“Inverse X-ray Photoemission Spectroscopy” with LIXS

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Principle of LIBS

LIBS = Laser Induced Breakdown Spectroscopy

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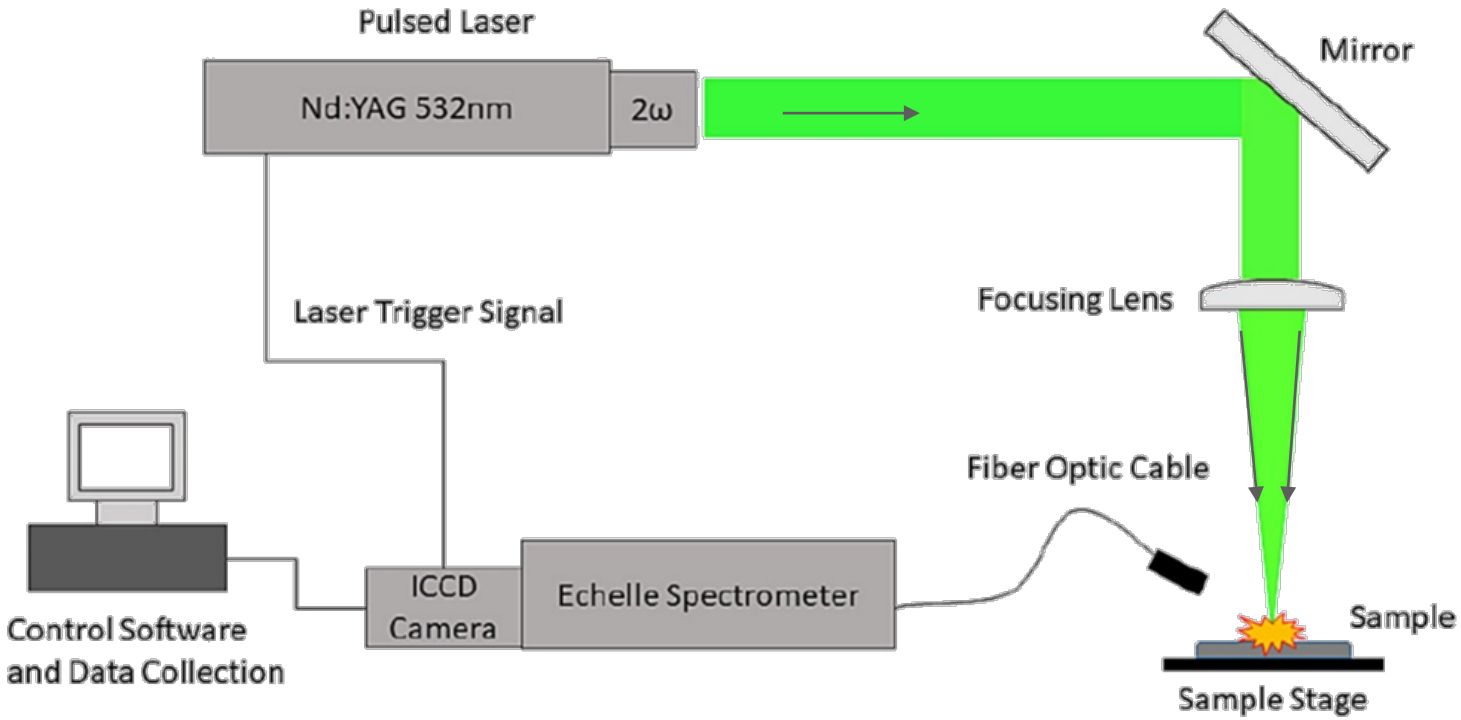
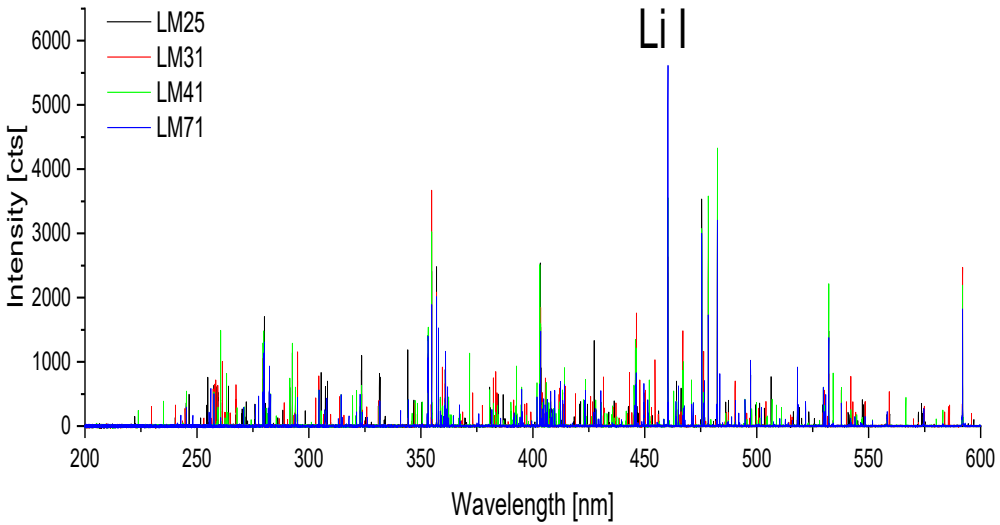
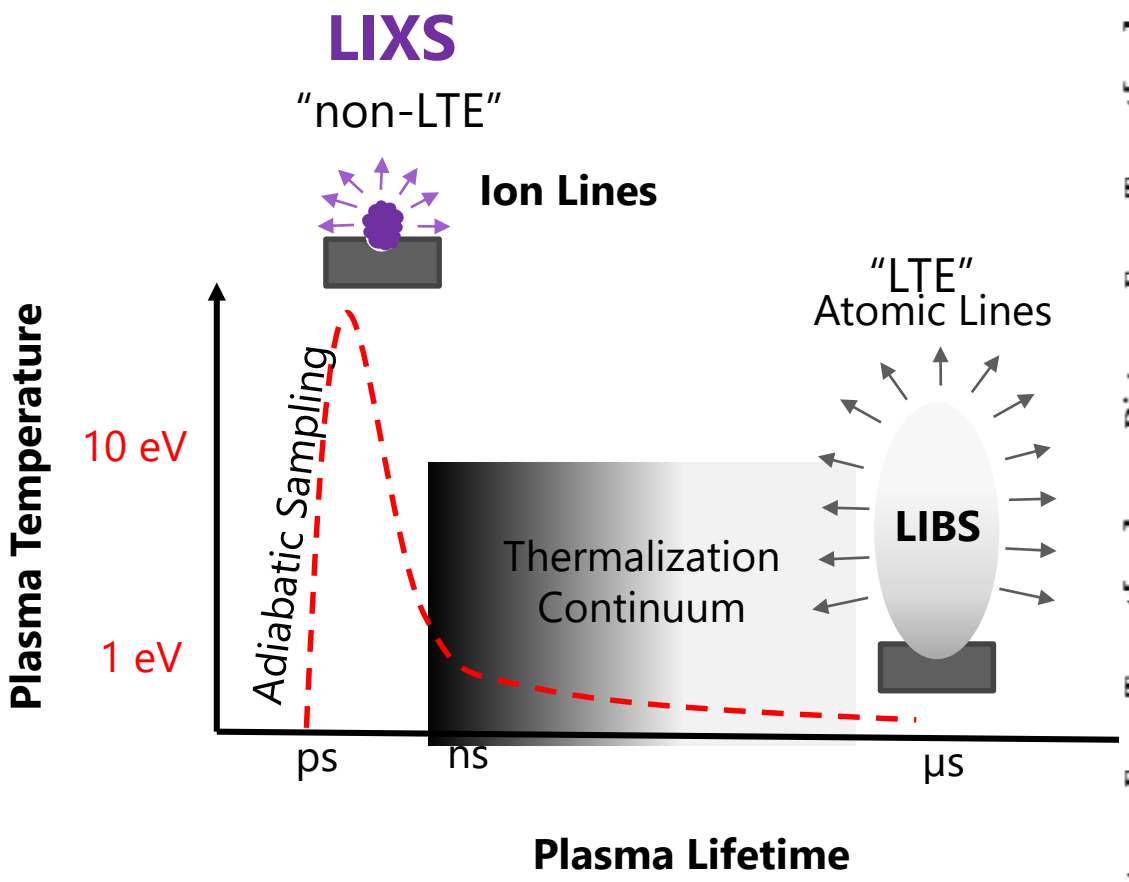


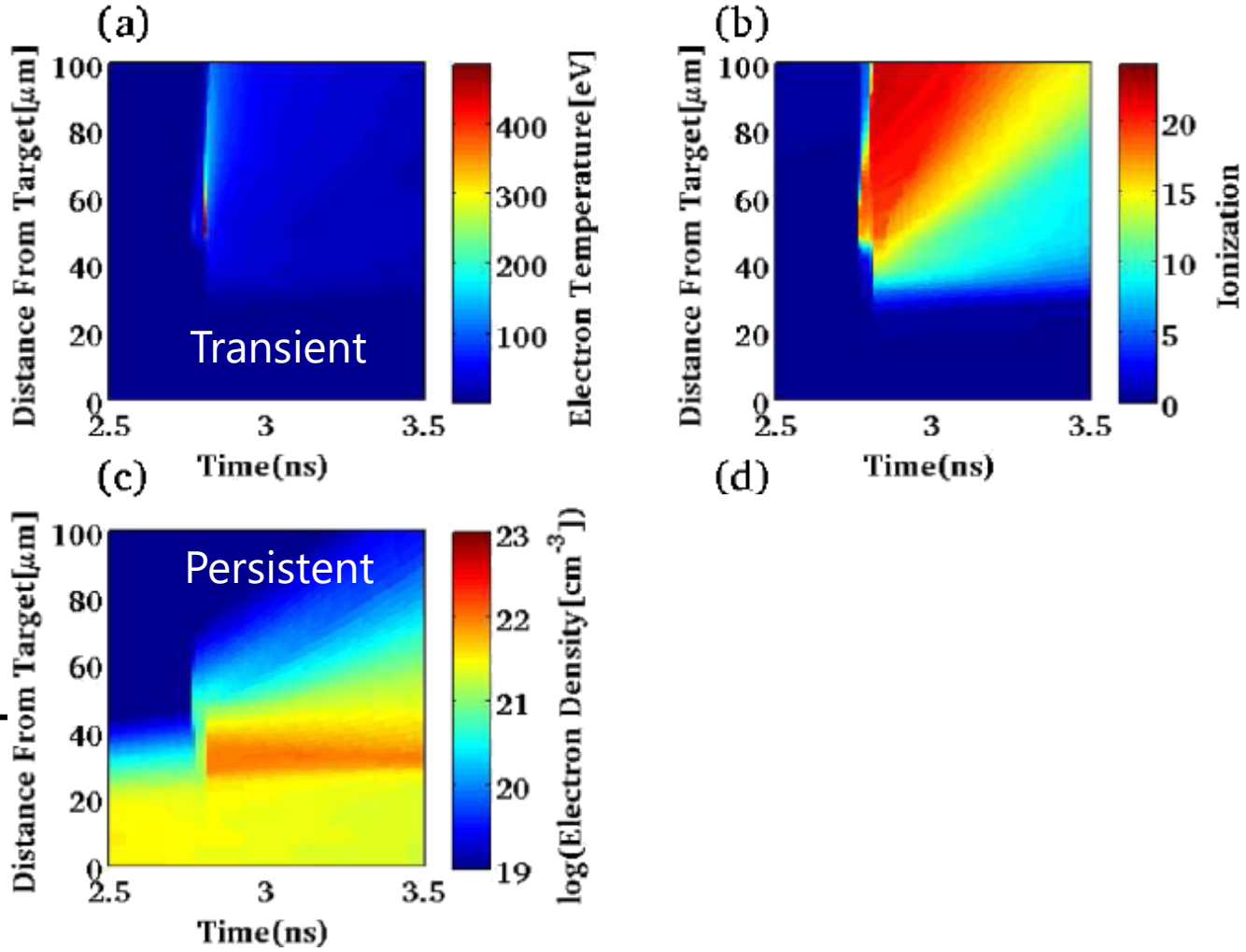


- LIBS has poor sensitivity for light elements and anions, e.g. Li, F
- LIBS suffers from to shot-to-shot poor reproducibility. e.g. >10%
- LIBS does not provide chemical information, e.g. Oxidation

Laser Plasma Evolution

LIXS = Laser Induced XUV Spectroscopy





Masoudnia L, Bleiner D. Optimum electron temperature and density for short-wavelength plasma-lasing from nickel-like ions. **Nuclear Instruments and Methods in Physics Research Section B: Beam Interactions with Materials and Atoms**. 2014 15;323:59-70.

Comparison of Spectroscopies

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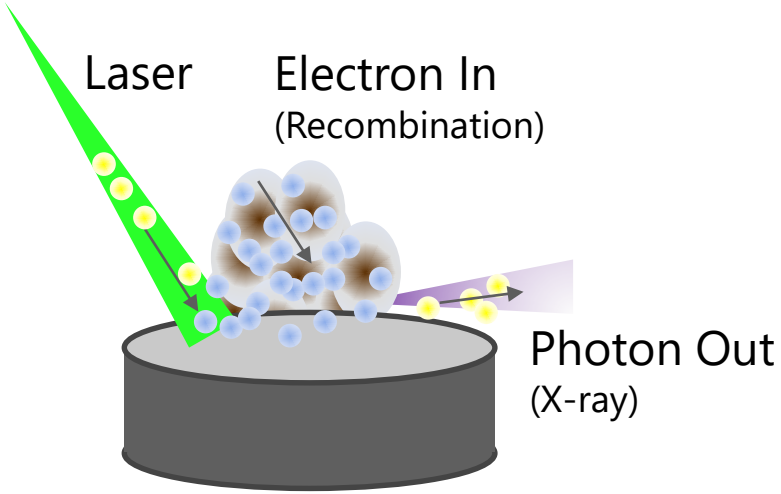
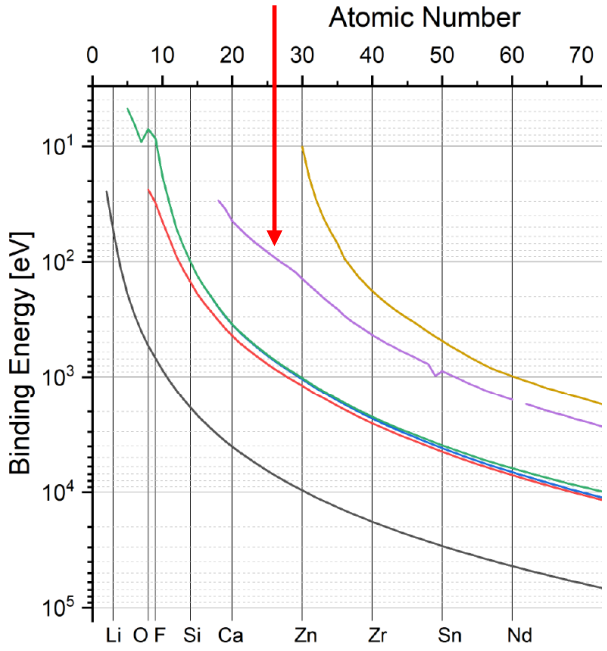


Plasma emission



Sommerfeld-Kossel Displacement Laws

1. The first spark (singly ionized) spectrum of an element is similar to the arc (neutral) spectrum of the preceding element

2. The Z+1 spark spectrum is similar to the Z spark spectrum of the preceding element.

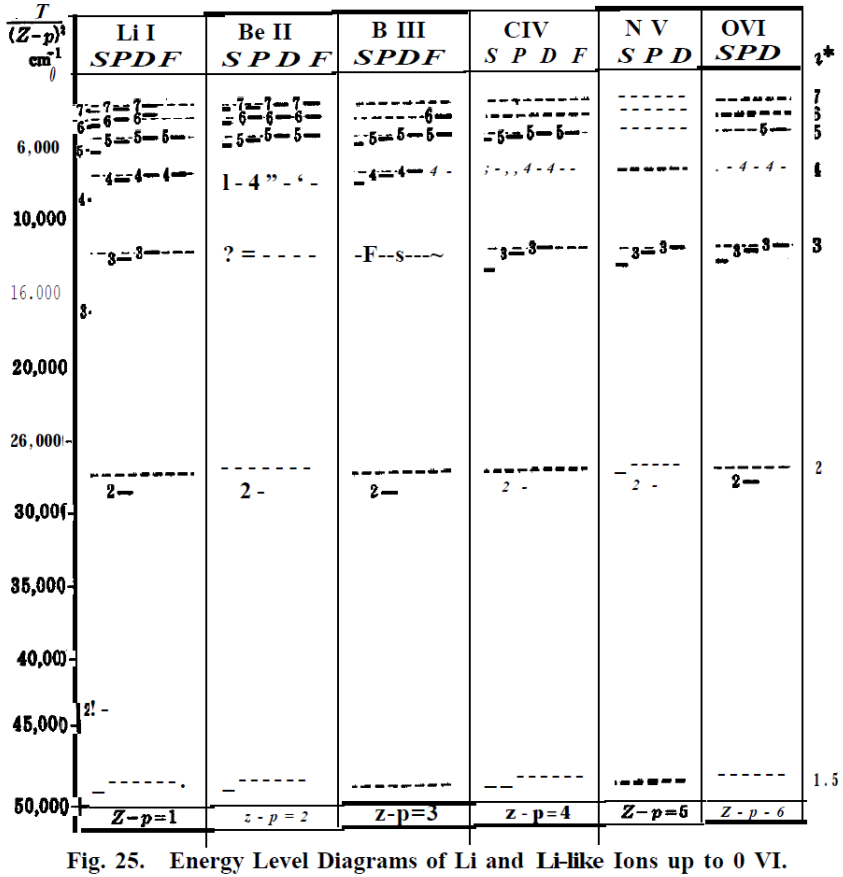
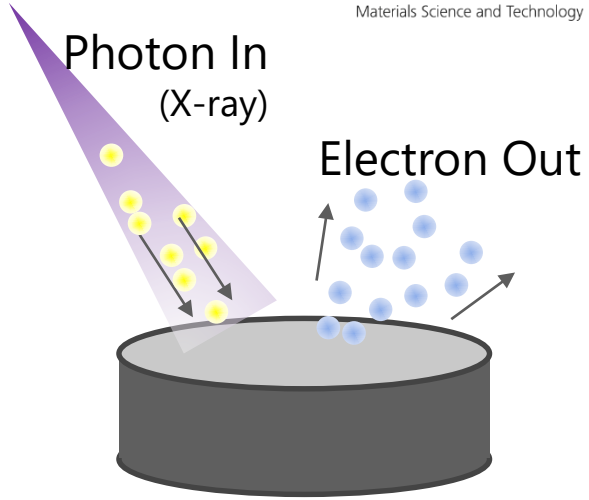
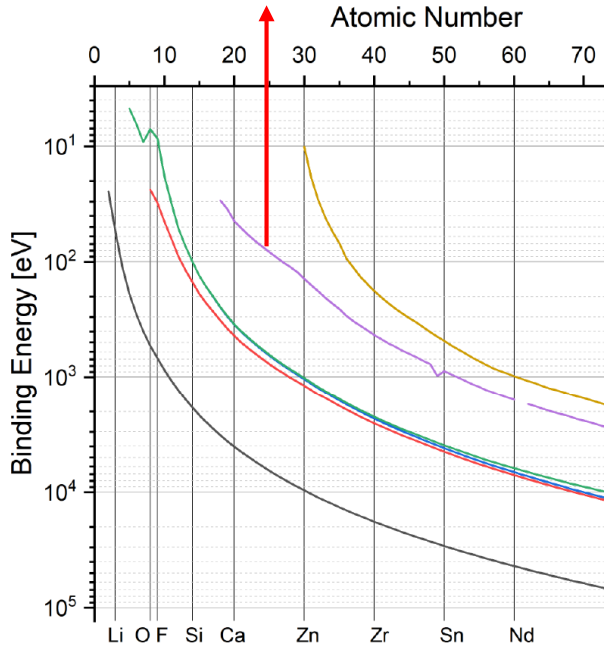


Fig. 25. Energy Level Diagrams of Li and Li-like Ions up to 0 VI.

Herzberg, 1944



Photoemission



Ionization Degree Alters the Emission Energy

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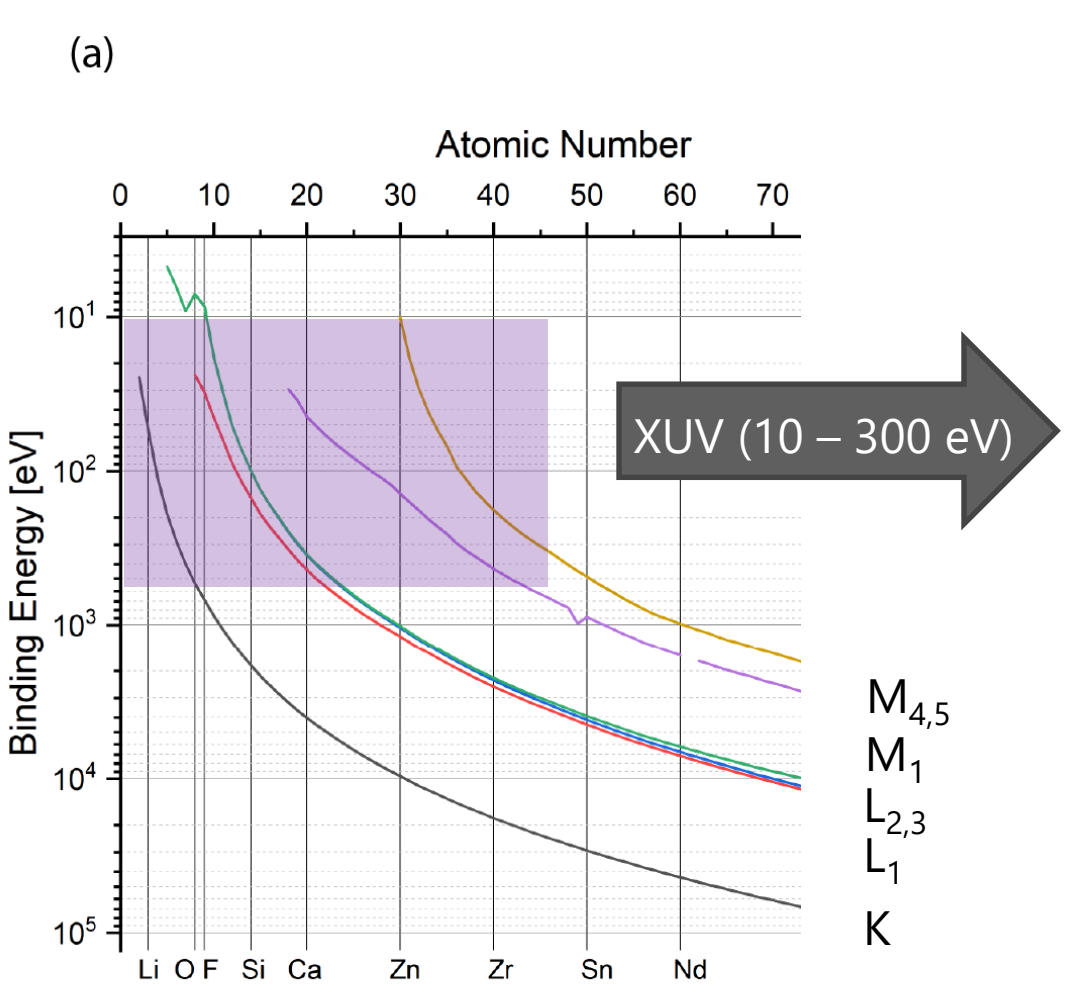
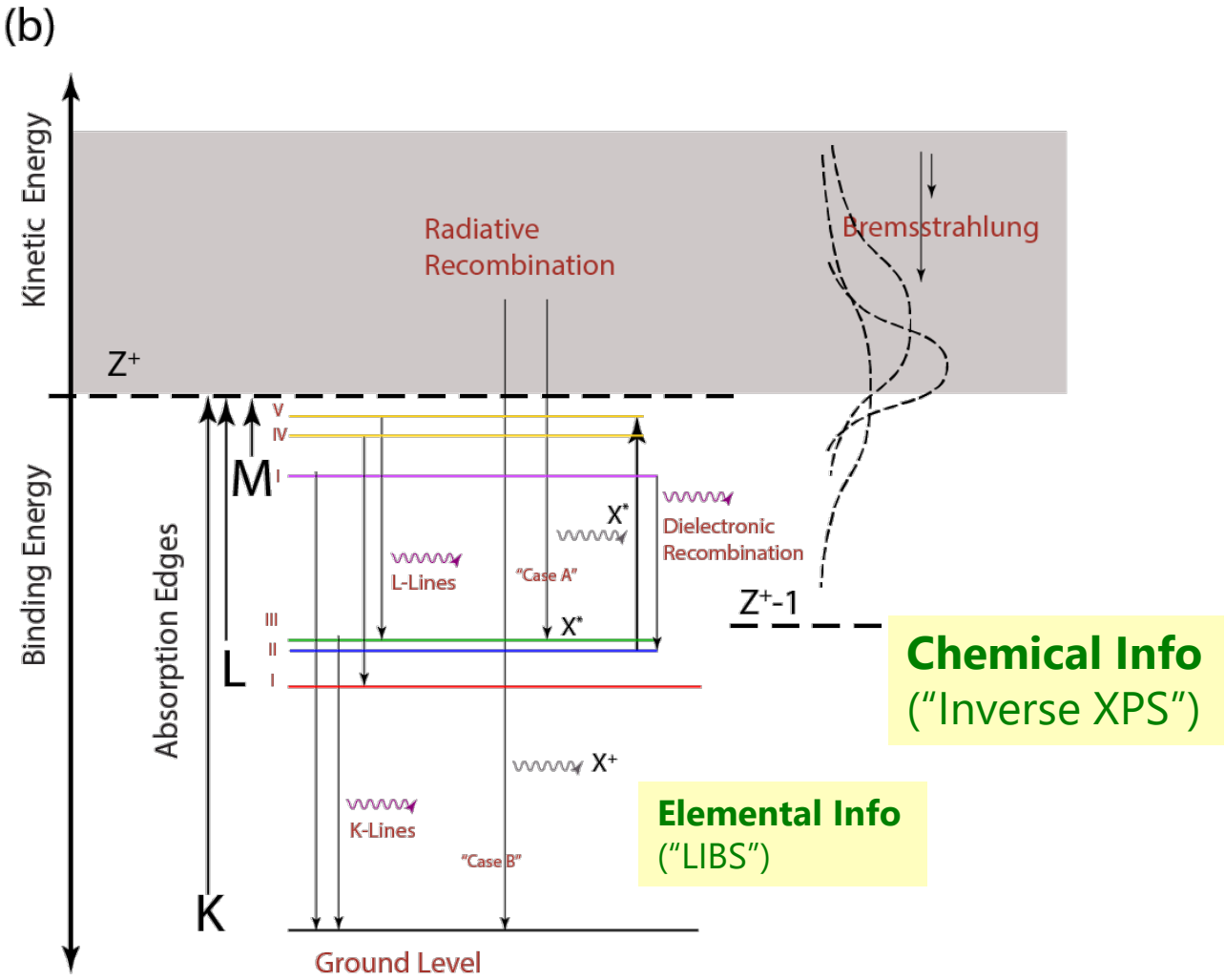




Bleiner, D, et al. "Laser-induced XUV spectroscopy (LIXS): From fundamentals to application for high-precision LIBS."
Spectrochimica Acta Part B: Atomic Spectroscopy (2023): 106668.

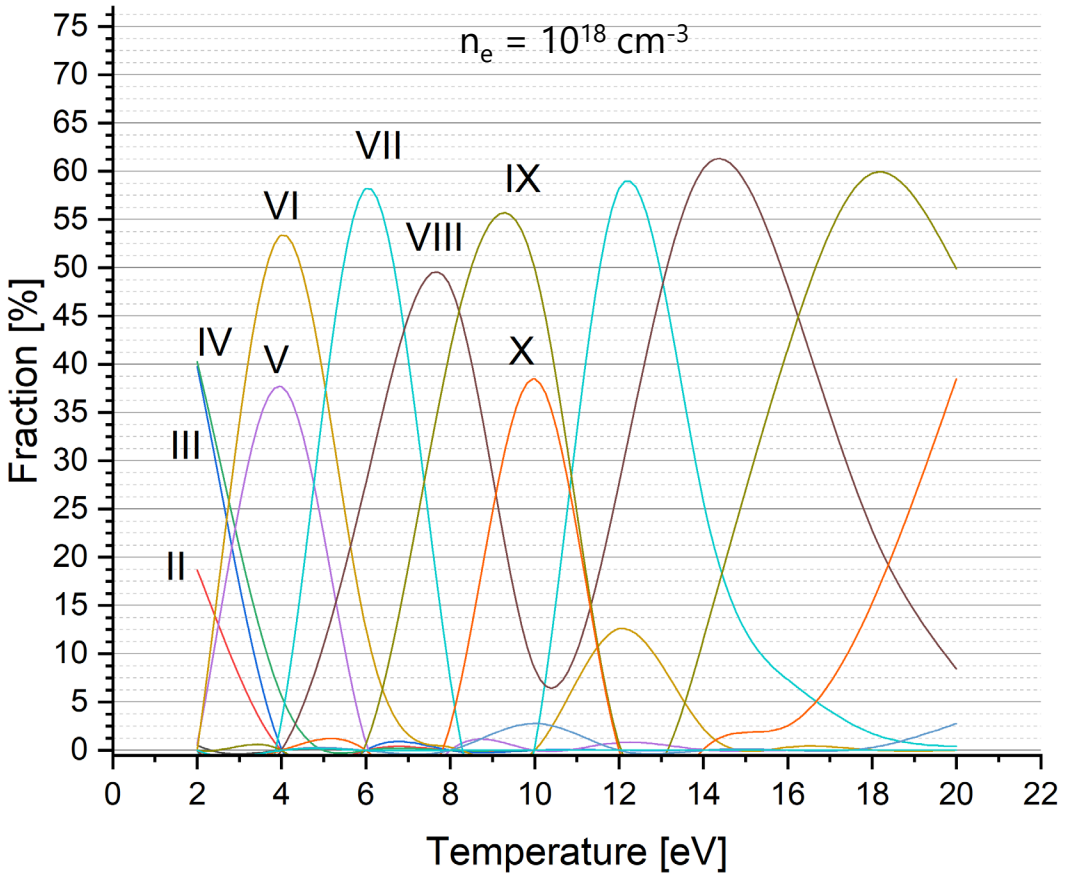
Ionization Stages in the non-LTE* Plasma

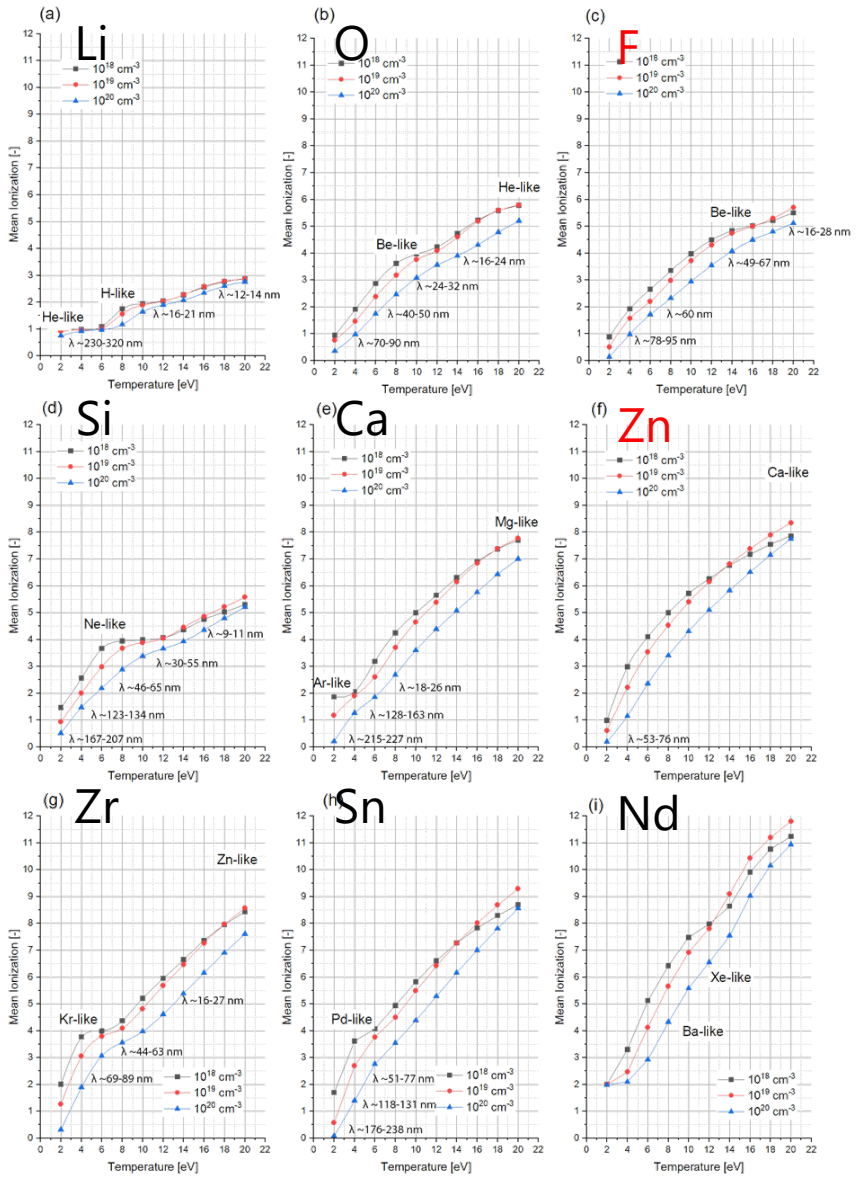
*Non Local Thermic Equilibrium

Zinc Ion Population

I II III

$Zn^{o} \rightleftharpoons Zn^{+1} \rightleftharpoons Zn^{+2} \rightleftharpoons \ldots$





Internal Standardization Eliminates Multiplicative Effects

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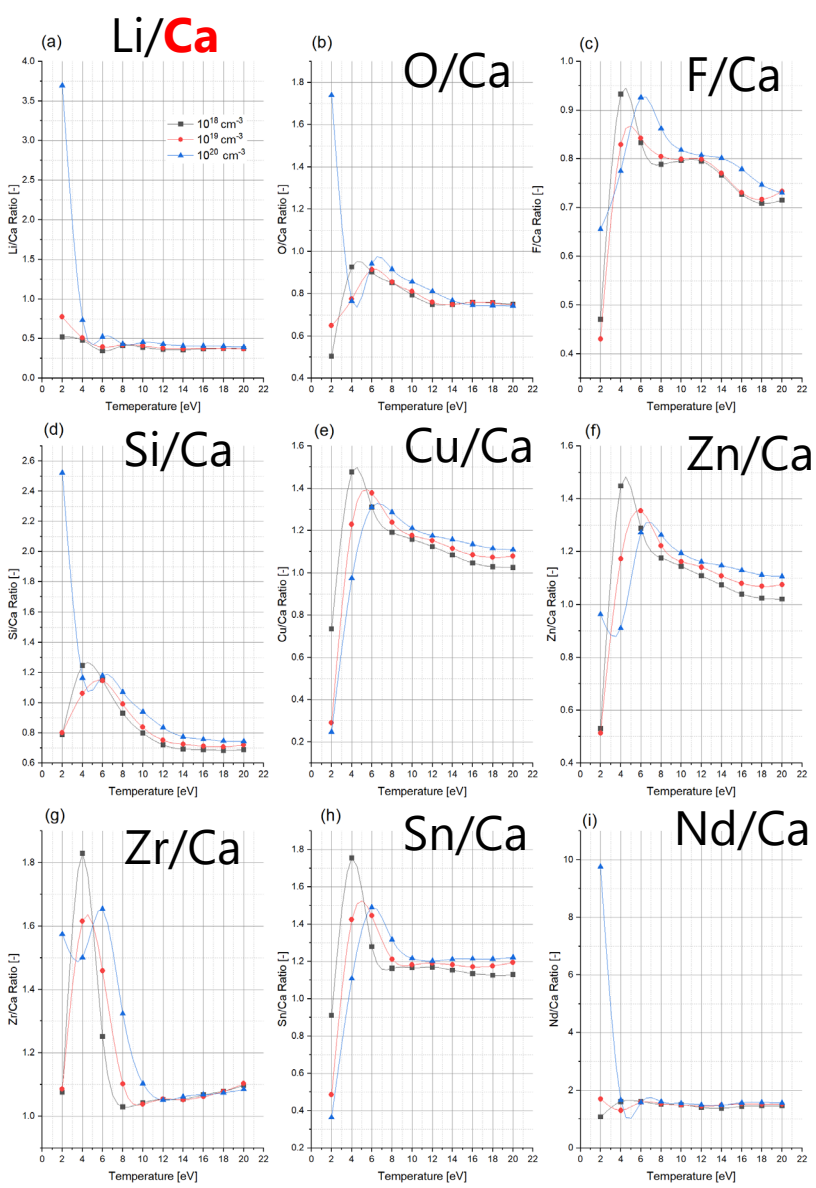

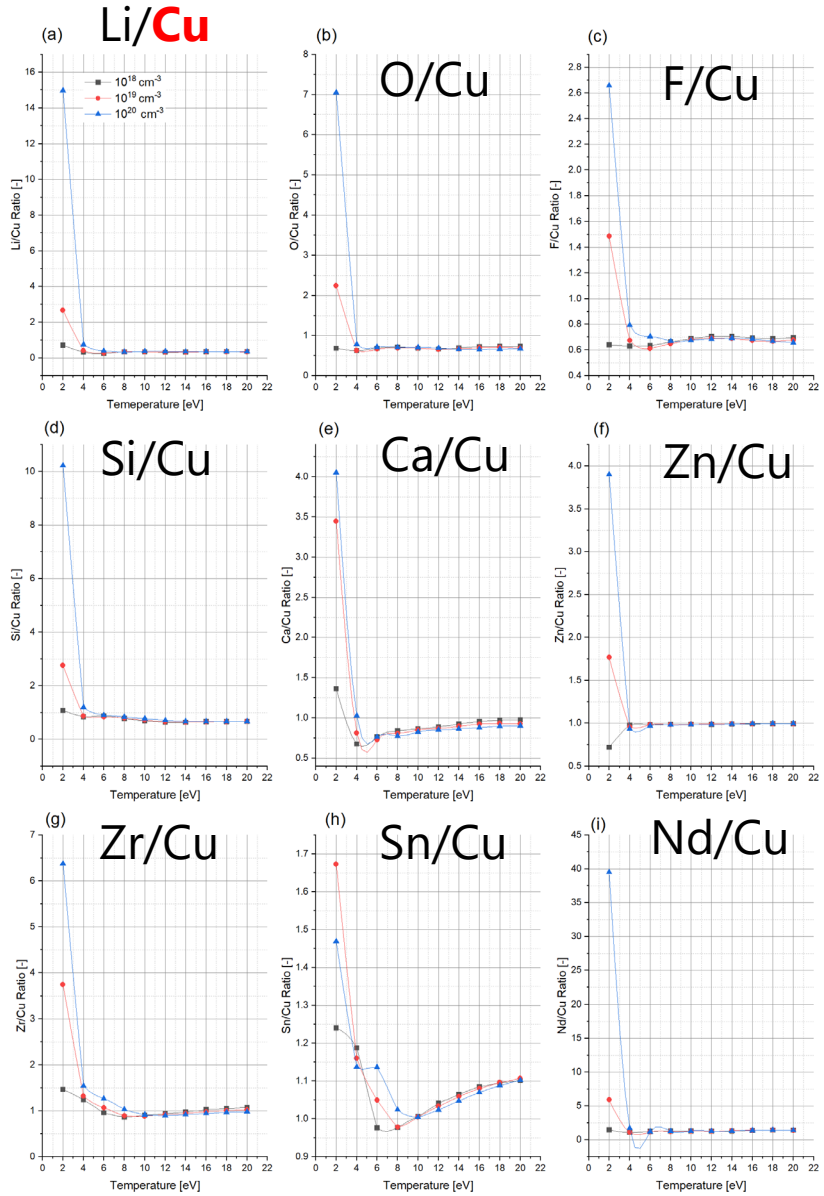

Further Readings

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ELSEVIER
Spectrochimica Acta Part B: Atomic Spectroscopy
Volume 204, June 2023, 106668

Laser-induced XUV spectroscopy (LIXS): From fundamentals to application for high-precision LIBS

Davide Bleiner [a b], Di Qu [a b], Kevin Kraft [a b], Oksana Shlyakhtun [b]

ELSEVIER
Spectrochimica Acta Part B: Atomic Spectroscopy
Volume 181, July 2021, 106214

High-precision mapping of fluorine and lithium in energy materials by means of laser-induced XUV spectroscopy (LIXS)

Di Qu [a b], Natacha Ohannessian [c d], Corino Wyder [a], Matthias Trottmann [a], Adrian Wichser [a], Thomas Lippert [c d], Davide Bleiner [a d b]

The Big 3 Challenges for LIXS

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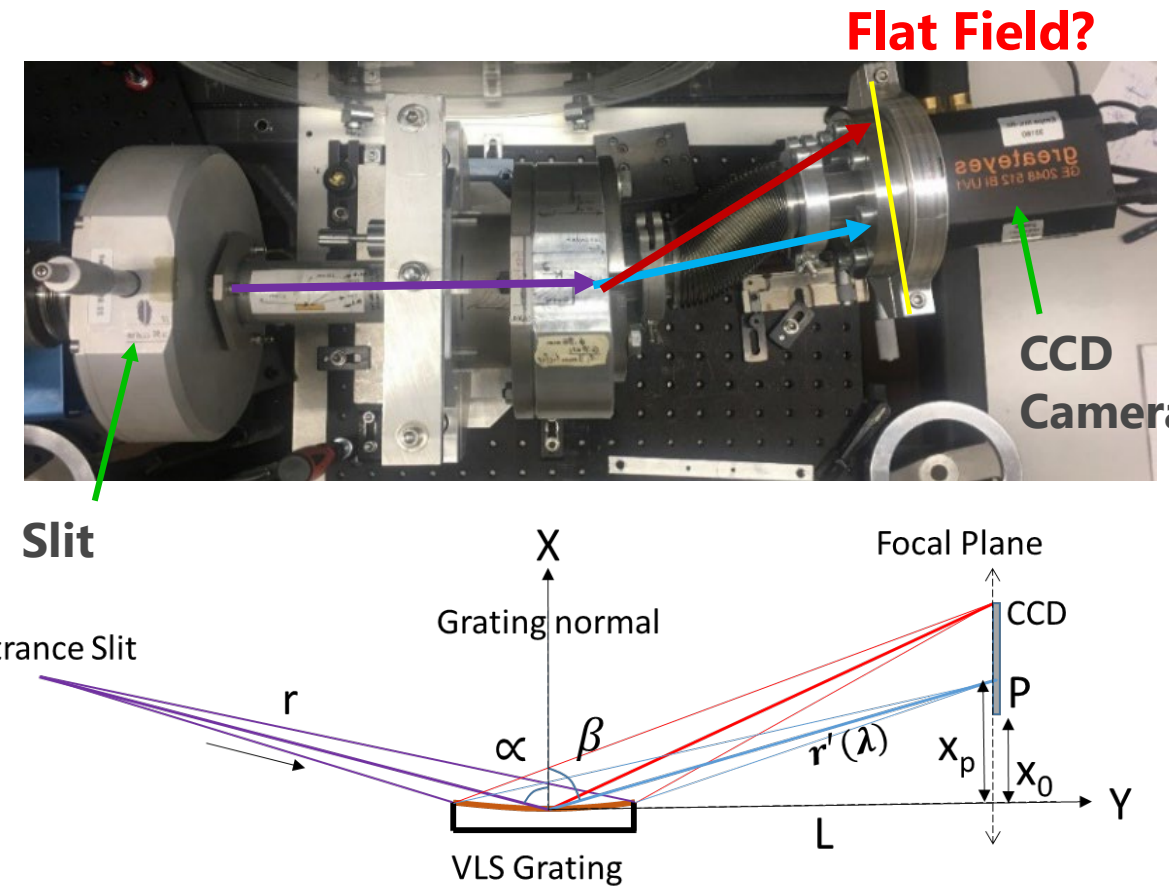
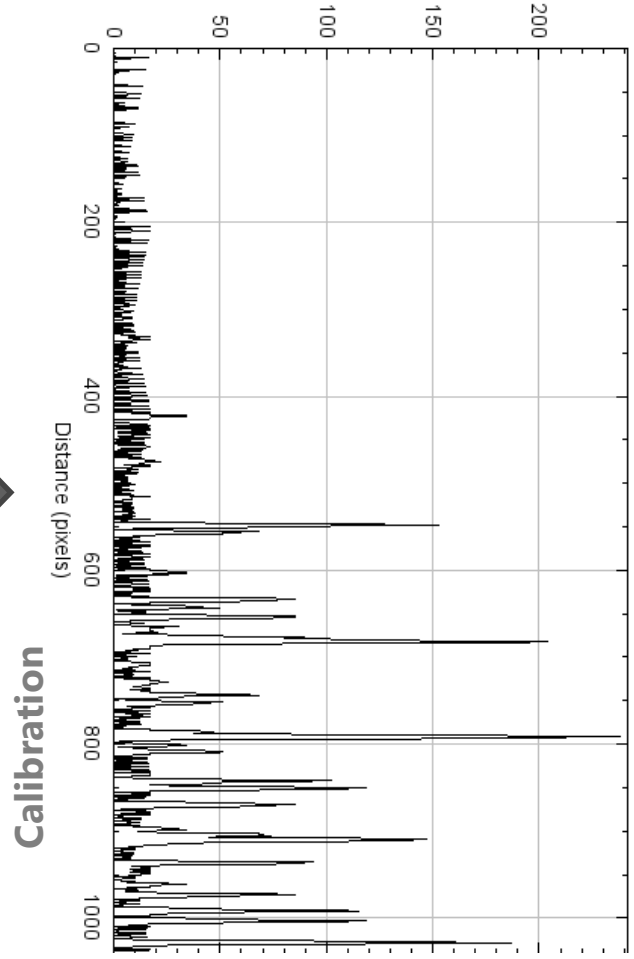
- Resolution of XUV Lines
- Flat-Field Collection
- Non-Linear Calibration



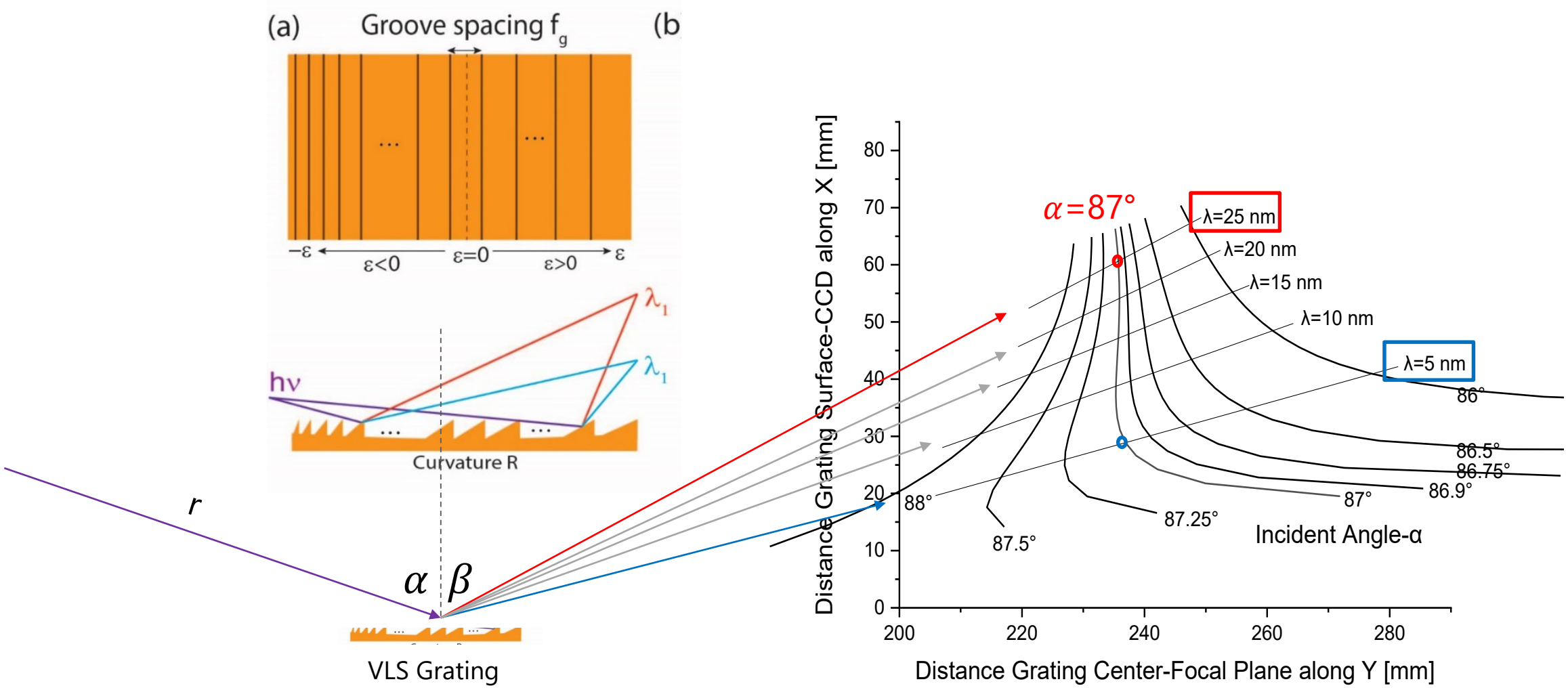
Resolution

Flat Field



Flat-Field Imaging of Spectrum using VLS*-Grating

*Varying Line Spacing



Dual Spectrometer Setup

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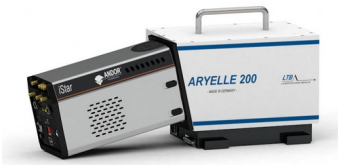
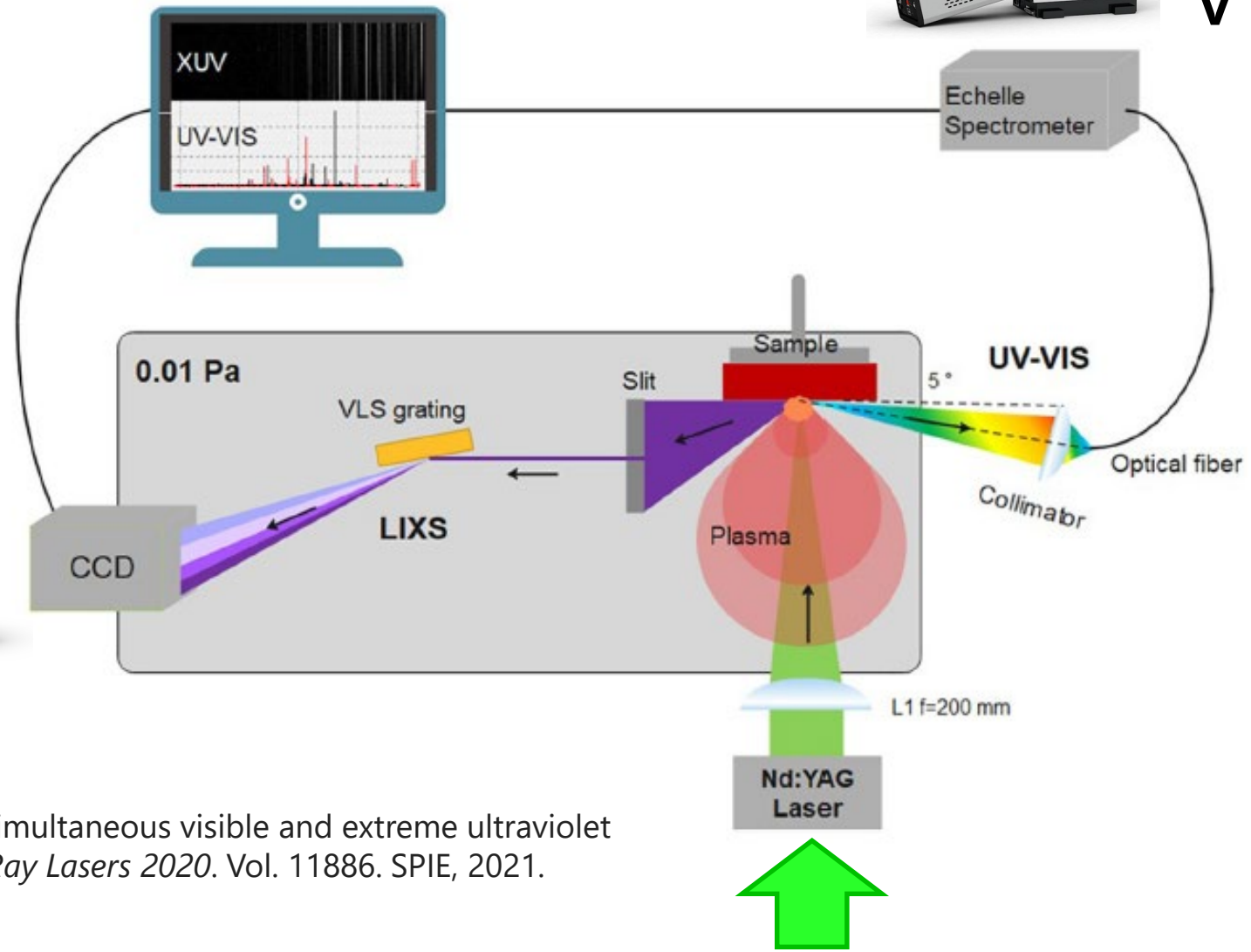
Spectral range		Δλ	20	nm
Slit Width		Ws	20	µm
N Pixels		n	2048	
Pixel Size		Wp	13	µm
		Ws/Wp	1.54	
Resolution Factor		RF	2	
Resolution		**Res**	**0.30**	Angström
			220	meV

XUV

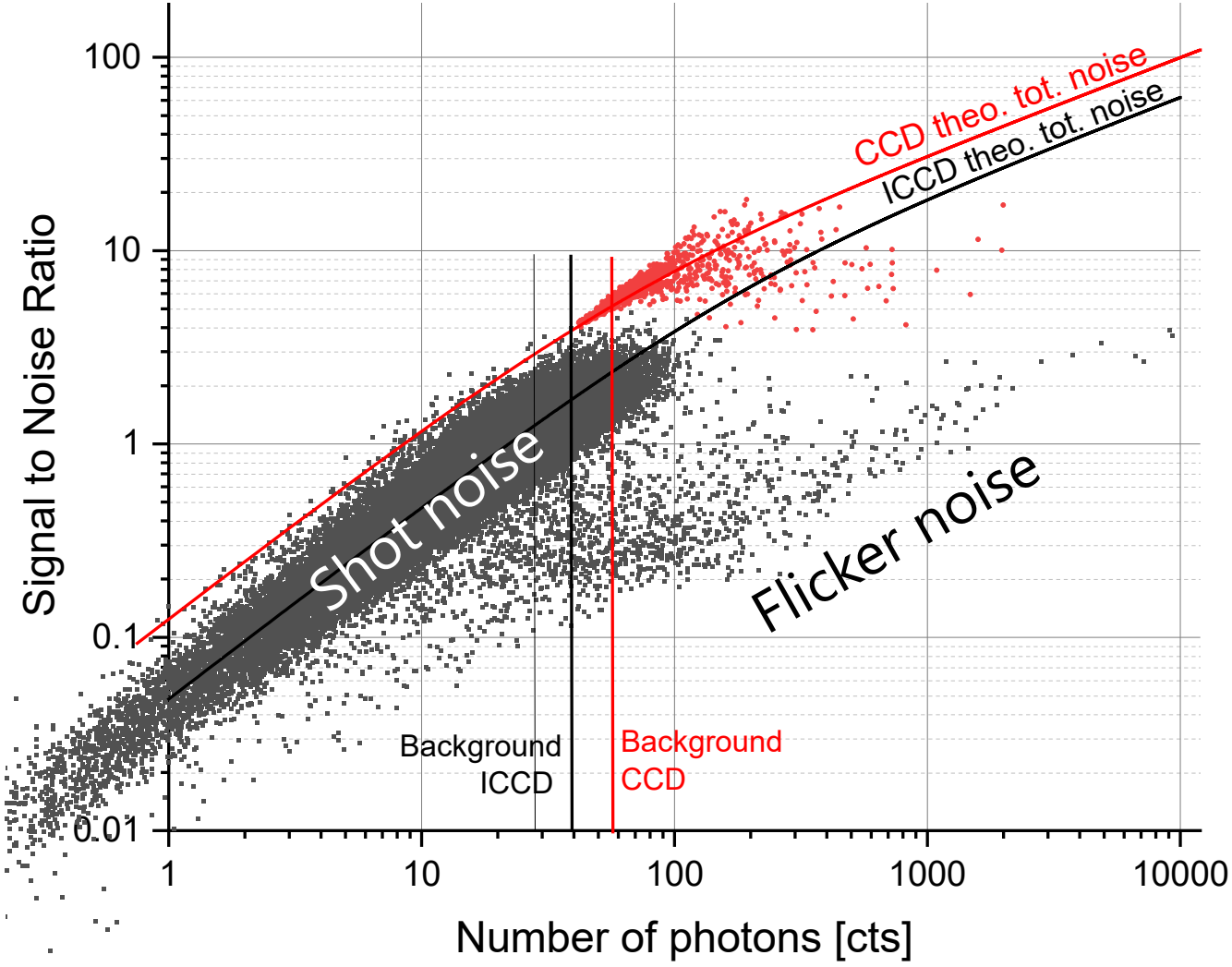


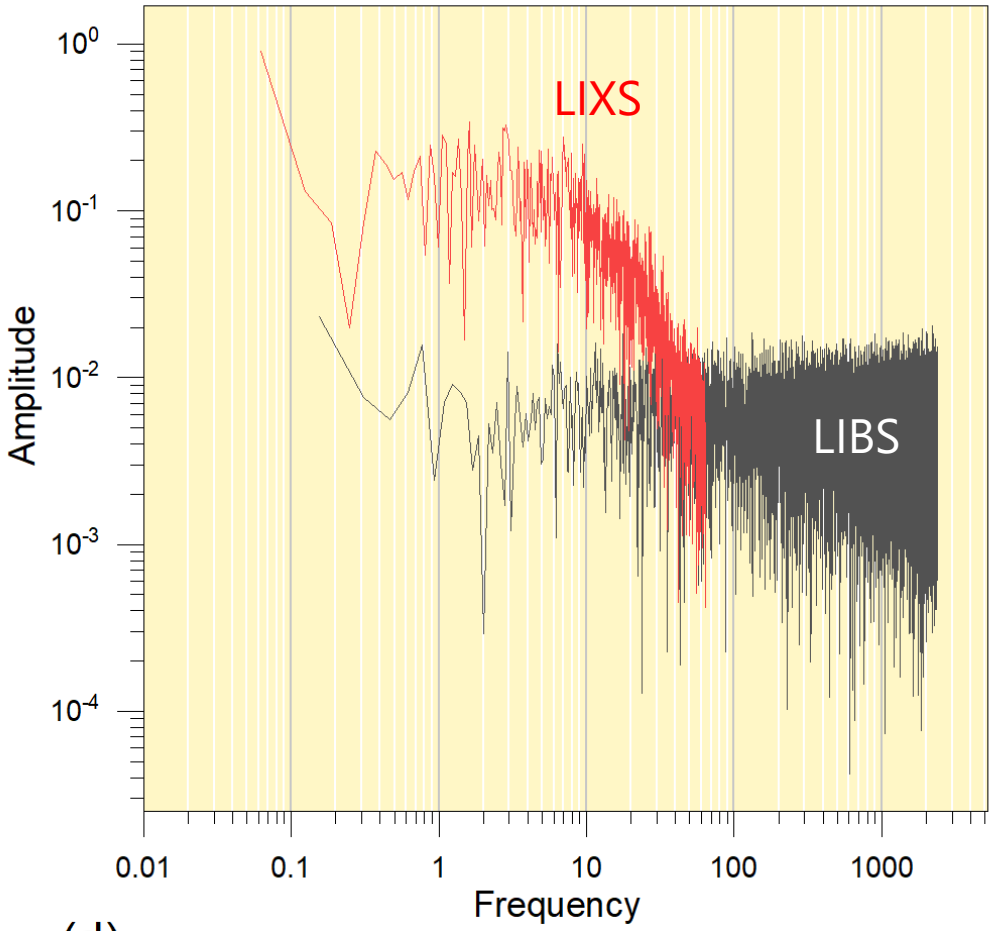
Vis



Qu, Di, et al. "Dual spectrometer for simultaneous visible and extreme ultraviolet LIBS." *International Conference on X-Ray Lasers 2020*. Vol. 11886. SPIE, 2021.

LIBS vs LIXS Information Capacity





Information Capacity* is Bandwidth-Limited

Shannon-Hartley Law

$$H = B \cdot Log_2\left(1 + \frac{S}{N}\right)$$

$$B = \frac{\Delta\lambda}{\lambda^2} c$$

LIXS ~ 100 LIBS

Bandwidth-limited Detection

Linear in Bandwidth,
Non-Linear in Power

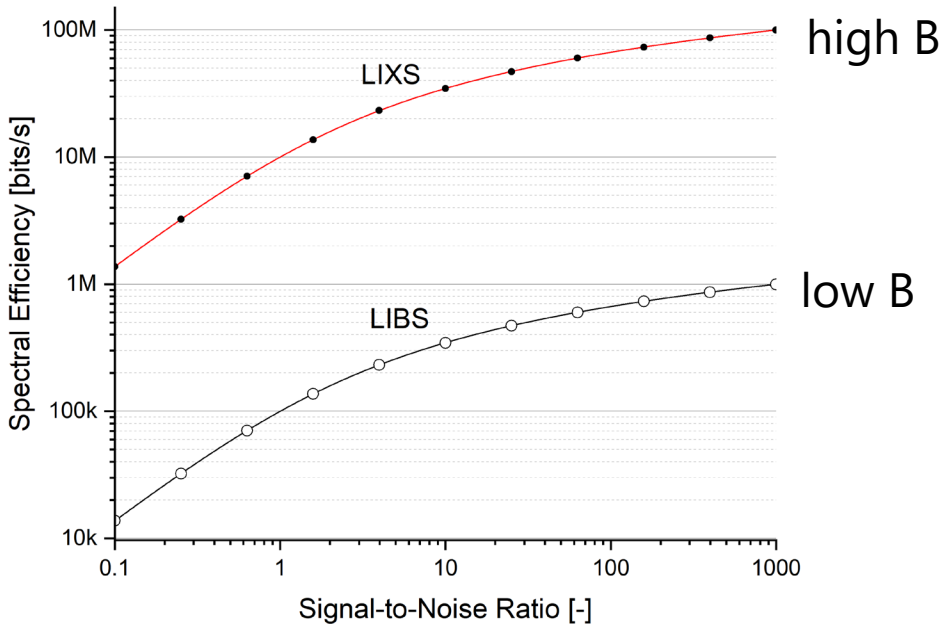
$$\frac{S}{N} \gg 1 \quad \approx Log_2\left(\frac{S}{N}\right)$$

LIXS ~3 LIBS

$$\frac{S}{N} \ll 1 \quad \approx 0$$

Power-limited Detection

Linear in Bandwidth and in Power



Bleiner, D, et al. "Laser-induced XUV spectroscopy (LIXS): From fundamentals to application for high-precision LIBS." *Spectrochimica Acta Part B: Atomic Spectroscopy* (2023): 106668.

LIXS in the Lab

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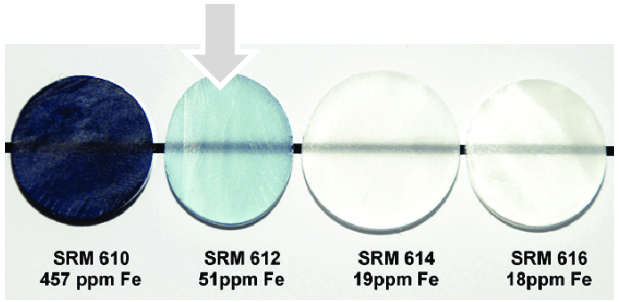
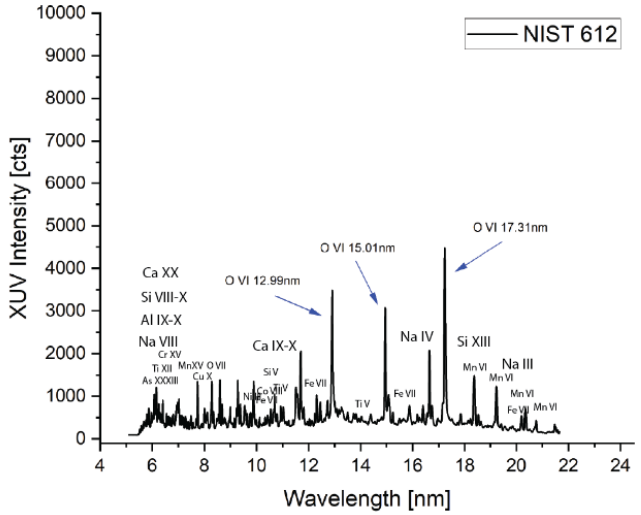
NIST612 Glass



(a)



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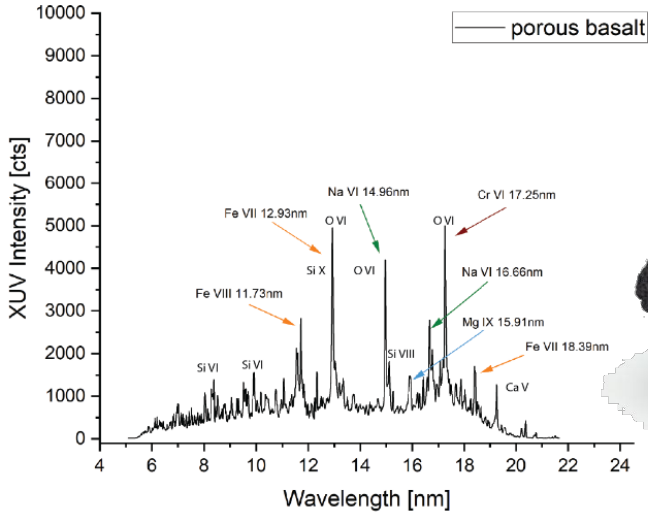
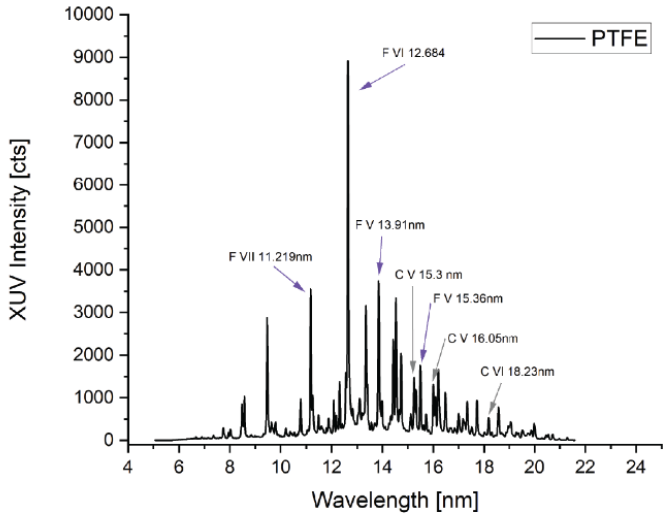


Basalt

Teflon

(c)



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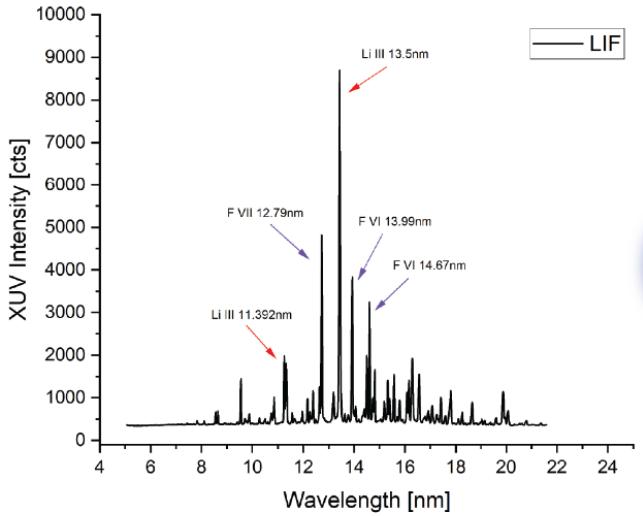
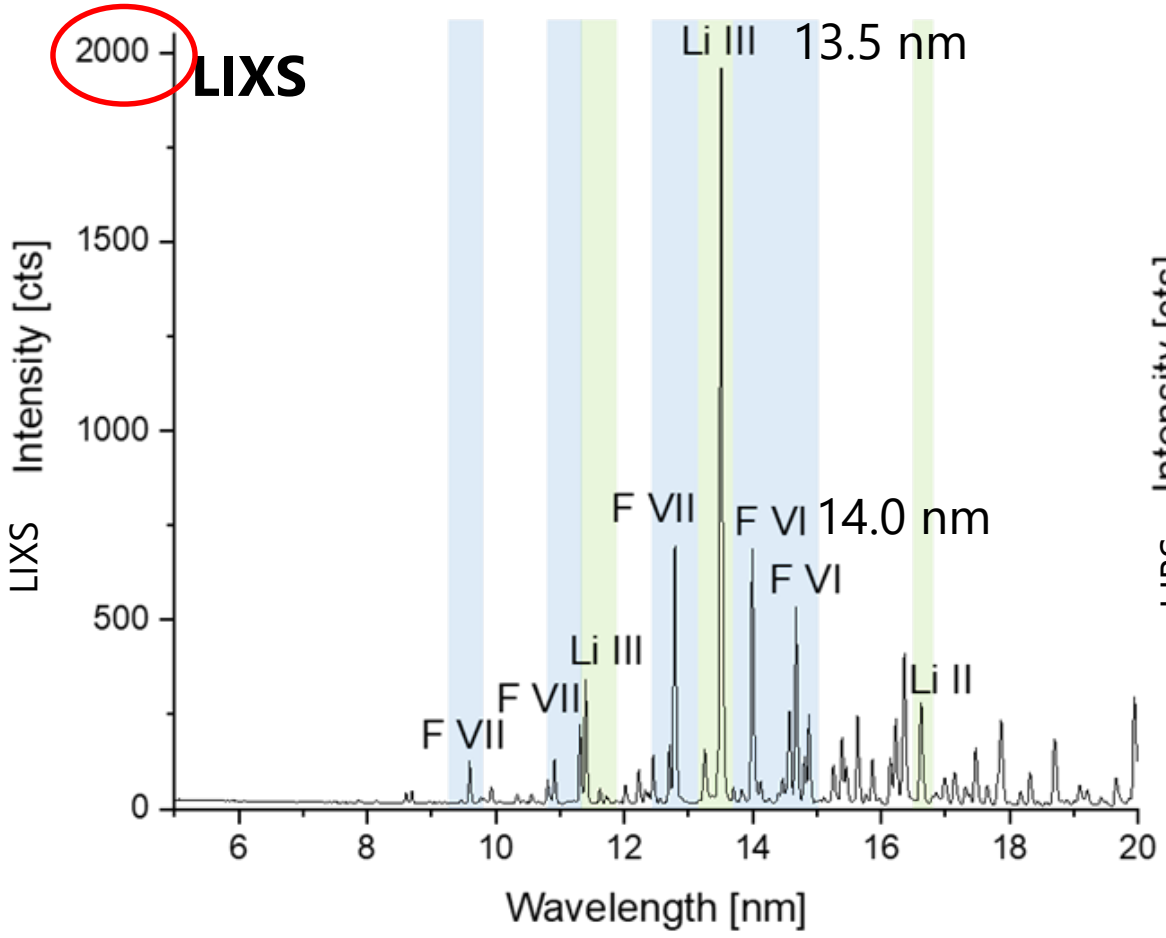
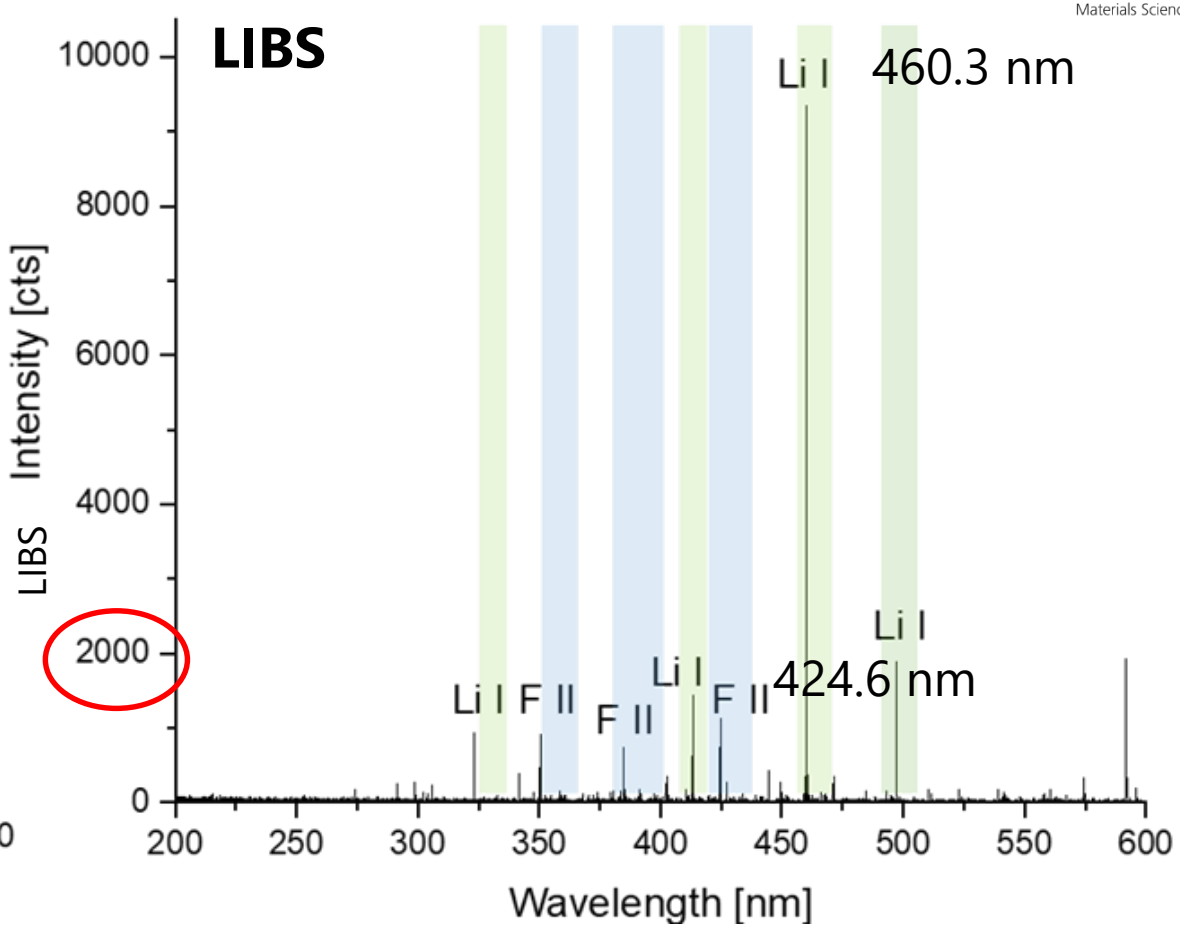


LiF Optics

LiF with LIXS vs LIBS

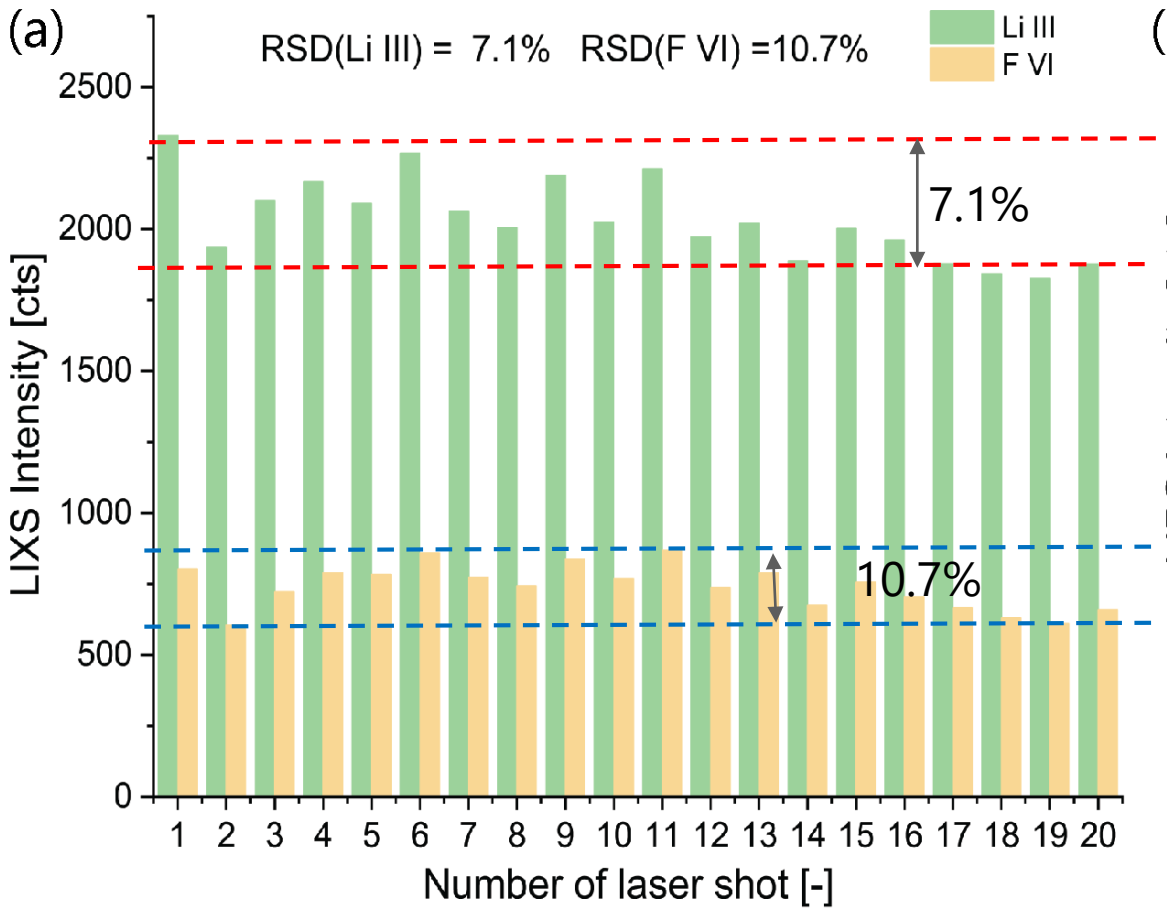




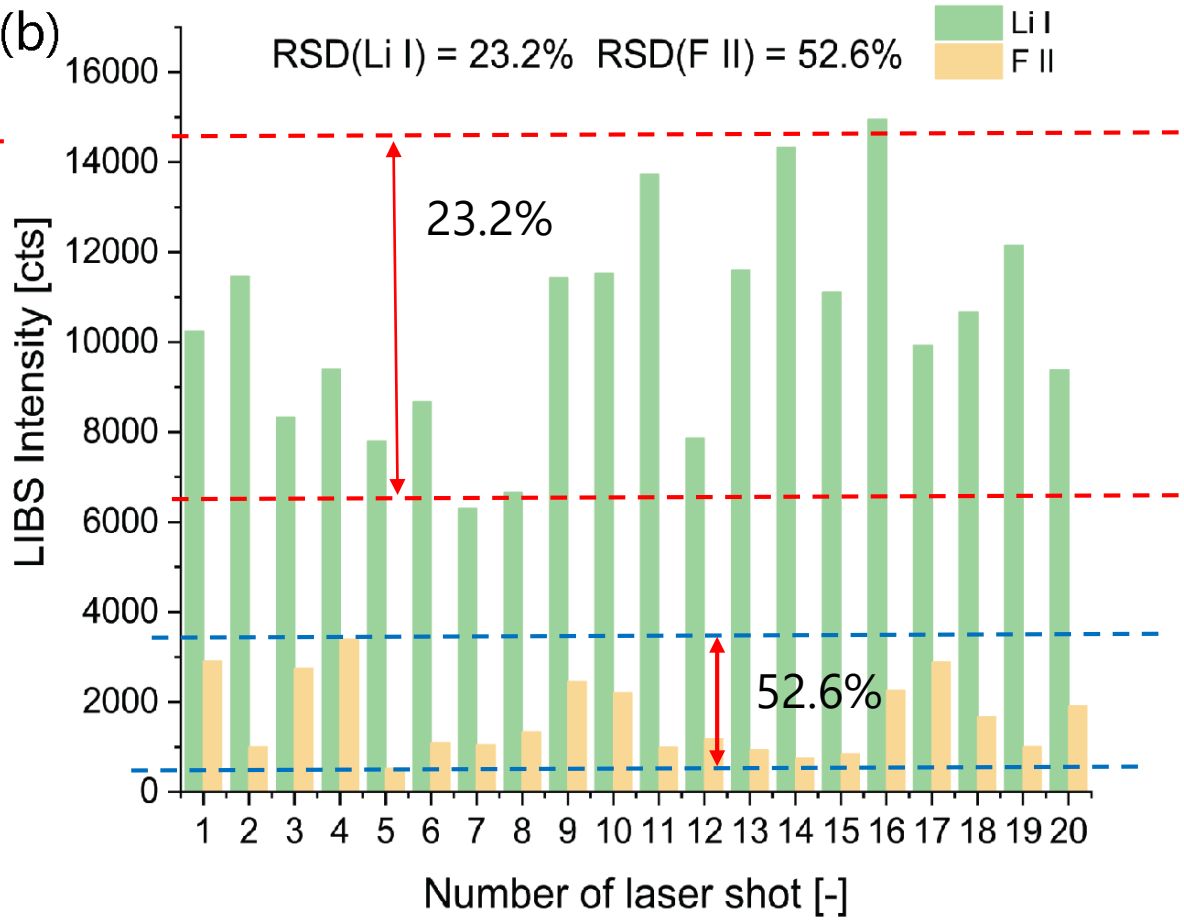
- Average LIBS spectra of 20 laser shots on the lithium fluoride (LiF) in XUV and UV-VIS
- Li III has strong emission at 13.5 nm, F VI and F VII lines in 9-18 nm.
- Lines from lower ionization level, Li I, F II

Shot to Shot Repeatability (No Int. Stand.)

LIXS



LIBS



Precursor Materials for Li Ion Manganese Battery (LMO)

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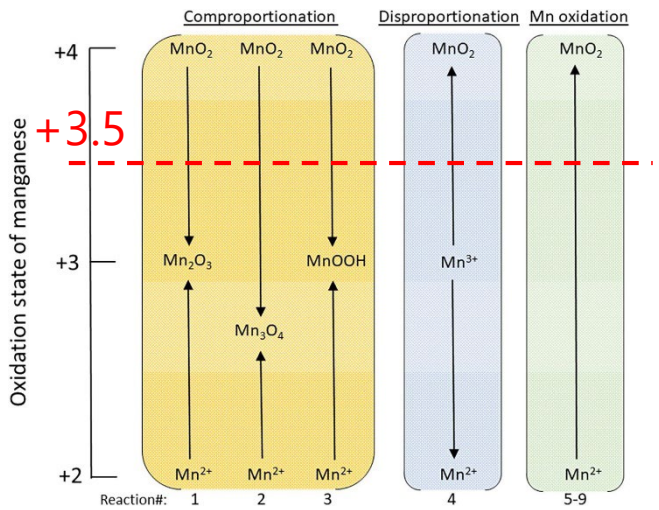
MnIII,IV
(+2,+3)

Hausmannite

General	
Category	Oxide mineral
Formula (repeating unit)	$Mn^{II}Mn^{III}{}_2O_4$, $MnO{\cdot}Mn_2O_3$, or Mn_3O_4
IMA symbol	Hsm[1]
Strunz classification	4.BB.10
Crystal system	Tetragonal
Crystal class	Ditetragonal dipyramidal (4/mmm) H-M symbol: (4/m 2/m 2/m)
Space group	$I4_1/amd$
Unit cell	a = 5.76 Å c = 9.46 Å; Z = 4



La Rowe, 2021

Hunter Disproportion.
Mn+3 → Mn+2 + Mn+4

At the Surface

MnIII
(+2)

Manganosite

Black manganosite crystals with zincite and sonolite

General	
Category	Oxide mineral
Formula (repeating unit)	Manganese oxide, MnO
IMA symbol	Mng[1]
Strunz classification	4.AB.25
Crystal system	Cubic
Crystal class	Hexoctahedral ($m\bar{3}m$) H-M symbol: (4/m $\bar{3}$ 2/m)
Space group	$Fm\bar{3}m$
Unit cell	a = 4.44 Å; Z = 4

MnV
(+4)

Pyrolusite

General	
Category	Oxide minerals
Formula (repeating unit)	MnO_2
IMA symbol	Pyl[1]
Strunz classification	4.DB.05
Crystal system	Tetragonal
Crystal class	Ditetragonal dipyramidal (4/mmm) H-M symbol: (4/m 2/m 2/m)
Space group	$P4_2/mnm$

LMO: LIBS vs. LIXS Signals: Experimental

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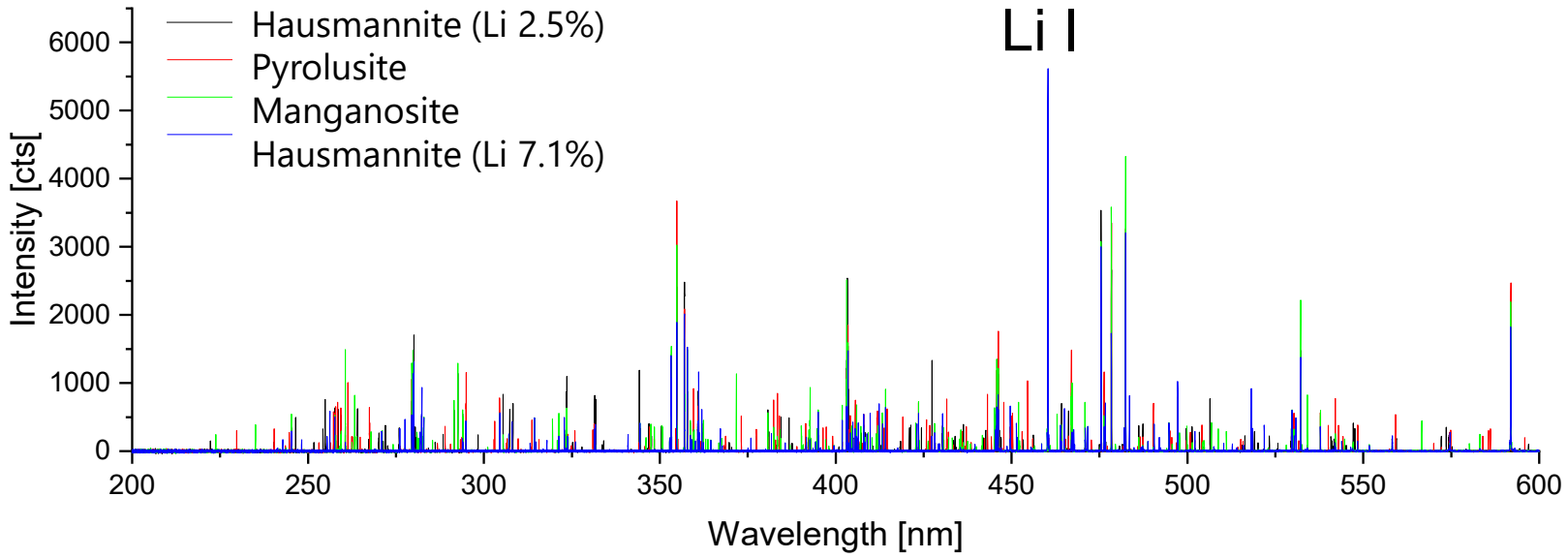
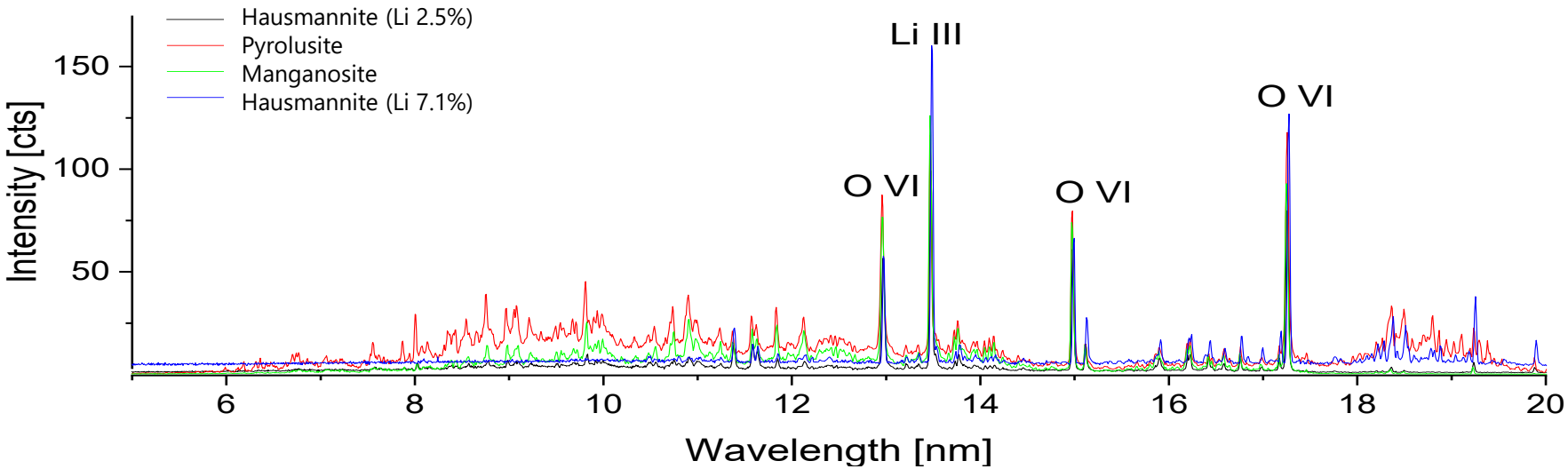


Formula	$Mn^{V}O_2$	$Mn^{III}O$	$Mn^{III}Mn^{IV}{}_3O_4$	$Mn^{III}Mn^{IV}{}_3O_4$
Name	**Pyrolusite**	**Manganosite**	**Hausmannite25**	**Hausmannite71**
Mn^{+2}	-	70.60%	22.70%	20.40%
Mn^{+3}	-	-	45.40%	40.70%
Mn^{+4}	59.00%	-	-	-
Li	3.10%	4.10%	2.50%	7.10%



LMO: LIBS vs. LIXS Signals: Theoretical Analysis

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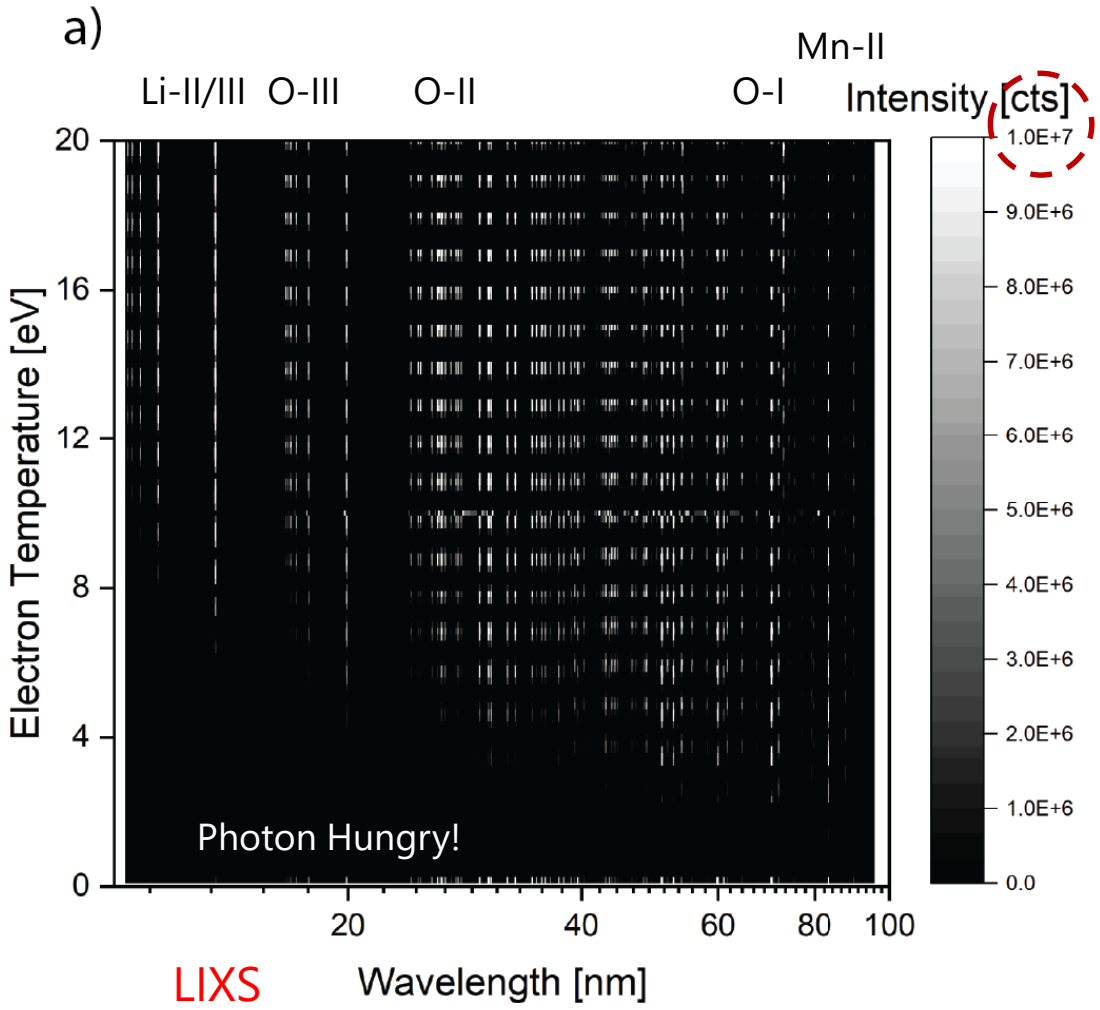

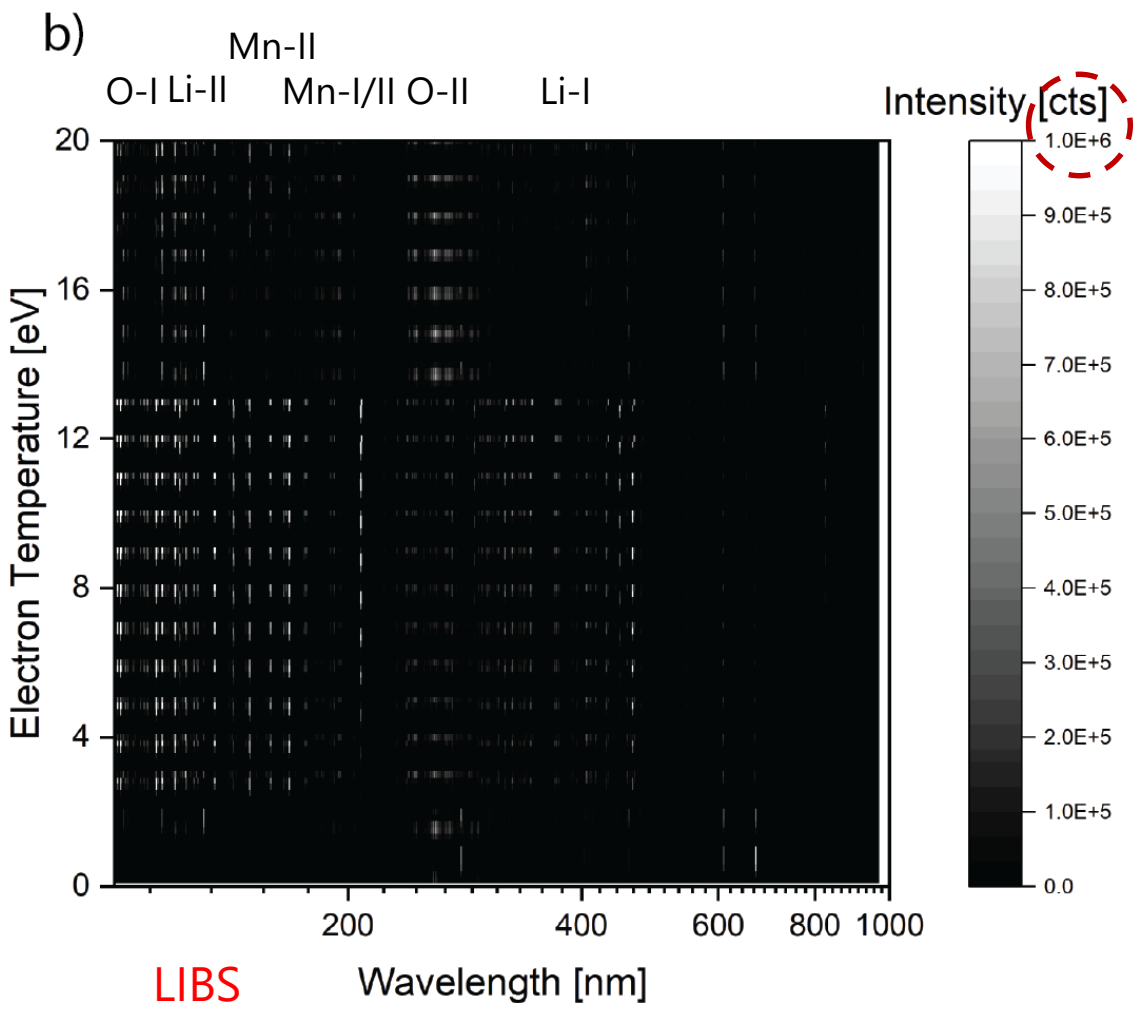

LMO / LIXS Signal

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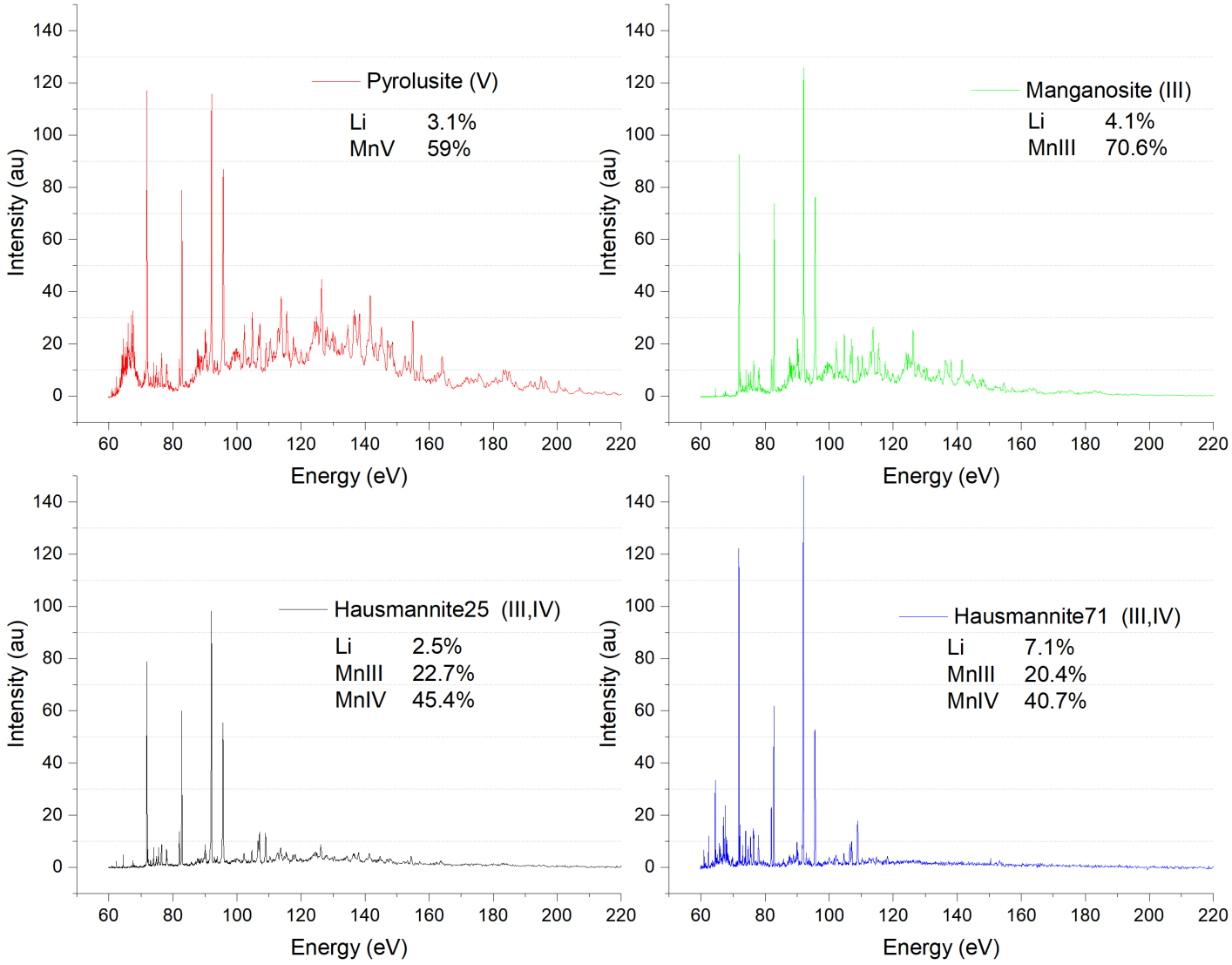
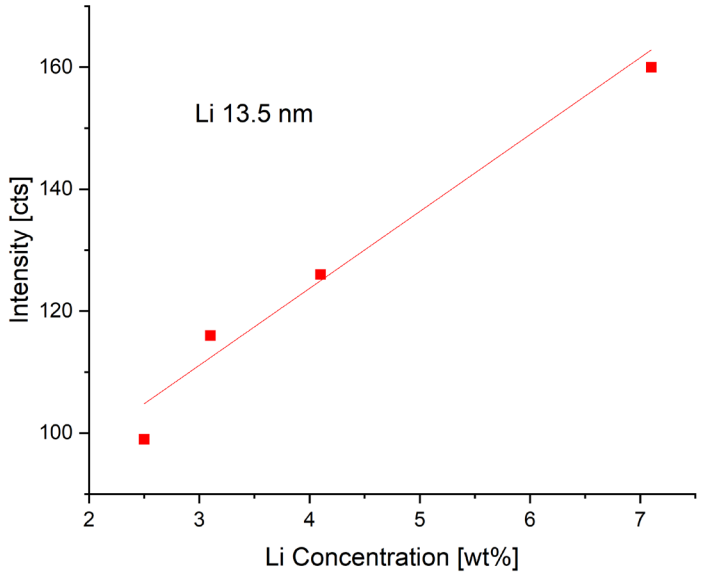
Clear Effect from Mn Oxidation



Li Signal Scales Linearly



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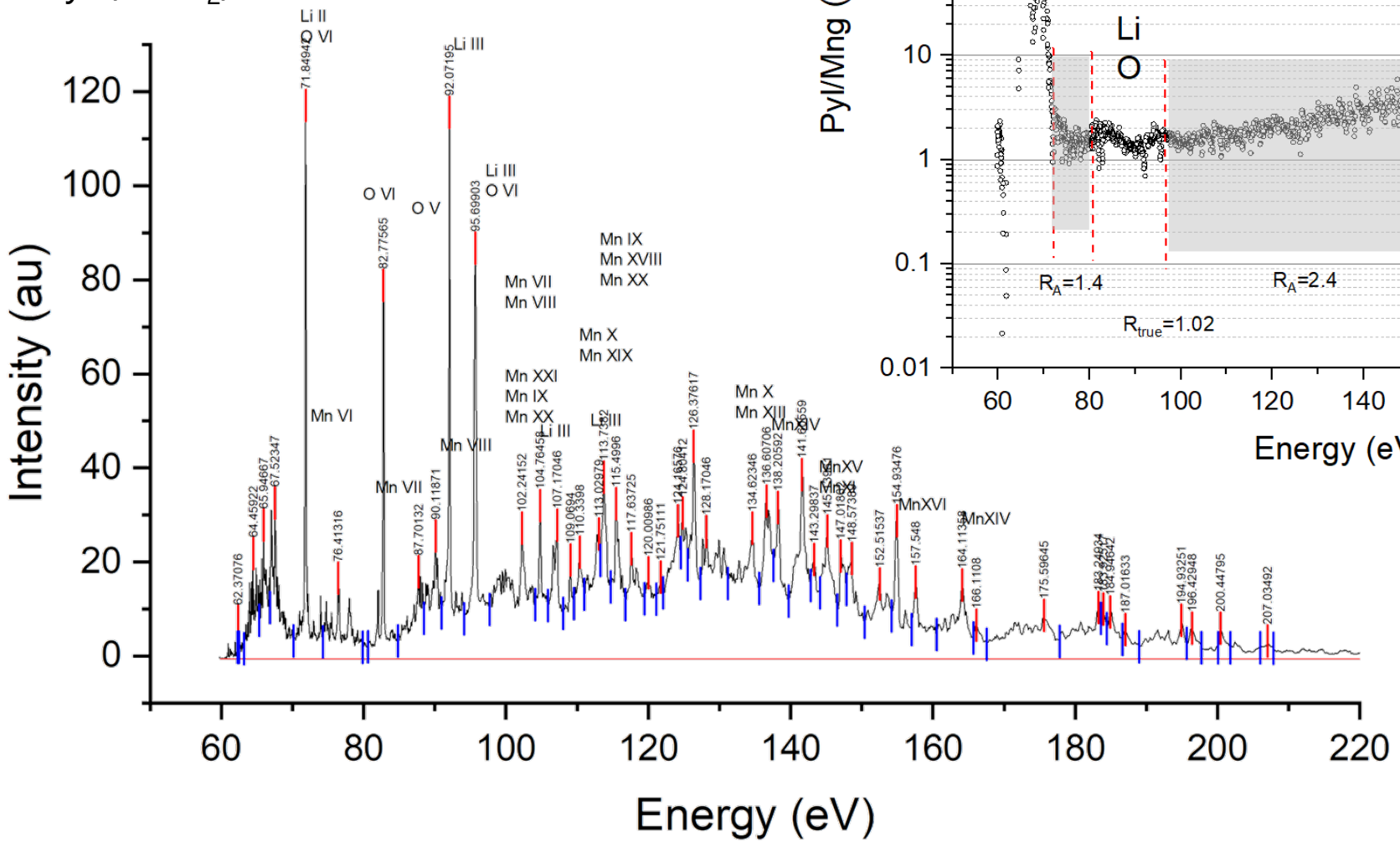
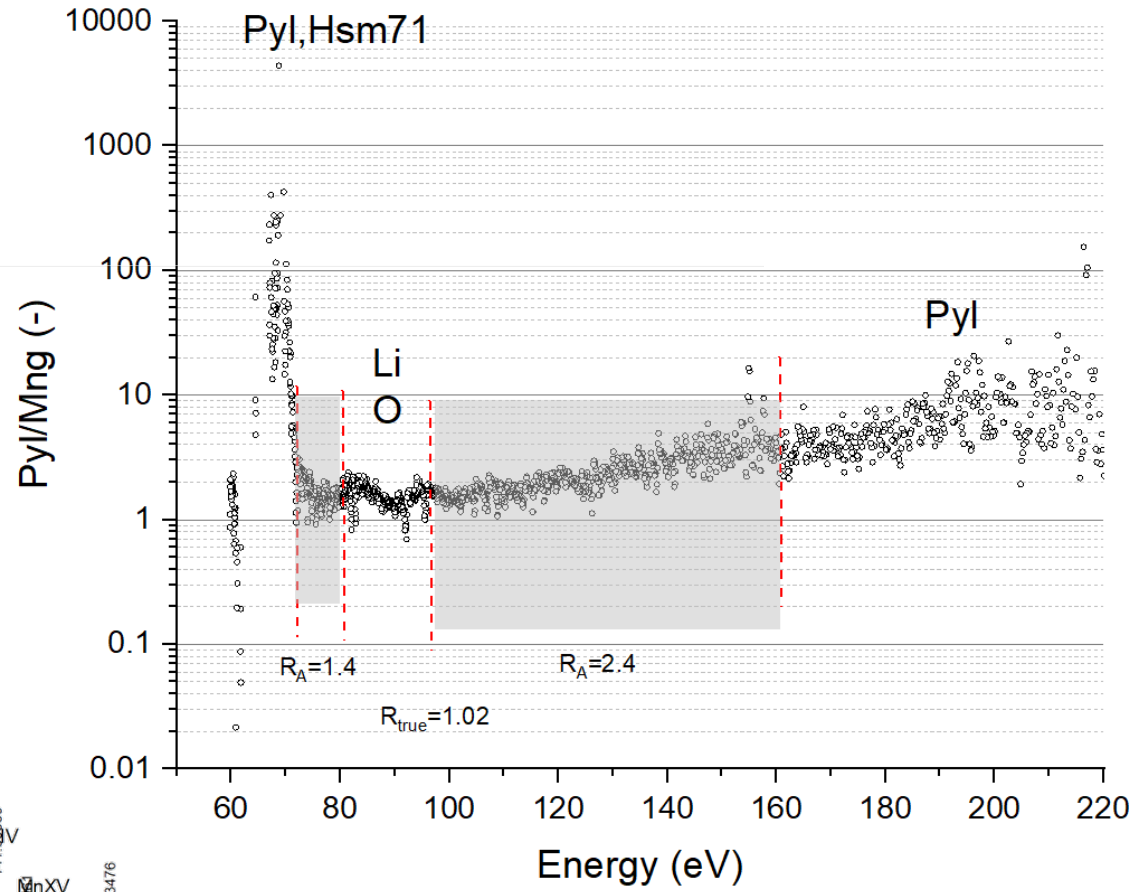
Pyl (MnO_2)





Discussion

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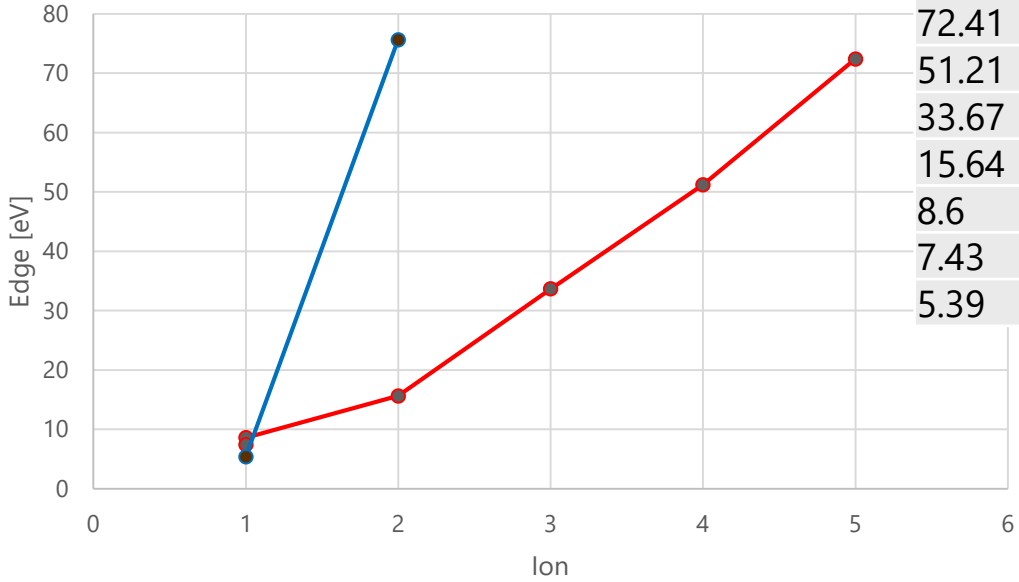
- Li Signal Scales Linearly
- Clear Effect from Mn Oxidation
  - Pyl and Hsm71 have a Strong Feature at Low Energy (62-67 eV)
  - Pyl and Mng is Constant in the Mid Energy (100-150 eV) increasing with Energy
  - Hsm Lacks Mid Energy Feature
- Interpretation:
  - Rad. Recombination adds progressively
  - Photoionization modifies the collisional ion balance
  - Closed shells are stable



Edge (eV)	Ion	Shell Term
75.64	Li+2	1s 2S1/2
72.41	Mn+5	3d2 3F2
51.21	Mn+4 (P)	3d3 4F3/2
33.67	Mn+3 (H)	3d4 5Do
15.64	Mn+2 (M, H)	3d5 6S5/2
8.6	Mn+1	3d5 4s 5S2
7.43	Mn+1	3d5 4s 7S3
5.39	Li+1	1s2 1So

Conclusions

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- **LIXS is LIBS in the X-ray but**
  - Less Plasma Flickering
  - Shell Population in Plasma is Critical
  - Chemical State → “Reverse XPS”

- **Outlook**
  - Replicate Preliminary Data
  - Deconvolution

Division Analytical Science / Swiss Chemical Society (SCS)

Events SCS - https://scg.ch/events

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AOFKA 10-13 September

Applied Surface and Solid Sample Analysis
ETH Zurich

https://aofka23.scg.ch

Euroanalysis 27-31 August

Geneva

www.euroanalysis2023.ch