Stimulated X-Ray Emission and Nonlinear Spectroscopy at XFELs

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Workshop on Frontiers of Physical Sciences with X-ray FELs
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HELMHOLTZ ASSOCIATION

DESY

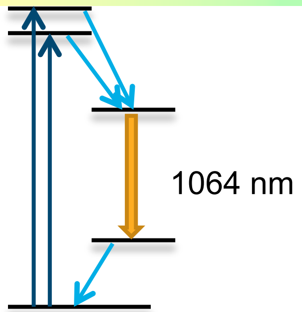
CFEL SCIENCE

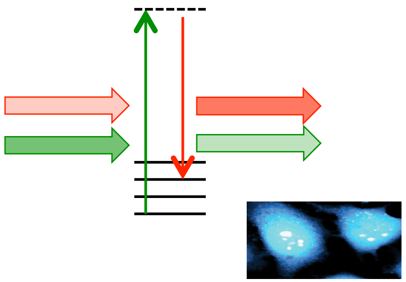
UH Universität Hamburg
DER FORSCHUNG | DER LEHRE | DER BILDUNG

Building blocks of nonlinear X-ray spectroscopy

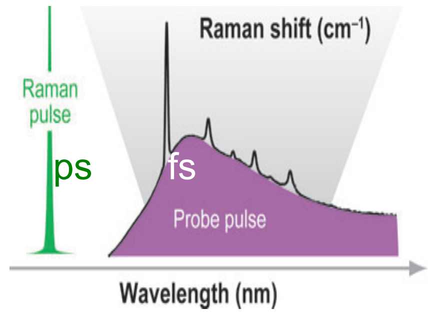
Transfer of nonlinear optical spectroscopies to the x-ray spectral domain

Optical Laser	Stimulated Raman scattering	Fs stimulated Raman spectroscopy



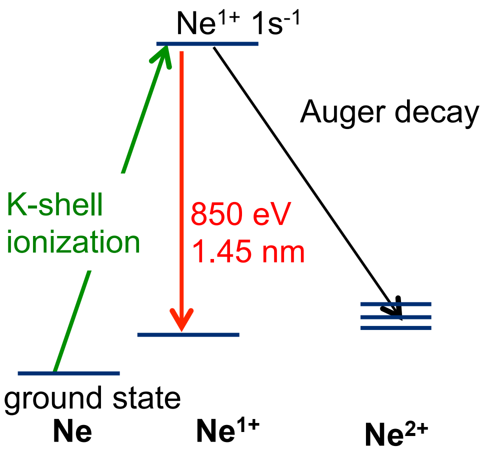


Background-free chemical imaging (microscopy)



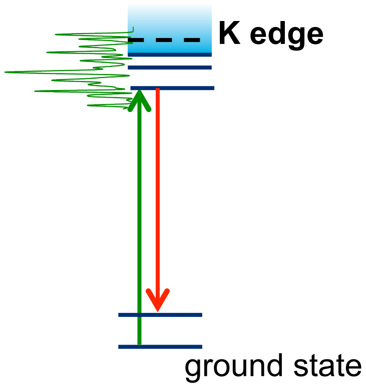
Grand challenge to transfer processes to the x-ray domain

Photoionization x-ray laser



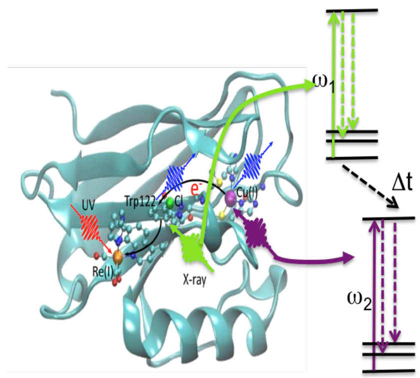
Realized in atomic gases, liquids (Mn salts), solids

Stimulated electronic x-ray Raman scattering (stimulated RIXS)



So far only in Neon

Stimulated electronic x-ray Raman pump-probe spectroscopy

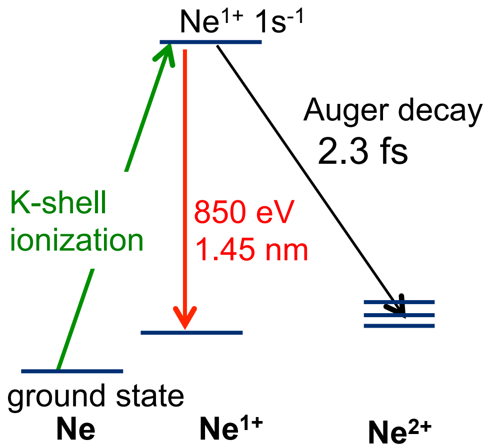


The future?

Amplified spontaneous x-ray emission

Photoionization K-α laser – from 1st demonstration to chemical analysis

Ne 849 eV (gas)

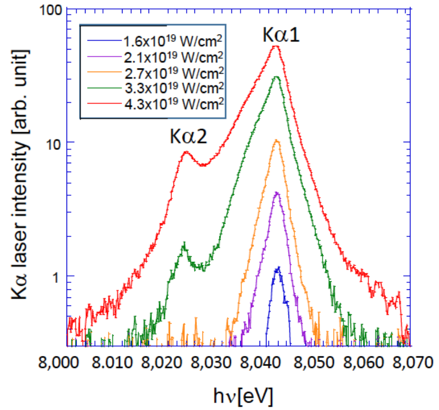


Rohringer et al.,
Nature **481**, 488 (2012).

Scheme first proposed by Duguay and Rentzepis, Appl. Phys. Lett. 10, 350 (1967).

Emission in forward direction, up to e^{21} amplification of spontaneous K-α emission

Cu 8,04 keV (solid)

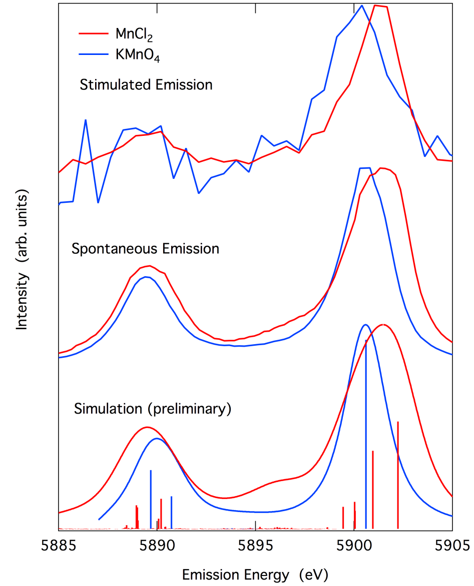


Yoneda et al.,
Nature **524**, 446 (2015).

Hard x-ray laser, seeded by 2-color FEL operation

Si L lines 70-100 eV (solid)
M. Beye et al.,
Nature **501**, 191 (2013)

Mn 5,9 keV (liquid)



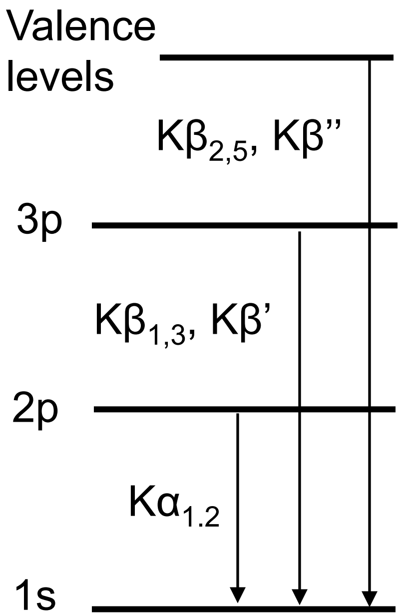
Kroll, et int., Rohringer, Bergmann,
Phys. Rev. Lett. **120**, 133203 (2018).

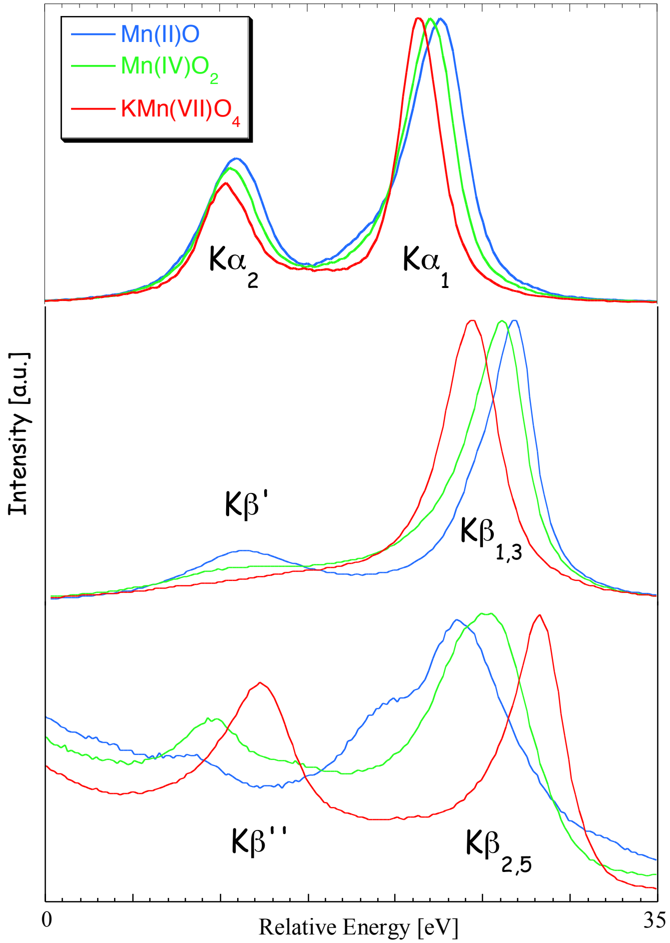
Stimulated X-Ray Emission Spectroscopy in Transition Metal Complexes

X-Ray Spectroscopy of transition metals

X-ray emission reveals chemically relevant information

Level Diagram





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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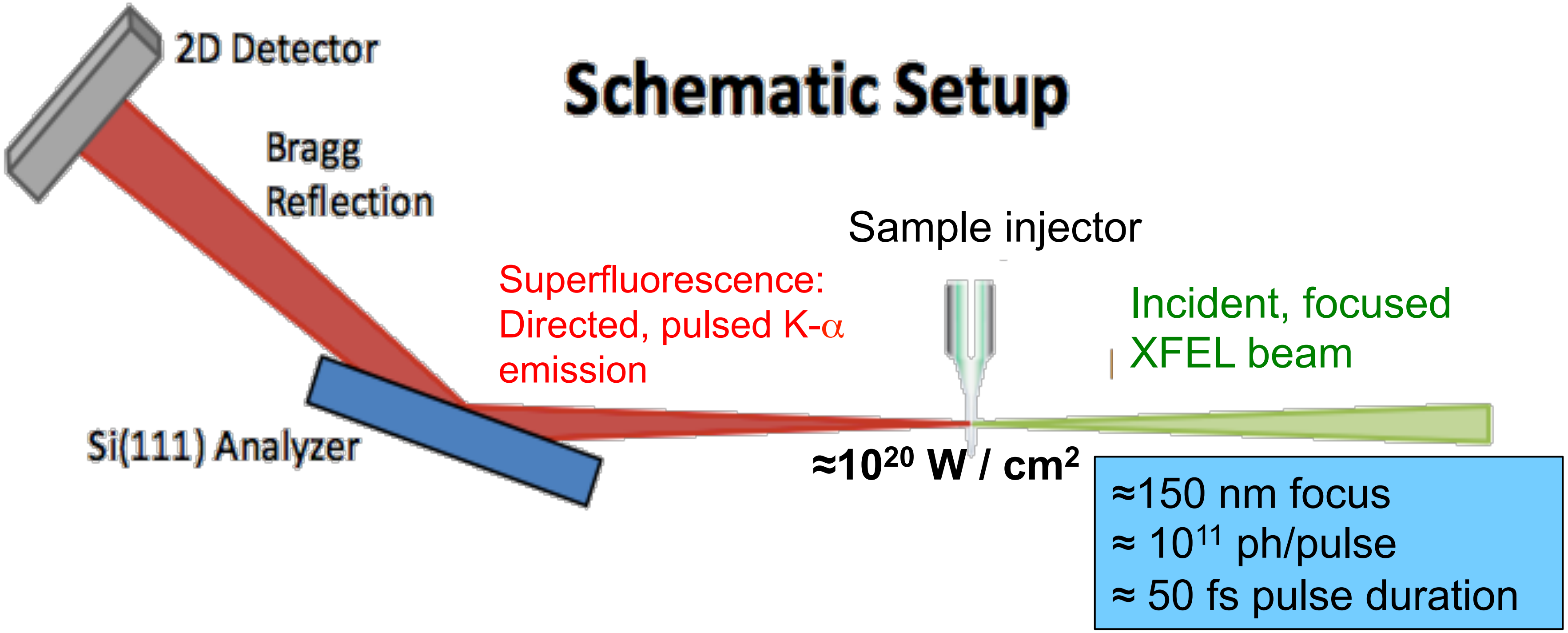
K-α lasing of Mn-salt aqueous solutions

10^{20} W/cm² on target creates population inversion on K-α transition



Samples: $MnCl_2$ solution (5 and 1 molar), $KMnO_4$ (0.4 molar)

Collect 100% of emission in forward direction

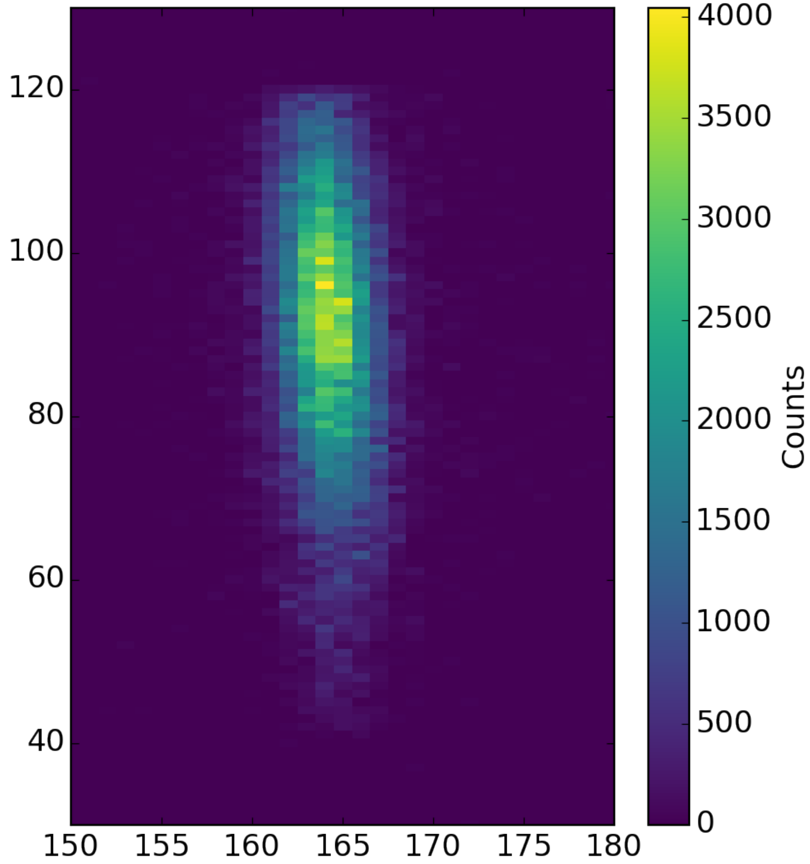
Use flat analyzer crystal – high efficiency

Experiment performed at CXI instrument, thanks to CXI team

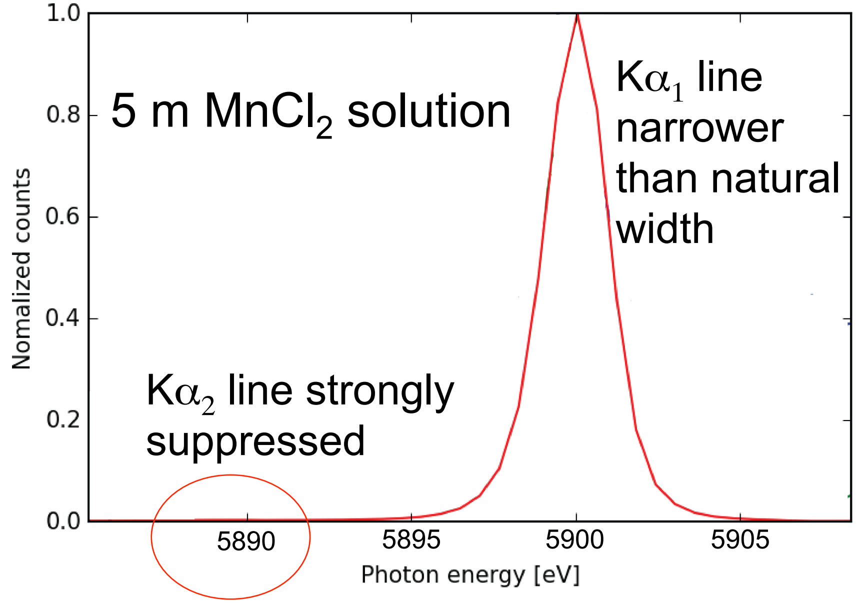
Observation of strong lasing at 5.9 keV Kα_1

Strong gain up to 10^6 detected Mn Kα photons

Raw CCD image of the Kα_1 lasing line



Single shot spectrum

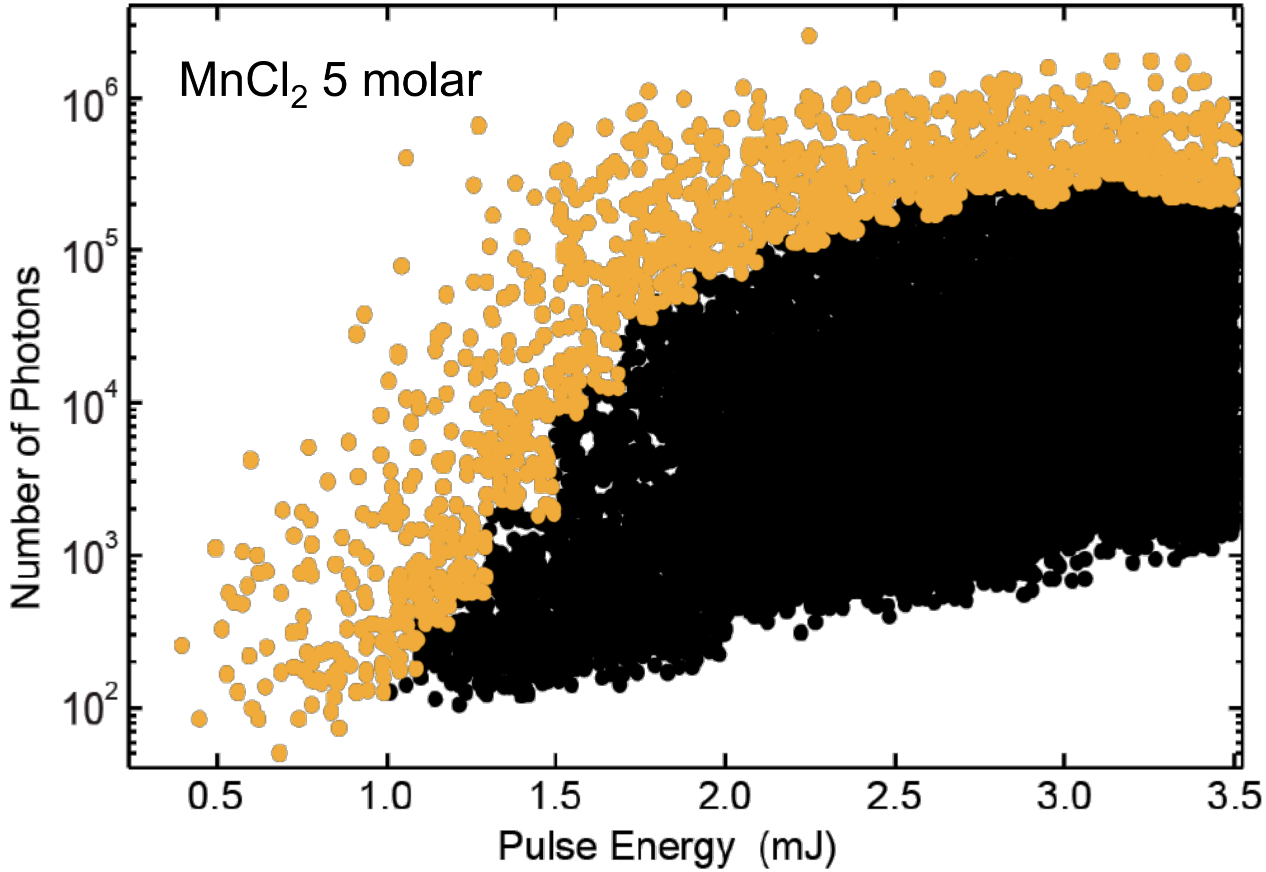


Kroll et al., *Phys. Rev. Lett.* **120**, 133203 (2018).

Gain curve of Mn K-α_1 emission

Exponential gain over 4 orders of magnitude reaching saturation

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

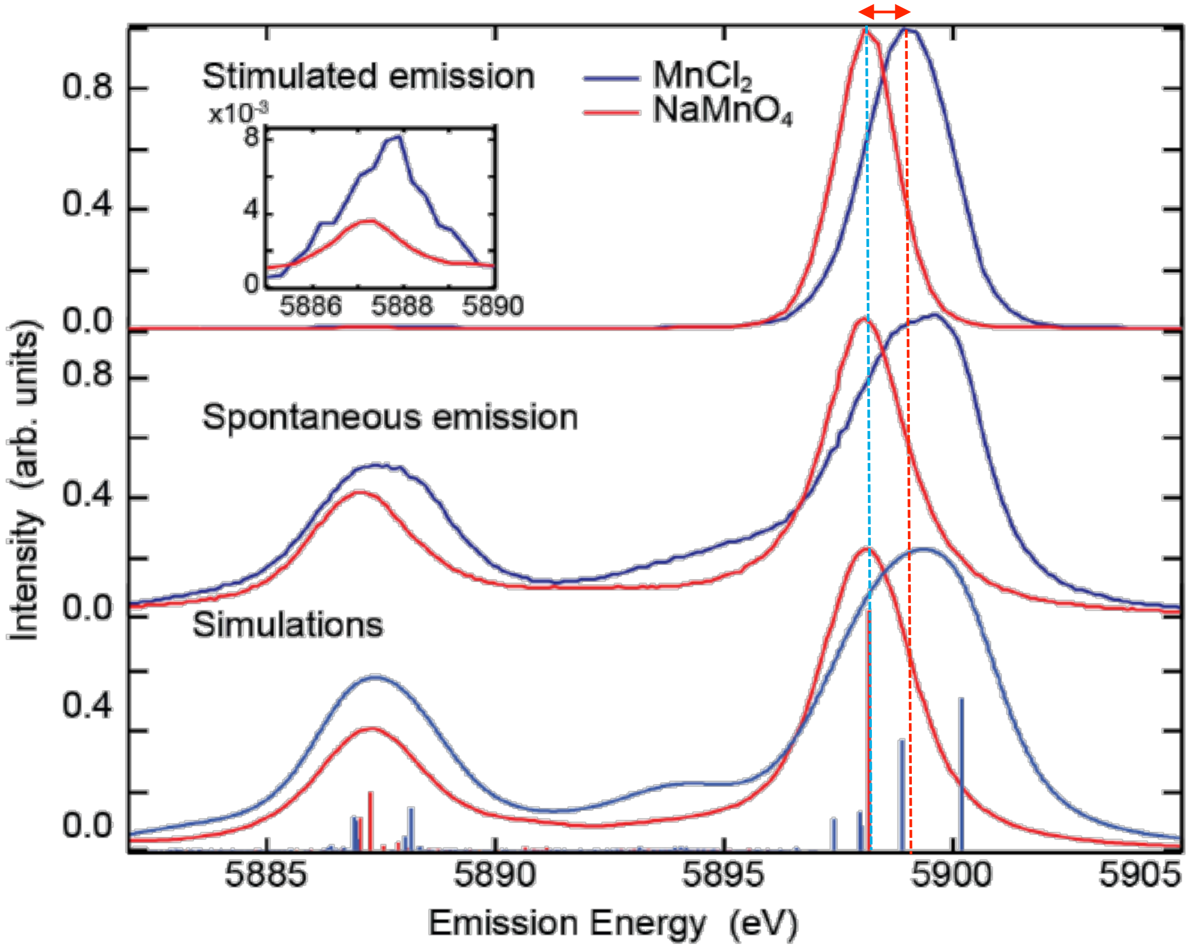


Extremely large shot-to-shot variation in the gain, (spatial jitter and temporal structure of FEL)

Kroll et al., *Phys. Rev. Lett.* **120**, 133203 (2018).

Spontaneous versus stimulated emission spectrum

Approaching chemically and biologically relevant samples



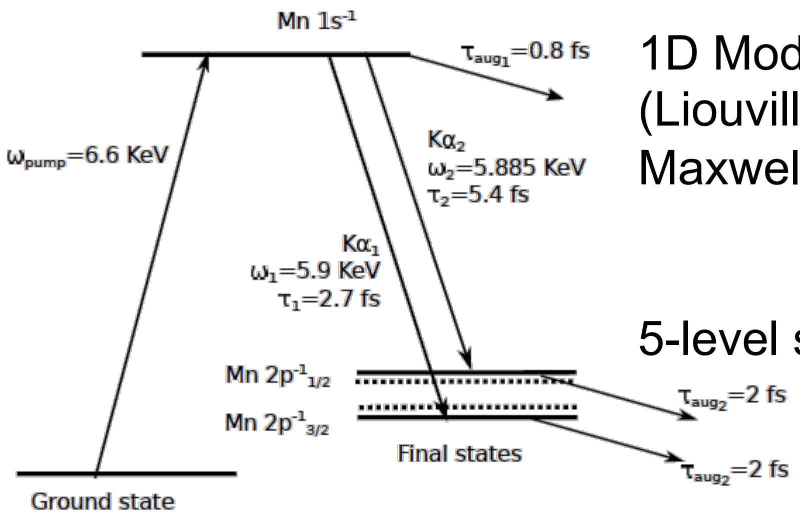
Sample spectra of Mn test compounds:
$Mn(II)Cl_2$ aqueous solution (5 and 1 molar), $NaMn(VII)_4$ (0.4 molar)

"Chemical shifts" differ in spontaneous and stimulated spectra

Kroll et al., *Phys. Rev. Lett.* **120**, 133203 (2018).

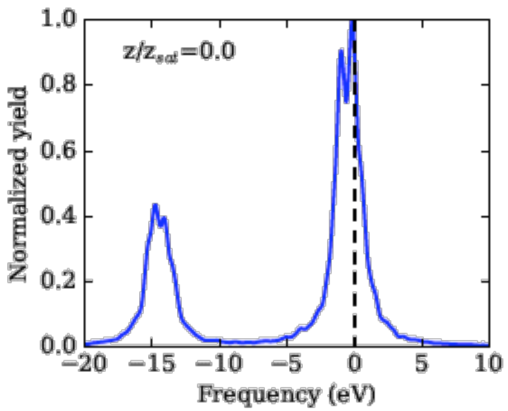
Strong-field effects in the x-ray spectral domain

Emission energies shift – coupled + driven oscillators

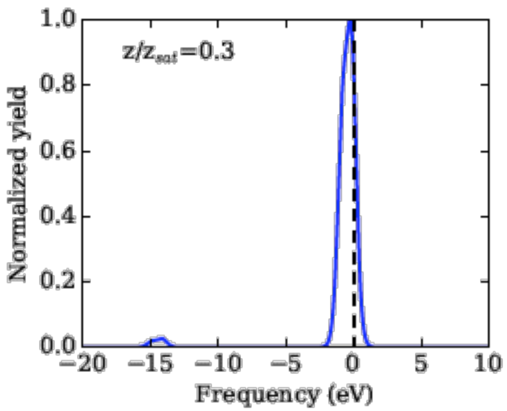


1D Model calculations (Liouville – von Neumann equ. Maxwell equ. in paraxial approx.)

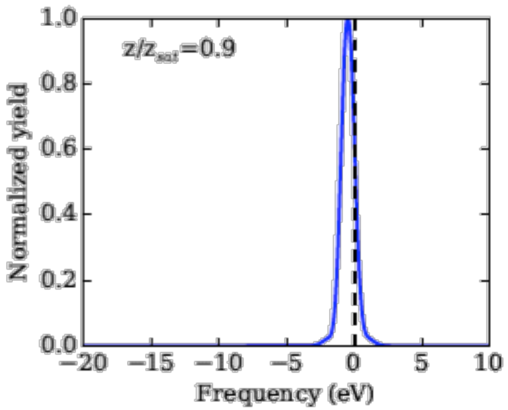
5-level scheme



Single-atom, “spontaneous” spectrum



Spectrum in “linear” gain region

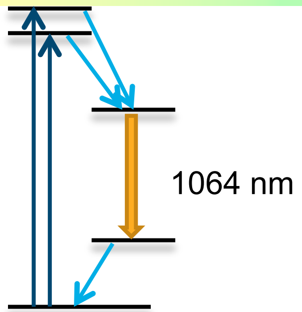


Gain-saturated spectrum

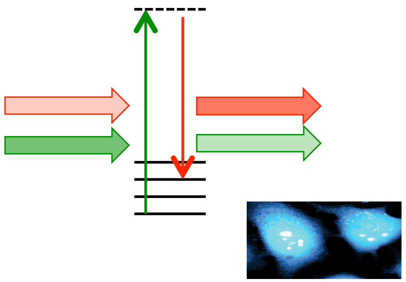
Building blocks of nonlinear X-ray spectroscopy

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

Optical Laser

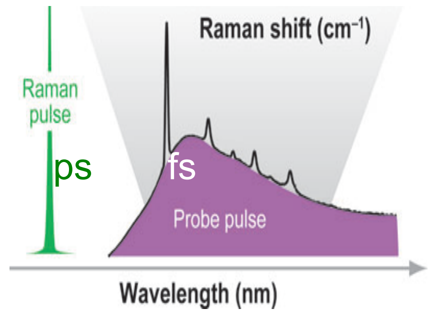


Stimulated Raman scattering



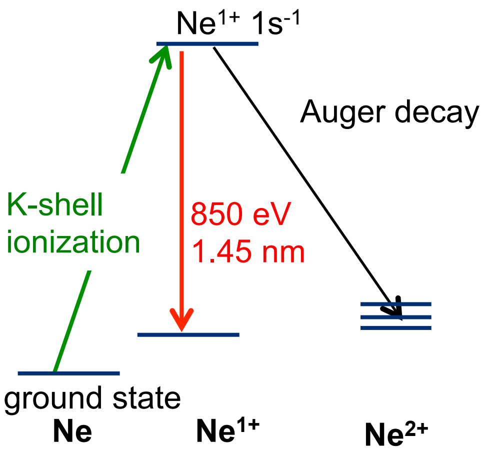
Background-free chemical imaging (microscopy)

Fs stimulated Raman spectroscopy



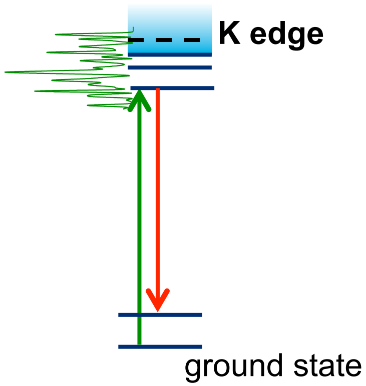
Grand challenge to transfer processes to the x-ray domain

Photoionization x-ray laser



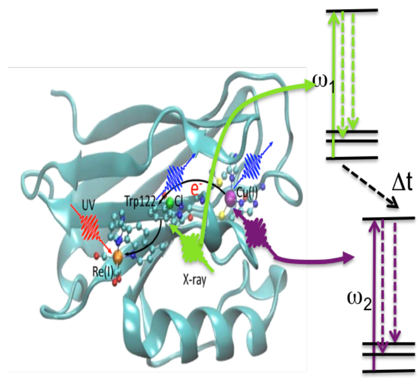
Realized in atomic gases, liquids (Mn salts), solids

Stimulated electronic x-ray Raman scattering (stimulated RIXS)



So far only in Neon

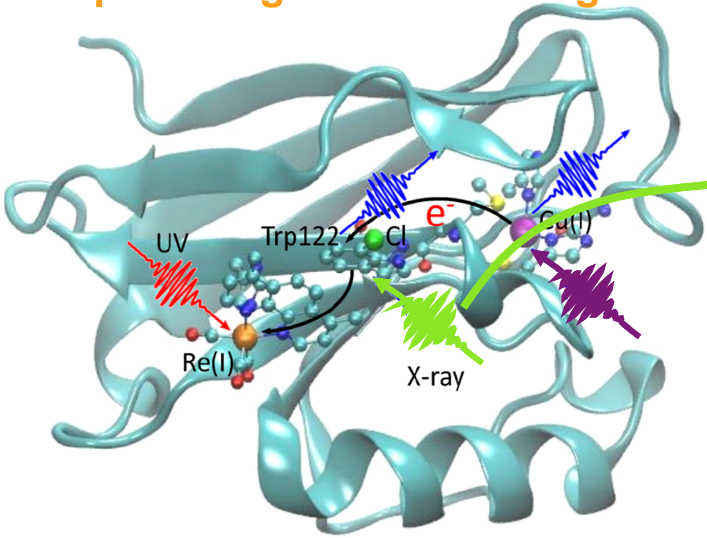
Stimulated electronic x-ray Raman pump-probe spectroscopy

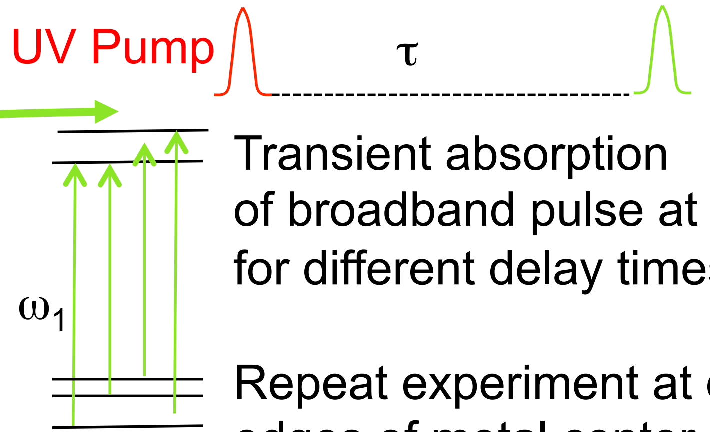


The future?

Linear x-ray spectroscopy - transient fs absorption

Example: Long-distance charge transfer in molecular complexes

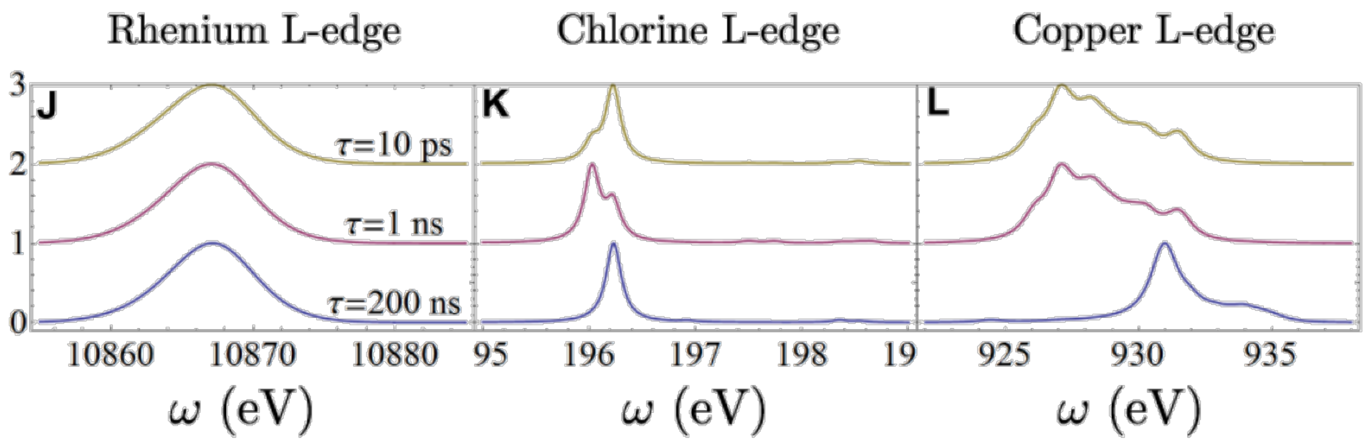




Transient absorption of broadband pulse at for different delay times

Repeat experiment at different edges of metal center

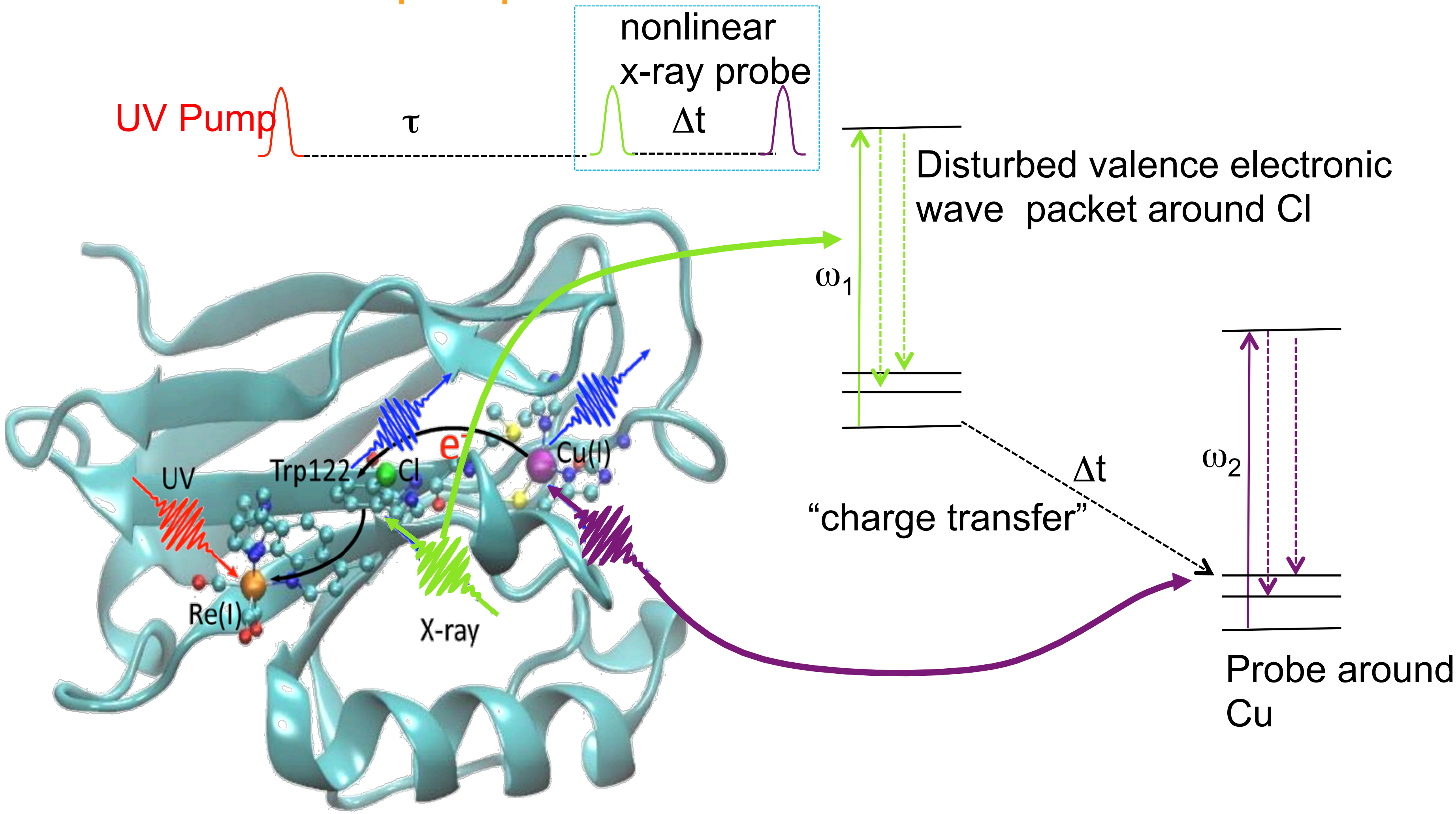
Simulated transient absorption spectra:



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

Stimulated electronic X-ray Raman spectroscopy

A coherent nonlinear probe process

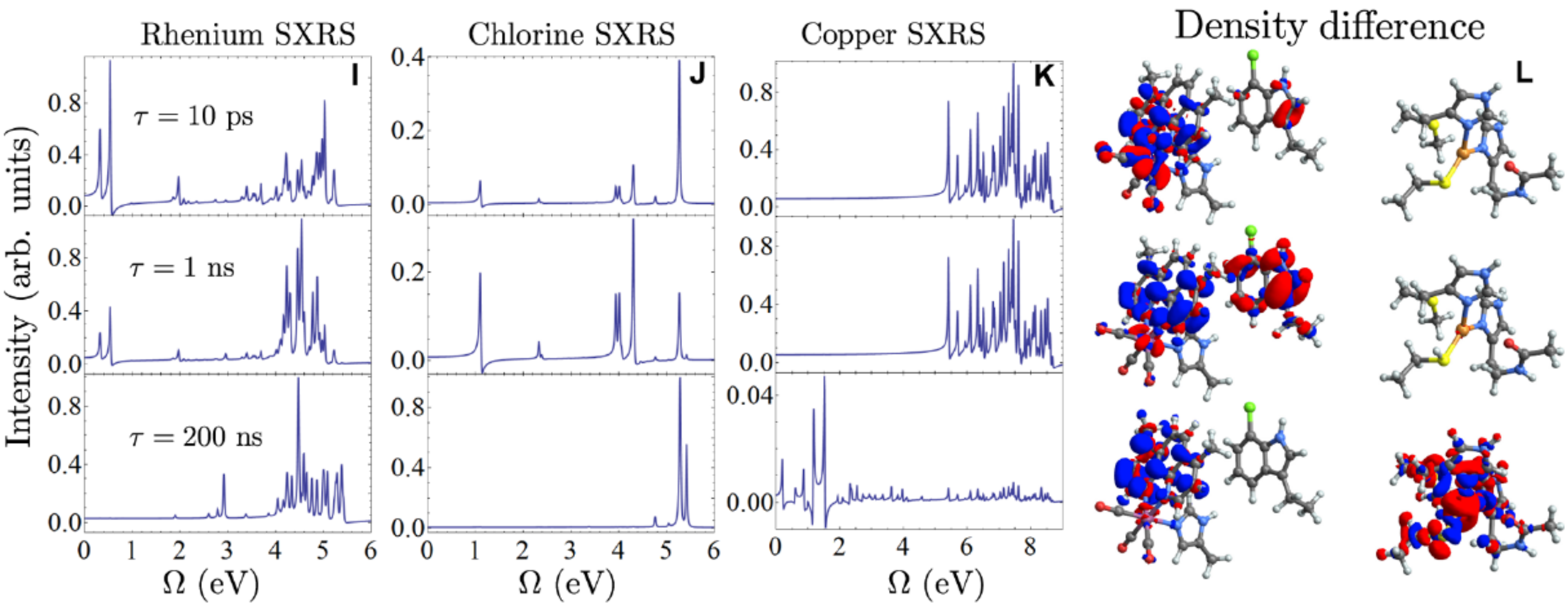


Shaul Mukamel et al. (PRL 89, 043001 (2002), PRB 72, 235110 (2005); PRA 76, 012504 (2007); PRB 79, 085108 (2009)

Simulated 1D Stimulated x-ray Raman spectra

τ…. Change pump-probe delay: on the 10 ps to 100 ns time scale
Δt…. Sampling time-delay: Δt varied up to 100 fs, in steps of 0.2 fs

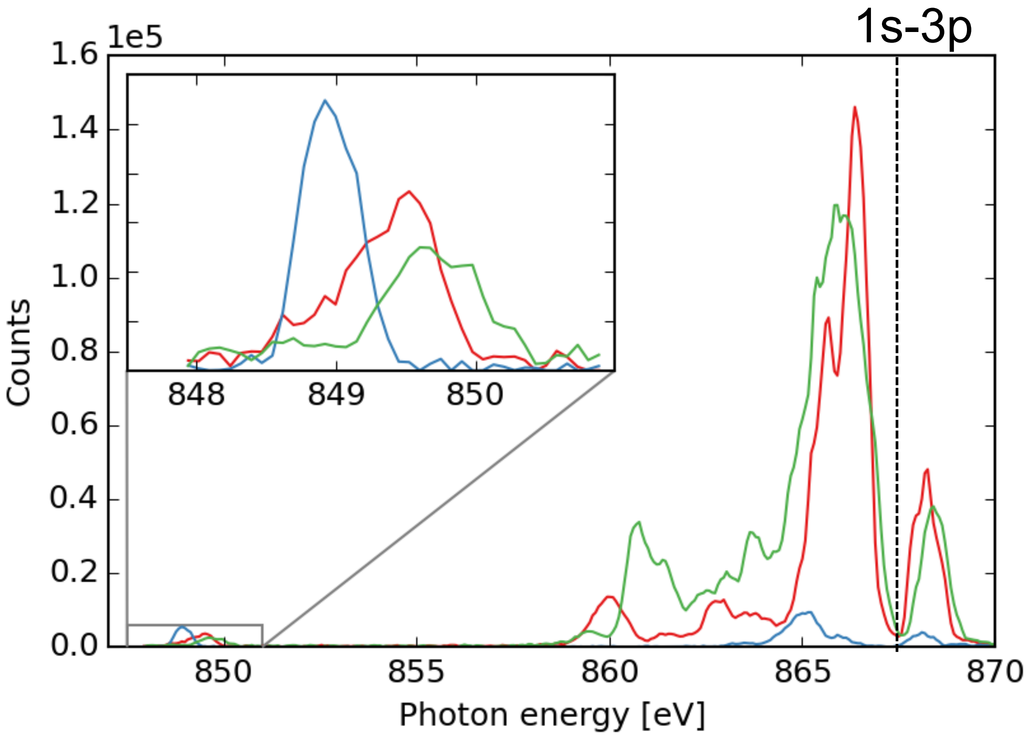
- Measure absorption of probe pulse (2nd x-ray pulse) does not need to be frequency resolved
- Take Fourier Transform with respect to Δt of total absorption
- Repeat for second x-ray pulse tuned to different edges (local metal centers)

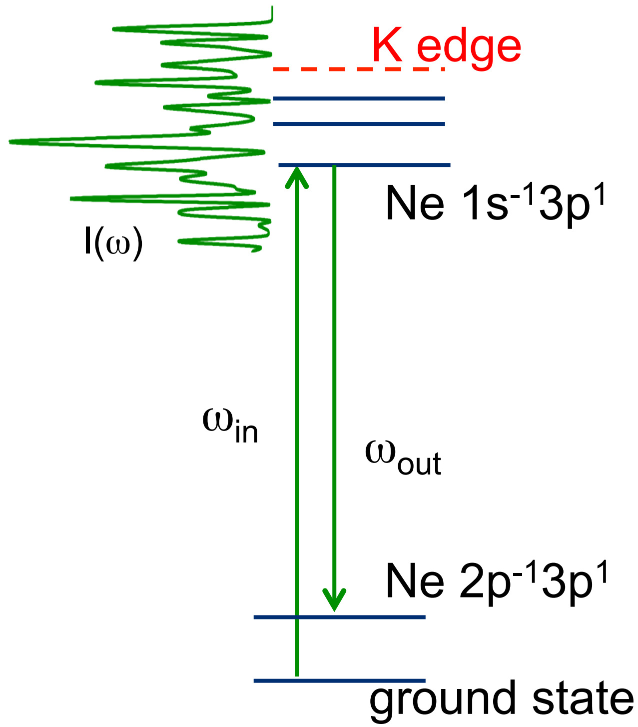


Y. Zhang et al., Phys. Chem. Lett. 5, 3656 (2014).

Stimulated resonant electronic x-ray Raman scattering in Neon

2 experimental demonstrations in Aug. 2012 and Feb. 2014



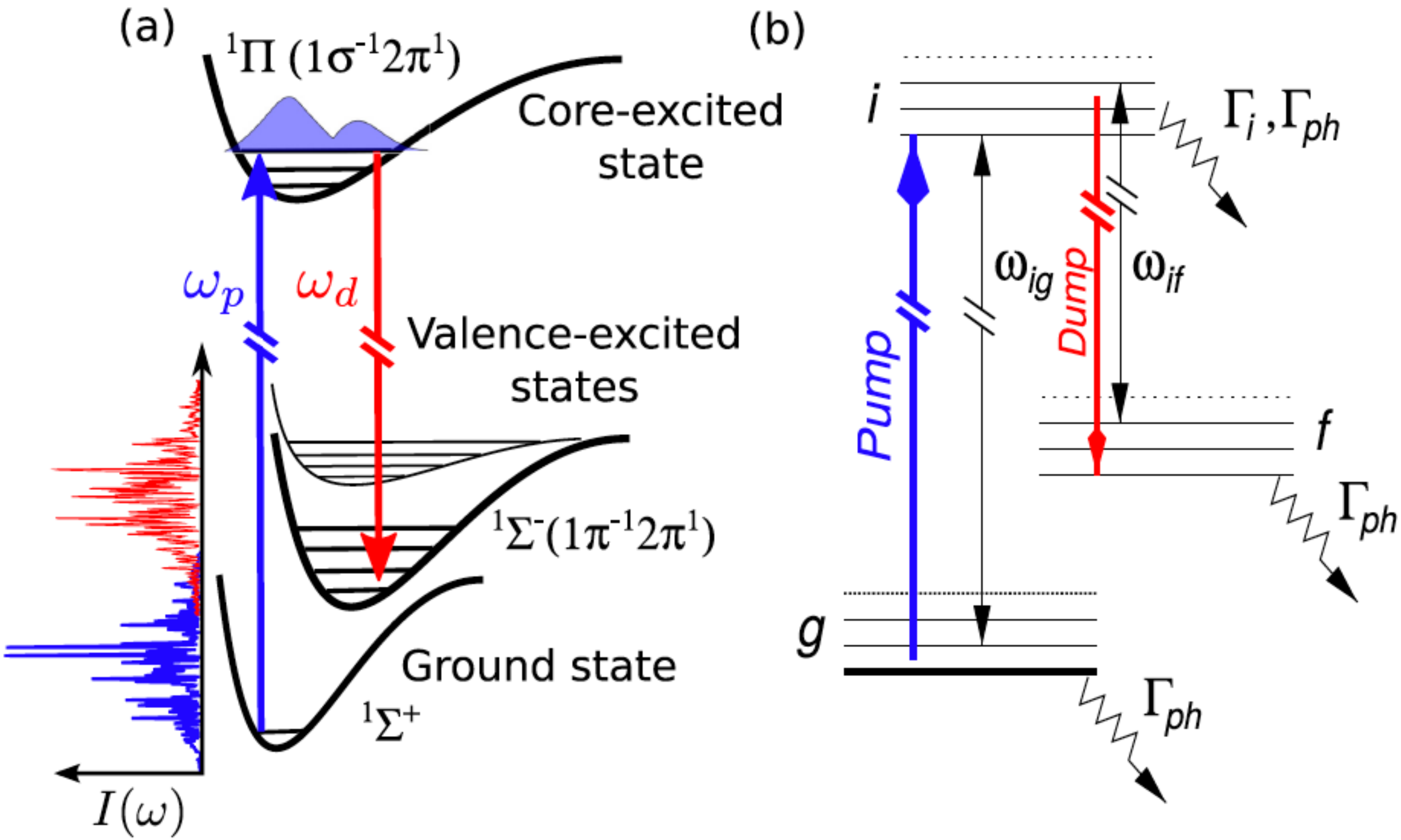


Spectral tail of SASE provides seeds photons
6 orders of magnitude of amplification (Raman gain)

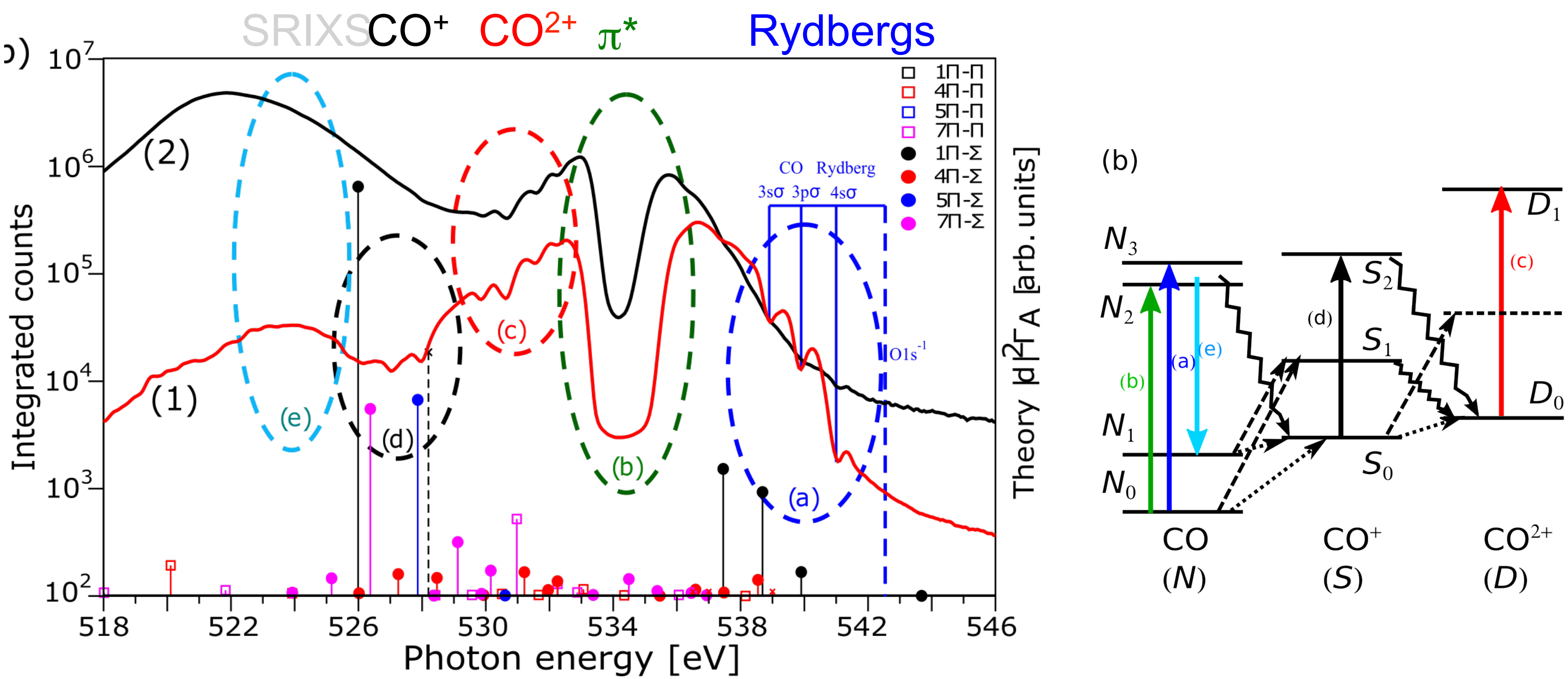
C. Weninger, N.R. et al., Phys. Rev. Lett. **111**, 233902 (2013)

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

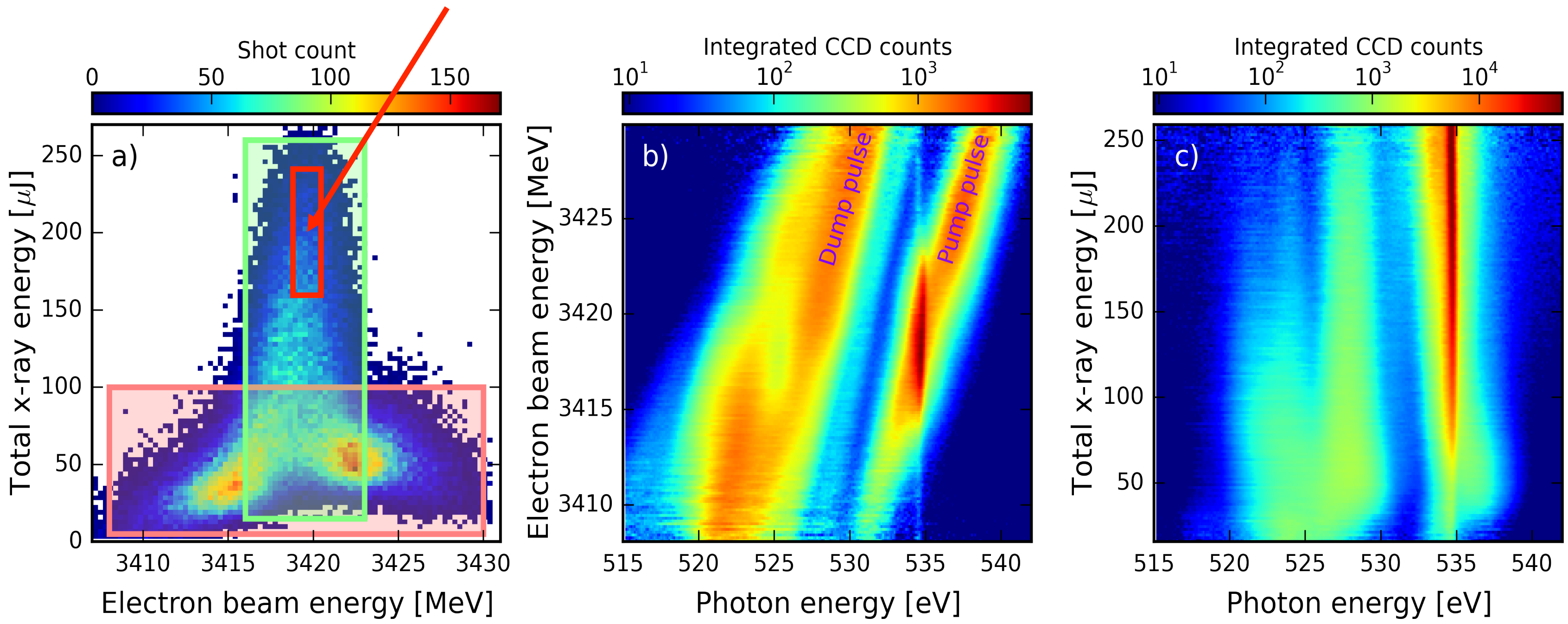
Similar changes of absorption spectrum due to sequential ionisation observed in water droplets (S. Schreck et al., *Phys. Rev. Lett.*, 2014, **113**, 153002.)

Kimberg et al., Faraday Discuss. **194**, 305 (2016). , DOI: 10.1039/C6FD00103C

Soft x-ray self-seeding mode to pump on the O π* resonance

X-ray energy / Electron-beam energy distribution to sort spectra

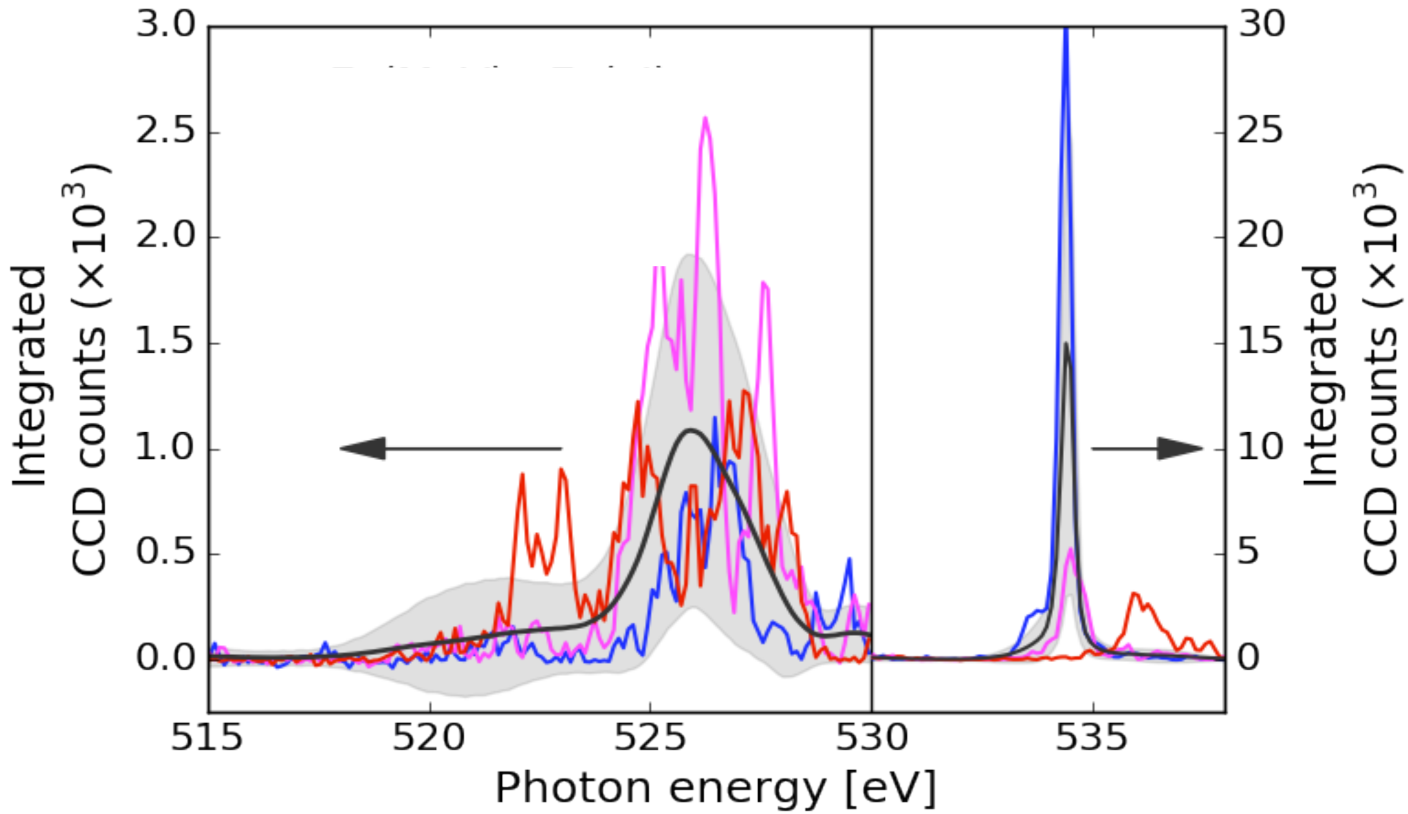
“Best region”, but low number of spectra…..



Kimberg et al., Faraday Discuss. **194**, 305 (2016). , DOI: 10.1039/C6FD00103C

Soft x-ray self-seeding mode to pump on the O π* resonance

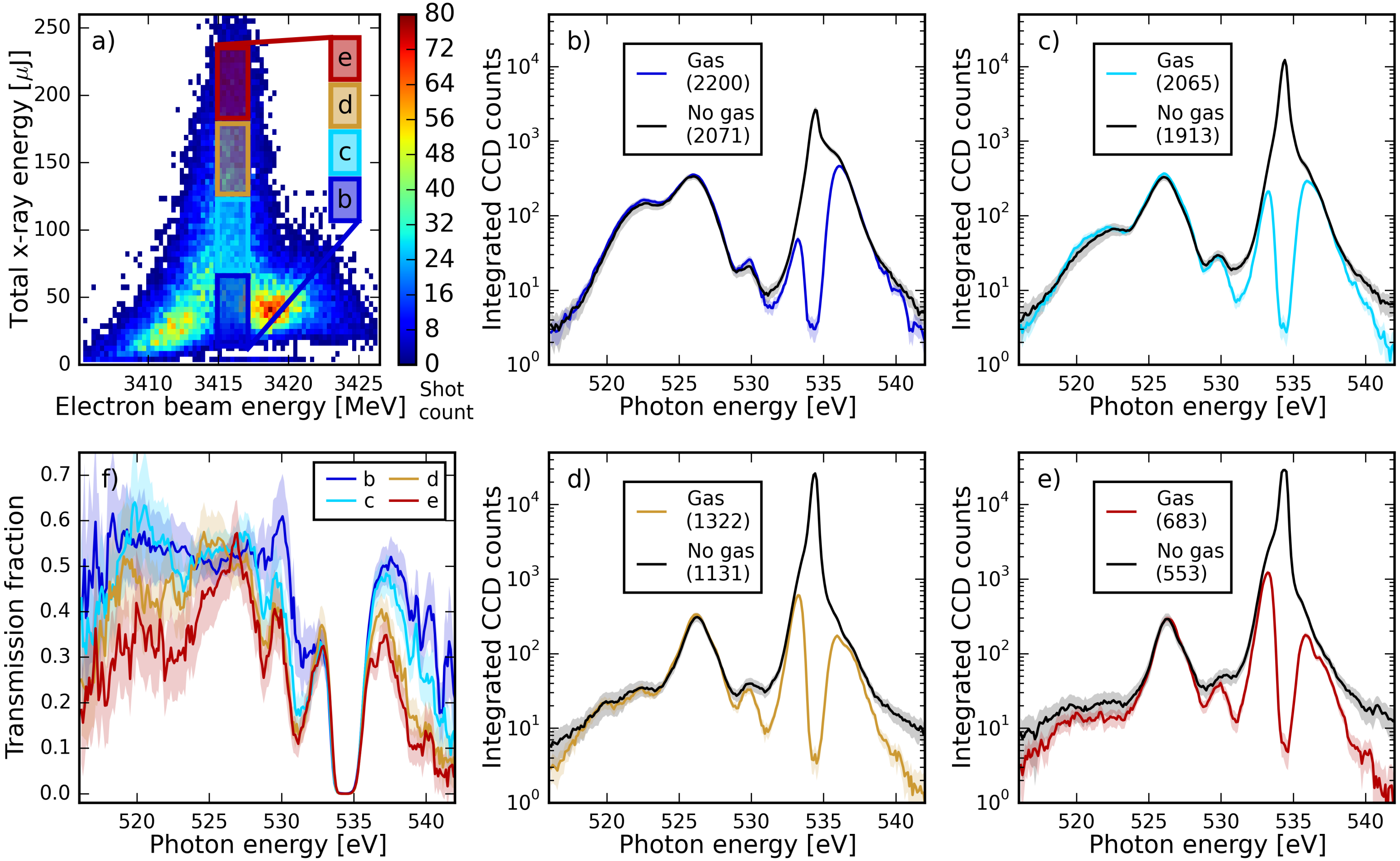
Self-seeded pulses are far from transform limit and shot-to-shot stability



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

Kimberg et al., Faraday Discuss. **194**, 305 (2016). , DOI: 10.1039/C6FD00103C

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



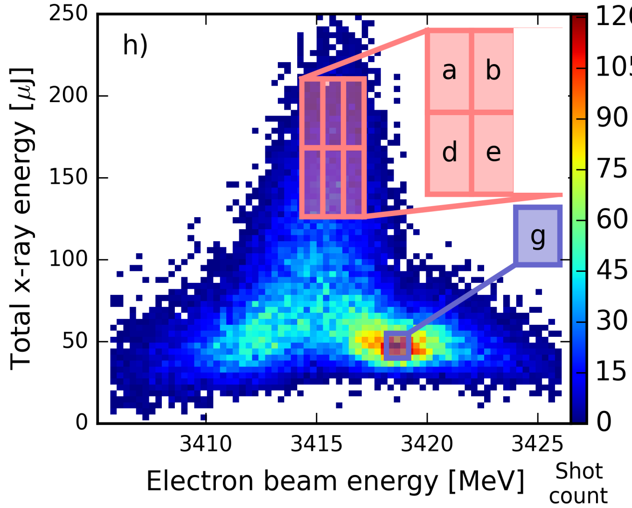
Absorption of transiently created ions visible in spectra!
No evidence for Stimulated Raman scattering

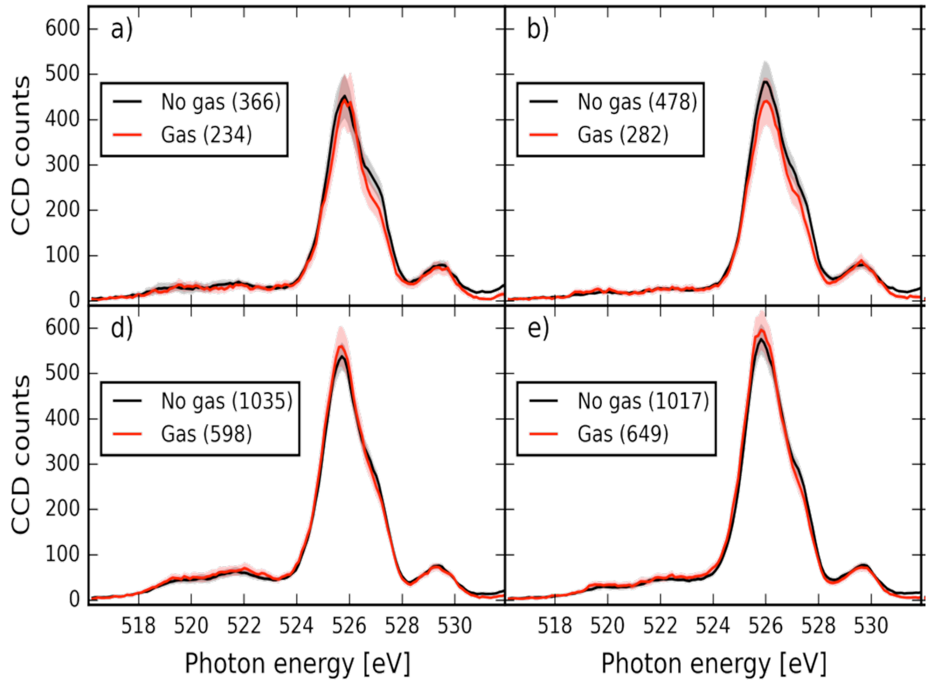
Gas pressure at 100 mbar

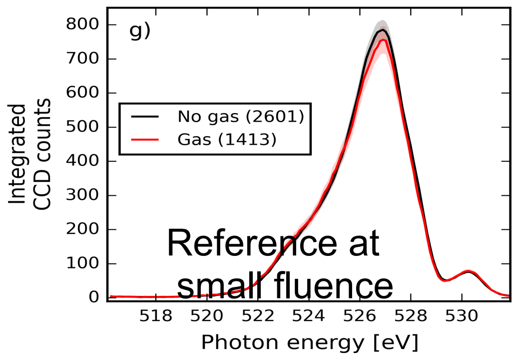
Kimberg et al., Faraday Discuss. **194**, 305 (2016). , DOI: 10.1039/C6FD00103C

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 !!!

Theory: **10^{11} photons in 35 fs, 6 μm**: Raman gain of 0.5

Conditions at experiment: $2\cdot 10^{8}$ photons/μm²/fs/eV (for 0.5 eV self-seeded pulses of 35 fs)

Kimberg et al., Faraday Discuss. **194**, 305 (2016). , DOI: 10.1039/C6FD00103C

Conclusion and outlook

Stimulated x-ray emission (superfluorescence) for targets relevant for chemistry

- K-α superfluorescence in Mn solutions demonstrated
- Chemical shifts are observable
- Strong-field effects: broadening and shifting of emission spectrum

- ➢ State-resolved spectroscopy difficult
- ➢ High cross-sections for Stimulated Raman involving spectator 2p-1s transitions
- ➢ Stimulated Raman experiments should be feasible with high-brilliance sources

Lessons learned from Stimulated Raman Experiments in gas-phase CO

- Broad-band SASE pulses lead to large background
- (Self)-seeded two-colour schemes reduce background for pulses with > 10 fs duration
- Statistical analysis is possible, but tedious
- In the soft x-ray region: $3x10^9$ photons/fs would give Raman gain of 0,5 OD

- ➢ LCLS XLEAP: promising for demonstrating Raman gain in soft- and hard x-ray region

What do we need to realize beyond proof-of-principle:

- ➢ Highly stable (seeded) sub-fs pulses of at least 2 different colors
- ➢ Pulse delays up to 100 fs, with 0.1 fs steps
- ➢ Experimental setup with 100 nm focus in the hard x-ray regime
- ➢ Well designed experimental stations with spectrometers of sub eV resolution