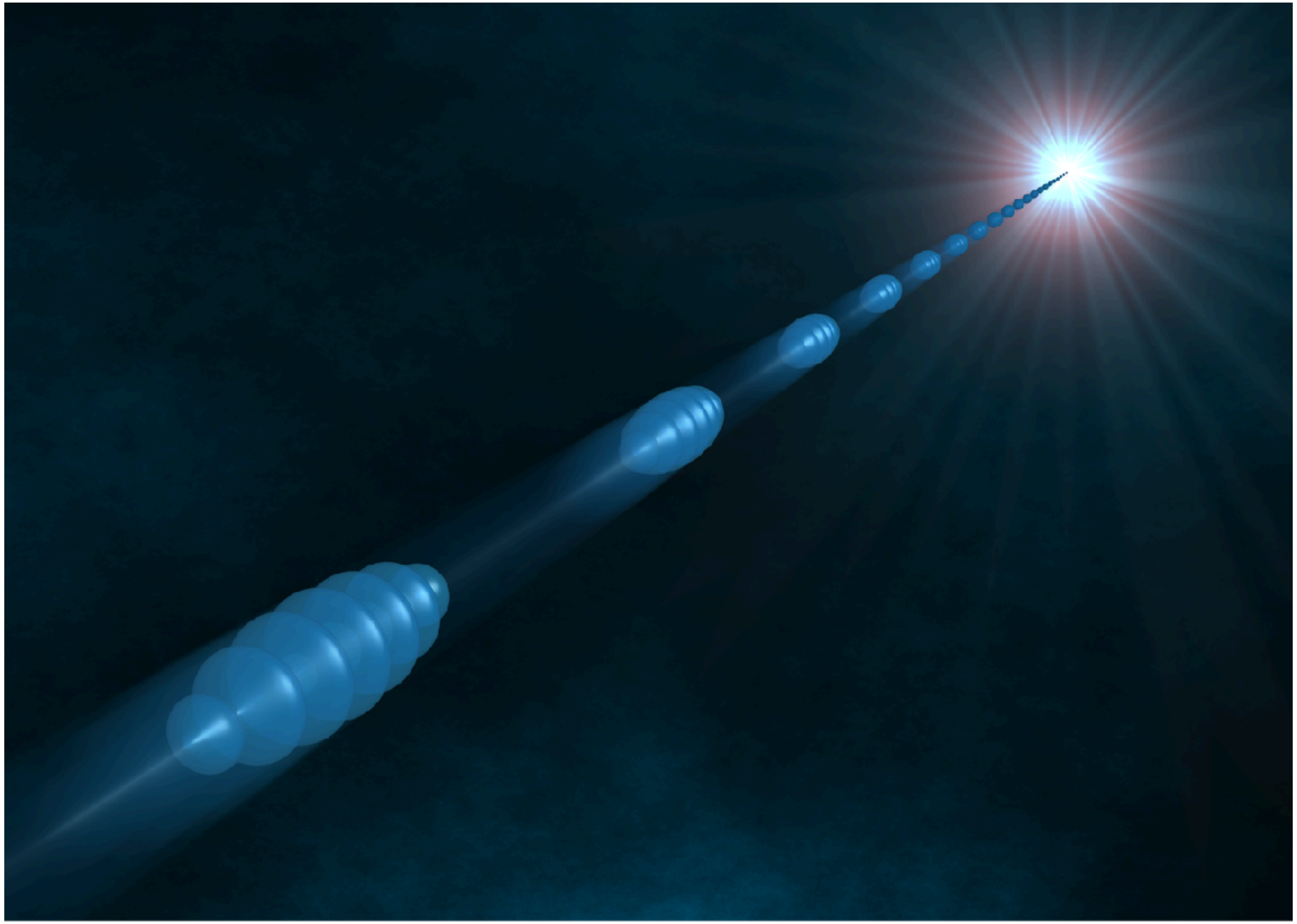
New opportunities for soft X-ray spectroscopy with free-electron lasers.



Martin Beye

Hamburg
2.3.2023

HELMHOLTZ

DESY.

Outline

- Introduction to free-electron lasers
- Soft X-ray spectroscopy with femtosecond resolution
- Towards non-linear X-ray spectroscopies

Free-electron lasers

Large scale facilities

European XFEL

HELMHOLTZ ZENTRUM DRESDEN ROSSENDORF
FELBE / TELBE at HZDR

Elettra Sincrotrone Trieste
FERMI at ELETTRA

Flash at DESY

NATIONAL ACCELERATOR LABORATORY
LCLS at SLAC

POHANG ACCELERATOR LABORATORY
PAL-XFEL

PAUL SCHERRER INSTITUT
Swiss FEL at PSI

lightsources.org

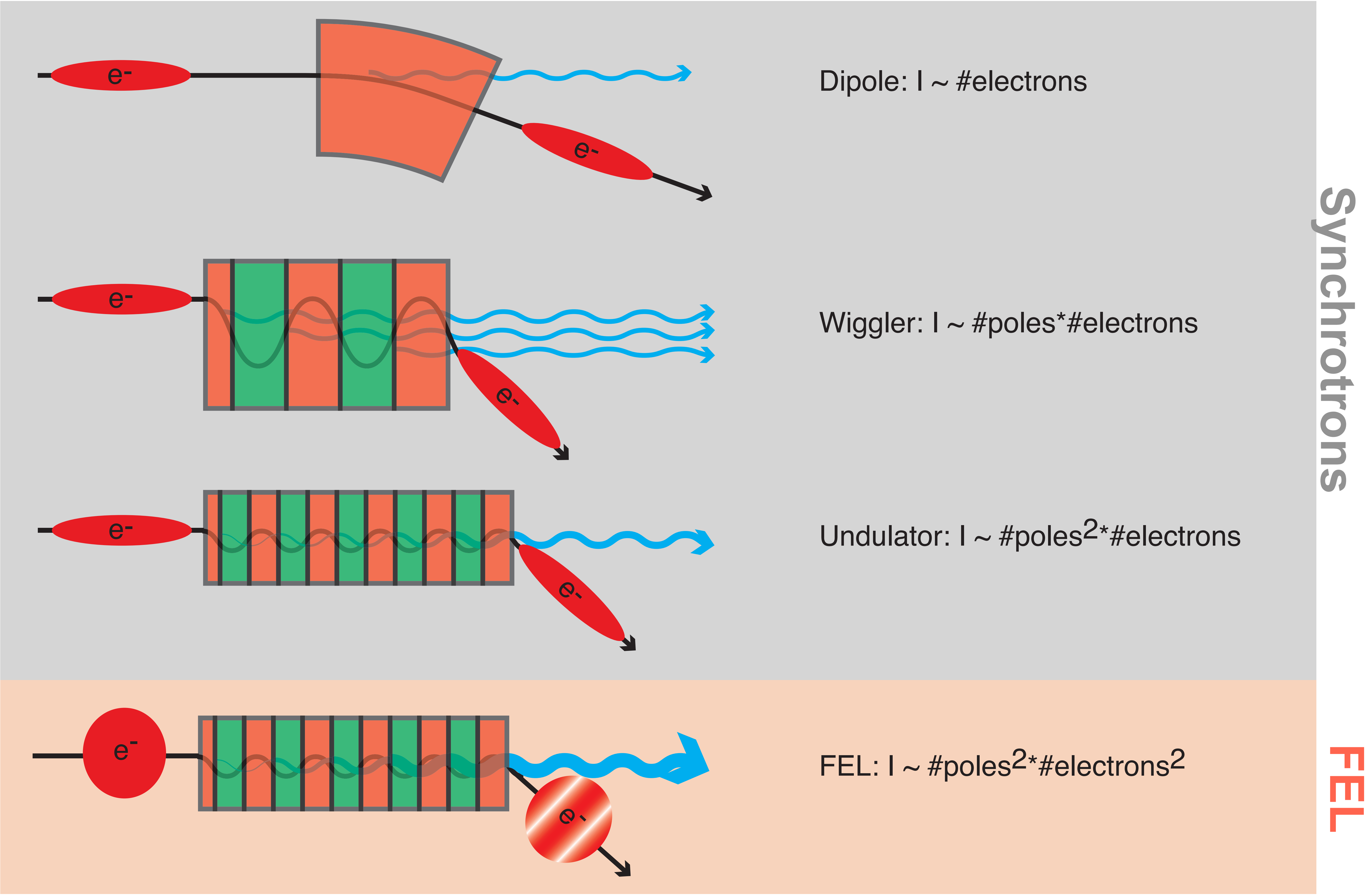
SACLA(XFEL)

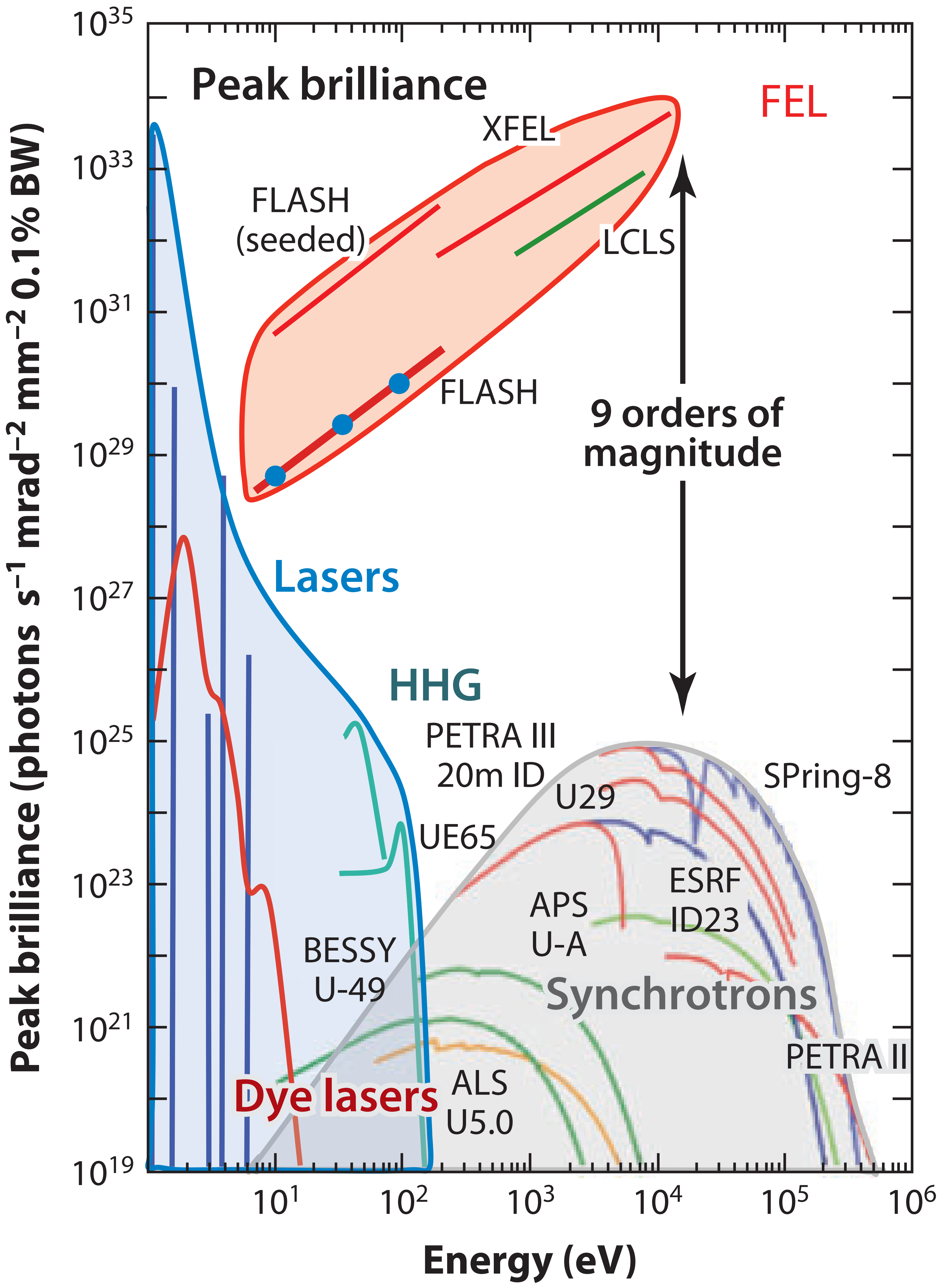
User access through proposals:

- typically twice a year
- free of charge for published research
- evaluated by international committees
- overbooking between 3- and 10-fold

From synchrotrons to free-electron lasers

Coherent interaction among electrons tremendously increases photon number

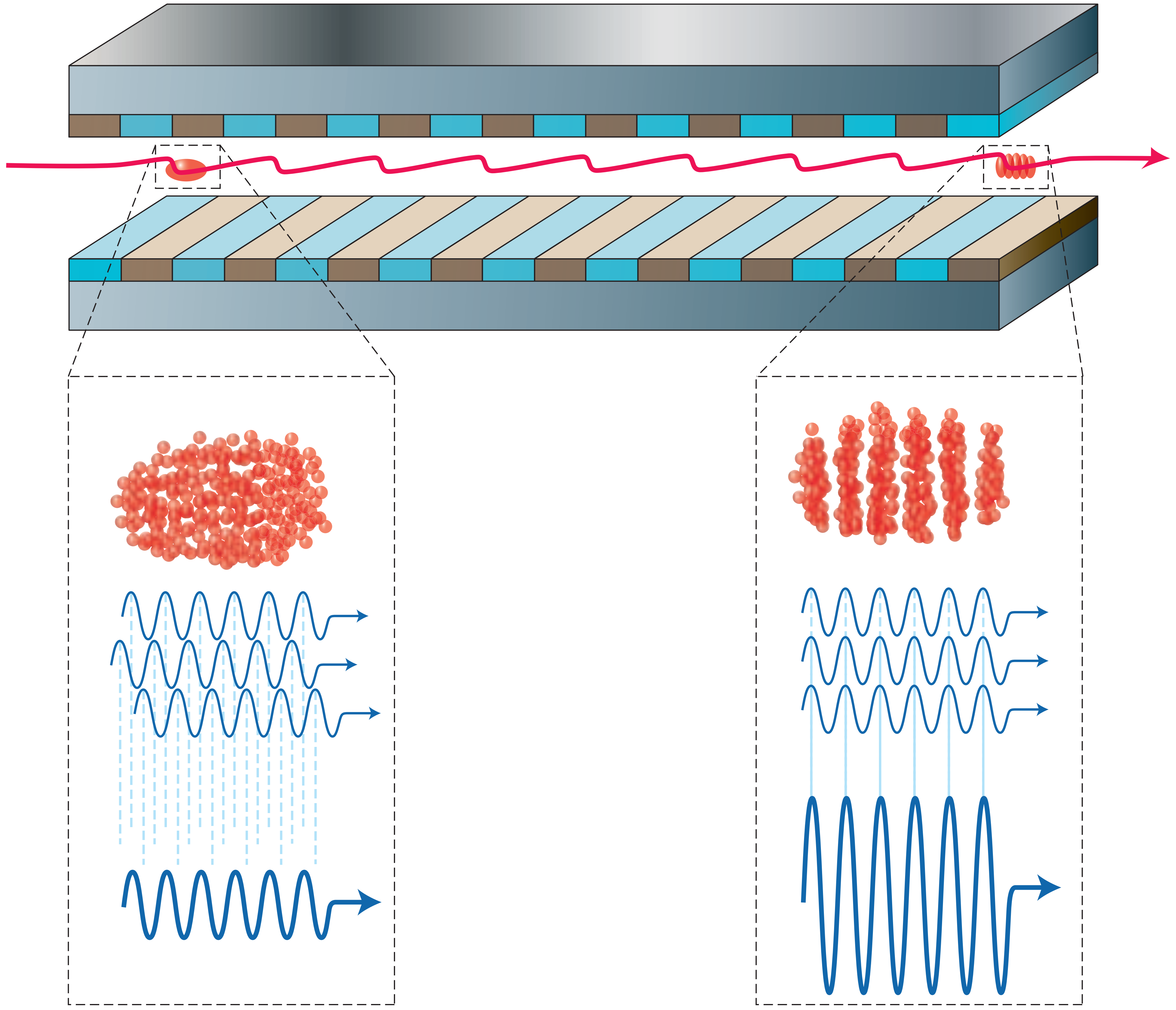




Ullrich et al., Ann. Rev. Phys. Chem. 63, 635 (2012)

How an FEL works

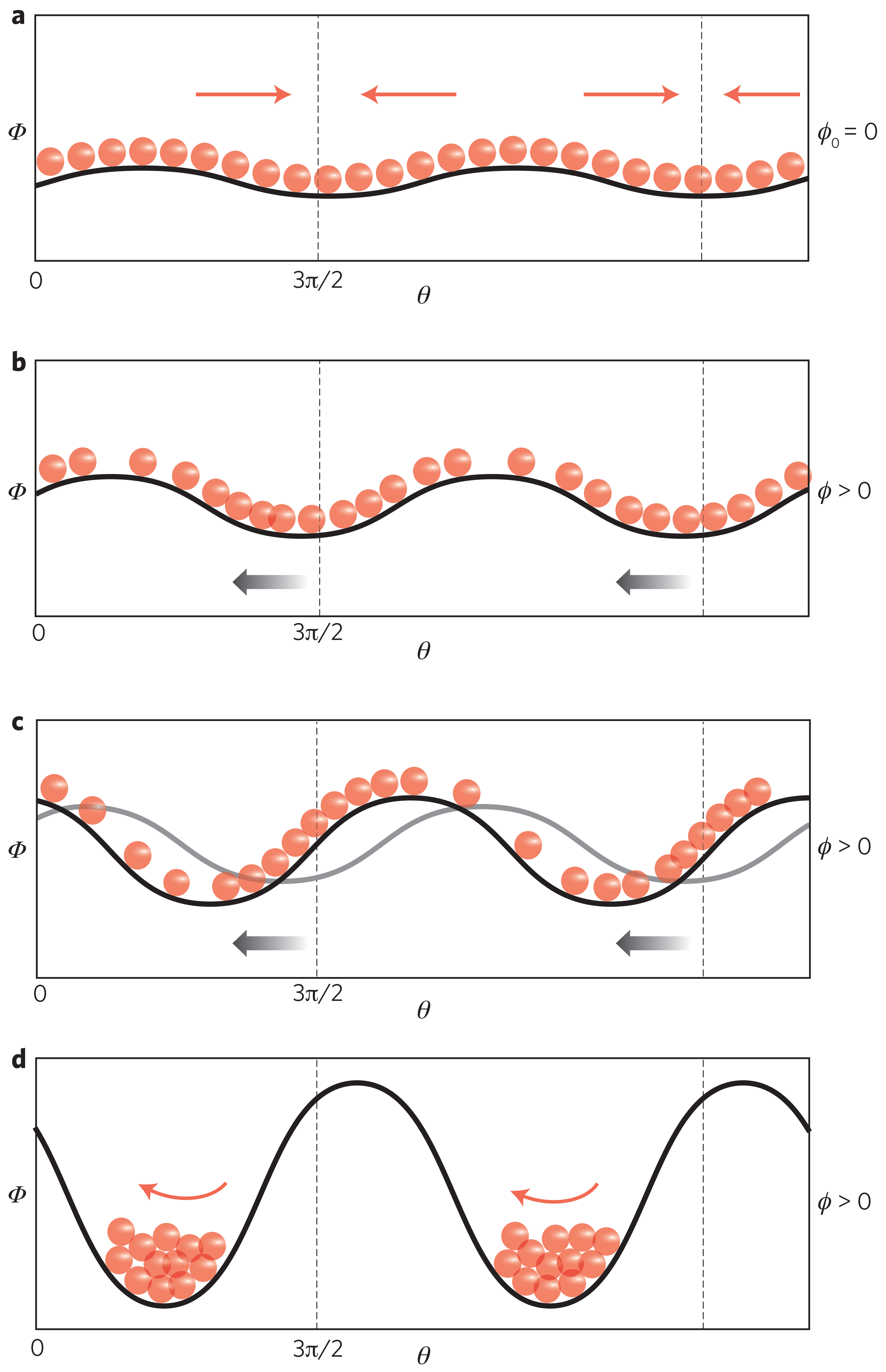
High density of relativistic electrons in an undulator interacts with the self-emitted field



Incoherent emission: electrons randomly phased

Coherent emission: electrons bunched at radiation wavelength

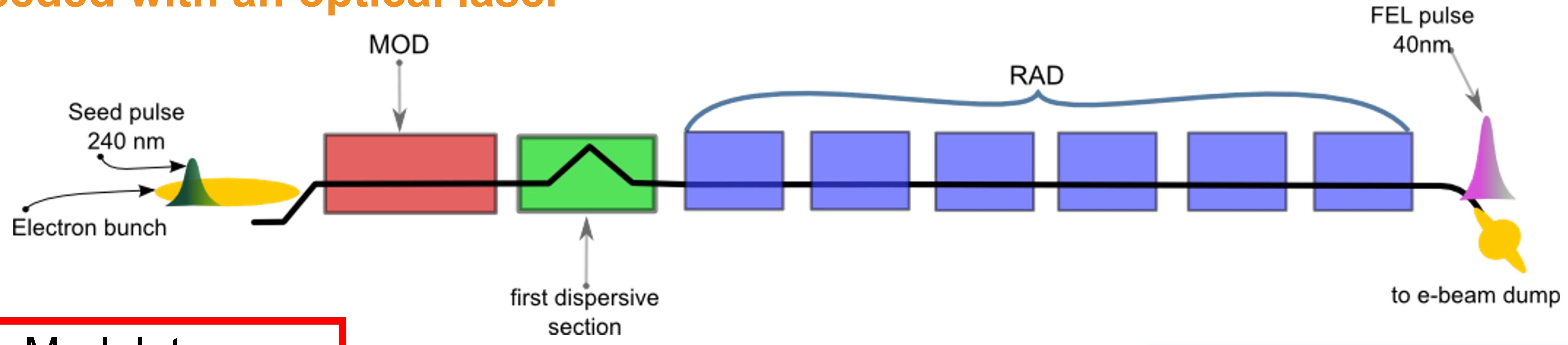
McNeil and Thompson, Nat. Phot. 4, 813 (2010)

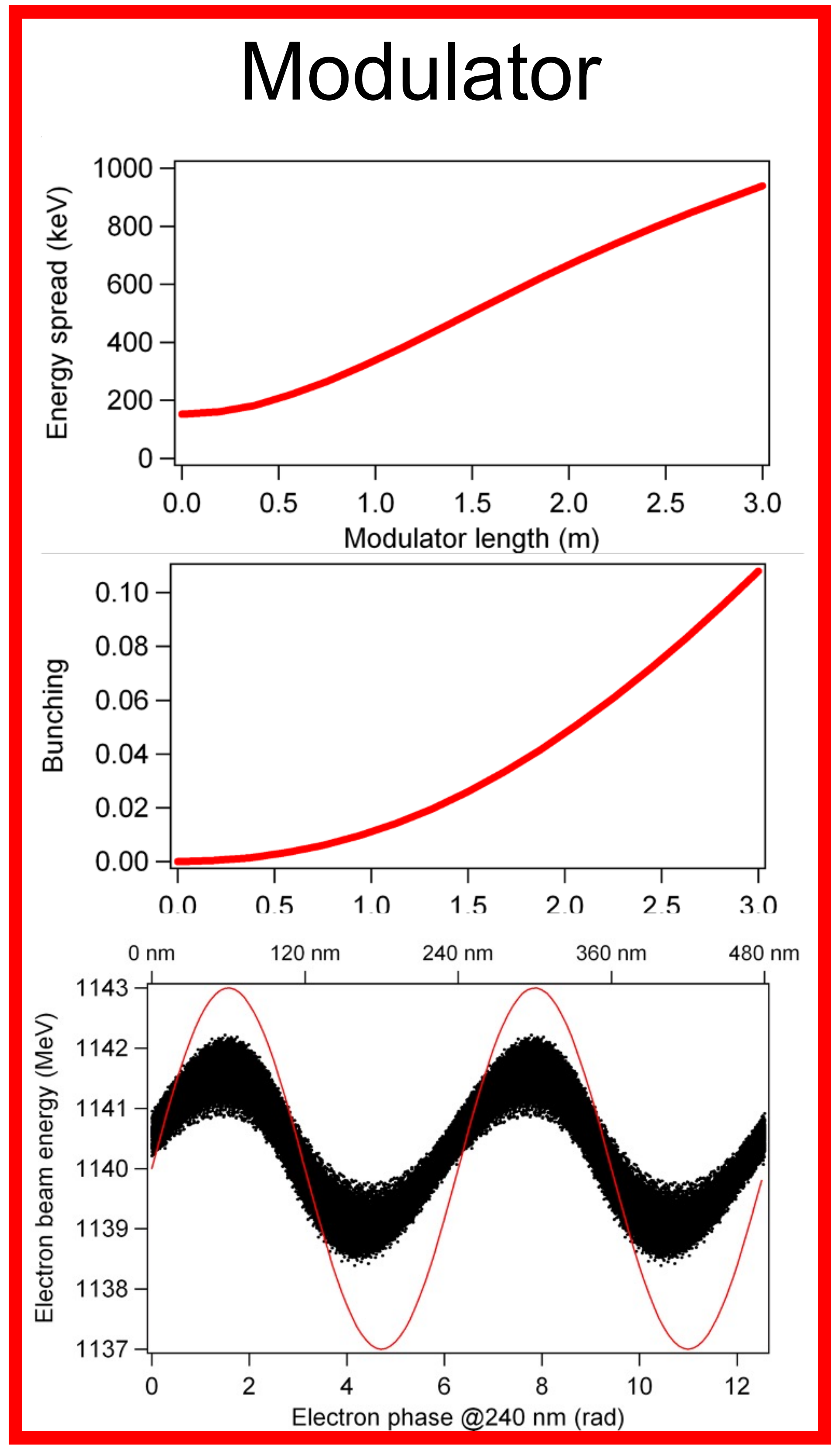


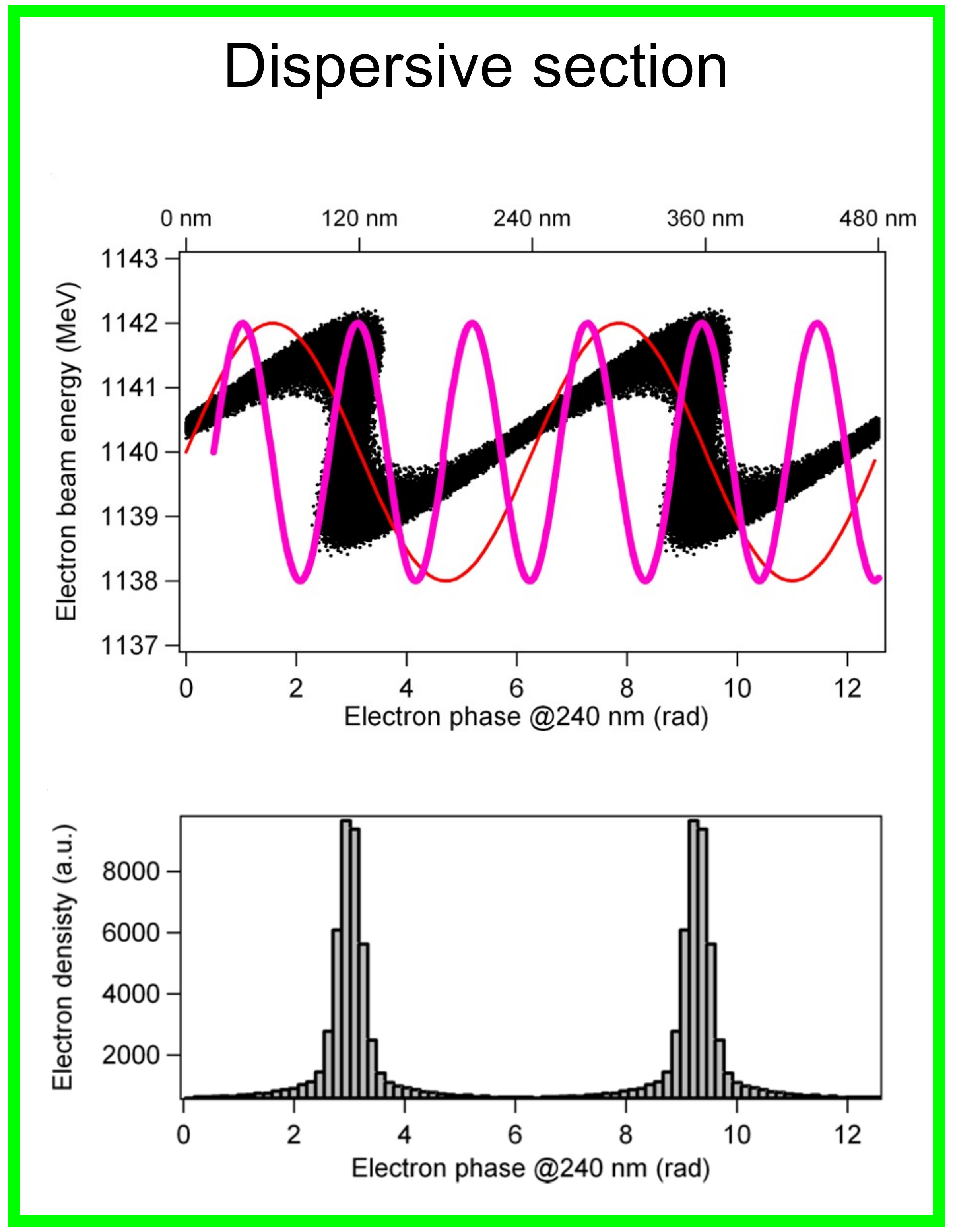
- The undulators in an FEL act like an amplifier.
- For SASE (self-amplification of spontaneous emission), they amplify the random spontaneous emission.
- In effect, they amplify any density modulation of the electron bunch at a wavelength within the amplifier bandwidth.
- Seeding needs to provide an electron bunch density modulation with Fourier components at the right wavelength.

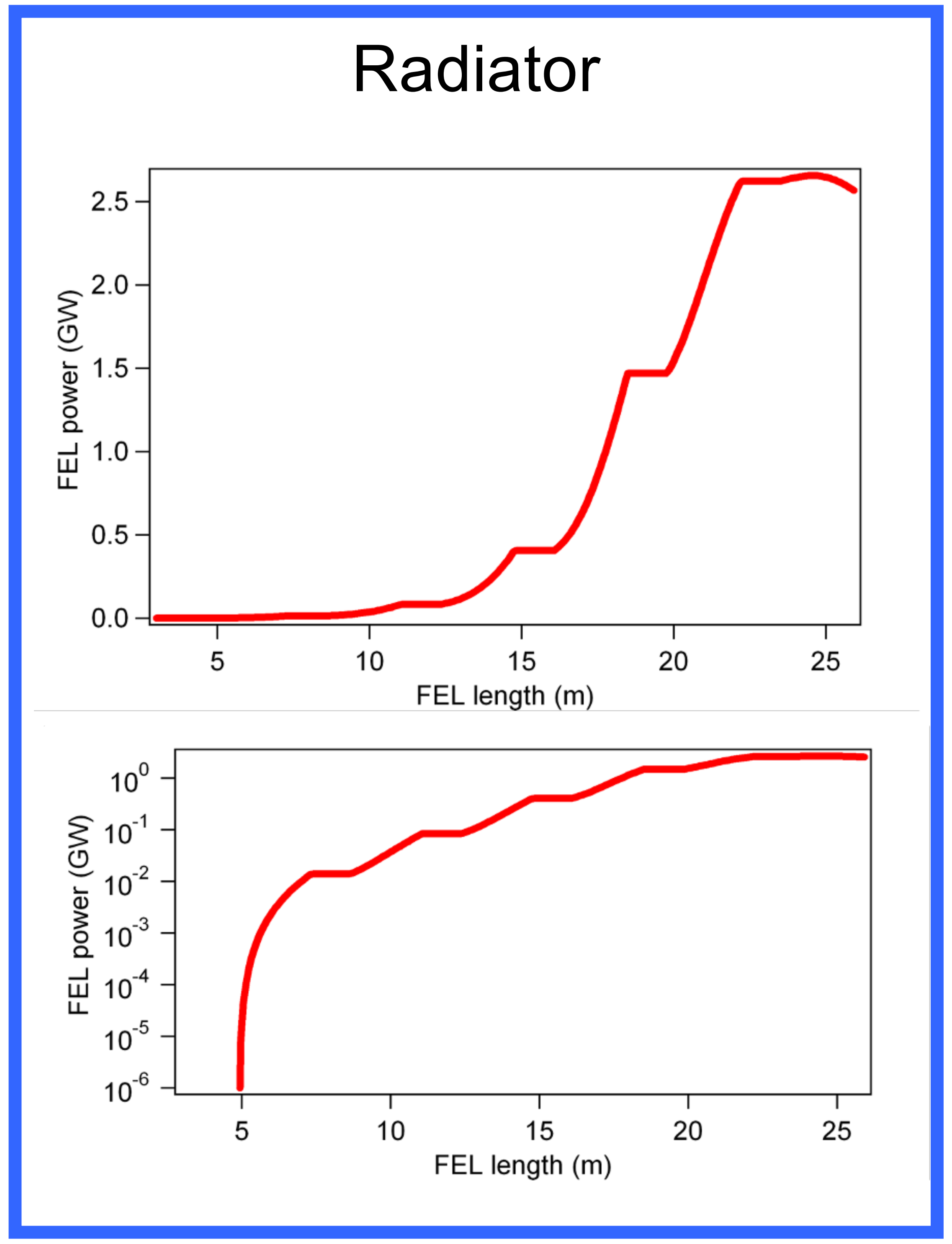
High gain harmonic generation (HGHG)

Externally seeded with an optical laser





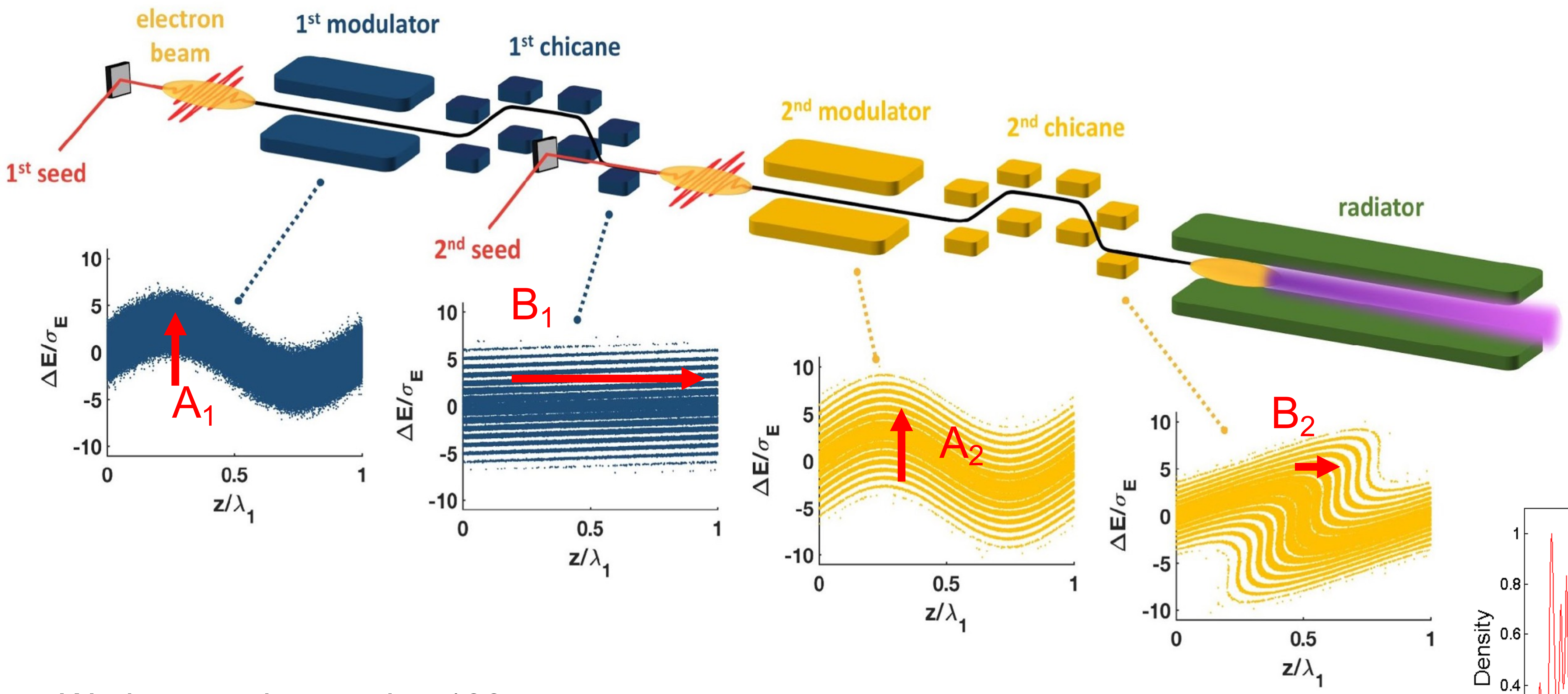


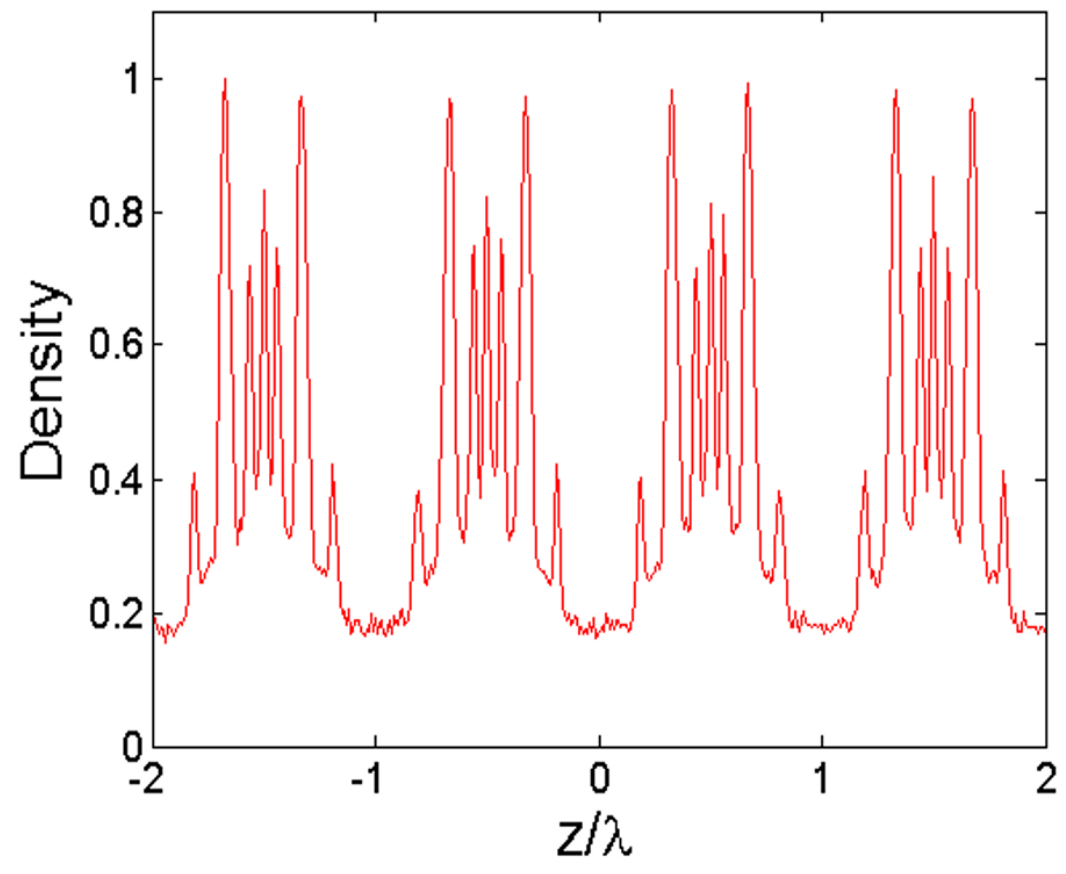


Energy modulation per energy spread must be larger than harmonic number (reasonable up to 10).

Echo-enabled harmonic generation (EEHG)

The way to get even higher harmonics, i.e. shorter wavelengths



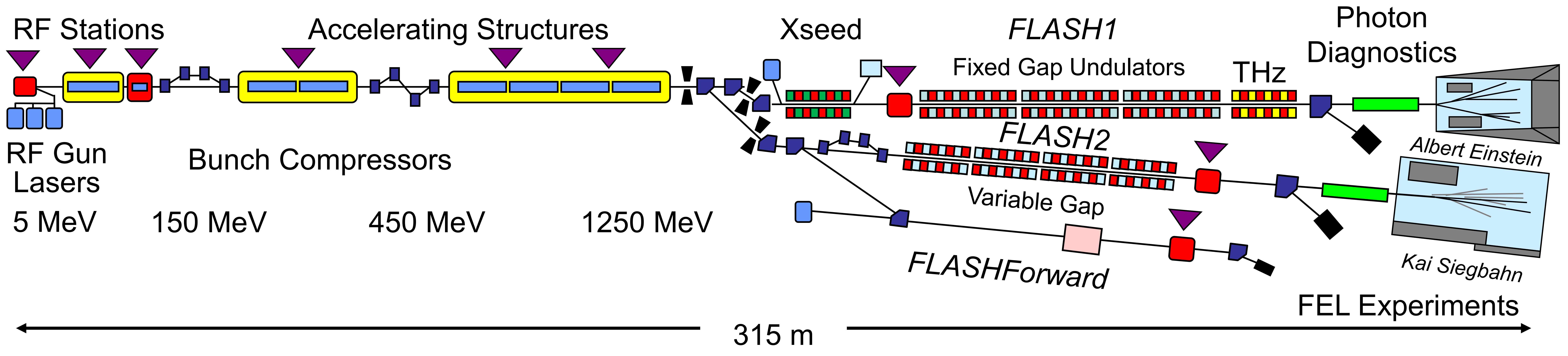


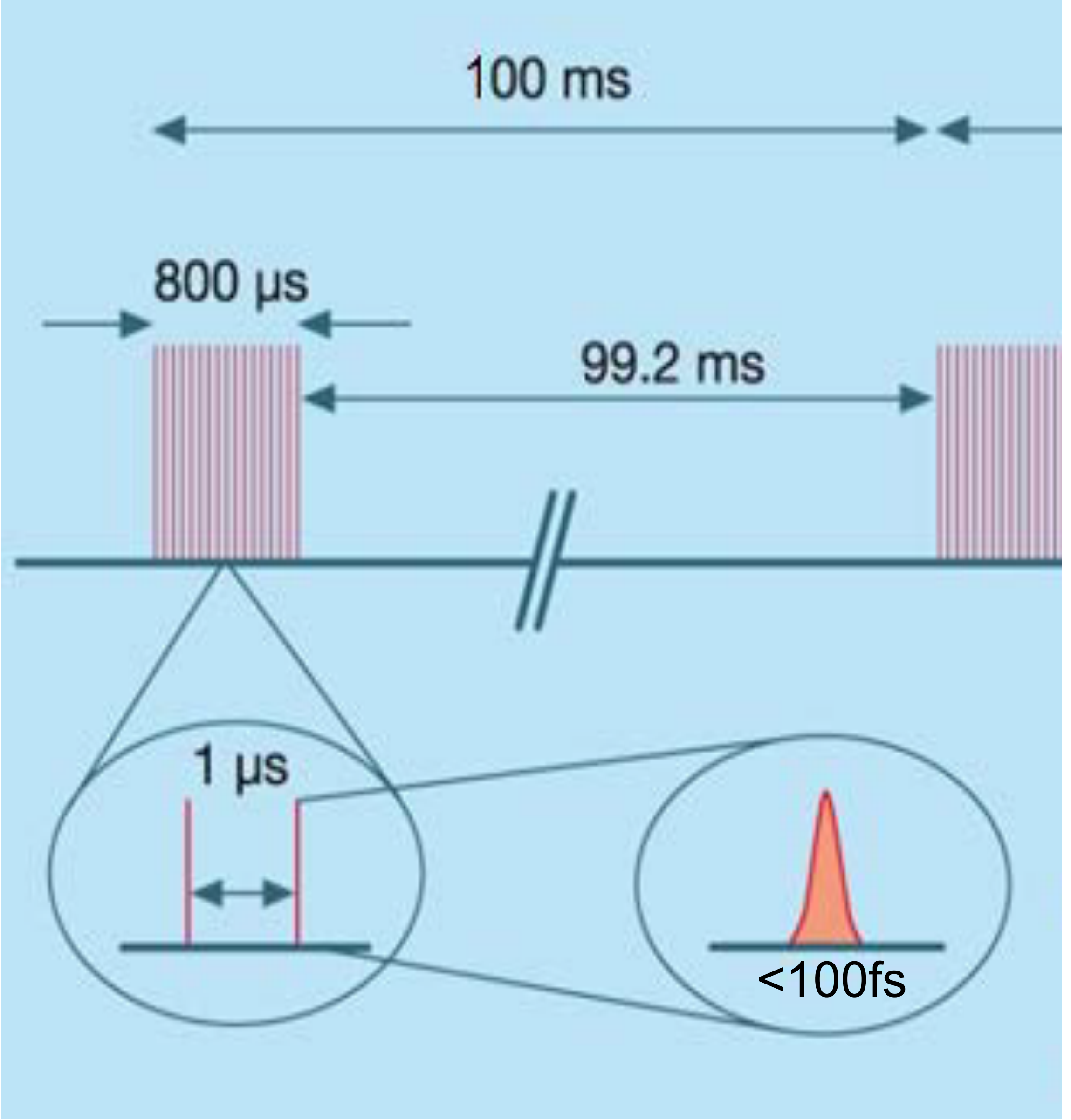
Works up to harmonic ~100.
Requires two lasers, modulators and chicanes.
Only one laser needs to be tunable.

FLASH overview (@ DESY, Hamburg, Germany)

High repetition rate free-electron laser with two undulator lines to generate XUV and soft X-ray pulses

FLASH today





- superconducting accelerator enables many thousand pulses per second
- operation in burst mode: up to 800µs RF filled with up to 800 electron pulses (1 MHz)
- usually, we serve in total 5000 pulses per second for two beam lines
- bursts repeated with 10Hz

Each experimental hall hosts:

- 2 open port beam lines (one monochromatic)
  - in total ~5 facility operated end stations or user supplied
- 2 fixed endstations at dedicated beam lines
- 1 split-and-delay-unit at an open port

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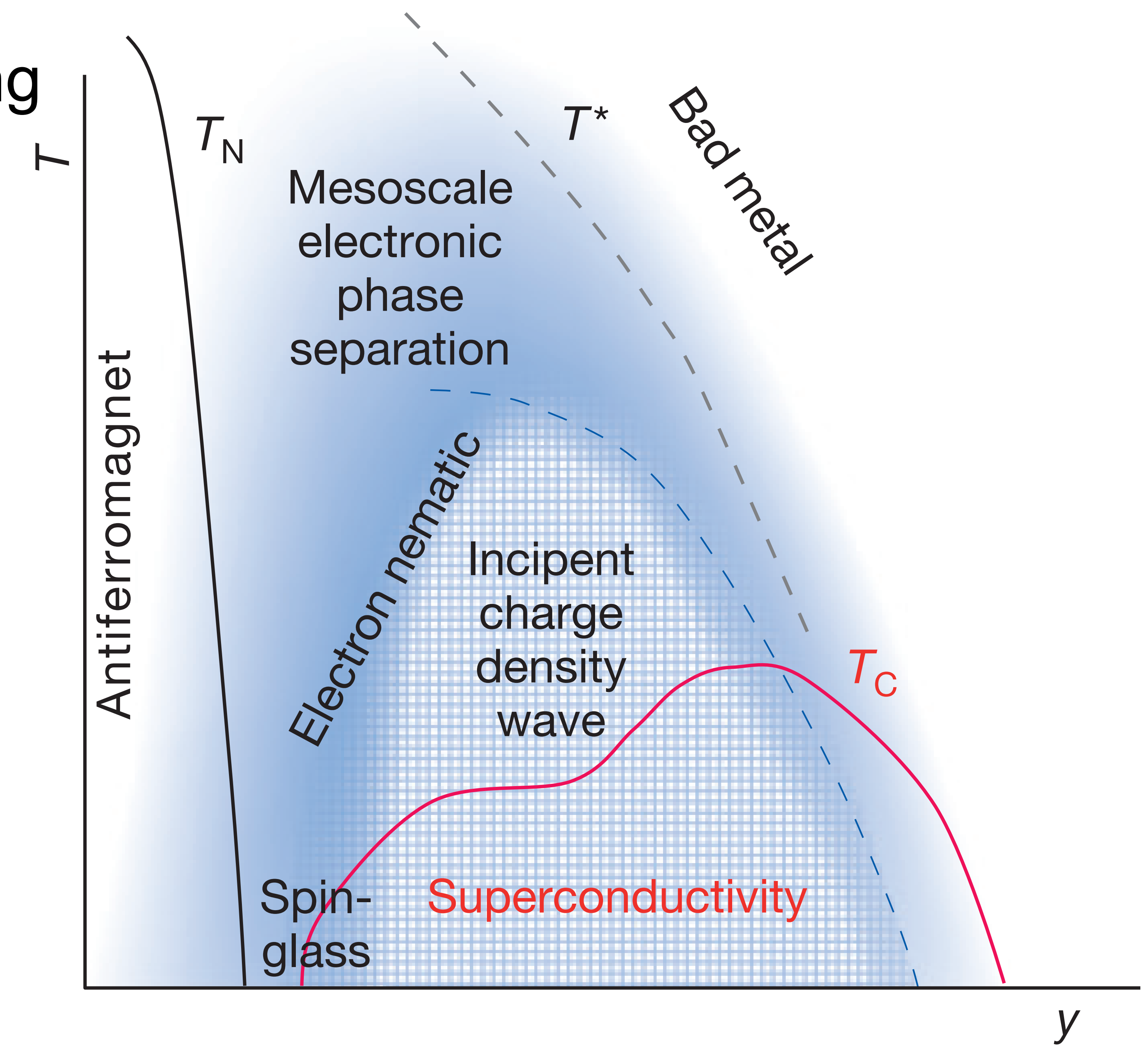
Low energy excitations at active sites

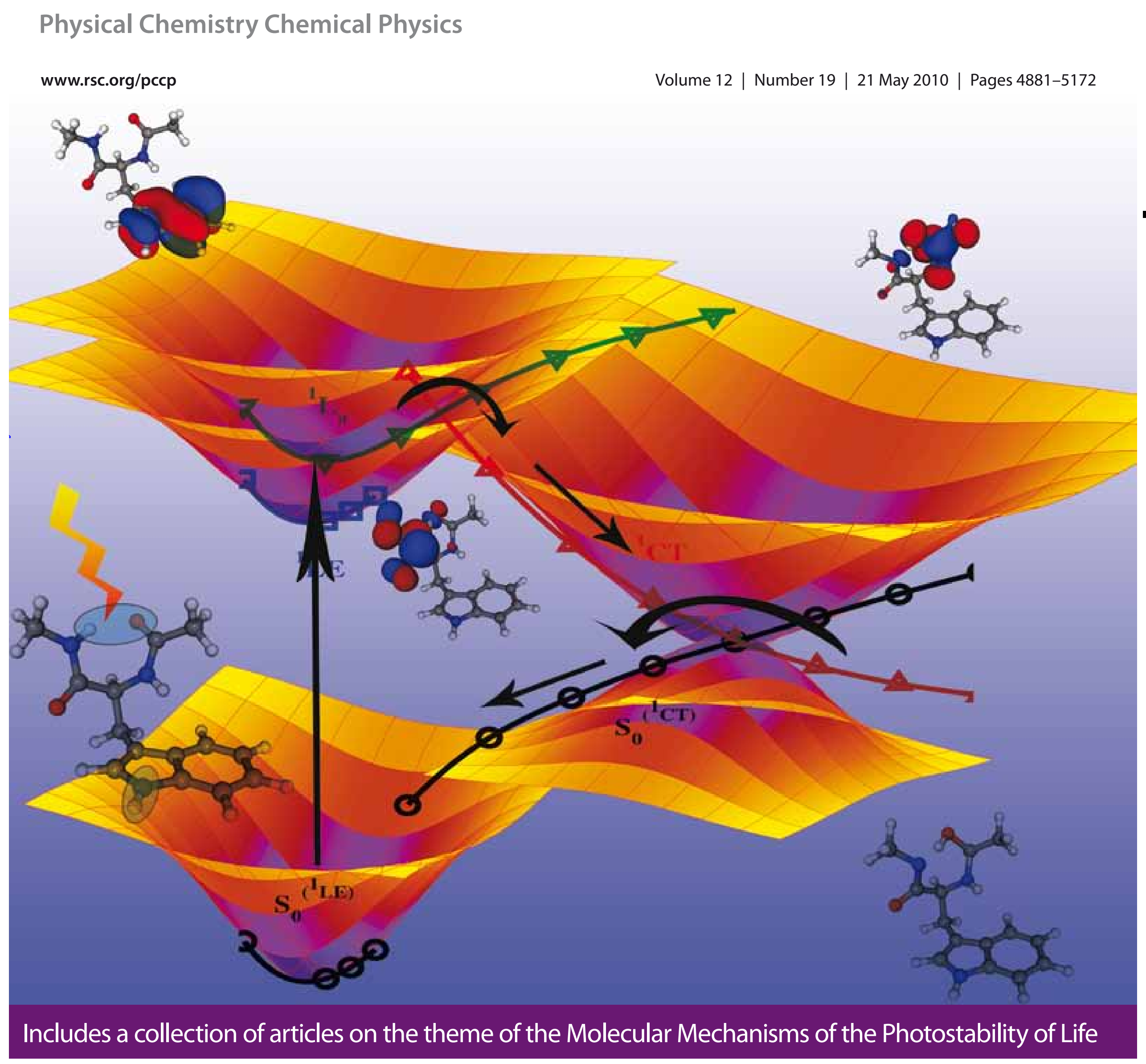
To understand and control functionality

> Correlated materials:
-Metal-to-Insulator Transitions
-Superconductors
-Magnetic switching
-Ferroelectrics



Fradkin, Kivelson, Nat. Phys. 8, 864 (2012)

> Photochemistry / Ultrafast chemical dynamics:
-Metal-to-Ligand charge transfer
-Artificial photosynthesis
-Solar fuels
-Heterogeneous catalysis



Low energy excitations at active sites

To understand and control functionality

> Correlated materials:

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> Photochemistry / Ultrafast chemical dynamics:

-Metal-to-Ligand charge transfer
-Artificial photosynthesis
-Solar fuels
-Heterogeneous catalysis

Excitation spectrum at the active site: Soft X-ray spectroscopy

Selectivity: Local electronic structure through specific core resonances

Core levels are element specific

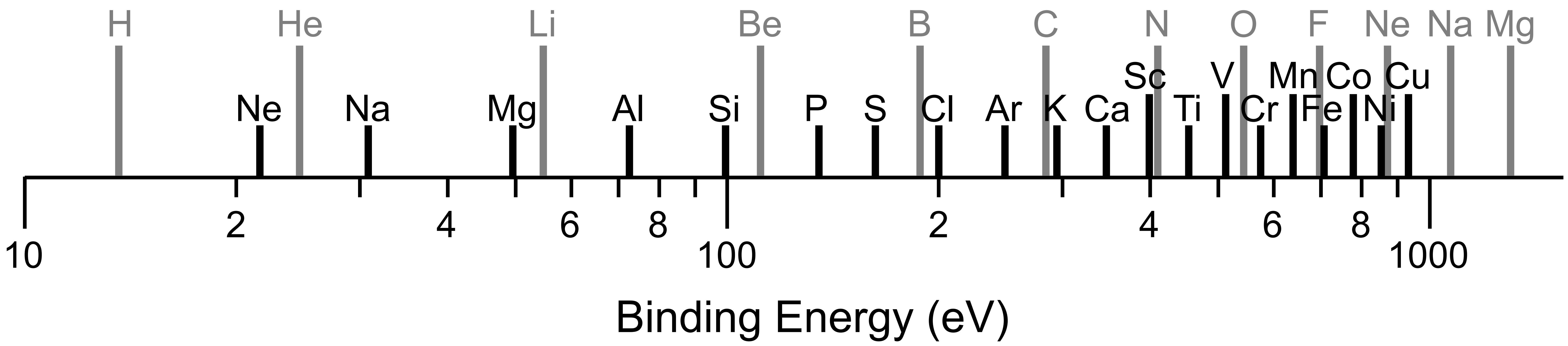


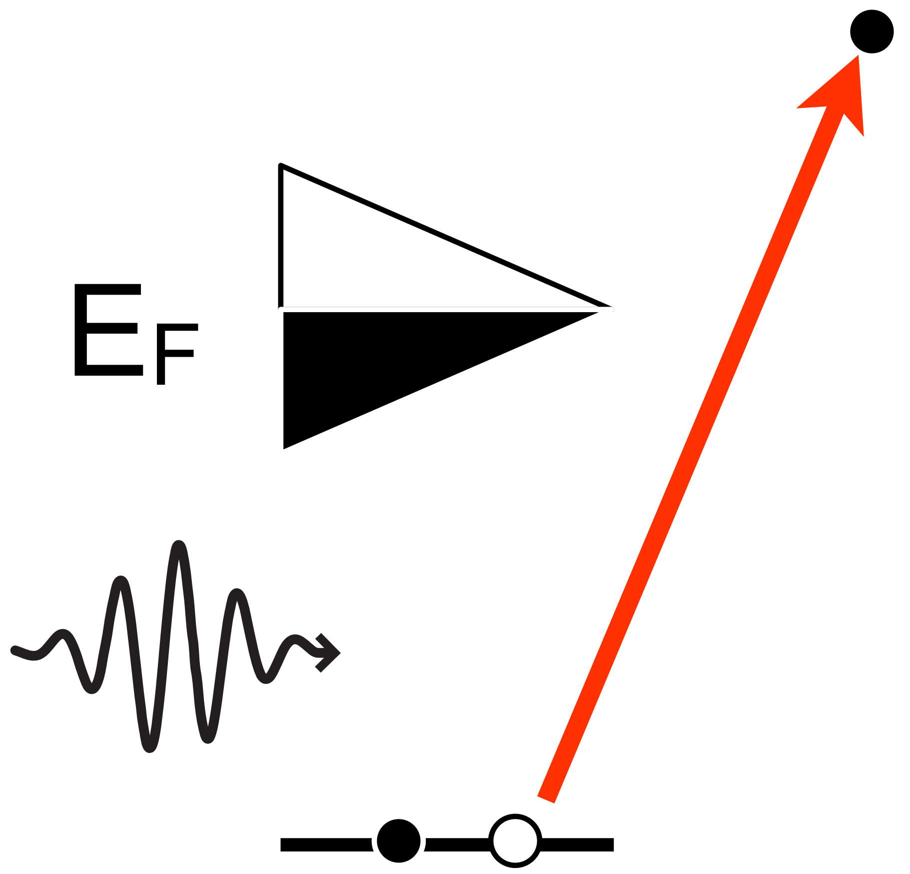
Table 1-1. *Electron binding energies, in electron volts, for the elements V to Ag in their natural forms.*

Element	K 1s	L_1 2s	L_2 $2p_{1/2}$	L_3 $2p_{3/2}$	M_1 3s	M_2 $3p_{1/2}$	M_3 $3p_{3/2}$	M_4 $3d_{3/2}$	M_5 $3d_{5/2}$	N_1 4s	N_2 $4p_{1/2}$	N_3 $4p_{3/2}$
23 V	5465	626.7†	519.8†	512.1†	66.3†	37.2†	37.2†					
24 Cr	5989	696.0†	583.8†	574.1†	74.1†	42.2†	42.2†					
25 Mn	6539	769.1†	649.9†	638.7†	82.3†	47.2†	47.2†					
26 Fe	7112	844.6†	719.9†	706.8†	91.3†	52.7†	52.7†					
27 Co	7709	925.1†	793.2†	778.1†	101.0†	58.9†	59.9†					
28 Ni	8333	1008.6†	870.0†	852.7†	110.8†	68.0†	66.2†					
29 Cu	8979	1096.7†	952.3†	932.7	122.5†	77.3†	75.1†					
30 Zn	9659	1196.2*	1044.9*	1021.8*	139.8*	91.4*	88.6*	10.2*	10.1*			
31 Ga	10367	1299.0*b	1143.2†	1116.4†	159.5†	103.5†	100.0†	18.7†	18.7†			
32 Ge	11103	1414.6*b	1248.1*b	1217.0*b	180.1*	124.9*	120.8*	29.8	29.2			
33 As	11867	1527.0*b	1359.1*b	1323.6*b	204.7*	146.2*	141.2*	41.7*	41.7*			
34 Se	12658	1652.0*b	1474.3*b	1433.9*b	229.6*	166.5*	160.7*	55.5*	54.6*			
35 Br	13474	1782*	1596*	1550*	257*	189*	182*	70*	69*			
36 Kr	14326	1921	1730.9*	1678.4*	292.8*	222.2*	214.4	95.0*	93.8*	27.5*	14.1*	14.1*
37 Rb	15200	2065	1864	1804	326.7*	248.7*	239.1*	113.0*	112*	30.5*	16.3*	15.3 *
38 Sr	16105	2216	2007	1940	358.7†	280.3†	270.0†	136.0†	134.2†	38.9†	21.3	20.1†
39 Y	17038	2373	2156	2080	392.0*b	310.6*	298.8*	157.7†	155.8†	43.8*	24.4*	23.1*

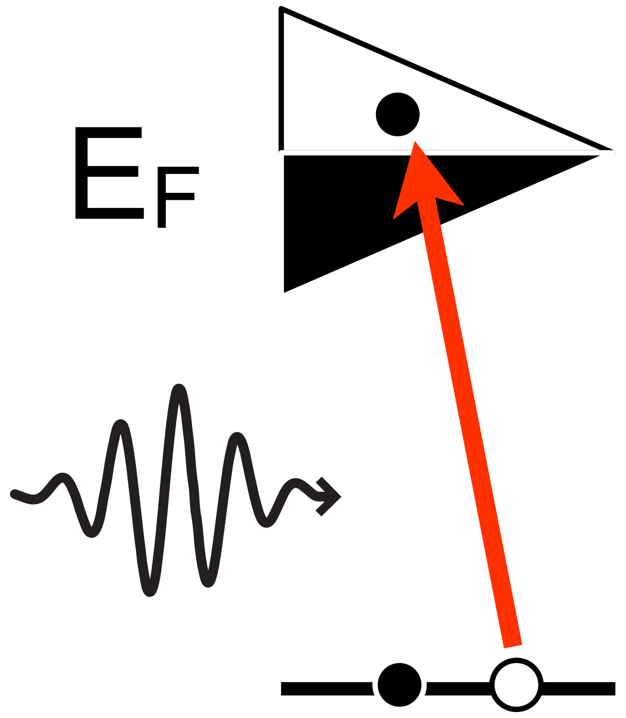
Spectroscopy toolbox

Different final states different probes

X-ray Photoelectron Spectroscopy (XPS)

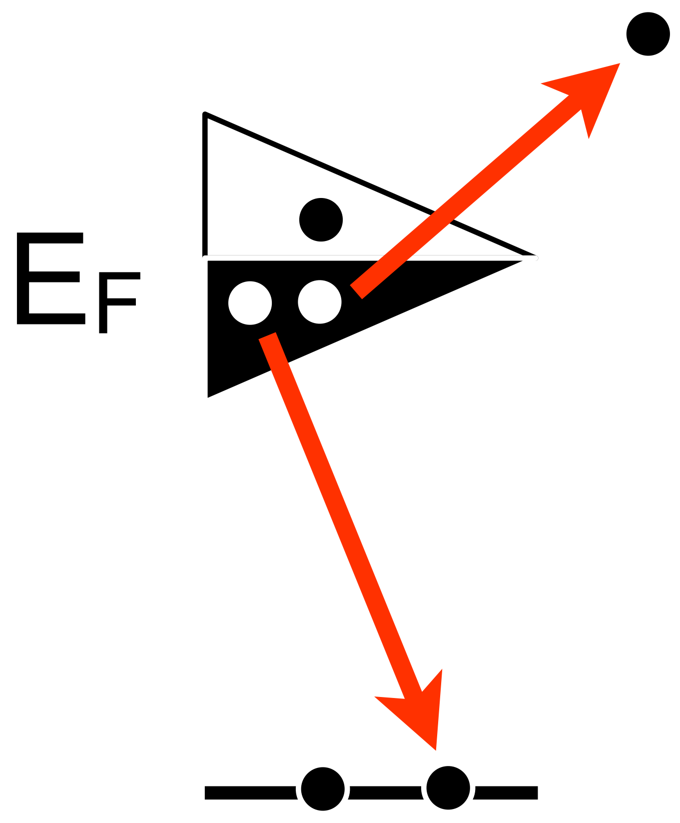


X-ray Absorption Spectroscopy (XAS)

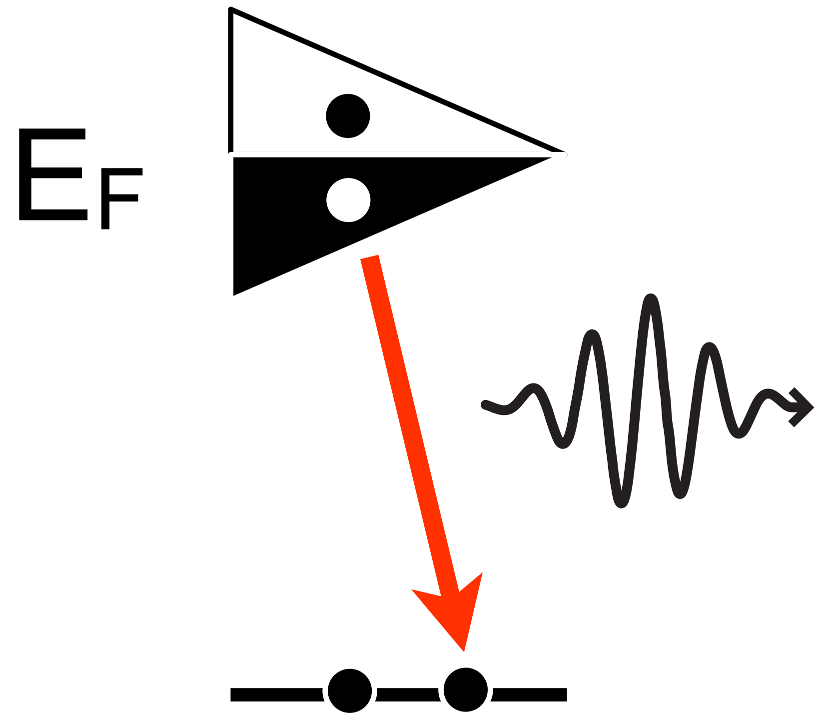


NEXAFS
XANES
EXAFS

Auger Emission Spectroscopy (AES)



X-ray Emission Spectroscopy (XES)

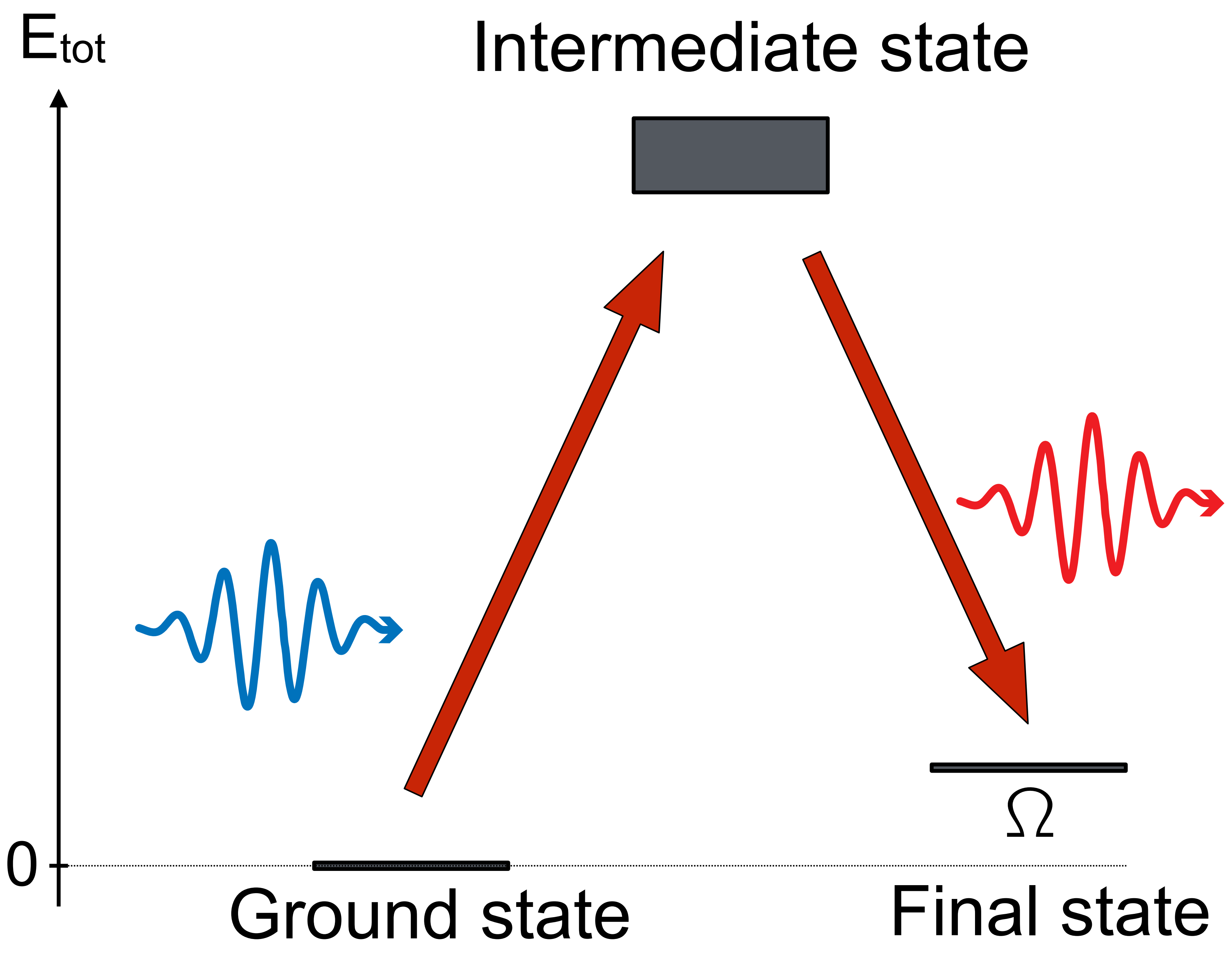


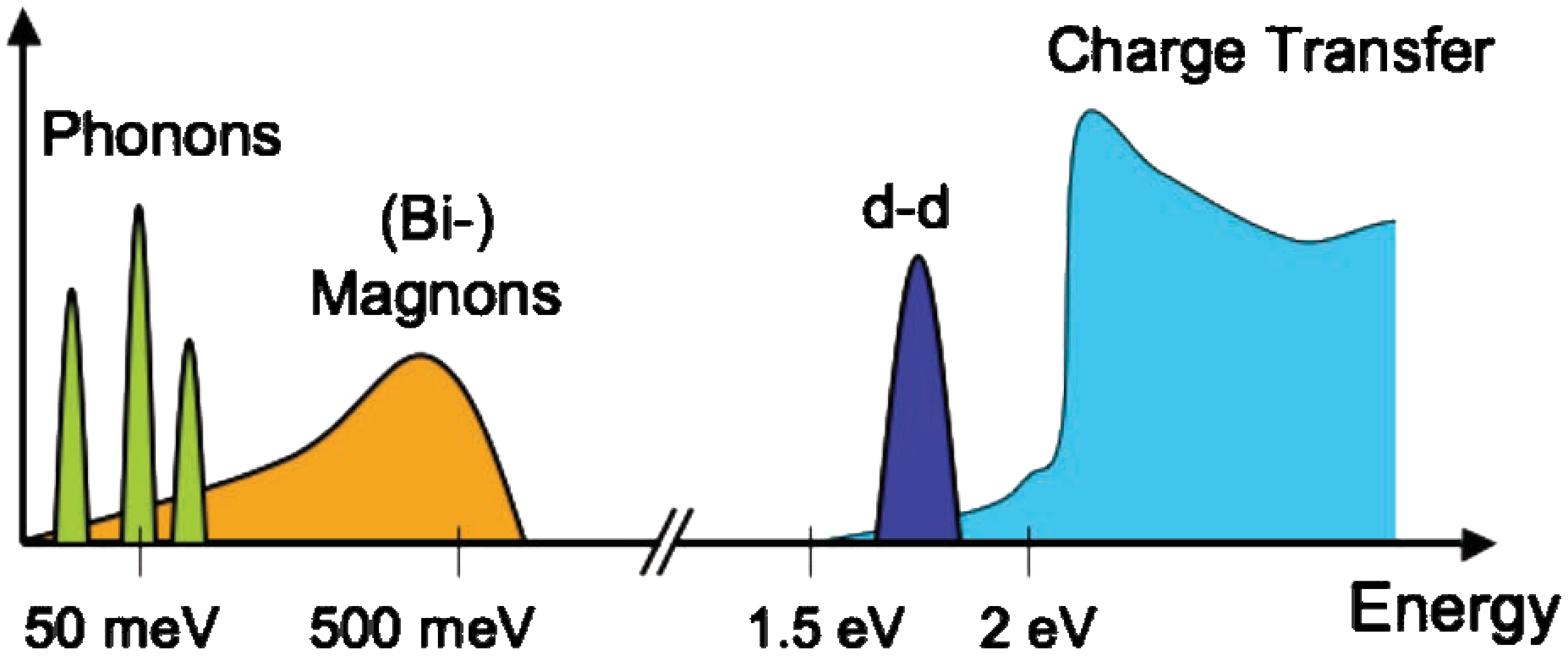
RIXS

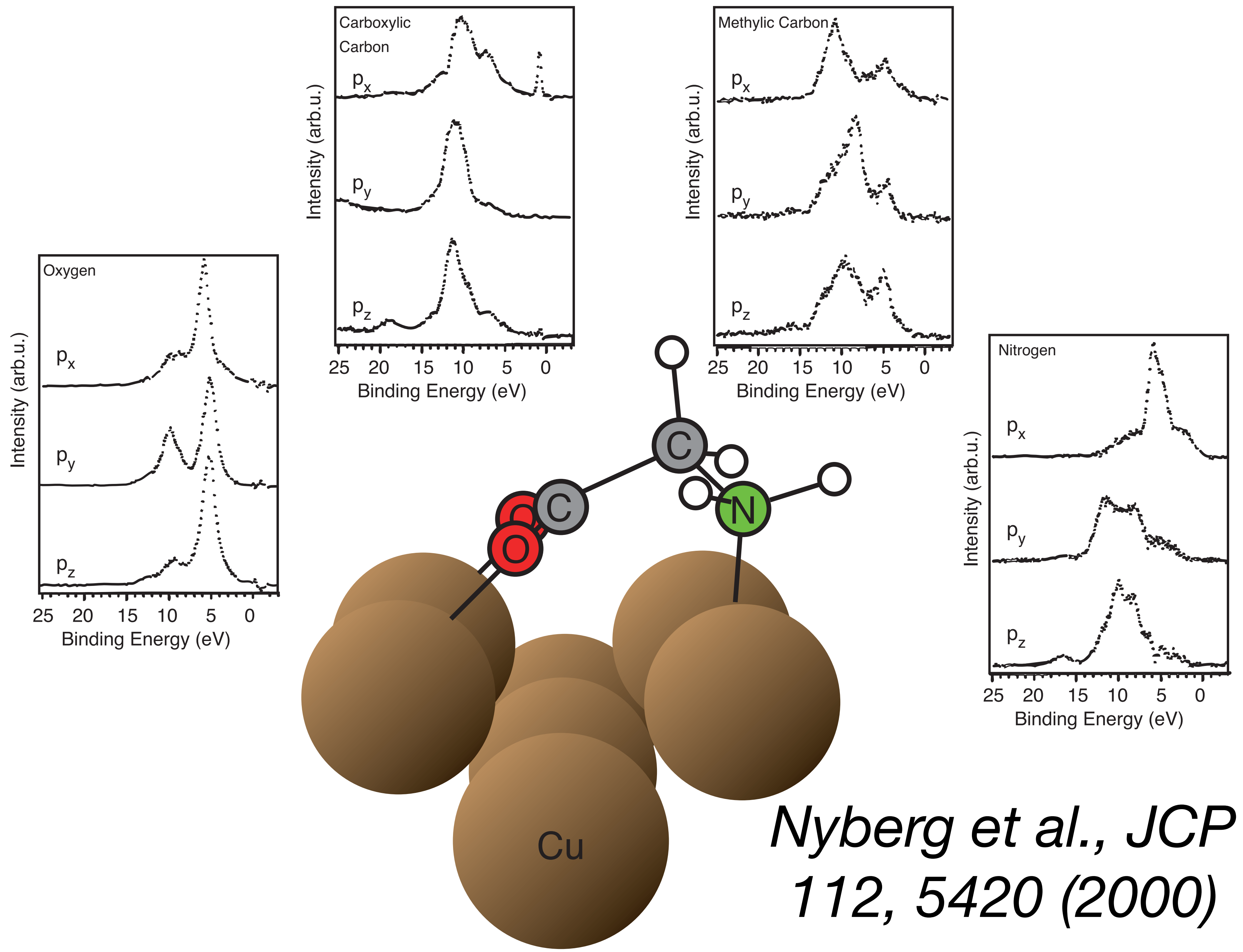
Resonant inelastic X-ray scattering (RIXS)

Photon-in photon-out

Ament et al, Rev Mod Phys 83, 705 (2011)







Nyberg et al., JCP 112, 5420 (2000)

Surface science at LCLS

Partners from Sweden, Germany, USA

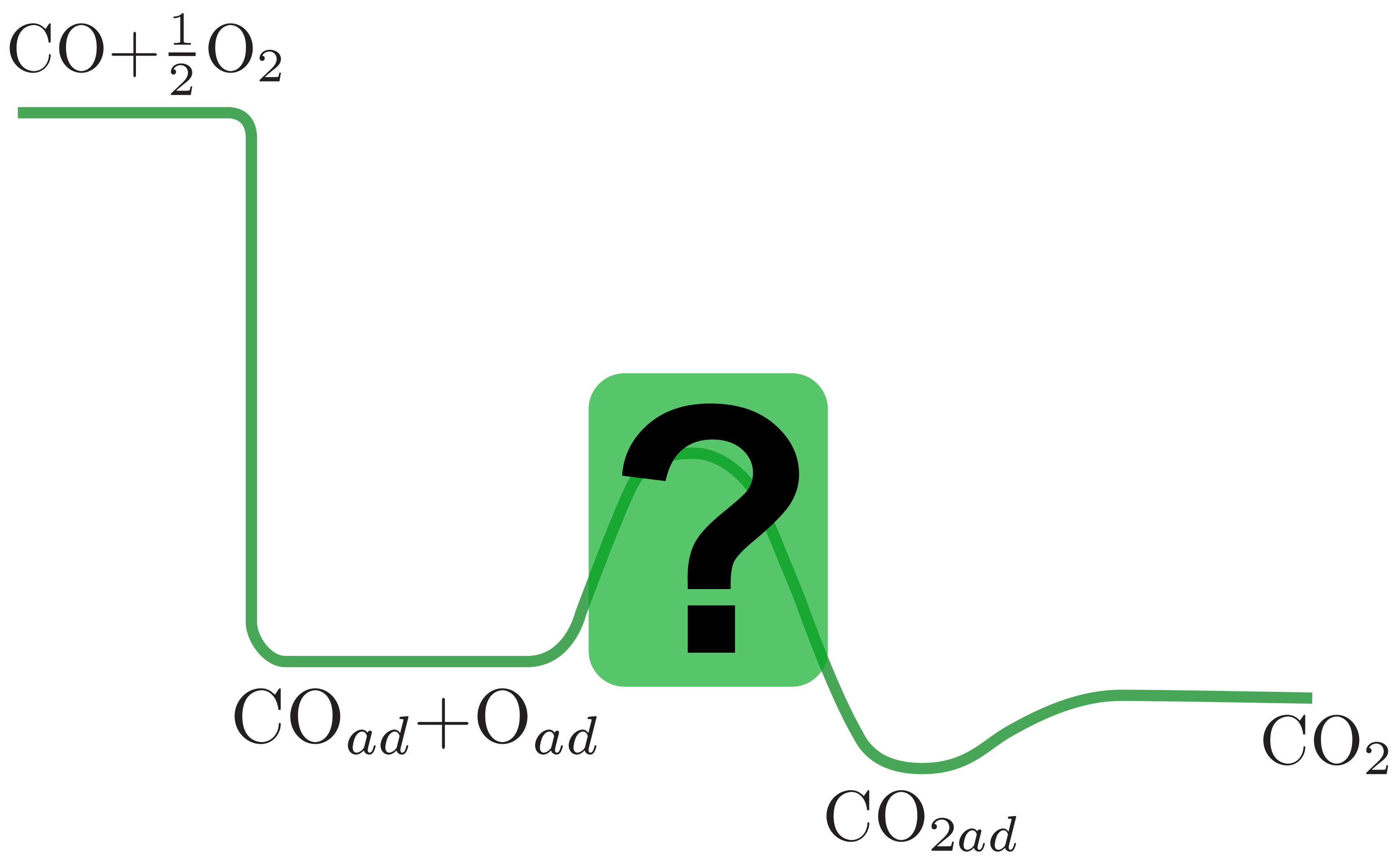
SLAC / Stanford University:
Frank Abild-Pedersen
Toyli Anniyev
Ryan Coffee
Georgi L. Dakovski
Tetsuo Katayama
Sarp Kaya
Jerry LaRue
Mike P. Minitti
Andreas Møgelhøj
May L. Ng
Anders R. Nilsson
Dennis Nordlund
Jens Nørskov
Hirohito Ogasawara
William F. Schlotter
Jonas A. Sellberg
Joshua J. Turner
Hongliang Xin

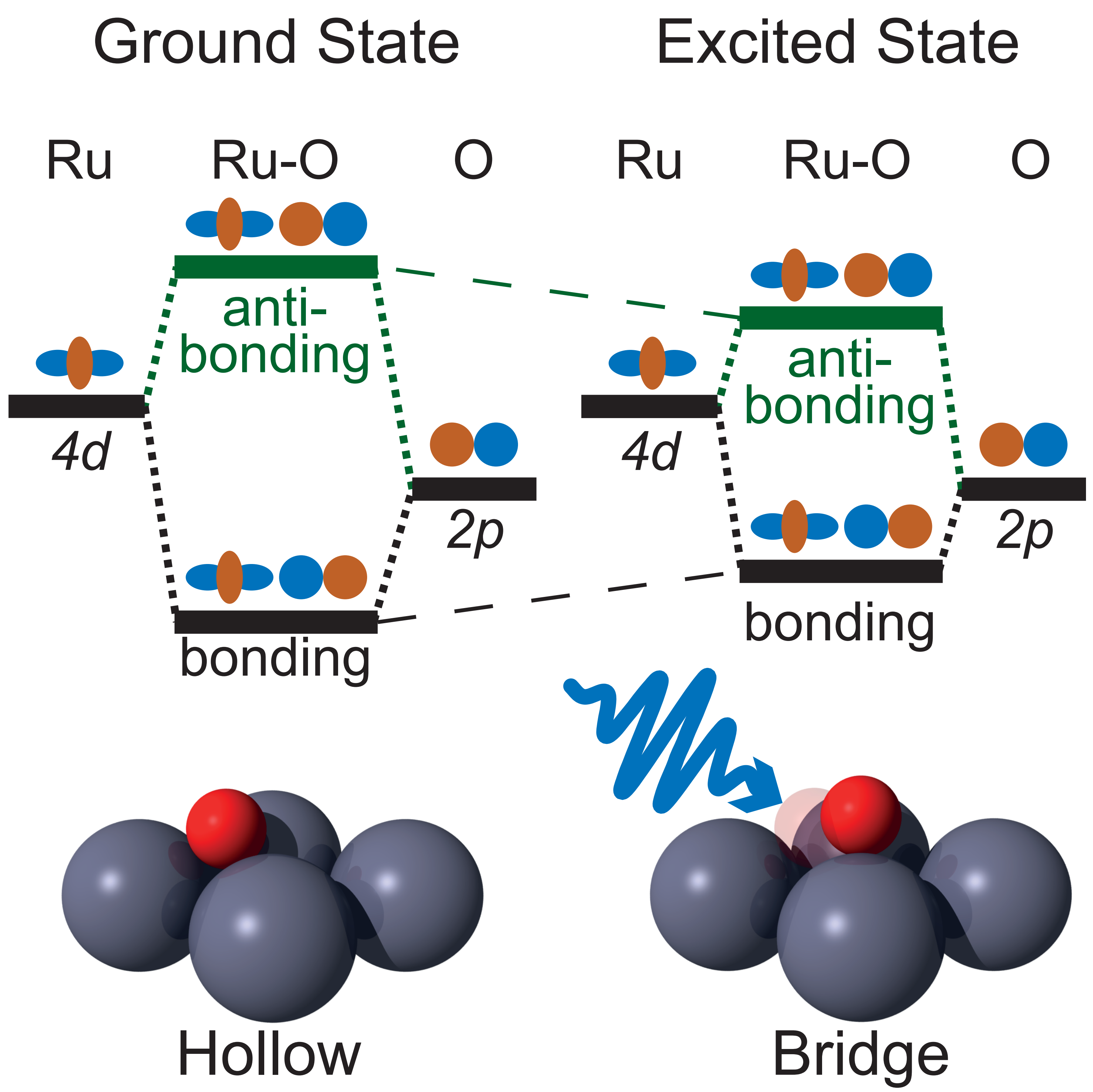
DESY:
Martin Beye
Wilfried Wurth
Universität Hamburg:
Martina Dell'Angela
Florian Hieke
Giuseppe Mercurio
Wilfried Wurth
Fritz-Haber Institut:
Martin Wolf
Helmholtz-Zentrum Berlin:
Alexander Föhlisch
Stockholm University:
Jörgen Gladh
Henrik Öberg
Henrik Öström
Lars Pettersson
Anders Nilsson

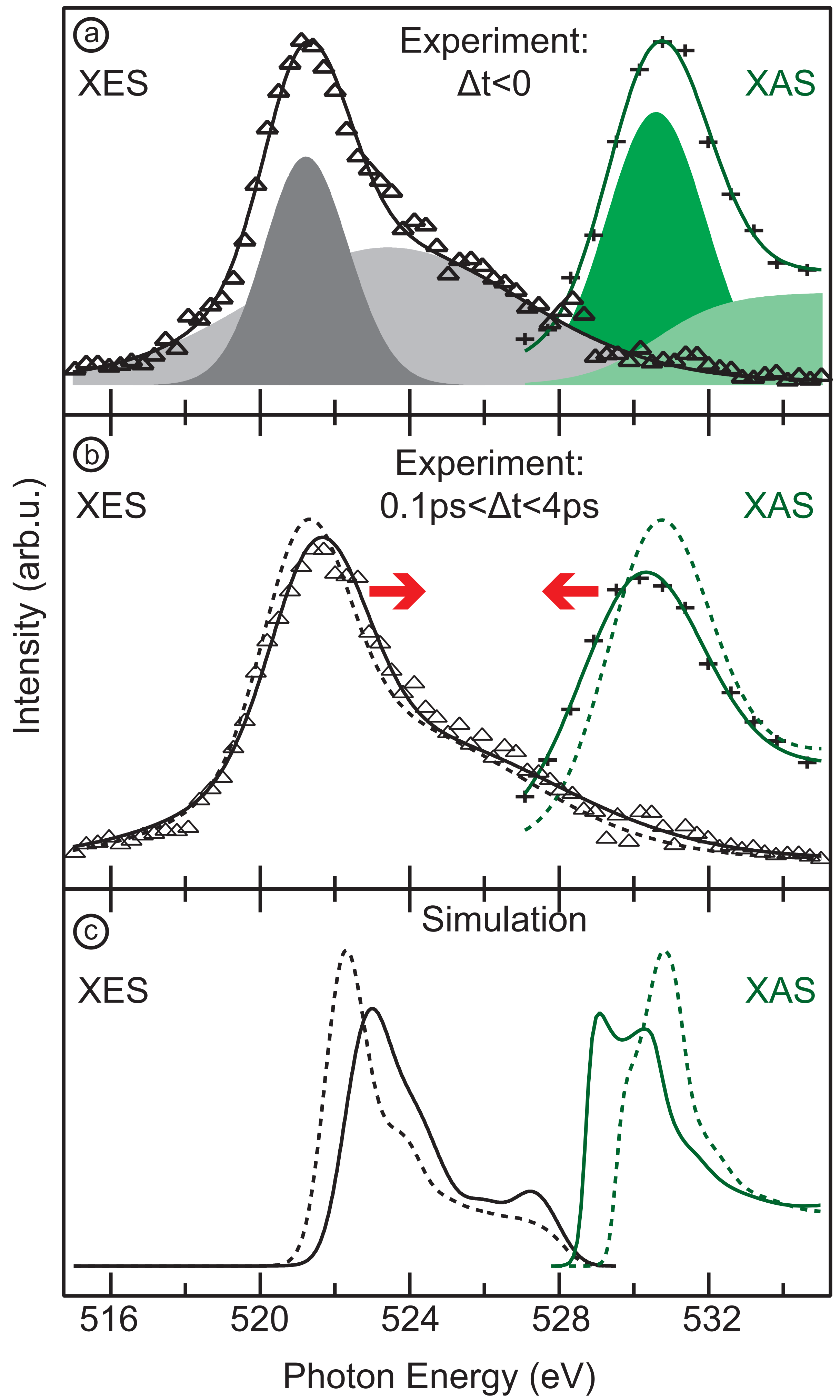
Activation of strongly bound O on Ru

Rate-limiting step, reduction of the bond strength (bonding-anti bonding splitting) directly observed

CO oxidation reaction
Nobel Prize for Chemistry in 2007: G. Ertl



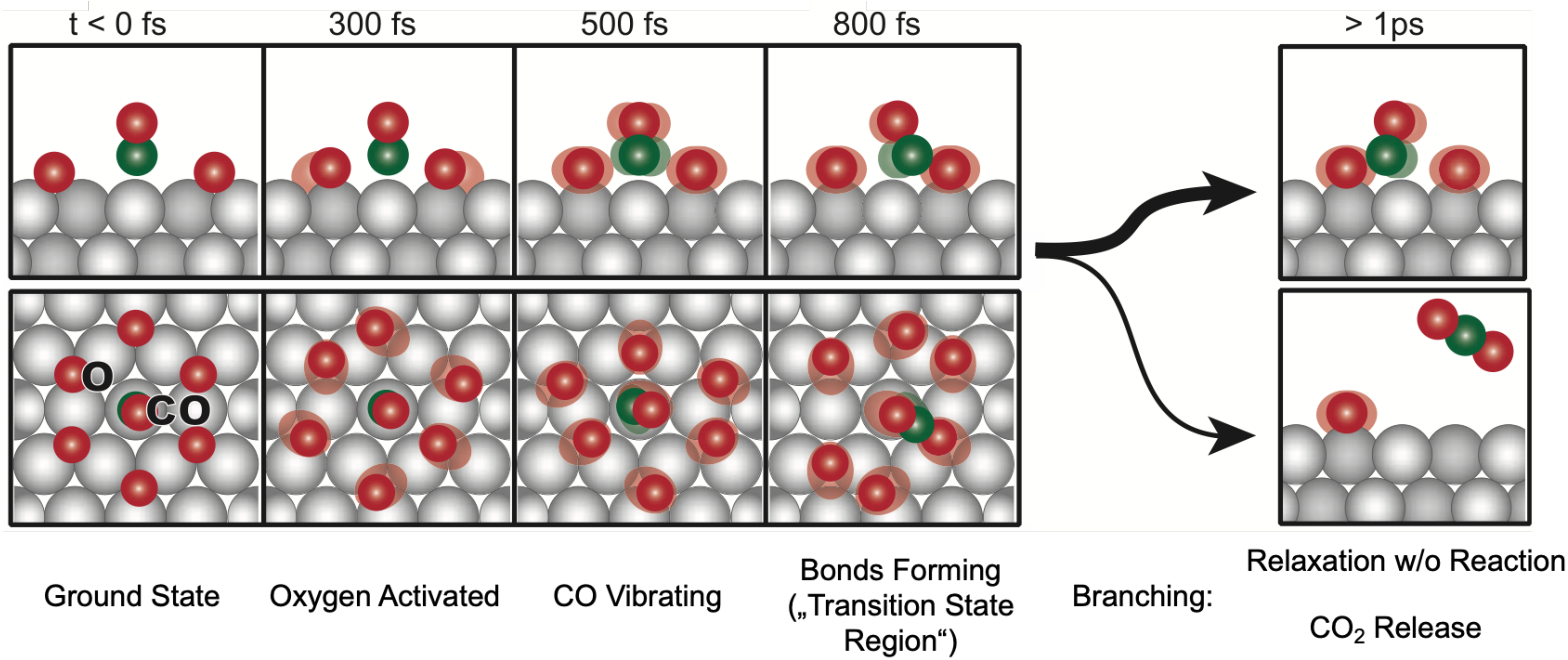




Beye et al., JPCL 7, 3647 (2016)

Transition State Region in CO Oxidation

Summary



H. Öström, et al., Science 347, 978 (2015)

Outline

- Introduction to free-electron lasers
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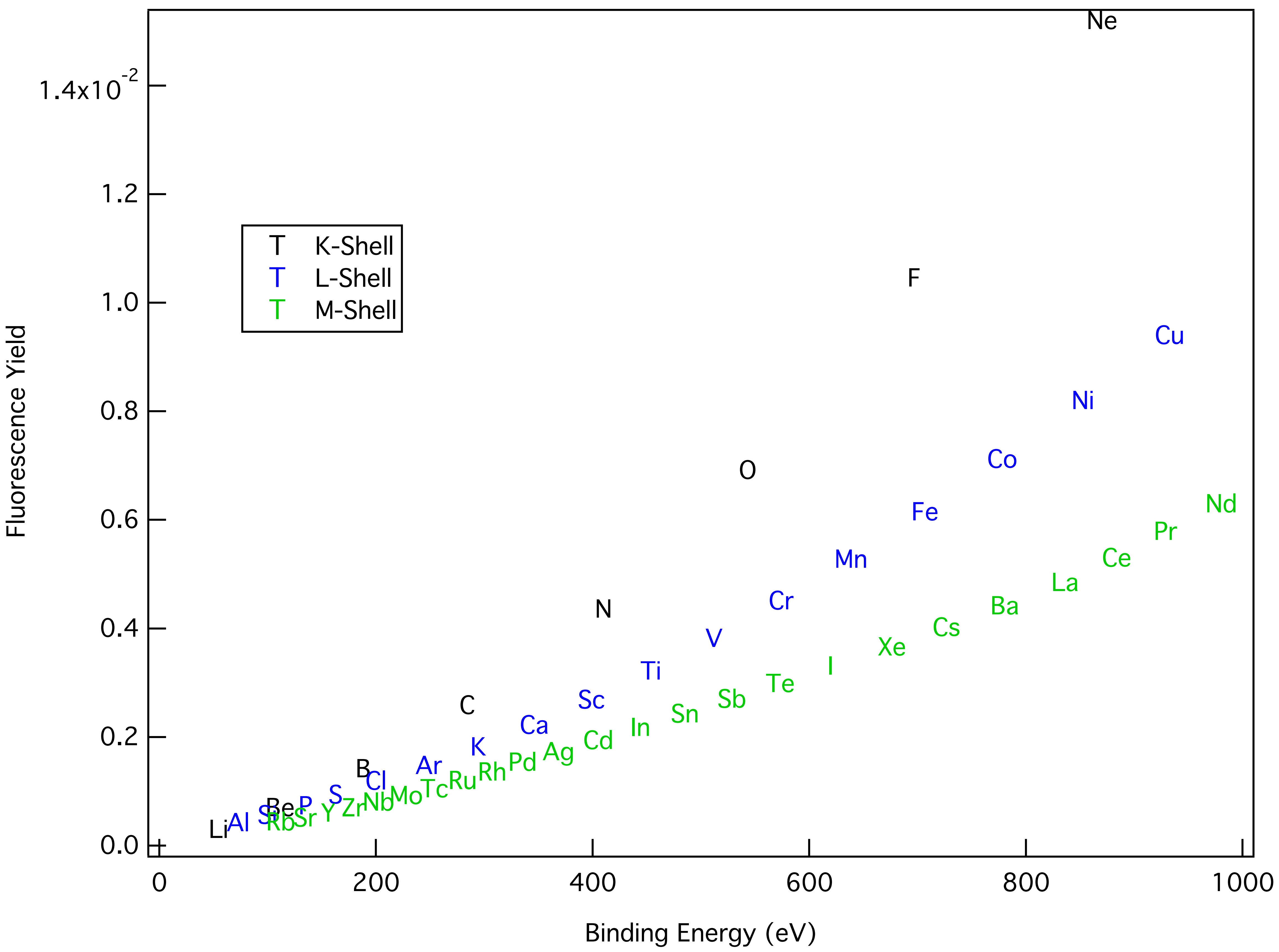
Soft X-ray RIXS limitations

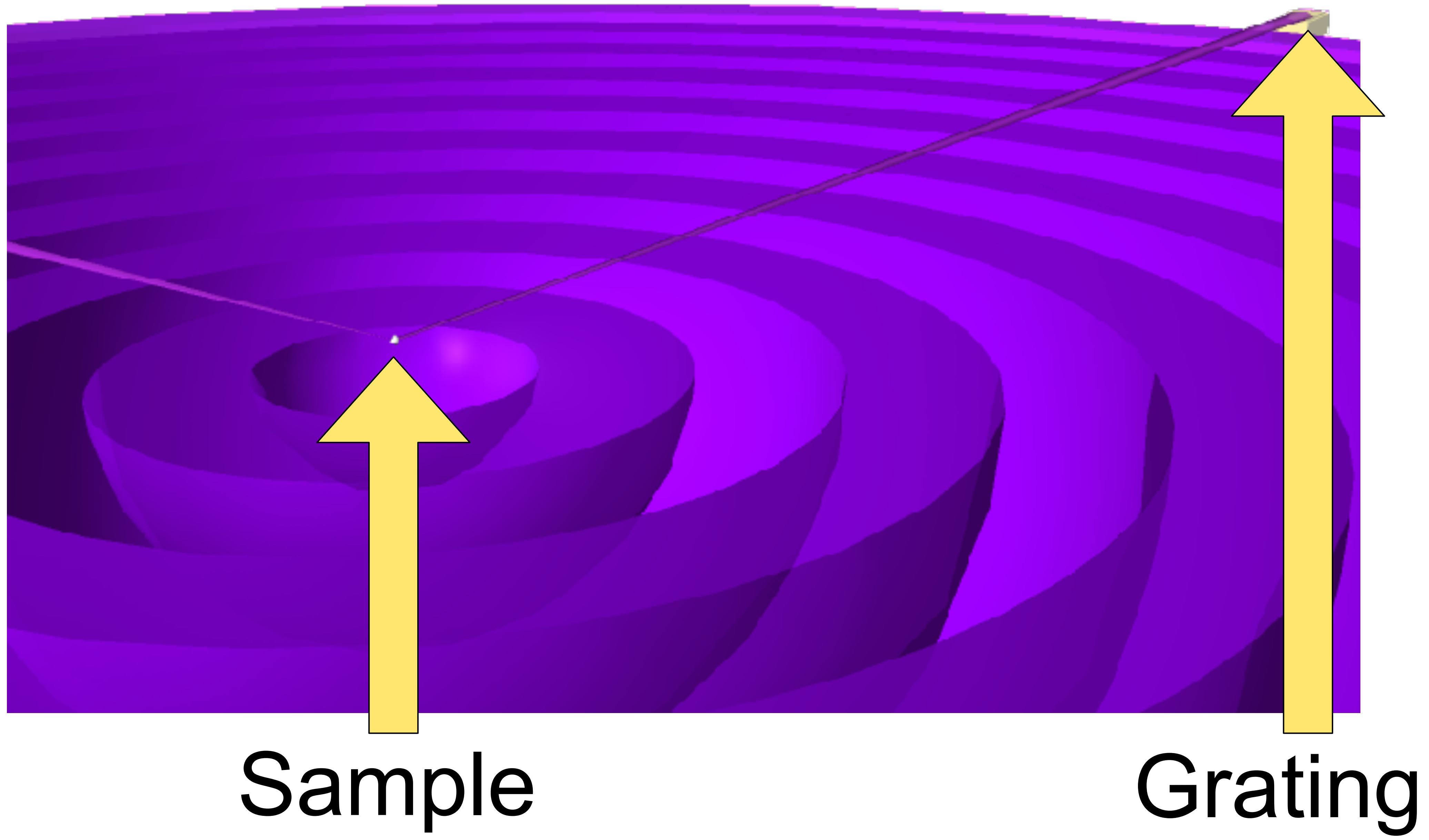
Low yield, low acceptance

Fluorescence yield of 10^{-2} to 10^{-3}



Hubbell, J. H. et al. J Phys Chem Ref Data ***23,*** *339 (1994)*

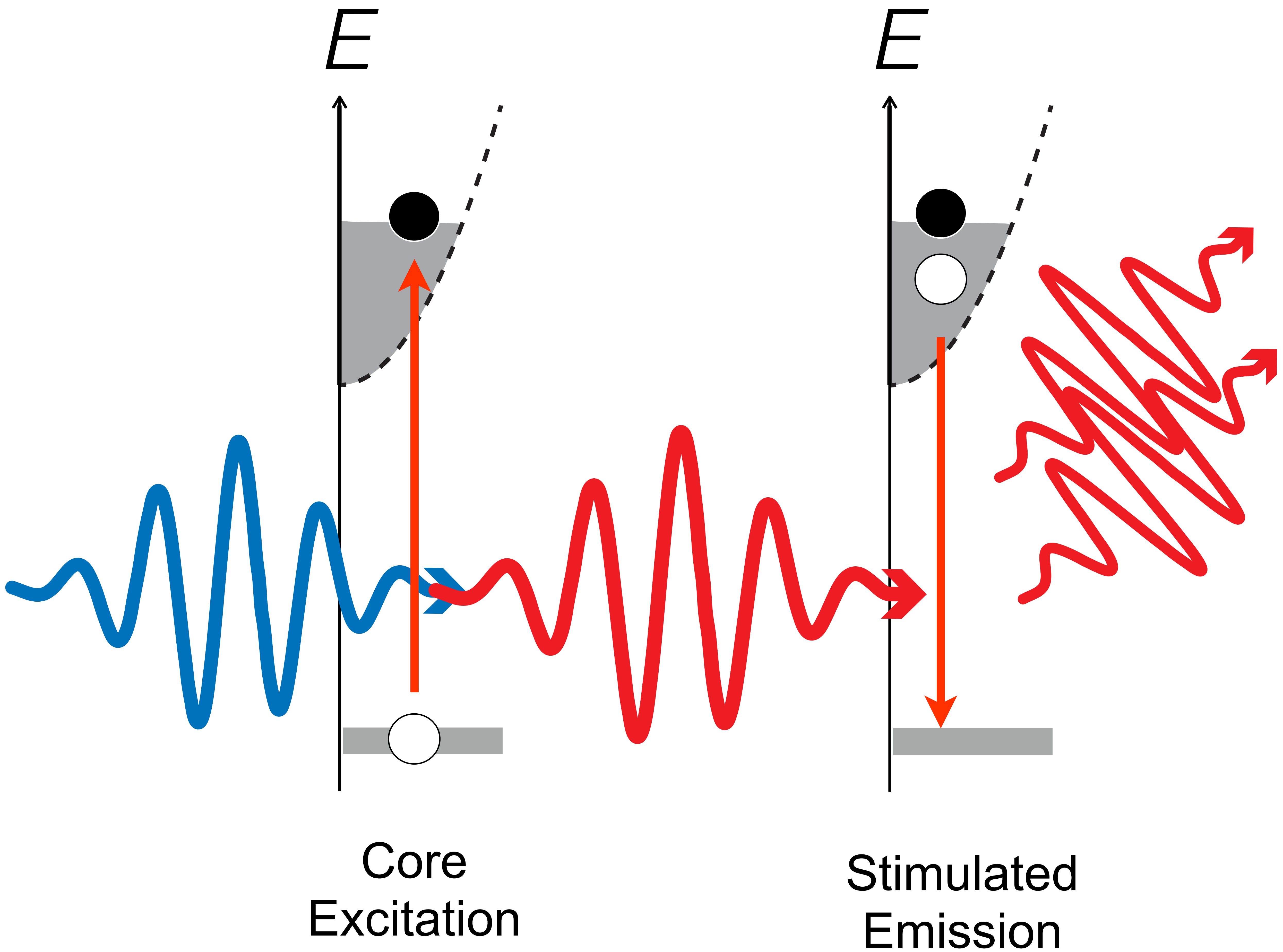
Isotropic Emission, but
Geometrical Spectrometer Acceptance
10^{-5} to 10^{-4} of 4π



Impulsively stimulated RIXS @ LCLS

Broadband short SASE pulses on Co metal

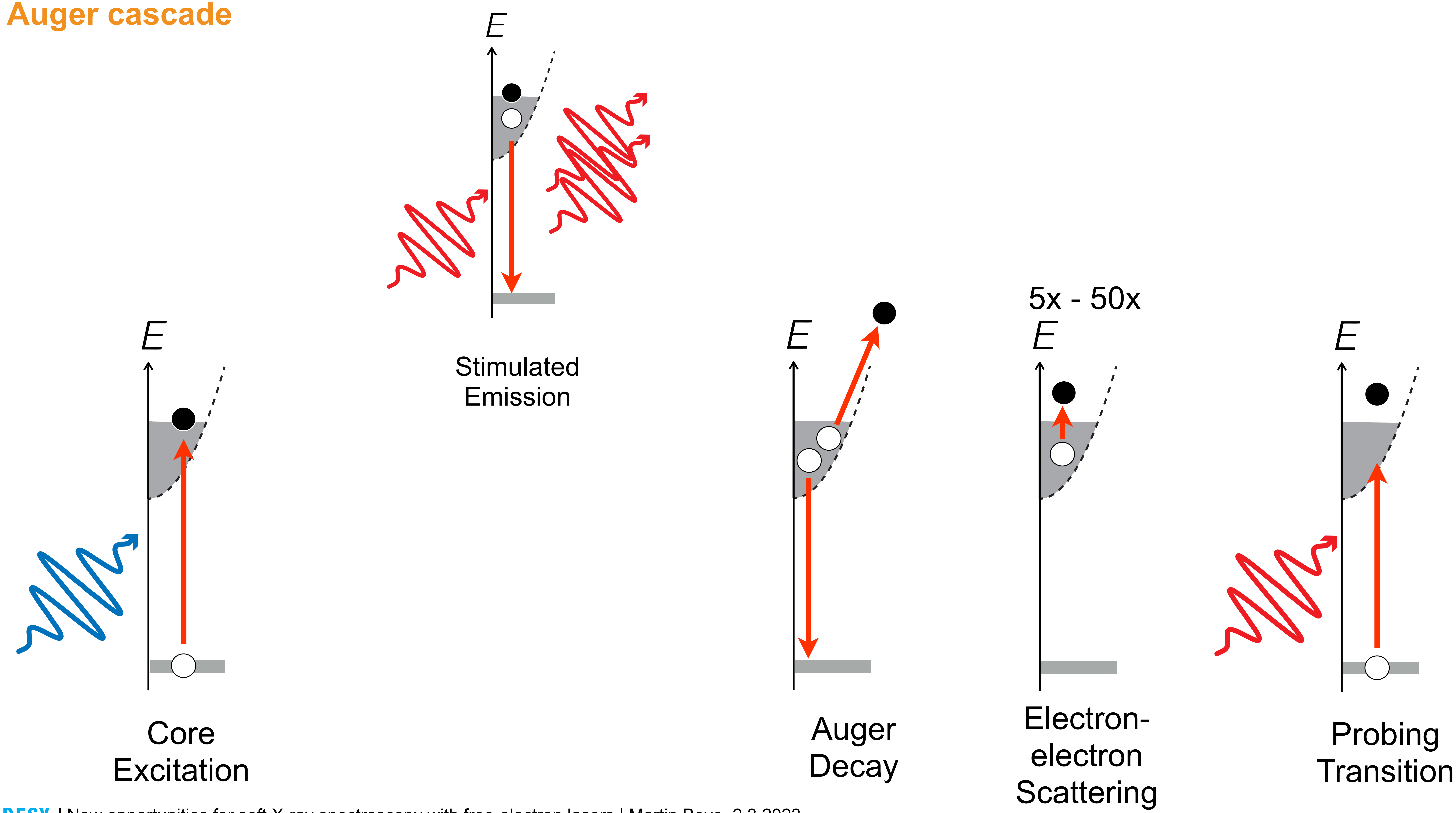
D. Higley
Z. Chen
M. Beye
M. Hantschmann
A. H. Reid
V. Mehta
O. Hellwig
G. L. Dakovski
A. Mitra
R. Y. Engel
T. Maxwell
Y. Ding
S. Bonetti
M. Bucher
S. Carron
T. Chase
E. Jal
R. Kukreja
T. Liu
A. Föhlisch
H. A. Dürr
W. F. Schlotter
J. Stöhr



Higley et al., Comm. Phys. 5, 83 (2022)

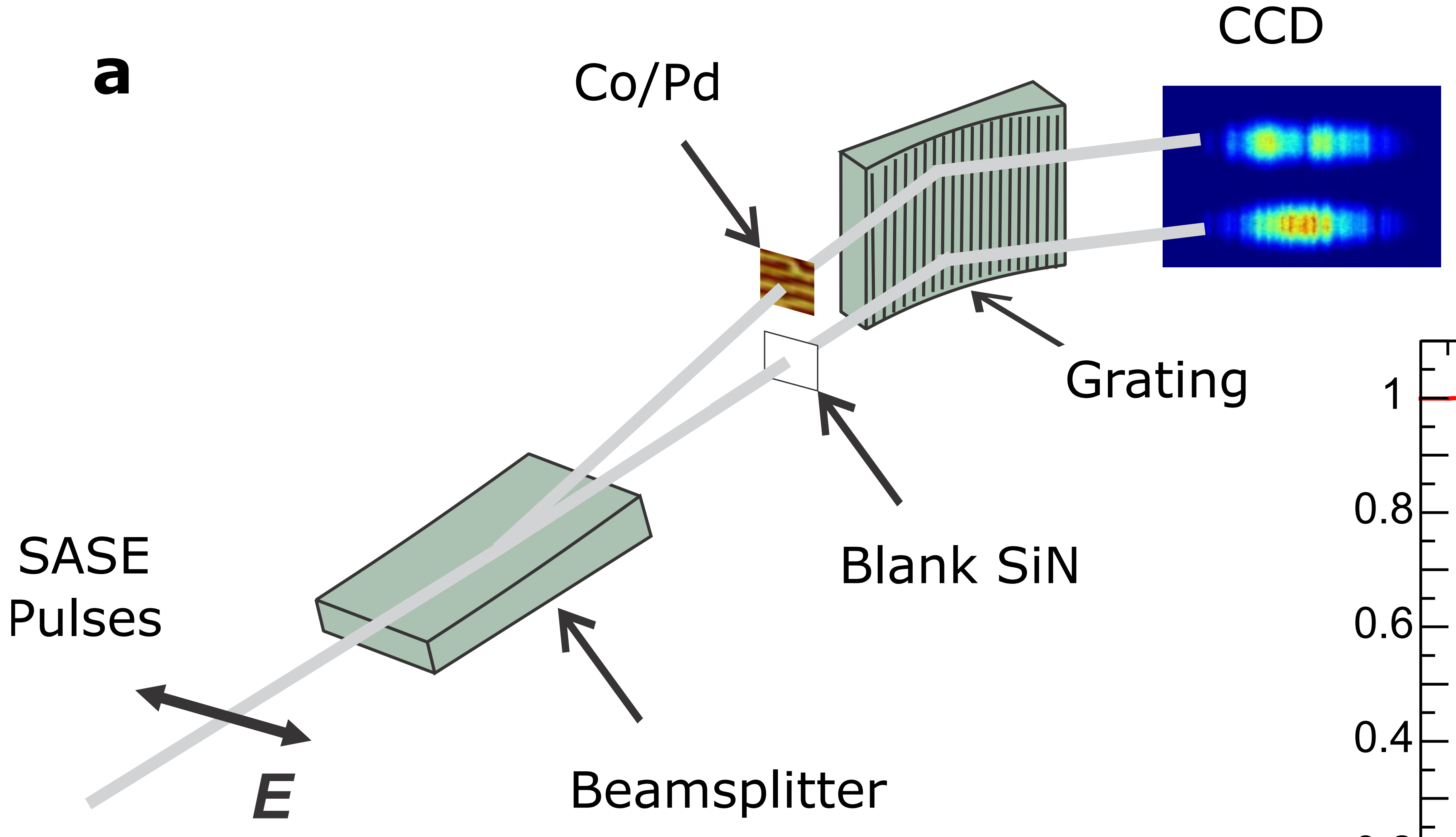
Concurrent processes

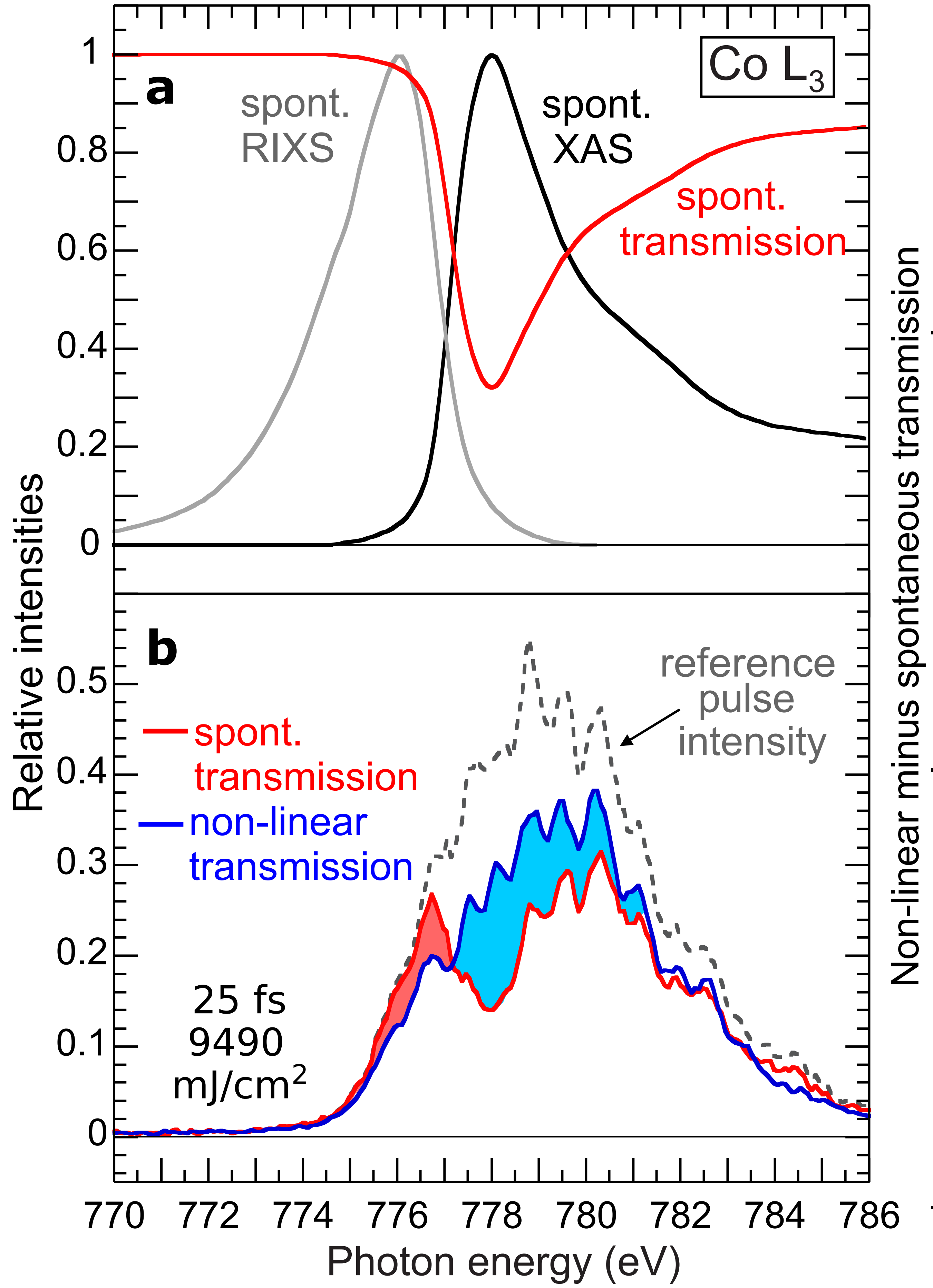
Auger cascade

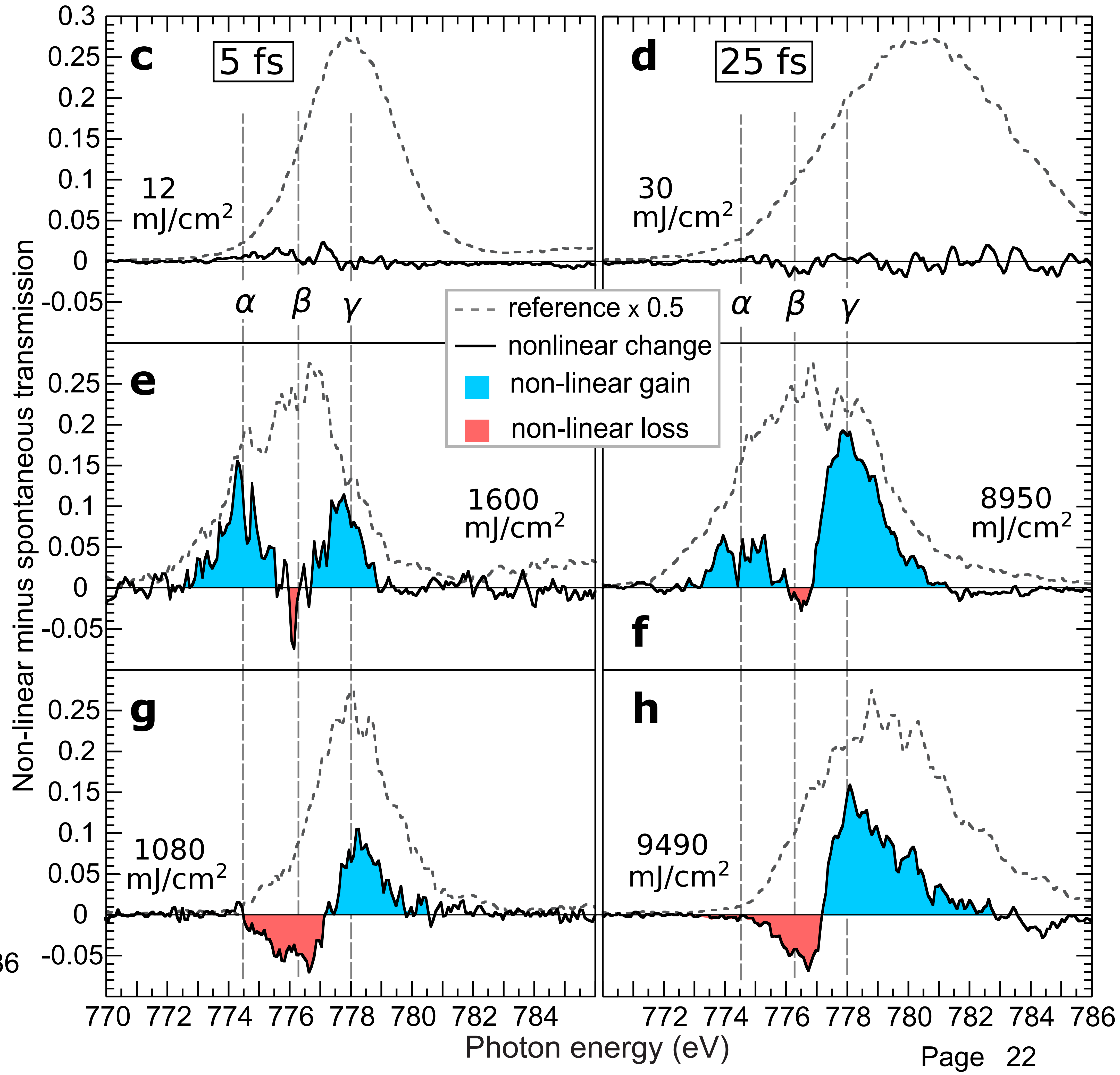


Impulsively stimulated RIXS

Next to Auger damage, stimulated emission is observed



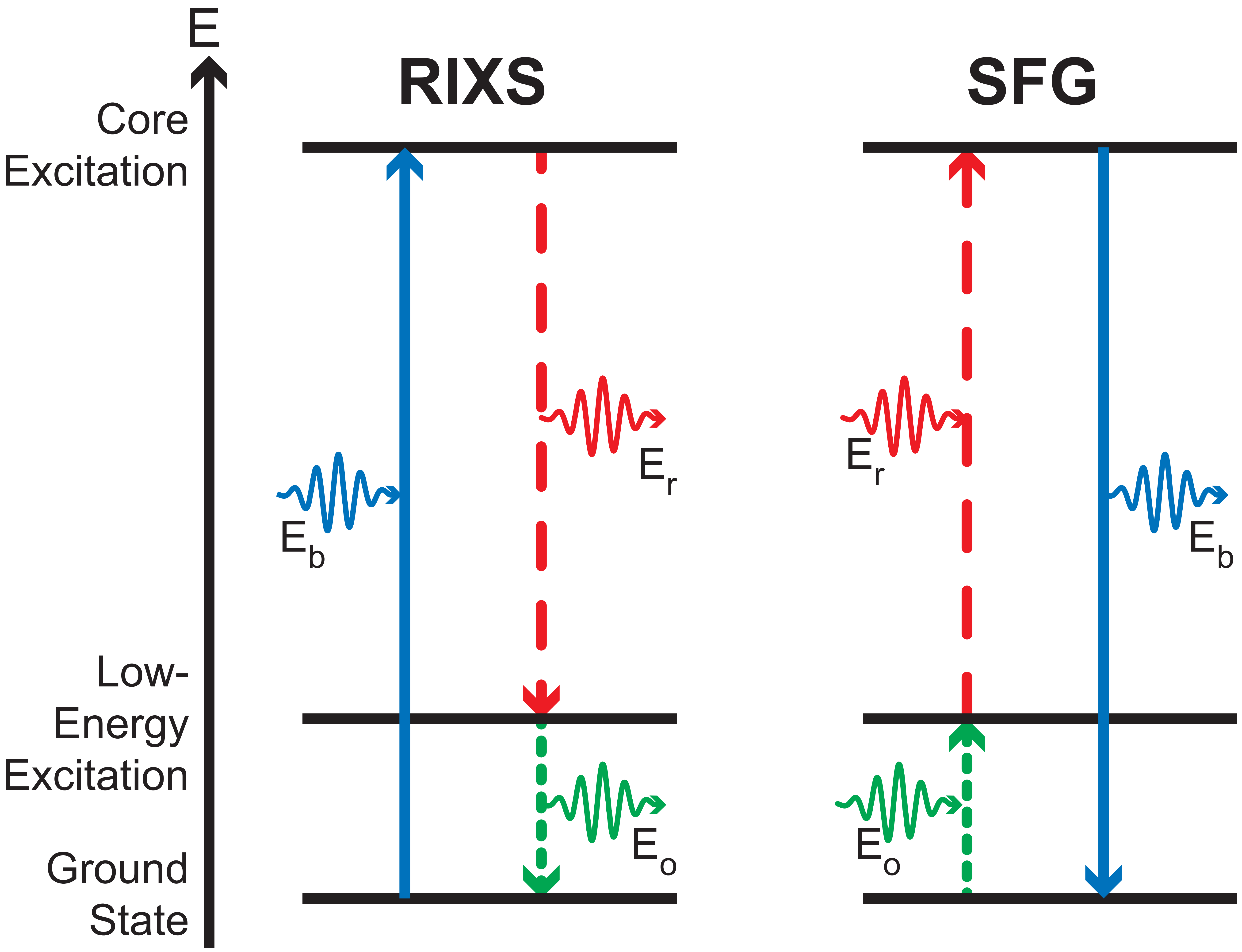




Higley et al., Comm. Phys. 5, 83 (2022)

Wave-mixing as a coherent alternative to RIXS?

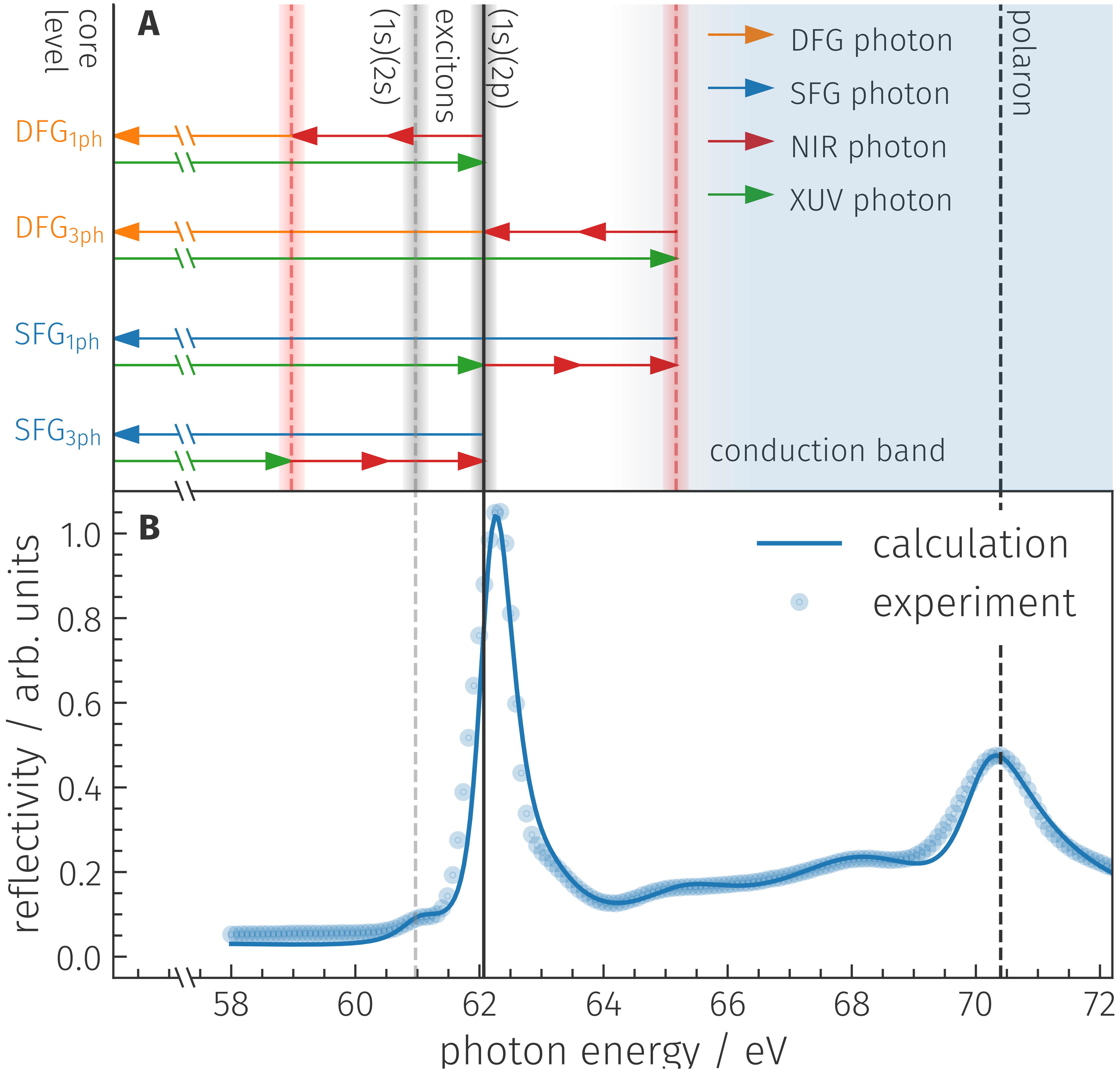
Similar excitations accessible, selection rules different, but coherent enhancement could be large

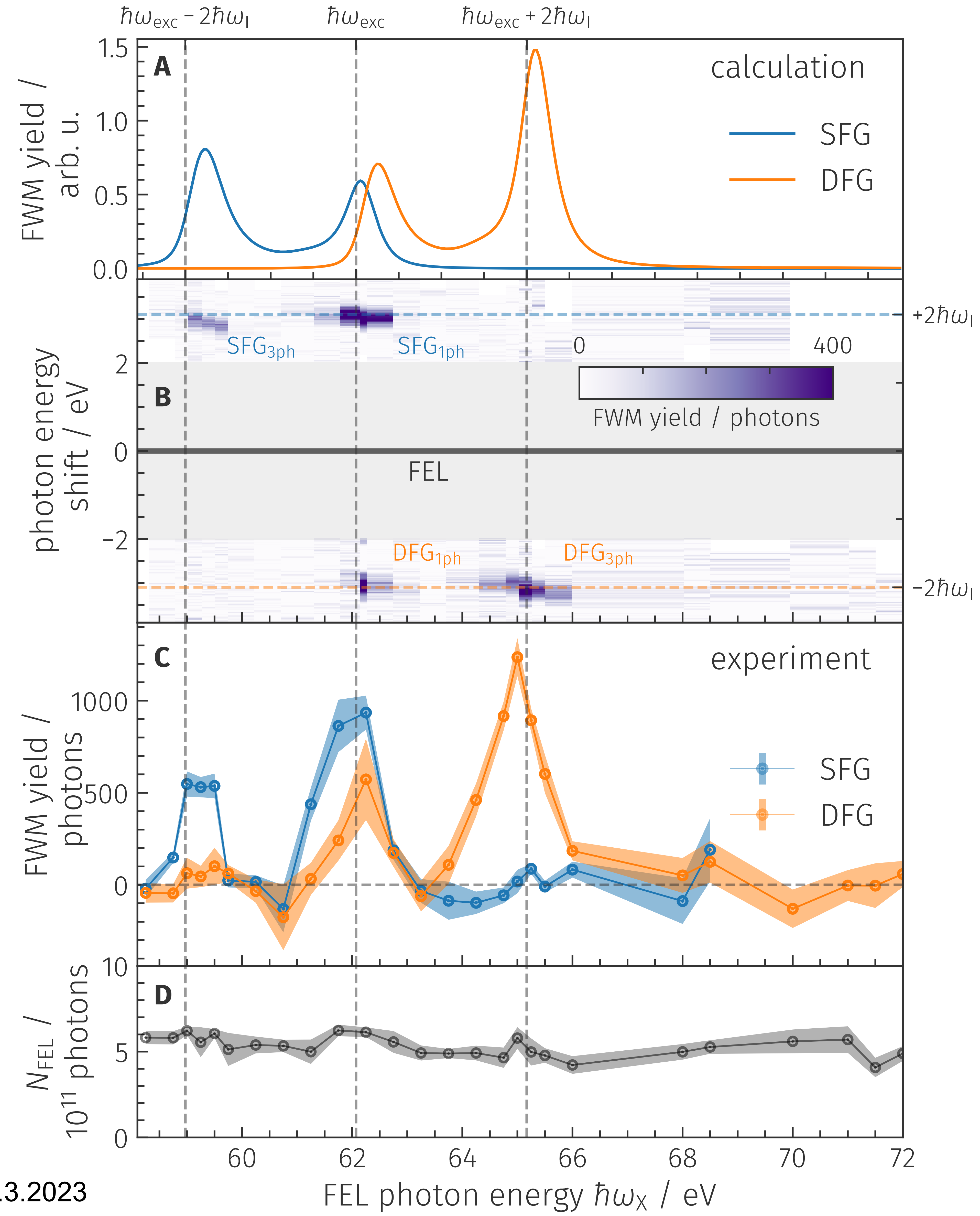


Beye et al., JPCM 31, 014003 (2019)

Wave-mixing as a coherent alternative to RIXS?

Four-wave mixing (2 optical ± 1 XUV = 1 new XUV) on LiF Li K-edge resonance





Rottke et al., Sci. Adv. eabn5127 (2022)

THANK YOU FOR YOUR ATTENTION.