Symmetry analysis of IR, Raman and high-order Raman scattering phenomena on the Bilbao Crystallographic Server

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BILBAO CRYSTALLOGRAPHIC SERVER

The Bilbao Crystallographic Server is a free web site with crystallographic databases and programs. It provides very useful information in studies related with crystal-structure symmetry, phase transitions and solid state problems. The available software is divided in several shells according to different topics:

- Basic crystallographic data (space groups and magnetic groups).
- Group-subgroup relations.
- Space group representations.
- Solid state problems.
- Structure tools.

New shell for the study of IR, Raman and high-order Raman scattering:

Raman and Hyper-Raman scattering (NEW)

SAM	Spectral Active Modes (IR, RAMAN and HYPER-RAMAN Selection Rules).
TENSOR TRANSFORM	Transformation of the Raman and Hyper-Raman Tensors
POLARIZATION SELECTION RULES	Polarization Selection Rules for Raman and Hyper-Raman Scattering processes
TWINS TENSORS	Raman or Hyper-Raman Tensors for Different Orientation Domains
CORRELATIONS POINTS	Relation between the symmetry modes in a high and low symmtry phases and their activity.
RAMAN CORRELATIONS SPACE	IR and Raman activity under a symmetry break for a given structures.
MORPHIC EFFECTS	Correlation relations for point groups under the action of an electric or magnetic field

TENSORS

- TENSOR TRANSFORM : Raman and Hyper-Raman (HR) tensors.

  Input: point group/space group and the orientation of the crystal.

  Point group: O_h (m-3m)

T_{1u},x			T_{1u},y			T_{1u},z			T_{2u}		
a	b	b	·	·	·	·	·	·	·	c	-c
·	·	·	b	a	b	·	·	·	-c	·	c
·	·	·	·	·	·	b	b	a	c	-c	·

Hyper-Raman tensor

45º rotation along the c axis → *tensor*

T_{1u},x			T_{1u},y			T_{1u},z			T_{2u}		
c'	c'	e'	d'	c'	e'	·	·	·	·	·	·
a'	a'	b'	d'	d'	e'	·	·	·	h'	h'	i'
·	·	·	·	·	·	f'	f'	g'	·	·	·

Hyper-Raman transform tensor

a'	b'	c'	d'	e'	f'	g'	h'	i'
-0.354b-0.354a	-0.707b	0.354b+0.354a	0.354a+0.354b	0.707b	b	a	-0.708c	1.414c

The relation of the coeffitiens between the initial and transform tensor

- TWIN DOMAINS
  - High and low symmetry structure
  - Transformation matrix

  → - Tensors in different orientation domains. - Intensity expressions.

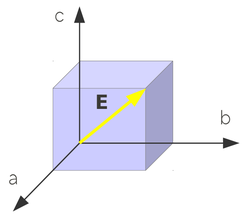
SPECTRA BEHAVIOUR

MORPHIC EFFECTS

- Symmetry break under an external field (**E** or **B**).
- Modes of the initial and perturbed systems.
- IR,Raman and Hyper-Raman activity information.

Example:

- Point group Oh (m-3m)
- An electric field (**E**) applied in the direction (1,1,1)



The symmetry of the system is reduced to C_{3v}(3m).

Relation between the modes of the initial and perturbed systems.

CORRELATION RELATIONS

- Relation between the symmetry modes in a high and low symmetry phases.
- IR, Raman and Hyper-Raman activity information.
- Very useful for phase transitions.

O_h (m-3m)	C_{3v} (3m)
A_{1g}	**A_1**
A_{1u}	A_2
A_{2g}	A_2
A_{2u}	**A_1**
E_g	**E**
E_u	**E**
T_{1g}	$A_2 + E$
T_{1u}	**$A_1 + E$**
T_{2g}	**$A_1 + E$**
T_{2u}	$A_2 + E$

Raman spectra

- Splitting of the mode T_{2g} in the low symmetry structure.
- Modes which are not active in the high symmetry are active in the low symmetry (A_{2u}, E_u and T_{1u}).

bold IR Active Modes

Raman Active Modes

Hyper-Raman Active Modes

Raman and Hyper-Raman Active Modes

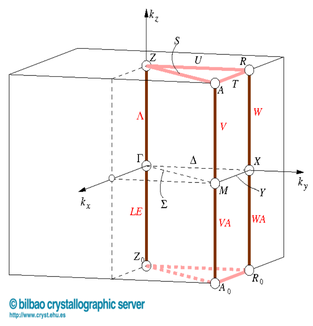
RAMAN CORRELATION SPACE

- High and low symmetry IR and Raman active modes and their compatibility relations.

k-vector	Modes behaviour	
	P4mm (No. 99)	*Cmm2* (No. 35)
Γ	A_1	A_1
	B_1	
	A_2	A_2
	B_2	
	E	B_1
	E	B_2
Z	Z_1	A_1
	Z_3	
	Z_4	A_2
	Z_2	
	Z_5	B_1
	Z_5	B_2

P4mm → Cmm2

(P,p) = a-b,a+b, 2c



P4mm (No. 99)	A_1	A_2	B_1	B_2	E
Cmm2 (No. 35)	A_1	A_2	B_1	B_2	

Raman Active / Raman Inactive

P4mm (No. 99)	A_1	A_2	B_1	B_2	E
Cmm2 (No. 35)	A_1	A_2	B_1	B_2	

IR Active / IR Inactive

SYMMETRY ADAPTED MODES

- New input: the structure can be introduced directly.
- HR selection rules and information about the tensors.
- Direct access to TENSOR TRANSFORM.
- Selection rules for second order IR and Raman processes.

POLARIZATION SELECTION RULES

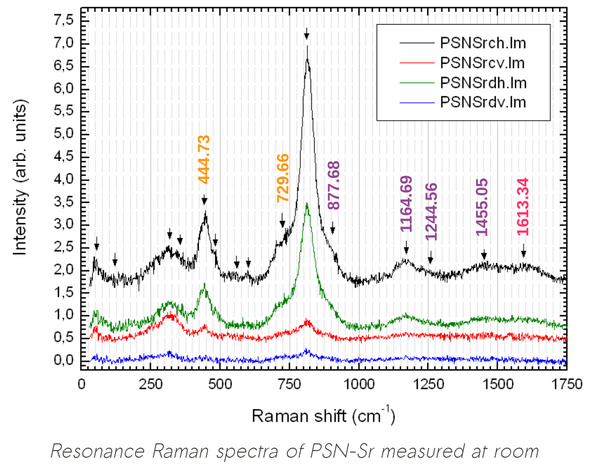
- Useful to choose the best geometrical configuration for Raman and HR experiments.
- The polarization selection rules can be calculated for different orientations and for different geometrical configurations:
  - Back scattering
  - Right angle scattering

	A_{1g}	E_g	T_{2g}
-X(YY)X	x	x	·
-X(YZ)X	·	·	x
-X(ZZ)X	x	x	·
-Y(XX)Y	x	x	·
-Y(XZ)Y	·	·	x
-Y(ZZ)Y	x	x	·
-Z(XX)Z	x	x	·
-Z(XY)Z	·	·	x
-Z(YY)Z	x	x	·

Polarization selection rules for Fm-3m (No. 225) in back scattering geometry

APPLICATION: STUDY OF RELAXORS

- Resonance Raman scattering RRS using the Bilbao Crystallographic Server.
- $PbSc_{0.5}Nb_{0.5}O_3$ (PSN-Sr): double perovskite structure Fm-3m (No. 225).



Resonance Raman spectra of PSN-Sr measured at room temperature in four different configurations.

First order RRS

Second order RRS

Third order RRS

⊗	A_g	A_u	^1E_g	^1E_u	^2E_g	^2E_u
A_g	**A_g**	A_u	**^1E_g**	^1E_u	**^2E_g**	^2E_u
A_u	·	**A_g**	^1E_u	**^1E_g**	^2E_u	**^2E_g**
^1E_g	·	·	**^2E_g**	^2E_u	**A_g**	A_u
^1E_u	·	·	·	**^2E_g**	A_u	**A_g**
^2E_g	·	·	·	·	**^1E_g**	^1E_u
^2E_u	·	·	·	·	·	**^1E_g**

Active / Inactive / **bold** Raman active modes

Second order selection rules

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