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Feasibility considerations for stimulated Raman scattering at an XFEL

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Outline

- Motivation
- Third-order susceptibility at X-ray wavelengths
- Spontaneous vs. stimulated X-ray Raman scattering
- Experimental considerations

Resonant Inelastic X-ray Scattering

RIXS at a synchrotron

- elemental (and chemical) specificity
- unrestricted by dipole selection rules (d-d)
- near L-edges (2p-3d): sensitive to valence, orbitals and spin
- in correlated electron materials:
  charge-transfer, crystal field, collective excitations
- photon-in / photon-out:
  bulk sensitive, ok in E and B fields

but:

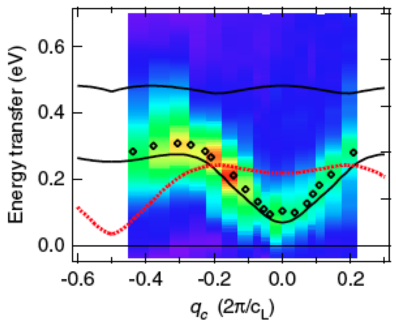
- photon hungry (dispersive detector)
- precludes time-resolved expts

RIXS in correlated electron materials

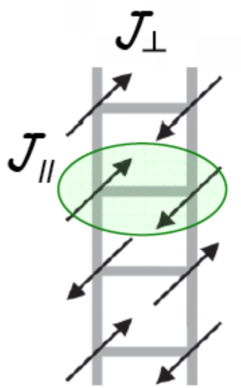
J Schlappa, *et al*, PRL 2009

Collective Magnetic Excitations in the Spin Ladder $Sr_{14}Cu_{24}O_{41}$ Measured Using High-Resolution Resonant Inelastic X-Ray Scattering

940 eV



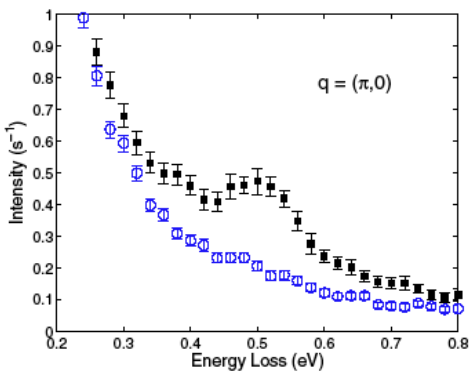
„two-triplon“ excitations at the Cu L_3 edge



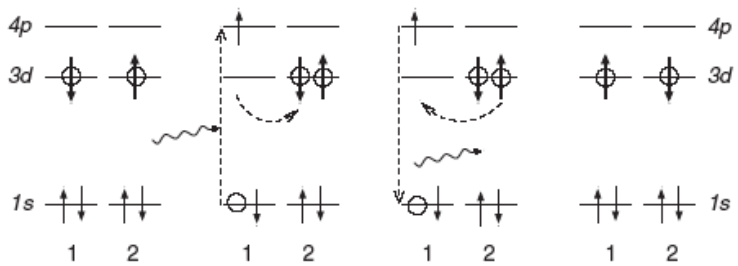
JP Hill, *et al*, PRL 2008

Observation of a 500 meV Collective Mode in $La_{2-x}Sr_xCuO_4$ and Nd_2CuO_4 Using Resonant Inelastic X-Ray Scattering

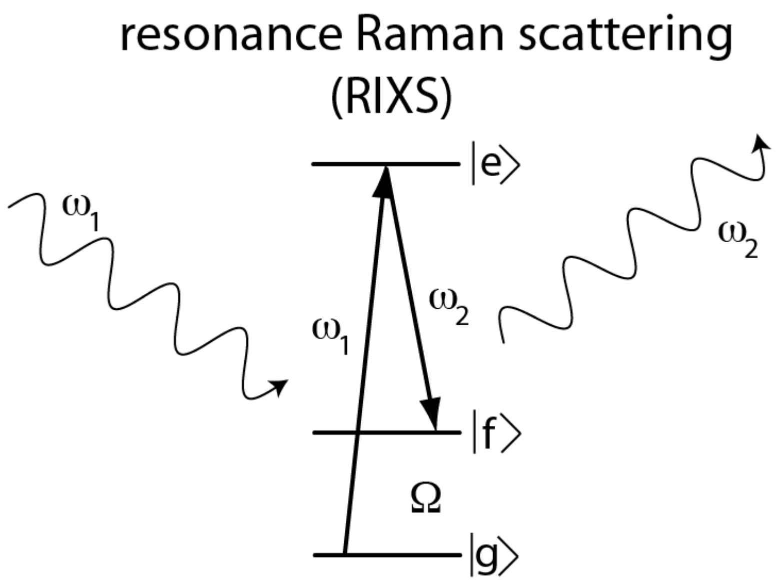
9 keV

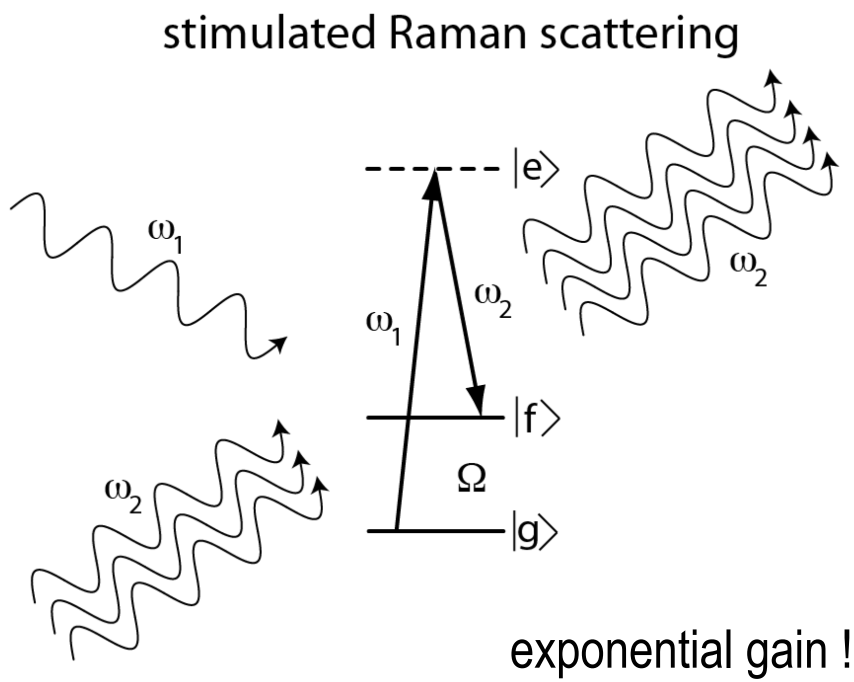


„multi-magnon“ excitations at the Cu *K* edge



Raman scattering





Both processes governed by 3rd-order NL susceptibility $\chi^{(3)}$.

Polarization and susceptibility

$$P(t) = \varepsilon_0\left[\chi^{(1)}E(t) + \chi^{(2)}E^2(t) + \chi^{(3)}E^3(t) + \cdots\right]$$
$$\equiv P^{(1)}(t) + P^{(2)}(t) + P^{(3)}(t) + \cdots$$
$$= -Ne\, x(t)$$

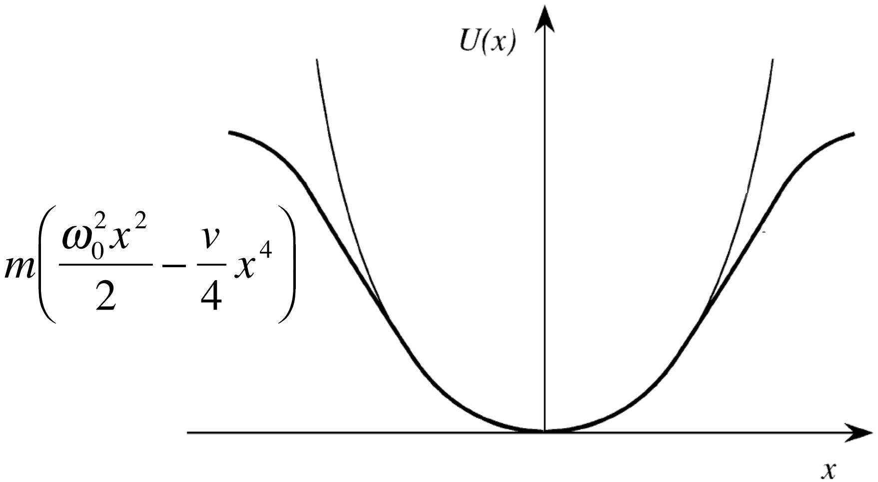
$$P^{(s)}(\omega_k) = \varepsilon_0\chi^{(s)}(\omega_k = \pm\omega_1 \pm \omega_2 \cdots \pm \omega_s)E(\pm\omega_1)E(\pm\omega_2)\cdots E(\pm\omega_s)$$

Raman scattering (spontaneous or stimulated) governed by:

$$\chi^{(3)}(\omega_2 = \omega_2 + \omega_1 - \omega_1)$$

Classical anharmonic oscillator

v = anharmonicity parameter



$$\ddot{x} + \gamma \dot{x} + \omega_0^2 x = \frac{-e}{m} E_x + v x^3$$

$$x \approx r_a \Rightarrow \omega_0^2 x^2 \approx v x^4$$

$$\Rightarrow v \approx \frac{\omega_0^2}{r_a^2} \qquad r_a = \text{atomic size}$$

$$\chi^{(3)}(\omega_2 = \omega_2 + \omega_1 - \omega_1) =$$

$$\frac{3Ne^4}{8\varepsilon_0 m^3 r_a^2} \frac{\omega_0^2}{\left|\omega_1^2 - \omega_0^2 - 2i\gamma\omega_1\right|^2 \left(\omega_2^2 - \omega_0^2 - 2i\gamma\omega_1\right)^2}$$

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$\chi^{(3)}$: optical frequency, non-resonant case

$$\gamma, \omega_1, \omega_2 << \omega_0; \hbar\omega_0 = 4.6\, eV; N = 4 \times 10^{22}\ cm^{-3}; r_a = 3\ \mathring{A}$$

$$\chi^{(3)}_{nr,opt} \approx \frac{Ne^4}{\varepsilon_0 m^3 r_a^2 \omega_0^6} = 0.3 \times 10^{-21} m^2 / V^2$$

experiment:

$$\chi^{(3)}_{nr,opt}(\mathrm{Al_2O_3}) = 0.21 \times 10^{-21}\ m^2 / V^2$$

$$(\mathrm{diamond}) = 1.8 \times 10^{-21}\ m^2 / V^2$$

$$(\mathrm{CdS}) = 98 \times 10^{-21}\ m^2 / V^2$$

$\chi^{(3)}$: X-ray frequency, resonant case

$$\omega_1 = \omega_0 = \omega_2 + \Omega; \gamma \approx \Omega << \omega_0; \ \hbar\gamma = 1\, eV$$

$$\chi^{(3)}_{res,X-ray} / N \approx \frac{e^4}{8\varepsilon_0 m^3 r_a^2 \omega_0^2 \gamma^4}$$

compare with „serious theory“:

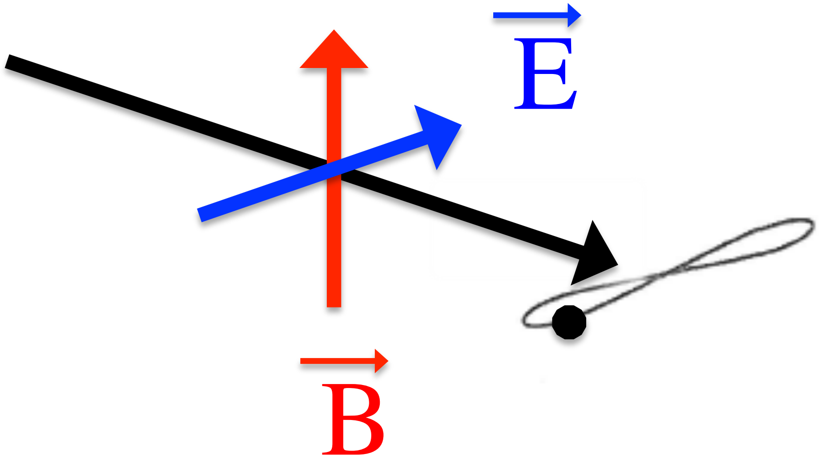
atom	r_a (Å)	$\hbar\omega_0$ (eV)	$\chi_{res,\,X\text{-}ray}/N$ (10^{-35} esu/atom)	literature value	
He	0.31	20.6	232	460 [Fill,1996]	$1^1S_0 \rightarrow 2^1S_0$
C	0.7	277	0.25	35 [Tanaka,2002]	$1s \rightarrow 2p$

Note:

$$\chi^{(3)}_{nr,opt} \approx \chi^{(3)}_{res,X-ray}$$

Classical free electron

include Lorentz force



$$\ddot{x} + \gamma\dot{x} = \frac{-e}{m}E_x + \frac{e}{m}\dot{z}B_y$$

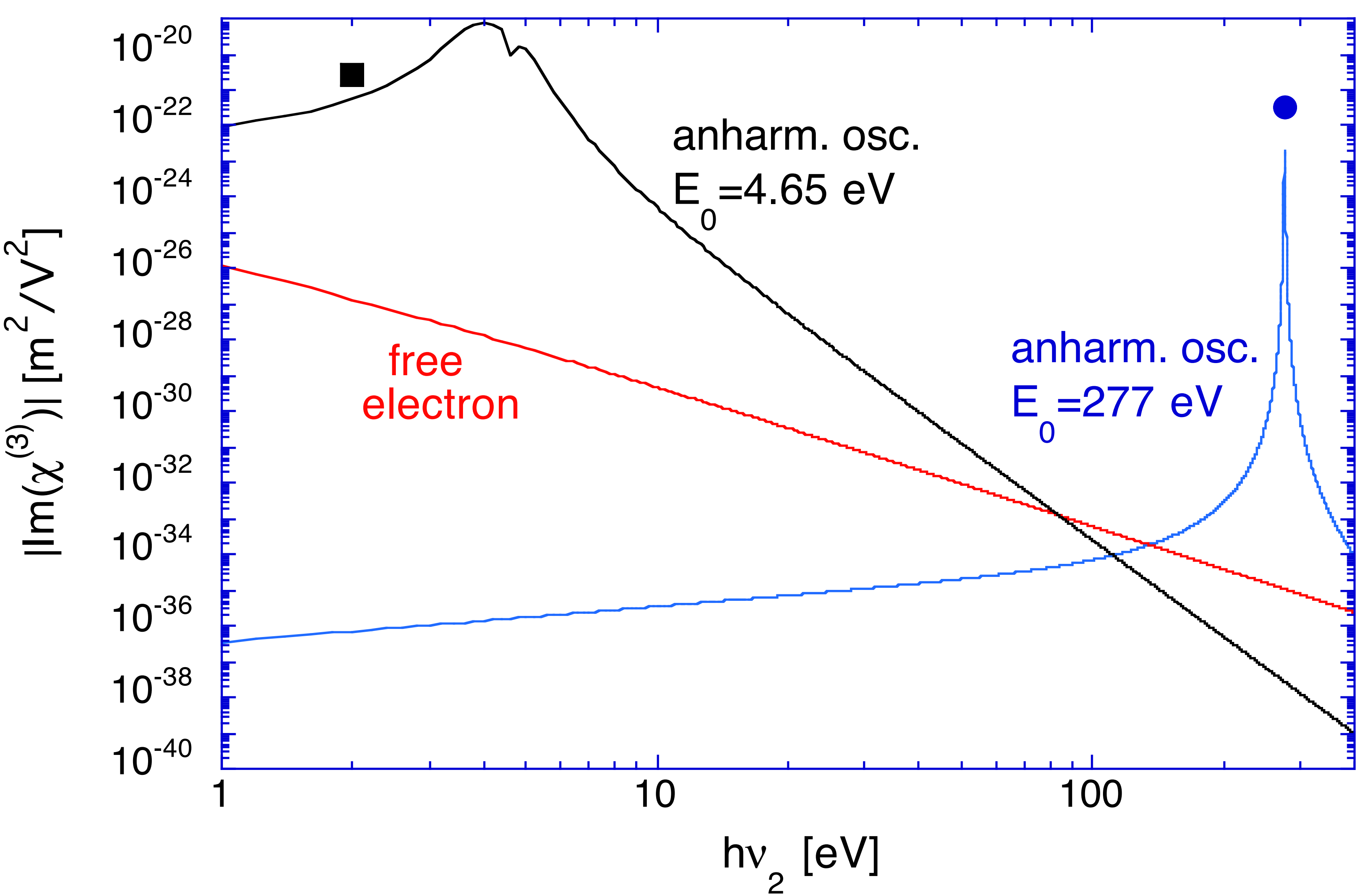
$$\ddot{z} + \gamma\dot{z} = \frac{-e}{m}\dot{x}B_y$$

$$B_y = \frac{1}{c}E_x$$

$$\chi^{(3)}(\omega_2 = \omega_2 + \omega_1 - \omega_1) \approx$$

$$\frac{Ne^4}{8\varepsilon_0 m^3 c^2}\frac{i\gamma}{\omega_1^2\omega_2(\omega_1 + \omega_2)(\omega_1 - \omega_2 + i\gamma)}$$

$\chi^{(3)}$ plots

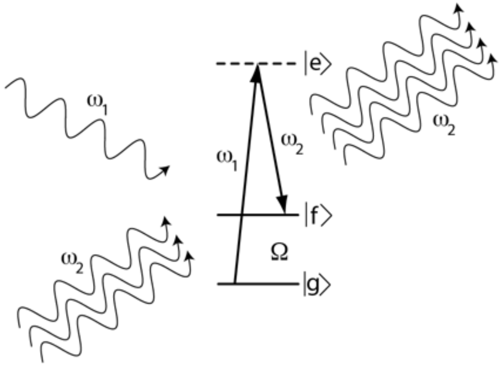


10^-20
10^-22
10^-24
10^-26
10^-28
10^-30
10^-32
10^-34
10^-36
10^-38
10^-40
|Im(χ^(3))| [m^2/V^2]
1
10
100
hν_2 [eV]
anharm. osc.
E_0=4.65 eV
free
electron
anharm. osc.
E_0=277 eV

When does *stimulated* compete with *spontaneous*?

Lee and Albrecht, 1985:

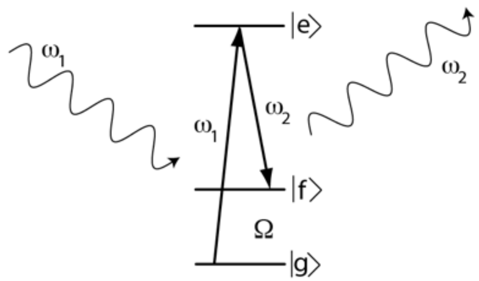
$$\frac{d^2\sigma_{stim}}{d\Omega_2 d\omega_2} = \frac{32\pi^2\hbar\omega_1\omega_2}{\varepsilon_0 c^2} F(\omega_2)\,\mathrm{Im}\left(\chi^{(3)}\right)/N$$



$F(\omega_2)$: spectral photon flux

Obtain the spontaneous case by setting $F = F_{bb\ zero\text{-}point} = \dfrac{\omega_2^2}{32\pi^3 c^2}$

$$\frac{d^2\sigma_{spon}}{d\Omega_2 d\omega_2} = \frac{\hbar\omega_1\omega_2^3}{\pi\varepsilon_0 c^4}\,\mathrm{Im}\left(\chi^{(3)}\right)/N$$



This corresponds to 4 x 10^9 photons (277 eV, 100 fs pulse, 0.5% bandwidth, $(100\ \mu m)^2$ focus).

XFEL delivers 10^{12} !

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The degeneracy parameter

Bloembergen, 1967:

... the stimulated effect will only be comparable to or larger than the spontaneous emission if the number of incident photons is so large that it exceeds the number of vacuum electromagnetic modes contained in the frequency interval of the linewidth.

Planck, 1911:

The black-body zero-point energy represents 1/2 photon per radiation mode.

Lengeler, 2001:

The number of photons/mode emitted by a source is given by the *degeneracy parameter* δ.

source	photon energy	δ
Hg lamp	4.9 eV	3×10^{-3}
synchrotron undulator	6.4 keV	2×10^{-3}
He-Ne laser	1.96 eV	2×10^{7}
XFEL	6.4 keV	2×10^{9}

Stimulated Raman pumping

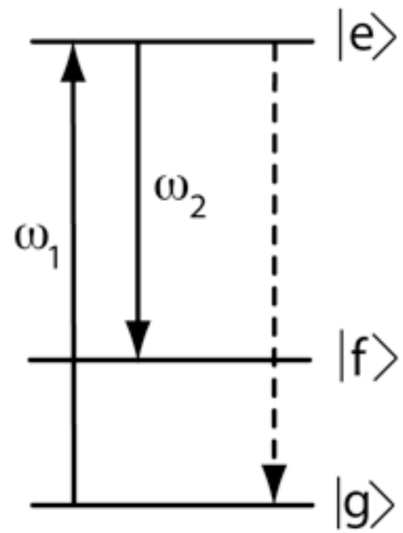
Use X-ray as a pump:

Devir and Bauer, 1978; Maier, et al, 1969:

rate of change of ground-state population:

$$\frac{\partial\Delta}{\Delta} = \frac{-32\pi^2 c^2 I_1 I_2 \tau}{\hbar^2 c^3 \omega_2^4 \gamma}\left(\frac{d\sigma_{spon}}{d\Omega_2}\right)$$

$$\approx \frac{-32\pi I_1 I_2 \tau}{\varepsilon_0 \hbar c^2}\mathrm{Im}\left(\frac{\chi^{(3)}}{N}\right)$$



Carbon (277 eV, 20 fs pulse):

$$\frac{\partial\Delta}{\Delta} = -1 \quad \text{for } I_1 = I_2 = 30\text{ MW}$$

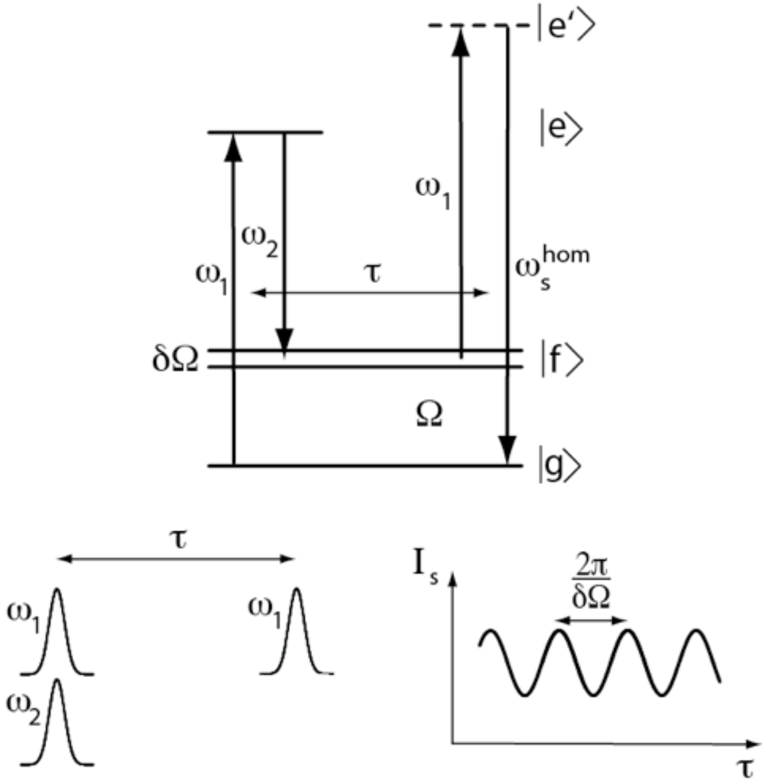
XFEL delivers 10 GW !

t-resolved Coherent Anti-Stokes Raman Scattering

X-ray pump – X-ray probe:

t-CARS : 4-wave mixing technique (also governed by $\chi^{(3)}$)

➔ t-resolved spectroscopy on superpositon of excited states



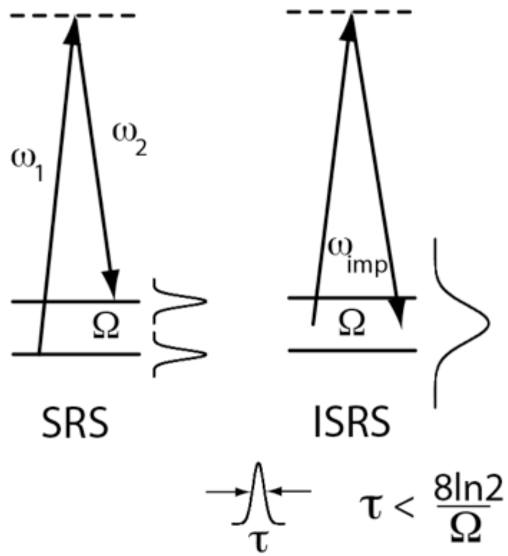
Impulsive stimulated Raman scattering [Nelson, 1987]

Supply ω_1 and ω_2 in a single pulse:

Minimum time-bandwidth product for a (Gaussian) pulse:

$$(\Delta E \cdot \tau)_{\min} = \hbar \Delta\omega_{FWHM} \tau_{FWHM} = 8\hbar \ln 2 = 3.65 \text{ eV fs}$$

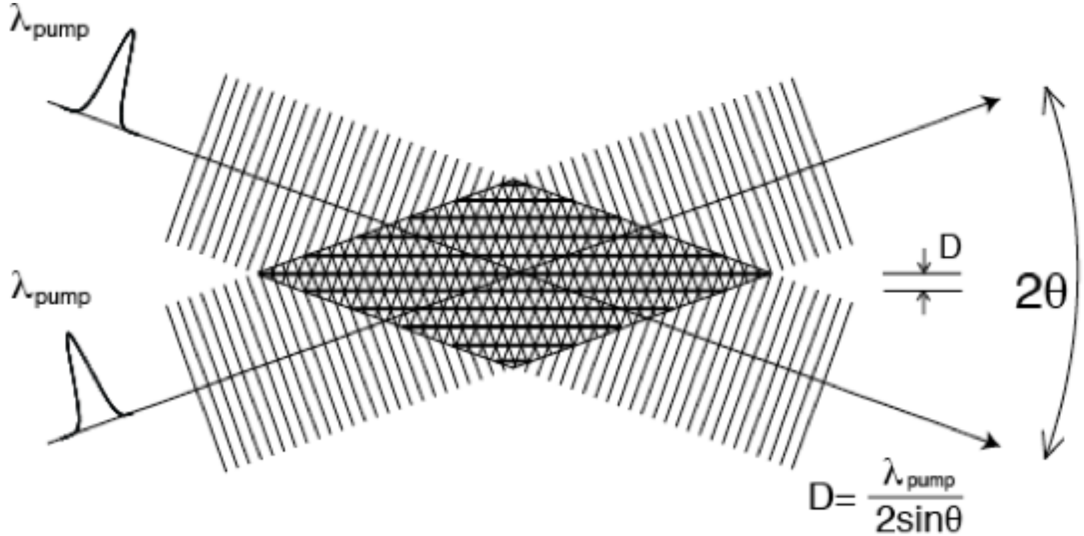
One sufficiently short XFEL pulse: delivers *both* frequencies required for stimulated Raman.



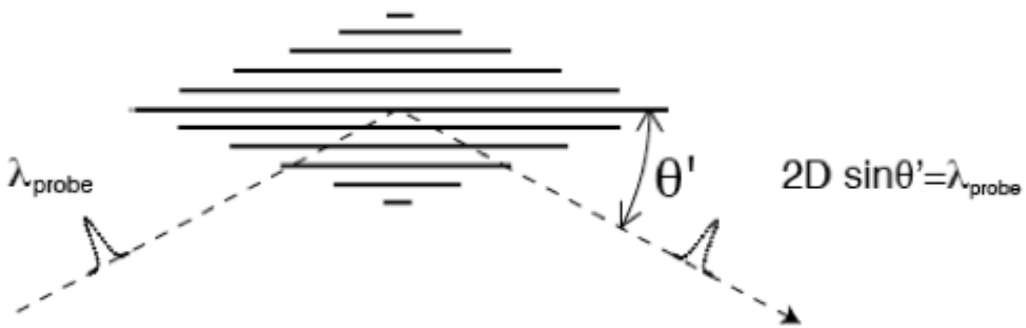
X-ray Transient Grating Spectroscopy

„Smart“ (q-selective) pump:

„Colliding“ pump pulses ➔ standing wave of excitation with given ω and q.



Transient grating queried by later probe pulse.

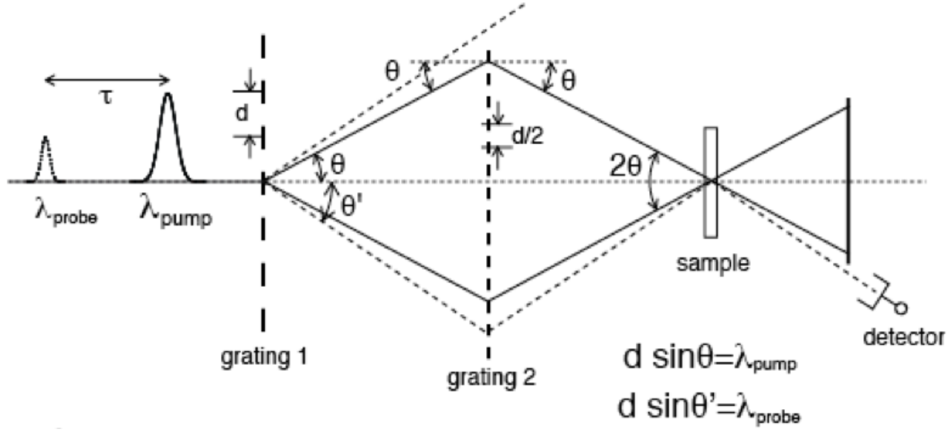


Examples of soft and hard XTGS experiments

soft

Spin excitations in $Sr_{14}Cu_{24}O_{41}$ at the
Cu $L_{2\text{-}3}$ edges (940 eV) [Schlappa, 2009]

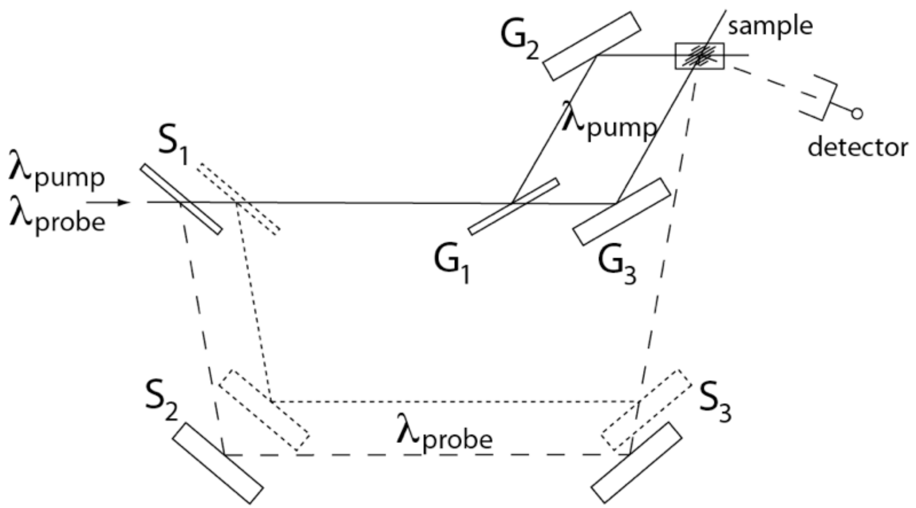
gratings: 300 nm diamond ridges, d=340 nm
3 µm substrate
T = 7%
η_{diff} = 12%
$T_{total} = 10^{-4}$; θ, θ' = 0.22, 0.25°



hard

Multi-magnon excitations in $La_{2-x}Sr_xCuO_4$ at the
Cu K edge (9 keV) [Hill, 2008]

thin Si crystals (30 µm) (T = 75%)
overall split-delay [Rosecker, 2009]: T = 1%



Need 2-color pulses – to differentiate pump and probe.

Summary

- Stimulated Raman: similar information as RIXS, with higher efficiency and t-resolution.

- $\chi^{(3)}$: estimated with classical models. Comparable values for non-resonant optical and resonant X-ray.

- Spontanteous Raman: stimulated by the bb zero-point field. At high degeneracy parameter, *stimulated* effect dominates. Efficient pumping to low-lying excited states.

- X-ray pump / X-ray probe analogs of t-CARS and TGS: promising possibilities at a (2-color) XFEL?

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