

PART B

Q1) Calculate electronic polarisability of

a) Hydrogen atom in ground state

To get polarisability we ~~use~~ need electric field \propto dipole moment

~~$\vec{p} = q\vec{r}$~~ $\vec{p} = \alpha \vec{E}$

to get \vec{E}

$q_{in} = \int \rho(r) dV$ Bohr's radius

$\rho(r) = \frac{q}{\pi a^3} e^{-2r/a}$ charge of e^-

$\therefore q_{in} = \int_0^\infty \int_0^\pi \int_0^{2\pi} \frac{q e^{-2r/a}}{\pi a^3} r^3 \sin\theta dr d\theta d\phi$

$= \frac{4q}{a^3} \left(e^{-2r/a} \times \left(\frac{a}{4} (2r^2 - 2ar + a^2) - a^3/4 \right) \right)$

$= q \left(1 - e^{-2r/a} \left(1 + \frac{2r}{a} + \frac{2r^2}{a^2} \right) \right)$

$\therefore E = \frac{q}{4\pi\epsilon_0 d^2} \left[1 - e^{-2d/a} \left(1 + \frac{2d^2}{a^2} + \frac{2d}{a} \right) \right]$

assuming $d/a \ll 1$ we can expand

$e^{-2d/a} = \left(1 - (2d/a) + \frac{1}{2} \left(\frac{2d}{a} \right)^2 - \frac{1}{6} \left(\frac{2d}{a} \right)^3 + \dots \right)$

$E = \frac{q}{4\pi\epsilon_0 d^2} \left[1 - \left(1 - \frac{2d}{a} + \frac{2d^2}{a^2} - \frac{4d^3}{3a^3} \right) \left(1 + \frac{2d}{a} + \frac{2d^2}{a^2} \right) \right]$

$= \frac{q}{4\pi\epsilon_0 d^2} \left[\cancel{1} - \cancel{1} - \cancel{2d/a} - \cancel{\frac{2d^2}{a^2}} + \cancel{\frac{2d}{a}} + \cancel{\frac{4d^2}{a^2}} + \cancel{\frac{4d^3}{a^3}} - \cancel{\frac{2d^2}{a^2}} - \cancel{4d^3/a^3} + \dots \right]$

$$= \frac{4}{3} \left(\frac{d}{a} \right)^3 + \dots$$

$$E = \frac{1}{4\pi\epsilon_0} \frac{q}{r^2} \cdot \left(\frac{4a^3}{3a^3} \right) = \frac{q}{(3\pi\epsilon_0 a^3)}$$

$$\therefore \boxed{\alpha = \frac{q^2}{3\pi\epsilon_0 a^3}}$$

Any molecule in ground state

a) For molecules it is not this simple to calculate electronic polarisability. This is because they polarize differently in different directions (non uniform distribution of charge, for atoms it is spherical → for ground state).
 CO_2 for instance has diff polarisabilities along diff axes: $(4.5 \times 10^{-40} \text{ C}^2\text{m/V}$ along the axis and $2 \times 10^{-40} \text{ C}^2\text{m/V}$ perpendicular)
 \therefore for a field in an arbitrary direction we must resolve it into parallel & perpendicular directions and multiply by the pertinent polarisability.

$$P = \alpha_{\perp} E_{\perp} + \alpha_{\parallel} E_{\parallel}$$

The induced dipole also may/may not be in the same direction as E . For CO_2 we still had only 2 unit directions (\perp and \parallel), for a completely asymmetrical molecule we must resolve it into the most general terms. We in general compute the polarisability tensor for the molecule

$$\begin{bmatrix} \alpha_{xx} & \alpha_{xy} & \alpha_{xz} \\ \alpha_{yx} & \alpha_{yy} & \alpha_{yz} \\ \alpha_{zx} & \alpha_{zy} & \alpha_{zz} \end{bmatrix}$$

Justification
Atkins

$$H(1), -\mu_2 E$$

$$\Delta E_2 = -\frac{1}{2} \alpha E^2$$

$$H(2), -\mu_2 E$$

$$E(2), E^2 \sum_n \frac{|\mu_{2,0n}|^2}{|E_0(0) - E_n(0)|}$$

transition dipole moment in z direction

$$\alpha_2 = 2 \sum_n \frac{|\mu_{2,0n}|^2}{E_n(0) - E_0(0)}$$

$$\alpha \approx \frac{2 e^2 R^2}{\Delta E}$$

size of the molecule

excitation energy

most generally speaking,

a) vibrational spectroscopy

Problem 12.16a) wavenumber of fundamental vibrational transition of $^{35}\text{Cl}_2$ is 564.9 cm^{-1} . calc. force constant of the bond ($m(^{35}\text{Cl}) = 34.9688 \text{ mu}$)

sol) Fundamental transition: $v = 1 \leftarrow 0$

$$\bar{\nu} = \frac{1}{2\pi c} \sqrt{\frac{k}{m_{\text{eff}}}}$$

also $m_{\text{eff}} = \frac{1}{2} m(^{35}\text{Cl})$

$$= \frac{1}{2} (34.9688 \text{ mu})$$

$$= \frac{1}{2} \times \frac{34.9688 \text{ u} \times 10^{-3} \text{ kg u}^{-1}}{6.023 \times 10^{23}}$$

20 ed

$$\frac{564.9 \text{ m}^{-1}}{100}$$

$$2 \sqrt{\frac{k}{\frac{34.9688 \text{ u}}{2 \times 6.023 \times 10^{23}} \text{ kg}^{-1} \text{ u}}} (3.14) (3 \times 10^8 \text{ m/s})$$

$$\therefore k = \frac{(564.9 \times 10^2 \text{ m}^{-1})^2 (2 \times 3.14 \times 3 \times 10^8 \text{ m/s})^2 \times 34.9688}{2 \times 6.023 \times 10^{26} \text{ kg}^{-1} \text{ u}}$$

$$k = 328.7 \text{ Nm}^{-1}$$

force constant

Problem 12.16b) for $^{79}\text{Br}^{81}\text{Br}$ is 323.2 cm^{-1} .
Calculate force constant ($m(^{79}\text{Br}) = 78.9183 \text{ mu}$,
 $m(^{81}\text{Br}) = 80.9163 \text{ mu}$)

sol) Fundamental transition: $v = 1 \leftarrow 0$.

$$\bar{\nu} = \frac{1}{2\pi c} \sqrt{\frac{k}{m_{\text{eff}}}}$$

$$m_{\text{eff}} = m_1^{-1} + m_2^{-1}$$

$$= (78.9183)^{-1} + (80.9163)^{-1}$$

$$= 0.01267 \text{ u}^{-1} + 0.012358 \text{ u}^{-1}$$

$$= 0.025029 \text{ u}^{-1}$$

$$323.2 \times 10^2 \text{ m}^{-1} = \sqrt{\frac{k}{\mu}} \quad \left(0.025029 \text{ u} \times 6.023 \times 10^{26} \text{ kg u}^{-1} \right)$$

$$2 \times 3.14 \times 3 \times 10^8 \text{ m/s}$$

$$k = \frac{(323.2 \times 10^2 \text{ m}^{-1})^2 (2 \times 3.14 \times 3 \times 10^8 \text{ m/s})^2}{0.025029 \text{ u} \times 6.023 \times 10^{26} \text{ kg u}^{-1}}$$

$$k = 245.9 \text{ Nm}^{-1}$$

Problem 12.20 a) First five vibrational energy levels of HCl are at 1481.86, 4367.50, 7149.00, 9826.48, and 12399.8 cm^{-1} . Calculate the dissociation energy of the molecule.

sol) Assuming the molecule is described by a Morse potential

$$\text{slope} = -2x_e \bar{\nu} = -104.11 \text{ cm}^{-1}$$

$$\therefore x_e \bar{\nu} = \frac{104.11 \text{ cm}^{-1}}{2} = 52.06 \text{ cm}^{-1}$$

$$\bar{\nu} - 2x_e \bar{\nu} = 2885.8 \text{ cm}^{-1}$$

$$\therefore \bar{\nu}_e = 2989.91 \text{ cm}^{-1}$$

$$D_e = \frac{\bar{\nu}_e^2}{4x_e \bar{\nu}_e} = \frac{\bar{\nu}_e^2}{4(52.06 \text{ cm}^{-1})}$$

$$= 42.93 \times 10^3 \text{ cm}^{-1}$$

$$= 42.93 \times 10^3 \text{ cm}^{-1} \left(\frac{1 \text{ eV}}{8065.5 \text{ cm}^{-1}} \right)$$

$$= 5.32 \text{ eV}$$

$$D_e = \frac{1}{2} \bar{\nu}_e$$

Dissociation energy =

$$= (42.93 \times 10^3 \text{ cm}^{-1}) - \frac{1}{2} (2989.91 \text{ cm}^{-1})$$

$$= [4.14 \times 10^4 \text{ cm}^{-1}]_{\text{or}}$$

$$4.14 \times 10^4 \text{ cm}^{-1} \times \frac{1 \text{ eV}}{8065.5 \text{ cm}^{-1}}$$

$$= [5.1373 \text{ eV}]$$

Problem 12.20 b) First five levels of HI are
 1144.83, 3374.90, 5525.51, 7596.86, 9588.35 cm^{-1} . Calculate dissociation energy

sol) slope = -76.65 cm^{-1}
 $\bar{V} - 2x_e \bar{V} = 2230.51 \text{ cm}^{-1}$

$\therefore \bar{V} = 2310.16 \text{ cm}^{-1}$

Assuming Morse potential

$D_e = \frac{\bar{V}}{4x_e} [12.38] = \frac{\bar{V}^2}{4x_e \bar{V}}$ ~~(12.38)~~

$= \frac{(2310.16 \text{ cm}^{-1})^2}{(4)(39.8 \text{ cm}^{-1})} = 33.50 \times 10^3 \text{ cm}^{-1}$
 $= 4.15 \text{ eV}$

Remaining zero potential energy

$D = D_e - \frac{1}{2} \bar{V} = (33.5 \times 10^3) - \frac{1}{2} (2310.16) \text{ cm}^{-1}$
 $= \boxed{3.235 \times 10^4 \text{ cm}^{-1}} = \boxed{4.01 \text{ eV}}$

b) Rotational spectroscopy

Problem 12.6a) wavenumber of $J=3 \leftarrow 2$ rotational transition of $^1\text{H}^{35}\text{Cl}$ (as rigid rotator) is 63.56 cm^{-1} .
 Calc a) Moment of inertia b) Bond length.

sol) $E_J = hc \tilde{B} J(J+1)$
 $\Delta E_J (3 \leftarrow 2) = hc \tilde{B} ((3)(4) - (2)(3))$
 $= 6hc \tilde{B}$

$\tilde{B} = \frac{h}{8\pi c I}$ $\bar{V} = 6\tilde{B}$ $\bar{V} = \frac{6h}{4\pi c I}$

$\bar{V} = 63.56 \text{ cm}^{-1}$ $c = 2.9978 \times 10^{10} \text{ cm}^{-1}$ $h = 1.0546 \times 10^{-34} \text{ Js}$

$I = \frac{(6) (1.0546 \times 10^{-34} \text{ Js})}{(4)(3.14)(2.998 \times 10^{10} \text{ cm}^{-1})(63.56 \text{ cm}^{-1})}$

$I = \boxed{2.644 \times 10^{-47} \text{ kg m}^2}$

$$I = m_{\text{eff}} R^2$$

$$\therefore R = \sqrt{\frac{I}{m_{\text{eff}}}}$$

bond length.

$$m_{\text{eff}} = \frac{m_H m_{Cl}}{m_H + m_{Cl}} = \frac{(1.0078)(34.9688)}{(1.0078 + 34.9688)} \left(1.66054 \times 10^{-27} \text{ kg} \right)$$

$$= 1.63 \times 10^{-27} \text{ kg}$$

$$\therefore R = \sqrt{\frac{2.644 \times 10^{-47} \text{ kg m}^2}{1.63 \times 10^{-27} \text{ kg}}} = \boxed{1.2736 \times 10^{-10} \text{ m}}$$

Problem 12.6b) $J = 1 \leftarrow 0$ for rotational for $^{1}\text{H}^{81}\text{Br}$ (mga) $= 16.93 \text{ cm}^{-1}$ Q1c d) 401 b) R

$$\text{sol) } \Delta J = hc \tilde{B} ((1)(2) - 0)$$

$$= 2hc\tilde{B}$$

$$\tilde{B} = \frac{h}{4\pi c I} \quad \tilde{\nu} = 2\tilde{B}$$

$$\therefore \tilde{\nu} = \frac{h}{2\pi c I} \quad \tilde{\nu} = 16.93 \text{ cm}^{-1}$$

$$I = \frac{1.0546 \times 10^{-34} \text{ Js}}{2 \times (3.14) (2.998 \times 10^{10} \text{ cm s}^{-1}) (16.93 \text{ cm}^{-1})}$$

$$\boxed{I = 3.309 \times 10^{-42} \text{ kg m}^2}$$

$$R = \sqrt{I / m_{\text{eff}}} \quad m_{\text{eff}} = \frac{m_H m_{Br}}{m_H + m_{Br}}$$

$$= \frac{(1)(81)}{(1+81)} \left(1.66054 \times 10^{-27} \text{ kg} \right)$$

$$= 1.64 \times 10^{-27} \text{ kg}$$

$$R = \sqrt{\frac{3.309 \times 10^{-42} \text{ kg m}^2}{1.64 \times 10^{-27} \text{ kg}}} = \boxed{1.4202 \times 10^{-10} \text{ m}}$$

Problem 12.8 a) Rotational constant of $^{127}\text{I}^{35}\text{Cl}$ is 0.1142 cm^{-1} . Calculate I-Cl bond length.
 $[m(^{35}\text{Cl}) = 34.9688 \text{ mu}, m(^{127}\text{I}) = 126.9045 \text{ mu}]$

Problem 12.5 a) Calculate freq of $J=4 \leftarrow 3$ transition in pure rotational spectrum of $^{14}\text{N}^{16}\text{O}$.
 eqb bond length is 115 pm

$$m_{\text{eff}} = \frac{m_{\text{N}} m_{\text{O}}}{m_{\text{N}} + m_{\text{O}}} = \frac{(14.003)(15.995)}{14.003 + 15.995} \left(\frac{1.6605 \times 10^{-27}}{1.66} \right)$$

$$m_{\text{eff}} = 1.24 \times 10^{-26} \text{ kg}$$

$$\text{MOI} = m_{\text{eff}} R^2 = (1.24 \times 10^{-26} \text{ kg})(115 \times 10^{-12} \text{ m})^2$$

$$I = 1.64 \times 10^{-46} \text{ kg m}^2$$

$$B = \frac{h}{4\pi c I} = \frac{1.0546 \times 10^{-34} \text{ Js}}{4 \times (3.14) (2.998 \times 10^8 \text{ ms}^{-1}) (1.64 \times 10^{-46})}$$

$$= 1.708 \text{ cm}^{-1}$$

$$\Delta \tilde{\nu} = 2\tilde{B}(J+1) = 2\tilde{B}(3+1) = 8(1.708 \text{ cm}^{-1})$$

$$\Delta \tilde{\nu} = 13.664 \text{ cm}^{-1}$$

$$\tilde{\nu} = \Delta \tilde{\nu} \times c = (13.664 \text{ cm}^{-1}) (2.998 \times 10^{10} \text{ cm s}^{-1})$$

$$\text{frequency} = 4.09 \times 10^{11} \text{ Hz}$$

Problem 12.5 b) $J=3 \leftarrow 2$ transition for $^{12}\text{C}^{16}\text{O}$.

eqb bond length = 112.81 pm

$$\Delta E = 2hc\tilde{B}J \rightarrow \text{upper state} = 6hc\tilde{B}$$

$$\tilde{B} = \frac{h}{4\pi c m_{\text{eff}} R^2} \quad \nu = 2c\tilde{B}J = \frac{hJ}{2\pi m_{\text{eff}} R^2}$$

$$m_{\text{eff}}^{-1} = m_{\text{C}}^{-1} + m_{\text{O}}^{-1} = \left(\frac{12}{12.000} + \frac{15.995}{15.995} \right)^{-1} \frac{1}{1.6605 \times 10^{-27}}$$

$$= 8.78348 \times 10^{25} \text{ kg}^{-1}$$

$$\nu = 8.78 \times 10^{25} \times 1.0546 \times 10^{-34} \times 3 = 3.4754 \times 10^{11} \text{ Hz}$$

$$2 \times (3.14) (112.81 \times 10^{-12})^2$$

c) Electronic spectroscopy

Numerical problem 1 from 13)

vibrational wavenumber in electronic ground state is $\bar{\nu} = 1580 \text{ cm}^{-1}$.

in first excited state $\bar{\nu}_1 = 700 \text{ cm}^{-1}$

$$\Delta E = 6.175 \text{ eV} = 6.175 \text{ eV} \left(\frac{8065.5 \text{ cm}^{-1}}{1 \text{ eV}} \right)$$

$$= 49804.4$$

transition is from $\nu=0$ to upper band
middle point will be the wavenumber of
lowest energy vibrational state so

$$\bar{\nu} \approx \bar{\nu}_e + \frac{1}{2}(\bar{\nu}_1 - \bar{\nu})$$

$$\approx 49804.4 + \frac{1}{2}(700 - 1580)$$

$$= 49364 \text{ cm}^{-1}$$

Resultant wave number is $\boxed{49364 \text{ cm}^{-1}}$

Problem 13.12 b) Light of wavelength 400 nm
passes through 3.5 mm of solution with conc
 $= 0.667 \text{ mmol dm}^{-3}$. Transmission is 65.5% .
alc. molar absorption coefficient.

a) According to Beer-Lambert law

$$\log \left(\frac{I}{I_0} \right) = -\epsilon [\text{C}] L \rightarrow \text{path length}$$

\swarrow \searrow \swarrow \searrow
 intensity of transmitted light intensity of incident light molar absorptivity coeff molar conc

$$\therefore \epsilon = \frac{-\log \frac{I}{I_0}}{[\text{C}] L} = \frac{-\log(0.655)}{(6.67 \times 10^{-4})(0.35)}$$

$$= 7.9 \times 10^2 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$$

$$\text{or } \boxed{7.9 \times 10^3 \text{ cm}^2 \text{ mol}^{-1}}$$

d) Raman spectroscopy

Problem 12.10 b) The wave number of incident radiation in a Raman spectrometer is $20,623 \text{ cm}^{-1}$. What is the wavenumber of scattered Stokes radiation for $J=4 \leftarrow 2$ transition of $^{16}\text{O}_2$.

sol) $\tilde{B}_2 = 1.4457 \text{ cm}^{-1} \rightarrow$ rotational const.

$$\Delta \tilde{V}_J = \tilde{B} J' (J'+1) - \tilde{B} J'' (J''+1)$$

$$= \tilde{B} [4(5) - 2(3)] = 14\tilde{B}$$

$$\Delta \tilde{V}_{\text{Stokes}} = \tilde{V}_i - \Delta \tilde{V}_J$$

$$= 20623 \text{ cm}^{-1} - 14(1.4457) \text{ cm}^{-1}$$

$$= \boxed{20603 \text{ cm}^{-1}}$$

Problem 12.11 b) Rotational Raman spectrum of $^{19}\text{F}_2$ (34.9688 mu) shows a series of Stokes lines separated by 3.5312 cm^{-1} and a series of anti-Stokes lines. Calculate bond length.

sol) separation of lines is $4\tilde{B}$

$$\tilde{B} = \frac{1}{4} (3.5312 \text{ cm}^{-1}) = 0.8828 \text{ cm}^{-1}$$

$$R = \sqrt{\left(\frac{h}{4\pi m_{\text{eff}} \tilde{B}} \right)}$$

$$m_{\text{eff}} = \frac{1}{2} m(^{19}\text{F}) = \frac{1}{2} \times 18.9984 \times (1.66 \times 10^{-27})$$

$$= 1.57734 \times 10^{-26} \text{ kg}$$

$$R = \frac{1.0546 \times 10^{-34}}{4\pi (1.57734 \times 10^{-26}) (2.998 \times 10^{10} \text{ cm s}^{-1}) (0.8828)}$$

$$\boxed{R = 1.4178 \times 10^{-10} \text{ m}}$$