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A New High-resolution Double Velocity Map Imaging Photoelectron Photoion Coincidence Spectrometer for Gas Phase Reaction Kinetics

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July 11, 2022

Molecular Interactions and Dynamics

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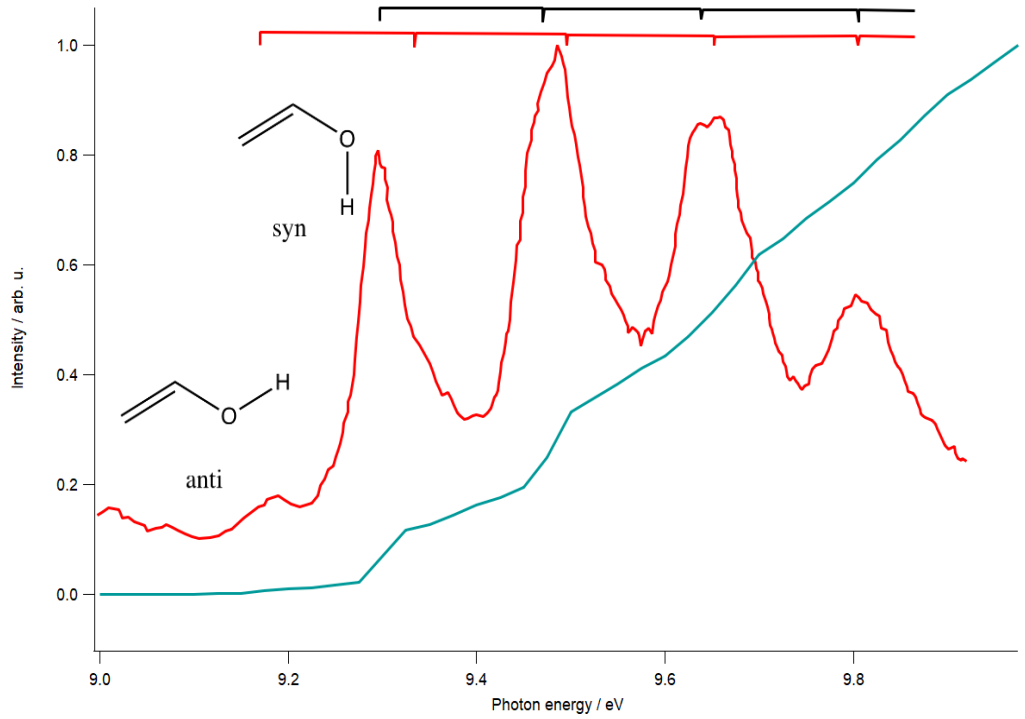
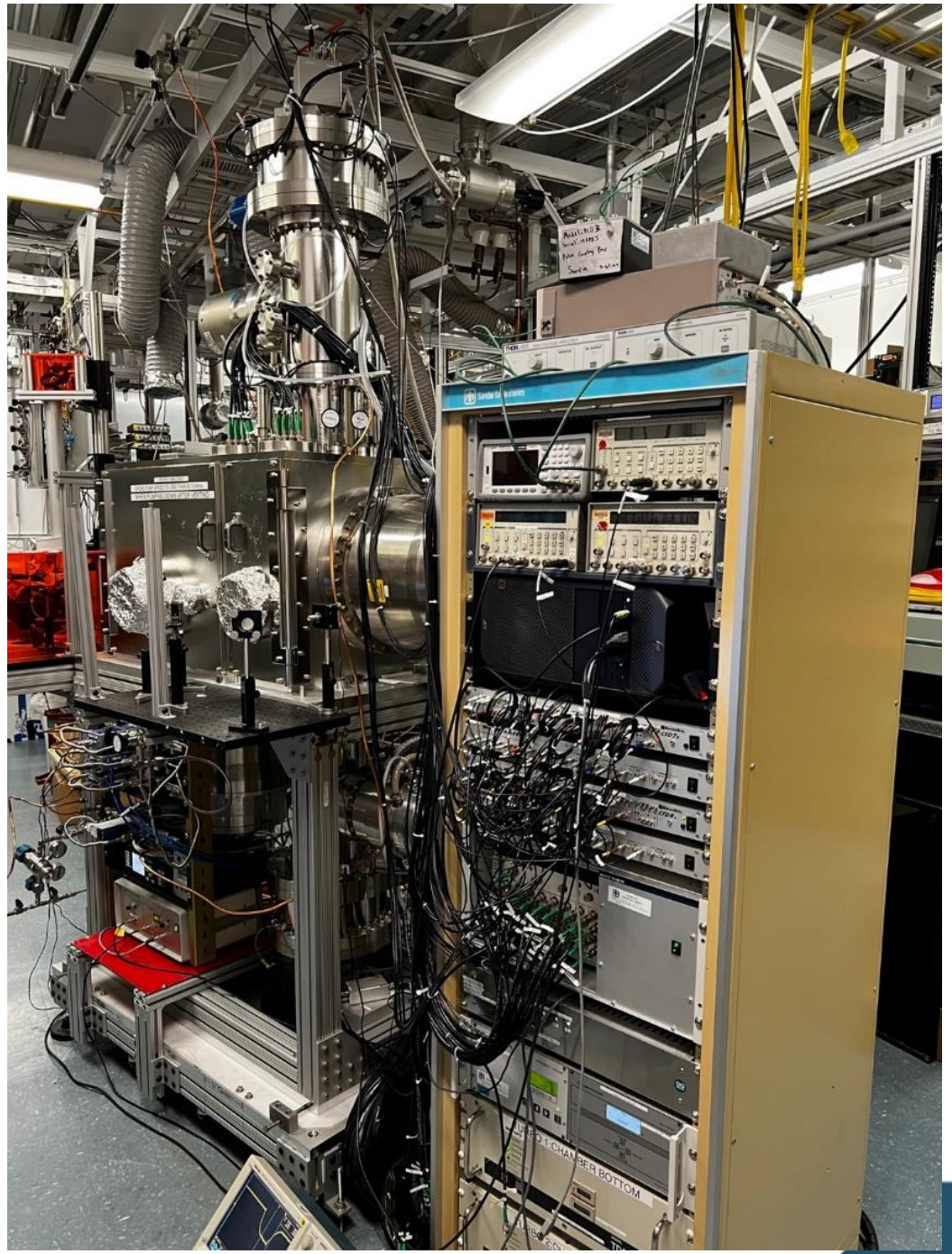
Design



PEPICO:

- Electrons and ions detected in coincidence
- TOF = $t_{ion} - t_{electron}$
- Mass resolved PES
- Electron and cation angular distributions
- Threshold and slow photoelectron spectra

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



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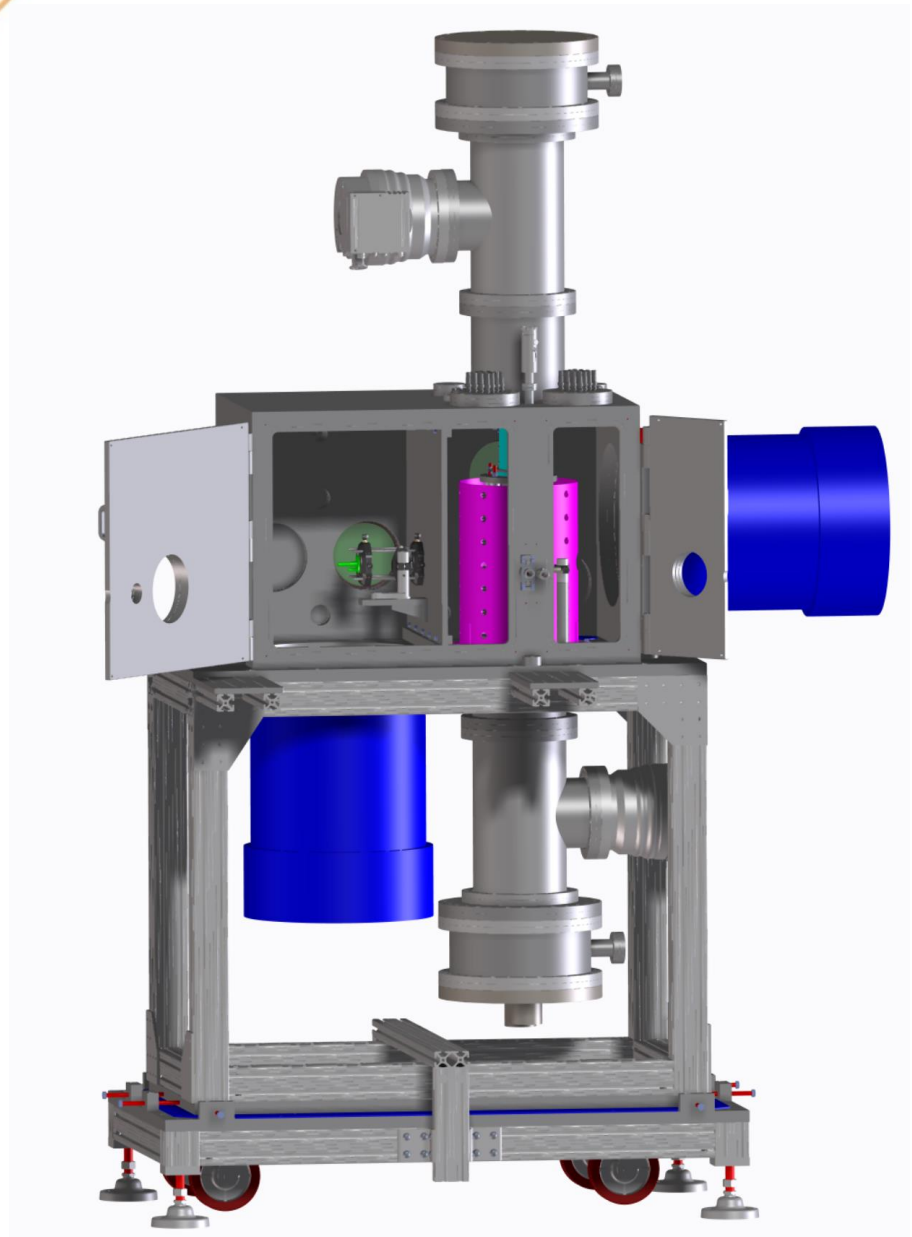

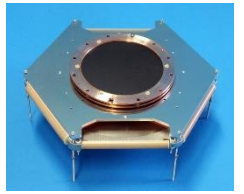

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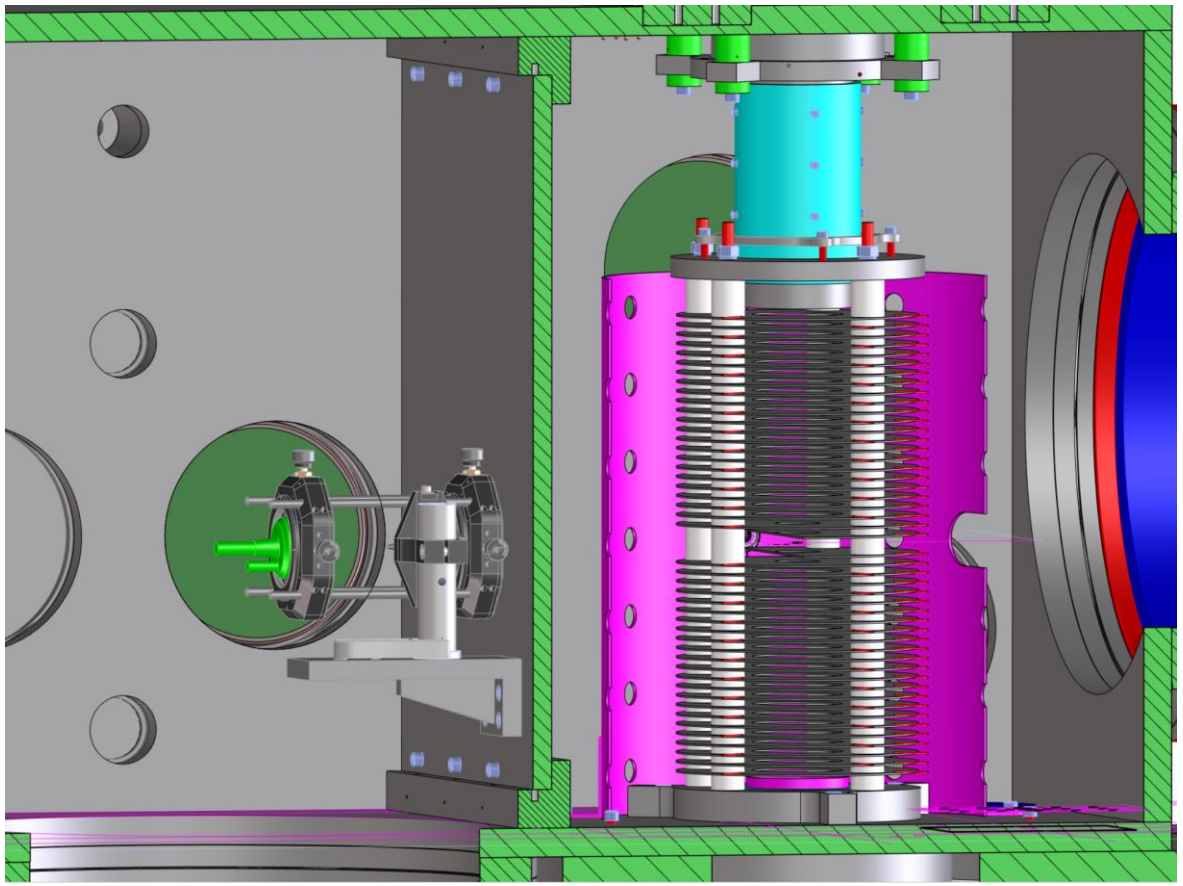

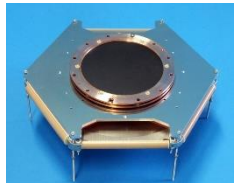

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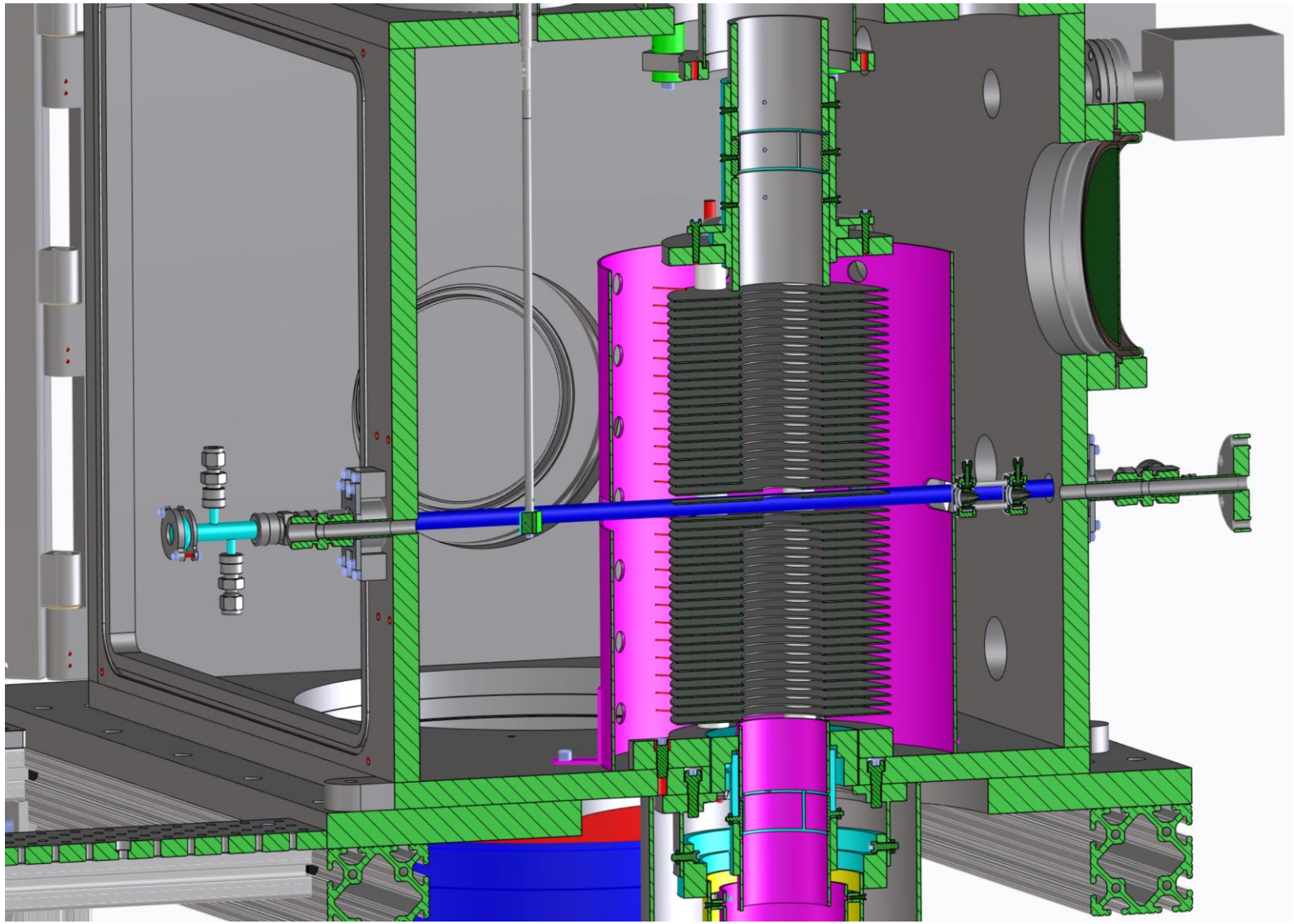
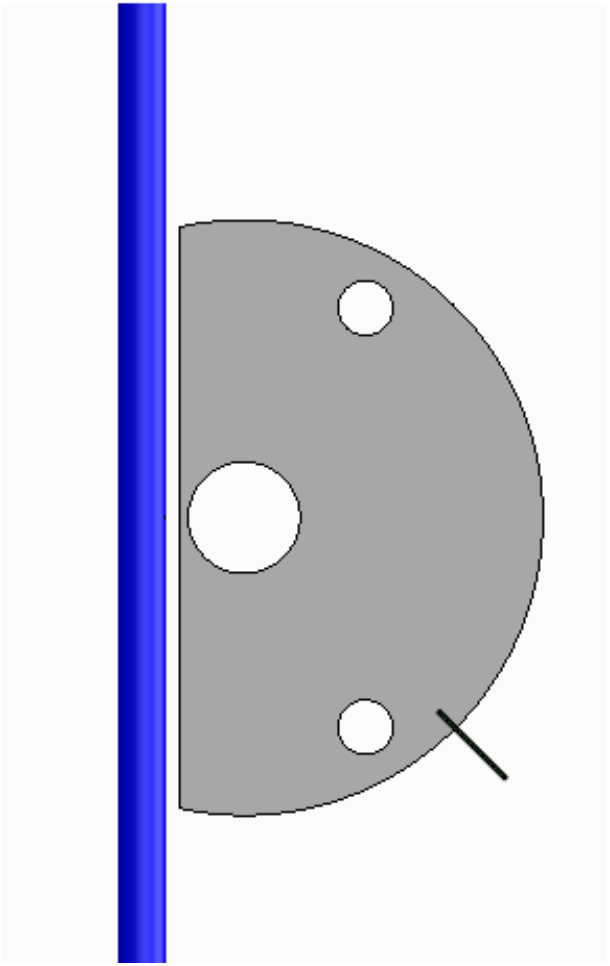
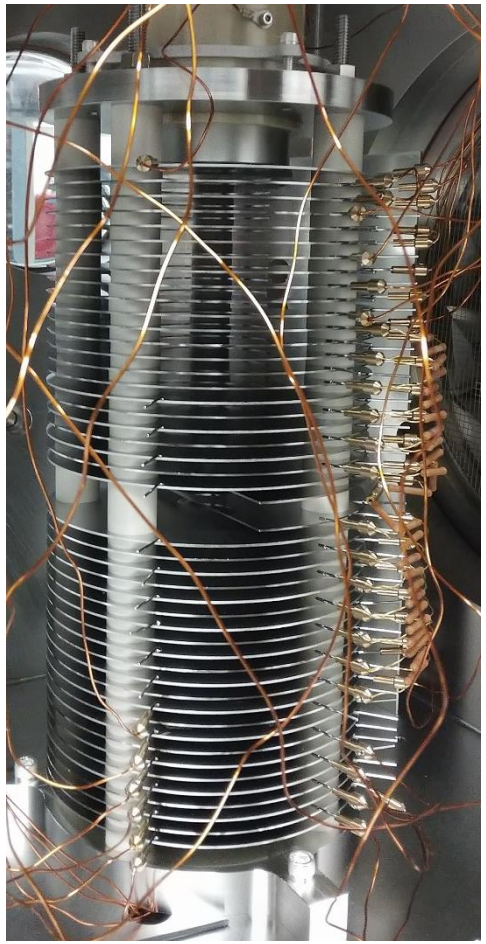
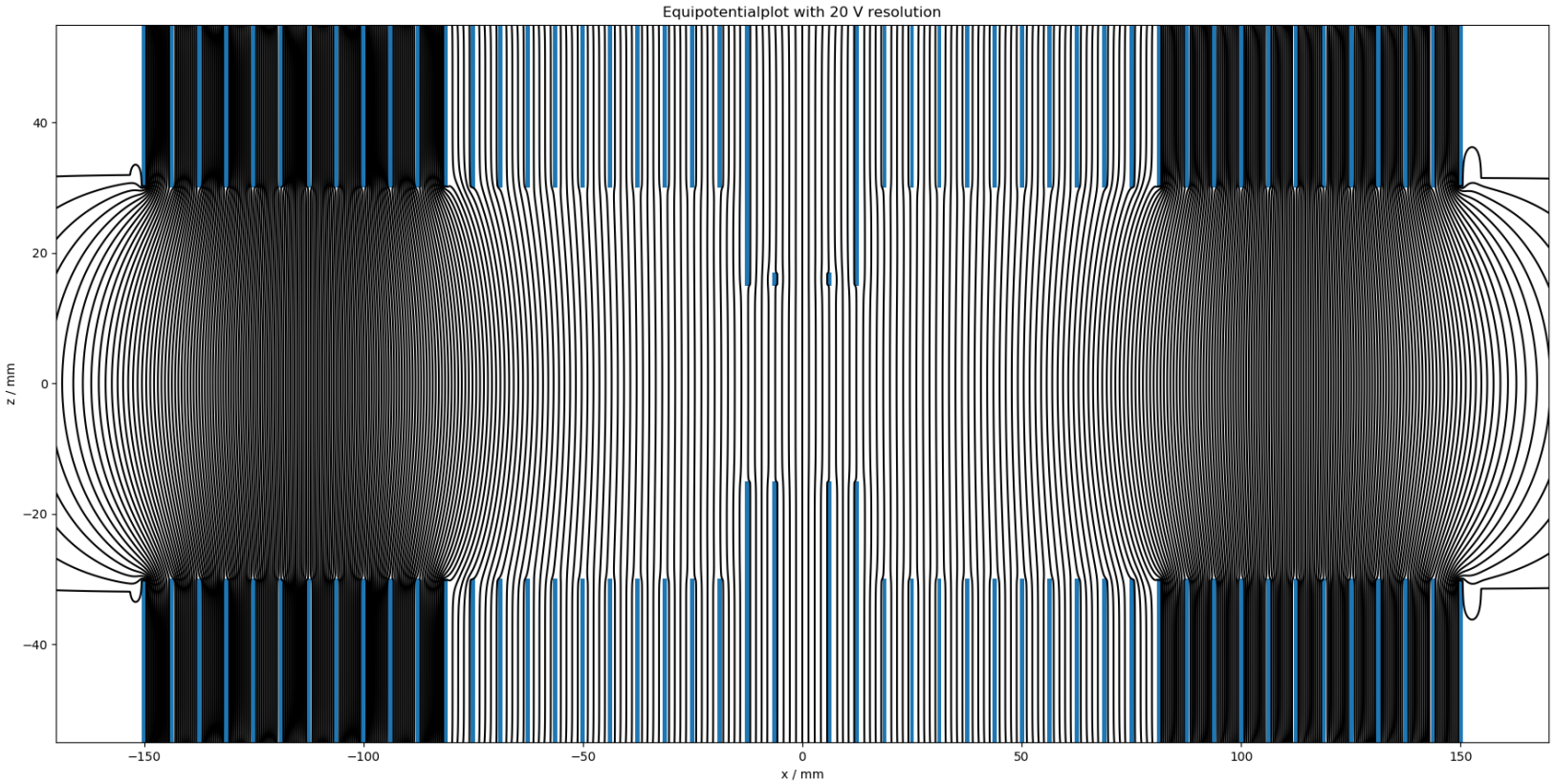




Ion Optics




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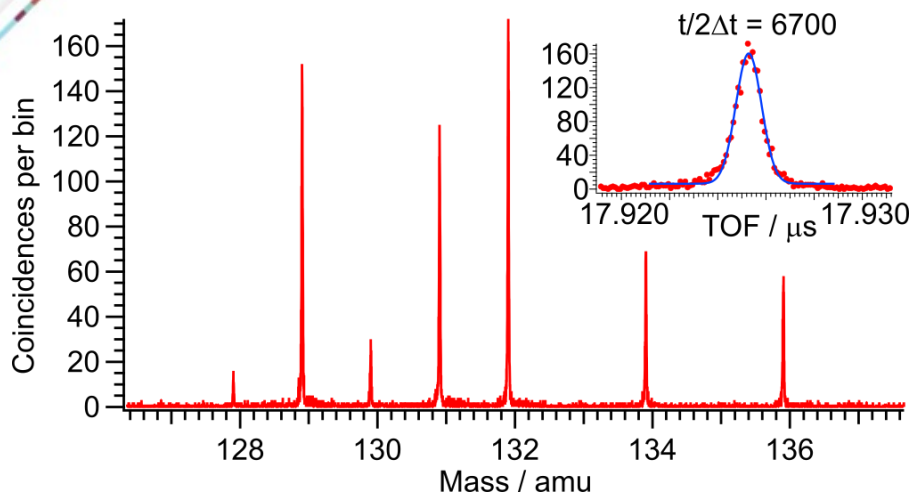
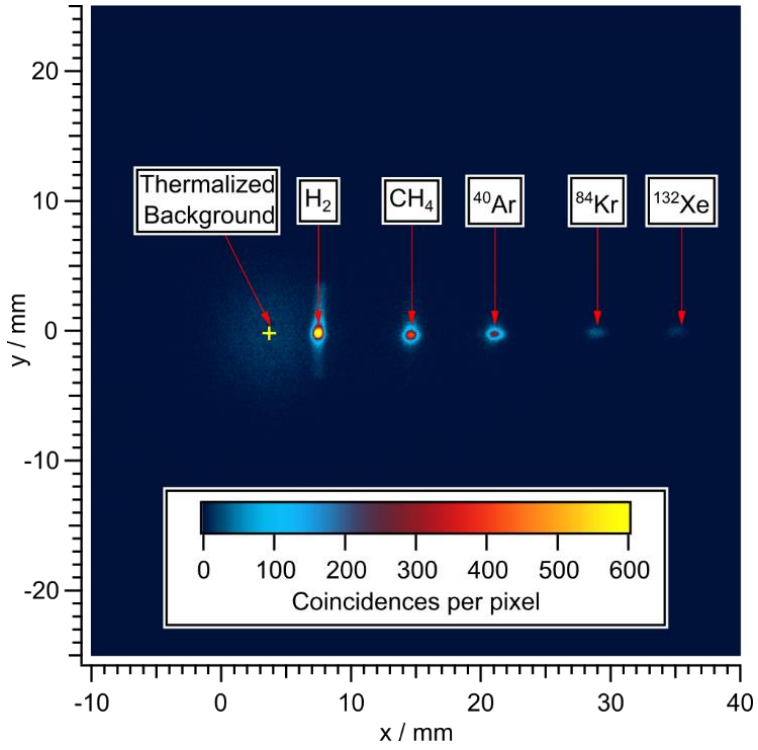
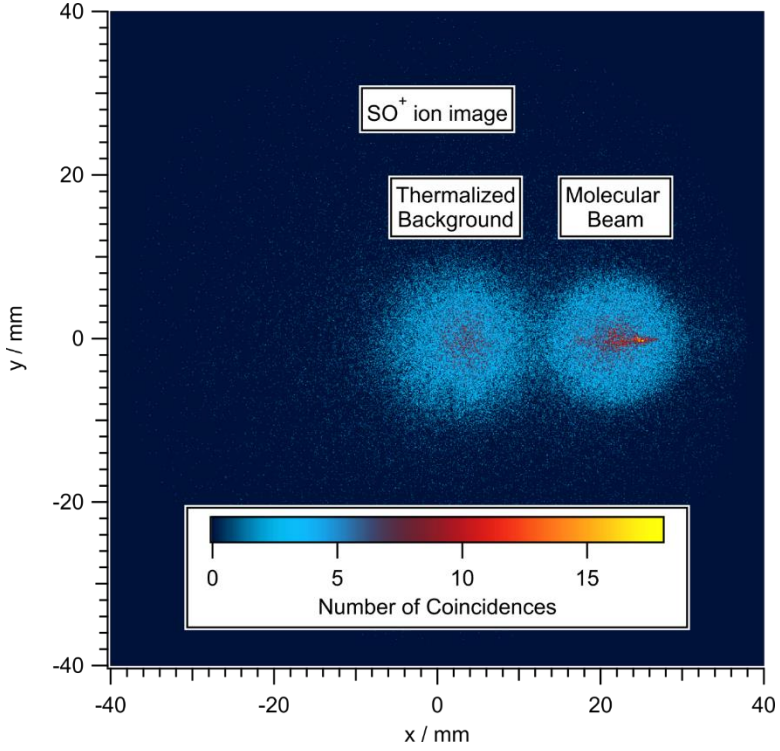
x / mm
40
20
0
−20
−40
−150
−100
−50
0
50
100
150

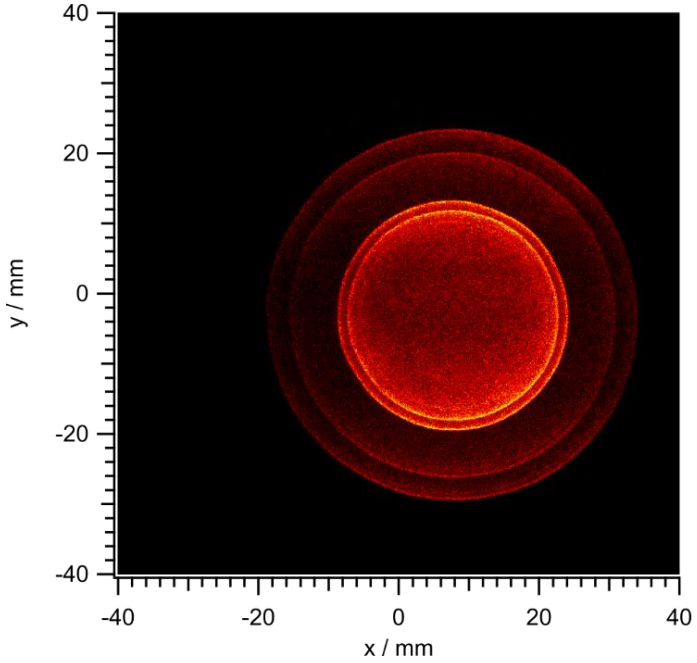
Performance

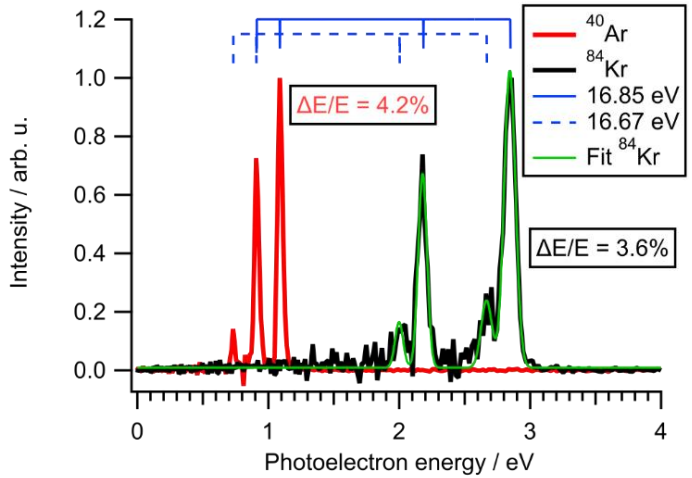




$$SO_2 \xrightarrow{h\nu} SO^+ + O$$





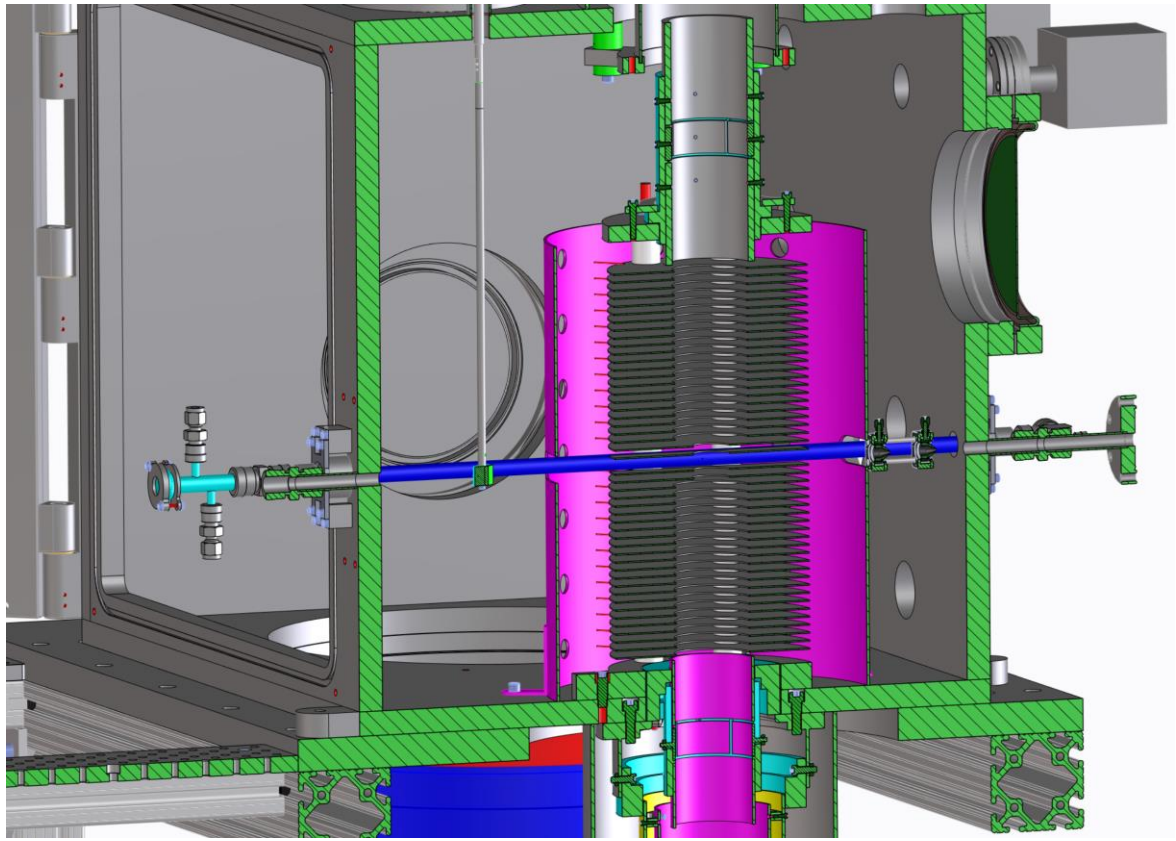


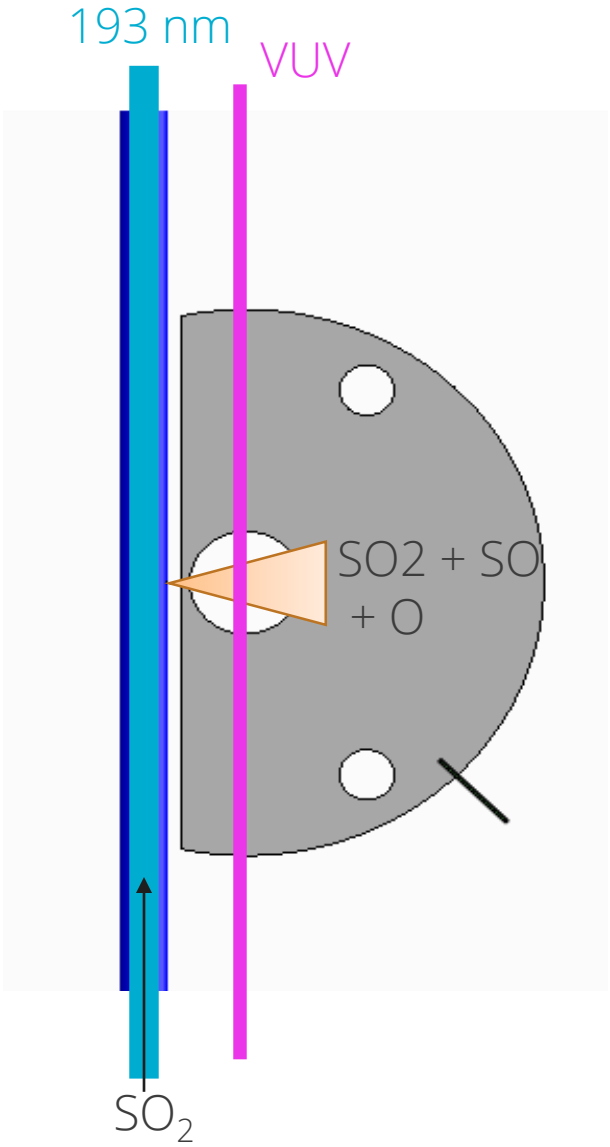
J. Phys. Chem. A 2022, 126, 1761

Performance – Time resolved experiments

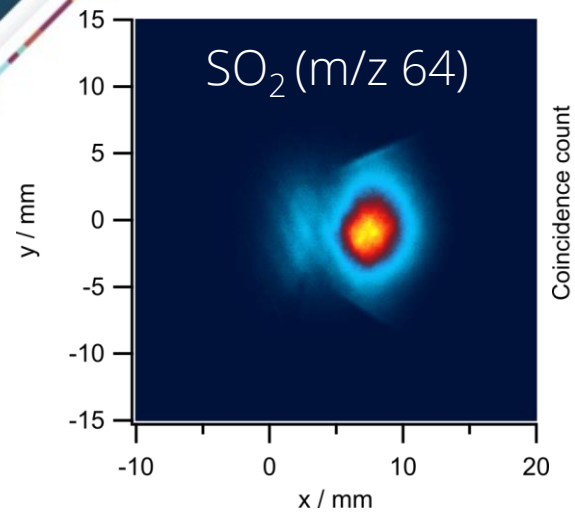
$SO_2 \xrightarrow{193\ nm} SO + O$

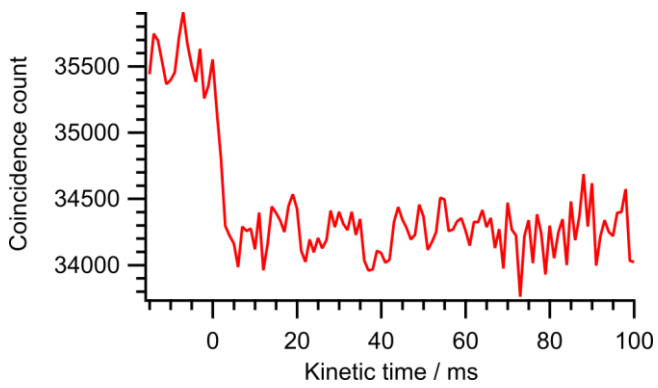
Excitation: $\tilde{C}(^1B_2) \leftarrow \tilde{X}(^1A_1)$
Products: $SO(\tilde{X}^3\Sigma^-) + O(^3P_j)$

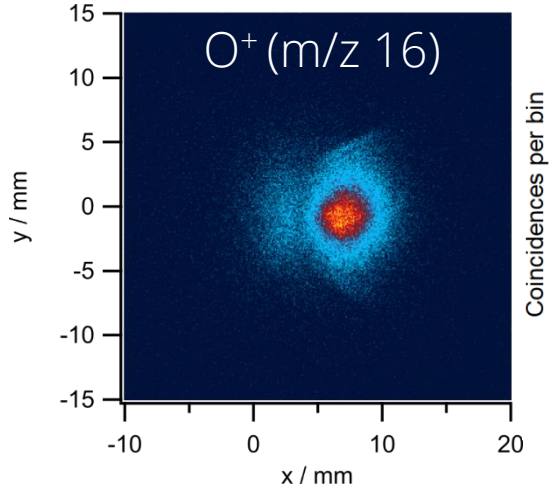


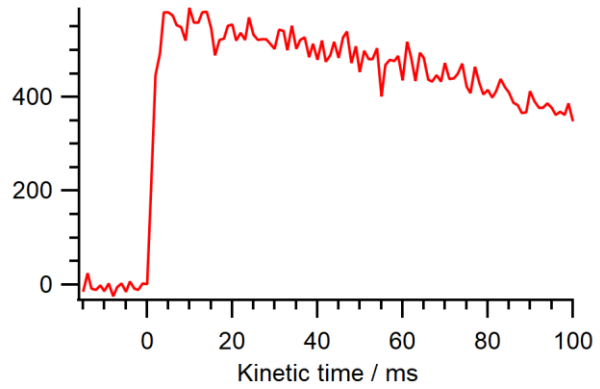


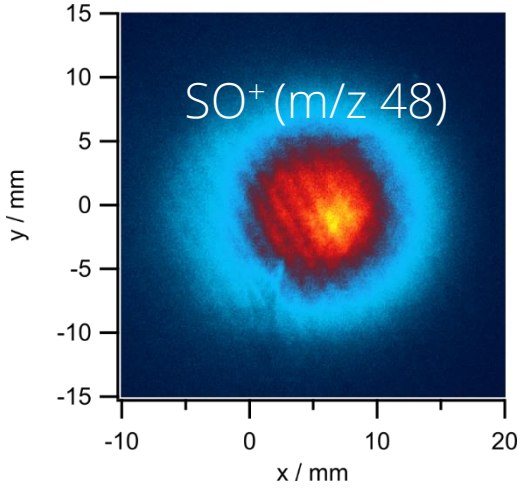
193 nm Dissociation of SO_2, VUV = 16.85 eV

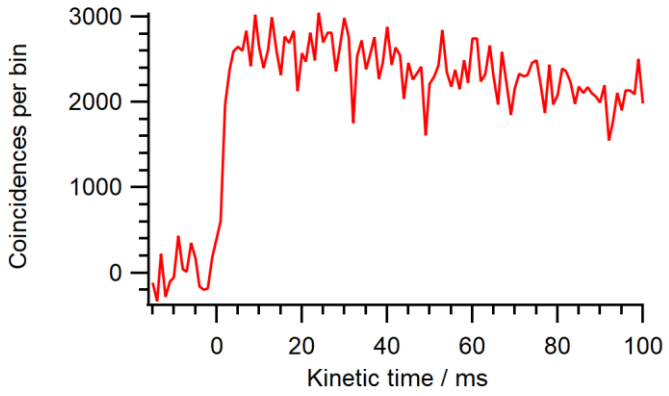


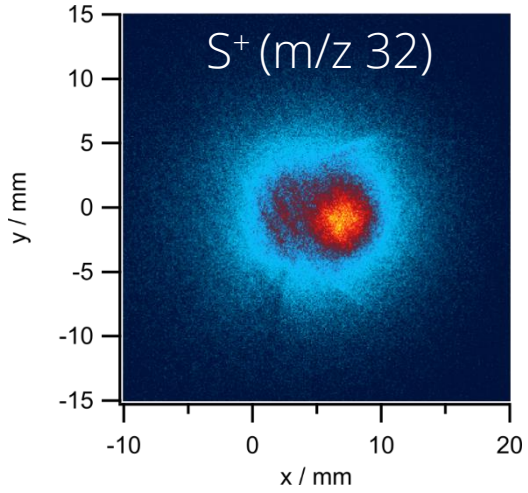


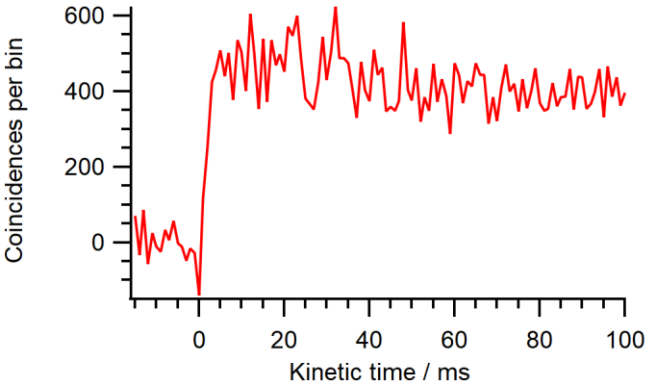




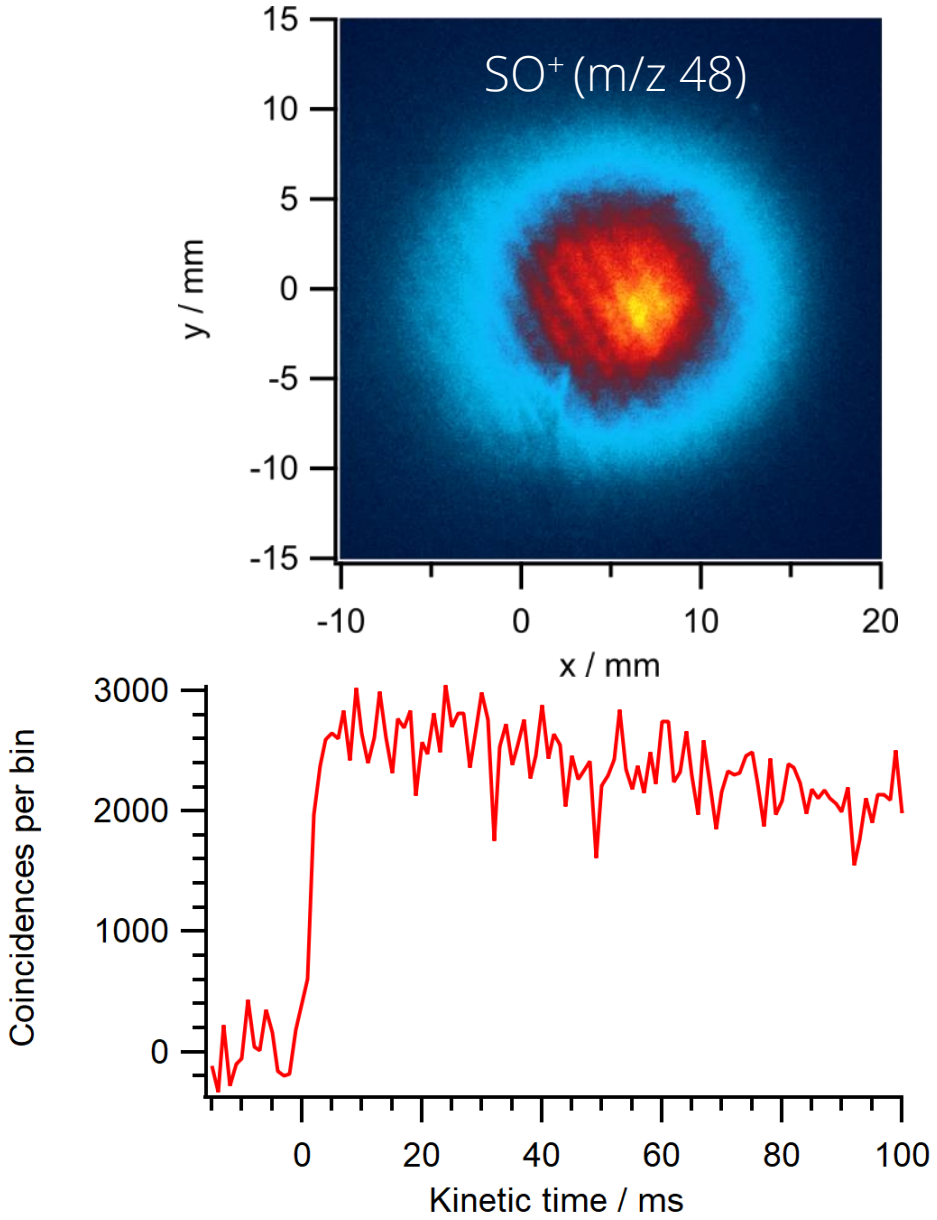






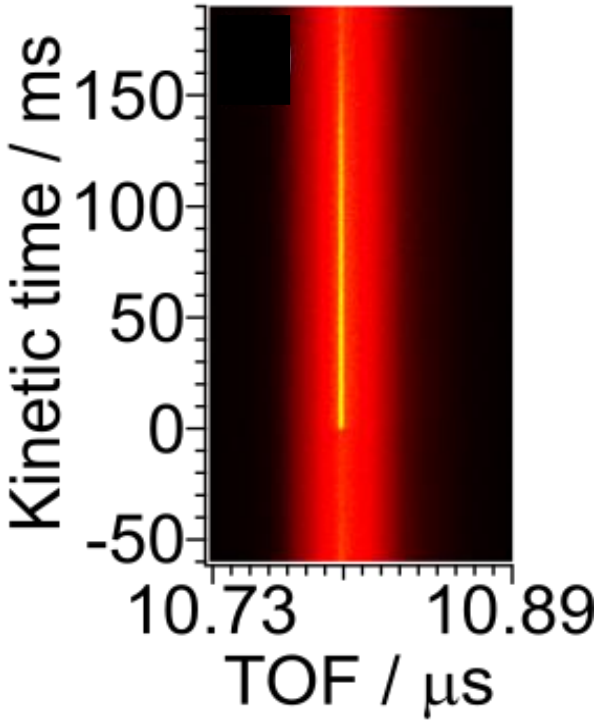


193 nm Dissociation of SO_2, VUV = 16.85 eV

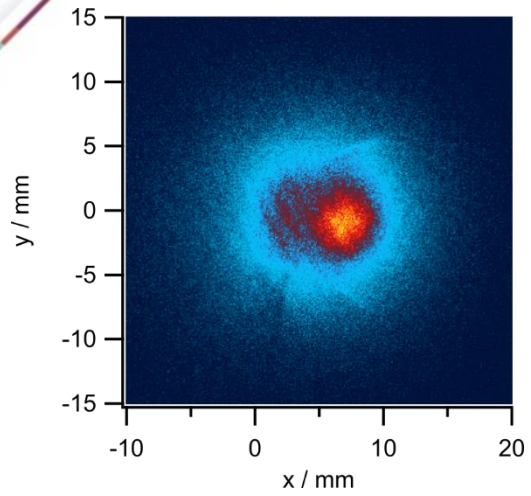


$$SO_2 \xrightarrow{h\nu} SO^+ + O$$

SO^+ appearance energy = 15.93 eV

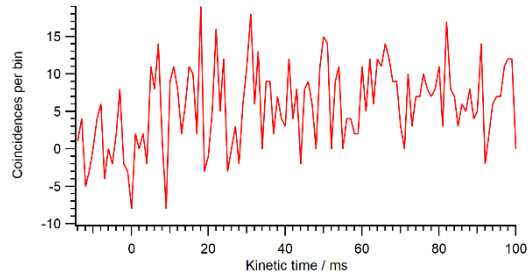


Performance – Time resolved experiments



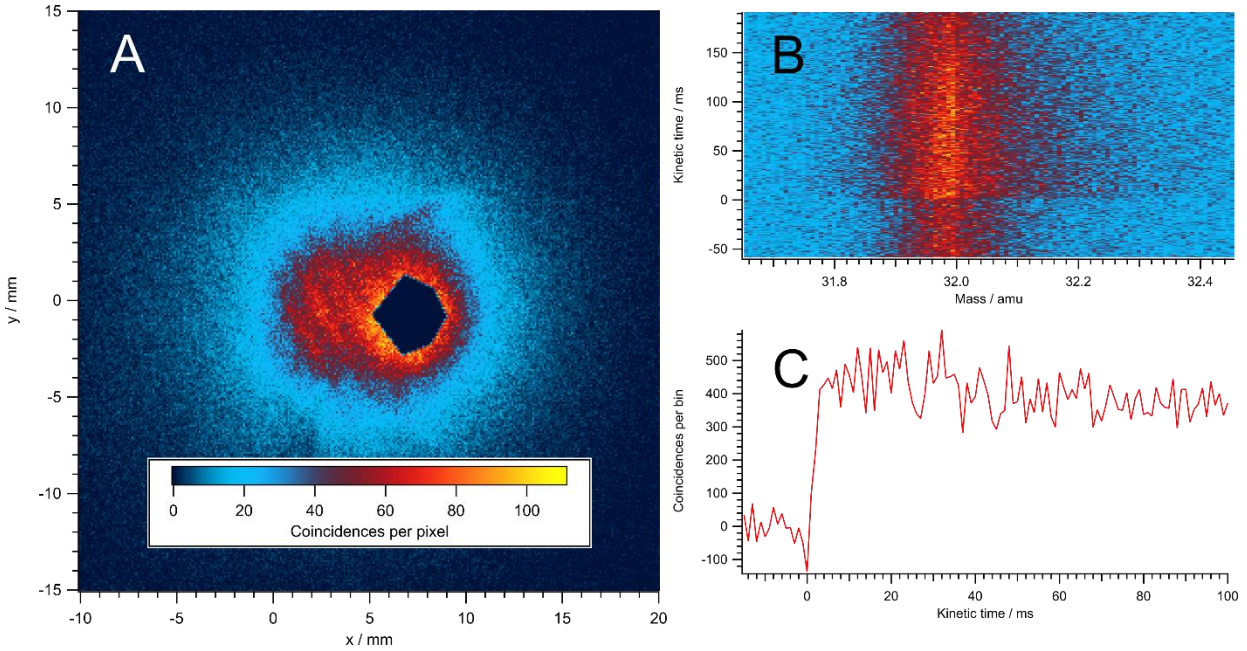
$SO \xrightarrow{h\nu} S^+ + O$

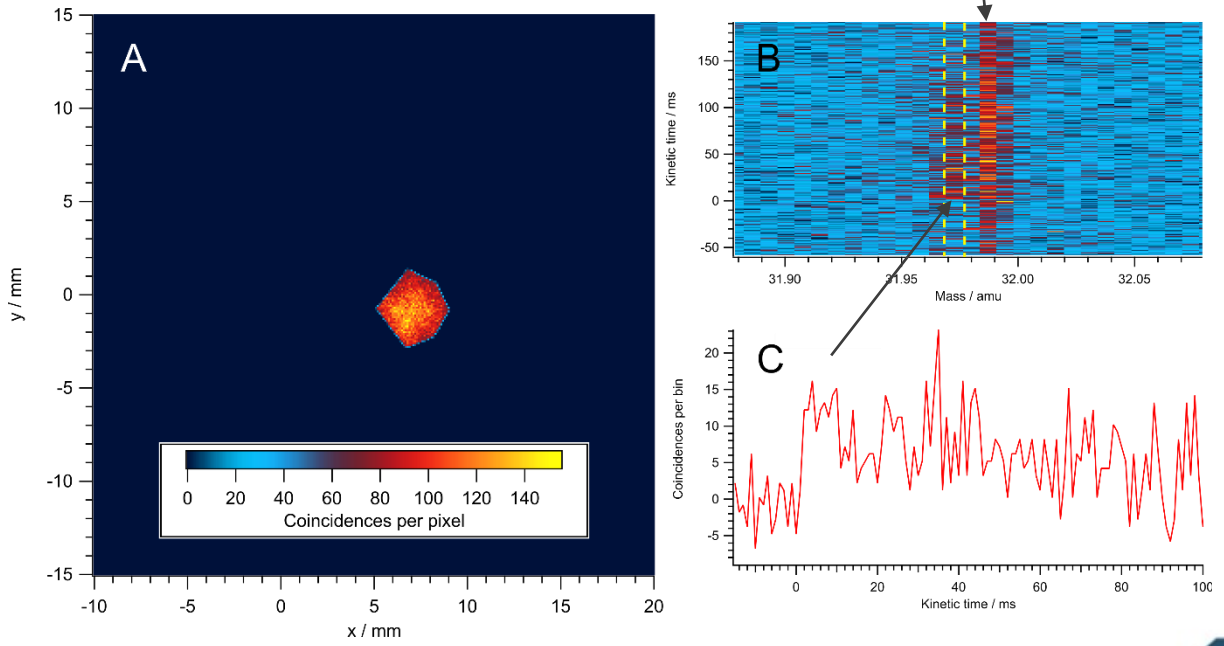
S^+ (m/z 32) appearance energy = 15.74 eV



m/z(^{32}S) = 31.972

m/z($^{16}O_2$) =31.989)

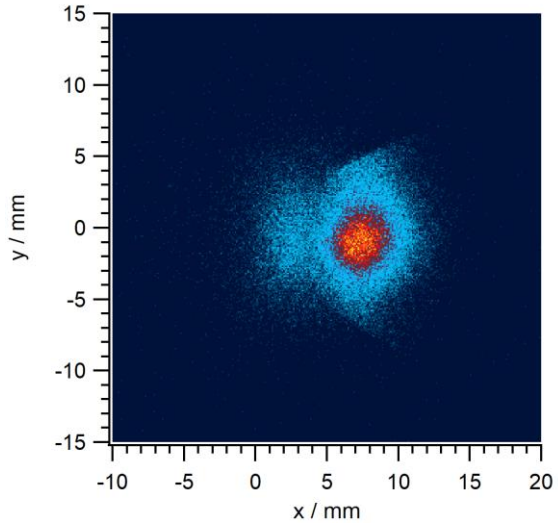


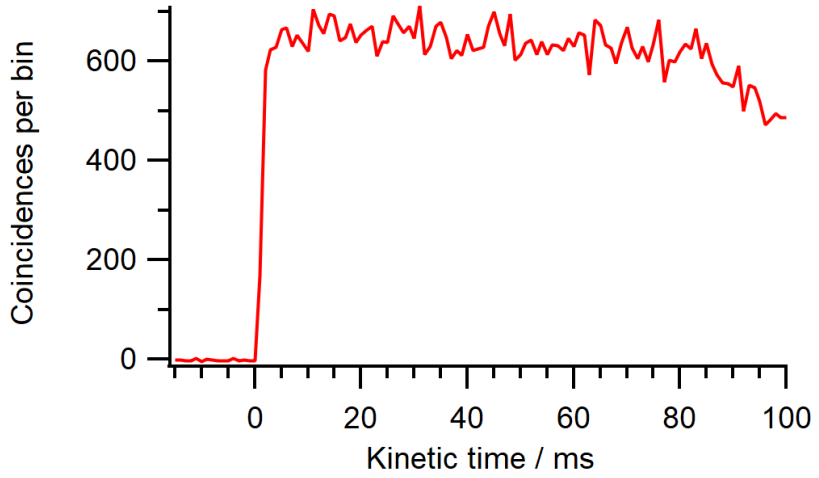


Performance – Time resolved experiments

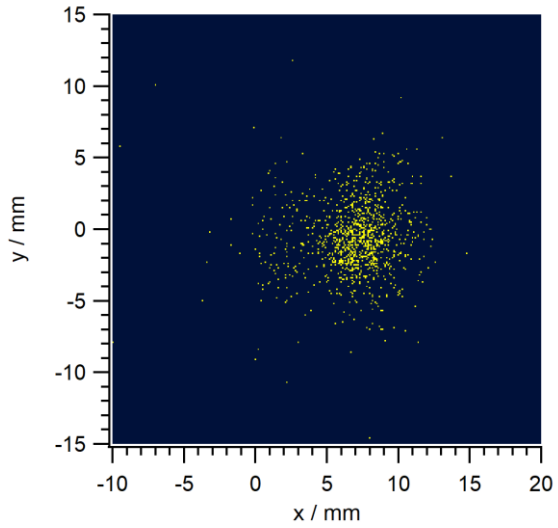
193 nm Dissociation of SO_2, using Ar-I VUV (11.62 & 11.83 eV)

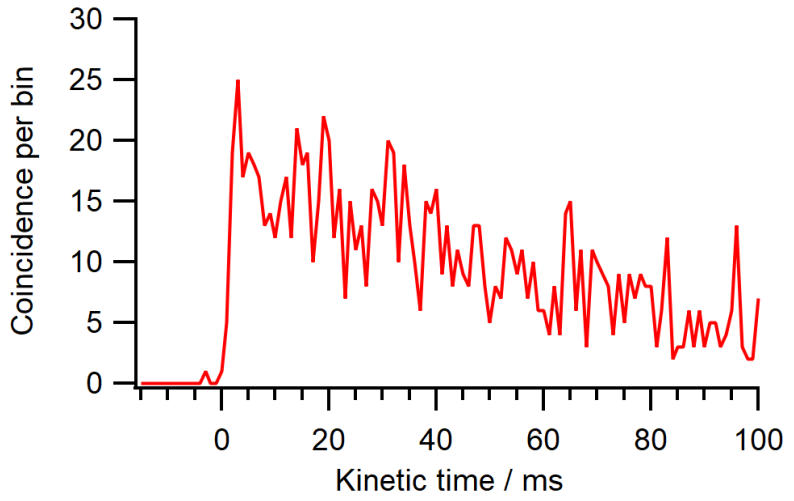
SO^+ (m/z 48)





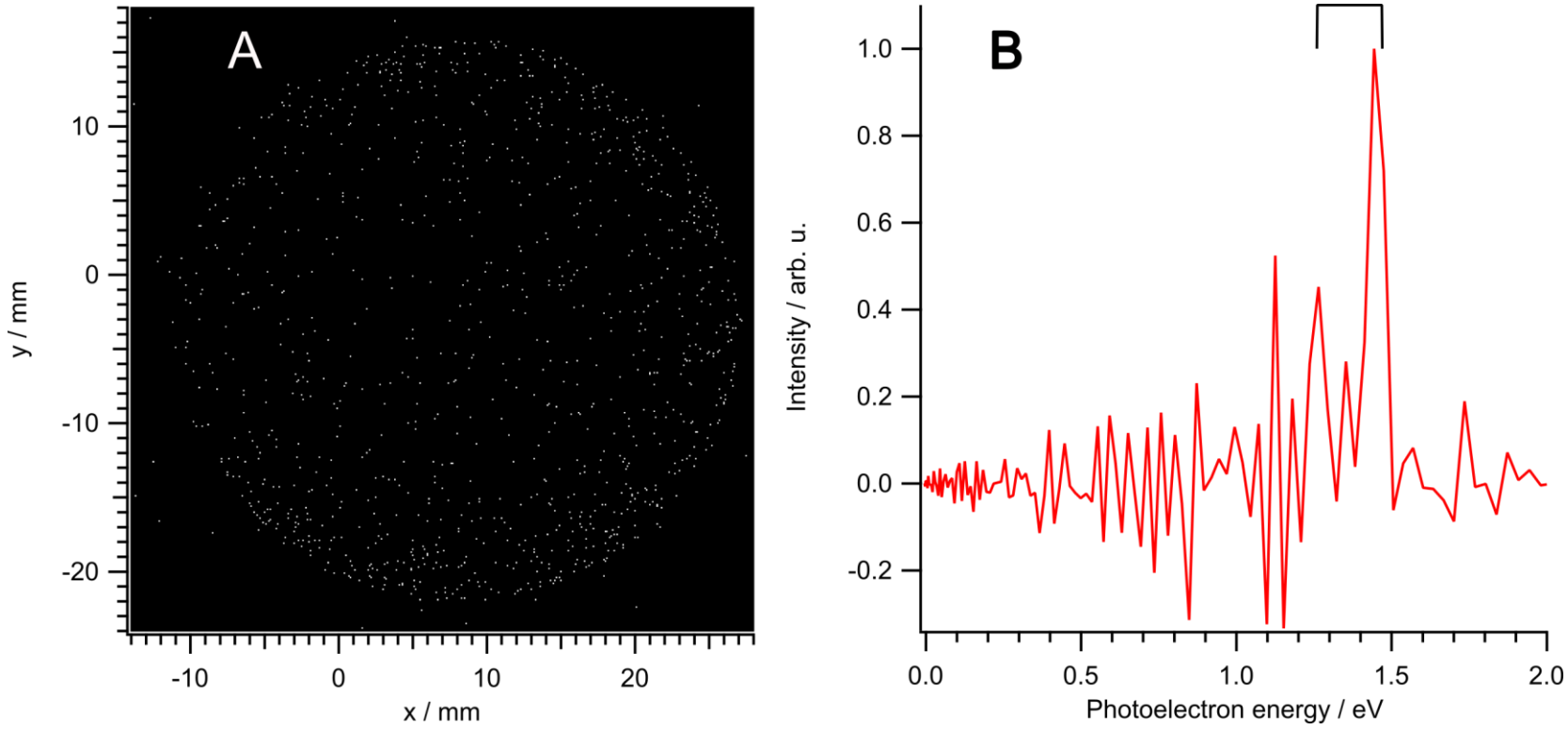
(m/z 32)





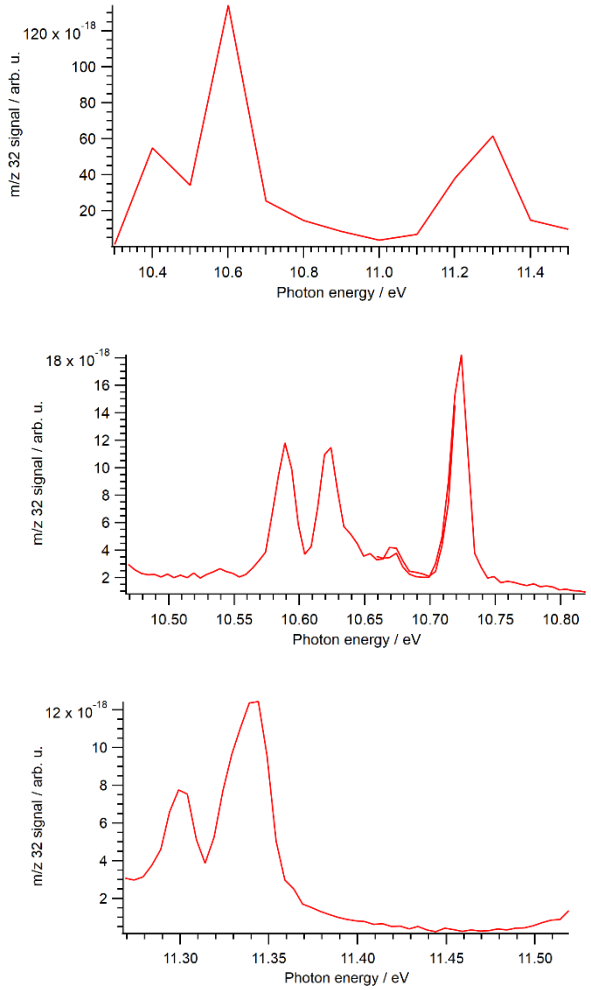
Performance – Time resolved experiments

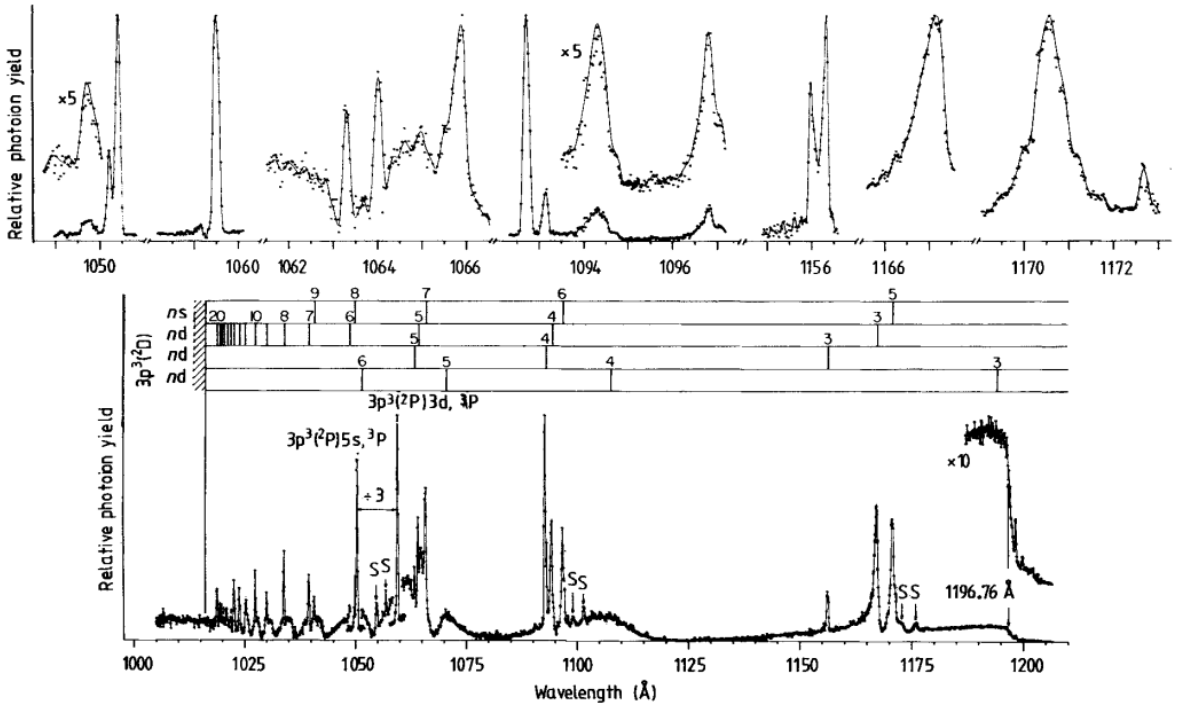
193 nm Dissociation of SO_2, using Ar-I VUV (11.62 & 11.83 eV)



SO_2 193 nm Dissociation with tunable VUV

Photoionization spectra of m/z 31.972 amu from SO_2 + 193 nm



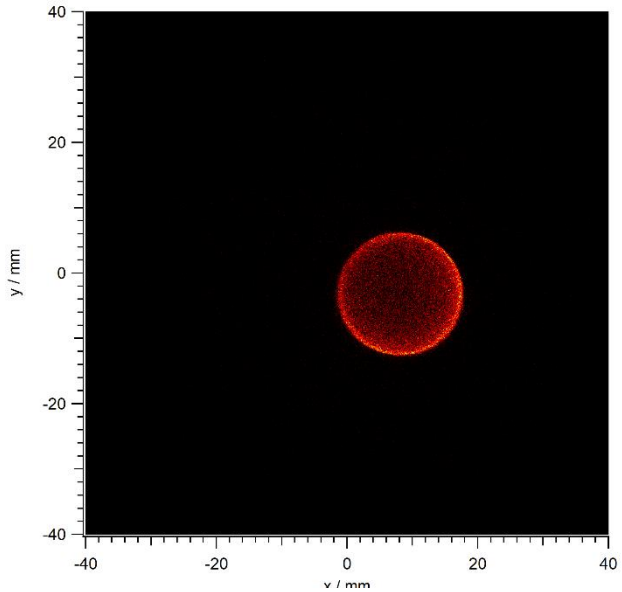


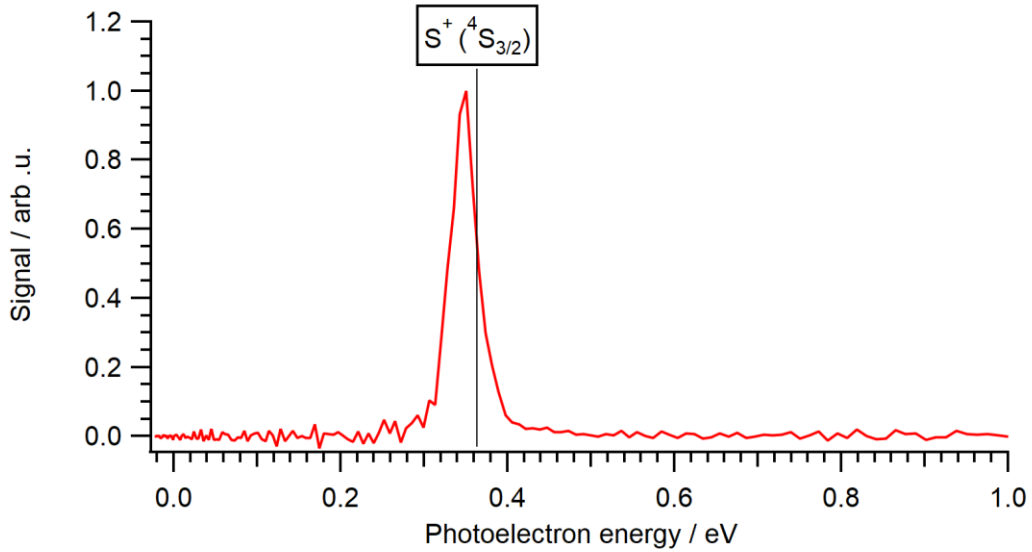
(Gibson & Berkowitz, J. Phys. B 19, 2825 (1986))

SO_2 193 nm Dissociation with tunable VUV

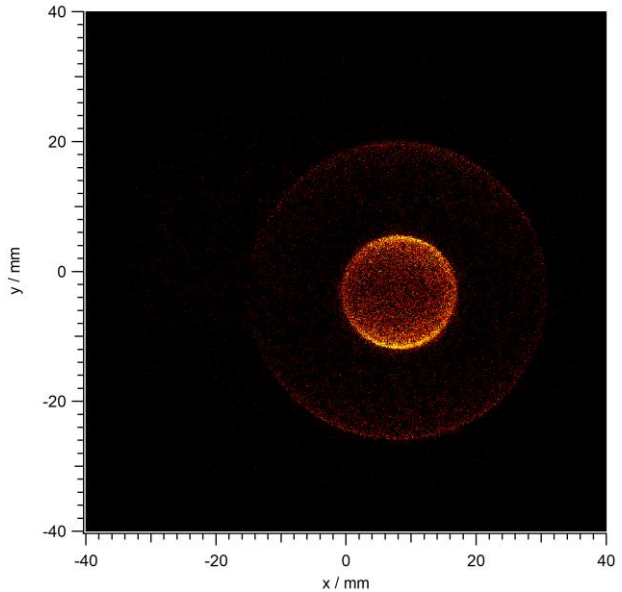
Photoelectron spectra of m/z 31.972 amu from SO_2 + 193 nm @ 10.742 eV

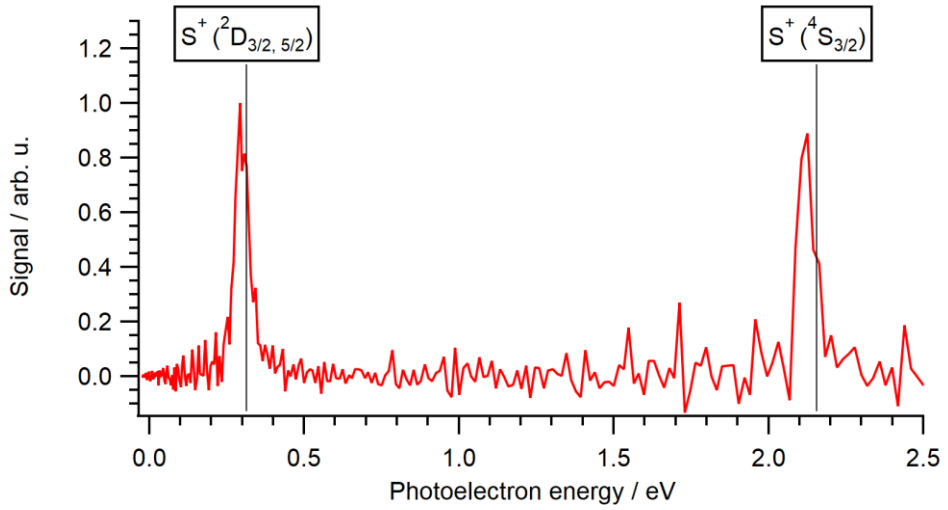
10.742 eV





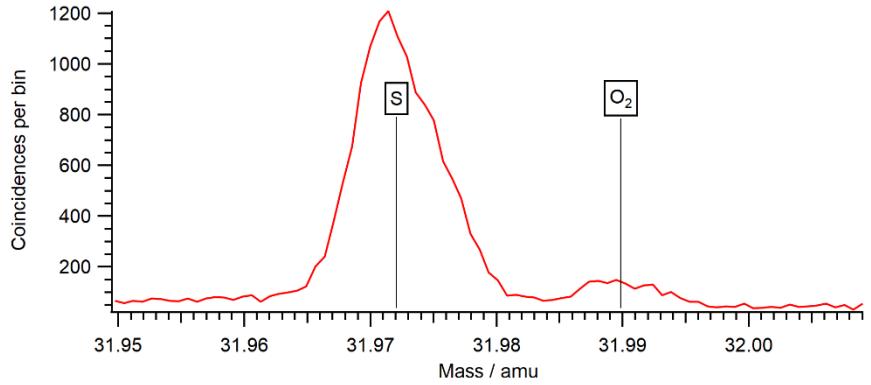
12.516 eV



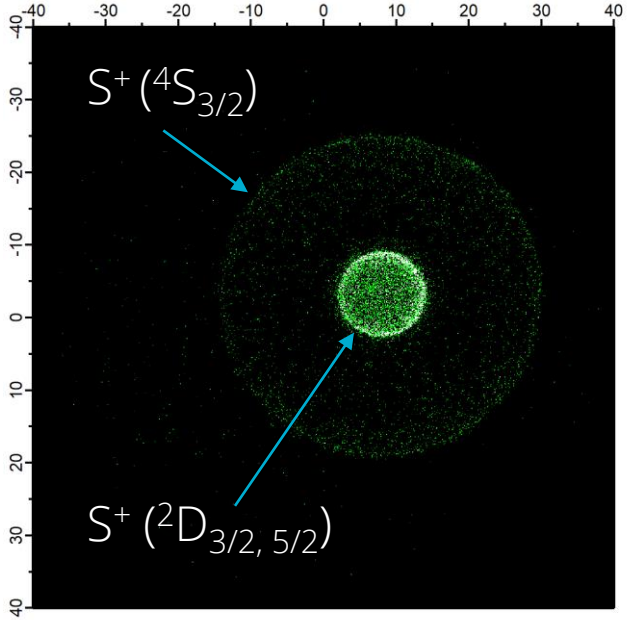


SO_2 193 nm Dissociation with tunable VUV

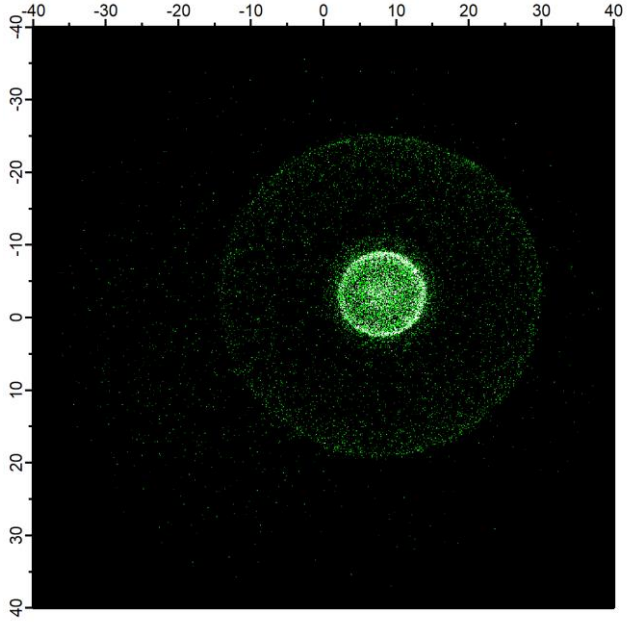
SO_2 + 193 nm @ 12.344 eV



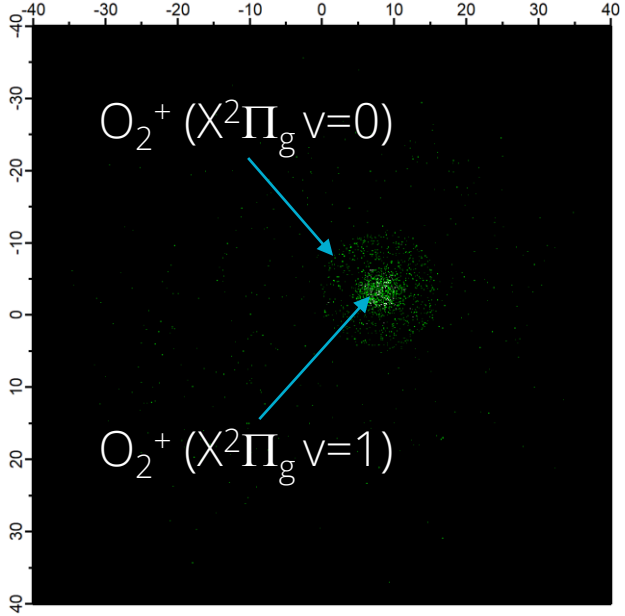
31.964-31.981 amu



31.950-32.009 amu

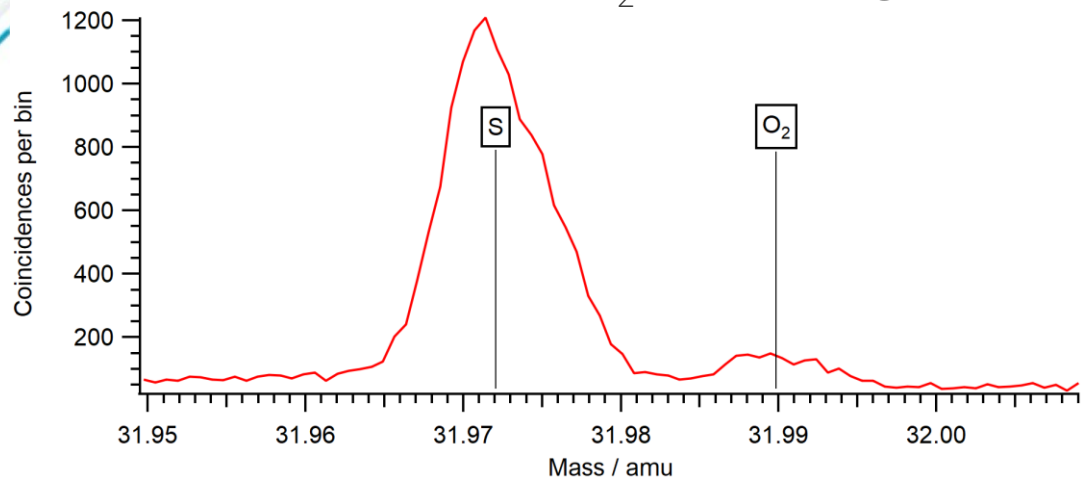


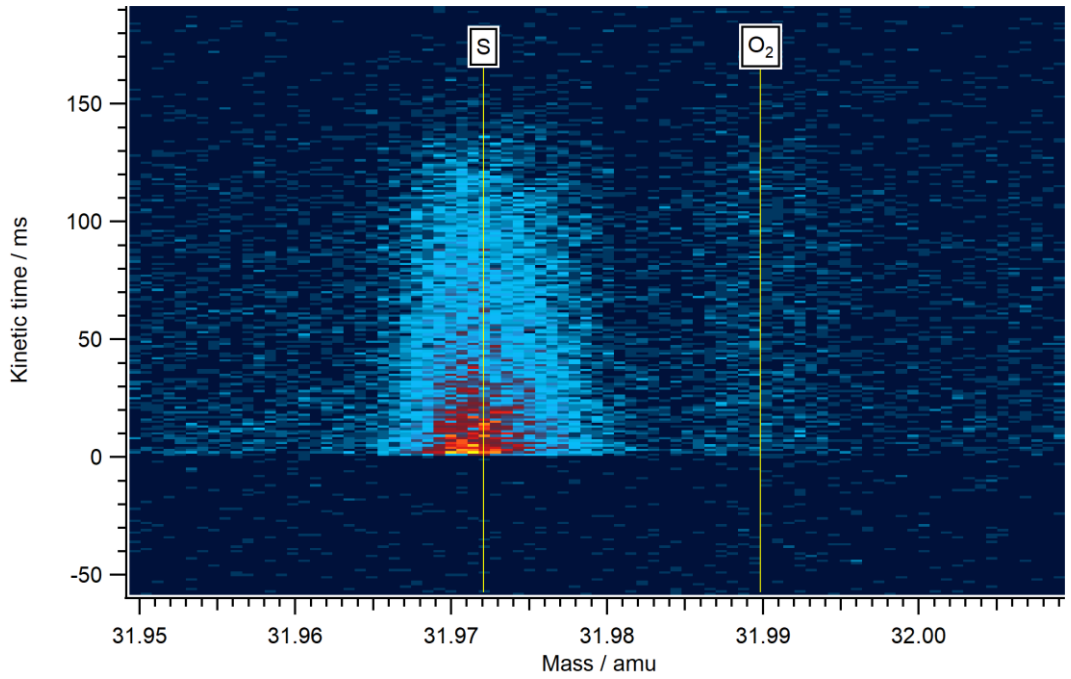
31.984-31.997 amu

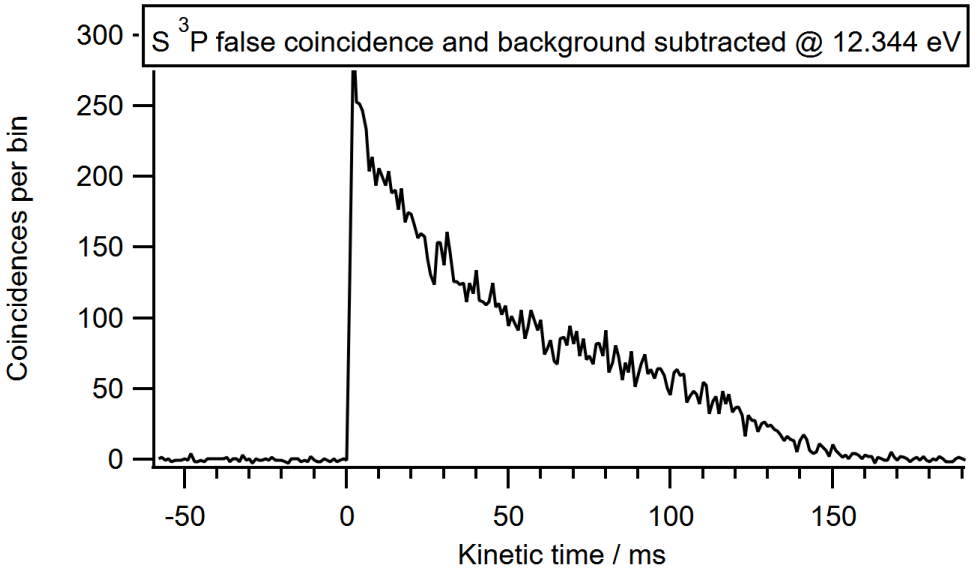


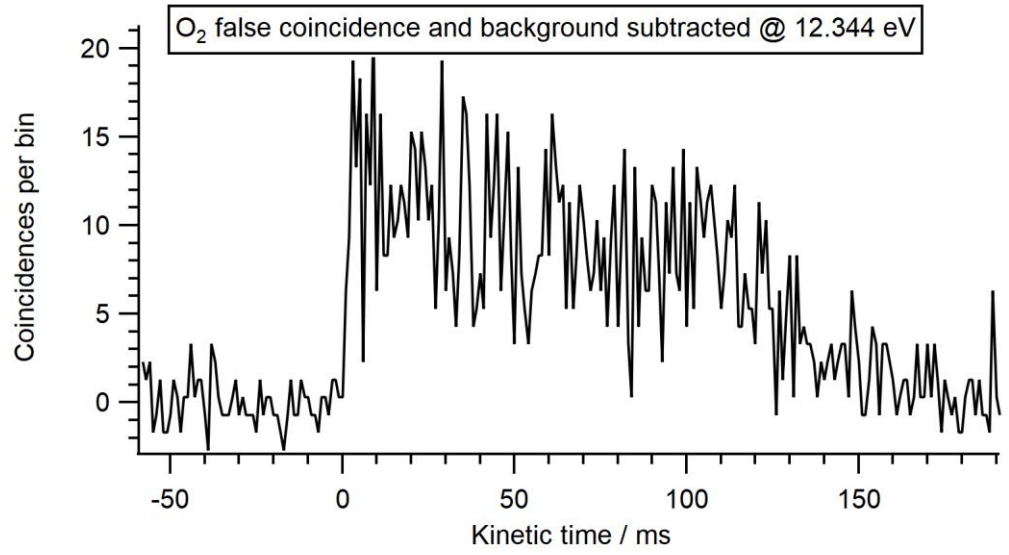
SO_2 193 nm Dissociation with tunable VUV

SO_2 + 193 nm @ 12.344 eV



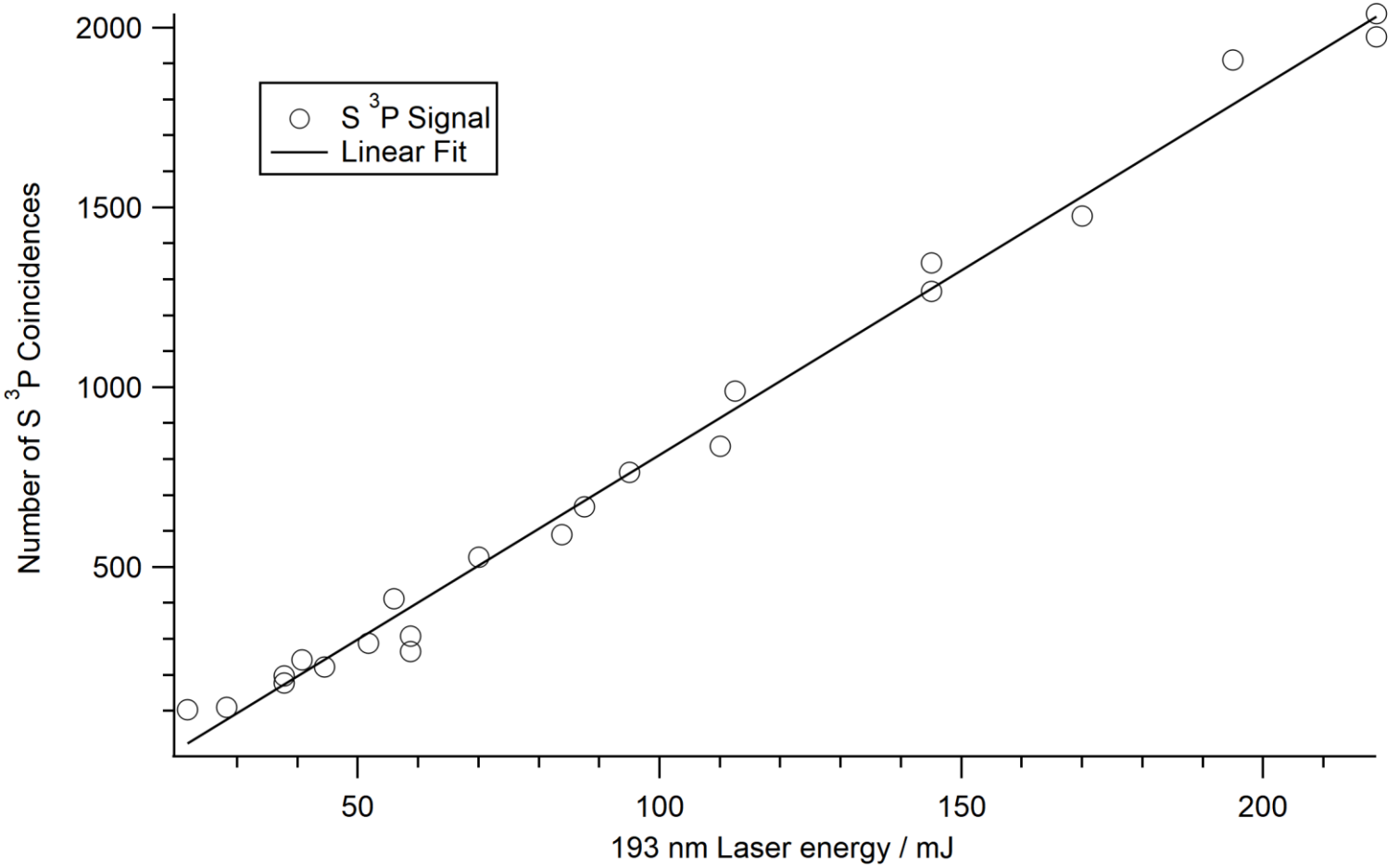






SO_2 193 nm Dissociation with tunable VUV

SO_2 + 193 nm Laser Power dependence

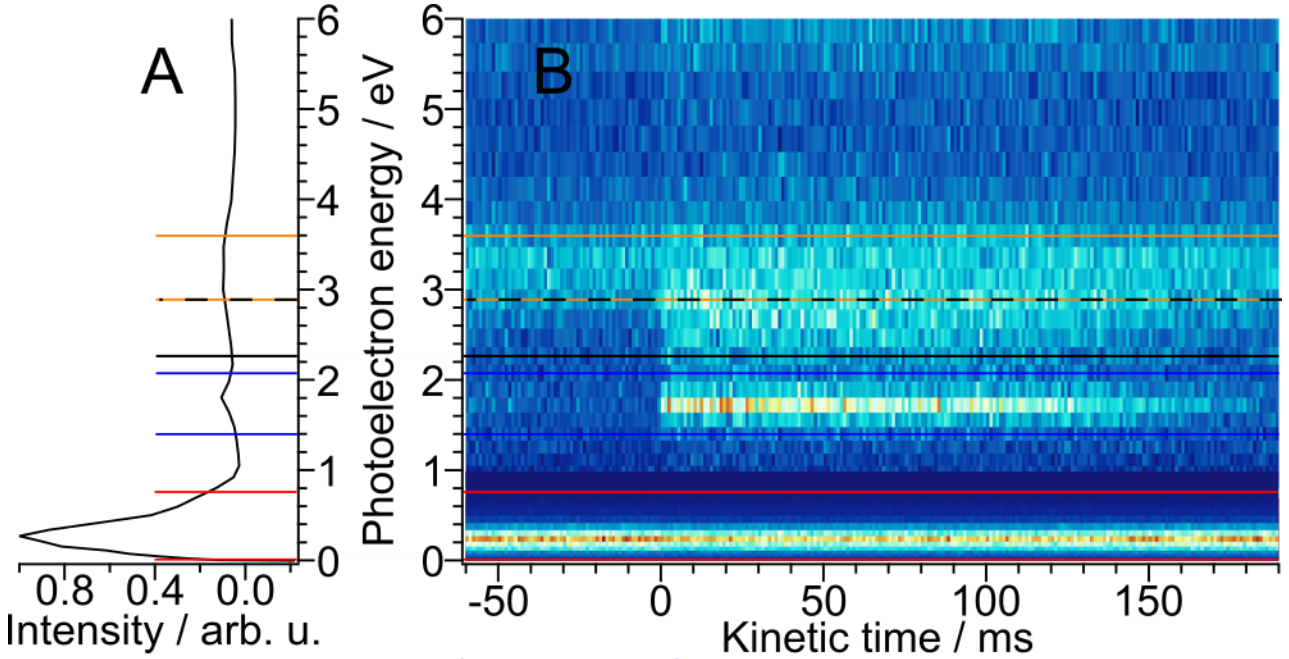


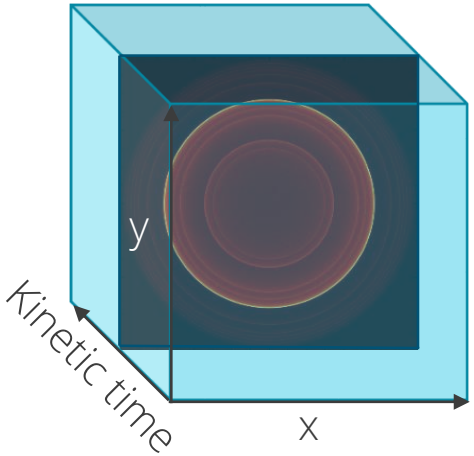
Conclusion

- We build a new high-resolution PEPICO for kinetics experiments
  - m/z > 10000 with Synchrotron radiation and > 6700 for discharge lamp
  - Photoelectron energy resolution dE/E ~ 4%
  - Powerful software allows for Coincidence filtering and analysis during data acquisition
- We tested the time-resolved performance by studying 193 nm dissociation of SO_2
  - We find a small yield of S + O_2 products that have not been previously observed

Thank you for your attention!

Time resolved Photoelectron spectra

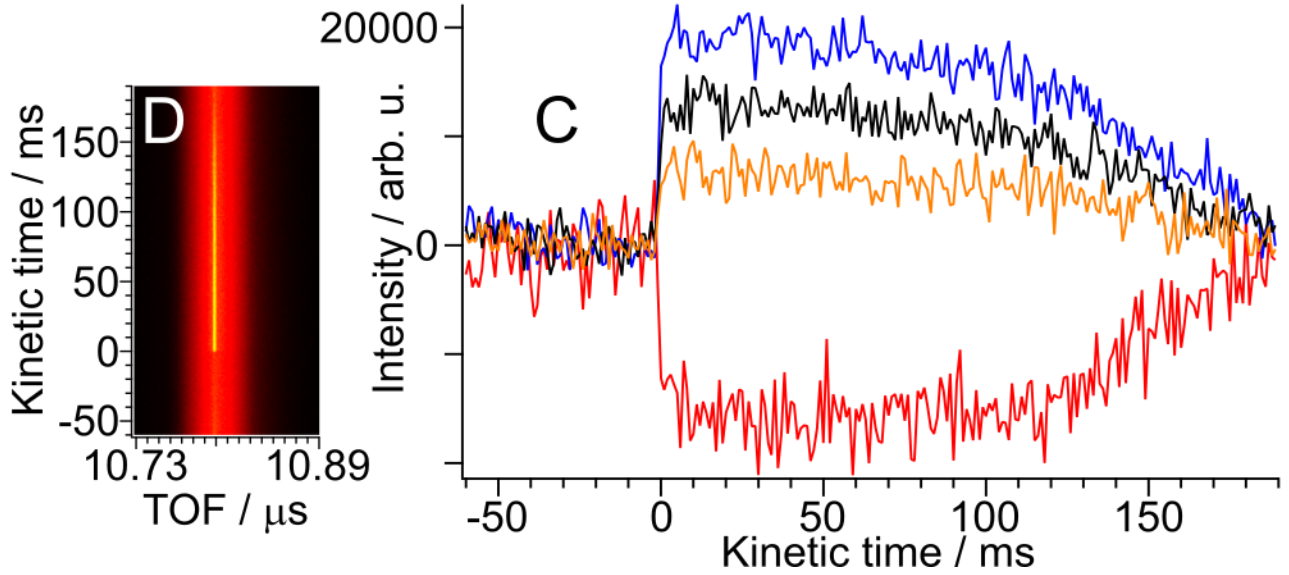




m/z 48 (SO)

$SO_2 \xrightarrow{h\nu} SO^+ + O$

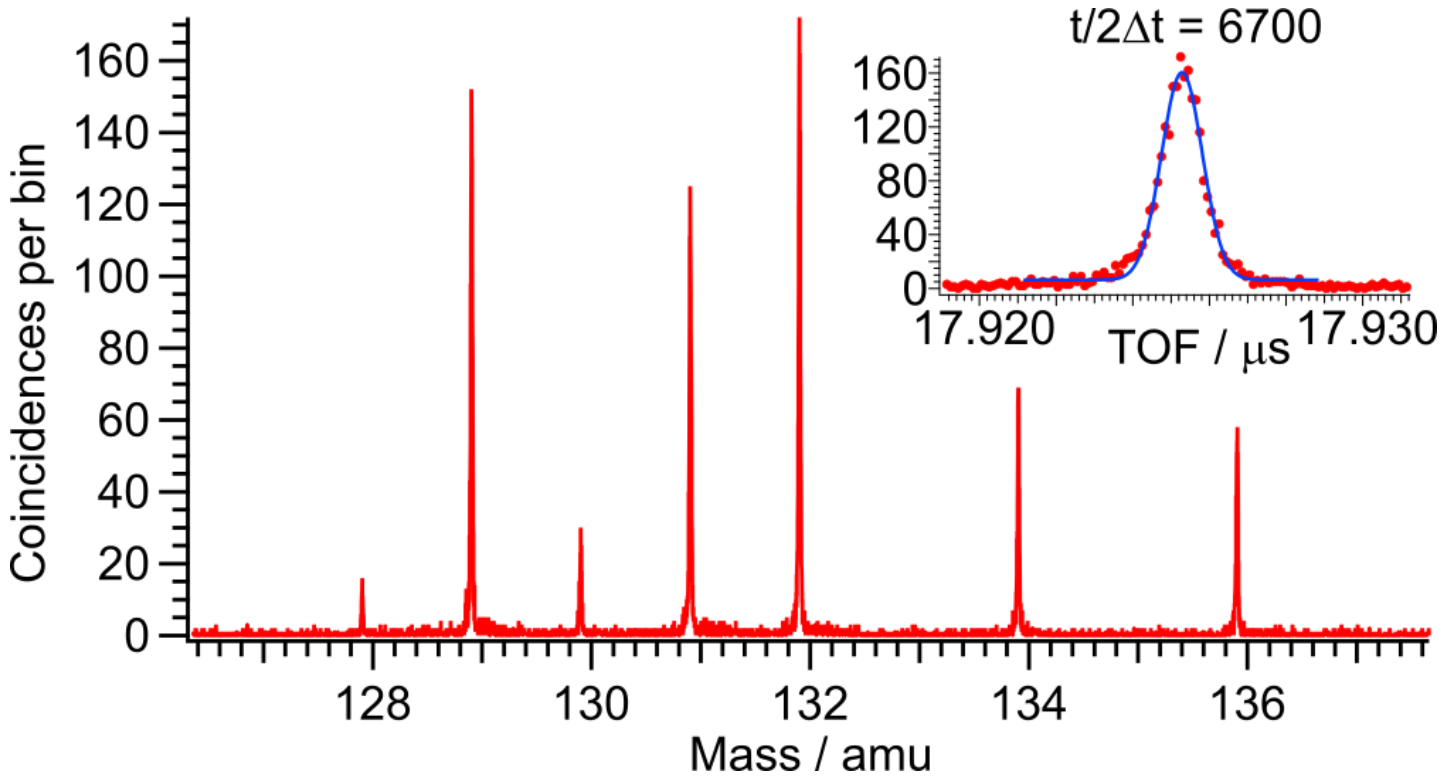
$SO \xrightarrow{h\nu} SO^+$



Performance – Molecular Beam Operation

10% H_2, 1% CH_4, 0.5% Ar, 0.5% Kr, 0.1% Xe in He

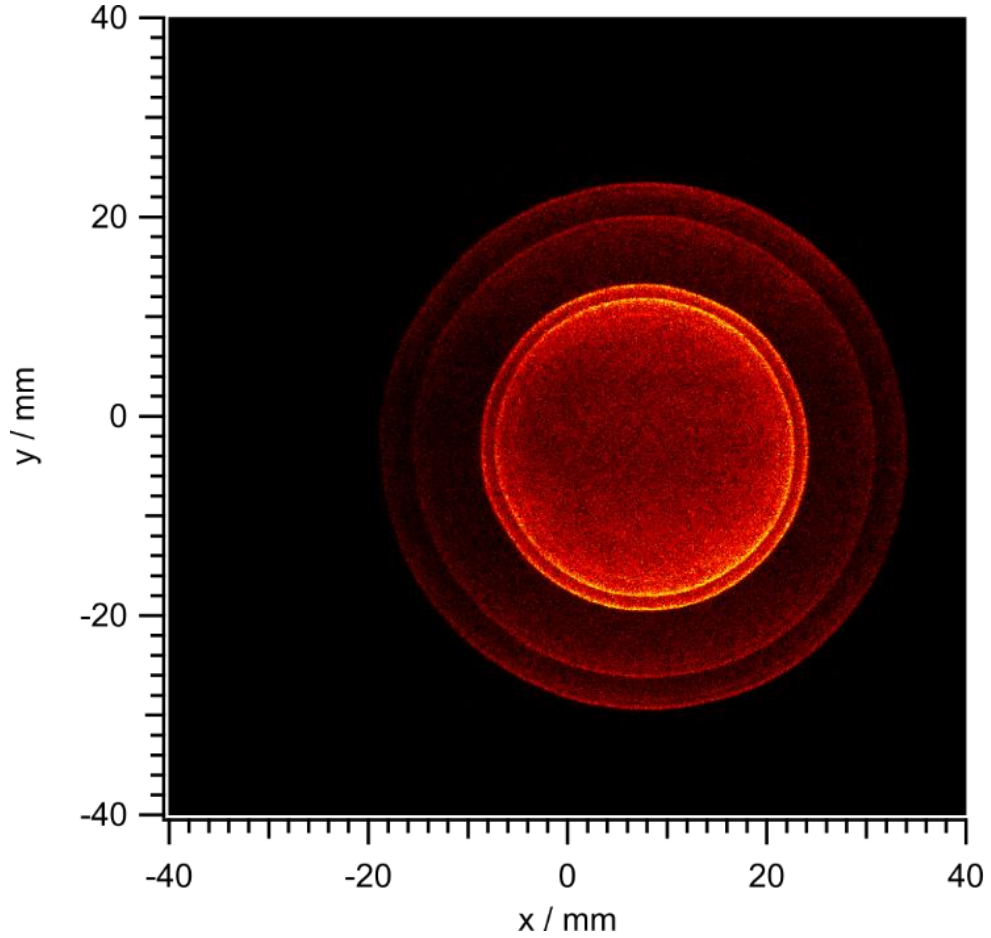
Coincidence Filter: Xe-TOF, ROI on Xe ions

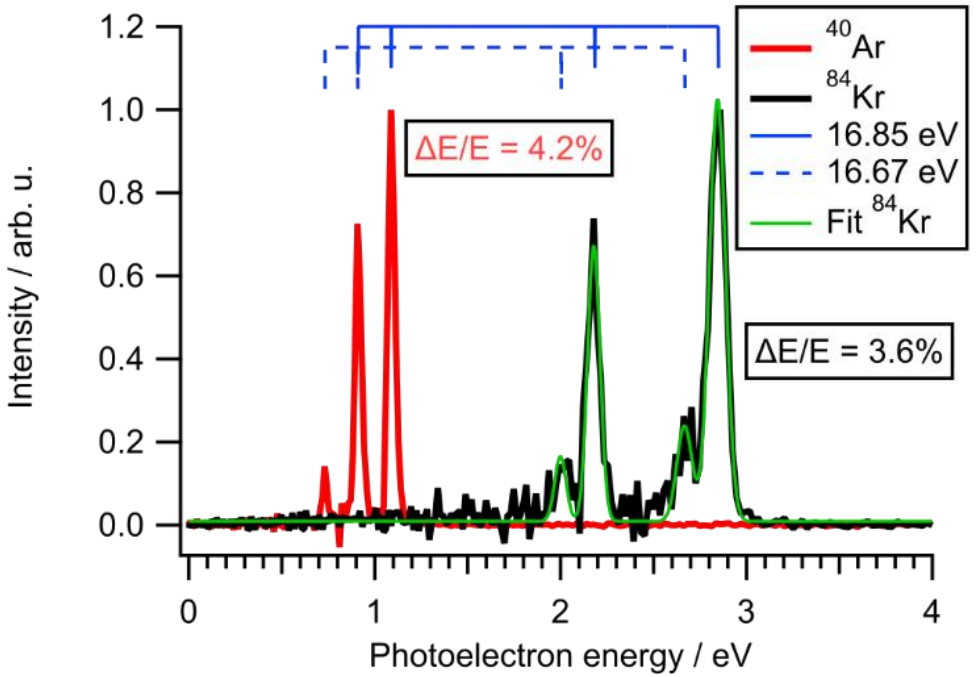


With Synchrotron VUV (ALS BL 9.0.2)
$t/2\Delta t = m/\Delta M > 10000$

Performance – Molecular Beam Operation

20% Ar and 20% Kr in He ionized by Ne-I VUV from discharge lamp

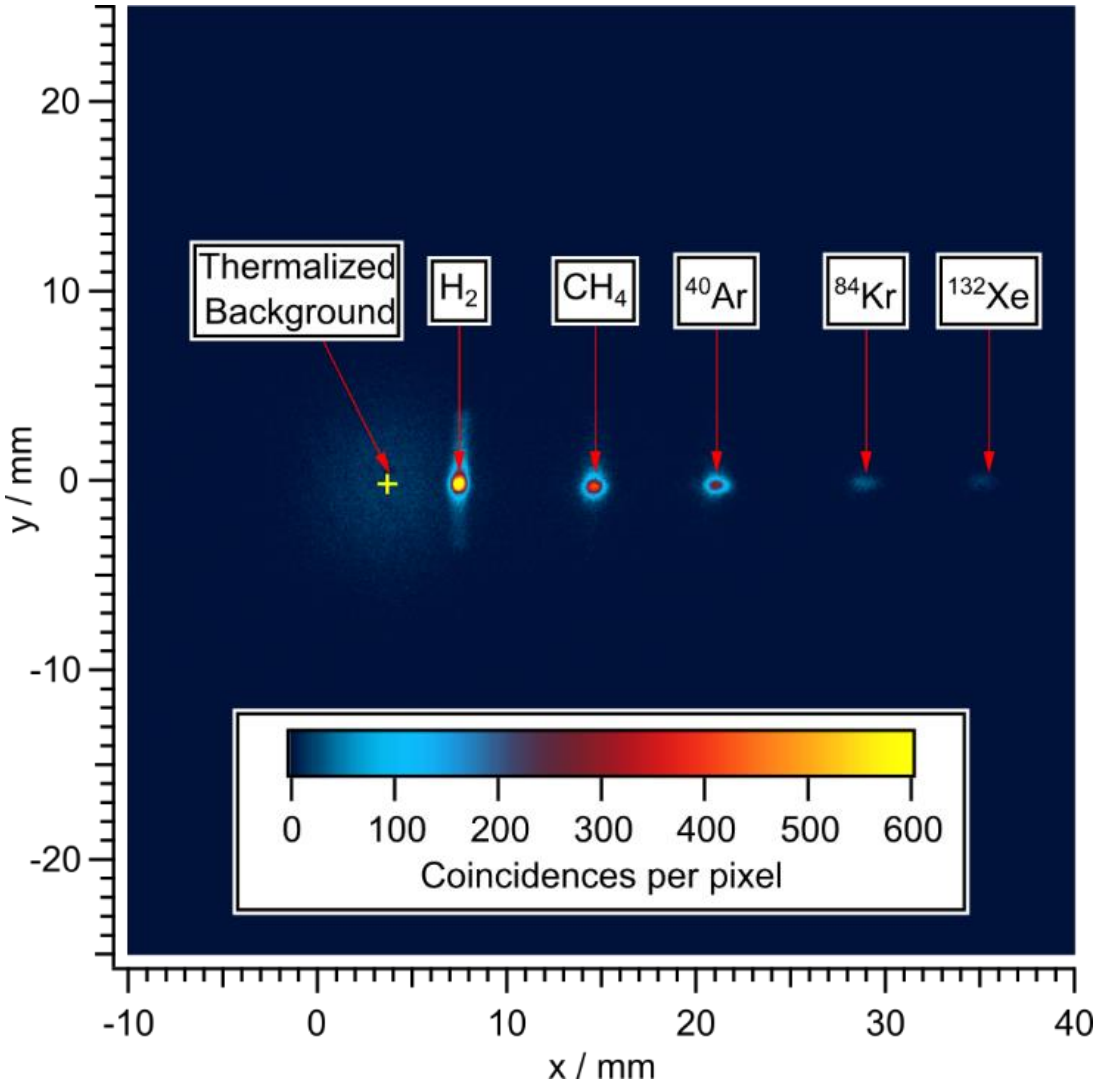


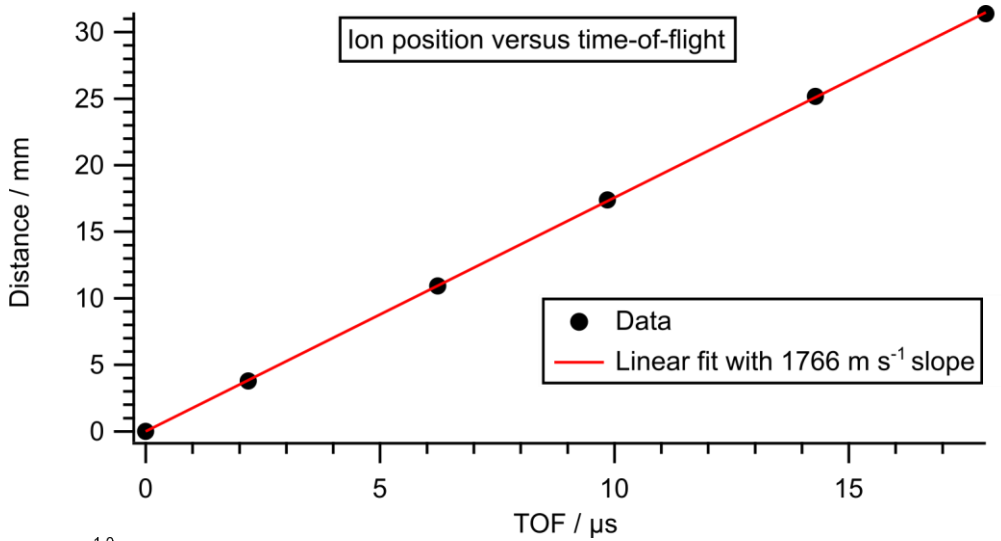


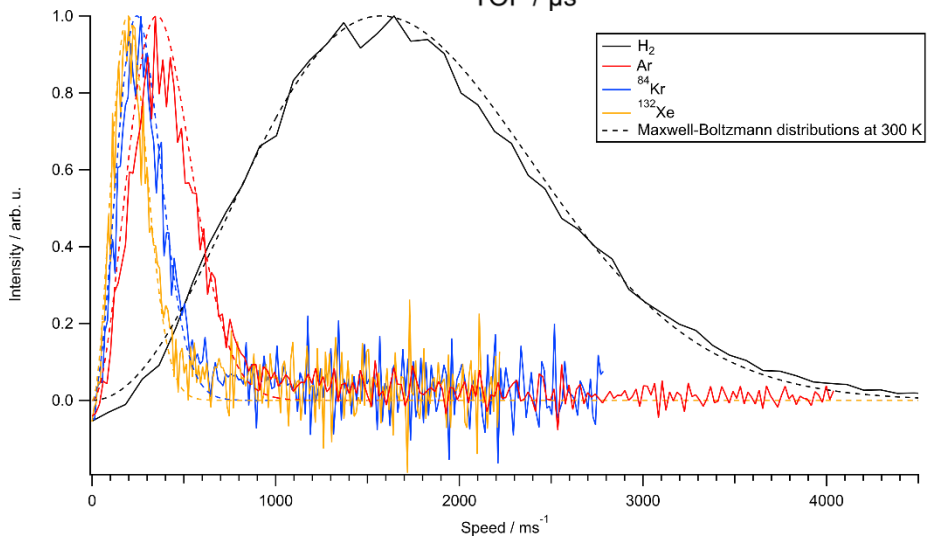
Performance – Molecular Beam Operation

10% H_2, 1% CH_4, 0.5% Ar, 0.5% Kr, 0.1% Xe in He

Coincidence Filter:25 us time-slice from center of MB

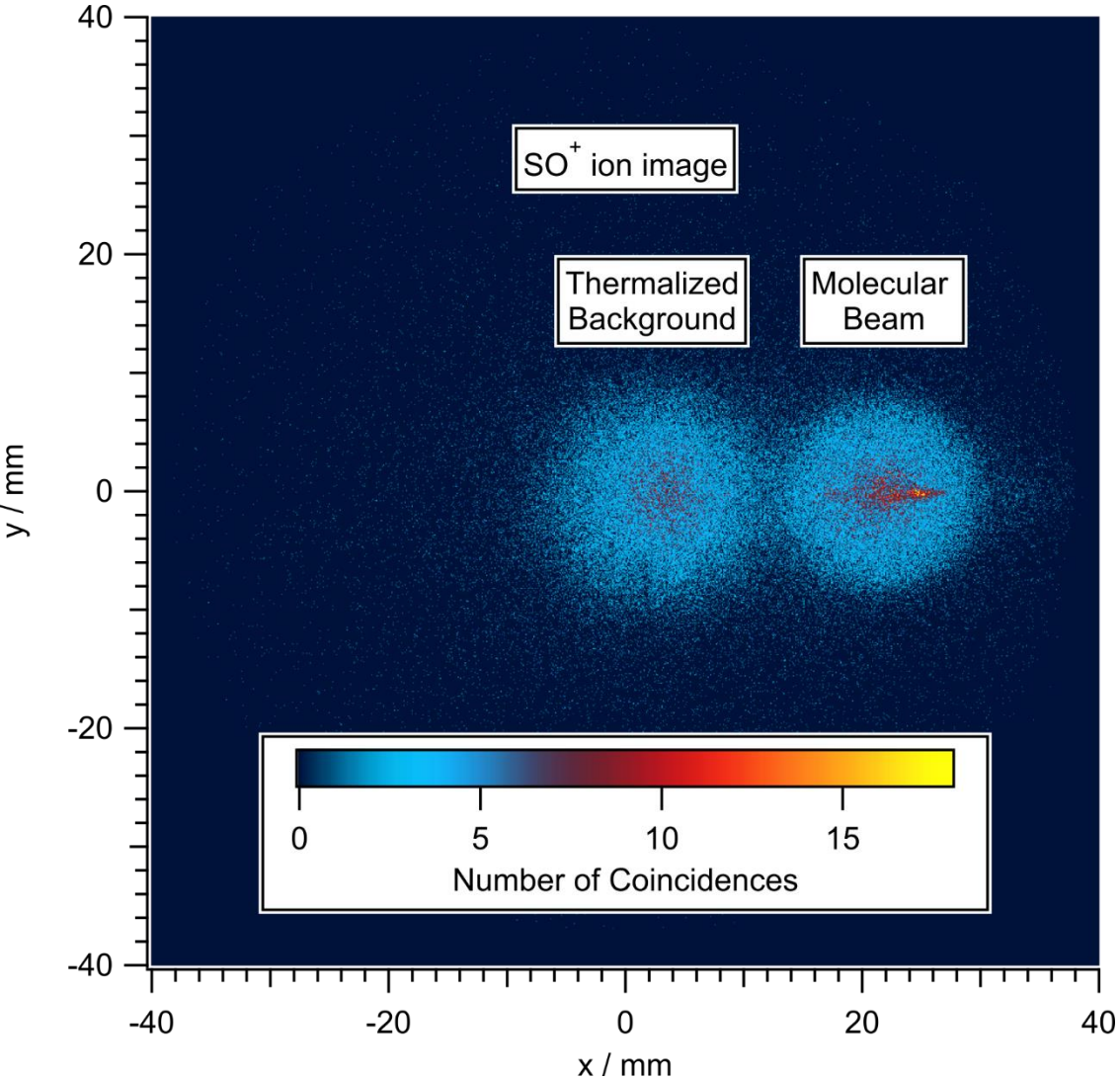


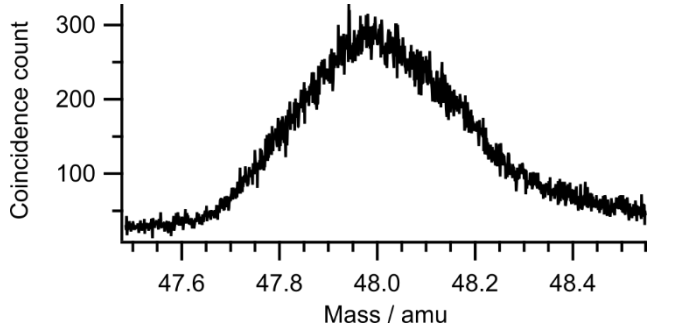


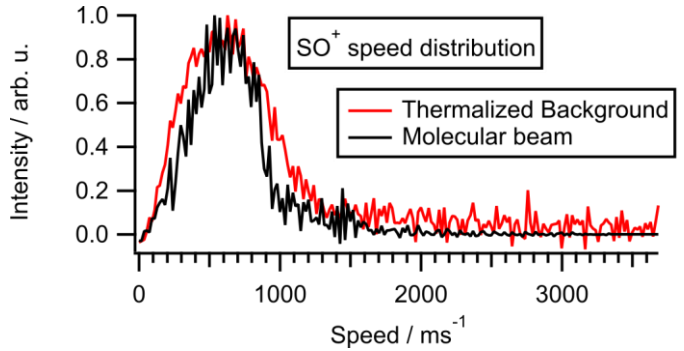


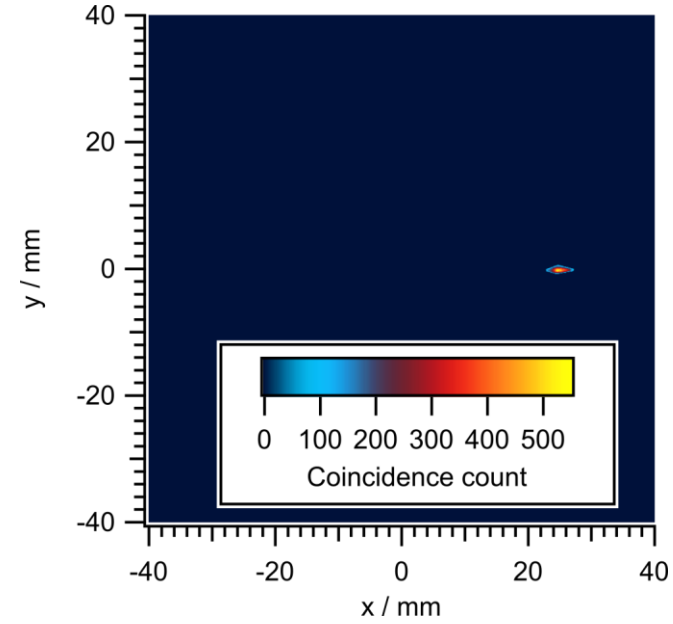
Performance – Molecular Beam Operation

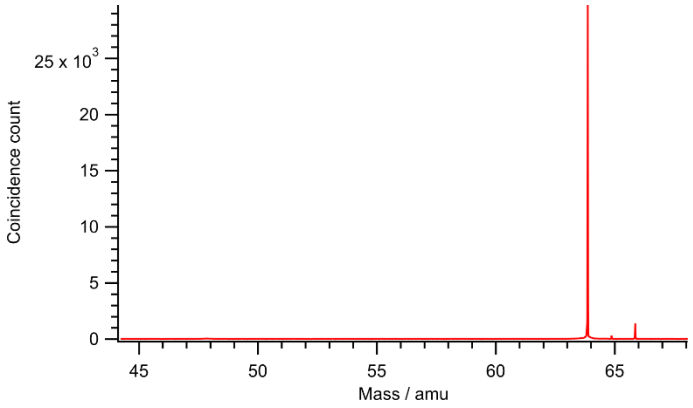
Dissociative ionization of 0.3% SO_2 in He, Photon energy = 16.85 eV
SO^+ appearance energy = 15.93 eV











SO_2 193 nm Dissociation with tunable VUV