$= \rho_{non}(\vec{r}) - \rho_{non}(\vec{r}) \pm \phi_{1s}^A(\vec{r})\phi_{1s}^B(\vec{r}) \mp S\left[\rho_{non}(\vec{r}) \pm \phi_{1s}^A(\vec{r})\phi_{1s}^B(\vec{r})\right]\left[1 \pm S + S^2 \pm \ldots\right]$

$= \pm\phi_{1s}^A(\vec{r})\phi_{1s}^B(\vec{r}) \pm \frac{S}{1 \pm S}\left[\rho_{non}(\vec{r}) \pm \phi_{1s}^A(\vec{r})\phi_{1s}^B(\vec{r})\right]$

$= \pm\left[\phi_{1s}^A(\vec{r})\phi_{1s}^B(\vec{r}) + \frac{S}{1 \pm S}\left(\rho_{non}(\vec{r}) \pm \phi_{1s}^A(\vec{r})\phi_{1s}^B(\vec{r})\right)\right]$

$= \pm\left(\phi_{1s}^A(\vec{r})\phi_{1s}^B(\vec{r})\right) \pm$ small terms.

$\approx \pm\frac{\alpha^3}{\pi}e^{-\alpha(r_A + r_B)}$

$\rho_{bonding}(\vec{r}) - \rho_{non}(\vec{r}) \approx \frac{\alpha^3}{\pi}e^{-\alpha(r_A + r_B)}$ → add a contribution to the electron density between the atoms.

$\rho_{antibonding}(\vec{r}) - \rho_{non}(\vec{r}) \approx -\frac{\alpha^3}{\pi}e^{-\alpha(r_A + r_B)}$ → subtract this contribution from the electron density between atoms.