Spectroscopie vibrationnelle appliquée à la détermination de la structure locale des verres silicatés

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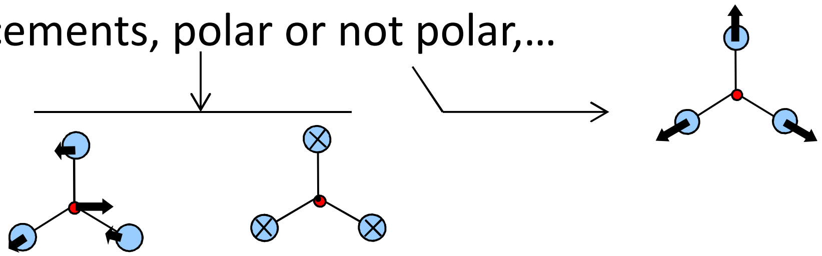
Outline

I- Vibrational spectroscopies

- Infrared, Raman and hyper-Raman scattering
- Nature of the vibrations in the glass formers SiO_2 and B_2O_3

Atomic displacements, polar or not polar,…



→ ***Quantitative description of the structural modifications in binary and ternary glasses***

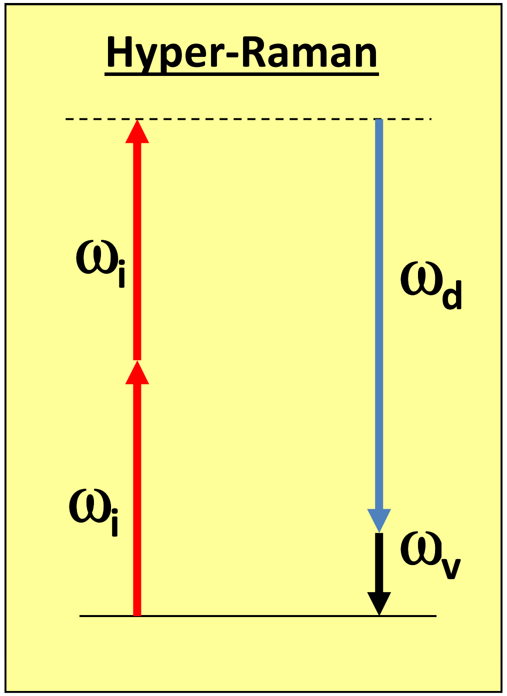
II- Hyper-Raman scattering: Coherent *vs* incoherent excitations

III- Si-O-Si angle distribution in silicates and borosilicates

IV- Signature of network modifier cations in the Raman spectra of aluminosilicate glasses

Vibrational spectroscopies

Scattered intensity: $$I(\omega,q) \propto TF\{\langle P(r,t)P(0,0)\rangle\}$$



- **Polarization :**

Induced polarization

Dipole moment — Polarizability — Hyper-Polarizability

$$P_T(r,t) = \mu(r,t) + \alpha(r,t)\,E_i + \beta(r,t)\,E_i\,E_i + \ldots$$

Infrared (IR) — Raman (RS) — Hyper-Raman (HRS)

Different selection rules in IR, RS, and HRS

Only polar modes in IR

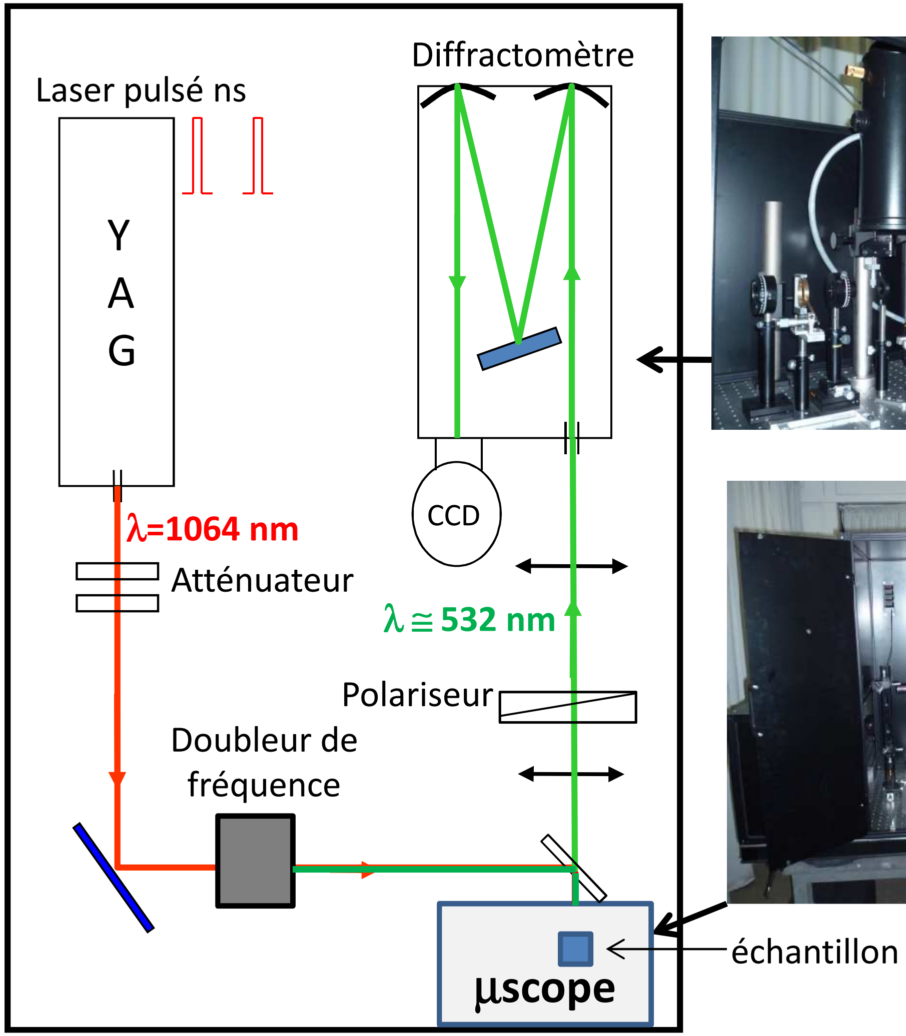
Polar and non-polar excitations in RS and HRS

Their exist excitations active in HRS not active in RS, and vice versa

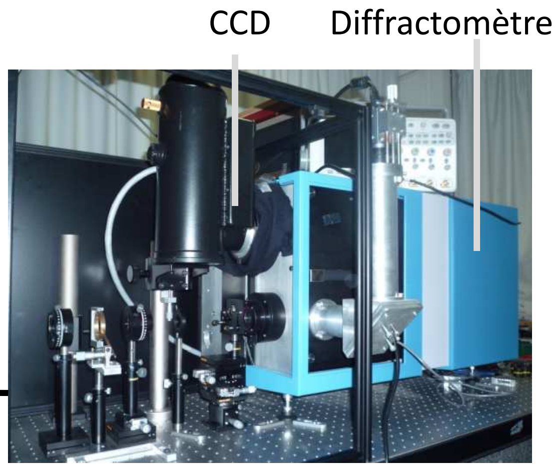
⇒ HRS complements IR and Raman techniques

Le spectromètre Hyper-Raman

$$\frac{I_{HRS}}{I_{RS}} \approx 10^{-6}$$ $\longrightarrow$ ***Nécessité d'un spectromètre très lumineux !!***



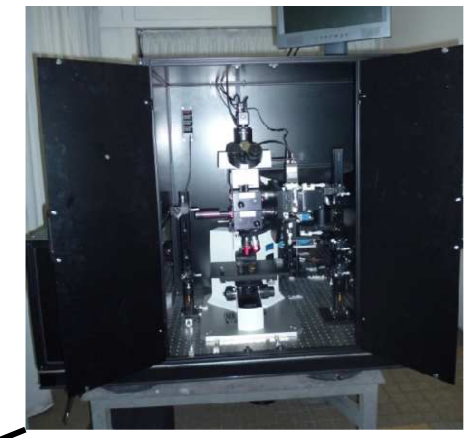
Raman



Diffractomètre :
- Haute résolution (~ 2cm^{-1})
- Haute luminosité

CCD :
-Très Sensible + faible bruit

Polariseur
- Spectres VV et VH



Microscope confocal
- Résolution spatiale qqes μm

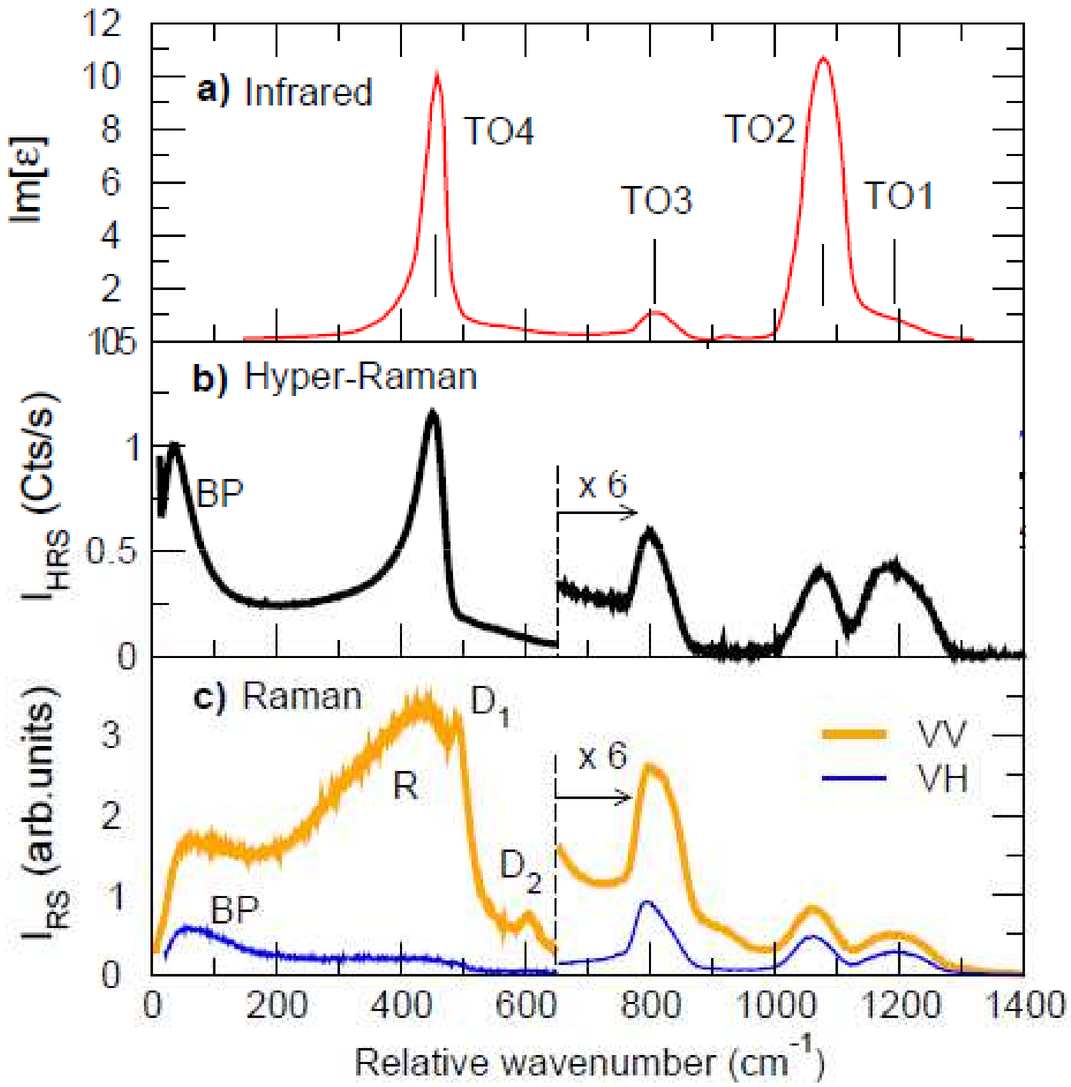
Doubleur de fréquence
$\longrightarrow$ Spectromètre Raman très lumineux

v-SiO_2: Vibrational spectroscopy

Only Polar modes

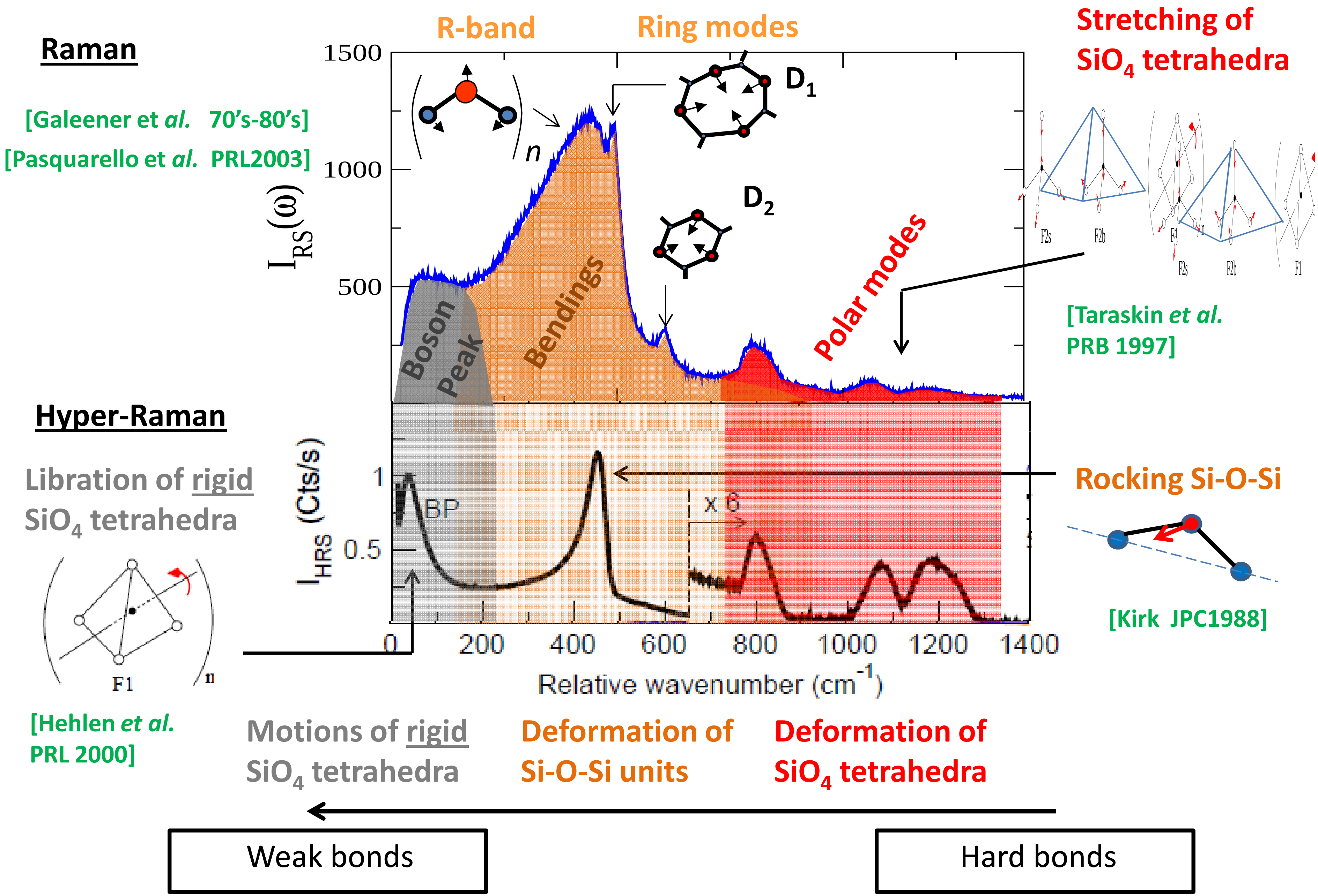
Polar modes + BP

Polar modes (but not TO4!) + BP



Selection rules partly apply !!

The vibrations of *v*-SiO_2



– II –

Hyper-Raman spectroscopy in *v*-SiO_2 :
Localized *vs* delocalized excitations

[B.Hehlen and G. Simon, JRS2012]

Hyper-Raman scattering

2^d order polarization fluctuation: $$\delta\vec{p} = \frac{\partial\chi^{(2)}}{\partial Q}\vec{E}\vec{E} = \beta\vec{E}\vec{E}$$

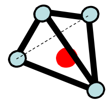
In glasses $$\beta = \beta_{Av} + \beta_{Loc}$$

Fluctuations from the average media

Local fluctuations

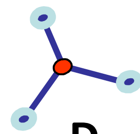
[Denisov *et al.* Phys. Rep. 1987]

- **β_{Loc} in liquids and gases**



T_d

  - Depends on the symmetry (point group) of the molecular units



D_{3h}

  - Isotropic averaging over all orientation $\longrightarrow$ **Incoherent**

$\longrightarrow$ **Scattering is independent on the wave vector q**

(intensity and depolarization ratio $\rho = I_{VH}/I_{VV}$)

HRS selection rules for β

• β_{Av} : **Isotropic average media → (∞∞m) symmetry group**

Scat. geometry	I_{VV}	I_{VH}	I_{HV}	I_{HH}
90°	$9a_{TO}^2$	$\frac{1}{2}a_{TO}^2+\frac{1}{2}a_{LO}^2$	a_{TO}^2	$\frac{1}{2}a_{TO}^2+\frac{1}{2}a_{LO}^2$
180°	$9a_{TO}^2$	a_{TO}^2	a_{TO}^2	$9a_{TO}^2$
0° (vert. slit)	$9a_{LO}^2$	a_{TO}^2	a_{LO}^2	$9a_{TO}^2$

No LOs (180° row)

Only LOs (0° (vert. slit), I_{VV})

⇒ **The scattering depends on q,**
intensities and depolarization ratios !!

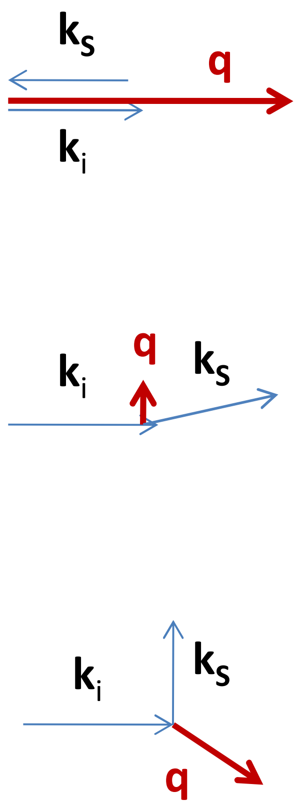
- LOs owing to their coupling with the long range electric field
- Strongly delocalized vibrations

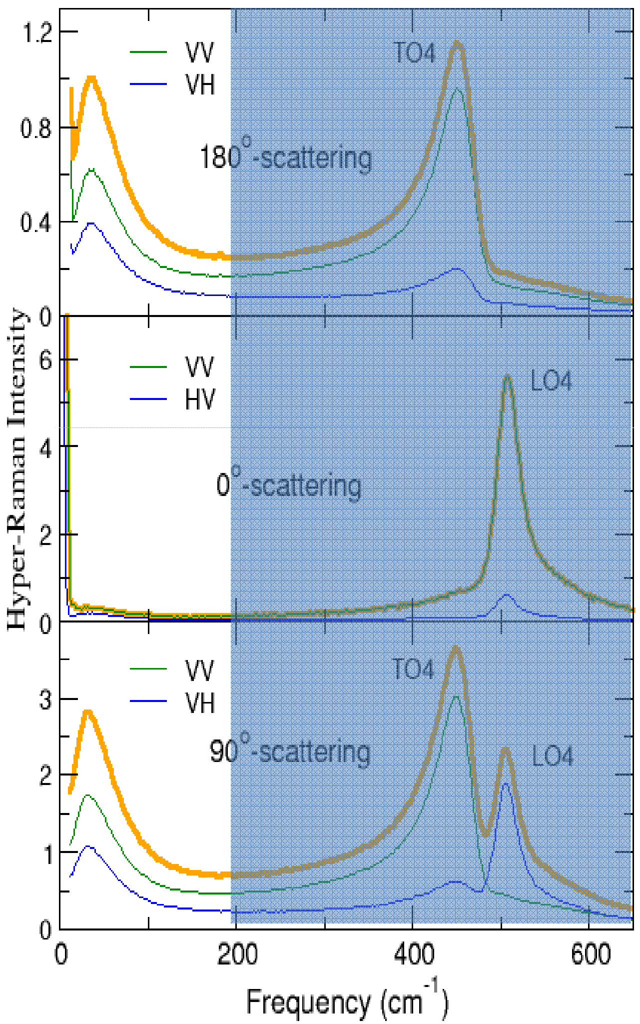
• **β in glasses: A complicated mixture of β_{Av} and β_{Loc}**

q-dependence of the HRS spectra

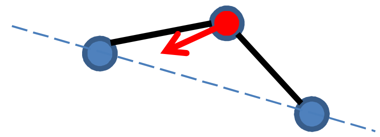
Depolarization ratio $\rho = \frac{I_{VH}}{I_{VV}}$

[B.Hehlen and G. Simon, JRS2012]





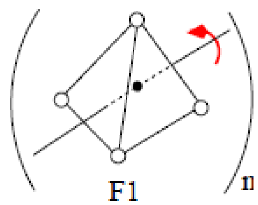
➢ **TO4-LO4 :**



ρ and I_{HRS} depend on q

→ **HRS efficiencies controled by β_{Av} ?**

➢ **HRS Boson peak :**

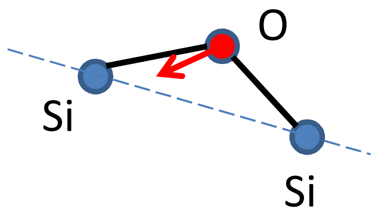


$$\rho_{BP} = 0.63 \pm 0.1$$

whatever the scattering geometry !!!

→ **HRS efficiency controled by β_{Loc}**

HRS efficiencies of the $(TO\text{-}LO)_4$ doublet



- **LO4 : fullfil the (∞∞m) average media selection rules**

  → Collective motions du to the coupling with the macroscopic E-field

- **TO4 : intermediate between (∞∞m) and local selection rules**

	Expe.	(∞∞m)
$I_{VV}^{180°} / I_{VH}^{180°}$	5.9	9
$I_{VV}^{90°} / I_{VH}^{90°}$	~10	18
$I_{VV}^{90°} / I_{VH}^{180°}$	~5.4	9

→ $\beta = \beta_{Loc} + \beta_{Av}$

→ Delocalized excitation !!

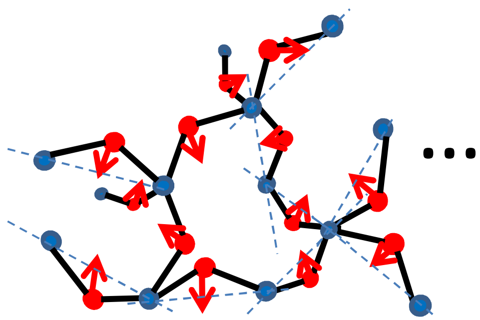
[M. Wilson *et al.* PRL 1996]

<u>Density fluctuations in *v*-SiO_2</u>

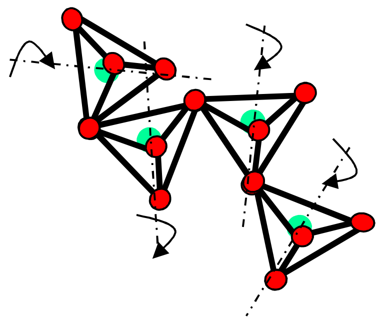
$\Delta\rho/\rho \cong 1.2\%$ in a volume of ~ $(2\ nm)^3$ → ~ 235 SiO_2 units

[A.M. Levelut and A. Guinier, Bull. Soc. Fr. Miné. Crist. 1967]

→ Up to ~100 Si-O-Si units could be involved !!



The Boson Peak



- **The <u>HRS</u> Boson Peak**
  - Scattering independent on q
  - Constant depolarization ratio $\rho = I_{VH}/I_{VV} = 0.63$

    $\rightarrow$ **Local or quasi-local excitations**

Librations of rigid SiO_4 tetrahedra [B. Hehlen *etal.*, PRL 2000]

- **Importance of librations at low-frequency in v-SiO_2**

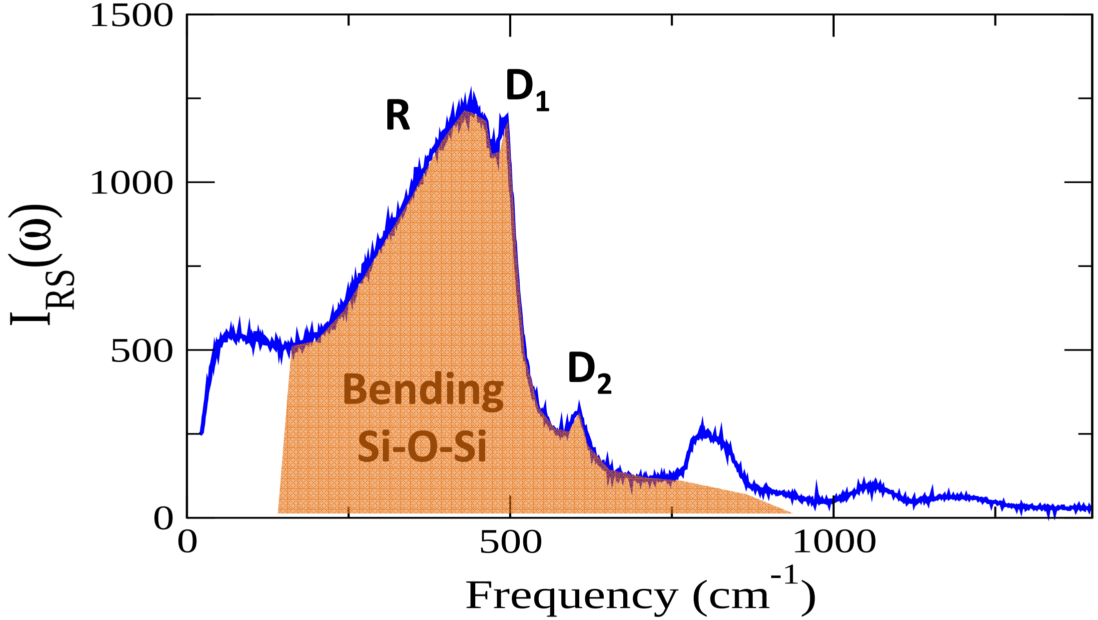
  - Soft mode of the α-β transition of α-quartz [Y. Tezuka *et al.*, PRL 1991]
  - Its frequency extrapolate to that of the glass at Tg [B. Hehlen *et al.*, JNCS 2002]
  - Supported by numerical simulations [B. Guillot *et al.*, PRL1997]
  - They participate to the total excess of low-ω vibrations [U. Buchenau *et al.*, PRL 1984]
  - Compatible with the Rigid Units Model (RUM) [K. Trachenko *et al.*, PRL 1998]

Boson Peak (excess of Cp/T^3 at low-T) :

Rigid librations + Translations

– III –
-O- bond angle of silicates extracted from their Raman spectra

[B.Hehlen, JPCM2010]



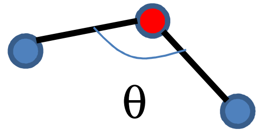
Raman is highly sensitivity to local structural modifications and very simple to operate but,… *it hardly provides quantitative estimates !!*

One example :

Bending modes R, D1, D2

What has to be known :

→ Si-O-Si angle θ

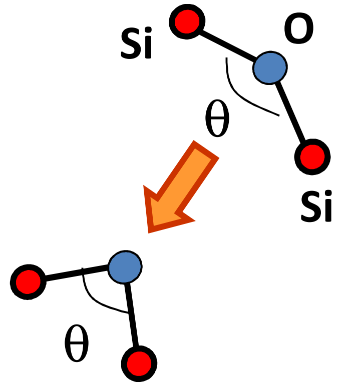


1	Coupling to light coefficient $C(\omega)$	$C(\omega) \propto \omega^2$
2	Coherent or incoherent scattering	No
3	Relation between the frequency or/and intensity and the structural property	$cos(\theta/2) = 7.33\ 10^{-4}\ \omega$
4	Effect of the surrounding on points 1-3	No

- After normalization by $C(\omega)$, the frequency of the R, D1 and D2 bands relates to the Si-O-Si angle through 3

- The transformation is however an approximation du to the unknowns 2 and 4

Raman Scattering in permanently densified silicas, *d*-SiO_2

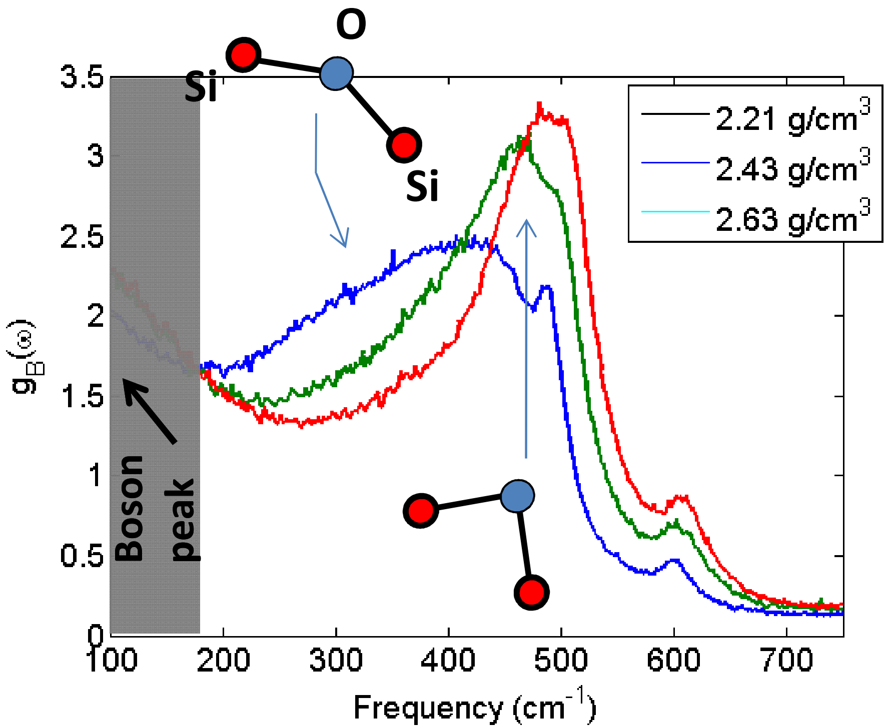


- **Permanent densification**

  - Reduction of the Si-O-Si angle θ in the network
  - SiO_4 tetrahedra remain unchanged [Y.Inamura *et al.* JNCS 2001]

  → **Puckering of the ring network + bond redistribution**

- **Density of states of bending modes**



Raman Intensity

$$g_B(\omega) \propto \frac{1}{\rho \omega_i \omega_s^3} \frac{\omega}{C_B(\omega)} \frac{I^{RS}(\omega)}{[n(\omega)+1]}$$

Glass density   Coupling function

For those $C_B(\omega) \propto \omega^2$

[B.Hehlen, JPCM2010]

$$g_B(\omega) \propto \frac{1}{\rho \omega_i \omega_s^3} \frac{I^{RS}(\omega)}{\omega \cdot [n(\omega)+1]}$$

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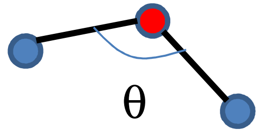

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4	Effect of the surrounding on points 1-3	No

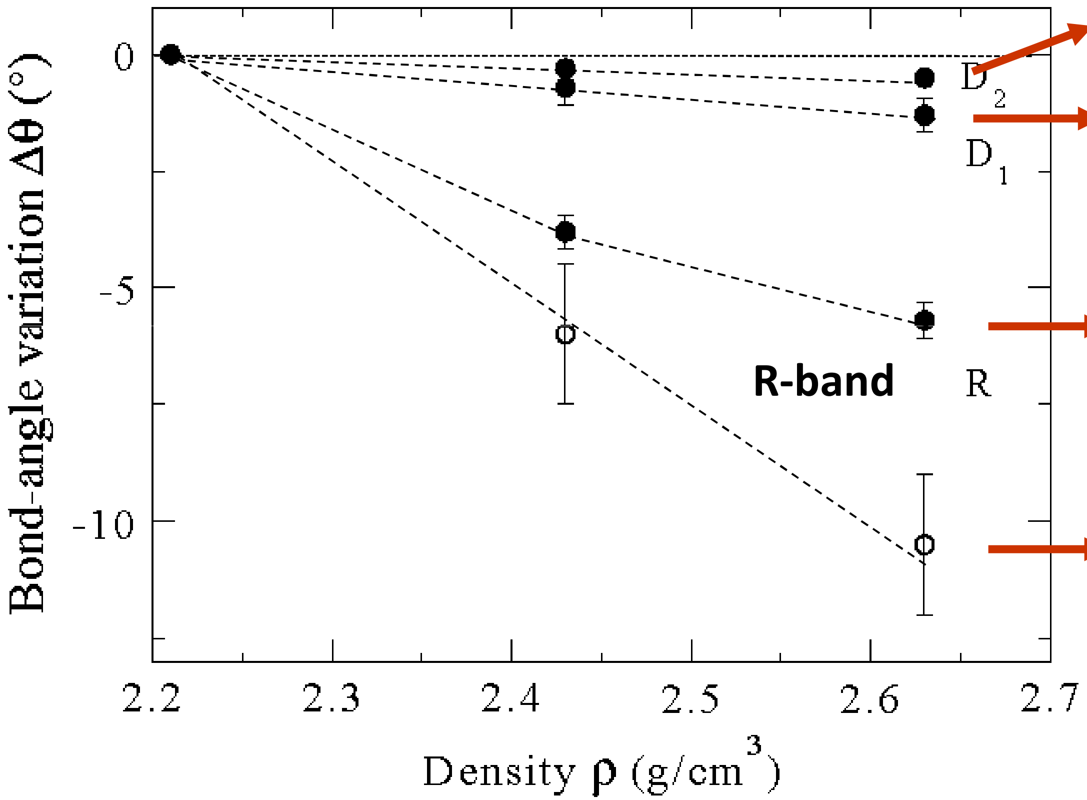
⇒ ~VDOS g(ω)

- After normalization by C(ω), the frequency of the R, D1 and D2 bands relates to the Si-O-Si angle through 3

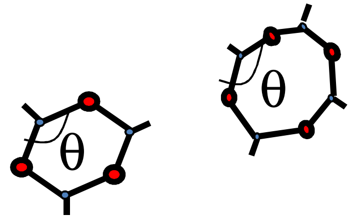
- The transformation is however an approximation du to the unknowns 2 and 4

Si-O-Si angle θ in *d*-SiO_2

[B. Hehlen, J.Phys.: Cond Matter 2010]



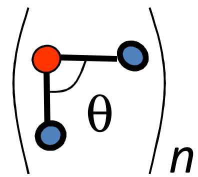
Small rings :



***n* = 3**

***n* = 4**

Network angle :

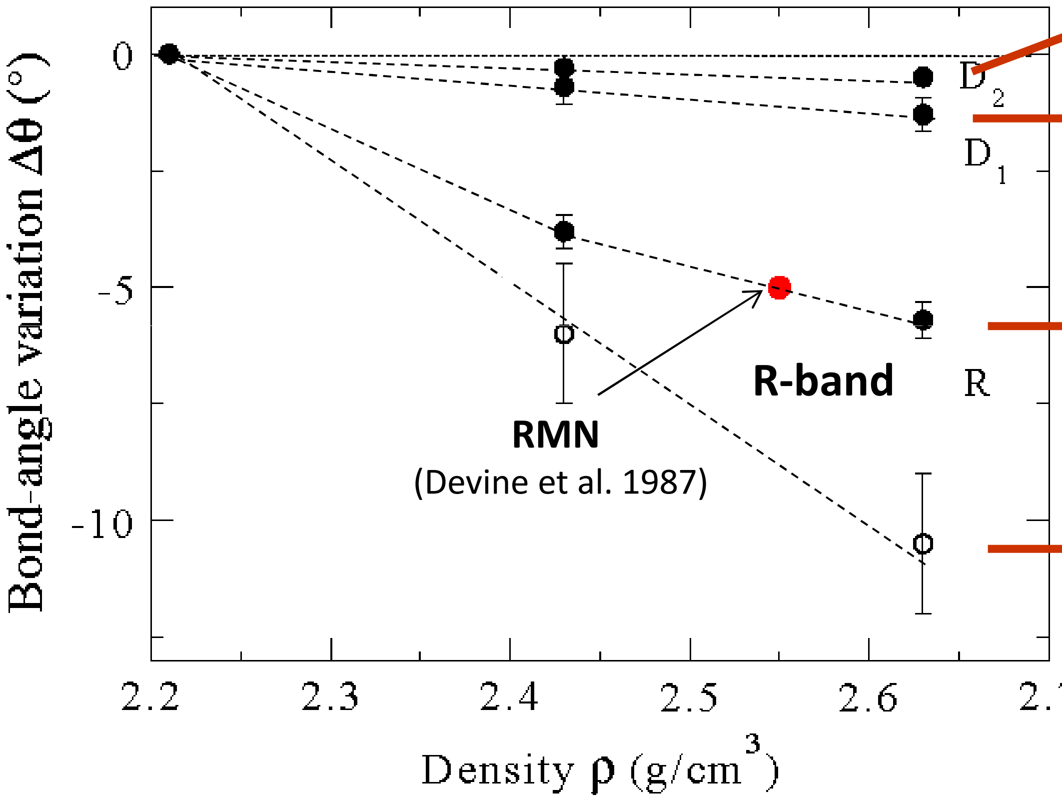


***n* ≅ 6** *Max. of the distribution*

***n* > 6** *Average angle*

Si-O-Si angle θ in *d*-SiO_2

[B. Hehlen, J.Phys.: Cond Matter 2010]



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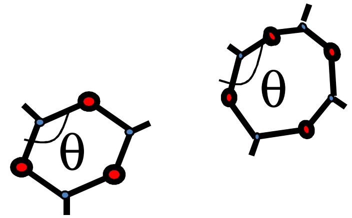

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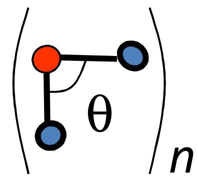

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Si-O-Si angle θ in *d*-SiO_2

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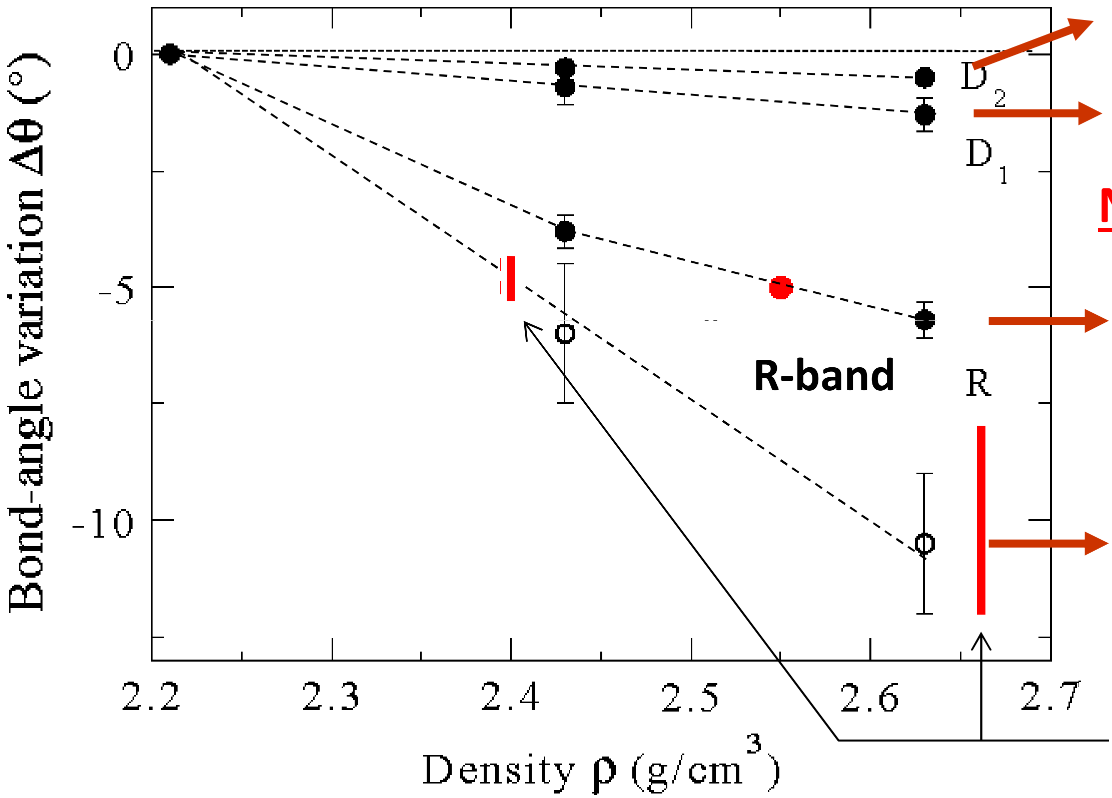

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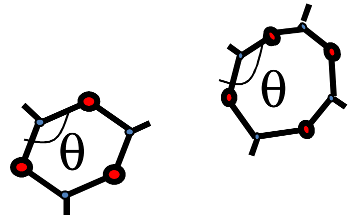
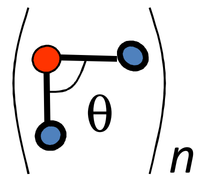


n **= 3**

n **= 4**

<u>Network angle :</u>



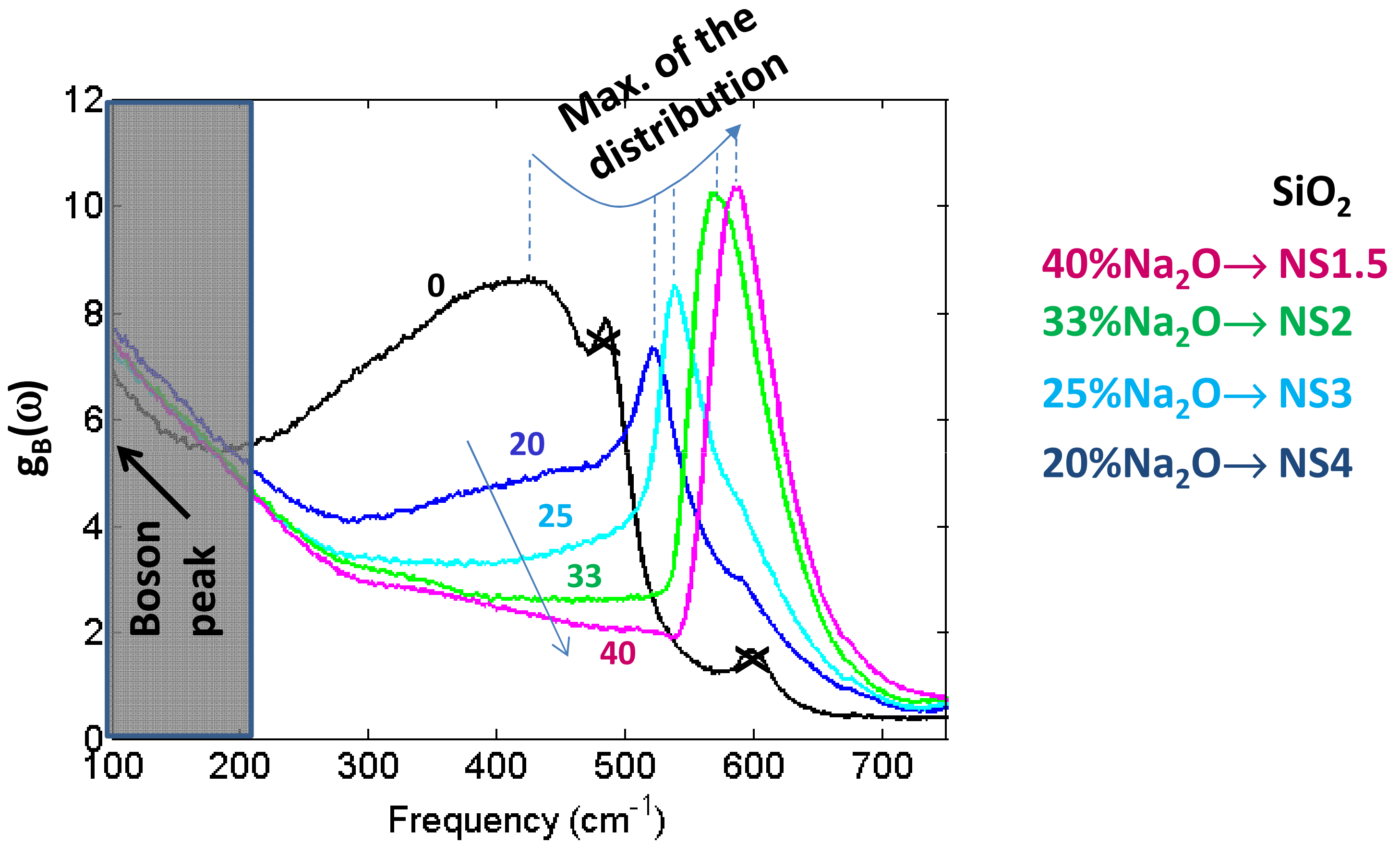
n **≅ 6** *Max. of the distribution*

n **> 6** *Average angle*

Simulations [Rahmani *et al.* PRB,2003]
[Matsubara , Ispas, Kob, 2009]

Si-O-Si angle in sodo-silicates

Density of states of bending modes

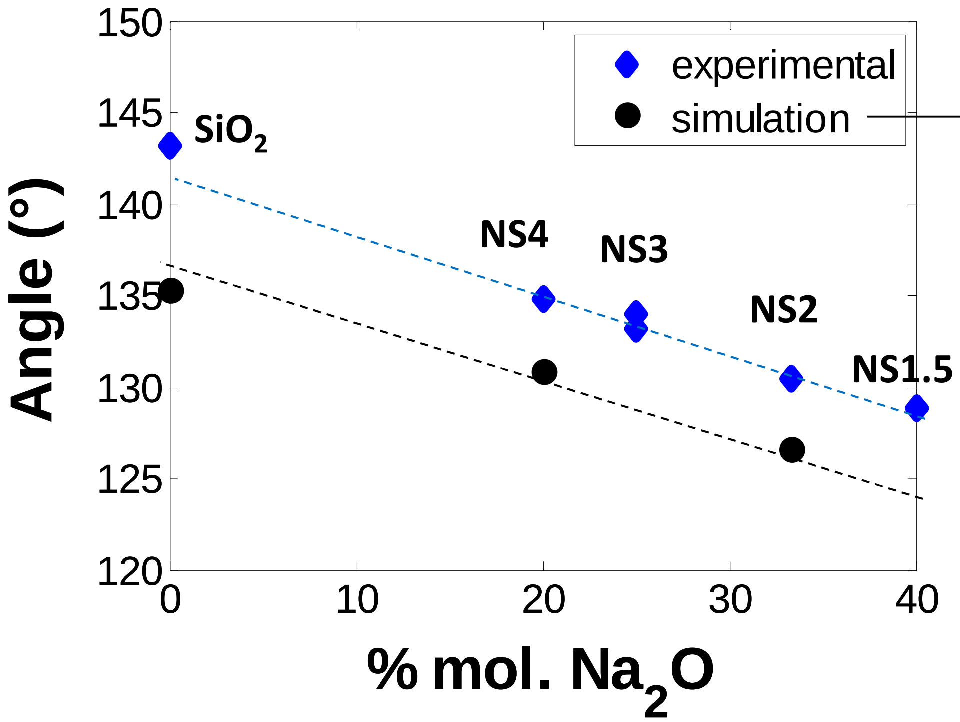


Bimodal angular population in sodo-silicates :

- A narrow and peaked one at high frequency
- A broad one at lower frequency

Si-O-Si angle in sodo-silicates

Most probable angle
(max. of the distribution)



[Truflandier, Ispas,Charpentier]

[Ispas et al PRB 2001]

Same trend !!

Depolymerization

reduces the Si-O-Si angle

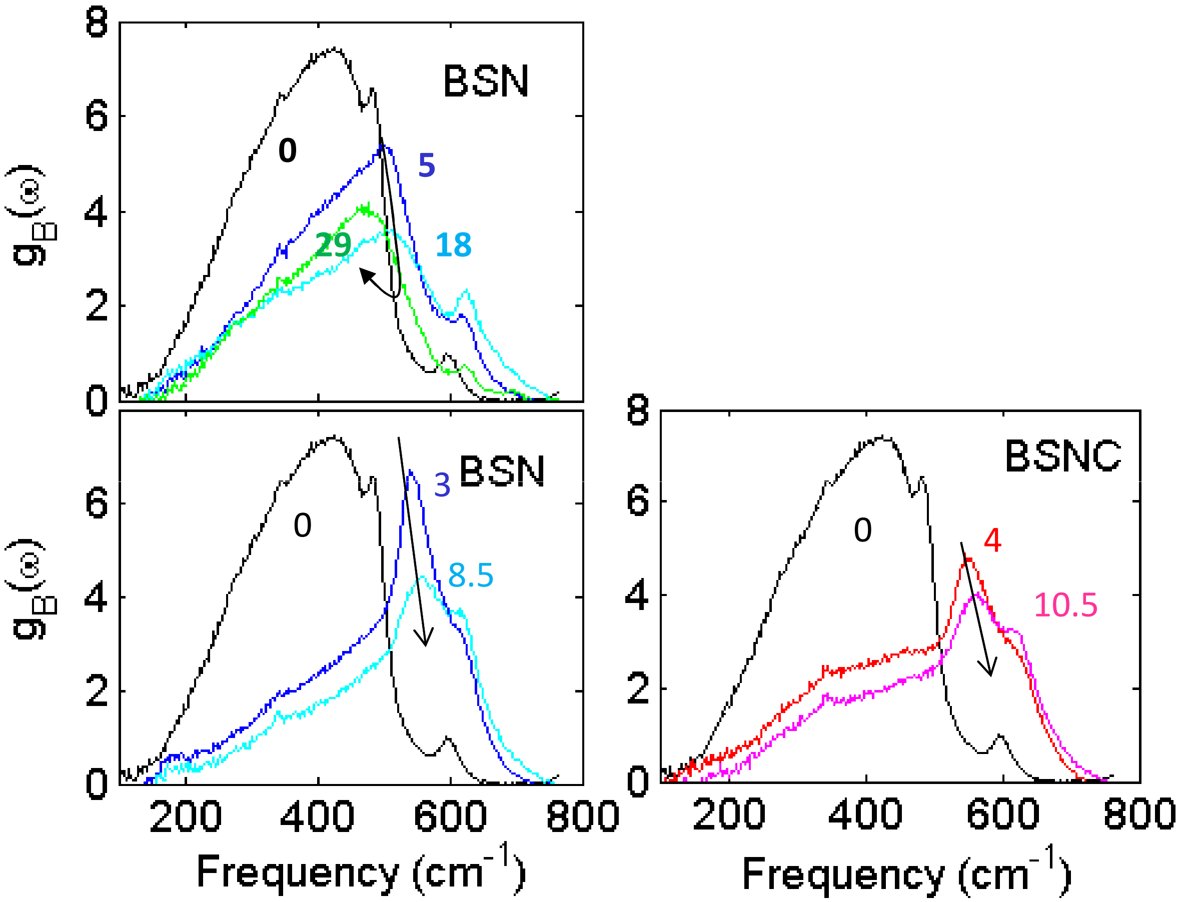
bond angle in boro-silicate glasses

BSN, BSNC

Raman density of states after subtraction of the BP signal :

15% Na_2O

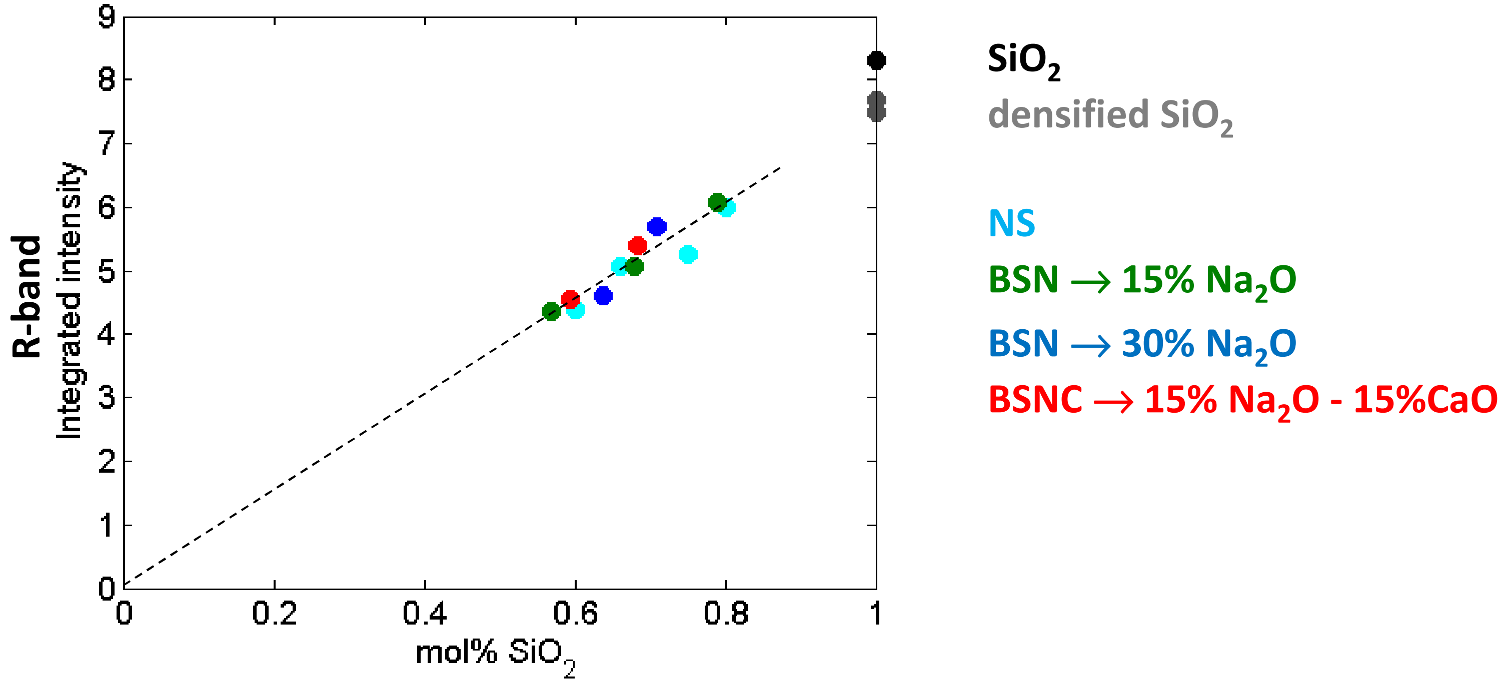
30% Na_2O



15% Na_2O
15% CaO

Integrated intensity :

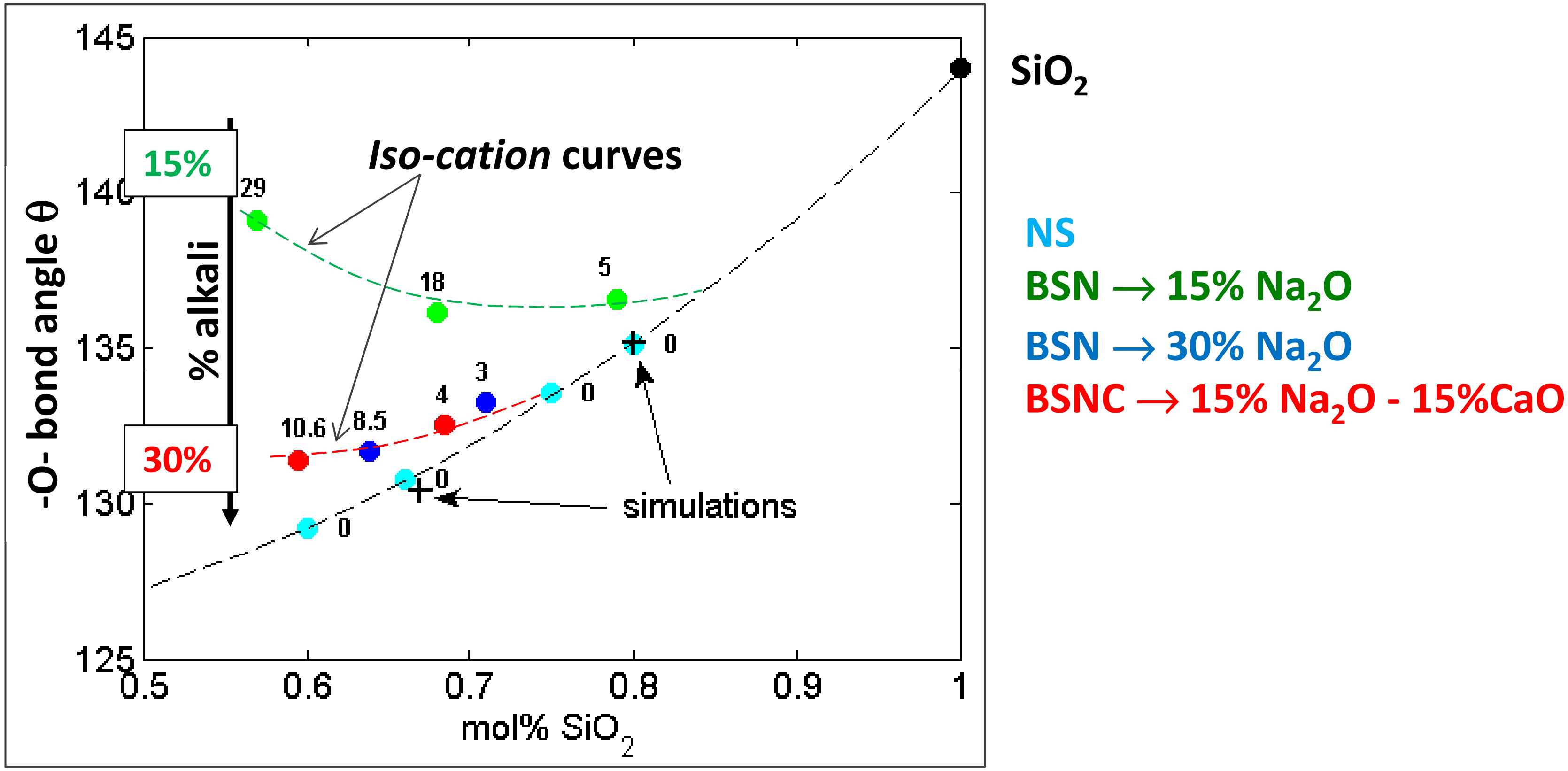
Strong correlation with the concentration of SiO_2 in the glass



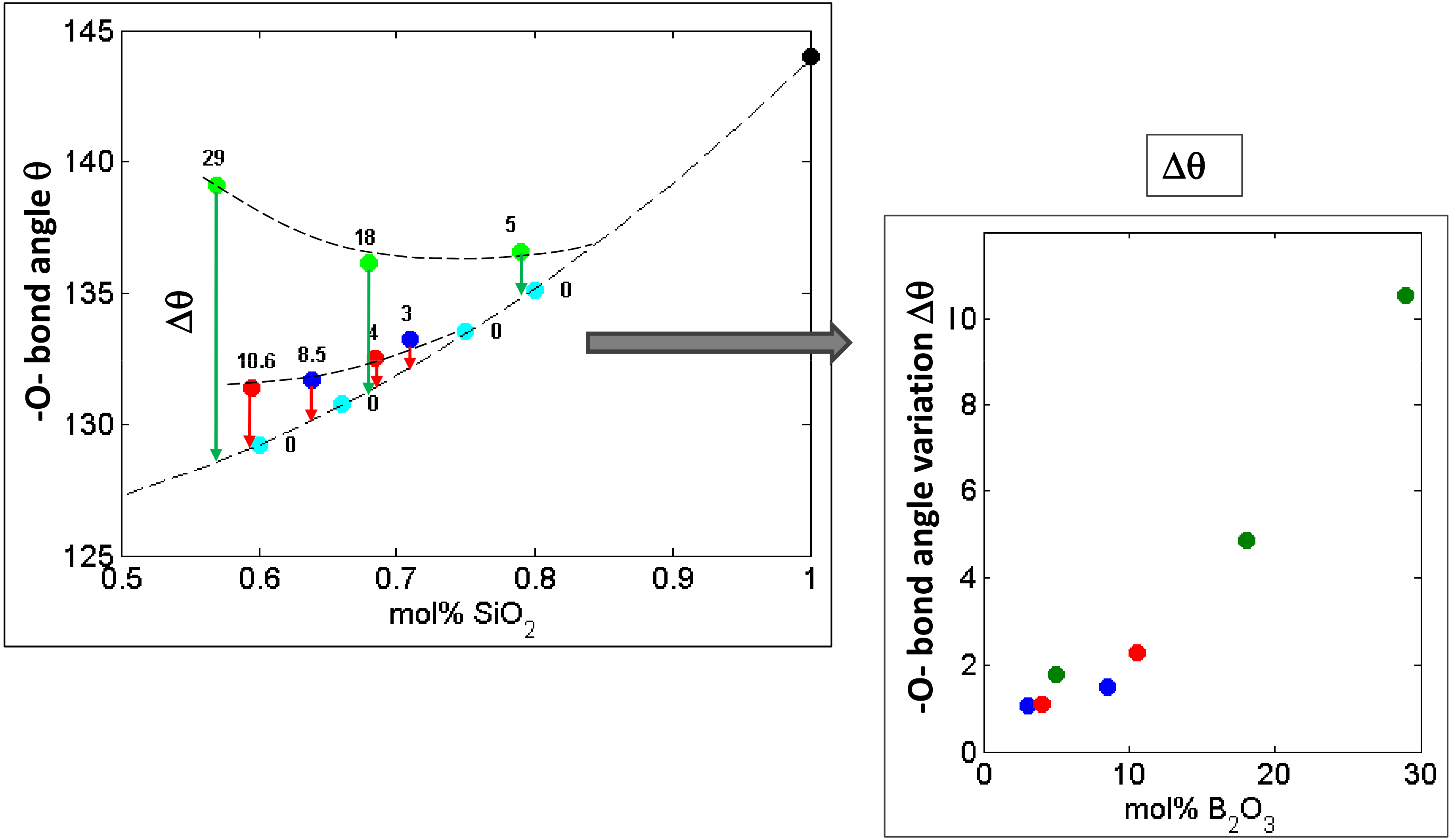
- The nature of the modes underlying the R-band (-O- bending) does not change with glass composition
- B-O-B bending give a very weak Raman signal (not shown here)

$\Rightarrow$ **R-Band in borosilicates : -O- bending, mostly with adjacent Si atoms.**

-O- bond angle *vs* SiO_2 mol%

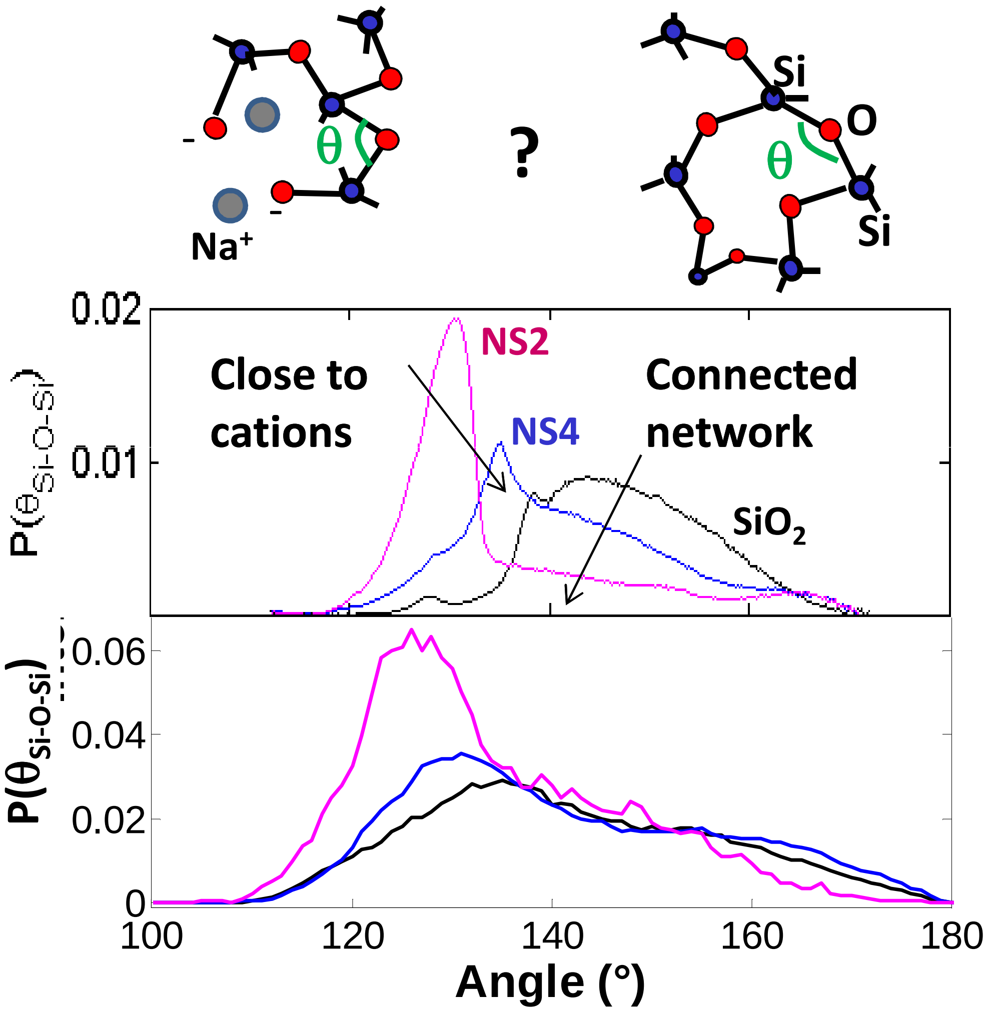


-O- bond angle *vs* B_2O_3 mol%



Distribution of Si-O-Si angles

- In sodo silicates



From Raman scattering

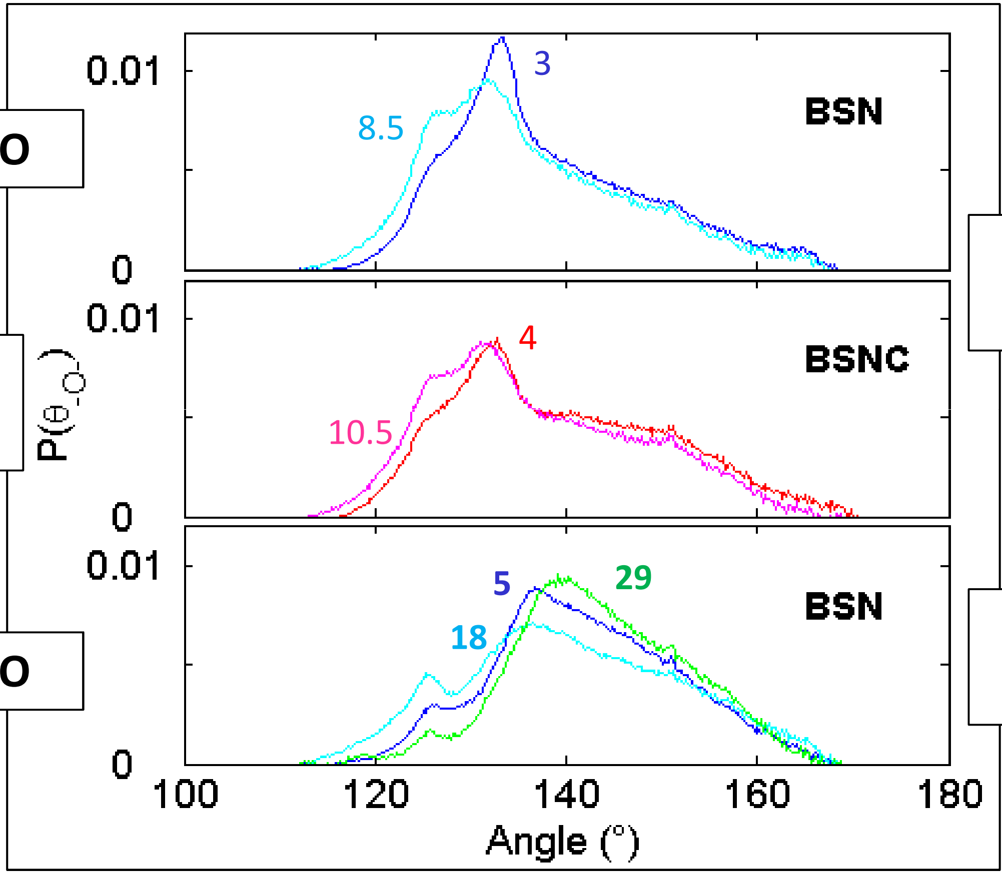
From Computer simulations

(Truflandier, Ispas,Charpentier)

(Ispas et al PRB 2001)

Distribution of –O – bond angles

- In boro-silicates



Depolymerized network

30% cations → Inhomogeneous angle distribution

Polymerized network

15% cations ~ Homogeneous angle distribution

→ Signature of an Inhomogeneous distribution of the cations in the glass ?

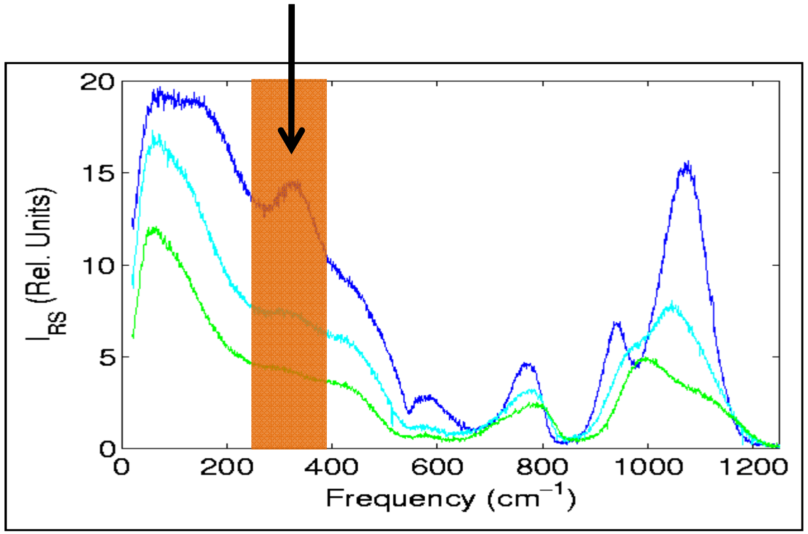
[Greaves]
[Mayer *et al.* PRB 2001]

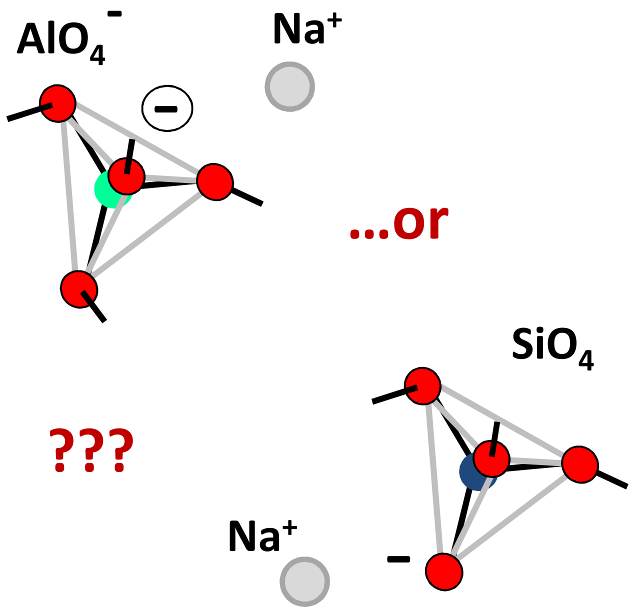
– IV –

Signature of network modifier cations in the Raman spectra

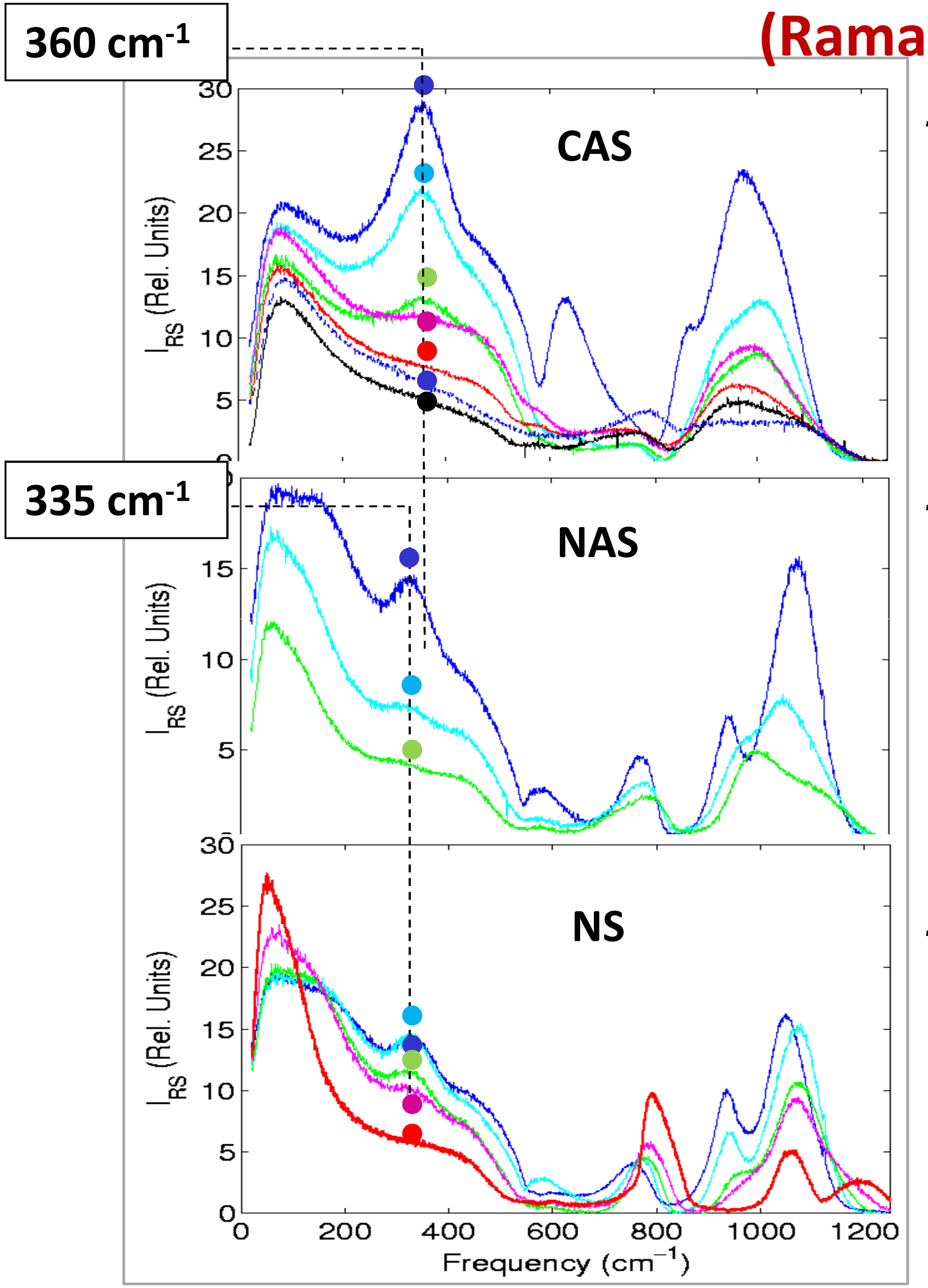
[B. Hehlen, D. Neuville]

- ✓ **Alumino-silicate glasses**
- ✓Depolarized Raman spectra, VH :
- ✓ Bending modes are inactives,
  allowing a clear observation of the <u>**cation band near 350 cm^{-1}**</u>

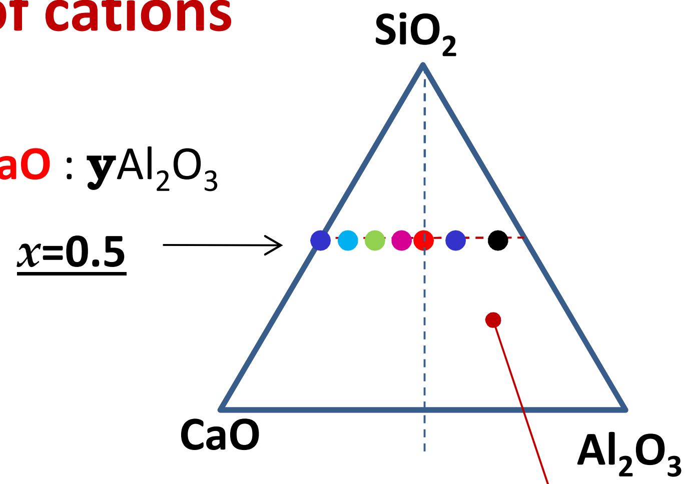




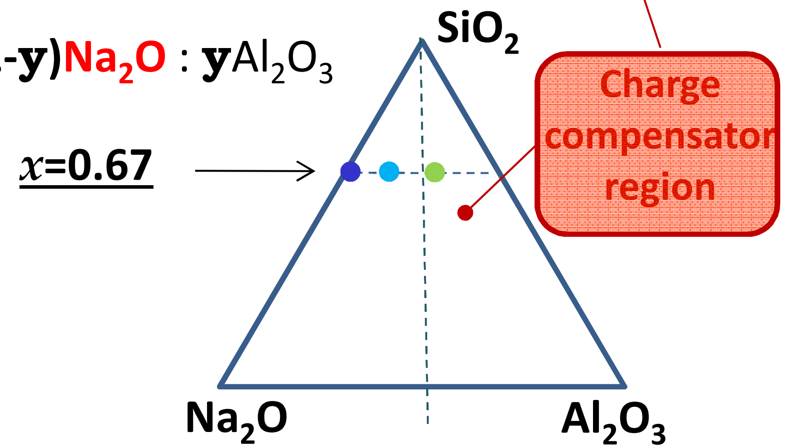
Modifier/compensator state of cations (Raman VH)



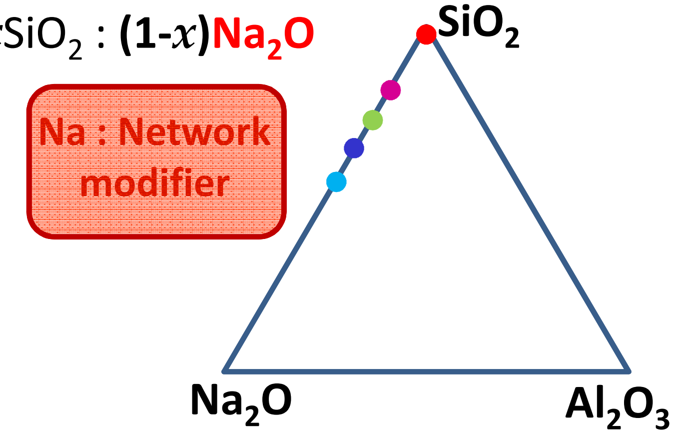
xSiO$_2$: (1-**y**)**CaO** : **y**Al$_2$O$_3$



xSiO$_2$: (1-**y**)**Na$_2$O** : **y**Al$_2$O$_3$



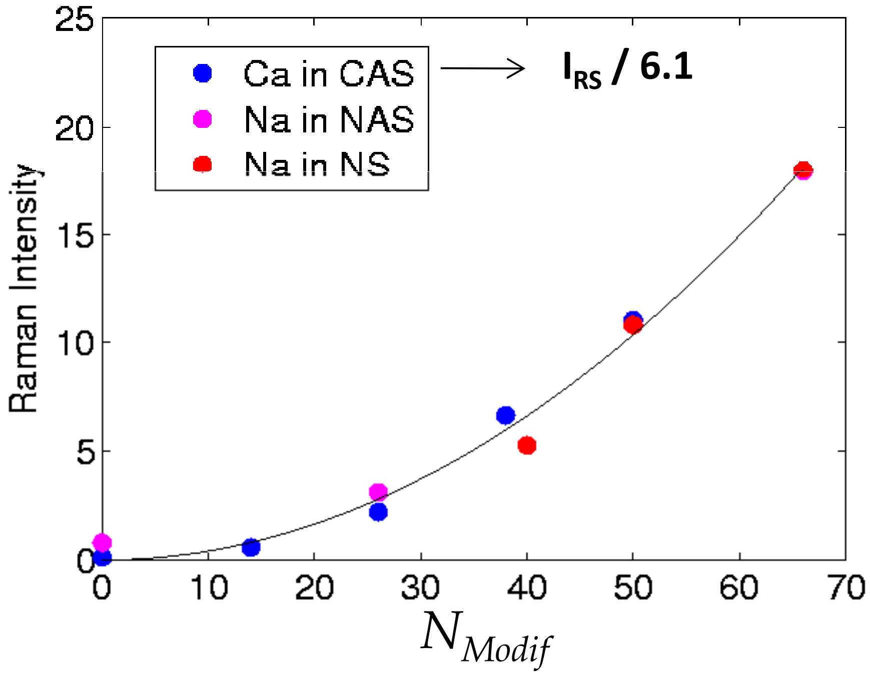
xSiO$_2$: (1-x)**Na$_2$O**



Raman intensity of the cation-band

Assuming al Aluminum atoms in AlO4$^-$ tetrahedra :

- $\mathbf{x}SiO_2$:$\mathbf{y}Na_2O$:$\mathbf{z}Al_2O_3$ 1 Na^+ Compensates 1 AlO4$^-$ ➡ N_{Modif}^{Na} = 2y-2z
- $\mathbf{x}SiO_2$:$\mathbf{y}CaO$:$\mathbf{z}Al_2O_3$ 1 Ca^{2+} Compensates 2 AlO4$^-$ ➡ N_{Modif}^{Ca} = y - z



- **Intensity dependences collapse in one master curve**
- **Raman signal goes to 0 when all cations are charge compensators**

➢ Raman-cation band near 340 cm^{-1} relates to <u>modifier</u> cations

Conclusions

Hyper-Raman :

Importance of librations of rigid SiO_4 tetrahedra in the boson peak of silica

Spatial coherence of the vibrations

TO4 : "chain" mode involving many rocking Si-O-Si units

HRS BP: localized or quasi-localized modes

Raman :

Si-O-Si bond angle value and distribution in silica and sodo silicates

-O- bond angle in borosilicates

Role of cations (modifier/compensator) in aluminosilicate glasses

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