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

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

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

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

13-7

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

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

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

13-14

$$R(0) = \tilde{\nu} + 2\tilde{B}_1 = 2642.60 \,\text{cm}^{-1} \tag{13.7}$$
$$R(1) = \tilde{\nu} - 2\tilde{B}_0 + 6\tilde{B}_1 = 2658.36 \,\text{cm}^{-1} \tag{13.8}$$
$$P(0) = \tilde{\nu} - 2\tilde{B}_0 = 2609.67 \,\text{cm}^{-1} \tag{13.9}$$
$$P(1) = \tilde{\nu} - 6\tilde{B}_0 - 2\tilde{B}_1 = 2592.51 \,\text{cm}^{-1} \tag{13.10}$$

thus

$$\tilde{B}_1 = 8.12 \,\text{cm}^{-1} \tag{13.11}$$
$$\tilde{B}_0 = 8.35 \,\text{cm}^{-1} \tag{13.12}$$

Then

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

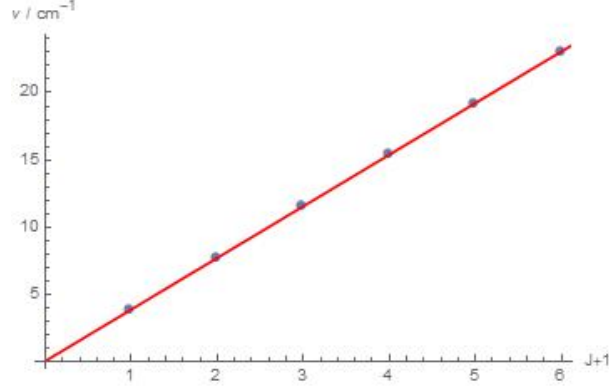$$\tilde{B}_0 = \tilde{B}_e - \frac{3}{2}\tilde{\alpha}_e = 8.35 \,\text{cm}^{-1} \tag{13.14}$$

$$\therefore$$

$$\tilde{B}_e = 8.47\,\text{cm}^{-1} \tag{13.15}$$

$$\tilde{\alpha}_e = 0.23\,\text{cm}^{-1} \tag{13.16}$$

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

$$2\tilde{B} = 3.845\,\text{cm}^{-1} \tag{13.18}$$

$$-4\tilde{D} = -2.555 \times 10^{-5}\,\text{cm}^{-1} \tag{13.19}$$

i.e.

$$\tilde{B} = 1.923\,\text{cm}^{-1} \tag{13.20}$$

$$\tilde{D} = 6.388 \times 10^{-6}\,\text{cm}^{-1} \tag{13.21}$$
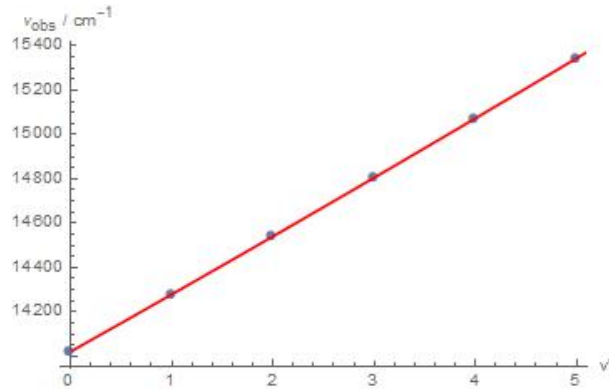
13-32 Since

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

Rewrite that as

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

thus we can fit the data as

and

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

thus

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

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

i.e.

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

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

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

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

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

$\therefore$

$$a_2^*(t)a_2(t) \approx \frac{1 - \mathrm{e}^{\mathrm{i}(E_2 - E_1 - h\nu)t/\hbar} - \mathrm{e}^{-\mathrm{i}(E_2 - E_1 - h\nu)t/\hbar} + 1}{(E_2 - E_1 - h\nu)^2}$$

$$\approx \frac{2 - 2\cos\dfrac{(E_2 - E_1 - h\nu)t}{\hbar}}{(E_2 - E_1 - h\nu)^2}$$

$$\approx \frac{\sin^2\dfrac{(E_2 - E_1 - h\nu)t}{2\hbar}}{(E_2 - E_1 - h\nu)^2}$$

$$\approx \frac{\sin^2\dfrac{(E_2 - E_1 - \hbar\omega)t}{2\hbar}}{(E_2 - E_1 - \hbar\omega)^2} \tag{13.35}$$

13-43

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

$$= \sqrt{\frac{2\alpha}{\pi}}\frac{\sqrt{\pi}}{2}$$

$$= \sqrt{\frac{\alpha}{2}} \tag{13.36}$$

$$I_{1\to 2} \approx \int_{-\infty}^{\infty} \psi_2(\xi)\xi\psi_1(\xi) = \sqrt{\frac{a}{\pi}}\int_{-\infty}^{\infty}\xi^2(2\xi^2 - 1)\,\mathrm{e}^{-\xi^2}\,\mathrm{d}\xi$$

$$= \sqrt{\frac{\alpha}{\pi}}\sqrt{\pi}$$

$$= \sqrt{\alpha} \tag{13.37}$$

thus

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

13-45 CH_2Cl_2 belongs to C_{2v} group, thus

	$\hat{E}$	$\hat{C}_2$	$\hat{\sigma}_v$	$\hat{\sigma}_v'$
Γ	15	-1	3	3

13-51