Advanced Physical Chemistry II
HW

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13 Molecular Spectroscopy

3, 7, 14, 18, 24, 28, 32, 37, 40, 43, 45, 51

13-3

$$\mu = \frac{1.01 \times 126.9}{1.01 + 126.9} \times 1823\,\mathrm{a.u.} = 1.827 \times 10^3\,\mathrm{a.u.} \tag{13.1}$$

$$\begin{aligned}\tilde{B} &= \frac{\hbar}{4\pi c\mu R_e^2} = \frac{1}{4\pi \times 137 \times 1.827 \times 10^3}\,\mathrm{a.u.} \times \frac{1}{(160.4\,\mathrm{pm})^2} \\ &= 1.682 \times 10^{-5}\,\mathrm{pm} \times \frac{1}{(160.4\,\mathrm{pm})^2} \\ &= 6.54\,\mathrm{cm}^{-1}\end{aligned} \tag{13.2}$$

$$c\tilde{B} = 3 \times 10^8\,\mathrm{m \cdot Hz} \times 6.54 \times 10^2\,\mathrm{m}^{-1} = 1.96 \times 10^5\,\mathrm{MHz} \tag{13.3}$$

13-7

$$\mu = \frac{38.96 \times 34.97}{38.96 + 34.97}\mathrm{amu} = 18.44\,\mathrm{amu} = 3.06 \times 10^{-26}\,\mathrm{kg} \tag{13.4}$$

$$k = \mu(2\pi c\tilde{\nu})^2 = 3.06 \times 10^{-26}(2\pi \times 3 \times 10^8 \times 27800)^2 = 84.0\,\mathrm{N \cdot m} \tag{13.5}$$

$$T = \frac{1}{c\tilde{\nu}} = \frac{1}{3 \times 10^8 \times 27800} = 1.20 \times 10^{-13}\,\mathrm{s} \tag{13.6}$$

13-14

$$R(0) = \tilde{\nu} + 2\tilde{B}_1 = 2642.60\,\mathrm{cm}^{-1} \tag{13.7}$$

$$R(1) = \tilde{\nu} - 2\tilde{B}_0 + 6\tilde{B}_1 = 2658.36\,\mathrm{cm}^{-1} \tag{13.8}$$

$$P(0) = \tilde{\nu} - 2\tilde{B}_0 = 2609.67\,\mathrm{cm}^{-1} \tag{13.9}$$

$$P(1) = \tilde{\nu} - 6\tilde{B}_0 - 2\tilde{B}_1 = 2592.51\,\mathrm{cm}^{-1} \tag{13.10}$$

thus

$$\tilde{B}_1 = 8.12\,\mathrm{cm}^{-1} \tag{13.11}$$

$$\tilde{B}_0 = 8.35\,\mathrm{cm}^{-1} \tag{13.12}$$

Then

$$\tilde{B}_1 = \tilde{B}_e - \frac{1}{2}\tilde{\alpha}_e = 8.12\,\mathrm{cm}^{-1} \tag{13.13}$$

$$\tilde{B}_0 = \tilde{B}_e - \frac{3}{2}\tilde{\alpha}_e = 8.35\,\mathrm{cm}^{-1} \tag{13.14}$$

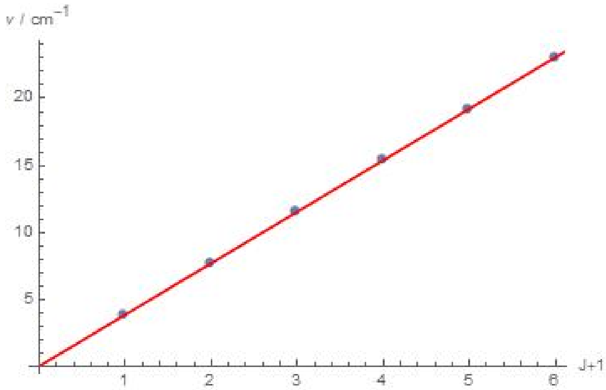
$\therefore$

$$\tilde{B}_e = 8.47\,\mathrm{cm}^{-1} \tag{13.15}$$
$$\tilde{\alpha}_e = 0.23\,\mathrm{cm}^{-1} \tag{13.16}$$

13-18 Since

$$\tilde{\nu}(J \to J+1) = 2\tilde{B}(J+1) - 4\tilde{D}(J+1)^3 \tag{13.17}$$

we can fit the $\tilde{\nu} \sim J+1$ curve as follows



and thus

$$2\tilde{B} = 3.845\,\mathrm{cm}^{-1} \tag{13.18}$$
$$-4\tilde{D} = -2.555 \times 10^{-5}\,\mathrm{cm}^{-1} \tag{13.19}$$

i.e.

$$\tilde{B} = 1.923\,\mathrm{cm}^{-1} \tag{13.20}$$
$$\tilde{D} = 6.388 \times 10^{-6}\,\mathrm{cm}^{-1} \tag{13.21}$$

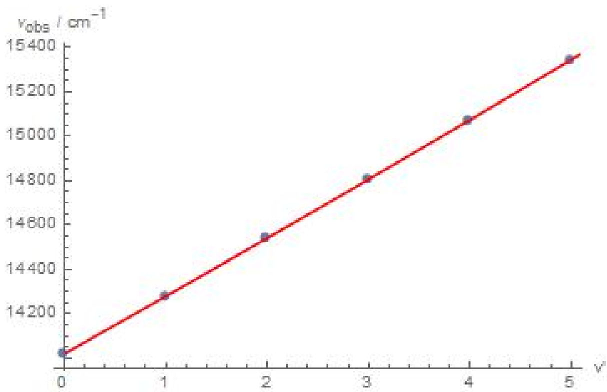
13-32 Since

$$\tilde{\nu}_{\mathrm{obs}} = \tilde{T}_e + \left(\frac{1}{2}\tilde{\nu}'_e - \frac{1}{4}\tilde{x}'_e\tilde{\nu}'_e\right) - \left(\frac{1}{2}\tilde{\nu}''_e - \frac{1}{4}\tilde{x}''_e\tilde{\nu}''_e\right) + (\tilde{\nu}'_e - \tilde{x}'_e\tilde{\nu}'_e)v' - \tilde{x}'_e\tilde{\nu}'_e v'^2 \tag{13.22}$$

Rewrite that as

$$\tilde{\nu}_{\mathrm{obs}}(v') = A + Bv' + Cv'^2 \tag{13.23}$$

thus we can fit the data as



and

$$\tilde{\nu}_{\mathrm{obs}}(v') = 14020.1 + 257.114v' + 1.57143v'^2 \tag{13.24}$$

thus

$$(\tilde{\nu}'_e - \tilde{x}'_e\tilde{\nu}'_e) = 257.114\,\mathrm{cm}^{-1} \tag{13.25}$$

$$\tilde{x}'_e\tilde{\nu}'_e = -1.571\,43\,\mathrm{cm}^{-1} \tag{13.26}$$

i.e.

$$\tilde{\nu}'_e = 255.542\,\mathrm{cm}^{-1} \tag{13.27}$$

$$\tilde{x}'_e\tilde{\nu}'_e = -1.571\,\mathrm{cm}^{-1} \tag{13.28}$$

13-37

$$I_{xx} = \sum_j m_j y_j^2 = m + 2m\sin^2 30° = \frac{3}{2}m \tag{13.29}$$

$$I_{yy} = \sum_j m_j x_j^2 = 0 + 2m\cos^2 30° = \frac{3}{2}m \tag{13.30}$$

$$I_{zz} = \sum_j m_j(x_j^2 + y_j^2) = m + m + m = 3m \tag{13.31}$$

13-40 Eq 13.55 reads

$$a_2(t) \approx (\mu_z)_{12}E_{0z}\left[\frac{1-\mathrm{e}^{\mathrm{i}(E_2-E_1+h\nu)t/\hbar}}{E_2-E_1+h\nu} + \frac{1-\mathrm{e}^{\mathrm{i}(E_2-E_1-h\nu)t/\hbar}}{E_2-E_1-h\nu}\right] \tag{13.32}$$

The second term dominates when $E_2 - E_1 \approx h\nu$, thus

$$a_2(t) \approx \frac{1-\mathrm{e}^{\mathrm{i}(E_2-E_1-h\nu)t/\hbar}}{E_2-E_1-h\nu} \tag{13.33}$$

$$a_2(t)^* \approx \frac{1-\mathrm{e}^{-\,\mathrm{i}(E_2-E_1-h\nu)t/\hbar}}{E_2-E_1-h\nu} \tag{13.34}$$

$\therefore$

$$\begin{aligned}
a_2^*(t)a_2(t) &\approx \frac{1-\mathrm{e}^{\mathrm{i}(E_2-E_1-h\nu)t/\hbar} - \mathrm{e}^{-\,\mathrm{i}(E_2-E_1-h\nu)t/\hbar} + 1}{(E_2-E_1-h\nu)^2} \\
&\approx \frac{2-2\cos\dfrac{(E_2-E_1-h\nu)t}{\hbar}}{(E_2-E_1-h\nu)^2} \\
&\approx \frac{\sin^2\dfrac{(E_2-E_1-h\nu)t}{2\hbar}}{(E_2-E_1-h\nu)^2} \\
&\approx \frac{\sin^2\dfrac{(E_2-E_1-\hbar\omega)t}{2\hbar}}{(E_2-E_1-\hbar\omega)^2}
\end{aligned} \tag{13.35}$$

13-43

$$\begin{aligned}
I_{0\to 1} &\approx \int_{-\infty}^{\infty} \psi_1(\xi)\xi\psi_0(\xi) = \sqrt{\frac{2a}{\pi}}\int_{-\infty}^{\infty} \xi^2\,\mathrm{e}^{-\xi^2}\,\mathrm{d}\xi \\
&= \sqrt{\frac{2\alpha}{\pi}}\frac{\sqrt{\pi}}{2} \\
&= \sqrt{\frac{\alpha}{2}}
\end{aligned} \tag{13.36}$$

$$\begin{aligned}
I_{1\to 2} &\approx \int_{-\infty}^{\infty} \psi_2(\xi)\xi\psi_1(\xi) = \sqrt{\frac{a}{\pi}}\int_{-\infty}^{\infty} \xi^2(2\xi^2-1)\,\mathrm{e}^{-\xi^2}\,\mathrm{d}\xi \\
&= \sqrt{\frac{\alpha}{\pi}}\sqrt{\pi} \\
&= \sqrt{\alpha}
\end{aligned} \tag{13.37}$$

thus

$$\frac{I_{0 \to 1}}{I_{1 \to 2}} = \frac{1}{\sqrt{2}} \tag{13.38}$$

13-45

13-51