UNIVERSITI SAINS MALAYSIA

Peperiksaan Semester Pertama

Sidang Akademik 1996/97

Oktober/November 1996

KTT 211 - Kimia Takorganik I

[Masa : 3 jam]

Jawab **LIMA** soalan sahaja. Soalan 1 hingga soalan 4 adalah wajib.

Pilih sebarang satu soalan daripada soalan 5 hingga soalan 7.

Hanya LIMA jawapan yang pertama sahaja akan diperiksa.

Jawab tiap-tiap soalan pada muka surat yang baru.

Kertas ini mengandungi TUJUH soalan dan Lampiran (17 mukasurat).

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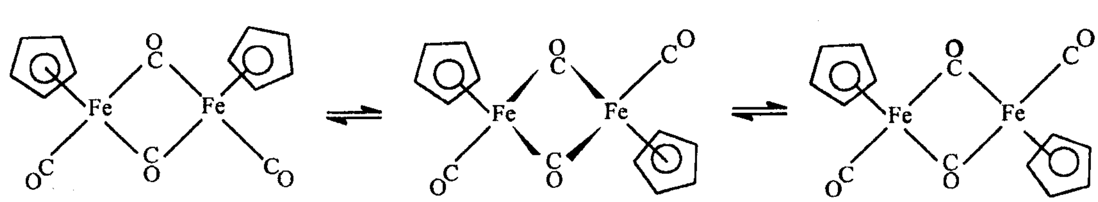
1. (a) Terangkan dengan ringkas tentang karakter bagi perwakilan tak terturunkan.

(4 markah)

(b) Kompleks $(\eta^5 - C_5H_5)_2Fe_2(CO)_4$ mungkin wujud sebagai isomer-isomer I, II, dan III seperti berikut :



I II III

(i) Senaraikan semua unsur simetri dan nyatakan kumpulan titik bagi tiap-tiap isomer I, II dan III.

(6 markah)

(b) Apakah nilai $\bar{B}$ dan $\bar{D}$ bagi $H^{37}Cl$ jika panjang ikatan dan pemalar daya dianggap sama bagi $H^{35}Cl$ dan $H^{37}Cl$?

(6 markah)

4. (a) Bincangkan kesan ketakharmonian terhadap spektrum getaran suatu molekul dwiatom.

(8 markah)

(b) Jalur asas ($v=O \longrightarrow v=1$) bagi molekul CO berpusat pada 2143.3 cm^{-1} dan nadakalian yang pertama ($v=O \longrightarrow v=2$) berpusat pada 4259.7 cm^{-1}. Kiralah frekuensi getaran ϖ_e (dalam unit cm^{-1}), pemalar ketakharmonian x_e dan pemalar daya bagi ikatan C — O.

(12 markah)

5. (a) Terangkan dengan ringkas isitilah-istilah berikut :

(i) Paksi putaran wajar bertertib n, C_n

(ii) Paksi putaran-pembalikan, bertertib n, S_n

(iii) Perwakilan tak-terturunkan.

(6 markah)

6. (a) Ungkapan taburan Boltzmann bagi populasi paras putaran dengan tenaga E_J adalah

$$E_J = (2J + 1)N_o \exp[-J(J + 1)\bar{B}\ hC/kT]$$

Parameter $\bar{B}$ adalah pemalar putaran dalam unit cm^{-1}.

Tunjukkan bahawa populasi didapati maksimum pada nilai angkabulat J yang hampir sama dengan

$$J_{maks} = (kT/2hc\bar{B})^{1/2} - 1/2$$

(8 markah)

(b) Bagi molekul HCl, populasi didapati maksimum pada nilai J = 3 pada 300 K. Anggarkan panjang ikatan bagi HCl dalam unit nm.

(12 markah)

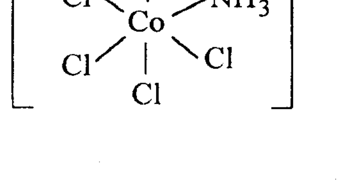
7. (a) Apakah kesan Raman? Terangkan dengan ringkas kesan Raman dengan menggunakan teori kuantum.

(10 markah)

(b) Bagi kompleks Co(II) berikut :

(i) Berikan kumpulan titik.

(ii) Dapatkan bilangan dan spesies simetri bagi getaran yang aktif dalam spektrum-spektrum Raman dan inframerah.



(10 markah)

oooOOOooo

THE NONAXIAL GROUPS

C_1	E
A	1

C_s	E	σ_h		
A'	1	1	x, y, R_z	x^2, y^2, z^2, xy
A''	1	−1	z, R_x, R_y	yz, xz

C_i	E	i		
A_g	1	1	R_x, R_y, R_z	$x^2, y^2, z^2, xy, xz, yz$
A_u	1	−1	x, y, z	

THE AXIAL GROUPS

► *The C_n Groups*

C_2	E	C_2		
A	1	1	z, R_z	x^2, y^2, z^2, xy
B	1	−1	x, y, R_x, R_y	yz, xz

C_3	E	C_3	C_3^2	$\varepsilon = \exp(2\pi i/3)$	
A	1	1	1	z, R_z	$x^2 + y^2, z^2$
E	$\begin{Bmatrix} 1 \\ 1 \end{Bmatrix}$	$\begin{matrix} \varepsilon \\ \varepsilon^* \end{matrix}$	$\begin{matrix} \varepsilon^* \\ \varepsilon \end{matrix}$	$(x, y), (R_x, R_y)$	$(x^2 - y^2, xy), (yz, xz)$

► *The* S_n *Groups*

S_4	E	S_4	C_2	S_4^3		
A	1	1	1	1	R_z	x^2+y^2, z^2
B	1	−1	1	−1	z	x^2-y^2, xy
E	$\{1$	i	−1	$-i\}$	$(x, y), (R_x, R_y)$	(xz, yz)
	$\{1$	$-i$	−1	$i\}$		

S_6	E	C_3	C_3^2	i	S_6^5	S_6	$\varepsilon = \exp(2\pi i/3)$	
A_g	1	1	1	1	1	1	R_z	x^2+y^2, z^2
E_g	$\{1$	ε	ε^*	1	ε	$\varepsilon^*\}$	(R_x, R_y)	(x^2-y^2, xy),
	$\{1$	ε^*	ε	1	ε^*	$\varepsilon\}$		(xy, yz)
A_u	1	1	1	−1	−1	−1	z	
E_u	$\{1$	ε	ε^*	−1	$-\varepsilon$	$-\varepsilon^*\}$	(x, y)	
	$\{1$	ε^*	ε	−1	$-\varepsilon^*$	$-\varepsilon\}$		

S_8	E	S_8	C_4	S_8^3	C_2	S_8^5	C_4^3	S_8^7	$\varepsilon = \exp(2\pi i/8)$	
A	1	1	1	1	1	1	1	1	R_z	x^2+y^2, z^2
B	1	−1	1	−1	1	−1	1	−1	z	
E_1	$\{1$	ε	i	$-\varepsilon^*$	−1	$-\varepsilon$	$-i$	$\varepsilon^*\}$	(x, y),	
	$\{1$	ε^*	$-i$	$-\varepsilon$	−1	$-\varepsilon^*$	i	$\varepsilon\}$	(R_x, R_y)	
E_2	$\{1$	i	−1	$-i$	1	i	−1	$-i\}$		(x^2-y^2, xy)
	$\{1$	$-i$	−1	i	1	$-i$	−1	$i\}$		
E_3	$\{1$	$-\varepsilon^*$	$-i$	ε	−1	ε^*	i	$-\varepsilon\}$		(xz, yz)
	$\{1$	$-\varepsilon$	i	ε^*	−1	ε	$-i$	$-\varepsilon^*\}$		

► *The* C_{nv} *Groups*

C_{2v}	E	C_2	$\sigma_v(xz)$	$\sigma_v'(yz)$		
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}	E	$2C_3$	$3\sigma_v$		
A_1	1	1	1	z	x^2+y^2, z^2
A_2	1	1	−1	R_z	
E	2	−1	0	$(x, y), (R_x, R_y)$	$(x^2-y^2, xy), (xz, yz)$

Character Tables

C_{4h}	E	C_4	C_2	C_4^3	i	S_4^3	σ_h	S_4		
A_g	1	1	1	1	1	1	1	1	R_z	x^2+y^2, z^2
B_g	1	−1	1	−1	1	−1	1	−1		x^2-y^2, xy
E_g	1	i	−1	$-i$	1	i	−1	$-i$		
	1	$-i$	−1	i	1	$-i$	−1	i	(R_x, R_y)	(xz, yz)
A_u	1	1	1	1	−1	−1	−1	−1	z	
B_u	1	−1	1	−1	−1	1	−1	1		
E_u	1	i	−1	$-i$	−1	$-i$	1	i		
	1	$-i$	−1	i	−1	i	1	$-i$	(x, y)	

C_{5h}	E	C_5	C_5^2	C_5^3	C_5^4	σ_h	S_5	S_5^7	S_5^3	S_5^9	$\varepsilon = \exp(2\pi i/5)$	
A'	1	1	1	1	1	1	1	1	1	1	R_z	x^2+y^2, z^2
E_1'	1	ε	ε^2	ε^{2*}	ε^*	1	ε	ε^2	ε^{2*}	ε^*		
	1	ε^*	ε^{2*}	ε^2	ε	1	ε^*	ε^{2*}	ε^2	ε	(x, y)	
E_2'	1	ε^2	ε^*	ε	ε^{2*}	1	ε^2	ε^*	ε	ε^{2*}		
	1	ε^{2*}	ε	ε^*	ε^2	1	ε^{2*}	ε	ε^*	ε^2		(x^2-y^2, xy)
A''	1	1	1	1	1	−1	−1	−1	−1	−1	z	
E_1''	1	ε	ε^2	ε^{2*}	ε^*	−1	$-\varepsilon$	$-\varepsilon^2$	$-\varepsilon^{2*}$	$-\varepsilon^*$		
	1	ε^*	ε^{2*}	ε^2	ε	−1	$-\varepsilon^*$	$-\varepsilon^{2*}$	$-\varepsilon^2$	$-\varepsilon$	(R_x, R_y)	(xz, yz)
E_2''	1	ε^2	ε^*	ε	ε^{2*}	−1	$-\varepsilon^2$	$-\varepsilon^*$	$-\varepsilon$	$-\varepsilon^{2*}$		
	1	ε^{2*}	ε	ε^*	ε^2	−1	$-\varepsilon^{2*}$	$-\varepsilon$	$-\varepsilon^*$	$-\varepsilon^2$		

C_{6h}	E	C_6	C_3	C_2	C_3^2	C_6^5	i	S_3^5	S_6^5	σ_h	S_6	S_3	$\varepsilon = \exp(2\pi i/6)$	
A_g	1	1	1	1	1	1	1	1	1	1	1	1	R_z	x^2+y^2, z^2
B_g	1	−1	1	−1	1	−1	1	−1	1	−1	1	−1		
E_{1g}	1	ε	$-\varepsilon^*$	−1	$-\varepsilon$	ε^*	1	ε	$-\varepsilon^*$	−1	$-\varepsilon$	ε^*		
	1	ε^*	$-\varepsilon$	−1	$-\varepsilon^*$	ε	1	ε^*	$-\varepsilon$	−1	$-\varepsilon^*$	ε	(R_x, R_y)	(xz, yz)
E_{2g}	1	$-\varepsilon^*$	$-\varepsilon$	1	$-\varepsilon^*$	$-\varepsilon$	1	$-\varepsilon^*$	$-\varepsilon$	1	$-\varepsilon^*$	$-\varepsilon$		
	1	$-\varepsilon$	$-\varepsilon^*$	1	$-\varepsilon$	$-\varepsilon^*$	1	$-\varepsilon$	$-\varepsilon^*$	1	$-\varepsilon$	$-\varepsilon^*$		(x^2-y^2, xy)
A_u	1	1	1	1	1	1	−1	−1	−1	−1	−1	−1	z	
B_u	1	−1	1	−1	1	−1	−1	1	−1	1	−1	1		
E_{1u}	1	ε	$-\varepsilon^*$	−1	$-\varepsilon$	ε^*	−1	$-\varepsilon$	ε^*	1	ε	$-\varepsilon^*$		
	1	ε^*	$-\varepsilon$	−1	$-\varepsilon^*$	ε	−1	$-\varepsilon^*$	ε	1	ε^*	$-\varepsilon$	(x, y)	
E_{2u}	1	$-\varepsilon^*$	$-\varepsilon$	1	$-\varepsilon^*$	$-\varepsilon$	−1	ε^*	ε	−1	ε^*	ε		
	1	$-\varepsilon$	$-\varepsilon^*$	1	$-\varepsilon$	$-\varepsilon^*$	−1	ε	ε^*	−1	ε	ε^*		

► *The* D_{nh} *Groups*

D_{2h}	E	$C_2(z)$	$C_2(y)$	$C_2(x)$	i	$\sigma(xy)$	$\sigma(xz)$	$\sigma(yz)$		
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	xz
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}	E	$2C_3$	$3C_2$	σ_h	$2S_3$	$3\sigma_v$	(x axis coincident with C_2)	
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)	(xz, yz)

D_{4h}	E	$2C_4$	C_2	$2C_2'$	$2C_2''$	i	$2S_4$	σ_h	$2\sigma_v$	$2\sigma_d$	(x axis coincident with C_2')	
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)	(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	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)	

D_{5h}	E	$2C_5$	$2C_5^2$	$5C_2$	σ_h	$2S_5$	$2S_5^3$	$5\sigma_v$	(x axis coincident with C_2)	
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 72°	2 cos 144°	0	2	2 cos 72°	2 cos 144°	0	(x, y)	
E_2'	2	2 cos 144°	2 cos 72°	0	2	2 cos 144°	2 cos 72°	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 72°	2 cos 144°	0	−2	−2 cos 72°	−2 cos 144°	0	(R_x, R_y)	(xz, yz)
E_2''	2	2 cos 144°	2 cos 72°	0	−2	−2 cos 144°	−2 cos 72°	0		

$\mathbf{D}_{4d}$	E	$2S_8$	$2C_4$	$2S_8^3$	C_2	$4C_2'$	$4\sigma_d$	(x axis coincident with C_2')	
A_1	1	1	1	1	1	1	1		x^2+y^2, z^2
A_2	1	1	1	1	1	−1	−1	R_z	
B_1	1	−1	1	−1	1	1	−1		
B_2	1	−1	1	−1	1	−1	1	z	
E_1	2	$\sqrt{2}$	0	$-\sqrt{2}$	−2	0	0	(x, y)	
E_2	2	0	−2	0	2	0	0		(x^2-y^2, xy)
E_3	2	$-\sqrt{2}$	0	$\sqrt{2}$	−2	0	0	(R_x, R_y)	(xz, yz)

$\mathbf{D}_{5d}$	1	$2C_5$	$2C_5^2$	$5C_2$	i	$2S_{10}^3$	$2S_{10}$	$5\sigma_d$	(x axis coincident with C_2)	
A_{1g}	1	1	1	1	1	1	1	1		x^2+y^2, z^2
A_{2g}	1	1	1	−1	1	1	1	−1	R_z	
E_{1g}	2	2 cos 72°	2 cos 144°	0	2	2 cos 72°	2 cos 144°	0	(R_x, R_y)	(xz, yz)
E_{2g}	2	2 cos 144°	2 cos 72°	0	2	2 cos 144°	2 cos 72°	0		(x^2-y^2, xy)
A_{1u}	1	1	1	1	−1	−1	−1	−1		
A_{2u}	1	1	1	−1	−1	−1	−1	1	z	
E_{1u}	2	2 cos 72°	2 cos 144°	0	−2	−2 cos 72°	−2 cos 144°	0	(x, y)	
E_{2u}	2	2 cos 144°	2 cos 72°	0	−2	−2 cos 144°	−2 cos 72°	0		

$\mathbf{D}_{6d}$	E	$2S_{12}$	$2C_6$	$2S_4$	$2C_3$	$2S_{12}^5$	C_2	$6C_2'$	$6\sigma_d$	(x axis coincident with C_2)	
A_1	1	1	1	1	1	1	1	1	1		x^2+z^2, z^2
A_2	1	1	1	1	1	1	1	−1	−1	R_z	
B_1	1	−1	1	−1	1	−1	1	1	−1		
B_2	1	−1	1	−1	1	−1	1	−1	1	z	
E_1	2	$\sqrt{3}$	1	0	−1	$-\sqrt{3}$	−2	0	0	(x, y)	
E_2	2	1	−1	−2	−1	1	2	0	0		(x^2-y^2, xy)
E_3	2	0	−2	0	2	0	−2	0	0		
E_4	2	−1	−1	2	−1	−1	2	0	0		
E_5	2	$-\sqrt{3}$	1	0	−1	$\sqrt{3}$	−2	0	0	(R_x, R_y)	(xz, yz)

THE CUBIC GROUPS

▸ *Tetrahedral Groups*

$\mathbf{T}$	E	$4C_3$	$4C_3^2$	$3C_2$	$\varepsilon = \exp(2\pi i/3)$	
A	1	1	1	1		$x^2+y^2+z^2$
E	$\left\{\begin{matrix}1\\1\end{matrix}\right.$	$\begin{matrix}\varepsilon\\\varepsilon^*\end{matrix}$	$\begin{matrix}\varepsilon^*\\\varepsilon\end{matrix}$	$\left.\begin{matrix}1\\1\end{matrix}\right\}$		$(2z^2-x^2-y^2, x^2-y^2)$
T	3	0	0	−1	$(R_x, R_y, R_z), (x, y, z)$	(xy, xz, yz)

► *The Icosahedral Groups*[a]

I_h	E	$12C_5$	$12C_5^2$	$20C_3$	$15C_2$	i	$12S_{10}$	$12S_{10}^3$	$20S_6$	15σ		
A_g	1	1	1	1	1	1	1	1	1	1		$x^2+y^2+z^2$
T_{1g}	3	$\frac{1}{2}(1+\sqrt{5})$	$\frac{1}{2}(1-\sqrt{5})$	0	−1	3	$\frac{1}{2}(1-\sqrt{5})$	$\frac{1}{2}(1+\sqrt{5})$	0	−1	(R_x, R_y, R_z)	
T_{2g}	3	$\frac{1}{2}(1-\sqrt{5})$	$\frac{1}{2}(1+\sqrt{5})$	0	−1	3	$\frac{1}{2}(1+\sqrt{5})$	$\frac{1}{2}(1-\sqrt{5})$	0	−1		
G_g	4	−1	−1	1	0	4	−1	−1	1	0		
H_g	5	0	0	−1	1	5	0	0	−1	1		$(2z^2-x^2-y^2,$ $x^2-y^2,$ $xy, yz, zx)$
A_u	1	1	1	1	1	−1	−1	−1	−1	−1		
T_{1u}	3	$\frac{1}{2}(1+\sqrt{5})$	$\frac{1}{2}(1-\sqrt{5})$	0	−1	−3	$-\frac{1}{2}(1-\sqrt{5})$	$-\frac{1}{2}(1+\sqrt{5})$	0	1	(x, y, z)	
T_{2u}	3	$\frac{1}{2}(1-\sqrt{5})$	$\frac{1}{2}(1+\sqrt{5})$	0	−1	−3	$-\frac{1}{2}(1+\sqrt{5})$	$-\frac{1}{2}(1-\sqrt{5})$	0	1		
G_u	4	−1	−1	1	0	−4	1	1	−1	0		
H_u	5	0	0	−1	1	−5	0	0	1	−1		

[a] For the pure rotation group I, the outlined section in the upper left is the character table; the g subscripts should, of course, be dropped and (x, y, z) assigned to the T_1 representation.

► *The Groups* $C_{\infty v}$ *and* $D_{\infty h}$ *for Linear Molecules*

$C_{\infty v}$	E	$2C_\infty^\phi$	⋯	$\infty\sigma_v$		
$A_1 \equiv \Sigma^+$	1	1	⋯	1	z	x^2+y^2, z^2
$A_2 \equiv \Sigma^-$	1	1	⋯	−1	R_z	
$E_1 \equiv \Pi$	2	$2\cos\phi$	⋯	0	$(x, y); (R_x, R_y)$	(xz, yz)
$E_2 \equiv \Delta$	2	$2\cos 2\phi$	⋯	0		(x^2-y^2, xy)
$E_3 \equiv \Phi$	2	$2\cos 3\phi$	⋯	0		
⋮	⋮	⋮	⋮	⋮		

$D_{\infty h}$	E	$2C_\infty^\phi$	⋯	$\infty\sigma_v$	i	$2S_\infty^\phi$	⋯	∞C_2		
$A_{1g} \equiv \Sigma_g^+$	1	1,	⋯	1	1	1	⋯	1		x^2+y^2, z^2
$A_{2g} \equiv \Sigma_g^-$	1	1	⋯	−1	1	1	⋯	−1	R_z	
$E_{1g} \equiv \Pi_g$	2	$2\cos\phi$	⋯	0	2	$-2\cos\phi$	⋯	0	(R_x, R_y)	(xz, yz)
$E_{2g} \equiv \Delta_g$	2	$2\cos 2\phi$	⋯	0	2	$2\cos 2\phi$	⋯	0		(x^2-y^2, xy)
⋯	⋯	⋯	⋯	⋯	⋯	⋯	⋯	⋯		
$A_{1u} \equiv \Sigma_u^+$	1	1	⋯	1	−1	−1	⋯	−1	z	
$A_{2u} \equiv \Sigma_u^-$	1	1	⋯	−1	−1	−1	⋯	1		
$E_{1u} \equiv \Pi_u$	2	$2\cos\phi$	⋯	0	−2	$2\cos\phi$	⋯	0	(x, y)	
$E_{2u} \equiv \Delta_u$	2	$2\cos 2\phi$	⋯	0	−2	$-2\cos 2\phi$	⋯	0		
$E_{3u} \equiv \Phi_u$	2	$2\cos 3\phi$	⋯	0	−2	$2\cos 3\phi$	⋯	0		
⋮	⋮	⋮	⋮	⋮	⋮	⋮	⋮	⋮		