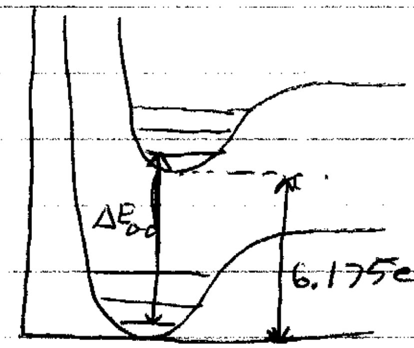
1. Atkins Problem 14.1



$\tilde{\nu}' = 700\ cm^{-1} \Rightarrow ZPE' = \frac{1}{2}hc\tilde{\nu}' = 6.934\times10^{-21}\ J$
$= 4.328\times10^{-2}\ eV$

$\tilde{\nu} = 1580\ cm^{-1} \Rightarrow ZPE = \frac{1}{2}hc\tilde{\nu} = 1.565\times10^{-20}\ J$
$= 9.769\times10^{-2}\ eV$

$\Delta E_{00} = 6.175\ eV + ZPE' - ZPE = 6.121\ eV$

$\tilde{\nu}_{0\text{-}0} = 6.121\ eV \cdot \frac{8065.5\ cm^{-1}}{eV} = 49{,}366\ cm^{-1}$

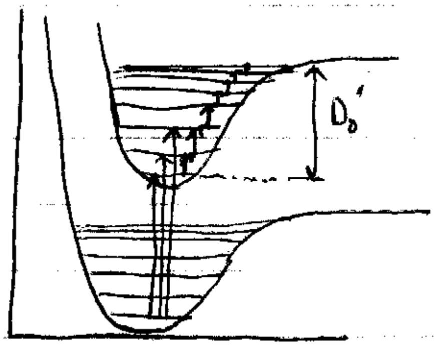
2. Atkins Problem 14.6

$^2\Pi_g \leftarrow {}^2\Sigma_u^+$ allowed ($\Delta S = 0$, parity change, $\Delta\Lambda = \pm 1$)

$^2\Pi_u \leftarrow {}^2\Sigma_u^+$ forbidden by parity

$^2\Sigma_g^+ \leftarrow {}^2\Sigma_u^+$ allowed ($\Delta S = 0$, parity change, $\Delta\Lambda = 0$, $^+\Sigma \leftrightarrow \Sigma^+$)

3. Atkins Problem 14.7



• Sum of red arrows $= \sum \Delta G_{v+\frac{1}{2}} = D_0'$

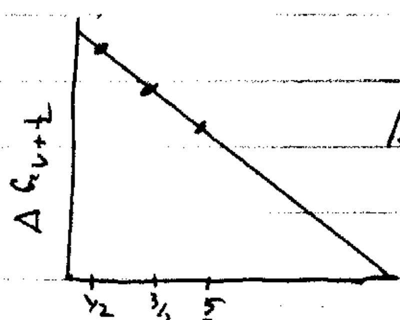
• Each red arrow is the difference between two black arrows

$\Downarrow$

$\Delta G_{1/2} = 50725.4 - 50062.6$ cm^{-1}

$\Delta G_{3/2} = 51369.0 - 50725.4$ cm^{-1}

etc



Birge-Sponer plot: Area under line $= D_0'$

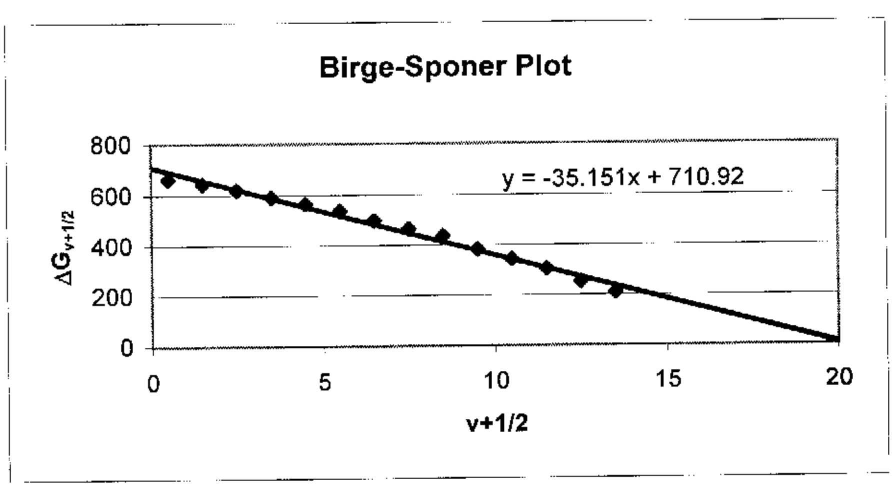
To do with Excel, plot straight line through points $\Rightarrow y = mx+b$

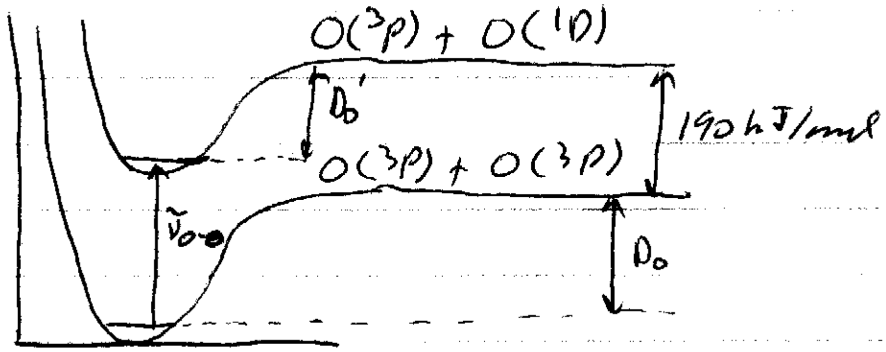
Area $= \frac{1}{2} y(x=0) \cdot x(y=0) = 7189.1$ cm^{-1}

$\boxed{D_0' = 7189.1 \text{ cm}^{-1} = 0.8913 \text{ eV}}$ $\quad 710.92 \qquad \frac{710.92}{35.151} = 20.22$

From plot below, this is overestimate.

wavenumber (cm^{-1})	v+1/2	$\Delta G_{v+1/2}$ (cm^{-1})
50062.6		
50725.4	0.5	662.8
51369	1.5	643.6
51988.6	2.5	619.6
52579	3.5	590.4
53143.4	4.5	564.4
53679.6	5.5	536.2
54177	6.5	497.4
54641.8	7.5	464.8
55078.2	8.5	436.4
55460	9.5	381.8
55803.1	10.5	343.1
56107.3	11.5	304.2
56360.3	12.5	253
56570.6	13.5	210.3





$$D_0 = \tilde{\nu}_{00} + D_0' - \underbrace{190\ \text{kJ/mol}}_{15870\ \text{cm}^{-1}} = 50062.6\ \text{cm}^{-1} + 7189.1\ \text{cm}^{-1} - 15870\ \text{cm}^{-1} = 41381.7\ \text{cm}^{-1} = 5.13\ \text{eV}$$

$$\boxed{D_0 = 41381.7\ \text{cm}^{-1} = 5.13\ \text{eV}}$$

4. Atkins Problem 14.8

$CH_3CH{=}CHCHO$

This molecule is a likely chromophore because of the C=C and C=O moieties. The likely transitions and wavenumbers can be judged from Table 14.3:

C=C	$\pi^* \leftarrow \pi$	46,950 cm⁻¹
C=O	$\pi^* \leftarrow n$	30,000 cm⁻¹

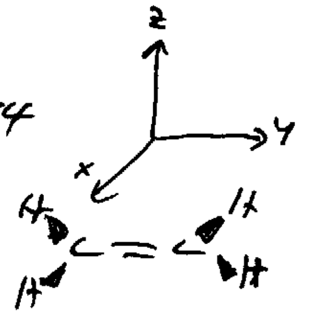
D_{2h}	E	$C_2(z)$	$C_2(y)$	$C_2(x)$	i	$\sigma(xy)$	$\sigma(xz)$	$\sigma(yz)$		
A_g	1	1	1	1	1	1	1	1		x^2, y^2, z^2
B_{1g}	1	1	−1	−1	1	1	−1	−1	R_z	xy
B_{2g}	1	−1	1	−1	1	−1	1	−1	R_y	xz
B_{3g}	1	−1	−1	1	1	−1	−1	1	R_x	yz
A_u	1	1	1	1	−1	−1	−1	−1		
B_{1u}	1	1	−1	−1	−1	−1	1	1	z	
B_{2u}	1	−1	1	−1	−1	1	−1	1	y	
B_{3u}	1	−1	−1	1	−1	1	1	−1	x	

Consult D_{2h} character table

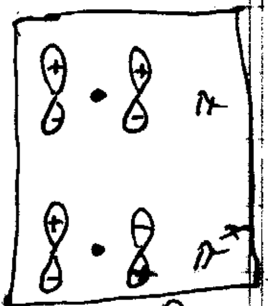
4

5. Atkins Problem 14.14

a) Ethene:



D_{2h}



$\pi = p_z(A) + p_z(B)$ $\qquad$ $\pi^* = p_z(A) - p_z(B)$

	E	$C_2(z)$	$C_2(y)$	$C_2(x)$	i	$\sigma(xy)$	$\sigma(xz)$	$\sigma(yz)$
$B_{1u} \Leftarrow \pi$	1	1	−1	−1	−1	−1	1	1
$B_{3g} \Leftarrow \pi^*$	1	−1	−1	1	1	−1	−1	1

$$\mu_{fi} = \int f_1 \underset{\downarrow}{\overset{\hat{\vec{\mu}}}{f_2}} f_3 \, d\tau \neq 0 \, ?$$

f_1: $b_{3g} \uparrow \pi^*$ $\qquad$ f_3: $b_{1u} \uparrow \pi$

Break into 3 integrals (3 components)

$f_2 = x$ $\quad B_{3u}$

y $\quad B_{2u}$

z $\quad B_{1u}$

x

	E	$C_2(z)$	$C_2(y)$	$C_2(x)$	i	$\sigma(xy)$	$\sigma(xz)$	$\sigma(yz)$
B_{3g}	1	−1	−1	1	1	−1	−1	1
B_{3u}	1	−1	−1	1	−1	1	1	−1
B_{1u}	1	1	−1	−1	−1	−1	1	1
$A_1 \neq B_{1g}$ =	1	1	−1	−1	1	1	−1	−1

y

	E	$C_2(z)$	$C_2(y)$	$C_2(x)$	i	$\sigma(xy)$	$\sigma(xz)$	$\sigma(yz)$
B_{3g}	1	−1	−1	1	1	−1	−1	1
B_{2u}	1	−1	1	−1	−1	1	−1	1
B_{1u}	1	1	−1	−1	−1	−1	1	1
=	1	1	1	1	1	1	1	1

z

	E	$C_2(z)$	$C_2(y)$	$C_2(x)$	i	$\sigma(xy)$	$\sigma(xz)$	$\sigma(yz)$
B_{3g}	1	−1	−1	1	1	−1	−1	1
B_{1u}	1	1	−1	−1	−1	−1	1	1
B_{1u}	1	1	−1	−1	−1	−1	1	1
$A_1 \neq B_{3g}$ =	1	−1	−1	1	1	−1	−1	1

The x and z components of $\vec{\mu}_{fi}$ are zero, but the y component is not. Therefore the $\pi^* \leftarrow \pi$ transition is $\boxed{\text{allowed}}$ in ethene, and the radiation absorbed is y-polarized.

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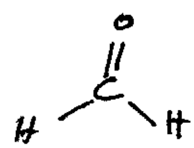
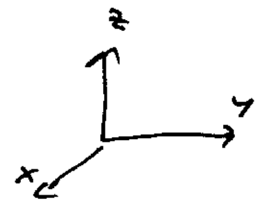
b) e.g. formaldehyde





Take the z-axis as coincident with the C–O bond, the y axis as in the plane of the molecule, and the x axis as perpendicular to the plane of the molecule.

The π^* orbital is perpendicular to the plane of the molecule and transforms as x. The n orbital is p_y.

Proceeding as before:

		E	C_2	$\sigma_v(xz)$	$\sigma_v'(yz)$
$B_2 \Leftarrow$	n	1	−1	−1	1
$B_1 \Leftarrow$	π^*	1	−1	1	−1

Character Table (Atkins)

C_{2v}	E	C_2	$\sigma_v(xz)$	$\sigma_v'(yz)$	$h=4$
A_1	1	1	1	1	z
A_2	1	1	−1	−1	
B_1	1	−1	1	−1	x
B_2	1	−1	−1	1	y

Need to evaluate $\int_{-\infty}^{\infty} \psi^* x\, \psi\, dx \quad \int_{-\infty}^{\infty} \psi^* y\, \psi\, dy \quad \int_{-\infty}^{\infty} \psi^* z\, \psi\, dz$

x is symmetry species B_1
y " " " B_2
z " " " A_1

Then we need the decomposition of these products:

$B_1 \times B_1 \times B_2$ (for x)
$B_1 \times B_2 \times B_2$ (for y)
$B_1 \times A_1 \times B_2$ (for z)

	E	C_2	σ_v	σ_v'	
B_1	1	−1	1	−1	
B_1	1	−1	1	−1	
B_2	1	−1	−1	1	
	1	−1	−1	1	$= B_2 \neq A_1$

B_1	1	−1	1	−1	
B_2	1	−1	−1	1	
B_2	1	−1	−1	1	
	1	−1	1	−1	$= B_1 \neq A_1$

B_1	1	−1	1	−1	
A_1	1	1	1	1	
B_2	1	−1	−1	1	
	1	1	−1	−1	$= A_2 \neq A_1$

A_1 does not occur in any product, so all 3 integrals are zero
$\Rightarrow$ transition forbidden

6. Exercise 15.1b

Table 15.2 $\quad {}^{19}F \quad I = \frac{1}{2} \quad \gamma = 25.177 \times 10^{7}\, T^{-1} s^{-1}$

$E_{m_I} = -\gamma \hbar B_0 m_I \qquad \Delta E = E_{-\frac{1}{2}} - E_{\frac{1}{2}} = \gamma \hbar B_0$

$$\nu = \frac{\Delta E}{h} = \frac{\gamma B_0}{2\pi} = \frac{(25.177 \times 10^{7}\, T^{-1} s^{-1})(16.2\,T)}{2\pi} = \quad \times 10^{8}\, s^{-1}$$
$$= 649\ MHz$$

Exercise 15.2b

Table 15.2 $\quad {}^{14}N \quad I = 1 \quad g = 0.404$

$\gamma \hbar = g_I \mu_N = 0.404 (5.051 \times 10^{-27}\, J\,T^{-1}) = 2.041 \times 10^{-27}\, J\,T^{-1}$

$E_{m_I} = -\gamma \hbar B_0 m_I = -g_I \mu_N B_0 m_I \qquad B_0 = 11.50\,T$

$m_I = 0, \pm 1 \Rightarrow \quad E_{+1} = -2.35 \times 10^{-26}\, J$
$\qquad E_0 = 0$
$\qquad E_{-1} = +2.35 \times 10^{-26}\, J$

Exercise 15.6b

$$\nu = \frac{\Delta E}{h} = \frac{\gamma B_o}{2\pi} \Longrightarrow B_o = \frac{2\pi\nu}{\gamma}$$

nucleus	γ	B_o at $\nu = 300$ MHz	B_o at $\nu = 750$ MHz
^{14}N	$1.93\times10^{7}\ T\,s^{-1}$	97.7 T	244 T
^{19}F	$25.177\times10^{7}\ T\,s^{-1}$	7.49 T	18.7 T
^{31}P	$10.840\times10^{7}\ T\,s^{-1}$	17.4 T	43.5 T

Exercise 15.7b

temp.

$$\frac{\delta N}{N} = \frac{N_\alpha - N_\beta}{N_\alpha + N_\beta} \approx \frac{\gamma\hbar B_o/kT}{2} \quad \text{(eq. 15.14b)}$$

Tesla

^{13}C $\gamma = 6.73\times10^{7}\ T^{-1}$ ... temp $= T = 25^\circ C = 298K$

a) $B_o = 0.50T$ $\quad \frac{\delta N}{N} = 4.3\times10^{-7}$

b) " $= 2.5T$ $\quad$ " $= 2.2\times10^{-6}$

c) " $= 15.5T$ $\quad$ " $= 1.34\times10^{-5}$

Exercise 15.8b

a) δ values are same

local field $\qquad$ applied field

b) ν and ν° depend on B: $\quad B = (1-\sigma)B_A \qquad \nu = \frac{\gamma B}{2\pi}$

$$\frac{[\nu-\nu^\circ] \text{ at } B_A = 800\,MHz}{[\nu-\nu^\circ] \text{ at } B_A = 60\,MHz} = \frac{[(1-\sigma)-(1-\sigma^\circ)]\cdot 800\,MHz}{[(1-\sigma)-(1-\sigma^\circ)]\cdot 60\,MHz} = \boxed{13.3}$$