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

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

$$\tilde{B} = \frac{\hbar}{4\pi c \mu R_e^2} = \frac{1}{4\pi \times 137 \times 1.827 \times 10^3} \text{ a. u. } \times \frac{1}{(160.4 \text{ pm})^2}$$

$$= 1.682 \times 10^{-5} \text{ pm} \times \frac{1}{(160.4 \text{ pm})^2}$$

$$= 6.54 \text{ cm}^{-1}$$
(13.2)

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

13-7

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

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

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

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

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

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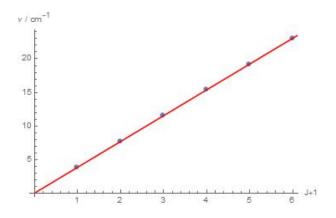
$$\tilde{B}_e = 8.47 \,\mathrm{cm}^{-1} \tag{13.15}$$

$$\tilde{\alpha}_e = 0.23 \,\mathrm{cm}^{-1}$$
 (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.

$$\tilde{B} = 1.923 \,\mathrm{cm}^{-1}$$
 (13.20)

$$\tilde{D} = 6.388 \times 10^{-6} \,\mathrm{cm}^{-1}$$
 (13.21)

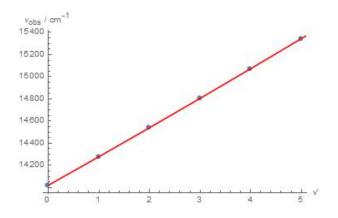
13-32 Since

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

Rewrite that as

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

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

$$\tilde{x}'_e \tilde{\nu}'_e = -1.57143 \,\mathrm{cm}^{-1}$$
 (13.26)

i.e.

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

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

13-37

$$I_{xx} = \sum_{j} m_j y_j^2 = m + 2m \sin^2 30^\circ = \frac{3}{2}m$$
 (13.29)

$$I_{yy} = \sum_{i} m_j x_j^2 = 0 + 2m\cos^2 30^\circ = \frac{3}{2}m$$
(13.30)

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

13-40 Eq 13.55 reads

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

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

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

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

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

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$$a_{2}^{*}(t)a_{2}(t) \approx \frac{1 - e^{i(E_{2} - E_{1} - h\nu)t/\hbar} - e^{-i(E_{2} - E_{1} - h\nu)t/\hbar} + 1}{(E_{2} - E_{1} - h\nu)^{2}}$$

$$\approx \frac{2 - 2\cos\frac{(E_{2} - E_{1} - h\nu)t}{\hbar}}{(E_{2} - E_{1} - h\nu)^{2}}$$

$$\approx \frac{\sin^{2}\frac{(E_{2} - E_{1} - h\nu)t}{2\hbar}}{(E_{2} - E_{1} - h\nu)^{2}}$$

$$\approx \frac{\sin^{2}\frac{(E_{2} - E_{1} - h\nu)t}{2\hbar}}{(E_{2} - E_{1} - \hbar\omega)t}$$

$$\approx \frac{\sin^{2}\frac{(E_{2} - E_{1} - \hbar\omega)t}{2\hbar}}{(E_{2} - E_{1} - \hbar\omega)^{2}}$$
(13.35)

13-43

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

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

$$a_{A_1} = \frac{1}{4}(15 - 1 + 3 + 3) = 5 \tag{13.39}$$

$$a_{A_2} = \frac{1}{4}(15 - 1 - 3 - 3) = 2 \tag{13.40}$$

$$a_{B_1} = \frac{1}{4}(15 + 1 + 3 - 3) = 4 \tag{13.41}$$

$$a_{B_2} = \frac{1}{4}(15 + 1 - 3 + 3) = 4 \tag{13.42}$$

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$$\Gamma_{3N} = 5A_1 + 2A_2 + 4B_1 + 4B_2 \tag{13.43}$$

Since

$$\Gamma_{\text{trans}} = A_1 + B_1 + B_2$$
(13.44)

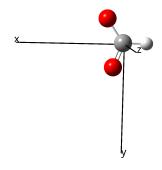
$$\Gamma_{\rm rot} = A_2 + B_1 + B_2 \tag{13.45}$$

we have

$$\Gamma_{\text{vib}} = 4A_1 + A_2 + 2B_1 + 2B_2 \tag{13.46}$$

and the A_2 vibrational mode is infrared inactive and the others are infrared active.

13-51 Construct Cartesian coordinates as below,



	X	У	${f z}$
С	0.0	0.0	0.0
O	43.1	112.2	0.0
Ο	75.5	-111.1	0.0
Н	-109.7	0.0	0.0

Table 1: the coordinates (pm) of each atom

thus the coordinates of center of mass is

$$\mathbf{r}_{CoM} = (39.7, 0.4, 0.0) \tag{13.47}$$

Recenter the frame to CoM frame, we get

	X	У	\mathbf{Z}
С	-39.7	-0.4	0.0
O	3.4	111.8	0.0
O	40.2	-111.5	0.0
Н	-149.4	-0.4	0.0

thus

$$I_{xx} = \sum_{i} m_i (y_i^2 + z_i^2) = 3.98 \times 10^5 \,\text{amu} \cdot \text{pm}^2$$
 (13.48)

$$I_{yy} = \sum_{i} m_i (x_i^2 + z_i^2) = 6.74 \times 10^4 \,\mathrm{amu \cdot pm^2}$$
 (13.49)

$$I_{zz} = \sum_{i} m_i (x_i^2 + y_i^2) = 4.65 \times 10^5 \,\mathrm{amu \cdot pm^2}$$
 (13.50)

$$I_{xy} = -\sum_{i} m_i x_i y_i = -6.53 \times 10^4 \,\mathrm{amu \cdot pm^2}$$
 (13.51)

$$I_{xz} = I_{yz} = 0 (13.52)$$

thus

$$\begin{vmatrix} 3.98 \times 10^{5} - \lambda & -6.53 \times 10^{5} & 0\\ -6.53 \times 10^{5} & 6.74 \times 10^{4} - \lambda & 0\\ 0 & 0 & 4.65 \times 10^{5} - \lambda \end{vmatrix} = 0$$
 (13.53)

$$\lambda = 5.50 \times 10^4, 4.10 \times 10^5, 4.65 \times 10^5 \tag{13.54}$$

thus

$$I_A = 4.10 \times 10^4 \tag{13.55}$$

$$I_B = 4.65 \times 10^4 \tag{13.56}$$

$$I_C = 5.50 \times 10^4 \tag{13.57}$$