

Ultrafast Spectroscopy of Coherent Phonon across the Pressure-Driven Insulator to Metal Phase Transition

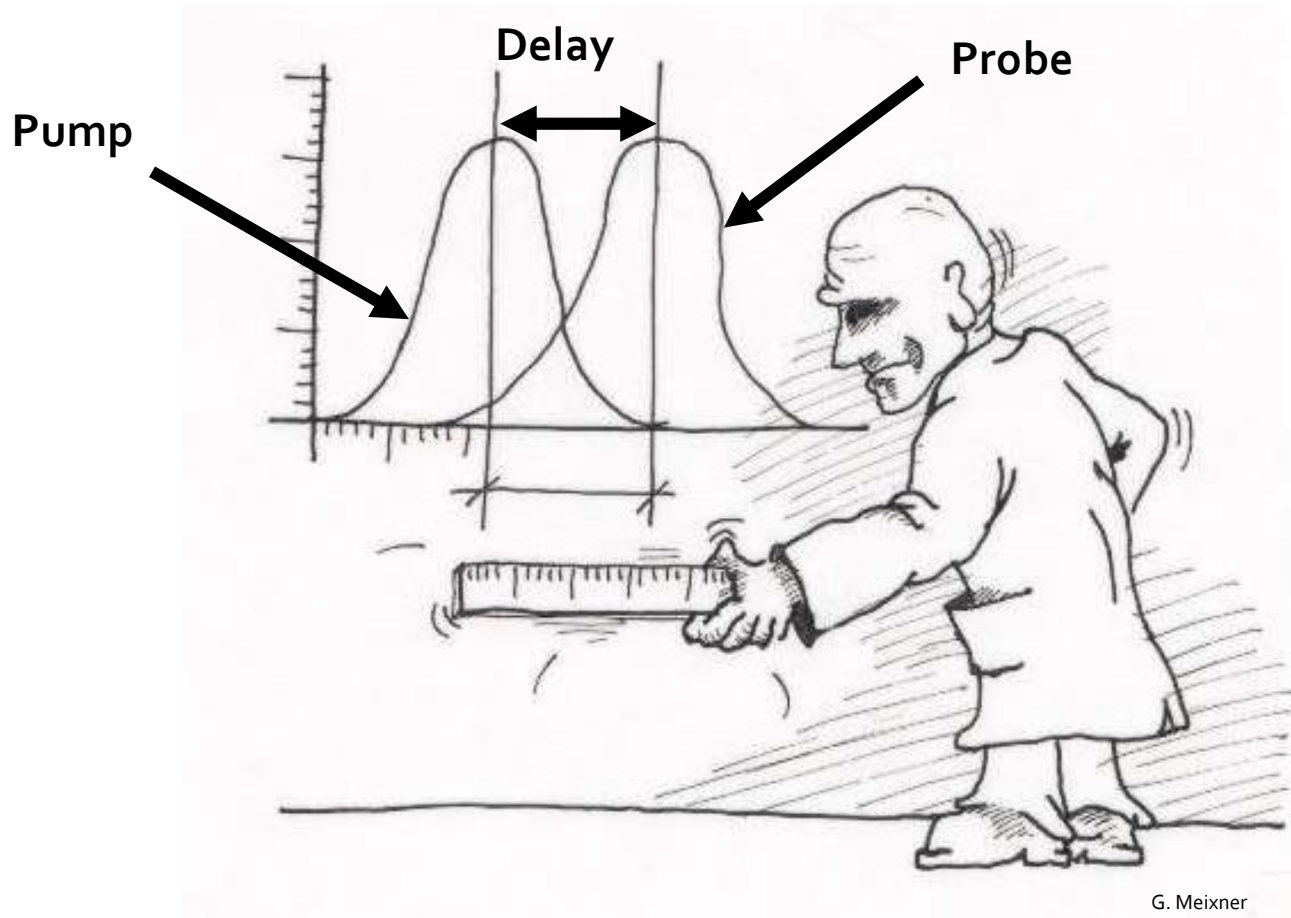
Roman Bertoni, Institut de Physique de Rennes, University of Rennes,
Materials & Light



Transformations of Correlated Electronic States by Electric or Optical Impacts.
International research school and workshop **IMPACT – 2024**

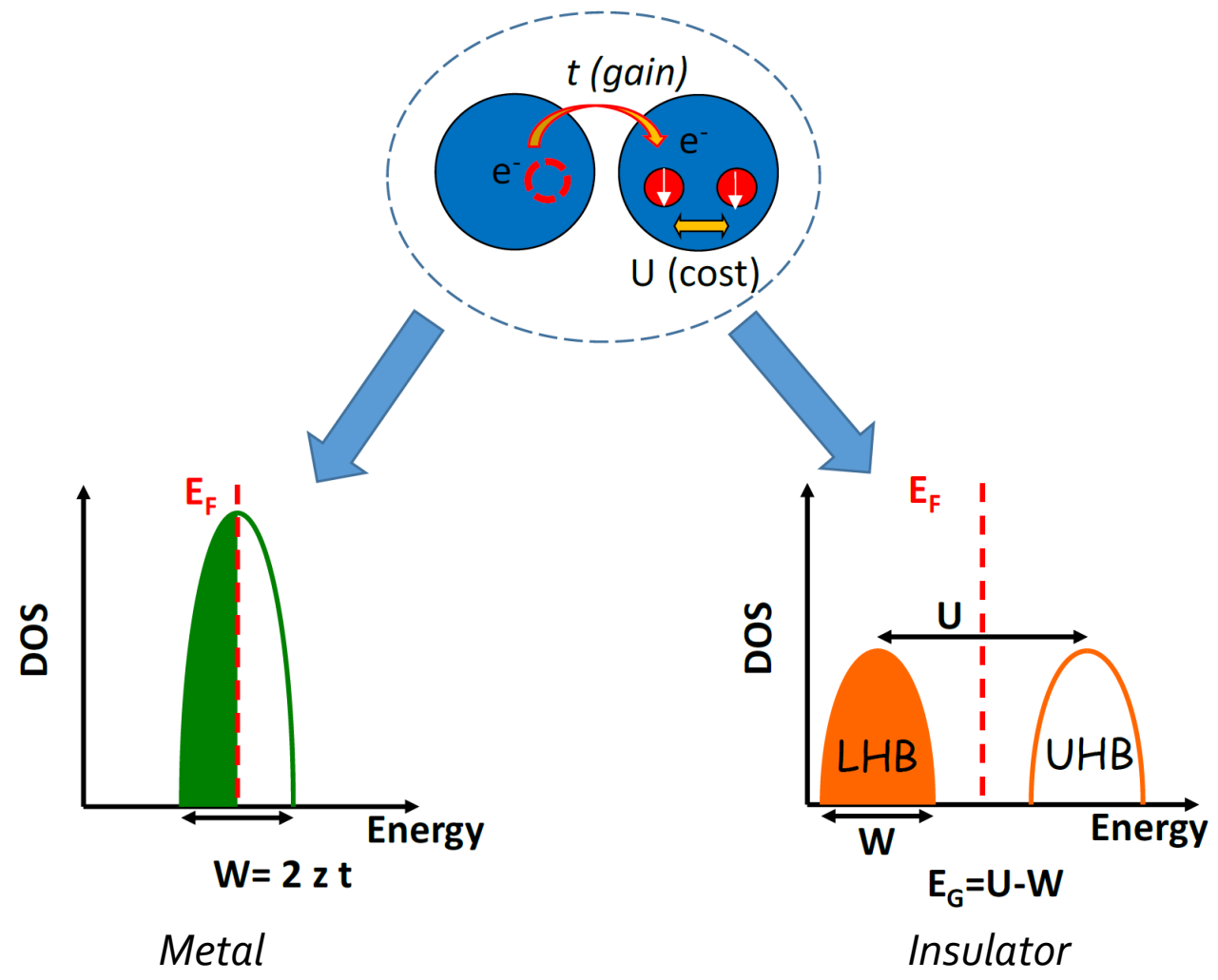
Ultrafast spectroscopy: Pump-Probe techniques

Monitoring the temporal evolution of the system after initial perturbation



Why?

- How fast is the transition occurring?
- What is the driving force?
- Can you control material properties with light?
- How and how fast energy dissipates?



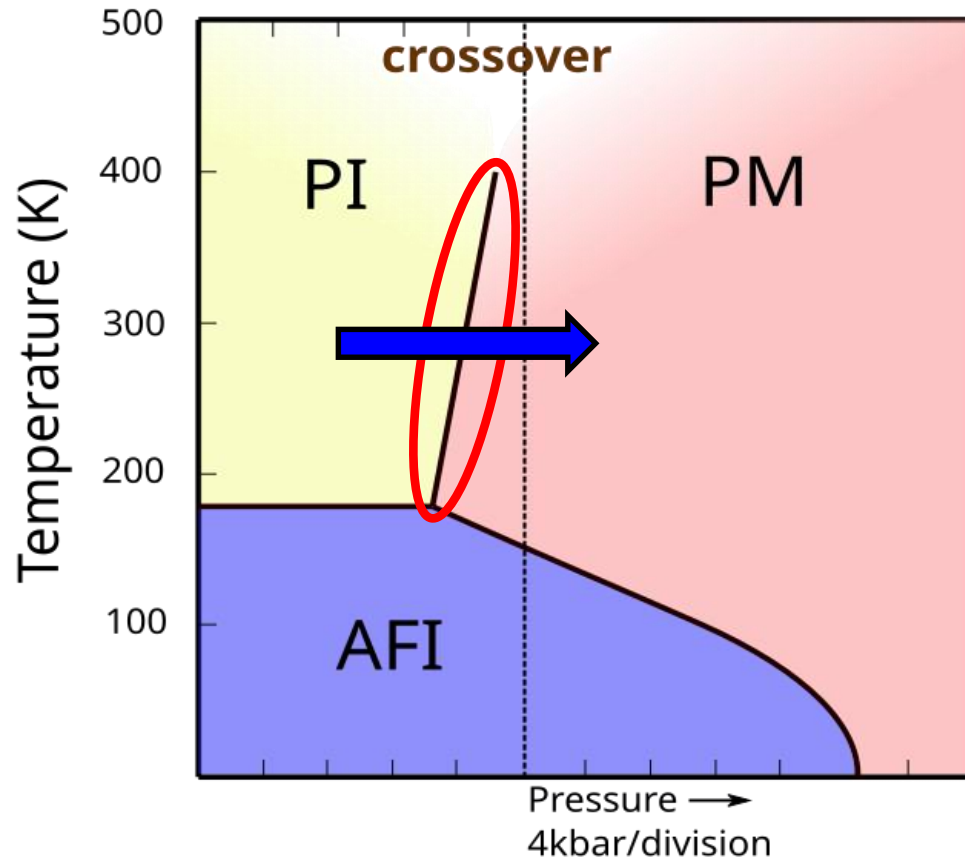
Insulator to Metal Transition through the prism of electronic correlation (Simple Mott-Hubbard model)



Ratio " U/W " control the state of the material

Tuning parameter ($W = \text{electronic bandwidth}$):

- **Hydrostatic pressure**



Textbook example: $(V_xCr_{1-x})_2O_3$

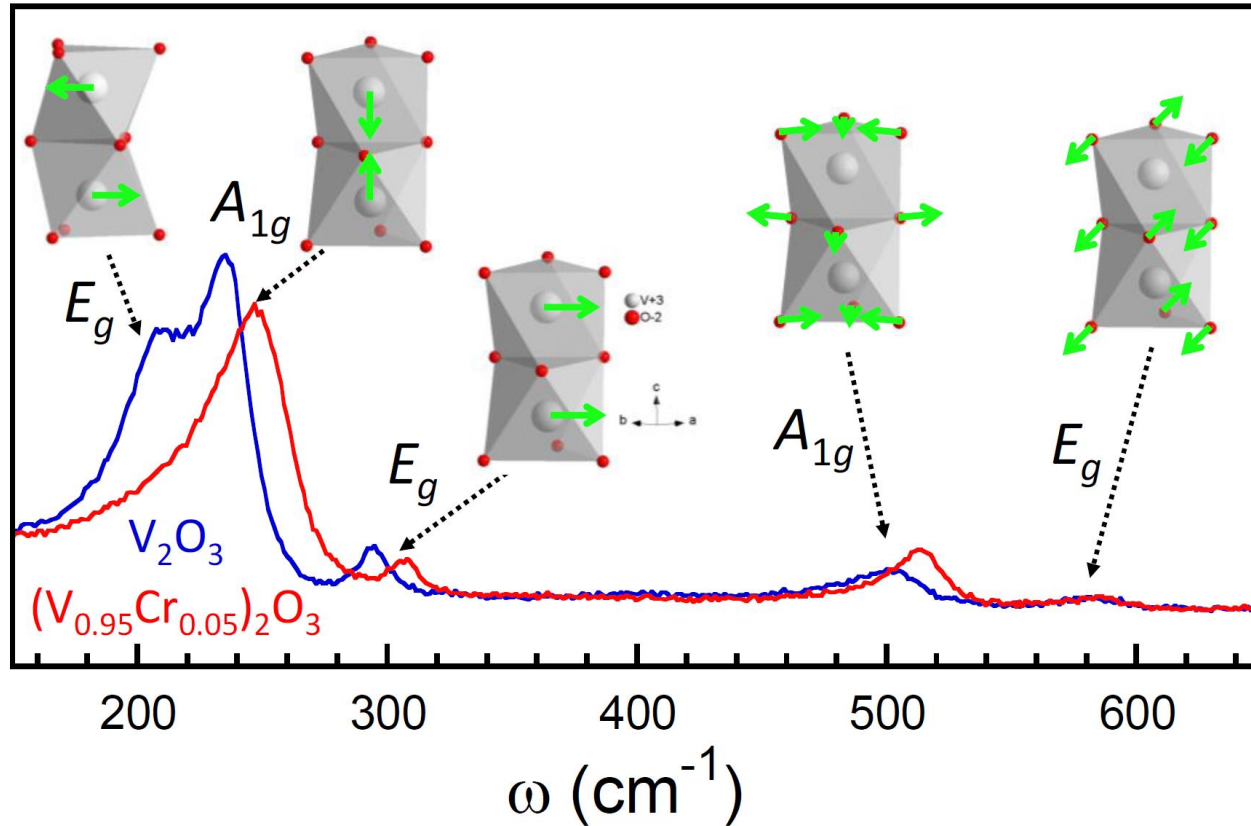
- Chemical substitution allows Insulating Phase under ambient conditions (1 bar, 300 K)
- Chemically pure V₂O₃ = PM phase

Paramagnetic Insulator (PI) to Paramagnetic Metal (PM) transition occurring at Room Temperature (Blue arrow):

- Isostructural (non symmetry breaking)
- Volume change (PI to PM → lattice contraction)
- First order (hysteresis + coexistence)

Structural signatures of Mott Transition?

Raman scattering intensity (arb. unit)



Raman spectrum on V_2O_3 single crystals

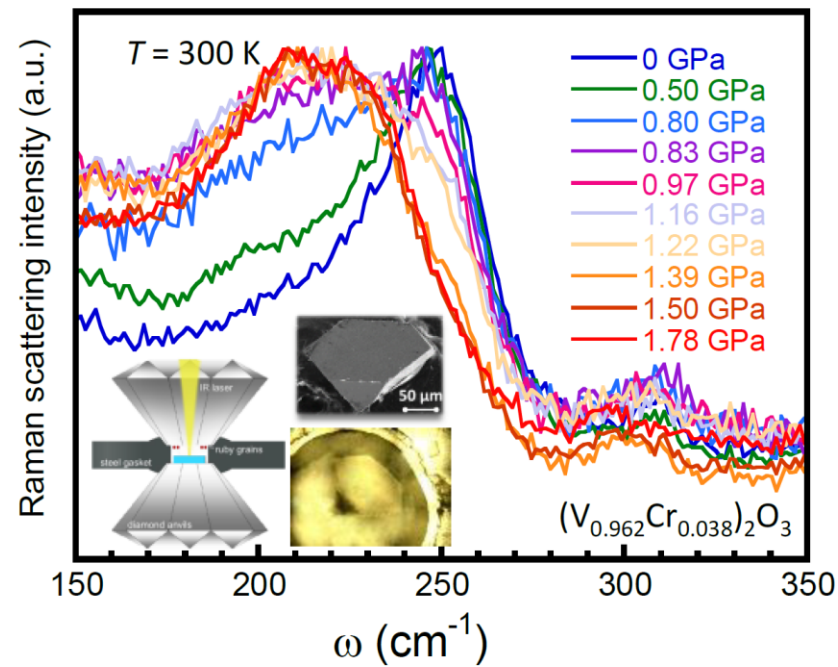
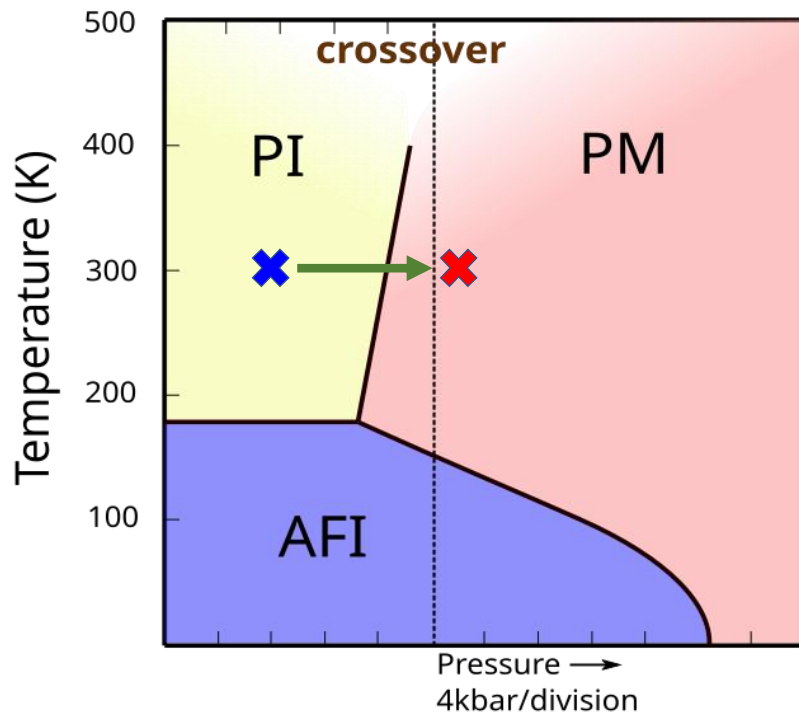
V_2O_3 = PM phase at room temperature

$(V_xCr_{1-x})_2O_3$ = PI phase at room temperature

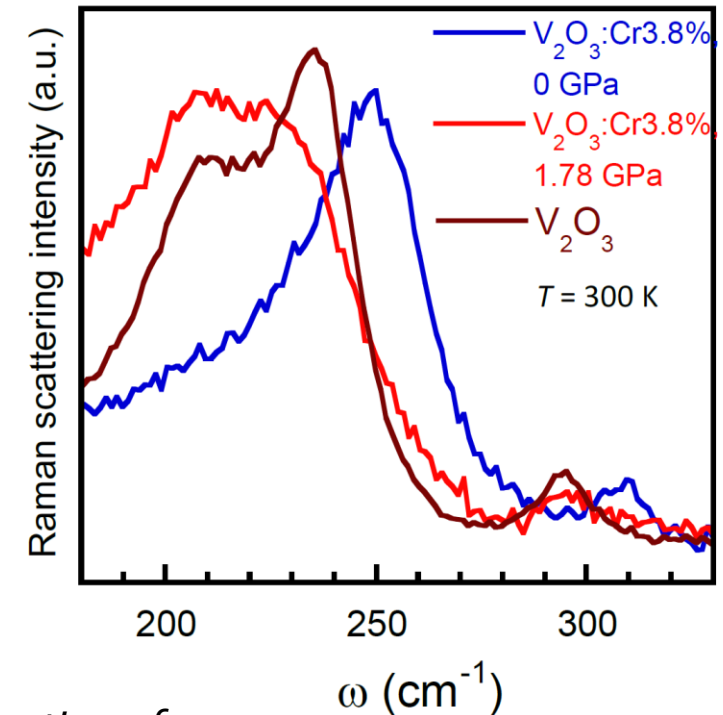
Lower frequencies in PM phase (few %)

- Optical phonon mode as possible spectroscopic marker of the non-symmetry breaking phase transition

Lattice volume change → shift in optical phonon frequency

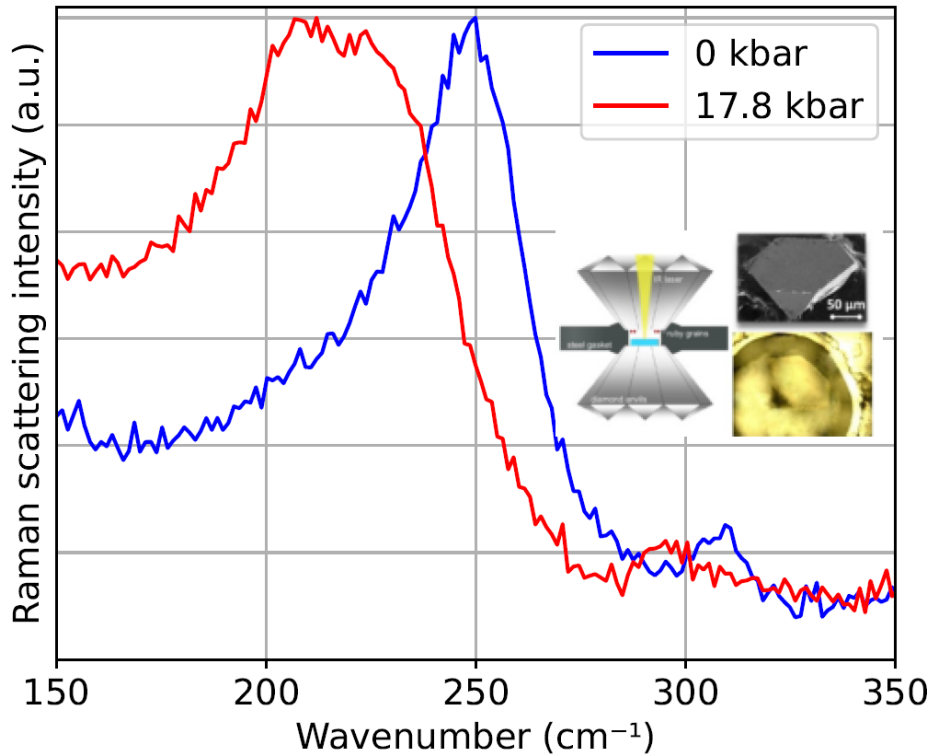


Raman spectrum on V_2O_3 single crystal as a function of pressure

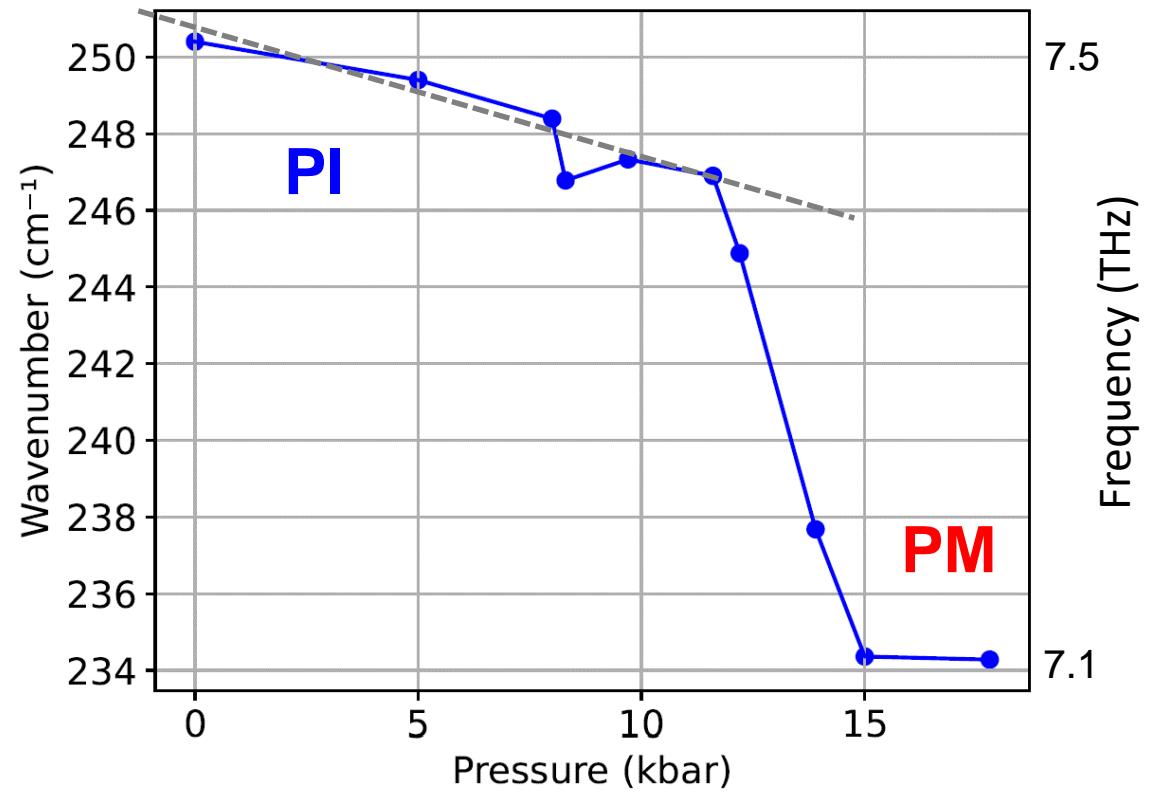


Pressure-induced PI to PM transition monitored by Raman Spectroscopy:

- Transition above 15 000 bars (1.5 GPa)
- Red shift of the A_{1g} frequency during IMT in the $(V_xCr_{1-x})_2O_3$ case



Raman spectrum on $(V_xCr_{1-x})_2O_3$ single crystal

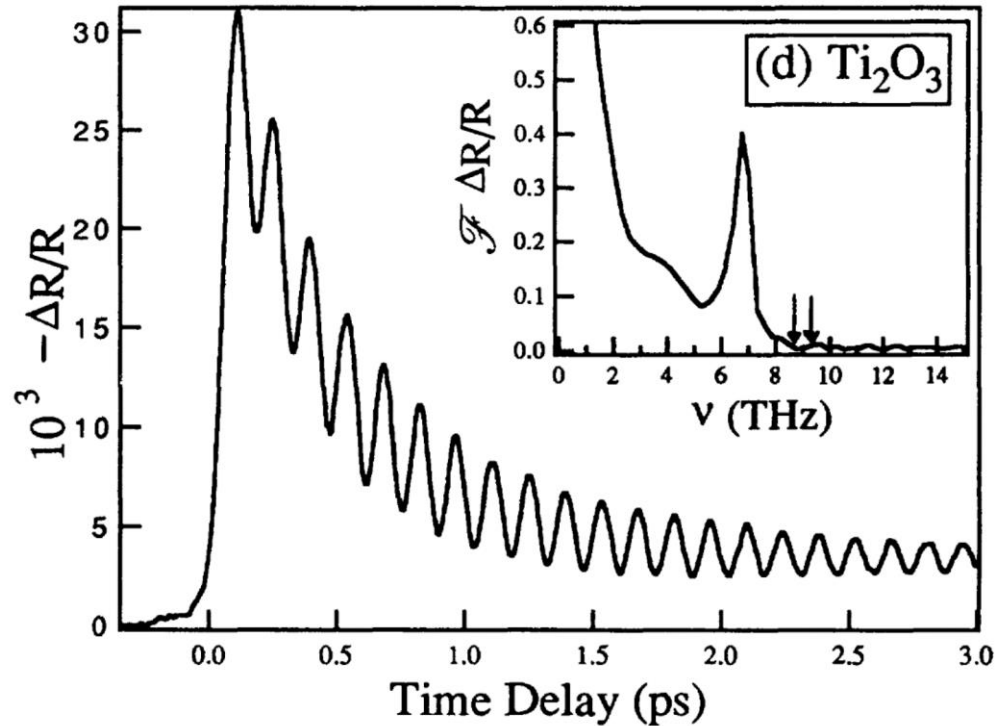


A_{1g} mode shift as a function of pressure

- A_{1g} shift as marker for the Mott Transition (plausible PM at 15 kbars)
- Small softening in the PI phase (-0.008 THz per 1000 bar)



- Single Crystal Cr doped



H. J. Zeiger, *Phys. Rev. B* 45 (2), 768 (1992)

- Modulation of the dielectric function or diffraction pattern at the optical phonon frequency (THz range)

Can be naively modelled by damped oscillating function

$$\frac{\Delta R}{R} \propto \left(\cos(\omega_{ph}t + \phi) \right) e^{-t/\tau}$$

3 quantities can be extracted

- Frequency
- Damping
- Phase

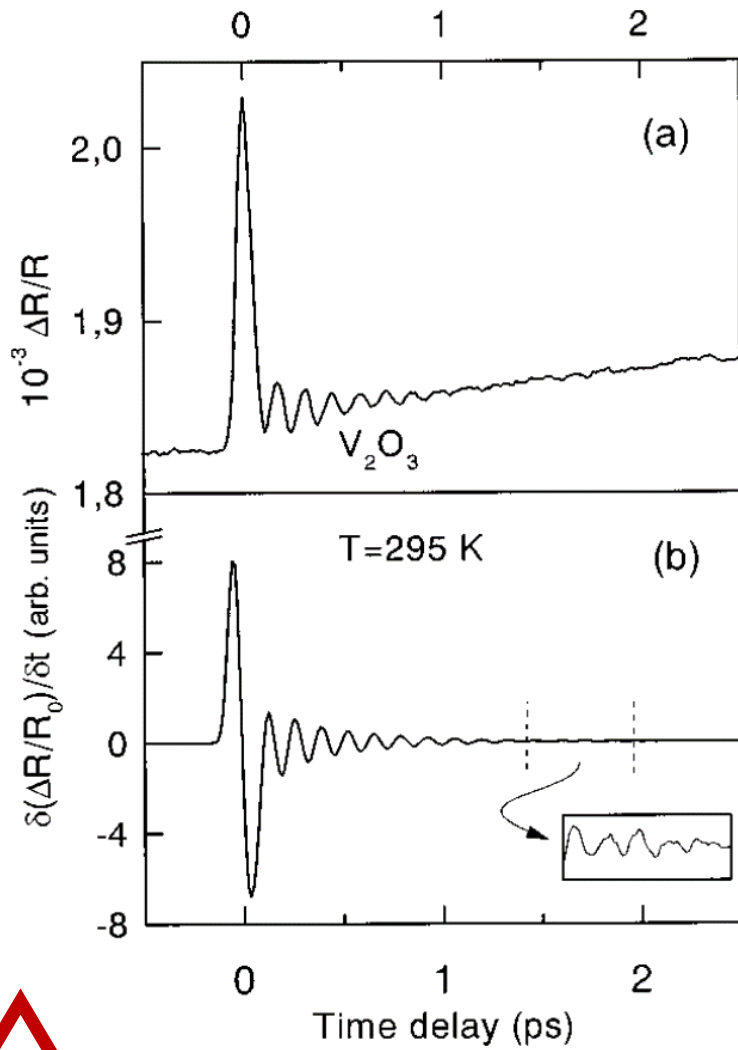
Two classifications unified through Raman formalism:

- **Displacive excitation of Coherent Phonon** (cosine like)
- Impulsive Raman Scattering (sine like)

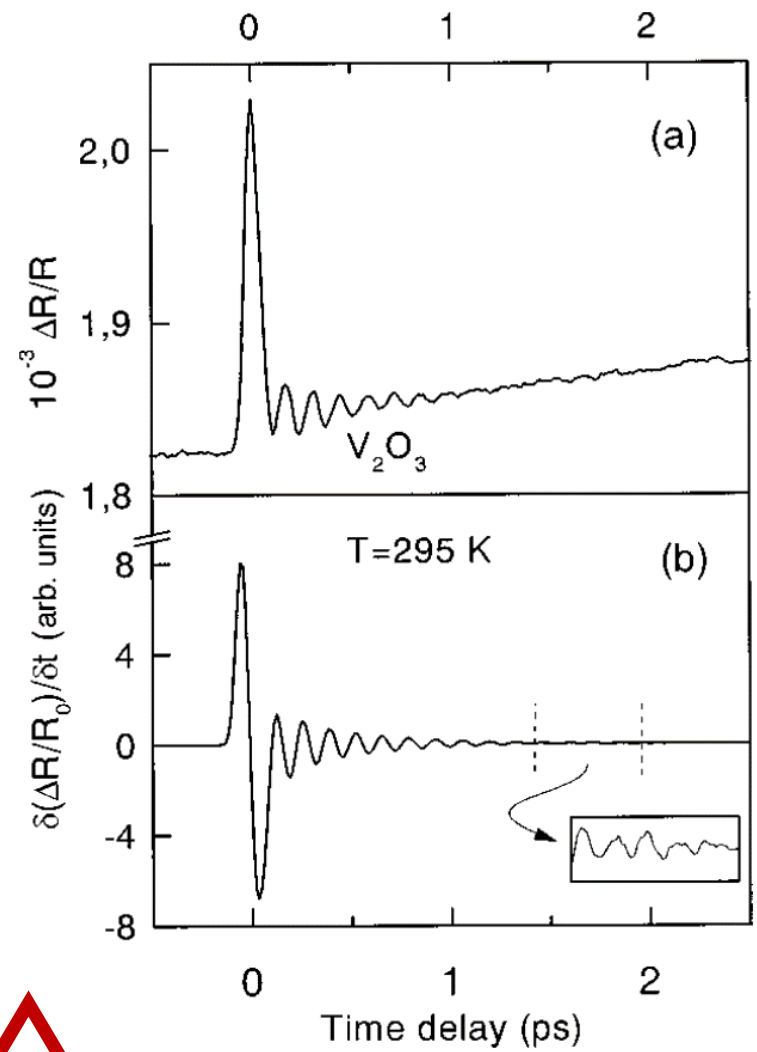



Electron phonon coupling →
Zone center optical phonon of A_{1g} character

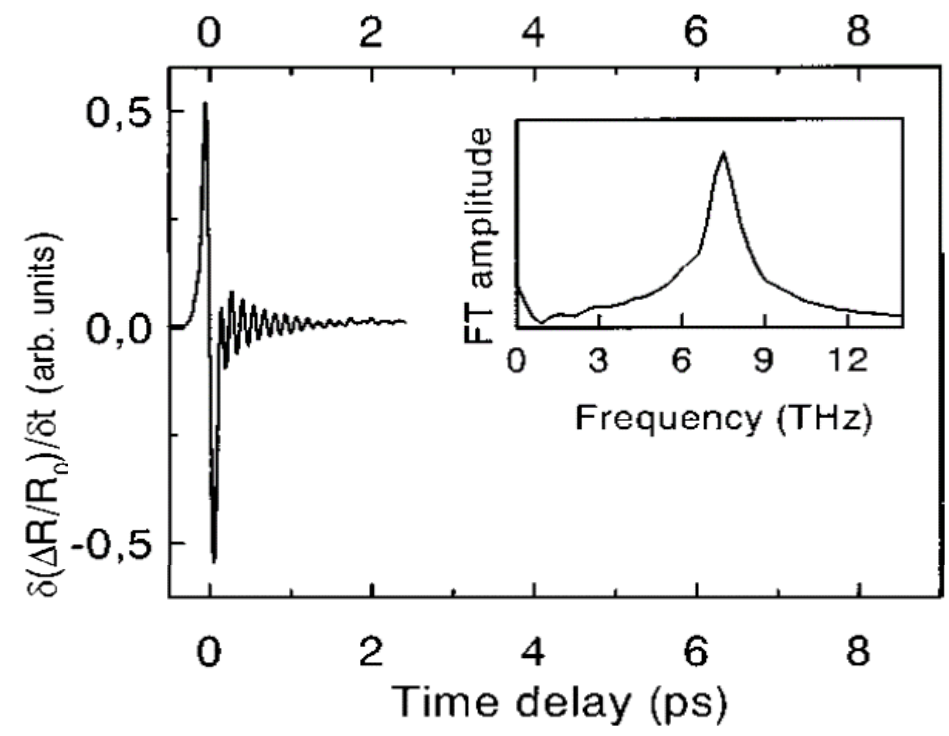
R. Merlin, *Solid State Communications* 102 (2), 207-220 (1997)



- Single Crystal V₂O₃
- Low excitation density



FFT




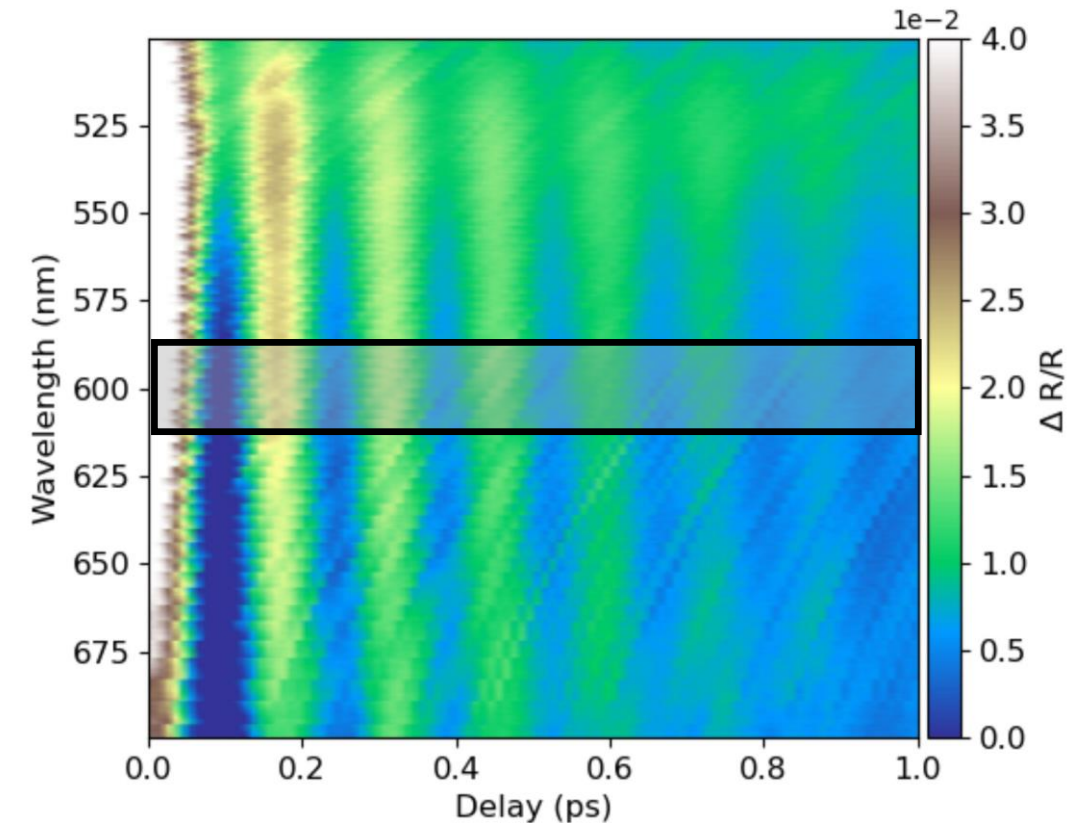
One single frequency observed at 7.4 THz (Instrumental Response Function ~ 100 fs) in pure V₂O₃

- Zone Center A_{1g} mode (2 modes: 7.4 and 15 THz)
- DECP like mechanism (genuine electronic excitation)



- Single Crystal V₂O₃
- Low excitation density

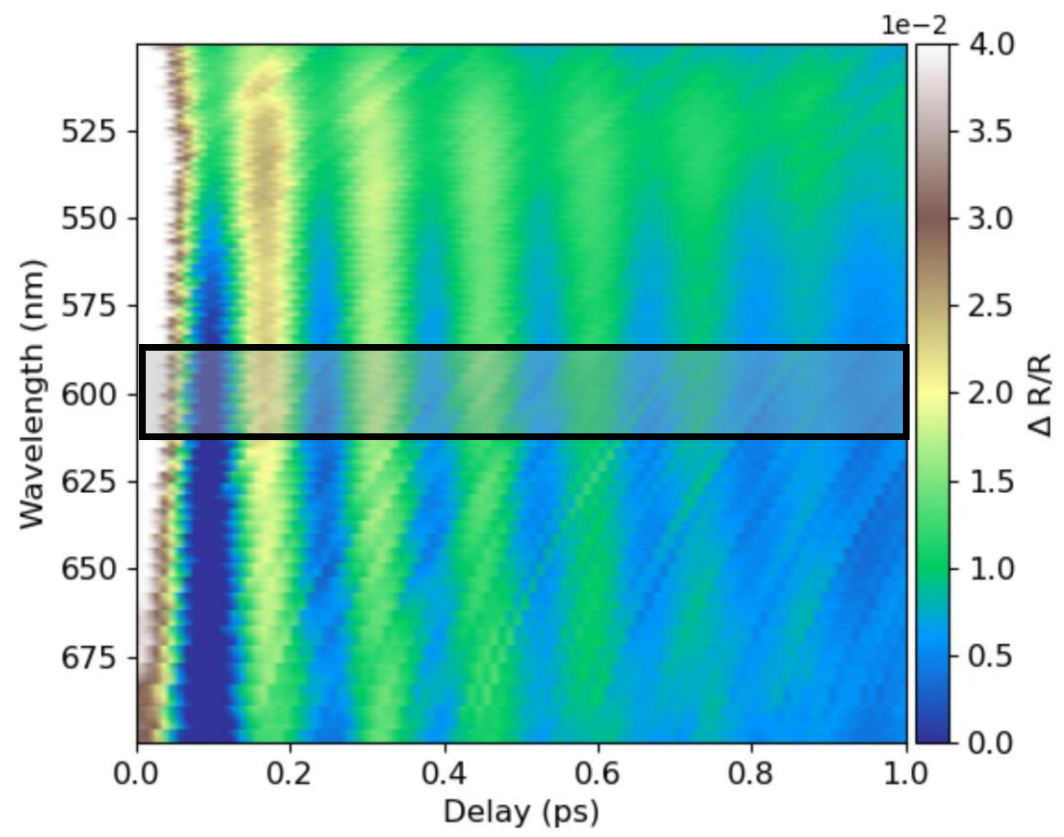
Nanometric thin film (~ 200 nm) of pure V_2O_3 (polycrystalline)
 \rightarrow PM phase at ambient temperature




Broadband transient reflectivity changes

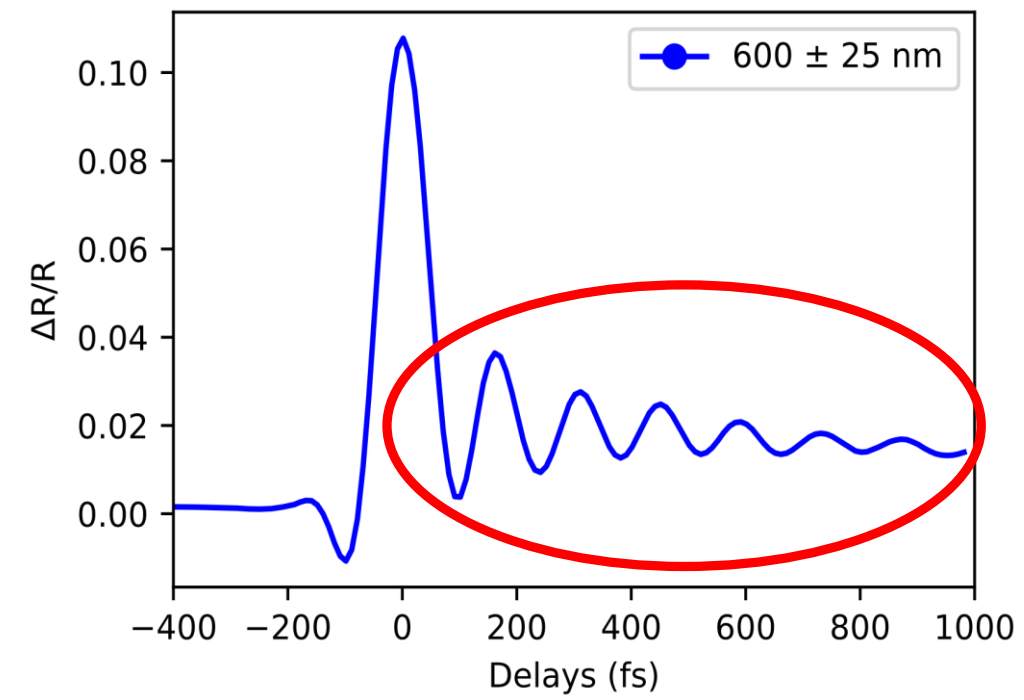
Pump at 800 nm \rightarrow electronic excitation

Nanometric thin film (~ 200 nm) of pure V_2O_3 (polycrystalline)
 \rightarrow PM phase at ambient temperature



Broadband transient reflectivity changes


 Single
wavelength
time trace

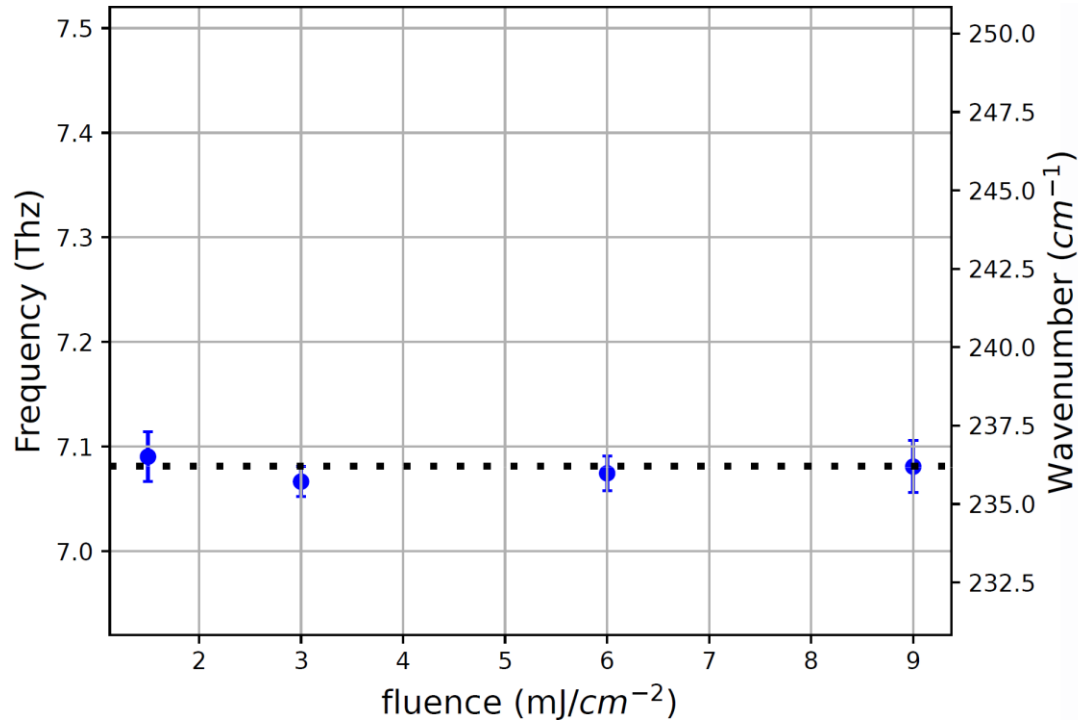


Coherent Phonon frequency ~ 7.1 THz

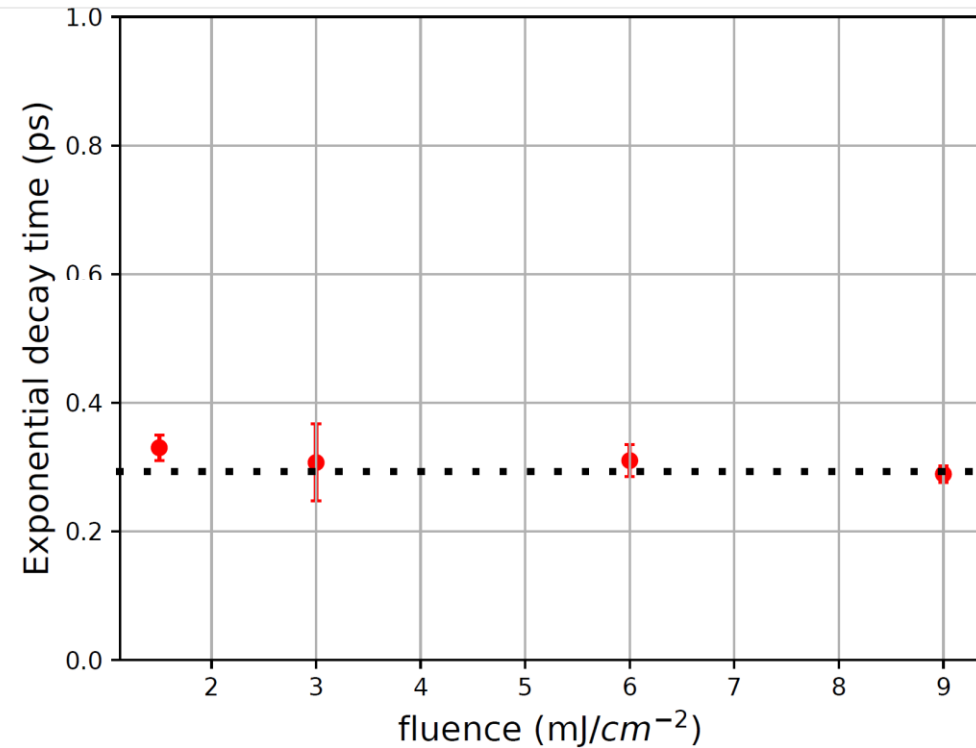
- Agreement with previous studies on similar sample

Pump at 800 nm \rightarrow electronic excitation

Nanometric thin film (~ 200 nm) of pure V_2O_3 (polycrystalline)
 \rightarrow PM phase at ambient temperature



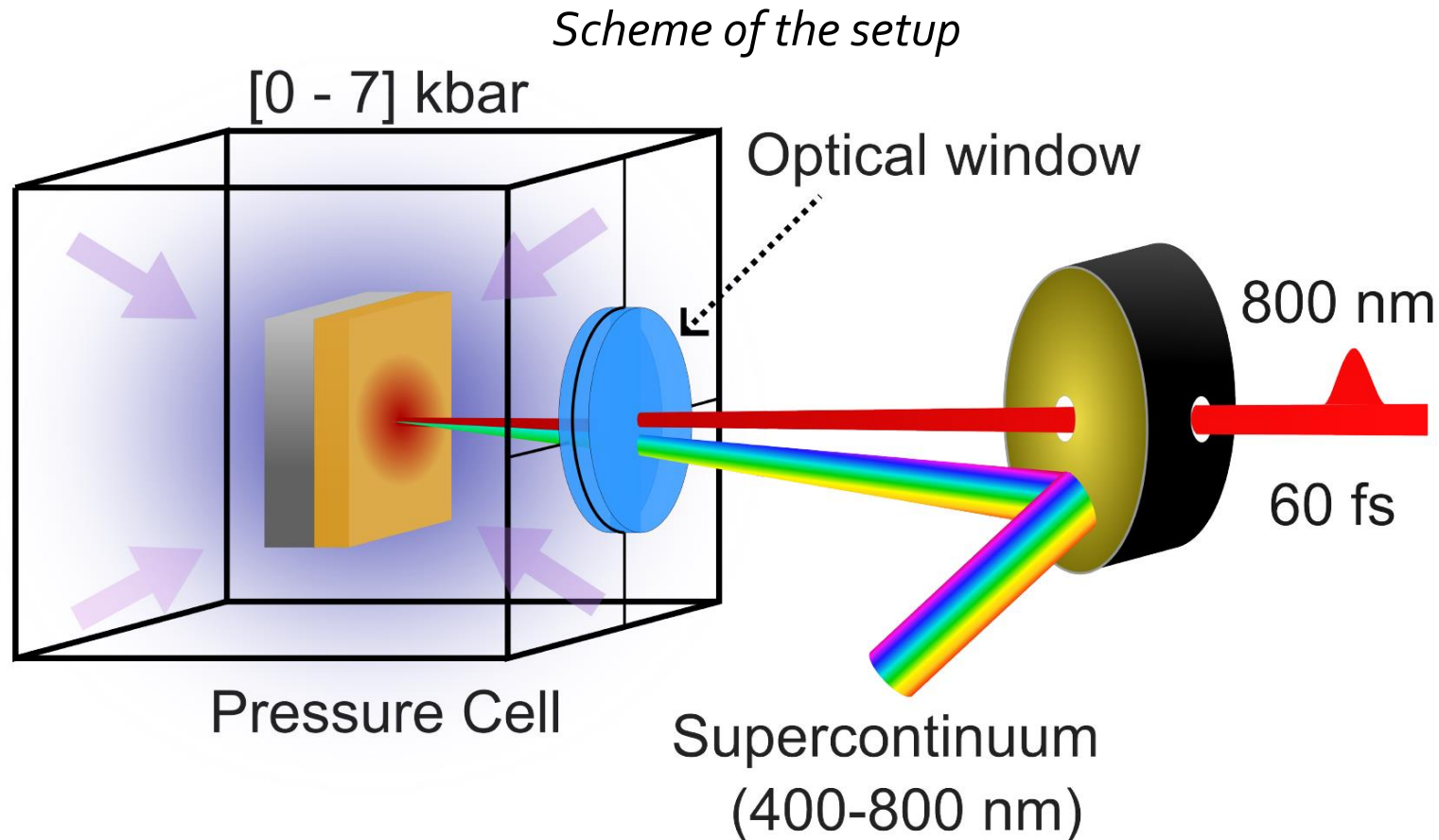
Phonon frequency as a function of excitation density



Damping time as a function of excitation density

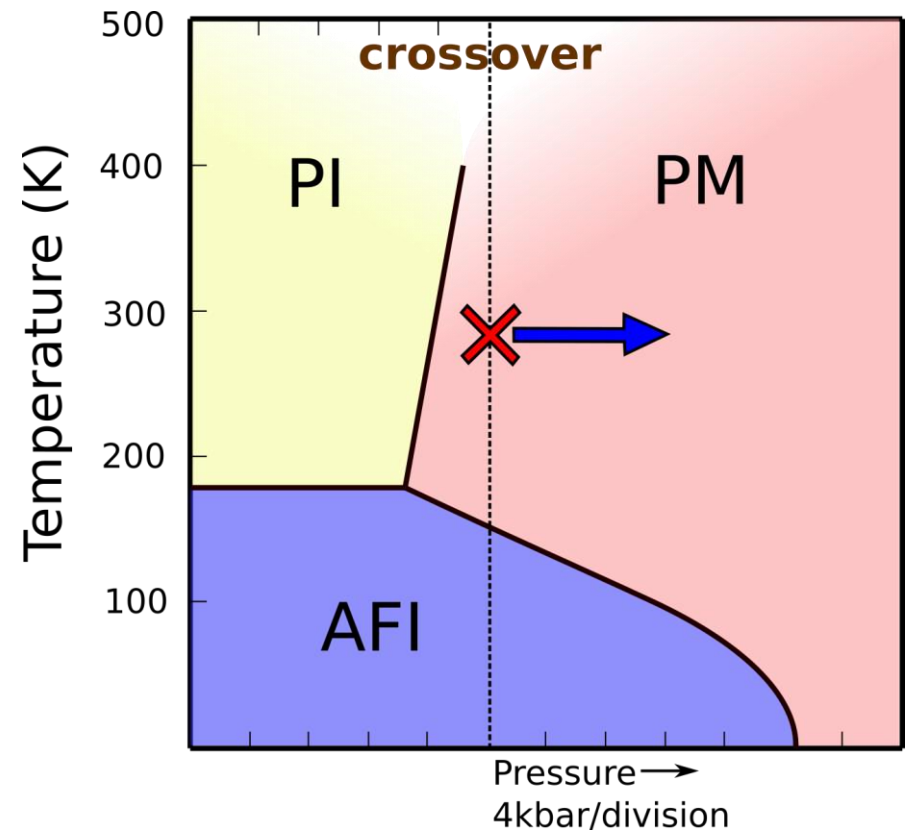
No influence of excitation density on phonon frequency nor damping time:

- In agreement with previous reports



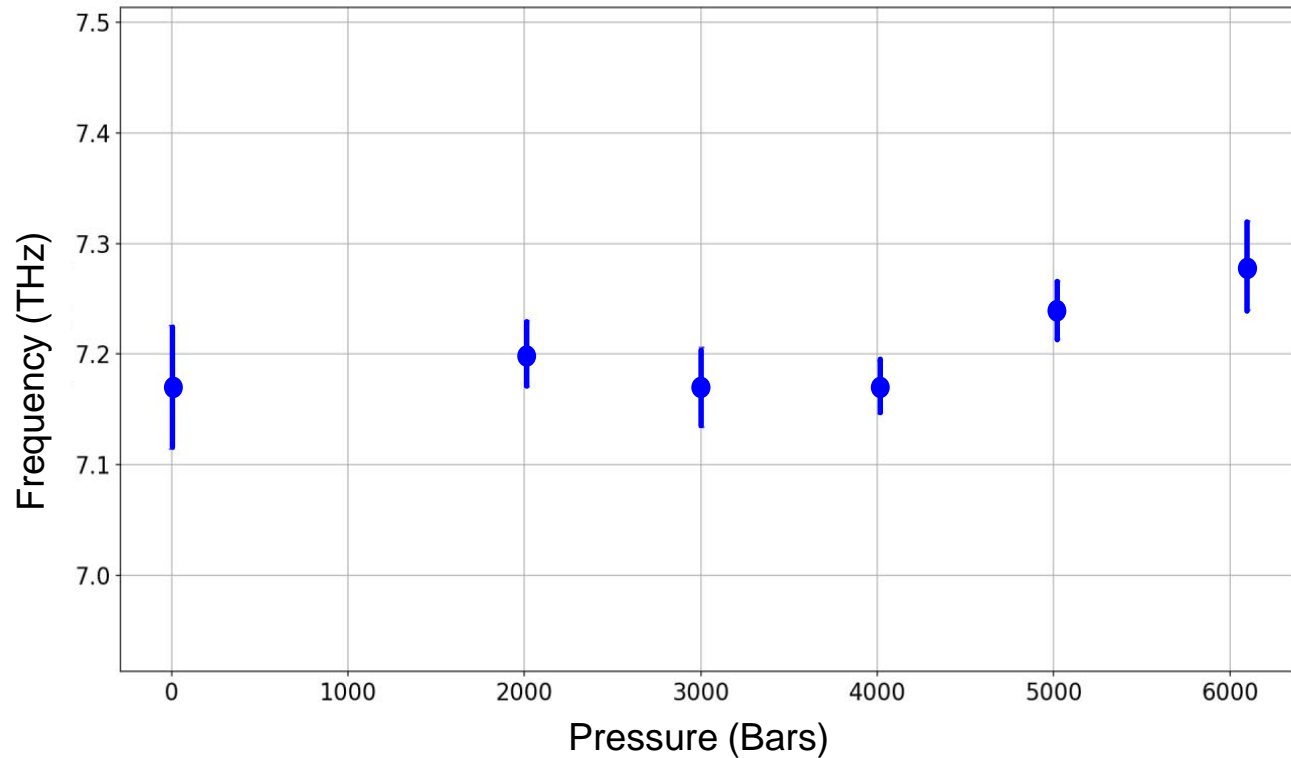
Combination of ultrafast optical spectroscopy and hydrostatic pressure:

- Spectrally- and time-resolved (visible range)
- Below 100 fs time resolution = able to track down coherent phonon up to 10 THz



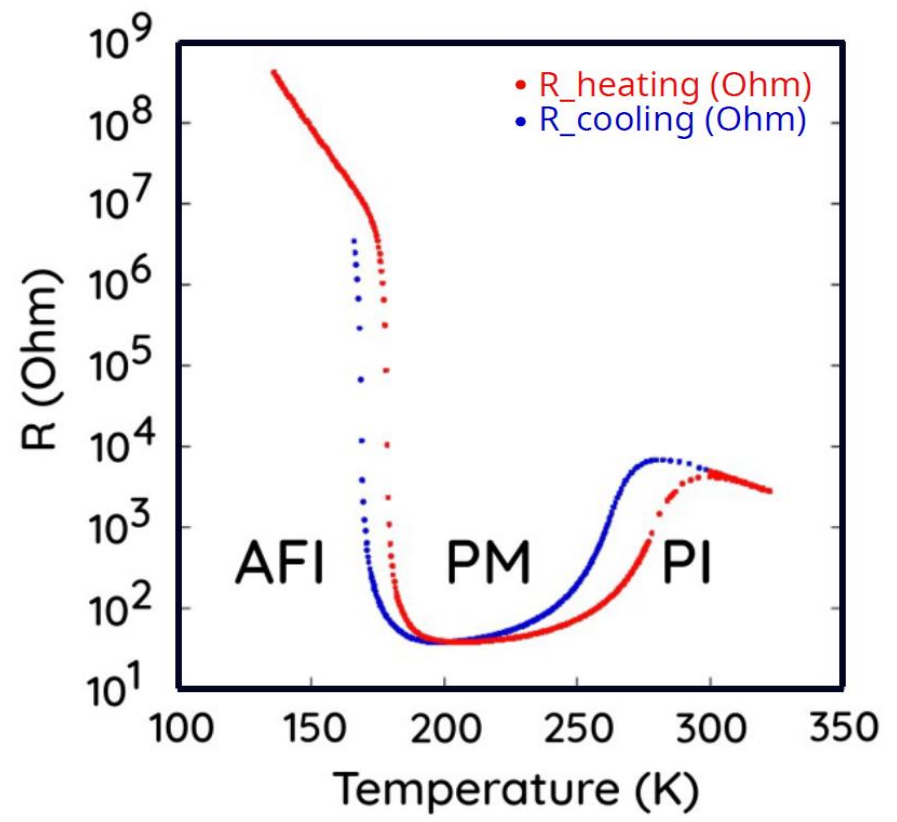
- Pure V_2O_3 without chemical substitution is a Paramagnetic "bad" Metal (PM) under standard thermodynamical conditions
- No expected phase transition under hydrostatic pressure
- Thin film of ~ 200 nm thickness

Effect of hydrostatic pressure on PM phase



- 7.17 ± 0.05 THz at ambient pressure
- Small hardening ($\sim 0,015$ THz per kbar)

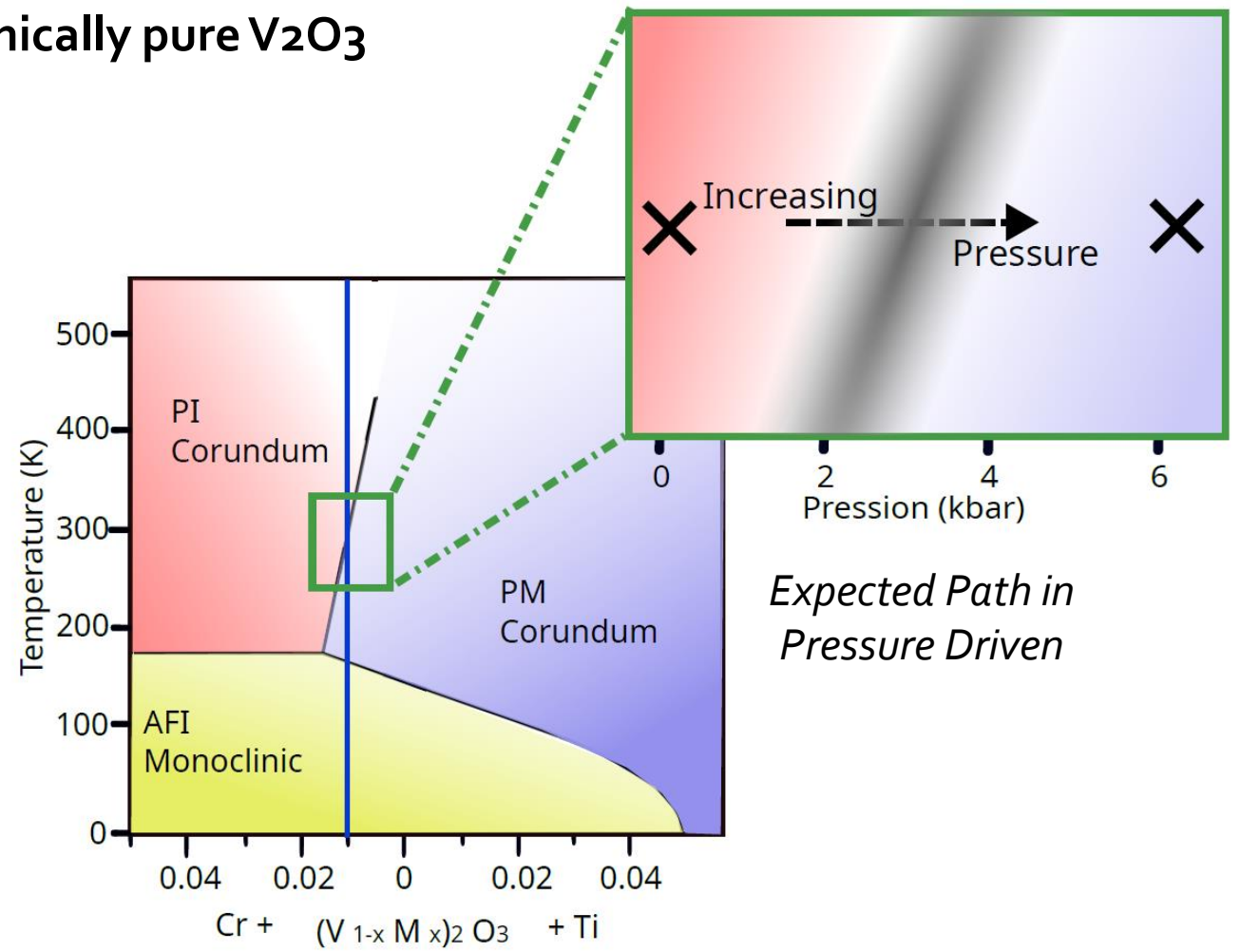
Evolution of the fitted phonon frequency (A_{1g} character)



Resistivity as a function of Temperature

- Double hysteresis feature:
- PI at Room Temperature
 - Expected critical pressure between 2-4 kbars

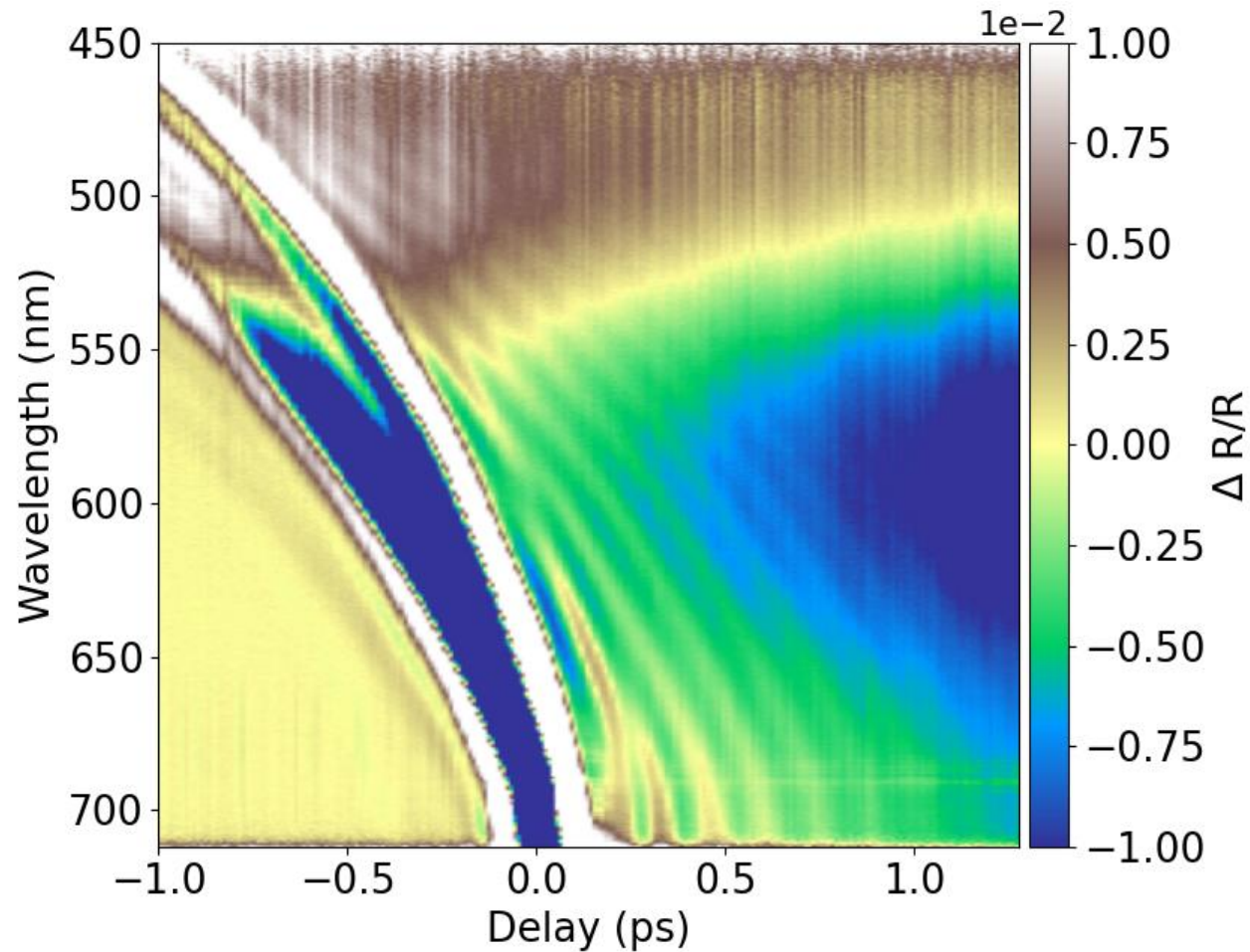
Chemically pure V₂O₃



Residual strain during annealing induces shift in the phase diagram

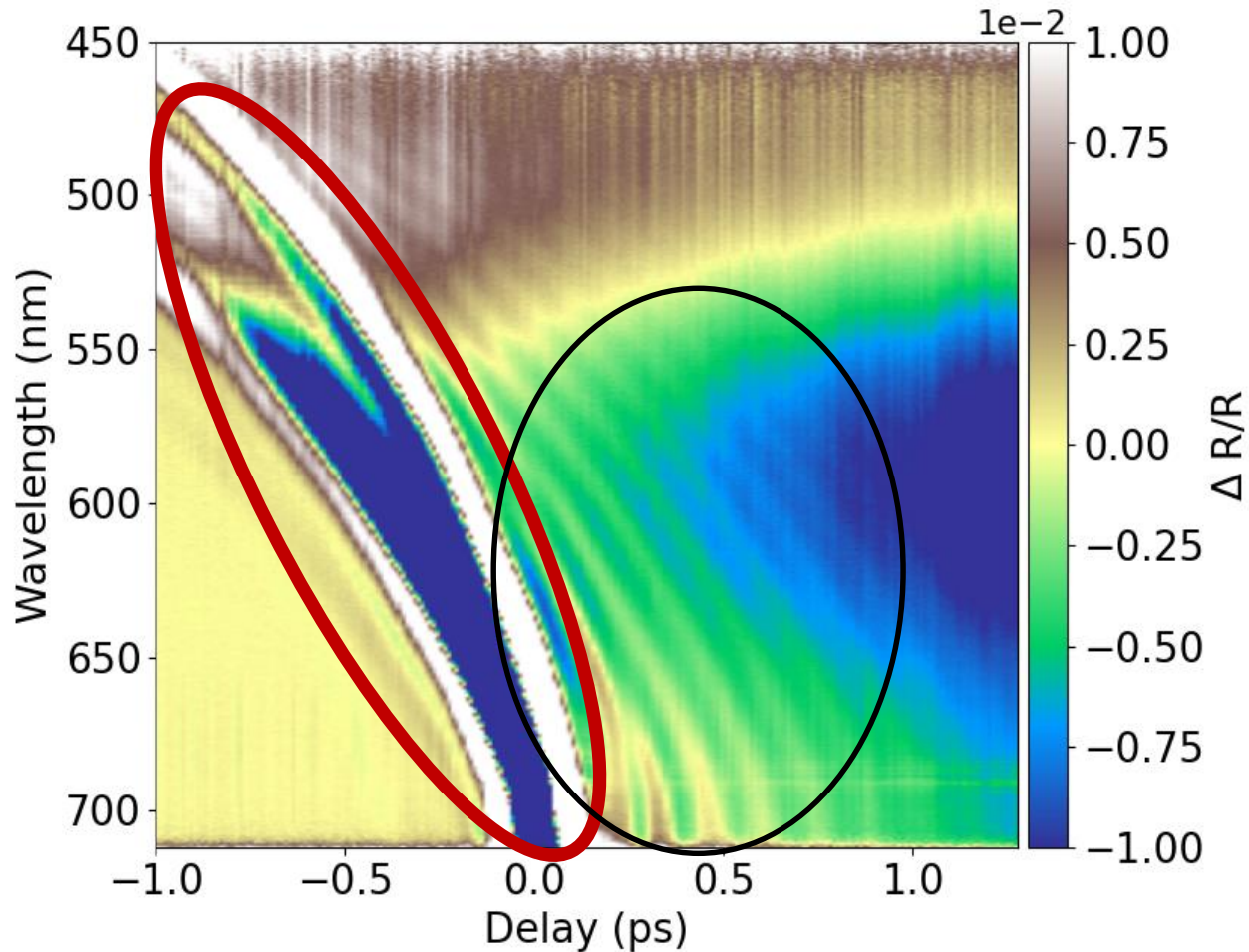
D. B. McWhan et al, *Phys. Rev. B*, 7, 1920-1931 (1973)

Transient changes of reflectivity following 800 nm photo-excitation



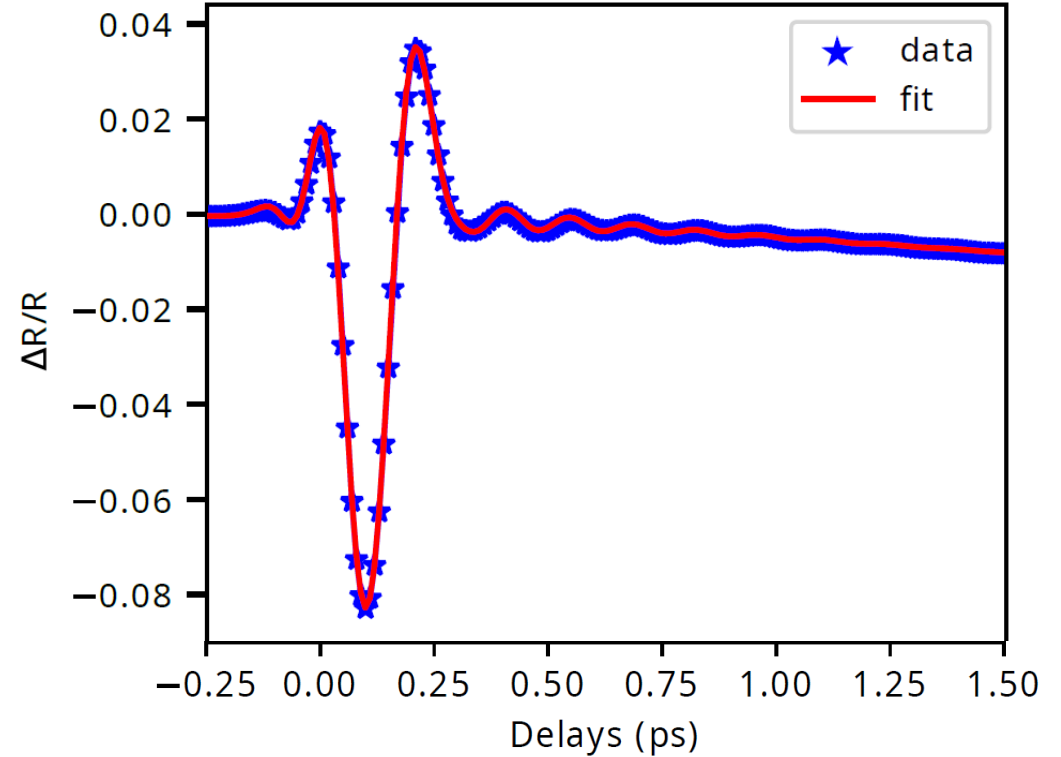
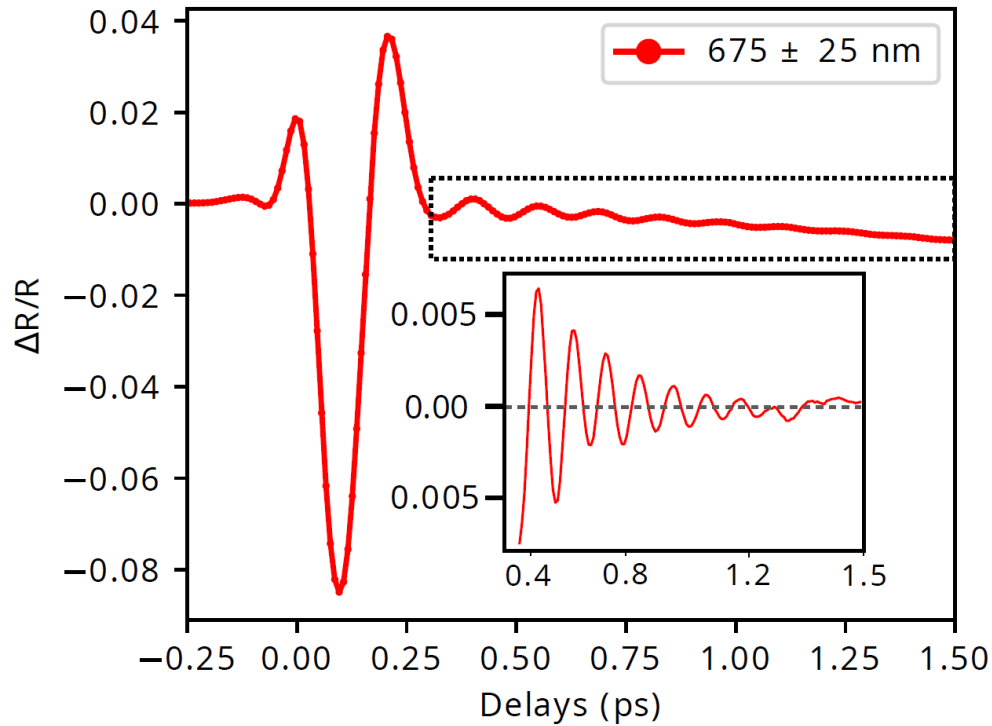
Raw data (no chirp corrected)

Transient changes of reflectivity following 800 nm photo-excitation



Raw data (no chirp corrected)

- First strong contribution from non linear artifacts (XPM contribution)
- Signatures of coherent phonon modulating the full spectrum + slow signal

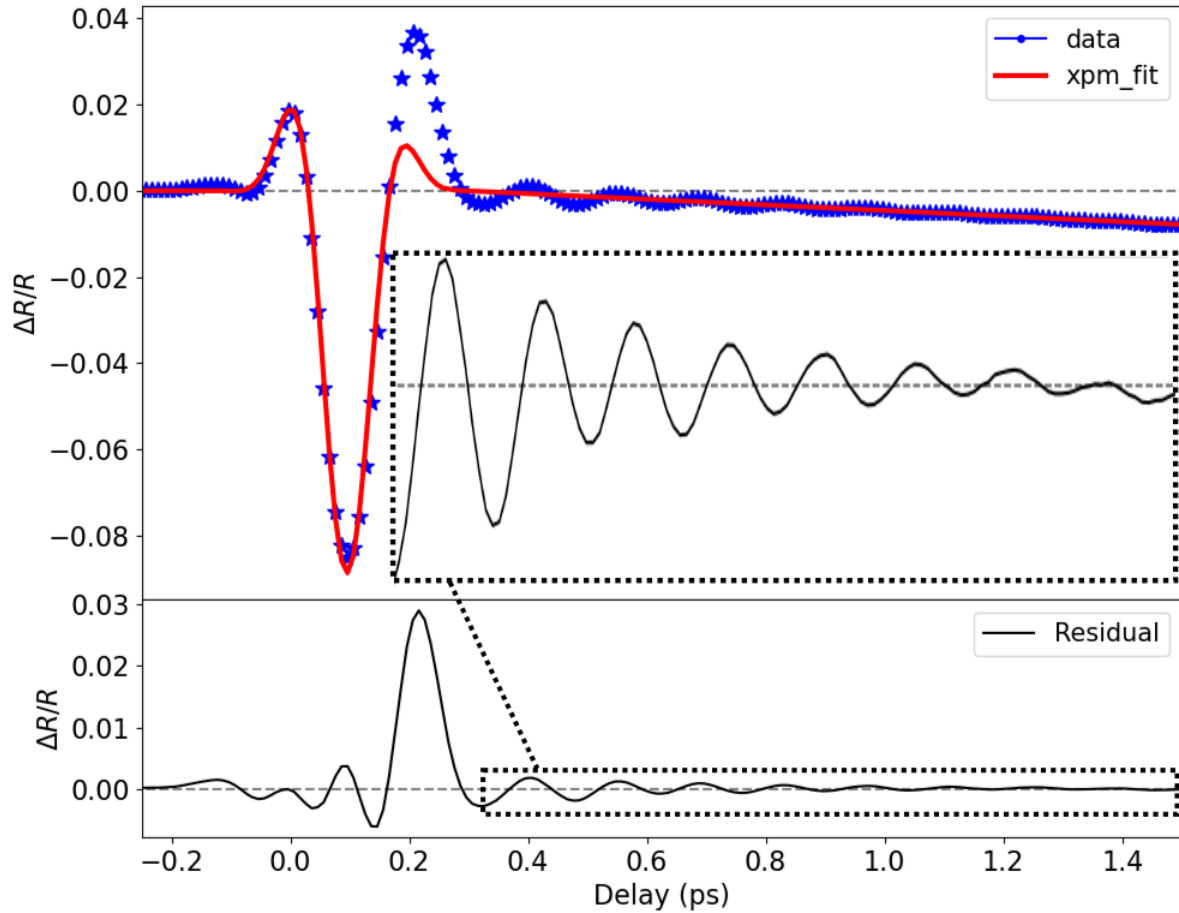


- Optical phonon lasting for 1,5 ps:
Enough to extract frequency and damping

Fitting single wavelength time-trace:

- Non linear optical component (XPM)
- Coherent phonon (Frequency + Damping)
- Affine function (thermo-elastic response)

675 nm probe



Top) Fitting of the raw data with XPM response

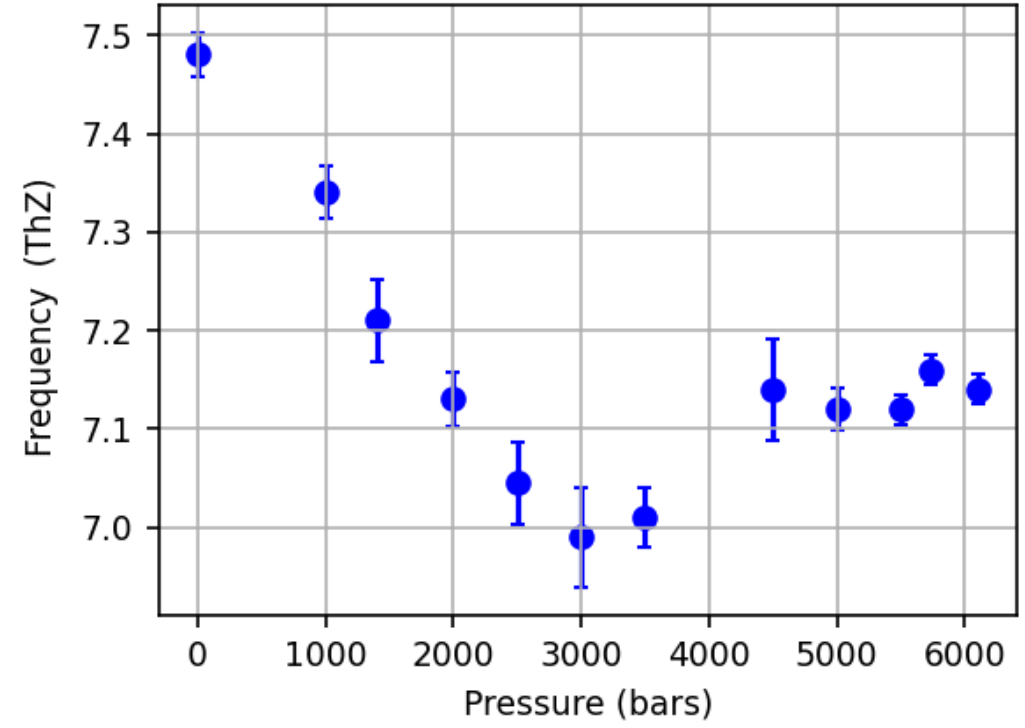
Bottom) Residual

Fitting the XPM signal with empiric function (1st derivate of Gaussian)

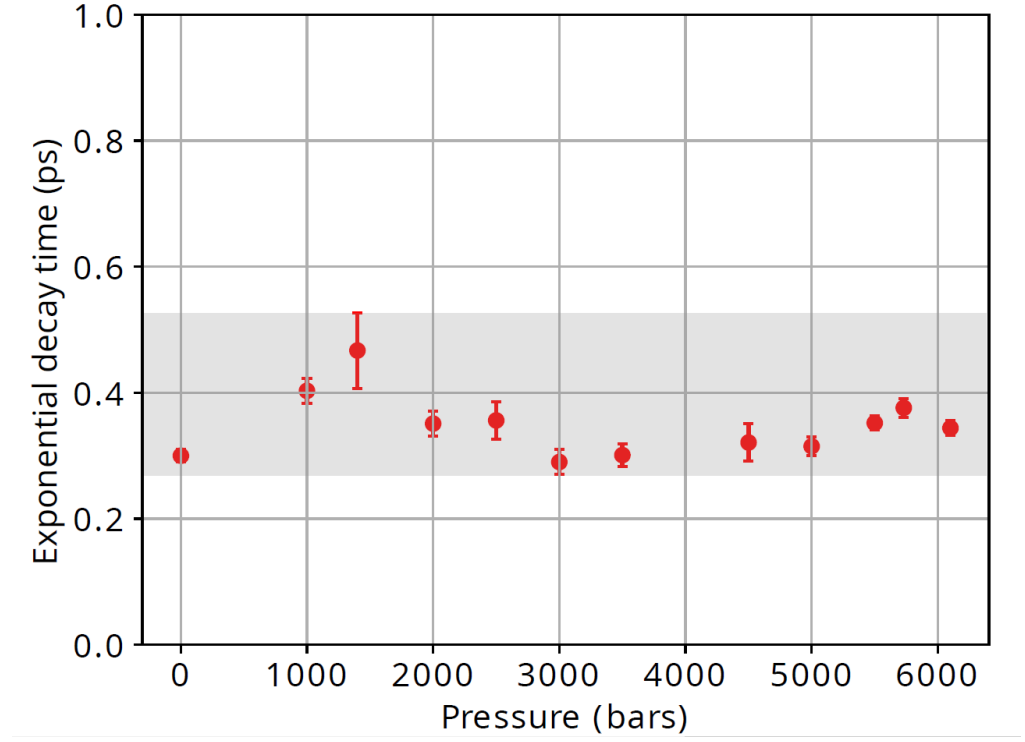
- Provide better view on the “coherent” response
- **Strong entanglement with a plausible electronic response at early time**



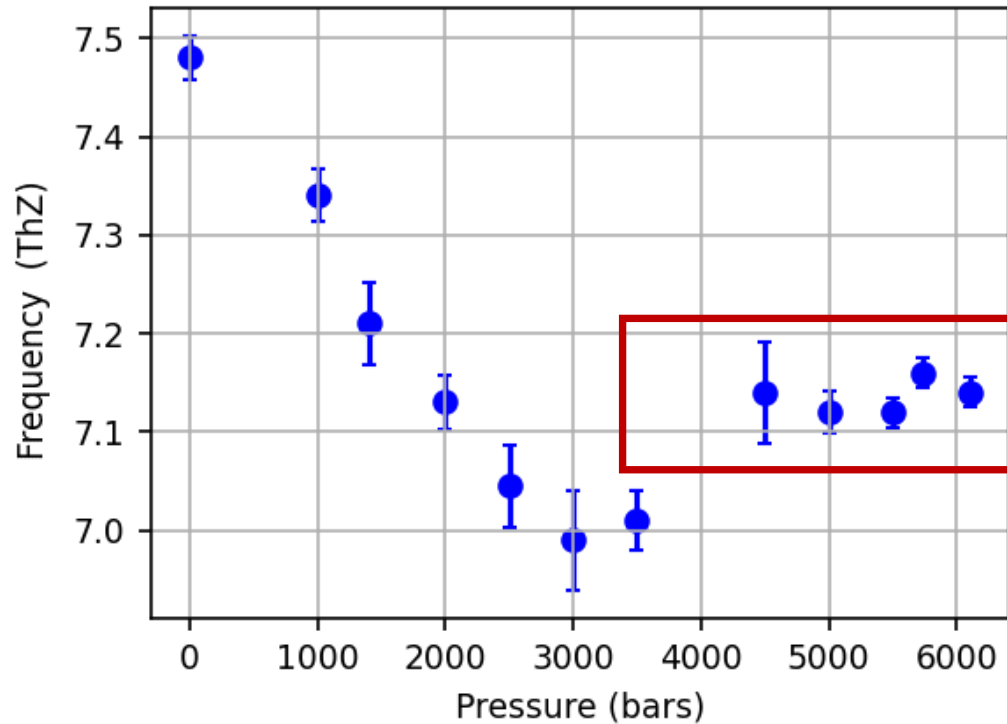
Electronic response cannot be investigate but phonon frequency and damping are extracted with confidence



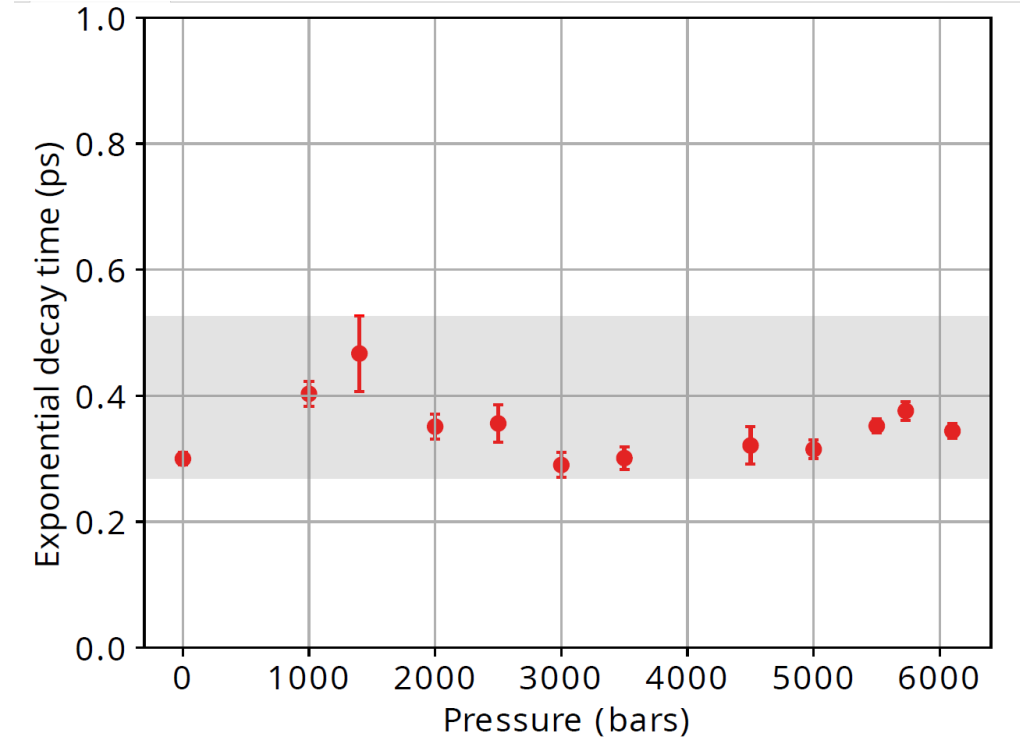
Phonon frequency as a function of pressure



Damping time as a function of pressure

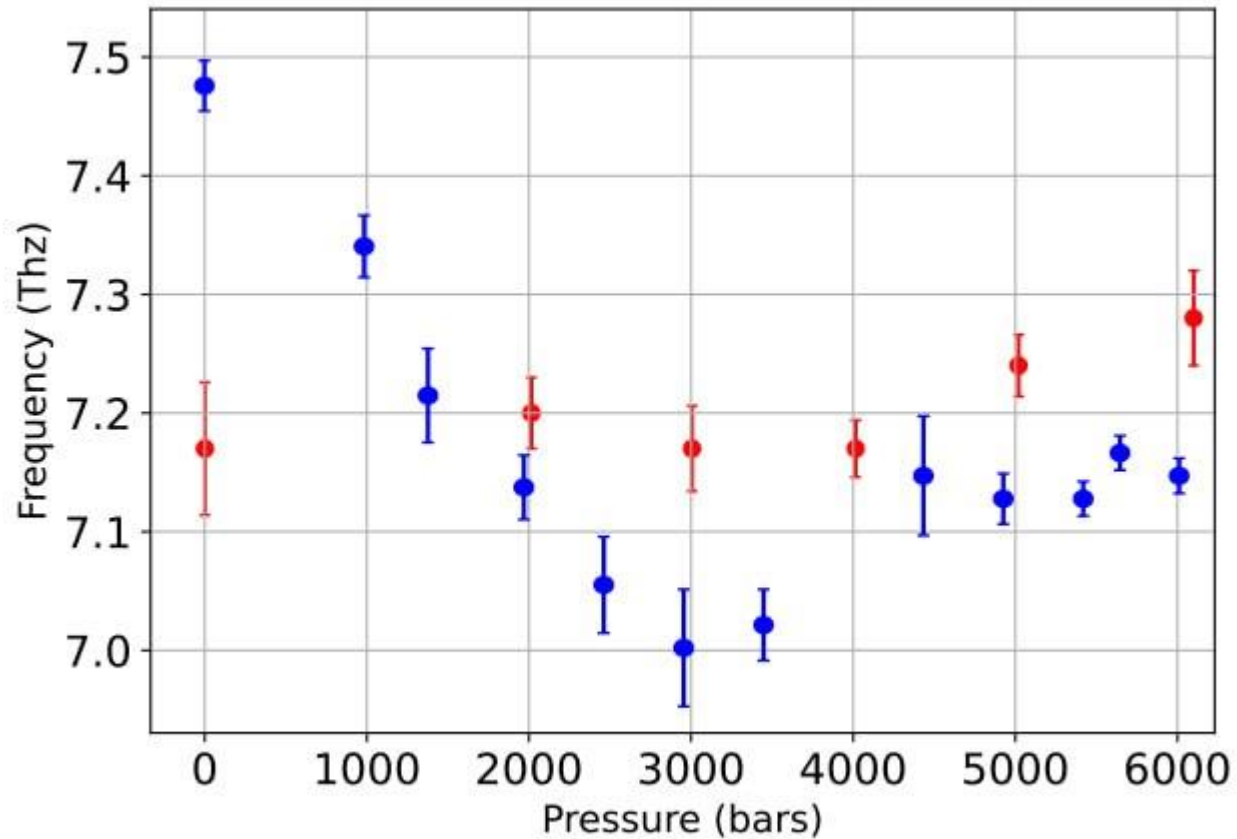


Phonon frequency as a function of pressure



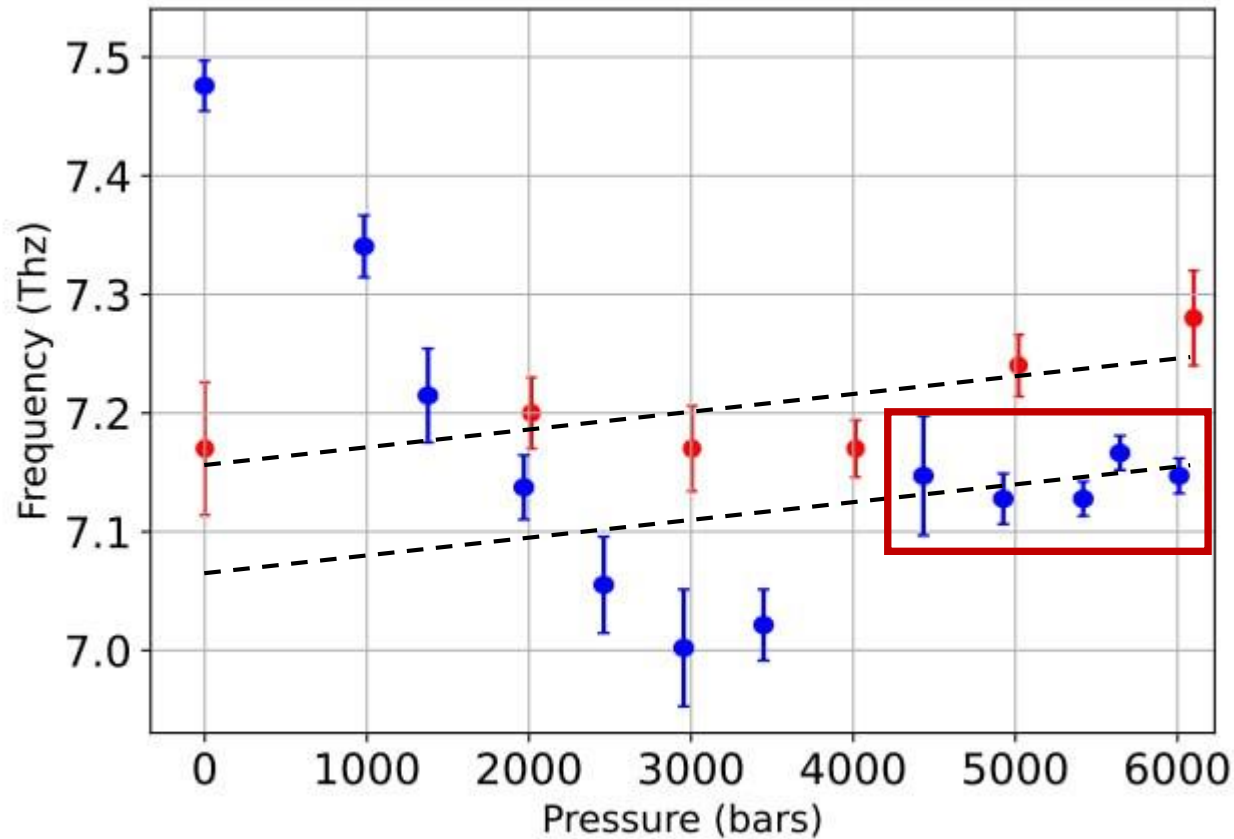
Damping time as a function of pressure

- Influence of hydrostatic on the phonon frequency (softening of 0.5 THz)
Plateau above 4500 bars: plausible PM phase?
- No obvious correlation between pressure and damping time

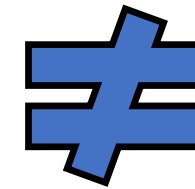


Unstrained V₂O₃ (PM at 1 bar)

Strained V₂O₃ (PI at 1 bar)



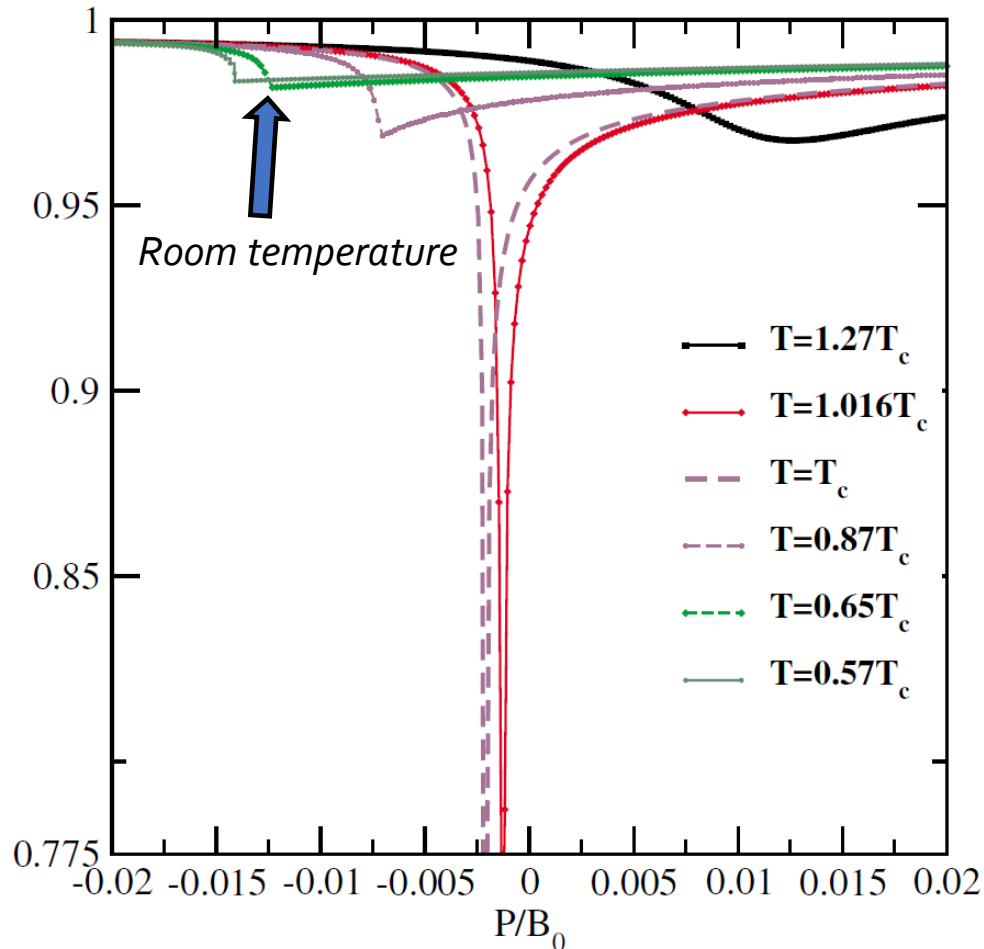
Unstrained V₂O₃



Strained V₂O₃

Same behavior for the plausible PM phase (dashed line) compared to unstrained

- Linear hardening with pressure (expected in simple material)



Simulation of sound velocity as a function of pressure in V_2O_3

S. R. Hassan et al, *Phys. Rev. Lett.*, 94, 036402 (2005)

One model: Compressible Hubbard model

- Consider both lattice and electronic contributions in the free energy calculation

$$F = F_0 - P_0(v - v_0) + \frac{1}{2}B_0 \frac{(v - v_0)^2}{v_0} + F_{el}[D(v)].$$

- B_0 = elastic bulk modulus
- F_{el} = electronic free energy (single band half filled)

One model: Compressible Hubbard model

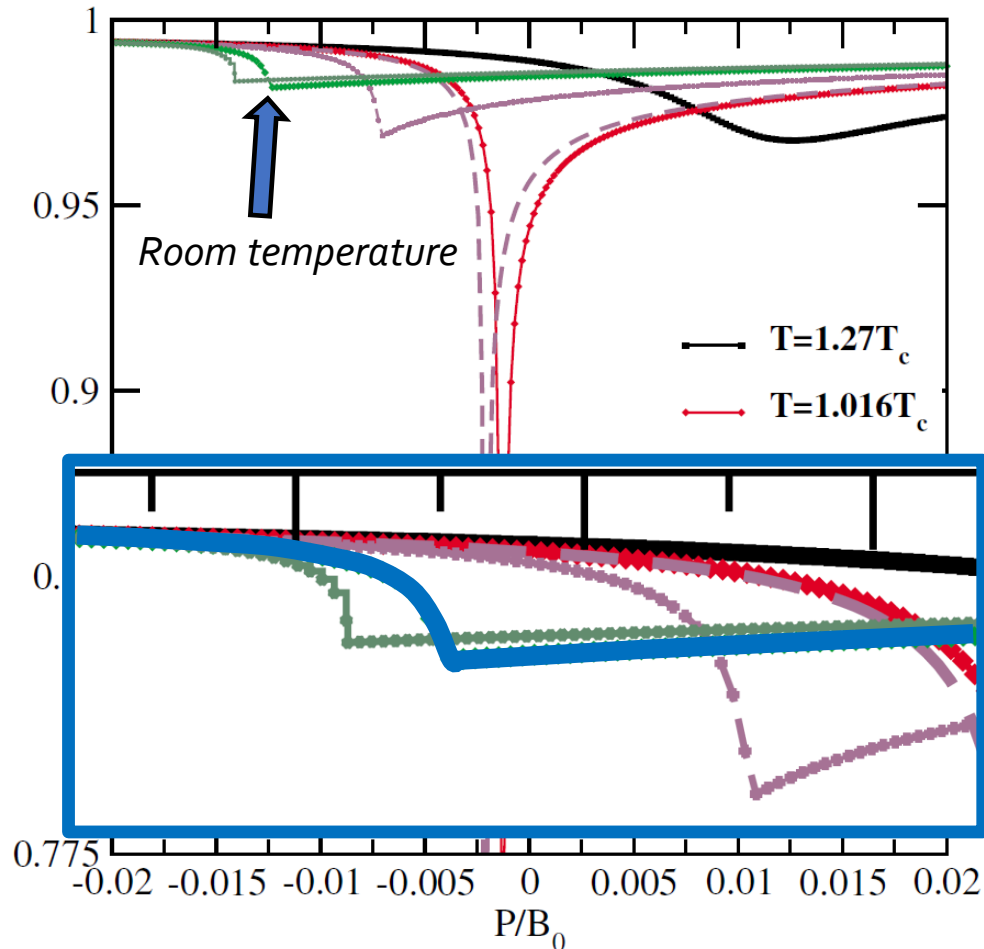
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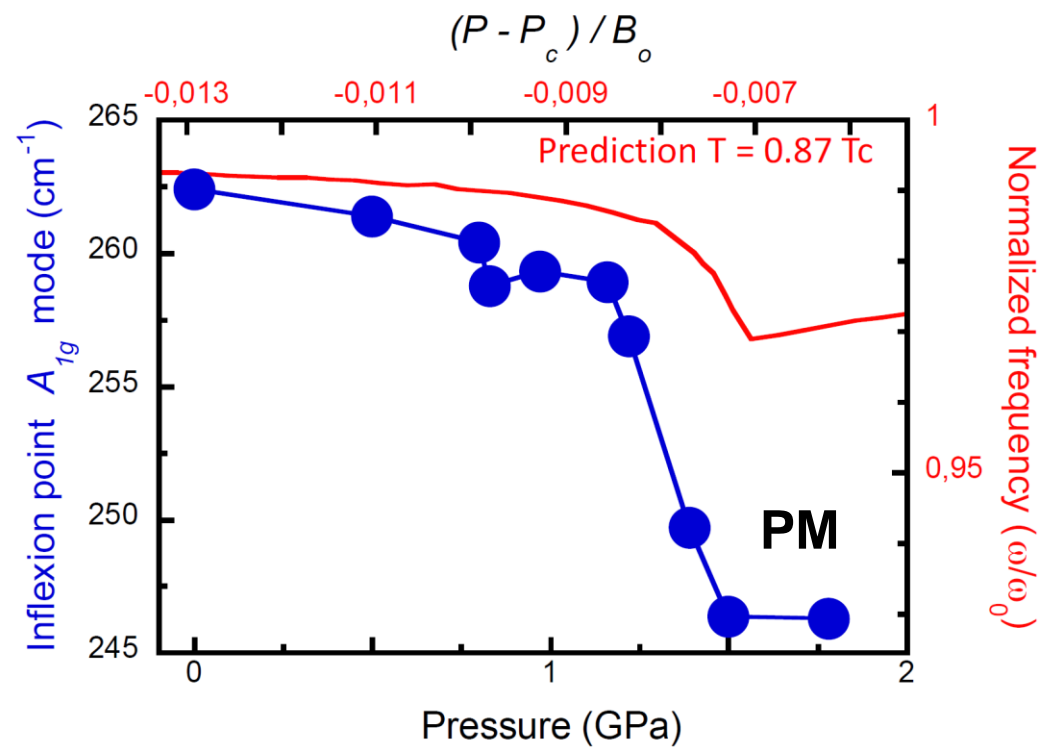
- B_0 = elastic bulk modulus
- F_{el} = electronic free energy (single band half filled)

Predict sound velocity anomaly \rightarrow softening of acoustic phonons

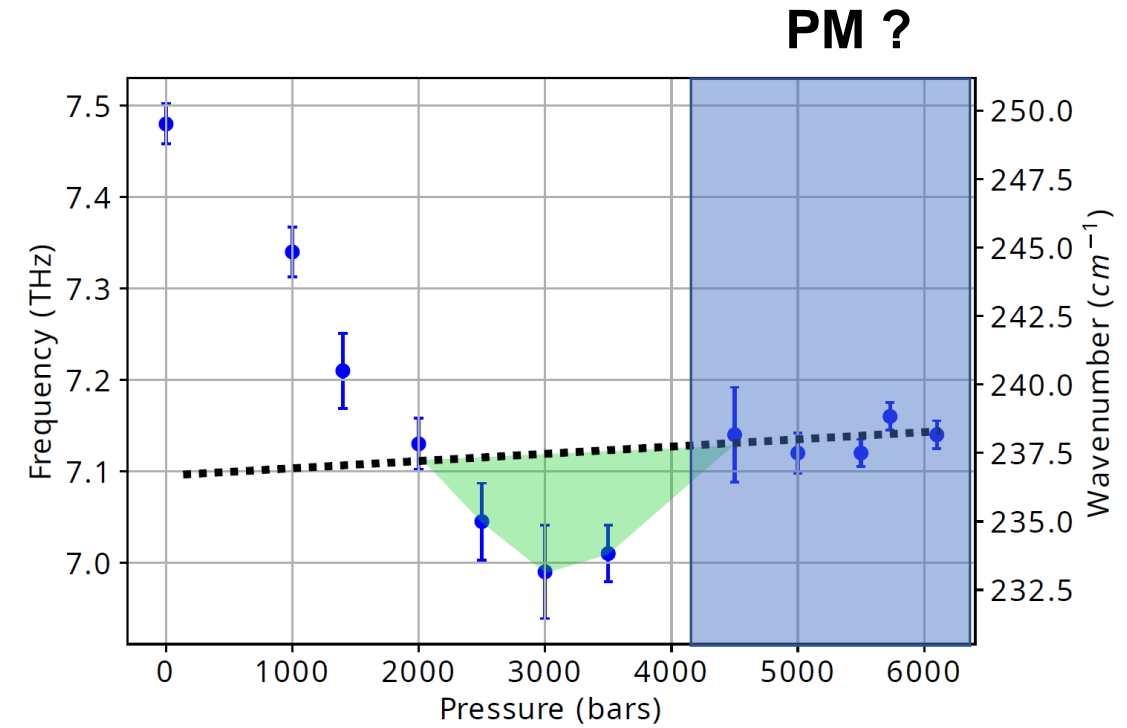
“Close to the Mott transition, lattice degrees of freedom react to the softening of electron degrees of freedom. This results in a change of lattice spacing, a diverging compressibility, and a critical anomaly of the sound velocity.”



Simulation of sound velocity as a function of pressure in V_2O_3

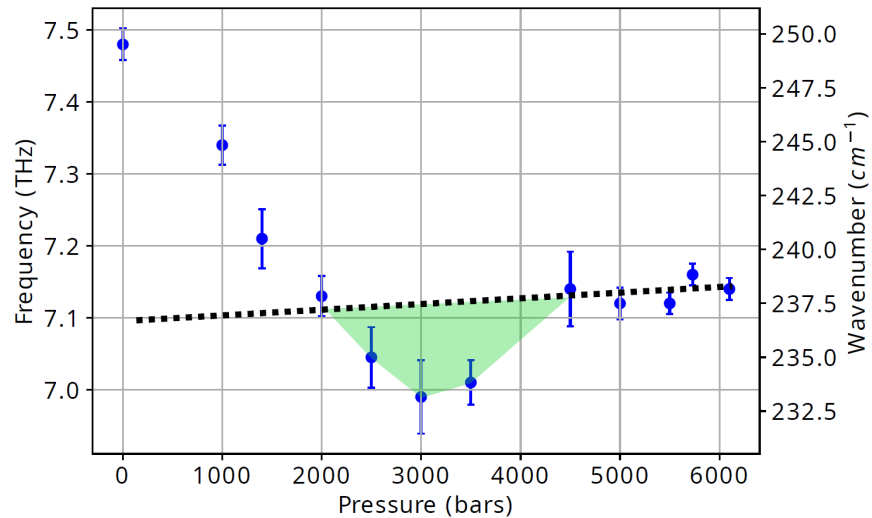
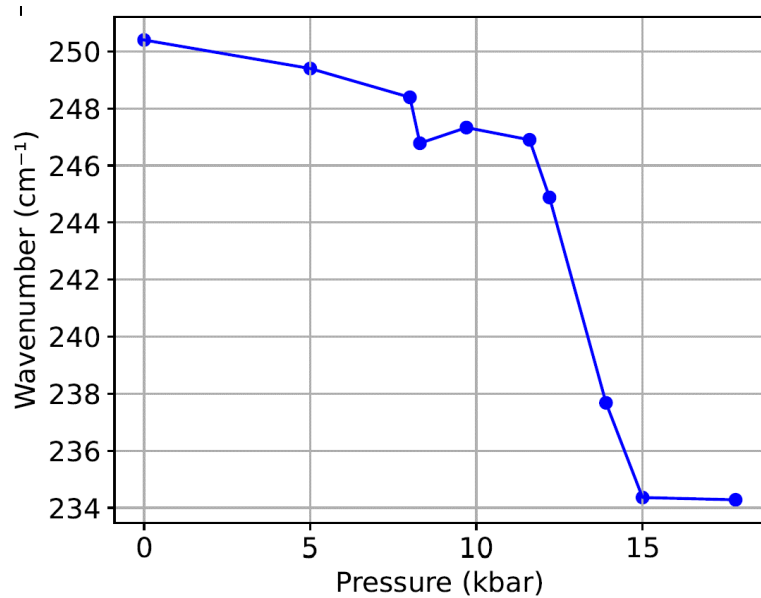


Raman spectroscopy on $(V_xCr_{1-x})_2O_3$ single crystal



Coherent phonon spectroscopy

- Similarity in behavior between the predicted softening (elastic modulus) and measured Raman mode frequency
- Softening of the coherent phonon beyond an extrapolation of PM phase (green area)
 - → Emergence of strong electron-lattice coupling probed in out-of-equilibrium case



- Agreement between static Raman (incoherent) and « coherent » phonon spectroscopy
- Strong indication of pressure induced Mott transition
- Strong electron phonon interactions observed in strongly out of equilibrium case
- Going beyond the Mott Hubbard model (key contribution of lattice)
- Lattice degrees of freedom must be consider near transition lines



This study is not aiming to look for PIPT!
Relevant spectral range is near IR

Accepted in *Physical Review Research*



Materials & Light team

Nicolas Godin

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Physics of Materials & Nanostructures

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Benoit Corraze

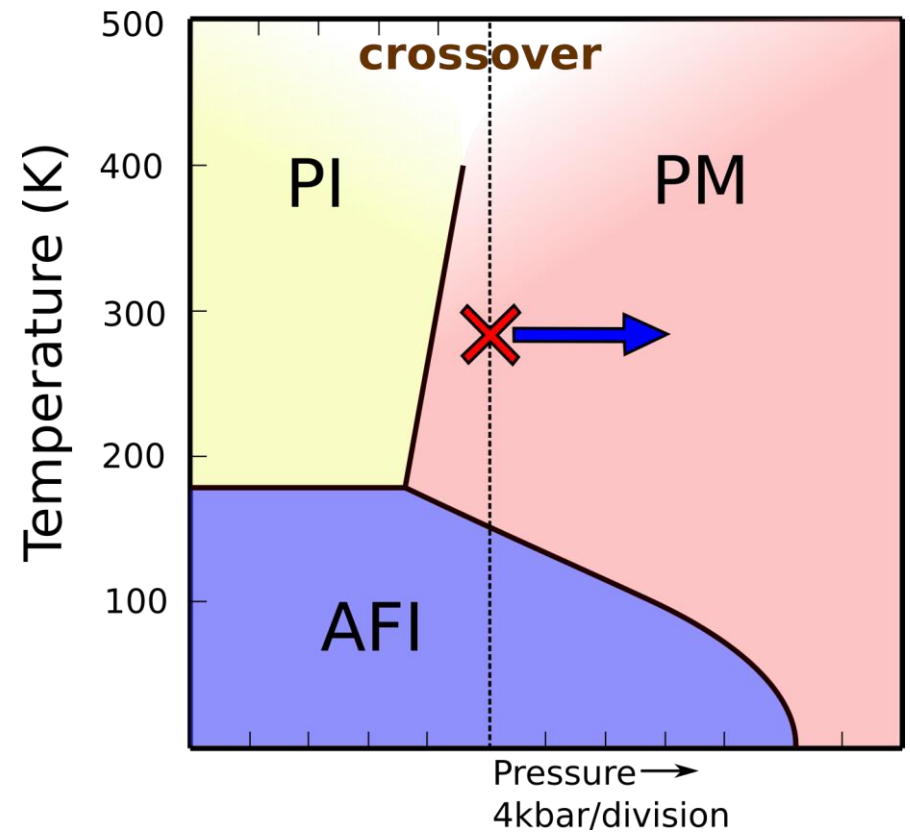
Laurent Cario

Julien Tranchant

Danylo Babich

Thanks for your attention

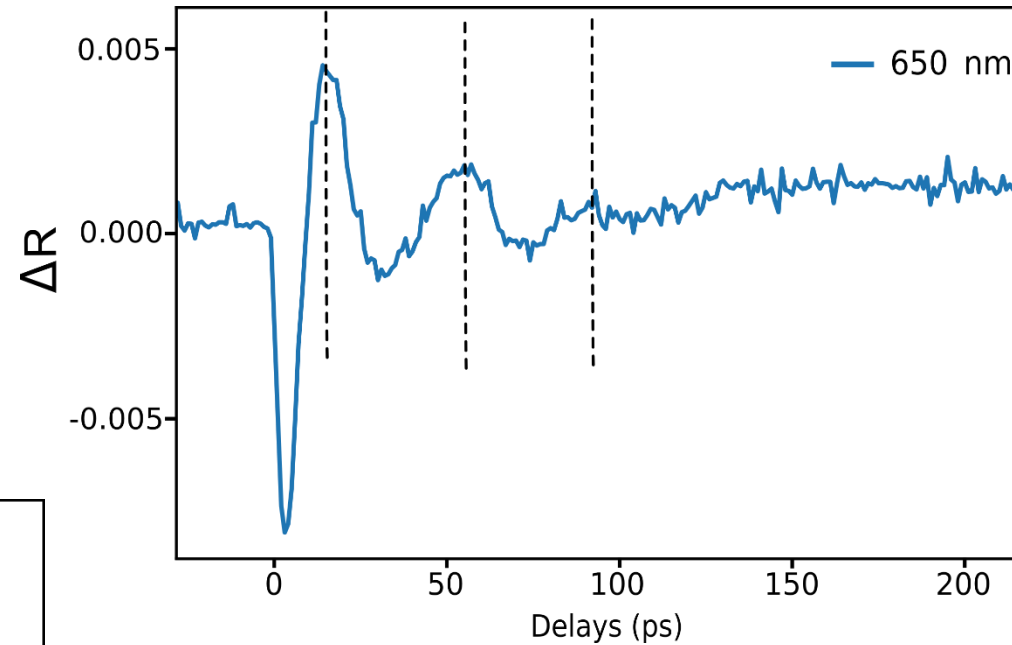
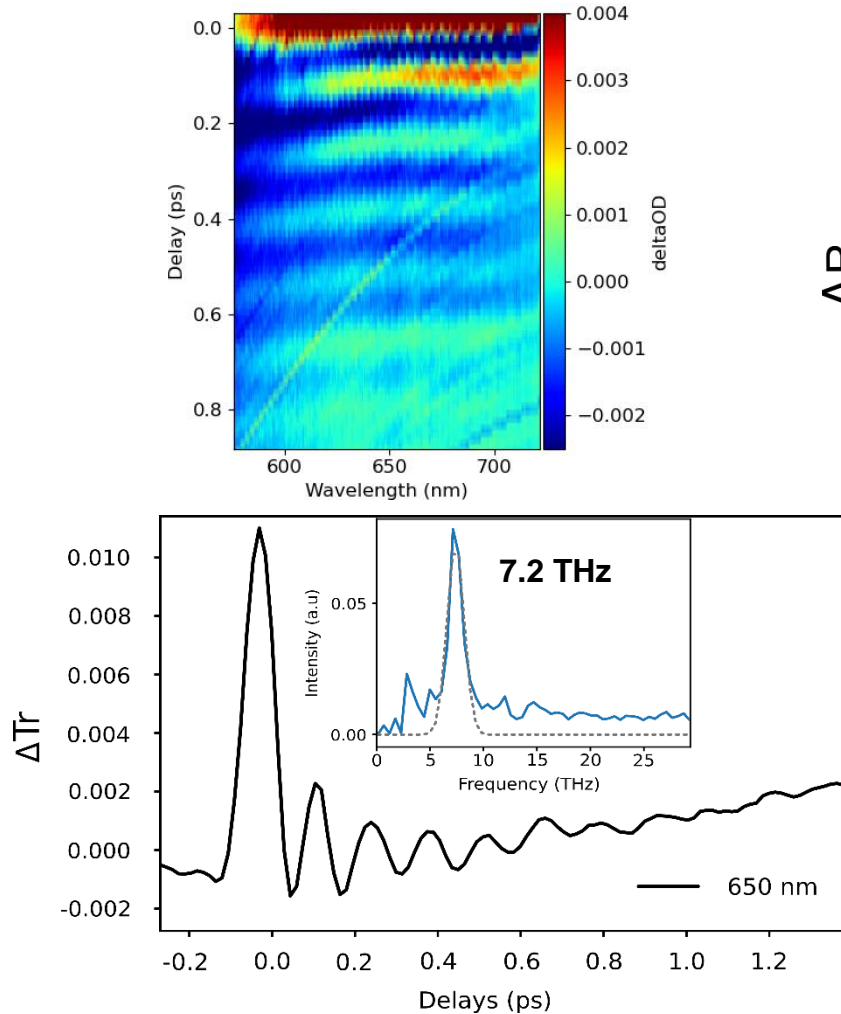
V_2O_3 → Benchmark of Mott physics



- Pure V_2O_3 without chemical substitution is a Paramagnetic "bad" Metal (PM) under standard thermodynamical conditions
- No expected phase transition under hydrostatic pressure
- Thin film of ~ 200 nm thickness

Inorganic materials → needs of several GPa (ten's of kbars)

D. B. McWhan et al, *Phys. Rev. B*, 7, 1920-1931 (1973)

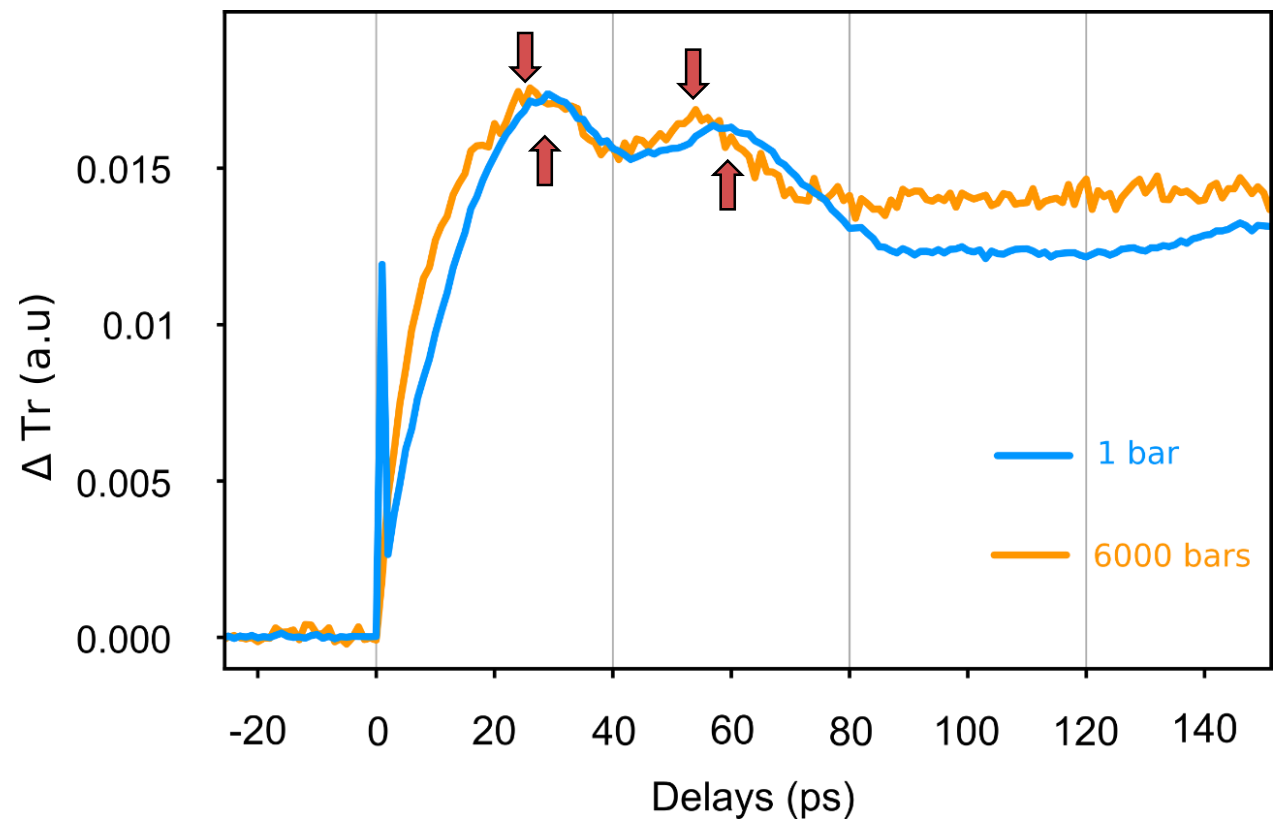


Oscillation phenomena linked to strain modulation (thermo-elastic).
 Related to film breathing?

Observation of coherent optical phonons:
 A_{1g} mode, agreement with literature

A. Levchuk et al., *Phys. Rev. B* 101, 180102 (2020)

B. Mansart et al, *EPL*, 92(3), 37007 (2010)



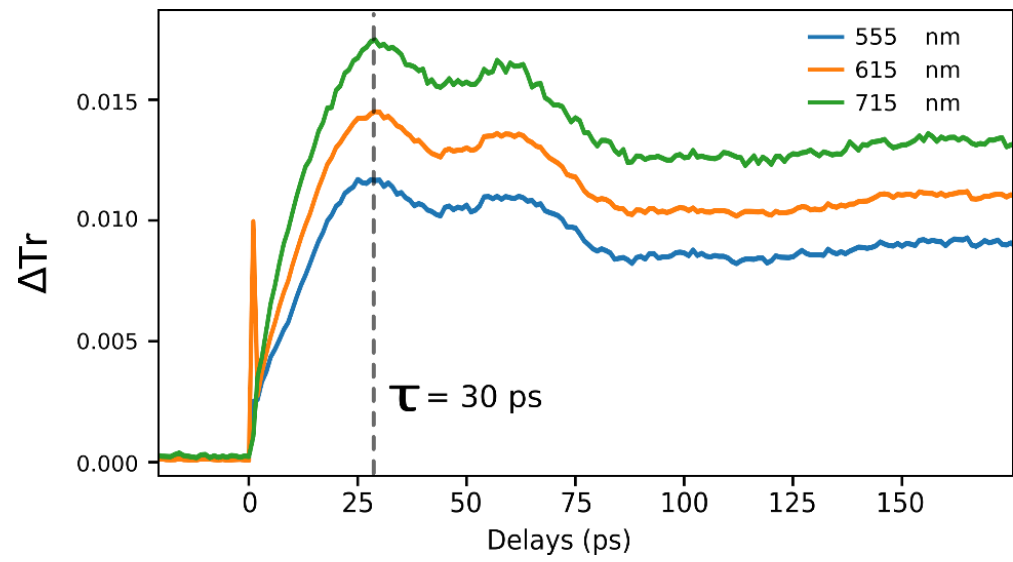
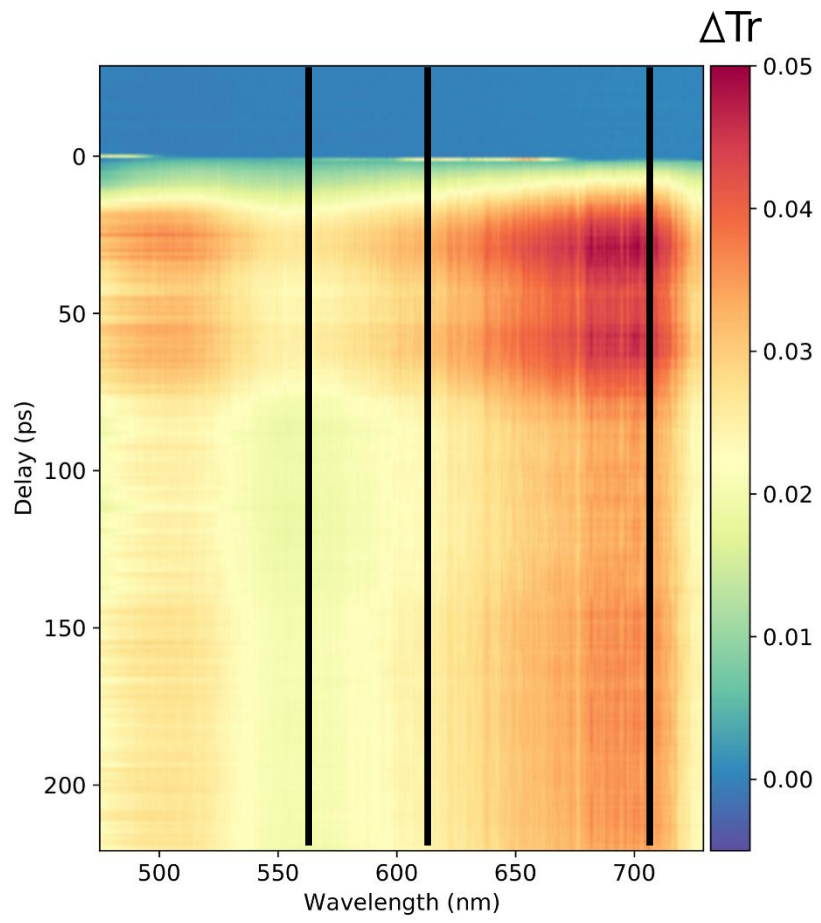
Normalized Transient Transmission at 650 nm

Shift of the rising time and oscillations (arrows) related to strain propagation effect:

Impact on speed of sound

Transmission

Pump 800 nm

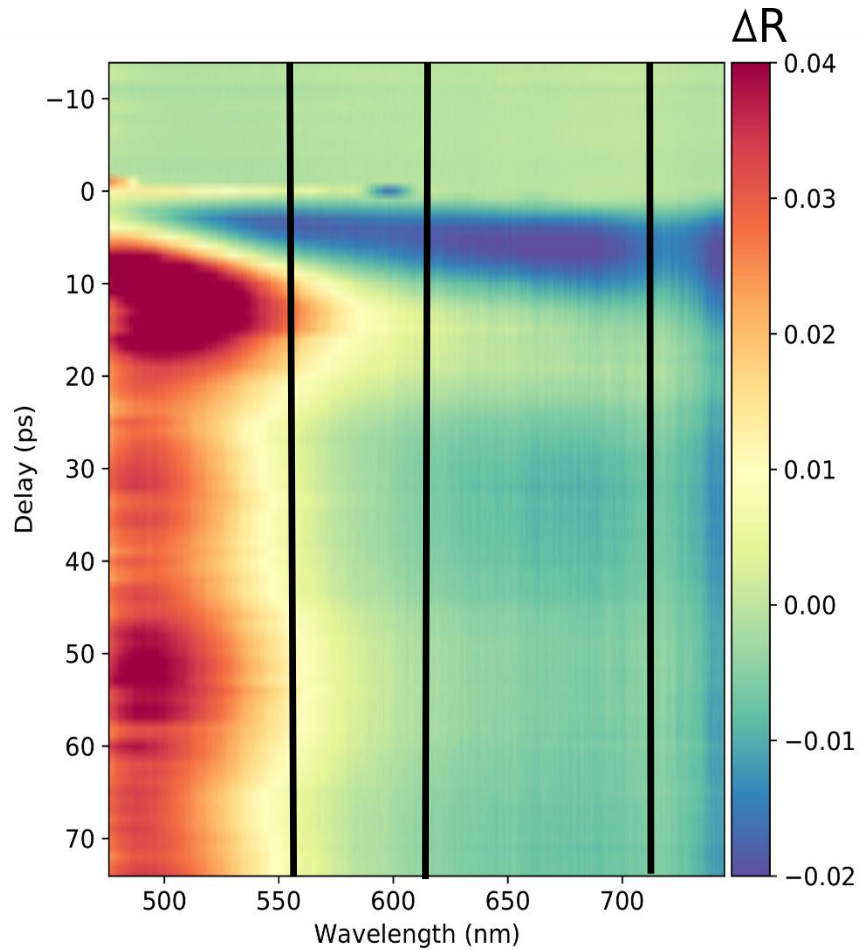


- Rising time ~ 30 ps
- Plateau at 100 ps and lasting ns

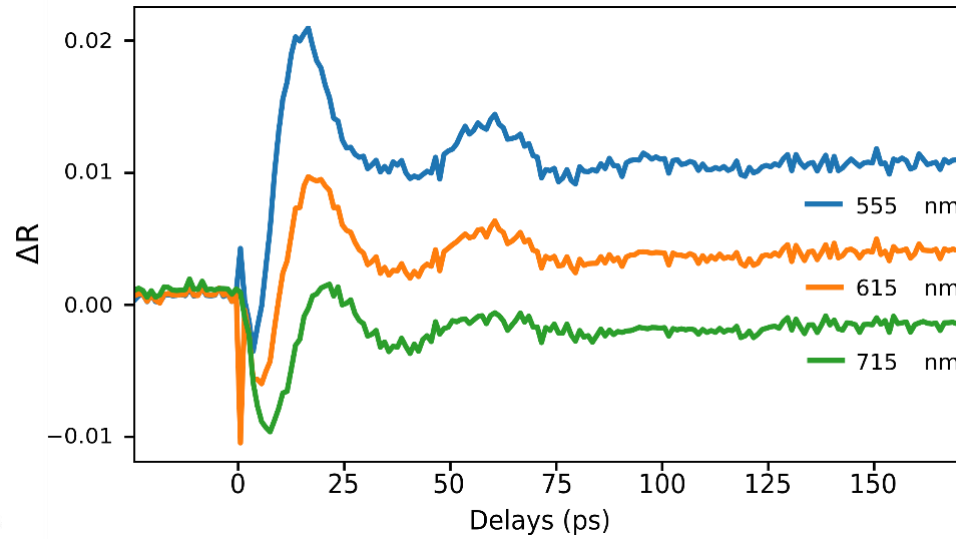
G. Huitric et al, *Faraday Discussion* (2022)

G. Privault et al, *submitted*

Reflectivity

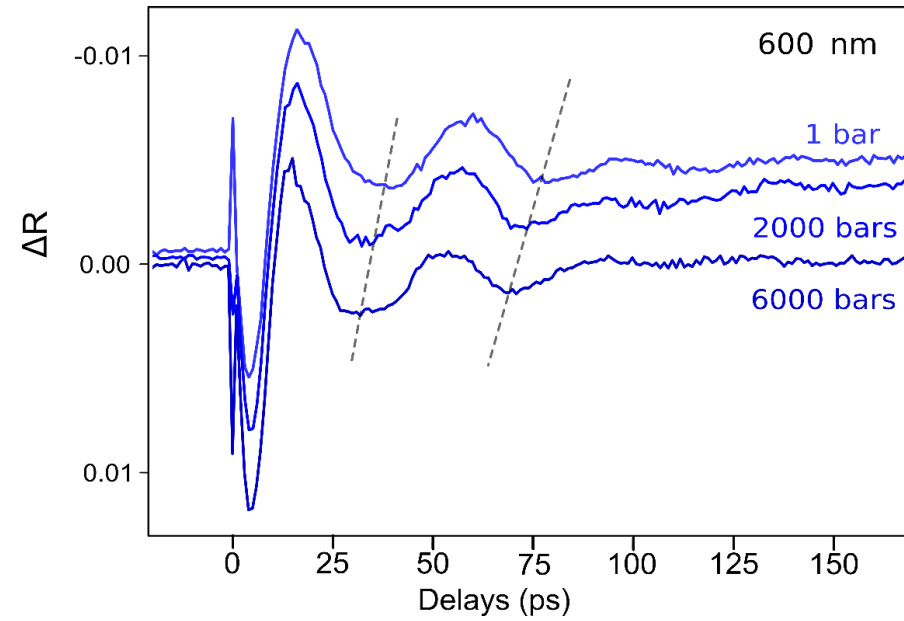
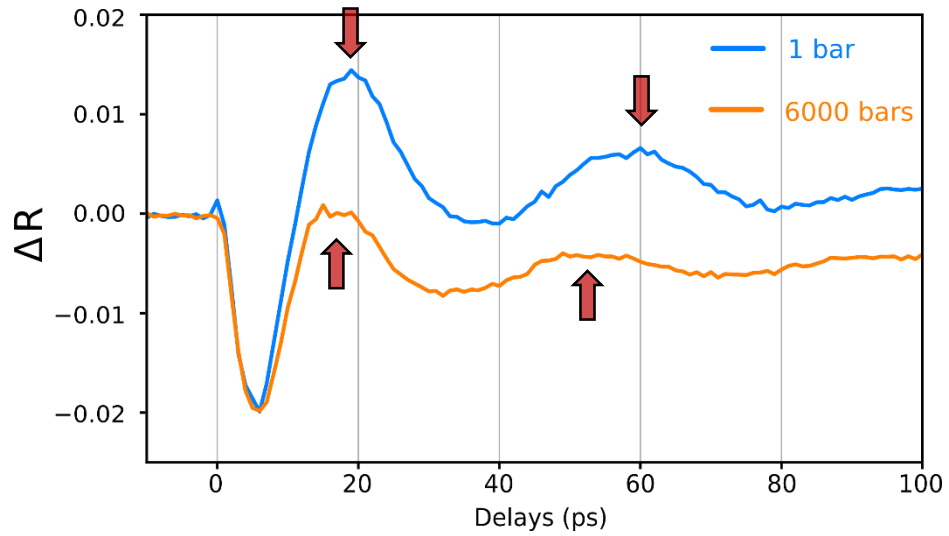


Pump 800 nm



- Oscillating/ Interference behavior
- Plateau at 100 ps and lasting up to ns

Acoustic properties

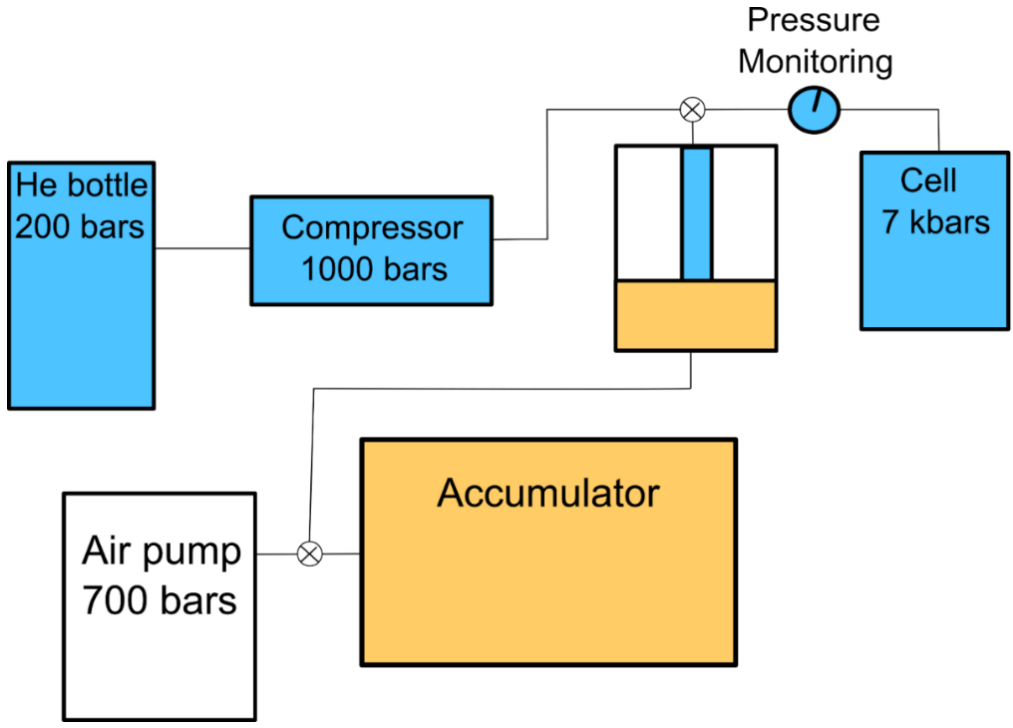


Blue shift of the “Brillouin” frequency under pressure

 Increase of speed of sound / stiffening

**Even in inorganic V_2O_3 , pressure below GPa acts on acoustic properties:
 may impact photo-induced strain effects**

Already used in pump-probe experiments with diamond anvil cell (lesser control)



Multi-stages He gas based cell



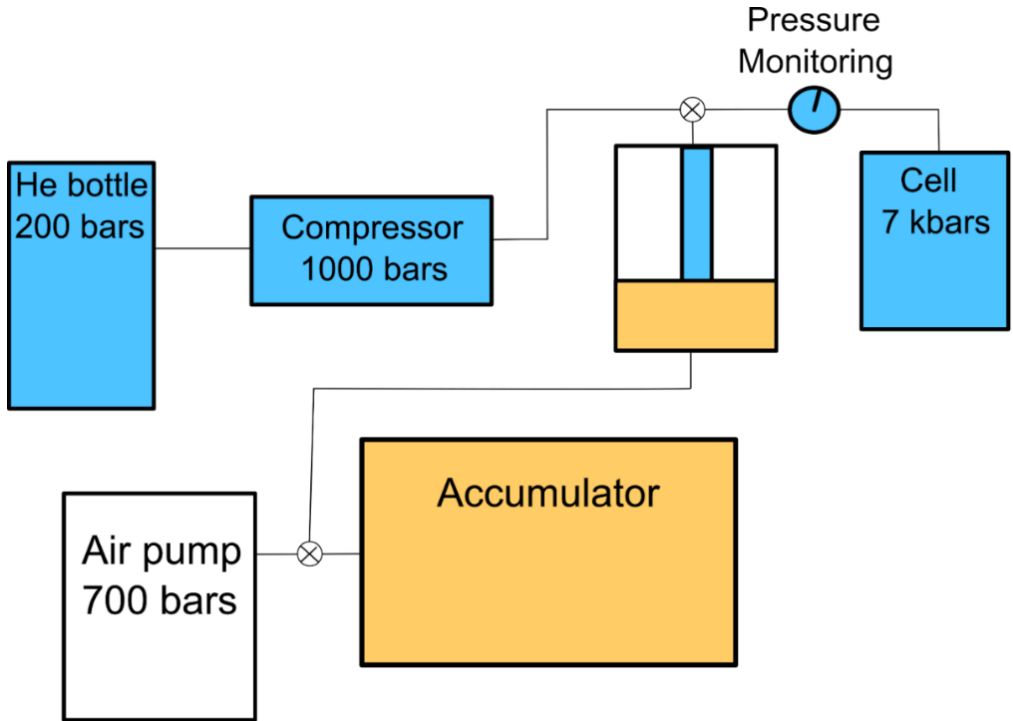
0-7 kbars (0-0.7 Gpa)
10-300 K
250-5000 nm

Specifications:

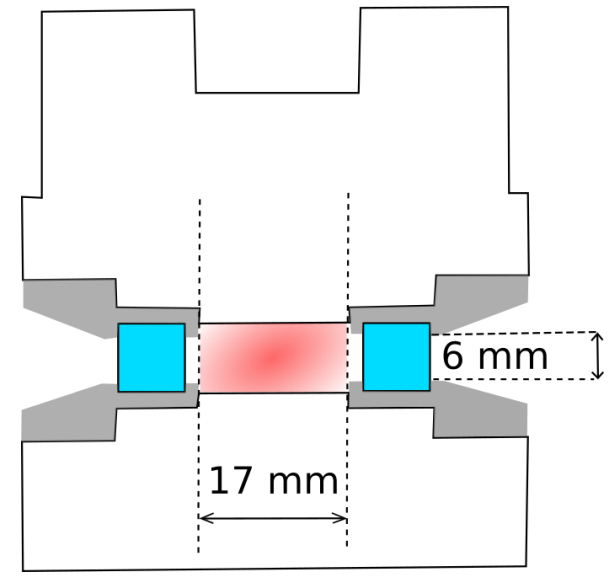
- Precision of few bars (measure in operando)
- Ramping up/down of few bars per minutes
- Sapphire windows allowing optical Transmission/Reflection

G. Privault et al., *T.E.P.J.S.T* 232 (13), 2195 (2023)

Already used in pump-probe experiments with diamond anvil cell (lesser control)



Multi-stages He gas based cell



0-7 kbars (0-0.7 Gpa)

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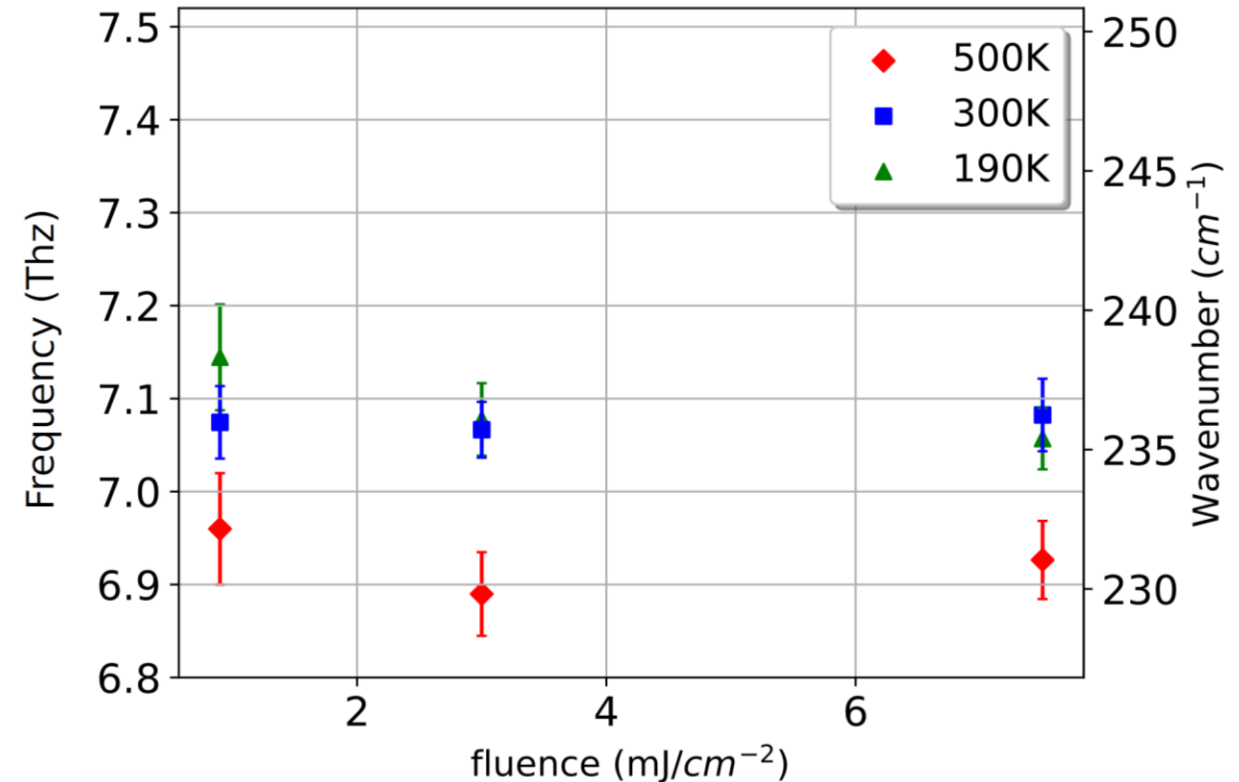
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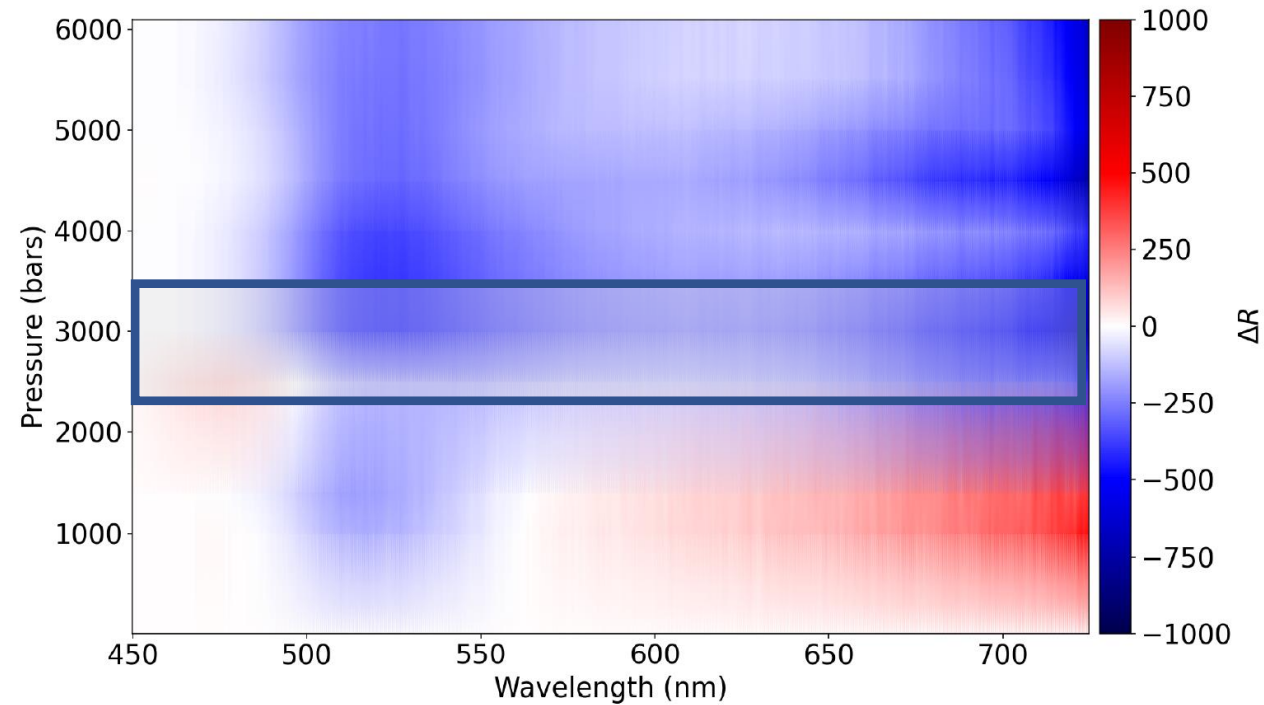
Tuning the temperature to explore the phase diagram



*Fitting of the
coherent phonon*



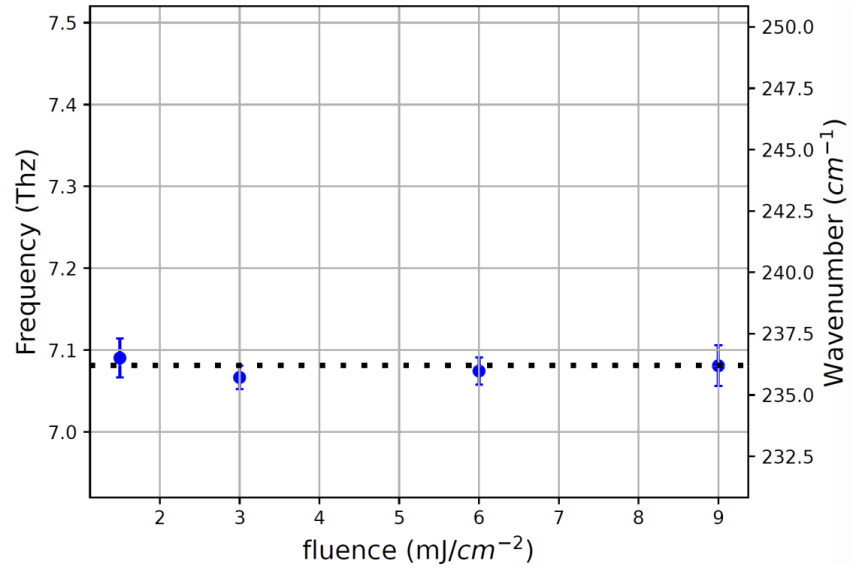
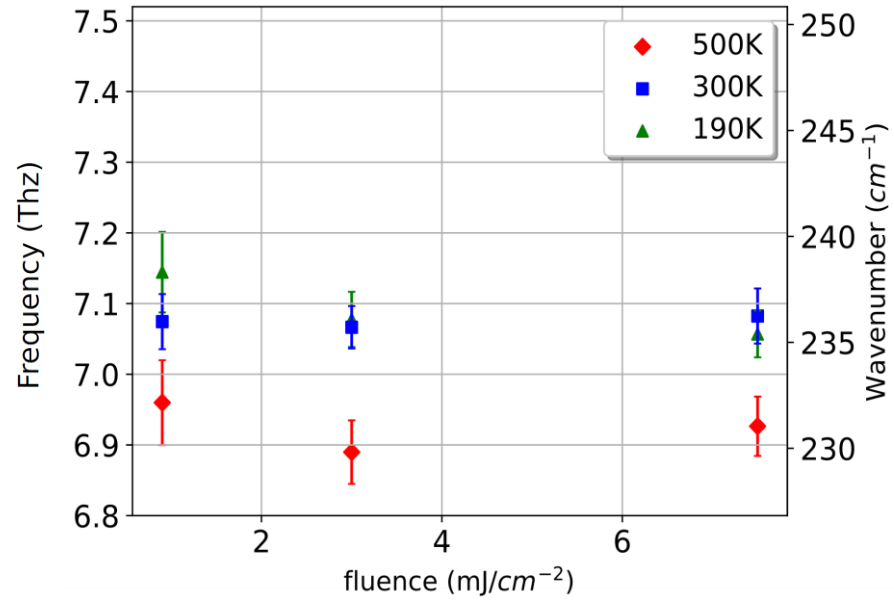
- Lower phonon frequency in the crossover region (6.9 THz).
- Frequency of coherent A_{1g} phonon is not affected by excitation density at Room temperature
- Slight softening near T_c (180K) ?

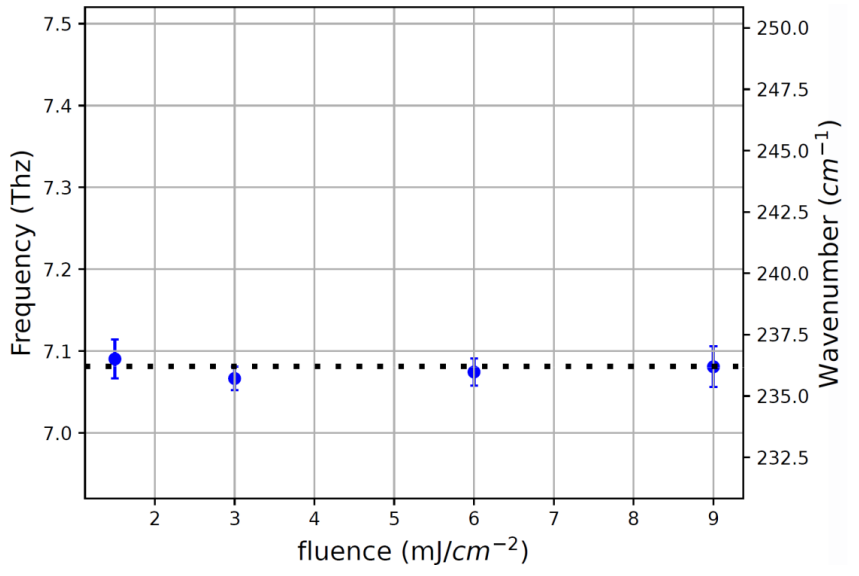
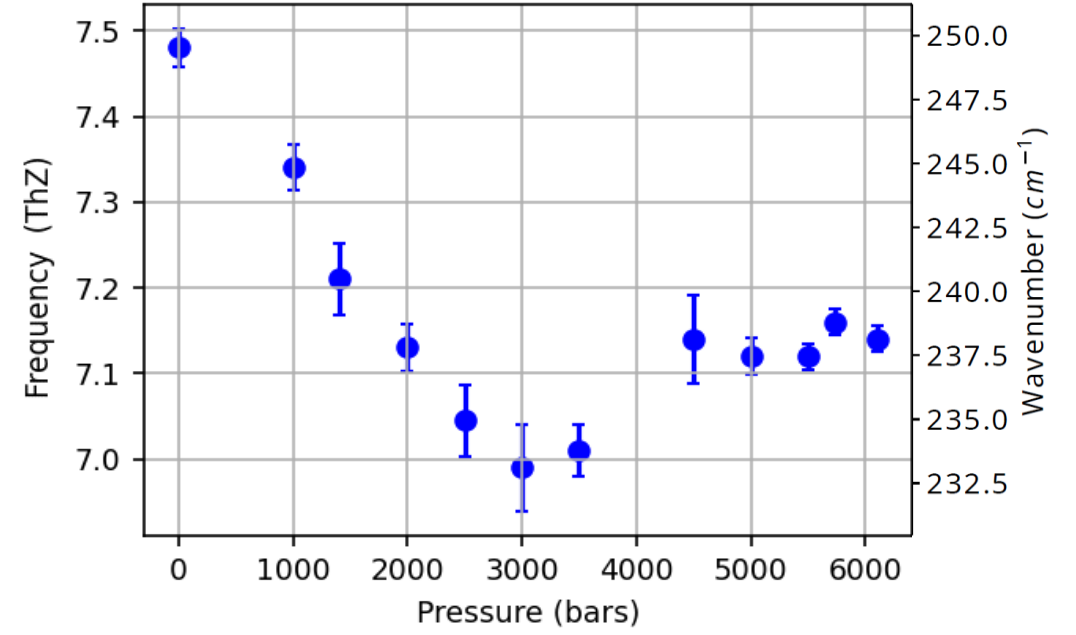
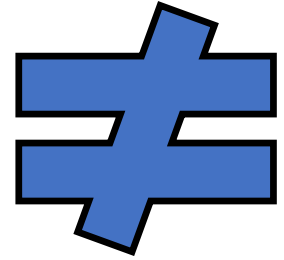
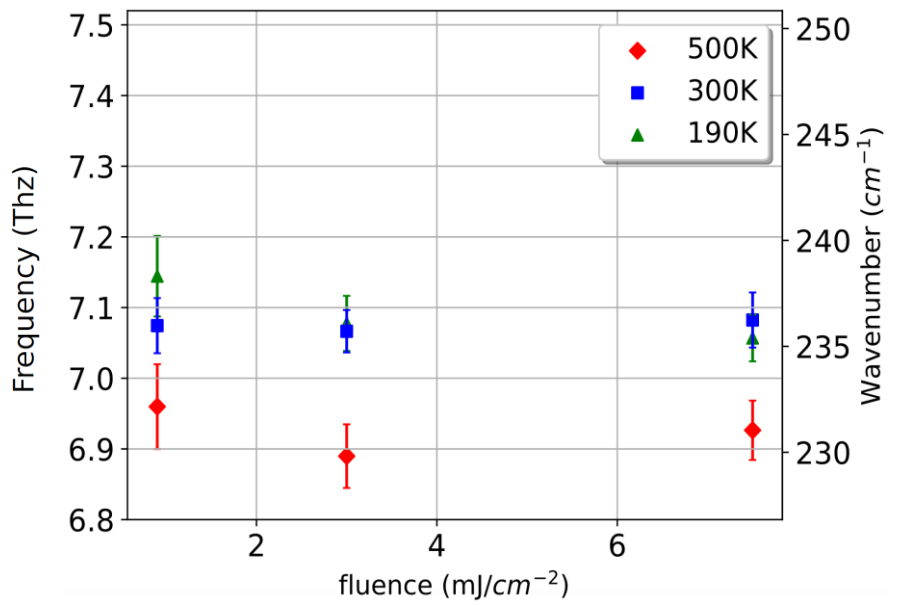


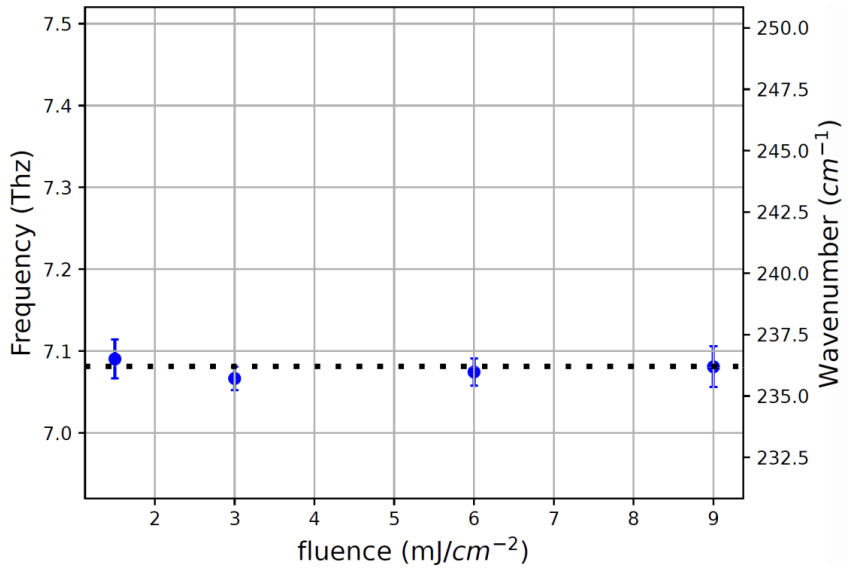
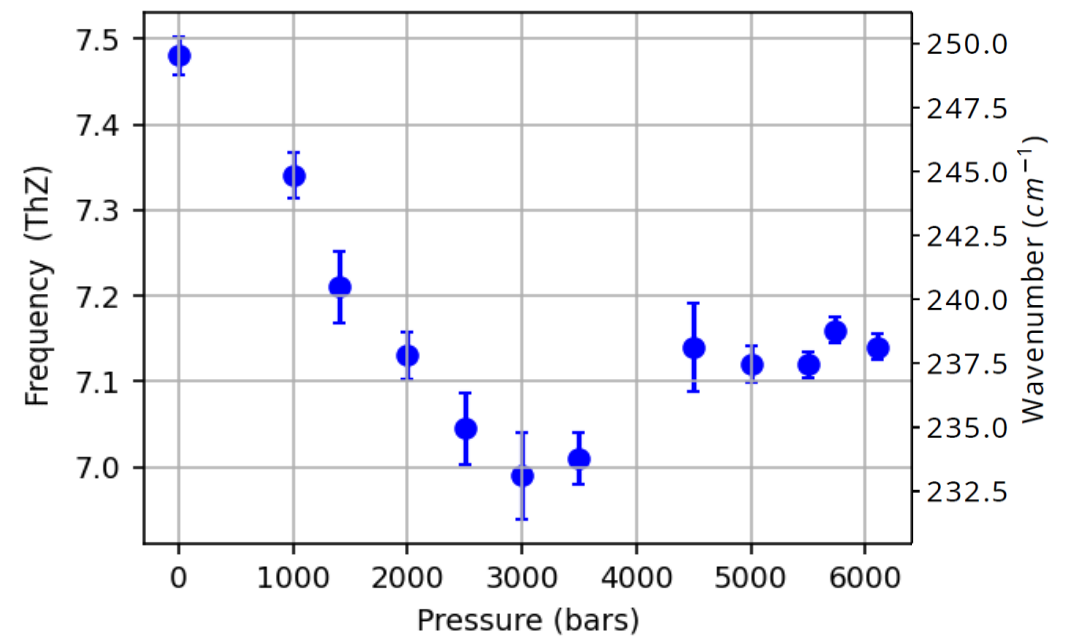
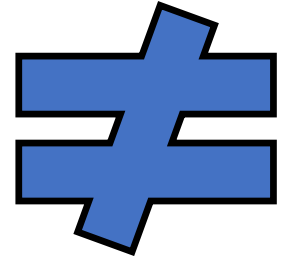
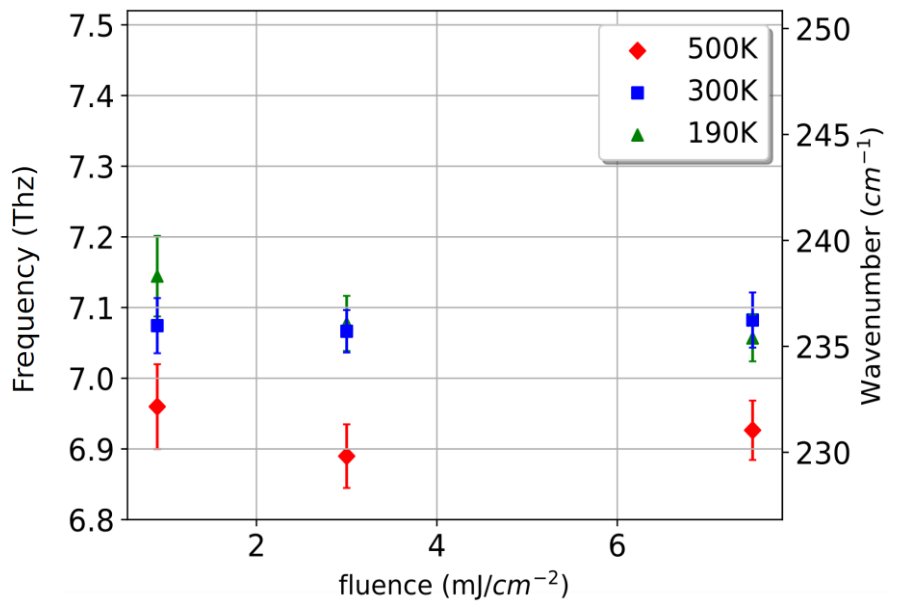
Differential reflectivity normalized with respect to ambient conditions

- Changes around 2500 to 3000 bars
- Indication of Mott transition ?

Is this behavior reflected in the out-of-equilibrium response? More complex signal?



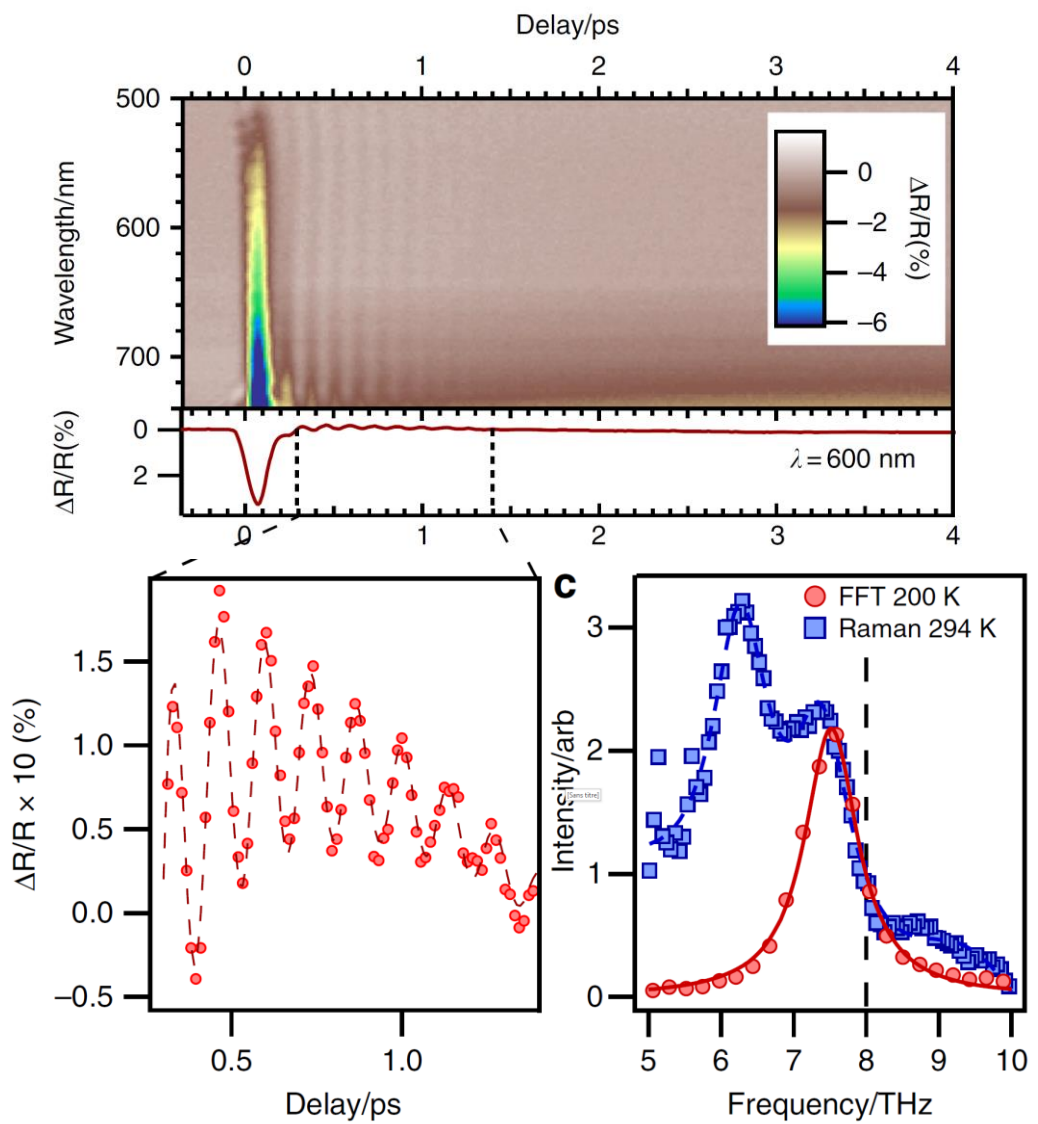




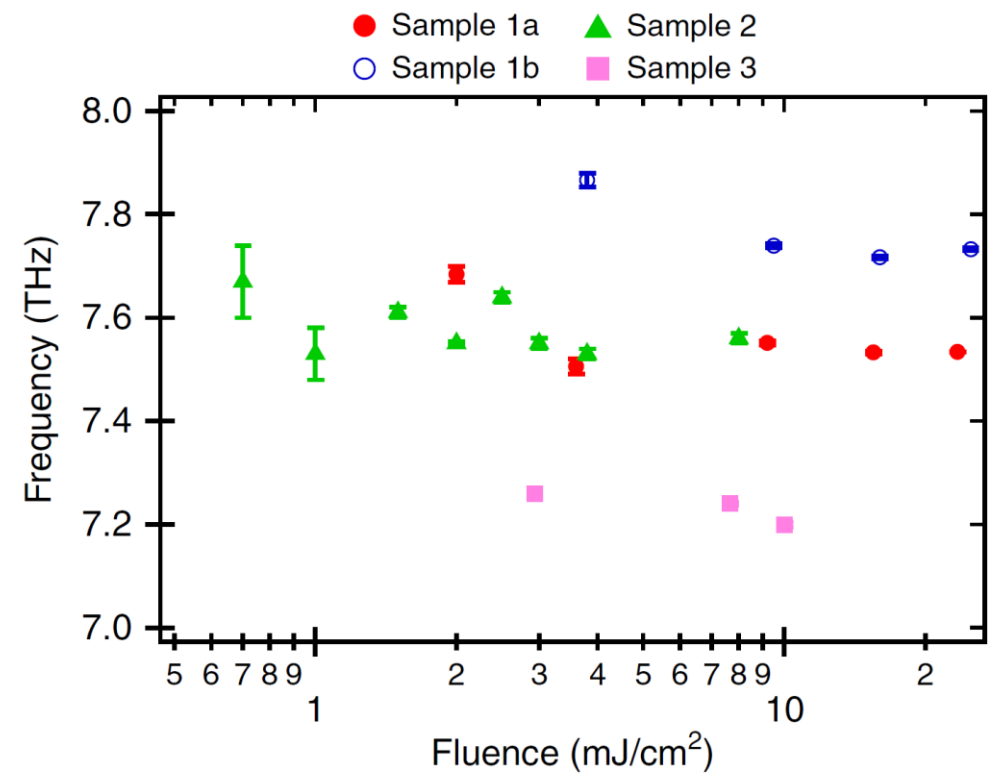
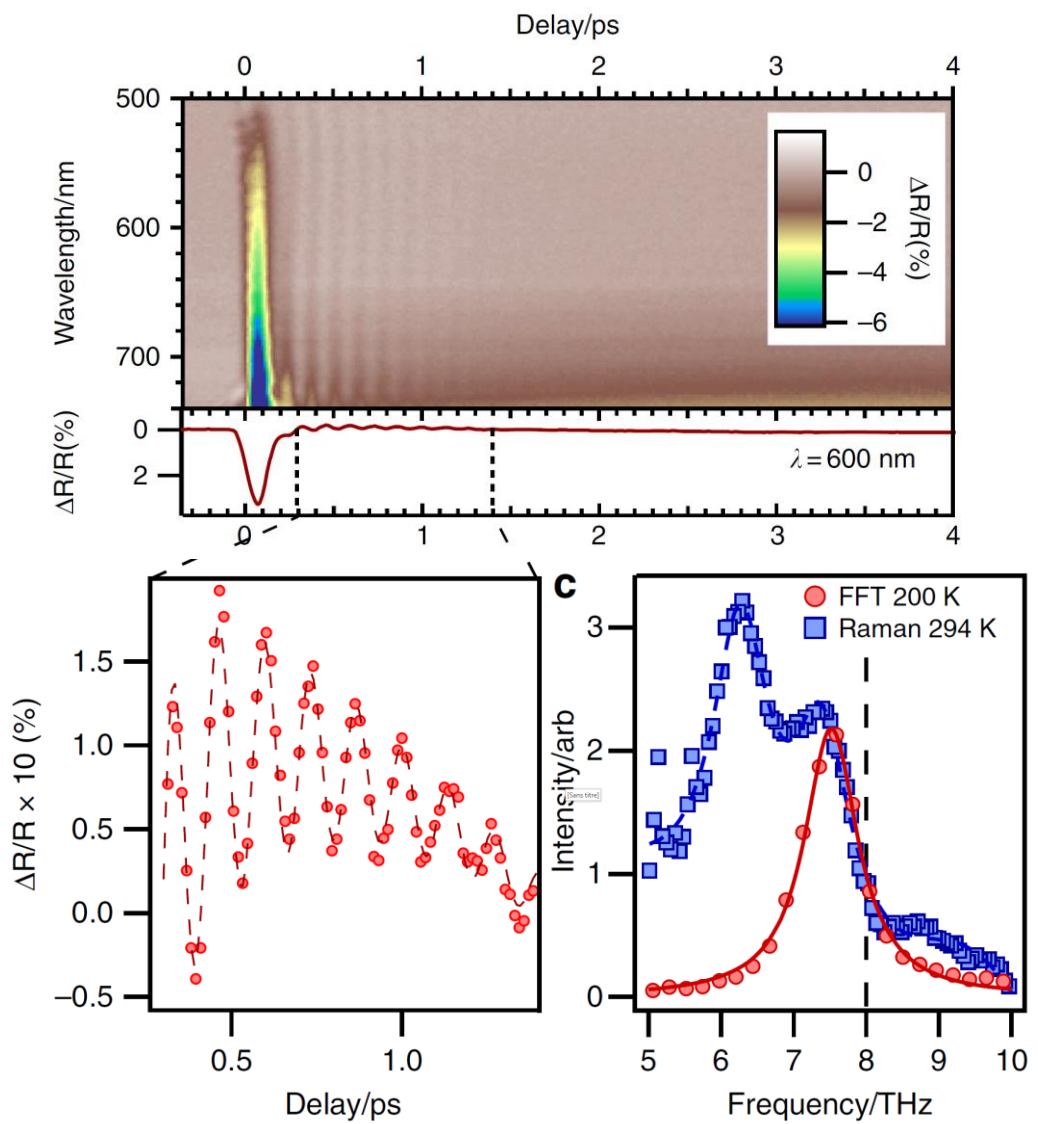
- Temperature/ Excitation density \rightarrow Small change of frequency
- Pressure \rightarrow Strong softening (0.5 THz) with local minimum around 3000 bars + plateau above 4500 bars

How should we understand this result?

- Pressure induced transition; is there more?



D. Moreno-Mencia et al , *Nat. Com.* , 10, 4034 (2019)



No obvious changes with excitation density

- The density of excited carriers is not changing the phonon frequency : neither softening or stiffening
- Sample growth modifies the frequency (strain, disorder, etc.)

