Character Tables II. General Approach

Chautauqua

General objective: Determine relationships between tensor elements not immediately obvious from direct inspection of the character tables.

$$\vec{\beta}^{\omega_{sum}} = \sum_n S_n(\omega_{ir}) \cdot (\vec{\alpha}_{0n} \otimes \vec{\mu}_{n0}) + NR$$

$$\vec{\beta}^{2\omega} = \sum_n S_n(2\omega) \cdot (\vec{\mu}_{0n} \otimes \vec{\alpha}_{n0}) + NR$$

Specific Objectives:

1. Illustrate the approach based on intuition for the C_4 operation.
2. Develop a linear algebra strategy to identify symmetry-allowed relationships.
3. Consider phase shifts in degenerate modes.

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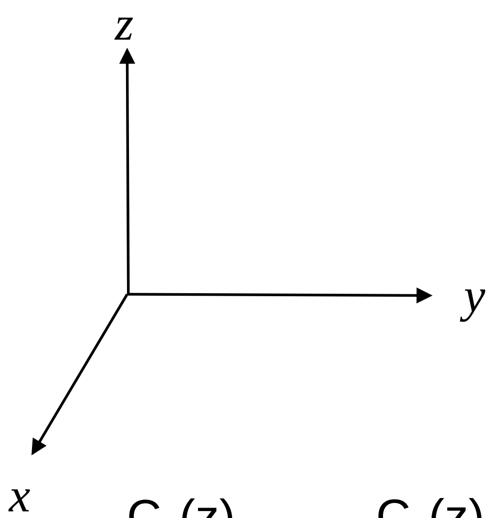
Note: Citations to the contents of these slides should reference the following textbook:
Simpson, Garth J. (2017) *Nonlinear Optical Polarization Analysis in Chemistry and Biology* (Cambridge University Press, ISBN 978-0-521-51908-3).

Guess and Check: C_4

Consider ir-vis SFG from an assembly with C_4 molecular symmetry.

$$\vec{\beta}^{\omega_{sum}} \cong S_n(\omega_{ir}) \cdot (\vec{\alpha}_{0n} \otimes \vec{\mu}_{n0}) + NR$$

C_4	E	C_4(z)	C_2(z)	3C_4(z)	Lin.	Quad.
A	1	1	1	1	z	x^2+y^2, z^2
B	1	-1	1	1	-	x^2-y^2, xy
E	1 1	i -i	-1 -1	-i i	(x,y)	(xz,yz)



C_2(z)	C_4(z)
$x \Rightarrow -x$	$x \Rightarrow y$
$y \Rightarrow -y$	$y \Rightarrow -x$
$z \Rightarrow z$	$z \Rightarrow z$

XXX	YXX	ZXX
XXY	YXY	ZXY
XXZ	YXZ	ZXZ
XYX	YYX	ZYX
XYY	YYY	ZYY
XYZ	YYZ	ZYZ
XZX	YZX	ZZX
XZY	YZY	ZZY
XZZ	YZZ	ZZZ

A more formal linear algebra approach exemplified for C_4 :*E*-transitions

C_4	E	$C_4(z)$	$C_2(z)$	$3C_4(z)$	Lin.	Quad.
A	1	1	1	1	z	x^2+y^2,z^2
B	1	-1	1	1	-	x^2-y^2,xy
E	1 1	i -i	-1 -1	-i i	(x,y)	(xz,yz)

Set of matrices corresponding to the $C_2(z)$ and $C_4(z)$ symmetry operations

$$C_n^1(z)=\begin{bmatrix}\cos(2\pi/n) & -\sin(2\pi/n) & 0\\ \sin(2\pi/n) & \cos(2\pi/n) & 0\\ 0 & 0 & 1\end{bmatrix}$$

$$\lambda\vec{\mu}'=C_4^1(z)\cdot\vec{\mu}=\begin{bmatrix}0 & -1 & 0\\ 1 & 0 & 0\\ 0 & 0 & 1\end{bmatrix}\cdot\begin{bmatrix}\mu_x\\ \mu_y\\ \mu_z\end{bmatrix}$$

$$eigenvalues\left[C_4^1(z)\right]=\begin{bmatrix}i\\ -i\\ 1\end{bmatrix}$$

$$eigenvec[i]=\begin{bmatrix}1\\ i\\ 0\end{bmatrix}$$

$$eigenvec[-i]=\begin{bmatrix}1\\ -i\\ 0\end{bmatrix}$$

$$\lambda\vec{\alpha}'=\left[C_4^1(z)\otimes C_4^1(z)\right]\cdot\vec{\alpha}$$

$$eigenvalues\left[C_4^1(z)\right]=\begin{bmatrix}1\\ i\\ -i\\ -1\end{bmatrix}$$

$$eigenvec[\pm i]=\begin{bmatrix}0\\0\\1\\0\\0\\\pm i\\0\\0\\0\end{bmatrix},\begin{bmatrix}0\\0\\0\\0\\0\\0\\1\\\pm i\\0\end{bmatrix}$$

Garth J. Simpson

A more formal linear algebra approach exemplified for C_4 : *A & B* -transitions

Set of matrices corresponding to the $C_2(z)$ and $C_4(z)$ symmetry operations

C_4	E	$C_4(z)$	$C_2(z)$	$3C_4(z)$	Lin.	Quad.
A	1	1	1	1	z	x^2+y^2, z^2
B	1	-1	1	1	-	x^2-y^2, xy
E	1 1	i -i	-1 -1	-i i	(x,y)	(xz,yz)

$$C_n^1(z) = \begin{bmatrix} \cos(2\pi/n) & -\sin(2\pi/n) & 0 \\ \sin(2\pi/n) & \cos(2\pi/n) & 0 \\ 0 & 0 & 1 \end{bmatrix}$$

$$\lambda\vec{\alpha}' = \left[C_4^1(z) \otimes C_4^1(z)\right] \cdot \vec{\alpha}$$

$$\lambda\vec{\mu}' = C_4^1(z) \cdot \vec{\mu} = \begin{bmatrix} 0 & -1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 1 \end{bmatrix} \cdot \begin{bmatrix} \mu_x \\ \mu_y \\ \mu_z \end{bmatrix}$$

$$eigenvalues\left[C_4^1(z)\right] = \begin{bmatrix} i \\ -i \\ 1 \end{bmatrix}$$

$$eigenvec[1] = \begin{bmatrix} 0 \\ 0 \\ 1 \end{bmatrix}$$

$$eigenvalues\left[C_4^1(z)\right] = \begin{bmatrix} 1 \\ i \\ -i \\ -1 \end{bmatrix}$$

$$eigenvec[1] = \begin{bmatrix} 1 \\ 0 \\ 0 \\ 0 \\ 1 \\ 0 \\ 0 \\ 0 \\ 0 \end{bmatrix}, \begin{bmatrix} 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 1 \end{bmatrix}$$

$$eigenvec[-1] = \begin{bmatrix} 1 \\ 0 \\ 0 \\ 0 \\ -1 \\ 0 \\ 0 \\ 0 \\ 0 \end{bmatrix}, \begin{bmatrix} 0 \\ 1 \\ 0 \\ -1 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \end{bmatrix}$$

How about β?

Parametric processes must transform as the totally symmetric group *A*.

$$\vec{\beta}' = \left[C_4^1(z) \otimes C_4^1(z) \otimes C_4^1(z) \right] \cdot \vec{\beta}$$

β_{zzz}

$\beta_{xxz} = \beta_{yyz}$

$\beta_{xyz} = -\beta_{yxz}$

$\beta_{xzx} = \beta_{yzy}$

$\beta_{zxx} = \beta_{zyy}$

$\beta_{xzy} = -\beta_{yzx}$

$\beta_{zxy} = -\beta_{zyx}$

How do we account for these complex terms in construction of β?

We don't!

Parametric processes must transform as the totally symmetric group *A*.

$$\vec{\beta}' = \left[C_4^1(z) \otimes C_4^1(z) \otimes C_4^1(z) \right] \cdot \vec{\beta}$$

β_{zzz} $\quad \beta_{xxz} = \beta_{yyz}$ $\quad \beta_{xzx} = \beta_{yzy}$ $\quad \beta_{xzy} = -\beta_{yzx}$

$\beta_{xyz} = -\beta_{yxz}$ $\quad \beta_{zxx} = \beta_{zyy}$ $\quad \beta_{zxy} = -\beta_{zyx}$

$$\vec{\beta}_{00} \cong S_n(\omega_{ir}) \vec{\alpha}_{0n} \otimes \vec{\mu}_{n0} + NR$$

$$\vec{\mu}_{n0} \quad \begin{bmatrix} 1 \\ \pm i \\ 0 \end{bmatrix} \qquad \vec{\alpha}_{00} \quad \begin{bmatrix} 0 \\ 0 \\ 1 \\ 0 \\ 0 \\ \mp i \\ 0 \\ 0 \\ 0 \end{bmatrix}, \begin{bmatrix} 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 1 \\ \mp i \\ 0 \end{bmatrix}$$

Resonantly-Enhanced SHG

How do thing change for SHG resonant at the second harmonic frequency?

Parametric processes must transform as the totally symmetric group *A*.

$$\vec{\beta}' = \left[C_4^1(z) \otimes C_4^1(z) \otimes C_4^1(z)\right] \cdot \vec{\beta}$$

β_{zzz}

$\beta_{xxz} = \beta_{yyz}$ $\quad$ $\beta_{xzx} = \beta_{yzy}$ $\quad$ $\beta_{xzy} = -\beta_{yzx}$

$\beta_{xyz} = -\beta_{yxz}$ $\quad$ $\beta_{zxx} = \beta_{zyy}$ $\quad$ $\beta_{zxy} = -\beta_{zyx}$

$$\vec{\beta} \cong S_n(2\omega)\, \vec{\mu}_{n0} \otimes \vec{\alpha}_{0n} + NR$$

$$\vec{\mu}_{0n} \quad \begin{bmatrix} 1 \\ \mp i \\ 0 \end{bmatrix} \qquad \vec{\alpha}_{n0} \quad \begin{bmatrix} 0 \\ 0 \\ 1 \\ 0 \\ 0 \\ \pm i \\ 0 \\ 0 \\ 0 \end{bmatrix}, \begin{bmatrix} 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 1 \\ \pm i \\ 0 \end{bmatrix}$$