Character Tables I. Introduction

General objective: Extend the general symmetry analysis to specific transitions by taking advantage of 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. Express the molecular hyperpolarizability in terms of the Kronecker product of a vector (transition moment) and matrix (Raman or two-photon absorption).
2. Identify transitions that are allowed by symmetry.
3. Identify the full set of resonantly enhanced tensor elements for a given transition.

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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).

Character Tables

Bottom up: Identification of the total set of unique molecular tensor elements based on symmetry.

Worked example: C_{2v}

-The A_1, B_1, and B_2 symmetries all have nonzero elements for both μ and α.

C_{2v}	E	C_2 (z)	$\sigma_v(xz)$	$\sigma_v(yz)$	Lin.	Quad.
A_1	1	1	1	1	z	x^2,y^2,z^2
A_2	1	1	-1	-1		xy
B_1	1	-1	1	-1	x	xz
B_2	1	-1	-1	1	y	yz

$$\beta_{ijk}\left(-\omega_3;\omega_1,\underline{\omega_2}\right)=\sum_n S_n\left(\omega_2\right)\alpha_{0n}\otimes\vec{\mu}_{n0}$$

$$\beta_{00}^{ijk}\left(-2\underline{\omega};\omega,\omega\right)=\sum_m S_m\left(2\omega\right)\vec{\mu}_{0m}\otimes\alpha_{m0}$$

SFG	$\alpha_{ij}\mu_k$
A_1	β_{xxz}, β_{yyz}, β_{zzz}
A_2	-
B_1	$\beta_{xzx} \cong \beta_{zxx}$
B_2	$\beta_{yzy} \cong \beta_{zyy}$

SHG	$\mu_i\alpha_{jk}$
A_1	β_{zxx}, β_{zyy}, β_{zzz}
A_2	-
B_1	$\beta_{xxz} = \beta_{xzx}$
B_2	$\beta_{yyz} = \beta_{yzy}$

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Character Tables

Let's consider the case of vibrational SFG with a molecule of B_1 symmetry.

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

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

C_{2v}	E	C_2 (z)	$\sigma_v(xz)$	$\sigma_v(yz)$	Lin.	Quad.
A_1	1	1	1	1	z	x^2,y^2,z^2
A_2	1	1	-1	-1		xy
B_1	1	-1	1	-1	x	xz
B_2	1	-1	-1	1	y	yz

$C_2(z)$ $\sigma_v(xz)$ $\sigma_v(yz)$

Character Tables

How does the transition moment transform for B_1 symmetry?

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

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

C_{2v}	E	C_2 (z)	σ_v(xz)	σ_v(yz)	Lin.	Quad.
A_1	1	1	1	1	z	x^2,y^2,z^2
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B_1	1	-1	1	-1	x	xz
B_2	1	-1	-1	1	y	yz

C_2(z) σ_v(xz) σ_v(yz)

Character Tables

How does the Raman matrix transform for B_1 symmetry?

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

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

C_{2v}	E	C_2 (z)	$\sigma_v(xz)$	$\sigma_v(yz)$	Lin.	Quad.
A_1	1	1	1	1	z	x^2,y^2,z^2
A_2	1	1	-1	-1		xy
B_1	1	-1	1	-1	x	xz
B_2	1	-1	-1	1	y	yz

$\sigma_v(yz)$

$$-\vec{\alpha}'_{0n} = \left[\sigma_v(yz) \otimes \sigma_v(yz)\right] \cdot \vec{\alpha}_{0n}$$

$$\begin{bmatrix} -1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix}$$

$$\begin{bmatrix} \alpha_{xx} \\ \alpha_{xy} \\ \alpha_{xz} \\ \alpha_{yx} \\ \alpha_{yy} \\ \alpha_{yz} \\ \alpha_{zx} \\ \alpha_{zy} \\ \alpha_{zz} \end{bmatrix}'_{0n} = -\begin{bmatrix} 1 & & & & & & & & \\ & -1 & & & & & & & \\ & & -1 & & & & & & \\ & & & -1 & & & & & \\ & & & & 1 & & & & \\ & & & & & 1 & & & \\ & & & & & & -1 & & \\ & & & & & & & 1 & \\ & & & & & & & & 1 \end{bmatrix} \cdot \begin{bmatrix} \alpha_{xx} \\ \alpha_{xy} \\ \alpha_{xz} \\ \alpha_{yx} \\ \alpha_{yy} \\ \alpha_{yz} \\ \alpha_{zx} \\ \alpha_{zy} \\ \alpha_{zz} \end{bmatrix}_{0n}$$

How does the Raman matrix transform for B_1 symmetry?

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

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

C_{2v}	E	C_2 (z)	σ_v(xz)	σ_v(yz)	Lin.	Quad.
A_1	1	1	1	1	z	x^2,y^2,z^2
A_2	1	1	-1	-1		xy
B_1	1	-1	1	-1	x	xz
B_2	1	-1	-1	1	y	yz

σ_v(xz)

$$\vec{\alpha}'_{0n} = \left[\sigma_v(xz) \otimes \sigma_v(xz)\right] \cdot \vec{\alpha}_{0n}$$

$$\begin{bmatrix} \alpha_{xx} \\ \alpha_{xy} \\ \alpha_{xz} \\ \alpha_{yx} \\ \alpha_{yy} \\ \alpha_{yz} \\ \alpha_{zx} \\ \alpha_{zy} \\ \alpha_{zz} \end{bmatrix}'_{0n} = \begin{bmatrix} 1 & & & & & & & & \\ & -1 & & & & & & 0 & \\ & & 1 & & & & & & \\ & & & -1 & & & & & \\ & & & & 1 & & & & \\ & & & & & -1 & & & \\ & & & & & & 1 & & \\ & 0 & & & & & & -1 & \\ & & & & & & & & 1 \end{bmatrix} \cdot \begin{bmatrix} \alpha_{xx} \\ \alpha_{xy} \\ \alpha_{xz} \\ \alpha_{yx} \\ \alpha_{yy} \\ \alpha_{yz} \\ \alpha_{zx} \\ \alpha_{zy} \\ \alpha_{zz} \end{bmatrix}_{0n} \quad \begin{bmatrix} \alpha_{xx} \\ \alpha_{xy} \\ \alpha_{xz} \\ \alpha_{yx} \\ \alpha_{yy} \\ \alpha_{yz} \\ \alpha_{zx} \\ \alpha_{zy} \\ \alpha_{zz} \end{bmatrix}_{0n} \quad \begin{bmatrix} \alpha_{xx} \\ \alpha_{xy} \\ \alpha_{xz} \\ \alpha_{yx} \\ \alpha_{yy} \\ \alpha_{yz} \\ \alpha_{zx} \\ \alpha_{zy} \\ \alpha_{zz} \end{bmatrix}_{0n}$$

$$\begin{bmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{bmatrix}$$

$$\begin{bmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{bmatrix}$$

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Molecular symmetry

SFG	$\alpha_{ij}\mu_k$
A_1	β_{xxz}, β_{yyz}, β_{zzz}
A_2	-
B_1	$\beta_{xzx} = \beta_{zxx}$
B_2	$\beta_{yzy} = \beta_{zyy}$

For a B_1 transition in vibrational SFG, one unique and two nonzero tensor elements survive.

$$\begin{bmatrix} xxx \\ xxy \\ xxz \\ xyx \\ xyy \\ xyz \\ xzx \\ xzy \\ xzz \\ yxx \\ yxy \\ yxz \\ yyx \\ yyy \\ yyz \\ yzx \\ yzy \\ yzz \\ zxx \\ zxy \\ zxz \\ zyx \\ zyy \\ zyz \\ zzx \\ zzy \\ zzz \end{bmatrix} \begin{bmatrix} 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 1 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 1 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \end{bmatrix} \cdot \left[\beta_{xzx}\right] = \boldsymbol{S} \cdot \vec{\beta}$$

Symmetry matrix ***S***, populating the full set of 27 elements from the subset of independent tensor elements (27×1 in this case).

Independent, nonzero elements within the molecular tensor.

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