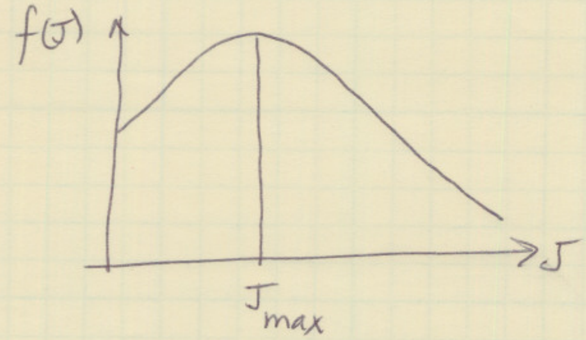
ADVANCED CHEMISTRY

QUANTUM MECHANICS - SPRING - WEEK 6

Chapter 13

13 $$f_J = (2J+1)\, e^{-[hcJ(J+1)B]/kT}$$



$$\therefore \text{ at } J_{max}, \left[\frac{d f(J)}{dJ}\right] = 0$$

$$\cancel{\frac{d f(J)}{dJ} = (2J+1)\left[-\right.}$$

$$f(J) = (2J+1)\left[e^{-hcB(J^2+J)/kT} \right]$$

$$\frac{d}{dJ}\left[f(J)\right] = (2J+1)\frac{d}{dJ}\left[e^{-hcB(J^2+J)/kT}\right] + 2\, e^{-hcB(J^2+J)/kT}$$

$$= (2J+1)\left[e^{-hcB(J^2+J)/kT}\left(\frac{-hcB}{kT}(2J+1)\right)\right] + 2\, e^{-hcB(J^2+J)/kT}$$

$$= e^{-hcB(J^2+J)/kT}\left[-\frac{hcB}{kT}(2J+1)^2 + 2\right]$$

at $J = J_{max}$ $\quad \frac{d}{dJ}\left[f(J)\right] = 0$

at $J = J_{max}$

$$-\frac{hcB}{kT}\left(2J_{max}+1\right)^2 + 2 = 0$$

$$\left(2J_{max}+1\right)^2 = \frac{2kT}{hcB}$$

$$2J_{max}+1 = \sqrt{\frac{2kT}{hcB}}$$

$$2J_{max} = \sqrt{\frac{2kT}{hcB}} - 1$$

$$J_{max} = \frac{1}{2}\sqrt{\frac{2kT}{hcB}} - \frac{1}{2}$$

$$= \frac{1}{2}\sqrt{\frac{2\times 2kT}{2\times hcB}} - \frac{1}{2} = \frac{1}{2}\sqrt{\frac{4kT}{2hcB}} - \frac{1}{2}$$

$$J_{max} = \sqrt{\frac{kT}{2hcB}} - \frac{1}{2}$$

14 For $H^{35}Cl$ $B = 10.5934\ cm^{-1}$ (from Table 13.4)

Room temperature $= 25°C = 298.15\ K$

$$= \left[\frac{(1.381\times 10^{-23}\ JK^{-1})(298.15\ K)}{\quad}\right]^{1/2} - \frac{1}{2}$$

$J_{max} = 2.628 \qquad \underline{\underline{J_{max} \approx 3}}$

at $J=0$ $N(0) = (2J+1)\, e^{-E_0/kT}$

$N(0) = e^{-hcBJ(J+1)/kT} = 1$

at $J=3$ $N(3) = 7\, e^{-hcB(12)kT}$

$N(3) = 7\, e^{-(6.626\times10^{-34}\,Js)(2.998\times10^{10}\,cm\,s^{-1})(10.5934\,cm^{-1})(12)/(1.381\times10^{-23}\,J\,K^{-1})(298.15\,K)}$

$= 3.79$

$\dfrac{N(3)}{N(0)} = \underline{\underline{3.79}}$

Energy at $J=0$ $\quad E_0 = 0$

Energy at $J=3$ $\quad E_3 = BJ(J+1) = 12B$

$E_3 - E_0 = 12B \quad \cancel{= \frac{12B}{kT}}$ ~~(in units of~~ kT)

$\dfrac{E_3 - E_0}{kT} = \dfrac{12B}{kT}$ (in units of kT)

$= \dfrac{12(10.5934\,cm^{-1})(6.626\times10^{-34}\,Js)(2.998\times10^{10}\,cm\,s^{-1})}{(1.381\times10^{-23}\,JK^{-1})(298.15\,K)}$

$= \underline{\underline{0.6134}}$

For ${}^{12}C^{16}O$ $\quad B = 1.93128\ cm^{-1}$

$$J_{max} = \left[\frac{(1.381\times10^{-23}\ JK^{-1})(298.15\ K)}{2(6.626\times10^{-34}\ Js)(2.998\times10^{10}\ cm s^{-1})(1.93128\ cm^{-1})}\right]^{1/2} - \frac{1}{2}$$

$$= 6.83 \approx \underline{\underline{7}}$$

$N(0) = 1$

$$N(7) = 15\, e^{-(6.626\times10^{-34}\ Js)(2.998\times10^{10}\ cm s^{-1})(1.93128\ cm^{-1})(56)/(1.381\times10^{-23}\ JK^{-1})(298\ K)}$$

$N(7) = 8.899$

$$\frac{N(7)}{N(0)} = \underline{\underline{8.89}}$$

$E_7 = BJ(J+1) = \cancel{8}\ 56B$

$$\frac{E_7 - E_0}{kT} = \frac{56B}{kT} = \frac{56(1.93128\ cm^{-1})(6.626\times10^{-34}\ Js)(2.998\times10^{10}\ cm s^{-1})}{(1.381\times10^{-23}\ JK^{-1})(298\ K)}$$

$$= \underline{\underline{0.1522}}$$

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$${}^{16}O \underbrace{=\!=}_{x} {}^{12}C \underbrace{=\!=}_{x} {}^{16}O \qquad I = 7.167\times10^{-46}\ kg\ m^2$$

$I = \sum m_i r_i^2 = m_0 x^2 + m_0 x^2$ where m_0 = mass of oxygen

$I = 2m_0 x^2$

$$x = 1.1612 \times 10^{-10}\, m \times \left(\frac{10^{10}\, \text{Å}}{m}\right) = 1.1612\ \text{Å}$$

CO bond length = $\underline{\underline{1.1612\ \text{Å}}}$

$$^{18}O \underbrace{=\!=\!=}_{x} {}^{12}C \underbrace{=\!=\!=}_{x} {}^{18}O$$

$$I = m_o x^2 + m_o x^2 = 2 m_o x^2$$
$$= 2\,(18\,amu)(1.1612 \times 10^{-10}\, m)^2 \times \left(\frac{1.661 \times 10^{-27}\, kg}{1\, amu}\right)$$
$$= \underline{\underline{8.063 \times 10^{-46}\, kg\, m^2}}$$

The moment of inertia for $^{16}O\,^{13}C\,^{16}O$ is the same as that of $^{16}O\,^{12}C\,^{16}O$ = $\underline{\underline{7.167 \times 10^{-46}\, kg\, m^2}}$

(17) NH_3 is a prolate top.

$$I_{\parallel} = I_a \qquad I_{\perp} = I_b = I_c$$

$$A = \frac{h}{8\pi^2 I_a c} = \frac{6.626 \times 10^{-34}\, Js}{8\pi^2 (4.41 \times 10^{-47}\, kg\, m^2)(2.998 \times 10^{10}\, cm\, s^{-1})}$$

$$A = \underline{\underline{6.3473\ cm^{-1}}}$$

$$B = \frac{h}{8\pi^2 I_b c} = \frac{6.626 \times 10^{-34}\, Js}{8\pi^2 (2.81 \times 10^{-47}\, kg\, m^2)(2.998 \times 10^{10}\, m s^{-1})}$$

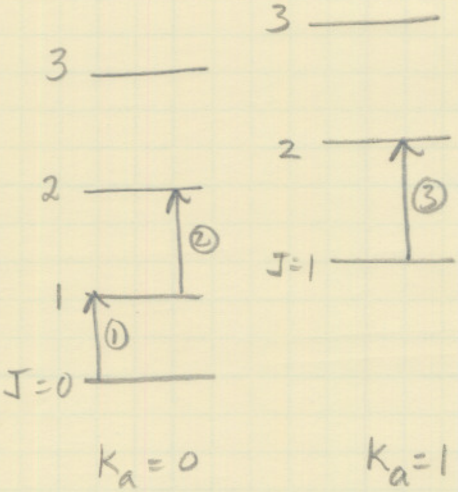
$$B = 9.9615\ cm^{-1}$$

$J=1 \quad E_1 = 2B$ $\qquad$ $J=0 \rightarrow J=1$

$$E_1 - E_0 = 2B$$

$J=0 \quad E_0 = 0$ $\qquad$ $= 19.9230\ cm^{-1}$

$$\text{wavelength} = \frac{1}{\cancel{2}(19.9230\ cm^{-1})} = 5.01932 \times 10^{-2}\ cm$$



There are two transitions that have $J=1 \rightarrow J=2$

② $J''=1 \quad J'=2 \quad K_a=0$

③ $J''=1 \quad J'=2 \quad K_a=1$

When $J''=1 \quad J'=2 \quad K_a=0$

$$F(J) = \cancel{2}BJ(J+1) + K_a^2(A-B)$$

$$F(J'') = BJ''(J''+1) + K_a^2(A-B) = 2B + K_a^2(A-B)$$

$$F(J') = 6B + K_a^2(A-B)$$

For the transition from $J''=1$ to $J'=2$

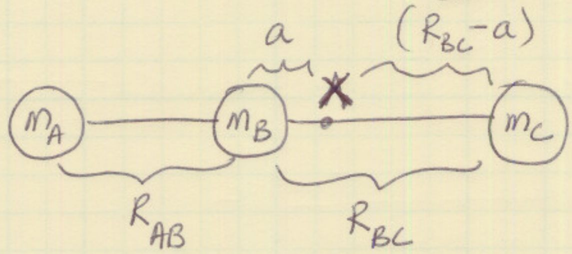
$$\Delta E = F(J') - F(J'') = 4B$$

Regardless of the value of K_a

$4(9.9615\ cm^{-1}) = 39.8460\ cm^{-1}$

∴ Both transitions with $J''=1 \rightarrow J''=2$ (regardless of K_a) will be at 2.5097×10^{-2} cm

(18)



let X = center of mass

For the center of mass condition;

$$m_A(R_{AB}+a) + m_B(a) = m_C(R_{BC}-a)$$

$$m_A R_{AB} + a m_A + a m_B = m_C R_{BC} - a m_C$$

$$a(m_A + m_B + m_C) = m_C R_{BC} - m_A R_{AB}$$

$$a = \frac{m_C R_{BC} - m_A R_{AB}}{(m_A + m_B + m_C)} = \frac{m_C R_{BC} - m_A R_{AB}}{M}$$

$$I = \sum m_i r_i^2$$

$$= m_A (R_{AB}+a)^2 + m_B a^2 + m_C (R_{BC}-a)^2$$

$$= m_A \left[R_{AB}^2 + 2a R_{AB} + a^2\right] + m_B a^2 + m_C \left[R_{BC}^2 - 2a R_{BC} + a^2\right]$$

$$= a^2\left[m_A + m_B + m_C\right] + 2a\left(m_A R_{AB} - m_C R_{BC}\right) +$$

$$m_A R_{AB}^2 + m_C R_{BC}^2$$

$$= a^2 M + 2a\left(m_A R_{AB} - m_C R_{BC}\right) + m_A R_{AB}^2 + m_C R_{BC}^2$$

$$= \frac{\left(m_C R_{BC} - m_A R_{AB}\right)^2}{M^2} \cdot M + 2\,\frac{\left(m_C R_{BC} - m_A R_{AB}\right)\left(m_A R_{AB} - m_C R_{BC}\right)}{M}$$

$$+ m_A R_{AB}^2 + m_C R_{BC}^2$$

$$= \frac{1}{M}\left[m_C^2 R_{BC}^2 - 2 m_C m_A R_{BC} R_{AB} + m_A^2 R_{AB}^2\right] +$$

$$\frac{2}{M}\left[m_C m_A R_{BC} R_{AB} - m_C^2 R_{BC}^2 - m_A^2 R_{AB}^2 + m_A m_C R_{AB} R_{BC}\right]$$

$$+ m_A R_{AB}^2 + m_C R_{BC}^2$$

$$= \frac{1}{M}\Big[m_C^2 R_{BC}^2 \cancel{- 2 m_C m_A R_{BC} R_{AB}} + m_A^2 R_{AB}^2 \cancel{+ 2 m_C m_A R_{BC} R_{AB}}$$

$$- 2 m_C^2 R_{BC}^2 - 2 m_A^2 R_{AB}^2 + 2 m_A m_C R_{AB} R_{BC}\Big]$$

$$+ m_A R_{AB}^2 + m_C R_{BC}^2$$

$$= \frac{-1}{M}\left[m_C^2 R_{BC}^2 - 2 m_A m_C R_{AB} R_{BC} + m_A^2 R_{AB}^2\right] +$$

$$m_A R_{AB}^2 + m_C R_{BC}^2$$

$$I = -\frac{1}{M}\left(m_C R_{BC} - m_A R_{AB}\right)^2 + m_A R_{AB}^2 + m_C R_{BC}^2$$

$$= -\frac{1}{\,}\left(m_C R_{BC} - m_A R_{AB}\right)^2 + \frac{M}{\,}\left(m_A R_{AB}^2 + m_C R_{BC}^2\right)$$

$$= \frac{1}{M}\Big\{ \cancel{-m_C^2 R_{BC}^2} + 2 m_A m_C R_{AB} R_{BC} - \cancel{m_A^2 R_{AB}^2} +$$
$$\cancel{m_A^2 R_{AB}^2} + m_A m_C R_{BC}^2 + m_A m_B R_{AB}^2 + m_B m_C R_{BC}^2$$
$$+ m_A m_C R_{AB}^2 + \cancel{m_C^2 R_{BC}^2} \Big\}$$

$$= \frac{1}{M}\left[m_A m_B R_{AB}^2 + m_B m_C R_{BC}^2 + m_A m_C \left(R_{AB}^2 + 2 R_{AB} R_{BC} + R_{BC}^2 \right) \right]$$

$$I = \frac{1}{M}\left[m_A m_B R_{AB}^2 + m_B m_C R_{BC}^2 + m_A m_C \left(R_{AB} + R_{BC} \right)^2 \right]$$

If $R_{AB} = R_{BC}$ and $m_A = m_C$

then

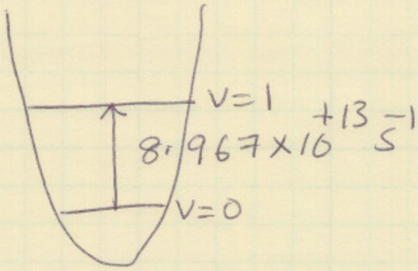
$$I = \frac{1}{M}\left[m_A m_B R_{AB}^2 + m_B m_A R_{AB}^2 + m_A^2 \left(R_{AB} + R_{AB} \right)^2 \right]$$

$$= \frac{1}{M}\left[2 m_A m_B R_{AB}^2 + m_A^2 \left(2 R_{AB} \right)^2 \right]$$

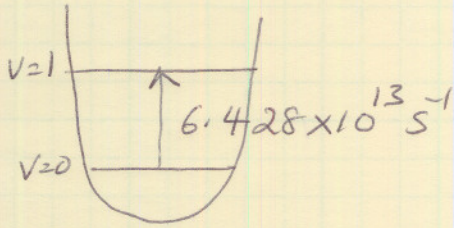
$$= \frac{1}{(m_A + m_B + m_C)}\left[2 m_A m_B R_{AB}^2 + 4 m_A^2 R_{AB}^2 \right]$$

$$= \frac{2 m_A R_{AB}^2 \cancel{(m_B + 2 m_A)}}{\cancel{(2 m_A + m_B)}} = 2 m_A R_{AB}^2$$

(19)



$H^{35}Cl$



$D^{35}Cl$

$$\nu = \frac{1}{2\pi}\sqrt{\frac{k}{\mu}}$$

$$\frac{\nu_{H^{37}Cl}}{\nu_{H^{35}Cl}} = \sqrt{\frac{\mu_{H^{35}Cl}}{\mu_{H^{37}Cl}}}$$ (since k is the same for the two isotopes)

$$= \sqrt{\frac{\left(\frac{1\times 35}{36}\right)\text{amu}}{\left(\frac{1\times 37}{38}\right)\text{amu}}} = 0.9992$$

$$\nu_{H^{37}Cl} = (8.967\times 10^{13}\ s^{-1})(0.9992) = 8.960\times 10^{13}\ s^{-1}$$

$$\lambda_{H^{35}Cl} = \frac{c}{\nu_{H^{35}Cl}} = \frac{2.99\times 10^{10}\ cm\ s^{-1}}{8.967\times 10^{13}\ s^{-1}} = 3.3344\times 10^{-4}\ cm$$

$$\tilde{\nu}_{H^{35}Cl} = 2998.9967\ cm^{-1}$$

$$\cancel{\lambda}\ \tilde{\nu}_{H^{37}Cl} = \frac{\nu_{H^{37}Cl}}{c} = \frac{8.960\times 10^{13}\ s^{-1}}{2.99\times 10^{10}\ cm\ s^{-1}} = 2996.6556\ cm^{-1}$$

$$\frac{\nu_{D^{37}Cl}}{\nu_{D^{35}Cl}} = \sqrt{\frac{\mu_{D^{35}Cl}}{\mu_{D^{37}Cl}}} = \sqrt{\frac{\left(\frac{2\times 35}{37}\right) amu}{\left(\frac{2\times 37}{39}\right) amu}} = 0.99854$$

$$\nu_{D^{37}Cl} = (6.428\times 10^{13}\ s^{-1})(0.99854) = 6.4186\times 10^{13}\ s^{-1}$$

$$\tilde{\nu}_{D^{37}Cl} = \frac{6.4186\times 10^{13}\ s^{-1}}{2.99\times 10^{10}\ cm\ s^{-1}} = 2.14669\times 10^{3}\ cm^{-1}$$

$$\tilde{\nu}_{D^{35}Cl} = \frac{6.428\times 10^{13}\ s^{-1}}{2.99\times 10^{10}\ cm\ s^{-1}} = 2.1498\times 10^{3}\ cm^{-1}$$

$$\tilde{\nu}_{D^{35}Cl} - \tilde{\nu}_{D^{37}Cl} = \underline{\underline{3.143\ cm^{-1}}}$$

(20)

	$\nu_e\ (cm^{-1})$
$^{127}I_2$	214.50
$^{79}Br_2$	325.321
$^{35}Cl_2$	559.7

$$\nu = \frac{1}{2\pi}\sqrt{\frac{k}{\mu}}$$

$$\mu_{I_2} = \left[\frac{127 \times 127}{2(127)}\right] amu \times \left(\frac{1.661\times 10^{-27} kg}{1 amu}\right)$$

$$= 1.0547\times 10^{-25}\ kg$$

$$k = \nu^2 4\pi^2 \mu \qquad \nu = \frac{c}{\lambda} = (2.99\times 10^{10}\ cm\ s^{-1})(214.50\ cm^{-1})$$

$$\nu = 6.4136\times 10^{12}\ s^{-1}$$

$$k = (6.4136\times 10^{12}\ s^{-1})^2\ 4\pi^2 (1.0547\times 10^{-25}\ kg)$$

$$= 171.27\ kg\ s^{-2} = \underline{\underline{171.27\ N\ m^{-2}}}$$

$$\mu_{Br_2} = \left(\frac{79 \times 79}{2 \times 79}\right) amu \times \left(\frac{1.661 \times 10^{-27} kg}{1 amu}\right) = 6.5609 \times 10^{-26} kg$$

$$\nu_{Br_2} = \left(2.99 \times 10^{10} cm\, s^{-1}\right)\left(325 \cancel{\times} 321\, cm^{-1}\right) = 9.7271 \times 10^{12} s^{-1}$$

$$k_{Br_2} = \left(9.7271 \times 10^{12} s^{-1}\right)^2 4\pi^2 \left(6.5609 \times 10^{-26} kg\right)$$

$$= 2.4507 \times 10^{2}\ N m^{-2}$$

$$= \underline{\underline{245.07\ N m^{-2}}}$$

$$\mu_{Cl_2} = \left(\frac{35 \times 35}{2 \times 35}\right) amu \times \left(\frac{1.661 \times 10^{-27} kg}{amu}\right) = 2.9067 \times 10^{-26} kg$$

$$\nu_{Cl_2} = \left(2.99 \times 10^{10} cm\, s^{-1}\right)\left(559.7\, cm^{-1}\right) = 1.6735 \times 10^{13} s^{-1}$$

$$k_{Cl_2}\ \left(1.6735 \times 10^{13} s^{-1}\right)^2 4\pi^2 \left(2.9067 \times 10^{-26} kg\right)$$

$$= \underline{\underline{321.38\ N M^{-2}}}$$

	I_2	Br_2	Cl_2
Bond energy (D_0)	1.5424 eV	1.9707 eV	2.4794 eV → increase
$k (N M^{-2})$	171.27	245.07	321.38 → increase