Chemistry 562 **Spring 2012**

Problem Set 9

Due Wednesday, March 28

(Make your reasoning clear. We need to understand your reasoning, not just see the final result.)

Note: Keep a copy for of your homework because the graded homework will not be returned before your exam.

1. *Self-test 10.9. Be sure to read Example 10.3*

   Expand the 3 X 3 determinant by hand and find the energies (Use the 3 x 3 analogue of Eqn. 10.42. There is also a good discussion at the bottom of page 396.). Use the energies in the secular equation along with normalization to determine the coefficients for each energy. (Use Eqn 10.44 as a guide, but with $S_{AA}=S_{BB}=1$ and $S_{AB}=S_{BA}=0$. In matrix notation, $(\mathbf{H}-E_i)\mathbf{c}_i=0$. This is Eqn 10.47 with **S** equal to the identity matrix.)

2. The table below gives some spectroscopic constants (in cm^{-1}) for the OH radical in its two lowest electronic states

	$X^2\Pi$	$A^2\Sigma^+$
$V(R_e)$	0	32682
$\tilde{\nu}$	3735.2	3180.6
$x_e\tilde{\nu}$	82.81	94.93
B	18.87	17.36

(a) Calculate the force constant and the equilibrium bond distance for both electronic states. Which is larger in each case?

(b) Predict the wavenumber of the vibrational overtone transition ($v=2 \leftarrow v=0$) *in the ground electronic state* ($X^2\Pi$).

(c) Predict the wavenumber of the electronic transition $A^2\Sigma^+(v=5, J=5) \leftarrow X^2\Pi\ (v=1, J=5)$.

(d) Plot the ground and exited electronic states and draw or plot the ground vibrational level on $X^2\Pi$ and the lowest five vibrational levels on $A^2\Sigma^+$. For plotting the electronic states, you should use the Morse potential equation, and determine a and D_e from:

$$x_e = \frac{a^2\hbar}{2\mu\omega} = \frac{\tilde{\nu}}{4D_e}$$

Be sure to use the correct equilibrium bond distances and to offset the excited electronic excited state by $V(R_e)$.

(e) Will $v_2=0$, 2, or 4 give the largest transition probability from $X^2\Pi$ (v=0, J=0) to $A^2\Sigma^+$ (v_2, J=0)? Why? (*Hint: Consider Franck-Condon Factors*)

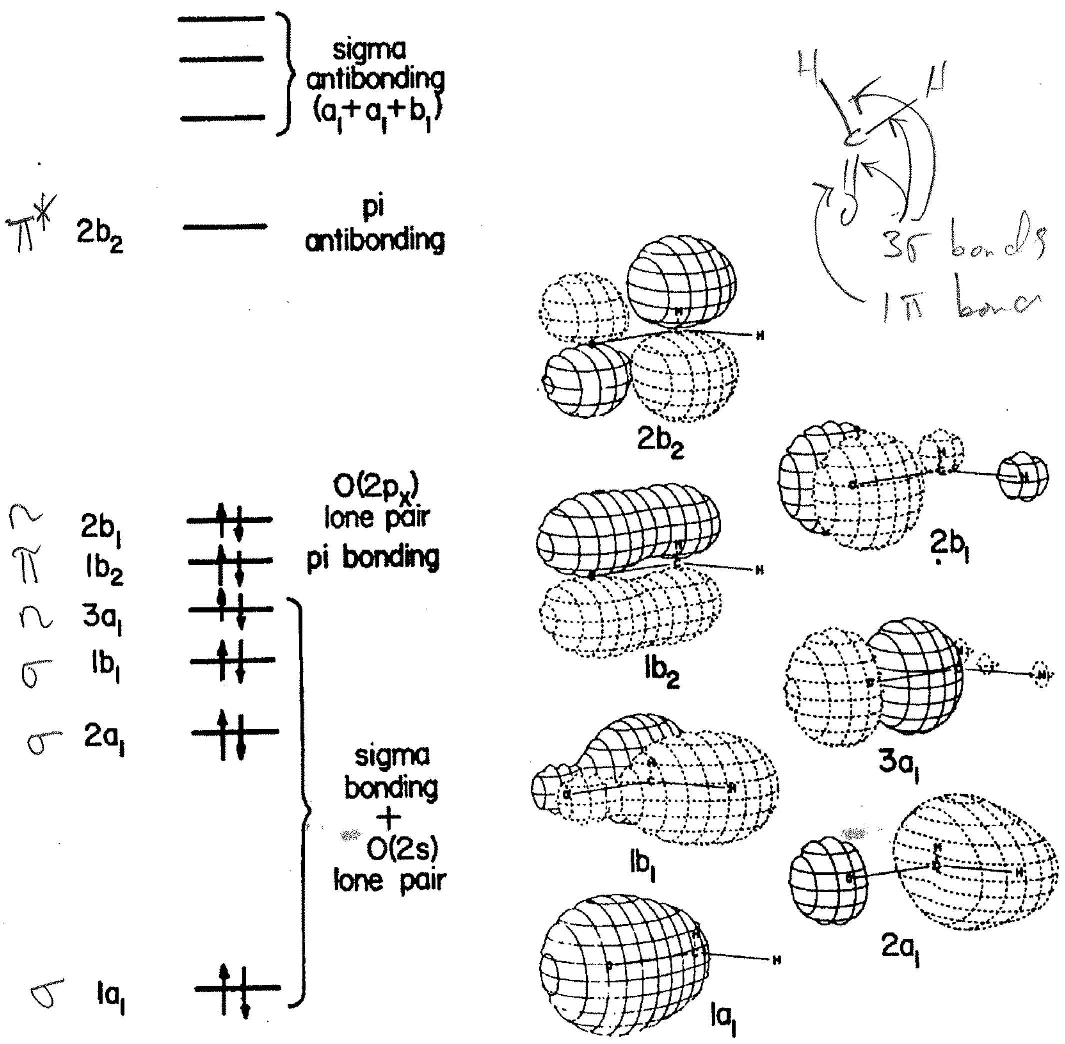
(f) Draw the MO energy level diagram of OH radical. (The ionization energy of oxygen atom is the same as the H atom, 13.6 eV). What type of transition is $A^2\Sigma^+ \leftarrow X^2\Pi$ ($\pi^* \leftarrow \pi$)?

(g) Sketch the absorption spectrum for $A^2\Sigma^+(v_2, J=0) \leftarrow X^2\Pi\ (v=0, J=0)$ for the range $v_2=0$ to $v_2=4$. (These are the Q-branches.)

3.) (a) The drawing below gives the molecular orbital diagram of formaldehyde along with drawings of the orbitals. (The symmetry designations are the same as in water since both are C_{2v} molecules.) There is one high energy orbital that is non-bonding. *Label it and its energy level with an n.* There is an antibonding orbital that is π^* in its local symmetry. *Label it.* (There is another non-bonding orbital. We will call it $3a_1$ even though the situation is actually more complicated because of the strong mixing of the atomic orbitals to make the three lowest a_1 orbitals. Each of them is partially bonding and nonbonding.)

Place electrons on the level diagram and work out the bond order for H_2CO. Is your result consistent with the Lewis dot structure?

Yes



(b) What will happen to the length of the C=O bond upon excitation of the $\pi^* \leftarrow n$ transition? The origin transition, $0 \leftarrow 0$, between the lowest vibrational levels in the ground and electronically excited state has a wavenumber of 28,200 cm^{-1}. Explain how the intensity of this transition compares to the intensity of other transitions.

Draw one-dimensional potential energy curves to illustrate your argument. Indicate the energy of the origin transition on your diagram.

1) Taking wes from butadiene example;


3 c-atoms w/ unhybridized p orbitals to use for π-bonding

$$\mathbb{H} = \begin{vmatrix} \alpha & \beta & 0 \\ \beta & \alpha & \beta \\ 0 & \beta & \alpha \end{vmatrix}$$

no interaction b/w non-neighbors

$$\alpha \equiv \int A \hat{H} A \, d\tau = \int B \hat{H} B \, d\tau \qquad S_{ij} = \delta_{ij} = \mathbb{I}$$

$$\beta = \int A \hat{H} B \, d\tau = \int B \hat{H} A \, d\tau$$

$$(\mathbb{H} - E_i \mathbb{S})\, c_i = 0$$

$$(\mathbb{H} - E_i \mathbb{I})\, c_i = 0$$

$$\mathbb{H} - E_i \mathbb{I} = \begin{vmatrix} \alpha - E & \beta & 0 \\ \beta & \alpha - E & \beta \\ 0 & \beta & \alpha - E \end{vmatrix}$$

solve for eigenvalues by taking determinant and setting equal to zero

$$\det(\mathbb{H} - E_i \mathbb{I}) = (\alpha - E) \begin{vmatrix} \alpha - E & \beta \\ \beta & \alpha - E \end{vmatrix} - \beta \begin{vmatrix} \beta & \beta \\ 0 & \alpha - E \end{vmatrix} - 0 \begin{vmatrix} \beta & \alpha - E \\ 0 & \beta \end{vmatrix}$$

$$= (\alpha - E)\left[(\alpha - E)^2 - \beta^2\right] - \beta\left[\beta(\alpha - E)\right] = \underbrace{(\alpha - E)}_{E = \alpha}\underbrace{\left((\alpha - E)^2 - 2\beta^2\right)}_{E = \alpha \pm \sqrt{2}\,\beta} = 0$$

Now plug eigenvalues in to $\mathbb{H} - E_i \mathbb{I}$ and solve for corresponding eigenvector c_i

1)(cont)

let $E = \alpha$

$$\begin{vmatrix} 0 & \beta & 0 \\ \beta & 0 & \beta \\ 0 & \beta & 0 \end{vmatrix} \begin{vmatrix} c_1 \\ c_2 \\ c_3 \end{vmatrix} = 0$$

$$\beta c_2 = 0 \quad \Rightarrow c_2 = 0$$

$$\beta c_1 + \beta c_3 = 0 \Rightarrow c_1 = -c_3$$

$$\beta c_2 = 0$$

$c_1^2 + c_2^2 + c_3^2 = 1$ (from normalization)

$$c_1^2 + (-c_1)^2 = 1 \qquad c_1 = \pm \frac{1}{\sqrt{2}} \quad c_3 = \mp \frac{1}{\sqrt{2}}$$

let $E = \alpha \pm \sqrt{2}\,\beta$

$$\begin{vmatrix} \mp\sqrt{2}\beta & \beta & 0 \\ \beta & \mp\sqrt{2}\beta & \beta \\ 0 & \beta & \mp\sqrt{2}\,\beta \end{vmatrix} \begin{vmatrix} c_1 \\ c_2 \\ c_3 \end{vmatrix} = 0$$

$$\begin{aligned} \mp\sqrt{2}\beta c_1 + \beta c_2 \quad &= 0 \\ \beta c_1 \mp \sqrt{2}\beta c_2 + \beta c_3 &= 0 \\ + \beta c_2 \mp \sqrt{2}\beta c_3 &= 0 \\ c_1^2 + c_2^2 + c_3^2 &= 1 \end{aligned}$$

$$c_2 = \pm\sqrt{2}\ c_1 \qquad \therefore \quad c_1 = c_3$$

$$c_2 = \pm\sqrt{2}\ c_3$$

$$c_1^2 + (\pm\sqrt{2}\,c_1^2)^2 + c_1^2 = 1 = 4c_1^2$$

$$c_1 = \pm \frac{1}{2}$$

$$c_2 = \frac{1}{\sqrt{2}}$$

$$c_3 = \pm \frac{1}{2}$$

$$\psi_3 = -\frac{1}{2}\chi_A + \frac{1}{\sqrt{2}}\chi_B - \frac{1}{2}\chi_C \ ; \ E = \alpha - \sqrt{2}\beta$$

$$\psi_2 = \frac{1}{\sqrt{2}}\chi_A + 0\chi_B + \frac{1}{\sqrt{2}}\chi_C \ ; \ E = \alpha$$

$$\psi_1 = \frac{1}{2}\chi_A + \frac{1}{\sqrt{2}}\chi_B + \frac{1}{2}\chi_C \ ; \ E = \alpha + \sqrt{2}\,\beta$$

NB
1) $\beta < 0$
2) ψ_1 has no nodes
↳ lowest E

ψ_3 has 2 nodes
↳ highest E

2) a) We have seen the Morse oscillator before.

If force is constant, we must be dealing with SHO language

$F = \underline{\underline{k}}x$, and we know these relations

$$\omega = \sqrt{\frac{k}{\mu}} \quad \text{or} \quad \tilde{\nu} = \frac{1}{2\pi c}\sqrt{\frac{k}{\mu}} \qquad (\text{eq. } 6.50, 6.51)$$

$$k = (\tilde{\nu}\, 2\pi c)^2 \cdot \mu$$

$$k_1 = (3735.2\ \cancel{cm^{-1}} \cdot 2 \cdot \pi \cdot 2.998 \times 10^{10}\ \cancel{cm}/s)^2 \cdot \left(\frac{1.007825 \cdot 15.99491}{(1.007825 + 15.99491}\right) \cancel{amu} \left(\frac{1.6605 \times 10^{-27}\ Kg}{\cancel{amu}}\right)$$

$$\underline{= 779.36\ \frac{Kg}{s^2}} \qquad N/m = \frac{Kg\ m/s^2}{m} = Kg/s^2 \quad ✓$$

$$k_2 = (3180.6\ cm^{-1} \cdot 2\pi \cdot 2.998 \times 10^{10}\ cm/s)^2 \cdot 1.5743 \times 10^{-27}\ Kg$$

$$\underline{= 565.10\ N/m}$$

$$B = \frac{\hbar}{4\pi c I} = \frac{\hbar}{4\pi c \mu R_e^2} \ ; \quad R_e = \left(\frac{\hbar}{4\pi c \mu B}\right)^{1/2}$$

$$R_e = \left(\frac{1.0545 \times 10^{-34}\ J \cdot s}{4\pi\ 2.998 \times 10^{10}\ cm/s \cdot 1.5743 \times 10^{-27}\ Kg \cdot 18.87\ cm^{-1}}\right)^{1/2} = 9.707 \times 10^{-11}\ m = \underline{0.9707\ \text{Å}}$$

$$\left(\frac{\frac{\cancel{Kg}\, m^2}{\cancel{s^2}} \cdot \cancel{s}}{\cancel{cm/s}\ \cancel{Kg}\ \cancel{cm^{-1}}}\right)^{1/2} = m \quad ✓$$

$$\underline{R_e' = 1.012\ \text{Å}}$$

The force constant is stronger in g.s. and the ~~g~~ bond length is shorter in the g.s.

b) $G(v+2) - G(v) = 2\tilde{\nu} - 2(v+3)x_e\tilde{\nu} + \ldots$ (eq. 6.58)

$v=0$

$= 2(3736.2\ \mathrm{cm^{-1}}) - 2(3)\,82.81\ \mathrm{cm^{-1}} = 6973.5\ \mathrm{cm^{-1}}$ ✓

c) $A^2\Sigma^+ (v=5, J=5) = G(v=5) + F(J=5)$

$= (5+\frac{1}{2})(3180.6\ \mathrm{cm^{-1}}) - (5+\frac{1}{2})^2\,94.93\ \mathrm{cm^{-1}}$

$+ 17.36\ \mathrm{cm^{-1}}(5)(6) = 15142.5\ \mathrm{cm^{-1}}$ (above $32682\ \mathrm{cm^{-1}}$)

$X^2\Pi (v=1, J=5) = G(v=1) + F(J=5)$

$= (1+\frac{1}{2})3735.2 - (1+\frac{1}{2})^2\,82.81 + 18.87(5)(6)$

$= 5982.58\ \mathrm{cm^{-1}}$ (above $0\ \mathrm{cm^{-1}}$) ✓

$(15142.5 + 32682)\ \mathrm{cm^{-1}} - (5982.58 + 0)\ \mathrm{cm^{-1}} = 41841.9\ \mathrm{cm^{-1}}$ ✓

(= 239 nm)

d, e) See Mathcad sheet

Some constants:

$N_A := 6.022 \cdot 10^{23}$ $\quad$ $amu := \dfrac{10^{-3} \cdot kg}{N_A}$ $\quad$ $wn := \dfrac{1}{cm}$

In general, Mathcad doesn't like wavenumbers the way we think about them

$Ang := 10^{-10} m$ $\quad$ $nm := 10^{-9} m$

$c := 2.9998 \cdot 10^{8} \cdot \dfrac{m}{s}$ $\quad$ $m_H := 1.007825 \cdot amu$ $\quad$ $h_{bar} := 1.0545 \cdot 10^{-34} \cdot J \cdot s$

$h := 6.626 \cdot 10^{-34} \cdot J \cdot s$ $\quad$ $m_O := 15.99491 \cdot amu$

Isotopes

These values are given in the problem. I like working in meters and wavenumbers

$R_{eX} := .9707 \cdot 10^{-10} m$ $\quad$ $R_{eA} := 1.012 \cdot 10^{-10} m$

$\tilde{\nu}_X := 3735.2 \cdot wn$ $\quad$ $\tilde{\nu}_A := 3180.6 \cdot wn$

$x_{eX} := \dfrac{82.81 wn}{\tilde{\nu}_X}$ $\quad$ $x_{eA} := \dfrac{94.93 wn}{\tilde{\nu}_A}$ $\quad$ x.e is unitless

$B_X := 18.87$ $\quad$ $B_A := 17.36$ $\quad$ (not used in worksheet)

We now calculate some of the following parameters that will be useful for plotting

$k_X := 779.36 \dfrac{N}{m}$ $\quad$ $k_A := 565.1 \dfrac{N}{m}$

$D_{eX} := \dfrac{\tilde{\nu}_X}{4 \cdot x_{eX}}$ $\quad$ $D_{eA} := \dfrac{\tilde{\nu}_A}{4 \cdot x_{eA}}$ $\quad$ ✓ in wavenumbers

$D_{eX} = 4.212 \times 10^{4} wn$ $\quad$ $D_{eA} = 2.664 \times 10^{4} wn$

$\mu := \dfrac{m_H \cdot m_O}{m_H + m_O}$ $\quad$ $h_{bar} \cdot \omega := h \cdot c \cdot \tilde{\nu}$ $\quad$ mass in Kg

$\omega_X := 2\pi \cdot c \cdot \tilde{\nu}_X$ $\quad$ $\omega_A := 2\pi \cdot c \cdot \tilde{\nu}_A$ $\quad$ in Hz/2pi

$\dfrac{c \cdot 2 \cdot \pi}{\omega_X} = 2.677 \times 10^{3} nm$ $\quad$ $\dfrac{c \cdot 2 \cdot \pi}{\omega_A} = 3.144 \times 10^{3} nm$ $\quad$ Resonable values (IR)!

$a_X := \left(\dfrac{x_{eX} \cdot 4 \cdot \pi \cdot c \cdot \tilde{\nu}_X \cdot \mu}{h} \right)^{0.5}$ $\quad$ $a_A := \left(\dfrac{2 \cdot \mu \cdot \omega_A \cdot x_{eA}}{h} \right)^{0.5}$ $\quad$ ✓

bar bar

$a_X = 2.159\,\frac{1}{Ang} \qquad a_A = 2.311\,\frac{1}{Ang}$

$X(r) := D_{eX}\cdot\left[1 - e^{-a_X\cdot\left(r-R_{eX}\right)}\right]^2$

$X\left(R_{eX}\right) = 0\,wn$ A good idea to check your function

$A(r) := D_{eA}\cdot\left[1 - e^{-a_A\cdot\left(r-R_{eA}\right)}\right]^2 + 32682wn$ Add an offset relative to g.s. curve

$A\left(R_{eA}\right) = 3.268\times 10^4\,wn$

Energy levels of Morse oscillator:

$G_X(v) := \left(v+\frac{1}{2}\right)\nu_X - \left(v+\frac{1}{2}\right)^2\cdot x_{eX}\cdot\nu_X$ Given in your text

$G_A(v) := \left(v+\frac{1}{2}\right)\nu_A - \left(v+\frac{1}{2}\right)^2\cdot x_{eA}\cdot\nu_A + 32682wn$ Again, don't forget the offset

$G_X(0) = 1.847\times 10^3\,wn$

$i := 0, 1 .. 4 \qquad w_i := i \qquad r_{X0} := .75Ang, .76Ang .. 1.5Ang$ Setting up some range variables for the plot

Let's plot the harmonic wf's and shift them by eye, this will be at least as good as drawing guess wf's on the curves:

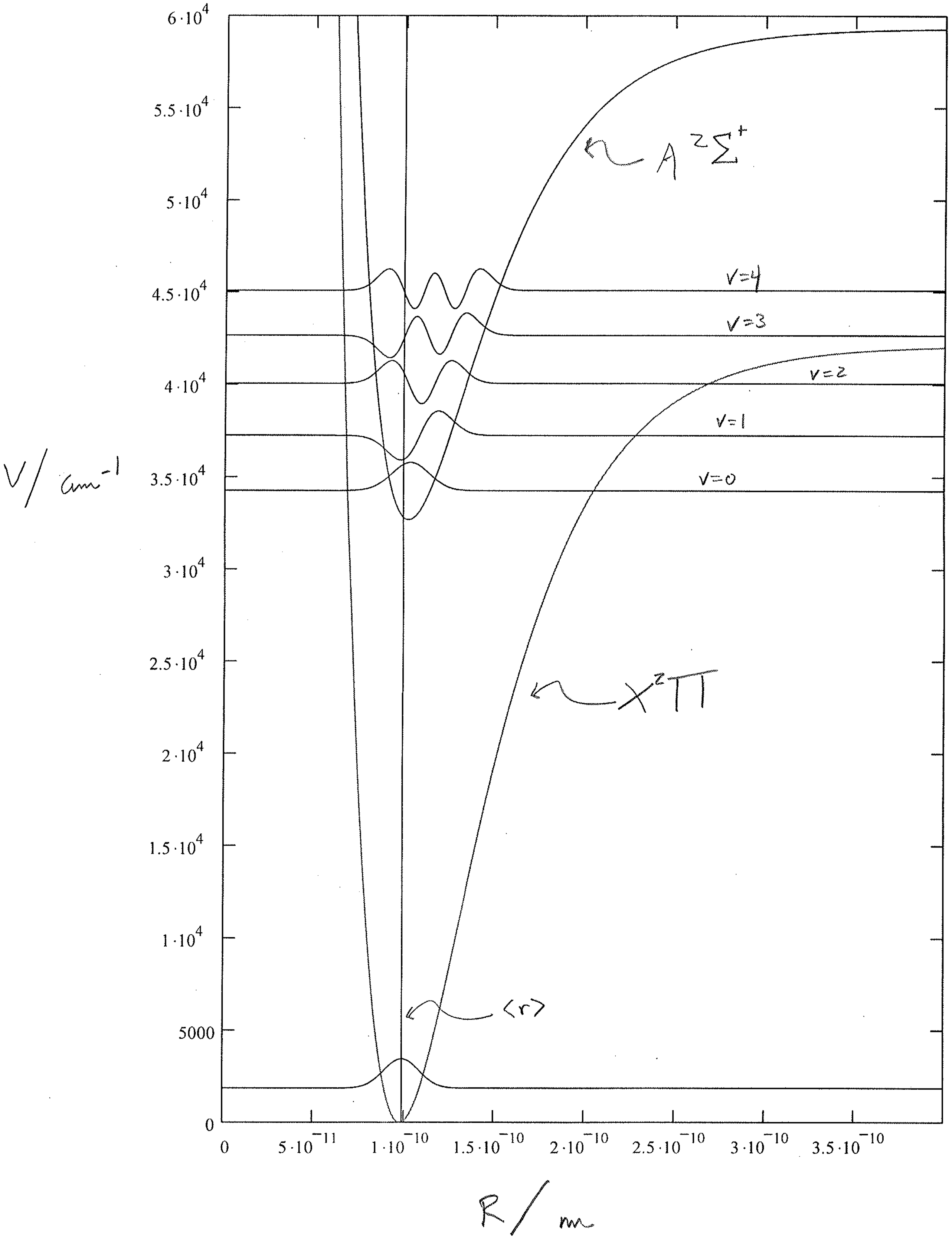
$\alpha_X := \left(\frac{h_{bar}^{\;2}}{\mu\cdot k_X}\right)^{.25} \qquad \alpha_A := \left(\frac{h_{bar}^{\;2}}{\mu\cdot k_A}\right)^{.25}$

$y_X(r) := \frac{r}{\alpha_X} \qquad y_A(r) := \frac{r}{\alpha_A}$

$N_X\left(v_x\right) := \left(\frac{1}{\alpha_X\cdot\pi^{0.5}\cdot 2^{v_x}\cdot v_x!}\right)^{.5} \qquad N_A\left(v_a\right) := \left(\frac{1}{\alpha_A\cdot\pi^{0.5}\cdot 2^{v_a}\cdot v_a!}\right)^{.5}$

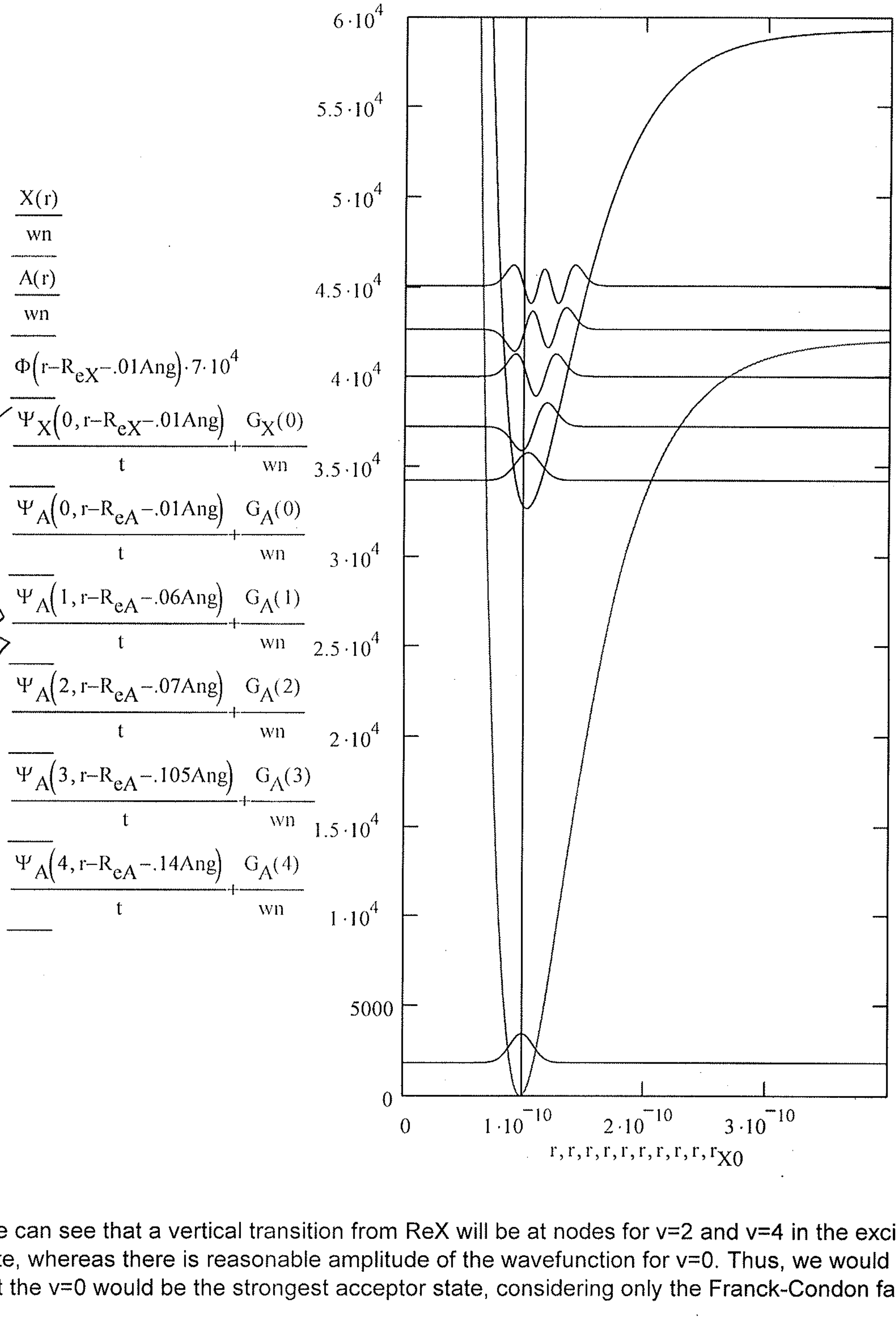
$\Psi_X\left(v_x, r\right) := N_X\left(v_x\right)\cdot Her\left(v_x, y_X(r)\right)\cdot e^{\frac{-y_X(r)^2}{2}} \qquad \Psi_A\left(v_a, r\right) := N_A\left(v_a\right)\cdot Her\left(v_a, y_A(r)\right)\cdot e^{\frac{-y_A(r)^2}{2}}$

$t := 15\cdot 10^1$ I will use this to scale the wf's on the plot below.



6·10^4
5.5·10^4
5·10^4
4.5·10^4
4·10^4
3.5·10^4
3·10^4
2.5·10^4
2·10^4
1.5·10^4
1·10^4
5000
0
0
5·10^−11
1·10^−10
1.5·10^−10
2·10^−10
2.5·10^−10
3·10^−10
3.5·10^−10
V/ cm^-1
R/ m
A ²Σ⁺
X ²Π
v=4
v=3
v=2
v=1
v=0
⟨r⟩

Same plot, showing you the arguments

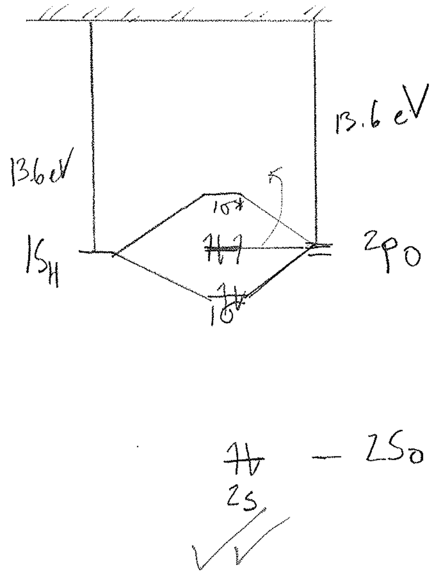


gives me vertical line

HO wf's

One can see that a vertical transition from ReX will be at nodes for v=2 and v=4 in the excited state, whereas there is reasonable amplitude of the wavefunction for v=0. Thus, we would expect that the v=0 would be the strongest acceptor state, considering only the Franck-Condon factor.

f)



This is a $\sigma^* \leftarrow n$ transition.

g) We need five lines that are the energy difference between the levels asked

$\mathrm{Abs}(v_2, v_1) := G_A(v_2) - G_X(v_1)$

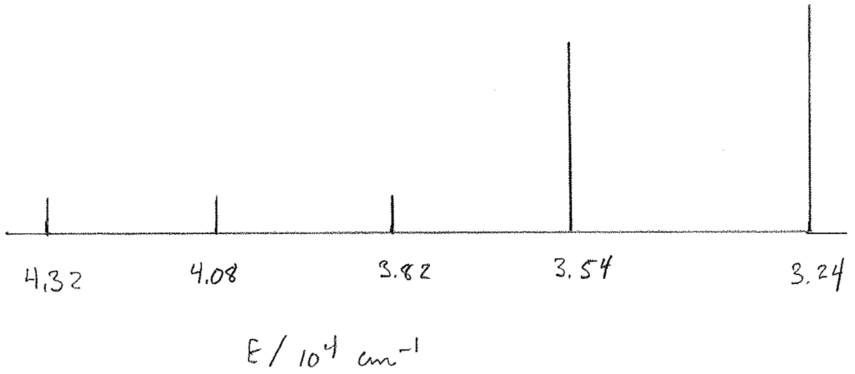
$j := 0, 1 .. 4$

$\mathrm{Abs}(j, 0) =$

$3.24 \cdot 10^4$
$3.539 \cdot 10^4$
$3.819 \cdot 10^4$
$4.08 \cdot 10^4$
$4.323 \cdot 10^4$

wn

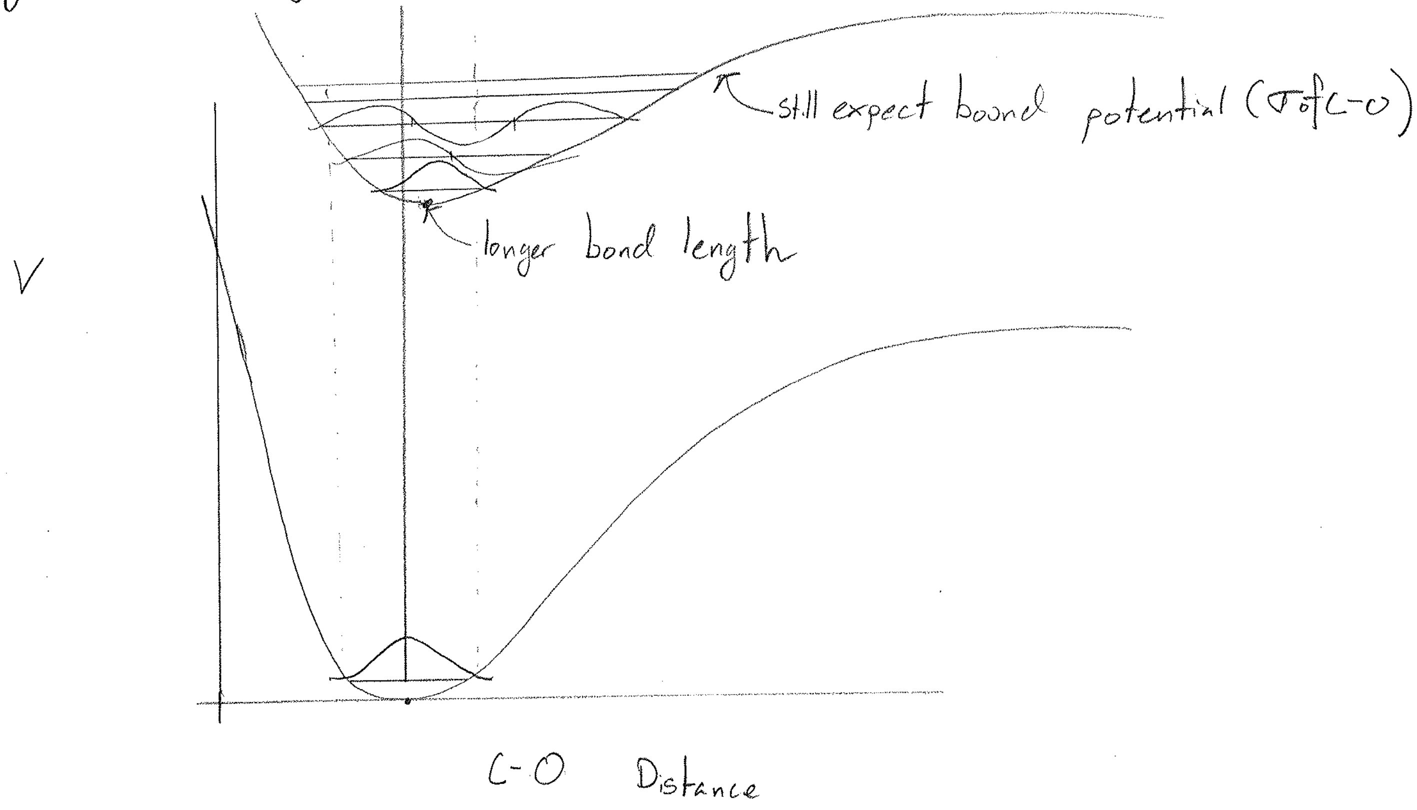
✓✓



These intensities reflect approximate Franck-Condon overlap for each transition

3) b) $\pi^* \leftarrow n$ meens we take an e^- from a non-bonding to an antibonding orbital, which at g.s. is unpopulated. Since the $2b_1$ orbital has a node between the C and O atoms, we should expect a weakening and lengthening of this bond.

Since the bond will be longer in the excited state, we would expect less than unity overlap in the $0 \leftarrow 0$ transition. One or two more quanta of excitation should give a stronger transition.



As drawn, we only clip the tail of v=0 w.f. in excited state (note this is only a qualitative arguement), but get a stronger overlap with v=1. Also note that $\int v_f^* v_i \, d\tau$ will begin to decrease for larger v_f as its w.f. extends well past the region of appreciable amplitude of v_i. (Recall, w.f. are normalized, mine are not.)