HEAVYMETAL VI 2026

Dual-Comb Spectroscopy of Heavy Metals (New Zr Oscillator Strengths!)

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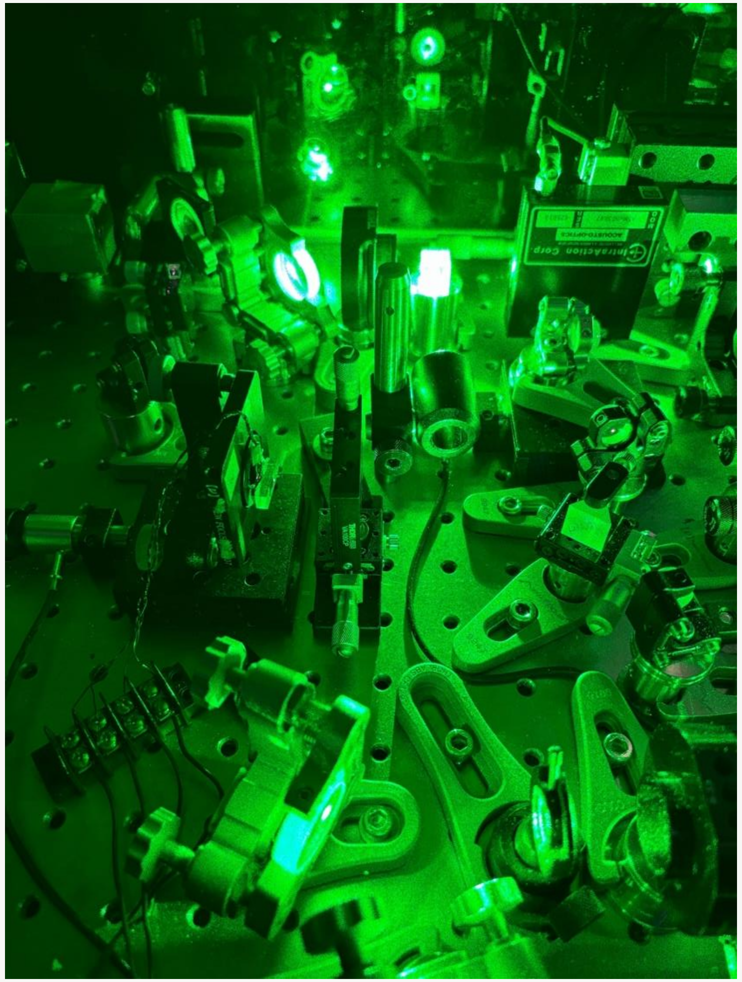
Wyant College of Optical Sciences

Overview

- **Experimental Setup**
  - Fundamental and second harmonic of Ti:s **simultaneously** probe solid samples using a laser produced plasma

- **Analysis**
  - Line Identifications (**tangent on databases**)
  - Plasma temperature and column densities
  - Extraction of **oscillator strengths**

- **Moving Forward**
  - Larger spectrum
  - Alloys as an anchor



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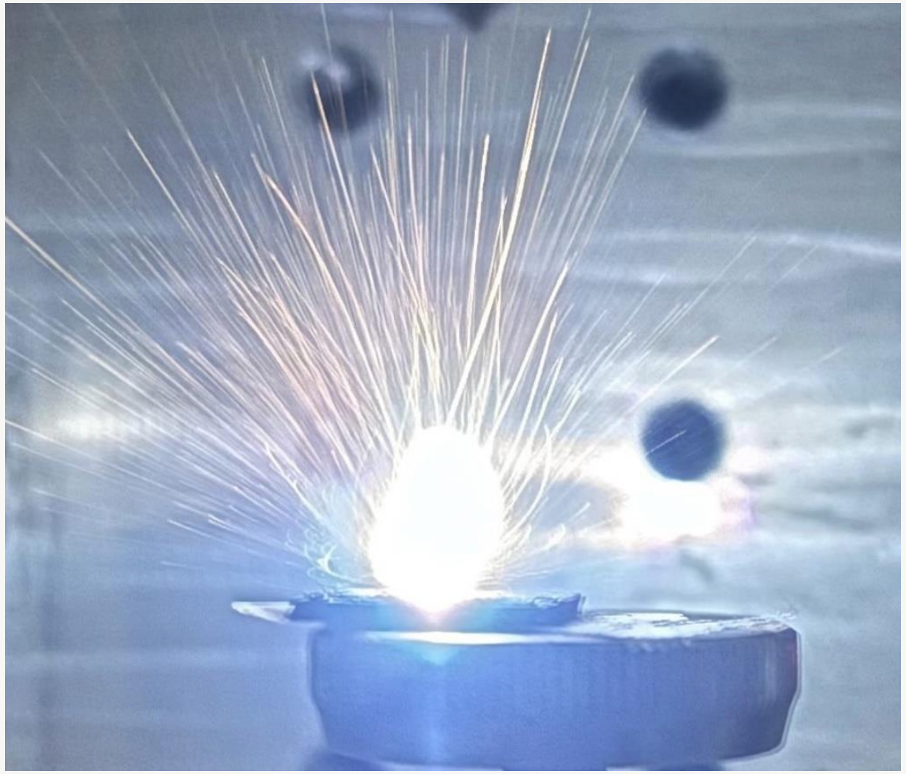
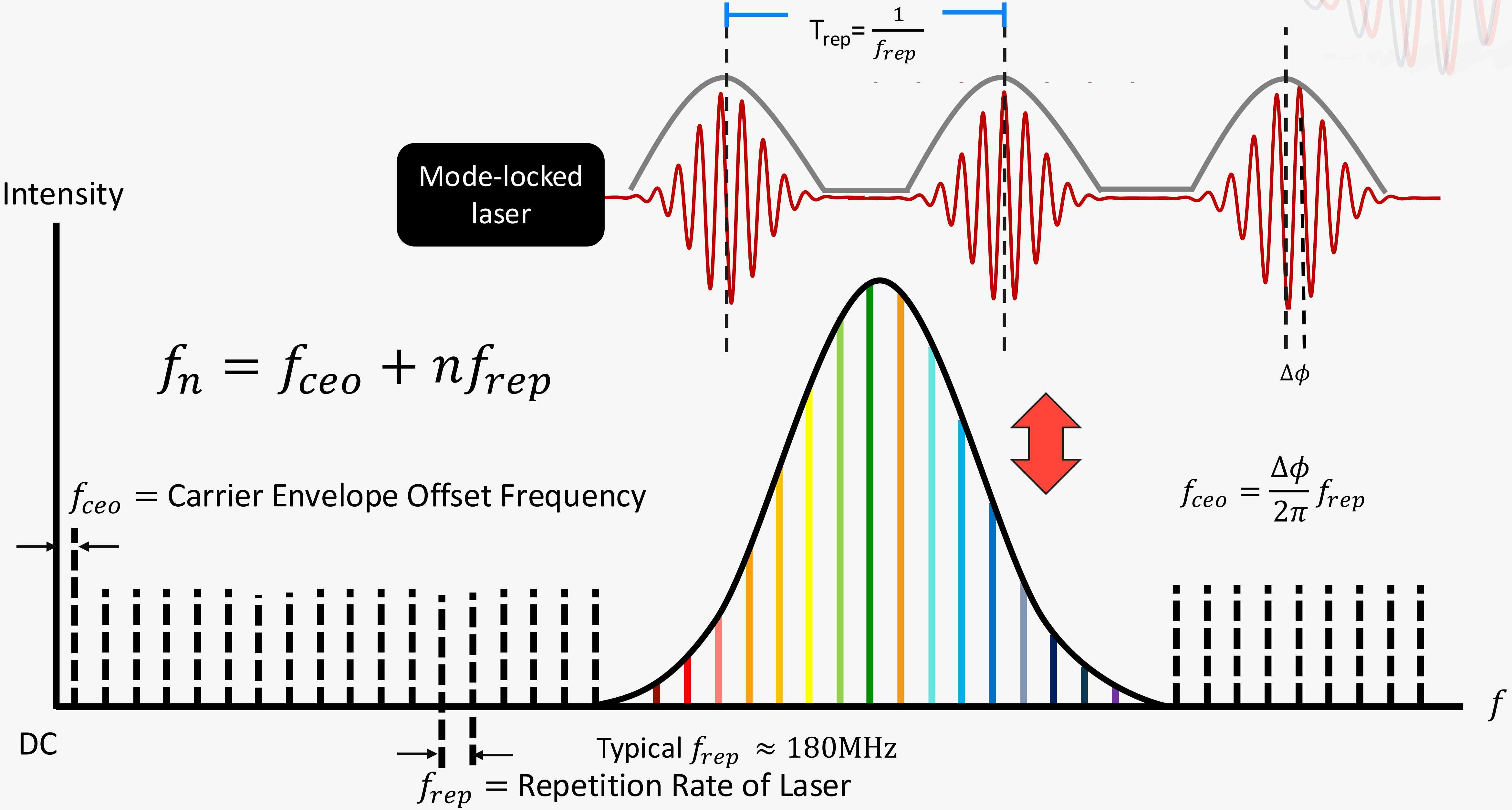
Laser Produced Plasmas

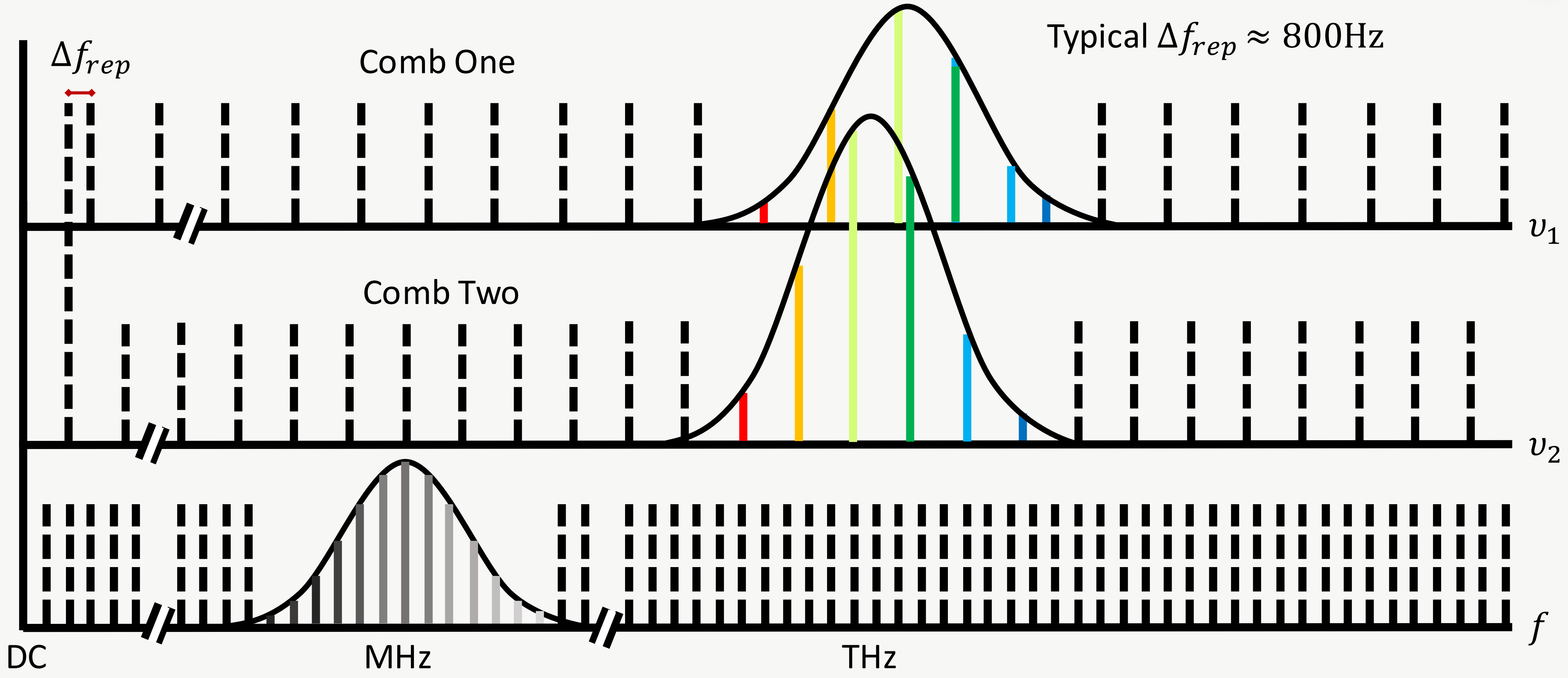
- **Convenient sample preparation**
- **Fundamental atomic/optical properties**
  - e.g. transitions and osc. strengths
- **Laser-Plasma dynamics & fundamentals**
  - ns-ms time scales
  - temperature 10,000+ K → 500 K
  - number densities 10^{21} → $10^{13}\ cm^{-3}$
  - species formation, plasma-chemistry
  - Tests of LTE conditions



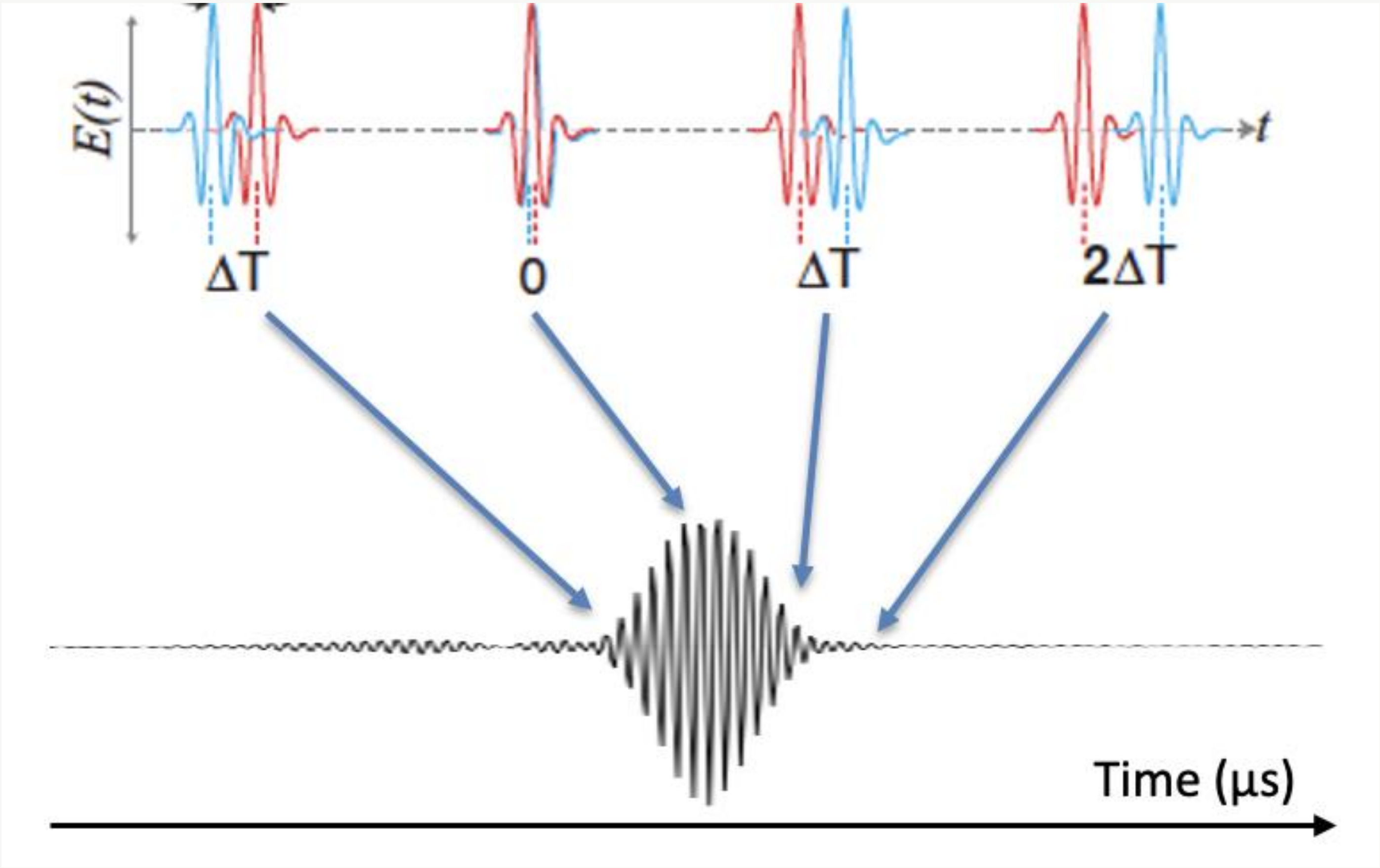
Frequency Combs



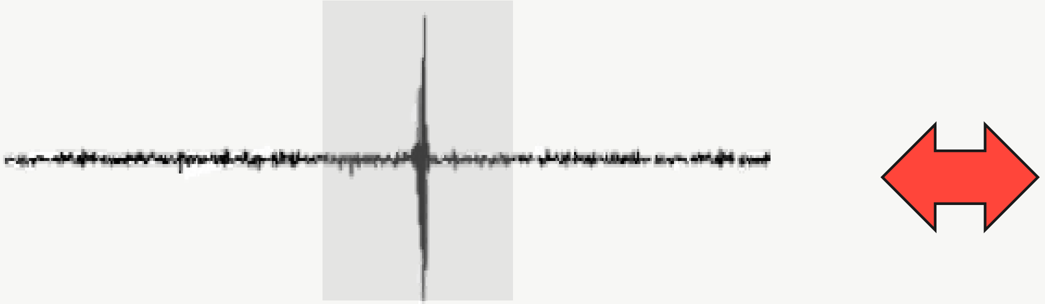
Dual-Comb Spectroscopy (DCS)



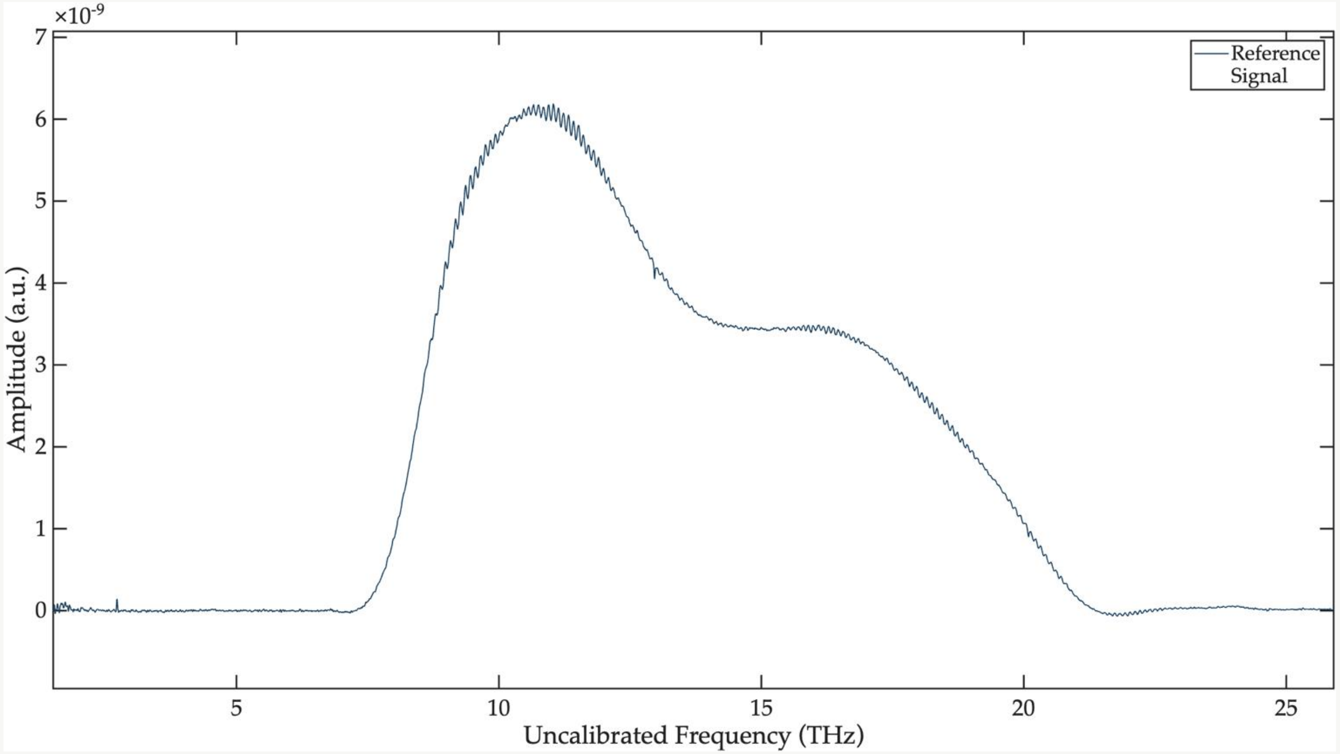
Dual-Comb Spectroscopy (DCS)



Fourier Transform spectroscopy



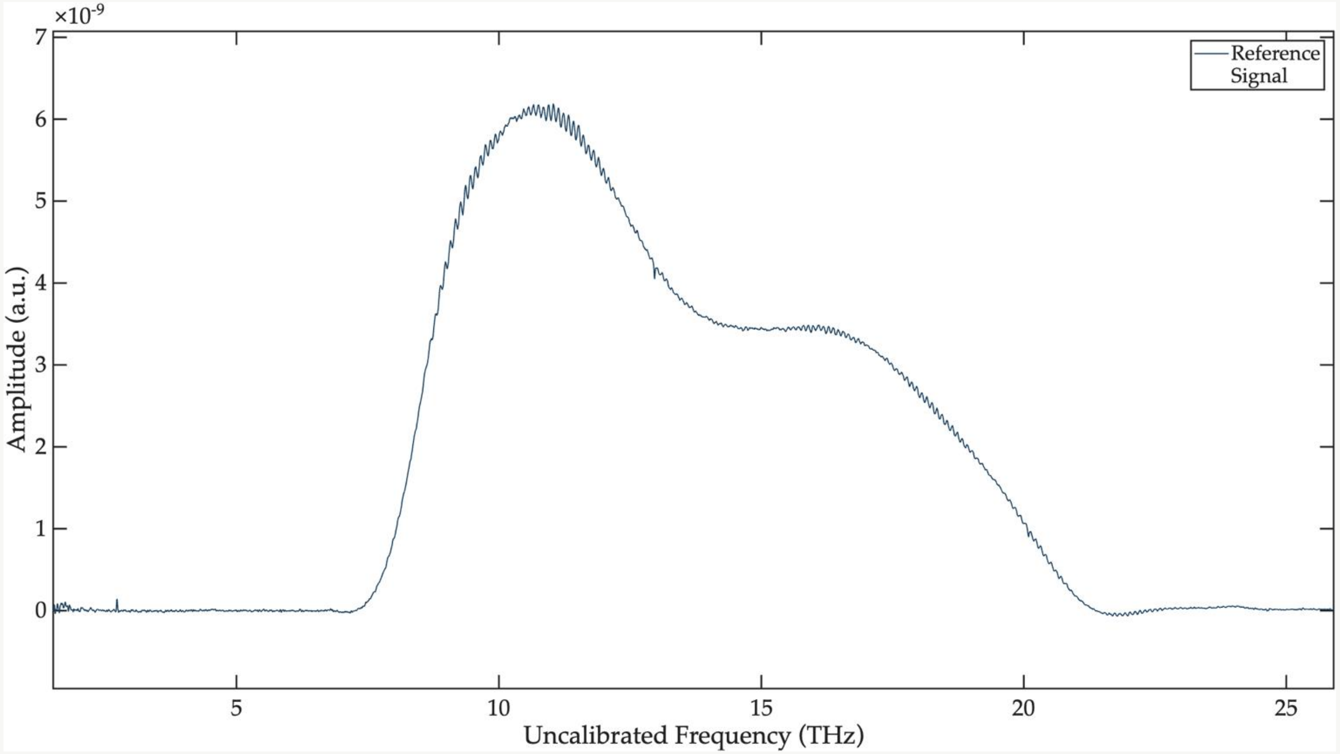
- Similar to Fourier Transform spectroscopy but no longer limited by a mechanical scanning arm!



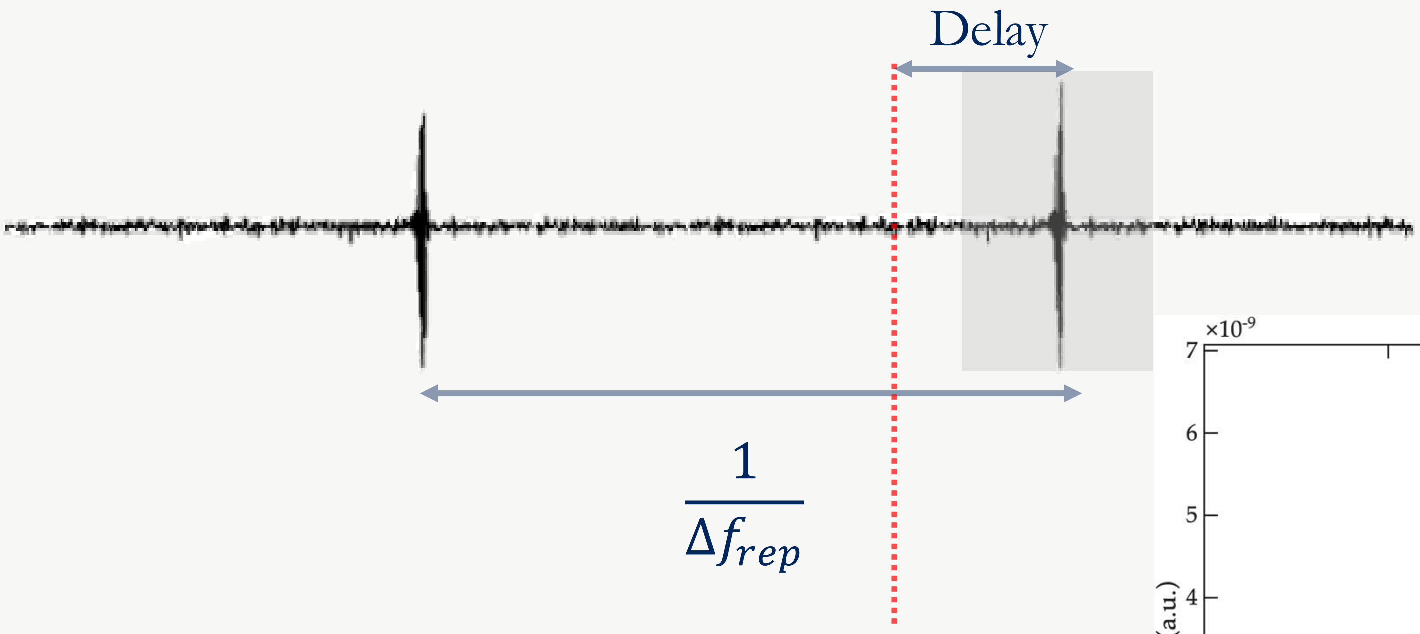
DCS Signal

$$\frac{1}{\Delta f_{rep}}$$

- $\Delta f_{rep} = 800$ Hz
- Able to collect both reference and signal

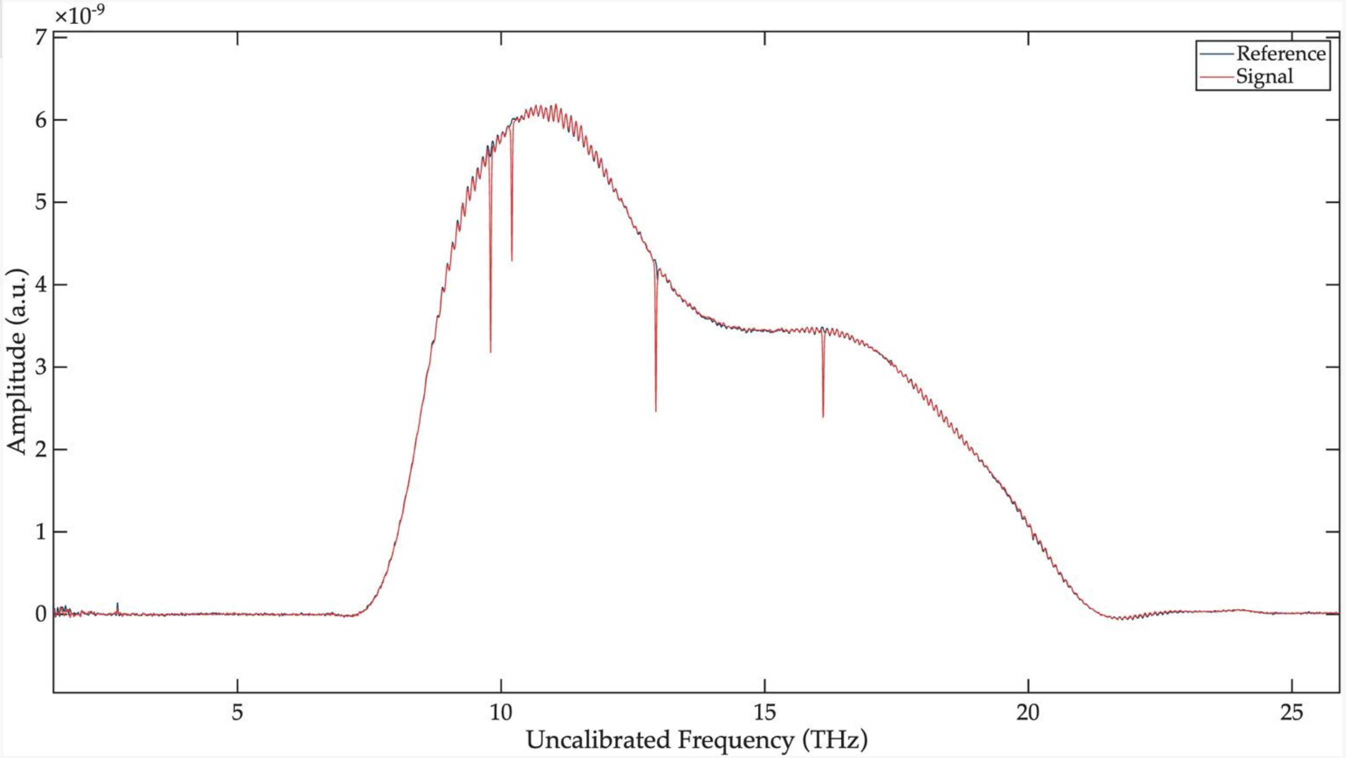


DCS Reference

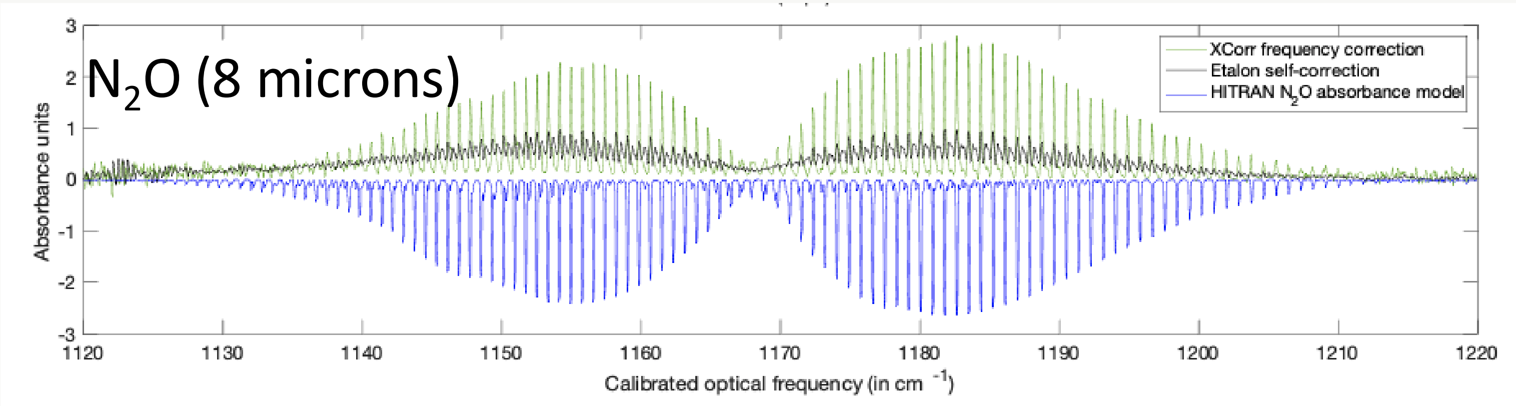


Absorbance:

$$A(\nu) = -\ln\left(\frac{I}{I_o}\right)$$

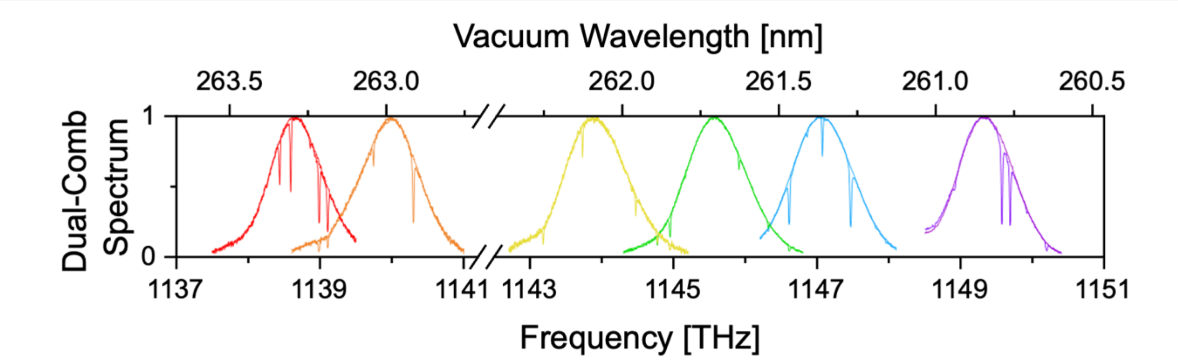


Dual Comb Spectroscopy: MIR to the VUV

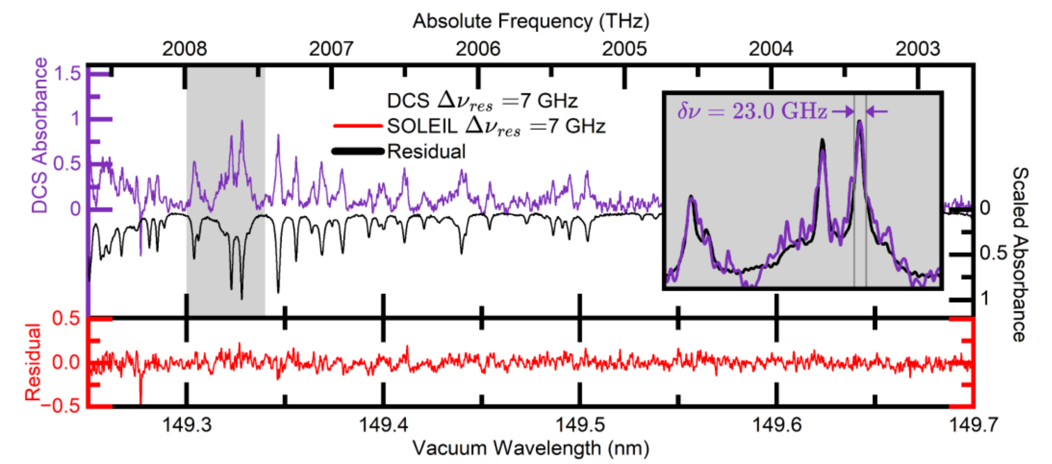


Resolving Power > 16,000,000

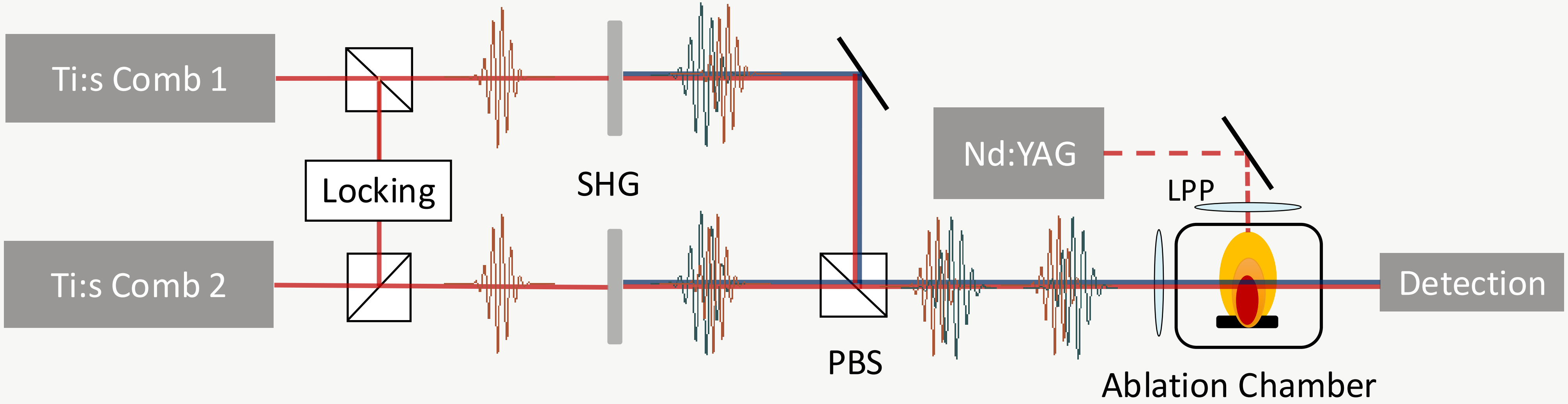
Fe in the DUV (260 nm)



ammonia VUV spectroscopy (148nm)

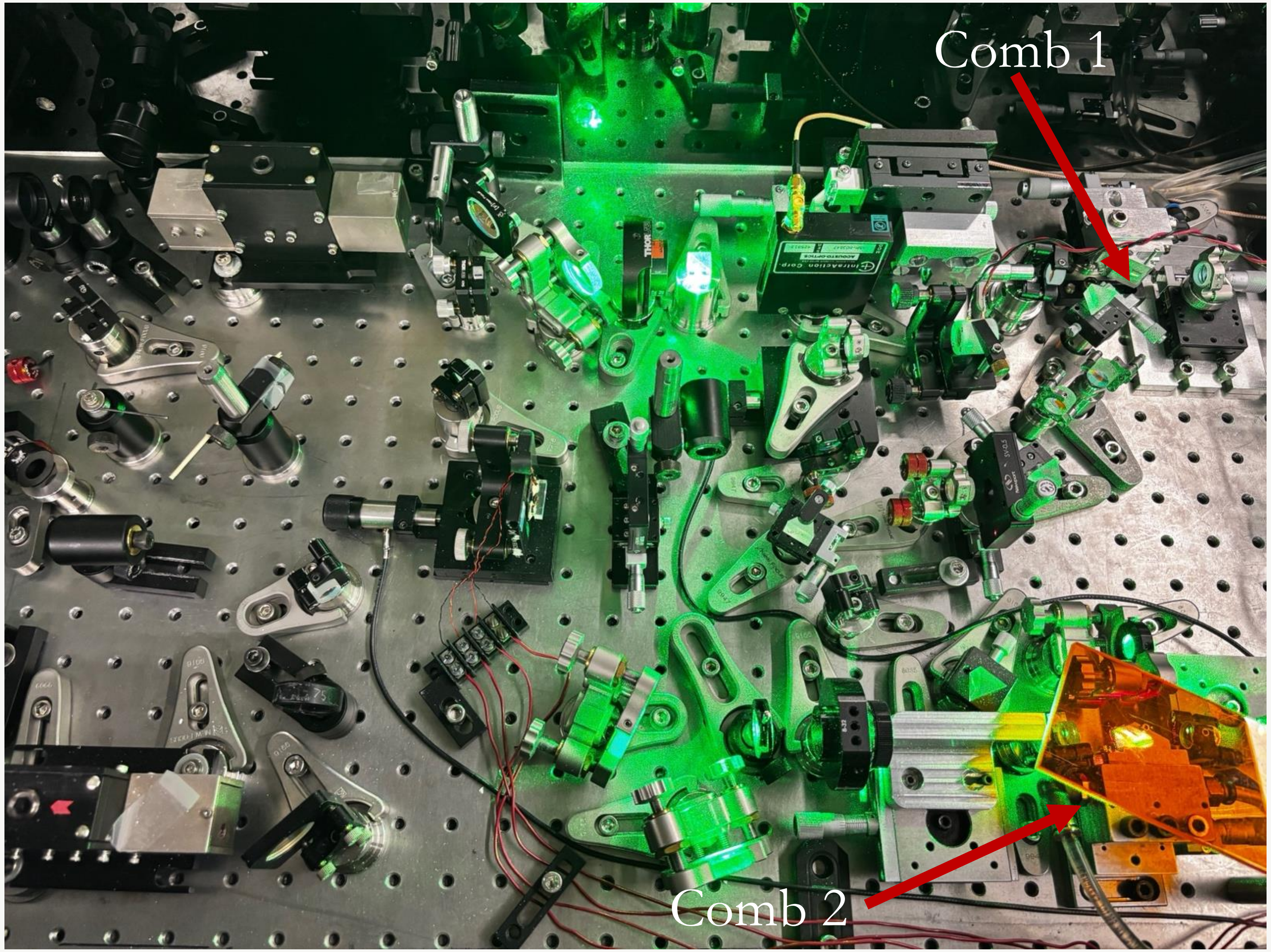


Experimental Setup

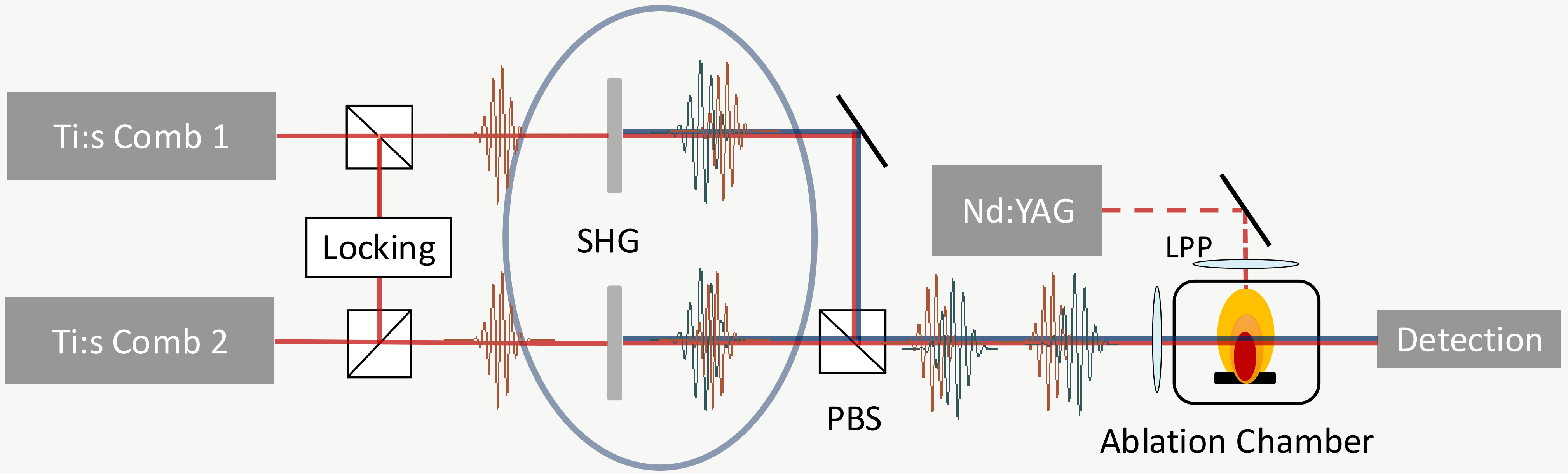


Home-Built Ti:s Combs

- 800nm center wavelength
- FWHM ~ 20nm
- Tunable over 50nm
- Rep Rate: 180 MHz



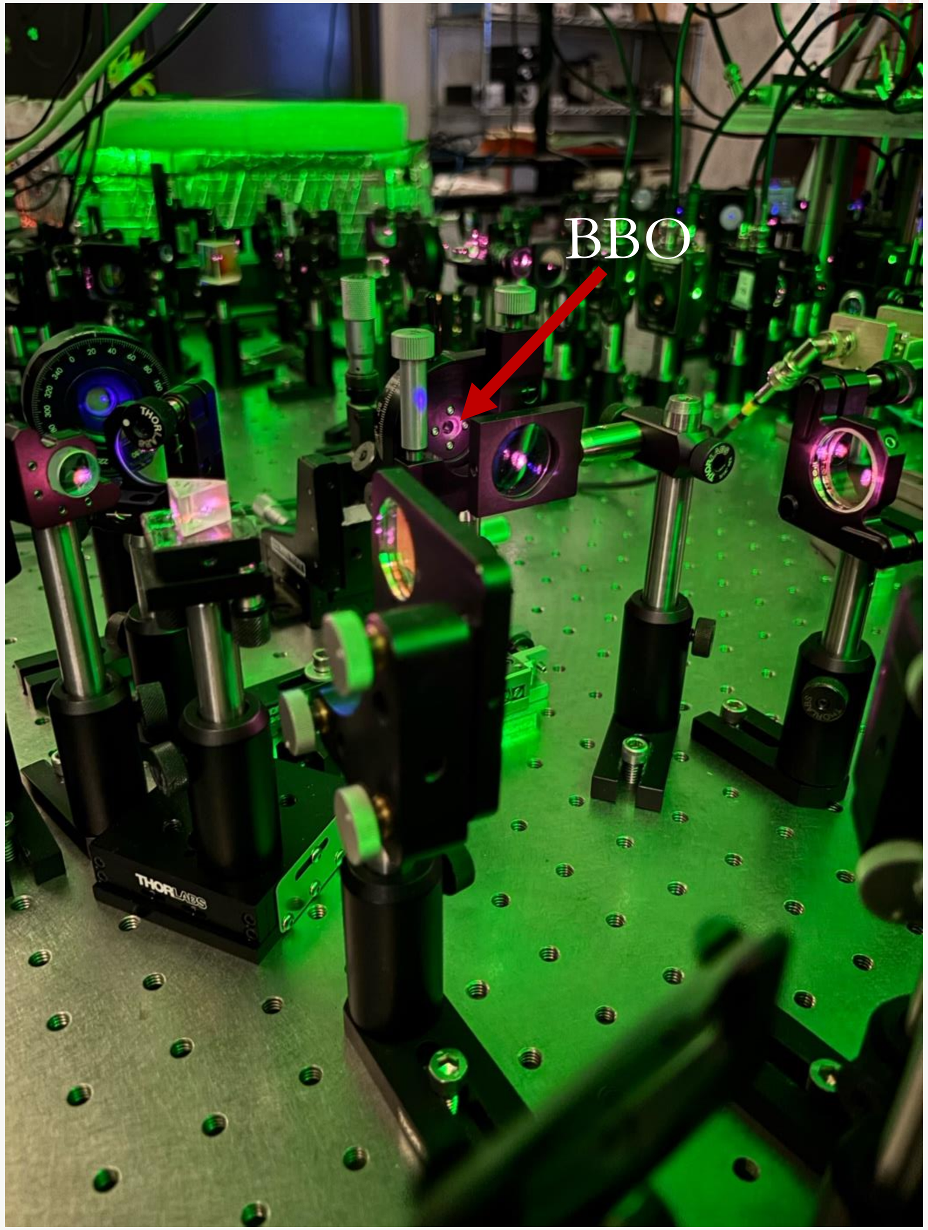
Second-Harmonic Generation



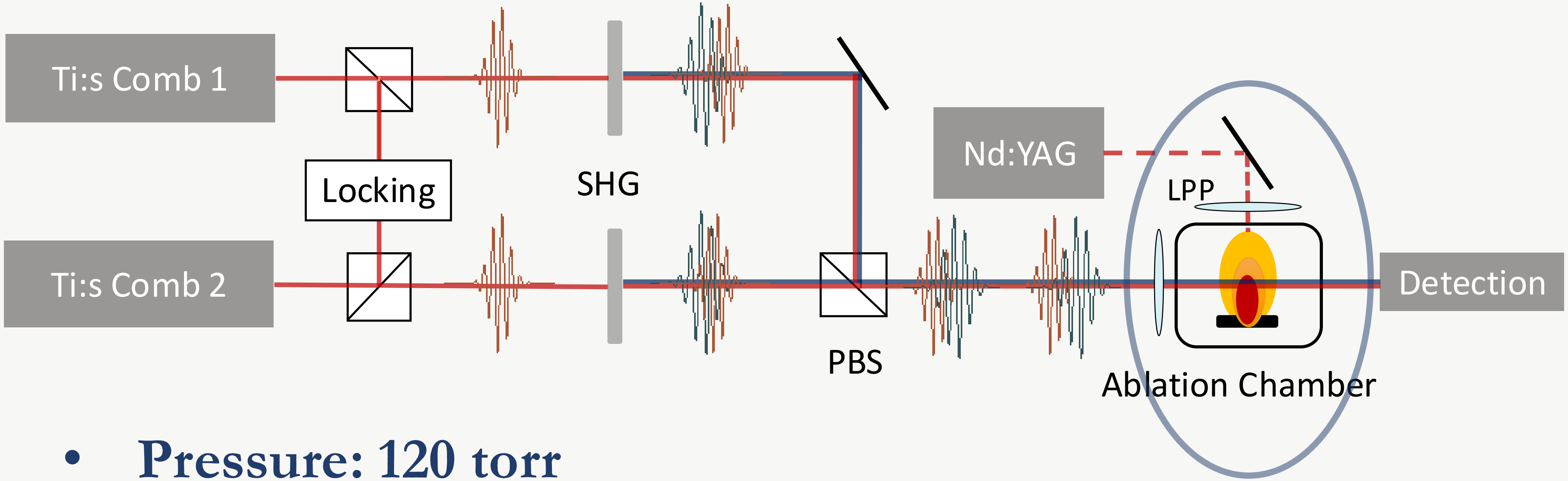
Second-Harmonic Generation

- Two BBOs used to frequency double the Ti:s combs from 800nm to 400nm

- FWHM ~ 10nm

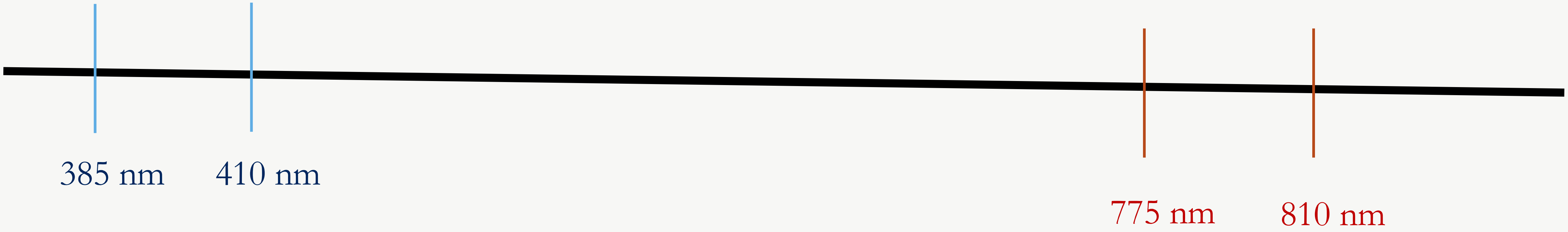


Laser Produced Plasma Conditions



- Pressure: 120 torr
- Beam Height: 2.5mm
- Flowing with 35 lpm of Ar

Current Wavelength Range



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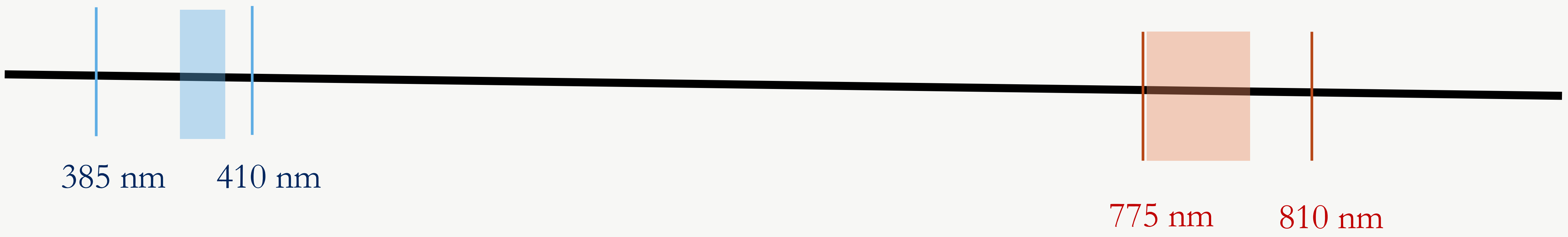
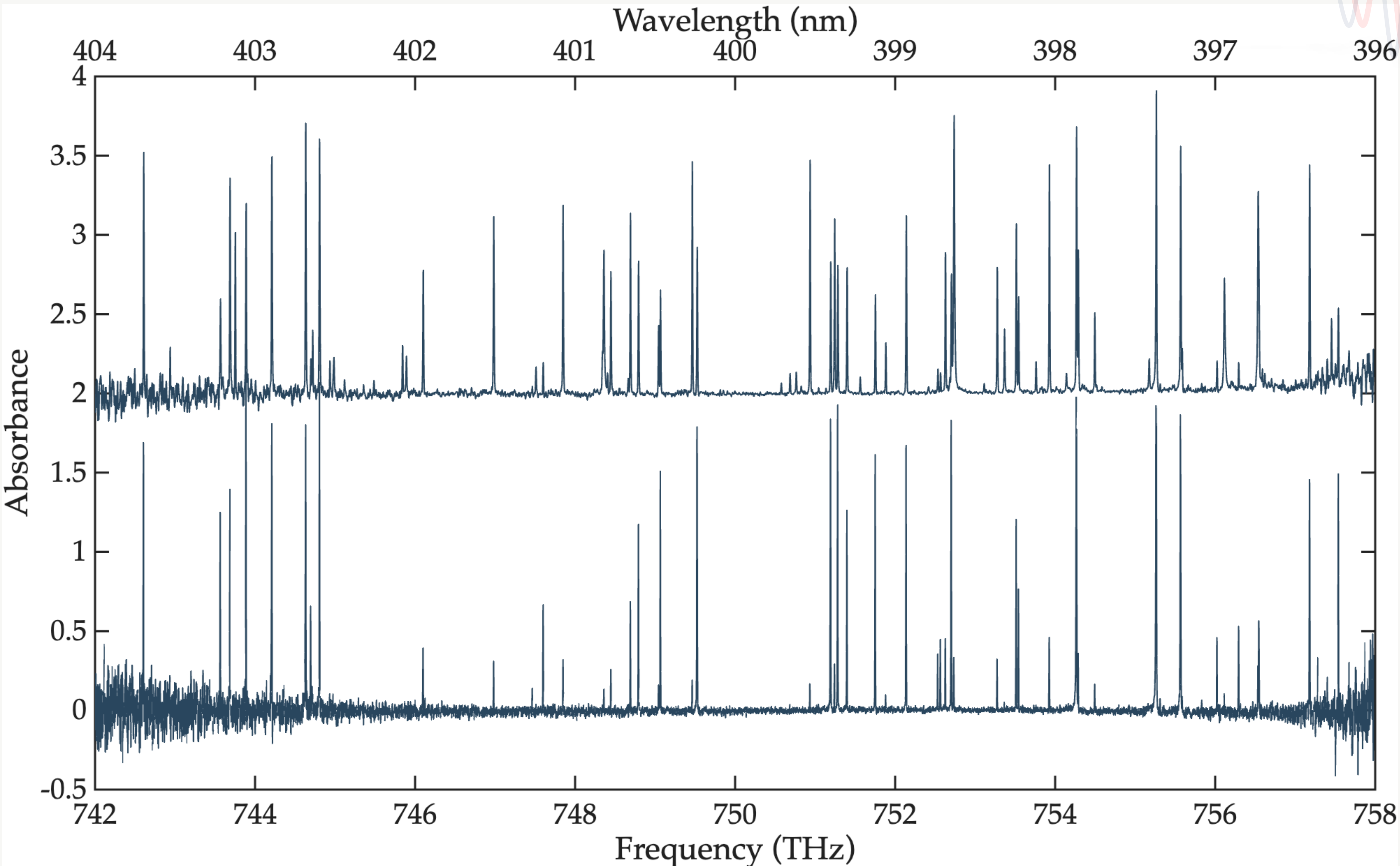
Data I Will Be Showing Today



Measured Zr absorbance

Resolution
~ 0.5 pm

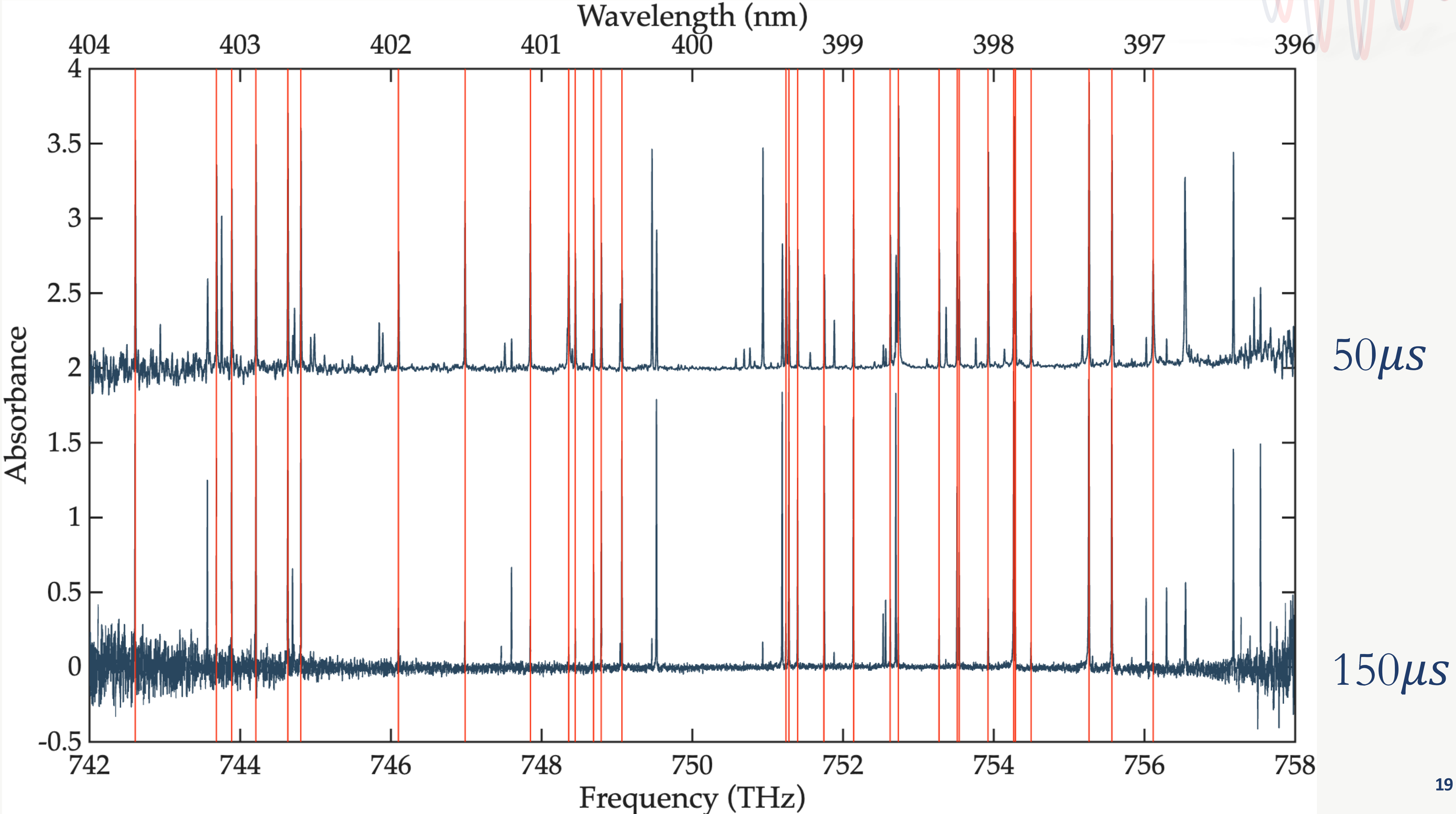


50μs

150μs

Red lines – Previously Identified Transitions

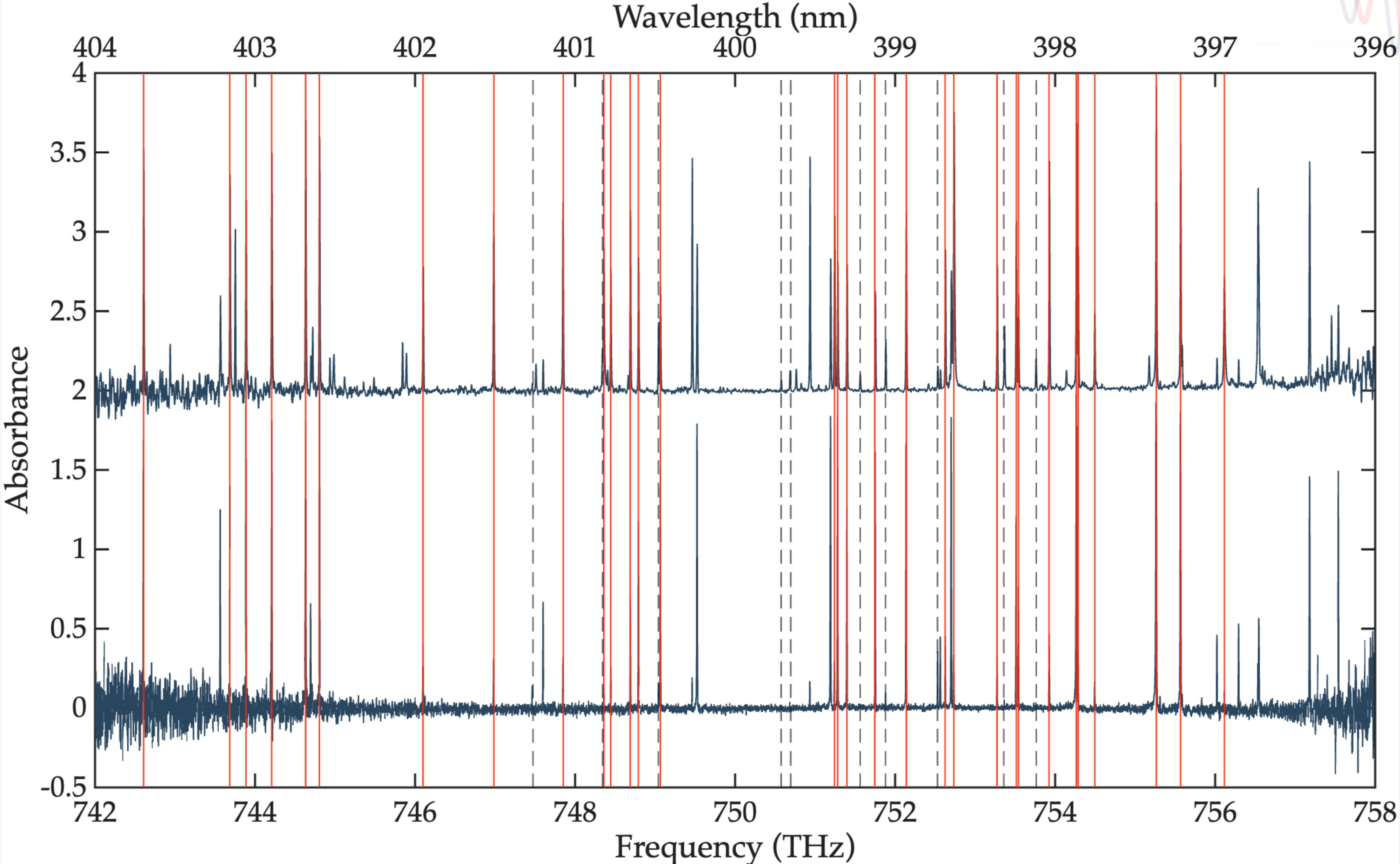
Resolution ~ 0.5 pm



Dashed lines – Newly Identified Transitions

Zirconium
40
Zr
91.224

Resolution
~ 0.5 pm

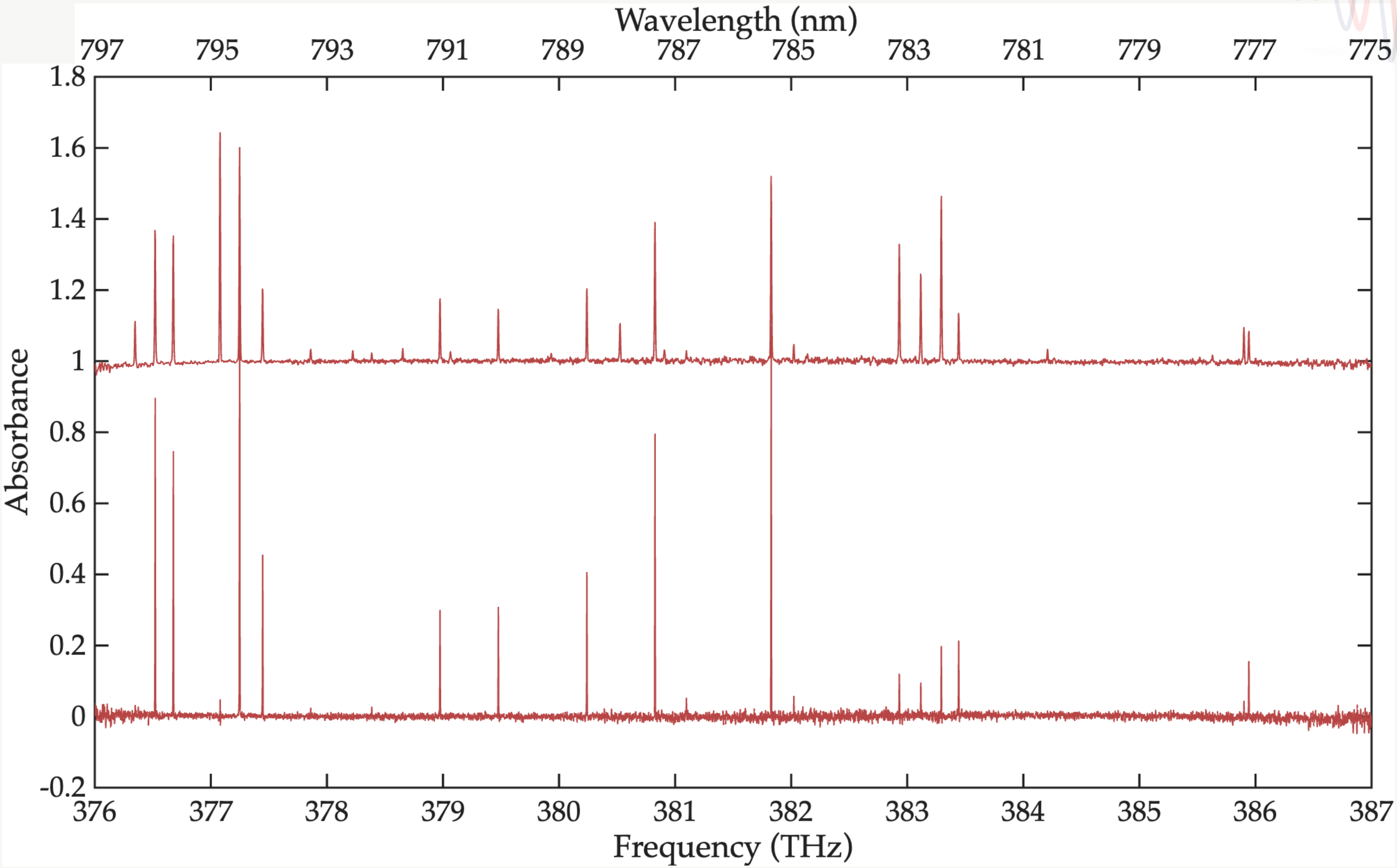


50μs

150μs

Measured Zr absorbance

Resolution ~ 0.5 pm



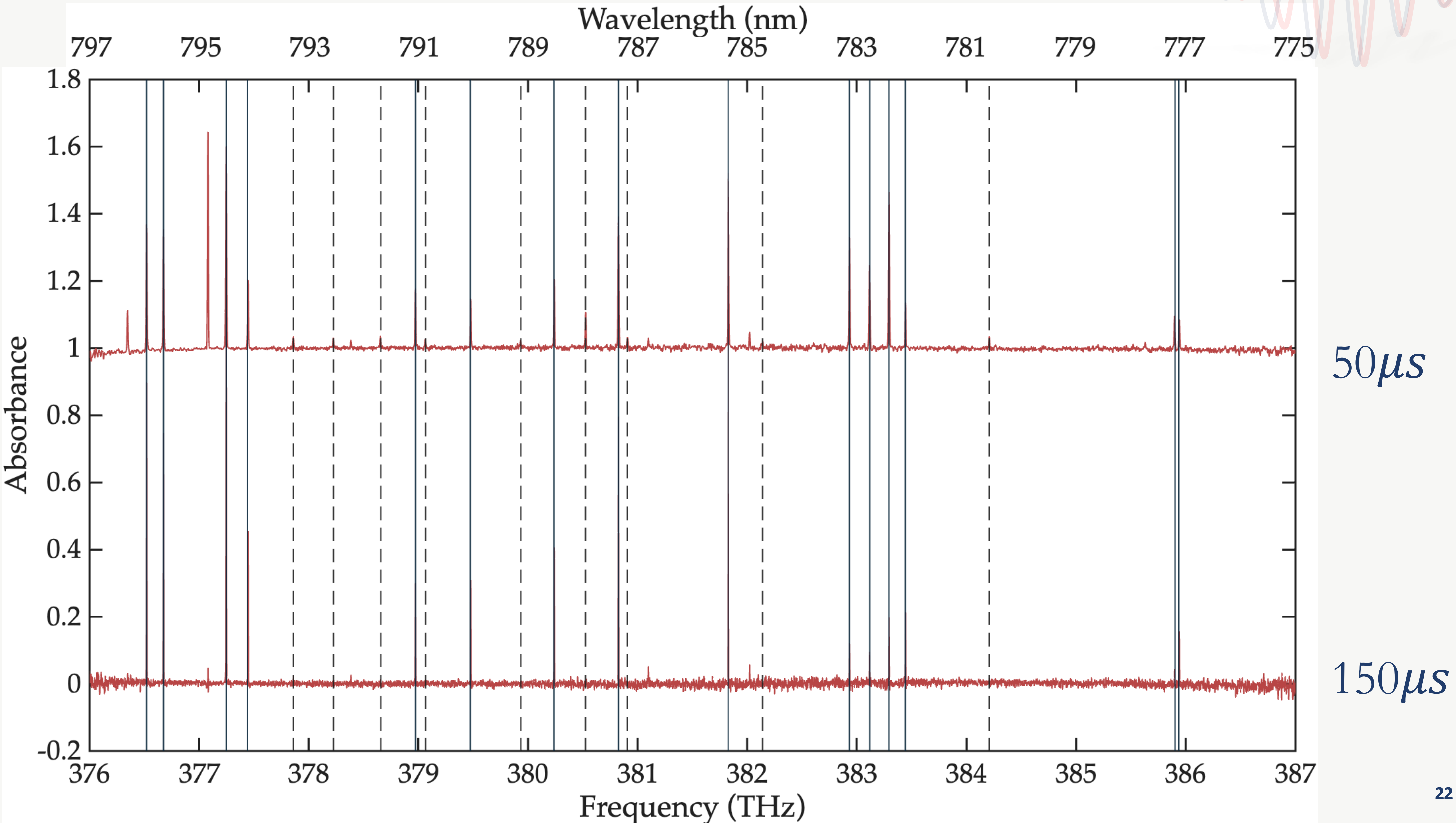
50μs

150μs

Identified Transitions

Zirconium 40 Zr 91.224

Resolution ~ 0.5 pm



Timeline of Key Zr Spectroscopy Studies

1930

THE STRUCTURE OF THE ARC SPECTRUM OF ZIRCONIUM

By C. C. Kiess and Harriet K. Kiess

1931

RP255

THE STRUCTURE OF THE SPECTRUM OF SINGLY IONIZED ZIRCONIUM

By C. C. Kiess and Harriet K. Kiess

1952

ATOMIC ENERGY LEVELS

As Derived From the Analyses of Optical Spectra

Volume II

The Spectra of Chromium, Manganese, Iron, Cobalt, Nickel, Copper, Zinc, Gallium, Germanium, Arsenic, Selenium, Bromine, Krypton, Rubidium, Strontium, Yttrium, Zirconium, and Niobium

BY CHARLOTTE E. MOORE

1961

Expanded - 1975

Tables of Spectral-Line Intensities

Part I - Arranged by Elements

Second Edition

William F. Meggers, Charles H. Corliss and Bourdon F. Scribner

Institute for Basic Standards
National Bureau of Standards
Washington, D.C. 20234

1962

Experimental Transition Probabilities for Spectral Lines of Seventy Elements

Derived From the NBS Tables of Spectral-Line Intensities

The wavelength, energy levels, transition probability, and oscillator strength of 25,000 lines between 2000 and 9000 A for 112 spectra of 70 elements.

Charles H. Corliss and William R. Bozman

Key Lessons

- **NIST does not have everything (this is known)**
  - Surprise: data from the 30s (where the energy levels were originally derived from - Moore) are left out of NIST.
- **Kurucz wavelengths are theory**
  - There are papers that are listed but this is **just for the oscillator strengths**.
  - Kurucz calculates energy levels and gives the Ritz transitions for lines that have oscillator strengths from experiments.
- **A lot of Zr I & II oscillator strengths are derived from relative intensities.**
  - There was a large dataset (Meggers) that had a known number density and arc temperature. The intensities were well characterized.
  - Then Corliss and Bozman calculated the oscillator strengths.
  - **These have been shown to have a large wavelength and intensity dependence.**

Boltzmann Plot Analysis

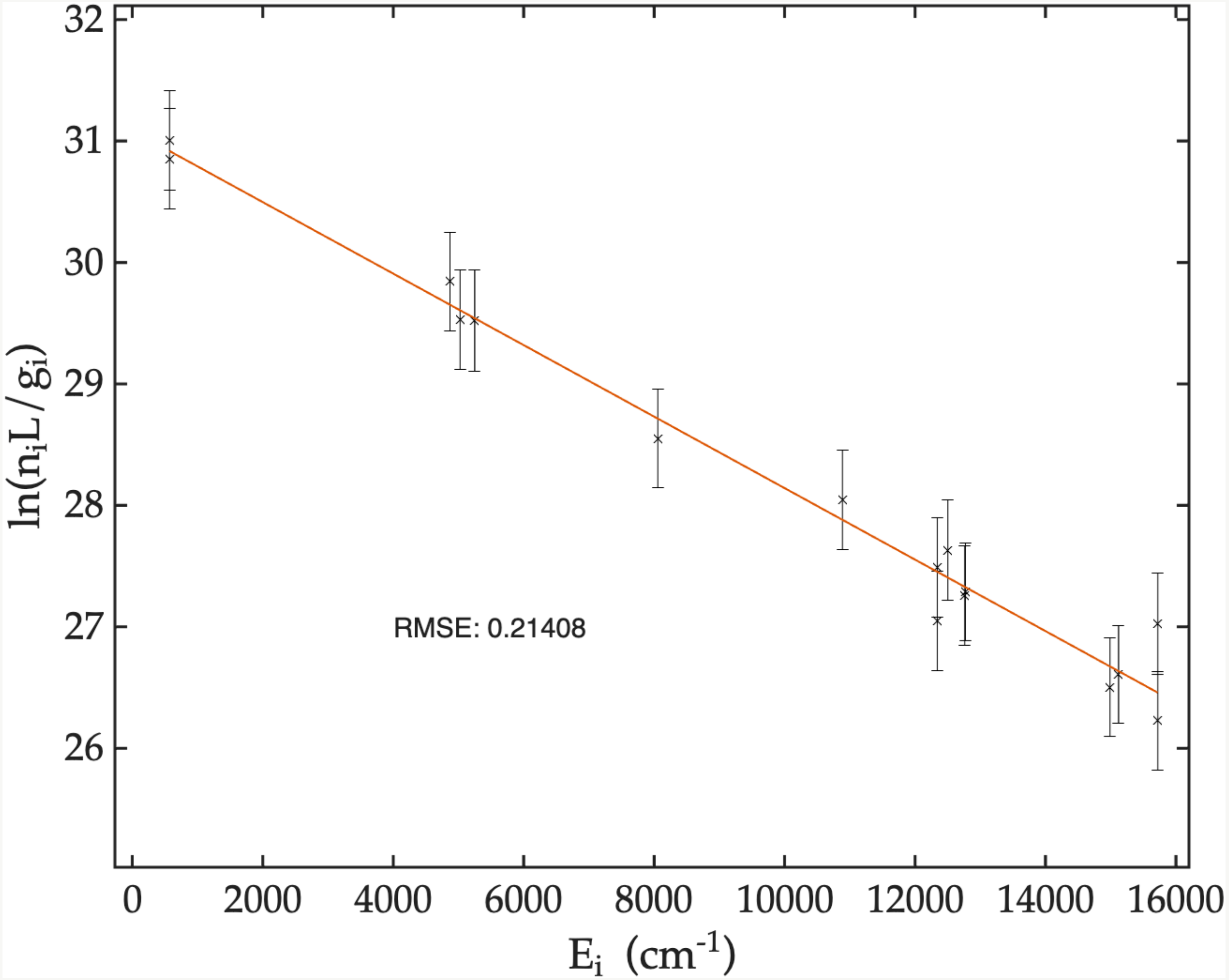
- **Calculate individually for each time delay**
- **Assumes LTE**

Boltzmann:

$$n_i = g_i \cdot n_{total} \cdot \frac{e^{\frac{-E_i}{k_B T}}}{Z(T)}$$

$$\ln\left(\frac{n_i L}{g_i}\right) = \ln\left(\frac{Area_{ij}}{\tilde{\sigma}_0 g_i f_{ij}}\right) = \ln\left(\frac{n_{tot} L}{Z(T)}\right) - \frac{E_i}{k_B T}$$

$$y = mx + b$$



Obtaining New Oscillator Strengths

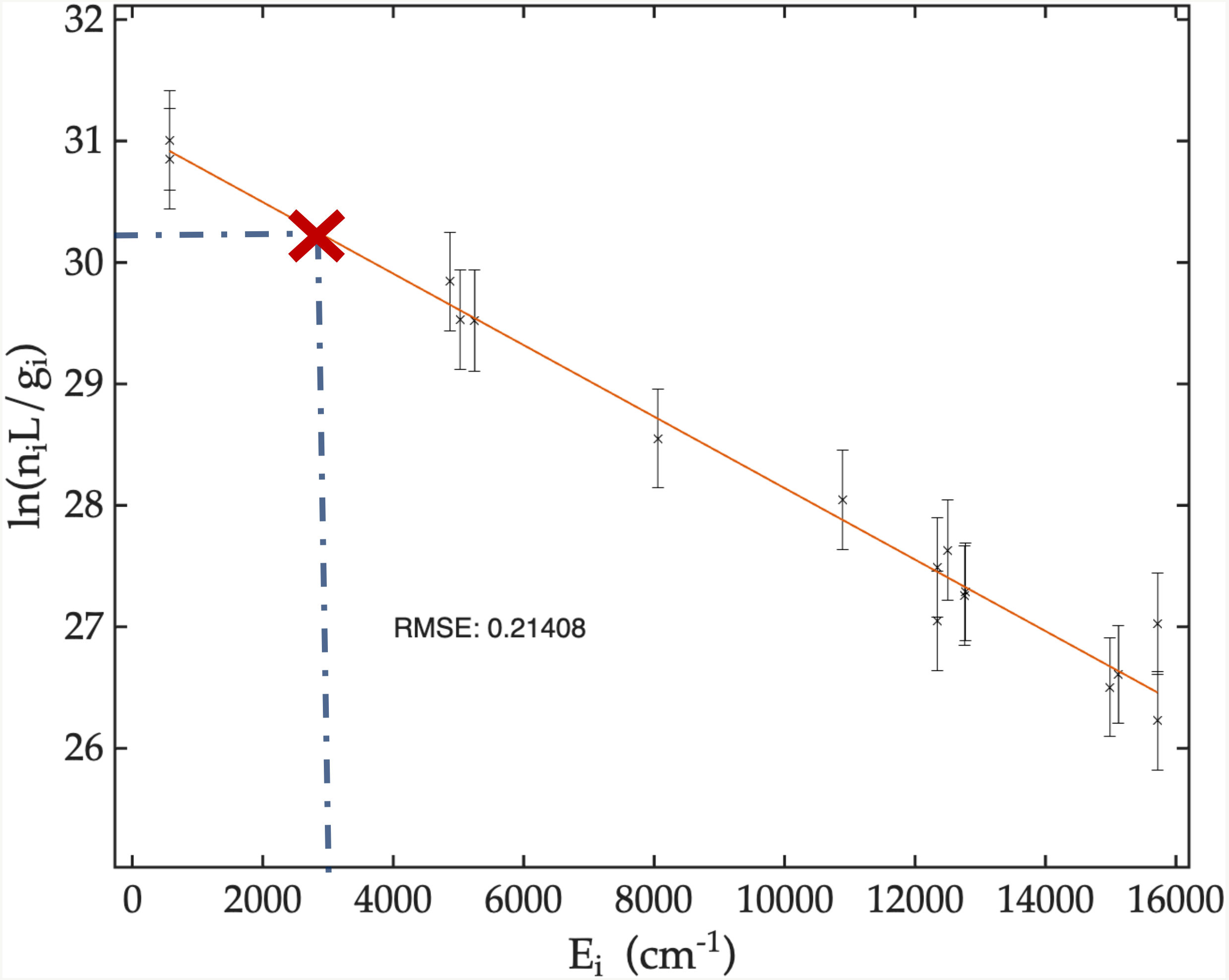
- T and $n_{tot}L$ now known
- $\longrightarrow$ solve for f_{ij}

Boltzmann:

$$n_i = g_i \cdot n_{total} \cdot \frac{e^{\frac{-E_i}{k_B T}}}{Z(T)}$$

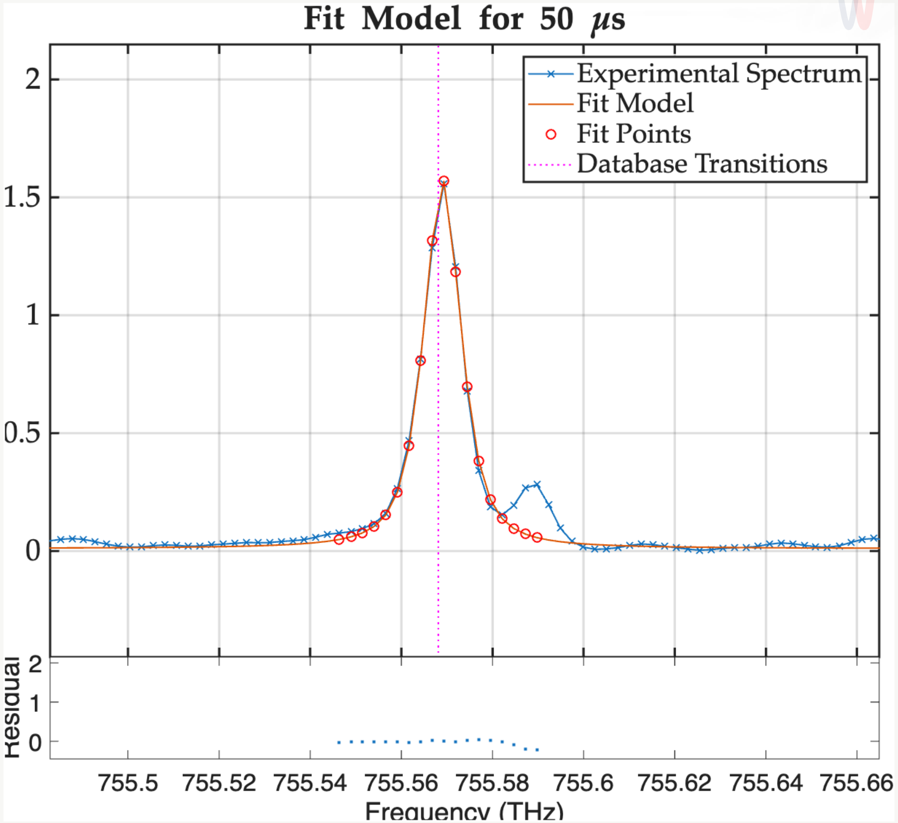
$$\ln\left(\frac{n_i L}{g_i}\right) = \ln\left(\frac{Area_{ij}}{\tilde{\sigma}_0 g_i f_{ij}}\right) = \ln\left(\frac{n_{tot}L}{Z(T)}\right) - \frac{E_i}{k_B T}$$

$$y = mx + b$$



Spectral Fitting

- **Each transition fit independently (e.g., peak area, Gaussian & Lorentzian widths)**
- **Fit includes instrument lineshape broadening**
- **Uncertainties calculated from fit statistics**



- Directly obtain **state resolved column densities** for each transition

$$A_i = \int -\ln\left(\frac{I(\nu)}{I_0(\nu)}\right)\cdot d\nu$$

$$= \int \alpha_i(\nu)\cdot L\cdot d\nu \approx \sigma_0 \cdot g_i \cdot f_{ij}\left(\frac{n_i}{g_i} - \frac{n_j}{g_j}\right)L$$

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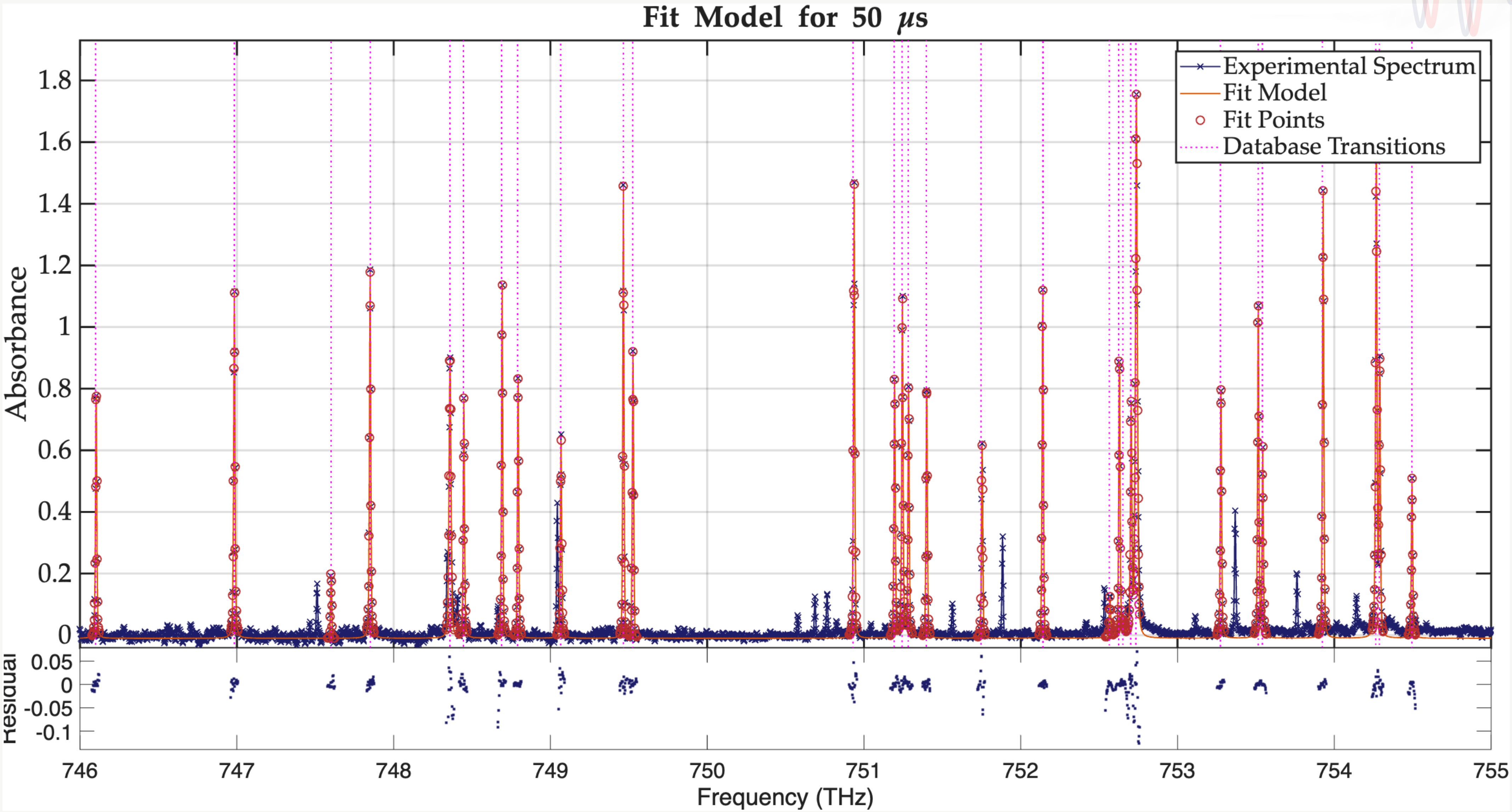
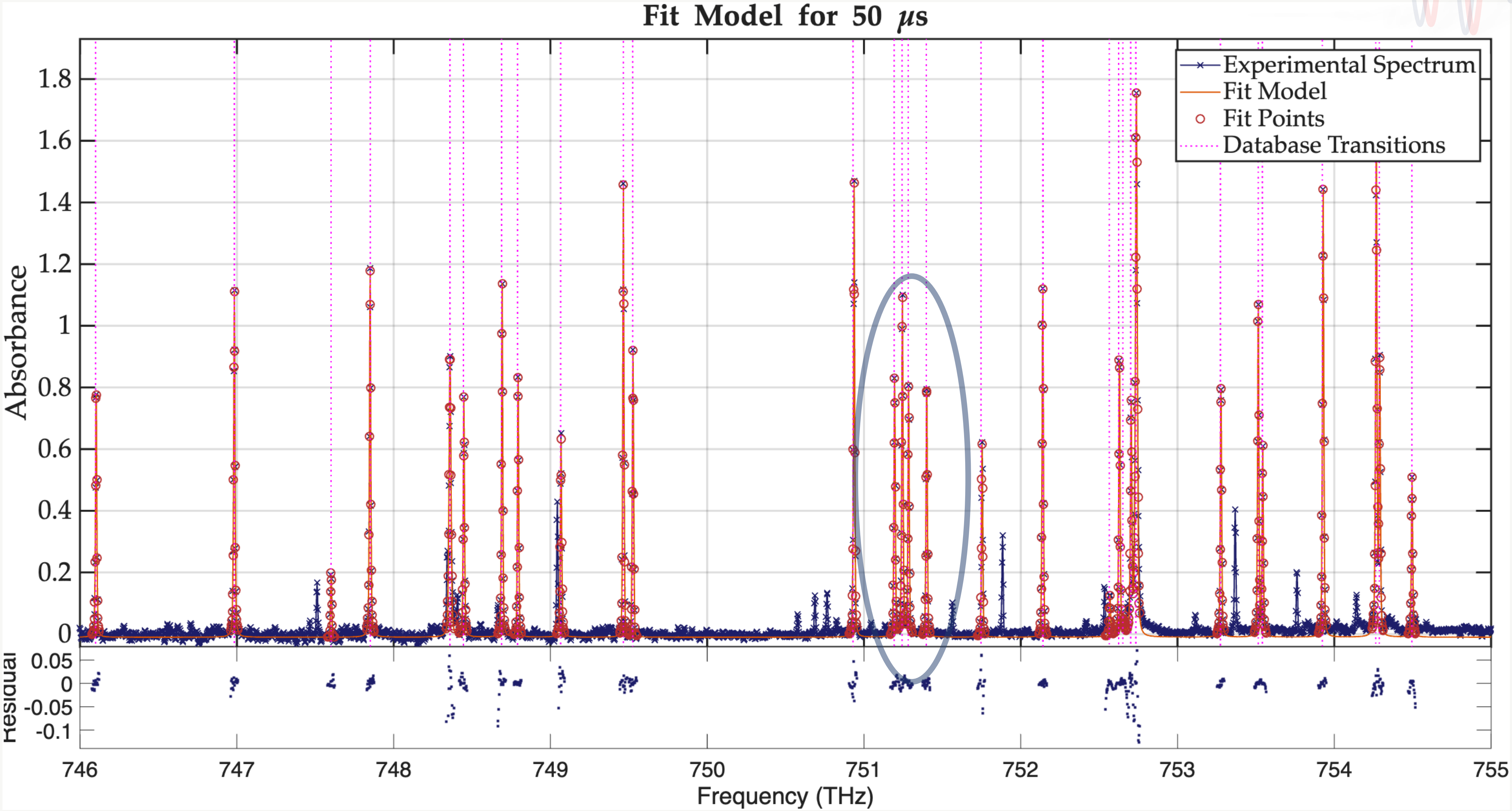
R. D. Weeks, et al. Spectrochimica Acta Part B (2021)

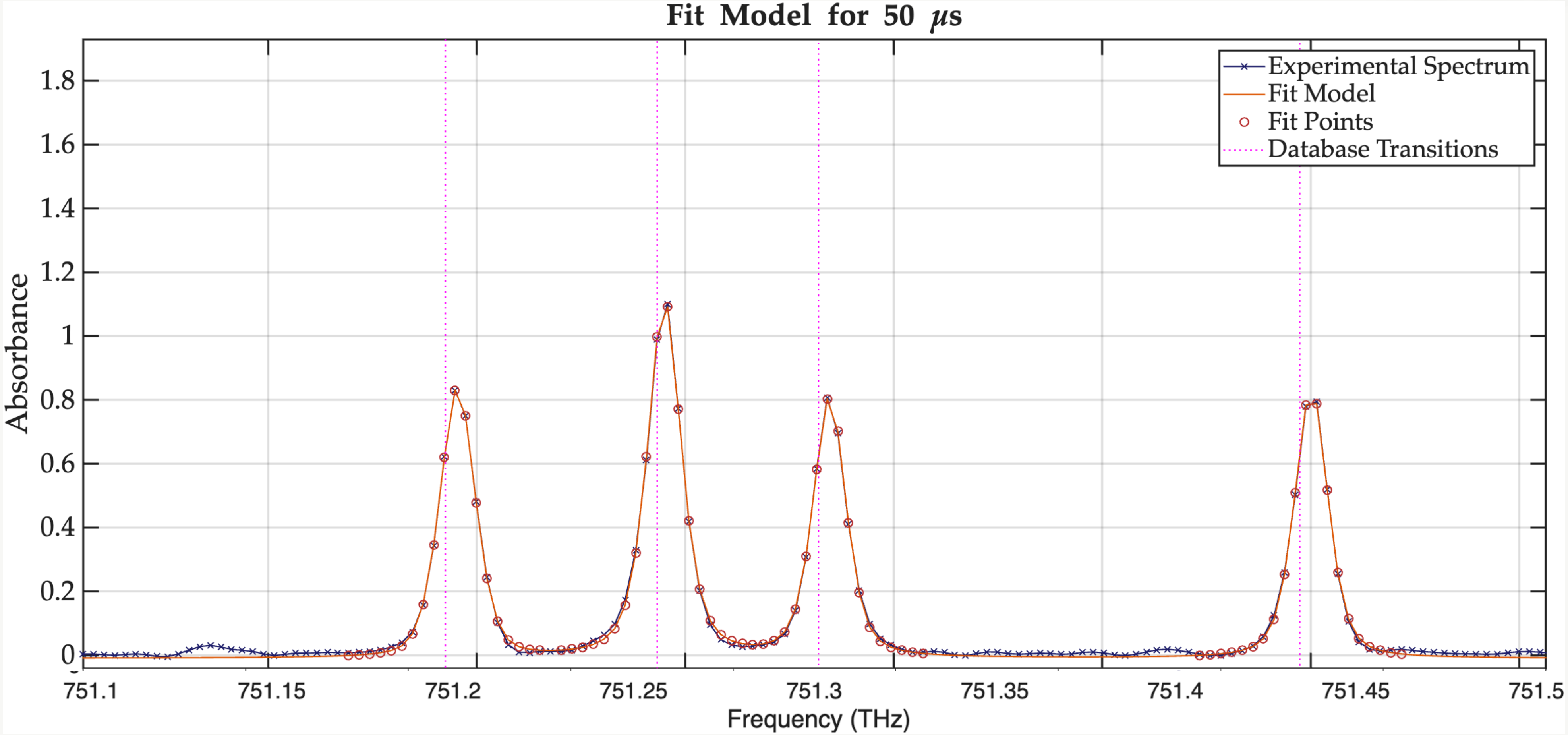
Fitting the Blue Region



Fitting the Blue Region



Fitting the Blue Region



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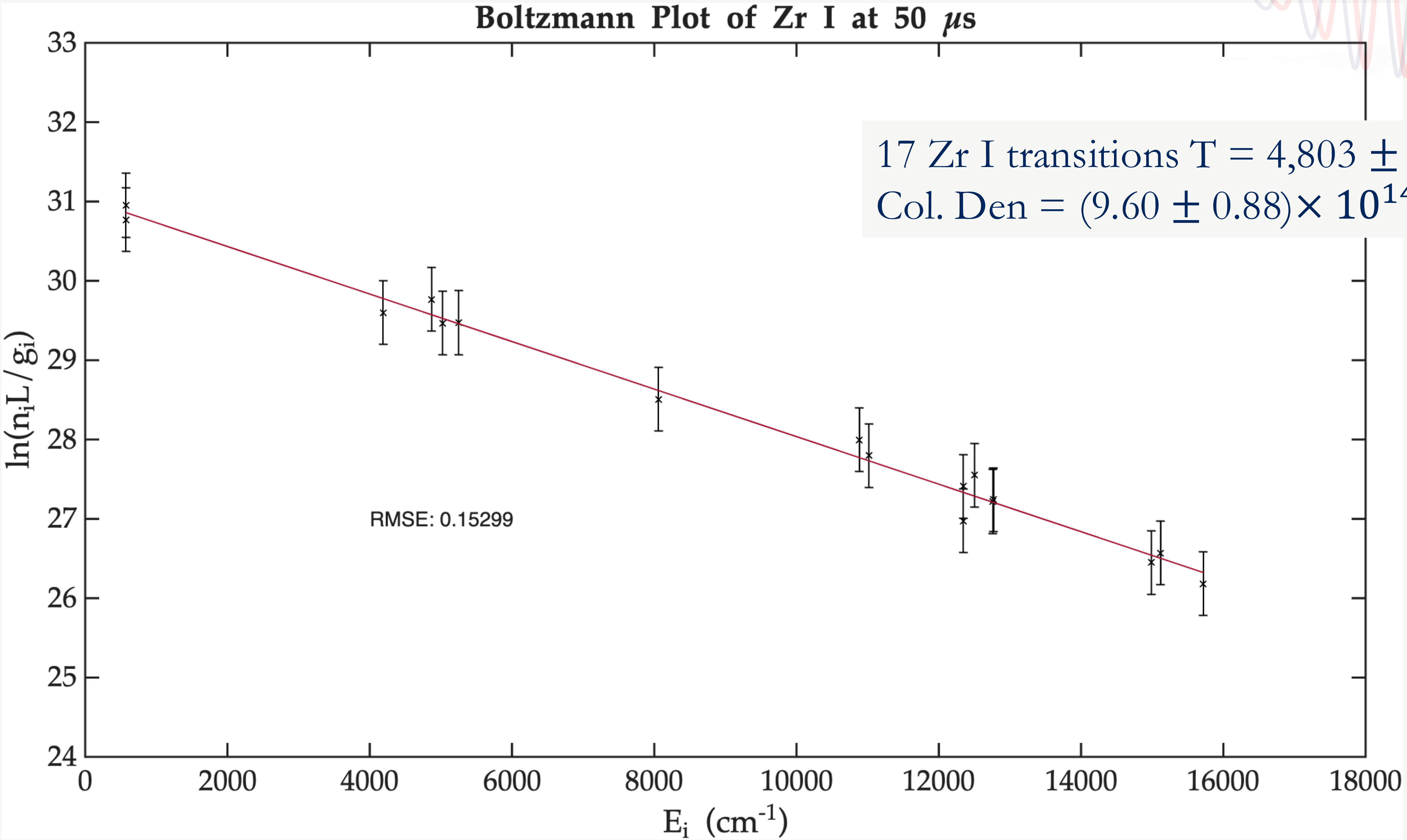
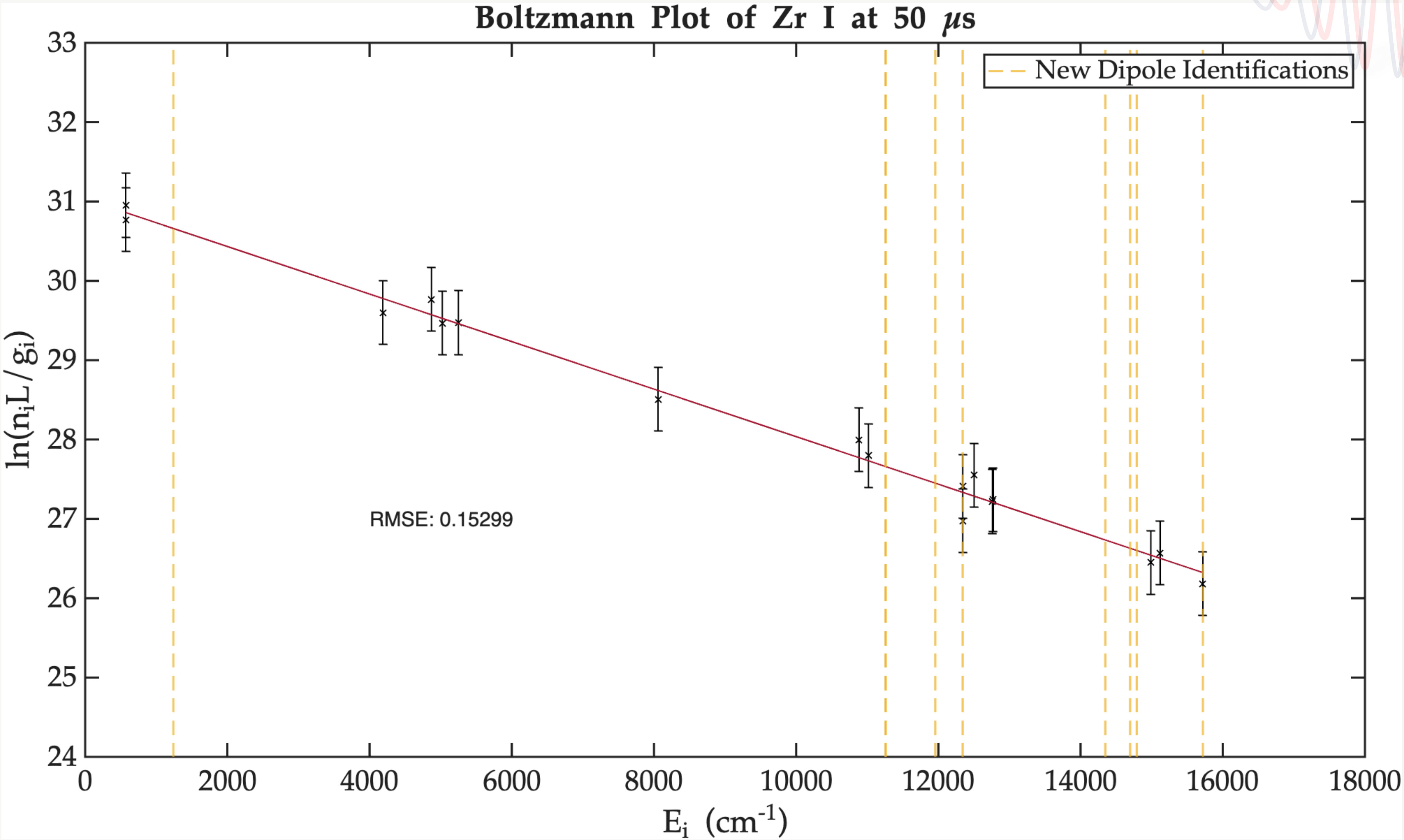
50 μs Blue - Boltzmann Plot Analysis



17 Zr I transitions T = 4,803 ± 190 K

Col. Den = (9.60 ± 0.88)$\times 10^{14}\ cm^{-2}$

Unidentified Oscillator Strengths



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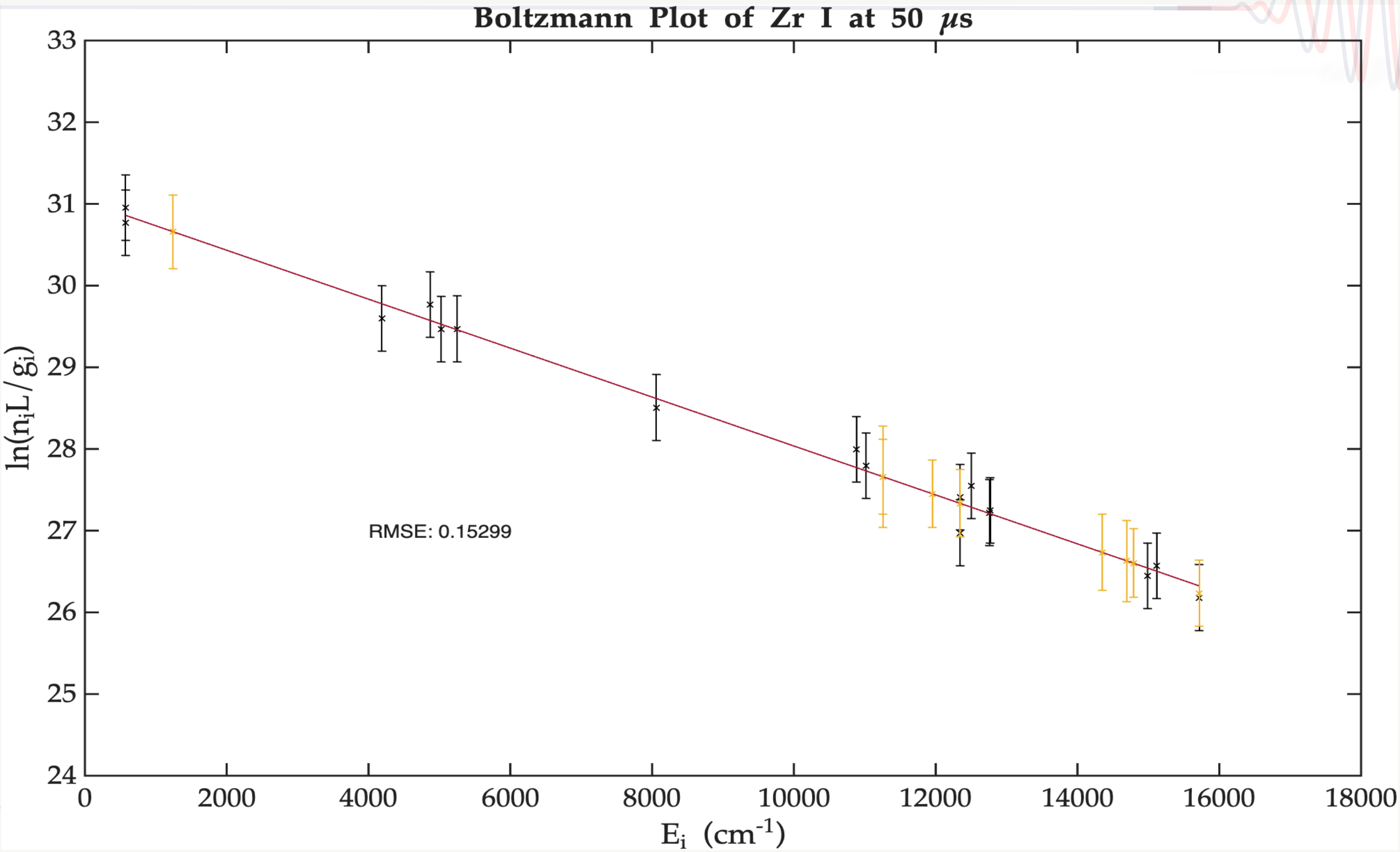
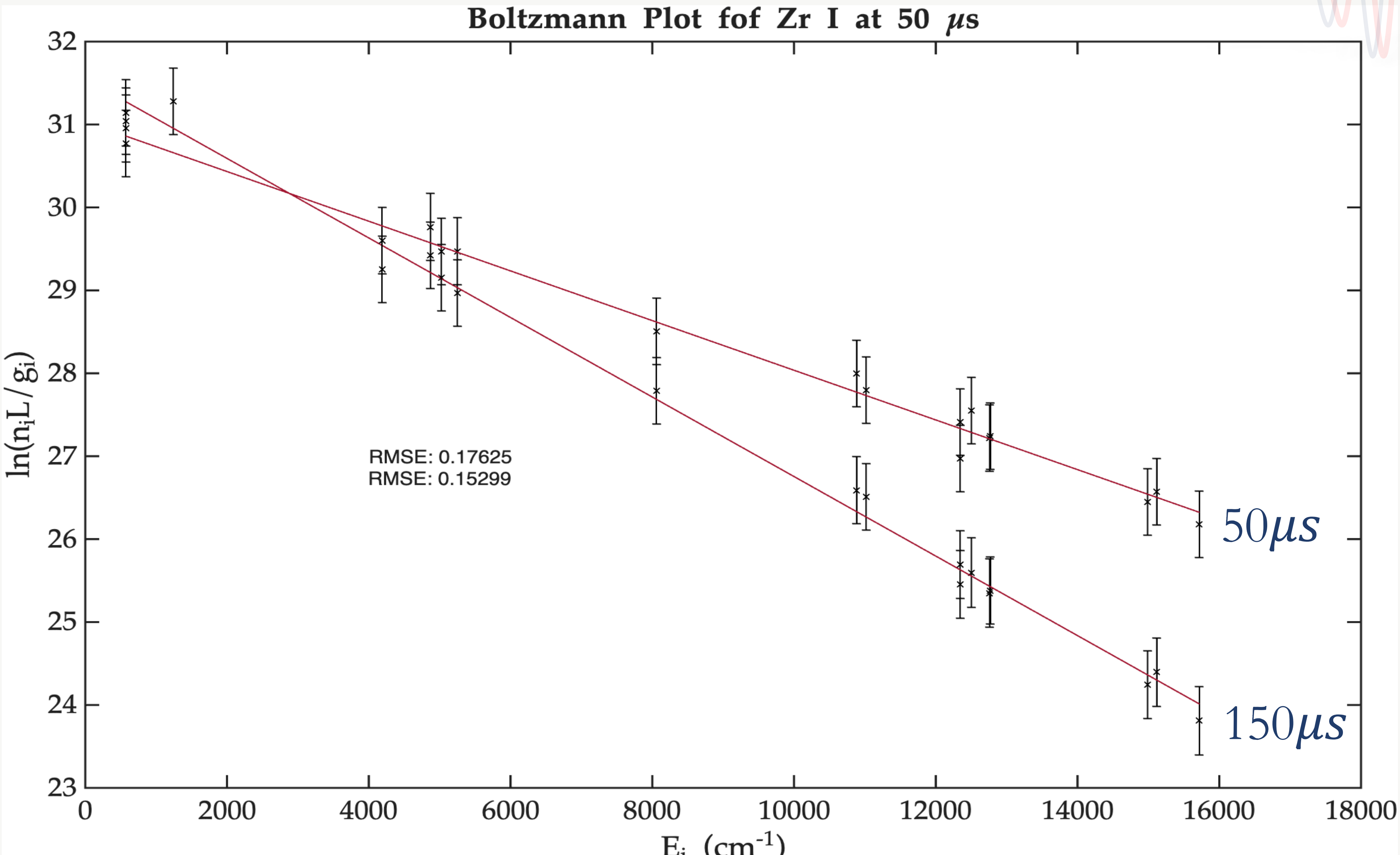
9 New Oscillator Strengths – 50μs



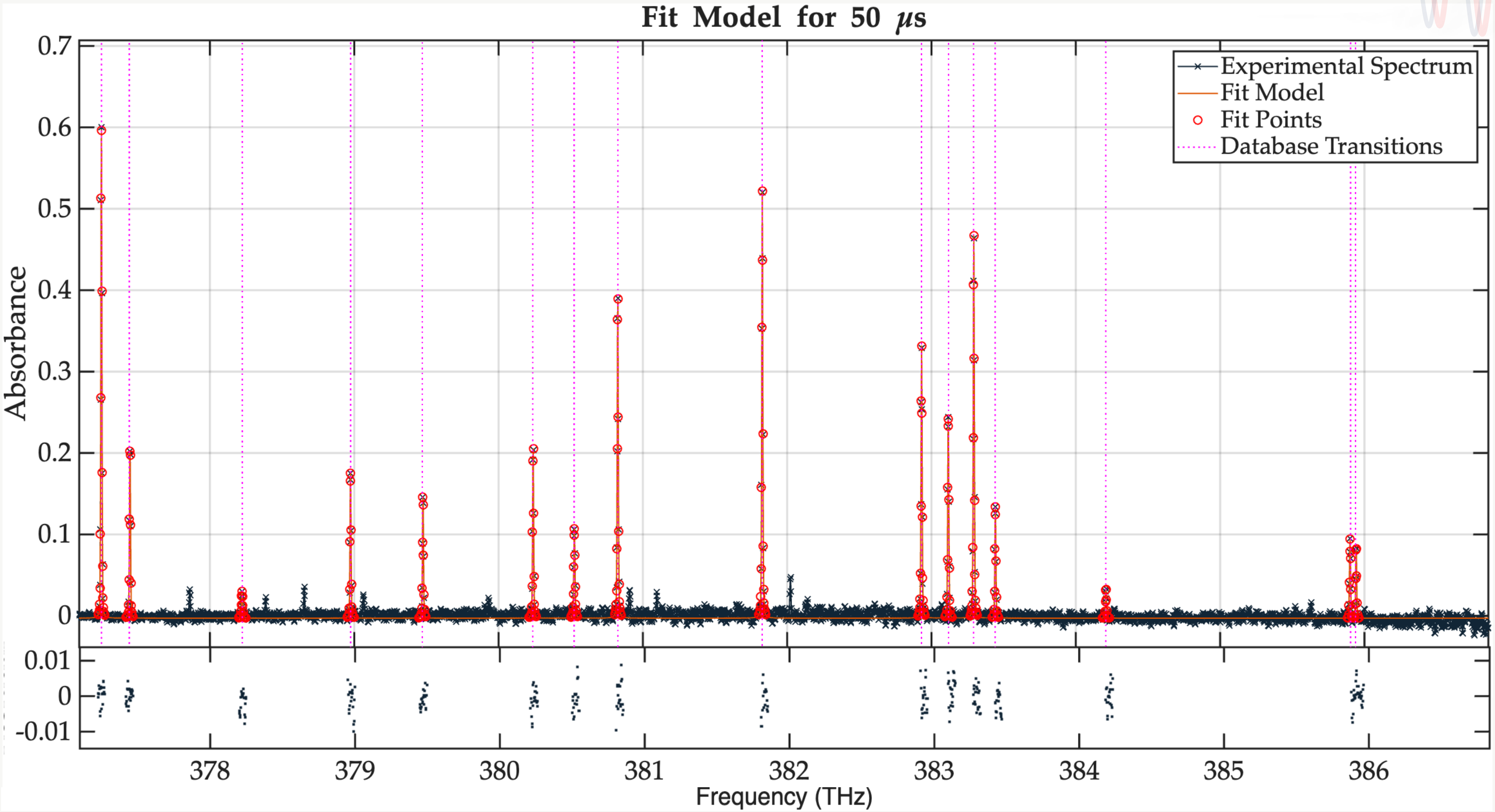
150 and 50 μs



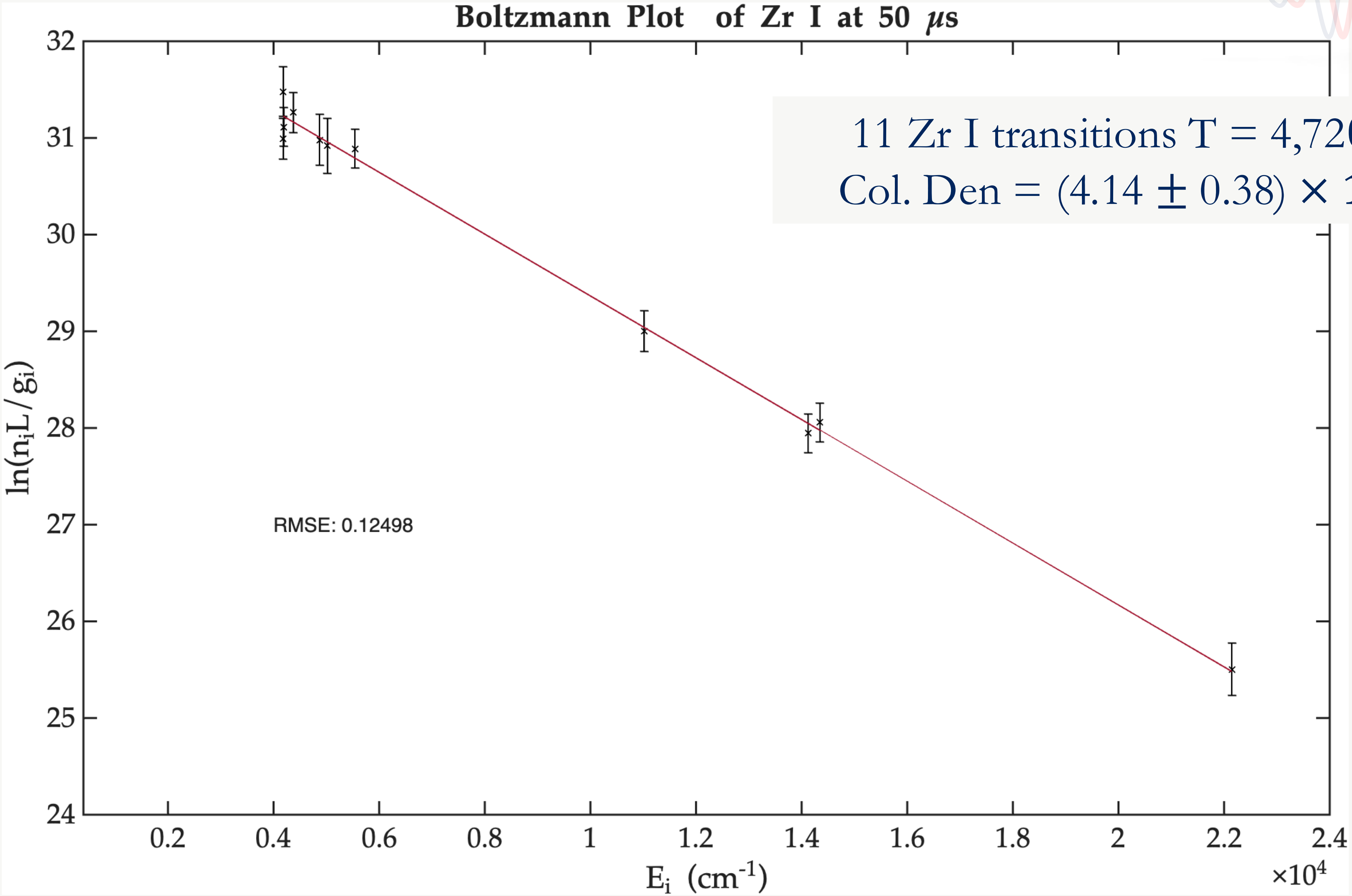
Oscillator Strength Agreement

Frequency (THz)	$\log(gf)$ ($50\mu s$)	Relative Uncertainty (dex)	$\log(gf)$ ($150\mu s$)	Relative Uncertainty (dex)
751.879	-0.75	0.05	-0.68	0.11
749.041	-0.69	0.05	-0.61	0.08
752.530	-2.45	0.10	-2.55	0.05

Red (800nm) – Fitting Results



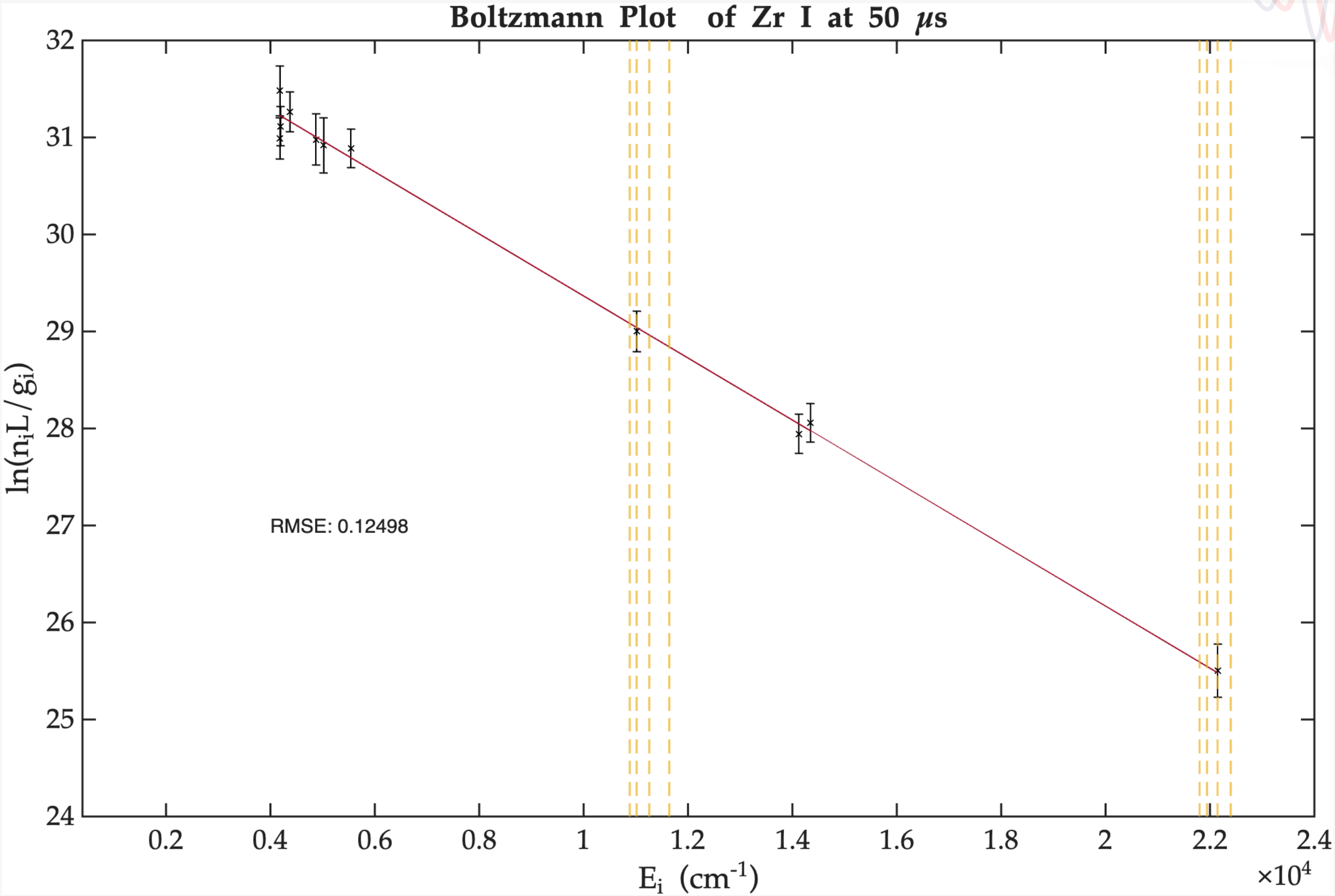
Red -Boltzmann Plot Analysis



11 Zr I transitions T = 4,720 $\pm$ 130 K

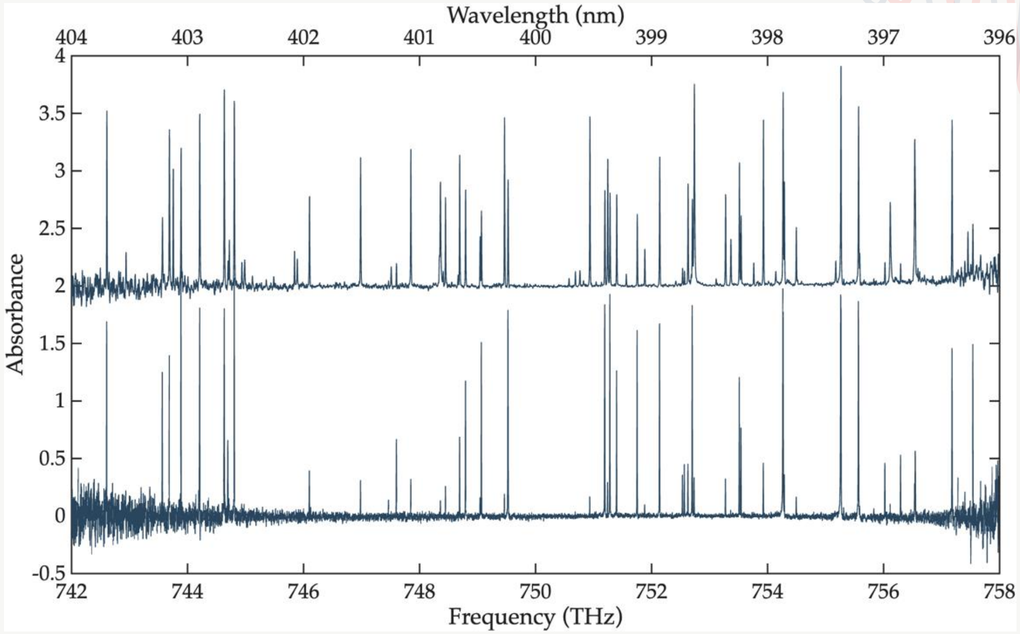
Col. Den = (4.14 $\pm$ 0.38) $\times\ 10^{15}\ cm^{-2}$

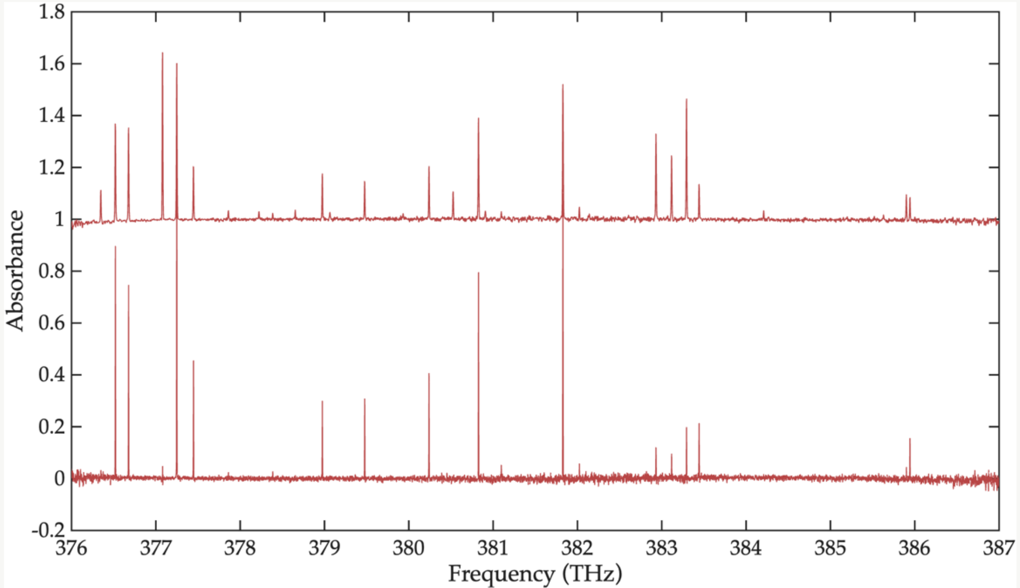
Potential Oscillator Strengths



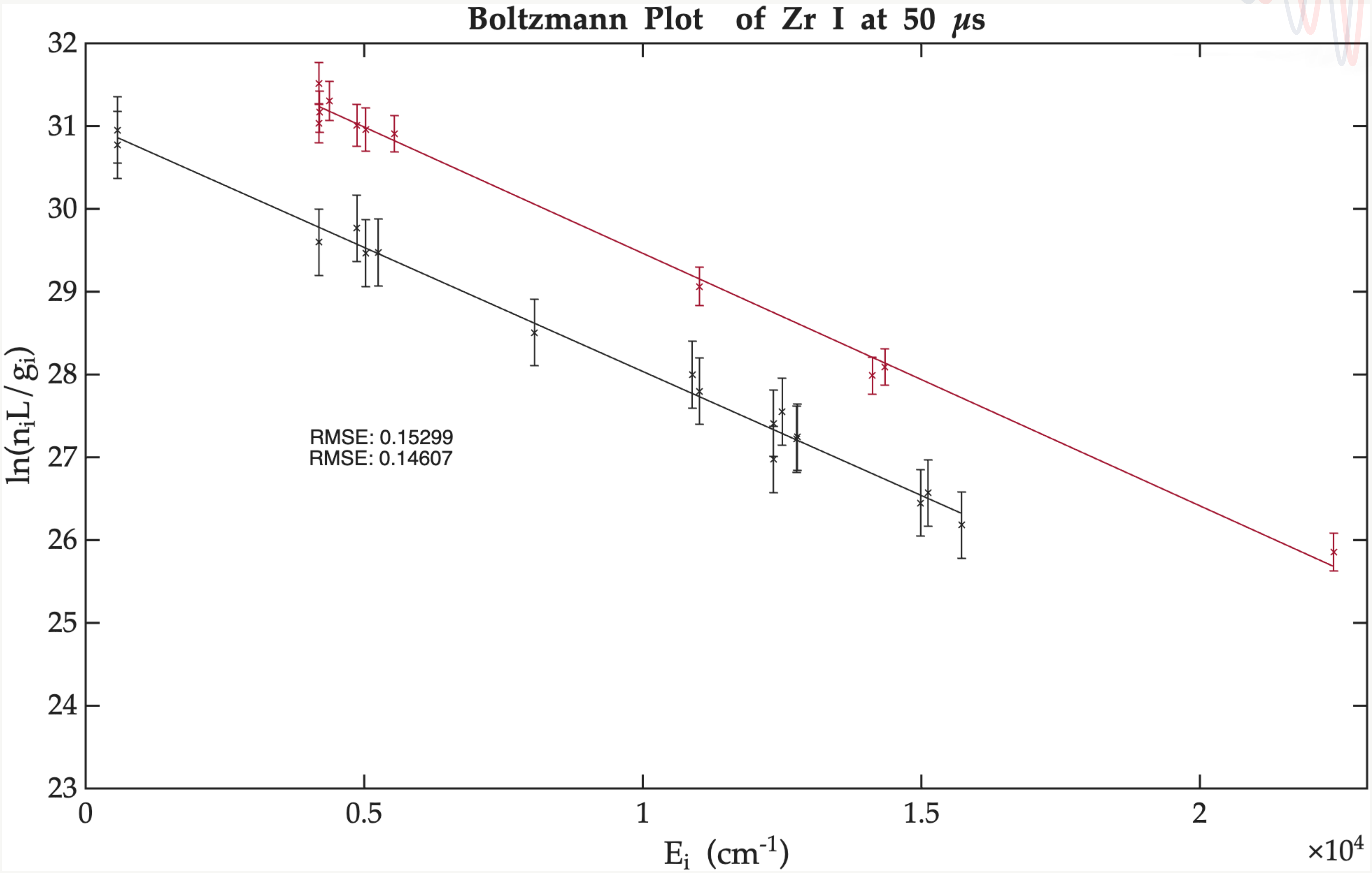
15 New Preliminary Oscillator Strengths !

Wavelength (nm)	Frequency (THz)	E_i (cm^{-1})	Log(gf)	Relative Uncertainty (dex)
400.6078	748.3440	11258	**-0.98**	0.10
400.2350	749.0410	11956	**-0.69**	0.05
399.4170	750.5751	11258	**-1.63**	0.21
399.3529	750.6956	14349	**-0.93**	0.11
398.8920	751.5629	14697	**-0.96**	0.13
398.7242	751.8792	12342	**-0.75**	0.05
398.3796	752.5297	1241	**-2.45**	0.10
397.9412	753.3587	15720	**-0.06**	0.04
397.7272	753.7640	14791	**-0.56**	0.07
787.0514	380.9058	22145	**-0.89**	0.08
789.0629	379.9348	21944	**-1.00**	0.10
790.8689	379.0672	11017	**-2.50**	0.09
791.7248	378.6574	11258	**-2.43**	0.08
793.3945	377.8605	10885	**-2.52**	0.08
784.5105	382.1395	11641	**-2.42**	0.11

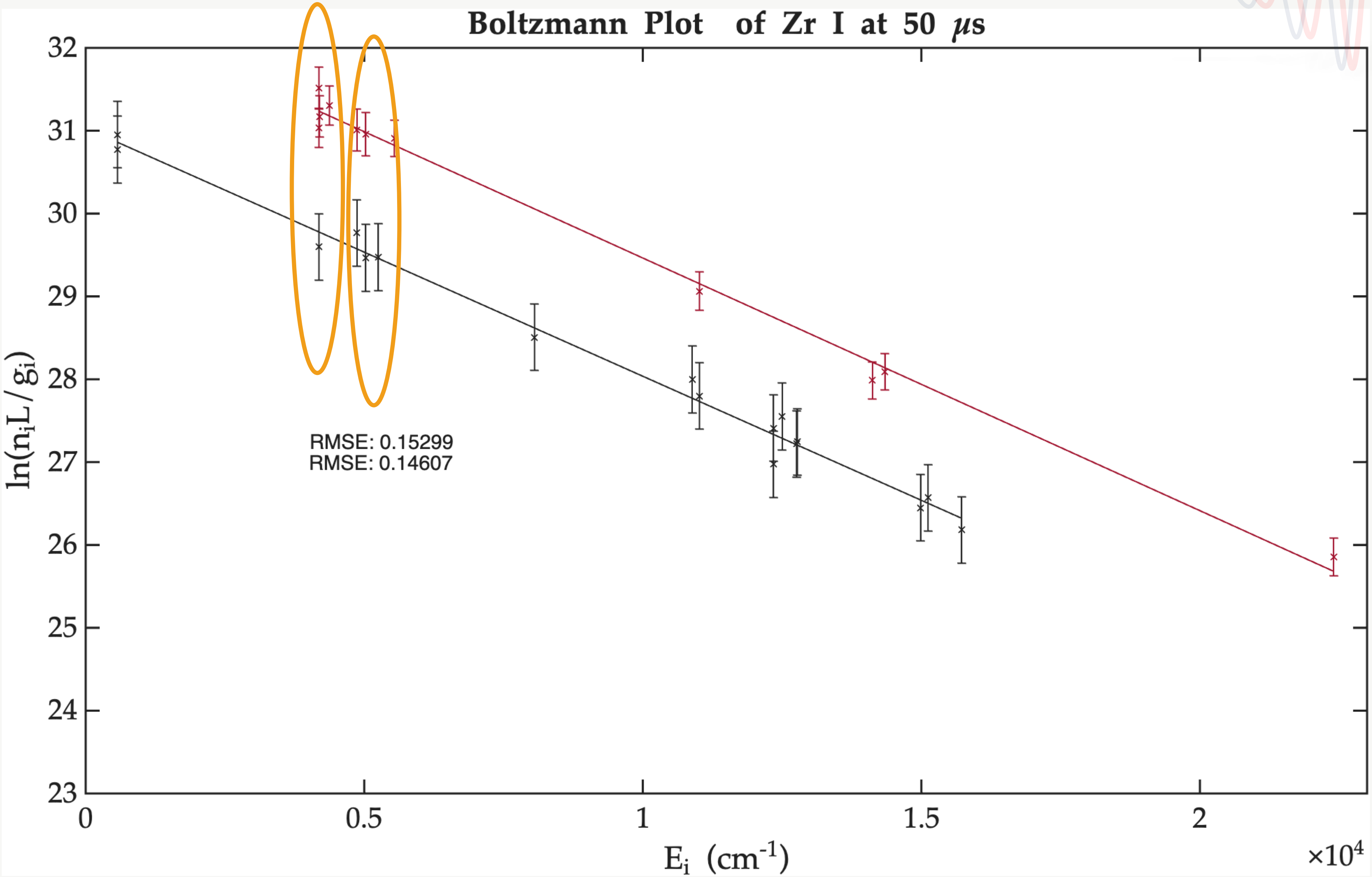




? The mystery ?


Boltzmann Plot of Zr I at 50 μs
ln(n_iL/g_i)
E_i (cm^-1)
×10^4
RMSE: 0.15299
RMSE: 0.14607
32
31
30
29
28
27
26
25
24
23
0
0.5
1
1.5
2

? The mystery ?



Boltzmann Plot of Zr I at 50 μs
RMSE: 0.15299
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ln(n_iL/g_i)
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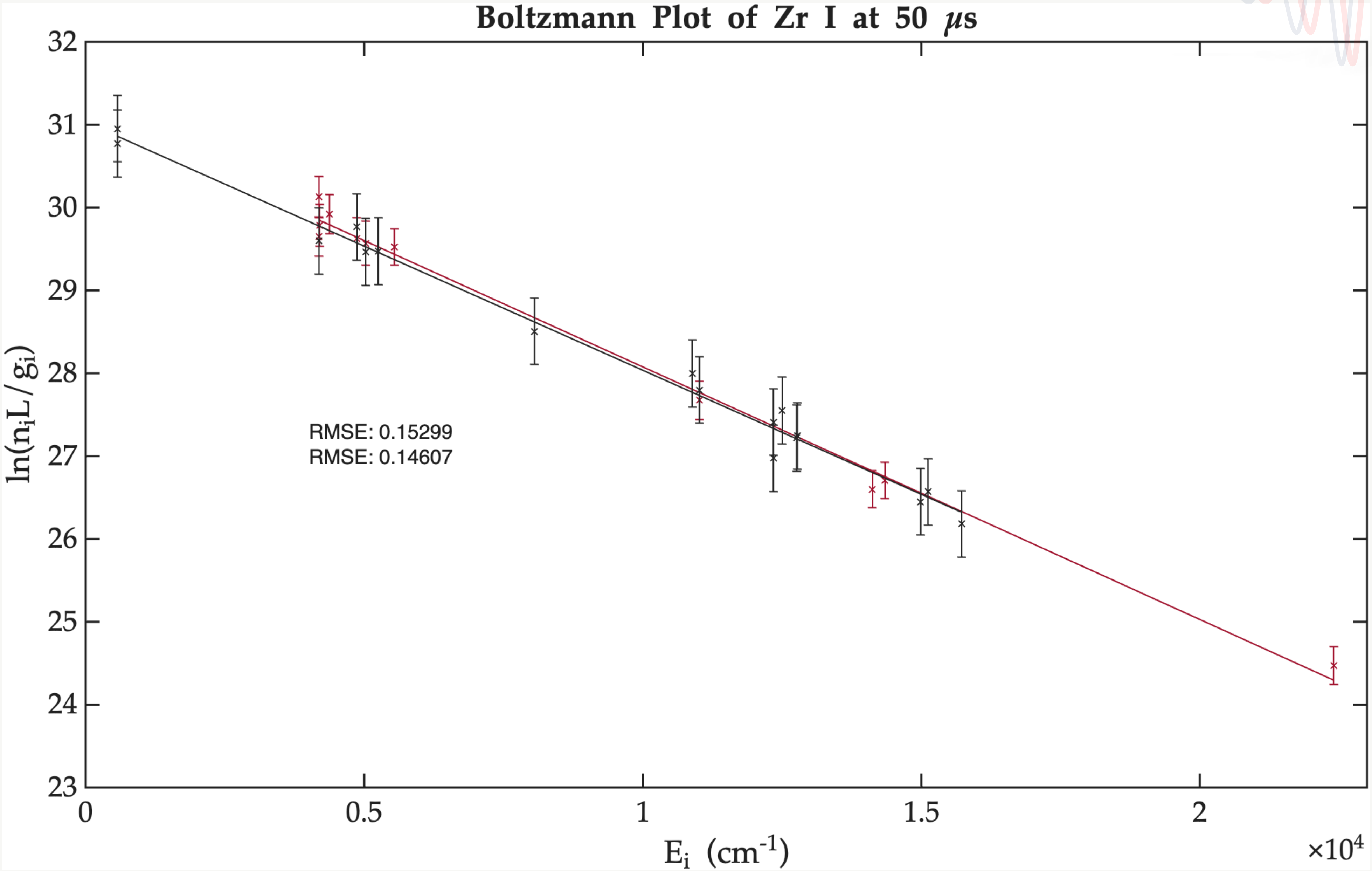
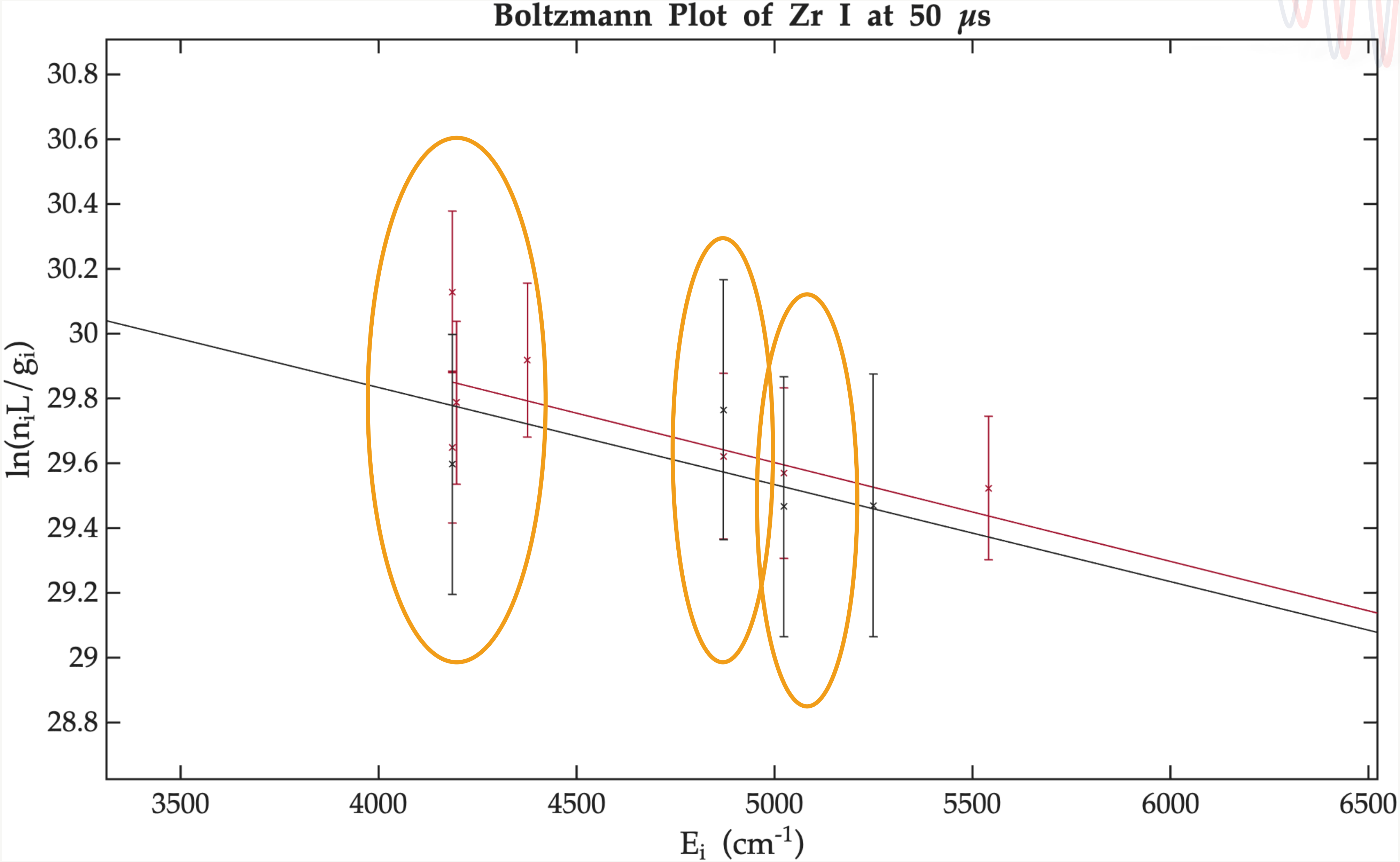
×10^4
32
31
30
29
28
27
26
25
24
23
0
0.5
1
1.5
2

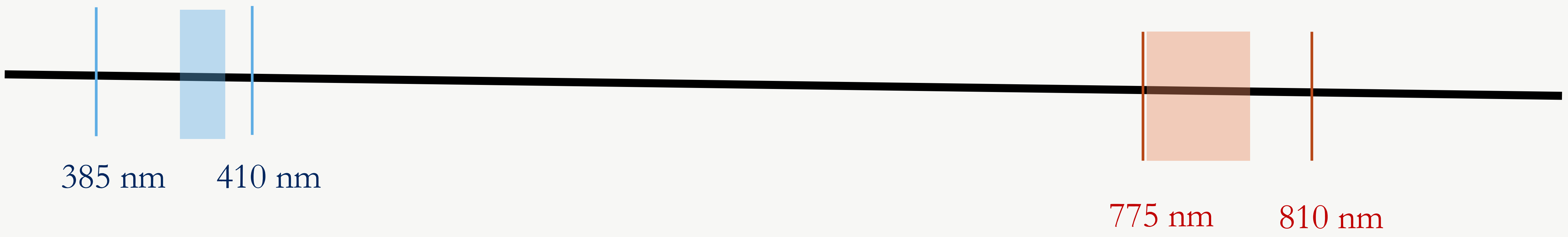
Accounting for the Factor of 4



Originating from the Same Energy Level

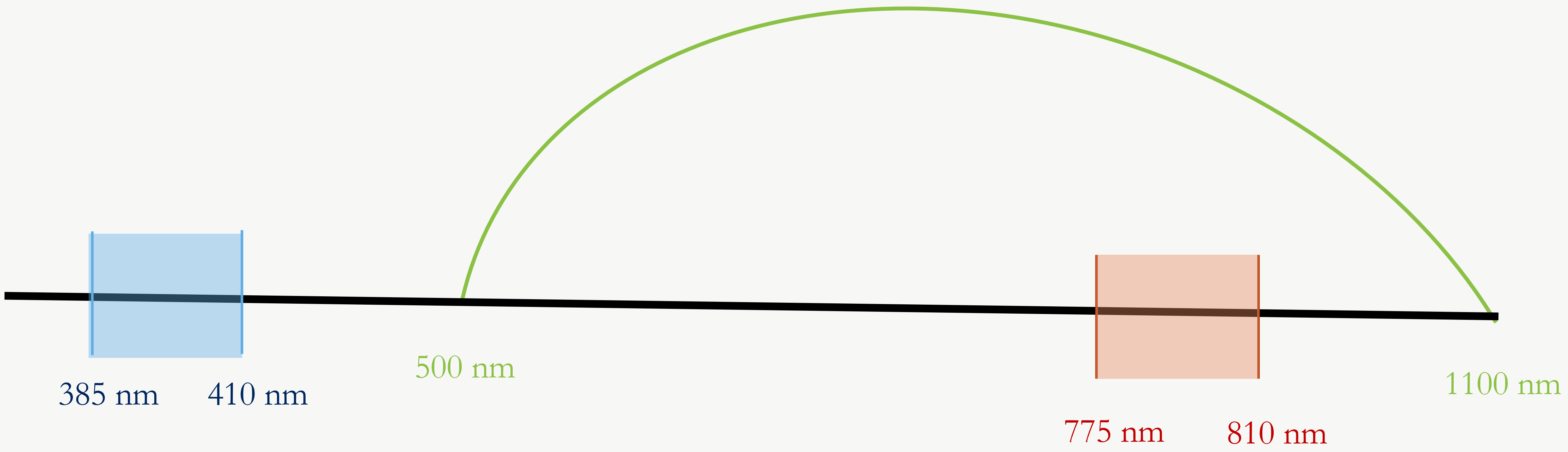


Current Wavelength Range



Extended Wavelength Range

Extending Analysis



Ongoing Work

Fundamental (780-810nm)

- 27 Zr transitions
- 3 new Zr I transitions

2nd harmonic (392-403nm)

- 70 Zr transitions
- 26 new Zr I transitions
- 4 new Zr II transitions

Total Range (500-1100nm)

- 217 New Transitions
- 193 Zr I
- 24 Zr II

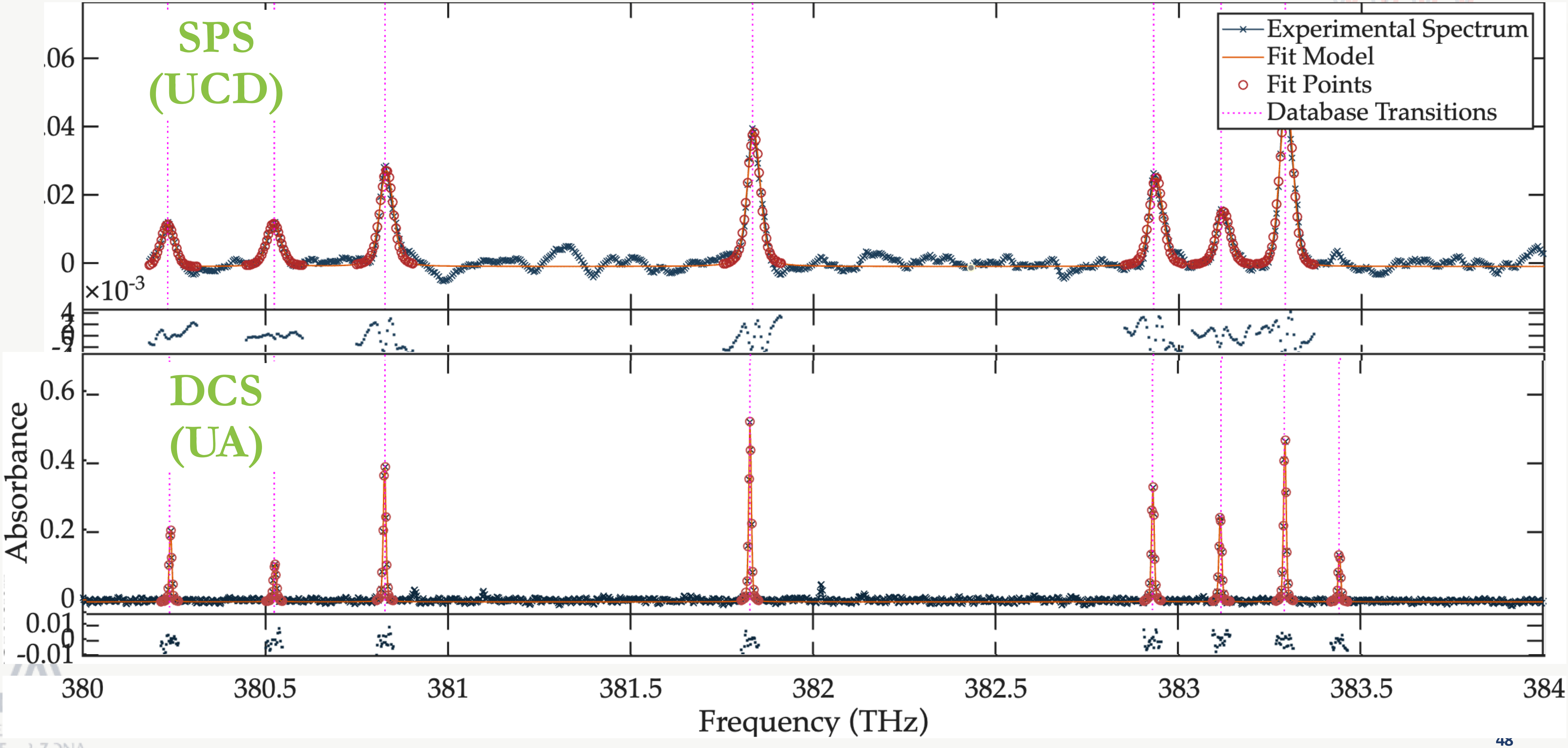
Paper In Review:

Valence Photoabsorption Spectroscopy of Zr and Zr^+ for Astrophysical Applications

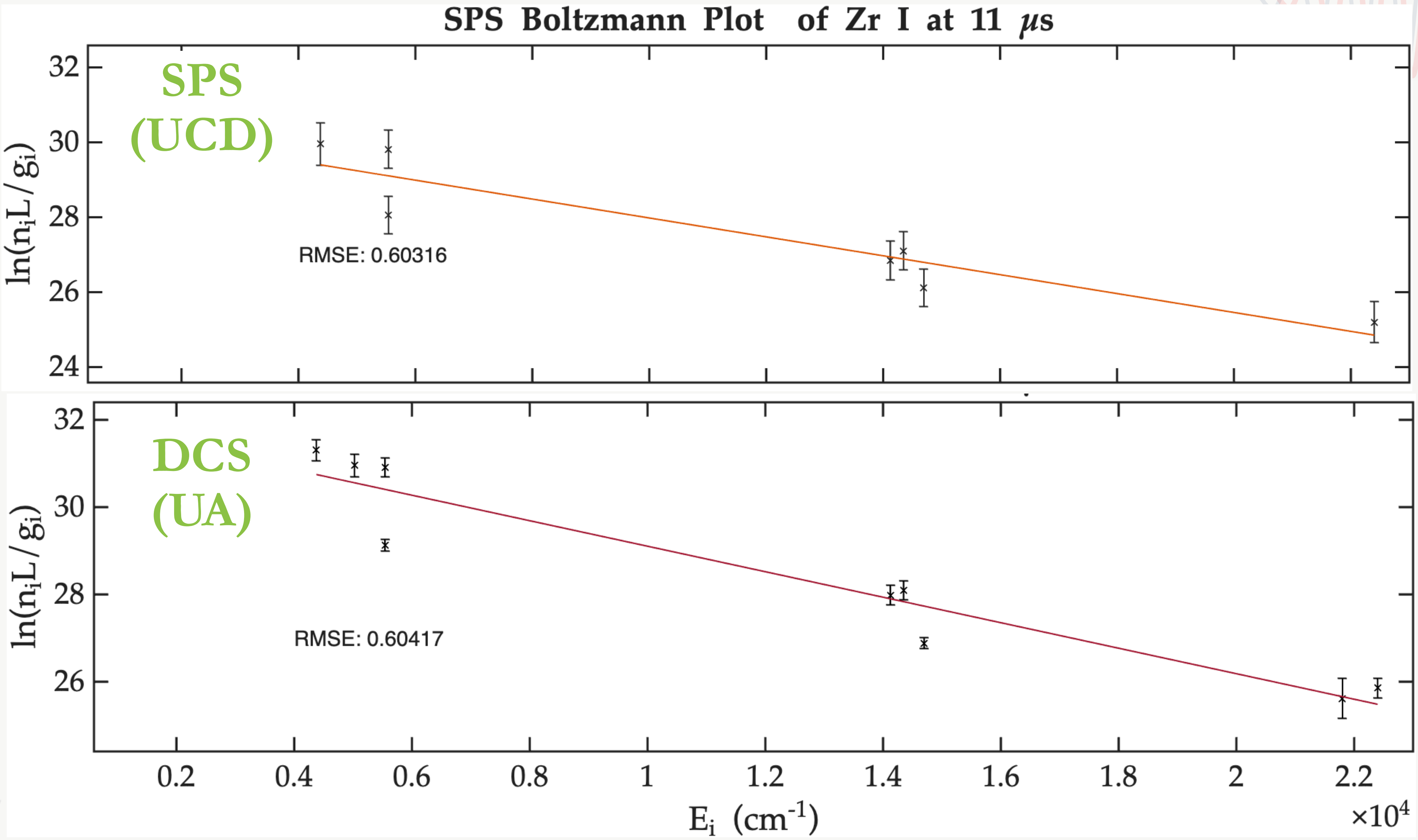
Kirsten Dowd,[1★] Hope Dannar,[2] Michael McCann,[3] R. Jason Jones,[2] Catherine A. Ramsbottom,[3] Andrew Jarymowycz,[2], Connor P. Ballance,[3] Padraig Dunne[1]

[1]*School of Physics, University College Dublin, Belfield, Dublin 4, Ireland*
[2]*Wyant College of Optical Sciences, University of Arizona, 1630 E. University Blvd., Tucson, AZ 85721, USA*
[3]*Astrophysics Research Centre, School of Mathematics & Physics, Queens University Belfast, BT7 1NN, Northern Ireland.*

Area Fit Comparison



Boltzmann Fit Comparison

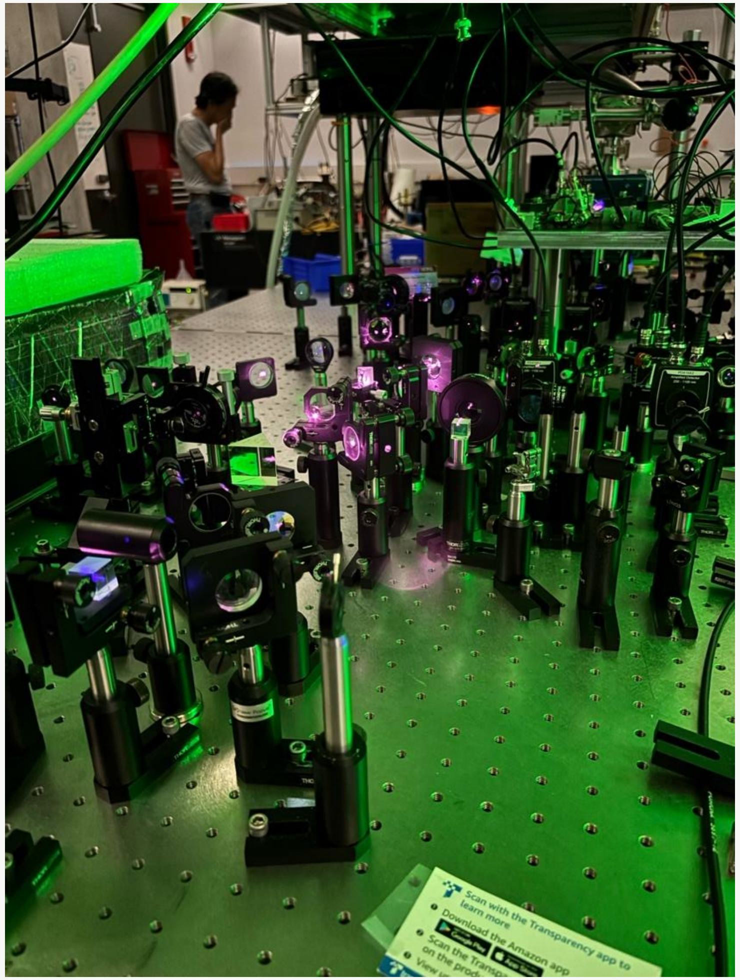


Frequency Combs for Astrophysics

- Approach-identifies new transitions, energy levels, and oscillator strengths, and can help reduce uncertainties in current data base.

- Using two spectral regions simultaneously provides greater coverage of neutral and ionic transitions, additional fitting constraints, improving the reliability of the resulting oscillator strengths.

- Going Forward: Alloys, broader bandwidth, and more species.



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Thank you

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