Problem Set 5

Q23.18 Why can you conclude that the energy of the antibonding MO in H$_2^+$ is raised more than the energy of the bonding MO is lowered?

The difference is due to the different denominators. The energy of the antibonding MO has a $1 - S_{ab}$ in the denominator, whereas the bonding MO has $1 + S_{ab}$. Because $S_{ab} > 0$, $1 + S_{ab} > 1$ and $1 - S_{ab} < 1$.

P23.5 Calculate the bond order in each of the following species and predict which of the two species in the following pairs has the higher vibrational frequency:

(a) Li$_2$ or Li$_2^+$

Li$_2$ has electron configuration $(1\sigma)(1\sigma^*)(2\sigma)$. The bond order is $(4-2)/2 = 1$.

Li$_2^+$ has electron configuration $(1\sigma)(1\sigma^*)(2\sigma)$. The bond order is $(3-2)/2 = 1/2$.

The species with the higher bond order has the stronger bond and higher vibrational frequency, so Li$_2$ in this case.

(b) C$_2$ or C$_2^+$

C$_2$: $(1\sigma)(1\sigma^*)(2\sigma)(2\sigma^*)(1\pi)$. The bond order is $(8-4)/2 = 2$.

C$_2^+$: $(1\sigma)(1\sigma^*)(2\sigma)(2\sigma^*)(1\pi)$. The bond order is $(7-4)/2 = 1.5$.

C$_2$ has the stronger bond and higher vibrational frequency.

(c) O$_2$ or O$_2^+$

O$_2$: $(1\sigma)(1\sigma^*)(2\sigma)(2\sigma^*)(3\sigma)(1\pi)(1\pi^*)$. The bond order is $(10-6)/2 = 2$.

O$_2^+$: $(1\sigma)(1\sigma^*)(2\sigma)(2\sigma^*)(3\sigma)(1\pi)(1\pi^*)$. The bond order is $(10-5)/2 = 2.5$.

O$_2^+$ has the stronger bond and higher vibrational frequency.

(d) F$_2$ or F$_2^+$

F$_2$: $(1\sigma)(1\sigma^*)(2\sigma)(2\sigma^*)(3\sigma)(1\pi)(1\pi^*)$. The bond order is $(10-8)/2 = 1$.

F$_2^+$: $(1\sigma)(1\sigma^*)(2\sigma)(2\sigma^*)(3\sigma)(1\pi)(1\pi^*)(3\sigma)$. The bond order is $(10-9)/2 = 0.5$.

F$_2$ has the stronger bond and higher vibrational frequency.
P23.6 Sketch the highest occupied molecular orbital (HOMO) for the following species:

(a) $N_2^+$

(b) $Li_2^+$

(c) $O_2^-$

(d) $H_2^-$

(e) $C_2^+$
P23.11 Arrange the following in terms of decreasing bond energy and bond length: O_2^+, O_2, O_2^-, and O_2^{2-}:

O_2^{2-}: (1\sigma)(1\sigma^*)(2\sigma(2\sigma^*)(3\sigma)(3\pi)(1\pi)(1\pi^*). The bond order is (10-8)/2 = 1.

O_2^-: (1\sigma)(1\sigma^*)(2\sigma)(2\sigma^*)(3\sigma)(3\pi)(1\pi). The bond order is (10-7)/2 = 1.5.

O_2: (1\sigma)(1\sigma^*)(2\sigma)(2\sigma^*)(3\sigma)(3\pi)(1\pi)(1\pi^*). The bond order is (10-6)/2 = 2.

O_2^+: (1\sigma)(1\sigma^*)(2\sigma)(2\sigma^*)(3\sigma)(3\pi)(1\pi)(1\pi^*). The bond order is (10-5)/2 = 2.5.

Bond Energy: O_2^+ > O_2 > O_2^- > O_2^{2-}. Bond Length: O_2^+ < O_2 < O_2^- < O_2^{2-}.

Q25.2 How can FRET give information about the tertiary structure of a biological molecule in solution?

The tertiary structure refers to the overall shape of the molecule. If a biological molecule is folded into a spherical shape, or is in the form of an a-helix or b-sheet, two common structural elements of a macromolecule (such as a protein), two regions of the molecule may end up close to each other even though, when the molecule is unfolded, the regions are in distant parts of the molecular backbone. By placing a donor and acceptor in two parts of the backbone, FRET can be used to determine if those parts lie near each other in the folded, tertiary structure.

Q25.4 What would the intensity versus frequency plot in Figure 25.10 look like if fluorescence were fast with respect to internal conversion?

In this case fluorescence would not necessarily occur from the ground vibrational state of the excited electronic state and the fluorescence and absorption spectra would be very close to each other.

P25.3 Ozone has an absorptivity at 300 nm of 0.00500 torr\(^{-1}\) cm\(^{-1}\). The amount of ozone in the atmosphere is quantified using the Dobson unit (DU), where 1 DU is equivalent to a 10\(^{-2}\) mm thick layer of ozone at 1 atm and 273.15 K.

a. Calculate the absorbance of the ozone layer at 300 nm for a typical coverage of 300 DU.

\[ A = e \cdot b \cdot c = (0.00500 \text{ torr}^{-1} \text{ cm}^{-1})(300 \text{ DU})(0.001 \text{ cm/DU})(1 \text{ atm x 760 torr/atm}) = 1.14, \text{ which corresponds to } T = 10^{-1.14} = 7.24\% \text{ transmittance.} \]

b. Calculate absorbance of ozone layer (300 nm) for reduced coverage of 120 DU.

\[ A = e \cdot b \cdot c = (0.00500 \text{ torr}^{-1} \text{ cm}^{-1})(120 \text{ DU})(0.001 \text{ cm/DU})(1 \text{ atm x 760 torr/atm}) = 0.0456, \text{ which corresponds to } T = 10^{-0.456} = 35.0\% \text{ transmittance.} \]
**P25.9** Green fluorescent protein (GFP) and variants have been developed for in vivo FRET studies. Two variants of GFP, CFP and YFP, form a FRET pair where $R_0 = 4.72$ nm. The excited state lifetime of the CFP donor in the absence of YFP is 2.7 ns.

(a) At what distance will the rate of energy transfer be equal to the excited state decay rate for isolated CFP, i.e., equal to the inverse of the excited state lifetime?

\[
k_{\text{ret}} = \frac{1}{\tau_D^*} \left( \frac{R_0}{r} \right)^6 = \frac{1}{2.7 \text{ ns}} \left( \frac{4.72 \text{ nm}}{r} \right)^6.
\]

\[
\therefore \quad r = 4.72 \text{ nm}
\]

(b) Determine the distance at which the energy transfer rate will be 5 times the excited state decay rate.

\[
k_{\text{ret}} = \frac{1}{\tau_D^*} \left( \frac{R_0}{r} \right)^6 = \frac{5}{2.7 \text{ ns}} = \frac{1}{2.7 \text{ ns}} \left( \frac{4.72 \text{ nm}}{r} \right)^6.
\]

\[
5 = \left( \frac{4.72 \text{ nm}}{r} \right)^6
\]

\[
\therefore \quad r = 3.61 \text{ nm}
\]

**Q28.12** Order the molecules CH$_3$I, CH$_3$Br, CH$_3$Cl, CH$_3$F in terms of increasing chemical shift. Explain.

Chemical shift increases as the electron-withdrawing character of the substrate increases. Thus, the more electronegative the halogen, the greater the chemical shift for the methyl protons. The ordering is therefore CH$_3$I < CH$_3$Br < CH$_3$Cl < CH$_3$F.

**P28.3** For a fixed frequency of the radiofrequency, $^1$H, $^{13}$C, $^{31}$P will be in resonance at different values of the static magnetic field. Calculate the value of $B_0$ for these nuclei to be in resonance if the radiofrequency field has a frequency of 250 MHz.

The condition for resonance is

\[
\nu = \frac{\hbar}{\gamma B_0}; \quad B_0 = \frac{\hbar \nu}{\gamma} = \frac{2\pi \nu}{\gamma}.
\]

We can find the values of $\gamma$ for the various nuclei in Table 28.1. For $^1$H:

\[
B_0 = \frac{2\pi \nu}{\gamma} = \frac{2\pi \nu}{\gamma} = \frac{2\pi(250 \times 10^6 \text{ s}^{-1})}{26.75 \times 10^7 \text{ rad} \cdot \text{T}^{-1} \cdot \text{s}^{-1}} = 5.87 \text{ T}
\]

Similarly, using $6.73 \times 10^7 \text{ rad T}^{-1} \text{ s}^{-1}$ for $^{13}$C we find $B_0 = 23.3 \text{ T}$ and using $10.84 \times 10^7 \text{ rad T}^{-1} \text{ s}^{-1}$ for $^{31}$P we find $B_0 = 14.5 \text{ T}$.