FEL based Nonlinear Spectroscopy

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FERMI

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nature photonics ARTICLES

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Highly coherent and stable pulses from the FERMI seeded free-electron laser in the extreme ultraviolet

E. Allaria *et al.**

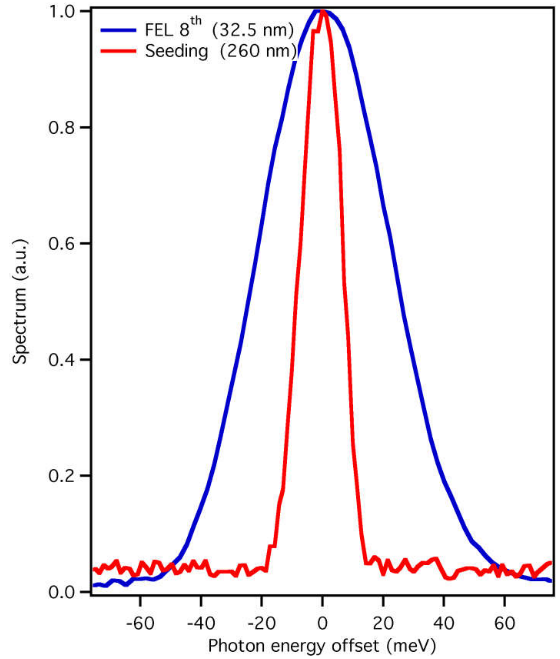
E ~ 20 - 400 eV

Δt < 100 fs (*superradiance 5 fs*)

Polarization

Two colors operation (*phase locked*)

Attosecond trains

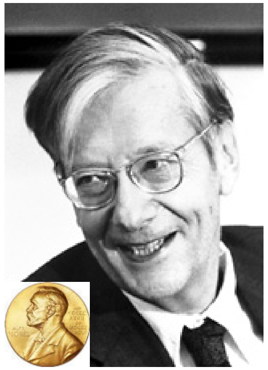


VOLUME 7, NUMBER 4 PHYSICAL REVIEW LETTERS AUGUST 15, 1961

WIKIPEDIA
The Free Encyclopedia

Famously, when published in the journal *Physical Review Letters*, the copy editor mistook the dim spot (at 347 nm) on the photographic paper as a **speck of dirt** and removed it from the publication.

Non-linear Optics



N. Bloembergen 1981

$$P_i = \chi^{(1)}_{ij} E_i + \chi^{(2)}_{ijk} E_j E_k + \chi^{(3)}_{ijkl} E_j E_k E_l + \cdots$$

Non linear techniques are **powerful** when one wants

to measure **sample properties** that cannot be addressed by ***conventional*** linear optical spectroscopy or to obtain spectroscopic information with a higher **sensitivity** than that associated with linear spectroscopy

$$\frac{\boldsymbol{P}^{(2)}}{\varepsilon_0} = [\chi^{(2)}(2\cdot\omega_1)\cdot \boldsymbol{E}_1'^2 \cdot \exp(-2\cdot i\cdot\omega_1\cdot t) + \chi^{(2)}(2\cdot\omega_2)\cdot \boldsymbol{E}_2'^2\cdot\exp(-2\cdot i\cdot\omega_2\cdot t)$$
$$+ 2\cdot\chi^{(2)}(\omega_1+\omega_2)\cdot \boldsymbol{E}_1'\cdot \boldsymbol{E}_2'\cdot\exp(-i\cdot(\omega_1+\omega_2)\cdot t)$$
$$+ 2\cdot\chi^{(2)}(\omega_1-\omega_2)\cdot \boldsymbol{E}_1'\cdot \boldsymbol{E}_2'\cdot\exp(-i\cdot(\omega_1-\omega_2)\cdot t) + \mathrm{C.C.}]$$
$$+ 2\cdot\chi^{(2)}(\omega=0)\cdot[\boldsymbol{E}_1'\cdot \boldsymbol{E}_2'^* + \boldsymbol{E}_1'^*\cdot \boldsymbol{E}_2']$$

SHG, SFG, DFG

$$I_i(\omega_3) \propto \left|\chi^{(2)}_{ijk}\right|^2 I_j I_k L^2 \cdot \mathrm{sinc}^2\left(\frac{\Delta k L}{2}\right)$$

$$\Delta k = \mathbf{k}_{out} - \sum \mathbf{k}_{in}$$

Non-linear Optics

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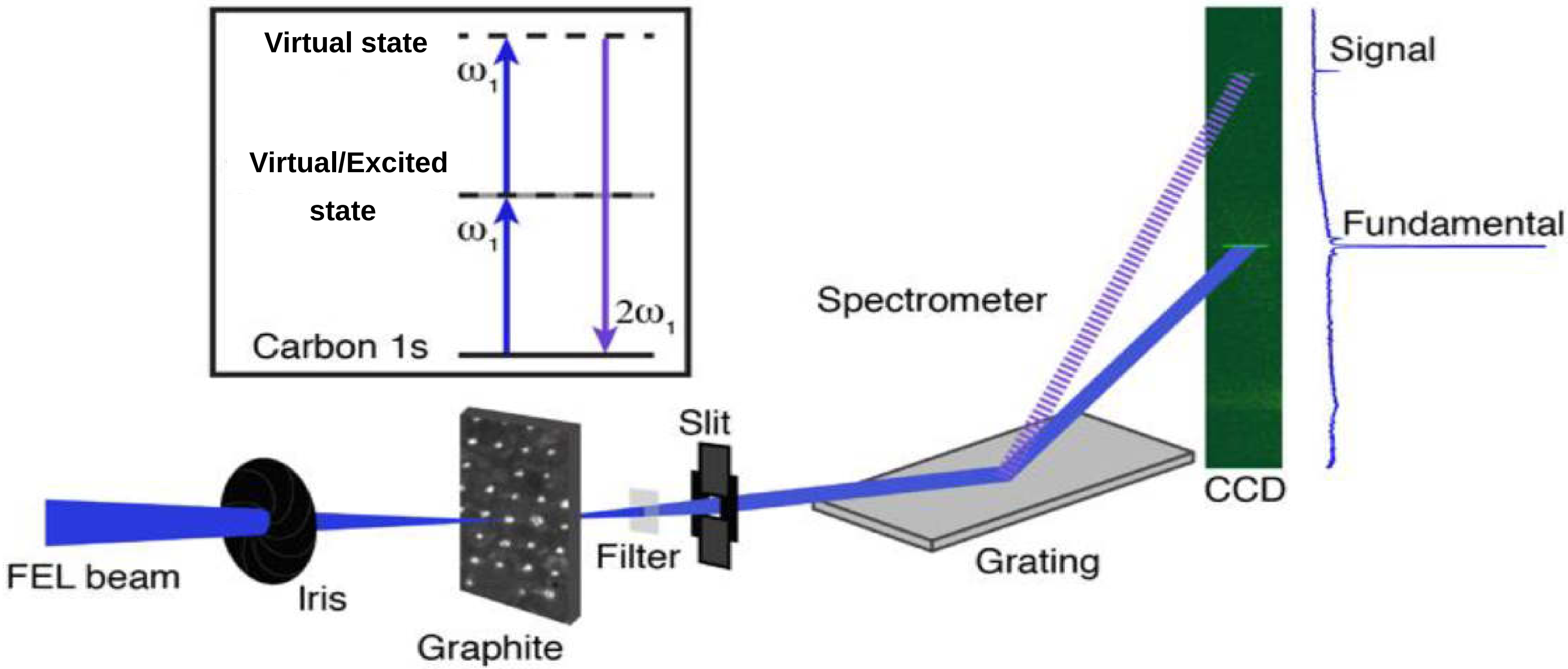
$$P_i = \chi^{(1)}_{ij} E_i + \chi^{(2)}_{ijk} E_j E_k + \chi^{(3)}_{ijkl} E_j E_k E_l + \cdots$$

SHG



R. Lam et al., PRL (2018)

Second Harmonic Generation at FERMI

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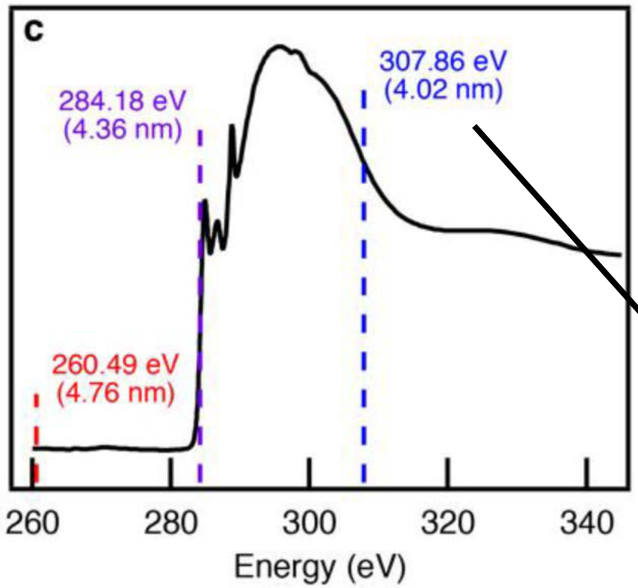
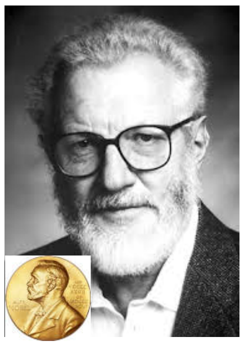
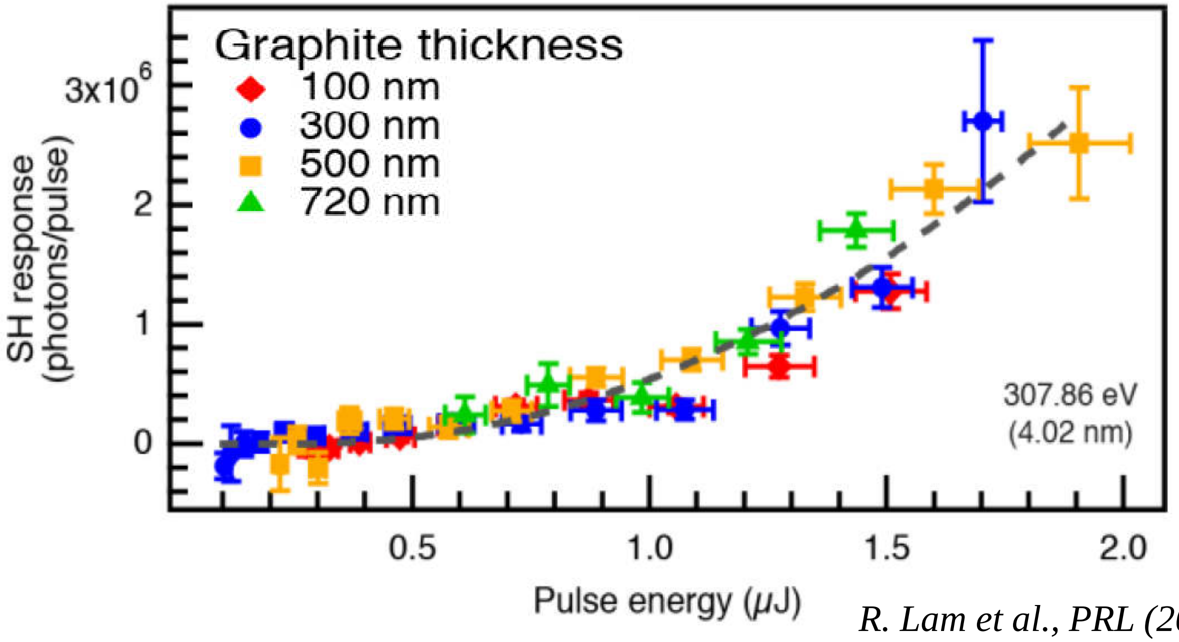


NO **thickness** dependence of SHG signal

Measure local geometric and/or electronic structure of a **single atomic layer**



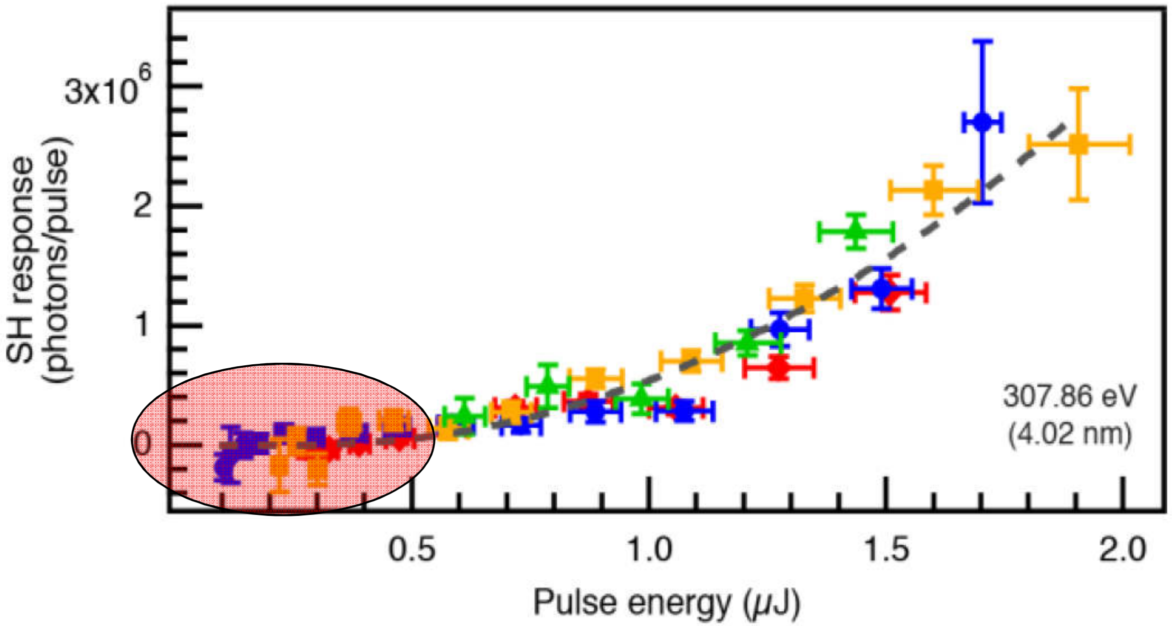
H. Kroemer 2000



<u>The interface is the device</u>!

R. Lam et al., PRL (2018)

Second Harmonic Generation at XFEL

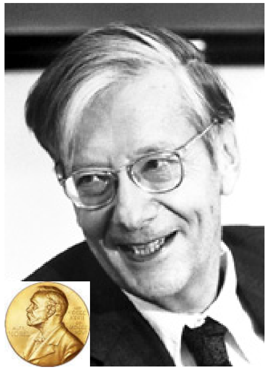


FEL based (**SHG**, **SFG**, **DFG**) would tremendously benefit from:

High Rep Rate → increase statistics → decrease the pulse intensity

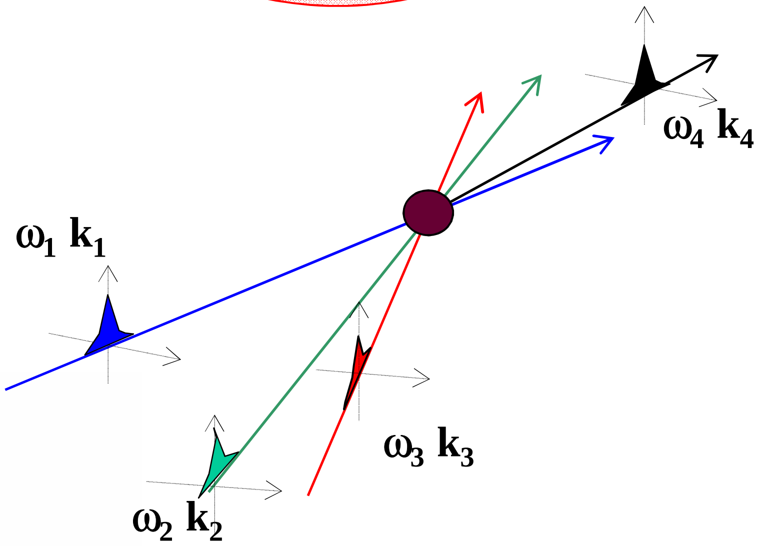
Soft X-ray at and beyond the **Water Window** (i.e. L-edges for magnetic materials)

Third Order Processes



N. Bloembergen 1981

$$P_i = \chi_{ij}^{(1)} E_i + \chi_{ijk}^{(2)} E_j E_k + \chi_{ijkl}^{(3)} E_j E_k E_l + \cdots$$



$$\omega_1 + \omega_2 + \omega_3$$

$$3\omega_j,\ \omega_j \qquad j=1,2,3$$

$$2\omega_i + \omega_j,\ 2\omega_i - \omega_j,\ \omega_i - 2\omega_j$$

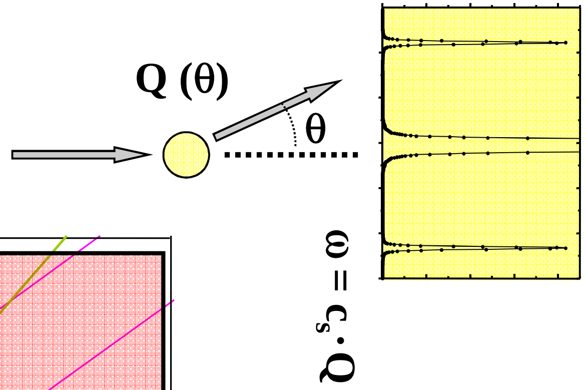
$$\omega_i + \omega_j - \omega_k,\ \omega_i - \omega_j - \omega_k$$

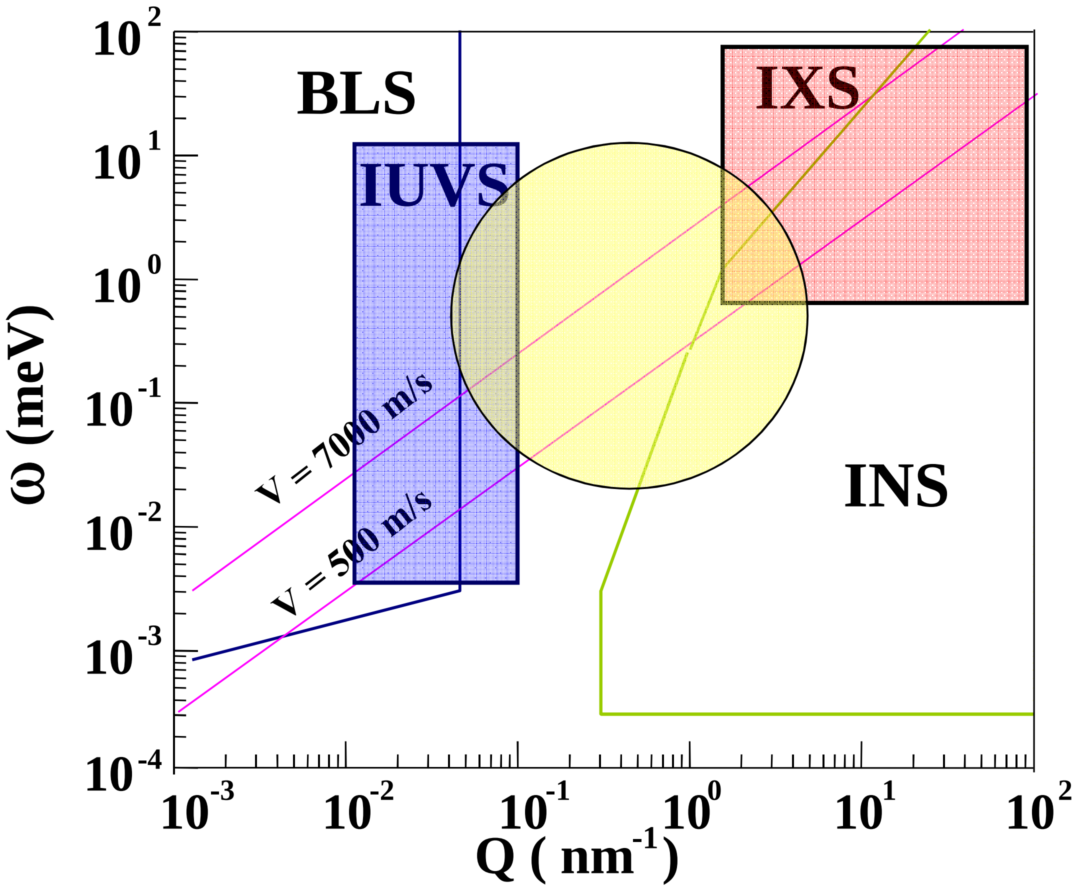
Collective Dynamics at the Nanoscale

To study Atomic and Molecular **Density Fluctuations** (i.e. sound modes) is of **great importance** to understand physical properties of gases, liquids and solids

Disordered Systems

Determination of the Dynamic Structure Factor: **S(Q,ω)**





Disordered Systems at the nanoscale

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The nature of the vibrational dynamics in **glasses** at the nanoscale is still unclear (V-SiO_2)

M. Foret *et al.*, *PRL* ***77***, 3831 (1996) → They are localized above ~ 1 nm^{-1}

P. Benassi *et al.*, *PRL* ***77***, 3835 (1996) → Existence of propagating excitations at high frequency

F. Sette *et al.*, *Science* ***280***, 1550 (1998) → They are acoustic-like

G. Ruocco *et al.*, *PRL* ***83***, 5583 (1999) → Change of sound attenuation mechanism at 0.1-1 nm^{-1}

B. Ruffle´ *et al.*, *PRL* ***90***, 095502 (2003) → Change is at 1 nm^{-1}

C. Masciovecchio *et al.*, *PRL* ***97***, 035501 (2006) → Change is at 0.2 nm^{-1}

W. Schirmacher *et al.*, *PRL* ***98***, 025501 (2007) → Model agrees with Masciovecchio et al.

B. Ruffle´ *et al.*, *PRL* ***100***, 015501 (2008) → Shirmacher model is not correct

G. Baldi *et al.*, *PRL* ***104***, 195501 (2010) → Change is at 1 nm^{-1}

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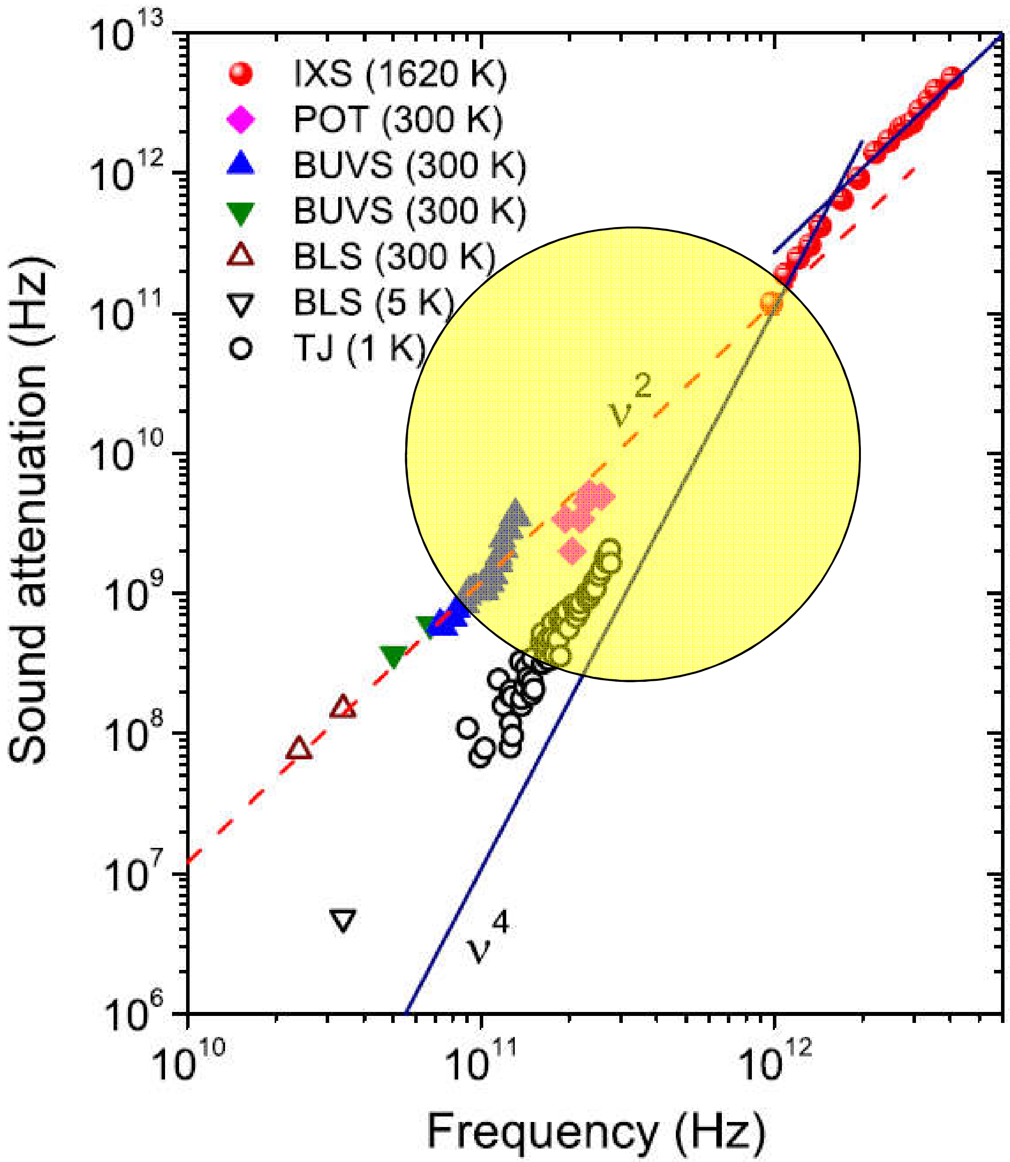
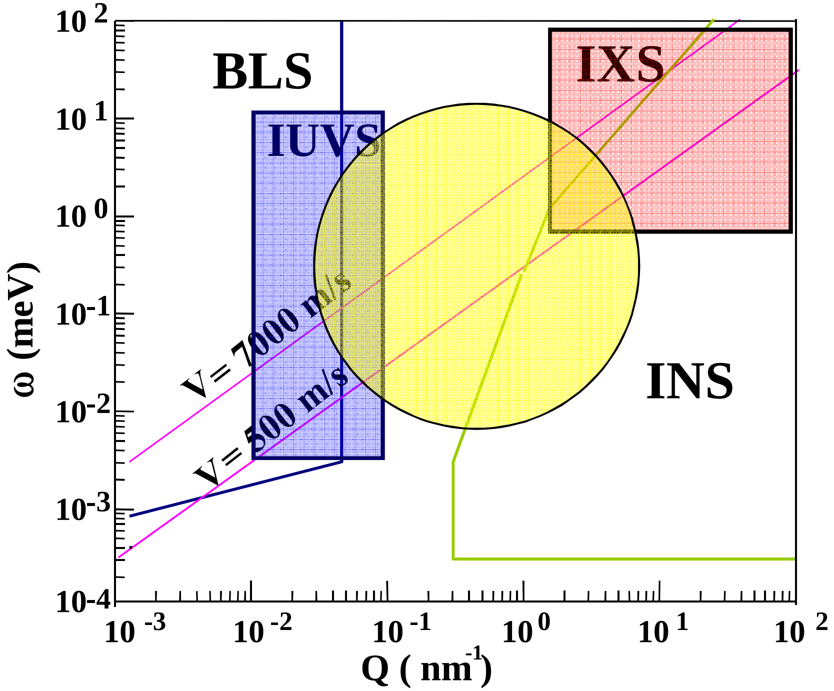
L. Wang et al., Nat. Comm. **10**, 26 (2019)

Fundamental to understand the low temperature anomalies in **glasses**

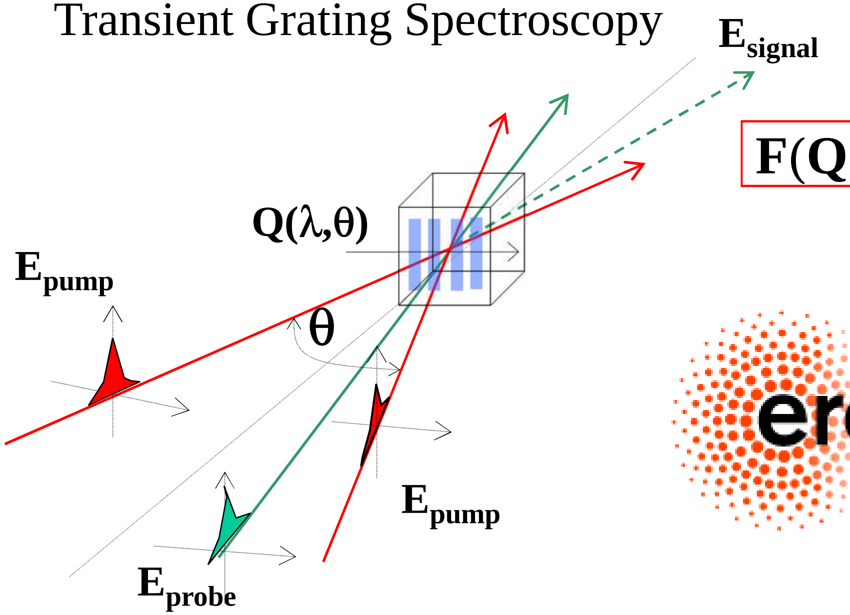
Disordered Systems at the nanoscale

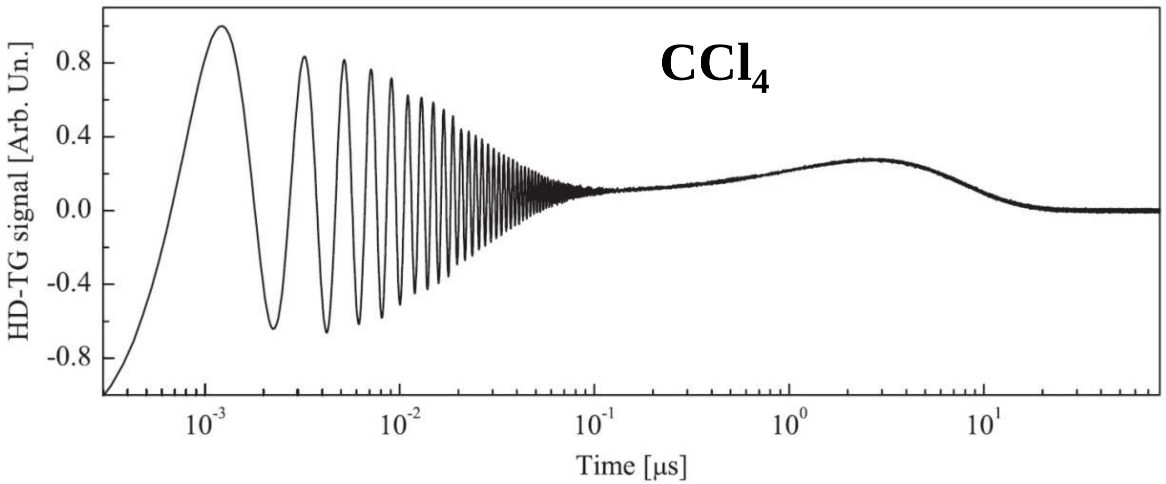


TIMER



Solution: Free Electron Laser based Transient Grating Spectroscopy





LETTER

doi:10.1038/nature1434

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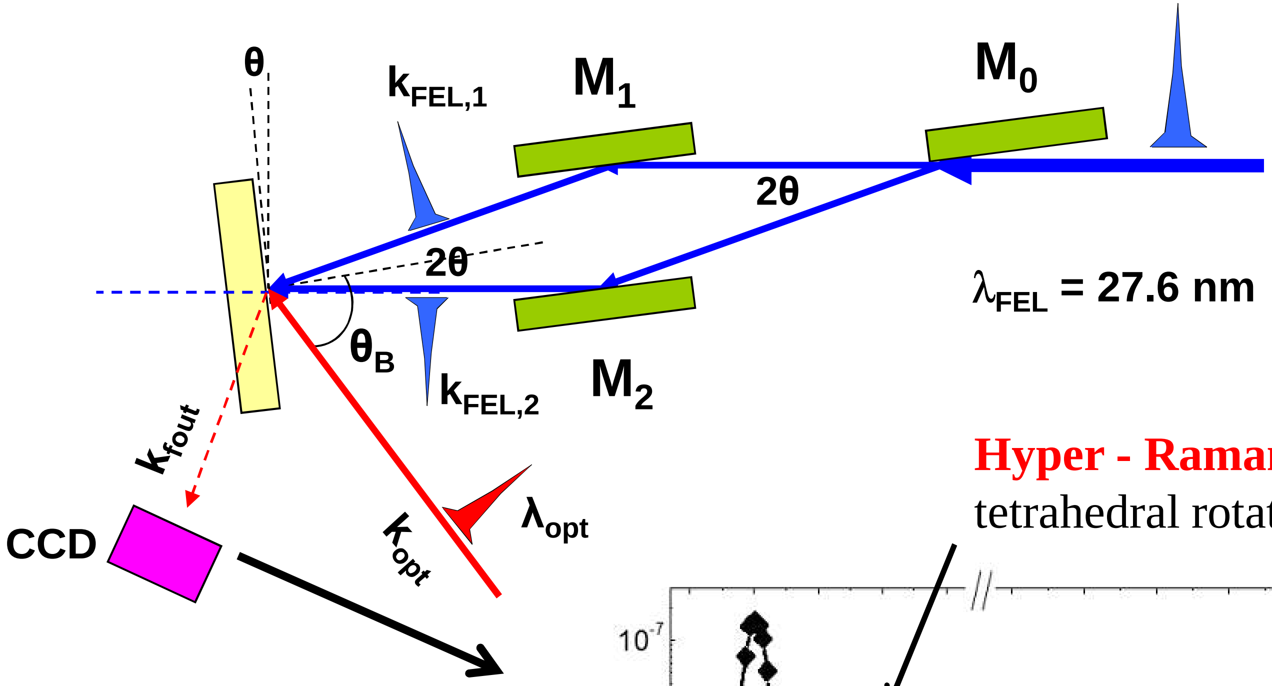
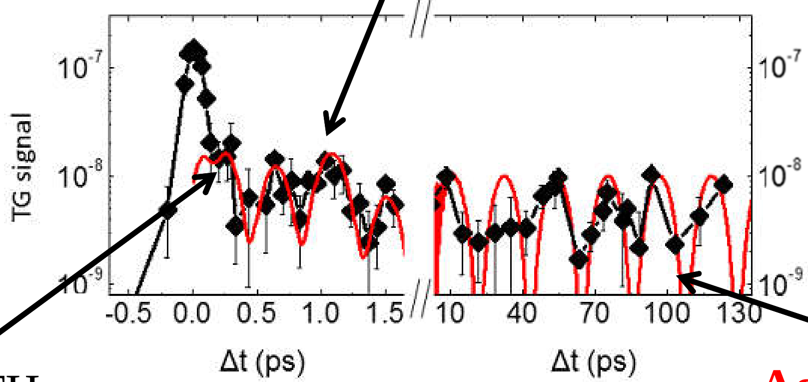
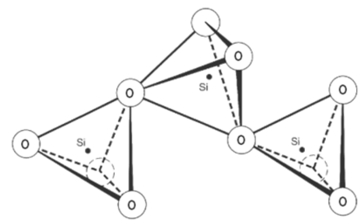
Four-wave mixing experiments with extreme ultraviolet transient gratings

F. Bencivenga et al., Nature 2015



Hyper - Raman modes → coupled tetrahedral rotations $\nu_2 \approx 4.1$ THz





Raman modes → tetrahedral bending $\nu_1 \approx 1.2$ THz

Acoustic-like excitations

Shorter λ

$Q = 2\pi/\lambda \sin\theta$ **(@ 10 nm → 0.5 nm^{-1})**

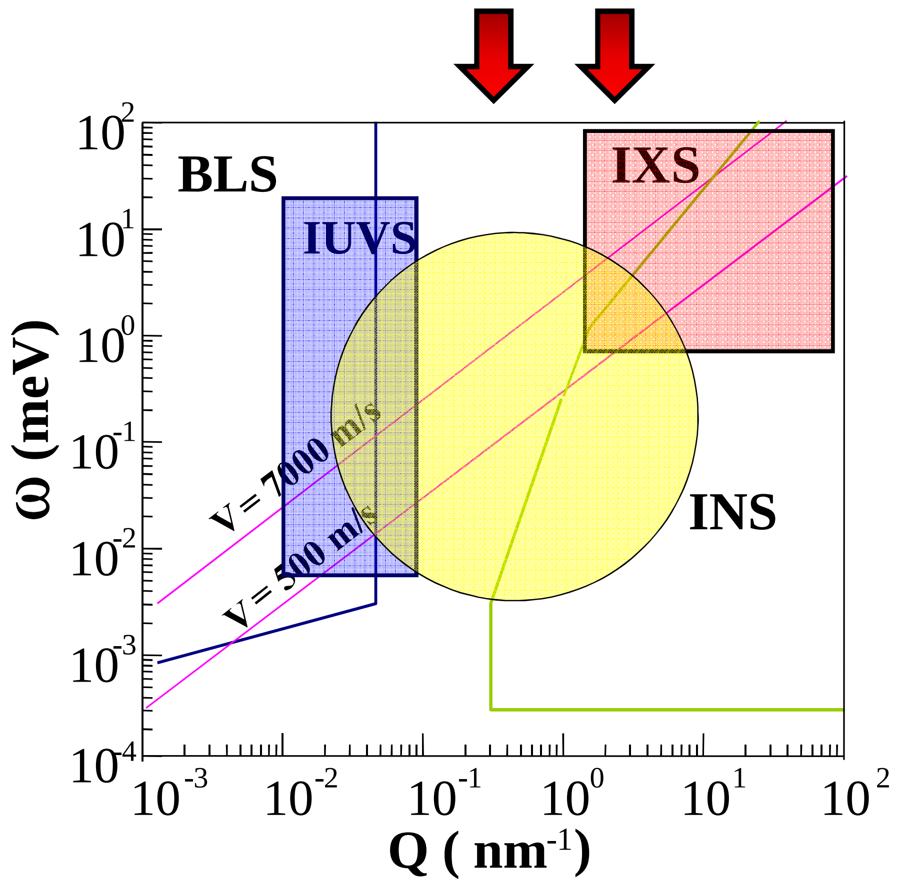
IXS @ Brookhaven (5 M €)

BRISP @ ILL (5 M €)

T-REX @ ESS → 20 M€

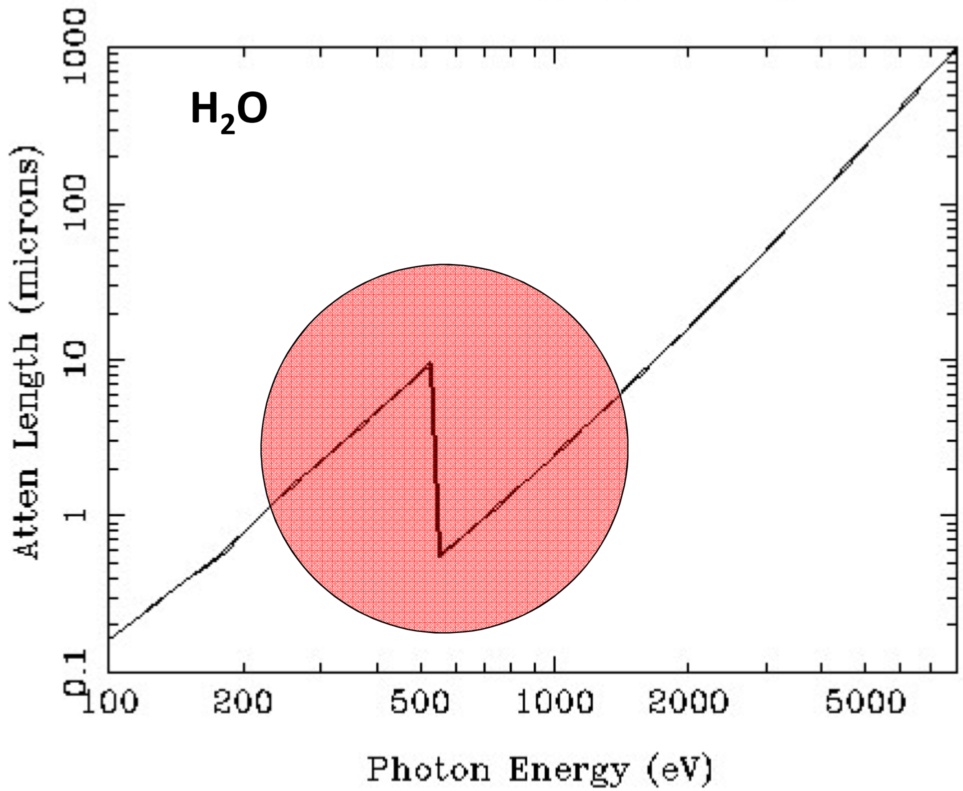
IXS @ XFEL (in progress)

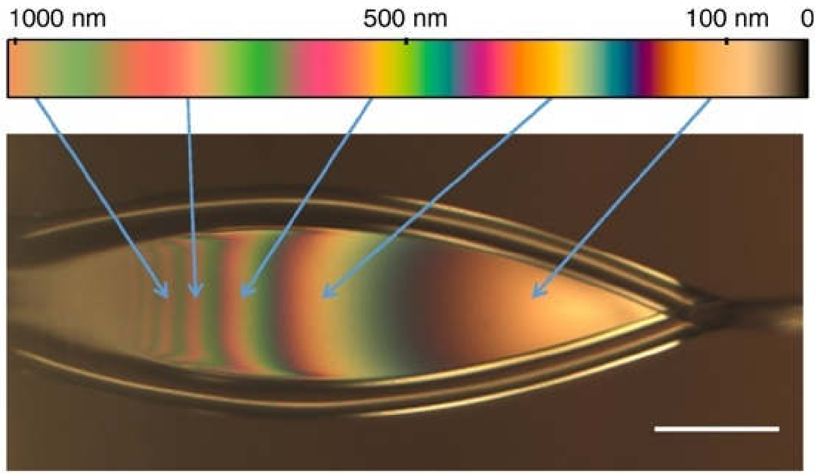
IXS @ SLS (in progress)



Can we extend **Transient Grating** in the IXS-INS kinematic region?

Shorter λ





J. D. Koralek et al., Nat. Comm. 2018

Transient Grating @ XFEL

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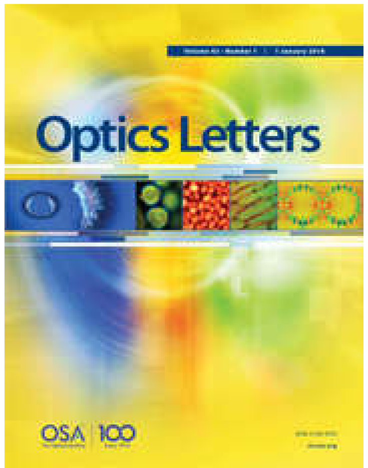
Advantages with respect IXS-INS: **resolution**

Advantages with respect FERMI:

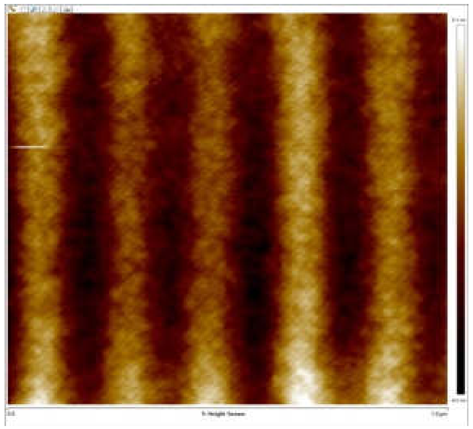
penetration depth of X-rays (easier **sample environment**)

rep-rate (→ decrease the pump fluence)

Is it possible at XFEL?



C. Svetina et al., Opt. Lett (2019)



100 nm pitch with **Talbot** effect for converging beams

E ≈ 3 keV

Transient Grating @ XFEL

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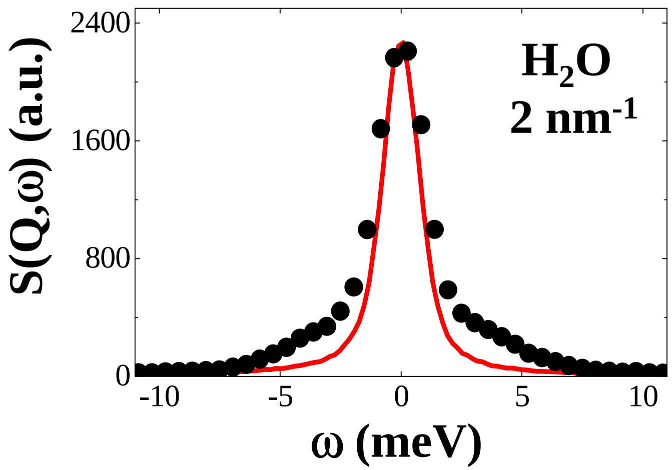
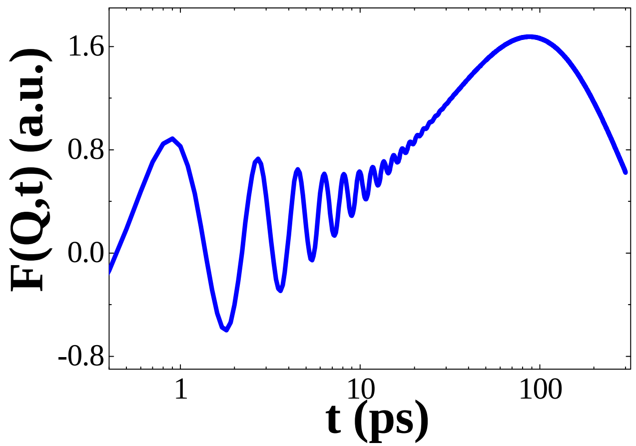
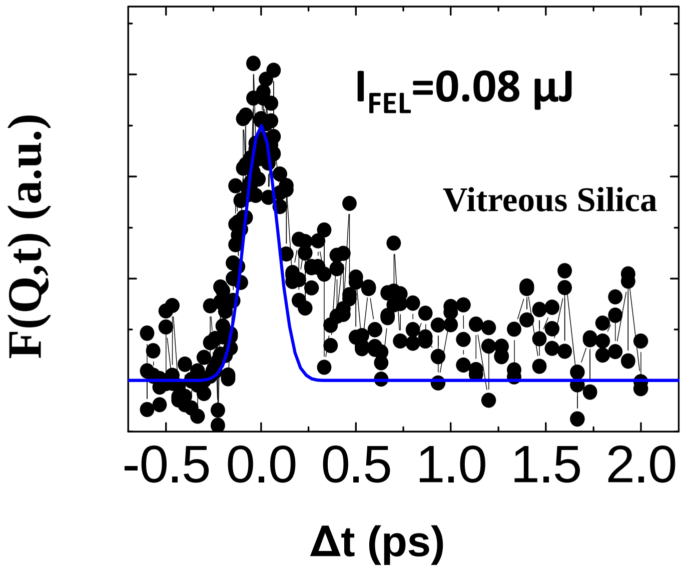
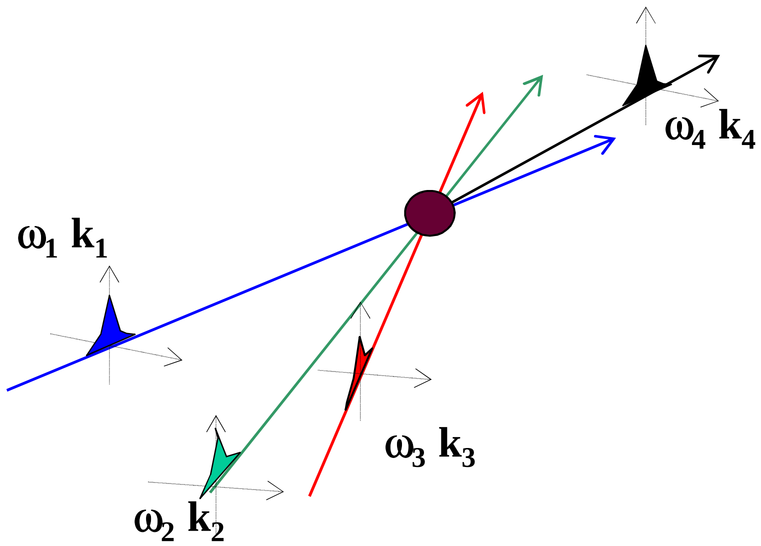






Spectra can be obtained at low intensity
High Rep Rate → Increasing the S/N ratio and statistics

Coherent Antistokes Raman Scattering

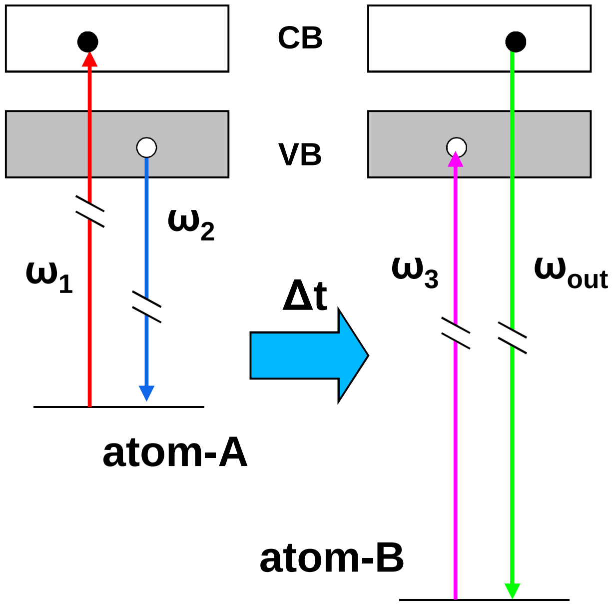


FWM techniques are: Stimulated Raman Gain Spectroscopy, **Transient Grating Spectroscopy**, Raman Induced Kerr Effect Spectroscopy, Femtosecond Stimulated Raman Scattering, Coherent Antistokes Raman Scattering (**CARS**), …………

Measure the coherence between the two different sites → tuning energies and time delay makes possible to chose where a given excitation is created, as well as where and when it is probed

↓

delocalization of electronic states and **charge/energy transfer** processes.



S. Tanaka and S. Mukamel, PRL (2002)

F. Bencivenga et al., submitted

TRUECARS

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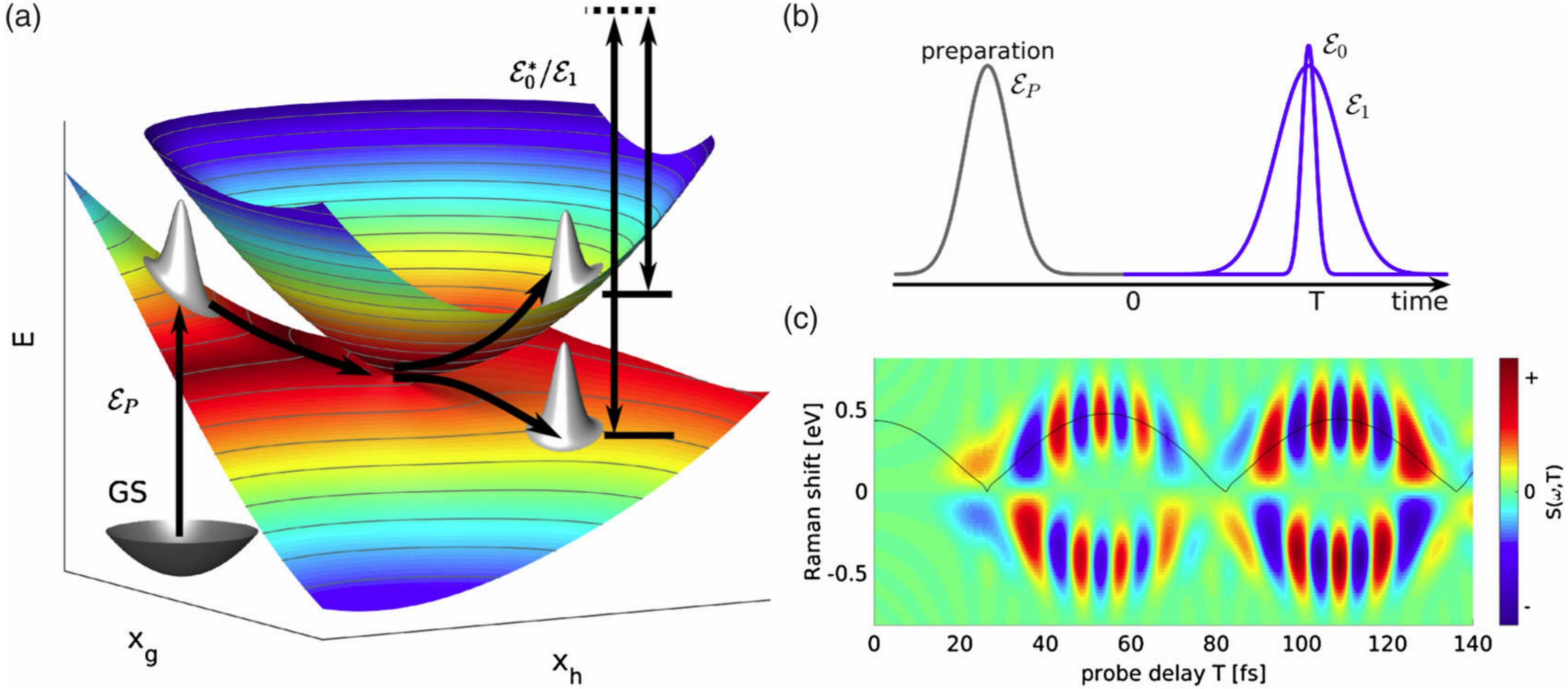
Conical Intersections (Molecular Funnels or Diabolic Points) → established paradigm for understanding **thermal chemistry**

A pump pulse → excited electronic state → non-stationary nuclear **wave packet** which then propagates towards the Conical Intersection (**CI**)



Electronic coherence builds up as the wave packet approaches the **CI** where the nonadiabatic intersurface coupling is present

Only Soft X-ray pulses provide the necessary temporal and spectral profiles (femtoseconds and few eV bandwidth) to detect electronic coherences

M. Kowalewski and S. Mukamel, PRL (2015)

Nonlinear Optics @ XFEL

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- High Rep Rate → Statistics, S/N, lower fluence
- Shorter λ → **Invade** INS, IXS kinematic region (much higher energy resolution)

  → **Sample environment**

Two **Colors** experiments:

CARS → measuring **Energy Transfer**

TRUECARS → measuring **Conical Intersections**

Acknowledgments


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M. Zangrando


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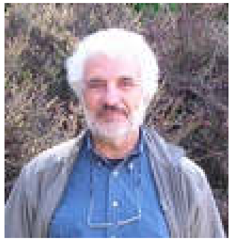
F. Parmigiani


M. Svandrlik

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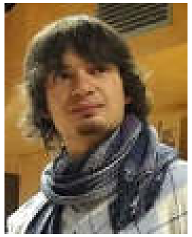
F. Bencivenga


F. Cilento


F. Capotondi


M. Di Fraia


E. Principi


C. Callegari


O. Plekan


A. Gessini


D. Naumenko


E. Pedersoli

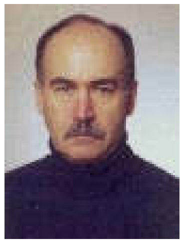

A. Perucchi

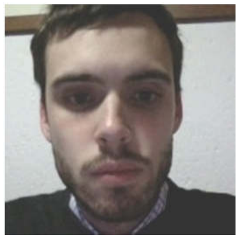

M. Malvestuto


M. Coreno


A. Simoncig


G. De Ninno


K. Prince


R. Mincigrucci


L. Foglia