

1. The rotational constant of $^{19}\text{F}^{19}\text{F}$ is 0.890 cm^{-1} . Calculate the bond length of the molecule.

Solution:

$$\tilde{B} = \frac{\hbar}{4\pi c I} \text{ where } I = \mu r^2 \text{ for a diatomic}$$

Recast this expression in terms of I and solve for r.

$$I = \frac{\hbar}{4\pi c \tilde{B}}, \text{ so } \mu r^2 = \frac{\hbar}{4\pi c \tilde{B}} \text{ and } r = \sqrt{\frac{\hbar}{4\pi \mu c \tilde{B}}}$$

Applying the appropriate numerical values. We first require the reduced mass in SI units.

$$\mu = \frac{m_F m_F}{(m_F + m_F)} = \frac{m_F}{2} = \frac{19}{2} 1.661 \times 10^{-27} \text{ kg} = 1.577 \times 10^{-26} \text{ kg}$$

$$r = \sqrt{\frac{1.054 \times 10^{-34} \text{ Js}}{4(3.141)(1.577 \times 10^{-26} \text{ kg})(2.997 \times 10^{10} \text{ cm/s})0.89 \text{ cm}^{-1}}}$$

$$= 1.41 \times 10^{-10} \text{ m} = 1.41 \text{ \AA}$$

2. The fundamental vibrational frequency of $^{12}\text{C}^{16}\text{O}$ is 2169.8 cm^{-1} . Calculate the force constant of stretching vibration of this diatomic molecule.

Solution:

$$k = \mu \omega^2 = \left(\frac{m_C m_O}{m_C + m_O} \right) 4\pi^2 \nu^2 = \left(\frac{m_C m_O}{m_C + m_O} \right) 4\pi^2 c^2 \tilde{\nu}^2$$

$$k = \left(\frac{12 \cdot 16}{(12 + 16)} \right) (1.661 \times 10^{-27} \text{ kg}) 4(3.141)^2 (2.99 \times 10^{10} \text{ cm/s})^2 (2169.8 \text{ cm}^{-1})^2$$

which gives $k = 1900 \text{ N/m}$.

3. Given the diagram below fill in the occupancy of the electrons in F_2 ($Z=9$).

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- a. What is the spin multiplicity of the ground state?

The total spin quantum number is $S = 0$ and the multiplicity is $2S + 1 = 1$

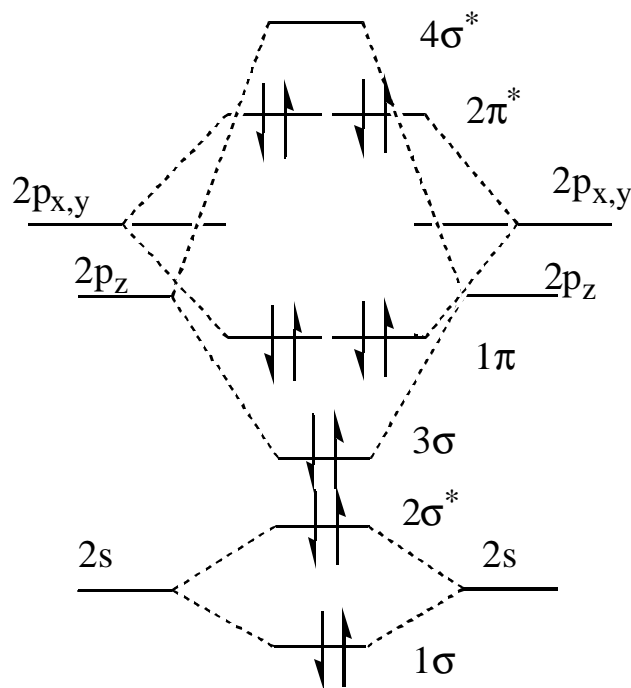
- b. Assign the lowest energy transition in diatomic fluorine using the molecular orbitals in the diagram. $2\pi^* \rightarrow 4\sigma^*$

- c. Give the bond order in the ground state.

Bond order = $\frac{1}{2}(8 \text{ bonding} - 6 \text{ anti-bonding}) = 1$

- d. Give the bond order of F_2^+ .

Bond order = $\frac{1}{2}(8 \text{ bonding} - 5 \text{ anti-bonding}) = 1.5$



4. A. Determine the solution concentration of oxymyoglobin given that the extinction coefficient is $180,000 \text{ M}^{-1}\text{cm}^{-1}$ at the peak of the Soret band ($\lambda_{\text{max}} = 418 \text{ nm}$). The absorbance of the sample is 0.3 in a 1 millimeter pathlength cell.

Solution: $A = \epsilon cd \rightarrow c = A/\epsilon d = 0.3/(180,000 \text{ M}^{-1}\text{cm}^{-1})(0.1 \text{ cm}) = 1.67 \times 10^{-5} \text{ M} = 16.7 \text{ mM}$

- B. Assuming that the photolysis yield for $\text{MbO}_2 \rightarrow \text{Mb} + \text{O}_2$ is $\Phi_{\text{photolysis}} = 0.75$ and that the absorbance of Mb is 0.1 at 418 nm, calculate the largest possible change in absorbance that can occur for laser photolysis of oxymyoglobin.

Solution: If all of the molecules are photoexcited then 25% will remain as MbO_2 ($A = 0.3 \times 0.25$) and will be unchanged and 75% will be converted to Mb ($A = 0.1 \times 0.75$). The change in absorbance is thus $\Delta A = (0.3 - 0.1)0.75 = 0.15$.