Quantum Chemistry

Corrections 4

1. *In the far infrared spectrum of $H^{79}Br$, there is a series of lines separated by 16.72 cm^{-1}. Calculate the moment of inertia and internuclear separation in $H^{79}Br$.*

Comme on l'a vu au cours, les transitions rotationnelles d'une molécule diatomique sont séparées, dans l'approximation du rotateur rigide, de $2B$ (en $\left[cm^{-1}\right]$), où $B = \frac{h}{8\pi^2 cI}$.

$$\left.\begin{array}{r} \Delta\tilde{\nu} = 2B = \dfrac{h}{4\pi^2 cI} \;\Rightarrow\; I = \dfrac{h}{4\pi^2 c\Delta\tilde{\nu}} \\ \Delta\tilde{\nu} = 16.72\left[cm^{-1}\right] \end{array}\right\} \Rightarrow\; I = 3.35\cdot 10^{-47}\left[kg\cdot m^2\right] = 2.02\left[uma\cdot \mathring{A}^2\right]$$

$$\left.\begin{array}{l} I = \mu r_0^{\,2} \;\Rightarrow\; r_0 = \sqrt{\dfrac{I}{\mu}} \\ \mu = \dfrac{m(H)\cdot m\left({}^{79}Br\right)}{m(H)+m\left({}^{79}Br\right)} = 0.995[uma] \end{array}\right\} \Rightarrow\; r_0 = 1.42\left[\mathring{A}\right]$$

2. *The $l=0 \rightarrow l=1$ transition for carbon monoxide ($^{12}C^{16}O$) occurs at $1.153 \cdot 10^5$ MHz. Calculate the bond length in carbon monoxide.*

La fréquence d'une transition rotationnelle vaut, $\nu = 2B(l+1)$
Dans notre cas, la transition a lieu de $l_{initial} = 1$ à $l_{final} = 0$, avec $\nu = 2B$ et $B = 5.765\cdot 10^{10}\, s^{-1}$

$$I = \frac{h}{8\pi^2 B} = \frac{6.626\cdot 10^{-34}\left[Js\right]}{8\pi^2\cdot 5.765\cdot 10^{10}\left[s^{-1}\right]} = 1.45\cdot 10^{-46}\, Kg\cdot m^2$$

$$\Rightarrow r = \sqrt{\frac{I}{\mu}} = \sqrt{\frac{1.45\cdot 10^{-47}\left[Kg\cdot m^2\right]}{\frac{48}{7}\cdot 1.66\cdot 10^{-27}\left[Kg\right]}} = 1.13\mathring{A}$$

ou

$$\nu_{1\leftarrow 0} = \frac{\Delta E_{1\leftarrow 0}}{h} = \frac{1}{h}\cdot\left(\frac{\hbar^2}{2I}\cdot 1\cdot 2 - \frac{\hbar^2}{2I}\cdot 0\cdot 1\right) = \frac{h}{4\pi^2 I}$$

$$\left.\begin{array}{l} I = \mu r_0^{\,2} = \dfrac{h}{4\pi^2\nu_{1\leftarrow 0}} \;\Rightarrow\; r_0 = \sqrt{\dfrac{h}{4\pi^2\nu_{1\leftarrow 0}\mu}} \\ \mu = \dfrac{m\left({}^{12}C\right)\cdot m\left({}^{16}O\right)}{m\left({}^{12}C\right)+m\left({}^{16}O\right)} = 6.856\left[uma\right] \end{array}\right\} \Rightarrow\; r_0 = 1.13\,\AA$$

3. *In Cartesian coordinates,*

$$\hat{L}_z = -i\hbar\left(x\frac{\partial}{\partial y} - y\frac{\partial}{\partial x}\right)$$

Use the following equations that relate Cartesian and spherical coordinates

$$x = r\sin\theta\cos\varphi \qquad r = \sqrt{x^2+y^2+z^2}$$

$$y = r\sin\theta\sin\varphi \qquad \varphi = \tan^{-1}\left(\frac{y}{x}\right)$$

$$z = r\cos\theta \qquad \theta = \cos^{-1}\left(\frac{z}{\sqrt{x^2+y^2+z^2}}\right)$$

to show that in spherical polar coordinates,

$$\hat{L}_z = -i\hbar\frac{\partial}{\partial\varphi}$$

On connaît $\hat{L}_z = -i\hbar\left(x\frac{\partial}{\partial y} - y\frac{\partial}{\partial x}\right)$ en coordonnées cartésiennes et on cherche à l'obtenir en coordonnées sphériques. Il faut donc exprimer *x*, *y*, $\frac{\partial}{\partial x}$ et $\frac{\partial}{\partial y}$ en fonction de *r*, θ et φ.

$$\frac{\partial}{\partial y} = \frac{\partial r}{\partial y}\frac{\partial}{\partial r} + \frac{\partial\theta}{\partial y}\frac{\partial}{\partial\theta} + \frac{\partial\varphi}{\partial y}\frac{\partial}{\partial\varphi}$$

$$\frac{\partial r}{\partial y} = \frac{2y}{2\sqrt{x^2+y^2+z^2}} = \frac{r\sin\theta\sin\varphi}{r} = \sin\theta\sin\varphi$$

$$\frac{\partial}{\partial x} = \frac{\partial r}{\partial x}\frac{\partial}{\partial r} + \frac{\partial\theta}{\partial x}\frac{\partial}{\partial\theta} + \frac{\partial\varphi}{\partial x}\frac{\partial}{\partial\varphi}$$

$$\frac{\partial r}{\partial x} = \frac{2x}{2\sqrt{x^2+y^2+z^2}} = \frac{r\sin\theta\cos\varphi}{r} = \sin\theta\cos\varphi$$

$$\frac{\partial\theta}{\partial y} = -\frac{1}{\sqrt{1-\frac{z^2}{x^2+y^2+z^2}}}\left(-\frac{1}{2}\right)\frac{z\cdot 2y}{\left(x^2+y^2+z^2\right)^{\frac{3}{2}}}$$

$$= \frac{yz}{\underbrace{\sqrt{x^2+y^2}}_{=r\sin\theta}\left(x^2+y^2+z^2\right)} = \frac{r\sin\theta\sin\varphi\cdot r\cos\theta}{r\sin\theta\cdot r^2}$$

$$= \frac{\cos\theta\sin\varphi}{r}$$

$$\frac{\partial\varphi}{\partial y} = \frac{1}{1+\frac{y^2}{x^2}}\cdot\frac{1}{x} = \frac{x}{x^2+y^2} = \frac{r\sin\theta\cos\varphi}{r^2\sin^2\theta} = \frac{\cos\varphi}{r\sin\theta}$$

$$\frac{\partial\theta}{\partial x} = -\frac{1}{\sqrt{1-\frac{z^2}{x^2+y^2+z^2}}}\left(-\frac{1}{2}\right)\frac{z\cdot 2x}{\left(x^2+y^2+z^2\right)^{\frac{3}{2}}}$$

$$= \frac{xz}{\underbrace{\sqrt{x^2+y^2}}_{=r\sin\theta}\left(x^2+y^2+z^2\right)} = \frac{r\sin\theta\cos\varphi\cdot r\cos\theta}{r\sin\theta\cdot r^2}$$

$$= \frac{\cos\theta\cos\varphi}{r}$$

$$\frac{\partial\varphi}{\partial x} = \frac{1}{1+\frac{y^2}{x^2}}\cdot\left(-\frac{y}{x^2}\right) = -\frac{y}{x^2+y^2} = -\frac{r\sin\theta\sin\varphi}{r^2\sin^2\theta} = -\frac{\sin\varphi}{r\sin\theta}$$

En effectuant maintenant les substitutions dans l’expression de départ, on obtient:

$$\hat{L}_z = -i\hbar\left[r\sin\theta\cos\varphi\left(\sin\theta\sin\varphi\frac{\partial}{\partial r}+\frac{\cos\theta\sin\varphi}{r}\frac{\partial}{\partial\theta}+\frac{\cos\varphi}{r\sin\theta}\frac{\partial}{\partial\varphi}\right)\right.$$

$$\left.-r\sin\theta\sin\varphi\left(\sin\theta\cos\varphi\frac{\partial}{\partial r}+\frac{\cos\theta\cos\varphi}{r}\frac{\partial}{\partial\theta}+\frac{\sin\varphi}{r\sin\theta}\frac{\partial}{\partial\varphi}\right)\right]$$

$$= -i\hbar\left(\cos^2\varphi\frac{\partial}{\partial\varphi}+\sin^2\varphi\frac{\partial}{\partial\varphi}\right) = -i\hbar\frac{\partial}{\partial\varphi}$$