Nonlinear X-ray-Matter interaction with X-ray Lasers

Andreas Scherz
European XFEL
Summary

Part 1 (Tuesday)
- Spectroscopy and Microscopy
- XFEL and SASE radiation
- Stimulated emission
- Nonlinear response at x-ray energies

Part 2 (Wednesday)
- Nonlinear absorption
- Three-wave mixing
- Four-wave mixing
SPECTROSCOPY AND MICROSCOPY
Resonant vs non-resonant x-ray processes

Resonant processes changes cross sections by orders of magnitude

Courtesy J. Stöhr
Transition rates of resonant X-ray Processes

X-Ray Absorption
- empty states
- valence shell
- $\hbar \omega_1$

X-Ray Emission
- empty states
- core shell
- $\hbar \omega_2$

Resonant Elastic Scattering
- empty states
- valence shell
- $\hbar \omega_1$
- $\hbar \omega_1$

Resonant Inelastic Scattering
- empty states
- core shell
- $\hbar \omega_1$
- $\hbar \omega_2$
Transition rates of resonant X-ray Processes

\[ T_{if} = \frac{2\pi}{\hbar} \left| \langle f | \mathcal{H}_{\text{int}} | i \rangle + \sum_j \frac{\langle f | \mathcal{H}_{\text{int}} | j \rangle \langle j | \mathcal{H}_{\text{int}} | i \rangle}{\varepsilon_i - \varepsilon_j} \right|^2 \delta(\varepsilon_i - \varepsilon_f) \rho(\varepsilon_f) \]

Fermi's Golden rule

Kramers - Heisenberg
Measurement of resonant X-ray Processes

- Elastic scattering
- Diffraction
- X-ray emission
- Inelastic scattering
- Absorption

Very low signal!

Courtesy J. Stöhr
X-ray Spectro-Microscopy

- X-ray tunability: elemental and chemical specificity
- X-ray polarization XMCD, XMLD
- Buried Structures

**X-ray view of Exchange Bias**

X-ray Spectro-Microscopy

- X-ray tunability: elemental and chemical specificity
- X-ray polarization XMCD, XMLD
- Buried Structures

Tuning to absorption resonances

Non-Resonant

XMCD

Photon energy (eV)

775  785

magnetic domains
Co/Pt multilayers

Transmission

October 4th/5th, 2016 - AlbaNova University Centre, Stockholm, Nordita School on Photon-Matter Interaction
Andreas Scherz, European XFEL
Tuning to absorption resonances

Resonant

magnetic domains
Co/Pt multilayers

Transmision
XMCD

Photon energy (eV)

775  785
Fourier Transform Spectro-Holography

**FTH Recording**  

- Using holographic mask
- Exploiting XMCD to image magnetic domains
- Resolution < 50nm

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**FTH Reconstruction**
- Need a sufficient amount of photons
- Need them in a very short time
- *Nonperturbative*: Damage to the sample must occur after snapshot
 XFEL and SASE radiation
Single shot image requires:
- Full field microscopy
- Coherent x-ray compatibility
- Robust and unique image reconstruction
- High photon efficient method

Single shot imaging to study:
- Non periodic structures in their “instant” state
- High resolution imaging beyond 10nm
- Fast dynamics on relevant length scales

European XFEL
- 1-100fsec
- 10mJ / pulse at soft x-ray wavelengths
- 0.1-1% bandwidth
- 10^14 photons/pulse
- Full transverse coherent
Facility overview

DESY-Bahrenfeld

- Electron source
- Linear accelerator begins
Nonlinear X-ray-Matter Interaction with X-ray Lasers

Facility overview

European XFEL

DESY-Bahrenfeld

- Electron source
- Linear accelerator begins

Superconducting electron accelerator
Facility overview

- Osdorfer Born
  - Electron beam to photon beamlines
  - Undulator systems begin

- DESY-Bahrenfeld
  - Electron source
  - Linear accelerator begins

Superconducting electron accelerator
Facility overview

Schenefeld
- Experiment hall
- Laboratories
- Offices

Osdorfer Born
- Electron beam to photon beamlines
- Undulator systems begin

DESY-Bahrenfeld
- Electron source
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Superconducting electron accelerator
### Optical beam transport and instruments

<table>
<thead>
<tr>
<th>Undulator Segment</th>
<th>FEL radiation energy [keV]</th>
<th>Wavelength [nm]</th>
</tr>
</thead>
<tbody>
<tr>
<td>SASE 1</td>
<td>3 - over 24</td>
<td>0.4 - 0.05</td>
</tr>
<tr>
<td>SASE 2</td>
<td>3 - over 24</td>
<td>0.4 - 0.05</td>
</tr>
<tr>
<td>SASE 3</td>
<td>0.27 - 3</td>
<td>4.6 – 0.4</td>
</tr>
</tbody>
</table>

- **Orange color**: X-ray optics & Beam Transport
- **430 m**

**Legend**
- electron tunnel
- photon tunnel
- undulator
- electron switch
- electron bend
- electron dump

**Additional Information**

- **Linear accelerator** for electrons (10.5, 14.0, 17.5 GeV)
- **SASE 2** 0.05 nm - 0.4 nm
- **SASE 1** 0.05 nm - 0.4 nm
- **SASE 3** 0.4 nm - 4.7 nm
### Hard X-rays

**SPB/SFX: Single Particles, Clusters, and Biomolecules and Serial Femtosecond Crystallography**
- Will determine the structure of single particles, such as atomic clusters, viruses, and biomolecules

**MID: Materials Imaging and Dynamics**
- Will be able to image and analyze nano-sized devices and materials used in engineering

**FXE: Femtosecond X-Ray Experiments**
- Will investigate chemical reactions at the atomic scale in short time scales—molecular movies

**HED: High Energy Density Physics**
- Will look into some of the most extreme states of matter in the universe, such as the conditions at the center of planets

### Soft X-rays

**SQS: Small Quantum Systems**
- Will examine the quantum mechanical properties of atoms and molecules.

**SCS: Spectroscopy and Coherent Scattering**
- Will determine the structure and properties of complex materials and nano-sized structures.
Statistical properties of SASE radiation and bandpass effects

SASE pulses after monochromator close to transform limit

SCS X-ray beam delivery using monochromator for time-resolved spectroscopy (100x100µm²)

(PINK BEAM: up to $10^{14}$ photons per pulse)

(Pink Beam: up to $10^{18}$-$10^{20}$ W/cm²)
Number of photons in coherence volume

<table>
<thead>
<tr>
<th>source</th>
<th>photon energy</th>
<th>$\delta$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hg lamp</td>
<td>4.9 eV</td>
<td>$3 \times 10^{-3}$</td>
</tr>
<tr>
<td>synchrotron undulator</td>
<td>6.4 keV</td>
<td>$2 \times 10^{-3}$</td>
</tr>
<tr>
<td>He-Ne laser</td>
<td>1.96 eV</td>
<td>$2 \times 10^{7}$</td>
</tr>
<tr>
<td>XFEL</td>
<td>6.4 keV</td>
<td>$2 \times 10^{9}$</td>
</tr>
</tbody>
</table>
number of simultaneous coherent x-rays

“simultaneous” is defined by atomic decay clock ~ 1 fs

Storage ring:

$10^{14}$ phot./eV/s $\rightarrow$ $10^{-1}$ phot./eV/fs “one photon at a time”
“simultaneous” is defined by atomic decay clock ~ 1 fs

Storage ring:

$10^{14}$ phot./eV/s $\rightarrow$ $10^{-1}$ phot./eV/fs “one photon at a time”

X-Ray lasers $10^9$ phot./fs

Typical x-ray pulse: $\hbar \omega = 778$ eV, $\Delta E = 1$ eV

- $\sim 50$ fs
- $\sim 15 \mu$m
- $\sim 1.8$ fs
- $\sim 550$ nm
- Coherent wave packet
Single-shot FTH

- Zero order beam and Circular Polarizer,
- >100 mJ/cm$^2$,
- 70fs pulse duration
Single-shot FTH

- Zero order beam and Circular Polarizer
- >100mJ/cm², 70fs pulse duration

Second shot
Single shot imaging of magnetic nanostructure

**Monochromator:** Co L3 edge (778.8eV) with 0.5eV bandwidth

**Photons after the polarizer:** $1 \times 10^9$ photons/pulse

**Focus at sample:** $10 \times 30 \mu m^2$

**Shot-shot intensity jitter:** Fluences from 1 to 30mJ/cm$^2$

**Nominal pulse durations:** 80fs and 360fs

Imaging threshold

1.5x10^5 photons detected in a 80fs x-ray pulse
Spatial multiplexing to improve image quality by up to a factor 4 (15 ref.)

Combination of resonant enhancement, phase recording and spatial multiplexing

Imaging threshold as low as 5mJ/cm^2
Single Shot Holography

- Using Fourier transform holography, obtain real-space image of magnetic domains.
- Diffraction from a single x-ray pulse (~5 mJ/cm²).
- We can combine this with pump-probe techniques to make time-resolved movies!
- Attain high resolution in single shot:

Critical time scale of stimulated x-ray processes

Stimulated processes must be triggered before spontaneous excited state decays

“atomic clock” = total decay time = a few femtoseconds
Amplified stimulated emission in a gas

LETTER

doi:10.1038/nature10721

Atomic inner-shell X-ray laser at 1.46 nanometres pumped by an X-ray free-electron laser

Nina Rohringer¹, Duncan Ryan², Richard A. London¹, Michael Purvis³, Felicie Albert¹, James Dunn¹, John D. Bozek³, Christoph Bostedt¹, Alexander Graf, Randal Hill¹, Stefan P. Hau-Riege¹ & Jorge J. Rocca²

Pulse length 40-80 fs
Pulse energy < 0.27 mJ
Power density < 2*10¹⁷ W/cm²

Atomic inner-shell X-ray laser

LETTER

Stimulated X-ray emission for materials science


$I = 1 \times 10^{16} \frac{W}{cm^2}$

Detected conversion is $10^{-11}$, stimulation enhancement by a factor $\sim 2$
Single shot diffraction atomic versus electronic structure

atomic structure: single shot pattern of virus or crystal

magnetic structure: Co/Pt domains
50 fs pulses

- 1 KJ/cm²
- 1 J/cm²
- 1 mJ/cm²
- 30 mJ/cm²
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- Four-wave mixing
NONLINEAR ABSORPTION
Extension to High Intensity Single Shots

Wu et al., PRL 117, 027401 (2016)
If diffraction scales linearly with intensity:

$$\text{High Intensity Pattern} = \text{Low Intensity Pattern} \times \text{Intensity Ratio}$$

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Increase intensity to \(~300\text{mJ/cm}^2\)

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Increase intensity to \( \sim 300 \text{mJ/cm}^2 \)
If diffraction scales linearly with intensity:

\[
\text{High Intensity Pattern} = \text{Low Intensity Pattern} \times \text{Intensity Ratio}
\]

Increase intensity to \(\sim 300 \text{mJ/cm}^2\)

- **Low Intensity**
  - 0.6 mJ/cm\(^2\)
  - \(x\,500\)

- **High Intensity**
  - 272 mJ/cm\(^2\)
  - 1500

Wu et al., PRL 117, 027401 (2016)
Two main observations:
1) Strong decrease in magnetic speckle intensity (loss of magnetic contrast)
2) Decrease in charge scattering
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Single shot diffraction of atomic versus magnetic structure

atomic structure: single shot pattern of virus or crystal

> $10^3$ difference in fluence!

magnetic structure: Co/Pt domains 50 fs pulses
$\psi_{tot}(r \simeq z) = \exp[ik_0z] + \frac{\exp[ikr]}{r} f(q)$

$\psi_{tot} \simeq \exp[ikz] \left\{ 1 + \frac{\exp[ik(x^2 + y^2)/2z]}{z} f(q \simeq 0) \right\}$

in the forward direction we require

$\int ds |\psi_{tot}|^2 = \pi R^2 - \frac{4\pi}{k} \text{Im} \{f(q = 0)\}$

$kR^2/z \gg 2\pi$ and $R/z \ll 1$

$\sigma_{sc} = 4\pi(f'^2 + f''^2)$

$\sigma_{abs} = \frac{\Gamma A}{\Gamma} 2\lambda f'''$

Optical constants, response function and their relation to the atomic scattering length

Refractive index and electric susceptibility

\[ n_\omega^2 = 1 + \chi(\omega) = 1 + \chi'(\omega) + i\chi''(\omega) \]

Optical constants

\[ n_\omega = 1 - \delta_\omega + i\beta_\omega \]

Atomic scattering length

\[ f(\omega) = r_0 Z + f'(\omega) - i f''(\omega) \]

\[ \delta_\omega = \frac{2\pi}{k^2} N_{at} (r_0 Z + f'(\omega)) \]

\[ \beta_\omega = \frac{2\pi}{k^2} N_{at} f''(\omega) \]
Stimulated resonant process

(a) Two-photon picture

(b) Single EM-wave picture

absorption

stim. scatt.

wave in

wave out
Polarisability

\[ P(t) = \varepsilon_0 \chi E(t) \]

\[ P(t) = \varepsilon_0 \left( \chi^{(1)} + \chi^{(2)} E(t) + \chi^{(3)} E^2(t) + \cdots \right) E(t) \]

\[ \equiv P^{(1)} + P^{(2)} + P^{(3)} + \cdots \]

\[ \chi = \chi^{(1)} + \chi^{(2)} E(t) + \chi^{(3)} E^2(t) + \cdots \]
Polarisability and nonlinear media response
Estimate of higher order response

Polarisability
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When NL terms compete with the linear term?
\[ \chi^{(n)} = \chi^{(n-1)} / |E| \approx \chi^{(n-1)} / |E_{\text{atom}}| \]
\[ \hbar \omega_{L23} = \int_{2p}^{3d} dr \, eE_{\text{atom}} = eE_{\text{atom}} |\mathcal{R}_{2p3d}| \]
\[ \mathcal{R}_{2p3d} = 6.2 \times 10^{-3} \text{ e nm} \]
Polarisability and nonlinear media response

Estimate of higher order response

Polarisability

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

When NL terms compete with the linear term?

\[ \chi^{(n)} = \chi^{(n-1)}/|E| \simeq \chi^{(n-1)}/|E_{\text{atom}}| \]
\[ \hbar \omega_{L23} = \int_{2p}^{3d} dr eE_{\text{atom}} = eE_{\text{atom}} |\mathcal{R}_{2p3d}| \]
\[ E_{\text{atom}} = 1.3 \times 10^{12} \frac{\text{V}}{\text{cm}} \]
The classical anharmonic oscillator model
off-resonant vs. resonant nonlinear response

\[ U(x) = \frac{1}{2} m\omega_0^2 x^2 - \frac{1}{4} mbx^4 \]

- Nonlinearity constant: \( b = \frac{\omega_0^2}{d^2 a_0^2} \)
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\[ \chi_{\text{off}}^{(3)}(\omega_0) = \frac{Ne^4}{\varepsilon_0 d^2 a_0^2 m^3 \omega_0^6} \]
The classical anharmonic oscillator model: off-resonant vs. resonant nonlinear response

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- Off-resonant Nonlinear response

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- Resonant Nonlinear response

\[ \chi^{(3)}_{\text{res}}(\omega_0) = \frac{Ne^4}{16\varepsilon_0 d^2 a_0^2 m^3 \omega_0^2 \gamma^4} \]
The classical anharmonic oscillator model
off-resonant vs. resonant nonlinear response

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\[ \chi_{\text{res}}^{(3)}(\omega_0) = \frac{Ne^4}{16\varepsilon_0 d^2a_0^2 m^3\omega_0^2\gamma^4} \]

- Co metal

\[ N = 90 \text{ at./nm}^3 \]
\[ d = 2.4 \text{ in units of the Bohr radius } a_0 \]
\[ \gamma \simeq 0.4 \text{ eV} \]
The classical anharmonic oscillator model
off-resonant vs. resonant nonlinear response

\[ U(x) = \frac{1}{2} m \omega_0^2 x^2 - \frac{1}{4} m b x^4 \]

- Nonlinearity constant: \( b = \frac{\omega_0^2}{d^2 a_0^2} \)

- Off-resonant Nonlinear response

\[ \chi^{(3)}_{\text{off}}(\omega_0) = \frac{N e^4}{\varepsilon_0 d^2 a_0^2 m^3 \omega_0^6} \]

- Resonant Nonlinear response

\[ \chi^{(3)}_{\text{res}}(\omega_0) = \frac{N e^4}{16\varepsilon_0 d^2 a_0^2 m^3 \omega_0^2 \gamma^4} \]

\[ \chi^{(3)}_{\text{off}}(\omega_0) \approx 1.1 \times 10^{-27} \text{ cm}^2 \text{ V}^{-2} \]

\[ \chi^{(3)}_{\text{res}}(\omega_0) \approx 2 \times 10^{-20} \text{ cm}^2 \text{ V}^{-2} \]

Nonlinear term at soft x-ray resonances becomes almost as large as the nonlinear term at optical wavelengths.
Optical Bloch equations of a two-level system

\[ \dot{\rho}_{21} = -i(\omega_{21} + \gamma)\rho_{21} + \frac{i}{\hbar} V_{21} \Delta \rho_{21} \]

\[ V_{21} = -\mu_{21} E(t) = -e \langle 1| \epsilon \rho |2 \rangle E e^{-i\omega t} \]

\[ \rho_{22} \quad \text{wave in} \quad \text{wave out} \quad \rho_{12}, \rho_{21} \]

\[ \rho_{11} \]

\[ \Gamma = \Gamma_x + \Gamma_a \]

\[ \gamma = \frac{1}{2} \Gamma_x + \frac{1}{2} \Gamma_a + \gamma_{el} \]
Excited state population in the Bloch picture

For $\tau_c \gg \hbar / \Gamma_A = 1.5 \text{fs}$ (Auger decay time)

Equilibrium excited state population:

Stöhr, Scherz, PRL 115, 107402 (2015)
Steady state response of the two level system

Polarisability

\[ P = \chi \varepsilon_0 E = n_a \text{tr} (\rho \mu) = n_a (\rho_{12} \mu_{21} + \rho_{21} \mu_{12}) \]

Susceptibility

\[ \chi = \frac{n_a |\mu_{21}|^2 (\omega - \omega_{21} - i\gamma) \Delta \rho_{21}^{\text{eq}}}{\varepsilon_0 \hbar \left[ (\omega - \omega_{21})^2 + \gamma^2 + 4\gamma / \Gamma V^2 \right]} \]

Rabi Frequency

\[ V = |\mu_{21}| |E| / \hbar \quad \Gamma_x = \frac{4\pi^2}{\varepsilon_0 \hbar \lambda^3} |\mu_{21}|^2 = \frac{4\pi^2 \hbar}{\varepsilon_0 \lambda^3} \frac{V^2}{|E|^2} \]
Nonlinear atomic scattering length

\[ \chi = \chi^{(1)} \frac{1}{1 + \mathcal{G} \frac{\Gamma_x \gamma}{\Delta^2 + \gamma^2} \langle n_x \rangle} = \chi^{(1)} \mathcal{B}_{NL} \quad \mathcal{V}^2 = \frac{1}{4} \mathcal{G} \Gamma_x \Gamma \langle n \rangle \]

\[ \chi^{(1)} = \frac{n_a \lambda^3}{4\pi^2} \frac{\Gamma_x (\Delta - i\gamma)}{\Delta^2 + \gamma^2} \Delta \rho_{21}^{eq} \]

atomic scattering length

\[ f' = -\frac{\lambda}{4\pi} \frac{\Gamma_x \Delta}{\Delta^2 + \gamma^2} \Delta \rho_{21}^{eq} \mathcal{B}_{NL} - r_0 Z = f' \mathcal{B}_{NL} - r_0 Z \]

\[ f'' = -\frac{\lambda}{4\pi} \frac{\Gamma_x \gamma}{\Delta^2 + \gamma^2} \Delta \rho_{21}^{eq} \mathcal{B}_{NL} = f'' \mathcal{B}_{NL} \]

\[ \mathcal{B}_{NL} = \frac{1}{1 + \frac{4\pi}{\lambda} f'' \mathcal{G} \langle n \rangle} \]
TABLE 1: Polarization dependent parameters for the $L_3$ resonances of Fe, Co, and Ni metals. Listed are the atomic number densities $\rho_a$, the resonance energies and wavelengths, and the polarization dependent ($q = 0, \pm$) peak experimental cross sections $\sigma_q^0$ ($1$ Mb $= 10^{-4} \text{ nm}^2$), assuming propagation along the magnetization direction. $\Gamma_q^\pm$ is the polarization dependent dipole transition width which includes the number of valence holes $N_h$, and $\Gamma$ is the natural decay energy width [15].

<table>
<thead>
<tr>
<th></th>
<th>$\rho_a$ [atoms/nm$^3$]</th>
<th>$\varepsilon_0$ [eV]</th>
<th>$\lambda_0$ [nm]</th>
<th>$\sigma_0^{+}$ [Mb]</th>
<th>$\sigma_0^{0}$ [Mb]</th>
<th>$\sigma_0^{-}$ [Mb]</th>
<th>$\Gamma^+ [\text{meV}]$</th>
<th>$\Gamma^0 [\text{meV}]$</th>
<th>$\Gamma^- [\text{meV}]$</th>
<th>$\Gamma [\text{eV}]$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe</td>
<td>84.9</td>
<td>707</td>
<td>1.75</td>
<td>8.8</td>
<td>6.9</td>
<td>5.0</td>
<td>1.37</td>
<td>1.08</td>
<td>0.78</td>
<td>0.36</td>
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<tr>
<td>Co</td>
<td>90.9</td>
<td>778</td>
<td>1.59</td>
<td>7.9</td>
<td>6.25</td>
<td>4.65</td>
<td>1.208</td>
<td>0.96</td>
<td>0.715</td>
<td>0.43</td>
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<tr>
<td>Ni</td>
<td>91.4</td>
<td>853</td>
<td>1.45</td>
<td>5.1</td>
<td>4.4</td>
<td>3.7</td>
<td>0.675</td>
<td>0.575</td>
<td>0.48</td>
<td>0.48</td>
</tr>
</tbody>
</table>
Onset of nonlinear contributions

High intensity

\[ B_{NL} = \frac{1}{1 + \frac{4\pi}{\lambda} f_0'' G \langle n \rangle} \]

Med intensity

\[ B_{NL} \simeq 1 - \frac{4\pi}{\lambda} G f_0'' \langle n \rangle \]

Low intensity

\[ B_{NL} \simeq 1 \quad f_0', f_0'' \]
First and third order response function

Co L3 edge

\[ \chi(1) \]

\[ \chi(3) [\text{cm}^2/\text{N}^2] \]

Photon Energy [eV]

\[ \times 10^{-19} \]
Gain Factor by coherent forward scattering

\[ I_{FW} = |E|^2 \approx I_0 \left[ 1 - 2\lambda n_a \Delta f'' + 2\lambda^2 n_a^2 \Delta^2 f''^2 \right] \]

Gain factor: \[ G = \frac{\lambda^2 N_a}{4\pi A} \]
Saturable X-ray absorption

(a) Co metal $L_3$ resonance

Eff. abs. cross section

Photon energy (eV)

(b) Trans. Intensity $I_0^0$ vs $I_0^0$

$I_0 [\text{mJ/cm}^2/\text{fs}]$

0.05 10 50 20 10 1 0.001

(c) XMCD $I_{\text{trans}}^0 / I_0^0 - I_{\text{trans}}^+ / I_0^+$

Sample thickness $d (\text{nm})$

$I_0 [\text{mJ/cm}^2/\text{fs}]$

0.001 1 10 20 50 100 1000

Stöhr, Scherz, PRL 115, 107402 (2015)
Experiment vs Theory

(a) Calculated SASE-stimulated coherent diffraction

(b) Integrated Intensity vs q (nm\(^{-1}\))

Low Intensity 0.6 mJ/cm\(^2\)/pulse
High Intensity 272 mJ/cm\(^2\)/pulse

Low Intensity 0.1 mJ/cm\(^2\)/pulse
High Intensity 270 mJ/cm\(^2\)/pulse

Contrast rel. to spontaneous

Wu et al., PRL 117, 027401 (2016)
Optical theorem

\[ \psi_{\text{tot}}(r \approx z) = \exp[i k_0 z] + \frac{\exp[i k r]}{r} f(q) \]

\[ \psi_{\text{tot}} \approx \exp[i k z] \left\{ 1 + \frac{\exp[i k (x^2 + y^2)/2z]}{z} f(q \approx 0) \right\} \]

in the forward direction we require

\[ k R^2 / z \gg 2\pi \text{ and } R/z \ll 1 \]

\[ \int d s |\psi_{\text{tot}}|^2 = \pi R^2 - \frac{4\pi}{k} \text{Im} \{ f(q = 0) \} \]

\[ \sigma_{\text{tot}} = \sigma_{\text{sc}} + \sigma_{\text{abs}} = \sigma_{\text{ex}} = \frac{4\pi}{k} \text{Im} f(0) \]

\[ \sigma_{\text{sc}} = 4\pi (f''^2 + f'''^2) \]

\[ \sigma_{\text{abs}} = \frac{\Gamma}{\Gamma} 2 \lambda f''' \]

THREE-WAVE MIXING
FOUR-WAVE MIXING
Wave mixing in response theory

\[ P(t) = \varepsilon_0 \left( \chi^{(1)} + \chi^{(2)} E(t) + \chi^{(3)} E^2(t) + \cdots \right) E(t) \]

\[ P^{(1)}(\omega_2) = \varepsilon_0 \chi^{(1)}(\omega_2 = \pm \omega_1) E(\omega_1) \]
Wave mixing in response theory

\[ P(t) = \varepsilon_0 \left( \chi^{(1)} + \chi^{(2)} E(t) + \chi^{(3)} E^2(t) + \cdots \right) E(t) \]

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Wave mixing in response theory

\[
P(t) = \varepsilon_0 \left( \chi^{(1)} + \chi^{(2)} E(t) + \chi^{(3)} E^2(t) + \cdots \right) E(t)
\]

\[
P^{(1)}(\omega_2) = \varepsilon_0 \chi^{(1)}(\omega_2 = \pm \omega_1) E(\omega_1)
\]

\[
P^{(2)}(\omega_3) = \varepsilon_0 \chi^{(2)}(\omega_3, \pm \omega_2, \pm \omega_1) E(\omega_2) E(\omega_1)
\]
Wave mixing in response theory

\[
    P(t) = \varepsilon_0 \left( \chi^{(1)} + \chi^{(2)} E(t) + \chi^{(3)} E^2(t) + \cdots \right) E(t)
\]

\[
P^{(1)}(\omega_2) = \varepsilon_0 \chi^{(1)}(\omega_2 = \pm \omega_1) E(\omega_1)
\]

\[
P^{(2)}(\omega_3) = \varepsilon_0 \chi^{(2)}(\omega_3, \pm \omega_2, \pm \omega_1) E(\omega_2) E(\omega_1)
\]

\[
P^{(3)}(\omega_4) = \varepsilon_0 \chi^{(3)}(\omega_4, \omega_3 \pm, \omega_2 \pm, \omega_1 \pm) E(\omega_3) E(\omega_2) E(\omega_1)
\]
Three wave mixing:
Second harmonic generation in diamond

\[ I = 1 \times 10^{16} \frac{W}{cm^2} \]

\[ \omega_2 = \omega_1 \]

\[ \omega_3 = 2\omega_1 \]

\[ \chi^2(7.3\, keV) \approx \sqrt{\nu_{\text{eff}}/E_{\omega_1}} = \sqrt{I_{\text{SHG}}/I_{\omega_1}}/E_{\omega_1} \]

\[ = 5.8 \times 10^{-11}/2.5 \times 10^9 \frac{V}{cm} = 2.3 \times 10^{-20} \frac{cm}{V} \]
Four wave mixing (FWM)

General four wave mixing scheme

Transient grating spectroscopy

resonance Raman scattering (RIXS)

stimulated Raman scattering

Bruce Patterson, SLAC-TN-10-026 (2010)
Transient grating spectroscopy at XUV wavelengths

Four-wave mixing experiments with extreme ultraviolet transient gratings

\[ \chi^{(3)} = \left( \frac{I_{\text{FWM}}}{I_0} \right)^{1/2} \left( \frac{E_{\text{EUV1}} E_{\text{EUV2}}}{E_{\text{EUV1}} E_{\text{EUV2}}} \right) \approx 6 \times 10^{-22} \text{m}^2 \text{V}^{-2} \]
Impulsively-driven coherent lattice dynamics

Transient Grating Experiments on V-SiO$_2$

Hyper- Raman modes due to coupled tetrahedral rotations $v_2 \approx 4.1$ THz

Raman modes due to tetrahedral bending $v_1 \approx 1.2$ THz

Acoustic-like excitations

Courtesy C. Masciovecchio
Two colour pulses schemes at XFEL’s

Two-colour pump-probe experiments with a twin-pulse-seed extreme ultraviolet free-electron laser

Courtesy C. Masciovecchio
CARS scheme using two-colour pulses from the machine and a x-ray split & delay line

Courtesy C. Masciovecchio
Beyond CARS
Coherent X-ray Raman spectroscopy

\[ S(\Omega_1, \Omega_3) = \int d\tau_1 e^{i\Omega_1 \tau_1} \int d\tau_3 e^{i\Omega_3 \tau_3} I_0^{\text{het}}(\tau_1, \tau_3) \]

Tanaka, Mukamel, PRL 89, 043001
## Acknowledgement

<table>
<thead>
<tr>
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Part 1 (Tuesday)
- Spectroscopy and Microscopy
- XFEL and SASE radiation
- Stimulated emission
- nonlinear response at x-ray energies

Part 2 (Wednesday)
- Nonlinear absorption
- Three-wave mixing
- Four-wave mixing
END