Approche multimodale par spectroscopies IR, Raman et hyper-Raman/hyper-Rayleigh: Relation structure/propriétés dans les verres TeO_2-$TaO_{5/2}$-Zn0

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Approche multimodale par spectroscopies IR, Raman et hyper-Raman/hyper-Rayleigh: Relation structure/propriétés dans les verres TeO_2-$TaO_{5/2}$-ZnO

G. Guéry (PhD work)

K. Richardson — CREOL, UCF, FL, USA

T. Cardinal — ICMCB, U Bordeaux, FR

M. Dussauze, F. Adamietz, V. Rodriguez — ISM, U Bordeaux, FR

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Quadratic Nonlinear Optics

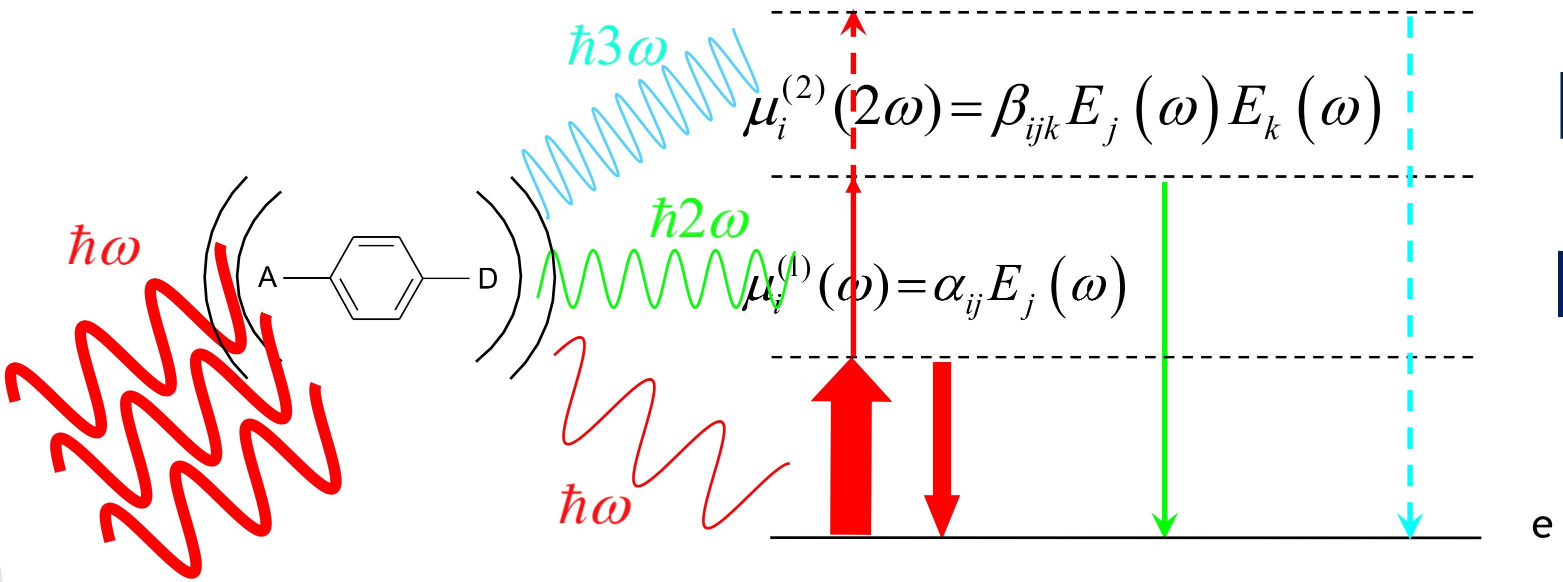
Molecular Dipolar electric response

$$P_i = \mu_i^{(0)} + \mu_i^{(1)}(\omega) + \mu_i^{(2)}(2\omega) + \mu_i^{(3)}(3\omega) + \ldots$$

$$\mu_i^{(3)}(3\omega) = \gamma_{ijkl} E_j(\omega) E_k(\omega) E_l(\omega)$$

$$\mu_i^{(2)}(2\omega) = \beta_{ijk} E_j(\omega) E_k(\omega)$$

$$\mu_i^{(1)}(\omega) = \alpha_{ij} E_j(\omega)$$

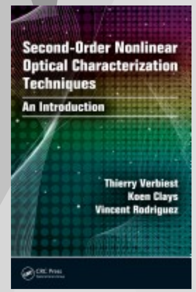


γ: second hyperpolarizability

β: first hyperpolarizability

α: polarizability

T. Verbiest, K. Clays, V. Rodriguez, « Second-order nonlinear optical characterizations techniques : An Introduction», CRC Press, Francis & Taylor Group, Boca Raton, 2009.



Quadratic Nonlinear Optics

Symmetry rules

$$\vec{P} = \vec{\mu}^{(0)} + \alpha\vec{E} + \beta\vec{E}\vec{E} + \gamma\vec{E}\vec{E}\vec{E} + \ldots$$

Isotropic, quadrupolar — α: polarizability

Isotropic, quadrupolar, hexacadecapolar — γ: second hyperpolarizability

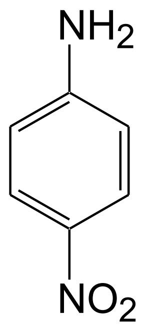
Always active /even terms

Dipolar, octupolar — β: first hyperpolarizability

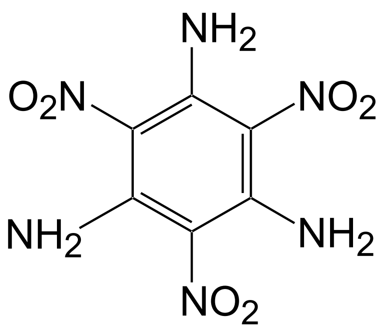
noncentrosymmetric molecules /odd term

1-D/push-pull

p-nitroaniline (PNA)



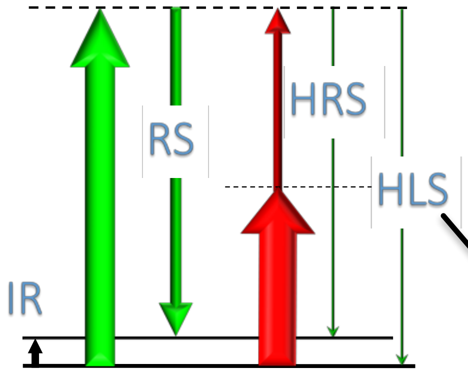
Octupolar



Triaminotrinitrobenzene (TATB)

Multimodal techniques

Extended vibrational studies: multipolar activity



IR: Infrared

RS: Raman scattering (spontaneous)

HRS: hyper-Raman scattering (spontaneous)

HLS: harmonic Light Scattering /hyper-Rayleigh (spontaneous)

$$\mu_i^{(2)}(2\omega) = \beta_{ijk} E_j(\omega) E_k(\omega)$$

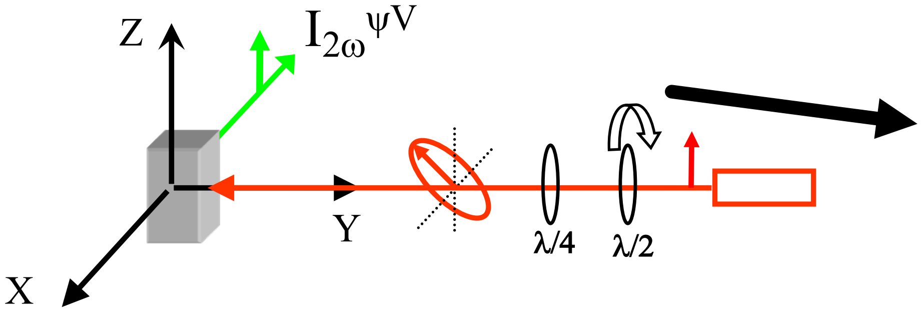
$$\left(\frac{dP_i}{dQ}\right)_{Q=0} = \left(\frac{d\mu_i^{(0)}}{dQ}\right)_{Q=0} + \left(\frac{d\alpha_{ij}}{dQ}\right)_{Q=0} E_j(\omega) + 1/2\left(\frac{d\beta_{ijk}}{dQ}\right)_{Q=0} E_j(\omega) E_k(\omega) + \ldots$$

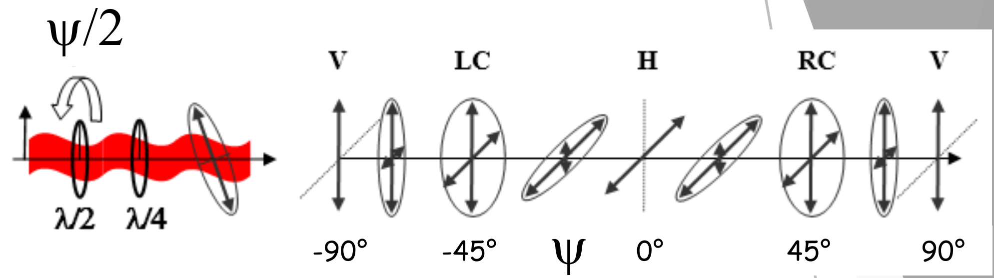
V. Rodriguez, J. Raman Spectrosc.,**2012**, 43, 627.

Hyper-Raman/hyper-Rayleigh and Raman setup

Hyper-Raman/hyper-Rayleigh setup

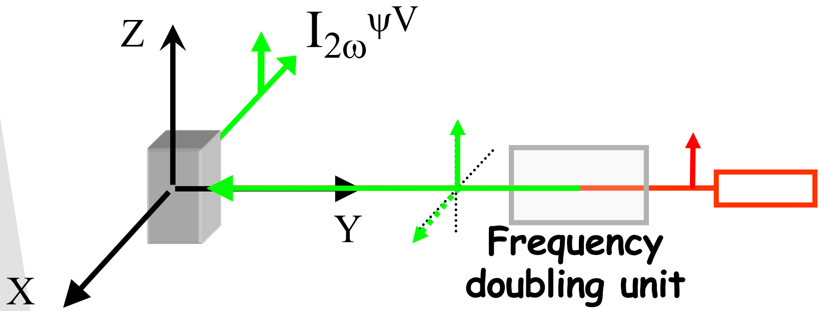
Polarization-resolved technique

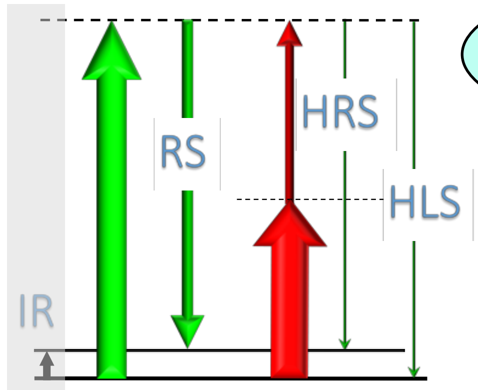




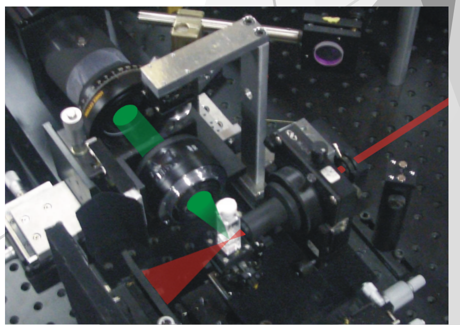
Laser Source : $Nd:YVO_4$ @1064 nm,
65 ps, 2kHz, E < 50 µj

Raman configuration (pulsed mode)





An optimized setup for the study of liquids, solids…

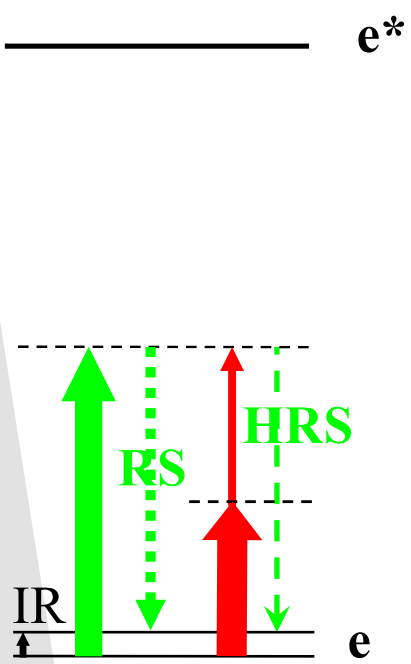


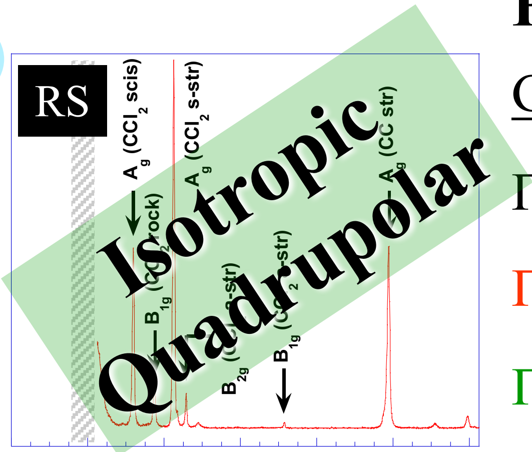
V. Rodriguez, J. Raman Spectrosc.,**2012**, 43, 627.

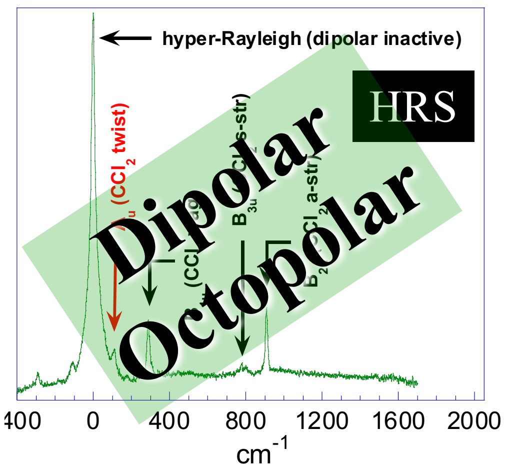
Extended vibrational studies: multipolar activity

A simple example

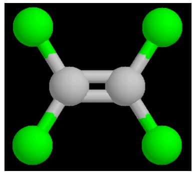
Combining the 3 techniques







Pure liquid C_2Cl_4

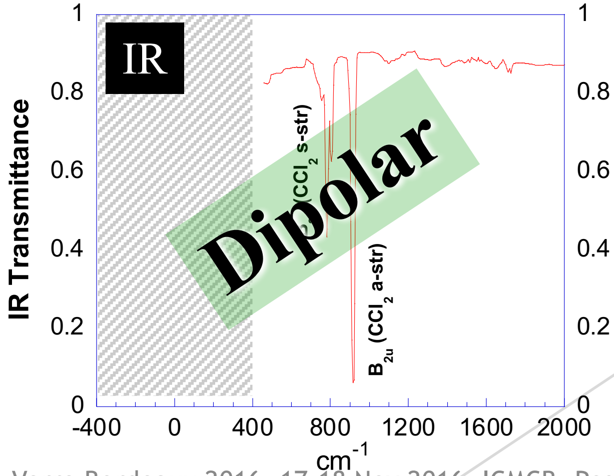


Group symmetry D_{2h}:

$\Gamma_{IR} = [B_{1u} \oplus 2\ B_{2u} \oplus 2\ B_{3u}]$

$\Gamma_{RS} = [3\ A_g] \oplus [2\ B_{1g} \oplus B_{2g}]$

$\Gamma_{HRS} = [\Gamma_{IR}] \oplus [A_u \text{ (silent mode)}]$



Extended vibrational studies: multipolar activity

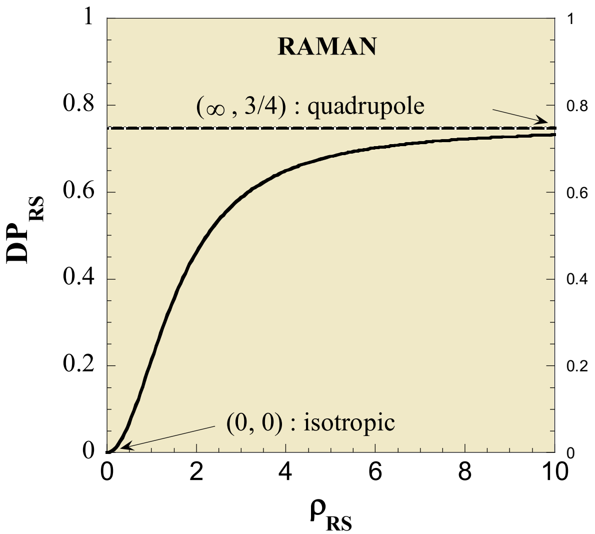
Symmetry rules in any isotropic media

…including glasses

$$\langle \alpha_{//}^2 \rangle \propto \frac{1}{3}\alpha_{J=0}^2 + \frac{2}{15}\alpha_{J=2}^2$$

$$\langle \alpha_{\perp}^2 \rangle \propto + \frac{1}{10}\alpha_{J=2}^2$$

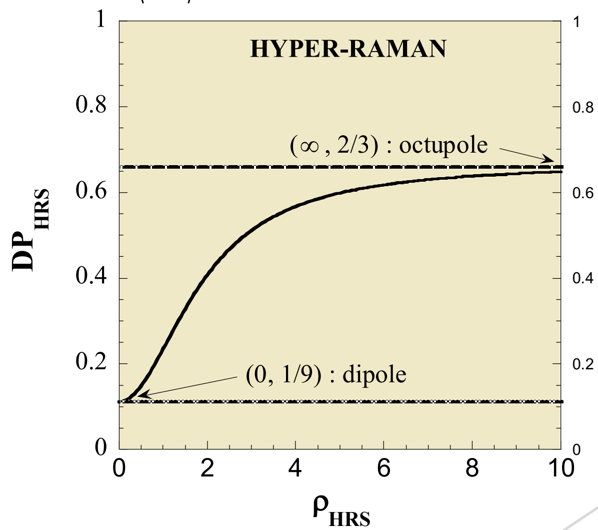
$$DP_{RS} = \frac{\langle \alpha_{\perp}^2 \rangle}{\langle \alpha_{//}^2 \rangle} = \frac{3\rho_{\mathrm{RS}}^2}{10+4\rho_{\mathrm{RS}}^2}; \quad \rho_{\mathrm{RS}} = \frac{\alpha_{J=2}}{\alpha_{J=0}}$$



$$\langle \beta_{//}^2 \rangle \propto \frac{1}{5}\beta_{J=1}^2 + \frac{2}{35}\beta_{J=3}^2$$

$$\langle \beta_{\perp}^2 \rangle \propto \frac{1}{45}\beta_{J=1}^2 + \frac{4}{105}\beta_{J=3}^2$$

$$DP_{HRS} = \frac{\langle \beta_{\perp}^2 \rangle}{\langle \beta_{//}^2 \rangle} = \frac{1}{9}\left[\frac{7+12\rho_{\mathrm{HRS}}^2}{7+2\rho_{\mathrm{HRS}}^2}\right]; \quad \rho_{\mathrm{HRS}} = \frac{\beta_{J=3}}{\beta_{J=1}}$$



$$I_{VV} = I_{\mathrm{P}}$$

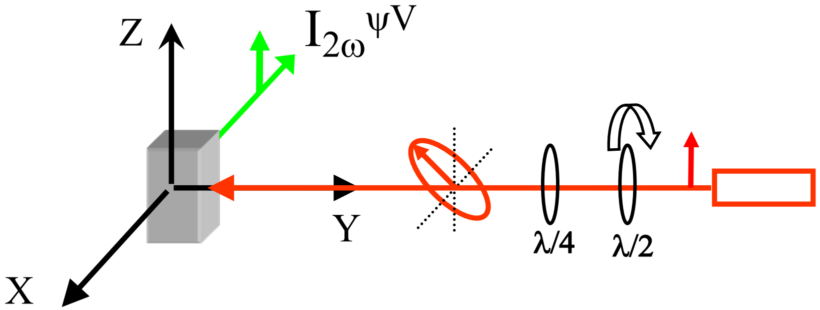
$$I_{HV} = I_{\perp}$$

Raman:
sensible to density fluctuation

Hyper-Raman:
sensible to orientational correlation (rotation)

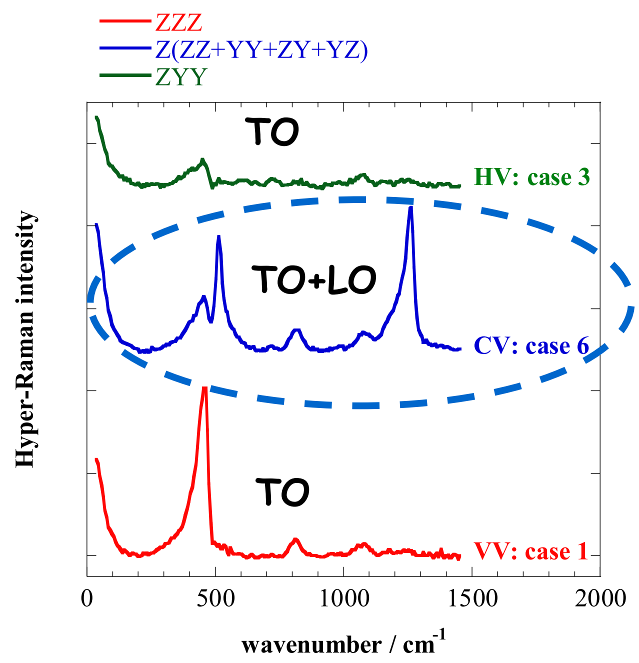
Extended vibrational studies: multipolar activity

Hyper-Raman/hyper-Rayleigh setup



Polarization-resolved technique

New additional TO-LO selection rules in hyper-Raman



SiO_2 – silica glass

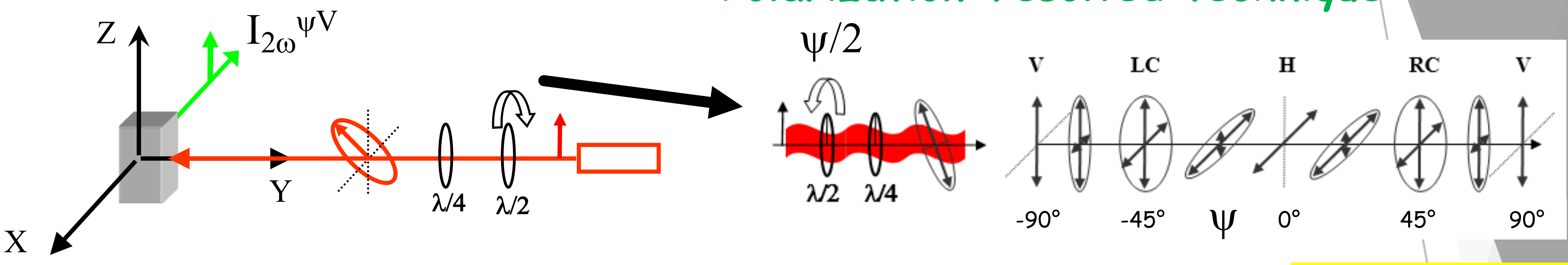
Vibrational Multipolar Decomposition
(with reduced RS and HRS intensities: at least corrected from Temperature)

$$\begin{aligned}
&Isotropic && (J=0:RS) && I_{l=0} \propto +3I_{RS}^{//} \quad -4I_{RS}^{\perp} \\
&Dipolar:TO && (J=1:HRS) && I_{l=1}^{TO} \propto +2I_{HRS}^{VV} \quad -3I_{HRS}^{HV} \;;\; (IR): \varepsilon''(\bar{\nu}) \propto Abs(\bar{\nu})/\bar{\nu} \\
&:LO && (J=1:HRS) && I_{l=1}^{LO} \propto +2I_{HRS}^{VH} \quad -I_{HRS}^{CH} \;;\; (IR): -\mathrm{Im}(1/\varepsilon) \\
&Quadrupolar && (J=2:RS) && I_{l=2} \propto I_{RS}^{\perp} \\
&Octupolar && (J=3:HRS) && I_{l=3} \propto -I_{HRS}^{VV} \quad +9I_{HRS}^{HV}
\end{aligned}$$

V. Rodriguez, J. Raman Spectrosc.,**2012**, 43, 627.

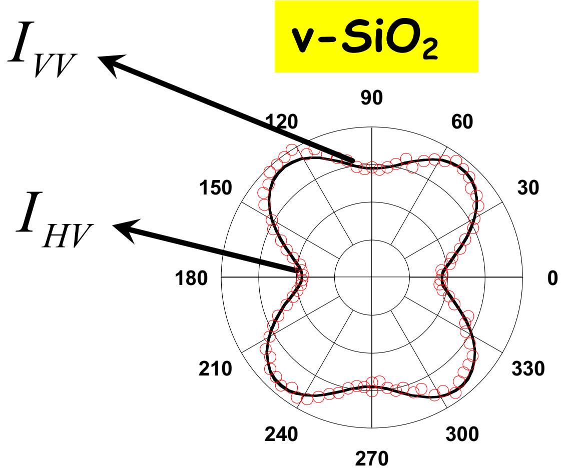
Hyper-Rayleigh Scattering: a unique tool to elucidate the (Nano) Structure of materials

Polarization-resolved technique



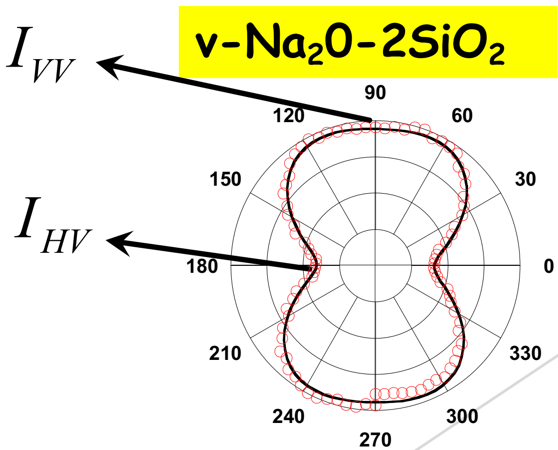
→ **gives an indication of the dipolar /octupolar nature of the ESU:** $\left(DR = I_{VV} / I_{HV}\right)$

ESU: Elementary Structural Unit



DR=3/2
Octupolar

Regular SiO_2 tetrahedra



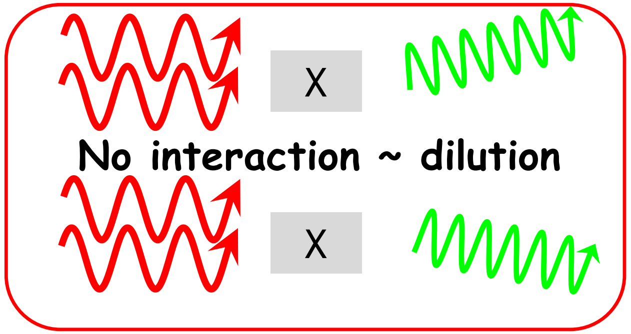
DR=2.34 > 3/2
Dipolar/octupolar

Distorted SiO_2 tetrahedra

Hyper-Rayleigh Scattering: a unique tool to elucidate the (Nano) Structure of materials

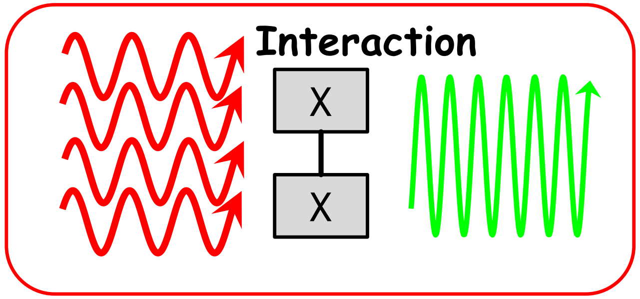
→ sensible to the special extent of the ESU

Structural Incoherent response



$$I^{2\omega}_{Incoherent} \propto [N_X] |\beta_X|^2$$

Structural Coherent response

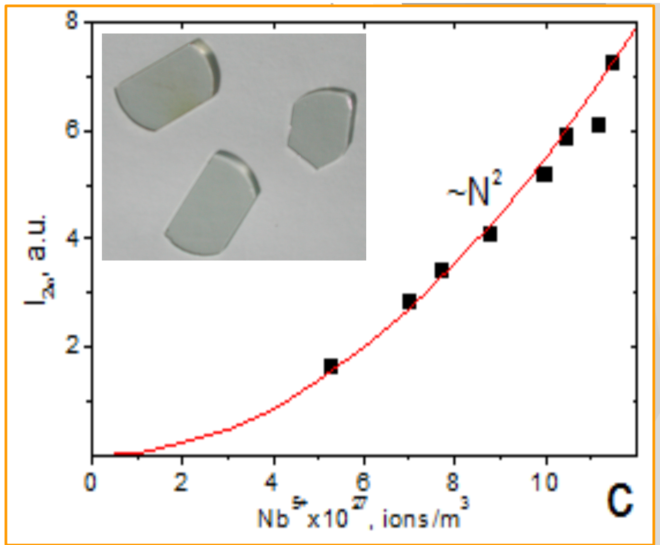


$$I^{2\omega}_{coherent} \propto [N_X]^2 |\beta_X|^2$$

Sodium Niobium Borophosphate

oxide glasses (BPNx)

$(1-x)[0,95NaPO_3+0,05Na_2B_4O_7]+xNb_2O_5$



→ sensible to nonlocal response of sizable nanoclusters (d> ~15 nm)
(Quadrupolar effective electric response)

Coherent response from highly correlated nanoclusters of NbO_3

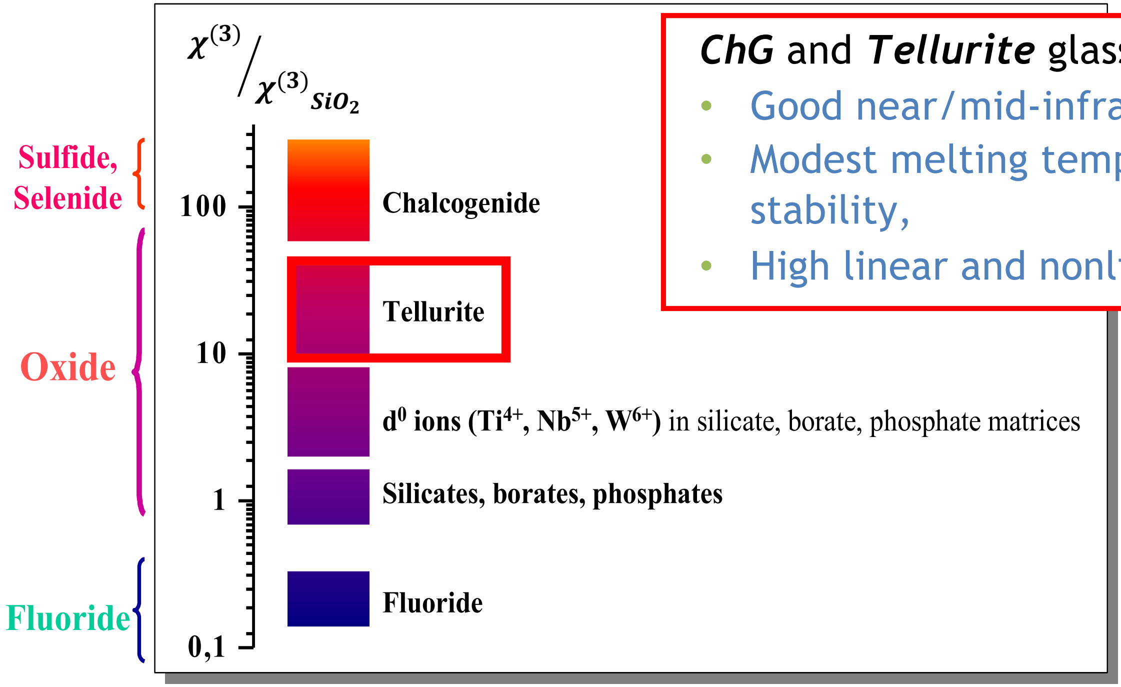
Te-based Glasses for Raman gain

$$P_i = \mu_i^{(0)} + \alpha_{ij} E_j + \beta_{ijk} E_j E_k + \gamma_{ijkl} E_j E_k E_l + \ldots$$

Third-order nonlinear polarization
(Stimulated Raman Gain-SRG)

Glass Families for nonlinear optical applications

Measured at 1.5 µm



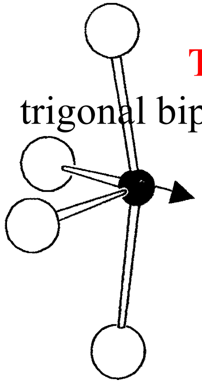
ChG and ***Tellurite*** glasses offer:

- Good near/mid-infrared transparency,
- Modest melting temperatures and good glass stability,
- High linear and nonlinear refractive indices.

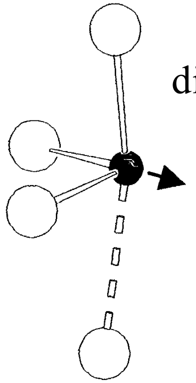
Te-based Glasses for Raman gain

Te^{4+} :
(Tellurite)

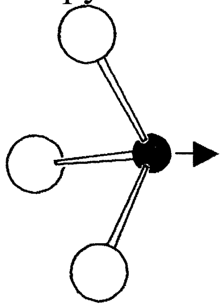
TeO_4
trigonal bipyramidal units

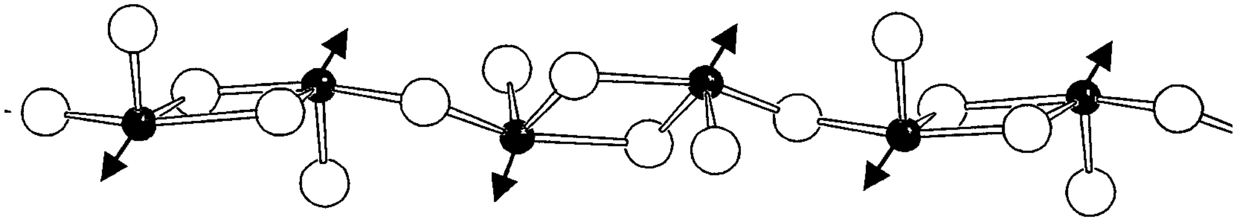


TeO_{3+1}
disphenoids



TeO_3
trigonal pyramidal units





TeO_2 chain-like arrangement, observed in paratellurite α-TeO_2

V. Rodriguez et al., *Hyper-Raman and Raman scattering in paratellurite TeO_2*. Journal of Raman Spectroscopy **2013**, 44, 739-745.

Te-based Glasses for Raman gain

TeO_2-$TaO_{5/2}$-ZnO glass system

Trade-off in the choice of the glass modifiers: ZnO helps for the fiber fabrication…
but what about the consequences ?

$(80+x)TeO_2$-$(20-x)TaO_{5/2}$

Glass modifier

impact of the glass structure ?

Raman gain response ?
NLO responses ?

$80TeO_2$-$(20-y)TaO_{5/2}$-yZnO

Glass former

V. Rodriguez et al., JPC C **2016**, 120, 23144.

vibrational responses and signatures ?

Effect of the glass polymerization ?

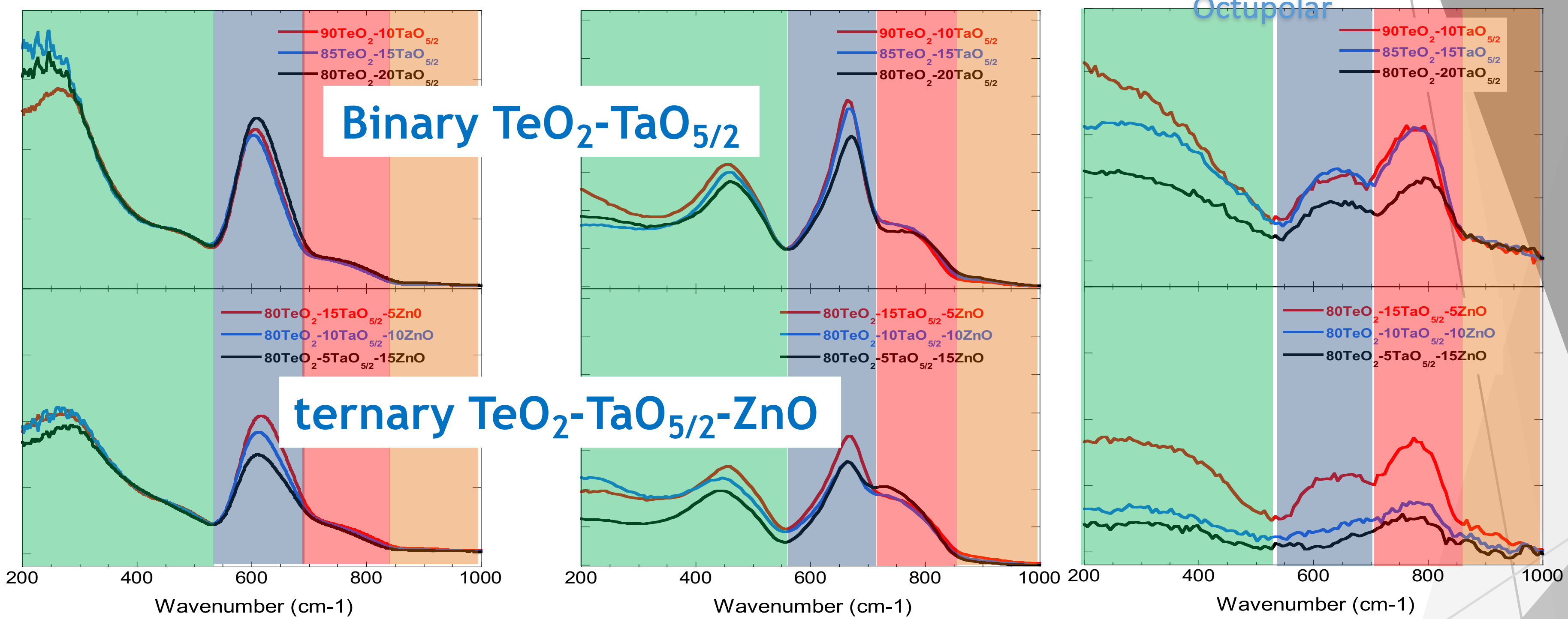
G. Guéry et al., Int. J. of Applied Glass Science **2014**, 5(2), 178

G. Guery et al., Chemical Physics Letters **2012,** 554, 123.

Te-based Glasses for Raman gain

Extended vibrational studies:

IR Dipolar **RS-VV** Isotropic, Quadrupolar **HRS-VV** Dipolar, Octupolar



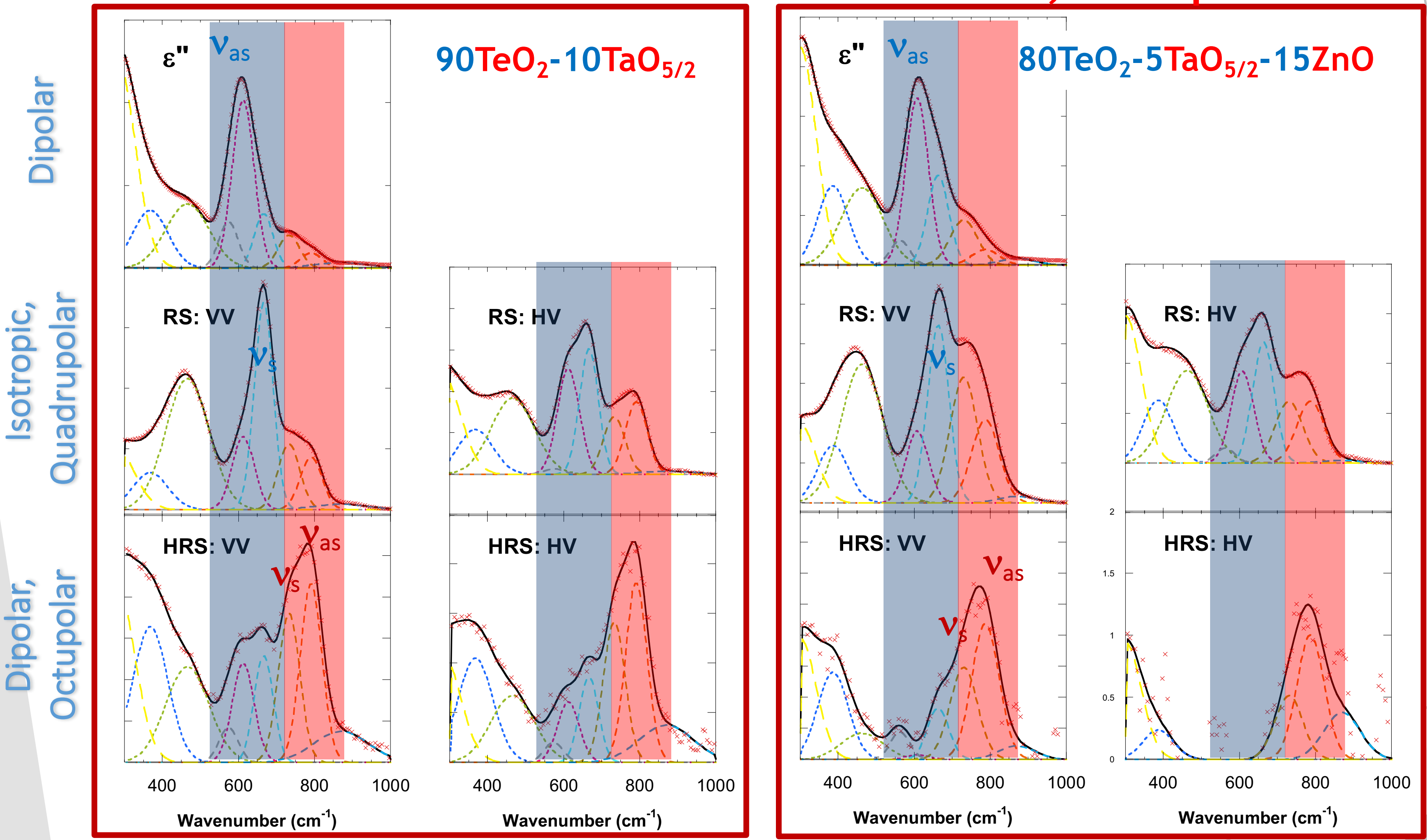
Te-O-Te
TeO_4
TeO_{3+1}
TaO_6

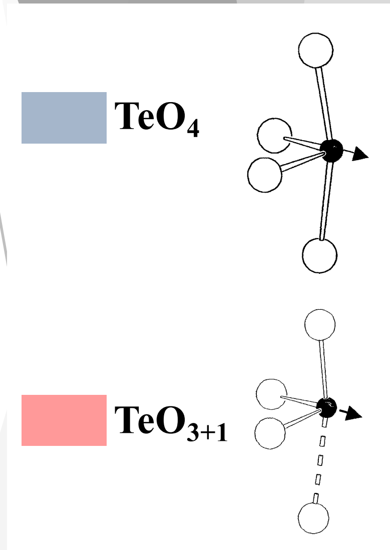
Vibrational spectra (IR, RS and HRS) are governed by the tellurite network
→ Need of spectrum deconvolution for obtaining the '*real*' species' contributions.

V. Rodriguez et al., JPC C **2016**, 120, 23144.

Te-based Glasses for Raman gain

Extended vibrational studies: one model, five spectra





Te-based Glasses for Raman gain

(80+x)TeO_2-(20-x)$TaO_{5/2}$

Glass modifier

impact of the glass structure ?

80TeO_2-(20-y)$TaO_{5/2}$-yZnO

Glass former

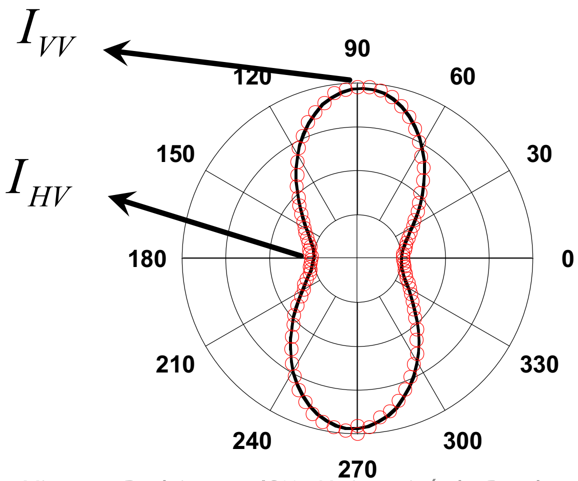
Effect of the glass polymerization ?

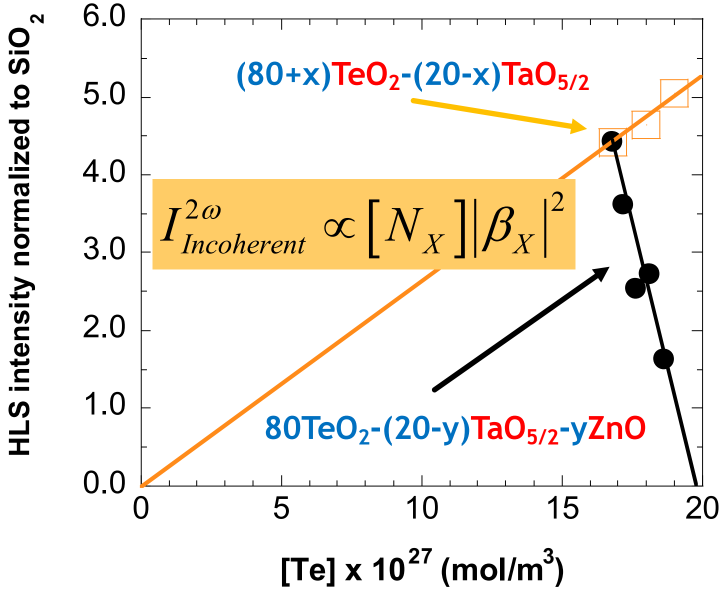
Structure insights from hyper-Rayleigh scattering

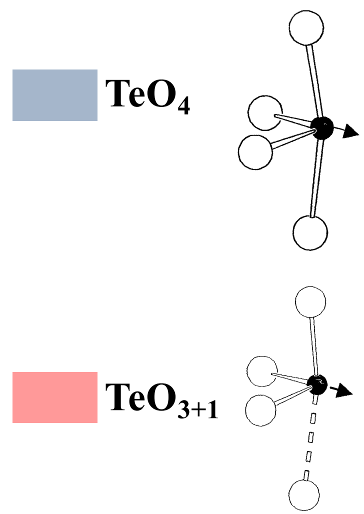
No change with composition

DR ~ 3.8 (more dipolar)

No change of ESU structure







Structural incoherent response:

Behavior of « diluted-like ESU »

Te-based Glasses for Raman gain

$(80+x)TeO_2$-$(20-x)TaO_{5/2}$

Glass modifier

impact of the glass structure ?

$80TeO_2$-$(20-y)TaO_{5/2}$-$yZnO$

Glass former

Effect of the glass polymerization ?

LO and NLO responses (HLS,Raman gain and Linear susceptibility)

Raman gain measured with spontaneous Raman (C. Rivero et al.)

$$\left|\chi^{(1)}\right|^2 = \left[\left(n^2-1\right)/4\pi\right]^2$$

@1064 nm

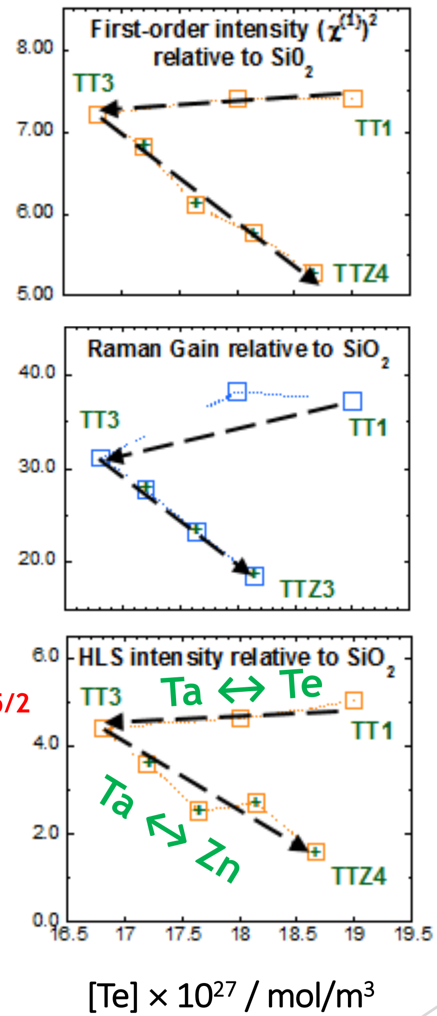
$$\left|\chi^{(3)}\right|^2$$

@752 nm (660 cm^{-1})

$80TeO_2$-$20TaO_{5/2}$

$$\left|\chi^{(2)}\right|^2$$

@1064 nm



Introduction of tantalum oxide slightly decreases the susceptibilities

Introduction of zinc oxide drastically decreases the susceptibilities

$80TeO_2$-$5TaO_{5/2}$-$15ZnO$

$90TeO_2$-$10TaO_{5/2}$

$80TeO_2$-$20ZnO$

C. Rivero, PhD thesis (2005) University of Central Florida, USA/University of Bordeaux, France

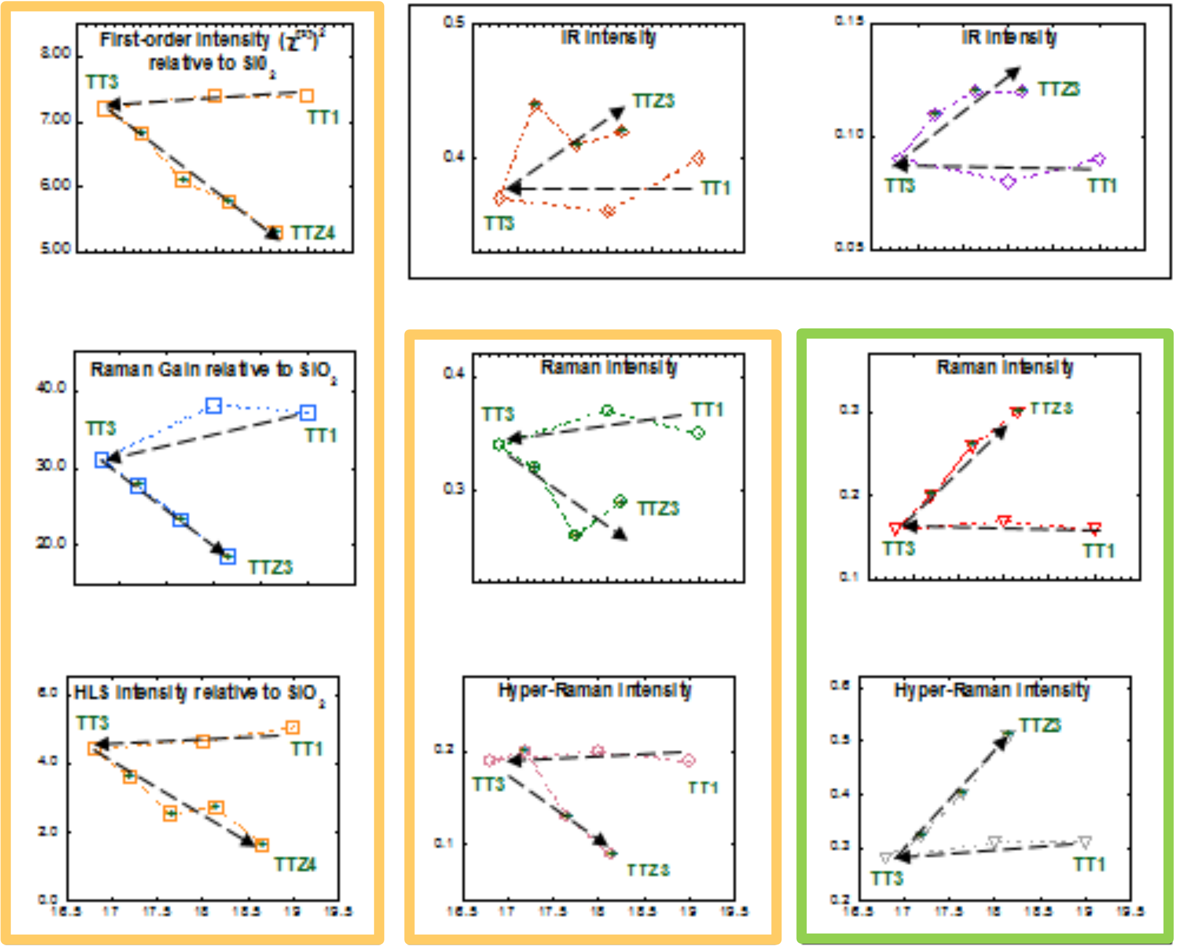
Te-based Glasses for Raman gain

Linear and Nonlinear optical Intensities

Vibrational Spectroscopies

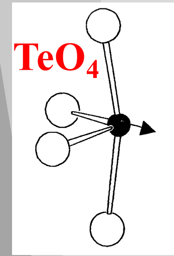
Modes 3 and 4 of TeO_4

Modes 5 and 6 of TeO_{3+1}

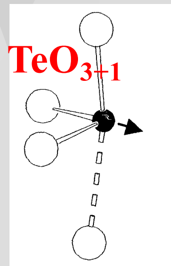


[Te] × 10^{27} / mol/m^3

Strong correlation of the decrease of the susceptibilities and the RS and HRS intensities of TeO_4…



… while RS and HRS intensities of TeO_{3+1} increase.



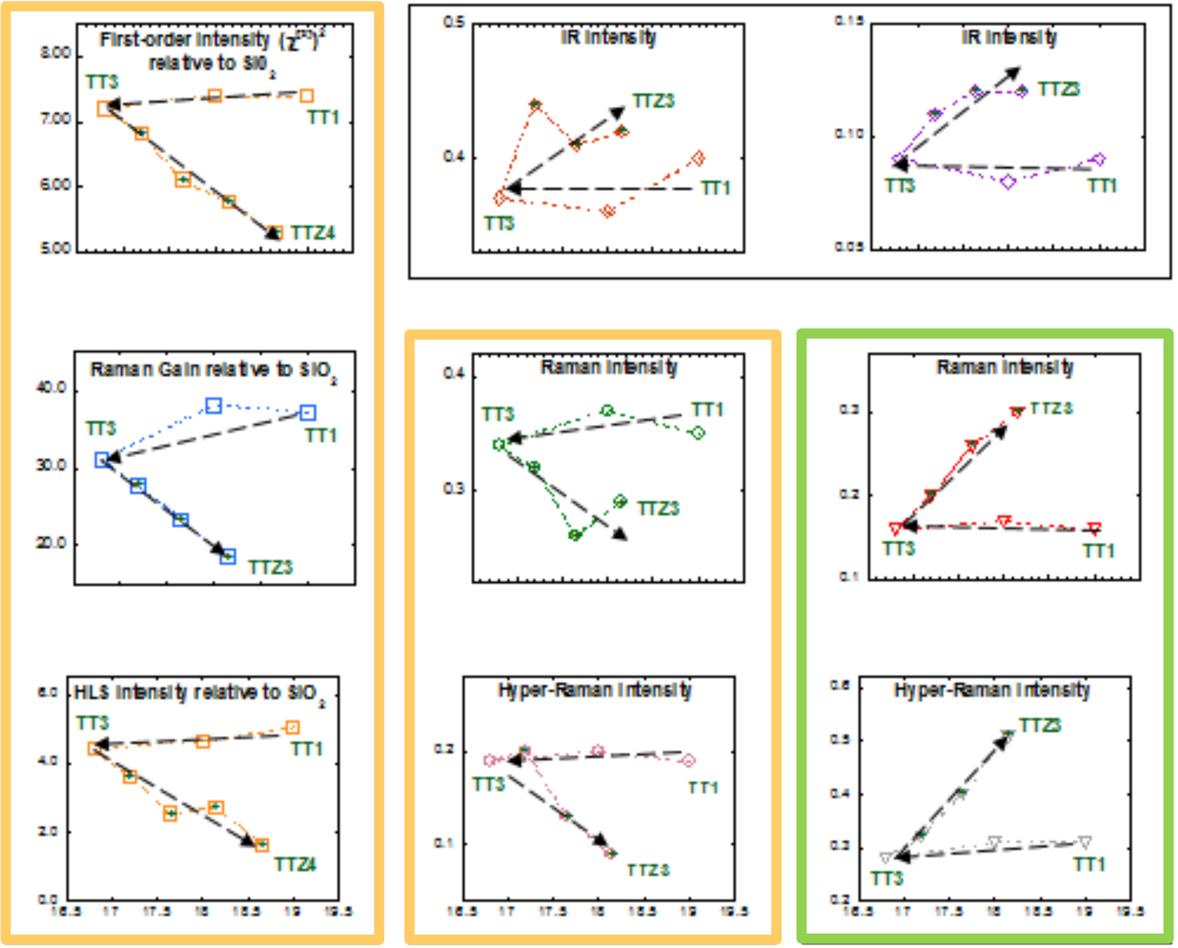
Te-based Glasses for Raman gain

Linear and Nonlinear optical Intensities

Vibrational Spectroscopies

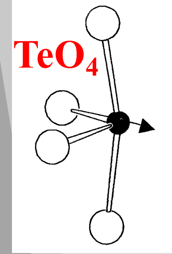
Modes 3 and 4 of TeO_4

Modes 5 and 6 of TeO_{3+1}

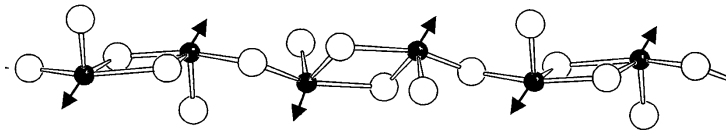


[Te] × 10^{27} / mol/m^3

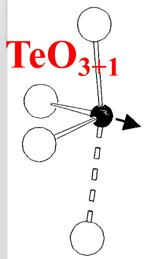
Strong correlation of the decrease of the susceptibilities and the RS and HRS intensities of TeO_4…



TeO_2 chain-like arrangement



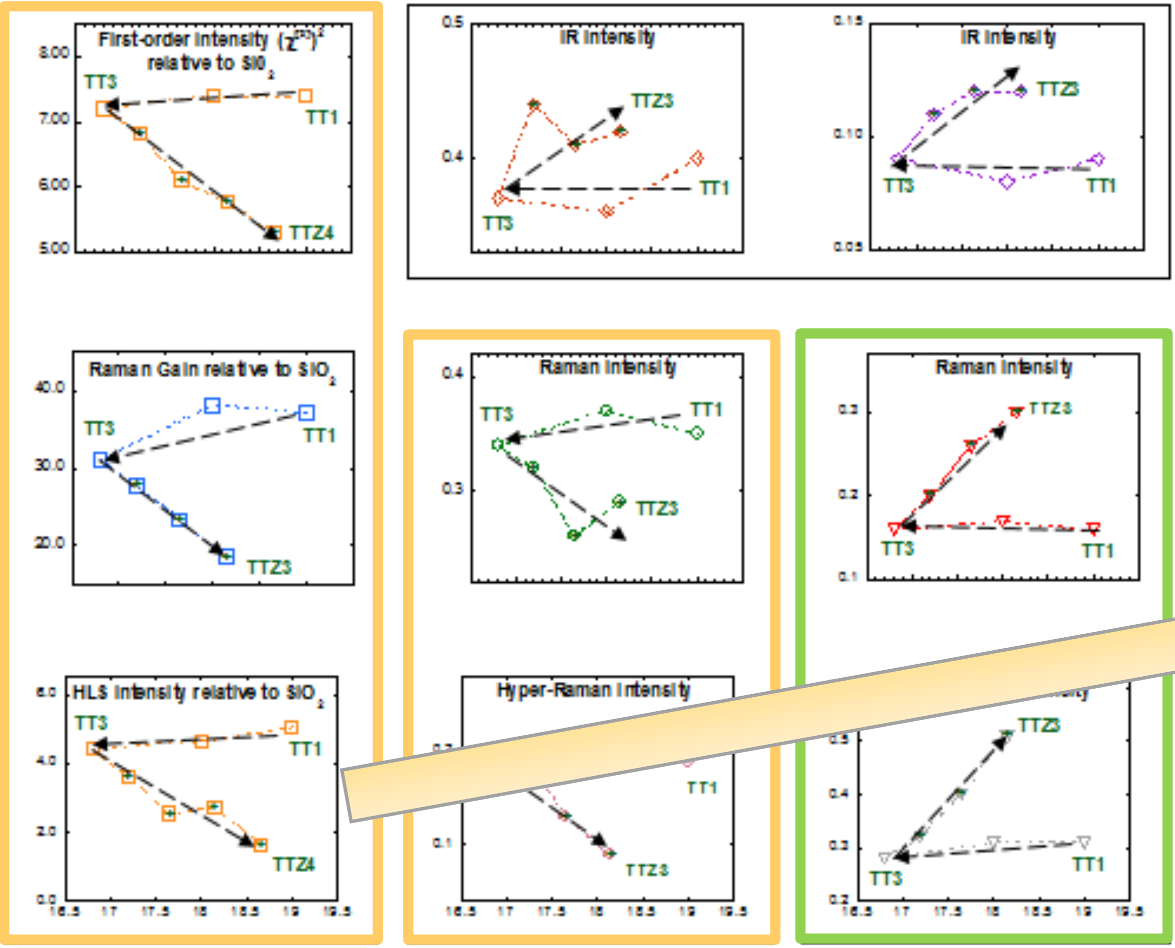
Discontinuity of Te-O-Te chains: change of the size of correlated chains



… while RS and HRS intensities of TeO_{3+1} increase.

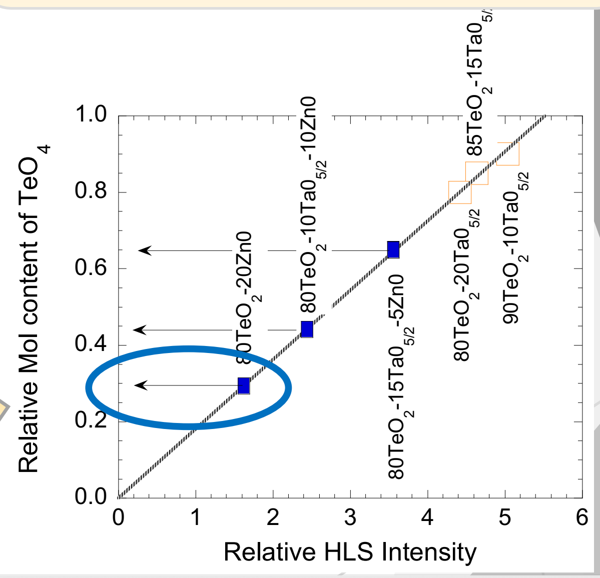
Te-based Glasses for Raman gain

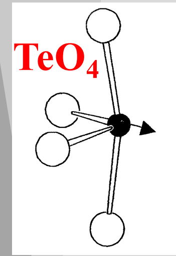
Linear and Nonlinear optical Intensities | Vibrational Spectroscopies: Modes 3 and 4 of TeO_4 | Modes 5 and 6 of TeO_{3+1}

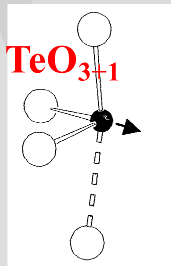


[Te] × 10^{27} / mol/m^3

Strong correlation of the decrease of the susceptibilities and the RS and HRS intensities of TeO_4…







In good accordance with neutron diffraction results of $80TeO_2$-$20ZnO$

Approche multimodale par spectroscopies IR, Raman et hyper-Raman/hyper-Rayleigh: Relation structure/propriétés dans les verres TeO_2-$TaO_{5/2}$-ZnO

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Quadratic Nonlinear Optics

Linear and nonlinear dielectric properties

The induced polarization of a medium is given by $P(\omega) = \sum_i \mu_i(\omega) = Nf_\omega[\alpha(\omega)E(\omega)] = \chi^{(1)}(\omega)E(\omega)$

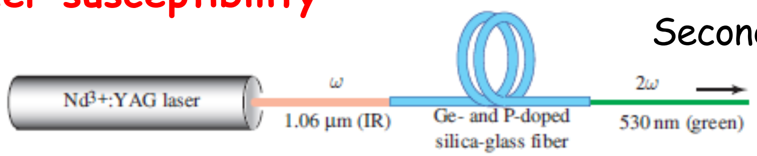
N: number density of molecules, $f_\omega = \frac{n_\omega^2 + 2}{3}$: local field factor (Lorentz-Lorenz)

$\chi^{(1)}$: first-order susceptibility (or linear susceptibility) $n_\omega^2 = \varepsilon_\omega = 1 + 4\pi\chi^{(1)}(\omega)$

→ Optical constants: $\hat{n}(\omega) = n(\omega) + ik(\omega)$ Maxwell (homogeneous medium): $(\hat{n}^2 = \varepsilon = \varepsilon' + i\varepsilon'')$

$\chi^{(2)}$: second-order susceptibility

Second Harmonic Generation (SFG, DFG, OR)



$\chi^{(3)}$: Third-order susceptibility

A lot of processes…. (Four waves mixing)

Raman gain (stimulated Raman)