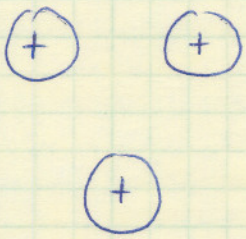
ADVANCED CHEMISTRY

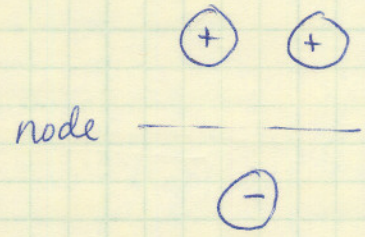
INORGANIC CHEMISTRY - WINTER - WEEK 9

Chapter 5

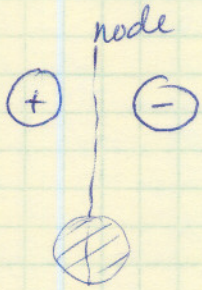
(13)



group orbital ①



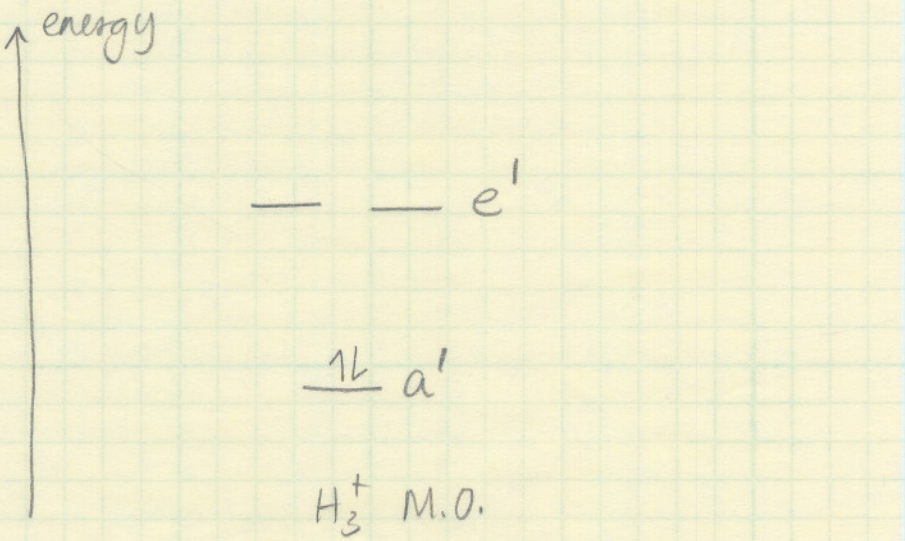
group orbital ②



group orbital ③

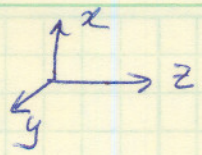
D_{3h} point group

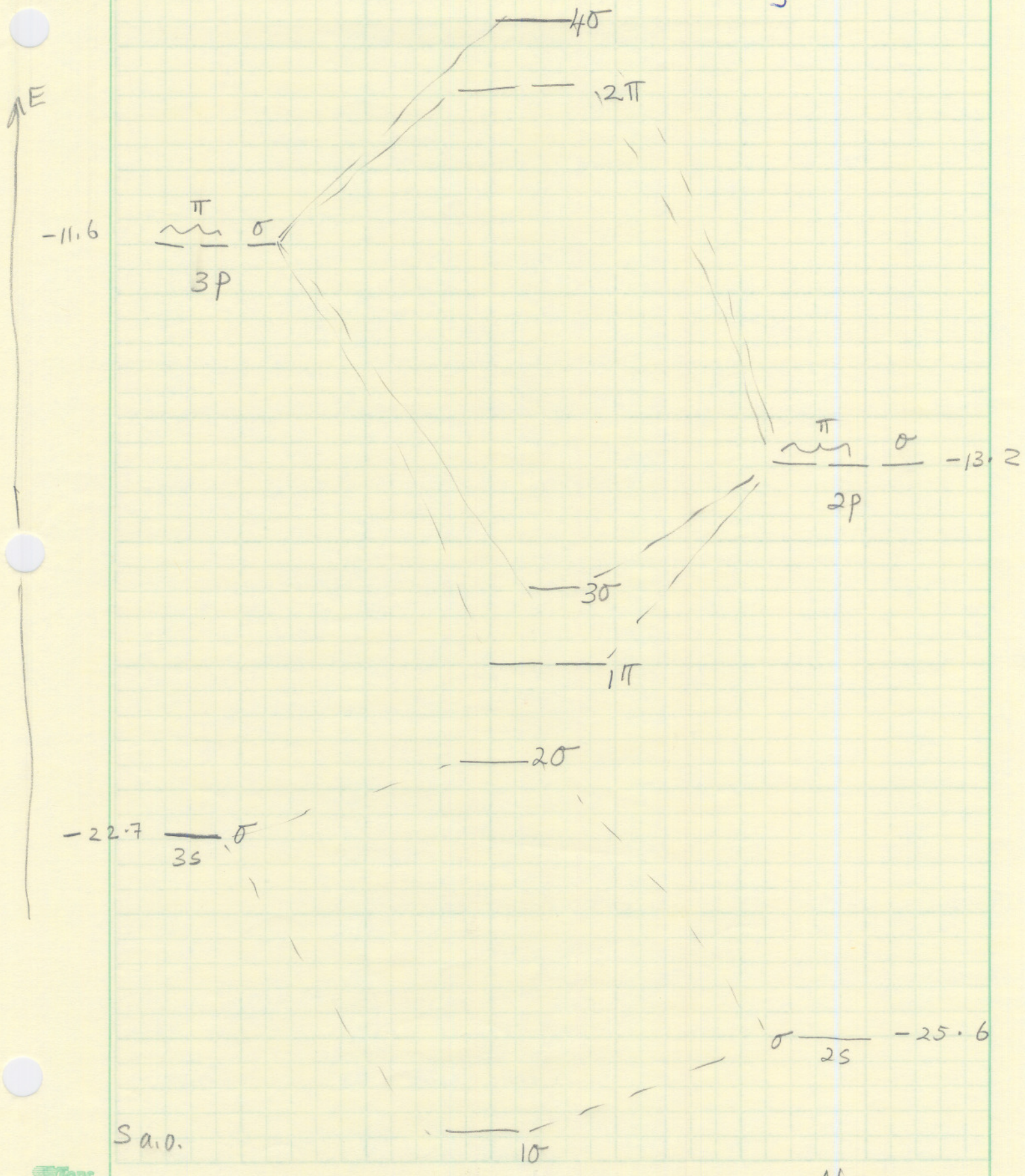
D_{3h}	E	$2C_3$	$3C_2$	σ_h	$2S_3$	$3\sigma_v$	
group ①	1	1	1	1	1	1	a_1'
② and ③	2			2		0	e'

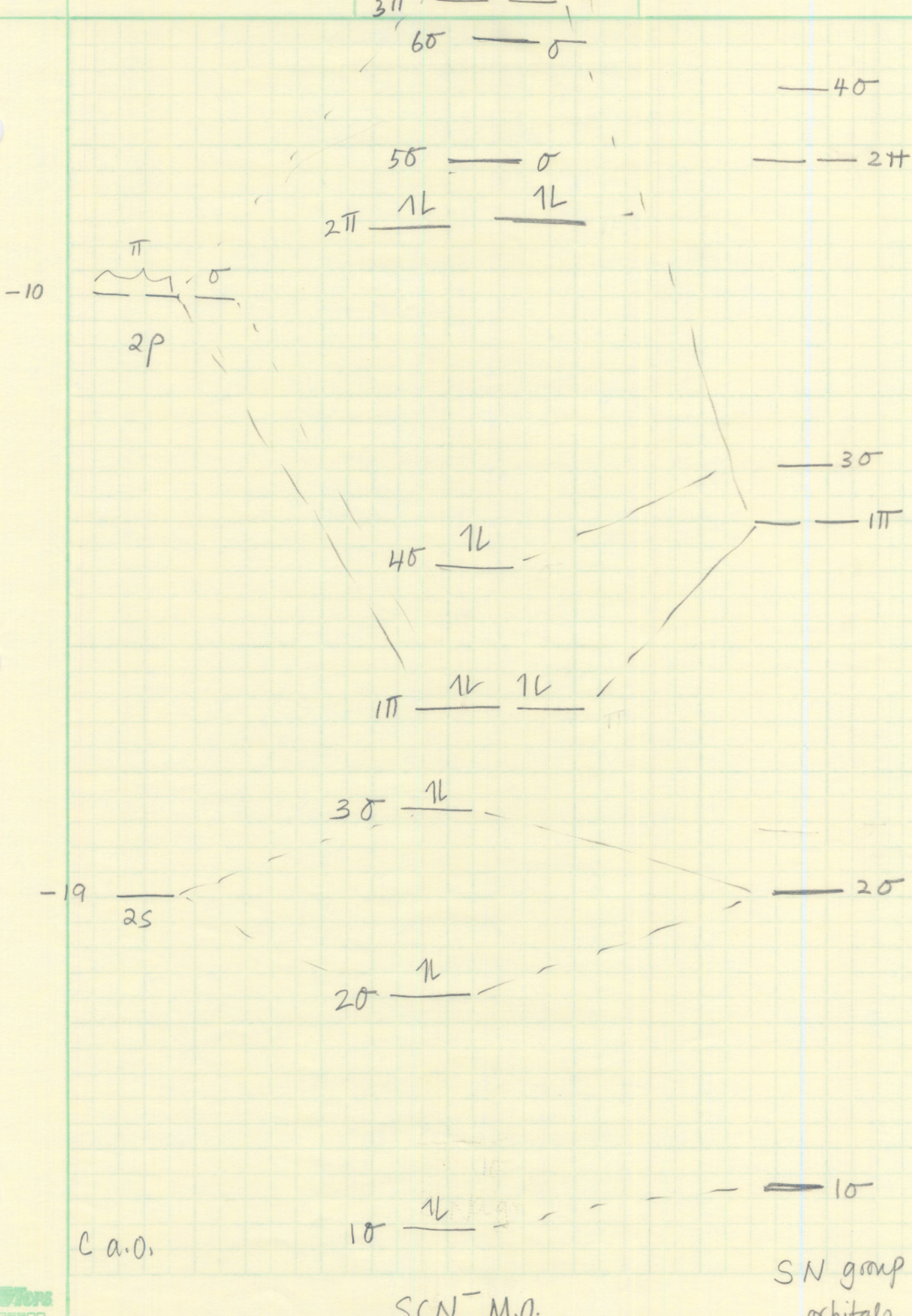


H_3^+ M.O.

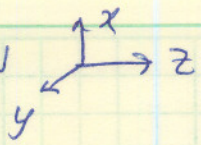
(15) SCN^- $C_{\infty v}$ point group S–C–N

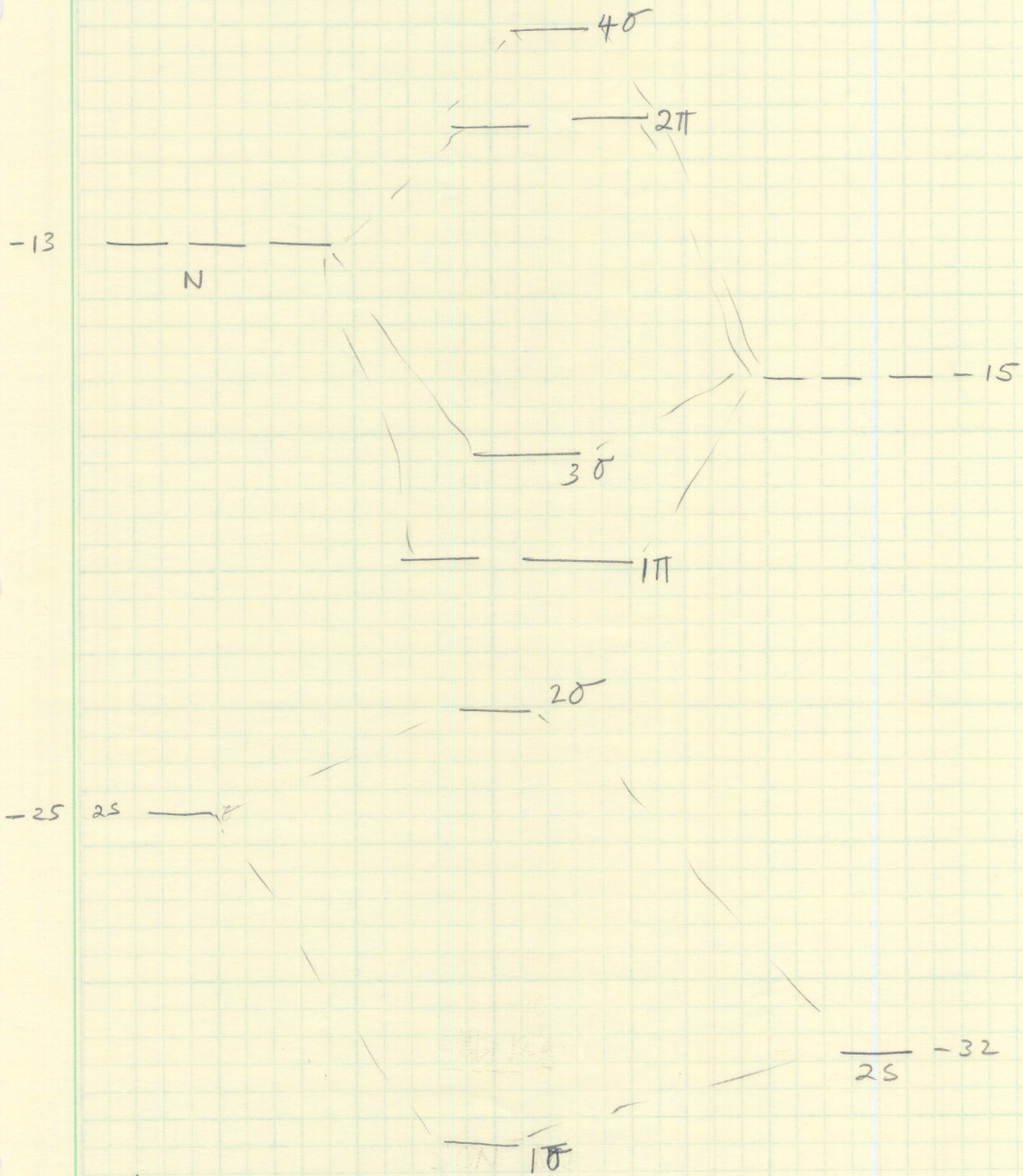




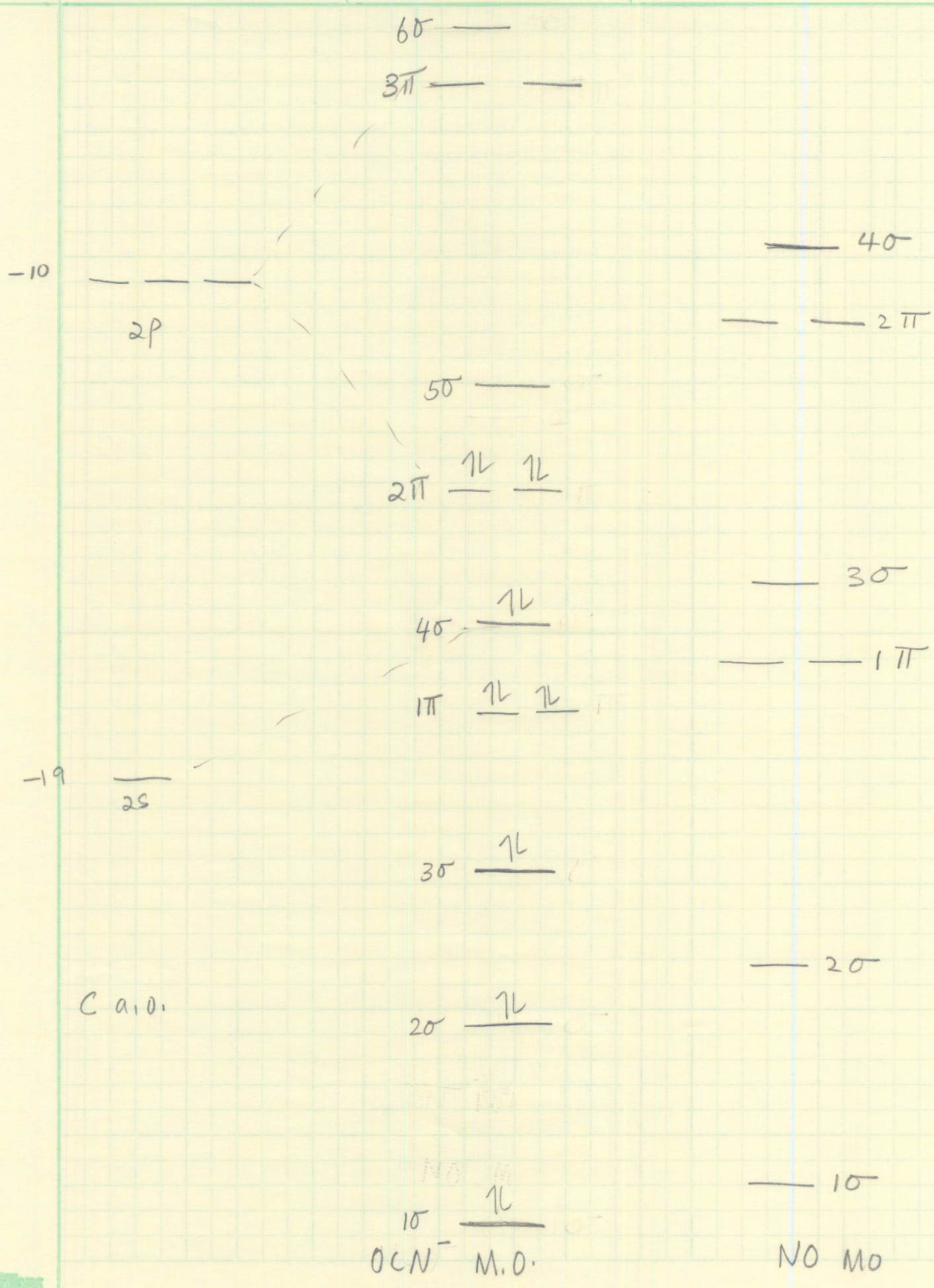

3π
6σ
σ
4σ
5σ
σ
2π
1L
1L
2π
π
σ
-10
2p
3σ
1π
4σ
1L
1π
1L
1L
3σ
1L
-19
2s
2σ
2σ
1L
1σ
1σ
1L
C a.O.
SCN⁻ M.O.
SN group orbitals

OCN^- $C_{\infty v}$ point group

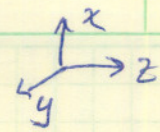


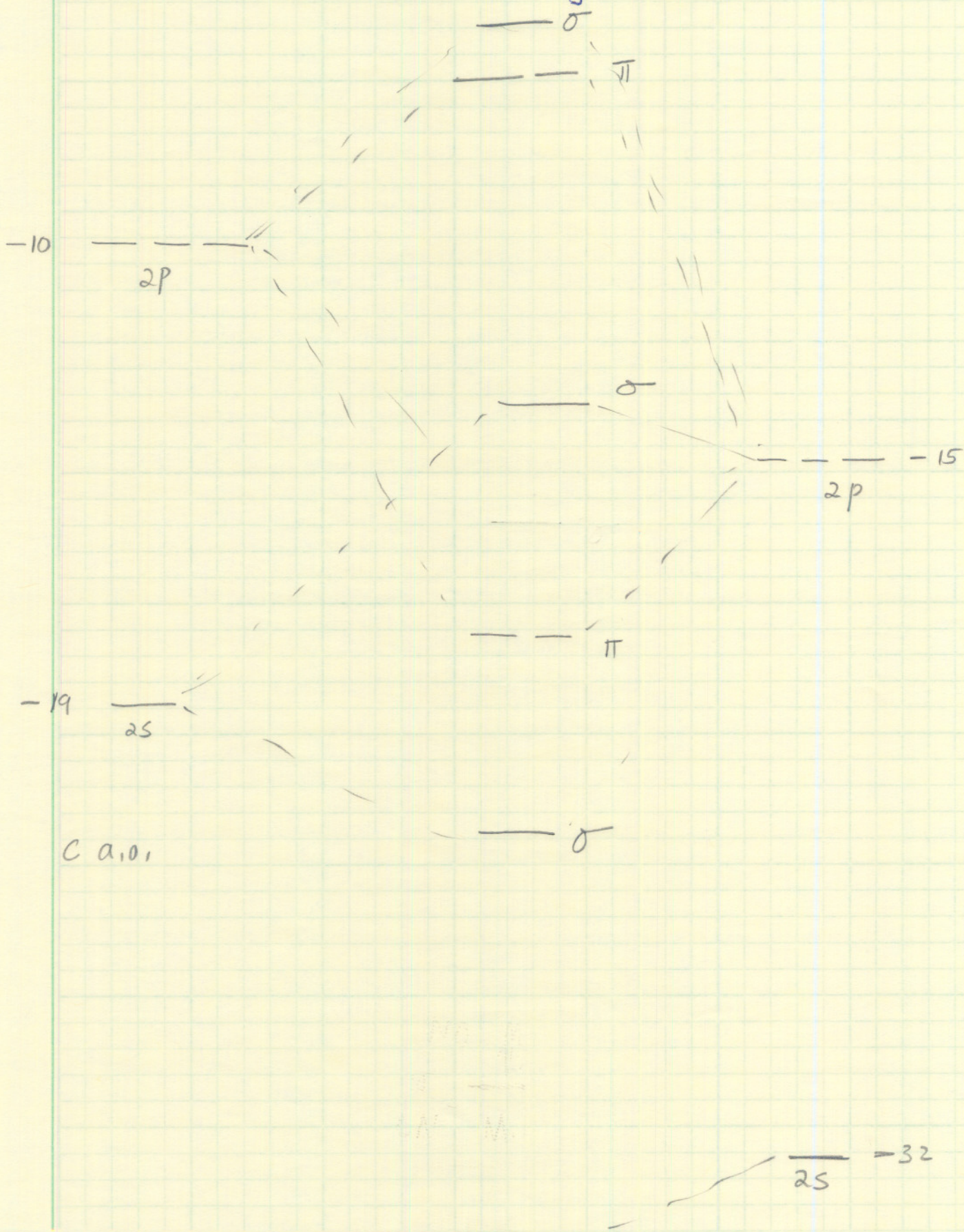


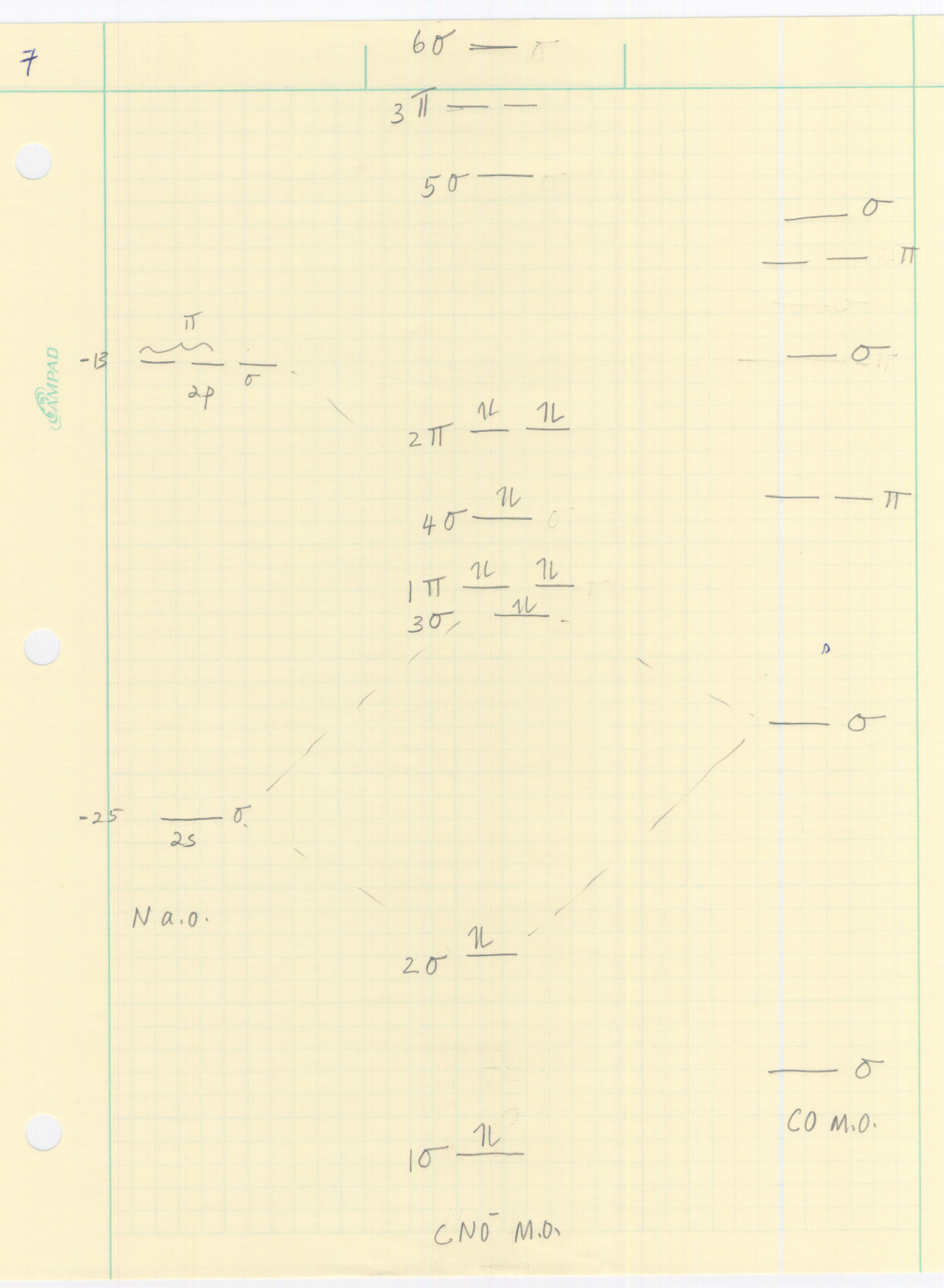
Na.O


6σ
3π
4σ
−10
2p
2π
5σ
2π
3σ
4σ
1π
1π
−19
2s
3σ
2σ
Ca.O.
2σ
1σ
1σ
OCN⁻ M.O.
NO MO

CNO^- $C_{\infty v}$ point group






6σ
3π
5σ
σ
π
π
σ
-13
2p
σ
2π
4σ
1π
3σ
σ
-25
2s
σ
Na.O.
2σ
σ
CO M.O.
1σ
CNO⁻ M.O.

In all three ions, the HOMO is a π orbital and the LUMO is a σ orbital.

(18) (a) $[\bar{I}\underline{N}-\bar{S}=\bar{O}I]^-$ $\longleftrightarrow$ $[I\bar{N}=\bar{S}-\underline{\bar{O}}I]^-$

$-2 \quad +1 \quad 0$ ← formal charges → $-1 \quad +1 \quad -1$

Preferred

$[I\bar{S}=\bar{N}-\underline{\bar{O}}I]^-$ $\longleftrightarrow$ $[\underline{I\bar{S}}-\bar{N}=\bar{O}I]^-$

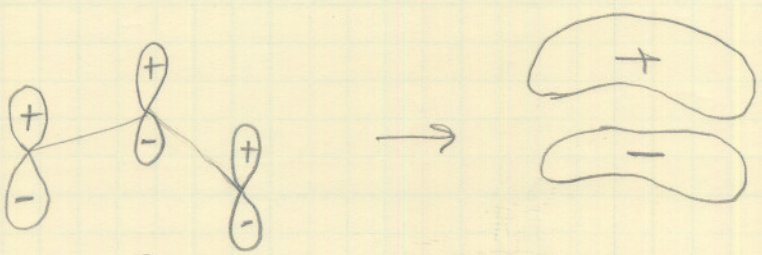
$0 \quad 0 \quad -1$ ← formal charges → $-1 \quad 0 \quad 0$

preffered

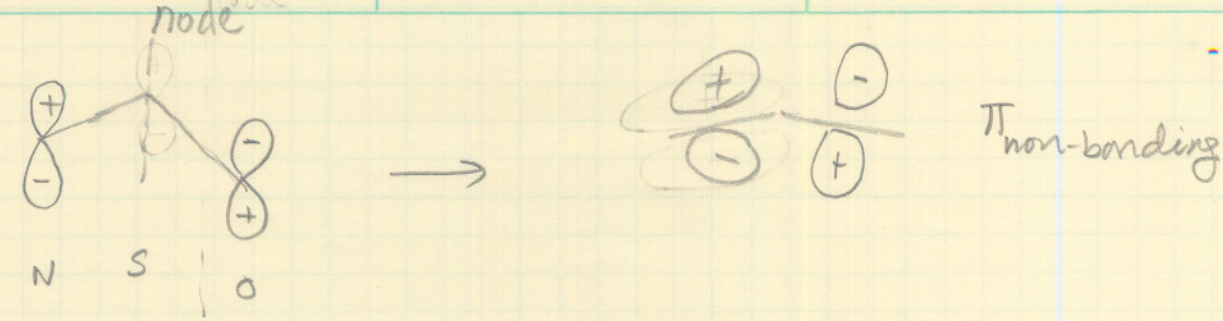
Based on the formal charges alone, SNO^- is the more stable ion.

In both ions S is double bonded to N (in the preferred structure based on formal charges)

(b) In forming the π bonds, the ~~2~~ valence p orbitals of the three atoms are involved.



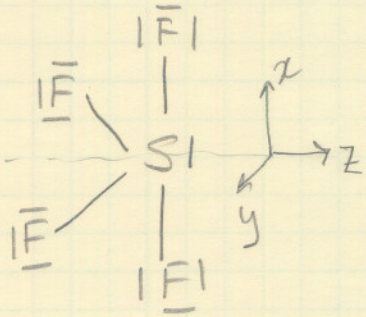
N S O



NSO^- will be similar.

(c) Since SNO^- is the more stable, it is reasonable to expect its bonds to be stronger (shorter bonds and higher vibrational frequency).

(19)



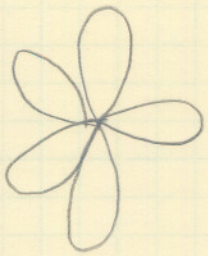
See-saw structure.

S has 5 electron pairs around it (one of them is a lone pair)

sp^3d hybridization to get 5 hybrid orbitals.

C_{2v} point group

Valence orbitals of S	symmetry in C_{2v} point grp
3s	a_1
$2p_z$	a_1
$3p_x$, ~~$3p_y$~~	b_1
$3p_y$	b_2
$3d_{z^2}$	a_1
$3d_{xy}$	a_2
$3d_{xz}$	b_1
$3d_{yz}$	b_2



C_{2v}	E	C_2	$\sigma_v(xz)$	$\sigma_v(yz)$
Γ_{sp^3d}	5	1	3	3

# of times A_1 is in $\Gamma = \frac{1}{4}[1+5+3+3] = 3$

# of times A_2 is in $\Gamma = \frac{1}{4}[5+1-3-3] = 0$

# of times B_1 is in $\Gamma = \frac{1}{4}[5-1+3-3] = 1$

# of times B_2 is in $\Gamma = \frac{1}{4}[5-1-3+3] = 1$

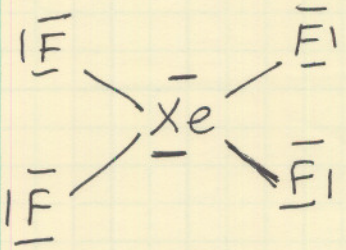
$$\Gamma = 3a_1 + b_1 + b_2$$

Orbitals involved in hybridization

$3s,\ 3p_x,\ 3p_y,\ 3p_z,\ 3d_{z^2}$

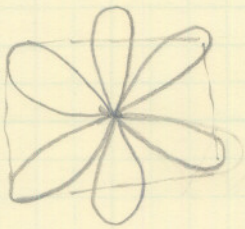
sp^3d hybridization

(21) square planar molecule D_{4h} point group.



The central atom has 6 electron pairs around it.

sp^3d^2 hybridization



D_{4h}	E	$2C_4$	C_2	$2C_2'$	$2C_2''$	i	$2S_4$	σ_h	$2\sigma_v$	$2\sigma_d$
$\Gamma_{sp^3d^2}$	6	2	2	2	0	0	0	4	4	2

# of times A_{1g} is in Γ $\} = \frac{1}{16}[6+4+2+4+4+8+4] = 2$

# of times B_{1g} is in Γ $\} = \frac{1}{16}[6-4+2+4+4+8-4] = 1$

# of times A_{2u} is in Γ $\} = \frac{1}{16}[6+4+2-4-4+8+4] = 1$

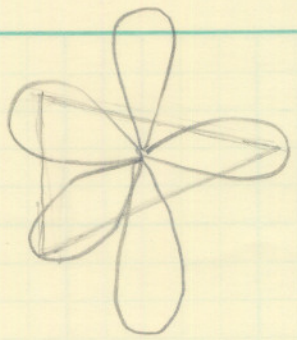
# of times E_u is in Γ $\} = \frac{1}{16}[12-4+8] = 1$

$$\Gamma_{sp^3d^2} = 2a_{1g} + b_{1g} + a_{2u} + e_u$$

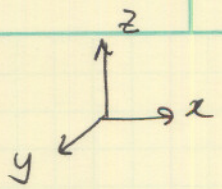
Valence orbitals of Xe	symmetry
5 S	a_{1g}
5 P_z	a_{2u}
5 P_x, 5 P_y	e_u
4 d_{z^2}	a_{1g}
4 $d_{x^2-y^2}$	b_{1g}
4 d_{xy}	b_{2g}
4 d_{xz}, 4 d_{yz}	e_g

sp^3d^2 hybridization

(22) (a)



D_{3h}



sp^3d hybridization

D_{3h}	E	$2C_3$	$3C_2$	σ_h	$2S_3$	$3\sigma_v$
Γ_{sp^3d}	5	2	1	3	0	3

# of times A_1' is in Γ $= \frac{1}{12}[5+4+3+3+9] = 2$

# of times e' is in Γ $= \frac{1}{12}[10-4+6] = 1$

# of times a_2'' is in Γ $= \frac{1}{12}[5+4-3-3+9] = 1$

$$\Gamma_{sp^3d} = 2a_1' + e' + a_2''$$

atomic orbitals of P	their symmetry
3s	a_1'
$3p_z$	a_2''
$3p_x, 3p_y$	e'
$3d_{z^2}$	a_1'
$3d_{x^2-y^2}, 3d_{xy}$	e''
$3d_{xz}, 3d_{yz}$	e''

involved in sp^3d hybridization.

(b) The 3s and $3p_x$, $3p_y$ orbitals bond with equitorial atoms.

$3p_z$ and $3d_{z^2}$ (along the z axis) bond with the axial atoms.

(c) The d_{z^2} orbital extends longer in space than any of the other orbitals involved in this hybridization model. Since d_{z^2} is binding to the axial atoms, the axial bonds are longer than equitorial bonds.
