Chemistry 327 **EXAM 3** Name_ KEY
Fall, 2009
Dr. Watson

Conversion factors and constants:

$$\frac{h}{8\pi^2 c} = 2.79928\times10^{-39}\ \text{g-cm}$$

$hc = 12398$ eV-Å $= 1.985\times10^{-25}$ J-m

$h = 6.626\times10^{-34}$ J-s $= 4.135\times10^{-15}$ eV-s

$c = 2.9979\times10^{8}$ m/s

$k = 1.380\times10^{-23}$ J/K $= 8.617\times10^{-5}$ eV/K

1 Å $= 1\times10^{-10}$ m

1 J $= 6.242\times10^{18}$ eV

electron rest mass $= 9.1095\times10^{-31}$ kg

electron rest mass energy (m_oc^2) $= 511\times10^{3}$ eV

proton rest mass $= 1.673\times10^{-27}$ kg

proton rest mass energy $= 936\times10^{6}$ eV

C_{3v}	E	$2C_3$	$3\sigma_v$		h = 6
A_1	1	1	1	z	z^2, x^2+y^2
A_2	1	1	-1		
E	2	-1	0	x, y,	(xy, x^2-y^2) (xz, yz)

1. a). Write all the possible the term symbol(s) for each of the electron configurations of the F_2 molecule given below.

6

2 • $2s\sigma_g^2 2s\sigma_u^2 2p\sigma_g^2 2p\pi_u^4 2p\pi_g^4$ $\Lambda=0$ $S=0$ → $^1\Sigma_g$

2+2 • $2s\sigma_g^2 2s\sigma_u^2 2p\sigma_g^2 2p\pi_u^4 2p\pi_g^3 2p\sigma_u^1$ $\Lambda=1$

$M_s = \frac{1}{2}+\frac{1}{2}=1$, $\frac{1}{2}-\frac{1}{2}=0$, $-\frac{1}{2}-\frac{1}{2}=-1$ } $S=1$

$-\frac{1}{2}+\frac{1}{2}=0$ $S=0$

$^3\Pi_u$, $^1\Pi_u$

b). Sketch the geometry of the XeF_4 molecule and specify the type of hybridization that is most appropriate for its valence-bond description.

6

Xe has 8 Ve
XeF_4 has 4bp + 2lp = 6 pairs
Hybridization is d^2sp^3

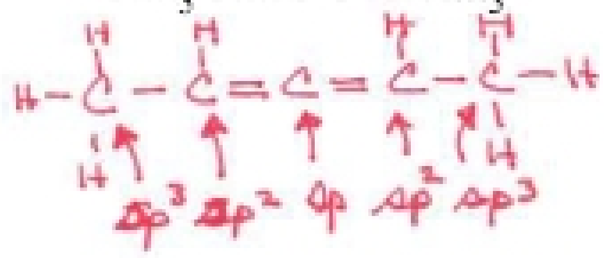
Square planar

c). Indicate the type of hybridization that is appropriate for each carbon atom in the molecule

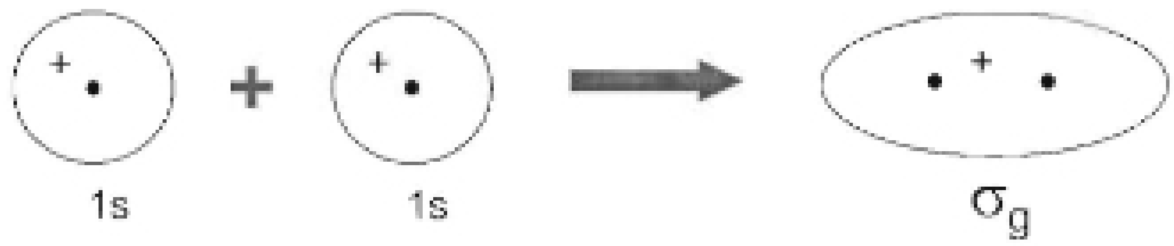
6

2

$CH_3CHCCHCH_3$



2. a). The formation of a σ_g molecular orbital for H_2 may be shown schematically as follows:



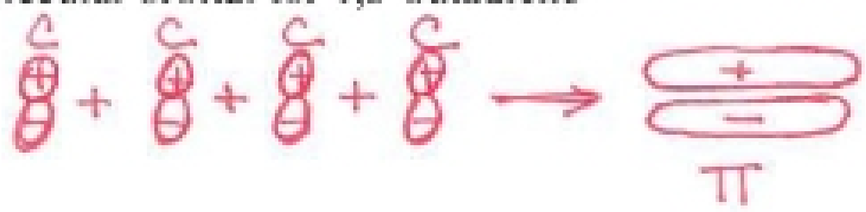
Draw a similar diagram for each of the following:

12 (2+2)

- a σ bonding molecular orbital for CO_2 using carbon and oxygen $2p_Z$ atomic orbitals

- a π antibonding molecular orbital for CO_2

- a π bonding molecular orbital for 1,3-butadiene



b). The bonding in the ally radical ($CH_2{=}CH{-}CH_2\,^\bullet$) may be described in terms of a σ-bond framework, formed from sp^2 hybridized orbitals, connecting each of the carbon atoms, and a delocalized π-bond involving <u>the remaining $2p_z$-electron on each carbon</u>. Set up the secular determinant for the π-orbitals using the Hückel approximation and solve for the energies in terms of α and β integrals.

8

$$\begin{vmatrix} \alpha-E & \beta & 0 \\ \beta & \alpha-E & \beta \\ 0 & \beta & \alpha-E \end{vmatrix} = 0$$

divide by β and let $x = \frac{\alpha-E}{\beta}$

$$\begin{vmatrix} x & 1 & 0 \\ 1 & x & 1 \\ 0 & 1 & x \end{vmatrix} = 0 \Rightarrow x\begin{vmatrix} x & 1 \\ 1 & x \end{vmatrix} - 1\begin{vmatrix} 1 & 1 \\ 0 & x \end{vmatrix} = 0$$

$$x(x^2-1) - x = 0$$

$$x^3 - 2x = x(x^2-2) = 0$$

$$x = 0, \pm\sqrt{2} = \frac{\alpha-E}{\beta}$$

$E_1 = \alpha + \sqrt{2}\beta$

$E_2 = \alpha$

$E_3 = \alpha - \sqrt{2}\beta$