

Character Tables I. Introduction



General objective: Extend the general symmetry analysis to specific transitions by taking advantage of character tables.

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

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

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Specific Objectives:

- Express the molecular hyperpolarizability in terms of the Kronecker product of a vector (transition moment) and matrix (Raman or two-photon absorption).
- Identify transitions that are allowed by symmetry.
- Identify the full set of resonantly enhanced tensor elements for a given transition.

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).





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)	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		ху
B ₁	1	-1	1	-1	X	XZ
B_2	1	-1	-1	1	y	yz

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

SFG
$$\alpha_{ij}\mu_{k}$$
 A_{1} $\beta_{xx}z, \beta_{yy}z, \beta_{zz}z$
 A_{2} -

 B_{1} $\beta_{xzx} \cong \beta_{zxx}$
 B_{2} $\beta_{yzy} \cong \beta_{zyy}$

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

SHG	$\mu_i lpha_{jk}$
A ₁	$eta_{\sf zxx},eta_{\sf zyy},eta_{\sf zzz}$
A_2	-
B ₁	$\beta_{xxz} = \beta_{xzx}$
B_2	$\beta_{yyz} = \beta_{yzy}$

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Let's consider the case of vibrational SFG with a molecule of B₁ symmetry.

$$\vec{\beta} = \sum_{n} S_{n} \left(\omega_{ir} \right) \vec{\alpha}_{0n} \otimes \vec{\mu}_{n0}$$

$\vec{eta} \cong S_n$ (ω_{i}	$\vec{\alpha}_{o}$	$\otimes \bar{\mu}_{0}$	+NR
$P = S_n$	$\langle \omega_{ir} \rangle$	$\int \alpha_{0n}$	$\smile \mu_{n0}$	1 1 1 1 1 1

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		ху
B ₁	1	-1	1	-1	X	XZ
B_2	1	-1	-1	1	у	yz

$$C_2(z)$$

$$\sigma_{v}(xz)$$

$$\sigma_v(yz)$$





How does the transition moment transform for B₁ 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.
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$$C_2(z)$$

$$\sigma_{v}(xz)$$

$$\sigma_v(yz)$$



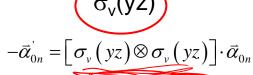


How does the Raman matrix transform for B₁ symmetry?

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

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

C _{2v}	Е	C ₂ (z)	$\sigma_{v}(xz)$	σ _v (yz)	Lin.	Quad.
A_1	1	1	1	1	z	X^2, Y^2, Z^2
A_2	1	1	-1	-1		ху
B ₁	1	(-1)	1	-1	X	\ XZ
B_2	1	-1	-1	1	У	yz /



$$\begin{bmatrix} \alpha_{xx} \\ \alpha_{xy} \\ \alpha_{xz} \\ \alpha_{yx} \\ \alpha_{yy} \\ \alpha_{yz} \\ \alpha_{zx} \\ \alpha_{zy} \end{bmatrix} = - \begin{bmatrix} 1 \\ -1 \\ -1 \\ -1 \\ 1 \end{bmatrix}$$

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

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

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

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

$$\begin{bmatrix} \alpha_{xx} \\ \alpha_{xy} \\ \alpha_{xz} \\ \alpha_{yx} \\ \alpha_{yz} \\ \alpha_{yz} \\ \alpha_{zy} \\ \alpha_{zz} \\ \alpha_{zz} \end{bmatrix}_{0n}$$



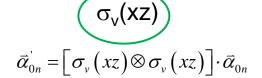


How does the Raman matrix transform for B₁ symmetry?

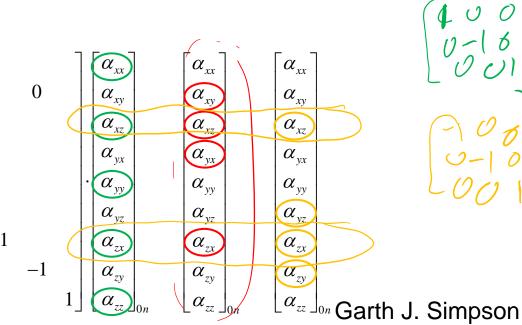
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$$\begin{bmatrix} \alpha_{xx} \\ \alpha_{xy} \\ \alpha_{xz} \\ \alpha_{yx} \\ \alpha_{yx} \\ \alpha_{yz} \\ \alpha_{zx} \\ \alpha_{zx} \\ \alpha_{zx} \end{bmatrix} = \begin{bmatrix} 1 & & & & & & \\ & -1 & & & & \\ & & & 1 & & \\ & & & -1 & & \\ & & & & -1 & \\ & & & & -1 & \\ & & & & & -1 & \\ & & & & & & -1 & \\ & & & & & & & \\ & & & & & & & \\ \end{bmatrix}$$





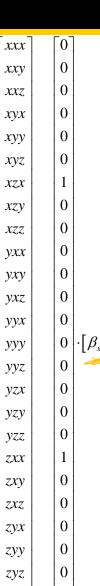


Molecular symmetry



SFG	$lpha_{ij}\mu_{k}$
A ₁	$eta_{xxz},eta_{yyz},eta_{zzz}$
A ₂	-
B ₁	$\beta_{xzx} = \beta_{zxx}$
B_2	$\beta_{yzy} = \beta_{zyy}$

For a B₁ transition in vibrational SFG, one unique and two nonzero tensor elements survive.



Z.Z.X

ZZZ

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

