

# Raman spectra simulation using first principles methods

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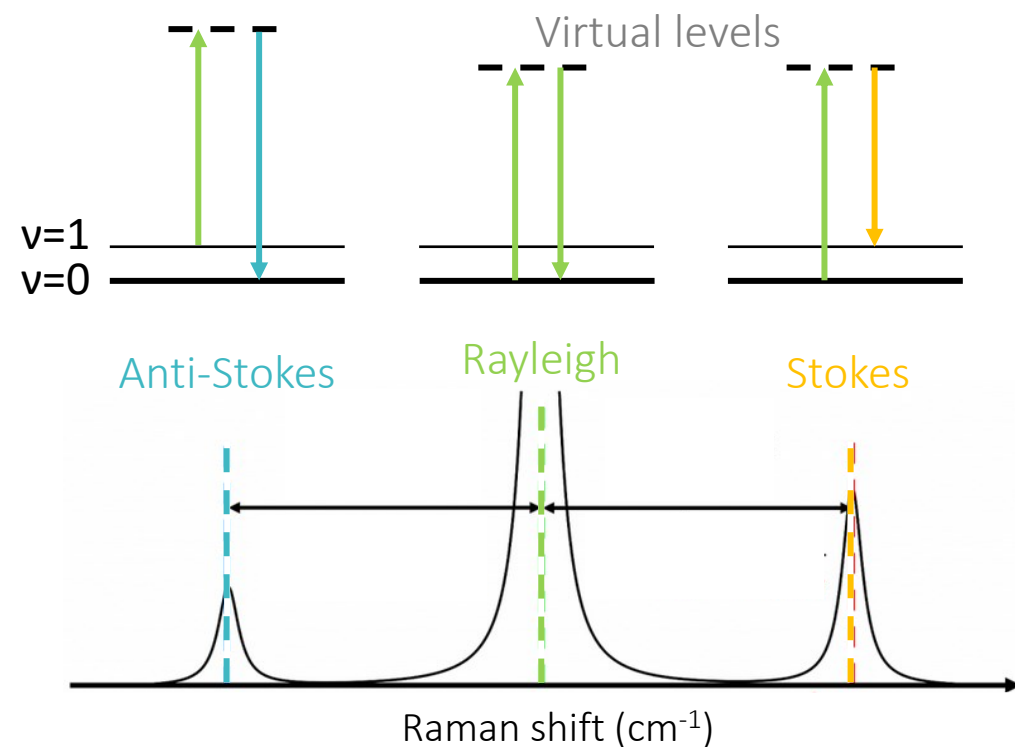
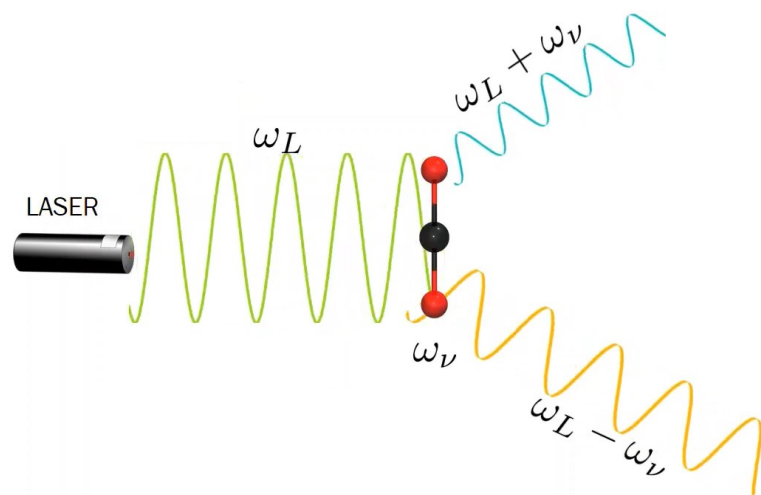
1. Brief introduction to Raman spectroscopy
2. What do we need to calculate Raman spectra ?
3. Density functional theory (DFT) methods
  - $\text{TiO}_2$  bulk
  - $\text{TiO}_2$  nanocrystals
  - Polystyrene
4. Ab initio molecular dynamics (AIMD)
5. Summary

# Brief introduction to Raman spectroscopy

Raman spectroscopy probes vibrational states of a material. It is based on inelastic scattering of light.

## Scattering of light :

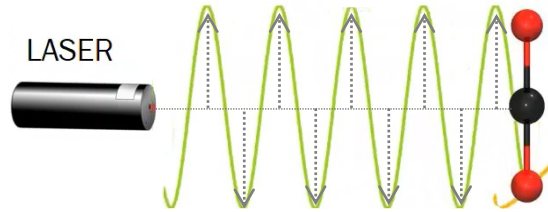
- Predominantly it is an **elastic scattering: Rayleigh**
- **Inelastic scattering of light : RAMAN**



Frequency difference between incident and scattered light corresponds to a vibrational state.

# Raman spectroscopy in more detail

## Oscillating electromagnetic wave



Electric field  $E$  interacts with electrons and perturbs electron cloud.  
The ability of electrons to be deformed under external electric field is called **polarizability**.

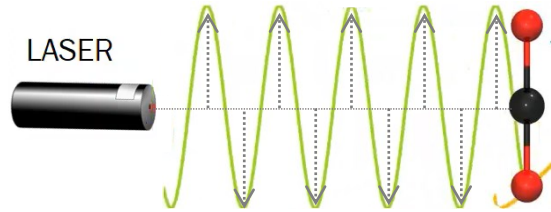


Perturbation of electron distribution can induce movement of ions (vibrations)



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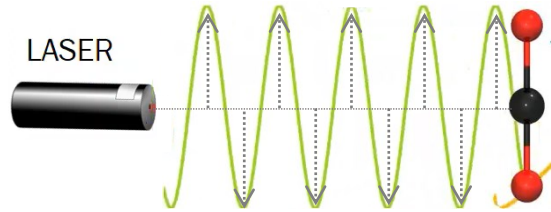


Light induces oscillating electric dipole in a material

$$\mathbf{p} = \alpha \cdot \mathbf{E}$$

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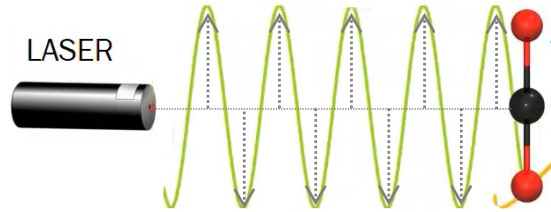
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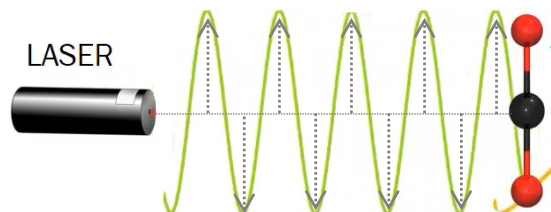
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Electric field applied along x direction induces polarization in all directions, each having their own polarizability constant

$$P_x = \alpha_{xx} E_x \quad P_y = \alpha_{yx} E_x \quad P_z = \alpha_{zx} E_x$$

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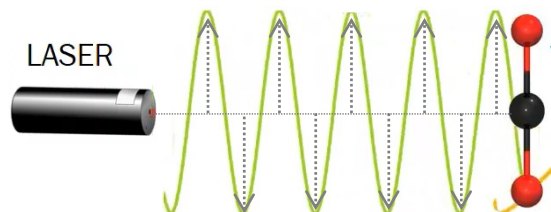
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$\alpha$  polarizability is a property of a material and depends on type of atoms and on the **bond distance**

$\alpha$  is a function of the nuclear coordinates and hence it is a function of atomic vibrational frequencies, i.e., If the polarizability is changing then it will oscillate at the same frequency that the atoms are vibrating

For a mode to be Raman active it must involve a change in the polarizability when the atoms are vibrating.

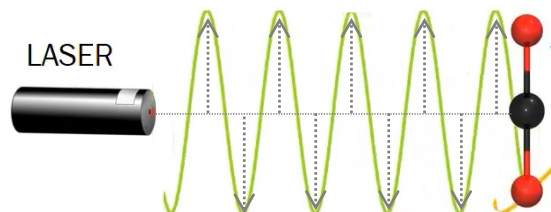
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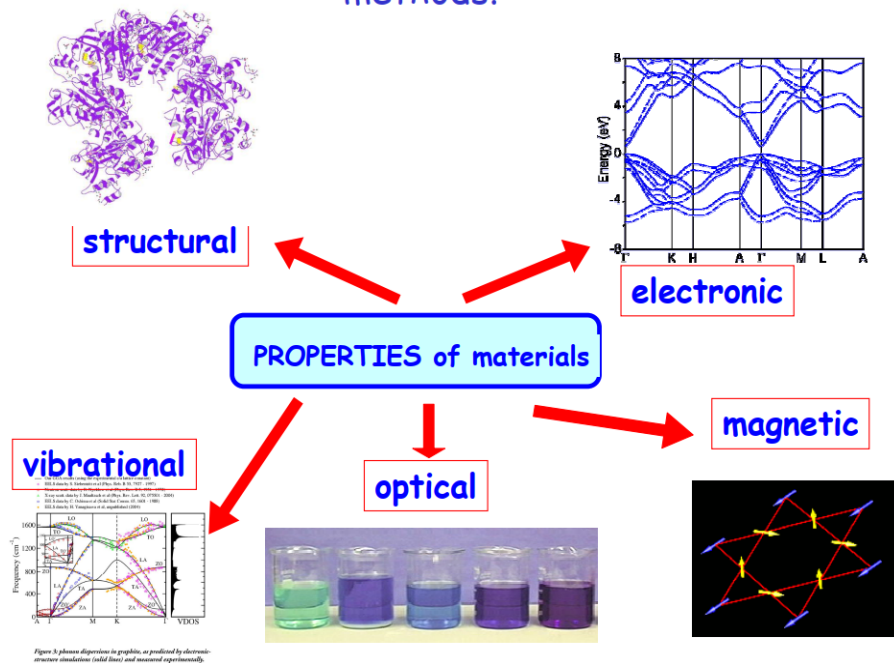
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We need to find a way to calculate **atomic vibrations** (give Raman frequencies) and the **change of polarizability** (give Raman intensities)

# Ab initio methods – from first principles

Goal: Describe properties of matter from ab initio methods.



In principle all properties of molecular system can be calculated starting from **Schrodinger equation** without need of experimental input; so, called *ab initio* „from first principles”

$$H\Psi = E\Psi$$



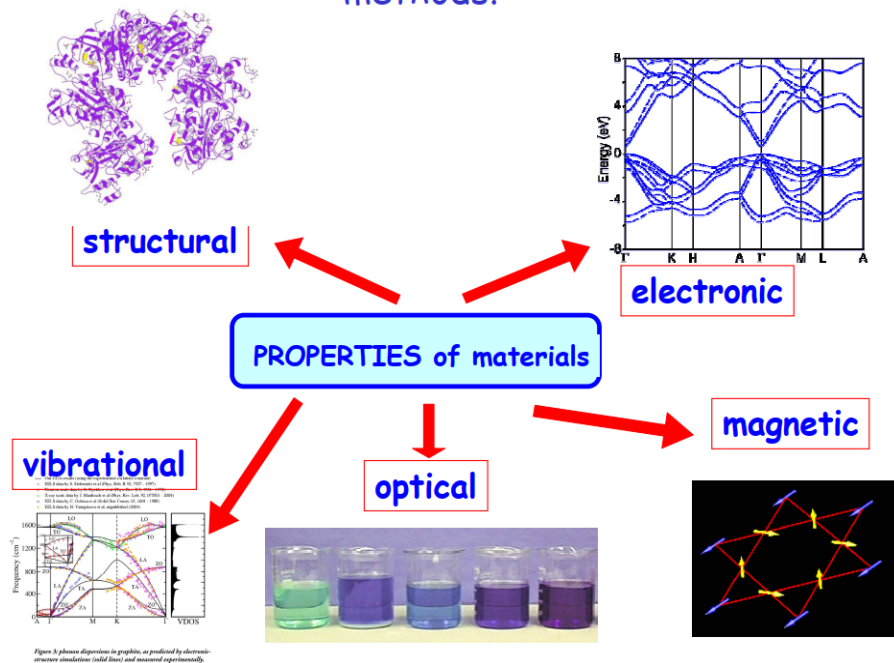
- Many body equation that includes all the interactions in a physical system
- We can get system observables (properties) when we evaluate total wave function)

Quantum Mechanics

$$\left[ -\sum_i^n \frac{1}{2} \Delta_i - \sum_a^m \frac{1}{2} \Delta_a + \sum_{i<j}^n \frac{1}{r_{ij}} + \sum_{a<b}^m \frac{Z_a Z_b}{R_{ab}} - \sum_i^n \sum_a^m \frac{Z_a}{r_{ia}} \right] \Psi(x_1 \cdots x_n X_1 \cdots X_m) = E\Psi(x_1 \cdots x_n X_1 \cdots X_m)$$

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→ No analytical solution!!

# Basics of Density Functional Theory (DFT)

Computational method that allows to investigate the electronic structure of many-body system, in particular atoms, molecules and the condensed phases.

## Basic assumptions that were made :

- **Decouple the electronic and nuclear degrees of freedom** nuclei are much heavier and thus much slower than electrons;
- Any property of a system can be evaluated from the system's ground state density instead of its full wave function.
- Ground state density of the many-body interacting system can be mapped on density of an auxiliary non-interacting independent particle system

Kohn-Sham equations

$$\left[ -\frac{\hbar^2}{2m} \nabla^2 + V_{\text{eff}}(\mathbf{r}) \right] \psi_i(\mathbf{r}) = \varepsilon_i \psi_i(\mathbf{r})$$

$$n(\mathbf{r}) = \sum_i^N f_i |\psi_i(\mathbf{r})|^2$$

$$V_{\text{eff}}[n(\mathbf{r})] = V_{\text{ext}}(\mathbf{r}) + V_H[n(\mathbf{r})] + V_{xc}(\mathbf{r})[n(\mathbf{r})]$$

Exchange-correlation potential

## Density Functional Theory

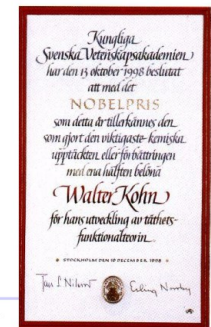
PHYSICAL REVIEW VOLUME 140, NUMBER 4A 15 NOVEMBER 1965

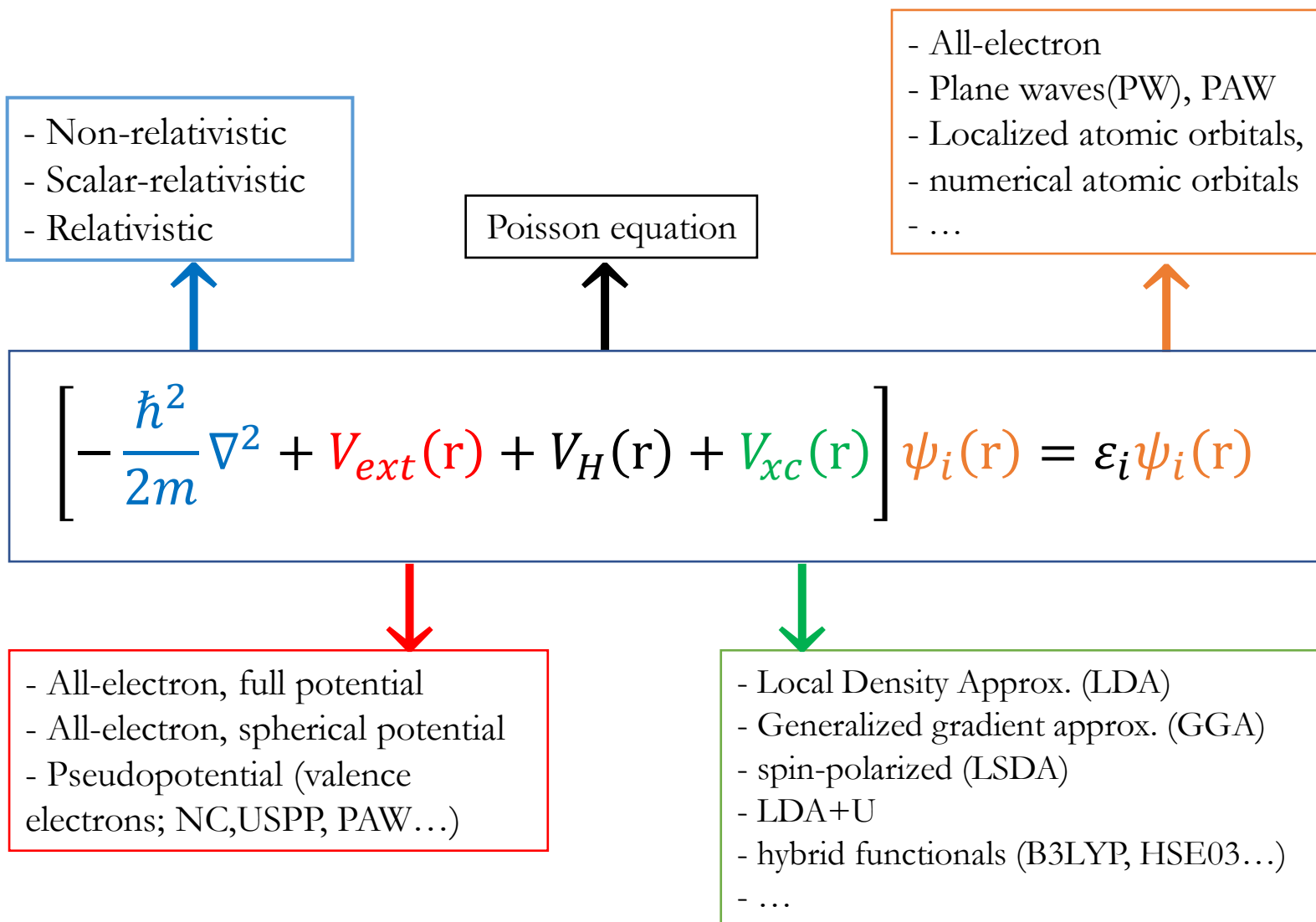
### Self-Consistent Equations Including Exchange and Correlation Effects\*

W. KOHN AND L. J. SHAM

main source of error. We do not expect an accurate description of chemical binding. In large atoms, of course,

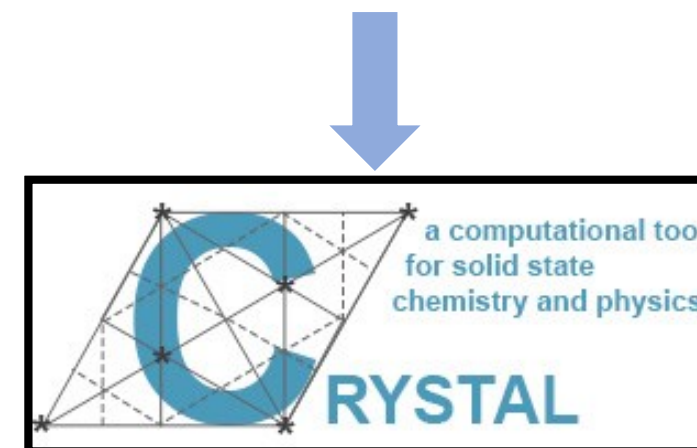
**Density functional theory is the most widely used method today for electronic structure calculations because of the approach proposed by Kohn and Sham**





## DIFFERENT DFT CODES AVAILABLE :

VASP, Quantum Espresso, ABINIT,  
CRYSTAL, GAUSSIAN, FHI-AIMES, CP2K,  
CASTEP, SIESTA, NewChem...

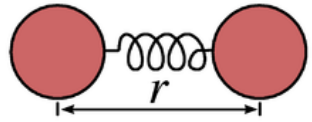


We need supercomputers !



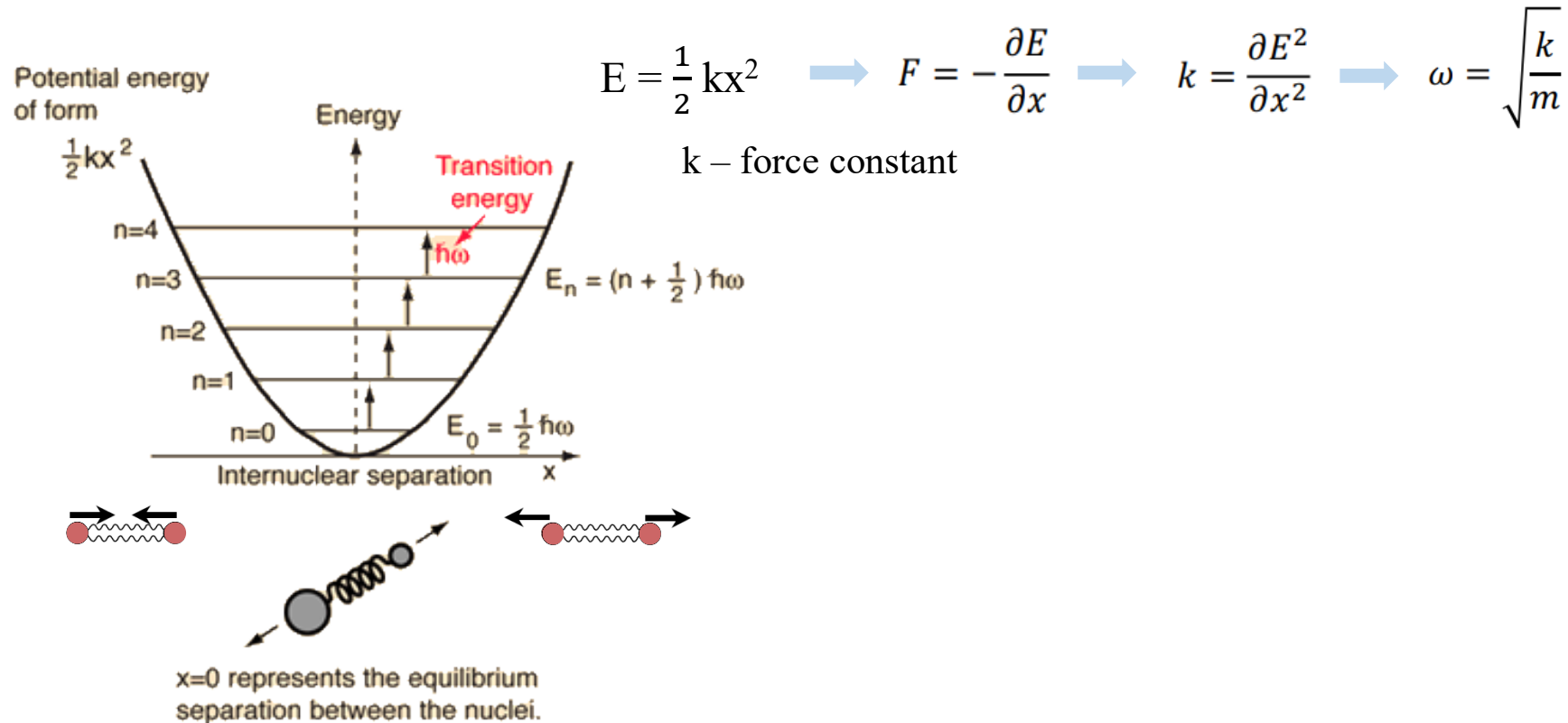
1. **Create a structural model corresponding to system that you want to study.**
2. **Optimize your structure** to be in minima of potential energy surface (Very important!).
3. Compute the normal modes of vibrations.
4. Compute the mode activity: **change of polarizability with respect to the normal modes displacements.**
5. Convolute the spectra with Gaussian or Lorentzian function to plot it.

# Atomic vibrations (normal modes)



## Simple case:

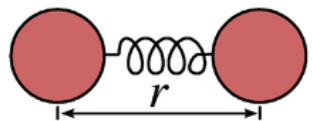
Vibrating diatomic molecule can be described as a harmonic oscillator



Vibrational frequency doesn't change ! Amplitude of vibration increases



# Atomic vibrations (normal modes)

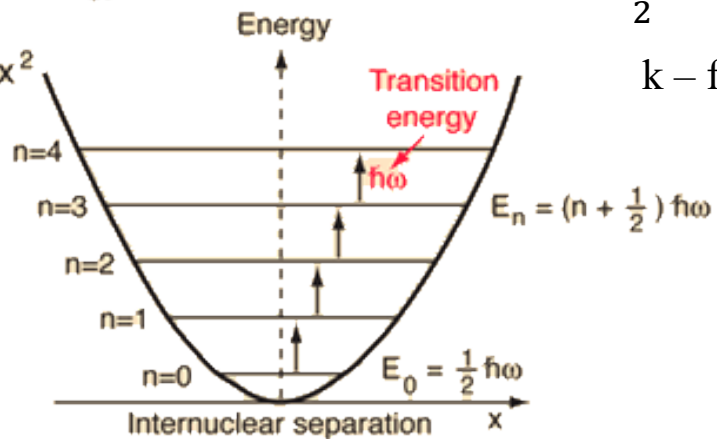


**Simple case:**

Vibrating diatomic molecule can be described as a harmonic oscillator

Potential energy of form

$$\frac{1}{2}kx^2$$



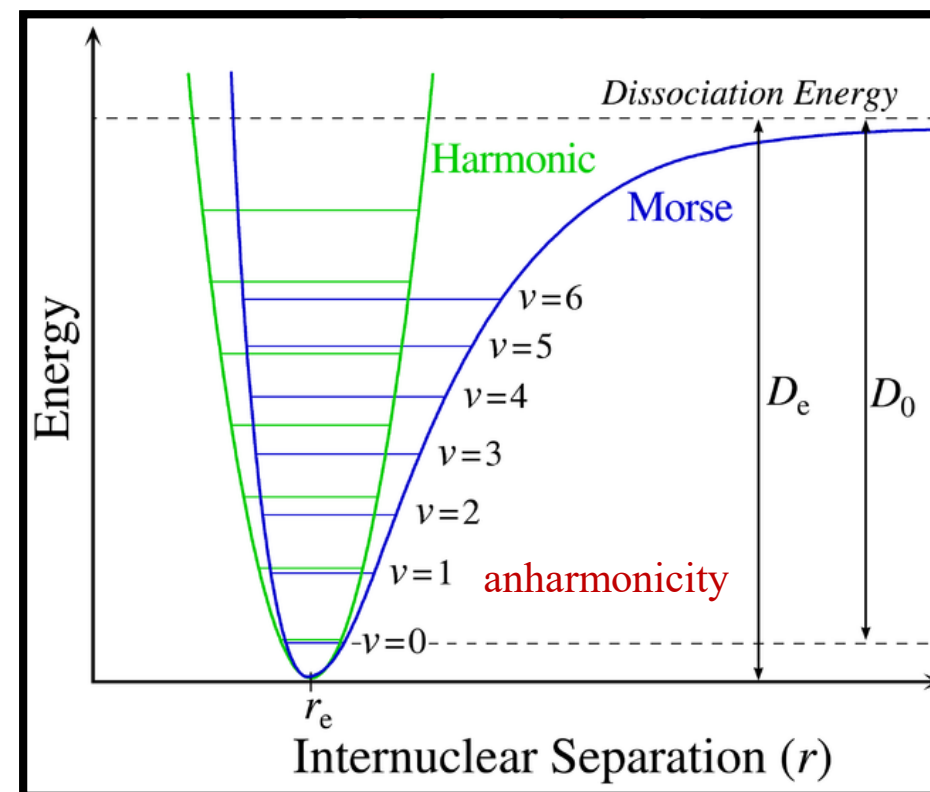
$$E = \frac{1}{2}kx^2 \quad \rightarrow \quad F = -\frac{\partial E}{\partial x} \quad \rightarrow \quad k = \frac{\partial^2 E}{\partial x^2} \quad \rightarrow \quad \omega = \sqrt{\frac{k}{m}}$$

k – force constant

Vibrational frequency doesn't change ! Amplitude of vibration increases

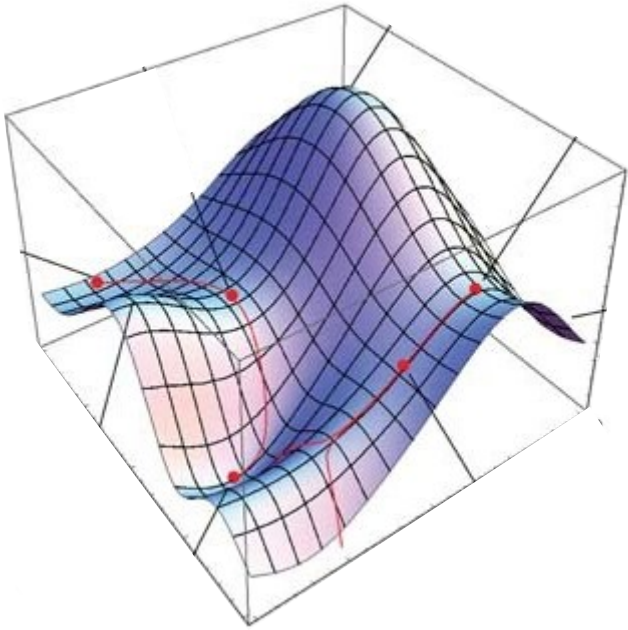


$x=0$  represents the equilibrium separation between the nuclei.



# Atomic vibrations (normal modes)

More realistic case



**Potential Energy Surface (PES)** can be quite complicated function of atomic positions.

But we still want to use harmonic approximation – we need to be in minimum of potential energy Surface (structure has to be optimized) !

We need to calculate force constants to get the frequencies !

Force constants  $\rightarrow$  matrix of second derivatives of energy with respect to atomic displacements (**Hessian matrix**)

$$\mathbf{H}_f = \begin{bmatrix} \frac{\partial^2 f}{\partial x_1^2} & \frac{\partial^2 f}{\partial x_1 \partial x_2} & \cdots & \frac{\partial^2 f}{\partial x_1 \partial x_n} \\ \frac{\partial^2 f}{\partial x_2 \partial x_1} & \frac{\partial^2 f}{\partial x_2^2} & \cdots & \frac{\partial^2 f}{\partial x_2 \partial x_n} \\ \vdots & \vdots & \ddots & \vdots \\ \frac{\partial^2 f}{\partial x_n \partial x_1} & \frac{\partial^2 f}{\partial x_n \partial x_2} & \cdots & \frac{\partial^2 f}{\partial x_n^2} \end{bmatrix}$$

3Nx3N matrix  
N-number of atoms

Hessian has to be diagonalized to obtain normal modes of vibration and frequencies !

Computationally expensive step (cost increases with the system size.)

**From DFT – Energy !**

## Assumptions:

- non-resonant conditions
- transition intensity depends only on wave functions of initial and final states (Placzek approximation )

Raman intensity  $I_{xy}^{\nu}$  for an oriented single-crystal associated to the mode with frequency  $\omega_{\nu}$  is given by :

$$I_{xy}^{\nu} \propto C \left( \frac{\partial \alpha_{xy}}{\partial Q_{\nu}} \right)^2$$

Change of polarizability tensor  $\alpha_{xy}$  with respect to normal modes displacements  $Q_{\nu}$ !

The prefactor C contains the laser frequency  $\omega_L$  and the temperature T dependence as follows

$$C \sim (\omega_L - \omega_{\nu})^4 \frac{1 + n(\omega_{\nu})}{30\omega_{\nu}}$$

where the Bose occupancy factor  $n(\omega_{\nu})$  is given by

$$1 + n(\omega_{\nu}) = \left[ 1 - \exp\left(-\frac{\hbar\omega_{\nu}}{K_B T}\right) \right]^{-1}$$

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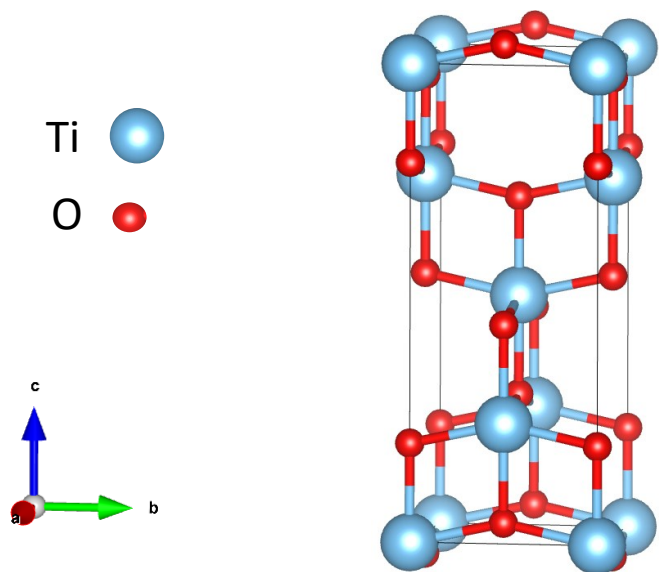
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The calculation of RAMAN intensities concerns single-crystal, but **CRYSTAL** automatically performs also the simulation of powder samples by computing integrals over all possible orientations of ideal bulk crystals.

# EXAMPLE 1 : bulk TiO<sub>2</sub> anatase

Let's start with something that is well known: Anatase form of TiO<sub>2</sub> with well defined structure and known Raman spectra

TiO<sub>2</sub> Anatase



Space group:  $I4_1/amd$  (141)

Six Raman active vibrations

$$A_{1g} + 2B_{1g} + 3E_g$$

CRYSTAL input file

```
anatase
CRYSTAL
0 0 1
141 .....> Space group number
3.785 9.515 .....> Lattice parameters
2 .....> Number of atoms in the
22 0.0 0.0 0.0 } cell
8 0.0 0.0 0.2066 } Atomic number and positions of atoms (direct coords)
OPTGEOM
END
END
```

We work using periodic boundary conditions !

# EXAMPLE 1 : bulk TiO<sub>2</sub> anatase

What information can we get from calculations?

Mode symmetry IR or Raman active

CRYSTAL output file

Modes	EIGV	FREQUENCIES	IRREP	IR INTENS	RAMAN
	(HARTREE**2)	(CM**-1) (THZ)		(KM/MOL)	
1- 1	0.0000E+00	0.0000 0.0000	(A2u)	A ( 0.00)	I
2- 3	0.1190E-21	0.0000 0.0000	(Eu)	A ( 0.00)	I
4- 5	0.3139E-06	<b>122.9715</b> 3.6866	(Eg)	I ( 0.00)	<b>A</b>
6- 7	0.6346E-06	<b>174.8333</b> 5.2414	(Eg)	I ( 0.00)	<b>A</b>
8- 9	0.9674E-06	<b>215.8729</b> 6.4717	(Eu)	A ( 7251.58)	I
10- 10	0.1938E-05	<b>305.5233</b> 9.1594	(A2u)	A ( 3485.00)	I
11- 11	0.2824E-05	<b>368.8387</b> 11.0575	(B1g)	I ( 0.00)	<b>A</b>
12- 13	0.3447E-05	<b>407.4995</b> 12.2165	(Eu)	A ( 4137.55)	I
14- 14	0.4970E-05	<b>489.2925</b> 14.6686	(B1g)	I ( 0.00)	<b>A</b>
15- 15	0.5170E-05	<b>499.0463</b> 14.9610	(A1g)	I ( 0.00)	<b>A</b>
16- 16	0.5726E-05	<b>525.1836</b> 15.7446	(B2u)	I ( 0.00)	I
17- 18	0.7655E-05	<b>607.2169</b> 18.2039	Eg)	I ( 0.00)	<b>A</b>

<RAMAN><RAMAN><RAMAN><RAMAN><RAMAN><RAMAN><RAMAN><RAMAN><RAMAN><RAMAN><RAMAN><RAMAN>  
<RAMAN><RAMAN><RAMAN><RAMAN><RAMAN><RAMAN><RAMAN><RAMAN><RAMAN><RAMAN><RAMAN><RAMAN>

# EXAMPLE 1 : bulk TiO<sub>2</sub> anatase

What information can we get from calculations?

```
--
POLYCRYSTALLINE ISOTROPIC INTENSITIES (ARBITRARY UNITS)

MODES  FREQUENCIES      I_tot  I_par  I_perp
-----
4- 5   122.9715 (Eg )    499.06 285.18 213.88
6- 7   174.8333 (Eg )      3.58  2.04  1.53
11- 11  368.8387 (B1g)    276.51 158.01 118.51
14- 14  489.2925 (B1g)     59.85  34.20  25.65
15- 15  499.0463 (A1g)    272.20 231.96  40.24
17- 18  607.2169 (Eg )   1000.00 571.43 428.57

--
SINGLE CRYSTAL DIRECTIONAL INTENSITIES (ARBITRARY UNITS)

MODES  FREQUENCIES      I_xx  I_xy  I_xz  I_yy  I_yz  I_zz
-----
4- 5   122.9715 (Eg )    0.00  0.00 499.07  0.00 499.05  0.00
6- 7   174.8333 (Eg )    0.00  0.00  3.58  0.00  3.58  0.00
11- 11  368.8387 (B1g)   553.02  0.00  0.00 553.02  0.00  0.00
14- 14  489.2925 (B1g)  119.70  0.00  0.00 119.70  0.00  0.00
15- 15  499.0463 (A1g)  433.14  0.00  0.00 433.14  0.00  8.55
17- 18  607.2169 (Eg )    0.00  0.00 1000.00  0.00 999.99  0.00

<RAMAN><RAMAN><RAMAN><RAMAN><RAMAN><RAMAN><RAMAN><RAMAN><RAMAN><RAMAN><RAMAN>
<RAMAN><RAMAN><RAMAN><RAMAN><RAMAN><RAMAN><RAMAN><RAMAN><RAMAN><RAMAN><RAMAN>
```

CRYSTAL output file

Info about total intensity as well as the parallel and perpendicular contributions.

Info about intensities for a single crystal.

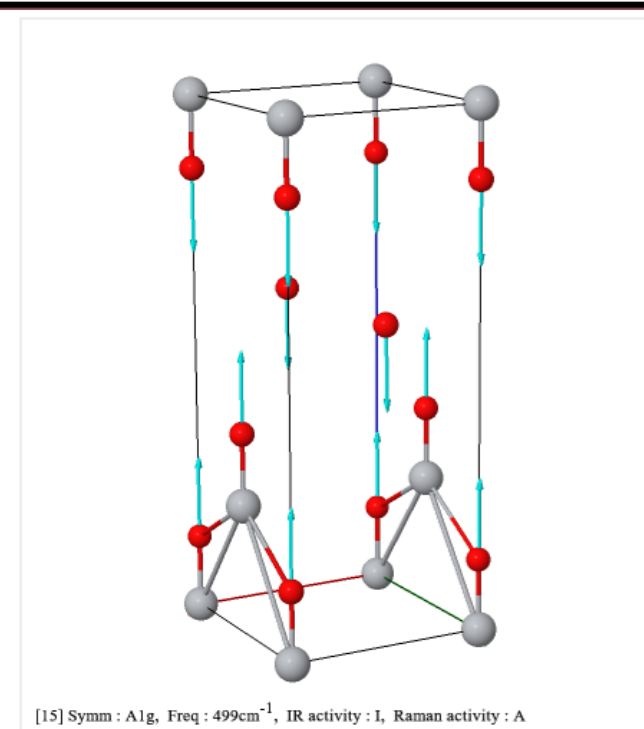
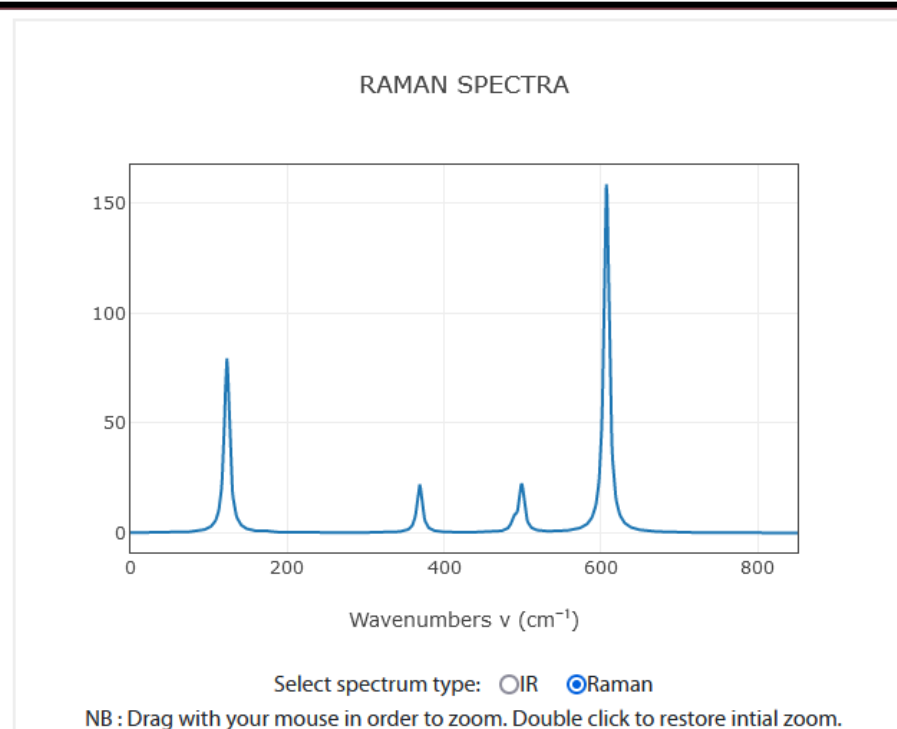
We get raw data for frequency and Raman intensity – to plot it, it has to be convoluted (this can be done automatically by the code).

# CRYSLOT

A modern and easy to use visualization environment for plotting properties of crystalline solids as computed by means of the CRYSTAL code.

[Learn more!](#)

- ✓ Online tool that can read and process directly CRYSTAL output file.
- ✓ We can visualize each mode of vibration, see what atoms are involved.
- ✓ Symmetry assignment of modes and their IR/Raman activity is done automatically by the code.



Modes

- 122.97
- 122.97
- 174.83
- 174.83
- 368.84
- 489.29
- 499.05
- 607.22
- 607.22

Filter modes

All  
 IR  
 Raman  
 Symmetry

A<sub>2u</sub>  
Eu  
E<sub>g</sub>  
B<sub>1g</sub>  
A<sub>1g</sub>

Ti O

Vibrations

Animation Scale:  1  2  3  
 Vectors Scale:  1  2  3

View

Cell  Perspective  
Along

Atoms size

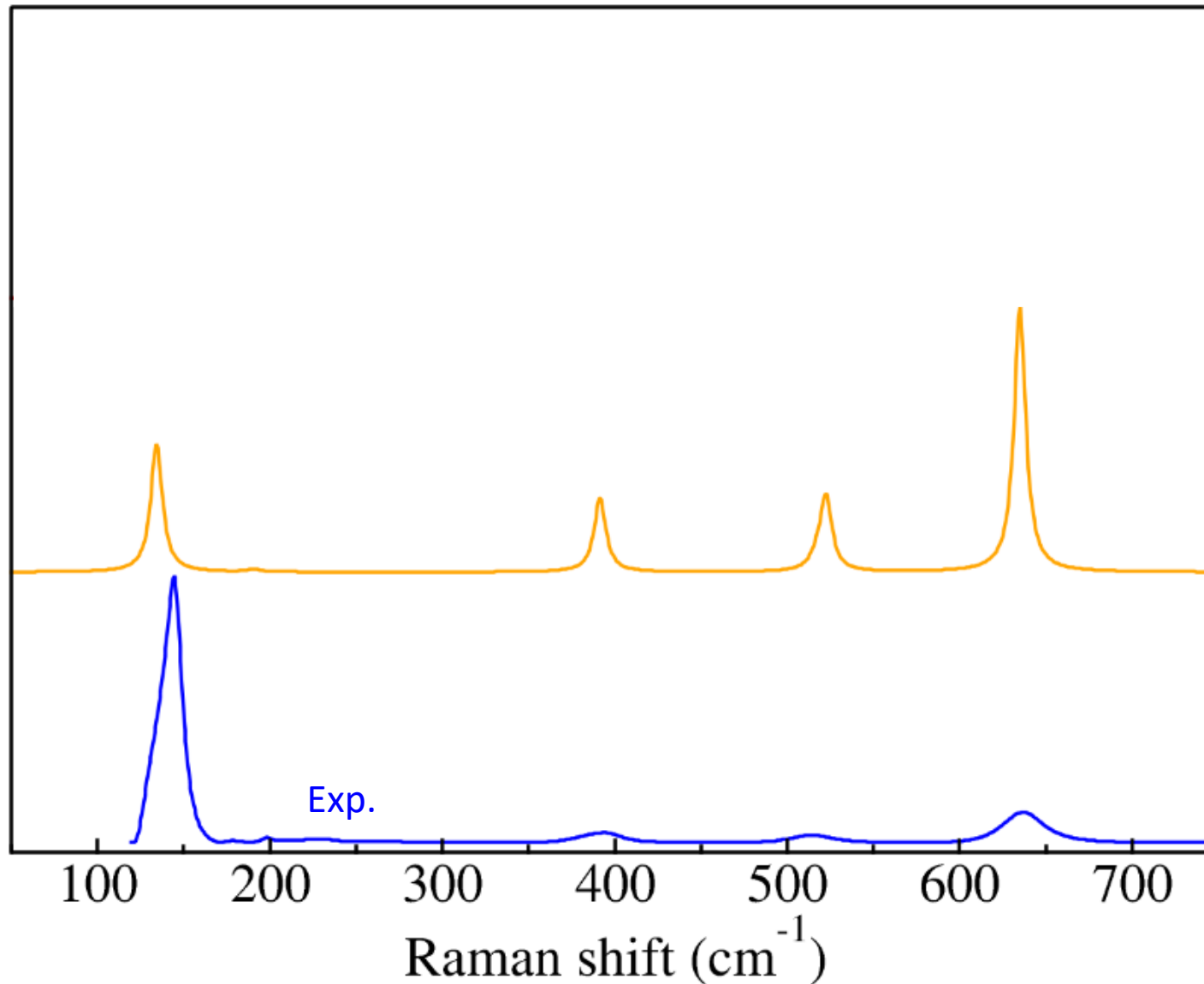
Tiny  Small  Big

Bond width

Thin  Thick



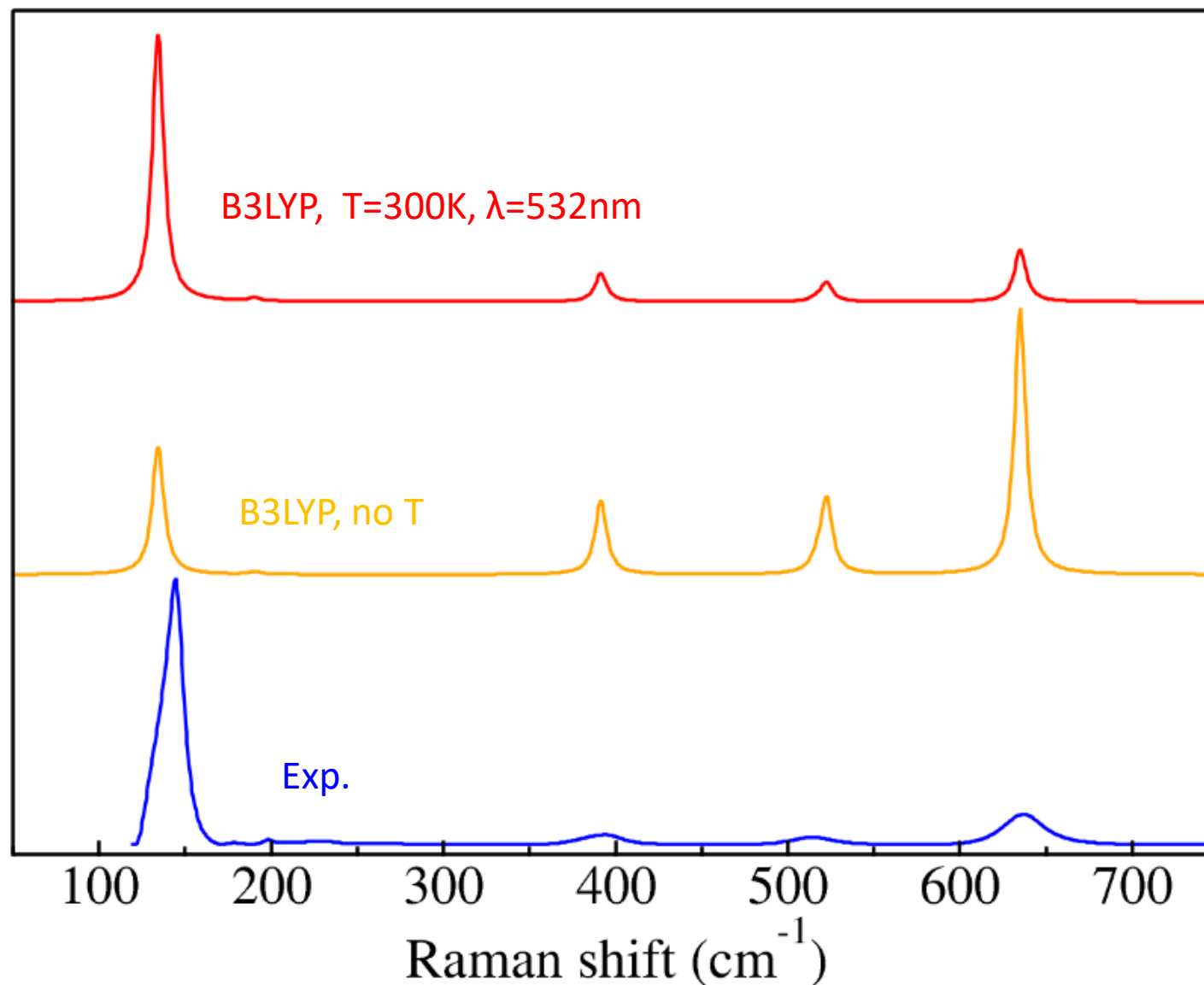
# EXAMPLE 1 : bulk TiO<sub>2</sub> anatase – theory vs experiment



Calculated frequencies are in a good agreement with experimental values.

☹ But relative intensities are not that good...

# EXAMPLE 1 : bulk TiO<sub>2</sub> anatase – theory vs experiment



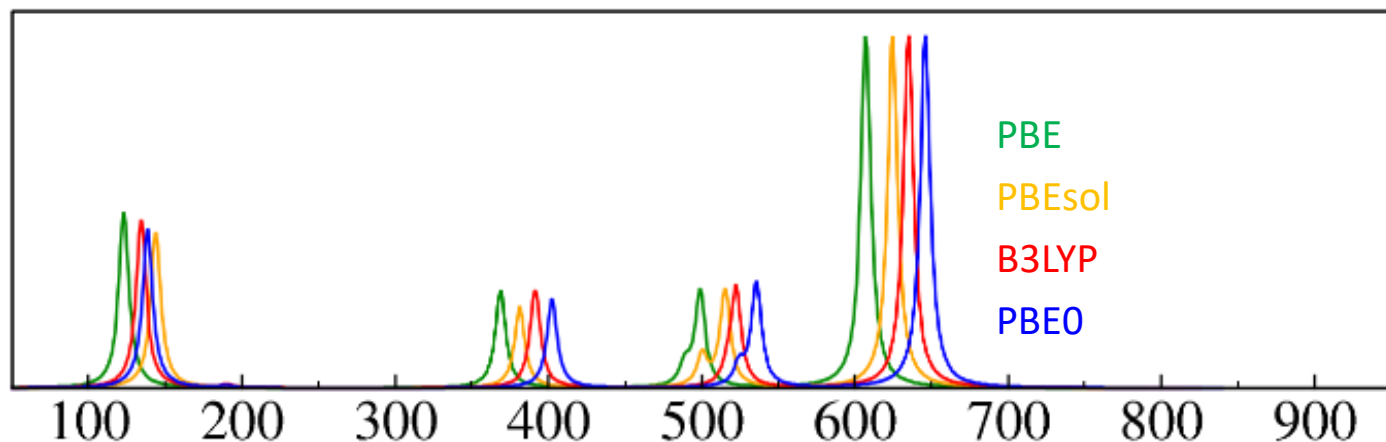
Calculated frequencies are in a good agreement with experimental values.

By including temperature & laser relative peaks intensities are changed. Frequency is not affected.

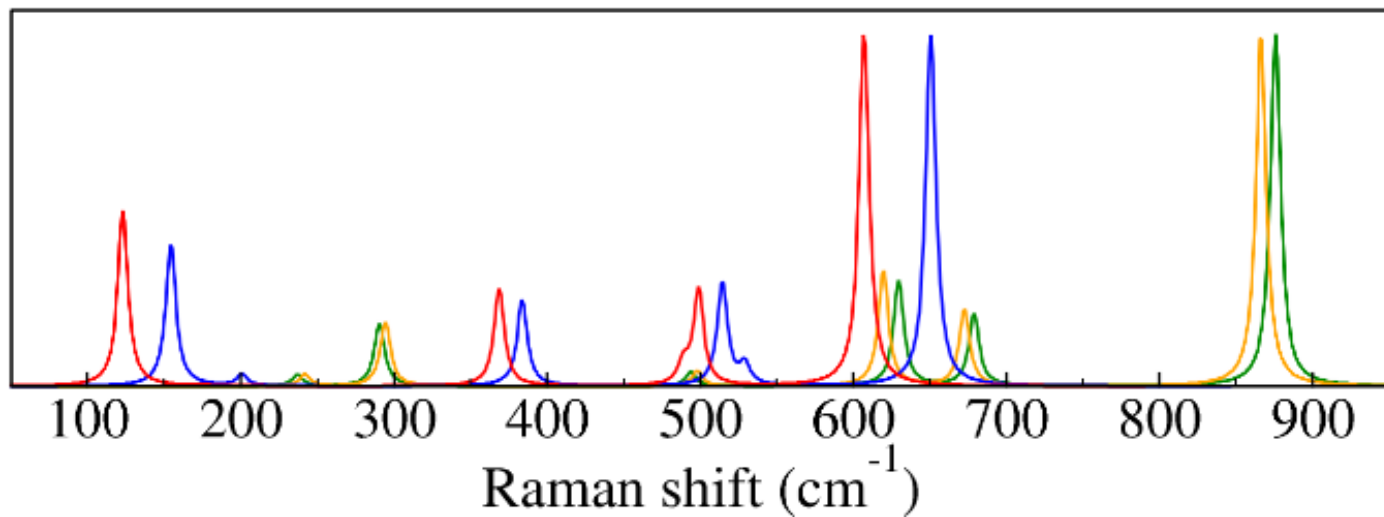
# EXAMPLE 1 : bulk TiO<sub>2</sub> anatase – computational setting

**Computational parameters are important !!!!**

Change of exchange-correlation functional or the basis set leads to shifts in frequency. Intensities are less affected.

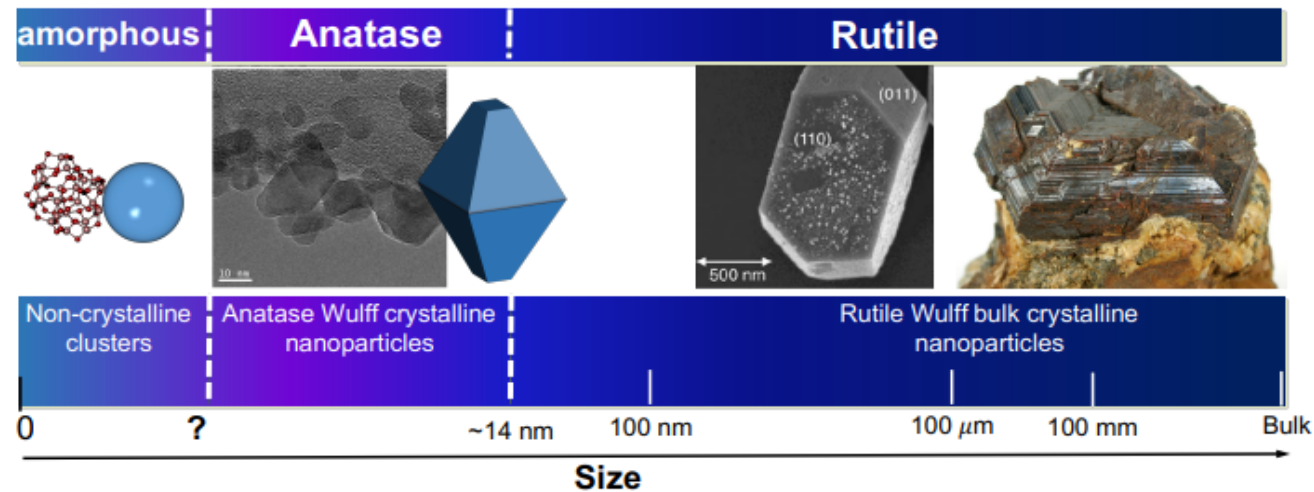


Different functional, the same basis set

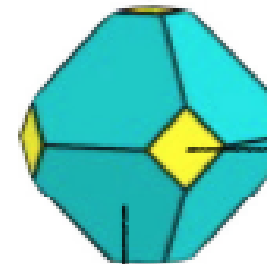


Different basis set, the same functional

# EXAMPLE 2 : TiO<sub>2</sub> nanocrystals (NC)

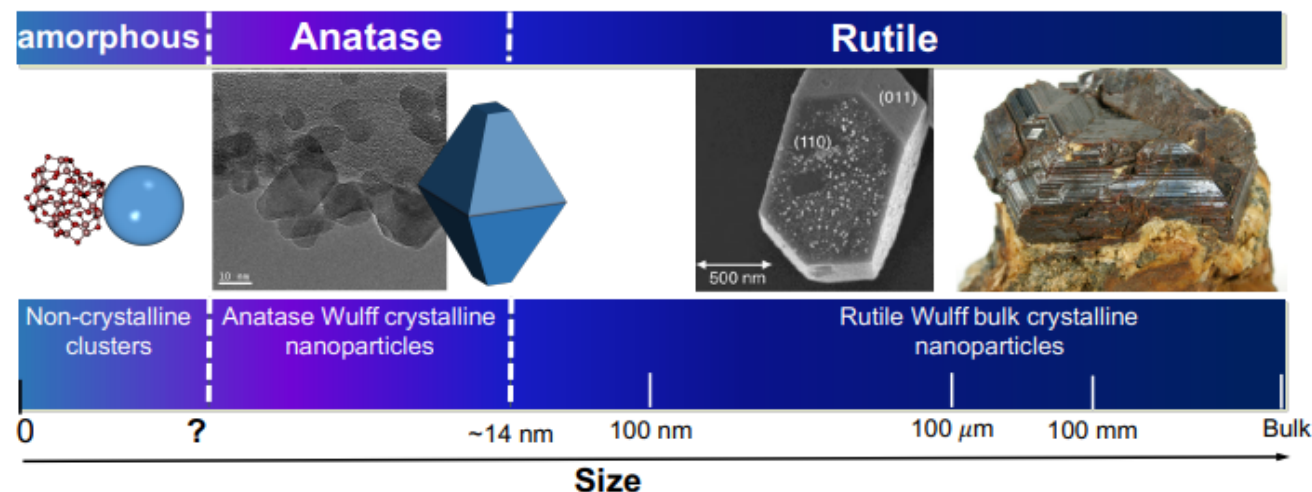


- TiO<sub>2</sub> nanoparticles are widely used in daily products (cosmetics or medicines) or in various technological applications ( for example as a catalyst).
- Properties are strongly depended on the size on NC and the surface that is exposed.
- Can different NC surfaces affect Raman spectra? Can we predict it from theory?

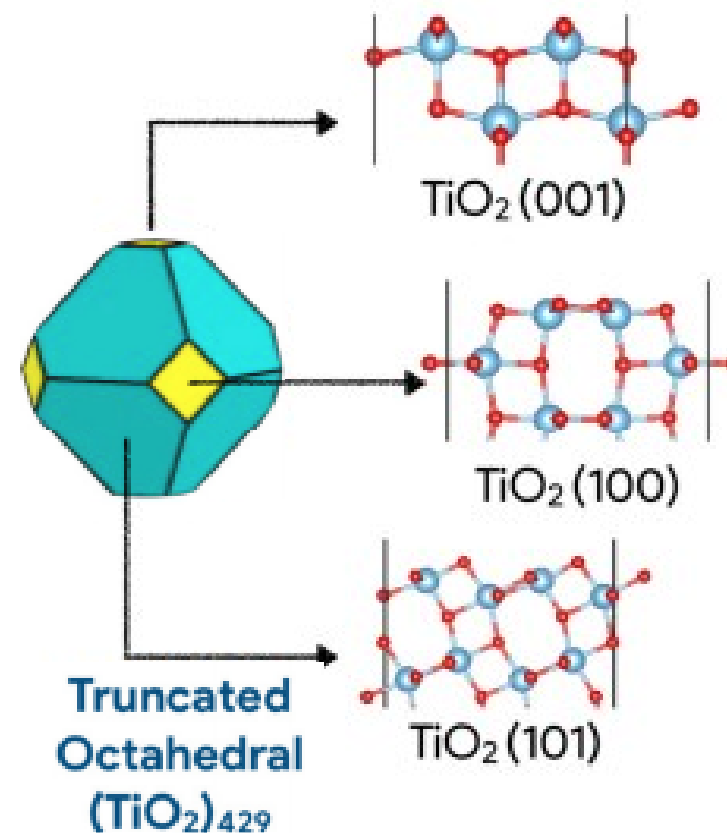


Truncated  
Octahedral  
(TiO<sub>2</sub>)<sub>429</sub>

# EXAMPLE 2 : TiO<sub>2</sub> nanocrystals (NC)



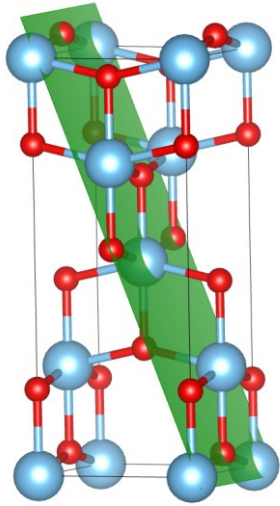
- TiO<sub>2</sub> nanoparticles are widely used in daily products (cosmetics or medicines) or in various technological applications (for example as a catalyst).
- Properties are strongly dependent on the size of NC and the surface that is exposed.
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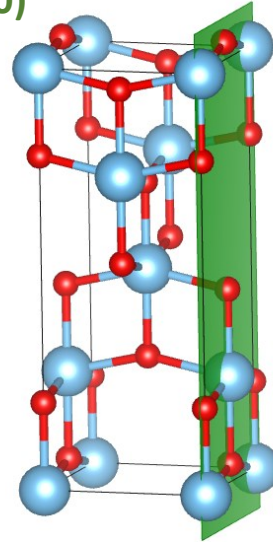
Each termination can be considered separately as a **surface of different termination**.

# EXAMPLE 2 : $\text{TiO}_2$ nanocrystals as surfaces with different terminations

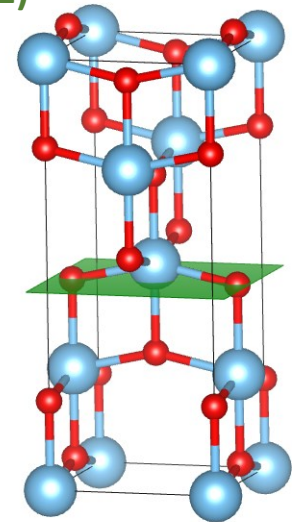
Plane (101)



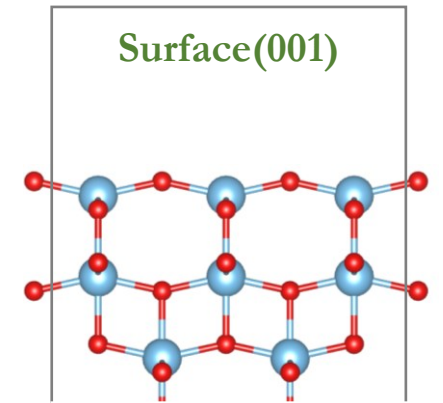
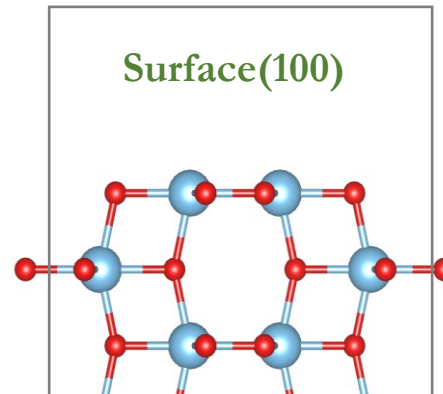
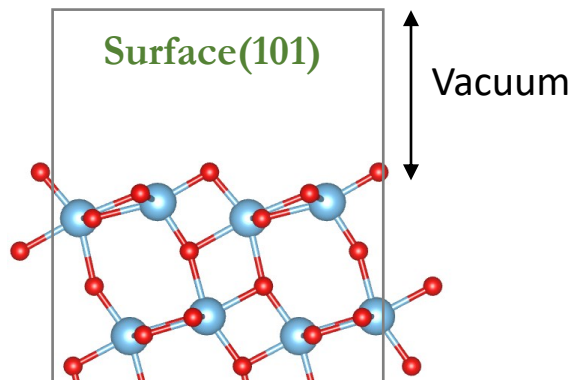
Plane (100)



Plane (001)



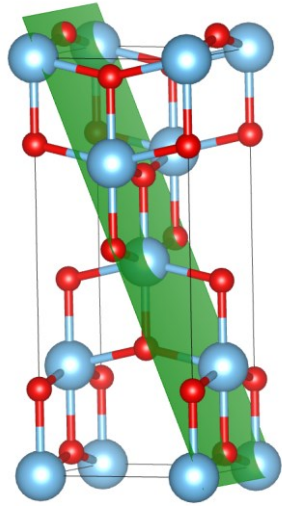
Bulk : 3D periodic structure



Surface : 2D periodicity in (x,y)

# EXAMPLE 2 : $\text{TiO}_2$ nanocrystals as surfaces with different terminations

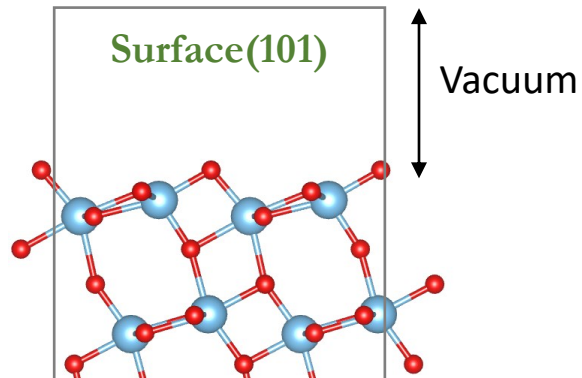
Plane (101)



Bulk : 3D periodic structure

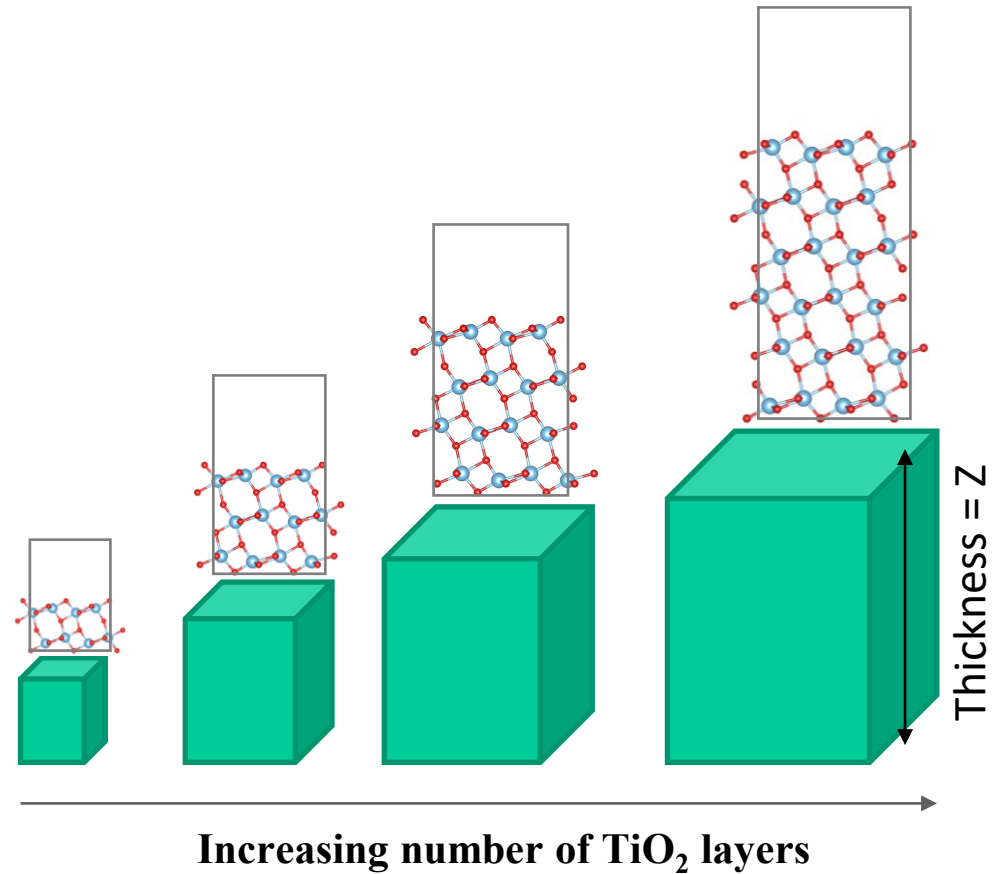


Surface(101)

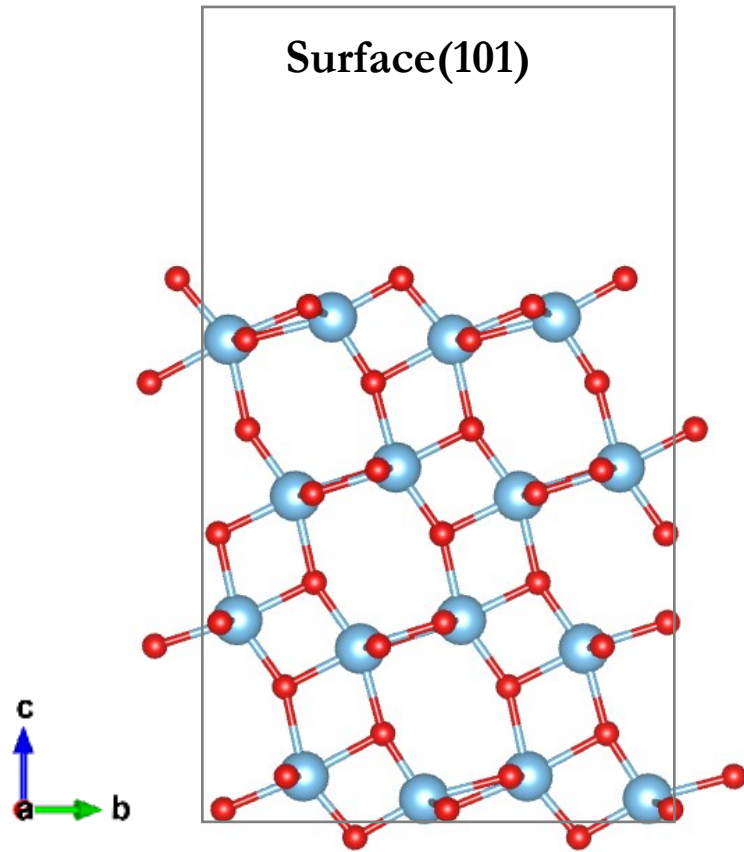


Surface : 2D periodicity in (x,y)

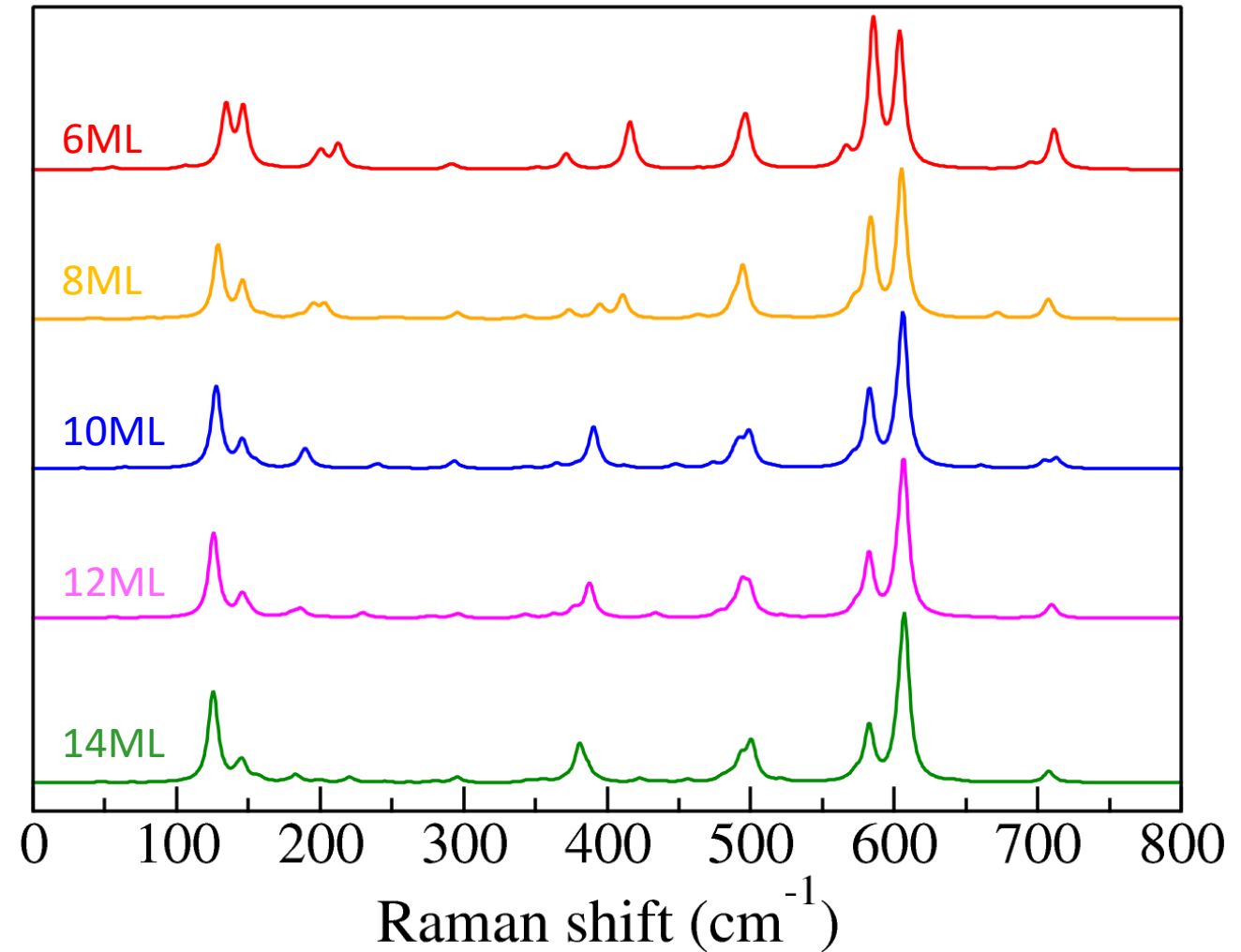
How many layers of  $\text{TiO}_2$  do you need?



# EXAMPLE 2 : TiO<sub>2</sub> nanocrystals as surfaces with different terminations



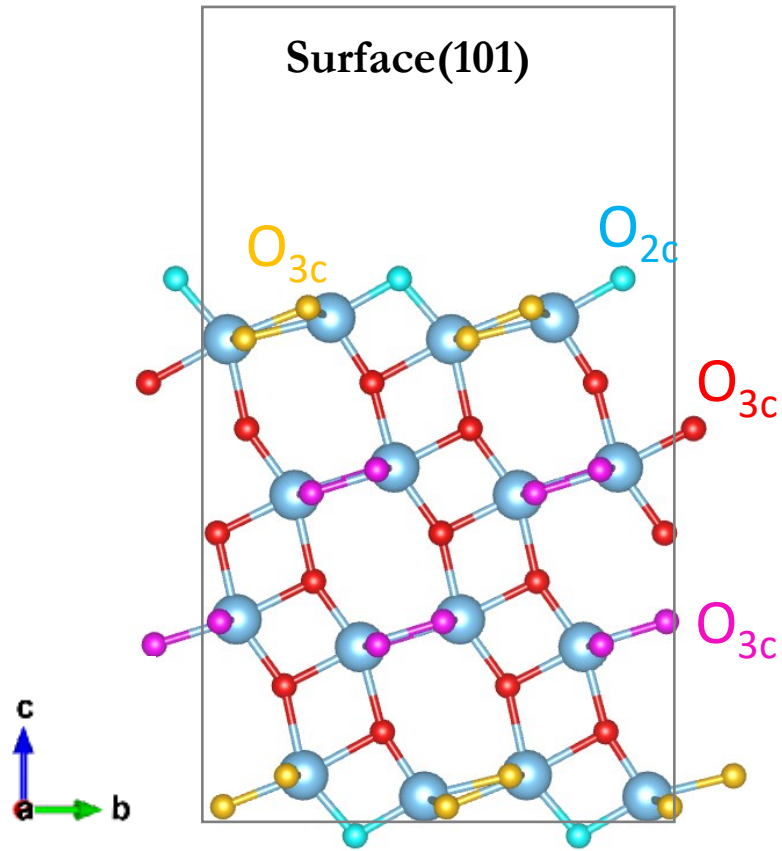
T = 0 K



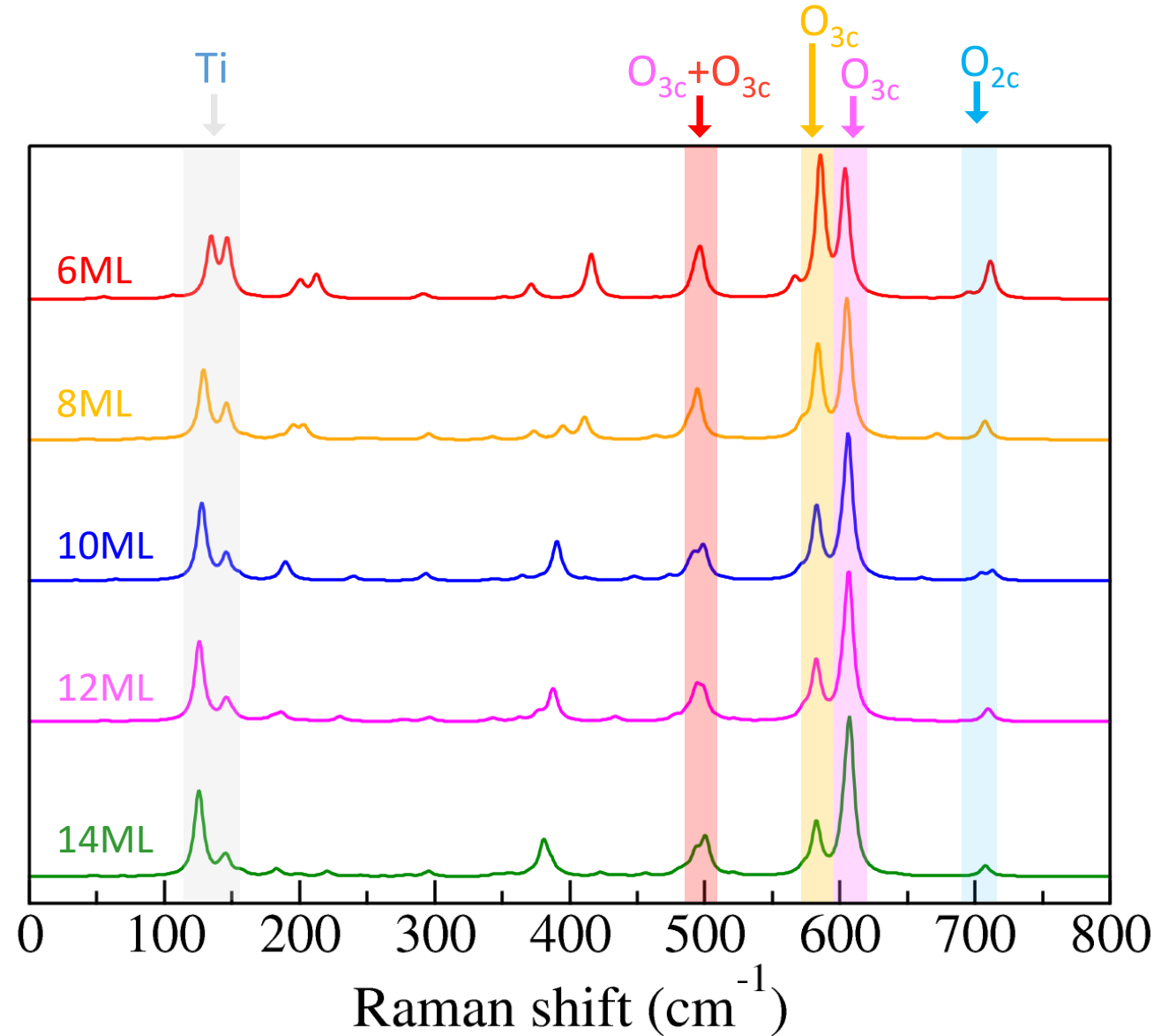
We can follow evolution of Raman spectra with slab thickness.



# EXAMPLE 2 : $\text{TiO}_2$ nanocrystals as surfaces with different terminations



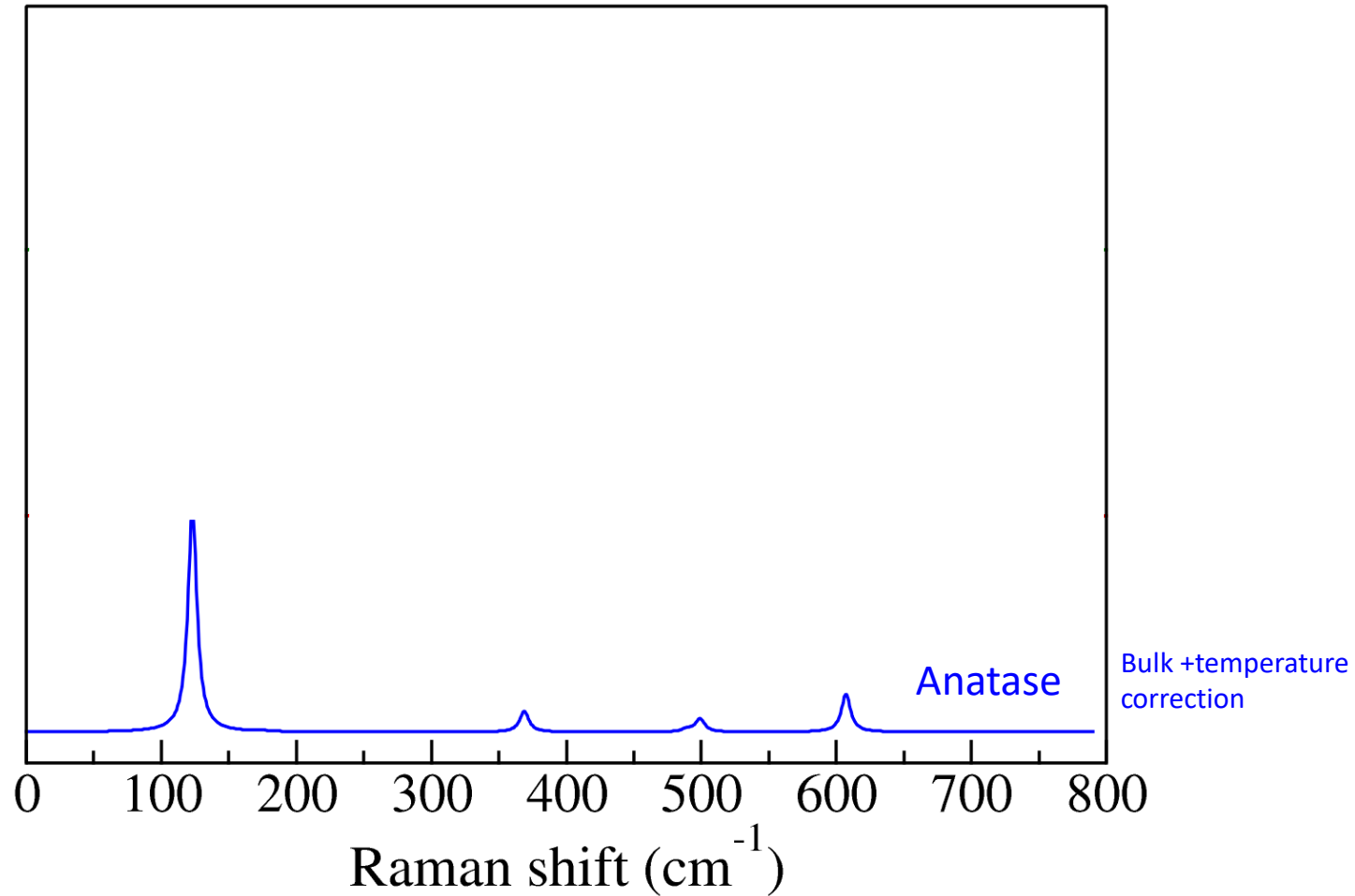
T = 0 K



We can assign different peaks in Raman spectra to particular atoms that are involved in a given mode !

# EXAMPLE 2 : TiO<sub>2</sub> nanocrystals as surfaces with different terminations

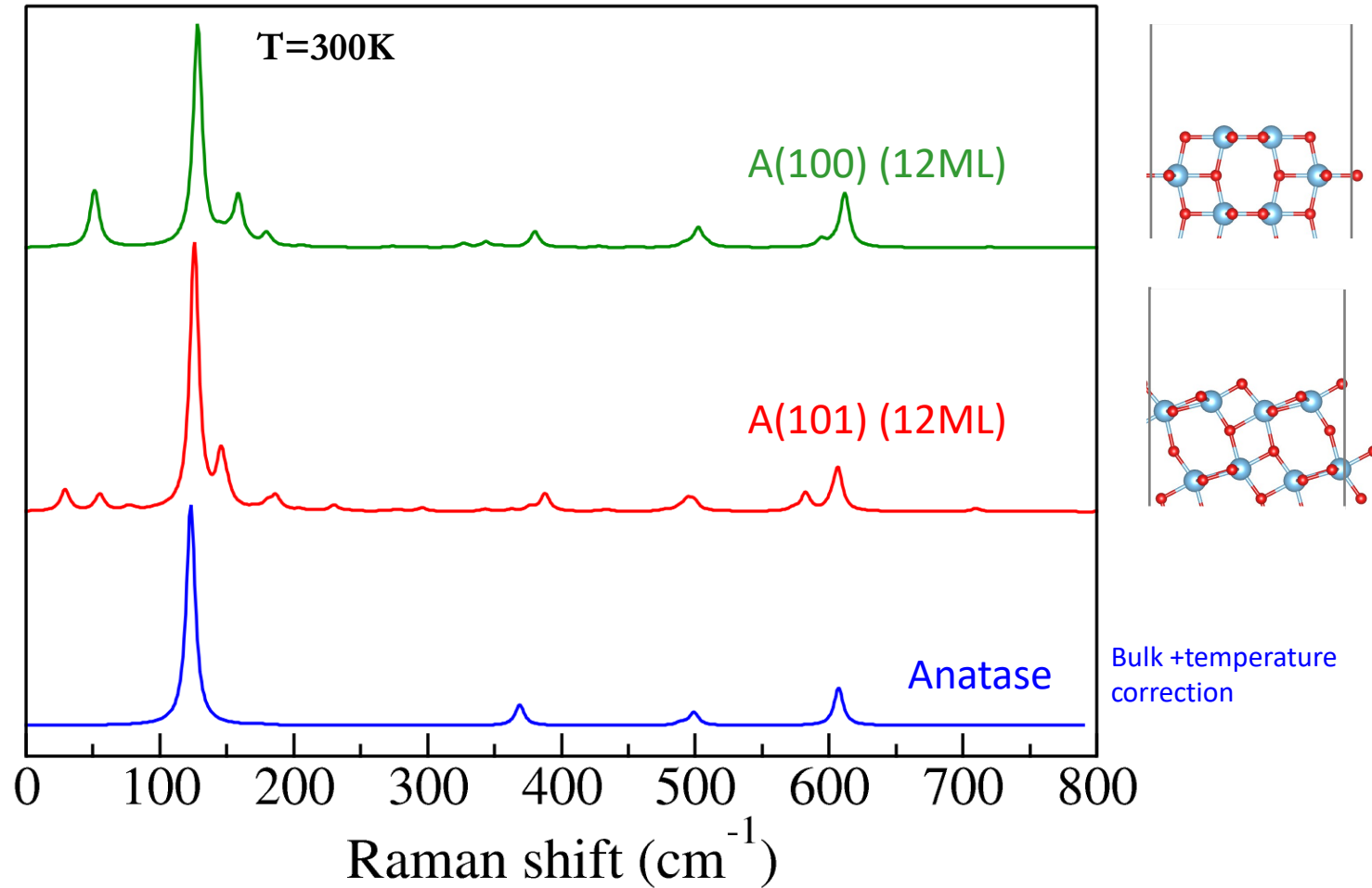
TiO<sub>2</sub> surfaces with respect to bulk anatase



Including temperature correction leads to changes in relative peaks intensities and improves agreement with experiment

# EXAMPLE 2 : TiO<sub>2</sub> nanocrystals as surfaces with different terminations

TiO<sub>2</sub> surfaces with respect to bulk anatase



Including temperature correction leads to changes in relative peaks intensities and improves agreement with experiment

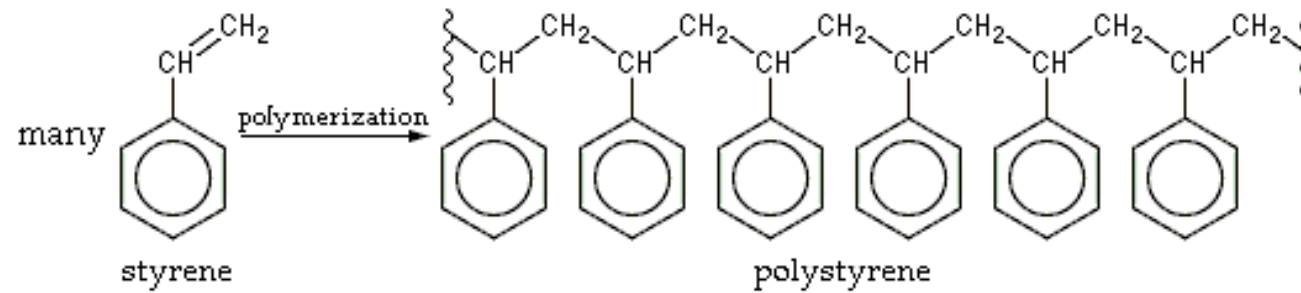
Raman spectra for surfaces converges to the anatase bulk spectra when number of TiO<sub>2</sub> layers increases

Some differences in spectra for different terminations are present (detectable?)

# EXAMPLE 3 : POLYSTYRENE

Polystyrene is a **well-known standard** for use in **Raman shift calibration**.

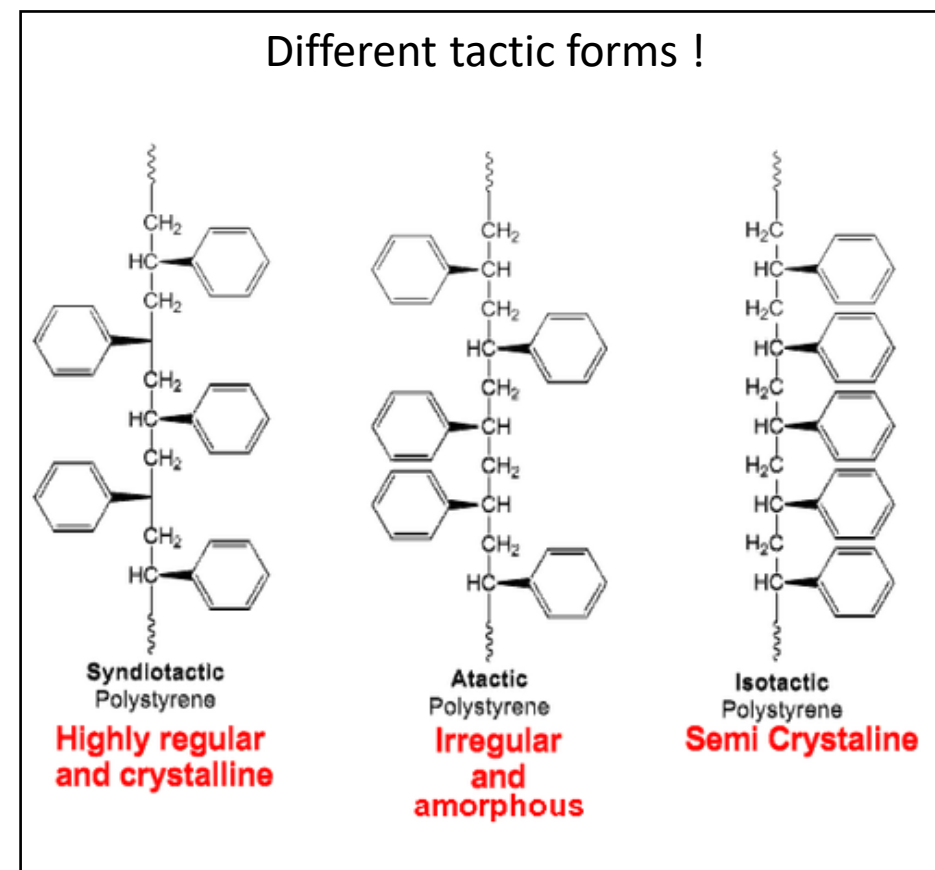
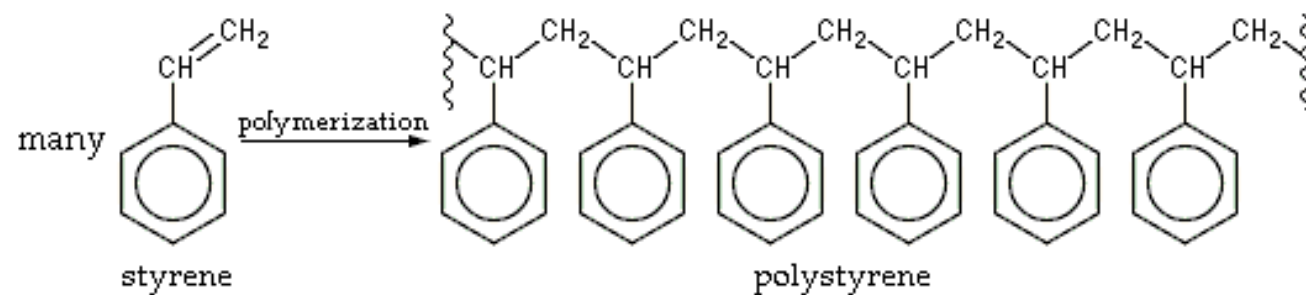
**Polystyrene** is a long chain hydrocarbon wherein **alternating carbon centres** are attached to **phenyl group** (a derivative of benzene).



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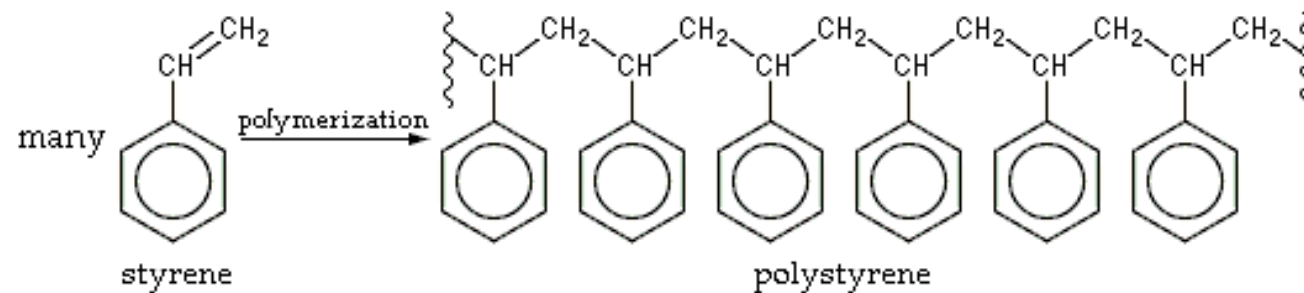
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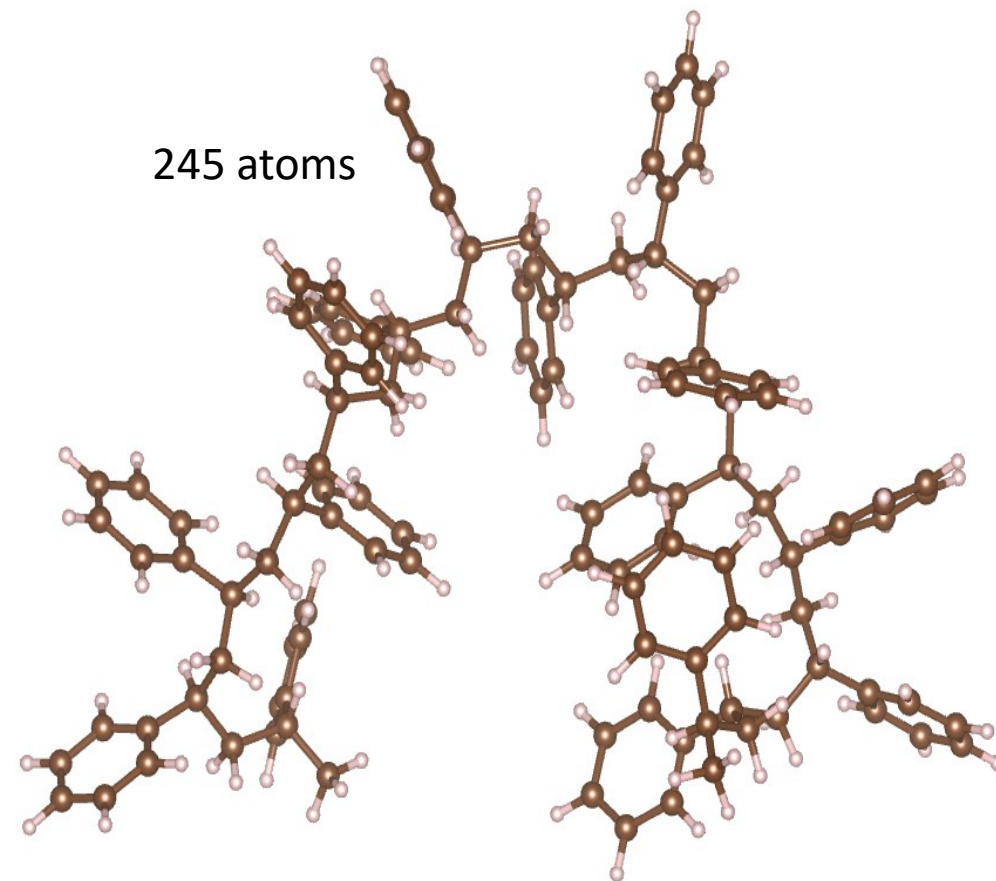
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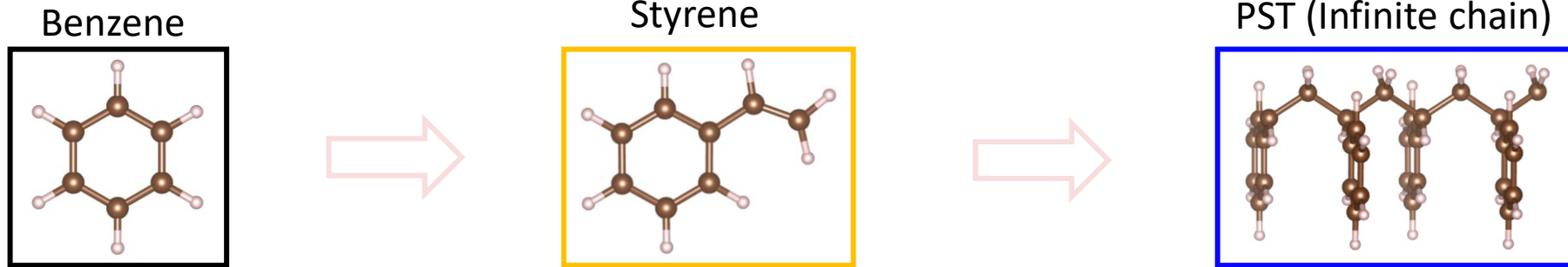
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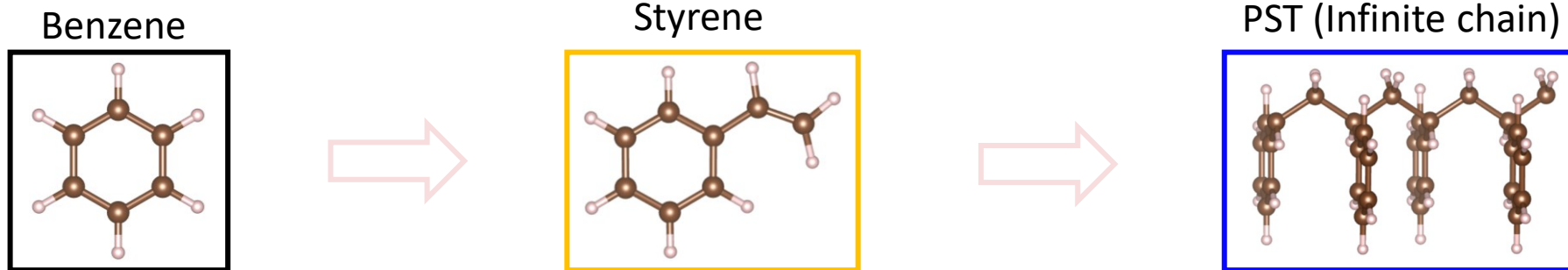
Quite big system – can we simplify the problem and start with something smaller??



# EXAMPLE 3 : POLYSTYRENE step by step

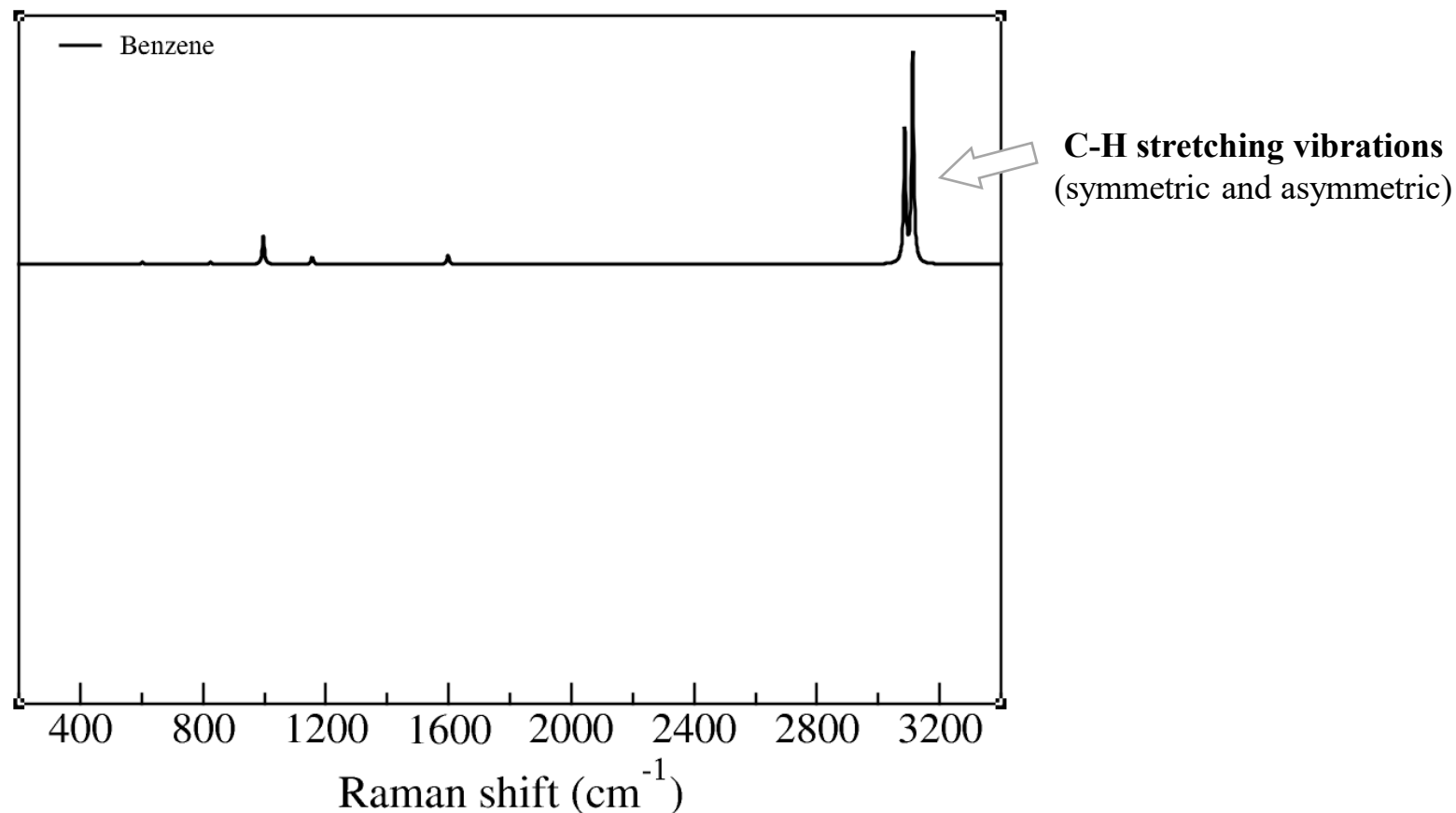


# EXAMPLE 3 : POLYSTYRENE step by step



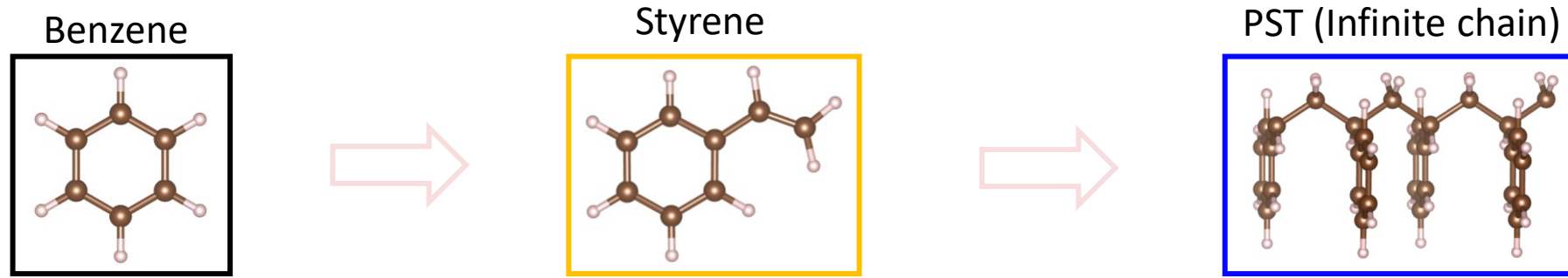
Small molecule allow to benchmark computational parameters (functional and basis set)

Symmetric/regular structure – sharp peaks in Raman spectra.



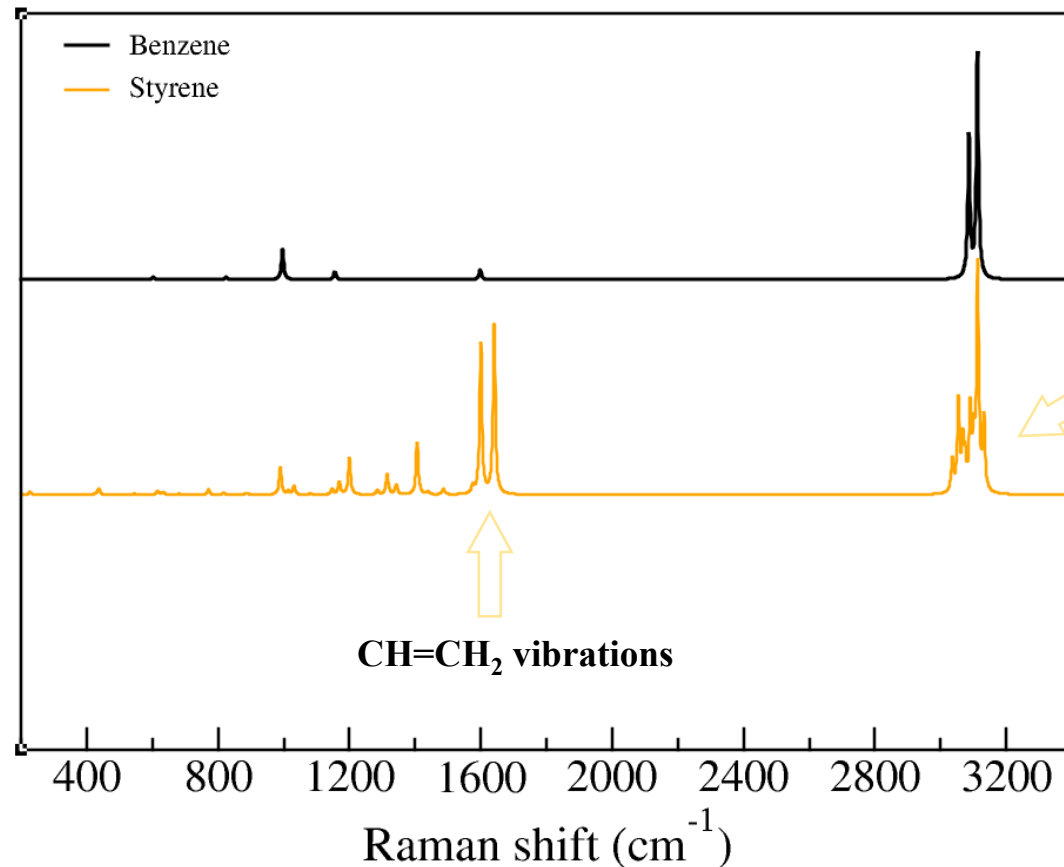


# EXAMPLE 3 : POLYSTYRENE step by step



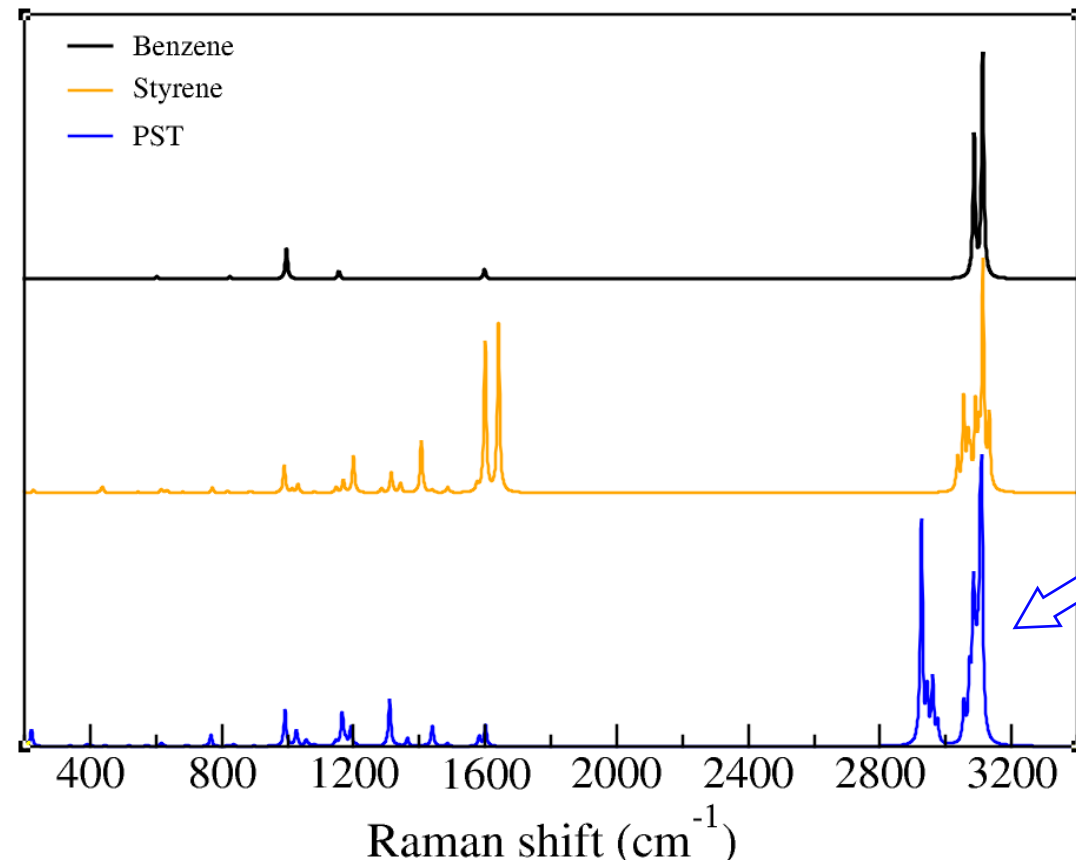
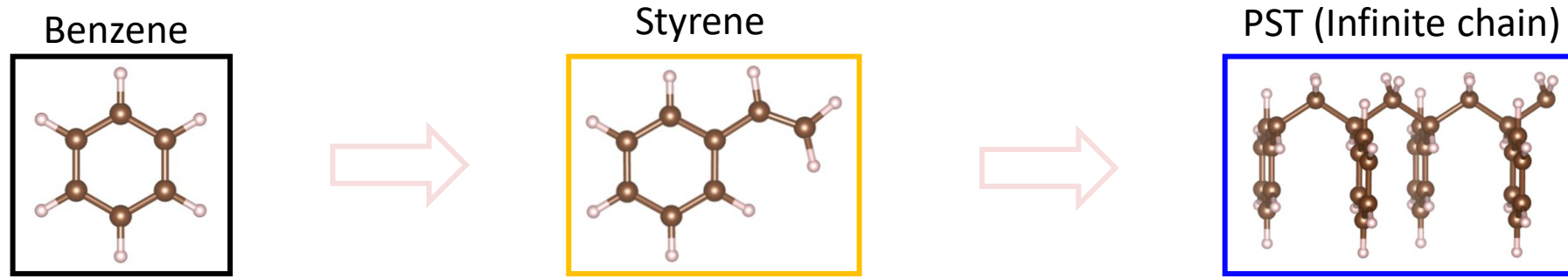
Less symmetric structure – more peaks in Raman spectra.

New features due to C=C double bonds



More peaks are associated with different C-H bonds

# EXAMPLE 3 : POLYSTYRENE step by step



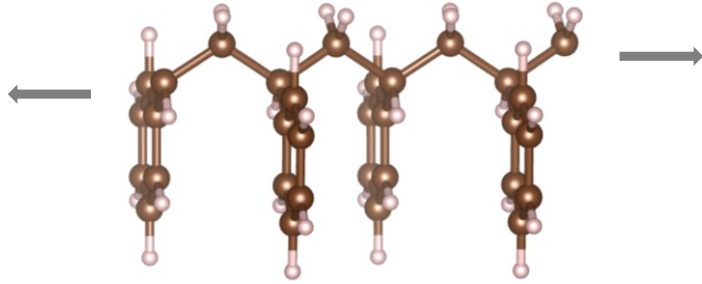
**C-H vibrations:**  
Above  $3000 \text{ cm}^{-1}$ : C-H in a phenyl group  
Below  $3000 \text{ cm}^{-1}$ : C-H in a carbon backbone

No double bonds!

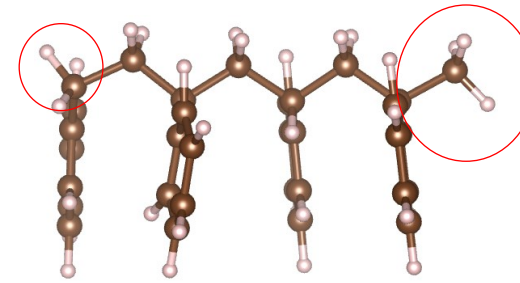
**Infinite chain** of styrene monomers.

# EXAMPLE 3: POLYSTYRENE Infinite and finite chain

**POLYMER (1D)** - infinite polymer chain in one direction

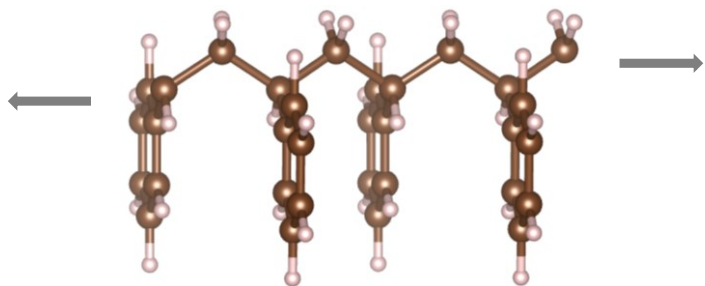


**MOLECULE (0D)** – no periodicity in any direction ( additional H at the end parts of polymer must be added to saturate dangling bonds (in green) )

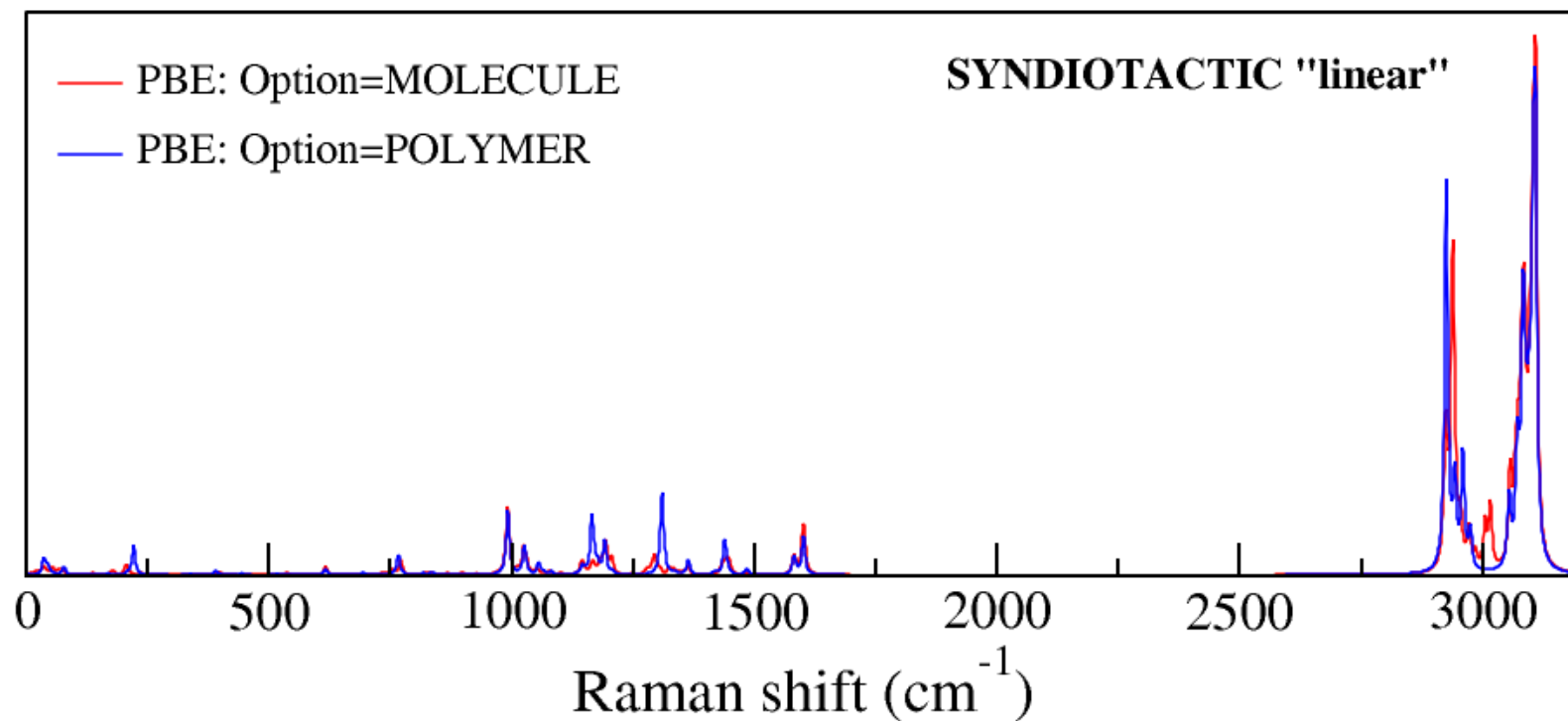
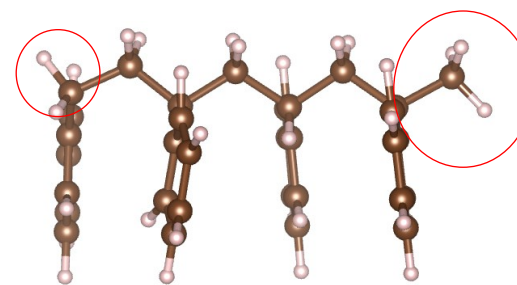


# EXAMPLE 3: POLYSTYRENE Infinite and finite chain

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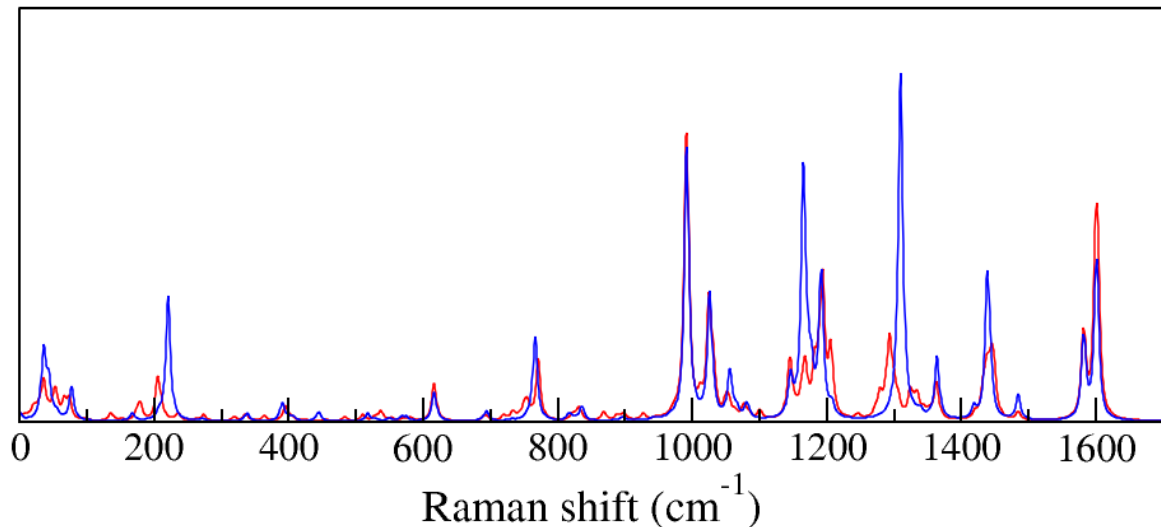
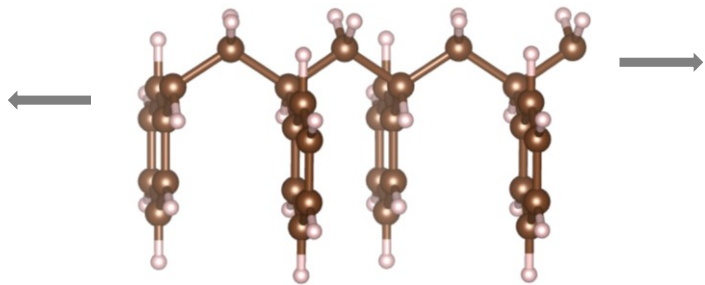


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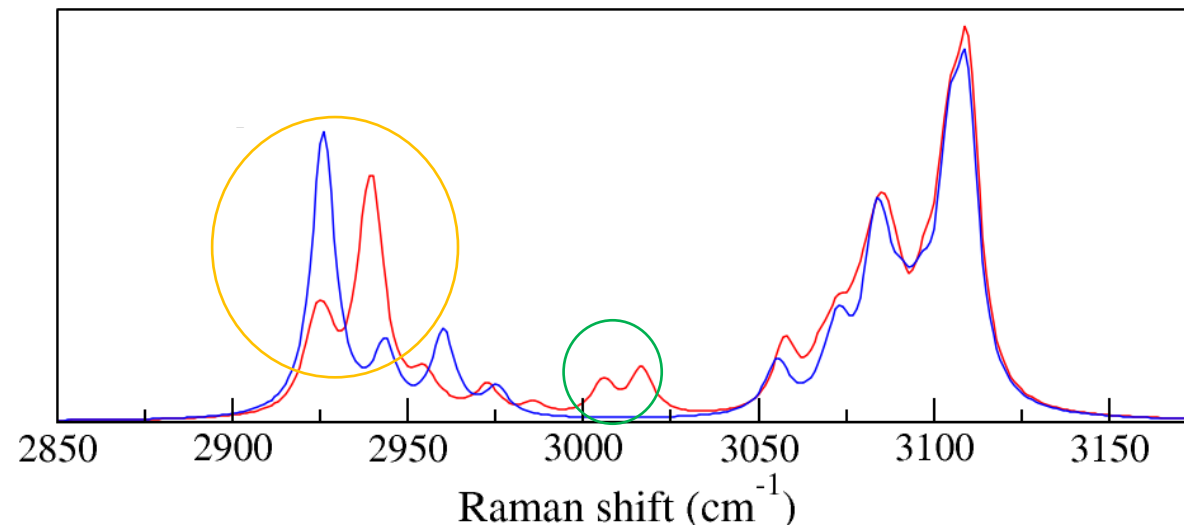
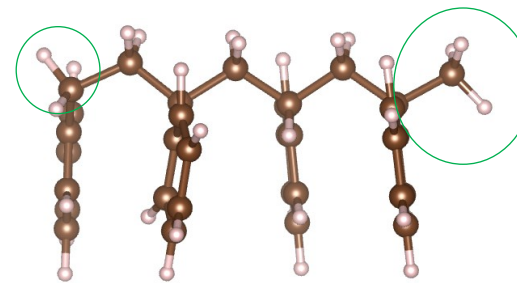
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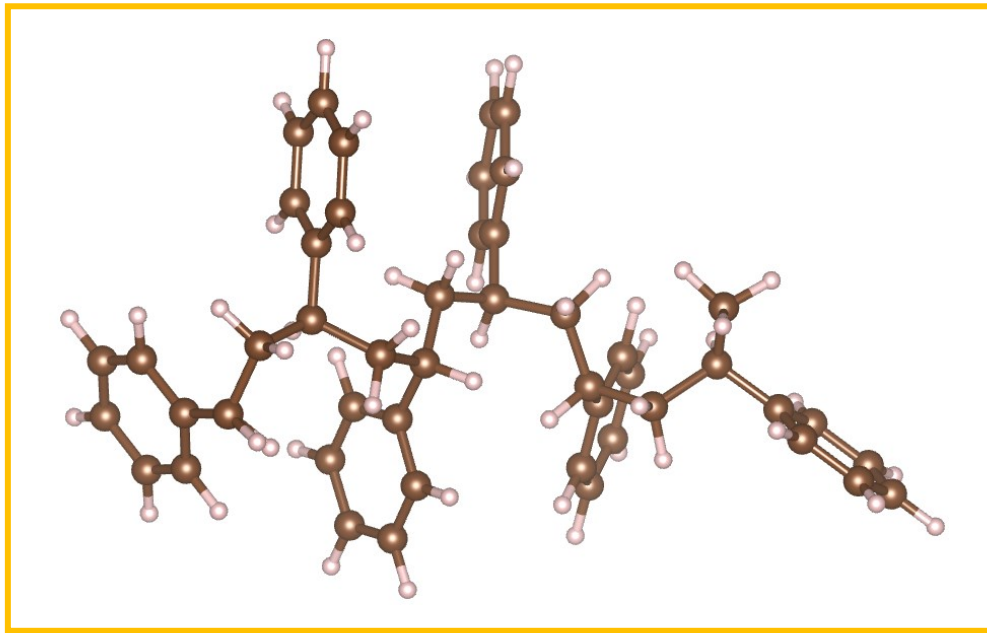
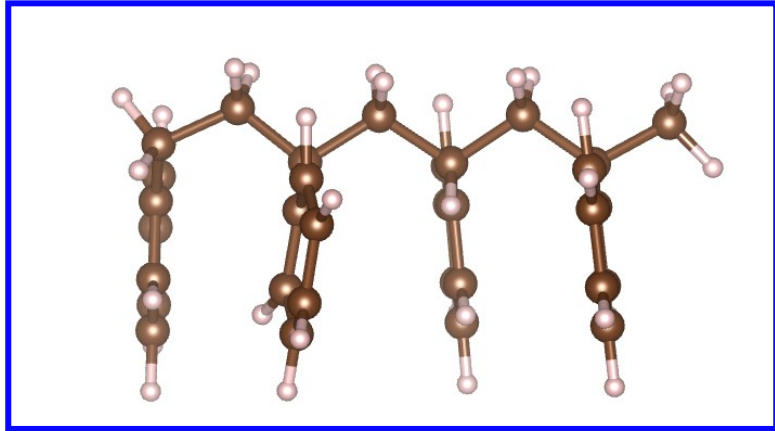
**Lower frequency region:**  
spectra are quite similar, small variations in the peaks' intensities

**MOLECULE (0D)** – no periodicity in any direction ( additional H at the end parts of polymer must be added to saturate dangling bonds (in green) )

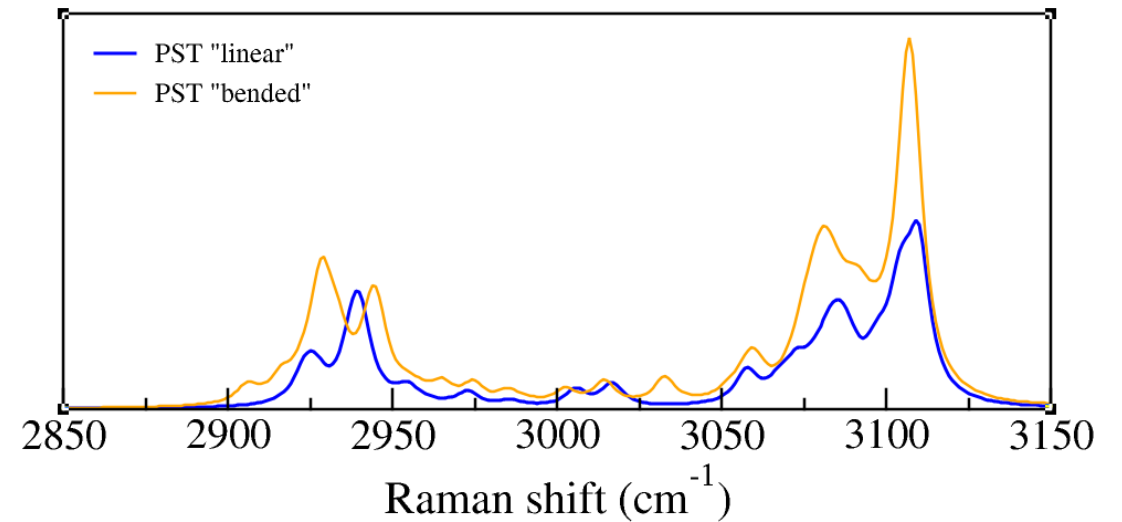
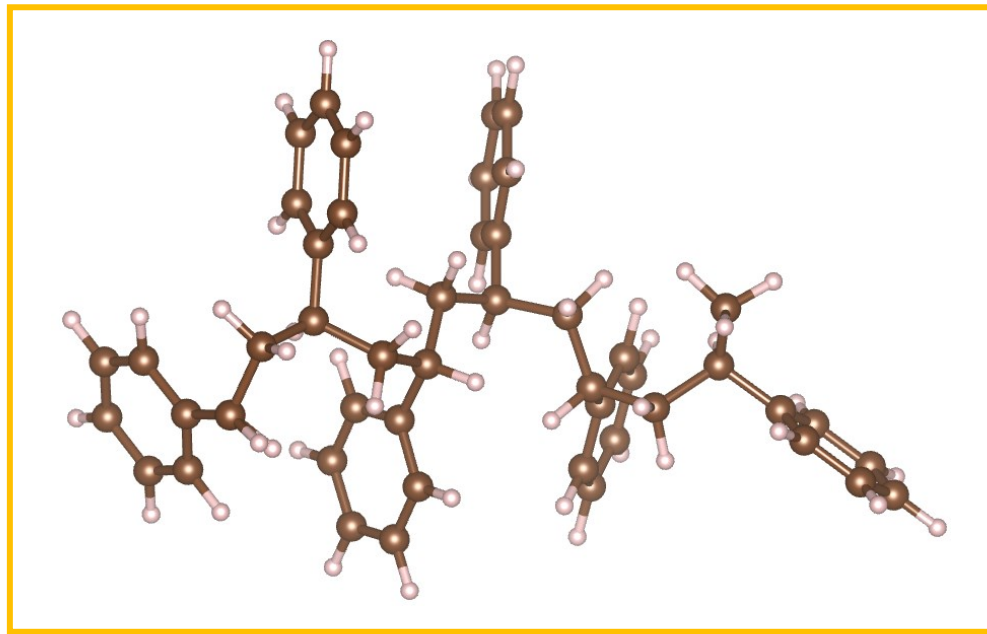
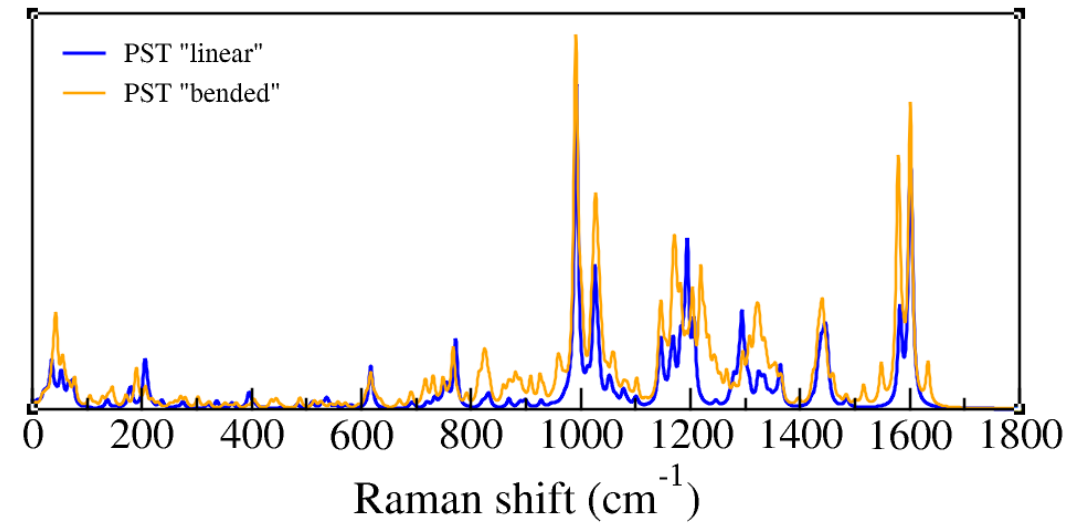
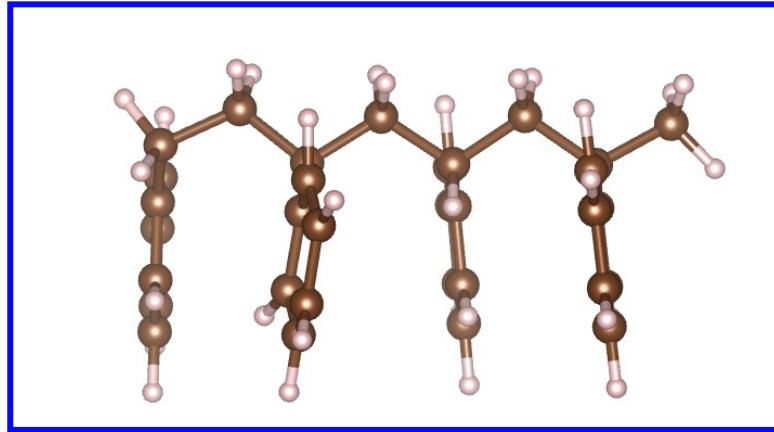


**Higher frequency region:** spectra are similar, but some new peaks emerge (in green) and changes in intensity (orange) (due to C-H in carbon backbone)  
New peaks can be due to saturation of ending bonds with H

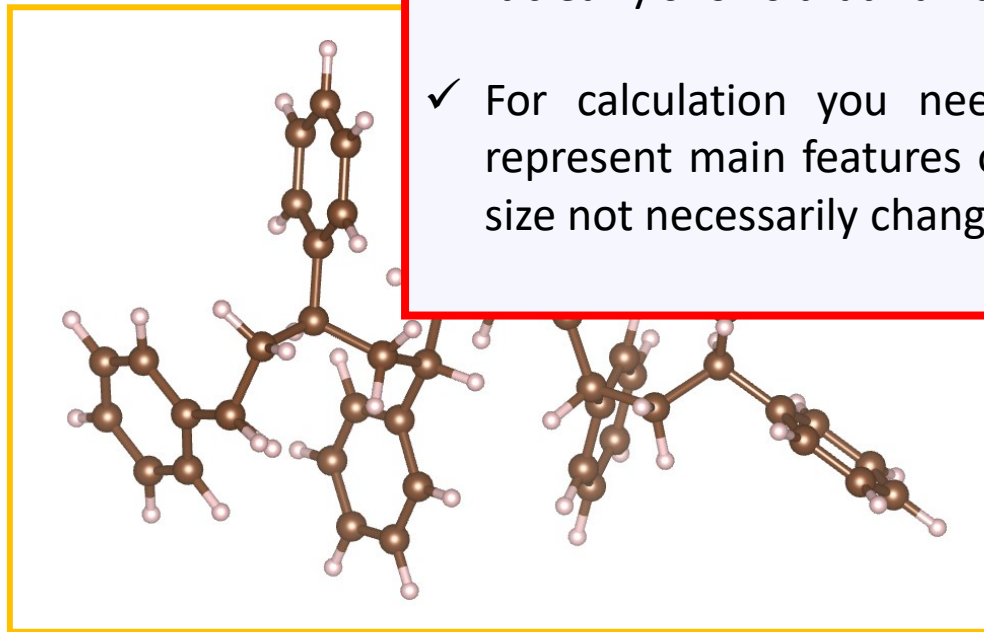
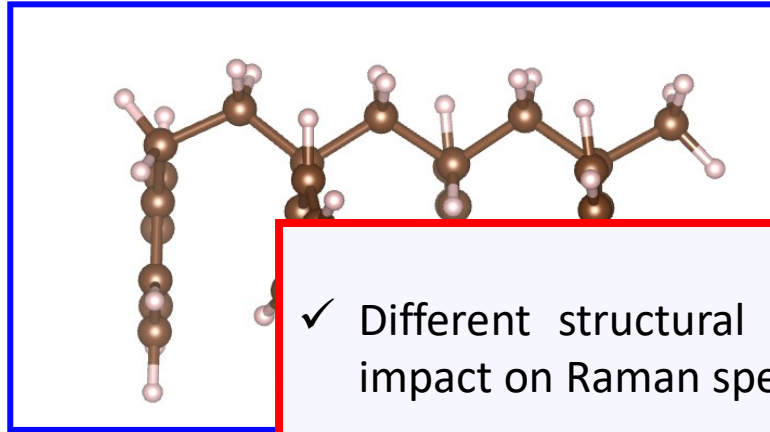
# EXAMPLE 3 : POLYSTYRNE „linear” and „bended” carbon chain



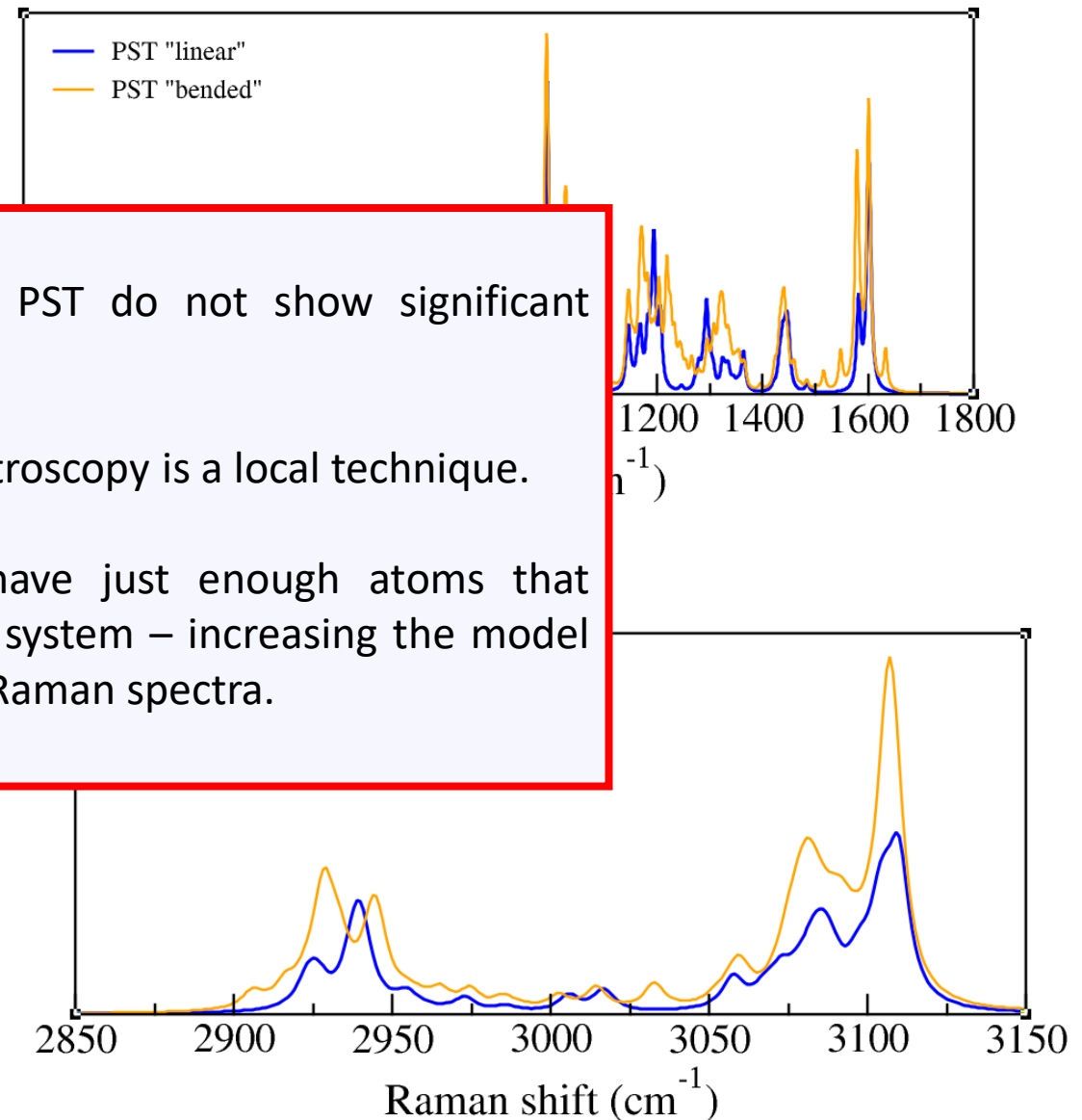
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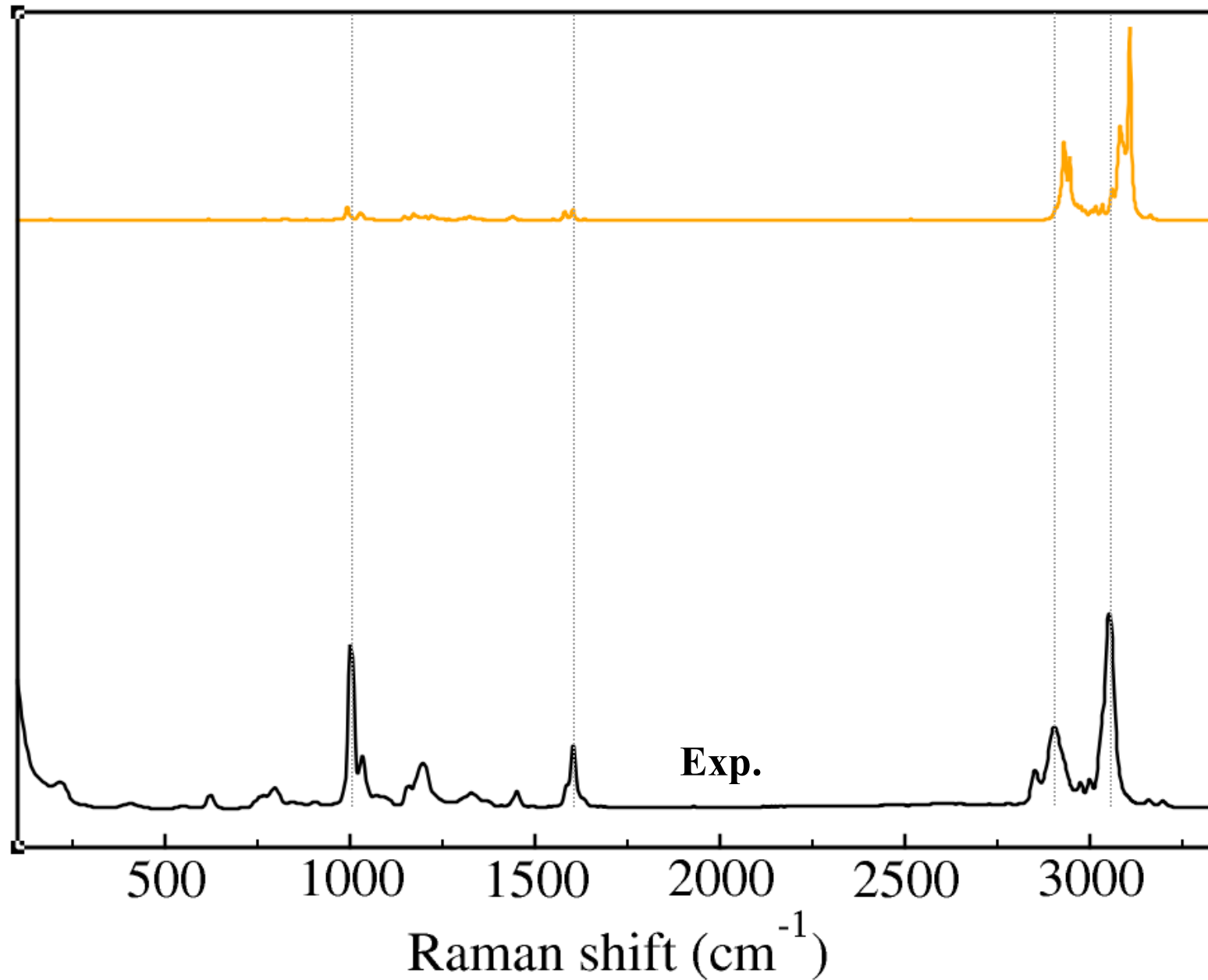


- ✓ Different structural models for PST do not show significant impact on Raman spectra.
- ✓ It clearly shows that Raman spectroscopy is a local technique.
- ✓ For calculation you need to have just enough atoms that represent main features of your system – increasing the model size not necessarily changes the Raman spectra.



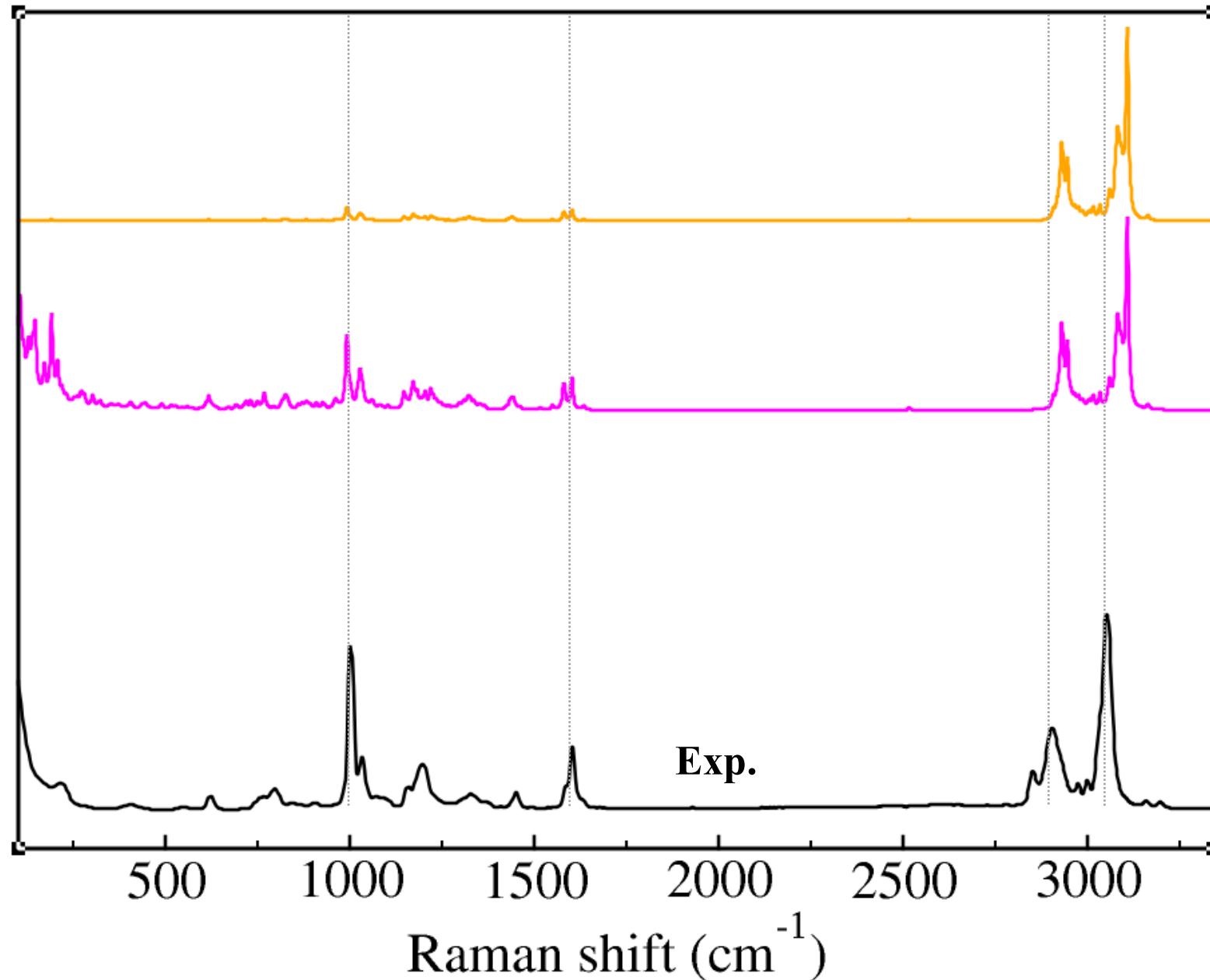


# EXAMPLE 3 : POLYSTYRNE Theory vs Experiment

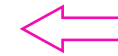


**C-H vibrations** higher in frequency by  
~50-65 cm<sup>-1</sup>  
← Wrong relative intensities...

# EXAMPLE 3 : POLYSTYRNE Theory vs Experiment

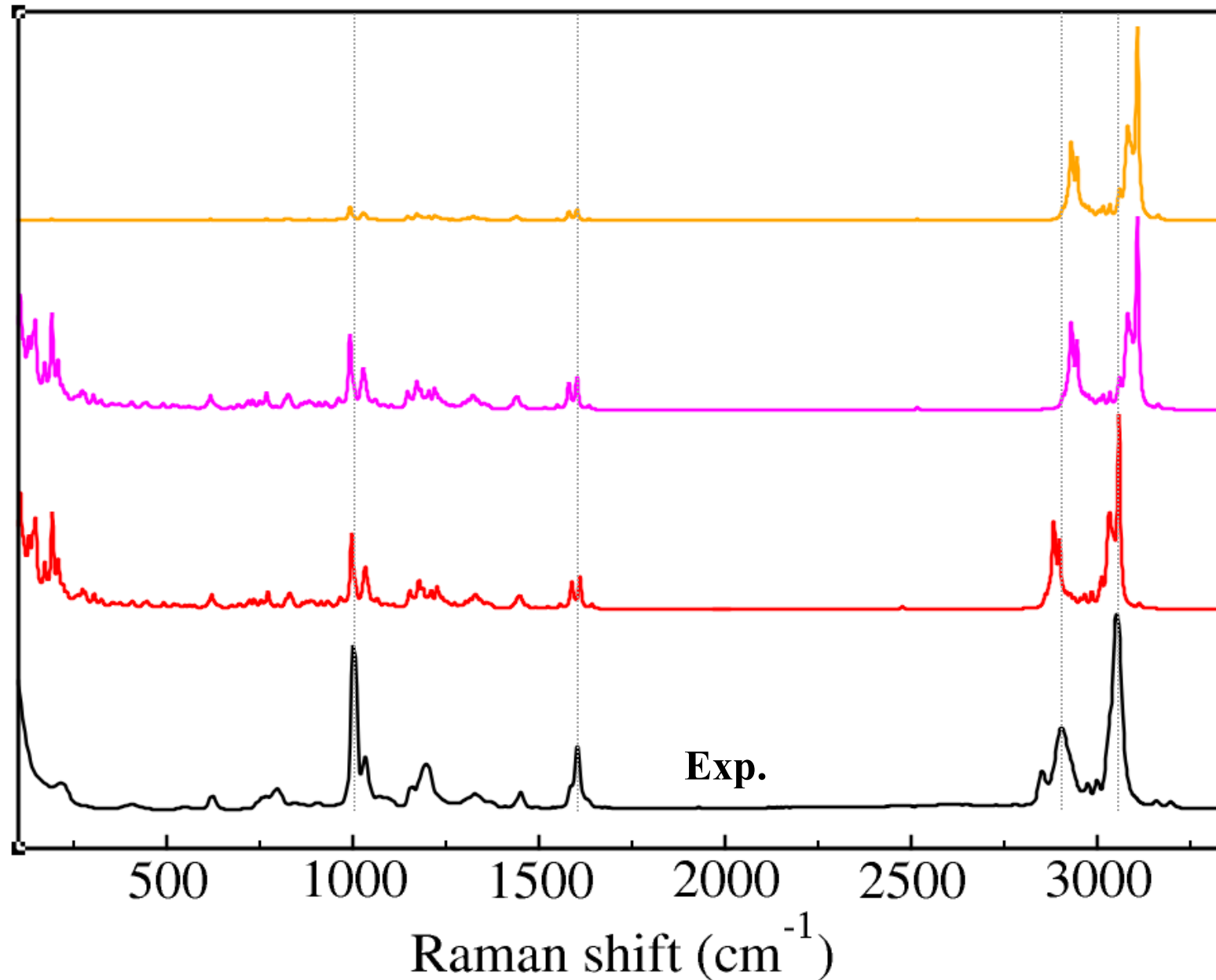


**C-H vibrations** higher in frequency by  $\sim 50\text{-}65 \text{ cm}^{-1}$



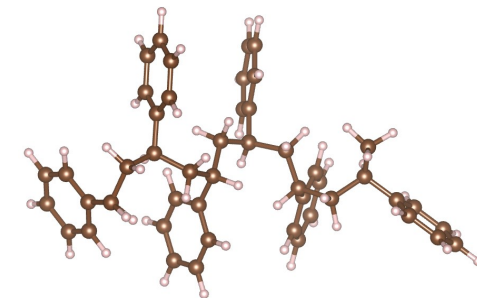
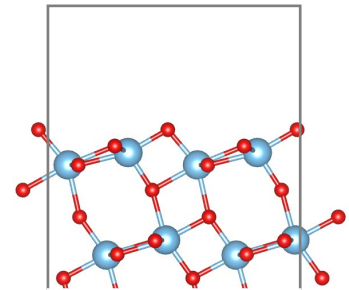
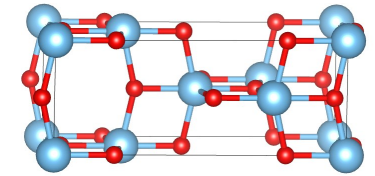
Relative intensities can be improved by including temperature correction in the calculations

# EXAMPLE 3 : POLYSTYRNE Theory vs Experiment



Frequencies can be rescale by using scalling factor

- ❖ DFT gives quite reasonable estimation of Raman spectra for various systems (we can model structures from 3D periodic to 0D molecular structures)
- ❖ Theory allows to build various models and study impact of different structural parameter on Raman spectra
- ❖ Frequency depends on computational parameters; relative intensities might not be that accurate (but as well as experimental ones)
- ❖ Relative intensities can be corrected/improved by including temperature (depends also on the system! )
- ❖ Most of the errors are due to lack of anharmonic effects
- ❖ Calculations at 0K

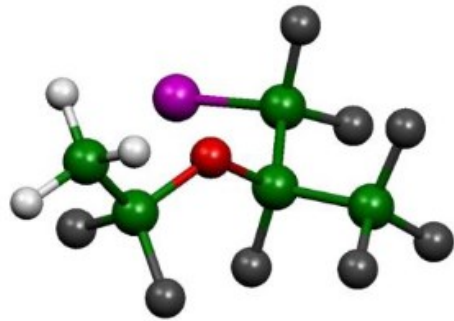


## **ADVANTAGES:**

- Much easier by far to include **temperature**, pressure and solvent effects; anharmonicity effects

## ADVANTAGES:

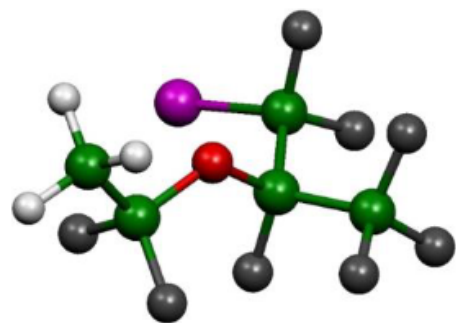
- Much easier by far to include **temperature**, pressure and solvent effects; anharmonicity effects
- **Sampling of the configurations**



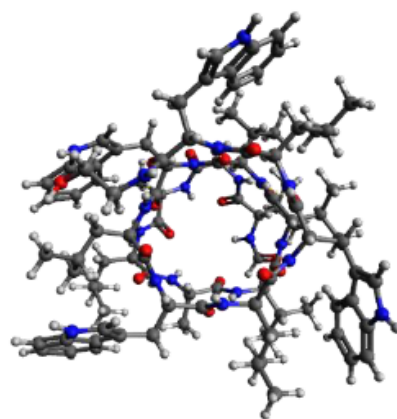
26 conformers

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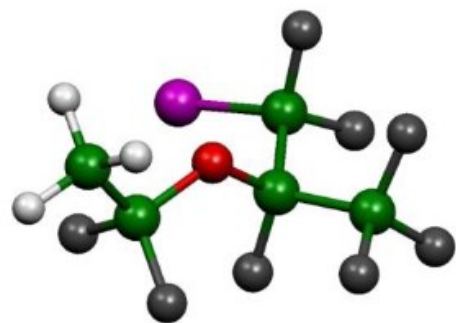
26 conformers



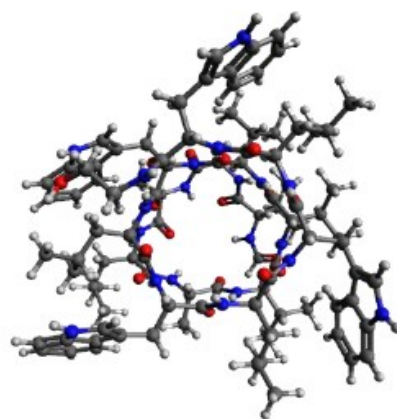
? conformers

## ADVANTAGES:

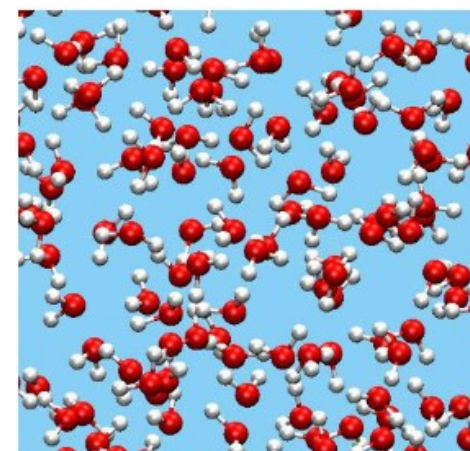
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26 conformers



? conformers

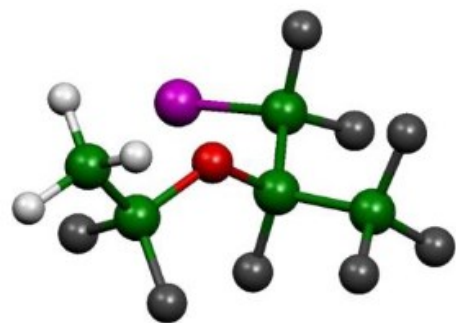


??? conformers

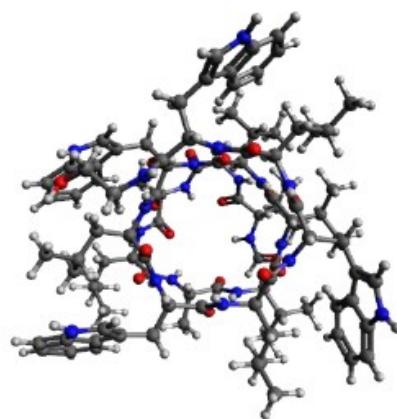


## ADVANTAGES:

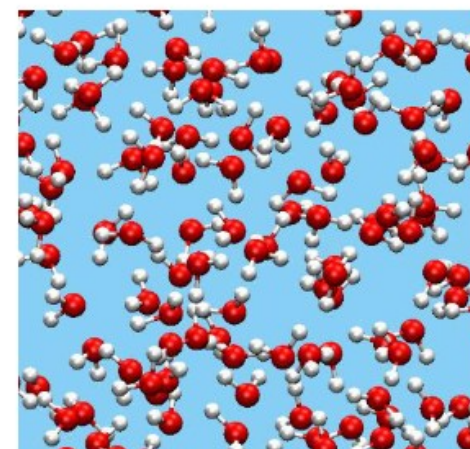
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26 conformers



? conformers



??? conformers

- **No need to calculate and diagonalize Hessian matrix**

## Born-Oppenheimer Molecular Dynamics

Electrons:  $H\Psi = E\Psi$

Nuclei:  $F = ma$

Initial configuration ( $t=0$ ):

$\Psi(t)$ ,  $\text{pos.}(t)$ ,  $\text{vel.}(t)$



$dt$  (=0.4 fs)

$\Psi(t+dt)$ ,  $\text{pos.}(t+dt)$ ,  $\text{vel.}(t+dt)$

$H\Psi = E\Psi \rightarrow$  DFT

$-\nabla E = F$

Integrate Newton eq.



$\{x_{i,t}, y_{i,t}, z_{i,t}, v_{x,i,t}, v_{y,i,t}, v_{z,i,t}\}$

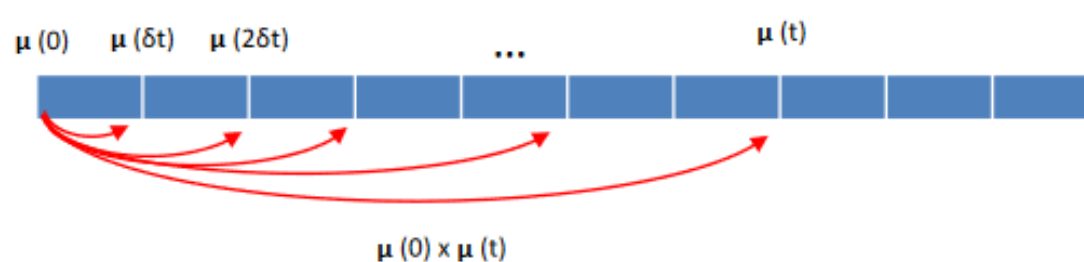
We work with  
periodic boundary  
conditions

- ✓ **Classical Newton equations** for movement of **ions** and **DFT** for **electrons**.
- ✓ Forces are computed on the fly from electronic structure calculations.
- ✓ Configurations of the phase space can easily be sampled, while at the same time, the electronic structure is treated
- ✓ Temperature and pressure are controlled by use of thermodynamical ensembles i.e., thermostats (like NVT-fixed number of particles, volumes and temperature or NVE – fixed number of particles, volume and Energy)

# Beyond classical DFT – *Ab initio* molecular dynamics (AIMD)

We run a molecular dynamics simulation and compute then compute the spectra by the Fourier transform of the time-correlation function of:

The dipol moment  $\rightarrow$  IR

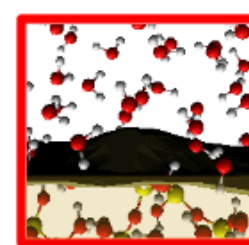
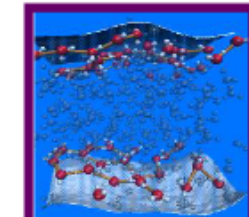
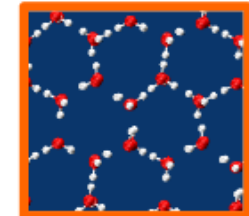
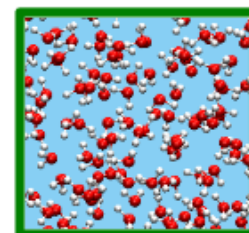
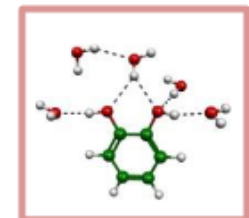
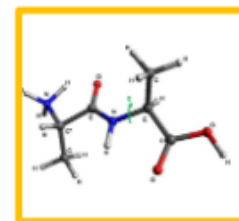
$$I(\omega) \propto \int dt e^{i\omega t} \langle \delta\mu(t) \delta\mu(0) \rangle$$


$\mu(0)$   $\mu(\delta t)$   $\mu(2\delta t)$  ...  $\mu(t)$

$\mu(0) \times \mu(t)$

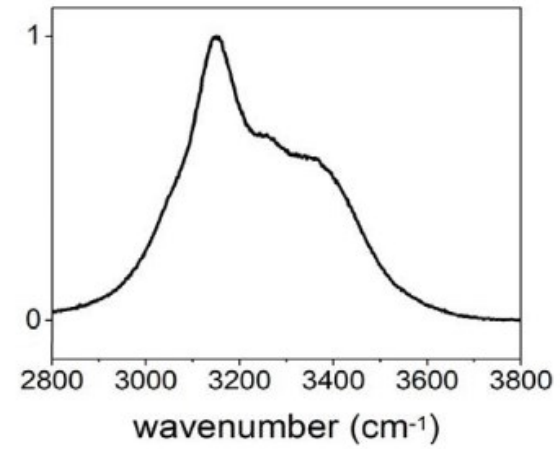
Of the polarizability tensor  $\rightarrow$  RAMAN

$$I(\omega) \propto \int dt e^{i\omega t} \langle \alpha(t) \alpha(0) \rangle$$



# EXAMPLE 1 : Raman spectrum of ice

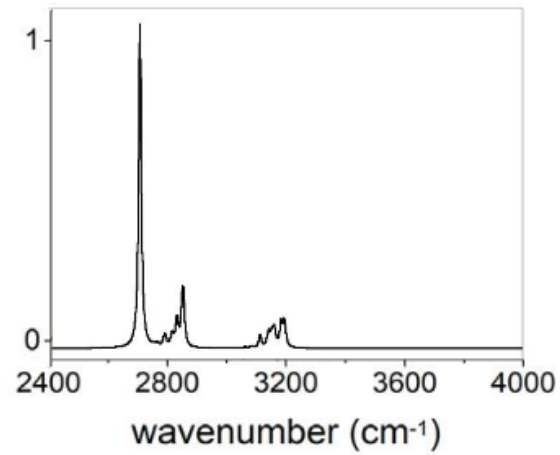
EXP.1



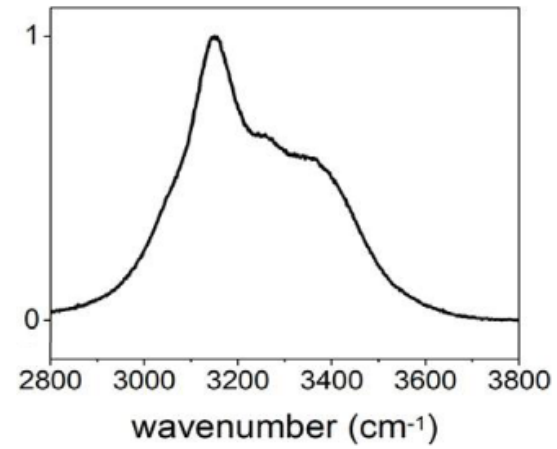
OH-stretching region : 2800-3800  $\text{cm}^{-1}$

# EXAMPLE 1 : Raman spectrum of ice

**"Static" DFT**



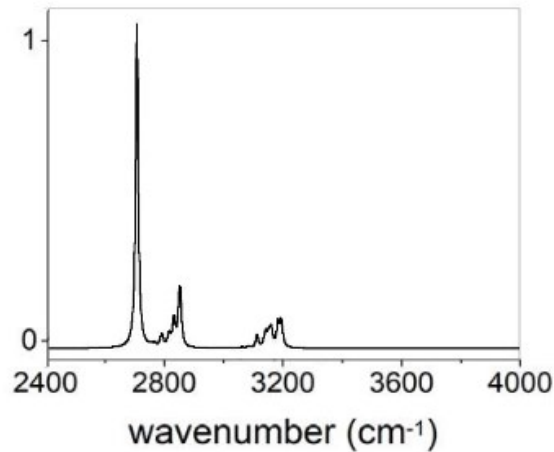
**EXP.1**



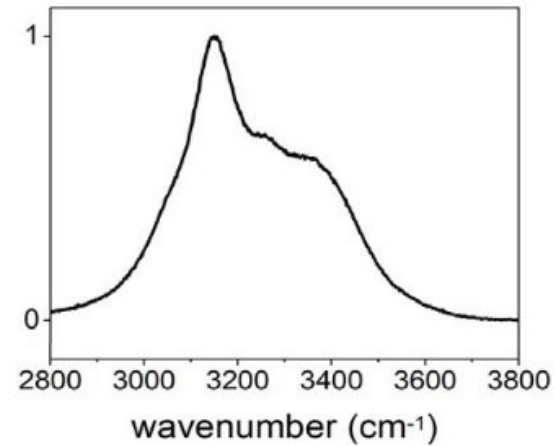
**OH-stretching region : 2800-3800 cm<sup>-1</sup>**

# EXAMPLE 1 : Raman spectrum of ice

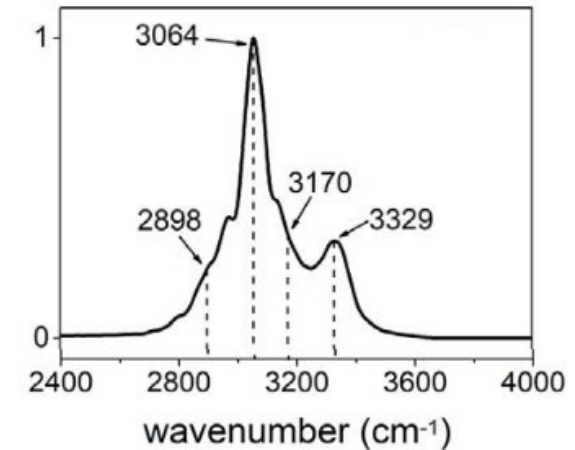
"Static" DFT



EXP.¹



DFT-MD ¹

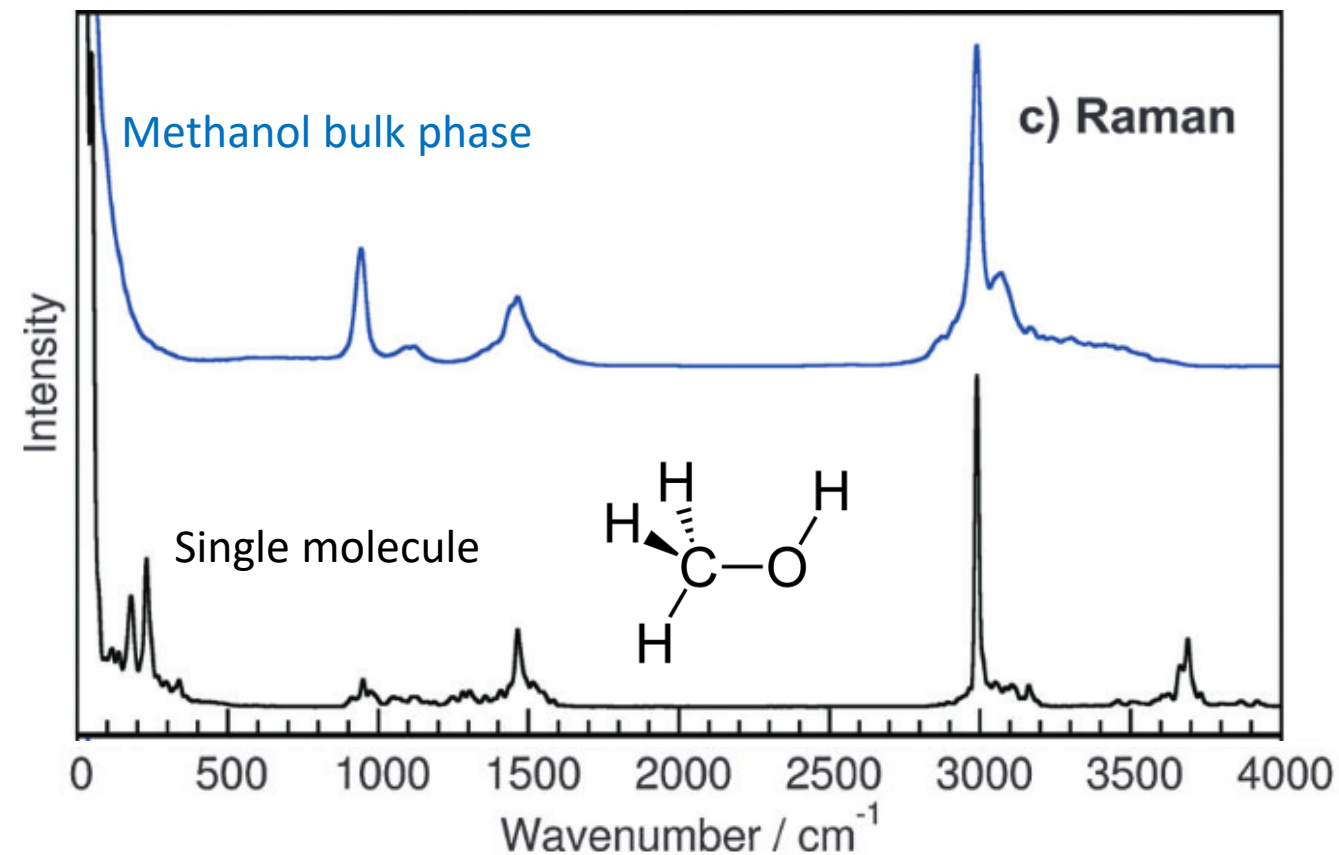


OH-stretching region : 2800-3800 cm<sup>-1</sup>

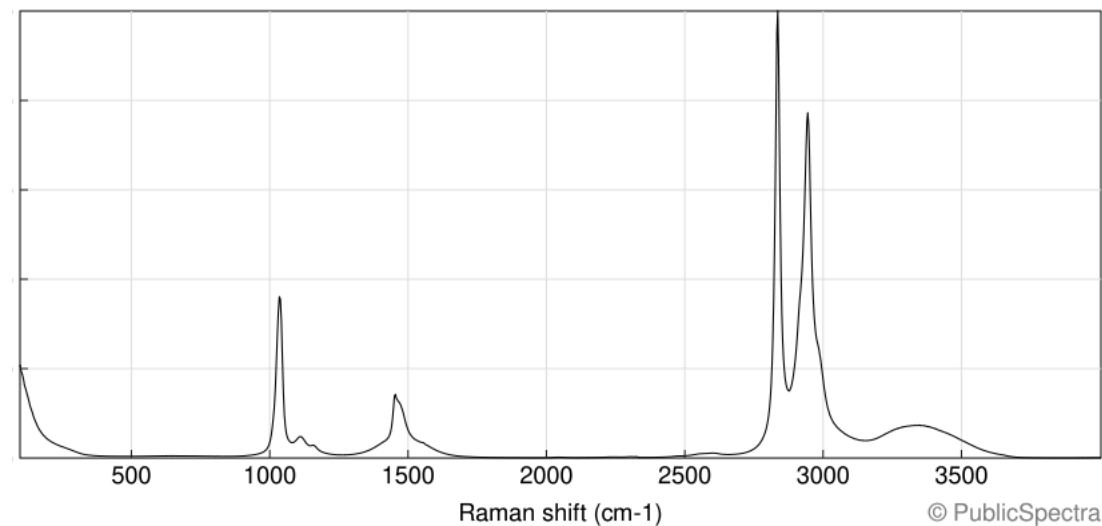
- MD reproduces well the broad Raman scattering observed in the OH stretching region
- Above 3170 cm<sup>-1</sup>: the calculated spectrum is slightly less broad than the experimental one and peaks also lack intensity compared to experiment : most probably due to the presence of **defects and grain boundaries in real ice**, contrary to perfect monocrystalline ice of the simulations.

# EXAMPLE 2 : Methanol (CH<sub>3</sub>OH)

C-H stretching

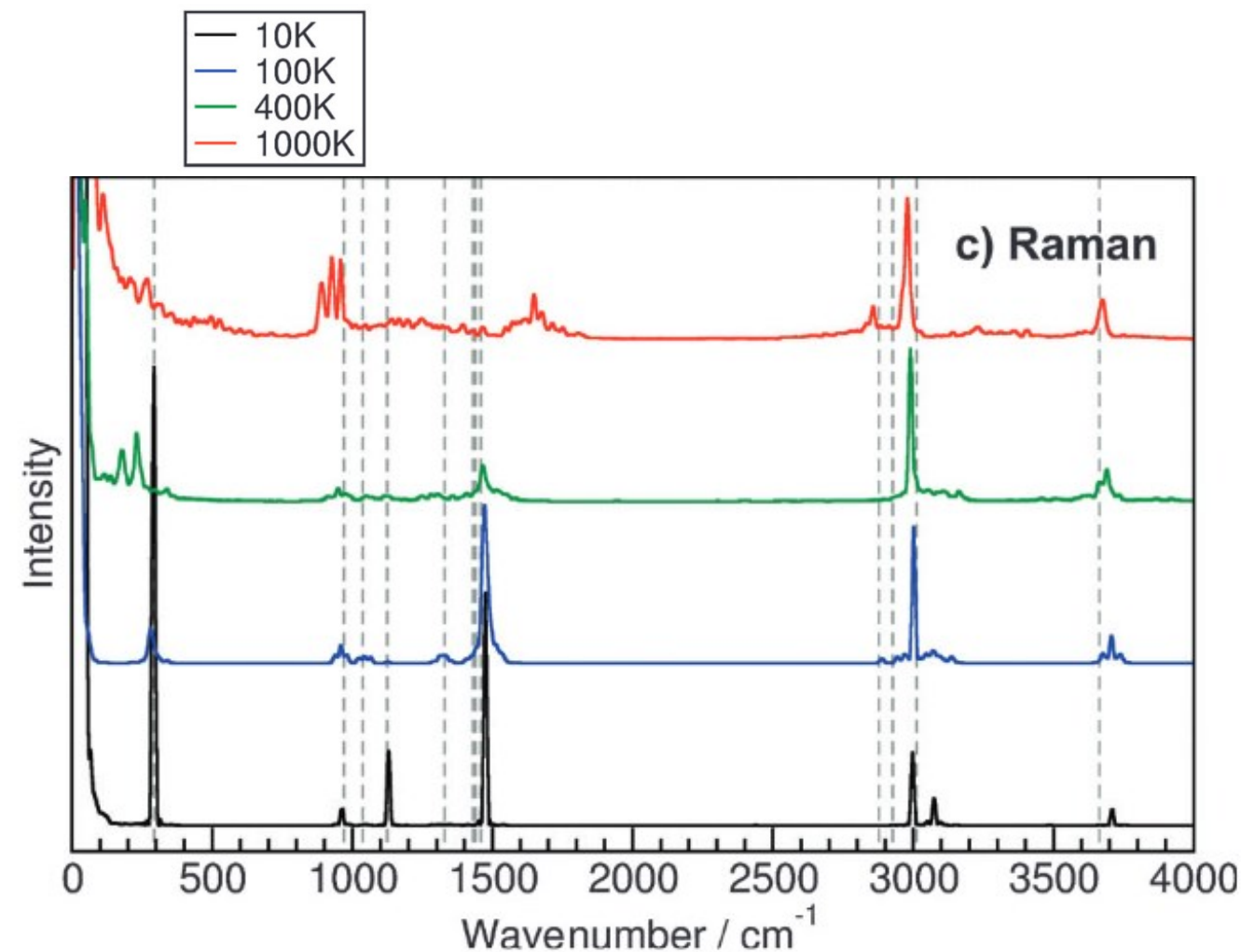


Raman Spectrum of Methanol



- Calculated Raman spectra for bulk like methanol is in a good agreement with experiment.
- Peak broadening comes directly from calculations.
- Hydrogen bonds are important !

# EXAMPLE 2 : Methanol (CH<sub>3</sub>OH)



## Temperature influence (NVT ensemble):

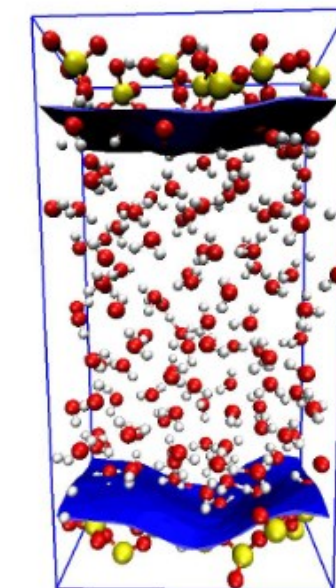
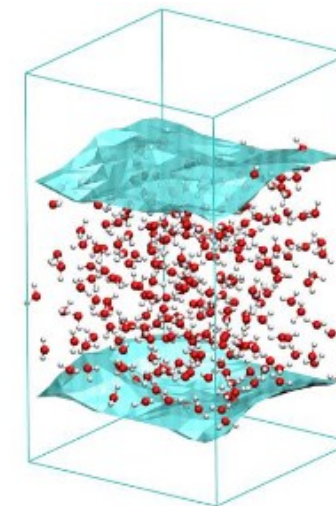
Temperature determines the amount of energy per vibrational degree of freedom, so the oscillation amplitude depends on it.

Higher temperatures lead to more pronounced anharmonicity effects ?

- ✓ Peaks are very sharp at lower temperatures – allows for more accurate determination of peaks positions
- ✓ Is more difficult to reach sufficient equilibration at lower temperatures and this reduces reliability of IR and Raman spectra
- ✓ Higher temperatures are required to sample the anharmonic region of the potential energy surface but too high temperatures become unsuitable.



- ❖ Thermostats are used to control temperature and pressure:
  - different thermostats available: NVT, NVE, NpT, NpV..
- ❖ Trajectory have to be sampled for a long enough time
- ❖ Proper time step !
- ❖ High computational cost to calculate dipole moments and polarizability especially in complex condensed matter systems like liquids, where the localization of the wave function is required
- ❖ Assignment of bands in terms of intra & intermolecular motions is much more complex



- ❖ We have theoretical methods that allow to predict Raman spectra for materials ranging from molecules through surfaces to solids or more complex systems.
- ❖ We can study evolution of the spectra depending on structural parameters and by adjusting our models accordingly.
- ❖ There are different theoretical approaches that can be used and each of them has their own advantages and limitations.
- ❖ We have to use approximation to make calculations possible so we can expect differences between theory and experiment.
- ❖ Regardless the method, there are always parameters to be set up on the way that might depend on the type of the system.

# Thank you!

Beata TAUDUL

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