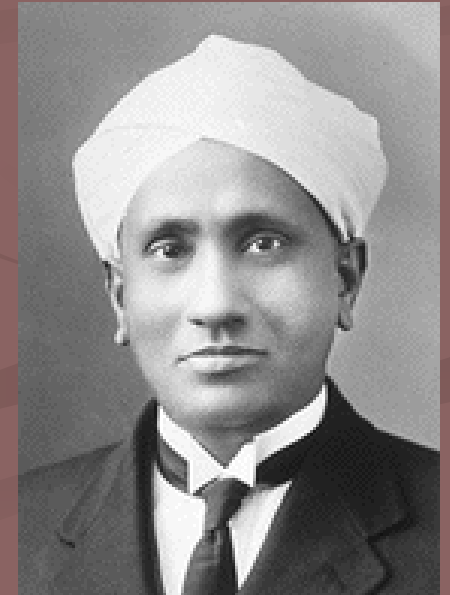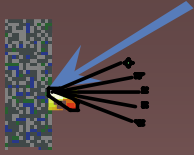# Raman: it's not just for noodles anymore
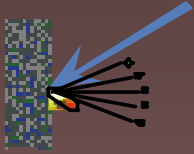
Part 2

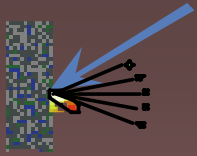Mario Affatigato

Physics Department

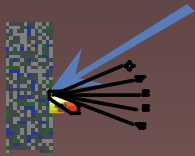Coe College

Outline - Day 2

- 4. Other Raman techniques
  - Raman microscopy
  - High pressure Raman spectroscopy
  - Surface enhanced Raman (SERS)
- 5. Vibrations and peak identification
- 6. Case studies
  - Silicates
  - Borates
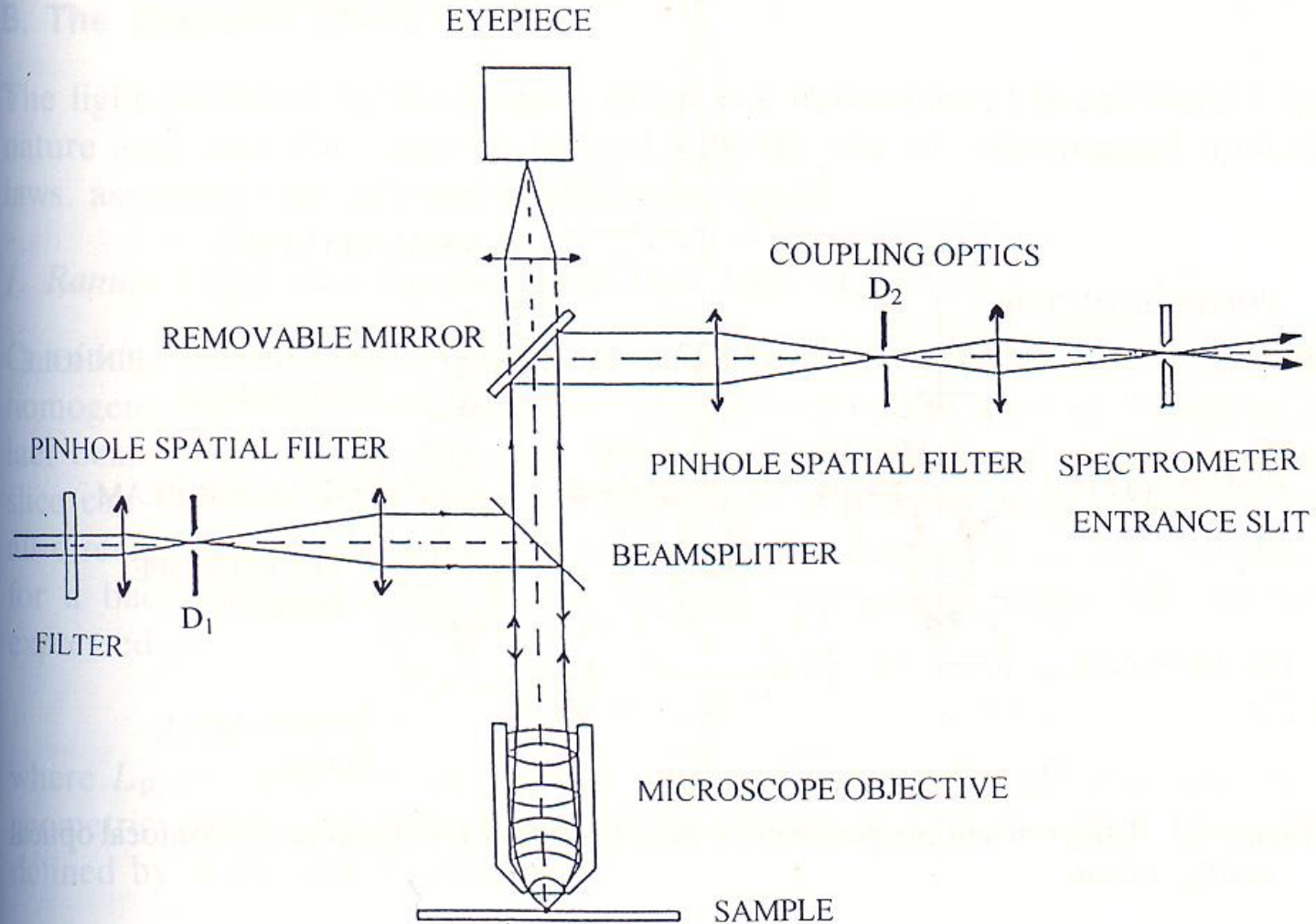 - Germanates
  - Other glass examples
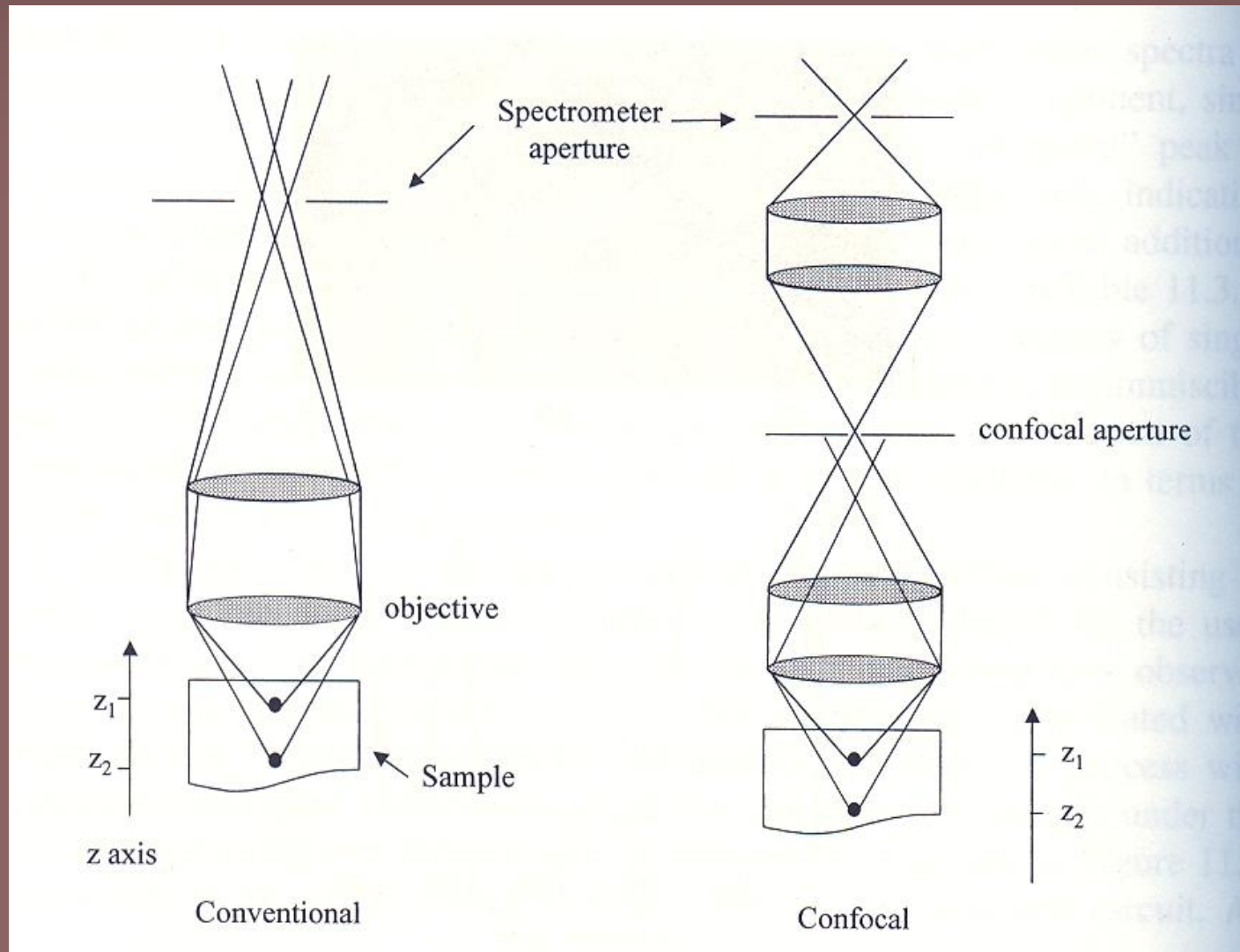- 7. References

4. Other Raman Techniques

Raman microscopes

Microscope schematic

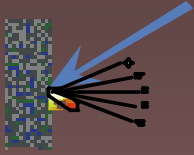# Conventional *vs.* Confocal

Raman microscopy

- Capability of imaging small features, composite materials, etc.
- Avoidance of large matrix effects
- Depth studies---up to a point
- Decrease in fluorescence, if that's a problem

BUT…

- Less light throughput (as less volume is effectively sampled)
- Some danger to lenses when using large Magnif.
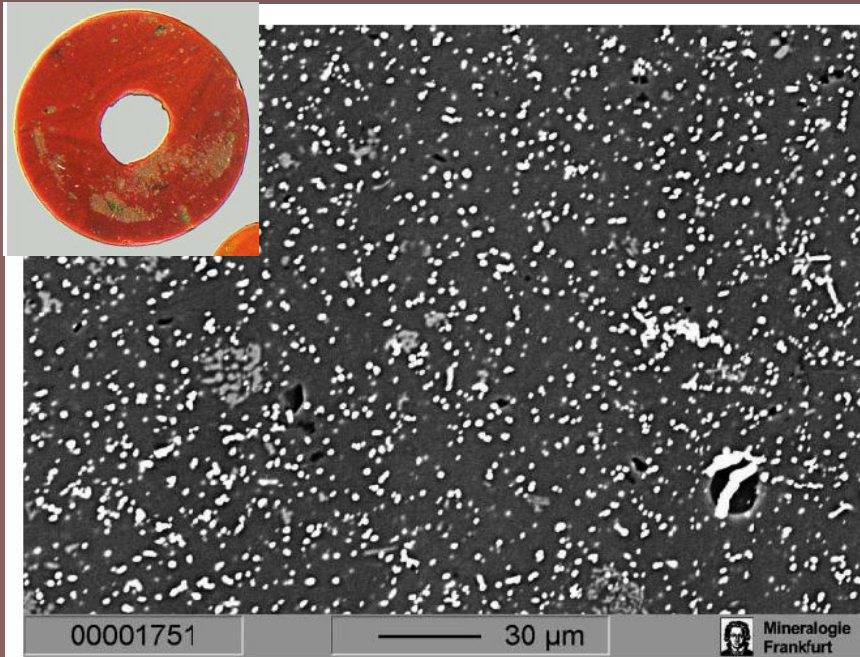- In confocal, less z-resolution than commonly believed.

Raman microscopy

Figure 4. Small cuprite crystals of micrometre size interspersed in the glass matrix of red opaque disc-shaped beads: back-scattered image.

Characterisation of inorganic pigments in ancient glass beads by means of Raman microspectroscopy, microprobe analysis and X-ray diffractometry
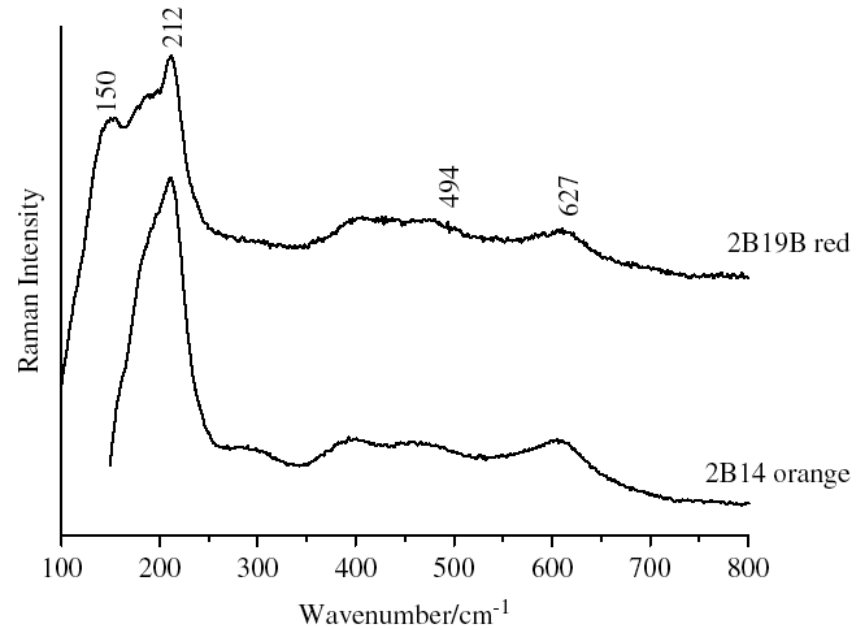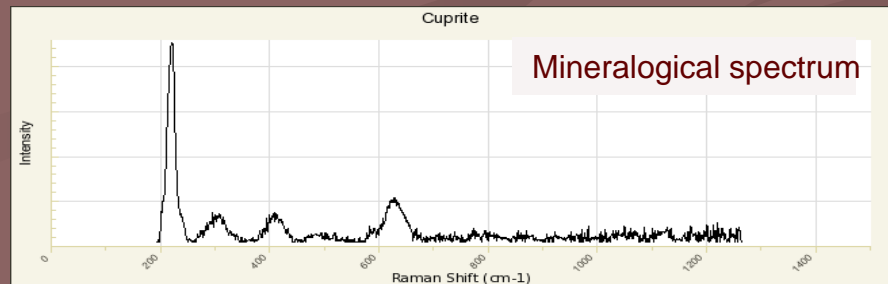
N. Welter,[1]* U. Schüssler[2] and W. Kiefer[1]

Figure 5. Raman spectra of cuprite (Cu_2O) in the red disc-shaped beads 2B19B and 2B14: excitation wavelength $\lambda = 514.5$ nm.

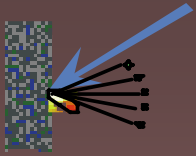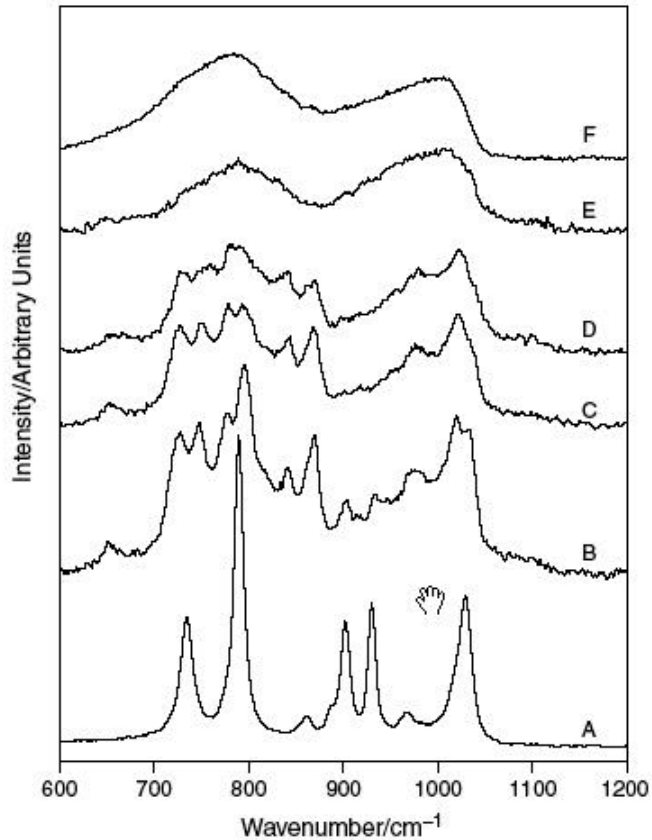Mineralogical spectrum

High pressure

High pressure and $Zr(WO_4)_2$

Figure 2. Evolution of the Raman spectra of zirconium tungstate.[22] (A) Sample at ambient pressure and (B)–(E) spectra obtained at 0.22, 0.75, 1.6 and 3.2 GPa, respectively. (F) Raman spectrum at ambient pressure for a sample recovered from high-pressure treatment in the DAC.

- On the left is an example of pressure-induced amorphization of zirconium tungstate. As the pressure increases the initial crystalline structure breaks down and does not return to the original state (see (F))

Raman spectroscopy as a probe for *in situ* studies of pressure-induced amorphization: some illustrative examples

A. S. Pereira,[1,2]* C. A. Perottoni[1,3] and J. A. H. da Jornada[1,4]
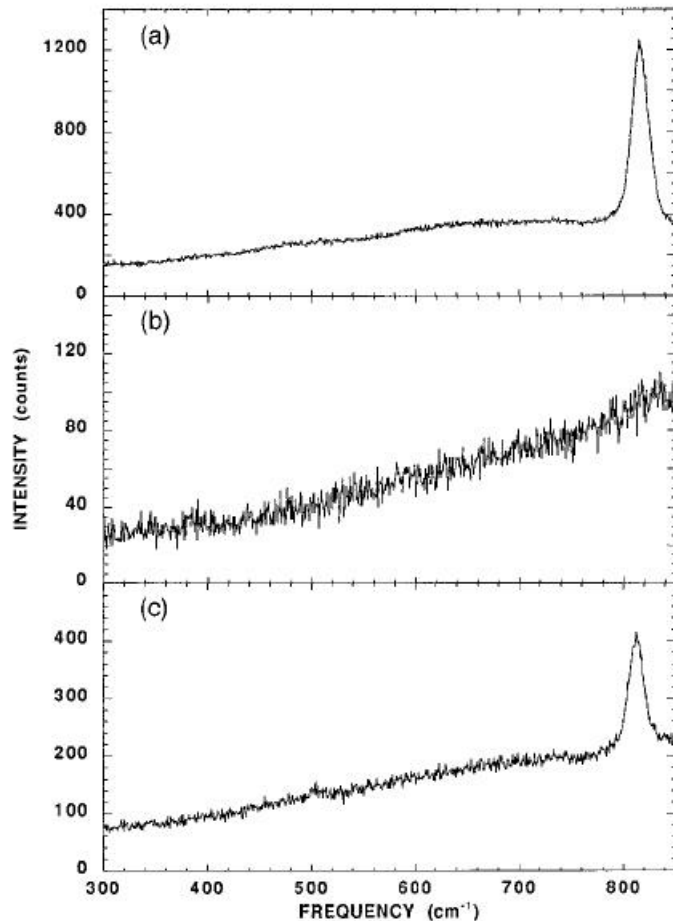
High pressure and B_2O_3

FIG. 1. Raman spectra of a-B_2O_3 at (a) 6 GPa just after loading, (b) at the maximum pressure 16 GPa, and (c) at 0 GPa after pressure release (still in the DAC).

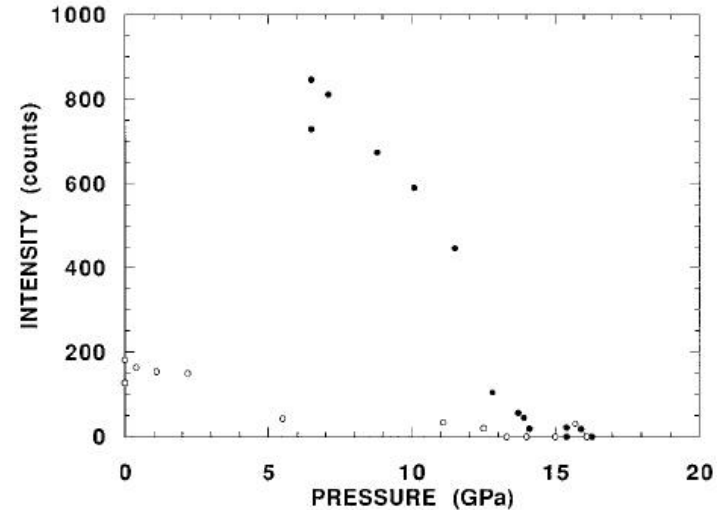FIG. 3. Intensity of the sharp peak vs pressure. The solid (open) symbols are taken with increasing (decreasing) pressure.

The disappearance of the 808 cm^{-1} band is due to the actual "dissolution" (break-up) of the boroxol rings, which form a more stable structure. Upon release of the pressure, a structural energy barrier prevents reformation.

From Grimsditch et al., PRB, 1996--see References
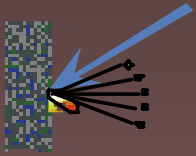
SERS

Surface-enhanced Raman

- Can increase the Raman signal by a factor of 10^4-10^6 regularly, with even 10^8-10^{14} for some systems.

- Surface selective, highly sensitive: allows for trace analysis and for better deconvolution

- Best when (Au, Ag, Cu) or (Li, Na, K) used

(From Veres, M. et al, 2004, see ref.)

The spectra at right show the regular spectra of a-C:H and a-C (bottom curves), and the SERS enhancement (top curves)

Nature of SERS

- Not extremely well understood. Arises from two effects:
  - Electromagnetic interactions
  - Chemical enhancement
- Electromagnetic: Dominant. Depends on the metal surfaces' roughness features, which can be attained via small metal particles. The metal particles create an EM field (plasmon) proximal to the analyte, enhancing its Raman signal.
- Chemical: Electronic coupling with the metal surface, creating a higher Raman scattering cross-section via a variety of pathways (charge-transfer intermediates, interactions with free electrons, etc.
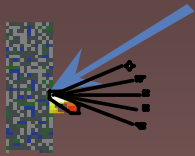
Raman of biocements

- SERS can also help with trace analysis. At right is an example of *picomole* quantities of proteins from a biocement (made by a seaworm) that are readily identifiable with SERS.

Pectinaria gouldii
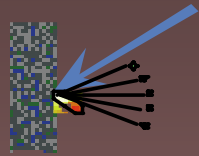
2005 Image courtesy of Prof. Maria Dean, Chemistry Dept., Coe Colle
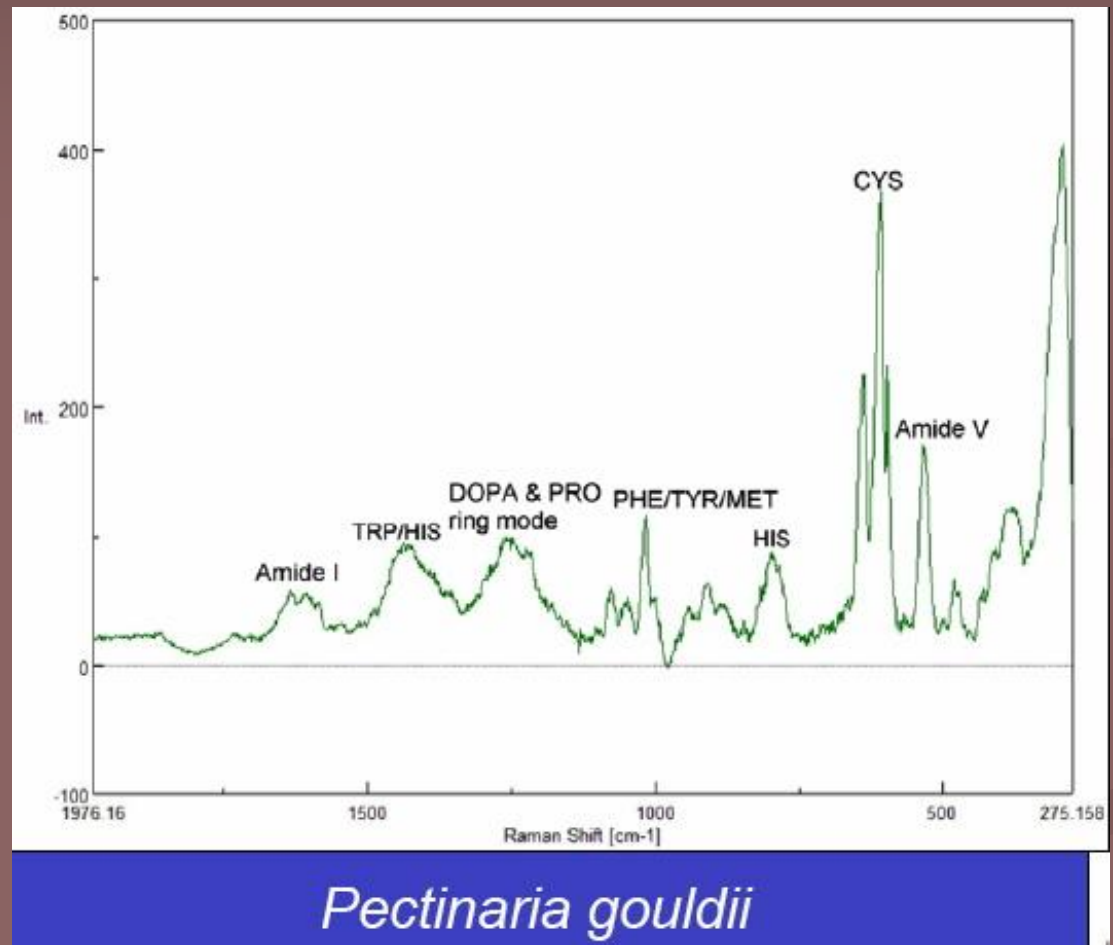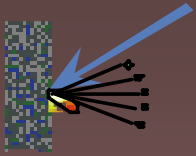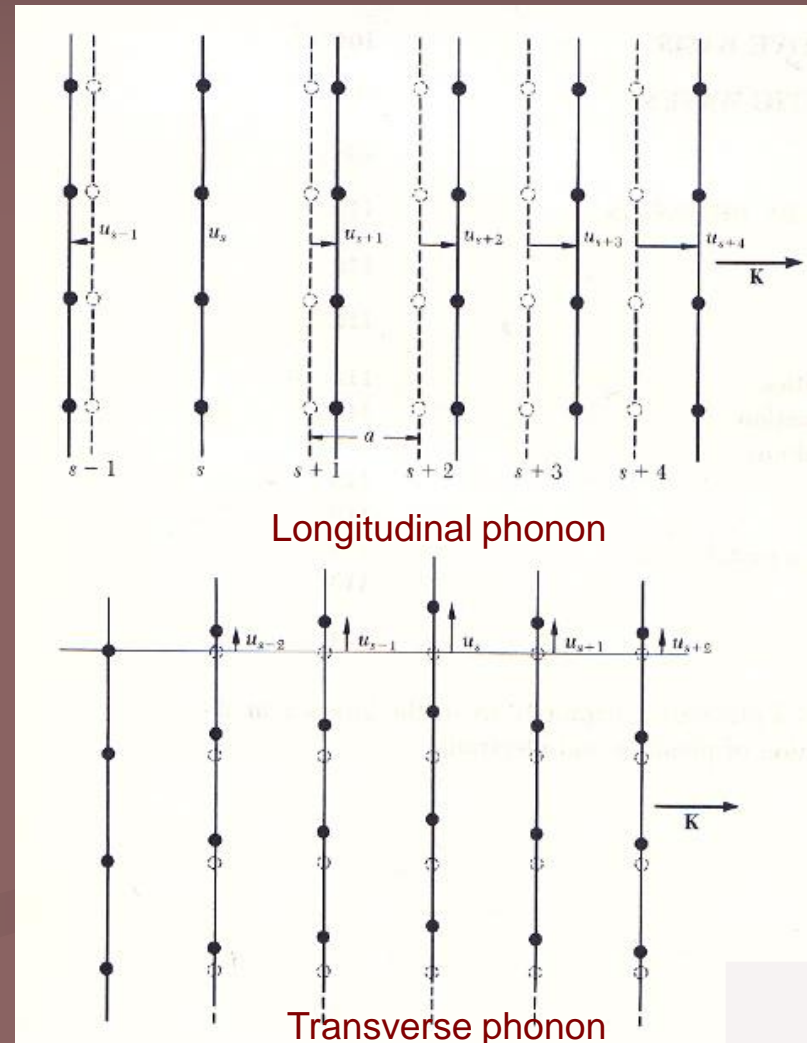
5. Identifying peaks
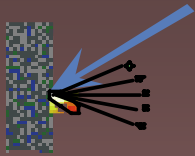
Crystals and phonons

To start with, we make the assumptions:

■ Bonds behave like springs and obey a linear response

■ Only the nearest neighbors matter

■ Then we get a force in the form of a "Hooke's law" for each atom in the basis

$$F_s = C\left(u_{s+1} - u_s\right) + C\left(u_{s-1} - u_s\right)$$

And so...

Longitudinal phonon

Transverse phonon

Crystals and phonons

$$M\ddot{u}_{2n} = f\left(u_{2n+1} + u_{2n-1} - 2u_{2n}\right)$$

$$m\ddot{u}_{2n+1} = f\left(u_{2n+2} + u_{2n} - 2u_{2n+1}\right)$$

Assuming the following solutions,

$$u_{2n} = y_1 Exp\left[i(2\pi\nu t + 2nka)\right]$$
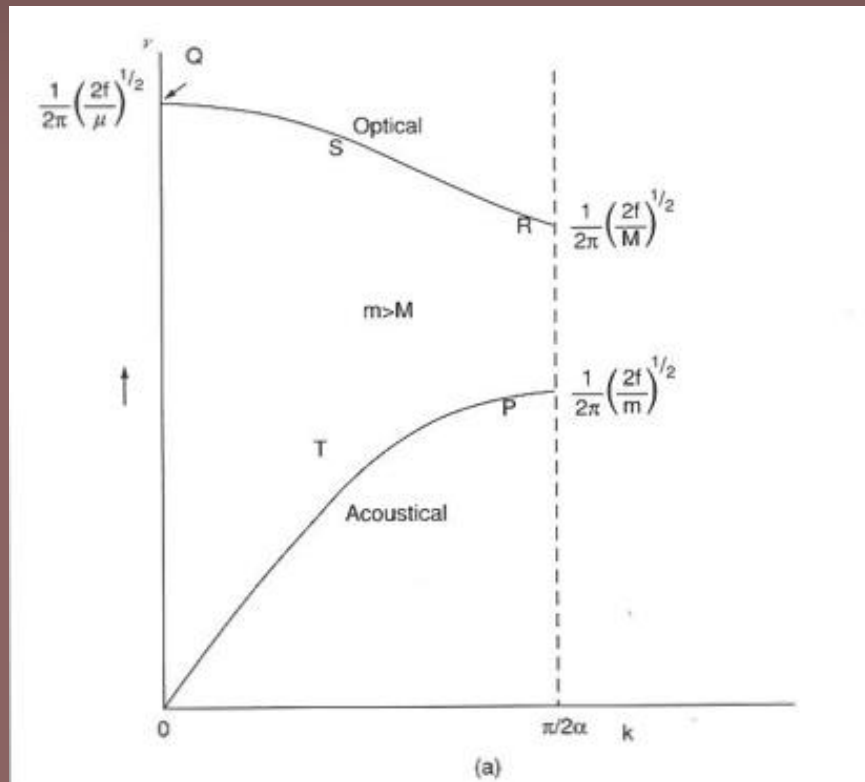
$$u_{2n+1} = y_2 Exp\left[i(2\pi\nu t + (2n+1)ka)\right]$$

we can get a dispersion relationship,

$$\nu^2 = \frac{1}{4\pi^2}\left|\frac{f}{\mu} \pm \left(\frac{f^2}{\mu^2} - \frac{4f^2 Sin^2 ka}{Mm}\right)^{1/2}\right|,$$

where μ is the reduced mass, and the two solutions (roots) for the frequency ν, given by

$$\nu_{op} = \frac{1}{2\pi}\left(\frac{2f}{\mu}\right)^{1/2}$$ Optical phonon

$$\nu_{ac} = \frac{1}{2\pi}\left(2f(M+m)\right)^{1/2} ka$$ Acoustic phonon

Raman phonons belong to the optical branch, and are more strongly associated with internal vibrations (as opposed to lattice modes)

Glasses and (sort of) phonons

- Something like the phonon dispersion relation can be obtained via Brillouin Neutron Scattering (inelastic scattering).

- But in reality the polarized character of the vibrations play a big role in creating the two phonon-like branches.
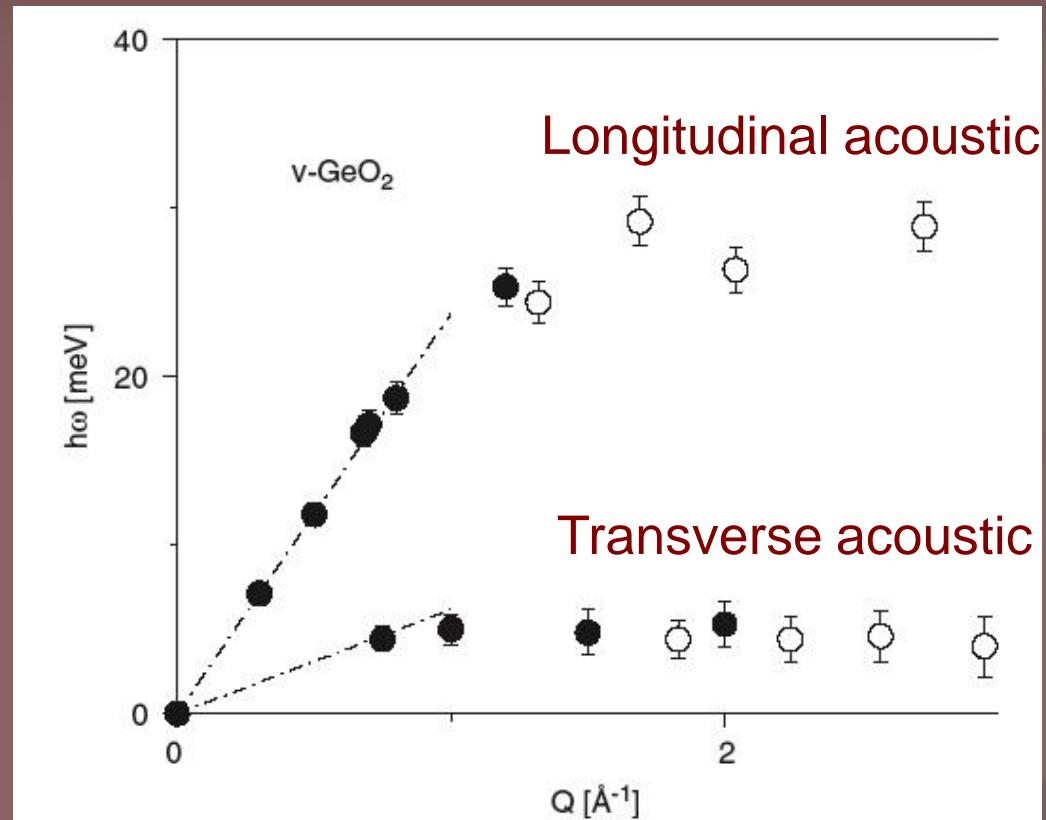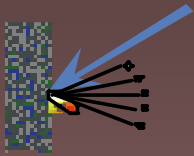

Longitudinal acoustic

Transverse acoustic

Fig. 8. Dispersion relations of v-GeO_2 as resulted from the fitting of the overall set of TAS data (full dots) and TOF [11] (open dots) data. The dashed lines are the L and T sound velocity as measured by Brillouin Light Scattering.

Considerations

- In general, we can assign bands in glass spectra by considering the following:

  - *Isolated molecular groups* (I.e., SiO_4 tetrahedra, BO_3 planar trigonal units, etc.). Easy to identify modes, important in glass. Computers can help.

  - *Coupled molecular groups* This can relax selection rules. Computers can help.

  - *Limited lattice models*. These are larger structures, such as longer chains or rings.

  - *Empirical assignment*. Comparison of glassy spectra and crystalline analogs; use of x-ray, EXAFS, or other information to make assignments. Use of isotopes can also help elucidate assignments.

Raman and FTIR bands

Functional Group/ Vibration	Region	Raman	InfraRed
Lattice vibrations in crystals, LA modes	10 - 200 cm-1	strong	strong
δ(CC) aliphatic chains	250 - 400 cm-1	strong	weak
υ(Se-Se)	290 -330 cm-1	strong	weak
υ(S-S)	430 -550 cm-1	strong	weak
υ(Si-O-Si)	450 -550 cm-1	strong	weak
υ(Xmetal-O)	150-450 cm-1	strong	med-weak
υ(C-I)	480 - 660 cm-1	strong	strong
υ(C-Br)	500 - 700 cm-1	strong	strong
υ(C-Cl)	550 - 800 cm-1	strong	strong
υ(C-S) aliphatic	630 - 790 cm-1	strong	medium
υ(C-S) aromatic	1080 - 1100 cm-1	strong	medium
υ(O-O)	845 -900 cm-1	strong	weak
υ(C-O-C)	800 -970 cm-1	medium	weak

| Functional Group/ Vibration	Region	Raman	InfraRed
δ(CH2) δ(CH3) asym	1400 - 1470 cm-1	medium	medium
υ(C-(NO2))	1340 - 1380 cm-1	strong	medium
υ(C-(NO2)) asym	1530 - 1590 cm-1	medium	strong
υ(N=N) aromatic	1410 - 1440 cm-1	medium	-
υ(N=N) aliphatic	1550 - 1580 cm-1	medium	-
δ(H2O)	~1640 cm-1	weak broad	strong
υ(C=N)	1610 - 1680 cm-1	strong	medium
υ(C=C)	1500 - 1900 cm-1	strong	weak
υ(C=O)	1680 - 1820 cm-1	medium	strong
υ(C≡C)	2100 - 2250 cm-1	strong	weak
υ(C≡N)	2220 - 2255 cm-1	medium	strong
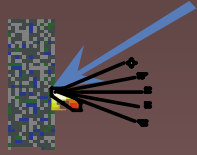
But must be careful…

■ Though the normal modes appear to match the spectrum, the ν_4 mode is not symmetric, yet the polarization measurements points to a totally-symmetric mode ($\rho<<0.75$). ν_1 is symmetric, but does not appear very polarized in the spectrum of v-SiO_2. Hence, looking at isolated molecular groups must be done carefully.
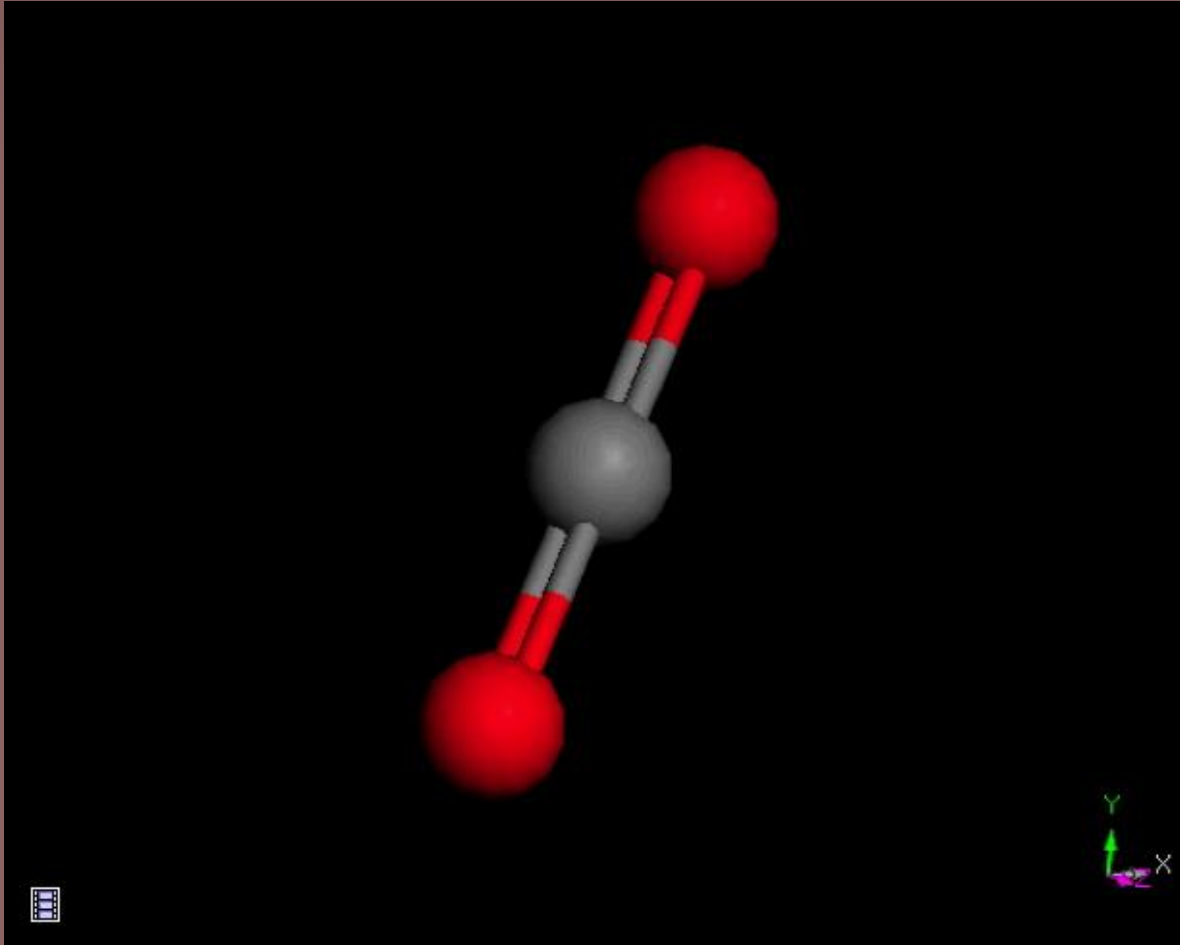
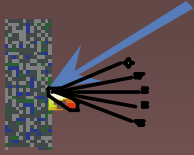Normal modes of isolated SiO_2 tetrahedron
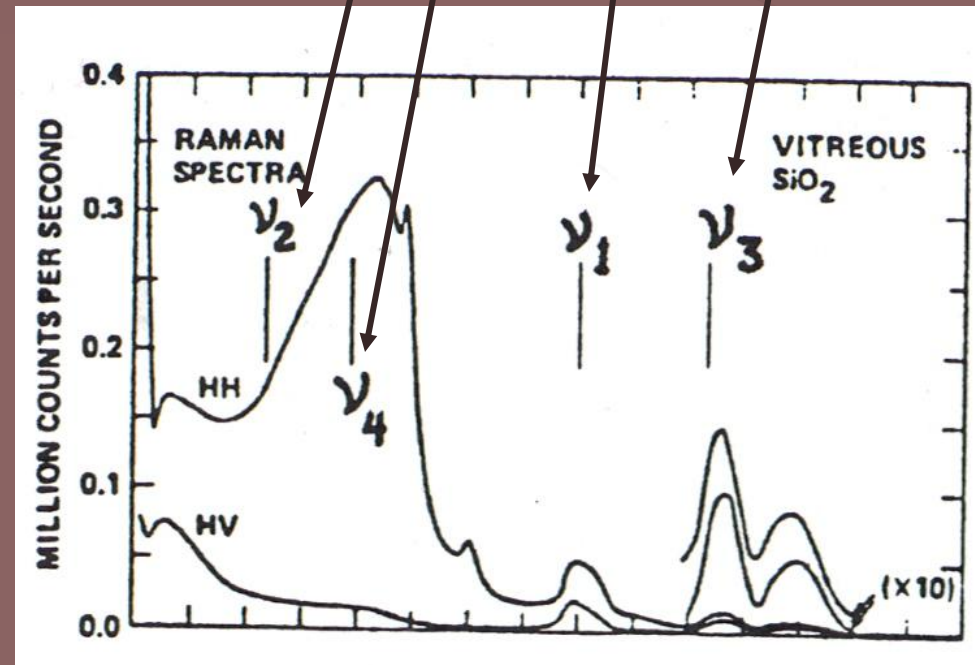
From B. Bendow, Infrared and Raman Analysis of Glasses, Ch. 2 in Experimental Techniques of Glass Science, see References.
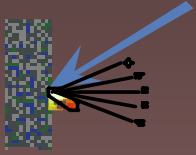
Computer modeling

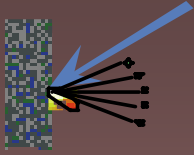Symmetric stretching mode. Calculated at 1486 cm^{-1}, really at 1340 cm^{-1} .
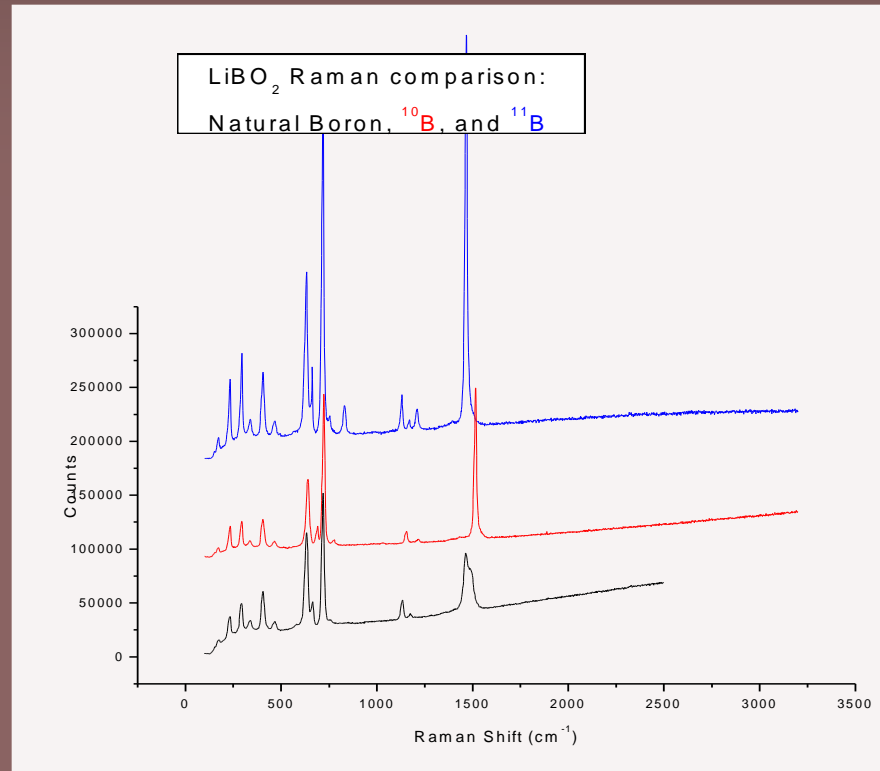
Still, we learn…

- …that a simple "molecule" model in which we treat the bond as a spring of constant *k* attached to atoms with a reduced mass *μ* gives us a natural frequency

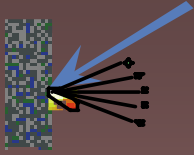$$f_{res} = \frac{1}{2\pi}\sqrt{\frac{k}{\mu}}, \; where \; \mu = \frac{m_1 m_2}{m_1 + m_2}$$

- Then bonds of higher masses and similar *k* values give lower resonant Raman frequencies.
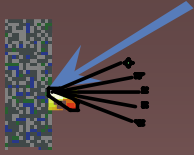
Isotopic substitution

LiBO$_2$ crystals with isotopic substitution. Data taken Spring 2006.

EXERCISE

- Given that one of the peaks of the ^{10}B-enriched spectrum (of crystalline $LiBO_2$) is centered at 1515 cm^{-1}, where would you estimate this same peak (same mode) will appear in the ^{11}B-enriched one? You may assume it arises from a B-O vibration.
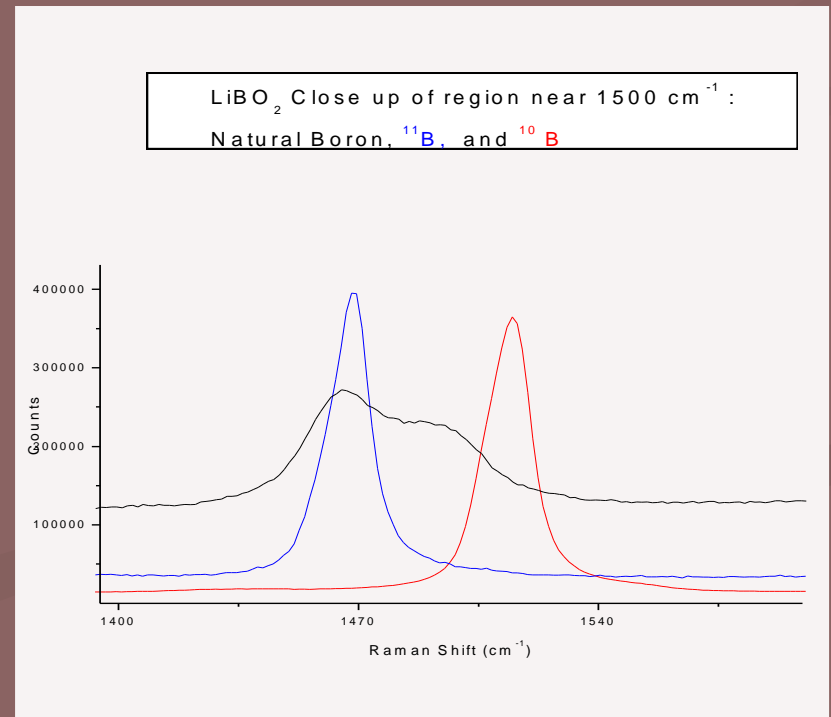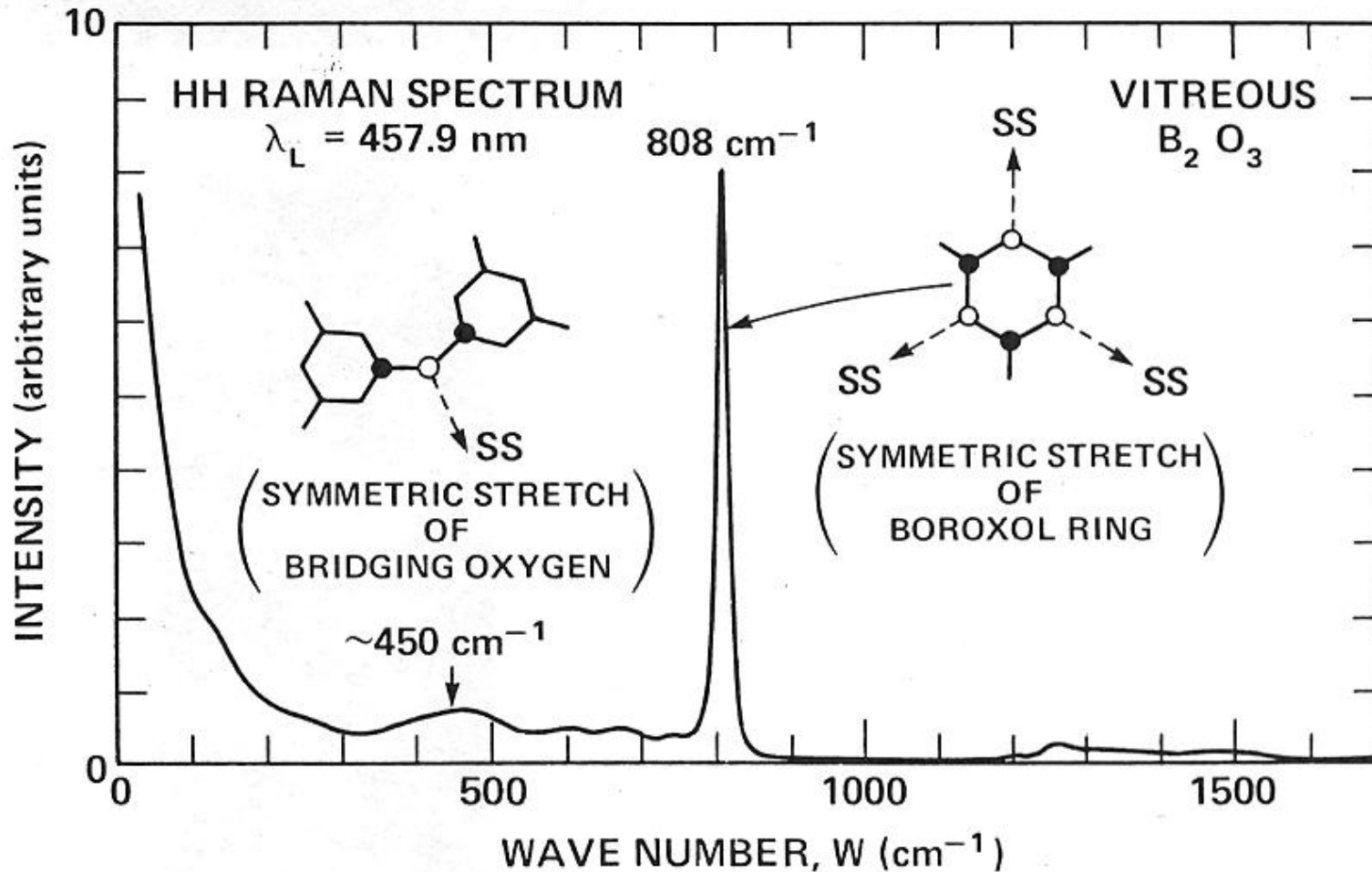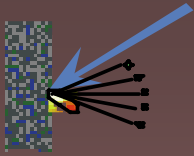
EXERCISE

- Given that one of the peaks of the ^{10}B-enriched spectrum (of crystalline $LiBO_2$) is centered at 1515 cm^{-1}, where would you estimate this same peak (same mode) will appear in the ^{11}B-enriched one? You may assume it arises from a B-O vibration.

The peak at 1515 cm^{-1} should shift to f_2 = f_1 * Sqrt(6.15/6.52), or
f_2=1515*0.971 ~ 1471 cm^{-1}. As you can see at the right, the ^{11}B peak does appear at a lower frequency, but also shows up at 1463 cm^{-1}

$$\frac{f_{res}^{(1)}}{f_{res}^{(2)}} = \frac{\sqrt{\frac{k}{\mu_1}}}{\sqrt{\frac{k}{\mu_2}}} = \sqrt{\frac{\mu_2}{\mu_1}}$$
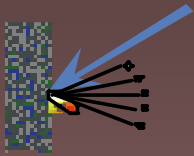
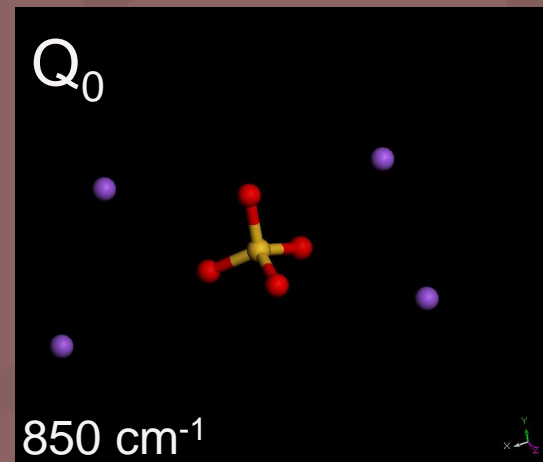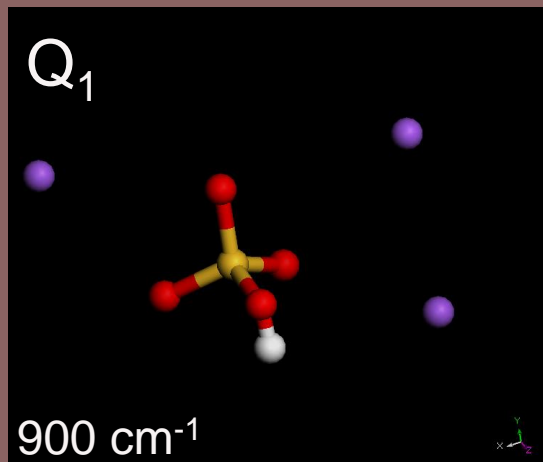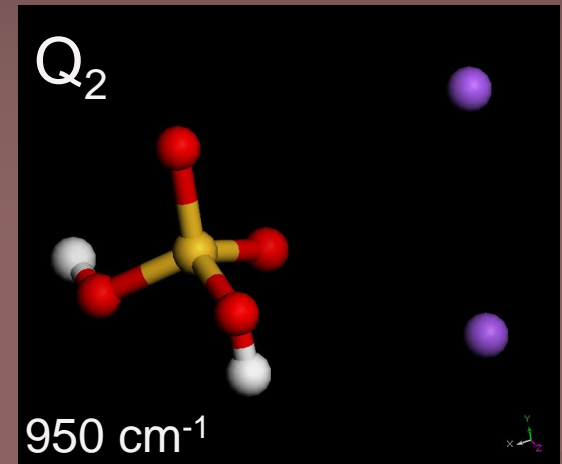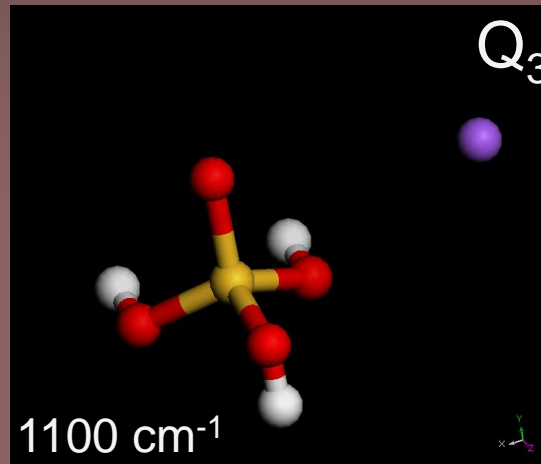LiBO$_2$ Close up of region near 1500 cm^{-1}: Natural Boron, ^{11}B, and ^{10}B

Classic example…

6. Case studies

Silicate units

Q_4

1060, 1200 cm^{-1}

Q_3

1100 cm^{-1}

Q_2

950 cm^{-1}

Q_1

900 cm^{-1}

Q_0
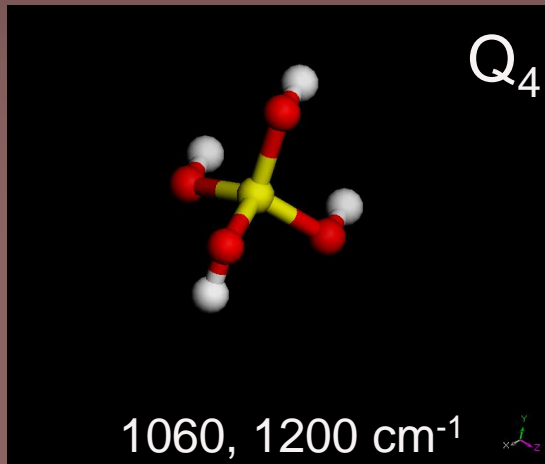
850 cm^{-1}

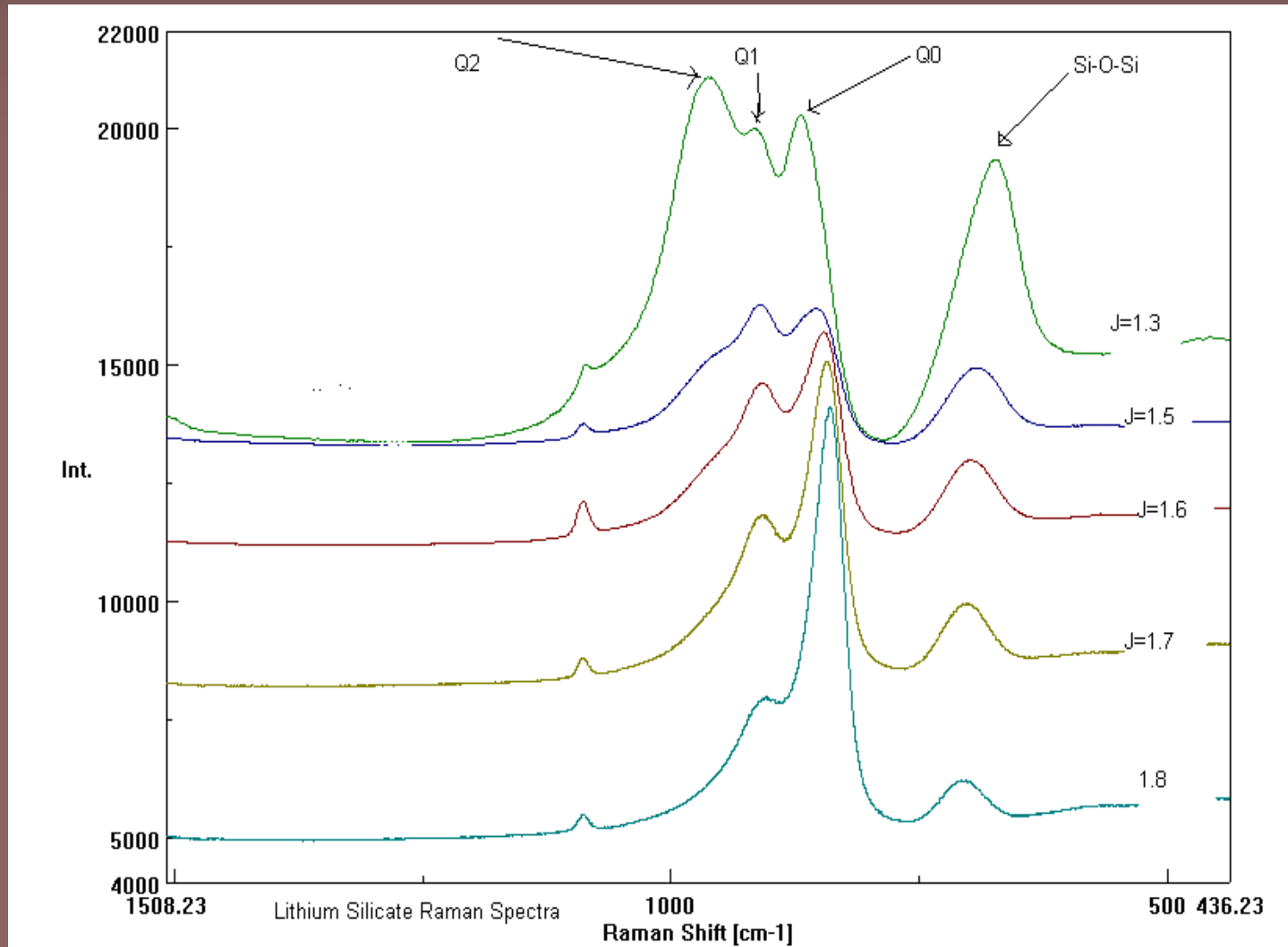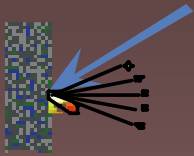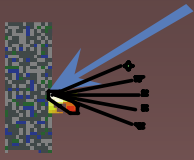*From Furukawa and White (1980) and Kamitsos et al. (1994)*

Alkali Silicates

EXERCISE

Based on the fractions on the right, sketch on the board a predicted Raman spectrum for the glass

$50Li_2O \bullet 50SiO_2$

Also recall that

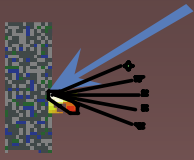--Q_4 at 1060, 1200 cm^{-1}

--Q_3 at 1100 cm^{-1}

--Q_2 at 950 cm^{-1}
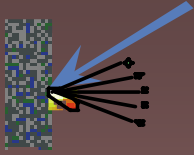
--Q_1 at 900 cm^{-1}

--Q_0 at 850 cm^{-1}

SYSTEM	COMPOSITION REGION (mol% R_2O)	EQUATIONS	FRACTIONAL EQUATIONS
Alkali Silicate	0–33.3	$Q_4 = 100-3x$	$f_3 = \dfrac{2x}{100-x}$
		$Q_3 = 2x$	
	33.3–50.0	$Q_3 = 200-4x$	$f_2 = \dfrac{3x-100}{100-x}$
		$Q_2 = 3x-100$	
	50.0–60.0	$Q_2 = 300-5x$	$f_1 = \dfrac{4x-200}{100-x}$
		$Q_1 = 4x-200$	
	60.0–66.7	$Q_1 = 400-6x$	$f_0 = \dfrac{5x-300}{100-x}$
		$Q_0 = 5x-300$	
Alkali Borate	0–30.0	$N_3 = 200-4x$	$N_4 = \dfrac{x}{100-x}$
		$N_4 = 2x$	
Alkali Germanate	0–?	$N_4 = 100-2x$	$N_6 = \dfrac{x}{100-x}$
		$N_6 = x$	

Shelby, J. Introduction to Glass Science and Technology, 2d ed.

EXERCISE
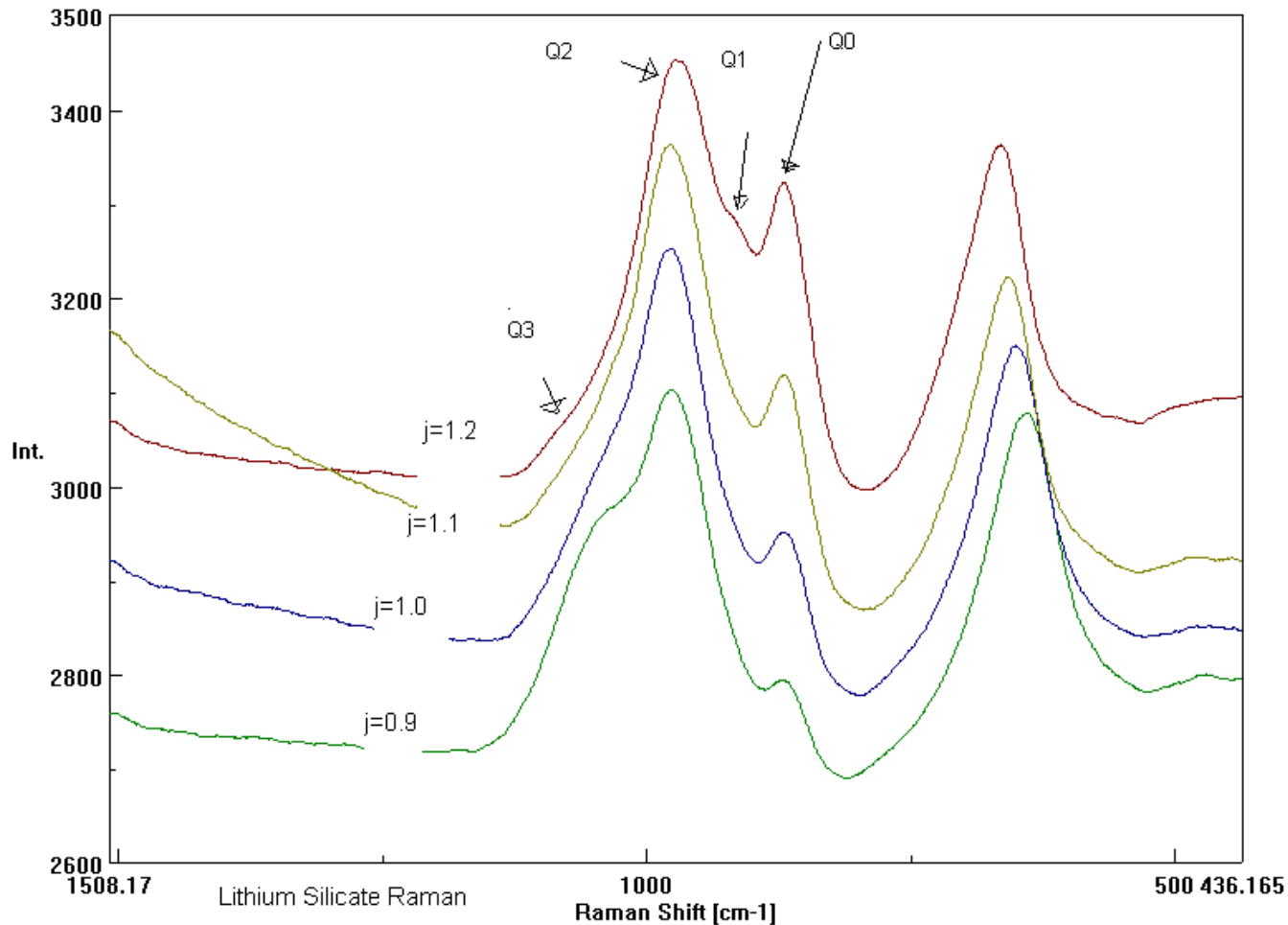
- **Answer is in the blue!**

NMR and Raman: Silicates

■ The fractions previously given were simplified. On the right is a graph of how they really look from NMR, along with results obtained from integrating Raman areas.
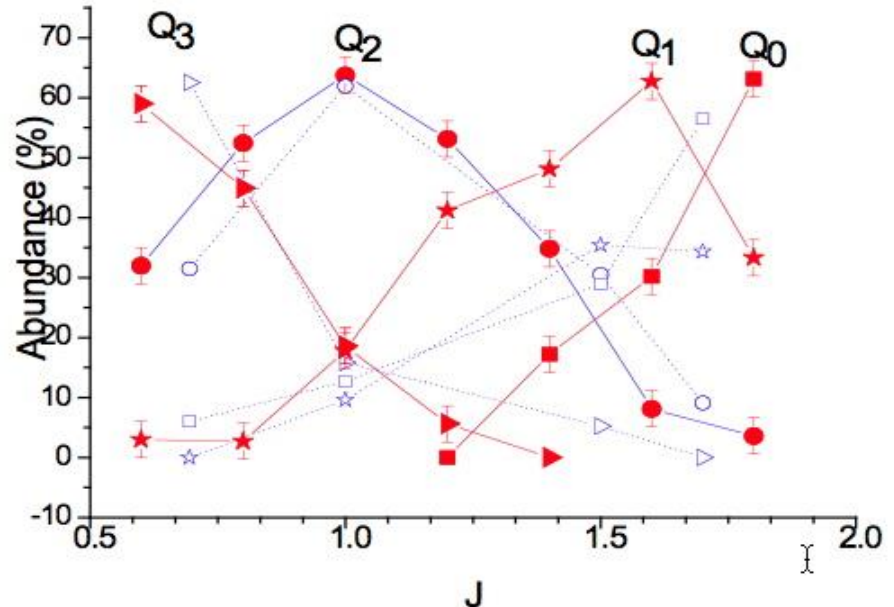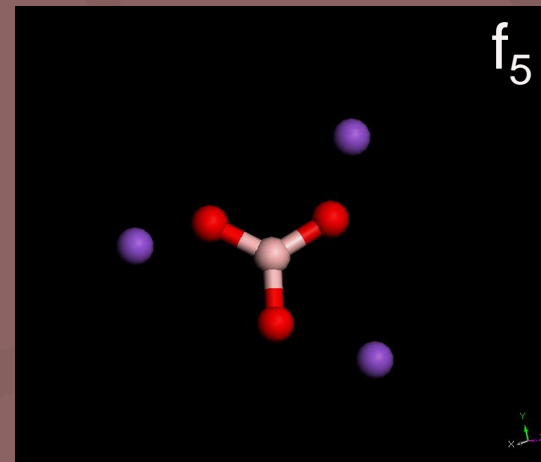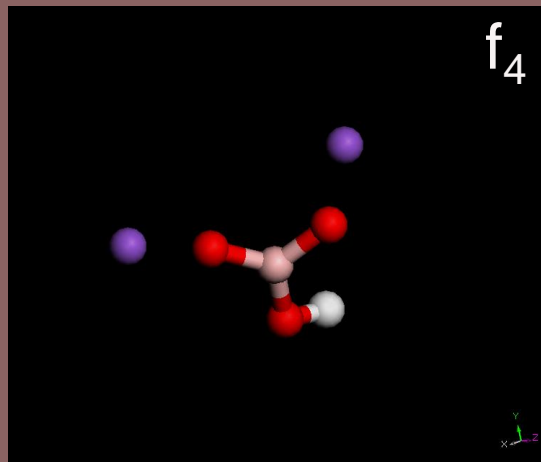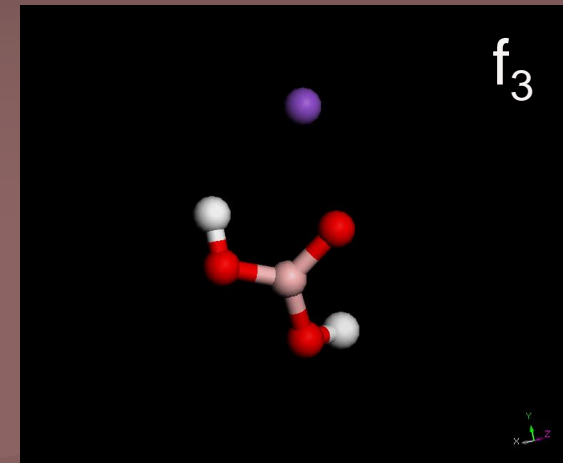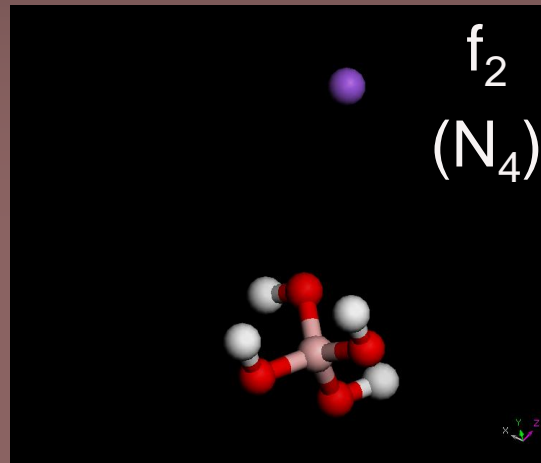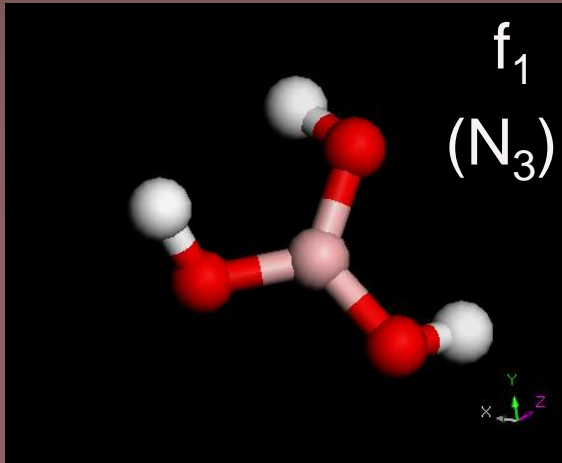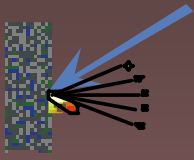

Figure 5: Comparison of the Q^n unit abundances from the present ^{29}Si MAS NMR data (solid symbols) and the Raman results (open symbols) from Umesaki et al.[9] The data are plotted as a function of J, the molar ratio of lithium oxide to silicon dioxide.

From C. Larson, J. Doerr, M. Affatigato, S. Feller, D. Holland, M.E. Smith, "A ^{29}Si MAS NMR Study of High Lithium-Content Silicate Glasses," J. Phys.: Condens. Matter 18 11323-11331 (2006).
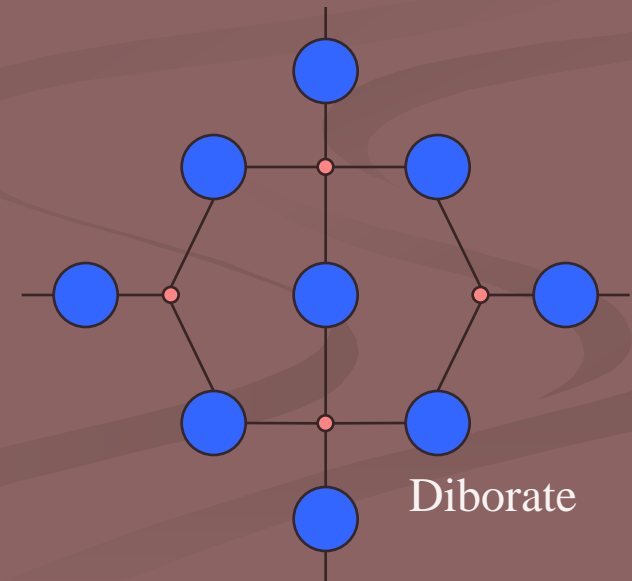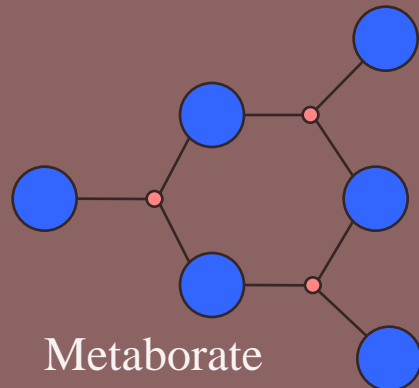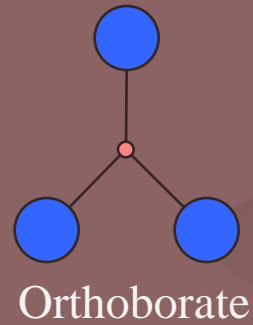
.
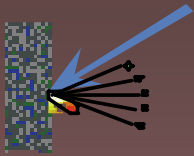
Borate (nano)units

Some borate mesounits

Di-pentaborate

Pyroborate

Orthoborate

Metaborate

Diborate

Boron
Oxygen
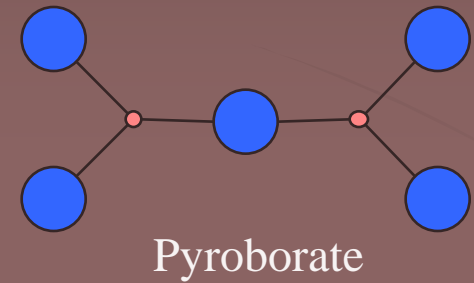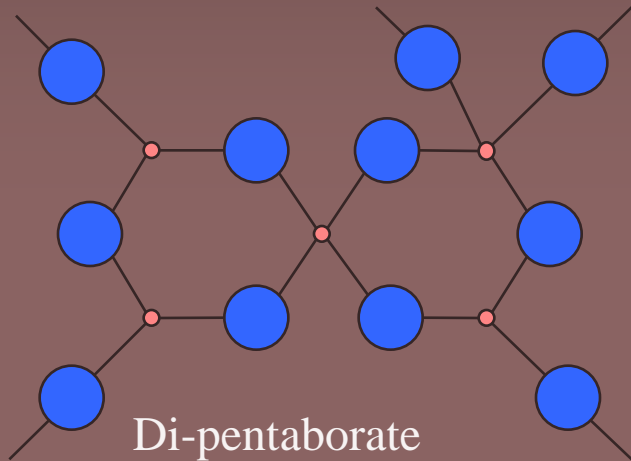
Data from alkali- and alkaline earth-borate crystals
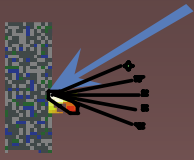
Lithium Borates

- **So how do we analyze the glass?**

- Look at systematic changes in the structure. Look at the literature. And look at isocompositional crystals of known structure. The $2Li_2O.B_2O_3$ (bottom) crystal is made up of pyroborate ($B_2O_5^{4-}$) units. Note how this peak grows in as the lithium content increases. The breadth of the band around 950 cm^{-1}, as well as the use of only two crystals, makes other assignments harder.
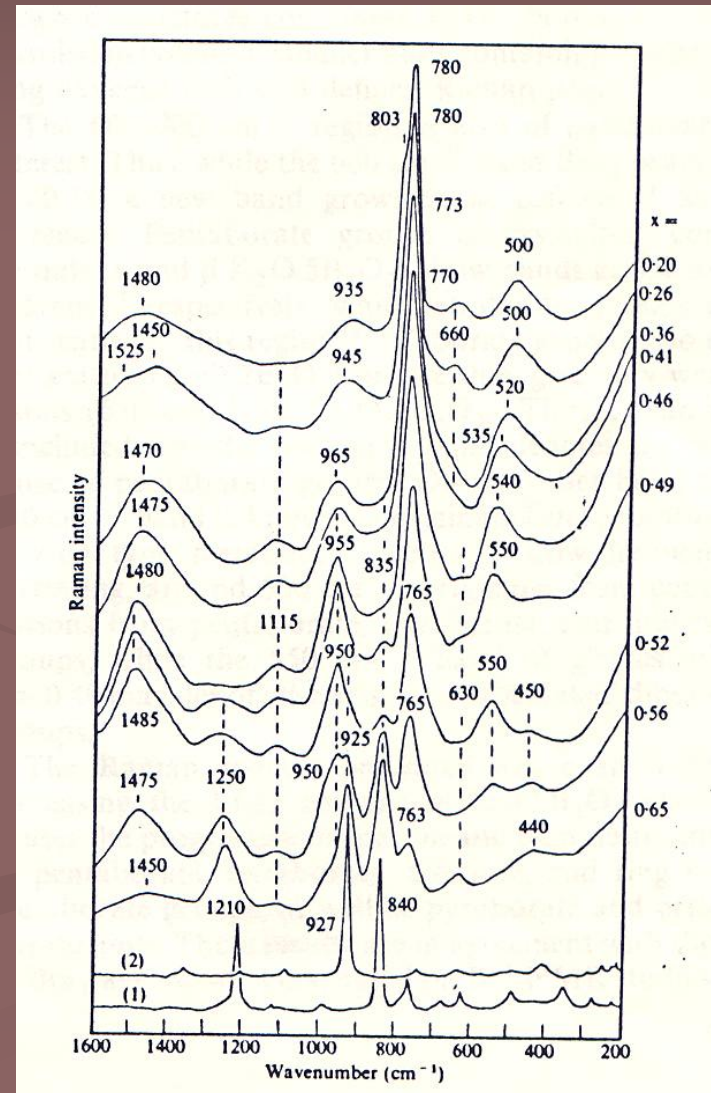
Quantification: Borates

- The graph on the right shows (deconvolved) polarized and depolarized bands for a series of Na borate glasses.
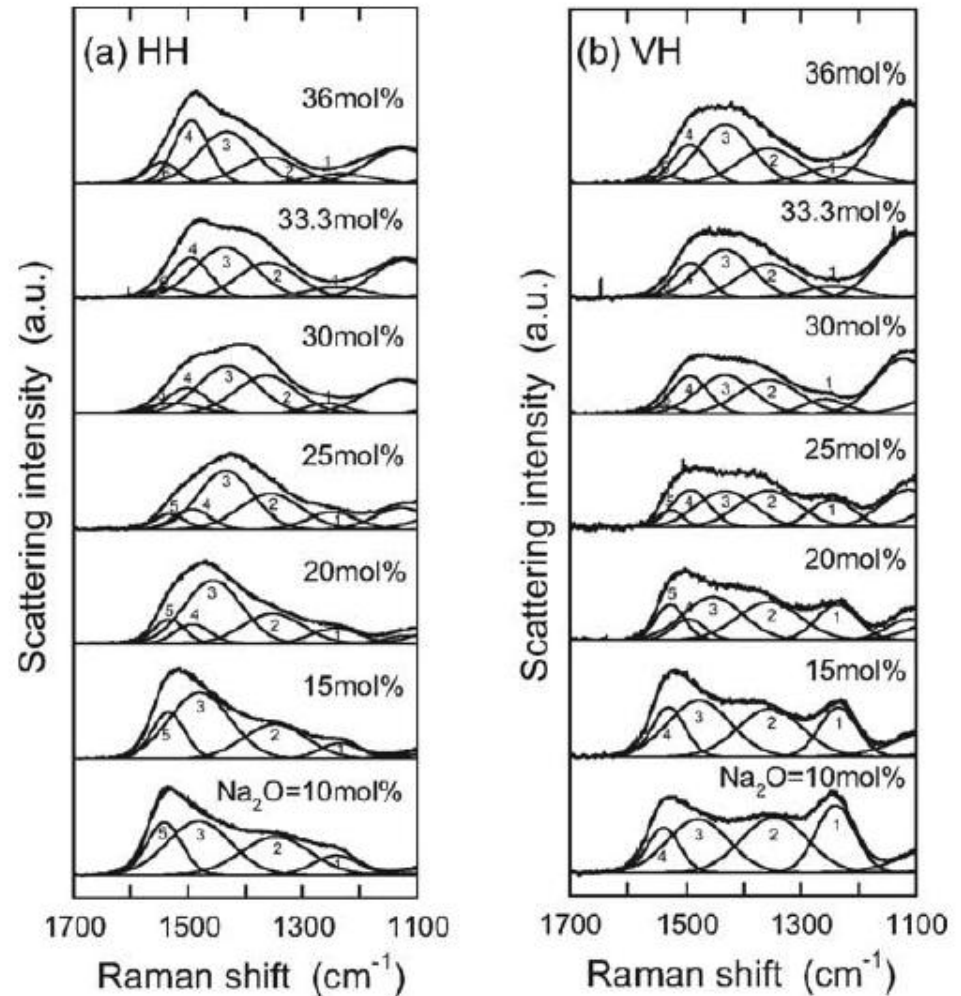
Structural investigation of sodium borate glasses and melts by Raman spectroscopy.
I. Quantitative evaluation of structural units

Tetsuji Yano *, Noboru Kunimine, Shuichi Shibata, Masayuki Yamane

Quantification: Borates

- By analyzing the intensity of the deconvoluted peaks we can obtain the ratio of the number of 3-coord. asymmetric boron units (N_{3a}) to the number of symmetric ones (N_{3s}). The results are compared to those obtained by NMR spectroscopy.

$$S = \frac{I_{SB4} + I_{SB6}}{I_{SB1} + I_{SB2} + I_{SB3} + I_{SB5}}$$

$$= \frac{(k_{SB4} + k_{SB6})N_{3a}}{(k_{SB1} + k_{SB2} + k_{SB3} + k_{SB5})N_{3s}} \propto \frac{N_{3a}}{N_{3s}},$$
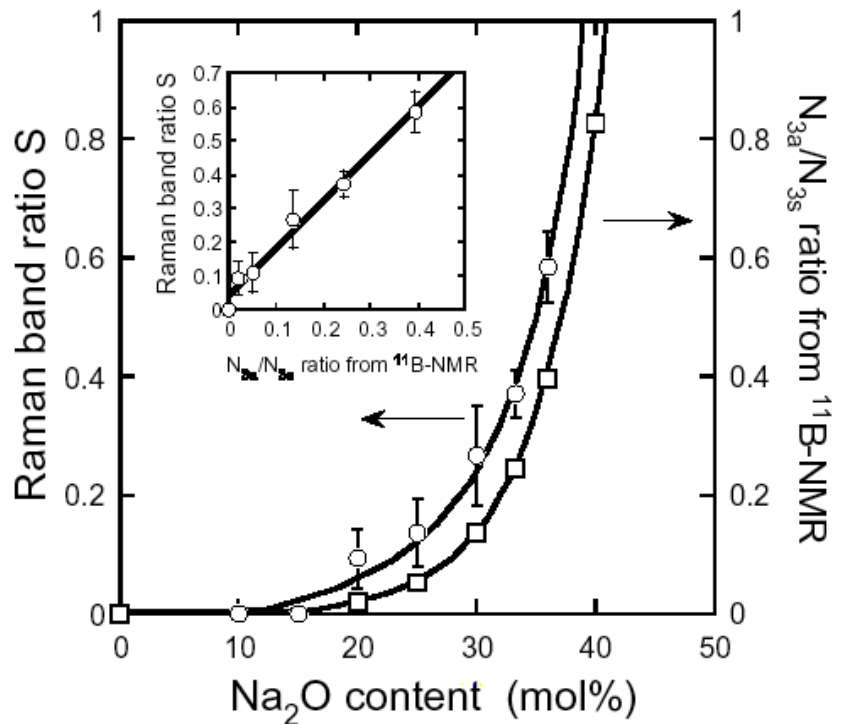
Quantification: Borates

- With more time, one can then obtain the abundance of larger species (mesounits)
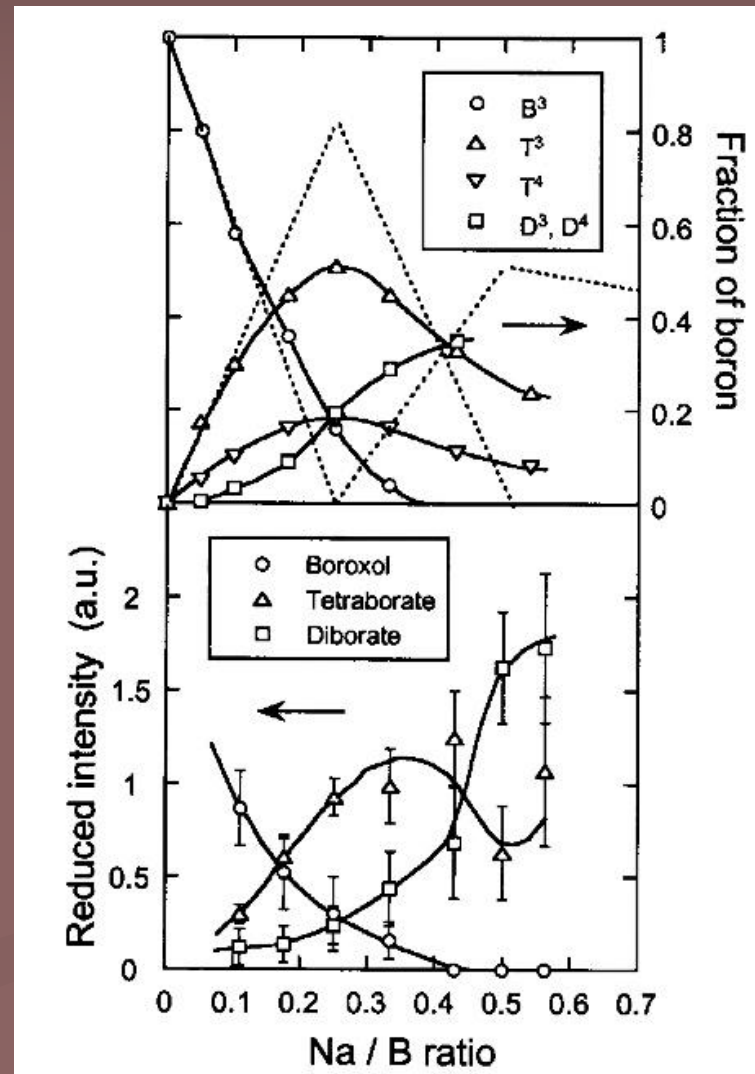
Borates and CO_2 retention

- At high alkali contents, borate glasses retain carbonate. The spectrum at right shows two glasses heated to 1000, 1150 °C.

- Most of the bands correspond to smaller borate units (e.g. pyroborates $B_2O_5^{4-}$, at 1210 cm-1; orthoborates BO_3^{3-} at 895 cm^{-1}, etc.).

- But the strongest band is at 1062 cm^{-1}, and is attributed to the vibrations of carbonate species in the glass. How do we know?
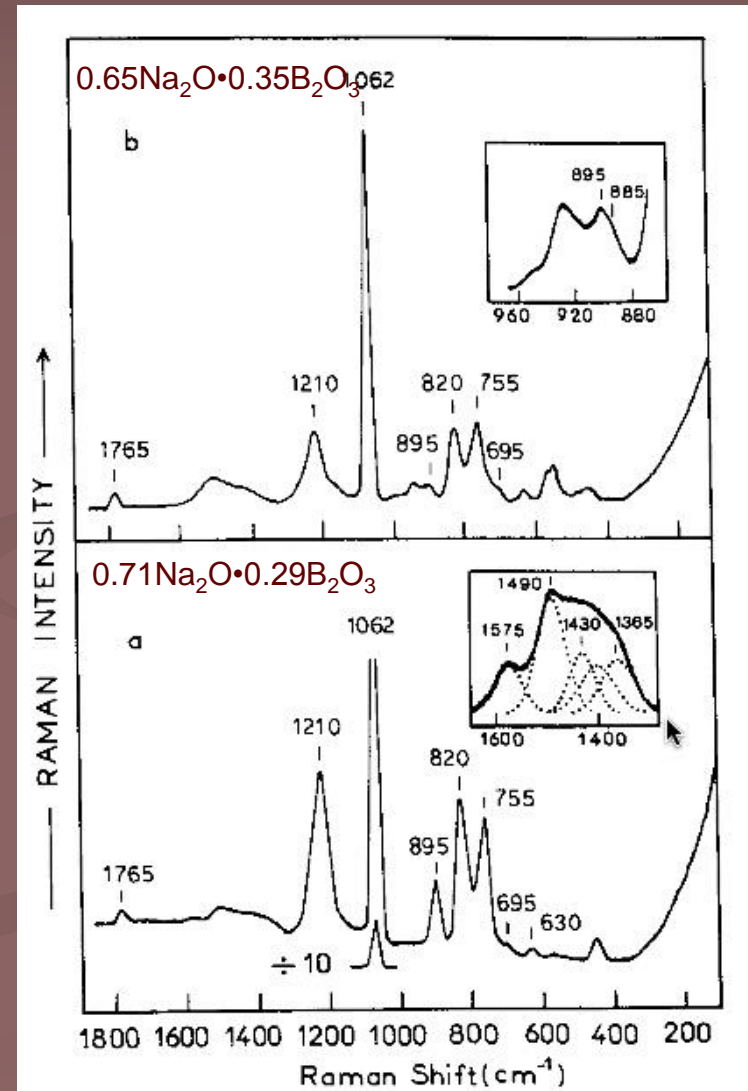
Borates and CO_2 retention

Table 2

Bands observed in the Raman and infrared spectra of Na_2CO_3 [15,16] and high sodium content borate glasses [a] (frequencies are in cm^{-1})

Assign-ment	Crystalline Na_2CO_3	Molten Na_2CO_3 [b] (750 °C)	Aqueous solution Na_2CO_3 (25 °C)	Borate glass
$\nu_1(A'_1)$	1079 s	1050 s,p	1067 s,p	1062 s
	1083 s		[1063] [c]	
$\nu_2(A''_2)$	[880] s	880 vw	[880]	885 sh [d]
	[886] s			[880]
$\nu_3(E')$	1422 m	1400 m	1380 m	1365 m
			1412 m	1430 m
	1431 m	1440 m	[1360]	[1436]
			[1405]	[1477]
$\nu_4(E')$	698 w	695 w	681 w	695 vw
	702 w			[700]
$2\nu_2$	1760 w	1758 w	NO	1765 m
	1771 w			

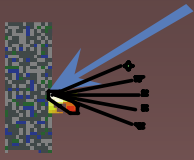[a] Results of this work. Only bands attributed to carbonates have been included.

[b] Eutectic composition: Na_2CO_3–NaCl (57 mol% NaCl, mp 640 °C).

[c] [   ] indicates an infrared value.

[d] This band was observed in the spectrum of the $x = 0.65$ Na–borate glass.

Abbreviations: s, strong; m, medium; w, weak; vw, very weak; p, polarised; sh, shoulder; NO, no band observed.

- Theory predicts four modes for the free carbonate ion (CO_3^{2-}). But changes such as coordination to metal cations, formation of cation-anion pairs, etc. destroy the symmetry.

- The behavior in the crystalline Na_2CO_3 is similar to that of the free ion (with splitting due to unit cell orientations). Thus, it is believed that the carbonate species are present as CO_3^{2-} ions dissolved in the glass matrix, with shifts due to interactions with Na cations and the borate network.

Germanate units

Q_4

$Q_{4'}$
(N_6)

Q_3

Q_2

Q_1

Q_0
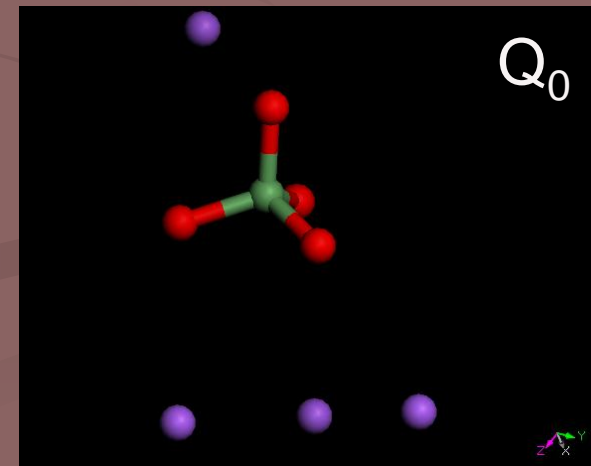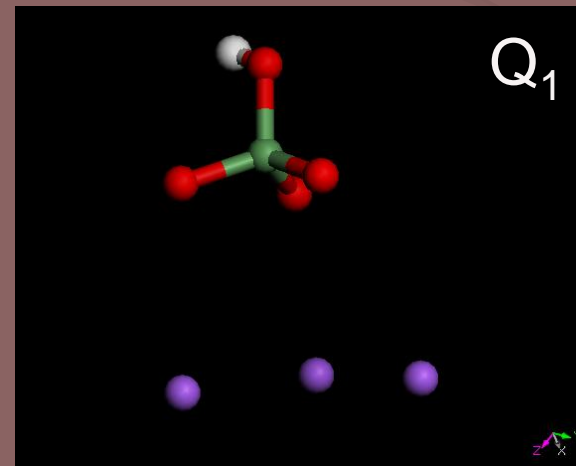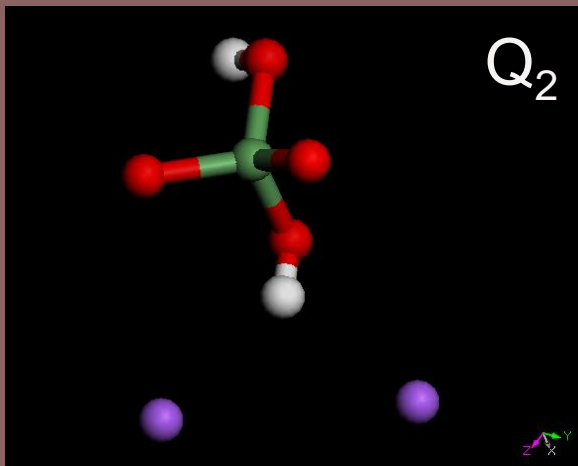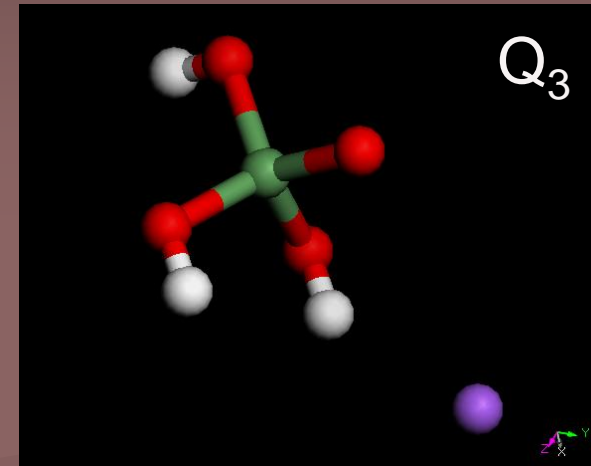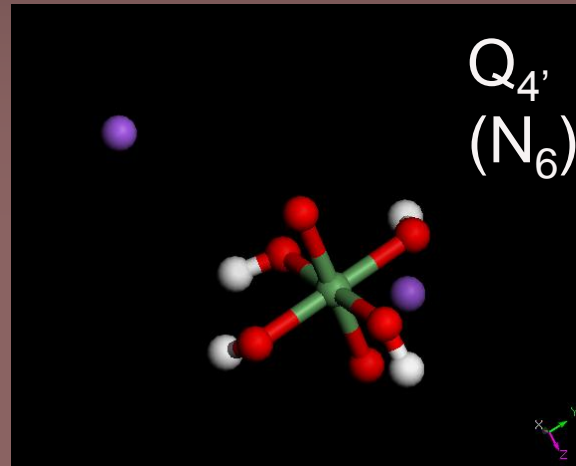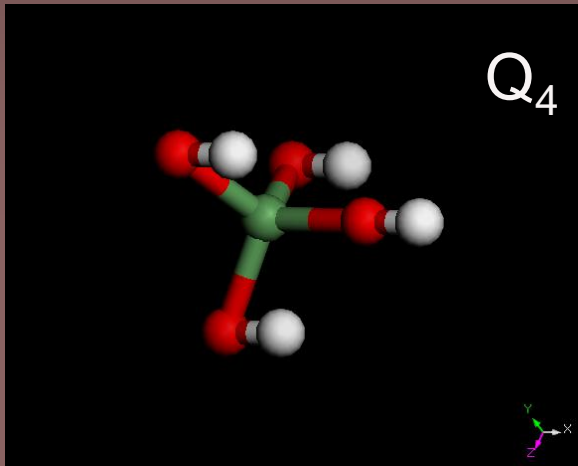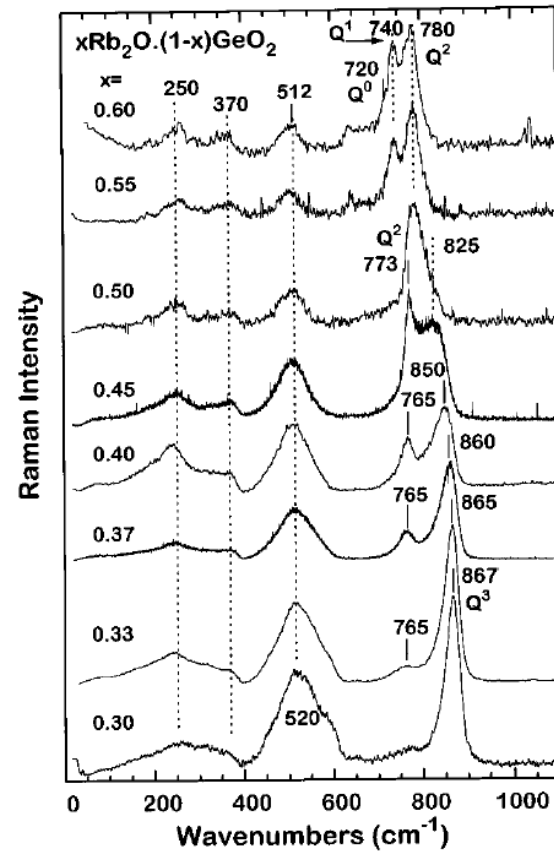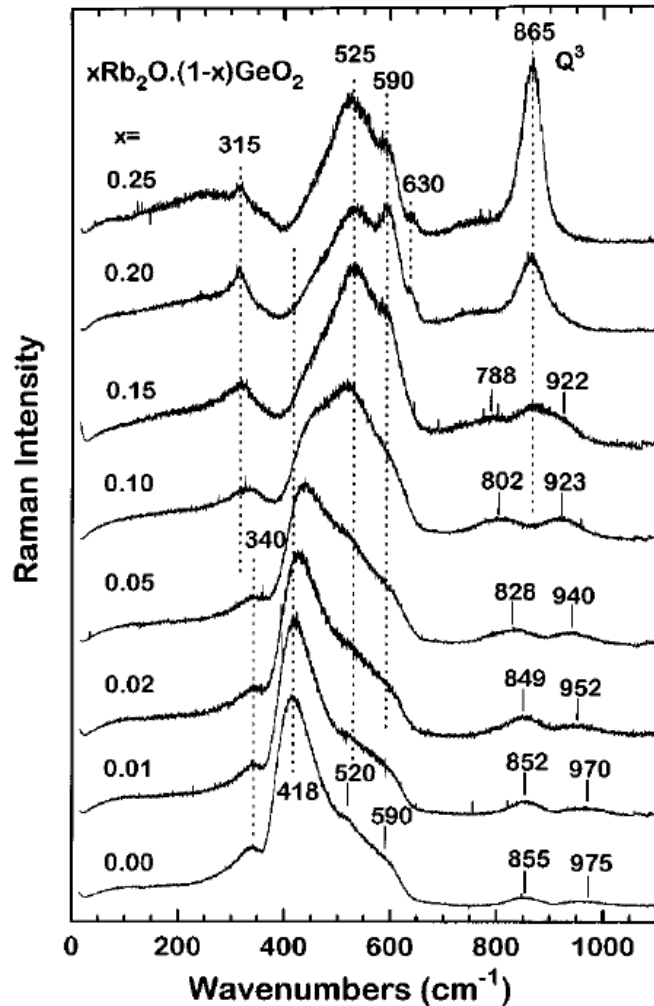
Germanates

11755

Raman and Infrared Structural Investigation of $xRb_2O\cdot(1 - x)GeO_2$ Glasses

E. I. Kamitsos,*,† Y. D. Yiannopoulos,† M. A. Karakassides,‡ G. D. Chryssikos,† and H. Jain§
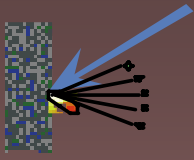
Germanates
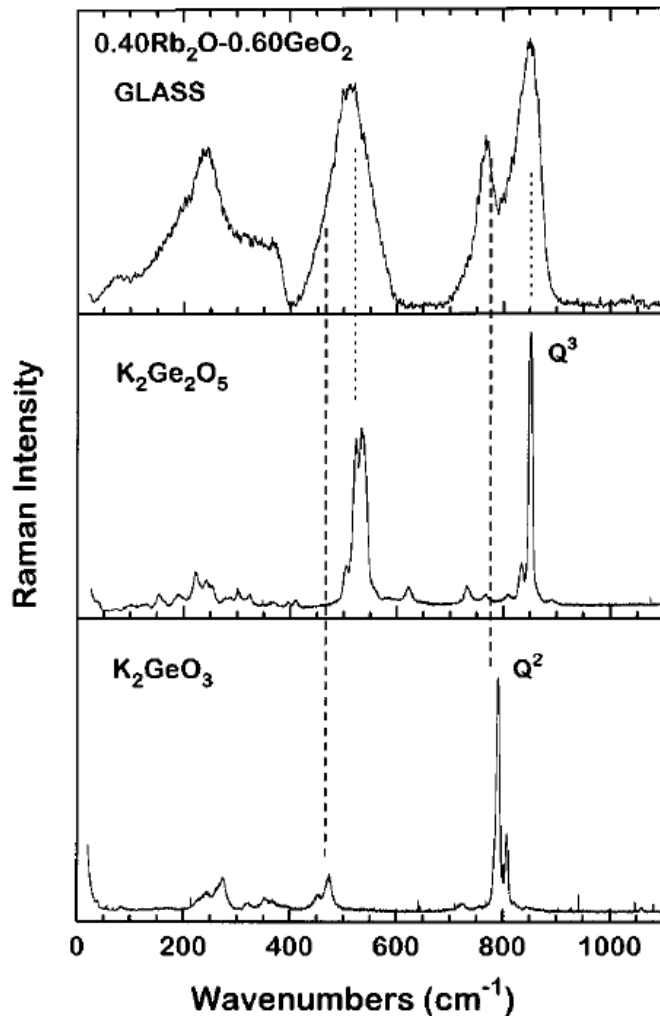
- The **Rb** glass spectrum above 400 cm^{-1} can be reproduced by the convolution of the two **K** crystalline ones, $K_2Ge_2O_5$ and K_2GeO_3. As the structure of these crystals is made up of Q_3 and Q_2 units, as well as $\nu_s(Ge(4)\text{-}O\text{-}Ge(4))$ bridges (515 cm^{-1}), we infer the glass structure to have the same building blocks.
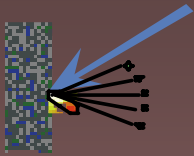
Sulfides

- The "attack" on the Raman of these glasses can be done by analogy. The lower frequency peak at 340 cm^{-1} is attributed to ν_s(Ge-S-Ge), while the three other main bands are associated with the equivalent Q_3, Q_2, Q_1 germanate units.
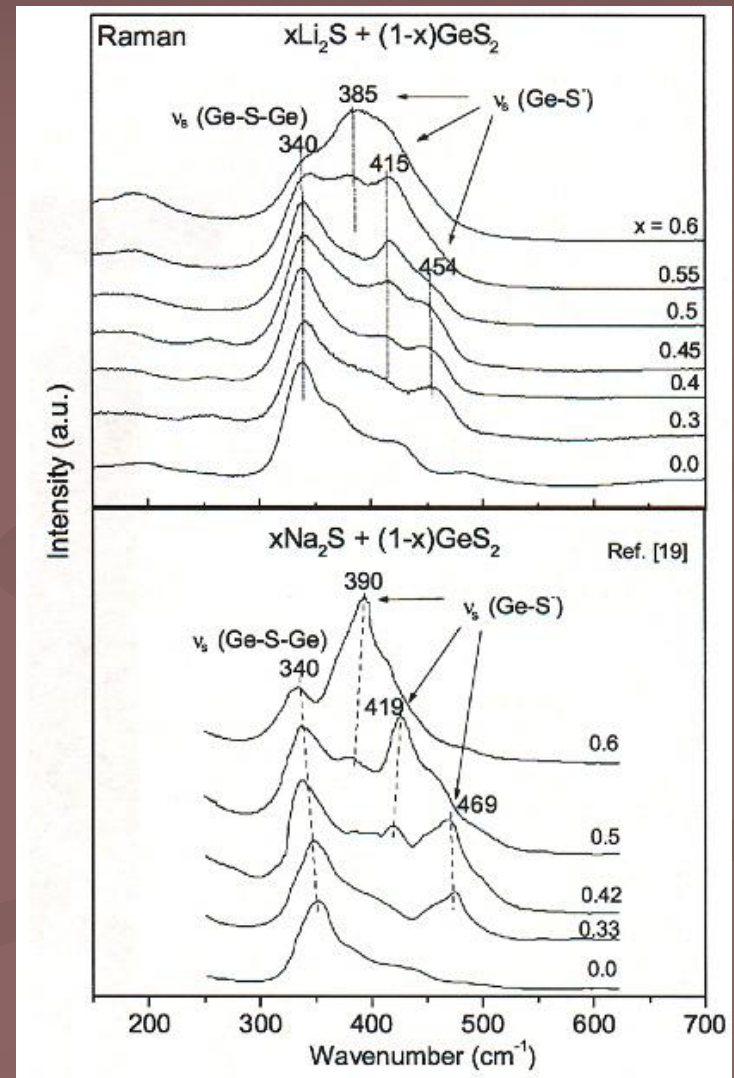
Warning (?): Lead vanadates

Before irradiation

After irradiation
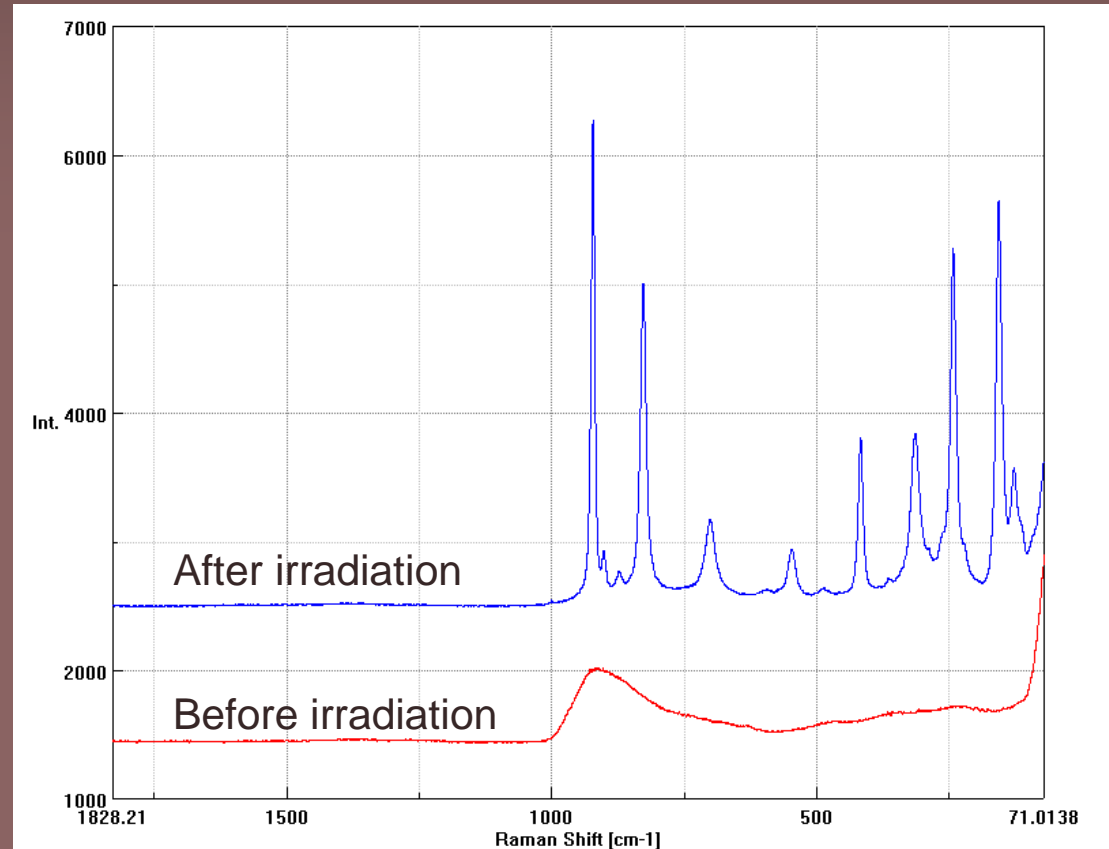
On the left, optical micrographs of a lead vanadate glass of composition $50PbO.50V_2O_5$, before and after irradiation at ~100 mW, 785 nm. Above, Raman spectra of the two locations, taken at very low powers.

(From Laser Induced Modification of Vanadate Glasses, B. Franta, T. Williams, C. Faris, S. Feller, M. Affatigato, submitted to Phys. Chem. Glasses.
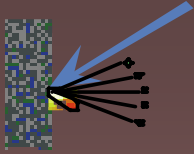
Miscellaneous
(if there is time. If not, Thank you!)
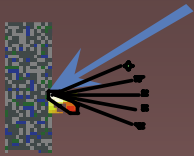
Raman in art

Figure 1 (a) Raman spectrum of a sample from a twelfth-century manuscript (Guineau, 1986). (b) Reference spectrum of ultramarine blue from lapis lazuli.

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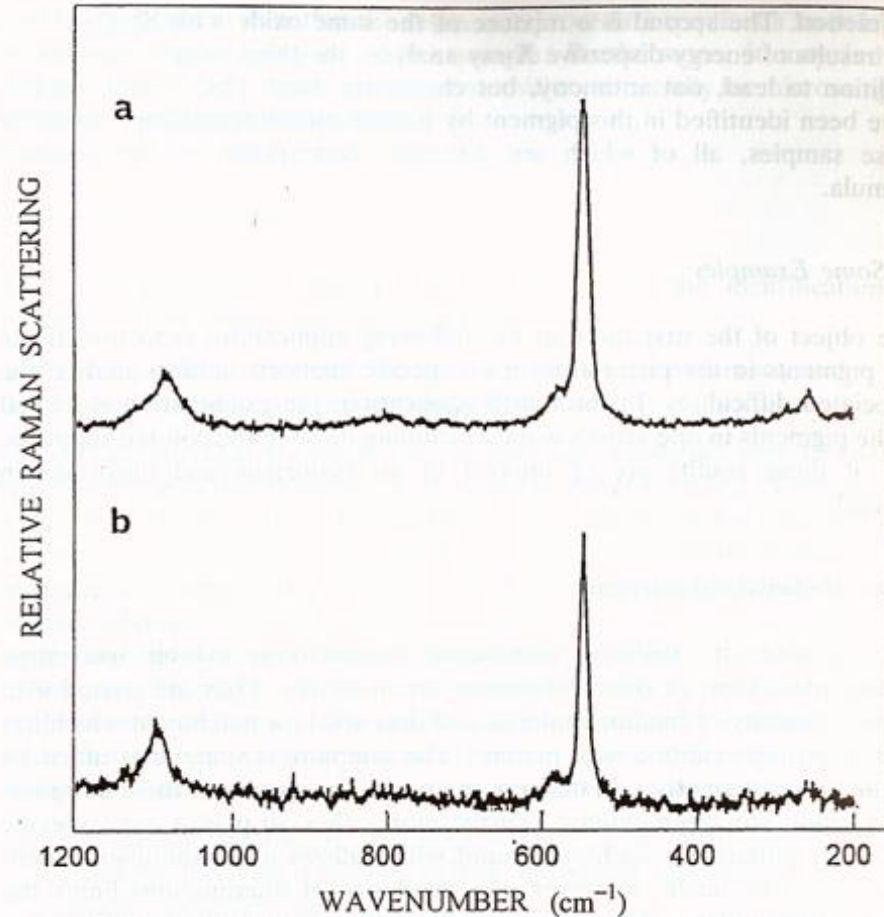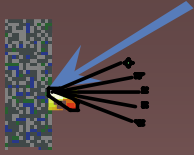- <u>Raman Spectroscopy for Chemical Analysis</u>, R.L. McCreery (Wiley Interscience, 2000).

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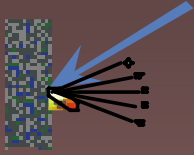
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