무기화학1 기말고사 2001. 무기1 기말

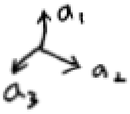
1. 다음 분자 또는 모형의 point group을 써라. (15점)

(a) cyclohexane (chair) (b) cyclohexane (boat) (c) 경북대학교 Mark

2. [illegible]Cl_{10}의 point group은 D_{2h} 이다. 분자 구조를 예측해 보아라. (10점)

3. 혼성오비탈(hybrid)의 형성을 Group Theory로 예측할 수 있다. 다음은 BCl_3에서 Boron(B) 원자에 hybrid가 형성되는 과정이다. (30점)

(a) BCl_3의 point group을 써라.



(b) 옆의 그림은 trigonal planar bond를 나타내는 세 벡타의 세트 (a set of three vectors)이다. 위 벡타 세트는 BCl_3의 point group의 reducible representation를 만드는 basis로 사용될 수 있다. 위 벡타 세트에 대한 BCl_3의 point group의 symmetry operation을 matrix 형태로 적어라.

$$E\begin{pmatrix}a_1\\a_2\\a_3\end{pmatrix}=\begin{pmatrix}1&0&0\\0&1&0\\0&0&1\end{pmatrix}\begin{pmatrix}a_1\\a_2\\a_3\end{pmatrix}=\begin{pmatrix}a_1\\a_2\\a_3\end{pmatrix}$$

(c) 각 operation에 대한 character를 적어라.

(e) (c)의 character 값들을 갖는 reducible representation을 Γ_1 이라고 하자. Γ_1은 어떠한 irreducible representation (symmetry type) 들의 합으로 이루어져 있는가?

(f) (e)에서 얻은 각 irreducible representation에 속하는 Boron의 원자오비탈들을 적어라.

(g) 따라서 reducible representation (Γ_1) 속하는 Boron의 원자오비탈들은 어떤 것들일까?

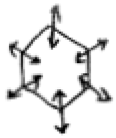
(h) (g)로부터 어떠한 hybrid가 형성되었을까 예측해 보아라.

4. 기체 상태의 Benzene의 vibrational spectroscopy 실험을 하면 ring-breathing mode가 992cm^{-1} 정도의 진동 에너지를 가지고 있음을 알 수 있다. 다음은 ring-breathing mode를 그림으로 나타낸 것이다. (20점)

(a) Benzene 의 point group은?

(b) ring-breathing mode에 대한 symmetry type을 결정하여라.

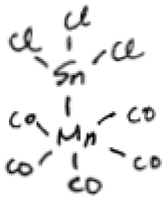
(c) 위의 vibrational spectroscopy는 Raman 이었을까? IR 이었을까?



5. (a) 수산화나트륨(NaOH) 용액 40.0 mL가 0.1M 황산(H_2SO_4)용액 400 mL로 적정된다. 이 수산화나트륨 용액 20 mL를 적정하는데 염산(HCl) 24mL가 소비되었다. 염산용액의 pH는 얼마인가? (10점)

6. 다음 반응에서 Lewis acid와 base를 지적하여라. (10점)

(a) $BF_3 + NH_3 \rightarrow F_3B\text{-}NH_3$ (b) $SnCl_3 + Mn(CO)_5 \rightarrow$

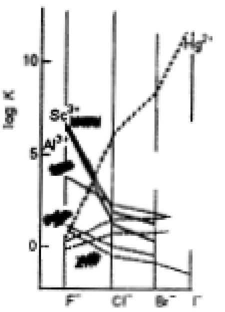


7. 이산화탄소는 물에 녹으면 산으로 작용한다. 그 이유는? (10점)

8. 다음의 Brønsted acid에서 산도(acidity)가 큰 것을 찾고 그 이유를 써라. (15점)

(a) H_2SO_4, $O_2SF(OH)$ (b) H_2SO_4, CF_3SO_3H (c) H_2SO_4, $O_2S(NH_2)OH$

9. 다음 그래프는 금속 양이온과 할로겐 음이온이 착물(complex)를 이룰 때 평형 상수 (K)의 값들을 표시한 것이다. 그림과 같은 경향을 보이는 이유를 써라. (15점)



C_{2v} (2mm)	E	C_2	$\sigma_v(xz)$	$\sigma'_v(yz)$	$h = 4$	
A_1	1	1	1	1	z	x^2, y^2, z^2
A_2	1	1	−1	−1	R_z	xy
B_1	1	−1	1	−1	x, R_y	xz
B_2	1	−1	−1	1	y, R_x	yz

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

D_{2h} (mmm)	E	$C_2(z)$	$C_2(y)$	$C_2(x)$	i	$\sigma(xy)$	$\sigma(zx)$	$\sigma(yz)$	$h = 8$	
A_g	1	1	1	1	1	1	1	1		x^2, y^2, z^2
B_{1g}	1	1	−1	−1	1	1	−1	−1	R_z	xy
B_{2g}	1	−1	1	−1	1	−1	1	−1	R_y	zx
B_{3g}	1	−1	−1	1	1	−1	−1	1	R_x	yz
A_u	1	1	1	1	−1	−1	−1	−1		
B_{1u}	1	1	−1	−1	−1	−1	1	1	z	
B_{2u}	1	−1	1	−1	−1	1	−1	1	y	
B_{3u}	1	−1	−1	1	−1	1	1	−1	x	

D_{3h} ($\bar{6}$m2)	E	$2C_3$	$3C_2$	σ_h	$2S_3$	$3\sigma_v$	$h = 12$	
A'_1	1	1	1	1	1	1		$x^2 + y^2, z^2$
A'_2	1	1	−1	1	1	−1	R_z	
E'	2	−1	0	2	−1	0	(x, y)	$(x^2 - y^2, xy)$
A''_1	1	1	1	−1	−1	−1		
A''_2	1	1	−1	−1	−1	1	z	
E''	2	−1	0	−2	1	0	(R_x, R_y)	(zx, yz)

D_{4h} (4/mmm)	E	$2C_4$	C_2	$2C'_2$	$2C''_2$	i	$2S_4$	σ_h	$2\sigma_v$	$2\sigma_d$	$h = 16$	
A_{1g}	1	1	1	1	1	1	1	1	1	1		$x^2 + y^2, z^2$
A_{2g}	1	1	1	−1	−1	1	1	1	−1	−1	R_z	
B_{1g}	1	−1	1	1	−1	1	−1	1	1	−1		$x^2 - y^2$
B_{2g}	1	−1	1	−1	1	1	−1	1	−1	1		xy
E_g	2	0	−2	0	0	2	0	−2	0	0	(R_x, R_y)	(zx, yz)
A_{1u}	1	1	1	1	1	−1	−1	−1	−1	−1		
A_{2u}	1	1	1	−1	−1	−1	−1	−1	1	1	z	
B_{1u}	1	−1	1	1	−1	−1	1	−1	−1	1		
B_{2u}	1	−1	1	−1	1	−1	1	−1	1	−1		
E_u	2	0	−2	0	0	−2	0	2	0	0	(x, y)	

T_d ($\bar{4}$3m)	E	$8C_3$	$3C_2$	$6S_4$	$6\sigma_d$	$h = 24$	
A_1	1	1	1	1	1		$x^2 + y^2 + z^2$
A_2	1	1	1	−1	−1		
E	2	−1	2	0	0		$(2z^2 - x^2 - y^2, x^2 - y^2)$
T_1	3	0	−1	1	−1	(R_x, R_y, R_z)	
T_2	3	0	−1	−1	1	(x, y, z)	(xy, yz, zx)

O_h (m3m)	E	$8C_3$	$6C_2$	$6C_4$	$3C_2$ $=(C_4^2)$	i	$6S_4$	$8S_6$	$3\sigma_h$	$6\sigma_d$	$h = 48$	
A_{1g}	1	1	1	1	1	1	1	1	1	1		$x^2 + y^2 + z^2$
A_{2g}	1	1	−1	−1	1	1	−1	1	1	−1		
E_g	2	−1	0	0	2	2	0	−1	2	0		$(2z^2 - x^2 - y^2, x^2 - y^2)$
T_{1g}	3	0	−1	1	−1	3	1	0	−1	−1	(R_x, R_y, R_z)	
T_{2g}	3	0	1	−1	−1	3	−1	0	−1	1		(xy, xz, yz)
A_{1u}	1	1	1	1	1	−1	−1	−1	−1	−1		
A_{2u}	1	1	−1	−1	1	−1	1	−1	−1	1		
E_u	2	−1	0	0	2	−2	0	1	−2	0		
T_{1u}	3	0	−1	1	−1	−3	−1	0	1	1	(x, y, z)	
T_{2u}	3	0	1	−1	−1	−3	1	0	1	−1		

C_{4v} (4mm)	E	$2C_4$	C_2	$2\sigma_v$	$2\sigma_d$	$h = 8$	
A_1	1	1	1	1	1	z	$x^2 + y^2, z^2$
A_2	1	1	1	−1	−1	R_z	
B_1	1	−1	1	1	−1		$x^2 - y^2$
B_2	1	−1	1	−1	1		xy
E	2	0	−2	0	0	$(x, y)(R_x, R_y)$	(zx, yz)

C_{5v}	E	$2C_5$	$2C_5^2$	$5\sigma_v$	$h = 10, \alpha = 72°$	
A_1	1	1	1	1	z	$x^2 + y^2, z^2$
A_2	1	1	1	−1	R_z	
E_1	2	$2\cos\alpha$	$2\cos 2\alpha$	0	$(x, y)(R_x, R_y)$	(zx, yz)
E_2	2	$2\cos 2\alpha$	$2\cos\alpha$	0		$(x^2 - y^2, xy)$

C_{6v} (6mm)	E	$2C_6$	$2C_3$	C_2	$3\sigma_v$	$3\sigma_d$	$h = 12$	
A_1	1	1	1	1	1	1	z	$x^2 + y^2, z^2$
A_2	1	1	1	1	−1	−1	R_z	
B_1	1	−1	1	−1	1	−1		
B_2	1	−1	1	−1	−1	1		
E_1	2	1	−1	−2	0	0	$(x, y)(R_x, R_y)$	(zx, yz)
E_2	2	−1	−1	2	0	0		$(x^2 - y^2, xy)$

$C_{\infty v}$	E	C_2	$2C_\phi$	$\infty\sigma_v$	$h = \infty$	
$A_1(\Sigma^+)$	1	1	1	1	z	$x^2 + y^2, z^2$
$A_2(\Sigma^-)$	1	1	1	−1	R_z	
$E_1(\Pi)$	2	−2	$2\cos\phi$	0	$(x, y)(R_x, R_y)$	(zx, yz)
$E_2(\Delta)$	2	2	$2\cos 2\phi$	0		$(xy, x^2 - y^2)$
⋮			⋮	⋮		

The groups D_{nh} (continued)

D_{5h}	E	$2C_5$	$2C_5^2$	$5C_2$	σ_h	$2S_5$	$2S_5^3$	$5\sigma_v$	$h = 20, \alpha = 72°$	
A'_1	1	1	1	1	1	1	1	1		$x^2 + y^2, z^2$
A'_2	1	1	1	−1	1	1	1	−1	R_z	
E'_1	2	$2\cos\alpha$	$2\cos 2\alpha$	0	2	$2\cos\alpha$	$2\cos 2\alpha$	0	(x, y)	
E'_2	2	$2\cos 2\alpha$	$2\cos\alpha$	0	2	$2\cos 2\alpha$	$2\cos\alpha$	0		$(x^2 - y^2, xy)$
A''_1	1	1	1	1	−1	−1	−1	−1		
A''_2	1	1	1	−1	−1	−1	−1	1	z	
E''_1	2	$2\cos\alpha$	$2\cos 2\alpha$	0	−2	$-2\cos\alpha$	$-2\cos 2\alpha$	0	(R_x, R_y)	(zx, yz)
E''_2	2	$2\cos 2\alpha$	$2\cos\alpha$	0	−2	$-2\cos 2\alpha$	$-2\cos\alpha$	0		

D_{6h} (6/mmm)	E	$2C_6$	$2C_3$	C_2	$3C'_2$	$3C''_2$	i	$2S_3$	$2S_6$	σ_h	$3\sigma_d$	$3\sigma_v$	$h = 24$	
A_{1g}	1	1	1	1	1	1	1	1	1	1	1	1		$x^2 + y^2, z^2$
A_{2g}	1	1	1	1	−1	−1	1	1	1	1	−1	−1	R_z	
B_{1g}	1	−1	1	−1	1	−1	1	−1	1	−1	1	−1		
B_{2g}	1	−1	1	−1	−1	1	1	−1	1	−1	−1	1		
E_{1g}	2	1	−1	−2	0	0	2	1	−1	−2	0	0	(R_x, R_y)	(zx, yz)
E_{2g}	2	−1	−1	2	0	0	2	−1	−1	2	0	0		$(x^2 - y^2, xy)$
A_{1u}	1	1	1	1	1	1	−1	−1	−1	−1	−1	−1		
A_{2u}	1	1	1	1	−1	−1	−1	−1	−1	−1	1	1	z	
B_{1u}	1	−1	1	−1	1	−1	−1	1	−1	1	−1	1		
B_{2u}	1	−1	1	−1	−1	1	−1	1	−1	1	1	−1		
E_{1u}	2	1	−1	−2	0	0	−2	−1	1	2	0	0	(x, y)	
E_{2u}	2	−1	−1	2	0	0	−2	1	1	−2	0	0		

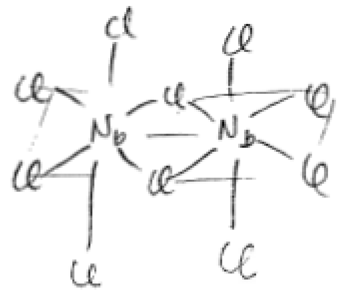
$D_{\infty h}$	E	$\infty C'_2$	$2C_\phi$	i	$\infty\sigma_v$	$2S_\phi$	$h = \infty$	
$A_{1g}(\Sigma_g^+)$	1	1	1	1	1	1		$z^2, x^2 + y^2$
$A_{1u}(\Sigma_u^+)$	1	−1	1	−1	1	−1	z	
$A_{2g}(\Sigma_g^-)$	1	−1	1	1	−1	1	R_z	
$A_{2u}(\Sigma_u^-)$	1	1	1	−1	−1	−1		
$E_{1g}(\Pi_g)$	2	0	$2\cos\phi$	2	0	$-2\cos\phi$	(R_x, R_y)	(zx, yz)
$E_{1u}(\Pi_u)$	2	0	$2\cos\phi$	−2	0	$2\cos\phi$	(x, y)	
$E_{2g}(\Delta_g)$	2	0	$2\cos 2\phi$	2	0	$2\cos 2\phi$		$(xy, x^2 - y^2)$
$E_{2u}(\Delta_u)$	2	0	$2\cos 2\phi$	−2	0	$-2\cos 2\phi$		
⋮	⋮	⋮	⋮	⋮	⋮	⋮		

1. (a) cyclohexane (chair) :  (D_{3d})

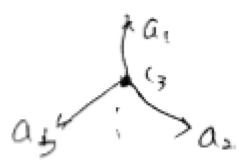
(b) cyclohexane (boat) :  (C_{2v})

(c) 벙블베찌는 Mark : C_{2v} (or C_s 뒷면이 모양이 없다고 할 때)

2.



3.



(a) D_{3h}

(b)

$$E\begin{pmatrix}a_1\\a_2\\a_3\end{pmatrix}=\begin{pmatrix}1&0&0\\0&1&0\\0&0&1\end{pmatrix}\begin{pmatrix}a_1\\a_2\\a_3\end{pmatrix}=\begin{pmatrix}a_1\\a_2\\a_3\end{pmatrix}\qquad C_3\begin{pmatrix}a_1\\a_2\\a_3\end{pmatrix}=\begin{pmatrix}0&0&1\\1&0&0\\0&1&0\end{pmatrix}\begin{pmatrix}a_1\\a_2\\a_3\end{pmatrix}=\begin{pmatrix}a_3\\a_1\\a_2\end{pmatrix}$$

$$C_2\begin{pmatrix}a_1\\a_2\\a_3\end{pmatrix}=\begin{pmatrix}1&0&0\\0&0&1\\0&1&0\end{pmatrix}\begin{pmatrix}a_1\\a_2\\a_3\end{pmatrix}=\begin{pmatrix}a_1\\a_3\\a_2\end{pmatrix},\ \sigma_h\begin{pmatrix}a_1\\a_2\\a_3\end{pmatrix}=\begin{pmatrix}1&0&0\\0&1&0\\0&0&1\end{pmatrix}\begin{pmatrix}a_1\\a_2\\a_3\end{pmatrix}=\begin{pmatrix}a_1\\a_2\\a_3\end{pmatrix}$$

$$S_3\begin{pmatrix}a_1\\a_2\\a_3\end{pmatrix}=\begin{pmatrix}0&0&1\\1&0&0\\0&1&0\end{pmatrix}\begin{pmatrix}a_1\\a_2\\a_3\end{pmatrix}=\begin{pmatrix}a_3\\a_1\\a_2\end{pmatrix}\qquad \sigma_v\begin{pmatrix}a_1\\a_2\\a_3\end{pmatrix}=\begin{pmatrix}1&0&0\\0&0&1\\0&1&0\end{pmatrix}\begin{pmatrix}a_1\\a_2\\a_3\end{pmatrix}=\begin{pmatrix}a_1\\a_3\\a_2\end{pmatrix}$$

(c)

D_{3h}	E	$2C_3$	$3C_2$	σ_h	$2S_3$	$3\sigma_v$
Γ_1	3	0	1	3	0	1

(e) $\Gamma_1 = A_1' + E'$

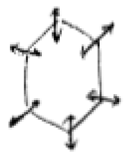
(f) A_1' : s E' : p_x, p_y

(g) $2s$, $2p_x$, $2p_y$

(h) sp^2

4\. (a) D_{6h}

(b)



D_{6h}	E	$2C_6$	$2C_3$	C_2	$3C_2'$	$3C_2''$	i	$2S_3$	$2S_6$	σ_h	$3\sigma_d$	$3\sigma_v$
A_{1g}	1	1	1	1	1	1	1	1	1	1	1	1

↑ ans.

(c) Raman

5

- NaOH 40ml + 0.1M H_2SO_4 400ml

$NV = N'V'$

$N_{NaOH} \times 40ml = 0.2N \times 400ml$ ∴ $N_{NaOH} = 2N$

- NaOH 20ml + HCl 24ml

$NV = N'V'$

$2N \times 20ml = N_{HCl} \times 24ml$ ∴ $N_{HCl} = 1.67N = 1.67M$

- HCl는 강산 ∴ $pH = -\log[H_3O^+] = -\log[H^+] = -\log(1.67)$

$HCl \rightarrow H^+ + Cl^-$
~100%

$= \underline{-0.223}$

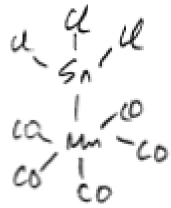
6\.

(a) BF_3 + $:NH_3$ → F_3B-NH_3

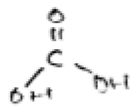
acid base

(b) $:SnCl_3$ + $Mn(CO)_5$ →

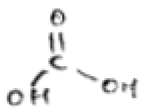
base acid



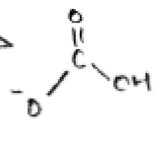
7\. $CO_2(g) + H_2O(l)$ →



(aq)

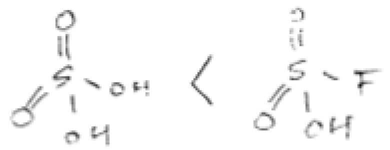


$+ H_2O(l)$ →



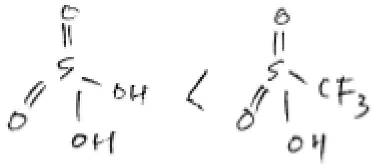
$+ H_3O^+(aq)$

8 (a) H_2SO_4 $O_2SF(OH)$



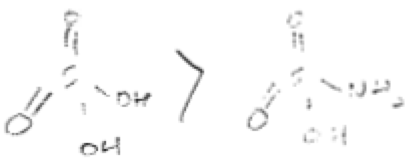
Electronegativity of F is bigger than that of OH to result in more effective charge on central S atom. This helps release of H^+.

(b) H_2SO_4, CF_3SO_3H



CF_3 is a strong electron-withdrawing group. Therefore as in (a), CF_3SO_3H is stronger acid.

(c) H_2SO_4 $O_2S(NH_2)OH$



NH_2 is an electron-donating group. This confers on S higher effective negative charge. This reduces the ability of releasing H^+.

9.

⟶ soft base

F^- Cl^- Br^- I^-

⟵ hard base

Hg^{2+} is a soft acid. Therefore, it makes complexes with soft bases more easily.

Al^{3+} is a hard acid. Therefore, it makes complexes with hard based more easily.