SSCHA SCHOOL · JUNE 8-12, 2026 - ONLINE

Vibrational spectroscopy of strongly anharmonic materials:

Calculation of Raman and IR spectra

Lorenzo Monacelli
Università di Roma «Sapienza», Dipartimento di Fisica

SAPIENZA UNIVERSITÀ DI ROMA

SSCHA

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Why vibrational spectroscopy?
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Static and dynamic response functions

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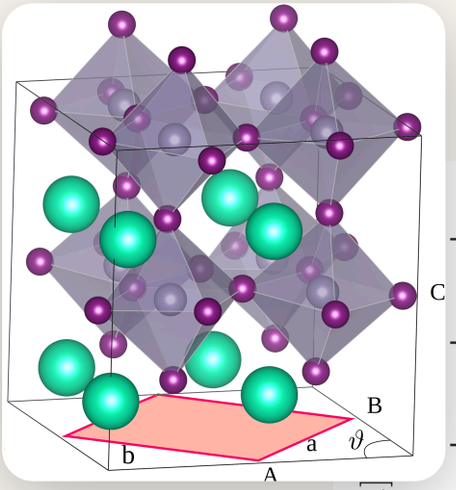
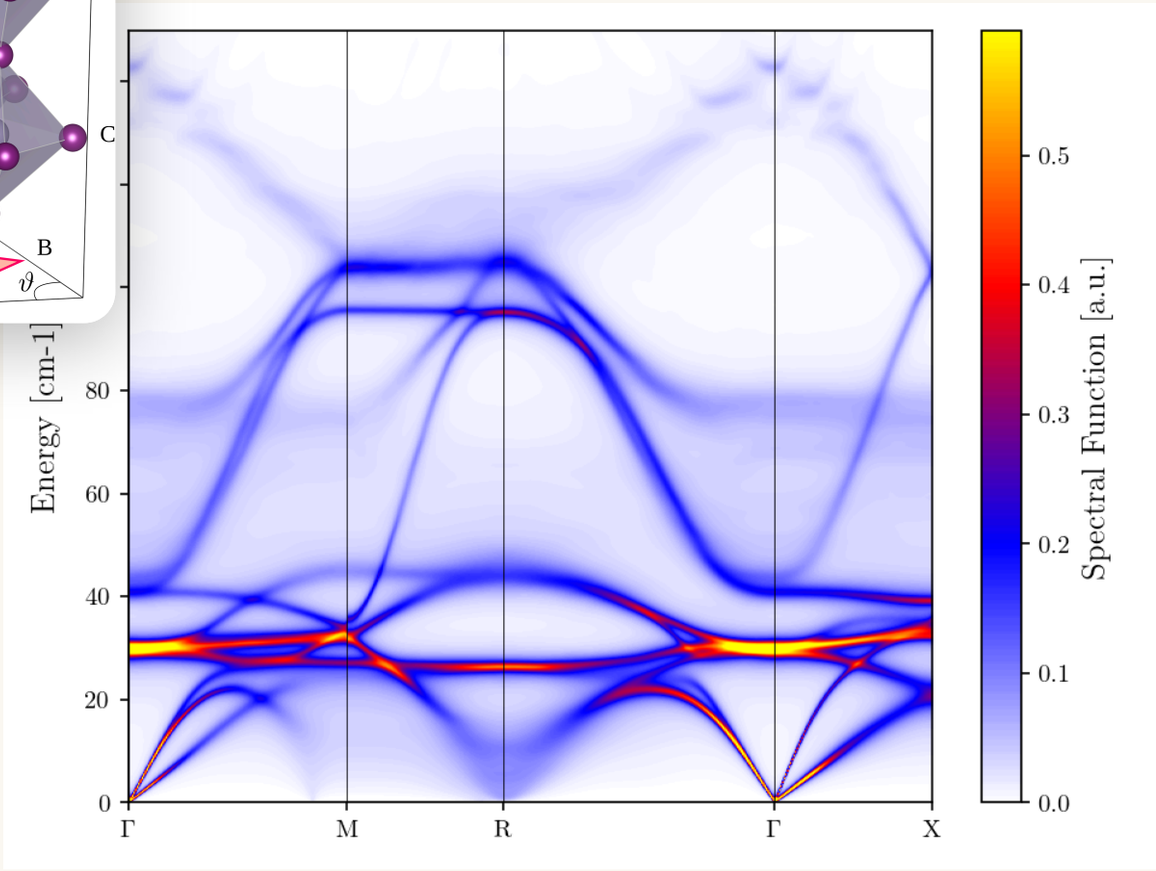
04 **Computing the Green's functions**
The Lanczos Algorithm

05 **Raman & IR vibrational spectra**
One and two-phonon properties





Why vibrational spectroscopy?

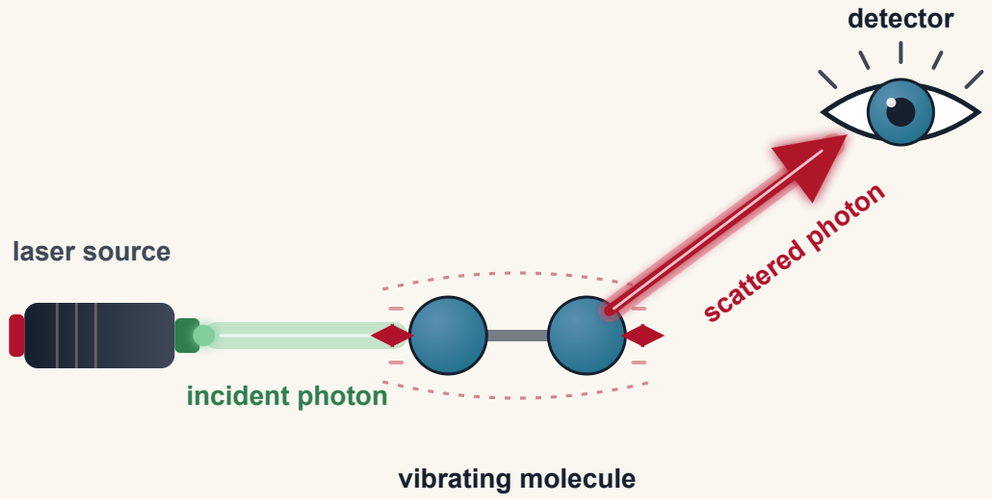
MOTIVATION

Vibrational Spectroscopy

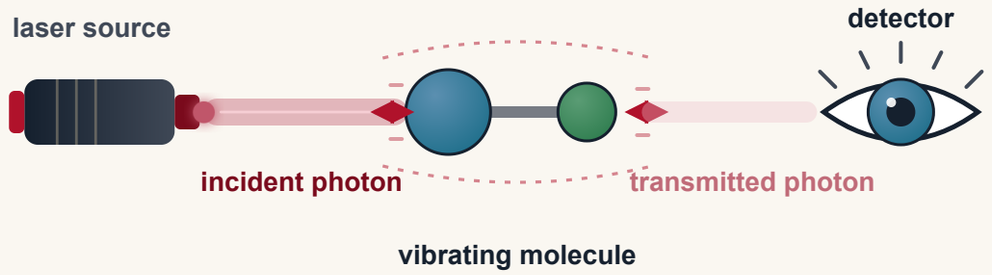
NONINVASIVE PROBE

- Easy to do and does not require custom setup
- Fast and does not destroy the sample
- Used in extreme environment (high-pressure)

Raman scattering



IR absorption



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Vibrational Spectroscopy

NONINVASIVE PROBE

- Easy to do and does not require custom setup
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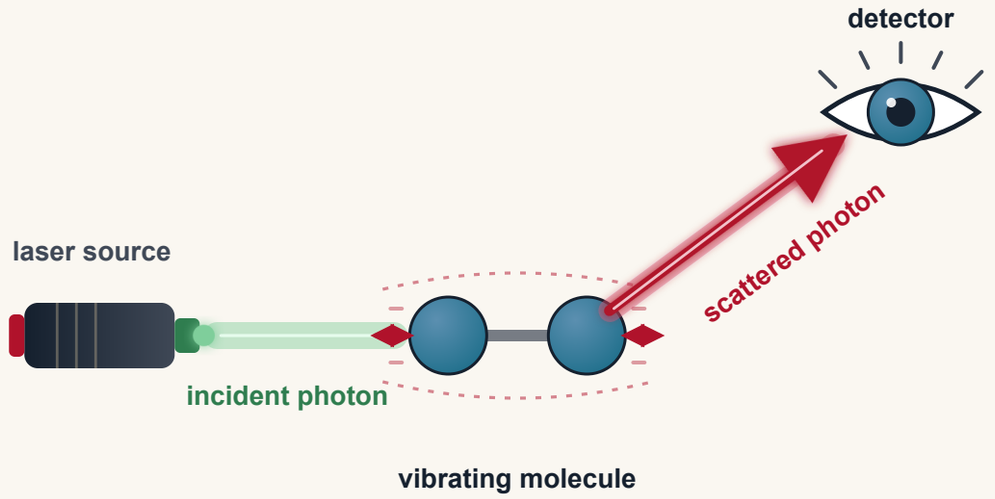
SENSITIVE TECHNIQUE

- Structural fingerprint
- Sensitive to local environment
- Identification of symmetry group
- Phase transitions

Raman scattering



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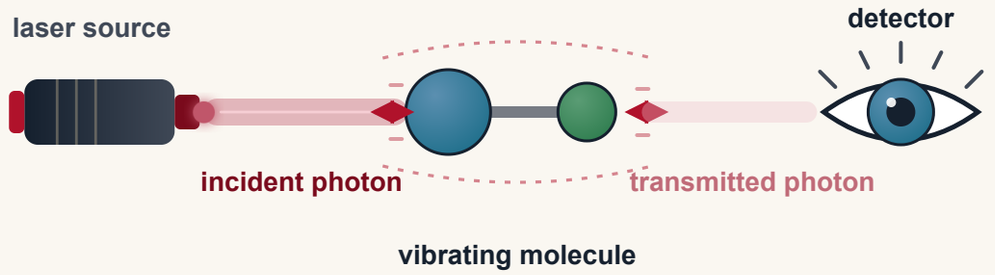

MOTIVATION

Probing the Brillouin zone

RAMAN & IR ONLY PROBE Γ PHONONS

Light in the far-IR/visible range, with $\lambda \geq 500$ nm.

$$q \sim \frac{1}{\lambda} \approx 2 \cdot 10^{-4}\ \mathring{A}^{-1} \approx 0\ \mathring{A}^{-1}$$

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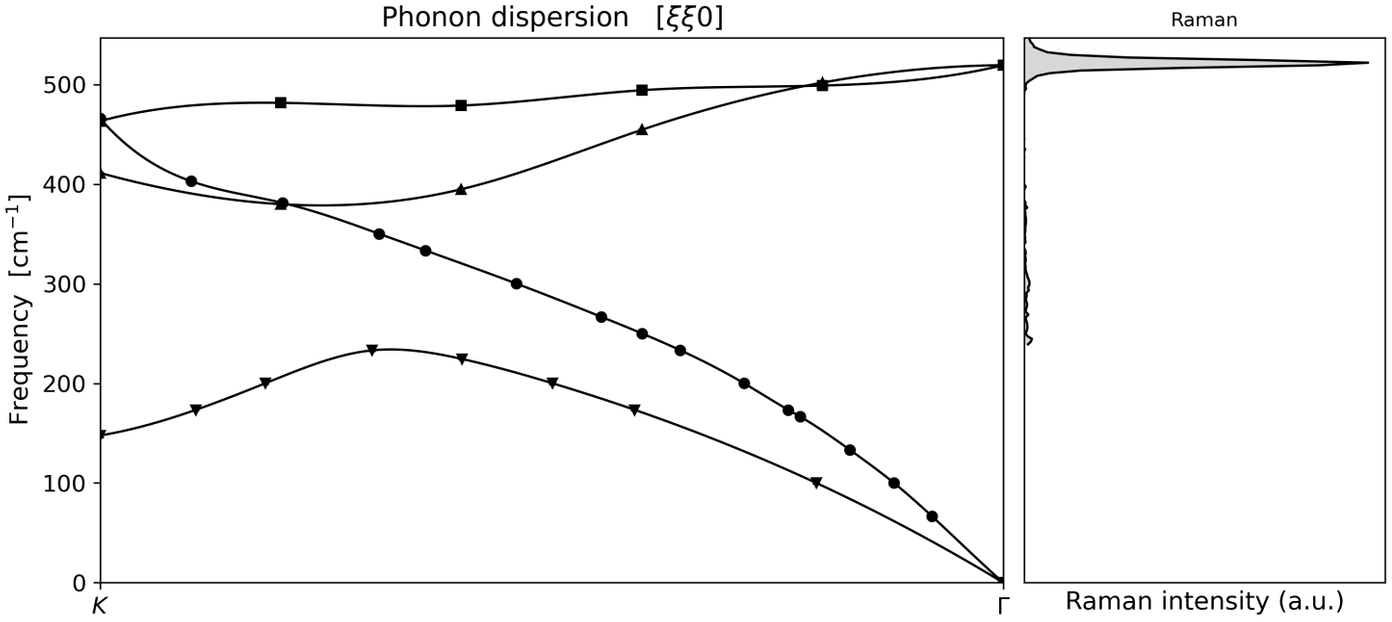

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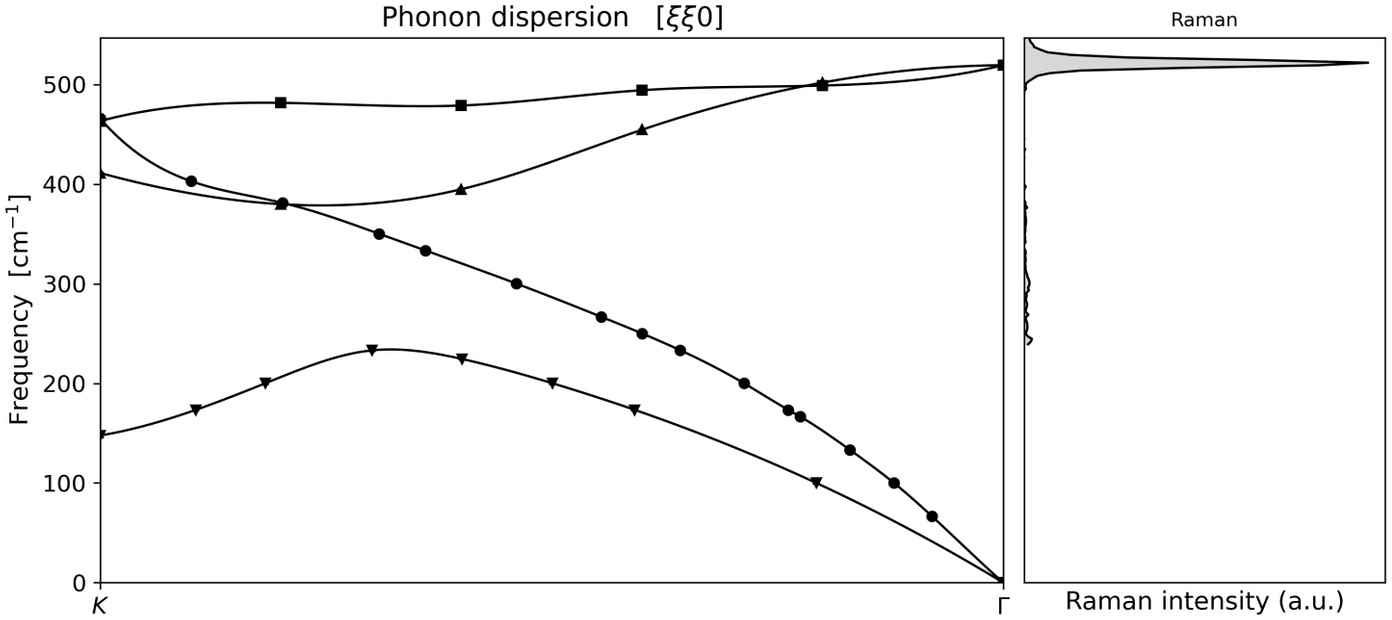


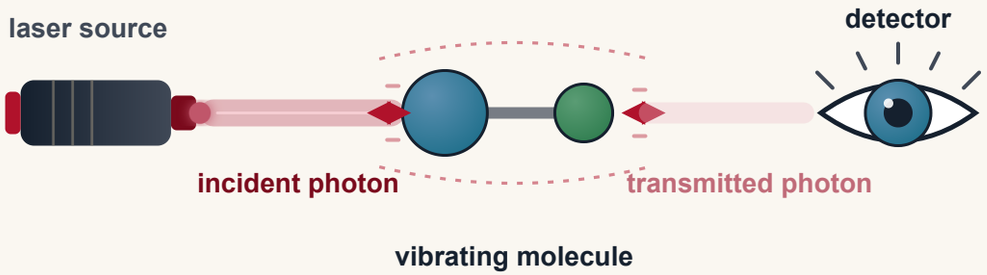
PROBING THE FULL BZ

- Inelastic neutron scattering
- Inelastic X-ray scattering
- Electron energy loss spectroscopy

Static and dynamic response functions

IR Absorption

IR absorption

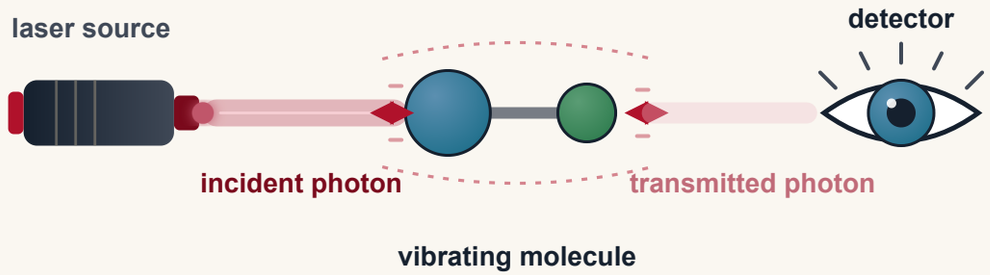


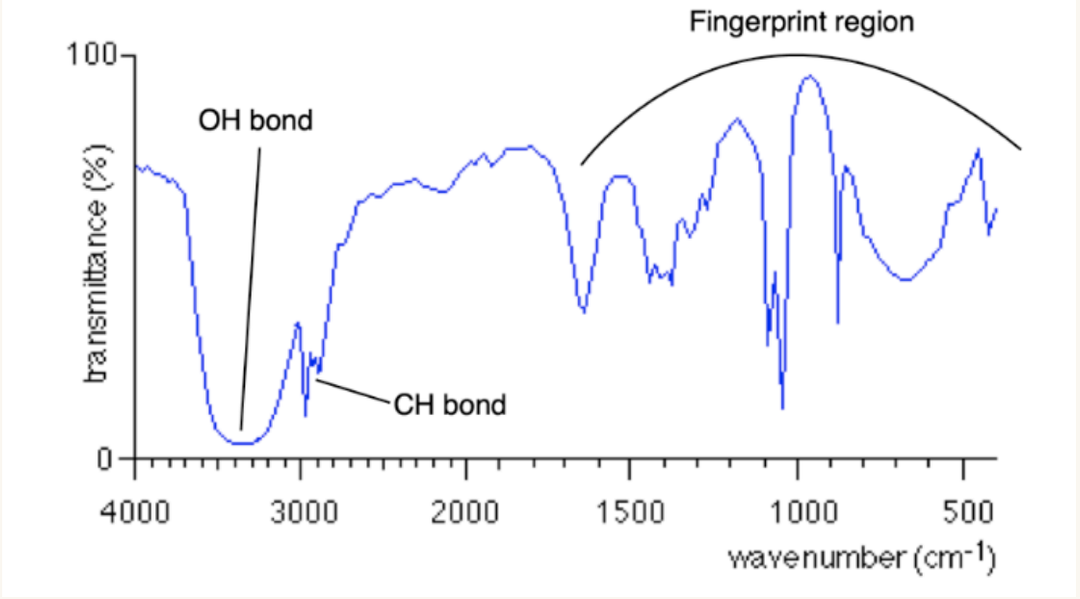
IR

- Infrared spectra is probed in absorption

IR Absorption

IR absorption



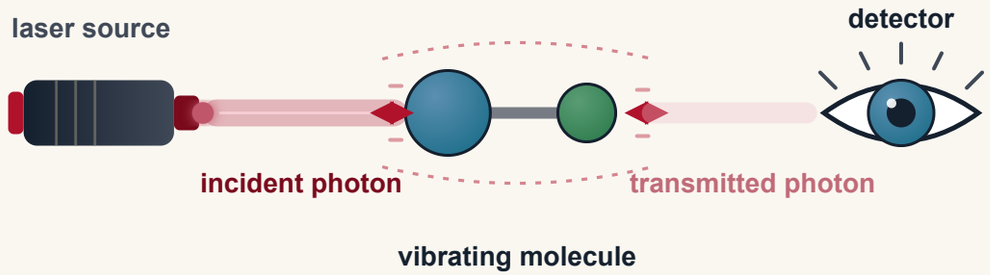


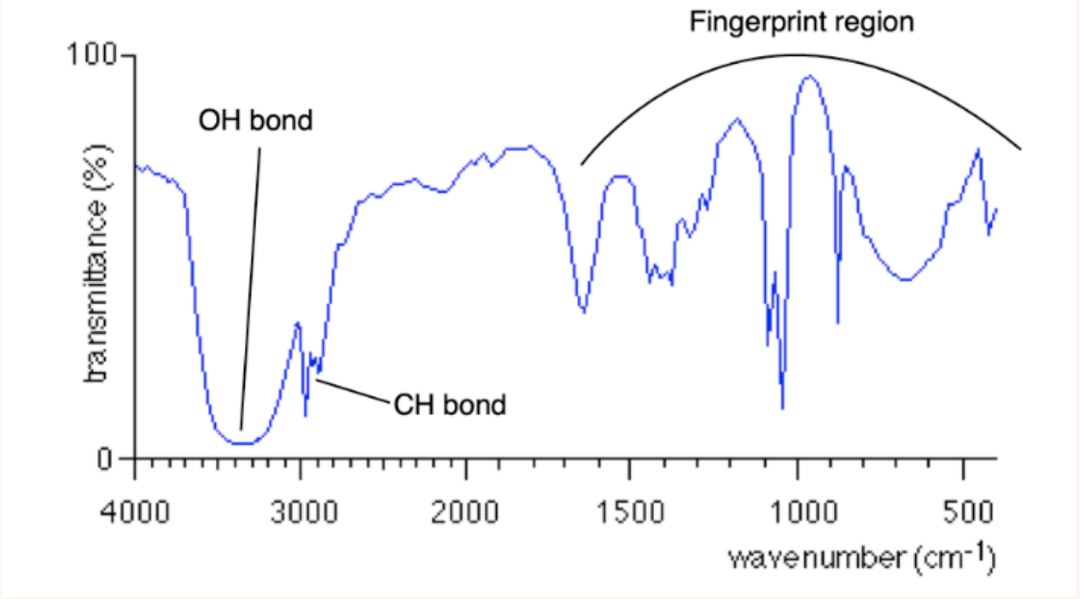
IR

- Infrared spectra is probed in absorption
- 1 photon is converted into 1 phonon

IR Absorption

IR absorption





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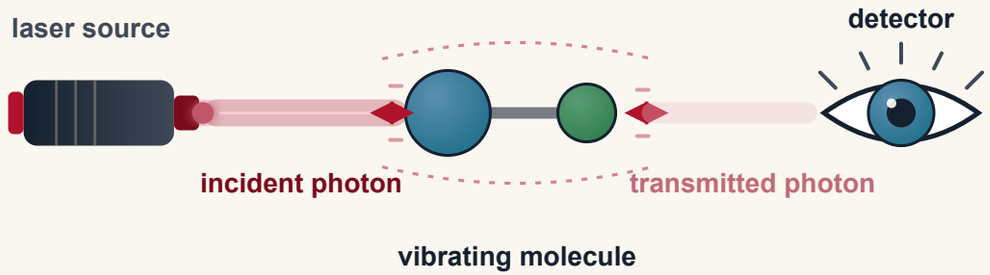

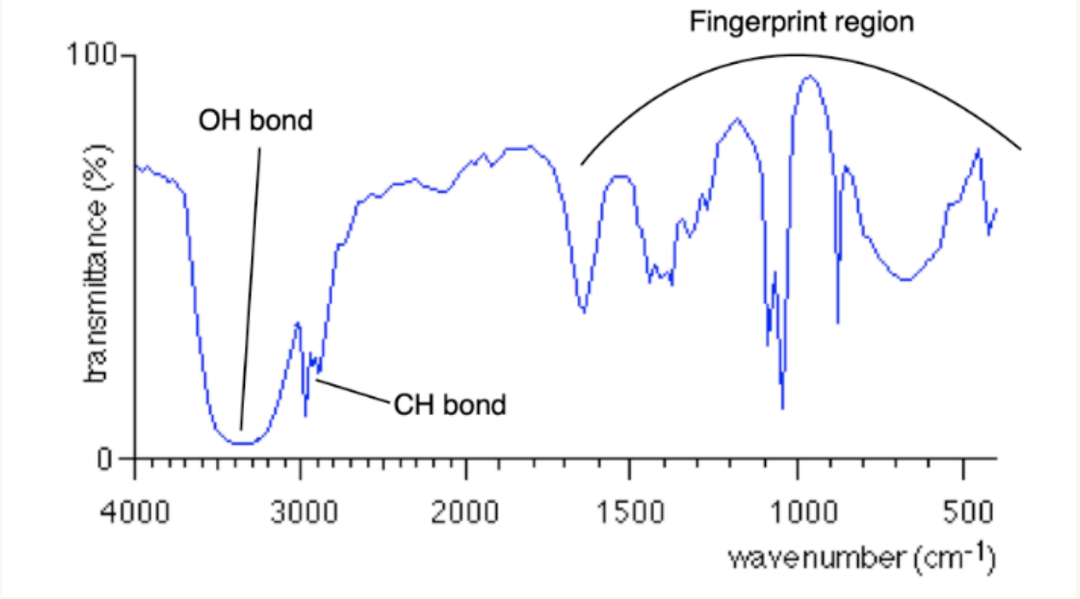

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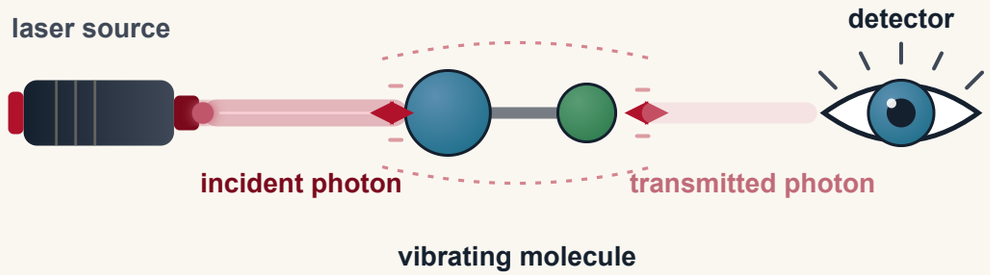
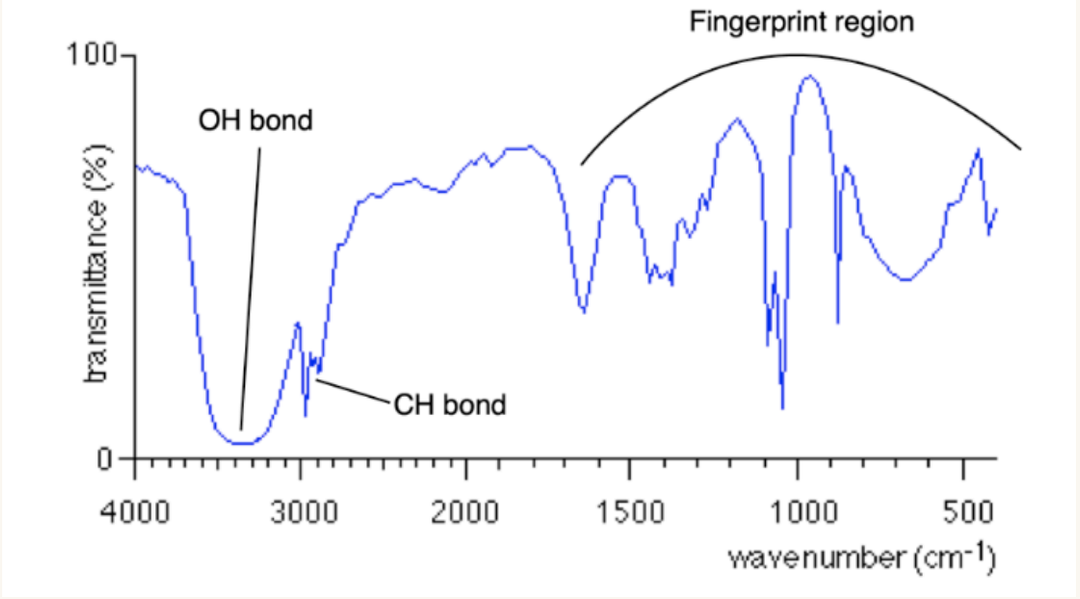


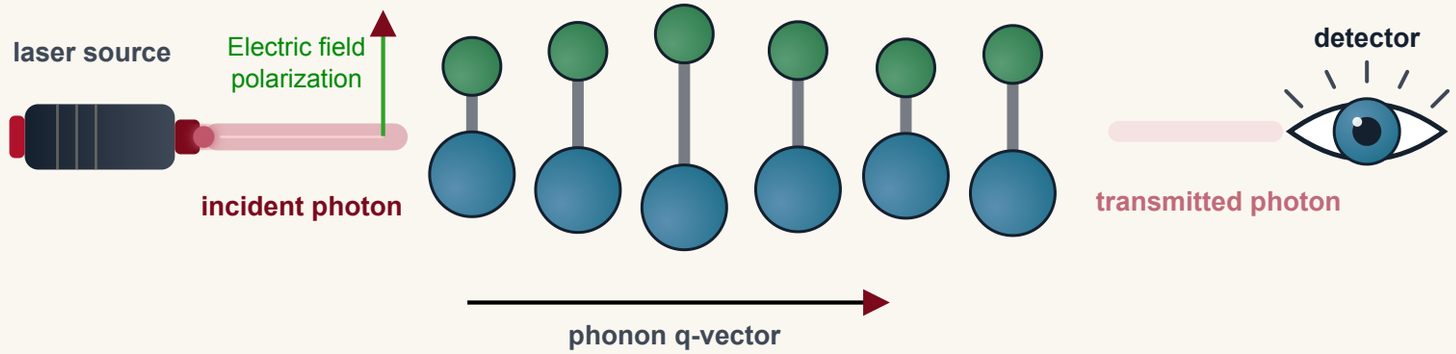


IR

- Infrared spectra is probed in absorption
- 1 photon is converted into 1 phonon
- Typical energy scale is 100-4000 cm^{-1}
- The electric dipole changes during vibration
- Only Γ phonons can be IR active

IR Absorption

IR absorption

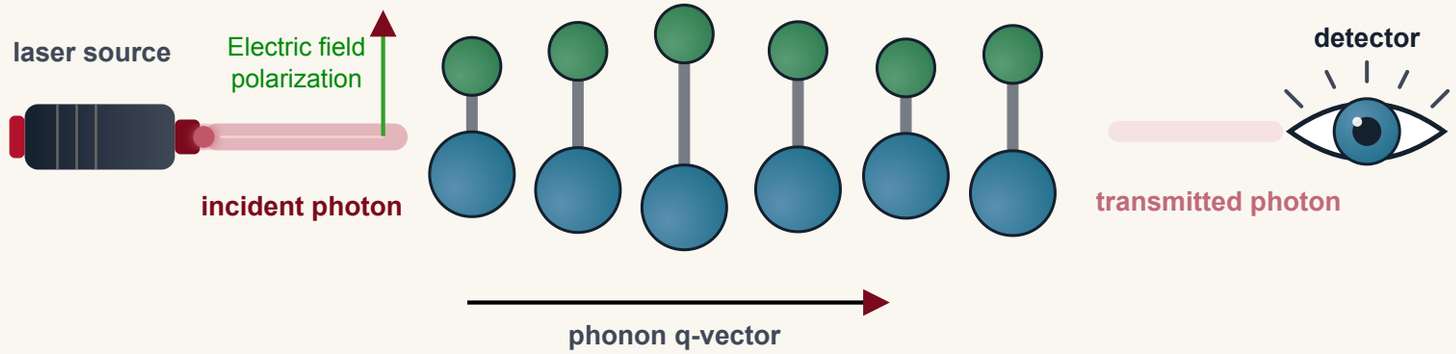


TO MODES

- IR probes mostly **transverse optical (TO)** modes in high-symmetry crystals
- The electric field is transverse to the photon propagation → couples to modes with polarization perpendicular to $\mathbf{q}$

IR Absorption

IR absorption



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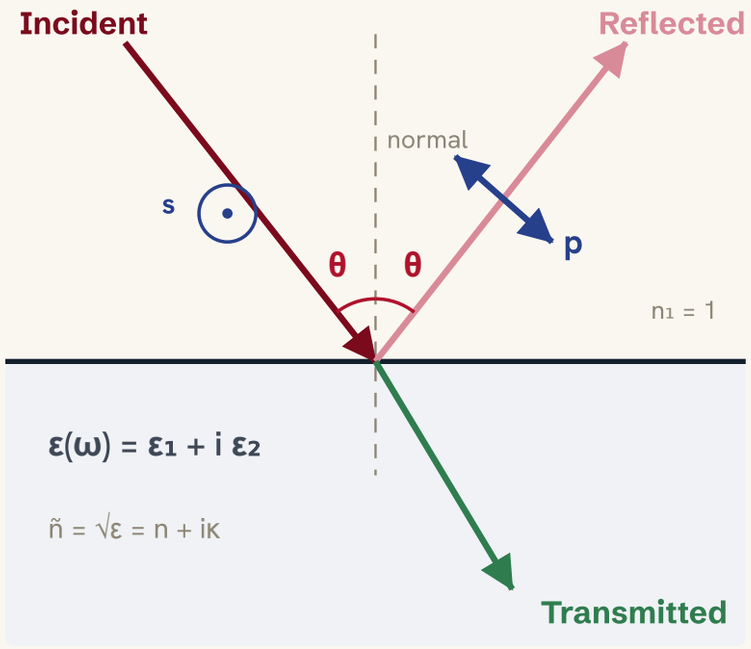
EXCEPTIONS

- In **non-isotropic** materials, LO and TO mix into quasi-LO and quasi-TO modes
- Near **surfaces** with non-normal incidence: broken isotropy enables LO coupling

IR Absorption

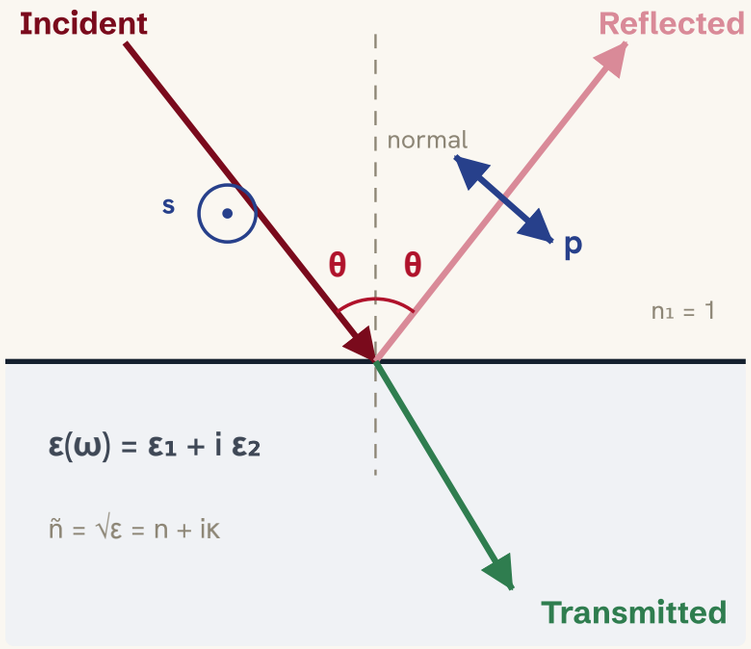


COMPLEX DIELECTRIC FUNCTION

$$\varepsilon(\omega) = \varepsilon_1(\omega) + i\varepsilon_2(\omega) \qquad \tilde{n}(\omega) = \sqrt{\varepsilon(\omega)} = n(\omega) + i\kappa(\omega)$$

$$\varepsilon_1 = n^2 - \kappa^2, \qquad \varepsilon_2 = 2n\kappa$$

IR Absorption



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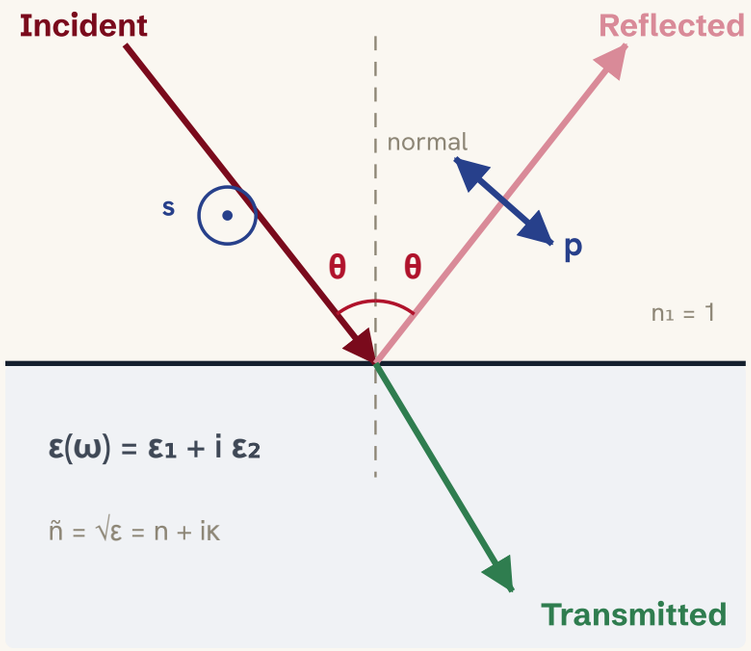
S-POLARIZATION

$$A_s(\omega) \propto \kappa(\omega)\cos^2\theta \qquad (\mathrm{E} \parallel \text{surface})$$

Absorption governed by **κ(ω)** — imaginary part of the refractive index

IR Absorption



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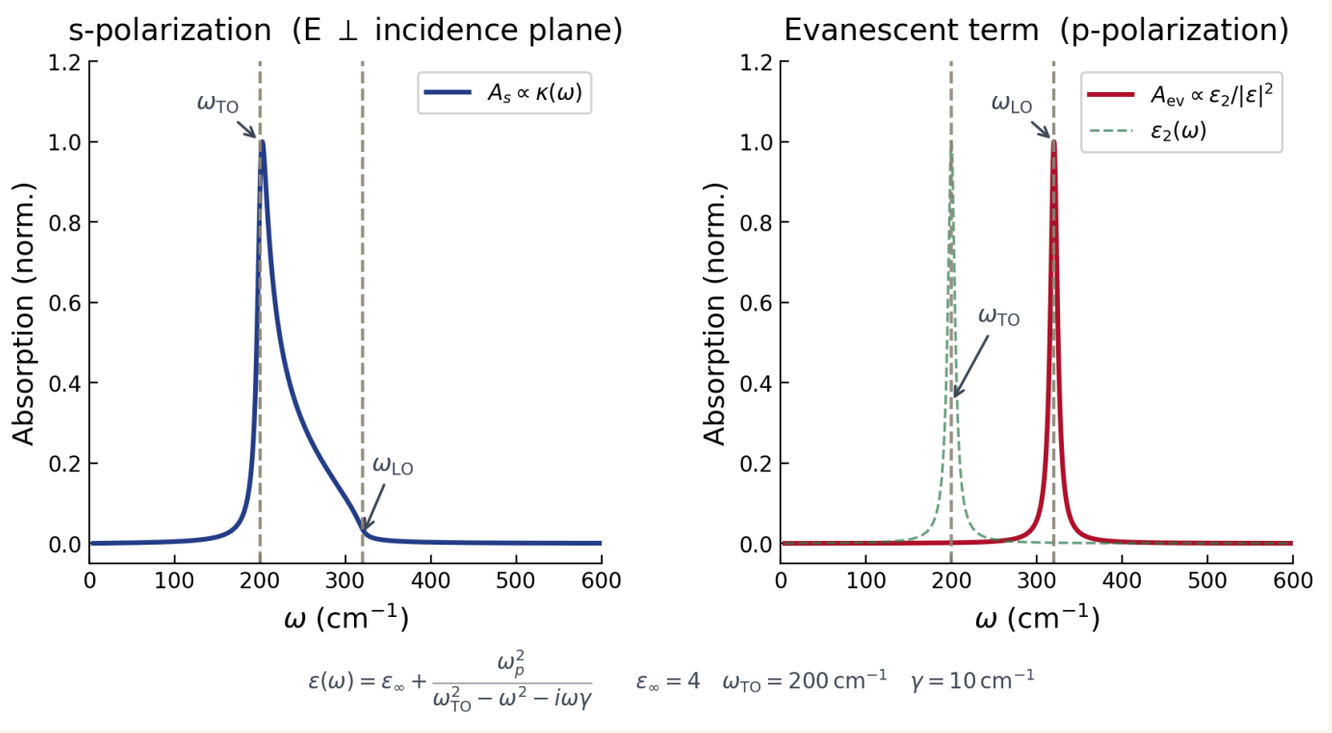
P-POLARIZATION

$$A_p(\omega) \propto \kappa(\omega)\cos^2\theta + \frac{\varepsilon_2(\omega)}{|\varepsilon(\omega)|^2}\sin^2\theta$$

Two distinct contributions:

· **κ(ω)** (traveling wave) · **ε₂(ω) / |ε(ω)|²** (evanescent term)

IR Absorption – Drude model



DRUDE-LORENTZ DIELECTRIC FUNCTION

$$\varepsilon(\omega) = \varepsilon_\infty + \frac{\omega_p^2}{\omega_{\mathrm{TO}}^2 - \omega^2 - i\omega\gamma}$$

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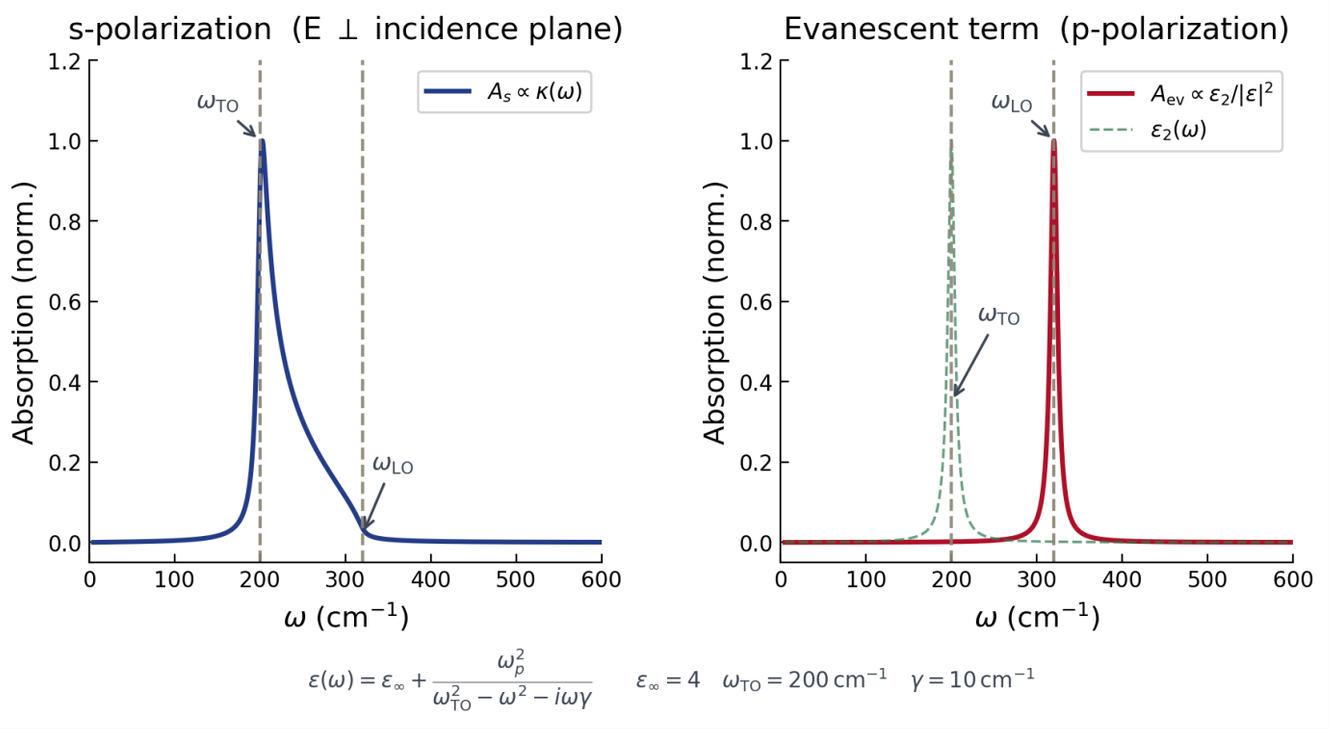

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$$A_s \propto \kappa(\omega) = \mathrm{Im}\sqrt{\varepsilon(\omega)}$$

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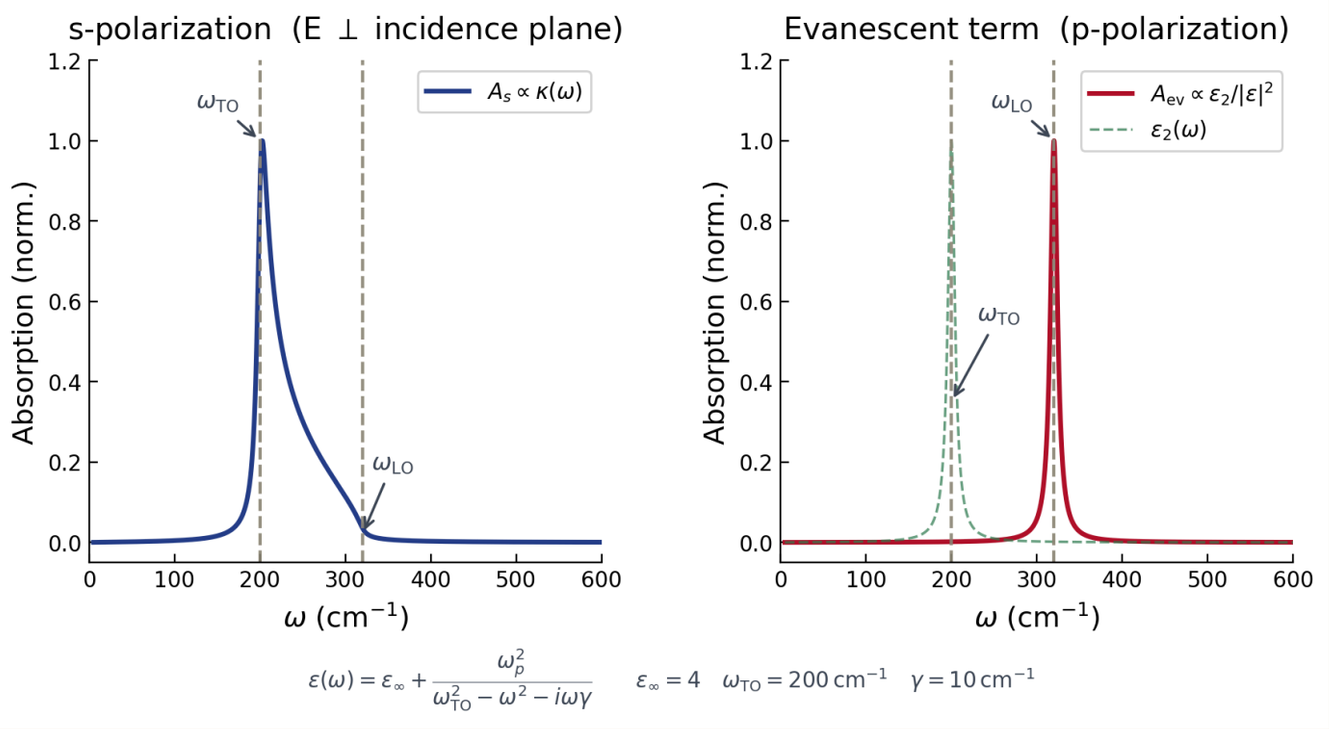

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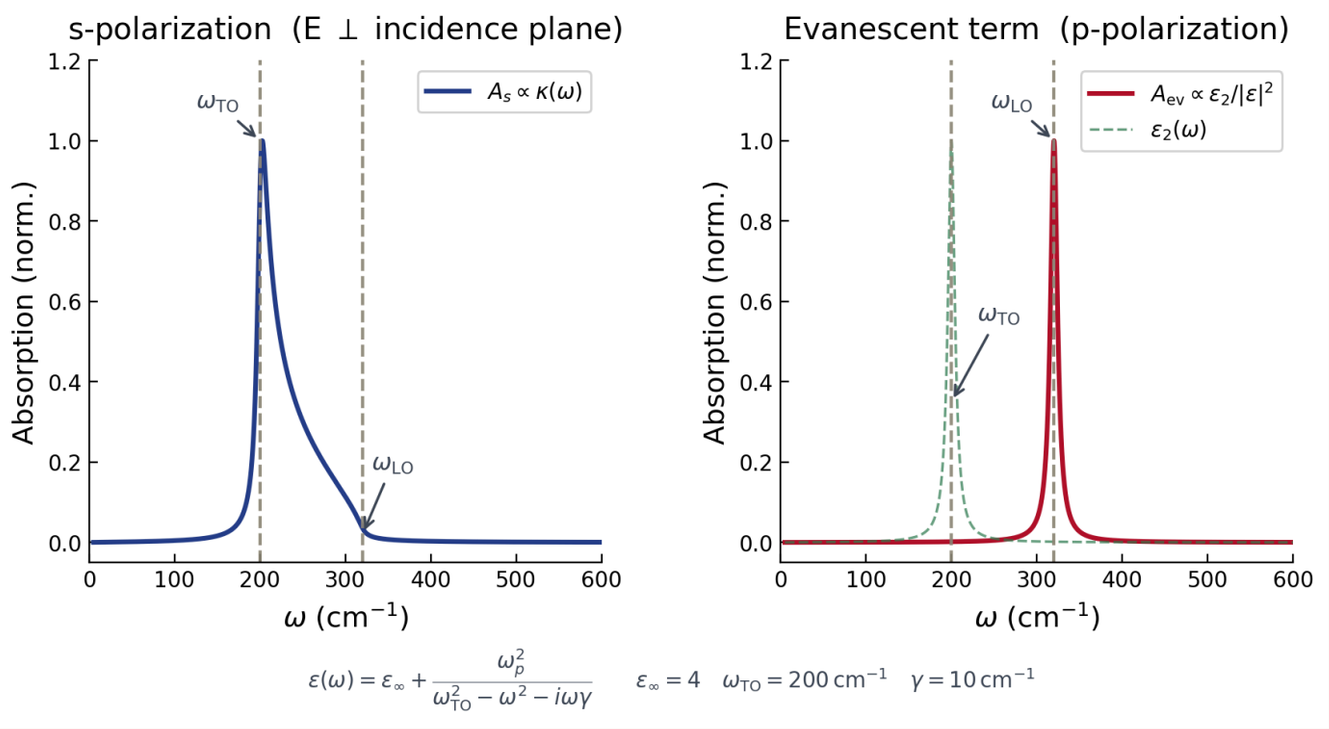

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- **LO phonon**: the evanescent term diverges when

$$\varepsilon(\omega_{\mathrm{LO}}) = 0 \quad \Rightarrow \quad \omega_{\mathrm{LO}}^2 = \omega_{\mathrm{TO}}^2 + \frac{\omega_p^2}{\varepsilon_\infty}$$

The dielectric function ε(ω)

DIPOLE-DIPOLE RESPONSE FUNCTION

To predict the IR spectrum we must compute $\varepsilon(\omega)$.
This is the **dipole–dipole response function** of the material. In CGS units it is

$$\varepsilon(\omega) = 1 + \frac{4\pi}{V}\,\chi_{\mu\mu}(\omega)$$

$\chi_{\mu\mu}(\omega)$: retarded correlation function of the total dipole moment $\vec{\mu}$

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The dipole susceptibility

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$$\langle\hat{\mu}_\alpha\rangle_{\hat{\rho}(t)} = \int_{-\infty}^{t} dt'\, \chi^{(\mathrm{ion})}_{\mu_\alpha\mu_\beta}(t-t')\, E_\beta(t')$$

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$$i\hbar\frac{\partial}{\partial t}\hat{\rho}(t) = [\hat{H} + \hat{H}'(t), \hat{\rho}(t)]$$

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- $\hat{H}$ is the Born-Oppenheimer hamiltonian, while $\hat{H}'(t)$ describes the coupling to the external field.

$$\hat{H} = \sum_{i=1}^{n}\frac{\hat{p}_i}{2m_i} + V(\hat{r}_1,\ldots,\hat{r}_n) \qquad \hat{H}'(t) = -\vartheta(t-t_0)\sum_{i=x,y,z}\hat{\mu}_i E_i(t)$$

  where $\hat{\mu}_i$ is the i-th component of the total dipole moment operator.

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DYNAMICAL SUSCEPTIBILITY

We need a time-dependent theory to solve the $\hat{\rho}(t)$

Solving the quantum nuclear dynamics

The time-dependent Gaussian density matrix

THE ANSATZ

We assume that the density matrix $\hat{\rho}(t)$ is a Gaussian in the nuclear coordinates and momenta.

$$\rho(\boldsymbol{R}, \boldsymbol{P}) = \mathcal{N} \exp\Bigg\{ -\frac{1}{2}\sum_{ab} \left[R_a - \mathcal{R}_a(t)\right] \alpha_{ab}(t) \left[R_b - \mathcal{R}_b(t)\right] - \frac{1}{2}\sum_{ab} \left[P_a - \mathcal{P}_a(t)\right] \beta_{ab}(t) \left[P_b - \mathcal{P}_b(t)\right] + \sum_{ab} \left[R_a - \mathcal{R}_a(t)\right] \gamma_{ab}(t) \left[P_b - \mathcal{P}_b(t)\right] \Bigg\}$$

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- The density matrix $\hat{\rho}$ is obtained with the Wigner transformation:

$$\rho(\boldsymbol{R}, \boldsymbol{P}) = \int d\boldsymbol{r} \frac{e^{-\frac{i}{\hbar}\boldsymbol{p}\cdot\boldsymbol{r}}}{(2\pi\hbar)^{3N}} \left\langle \boldsymbol{R} + \frac{\boldsymbol{r}}{2} \middle| \hat{\rho}(t) \middle| \boldsymbol{R} - \frac{\boldsymbol{r}}{2} \right\rangle$$

The time-dependent Gaussian density matrix

THE ANSATZ

We assume that the density matrix $\hat{\rho}(t)$ is a Gaussian in the nuclear coordinates and momenta.

$$\rho(\boldsymbol{R},\boldsymbol{P}) = \mathcal{N}\exp\Bigg\{ -\frac{1}{2}\sum_{ab}\left[R_a - \mathcal{R}_a(t)\right]\alpha_{ab}(t)\left[R_b - \mathcal{R}_b(t)\right] - \frac{1}{2}\sum_{ab}\left[P_a - \mathcal{P}_a(t)\right]\beta_{ab}(t)\left[P_b - \mathcal{P}_b(t)\right] + \sum_{ab}\left[R_a - \mathcal{R}_a(t)\right]\gamma_{ab}(t)\left[P_b - \mathcal{P}_b(t)\right]\Bigg\}$$

- The density matrix $\hat{\rho}$ is obtained with the Wigner transformation:

$$\rho(\boldsymbol{R},\boldsymbol{P}) = \int d\boldsymbol{r}\,\frac{e^{-\frac{i}{\hbar}\boldsymbol{p}\cdot\boldsymbol{r}}}{(2\pi\hbar)^{3N}}\left\langle \boldsymbol{R}+\frac{\boldsymbol{r}}{2}\middle|\,\hat{\rho}(t)\,\middle|\boldsymbol{R}-\frac{\boldsymbol{r}}{2}\right\rangle$$

- $$\langle\delta\boldsymbol{R}\delta\boldsymbol{R}\rangle_{\hat{\rho}(t)} = (\boldsymbol{\alpha}-\boldsymbol{\gamma}\boldsymbol{\beta}^{-1}\boldsymbol{\gamma}^{\dagger})^{-1} \qquad \langle\delta\boldsymbol{R}\delta\boldsymbol{P}\rangle_{\hat{\rho}(t)} = -\left(\boldsymbol{\gamma}^{\dagger}-\boldsymbol{\beta}\boldsymbol{\gamma}^{-1}\boldsymbol{\alpha}\right)^{-1} \qquad \langle\delta\boldsymbol{P}\delta\boldsymbol{P}\rangle_{\hat{\rho}(t)} = \left(\boldsymbol{\beta}-\boldsymbol{\gamma}^{\dagger}\boldsymbol{\alpha}^{-1}\boldsymbol{\gamma}\right)^{-1}$$

The least action principle

- The Dirac action

$$A = \frac{1}{t_1 - t_0} \int_{t_0}^{t_1} \langle \psi | \, \hat{H} + \hat{H}'(t) - i\hbar \frac{\partial}{\partial t} \, | \psi \rangle$$

- is stationary around the exact solution

$$\delta A = 0$$

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- From which we get the complete equations of motions:

$$\frac{\delta A}{\delta \mathcal{R}(t)} = 0 \qquad \frac{\delta A}{\delta \mathcal{P}(t)} = 0 \qquad \frac{\delta A}{\delta \langle \delta \boldsymbol{R} \delta \boldsymbol{R} \rangle (t)} = 0 \qquad \cdots$$

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- This is equivalent to solve the self-consistent time-dependent equation

$$i\hbar \frac{\partial \hat{\rho}}{\partial t} = \left[\hat{\mathcal{H}}[\hat{\rho}](t), \hat{\rho}(t) \right]$$

  where $\hat{\mathcal{H}}(t)$ is a harmonic Hamiltonian whose parameter depend self-consistently from the $\hat{\rho}$ state itself.

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Newton's equations

$$\frac{d}{dt}\left\langle \tilde{\boldsymbol{R}} \right\rangle = \left\langle \tilde{\boldsymbol{P}} \right\rangle \qquad \frac{d}{dt}\left\langle \tilde{\boldsymbol{P}} \right\rangle = -\left\langle \frac{dV}{d\tilde{\boldsymbol{R}}} \right\rangle$$

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Quantum dynamics

$$\frac{d}{dt}\left\langle \delta\tilde{\boldsymbol{R}}\delta\tilde{\boldsymbol{R}} \right\rangle = \left\langle \delta\tilde{\boldsymbol{R}}\delta\tilde{\boldsymbol{P}} \right\rangle + h.c.$$

$$\frac{d}{dt}\left\langle \delta\tilde{\boldsymbol{P}}\delta\tilde{\boldsymbol{P}} \right\rangle = -\left\langle \frac{d^2V}{d\tilde{\boldsymbol{R}}d\tilde{\boldsymbol{R}}} \right\rangle \left\langle \delta\tilde{\boldsymbol{R}}\delta\tilde{\boldsymbol{P}} \right\rangle + h.c.$$

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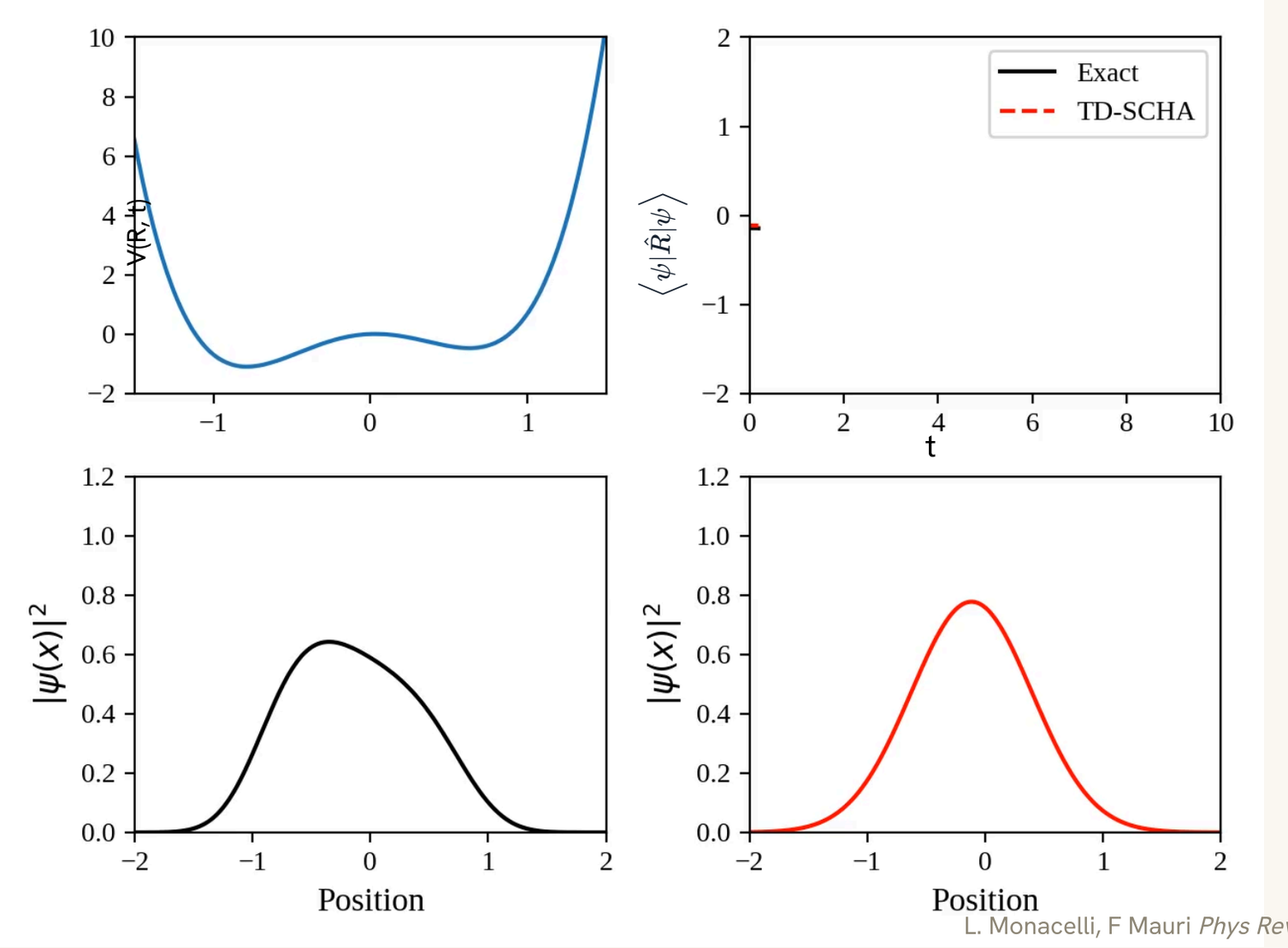
Benchmarking the dynamics



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Linear response theory

LINEAR PERTURBATION

We have an external perturbation $f(t)$ coupled to the ions through an operator $\hat{A}$

$$\hat{H}(t) = \hat{H}_0 + \hat{A} f(t)$$

- The system is in equilibrium for $t < t_0$, and the perturbation is switched on at $t = t_0$.

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- Plugging it into the TD-SCHA equations we get:

$$i\hbar \frac{d\hat{\rho}^{(1)}}{dt} = \underbrace{\left[\hat{\mathcal{H}}[\hat{\rho}_0], \hat{\rho}^{(1)}\right]}_{\text{Harmonic evolution}} + \overbrace{\left[\hat{\mathcal{H}}[\hat{\rho}^{(1)}(t)], \hat{\rho}_0\right]}^{\text{self-energy correction}}$$

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- In linear response, we can compress the full time dependency in only few variables:

$$\hat{\rho}^{(1)}(t) = \begin{pmatrix} \tilde{\boldsymbol{R}}^{(1)}(t) \\ \left\langle \delta\tilde{\boldsymbol{R}}\delta\tilde{\boldsymbol{R}} \right\rangle_{(1)}(t) \\ \left\langle \delta\tilde{\boldsymbol{P}}\delta\tilde{\boldsymbol{P}} \right\rangle_{(1)}(t) \end{pmatrix} \quad \Longrightarrow \quad \left(\mathcal{L} + \omega^2\right) \begin{pmatrix} \tilde{\boldsymbol{R}}^{(1)}(\omega) \\ \left\langle \delta\tilde{\boldsymbol{R}}\delta\tilde{\boldsymbol{R}} \right\rangle_{(1)}(\omega) \\ \left\langle \delta\tilde{\boldsymbol{P}}\delta\tilde{\boldsymbol{P}} \right\rangle_{(1)}(\omega) \end{pmatrix} = \begin{pmatrix} \left\langle \frac{\partial A}{\partial \tilde{R}_a} \right\rangle_{(0)} \\ \left\langle \frac{\partial^2 A}{\partial \tilde{R}_a \partial \tilde{R}_b} \right\rangle_{(0)} \\ \left\langle \frac{\partial^2 A}{\partial \tilde{P}_a \partial \tilde{P}_b} \right\rangle_{(0)} \end{pmatrix} f(\omega)$$

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- $\left(\mathcal{L} + \omega^2\right) \hat{\boldsymbol{\rho}}^{(1)}(\omega) = \boldsymbol{a} f(\omega) \qquad \mathcal{L} = \mathcal{L}_{\text{harm}} + \mathcal{L}_{\text{anharm}}$

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The dynamical matrix decomposition

$$\mathcal{L}_{\text{harm}}(\omega) = \begin{pmatrix} \sim^{-1} & 0 & 0 \\ 0 & \rightrightarrows^{-1} & 0 \\ 0 & 0 & \rightleftarrows^{-1} \end{pmatrix}$$

$$\mathcal{L}_{\text{anh}}(\omega) = \begin{pmatrix} 0 & - & - \\ - & - & - \\ - & - & - \end{pmatrix}$$

$$\hat{\rho}^{(1)}(t) = \begin{pmatrix} \tilde{\boldsymbol{R}}^{(1)}(t) \\ \left\langle \delta\tilde{\boldsymbol{R}}\delta\tilde{\boldsymbol{R}} \right\rangle_{(1)}(t) \\ \left\langle \delta\tilde{\boldsymbol{P}}\delta\tilde{\boldsymbol{P}} \right\rangle_{(1)}(t) \end{pmatrix}$$

$\sim = \mathcal{G}^{(0)}(\omega)$

$\rightrightarrows = \chi^{(0)}_{\pm}(\omega)$

$\blacktriangleright = \overset{(3)}{D}$

$\blacksquare = \overset{(4)}{D}$

$$\overset{(3)}{D}_{abc} = \left\langle \frac{\partial^3 V}{\partial\tilde{R}_a\,\partial\tilde{R}_b\,\partial\tilde{R}_c} \right\rangle_{(0)}$$

$$\overset{(4)}{D}_{abcd} = \left\langle \frac{\partial^4 V}{\partial\tilde{R}_a\,\partial\tilde{R}_b\,\partial\tilde{R}_c\,\partial\tilde{R}_d} \right\rangle_{(0)}$$

TD-SCHA response functions

$$\hat{\rho}^{(1)}(\omega) = \begin{pmatrix} \tilde{\boldsymbol{R}}^{(1)}(\omega) \\ \left\langle \delta\tilde{\boldsymbol{R}}\delta\tilde{\boldsymbol{R}} \right\rangle_{(1)}(\omega) \\ \left\langle \delta\tilde{\boldsymbol{P}}\delta\tilde{\boldsymbol{P}} \right\rangle_{(1)}(\omega) \end{pmatrix}$$

$$(\mathcal{L} + \omega^2)\, \hat{\rho}^{(1)}(\omega) = \boldsymbol{a}\, f(\omega)$$

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For an observable $\hat{B}$, we can compute its perturbed average as

$$\langle B \rangle_{(1)}(\omega) = \sum_a \left\langle \frac{\partial B}{\partial \tilde{R}_a} \right\rangle_{(0)} \tilde{R}_a{}^{(1)}(\omega) + \sum_{ab} \left\langle \frac{\partial^2 B}{\partial \tilde{R}_a \partial \tilde{R}_b} \right\rangle_{(0)} \langle \delta\tilde{R}_a \delta\tilde{R}_b \rangle_{(1)}(\omega) + \sum_{ab} \left\langle \frac{\partial^2 B}{\partial \tilde{P}_a \partial \tilde{P}_b} \right\rangle_{(0)} \langle \delta\tilde{P}_a \delta\tilde{P}_b \rangle_{(1)}(\omega) \equiv \boldsymbol{b}^\top \cdot \hat{\rho}^{(1)}(\omega)$$

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Perturbation coupling:

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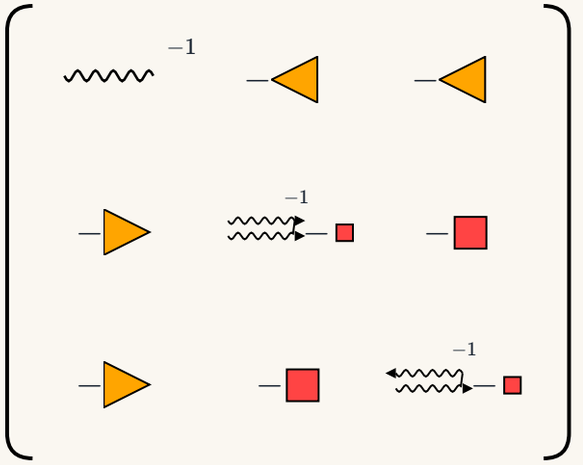
Observable gradient:

$$\boldsymbol{b} = \begin{pmatrix} \left\langle \frac{\partial B}{\partial \tilde{\boldsymbol{R}}} \right\rangle_{(0)} \\ \left\langle \frac{\partial^2 B}{\partial \tilde{R}_a \partial \tilde{R}_b} \right\rangle_{(0)} \\ \left\langle \frac{\partial^2 B}{\partial \tilde{P}_a \partial \tilde{P}_b} \right\rangle_{(0)} \end{pmatrix}$$

$$\mathcal{L} + \omega^2 =$$



Phonon Green's function

PHONON GREEN'S FUNCTION

The phonon propagation is define by the mass-rescaled displacement-displacement susceptibility:

$$G_{ab}(t) = \left\langle \sqrt{m_a}(\hat{R}(t) - \mathcal{R}_a^{(0)})\sqrt{m_b}(\hat{R}(0) - \mathcal{R}_b^{(0)}) \right\rangle_0 \qquad G_{ab}(\omega) = \chi_{\tilde{R}_a \tilde{R}_b}(\omega)$$

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$$\hat{A} = \sqrt{m_a}(\hat{R} - \mathcal{R}_a^{(0)}) \qquad \hat{B} = \sqrt{m_b}(\hat{R} - \mathcal{R}_b^{(0)}) \qquad \boldsymbol{a} = \begin{pmatrix} \delta_{ai} \\ 0 \\ 0 \end{pmatrix} \qquad \boldsymbol{b} = \begin{pmatrix} \delta_{bi} \\ 0 \\ 0 \end{pmatrix}$$

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$$G_{ab}(\omega) = \chi_{\tilde{R}_a\tilde{R}_b}(\omega) = \left(\mathcal{L} + \omega^2\right)^{-1}_{ab}$$

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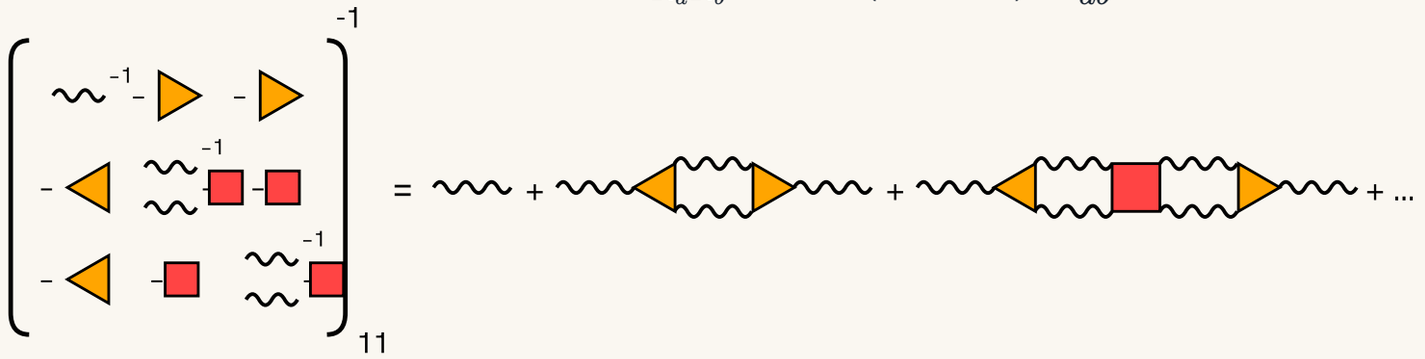


TIME-DEPENDENT SSCHA

Phonon Green's function

ONE PHONON PROPAGATOR

$$\mathcal{G}(\omega) = \left(\omega^2 - \boldsymbol{D}\right)^{-1} =$$

$$\boldsymbol{G}(\omega) = \left(\omega^2 - \boldsymbol{D} - \boldsymbol{\Pi}(\omega)\right)^{-1}$$

TWO PHONONS PROPAGATOR

$$\boldsymbol{\chi}^{(+)}_{\mu\nu}(\omega) = \frac{(1 + n_\mu + n_\nu)(\omega_\mu + \omega_\nu)}{\omega^2 - (\omega_\mu + \omega_\nu)^2} =$$

$$\boldsymbol{\chi}^{(-)}_{\mu\nu}(\omega) = \frac{(\omega_\mu - \omega_\nu)(n_\mu - n_\nu)}{\omega^2 - (\omega_\mu - \omega_\nu)^2} =$$

Phonon Green's function

ONE PHONON PROPAGATOR

$$\mathcal{G}(\omega) = \left(\omega^2 - \boldsymbol{D}\right)^{-1} =$$

$$\boldsymbol{G}(\omega) = \left(\omega^2 - \boldsymbol{D} - \boldsymbol{\Pi}(\omega)\right)^{-1}$$

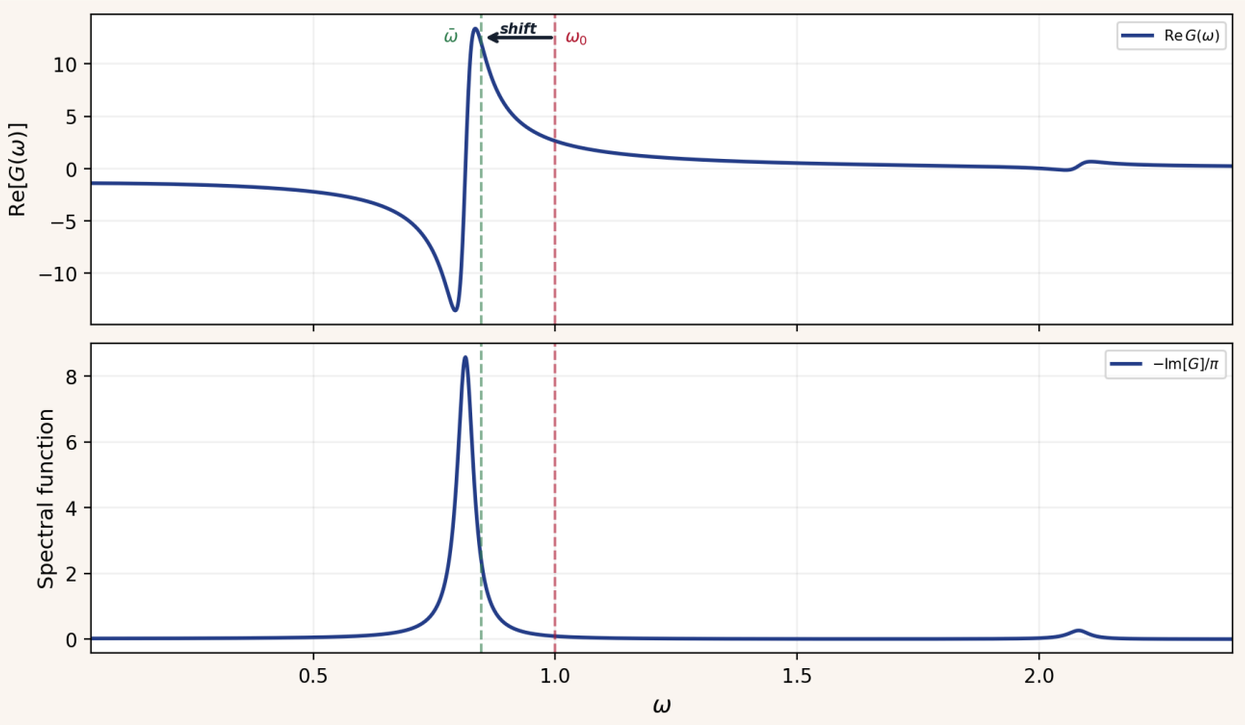
TWO PHONONS PROPAGATOR

$$\boldsymbol{\chi}^{(+)}_{\mu\nu}(\omega) = \frac{(1 + n_\mu + n_\nu)(\omega_\mu + \omega_\nu)}{\omega^2 - (\omega_\mu + \omega_\nu)^2} =$$

$$\boldsymbol{\chi}^{(-)}_{\mu\nu}(\omega) = \frac{(\omega_\mu - \omega_\nu)(n_\mu - n_\nu)}{\omega^2 - (\omega_\mu - \omega_\nu)^2} =$$

The free energy Hessian is the static limit of $\boldsymbol{G}(\omega)$

$$\frac{d^2F}{d\tilde{R}_a d\tilde{R}_b} = -\lim_{\omega\to 0}\left[\boldsymbol{G}(\omega)\right]^{-1}_{ab}$$



Computing the phonon Green's functions

The Lanczos algorithm

$$\chi_{AB}(\omega) = \boldsymbol{b}^\top (\mathcal{L} + \omega^2)^{-1} \boldsymbol{a}$$

THE PROBLEM

$\mathcal{L}$ is a $(6N)^2 \times (6N)^2$ **matrix** — it acts on the full space of $\tilde{\boldsymbol{R}}^{(1)}$, $\langle \delta\tilde{\boldsymbol{R}} \delta\tilde{\boldsymbol{R}} \rangle_{(1)}$, and $\langle \delta\tilde{\boldsymbol{P}} \delta\tilde{\boldsymbol{P}} \rangle_{(1)}$.

Direct inversion for **each** ω costs $O(N^6)$ — completely intractable even for a few atoms!

KRYLOV SUBSPACE

$$\mathcal{K}_M = \mathrm{span}\{\boldsymbol{a},\ \mathcal{L}\boldsymbol{a},\ \mathcal{L}^2\boldsymbol{a},\ \ldots,\ \mathcal{L}^{M-1}\boldsymbol{a}\}$$

$M \ll (6N)^2$. The Lanczos algorithm orthogonalises $\mathcal{K}_M$, yielding a **tridiagonal** $M \times M$ matrix $\boldsymbol{T}_M$.

LANCZOS RECURRENCE

Start with $\beta_1 \boldsymbol{v}_1 = \boldsymbol{a}$, $\boldsymbol{v}_0 = \boldsymbol{0}$. For $n = 1, \ldots, M$:

$$\beta_{n+1}\boldsymbol{v}_{n+1} = \mathcal{L}\boldsymbol{v}_n - \alpha_n \boldsymbol{v}_n - \beta_n \boldsymbol{v}_{n-1}$$

$$\alpha_n = \langle \boldsymbol{v}_n | \mathcal{L} | \boldsymbol{v}_n \rangle, \qquad \beta_{n+1} = \| \boldsymbol{w}_{n+1} \|$$

Tridiagonal projection

$$\boxed{\chi_{AB}(\omega) \approx |\boldsymbol{a}|^2 \left[(\boldsymbol{T}_M + \omega^2)^{-1} \right]_{11}}$$

LANCZOS RESULT

After M iterations, $\mathcal{L}$ is projected onto the tridiagonal $M \times M$ matrix:

$$\boldsymbol{T}_M = \begin{pmatrix} \alpha_1 & \beta_1 & & & \\ \beta_1 & \alpha_2 & \beta_2 & & \\ & \beta_2 & \ddots & \ddots & \\ & & \ddots & \ddots & \beta_{M-1} \\ & & & \beta_{M-1} & \alpha_M \end{pmatrix} \qquad \boldsymbol{T}_M \boldsymbol{v}_n = \beta_{n-1}\boldsymbol{v}_{n-1} + \alpha_n \boldsymbol{v}_n + \beta_n \boldsymbol{v}_{n+1}$$

Inverting $(\boldsymbol{T}_M + \omega^2)$ costs only $O(M)$ flops per ω — **trivial** compared to $O(N^6)$.
The $(1,1)$ element of the inverse has a **continued fraction** representation.

Continued fraction representation

$(\boldsymbol{T}_M + \omega^2)^{-1}_{11}$ admits a closed **continued fraction** form:

$$\left[(\boldsymbol{T}_M + \omega^2)^{-1}\right]_{11} = \cfrac{1}{\omega^2 + \alpha_1 - \cfrac{\beta_1^2}{\omega^2+\alpha_2 - \cfrac{\beta_2^2}{\cdots - \cfrac{\beta_{M-1}^2}{\omega^2+\alpha_M}}}}$$

From response functions to experiments

IR: the dielectric response

$$\varepsilon_{\alpha\beta}(\omega) = \varepsilon^{\infty}_{\alpha\beta} + \frac{4\pi}{V}\chi^{\text{ion}}_{M_\alpha M_\beta}(\omega)$$

PERTURBATION

The electric field couples to the ionic dipole:

$$\hat{H}'(t) = -\hat{M}_\beta(\hat{\boldsymbol{R}})\, E_\beta(t)$$

OBSERVABLE

The response is the induced dipole:

$$\left\langle \hat{M}_\alpha \right\rangle_{(1)}(\omega) = \chi^{\text{ion}}_{M_\alpha M_\beta}(\omega)\, E_\beta(\omega)$$

$$\chi^{\text{ion}}_{M_\alpha M_\beta}(\omega) = \boldsymbol{a}_\alpha^{\top}(\boldsymbol{\mathcal{L}} + \omega^2)^{-1}\boldsymbol{a}_\beta$$

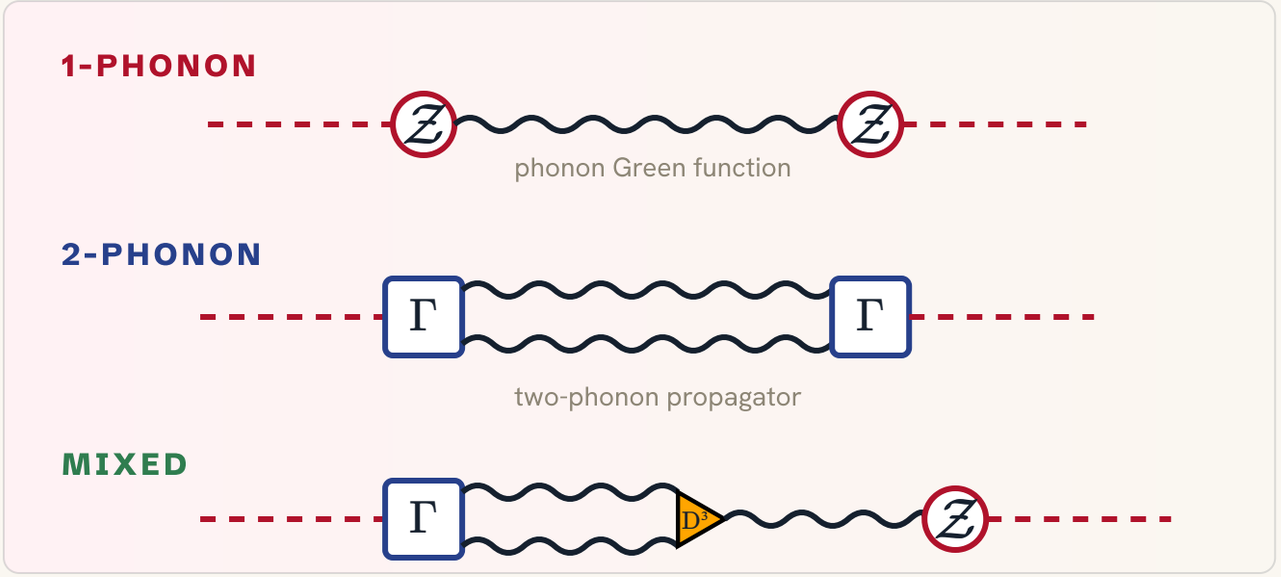
IR: building the a and b vectors

RESPONSE VECTOR

$$\boldsymbol{a}_\beta = \begin{pmatrix} \left\langle \frac{\partial M_\beta}{\partial \tilde{R}_a} \right\rangle_0 \\ \left\langle \frac{\partial^2 M_\beta}{\partial \tilde{R}_a \partial \tilde{R}_b} \right\rangle_0 \\ 0 \end{pmatrix} = \begin{pmatrix} \left\langle Z^*_{\beta a} \right\rangle_0 / \sqrt{m_a} \\ \left\langle \frac{\partial Z^*_{\beta b}}{\partial \tilde{R}_a} \right\rangle_0 / \sqrt{m_b} \\ 0 \end{pmatrix}$$

BORN EFFECTIVE CHARGE

$$Z^*_{\beta a}(\boldsymbol{R}) = \frac{\partial M_\beta(\boldsymbol{R})}{\partial R_a} \qquad \frac{\partial Z^*_{\beta b}}{\partial R_a} = \frac{\partial^2 M_\beta}{\partial R_a \partial R_b}$$



$$\mathcal{Z}_{\alpha a} = \frac{\langle Z^*_{\alpha a} \rangle_0}{\sqrt{m_a}},$$

$$\Gamma_{\alpha,ab} = \frac{\langle \partial_{R_a} Z^*_{\alpha b} \rangle_0}{\sqrt{m_a m_b}}$$

IR RESPONSE

IR: practical spectrum

CONSTANT BORN CHARGES

If Z^* is independent of the ionic configuration, only the one-phonon block is needed:

$$\chi^{\text{ion}}_{M_\alpha M_\beta}(\omega) = \sum_{ab} \frac{Z^*_{\alpha a}}{\sqrt{m_a}} G_{ab}(\omega) \frac{Z^*_{\beta b}}{\sqrt{m_b}}$$

WHAT IS COMPARED TO EXPERIMENT?

Experiments measure absorption of light, which is related to the dielectric tensor.

$$\varepsilon_{\alpha\beta}(\omega) = \varepsilon^{(\infty)}_{\alpha\beta} + \frac{4\pi}{V}\chi^{\text{ion}}_{M_\alpha M_\beta}(\omega)$$

$$\tilde{n}(\omega) = \sqrt{\varepsilon(\omega)} = n(\omega) + i\kappa(\omega)$$

Absorption follows $\kappa(\omega)$.

IR RESPONSE

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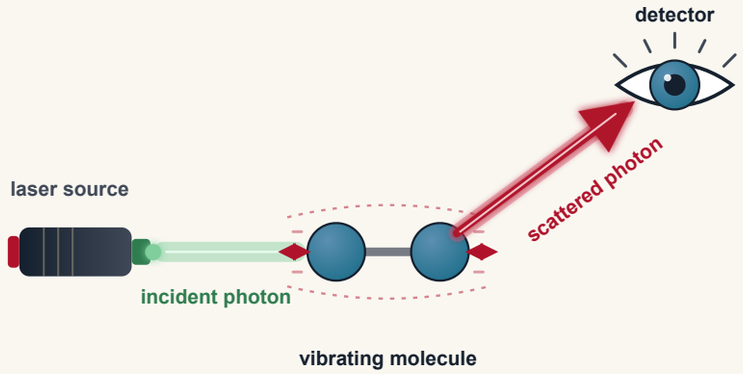
Absorption follows $\kappa(\omega)$.

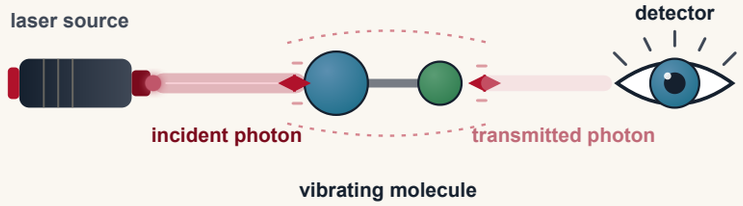
$$\text{Born charges} + \text{TD-SCHA Green function} \Longrightarrow \varepsilon(\omega) \Longrightarrow \text{IR spectrum}$$

Raman is a scattering process

Raman scattering



IR absorption



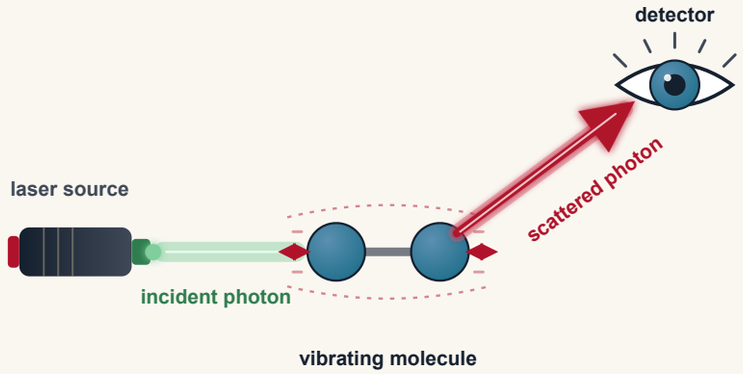
LIGHT IN, LIGHT OUT

A process where a photon is firstly absorbed and emitted.
The rate is provided by the Fermi golden rule

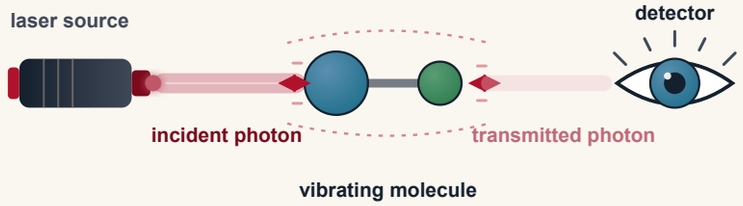
$$I(\omega) \propto \sum_{i,f} p_i \left|\langle i|\hat{\alpha}|f\rangle\right|^2 \delta\left(\omega - \frac{E_f - E_i}{\hbar}\right)$$

Raman is a scattering process

Raman scattering



IR absorption



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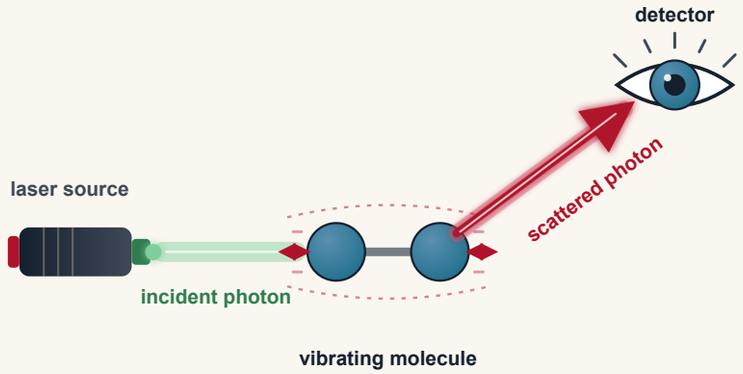
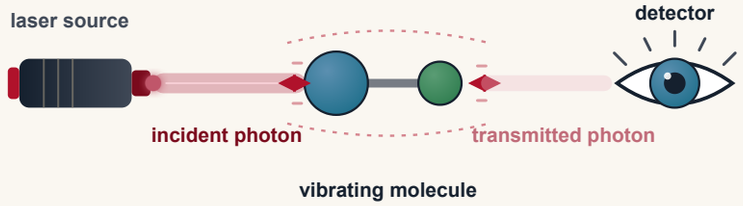
- **Stokes:** $\omega_{\text{out}} = \omega_L - \Omega$; a phonon is created.

Raman is a scattering process

Raman scattering



IR absorption



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- **Stokes:** $\omega_{\text{out}} = \omega_L - \Omega$; a phonon is created.
- **Anti-Stokes:** $\omega_{\text{out}} = \omega_L + \Omega$; a thermal phonon is annihilated.

From Fermi golden rule to the autocorrelation

$$I(\omega) \propto \sum_{i,f} p_i \left|\langle i|\,\hat{\alpha}\,|f\rangle\right|^2 \delta\left(\omega - \frac{E_f - E_i}{\hbar}\right)$$

From Fermi golden rule to the autocorrelation

$$I(\omega) \propto \sum_{i,f} p_i \left|\langle i|\,\hat{\alpha}\,|f\rangle\right|^2 \delta\left(\omega - \frac{E_f - E_i}{\hbar}\right)$$

$$\delta(\omega) = \frac{1}{2\pi}\int_{-\infty}^{\infty} dt\, e^{i\omega t} \qquad \langle i|\hat{\alpha}|f\rangle\, e^{i(E_f-E_i)t/\hbar} = \langle i|\hat{\alpha}(t)|f\rangle$$

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$$I(\omega) \propto \frac{1}{2\pi}\int_{-\infty}^{\infty} dt\, e^{-i\omega t} \sum_i p_i \,\langle i|\,\hat{\alpha}(t)\hat{\alpha}(0)\,|i\rangle$$

From Fermi golden rule to the autocorrelation

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$$\boxed{I(\omega) \propto \int_{-\infty}^{\infty} dt\, e^{-i\omega t} \left\langle \hat{\alpha}(t)\hat{\alpha}(0)\right\rangle \equiv C_{\alpha\alpha}(\omega)}$$

RAMAN RESPONSE

From Fermi golden rule to the autocorrelation

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STOKES ($\Omega_{\mathrm{OUT}} = \Omega_L - \Omega$)

$E_f > E_i$ The δ picks ω, so

$$I_{\mathrm{S}}(\omega) = C_{\alpha\alpha}(\omega)$$

ANTI-STOKES ($\Omega_{\mathrm{OUT}} = \Omega_L + \Omega,\ \Omega > 0$)

$E_f < E_i$, the δ picks $-\omega$. Exchanging $i \leftrightarrow f$,

$$I_{\mathrm{AS}}(\omega) = C_{\alpha\alpha}(-\omega)$$

Fluctuation–dissipation: from $C(\omega)$ to $\chi(\omega)$

FLUCTUATION-DISSIPATION THEOREM

$$C(\omega) = -\frac{\hbar\,[1 + n(\omega)]}{\pi}\,\operatorname{Im}\chi(\omega)$$

RAMAN RESPONSE

Fluctuation–dissipation: from $C(\omega)$ to $\chi(\omega)$

FLUCTUATION-DISSIPATION THEOREM

$$C(\omega) = -\frac{\hbar\,[1 + n(\omega)]}{\pi}\,\mathrm{Im}\,\chi(\omega)$$

Stokes

$$I_{\mathrm{S}}(\omega) \propto -\,[1 + n(\omega)]\,\mathrm{Im}\,\chi_{\alpha\alpha}(\omega)$$

Anti-Stokes

$$I_{\mathrm{AS}}(\omega) \propto -\underbrace{[1 + n(-\omega)]}_{-n(\omega)}\,\mathrm{Im}\,\chi_{\alpha\alpha}(-\omega)$$

$$I_{\mathrm{AS}}(\omega) \propto -n(\omega)\,\mathrm{Im}\,\chi_{\alpha\alpha}(\omega)$$

RAMAN RESPONSE

Fluctuation–dissipation: from $C(\omega)$ to $\chi(\omega)$

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$$I_{\mathrm{AS}}(\omega) \propto -n(\omega)\,\mathrm{Im}\,\chi_{\alpha\alpha}(\omega)$$

SPECTRAL FUNCTION

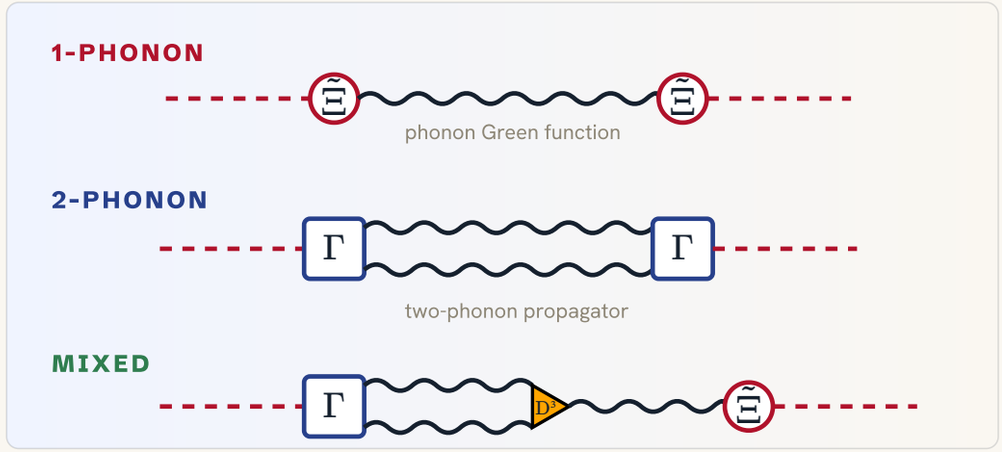
The Raman response is proportional to the polarizability-polarizability spectral function, multiplied by the appropriate Bose occupation number

Raman: building the a vector

$$\chi_{\alpha\alpha}(\omega) = \boldsymbol{a}^{\top}(\mathcal{L} + \omega^2)^{-1}\boldsymbol{a}$$

RESPONSE VECTOR

$$\boldsymbol{a}_{\alpha} = \begin{pmatrix} \left\langle \frac{\partial \alpha}{\partial \tilde{R}_a} \right\rangle_0 \\ \left\langle \frac{\partial^2 \alpha}{\partial \tilde{R}_a \partial \tilde{R}_b} \right\rangle_0 \\ 0 \end{pmatrix} = \begin{pmatrix} \langle \Xi_a \rangle_0 / \sqrt{m_a} \\ \left\langle \frac{\partial \Xi_b}{\partial \tilde{R}_a} \right\rangle_0 / \sqrt{m_b} \\ 0 \end{pmatrix}$$



ATOMIC RAMAN TENSOR

$$\Xi_{a\alpha\beta}(\boldsymbol{R}) = \frac{\partial \alpha_{\alpha\beta}(\boldsymbol{R})}{\partial R_a}$$

$$\frac{\partial \Xi_{b\alpha\beta}}{\partial R_a} = \frac{\partial^2 \alpha_{\alpha\beta}}{\partial R_a \partial R_b}$$

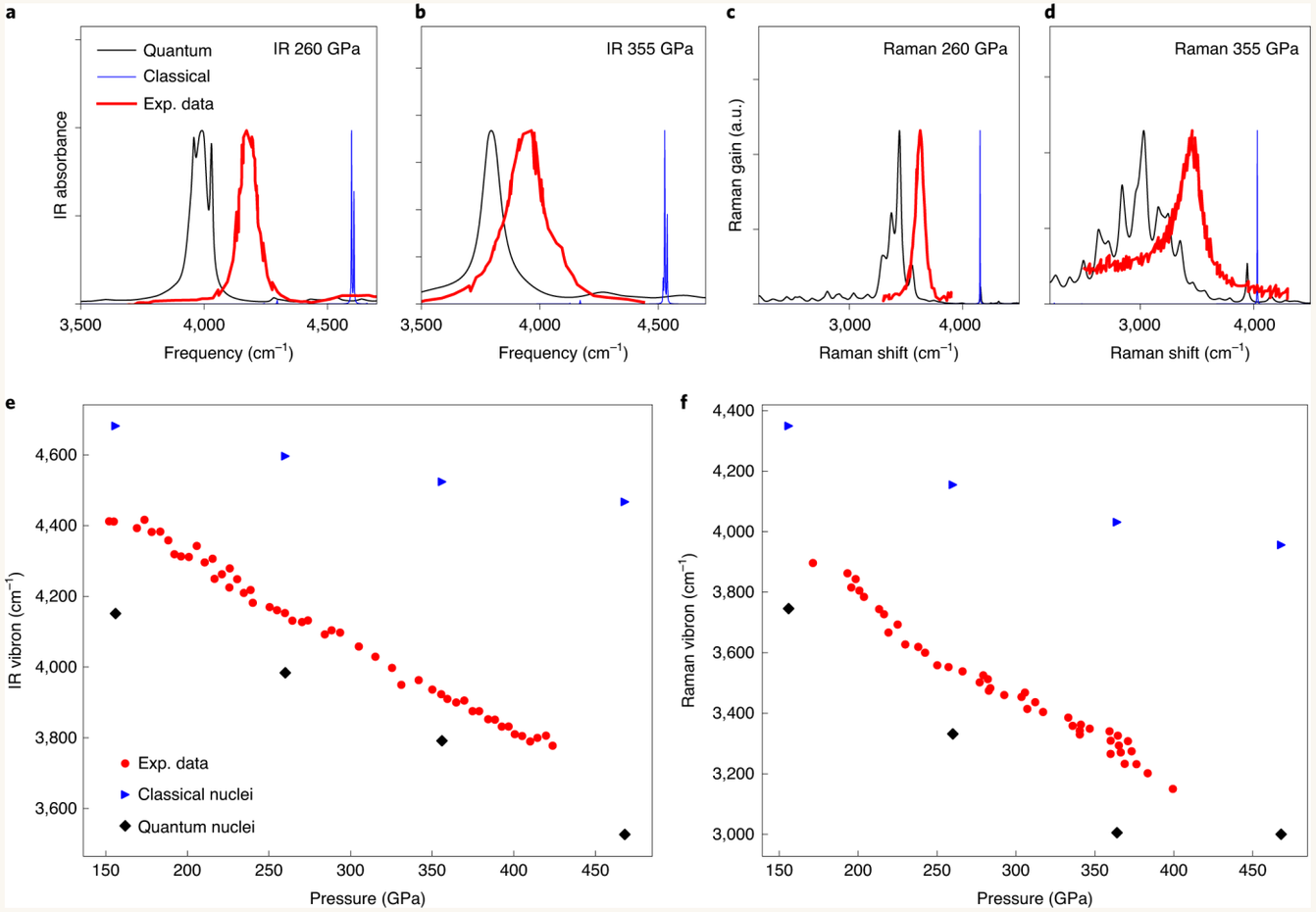
$$\tilde{\Xi}_a = \frac{\langle \Xi_{a\alpha\beta} \rangle_0}{\sqrt{m_a}},$$

$$\Gamma_{ab} = \frac{1}{\sqrt{m_a m_b}} \left\langle \frac{\partial \Xi_{a\alpha\beta}}{\partial R_b} \right\rangle_0$$

APPLICATIONS

TD-SCHA in practice

TD-SCHA benchmark: high-pressure hydrogen



PHASE III OF HYDROGEN @ 300 GPA

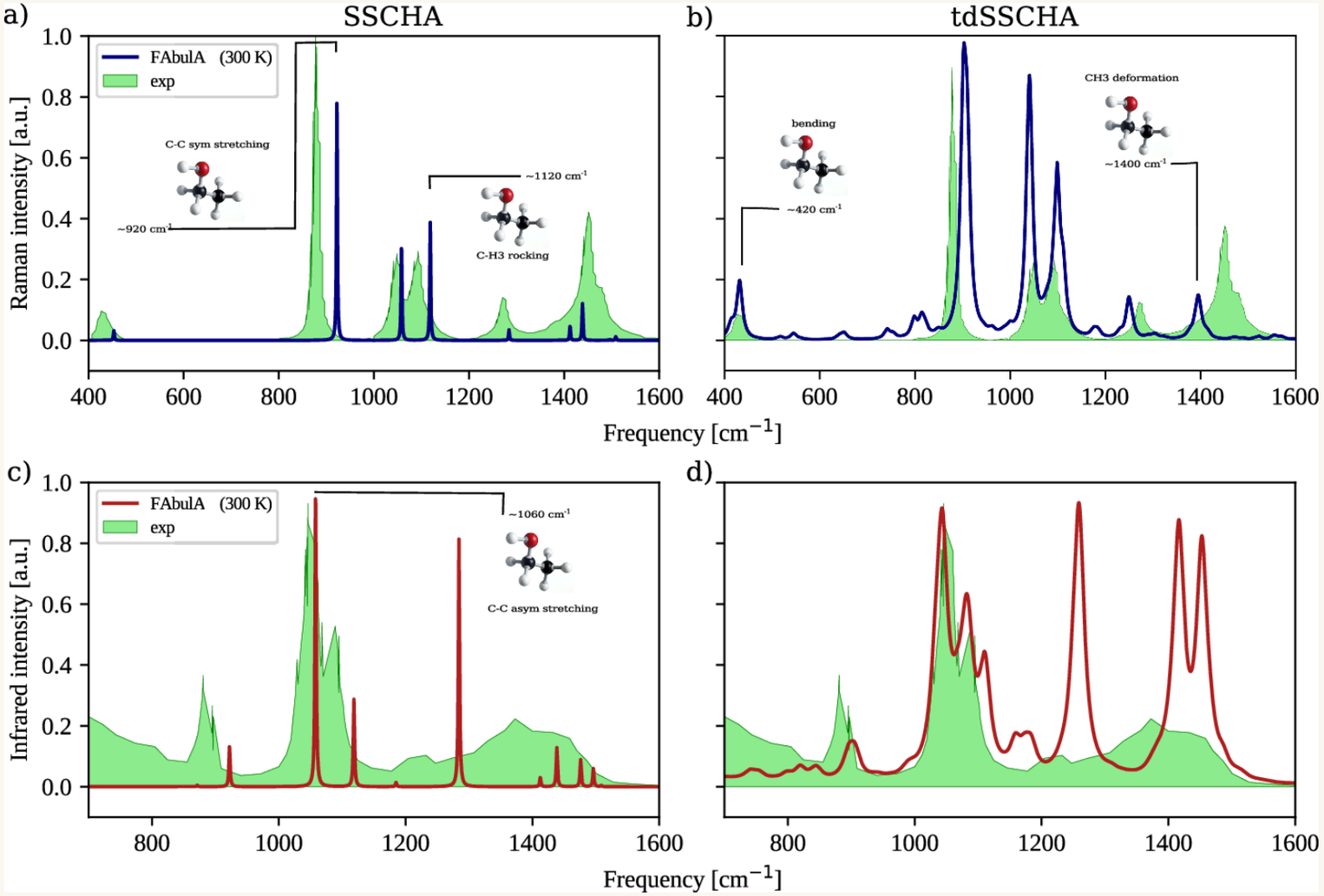
The IR and Raman spectrum of high-pressure hydrogen.

- Phase identification

L. Monacelli & F. Mauri, *Phys. Rev. B* **103**, 104305 (2021)
L. Monacelli *et al.*, *Nature Phys.* **17**, 63 (2021)

APPLICATIONS

Vibrational spectroscopy of organic molecules



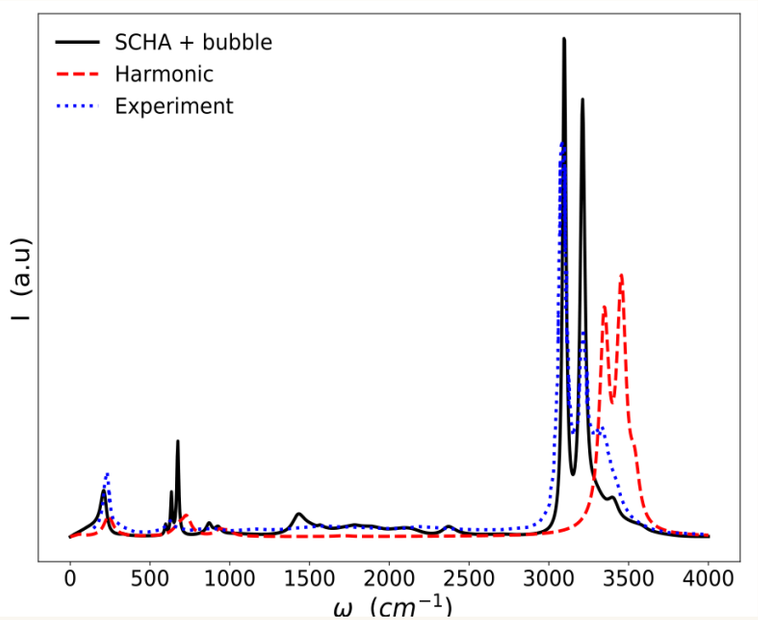
ETHANOL — RAMAN & IR

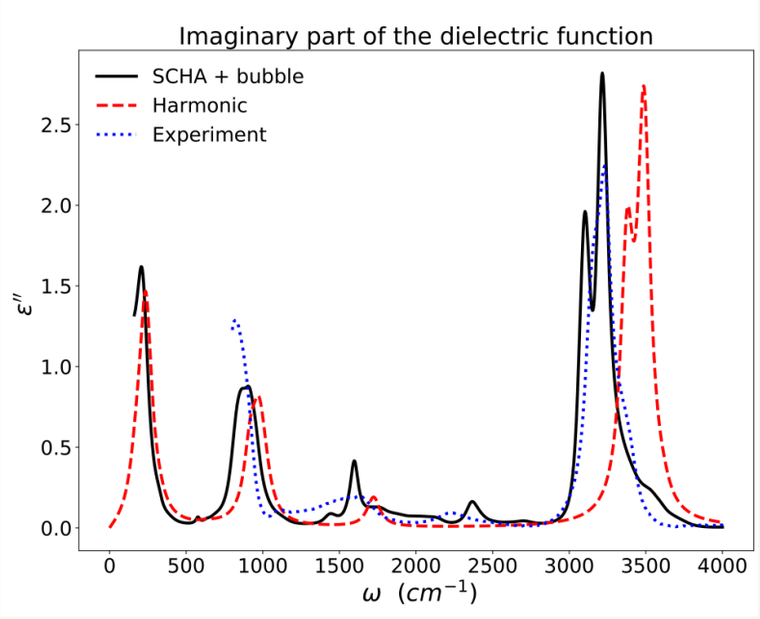
- Raman and IR spectrum of organic molecules

M. Miotto & L. Monacelli, *npj Comput. Mater.* **10**, 240 (2024)

APPLICATIONS

Ice XI: Raman scattering & dielectric function





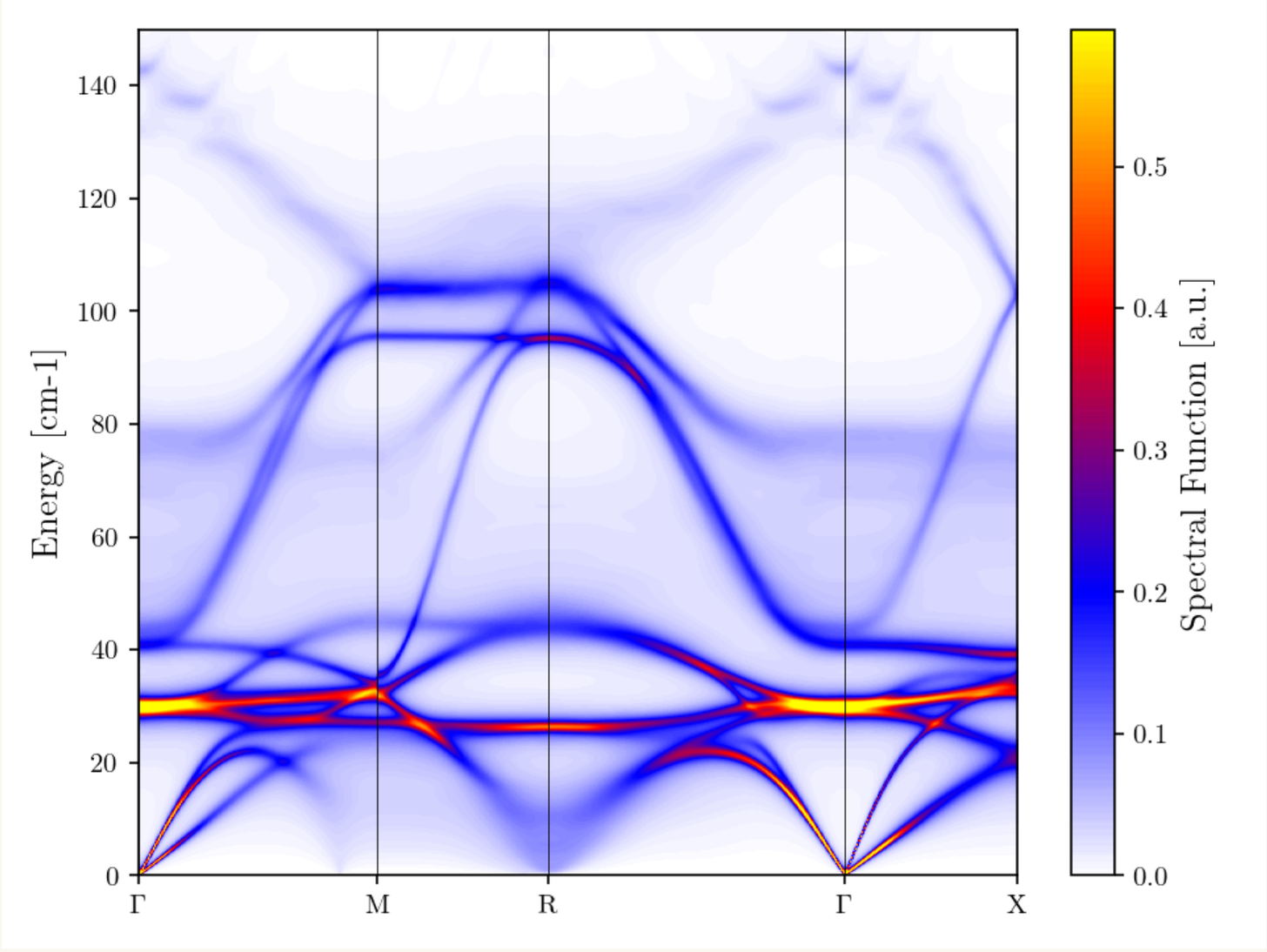
ICE XI — H2O & D2O @ 200 K

The TD-SCHA reproduces the Raman spectrum and the imaginary part of the dielectric function of ice XI

M. Cherubini, L. Monacelli & F. Mauri, *J. Chem. Phys.* **155**, 184502 (2021)

APPLICATIONS

CsSnI3: spectral functions at any q-point



B-A CSSNI3 @ 450 K

Phonon spectral functions are **not limited to Γ** — the TD-SCHA Lanczos algorithm gives access to the full q-resolved spectrum.

L. Monacelli & N. Marzari, *Chem. Mater.* **35**, 1702 (2023)

IN SUMMARY

Thank you

www.sscha.eu

github.com/SSCHAcode

01 **Experimental spectra are susceptibilities**

IR absorption, Raman scattering, neutron and X-ray scattering are all described by a **susceptibility** $\chi_{AB}(\omega)$. Evaluating the right χ_{AB} with the correct operators A and B directly yields the measured spectrum.

02 **Observed phonons $\neq$ SSCHA frequencies**

The **physical phonon peaks** are the poles of the interacting Green's function $G(\omega)$, which differ from both the harmonic Hessian frequencies and the SSCHA auxiliary frequencies. Only the dynamical theory reveals the true phonon spectrum.

03 **TD-SCHA computes it all**

The Lanczos algorithm within TD-SCHA efficiently evaluates the **phonon Green's function** and any susceptibility $\chi_{AB}(\omega)$. From these, Raman, IR, and inelastic scattering spectra follow directly, with ab-initio linewidths and at any q-point.

> The **dynamical structure factor** $S(q,\omega)$ is also the density-density susceptibility. Therefore **neutron scattering**, **inelastic X-ray scattering** are equally accessible within the same TD-SCHA + Lanczos framework.

Lorenzo Monacelli
Università di Roma «Sapienza», Dipartimento di Fisica

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