Answers HW # 5 Chem 1410

5-13. For $H^{79}Br$ $\tilde{\nu} = 2630\ cm^{-1}$. What is k and τ?

$$k = (2\pi c \tilde{\nu})^2 \mu$$

$$\mu = \frac{(1.68 \times 10^{-27})(1.33 \times 10^{-35})}{1.348 \times 10^{-25}} = 1.66 \times 10^{-27}\ Kg$$

$$k = \left[2\pi\, (2.998 \times 10^{8}\ \tfrac{m}{s})(2630\ cm^{-1})\left(\tfrac{100\ cm}{m}\right)\right]^2 \cdot 1.66 \times 10^{-27}\ Kg$$

$$= 407\ N/m$$

$$\tau = \frac{1}{\nu} = \frac{1}{c\tilde{\nu}} = \frac{1}{(2.998 \times 10^{8}\ \frac{m}{s})(2630\ cm^{-1})\left(\frac{100\ cm}{m}\right)}$$

$$\tau = 1.27 \times 10^{-14}\ sec$$

5-25. For the harmonic oscillator problem calculate $\langle p \rangle$ and $\langle p^2 \rangle$.

$\int \psi_v^* \hat{p}\, \psi_v\, dx = 0$ because the integrand is an odd function.

if ψ_v is even $\rightarrow$ $\hat{p}\psi_v$ is odd

if ψ_v is odd $\rightarrow$ $\hat{p}\psi_v$ is even

$$\langle p^2 \rangle = \int \psi_v \, \hat{p}^2 \, \psi_v \, dx = \int \psi_v \left(-\hbar^2 \frac{d^2}{dx^2} \right) \psi_v \, dx$$

So we need to consider $\int \psi_v \frac{d^2}{dx^2} \psi_v \, dx$

$$\psi_v = N_v H_v(\xi) \, e^{-\xi^2/2}$$

$$\frac{d}{d\xi} H_v e^{-\xi^2/2} = \left(\frac{dH_v}{d\xi} - \xi H_v \right) e^{-\xi^2/2}$$

$$= \left(2v H_{v-1} - \frac{H_{v+1}}{2} - v H_{v-1} \right) e^{-\xi^2/2}$$

$$= \left(v H_{v-1} - \frac{H_{v+1}}{2} \right) e^{-\xi^2/2}$$

$$\frac{d}{d\xi} \left(v H_{v-1} - \frac{H_{v+1}}{2} \right) e^{-\xi^2/2} =$$

$$\left(v H_{v-1}' - \frac{H_{v+1}'}{2} \right) e^{-\xi^2/2} + \left(v H_{v-1} - \frac{H_{v+1}}{2} \right) (-\xi) \, e^{-\xi^2/2}$$

$$\left[2v(v-1) H_{v-2} - \frac{2}{2}(v+1) H_v - v \left(\frac{H_v}{2} + \frac{2(v-1)}{2} H_{v-2} \right) + \frac{1}{2} \left(\frac{H_{v+2}}{2} + \frac{2(v+1)}{2} H_v \right) \right] e^{-\xi^2/2}$$

$$= \left[v(v-1) H_{v-2} + \left(-v - \frac{1}{2} \right) H_v + \frac{1}{4} H_{v+2} \right] e^{-\xi^2/2}$$

We can ignore these two terms as they will not contribute to the integral.

We are left with

$$\langle p^2 \rangle = -\hbar^2 \alpha \left(-v - \frac{1}{2} \right) \underbrace{\int_{-\infty}^{\infty} \psi_v \psi_v \, dx}_{1} = \hbar \sqrt{k\mu} \left(v + \frac{1}{2} \right)$$

$d/dx = \sqrt{\alpha} \, d/d\xi$

5-37

a) $\hat{L}^2 \sqrt{\frac{1}{4\pi}} = 0$

b) $\hat{L}^2 \sqrt{\frac{3}{4\pi}} \cos\theta = \sqrt{\frac{3}{4\pi}} \left(\frac{-\hbar^2}{\sin\theta}\right) \frac{d}{d\theta} \sin\theta(-\sin\theta)$

$= \sqrt{\frac{3}{4\pi}} \left(\frac{\hbar^2}{\sin\theta}\right)(2\sin\theta\cos\theta) = \sqrt{\frac{3}{4\pi}}\, 2\hbar^2 \cos\theta$

the eigenvalue is $2\hbar^2$

c) $\hat{L}^2 \sqrt{\frac{3}{8\pi}} \sin\theta\, e^{i\phi} = \sqrt{\frac{3}{8\pi}} \left(\frac{-\hbar^2}{\sin\theta}\right) \Big[\frac{d}{d\theta} \sin\theta\cos\theta\, e^{i\phi}$

$+ \frac{1}{\sin\theta} \sin\theta \frac{d^2}{d\phi^2} e^{i\phi}\Big]$

$= \sqrt{\frac{3}{8\pi}} (+\hbar^2) \left\{ \frac{\sin^2\theta - \cos^2\theta}{\sin\theta} + \frac{\sin\theta}{\sin^2\theta} \right\} e^{i\phi}$

$= \sqrt{\frac{3}{8\pi}}\, \hbar^2 \left\{ \frac{\sin^2\theta - \cos^2\theta + 1}{\sin\theta} \right\} e^{i\phi}$

$= \sqrt{\frac{3}{8\pi}}\, \hbar^2 \left\{ \frac{\sin^2\theta - \cos^2\theta + \sin^2\theta + \cos^2\theta}{\sin\theta} \right\} e^{i\phi} = \sqrt{\frac{3}{8\pi}} (2\hbar^2) \sin\theta\, e^{i\phi}$

the eigenvalue is $2\hbar^2$

d) $\hat{L}^2 \sqrt{\frac{3}{8\pi}} \sin\theta\, e^{-i\phi} = \sqrt{\frac{3}{8\pi}} (2\hbar^2) \sin\theta\, e^{-i\phi}$

the eigenvalue is $2\hbar^2$. The steps for proving (d) are the same as for (c).

(b), (c), (d) all have the same eigenvalue.

5-47. Spectra of D vs. H.

$$\mu_H = \frac{m_e m_H}{m_e + m} \qquad \mu_D = \frac{m_e m_D}{m_e + m_D}$$

$$\frac{\mu_D}{\mu_H} = \frac{m_e m_D}{m_e + m_D} \cdot \frac{m_e + m_H}{m_e m_H} = \frac{m_D}{m_H} \frac{m_e + m_H}{m_e + m_D}$$

$m_e = 9.109 \times 10^{-31}$ Kg

$m_p = 1.6726 \times 10^{-27}$ Kg

$m_D = 3.3436 \times 10^{-27}$ Kg

Here m_H and m_D are the masses of the nuclei <u>not</u> the total atomic masses. So m_H actually is m_p.

$$\frac{\mu_D}{\mu_H} = \frac{3.3436}{1.6726} \frac{1.6726 + .0009}{3.3436 + .0009} = 1.00027$$

Now the Energy levels of the H atom are $\propto \mu$.

So the ratio of the spectral transitions of deuterium and hydrogen goes as 1.00027.