LECTURE 24/36 = $\frac{2}{3}$ NOV-4-02

TRIATOMIC MOLECULES
POLYATOMIC MOLECULES
SPECTROSCOPY

READ: TODAY'S LEC GRAY CH4 P 126-144

NEXT LEC GRAY CH 5 P148-156

PS 4 MORE PROBLEMS

P7.- USE MOLECULAR-ORBITAL THEORY TO EXPLAIN WHY THE DISSOCIATION ENERGY OF N_2 IS GREATER THAN THAT OF N_2^+, BUT THE DISSOCIATION ENERGY OF O_2^+ IS GREATER THAN THAT OF O_2

P8.- PREDICT THE RELATIVE STABILITIES OF THE SPECIES N_2, N_2^+, AND N_2^-.

P9.- FOR A LINEAR XY_2 MOLECULE, DRAW A SCHEMATIC REPRENTATION OF THE $1\pi_u$, $2\pi_u$, AND $1\pi_g$ ORBITALS

P10.- EXPLAIN WHY THE DOUBLY DEGENERATE $1\pi_u$ ORBITALS FOR A LINEAR XY_2 MOLECULE DO NOT REMAIN DEGENERATE WHEN THE MOLECULE IS BENT

TRIATOMIC MOLECULES

LINEAR CO_2 N_2O OCS, NO_2^{2+}

BENT NO_2, O_3, NF_2, NO_2^-

WE LOCALIZE ORBITAL FOR THE σ BONDS AND DELOCALIZED FOR THE π BONDS

LINER

HYBRIDIZE S P_z FOR THE CENTRAL ATOM

FOR THE OUTER ATOMS JUST CONSIDER THE P ORBITALS. AND USE P_z FOR σ BONDING WITH AN SP HYBRID.

THE 2σ BONDS ARE FILLED WITH 2 PAIR OF ELECTRONS

NOW WE USE THE P_x AND P_y ORBITALS OF THE 3 ATOMS TO MAKE UP DELOCALIZED MO.

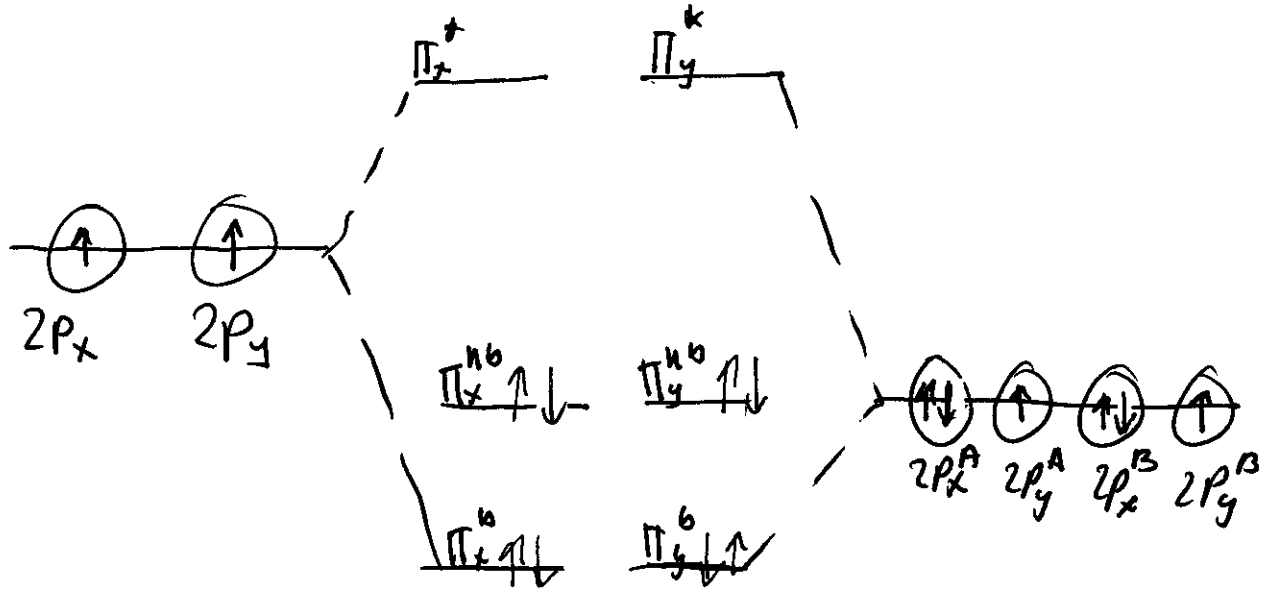
$$\psi_1 = C_1 p_x^A + C_2 p_x^B + C_3 p_x^C \quad \text{BONDING}$$

$$\psi_2 = C_4 p_x^A - C_5 p_x^B + C_6 p_x^C \quad \text{ANTI BONDING}$$

$$\psi_3 = C_7 p_x^A - C_8 p_x^C \quad \text{NON BONDING}$$

CENTRAL ATOM C

OUTER ATOMS O



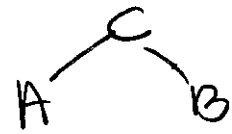
TOTAL OF 6 e⁻/atom

2 → 2S

1 → σ

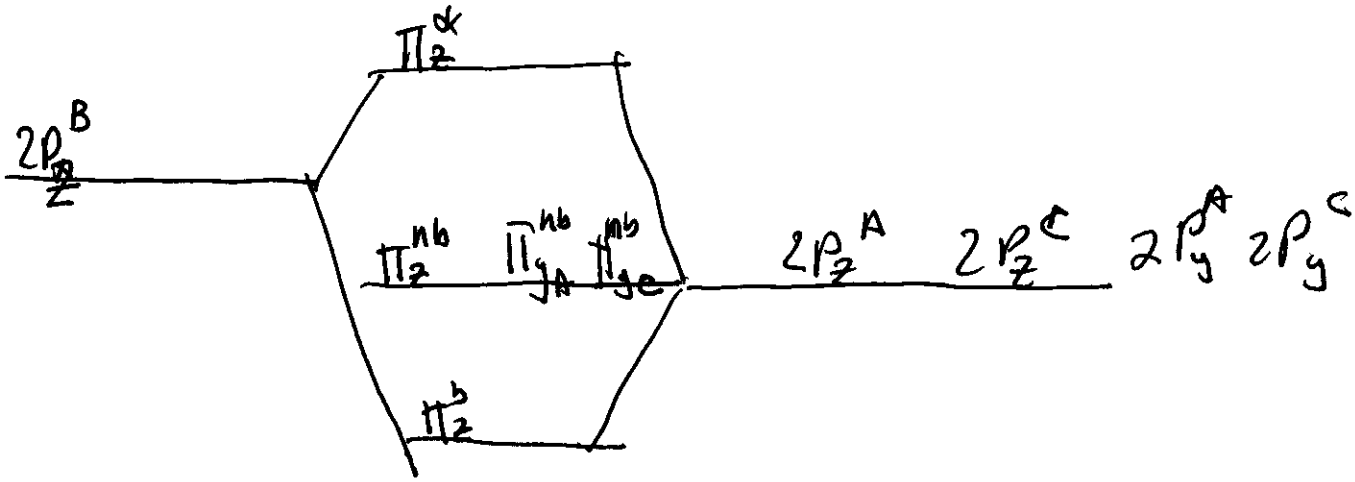
$$BO = \underset{\sigma}{2} + \underset{\pi}{2} = 4$$

BENT MOLECULES



CONSIDER sp^2 $(s\,p_x\,p_y)$ FOR THE CENTRAL ATOM AND USE TWO FOR BONDING AND THE THIRD FOR A LONE PAIR. FOR THE OUTER ATOMS PUT 2e IN THE 2S(A) ORBTAL AND TAKE ONE THAT POINTS TO THE CENTRAL ATOM, p_z WILL BOND WITH THE p_z OF THE CENTRAL ATOM AND THE OTHER IS A NONBONDING ORBITAL

THE 3 p_z ORBITAL CAN BE COMBINED INTO BONDING, NONBONDING AND ANTIBONDING π ORBITALS



B ATOM $\boxed{2s^2 \quad 2p_x^1 \quad 2p_y^1}$ $2p_z^1$

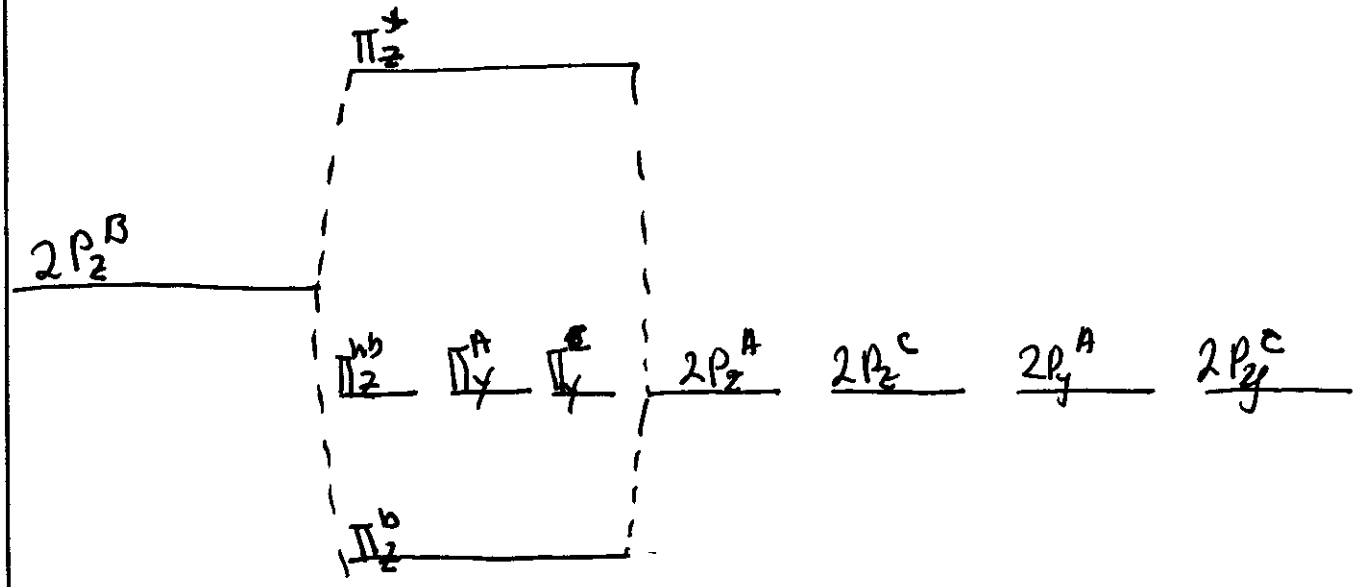
3 sp^2

4. σ sp^2 $2p_z^1$

A AND B ATOMS $(2s)^2$ $2p_x^1$ $2p_y^1$ $2p_z^1$

ONE $sp^2 + 2p_x^1$

σ $2p_y^1$ $2p_z^1$



THE CENTRAL ATOM ACCOMODATES $2e^-$ (LONE PAIR) ON ONE sp^2 AND $2e^-$ ON THE OTHER 2 sp^2 FOR BONDING. THE OUTER ATOMS CAN ACCOMODATE $4e^-$ ON THE LOCALIZED 2S AO AND $2e^-$ ON THE sp^2 BONDING ORBITALS. THE REST OF THE e^- ARE PLACED ON π ORBITALS. THUS THE CENTRAL ATOM NEEDS AT LEAST $5e^-$ FOR π BONDING AND THE OUTER ATOM $4e^-$.

C $2s^2$ $2p^2$

N $2s^2$ $2p^3$

O $2s^2$ $2p^4$

CO_2 $16e^-$

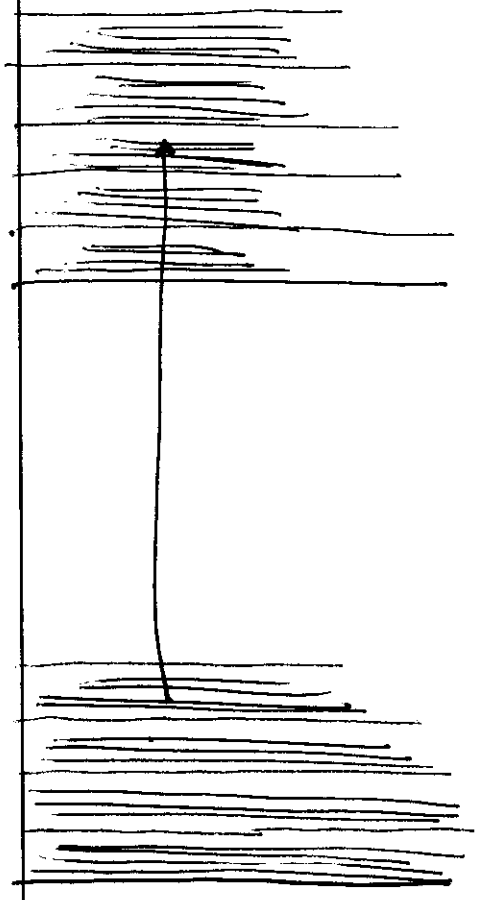
NO_2 $17e^-$

O_3 $18e^-$

FOR TRIATOMIC NON HYDRIDES: $16e^-$ → LINEAR
$(17-20)e^-$ → BENT

MOLECULAR SPECTROSCOPY

$$E_{TOTAL} = E_{elec} + E_{vib} + E_{rot}$$



FIRST (electronic) EXCITE STATE

GROUND STATE

UV-vis → ELECTRONIC TRANSITIONS

Infra Red - IR → Vibrational Trans

MICRO WAVE → ROTATIONAL