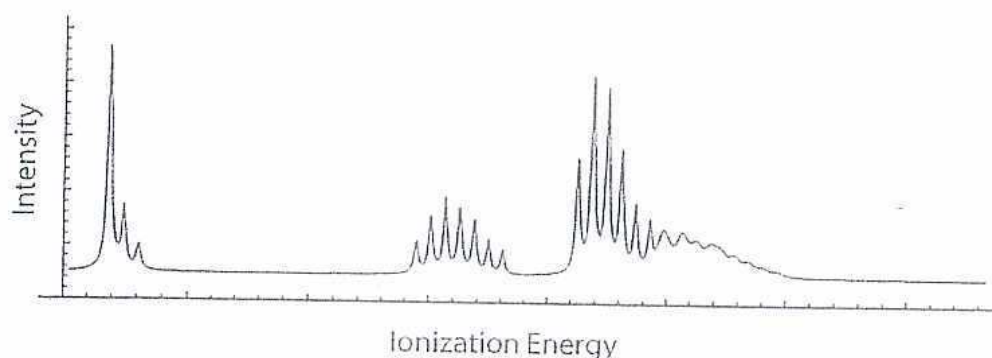


Q15.2) ~~Q15.2)~~ The relative intensities of vibrational peaks in an electronic spectrum are determined by the Franck-Condon factors. How would the potential curve for the excited state in Figure 26.2 need to be shifted along the distance axis for the  $n = 0 \rightarrow n' = 0$  transition to have the highest intensity? The term  $n$  refers to the vibrational quantum number in the ground state, and  $n'$  refers to the vibrational quantum number in the excited state.

It would need to be shifted to the left, corresponding to a shorter bond length. The  $n = 0 \rightarrow n' = 0$  transition will have the highest intensity if the bond length in the ground and excited states is the same.

Q15.3) ~~Q15.3)~~ Suppose you obtain the UV photoelectron spectrum shown here for a gas-phase molecule. Each of the groups corresponds to a cation produced by ejecting an electron from a different MO. What can you conclude about the bond length of the cations in the three states formed relative to the ground-state neutral molecule? Use the relative intensities of the individual vibrational peaks in each group to answer this question.



Because the most intense peak in the first group corresponds to  $n = 0$ , we conclude that the bond length in the cation is very similar to that in the ground state. The most intense peak in the second and third groups correspond to  $n = 3$ , and  $n = 4$  respectively. We conclude that the bond length in the cations corresponding to both groups of peaks is longer than that in the ground state. The cation corresponding to the second group of peaks has the longest bond.

Q15.6) ~~Q15.6)~~ Explain why the fluorescence and absorption groups of peaks in Figure 26.10 are shifted and show mirror symmetry for idealized symmetrical ground-state and excited-state potentials.

The absorption event is initiated from the  $n = 0$  vibrational level of the ground state. The relative order of peak intensities for different vibrational quantum

numbers of the excited state is governed by the Franck-Condon principle. Assume, as is often the case, that the excited state has a longer bond. In that case the maximum intensity is observed for  $n' > 0$ , where the prime refers to the excited state. The molecule will quickly lose energy, and be in the  $n' = 0$  vibrational level. Because fluorescence to the ground state occurs from this level, the whole fluorescence spectrum is shifted to lower frequencies relative to the absorption spectrum. The reason for the mirror symmetry can best be understood by looking at Figure 26.10. For a symmetric potential, the progression from the maximum to the minimum overlap leads to a decrease in the frequency of the absorption transition, but to an increase in the frequency of the fluorescence transition.

Q15.11)

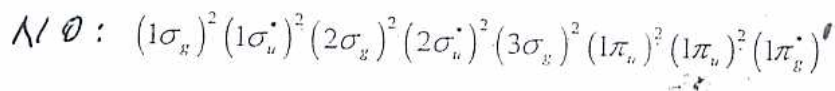
~~Q15.11~~) Because internal conversion is in general very fast, the absorption and fluorescence spectra are shifted in frequency as shown in Figure 26.10. This shift is

crucial in making fluorescence spectroscopy capable of detecting very small concentrations. Can you explain why?

In the experiment, the sample is constantly being illuminated with light to effect the transition of interest. If fluorescence occurred at exactly the same frequency as absorption, the signal would not be detectable because it is indistinguishable for the light used to excite the molecule. Because the fluorescence spectrum is shifted to lower frequencies, a filter can be used in front of the detector that will block light at the absorption frequency. Consequently, the signal has a very low background.

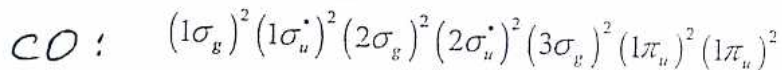
1) Number of Unpaired Electrons in a Molecule

i) NO has 15 electrons and the configuration:



It has one unpaired electron.

ii) CO has 14 electrons and the configuration:



It has no unpaired electrons.

## Problem Set 11: solution to Problem 2

2) First, define  $\alpha = \sqrt{k/\hbar}$ . Now ...

a) Since the ground state vibrational level is the same for both potential curves, namely,  $E_0^{(g)} = E_0^{(e)} = \hbar\omega/2$ , then the energy gap between these levels is simply the energy gap between the minima of the two potential curves, namely  $V_0$ . Thus the frequency of the photon absorbed to make a transition between these energy levels is  $\nu = V_0/h$ .

b) Writing down the overlap integral itself:

$$J = \int_{-\infty}^{\infty} dx \psi_0^{(g)}(x) \psi_0^{(e)}(x) = \int_{-\infty}^{\infty} dx \frac{1}{\sqrt{\pi}} \exp\left(-\frac{\alpha^2}{2}x^2\right) \frac{1}{\sqrt{\pi}} \exp\left(-\frac{\alpha^2}{2}(x-a)^2\right)$$

$$= \frac{1}{\pi} \int_{-\infty}^{\infty} dx \exp\left(-\frac{\alpha^2}{2}x^2 - \alpha^2 x a + \frac{\alpha^2}{2}a^2\right) = \frac{1}{\pi} \exp\left(\frac{\alpha^2}{2}a^2\right) \int_{-\infty}^{\infty} dx \exp\left(-\frac{\alpha^2}{2}x^2 - \alpha^2 x a\right)$$

[Note: we've used the Gaussian integral identity:  $\int_{-\infty}^{\infty} dx \exp(-Ax^2 - Bx) = \sqrt{\pi/A} \exp\left(\frac{B^2}{4A}\right)$ .]

Thus:  $I = |J|^2 = \exp\left(-\alpha^2 a^2\right)$ .

Note that  $I$  decreases monotonically from the value of 1 when  $a=0$ , to 0 when  $a \rightarrow \pm\infty$  [why?].