3rd International ABINIT Developer Workshop

First-principles modelling of experimental phonon spectra

Patrick Hermet

Groupe de physique théorique des matériaux

Université de Liège

patrick.hermet@ulg.ac.be

Wednesday 31 January 2007

Outline

1. Background before modelling phonon spectra

2. Inelastic neutron scattering response

- Fundamental equations
- Application to α-bithiophene

3. Infrared transmission response

- Fundamental equations
- Case of polycrystalline powder
- Application to α-quaterthiophene

4. Nonresonant Raman scattering response

- Fundamental equations
- Application to α-bithiophene

Background before modelling phonon spectra

Dynamical matrix

Calculation of phonons

↓

Knowledge of dynamical matrix : $D_{\alpha\beta}(\mathbf{q} ; \kappa, \kappa')$

→ Frozen phonon

→ Linear response

↓ Diagonalization for a fixed **q**

3pκ eigenvalues ⟶ the square of vibrational frequencies of the mode *s* : $\omega^2_s(\boldsymbol{q})$

3pκ eigenvectors ⟶ the polarization vectors of the mode *s* : $\boldsymbol{e}(\kappa ; s, \boldsymbol{q})$

where

α, β = Cartesian directions

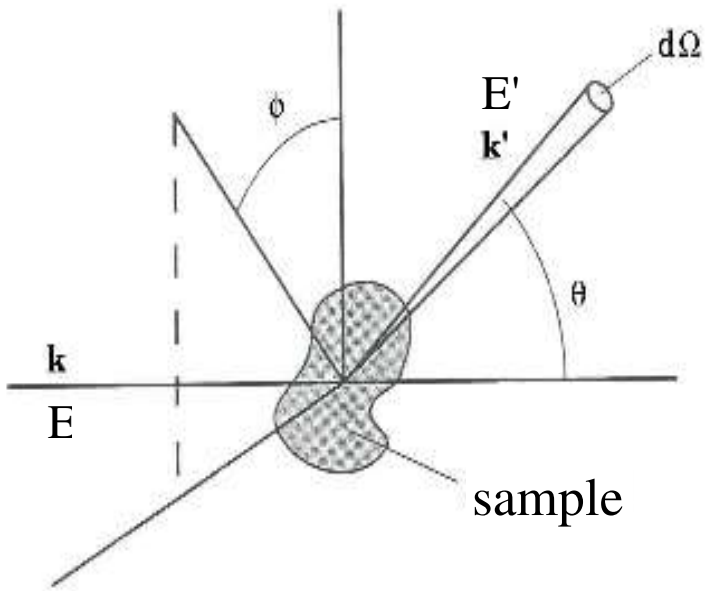
κ, κ' = atom numbers

p = space dimension

q = phonon wavevector within the first Brillouin zone

Inelastic neutron scattering

Principles



E (resp. E') : energy of incident (resp. scattered) neutrons

k (resp. **k'**) : wavevector of incident (resp. scattered) neutrons

|m> (resp. |m'>) : initial (resp. final) state of the sample

|i> = |**k**>|m> : initial state of the neutron-sample system

|f> = |**k'**>|m'> : final state of the neutron-sample system

Momentum conservation : $\hbar \mathbf{K} = \hbar(\mathbf{k} - \mathbf{k}')$

Energy conservation : $\hbar\omega = E_m - E_{m'} = E - E'$

In a INS experiment, we measure the number of scattered neutrons (dN), by time unit, within the solid angle (dΩ), and with an energy included between E' and dE'.

This number, dN, is proportional to the differential scattering cross section given by :

$$\frac{d^2\sigma}{d\Omega\, dE'} = \frac{dN}{\phi\, d\Omega\, dE'},$$

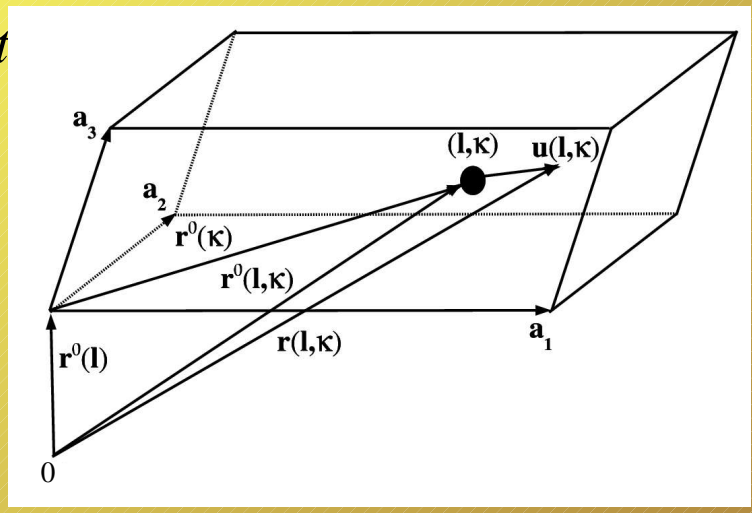
where ϕ is the incident flux of neutrons

Inelastic neutron scattering

Fundamental equations

Using a hard-core potential for neutron-nucleus, $U(r)=2\pi\hbar\sum_{j=1}^{N}\frac{b_j}{m_j}\delta(r-r_j)$, and the Fermi's golden rule, $W_{if}=\frac{2\pi}{\hbar}|\langle \boldsymbol{k}'m'|U|\boldsymbol{k}m\rangle|^2\,\delta(\hbar\omega+E_m-E_{m'})$, the differential scattering cross section is given by:

$$\frac{d^2\sigma}{d\Omega\,dE'}=\frac{k'}{k}\frac{1}{2\pi\hbar}\sum_{jj'}\int_{-\infty}^{+\infty}e^{i\omega t}<b_j b_{j'}e^{i\boldsymbol{K}\boldsymbol{r}_j(t)}e^{-i\boldsymbol{K}\boldsymbol{r}_{j'}(0)}>dt$$



In a crystal, the instantaneous position of the κ-nucleous belonging to the **l**-cell is :

$$\boldsymbol{r}_j=\boldsymbol{r}(\boldsymbol{l},\kappa)=\boldsymbol{r}^0(\boldsymbol{l},\kappa)+\boldsymbol{u}(\boldsymbol{l},\kappa)\longrightarrow j=(\boldsymbol{l},\kappa)$$

Thus, the differential scattering cross section is :

$$\frac{d^2\sigma}{d\Omega\,dE'}=\frac{k'}{k}\frac{1}{2\pi\hbar}\sum_{l\kappa'}\sigma_{inc}(\kappa)e^{-2W_\kappa(\boldsymbol{K})}\int_{-\infty}^{+\infty}e^{i\omega t}<e^{i\boldsymbol{K}\boldsymbol{u}(\boldsymbol{l},\kappa;t)\boldsymbol{K}\boldsymbol{u}(\boldsymbol{l},\kappa;0)}>dt$$

where $\sigma_{inc}(\kappa)=\overline{b_\kappa^2}-\bar{b}_\kappa^2$ and $W_\kappa(\boldsymbol{K})=\frac{1}{2}\langle[\boldsymbol{K}\boldsymbol{u}(\boldsymbol{l},\kappa;0)]^2\rangle$

Inelastic neutron scattering

Fundamental equations

After developing in series the exponential and using the Fourier transform of the displacement-displacement autocorrelation function,

$$\int_{-\infty}^{+\infty} e^{i\omega t}\langle \boldsymbol{u}(\boldsymbol{l},\kappa;t)\boldsymbol{u}(\boldsymbol{l}',\kappa';0)\rangle dt = \frac{2\pi\hbar[n(\omega)+1]}{\sqrt{m_\kappa m_{\kappa'}}}\sum_{s,\boldsymbol{q}} e_\alpha(\kappa;s,\boldsymbol{q})e^*_\beta(\kappa';s,\boldsymbol{q})e^{i\boldsymbol{q}[\boldsymbol{r}(\boldsymbol{l})-\boldsymbol{r}(\boldsymbol{l}')]}\frac{1}{2\omega_s(\boldsymbol{q})}$$
$$[\delta(\omega-\omega_s(\boldsymbol{q}))-\delta(\omega+\omega_s(\boldsymbol{q}))],$$

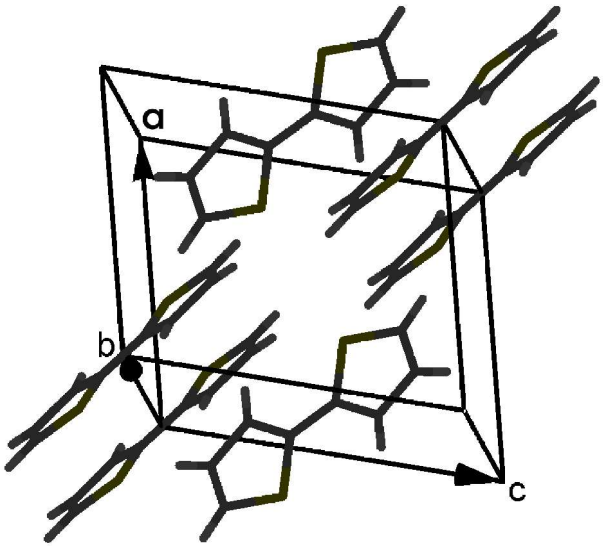
we have the famous equation of inelastic neutron scattering :

$$\frac{d^2\sigma}{d\Omega\, dE'} = \frac{k'}{k}[n(\omega)+1]\sum_\kappa \frac{\sigma_{inc}(\kappa)}{m_\kappa}\sum_{s,\boldsymbol{q}}|\boldsymbol{K}\,\boldsymbol{e}(\kappa;s,\boldsymbol{q})|^2\, e^{-2W_\kappa(\boldsymbol{K})}\frac{1}{2\omega_s(\boldsymbol{q})}[\delta(\omega-\omega_s(\boldsymbol{q}))-\delta(\omega-\omega_s(\boldsymbol{q}))]$$

where $n(\omega)$ is the Bose factor

Inelastic neutron scattering

Application: the α-bithiophene



Monoclinic unit cell ($P2_1/c$) :

$a = 7.734$ Å

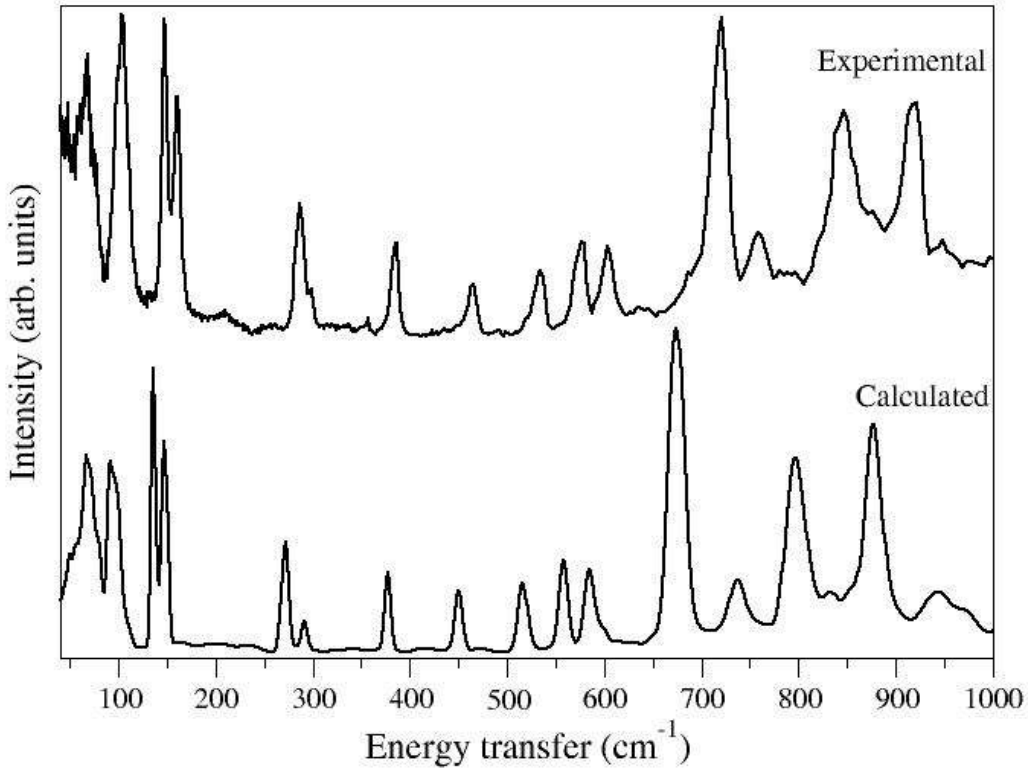
$b = 5.729$ Å

$c = 8.933$ Å

$\beta = 106.72°$

$Z = 2$

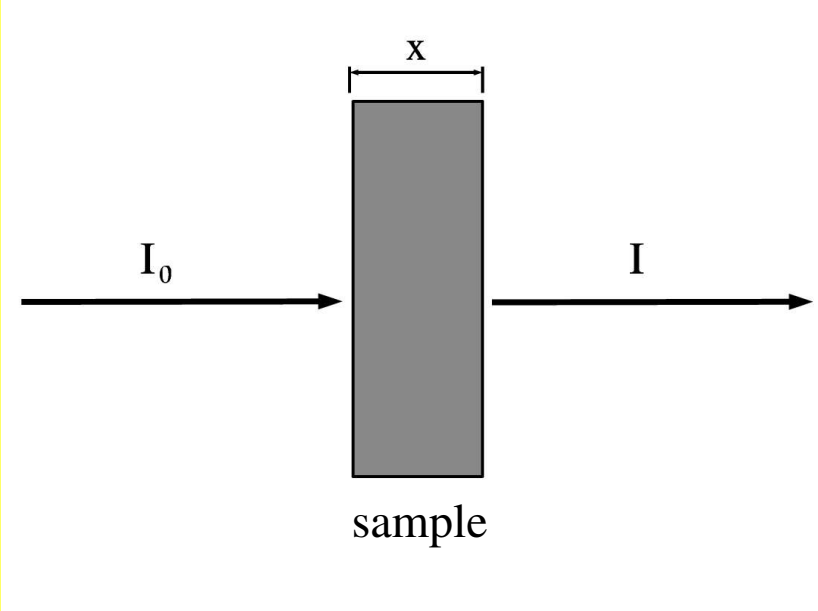
32 atoms



P. Hermet *et al*, J. Phys.: Condens. Matter **16** (2004) 7385

Infrared response

Principles



I_0 : intensity of incident radiation

I : intensity of transmitted radiation

x : width of sample

n : refraction index of the sample

ω : frequency of the radiation

Beer-Lambert law : $\frac{I}{I_0} = e^{-\mu x}$ where $\mu = \frac{\omega}{nc} \Im \chi$

with χ is the dielectric susceptibility of sample

c is the speed of light

Infrared response

Fundamental equations

Hamiltonian of system : $H = H_0 + H'$ with $H_o\,|n\rangle = E\,|n\rangle$ and $H' = -\,\mathbf{M}\,.\,\mathbf{E}$

where **M** is the dipolar moment, and **E** is the electric field

Under the electric field, the system is not at the equilibrium and a polarization, **P**, appears :

$$\langle P_\alpha(t)\rangle = Tr(\rho P_\alpha) = \epsilon_0 \sum_\beta \int_{-\infty}^{t} \chi_{\alpha\beta}(t-t')E_\beta(t')dt', \qquad \alpha, \beta = x, y, z$$

where the density operator, ρ, obeys at the evolution equation :

$$i\hbar\frac{\partial\rho}{\partial t} = [H, \rho]$$

After some developments, we have :

$$\chi_{\alpha\beta}(\tau) = \frac{1}{\epsilon_0 V}\frac{i}{\hbar}\langle[M_\alpha(\tau), M_\beta(0)]\rangle\theta(\tau),$$

where θ is the Heaviside function and $\tau = t - t'$

Infrared response

Fundamental equations

Using the dipolar moment is given by : $M_\alpha = \sum_{\beta, l', \kappa} Z^*_{\alpha\beta}(\kappa) u_\beta(l', \kappa),$

where $Z^*(\kappa)$ is the Born effective charge tensor and $u(l', \kappa)$ is the displacement of the κ-atom within the l'-cell, the dielectric susceptibility is :

$$\chi_{\gamma\delta}(\tau) = \frac{1}{\epsilon_0 V} \frac{i}{\hbar} \sum_{\alpha, l, \kappa} \sum_{\beta, l', \kappa'} Z^*_{\gamma\alpha}(\kappa) Z^*_{\delta\beta}(\kappa') \langle [u_\alpha(l, \kappa; \tau), u_\beta(l', \kappa'; 0)] \rangle \theta(\tau)$$

Taking the Fourier transform and using the fluctuation-dissipation theorem, we have :

$$\Im \chi_{\gamma\delta}(\tau) = \frac{1}{\epsilon_0 V} \frac{1}{2\hbar} \sum_{\alpha, l, \kappa} \sum_{\beta, l', \kappa'} Z^*_{\gamma\alpha}(\kappa) Z^*_{\delta\beta}(\kappa') (1 - e^{-\beta\hbar\omega}) \int_{-\infty}^{+\infty} \langle u_\alpha(l, \kappa; \tau) u_\beta(l', \kappa'; 0) \rangle e^{i\omega\tau} d\tau$$

Finally, using the expression of the Fourier transform of the displacement-displacement autocorrelation function, the imaginary part of the dielectric susceptibility is (for $q = 0$) :

$$\Im \chi_{\gamma\delta}(\omega) = \frac{\pi}{\epsilon_0 V} \sum_s \frac{A_{\gamma\delta}(s)}{2\omega_s} [\delta(\omega - \omega_s) - \delta(\omega + \omega_s)]$$

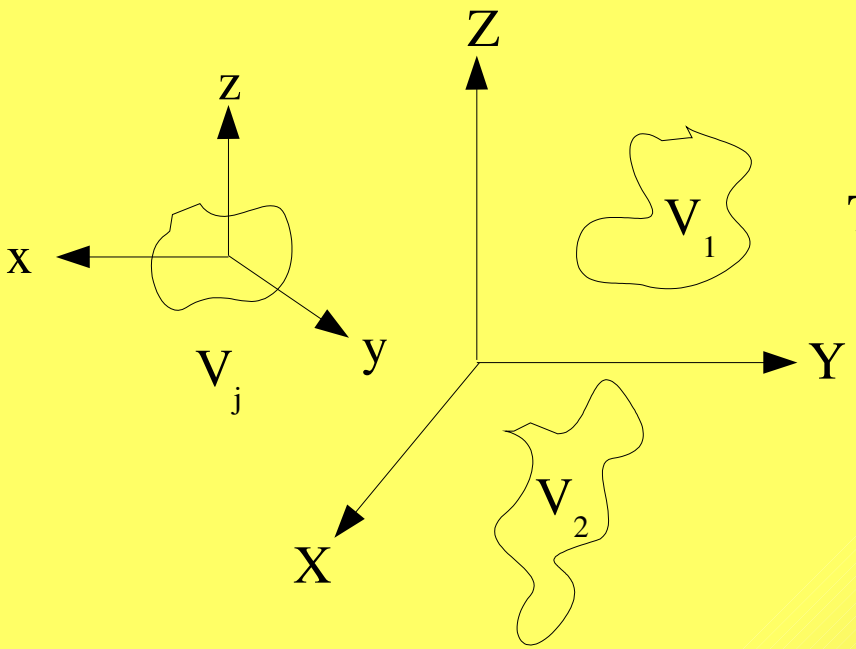
where

$$A_{\gamma\delta}(s) = [\sum_{\alpha\kappa} \frac{Z^*_{\gamma\alpha}(\kappa)}{\sqrt{m_\kappa}} e_\alpha(\kappa, s)] [\sum_{\beta\kappa'} \frac{Z^*_{\delta\beta}(\kappa')}{\sqrt{m_{\kappa'}}} e_\beta(\kappa', s)]$$

Infrared response

Polycrystalline powder

We consider a system with a volume V and constituted of N subsystems



XYZ : laboratory referential

xyz : subsystem referential

The dielectric polarization of the total system is given by :

$$P_\alpha = \frac{1}{V}\sum_j V^j P_\alpha^j = \frac{\epsilon_0}{V}\sum_j V^j \sum_\beta \chi_{\alpha\beta}^j E_\beta^j$$

where P^j, V^j, and χ^j are respectively the polarization, the volume and the susceptibility of the *j*-subsystem

We suppose that the macroscopic electric field $\boldsymbol{E}$ is the same as the electric fields $\boldsymbol{E}^j$ acting on each subsystem, and there is no electromagnetic interaction between each subsystem (true if the (particles are not metallic and the particles are not too close each others). Within these hypothesis, we have :

$$\chi_{\alpha\beta} = \frac{1}{V}\sum_{j=1}^{N} V^j \chi_{\alpha\beta}^j$$

Now, we suppose that the subsystems are identical (V^j are equal), and connected only by a rigid rotation

→ The *j*-index can be represented by 3 angles : Ψ, θ and ϕ (the Euler's angle)

Infrared response

Polycrystalline powder

The susceptibility of the different subsystems can be obtained as :

$$\chi^{j}_{\alpha\beta} = \sum_{\gamma\delta} R^{j}_{\alpha\gamma}\,\chi^{0}_{\gamma\delta}\,(R^{j}_{\delta\beta})^{-1}$$ where R is the rotation matrix given by :

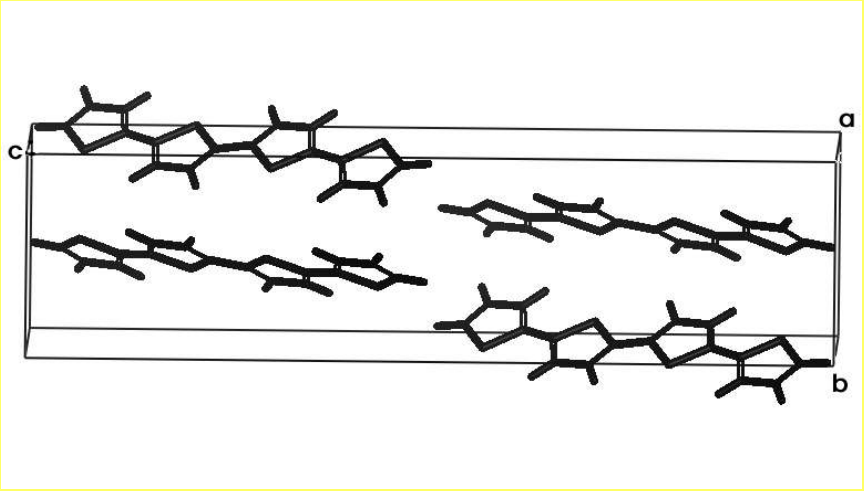
$$R^{j}=R^{(\Psi,\theta,\phi)}=\begin{pmatrix} \cos\Psi\cos\theta\cos\phi-\sin\Psi\sin\theta & \cos\Psi\cos\theta\sin\phi+\sin\Psi\cos\phi & \cos\Psi\cos\theta \\ -\sin\Psi\cos\theta\cos\phi-\cos\Psi\sin\theta & -\sin\Psi\cos\theta\sin\Psi+\cos\Psi\cos\phi & -\sin\Psi\sin\theta \\ -\cos\phi\cos\theta & -\sin\phi\sin\theta & \cos\theta \end{pmatrix}$$

The susceptibility of the total system is :

$$\chi_{\alpha\beta} = \int_0^{2\pi} d\phi \int_0^{\pi} \sin\theta\, d\theta \int_0^{2\pi} d\Psi \left[R^{(\Psi,\theta,\phi)}\chi^{0}\,(R^{(\Psi,\theta,\phi)})^{-1}\right]_{\alpha\beta}$$

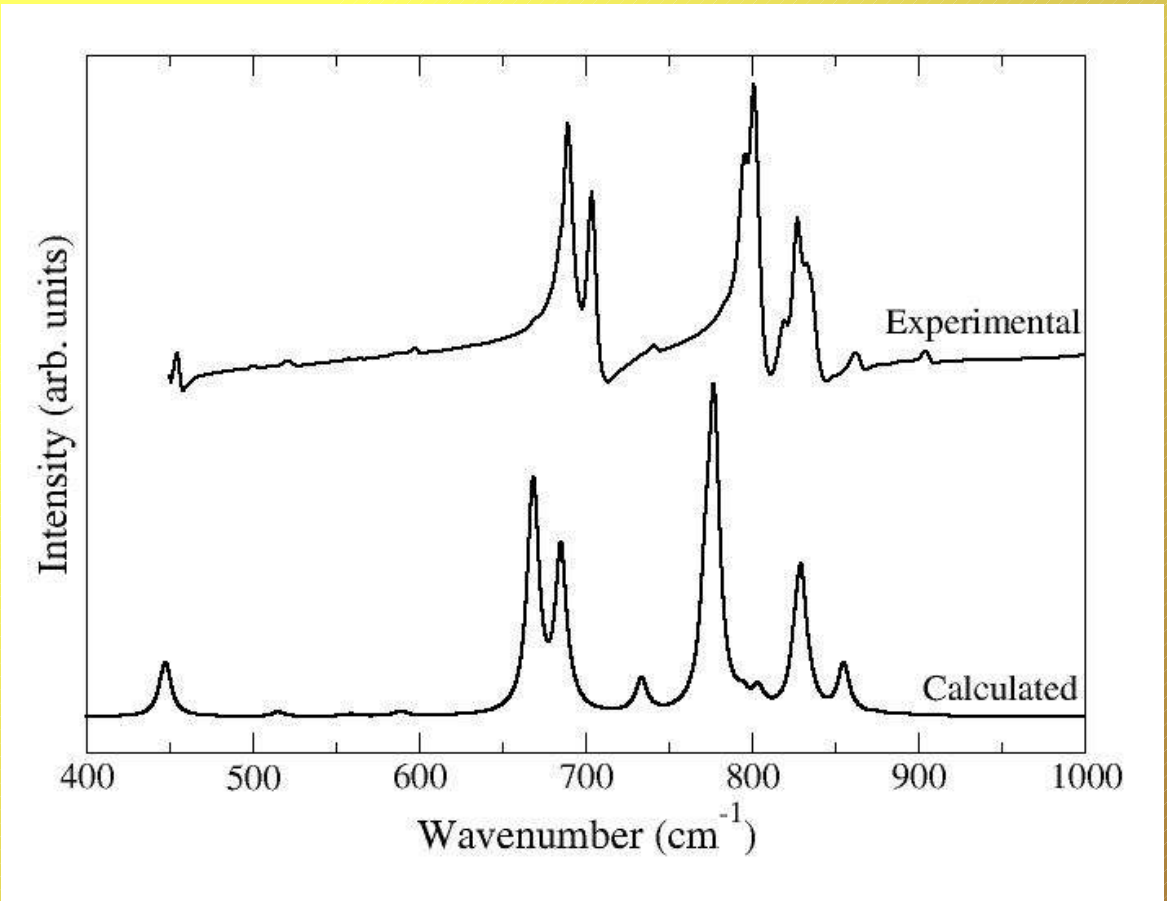
Infrared response

Application : the α-quaterthiophene



Monoclinic unit cell ($P2_1/c$)

- a = 6.085 Å
- b = 7.858 Å
- c = 30.483 Å
- β = 91.81°
- Z = 4
- 120 atoms



P. Hermet *et al*, Synth. Metals **156** (2006) 519

Nonresonant Raman scattering response

Fundamental equations

We show that the differential cross section is proportional to :

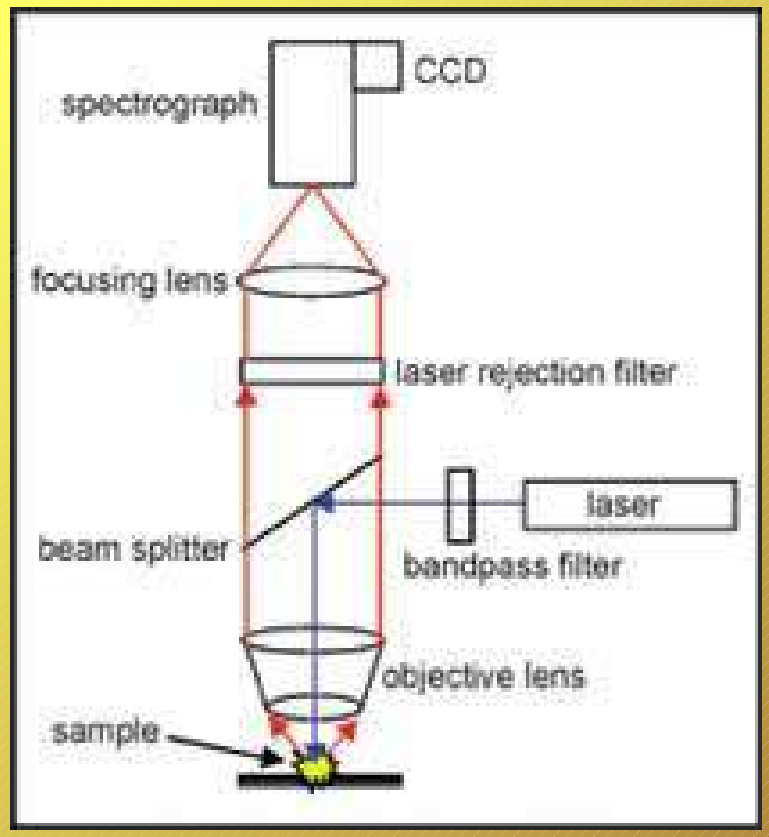
$$\frac{d^2\sigma}{d\Omega\, d\omega_d} \propto \int_{-\infty}^{+\infty} \langle \boldsymbol{A}^*(\boldsymbol{r},t)\,\boldsymbol{A}(\boldsymbol{r},t+\tau)\rangle e^{i\omega_f \tau}\, d\tau$$

After the electromagnetism rules, we have :

$$\Delta \boldsymbol{A}(\boldsymbol{r},t) - \frac{1}{c^2}\frac{\partial^2 \boldsymbol{A}(\boldsymbol{r},t)}{\partial t^2} = -\mu_0 \frac{\partial \boldsymbol{P}(\boldsymbol{r},t)}{\partial t}$$

and the solutions are given by :

$$\boldsymbol{A}(\boldsymbol{r},t) = \frac{\mu_0}{4\pi}\int \frac{\delta\left(t - t' - \frac{|\boldsymbol{r}-\boldsymbol{r}'|}{c}\right)}{|\boldsymbol{r}-\boldsymbol{r}'|}\frac{\partial \boldsymbol{P}(\boldsymbol{r}',t')}{\partial t'}\, dt'\, d^3 r'$$



Under the electric field, $E_i = E_i^0\ e^{i(\boldsymbol{k}_i \boldsymbol{r} - \omega_i t)}$, a polarization appears in the medium given by : $\boldsymbol{P}(\boldsymbol{r},t) = \epsilon_O \chi(\boldsymbol{r},t)\boldsymbol{E}_i$

Nonresonant Raman scattering response

Fundamental equations

If we suppose that the polarizability is due to the fluctuation of susceptibility, we have :

$$\delta P(\boldsymbol{r},t)=\epsilon_O \delta\chi(\boldsymbol{r},t)\boldsymbol{E}_i \quad \text{with} \quad \delta\chi_{\alpha\gamma}=\sum_{\delta\kappa}\left(\frac{\partial\chi_{\alpha\gamma}}{\partial u_\delta(\kappa)}\right)_0 u_\delta(\kappa)$$

Then, using the annihilation-creation operators to express the displacement :

$$u_\delta(\kappa,t)=\sum_s\sqrt{\frac{\hbar}{2\omega_s}}\left[\frac{e_\delta(\kappa,s)}{\sqrt{m_\kappa}}a_s e^{-i\omega_f t}+\frac{e_\delta(\kappa,s)}{\sqrt{m_\kappa}}a_s^+ e^{-i\omega_f t}\right]$$

and using the averages : $\langle a_s a_{s'}^+\rangle=\delta_{ss'}(n_s+1)$ and $\langle a_s^+ a_{s'}\rangle=\delta_{ss'}n_s$ where n_s is the Bose factor, we have the differential cross section :

$$\frac{d^2\sigma}{d\Omega\, d\omega_f}=\frac{\omega_f^4}{8\pi^2c^2}[n(\omega)+1]\hbar\sum_{\alpha\beta\gamma\lambda}v_\alpha v_\beta I_{\alpha\gamma\beta\lambda}(\omega)w_\gamma w_\lambda$$

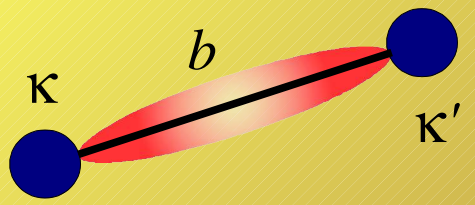
with, $$I_{\alpha\gamma\beta\lambda}(\omega)=\sum_s a^*_{\alpha\gamma}(s)a_{\beta\lambda}(s)\frac{1}{2\omega_s}\left[\delta(\omega-\omega_s)-\delta(\omega+\omega_s)\right]$$

and, $$a_{\alpha\gamma}(s)=\sqrt{V}\sum_{\kappa\delta}\frac{1}{\sqrt{m_\kappa}}\pi^\kappa_{\alpha\gamma,\delta}\,e_\delta(\kappa,s) \quad \text{where} \quad \pi^\kappa_{\alpha\gamma,\delta}=\left(\frac{\partial\chi_{\alpha\gamma}}{\partial u_\delta(\kappa)}\right)_0$$

Nonresonant Raman scattering response

Calculation of π–tensors: the bond polarizability model

The susceptibility χ of the crystal can be decomposed into individual contributions, arising only from the polarizability α of bond *b* between nearrest-neighbor atoms :



$$\chi_{\alpha\gamma} = \frac{1}{V}\sum_{b} \alpha^{b}_{\alpha\gamma}$$

and the polarizability of a particular bond *b* is given by the empiric equation :

$$\alpha^{b}_{\alpha\gamma}(r) = \frac{1}{3}(\alpha_l + 2\alpha_p)\,\delta_{\alpha\gamma} + (\alpha_l - \alpha_p)\left(\hat{r}_\alpha \hat{r}_\gamma - \frac{1}{3}\delta_{\alpha\gamma}\right)$$

Now, we suppose that the BP parameters are functions of the bond lengths only, so that

$$\pi^{\kappa}_{\alpha\gamma,\delta} = \frac{1}{V}\sum_{b}\left[\frac{1}{3}\underbrace{(2\alpha'_p + \alpha'_l)}_{\bar{\alpha}}\,\delta_{\alpha\gamma}\hat{r}_\delta + \underbrace{(\alpha'_l - \alpha'_p)}_{\bar{\beta}}\left(\hat{r}_\alpha \hat{r}_\gamma - \frac{1}{3}\delta_{\alpha\gamma}\right)\hat{r}_\delta + \underbrace{\frac{\alpha_l - \alpha_p}{r}}_{\bar{\gamma}}\left(\delta_{\alpha\delta}\hat{r}_\gamma + \delta_{\gamma\delta}\hat{r}_\alpha - 2\hat{r}_\alpha \hat{r}_\gamma \hat{r}_\delta\right)\right]$$

$\bar{\alpha}, \bar{\beta}, \bar{\gamma}$ are determined by fitting the experimental intensities of Raman spectrum

M.V. Wolkenstein, *C.R. Acad. Sci. URSS* **30** (1941) 791

Nonresonant Raman scattering response

Calculation of π–tensors: the nonlinear response

π-tensors are related to a mixed third-order derivative with respect to two electric fields and one atomic displacement of the field-dependent energy functional, F = $\mathcal{E}$ - V **E . P**, where $\mathcal{E}$ is the total energy in zero field and **E** (respectively **P**) are the macroscopic electric field (respectively polarization) :

$$\pi^{\kappa}_{\beta\gamma,\delta} = -\frac{1}{V}\frac{\partial^3 F}{\partial E_\beta \partial E_\gamma \partial u_\delta(\kappa)}$$

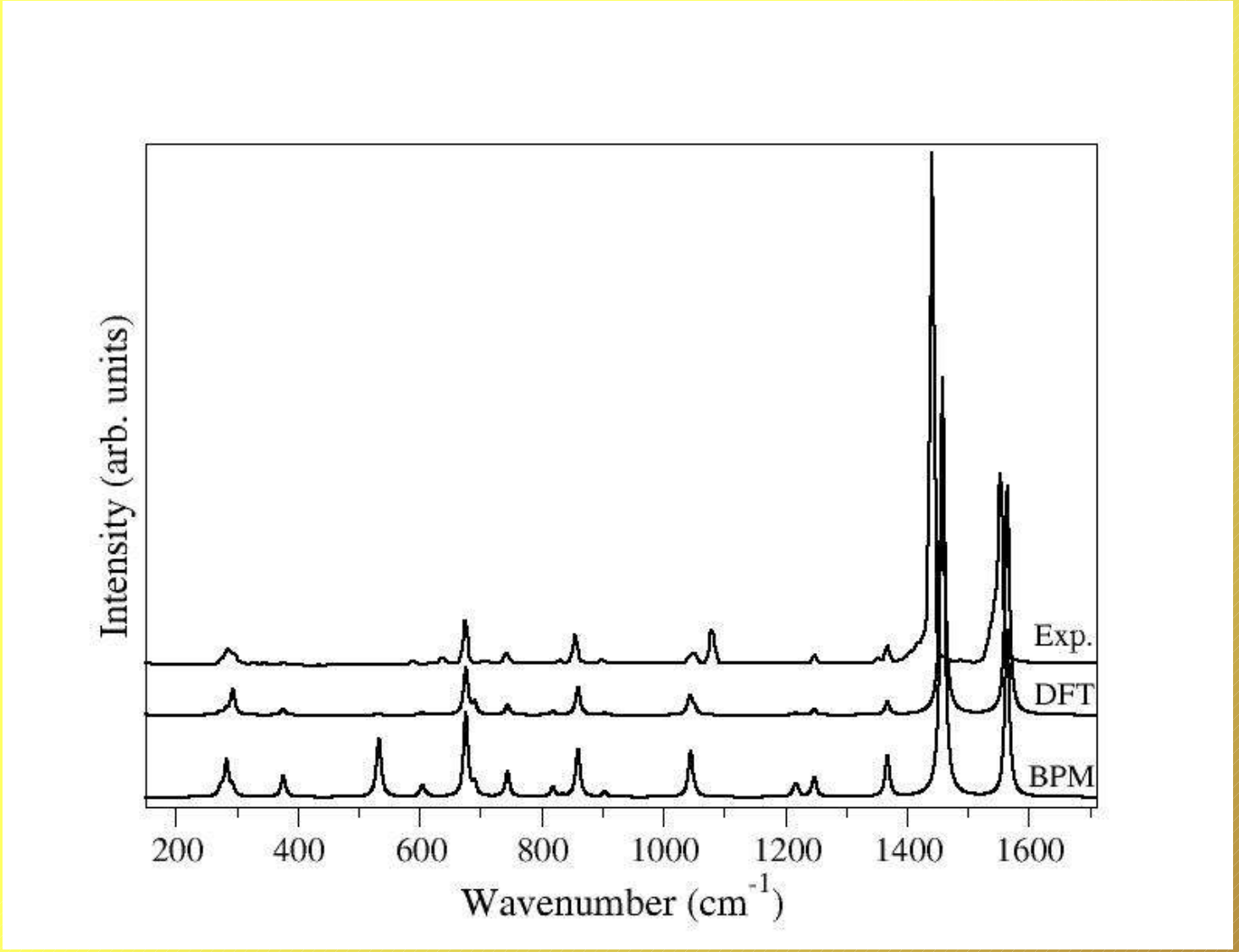
These derivatives are obtained within a nonlinear response formalism, taking advantage of the (2n +1) theorem

M.Veithen *et al*, Phys. Rev. Lett. **93** (2004) 187401

M.Veithen *et al*, Phys. Rev. B **71** (2005) 125107

Nonresonant Raman scattering response

Application : the α-bithiophene



P. Hermet *et al*, J. Phys. Chem. B **110** (2006) 24869

Conclusions

- Abinit and anaddb compute independently all quantities required to simulate the INS, IR and Raman responses ⟶ It could be interesting to do a subroutine with the equations for the 3 spectroscopies to help spectroscopists in the understanding of their phonon spectra

- For Raman response : since the calculations of π-tensors, via the nonlinear response, require a very important computing time for large systems, it could be interesting to implement the bond polarizability model in anaddb