Exploring the phase-diagram of molecular crystals during ultrafast photo-induced non-equilibrium dynamics

Roman Bertoni, Materials & Light Team

University Rennes 1 , Institut de Physique de Rennes

ECRYS 2022, Cargese, 8 - 20 August 2022

Acknowledgments

Materials & Light team

- Nicolas Godin
- Jean-Claude Ameline
- Ela Trzop
- Gaël Privault
- Guénolé Huitric
- Marius Hervé
- Giovanni Azzolina

Physics of Materials & Nanostructures

- Etienne Janod
- Zohra Khaldi
- Julien Tranchant
- Laurent Cario
- Benoit Corraze

Division of Chemistry

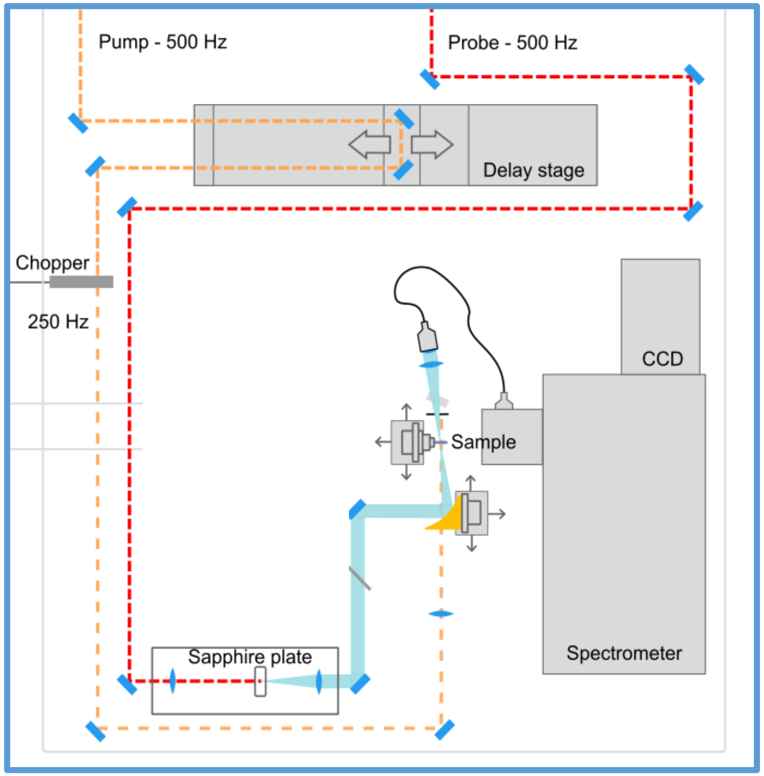
- Mitsuhiko Maesato
- Gunzi Saito

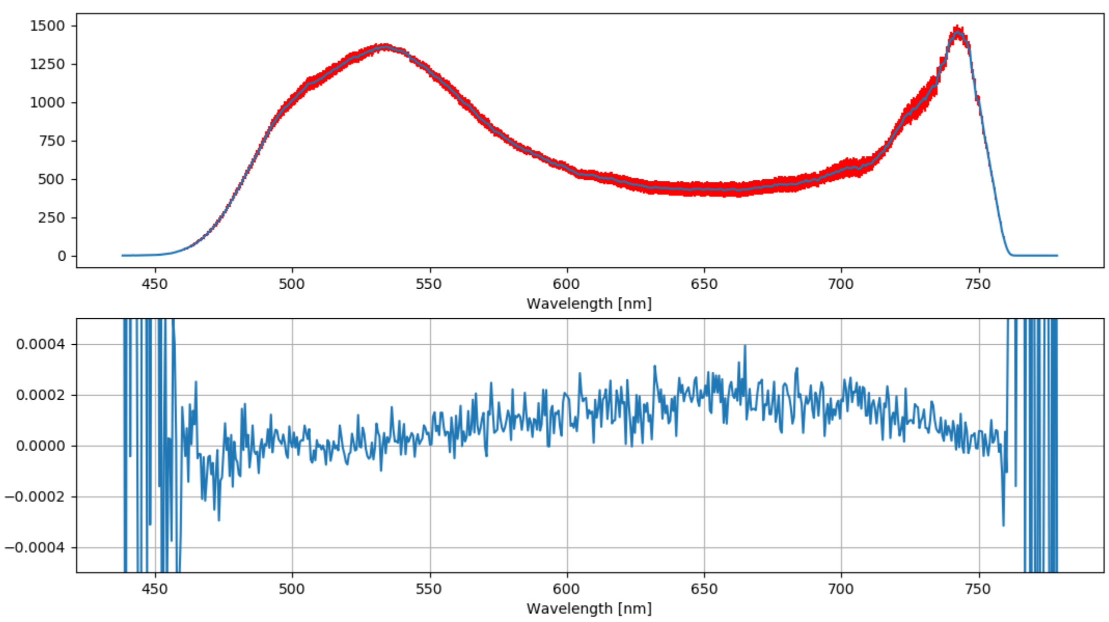
Goal

Ultrafast photo-induced dynamics of materials

- Goal ⇨ beyond the sole use of temperature as external thermodynamical control parameter
- Exploring the Pressure Temperature Phase Diagram of Molecular Material
- Seek for peculiar the Photo-Induced Dynamics in well defined parts of the Phase Diagram

Optical Setup





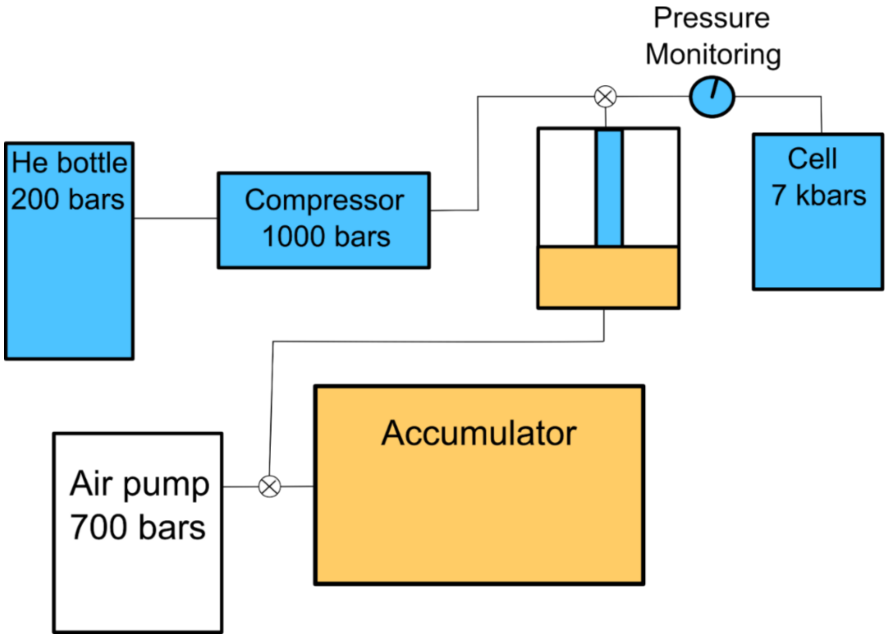
Supercontinuum/ White light Spectroscopy

- (470-750 nm)
- Time resolution ~ 100 fs
- Sensitivity ~ 0.1 mOD (10^{-4})
- Pump (450-2200 nm) → 800 nm

With courtesy of G. Azzolina

High Pressure Setup

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

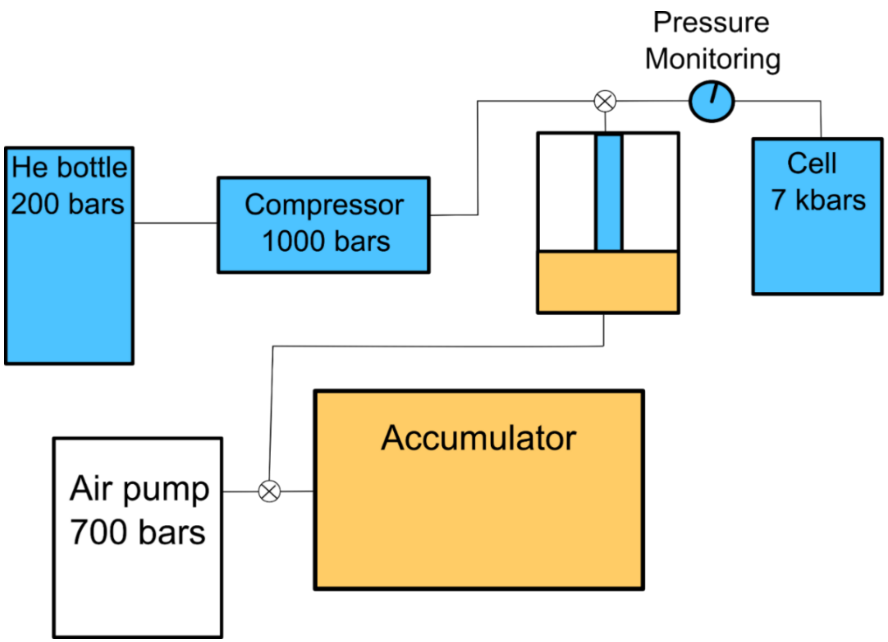
250-5000 nm

Specifications:

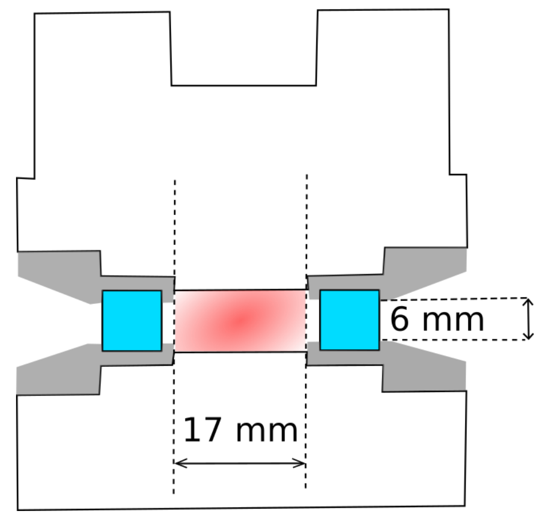
- Precision of few bars (measure in operando)
- Ramping up/down of few bars per minutes
- Sapphire windows allowing optical Transmission/Reflection

High Pressure Setup

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



Multi-stages He gas based cell



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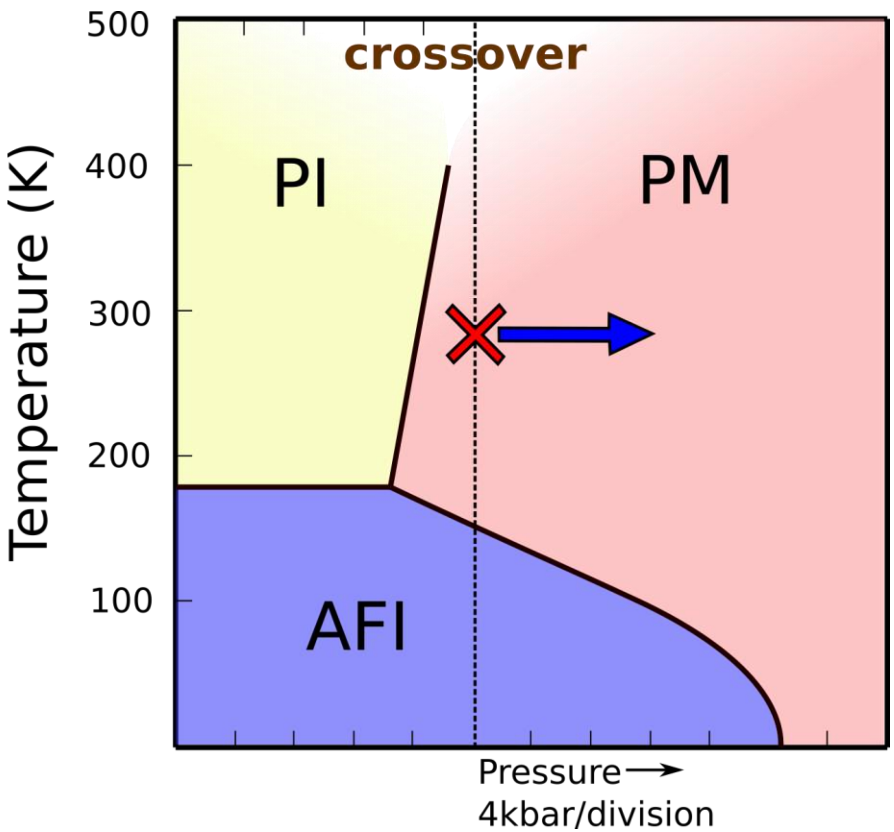
V_2O_3 Phase Diagram

First a "*counter*" example: V_2O_3 ➡ Benchmark of Mott physics



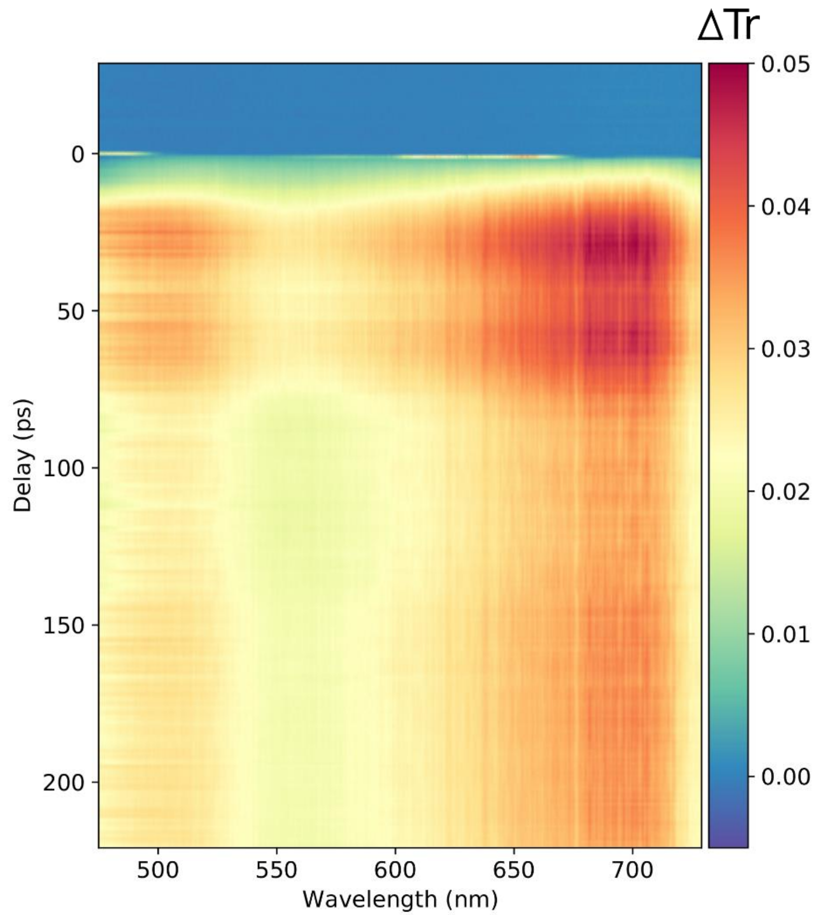
- Pure V_2O_3 without chemical substitution is a Paramagnetic "bad" Metal (PM) under standard thermodynamical conditions
- No expected phase transition under hydrostatic pressure
- Thin film of ~ 190 nm thickness

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

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

Photo-induced dynamics in V_2O_3

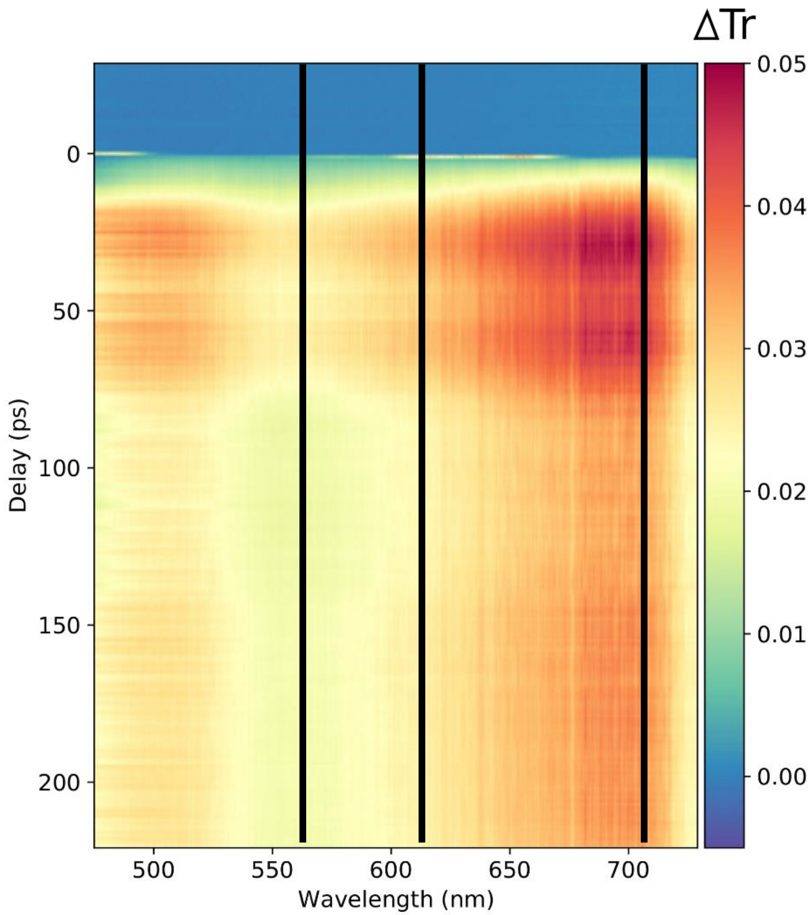
Transmission



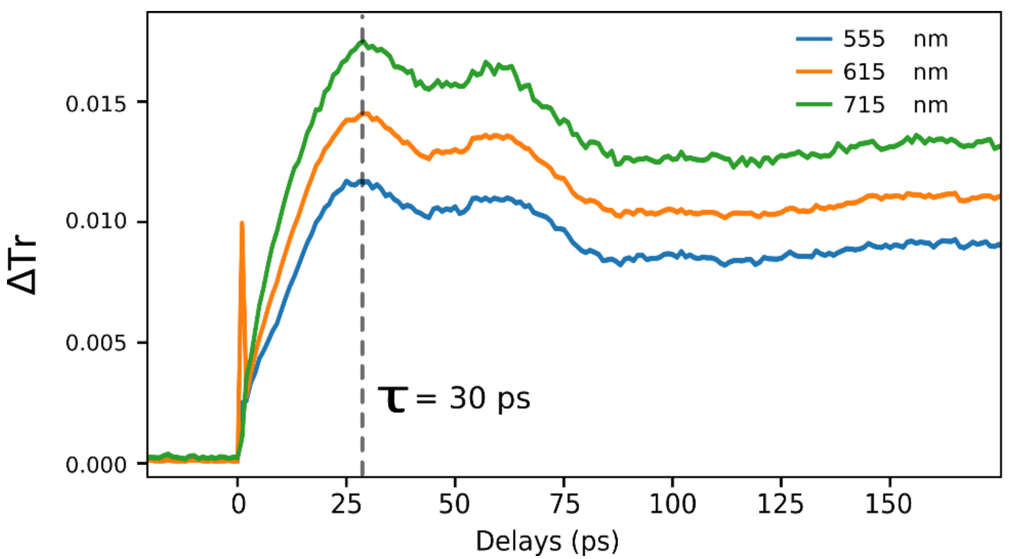
Pump 800 nm

Photo-induced dynamics in V_2O_3

Transmission



Pump 800 nm



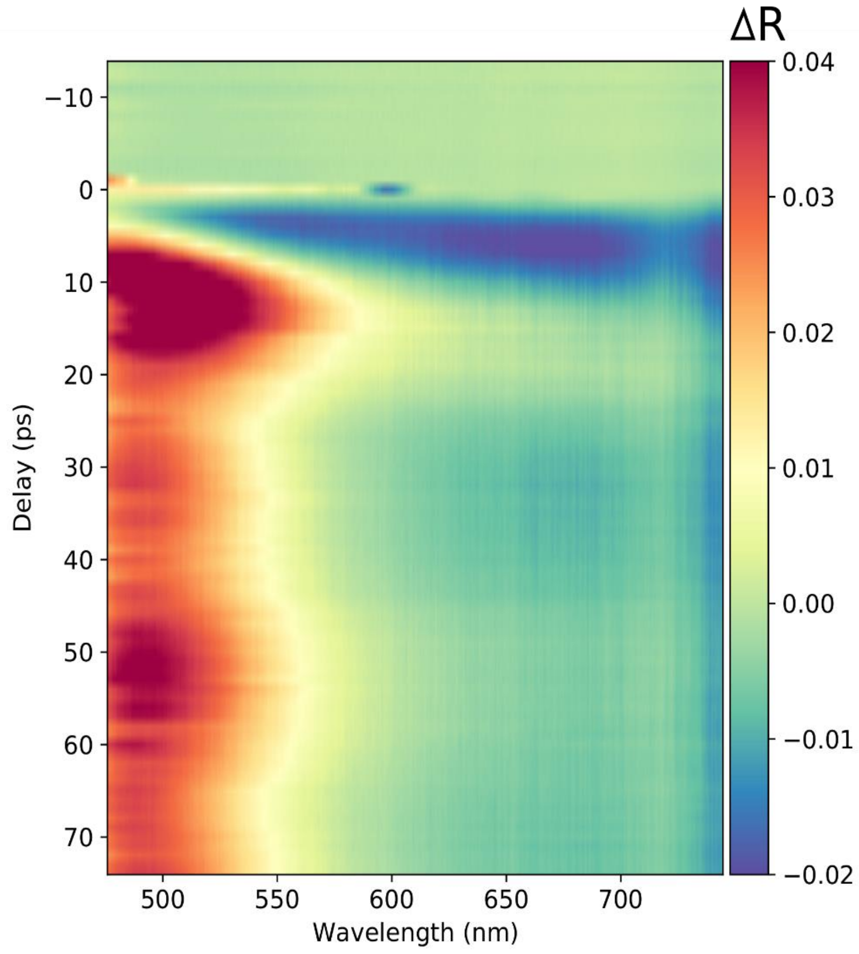
- Rising time ~ 30 ps
- Plateau at 100 ps and lasting ns

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

G. Privault et al, *submitted*

Photo-induced dynamics in V_2O_3

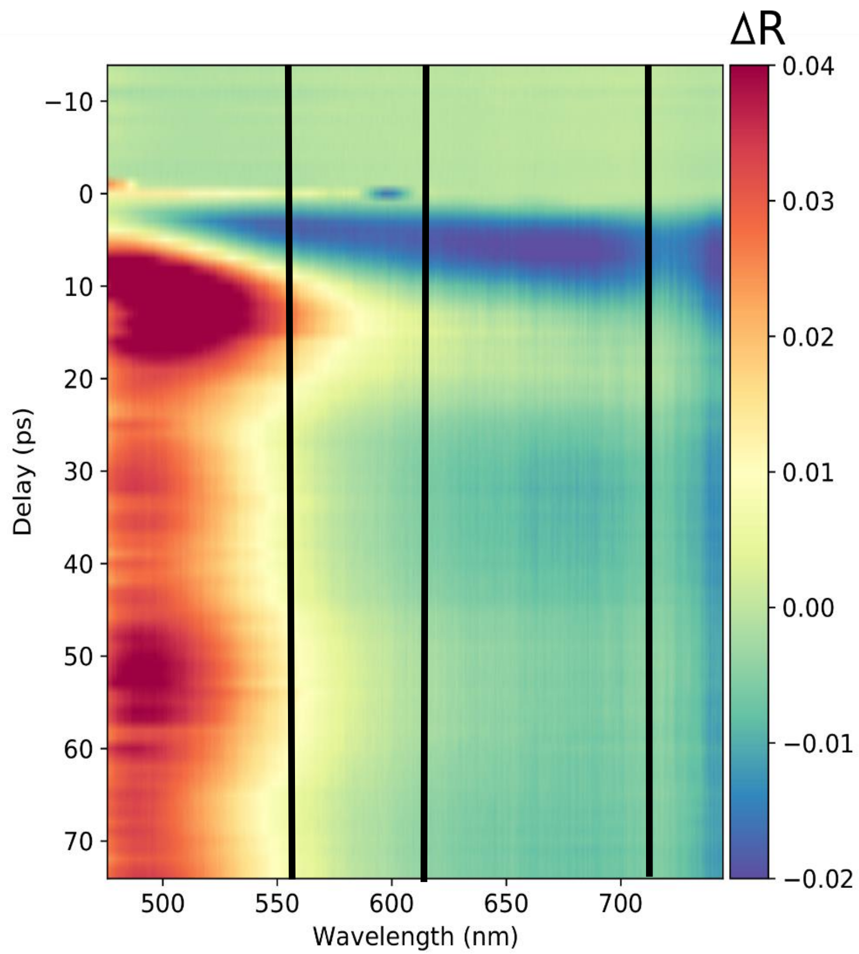
Reflectivity



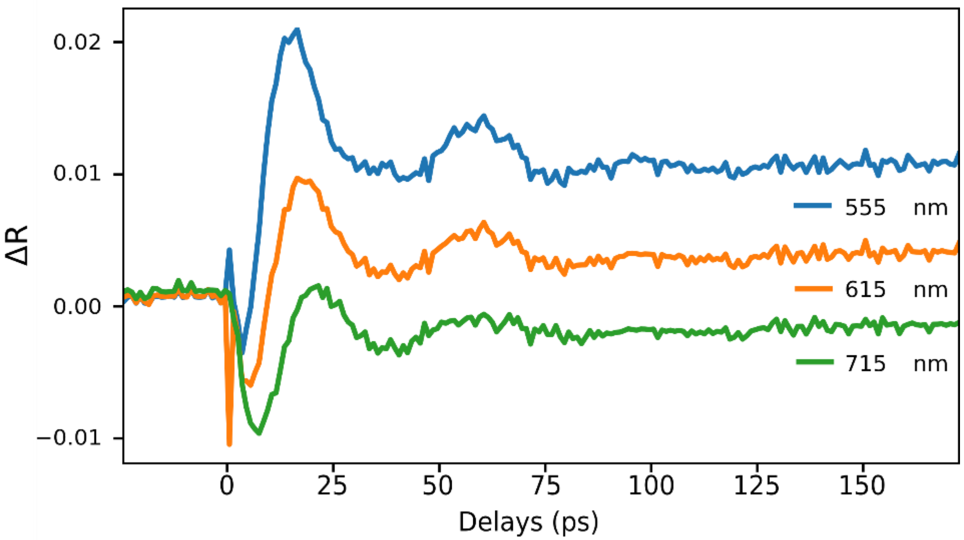
Pump 800 nm

Photo-induced dynamics in V_2O_3

Reflectivity

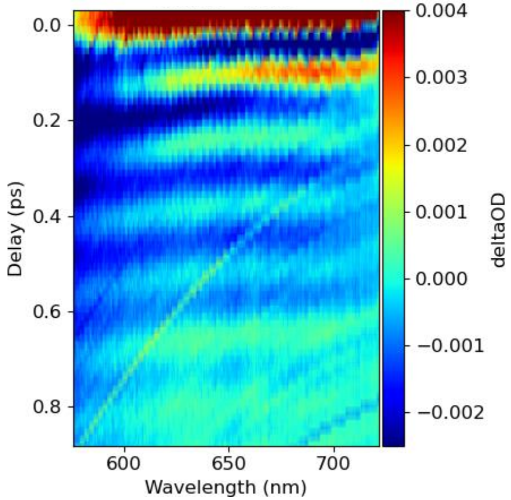


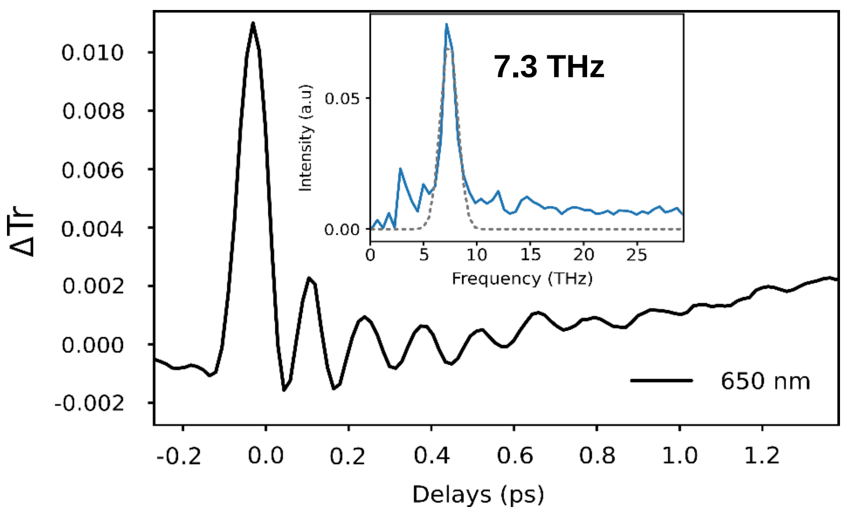
Pump 800 nm



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

Photo-induced dynamics in V_2O_3

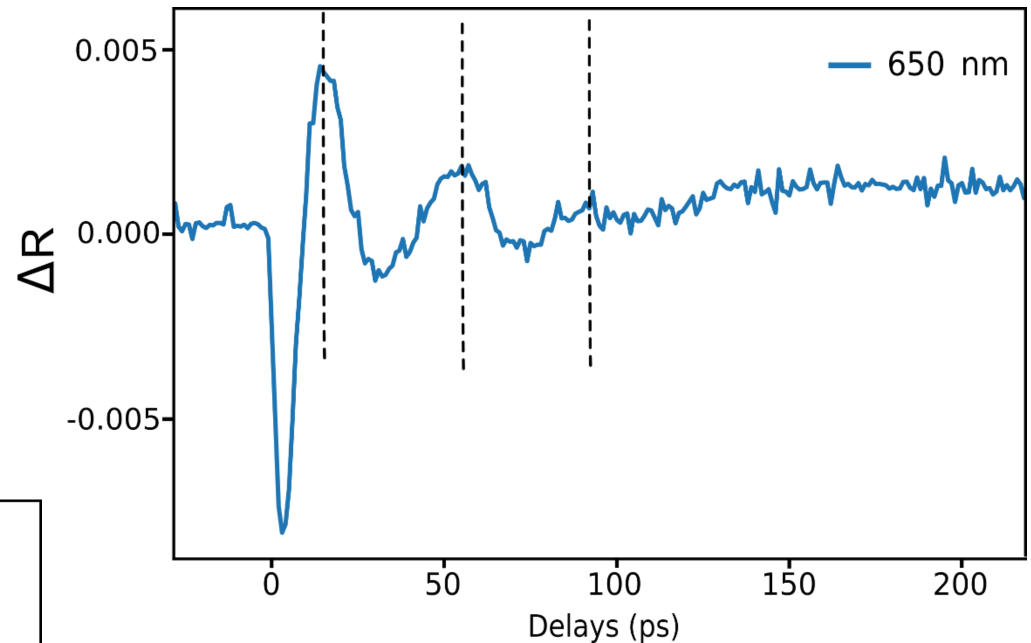




Observation of coherent optical phonons:

A_{1g} mode, agreement with literature

G.Lantz et al , *Nature communications*, 8(1), 1-7 (2017)



Oscillation phenomena linked to strain modulation (thermo-elastic).

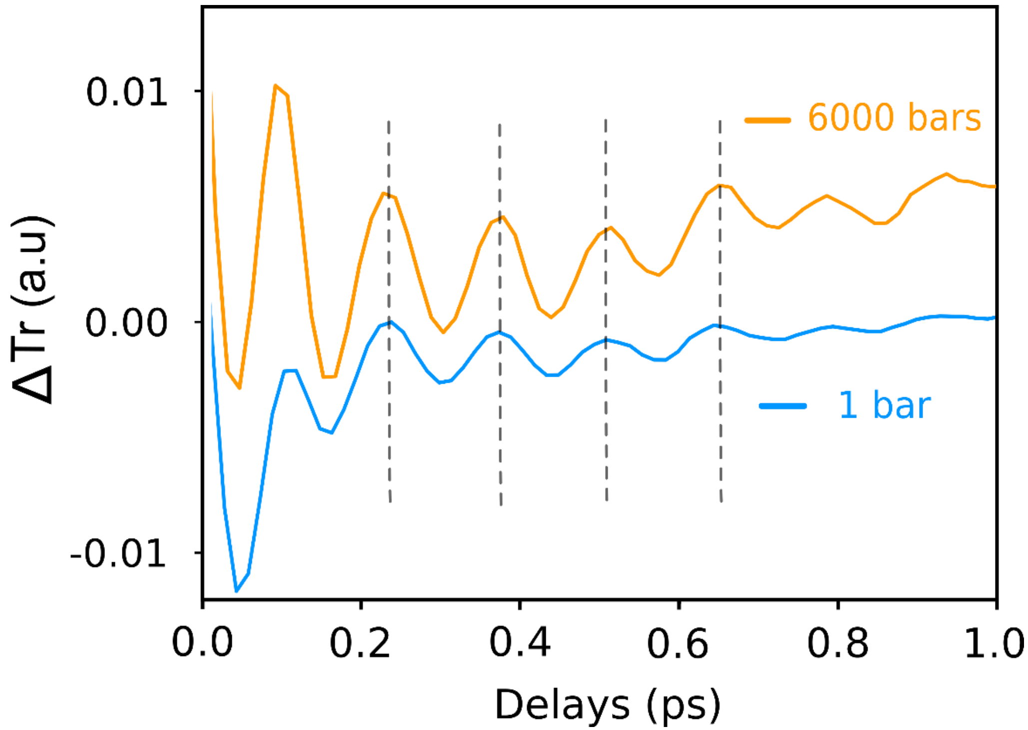
Related to film breathing?

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

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

Photo-induced dynamics in V_2O_3

Phonon potential

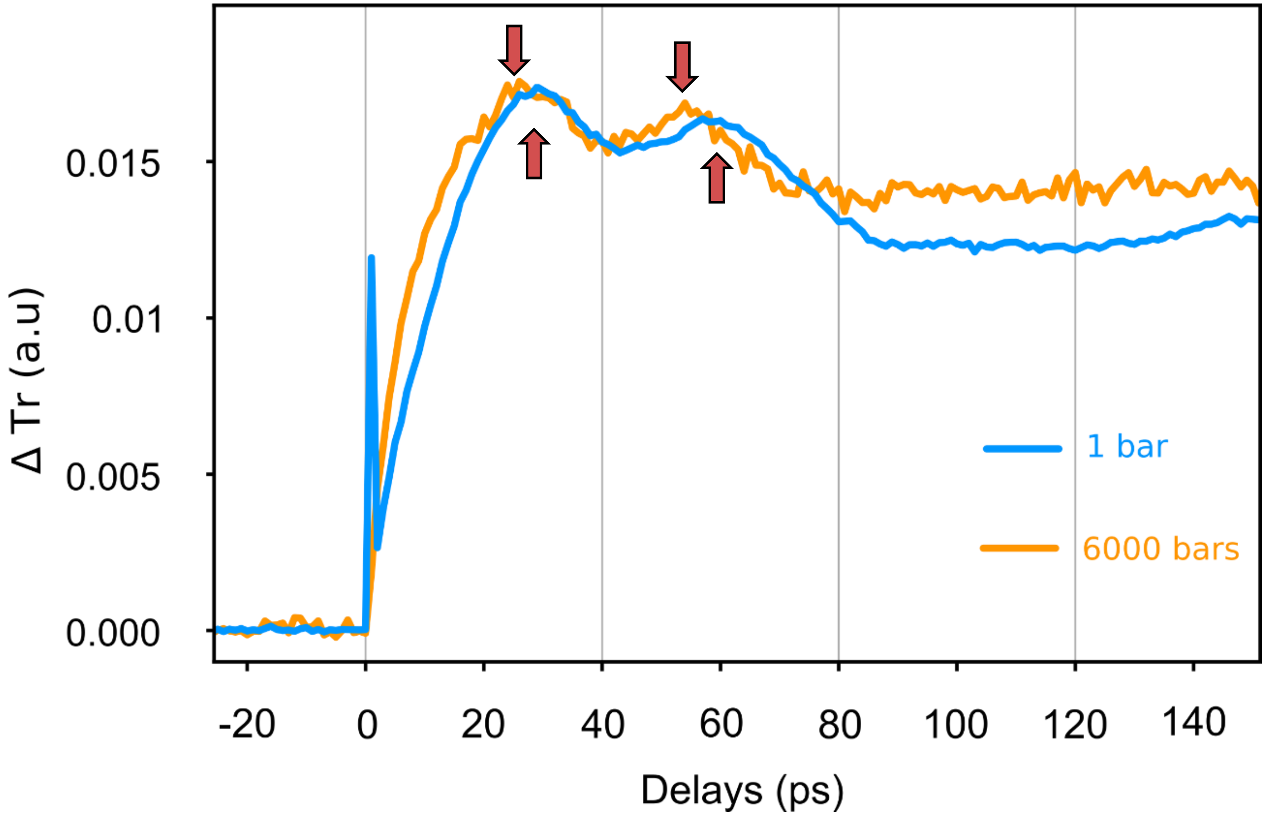


Residual of short timescale at 650 nm

No apparent shift in A_{1g} frequency

No observable modification of the A_{1g} phonon potential (0-6 kbars)

Photo-induced dynamics in V_2O_3



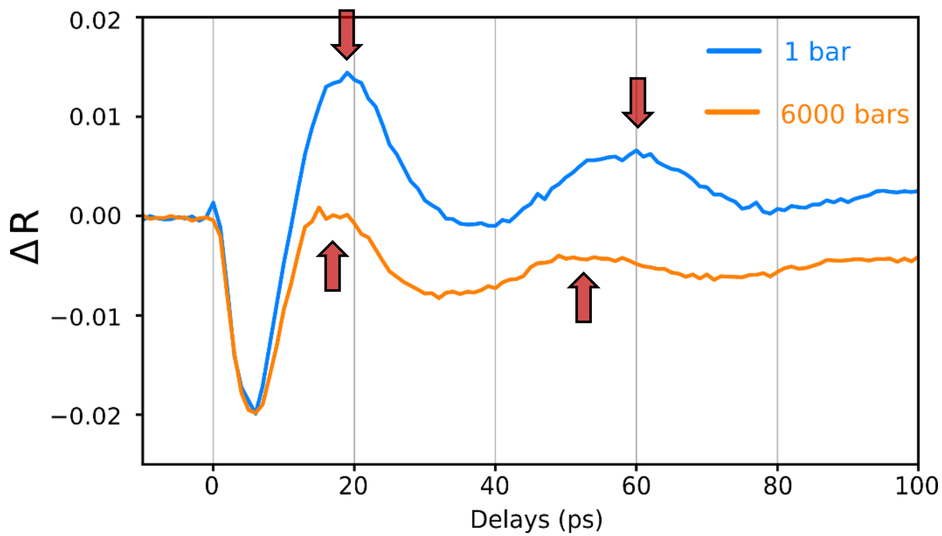
Normalized transient transmission at 650 nm

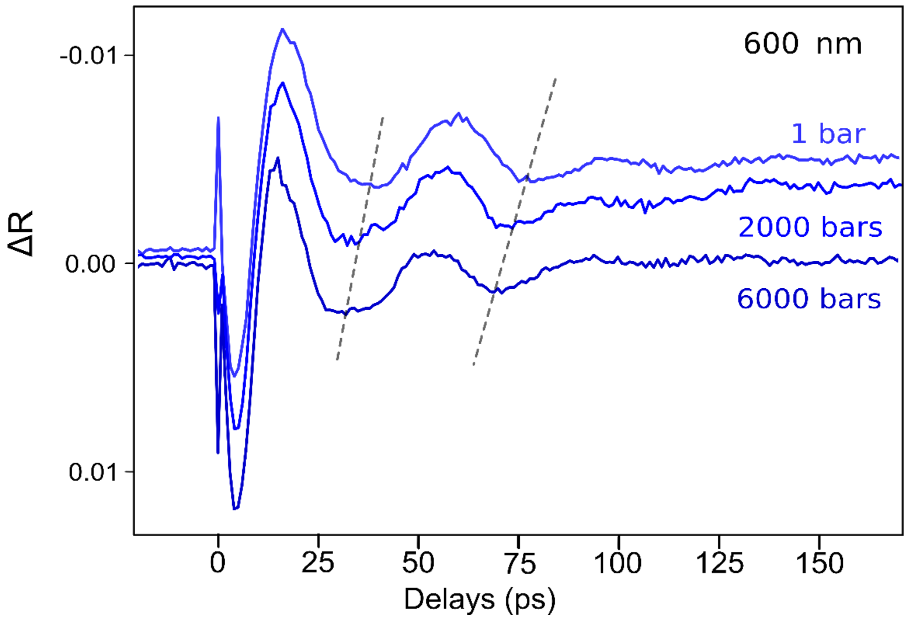
Shift of the rising time and oscillations (arrows) related to strain propagation effect:

Impact on speed of sound

Photo-induced dynamics in V_2O_3

Acoustic properties





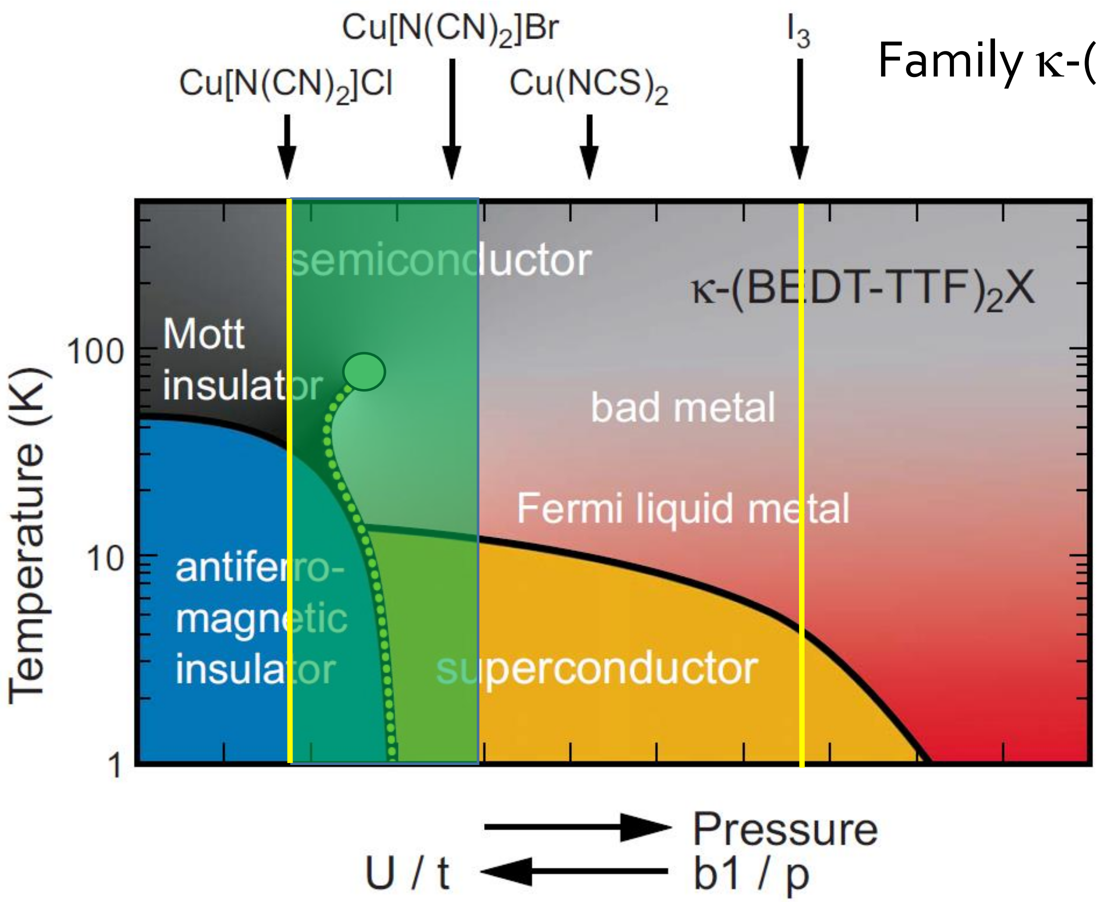
Blue shift of the "Brillouin" frequency under pressure

→ Increase of speed of sound / stiffening

Even in inorganic V2O3, pressure below GPa acts on acoustic properties: may impact photo-induced strain effects

Phase Diagram of MOC

MOC: Molecular Conductors



Family κ-(-BEDT-TTF)$_2$X

- Several competiting orders
- Accessible with ten's of kbars
- Critical end-point around 40 K

Other pathway:
Chemical substition to move along the phase diagram.
Very sensitive to disorder.

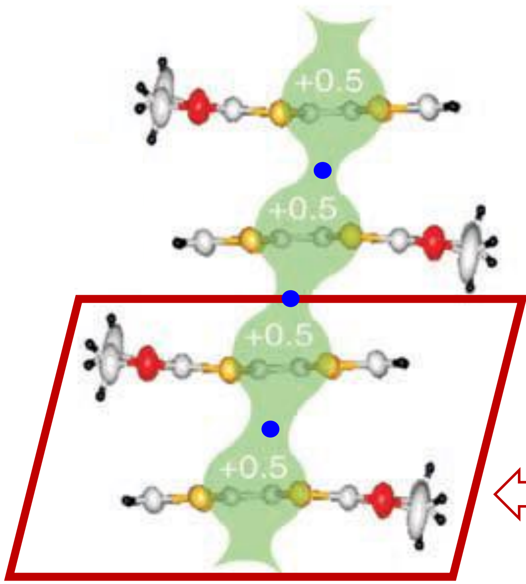
D. Faltermeier et al., *Phys. Rev. B* 76 (16), 165113 (2007)

E. Gati et al., *Science Advances*, 2, 12 (2016)

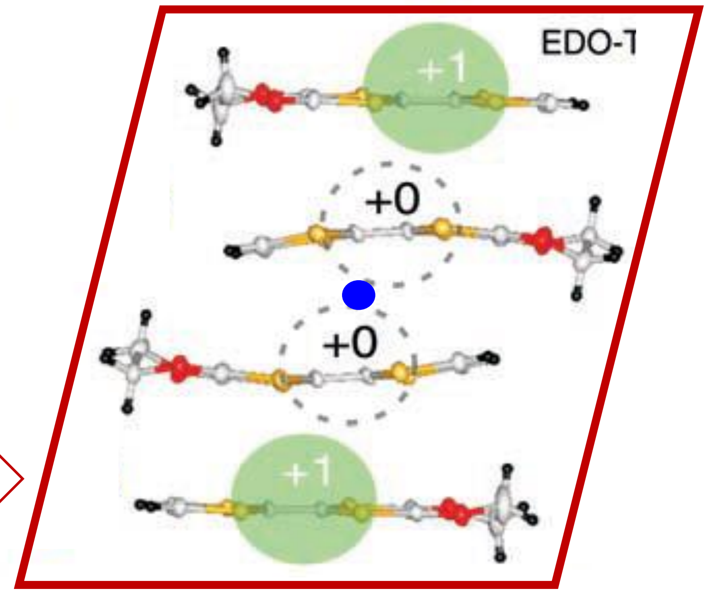
(EDO-TTF)-XF_6

System displaying **Metal to Insulator (MIT) Phase Transition**

High Temperature Phase



Low Temperature Phase



T_c = 240 k

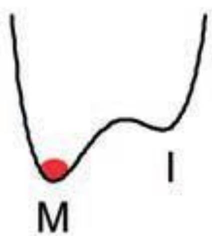
P_c = 2200 bars

Unit cell

Metallic

½-½-½-½-½

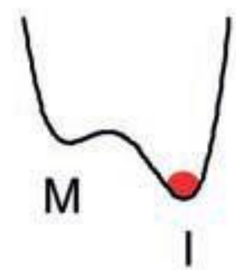
● Inversion symmetry center



Charge-Order Insulator

0-0-1-1-0-0

Cell-doubling



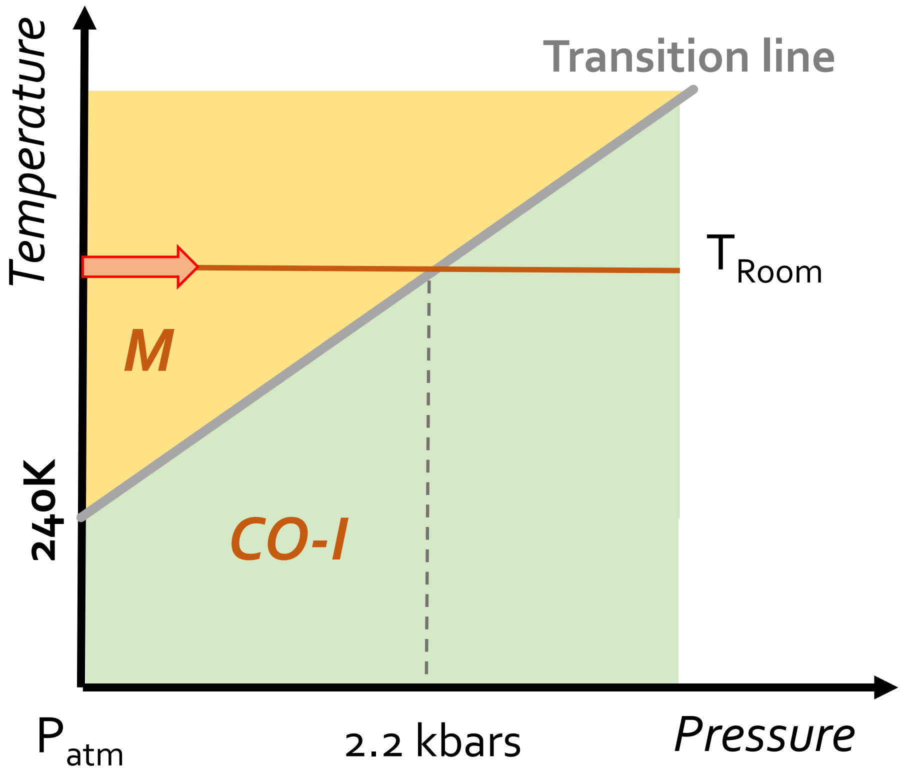
A. Ota et al., *J. Mat. Chem.* 12 (9), 2600 (2002)

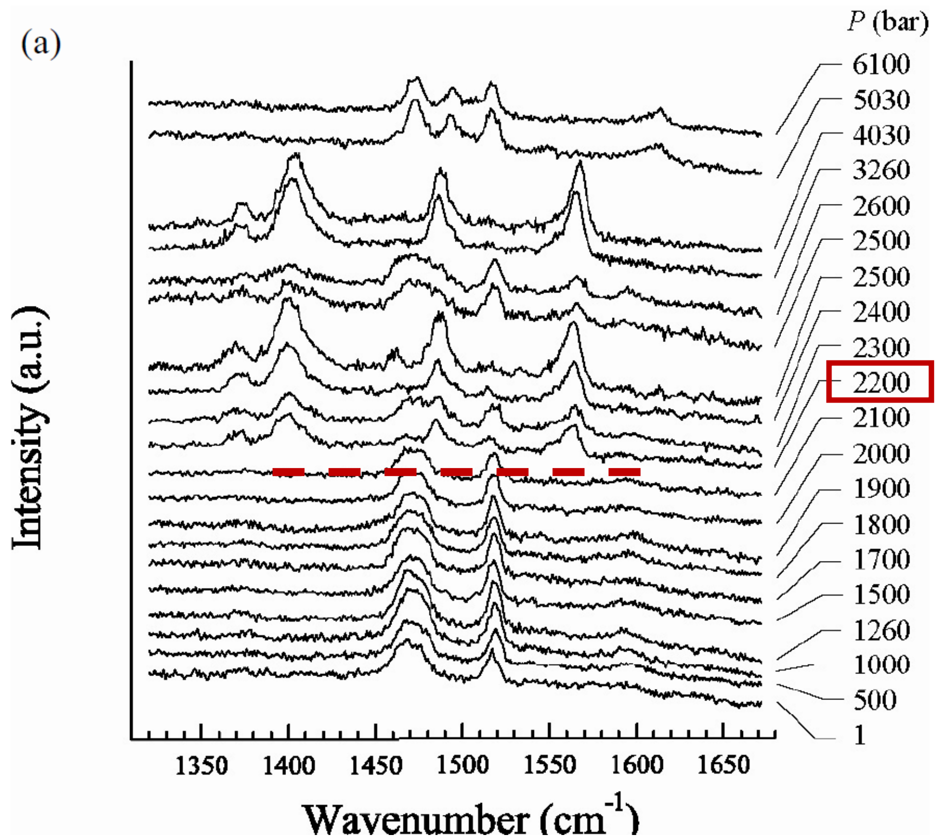
M. Chollet et al, *Science*, 307 (5706) 86 (2005)

H. Yamochi et al, *Science and Technology of Advanced Materials*, 10(2), 024305 (2009).

Tentative Phase Diagram of (EDO-TTF)-XF_6

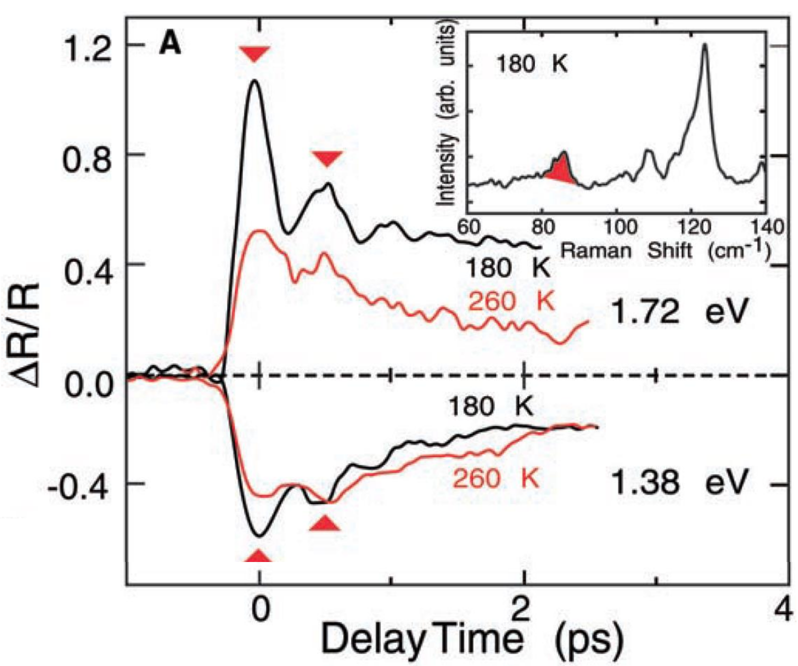
1st Order Phase Transition

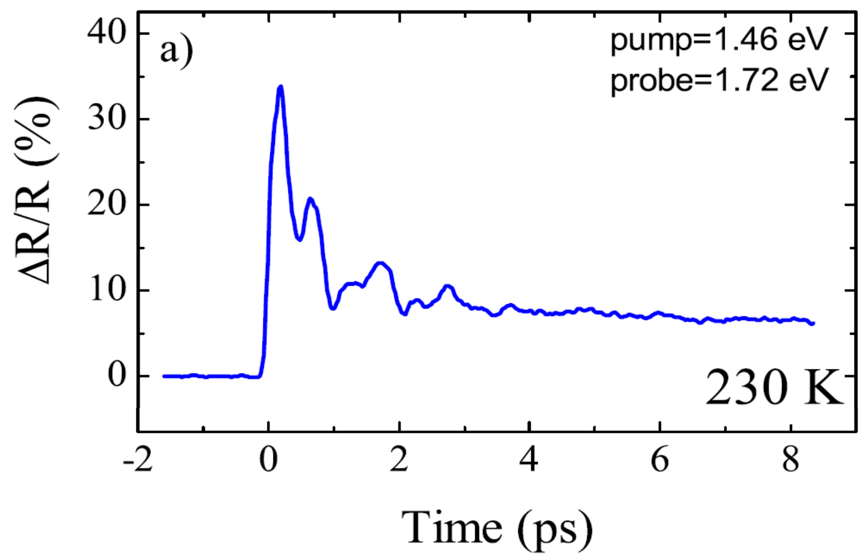




M. Maesato et al, *J. of Phys.: Conference Series* 148 (1), 012004, (2009)

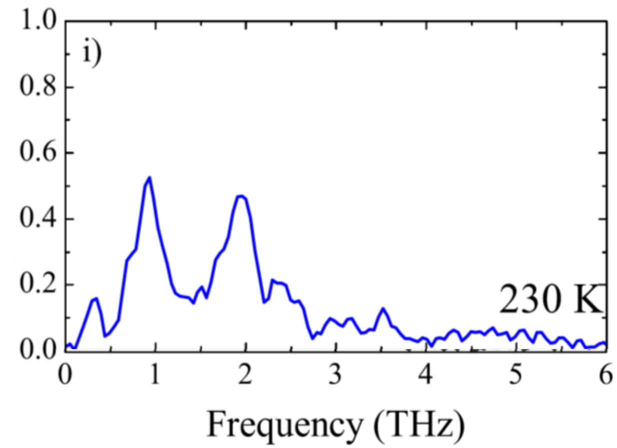
Photo-Induced Dynamics in $(EDO\text{-}TTF)\text{-}XF_6$





System displaying reflectivity changes up to 100 % upon photo-excitation :
Related to the collapse of electronic charge order.

Strongly related to atomic structure as coherent phonons modulate reflectivity up to 10 %



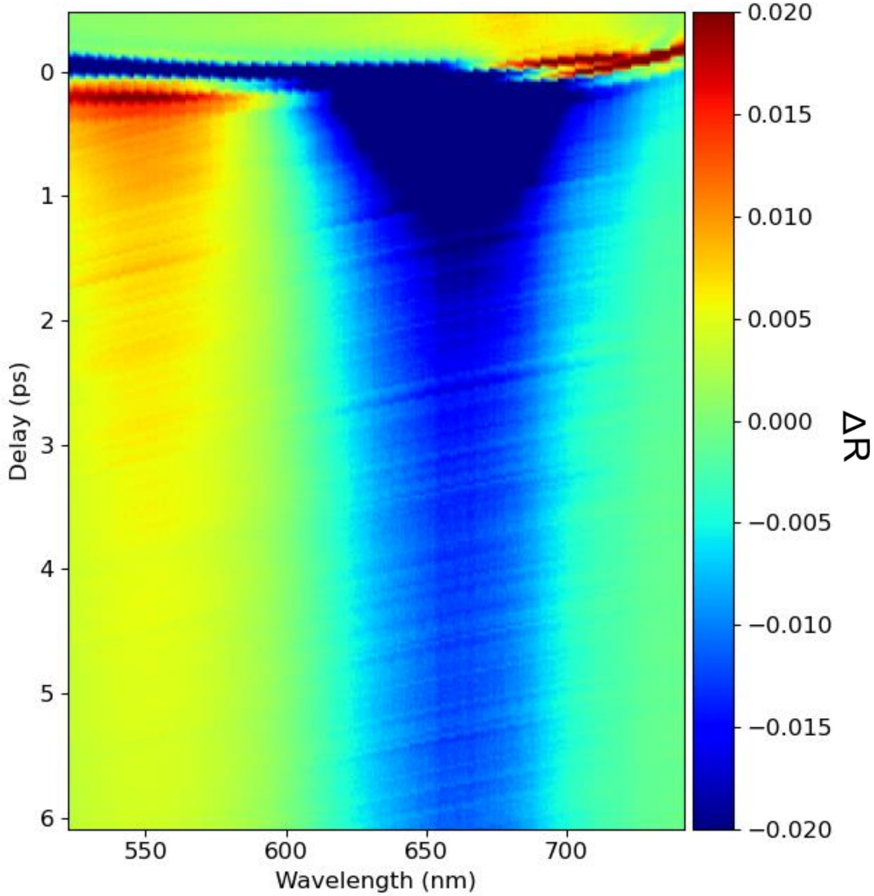
M. Chollet et al, *Science*, 307 (5706) 86 (2005)

M. Servol et al, *Phys. Rev. B* , 92(2) 024304 (2015)

Ambient Pressure P-I dynamics in (EDO-TTF)-XF_6

Pump 800 nm

picosecond timescale / 1 bar

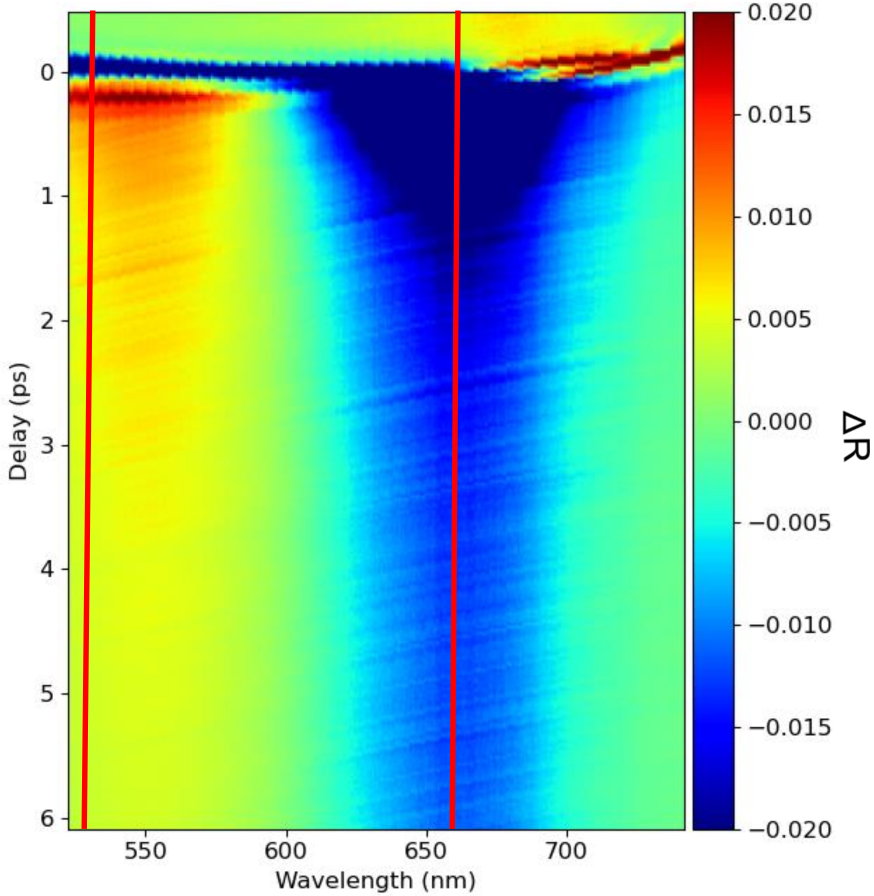


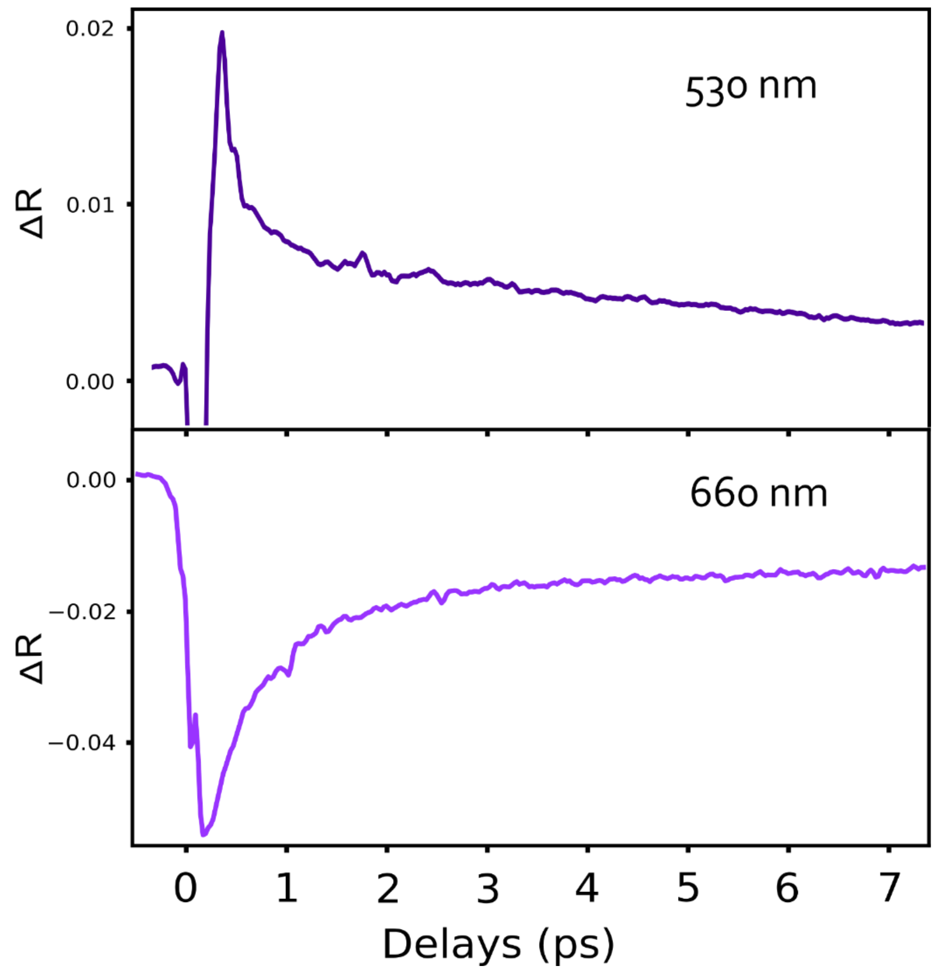
Broadband reflectivity changes after 800 nm pumping

Ambient Pressure P-I dynamics in (EDO-TTF)-XF_6

Pump 800 nm

picosecond timescale / 1 bar

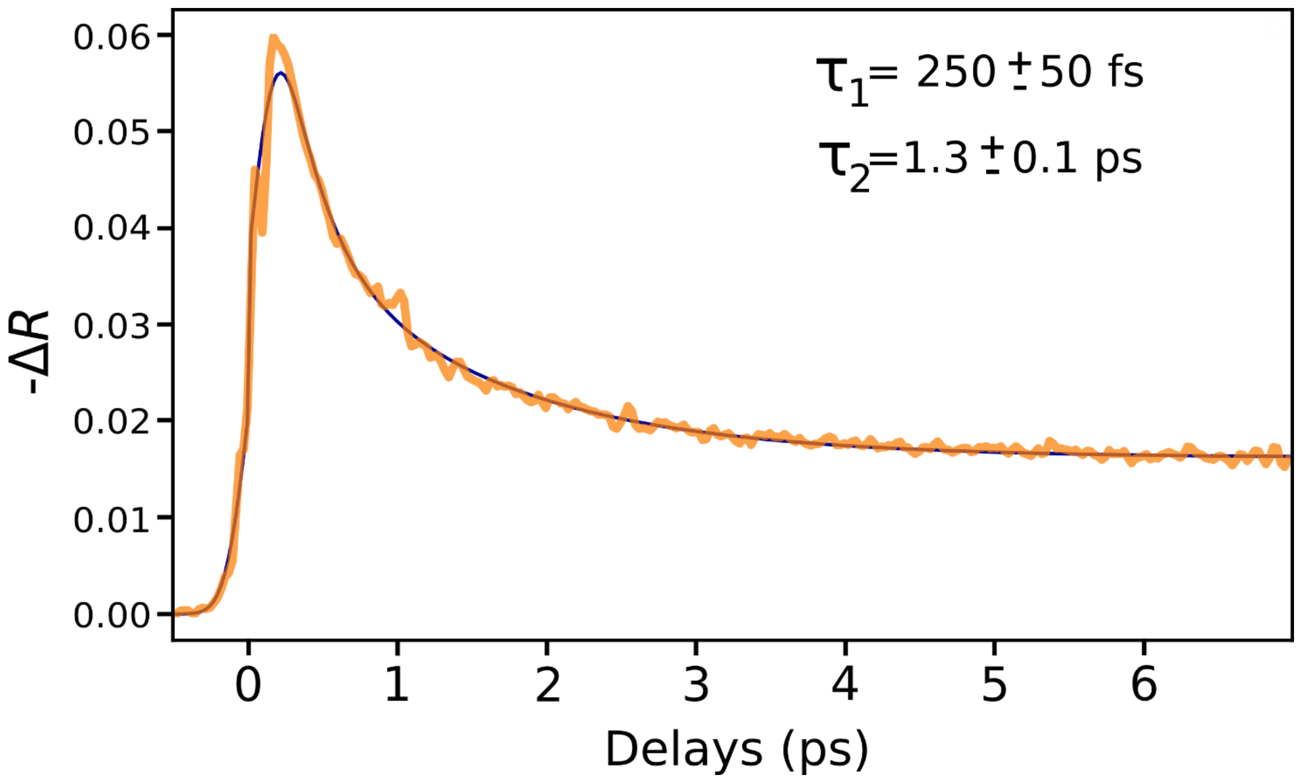




Broadband reflectivity changes after 800 nm pumping

Ambient Pressure P-I dynamics in (EDO-TTF)-XF_6

Transient reflectivity at 660 nm



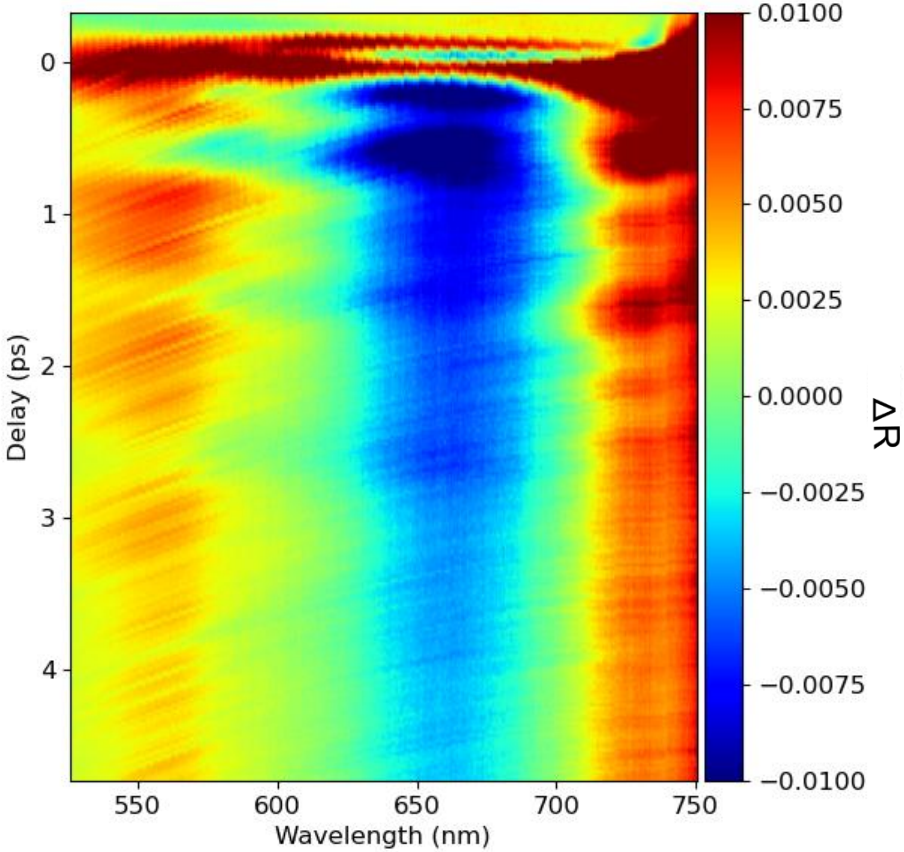
Model with bi-exponential decay:

- 250 fs, electron-electron?
- 1.3 ps, electron-phonon?

Relaxation of excited carriers

High Pressure P-I dynamics in (EDO-TTF)-XF_6

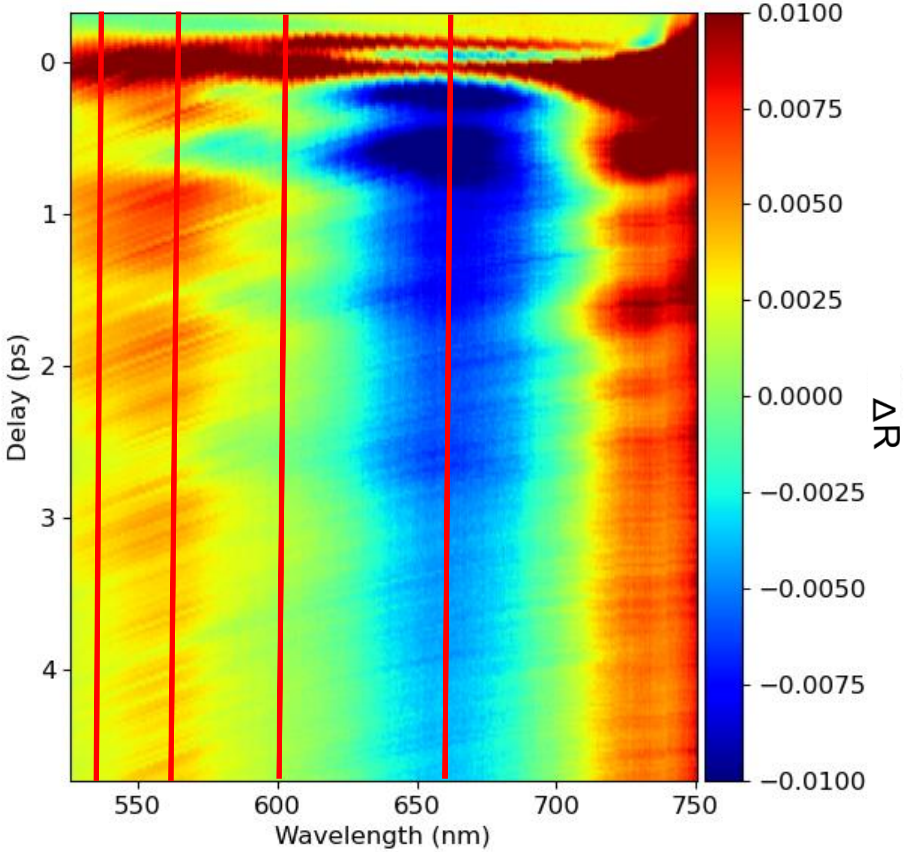
picosecond timescale / 3000 bars



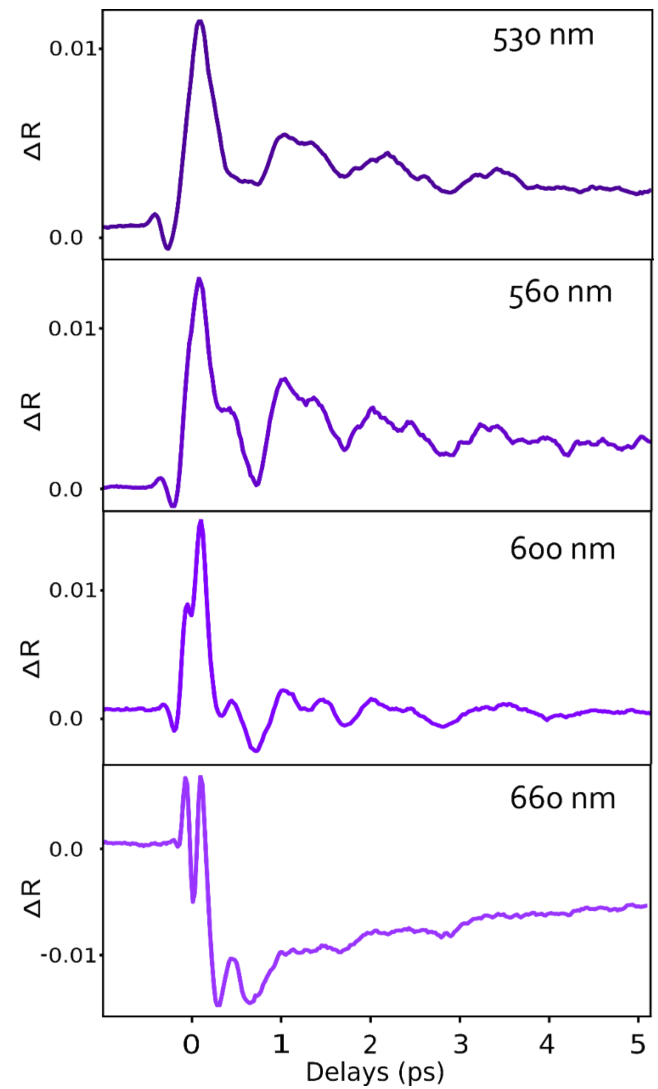
Broadband reflectivity changes after 800 nm pumping

High Pressure P-I dynamics in $(EDO\text{-}TTF)\text{-}XF_6$

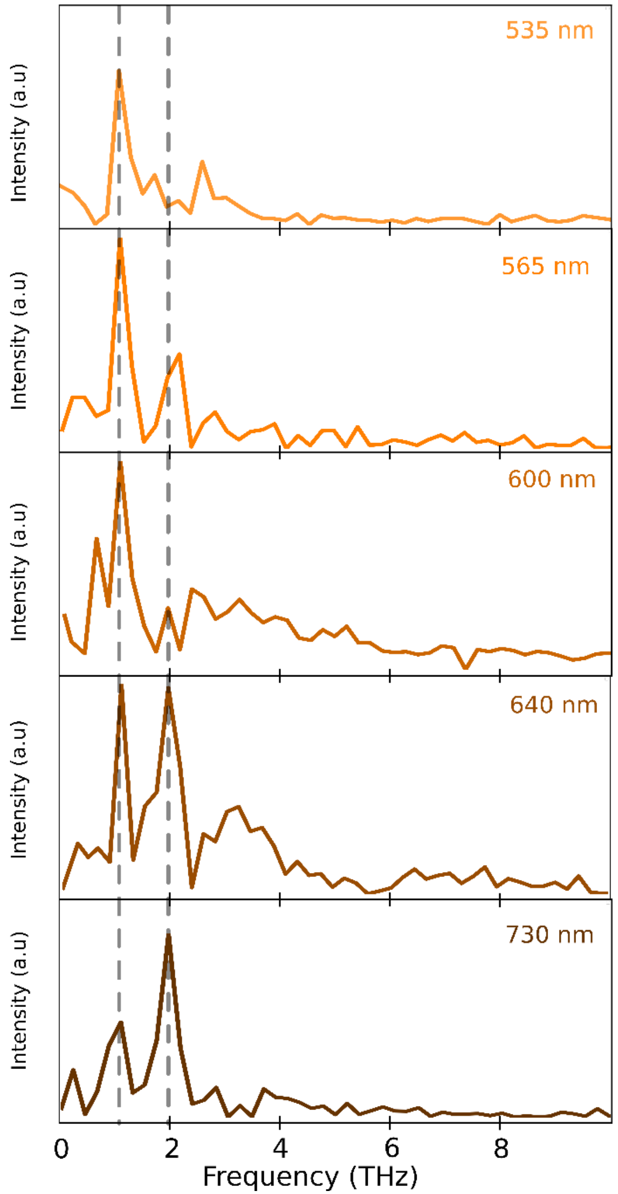
picosecond timescale / 3000 bars



Broadband reflectivity changes after 800 nm pumping

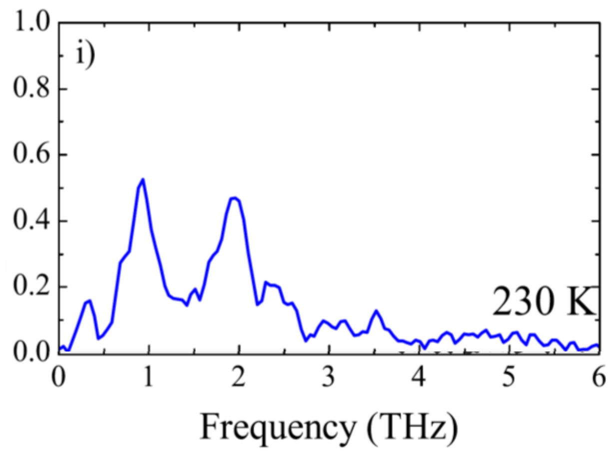


High Pressure P-I dynamics in (EDO-TTF)-XF_6

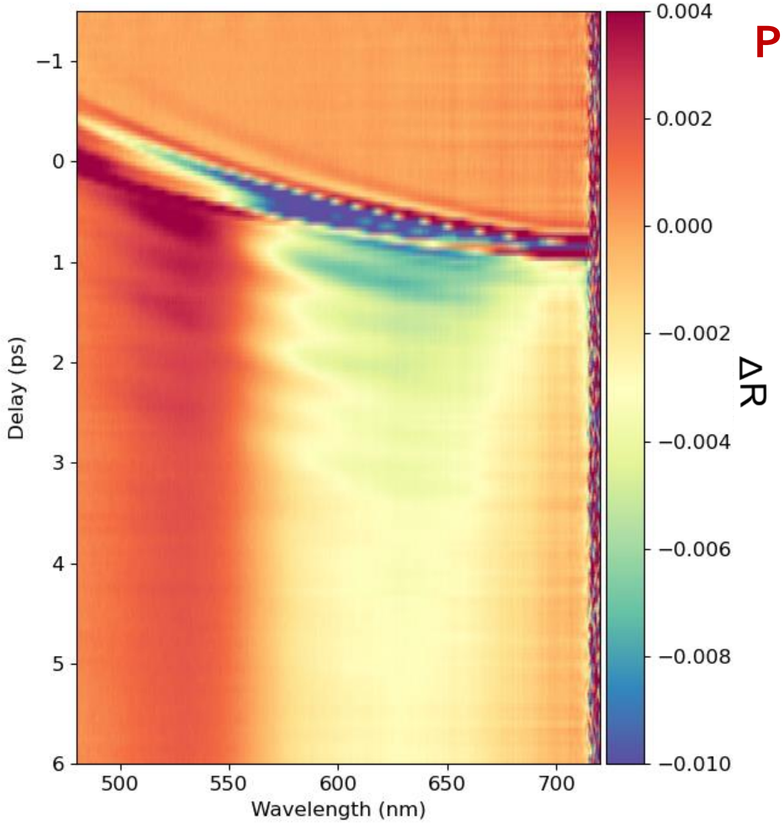


FFT at several wavelengths:

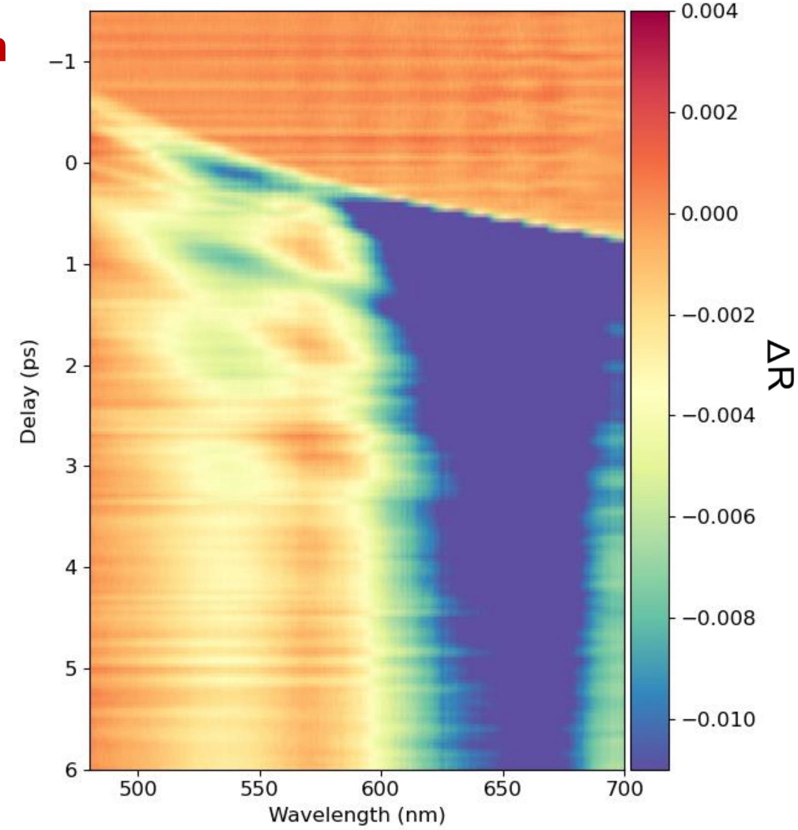
- Observation of several modes (1 THz, 2THz)
  - Match the thermally driven case



High Pressure P-I dynamics in (EDO-TTF)-XF_6



Pump 800 nm



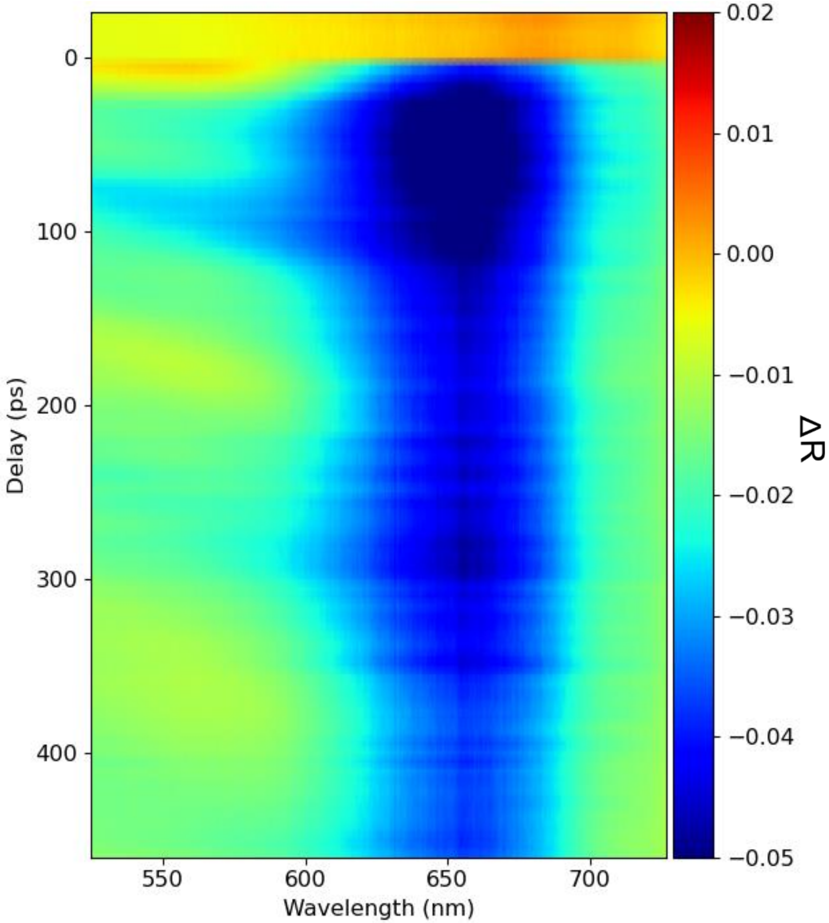
E // to stacking axis

E ⊥ to stacking axis

anisotropic response expected for 1 D conductors

Time Dependent Brillouin Scattering in (EDO-TTF)-XF_6

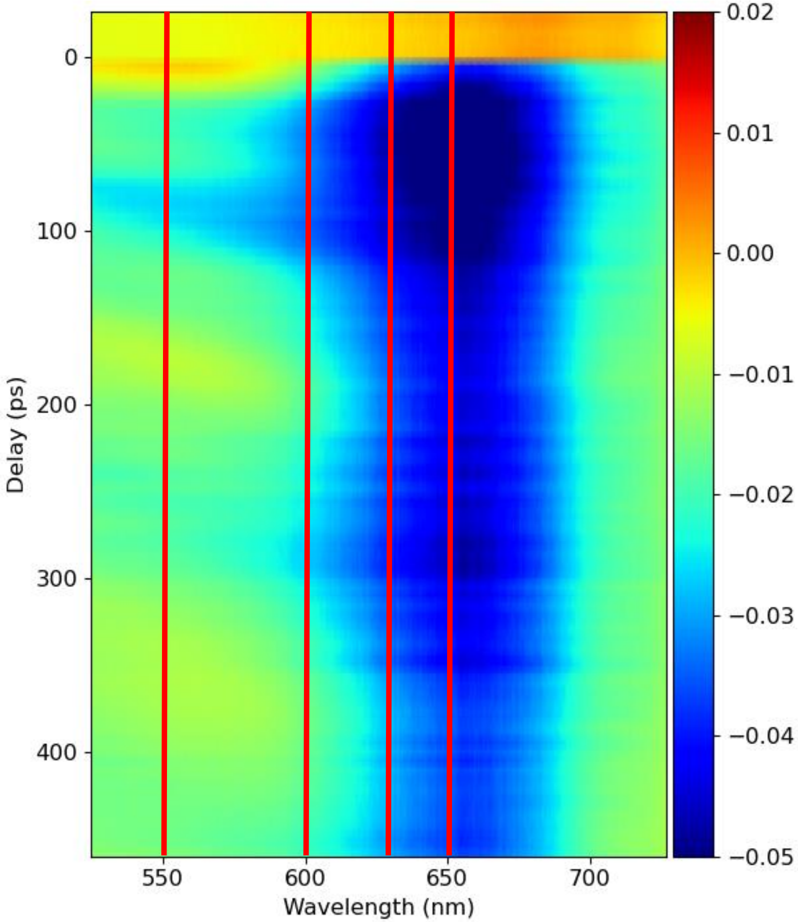
acoustic timescale / 1 bar



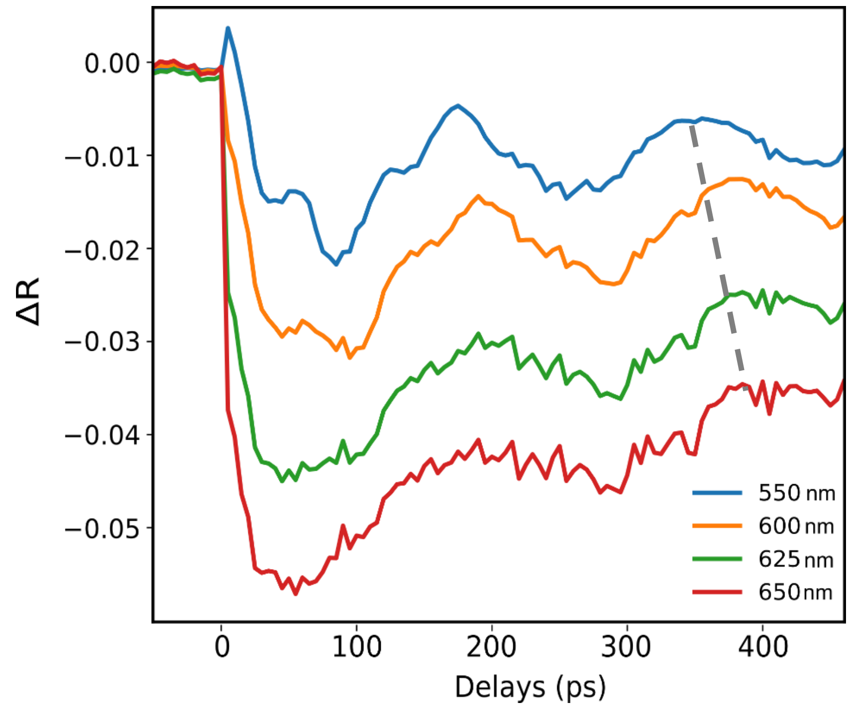
Broadband reflectivity changes after 800 nm pumping

Time Dependent Brillouin Scattering in (EDO-TTF)-XF_6

acoustic timescale / 1 bar



Broadband reflectivity changes after 800 nm pumping



Red Shift of oscillations with longer wavelength

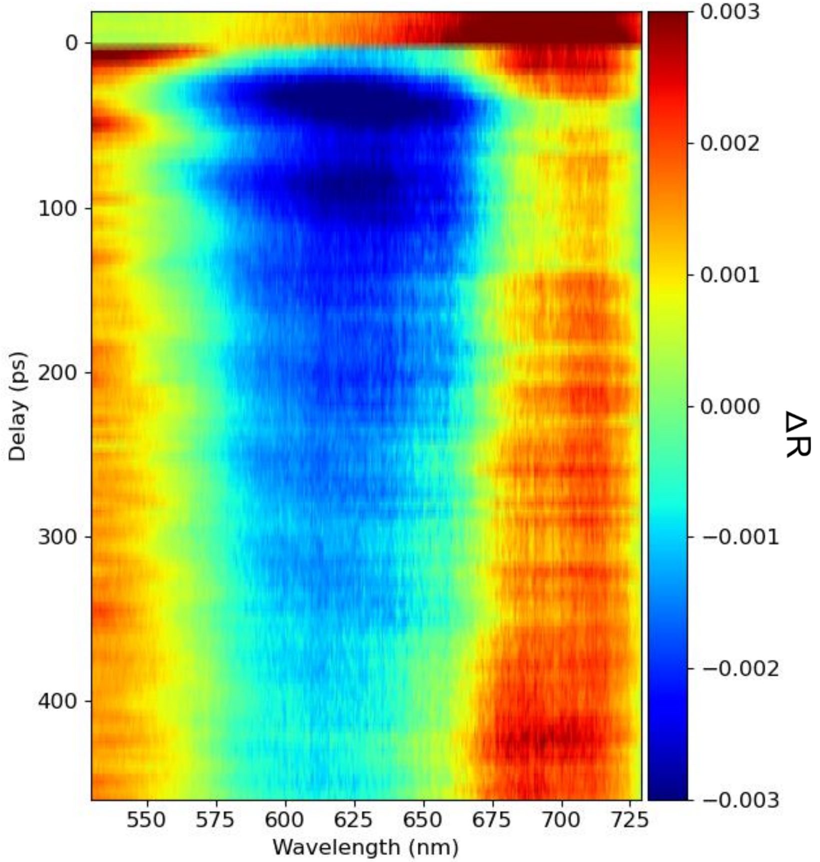
Time Domain Brillouin Scattering dependent of speed of sound (v), refractive index (n) and probing wavelength (λ):

$$F_B = \frac{2\,n\,v}{\lambda}$$

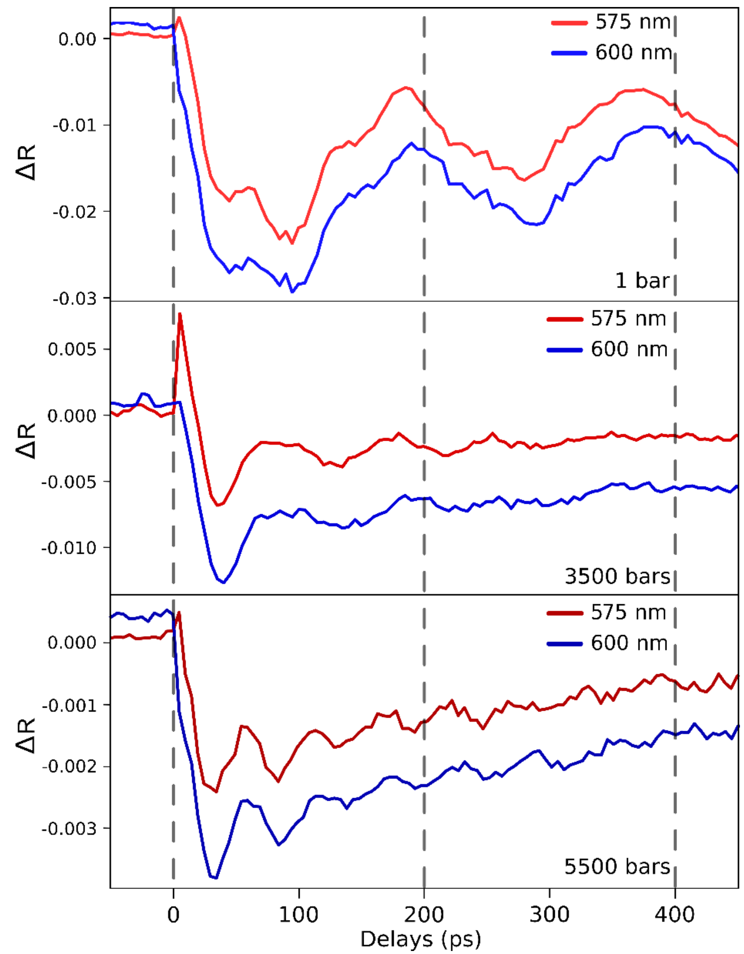
T. Parpiiev et al , *Appl. Phys. Lett.* , 111, 151901 (2017)

Time Dependent Brillouin Scattering in (EDO-TTF)-XF_6

acoustic timescale / 5500 bars



Broadband reflectivity changes after 800 nm pumping



Increase of Brillouin frequency F_B:

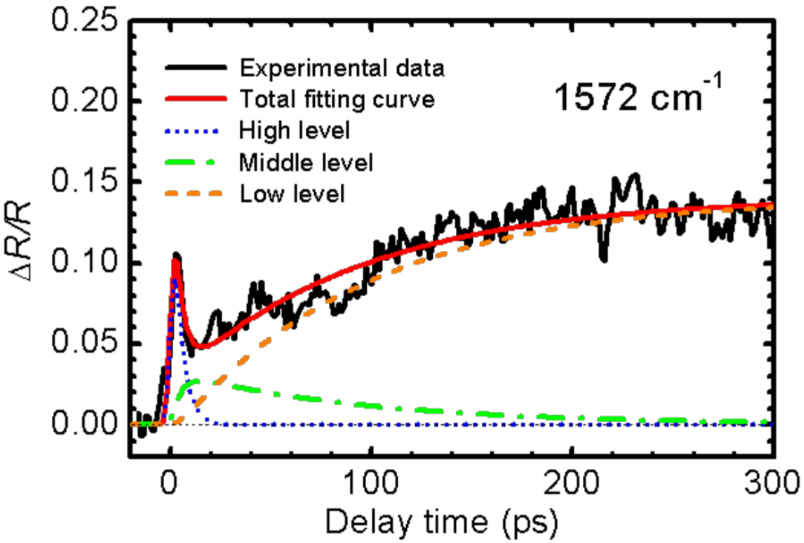
- 5.5 GHz (1 bar) to 15 GHz (5500 bars)

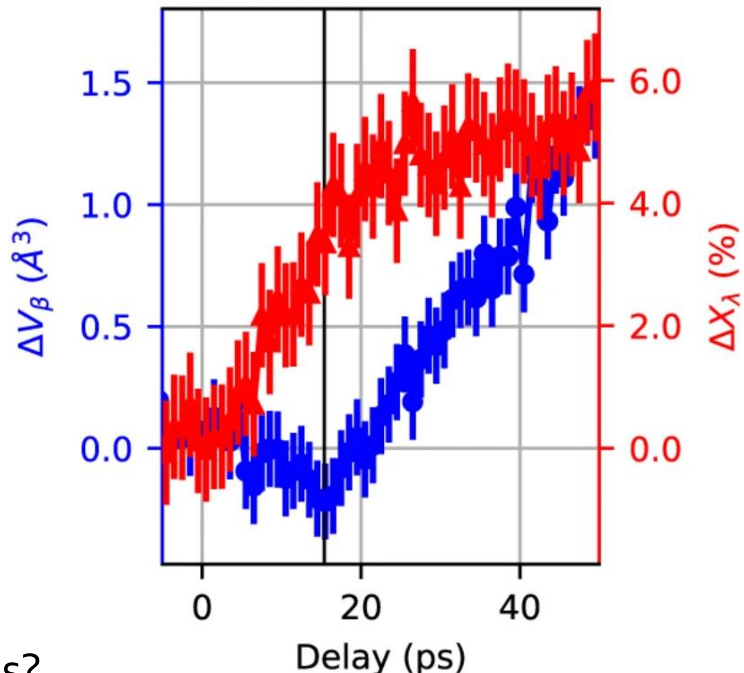
Photo-induced strain effects

Article | Open Access | Published: 23 February 2021

Strain wave pathway to semiconductor-to-metal transition revealed by time-resolved X-ray powder diffraction

Transient IR reflectivity on (EDO-TTF)PF_6





Slower dynamics on 100's ps? Acoustic contributions?

Acoustic/strain processes might be relevant in the establishment of a new macroscopic phase and likely to occur in the 10 to 100 ps timescale

T. Ishikawa et al , *Crystals*, 2(3), 1067 (2012)

C. Mariette et al , *Nat Com*, 12(1), 1-11 (2021)

Take Home Messages

- Broadand ultrafast optical spectroscopy under high pressure (0-6kbars)
- Time resolution as good as ~100 fs
- Observation of coherent optical phonons and thermo-elastic processes
- Strong modification of (v/n) in molecular materials