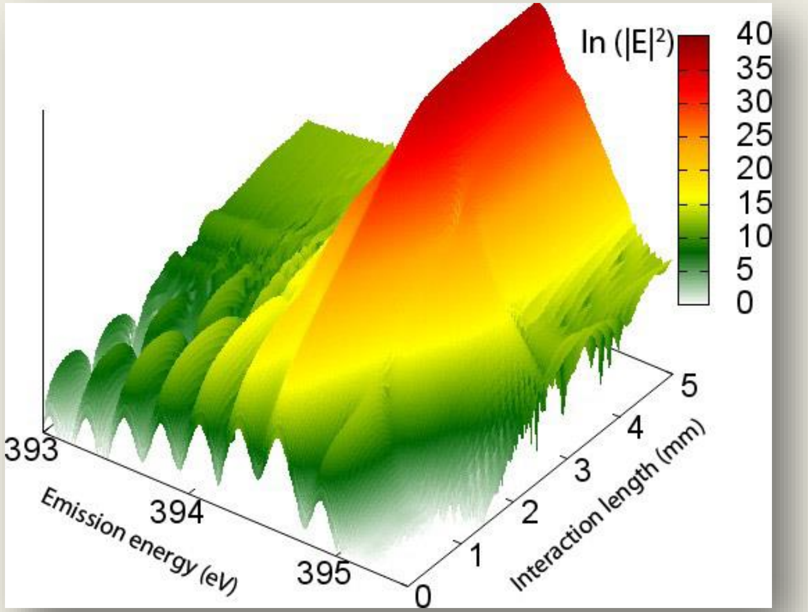
Stimulated X-ray emission in molecules: experience and perspectives



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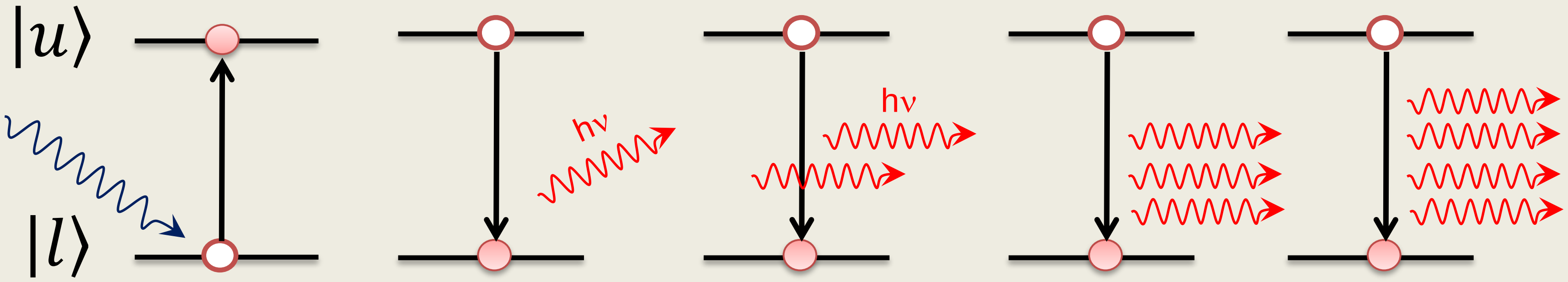
Workshop on 1D-imaging Soft X-ray Spectroscopy at SQS, The EuroXFEL 21/10/21

Stimulated X-ray emission in molecules: theoretical experience and perspectives at SQS

- Basics of stimulated emission, amplified spontaneous X-ray emission in atoms
- Theory of SXE in molecules: new opportunities and challenges
- Stimulated X-ray Raman (RIXS): new dimensions for two X-ray color schemes
- Theory vs experiment

- **New possibilities with 1D imaging Soft X-ray spectroscopy at SQS:**
  - IR+X-ray: molecular alignment for SXE
  - IR+X-ray: IR-pump vibrational dynamics observed in fluorescence
  - Study of electron wave packet in a confinement: shape resonance tunneling time
  - Observation of the pulse slow down in two-color delayed X-ray pulse mode

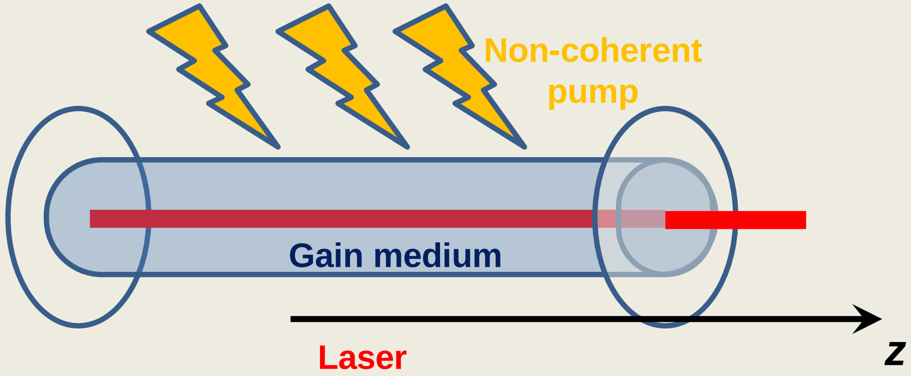
Stimulated emission and lasing



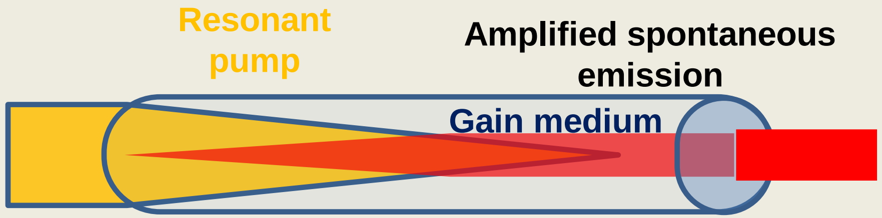
Absorption

Spontaneous emission

Stimulated emission
Coherent radiation



Laser



Cavityless laser

$$\left(\frac{1}{c}\frac{\partial}{\partial t}+\frac{\partial}{\partial z}\right)I = gI,\ g = \sigma_{stim}\left(N_u - N_l\right)$$

$$I \approx I_0 \exp(gNz)$$

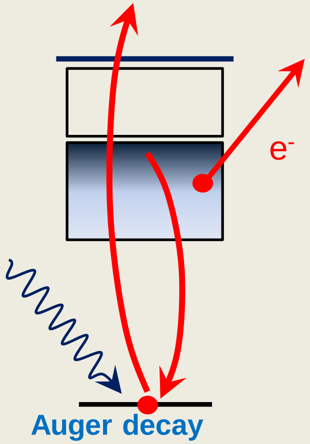
Towards x-ray nonlinearity: x-ray lasing

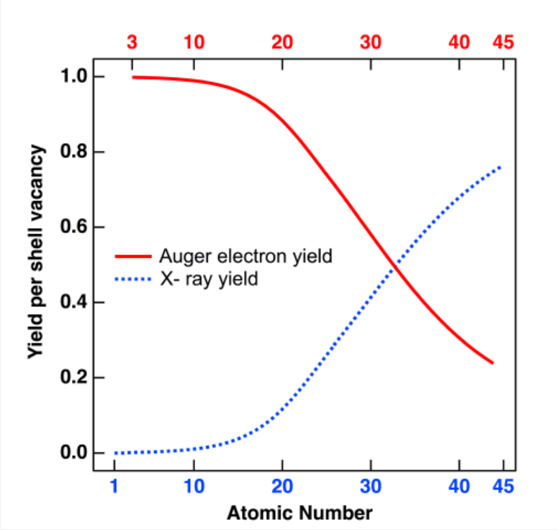
- **X-ray lasing scheme was proposed in 60th**
  Duguay & Rentzepis, Appl. Phys. Lett. ***10*** *350 (1967)*

- **Strong nonradiative Auger decay channel**
  - Short core-hole lifetime: **1-10 fs**
  - Small transition dipole moments (TFY ~ $10^{-2} – 10^{-3}$)

- **Create gain media**
  - Pump rate faster than Auger rate!
  - Source: High photon flux and photon energy
  Rohringer & London, PRA 80, 013809 (2009)
  Sun et al., Phys Rev A 81 (2010) 013812

- **1st demonstration of the XFEL pumped x-laser**
  - 2010: LCLS soft X-ray FEL in operation
  - Gas phase Neon: Kα soft x-ray lasing: *Rohringer et al., Nature* ***481****, 488 (2012)*





1st experiment on x-ray nonlinear effects: X-ray lasing in Ne gas

- ☐ LCLS pump: hv=960 eV, 40 fs, focus 2 mkm
- ☐ **Single shot of highest intensity:** ~ 10^{12} photons per XFEL pulse
- ☐ **X-ray emission:** 8×10^9 photons in Ne K-α line
  - ✓ **conversion efficiency ~ 4 x 10^{-3}**

Rohringer *et al.*, *Nature* **481**, 488 (2012)

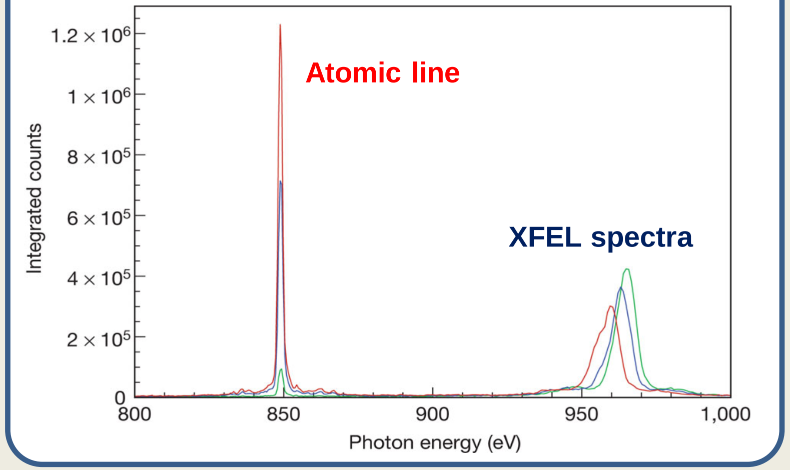
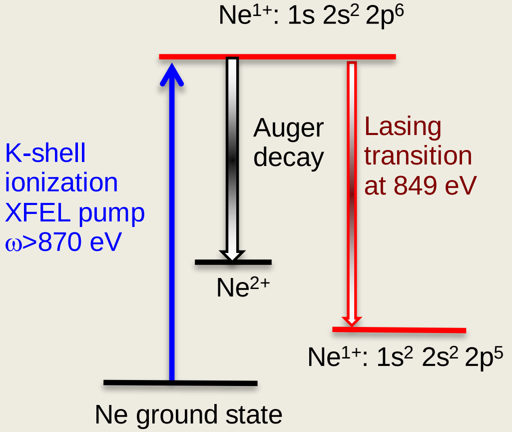
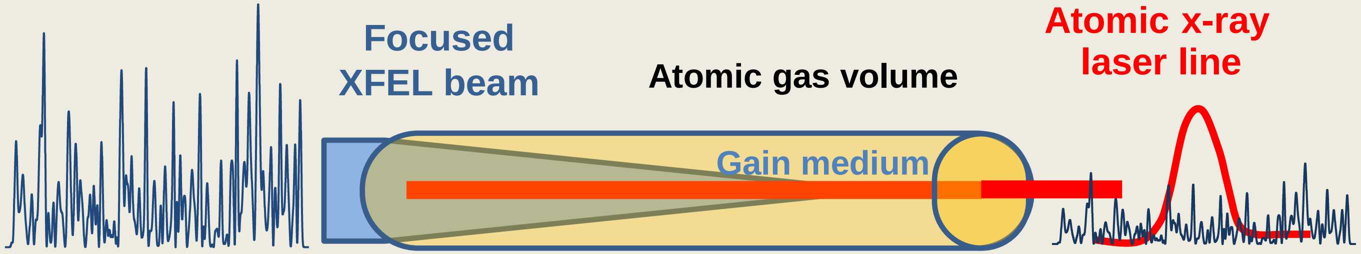
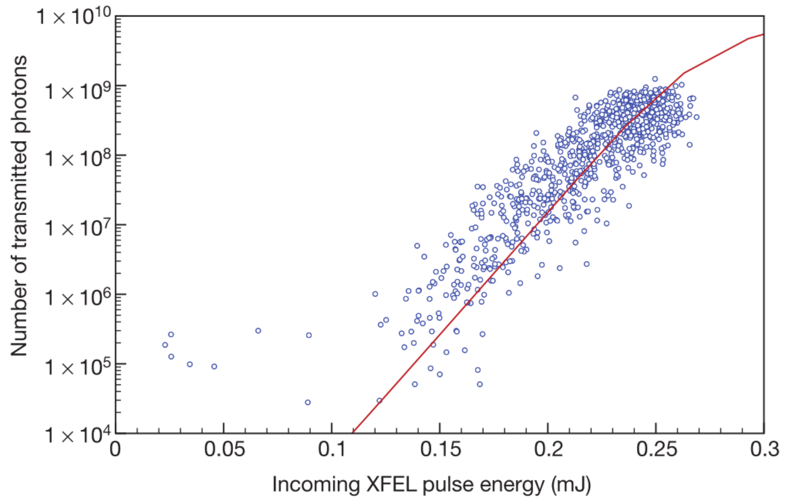


Photo-ionization pumping



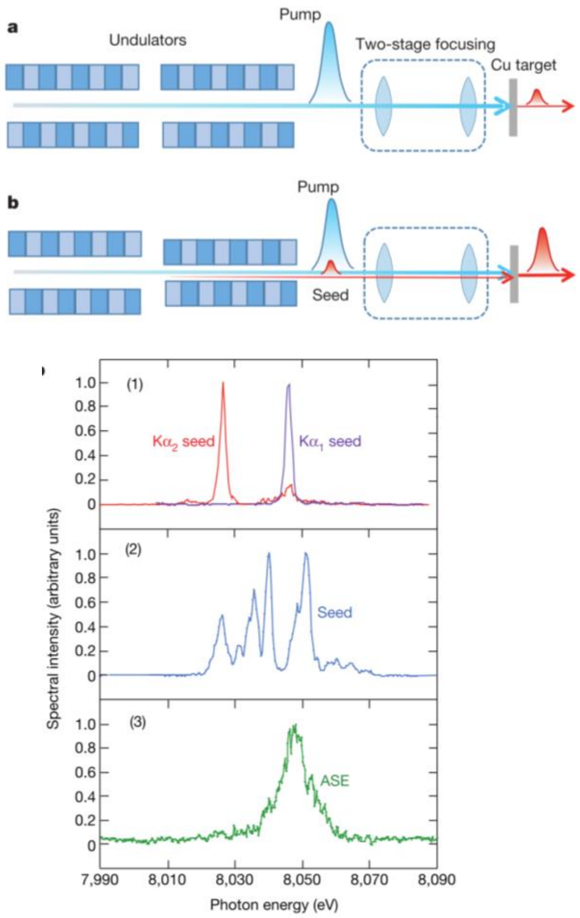


Dependence of the XRL output on pump power.

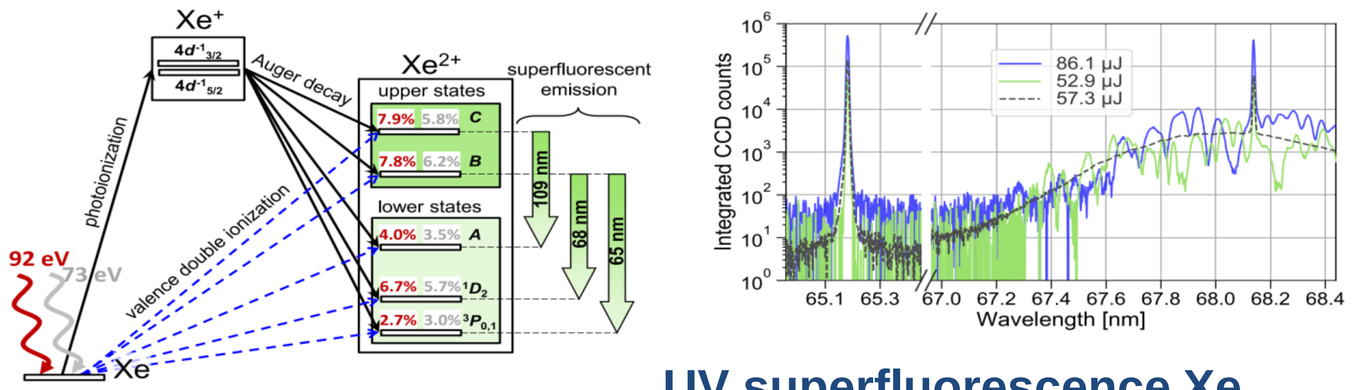


Duguay & Rentzepis, Appl. Phys. Lett. ***10*** *350 (1967)*
Rohringer & London, PRA ***80****, 013809 (2009)*
Rohringer et al., Nature ***481****, 488 (2012)*

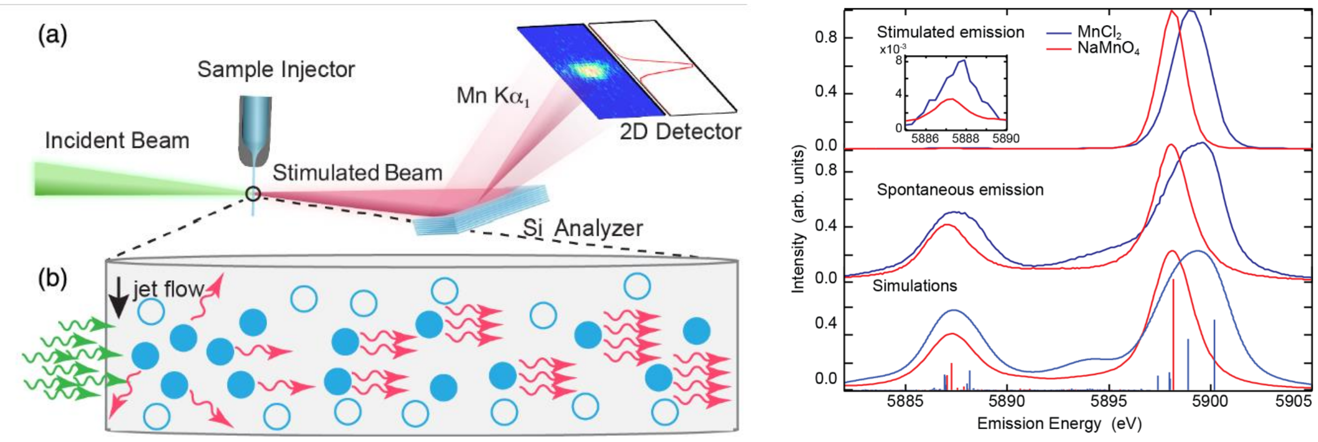
Cu Kα line laser: 8 keV



PHYSICAL REVIEW LETTERS **123,** 023201 (2019)



UV superfluorescence Xe



Stimulated X-Ray Emission in TM Complexes

…..

Cu Ka laser, 8 keV: *Yoneda, H. et al. Nature* ***524,*** *446–449 (2015).*

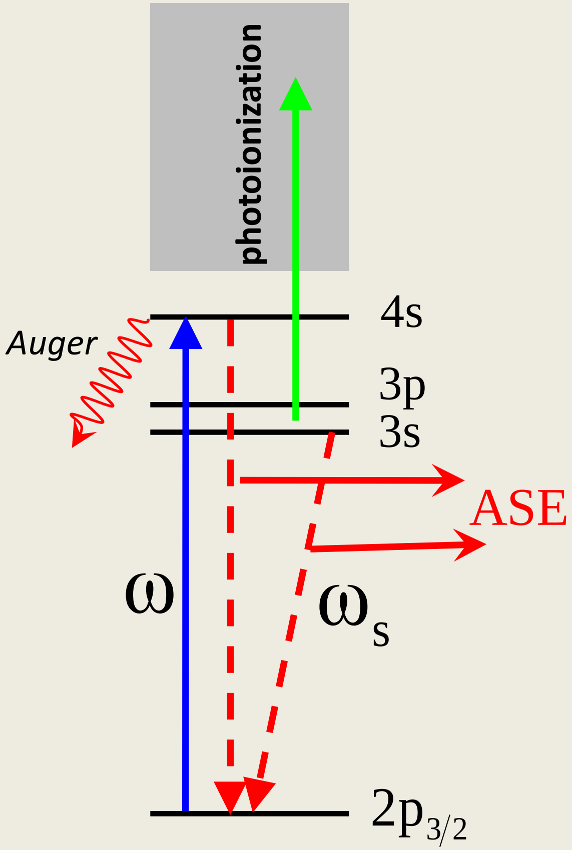
Superfuorescence, FWM in He: *J. R. Harries et al., Phys. Rev. Lett, 121, 263201 (2018)*

SRIXS and ASXE Mn Ka, Kb: *Kroll et al., PRL 120, 133203 (2018), PRL 125, 037404 (2020)*

Superfluorescence Xe: *L. Mercadier et al., Phys. Rev. Lett., 123, 023201 (2019)*

…..

Theoretical predictions: nonlinear effects for strong X-ray pulse propagating in resonant gas media



- *Ar* gas medium
- Strong Auger decay and photoionization: an open quantum system is considered

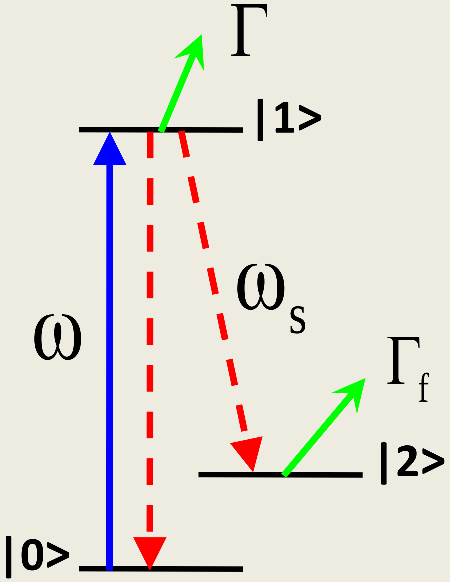
$$\Gamma = \Gamma_{decay} + \gamma_{photoionization}$$

$$\rho_{00} + \rho_{11} + \rho_{22} \approx \rho_{00} e^{-\Gamma\tau} < 1$$

- Scheme of transitions uses

$$|1\rangle = |2p_{3/2}^{-1} 4s\rangle$$

$$|2\rangle = |3s^{-1} 4s\rangle$$



Sun et al., Phys Rev A 81 (2010) 013812
Sun et al., Phys Rev A 81 (2010) 043412

Courtesy of F. Gelmukhanov

Coupled density matrix and Maxwell's equations

Density-matrix equations

$$[\frac{\partial}{\partial t} + \Gamma_{11} + \gamma_{ph}^{(1)}(t)]\rho_{11} = W = 2\Im\sum_{n=0,2}(V_{1n}\rho_{n1})$$

$$[\frac{\partial}{\partial t} + \Gamma_{22} + \gamma_{ph}^{(2)}(t)]\rho_{22} = 2\Im(V_{21}\rho_{12})$$

$$[\frac{\partial}{\partial t} + \Gamma_{00} + \gamma_{ph}^{(0)}(t)]\rho_{00} = 2\Im(V_{01}\rho_{10})$$

$$[\frac{\partial}{\partial t} + \Gamma_{10} + \gamma_{ph}^{(10)}(t)]\rho_{10} = iV_{10}(\rho_{11} - \rho_{00}) - iV_{12}\rho_{20}$$

$$[\frac{\partial}{\partial t} + \Gamma_{12} + \gamma_{ph}^{(12)}(t)]\rho_{12} = iV_{12}(\rho_{11} - \rho_{22}) - iV_{10}\rho_{02}$$

$$[\frac{\partial}{\partial t} + \Gamma_{20} + \gamma_{ph}^{(20)}(t)]\rho_{20} = -iV_{21}\rho_{10} + i\rho_{21}V_{10}$$

Maxwell equations

$$\frac{\partial E}{\partial z} + \mu_0\frac{\partial H}{\partial t} = 0$$

$$\frac{\partial H}{\partial z} + \varepsilon_0\frac{\partial E}{\partial t} = -\frac{\partial P}{\partial t}$$

$$\boxed{\begin{aligned} P(t,z) &= NTr(d\rho) \\ &= 2N\Re(d_{10}\rho_{01}e^{i\omega_{10}t} + d_{12}\rho_{21}e^{i\omega_{12}t}) \end{aligned}}$$

Macroscopic nonlinear polarisation

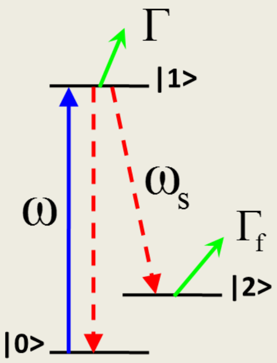
$$\mathrm{V}_{mn} = -E(t,z)d_{nm}e^{i\omega_{mn}t}/\hbar$$

$$\gamma_{ph}^{(nm)}(t) = \frac{1}{2}\left[\gamma_{ph}^{(n)}(t) + \gamma_{ph}^{(m)}(t)\right], \quad \gamma_{ph}^{(n)}(t) = \sigma_{ph}^{(n)}\frac{I(t)}{\hbar\omega}$$

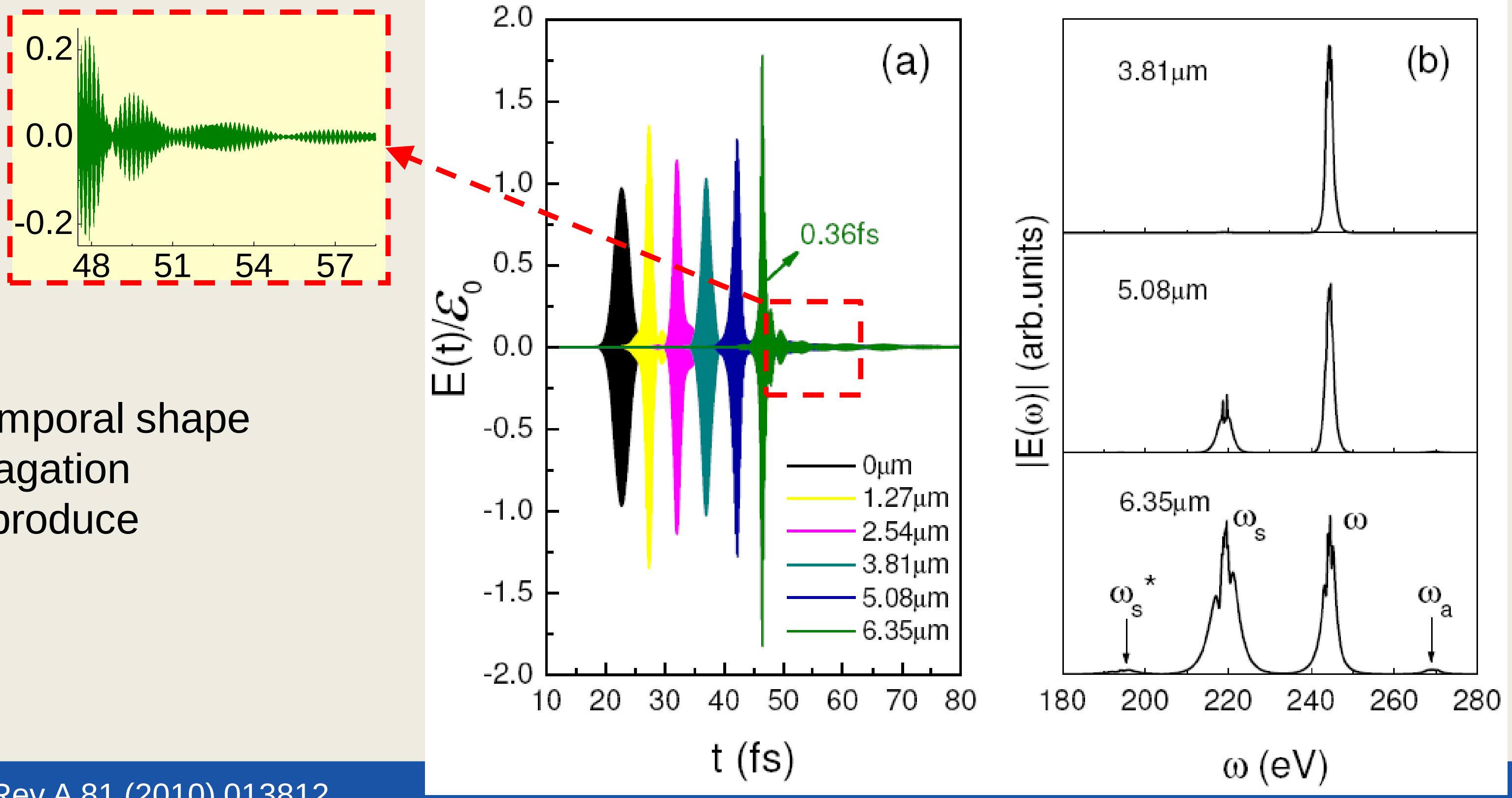
Numerical solution: Finite-Difference Time Domain method

Pulse compression, pulse modulation and four-wave mixing

- Coherent x-ray pulse 2 fs duration, 3π pulse area resonant to Ar transition
- Pulse (Burnham-Chiao) modulations: gain in an inverted medium and the sign-changing modulation of the envelope in the region where the inversion is absent.

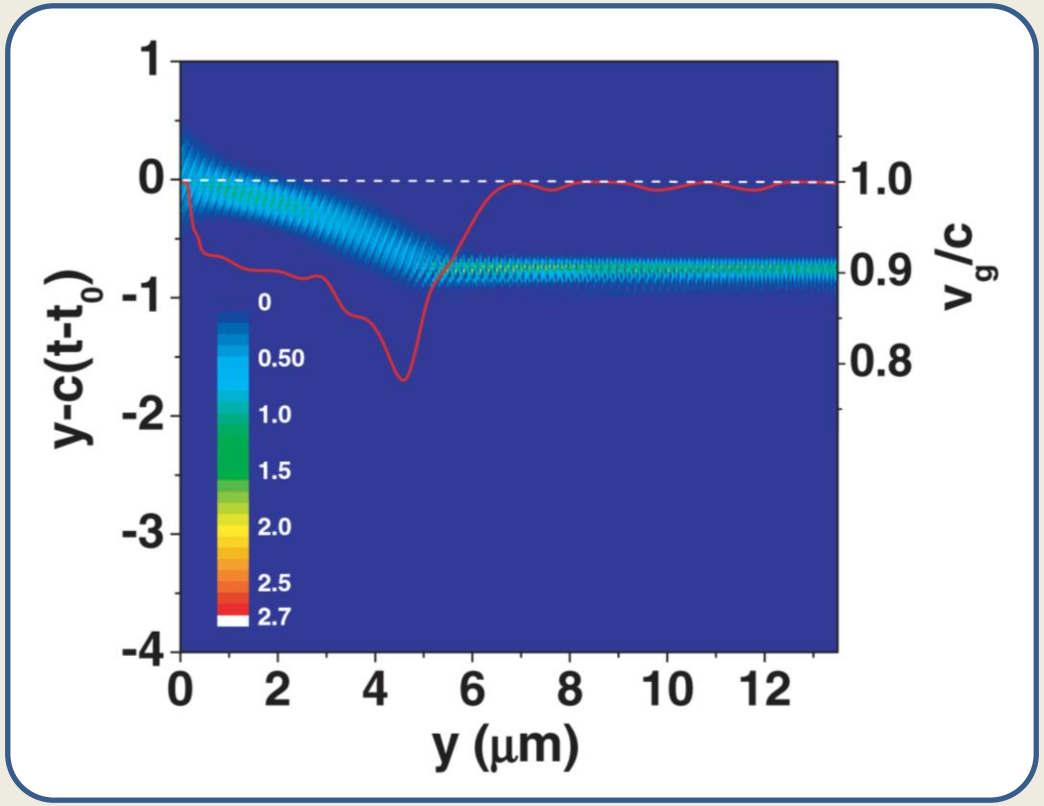


- The pump component change the temporal shape (pulse compression) during the propagation
- Corresponding spectral broadening produce seeding for the Stokes line



Sun et al., Phys Rev A 81 (2010) 013812

Slowdown of XFEL pulse



- High intensity of XFEL pulse results in a change of the refractive index
- Nonlinear refractive index

$$n = n_0 + n_{nl} \approx 1 + n_{nl}$$

- Slowdown of the pulse

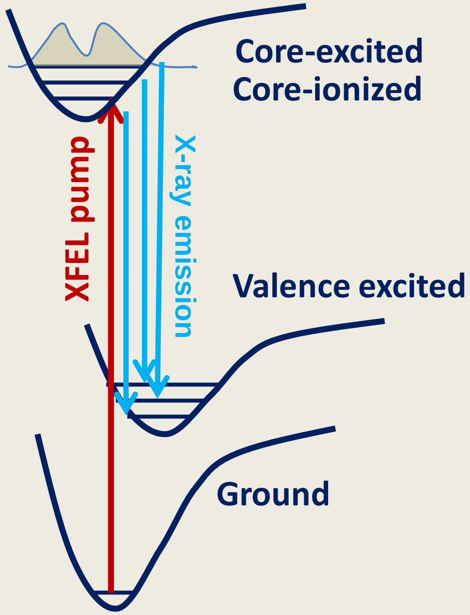
$$v_g = \frac{v}{n - \lambda\, dn / d\lambda}$$

Well-known in the optical region, but in x-ray n is very close to 1.

- The reported nonlinear change of the refraction index of the order 0.1–1

Sun et al., Phys Rev A 81 (2010) 013812

Stimulated resonant x-ray emission in molecules: Opportunities or difficulties?



What nuclear degrees of freedom can give us?

- **Broader absorption and emission energy ranges:**

+ various electronic and vibrational transitions, chemical shifts
+ effective pump on broadened transition
- weaker emission efficiency

- **Various schemes**:

+ choosing potentials of the core-excited and final states
+ variation and control of the nuclear coordinates
- numerous competing channels

- **X-ray polarization control:**

+ using the molecular alignment with additional IR field
+ pump-probe with IR excitation
- low efficiency due to chaotic orientation of soft matter

Miao *et al*, *Phys. Rev. Lett.* **109** 233905 (2012)
Kimberg & Rohringer, *Phys. Rev. Lett.* **110** 043901 (2013)
Kimberg *et al, J. Phys.: Conf. Ser.* **488** 012025 (2014)
V. Kimberg et al, Faraday Discussions **194** 305 (2016)

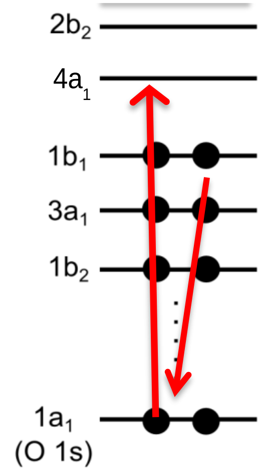
Local structure and nuclear dynamics in RIXS

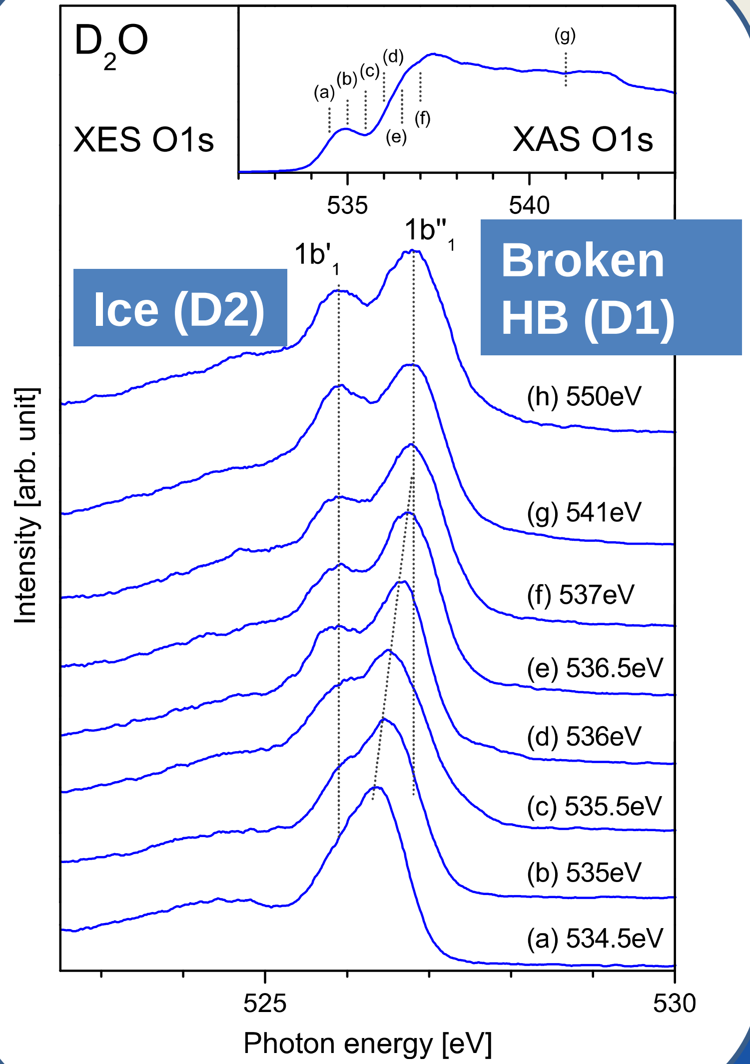
$1b_1$ structure splitting in RIXS: structure vs dynamics

Structure

- Nat.Comm. 6, 8998 (2015)
- J.Chem Phys. 148, 144507(2018)

$1b_1$: first inelastic RIXS channel



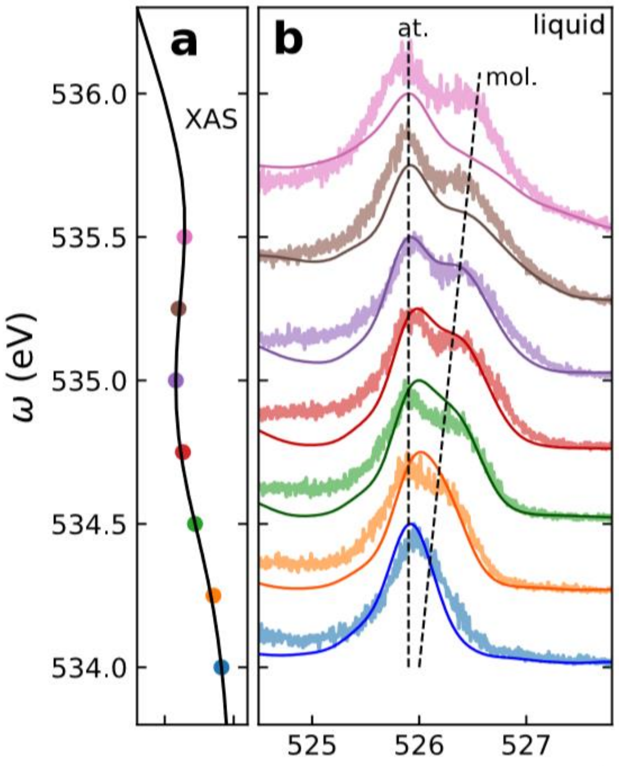


Nuclear dynamics

- PRL, 100, 027801(2008); PRL, 114, 088302(2015); PRB, 79, 144204(2009)
- This mechanism supported by isotope sensitivity of RIXS

Dynamics in real-time XFEL measurements

Pre-edge1)



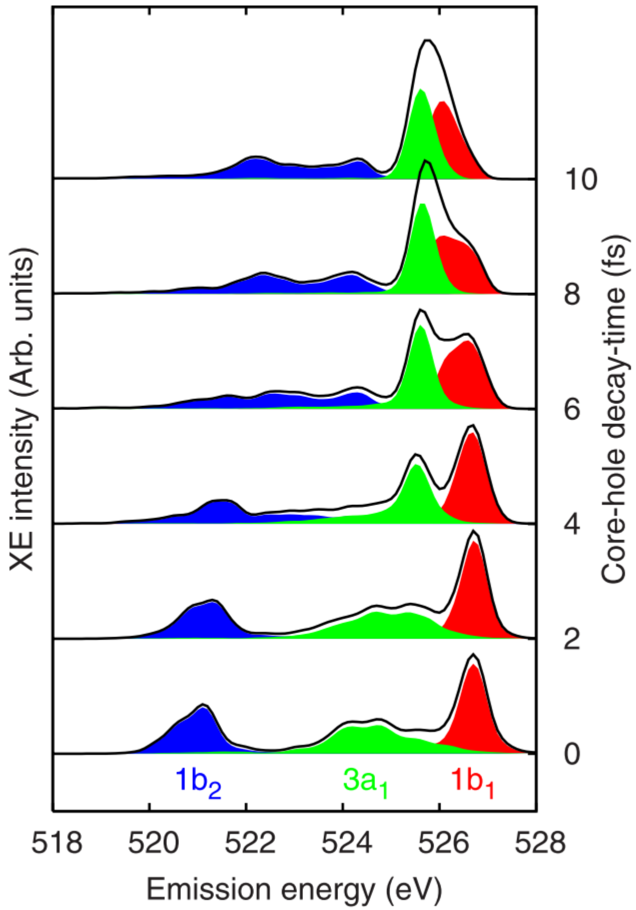
Effective scattering duration time:

$$\tau_s = \frac{1}{\sqrt{\Omega^2 + \Gamma^2}}$$

Structure vs dynamics problem in water

- "Time-dependent" XES modelling with MD2)
- Can be measured in XFEL all X-ray pump-probe scheme with **stimulated X-ray emission** via $3a_1$ and $1b_1$ channels
- Different polarization dependence for $3a_1$ and $1b_1$ peaks can be traced in stimulated resonant X-ray emission

Post-edge2)



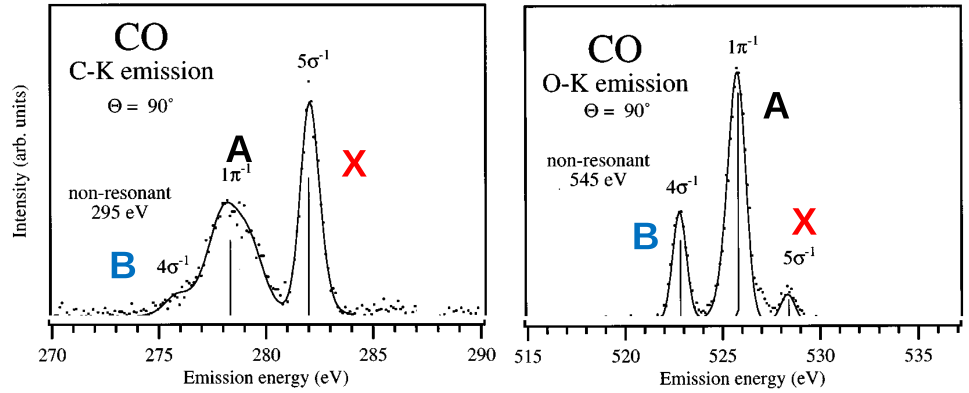
[1] V. Vaz da Cruz, et al, Nat Commun. **10**, 1013 (2019)

[2] M. Odelius, Phys. Rev. B 79, 144204 (2009)

Stimulated X-ray emission in CO

- Two core-ionization edges: CK (296 eV) and OK (542 eV)
- Lifetime of O1s^{-1} core-hole is twice shorter than C1s^{-1}: different nuclear dynamics

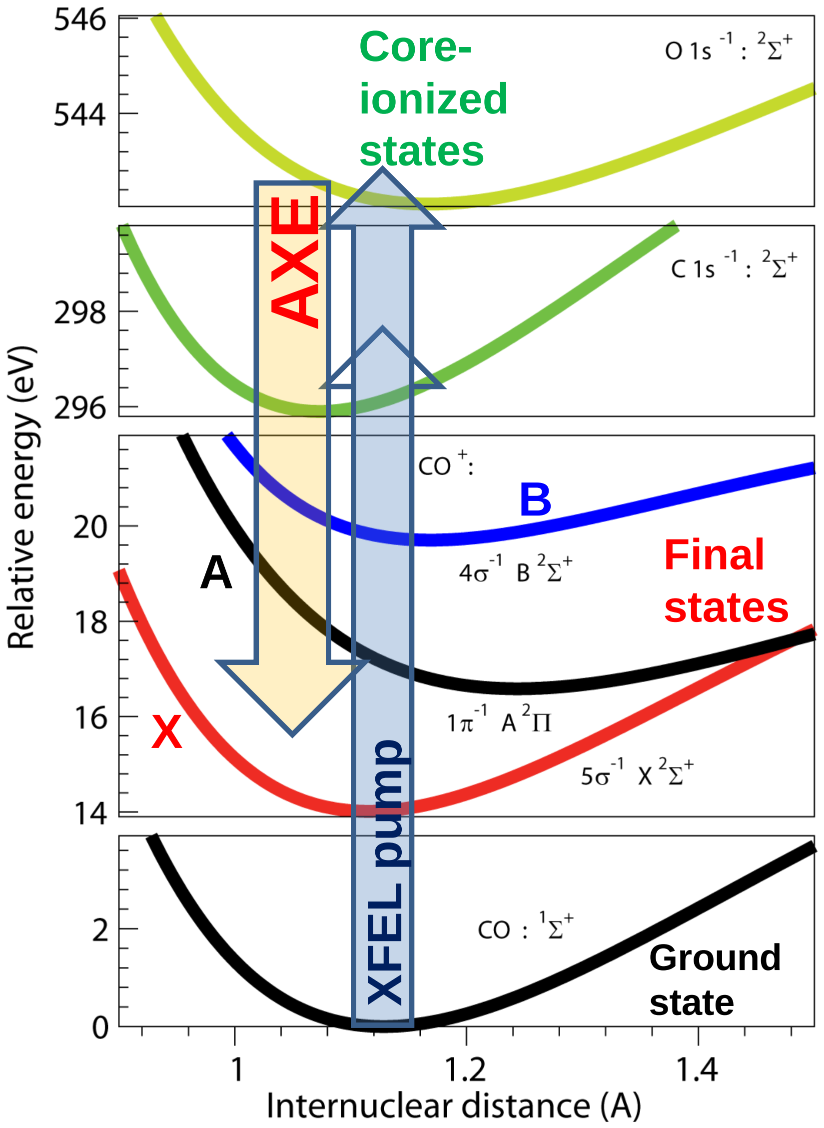
Skytt et al, *Phys Rev A* **55** 134 (1997)



- Strongest transitions :

C1s^{-1}→X, O1s^{-1}→A, O1s^{-1}→B

- Different PECs of the final states: vary the nuclear dynamics and x-ray emission process
- Different transition symmetries



V. Kimberg, S. Zhang, and N. Rohringer, *J. Phys. B At. Mol. Opt. Phys.* **46**, 164017 (2013)

Theoretical framework

Coupled Maxwell and Density Matrix equations

Wave equation for propagation and amplification of the complex field (SVA)

$$\left(\frac{\partial}{\partial z}+\frac{1}{c}\frac{\partial}{\partial t}\right)E^{+}=-i\frac{2\pi\omega_L}{c}P^{+}$$

Nonlinear polarization includes all vibrational transitions

$$P^{+}=\sum_{i,f}\rho_{if}(\theta)d_{if}\cos(\theta)e^{i(\omega_{if}-\omega_L)t} \qquad d_{if}=d_e\langle\nu_i|\nu_f\rangle,\ \theta=\angle(\mathbf{E},\mathbf{d})$$

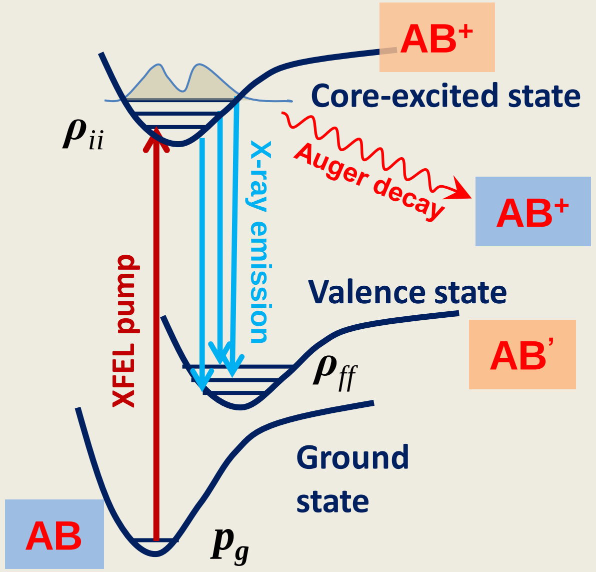
Born-Oppenheimer and Franck-Condon approximations

Reduced density matrix equations

$$\dot{\rho}_{ii'}(\theta;z,t)=-\Gamma_i\rho_{ii'}+P_{ii'}+i\sum_f\left(\rho_{fi'}R^{*}_{if}-\rho_{if}R^{*}_{i'f}\right)$$

$$\dot{\rho}_{if}(\theta;z,t)=-\frac{\Gamma_i}{2}\rho_{if}+i\sum_{f'}\rho_{f'f}R^{*}_{if'}-i\sum_{i'}\rho_{ii'}R^{*}_{i'f}+\left(\rho_{ii}-\rho_{ff}\right)S(z,t)$$

$$\dot{\rho}_{ff'}(\theta;z,t)=i\sum_i\left(\rho_{if'}R_{if}-\rho_{fi}R_{if'}\right)$$

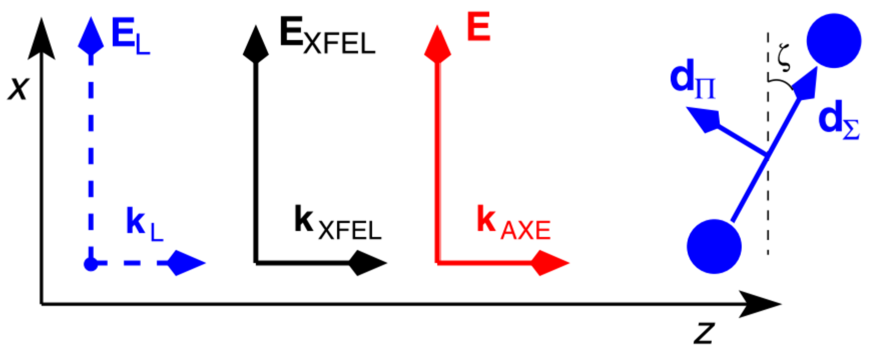


$$j=\{j_e,\nu_j\}$$

$$R_{if}=E^{+}d_{if}\cos(\theta)e^{i(\omega_L-\omega_{if})t}$$

Nonlinear polarization is averaged over molecular orientation (cos θ) and source term S(z,t)

Field-free IR molecular alignment

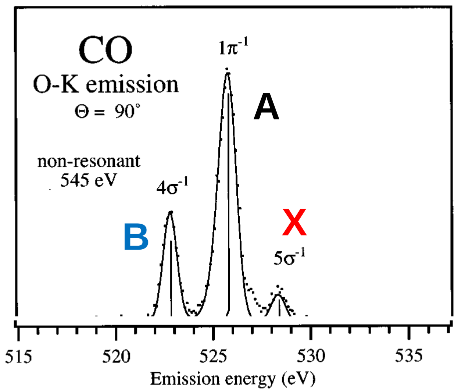


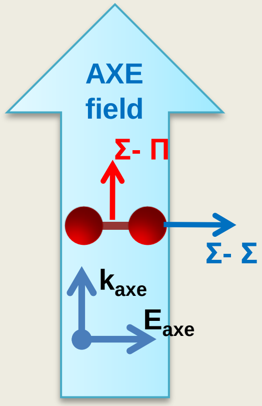
- Transition symmetry is important :

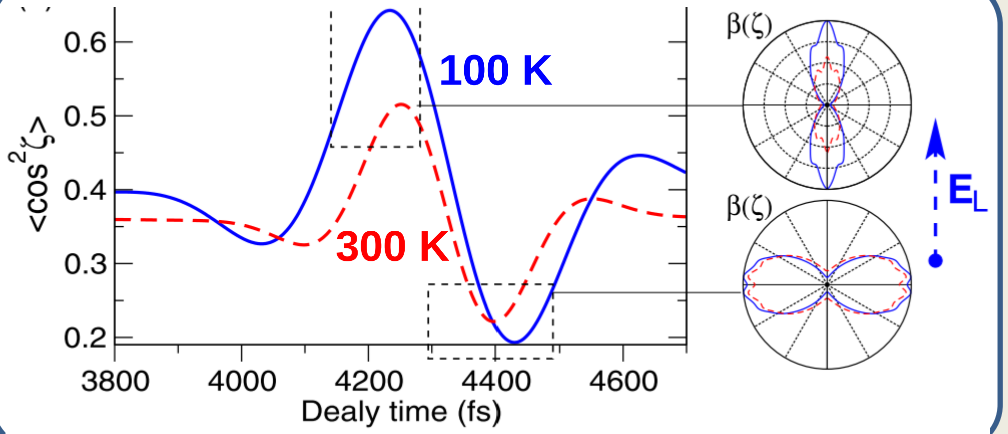
O1s-1 → A (Σ-Π) dominates for the anti-aligned ensemble
O1s-1 → B (Σ-Σ) dominates for the aligned ensemble

IR-pulse used in simulations:
800 nm, 100 fs, 1.26e14 W/cm^2

Skytt et al, *Phys Rev A* **55** 134 (1997)

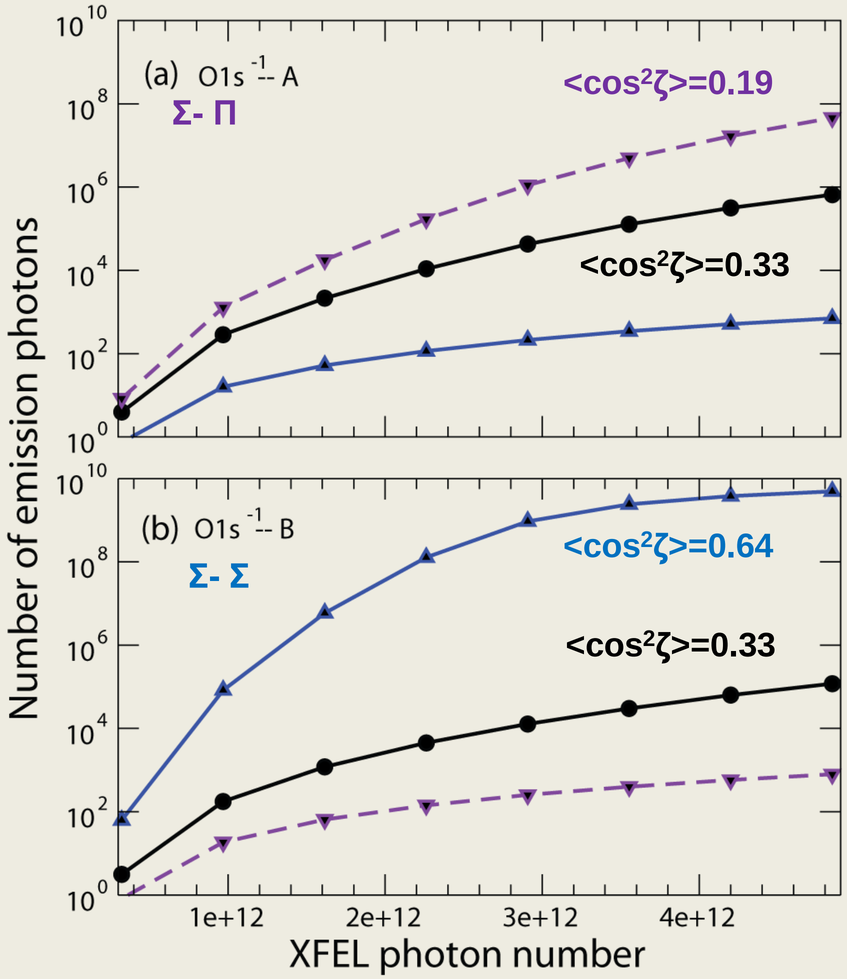






IR laser synchronized with XFEL creates great opportunities for molecular AXE at SQS

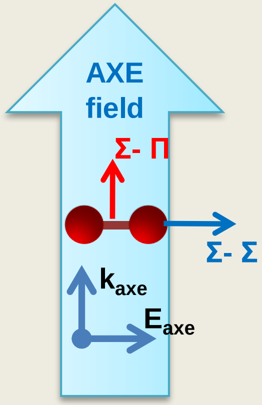
Amplified spontaneous X-ray emission: various lasing channels

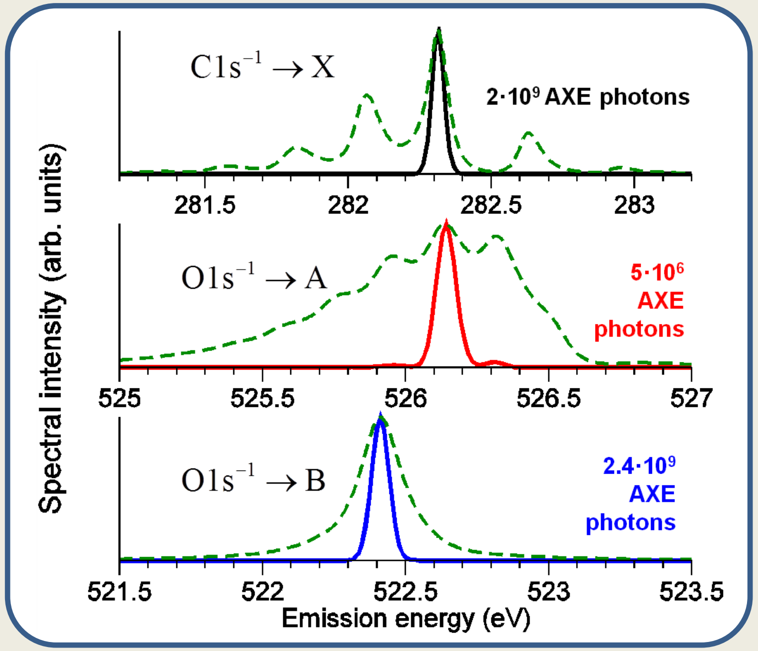


- Transition symmetry is important :

O1s-1 → A (Σ-Π) dominates for the anti-aligned ensemble

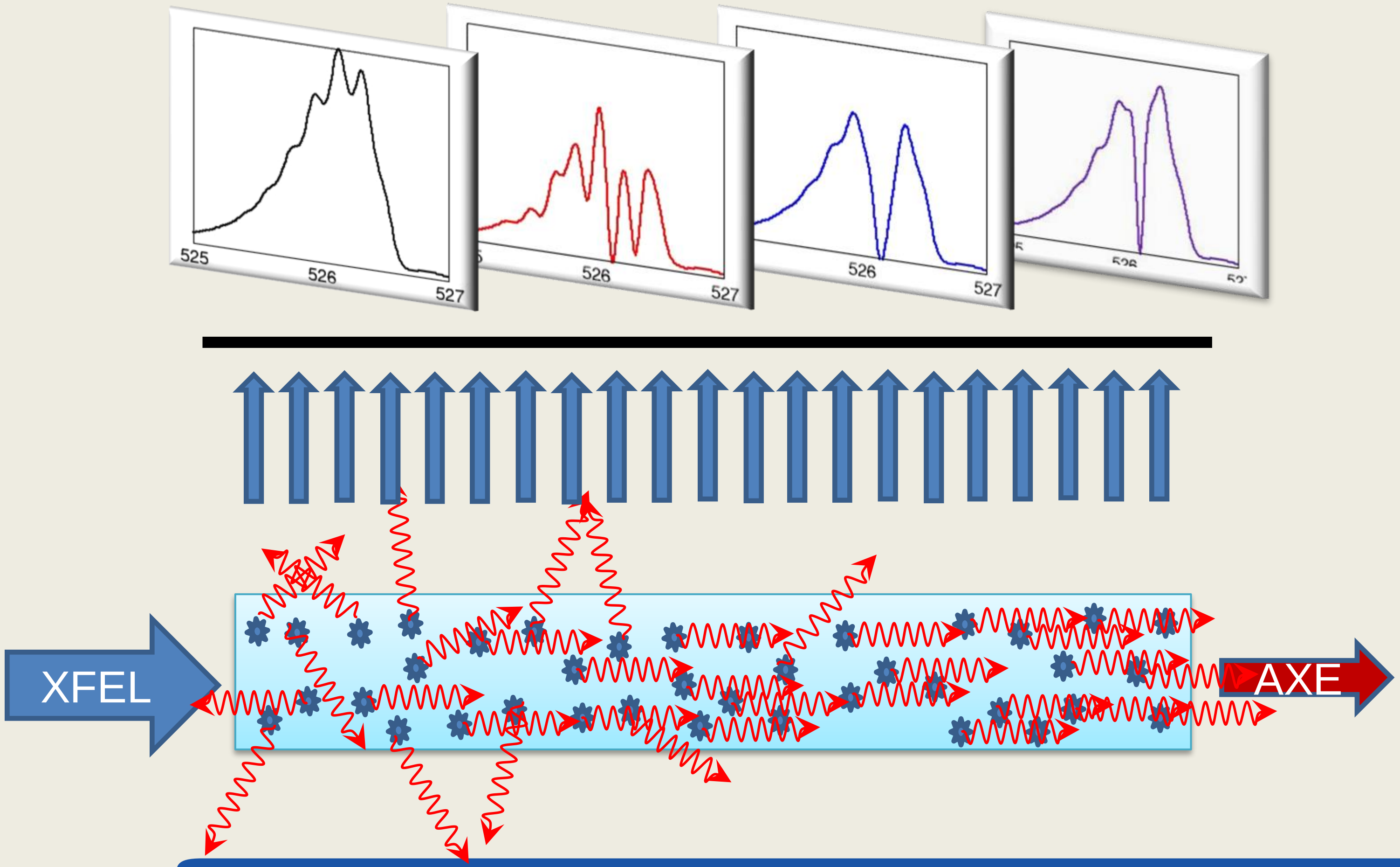
O1s-1 → B (Σ-Σ) dominates for the aligned ensemble

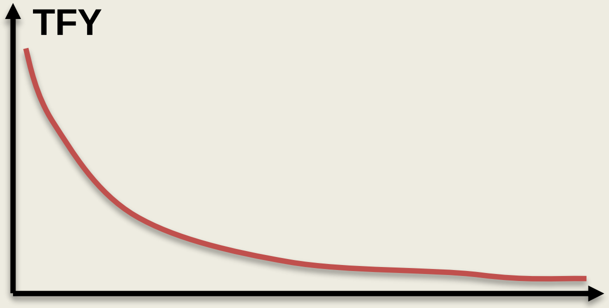


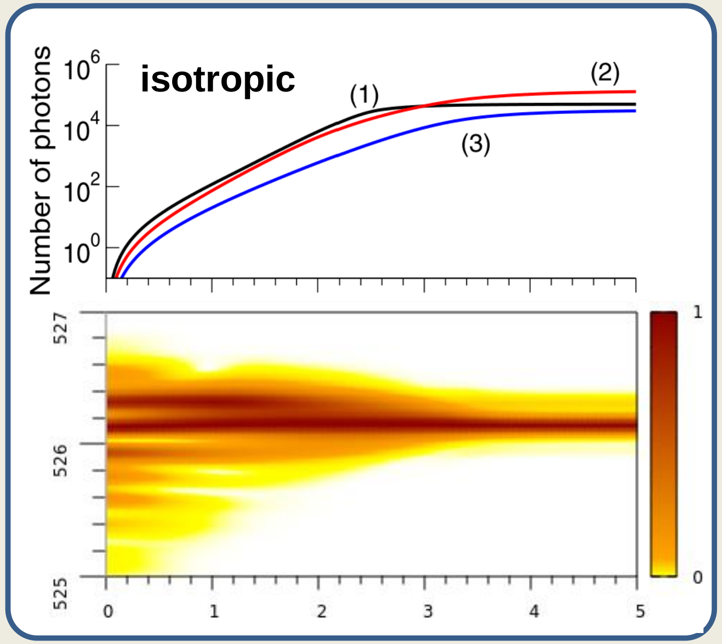


IR laser synchronized with XFEL creates great opportunities for molecular AXE at SQS

1D-imaging of the nonlinear propagation in fluorescence



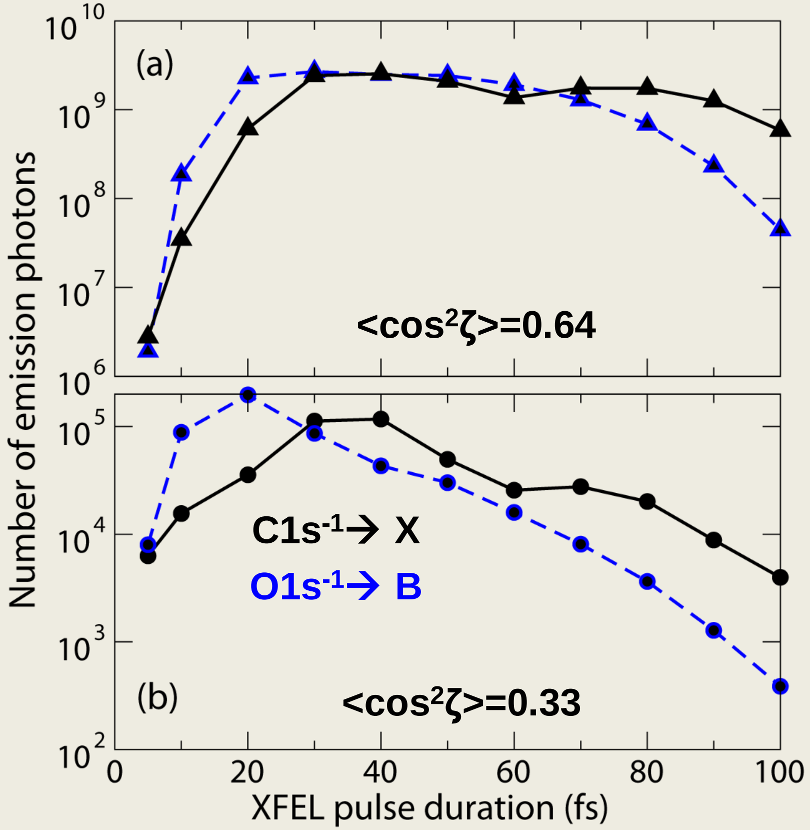




Suppression of TFY and change of XE spectra of 1D IXS are the fingerprints of the SXE

Pump pulse duration

XFEL photon flux=const



- Pump pulse duration allows to optimize lasing conditions for according to the core-hole lifetime

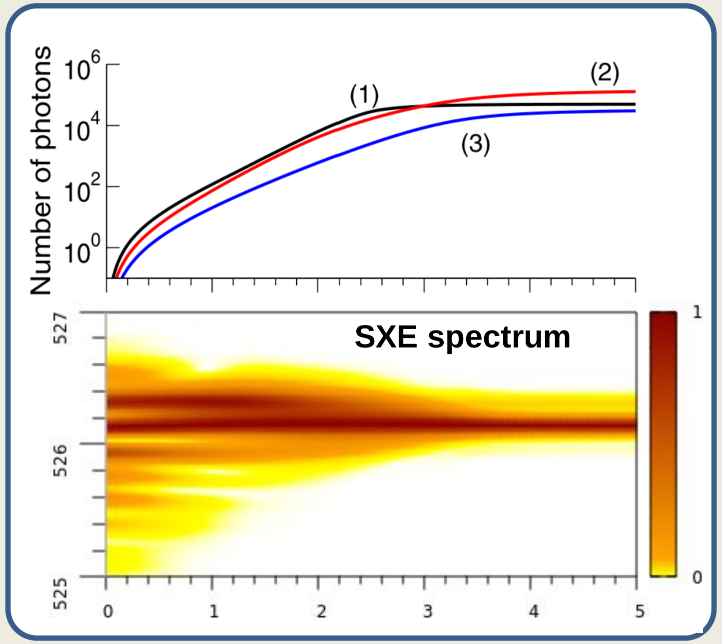
- Same photon flux, different pulse length
    - Shorter pulse is more efficient for shorter lifetime
    - Optimal conditions are broader for the aligned ensemble

- The higher pumping rate (shorter pump pulse) beats the stronger Auger decay and results in a larger AXE efficiency

Dynamics of amplified x-ray emission in CO

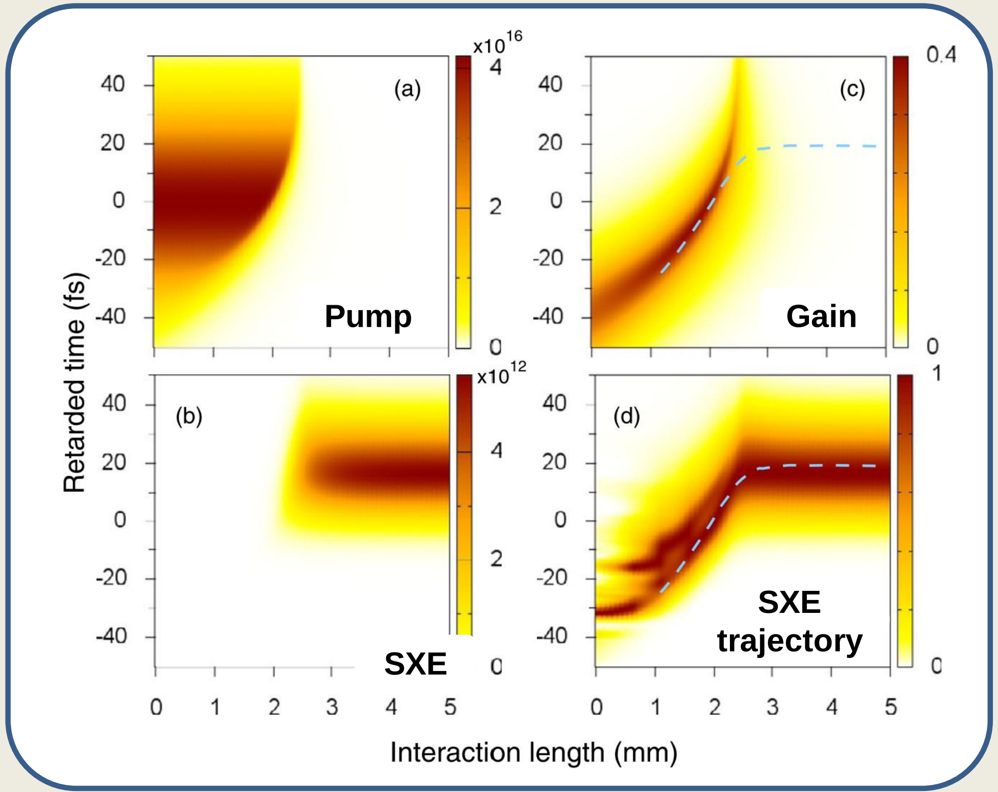
❑ **Spectral dynamics**

- Low intensity: broadband emission
- Narrow line in the linear gain region
- Broadening and shift of the spectral line due to strong field (nonlinear) effects above the saturation (z>3 mm)



❑ Group velocity of pulse propagating in high gain resonance medium is slowdown1)

- Gain "catch-up" effect2) (not observed without pump absorption)
- **Strong absorption** results in a shift of the XFEL front -> population inversion shifts to later times as well



Nonlinear effects and pulse delay by about 40 fs

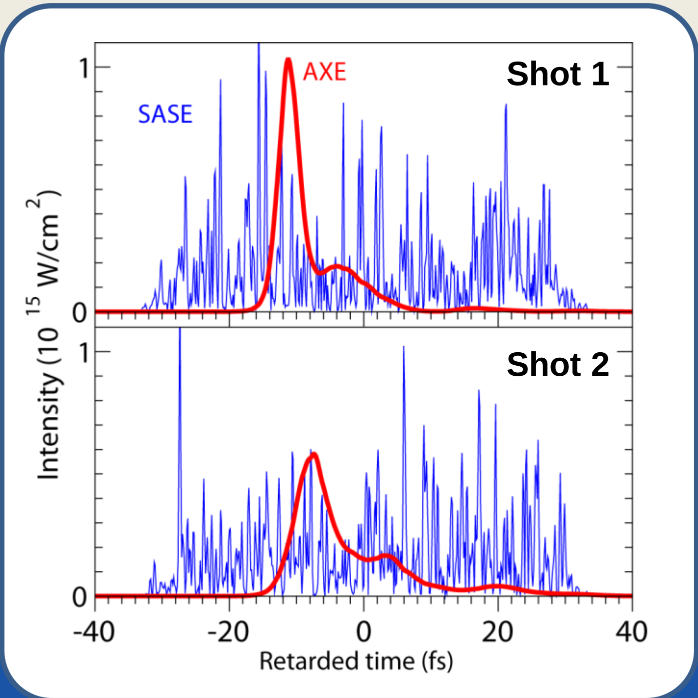
1)Casperson & Yariv, PRL **29**, 293 (1971)
2)Miao et al PRL **109** 233905 (2012)

SASE pump pulse: N_2 showcase

- Broad-band excitation (~ 8 eV)
- Core-ionization: due to the off-resonant excitation SASE show no drawback as compared to Gaussian profile
- **AXE conversion:** broadband **SASE pulse** to a narrow band (0.1 eV) short (~5-10 fs) **AXE pulse**
- Shot to shot results are slightly different: averaging over large number of SASE pulses

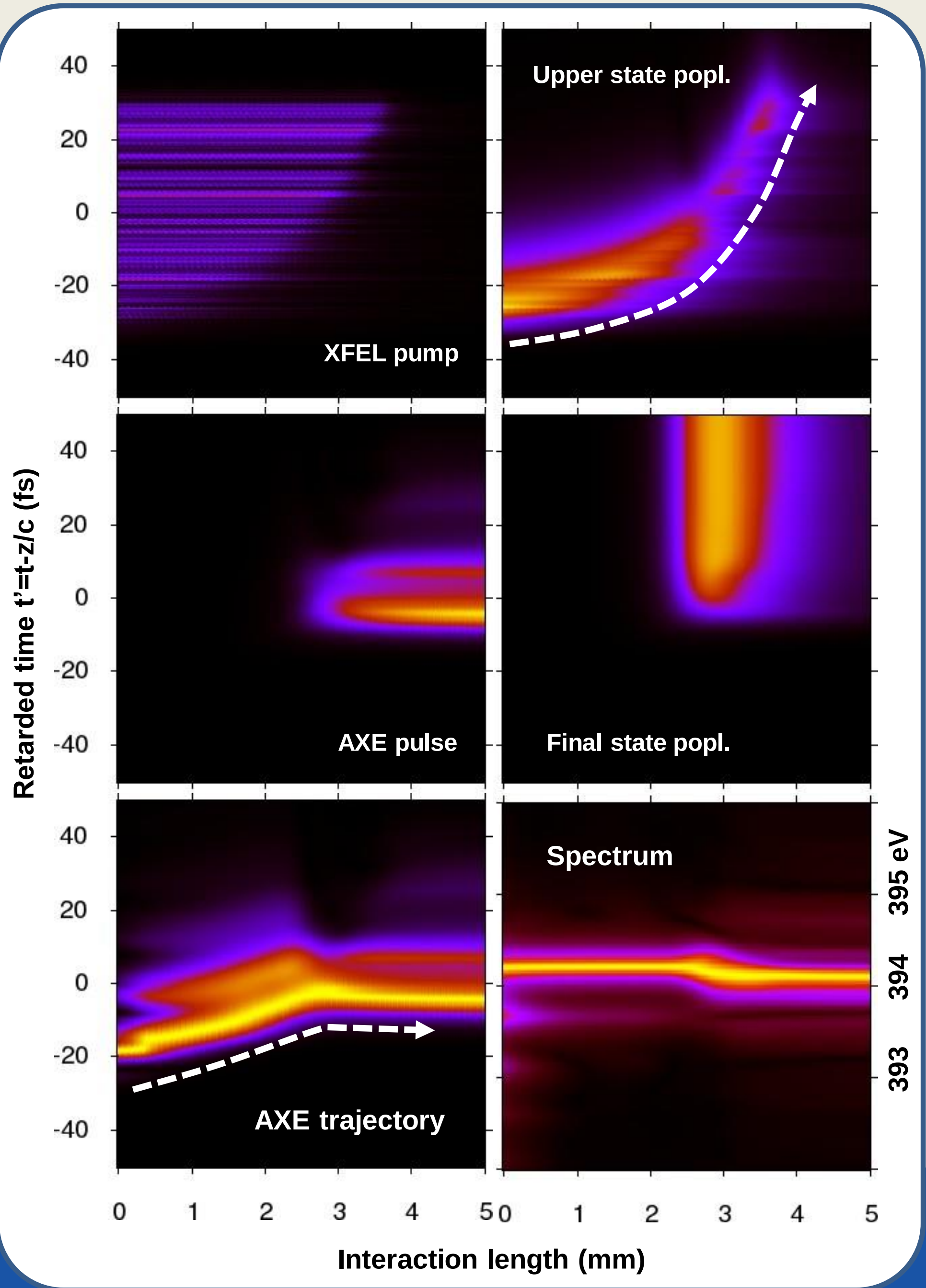
❑ **Spectral dynamics**

- Low intensity: broadband emission, narrow line in the linear gain region
- Broadening and shift of the spectral line due to strong field (nonlinear) effects above the saturation (z>3 mm)



❑ Group velocity of pulse propagating in high gain resonance medium is slowdown[1)]

- Gain "catch-up" effect[2)] (not observed without pump absorption)
- **Strong absorption** results in a shift of the XFEL front -> population inversion shifts to later times as well

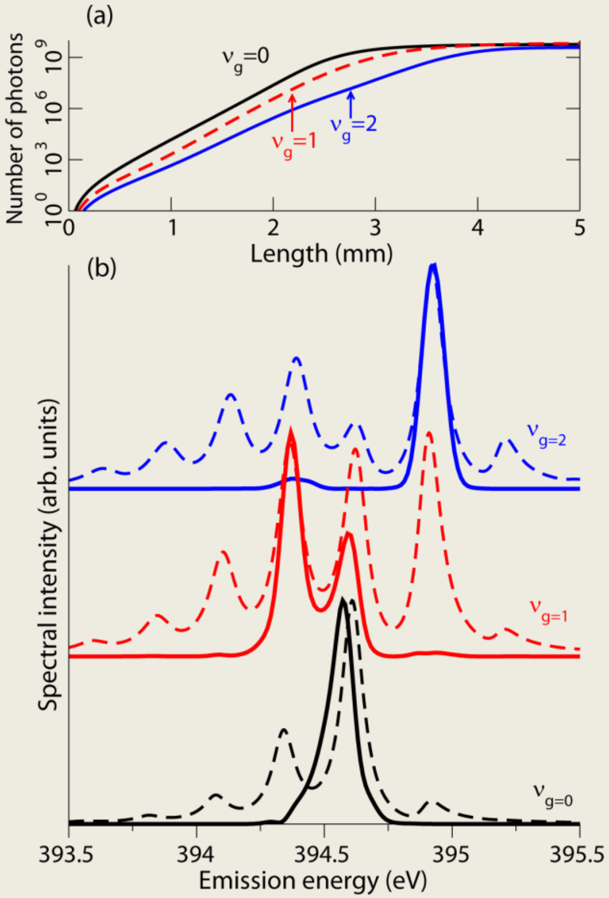


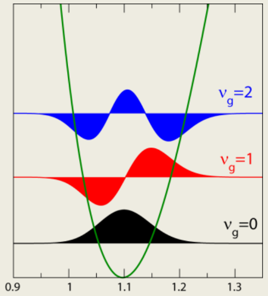
[1)] Casperson & Yariv, PRL **29**, 293 (1971)

[2)] Miao et al PRL **109** 233905 (2012)

Stimulated X-ray emission from IR-excited molecules

❑ **By fixing the initial vibrational quantum state (e.g. IR Raman), a shift of the SXE to the maximum of the fluorescence spectrum can be achieved (N_2 showcase).**



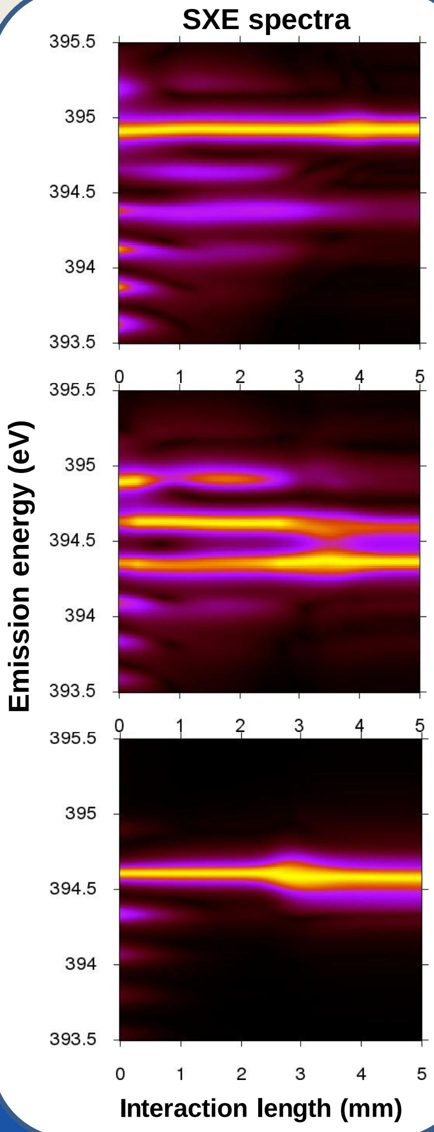


- Simulations for the cases when only the v_g=0, 1 or 2 vibrational sublevel of the ground electronic state is initially populated.

- Difference in the gain is due to the different Franck-Condon factors

- The propagation spectral dynamics is more complex in the cases of the broad vibrational band excitation

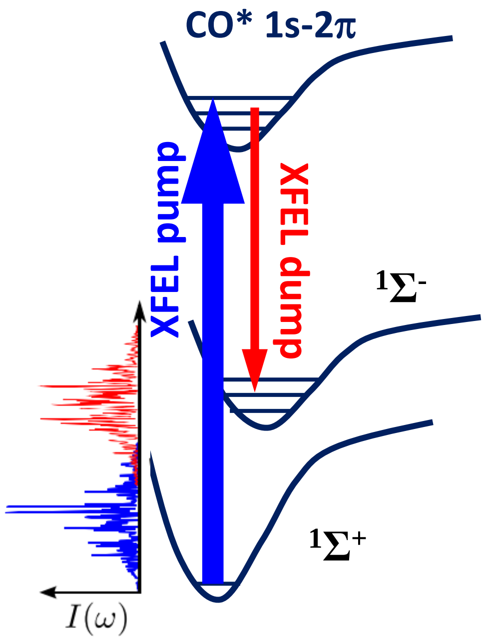
- Any coherent superposition of the vibrational states which differs sufficiently from the v_g=0 results in a change of the AXE spectrum.

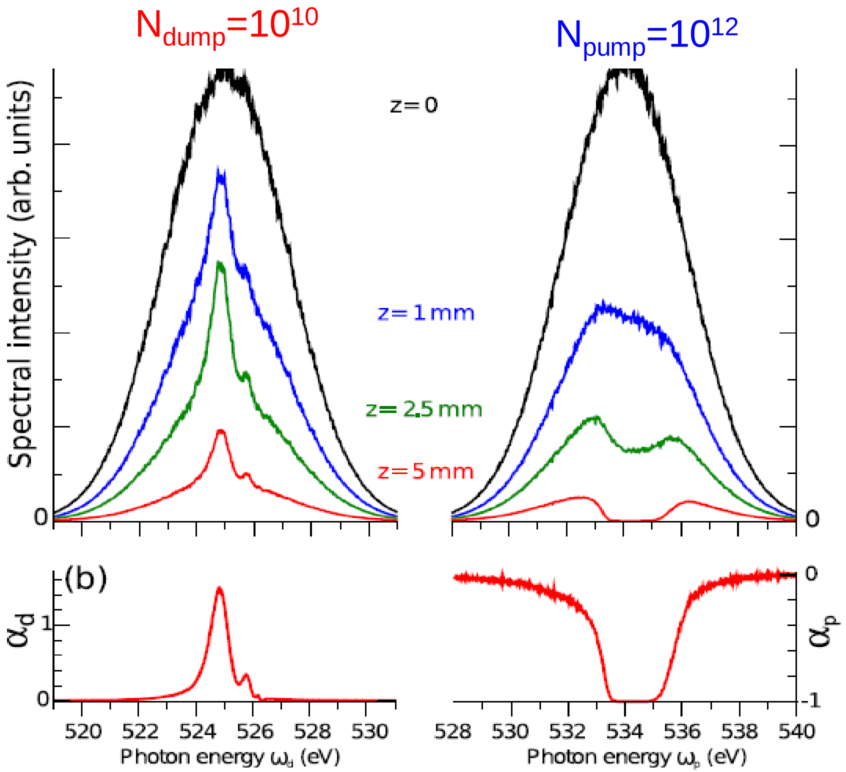


IR laser synchronized with XFEL creates great opportunities for IR-pump X-ray probe at SQS

Stimulated RIXS in two-color regime

- High flux pump pulse: 10^{12} photons per target (3 mkm focus, 100 fs)
- Population inversion and amplified stimulated emission conditions
- Gross features in x-ray amplified emission
- Feasibility study for the experiment (LCLS, AMO beam line at 2014)



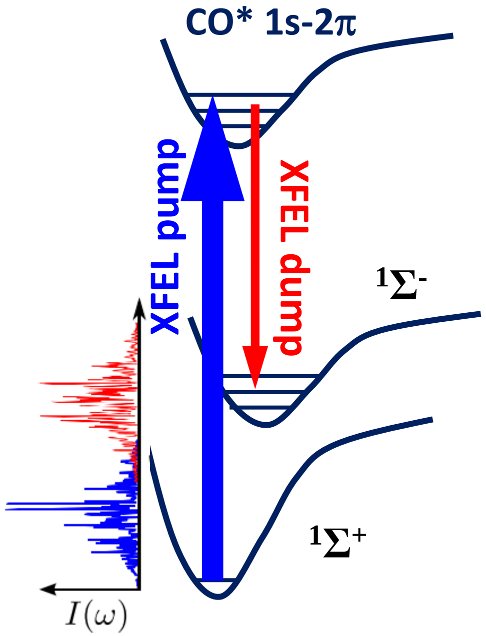


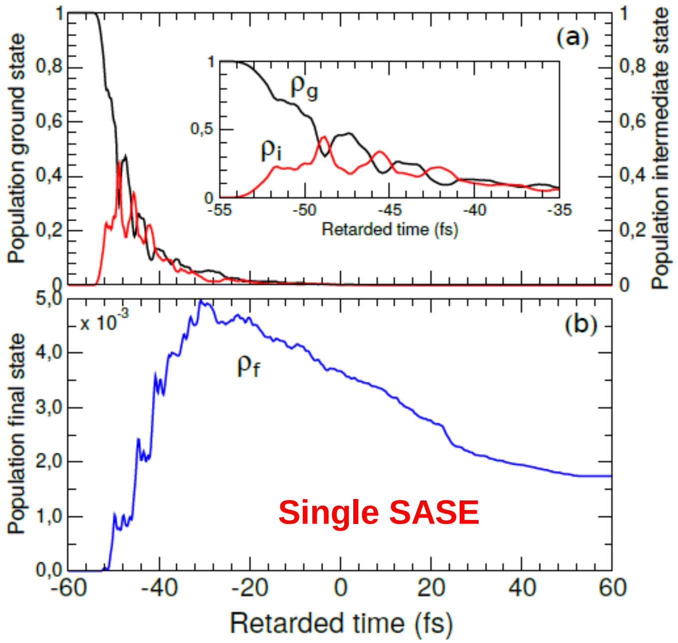
V. Kimberg & N. Rohringer, Structural Dynamics **3**, 034101 (2016)

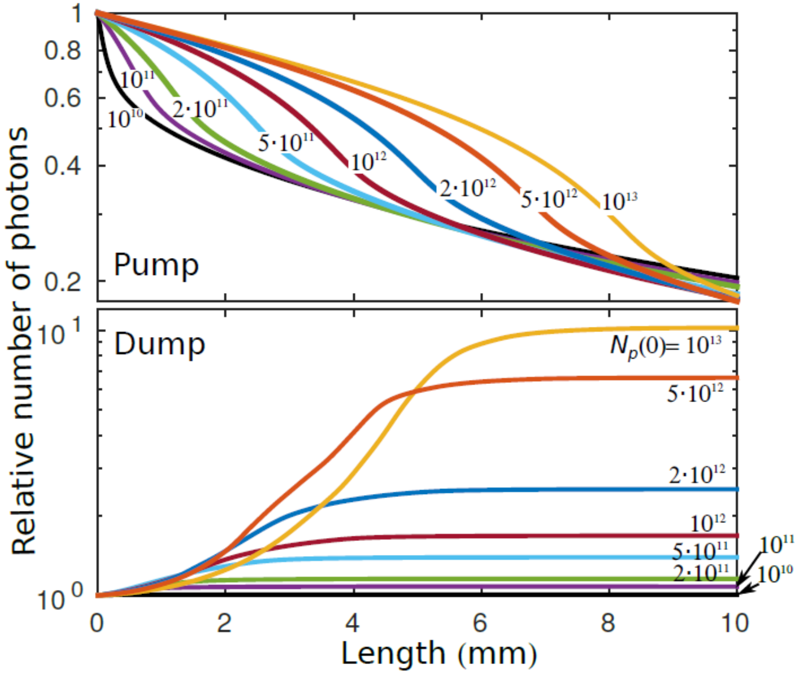
Averaged over 1000 SASE shots

Stimulated RIXS in strong pump regime

- Population inversion and amplified stimulated emission conditions
- Dipole moment (dump) < dipole moment (pump)
- Gross features in x-ray amplified emission
- Feasibility study for the experiment (LCLS, AMO beam line at 2014)



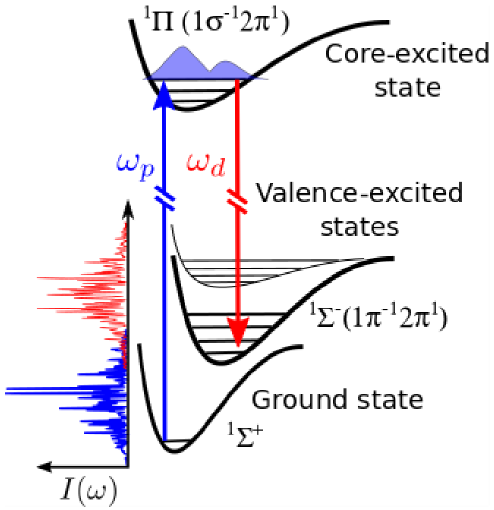




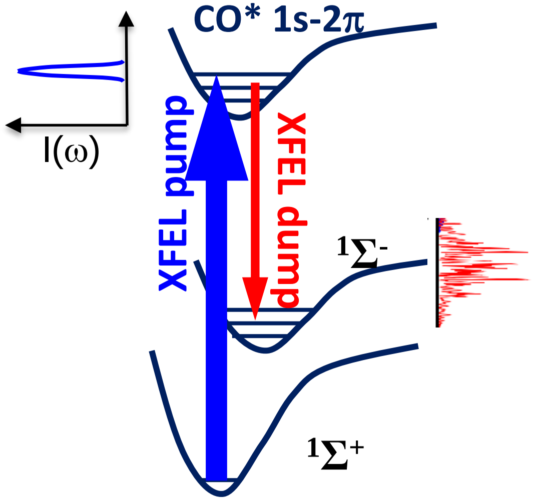
V. Kimberg & N. Rohringer, Structural Dynamics **3**, 034101 (2016)

Two 2-color SRIXS schemes

- SASE pump – SASE dump



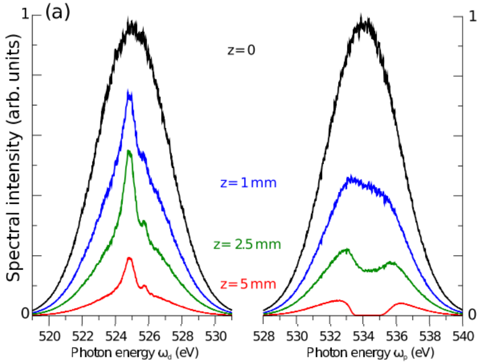
- Self-seeded pump – SASE dump



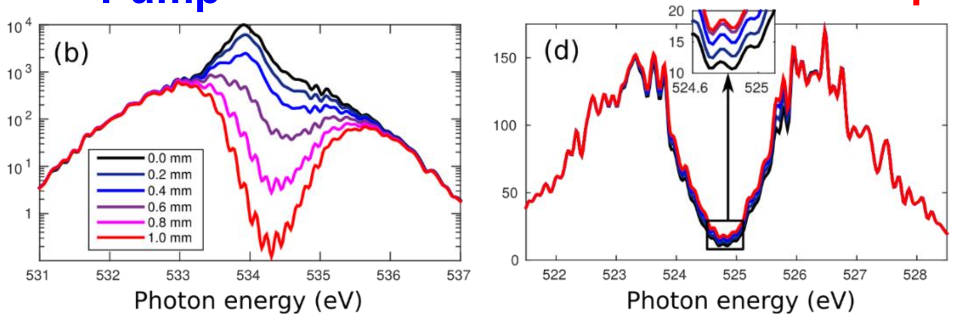
Theory predictions

~10^{12} photons/target

Dump **Pump**



Pump **Dump**



~10^{11} photons/target

LCLS Feb 2014
AMO beamline

Experiments

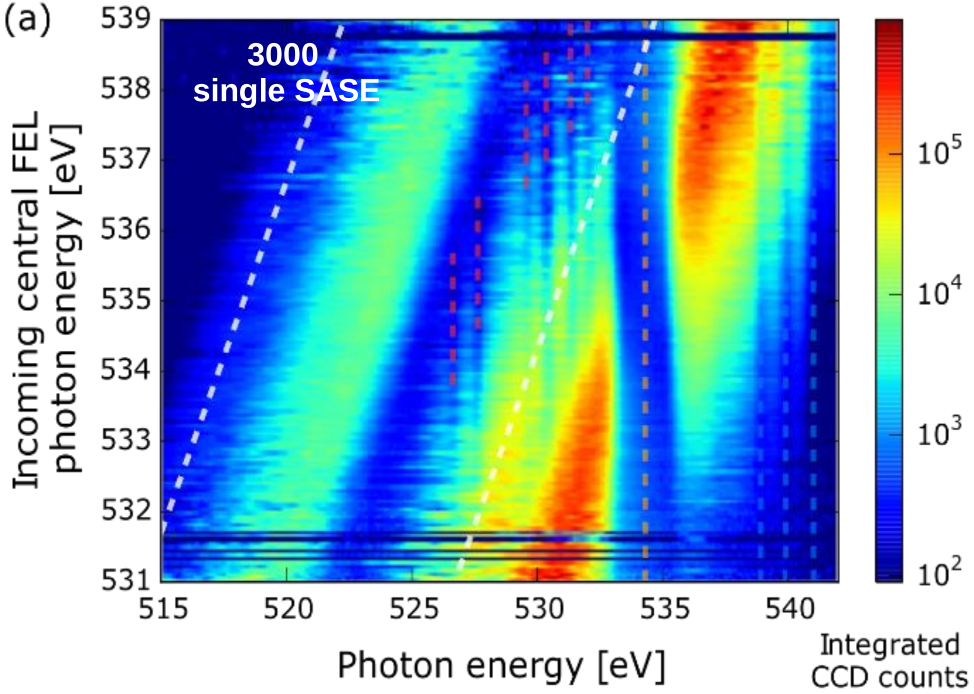
LCLS Jul 2015
AMO beamline

V. Kimberg & N. Rohringer, *Structural Dynamics* **3**, 034101 (2016)

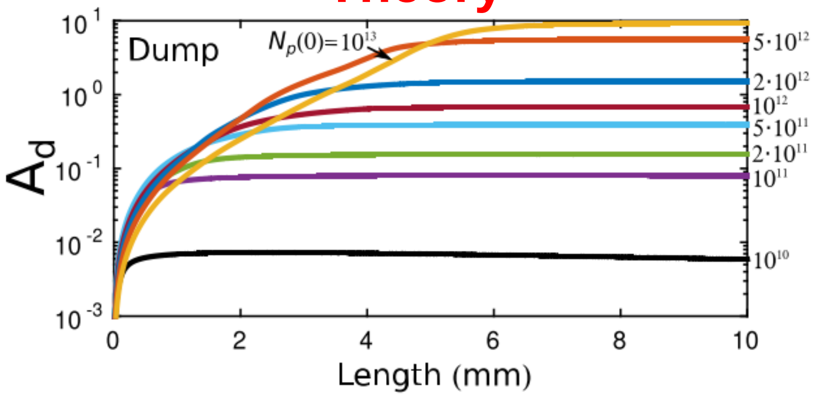
V. Kimberg et al, Faraday Discussions **194** 305 (2016)

Critical assessment: pump intensity

LCLS 2014



Theory



$$A_d = N_d \exp(\sigma_{ph} N z)/N_d(0) - 1$$

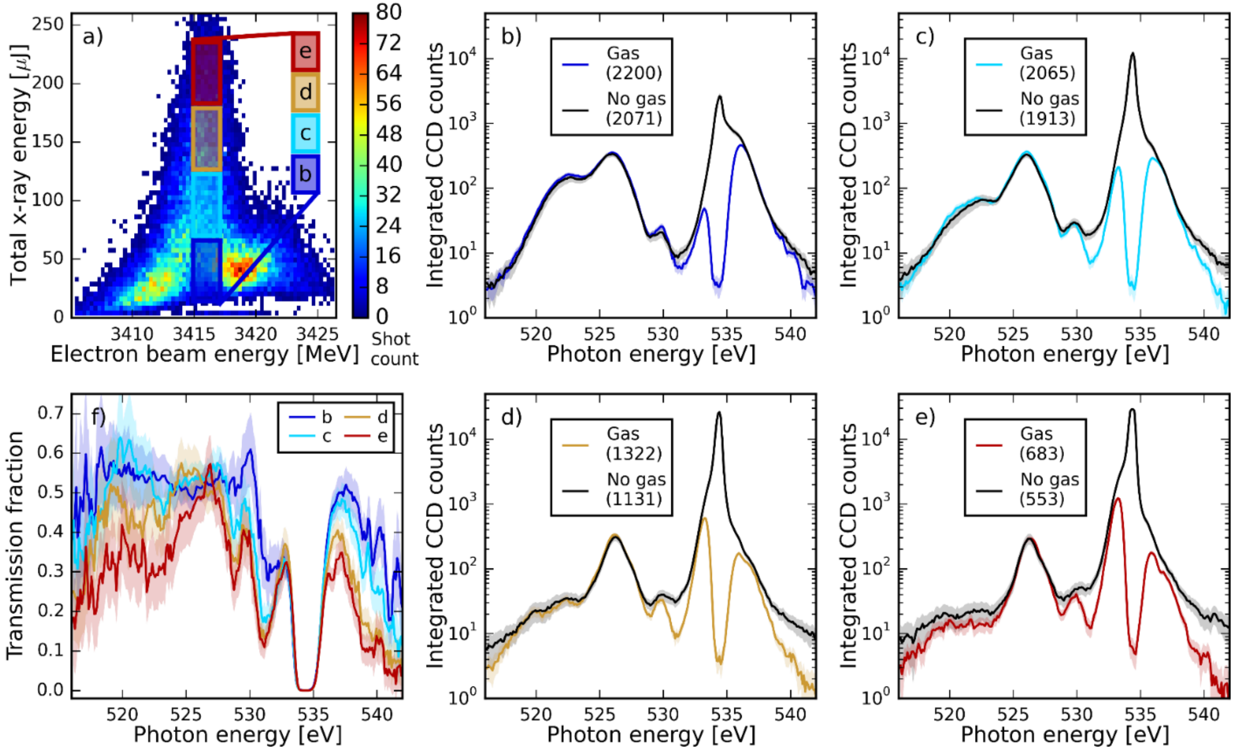
- Stimulated RIXS using 2-color SASE/SS scheme: ***no evidence of SRIXS***
- *Main requirement:* high spectral intensity of the pump overlapping with resonance

- **Intensities were on border of attainability!**
- Degradation of transmission and focusing x-ray optics, non-collinearity of pump/dump in the gas cell...
- Solution: pushing up XFEL intensities, using molecules alignment

Advanced analysis of the experimental data

- New measuring protocol for **weak signal measurement**
  - Gas/no-gas average spectra comparison for different pressure; Partial averaging of restricted ensembles (e-beam/pulse energy)

LCLS 2015
AMO, LAMP



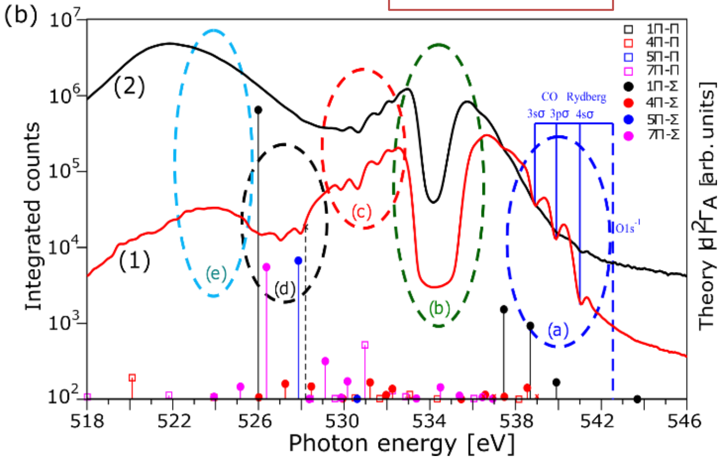
- High x-ray beam energies are only around certain e-beam energy interval
- High fluctuation of the total x-pulse energy
- The average spectrum is different for different regions on the correlation plot
- Fluctuations complicate the detection of a small SRIXS signal

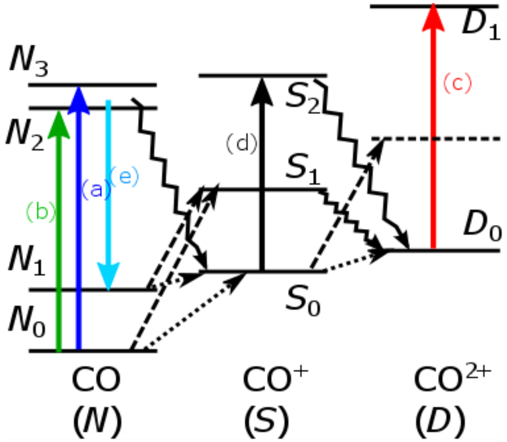
Despite fluctuations, averaged spectra are well reproducible
Relative differences > 0.05% observable !!!

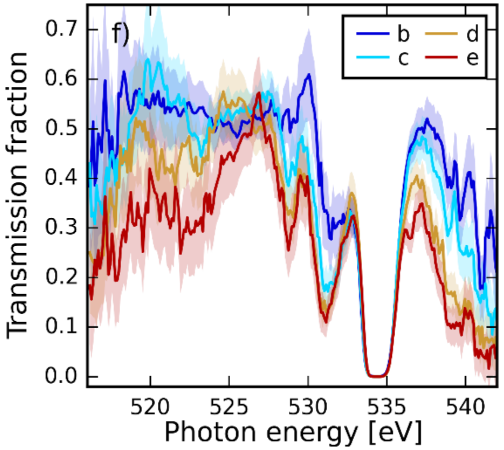
V. Kimberg et al, Faraday Discussions (2016)

Absorption features of transiently created ions

LCLS 2014





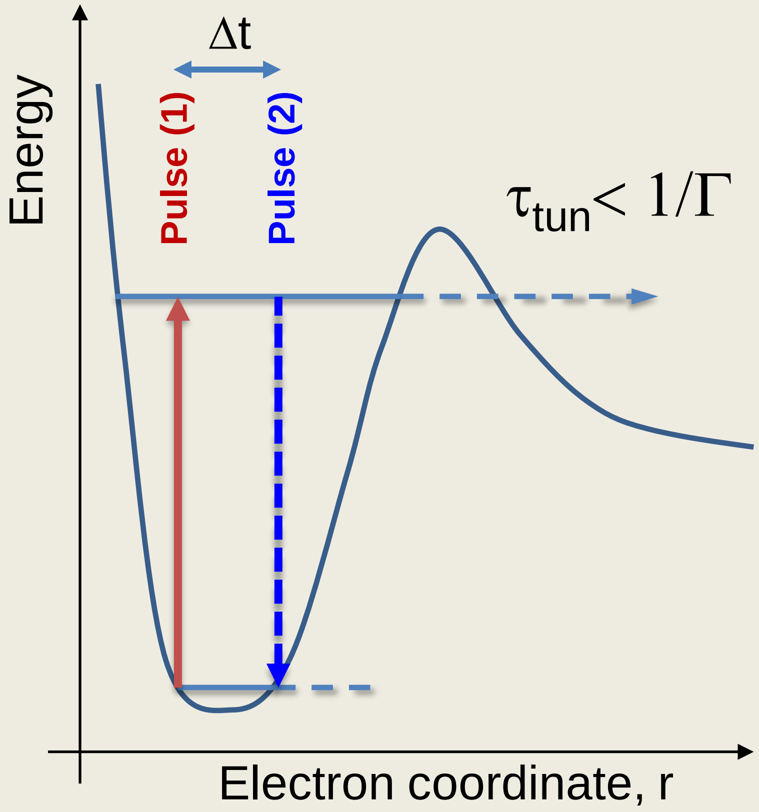


LCLS 2015

(a) high energy 539-541 eV:
Rydberg states absorption by neutral CO
(b) 1s-π* resonance at 534 eV
(c) middle energy 529-533 eV:
Tentatively assigned to absorption lines in CO^{++}
(d) low energy 525-528 eV :
O1s excitation of single-charge CO$^+$ (confirmed by XES)
(e) expected SRIXS region

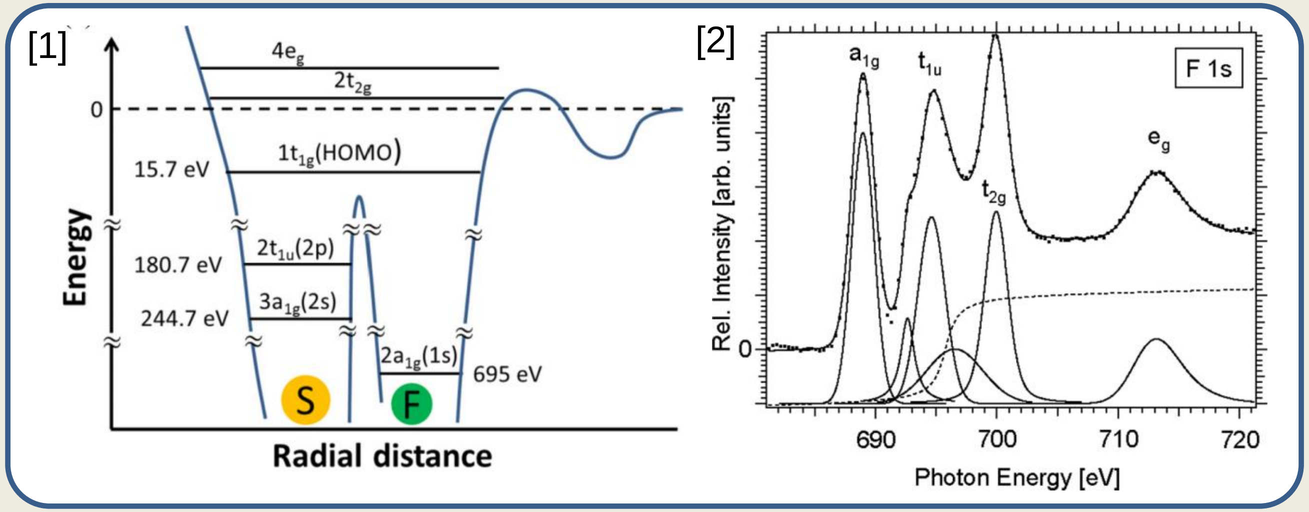
- 1D imaging: different channels will be visible via fluorescence measurement at different propagation length, giving complementary information for SRIXS

Electron tunnelling time at the shape resonances



- SF_6 molecule or SF_6 cluster (for example)
- No pulse (2) or $\Delta t > \tau_{tun}$: we will see X-ray fluorescence during $1/\Gamma$
- $\Delta t < \tau_{tun}$: fluorescence is absent as core-hole is filled by SXE

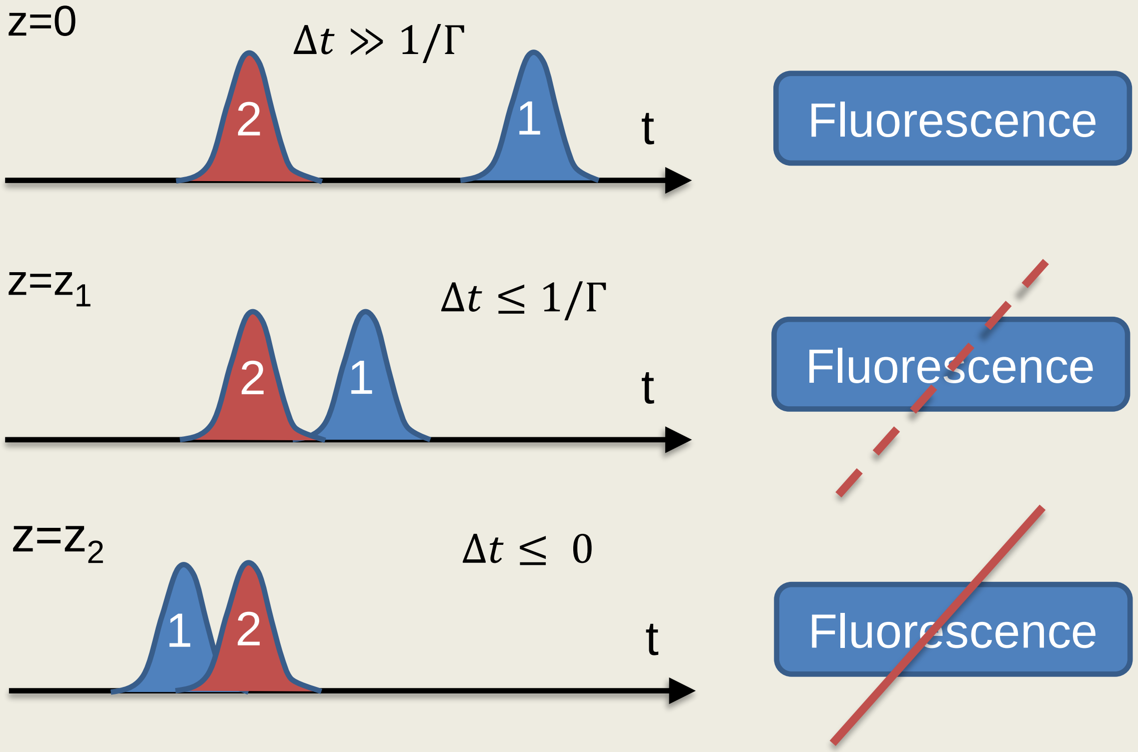
- Direct measurements of the tunnelling time and electron dynamics for various molecular systems and cluster size
- Dynamical features along the medium as pulse intensities are changed



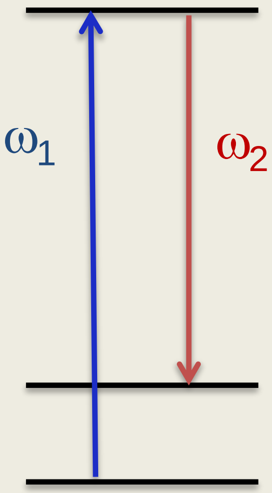
1) Nguyen,et al., Phys Rev A 93, 063419 (2016)
2) Grunewald, et al., Zeitschrift für Physikalische Chemie 234, 1371 (2020)

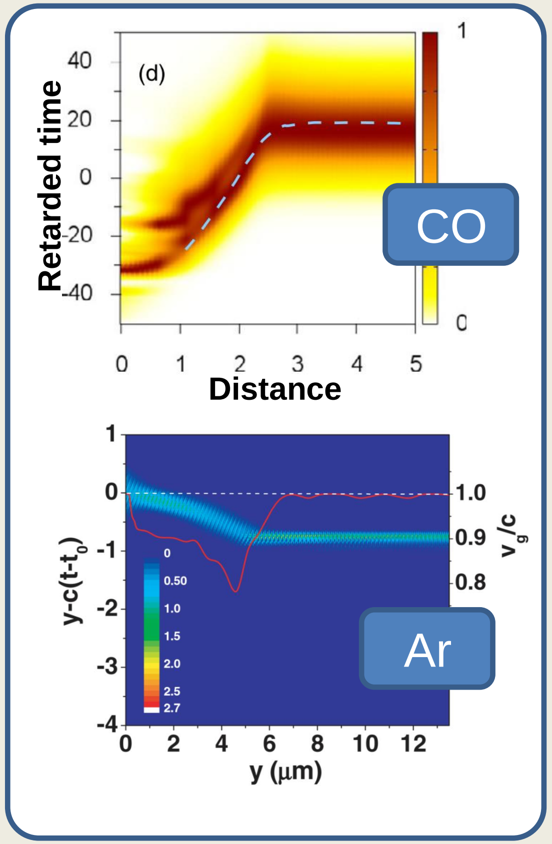
Pulse slowdown on resonant X-ray transition

Time ⟷ Distance



Ne (GS, $1s^{-1}3p^1$, $2p^{-1}3^{-1}$)
CO (GS, $1\sigma^{-1}2\pi^1$, $1\pi^{-1}2\pi^1$)
etc...

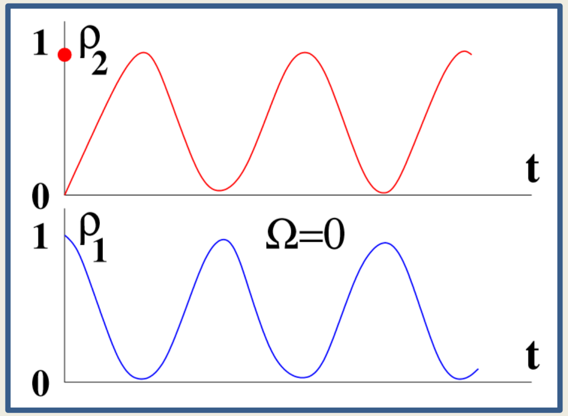


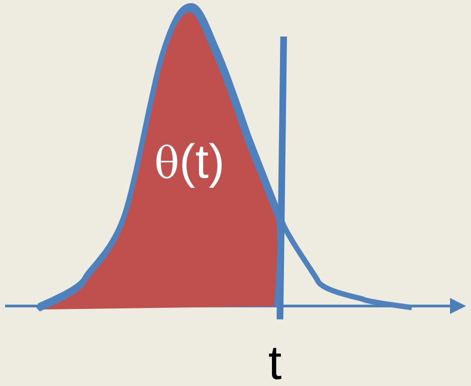


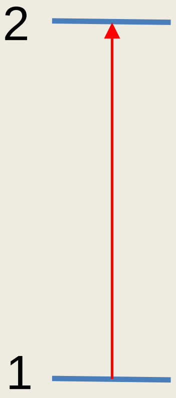
Delay of several tens fs

1D-imaging spectrometer allows to collect spatial information on nonlinear propagation which can be converted to temporal description of slowdown of the X-ray pulses

Pulse: *n*π-pulses and area theorem







- Another important case: resonant interaction Ω=0

$$\dot{a}_1 = i\frac{G(t)}{2}a_2,\quad \dot{a}_2 = i\frac{G(t)}{2}a_1$$

- Can be decoupled using $a_\pm = a_1 \pm a_2$

$$\dot{a}_+ = i\frac{G(t)}{2}a_+,\quad \dot{a}_- = i\frac{G(t)}{2}a_-$$

- Solution is

$$a_\pm(t) = A_\pm e^{\pm i\theta(t)/2},\quad \theta(t) = \int_{-\infty}^{t} G(t_1)dt_1 = d_{12}\int_{-\infty}^{t} E(t_1)dt_1$$

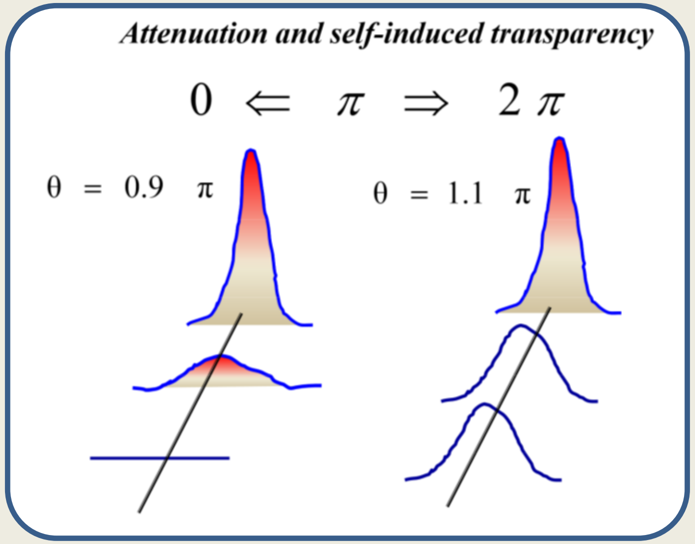
- Taking into account initial condition ($a_1=1$, $a_2=0$) : $A_+=A_-=1$

$$\rho_1(t) = \left|a_1(t)\right|^2 = \cos^2\frac{\theta(t)}{2},\quad \rho_2(t) = \left|a_2(t)\right|^2 = \sin^2\frac{\theta(t)}{2}$$

$$\rho_1(\infty) = \cos^2\frac{\theta}{2},\quad \rho_2(\infty) = \sin^2\frac{\theta}{2}$$

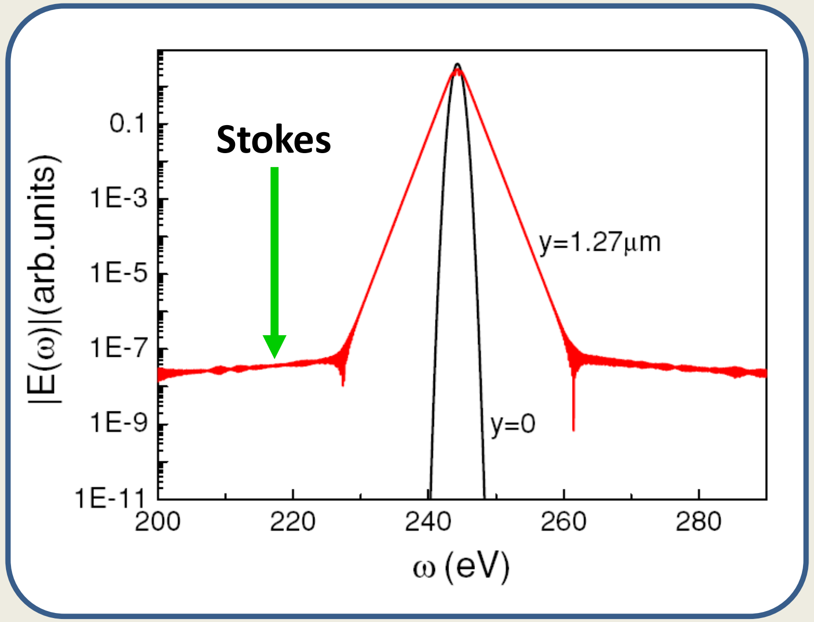
- ✓ Area theorem (Mc Call-Hahn): the system is inverted when pulse area is (2n+1)π (unstable)
- ✓ Self induced transparency: for 2nπ pulse the system stays in the ground state, no absorption!
- ✓ Control over population transfer using pulse area

Pulse compression and seeding for the Stokes line

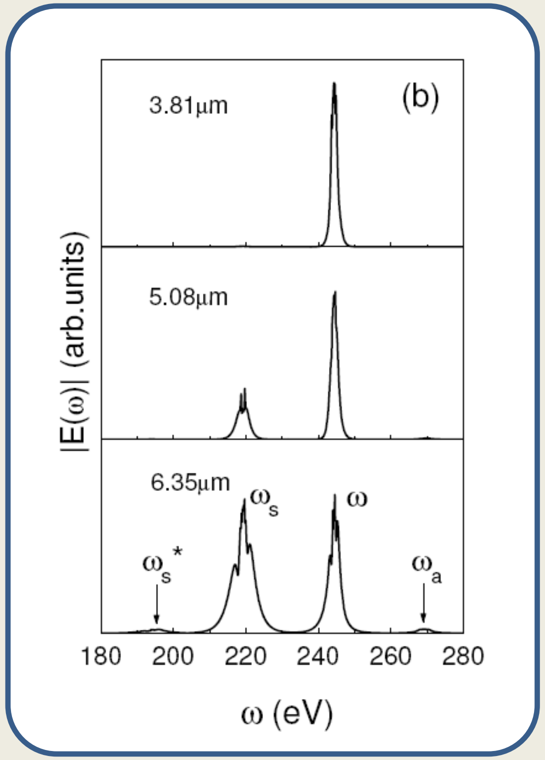


- For pulses with $\theta<\pi$: $\theta\rightarrow 0$
- For pulses with $\theta>\pi$: $\theta\rightarrow 2\pi$
- Energy conservation low

$$E_{3\pi}^2\tau_{3\pi} = E_{2\pi}^2\tau_{2\pi}$$



- Burnham-Chiao modulation of the XFEL pulse results in the broadening while the envelope of the BC oscillations forms the spectral tail
- This spectral tail gives the seed radiation for Stokes and four-wave mixing fields



Sun et al., Phys Rev A 81 (2010) 013812

Summary

❑ Stimulated X-ray emission (SXE) and related processes in molecules

- Amplifies X-ray emission (single X-ray pulse)
- Stimulated RIXS schemes (two-color X-ray)

❑ Application of 1D-imaging X-ray spectrometer at SQS

- ➢ IR+X-ray: molecular alignment for an efficient AXE
- ➢ IR+X-ray: pumped vibrational dynamics observed with X-ray fluorescence
  - ➢ SXE near shape resonances: study of the electron wave packet dynamics in a confinement
  - ➢ Slow down of resonant X-ray pulse measured in two X-ray pulse mode
    - ➢ Pulse broadening and compressing, self-induced transparence, four-wave mixing, …

Acknowledgements: *Swedish Research Council and Russian Science Foundation*