Glass networks & vibrational methods

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Content

1. From atoms motion to its interaction with light
2. Interaction light/matter
3. equipment and the parameters to consider
4. Assignment in silicate glasses and polymerization
5. In situ observation of the glass transition
6. Evolution of glasses at high pressure

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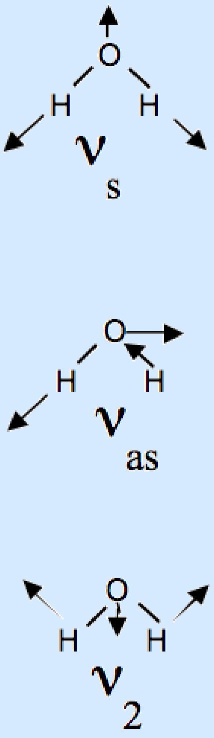
1.1. atom motions

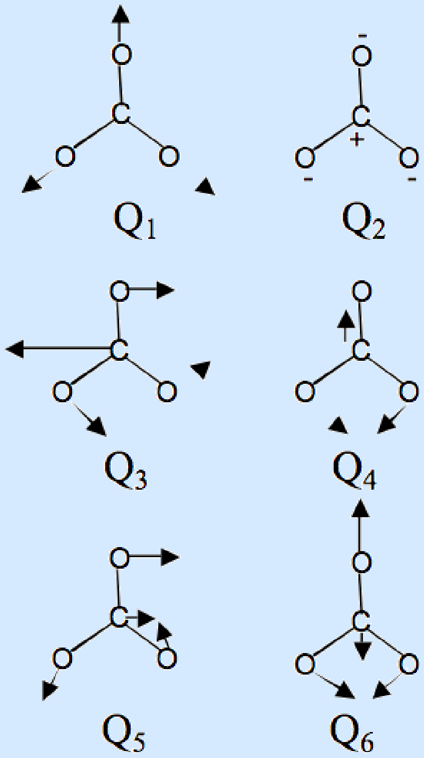
3 degrees of freedom by atom

For one molecule of n atoms

- 3 translations
- 3 rotations
- 3n-6 vibrations

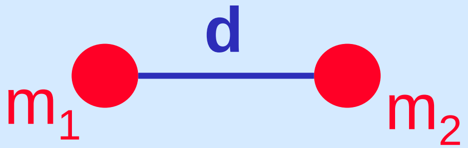


Ex: H_2O



Ex: CO_3

1.2. atom vibrations



Oscillation frequency from the hook law:

$$\nu = 1/2\ (K_r/m)^{1/2}$$

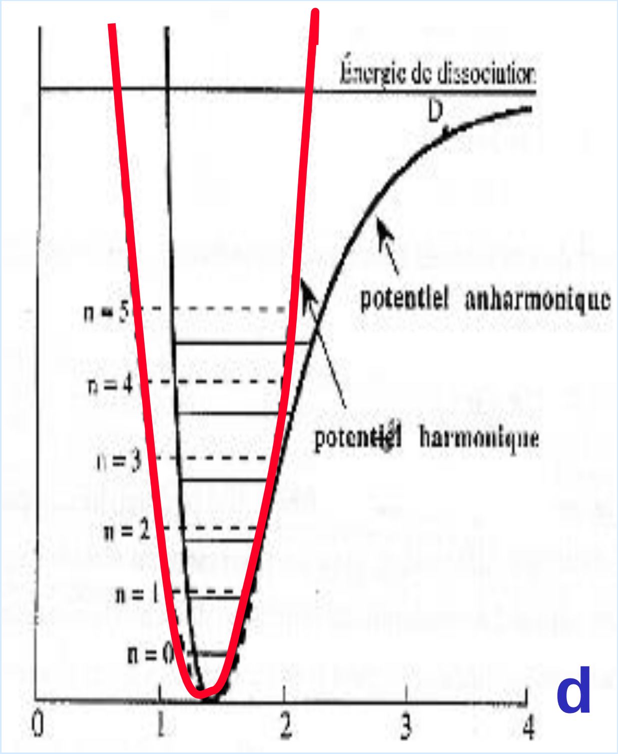
m is the reduce mass $m=m_1m_2/(m_1+m_2)$.

Order of magnitude :

10^{12} to 10^{14} s^{-1}

3.10^{-4} to 3.10^{-6} m

33 à 3333 cm^{-1}



1.3. wave and wavenumber

Wave equation $$\frac{\partial^2 u}{\partial t^2} = c^2 \nabla^2 u$$

Solution of the shape $u(\mathbf{r}, t) = f(\mathbf{n}.\mathbf{r} - vt)$

If sinusoidal $u(\mathbf{r}, t) = u_0 \cos(wt - \mathbf{K}.\mathbf{r})$

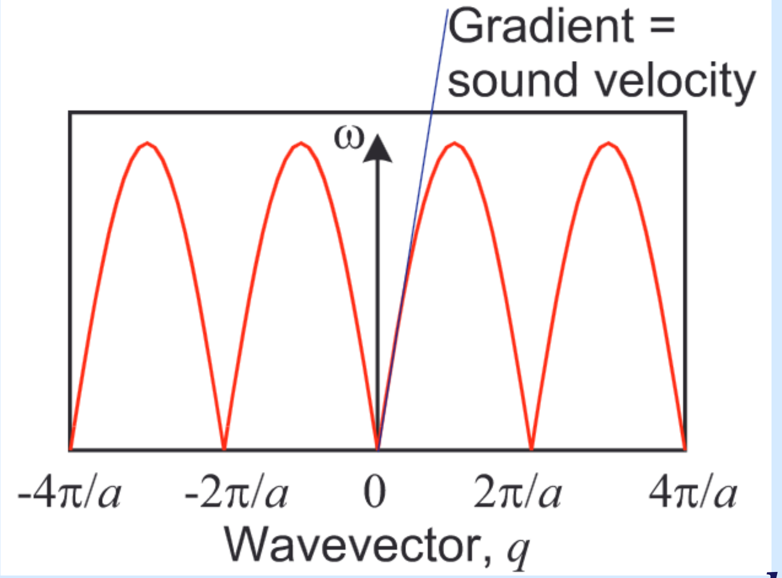
$$T = \frac{2\pi}{\omega} \qquad \lambda = \frac{2\pi v}{\omega} = vT \qquad \vec{K} = \frac{2\pi}{\lambda}\vec{u}$$

Phase velocity $$v = \frac{\omega}{K}$$

1.4. monoatomic chain

Dispersion relation

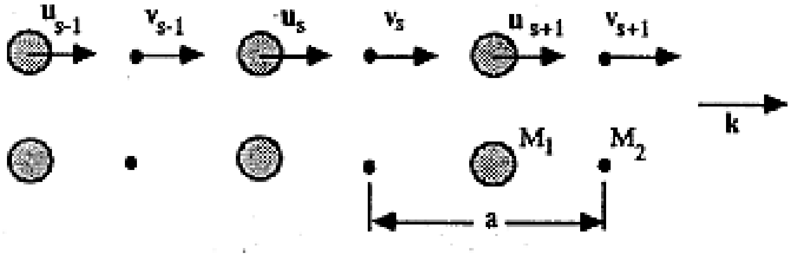
$$\omega^2 = \frac{2C}{M}(1 - cosKa)$$

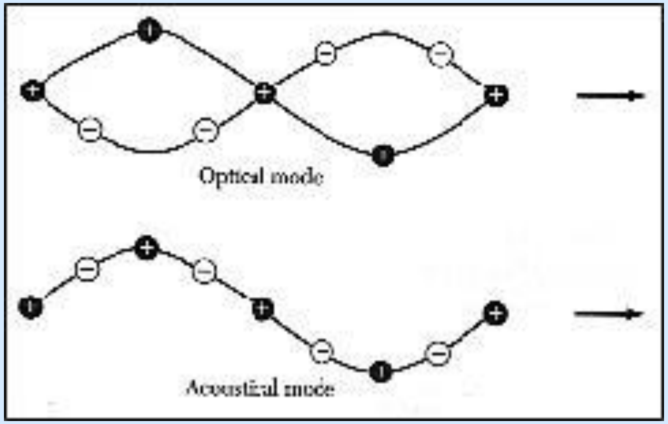


Group velocity

$$v_g = \frac{d\omega}{dK}$$

1.5. diatomic chain

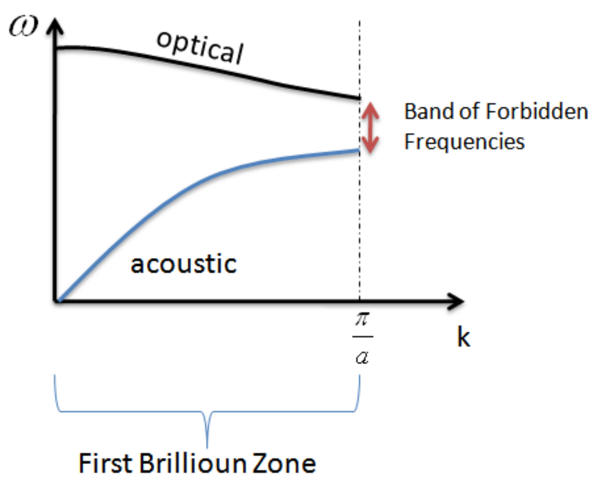




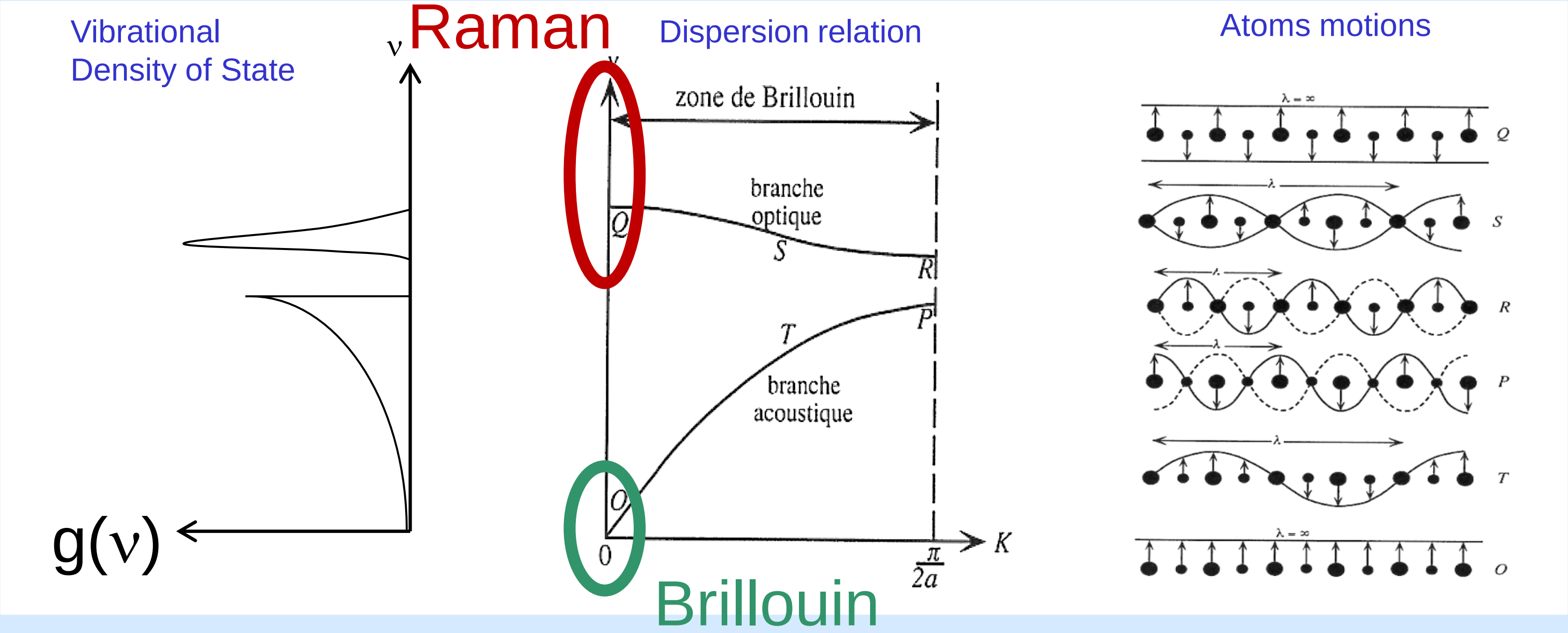
Dispersion relations

$$\omega^2 \cong 2C\left(\frac{1}{M_1}+\frac{1}{M_2}\right)$$

$$\omega^2 \cong \frac{0.5\ C}{M_1+M_2}\ K^2a^2$$



1.6. Vibrations in a solid


Vibrational Density of State

Dispersion relation

Atoms motions

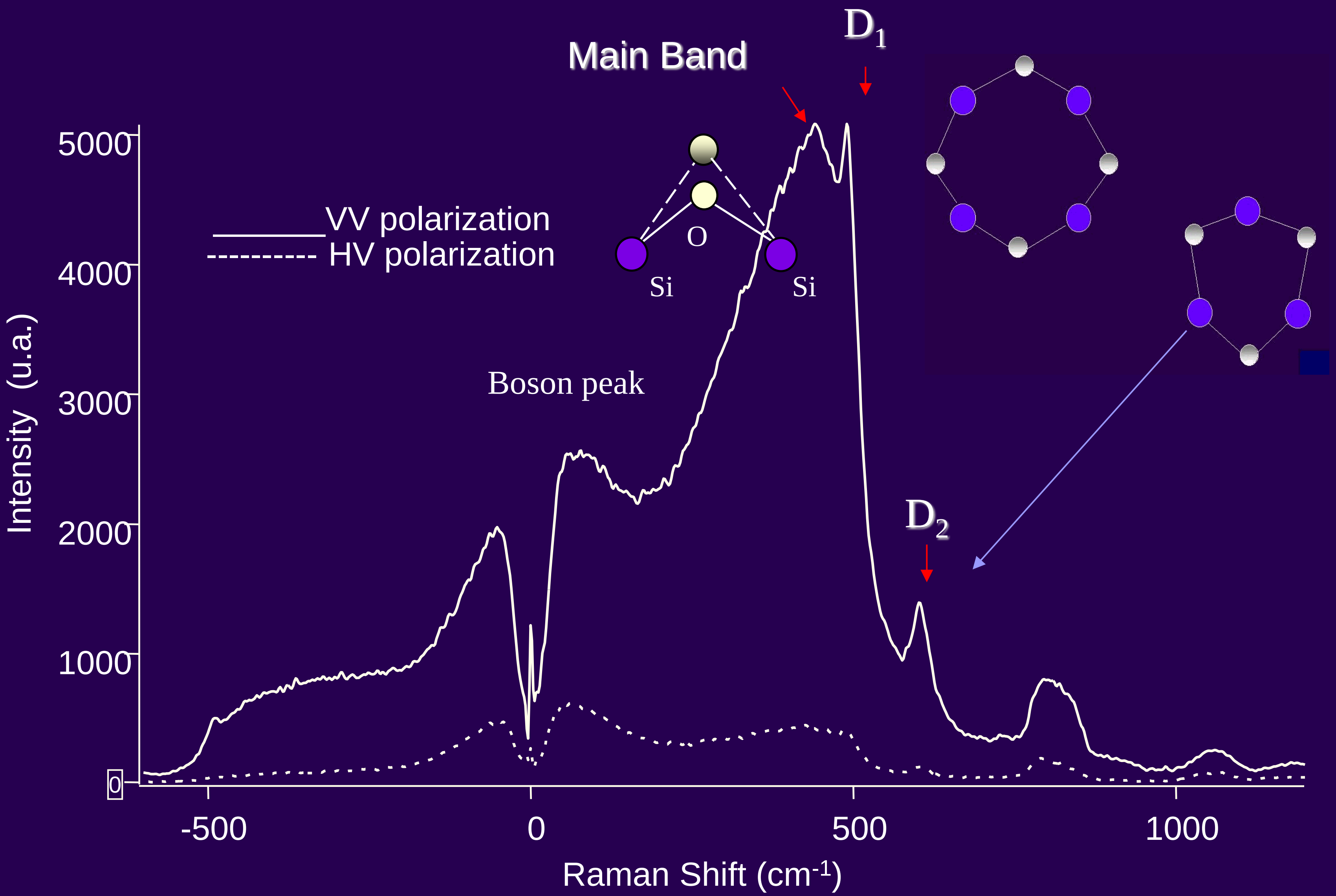
Solide with n atoms and n is big so 3n-6 ≅ 3n

Cell with Z formular units of N atoms:

- 3 acoustic modes (1 Longitudinal and 2 Tranverse)
- 3NZ-3 optical modes

Integral of g(n) is egual to 3NZ
Important to normalization

1.7. Silica glass Raman spectra



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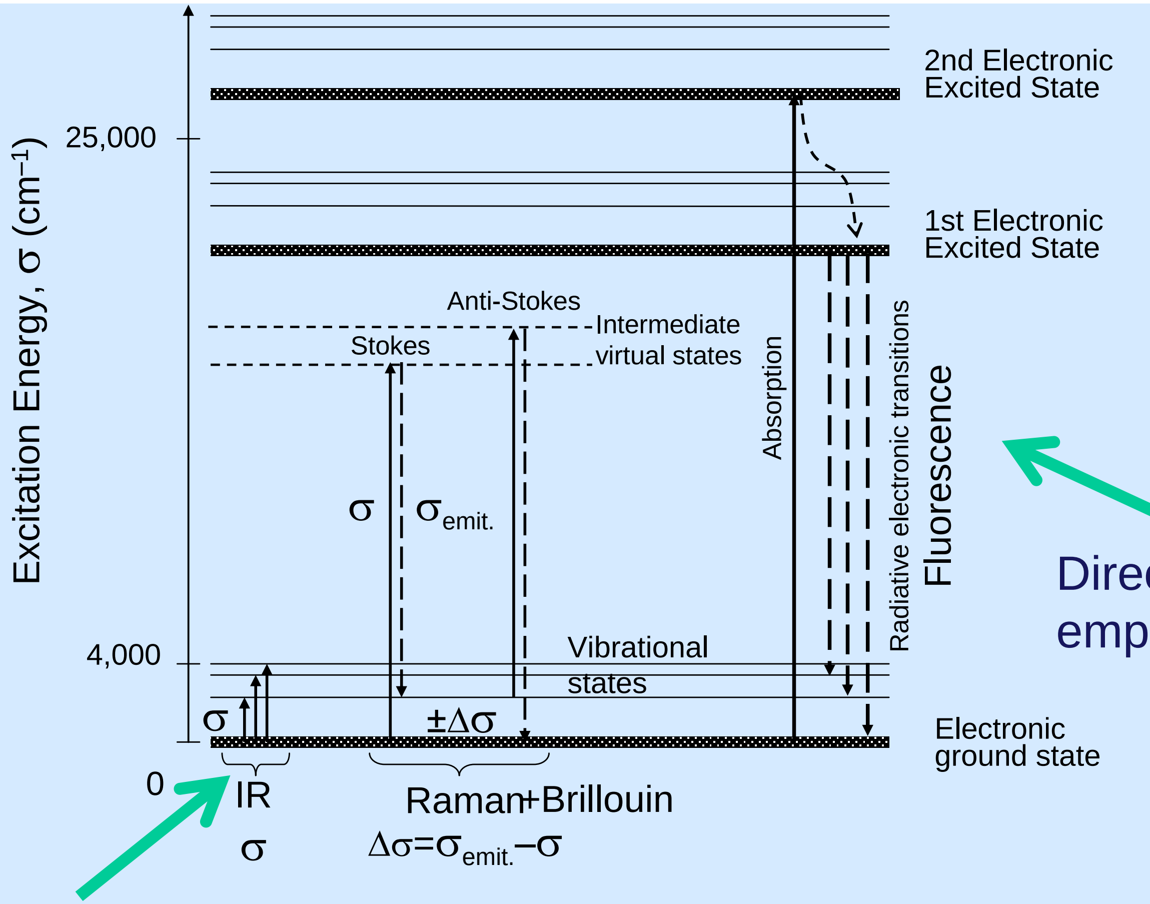
2.1. Fluorescence / Raman / absorption IR



Direct absorption if empty orbital

Direct absorption if a dipolar momentum present

Neuville et al. 2014

2.2. Induced dipole

Interaction between electric field of incident photon and molecule

Electric field oscillating with incident frequency v_i:

$$E_i = E_0 \cos(2\pi v_i t)$$

Induces molecular electric dipole (p):

$$\vec{p} = \alpha \vec{E}$$

Proportional to molecular polarizability, α

Polarization results in nuclear displacement

2.3. Induced dipole Classic physic treatment of Raman scattering

- For small distortions, polarizability is linearly proportional to the displacement

$$\alpha = \alpha_o + (\frac{\delta\alpha}{\delta q})_o q + \cdots$$

- Resultant dipole:

$$\vec{\mu} = \alpha\vec{E} = \alpha_o E_o \cos(2\pi\nu_i t) + $$

Rayleigh Scattering

$$\frac{1}{2}E_0 q_0 \left(\frac{\partial\alpha}{\partial q}\right)_0 \left\{\cos\left[2\pi(\nu_i + \nu_R)t\right] + \cos\left[2\pi(\nu_i - \nu_R)t\right]\right\}$$

Anti-Stokes

Stokes

2.4. Selection rule in Raman and Infra-Red Absorption

IR

Interaction between electrical field and the dipolar momentum μ of the molecule
Signal condition: possible change of μ along the propagating vibration

Raman

The molecule must be polarizable, i.e. induced dipolar moment induced: $\mu = \alpha E$ where α is the polarizability tensor.

Selection Rules

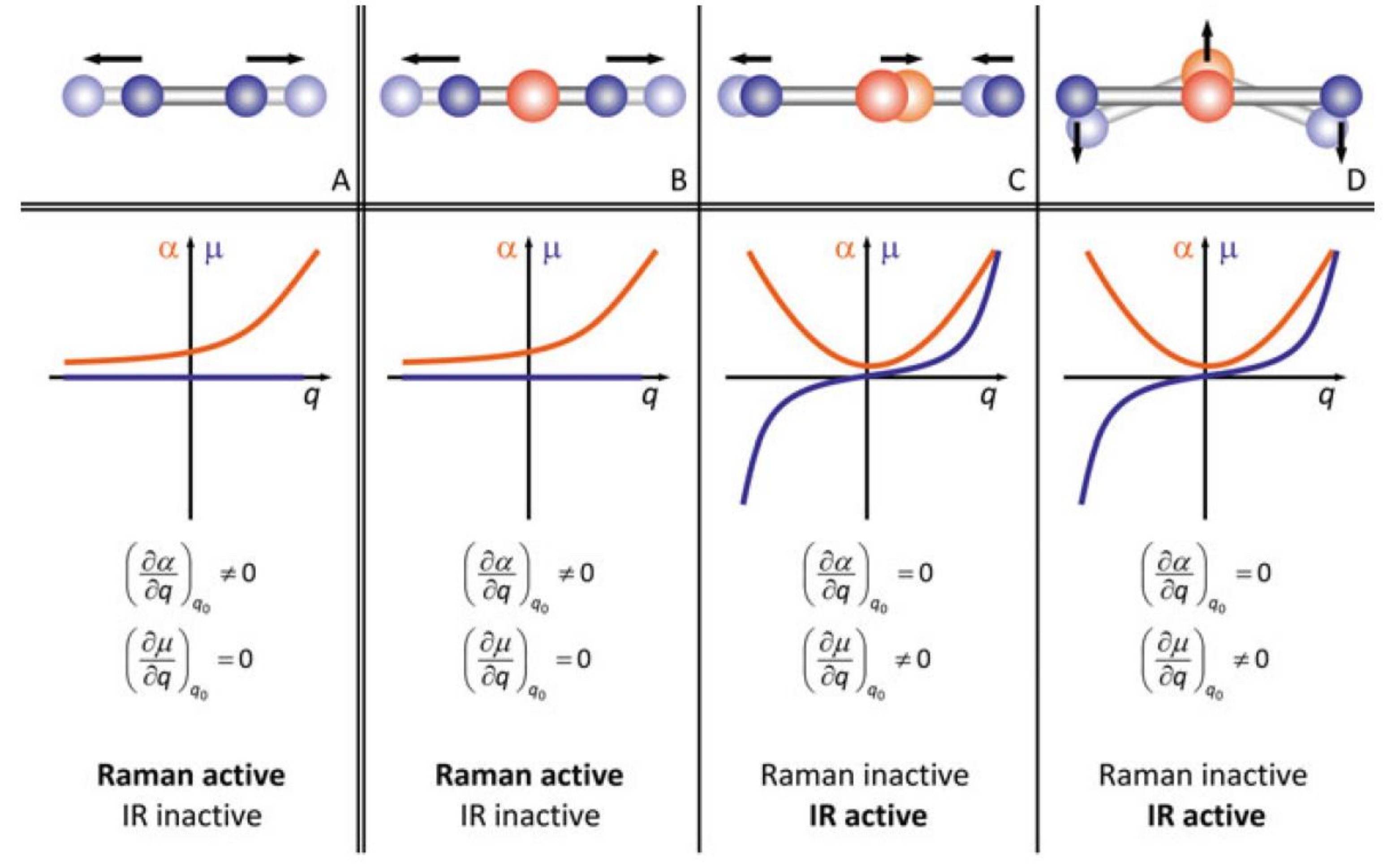
μ in IR (x y z)
α in Raman (x^2, y^2, z^2, xy, yz, xz)
Using the two last colums of the character table of the space group

Glass?

Exclusion rule if an inversion center is present

- polar mode polar: inactive in Raman (active en IR)
- non-polar mode: active in Raman (inactive en IR)

2.4. Selection rule example



2.5. Intrinsic Raman Intensity

$$I = I_{obs} R = C(\nu)\, g(\nu)$$

$$R = \frac{\nu . \nu_0^{\,3}\left(1 - e^{-\frac{hc\nu}{kT}}\right)}{(\nu_0 - \nu)^4}$$

Bose factor
Thermal population

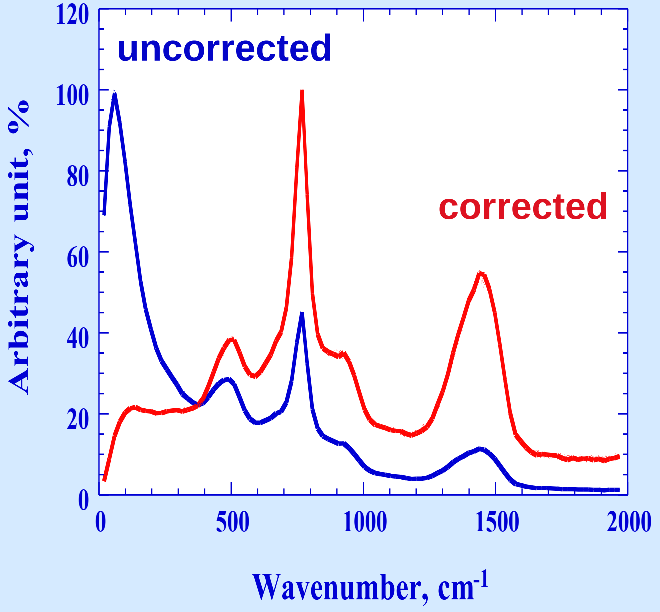
Rayleigh

h=1.05458.10^{-34} Js,
k=1.38066.10^{-23} JK^{-1},
c=2.9979.10^{10} cms^{-1}
T temperature en K,
ν_o wavenumber of the exiting light
laser Ar^+ at 514nm , ν_o = 19435.1 cm^{-1})
ν wavenumber in cm^{-1}.

Laser UV more efficient than IR

Different factors affecting polarisability and C(ν):

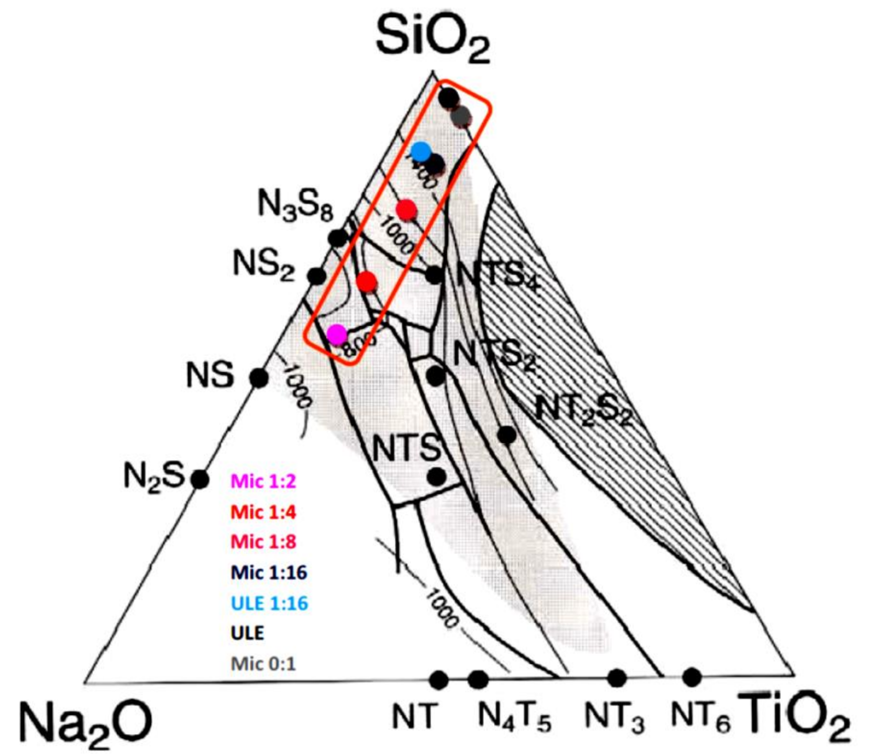
- -Selection Rules – Group theory
- -Laser and emission polarisization
- -Species concentration
- -Atomes with high Z
- -Covalent bonds



Strategy of normalization complex
if change of CN or chemistry

2.6 example titanosilicates

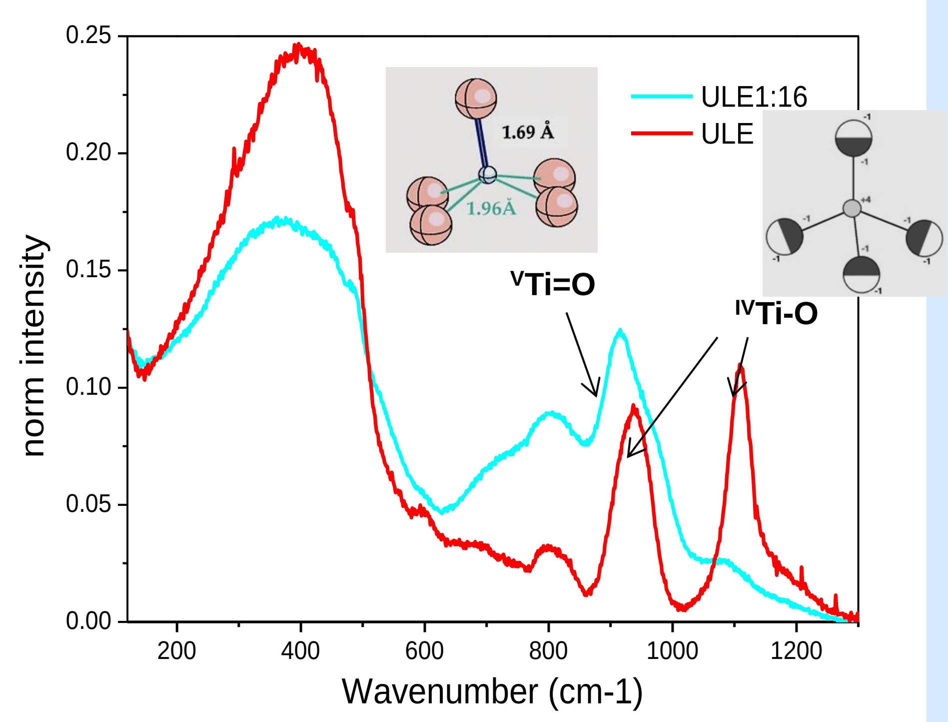
10 mol% of TiO2 for the Mic series
6 mol% of TiO2 for the ULE

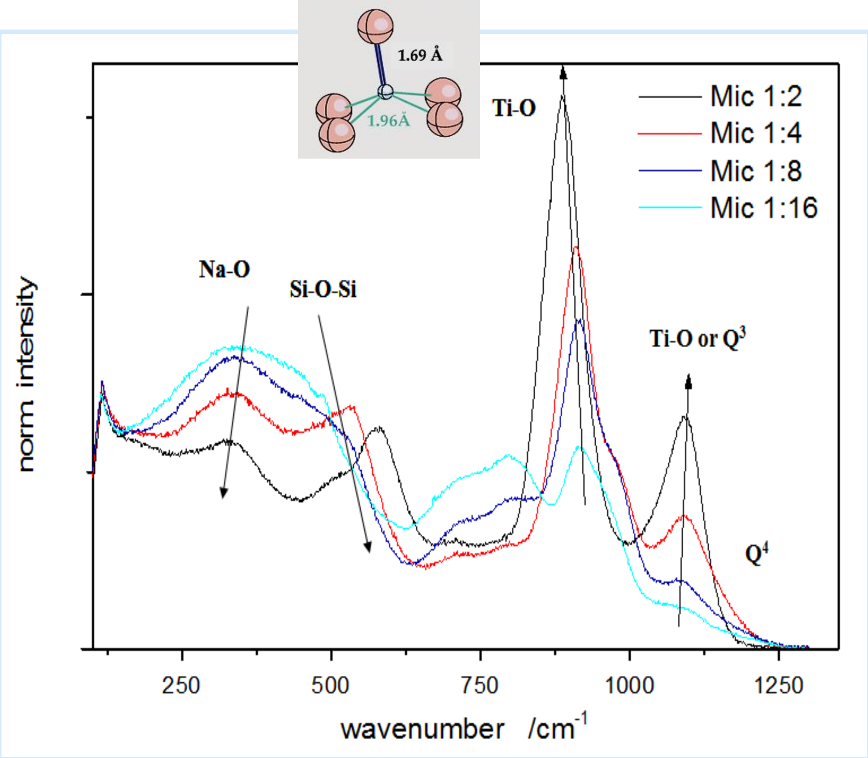


Sample	Na_2O /mol%	SiO_2 /mol%	TiO_2 /mol%	M /g mol^{-1}
Mic 1:2	35	56	9	43,91
Mic 1:4	22	68	10	45,00
Mic 1:8	12	78	10	45,79
Mic 1:16	6	85	9	46,20
ULE 1:16	6	87	7	46,05
ULE	0	94	6	46,45

Constant TiO_2 concentration
Ti higher Z than Si

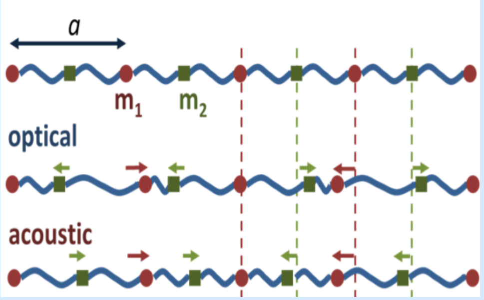
2.6. example titanosilicates



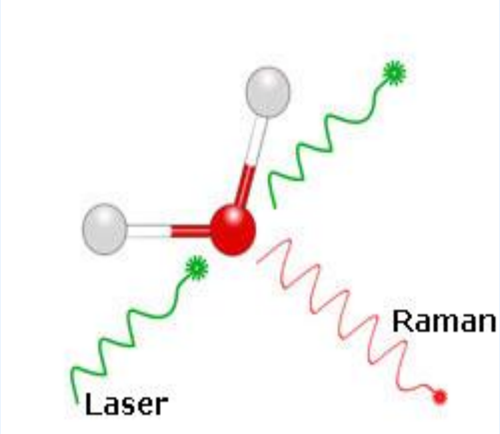


- ULE with $^{[4]}$Ti and very similar to pure silica
- With the increase of Na$_2$O content Ti changes CN from 4 to 5
- The double bond of $^{[5]}$Ti has a very strong Raman activity

2.7. Inelastic light scattering Raman versus Brillouin

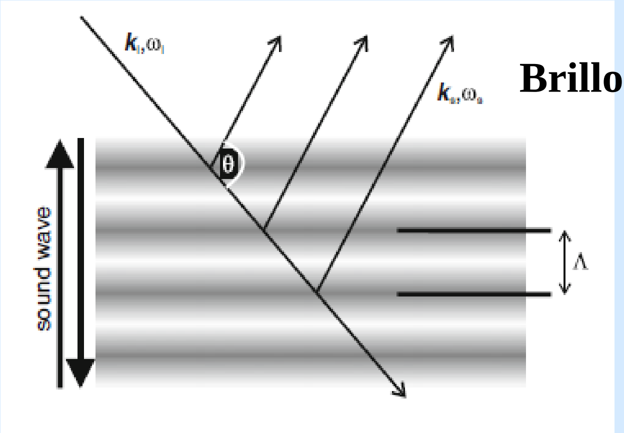


Scattering on optical phonons



typical energies 10-1000 cm^{-1}

Scattering on acoustic phonons



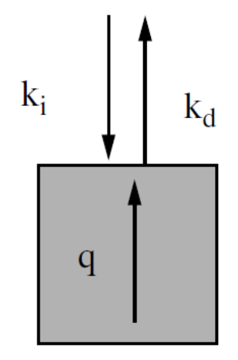
typical energies < 10 cm^{-1}

2.8. Brillouin spectroscopy and Elastic properties

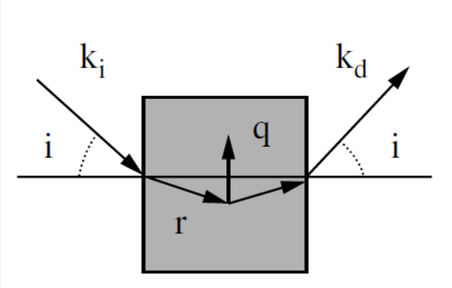
Back scattering geometry

Platelet geometry

$$\Delta\nu_{180} = \frac{2n\,.\,c}{\lambda}$$



$$\Delta\nu_i = \frac{2\sin i\,.\,c}{\lambda}$$



Refractive index needed
Only Longitudinal

No index
Transverse and Longitudinal
Angle very critical
Parallel plates of 20 microns thick

$$c_l = \sqrt{\frac{K + \frac{4}{3}G}{\rho}} = \sqrt{\frac{M}{\rho}}$$

$$c_t = \sqrt{\frac{G}{\rho}}$$

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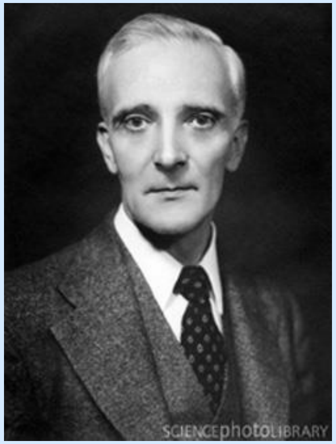
3.1. Raman and Brillouin Spectroscopy - Discovery



Léon Brillouin predicted the scattering in 1914

No Nobel price….Because he moved out of France

Sir C.V. Raman discovered the Raman effect in 1928 with his student K.S. Krishnan

He obtained the Nobel price in Physic en 1930

3.2. Raman and Brillouin Shift

Raman shift is expressed has a **wavenumber in cm^{-1}**

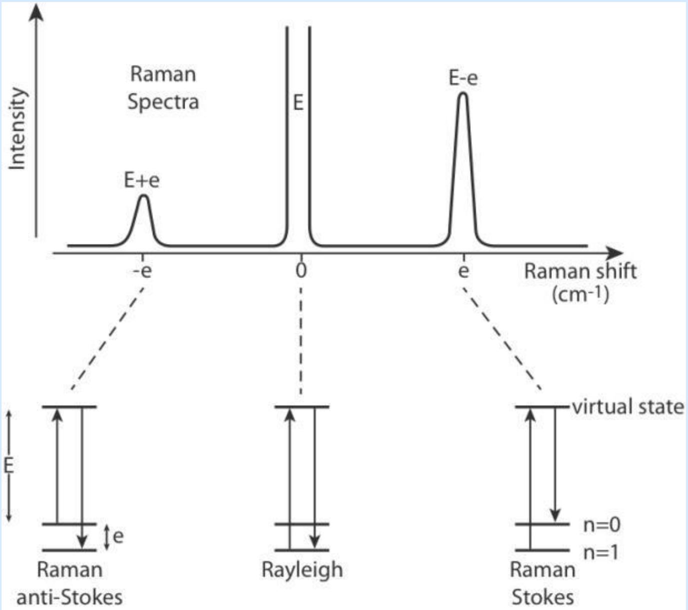
Example:

Laser at λ_0 = 532 nm = 532.10^{-7}cm d'où ν_0 = 18797 cm^{-1}

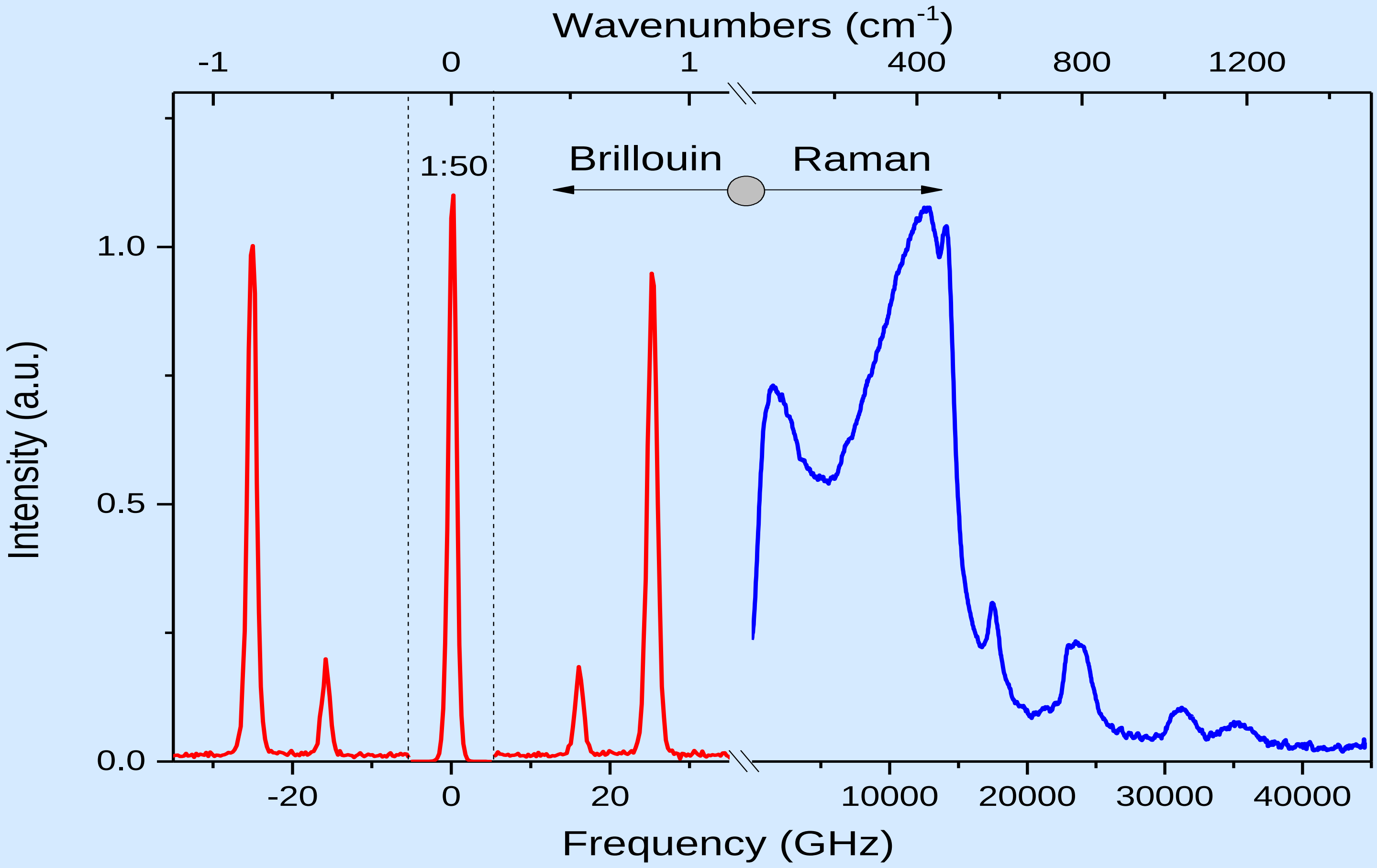
Frequency f = c. ν = 3. 10^{6} x 500 = 1.5 10^{9} s^{-1} = 1.5 GHz

For a shift of ν = 500 cm^{-1}
In Stock
ν_0- ν = 18797 – 500 = 18297 cm^{-1} soit λ_S = 547 nm
In Anti Stock
ν_0+ ν = 18797 + 500 = 19297 cm^{-1} soit λ_{AS} = 518 nm

In Brillouin people prefer to use the GHz



3.3. Raman and Brillouin spectra: SiO_2 glass

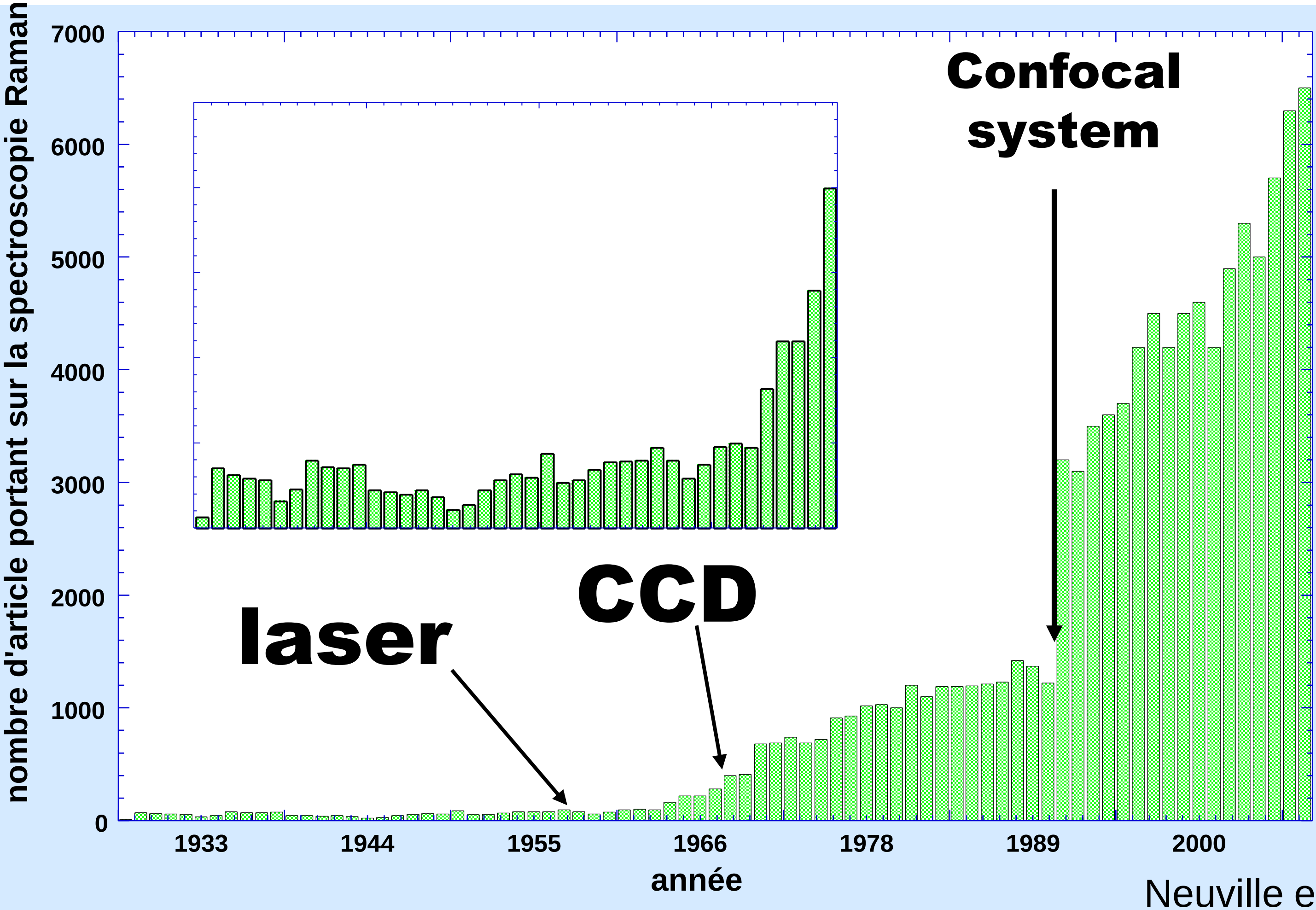


3.4. Light Scattering intensities

- Major part of incident beam is TRANSMITTED
- No change of wavelength ELASTIC scattering $1/10^4$
- Change of wavelength INELASTIC scattering:
  - BRILLOUIN $1/10^6$
  - RAMAN $1/10^8$

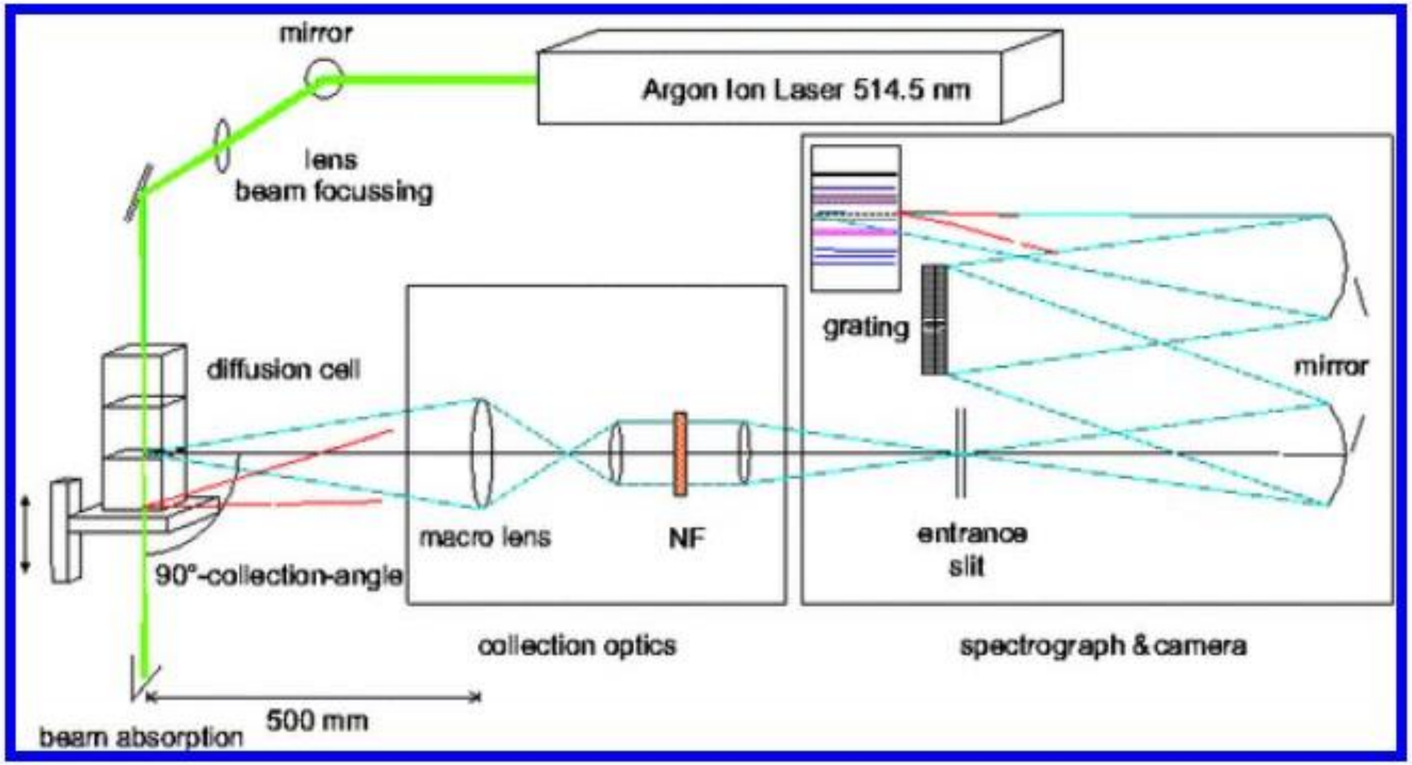
Experimental challenge in detection level and spectral resolution

3.5. Technological advances

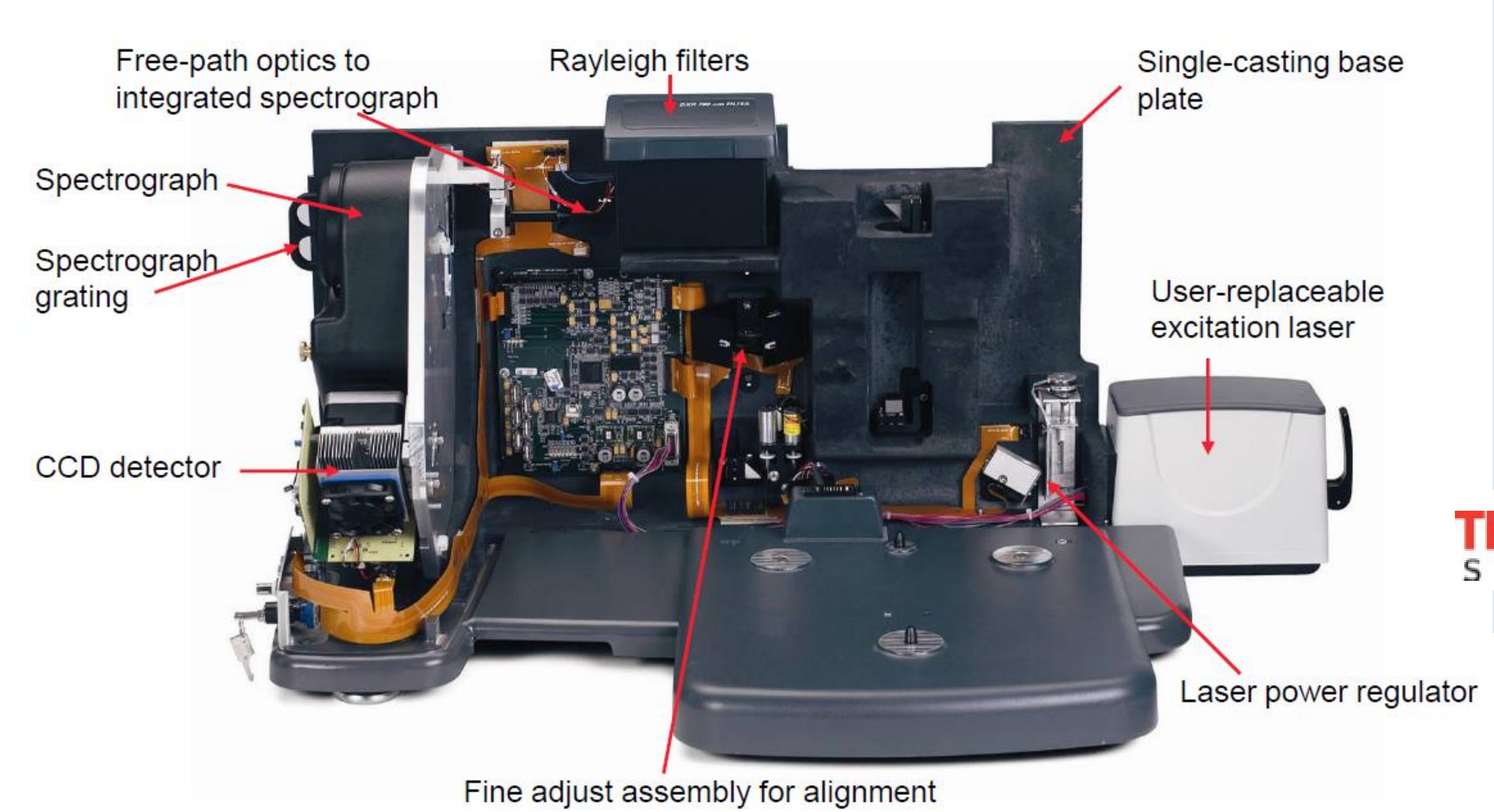


Neuville et al. 2014

3.6. General design of Raman spectrometer

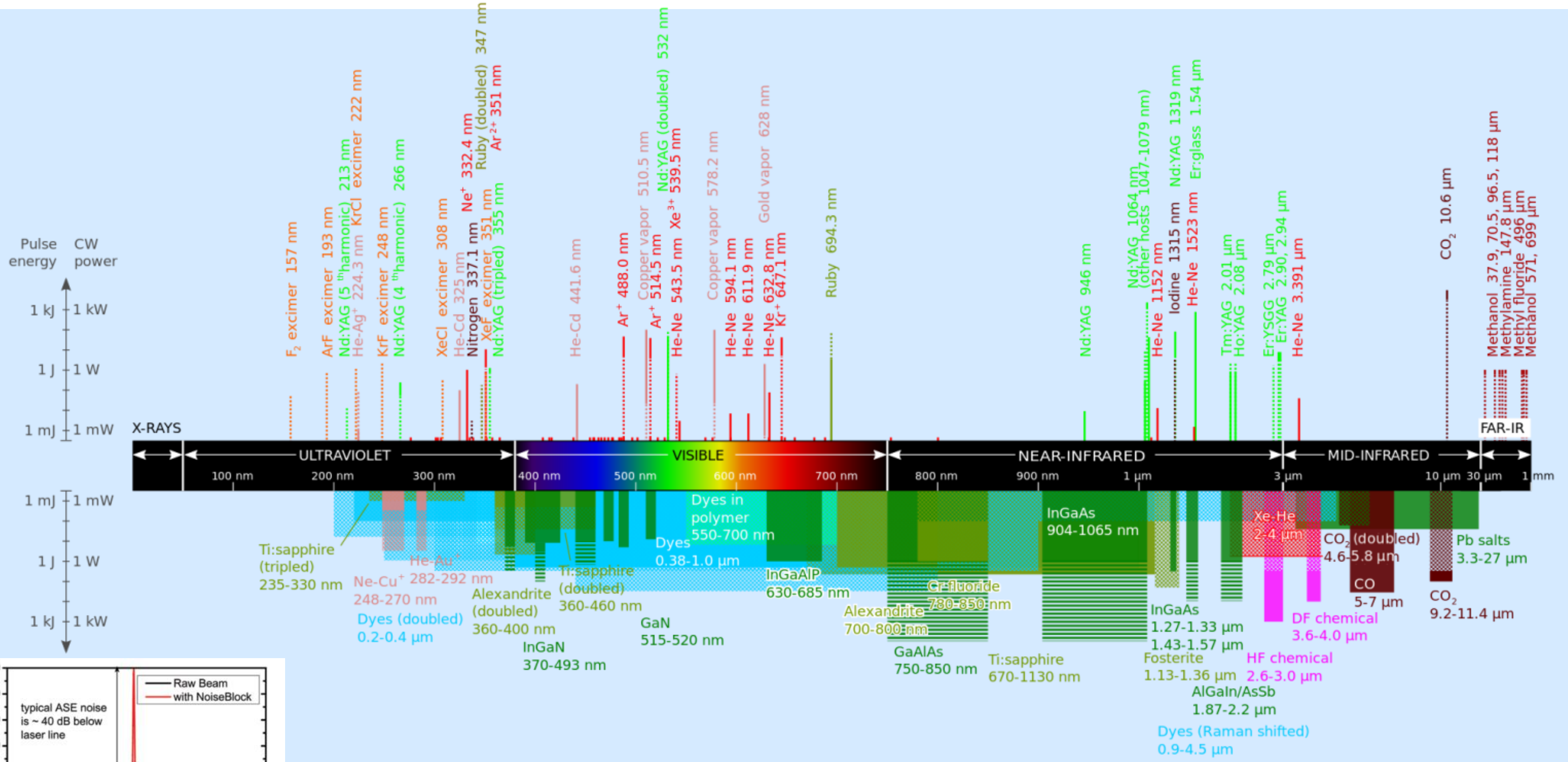


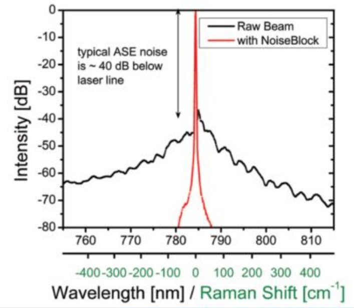
3.6. General design



ThermoFisher SCIENTIFIC

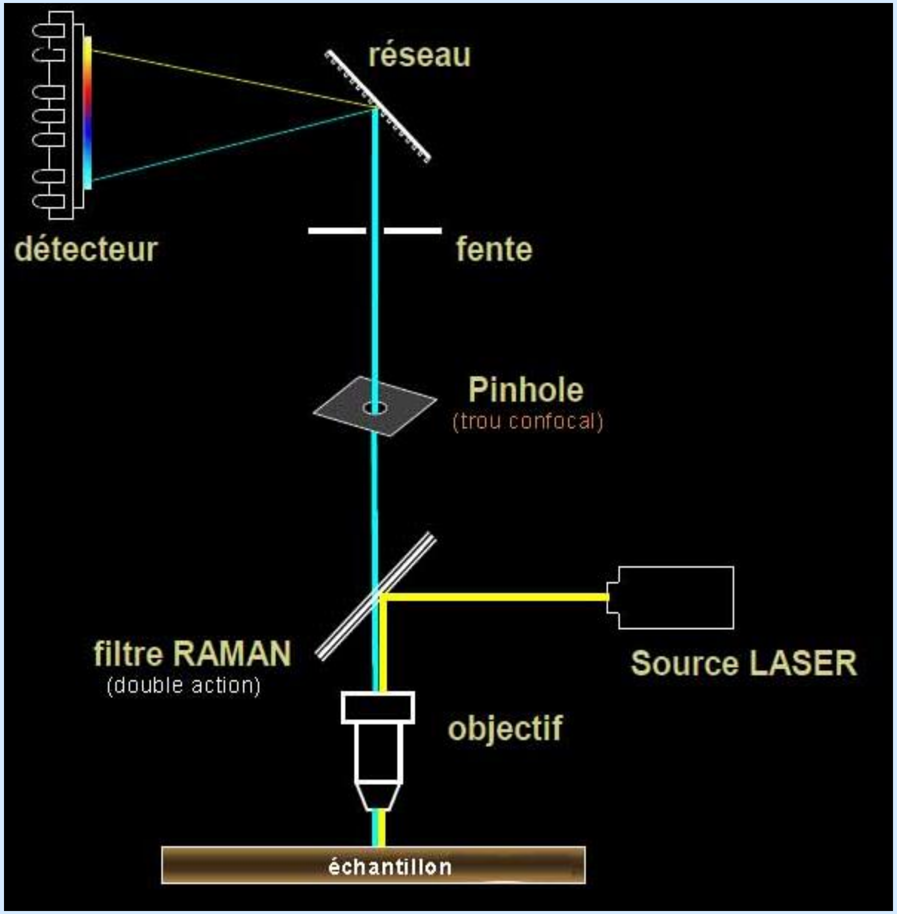
3.7. Laser

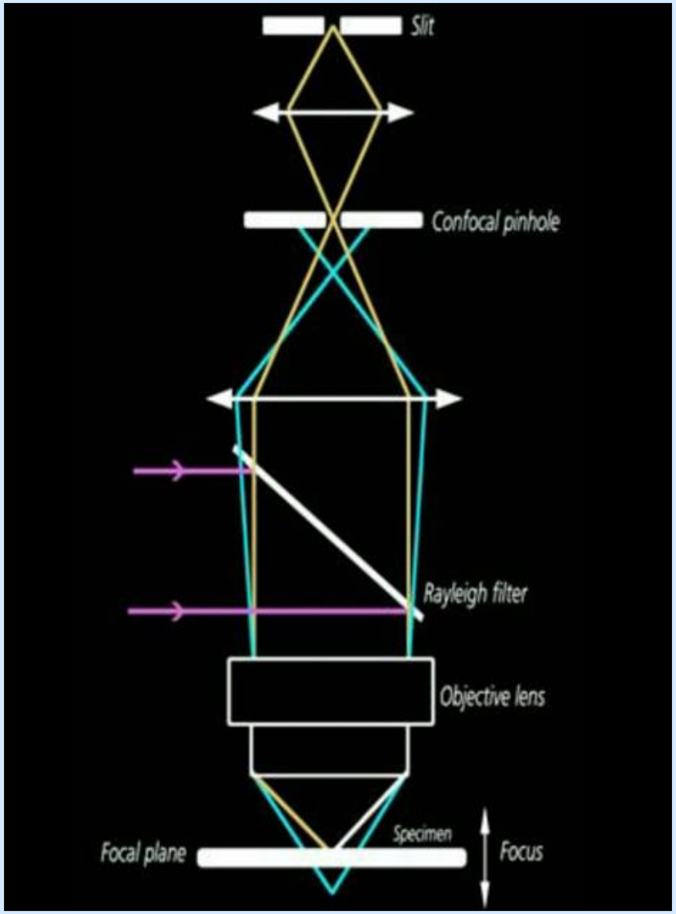




Quality factor of the laser need to be good enough
Single mode critical to Brillouin spectroscopy

3.8. Confocal


réseau
détecteur
fente
Pinhole
(trou confocal)
filtre RAMAN
(double action)
Source LASER
objectif
échantillon


Slit
Confocal pinhole
Rayleigh filter
Objective lens
Specimen
Focal plane
Focus

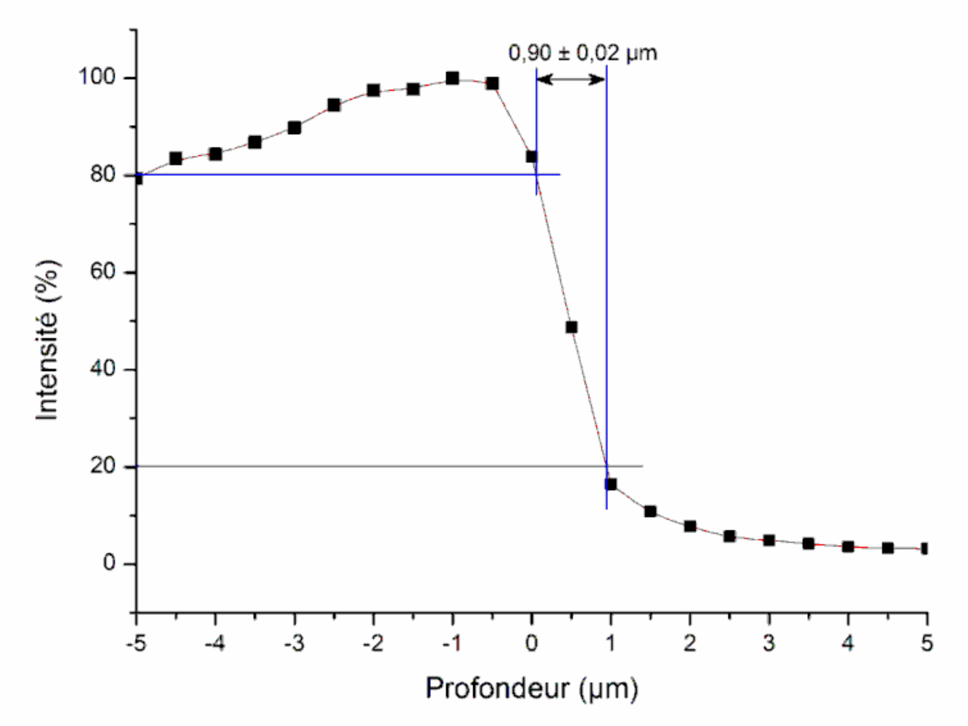
3.9. Spatial resolution

Horizontal spatial resolution depends on the objectif and the laser wavelength

$$D = \frac{1.22\,\lambda}{NA}$$

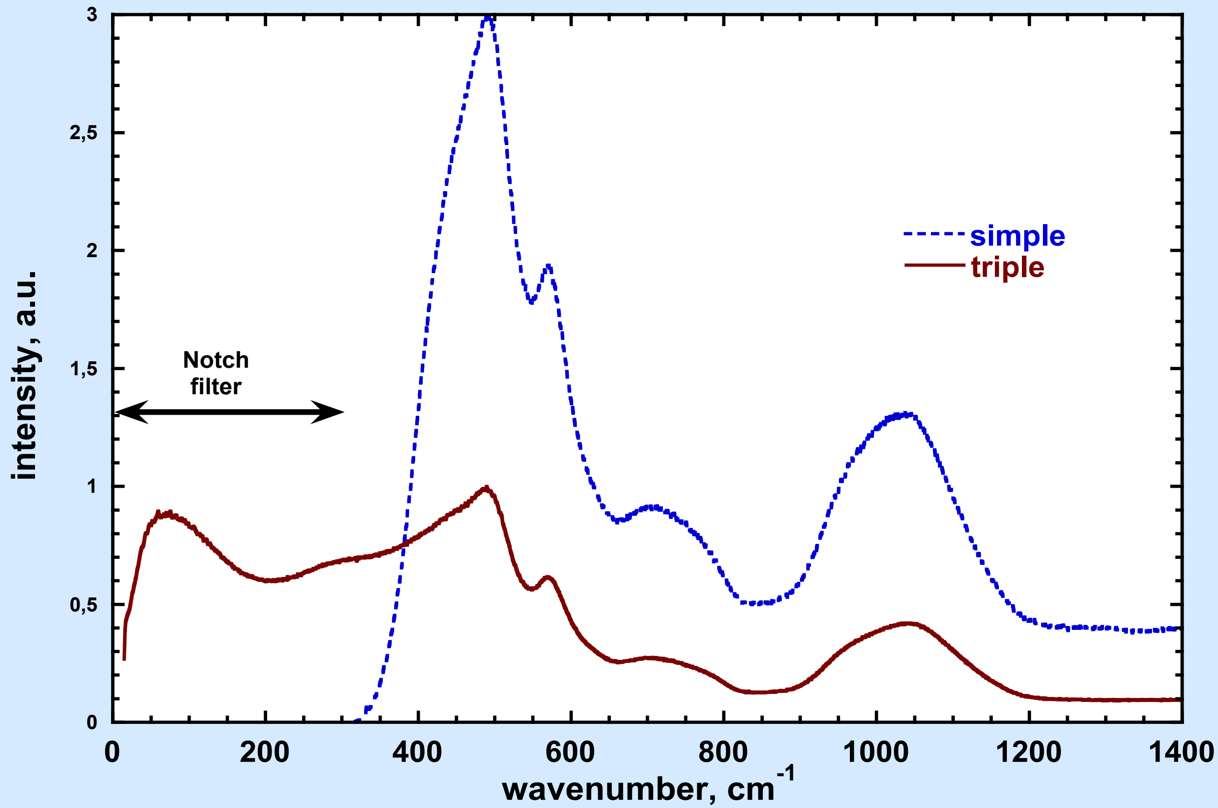
Vertical resolution around 1 µm in confocal mode with a X100 objectif

$$d.o.f. = \frac{4\lambda}{NA^2}$$



de Bonfils 2007

3.10. Filter and Rayleigh rejection

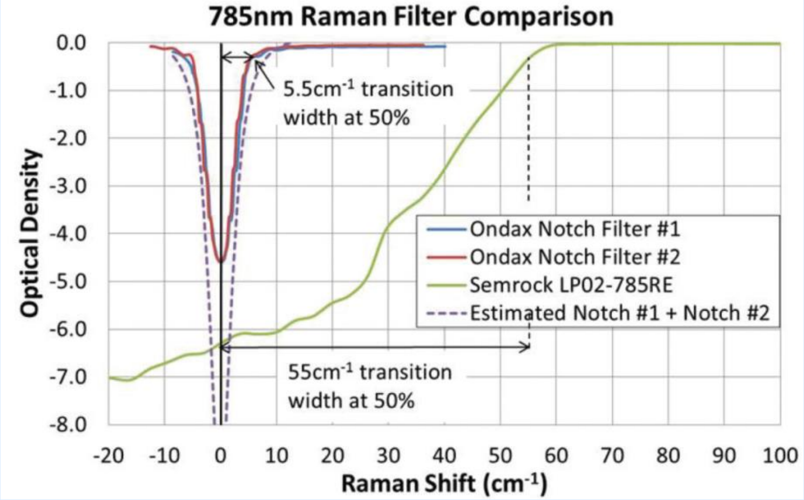


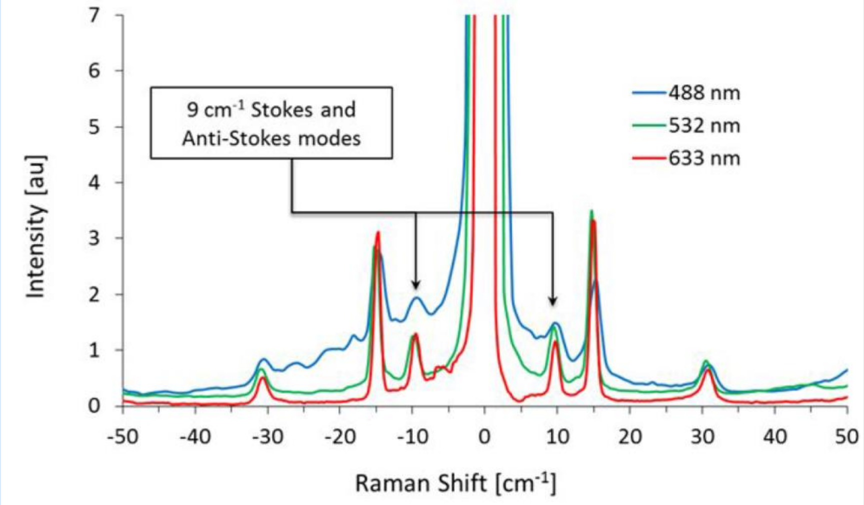
Neuville et al. 2014

Use of monochromators

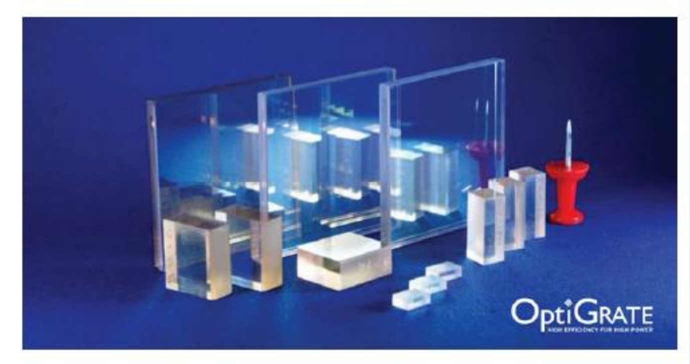
- Not specific of an exitation wavelength
- Low brightness

3.10. Filter and Rayleigh rejection

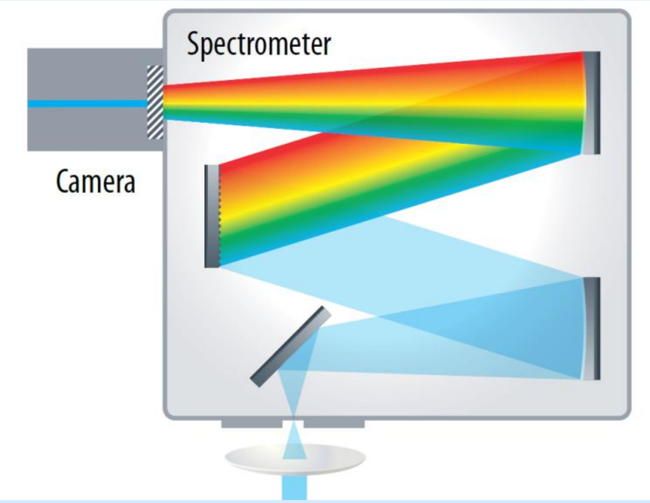


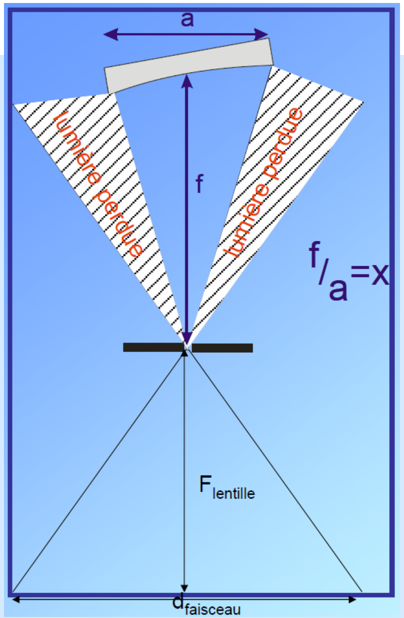


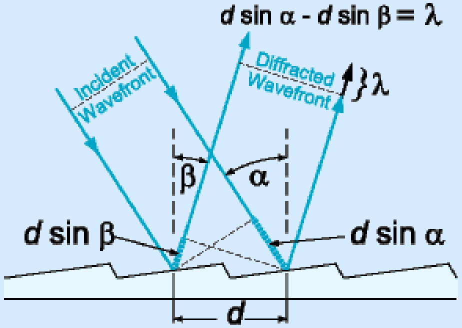
New trend with volume Bragg gratings
One filter for one wavelength



3.11. Spectrometer and Gratings







Grating Equation:

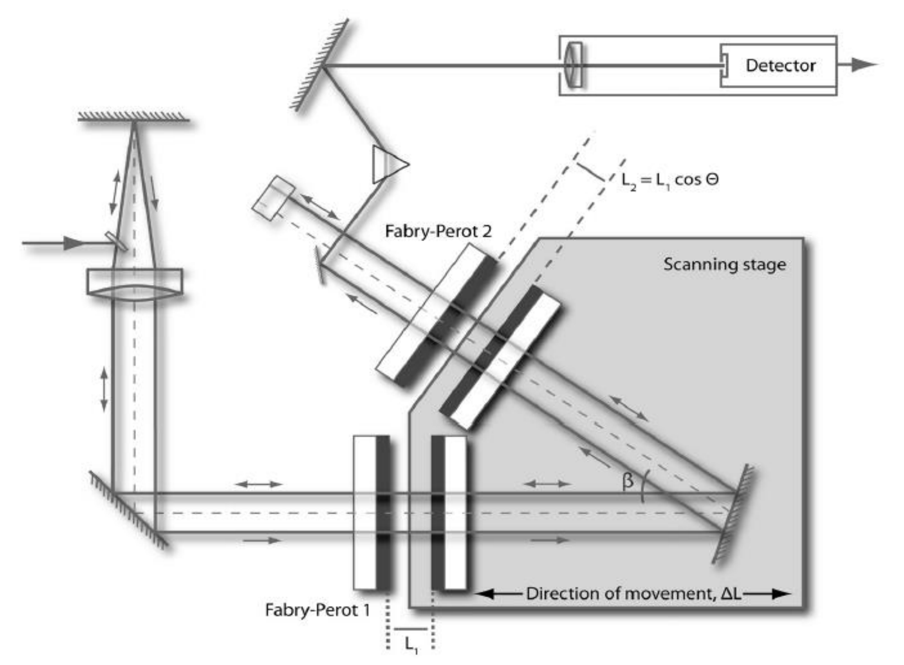
$m\lambda = d(\sin\alpha \pm \sin\beta)$

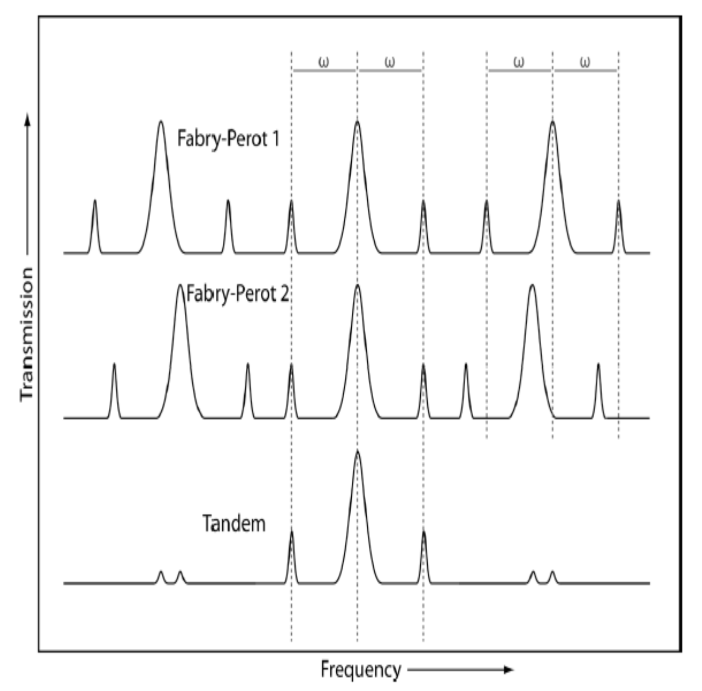
Fig 4.9 Diffraction grating

Frequency resolution is fonction of the spectrometer focal length and of the gratings

but way too bad for Brillouin spectroscopy

3.12. Brillouin spectroscopy: Fabri-Perot interferometer





Maximum transmission at:

$$\lambda = \frac{2d}{m}.$$

d – mirror space
m - integer

Very good spectral resolution
Rejection of the Rayleigh done by a shutter

3.13. Intensity and experimental conditions

Collection conditions

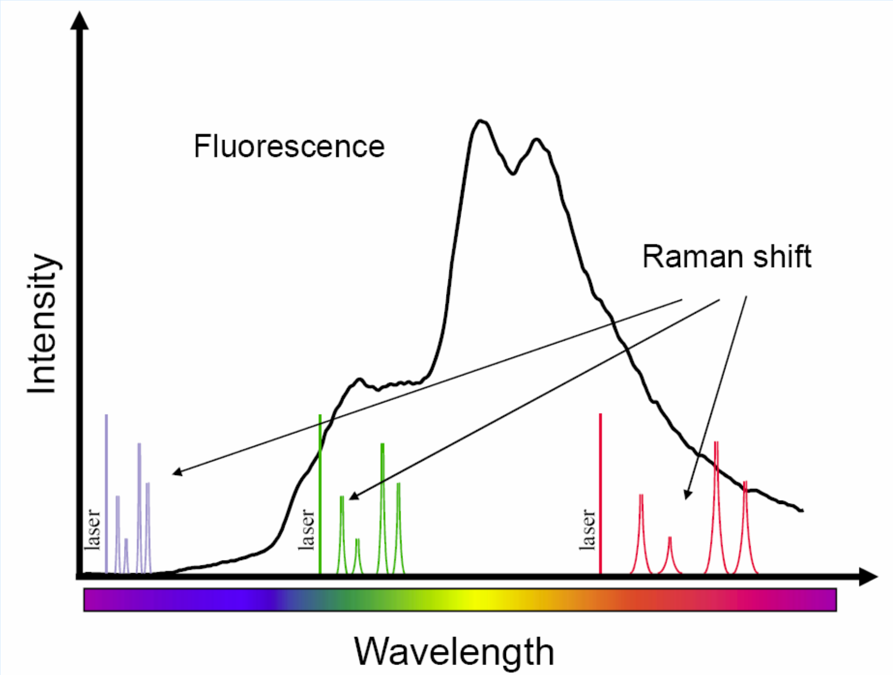
- experimental parameters (counting time, numbre of accumulations)
- confocal pinhole diameter
- objectif
- optical path: global responce of the apparatus (grating)
- wavelength of excitation in relation with detector sensitivity

Sample preparation

- surface of the sample (flat and polish always better)
- heterogeneitis diffusing light (bubles or cristals)
- sample absorption at the excitation wavelength
- refraction index

3.14. Raman versus Luminescence

	Fluorescence	**Diffusion élastique**	**Diffusion Raman**
Probability (~)	10^{-4} à 10^{-2}	10^{-2} à 10^{-1}	10^{-7} à 10^{-14}

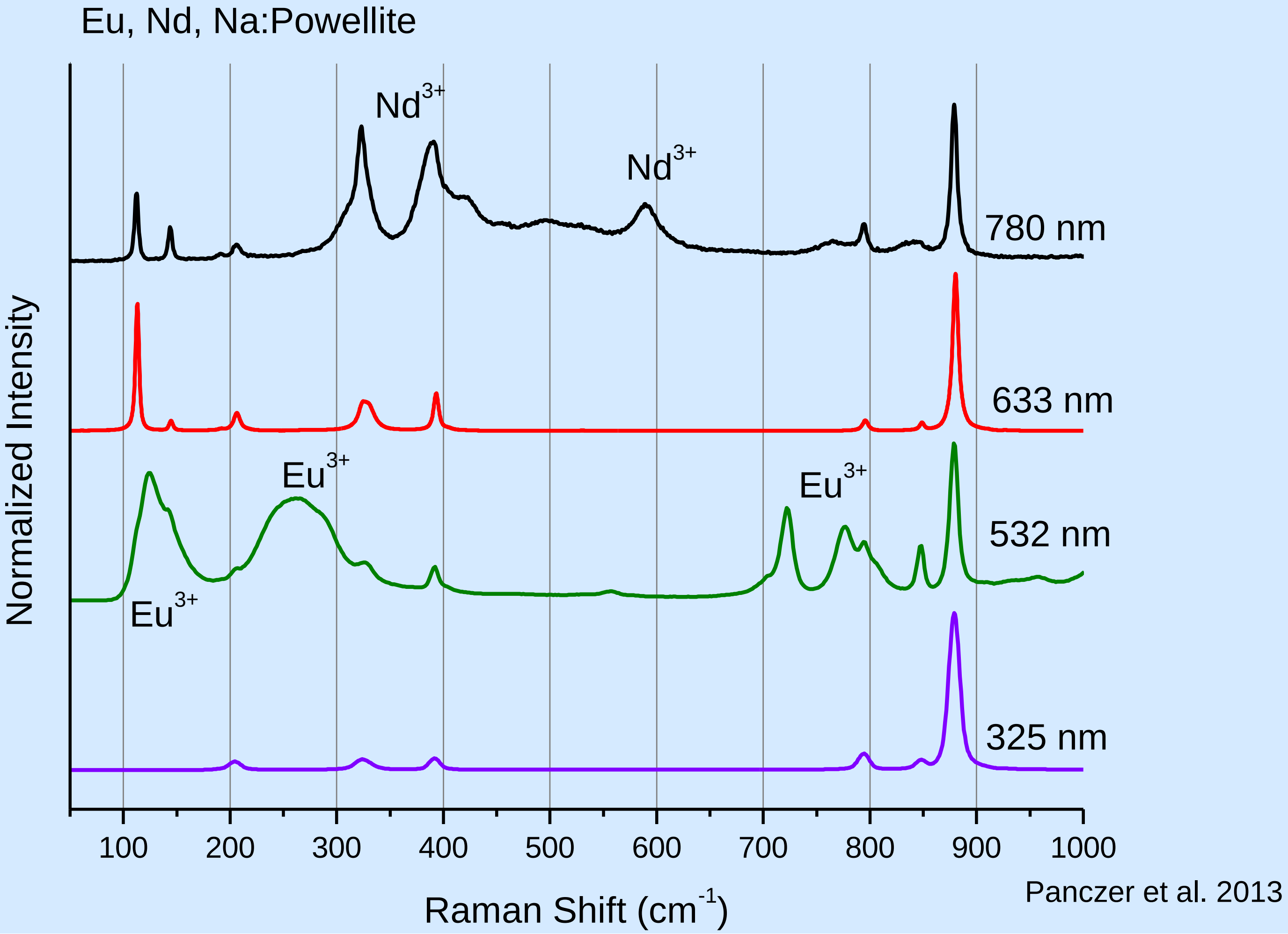


Panczer et al. 2013

There is always a possible luminescence or a tail of luminescence

Baseline correction often needed and of different shapes

3.14. Raman shift = relative wavenumber (cm^{-1})



Panczer et al. 2013

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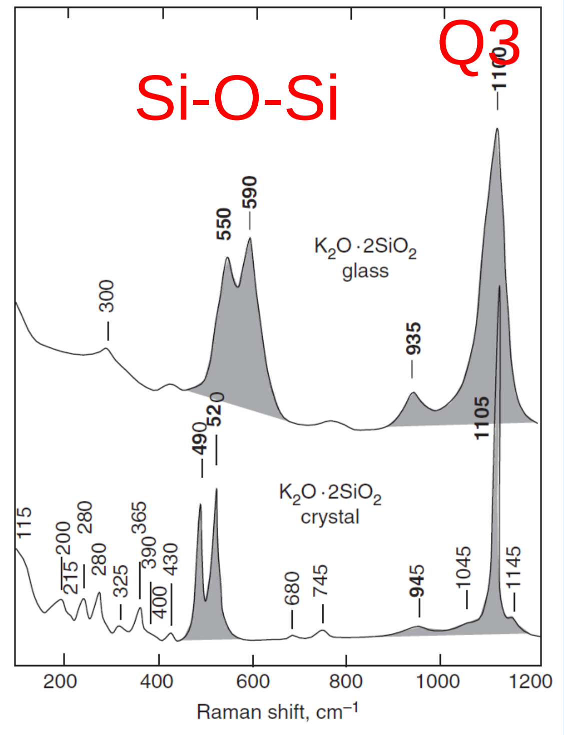
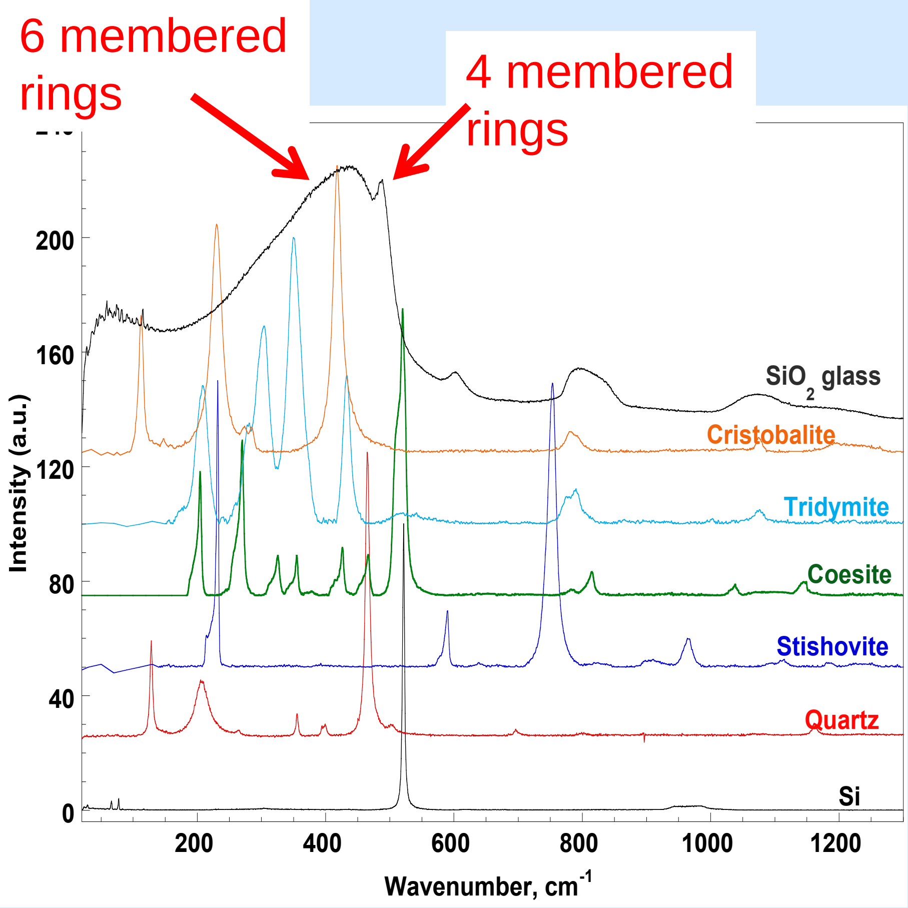
4.1. Finger print with crystals



Si-O-Si

Q3

Richet & Mysen, 1999

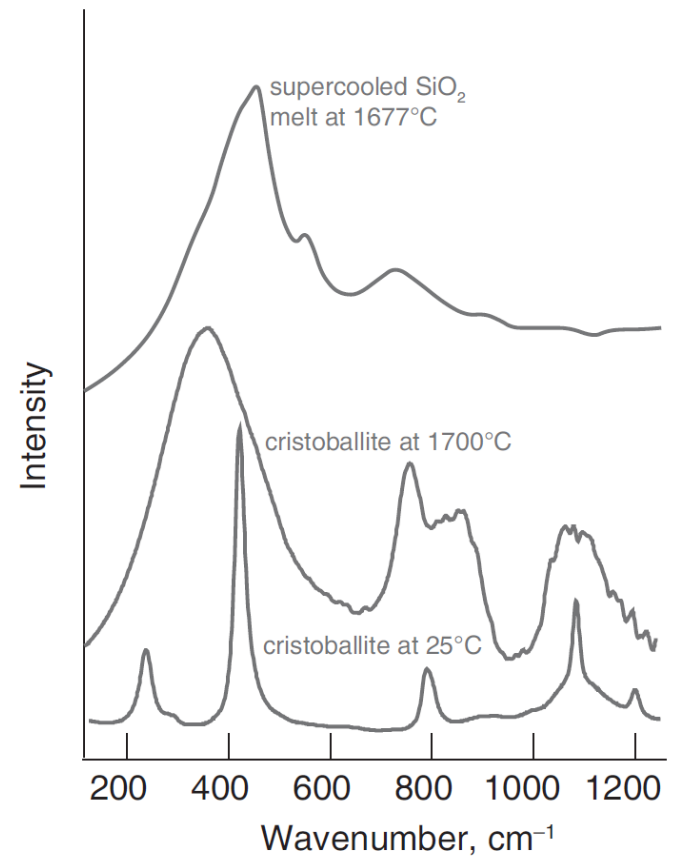


6 membered rings

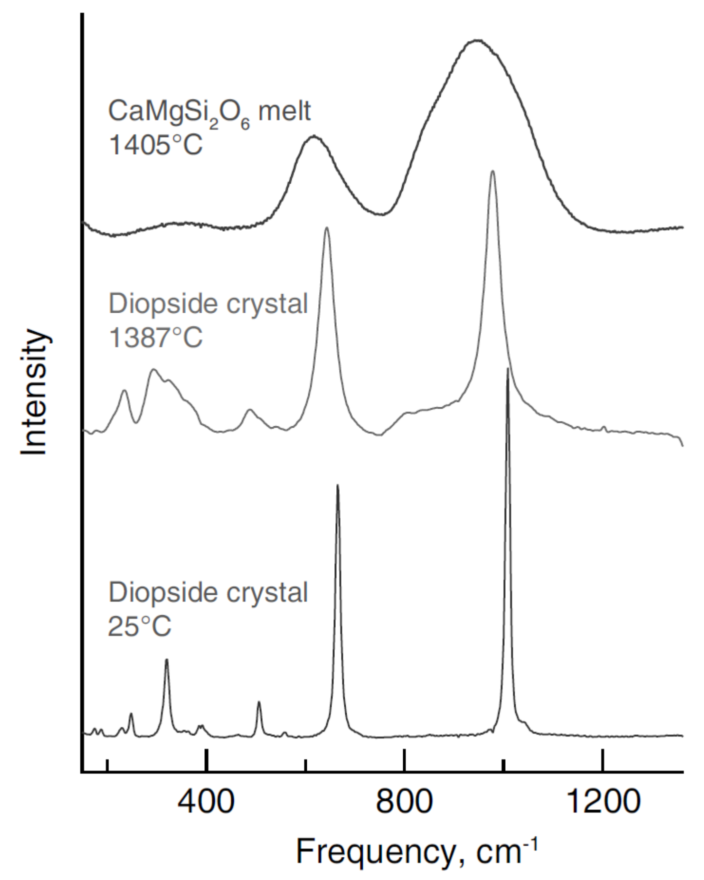
4 membered rings

Neuville et al. 2014

4.2. Finger print close to melting point



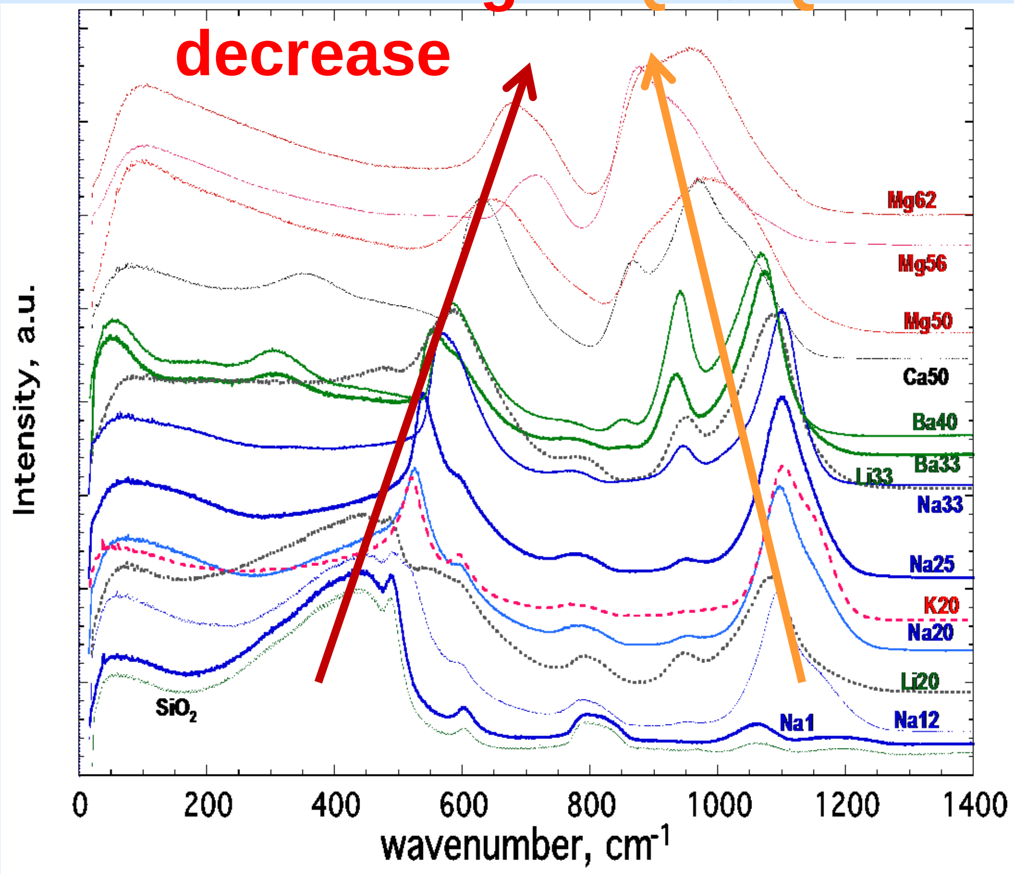
Richet & Mysen, 1999



Kushiro, 1969

4.3. Polymerization

Si-O-Si angle decrease **Q0←Q4**

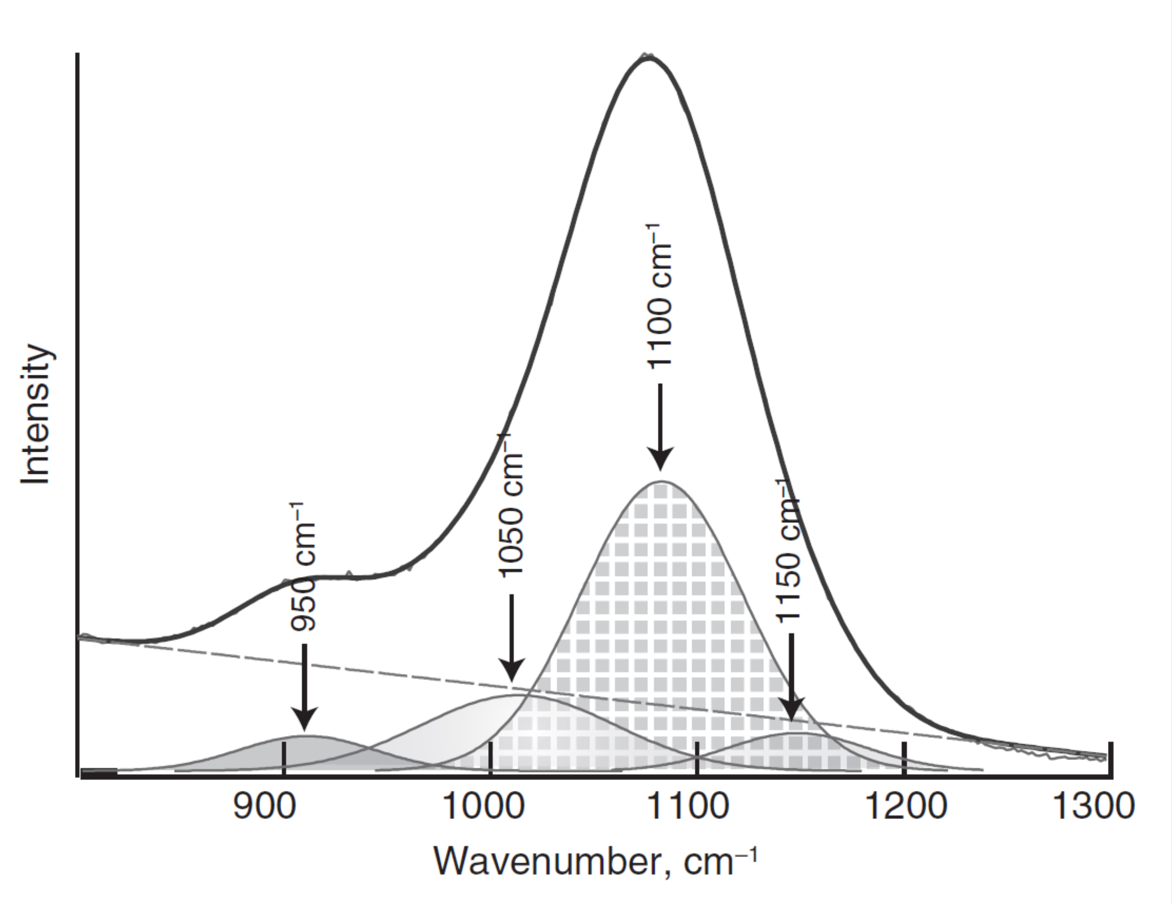


Neuville et al. 2014

modifier

Strong increase of intensity in the Qn stretching region compare to the bend region

4.4. Peak fitting



Rossano and Mysen 2012

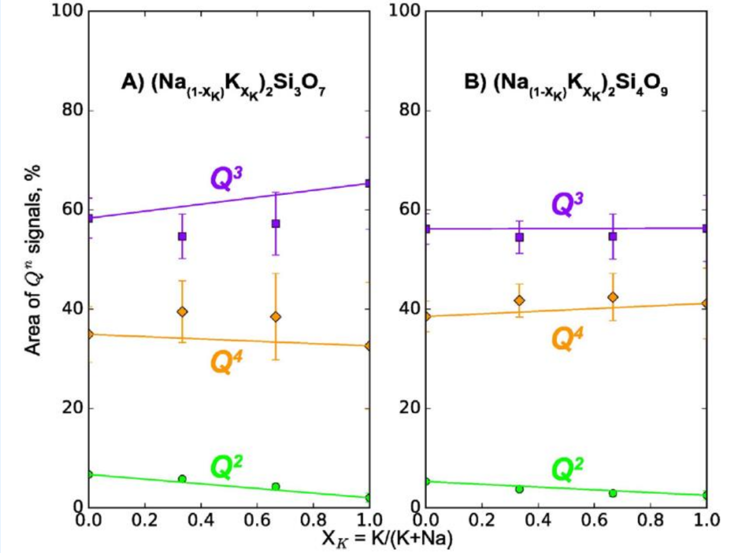
Determination of the Qn species by peak fitting

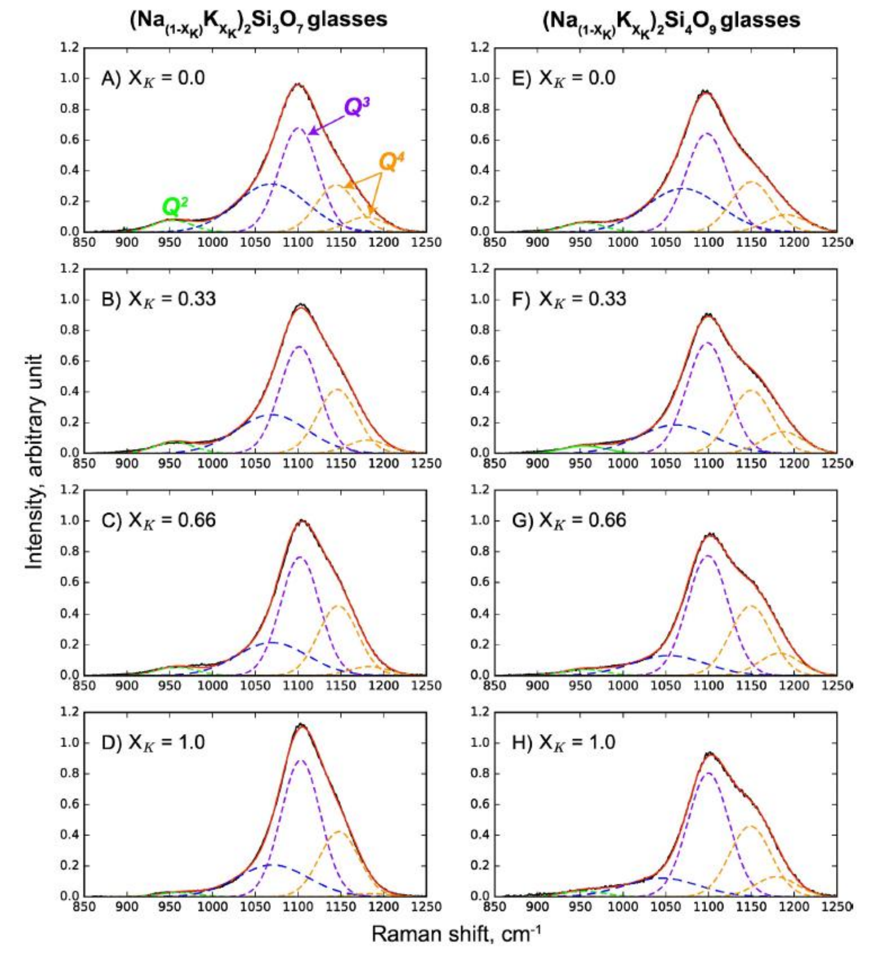
4.5. Example of the use of deconvolution

Molecular structure, configurational entropy and viscosity of silicate melts: Link through the Adam and Gibbs theory of viscous flow

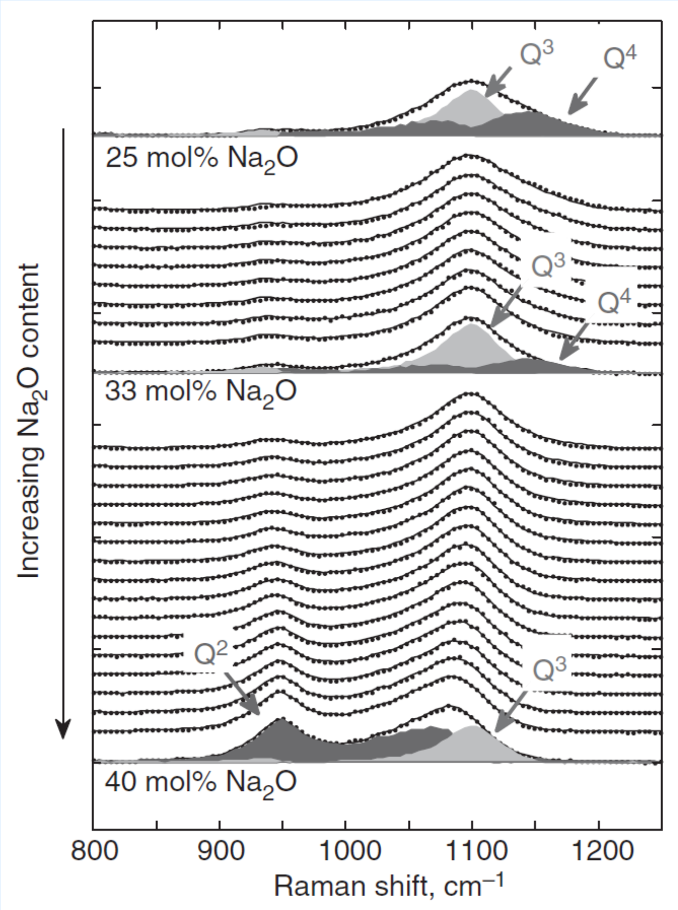
Charles Le Losq [a,*], Daniel R. Neuville [b]

Journal of Non-Crystalline Solids 463 (2017) 175–188





4.6. Principal component analysis



Malfait et al., 2008

Principal component analysis to determine the characteristic spectra of each Qn

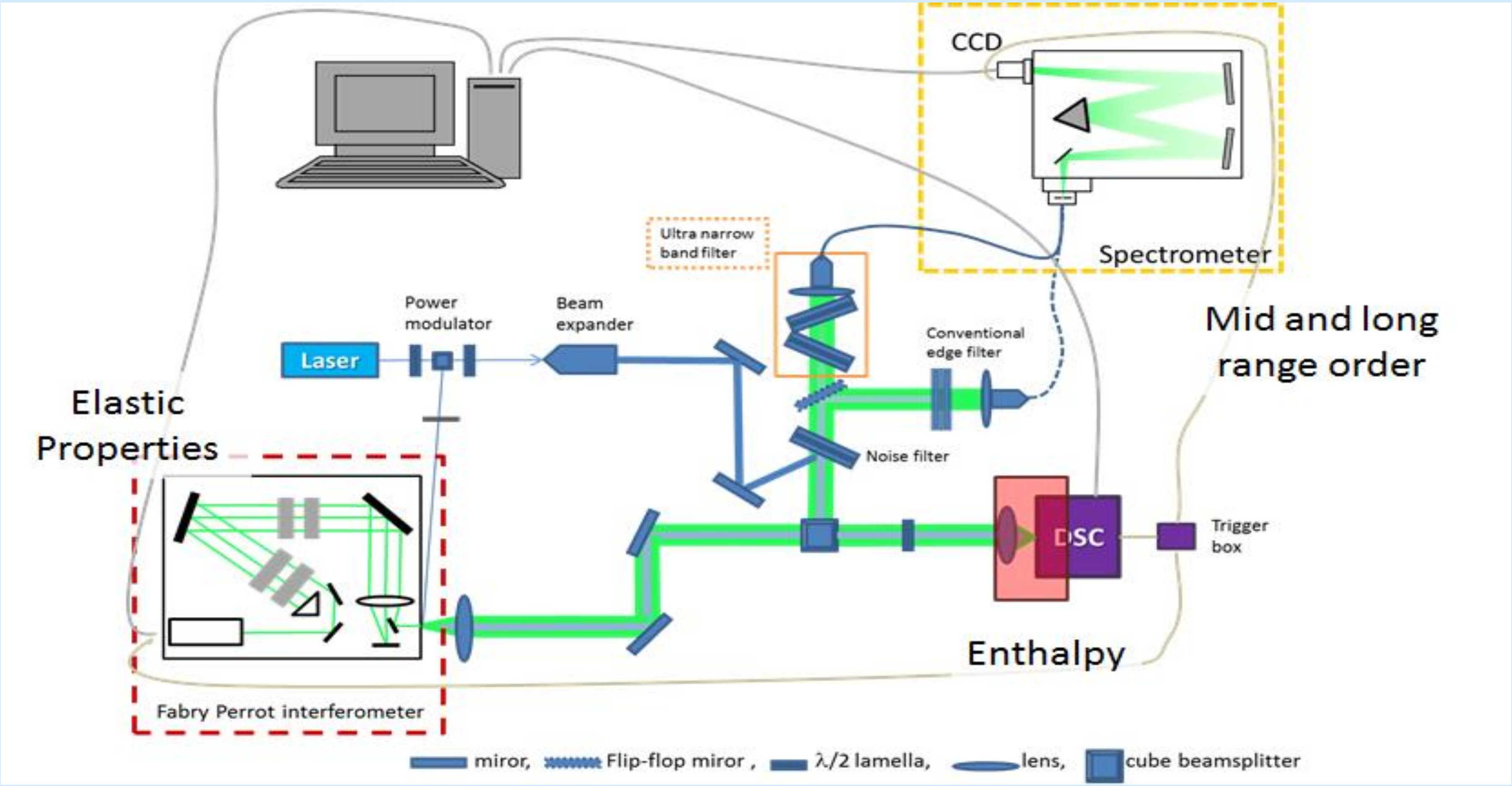
Very powerful however these characteristic Qn spectra evolve with the modifier cation

Content

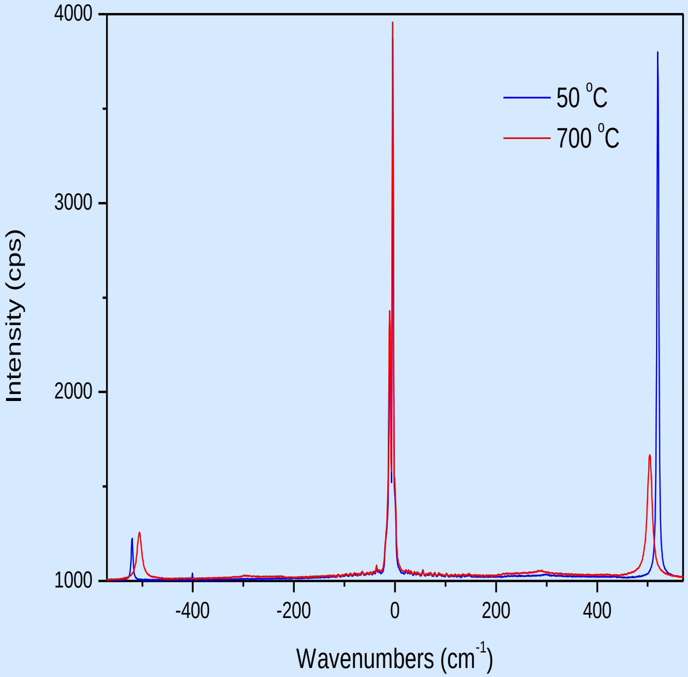
1. From atoms motion to its interaction with light
2. Interaction light/matter
3. equipment and the parameters to consider
4. Assignment in silicate glasses and polymerization
5. In situ observation of the glass transition
6. Evolution of glasses at high pressure

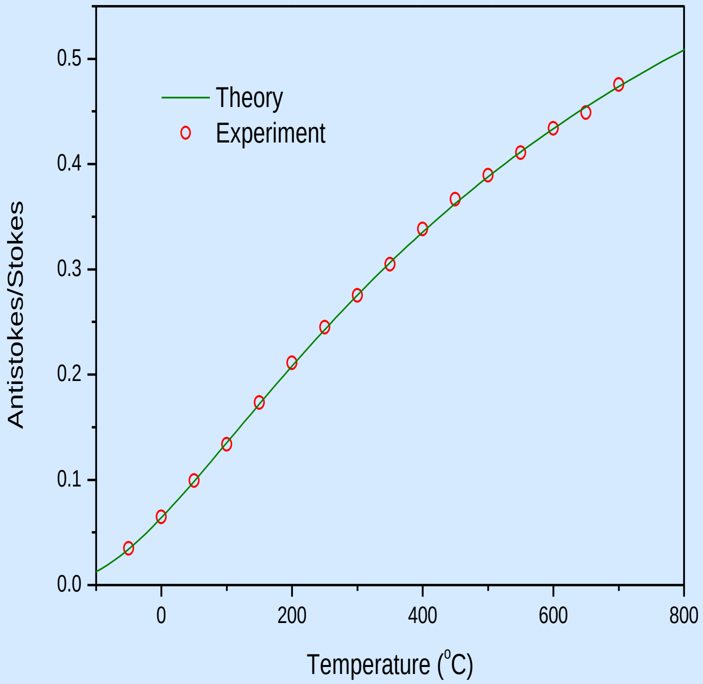
5.1. Experimental setup: ARABICA

Associated RAman BrIllouin CAlorimeter



5.2. Antistokes/stokes Raman spectra of Silicon



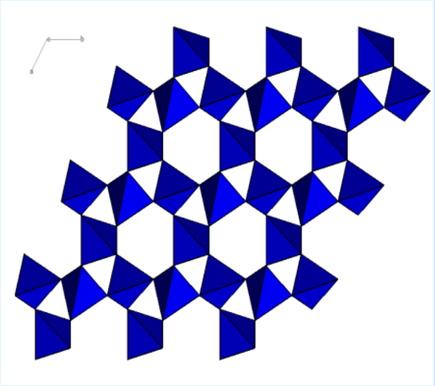


Temperature from DSC calibration is in very good agreement with the temperature obtained by the Antistokes/stokes ratio.

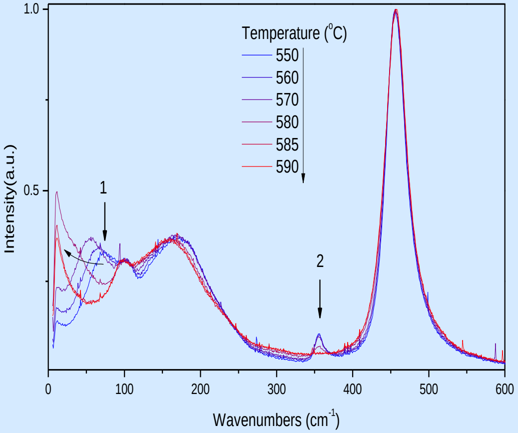
Ability to know the temperature of the probed sample.

5.3. Quartz alpha-beta transition

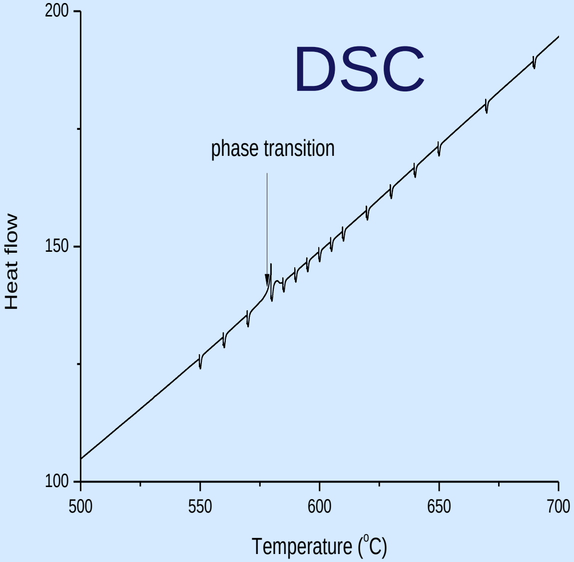
Animation of transformation from trigonal alpha- to hexagonal beta-quartz



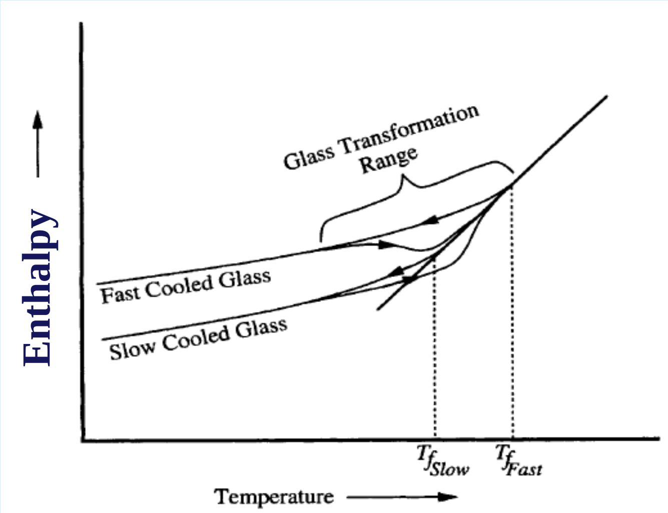
Raman spectra



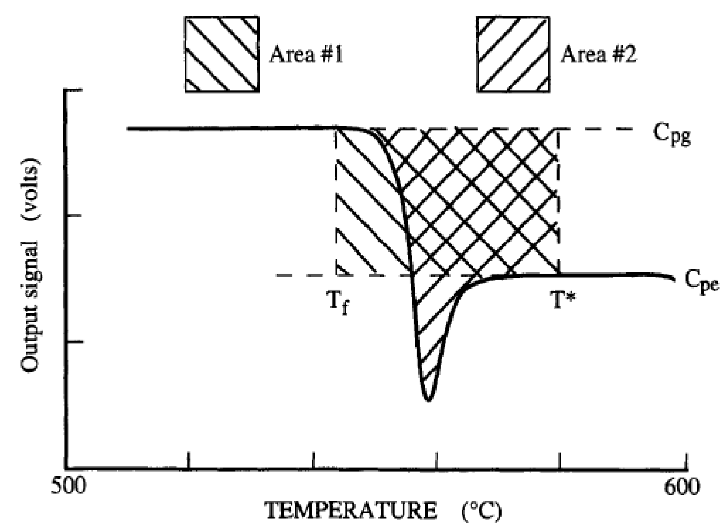
DSC



5.4. Glass transition



$$\int_{T^*}^{T_f} (C_{pe} - C_{pg})\,dT_f = \int_{T^*}^{T^\#} (C_p - C_{pg})\,dT$$



Higher the cooling rate higher the fictive temperature

5.5 Sample

$60NaPO_3\text{-}20Ca(PO3)_2$

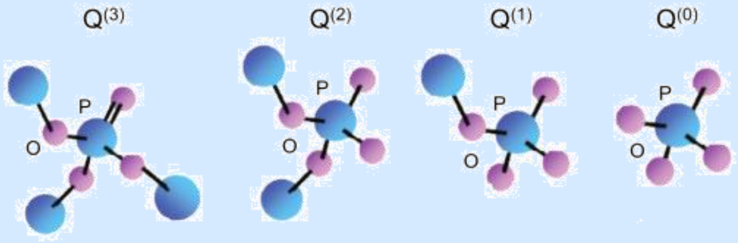
Thermal properties:

Tg ~ 350 ^{o}C

Tm ~ 735 ^{o}C

Tx ~ 547 ^{o}C

Known structure

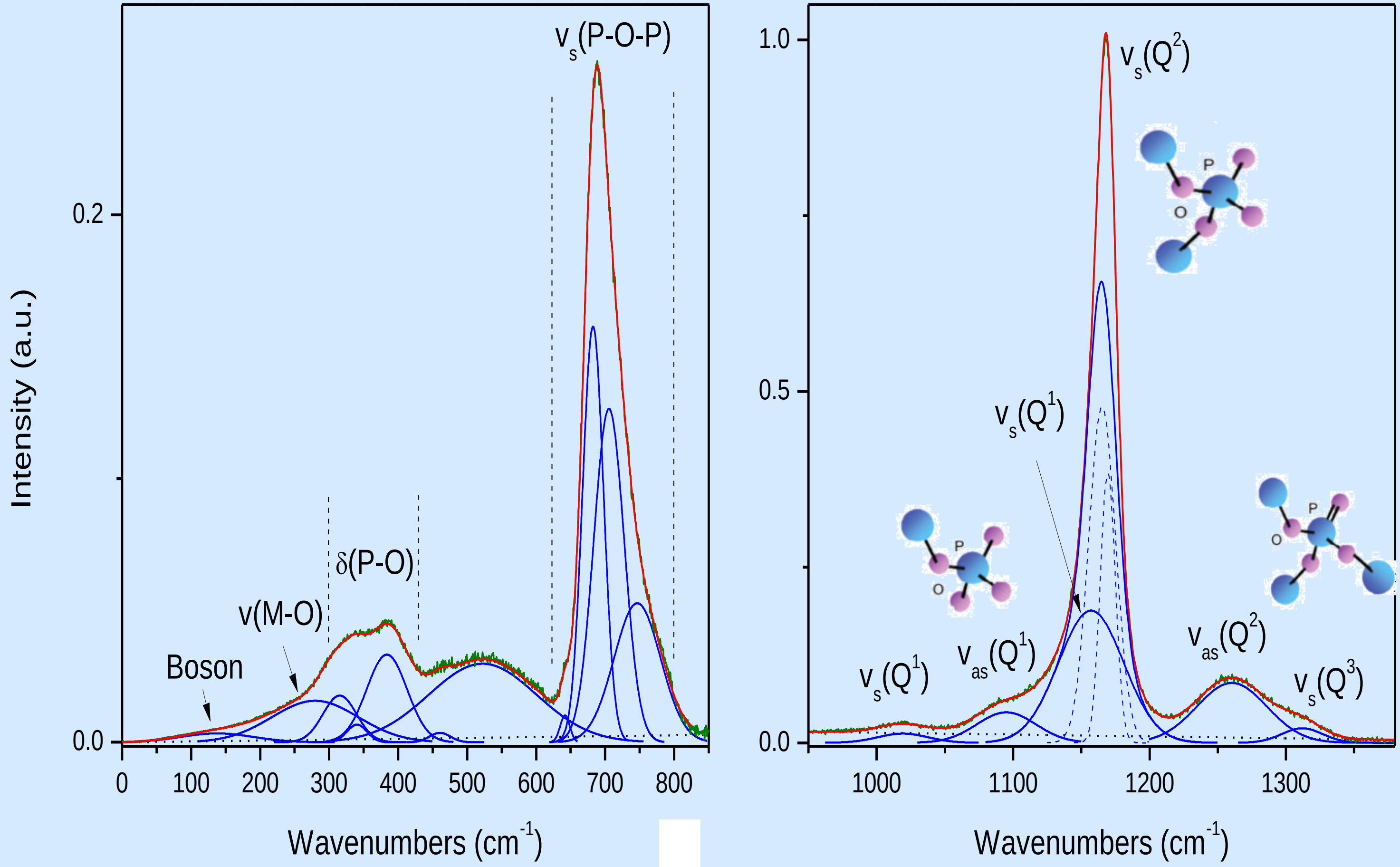


Cooling with different rates
Measuring properties during heating with a constant heating rate of 10 K/min

Heat flow was calibrated using a sapphire disc

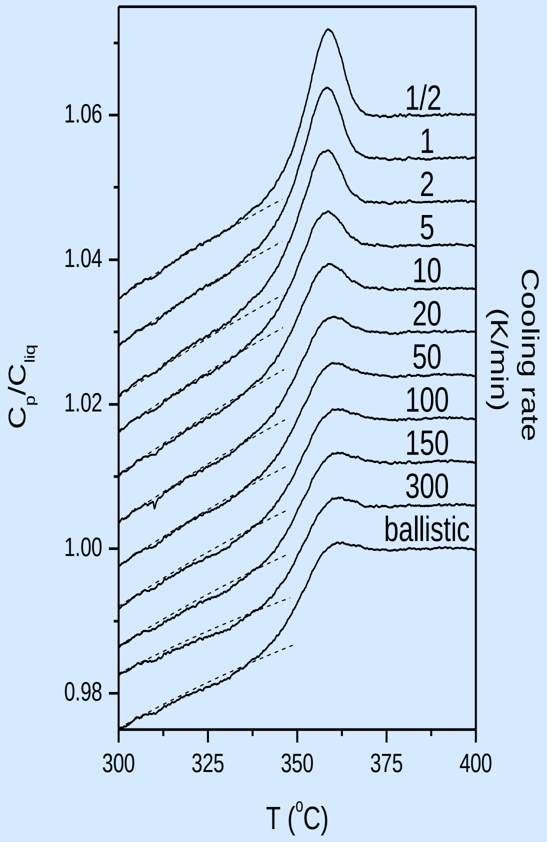
Luke B. Fletcher et al. Opt. Mater. Express 1, 845-855 (2011)

5.6. Deconvolution of the observed Raman spectra

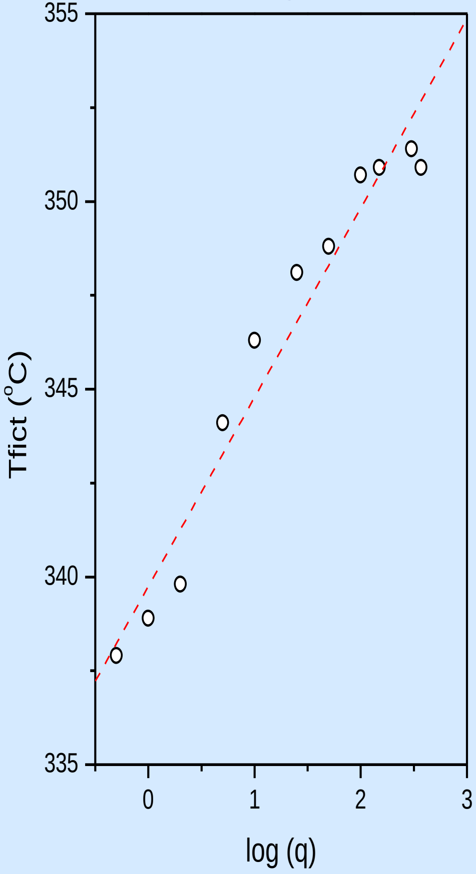


5.6. Glass transition: DSC

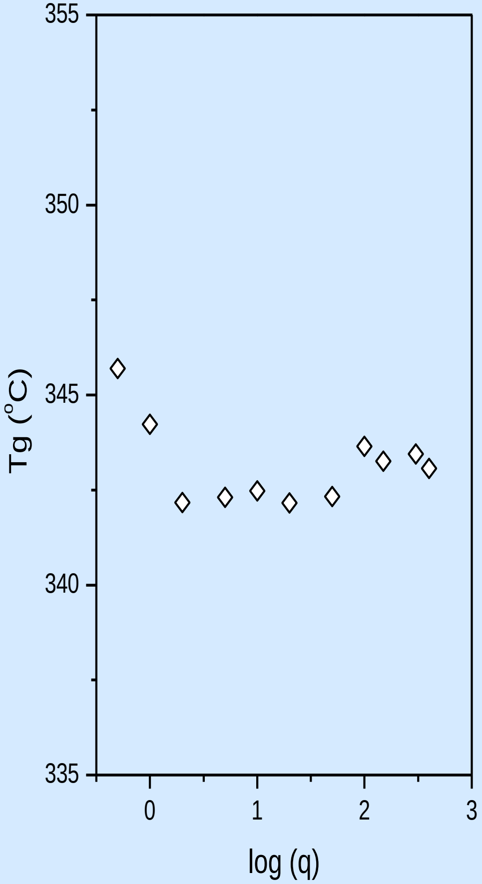
Heat capacity normalized to liquid state value



Fictive temperature vs cooling rate

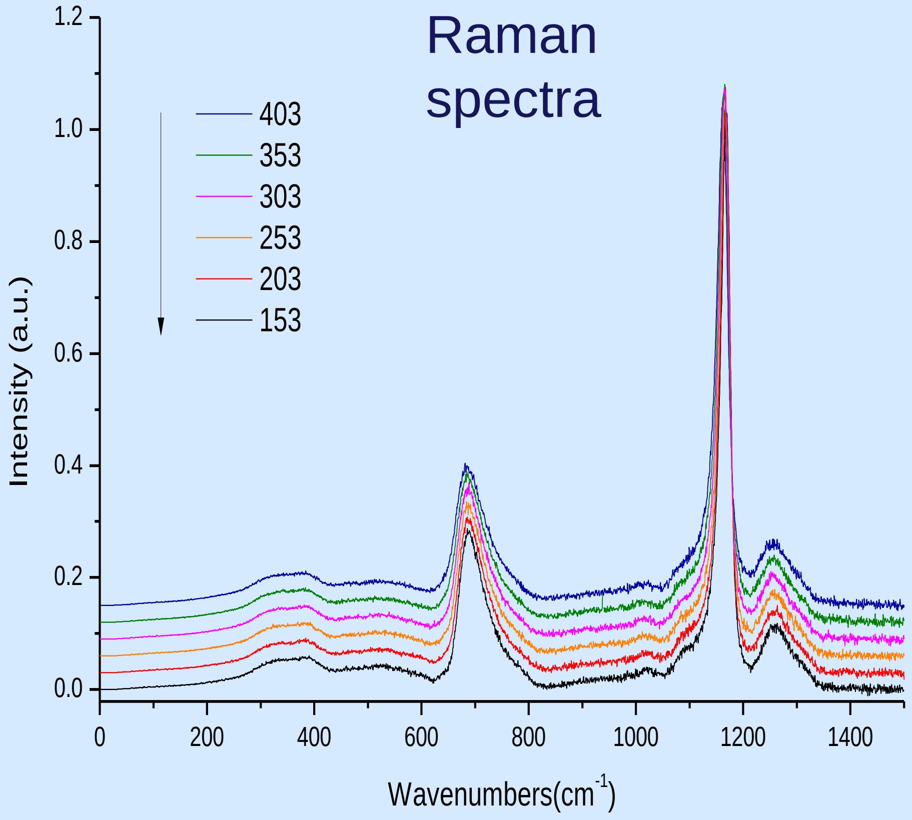


Formal Tg vs cooling rate

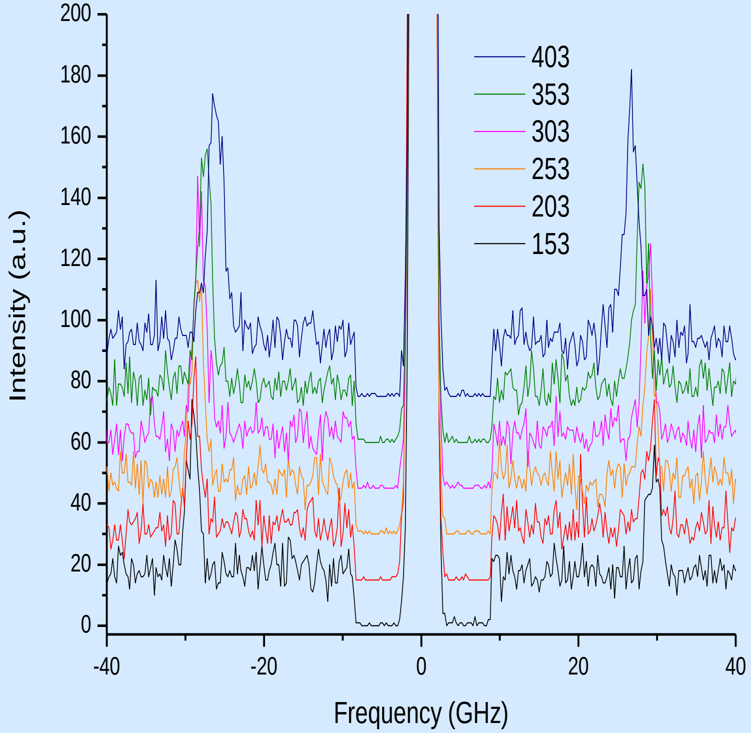


5.7. Raman and Brillouin in temperature

Raman spectra



Brillouin spectra



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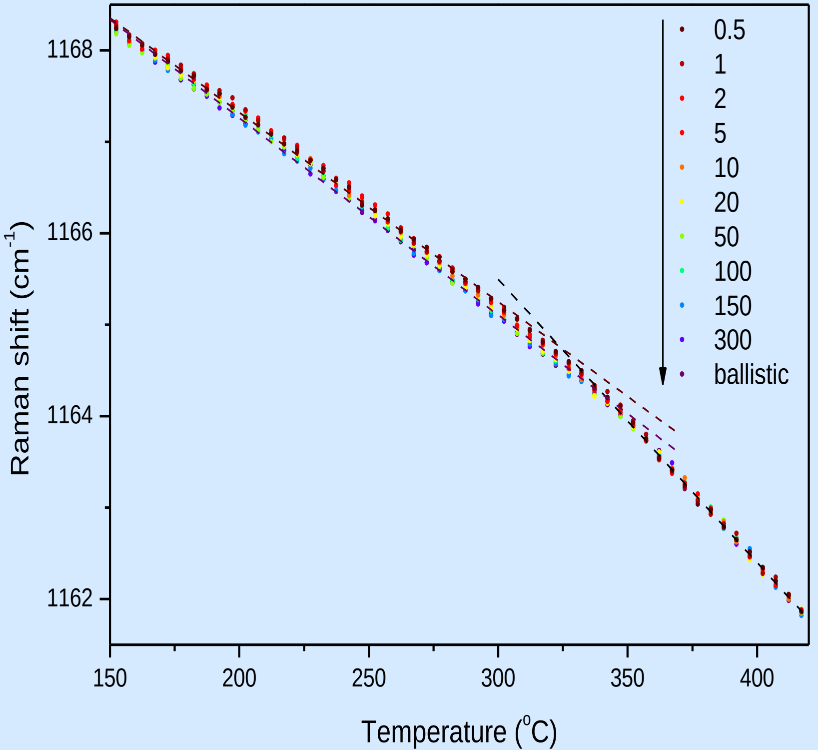
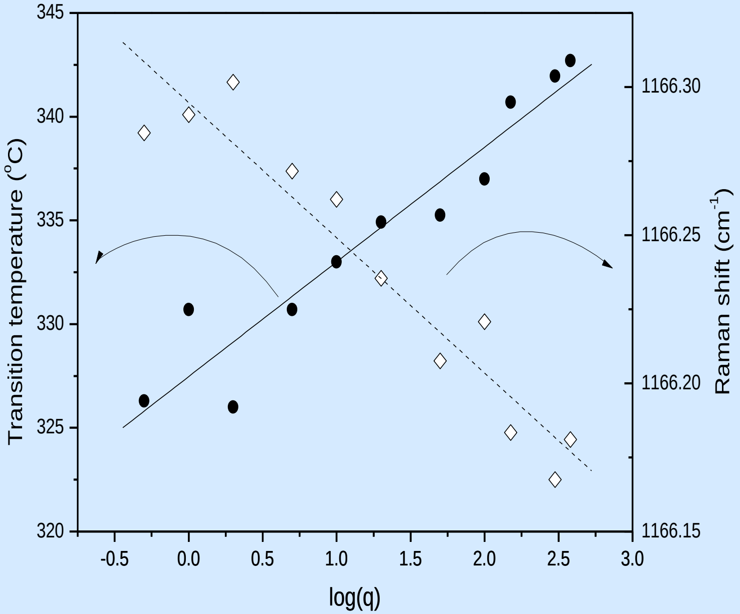
5.8. Analysis of the main Raman band behavior

Band position vs temperature



Raman fictive temperature and Raman shift at 250 °C vs cooling rate



Very weak effect on the short range order

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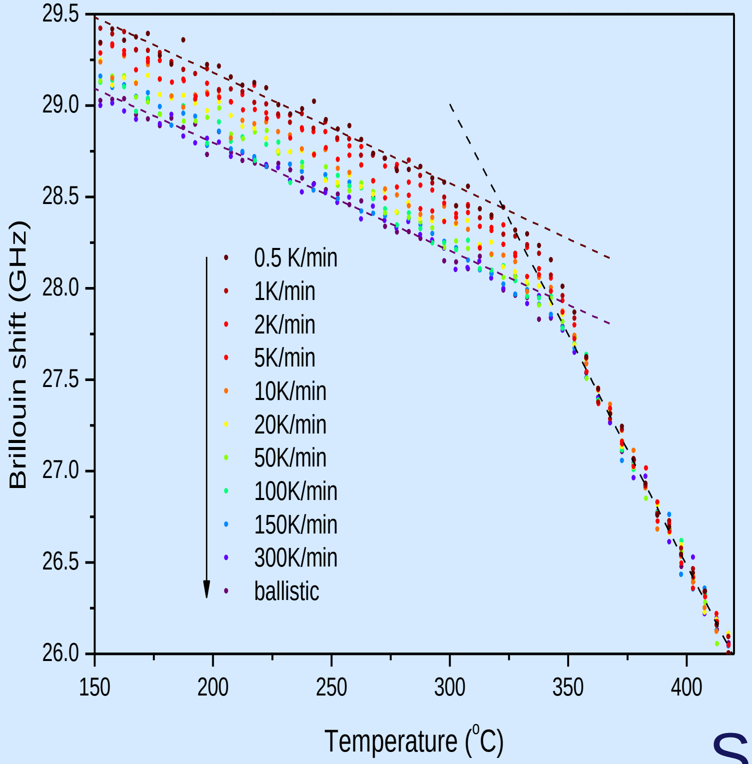
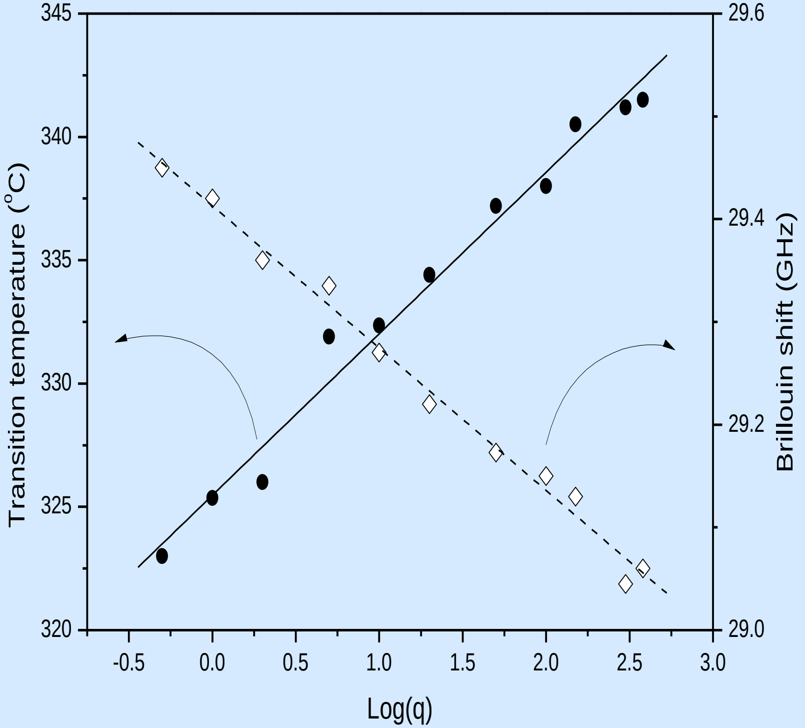
WW3

5.8. Analysis of the Brillouin behavior

Brillouin shift vs temperature



Brillouin fictive temperature and Brillouin shift at 150 °C vs cooling rate



Strong effect on the long range order

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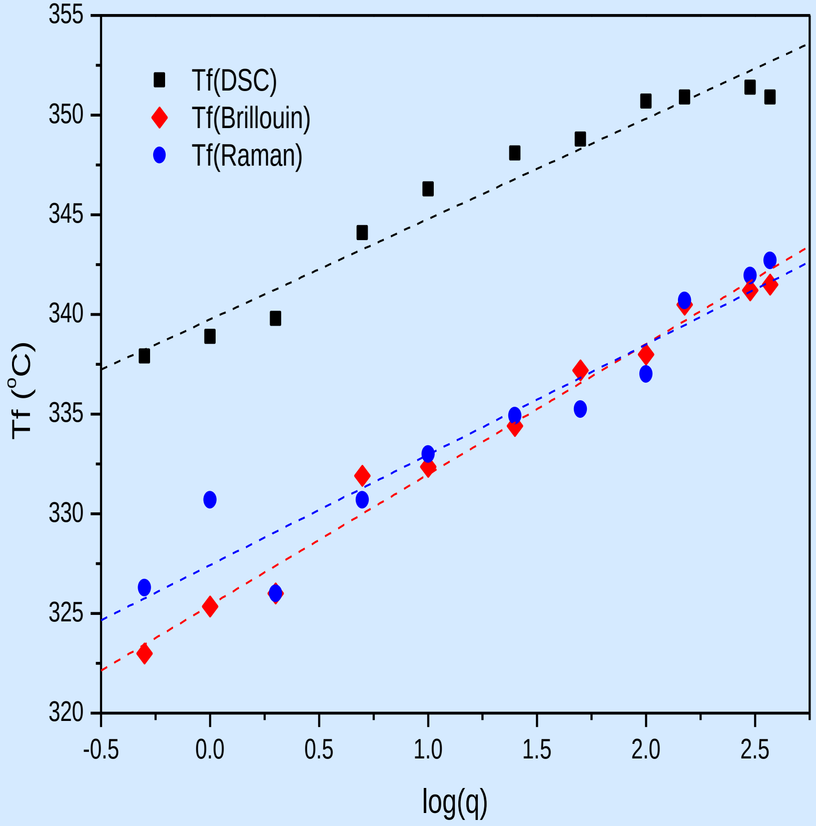
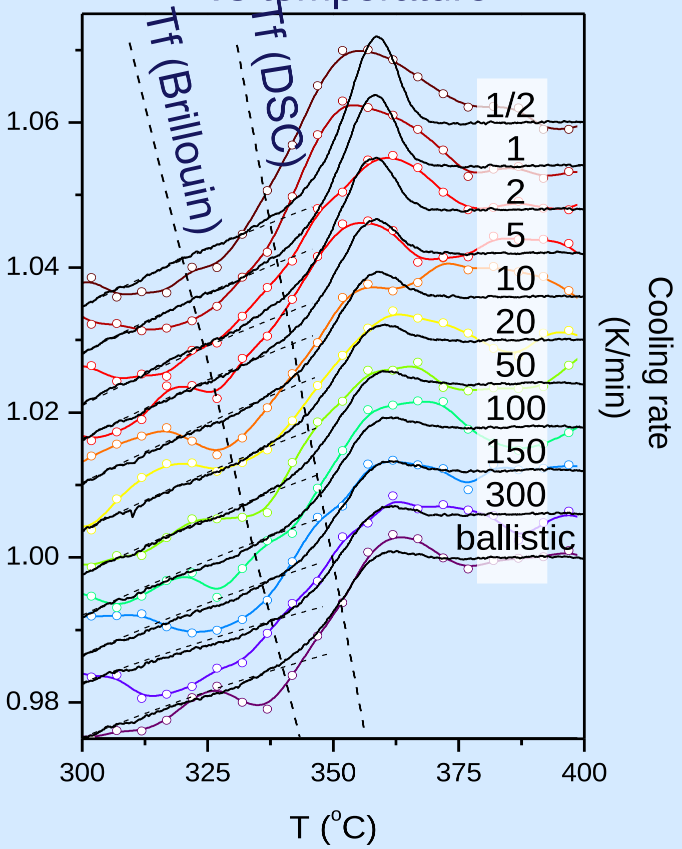
5.9. Comparison of thermal properties

Fictive temperature from DSC, Brillouin and Raman data vs the cooling rate



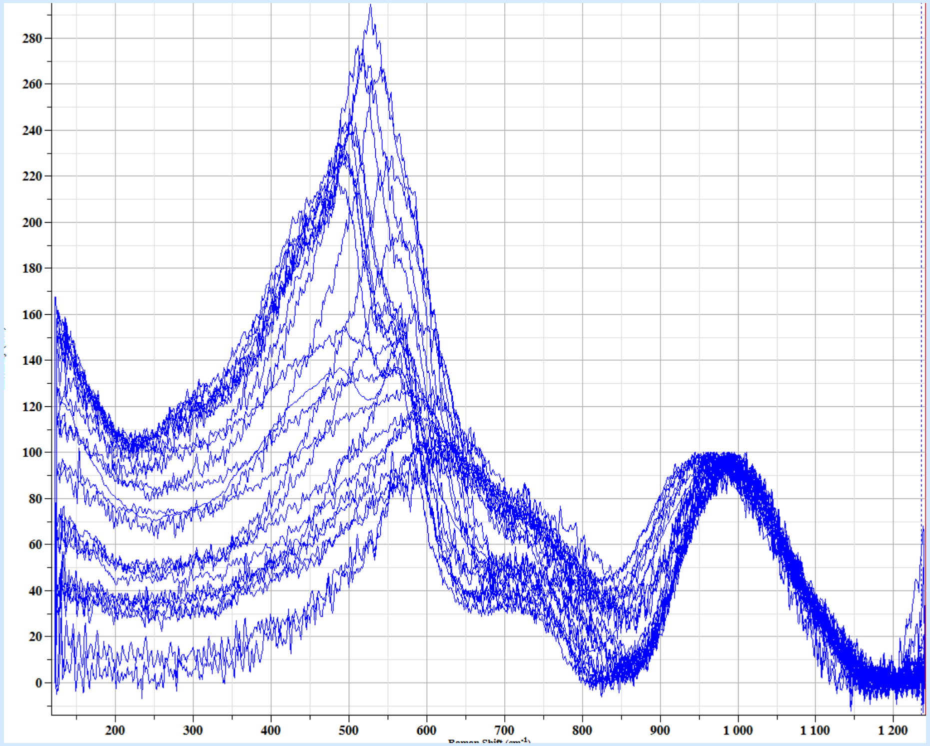
Brillouin shift derivative and the heat capacity (DSC) vs temperature



Content

6.1. $NaAlSiO_4$ under pressure

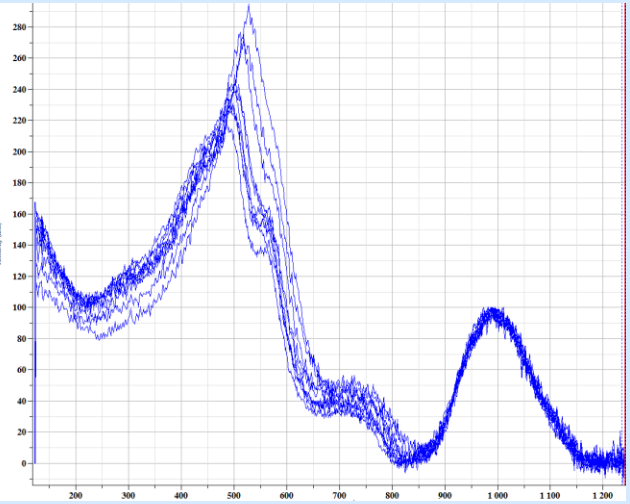
Glass fully polymerised with Al and Si in equal proportion in the thetraderals



Normalised on the max intensity of the Qn region

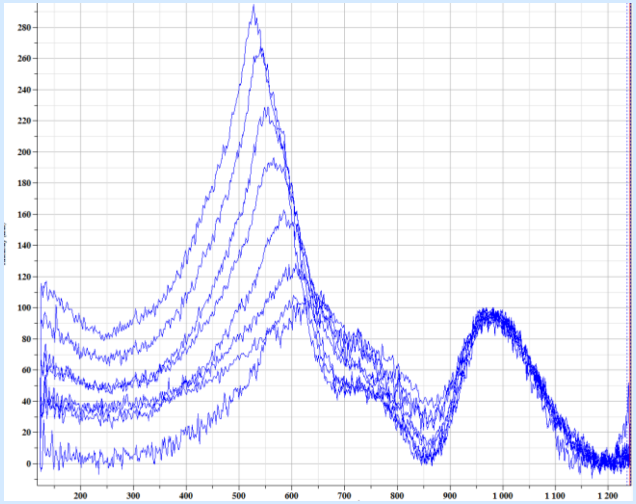
6.2. $NaAlSi_2O_6$ under pressure

0-8GPa



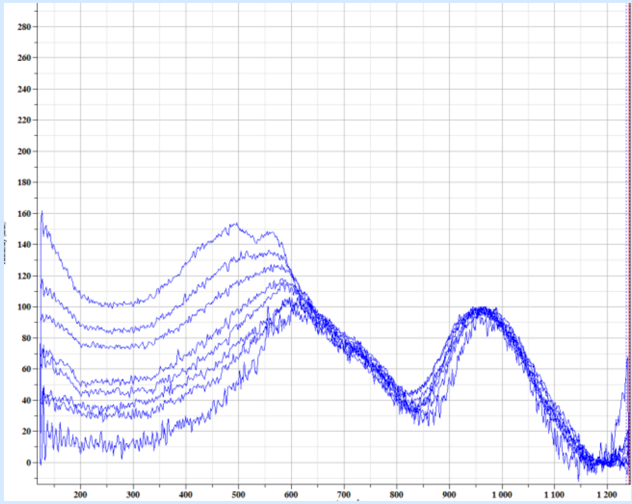
Modification of the angle between the tetrahedrals

8-16GPa



Change of CN of Al and Si

16-0GPa



Partial change back of CN and angles

Destruction of the mid range order

High coordinated Al? Modifier?

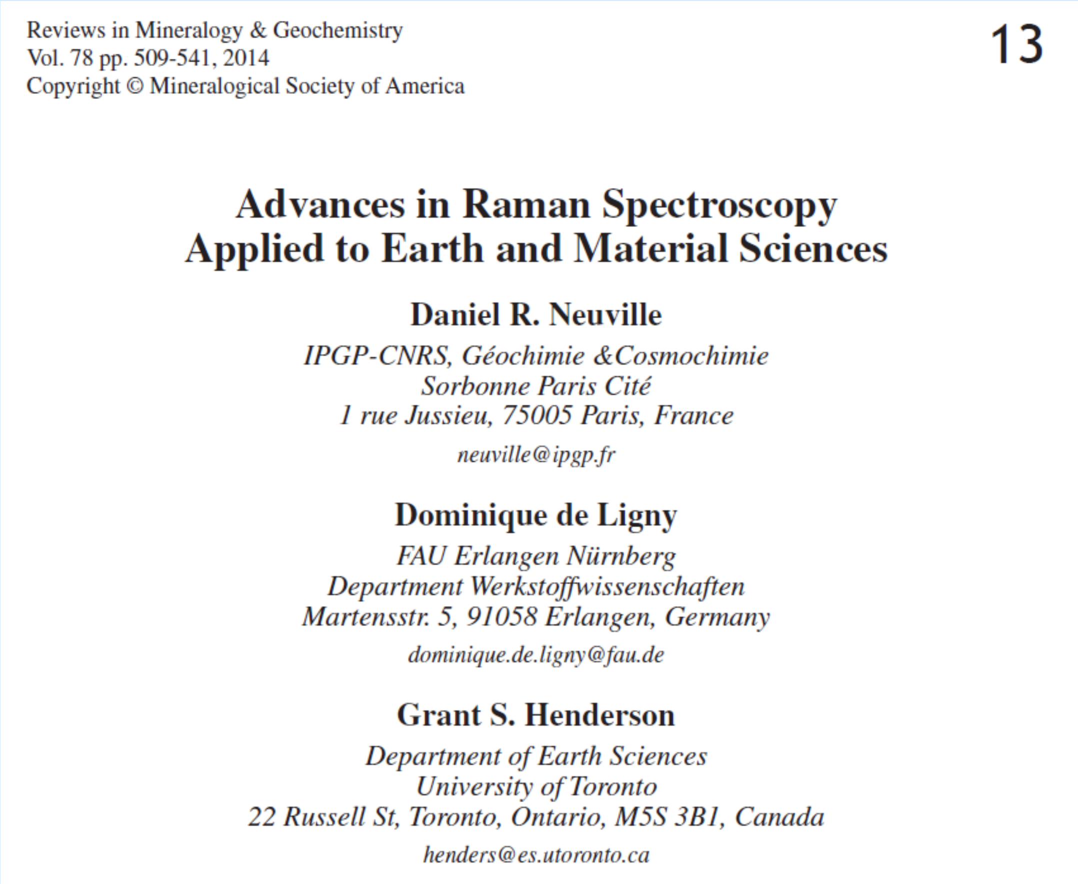
7. Conclusion

- Brillouin and Raman spectroscopy are very sensitive techniques
- Easy preparation of the sample
- Flexible sample environment

- Sensitive mostly to the network formers
- In polymerized glass same dynamic of the answer at short and long range order

- Difficult control of luminescence
- Baseline and normalization always questionable
- Assignment not always straight forward

- There is plenty things happening in the mid range order that have unfortunately no signature



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Advances in Raman Spectroscopy Applied to Earth and Material Sciences

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