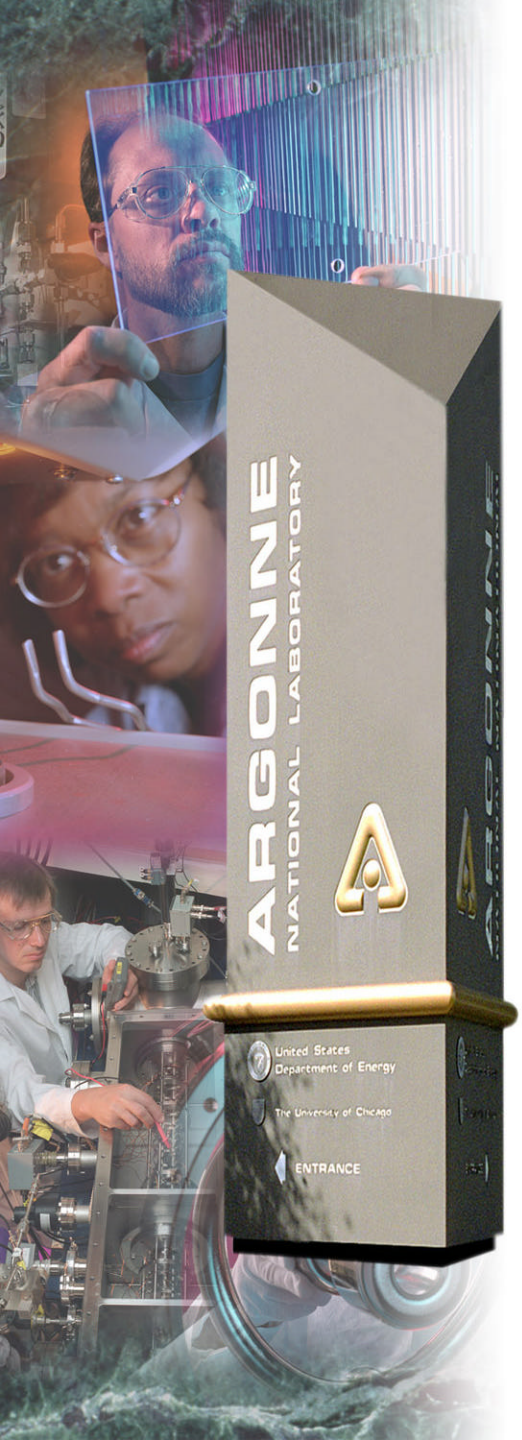


LPI SNMS with VUV FEL

Igor Veryovkin

and many more people involved

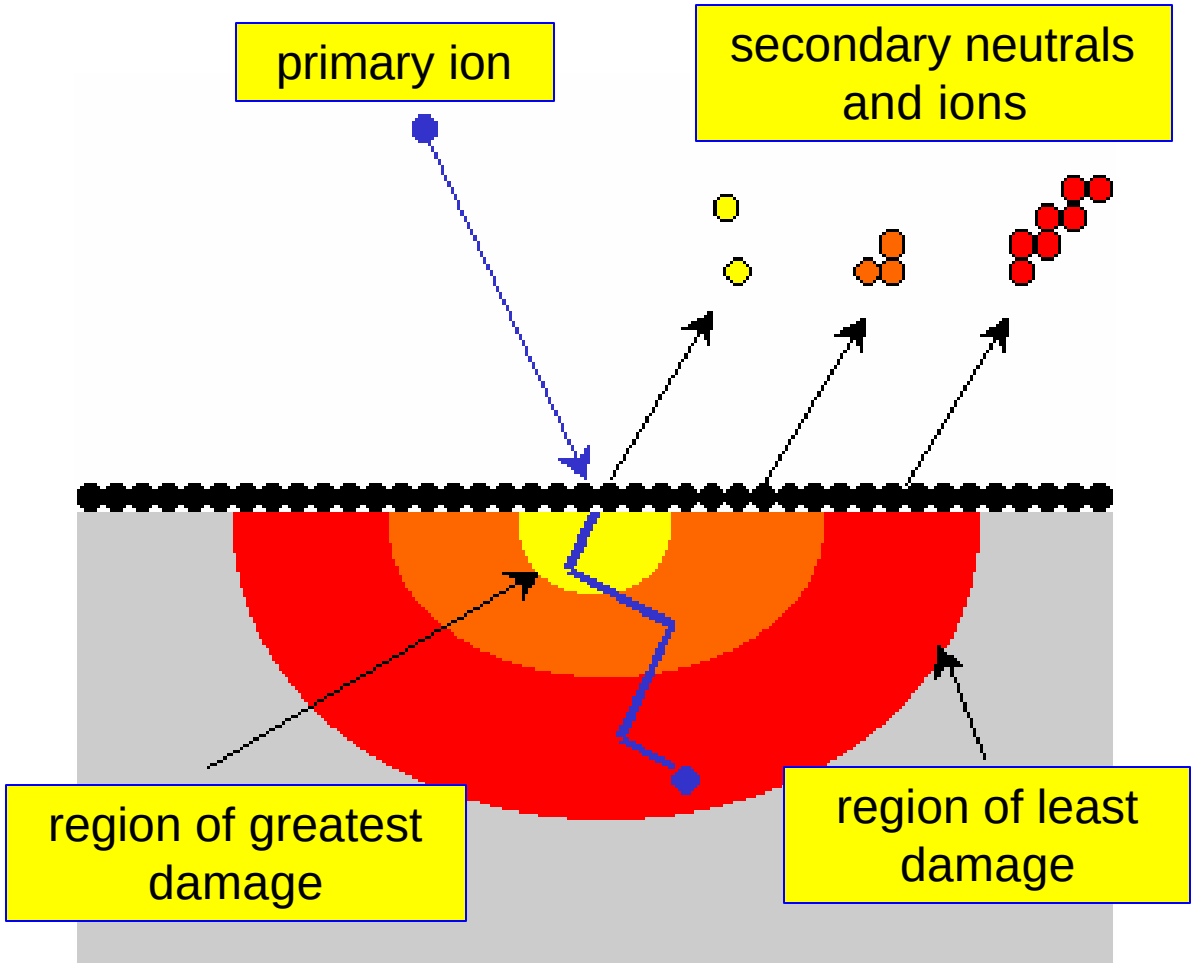
(such as Wallis Calaway, Jerry Moore, Michael Pellin, Bruce King, Mladen Petravic, Andreas Wucher….)

Argonne National Laboratory

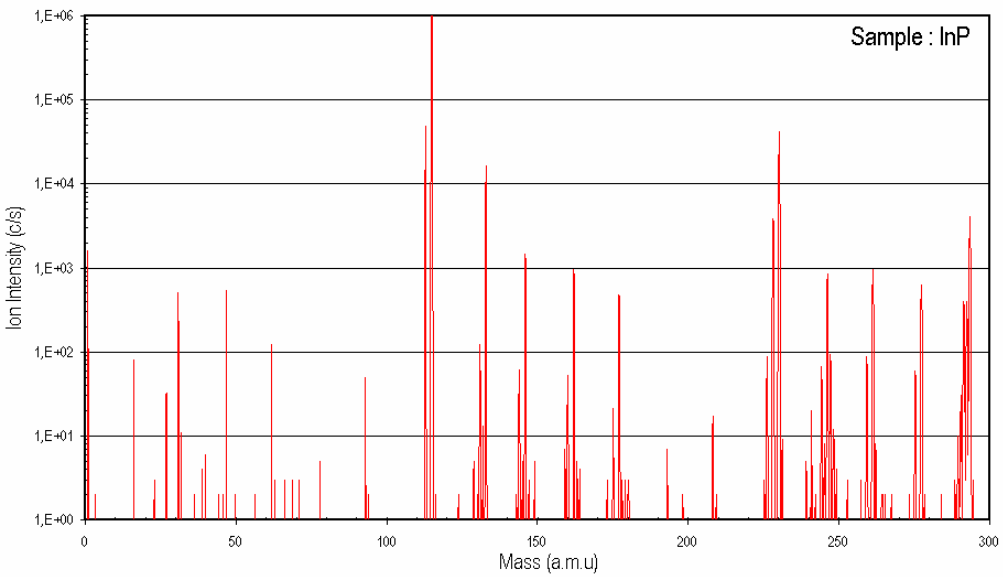
Office of Science
U.S. Department of Energy

A U.S. Department of Energy
Office of Science Laboratory
Operated by The University of Chicago

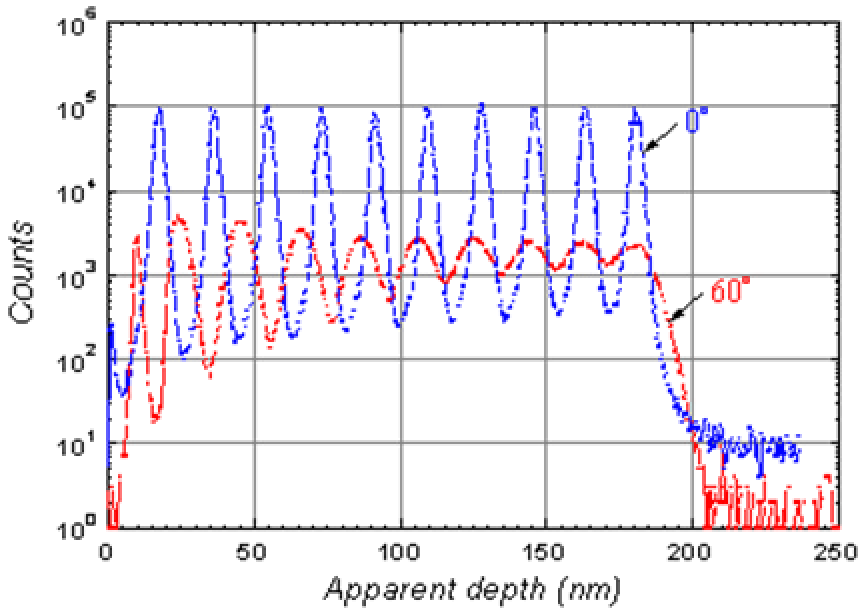
Emission of secondary neutrals and ions under energetic ion bombardment



The most important capabilities of ion sputtering based family of analytical techniques – surface analysis and depth profiling

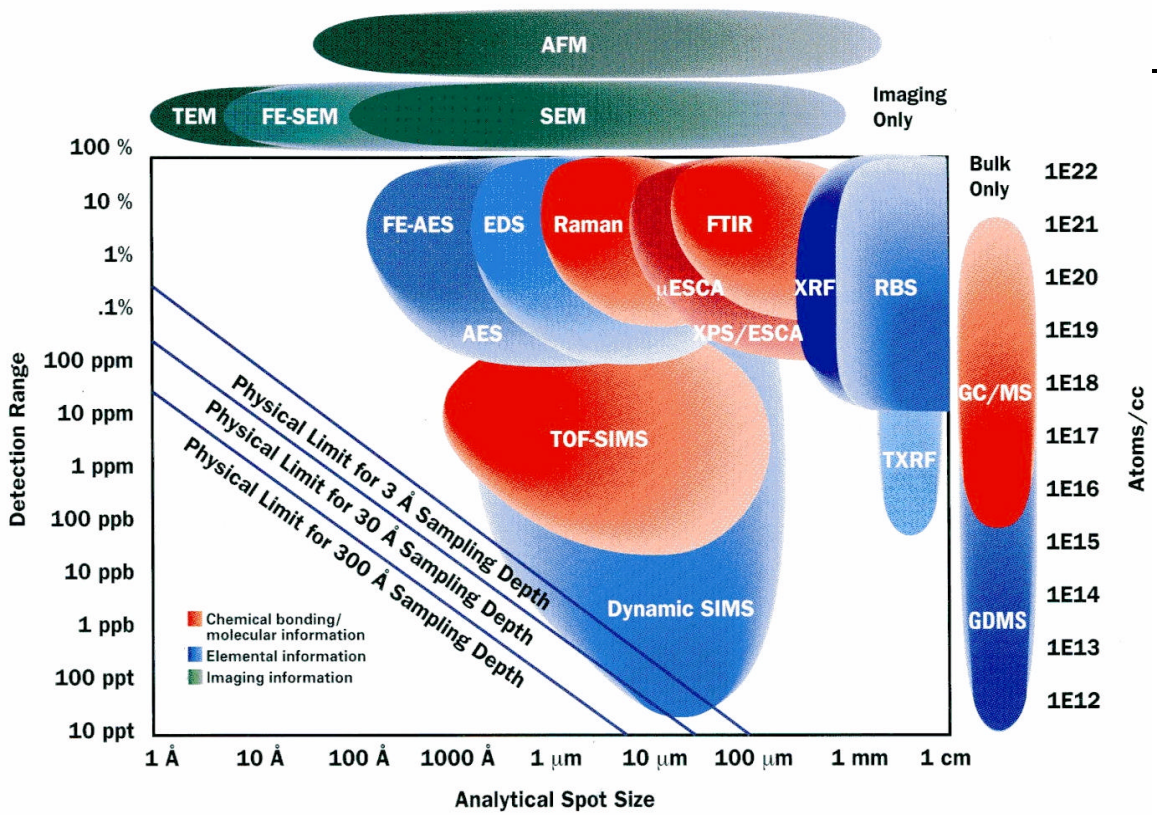


Typical mass spectrum

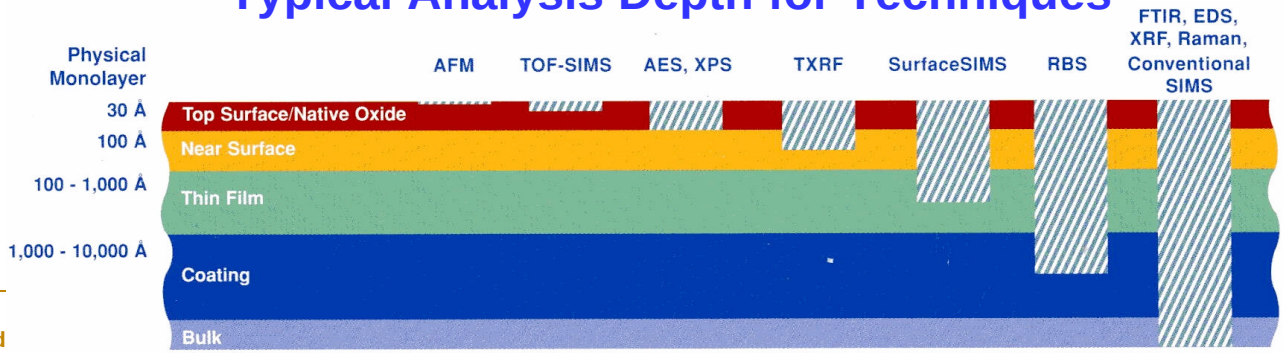


Typical depth profile of multilayered material

Analytical Resolution versus Detection Limit



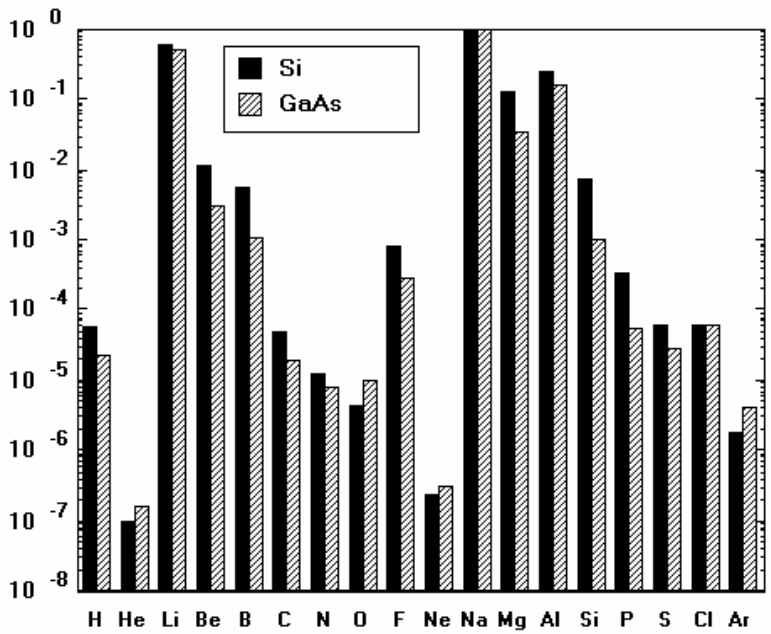
Typical Analysis Depth for Techniques



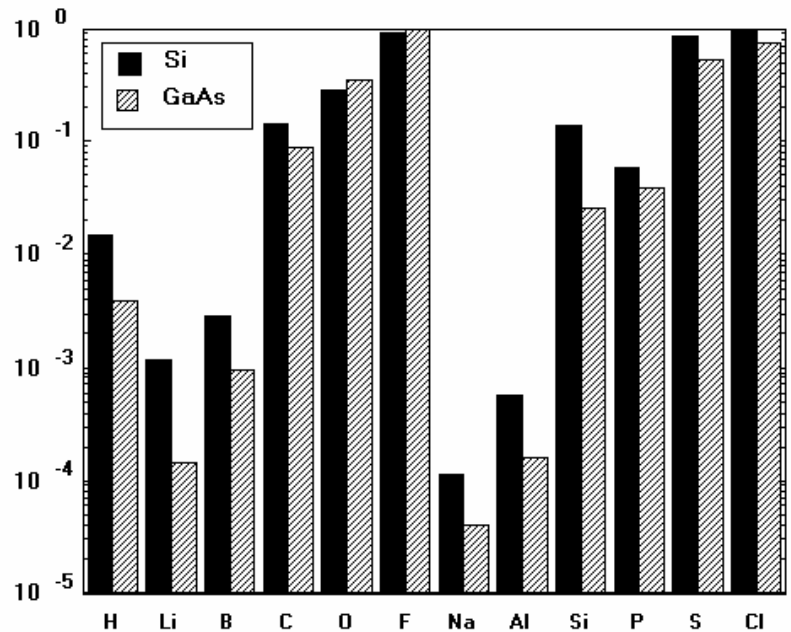
The greatest drawback of SIMS - Matrix effects

- ionization efficiencies for different elements can differ orders of magnitude
- even the same elements sputtered from different samples have different ionization efficiency

O_2^+ ion bombardment



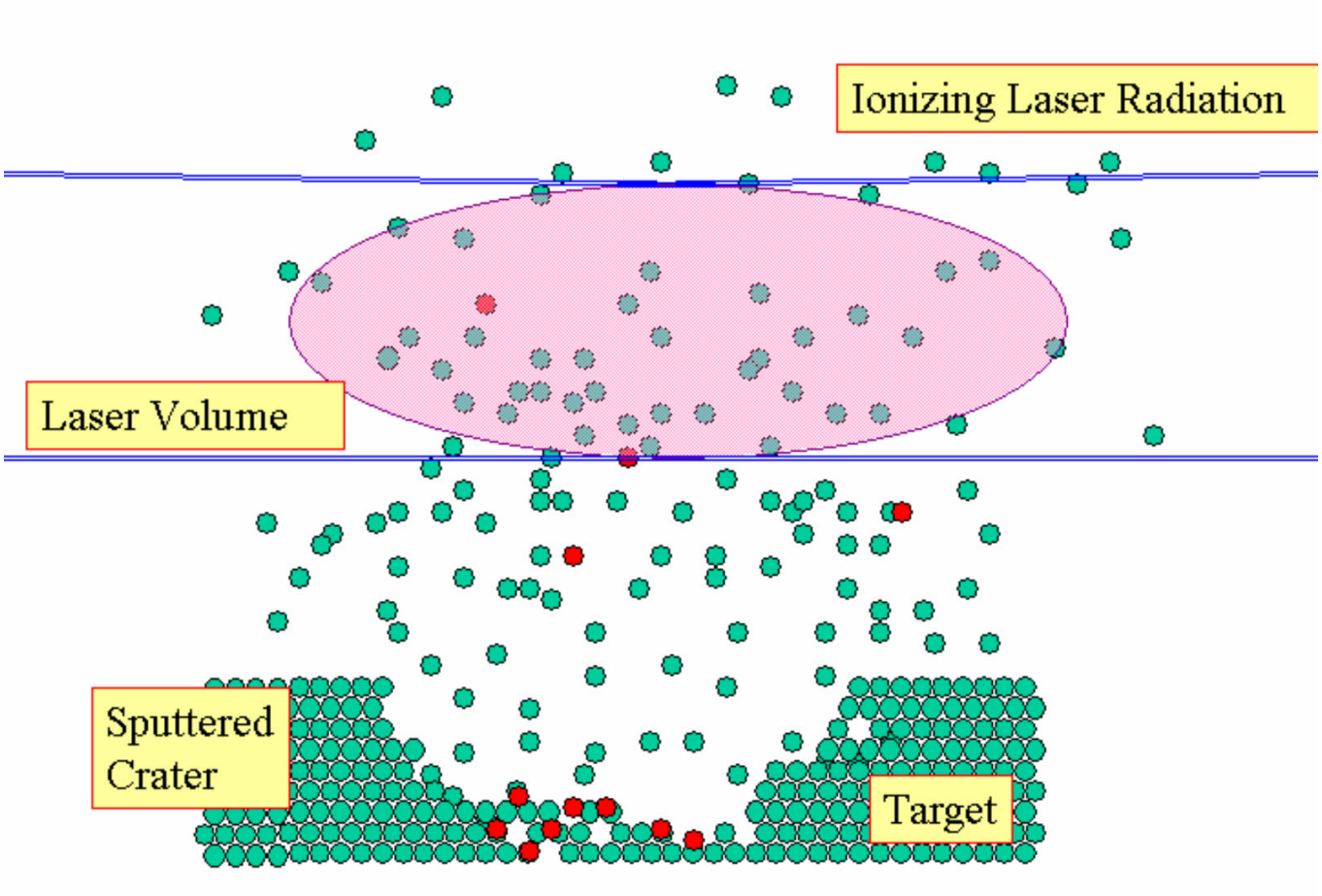
Cs^+ ion bombardment



Positive secondary ions **Negative secondary ions**

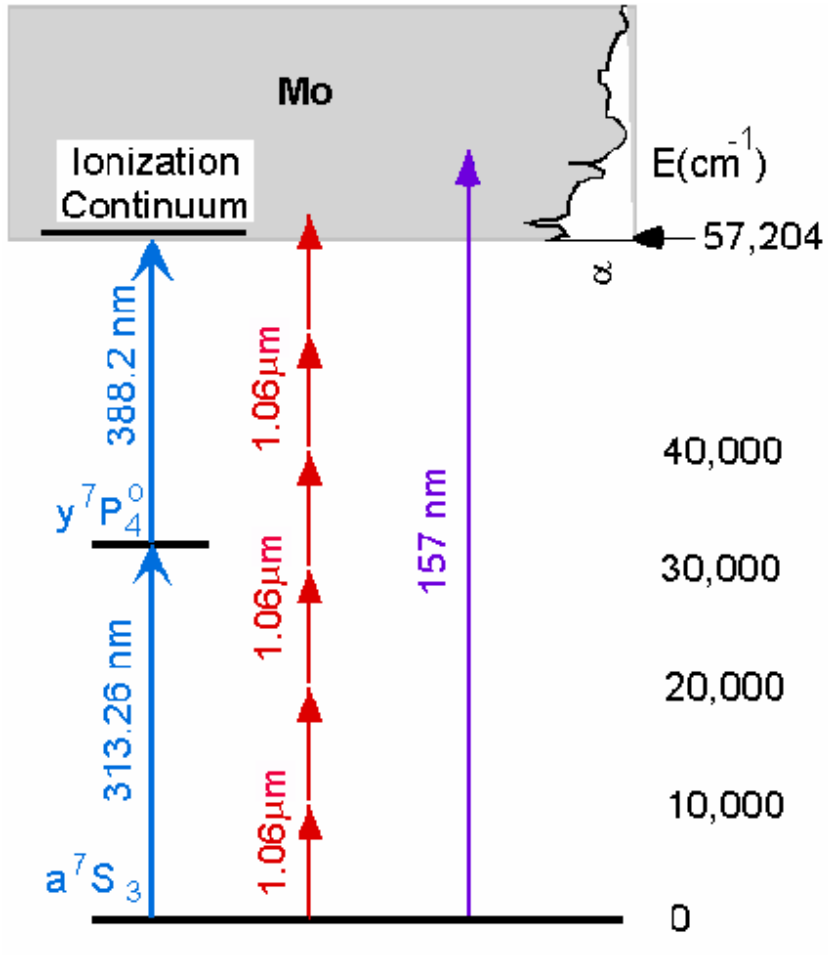
This limits both the accuracy and the sensitivity of analysis

Laser post-ionization SNMS is potentially free of the drawbacks of SIMS



Desorbed flux in the volume above the target is a very complex mixture of neutrals and ions, which is **dominated by the neutral component**.

Photo-ionization regimes



- *Non-resonant Multi-Photon Ionization (MPI)*
  - Universal ionization
  - Quantification more difficult: hard to saturate
  - Very high intensity lasers required for saturation
- *Resonantly Enhanced Multi-Photon Ionization (REMPI)*
  - Single element specific
  - Quantification (saturation) easier
  - Tunable lasers required for resonance mode
- *Single Photon Ionization (SPI)*
  - Photon energy must exceed Ionization Potential (IP)
  - Quantification easier
  - Resonance (auto-ionizing) regime is possible with the new VUV FEL

PERIODIC TABLE

Atomic Properties of the Elements

NIST
National Institute of Standards and Technology
Technology Administration, U.S. Department of Commerce

Physics Laboratory
physics.nist.gov

Standard Reference Data Group
www.nist.gov/srd

Frequently used fundamental physical constants

For the most accurate values of these and other constants, visit physics.nist.gov/constants

1 second = 9 192 631 770 periods of radiation corresponding to the transition between the two hyperfine levels of the ground state of ^{133}Cs

speed of light in vacuum	c	299 792 458 m s^{-1}	(exact)
Planck constant	h	6.6261×10^{-34} J s	($\hbar = h/2\pi$)
elementary charge	e	1.6022×10^{-19} C	
electron mass	m_e	9.1094×10^{-31} kg	
	$m_e c^2$	0.5110 MeV	
proton mass	m_p	1.6726×10^{-27} kg	
fine-structure constant	α	1/137.036	
Rydberg constant	R_∞	10 973 732 m^{-1}	
	$R_\infty c$	$3.289\,842 \times 10^{15}$ Hz	
	$R_\infty hc$	13.6057 eV	
Boltzmann constant	k	1.3807×10^{-23} J K^{-1}	

Solids
Liquids
Gases
Artificially Prepared

Group 1 IA | 2 IIA | 3 IIIB | 4 IVB | 5 VB | 6 VIB | 7 VIIB | 8 | 9 | 10 VIII | 11 IB | 12 IIB | 13 IIIA | 14 IVA | 15 VA | 16 VIA | 17 VIIA | 18 VIIIA

Period

Atomic Number	Symbol	Name	Ground-state Level	Atomic Weight†	Ground-state Configuration	Ionization Energy (eV)
1	H	Hydrogen	$^2S_{1/2}$	1.00794	1s	13.5984
2	He	Helium	$^1S_0$	4.002602	$1s^2$	24.5874
3	Li	Lithium	$^2S_{1/2}$	6.941	$1s^2 2s$	5.3917
4	Be	Beryllium	$^1S_0$	9.012182	$1s^2 2s^2$	9.3227
5	B	Boron	$^2P^\circ_{1/2}$	10.811	$1s^2 2s^2 2p$	8.2980
6	C	Carbon	$^3P_0$	12.0107	$1s^2 2s^2 2p^2$	11.2603
7	N	Nitrogen	$^4S^\circ_{3/2}$	14.0067	$1s^2 2s^2 2p^3$	14.5341
8	O	Oxygen	$^3P_2$	15.9994	$1s^2 2s^2 2p^4$	13.6181
9	F	Fluorine	$^2P^\circ_{3/2}$	18.9984032	$1s^2 2s^2 2p^5$	17.4228
10	Ne	Neon	$^1S_0$	20.1797	$1s^2 2s^2 2p^6$	21.5645
11	Na	Sodium	$^2S_{1/2}$	22.989770	[Ne]3s	5.1391
12	Mg	Magnesium	$^1S_0$	24.3050	$[Ne]3s^2$	7.6462
13	Al	Aluminum	$^2P^\circ_{1/2}$	26.981538	$[Ne]3s^2 3p$	5.9858
14	Si	Silicon	$^3P_0$	28.0855	$[Ne]3s^2 3p^2$	8.1517
15	P	Phosphorus	$^4S^\circ_{3/2}$	30.973761	$[Ne]3s^2 3p^3$	10.4867
16	S	Sulfur	$^3P_2$	32.065	$[Ne]3s^2 3p^4$	10.3600
17	Cl	Chlorine	$^2P^\circ_{3/2}$	35.453	$[Ne]3s^2 3p^5$	12.9676
18	Ar	Argon	$^1S_0$	39.948	$[Ne]3s^2 3p^6$	15.7596
19	K	Potassium	$^2S_{1/2}$	39.0983	[Ar]4s	4.3407
20	Ca	Calcium	$^1S_0$	40.078	$[Ar]4s^2$	6.1132
21	Sc	Scandium	$^2D_{3/2}$	44.955910	$[Ar]3d4s^2$	6.5615
22	Ti	Titanium	$^3F_2$	47.867	$[Ar]3d^2 4s^2$	6.8281
23	V	Vanadium	$^4F_{3/2}$	50.9415	$[Ar]3d^3 4s^2$	6.7462
24	Cr	Chromium	$^7S_3$	51.9961	$[Ar]3d^5 4s$	6.7665
25	Mn	Manganese	$^6S_{5/2}$	54.938049	$[Ar]3d^5 4s^2$	7.4340
26	Fe	Iron	$^5D_4$	55.845	$[Ar]3d^6 4s^2$	7.9024
27	Co	Cobalt	$^4F_{9/2}$	58.933200	$[Ar]3d^7 4s^2$	7.8810
28	Ni	Nickel	$^3F_4$	58.6934	$[Ar]3d^8 4s^2$	7.6398
29	Cu	Copper	$^2S_{1/2}$	63.546	$[Ar]3d^{10} 4s$	7.7264
30	Zn	Zinc	$^1S_0$	65.409	$[Ar]3d^{10} 4s^2$	9.3942
31	Ga	Gallium	$^2P^\circ_{1/2}$	69.723	$[Ar]3d^{10} 4s^2 4p$	5.9993
32	Ge	Germanium	$^3P_0$	72.64	$[Ar]3d^{10} 4s^2 4p^2$	7.8994
33	As	Arsenic	$^4S^\circ_{3/2}$	74.92160	$[Ar]3d^{10} 4s^2 4p^3$	9.7886
34	Se	Selenium	$^3P_2$	78.96	$[Ar]3d^{10} 4s^2 4p^4$	9.7524
35	Br	Bromine	$^2P^\circ_{3/2}$	79.904	$[Ar]3d^{10} 4s^2 4p^5$	11.8138
36	Kr	Krypton	$^1S_0$	83.798	$[Ar]3d^{10} 4s^2 4p^6$	13.9996
37	Rb	Rubidium	$^2S_{1/2}$	85.4678	[Kr]5s	4.1771
38	Sr	Strontium	$^1S_0$	87.62	$[Kr]5s^2$	5.6949
39	Y	Yttrium	$^2D_{3/2}$	88.90585	$[Kr]4d5s^2$	6.2173
40	Zr	Zirconium	$^3F_2$	91.224	$[Kr]4d^2 5s^2$	6.6339
41	Nb	Niobium	$^6D_{1/2}$	92.90638	$[Kr]4d^4 5s$	6.7589
42	Mo	Molybdenum	$^7S_3$	95.94	$[Kr]4d^5 5s$	7.0924
43	Tc	Technetium	$^6S_{5/2}$	(98)	$[Kr]4d^5 5s^2$	7.28
44	Ru	Ruthenium	$^5F_5$	101.07	$[Kr]4d^7 5s$	7.3605
45	Rh	Rhodium	$^4F_{9/2}$	102.90550	$[Kr]4d^8 5s$	7.4589
46	Pd	Palladium	$^1S_0$	106.42	$[Kr]4d^{10}$	8.3369
47	Ag	Silver	$^2S_{1/2}$	107.8682	$[Kr]4d^{10} 5s$	7.5762
48	Cd	Cadmium	$^1S_0$	112.411	$[Kr]4d^{10} 5s^2$	8.9938
49	In	Indium	$^2P^\circ_{1/2}$	114.818	$[Kr]4d^{10} 5s^2 5p$	5.7864
50	Sn	Tin	$^3P_0$	118.710	$[Kr]4d^{10} 5s^2 5p^2$	7.3439
51	Sb	Antimony	$^4S^\circ_{3/2}$	121.760	$[Kr]4d^{10} 5s^2 5p^3$	8.6084
52	Te	Tellurium	$^3P_2$	127.60	$[Kr]4d^{10} 5s^2 5p^4$	9.0096
53	I	Iodine	$^2P^\circ_{3/2}$	126.90447	$[Kr]4d^{10} 5s^2 5p^5$	10.4513
54	Xe	Xenon	$^1S_0$	131.293	$[Kr]4d^{10} 5s^2 5p^6$	12.1298
55	Cs	Cesium	$^2S_{1/2}$	132.90545	[Xe]6s	3.8939
56	Ba	Barium	$^1S_0$	137.327	$[Xe]6s^2$	5.2117
72	Hf	Hafnium	$^3F_2$	178.49	$[Xe]4f^{14} 5d^2 6s^2$	6.8251
73	Ta	Tantalum	$^4F_{3/2}$	180.9479	$[Xe]4f^{14} 5d^3 6s^2$	7.5496
74	W	Tungsten	$^5D_0$	183.84	$[Xe]4f^{14} 5d^4 6s^2$	7.8640
75	Re	Rhenium	$^6S_{5/2}$	186.207	$[Xe]4f^{14} 5d^5 6s^2$	7.8335
76	Os	Osmium	$^5D_4$	190.23	$[Xe]4f^{14} 5d^6 6s^2$	8.4382
77	Ir	Iridium	$^4F_{9/2}$	192.217	$[Xe]4f^{14} 5d^7 6s^2$	8.9670
78	Pt	Platinum	$^3D_3$	195.078	$[Xe]4f^{14} 5d^9 6s$	8.9588
79	Au	Gold	$^2S_{1/2}$	196.96655	$[Xe]4f^{14} 5d^{10} 6s$	9.2255
80	Hg	Mercury	$^1S_0$	200.59	$[Xe]4f^{14} 5d^{10} 6s^2$	10.4375
81	Tl	Thallium	$^2P^\circ_{1/2}$	204.3833	[Hg]6p	6.1082
82	Pb	Lead	$^3P_0$	207.2	$[Hg]6p^2$	7.4167
83	Bi	Bismuth	$^4S^\circ_{3/2}$	208.98038	$[Hg]6p^3$	7.2855
84	Po	Polonium	$^3P_2$	(209)	$[Hg]6p^4$	8.414
85	At	Astatine	$^2P^\circ_{3/2}$	(210)	$[Hg]6p^5$	
86	Rn	Radon	$^1S_0$	(222)	$[Hg]6p^6$	10.7485
87	Fr	Francium	$^2S_{1/2}$	(223)	[Rn]7s	4.0727
88	Ra	Radium	$^1S_0$	(226)	$[Rn]7s^2$	5.2784
104	Rf	Rutherfordium	$^3F_2$?	(261)	$[Rn]5f^{14} 6d^2 7s^2$?	6.0 ?
105	Db	Dubnium		(262)		
106	Sg	Seaborgium		(266)		
107	Bh	Bohrium		(264)		
108	Hs	Hassium		(277)		
109	Mt	Meitnerium		(268)		
110	Uun	Ununnilium		(281)		
111	Uuu	Unununium		(272)		
112	Uub	Ununbium		(285)		
114	Uuq	Ununquadium		(289)		
116	Uuh	Ununhexium		(292)		
57	La	Lanthanum	$^2D_{3/2}$	138.9055	$[Xe]5d6s^2$	5.5769
58	Ce	Cerium	$^1G^\circ_4$	140.116	$[Xe]4f5d6s^2$	5.5387
59	Pr	Praseodymium	$^4I^\circ_{9/2}$	140.90765	$[Xe]4f^3 6s^2$	5.473
60	Nd	Neodymium	$^5I_4$	144.24	$[Xe]4f^4 6s^2$	5.5250
61	Pm	Promethium	$^6H^\circ_{5/2}$	(145)	$[Xe]4f^5 6s^2$	5.582
62	Sm	Samarium	$^7F_0$	150.36	$[Xe]4f^6 6s^2$	5.6437
63	Eu	Europium	$^8S^\circ_{7/2}$	151.964	$[Xe]4f^7 6s^2$	5.6704
64	Gd	Gadolinium	$^9D^\circ_2$	157.25	$[Xe]4f^7 5d6s^2$	6.1498
65	Tb	Terbium	$^6H^\circ_{15/2}$	158.92534	$[Xe]4f^9 6s^2$	5.8638
66	Dy	Dysprosium	$^5I_8$	162.500	$[Xe]4f^{10} 6s^2$	5.9389
67	Ho	Holmium	$^4I^\circ_{15/2}$	164.93032	$[Xe]4f^{11} 6s^2$	6.0215
68	Er	Erbium	$^3H_6$	167.259	$[Xe]4f^{12} 6s^2$	6.1077
69	Tm	Thulium	$^2F^\circ_{7/2}$	168.93421	$[Xe]4f^{13} 6s^2$	6.1843
70	Yb	Ytterbium	$^1S_0$	173.04	$[Xe]4f^{14} 6s^2$	6.2542
71	Lu	Lutetium	$^2D_{3/2}$	174.967	$[Xe]4f^{14} 5d6s^2$	5.4259
89	Ac	Actinium	$^2D_{3/2}$	(227)	$[Rn]6d7s^2$	5.17
90	Th	Thorium	$^3F_2$	232.0381	$[Rn]6d^2 7s^2$	6.3067
91	Pa	Protactinium	$^4K_{11/2}$	231.03588	$[Rn]5f^2 6d7s^2$	5.89
92	U	Uranium	$^5L^\circ_6$	238.02891	$[Rn]5f^3 6d7s^2$	6.1941
93	Np	Neptunium	$^6L_{11/2}$	(237)	$[Rn]5f^4 6d7s^2$	6.2657
94	Pu	Plutonium	$^7F_0$	(244)	$[Rn]5f^6 7s^2$	6.0260
95	Am	Americium	$^8S^\circ_{7/2}$	(243)	$[Rn]5f^7 7s^2$	5.9738
96	Cm	Curium	$^9D^\circ_2$	(247)	$[Rn]5f^7 6d7s^2$	5.9914
97	Bk	Berkelium	$^6H^\circ_{15/2}$	(247)	$[Rn]5f^9 7s^2$	6.1979
98	Cf	Californium	$^5I_8$	(251)	$[Rn]5f^{10} 7s^2$	6.2817
99	Es	Einsteinium	$^4I^\circ_{15/2}$	(252)	$[Rn]5f^{11} 7s^2$	6.42
100	Fm	Fermium	$^3H_6$	(257)	$[Rn]5f^{12} 7s^2$	6.50
101	Md	Mendelevium	$^2F^\circ_{7/2}$	(258)	$[Rn]5f^{13} 7s^2$	6.58
102	No	Nobelium	$^1S_0$	(259)	$[Rn]5f^{14} 7s^2$	6.65
103	Lr	Lawrencium	$^2P^\circ_{1/2}$?	(262)	$[Rn]5f^{14} 7s^2 7p$?	4.9 ?

Lanthanides
Actinides

†Based upon ^{12}C. () indicates the mass number of the most stable isotope.

For a description of the data, visit physics.nist.gov/data

NIST SP 966 (September 2003)

Periodic Table of Photo-ionization:

SPI with F_2 laser (157.63 nm ~ 7.866 eV and 157.52 nm ~ 7.871 eV)

Atomic number — no — yes — Element

Ionization Potential (eV)

1 H 13.6																	2 He 24.59
3 Li 5.39	4 Be 9.32						1 H 13.6					5 B 8.30	6 C 11.26	7 N 14.53	8 O 13.82	9 F 17.42	10 Ne 21.57
11 Na 5.14	12 Mg 7.65											13 Al 5.99	14 Si 8.15	15 P 10.49	16 S 10.36	17 Cl 12.97	18 Ar 15.76
19 K 4.34	20 Ca 6.11	21 Sc 6.56	22 Ti 6.83	23 V 6.75	24 Cr 6.77	25 Mn 7.43	26 Fe 7.90	27 Co 7.88	28 Ni 7.64	29 Cu 7.73	30 Zn 9.39	31 Ga 6.0	32 Ge 7.90	33 As 9.79	34 Se 9.75	35 Br 11.81	36 Kr 14.0
37 Rb 4.18	38 Sr 5.70	39 Y 6.22	40 Zr 6.63	41 Nb 6.76	42 Mo 7.09	43 Tc 7.28	44 Ru 7.36	45 Rh 7.46	46 Pd 8.34	47 Ag 7.58	48 Cd 8.99	49 In 5.79	50 Sn 7.34	51 Sb 8.61	52 Te 9.01	53 I 10.45	54 Xe 12.12
55 Cs 3.89	56 Ba 5.21	57 La* 5.58	72 Hf 6.83	73 Ta 7.55	74 W 7.86	75 Re 7.83	76 Os 8.44	77 Ir 8.97	78 Pt 8.96	79 Au 9.23	80 Hg 10.44	81 Tl 6.11	82 Pb 7.42	83 Bi 7.29	84 Po 8.42	85 At 9.65	86 Rn 10.76
87 Fr 4.07	88 Ra 5.28	89 Ac~ 5.17	104 Rf 6.0 ?	105 Db	106 Sg	107 Bh	108 Hs	109 Mt									
Lanthanide Series *		58 Ce 5.54	59 Pr 5.47	60 Nd 5.53	61 Pm 5.58	62 Sm 5.64	63 Eu 5.67	64 Gd 6.15	65 Tb 5.86	66 Dy 5.94	67 Ho 6.02	68 Er 6.11	69 Tm 6.18	70 Yb 6.25	71 Lu 5.43		
Actinide Series ~		90 Th 6.31	91 Pa 5.89	92 U 6.19	93 Np 6.27	94 Pu 6.03	95 Am 5.97	96 Cm 5.99	97 Bk 6.20	98 Cf 6.28	99 Es 6.42	100 Fm 6.50	101 Md 6.58	102 No 6.65	103 Lr 4.9 ?		

Periodic Table of Photo-ionization:

SPI with Conventional Tunable Lasers (³200 nm ~ £6.2 eV)

Atomic number

Ionization Potential (eV)

Element

1 H 13.6																	2 He 24.59
3 Li 5.39	4 Be 9.32											5 B 8.30	6 C 11.26	7 N 14.53	8 O 13.82	9 F 17.42	10 Ne 21.57
11 Na 5.14	12 Mg 7.65											13 Al 5.99	14 Si 8.15	15 P 10.49	16 S 10.36	17 Cl 12.97	18 Ar 15.76
19 K 4.34	20 Ca 6.11	21 Sc 6.56	22 Ti 6.83	23 V 6.75	24 Cr 6.77	25 Mn 7.43	26 Fe 7.90	27 Co 7.88	28 Ni 7.64	29 Cu 7.73	30 Zn 9.39	31 Ga 6.0	32 Ge 7.90	33 As 9.79	34 Se 9.75	35 Br 11.81	36 Kr 14.0
37 Rb 4.18	38 Sr 5.70	39 Y 6.22	40 Zr 6.63	41 Nb 6.76	42 Mo 7.09	43 Tc 7.28	44 Ru 7.36	45 Rh 7.46	46 Pd 8.34	47 Ag 7.58	48 Cd 8.99	49 In 5.79	50 Sn 7.34	51 Sb 8.61	52 Te 9.01	53 I 10.45	54 Xe 12.12
55 Cs 3.89	56 Ba 5.21	57 La* 5.58	72 Hf 6.83	73 Ta 7.55	74 W 7.86	75 Re 7.83	76 Os 8.44	77 Ir 8.97	78 Pt 8.96	79 Au 9.23	80 Hg 10.44	81 Tl 6.11	82 Pb 7.42	83 Bi 7.29	84 Po 8.42	85 At 9.65	86 Rn 10.76
87 Fr 4.07	88 Ra 5.28	89 Ac~ 5.17	104 Rf 6.0 ?	105 Db	106 Sg	107 Bh	108 Hs	109 Mt									
Lanthanide Series *		58 Ce 5.54	59 Pr 5.47	60 Nd 5.53	61 Pm 5.58	62 Sm 5.64	63 Eu 5.67	64 Gd 6.15	65 Tb 5.86	66 Dy 5.94	67 Ho 6.02	68 Er 6.11	69 Tm 6.18	70 Yb 6.25	71 Lu 5.43		
Actinide Series ~		90 Th 6.31	91 Pa 5.89	92 U 6.19	93 Np 6.27	94 Pu 6.03	95 Am 5.97	96 Cm 5.99	97 Bk 6.20	98 Cf 6.28	99 Es 6.42	100 Fm 6.50	101 Md 6.58	102 No 6.65	103 Lr 4.9 ?		

Periodic Table of Photo-ionization:

REMPI with Conventional Tunable Lasers

Atomic number

Ionization Potential (eV)

Element

1 H 13.6																	2 He 24.59
3 Li 5.39	4 Be 9.32											5 B 8.30	6 C 11.26	7 N 14.53	8 O 13.82	9 F 17.42	10 Ne 21.57
11 Na 5.14	12 Mg 7.65											13 Al 5.99	14 Si 8.15	15 P 10.49	16 S 10.36	17 Cl 12.97	18 Ar 15.76
19 K 4.34	20 Ca 6.11	21 Sc 6.56	22 Ti 6.83	23 V 6.75	24 Cr 6.77	25 Mn 7.43	26 Fe 7.90	27 Co 7.88	28 Ni 7.64	29 Cu 7.73	30 Zn 9.39	31 Ga 6.0	32 Ge 7.90	33 As 9.79	34 Se 9.75	35 Br 11.81	36 Kr 14.0
37 Rb 4.18	38 Sr 5.70	39 Y 6.22	40 Zr 6.63	41 Nb 6.76	42 Mo 7.09	43 Tc 7.28	44 Ru 7.36	45 Rh 7.46	46 Pd 8.34	47 Ag 7.58	48 Cd 8.99	49 In 5.79	50 Sn 7.34	51 Sb 8.61	52 Te 9.01	53 I 10.45	54 Xe 12.12
55 Cs 3.89	56 Ba 5.21	57 La* 5.58	72 Hf 6.83	73 Ta 7.55	74 W 7.86	75 Re 7.83	76 Os 8.44	77 Ir 8.97	78 Pt 8.96	79 Au 9.23	80 Hg 10.44	81 Tl 6.11	82 Pb 7.42	83 Bi 7.29	84 Po 8.42	85 At 9.65	86 Rn 10.76
87 Fr 4.07	88 Ra 5.28	89 Ac~ 5.17	104 Rf 6.0 ?	105 Db	106 Sg	107 Bh	108 Hs	109 Mt									
Lanthanide Series *		58 Ce 5.54	59 Pr 5.47	60 Nd 5.53	61 Pm 5.58	62 Sm 5.64	63 Eu 5.67	64 Gd 6.15	65 Tb 5.86	66 Dy 5.94	67 Ho 6.02	68 Er 6.11	69 Tm 6.18	70 Yb 6.25	71 Lu 5.43		
Actinide Series ~		90 Th 6.31	91 Pa 5.89	92 U 6.19	93 Np 6.27	94 Pu 6.03	95 Am 5.97	96 Cm 5.99	97 Bk 6.20	98 Cf 6.28	99 Es 6.42	100 Fm 6.50	101 Md 6.58	102 No 6.65	103 Lr 4.9 ?		

Periodic Table of Photo-ionization:

SPI with the new VUV FEL (55 nm ¸ 450 nm ~ 2.75 eV ¸ 22.54 eV)

Atomic number

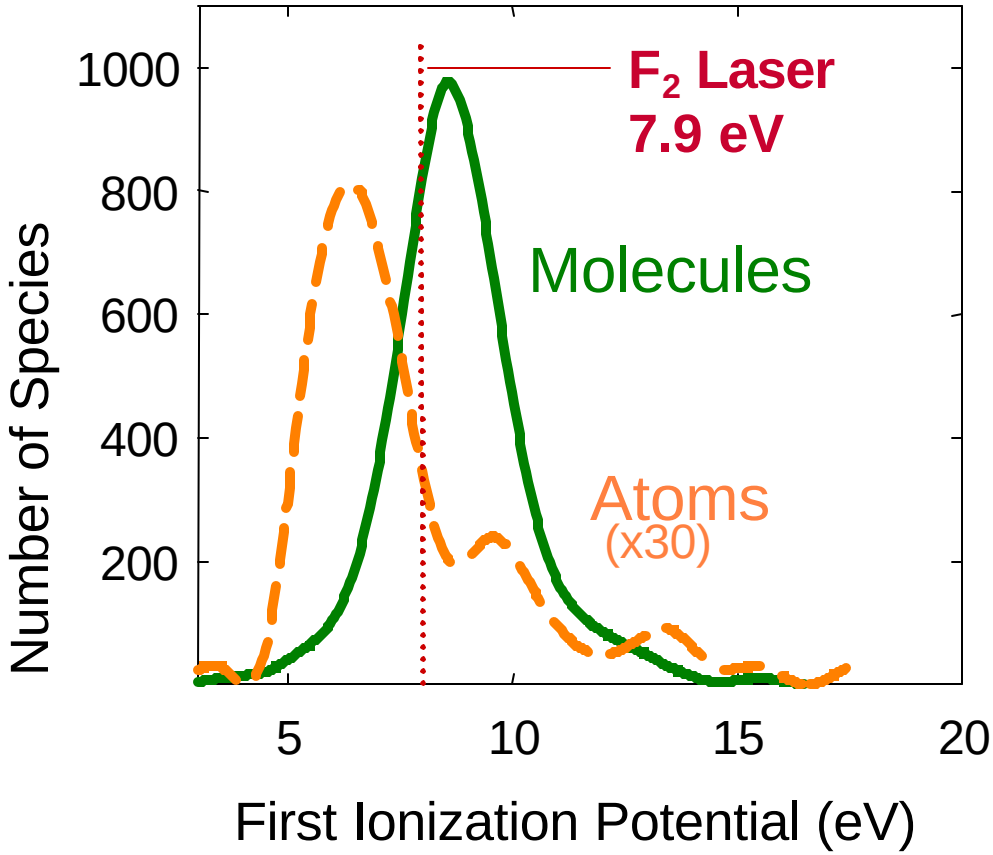
Ionization Potential (eV)

Element

1 H 13.6																	2 He 24.59
3 Li 5.39	4 Be 9.32											5 B 8.30	6 C 11.26	7 N 14.53	8 O 13.82	9 F 17.42	10 Ne 21.57
11 Na 5.14	12 Mg 7.65											13 Al 5.99	14 Si 8.15	15 P 10.49	16 S 10.36	17 Cl 12.97	18 Ar 15.76
19 K 4.34	20 Ca 6.11	21 Sc 6.56	22 Ti 6.83	23 V 6.75	24 Cr 6.77	25 Mn 7.43	26 Fe 7.90	27 Co 7.88	28 Ni 7.64	29 Cu 7.73	30 Zn 9.39	31 Ga 6.0	32 Ge 7.90	33 As 9.79	34 Se 9.75	35 Br 11.81	36 Kr 14.0
37 Rb 4.18	38 Sr 5.70	39 Y 6.22	40 Zr 6.63	41 Nb 6.76	42 Mo 7.09	43 Tc 7.28	44 Ru 7.36	45 Rh 7.46	46 Pd 8.34	47 Ag 7.58	48 Cd 8.99	49 In 5.79	50 Sn 7.34	51 Sb 8.61	52 Te 9.01	53 I 10.45	54 Xe 12.12
55 Cs 3.89	56 Ba 5.21	57 La* 5.58	72 Hf 6.83	73 Ta 7.55	74 W 7.86	75 Re 7.83	76 Os 8.44	77 Ir 8.97	78 Pt 8.96	79 Au 9.23	80 Hg 10.44	81 Tl 6.11	82 Pb 7.42	83 Bi 7.29	84 Po 8.42	85 At 9.65	86 Rn 10.76
87 Fr 4.07	88 Ra 5.28	89 Ac~ 5.17	104 Rf 6.0 ?	105 Db	106 Sg	107 Bh	108 Hs	109 Mt									
Lanthanide Series *		58 Ce 5.54	59 Pr 5.47	60 Nd 5.53	61 Pm 5.58	62 Sm 5.64	63 Eu 5.67	64 Gd 6.15	65 Tb 5.86	66 Dy 5.94	67 Ho 6.02	68 Er 6.11	69 Tm 6.18	70 Yb 6.25	71 Lu 5.43		
Actinide Series ~		90 Th 6.31	91 Pa 5.89	92 U 6.19	93 Np 6.27	94 Pu 6.03	95 Am 5.97	96 Cm 5.99	97 Bk 6.20	98 Cf 6.28	99 Es 6.42	100 Fm 6.50	101 Md 6.58	102 No 6.65	103 Lr 4.9 ?		

This is a Universal Ionization!

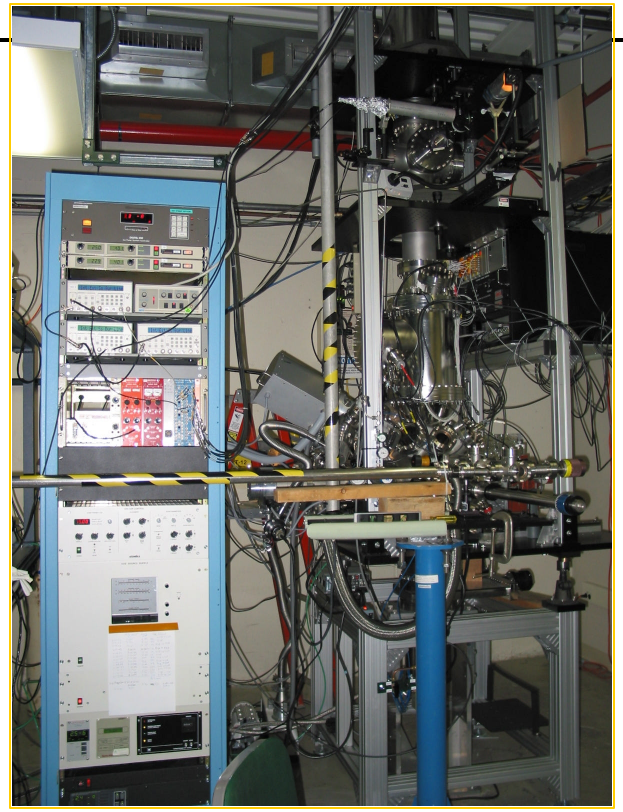
Distribution of First Ionization Potentials

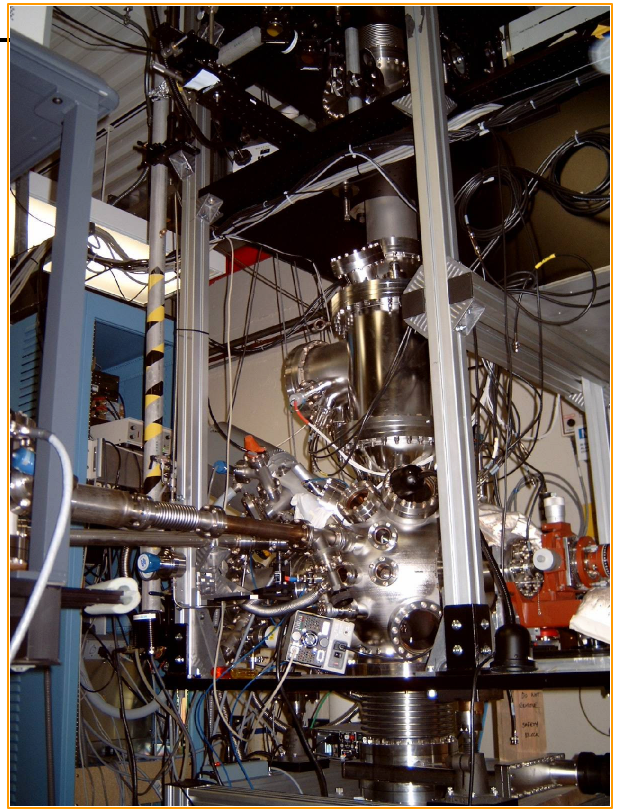


The new VUV FEL with the photon energy tunable up to 22.54 eV and 100 mJ/pulse will make possible saturation of the resonance SPI for almost every species!

It Would Be Great If There Was An Instrument That Could Take Full Advantage Of These Unique Opportunities…

We have already built one at the end station of the APS FEL!





First measurements with FEL: August 2002

Additional F_2 laser operational: March 2003

VUV optical spectrometer and power meters are operational: June 2003

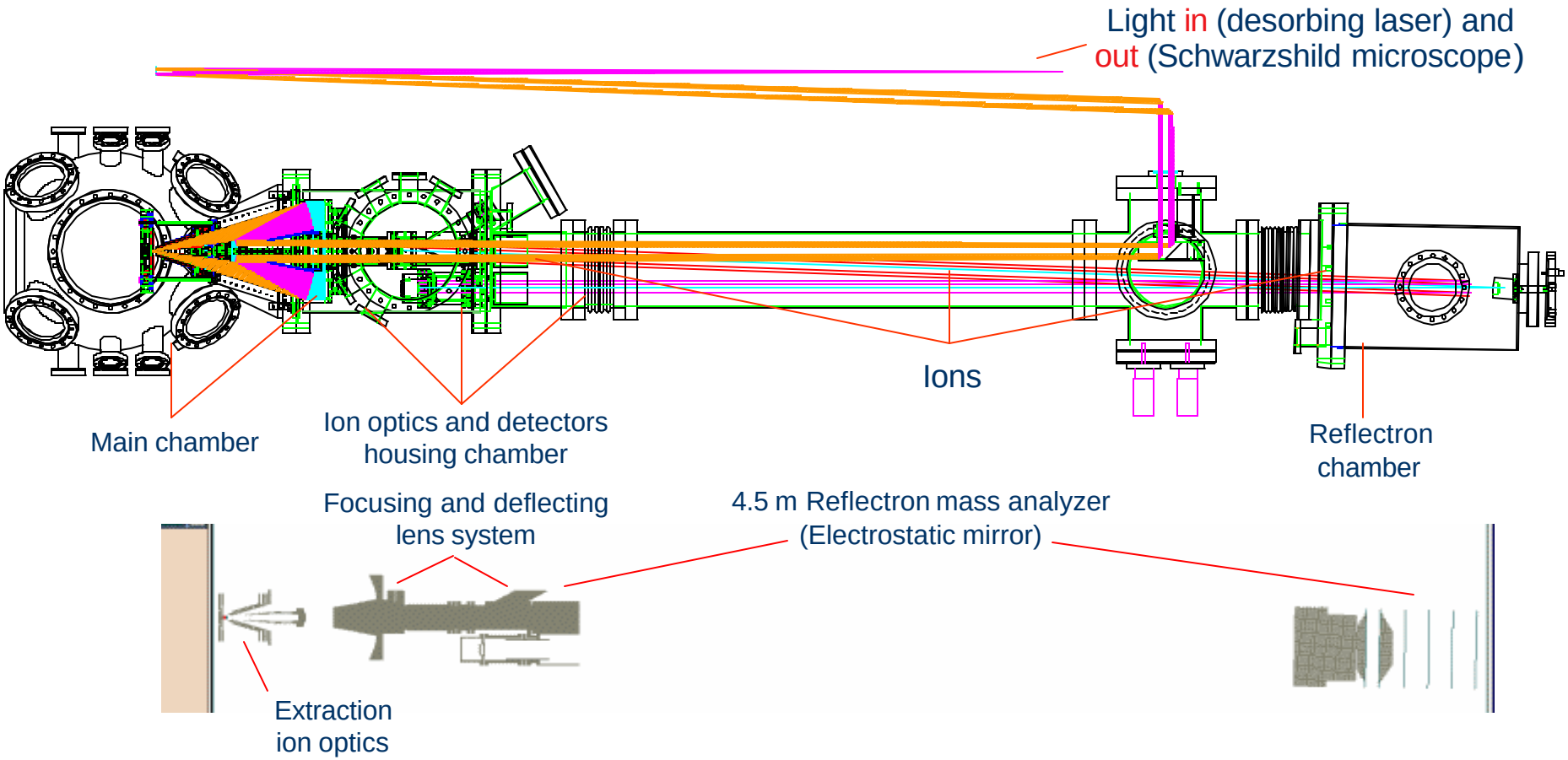
SPIRIT – Single Photon Ionization Resonance Ionization to Threshold – *is now fully operational LPI SNMS instrument with superb analytical capabilities*

The INSTRUMENT

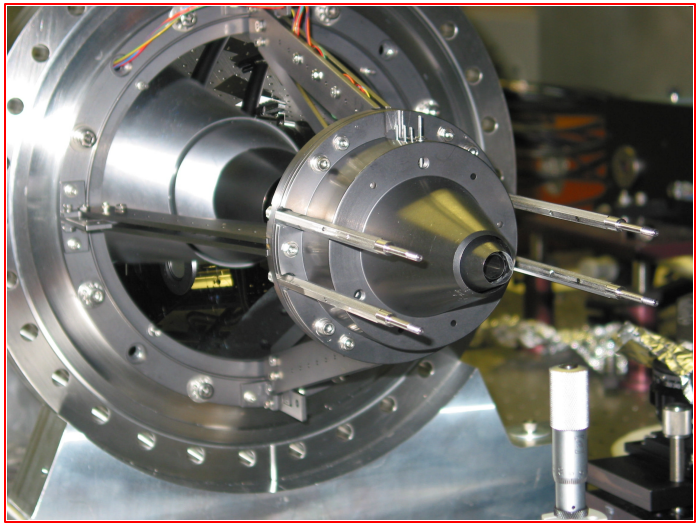
The development of this instrument was based on extensive computer modeling implementing virtual reality concept

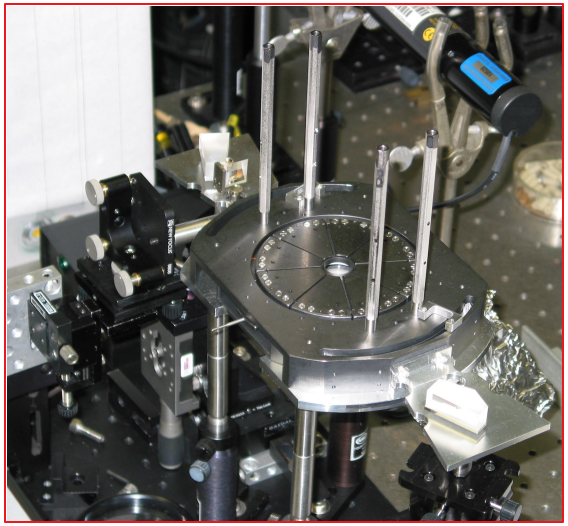
- Three-dimensional computer modeling of ion optics aided inventions of new ion optical systems. SIMION 3D© software was extensively used ion trajectory simulations.
- New data processing algorithms for results of ion trajectory simulations were developed. These algorithms used data base managing principles and distributed parallel computing.
- Three-dimensional design of all new components was aided by AutoCAD©.
- Characterization of analytical capabilities of SPIRIT was performed prior to their construction using computer modeling, whose accuracy was proven with real LPI SNMS instruments operated in our lab.

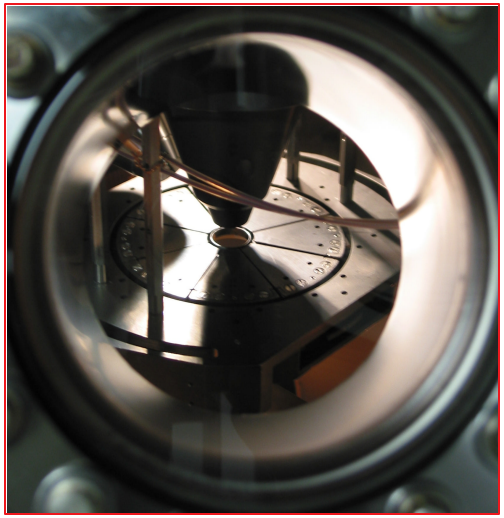
The INSTRUMENT: how it works

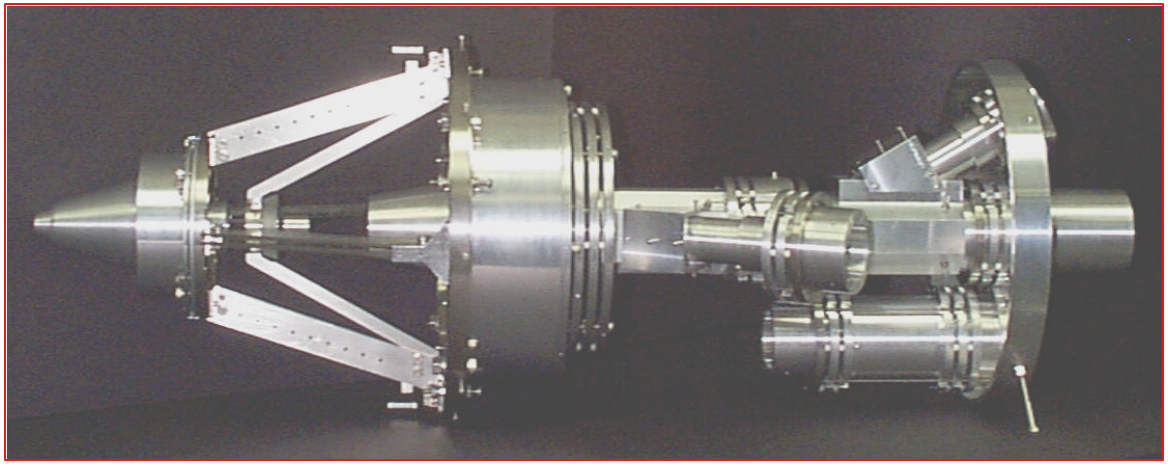


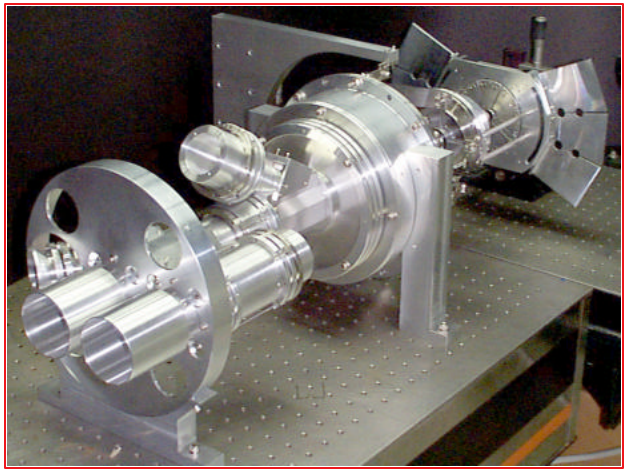
The INSTRUMENT: what is inside – ion and light optics



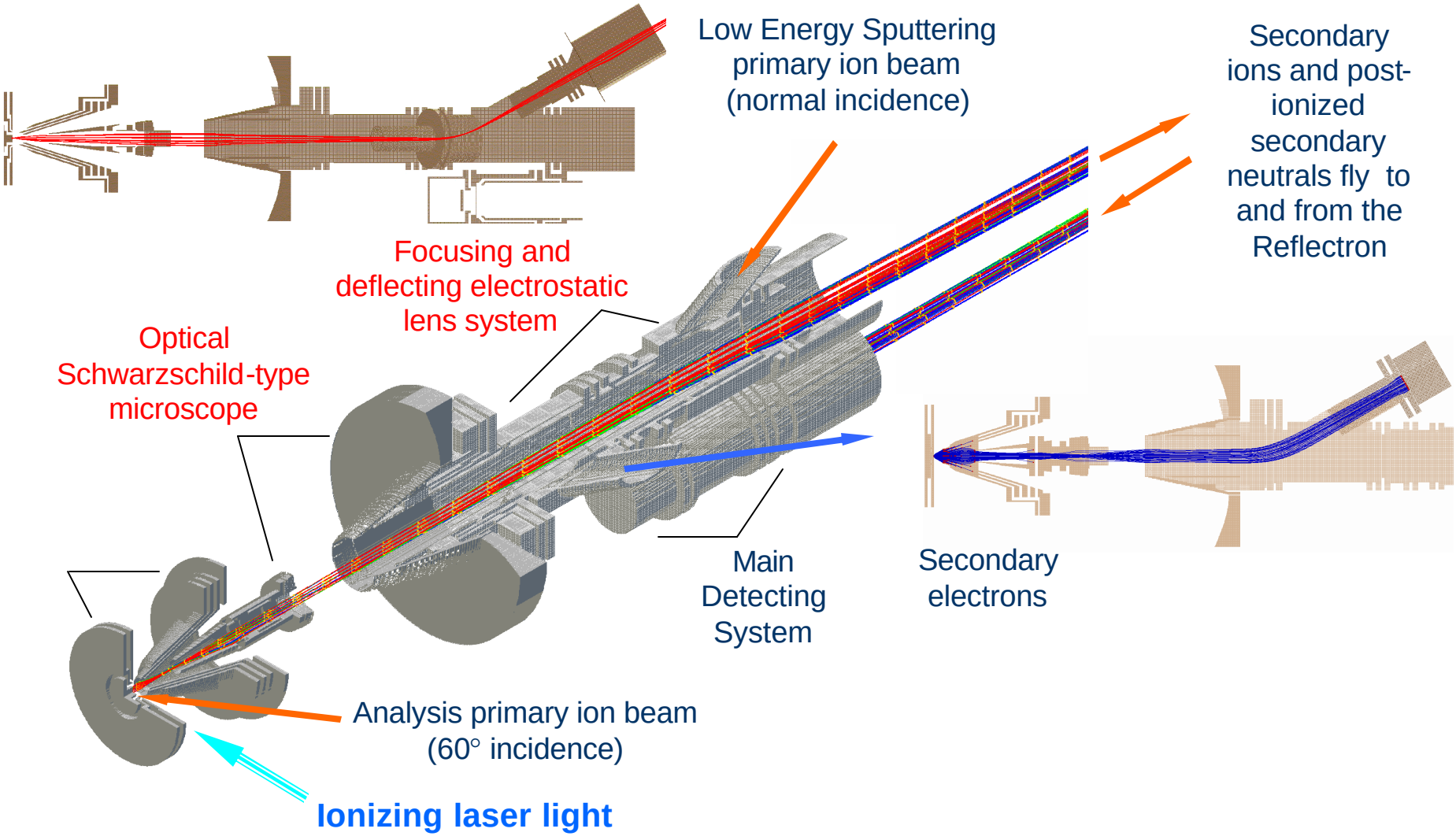






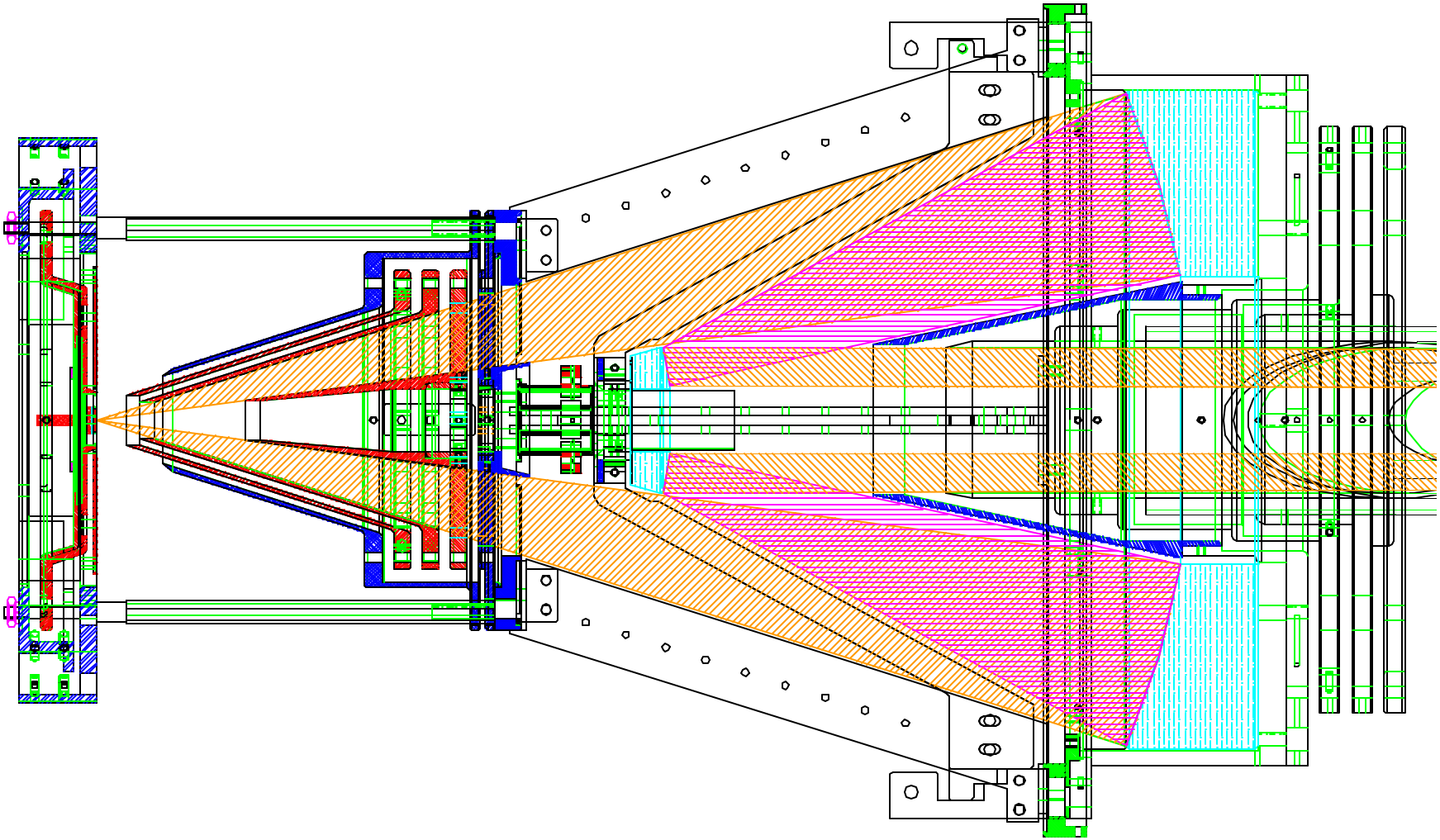


The INSTRUMENT: ion optics innovations



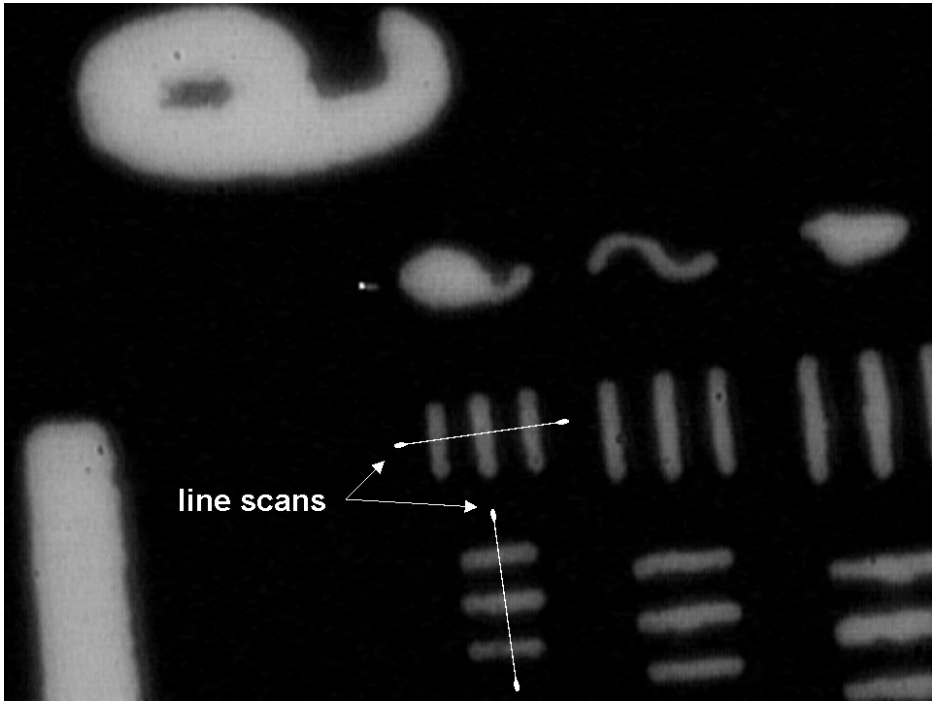
The INSTRUMENT:

ion optics incorporates high resolution light microscope



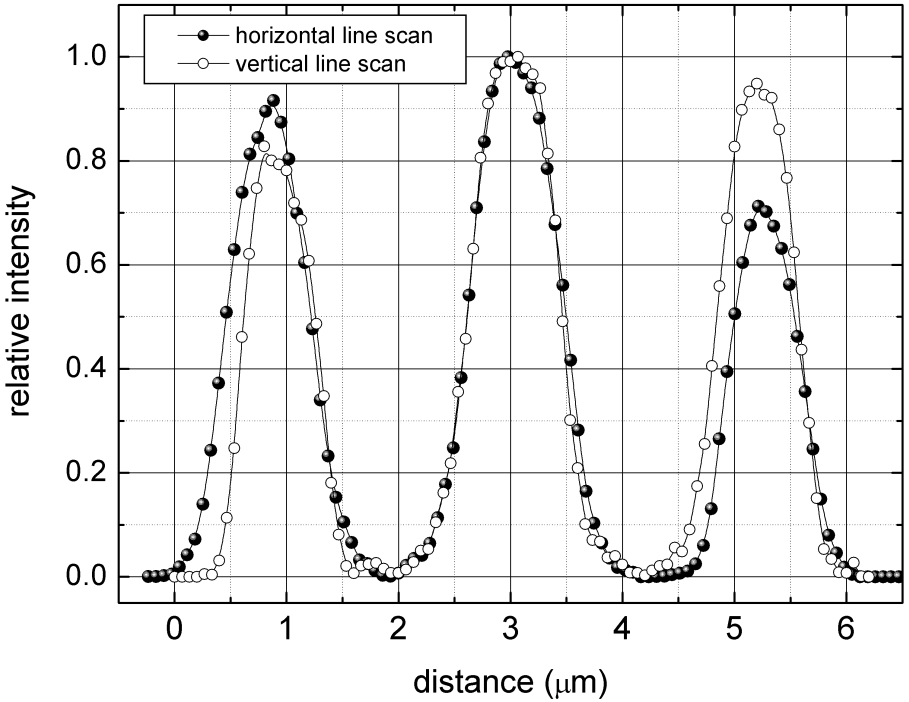
The INSTRUMENT: how it sees the samples under the optical Schwarzschild microscope

Air Force test pattern as viewed with the new Schwarzschild microscope after installation.



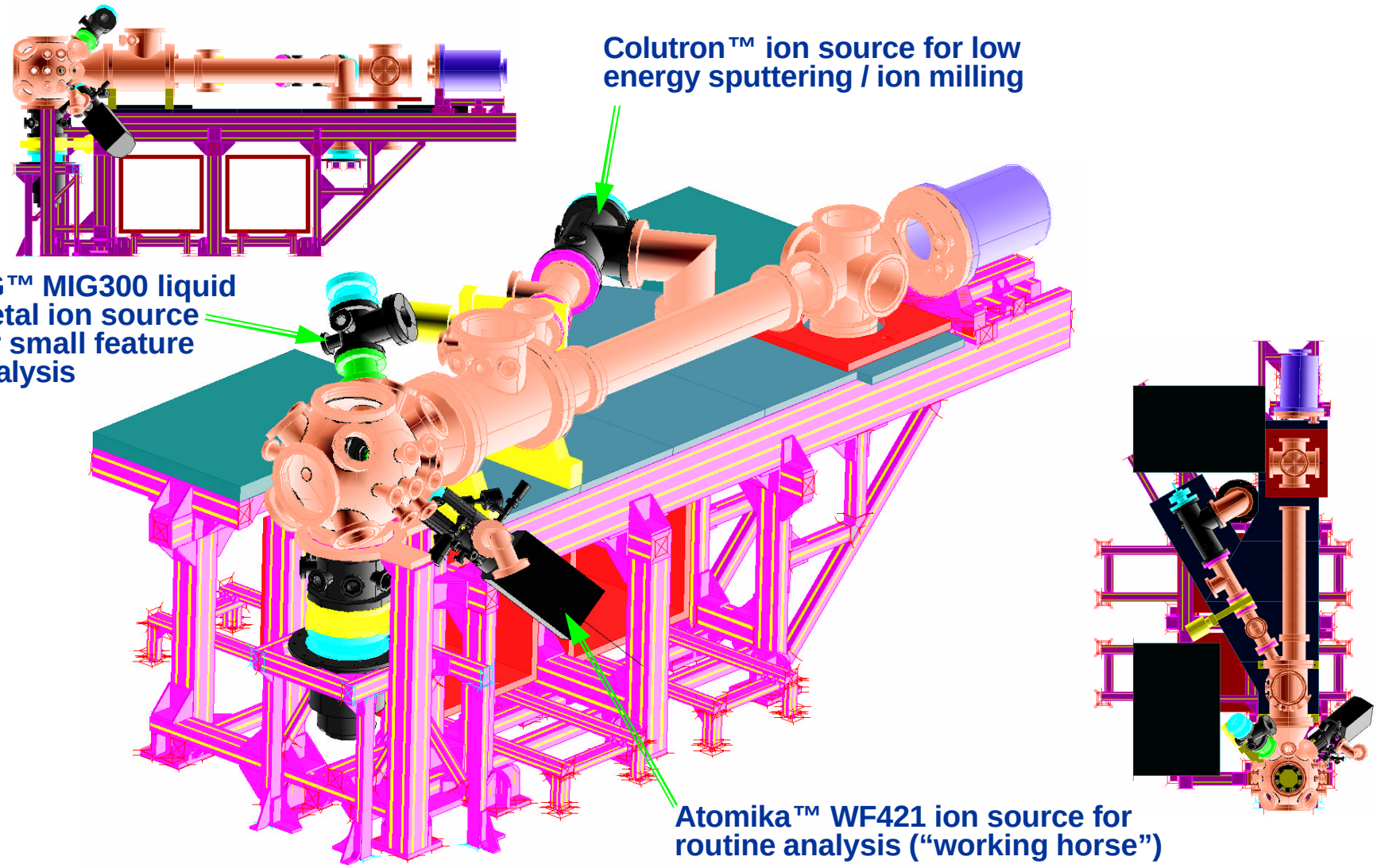
Line spacing = 2.2 µm.

Line scans show that the theoretical resolution of 0.5 µm is achieved.

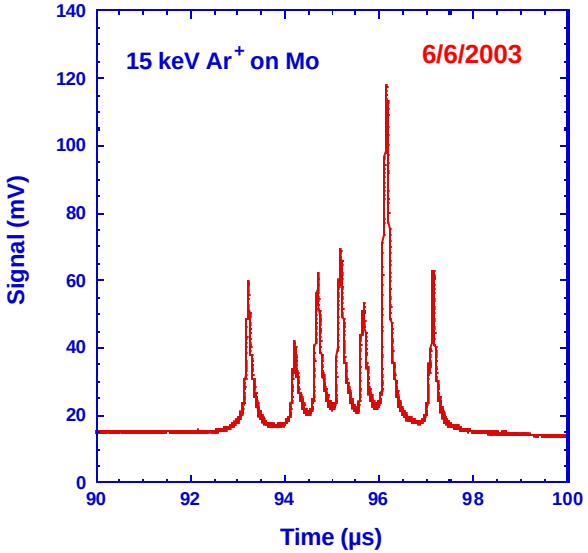


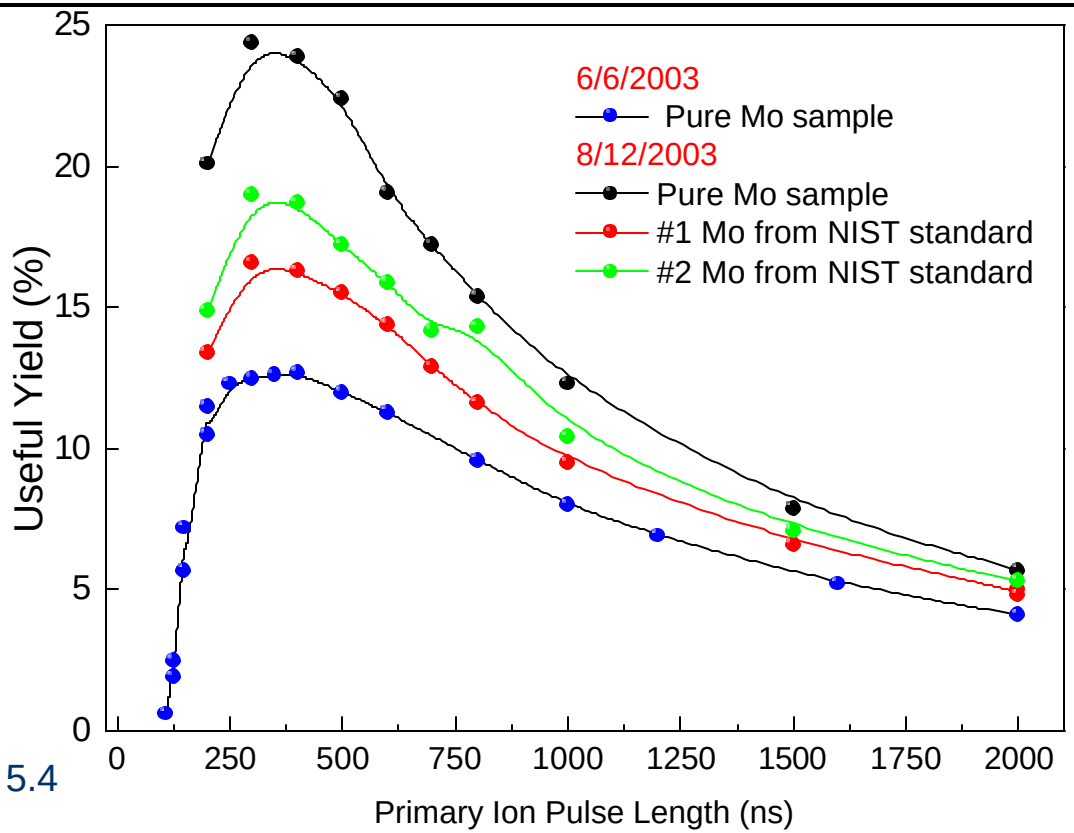
The INSTRUMENT:

two more machines identical to SPIRIT in our lab in Building 200 (Chemistry)



The INSTRUMENT: what it is capable of



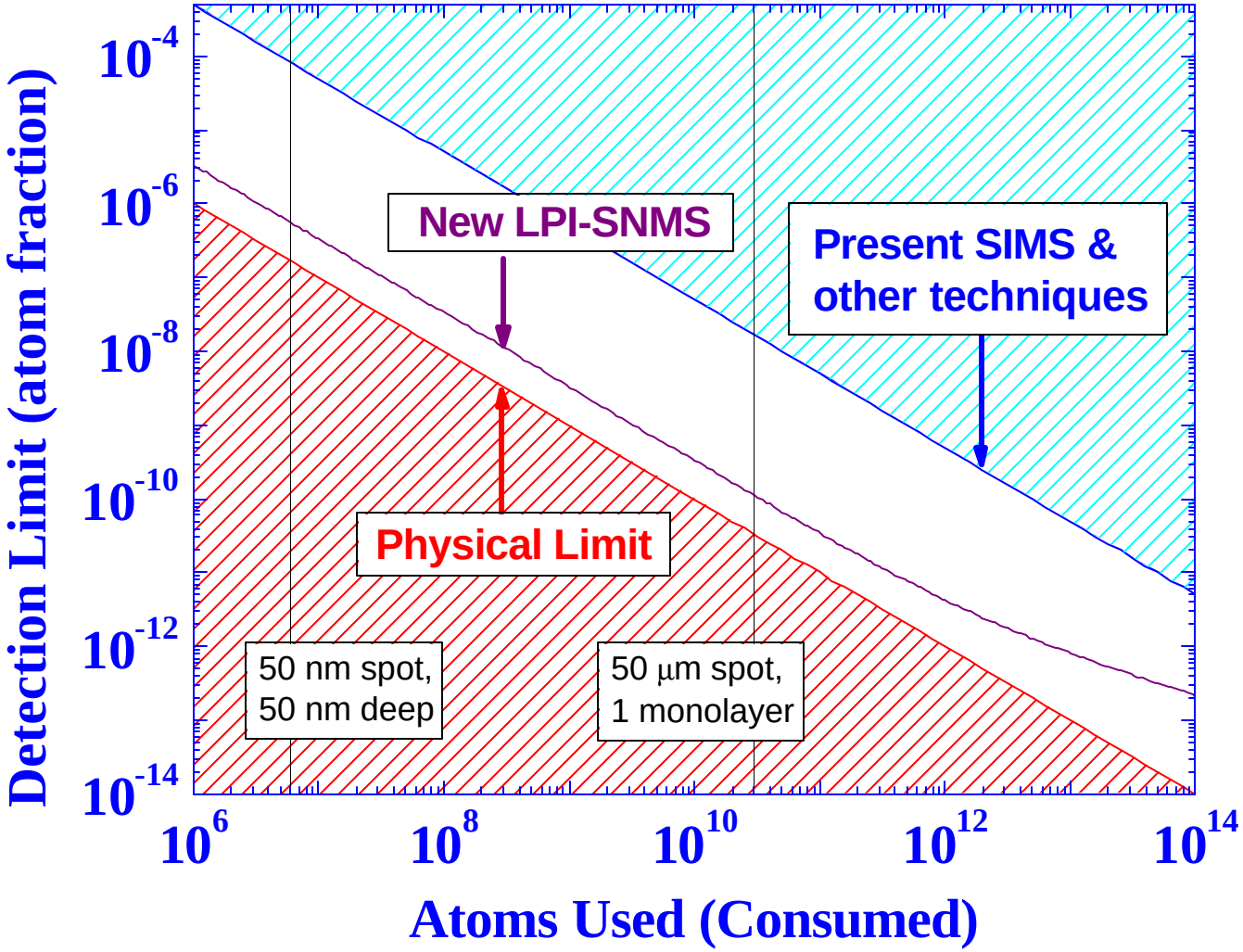


- Ion current = 1.6 μA
- Ion beam pulse width = 200 ns
- Ions to Target = 2.0×10^6
- Mo Sputter Yield (15 keV Ar^+ @ 60º) = 5.4
- Atoms Removed = 1.1×10^7
- Atoms Detected = 1.3×10^6
- Useful Yield = $1.3 \times 10^6 / 1.1 \times 10^7$ ~ 12%

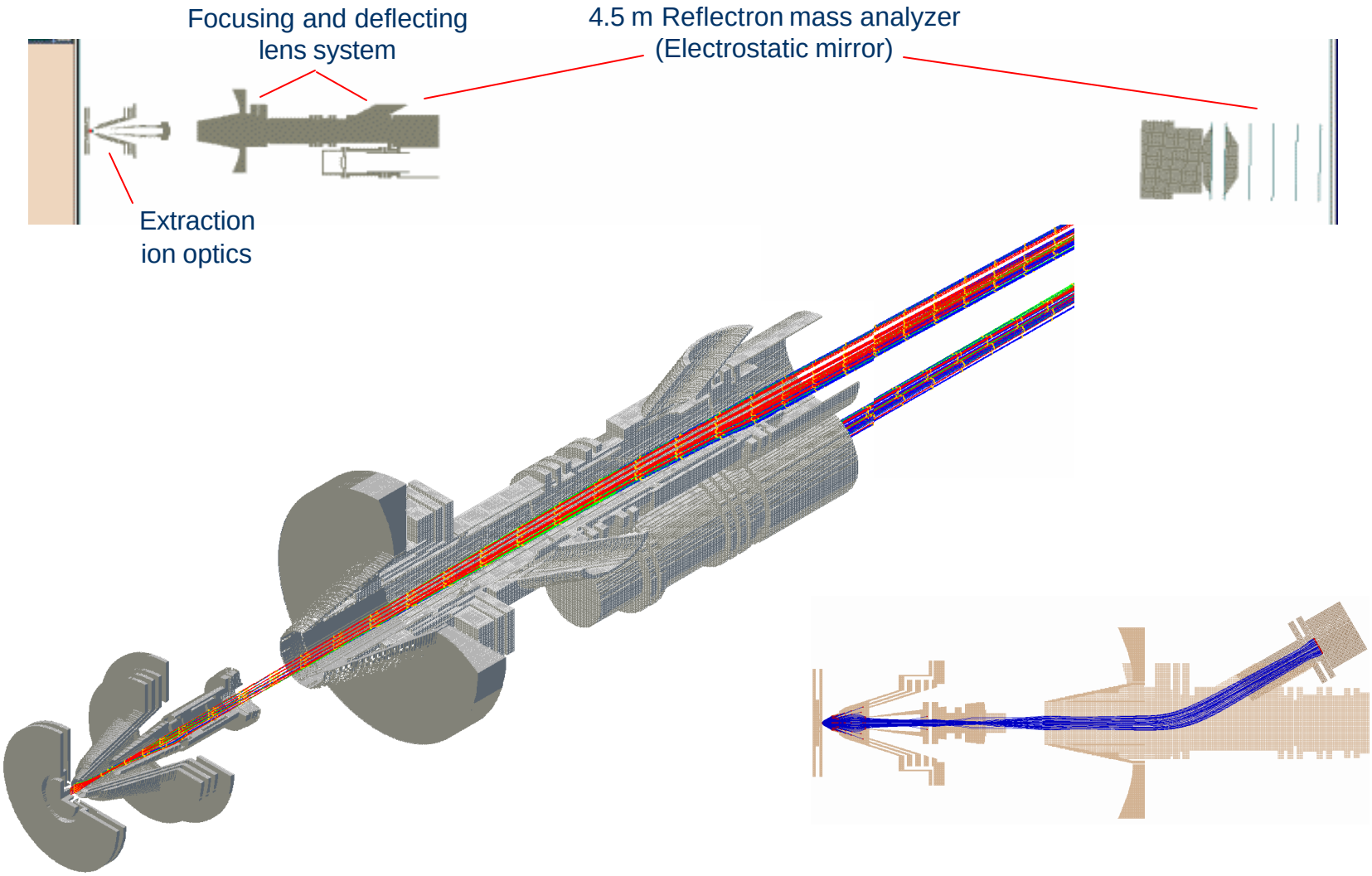
The most recent experiments aimed at characterization of the useful yield confirmed that it is as high as was predicted by computer simulations

The INSTRUMENT:

Detection limits in the LPI SNMS operation mode predicted by computer simulations



This is true now!

The INSTRUMENT:

What can we do with fragment ions?