Quiz - I (Solution) Jan_29_016

1]

$$D_{min}^{47} = \frac{1}{4\pi\epsilon_0} \frac{47 \times 2 \times 1.6\times10^{-19}}{10\times10^{6}}$$

$$D_{min} = \frac{q_1 q_2}{KE}$$

$$D_{min}^{79} = \frac{1}{4\pi\epsilon_0} \frac{79 \times 2 \times 1.6\times10^{-19}}{5\times10^{6}}$$

$$D_{min}^{79} > D_{min}^{47}$$

$$\chi = 2\tan^{-1}\left(\frac{D_{min}}{2b}\right) \qquad \chi^{79} > \chi^{47}$$

For Gold deflection will be larger.

$$r_{min} = \frac{b \cos \chi/2}{1 - \sin \chi/2} \qquad \text{So } r_{min}^{79} > r_{min}^{47}$$

This implies that size of nucleus with $Z = 47$ will be smaller than nucleus with $Z = 79$

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2. Silver Atom in $L = 1$ state.

$m_\ell = +1, 0, -1$

There should be three spots on the screen.

There observation is not consistent with their assumption.

electronic configuration of silver atom $[Kr]\, 4d^{10}\, 5s^1$

Closed shell with one free electron. Idea about e^- spin which can take only two values

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3] Binding energy : $E = -\frac{1}{2}\frac{Z^2}{n_1^2} - \frac{1}{2}\frac{(Z-\epsilon)^2}{n_2^2}$

From $1s^2$ configuration $\epsilon = 0.656$

$$1s\,2s = -\frac{1}{2}\frac{Z^2}{n_1^2} - \frac{1}{2}\frac{(Z-0.656)^2}{n_2^2} = -2 - \frac{1}{8}(2-0.656)^2$$

$$= -2.2294$$

5) $1s\,2p$ state

$l_1 = 0 \qquad l_2 = 1$

$m_{s_1} = 1/2 \qquad m_{s_2} = 1/2, -1/2$

L-S coupling $\quad$ ~~L = 1~~ $\quad S = 0, 1 \qquad L = 1$

$J = 0, 1, 2$

(1) for $S = 0 \quad L = 1$

$J = 1$

singlet state $\quad {}^1P_1$

(2) $L = 1 \quad S = 1$

$J = 0, 1, 2$

$\equiv$ Triplet state $\quad {}^3P_{0,1,2}$

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6) J - J coupling.

$J_1 = 1/2 \qquad J_2 = 3/2, 1/2$

for $J_1 = 1/2 \quad J_2 = 3/2$

$J = J_1 + J_2 \quad J_1 - J_2$

$= 1, 2$

for $J_1 = 1/2 \quad J_2 = 1/2$

$J = 0, 1$

$l_1 + l_2 = 1$

$S_1 + S_2 = 0, 1$

${}^1P_0, \; {}^3P_0$

${}^1P_1 \quad {}^1P_2 \quad {}^3P_1 \quad {}^3P_2$

Total state $\quad {}^1P_0 \qquad {}^3P_{0,1,2}$

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3) Nuclear spin 1

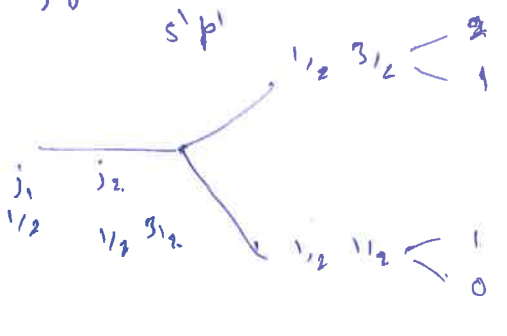
$f = 3/2 \quad 1/2$

$$S_N \cdot S_e = \frac{\hbar^2}{2}\left[f(f+1) - S_N(S_N+1) - S_e(S_e+1)\right]$$

$$= \frac{\hbar^2}{2}\left(f(f+1) - 2 - 3/4\right)$$

$$= \frac{\hbar^2}{2}\left[f(f+1) - \frac{11}{4}\right]$$

jj



for High Z atoms

$F = 1, 0$

1

[Solution Quiz - 2]

1) Term Symbol for

B_2 : $(1\sigma_g)^2 (1\sigma_u)^2 (2\sigma_g)^2 (2\sigma_u)^2 (1\pi_u)^2$

C_2 : $(1\sigma_g)^2 (1\sigma_u)^2 (2\sigma_g)^2 (2\sigma_u)^2 (1\pi_u)^4$

For B_2 : ~~Outsh~~ Outershell $(1\pi_u)^2$ [2 electrons both are in π state] $l = 1$

According to Pauli's exclusion principle.

m_{l_1}	m_{s_1}	m_{l_2}	m_{s_2}	M_L	M_S
+1	+1/2	+1	-1/2	2	0
+1	+1/2	-1	+1/2	0	1
+1	+1/2	-1	-1/2	0	0
+1	-1/2	-1	+1/2	0	0
+1	-1/2	-1	-1/2	0	-1
-1	+1/2	-1	-1/2	-2	0

$M_L = 2$ $M_S = 0$ $^1\Delta$

$M_L = 0$ $M_S = 1$ $^3\Sigma$

$M_L = 0$ $M_S = 0$ $^1\Sigma$

For C_2 : All the shell are fully filled. Term symbol $^1\Sigma$

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2) Transition from (v, J) to (v', J')

$$\Delta E = E_{v'J'} - E_{vJ}$$

$$= h\nu_0 (v' - v) + B'hc J'(J'+1) - Bhc J(J+1)$$

rigid rotor $B' = B$

$\Delta E = h\nu_0 + 2Bhc(J+1)$ for R branch $\Delta J = +1$

$\Delta E = h\nu_0 - 2BJ$ for P branch $\Delta J = -1$

For this line spacing is equal to $2B$ (Constant)

But when we consider ro-vibrational coupling.

$$\underbrace{B'}_{\text{rotational constant.}} = B_0 - \alpha_e (v + 1/2)$$

$$\Delta E = h\nu_0 (v' - v) + hcB' J'(J'+1) - Bhc\, J(J+1)$$

Line spacing. (for R branch)

$$\tilde{\nu} = \left[\left[B_0 - \frac{3\alpha_e}{2}\right](J+2)(J+3) - (B_0 \cancel{- \frac{3\alpha_e}{2}})(J+1)(J+2)\right]$$

$$- \left[\left(B_0 - \frac{3\alpha_e}{2}\right)(J+1)(J+2) - B_0 (J)(J+1)\right]$$

$$= \left[-\frac{3\alpha_e}{2}\left[J^2 + 5J + 6\right] + B_0 (J^2 + 5J + 6) - B_0 (J^2 + 3J + 2)\right]$$

$$- \left[B_0 (J^2 + 3J + 2) - \frac{3\alpha_e}{2}(J^2 + 3J + 2) - B_0 (J^2 + J)\right]$$

$$= \frac{-3\alpha_e}{2} \Big[\quad \quad J J^2 + C \quad J J + \text{Constant.}$$

~~Quad~~ Quadratic in J.

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3) Population distribution for any energy level J is given by Boltzmann distribution.

$$N_J = N_0 (2J+1)\, e^{\left(-\frac{\Delta E}{k_B T}\right)}$$

$$E = Bhc (J)(J+1)$$

Most populated level is determined as $\frac{dN_J}{NJ} = 0$ (zero at maxima of N_J distribution)

$$\frac{dN_J}{dJ} = N_0 \left[2 e^{-\frac{Bhc\, J(J+1)}{k_B T}} + (2J+1) e^{-\frac{Bhc\, J(J+1)}{k_B T}} \left(-\frac{Bhc\,(2J+1)}{k_B T} \right) \right] = 0$$

$$= N_0 e^{-\frac{Bhc\, J(J+1)}{k_B T}} \left[2 + (2J+1) \left(-\frac{Bhc\,(2J+1)}{k_B T} \right) \right] = 0$$

$$\Rightarrow \quad 2 + (2J+1)^2 \left(-\frac{Bhc}{k_B T} \right) = 0$$

$$\Rightarrow \quad (2J+1)^2 = \frac{2 k_B T}{Bhc}$$

$$\Rightarrow \quad (2J+1) = \sqrt{\frac{2 k_B T}{Bhc}}$$

$$\Rightarrow \quad J_{max} = \sqrt{\frac{k_B T}{2Bhc}} - \frac{1}{2}$$

(i) Room Temp. $T = 300\,k$ $\qquad k_B = 1.38 \times 10^{-23}\ J/k$

$B = 10.6\ cm^{-1}$ $\qquad J_{max} = 2.6$

$= 1060\ m^{-1}$

(ii) At $100°c$. $\qquad T = 373\ k$

$J_{max} = 2.95$

As it is clearly seem for the temp difference of ~~75~~ $73°c$

change in J_{max} is ~~very~~ not much. ~~Effe~~.

J_{max} can not be used for accurated measurent of temperature of sample because — — — — —

Que : 4 Centrifugal Distortion.

A real molecule is not rigid. When it rotates, the centrifugal forces act on the atom and internuclear distance widens. This force is compensated by restoring force $\vec{F_r}$ which depends on the slope of potential energy.

In the vicinity of equilibrium R_e.

$$F_r = -k\,(R - R_e)\,\hat{R}$$

So
$$\frac{J(J+1)\hbar^2}{mR^3} = k\,(R - R_e)$$

$$R = R_e + \frac{J(J+1)\hbar^2}{MkR^3}$$

$$R = R_e\left(1 + \frac{J(J+1)\hbar^2}{MkR_e^4}\right)$$

$$\frac{1}{R^2} = \frac{1}{R_e^2}\left[1 - \frac{2J(J+1)\hbar^2}{MkR_e^4} + \frac{3J^2(J+1)^2\hbar^2}{M^2k^2R_e^8} + \cdots\right]$$

$$E_{rot} = \frac{J(J+1)\hbar^2}{2MR^2} = \frac{J(J+1)\hbar^2}{2MR_e^2} - \frac{J^2(J+1)^2\hbar^4}{2M^2kR_e^6}$$

$$B_e \propto \frac{1}{R_e^2} \qquad \underbrace{D_e \propto \frac{1}{R_e^6}}_{\text{Centrifugal distortion term}}$$

$$\underbrace{D_v \propto \int \psi^*_{vibr}\,\frac{1}{R^6}\,\psi_{vib}\,dR}$$

Ques 6.

$$G(n) = \omega_e\left(n+\tfrac{1}{2}\right) - x_e\omega_e\left(n+\tfrac{1}{2}\right)^2$$

$$G(n+1) - G(n) = \omega_e\left(n+1+\tfrac{1}{2}\right) - \omega_e\left(n+\tfrac{1}{2}\right) - x_e\omega_e\left(n+1+\tfrac{1}{2}\right)^2 + x_e\omega_e\left(n+\tfrac{1}{2}\right)^2$$

$$\Rightarrow \omega_e - x_e\omega_e\left[n^2+\tfrac{9}{4}+3n\right] + x_e\omega_e\left(n^2+\tfrac{1}{4}+n\right)$$

$$\Rightarrow \omega_e - \cancel{x_e\omega_e n^2} - x_e\omega_e\tfrac{9}{4} - 3n x_e\omega_e + \cancel{x_e\omega_e n^2} + \frac{x_e\omega_e}{4} + n x_e\omega_e$$

$$\Rightarrow \omega_e - 2x_e\omega_e - 2n x_e\omega_e$$

$$G(n+2) - G(n+1) = \omega_e\left(n+2+\tfrac{1}{2}\right) - \omega_e\left(n+1+\tfrac{1}{2}\right) - x_e\omega_e\left(n+2+\tfrac{1}{2}\right)^2 + x_e\omega_e\left(n+1+\tfrac{1}{2}\right)^2$$

$$\Rightarrow \omega_e - x_e\omega_e\left(n^2+\tfrac{25}{4}+5n\right) + x_e\omega_e\left(n^2+\tfrac{9}{4}+3n\right)$$

$$\Rightarrow \omega_e - \cancel{x_e\omega_e n^2} - \tfrac{25}{4}x_e\omega_e - 5n x_e\omega_e + \cancel{x_e\omega_e n^2} + \tfrac{9}{4}x_e\omega_e + 3n x_e\omega_e$$

$$\Rightarrow \omega_e - 4x_e\omega_e - 2n x_e\omega_e$$

Δ spacing $\Rightarrow$ $\cancel{\omega_e} - 4x_e\omega_e - \cancel{2n x_e\omega_e} - \cancel{\omega_e} + 2x_e\omega_e + \cancel{2n x_e\omega_e}$

$$\Rightarrow -2x_e\omega_e$$

Given Spectrum / Energy level: 2886, 5668, 8347, 10923

ΔE ~~spacing $\Rightarrow$ 2782, 2679, 2576~~

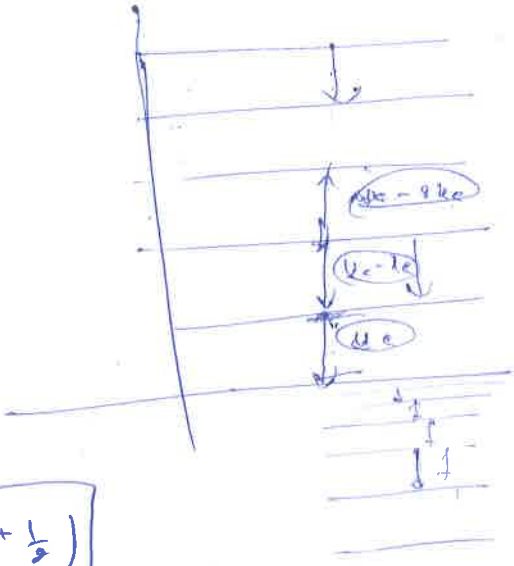
Spacing: −103, −103, −103

$$-2x_e\omega_e = -103$$

$$\boxed{x_e\omega_e = 51.5\ \text{cm}^{-1}}$$

$G(v) = w_e ($

$G(v) = \boxed{w_e - 2x_e w_e - (3n) x_e w_e}$



Harmonic Oscillator.

Transition between any two level has same energy $\boxed{\hbar\omega\left(n+\frac{1}{2}\right)}$

But Morse potential gives that with increase in line energy difference b/w two level keep on decreasing (which is directly proportional to n)

We

$\hbar\omega\left(n+\frac{1}{2}\right)$

$\hbar\omega$

$G(v)$

$\boxed{w_e - n \times 2}$