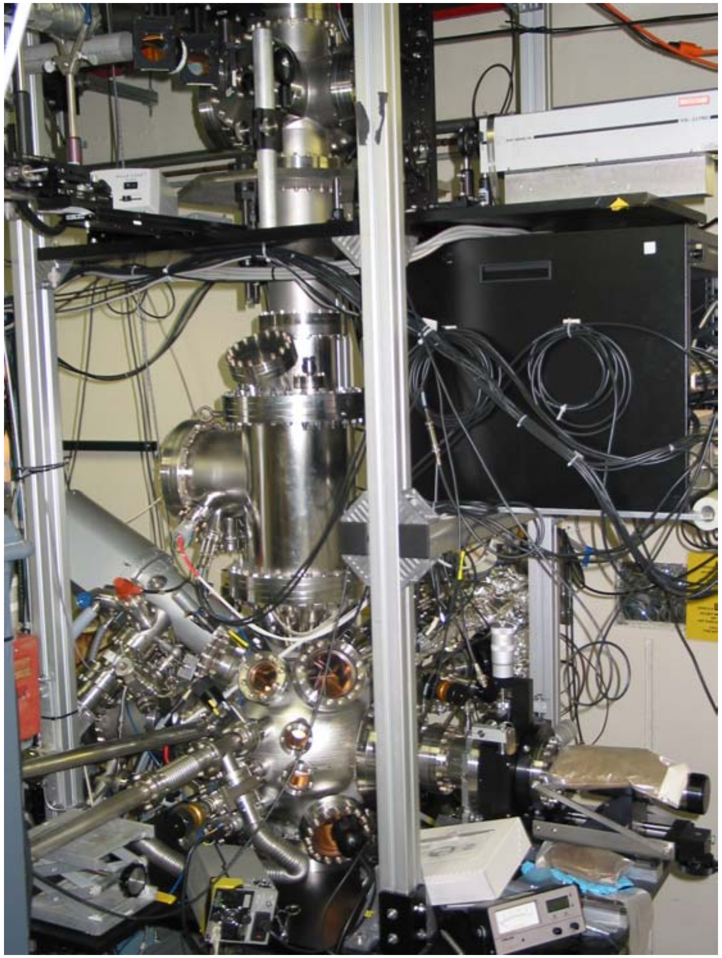
# SPIRIT - Photoionisation of Atoms and Molecules using LEUTL

Bruce King
*University of Newcastle, Australia*

SPIRIT - Single Photon Ionisation or Resonant Ionisation to Threshold



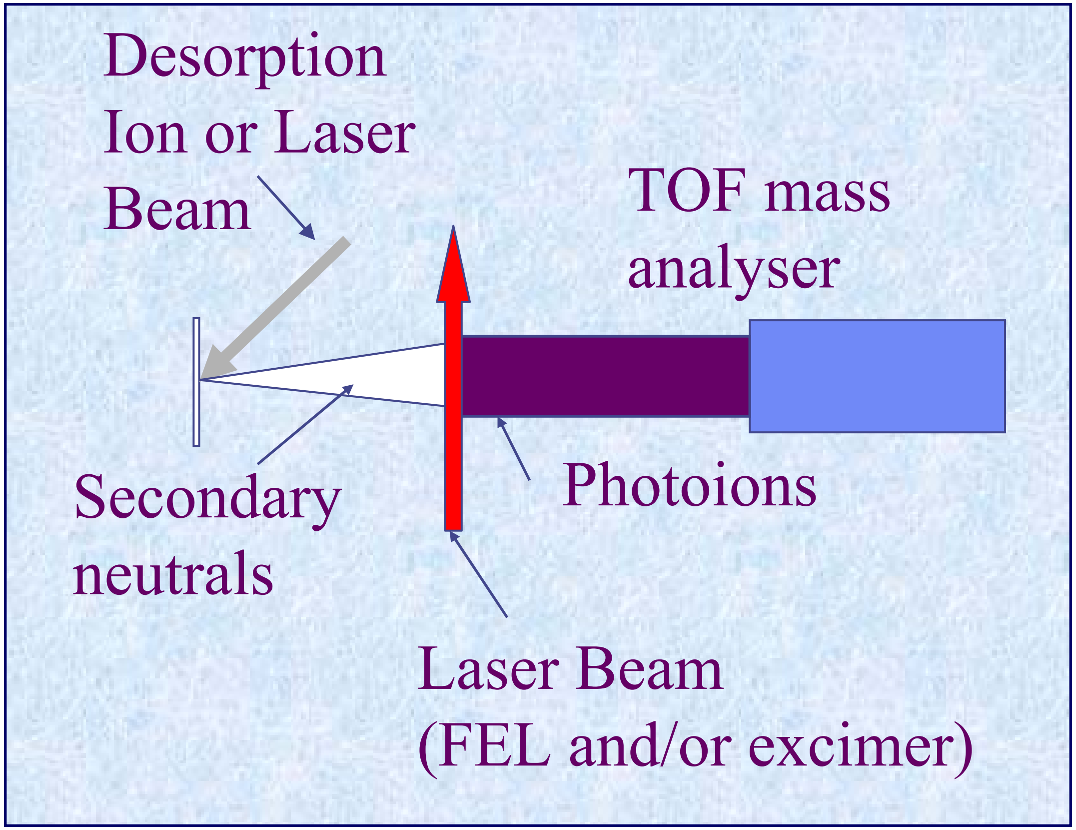
# Collaborators

| | |
|---|---|
| Jerry Moore, Wally Calaway, Igor Veryovkin, Michael Pellin | |
| | Materials Science Division |
| John Lewellen, Steven Milton, Kwang-Je Kim, Yuelin Li, Alex Lumpkin, Elizabeth Moog, Patric DenHartog, Mark Erdmann, Brian Tieman | |
| | Advanced Photon Source |
| Bruce King | University of Newcastle (Australia) |
| Mladin Petravic | Australian National University |
| Typhoon Lee and Chun-Yen Chen | Academia Sinica (Taiwan) |
| Andreas Wucher | University of Essen (Germany) |
| Don Burnett | California Institute of Technology |
| Gayle Woloschak | Northwestern University |
| Luke Hanley and Carrie Pavloski | University of Illinois Chicago |

# Schematic of SPIRIT Technique

•Laser postionisation using excimer and/or free electron lasers

•A sensitive mass spectrometer




•Analyse majority desorbed species

•Laser schemes to

✓Photoionise with near 100% efficiency

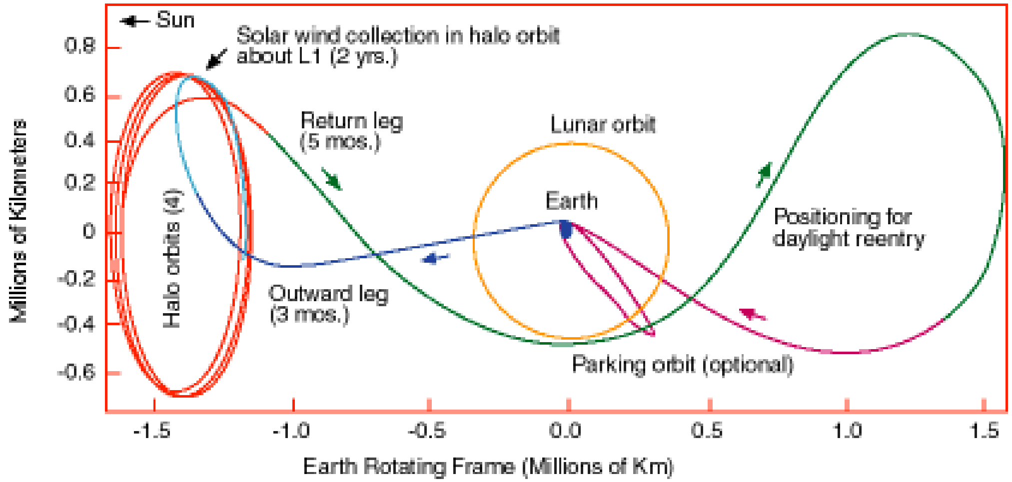
✓Minimise molecular fragmentation

# Motivation for Postionisation
# -Elemental Trace Analysis of Small Samples

| Monolayer | Nanoparticle |
|---|---|
| 1 µm square | **50 nm cube** |
| $1.5\times10^{7}$ atoms | **$6 \times 10^{6}$ atoms** |
| 70 ppb = 1 atom | **160 ppb = 1 atom** |

- With so few atoms, every atom counts.
- Characterisation must be accomplished before consuming the total number of atoms available.
- Define

$$Useful\ Yield = \frac{measured\ atoms}{desorbed\ atoms}$$



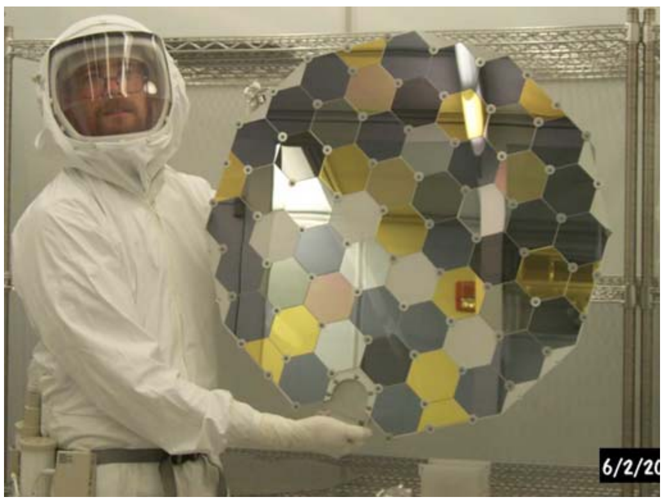

The NASA Genesis Discovery Mission will collect solar wind into pure Si wafers and return them to earth for analysis.

**Near Surface**

**100 nm deep**

**1mm x 1mm spot**

**1 ppt = 6000 atoms**



## Average Concentration (ppt) Expected in Top 100 nm

$^{93}Nb = 0.9$

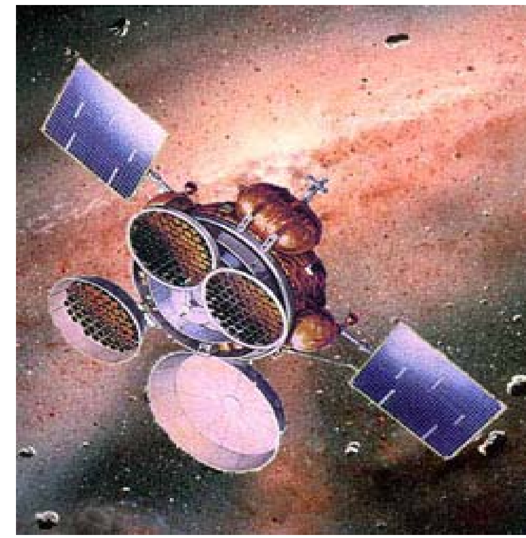
$^{103}Rh = 0.4$

$^{106}Pd = 0.5$

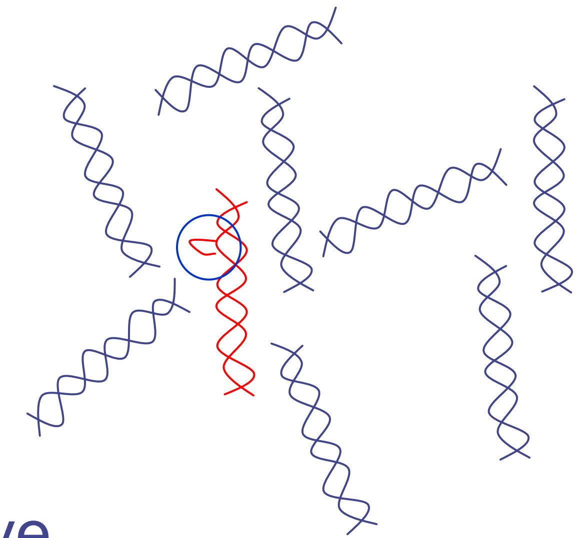
$^{114}Cd = 0.7$

$^{115}In = 0.2$

$^{120}Sn = 2.5$



# Motivation for Postionisation
# -Trace Analysis of Biomolecules



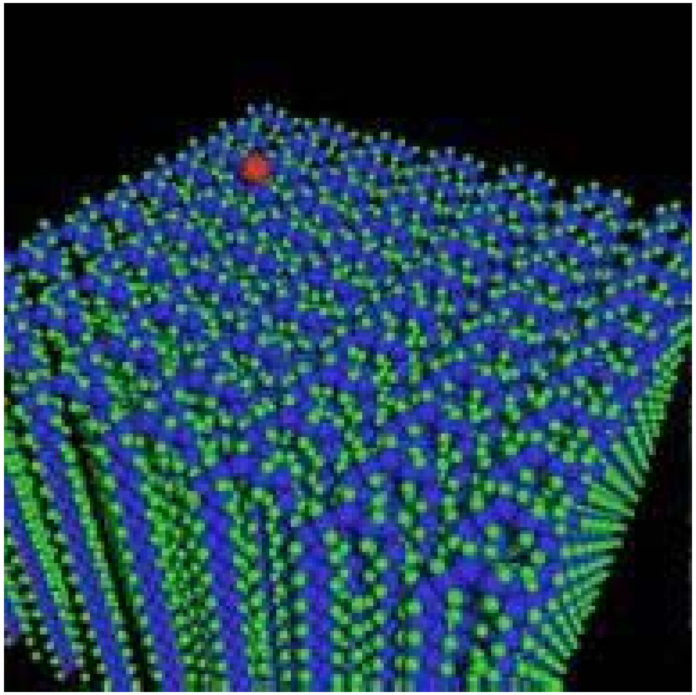
• Many cancers begin with chemicals modifying DNA

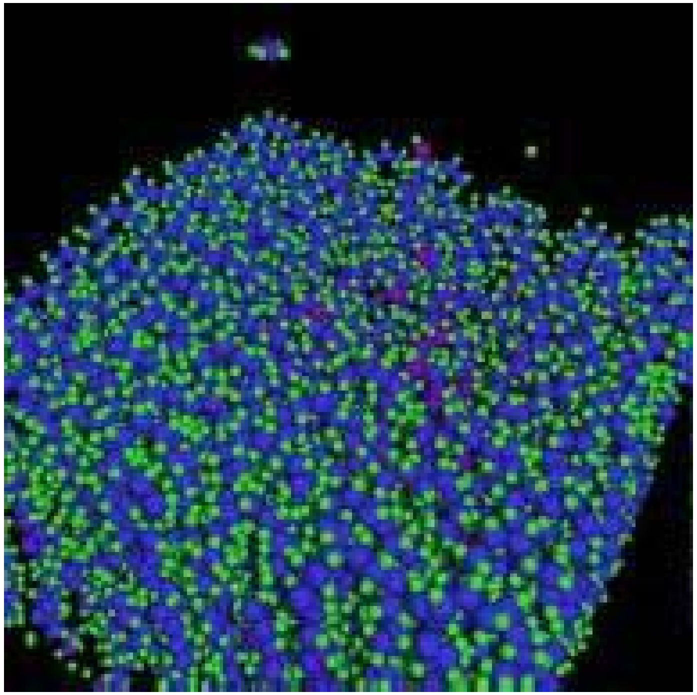
•Carcinogen-DNA adducts can be effective biomarkers for cancer

•Paul Chiarelli (National Center for Toxicological Research/Loyola) – measured from kg scale tissue digests (population averages)

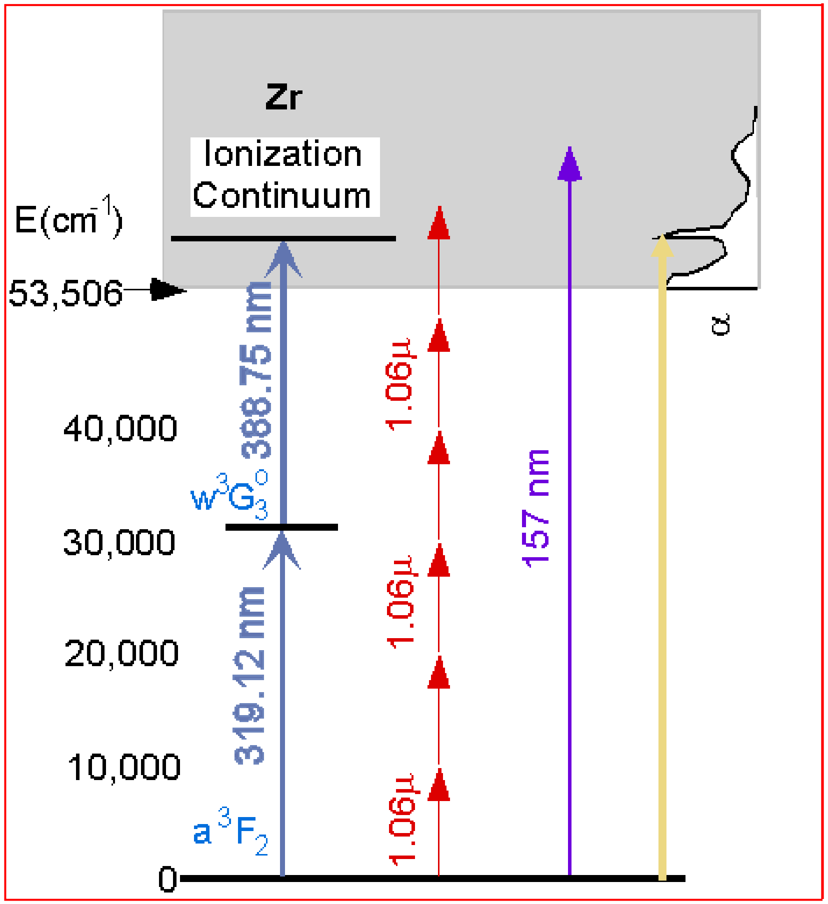
**4-5 orders of magnitude** better sensitivity desirable

# Motivation for Postionisation
## -Understanding mechanisms of neutral ejection from surfaces





# Laser Ionisation Schemes




Resonant multiphoton ionisation

Nonresonant multiphoton ionisation

Single photon ionisation (from excimer laser)

Tunable single photon ionisation (VUV FEL)

# Single Photon Ionisation

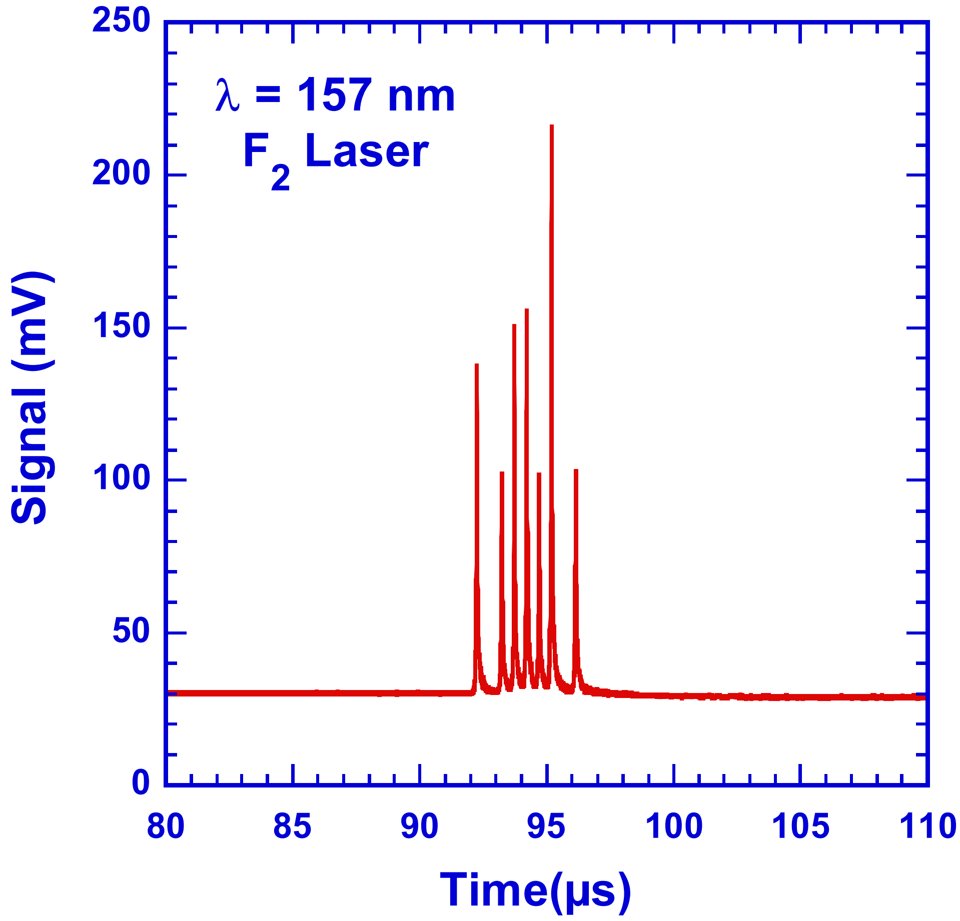
- The ideal is saturation – all absorbing species in laser volume are ionised

SPI cross-section ~ $10^{-17}$cm$^{2}$

Corresponds to 1mJ/pulse at 157nm.

- ALFF (200μJ/pulse) will permit saturation with smaller beam spots and multiple pass optics in chamber
- Laser fluctuations become irrelevant so SASE OK
- Quantification possible without knowing cross sections
- But with SPI, quantification also possible at lower intensities

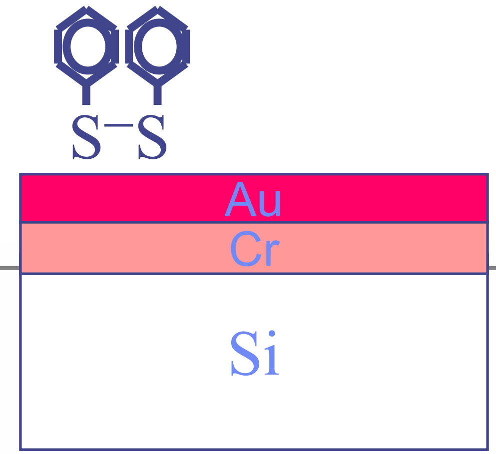
# Single Photon Ionisation with an excimer laser

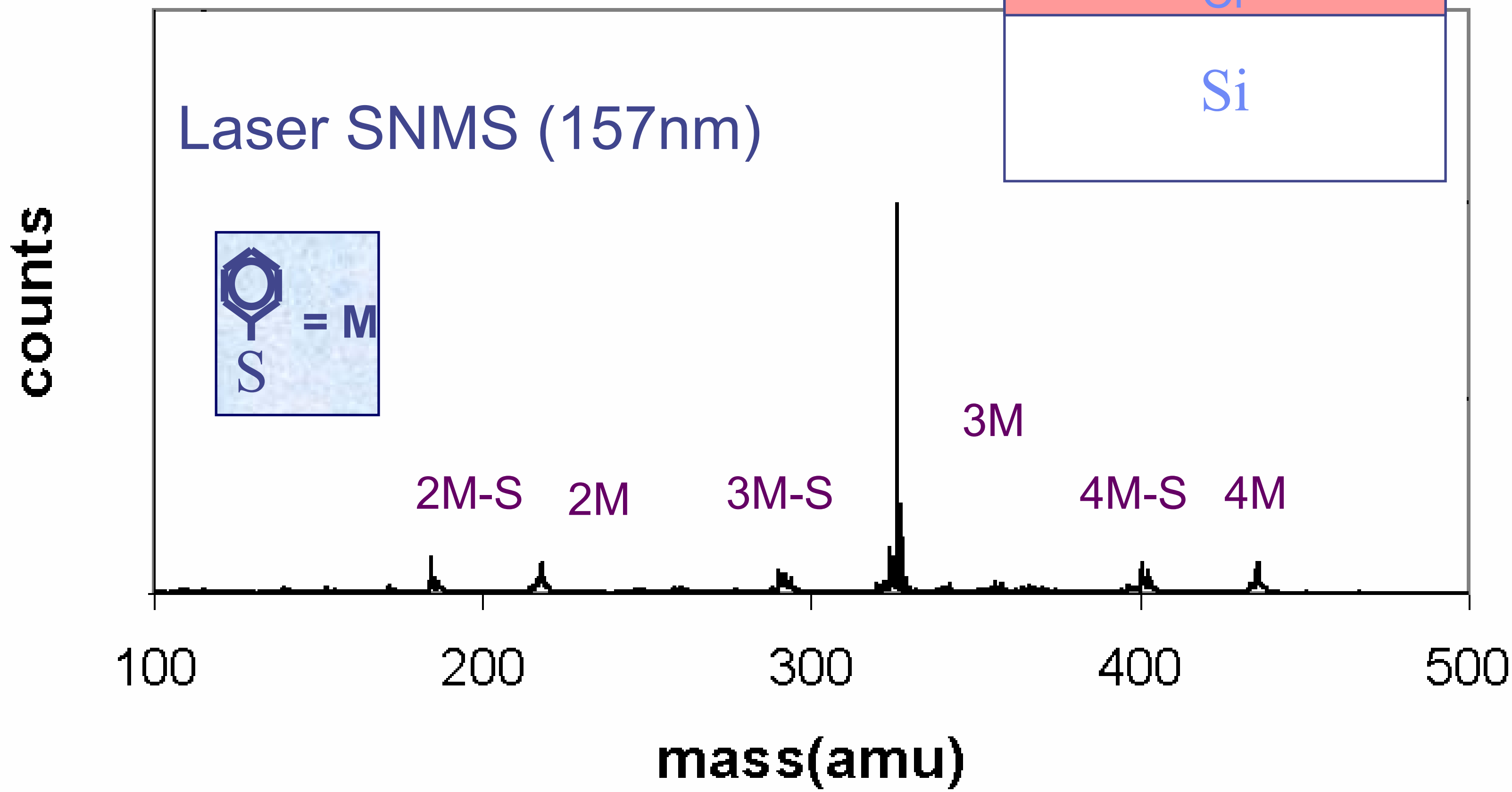



24% useful yield for Mo with SPIRIT

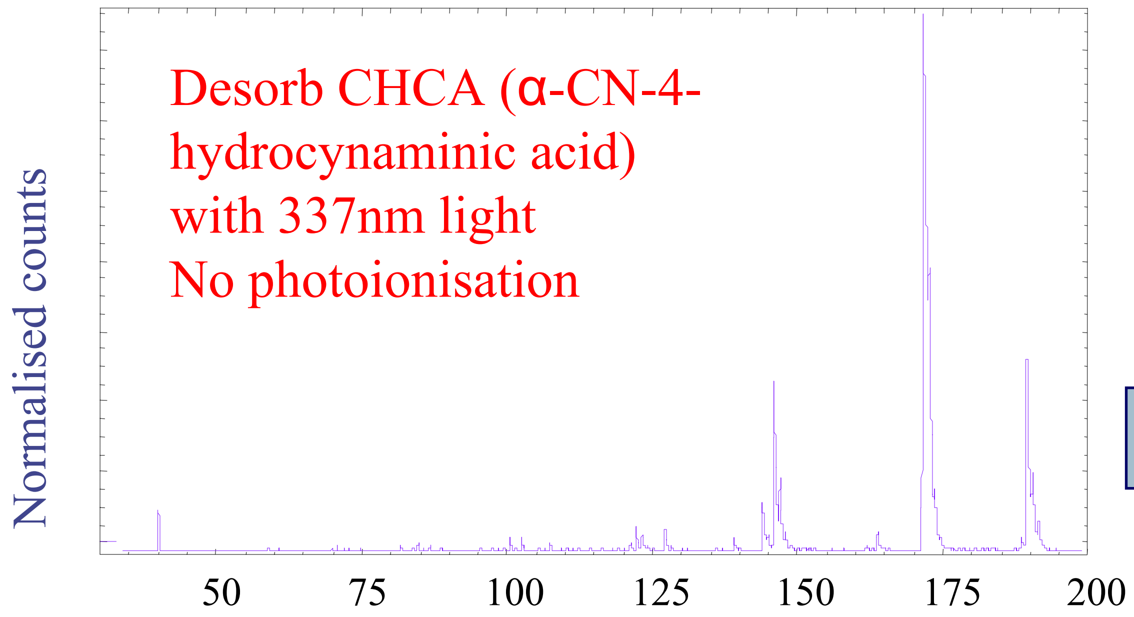
Sub-ppb analysis possible in top layer with 100 micron diameter beam

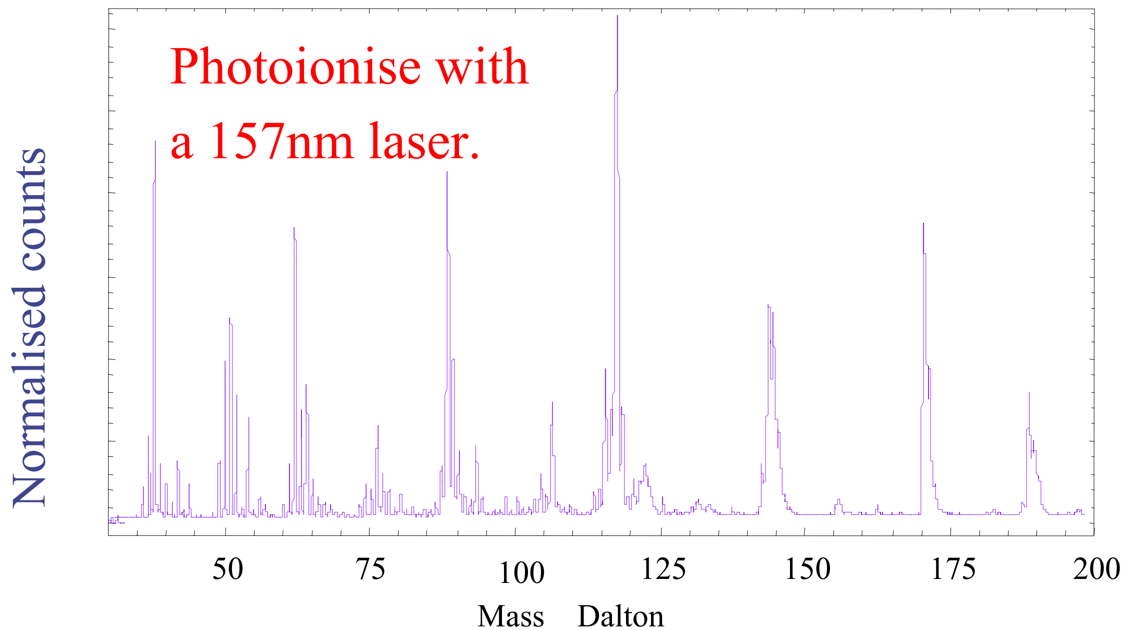
# SAM of Diphenyl Disulphide
$(C_6H_5S)_2 = 2M$




Useful yield of large fragments = 0.5%



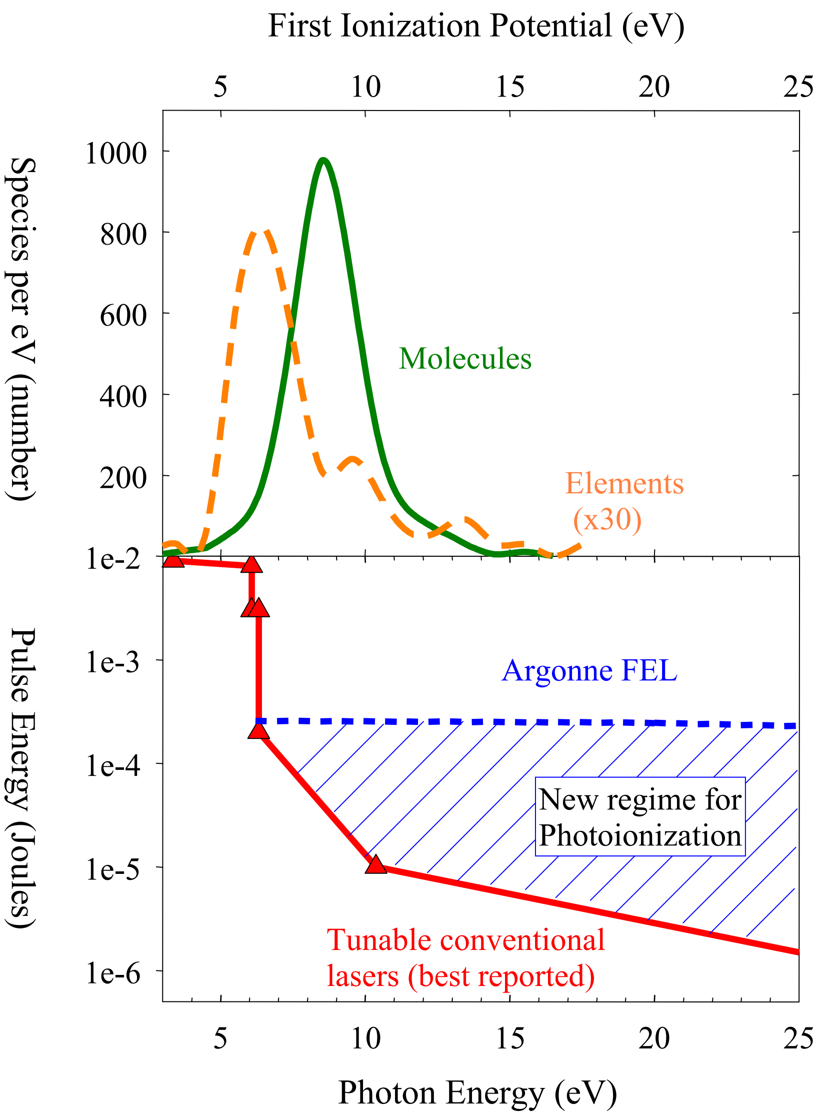



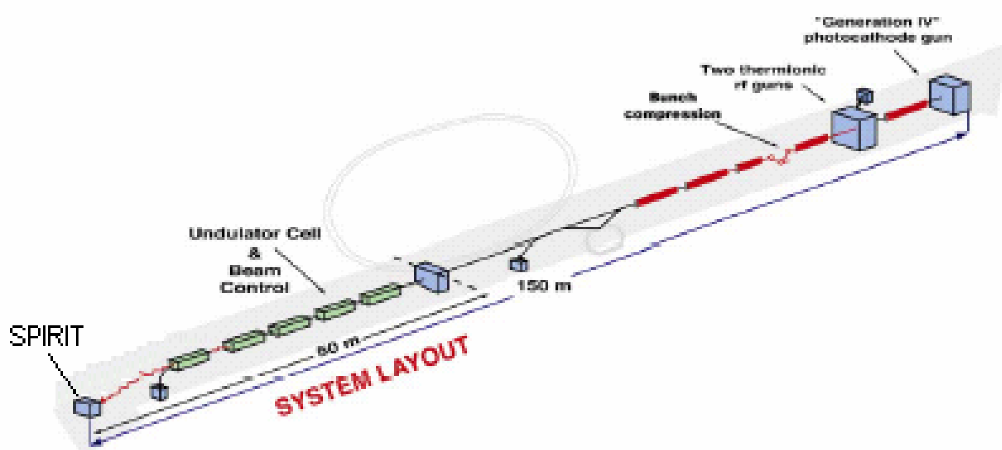

Up to 300x
signal increase

We need a better laser!

An intense tunable VUV laser is required for sensitive analysis of

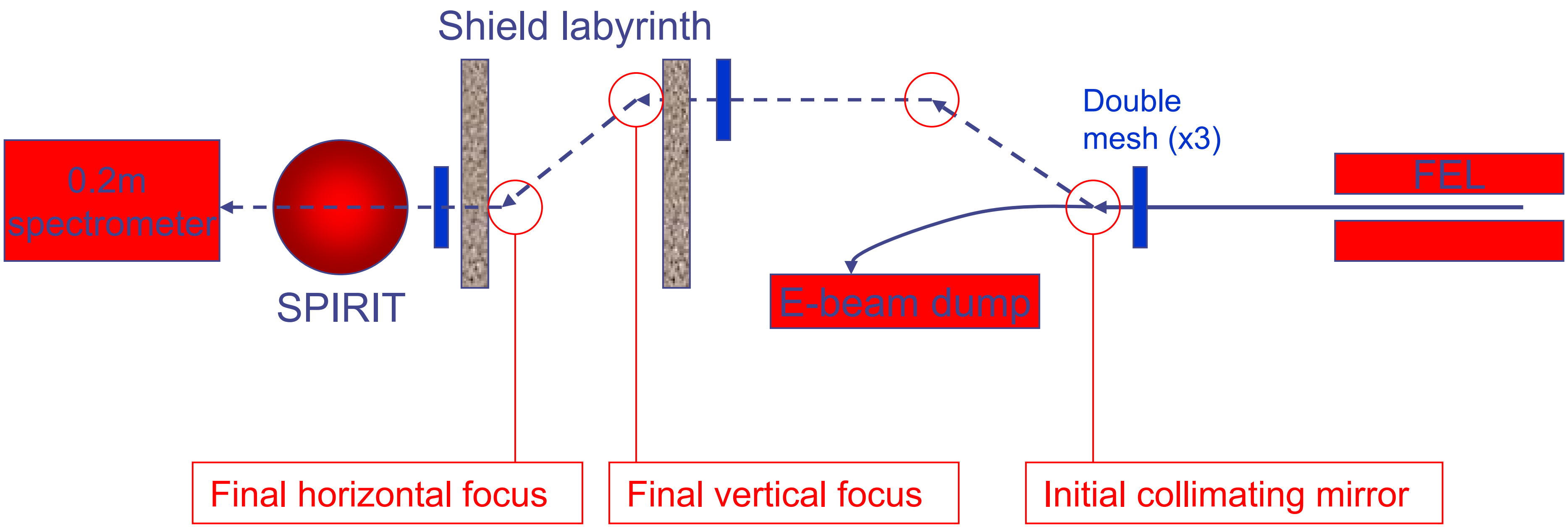
- elements with high ionisation potentials(eg C,N,O,H)
- most molecules



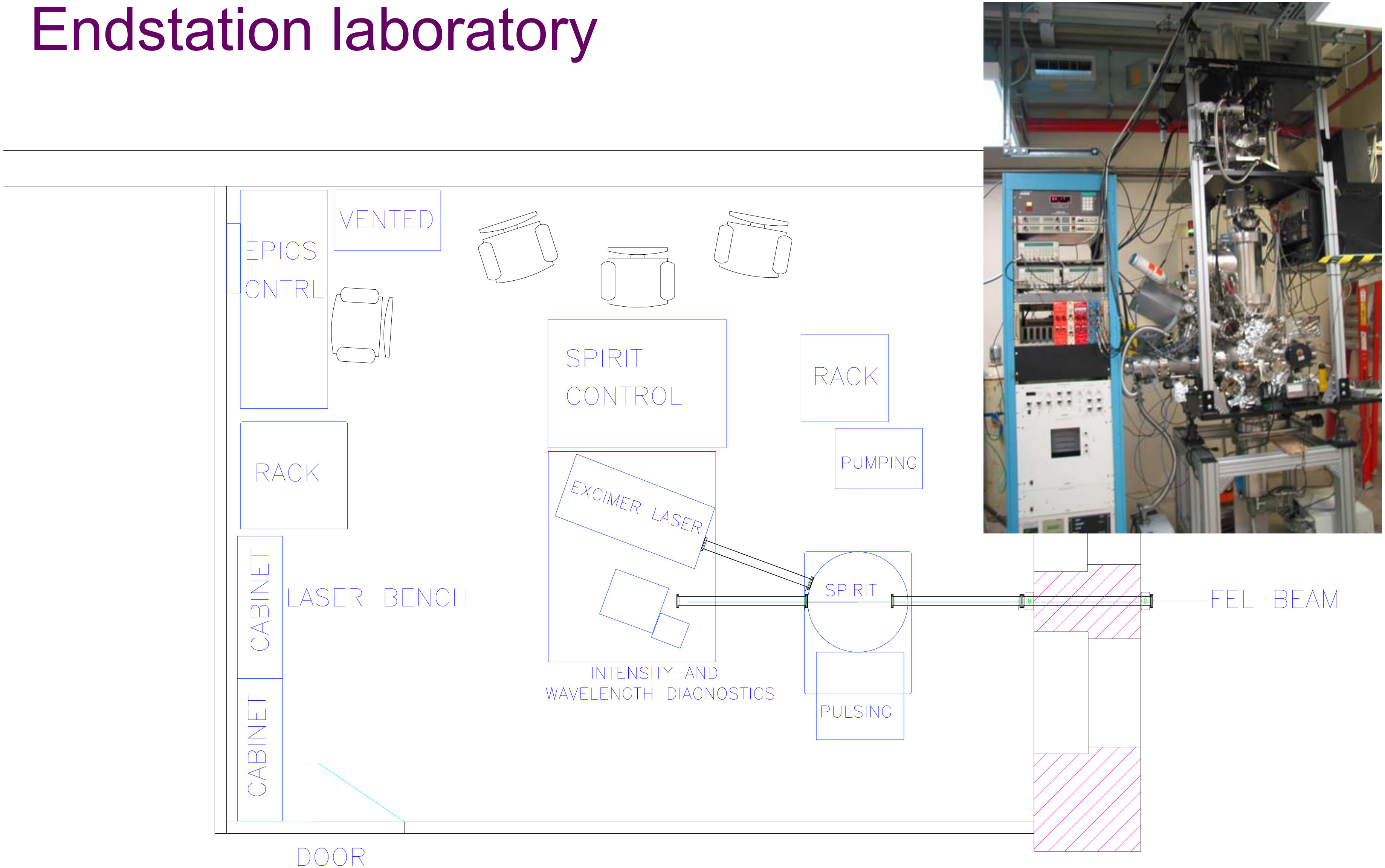

"Generation IV" photocathode gun
Two thermionic rf guns
Bunch compression
Undulator Cell & Beam Control
150 m
60 m
SPIRIT
SYSTEM LAYOUT

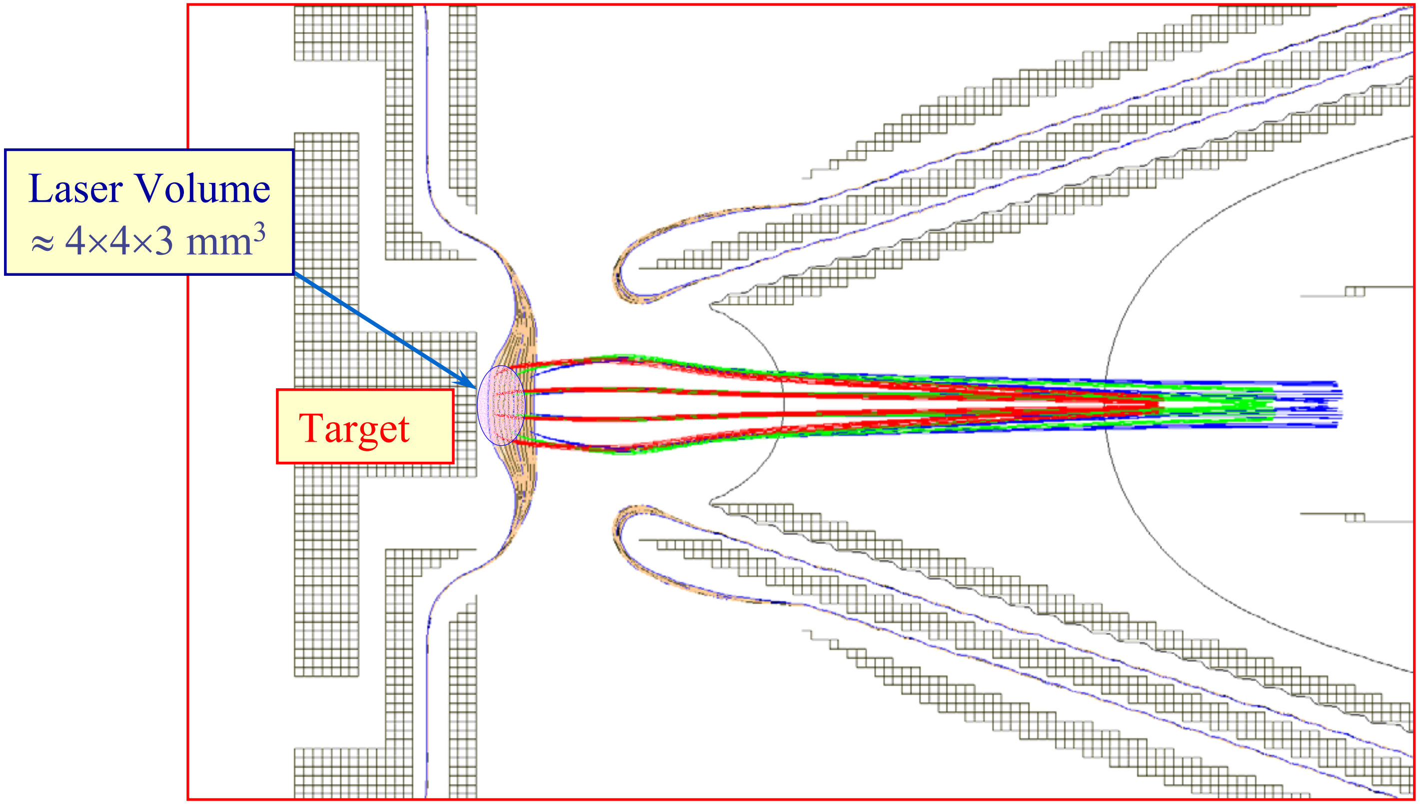

OPTRONICS
CAUTION
CAUTION

# FEL Beam transport schematic

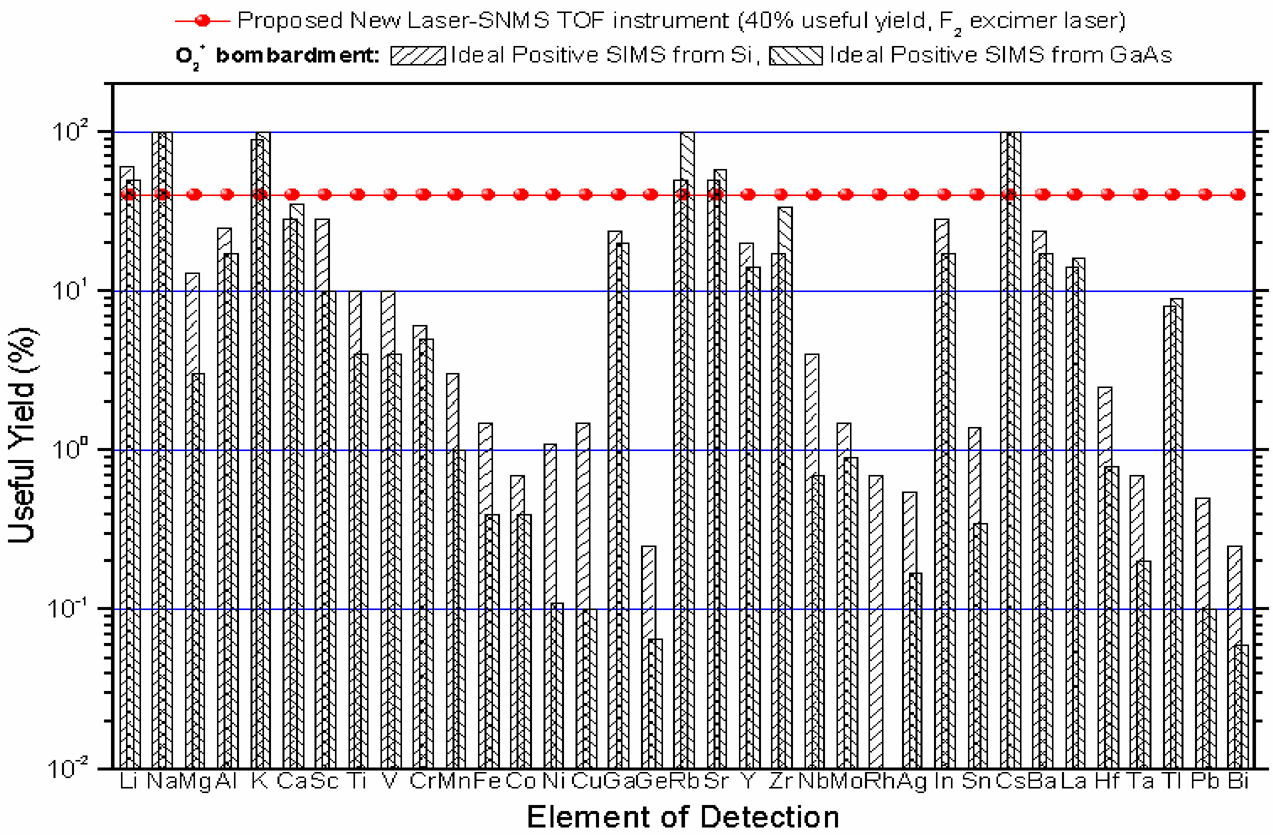


# Endstation laboratory



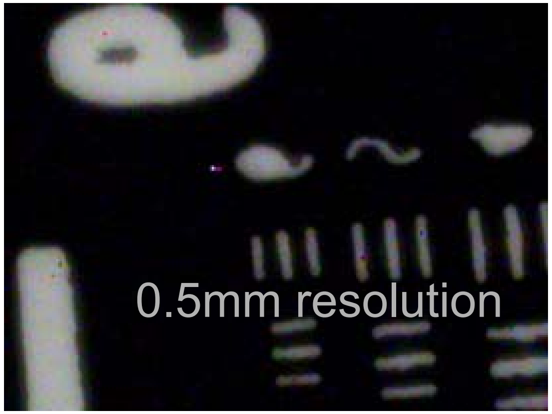



| Instrument | Sputtered Fraction | **Ionization Efficiency** | Spectrometer Transmission | Detector Efficiency | Useful Yield |
|---|---|---|---|---|---|
| SPIRIT | 0.43 | **0.95** | 0.98 | 0.75 | 30% |

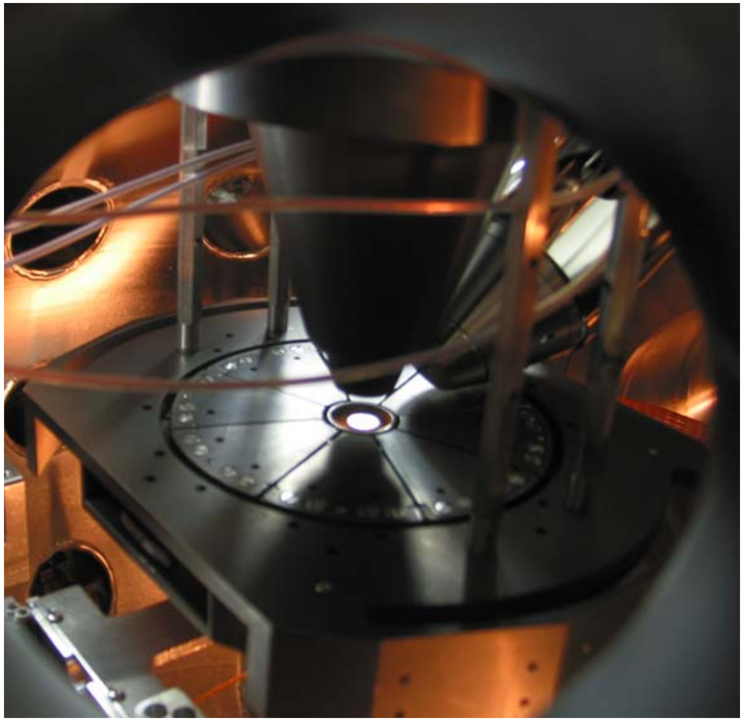


Proposed New Laser-SNMS TOF instrument (40% useful yield, F2 excimer laser)
O2+ bombardment: Ideal Positive SIMS from Si, Ideal Positive SIMS from GaAs
Useful Yield (%)
10^2
10^1
10^0
10^-1
10^-2
Li Na Mg Al K Ca Sc Ti V Cr Mn Fe Co Ni Cu Ga Ge Rb Sr Y Zr Nb Mo Rh Ag In Sn Cs Ba La Hf Ta Tl Pb Bi
Element of Detection

- Novel mass spectrometer optimised for postionisation
- Highest useful yield of any such instrument worldwide
  - measured 24% so far (one in four atoms counted)
- Low noise and background – vital for ultratrace measurements
- Integrated optical microscope for imaging and laser desorption
- Wide mass range and dynamic range

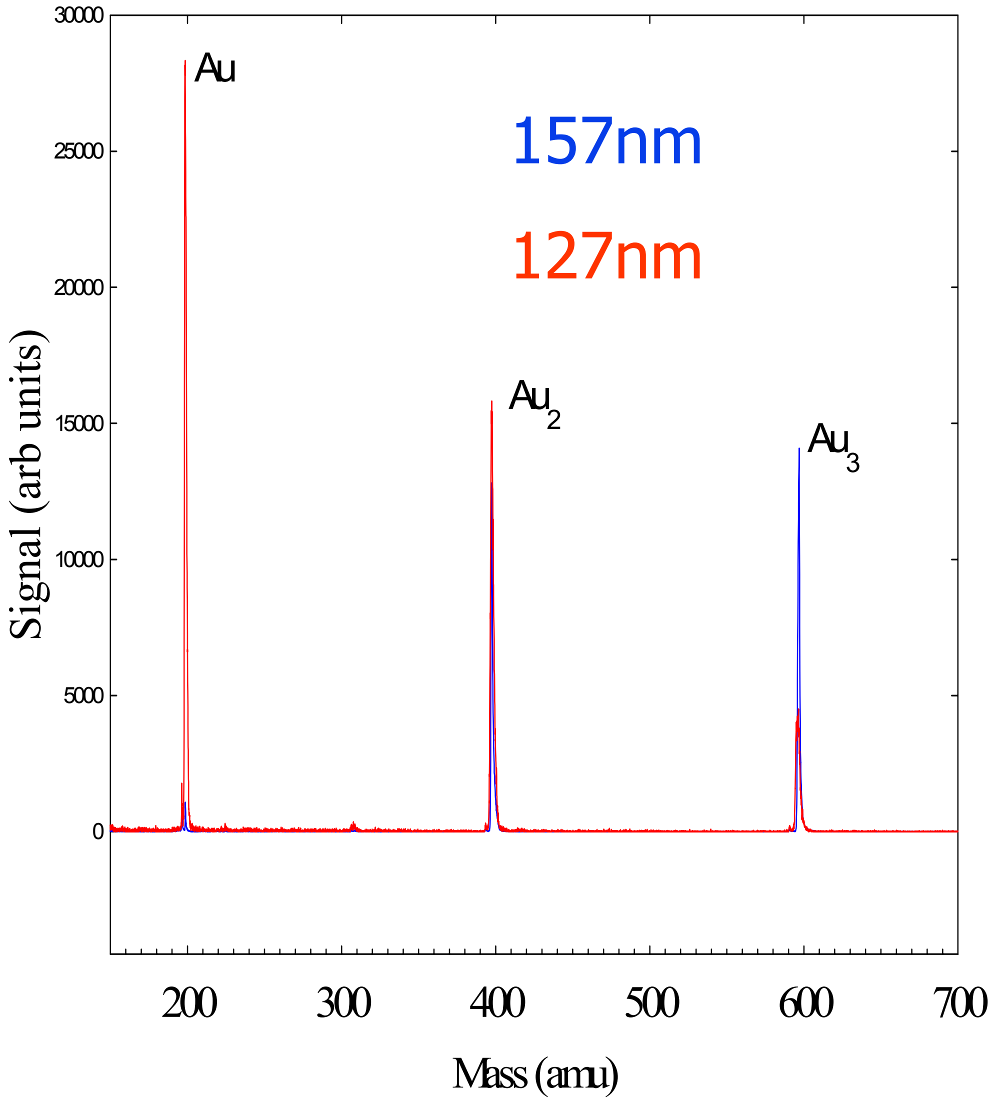


# FEL Photoionisation of Au and $Al_4Au$



- IP of Al is 6eV
- IP of Au is 9.2eV (134nm).
- Au above $F_2$ laser wavelength (157nm)
- Tune the FEL above and below the IP of gold

# Photoionisation of Sputtered Gold



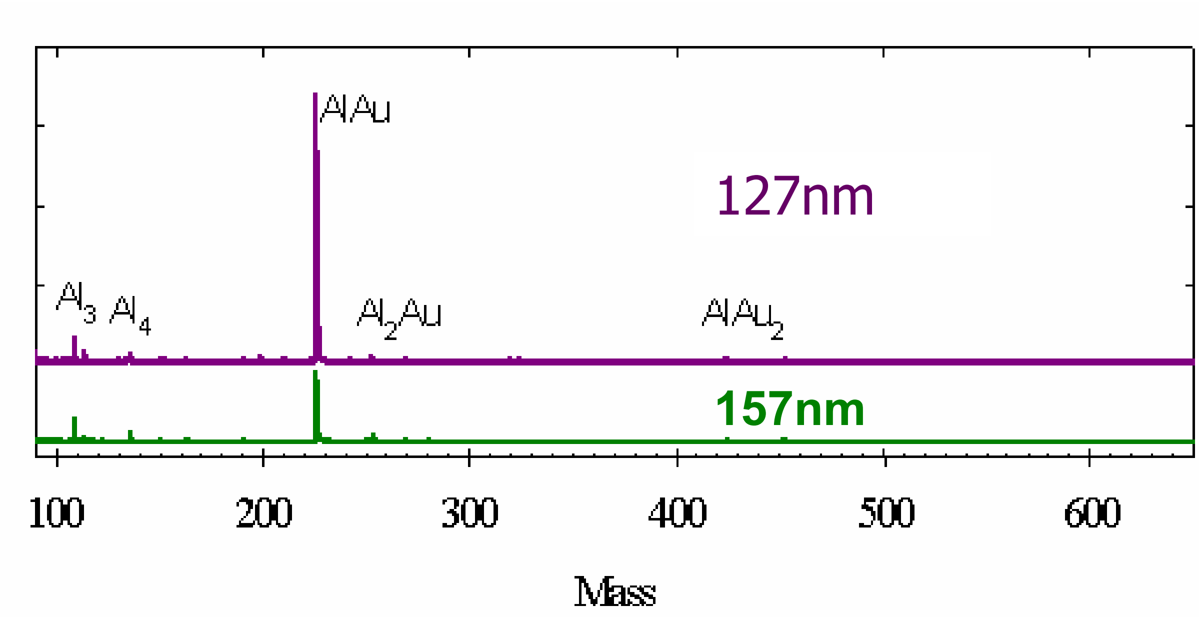

- Photoions of Au atoms, dimers and trimers observed
- Atoms dramatically enhanced when photons are above IP
- We can turn signals on and off by tuning the VUV wavelength

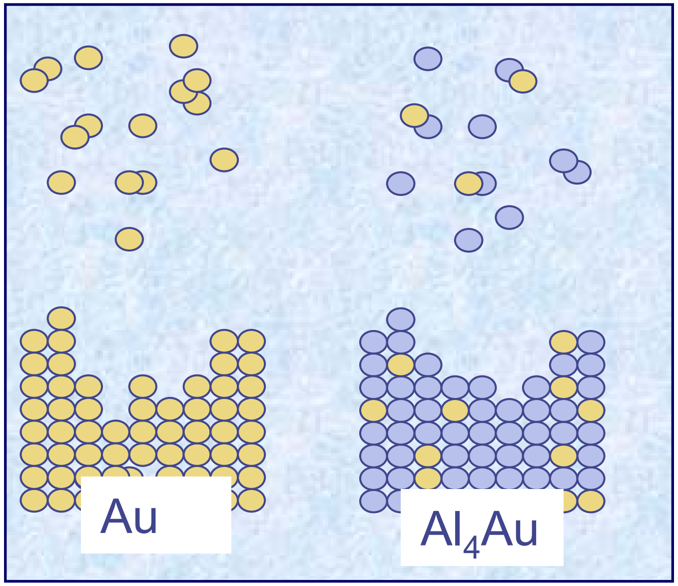
151 years ago W.R. Grove made the first recorded observation of sputtering

(Phil Trans, 142 (1852) 87)

But we are still surprised by new results!

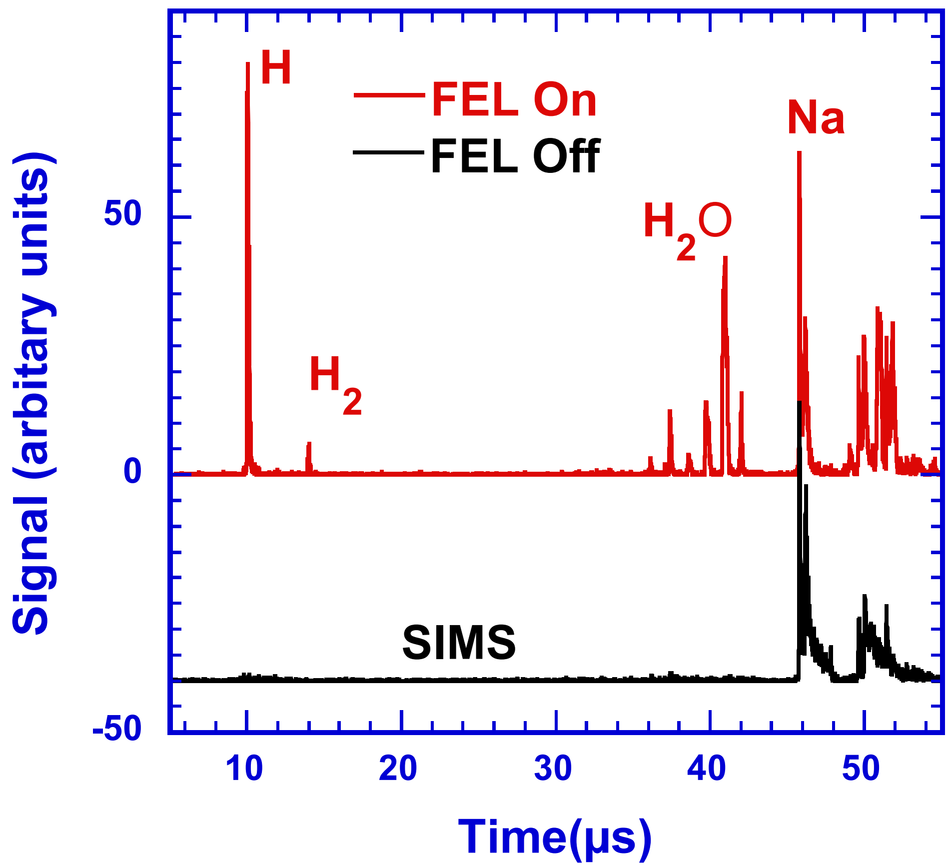
# Photoionisation of Sputtered $Al_4Au$



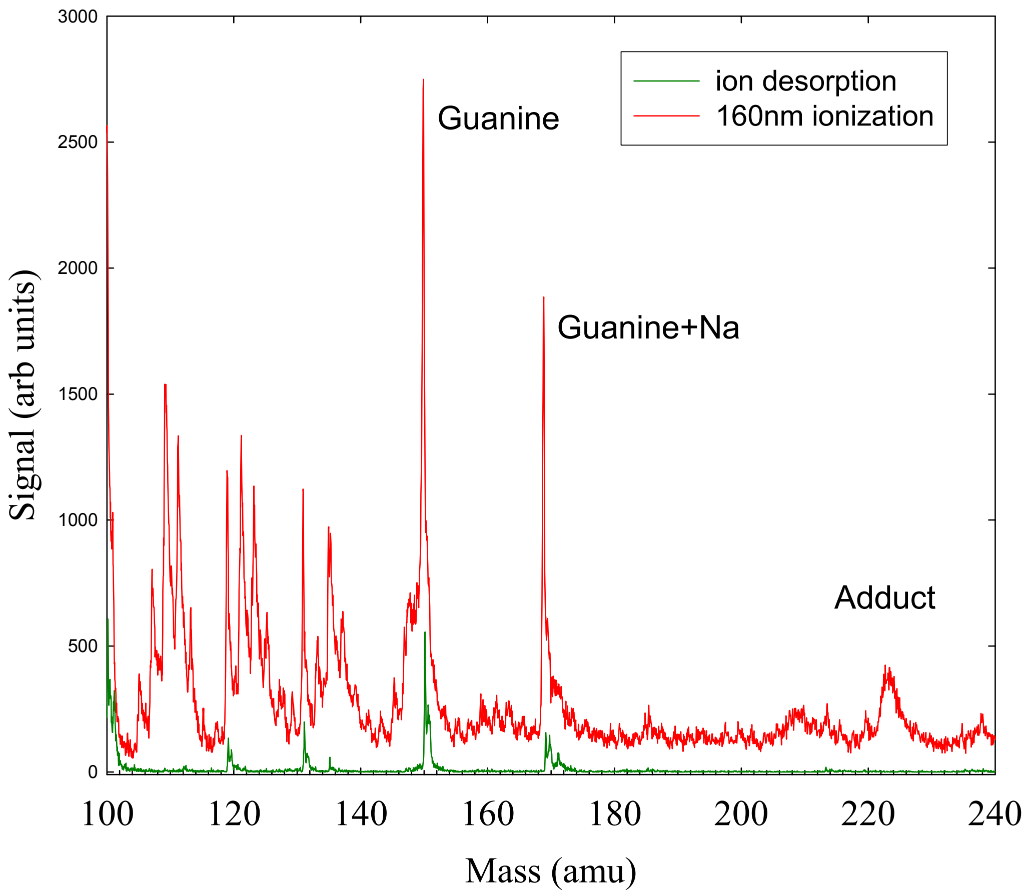

Sputtered $Al_4Au$ gives Au essentially only in clusters

# Multiphoton Photoionisation of Light Elements




- Photoions of gas phase H, $H_2$, $H_2O$, N and NH observed (at 162nm)
- Driving nonlinear processes possible, even with LEUTL

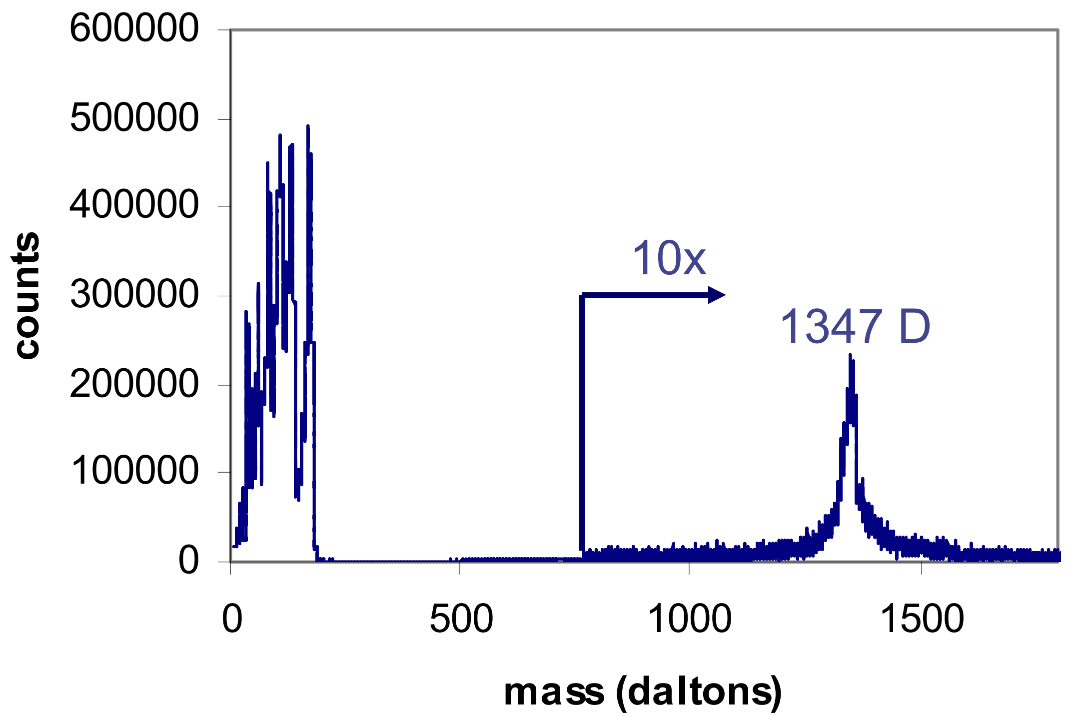
# Photoionisation of sputtered guanine adducts




- See similar enhancements using the FEL to those seen for $F_2$ laser
- 5x enhancement for guanine
- 100x enhancement for adduct and fragments
- In the future $C_{60}$ beams for minimised fragmentation

# Peptide Analysis

## Laser Ablation of Substance P in CHCA



# Conclusion & Present Status of SPIRIT

- SPIRIT instrument completed and thoroughly tested – 24% useful yield measured
- FEL VUV beam transport and diagnostics developed
- Photoionisation with $F_2$ laser (157nm) or FEL (266-120nm)
- Elements, pure organic molecules, and mixtures have been studied
    - *Matrix effect demonstrated in metal alloy systems*
    - *High efficiency in guanine adduct detection*
    - *Peptide desorption and multiphoton ionisation have been observed*

## Some future experiments with LEUTL

- Optimise SPIRIT for peptide samples
- Demonstrate 2 photon ionisation schemes using excimer laser and FEL
- Expand analysis of gold alloys to explain anomalous sputtering

## Some future experiments with ALFF

- Saturation of single photon ionisation for analysis of C,N,O,H with high sensitivity
- Measurement of sputtering into various ion and neutral channels for a complete analysis of sputtering