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WINTER COLLEGE ON LASERS, ATOMIC AND MOLECULAR PHYSICS

(21 January - 22 March 1985)

THEORY OF POINT GROUPS

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THEORY OF POINT GROUPS

1) Case of the XY_2 non-linear symmetrical molecules

- Physical system (Fig. 1)
- Choice of xyz (Fig. 2)
- Symmetry operations (Fig. 3)

	I	$C_z(\pi)$	σ_{xz}	σ_{yz}
I	I	$C_z(\pi)$	σ_{xz}	σ_{yz}
$C_z(\pi)$	$C_z(\pi)$	I	σ_{yz}	σ_{xz}
σ_{xz}	σ_{xz}	σ_{yz}	I	$C_z(\pi)$
σ_{yz}	σ_{yz}	σ_{xz}	$C_z(\pi)$	I

(1)

- Transformation of the components of a vector (Fig. 4)

$$M_{\gamma'} = \chi\, M_{\gamma} \qquad (\gamma = x\,y\,z) \qquad (2)$$

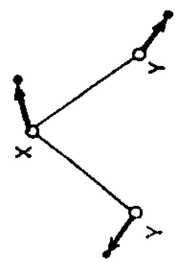


Fig. 1

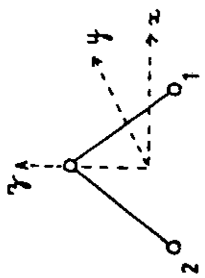


Fig. 2

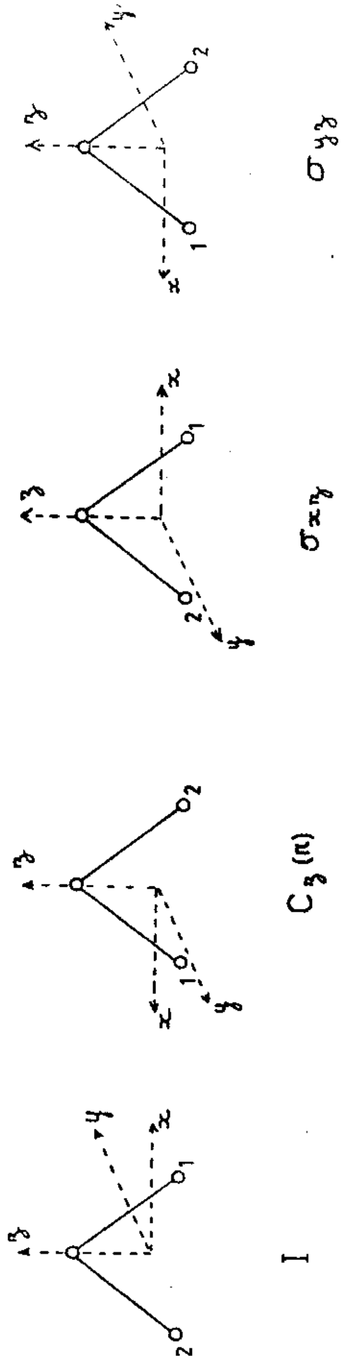


Fig. 3

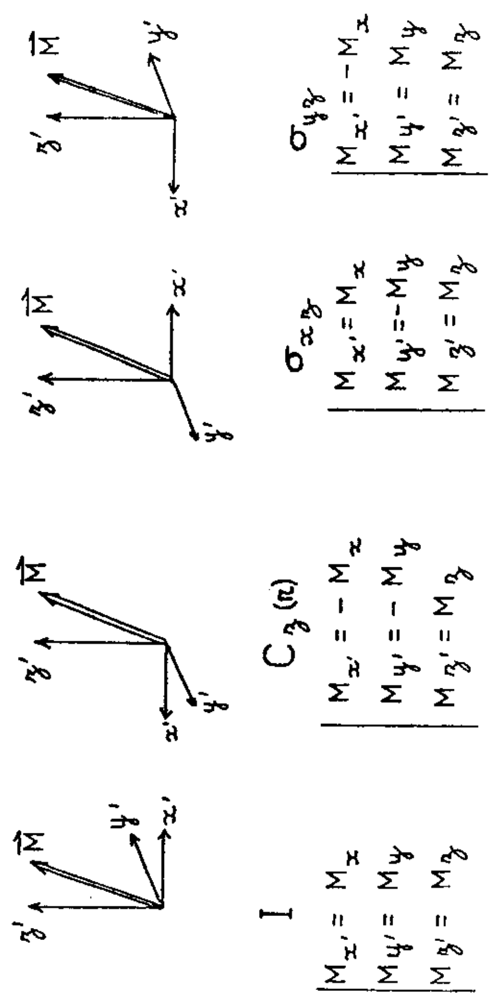


Fig. 4

	I	$C_z(\pi)$	σ_{xz}	σ_{yz}
M_x	1	-1	1	-1
M_y	1	-1	-1	1
M_z	1	1	1	1

(3)

- Tranformation of the components of a tensor

$$M_{x'} M_{y'} = \chi M_x M_y \quad (4)$$

	I	$C_z(\pi)$	σ_{xz}	σ_{yz}
$M_x M_y$	1	1	-1	-1

(5)

- Symmetry species

	I	$C_z(\pi)$	σ_{xz}	σ_{yz}
A_1	1	1	1	1
A_2	1	1	-1	-1
B_1	1	-1	1	-1
B_2	1	-1	-1	1

(6)

A_1	scalars	M_z	$\alpha_{xx}\ \alpha_{yy}\ \alpha_{zz}$	
A_2			α_{xy}	(7)
B_1		M_x	α_{xz}	
B_2		M_y	α_{yz}	

- Symmetry species of a product

$A_1 \cdot A_1 = A_1$	$A_1 \cdot A_2 = A_2$	$A_2 \cdot B_1 = B_2$	
$A_2 \cdot A_2 = A_1$	$A_1 \cdot B_1 = B_1$	$A_2 \cdot B_2 = B_1$	(8)
$B_1 \cdot B_1 = A_1$	$A_1 \cdot B_2 = B_2$	$B_1 \cdot B_2 = A_2$	
$B_2 \cdot B_2 = A_1$			

- Symmetry species of normal coordinates

$$Q_{s\sigma} = \sum_{i\,\alpha} \ell^{\alpha}_{i\,s\sigma}\ m_i^{\frac{1}{2}}\ \Delta\alpha_i \qquad (9)$$

- Symmetry species of vibrational wave functions

$$H = H(1) + H(2) + H(3) \qquad (10)$$

$$\Psi_{v_1 v_2 v_3}(Q_1 Q_2 Q_3) = \Psi_{v_1}(Q_1)\,\Psi_{v_2}(Q_2)\,\Psi_{v_3}(Q_3) \qquad (11)$$

$$\Psi_{v_s}(-Q_s) = \Psi_{v_s}(Q_s) \quad \text{if } \underline{v_s \text{ even}}$$
$$\Psi_{v_s}(-Q_s) = -\Psi_{v_s}(Q_s) \quad \text{if } \underline{v_s \text{ odd}} \qquad (12)$$

$$A_1 \cdot A_1 \cdot A_1 = A_1$$
$$A_1 \cdot A_1 \cdot B_1 = B_1 \qquad (13)$$

$$\Psi_{v_1 v_2 v_3}(Q_1 Q_2 Q_3) \text{ is } \begin{cases} A_1 & \text{if } v_3 \text{ is even} \\ B_1 & \text{if } v_3 \text{ is odd} \end{cases} \qquad (14)$$

- Vibrational selection rules

$$\mathfrak{J} = \int_\tau \overline{\Psi}_m\ R\ \Psi_n\ d\tau \qquad (15)$$

$$\Psi_m \Psi_n \text{ is } \begin{cases} A_1 & \text{if } \Delta v_3 \text{ is even} \\ B_1 & \text{if } \Delta v_3 \text{ is odd} \end{cases} \qquad (16)$$

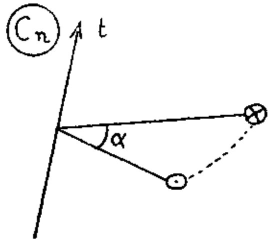
Emission absorption :

$$\int_\tau \overline{\psi}_m\ M_x\ \psi_n\ d\tau \neq 0 \quad \text{if} \quad \Delta v_3 = \pm 1, \pm 3, \pm 5, \ldots \qquad (17)$$

$$\int_\tau \overline{\psi}_m\ M_z\ \psi_n\ d\tau \neq 0 \quad \text{if} \quad \Delta v_3 = \pm 0, \pm 2, \pm 4, \ldots \qquad (18)$$

Rotation

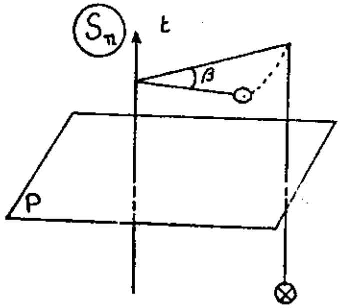
$C_t(\alpha)$



$\alpha = \frac{2\pi}{n}, \frac{4\pi}{n}, \frac{6\pi}{n}, \ldots$

Rotation-reflection

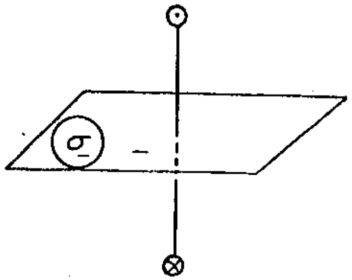
$S_t(\beta)$



$\beta = \frac{2\pi}{n}, \frac{6\pi}{n}, \frac{10\pi}{n}, \ldots$

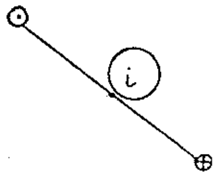
Reflection

σ



Inversion

i



A symmetry operation transforms point ⊙ into point ⊗

Fig . 5

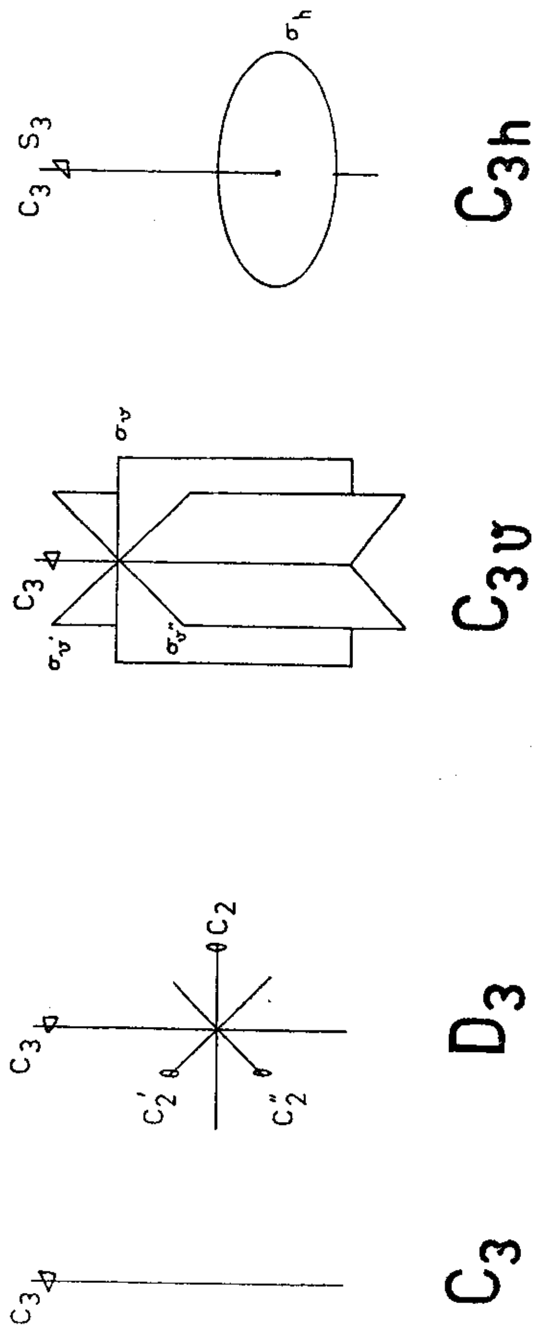


Fig. 6

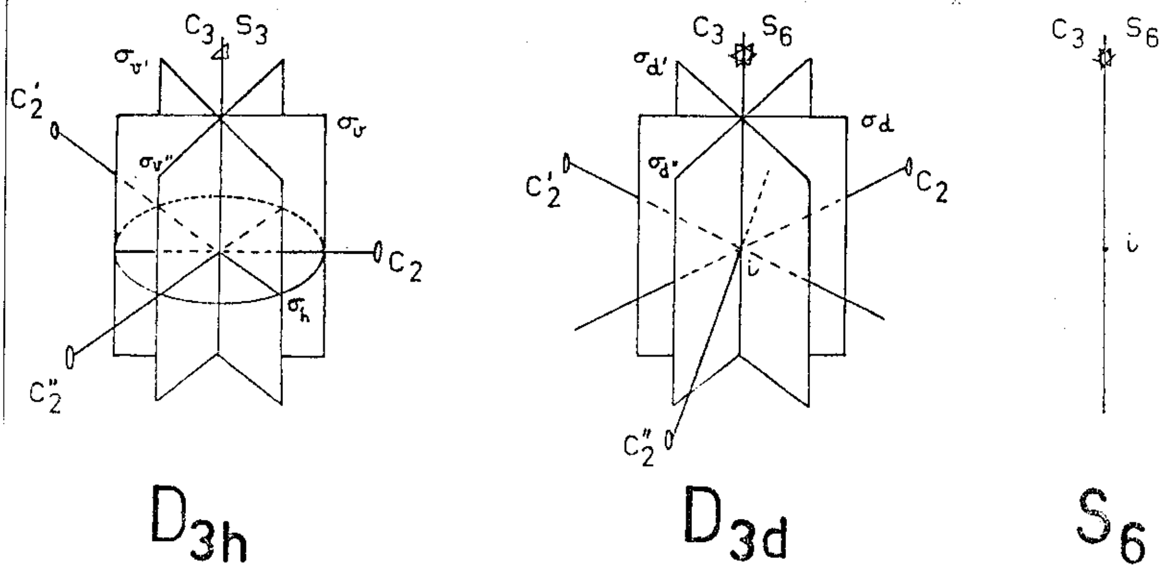


Fig.6 (continued)

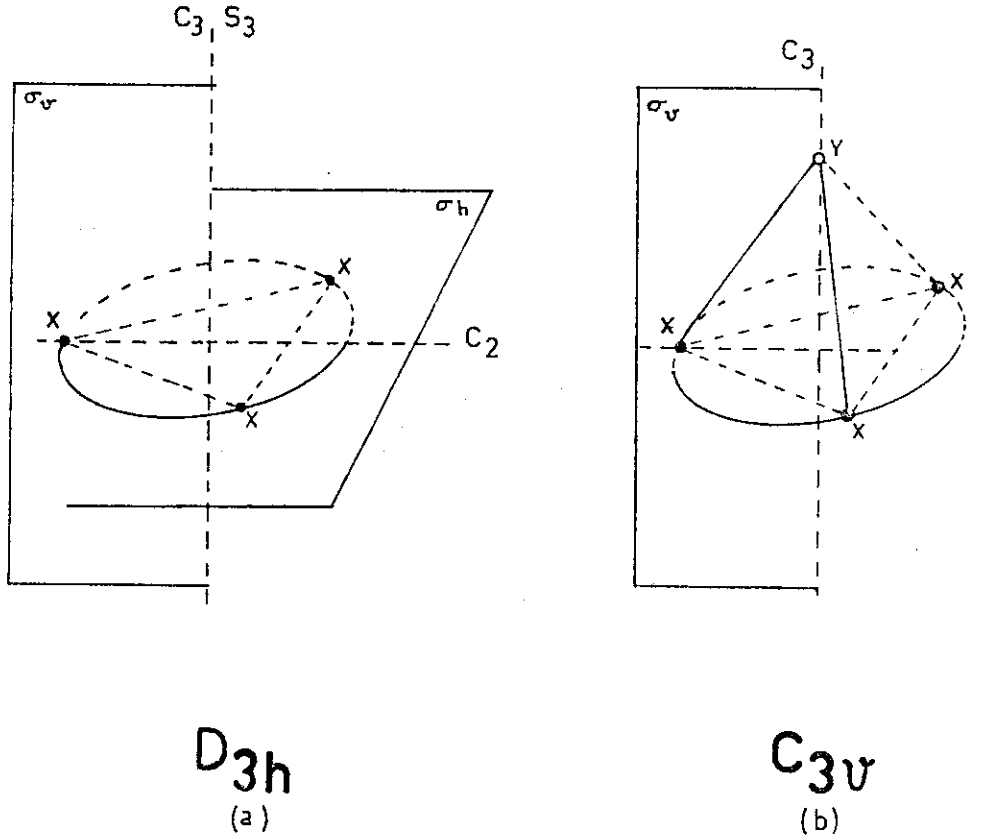
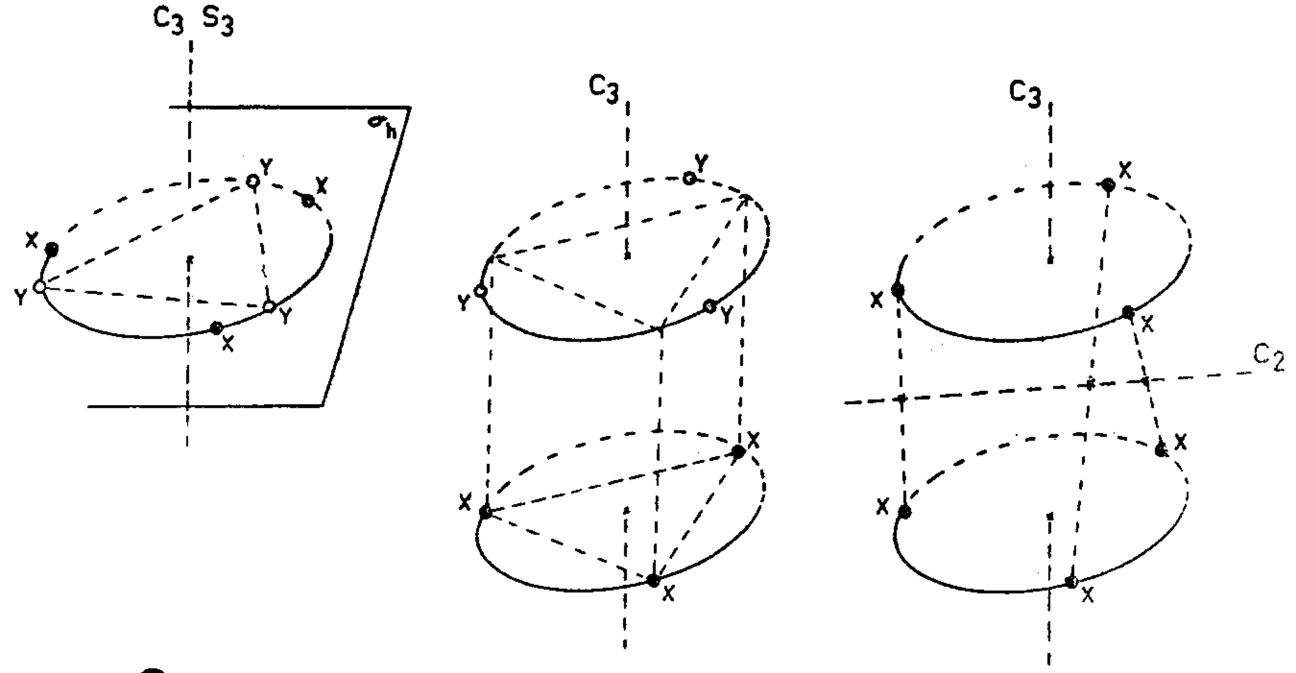


Fig.7

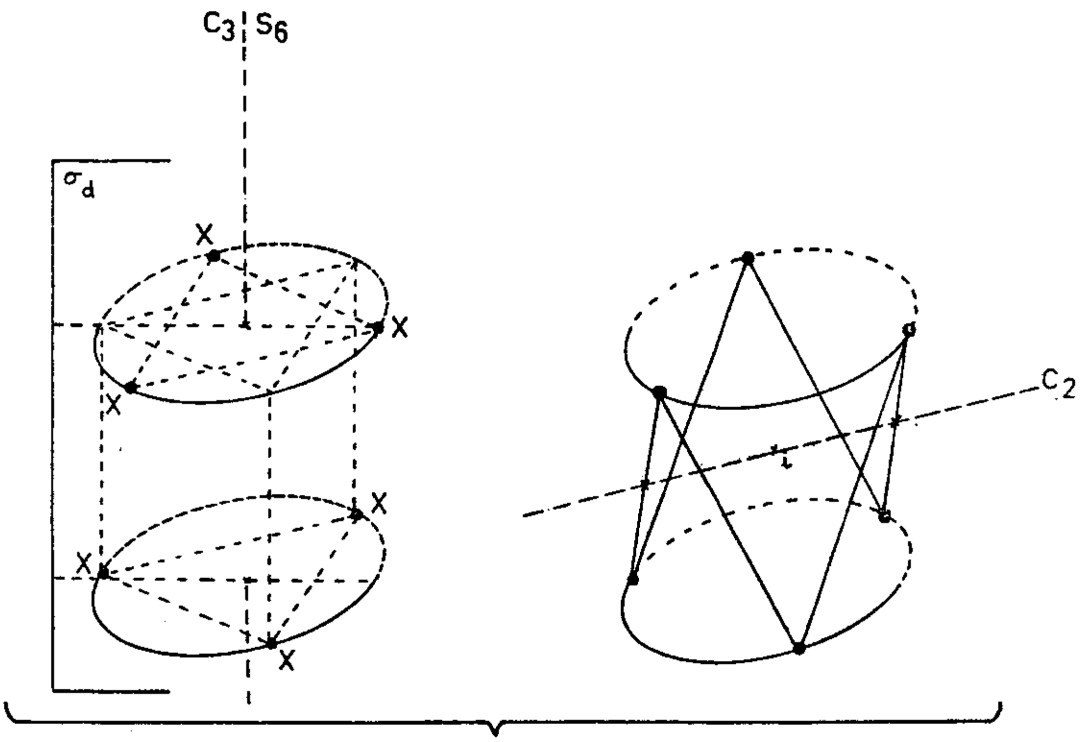


C_{3h}
(c)

C_3
(d)

D_3
(e)

Fig . 7 (continued)



D_{3d}
(f)

Fig. 7 (end)

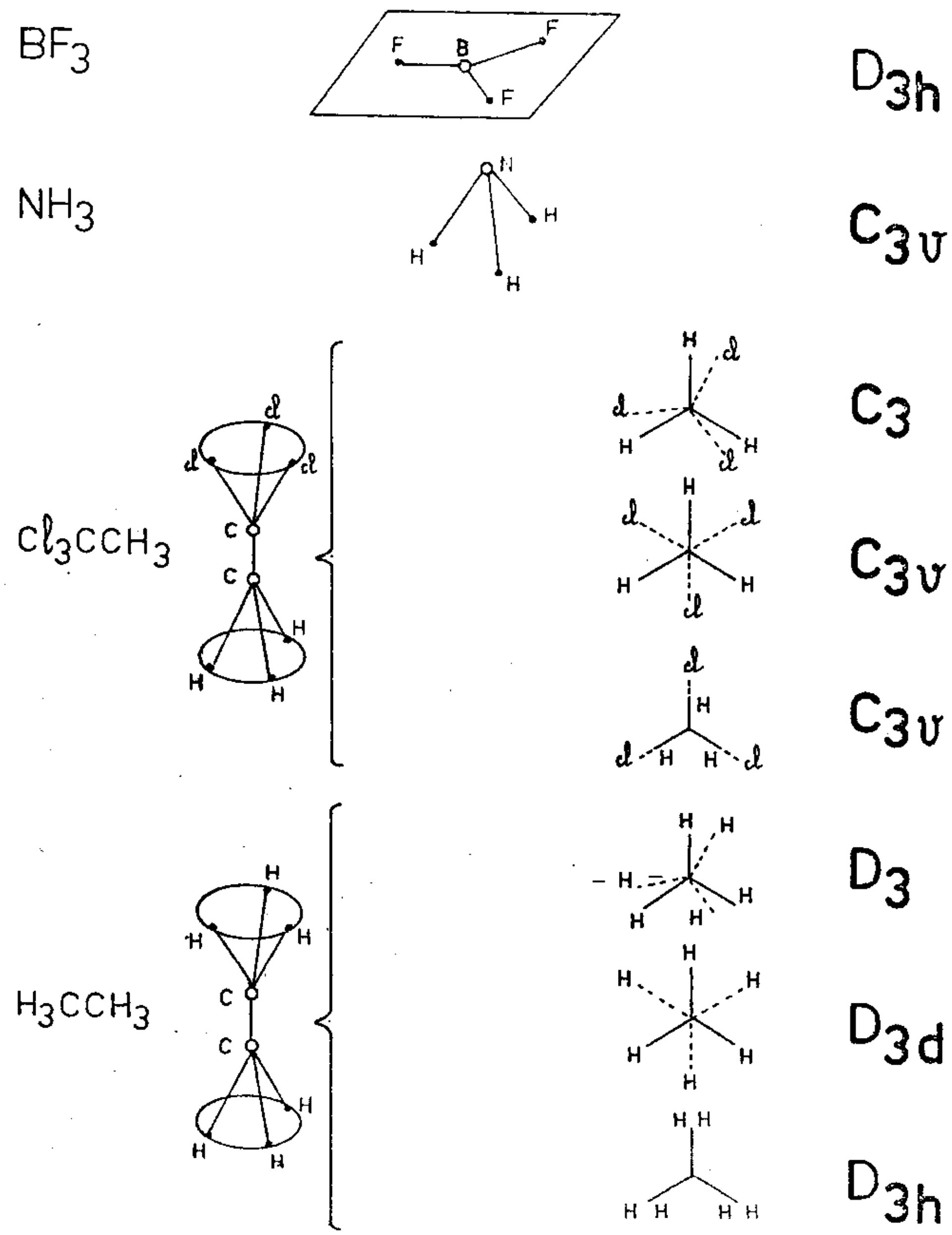


Fig. 8

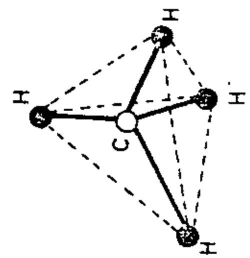


Fig. 11

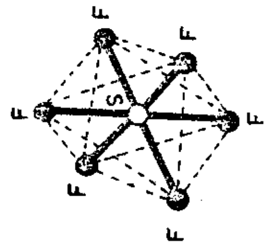


Fig. 12

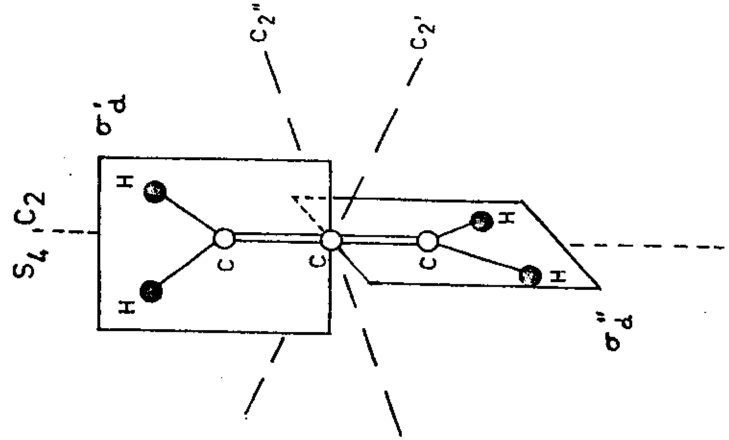


Fig. 10

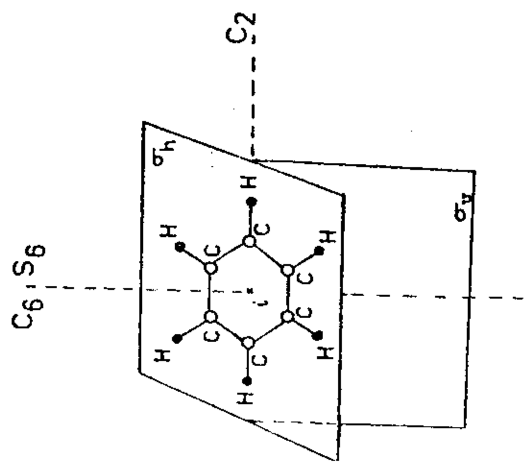


Fig. 9

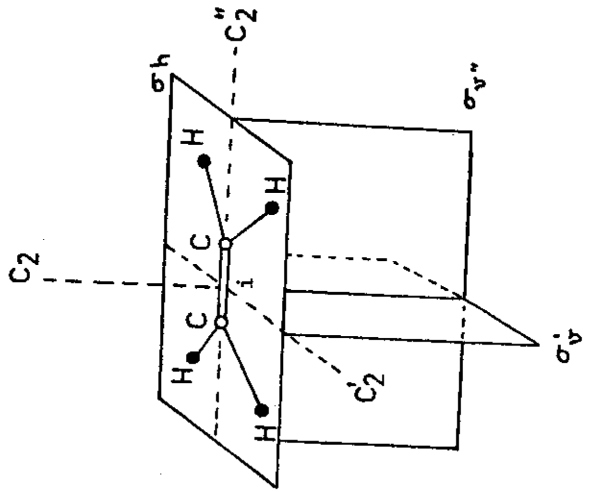


Fig. 14

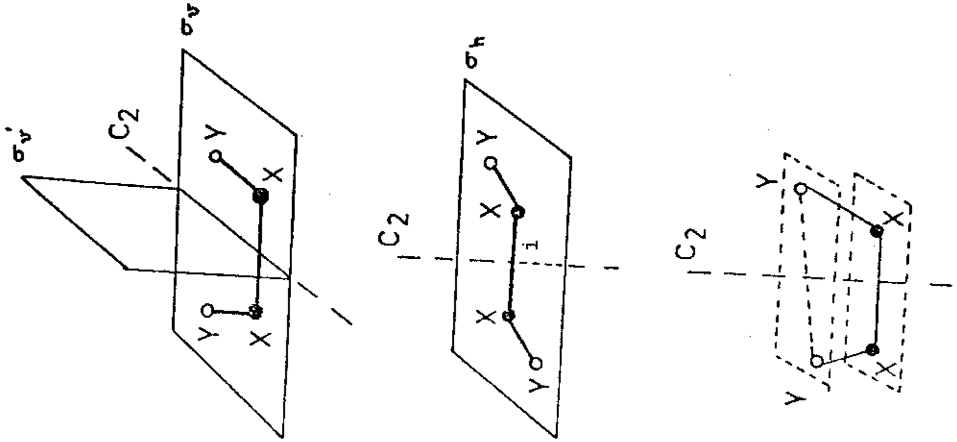


Fig. 13

TABLE I

Group	Elements of symmetry	Order	Operations of symmetry
C_3	C_3	3	(3) $C_z\left(k\frac{2\pi}{3}\right)$ including I
D_3	C_3 $3C_2$	6	(3) $C_z\left(k\frac{2\pi}{3}\right)$ " I (3) $C_w(\pi)$
C_{3v}	C_3 $3\sigma_v$	6	(3) $C_z\left(k\frac{2\pi}{3}\right)$ " I (3) σ_v
C_{3h}	C_3 S_3 σ_h	6	(3) $C_z\left(k\frac{2\pi}{3}\right)$ " I (3) $S_z\left(k\frac{2\pi}{3}\right)$ " σ_h
D_{3h}	C_3 S_3 $3C_2$ $3\sigma_v$ σ_h	12	(3) $C_z\left(k\frac{2\pi}{3}\right)$ " I (3) $C_w(\pi)$ (3) $S_z\left(k\frac{2\pi}{3}\right)$ " σ_h (3) σ_v
D_{3d}	C_3 S_6 $3C_2$ $3\sigma_d$ i	12	(3) $C_z\left(k\frac{2\pi}{3}\right)$ " I (3) $C_w(\pi)$ (3) $S_z\left((2k+1)\frac{\pi}{3}\right)$ " i (3) σ_d
S_6	C_3 S_6 i	6	(3) $C_z\left(k\frac{2\pi}{3}\right)$ " I (3) $S_z\left((2k+1)\frac{\pi}{3}\right)$ " i

TABLE II

N = 3	C_3	D_3	C_{3v}	C_{3h}	D_{3h}	D_{3d}	S_6		
N = 4	C_4	D_4	C_{4v}	C_{4h}	D_{4h}			D_{2d}	S_4
N = 5	C_5	D_5	C_{5v}	C_{5h}	D_{5h}	D_{5d}	S_{10}		
N = 6	C_6	D_6	C_{6v}	C_{6h}	D_{6h}				
N = 7	C_7	D_7	C_{7v}	C_{7h}	D_{7h}	D_{7d}	S_{14}		
N = 8	C_8	D_8	C_{8v}	C_{8h}	D_{8h}			D_{4d}	S_8

....

2) General method

a) Symmetry group of the equilibrium configuration

- elements of symmetry (Fig. 5)
- operations of symmetry (Fig. 5)
- case of an axially symmetric molecule with $n = 3$ (Fig. 6, 7, 8) (Table I)
- axially symmetric molecules (Table II)

$$C_n \ , \ D_n \ , \ C_{nv} \ , \ C_{nh} \ , \ D_{nh} \qquad n \geqslant 3$$

$$D_{nd} \ , \ S_{2n} \qquad n \geqslant 2 \tag{19}$$

Examples : D_{6h} (Fig. 9)
D_{2d} (Fig. 10)

- linear molecules
- spherical top molecules (Fig. 11, 12)
- asymmetric molecules (Fig. 13, 14)

b) Laws of transformation of the various properties of the molecule

- representations

$$S' = \chi_i \ S \qquad (\chi_i = \pm 1) \tag{20}$$

	Operations				
	I	...	O_1	O_j	...
S	$S^{(I)} = S$	...	$S^{(i)} = \chi_1 S$	$S^{(j)} = \chi_j S$	...

(21)

	Operations				
	I	...	O_i	O_j	...
S_1	$S_1^{(I)} = S_1$	...	$S_1^{(i)} = \beta^i_{11} S_1 + \beta^i_{12} S_2$	$S_1^{(j)} = \beta^j_{11} S_1 + \beta^j_{12} S_2$	...
S_2	$S_2^{(I)} = S_2$	...	$S_2^{(i)} = \beta^i_{21} S_1 + \beta^i_{22} S_2$	$S_2^{(j)} = \beta^j_{21} S_1 + \beta^j_{22} S_2$	...

(22)

$$\begin{Bmatrix} 1 & 0 \\ 0 & 1 \end{Bmatrix} \quad \cdots \quad \begin{Bmatrix} \beta^i_{11} & \beta^i_{12} \\ \beta^i_{21} & \beta^i_{22} \end{Bmatrix} \quad \begin{Bmatrix} \beta^j_{11} & \beta^j_{12} \\ \beta^j_{21} & \beta^j_{22} \end{Bmatrix} \quad \cdots \qquad (23)$$

$$\begin{cases} O_k = O_i \, O_j \\ \{\beta^k\} = \{\beta^i\}\{\beta^j\} \end{cases} \qquad (24)$$

- characters

$$\chi_i = \beta^i_{11} + \beta^i_{22} \qquad (25)$$

	Operations				
	I	...	O_i	O_j	
S_1, S_2	2	...	$\chi_i \left(= \beta^i_{11} + \beta^i_{22}\right)$	$\chi_j \left(= \beta^j_{11} + \beta^j_{22}\right)$	...

(26)

	Operations				
	I	...	O_i	O_j	...
S	1	...	χ_i	χ_j	...

(27)

- symmetry species ; example : group C_{3v}

	I	$C_z\left(\frac{2\pi}{3}\right)$	$C_z\left(\frac{4\pi}{3}\right)$	σ_v	$\sigma_{v'}$	$\sigma_{v''}$
A_1	1	1	1	1	1	1
A_2	1	1	1	-1	-1	-1
E	2	-1	-1	0	0	0

(28)

	I	$2C_z$	$3\sigma_v$
A_1	1	1	1
A_2	1	1	-1
E	2	-1	0

(29)

- vibrational selection rules

$$\int_\tau \overline{\Psi_m} \; R \; \Psi_n \, d\tau \qquad (30)$$

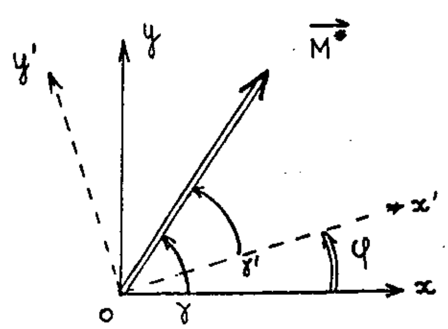
3) Case of the non-symmetrical linear molecule

- Group $C_{\infty v}$
- Transformation of M_x M_y M_z P_z

	Operations				
	I	$C_z(\varphi)$	...	$\sigma_{v\theta}$	...
M_z	$M_z^{(I)} = M_z$	$M_z^{(C)} = M_z$	...	$M_z^{(\sigma)} = M_z$	...
	$\{1\}$	$\{1\}$	...	$\{1\}$	...

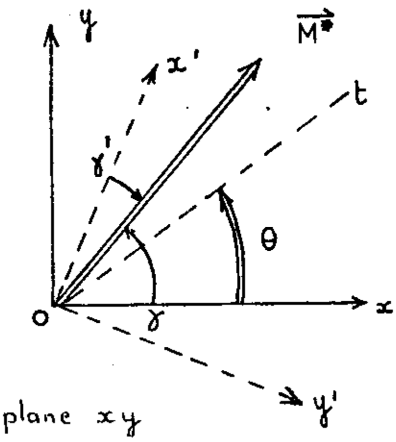
(31)

Rotation by an angle φ about the origin



Reflection with respect to t

[(Ox, Ot) = θ]



$$\begin{cases} M_x = \rho\cos\gamma \\ M_y = \rho\sin\gamma \end{cases}$$

$$\begin{cases} M_{x'} = \rho\cos\gamma' \\ M_{y'} = \rho\sin\gamma' \end{cases}$$

ρ : modulus of $\vec{M}^*$

$\vec{M}^*$: Projection of $\vec{M}$ on the plane xy

Rotation:

$$\boxed{\gamma' = \gamma - \varphi}$$

$$\begin{cases} M_{x'} = \rho\,(\cos\gamma\cos\varphi + \sin\gamma\sin\varphi) \\ M_{y'} = \rho\,(\sin\gamma\cos\varphi - \cos\gamma\sin\varphi) \end{cases}$$

$$\begin{cases} M_{x'} = M_x\cos\varphi + M_y\sin\varphi \\ M_{y'} = -M_x\sin\varphi + M_y\cos\varphi \end{cases}$$

Reflection:

$$\boxed{\gamma' = -\gamma + 2\theta}$$

$$\begin{cases} M_{x'} = \rho\,(\cos\gamma\cos 2\theta + \sin\gamma\sin 2\theta) \\ M_{y'} = \rho\,(\cos\gamma\sin 2\theta - \sin\gamma\cos 2\theta) \end{cases}$$

$$\begin{cases} M_{x'} = M_x\cos 2\theta + M_y\sin 2\theta \\ M_{y'} = M_x\sin 2\theta - M_y\cos 2\theta \end{cases}$$

Fig.15

Operations

	I	$C_z(\varphi)$	...	$\sigma_{v\theta}$	...	
M_x	$M_x^{(I)} = M_x$	$M_x^{(C)} = M_x\cos\varphi + M_y\sin\varphi$	...	$M_x^{(\sigma)} = M_x\cos 2\theta + M_y\sin 2\theta$	...	(32)
M_y	$M_y^{(I)} = M_y$	$M_y^{(C)} = -M_x\sin\varphi + M_y\cos\varphi$	...	$M_y^{(\sigma)} = M_x\sin 2\theta - M_y\cos 2\theta$	...	

$$\begin{Bmatrix} 1 & 0 \\ 0 & 1 \end{Bmatrix} \quad \begin{Bmatrix} \cos\varphi & \sin\varphi \\ -\sin\varphi & \cos\varphi \end{Bmatrix} \quad \cdots \quad \begin{Bmatrix} \cos 2\theta & \sin 2\theta \\ \sin 2\theta & -\cos 2\theta \end{Bmatrix} \quad \cdots \tag{33}$$

$$\vec{P} = \vec{V} \wedge \vec{W} \tag{34}$$

$$P_z = V_x W_y - V_y W_x \tag{35}$$

$$P_z = \rho\sigma(\cos\gamma\sin\delta - \sin\gamma\cos\delta) = \rho\sigma\sin(\delta - \gamma) \tag{36}$$

Operations

	I	$C_z(\varphi)$	...	$\sigma_{v\theta}$	...	
P_z	$P_z^{(I)} = P_z$	$P_z^{(C)} = P_z$	...	$P_z^{(\sigma)} = -P_z$	...	(37)
	$\{1\}$	$\{1\}$	...	$\{-1\}$	...	(38)

	Operations				
	I	$C_z(\varphi)$	...	$\sigma_{v\theta}$	...
M_z	1	1	...	1	...
P_z	1	1	...	-1	...
$M_x\ M_y$	2	$2\cos\varphi$	...	0	...

(39)

- Table of characters

	I	$2\,C_z(\varphi)$	...	$\infty\,\sigma_v$
Σ^+	1	1	...	1
Σ^-	1	1	...	-1
Π	2	$2\cos\varphi$	...	0
Δ	2	$2\cos 2\varphi$	...	0
Φ	2	$2\cos 3\varphi$	...	0
Γ	2	$2\cos 4\varphi$	...	0
...	...	...	...	...

(40)

- Transformation of normal coordinates (Fig. 16)
- Transformation of vibrational wave functions

$$\Psi_{v_1 v_2 \ell_2 v_3}(Q_1\ r\chi\ Q_3) = \Psi_{v_1}(Q_1)\,\Psi_{v_2\ell_2}(r\ \chi)\,\Psi_{v_3}(Q_3) \qquad (41)$$

$$\left.\begin{aligned} Q_{21} &= r\cos\chi \\ Q_{22} &= r\sin\chi \end{aligned}\right\}\ \text{(Fig. 17)} \qquad (42)$$

$$\Psi_{v_2\ell_2}(r,\chi) = F_{v_2|\ell_2|}(r)\, e^{i\ell_2\chi} \qquad (43)$$

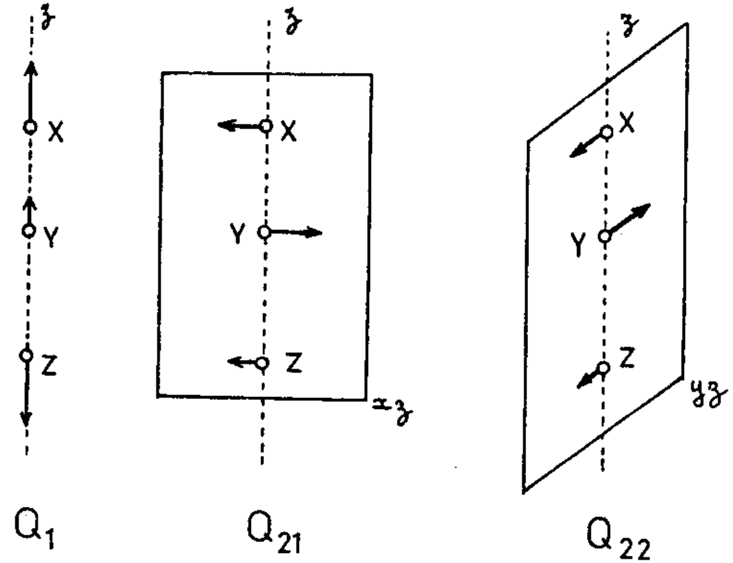


Fig.16

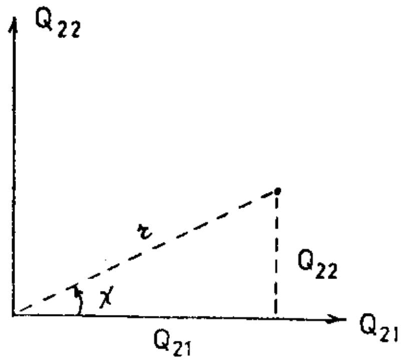


Fig.17

Operation I	$r,\chi \rightarrow r,\chi$	
Operation $C_z(\varphi)$	$r,\chi \rightarrow r,\chi-\varphi$	(44)
Operation $\sigma_{v\theta}$	$r,\chi \rightarrow r,2\theta-\chi$	

	Operations				
	I	$C_z(\varphi)$	....	$\sigma_{v\theta}$	...
$\Psi_{v_2\ell_2}$	$\Psi^{(I)}_{v_2\ell_2}=\Psi_{v_2\ell_2}$	$\Psi^{(C)}_{v_2\ell_2}=e^{-i\ell_2\varphi}\,\Psi_{v_2\ell_2}$	....	$\Psi^{(\sigma)}_{v_2\ell_2}=e^{2i\ell_2\theta}\Psi_{v_2-\ell_2}$	...
$\Psi_{v_2-\ell_2}$	$\Psi^{(I)}_{v_2-\ell_2}=\Psi_{v_2-\ell_2}$	$\Psi^{(C)}_{v_2-\ell_2}=e^{i\ell_2\varphi}\,\Psi_{v_2-\ell_2}$	....	$\Psi^{(\sigma)}_{v_2-\ell_2}=e^{-2i\ell_2\theta}\Psi_{v_2\ell_2}$	...

(45)

$$\begin{Bmatrix} 1 & 0 \\ 0 & 1 \end{Bmatrix} \qquad \begin{Bmatrix} e^{-i\ell_2\varphi} & 0 \\ 0 & e^{i\ell_2\varphi} \end{Bmatrix} \qquad \cdots\cdots \qquad \begin{Bmatrix} 0 & e^{2i\ell_2\theta} \\ e^{-2i\ell_2\theta} & 0 \end{Bmatrix} \qquad \cdots \tag{46}$$

	Operations				
	I	$C_z(\varphi)$	...	$\sigma_{v\theta}$	...
$\Psi_{v_2\ell_2},\Psi_{v_2-\ell_2}$	2	$2\cos\ell_2\varphi$	...	0	...

(47)

$$\overline{\Psi'_v}\,\Psi''_v = \Psi'_1\ \Psi''_1\ \Psi'_3\ \Psi''_3\ {}_{F'F''}\ e^{i(\ell''_2-\ell'_2)\chi} \tag{48}$$

$\overline{\Psi'_v}\,\Psi''_v$ is Σ, when $\Delta\ell_2 = 0$
Π, when $\Delta\ell_2 = \pm 1$ (49)
Δ, when $\Delta\ell_2 = \pm 2$

- Products of symmetry species

$$\Pi\,\Delta = \Phi + \Pi \tag{50}$$

$$\Pi\,\Pi = \Delta + \Sigma + \Sigma \tag{52}$$

$$\left\{\begin{array}{l} e^{\pm i\chi_1}\,e^{\pm 2i\chi_2} = e^{\pm i(\chi_1+2\chi_2)} \\ e^{\mp i\chi_1}\,e^{\pm 2i\chi_2} = e^{\pm i(-\chi_1+2\chi_2)} \end{array}\right. \tag{51}$$

$$\left\{\begin{array}{l} e^{\pm i\chi_1}\,e^{\pm i\chi_2} = e^{\pm i(\chi_1+\chi_2)} \\ e^{\pm i\chi_1}\,e^{\pm i\chi_2} = e^{\pm i(-\chi_1+\chi_2)} \end{array}\right. \tag{53}$$

$$\Pi\,\Pi = \Delta + \Sigma^+ + \Sigma^- \tag{54}$$

$(\Delta\ell=0)$	$(\Delta\ell=\pm1)$	$(\Delta\ell=\pm2)$	etc...
$\Sigma^+\Sigma^+=\Sigma^+$	$\Sigma^+\Pi=\Pi$	$\Sigma^+\Delta=\Delta$	
$\Sigma^-\Sigma^-=\Sigma^+$	$\Sigma^-\Pi=\Pi$	$\Sigma^-\Delta=\Delta$	
$\Sigma^+\Sigma^-=\Sigma^-$	$\Pi\Delta=\Phi+\Pi$	$\Pi\ \Phi=\Gamma+\Delta$	(55)
$\Pi\,\Pi=\Delta+\Sigma^++\Sigma^-$	etc ...	etc ...	
$\Delta\Delta=\Gamma+\Sigma^++\Sigma^-$			
etc			

$$\left\{\begin{array}{ll} V_xW_x + V_yW_y & \Sigma^+ \\ V_xW_y - V_yW_x & \Sigma^- \\ \left.\begin{array}{l} V_xW_x - V_yW_y \\ V_xW_y + V_yW_x \end{array}\right\} & \Delta \end{array}\right. \qquad (56)$$

	Operations				
	I	$C_z(\varphi)$	...	$\sigma_{v\theta}$	...
$V_xW_x - V_yW_y$ $V_xW_y + V_yW_x$	$\begin{Bmatrix} 1 & 0 \\ 0 & 1 \end{Bmatrix}$	$\begin{Bmatrix} \cos 2\varphi & \sin 2\varphi \\ -\sin 2\varphi & \cos 2\varphi \end{Bmatrix}$	...	$\begin{Bmatrix} \cos 4\theta & \sin 4\theta \\ \sin 4\theta & -\cos 4\theta \end{Bmatrix}$	... (57)

$$\begin{array}{ll|l} V_xW_x\ , & V_yW_y & \Sigma^+,\ \Delta \\ V_xW_y\ , & V_yW_x & \Sigma^-,\ \Delta \end{array} \qquad (58)$$

- Components of a tensor

	species
$T_{xx} + T_{yy}$	Σ^+
$T_{xx} - T_{yy}$	Δ
$T_{xy} + T_{yx}$	Δ
$T_{xy} - T_{yx}$	Σ^-

	species
T_{zz}	Σ^+
T_{xz}	Π
T_{yz}	Π
T_{zx}	Π
T_{zy}	Π

(59)

- vibrational selection rules

Polarisability

α_{xx}	$\Sigma^+\ \Delta$
α_{yy}	$\Sigma^+\ \Delta$
α_{zz}	Σ^+
$\alpha_{xy}\ (=\alpha_{yx})$	Δ
$\alpha_{yz}\ (=\alpha_{zy})$	Π
$\alpha_{zx}\ (=\alpha_{xz})$	Π

Electric dipole moment

M_x	Π
M_y	Π
M_z	Σ^+

(60)

(Emission, absorption) : $\Delta\ell_2 = 0, \pm 1$ (61)

(Raman scattering) $\Delta\ell_2 = 0, \pm 1, \pm 2$ (62)

If $\Delta\ell_2 = 0$ (E, A, RS) and $\ell_2 = 0$: $\Sigma^+ \leftrightarrow \Sigma^+\ ,\ \Sigma^- \leftrightarrow \Sigma^-\ ,\ \Sigma^+ \not\leftrightarrow \Sigma^-$ (63)

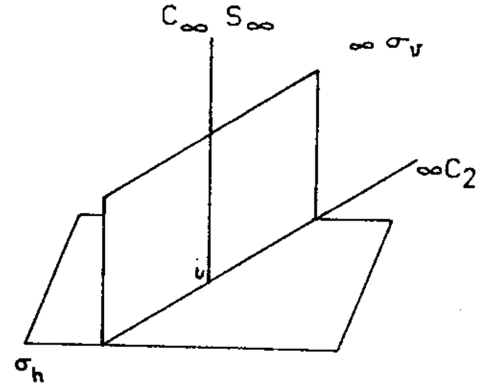


Fig. 18

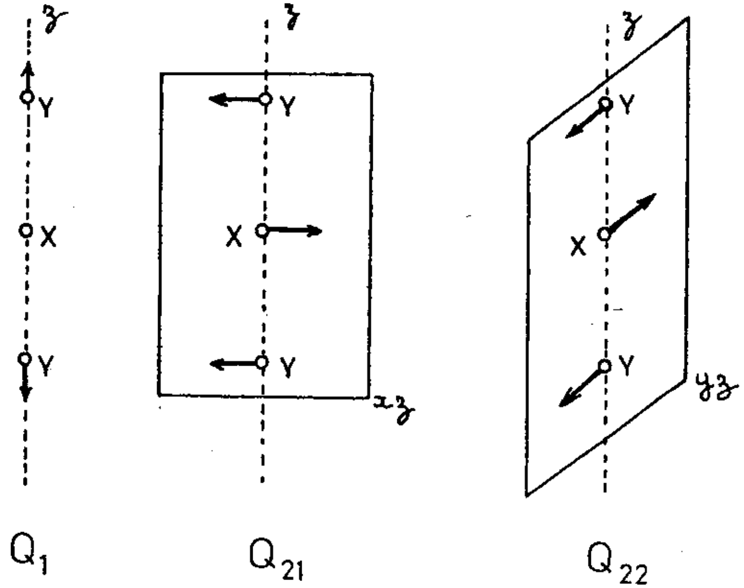


Fig. 19

4) Case of the symmetrical linear molecules

- Group $D_{\infty h}$ (Fig. 18)
- Table of characters

	I	$2\,C_z(\varphi)$	...	$2\,S_z(\varphi)$	...	σ_h	i	$\infty\,\sigma_v$	$\infty\,C_2$
Σ_g^+	1	1	...	1	...	1	1	1	1
Σ_u^+	1	1	...	-1	...	-1	-1	1	-1
Σ_g^-	1	1	...	1	...	1	1	-1	-1
Σ_u^-	1	1	...	-1	...	-1	-1	-1	1
Π_g	2	$2\cos\varphi$	...	$-2\cos\varphi$	...	-2	2	0	0
Π_u	2	$2\cos\varphi$	...	$2\cos\varphi$	...	2	-2	0	0
Δ_g	2	$2\cos 2\varphi$	...	$2\cos 2\varphi$	...	2	2	0	0
Δ_u	2	$2\cos 2\varphi$	...	$-2\cos 2\varphi$	...	-2	-2	0	0
...	...	....	...	....	...	...	...	...	...

(64)

- Species of M_γ and $\alpha_{\gamma\gamma'}$

α_{xx}	Σ_g^+ Δ_g
α_{yy}	Σ_g^+ Δ_g
α_{zz}	Σ_g^+
α_{xy} $(=\alpha_{yx})$	Δ_g
α_{yz} $(=\alpha_{zy})$	Π_g
α_{zx} $(=\alpha_{xz})$	Π_g

M_x	Π_u
M_y	Π_u
M_z	Σ_u^+

(65)

- Species of normal coordinates (Fig. 19)

$$\begin{cases} Q_1 & : \quad \Sigma_g^+ \\ Q_{21} \text{ and } Q_{22} & : \quad \Pi_u \\ Q_3 & : \quad \Sigma_u^+ \end{cases} \qquad (66)$$

- Species of vibrational wave functions

$$\Psi_{v_1 v_2 \ell_2 v_3} \quad \text{is} \quad \Sigma^+, \Pi, \Delta, \Phi, \Gamma \ldots \qquad (67)$$

when $\ell_2 = 0, \pm 1, \pm 2, \pm 3, \pm 4, \ldots$ respectively

$$\Psi_{v_1 v_2 \ell_2 v_3} \quad \text{is} \quad \begin{cases} \underline{g} & \text{when} \quad v_2 + v_3 \quad \text{is even} \\ \underline{u} & \text{when} \quad v_2 + v_3 \quad \text{is odd} \end{cases} \qquad (68)$$

Examples :

00^00	Σ_g^+	20^00	Σ_g^+	11^10	Π_u
10^00	Σ_g^+	02^00	Σ_g^+	10^01	Σ_u^+
01^10	Π_u	02^20	Δ_g	01^11	Π_g
00^01	Σ_u^+	00^02	Σ_g^+	etc...	

(69)

- Species of a product

$$g.g = g$$
$$u.u = g$$
$$g.u = u \qquad (70)$$
$$u.g = u$$

$$\overline{\Psi'_v} \; \Psi''_v \quad \text{is} \quad \begin{cases} \underline{g} & \text{when} \quad \Delta v_2 + \Delta v_3 \quad \text{is even} \\ \underline{u} & \text{when} \quad \Delta v_2 + \Delta v_3 \quad \text{is odd} \end{cases} \qquad (71)$$

- Vibrational selection rules

(Emission, absorption) $\begin{cases} \Delta \ell_2 = 0, \pm 1 \\ \Delta v_2 + \Delta v_3 \quad \text{odd} \end{cases}$ (72)

$\Sigma^+ \leftrightarrow \Sigma^+$, $\Sigma^- \leftrightarrow \Sigma^-$, $\Sigma^+ \not\leftrightarrow \Sigma^-$ (73)

(Emission, absorption) $g \leftrightarrow u$, $g \not\leftrightarrow g$, $u \not\leftrightarrow u$ (74)

(Raman scattering) $\begin{cases} \Delta \ell_2 = 0, \pm 1, \pm 2 \\ \Delta v_2 + \Delta v_3 \quad \text{even} \end{cases}$ (75)

$\Sigma^+ \leftrightarrow \Sigma^+$, $\Sigma^- \leftrightarrow \Sigma^-$, $\Sigma^+ \not\leftrightarrow \Sigma^-$ (76)

(Raman scattering) $g \leftrightarrow g$, $u \leftrightarrow u$, $g \not\leftrightarrow u$) (77)

5) Theory of representations

- Representations

$$\begin{array}{llll} & \multicolumn{3}{c}{\overbrace{\hspace{6cm}}^{\text{Operations}}} \\ \text{Basis :} & O_i & O_j & \cdots \\ \begin{matrix} S_1 \\ S_2 \\ S_3 \end{matrix} & \boxed{\begin{matrix} x & x & x \\ x & x & x \\ x & x & x \end{matrix}} & \boxed{\begin{matrix} x & x & x \\ x & x & x \\ x & x & x \end{matrix}} & \cdots \\ & \{\Gamma_i\} & \{\Gamma_j\} & \cdots \\ & \multicolumn{3}{c}{\underbrace{\hspace{6cm}}_{\text{Matrices of transformation}}} \end{array} \tag{78}$$

$$\begin{Bmatrix} S_1^{(j)} \\ S_2^{(j)} \\ S_3^{(j)} \end{Bmatrix} = \{\Gamma_j\} \begin{Bmatrix} S_1 \\ S_2 \\ S_3 \end{Bmatrix} \tag{79}$$

- Equivalent representations

$$\begin{aligned} S_1^* &= a\ S_1 + b\ S_2 + c\ S_3 \\ S_2^* &= d\ S_1 + e\ S_2 + f\ S_3 \\ S_3^* &= g\ S_1 + h\ S_2 + i\ S_3 \end{aligned} \tag{80}$$

$$\begin{Bmatrix} S_1^* \\ S_2^* \\ S_3^* \end{Bmatrix} = \{T\} \begin{Bmatrix} S_1 \\ S_2 \\ S_3 \end{Bmatrix} \tag{81}$$

$$\{T\} = \begin{Bmatrix} a & b & c \\ d & e & f \\ g & h & i \end{Bmatrix} \tag{82}$$

$$\begin{Bmatrix} S_1^{*(j)} \\ S_2^{*(j)} \\ S_3^{*(j)} \end{Bmatrix} = \{\Gamma_j^*\} \begin{Bmatrix} S_1^* \\ S_2^* \\ S_3^* \end{Bmatrix} \tag{83}$$

$$\begin{Bmatrix} S_1^{*(j)} \\ S_2^{*(j)} \\ S_3^{*(j)} \end{Bmatrix} = \{\Gamma_j^*\}\{T\} \begin{Bmatrix} S_1 \\ S_2 \\ S_3 \end{Bmatrix} = \{T\}\{\Gamma_j\} \begin{Bmatrix} S_1 \\ S_2 \\ S_3 \end{Bmatrix} \tag{84}$$

$$\Gamma_j^*\ T = T\ \Gamma_j \tag{85}$$

$$\Gamma_j^* = T\ \Gamma_j\ T^{-1} \tag{86}$$

$$\text{trace}\ T\ \Gamma_j\ T^{-1} = \text{trace}\ \Gamma_j \tag{87}$$

Operations

Bases	O_i	O_j	...
$S_1\ S_2\ S_3$	Γ_i	Γ_j	...
$S_1^*\ S_2^*\ S_3^*$	Γ_i^* $(=T\ \Gamma_i T^{-1})$	Γ_j^* $(=T\ \Gamma_j\ T^{-1})$	...

(88)

- Reduction of a representation

Basis: S_1^*, S_2^*, S_3^* — Operations O_i, O_j, ...

O_i		
x	0	0
0	x	x
0	x	x

O_j		
x	0	0
0	x	x
0	x	x

$\{\Gamma_i^*\}$ $\{\Gamma_j^*\}$ ... (89)

Bases — Operations O_i, O_j ...

S_1^*: [x] [x] ...

S_2^*, S_3^*:

x	x
x	x

x	x
x	x

... (90)

Basis — Operations O_i, O_j ...

S_2^{**}, S_3^{**}:

x	0
0	x

x	0
0	x

... (91)

Bases — Operations O_i, O_j ...

S_2^{**}: [x] [x] ...

S_3^{**}: [x] [x] ... (92)

(93)

representation

x	x	x
x	x	x
x	x	x

either irreducible or equivalent to

x	0	0
0	x	x
0	x	x

i.e. reducible into [x] (irreducible) and

x	x
x	x

representation

x	x
x	x

either irreducible or equivalent to

x	0
0	x

i.e. reducible into [x] and [x] (both irreducible)

Addendum

Symmetry species ($\equiv$ Irreducible representations) for Point groups associated with Axially symmetric molecules

---

$A, B, E_1, E_2, \ldots$ We perform operation $\mathcal{O}$ (defined below); let $\Gamma(\mathcal{O})$ be the matrix corresponding to $\mathcal{O}$ in the representation Γ

$\Gamma(\mathcal{O})$	$\{+1\}$	$\{-1\}$	$\begin{Bmatrix} \cos\frac{2\pi a}{n} & \delta\sin\frac{2\pi a}{n} \\ -\delta\sin\frac{2\pi a}{n} & \cos\frac{2\pi a}{n} \end{Bmatrix}$	$a = 1, 2, \ldots \ldots \frac{n-1}{2}$ or $\frac{n-2}{2}$; $\delta = \pm 1$
Species	A	B	E_a	

Remarks
- The various species are associated with distinct values of $\cos\frac{2\pi a}{n}$ (see fig 1)
- B can occur only if n is even
- if $n = 3$ or 4, one writes E for E_1

Operation $\mathcal{O}$
- C_n, D_n, C_{nv}, D_{nh}, S_{2n} (n odd), D_{nd} (n odd): $\mathcal{O} = C_z\left(\frac{2\pi}{n}\right)$
- S_{2n} (n even), D_{nd} (n even): $\mathcal{O} = S_z\left(\frac{2\pi}{2n}\right)$

$(A \text{ or } B)_{1,2}$ We perform operation $\mathcal{O}'$ (defined below)

$\Gamma(\mathcal{O}')$	$\{+1\}$	$\{-1\}$
Species	1	2

Operation $\mathcal{O}'$
- D_n, D_{nh}, D_{nd}: $\mathcal{O}' = C_\theta(\pi)$ $\quad \theta = (zx, zC_2)$
- C_{nv}: $\mathcal{O}' = \sigma_\theta$ $\quad \theta = (zx, \sigma_v)$

Point groups:

- I a: C_{Nv}, D_N, D_{Nh}, D_{Nd} (N odd)
- I b: $D_{\frac{N}{2}d}$ ($\frac{N}{2}$ even)
- II a: C_N, C_{Nh}, S_{2N} (N odd)
- II b: S_N ($\frac{N}{2}$ even)

- I : species defined by $\mathcal{O} + \mathcal{O}'$
- II : species defined by $\mathcal{O}$
- a : $\mathcal{O} = C_z\left(\frac{2\pi}{N}\right)$
- b : $\mathcal{O} = S_z\left(\frac{2\pi}{N}\right)$

Definition of n : let us consider the proper rotations $C_z(\varphi)$ belonging to the group : the smallest non-zero φ is equal to $\frac{2\pi}{n}$

Definition of N : $\mathcal{O} \equiv C_z\left(\frac{2\pi}{N}\right)$ or $S_z\left(\frac{2\pi}{N}\right)$

$N \equiv n$ except for $\underbrace{D_{nd}, S_{2n}}_{(n \text{ even})}$ for which $N = 2n$

′ ″ means sym. or antisym. with respect to σ_h only for $\underbrace{C_{nh}\ D_{nh}}_{(n \text{ odd})}$.

g u means sym. or antisym. with respect to i only for $\underbrace{C_{nh}\ D_{nh}}_{(n \text{ even})}$ $\underbrace{S_{2n}\ D_{nd}}_{(n \text{ odd})}$

TABLEAU I

Groupe	Opérations du type 1		Opérations du type 2		Nombre des opérations du type 1 (G_1)	Nombre des opérations du type 2 (G_2)	Ordre du groupe (G)
C_n	$C_z\left(2\pi\frac{k}{n}\right)$				n		n
S_{2n}	$C_z\left(2\pi\frac{k}{n}\right)$	$S_z\left(2\pi\frac{2k+1}{2n}\right)$			$2n$		$2n$
C_{nh}	$C_z\left(2\pi\frac{k}{n}\right)$	$S_z\left(2\pi\frac{k}{n}\right)$			$2n$		$2n$
D_n	$C_z\left(2\pi\frac{k}{n}\right)$		$C_\theta(\pi)$		n	n	$2n$
C_{nv}	$C_z\left(2\pi\frac{k}{n}\right)$			σ_θ	n	n	$2n$
D_{nh}	$C_z\left(2\pi\frac{k}{n}\right)$	$S_z\left(2\pi\frac{k}{n}\right)$	$C_\theta(\pi)$	σ_0	$2n$	$2n$	$4n$
D_{nd}	$C_z\left(2\pi\frac{k}{n}\right)$	$S_z\left(2\pi\frac{2k+1}{2n}\right)$	$C_\theta(\pi)$	σ_θ	$2n$	$2n$	$4n$

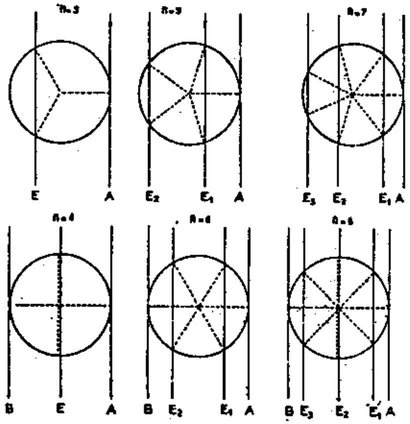


FIG. 1.

TABLEAU II

Nomenclature des représentations irréductibles des différents groupes « axiaux » (Types de symétrie).

C_3	AE	C_{3v}, D_3	A_1A_2E
C_4	ABE	C_{4v}, D_4	$A_1A_2B_1B_2E$
C_5	AE_1E_2	C_{5v}, D_5	$A_1A_2E_1E_2$
C_6	ABE_1E_2	C_{6v}, D_6	$A_1A_2B_1B_2E_1E_2$
S_4	ABE	D_{3h}	$A'_1A''_1A'_2A''_2E'E''$
S_6	$A_gA_uE_gE_u$	D_{4h}	$A_{1g}A_{1u}A_{2g}A_{2u}B_{1g}B_{1u}B_{2g}B_{2u}E_gE_u$
S_8	$ABE_1E_2E_3$	D_{5h}	$A'_1A''_1A'_2A''_2E'_1E''_1E'_2E''_2$
		D_{6h}	$A_{1g}A_{1u}A_{2g}A_{2u}B_{1g}B_{1u}B_{2g}B_{2u}E_{1g}E_{1u}E_{2g}E_{2u}$
C_{3h}	$A'A''E'E''$	D_{2d}	$A_1A_2B_1B_2E$
C_{4h}	$A_gA_uB_gB_uE_gE_u$	D_{3d}	$A_{1g}A_{1u}A_{2g}A_{2u}E_gE_u$
C_{5h}	$A'A''E'_1E''_1E'_2E''_2$	D_{4d}	$A_1A_2B_1B_2E_1E_2E_3$
C_{6h}	$A_gA_uB_gB_uE_{1g}E_{1u}E_{2g}E_{2u}$	D_{5d}	$A_{1g}A_{1u}A_{2g}A_{2u}E_{1g}E_{1u}E_{2g}E_{2u}$