Time-resolved non-linear spectroscopy at FEL sources

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Outline

• Ultrafast time-resolved Raman in the visible regime
  • Frequency domain (FSRS) vs Time domain (IVS): molecular movies of heme proteins and structural rearrangements induced by photo-carriers in hybrid perovskites.

• Nonlinear optics in the soft X-Ray regime
  • Manipulating the spectral properties of soft X-ray pulses.

• X-rays perspectives
Making molecular movies using light flashes: the pump-probe scheme

\[ \Delta t \leq 10^{-12} \text{ s} \]
\[ \Delta x \leq 10^{-10} \text{ m} \]
#1: Time Resolved Diffraction
#2: Time Resolved Raman
Raman for pedestrians

Inelastic light scattering

\[ P(t) = \alpha(t)E(t) \]
(spontaneous) time resolved Raman for pedestrians

Inelastic light scattering

\[ P(t) = \alpha(t)E(t) \]
Transient spontaneous Raman spectroscopy

Raman Spectrum: Structural Sensitivity

Pulsed Raman excitation (FT limited)

Fourier Transform Limit: $\delta \omega \delta t \geq 15 \text{ ps cm}^{-1}$
Two Approaches

**FSRS:** Femtosecond Stimulated Raman Spectroscopy (frequency-domain Raman)

**IVS:** Impulsive Vibrational Spectroscopy (time-domain Raman)

FSRS-Probe

IVS-Probe

Photo-reaction coordinate(s)
Two Approaches

FSRS: Femtosecond Stimulated Raman Spectroscopy (frequency-domain Raman)

IVS: Impulsive Vibrational Spectroscopy (time-domain Raman)
FSRS in a nutshell:

\[ \frac{d^2 Q}{dt^2} + 2\gamma \frac{dQ}{dt} + \omega_0^2 Q = \alpha_0' |\tilde{E}(\vec{r}, t)|^2 \]

\[ \frac{\partial^2 E(z, t)}{\partial z^2} - \frac{1}{c^2} \frac{\partial^2 E(z, t)}{\partial t^2} \approx \frac{4\pi}{c^2} N\alpha_0' \frac{\partial^2 (QE(z, t))}{\partial t^2} \]
FSRS in a nutshell:

Combining spectral and temporal resolution

“Reaction” coordinate

Energy

Timeline
How it works: the Heme-proteins case

O₂ transport, storage and sensing. Intracellular trafficking, oxygen sensing, NO synthesis and regulation, oxidative metabolism, apoptosis and regulation of DNA expression.

Function $\leftrightarrow$ bond breaking and recombination
FSRS at work: sub-ps in Mb

 Mb deOxy

Mb CO

\( \Delta t = 0.25 \text{ ps} \)

\( \Delta t = 0 \text{ ps} \)

\( \Delta t = 30 \text{ ps} \)

\( \Delta t = 5.0 \text{ ps} \)

\( \Delta t = 3.0 \text{ ps} \)

\( \Delta t = 1.5 \text{ ps} \)

\( \Delta t = 0.40 \text{ ps} \)

\( \Delta t = 0.30 \text{ ps} \)

\( \Delta t = -10 \text{ ps} \)

\( \tau_\sim = 0.29 \text{ ps} \)

\( \tau_\sim = 5.2 \text{ ps} \)

Analysis of the \( \nu_4 \) Mb deOxy MbCO

Transient spontaneous Raman spectroscopy
Two Approaches

FSRS: Femtosecond Stimulated Raman Spectroscopy (frequency-domain Raman)

IVS: Impulsive Vibrational Spectroscopy (time-domain Raman)
Two femtosecond pulses are exploited for measuring the vibrational spectrum.

The coherently stimulated third-order polarization oscillates in T and modulates the transmitted probe pulse.
IVS in a nutshell:

- Two femtosecond pulses are exploited for measuring the vibrational spectrum.
- The coherently stimulated third-order polarization oscillates in $\Delta T$ and modulates the transmitted probe pulse.

Raman features can be extracted by Fast Fourier Transforming (FFT).
Two femtosecond pulses are exploited for measuring the vibrational spectrum.

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IVS in a nutshell:

- Two femtosecond pulses are exploited for measuring the vibrational spectrum.
- The coherently stimulated third-order polarization oscillates in $T$ and modulates the transmitted probe pulse.
Two Approaches

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IVS: Impulsive Vibrational Spectroscopy (time-domain Raman)

Key ingredients: Ultrashort pulses, with large spectral tunability.
Non-linear spectroscopy at FEL sources

Controlling the spectral properties of X-Ray pulses would provide novel opportunities for non-linear photonics and time-resolved spectroscopy at FEL facilities.

At visible wavelengths self-phase modulation (SPM) represents one of the primary tools used for tuning the spectral bandwidth by Kerr effect in transparent media.

Idea: studying similar nonlinear effects, but in the X-Ray regime, at EIS-TIMEX of the FERMI FEL in Trieste

Non-linear spectroscopy at FEL sources

Experimental results on Mg samples

Spectral modification as a function of pulse fluence and energy

Strong dependence on the interaction process between light and core electrons

Studying similar nonlinear effects, but in the X-Ray regime, at EIS-TIMEX of the FERMI FEL in Trieste

Non-linear spectroscopy at FEL sources

Experimental results on Mg samples

Above abs. edge:

- The dispersive lineshapes in the differential spectra indicate a pronounced blue-shift: SPM effect induced by photo-induced core electron ionization.

Core photoelectrons are promoted nearly above the Fermi level, generating a transient hot dense ionized plasma.
Non-linear spectroscopy at FEL sources

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\[ E(r, t) = \Re \{ \psi(r, t) e^{ik_0z - i\omega_0 t} \hat{n} \} \]

SPM induced phase

\[ \phi_{\text{NL}}(r, t) = \chi^{(3)} |\psi(r, t)|^2 k_0 L \]

Delayed thermal response of electrons (DTRE)

\[ \phi_{\text{DTRE}}(r, t) = \int dt' h(t') |\psi(r, t - t')|^2 k_0 L \]

SPM alone does not account for the red-shift at low fluences
Non-linear spectroscopy at FEL sources

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Strong dependence on the interaction process between light and core electrons

\[ E(r, t) = \text{Re}[\psi(r, t)e^{ik_0z - i\omega_0 t \hat{n}}] \]

SPM + DTRE

\[ \phi_{\text{NL}}(r, t) = \chi^{(3)}|\psi(r, t)|^2 k_0 L \]
\[ \phi_{\text{DTRE}}(r, t) = \int dt' h(t')|\psi(r, t - t')|^2 k_0 L \]
Non-linear spectroscopy at FEL sources

Experimental results on Mg samples

Spectral modification as a function of pulse fluence and energy:
- Blue shift for above edge interaction,
- Red shift for below edge interaction at low fluences
- Spectral broadening for below edge interaction at high fluences

Demonstrated self-induced spectral beam modification by interaction with sub-micrometric foils of selected monoatomic materials in the EUV
Time-Resolved nonlinear Raman Spectroscopy: X ray perspectives...
#1: FSRS with X ray pump

Capturing structural evolution during photofragmentation
#2: IVS with X ray probe

Motivation:

The key iron-histidine mode is very weak in the Soret Resonant Raman spectrum.
#2: FSRS with X ray probe

Generate **ground state** coherences with VIS, reaction pathway resonantly probed with X-rays


The congested FSRS spectrum cannot uniquely identify the reaction pathway

Sharpening Raman resonance at the atomic level: Carbon motions in Rhodopsin