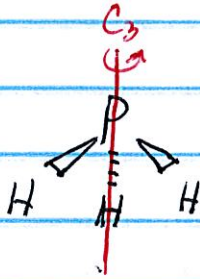SOLUTIONS

PROBLEM SET 11

CHM 3411, Dr. Chatfield

1. $^{31}P^1H_3$ Calculate moment of inertia about C_3 axis and $\tilde{B}$. Given: $r_{PH} = 142\,pm$, $\theta_{HPH} = 93.5°$

C_3 is the figure axis. The moment of inertia about it is $I_{\parallel}$

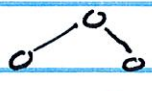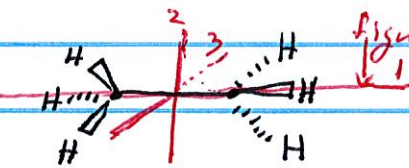From the table of moments of inertia, we find:

$$I_{\parallel} = 2\,m_H\,(1-\cos\theta)\,r^2 \quad \text{(for molecule of this symmetry)}$$
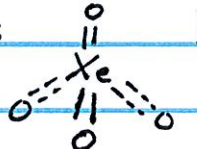
93.5°

$142\,pm = 1.42\times10^{-10}\,m$

$1\,amu = 1.066\times10^{-27}\,kg$

$$I_{\parallel} = 7.10\times10^{-47}\,kg\,m^2$$

$$\tilde{A} = \frac{\hbar}{4\pi c\,I_{\parallel}} = 394\,m^{-1} = 3.94\,cm^{-1}$$
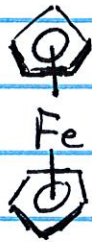
2. O_3 asymmetric top   (see next p. for expl.)

$CH_3 CH_3$ symmetric top   figure axis

$I_2 = I_3 \neq I_1$
by symmetry

XeO_4 spherical top (tetrahedral:)

$FeCp_2$ symm. top
(see following
for expl.)   Fe   ferrocene

3. HCN is linear, so we can use a table of moments of inertia for particular symmetries (e.g. Table 12B.1 in Atkins 10e). There we find:

$$m_A \underset{B}{\rule{1cm}{0.4pt}} m_B \underset{}{\rule{1cm}{0.4pt}} R' \; m_C \qquad I = m_A R^2 + m_C R'^2 - \frac{(m_A R - m_C R')^2}{m}$$

$$m = m_A + m_B + m_C$$

In our case, $m_A = m_H$, $m_B = m_C$ (carbon), $m_C = m_N$, $R = R_{CH}$, $R' = R_{CN}$

We have 2 different isotopomers, each with a different moment of inertia and mass:

$$^1H\,^{12}C\,^{14}N \rightarrow I, m \qquad ^2H\,^{12}C\,^{14}N \rightarrow I', m'$$

The moments of inertia are determined from B:

$$B = c\tilde{B} = \frac{\hbar}{4\pi I} \implies I = \frac{\hbar}{4\pi B}$$

$$B = 44.316 \, GHz = 44.316 \times 10^9 \, s^{-1} \implies I = 1.8937 \times 10^{-46} \, kg \, m^2$$
$$B' = 36.208 \, " \quad = 36.208 \quad " \quad " \implies I' = 2.3177 \times 10^{-46} \, kg \, m^2$$

The expressions for I and I' constitute 2 equations in 2 unknowns, R and R', and so we can solve for R and R'. The algebra is a little involved (next p.):

Rearranging the first equation above yields:

$$I_m = m_A m R^2 + m_c m R'^2 - (m_A R - m_c R')^2$$

$$= m_A(m_B + m_c)R^2 + m_c(m_A + m_B)R'^2 + 2m_A m_c RR'$$

$$\frac{I_m}{m_A} = (m_B + m_c)R^2 + \frac{m_c}{m_A}(m_A + m_B)R'^2 + 2m_c RR'$$

$$\frac{I'm'}{m_A'} = (m_B + m_c)R^2 + \frac{m_c}{m_A'}(m_A' + m_B)R'^2 + 2m_c RR'$$

Subtract: $\quad \dfrac{I_m}{m_A} - \dfrac{I'm'}{m_A'} = \left[\dfrac{m_c}{m_A}(m_A + m_B) - \dfrac{m_c}{m_A'}(m_A' + m_B) \right] R'^2$

This can be solved for R'. Remember the constants: $m_A = m_{^1H} = 1 m_u$ (atomic mass unit)

$$m_A' = m_{^2H} = 2m_u \qquad m_B = m_{^{12}C} = 12 m_u \qquad m_c = M_{^{14}N} = 14 m_u$$

$$m = m_A + m_B + m_c = 27 m_u$$

$$m' = m_A' + m_B + m_c = 28 m_u$$

$$I = 1.8937 \times 10^{-46} \, kg \, m^2 = 1.1407 \times 10^{-19} \, m_u \, m^2$$

$$I' = 2.3177 \times 10^{-46} \, kg \, m^2 = 1.3958 \times 10^{-19} \, m_u \, m^2$$

Substituting into the equation above and solving for R' yields: $\quad R' = R_{CN} = 115.7 \, pm$

Substituting and solving for R yields: $\quad R = R_{CH} = 106.7 \, pm$

(requires quadratic eq.

Literature values: $R_{CN} = 115.6 \, pm$, $R_{CH} = 106.8 \, pm$

$\Rightarrow$ Good Agreement

4. μ-wave spectrum of CO

(a) Spacing of peaks is 2B, so:

$$B = \frac{1}{2}(698.81 - 579.01)\,GHz = 57.9\,GHz = 5.79 \times 10^{10}\,s^{-1}$$

$$\tilde{B} = \frac{B}{c} = \frac{5.79 \times 10^{10}\,s^{-1}}{2.998 \times 10^{10}\,cm \cdot s^{-1}} = 1.93\,cm^{-1}$$

(b) $\tilde{B} = \frac{\hbar}{4\pi c I}$ $I = \frac{\hbar}{4\pi c \tilde{B}} = 1.45 \times 10^{-46}\,kg\,m^2$

$$I = \mu R^2 \implies R = \left(\frac{I}{\mu}\right)^{1/2} \qquad \mu = \frac{m_{12_C}\,m_{16_O}}{m_{12_C} + m_{16_O}} = \frac{12.16}{28}\,m_u$$

$$\underset{amu}{\uparrow}$$

$$R = 113\,pm \qquad\qquad\qquad = 6.857\,m_u = 1.139 \times 10^{-26}\,kg$$

(c) $579.01\,GHz$ is for a transition from J to $J+1$

$$F(J) = BJ(J+1) \qquad F(J+1) = B(J+1)(J+2)$$

$$579.01\,GHz = \Delta F = F(J+1) - F(J) = B\left[(J^2 + 3J + 2) - (J^2 + J)\right]$$

$$\qquad\qquad\qquad\qquad\qquad\qquad = B(2J+2)$$

$$J = \left(\frac{579.01\,GHz}{57.9\,GHz} - 2\right) \cdot \frac{1}{2} \qquad \underset{57.9\,GHz}{\uparrow}$$

$$= 4$$

$$\therefore \quad 579.01\,GHz \text{ peak: } J=5 \leftarrow J=4$$

$$694.81 \quad \text{''} \qquad \text{''} \quad \text{: } J=6 \leftarrow J=5$$

(d) The ratio of intensities equals the ratio of the populations of the initial states for the transitions

degeneracy: $g_J = 2J+1$

$$\text{Population} = N_J \propto g_J \, e^{-E_J/kT}$$

$$\frac{I(J_{init} = 5)}{I(J_{init} = 4)} = \frac{N_5}{N_4} = \frac{25}{24} \, e^{-\Delta E/kT} \qquad [\; E_5 - E_4$$

ratio = 1.19

$$\frac{g_5}{g_4} = \frac{2 \cdot 5 + 1}{2 \cdot 4 + 1} = 1.222$$

$$\Delta E = hB(5)(6) - hB(4)(5) \qquad (\text{from } E = hBJ(J+1)$$
$$= 10 hB = 3.837 \times 10^{-22} \, J \qquad\qquad = hc\tilde{B} J(J+1))$$

$$\ln\left(\frac{1.19}{1.22}\right) = -\frac{\Delta E}{kT} \quad \Rightarrow \quad T = \frac{-\Delta E}{k \ln(1.19/1.22)} = 1,120 K$$

$$\text{hot!}$$

(e) $B = \dfrac{\hbar}{4\pi I} = \dfrac{\hbar}{4\pi \mu R^2}$ It is a good assumption that B is same for both isotopomers.

$$\frac{B(^{14}C^{16}O)}{B(^{12}C^{16}O)} = \frac{\mu(^{12}C^{16}O)}{\mu(^{14}C^{16}O)} = \frac{14+16}{14 \cdot 16} \cdot \frac{12 \cdot 16}{12+16} = 0.9123$$

$$B(^{14}C^{16}O) = 0.9123 \, B(^{12}C^{16}O) = 53.2 \, GHz$$

$$\Delta F(J=5 \leftarrow J=4) = 532 \, GHz \; \Big\} \text{ for } ^{14}C^{16}O$$
$$\Delta F(J=6 \leftarrow J=5) = 638 \quad \text{``} \quad \Big\}$$

5. $\tilde{\nu} = \frac{1}{2\pi c} \sqrt{\frac{k}{\mu}}$ Let 1 represent $^1H^{35}Cl$, 2 repr. $^2H^{37}Cl$

$\frac{\tilde{\nu}_1}{\tilde{\nu}_2} = \sqrt{\frac{\mu_2}{\mu_1}}$ $\mu_1 = \frac{m_{^1H} \cdot m_{^{35}Cl}}{m_{^1H} + m_{^{35}Cl}} = \frac{35}{36}$ amu $= 0.97222$ amu

$\mu_2 = \frac{m_{^2H} \cdot m_{^{37}Cl}}{m_{^2H} + m_{^{39}Cl}} = \frac{74}{39}$ amu $= 1.89744$ amu

$\frac{\tilde{\nu}_1}{\tilde{\nu}_2} = 0.512$

$\frac{\tilde{\nu}_1 - \tilde{\nu}_2}{\tilde{\nu}_1} \times 100\% = 48.8\%$

6. $\tilde{\nu} = \frac{1}{2\pi c}\sqrt{\frac{k}{\mu}}$ $\implies$ $k = (2\pi c)^2 \tilde{\nu}^2 \mu$

$\mu = \frac{m(^{79}Br)\cdot m(^{81}Br)}{m(^{79}Br)+m(^{81}Br)} = \frac{79\cdot81}{79+81}\ amu = 39.99375\ amu$
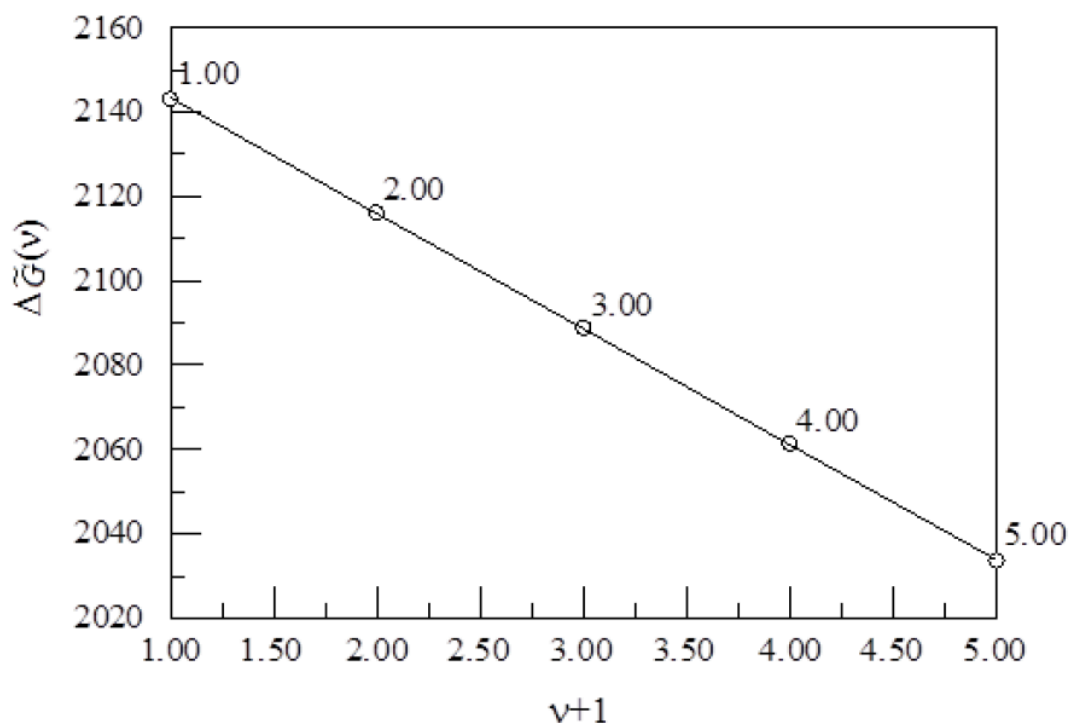
$1.660539\times10^{-27}\ kg$ $\downarrow$

$k = 244.8\ kg\ s^{-2}$

7.

See Fig. 12D.3 for a plot of $\Delta\tilde{G}(v) = \tilde{v} - 2(v+1)x_e\tilde{v}$ [12D.14] against $v + 1$.

Figure 12D.3

The intercept gives $\boxed{\tilde{v} = 2170.8 \text{ cm}^{-1}}$ and the slope gives $2x_e\tilde{v} = 27.4 \text{ cm}^{-1}$; thus, $\boxed{x_e\tilde{v} = 13.7 \text{ cm}^{-1}}$.

8.

we note first that only two data are provided; yet we have four distances to calculate: $R(CC)$, for both C_2H_2 and C_2D_2, $R(CH)$, and $R(CD)$. Consequently we must make some reasonable approximations in order to solve this problem. We will assume that the CC and CH distances are the same in both molecules. Our procedure will be first to calculate the moments of inertia of the molecules from the given rotational constants and then from the moments of inertia and the known masses of the atoms to calculate the interatomic distances.

$$\tilde{B} = \frac{\hbar}{4\pi cI} \text{ hence } I = \frac{\hbar}{4\pi c\tilde{B}}$$

The formulas for the moments of inertia in terms of the masses and distances are:

$$I(C_2H_2) = 2m_C a^2 + 2m_H b^2 \text{ (eqn 1) and } I(C_2D_2) = 2m_C a^2 + 2m_D b^2 \text{ (eqn 2)}$$

where a is the distance from the center of mass to the C atom, which is half the CC interatomic distance, and b is the distance from the center of mass to the H or D atom.

$$\tilde{B}(C_2H_2) = \frac{2.352 \text{ cm}^{-1}}{2} = 1.176 \text{ cm}^{-1} \text{ and } \tilde{B}(C_2D_2) = \frac{1.696 \text{ cm}^{-1}}{2} = 0.848 \text{cm}^{-1}$$

Therefore,

$$I(C_2H_2) = \frac{\hbar}{4\pi c \times 1.176 \text{ cm}^{-1}} = 2.3804 \times 10^{-46} \text{ kg m}^2 \text{ and}$$

$$I(C_2D_2) = \frac{\hbar}{4\pi c \times 0.848 \text{ cm}^{-1}} = 3.3010 \times 10^{-46} \text{ kg m}^2$$

The masses are $m_C = 12.0000$ u, $m_H = 1.0078$ u, and $m_D = 2.0140$ u; u is the atomic mass unit. Substituting these values into eqns. 1 and 2 above and solving the equations simultaneously for distances a and b we obtain:

$$a = 0.6049 \times 10^{-10} \text{ m and } b = 1.6598 \times 10^{-10} \text{ m}$$

$$R(CC) = 2a = 1.2098 \times 10^{-10} \text{ m} = \boxed{121.0 \text{ pm}} \text{ and}$$

$$R(CH) = R(CD) = b - a = 1.055 \times 10^{-10} \text{ m} = \boxed{105.5 \text{ pm}}$$

9. $C_6H_6 \Rightarrow N = 12$ atoms nonlinear $\Rightarrow$ # vib. modes $= 3N-6 = 30$

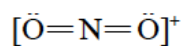$C_6H_5CH_3$ (this must be what was meant — typo in Atkins 10e)
$\Downarrow$
$N = 14$ atoms nonlinear $\Rightarrow$ # modes $= 3N-6 = 36$

$H \equiv C - C \equiv C - H \Rightarrow N = 5$ linear $\Rightarrow$ # modes $= 3N-5 = 10$

10.

The Lewis structure is

$$[\ddot{O}{=}N{=}\ddot{O}]^+$$

VSEPR indicates that the ion is linear and has a centre of symmetry. The activity of the modes is consistent with the rule of mutual exclusion; none is both infrared and Raman active. These transitions may be compared to those for CO_2 (Fig. 12E.2 of the text) and are consistent with them. The Raman active mode at 1400 cm^{-1} is due to a symmetric stretch $(\tilde{\nu}_1)$, that at 2360 cm^{-1} to the antisymmetric stretch $(\tilde{\nu}_3)$ and that at 540 cm^{-1} to the two perpendicular bending modes $(\tilde{\nu}_2)$. There is a combination band, $\tilde{\nu}_1 + \tilde{\nu}_3 = 3760$ $cm^{-1} \approx 3735$ cm^{-1}, which shows a weak intensity in the infrared.

10. cont'd (Spartan calculation

Frequencies below are in cm^{-1}. NO bond length, b, is in pm.

	B3LYP/6-31G*
$\tilde{\nu}_1$ (degenerate)	628.309
$\tilde{\nu}_2$	1448.757
$\tilde{\nu}_3$	2449.337
b	112.9

IR intensity: Mode 2 has an IR intensity of 0, consistent with the fact that the Raman spectrum has a peak at 1400 cm^{-1} but the IR spectrum does not. Mode 1 has a moderate IR intensity, and mode 3 has a large intensity. These computed data are consistent with the spectra.

The molecule is linear. When optimized from a bent geometry, the bond angle becomes 179.99^o, and the lowest frequency mode is not assigned. Therefore we can be confident that 180° is the true optimized ground-state geometry. When the bond angle is set to exactly 180°, the mode's frequency mode is assigned, and the energy is unchanged to 5 decimal places. The values in the table above pertain to the 180° geometry.

The modes were visualized with Spartan:
Mode 1 is a bending mode
Mode 2 is a symmetric stretch
Mode 3 is an antisymmetric stretch

According to Atkins 10e, experimental values for the bending and antisymmetric stretch modes are 540 cm^{-1} and 2360 cm^{-1}, respectively. On the other hand, the NIST webbooks lists the bending mode as having a frequency or 627.7 cm^{-1}, and two values are given for the antisymmetric stretch, measured with different techniques, 2376.5 and 2348.2 cm^{-1} (these are the values for the ground state). Overall, the B3LYP/6-31G* is in good agreement with the NIST Webbook values.

An experimental bond length is not available. Very high-level calculated bond lengths are available at NIST, and the consensus value is approximately 112 pm (e.g. CCSD(T)=Full/aug-cc-pVQZ), which is in close agreement with our B3LYP/6-31G* value.