

# Perspectives of multi-colour nonlinear x-ray Raman scattering with high-brilliance XFELs



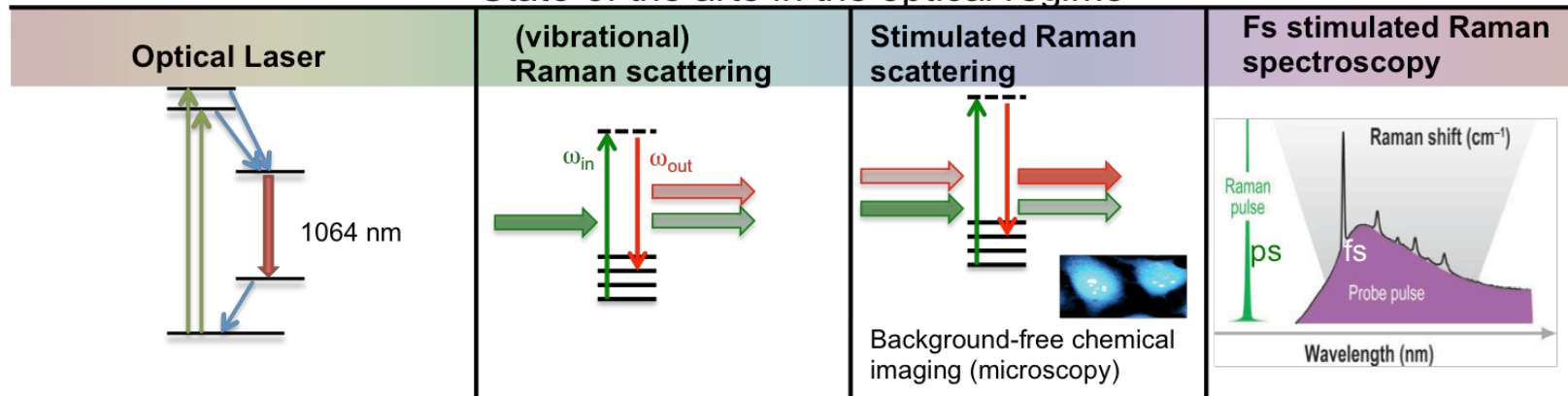
**Nina Rohringer,**  
**New Scientific Capabilities at the European XFEL, March 26, 2019**



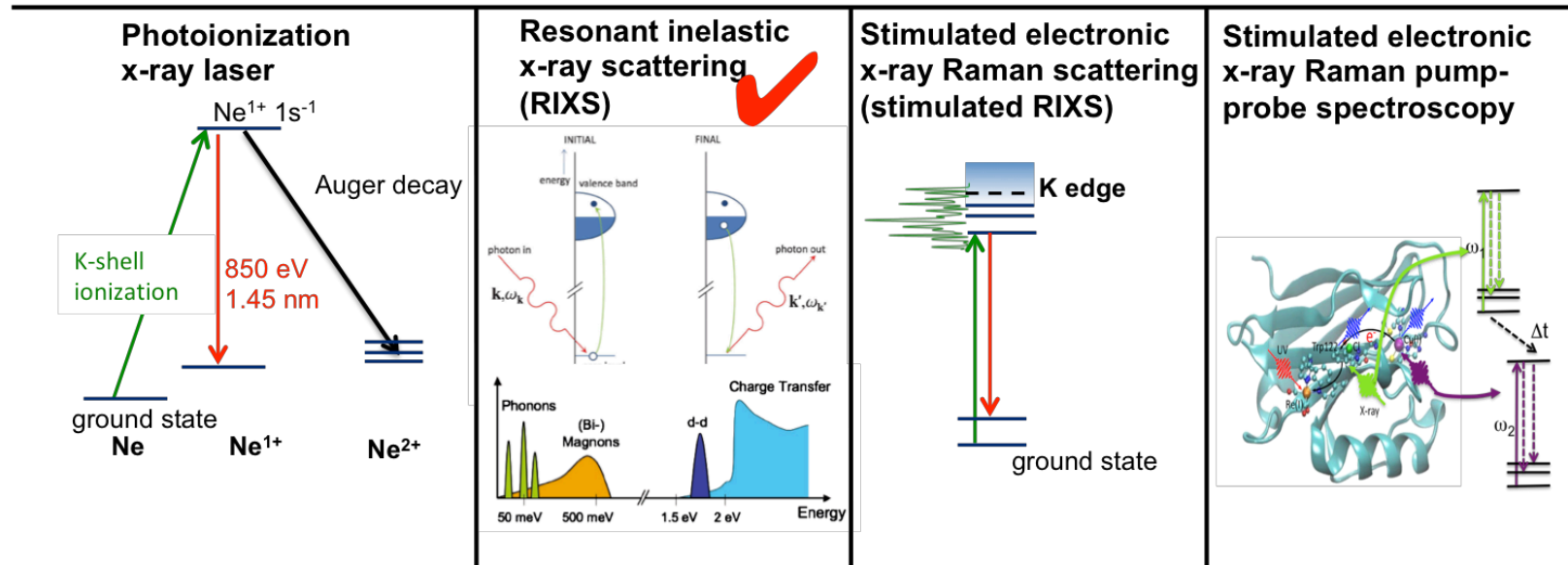
# Stimulated x-ray emission

Transfer of nonlinear optical effects to the x-ray spectral domain

State-of the arte in the optical regime

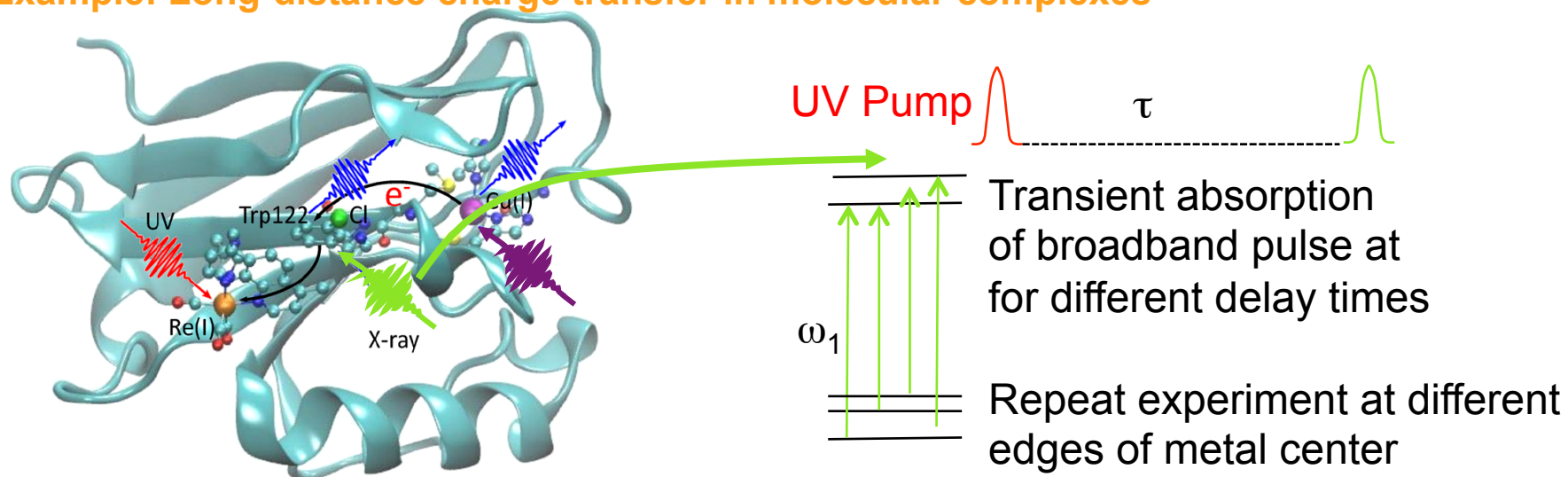


Grand challenge to transfer processes to the x-ray domain

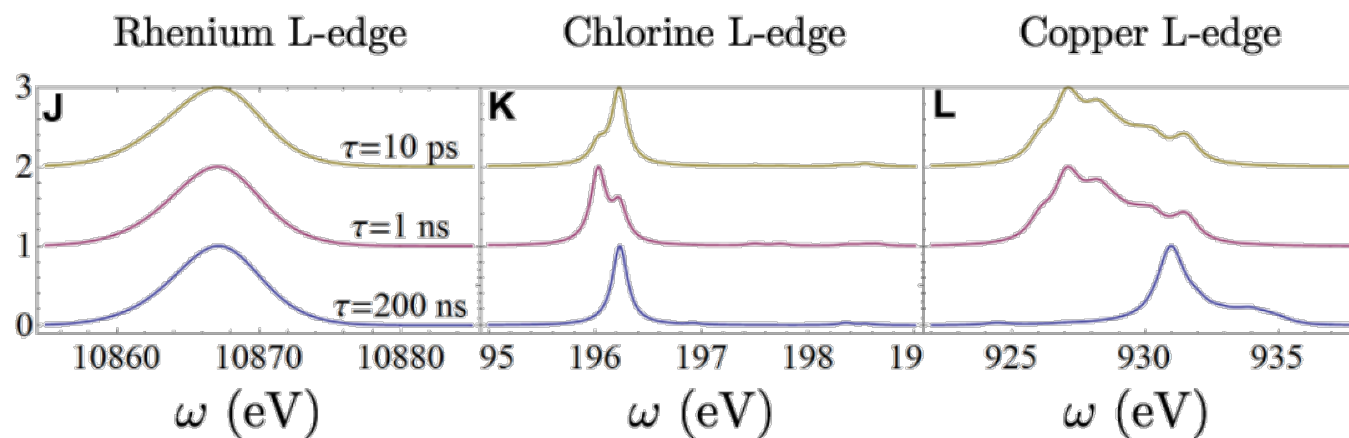


# Linear x-ray spectroscopy - transient fs absorption

Example: Long-distance charge transfer in molecular complexes

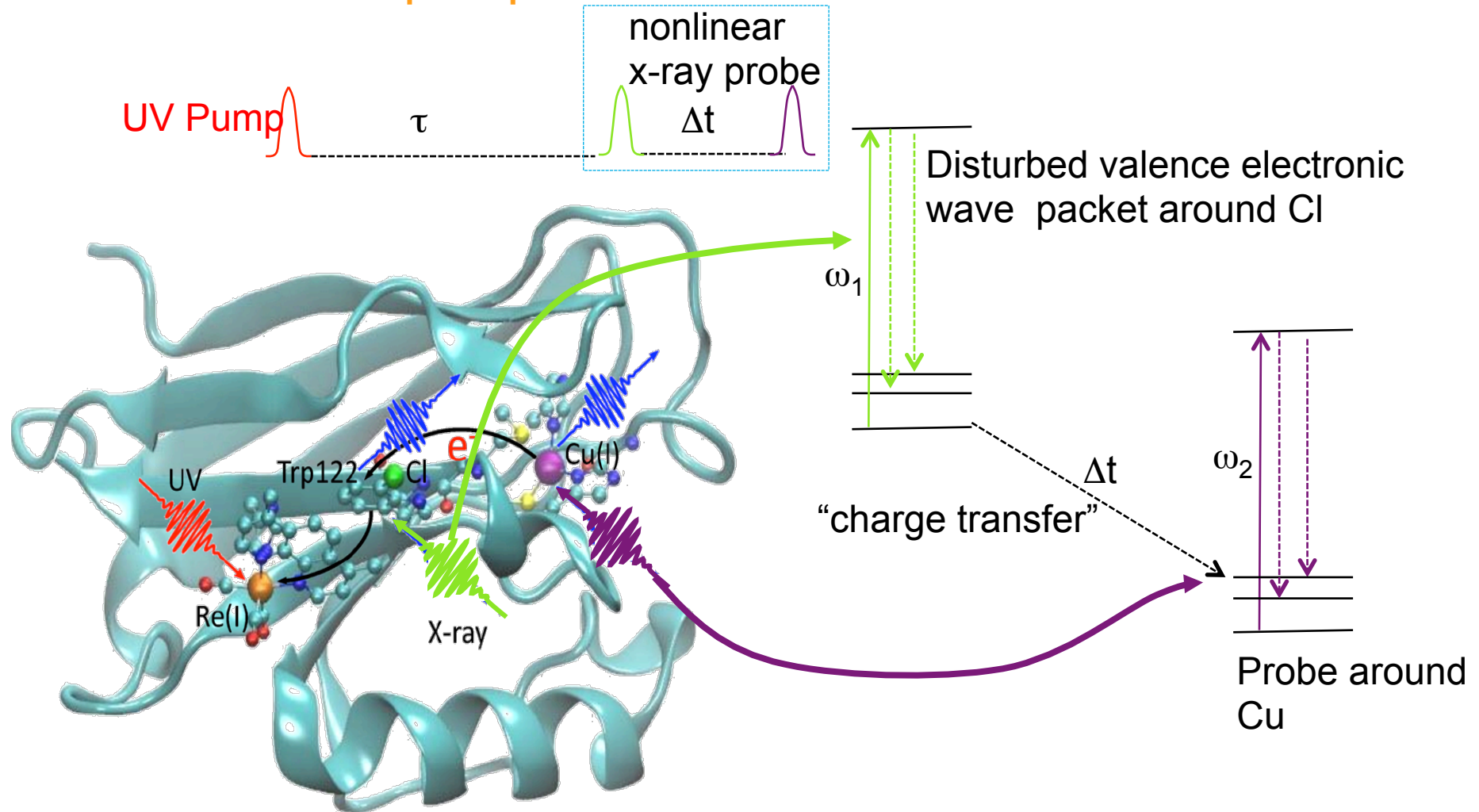


Simulated transient absorption spectra:



# Stimulated electronic X-ray Raman spectroscopy

A coherent nonlinear probe process



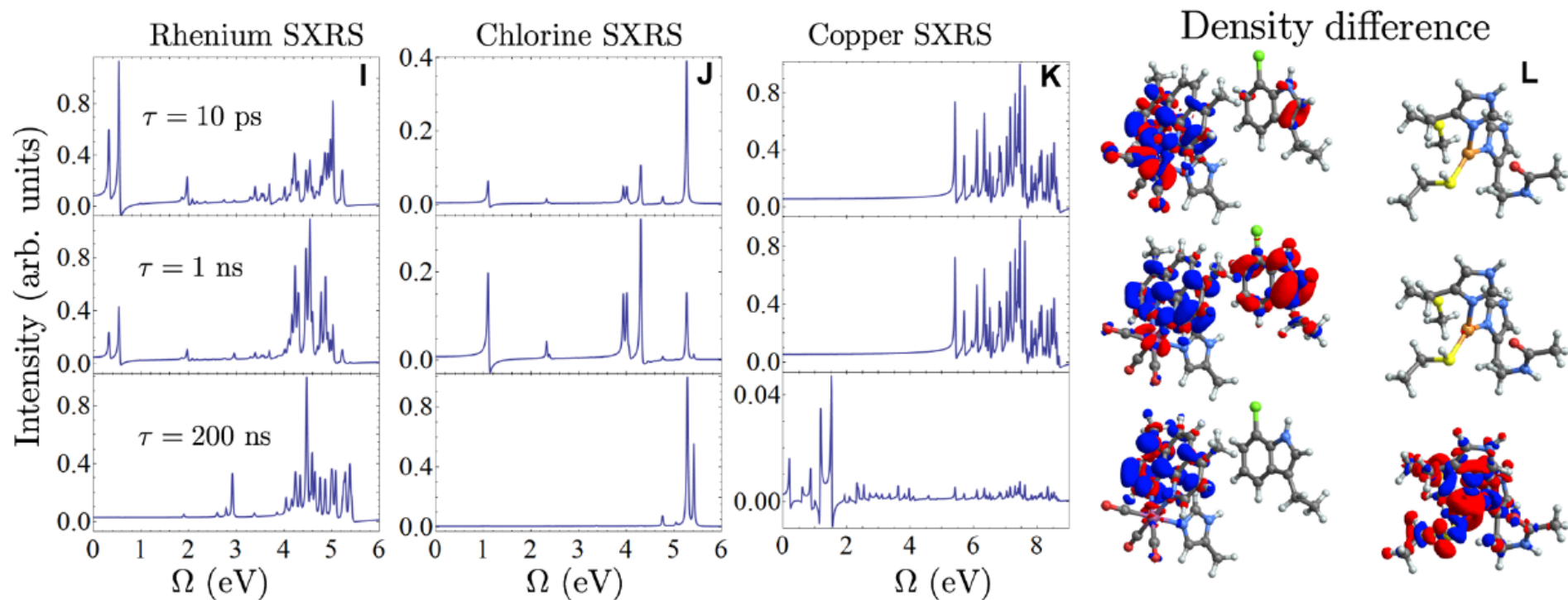
Shaul Mukamel et al. ( PRL 89, 043001 (2002), PRB 72, 235110 (2005); PRA 76, 012504 (2007); PRB 79, 085108 (2009)

# Simulated 1D Stimulated x-ray Raman spectra

$\tau$ .... Change pump-probe delay: on the 10 ps to 100 ns time scale

$\Delta t$ .... Sampling time-delay:  $\Delta t$  varied up to 100 fs, in steps of 0.2 fs

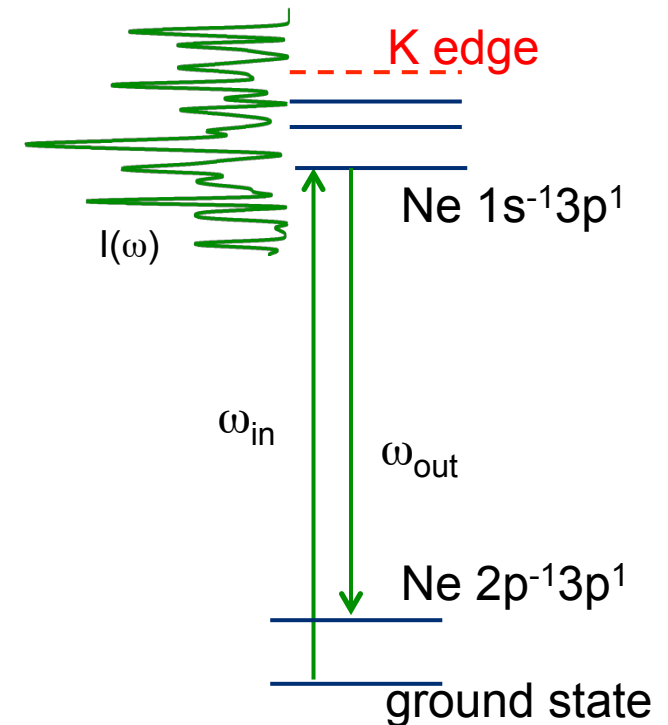
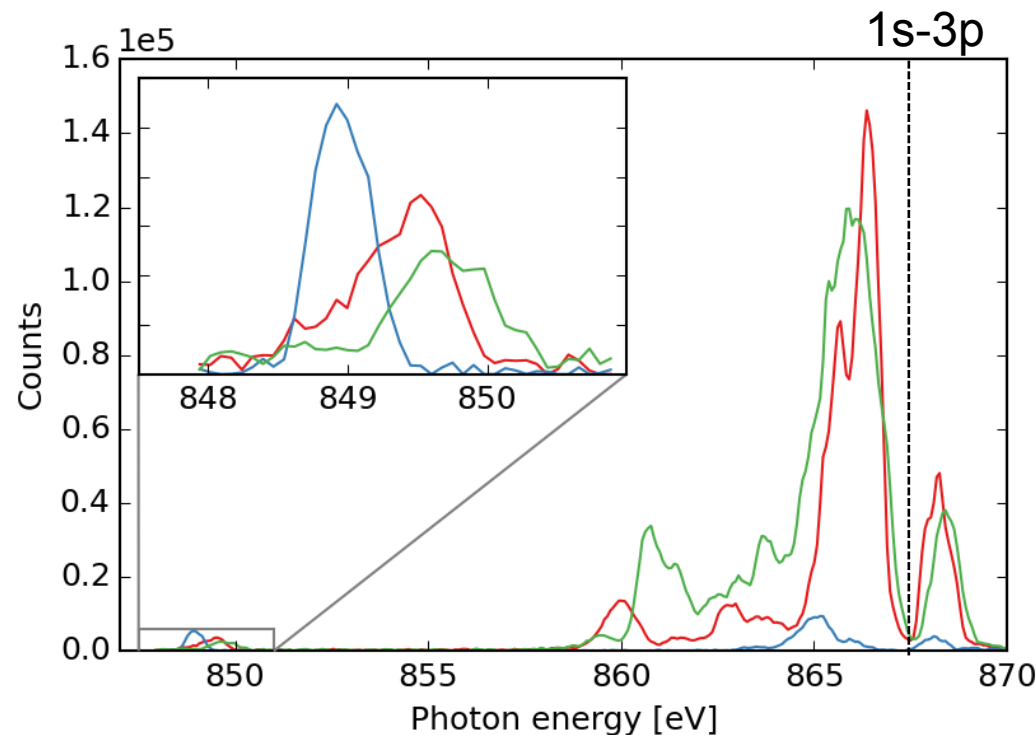
- Measure absorption of probe pulse (2<sup>nd</sup> x-ray pulse) does not need to be frequency resolved
- Take Fourier Transform with respect to  $\Delta t$  of total absorption
- Repeat for second x-ray pulse tuned to different edges (local metal centers)



Y. Zhang et al., Phys. Chem. Lett. 5, 3656 (2014).

# Stimulated resonant electronic x-ray Raman scattering in Neon

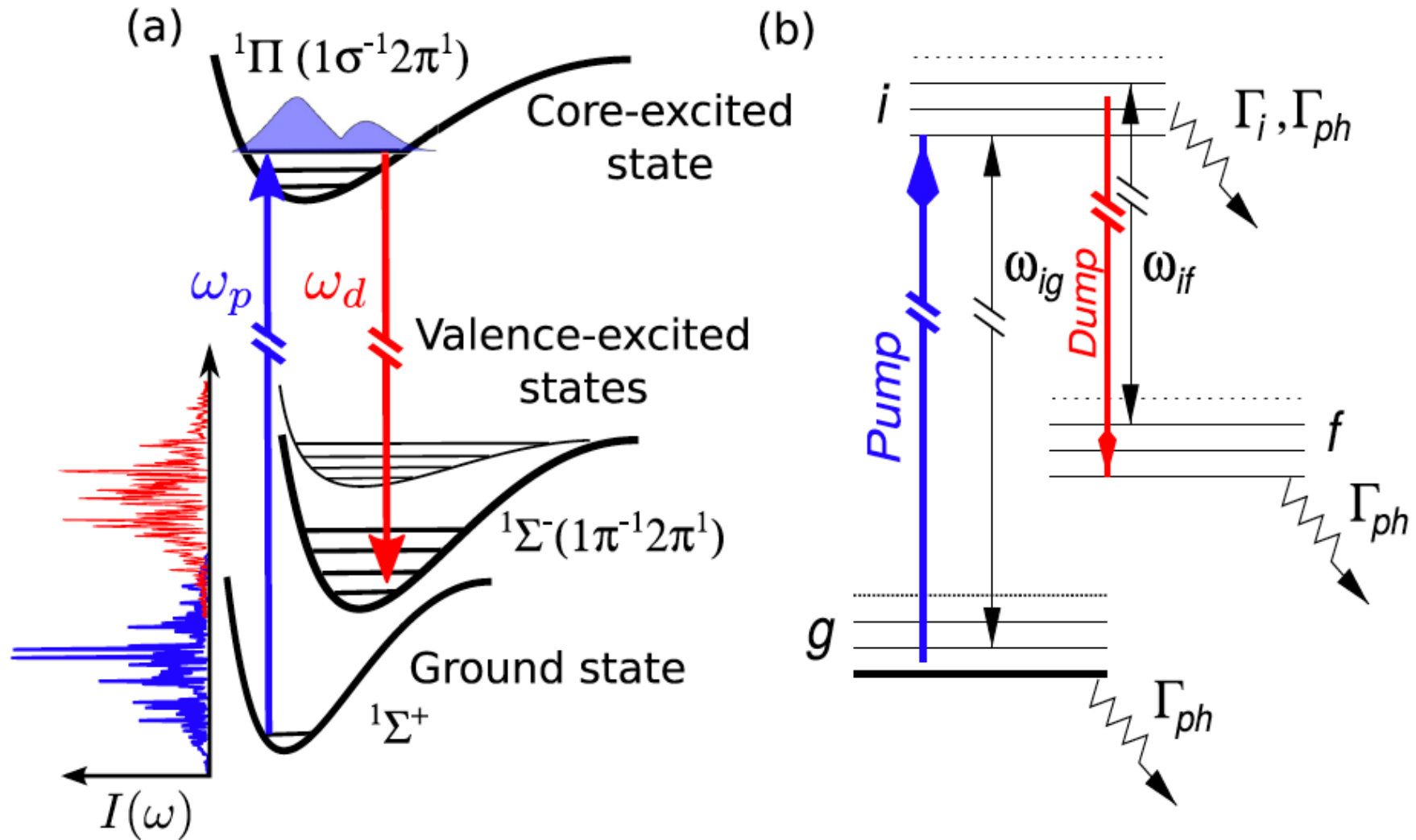
2 experimental demonstrations in Aug. 2012 and Feb. 2014



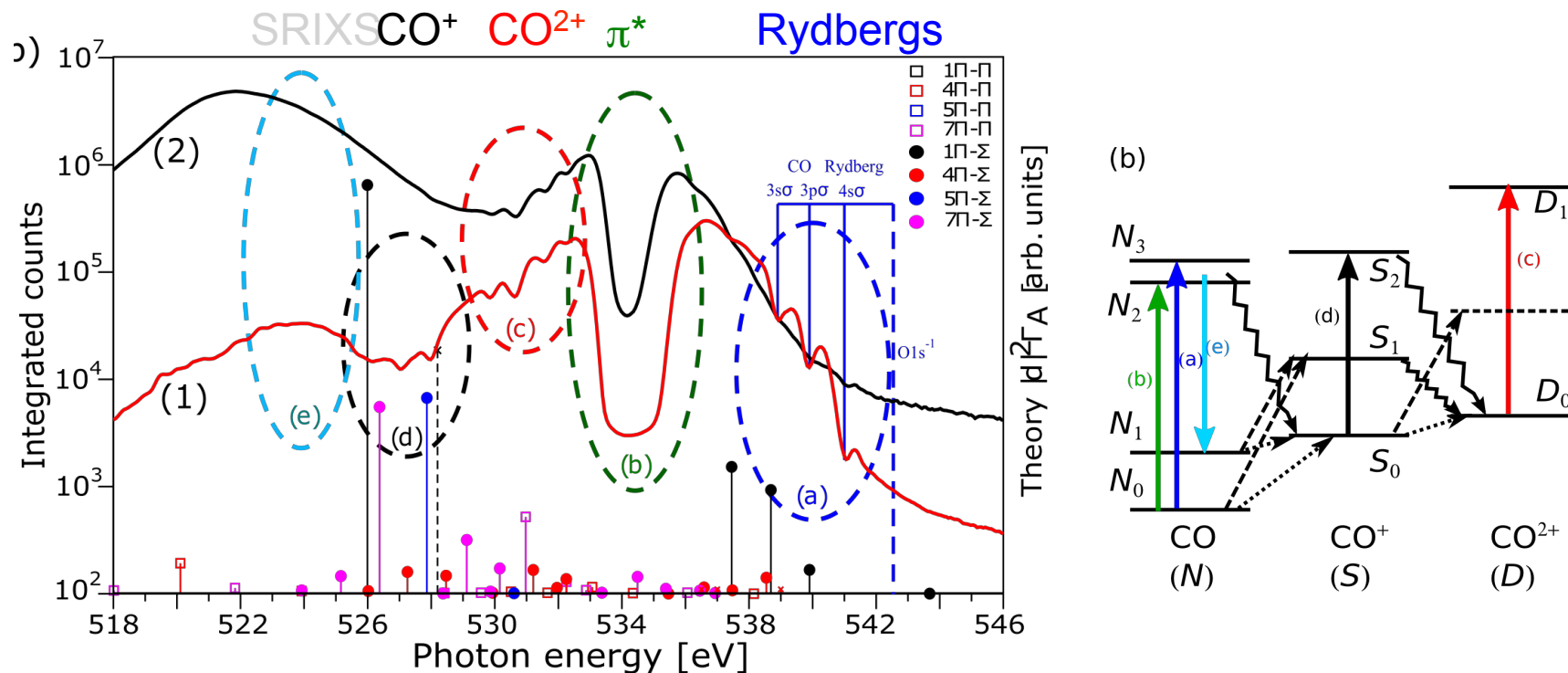
Spectral tail of SASE provides seeds photons  
6 orders of magnitude of amplification (Raman gain)

# Stimulated electronic x-ray Raman scattering in CO

Experiment with 2-colour SASE pulses



# High-fluence pulses result in the creation of large absorption features of higher charged ions

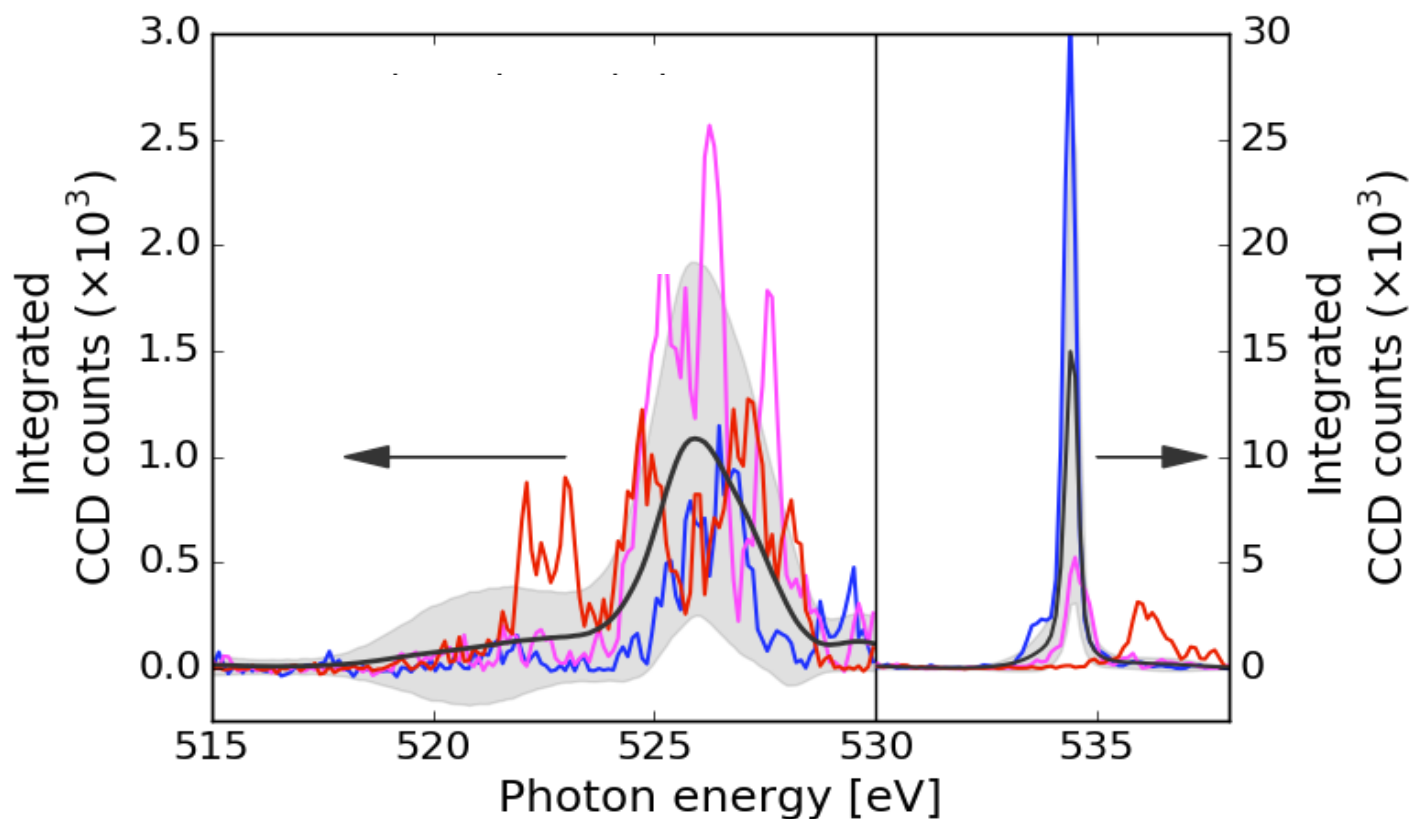


-> replace pump pulse by low-fluence, high brilliance self-seeded XFEL pulse

Similar changes of absorption spectrum due to sequential ionisation observed in water droplets (S. Schreck et al., *Phys. Rev. Lett.*, 2014, **113**, 153002. )

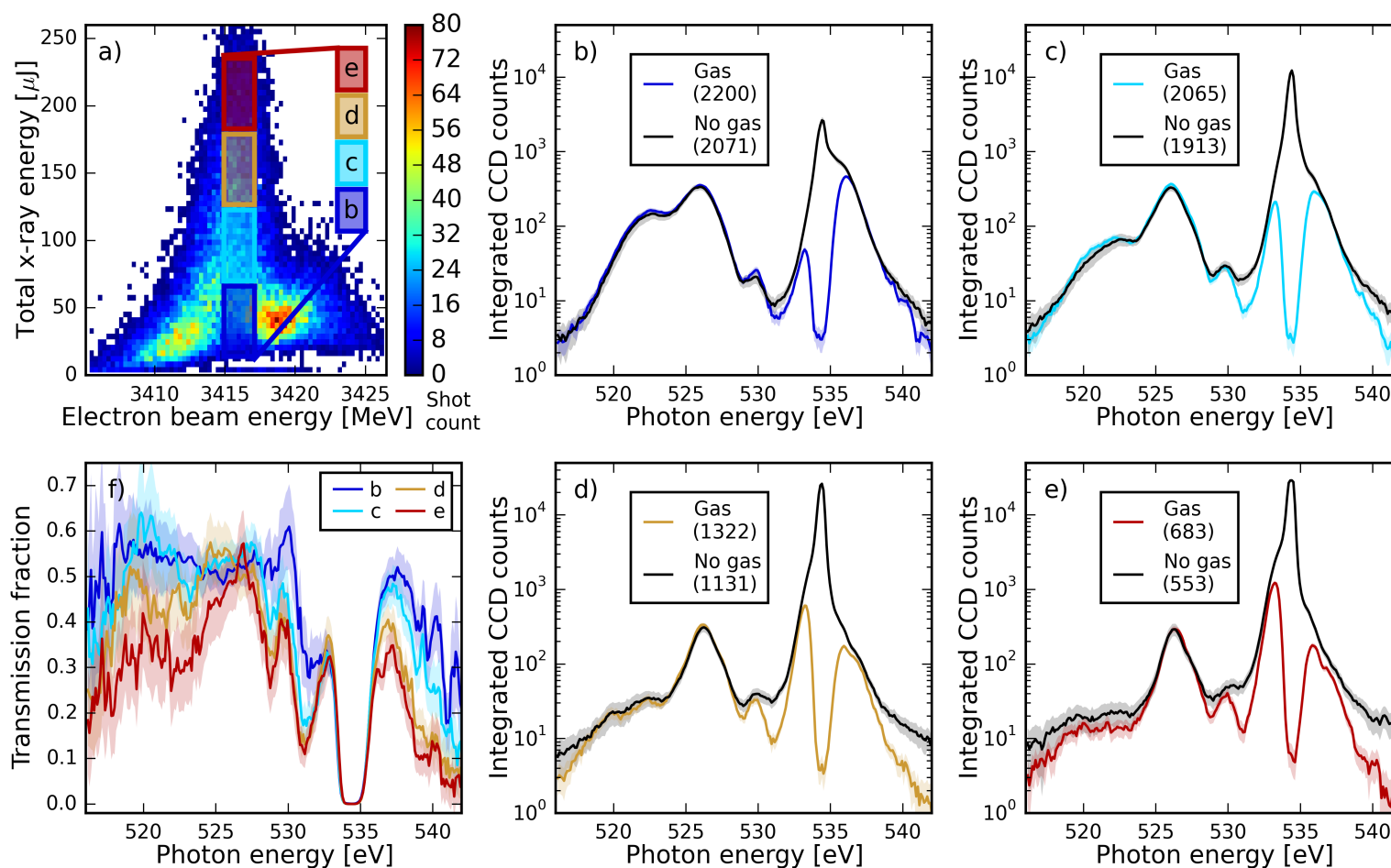
## Soft x-ray self-seeding mode to pump on the O $\pi^*$ resonance

Self-seeded pulses are far from transform limit and shot-to-shot stability



**Are small Raman Gains and transient absorption signals measurable with this highly fluctuating source?**

# Averaged spectra in the “pump” and “dump” region

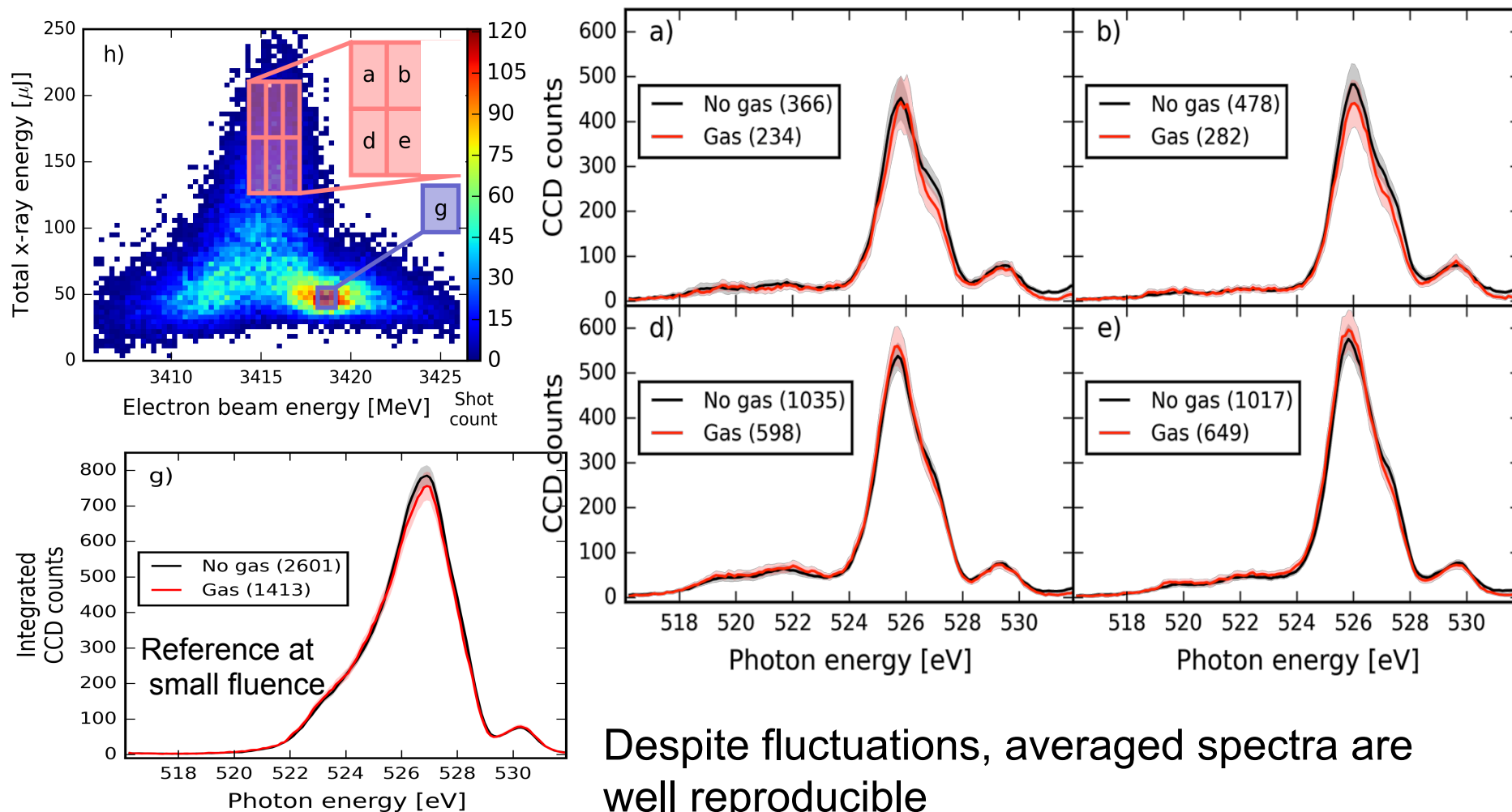


Absorption of transiently created ions visible in spectra!

No evidence for Stimulated Raman scattering

Gas pressure at 100 mbar

# Analysis of stability of XFEL self-seeded two-color source (peak of seeded pulses at 534.43 eV, 100mbar CO)

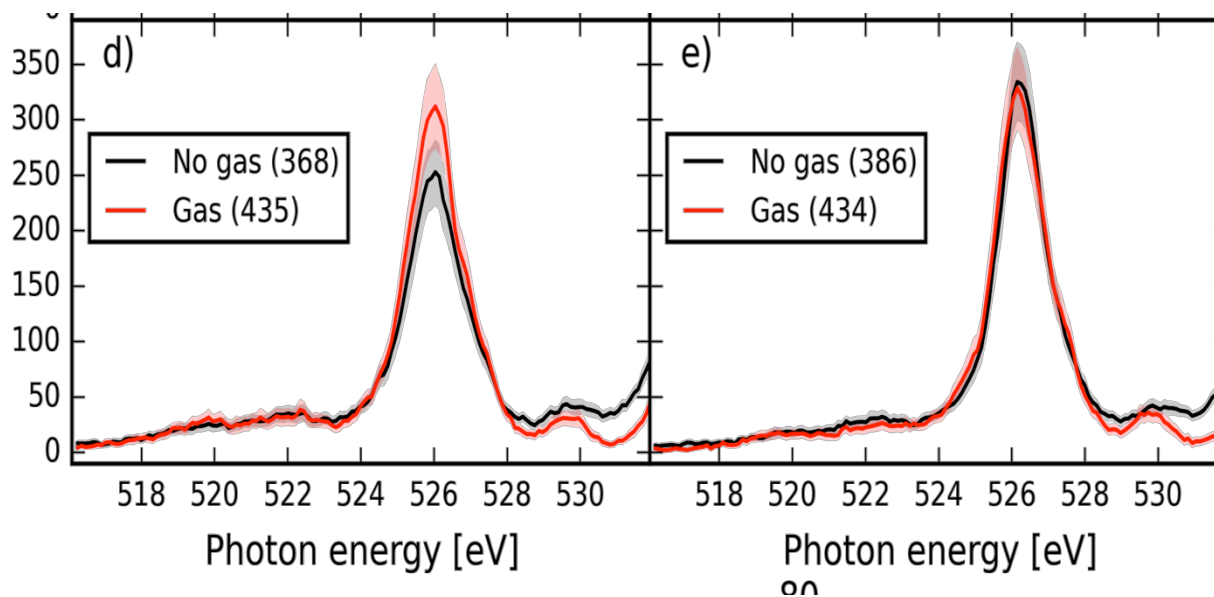
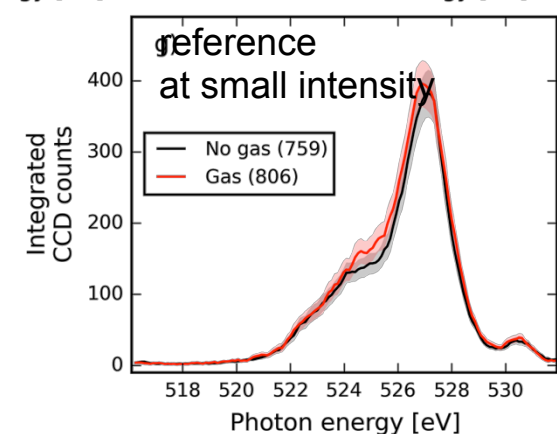
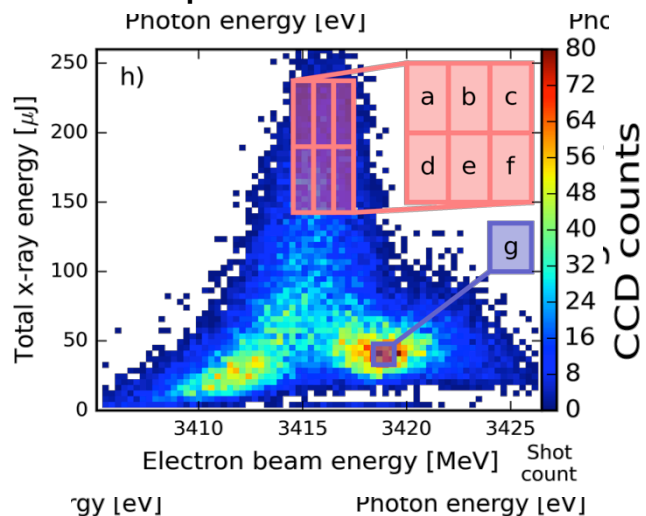


Despite fluctuations, averaged spectra are well reproducible

**Relative differences > 0.05 OD observable !!!**

# Statistically relevant differences for different XFEL setting (peak of seeded pulse at 534.32 eV)

Gas pressure at 100 mbar

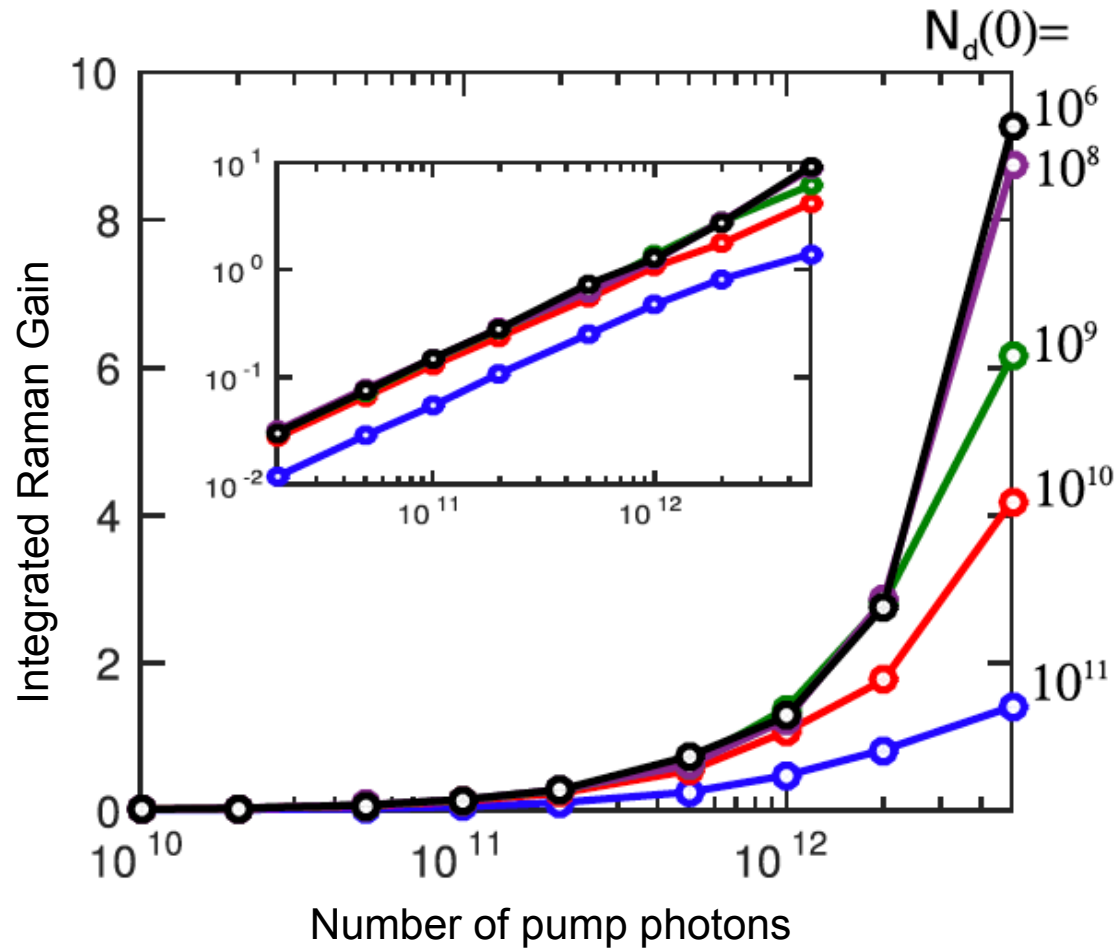


**We need higher pulse energies !**

Theory:  $10^{11}$  photons in 35 fs, 6  $\mu$ m: Raman gain of 0.5  
 Conditions at experiment:  $2 \cdot 10^8$  photons/ $\mu$ m<sup>2</sup>/fs/eV (for 0.5 eV self-seeded pulses of 35 fs)

# Stimulated electronic x-ray Raman scattering @ high-brilliance XFELs

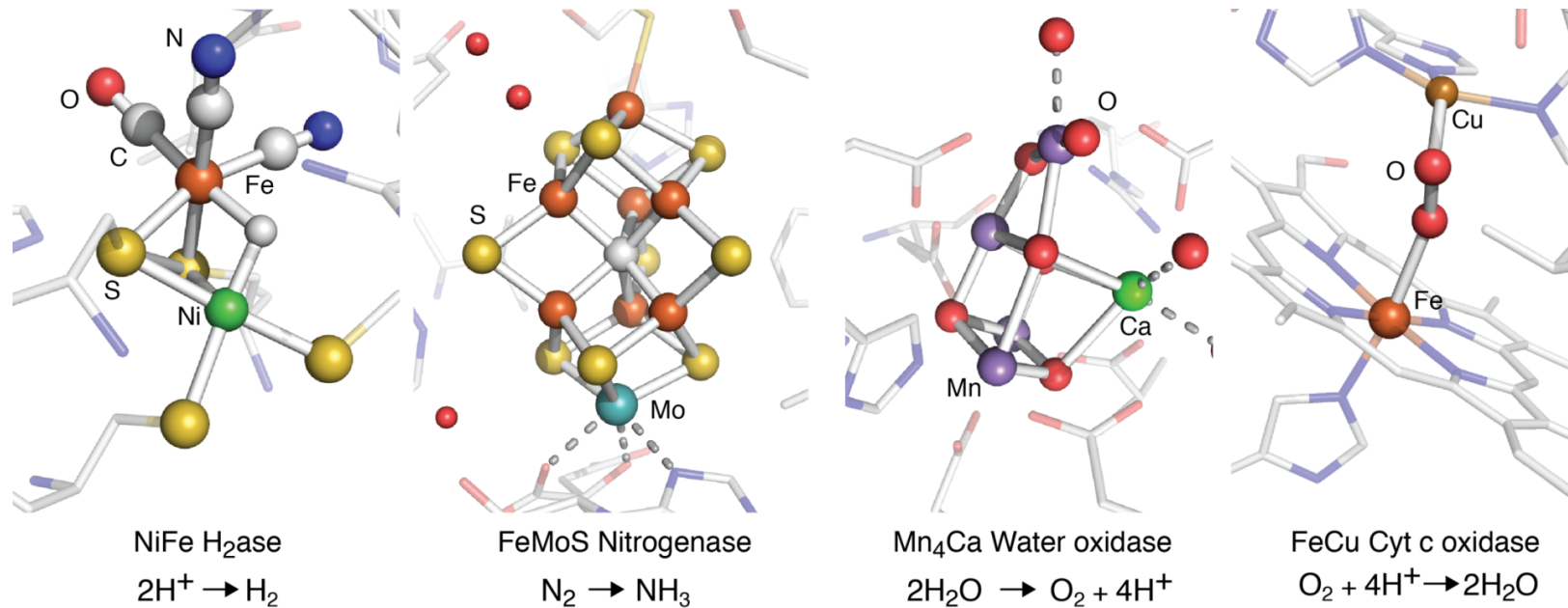
$10^{12}$  to  $10^{13}$  photons per pulse implies ODs  $\approx 10$



Number of photons in the “dump” pulse

# Importance of Metals in Biological Systems

Holy Grail: Characterization of the Catalytic Pathways and Intermediates

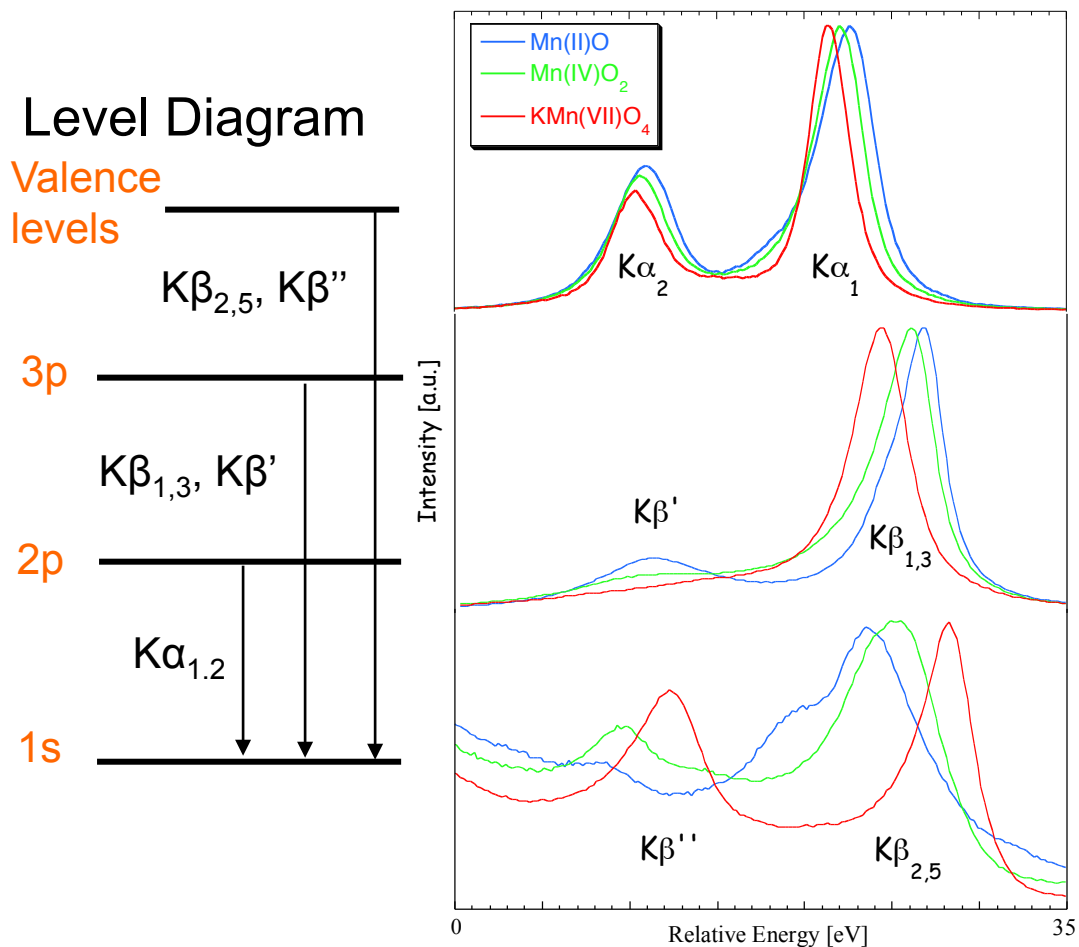


Respiration  
Photosynthesis  
Nitrogen fixation  
RNA synthesis, Detoxification...

Catalyze thermodynamically demanding reactions under physiological conditions with minimized driving force!

# X-Ray Spectroscopy of transition metals

X-ray emission reveals chemically relevant information



Spin/oxidation state of transition metals

Valence orbitals: ligand type, structure, covalency, ligand protonation, etc.

Bergmann et al.,  
*J. Synchr. Rad.* 8, 199 (2001)

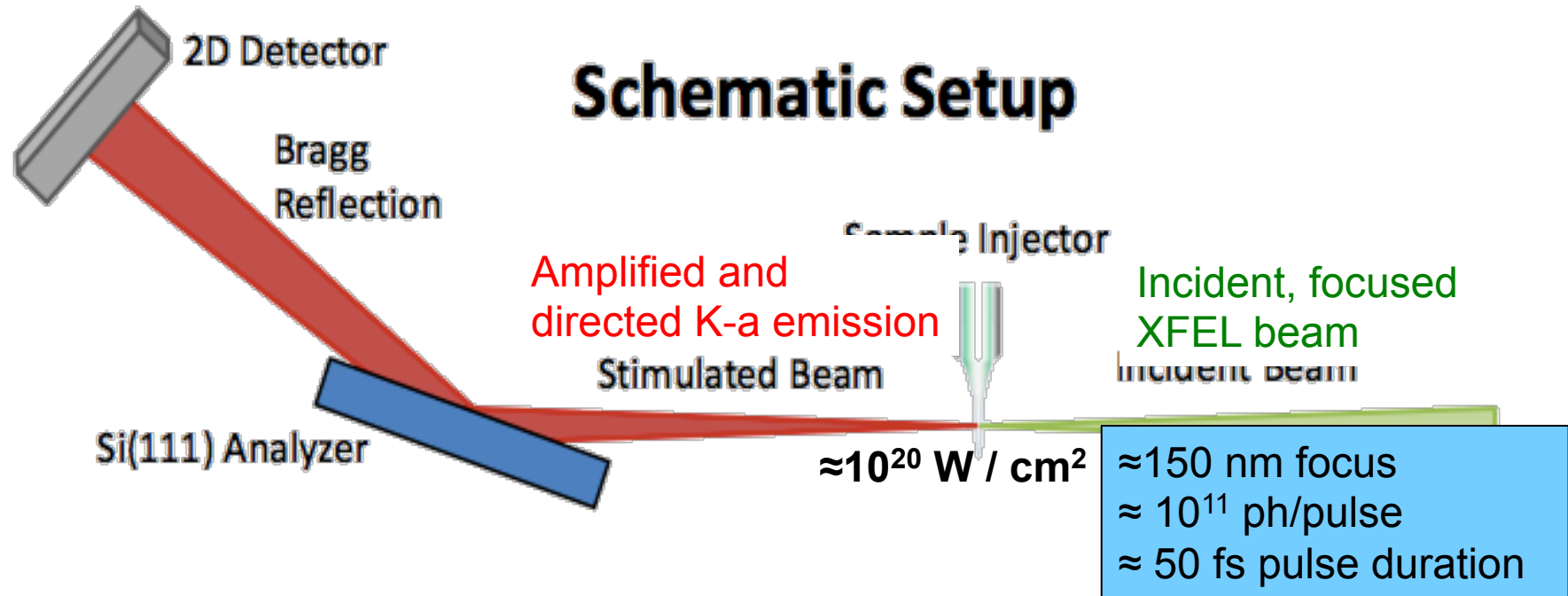
For reviews see: Glatzel & UB, *Coord. Chem. Rev.*, **249**, 65-95, (2005)

Pollock & DeBeer, *Accounts of Chemical Research* (2015)

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# K- $\alpha$ lasing of Mn-salt aqueous solutions

$10^{20}$  W/cm<sup>2</sup> on target creates population inversion on K- $\alpha$  transition



Samples: MnCl<sub>2</sub> solution (5 and 1 molar), KMnO<sub>4</sub> (0.4 molar)

Collect 100% of emission in forward direction

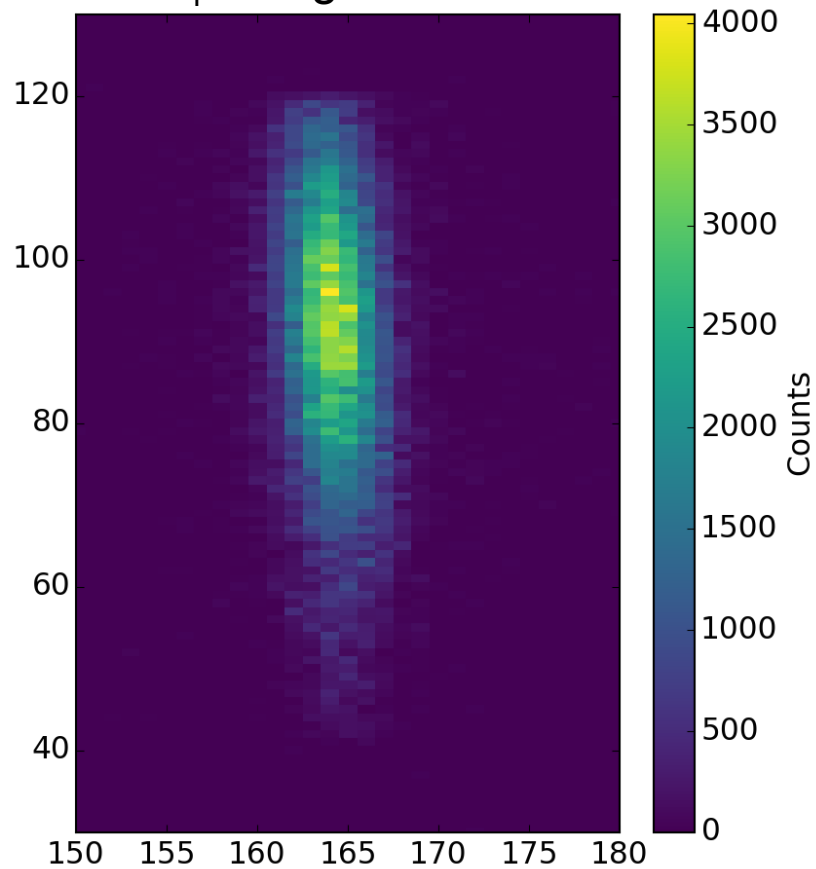
Use flat analyzer crystal – high efficiency

Experiment performed at CXI instrument, thanks to CXI team

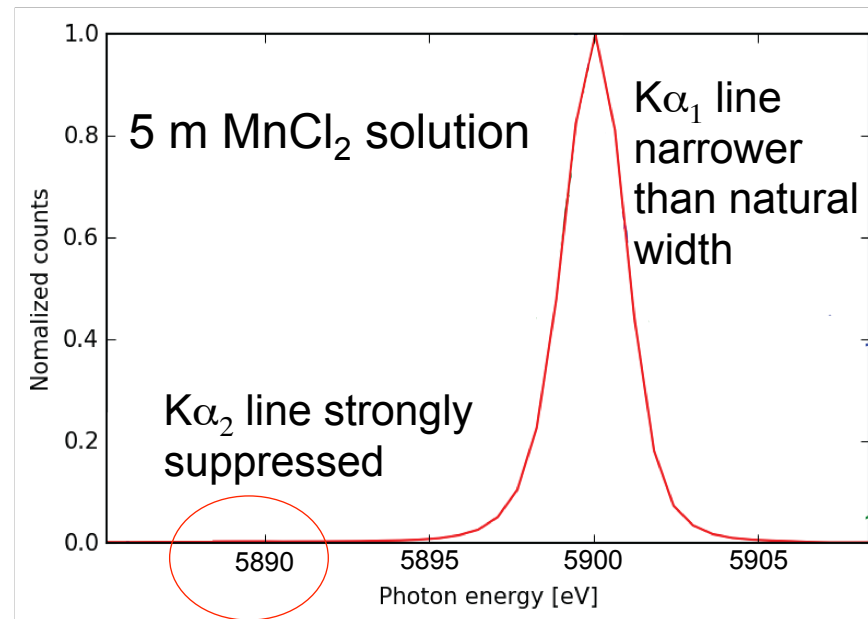
# Observation of strong lasing at 5.9 keV $K\alpha_1$

Strong gain up to  $10^6$  detected Mn  $K\alpha$  photons

Raw CCD image of the  $K\alpha_1$  lasing line



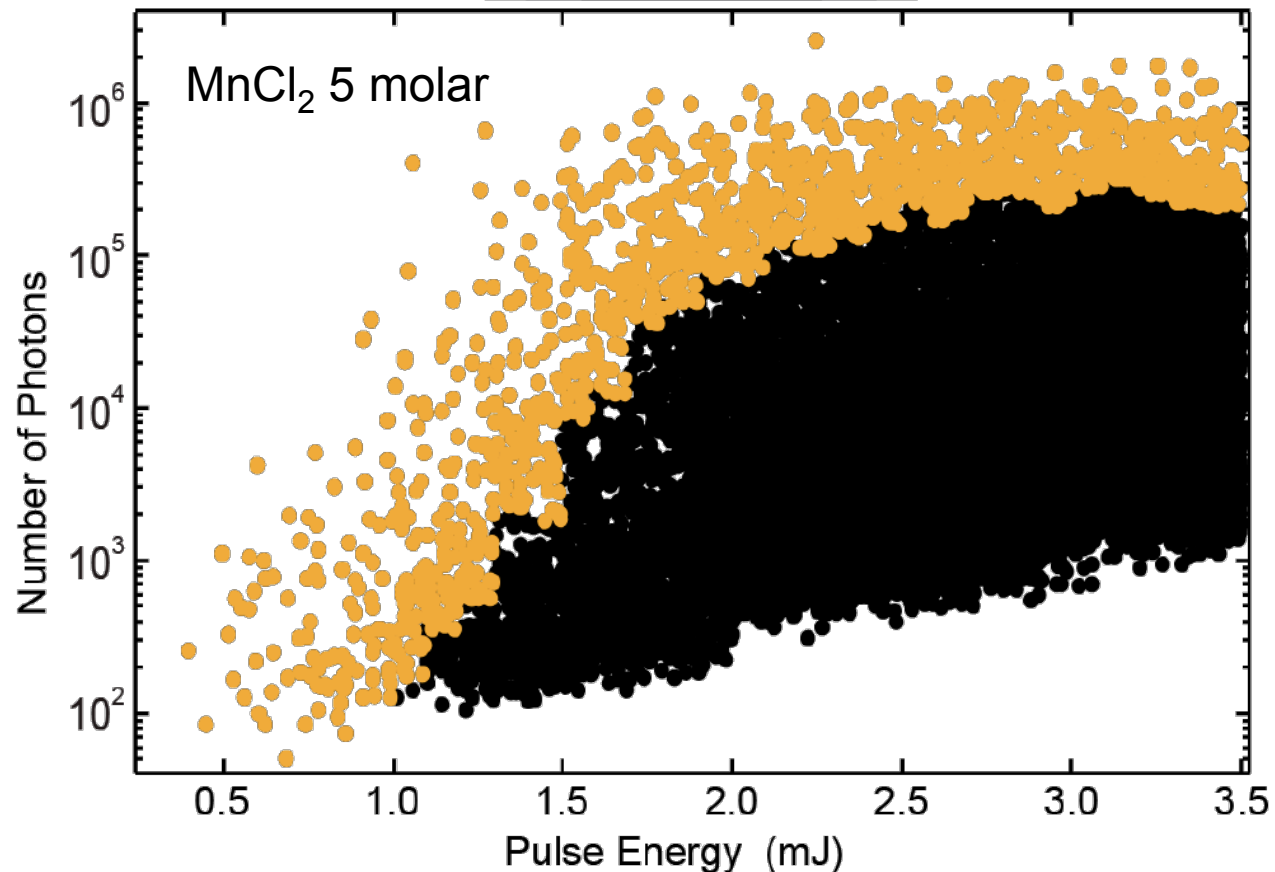
## Single shot spectrum



# Gain curve of Mn K- $\alpha_1$ emission

Exponential gain over 4 orders of magnitude reaching saturation

Single-shot emission yield as a function of incoming FEL-pulse energy

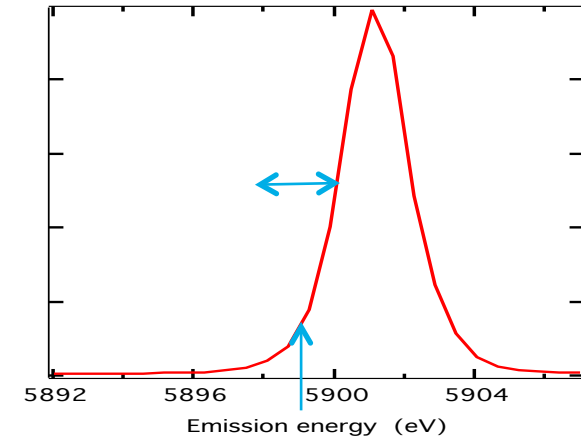
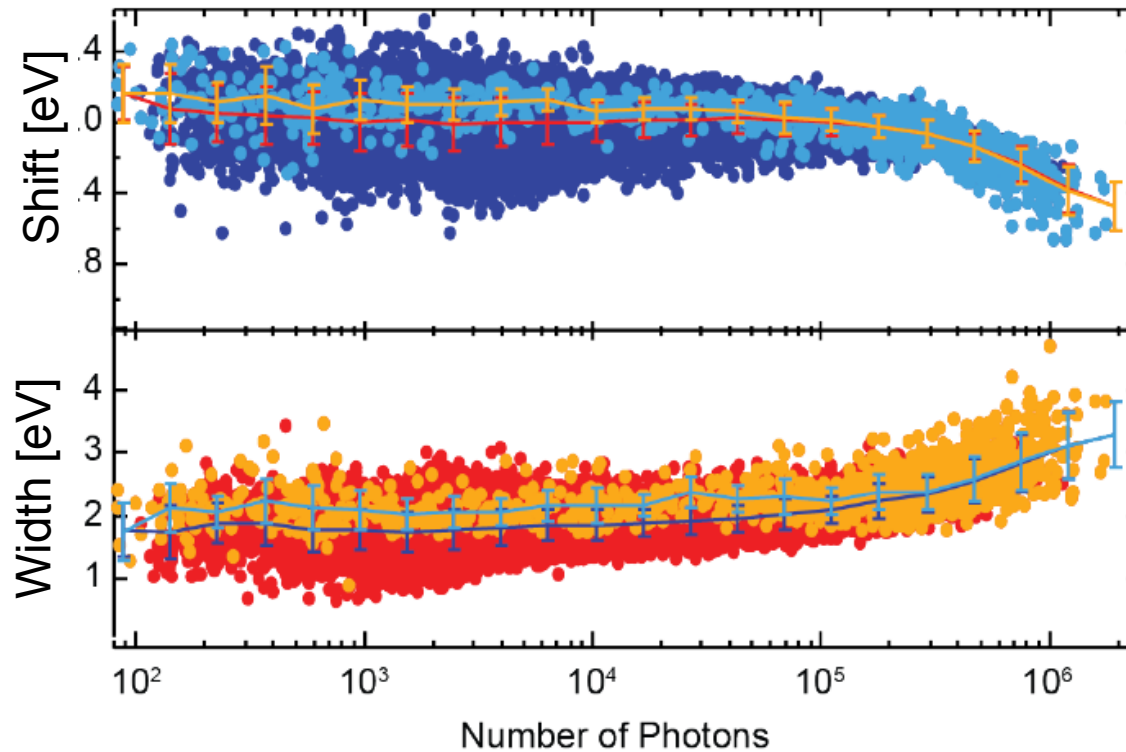


Extremely large shot-to-shot variation in the gain, (spatial jitter and temporal structure of FEL)

# Line-width dependence of the emission

Spectral analysis of K- $\alpha$  radiation over 4 orders of magnitude of amplification

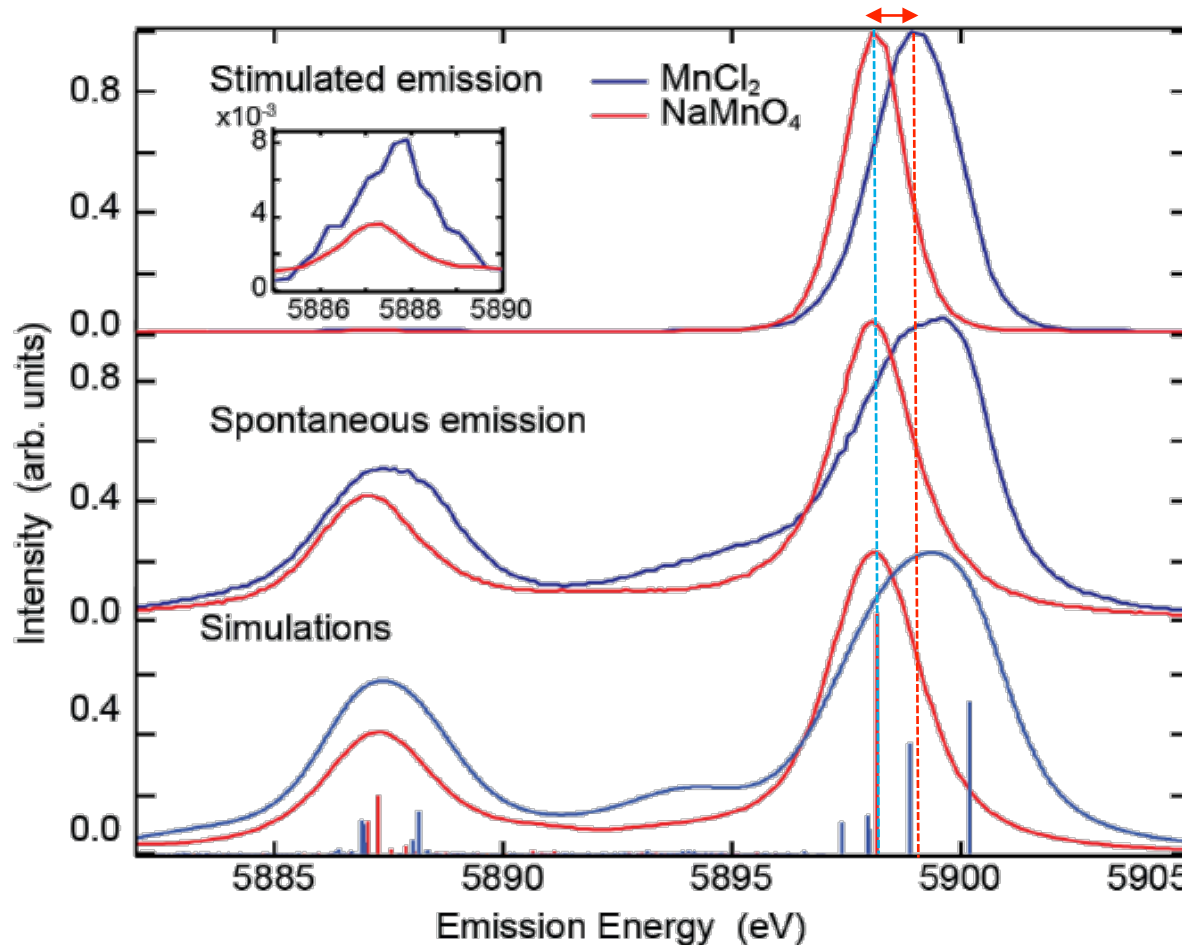
Peak position and width:



- Gain narrowing at the onset of amplification (ASE)
- Broadening of emission line in exponential amplification (Superfluorescence)
- At saturation: Rabi-Flopping induces broadening, shift to lower energies

# Spontaneous versus stimulated emission spectrum

Approaching chemically and biologically relevant samples



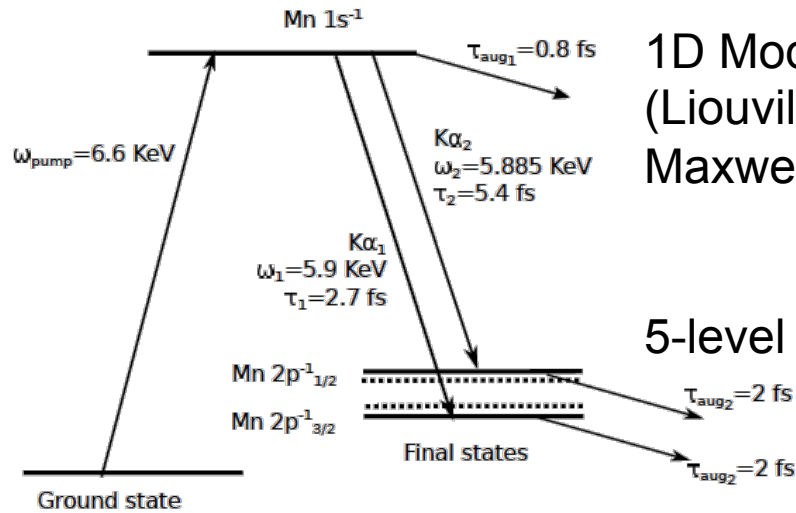
“Chemical shifts” differ in spontaneous and stimulated spectra

Sample spectra of Mn test compounds:

Mn(II)Cl<sub>2</sub> aqueous solution (5 and 1 molar), NaMn(VII)<sub>4</sub> (0.4 molar)

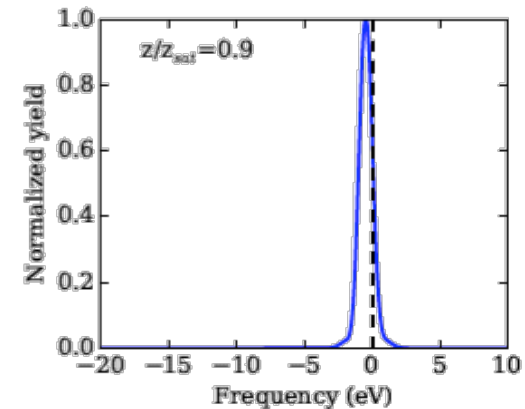
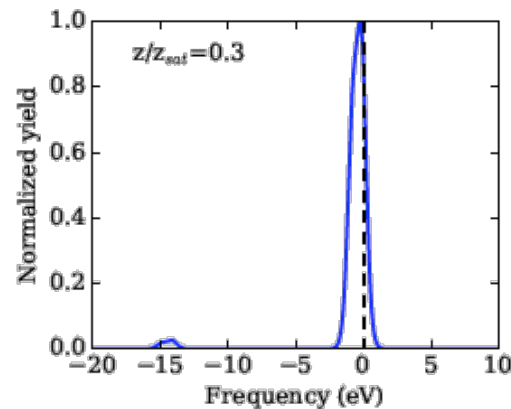
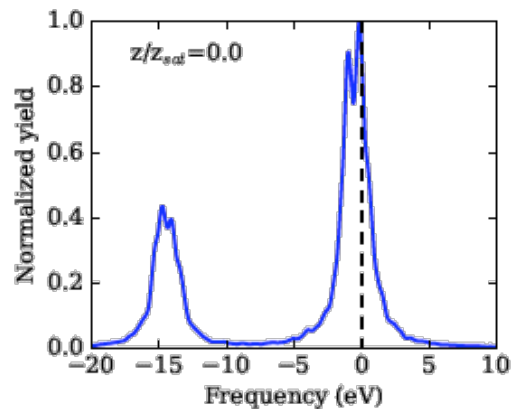
# Strong-field effects in the x-ray spectral domain

Emission energies shift – coupled + driven oscillators



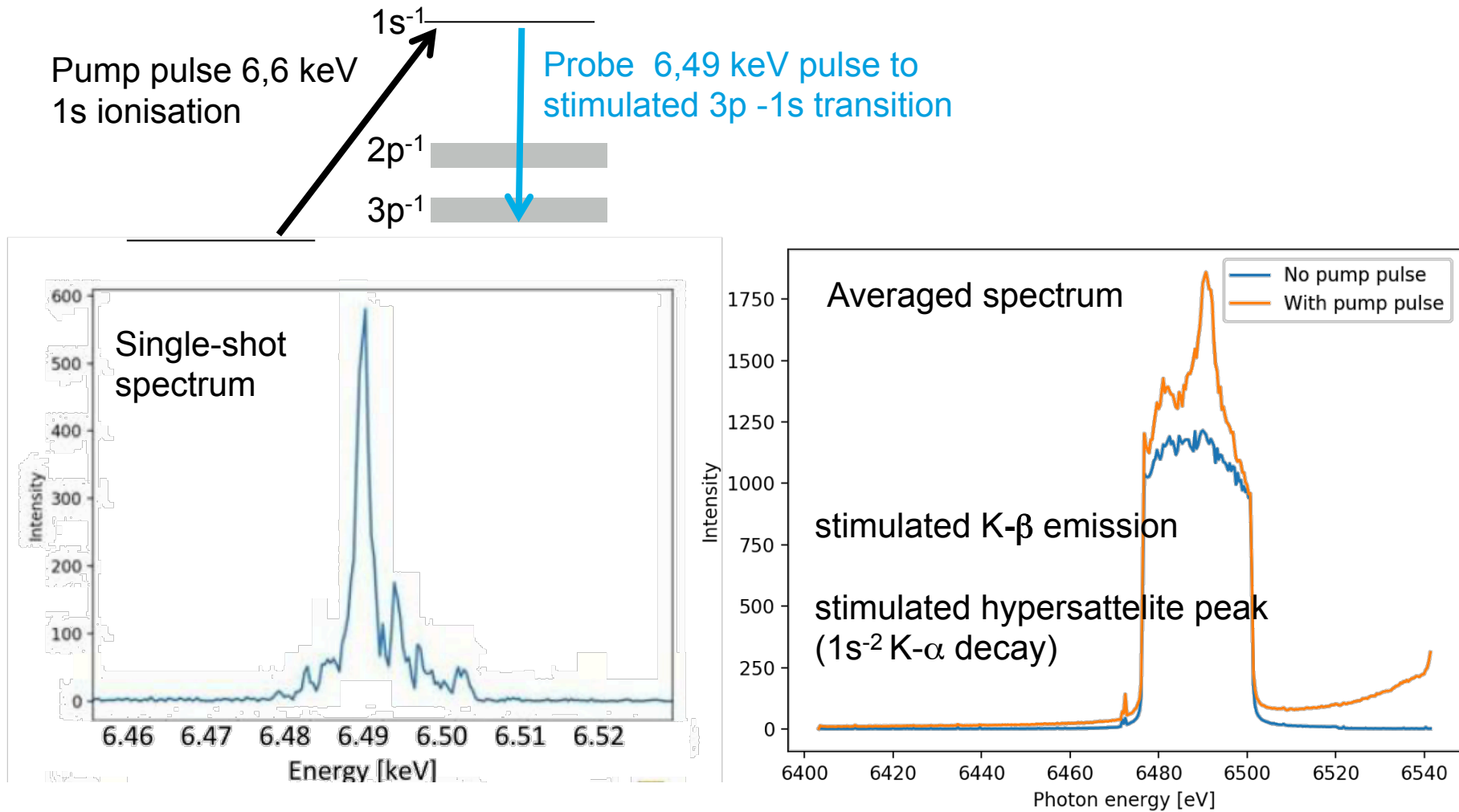
1D Model calculations  
(Liouville – von Neumann equ.  
Maxwell equ. in paraxial approx.)

5-level scheme



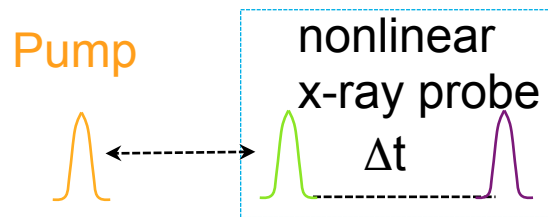
# 1<sup>st</sup> observation of stimulated K- $\beta$ emission

Towards valence to core stimulated hard x-ray emission spectroscopy



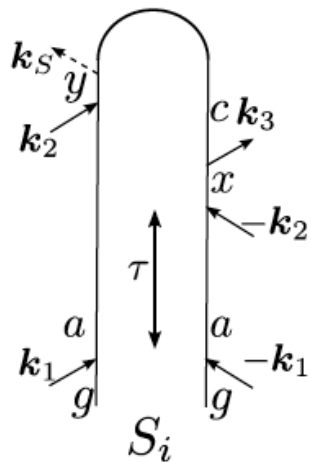
# Dedicated nonlinear spectroscopy beamline

Ideal parameters would be



## 2-colour pulses of

- 10-100s as to fs pulse duration
- (Reproducible) transform limited pulses, or controlled chirp
- Controllable delay from fs to ps, in fs to sub-fs steps



## Beam line that can adjust angle of incidence of x-ray pulses for

- wave-vector matching (choose different nonlinear diagrams)
- homodyne versus heterodyne, background free signal emission

## In the case that x-ray pulses are non reproducible:

- Measure spectrum of incoming and outgoing x-ray pulses