2005년도 무기화학1 기말고사 (2005년 6월 17일)

- 시험시간 7:00PM-10:00 PM
- 학생들 사이의 계산기 교환은 허락하지 않음.
- 휴대전화의 전원은 무조건 끌 것. 감독관의 눈에 전화기가 보이면 이유여하를 막론하고 부정행위로 간주 함.
- 여러 가지 상수는 시험지의 끝 부분에 있음.

1. 다음표의 빈칸을 채우시오. (표를 반드시 그릴 것)

원자번호	원소 기호	이름	족 (Family)	주기 (Period)
4				
	In			
		Xenon		
76				
	Lr			
		Hassium		

2. 다음의 빈칸을 채워라.

(a) For N atoms, there are 3N total motions, known as [세단어].

(b) [두단어], the mathematical treatment of the properties of groups, can be used to determine the molecular orbitals, vibrations, and other properties of the molecules.

(c) [한단어] compounds are attracted by an external magnetic field. This attraction is a consequence of one or more [한단어] electrons behaving as tiny magnets. [한단어] compounds, on the other hand, have no [한단어] electrons and are repelled slightly by magnetic fields.

(d) The [두단어], which states that orbitals of the same symmetry interact so that their energies never cross.

(e) A [세단어] (S_n) requires rotation of 360°/n, followed by reflection through a plane perpendicular to the axis of rotation.

(f) The ability of chiral molecules to rotate plane-polarized light is termed [두단어] and may be measured experimentally.

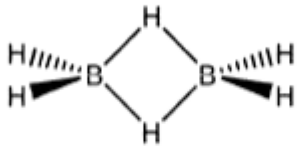
(g) One of the principles of quantum mechanics is that any energy calculated will be equal to or [한단어] than the true energy, so we can be confident that the energy calculated is not [한단어] the true value.

3. 다음 분자 또는 모형의 point group은?

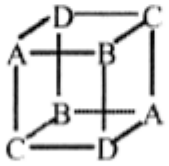
(a) whiffle ball

whiffle ball은 플라스틱으로 만들어져 있다. 공의 표면에 있는 글씨나 그림은 모두 무시하고 생각하라.

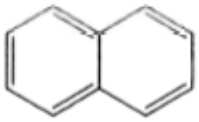
(b) diborane



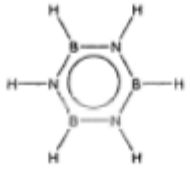
(c)



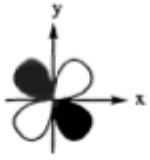
(d) naphtalene (답을 5점을 주고 살 수 있다.)



(e) borazine (planar)

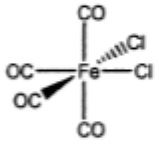


(f) d_{xy}

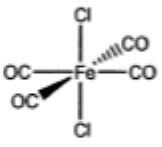


4. 다음 착물들을 생각하여 보자.

a. *cis*-$Fe(CO)_4Cl_2$



b. *trans*-$Fe(CO)_4Cl_2$

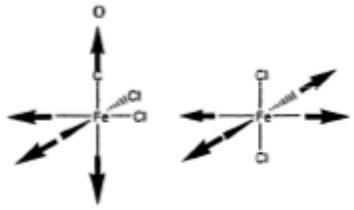


위의 착물들에서 Raman-active한 υ(C-O) stretching vibrational mode들을 찾아 보려고 한다.

(a) a, b 의 point group은? (각 5점을 주고 답을 살수 있다. 틀리면 뒤의 문제들은 무조건 0점)

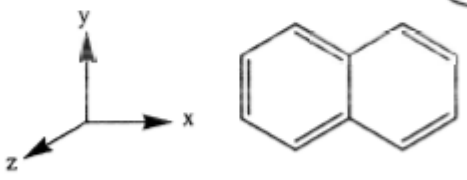
(b) 각 υ(C-O) stretching mode를 하나의 vector로 표시하고 이 때 이들의 reducible representation (Γ_a, Γ_b)을 구하라.

Γ_a Γ_b



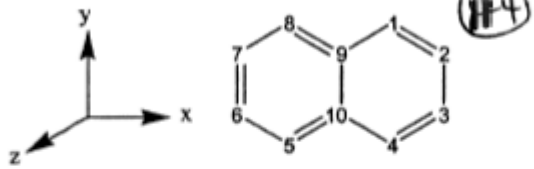
(c) (b)의 Γ_a, Γ_b 를 irreducible representation 들의 합으로 표시하라.
(d) a, b의 υ(C-O) stretching vibrational mode 들 중에서 Raman-active 한 mode들은 (symmetry types)?
(e) (d)의 Raman-active 한 mode들에 대하여 어떠한 stretching mode들인지 그림으로 표시하라.

5. 문제 3(d)가 틀리면 이번 문제는 무조건 0점. (58)



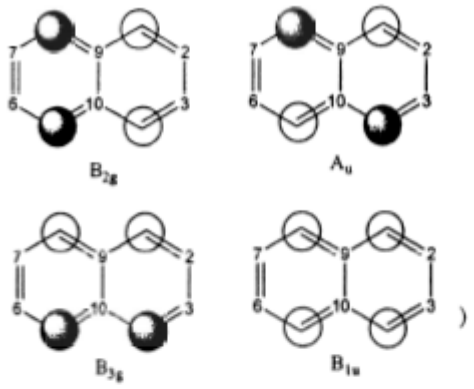
(a) Naphtalene ($C_{10}H_8$)의 3N total motion들에 대한 reducible representation (Γ)은?
(b) (a)의 Γ를 irreducible representation의 합으로 표시하라.
(c) (b)의 irreducible representation을 translational, rotational, vibrational mode 들로 분류하라.
(d) (c)의 vibrational mode 들 중에서 IR-active 한 mode들은?

6. Naphthalene의 π-bonding system (bonding, antibonding, nonbonding) 은 10개의 탄소(C) p_z orbital 들을 사용하여 건설할 수 있다. 이제 그 모양을 알아보려 한다. (문제 3(d)가 틀리면 이번 문제는 무조건 0점.) (44)

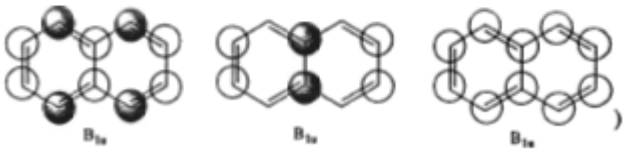


(a) naphtalene의 ^{13}C NMR 스펙트럼을 얻으면 몇 개의 ^{13}C peak가 나오는가? (즉, C에 대하여 몇 종류의 equivalent atom들이 있는 가를 물어보는 문제)
(b) (a)의 각 equivalent atom들을 그룹으로 나누어라. (답의 예: A{1,4,5,8}, B{...}, C{...}, D{..}, E{..})
(c) (b)의 각 그룹에 대하여 reducible representation (Γ_A, Γ_B, ..) 을 구하라.
(답의 예: Γ_A= 4 0 0 0 0 -4 0 0)
(d) (c)의 각 reducible representation을 irreducible representation의 합으로 표시하라.
(답의 예: $\Gamma_A = B_{2g} + B_{3g} + A_u + B_{1u}$)
(e) (d)의 irreducible representation의 symmetry type을 참고로 하여 SALC (group orbital) 의 그림을 그려라.

(답의 예: A(1, 4, 5, 8)



(f) (e)의 SALC들을 바탕으로 하여 naphthalene의 π-bonding system의 10개의 molecular orbitals 들을 그려라.
(답의 예: 3개의 B_{1u} orbital들



7. 주어진 symmetry adapted orbital 그림을 바탕으로 NH_3 의 MO를 건설하여보자. (84)

(a) 3개의 수소 1s orbital로 만들어지는 SALC (group orbital)을 그려라. (symmetry type도 쓸 것)
(b) 질소 원자의 2s와 2p orbital들의 symmetry type은?
(c) (a)와 (b)를 바탕으로 NH_3의 MO의 예상되는 모양을 그려라.
(d) (c)의 MO의 에너지 준위 그림을 그려라.
(e) NH_3의 ground state 와 first excited state의 electron configuration을 써라.

8. PCl_5는 D_{3h}의 point group에 속한다. P와 Cl 사이에 형성되는 σ-결합에 사용되는 P의 hybride orbital을 결정하여라 (30)

9. (보너스) 이번 학기 강의에서 좋은점, 나쁜점에 대하여 쓰고 다음 학기 강의에서 바라는 점에 대해서 써라. (10줄 이상 쓸 것) (30)

2005년 무기화학 I 기말고사 정답

1

2×24 = 48.

원자번호	원소기호	이름	족	주기
4	Be	Beryllium	2 (IIA)	2
49	In	Indium	13 (IIIA)	5
54	Xe	Xenon	18 (VIIIA)	5
76	Os	Osmium	8 (VIIIB)	6
103	Lr	Lawrencium	Actinide (악티늄)	7
108	Hs	Hassium	8 (VIIIB)	7

2 96

(a) degree of freedom 3×2

(b) Group theory 2×2

(c) Paramagnetic, unpaired, diamagnetic, unpaired 4×2

(d) noncrossing rule 2×2

(e) rotation reflection operation 3×2

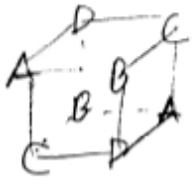
(f) optical activity (optically active) 2×2

(g) greater, below 2×2

3 (20)

(a) wiffle ball C_{8v} 5

(b) diborane D_{2h} 5

(c) 

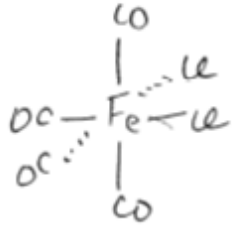
C_i 5

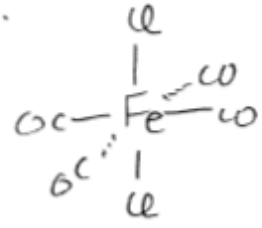
(d) naphthalene D_{2h} 5

(e) borazine D_{3h} 5

(f) dxy D_{2h} 5

4 (107)

a. 

b. 

(a) a. C_{2v} 5 b. D_{4h} 5

(b) a.

C_{2v}	E	C_2	$\sigma_v(xz)$	$\sigma_v'(yz)$	
Γ_a	4	0	2	2	7

b. 7

D_{4h}	E	$2C_4$	C_2	$2C_2'$	$2C_2''$	i	$2S_4$	σ_h	$2\sigma_v$	$2\sigma_d$
original → Γ_b	4	0	0	2	0	0	0	4	2	0
5로 Γ_b' →				(0	2)				(0	2)

나눈 개수로

4 (cont'd)

(c) $\Gamma_a = 2A_1 + B_1 + B_2$ 10

Γ_b =>

D_{4h}	E	$2C_4$	C_2	$2C_2'$	$2C_2''$	i	$2S_4$	σ_h	$2\sigma_v$	$2\sigma_d$	h=16
Γ_b	4	0	0	2	0	0	0	4	2	0	
A_{1g}	1	1	1	1	1	1	1	1	1	1	
$D_{4h}\times\Gamma_b\times A_{1g}$	4	0	0	4	0	0	0	4	4	0	sum 16 → coeff 1
B_{1g}	1	-1	1	1	-1	1	-1	1	1	-1	
$D_{4h}\times\Gamma_b\times B_{1g}$	4	0	0	4	0	0	0	4	4	0	16 → 1
$\Gamma_b - A_{1g} - B_{1g}$	2	0	-2	0	0	-2	0	2	0	0	⇒ E_u

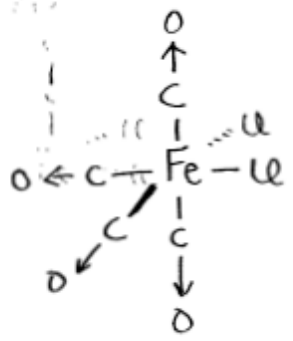
$\therefore \Gamma_b = A_{1g} + B_{1g} + E_u$ 15

$\Gamma_b' = A_{1g} + B_{2g} + E_u$

(d) a. $2A_1, B_1, B_2$ 5

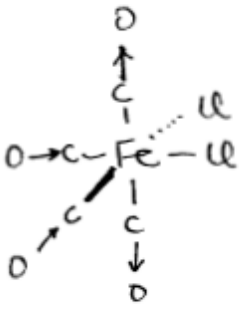
b. A_{1g}, B_{1g} (또는 Γ_b'의 activity) 5
A_{1g}, B_{2g}

(e) a. A_1



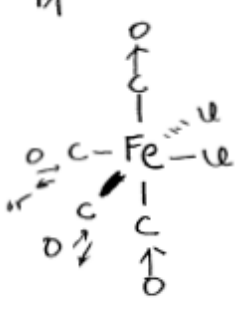
8

A_1



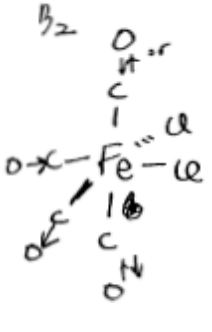
8

B_1



8

B_2

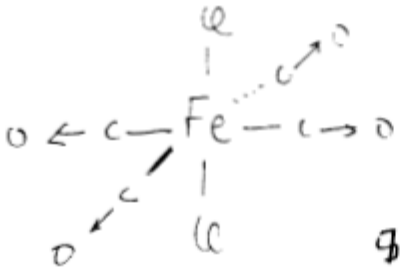


8

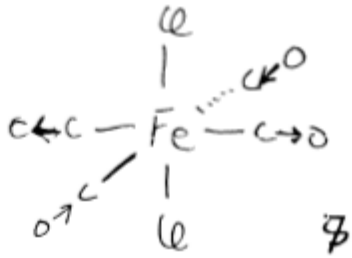
④ (cont'd)

b

A_{1g}

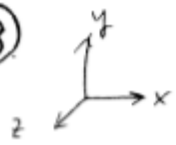


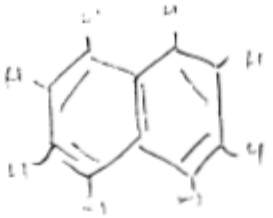
B_{1g}



4

5 (58)





$C_{10}H_8$

(a)

D_{2h}	E	$C_2(z)$	$C_2(y)$	$C_2(x)$	i	$\sigma(xy)$	$\sigma(xz)$	$\sigma(yz)$
Γ	54	0	−2	0	0	18	0	2

10

(b) $\Gamma = 9A_g + 9B_{1g} + 4B_{2g} + 5B_{3g} + 4A_u + 5B_{1u} + 9B_{2u} + 9B_{3u}$

20

(c) $\Gamma_{translation} = B_{1u} + B_{2u} + B_{3u}$ 6

$\Gamma_{rotation} = B_{1g} + B_{2g} + B_{3g}$ 4

$\Gamma_{vibration} = 9A_g + 8B_{1g} + 3B_{2g} + 4B_{3g} + 4A_u + 4B_{1u} + 8B_{2u} + 8B_{3u}$

(d) IR-active vibrational modes

$4B_{1u}, 8B_{2u} + 8B_{3u}$ 6

10

(5)

6 (14)

(a) 3>H 10

(b) A {1, 4, 5, 8}

B {2, 3, 7, 6}) 5

C {9, 10}

(c)

D_{2h}	E	$C_2(x)$	$C_2(y)$	$C_2(z)$	i	$\sigma(xy)$	$\sigma(xz)$	$\sigma(yz)$	
Γ_A	4	0	0	0	0	-4	0	0	
Γ_B	4	0	0	0	0	-4	0	0	7
Γ_C	2	0	-2	0	0	-2	0	2	7

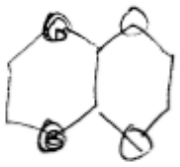
(d) $\Gamma_A = B_{2g} + B_{3g} + A_u + B_{1u}$ 10 . 9.5

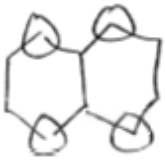
$\Gamma_B = B_{2g} + B_{3g} + A_u + B_{1u}$ 10 .

$\Gamma_C = B_{3g} + B_{1u}$ 10

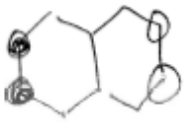
6 (cont'd)

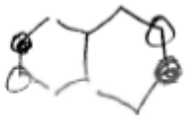
(e) * A{ 4, 5, 8 }

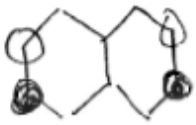
B_{2g}  A_u 

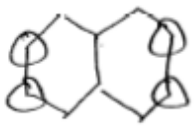
B_{3g}  B_{1u} 

* B{ 2, 3, 7, 6 }

B_{2g}  5

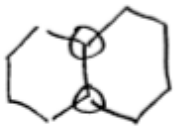
A_u  5

B_{3g}  5

B_{1u}  5

* C{ 9, 10 }

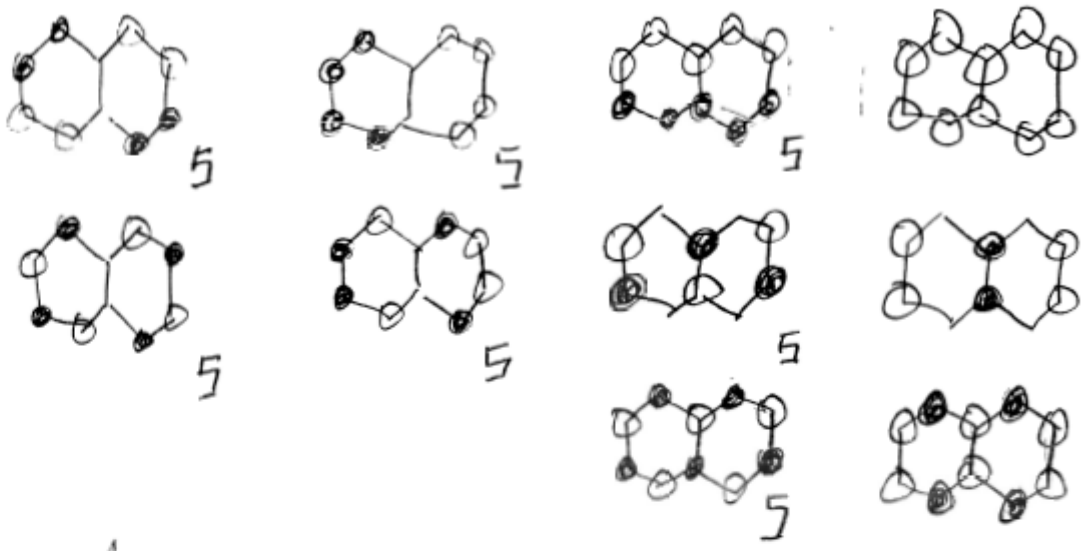
B_{3g}  5

B_{1u}  5

15

6 (cont'd)

(f)



A_u B_{2g} B_{3g} B_{1u}

7 (30) NH_3, C_{3v}

(a)

A_1 5 E 5

(b) N 2s  A_1 5

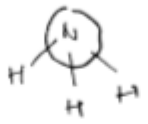
N $2p_z$: A_1 5

N $2p_x, 2p_y$ E 5

13

7 (cont'd)

(c) $1a_1$



$2a_1$

5 서로의 ok 모양 5

$3a_1$

5

$1e$

5

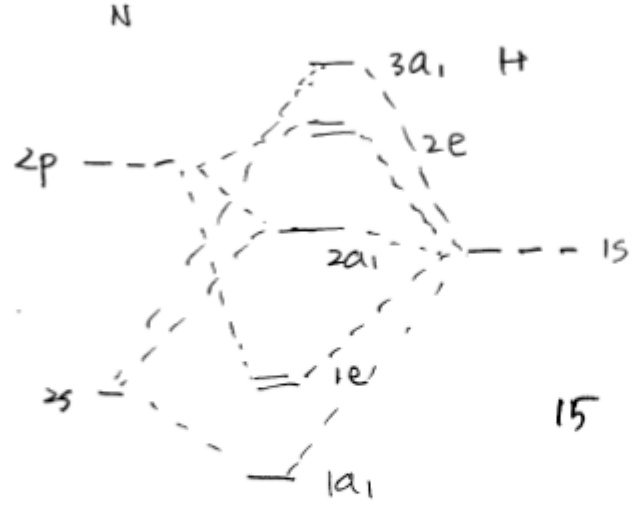
5

$2e$

5

5

(d)



15

(e)

$(1a_1)^2(1e)^4(2a_1)^2$

ground state

7

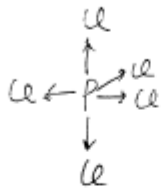
$(1a_1)^2(1e)^4(2a_1)^1(2e)^1$

1st excited state

7

8 (30)

PCl_5 D_{3h}



D_{3h}	E	$2C_3$	$3C_2$	σ_h	$2S_3$	$3\sigma_v$	
Γ	5	2	1	3	0	3	10

$\Gamma = 2A' + E' + A_2''$ 10

A' → s, d_{z^2}

E' → (p_x, p_y) or $(d_{x^2-y^2}, d_{xy})$ 10

A_2'' → p_z

$\therefore$ dsp^3 or d^3sp