Approches expérimentale et de simulation de la spectroscopie vibrationnelle pour l'étude des matériaux

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Outline

Introduction

Context of the presented introduction studies

First example : Scandium Oxide – Sc_2O_3

Experimental spectrum
Calculated spectrum

Second Example : Uranium Oxide – UO_2

Experimental spectrum
Calculated spectrum

Perspectives

Goal

Coupling Experimental and Computational Tools

Experimental Physics – Chemical physics

Solid state – Chemical Physics laboratory :

Glasses, Nuclear Materials…

Experimental physics :

Vibrational spectroscopy, Cyclotron, NMR, Brillouin scattering

X-Ray Diffusion…

Unusual environments :

HT, Irradiation, in situ measurements…

All the experiments at located in our laboratory and we have a privileged access to the synchrotron facility « SOLEIL »

Goal

Coupling Experimental and Computational Tools

Computational physics

Why? :

Difficult experiments:

Nuclear Materials, extreme conditions…

Experimental spectra :

Sometimes ambiguous mode assignments

Predicting spectra for some « exotic materials »:

Transition species (short live times, unstable…)

That's a approach we want to develop in our Laboratory!

Crystallography

First example : Scandium Oxide

Interest : Component for the « Megajoule LASER » : scintillator

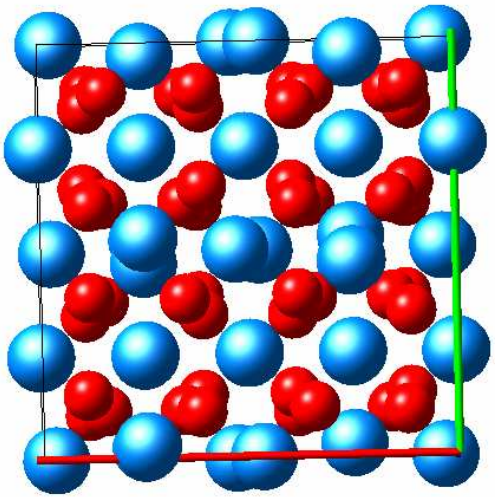
Cell parameters:

Parameter	Value
a	9.810000
b	9.810000
c	9.810000
alpha	90
beta	90
gamma	90

Density: 3.881 Mg/m^3

Crystal Point Group: T_h (m-3)

Cubic body centered



The oxygen and the scandium atoms are organized like « waves »

Experimental Spectrum

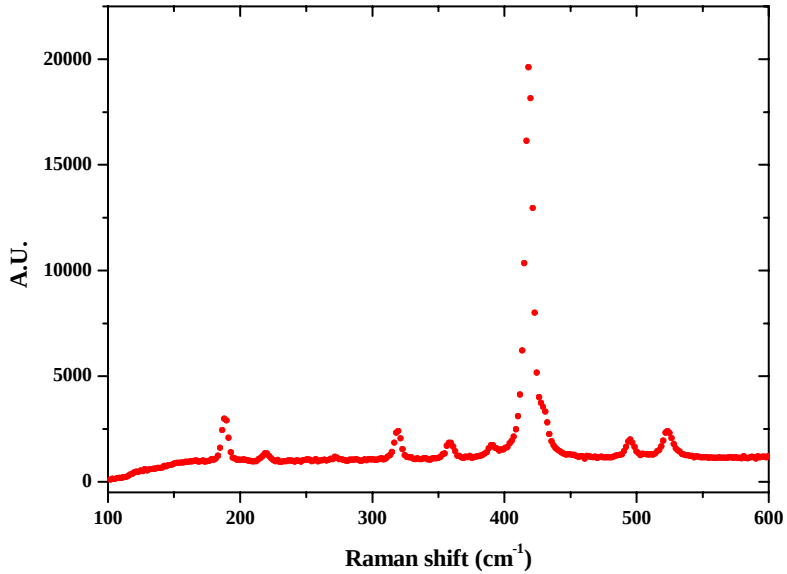
First example : Scandium Oxide

Observed modes (cm-1)
180
212
270
318
362
385
422
444
493
515

Modes : 10

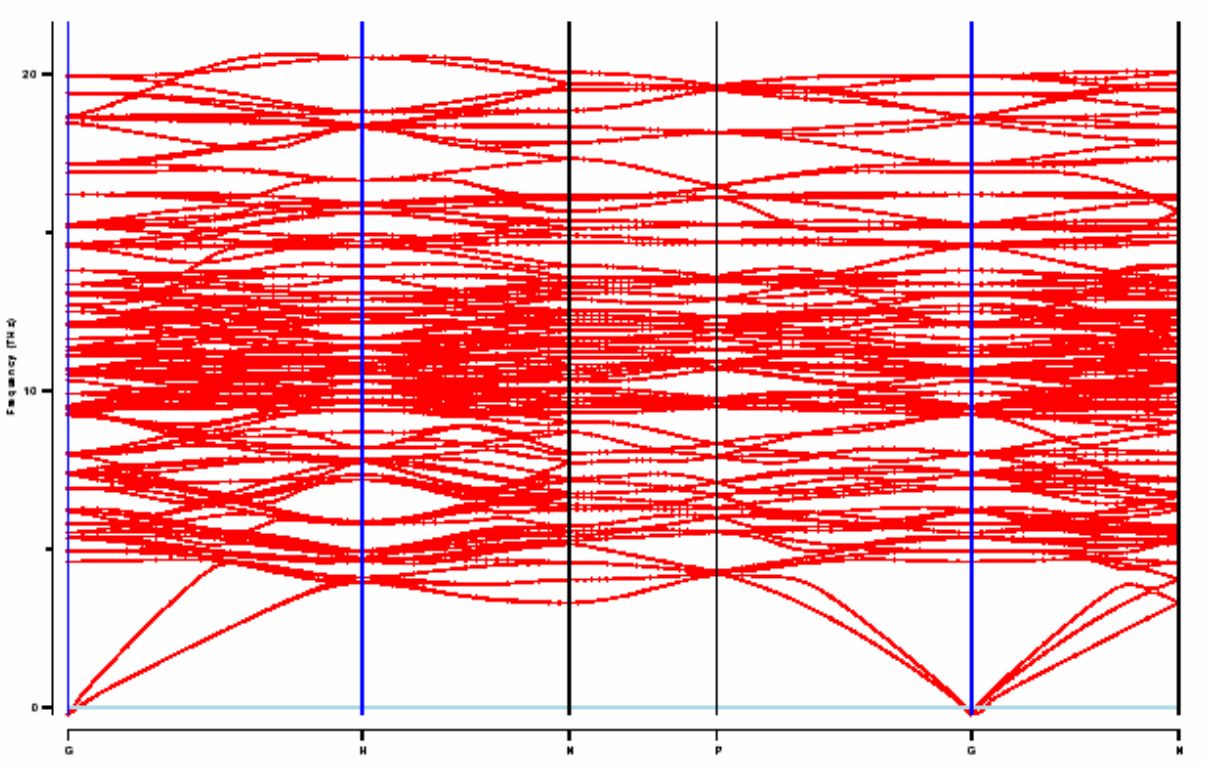
Experimental Conditions

Laser : Ar/Kr (514.5 nm)
Micro Raman on a polycrystalline sample



Calculated phonon modes

First example : Scandium Oxide



MEDEA

(VASP and Phonon)

Default VASP parameters

Using GGA-PBE / PAW

Supercell with 80 atoms

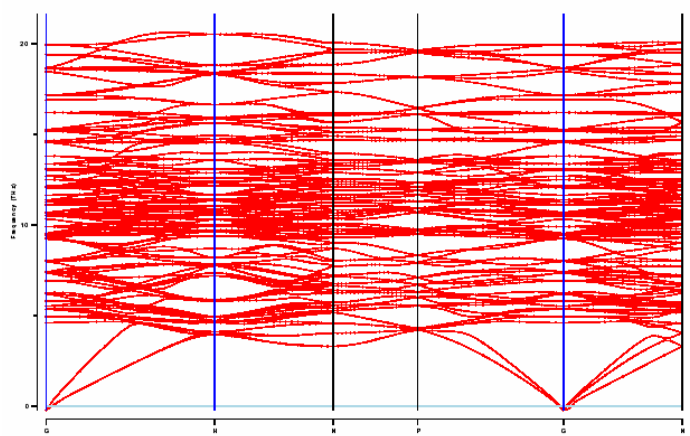
GGA-PBE
Generalized Gradient Approximation
by Perdew, Burke and Enzenhofer

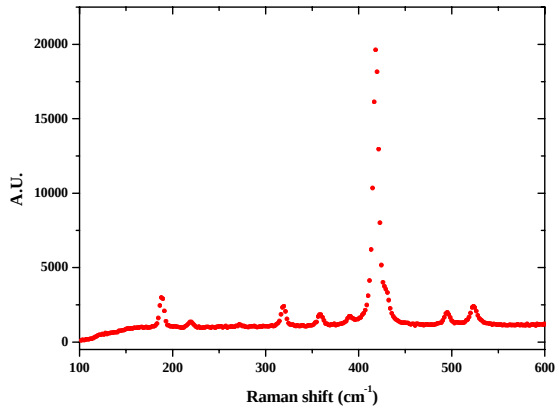
PAW
Plane augmented Waves

Calculated and observed phonon modes

First example : Scandium Oxide

Multiplicity	ω (Thz)	ω (cm-1)	Observed modes (cm-1)	Irreductible representation
3	-0,20	-7		Tu(I)
1	4,62	155		Au
3	4,95	166		Tu(I)
3	5,37	180	180	Tg(R)
2	5,53	185		Eu
3	5,81	195		Tg(R)
3	6,20	208		Tu(I)
1	6,25	210	212	Ag(R)
3	6,92	232		Tu(I)
3	7,38	248		Tg(R)
3	7,40	248		Tu(I)
3	8,00	268		Tu(I)
2	8,04	269	270	Eg(R)
3	9,22	309		Tu(I)
1	9,29	311		Au
3	9,42	316	318	Tg(R)
3	9,52	319		Tg(R)
2	9,54	320		Eu
3	9,91	332		Tu(I)
1	10,33	346		Au
3	10,51	352	362	Tg(R)
2	10,63	356		Eg(R)
3	10,63	357		Tg(R)
3	10,70	359		Tu(I)
3	11,12	373		Tu(I)
3	11,27	378	385	Tg(R)
3	11,38	382		Tu(I)
1	11,64	390		Ag(R)
2	12,06	404		Eu
3	12,14	407		Tu(I)
3	12,50	419	422	Tg(R)
2	12,69	426		Eg(R)
2	13,04	437		Eu
3	13,11	440		Tu(I)
3	13,36	448	444	Tg(R)
3	13,80	463		Tu(I)
4	14,55	488	493	Ag(R) + Tg(R)
1	14,64	491		Au
3	15,19	509		Tu(I)
3	15,27	512	515	Tg(R)
3	16,19	543		Tu(I)
1	16,89	566		Au
3	17,16	576		Tg(R)
1	18,45	619		Ag(R)
3	18,63	625		Tu(I)
2	18,66	626		Eg(R)
2	19,38	650		Eu
3	19,93	668		Tg(R)





Calculated Modes : 120

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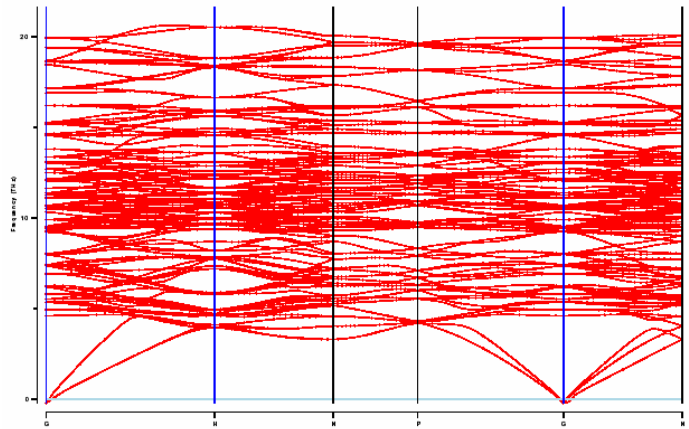
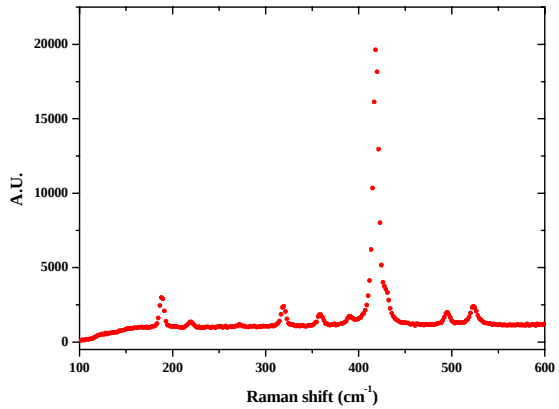
Calculated and observed phonon modes

First example : Scandium Oxide

Multiplicity	ω (Thz)	ω (cm-1)	Observed modes (cm-1)	Irreductible representation
3	5,37	180	180	Tg(R)
3	5,81	195		Tg(R)
1	6,25	210	212	Ag(R)
3	7,38	248		Tg(R)
2	8,04	269	270	Eg(R)
3	9,42	316	318	Tg(R)
3	9,52	319		Tg(R)
3	10,51	352	362	Tg(R)
2	10,63	356		Eg(R)
3	10,63	357		Tg(R)
3	11,27	378	385	Tg(R)
1	11,64	390		Ag(R)
3	12,50	419	422	Tg(R)
2	12,69	426		Eg(R)
3	13,36	448	444	Tg(R)
4	14,55	488	493	Ag(R) + Tg(R)
3	15,27	512	515	Tg(R)
3	**17,16**	**576**		**Tg(R)**
1	**18,45**	**619**		**Ag(R)**
2	**18,66**	**626**		**Eg(R)**
3	**19,93**	**668**		**Tg(R)**





Calculated Raman Active Modes :

54

Some Previous Conclusions

Coupling Experimental and Computational Tools

For this example seems to be OK

Our interest:

Precise identification of the modes corresponding to the tested structure

Some observed modes are experimentally “degenerated” (example : 362 cm^{-1})

And now?:

Performing high resolution polarized Raman spectrometry on a monocrystal to test the selection rules.

That’s very promising!

Crystallography

Second example : Uranium Oxide

Interests :

1) Well known structure

2) Good candidate to validate the calculation setup for further uranium derivatives

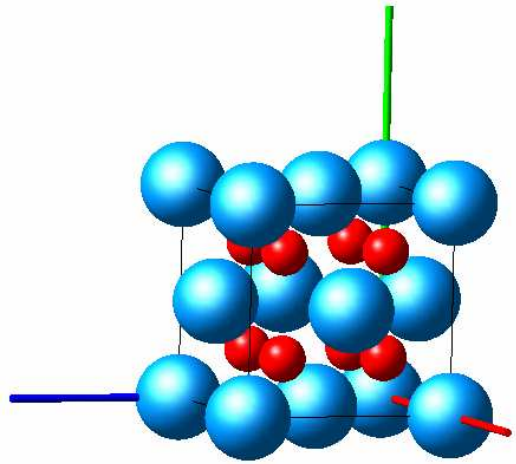
Cell parameters:

Parameter	Value
a	5.4682
b	5.4682
c	5.4682
alpha	90
beta	90
gamma	90

Density: 10.969 Mg/m^3

Crystal point group O_h (m3m)

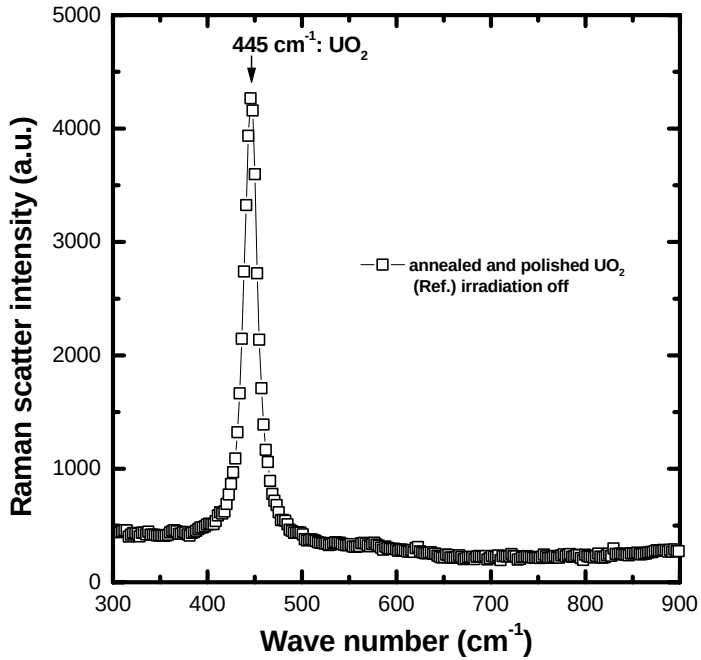
Cubic



Fluorine structure

Experimental Spectrum

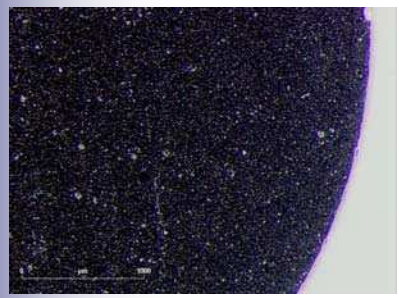
Second example : Uranium Oxide



Experimental Conditions

Laser : Ar/Kr (647 nm)
Micro Raman on a polycrystalline sample

Raman ex-situ : no irradiation



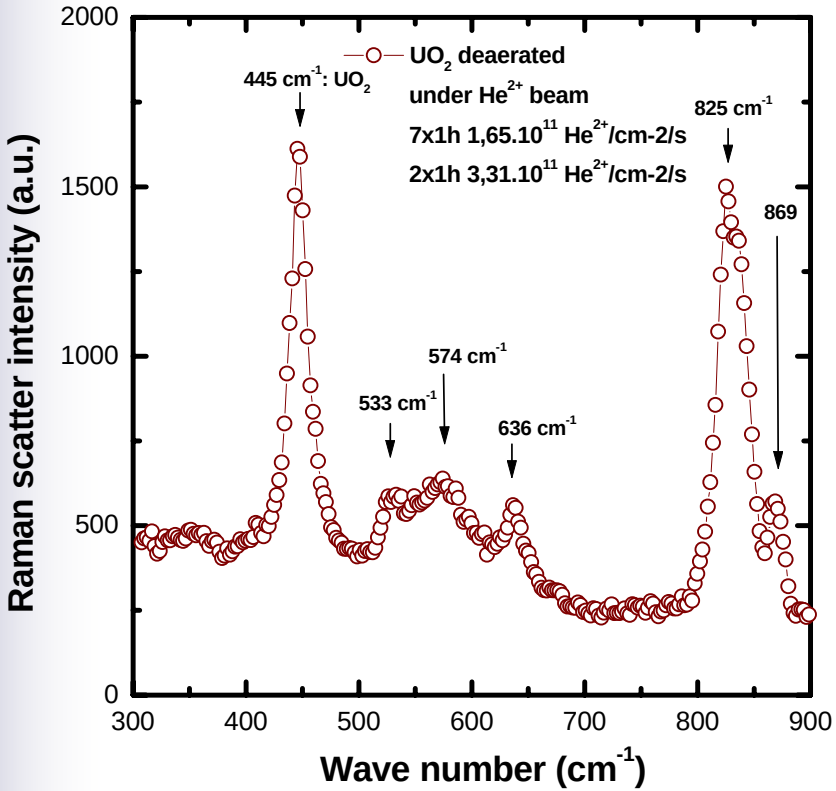
1 mode 445 cm^{-1} : UO_2
(1 active Raman mode for Fluorine structure)

(G. Allen et al. 1987)

No surprise, our samples are pure

Experimental Spectrum

Second example : Uranium Oxide



Expérimental Conditions

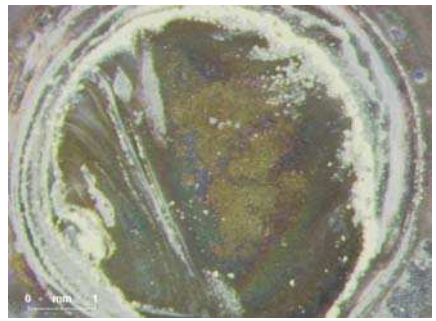
Laser : Ar/Kr (647 nm)
Micro Raman on a polycrystaline sample

Raman ex-situ : after irradiation He^{2+} +H_2O

1 mode 445 cm^{-1} : UO_2
(1 active Raman mode for fluorine structure)

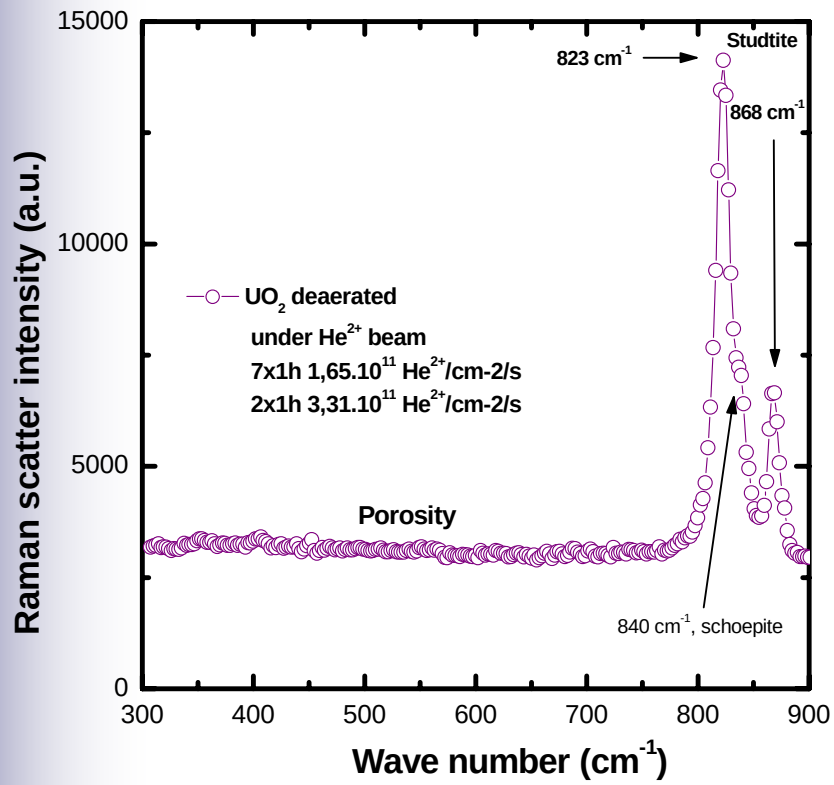
But :

New modes appear !



Experimental Spectrum

Second example : Uranium Oxide



Usual assignments

825 et 868 cm^{-1}
Studtite
$UO_2O_2.4H_2O$

840 cm^{-1}
Schoepite $UO_3.2H_2O$

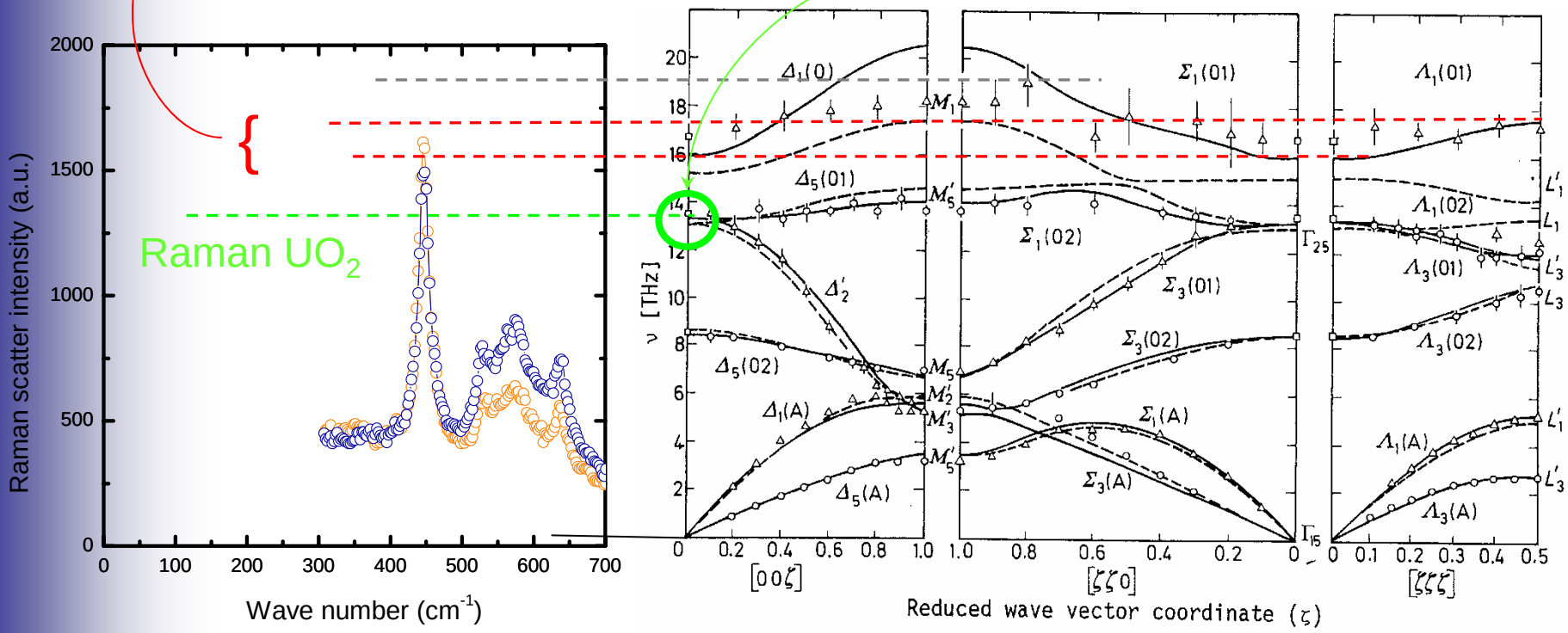
These assignments are not attributed to some particular modes.
Experimentally more precise Raman experiments are not possible at the moment :
Radioactive materials and no very stable in time.

Second example : Uranium Oxide

Experimental Spectrum and Phonons

local disorder → Partial lifting of the Raman selection rules

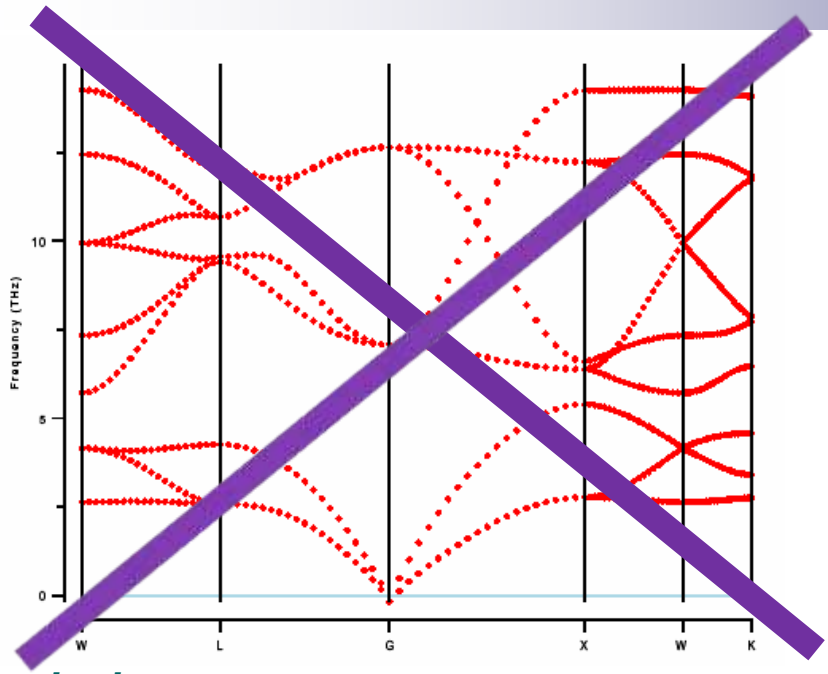
UO_2 - fluorine : 1 Raman mode



Phonons dispersion curves (inélastiques neutrons)
Dolling, Cowley et Woods, Can. J. Phys. **43**, 1397 (1965)
Cowley et Dolling, Phys. Rev. B **167**, 464 (1968)

Second example : Uranium Oxide

Calculated phonon dispersion



Default VASP parameters

Using GGA-PBE / PAW

Supercell with 96 atoms

MEDEA

(VASP and Phonon)

Conclusion:

The results are strongly wrong

Even when we are only interested by the Raman modes this approach is too optimistic

What kind of ameliorations :

Taking into account the spin orbit coupling

Taking into account the strong correlation of the electrons in this system

Perspectives

Coupling Experimental and Computational Tools
is very promising in the field of our activities

First example : Scandium Oxide – Sc_2O_3

The experiment and the simulation are in good agreement
We have to develop our experimental tool

Second Example : Uranium Oxide – UO_2

The experience opens a large field of investigations in (experimental and computational physics)
Our first approach was optimistic we have to taking into account the correlation effects (f e^-)

Difficulties :

The experiments are very difficult to perform : in the future we will try to made in-situ time resolved Raman Measurements
The systems contain a lot of atoms and their computational treatment increases the “computer cost” every time we try to be more precise (coupling, correlation…)

Thanks a lot for your attention

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