

ABINIT School on ground state, linear response properties and dynamics  
Prague, Sept. 2-6, 2019



FROM RESEARCH TO INDUSTRY



# DFPT non linear response

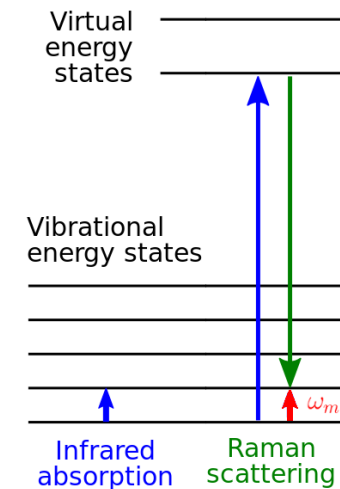
## Raman spectra using “full DFPT”

*Marc Torrent*  
*CEA, DAM, DIF, Arpajon, F-91297 France*

- Raman scattering basics
- PEAD approach vs Full DFPT approach
- 2<sup>nd</sup> order Sternheimer equation
- How to use ABINIT
- How to get Raman spectra

- Stokes mechanism : inelastic scattering of an incident photon interacting with a phonon  $\Rightarrow$  Frequency shift between the incident and scattered light :  $\Delta\omega = \omega_m$
- We treat only non resonant scattering :  $E_\gamma < E_{\text{gap}}$   
 $\Rightarrow$  Relevant only for insulators
- Measured intensity  $\approx$  sum of Lorentzian functions:

$$I(\omega) \approx \sum_m^{\text{active}} \frac{I_m}{\pi} \frac{C_m}{(\omega - \omega_m)^2 + C_m^2}$$

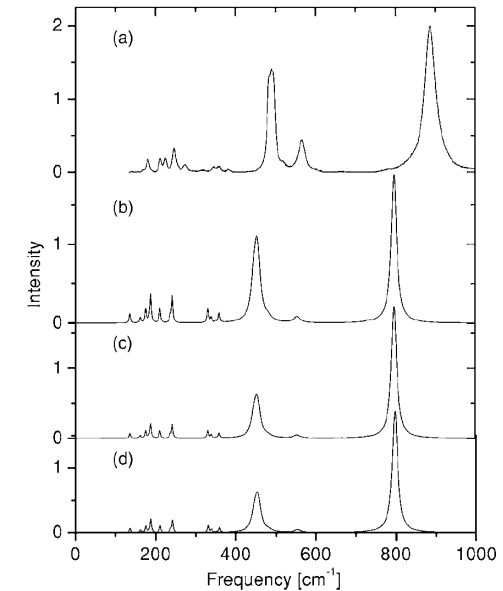


- Only active phonon modes contribute:
  - They have a null wave vector ( $q = 0$ ).
  - They follow selection rules depending on crystal symmetries and photon polarization

$$I(\omega) \approx \sum_m^{\text{active}} \frac{I_m}{\pi} \frac{C_m}{(\omega - \omega_m)^2 + C_m^2}$$

Peak properties :

- Position:  $\omega_m$  phonon frequency  
⇒ 2<sup>nd</sup> derivatives of the total energy  $E$
- Intensity:  $I_m$   
⇒ 3<sup>rd</sup> derivatives of the total energy  $E$
- Width :  $C_m$   
⇒ 3<sup>rd</sup> and 4<sup>th</sup> derivatives of the total energy  $E$



For a single crystal :

$$I_m \propto \frac{(\omega_0 - \omega_m)^4}{\omega_m} |\mathbf{e}_S \cdot \alpha^m \cdot \mathbf{e}_I|^2$$

For polycrystals : mean over all possible angles between  $\mathbf{e}_I$  and  $\mathbf{e}_S$ .

- $\omega_0/\omega_m$  : light / phonon frequency
- $\mathbf{e}_I/\mathbf{e}_S$  : incident / scattered photon polarization direction
- $\alpha^m$  : **Raman tensor**, depending on crystal properties

Raman tensor :

$$\alpha_{ij}^m = \sqrt{\Omega_0} \sum_{\kappa, \beta} \frac{d\chi_{ij}}{d\tau_{\kappa\beta}} u_m(\kappa\beta)$$

- $\Omega_0$  : crystal volume
- $u_m(\kappa\beta)$  : eigendisplacement  $m$  of atom  $\kappa$  along direction  $\beta$
- $\frac{d\chi_{ij}}{d\tau_{\kappa\beta}}$  : derivative of the electric susceptibility with respect to the displacement of atom  $\kappa$  along direction  $\beta$  (at  $\tau_{\kappa\beta} = 0$ )

$$\frac{d\chi_{ij}}{d\tau_{\kappa\beta}} = \frac{\partial\chi_{ij}}{\partial\tau_{\kappa\beta}} + \sum_k \frac{\partial\chi_{ij}}{\partial\mathcal{E}_k} \frac{\partial\mathcal{E}_k}{\partial\tau_{\kappa\beta}} \quad \chi_{ij}(\mathcal{E}) = \chi_{ij}^{(1)} + \sum_k \chi_{ijk}^{(2)} \mathcal{E}_k + O(\mathcal{E}^2)$$

For transverse optical modes (TO) :

$$\alpha_{ij}^{m_{TO}} = \sqrt{\Omega_0} \sum_{\kappa,\beta} \frac{\partial\chi_{ij}^{(1)}}{\partial\tau_{\kappa\beta}} u_m(\kappa\beta)$$

For longitudinal optical modes (LO) :

$$\alpha_{ij}^{m_{LO}} = \sqrt{\Omega_0} \sum_{\kappa,\beta} \left( \frac{\partial\chi_{ij}^{(1)}}{\partial\tau_{\kappa\beta}} - \frac{8\pi}{\Omega_0} \sum_k \chi_{ijk}^{(2)} \sum_l \epsilon_{kl}^{-1} Z_{\kappa\beta,l}^* \right) u_m(\kappa\beta)$$

- $\epsilon_{ij}^{-1}$  : inverse of the dielectric tensor (  $\epsilon_{ij} = 4\pi\chi_{ij}^{(1)} - 1$  )
- $Z_{\kappa\beta,l}^*$  : Born effective charges tensor

- We need the derivatives of the total energy  $E$  with respect to:
  - $\tau_{\kappa\alpha}$  : atomic displacement ( $\mathbf{q} = 0$ )
  - $\mathcal{E}_j$  : uniform electric field

2<sup>nd</sup> derivatives :

$$E^{(\tau_{\kappa\alpha}\tau_{\kappa'\beta})} = C_{\kappa\alpha,\kappa'\beta} \Rightarrow D_{\kappa\alpha,\kappa'\beta}(\mathbf{q} = 0) \Rightarrow \{\omega_m, u_m(\kappa, \beta)\}$$

$$E^{(\mathcal{E}_i\mathcal{E}_j)} = -\Omega_0 \chi_{ij}^{(1)} \quad E^{(\tau_{\kappa\beta}\mathcal{E}_i)} = -Z_{\kappa\beta,i}^*$$

3<sup>rd</sup> derivatives :

$$E^{(\tau_{\kappa\beta}\mathcal{E}_i\mathcal{E}_j)} = -\Omega_0 \frac{\partial \chi_{ij}^{(1)}}{\partial \tau_{\kappa\beta}} \quad E^{(\mathcal{E}_i\mathcal{E}_j\mathcal{E}_k)} = -2\Omega_0 \chi_{ijk}^{(2)}$$

Notation :

$$X^{(\lambda_1)} \equiv \left. \frac{dX}{d\lambda_1} \right|_{\lambda_1=0} \quad X^{(\lambda_1\lambda_2)} \equiv \left. \frac{d^2X}{d\lambda_1 d\lambda_2} \right|_{\lambda_1=\lambda_2=0}$$

*See Ph. Ghosez's talk...*

- The PEAD (Perturbation Expansion After Discretization) approach:
  - Gives access to 3<sup>rd</sup> order derivatives of energy
  - Is a mixing of DFPT and “Berry phase” formalism
  - Was implemented in ABINIT since 2005 (only for NC pseudopotentials)
  - Uses a discretized version of  $\nabla_k$
  - Doesn't need 2<sup>nd</sup> order derivatives of wave functions:  $|\Psi_{nk}^{(k_i \varepsilon_j)}\rangle, |\Psi_{nk}^{(k_i k_j)}\rangle$
- Alternate solution : get rid of the Berry phase formalism, need of 3<sup>rd</sup> derivatives of E in a “full DFPT” way.



From the  $2n + 1$  theorem, to compute 3<sup>rd</sup> derivatives of the energy requires only ground state wave functions  $|\Psi_{nk}^{(0)}\rangle$  and its first derivatives :

$$|\Psi_{nk}^{(\tau_{\kappa\beta})}\rangle \quad |\Psi_{nk}^{(\mathcal{E}_i)}\rangle$$

⇒ They are obtained solving 1<sup>st</sup> order Sternheimer equations.

However, the electric field perturbation brings a difficulty :

$$V(\mathcal{E}) = \mathcal{E} \cdot \mathbf{r} = \mathcal{E} \cdot "i\nabla_{\mathbf{k}}"$$

For 2<sup>nd</sup> derivatives of E, one also needs :  $|\Psi_{nk}^{(k_i)}\rangle$

and for 3<sup>rd</sup> derivatives :  $|\Psi_{nk}^{(k_i\mathcal{E}_j)}\rangle$  ,  $|\Psi_{nk}^{(k_i k_j)}\rangle$

⇒ We need to solve two 2<sup>nd</sup> order Sternheimer equations !

- The Sternheimer equations have the form  $Ax = B$  where  $A^\dagger = A$   
 $\Rightarrow$  Solved with a conjugate gradient algorithm.

$$1^{\text{st}} \text{ order : } (P^c)^\dagger (H^{(0)} - \epsilon_n S^{(0)}) P^c |\psi_n^{(\lambda_1)}\rangle = - (P^c)^\dagger (H^{(\lambda_1)} - \epsilon_n S^{(\lambda_1)}) |\psi_n^{(0)}\rangle$$

$$2^{\text{nd}} \text{ order : } (P^c)^\dagger (H^{(0)} - \epsilon_n S^{(0)}) P^c |\psi_n^{(\lambda_1 \lambda_2)}\rangle = - (P^c)^\dagger (H^{(\lambda_1 \lambda_2)} - \epsilon_n S^{(\lambda_1 \lambda_2)}) |\psi_n^{(0)}\rangle \\
- (P^c)^\dagger (H^{(\lambda_1)} - \epsilon_n S^{(\lambda_1)}) |\psi_n^{(\lambda_2)}\rangle - (P^c)^\dagger (H^{(\lambda_2)} - \epsilon_n S^{(\lambda_2)}) |\psi_n^{(\lambda_1)}\rangle \\
+ \sum_m^{\text{occ}} \Lambda_{mn}^{(\lambda_1)} (P^c)^\dagger (S^{(\lambda_2)} |\psi_m^{(0)}\rangle + S^{(0)} |\psi_m^{(\lambda_2)}\rangle) + \sum_m^{\text{occ}} \Lambda_{mn}^{(\lambda_2)} (P^c)^\dagger (S^{(\lambda_1)} |\psi_m^{(0)}\rangle + S^{(0)} |\psi_m^{(\lambda_1)}\rangle)$$

3<sup>rd</sup> order energy expression

$$E^{(\lambda_1 \lambda_2 \lambda_3)} = \frac{1}{6} \left( \tilde{E}^{(\lambda_1 \lambda_2 \lambda_3)} + \tilde{E}^{(\lambda_1 \lambda_3 \lambda_2)} + \tilde{E}^{(\lambda_2 \lambda_1 \lambda_3)} + \tilde{E}^{(\lambda_2 \lambda_3 \lambda_1)} + \tilde{E}^{(\lambda_3 \lambda_1 \lambda_2)} + \tilde{E}^{(\lambda_3 \lambda_2 \lambda_1)} \right)$$

$$\begin{aligned} \tilde{E}^{(\lambda_1 \lambda_2 \lambda_3)} &= \sum_{\mathbf{k} \in \mathcal{B}} \sum_n^{\text{occ}} \left( \langle \Psi_{n\mathbf{k}}^{(\lambda_1)} | H^{(\lambda_2)} - \epsilon_{n\mathbf{k}}^{(0)} S^{(\lambda_2)} | \Psi_{n\mathbf{k}}^{(\lambda_3)} \rangle + \langle \Psi_{n\mathbf{k}}^{(0)} | H_{\mathbf{KV}}^{(\lambda_1 \lambda_2)} | \Psi_{n\mathbf{k}}^{(\lambda_3)} \rangle + \langle \Psi_{n\mathbf{k}}^{(\lambda_1)} | H_{\mathbf{KV}}^{(\lambda_2 \lambda_3)} | \Psi_{n\mathbf{k}}^{(0)} \rangle \right) \\ &- \sum_{\mathbf{k} \in \mathcal{B}} \sum_{n,m}^{\text{occ}} \Lambda_{nm\mathbf{k}}^{(\lambda_1)} \left( \langle \Psi_{n\mathbf{k}}^{(\lambda_2)} | S^{(0)} | \Psi_{m\mathbf{k}}^{(\lambda_3)} \rangle + \langle \Psi_{n\mathbf{k}}^{(\lambda_2)} | S^{(\lambda_3)} | \Psi_{m\mathbf{k}}^{(0)} \rangle + \langle \Psi_{n\mathbf{k}}^{(0)} | S^{(\lambda_2)} | \Psi_{m\mathbf{k}}^{(\lambda_3)} \rangle \right) \\ &+ \frac{1}{6} \int d\mathbf{r} E_{\text{xc}}'''[\mathbf{r}, \tilde{n}^{(0)}] \tilde{n}^{(\lambda_1)}(\mathbf{r}) \tilde{n}^{(\lambda_2)}(\mathbf{r}) \tilde{n}^{(\lambda_3)}(\mathbf{r}) \\ &+ \frac{1}{6} \sum_a \int_{\Omega_a} d\mathbf{r} \left( E_{\text{xc}}'''[\mathbf{r}, n_a^{(0)}] n_a^{(\lambda_1)}(\mathbf{r}) n_a^{(\lambda_2)}(\mathbf{r}) n_a^{(\lambda_3)}(\mathbf{r}) - E_{\text{xc}}'''[\mathbf{r}, \tilde{n}_a^{(0)}] \tilde{n}_a^{(\lambda_1)}(\mathbf{r}) \tilde{n}_a^{(\lambda_2)}(\mathbf{r}) \tilde{n}_a^{(\lambda_3)}(\mathbf{r}) \right) \\ &+ \frac{1}{2} \int d\mathbf{r} E_{\text{Hxc}}''[\mathbf{r}, \tilde{n}^{(0)}] \tilde{n}^{(\lambda_1)}(\mathbf{r}) \tilde{n}^{(\lambda_2 \lambda_3)}(\mathbf{r}) \\ &+ \frac{1}{2} \sum_a \int_{\Omega_a} d\mathbf{r} \left( E_{\text{Hxc}}''[\mathbf{r}, n_a^{(0)}] n_a^{(\lambda_1)}(\mathbf{r}) n_a^{(\lambda_2 \lambda_3)}(\mathbf{r}) - E_{\text{Hxc}}''[\mathbf{r}, \tilde{n}_a^{(0)}] \tilde{n}_a^{(\lambda_1)}(\mathbf{r}) \tilde{n}_a^{(\lambda_2 \lambda_3)}(\mathbf{r}) \right) \end{aligned}$$

## Using PEAD approach

- Dataset 1 : ground state  
 $\Rightarrow \Psi_{nk}^{(0)}, \epsilon_{nk}^{(0)}, n^{(0)}(\mathbf{r}), \dots$
- Dataset 2 : 1st order Sternheimer (and 2de derivatives of E)  
*rfddk = 1, rfphon = 1, rfelfd = 1*  
 $\Rightarrow \Psi_{nk}^{(k_i)}, \Psi_{nk}^{(\tau_{\kappa\beta})}, \Psi_{nk}^{(\mathcal{E}_i)}$
- Dataset 3 : 3rd derivatives of E  
optdriver=5  
d3e\_pert1\_phon=1, d3e\_pert1\_elfd=1

## Using DFPT approach

- Dataset 1 : ground state  
 $\Rightarrow \psi_{nk}^{(0)}, \epsilon_{nk}^{(0)}, n^{(0)}(\mathbf{r}), \dots$
- Dataset 2 : 1st order Sternheimer (and 2de derivatives of E)  
 $rfddk = 1, rfphon = 1, rfelfd = 1$   
 $\Rightarrow \psi_{nk}^{(k_i)}, \psi_{nk}^{(\tau_{\kappa\beta})}, \psi_{nk}^{(\mathcal{E}_i)}$
- Dataset 3 : 2nd order Sternheimer  
 $rf2\_dkdk = 1$   
 $\Rightarrow \psi_{nk}^{(k_i k_j)}$
- Dataset 4 : 2nd order Sternheimer  
 $rf2\_dkde = 1$   
 $\Rightarrow \psi_{nk}^{(k_i \mathcal{E}_j)}$
- Dataset 5 : 3rd derivatives of E  
 $optdriver=5, usepead=0$  (default : 1)  
 $d3e\_pert1\_phon=1, d3e\_pert1\_elfd=1$

New in 2018  
 Available in ABINIT v8.10.3  
 Mandatory for PAW

Due to symmetries : only 1 degree of liberty in the tensors

$$a_{xyz}(AI) = -E^{(\tau_{AI,x}\varepsilon_y\varepsilon_z)}$$

$N_{\mathbf{k}}$  : number of k-points in the Brillouin zone

DFPT : current work

PEAD : previous ABINIT implementation

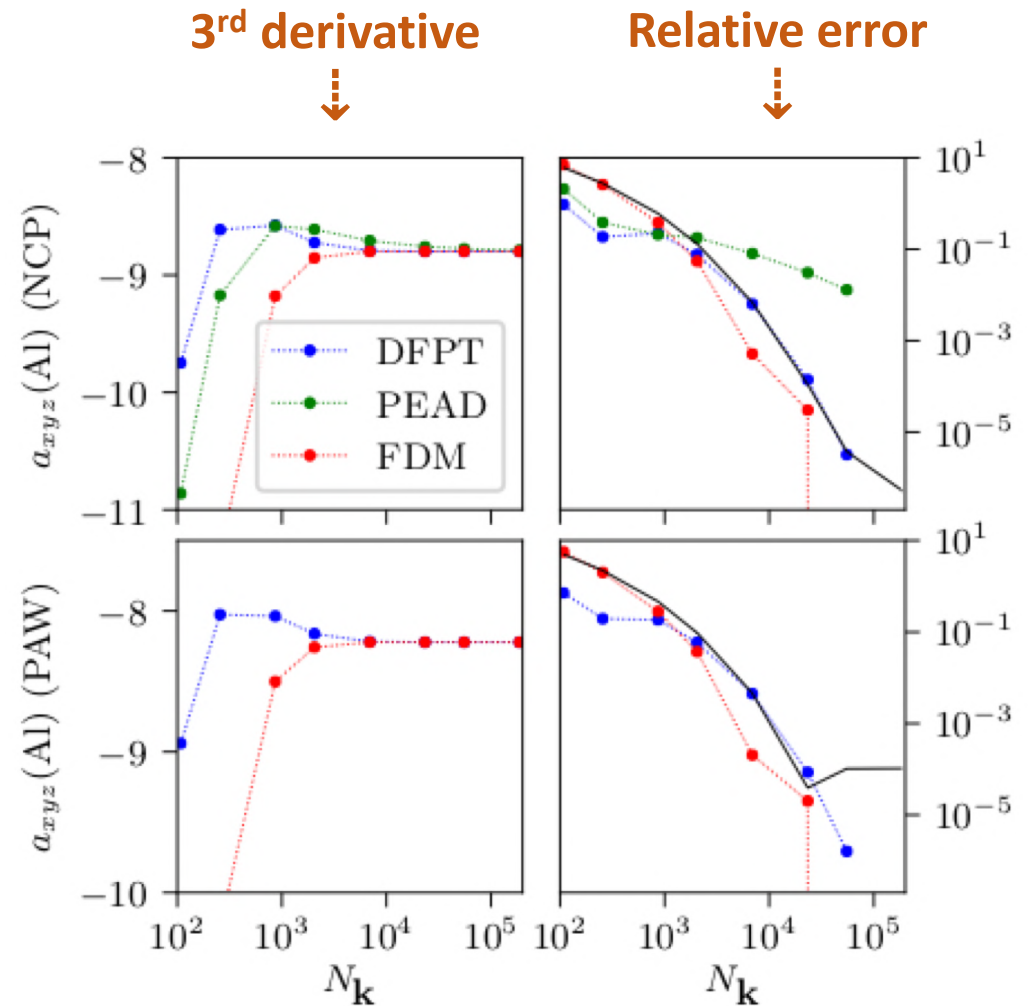
FDM : Finite Difference Method :

$$E_{FDM}^{(\tau_{AI,x}\varepsilon_y\varepsilon_z)} \equiv \frac{E_{AI=+\Delta x}^{(\varepsilon_y\varepsilon_z)} - E_{AI=-\Delta x}^{(\varepsilon_y\varepsilon_z)}}{2\Delta x}$$

$\alpha$ -quartz

NCP →

PAW →



## Transverse optical modes

(I) : ABINIT : compute DDB:  $E^{(\tau_{\kappa\alpha}\tau_{\kappa'\beta})}(\mathbf{q} = 0)$ ,  $E^{(\tau_{\kappa\beta}\varepsilon_i\varepsilon_j)}$

(II) : MRGDDB + ANADDB : diagonalize the dynamical matrix, and compute the Raman tensor  $\alpha^m$  for every phonon mode  $m$ :

$$\alpha_{ij}^m(\mathbf{q} = 0) = -\frac{1}{\sqrt{\Omega_0}} \sum_{\kappa,\beta} E^{(\tau_{\kappa\beta}\varepsilon_i\varepsilon_j)} u_{m,\mathbf{q}=0}(\kappa\beta)$$

(III) : RAMAN\_SPEC.PY : compute Raman intensities (from the Raman tensor)

Parameters depending on experimental setup : laser frequency ( $\omega_0$ ) and polarization ( $\mathbf{e}_I$ ,  $\mathbf{e}_S$ ), temperature ( $T$ )

$$I_m = \frac{\hbar}{2\omega_m} (n_m + 1) \frac{(\omega_0 - \omega_m)^4}{c^4} |\mathbf{e}_S \cdot \alpha^m \cdot \mathbf{e}_I|^2 \quad n_m = \frac{1}{e^{\hbar\omega_m/k_B T} - 1}$$

Can also compute the intensity of a powder.

## Longitudinal optical modes

(I) : ABINIT : compute DDB:  $E^{(\tau_{\kappa\alpha}\tau_{\kappa'\beta})}(\mathbf{q} = 0)$ ,  $E^{(\tau_{\kappa\beta}\epsilon_i\epsilon_j)}$ ,  $E^{(\epsilon_i\epsilon_j)}$ ,  $E^{(\tau_{\kappa\beta}\epsilon_i)}$ ,  $E^{(\epsilon_i\epsilon_j\epsilon_k)}$

(II) : MRGDDB + ANADDB : diagonalize the dynamical matrix, and compute the Raman tensor  $\alpha^m$  for every phonon mode  $m$ :

$$TO : \alpha_{ij}^m(\mathbf{q} = 0) = -\frac{1}{\sqrt{\Omega_0}} \sum_{\kappa,\beta} E^{(\tau_{\kappa\beta}\epsilon_i\epsilon_j)} u_{m,\mathbf{q}=0}(\kappa\beta)$$

For different  $\mathbf{q}$  directions:

$$LO : \alpha_{ij}^m(\mathbf{q} \rightarrow 0) = -\frac{1}{\sqrt{\Omega_0}} \sum_{\kappa,\beta} E^{(\tau_{\kappa\beta}\epsilon_i\epsilon_j)} u_{m,\mathbf{q}\rightarrow 0}(\kappa\beta) + \sum_{\kappa,\beta} \frac{4\pi}{\Omega_0^2} \left( \sum_k E^{(\epsilon_i\epsilon_j\epsilon_k)} q_k \right) \frac{\sum_k Z_{\kappa,\beta,k}^* q_k}{\sum_{k,l} \epsilon_{kl} q_k q_l} u_{m,\mathbf{q}\rightarrow 0}(\kappa\beta)$$

(III) : RAMAN\_SPEC.PY : compute Raman intensities (from the Raman tensor)

Parameters depending on experimental setup : laser frequency ( $\omega_0$ ) and polarization ( $\mathbf{e}_I$ ,  $\mathbf{e}_S$ ), temperature ( $T$ )

$$I_m = \frac{\hbar}{2\omega_m} (n_m + 1) \frac{(\omega_0 - \omega_m)^4}{c^4} |\mathbf{e}_S \cdot \alpha^m \cdot \mathbf{e}_I|^2 \quad n_m = \frac{1}{e^{\hbar\omega_m/k_B T} - 1}$$

**WARNING :** For LO modes,  $I_{\text{powder}}$  cannot be obtained directly from *RAMAN\_SPEC.PY* : numerical integration on  $\mathbf{q}$  directions is needed!



$\alpha$ -quartz

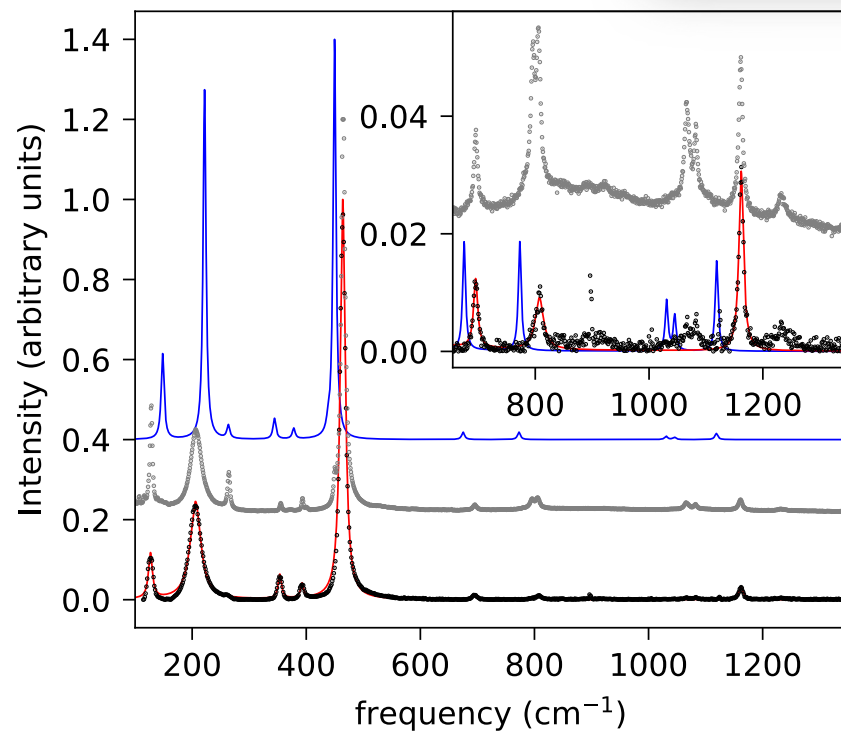
$$I(\omega) \approx \sum_m^{\text{active}} \frac{I_m}{\pi} \frac{\Gamma_m}{(\omega - \omega_m)^2 + \Gamma_m^2}$$

**Blue line** (offset=0.4): theoretical spectrum - PAW+LDA ( $\Gamma_m = 4 \text{ cm}^{-1}$ )

**Grey dots** (offset=0.2) : experimental spectrum (Handbook of Minerals Raman Spectra)

**Black dots** (no offset) : experimental spectrum (RRUFF project)

**Red line** : Fit of RRUFF data



PAW+LDA		Fit of RRUFF		
$\omega$	$I/I_{\text{ref}}$	$\omega$	$I/I_{\text{ref}}$	$\Gamma$
148	0.214	127	0.089	4.1
222	0.875	206	0.521	11.1
263	0.033			
344	0.052	354	0.040	3.5
378	0.027	393	0.021	3.0
438	0.019			
450	1.000	464	1.000	5.2
675	0.018	695	0.010	4.4
773	0.019	807	0.014	8.6
1031	0.009			
1045	0.006			
1119	0.015	1162	0.028	4.8

**Preliminary results on LiCoO<sub>2</sub>:**

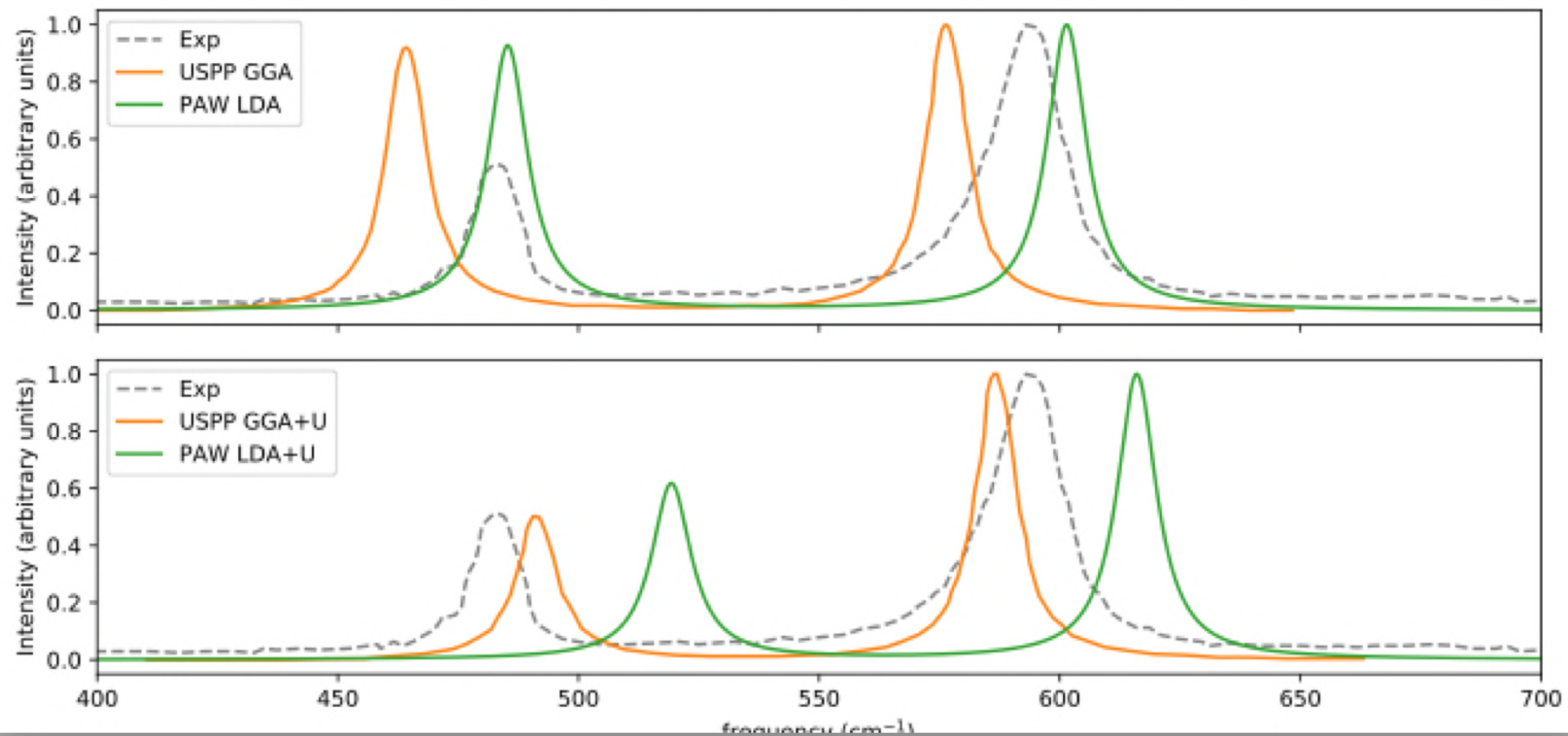
With "+U", relative error between DFPT and finite difference (FD) on the Raman tensor :  $|\alpha_{ij}^{DFPT} - \alpha_{ij}^{FD}| / |\alpha_{ij}^{DFPT}| < 0.2\%$

Comparison between PAW LDA / LDA+U (this work) and Ultrasoft (USPP) GGA / GGA+U (Miwa PRB 97, 075143 (2018)):

- **U and J not computed for LDA+U**, chosen as the same values than GGA+U ( $U = 5.6$  eV,  $J = 0.8$  eV).
- Cell optimization for LDA and LDA+U

Experimental values also taken from Inaba *et al*, Chem. Lett. 24, 889 (1995).

Theoretical spectra : lorentzian width =  $5 \text{ cm}^{-1}$ , depend on three parameters only :  $\omega_1, \omega_2, I_1/I_2$ .



- **PEAD approach**
  - Norm-conserving pseudopotentials
  - LDA exchange correlation only
  - No spins
  - Is a mixing of DFPT and “Berry phase” formalism
- **Full DFPT approach**
  - Norm-conserving pseudopotentials and Projector Augmented-Wave
  - LDA exchange correlation only  
*Need “pawxcdev=0” keyword (no accelerated XC)*
  - Spins, but no spinors
  - DFT+U (electronic correlations)

- “Full DFPT” approach is an alternative to PEAD approach to apply non-linear response formalism.
- It is available for both NCPP and PAW formalisms.
- It needs more computational steps.
- It converges better with respect to the k-point grid.

- [1] *Density-functional perturbational theory for dielectric tensors in the ultrasoft pseudopotential scheme*, Umari, Gonze, Pasquarello, PRB 69, 235102 (2004)
- [2] *Nonlinear optical susceptibilities, Raman Efficiencies, and eletro-optic tensors from first-principle density functional perturbation theory*, Veithen, Gonze, Ghosez, PRB 71, 125107 (2005)
- [3] *Projector Augmented-Wave approach to density-functional perturbation theory*, Audouze, Jollet, Torrent, Gonze, PRB 73, 235101 (2006)
- [4] *Prediction of Raman spectra with ultrasoft pseudopotentials*, PRB 84, 094304 (2011)
- [5] *Computation of Raman spectra within the Density Functional Perturbation Theory coupled with the Projector Augmented-Wave method*, Baguet, Torrent, in preparation

