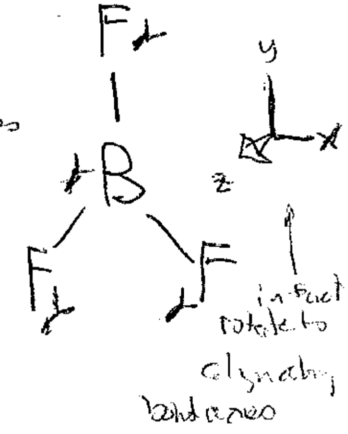
out 04 Mar 2015
due 16 Mar 2015

Chem 776 . Solutions to Ass #1

1 (a) symmetry species of BF_3 point group D_{3h}

3N - coord.
$3N-6 = 6$ vibr. modes



$\boxed{D_{3h}}$		E	$2C_3$	$3C_2$	σ_h	$2S_3$	$3\sigma_v$
	Γ_{3N}	12	0	−2	4	−2	2
$E' + A_2''$	Γ_{trans}	3	0	−1	1	−2	1
$A_2' + E''$	Γ_{rot}	3	0	−1	−1	2	−1
$\Gamma_{3N}-\Gamma_t-\Gamma_r =$	Γ_{vib}	6	0	0	4	−2	2

$$a_{A_1'} = \tfrac{1}{12}\left(1\cdot(6)\cdot 1 + 1\cdot(4)\cdot 1 + 2\cdot(-2)\cdot 1 + 3\cdot(2)\cdot 1\right) = (6+6)/12 = 1$$
$$a_{A_2'} = \tfrac{1}{12}\left(1\cdot 6\cdot 1 + 1\cdot 4\cdot 1 + 2\cdot(-2)\cdot 1 + 3\cdot(2)\cdot(-1)\right) = (6-6)/12 = 0$$
$$a_{E'} = \tfrac{1}{12}\left(1\cdot 6\cdot 2 + 1\cdot 4\cdot 2 + 2\cdot(-2)\cdot(-1) + 3\cdot 2\cdot(0)\right) = (12+8+4)/12 = 2$$
$$a_{A_1''} = \tfrac{1}{12}\left(1\cdot 6\cdot 1 + 1\cdot 4\cdot(-1) + 2(-2)(-1) + 3\cdot 2\cdot(-1)\right) = (6-6)/12 = 0$$
$$a_{A_2''} = \tfrac{1}{12}\left(1\cdot 6\cdot 1 + 1\cdot 4(-1) + 2(-2)(-1) + 3\cdot 2(+1)\right) = (6+6)/12 = 1$$
$$a_{E''} = \tfrac{1}{12}\left(2\cdot 6\cdot 1 + 1\cdot 4(-2) + 2(-2)(1) + 3\cdot 2\cdot(0)\right) = (12-8-4)/12 = 0$$

$$\Gamma_{vib} = a_1' + 2e' + a_2''$$

NB each E' mode is doubly degenerate

(b) a_2'' and $2e'$ are IR active
a_1' and $2e'$ are Raman active
there are no silent modes

---

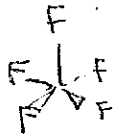
2. NB only $\Gamma_{stretch}$ was to be identified

$\boxed{D_{3h}}$	E	$2C_3$	$3C_2$	σ_h	$2S_3$	$3\sigma_v$
Γ_{str}	5	2	1	3	0	3

$$a_1' = \tfrac{1}{12}\left[(1\cdot 5\cdot 1) + (2\cdot 2\cdot 1) + (3\cdot 1\cdot 1) + (1\cdot 3\cdot 1) + (2\cdot 0\cdot 1) + (3\cdot 3\cdot 1)\right] = \tfrac{24}{12} = 2$$
$$a_2' = \left(\tfrac{1}{12}\right)\left[\;1 \quad +1 \quad -1 \quad 1 \quad 0 \quad -1\;\right] = 0$$
$$e' = \left(\tfrac{1}{12}\right)\left[\;2 \quad -1 \quad 0 \quad 2 \quad -1 \quad 0\;\right] = \tfrac{12}{12} = 1$$
$$a_1'' = \tfrac{1}{12}\left[\;1 \quad 1 \quad 1 \quad -1 \quad -1 \quad -1\;\right] = \tfrac{0}{12} = 0$$
$$a_2'' = \tfrac{1}{12}\left[\;1 \quad 1 \quad -1 \quad -1 \quad -1 \quad 1\;\right] = \tfrac{12}{12} = 1$$
$$e'' = \tfrac{1}{12}\left[\;2 \quad -1 \quad 0 \quad -2 \quad 1 \quad 0\;\right] = \tfrac{0}{12} = 0$$

$2a_1' \oplus e' \oplus a_2''$

2 cont'd

C_{4v} 

	E	$2C_4$	C_2	$2\sigma_v$	$2\sigma_d$		
Γ_{str}	5	1	1	3	1		

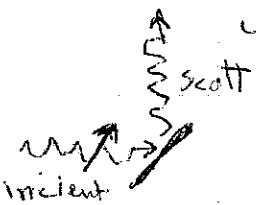
$2a_1$ (+)
b_1 (+)
e

$$
\begin{cases}
a_1 = \frac{1}{8}[1\cdot5\cdot1 + 2\cdot1\cdot1 + 1\cdot1\cdot1 + 2\cdot3\cdot1 + 2\cdot1\cdot1] = \frac{16}{8} = 2 \\
a_2 = \frac{1}{8}[\;1 \quad 1 \quad 1 \quad -1 \quad -1\;] = \frac{0}{8} = 0 \\
b_1 = \frac{1}{8}[\;1 \quad -1 \quad 1 \quad 1 \quad -1\;] = \frac{8}{8} = 1 \\
b_2 = \frac{1}{8}[\;1 \quad -1 \quad 1 \quad -1 \quad 1\;] = \frac{0}{8} = 0 \\
e = \frac{1}{2}[\;2 \quad 0 \quad -2 \quad 0 \quad 0\;] = \frac{8}{8} = 1
\end{cases}
$$

			# stretch bonds
(ii) D_{3h} structure	$2a_1$, e'	Raman active	3
(iii)	e', a_2''	IR active	2
C_{4v} structure	$2a_1$, b_1, e	Raman	~~3~~ 4
	$2a_1$, e	IR	3

(iv) Raman polarization
for D_{3h} structure: 2 polarized modes 1 unpolarized
for C_{4v} structure: 2 polarized, 2 unpolarized.

NB Γ_{TS} (a_1) modes are polarized – large intensity change for $E_{\parallel}$, $E_{\perp}$
non TS modes are unpolarized – very little change in intensity between $E_{\parallel}$, $E_{\perp}$



where $E_{\parallel}$ is when the $\underline{E}$ of the incident (excitation light) is parallel to the $\underline{E}$ of the collected (inelastic scatt) light
$E_{\perp}$ is when the $\underline{E}$ of the incident light is perpendicular to the $\underline{E}$ of the collected (inel. scatt) light

see e.g. www.youtube.com/watch?v=53wsLZ5FgbM

(v)		D_{3h}	C_{4v}
IR	– 2 modes	2	3
Ram	– 3 modes, 2 polarized.	3 (2pol)	4 (2pol)

} consistent with D_{3h} trigonal bipyramidal structure

ref J Chem Phys 44 (1966) 4039.

3. $\nu = \frac{1}{2\pi}\sqrt{\frac{k}{\mu}}$ $\quad \mu = \frac{m_1 \cdot m_2}{m_1 + m_2}$

μ_{gas}	C_{DOWN}	O_{DOWN}
6.86	16	12
	0.65	0.76
	0.58	0.67

(a) if k is unchanged $\frac{\nu_{surf}}{\nu_{gas}} = \left(\frac{\mu_g}{\mu_c}\right)^{1/2}$

(b) if k decreases by 20% $\frac{\nu_{surf}}{\nu_{gas}} = \left(\frac{\mu_g}{k_g}\,\frac{k_s}{\mu_s}\right)^{1/2} = \sqrt{0.8}\left(\frac{\mu_g}{\mu_c}\right)^{1/2}$

---

4. Balmer line at 4341.7 Å is n = 5 → n = 2 line

<u>for H</u> $\Delta E = \left(\frac{R_H}{n_1^2} - \frac{R_H}{n_2^2}\right) = \frac{hc}{\lambda}$ or $\lambda_H = \frac{hc}{R_H}\cdot\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)^{-1}$

$R_H = \frac{\mu e^4}{8h^3 \varepsilon_0^2 c} = 1.096776 \times 10^7 \text{ m}^{-1}$ (Hollas, p 5)

$\lambda_D = \frac{R_H}{R_D}\lambda_H = \frac{\mu_H}{\mu_D}\lambda_H$ $\quad \mu_H = \frac{m_e m_p}{m_e + m_p}$

$\mu_D = \frac{m_e (m_D)}{m_e + m_D}$

$\lambda_D = \left(\frac{\cancel{m_e}\cdot m_p}{m_e + m_p}\right)\left(\frac{m_e + m_D}{\cancel{m_e} m_D}\right)\lambda_H$

$m_e = 9.1093829(4) \times 10^{-31}$ kg
$m_p = m_H = 1.67262178(7) \times 10^{-27}$ "
$m_D = 3.3435835(2) \times 10^{-27}$ kg
7 sig fig.

$= \left[\left(\frac{1.67262178}{3.3435835}\right)\left(\frac{3.3444944}{1.67353272}\right)\right]\lambda_H$
$= 0.9997280\ \lambda_H$
$= 4340.52$ Å

726 A#1
4

$$\begin{pmatrix} \ln(0.45) = 0.80 \\ \ln(0.77) = 0.26 \end{pmatrix}$$

5.

$\lambda =$	$\varepsilon\,(l \cdot mol^{-1} cm^{-1})$ 255	269
benzene	234	12.5
toluene	210	267

$T(255) = 0.45$ $A_{255} = 0.347$
$T(269) = 0.77$ $A_{269} = 0.114$

NB in optical region use $\log_{10}$ (X-ray use $\ln = \log_e$)

$$A = -\log_{10} T = \varepsilon \cdot c \cdot l$$

2 eqns & 2 unknowns
$c_B = [C_6H_6]$
$c_T = [C_7H_8]$

at 255 nm $0.347 = 234\, c_B + 210\, c_T$ ①
at 269 nm $0.114 = 12.5\, c_B + 267\, c_T$ ②

from ② $c_T = (0.114 - 12.5\, c_B)/267$

→ ① $0.347 = 234\, c_B + \frac{210}{267}(0.114 - 12.5\, c_B)$

$0.347 = c_B(234 - 9.83) + 0.0897$

$c_B = 1.15 \times 10^{-3}$ M

$c_T = 3.73 \times 10^{-4}$ M

---

6. D_{2h} $B_{3g} \otimes A_g = B_{3g}$ di.pole allowed trans $\subset b_{1u}, b_{2u}\, b_{3u}$

So vibrational mode that could make this transition allowed are ones where

$$\Gamma_{vib} \otimes B_{3g} \subset b_{1u}, b_{2u}, b_{3u}$$

these are those among the u symmetry species since $g \times u = u$

$a_u \otimes b_{3g} = b_{3u}$
$b_{1u} \otimes b_{3g} = b_{2u}$ $1 \times 3 = 2$
$b_{2u} \otimes b_{3g} = b_{1u}$ $2 \times 3 = 1$
$b_{3u} \otimes b_{3g} = a_u$ $(3 \times 3 = 0 = 1)$

a_u, b_{1u} and b_{2u} modes could make the $B_{3g} \leftrightarrow A_g$ an allowed vibronic transition