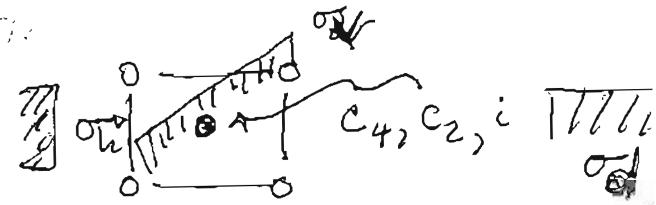
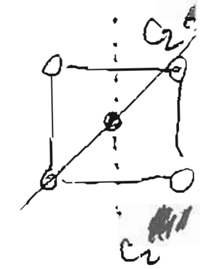
FROM PROBLEM SET 3

XeF_4 POINT GROUP D_{4h}





D_{4h}	E	$2C_4$	C_2	$2C_2'$	$2C_2''$	i	$2S_4$	σ_h	$2\sigma_v$	$2\sigma_d$		
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_{4h} Character Table

D_4	A_1	A_2	B_1	B_2	E	Operators
A_1	A_1	A_2	B_1	B_2	E	x^2+y^2, z^2
A_2	A_2	A_1	B_2	B_1	E	z, R_z
B_1	B_1	B_2	A_1	A_2	E	x^2-y^2
B_2	B_2	B_1	A_2	A_1	E	xy
E	E	E	E	E	$A_1 \oplus A_2 \oplus B_1 \oplus B_2$	x, y, R_x, R_y, xz, yz

D_4 Direct Product Table

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Number of vibrations $3N-6 = 9$

	E	$2C_4$	C_2	$2C_2'$	$2C_2''$	i	$2S_4$	σ_h	$2\sigma_v$	$2\sigma_d$
Γ_{CART}	15	1	−1	−3	−1	−3	−1	5	3	1

$\chi_E \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} = 3$, 5 unshifted 15

$\chi_{\sigma_h} \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -1 \end{pmatrix} = 1$, 5 unshifted 5

$\chi_i \begin{pmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{pmatrix} = -3$, 1 unshifted -3

$\chi_{C_4} \begin{pmatrix} \cos 90 & \sin 90 & 0 \\ -\sin\theta & \cos\theta & 0 \\ 0 & 0 & 1 \end{pmatrix} = \begin{pmatrix} 0 & & \\ & 0 & \\ & & 1 \end{pmatrix} = 1$, 1 unshifted 1

$\chi_{C_2} \begin{pmatrix} \cos 180 & \sin 180 & 0 \\ -\sin 180 & \cos 180 & 0 \end{pmatrix} = \begin{pmatrix} -1 & & \\ & -1 & \\ & & 1 \end{pmatrix} = -1$, 1 unshifted -1

$\chi_{C_2'} = -1$, 3 unshifted -3

$\chi_{C_2''} = -1$, 1 unshifted -1

$$\chi_{S_4} = \begin{pmatrix} \cos 90 & \sin 90 & 0 \\ \sin 90 & \cos 90 & 0 \\ 0 & 0 & -1 \end{pmatrix} = -1 \text{ , 1 unshifted} \quad -1$$

$$\chi_{\sigma_v} = \begin{pmatrix} 1 & & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -1 \end{pmatrix} = 1 \text{ , 3 unshifted} \quad -3$$

$\chi_{\sigma_d} = 1$, 1 unshifted 1

$$\boxed{\begin{array}{c|cccccccccc} & E & 2C_4 & C_2 & 2C_2' & 2C_2'' & i & 2S_4 & \sigma_h & 2\sigma_v & 2\sigma_d \\ \Gamma_{x,y,z} & 3 & 1 & -1 & -1 & -1 & -3 & -1 & 1 & 1 & 1 \end{array}}$$

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<u>ORDER</u> $\quad h = 16$

$$a_i = \frac{1}{h} \sum_R \chi(R) \chi_i(R) \qquad \text{"OPERATIONS"}$$

RED IRRED

OR

$$a_i = \frac{1}{h} \sum_{\text{CLASSES}} \chi(R)\, g\, \chi_i(R) \qquad \text{"CLASSES"}$$

EXAMPLES

USE V.I.F.

Γ_{RED}	E	$2C_4$	C_2	$2C_2'$	$2C_2''$	i	$2S_4$	σ_h	$2\sigma_v$	$2\sigma_d$
	15	1	−1	−3	−1	−3	−1	5	3	1

a_{1g} $\frac{1}{16}\Big[(15)(1)(1) + (2)(1)(1) + (1)(-1)(1) + (2)(-3)(1) + (2)(-1)(1)$
$+ (1)(-3)(1) + (2)(-1)(1) + (1)(5)(1) + (2)(3)(1) + (2)(1)(1)\Big]$

$\frac{1}{16}\left[15 + 2 - 1 - 6 - 2 - 3 - 2 + 5 + 6 + 2\right] = \frac{1}{16}(16) = 1$

e_g $\frac{1}{16}\Big[(15)(1)(2) + (-1)(1)(-2) + (1)(2)(-3) + (5)(1)(-2)\Big] = \frac{1}{16}(16) = 1$

e_u $\frac{1}{16}\Big[(15)(1)(2) + (-2)(-1)(1) + (-2)(-3)(1) + (5)(2)(1)\Big] = \frac{1}{16}(48) = 3$

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AND SO ON

A_{1g}	1
A_{2g}	1
B_{1g}	1
B_{2g}	1
E_g	1
A_{1u}	1
A_{2u}	2
B_{1u}	0
B_{2u}	1
E_u	3
	15

$$\Gamma_{TRANS} = A_{2u} + E_u$$
$$\Gamma_{ROT} = A_{2g} + E_g$$

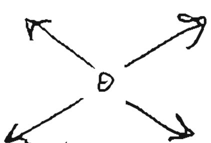
} FROM CHARACTER TABLES

$$\Gamma_{VIB} = \Gamma_{CART} - \Gamma_{TRANS} - \Gamma_{ROT}$$
$$= (A_{1g} + A_{2g} + B_{1g} + B_{2g} + E_g + 2A_{2u} + B_{2u} + 3E_u) - (A_{2u} + E_u) - (A_{2g} + E_g)$$

$$\Gamma_{VIB} = A_{1g} + B_{1g} + 2E_u + A_{2u} + B_{2u} + B_{2g}$$ (9)

σ_h $\quad A_{2u}$ $\quad B_{2u}$ $\quad$ oop (2)

A_{1g} $\quad B_{1g}$ $\quad B_{2g}$ $\quad 2E_u$ $\quad$ ip



D_{4h}

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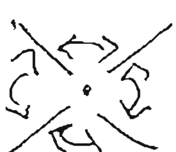
D_{4h}	E	$2C_4$	C_2	$2C_2'$	$2C_2''$	i	$2S_4$	σ_h	$2\sigma_v$	$2\sigma_d$
Γ_{STR}	4	0	0	2	0	0	0	4	2	0

$$\Gamma_{STR} = A_{1g} + B_{1g} + E_u$$ (4)



D_{4h}

	E	$2C_4$	C_2	$2C_2'$	$2C_2''$	i	$2S_4$	σ_h	$2\sigma_v$	$2\sigma_d$
Γ_{BEND}	4	0	0	0	2	0	0	4	0	2

$$\Gamma_{BEND} = \cancel{A_{1g}} + B_{2g} + E_u$$ (3)

(9)

z A_{2u} IR active

x, y $2E_u$

x^2+y^2, z^2 A_{1g}

x^2-y^2 B_{1g} RAMAN active

xy B_{2g}

(B_{2u} inactive)

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FIRST OVERTONE $(\ )^2$ A_{1g} • IR ACTIVE NONE

SECOND OVERTONE $(\ )^2(\ )^1$ SAME AS FUNDAMENTALS

COMBINATION BAND

$$A_{1g} \otimes A_{2u} = A_{2u}$$

$$B_{1g} \otimes B_{2u} = A_{2u}$$

z polarization

IR ACTIVE

THE QUESTION

(a.) Determine the number and symmetries of the vibrational modes of XeF_4.
(b.) Determine which vibrational modes are in-plane and which are out-of-plane.
(c.) Discuss the contributions of bends and stretches to the various modes.
(d.) Determine the spectral activity of each mode.
(e.) Consider the nondegenerate normal modes. Which of these would be expected to br infrared and Raman active as first overtones?
(f.) Which combination bands of the nondegenerate normal modes would be IR active?

FROM PROBLEM
SET 4

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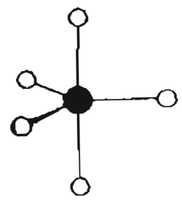
1. Determine the number and symmetries of the vibrational modes of PCl_5. Determine the contributions of bond stretches to the various vibrational modes. Determine the spectral activity of each mode. Give examples of combination bands which would be (a) infrared active and (b) Raman active.

ANSWERS



POINT GROUP D_{3h}

NUMBER OF VIBRATIONS $3N-6 = 12$

CHARACTER TABLE

D_{3h}	E	$2C_3$	$3C_2$	σ_h	$2S_3$	$3\sigma_v$		
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)

DIRECT PRODUCT TABLE

D_{3h}	A_1'	A_2'	A_1''	A_2''	E'	E''	Operators
A_1'	A_1'	A_2'	A_1''	A_2''	E'	E''	x^2+y^2, z^2
A_2'	A_2'	A_1'	A_2''	A_1''	E'	E''	R_z
A_1''	A_1''	A_2''	A_1'	A_2'	E''	E'	
A_2''	A_2''	A_1''	A_2'	A_1'	E''	E'	z
E'	E'	E'	E''	E''	$A_1' \oplus A_2' \oplus E'$	$A_1'' \oplus A_2'' \oplus E''$	x, y, x^2-y^2, xy
E''	E''	E''	E'	E'	$A_1'' \oplus A_2'' \oplus E''$	$A_1' \oplus A_2' \oplus E'$	R_x, R_y, xz, yz

D_{3h}	E	$2C_3$	$3C_2$	σ_h	$2S_3$	$3\sigma_v$
Γ_{CART}	18	0	−2	4	−2	4

$$\Gamma_{CART} = A_2' + 2E'' + 4E' + 2A_1' + 3A_2''$$ (18) FROM V.I.F

$$\Gamma_{ROT} = A_2' + E''$$

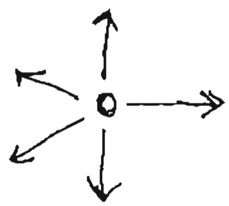
$$\Gamma_{TRANS} = A_2'' + E'$$

} FROM CHARACTER TABLE

$$\Gamma_{VIB} = \Gamma_{CART} - \Gamma_{ROT} - \Gamma_{TRANS}$$

$$\Gamma_{VIB} = 2A_1' + 2A_2'' + 3E' + E'' \qquad (12)$$

STRETCHES



	E	$2C_3$	$3C_2$	σ_h	$2S_3$	$3\sigma_v$
Γ_{STR}	5	2	1	3	0	3

V.I.F.

$$\Gamma_{STR} = 2A_1' + A_2'' + E'$$

Γ z A_2''

Γ x, y E'

DIPOLE OPERATOR FROM CHARACTER TABLES

Γ z^2, x^2+y^2 A_1'

Γ x^2-y^2, xy E'

Γ xz, yz

POLARIZABILITY COMPONENTS

A_2'', E' INFRARED ACTIVE

$2A_1'$, E', E'' RAMAN ACTIVE

e.g. COMBINATION BANDS

IR ACTIVE

$A_2'' + A_1'$ $\quad A_2'' \otimes A_1' = A_1'$

RAMAN ACTIVE

$A_1' + E'$

$A_1' \otimes E' = E$

FROM
PROBLEM SET 4

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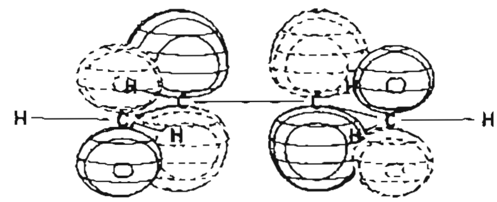
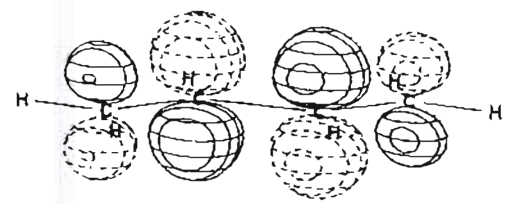
OUTLINE

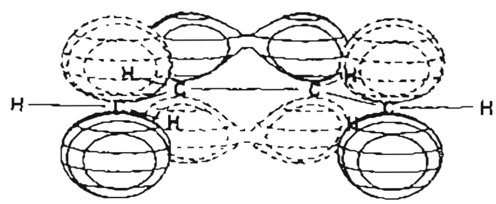
2. Compare the electronic spectra of cis- and trans-butadioene. Consider the two highest occupied and two lowest unoccupied π molecular orbitals. Determine the orbitally allowed electric dipole transitions and the polarization of each transition. Determine whether any orbitally forbidden electric dipole transitions may be vibronically allowed.



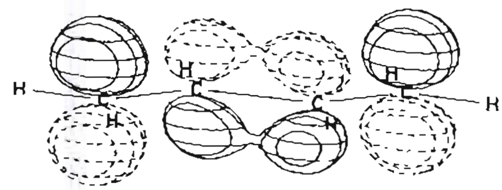
→ $2A_2$ E= 0.289 π^*_4



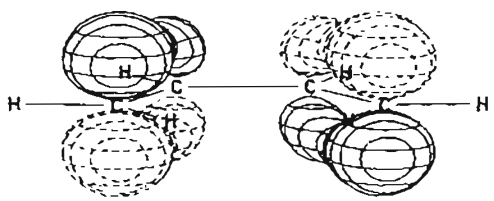
→ $2B_g$ E= 0.283 π^*_4



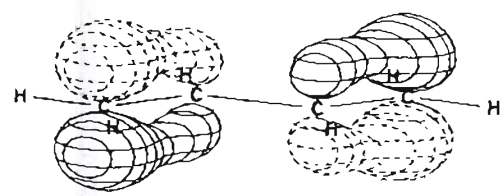
→ $2B_1$ E= 0.120 π^*_3



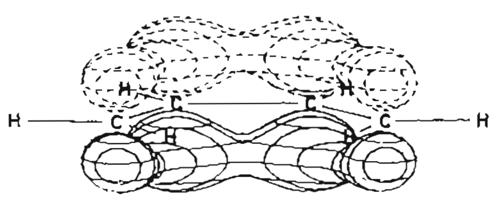
→ $2A_u$ E= 0.127 π^*_3



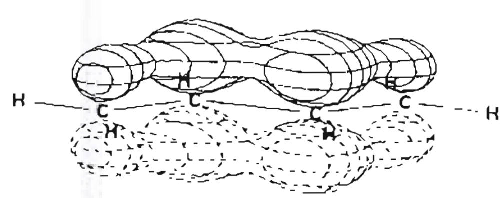
→ $1A_2$ E=-0.354 π_2



→ $1B_g$ E=-0.358 π_2



→ $1B_1$ E=-0.477 π_1



→ $1A_u$ E=-0.477 π_1

$3N-6 = 24$

cis	trans
C_{2v}	C_{2h}

→ NOTE ORBITAL SYMMETRIES HAVE BEEN GIVEN TO YOU.

C_{2v}	A_1	A_2	B_1	B_2	Operators
A_1	A_1	A_2	B_1	B_2	z, x^2, y^2, z^2
A_2	A_2	A_1	B_2	B_1	R_z, xy
B_1	B_1	B_2	A_1	A_2	x, R_y, xz
B_2	B_2	B_1	A_2	A_1	y, R_x, yz

C_{2v} DIRECT PRODUCT TABLE

C_{2h}	A_g	A_u	B_g	B_u	Operators
A_g	A_g	A_u	B_g	B_u	R_z, x^2, y^2, z^2, xy
A_u	A_u	A_g	B_u	B_g	z
B_g	B_g	B_u	A_g	A_u	R_x, R_y, xz, yz
B_u	B_u	B_g	A_u	A_g	x, y

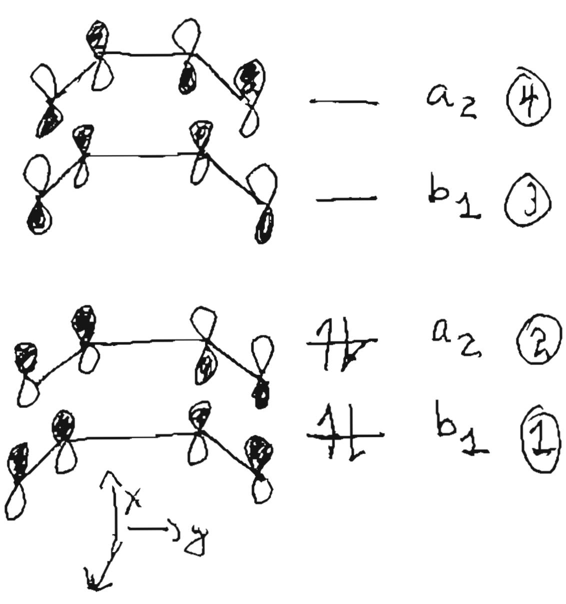
C_{2h} DIRECT PRODUCT TABLE

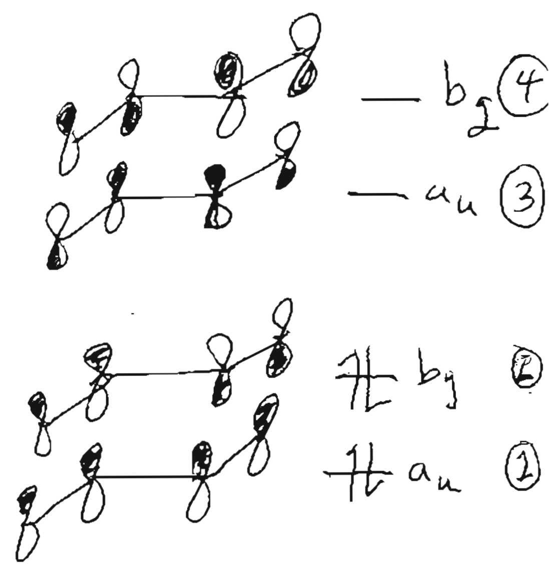
C_{2v} CHARACTER TABLE

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_{2h} CHARACTER TABLE

C_{2h}	E	C_2	i	σ_h		
A_g	1	1	1	1	R_z	x^2, y^2, z^2, xy
B_g	1	−1	1	−1	R_x, R_y	xz, yz
A_u	1	1	−1	−1	z	
B_u	1	−1	−1	1	x, y	





e.g. CONSIDER HOMO → LUMO
HOMO → LUMO + 1

cis C_{2v} | **trans** C_{2h}

$(a_2)^2 \rightarrow (a_2)^1(b_1)$ | $(b_g)^2 \rightarrow (b_g)^1(a_u)^1$

$(a_2)^2 \rightarrow (a_2)^1(a_2^1)$ | $(b_g)^2 \rightarrow (b_g)^1(b_g)^1$

$a_2 \otimes b_1$ b_2 allowed y | $b_g \otimes a_u$ b_u allowed x, y

$a_2 \otimes a_2$ a_1 allowed z | $b_g \otimes b_g$ a_g forbidden

x b_1
y b_2
z a_1

x, y b_u
z a_u

DIPOLE
OPERATORS

I ORBTAL II

I VIBRONIC II

Allowed b_1, b_2, a_1 Vibrations | Allowed b_u or a_u Vibrations

C_{2v}	E	C_2	$\sigma(xz)$	$\sigma(yz)$
	30	0	0	30

C_{2h}	E	C_2	i	σ_h
Γ_{CART}	30	0	0	10

V.I.F → $\Gamma_{CART} =$

VIF → $\Gamma_{CART} = 10a_g + 5b_g + 5a_u + 10$

$\Gamma_{ROT+TRANS} = a_1 + b_1 + b_2 + a_2 + b_1 + b_2$

$\Gamma_{ROT+TRANS} = a_u + 2b_u + a_g + 2b$

$\Gamma_{vib} =$

$\Gamma_{vib} = 9a_g + 3b_g + \underline{\underline{4a_u}} + \underline{\underline{8b_u}}$

Our Goal - TO LEARN SOMETHING ABOUT STRUCTURE AND SPECTRA OF MOLECULES FROM SYMMETRY ONLY

- NO 'TOUGH' NUMERICAL WORK.
- ZERO/NONZERO INTEGRALS.

In The Beginning -

$\boxed{\text{PRECISE CHARACTERIZATION SYMMETRY}}$

- GROUP
- SYMMETRY ELEMENTS
- SYMMETRY OPERATIONS
- GROUP MULTIPLICATION TABLE

$\boxed{\text{POINT SYMMETRY GROUPS}}$

- FLOWCHARTS

IMPORTANT BUT RELATIVELY STRAIGHTFORWARD

POINT GROUP

- DIPOLE MOMENT? $\vec{\mu}$
- CHIRAL?

OPTICALLY ACTIVE

CLASS STRUCTURE

- EQUIVALENT SYMMETRY ELEMENTS

SYMMETRY OPERATIONS BY MATRICES

$$\underline{\underline{C}}_\theta = \begin{pmatrix} \cos\theta & \sin\theta & 0 \\ -\sin\theta & \cos\theta & 0 \\ 0 & 0 & 1 \end{pmatrix} \qquad z$$

$$\underline{\underline{I}} = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} \qquad \underline{\underline{i}} = \begin{pmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{pmatrix}$$

$$\underline{\underline{\sigma}} = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -1 \end{pmatrix} \qquad \underline{\underline{S}}_\theta = \begin{pmatrix} \cos\theta & \sin\theta & 0 \\ -\sin\theta & \cos\theta & 0 \\ 0 & 0 & -1 \end{pmatrix}$$

TRACES $\chi(\underline{\underline{C}})$

MATRICES AS **REPRESENTATIONS** OF GROUPS.

$\left.\begin{array}{l}\text{REDUCIBLE}\\ \text{IRREDUCIBLE}\end{array}\right\}$ REPRESENTATIONS

GREAT

ORTHOGONALITY

THEOREM

G.O.T.

GREAT BUT 'COMPLICATED'.
SIMPLER TO USE **CHARACTERS**.

$$\boxed{a_i = \frac{1}{h}\sum_R \chi(R)\,\chi_i(R)}$$!!!!

SYMMETRY CLASSIFICATION.

Ψ AS BASES IRREDUCIBLE REPRESENTATIONS.

DIRECT $\boxed{\otimes}$ PRODUCT

NORMAL MODES

$(3N - 6)$

3N CARTESIAN COORDINATE VECTORS BASES

$\Downarrow$

Γ_{CART} REDUCIBLE

$$a_i = \frac{1}{h} \sum_R \chi(R) \chi_i(R)$$

$- \Gamma_{TRANS}$

$- \Gamma_{ROT}$

Γ_{VIB}

Γ_{STR}

Γ_{BEND}

CHARACTER TABLES

$x \quad y \quad z$

$R_x \quad R_y \quad R_z$

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CARE WITH "A_1" BENDS

$\psi_i(v=0) \quad A_1$

$\boxed{\text{IR ACTIVE FUNDAMENTAL}}$ $\Gamma\begin{pmatrix} x \\ y \\ z \end{pmatrix} \otimes \Gamma\psi_j(v=1) = A_1$

$\boxed{\text{RAMAN ACTIVE FUNDAMENTAL}}$ $\Gamma\begin{pmatrix} x^2 \\ y^2 \\ z^2 \end{pmatrix} \otimes \Gamma\psi_j(v=1) = A_1$

$xy \ldots$

CENTROSYMMETRIC

$i \rightarrow g$ RAMAN

$i \rightarrow u$ IR

$\boxed{\text{COMBINATION}}$

IR $\Gamma\begin{pmatrix} x \\ y \\ z \end{pmatrix} \otimes \Gamma_{\psi_j(v=1)} \otimes \Gamma_{\psi_k(v=}$

$= A_1$

$\boxed{\text{GROSS SELECTION RULES}}$

IR $\frac{\partial \mu_i}{\partial \Phi} \neq 0$

RAMAN CHANGE POLARIZABILI

RAMAN - BLUE SKY

- STOKES & ANTISTOKES

ELECTRONIC SPECTRA

SPIN $\qquad \Delta S = 0$ ALLOWED

ORBITALS $\longrightarrow$ STATES

$$(\ )^2 \qquad a_1$$

$$(\ )^1 \otimes (\ )^1 \rightarrow {}^{1,3}\underline{\quad}$$

$\boxed{\text{ORBITALLY ALLOWED}}$

$$\Gamma\begin{pmatrix}x\\y\\z\end{pmatrix} \otimes \Gamma\psi_j(el) = A_1$$

$\boxed{\text{VIBRONIC}}$

$$\Gamma\begin{pmatrix}x\\y\\z\end{pmatrix} \otimes \Gamma\psi_j\, el \otimes \Gamma\psi_j\, vib\,(v=1) = A_1$$

$\boxed{\text{JABLONSKI}}$ $\qquad$ $\boxed{\text{TYPES OF TRANSIT}^{N}}$