

Hyper-Raman spectroscopy from boron oxide

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Hyper-Raman scattering

Polarisation: $P_i(r,t) = \mu(r,t) + \alpha_{ij}(r,t) E_j + \beta_{ijk}(r,t) E_j E_k + \dots$

Hyper-Raman selection rules:

- IR modes active in hyper-Raman scattering
- It exits modes forbidden in both Raman and IR but active in hyper-Raman
- Acoustics modes forbidden in hyper-Raman

LASER YAG Q Switch

- wavelength: 1064 nm
- average power at 10 kHz: ≥ 8 W
- pulse duration: < 30 ns
- peak power: ≥ 60 kW

Spectrometer

- Resolution: grating 1800 g/mm: 2 cm^{-1} ; grating 600 g/mm: 6 cm^{-1}
- HRS and RS on the same apparatus
- Relative intensity $\frac{I_{HR}}{I_R}$

Selection rules in glasses

Properties of $\bar{\beta}$:

Polar modes polarized along x axis (same along y or z):

$$D(x) = \begin{pmatrix} 3a & a & a \\ 0 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix}$$

$\bar{\beta}_{xx} = 3a = \bar{\beta}_{yy}$ - The value of a depends on the mode
 $\bar{\beta}_{yx} = a = \bar{\beta}_{xy}$ - different for TO and LO

I_{VV} : projection of TO and LO on V axis $\rightarrow \infty 9a^2_{TO}$
 I_{VH} : projection of TO and LO on H axis $\rightarrow \infty 0.5a^2_{TO} + 0.5a^2_{LO}$

Properties of $\Delta\beta$: Depend on the local symmetry of B_2O_3 :

- Planar BO_3 triangles and B_3O_3 boroxol rings belong to the point group D_{3h}
- Irreducible representation: for one BO_3 and one $B_3O_3 = 2(B_2O_3)$
- $[1,2] A_1'(R,HR) + [3,4] E'(IR,R,HR) + [2,2] A_2''(IR,HR)$
- $[1,2] A_2'(R,HR) + [1,2] E''(R,HR)$

Triangles and rings in the ratio 1/1

Optical spectroscopies from boron oxide

Mode	IR	R	HR	Representation for triangles
A_1'		$(\alpha_{xx} + \alpha_{yy}, \alpha_{zz})$	$(\beta_{xxx} - 3\beta_{yyy})$	
E'	(μ_x, μ_y)	$(\alpha_{xx} - \alpha_{yy}, \alpha_{zz})$	$(\beta_{xxx} + \beta_{yyy}, \beta_{xyx} + \beta_{xyy}, \beta_{xxy} + \beta_{yyx})$	
A_2''	μ_z		$(\beta_{yyy} + \beta_{xxx})$	
A_2'			$(\beta_{yyy} - 3\beta_{xxx})$	R_z In-plane librations
E''	$(\alpha_{xx}, \alpha_{yy})$		$(\beta_{yyx} - \beta_{xxy}, \beta_{xyx})$	R_x, R_y Out-of-plane librations

Coherence effect on the Boson Peak

For incoherent scatterers: $I_{\xi} \propto \left| \sum_i P_i^{\xi} \right|^2 = \sum_i |P_i^{\xi}|^2$

If structural units vibrate with a fixed phase relationship: $I_{\xi} \propto \left| \sum_i P_i^{\xi} \right|^2$

Coherence for two types of modes

- Polar modes: Reflect partially the average D_{3h} symmetry
- External modes for which nearby atoms move together

Experimentally we observe

- Hyper-Raman intensity: $I_{Polar\ modes} \approx I_{Boson\ peak} \gg I_{A_1'}$
- Relative RS and HRS Intensity: $\frac{I_{HR}^{BP}}{I_R^{BP}} \approx 50$
- Enhancement of the boson peak signal in HRS not in RS

Possible origin

$D_{3h} \Rightarrow$ The sign of β is reversed by inversion (but α is always a positive value)

The HRS signal of two adjacent rings add coherently while it subtracts in RS

Consistent with out-of-phase librations of neighbouring boroxols
 An average of $N=7$ boroxols might vibrate coherently

Selection rules analysis

A_1' : Breathing motions of boroxol rings

A_2' : Out-of-plane polar motions

E' : In-plane polar motions

The boroxol structure is destroyed by lithium substitution

Comparison between B_2O_3 and $Li_2O:4B_2O_3$

The boson peak

\Rightarrow HRS allows to separate TO and LO

\Rightarrow Out-of-plane libration motions of rings and triangles (E'' symmetry)

\Rightarrow Originate mainly from boroxols rings

Difference between RS, HRS and Neutron BP

- Same modes scatter in RS and HRS (cf. table)
- RS sees the incoherent boroxol contribution while HRS is sensitive to coherent effects
- Difference between RS and HRS: Modes involving larger than average N boroxols, which scatter more strongly, have also a lower than average frequency