Time-resolved non-linear spectroscopy at FEL sources

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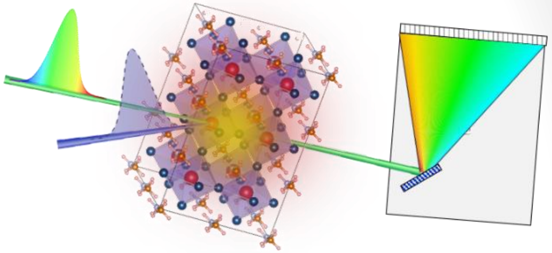
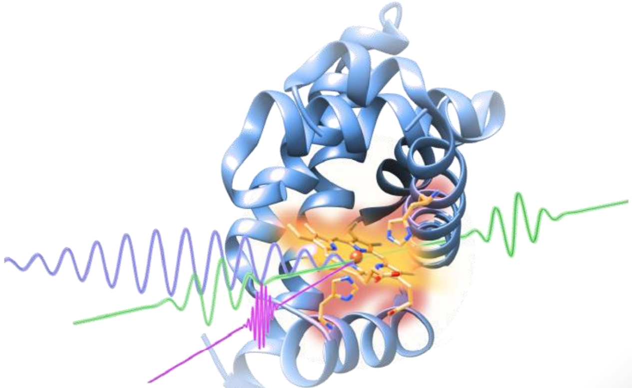
Outline

- 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.



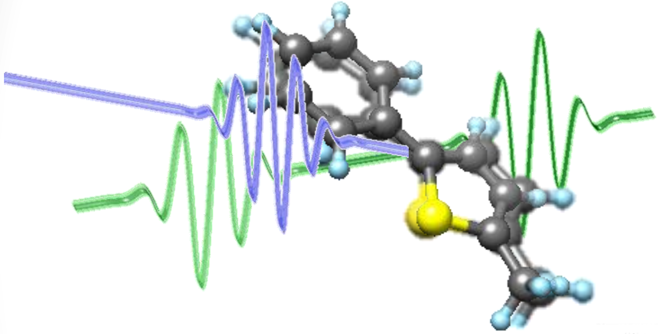
- Nonlinear optics in the soft X-Ray regime
    - Manipulating the spectral properties of soft X-ray pulses.
- X-rays perspectives

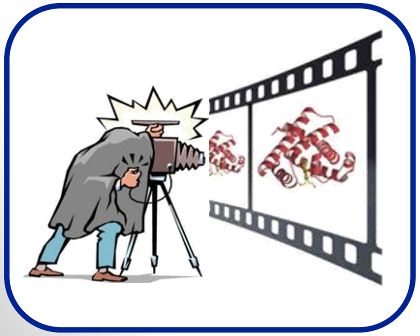


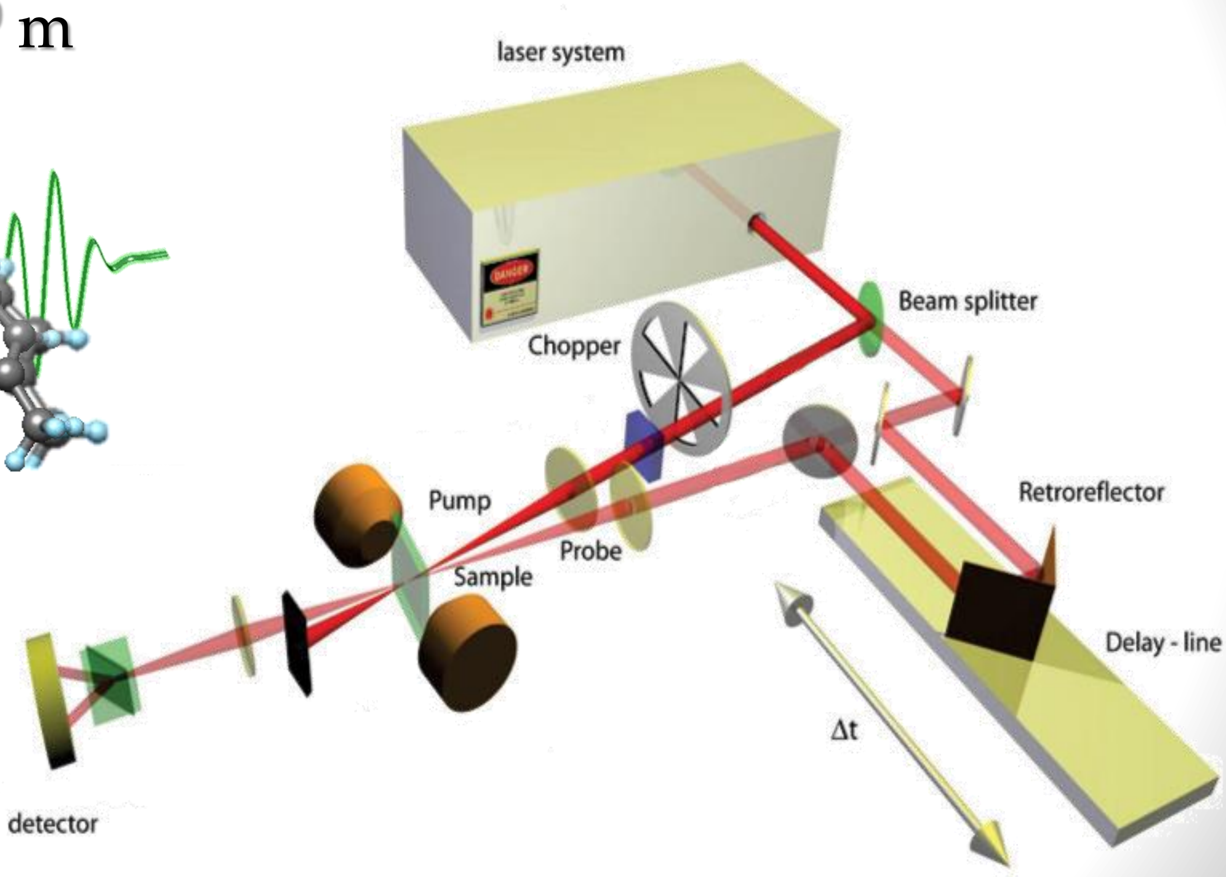
Making molecular movies using light flashes: the pump-probe scheme

$\Delta t \leq 10^{-12}$ s

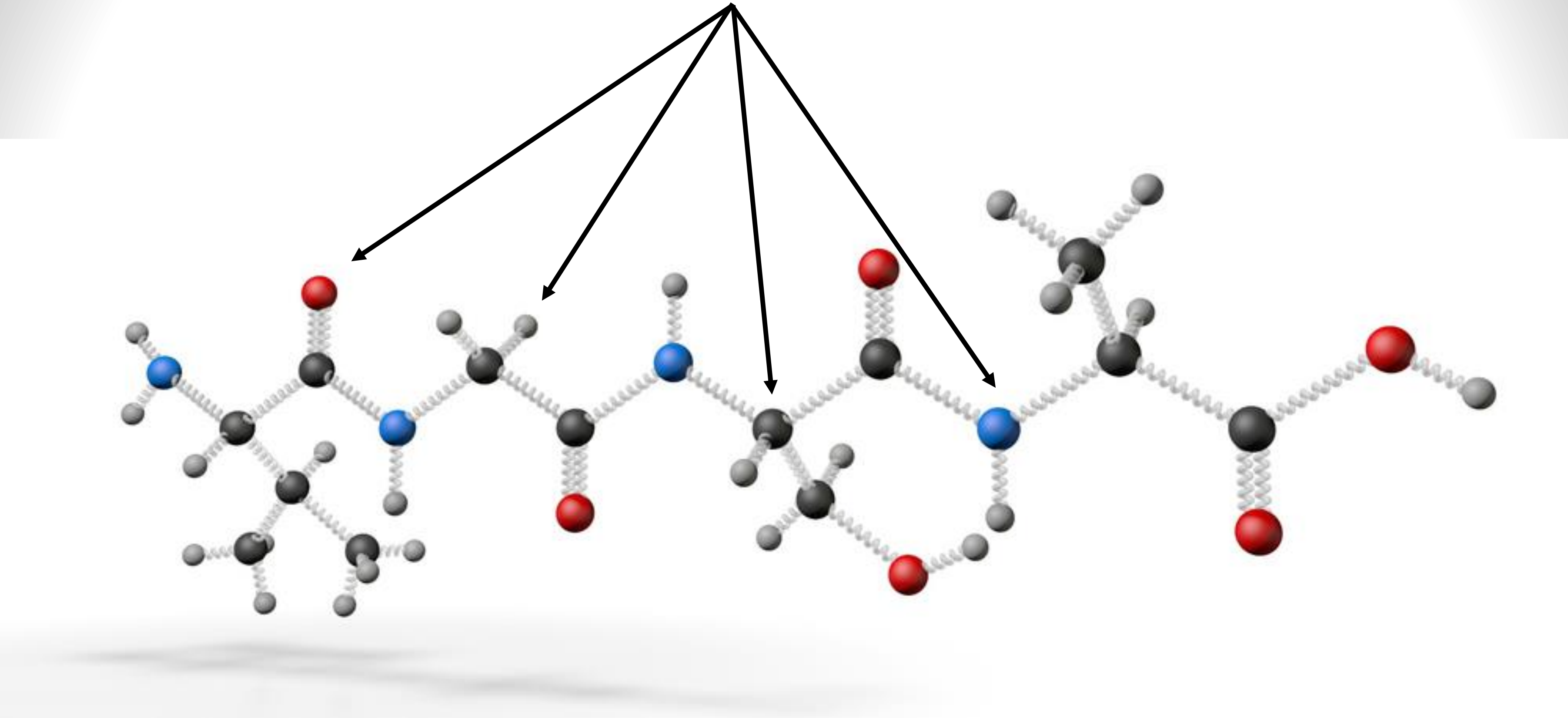
$\Delta x \leq 10^{-10}$ m



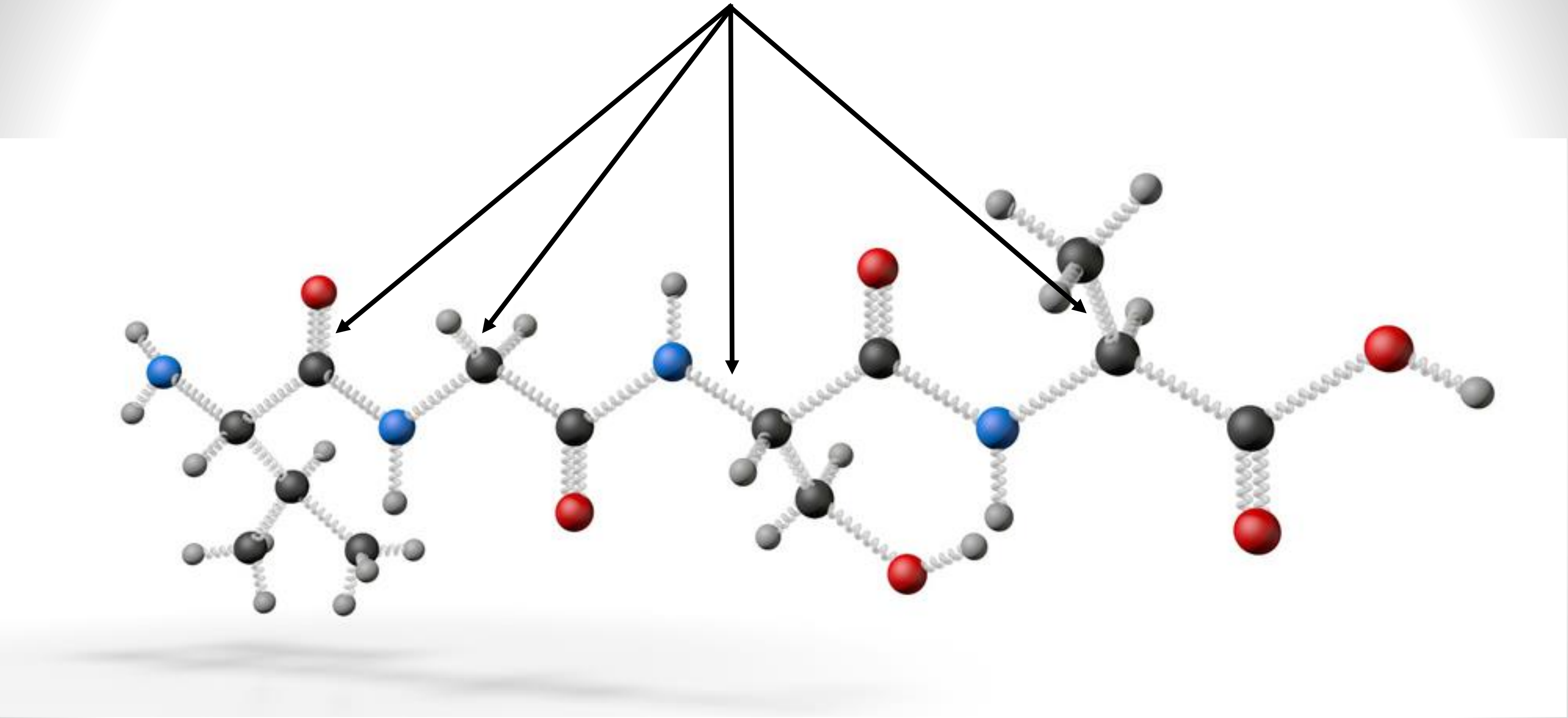




#1: Time Resolved Diffraction

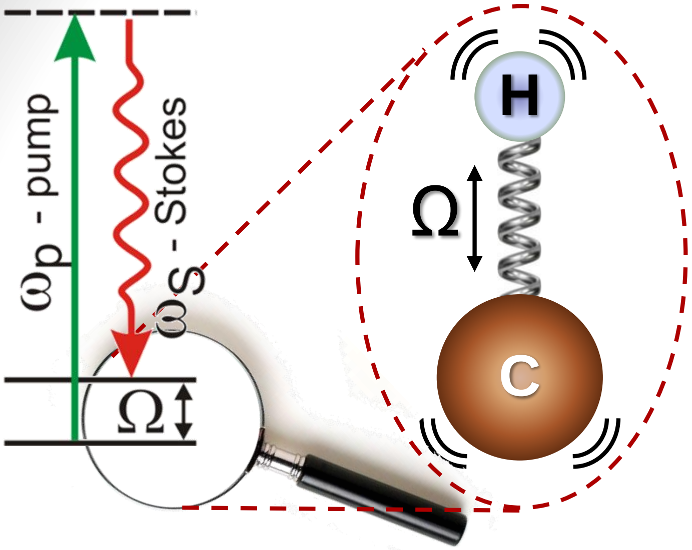


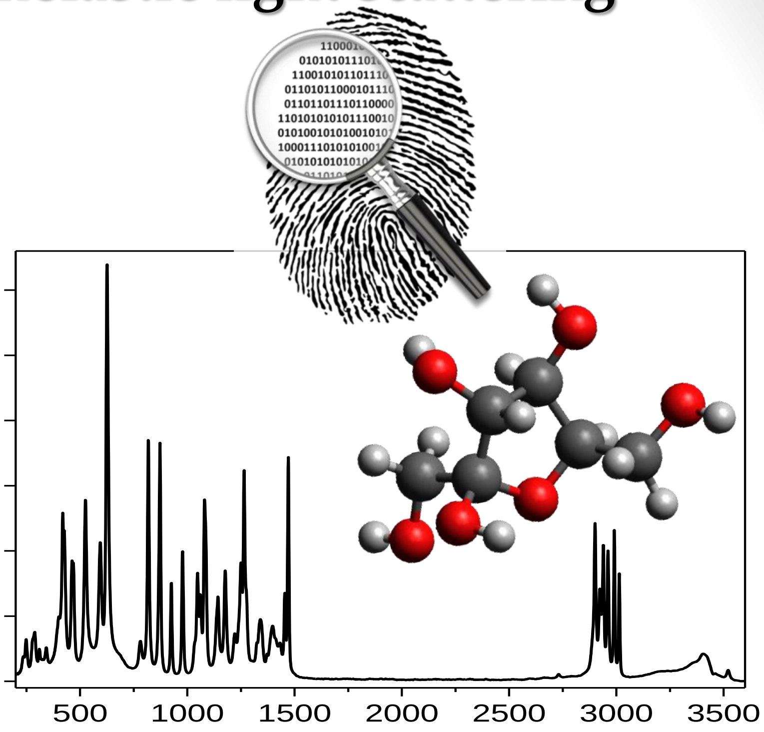
#2: Time Resolved Raman



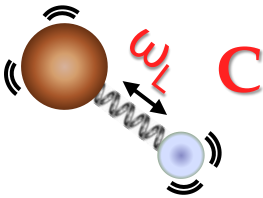
(spontaneous) Raman for pedestrians

Inelastic light scattering





$$P(t) = \alpha(t)E(t)$$



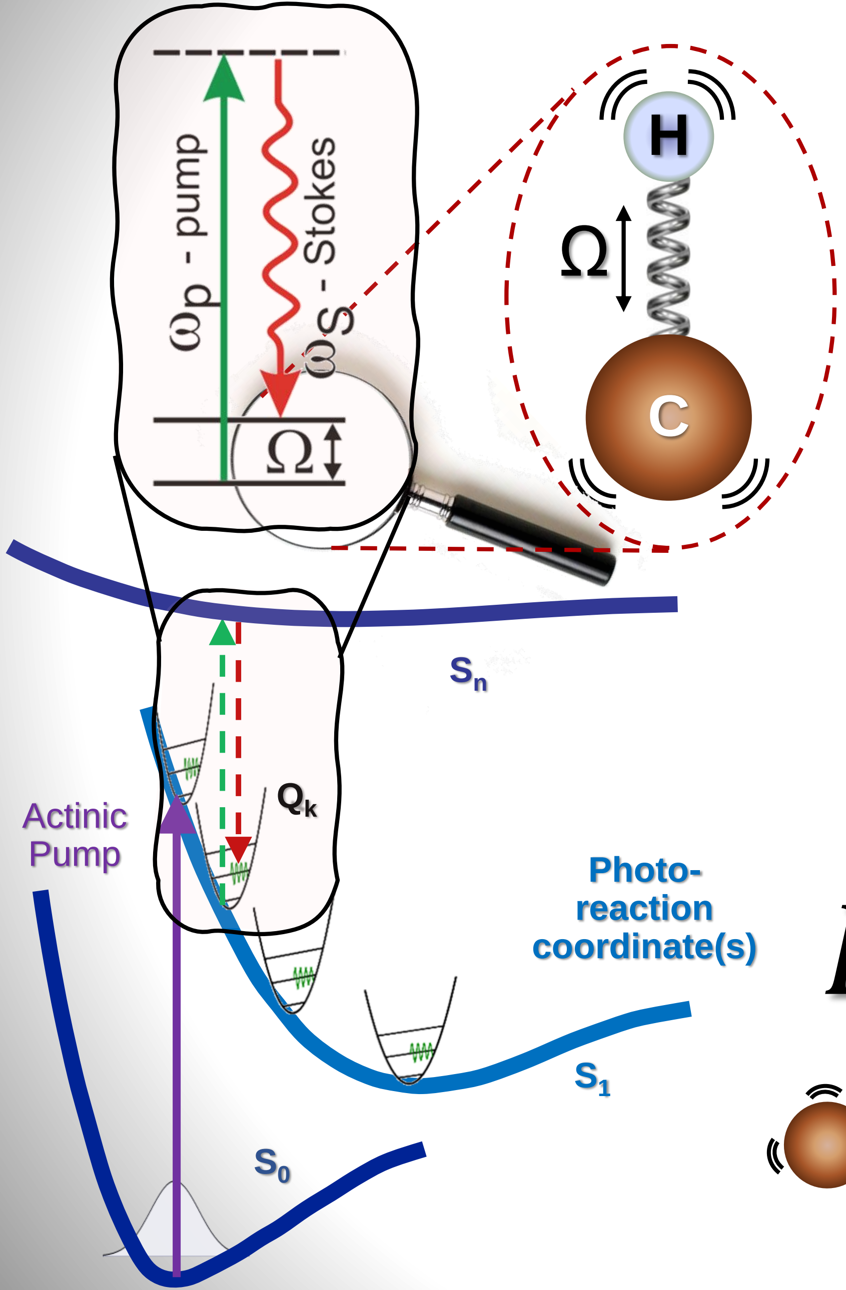
Chemistry

Low frequency
~30 Thz

Optics

High frequency
~600 Thz

(spontaneous) time resolved **Raman for pedestrians**



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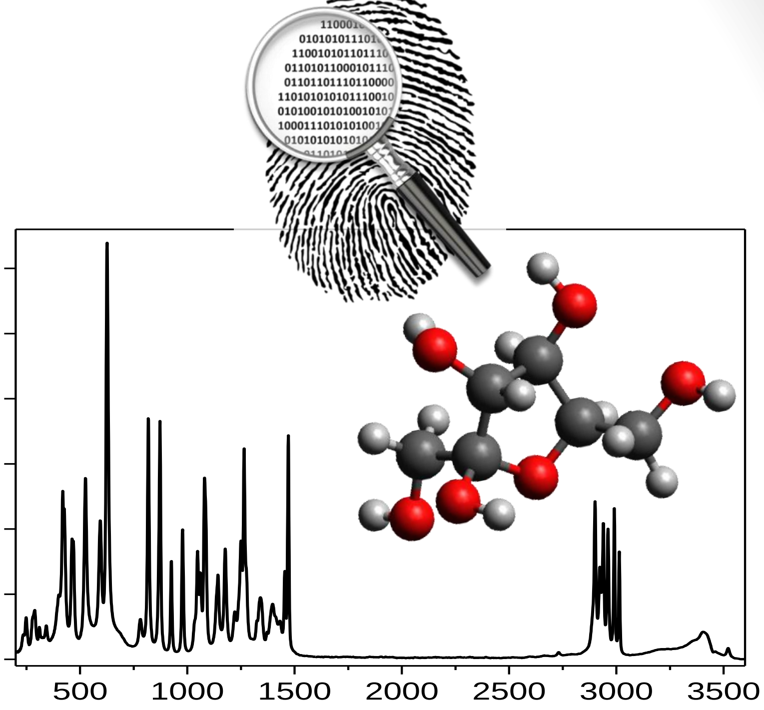

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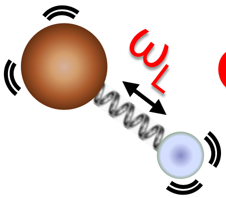

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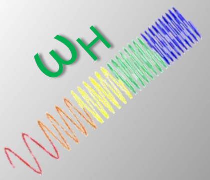
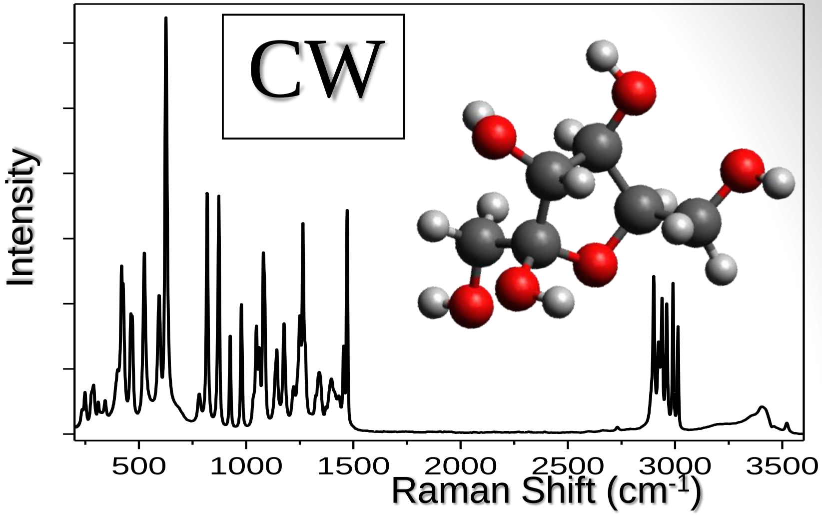
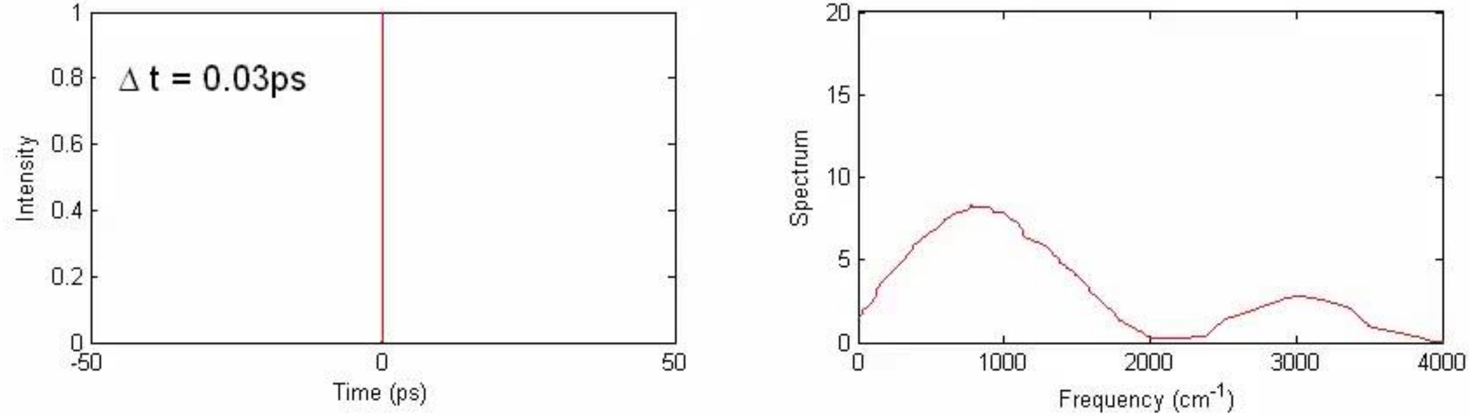


Transient spontaneous Raman spectroscopy

Raman Spectrum:
Structural Sensitivity



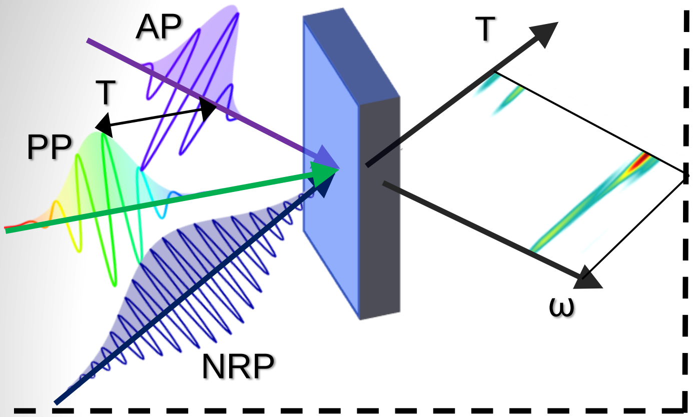
Pulsed Raman excitation (FT limited)



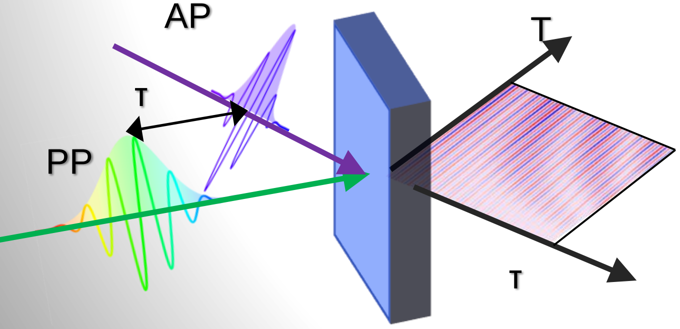
Fourier Transform Limit: $\delta\omega \, \delta t \geq 15 \ ps \ cm^{-1}$

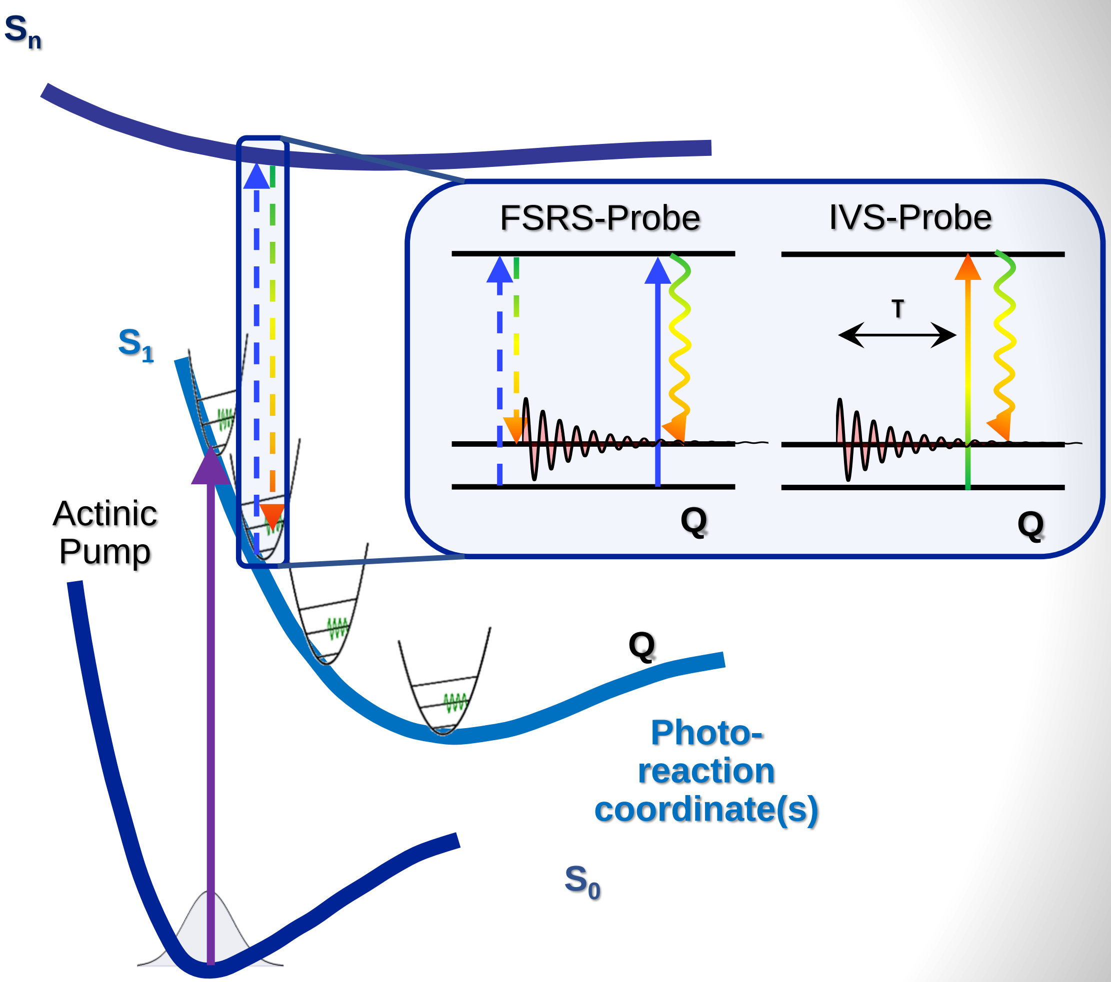
Two Approaches

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



IVS: Impulsive Vibrational Spectroscopy (time-domain Raman)





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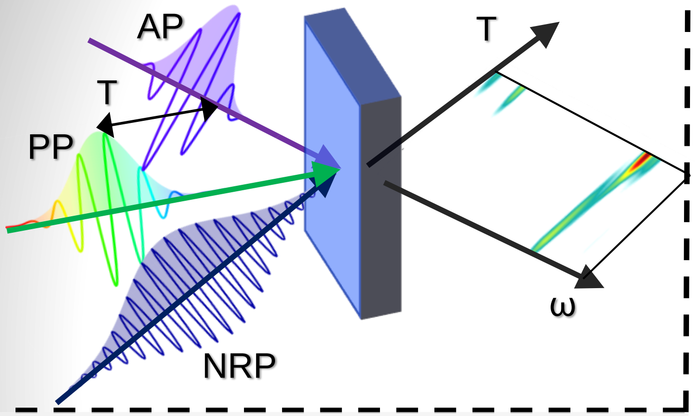

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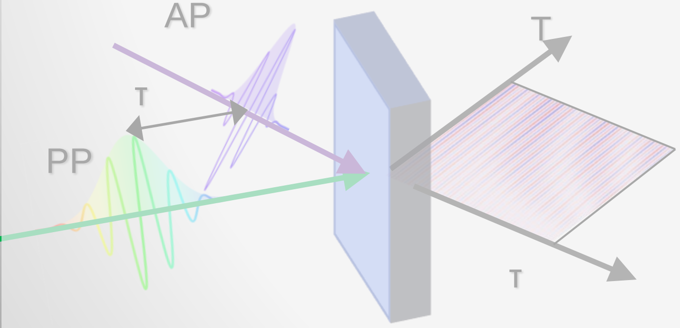
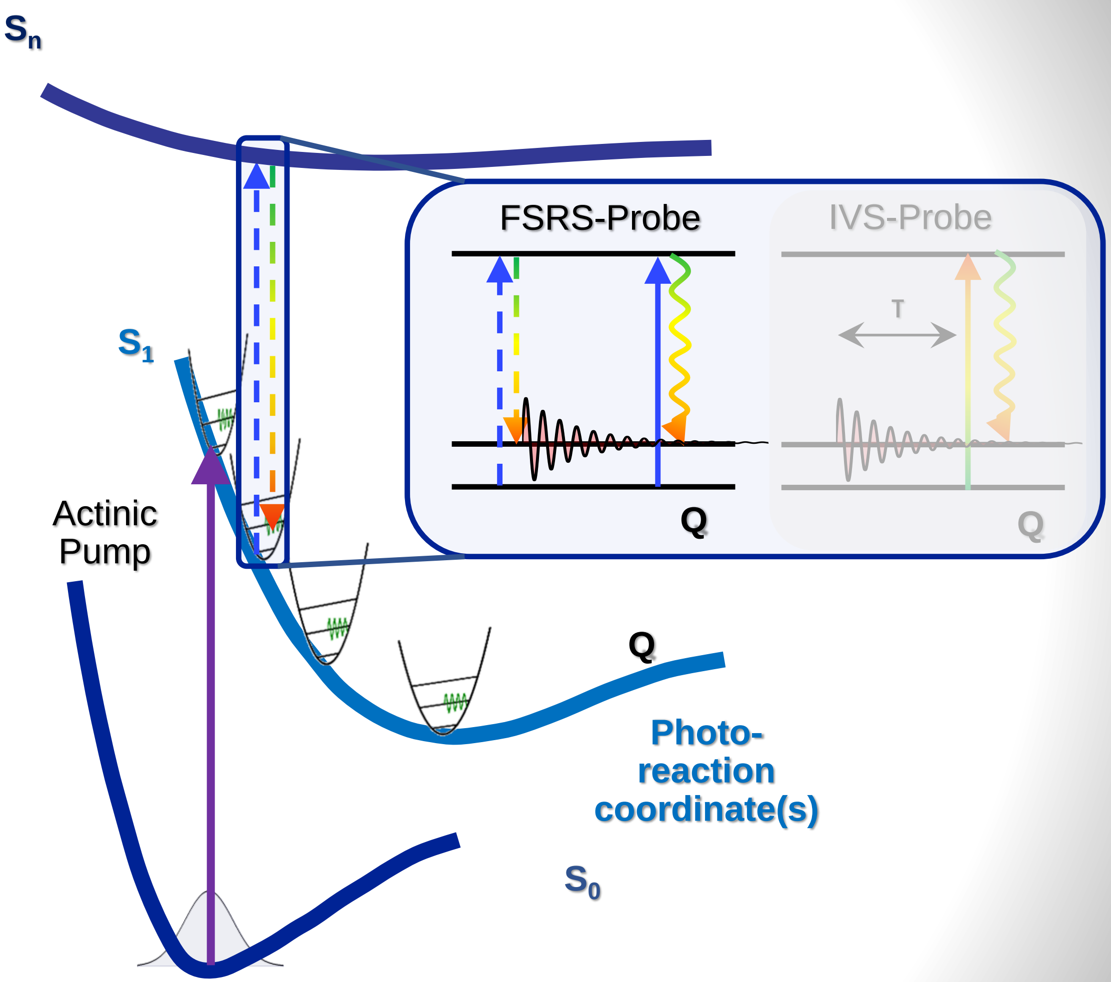
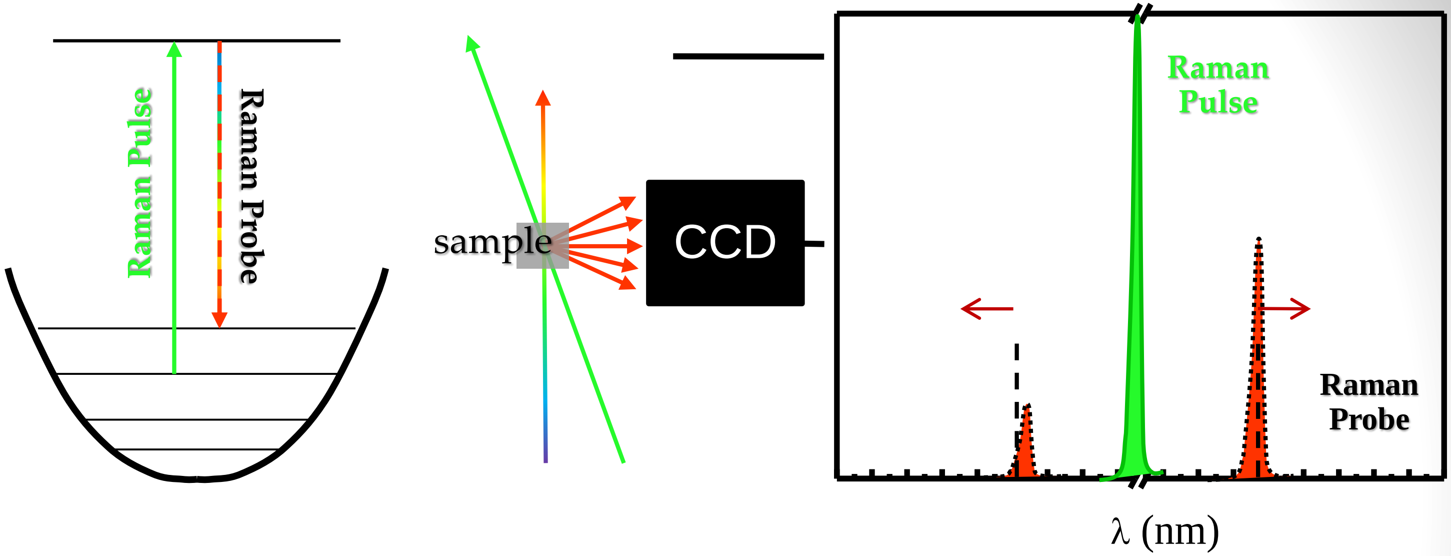


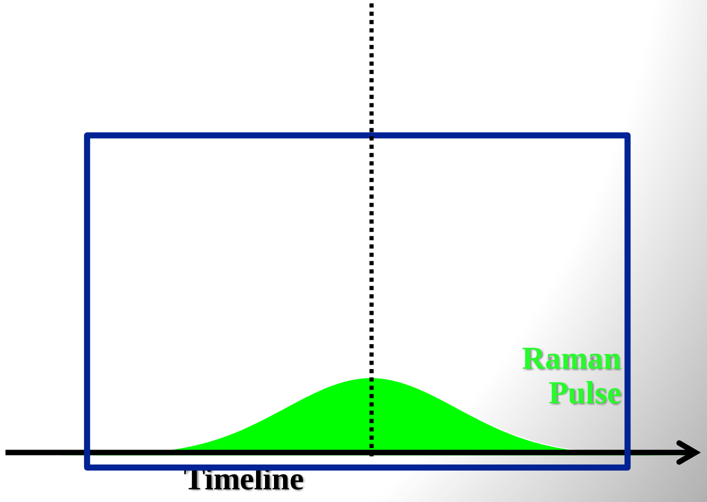


FSRS in a nutshell:



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

$$\frac{\partial^2E(z,t)}{\partial z^2}-\frac{1}{c^2}\frac{\partial^2E(z,t)}{\partial t^2}\approx\frac{4\pi}{c^2}N\alpha_0'\frac{\partial^2(QE(z,t))}{\partial t^2}$$



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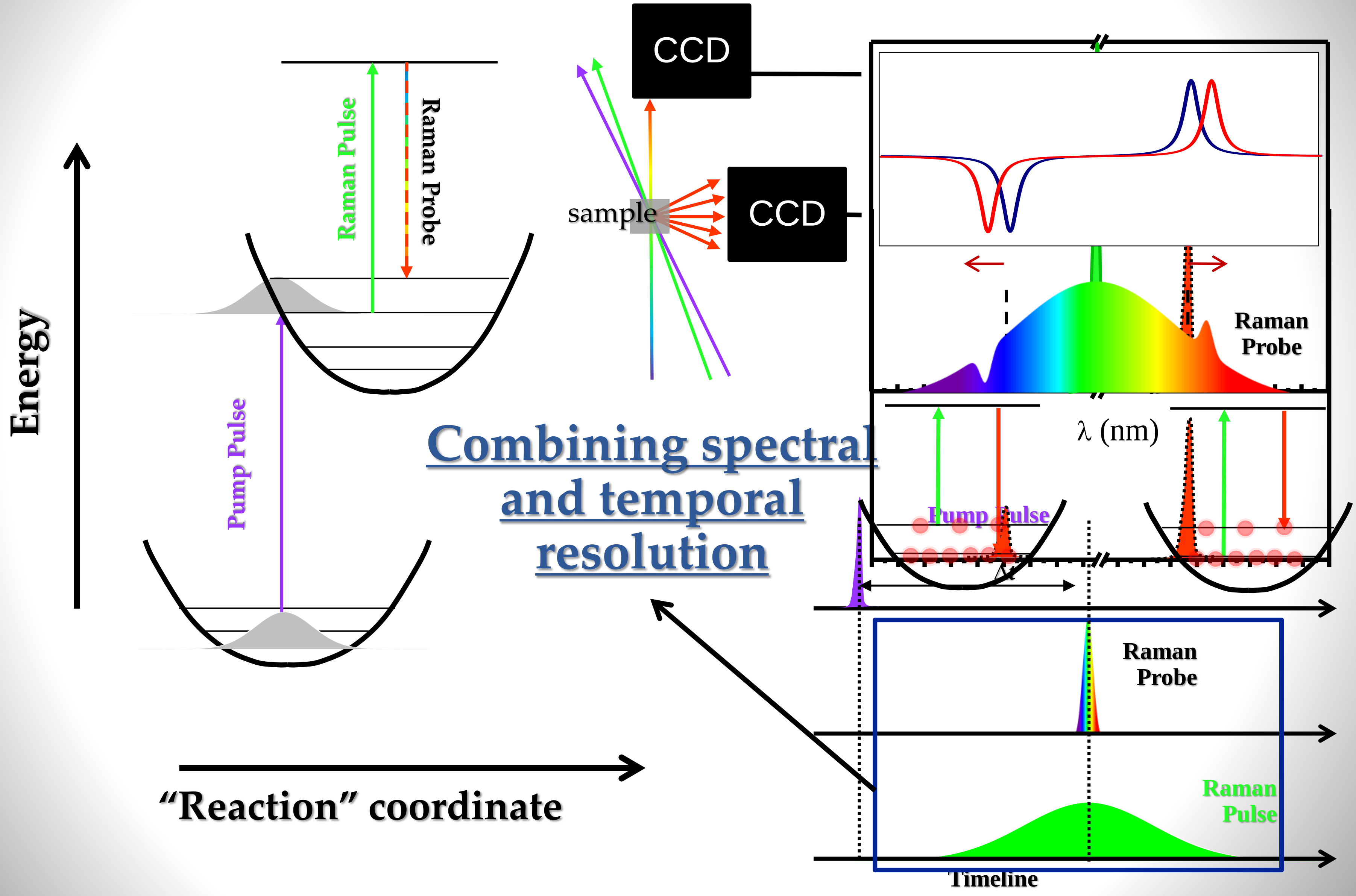
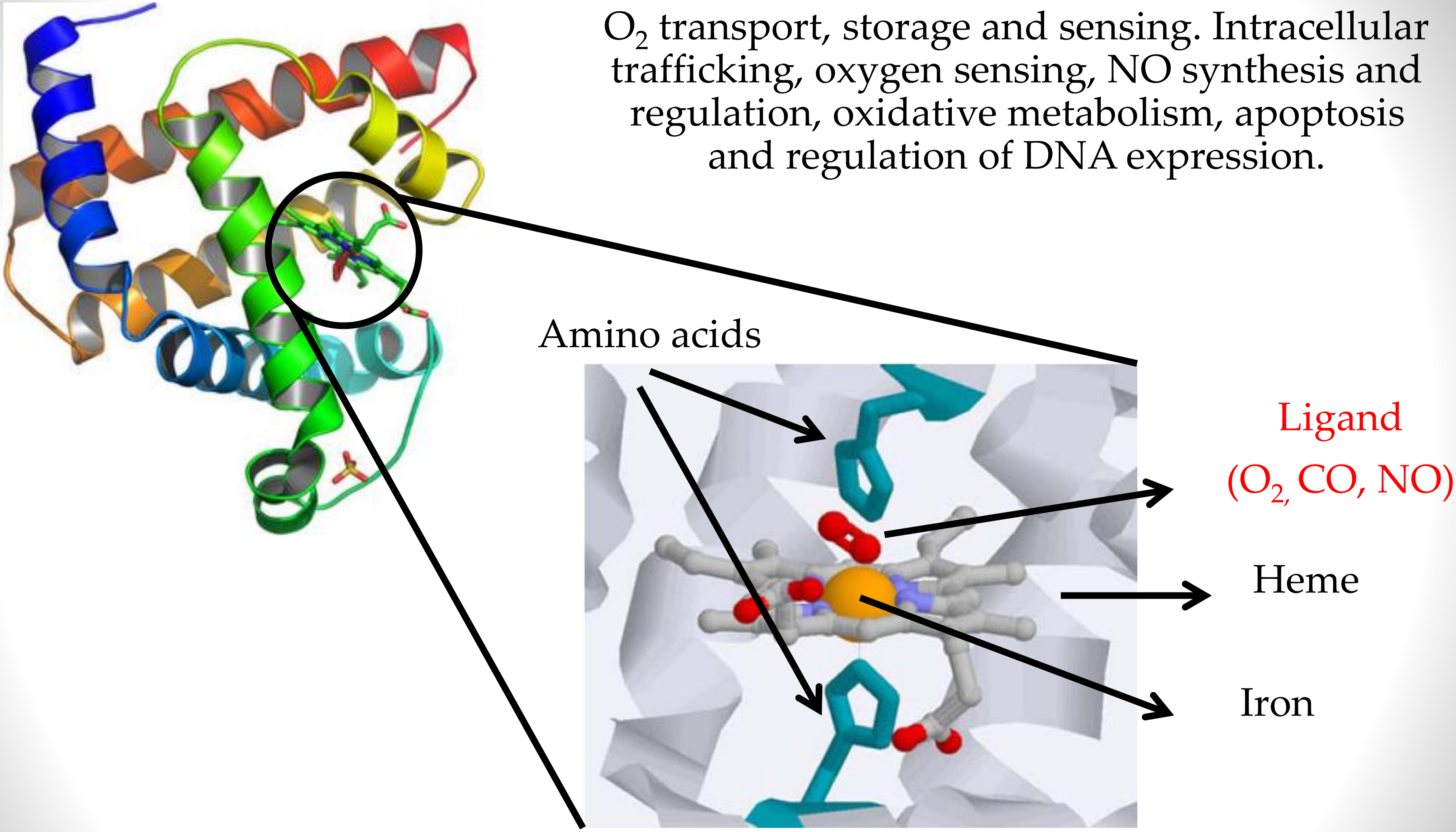


Combining spectral and temporal resolution

How it works: the Heme-proteins case

O_2 transport, storage and sensing. Intracellular trafficking, oxygen sensing, NO synthesis and regulation, oxidative metabolism, apoptosis and regulation of DNA expression.



Amino acids

Ligand

(O_2, CO, NO)

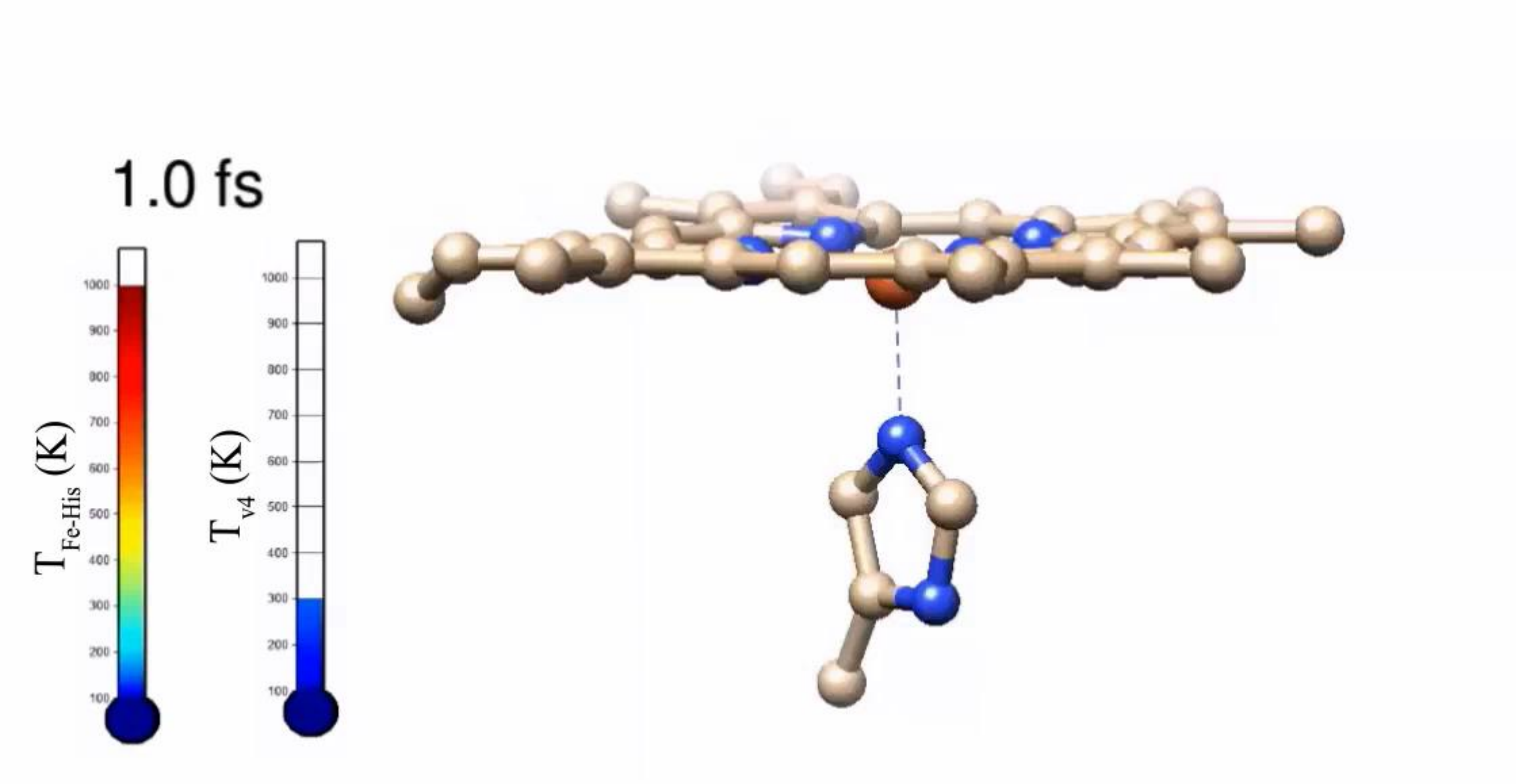
Heme

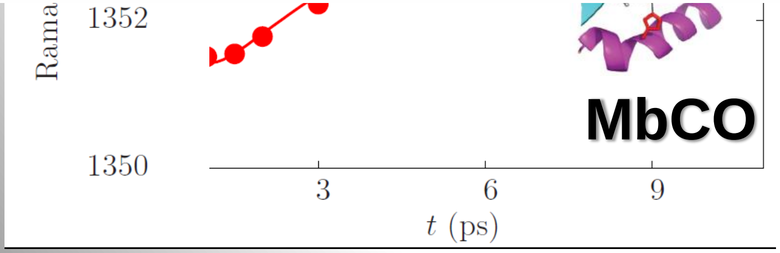
Iron

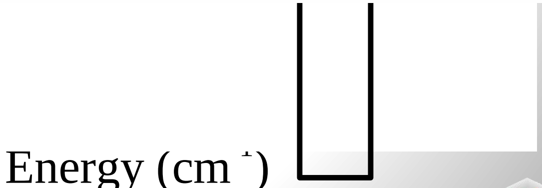
Function ←→ bond breaking and recombination

FSRS at work: sub-ps in Mb

Mb deOxy







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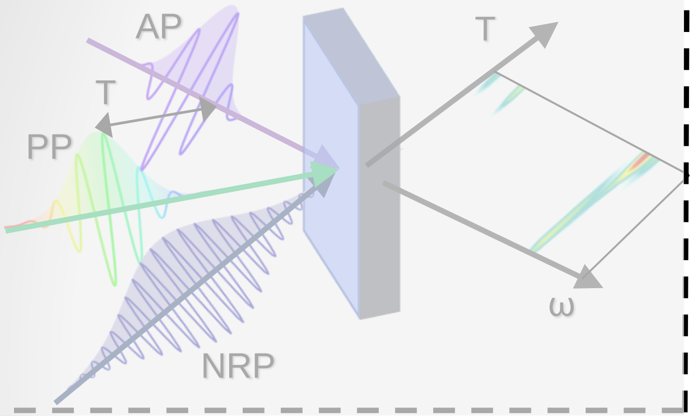

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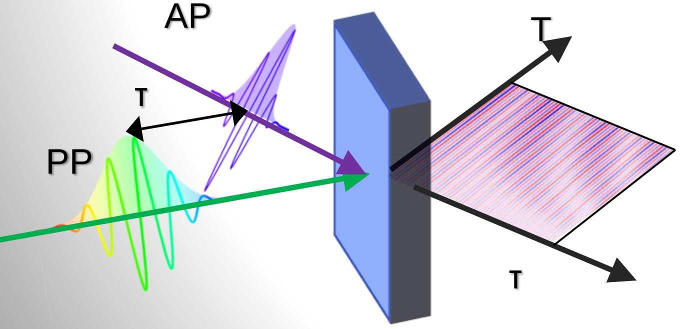

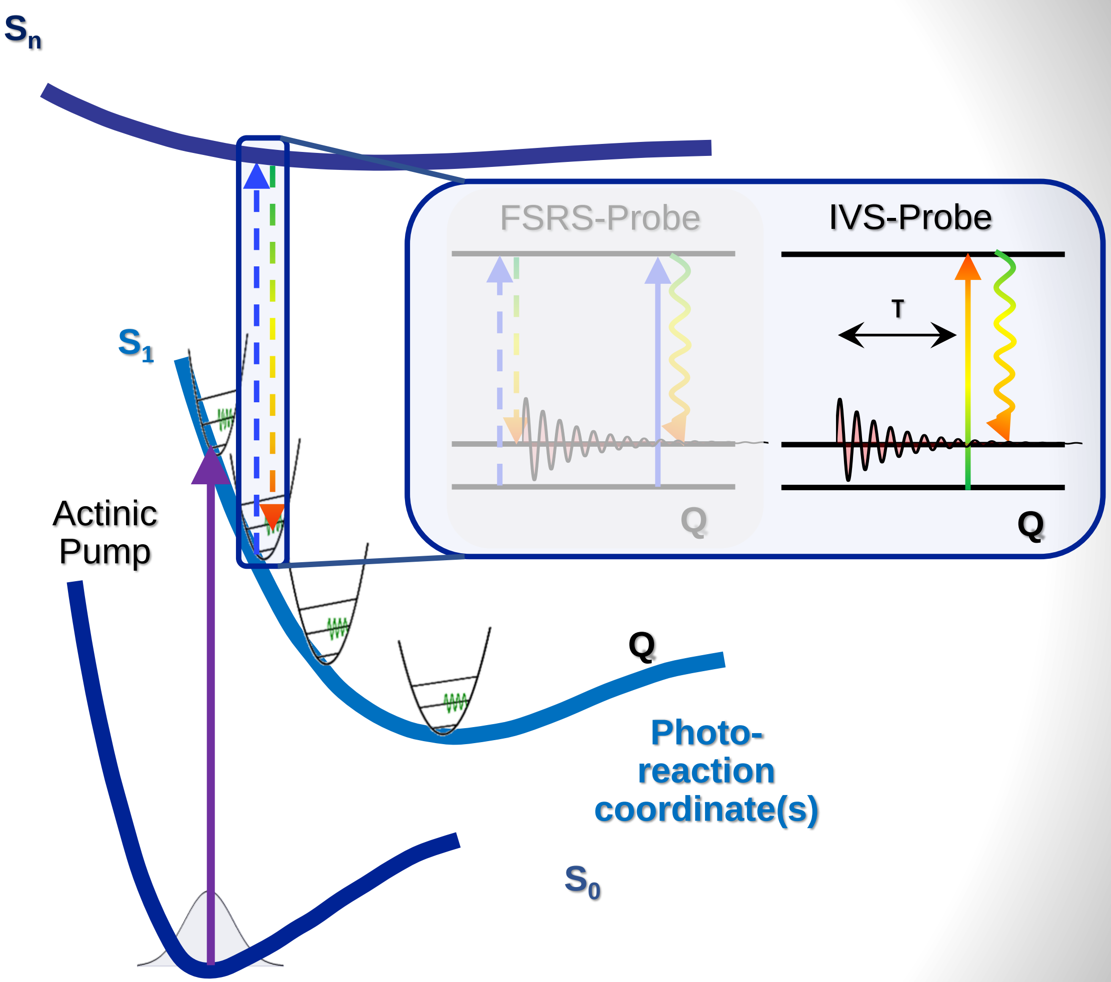

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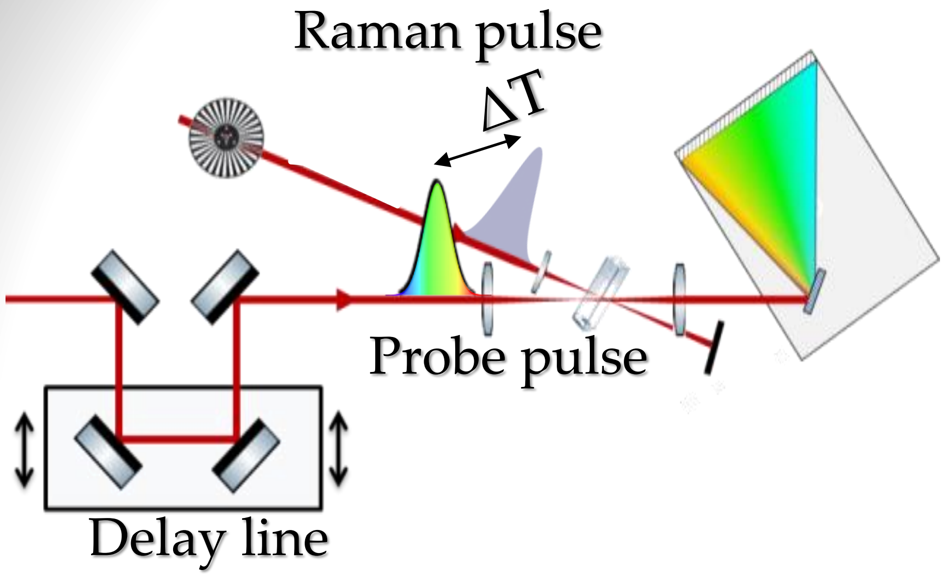

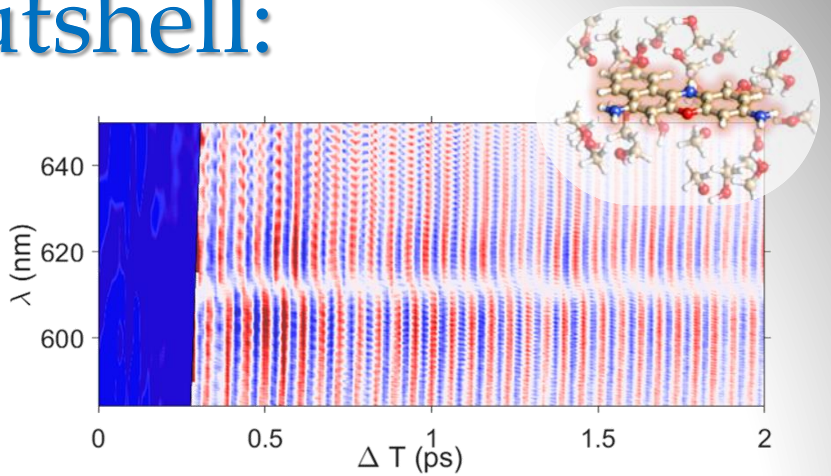

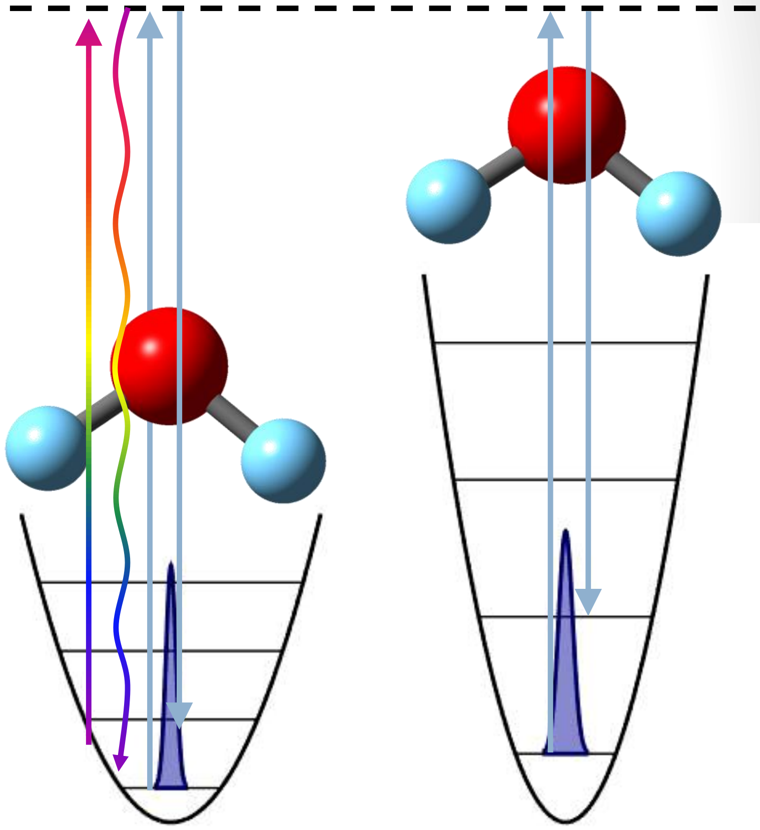

- Two femtosecond pulses are exploited for measuring the vibrational spectrum
- The coherently stimulated third-order polarization oscillates in T and modulates the transmitted probe pulse.

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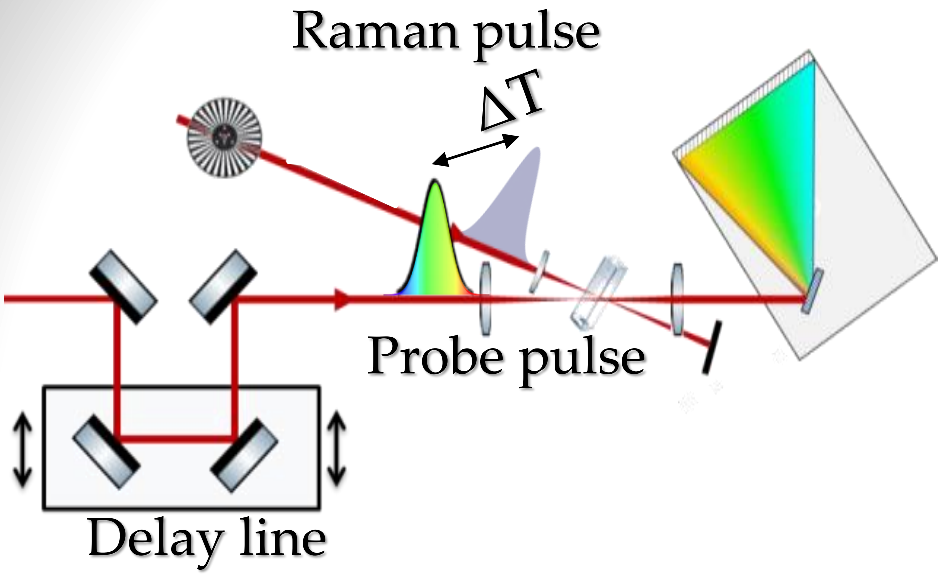

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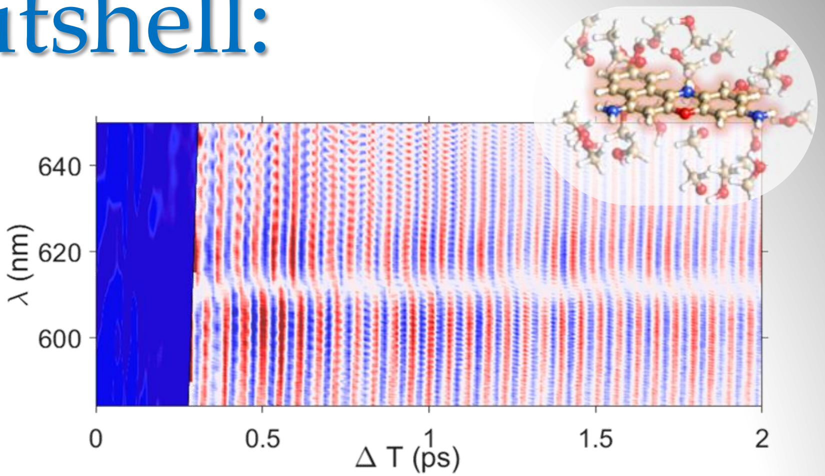
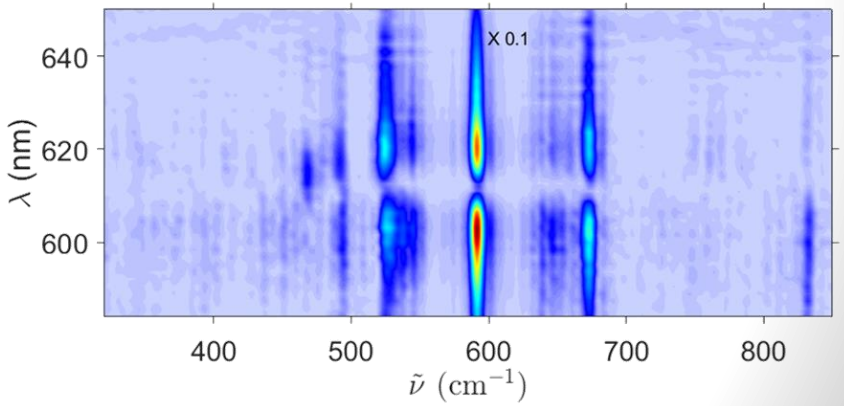


FFT



Raman features can be extracted by Fast Fourier Transforming

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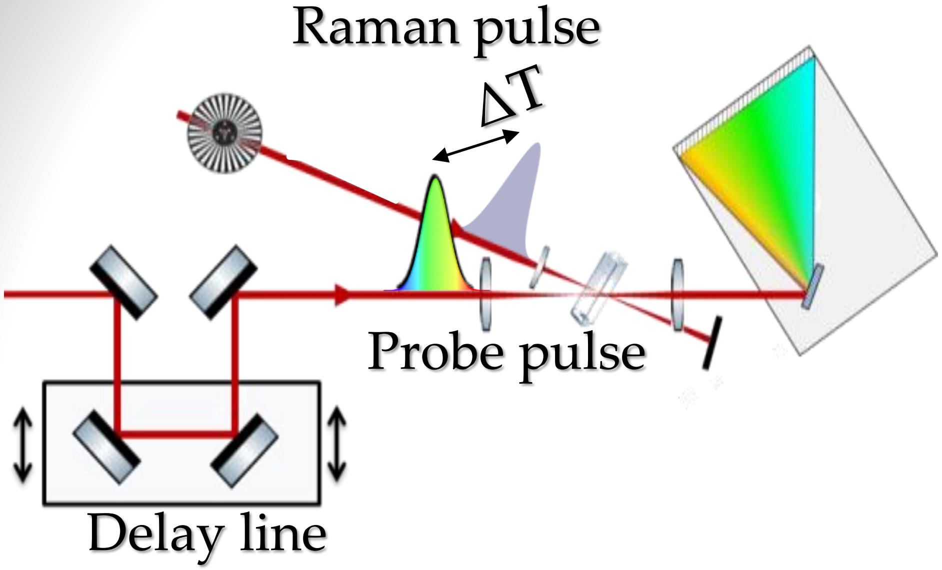

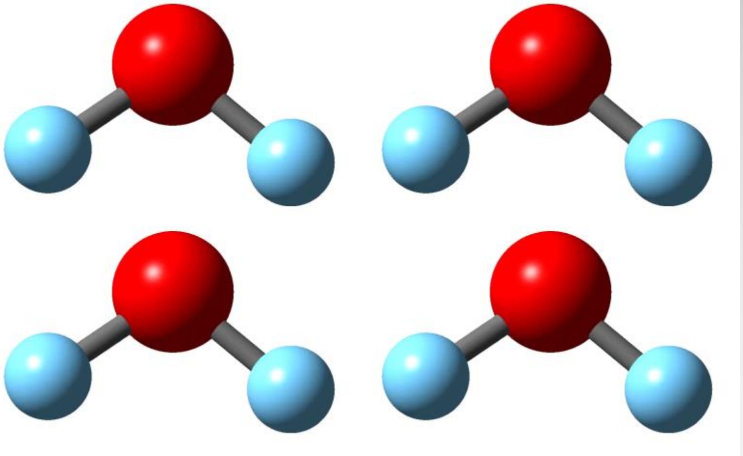

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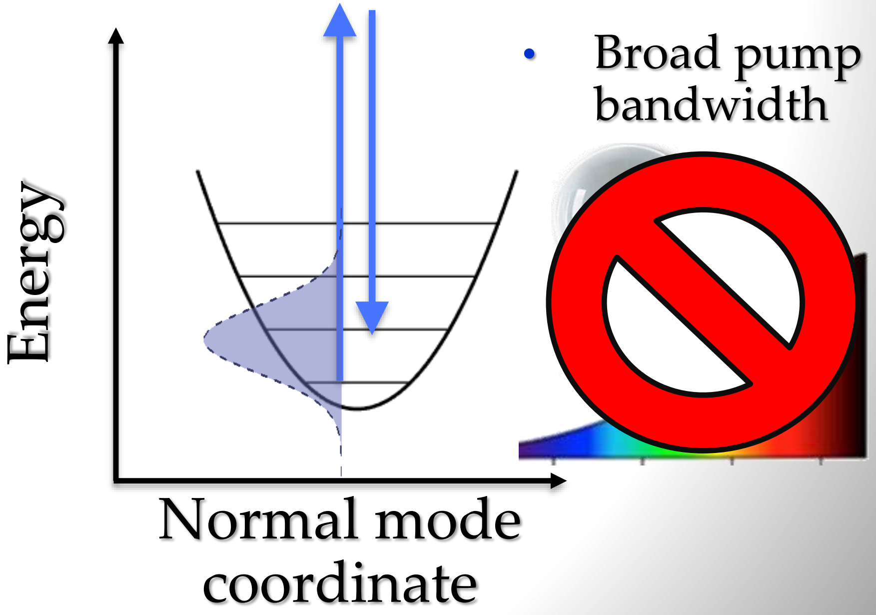

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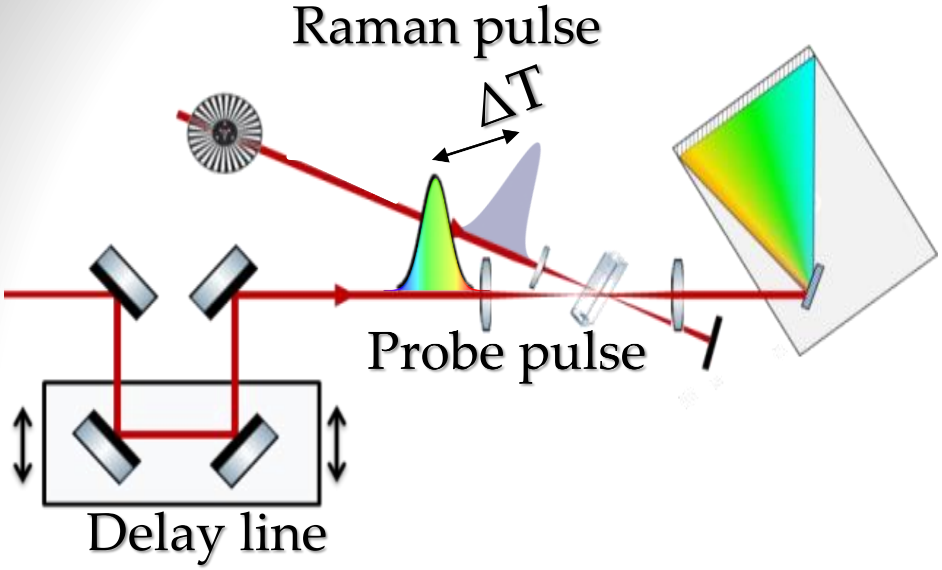

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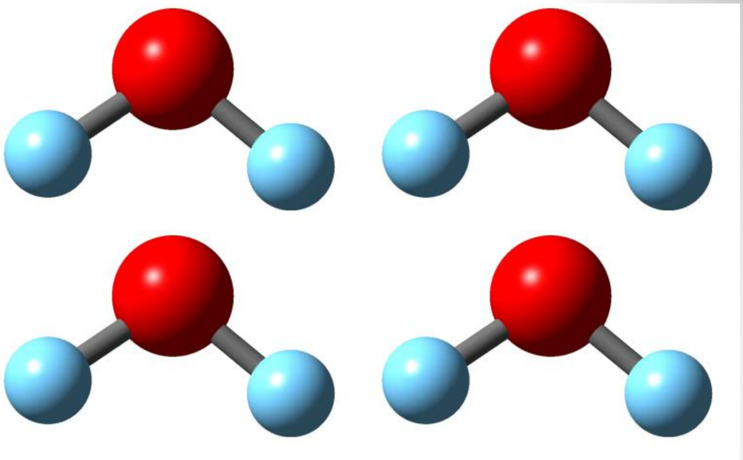
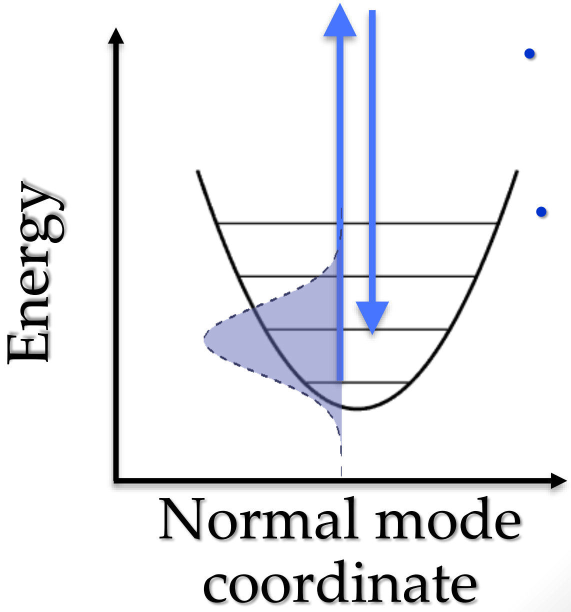
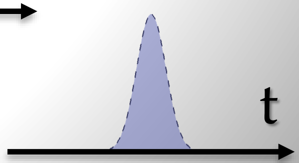




- Broad pump bandwidth
- Pump duration shorter than vibrational periods



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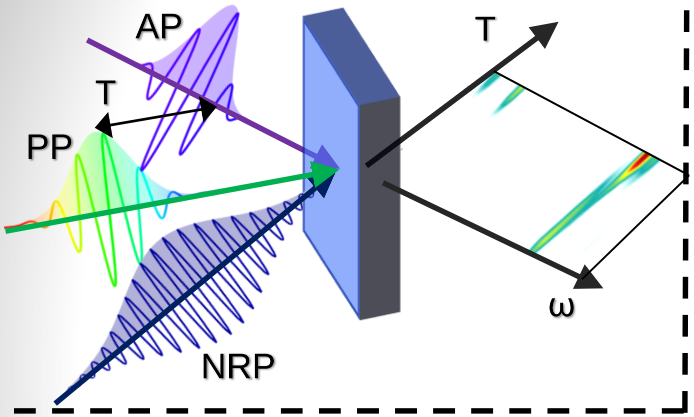

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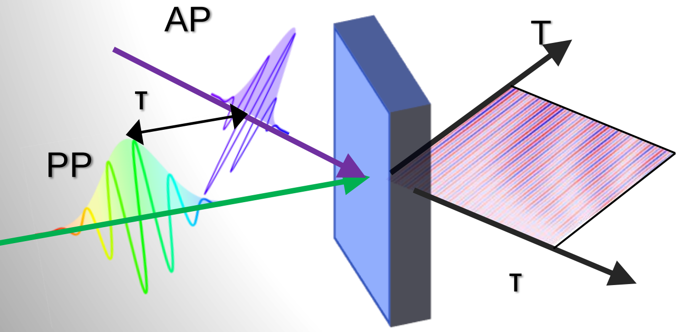
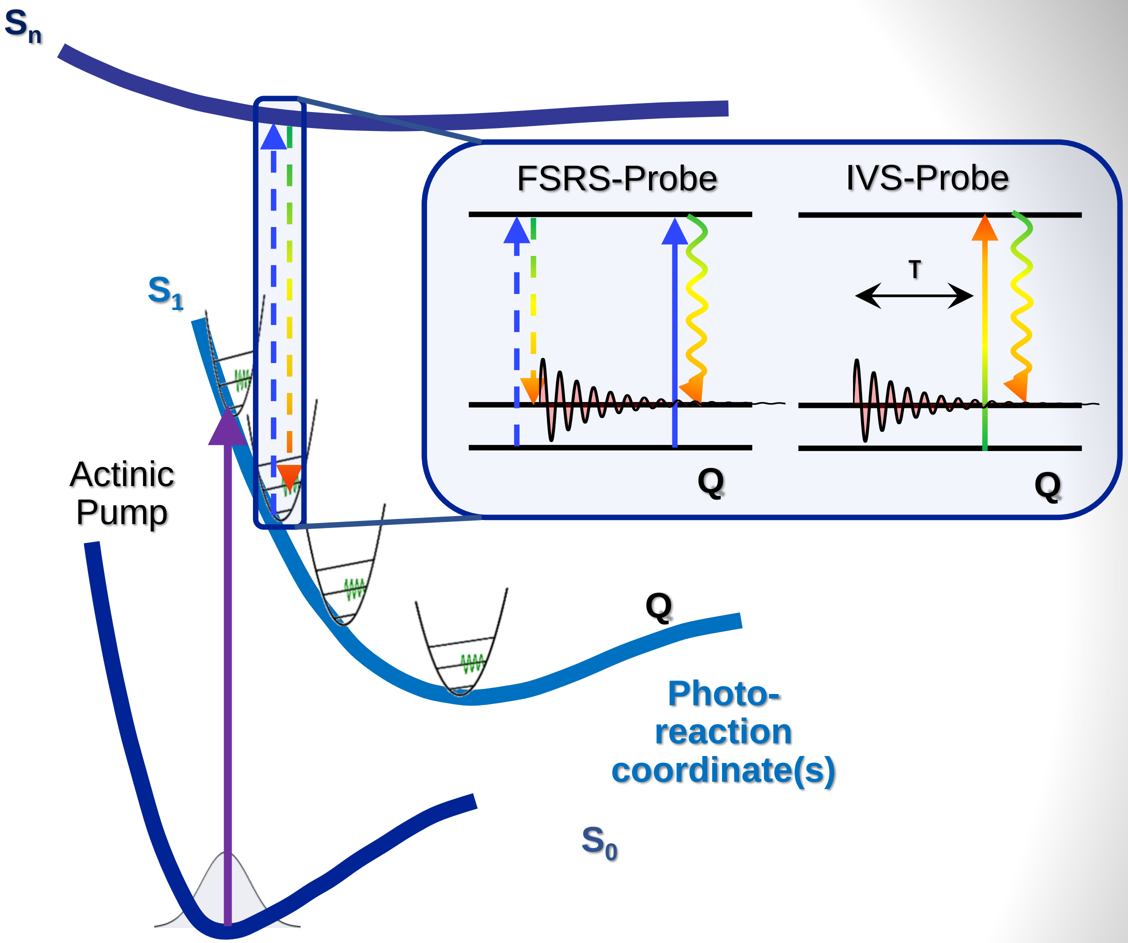
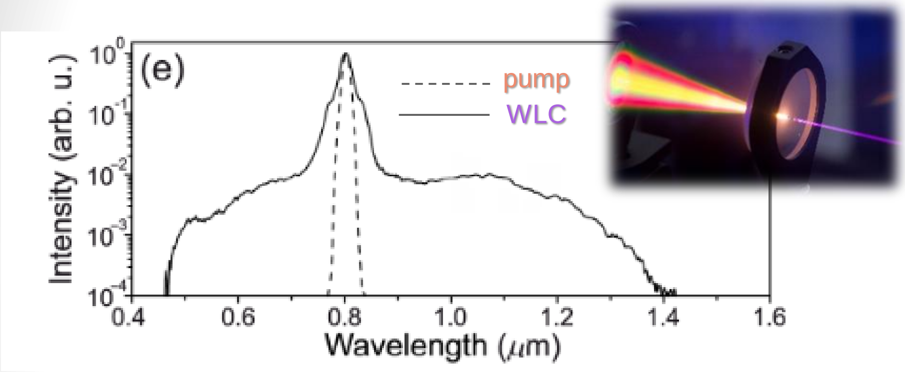




Key ingredients: Ultrashort pulses, with large spectral tunability.

Non-linear spectroscopy at FEL sources

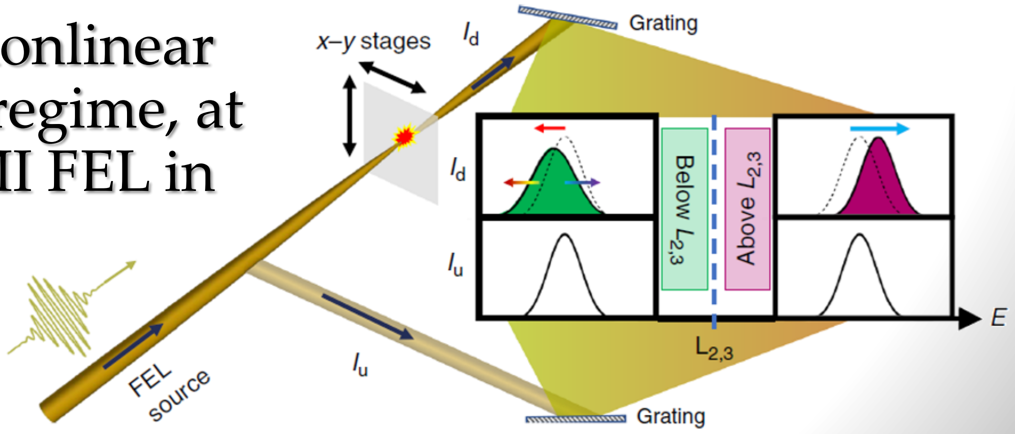
Controlling the spectral properties of X-Ray pulses would provide novel opportunities for non-linear photonics and time-resolved spectroscopy at FEL facilities.



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.

$$n = n_0 + \frac{3\chi^{(3)}}{8n_0}\left|\mathbf{E}_\omega\right|^2 = n_0 + n_2 I$$

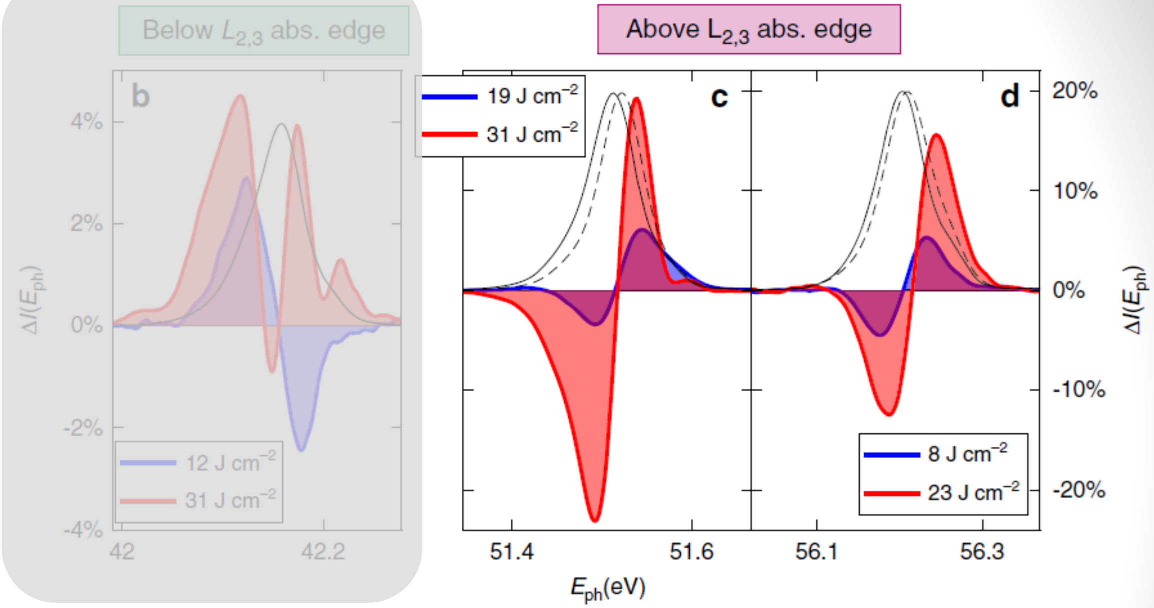
Idea: studying similar nonlinear effects, but in the X-Ray regime, at EIS-TIMEX of the FERMI FEL in Trieste



From: *"Non-linear self-driven spectral tuning of Extreme Ultraviolet Femtosecond Pulses in monoatomic materials"* by C. Ferrante et al., Light: Science & Applications (2021) 10:92

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

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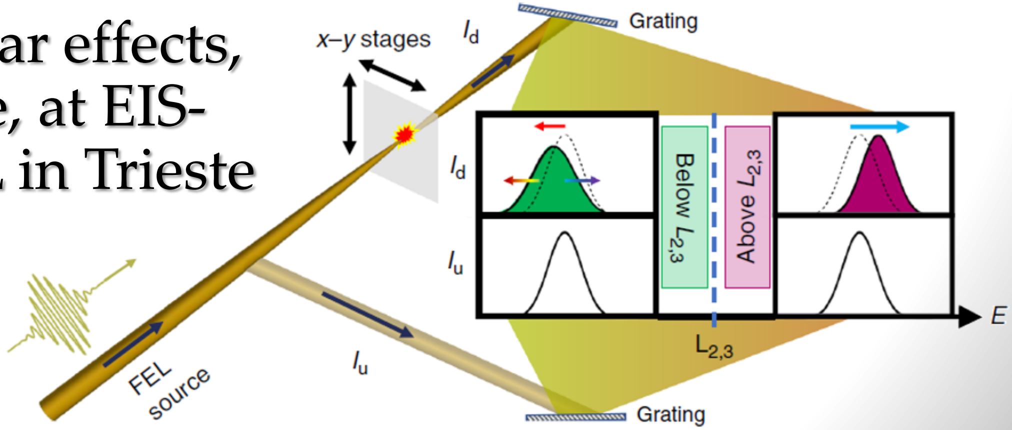

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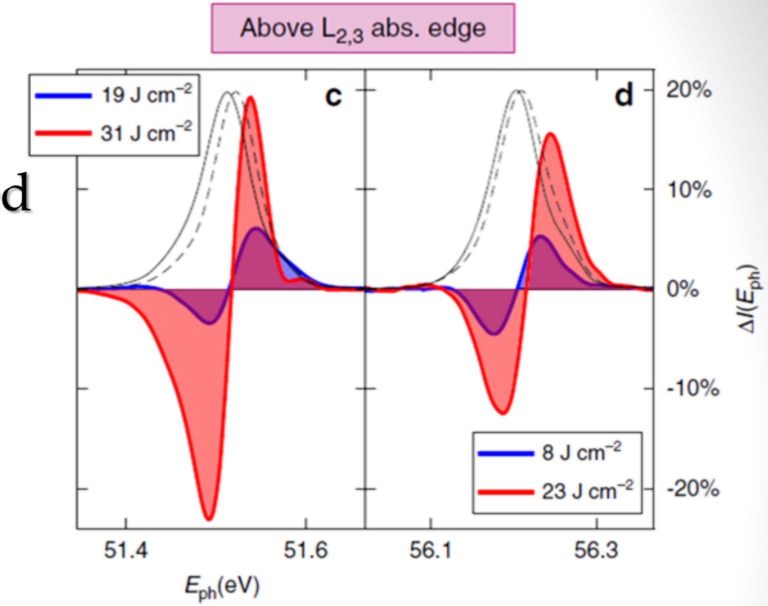
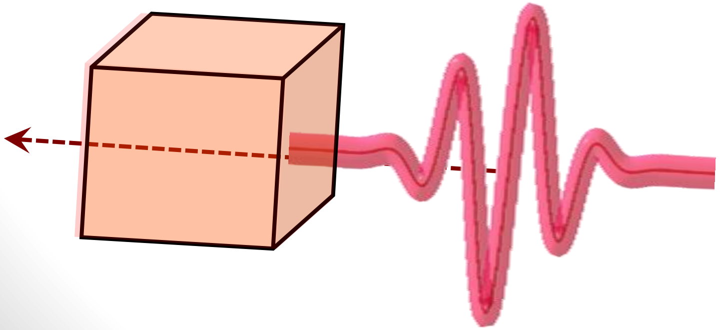
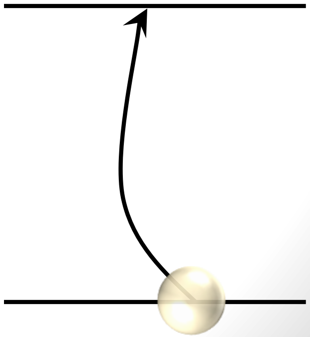


Core photoelectrons are promoted nearly above the Fermi level, generating a transient hot dense ionized plasma





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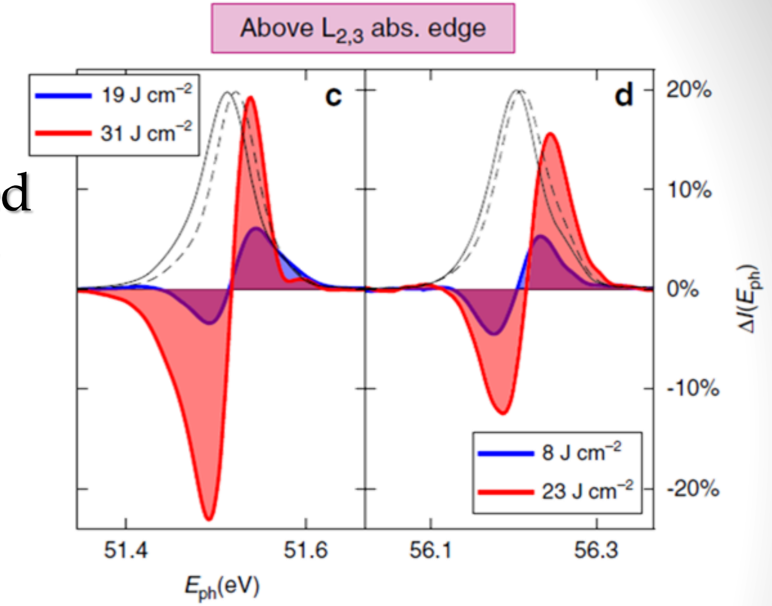

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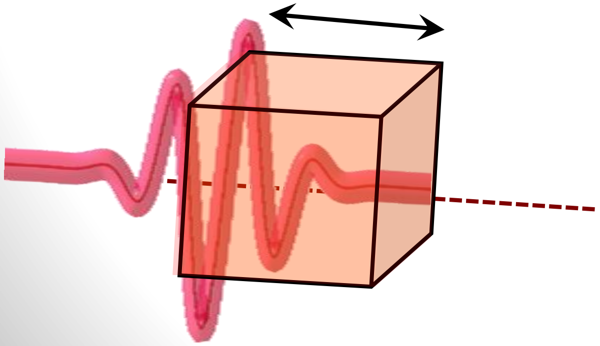
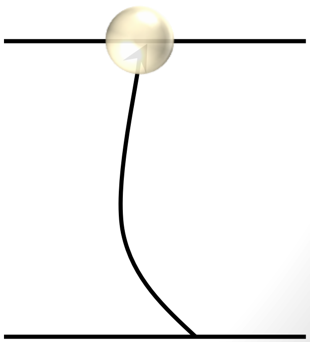


The trailing part of the pulse experiences a reduced refractive index and is hence accelerated: this results in a spectral blue-shift



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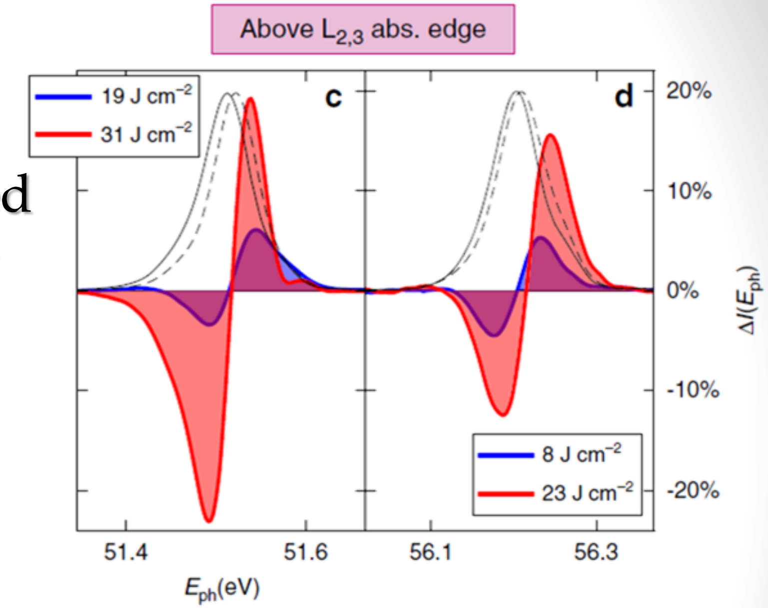

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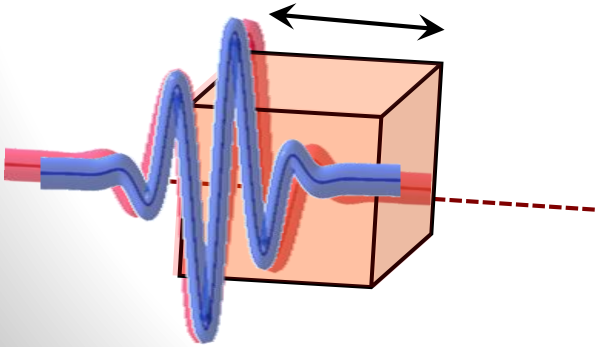

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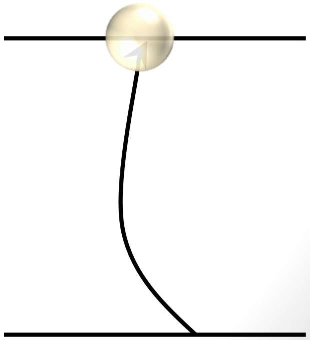

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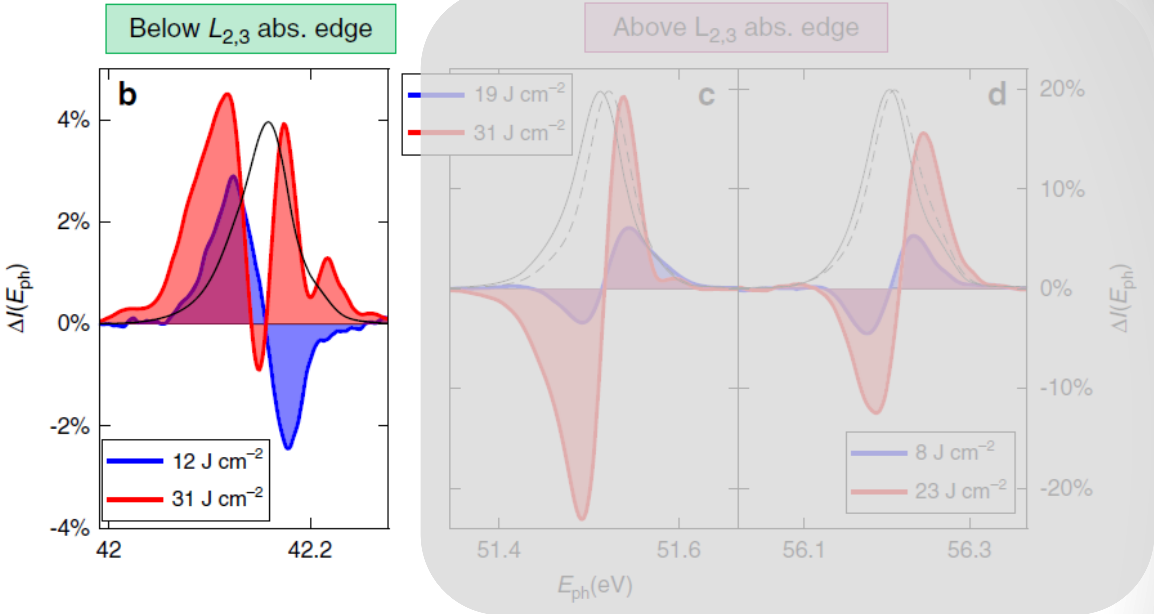
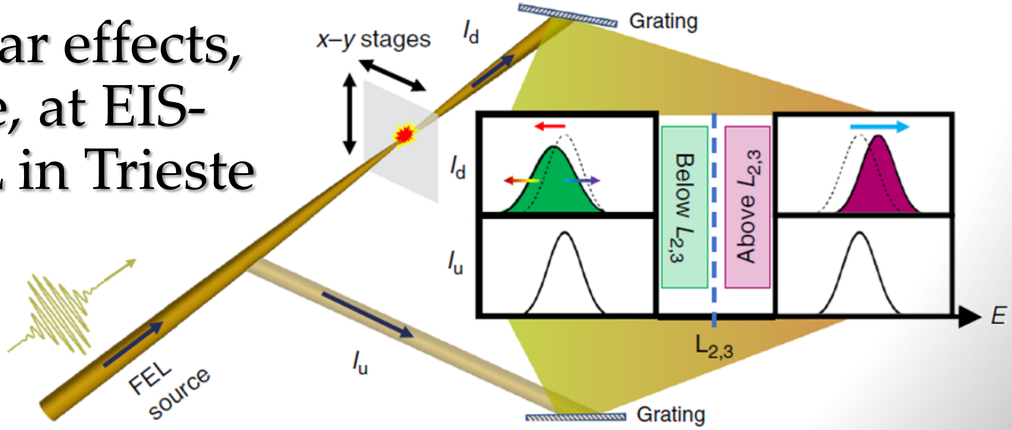
Strong dependence on the interaction process between light and core electrons

Experimental results on Mg samples



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

Spectral modification as a function of pulse fluence and energy

Strong dependence on the interaction process between light and core electrons

$$\mathbf{E}(\mathbf{r},t) = \mathrm{Re}[\psi(\mathbf{r},t)e^{ik_0 z - i\omega_0 t}\hat{\mathbf{n}}]$$

SPM induced phase

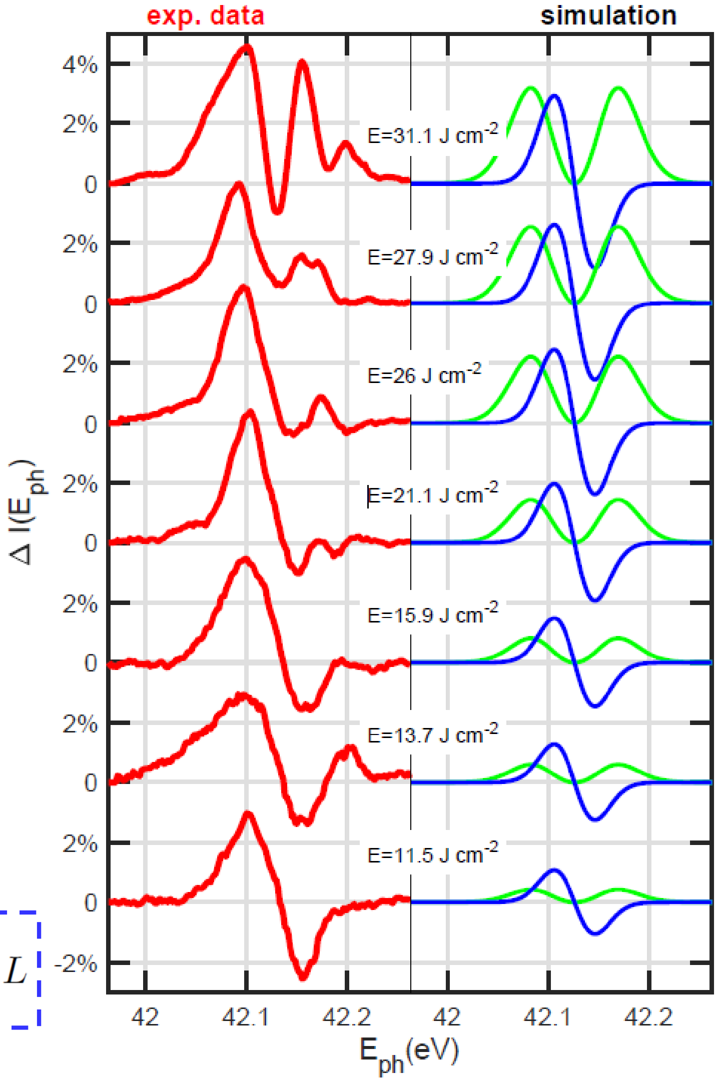
$$\phi_{\mathrm{NL}}(\mathbf{r},t) = \chi^{(3)}|\psi(\mathbf{r},t)|^2 k_0 L$$

Delayed thermal response of electrons (DTRE)

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

Experimental results on Mg samples

Below $L_{2,3}$ abs. edge



SPM alone does not account for the red-shift at low fluences

Non-linear spectroscopy at FEL sources

Spectral modification as a function of pulse fluence and energy

Strong dependence on the interaction process between light and core electrons

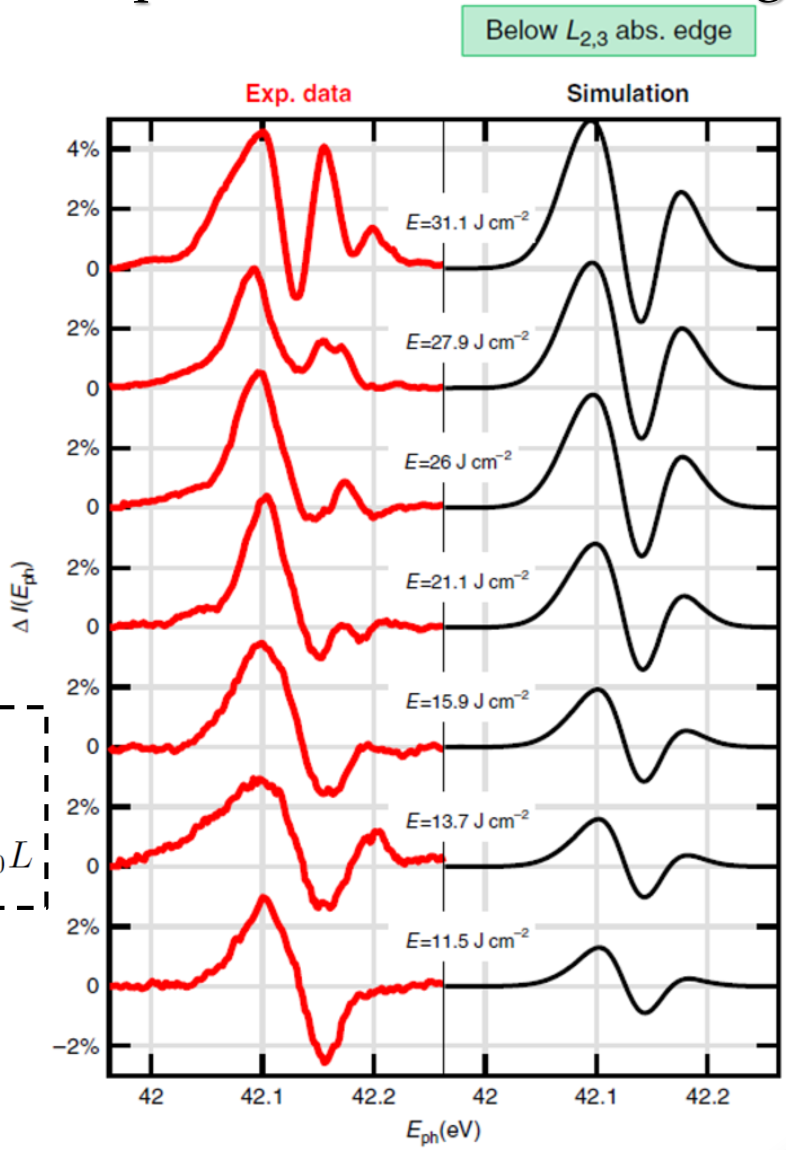
$$\mathbf{E}(\mathbf{r},t) = \mathrm{Re}[\psi(\mathbf{r},t)\mathrm{e}^{ik_0 z - i\omega_0 t}\hat{\mathbf{n}}]$$

SPM +DTRE

$$\phi_{\mathrm{NL}}(\mathbf{r},t) = \chi^{(3)}|\psi(\mathbf{r},t)|^2 k_0 L$$

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

Experimental results on Mg samples



Non-linear spectroscopy at FEL sources

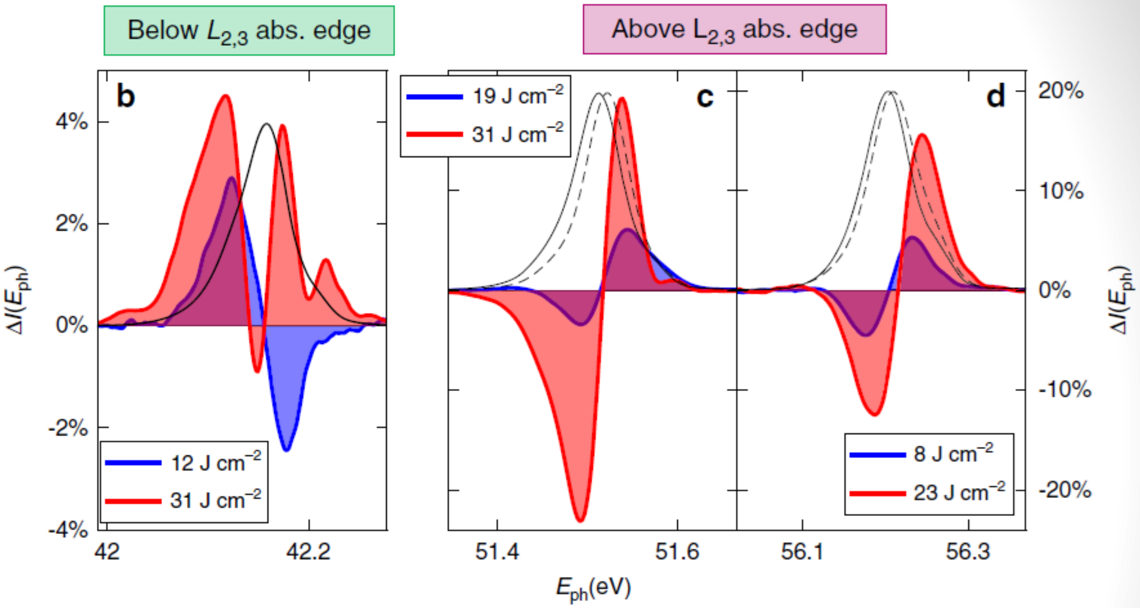
Spectral modification as a function of pulse fluence and energy:

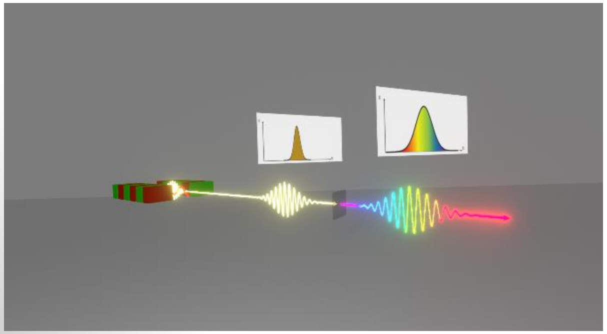
Blue shift for above edge interaction,

Red shift for below edge interaction at low fluences

Spectral broadening for below edge interaction at high fluences

Experimental results on Mg samples

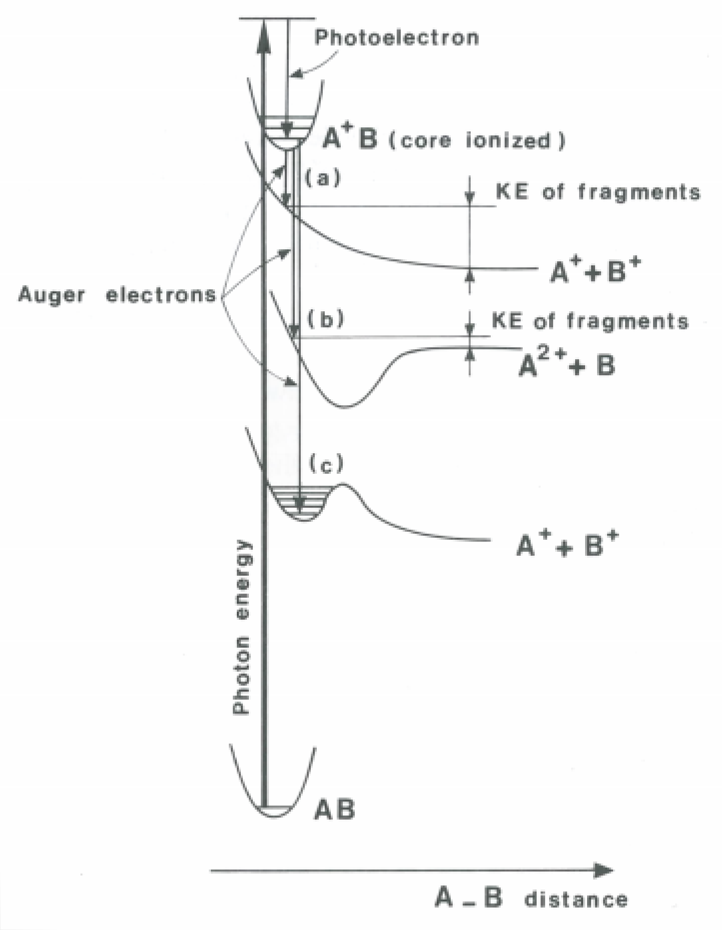




Demonstrated self-induced spectral beam modification by interaction with sub-micrometric foils of selected monoatomic materials in the EUV

Time-Resolved nonlinear Raman Spectroscopy: X ray perspectives…

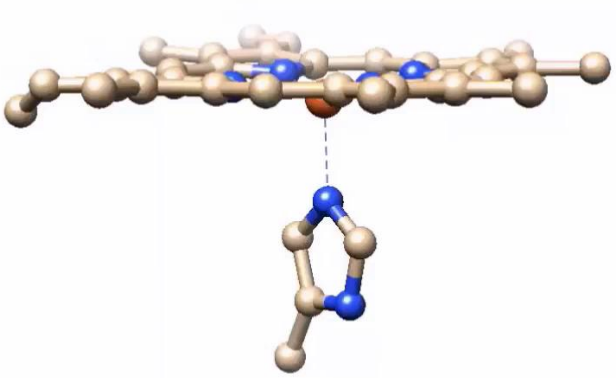
#1: FSRS with X ray pump

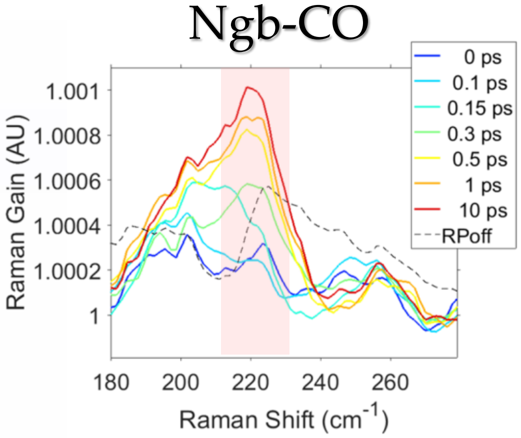


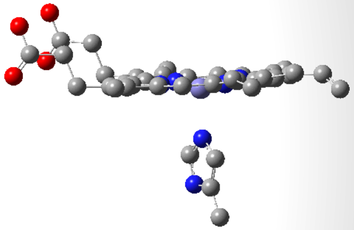
Capturing structural evolution during photofragmentation

#2: IVS with X ray probe

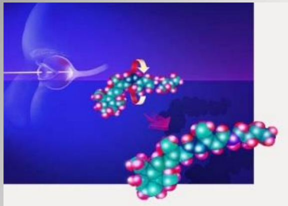
Motivation:





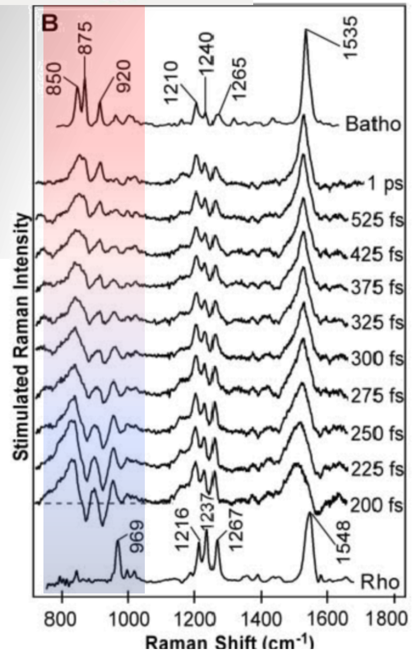


The key iron-histidine mode is very weak in the Soret Resonant Raman spectrum



#2: FSRS with X ray probe

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



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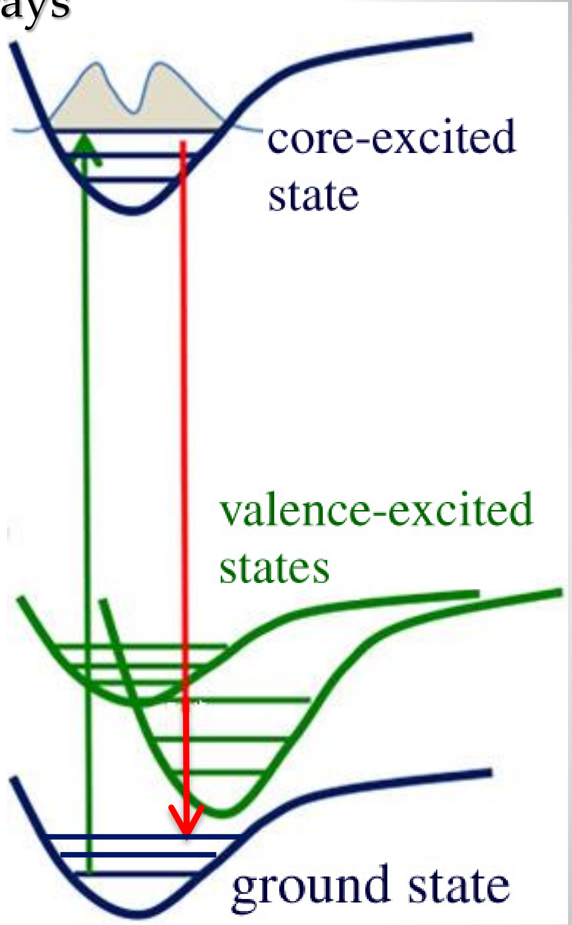
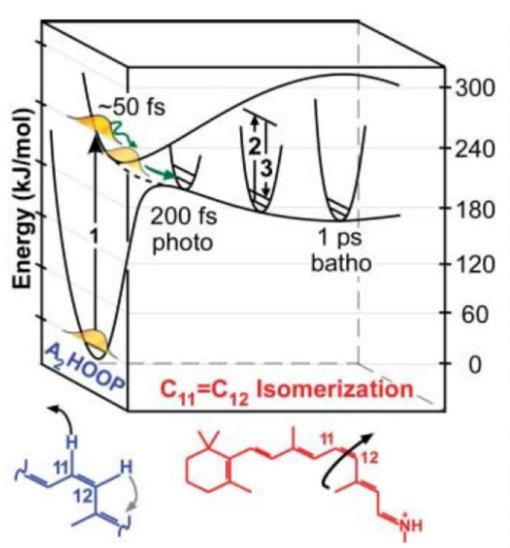


The congested FSRS spectrum cannot uniquely identify the reaction pathway



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