Calculation of vibrational frequencies and tools for their analysis

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Harmonic frequency in solids with CRYSTAL

Building the Hessian matrix

$$v_j = \frac{\partial V}{\partial u_j}$$

$$H_{ji} = \left[\frac{\partial v_j}{\partial u_i}\right]_0 \approx \frac{v_j(0,....,u_i,...) - v_j(0,....,-u_i,...)}{2u_i}$$

analytical first derivative

numerical second derivative

$$W_{ij}(k=0) = \sum_G \frac{H_{ij}^{0G}}{\sqrt{M_i M_j}}$$

Harmonic frequencies at the central zone are obtained by diagonalising the mass weighted Hessian matrix, W

Isotopic shift can be calculated at no cost!

CRYSTAL frequency calculation input

The minimum input is very simple :

FREQCALC

END

Several examples of options:

RESTART

MODES

ISOTOPES

NOINTENS

```
8    -2.341515086604E-01   9.118215424311E-02   2.50
8     2.246634517568E-01   4.466057545545E-01   2.50
8     2.746171575544E-01   1.624588255974E-01   3.21
FREQCALC
END
END
12  5
 0 0 8 2. 1.
 68371.875        0.0002226
  9699.34009      0.0018982
```

At the end of the geometry bloc

CRYSTAL frequency calculation output

Frequencies, symmetry analysys, IR intensities, IR and Raman activities

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HHHHHHHHHHHHHHHHHHHHHHHHHHHHHHHHHHHHHHHHHHHHHHHHHHHHHHHHHHHHHHHHHHHHHHHHHH
```

MODES		EV (AU)	FREQUENCIES (CM**-1)	(THZ)	IRREP	IR	INTENS (KM/MOL)	RAMAN
1-	1	0.00000000	-0.0119	-0.0004	(A2U)	A (	0.00)	I
2-	3	0.00000000	-0.0063	-0.0002	(EU)	A (	0.00)	I
4-	5	0.00292461	277.9957	8.3341	(EG)	I (	0.00)	A
6-	7	0.00501644	364.0844	10.9150	(EU)	A (	521.22)	I
8-	8	0.00778792	453.6439	13.5999	(A1G)	I (	0.00)	A
9-	10	0.00796426	458.7511	13.7530	(EU)	A (	1118.00)	I
11-	11	0.00940657	498.5628	14.9465	(A2U)	A (	267.76)	I
12-	13	0.02442204	803.3324	24.0833	(EG)	I (	0.00)	A
14-	14	0.56009552	3847.1164	115.3336	(A1G)	I (	0.00)	A
15-	15	0.56772589	3873.2330	116.1166	(A2U)	A (	193.78)	I

```
HHHHHHHHHHHHHHHHHHHHHHHHHHHHHHHHHHHHHHHHHHHHHHHHHHHHHHHHHHHHHHHHHHHHHHHHHH
```

- Document the accuracy (with respect to experiment, when experiment is accurate)

- Document the numerical stability of the computational process

- Interpret the spectrum and attribute the modes

The garnet example will be used

Garnets: $X_3Y_2(SiO_4)_3$

X	Y	Name
Mg	Al	Pyrope
Ca	Al	Grossular
Ca	Fe	Andradite
Ca	Cr	Uvarovite
Mn	Al	Spessartine

Space Group: Ia-3d

80 atoms in the primitive cell (240 modes)

$$\Gamma^{rid} = 3A_{1g} + 5A_{2g} + 8E_g + 14\,F_{1g} + 14\,F_{2g} + 5A_{1u} + 5\,A_{2u} + 10E_u + 18F_{1u} + 16F_{2u}$$

17 IR (F_{1u}) and 25 RAMAN (A_{1g}, E_g, F_{2g}) active modes

Silicate garnet grossular structure: $Ca_3Al_2(SiO_4)_3$

O

Ca

distorted dodecahedra

O

Si

O

tetrahedra

O

Al
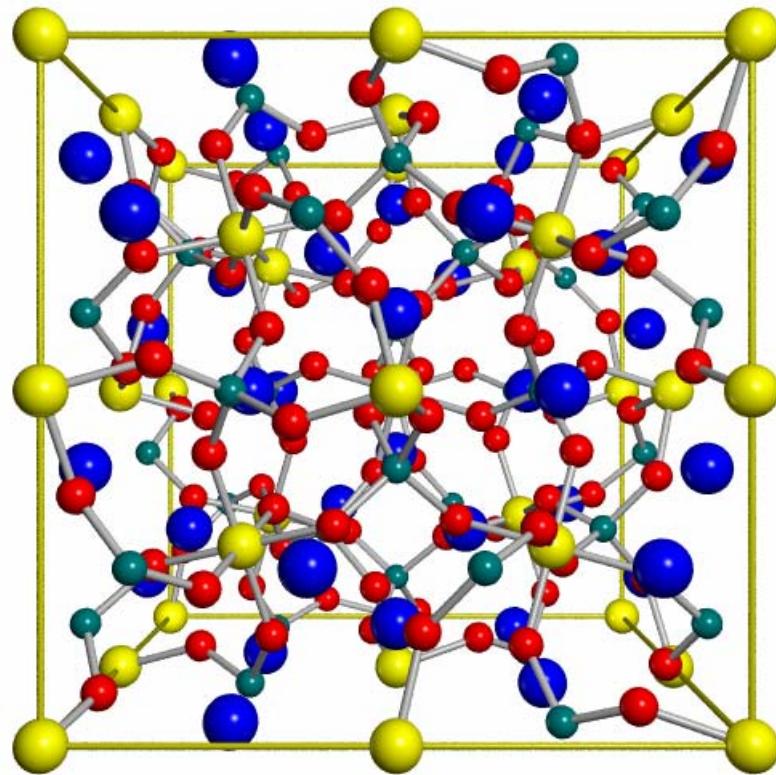
octahedra

- Cubic **Ia-3d**
- 160 atoms in the UC (80 in the primitive)
- O general position (48 equivalent)
- Ca (24e) Al (16a) Si (24d) site positions

Garnets geometry

**Cell parameter** (in Å)
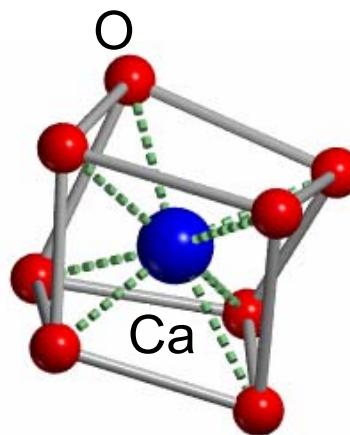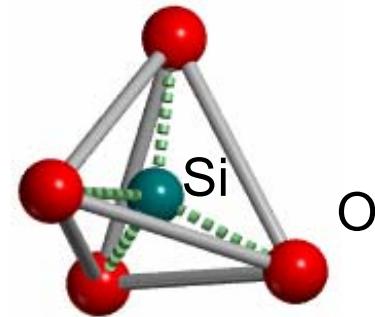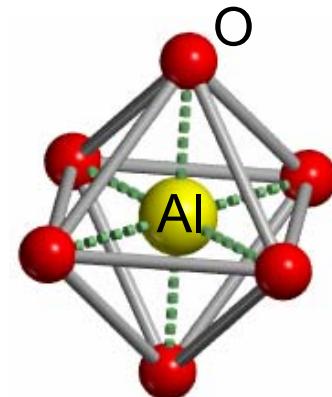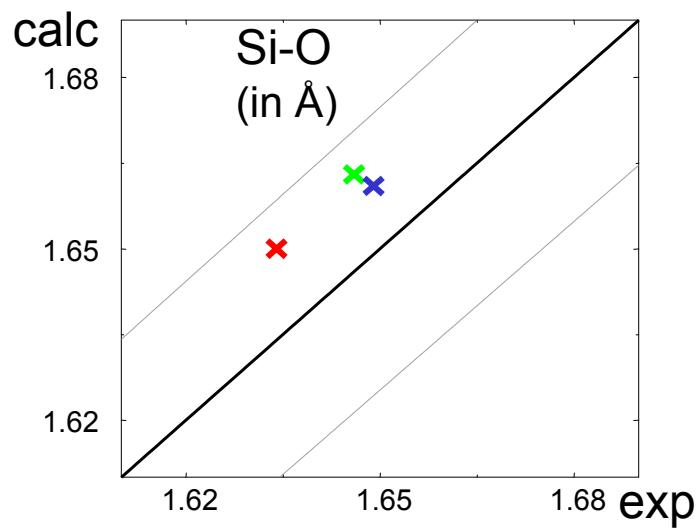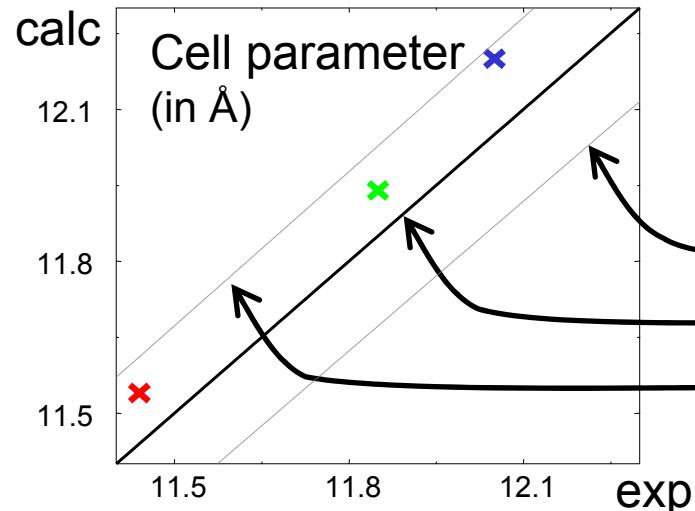
B3LYP vs experiment
(**pyrope**, **grossular** and **andradite**)

- 1.5 %

Perfect agreement

+ 1.5 %

Si-O (in Å)

X-O and Y-O (in Å)
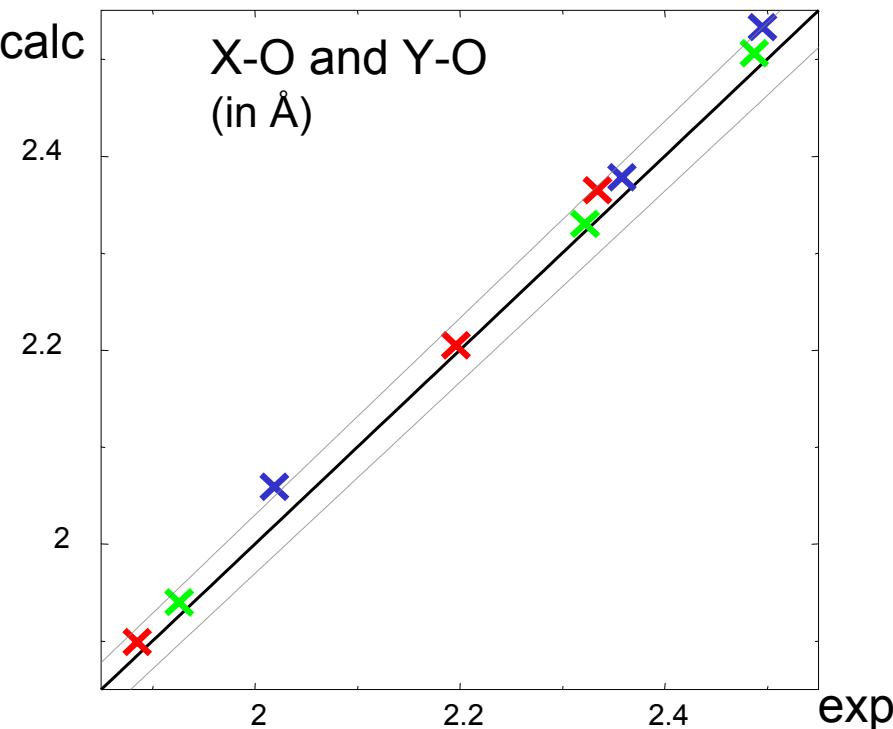
Pyrope & andradite : Armbruster T. and Geiger C., *Eur. J. Mineral.* **1993.** *5.* 59 ; Grossular : Mittal. et. al. *Phys. Rev. B.* **2001.** *64,* 094302

Hessian construction and Symmetry
(Garnet example)

Each SCF+Gradient calculation provides one line of H_{ik}

80 atoms = 240+1 SCF+G calculations with low (null) symmetry

1. Point symmetry is used to generate lines of atoms symmetry related

2. Other symmetries (among x, y, z lines; translational invariance) further reduce the required lines

$\Rightarrow$ At the end only 9 SCF+G calculations are required

Numerical stability of the computational process

• <u>DFT integration grid</u>

$|\overline{\Delta}|$ is the mean absolute deviation of frequencies between 2 values of an option. (in cm^{-1})

XLarge
$\overline{|\Delta|}$ =0.7 → Large
$\overline{|\Delta|}$ =0.6 → Standard

Grid	(Rad,Ang)
Standard	(55,434)
Large	(75,974)
XLarge	(99,1454)
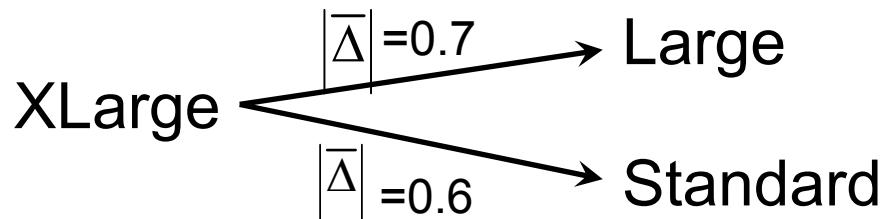
$\Rightarrow$ Standard grid is enough

(For the pyrope case)

• <u>SCF convergence</u>

$Tol_{\Delta E}=10^{-10}$ (UA) $\xrightarrow{\overline{|\Delta|}=0.2}$ $Tol_{\Delta E}=10^{-11}$ (UA)
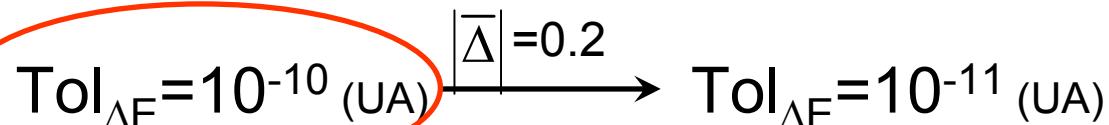
Calculated frequencies stability : Hessian construction

N=2

N : Number of points

N=3

u : Step size

dE/dx

x

u

dE/dx

x

u

u
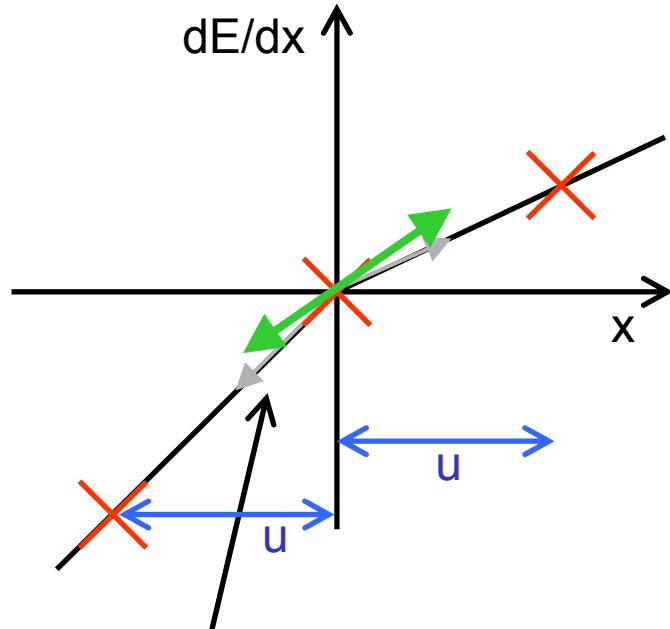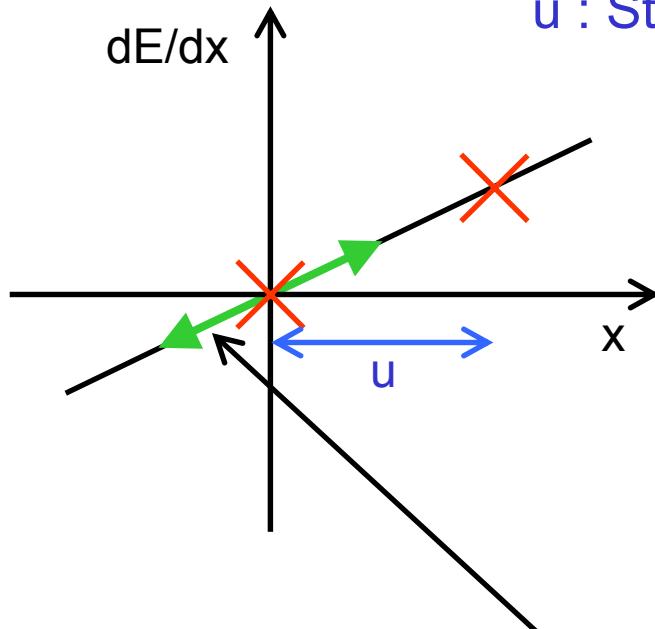
Numerical estimation of d^2E/dx^2

$N=2 \xrightarrow{\ |\overline{\Delta}|=0.1\ } N=3$

$u=0.001 \text{ Å} \xrightarrow{\ |\overline{\Delta}|=0.4\ } u=0.003 \text{ Å}$

Basis set effect

	BSA	BSB	BSC
Mg	8-511G(d)	-	-
Al	8-511G(d)	+sp	-
Si	8-631G(d)	+sp	+d
O	8-411G(d)	-	+d

Description of the three basis sets adopted for the calculation of the vibrational frequencies of <u>pyrope</u>. 8-511G(d) means that a 8G contraction is used for the 1s shell; a 5G contraction for the 2sp, and a single G for the 3sp and 4sp shells, plus a single G d shell (1+4+4+4+5=18 AOs per Mg or Al atom).

 +sp and +d means that a diffuse sp or d shell has been added to basis set A.

Basis set effect : IR frequencies of Pyrope

Calculated Modes						Exp a)
BSA		**BSB**		**BSC**		
υ	$\Delta\upsilon$	υ	$\Delta\upsilon$	υ	$\Delta\upsilon$	
988	16	970	-2	964	-8	972
913	11	896	-6	890	-12	902
882	11	865	6	859	-12	871
691	41	674	24	673	23	~650
594	13	583	2	581	-0	581
538	3	533	-2	532	-3	535
505	27	484	6	481	3	478
471	16	459	4	457	2	455
428	6	423	1	423	1	422
390	7	383	0	383	-0	383
353	17	349	13	349	13	336
338	2	334	-2	335	-1	336
261	2	260	1	259	-0	259
220	-1	216	-5	217	-4	221
193	-2	189	-6	191	-4	195
142	8	140	6	140	6	134
133	-1	121	-13	120	-14	134

IR-TO modes (F_{1u}) of pyrope as a function of the basis set size. Frequency differences ($\Delta\upsilon$) are evaluated with respect to experimental data. υ and $\Delta\upsilon$ in cm^{-1}.

a) Hofmeister et. al. *Am. Mineral.* **1996**. *81*, 418

$|\Delta\upsilon|$ 0   5   10   15   20   +

$\rightarrow$
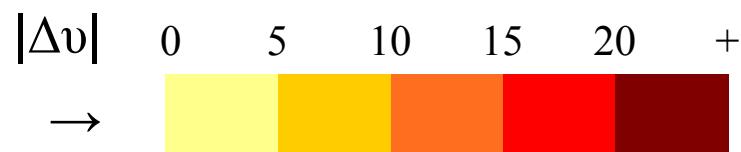
- BSA is to small

- BSB and BSC are good
  $\Rightarrow$ Let's use BSB

Why so large differences with exp for this mode?
See next slide

Pyrope : IR intensities

Calculated Modes (BSB)			Exp a)
υ cm^{-1}	$\Delta\upsilon$ cm^{-1}	Calculated Intensity (kM/mol)	υ cm^{-1}
970	-2	5715	972
896	-6	5648	902
865	-6	14028	871
674	24	4	~650
583	2	1326	581
533	-2	869	535
484	6	753	478
459	4	13721	455
423	1	1309	422
383	0	3552	383
349	13	85	336
334	-2	6296	336
260	1	720	259
216	-5	8	221
189	-6	3330	195
140	6	24	134
121	-13	2904	134

IR-TO modes of **pyrope** and their intensity. Frequency differences ($\Delta\upsilon$) are evaluated with respect to experimental data.

a) Hofmeister et. al. *Am. Mineral*. **1996**. *81*, 418

When the mode intensity is to small, the mode frequency can not be accurately determined by experiment.

Or sometimes can't be observed at all ! See next slide

Grossular : IR intensities

Calculated Modes			Exp a)
υ	$\Delta\upsilon$	Intensity (kM/mol)	υ
903	-11	6652	914
851	-9	3148	860
830	-13	16321	843
627	9	739	618
547	5	740	542
509	4	148	505
481	7	326	474
441	-8	19909	449
424	-6.	88	430
407	**-**	**18**	**-**
395	-4	9164	399
357	1	162	356
303	1	751	302
242	-3	1176	245
207	2	322	205
183	-3	939	186
153	-6	293	159

IR-TO modes (F_{1u}) of **grossular** and their intensity. Frequency differences ($\Delta\upsilon$) are evaluated with respect to experimental data.

a) Hofmeister et. al. *Am. Mineral.* **1996**. *81*, 418

Pyrope raman modes : Calc vs Exp

Calculated Modes		Observed Modes		
BSB		Exp. a)	Exp. b)	Exp. c)
υ	$\Delta\upsilon$ a)	υ	υ	υ
1063	-3	1066	1062	1066
930	-15	945	938	-
921	-7	928	925	927
890	-12	902	899	-
861	-	-	911(867)	-
855	-16	871	866	870
654	3	651	648	648
635	-	-	626	-
604	6	598	598	-
565	2	563	562	561
529	4	525	524	-
514	2	512	510	511
494	2	492	490	492

Frequency differences ($\Delta\upsilon$) are evaluated with respect to experimental data of Kolesov, 1998. υ and $\Delta\upsilon$ in cm^{-1}.

in parentheses unpublished results reported by Chaplin et al, *Am. Mineral*, **1998.** 83, 841

The Eg mode at 439 cm^{-1} and F2g mode at 285 cm^{-1} reported by Hofmeiser and Chopelas have not been included in the table, because they do not correspond to any calculated frequency.

a) Kolesov et. al.
   Phys. Chem. Min. **1998**. *25*, 142
b) *Hofmeister et. al.*
   Phys. Chem. Min. **1991**. *17*, 503
c) Kolesov et. al.
   Phys. Chem. Min. **2000**. *27*, 645

Pyrope raman modes : Calc vs Exp

Calculated Modes		Observed Modes		
BSB		Exp. a)	Exp. b)	Exp. c)
υ	$\Delta\upsilon$ a)	υ	υ	υ
383	-0	383	379	384
379	4	375	365(379)	-
356	-8	364	362	363
353	-0	353	350	352
337	-8	345	-	343
320	-2	322	318(342)	320
309	25	284	342(309)	-
269	-	-	272	273
204	-9	213	230	209
209	-2	211	203	-
173	-	-	208	-
106	-31	137	-	127

Frequency differences ($\Delta\upsilon$) are evaluated with respect to experimental data of Kolesov, 1998. υ and $\Delta\upsilon$ in cm^{-1}.

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c) Kolesov et. al.
   Phys. Chem. Min. **2000**. *27*, 645

Garnets : Satistics

	Systems	$\left|\overline{\Delta}\right|$	$\overline{\Delta}$	Δ_{max}
Raman a) and c)	**Grossular**	7.5	3.0	32
	Pyrope	7.6 (3.6)	-3.2 (-2.4)	31 (21)
	Andradite	5.3	-5.1	11
	Uvarovite	4.2	-0.4	22
IR b)	**Grossular**	7.5	-2.1	13
	Pyrope	4.6	-0.7	13
	Andradite	8.5	-8.5	17

a) Kolesov et. al.
Phys. Chem. Min. **1998.** *25*, 142

b) Hofmeister et. al.
Am. Mineral, **1998**. *83*, 841

c) Kolesov et al.
Phys. Chem. Min. **2000.** *27*, 645

Statistical analysis of calculated IR and Raman modes of garnets compared with experimental data. For Pyrope in parentheses experimental [c] data from Kolesov et. al. 2000.

The isotopic shift

- As a tool for the assignement of the modes and for the interpretation of the spectrum.

- Each atom at a time

- In some cases also infinite mass

Pyrope : $^{24}Mg \rightarrow ^{26}Mg$
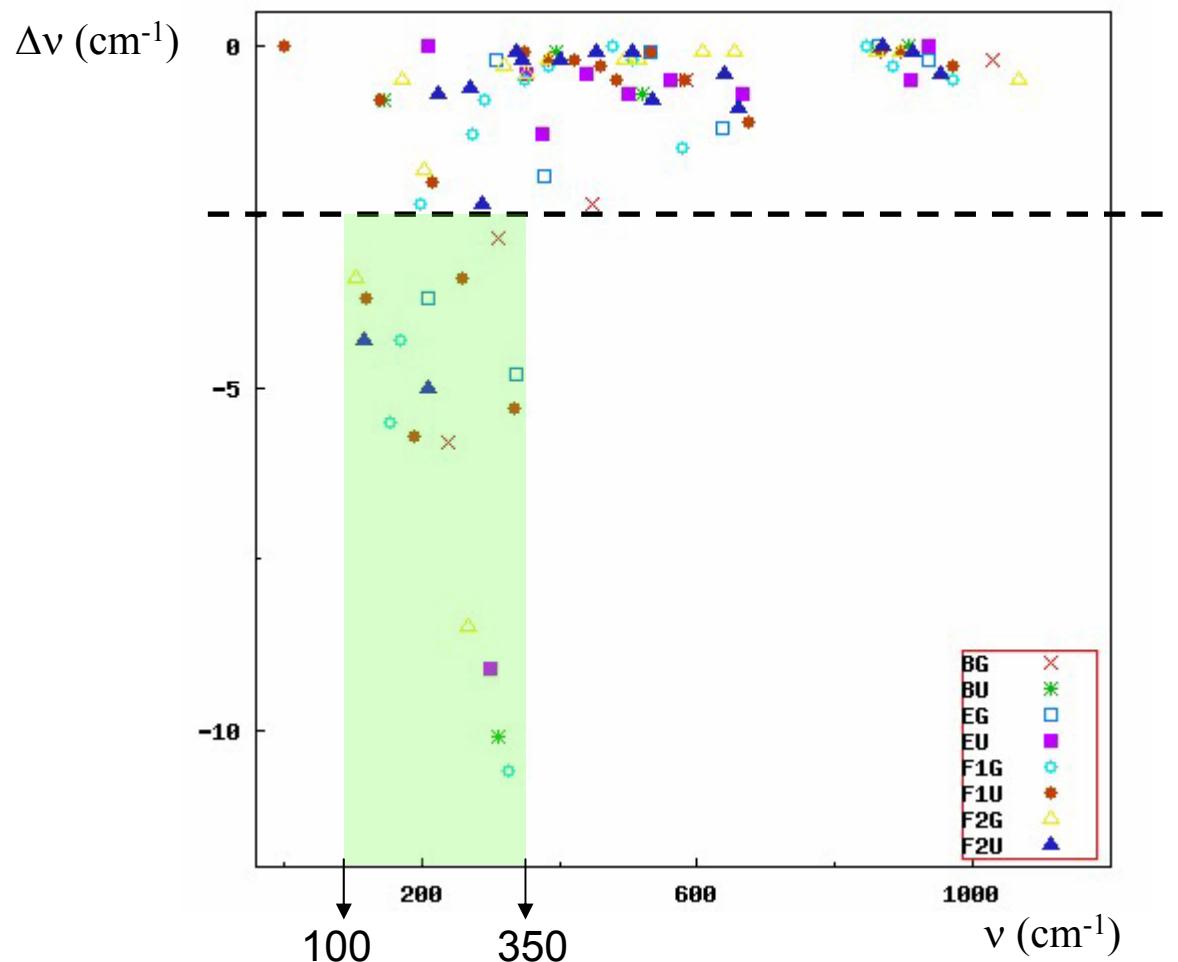
Isotopic shift on the vibrational frequencies of pyrope when ^{26}Mg is substituted for ^{24}Mg.

Pyrope : $^{27}Al \rightarrow {}^{29}Al$
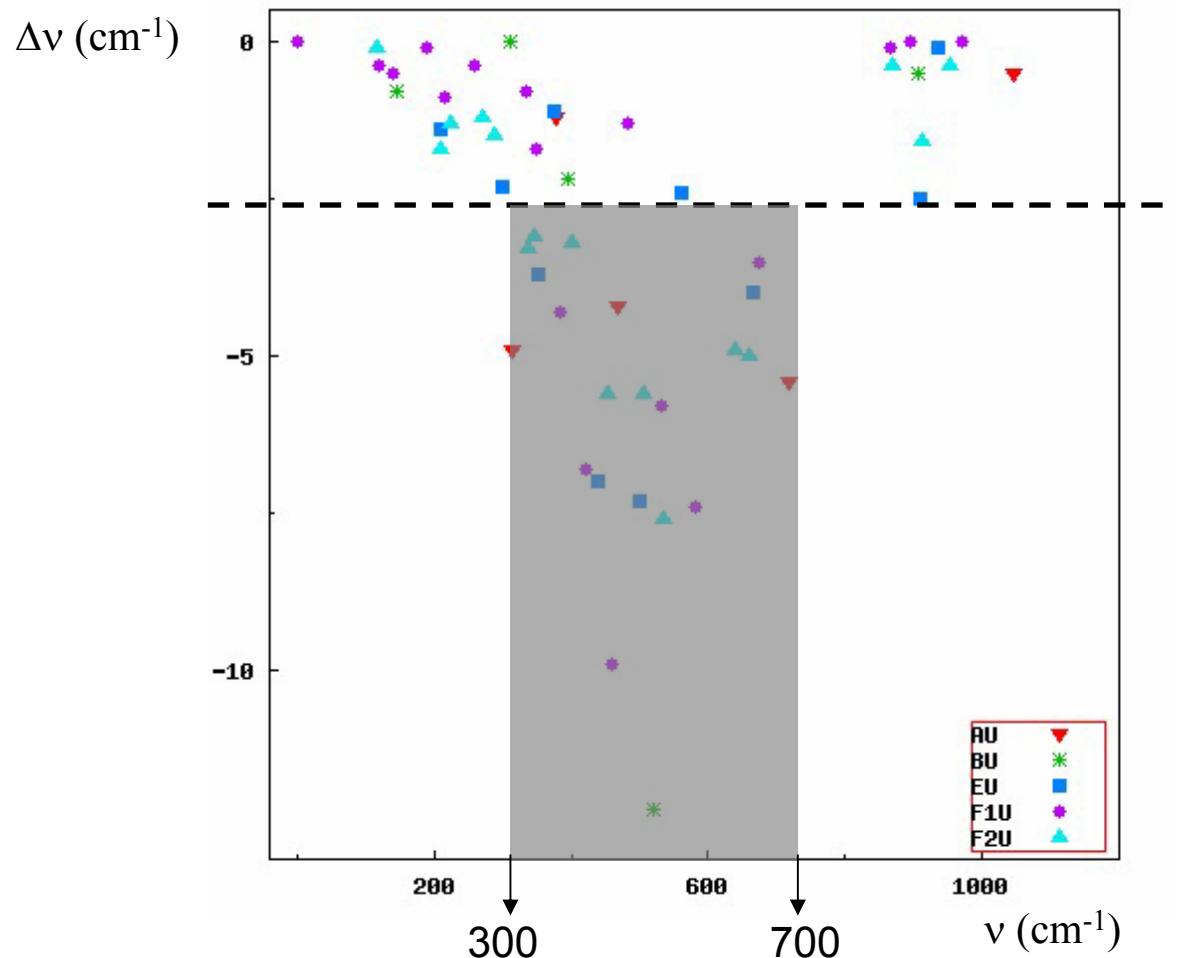
Isotopic shift on the vibrational frequencies of pyrope when ^{29}Al is substituted for ^{27}Al.

Pyrope : $^{16}O \rightarrow {}^{18}O$
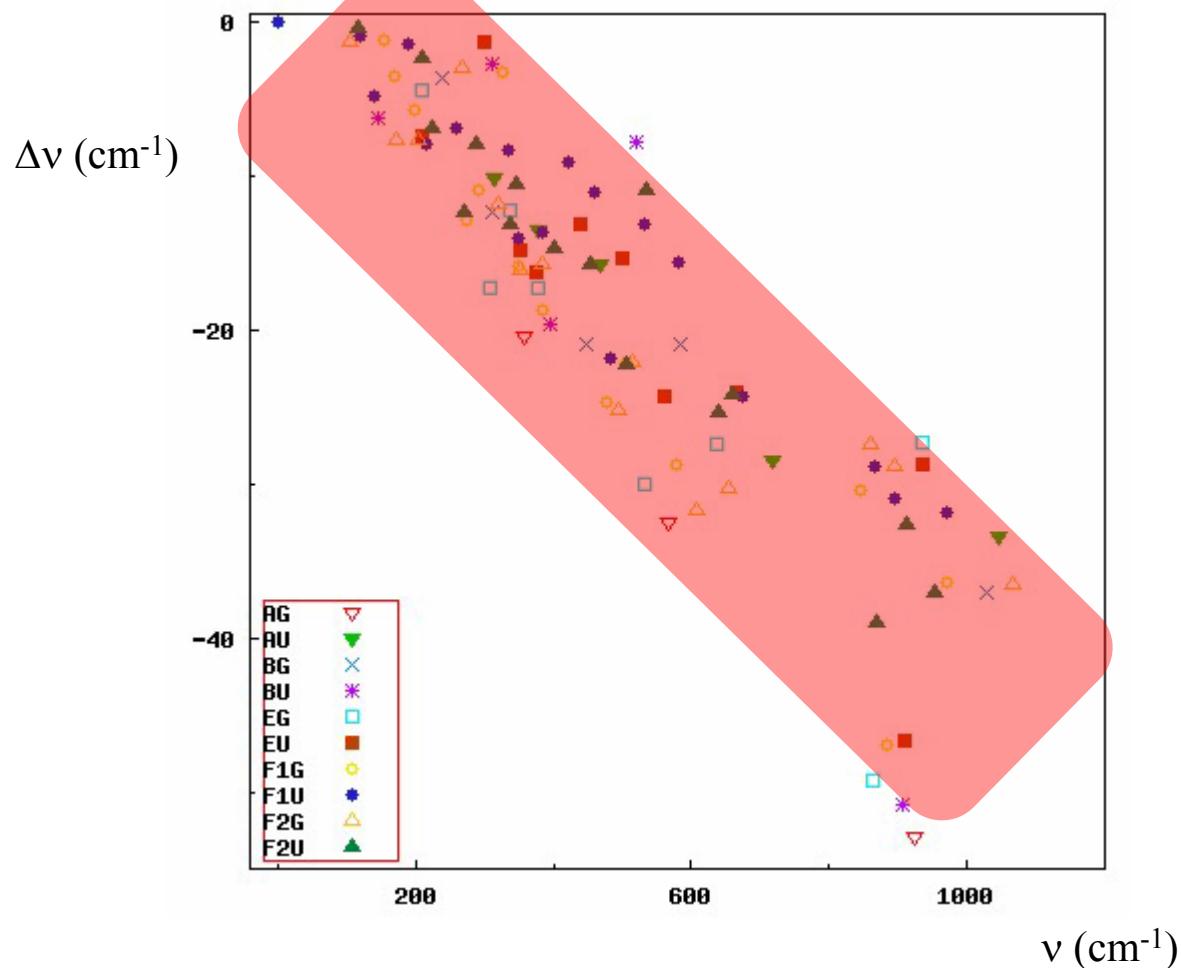
Isotopic shift on the vibrational frequencies of pyrope when ^{18}O is substituted for ^{16}O.

Pyrope : $^{28}Si \rightarrow$ ^{30}Si
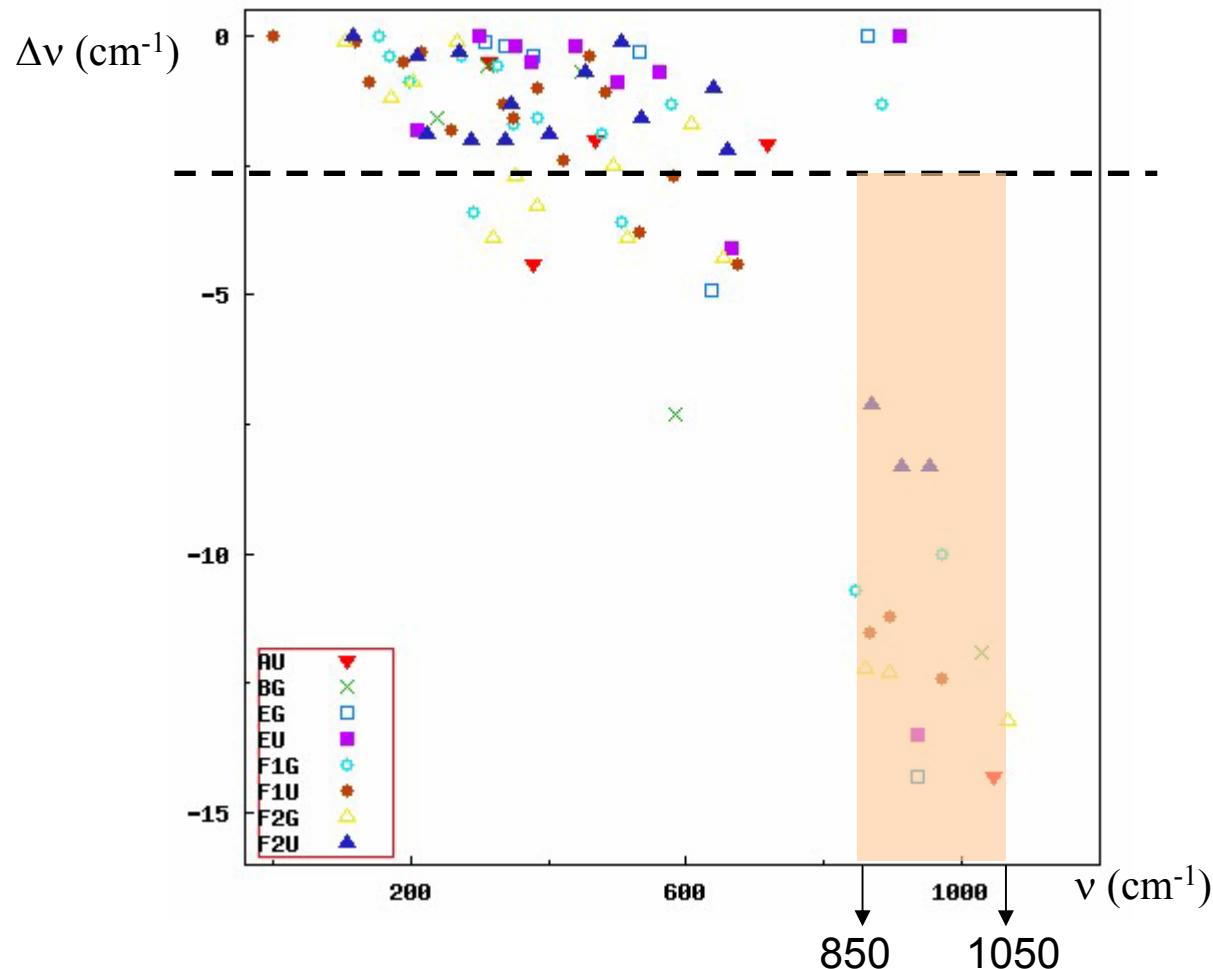
Isotopic shift on the vibrational frequencies of pyrope when ^{30}Si is substituted for ^{28}Si.

Internal/external modes

Si-O bonds stronger than the others

$\Rightarrow$ Modes separated in 2 types:

- Internal modes (deformation of the tetrahedra)
- External modes (solid tetrahedra)

Isolated tetrahedra modes (internal modes)

Streching
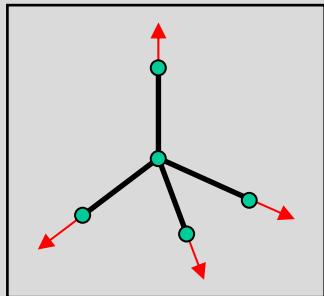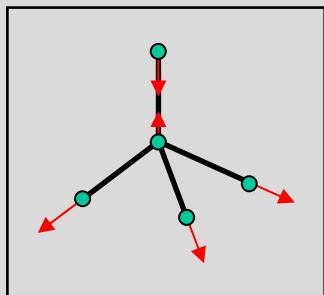
Bending

υ_1 : Symmetric
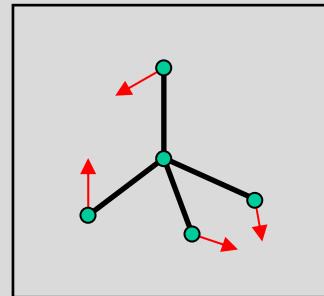
υ_2 : Symmetric
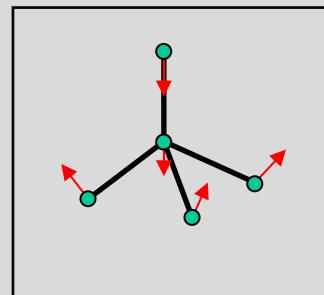
υ_3 : Asymmetric

υ_4 : Asymmetric

Pyrope : Stretching modes
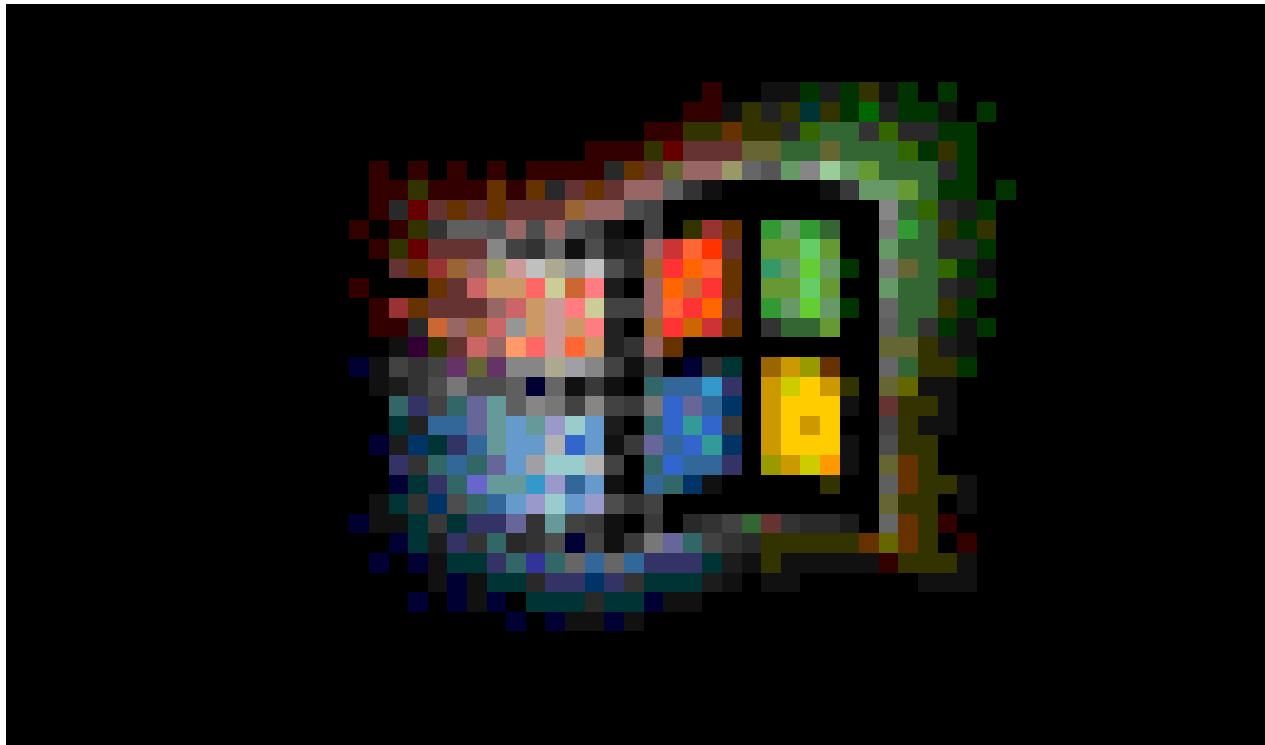
Symmetric stretching υ_1 921 cm^{-1}	Asymmetric stretching υ_3 890 cm^{-1}

Mg **Al** **Si** **O**

Pyrope : normal modes attribution
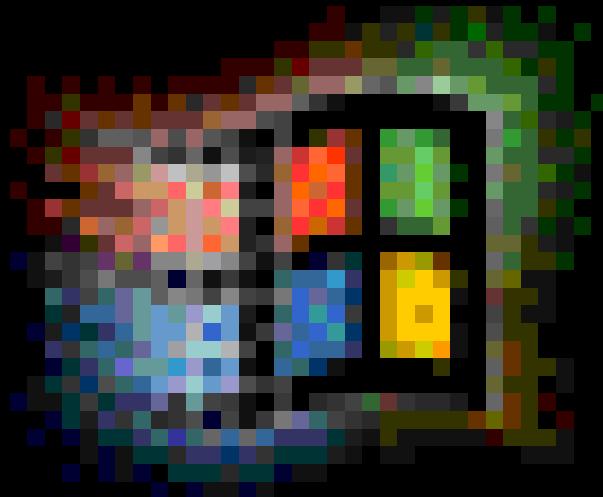
υ_2 SiO$_4$ bending	SiO$_4$ rotation	Mainly
476 cm^{-1}	+ Mg translation	Mg translation
	200 cm^{-1}	117cm^{-1}

Mg	Al	Si	O

A related family:

From Garnets to Hydrogarnets

a) R. Orlando et. al. *J. Phys. Chem. B.* 2006. *110*, 692

Grossular and katoite: a detailed view
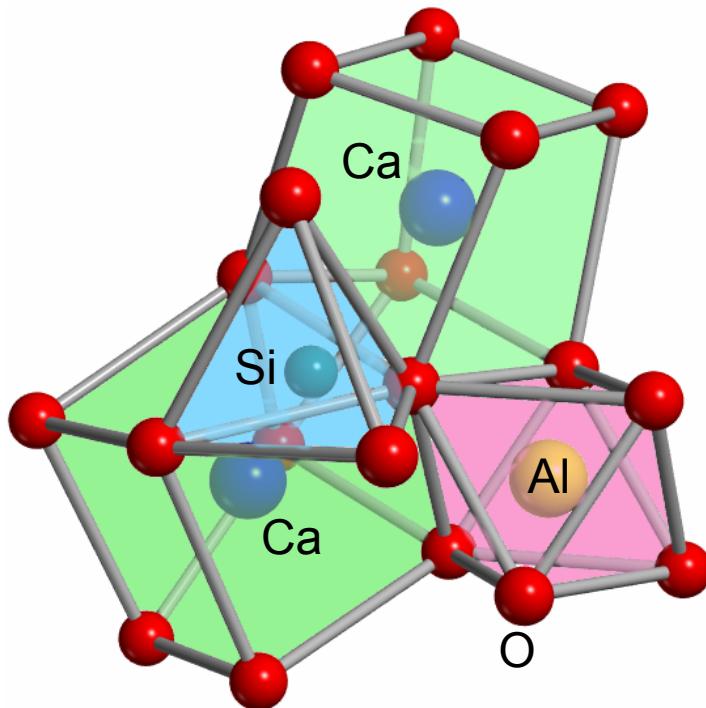
Grossular $Ca_3Al_2(SiO_4)_3$

$-Si^{4+}$

$+4H^+$
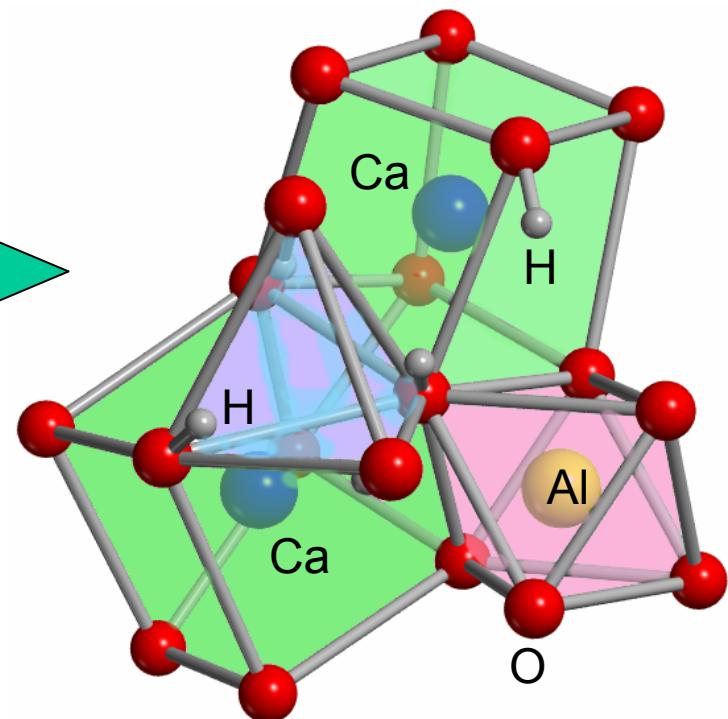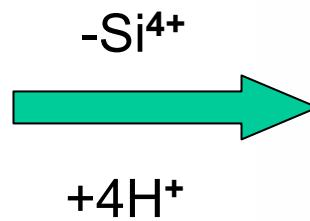
Katoite $Ca_3Al_2((OH)_4)_3$

The disparition of the Si-O bonds makes katoite softer than grossular

The unit cell content of katoite $Ca_3Al_2[(OH)_4]_3$

H

O

Ca
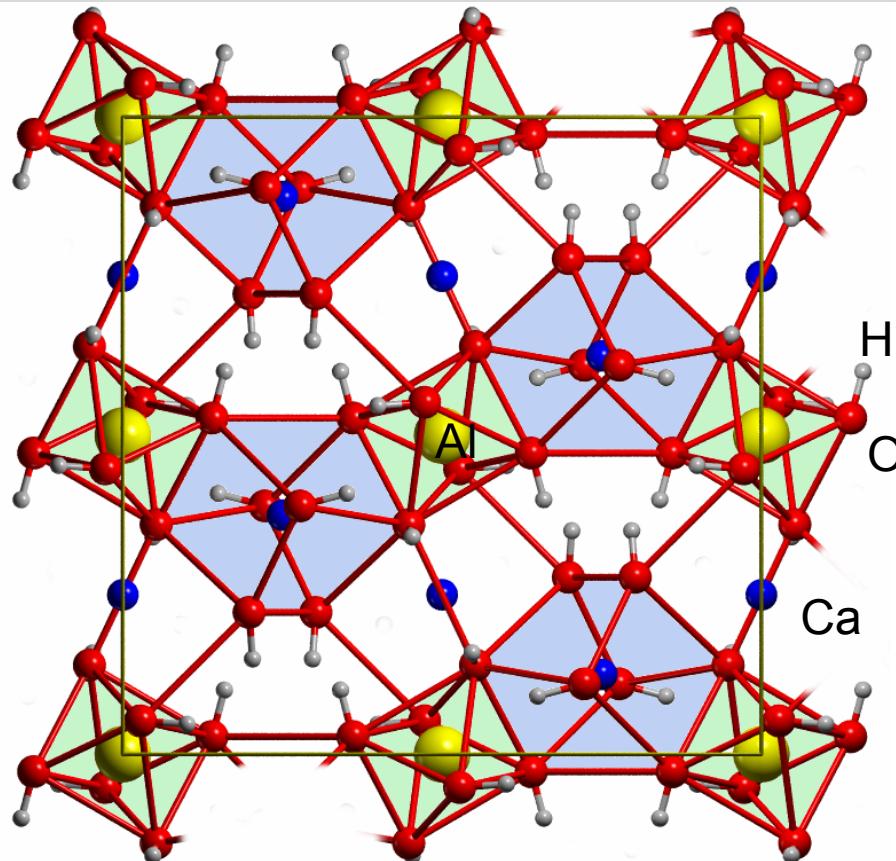
- There are 8 $Al(OH)_6^{3-}$ octahedra in the unit cell;
- The space between octahedra is filled by 12 Ca^{2+} ions.
- The SiO_4 tetrahedra of garnets are here replaced by $(OH)_4$ tetrahedral "defects".

- how to interpret the vibrational spectrum?
- is it possible to factorize it in terms of subunits?
- who is responsible for the very low frequencies?

The role of Hydrogen

- Is it possible to identify H modes?

- Can we define, in particular:

a) O-H stretching

b) Al-O-H bending

c) H rotations with respect to the Al-O axis?

Infinite mass substitution

Katoite : $Ca_2Al_3(OH)_{12}$

116 atoms in the unit cell

$\rightarrow$ 348 modes

To many modes to analyse

Aluminium octahedra are no more

bonded through Si tetrahedra

$\rightarrow$ Focus on a single $Al(OH)_6$ octahedron
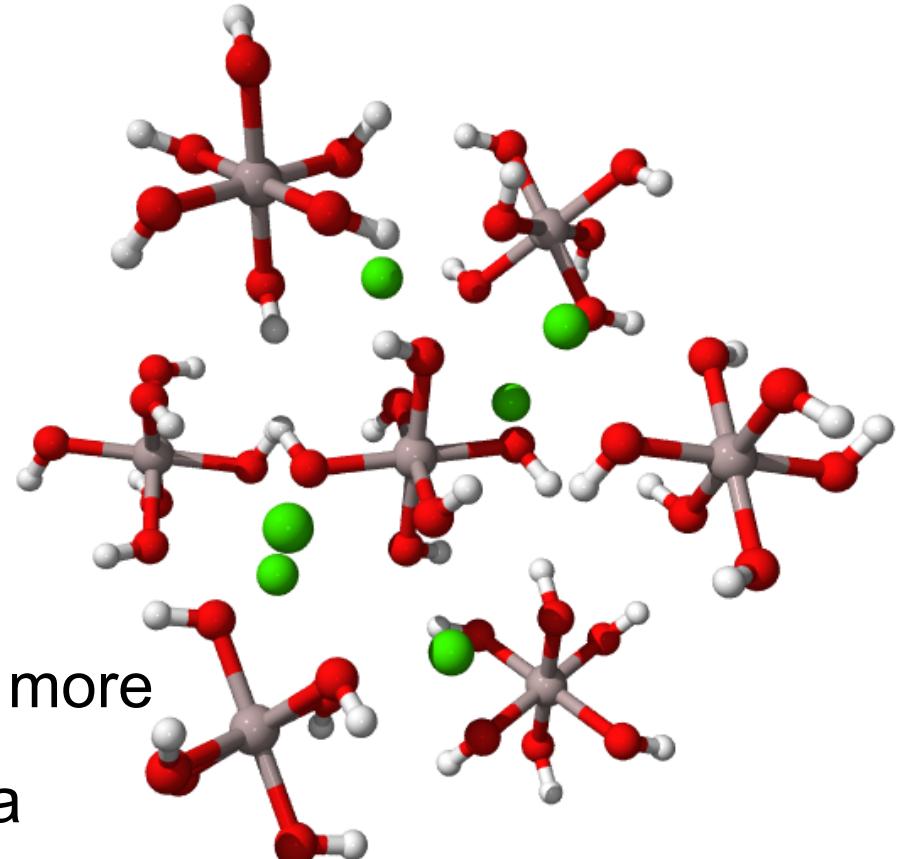
Infinite mass substitution

→ Focus on a single octahedron

How to proceed ?

→ Performing an isotopic substitution (at no cost) where all atoms except one Al(OH)$_6$ octahedron have an infinite mass
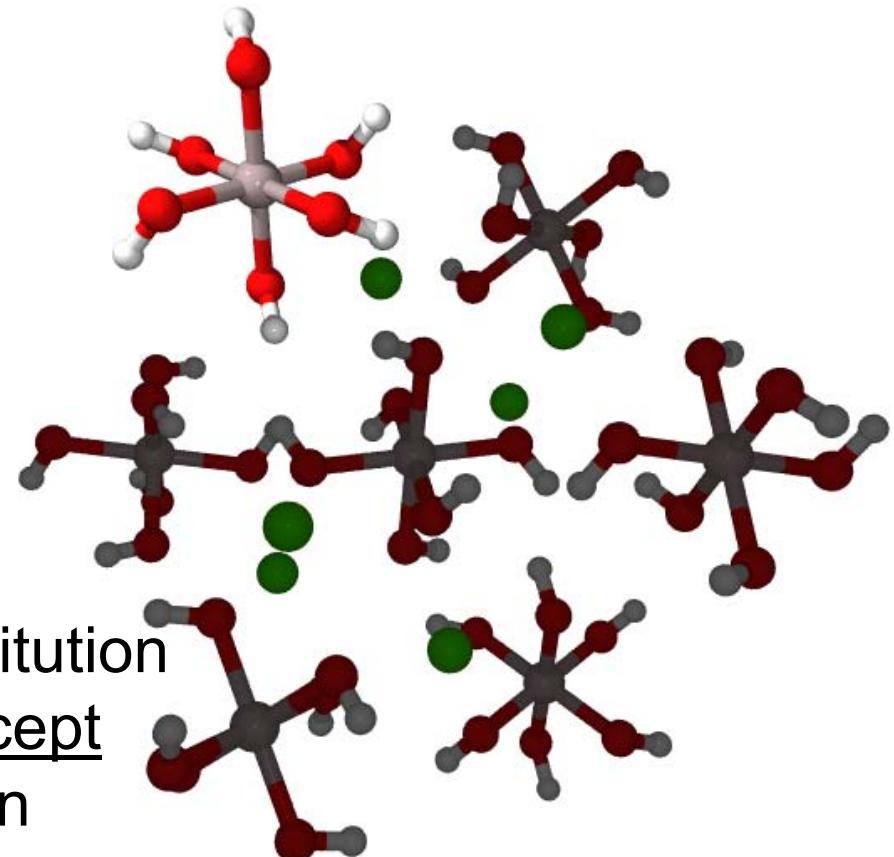
The isotopic effect

2 types of isotopic effects:

- **Infinite mass attributed to a fraction of the atoms.**

Advantages with respect to subunits investigated with clusters (ex: isolated $Al(OH)_6$):

a) the atoms move in the field created by the infinite system.
b) and in the presence of the other atoms
c) and the hessian matrix is the correct one

- **Isotopic substitution (ex: ^{29}Al for ^{27}Al)**

Octahedron fragment in katoite
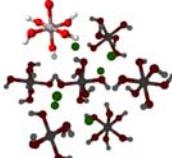
Assignment		^{29}Al	^{18}O	D
	υ	$\Delta\upsilon$	$\Delta\upsilon$	$\Delta\upsilon$
Octahedron Translation	163.8	-1.9	-6.3	-3.2
	194.7	-1.6	-8.6	-2.3
Octahedron Rotation	198.3	0	-11.2	-1.9
	200.4	0	-10.9	-5.2
AlO$_6$ Modes	264.5	-0.1	-14.4	-7.5
	286.8	-0.1	-15.3	-10.9
	357	0	-18.9	-17.4
	374.9	0	-18.8	-26.7
	398.9	0	-22.2	-7.2
	400	-1.7	-17.8	-24.4
	423.3	-4.8	-15.9	-22
	524.5	-9	-12.9	-101.3
	538.4	0	-29.4	-142.3
	547.9	-7.7	-15.2	-61.7

Lowest part :
modes < 55Ocm^{-1}

Calculated modes of octahedron fragment and the effect of ^{29}Al, ^{18}O and D isotopic substitution.

Octahedron fragment in katoite

Assignment	Al(OH)$_6$ υ	H$_6$ υ^*	^{29}Al $\Delta\upsilon$	^{18}O $\Delta\upsilon$	D $\Delta\upsilon$
Rotation H	553.5	549.6	0	-0.6	-33.3
	599.5	590.4	-0.2	-2	-71.1
	662.9	658.1	0	-0.6	-187.1
	669.2	656.9	-0.2	-1.5	-145.3
Bending H-O-Al	802.5	770.5	0	-4.2	-200.4
	825.4	787.8	-1.2	-3.6	-185.8
	855.5	795	-1.8	-5.2	-190.2
	867.7	820.6	0	-6.4	-199.2
Stretching O-H	3847.8	3735.2	0	-12.5	-1038.1
	3849.4	3736.4	0	-12.5	-1039.1
	3850.7	3738.5	0	-12.4	-1039.9
	3851.4	3739.6	0	-12.4	-1039.5
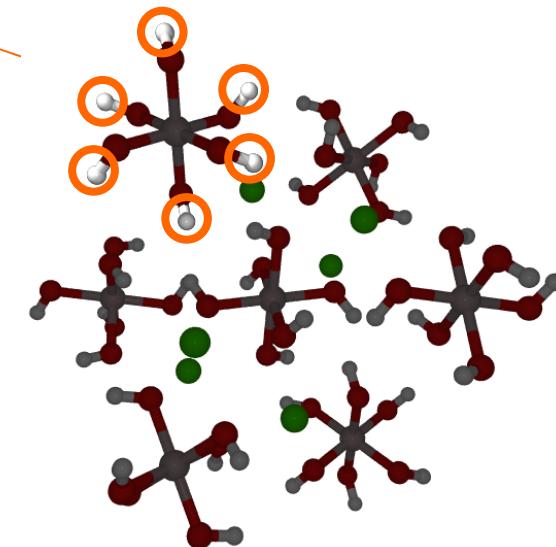
The H$_6$ modes are obtained by "freezing" all atoms but the six hydrogen atoms of the single octahedron

υ^* corresponds to the modes of free hydrogen in the octahedron fragment

Highest part :
modes > 55Ocm^{-1}

Katoite : Isotopic substitution

$Ca^{40\rightarrow44}$

$Al^{27\rightarrow29}$

$O^{16\rightarrow18}$

H→D (low freq)

H→D (high freq)
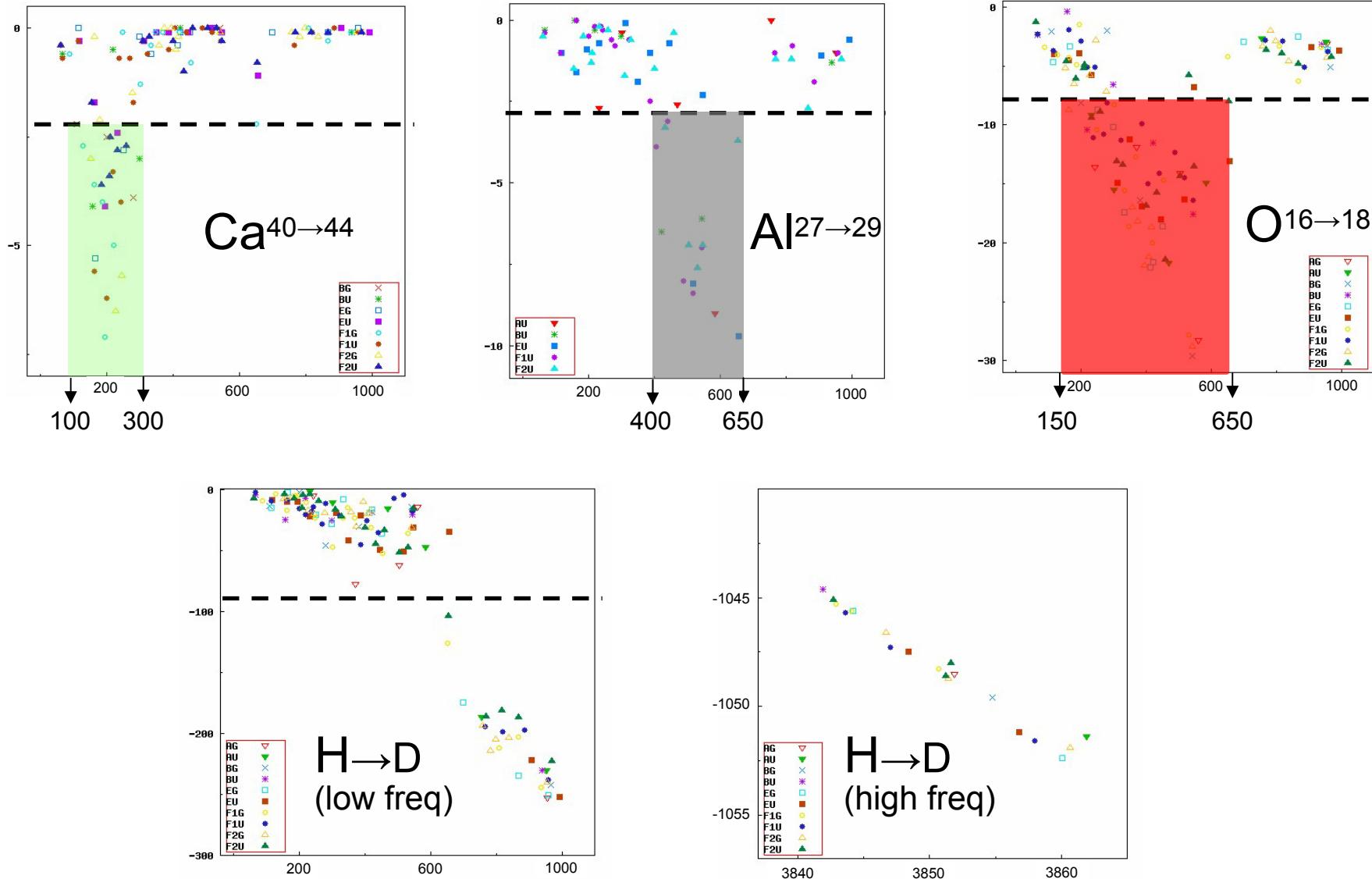
Simulated vibrational spectrum

- 🔴 **Stretching OH**
- 🔵 **Bending Al-O-H**
- 🟢 **H- Rotation???**
- 🟡 **??? + (AlOH)$_6$ transl and rot**
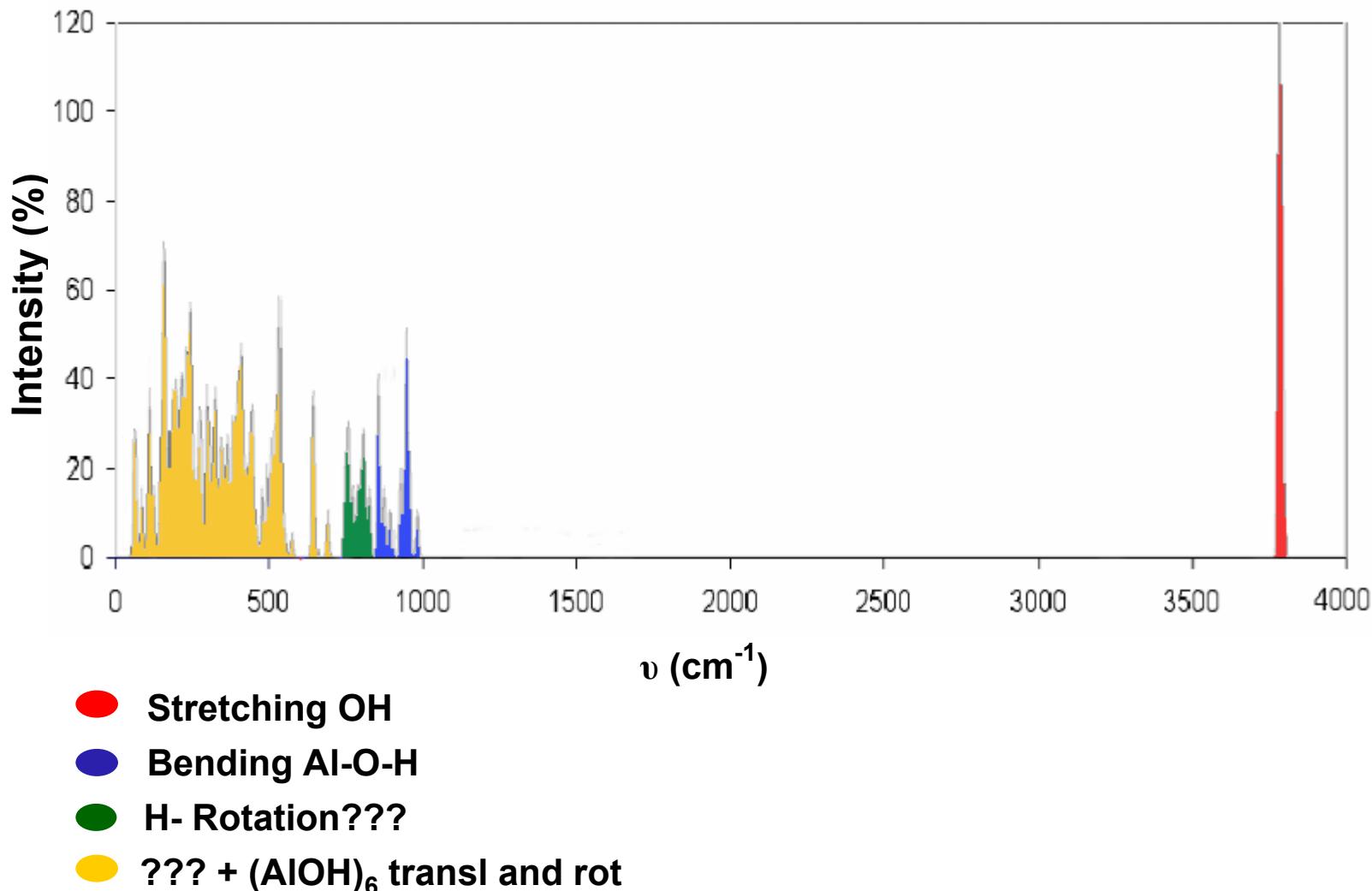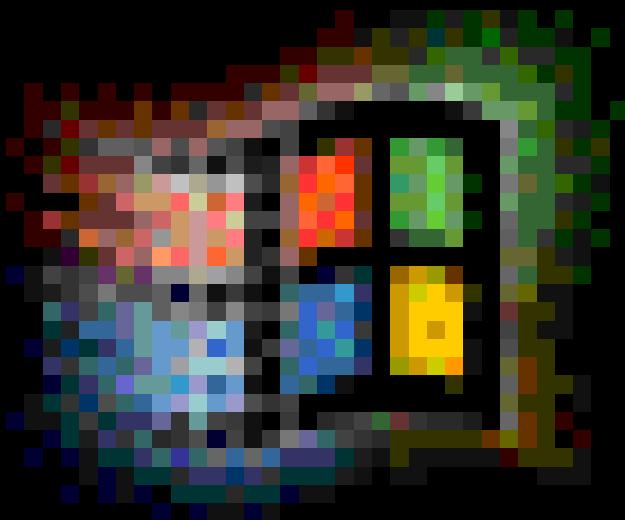
Katoite : H modes

| 3852 cm^{-1} OH Stretching | 868 cm^{-1} AlOH Bending | 652 cm^{-1} H-Rotation |

Mg **Al** **H** **O**

Katoite : Al octahedra modes
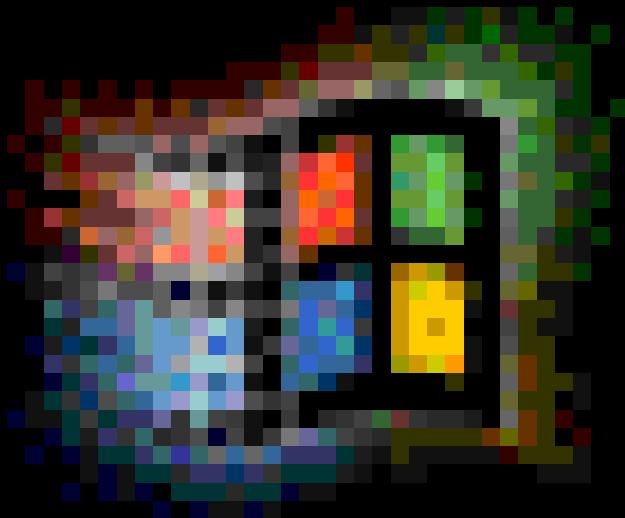
| O-Al Stretching 541 cm^{-1} | Octahedron Rotation 179 cm^{-1} | Octahedron Traslation 156 cm^{-1} |

Mg **Al** **H** **O**

Calculated and experimental O-H stretching modes of katoite. The calculated modes have been corrected by using the anharmonicity constant (86 cm^{-1}) obtained for the fully decoupled OH stretching. υ and $\Delta\upsilon$ in cm^{-1}.

	Calc.		Exp.[a]		Exp.[b]	
	υ	Δ	υ	Δ	υ	Δ
IR	3672-3689	17	3655-3701	46	3663-3703	40
Raman	3672-3686	14	3648-3699	44	-	-

a) Kolesov and Geiger *Am. Mineral.*. **2005.** *90*, 1335
b) Rossman and Aines. *Am. Mineral.* **1991.** *76*, 1153

Experimental data (only one IR mode)

3663 cm^{-1} [WHBH   40 cm^{-1}] Rossman &Aines, Am. Mineral 1991

Calculated anharmonic frequency

3682 cm^{-1} [isolated H; the A$_{1g}$ mode of the 48 H is 9 cm^{-1} lower]

How is changing with pressure?

see next slide

O-H stretching region *vs* pressure
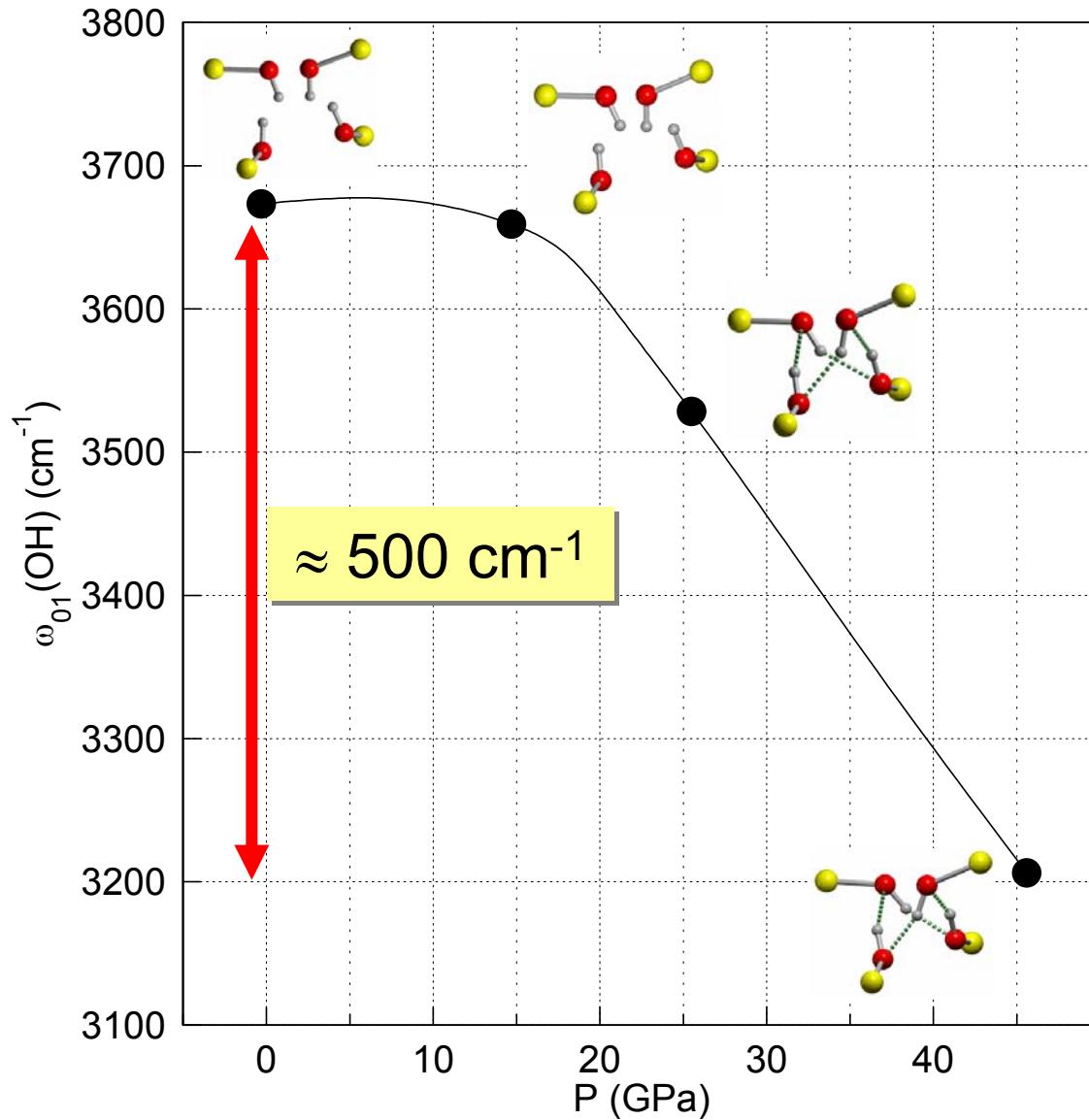
References

- **Pyrope:**   Pascale F.; Zicovich-Wilson C.M.; Orlando R.; Ugliengo P.; Dovesi R.

  "Vibration frequencies of $Mg_3Al_2Si_3O_{12}$ Pyrope: An ab-inito study with Crystal code"
  J. Phys. Chem. B. **2005**. *109,* 6146.

- **Andradite:**   Pascale F.; Catti M.; Damin. A.; Orlando R.; Saunders V.R.; Dovesi R.

  "Vibration frequencies of $Ca_3Fe_2Si_3O_{12}$ Andradite: An ab-inito study with Crystal code"
  J. Phys. Chem. B. **2005.** *109,* 18522**.**

- **Grossular:**   Zicovich-Wilson C.M.; Torres F. J.; Pascale F.; Orlando R.; Dovesi R. (2005)

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  "Vibrational Spectrum of Katoite $Ca_3Al_2[(OH)_4]_3$: a periodic ab-inito study"
  J. Phys. Chem. B. **2006.** *110,* 692**.**

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