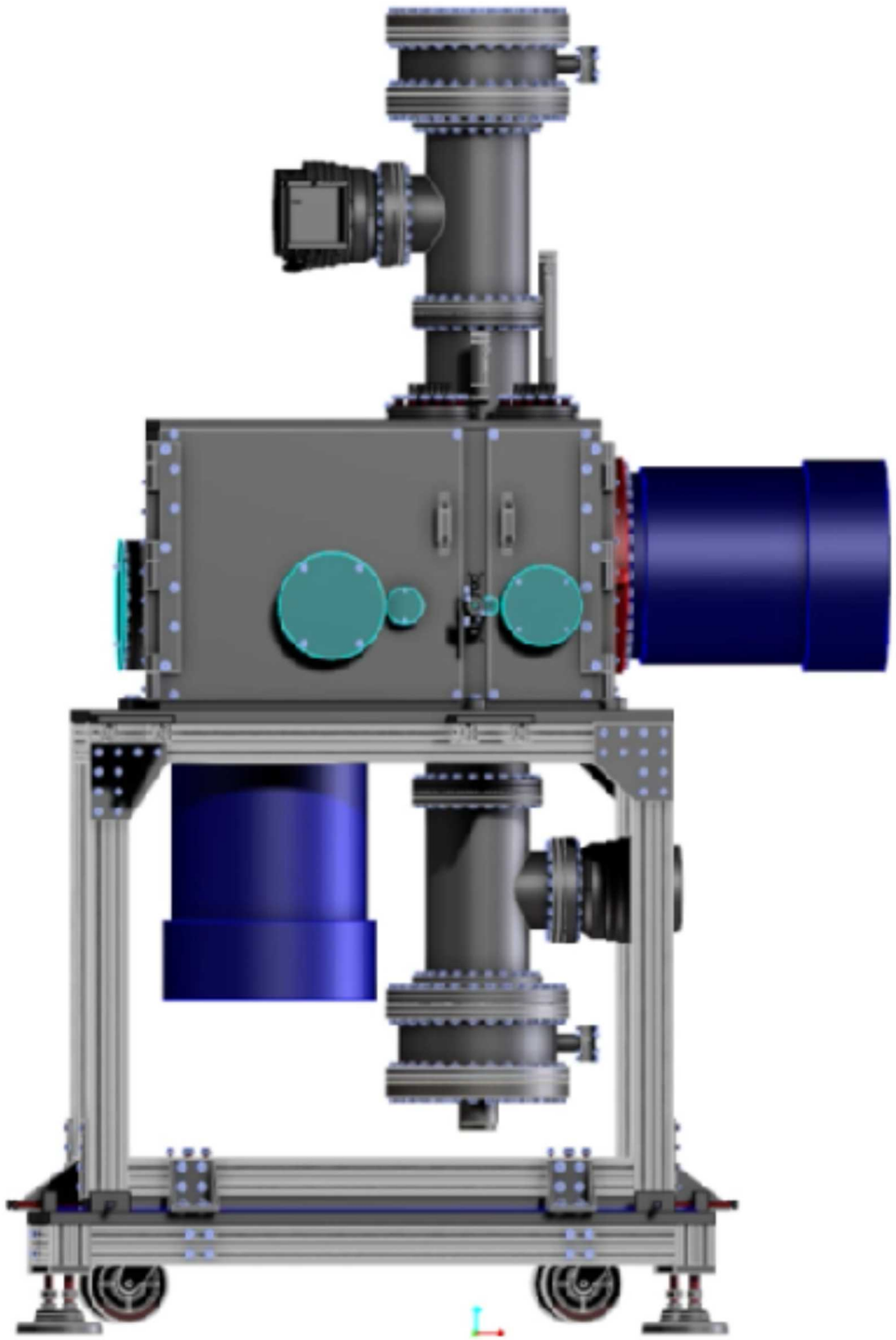
Design of the CRF-PEPICO a next generation multiplexed spectrometer for studying gas-phase kinetics of combustion and atmospheric reactions

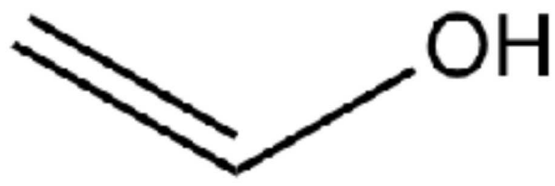
SAND2018-11653PE

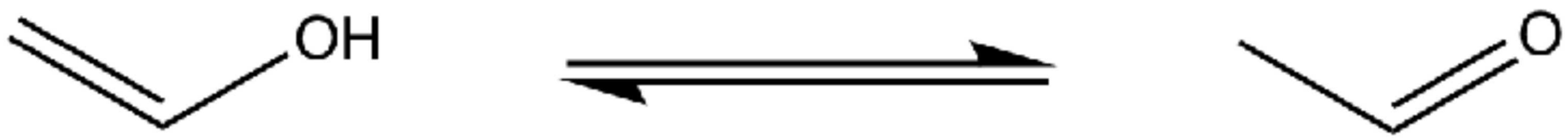


Postdoc seminar 10/11/2018

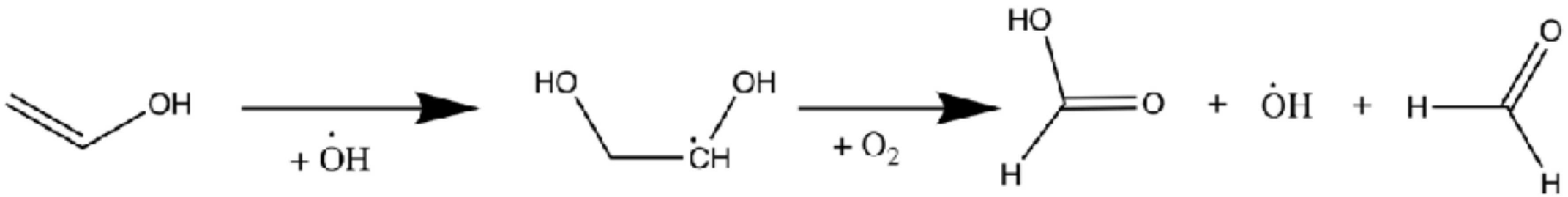
Daniel Neeson

Vinyl alcohol





Vinyl alcohol



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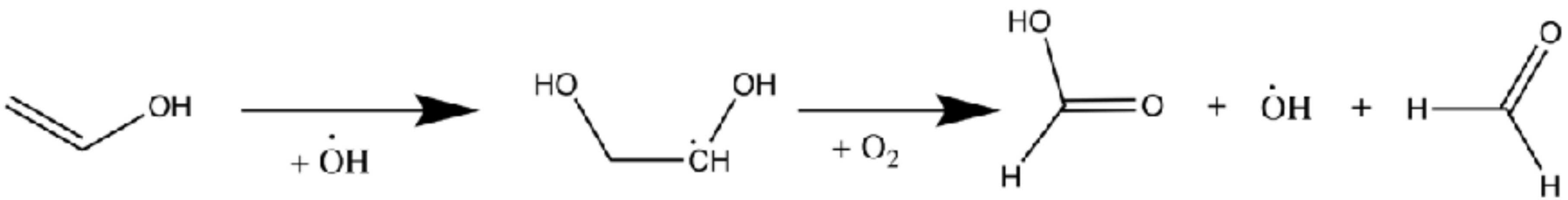

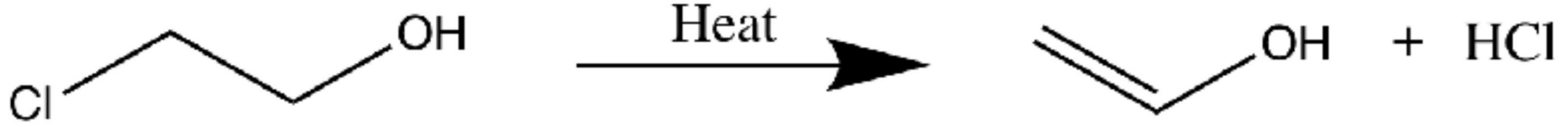

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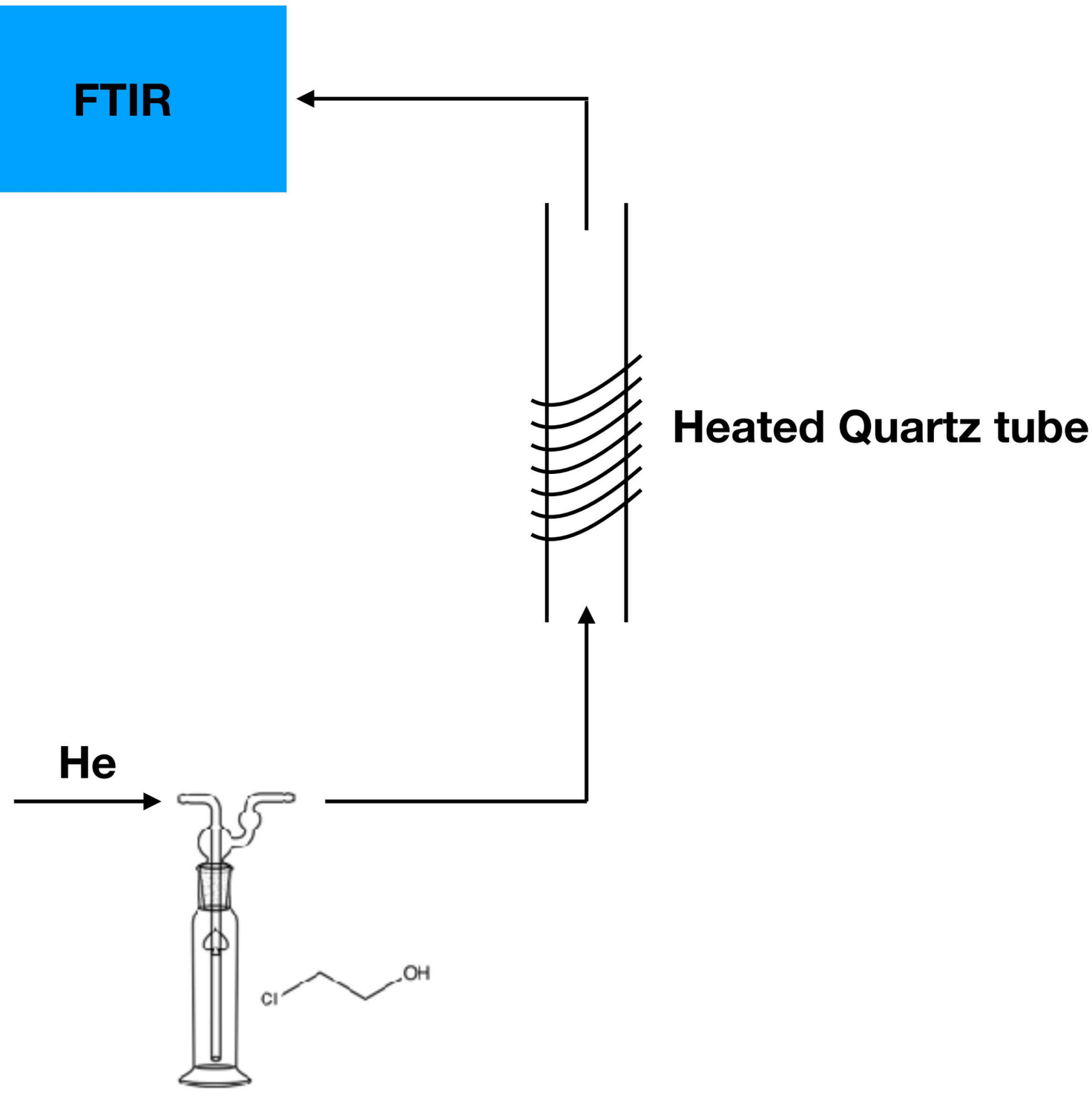

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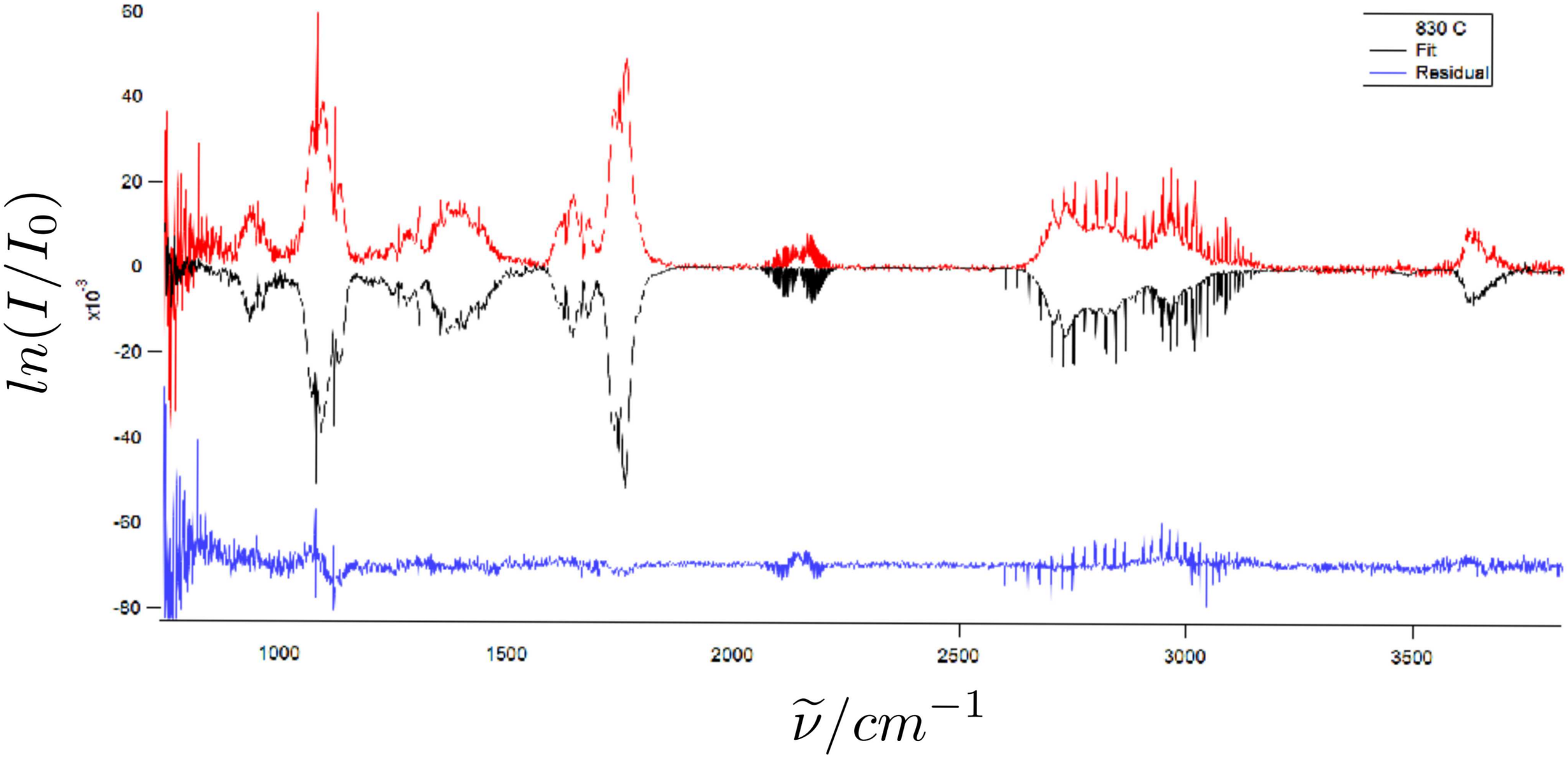
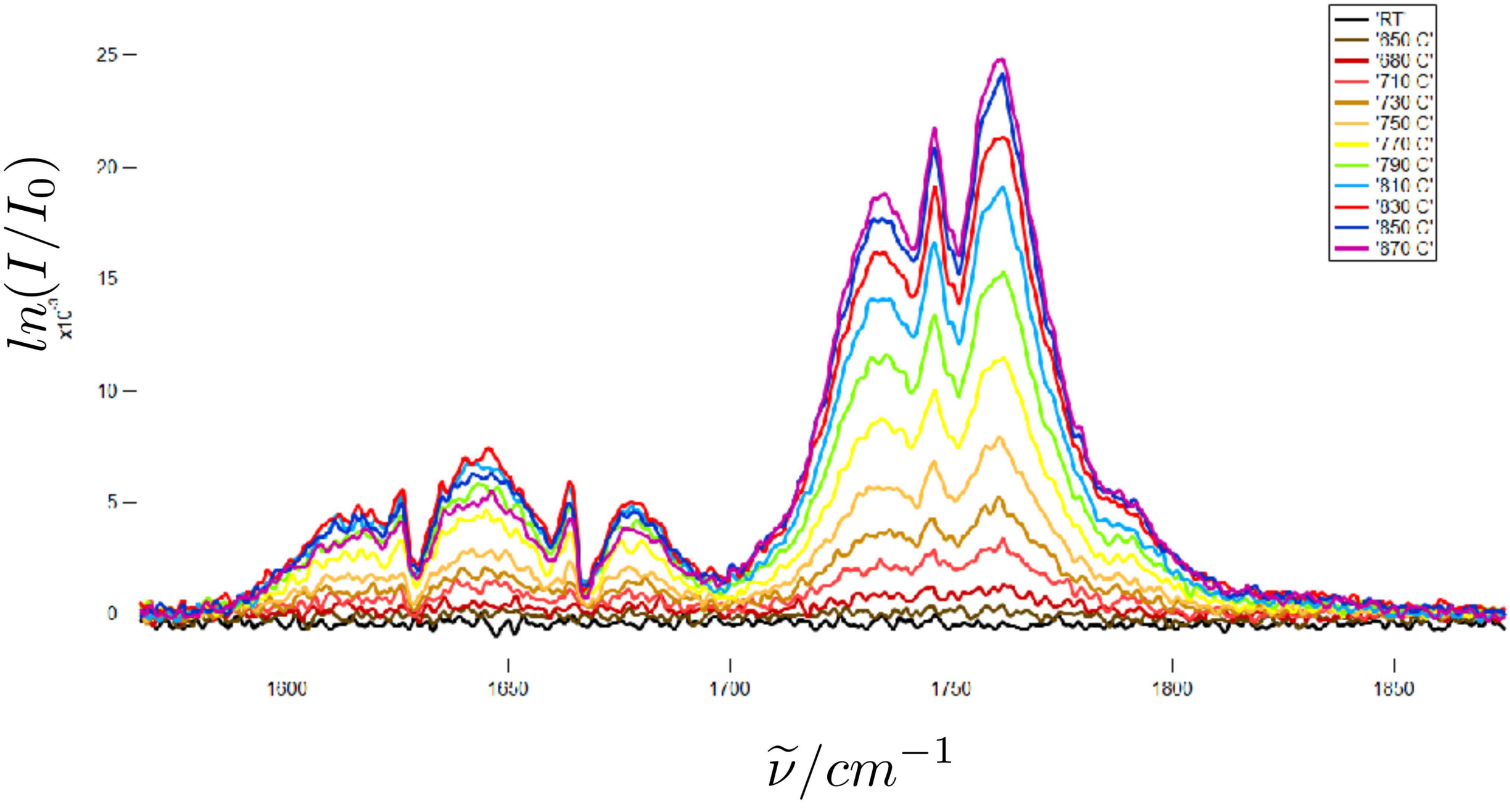
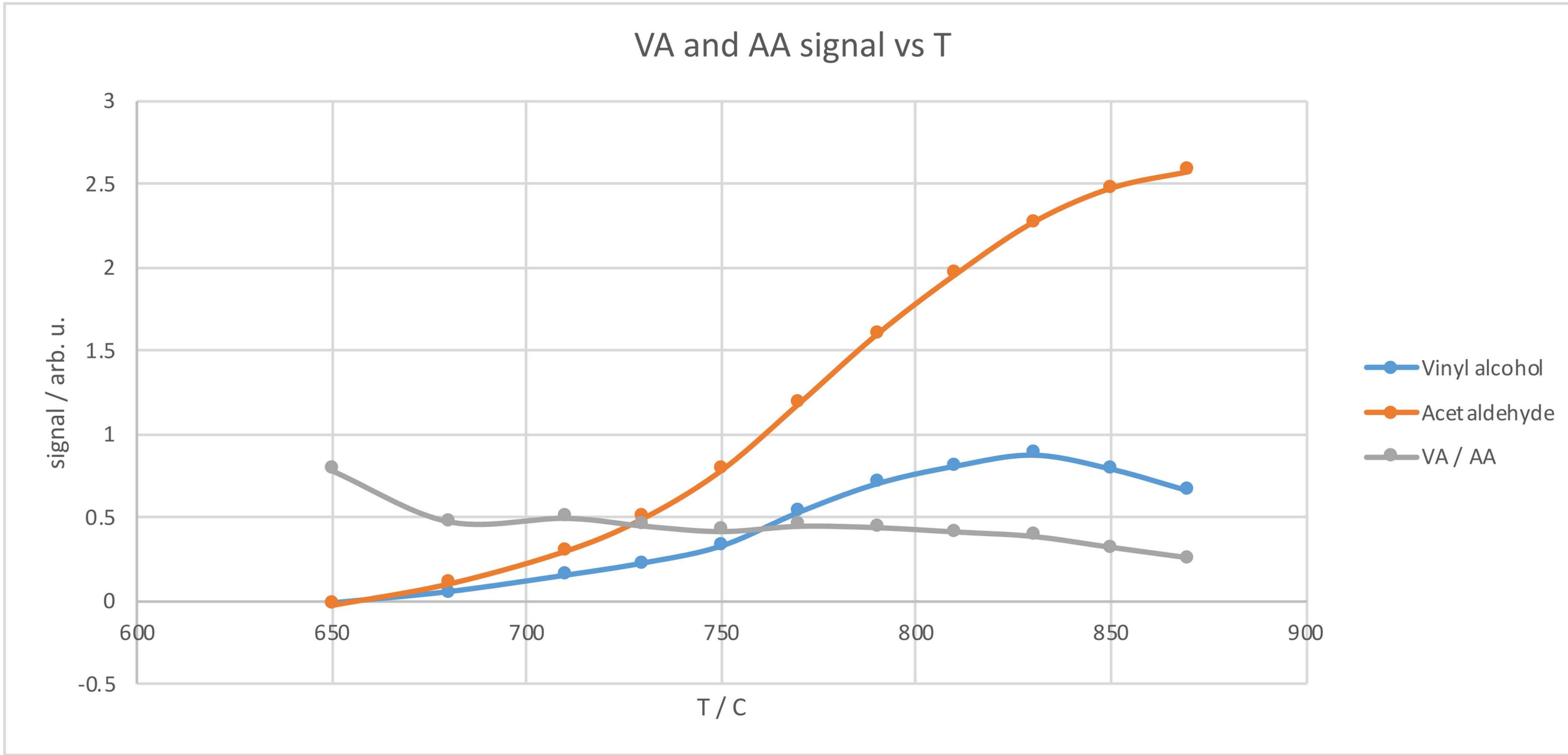


Fit =  + CO + + + CH_4 + HCl

Vinyl alcohol



Vinyl alcohol



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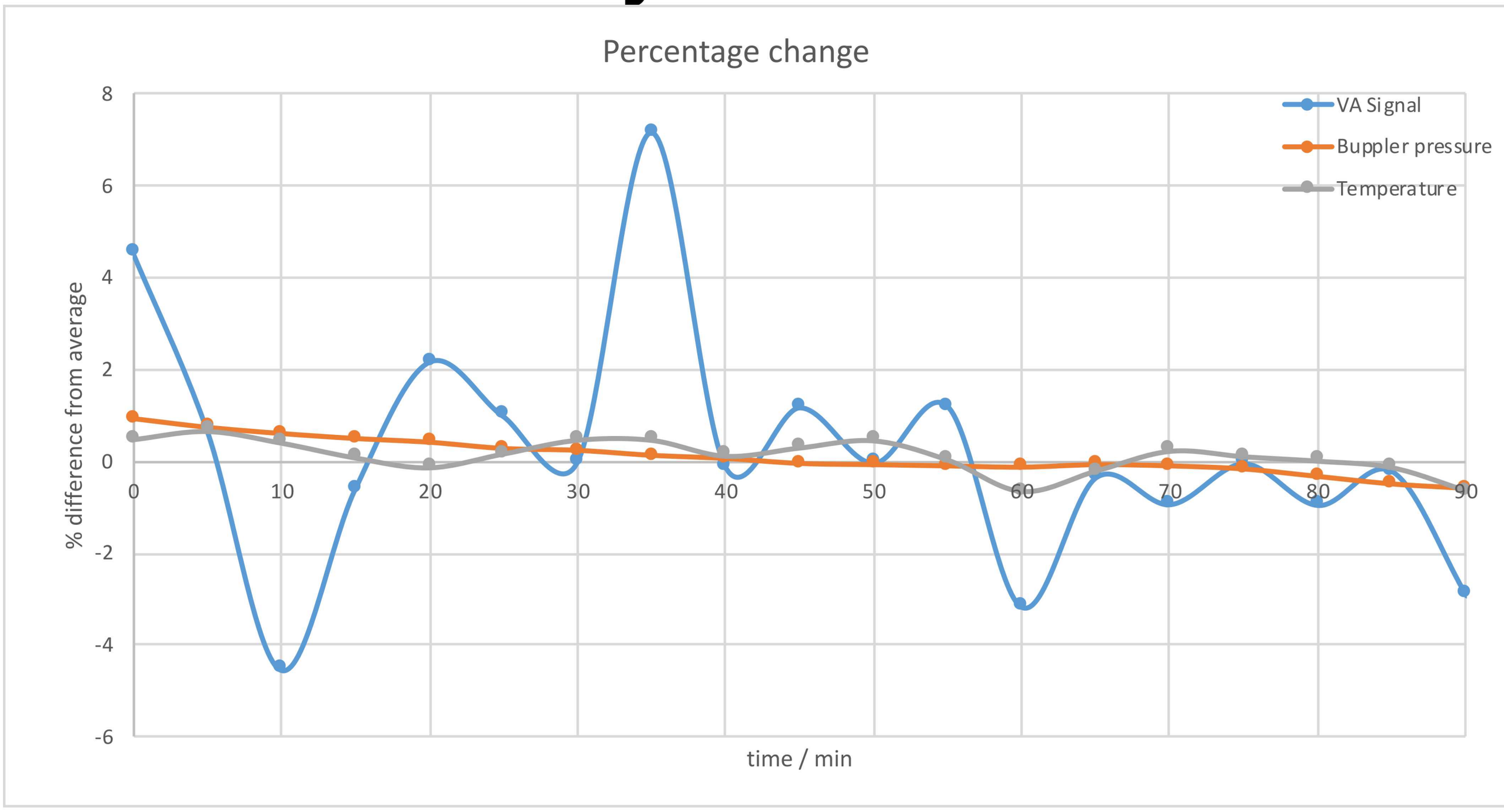
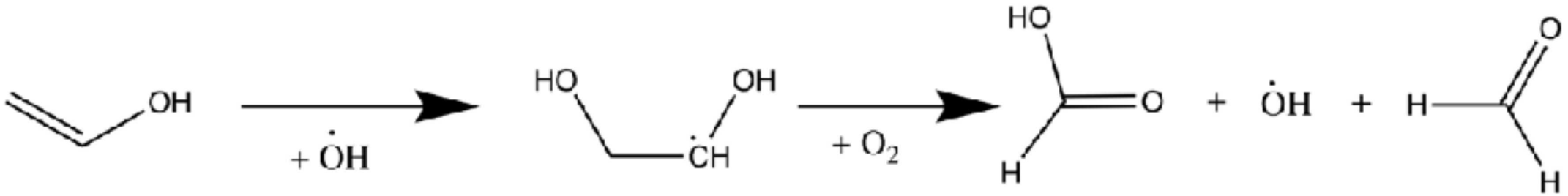
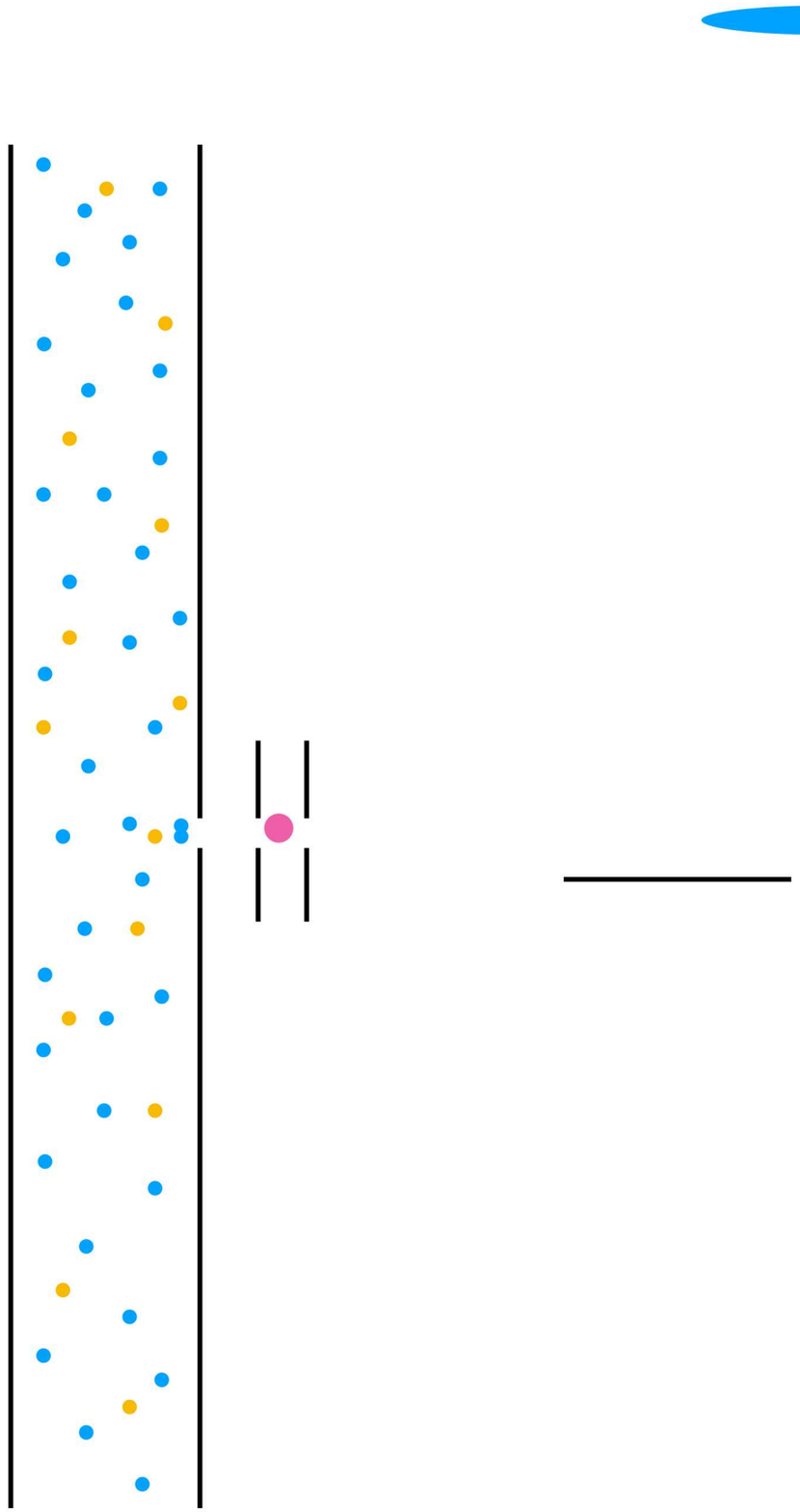


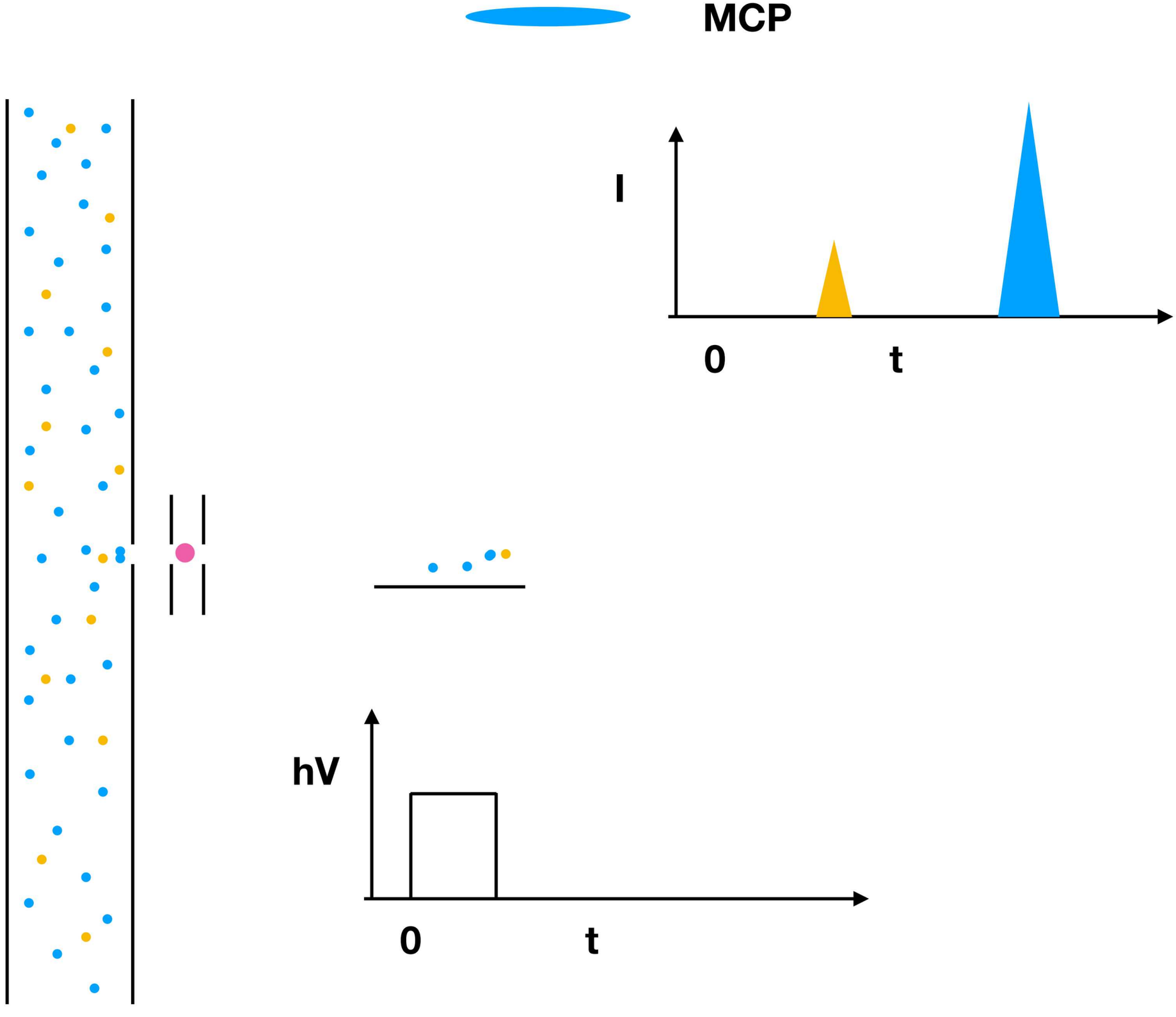
Vinyl alcohol

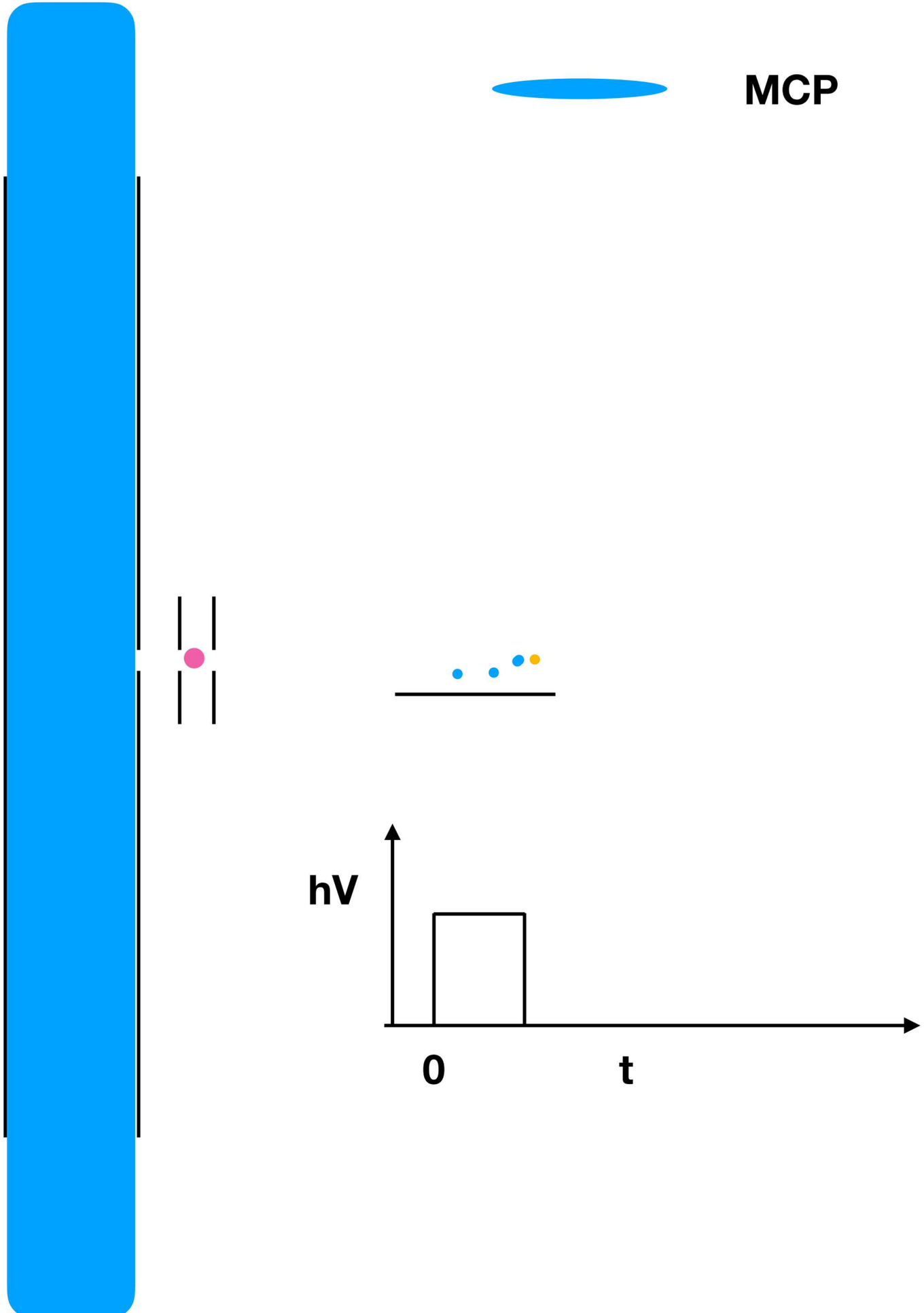


Multiplexed ionization mass spectrometry (MPIMS)



Multiplexed ionization mass spectrometry (MPIMS)

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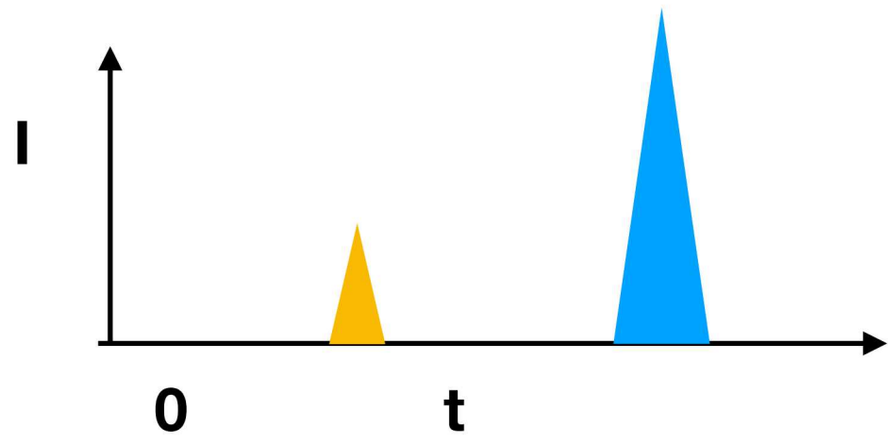
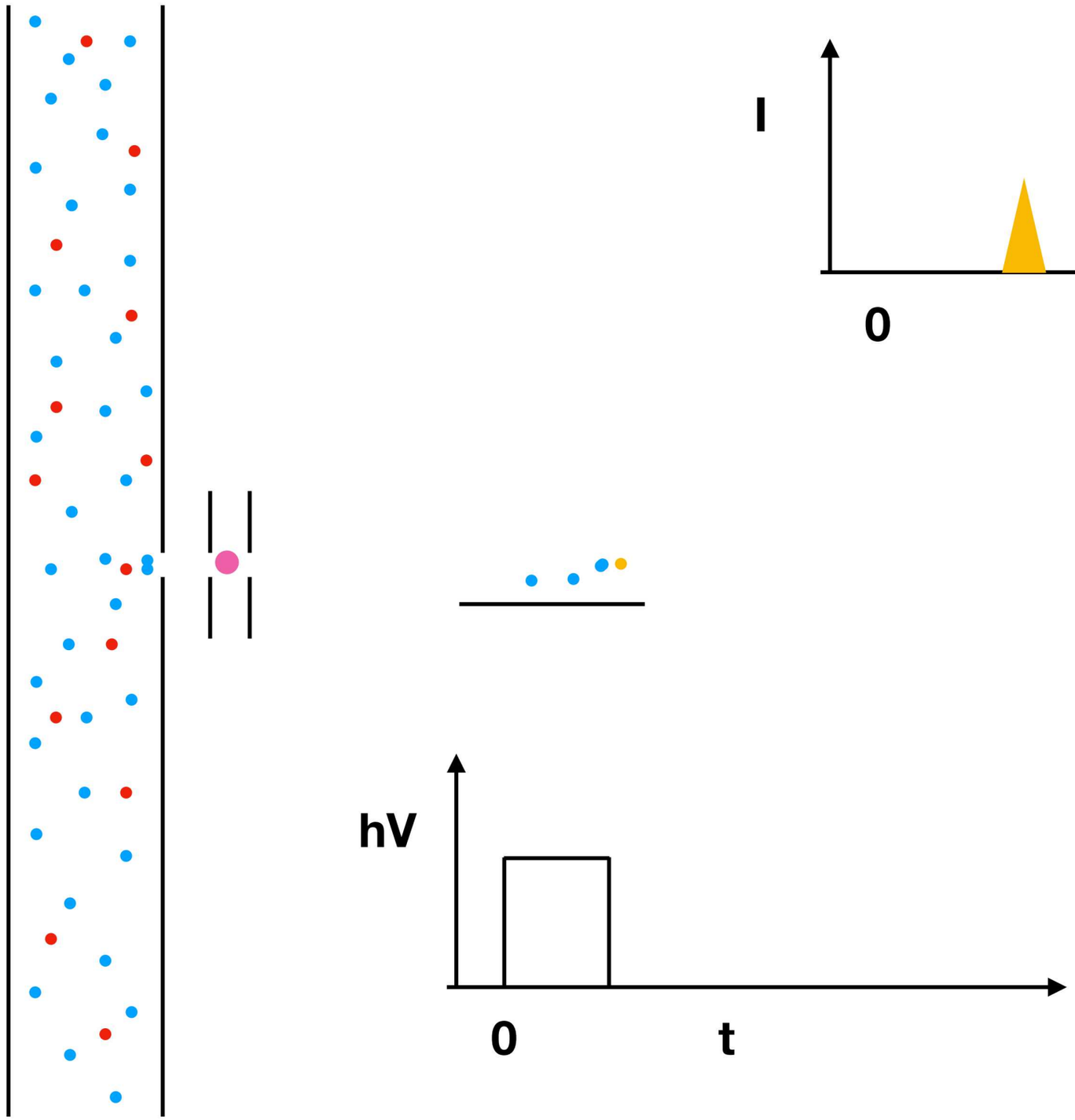
MCP





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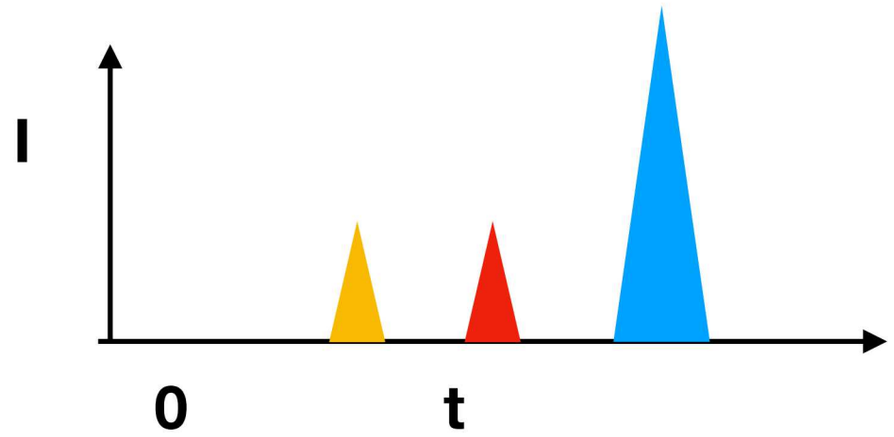
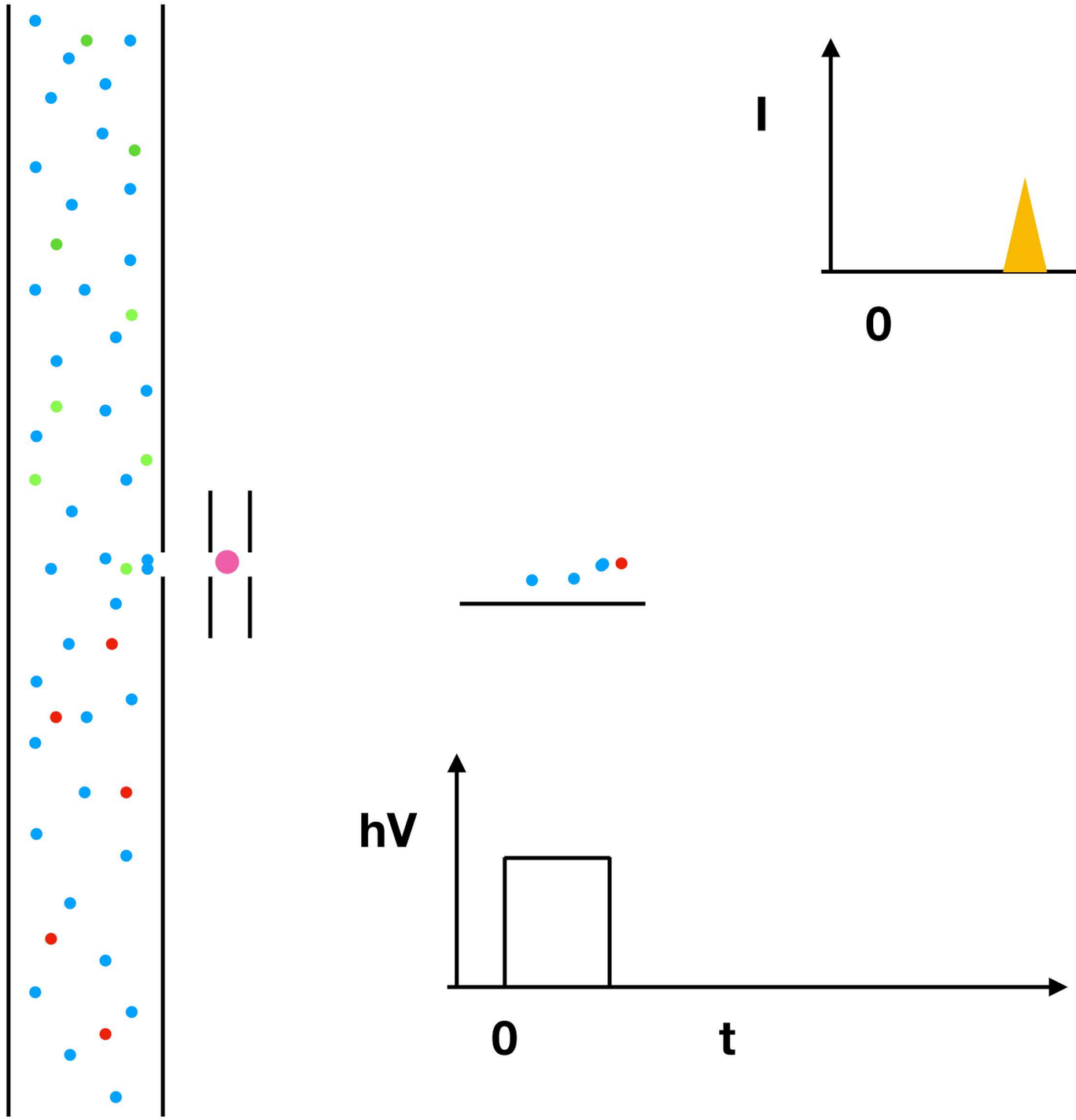
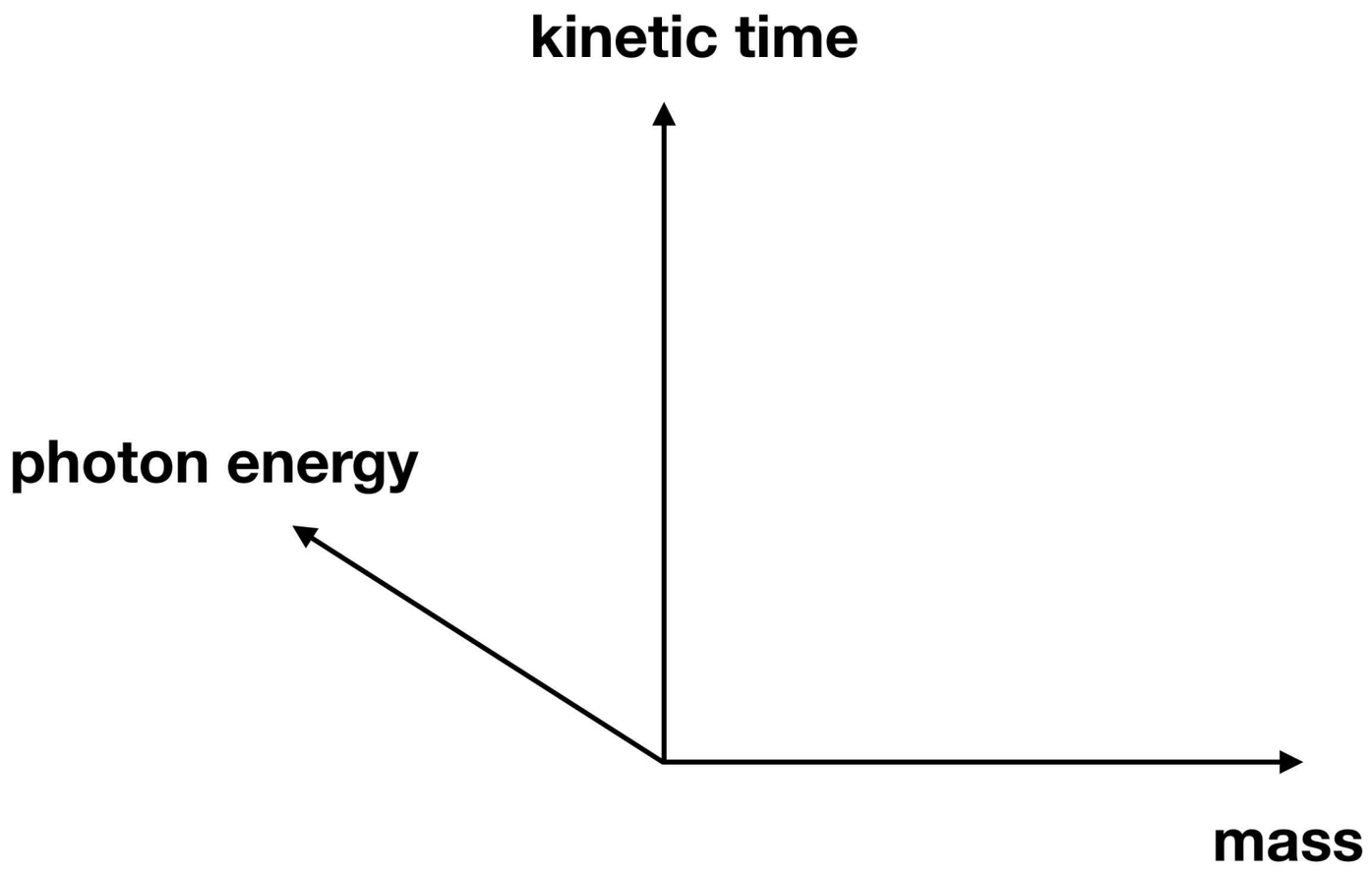




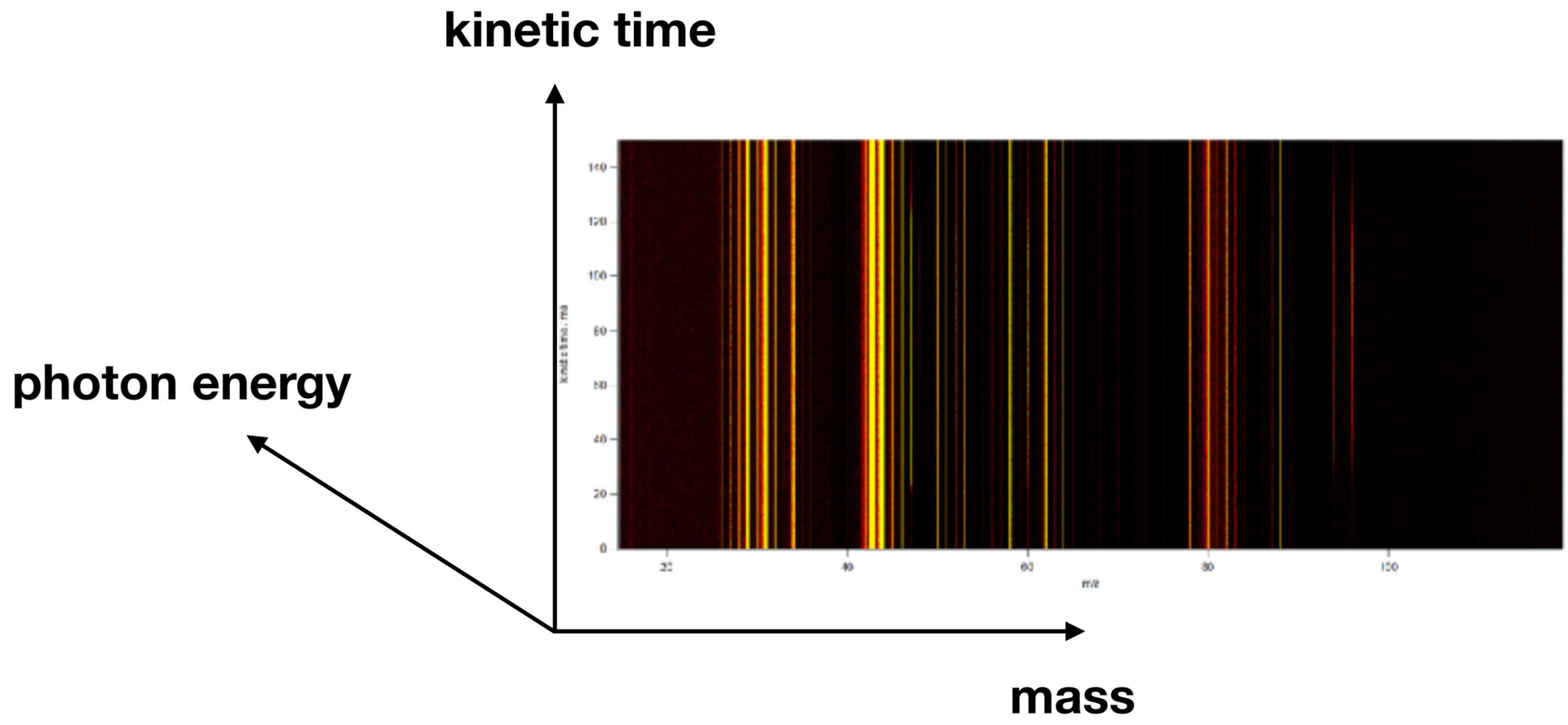
Multiplexed ionization mass spectrometry (MPIMS)

3 dimensional data set



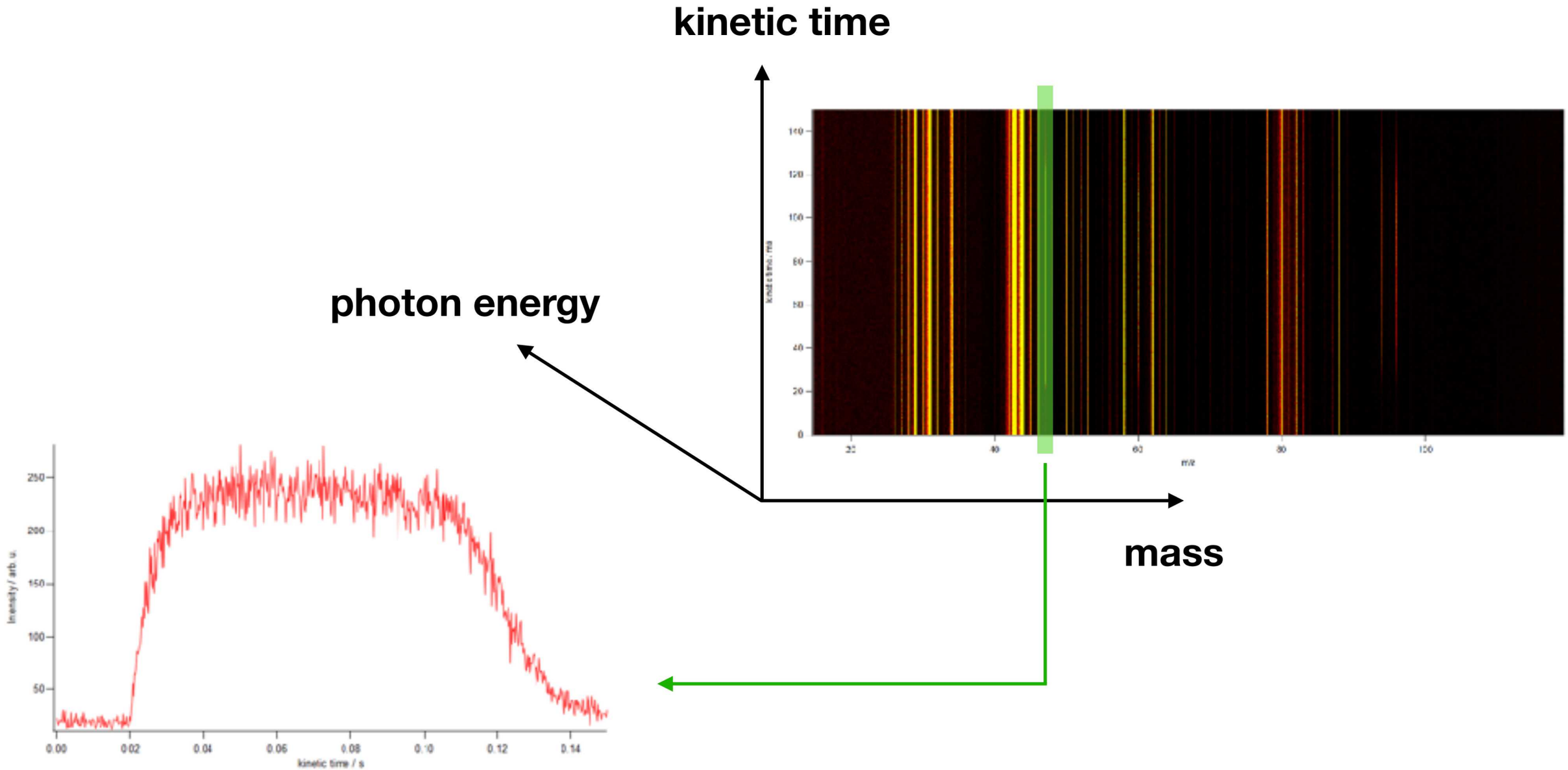
Multiplexed ionization mass spectrometry (MPIMS)

3 dimensional data set

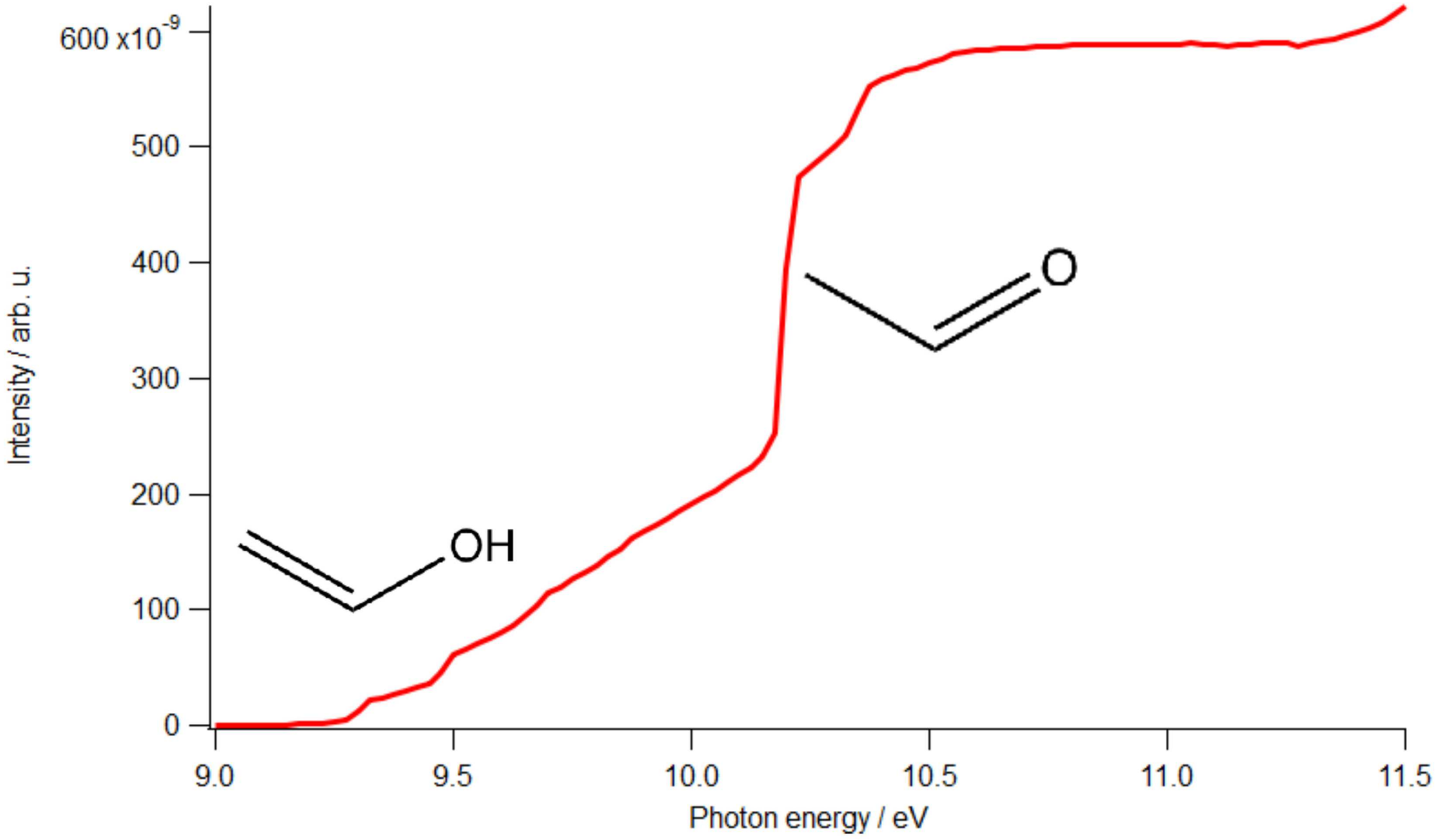


Multiplexed ionization mass spectrometry (MPIMS)

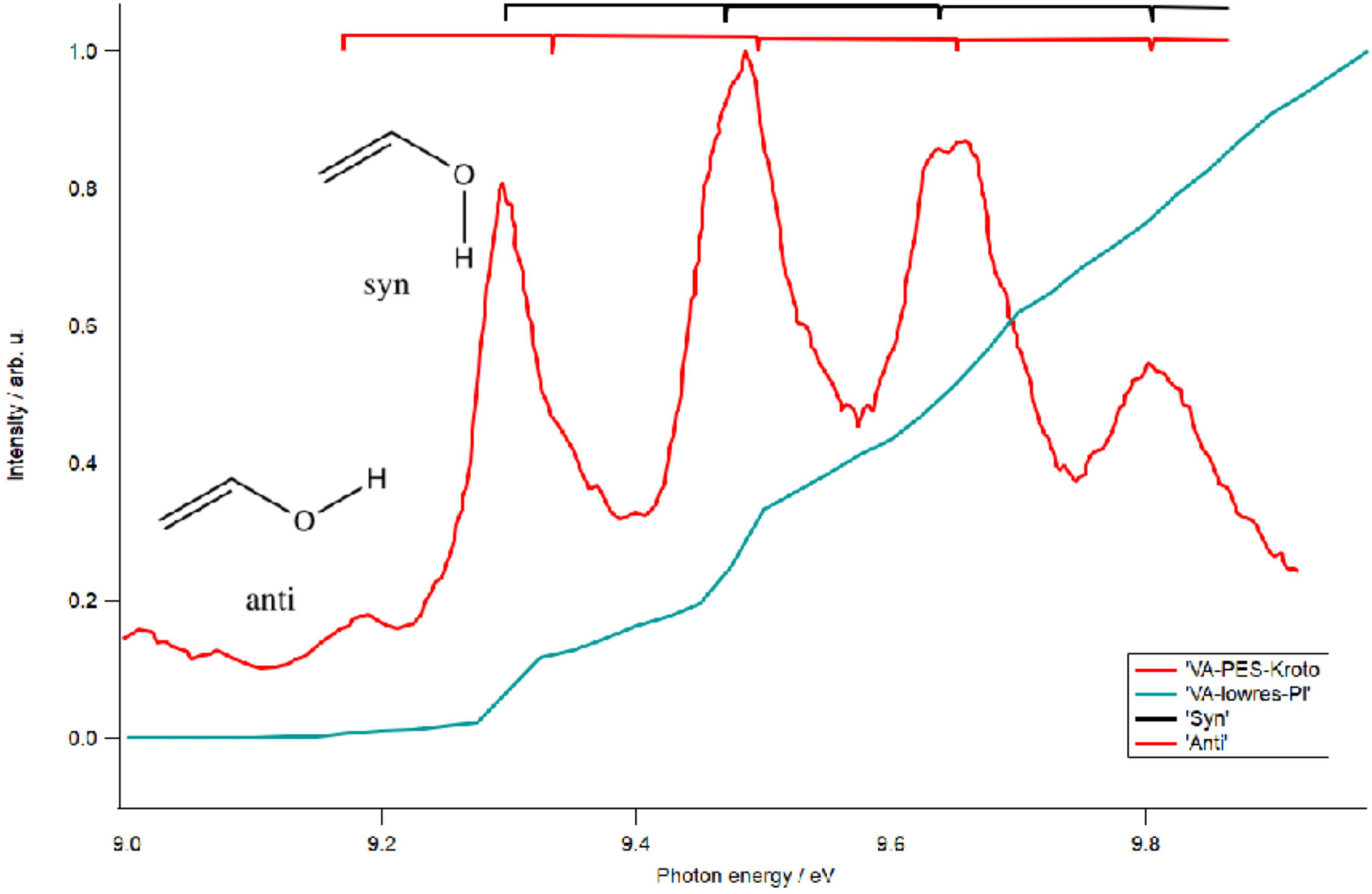
3 dimensional data set



Photoionization (PI) Spectrum



PIS vs PES



J. Electron. Spectrosc. Relat. Phenom. **1989,** 49, 195-201

Photoelectron photoion coincidence spectroscopy (PEPICO)

MCP

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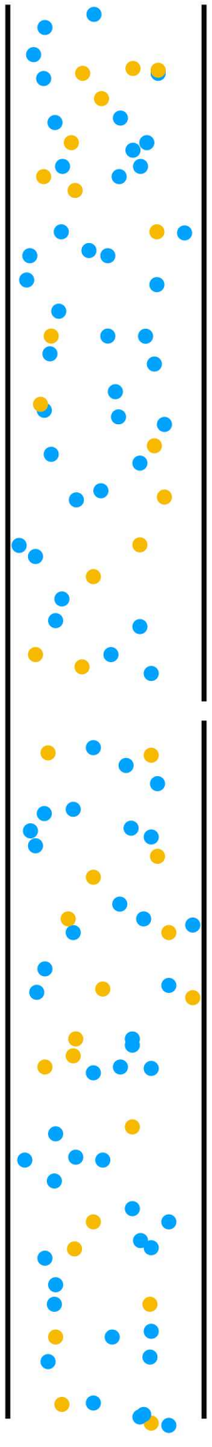
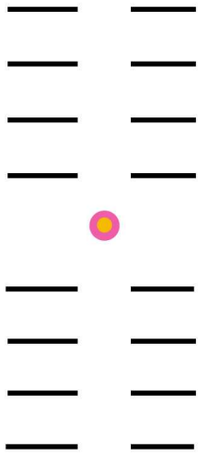
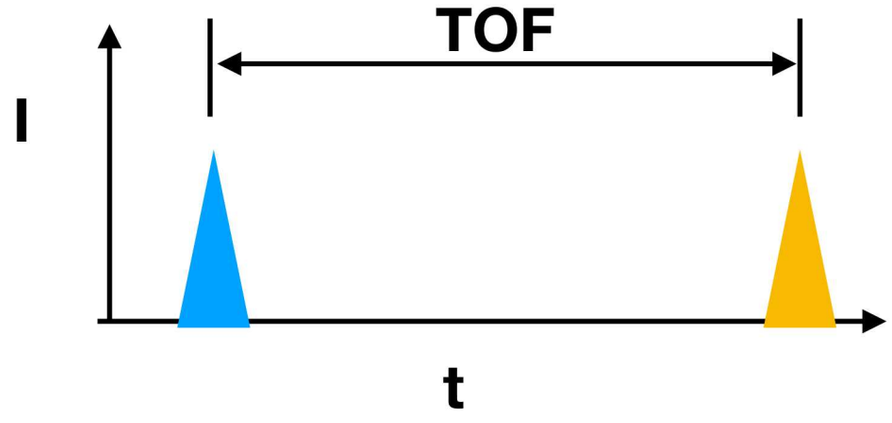
MCP

MCP

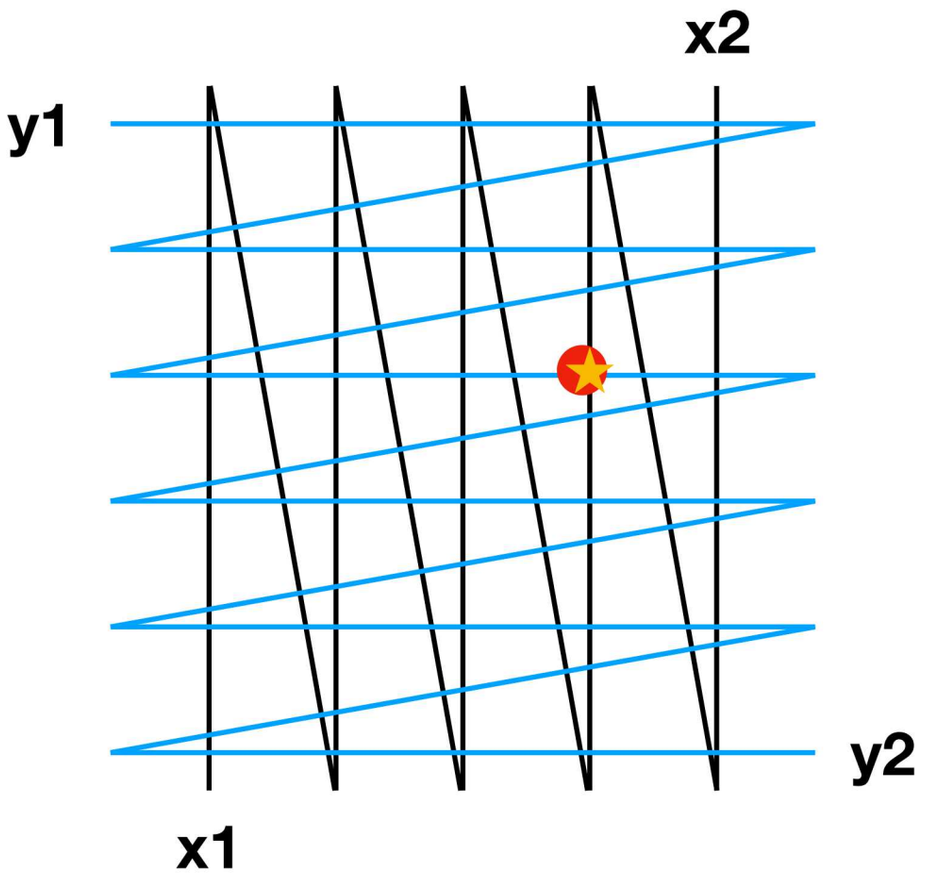


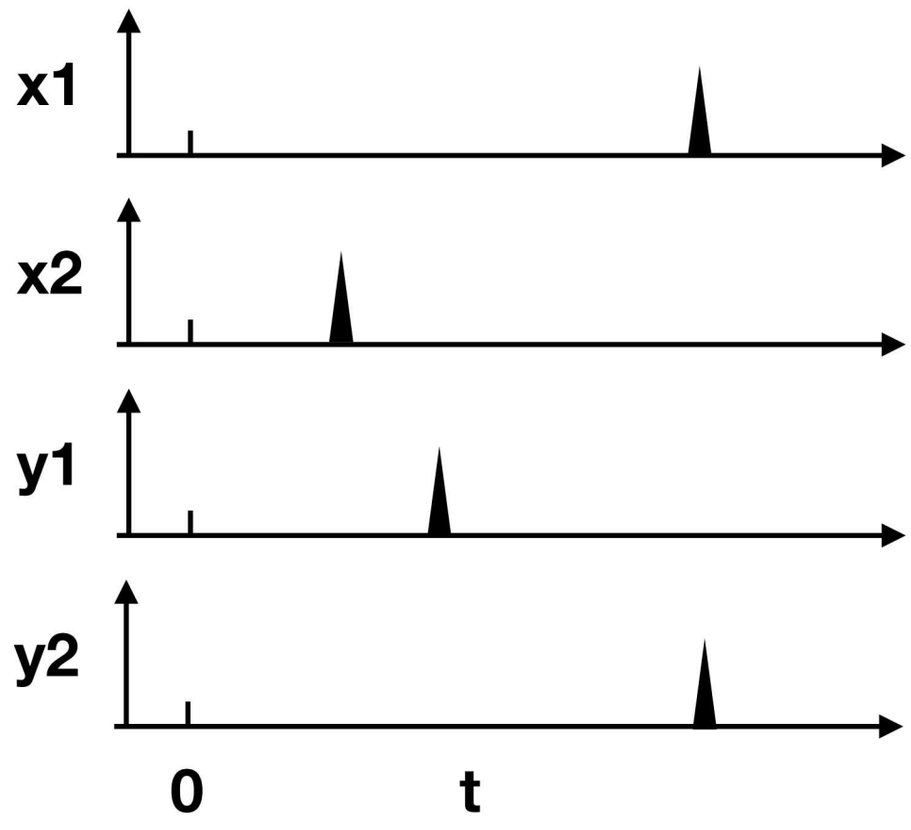


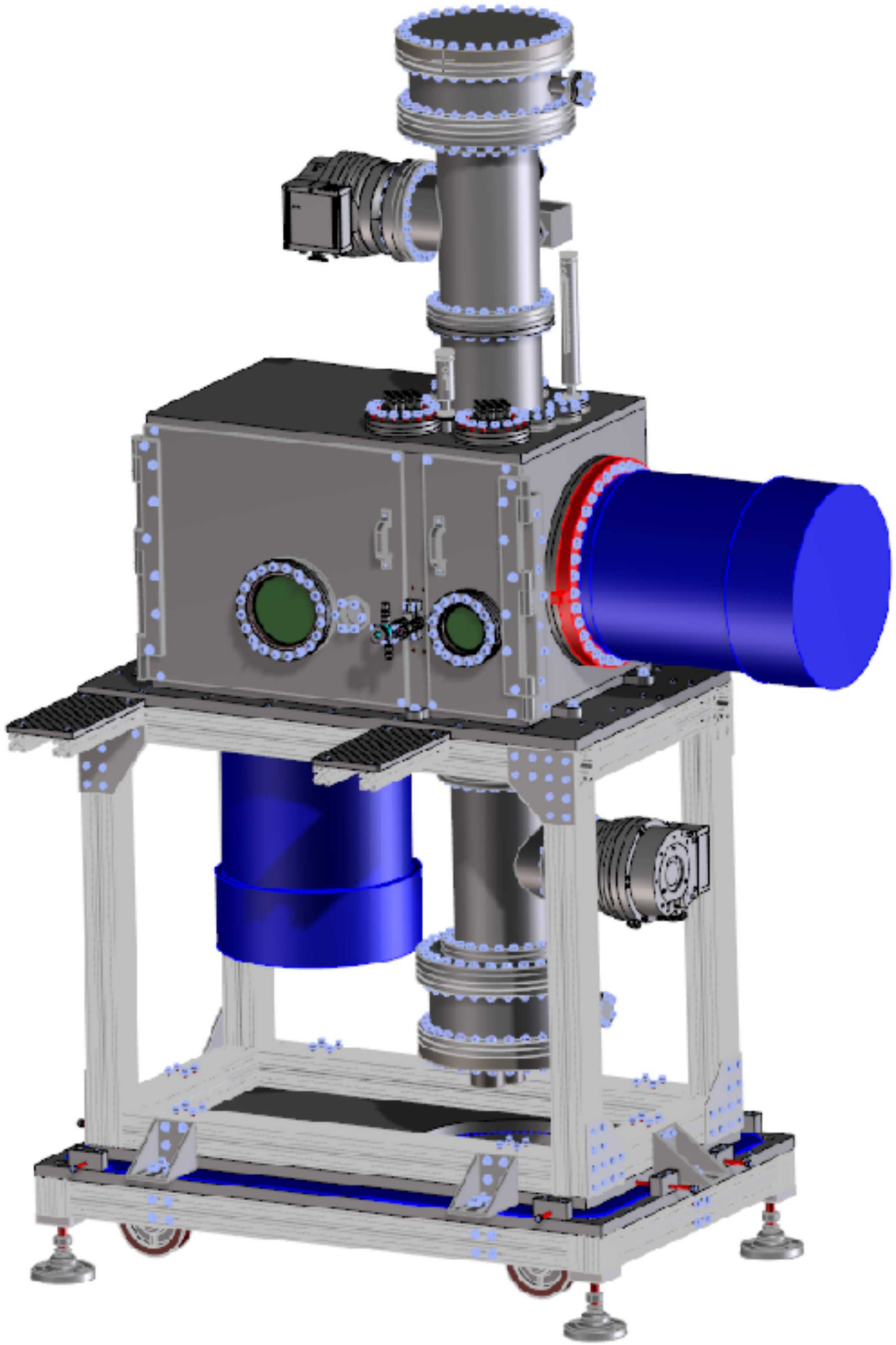


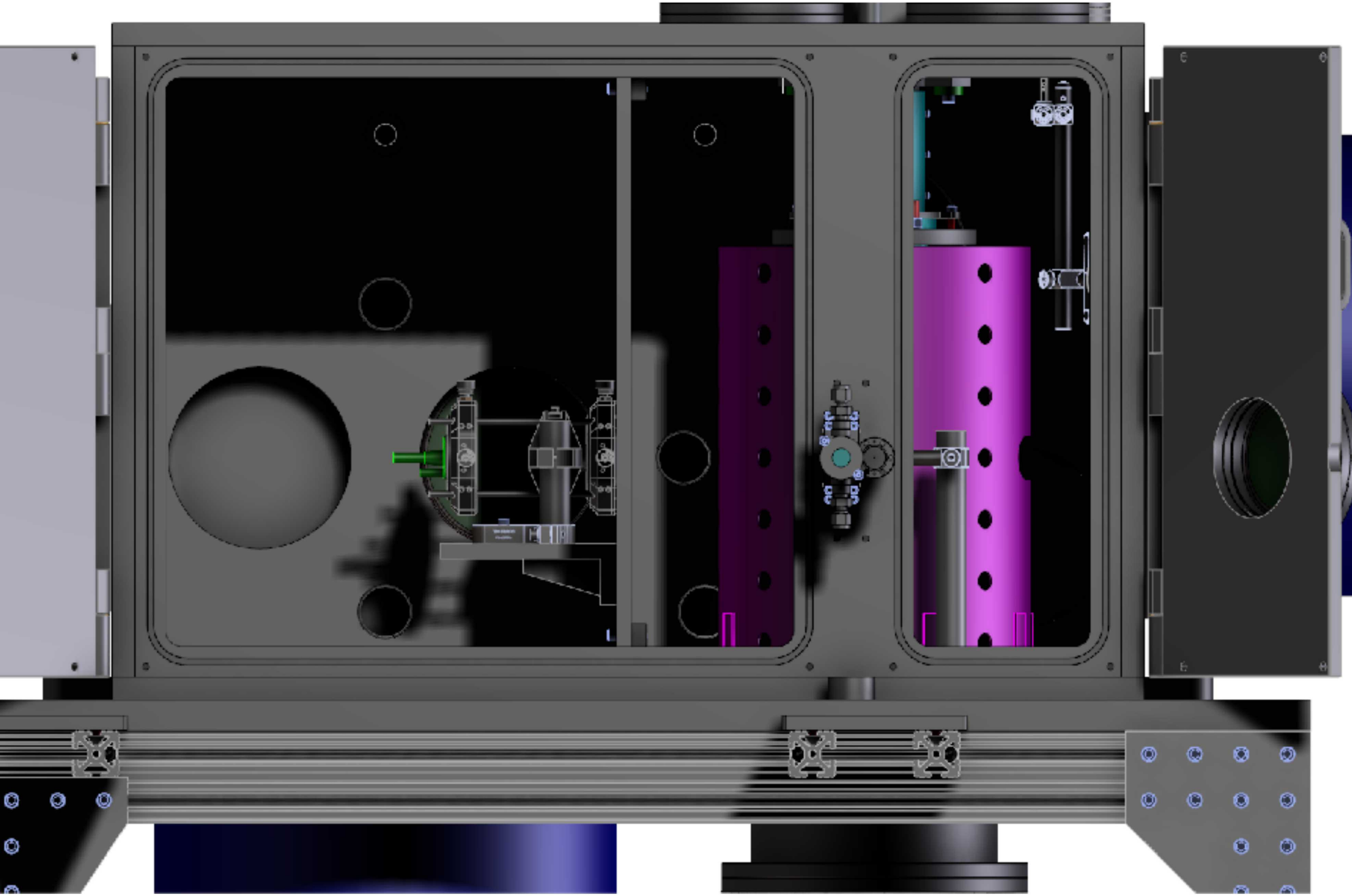
MCP

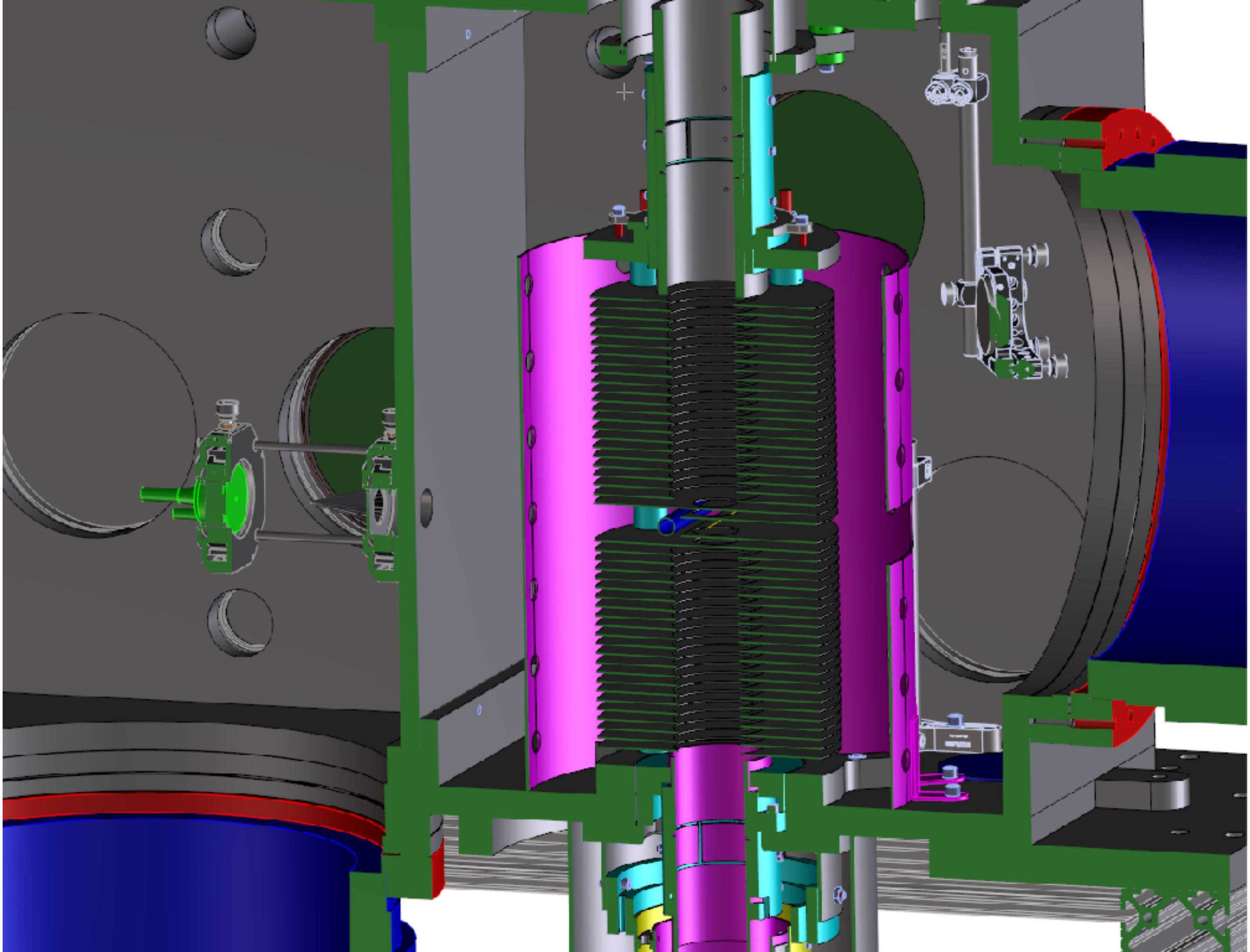
Delay line anode detector



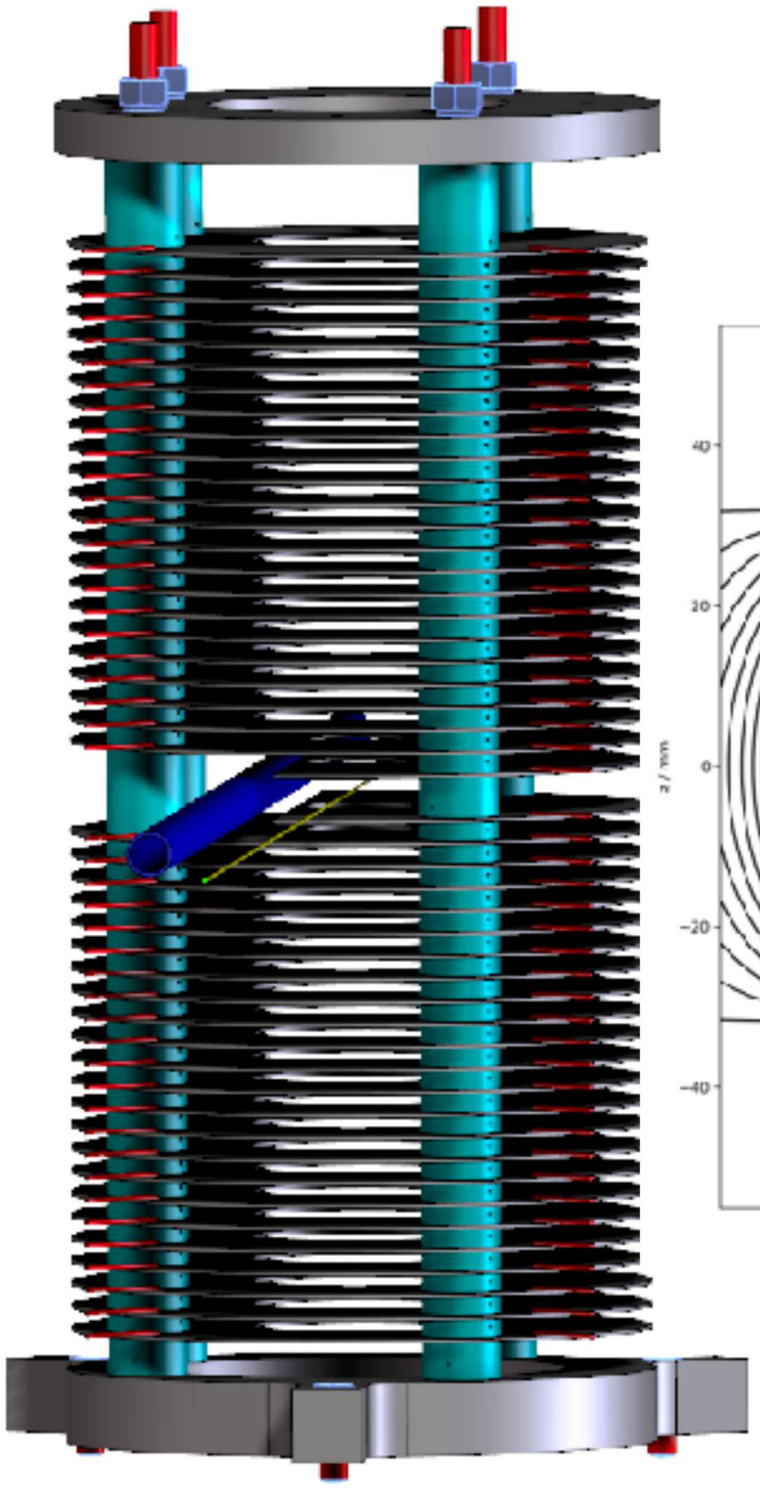


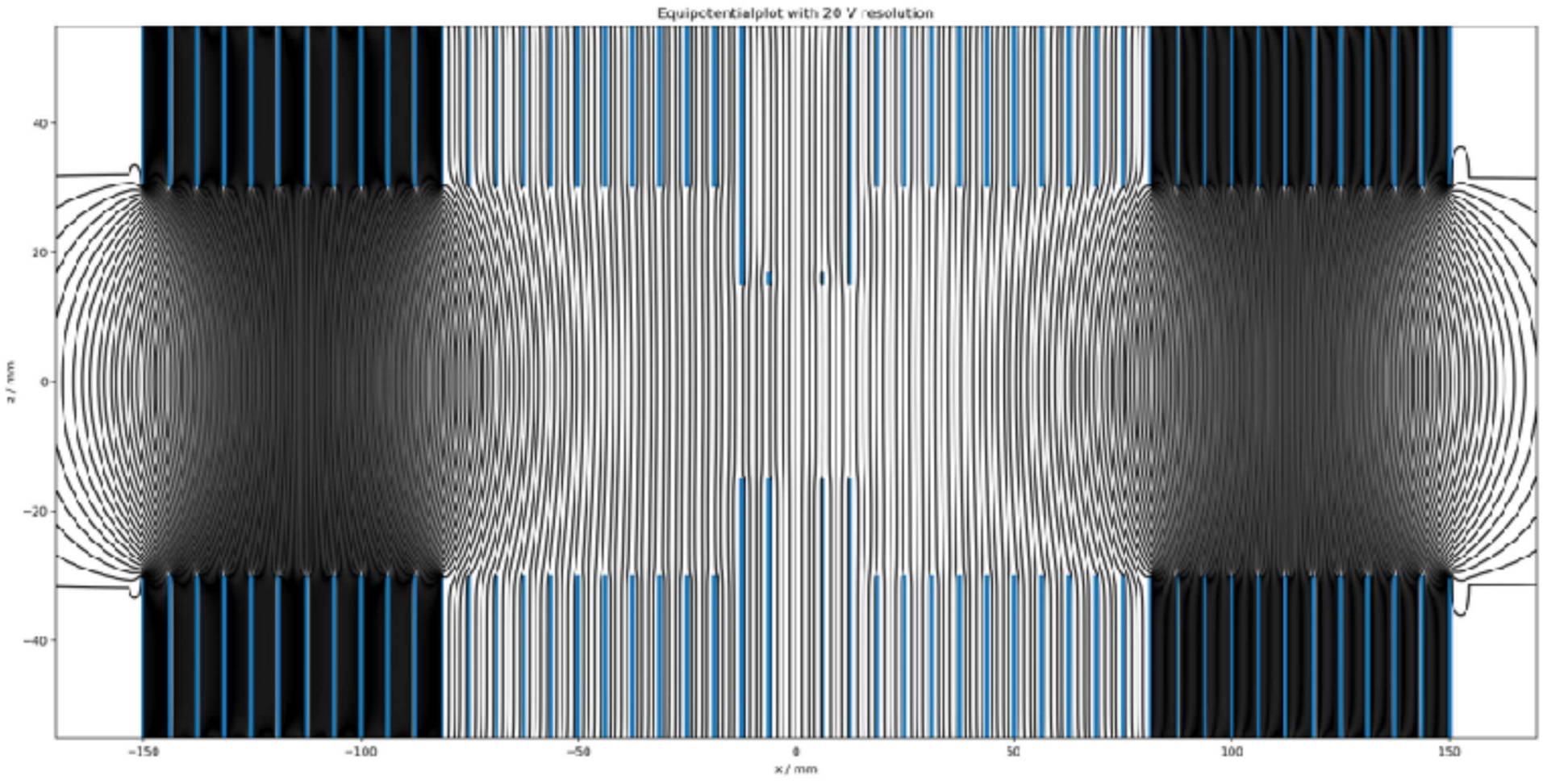






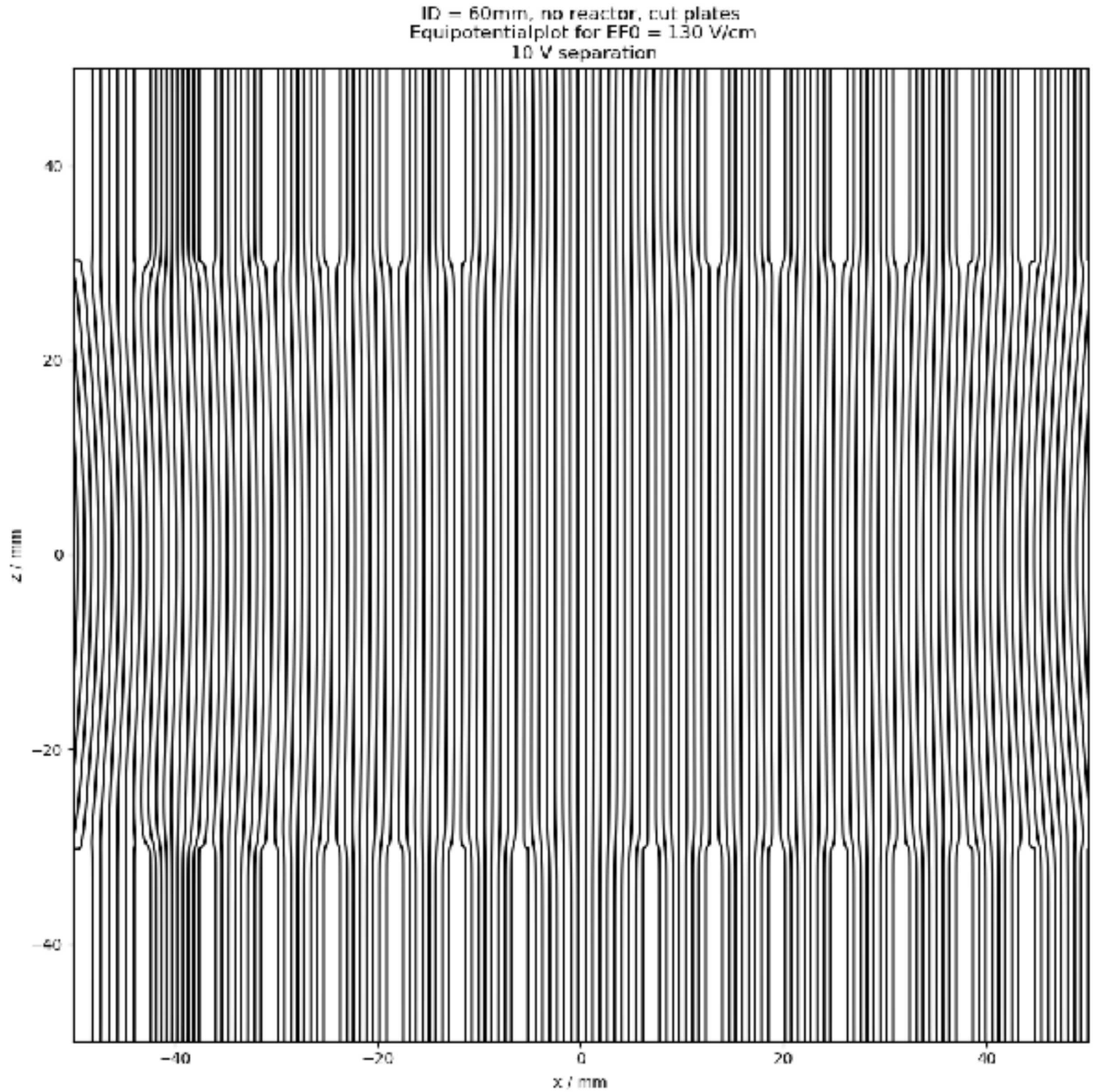
Ion Optics




Equipotentialplot with 20 V resolution
40
20
0
−20
−40
z / mm
−150
−100
−50
0
50
100
150
x / mm

Ion Optics

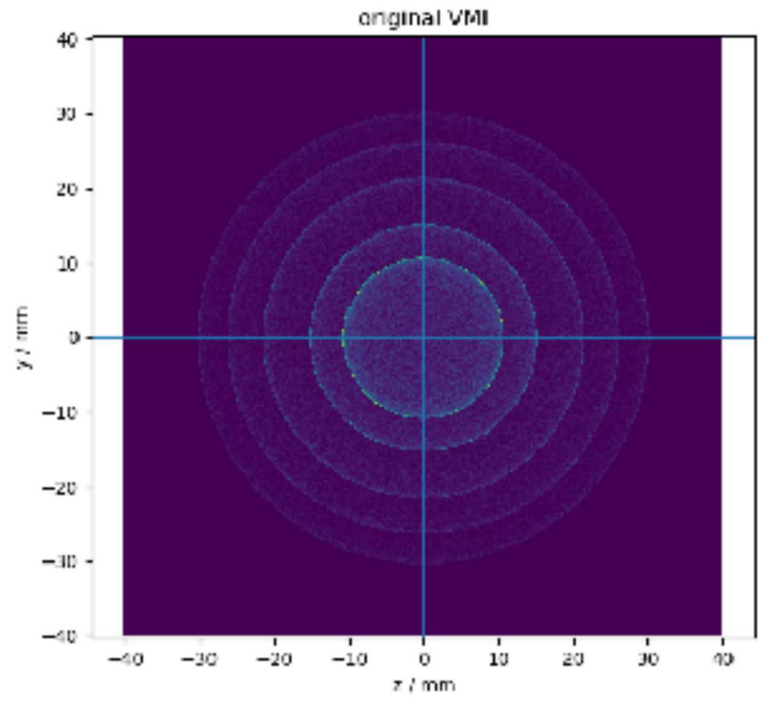
No Reactor

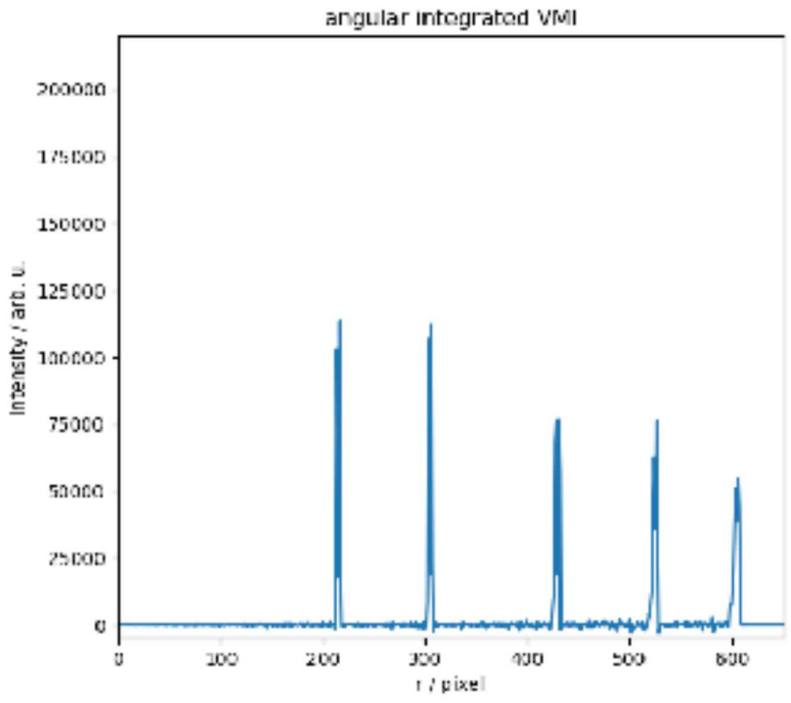


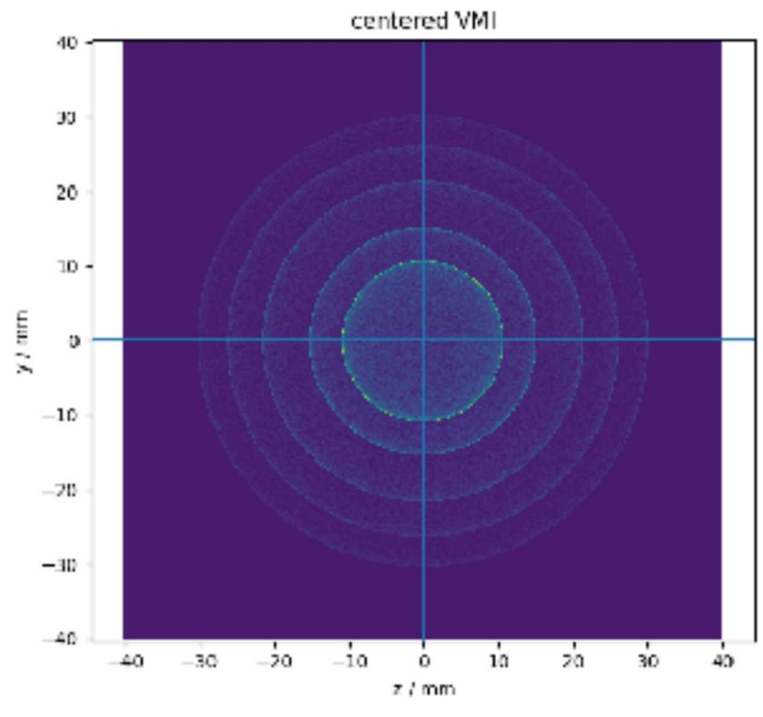
Ion Optics

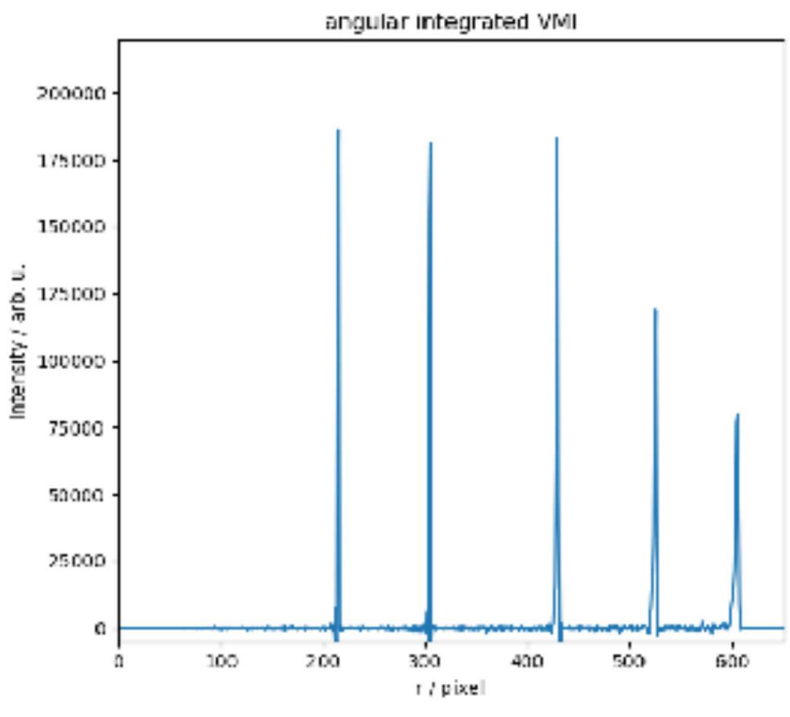
No Reactor

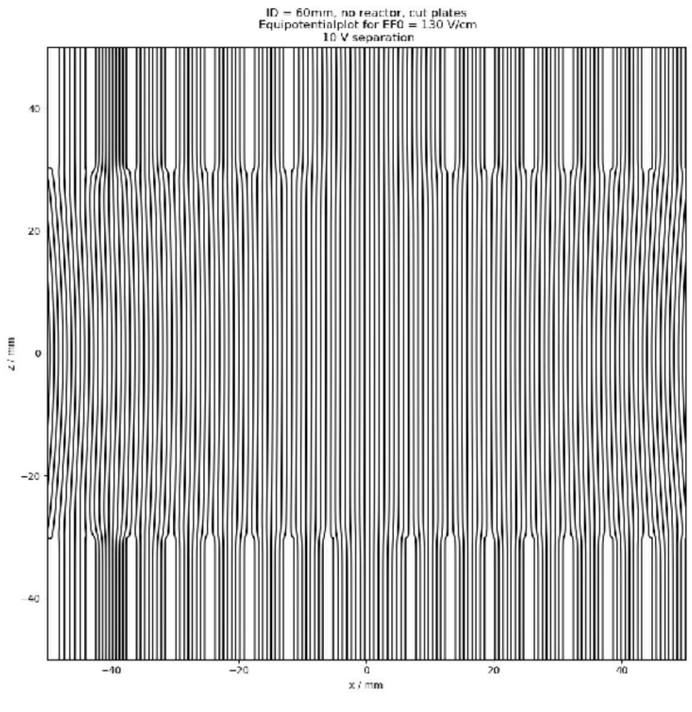
ΔE/E = 2ΔR/R = 1.2%





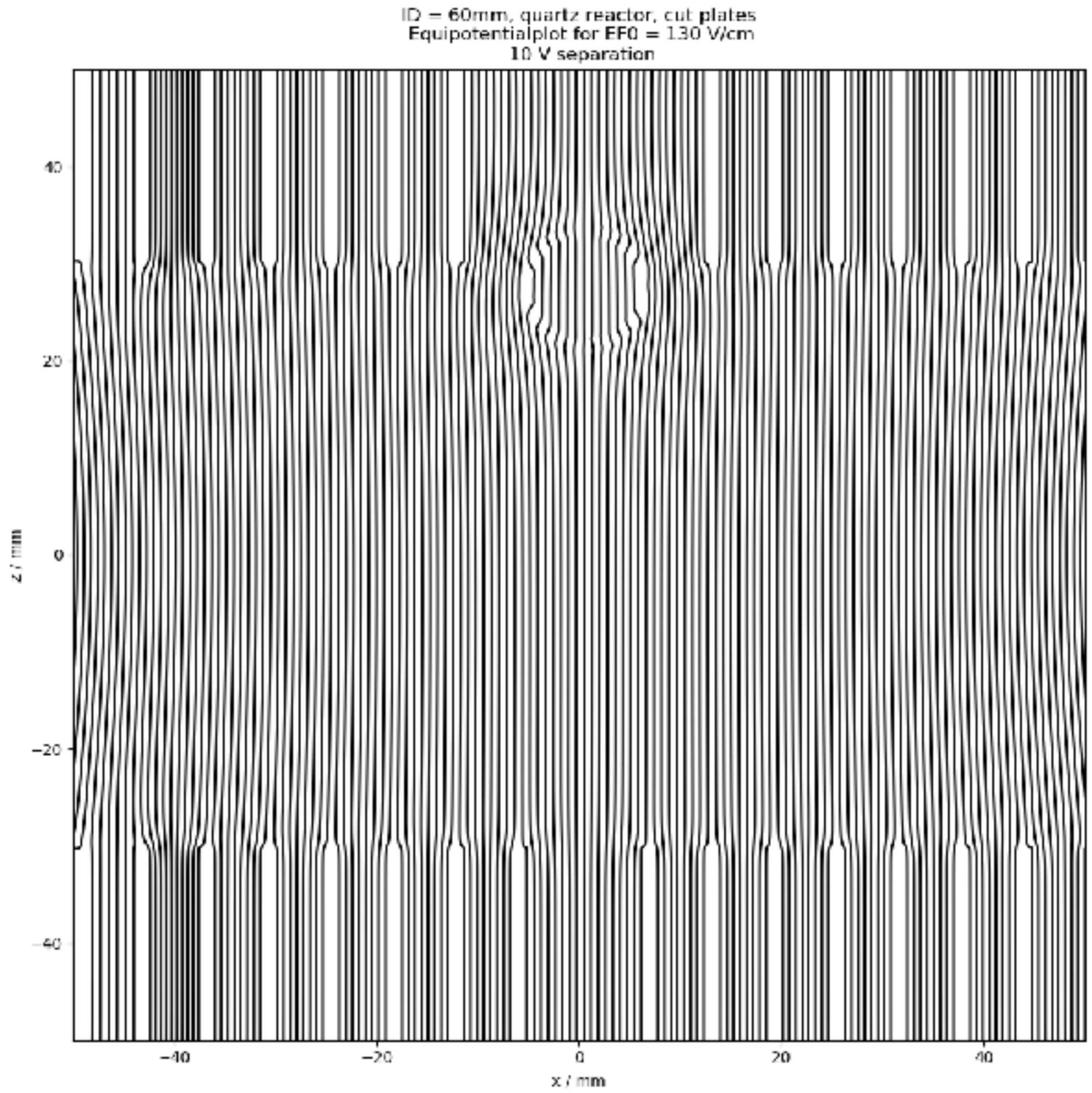






Ion Optics

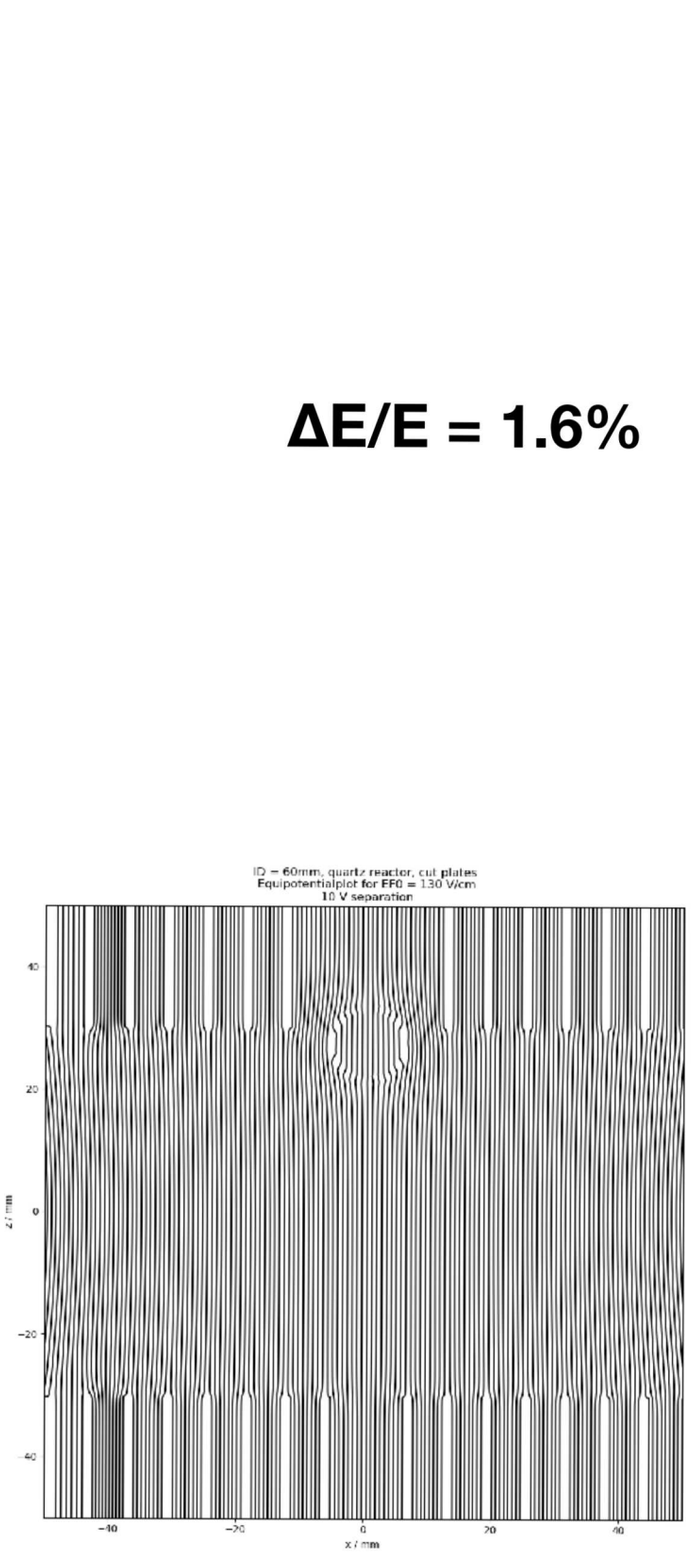
Quartz Reactor

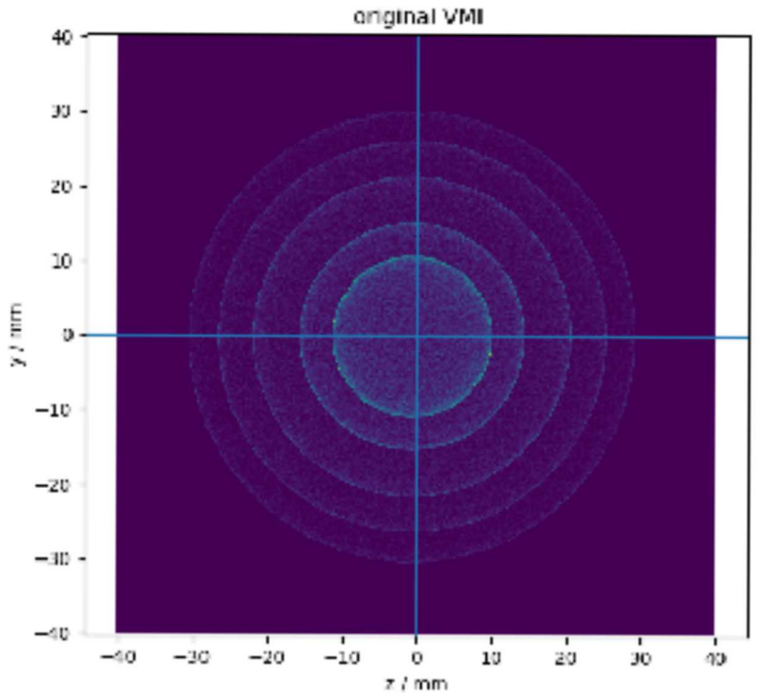


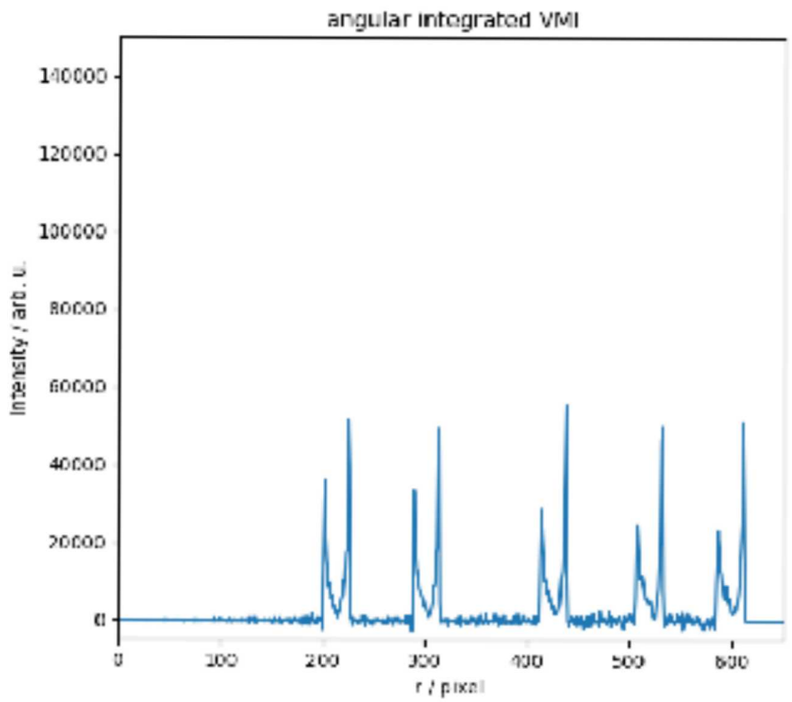
Ion Optics

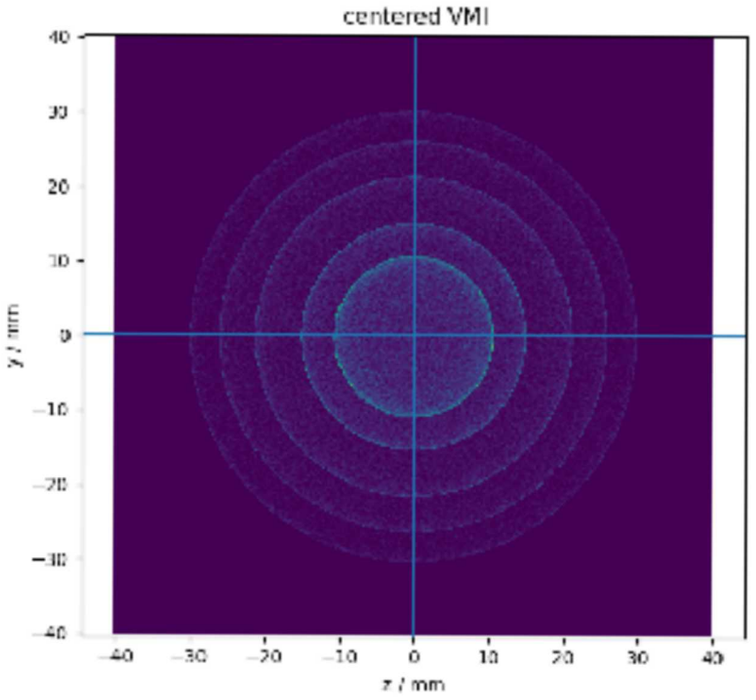
Quartz Reactor

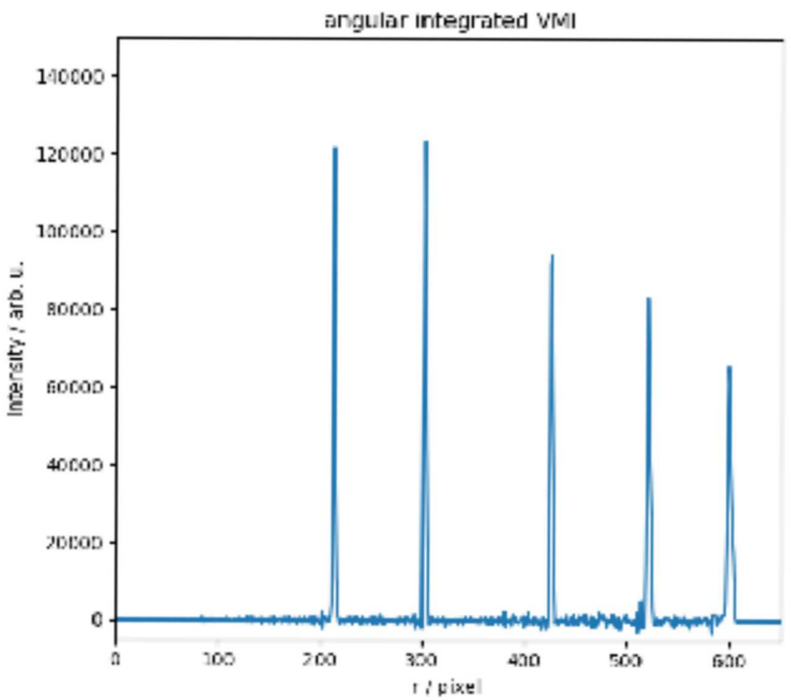
ΔE/E = 1.6%





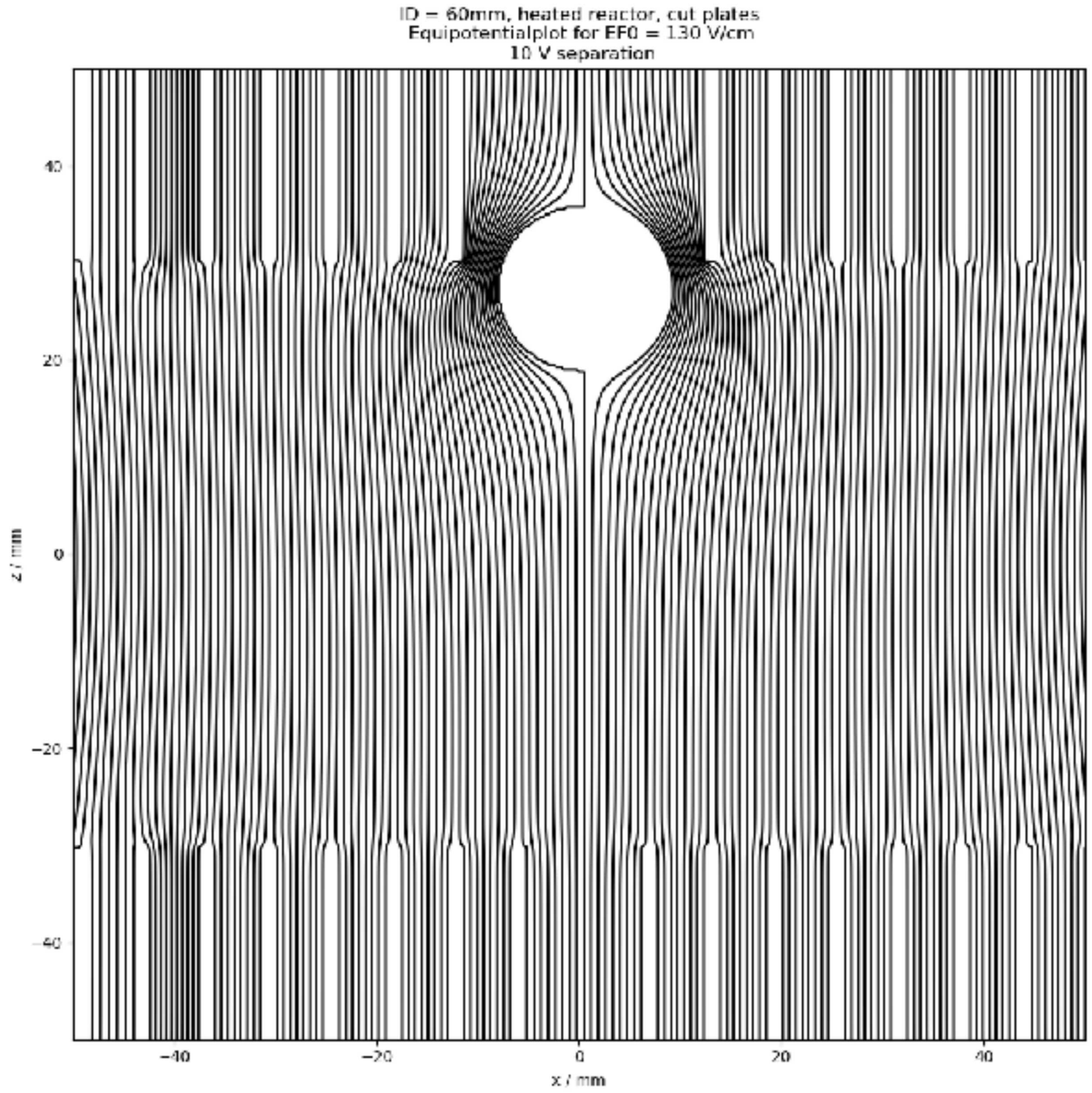






Ion Optics

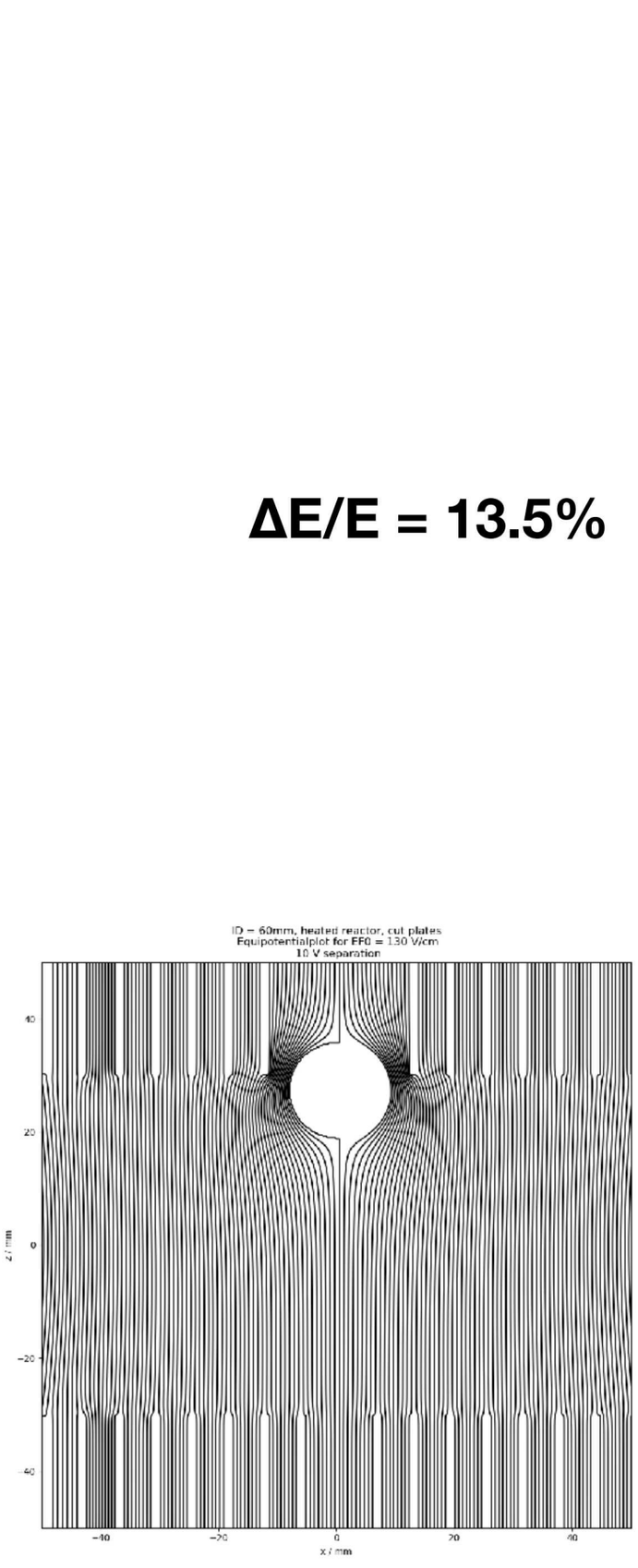
Metal Reactor

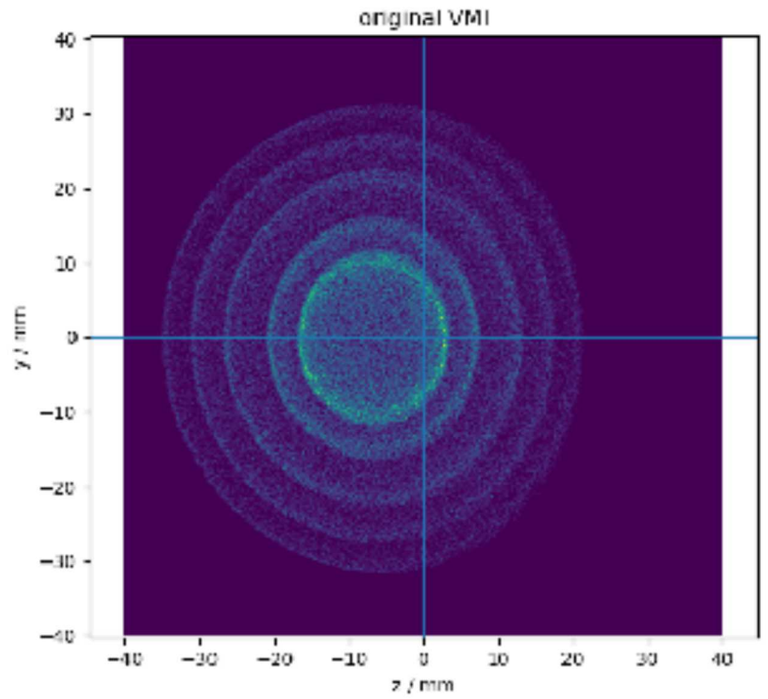


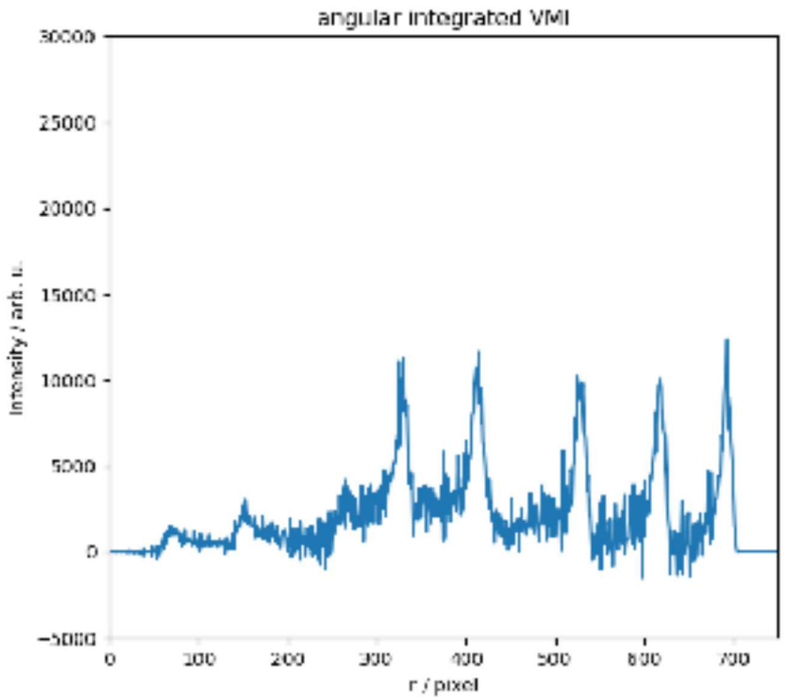
Ion Optics

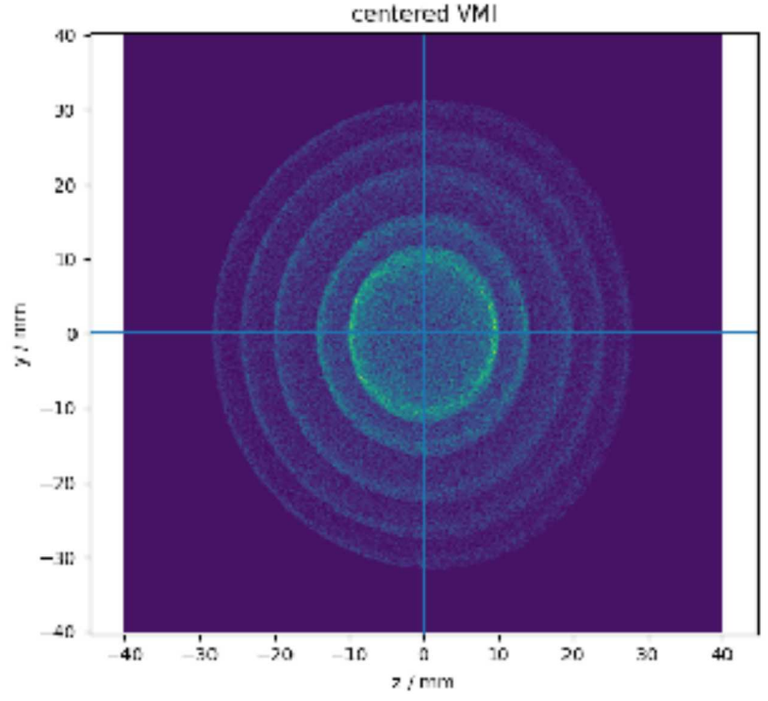
Metal Reactor

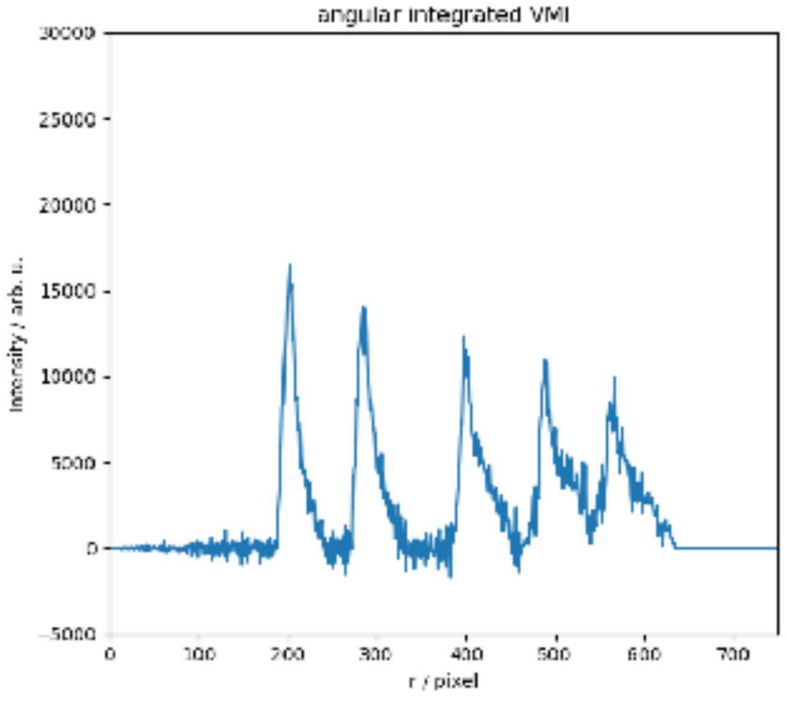
ΔE/E = 13.5%





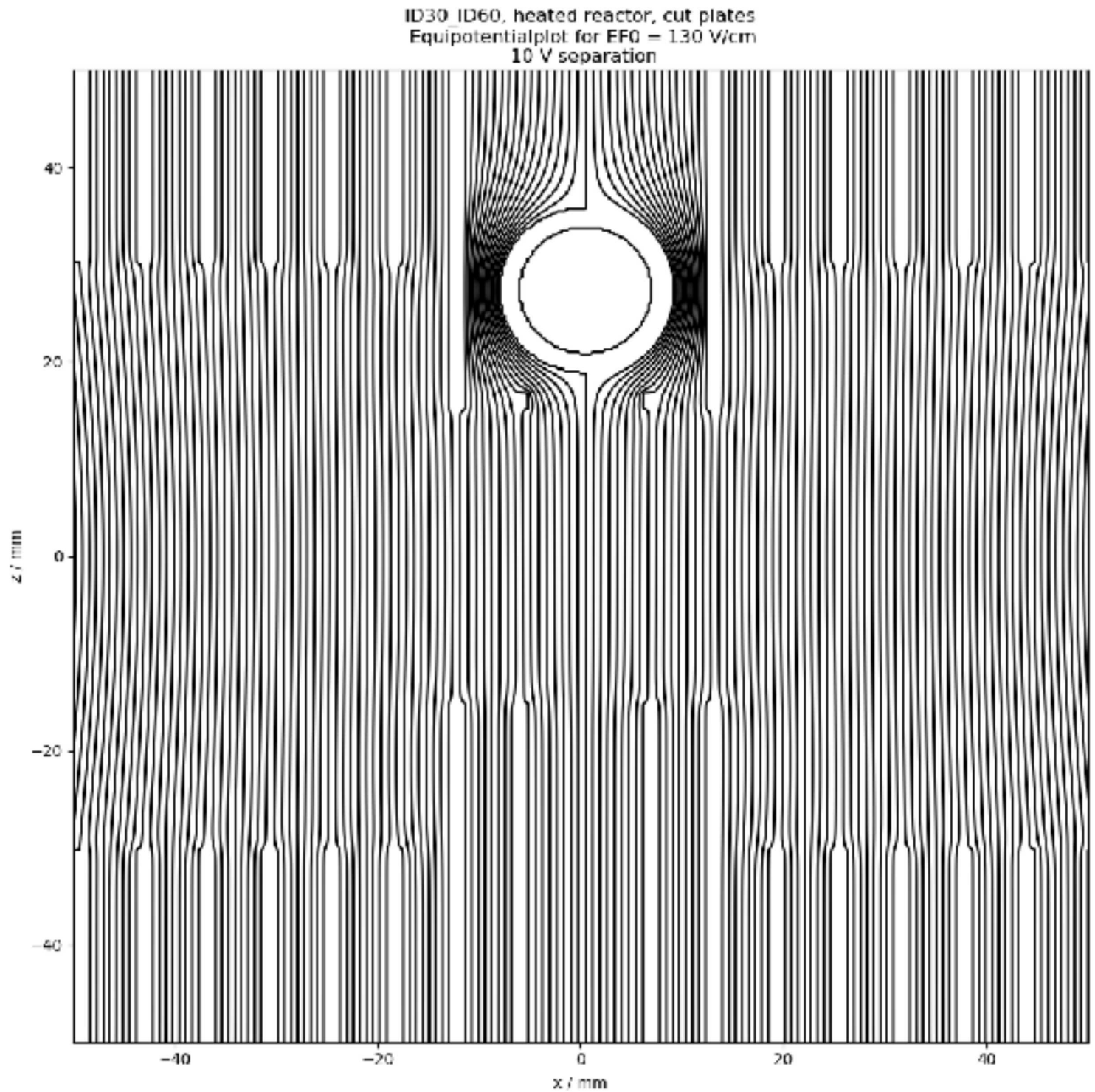






Ion Optics

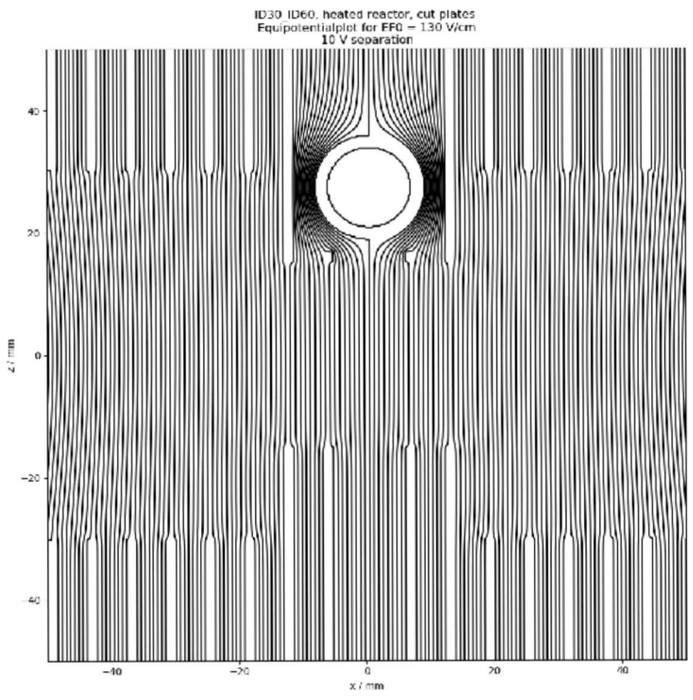
Metal Reactor

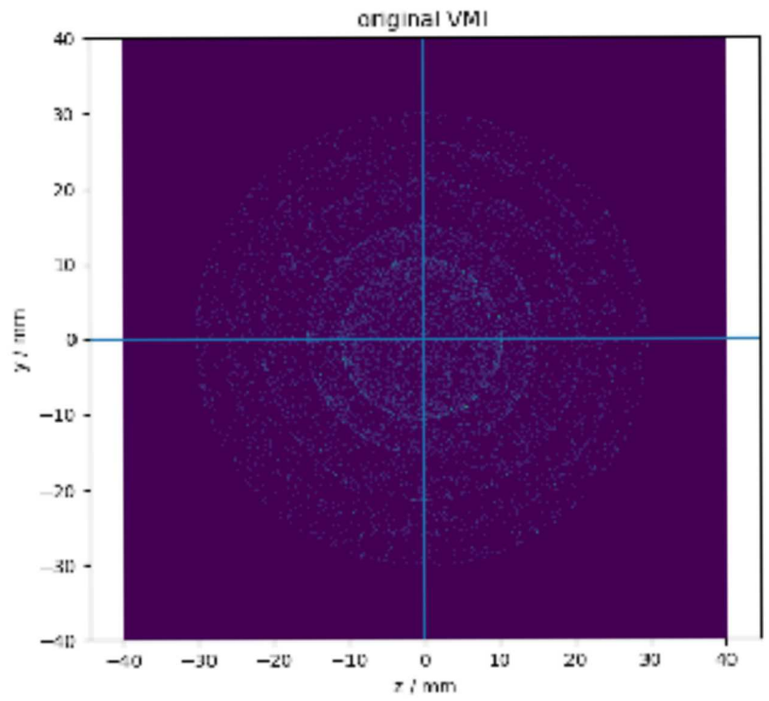


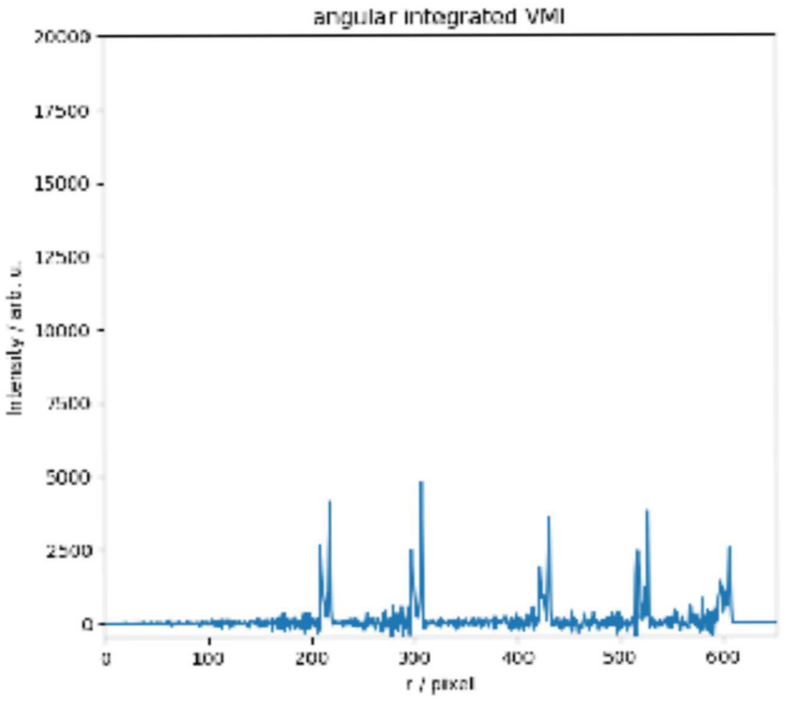
Ion Optics

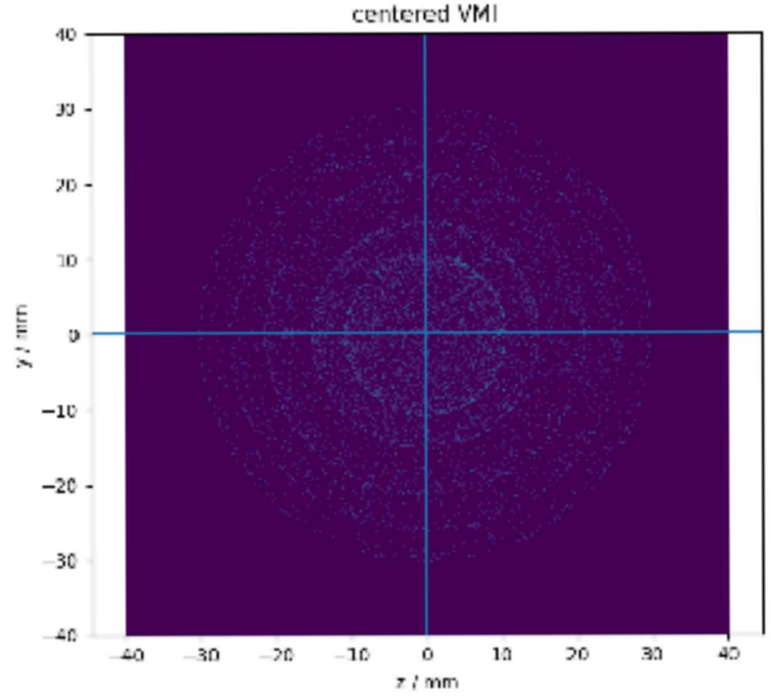
Metal Reactor

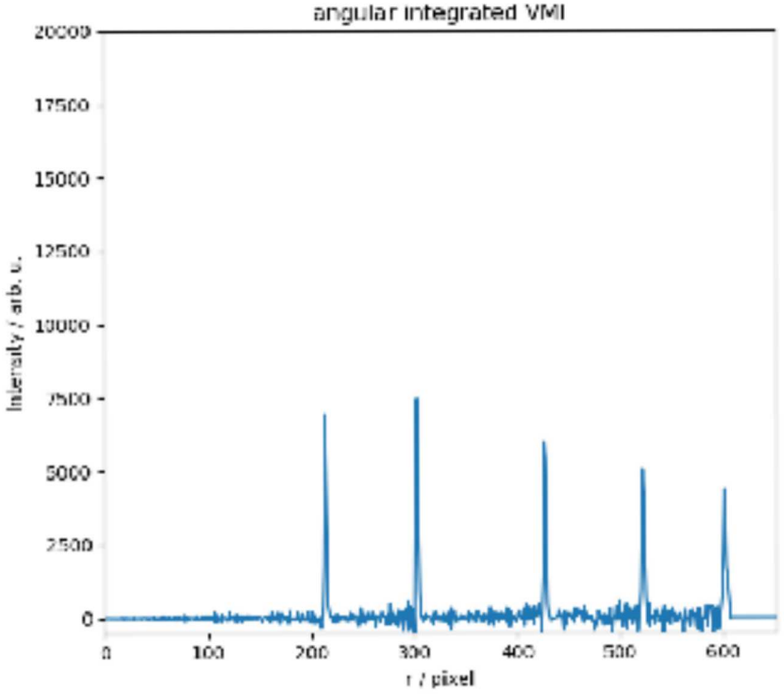
ΔE/E = 1.3%



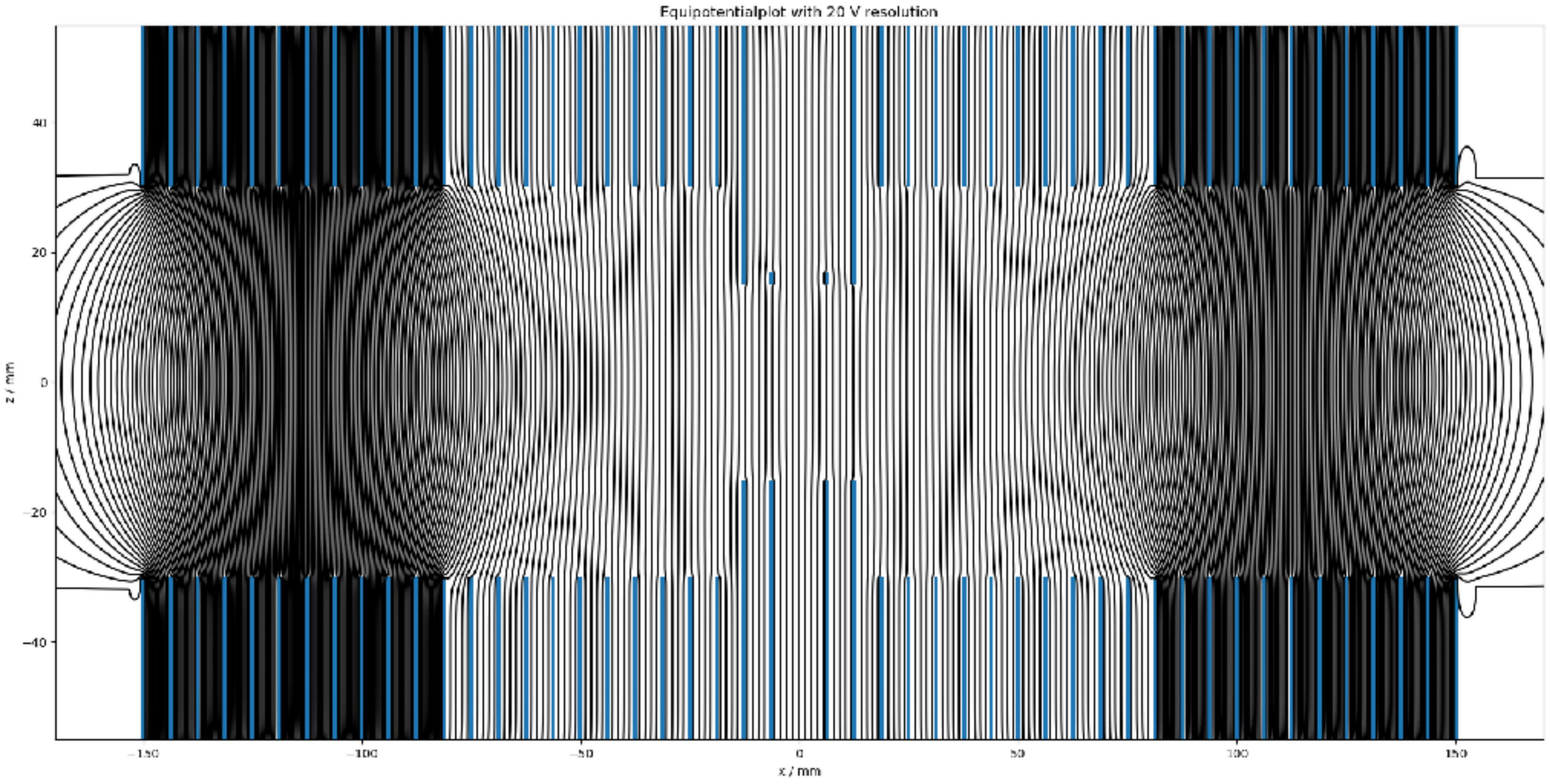






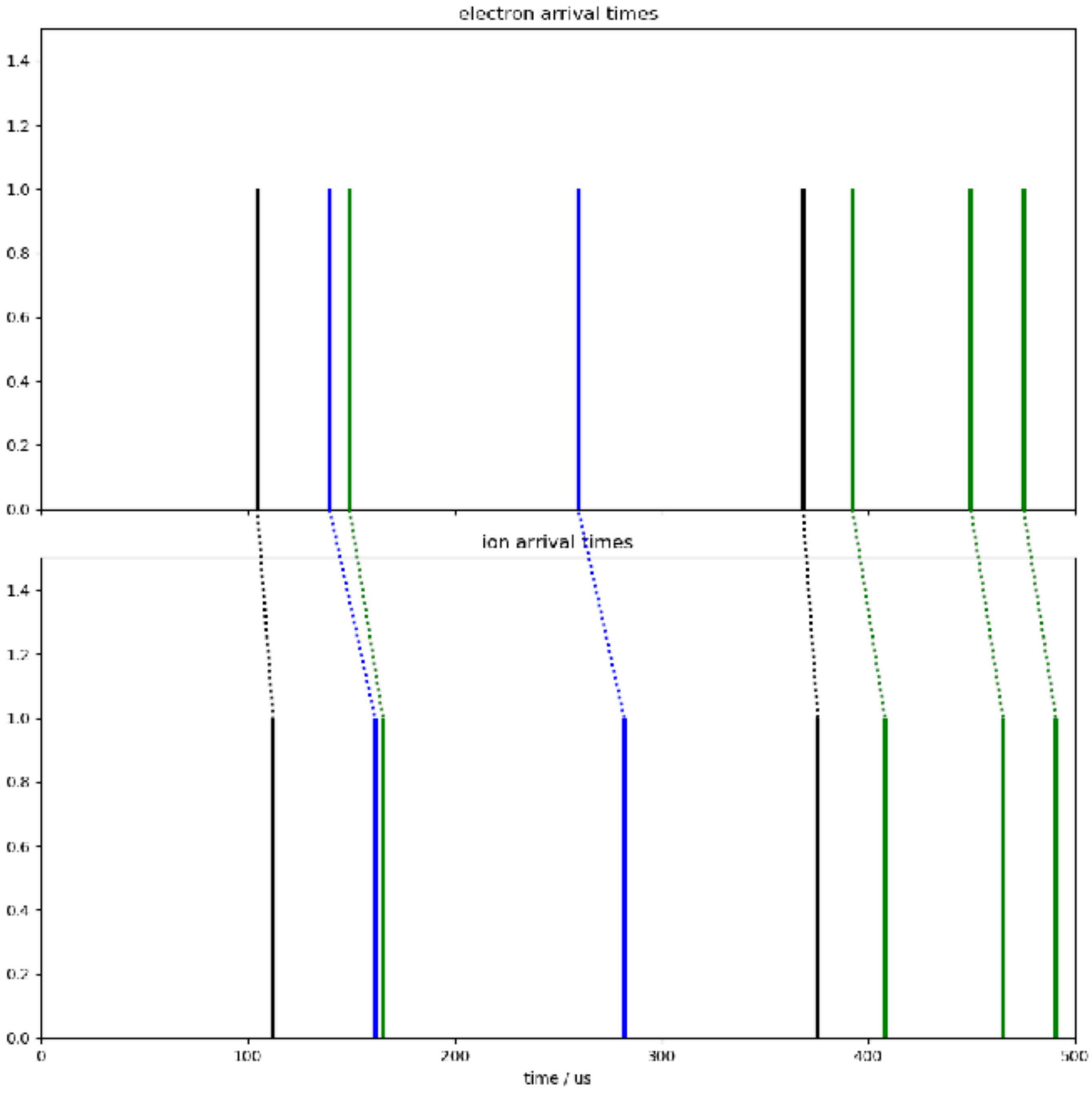


Ion Optics



Photoelectron energy resolution ΔE/E = 1.0 - 1.3 %
Ion time-of-flight resolution m/Δm = 2300 - 3000

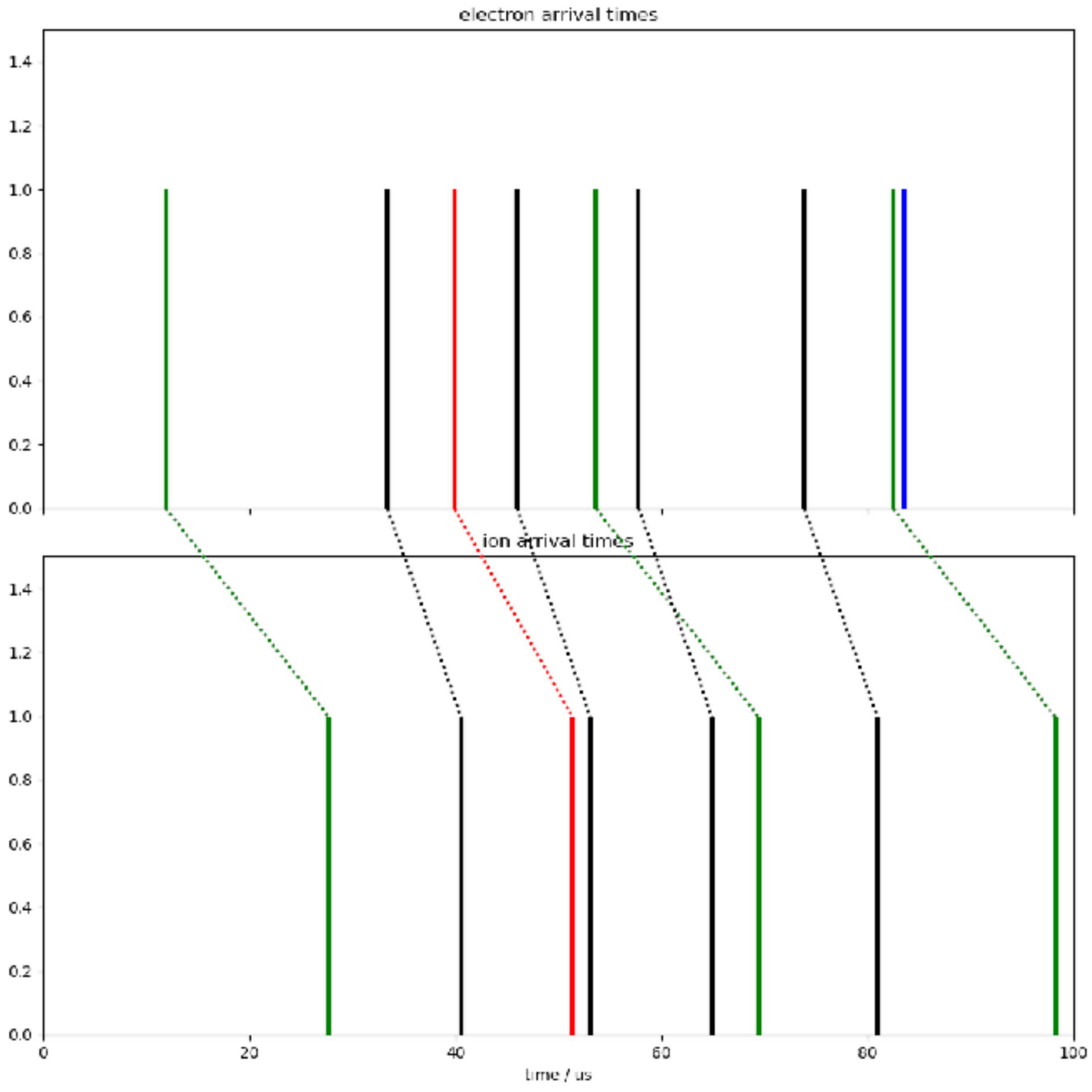
Coincidence Detection



TOFs: 7.1, 11.5, 15.8, 22.3

10 kHz ionization rate

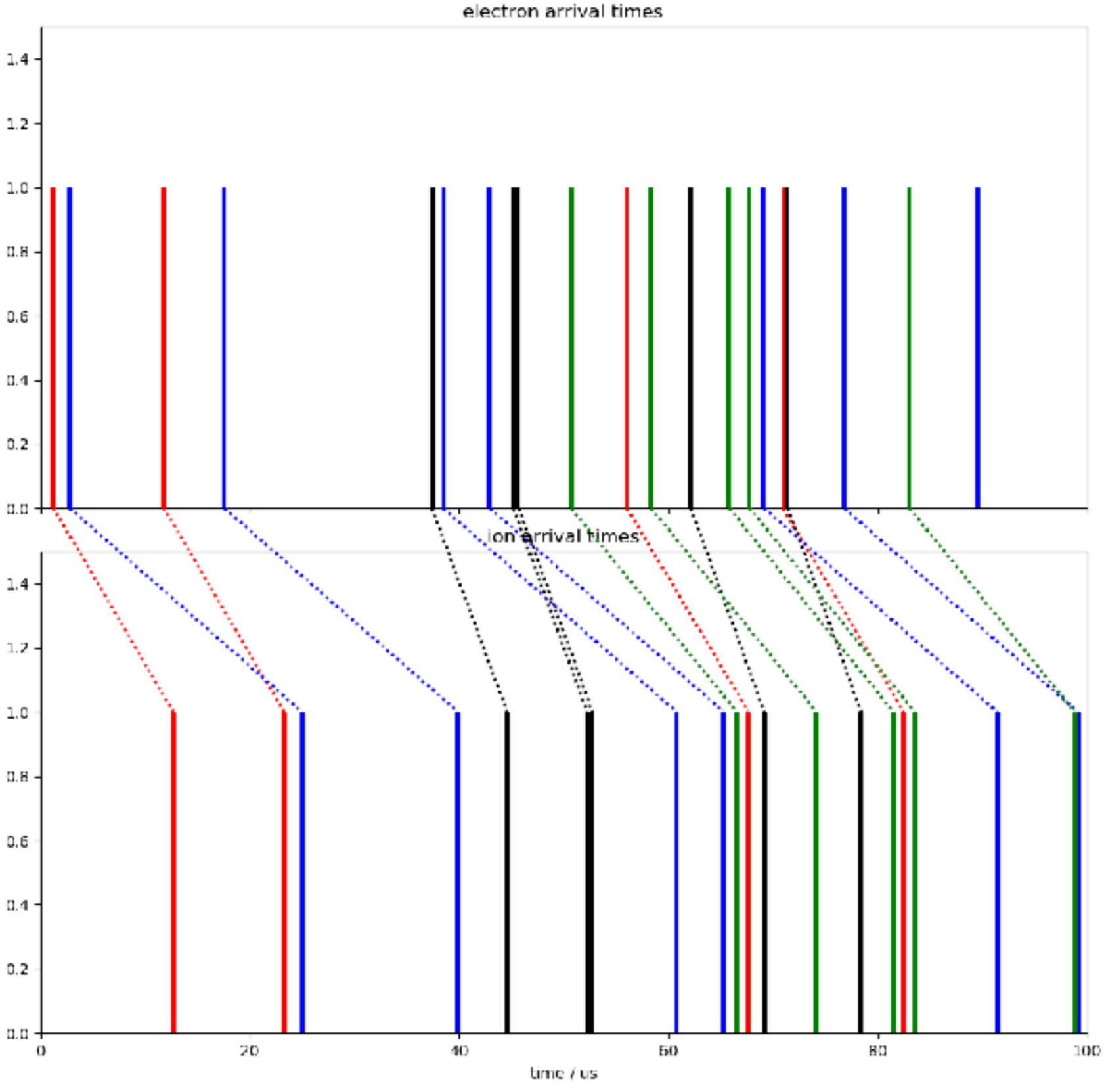
Coincidence Detection



TOFs: 7.1, 11.5, 15.8, 22.3

100 kHz ionization rate

Coincidence Detection

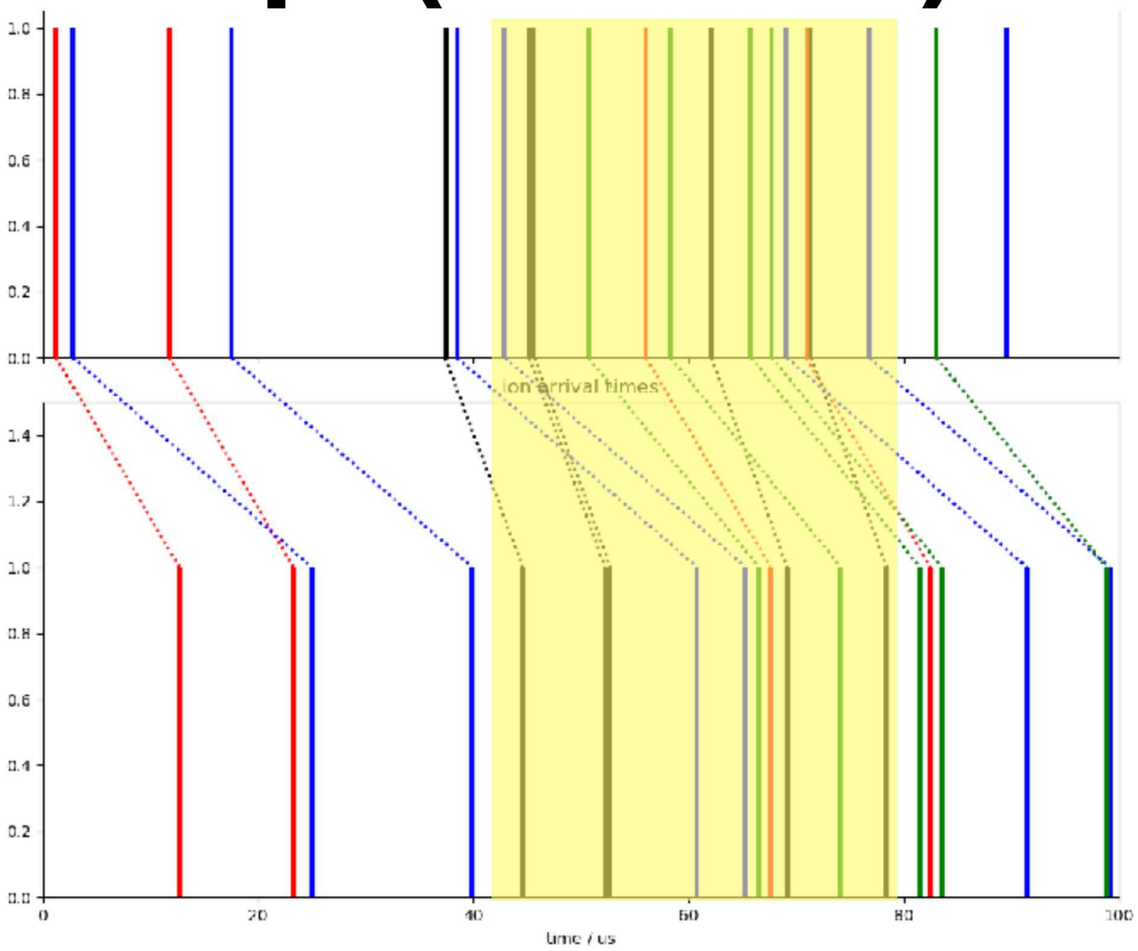


TOFs: 7.1, 11.5, 15.8, 22.3

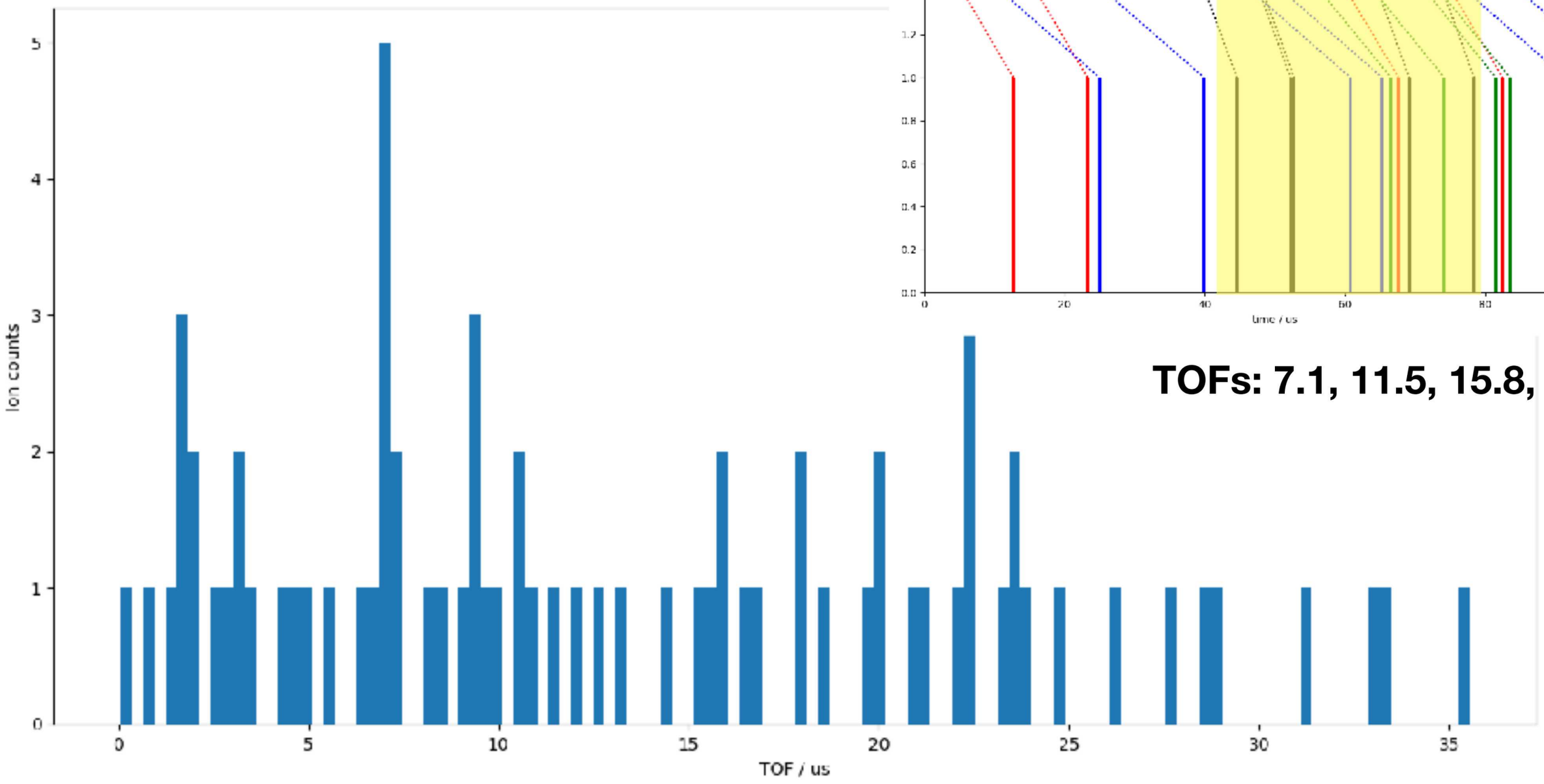
250 kHz ionization rate

Multi Start Multi Stop (MSMS)

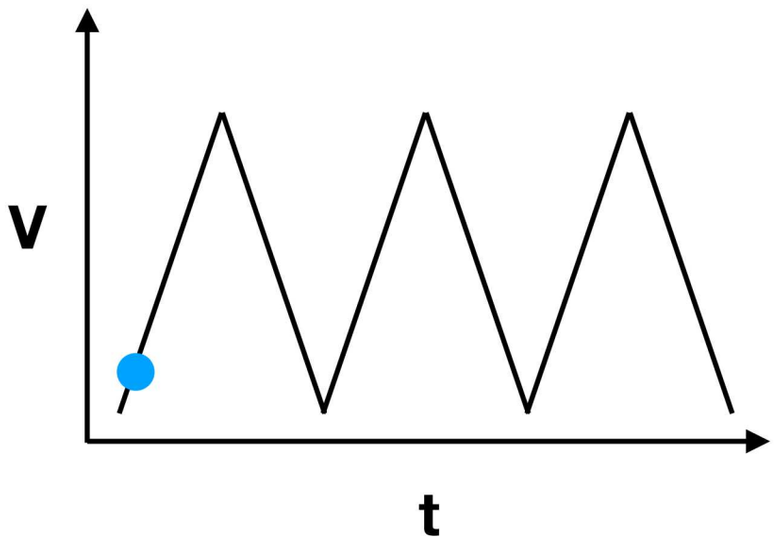
250 kHz ionization rate
40 - 80 us time window

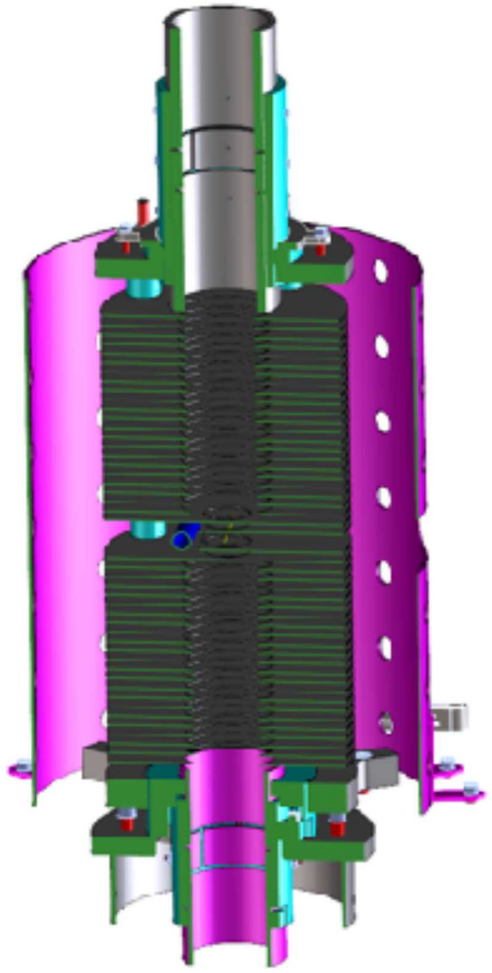


TOFs: 7.1, 11.5, 15.8, 22.3

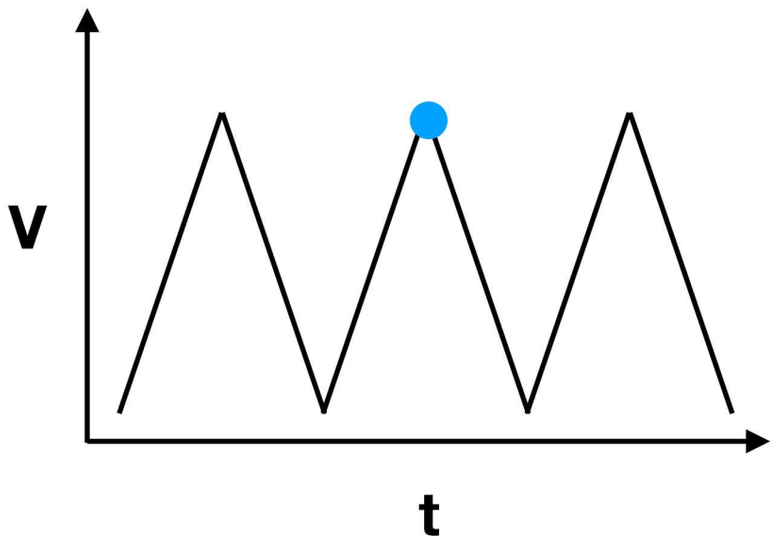


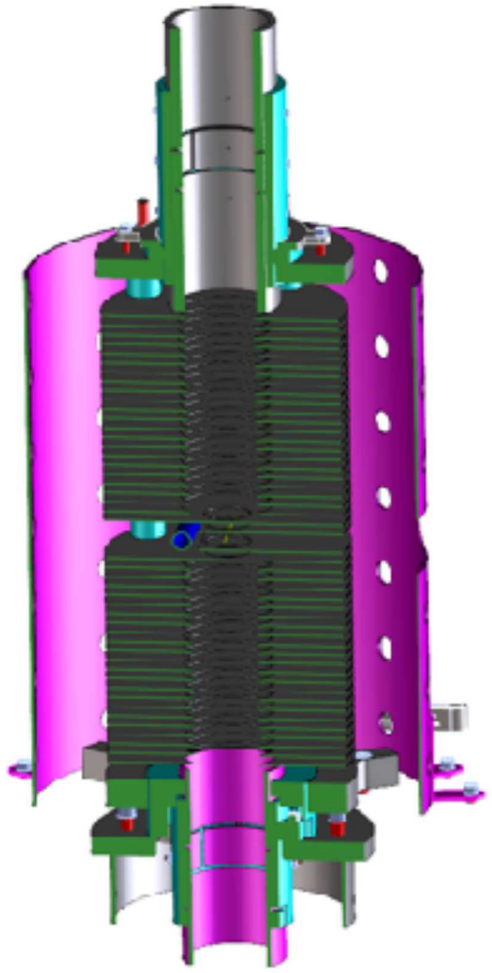
False Coincidence Rejection (FCR)



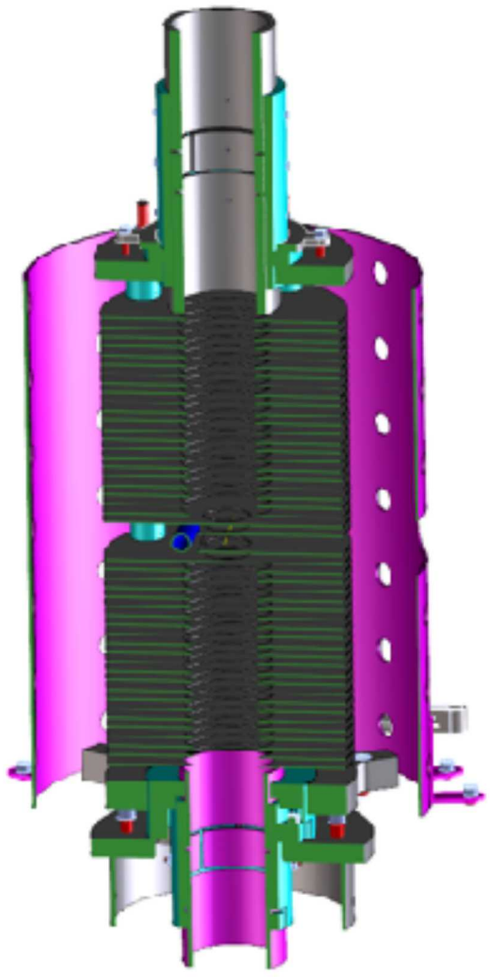


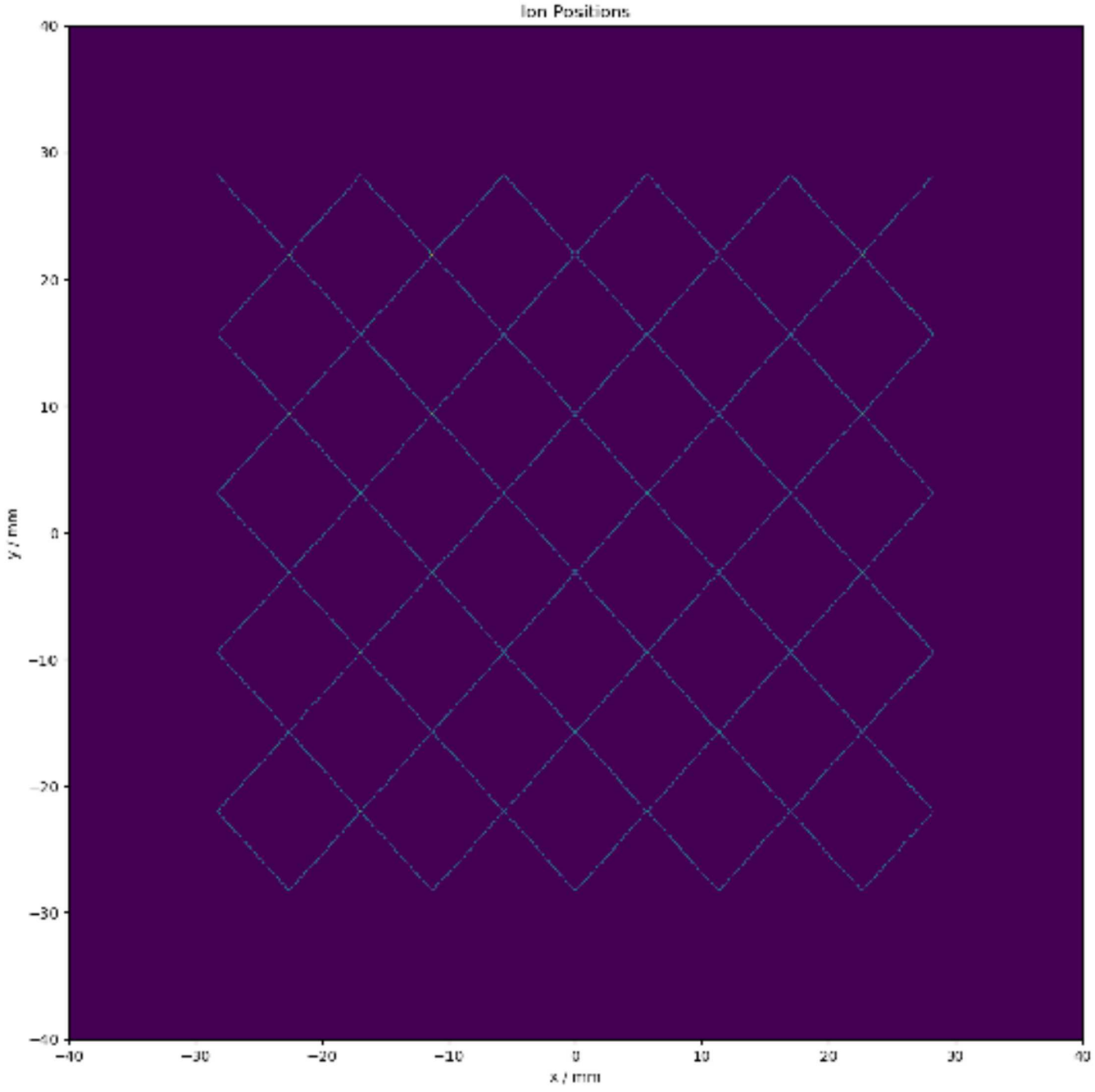
False Coincidence Rejection (FCR)



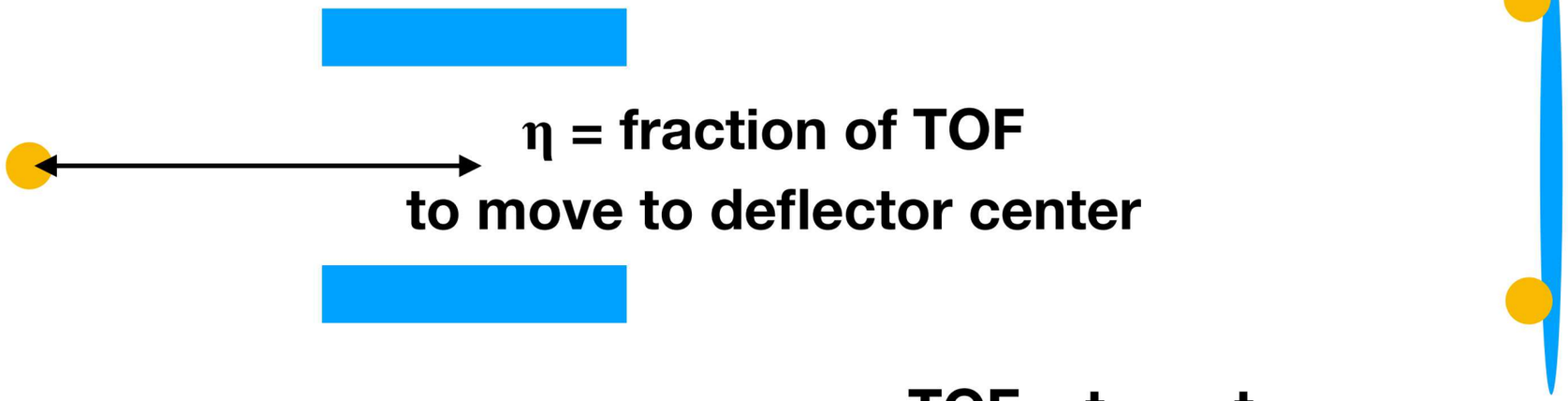


False Coincidence Rejection (FCR)



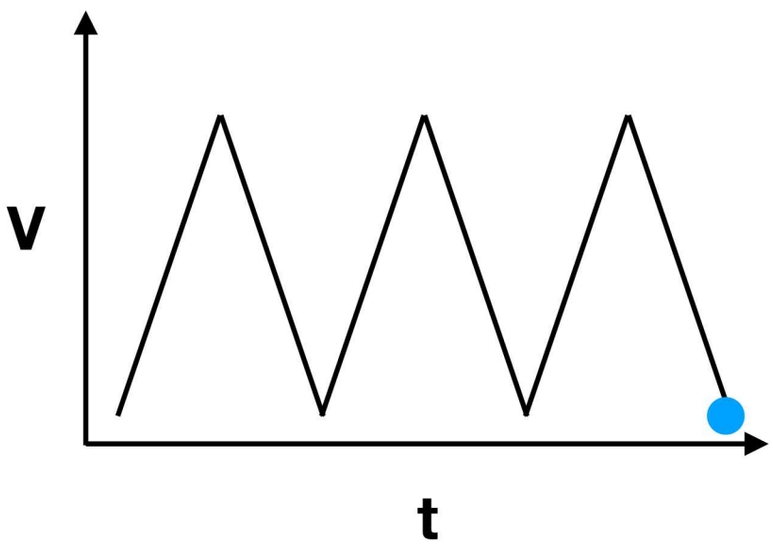


False Coincidence Rejection (FCR)



$TOF = t_{elec} - t_{ion}$

$t_{defl} = t_{elec} + TOF \times \eta$

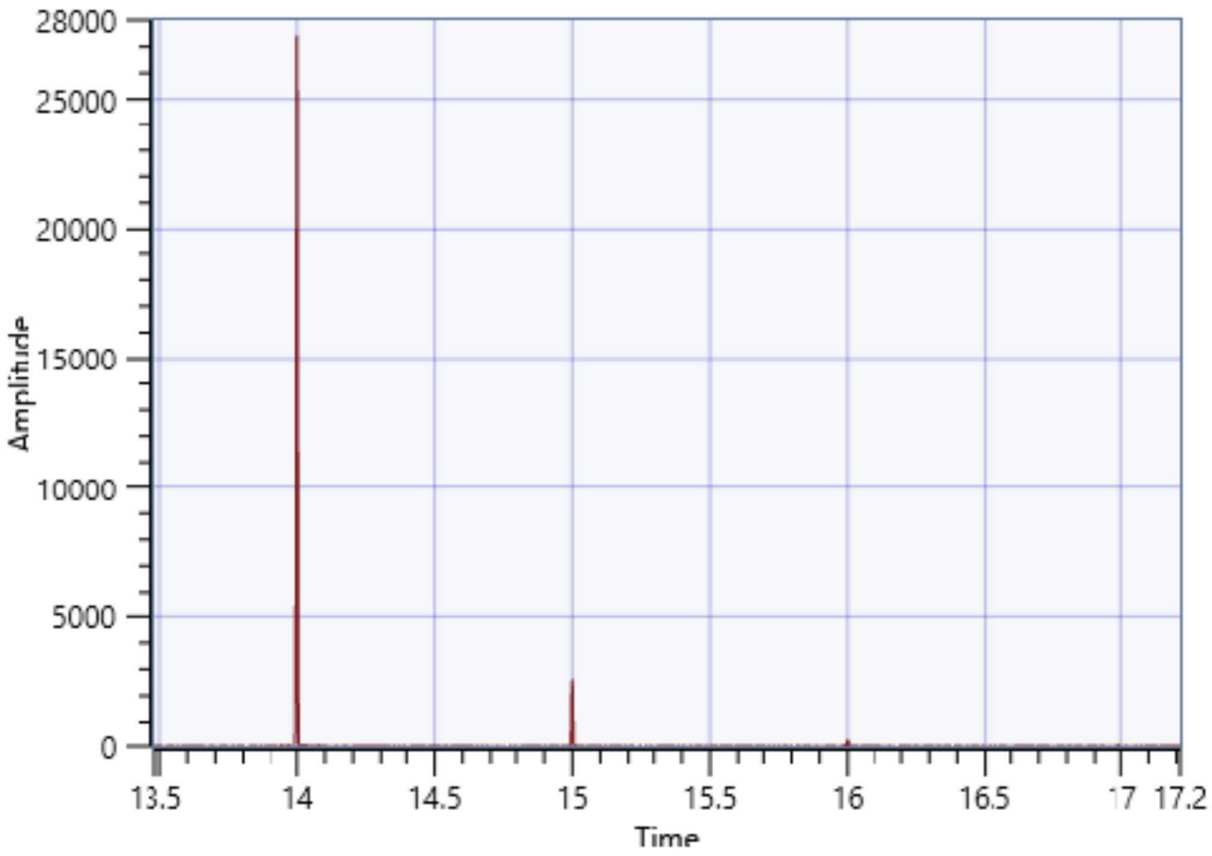


If calculated ion position does not match experimental position
-> reject coincidence

MSMS vs FCR

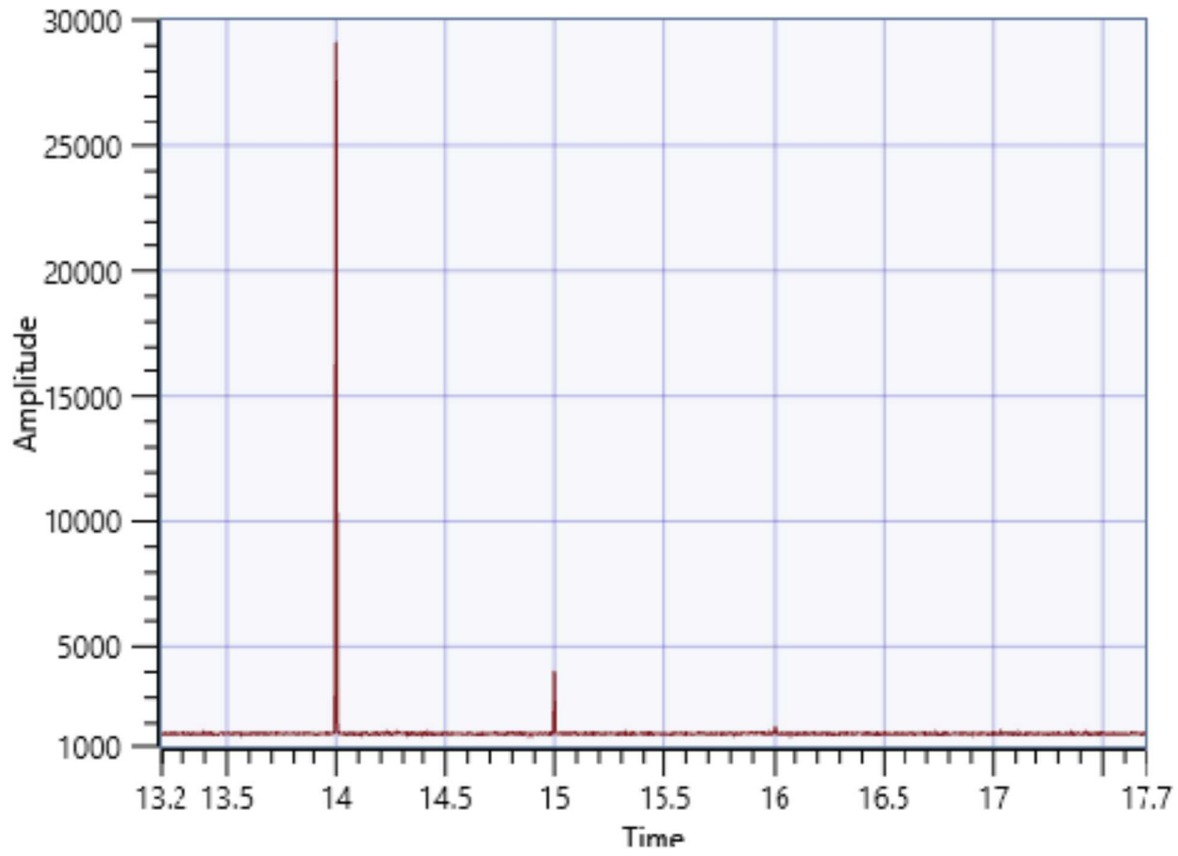
FCR Total Coincidences

15.17 M



MSMS Total Coincidences

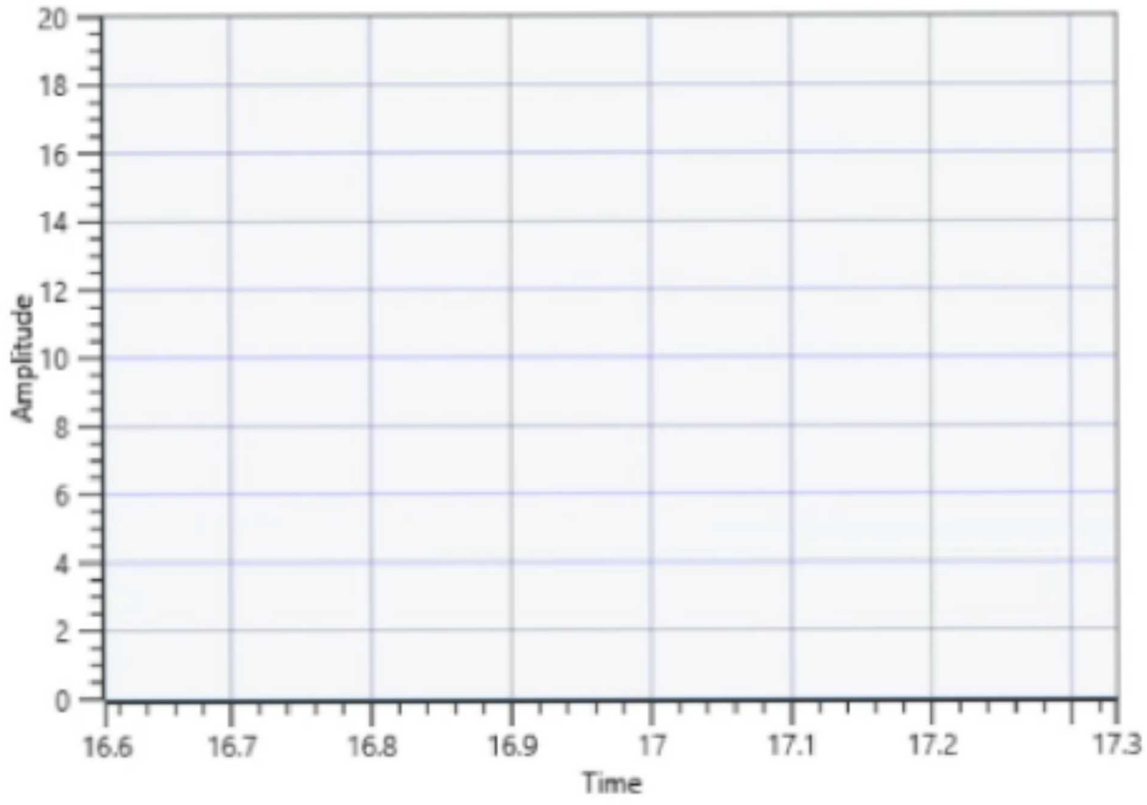
74.5 M



MSMS vs FCR

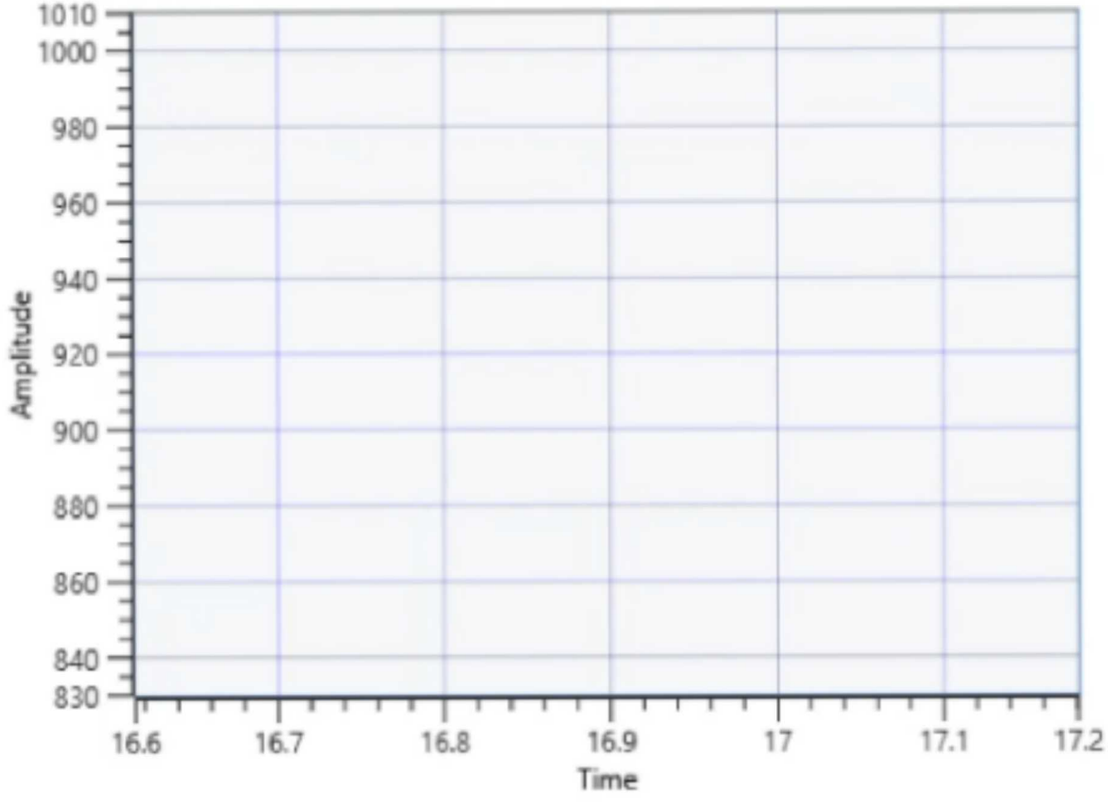
FCR Total Coincidences

102.5 k



MSMS Total Coincidences

45.98 M



FCR last dll call time [ms]

379

MSMS last dll call time [ms]

342

Stop

PEPICO data processing

$$Coincidence = \begin{pmatrix} t_{elec} \\ tof \\ t_{kinetic} \\ h\nu \\ x_{elec} \\ y_{elec} \\ x_{ion} \\ y_{ion} \end{pmatrix}$$

PEPICO data processing

$$Coincidence = \begin{pmatrix} t_{elec} \\ tof \\ t_{kinetic} \\ h\nu \\ x_{elec} \\ y_{elec} \\ x_{ion} \\ y_{ion} \end{pmatrix}$$

8 x 64 bit

@ 100 kHz ionization rate -> 6.4 Mb/s = 23.04 Gb/h = 368.64 Gb/16h

PEPICO data processing

$$Coincidence = \begin{pmatrix} t_{elec} \\ tof \\ t_{kinetic} \\ h\nu \\ x_{elec} \\ y_{elec} \\ x_{ion} \\ y_{ion} \end{pmatrix}$$

8 x 64 bit

@ 100 kHz ionization rate ->
6.4 Mb/s = 23.04 Gb/h =
368.64 Gb/16h

Can we analyze the data on the fly and only keep the results?

PEPICO simulator

Generates PEPICO events randomly from supplied parameters:

- **ion TOF, FWHM**
- **ionization probability**
- **rate constants**
- **ionization potentials**
- **photon energy**

Output:

$$Electrons = \begin{pmatrix} t_{elec} \\ x_{elec} \\ y_{elec} \end{pmatrix} \qquad Ions = \begin{pmatrix} t_{ion} \\ x_{ion} \\ y_{ion} \end{pmatrix}$$

PEPICO simulator

Output:

$$Electrons = \begin{pmatrix} t_{elec} \\ x_{elec} \\ y_{elec} \end{pmatrix} \qquad Ions = \begin{pmatrix} t_{ion} \\ x_{ion} \\ y_{ion} \end{pmatrix}$$

# PEPICO events	CPU	GPU (CUDA)
10^5	710 ms	330 ms
2.5x10^5	1.8 s	800 ms
10^6	6.7 s	3.2 s

CPU: Intel Core i7-3610QM @ 2.3 GHz, 8GB RAM
GPU: NVIDIA Quadro K3000M @ 653 MHz, 2 GB GDDR5

PEPICO simulator

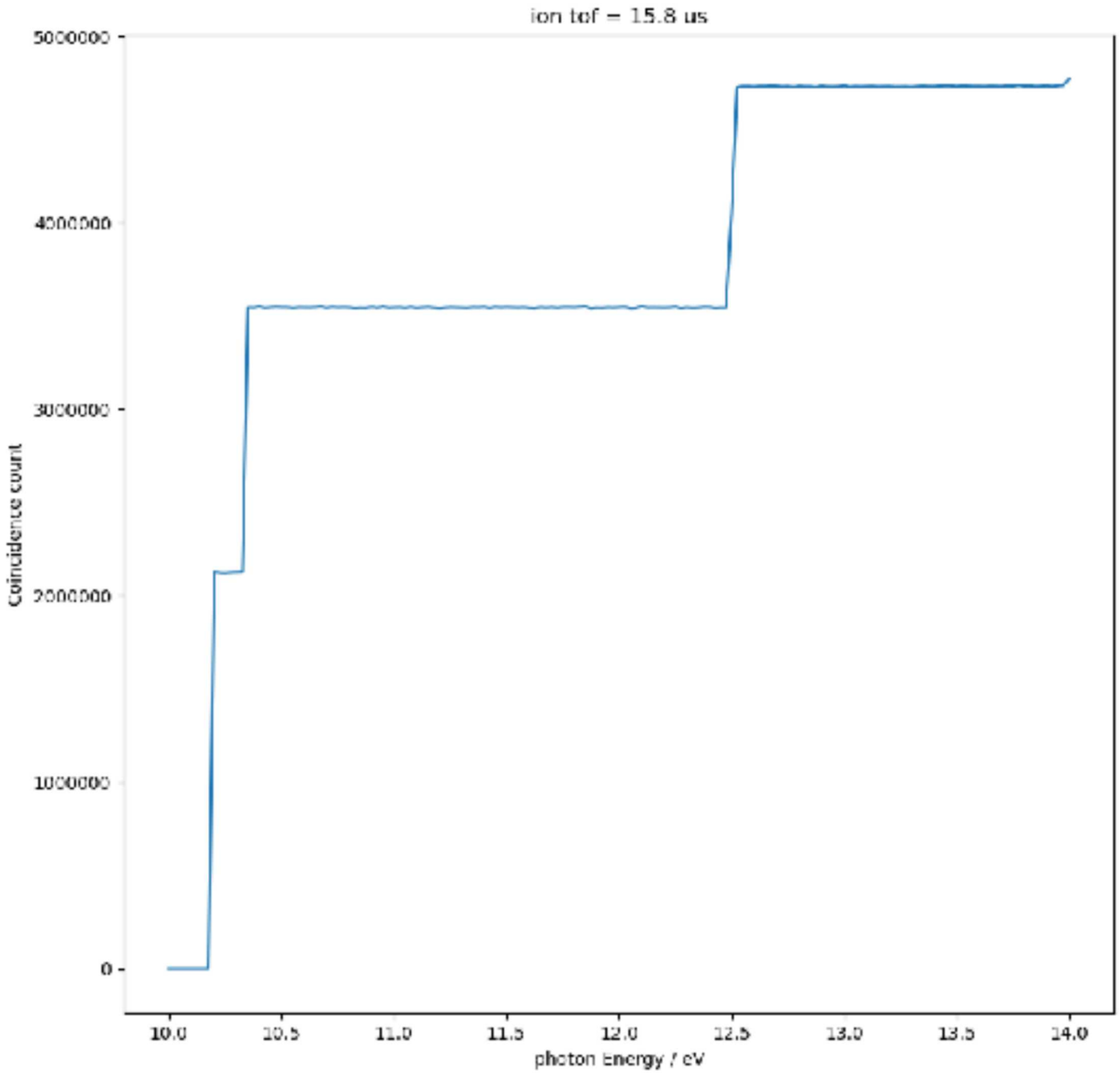
FCR vs MSMS:

rep. rate / kHz	# PEPICO events	FCR	FCR Coincidences	MSMS	MSMS Coincidences
100	10^5	55 ms	~ 1.02 * 10^5	110 ms	~ 5 * 10^5
250	2.5x10^5	230 ms	~ 2.66 * 10^5	550 ms	~ 2.75 * 10^6
1000	10^6	1600 ms	~ 1.23 * 10^6	6200 ms	~ 3.27 * 10^7

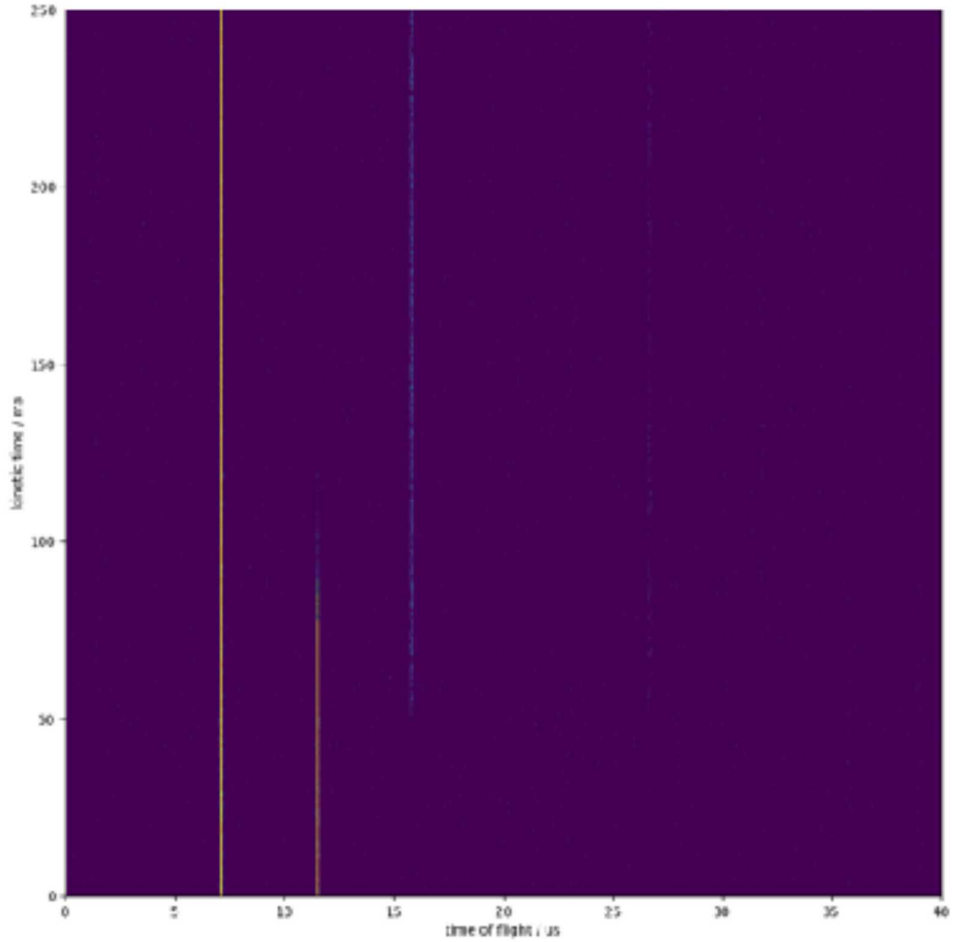
Real time coincidence analysis with 250 kHz is possible.

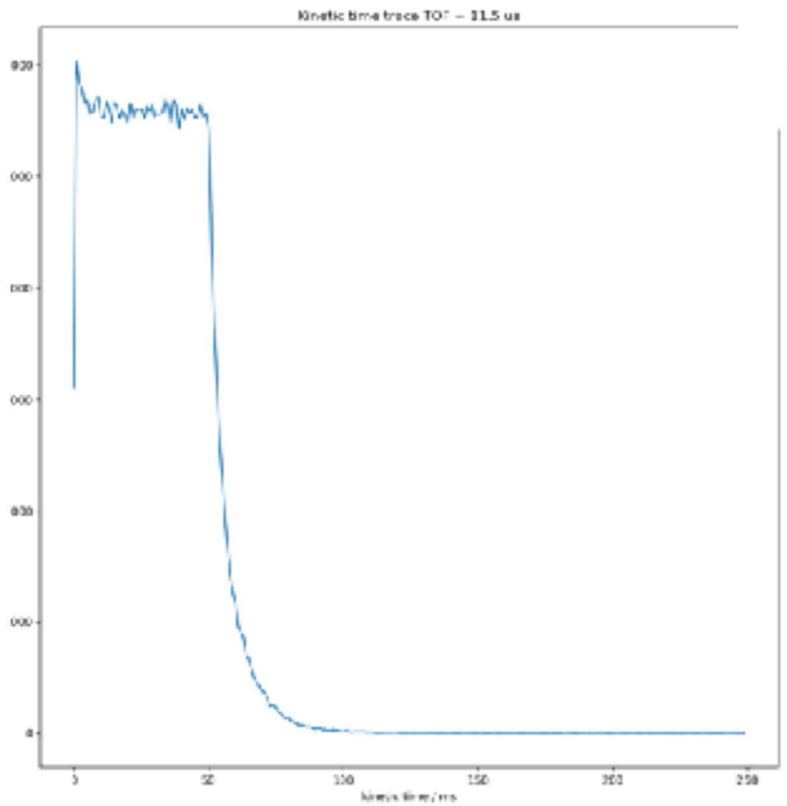
PEPICO simulation

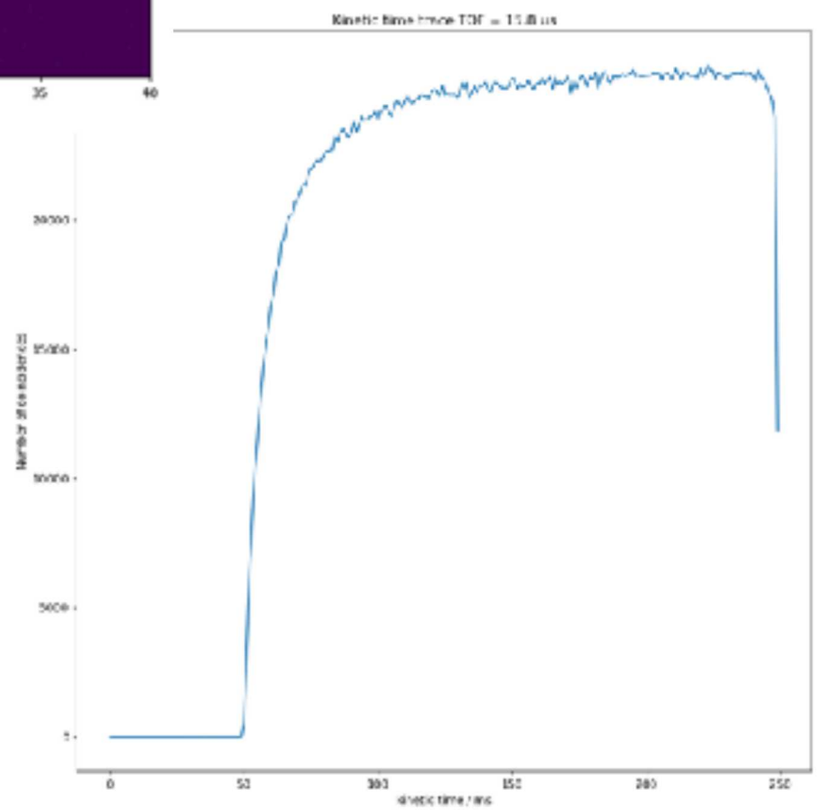
Photon energy: 10 - 14 eV, 25 meV steps
100 kHz
TOF: 7.1, 11.5, 15.8, 22.3, 26.7, 28.0 µs



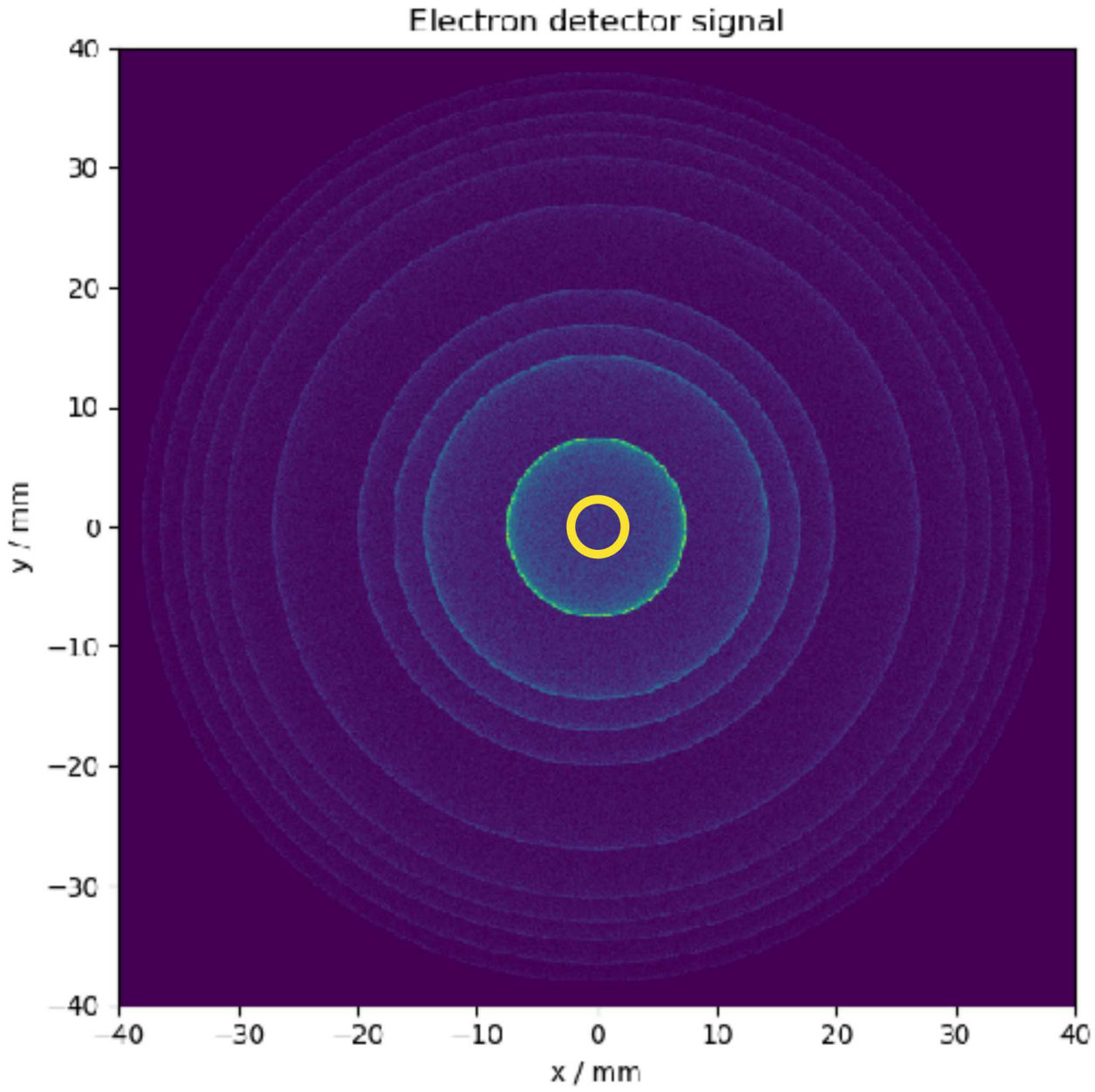
PEPICO simulation







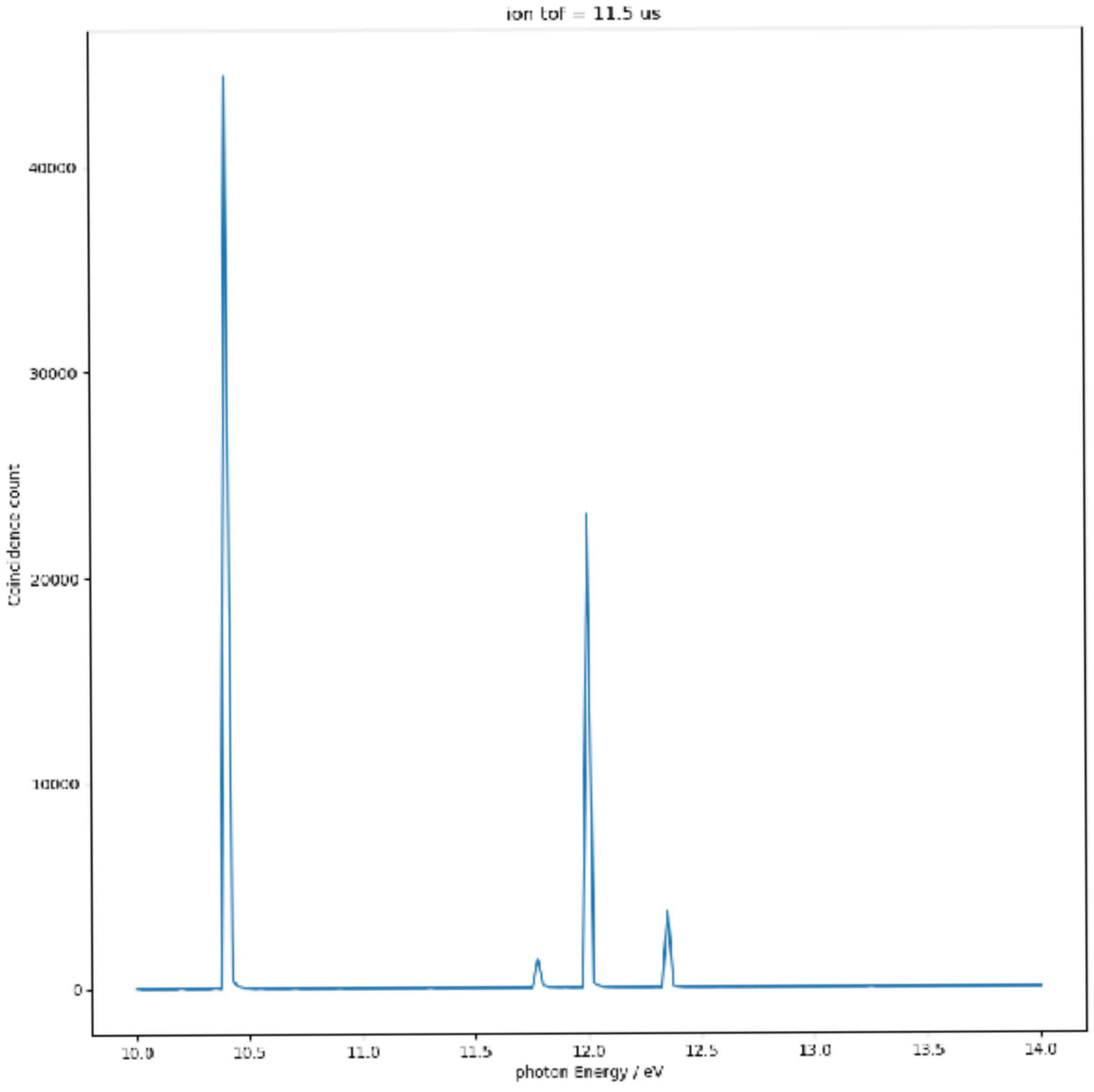
PEPICO simulation



Select only Coincidences with electrons with zero kinetic energy

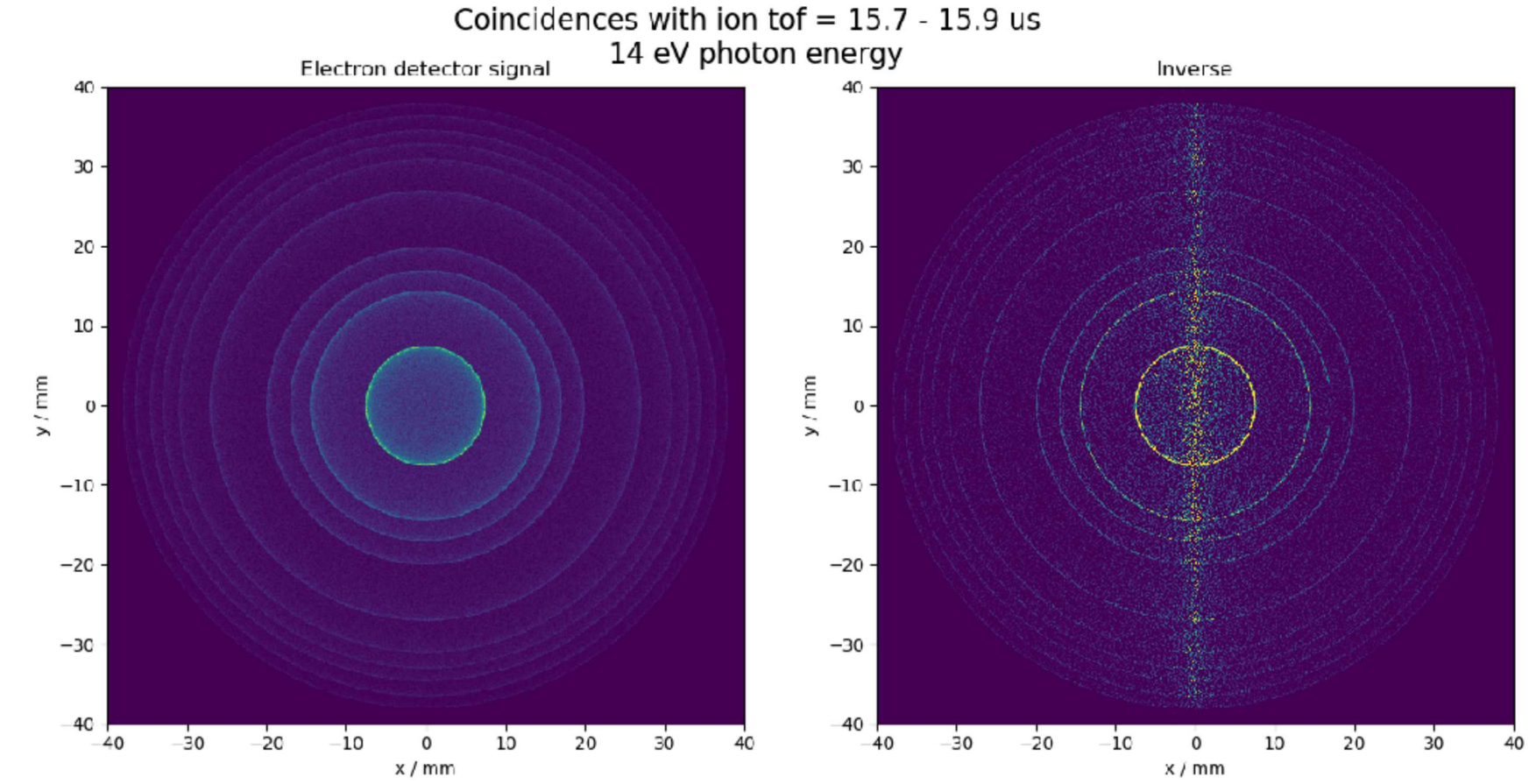
PEPICO simulation

Threshold photoelectron spectra (TPES)



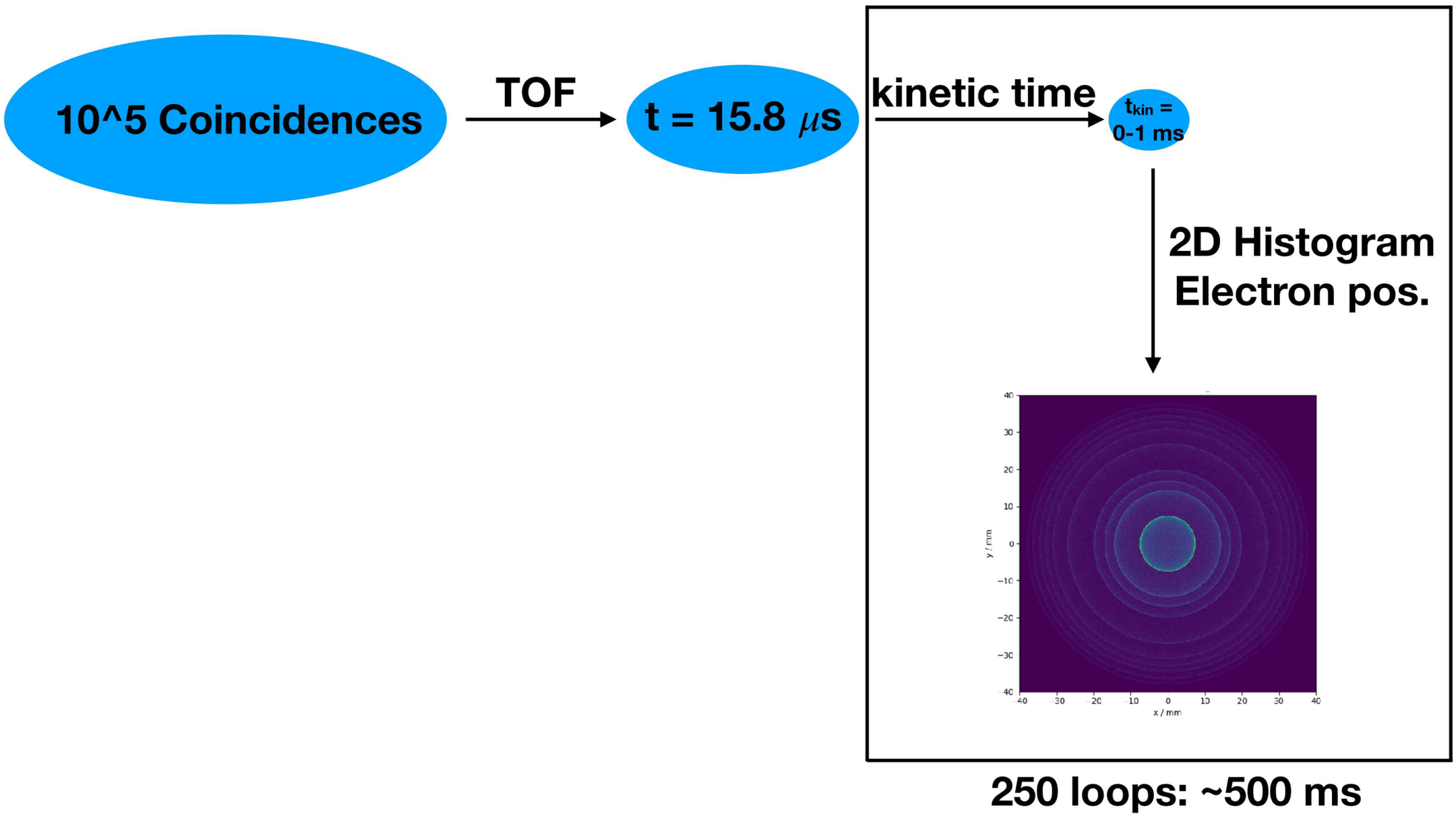
PEPICO simulation

Two isomers at TOF 15.8 µs with identical ionization probability but different ionization potentials and rate constants



PEPICO simulation

Two isomers at TOF 15.8 µs with identical ionization probability but different ionization potentials and rate constants



PEPICO simulation

Two isomers at TOF 15.8 µs with identical ionization probability but different ionization potentials and rate constants

10^5 Coincidences

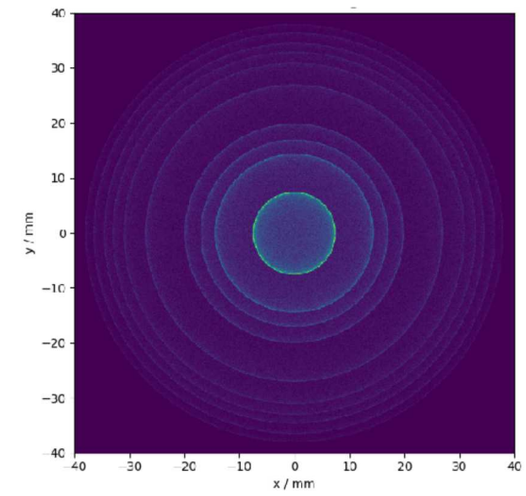
TOF

t = 15.8 μs

kinetic time

t_{kin} = 0-1 ms

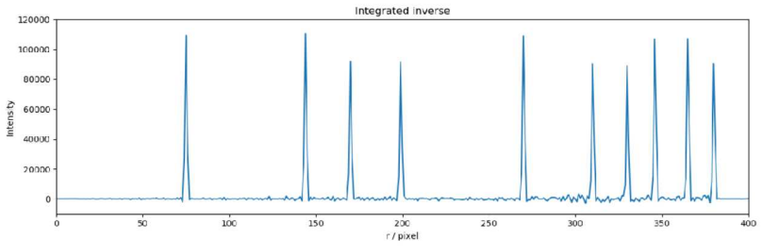
2D Histogram Electron pos.



250 loops: ~500 ms

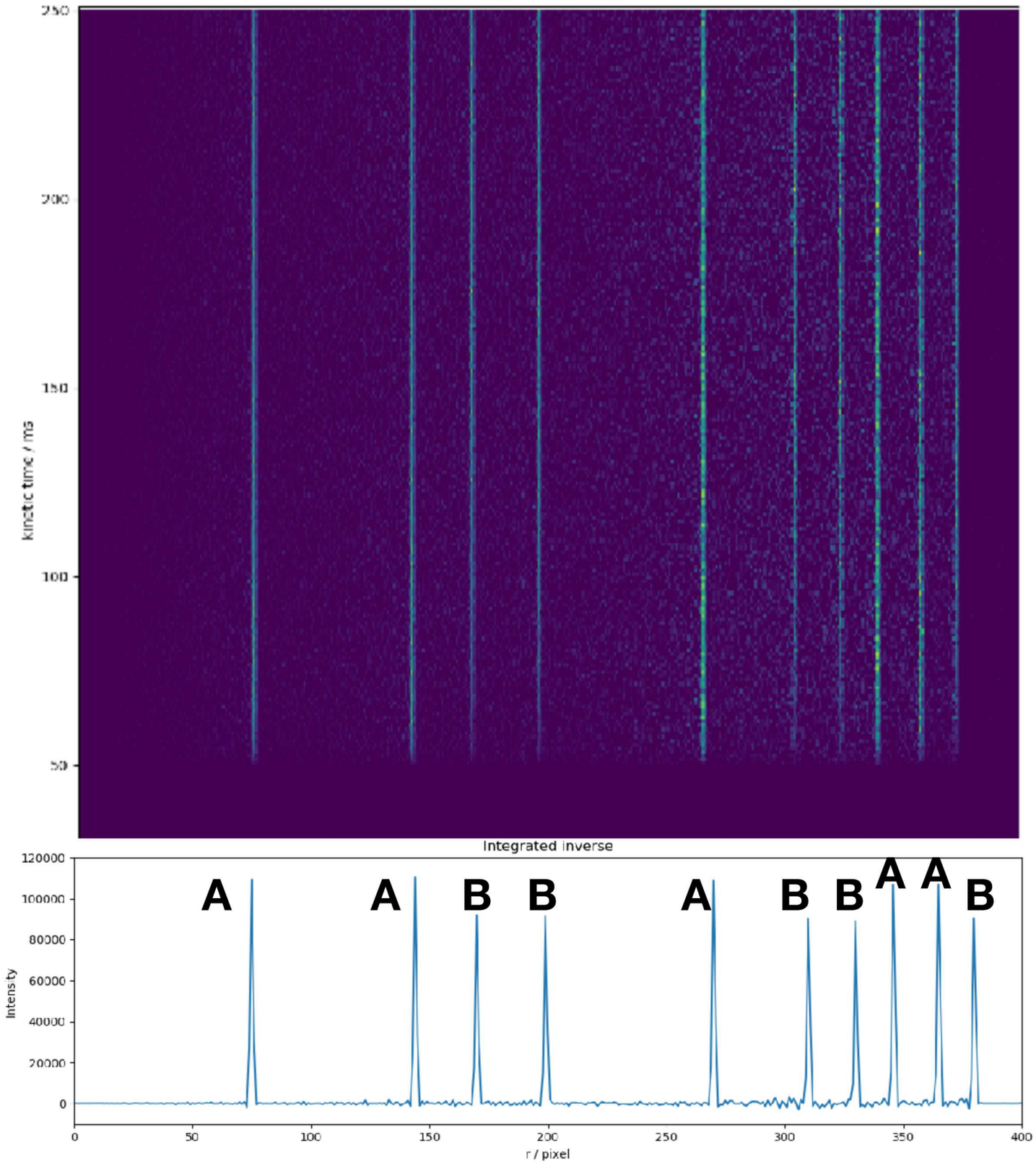
Inverse and Integration

PyAbel Basex : ~1.5 s
DAVIS: <100 ms



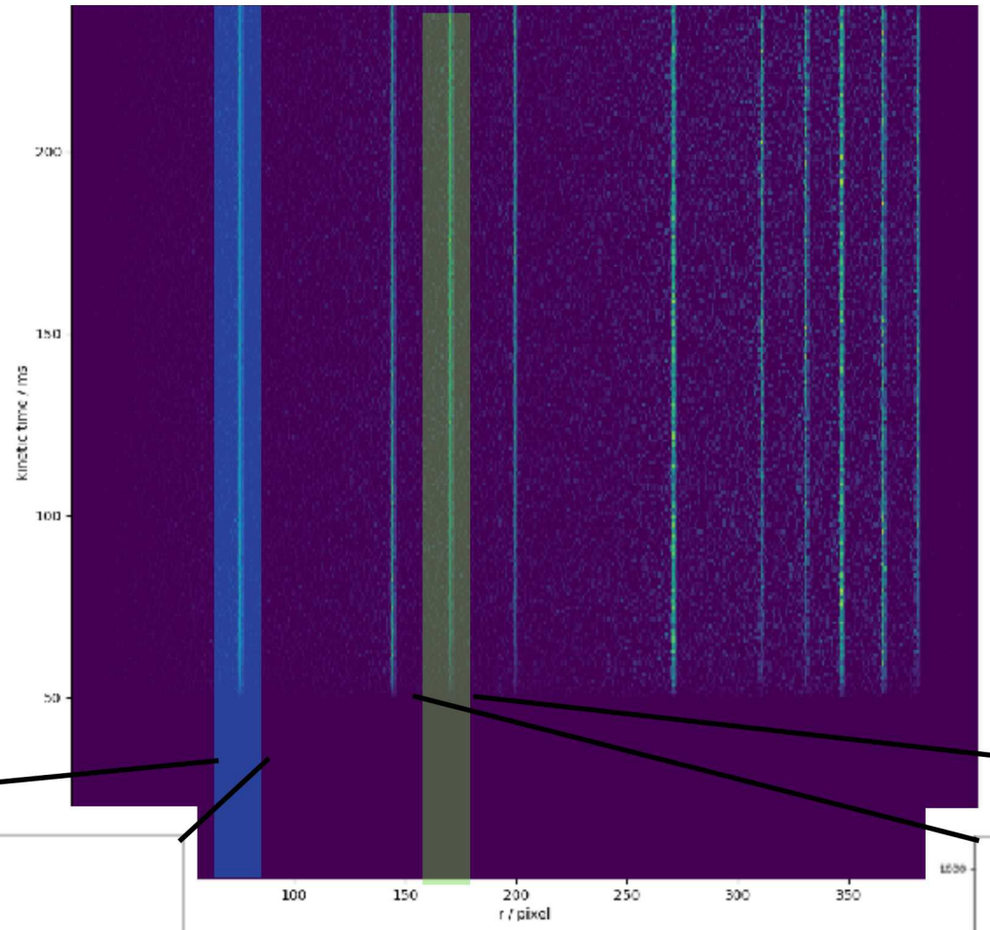
DAVIS: J. Chem. Phys. **148**, 194101 (2018)

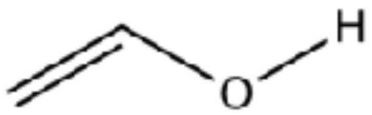
PEPICO simulation



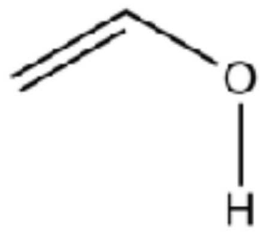
PEPICO simulation

Kinetic time resolved PES





anti



syn

Conclusion

- **PEPICO enables reaction studies of conformers that are not accessible with MPIMS**
- **PEPICO yields PES which is a better molecular fingerprint than PIS**
- **Real time analysis of 100-250 kHz count rate experiment is possible**
- **Faster count rates should be possible with better computing hardware and code optimizations**
- **Design of the instrument is finished and manufacturing will start soon**

Thank you for your attention