

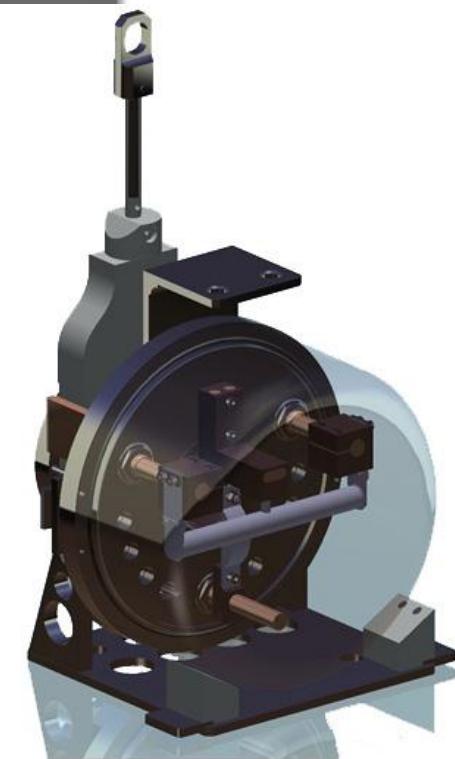
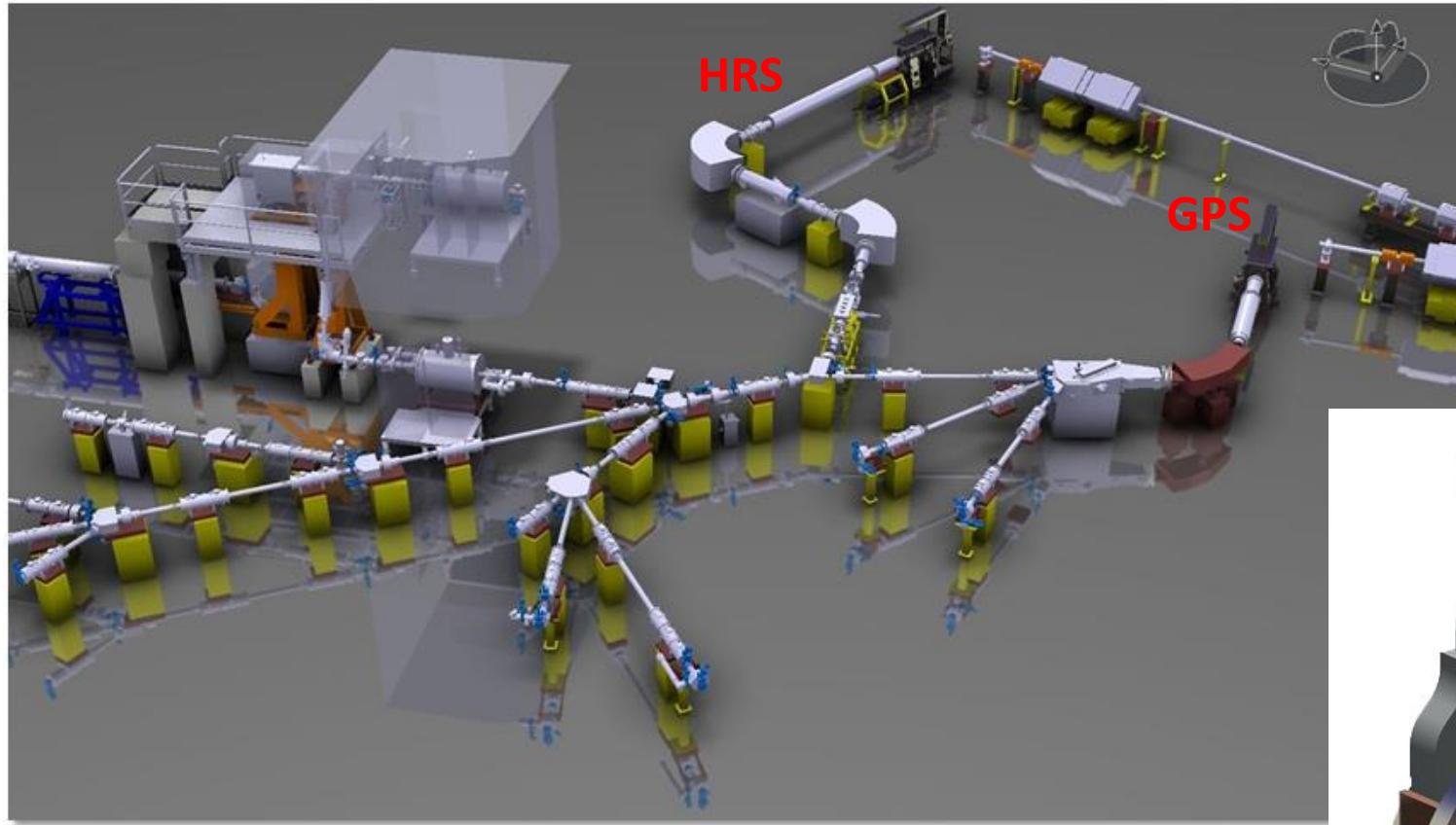
Exploratory studies of laser interaction with volatile refractory elements

Christoph Seiffert

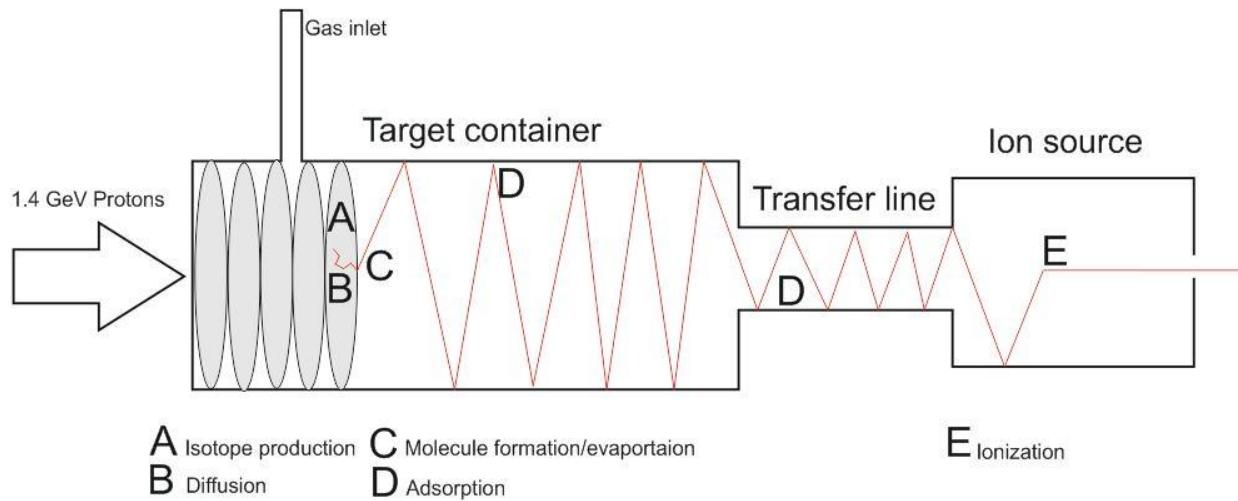


- Introduction
 - Radioactive ion beam production at ISOLDE
 - Limitations of the ISOL method
- Steps of molecular beam development
 - Considerations of elements and chemical equilibrium
- Laser induced breakup of molecules
 - Status of work

Radioactive beam production

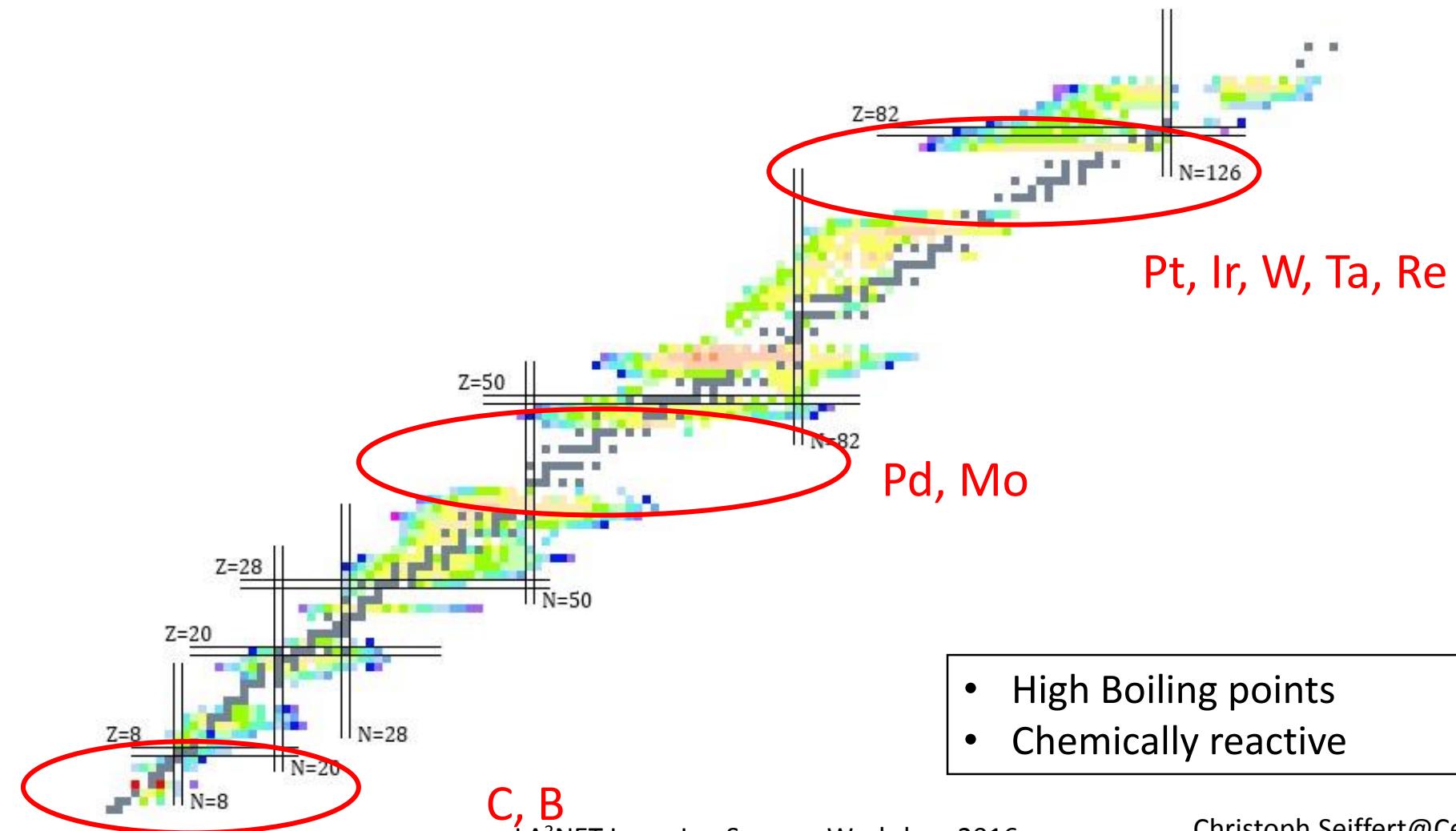


Radioactive beam production



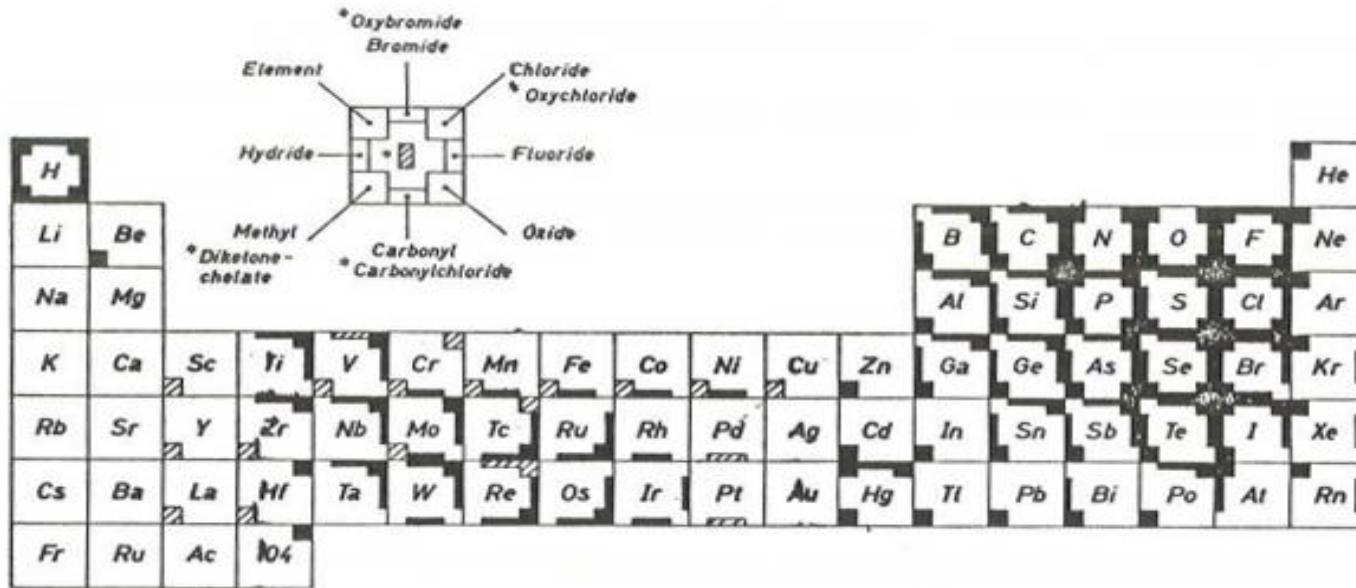
$$N(t) = N_0 * e^{-\lambda*(t_{ads}+t_{trans}+t_{diff})} * \epsilon_{diff} * \epsilon_{formation} * \epsilon_{trans} * \epsilon_{ion}$$

Available Isotopes at ISOLDE



- High Boiling points
- Chemically reactive

Molecular Extraction



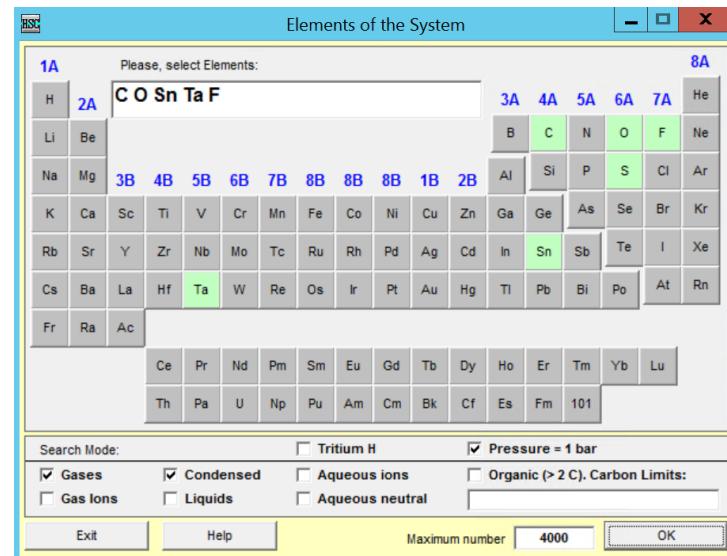
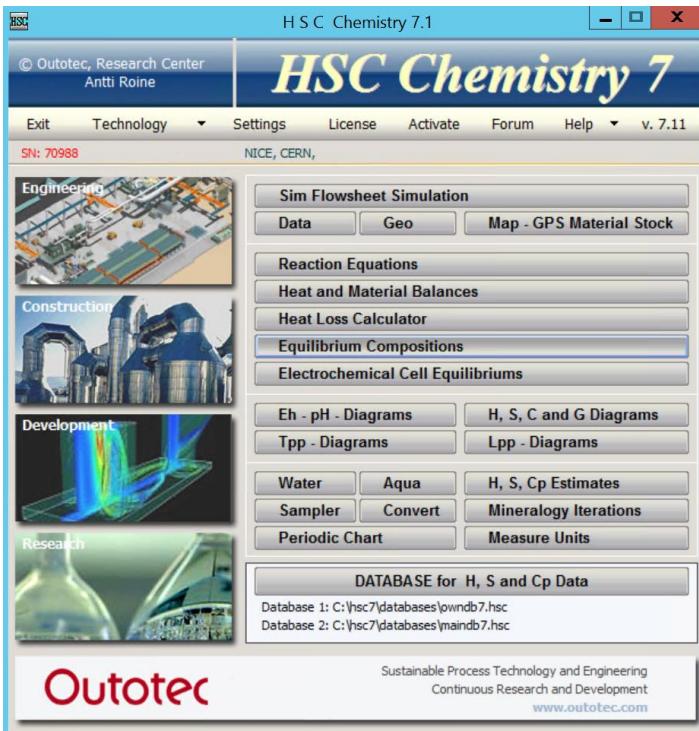
Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lw

Element	Boiling point [°C]	Molecular sideband	Boiling point [°C]
C	4827	CO	-191.5
B	3927	BF ₃	-100.3
Mo	4639	Mo(CO) ₆	156
W	5555	W(CO) ₆	175

- e.g. CO, CO₂, BF_n, TiF_n

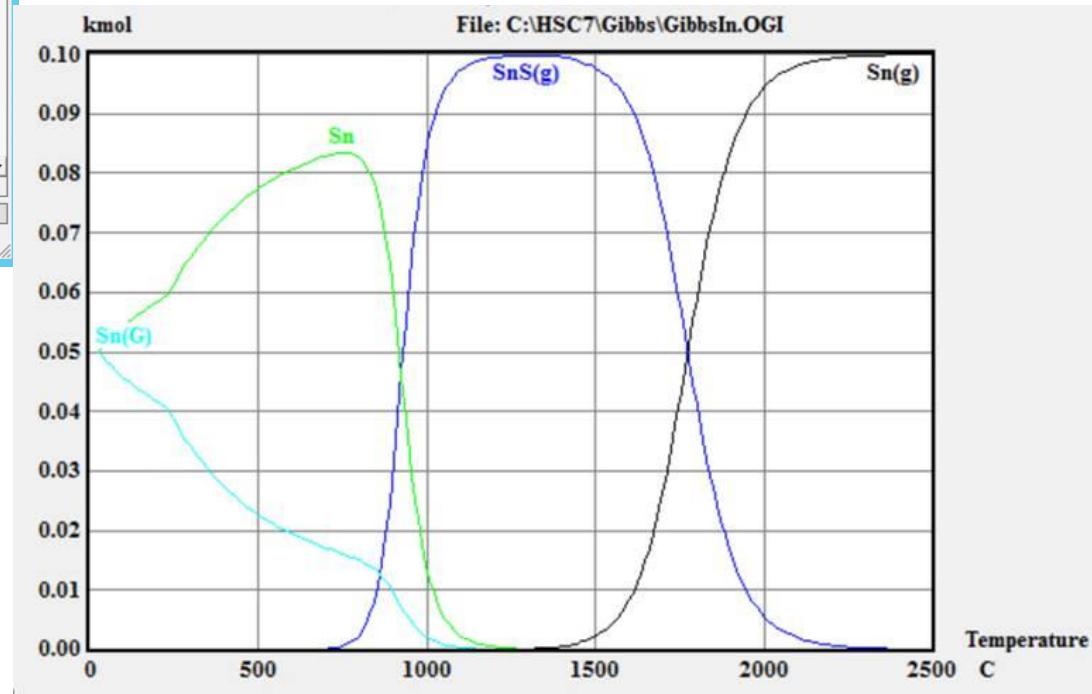
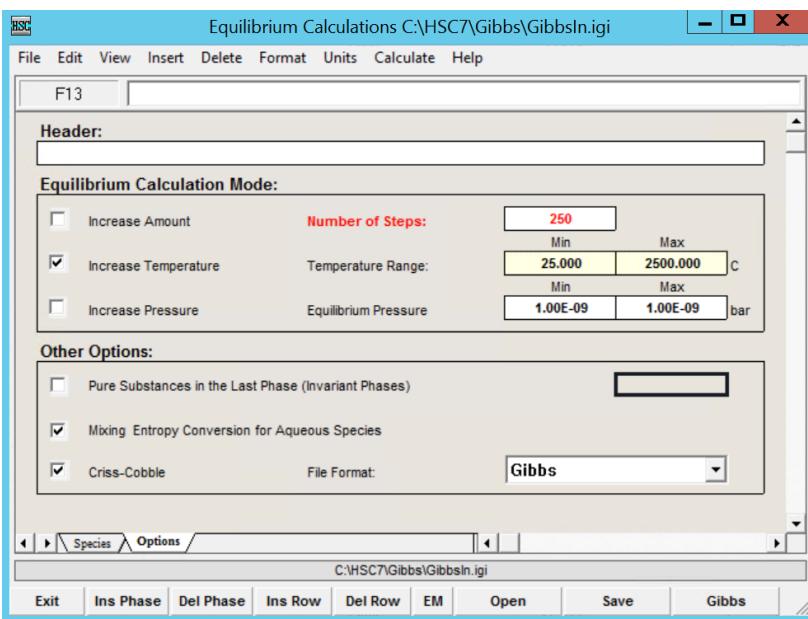
In-Target Chemistry

- Access chemical equilibrium in target container
- HSC Chemistry 7 software
- Calculation based on Gibbs free energy



Equilibrium Calculations C:\HSC7\Gibbs\GibbsIn.igi							
File Edit View Insert Delete Format Units Calculate Help							
C110 0.1							
	SPECIES Formula	Temper. C	Amount kmol	Amount %	Step kmol	Step %	Activity Coeff.
98	Ta2O5		25.000				1.000
99	CARBIDES, etc.						
100	TaC0.7		25.000				1.000
101	TaC0.99		25.000				1.000
102	TaC		25.000				1.000
103	Ta2C		25.000				1.000
104	ELEMENTS		11.000	100.000			
105	C		25.000	1.000	9.091		1.000
106	(C,A)		25.000				1.000
107	C(D)		25.000				1.000
108	C60		25.000				1.000
109	C70		25.000				1.000
110	Sn		25.000	0.1			1.000
111	Sn(G)		25.000				1.000
112	Ta		25.000	10.000	90.909		1.000
113							
114							
115							

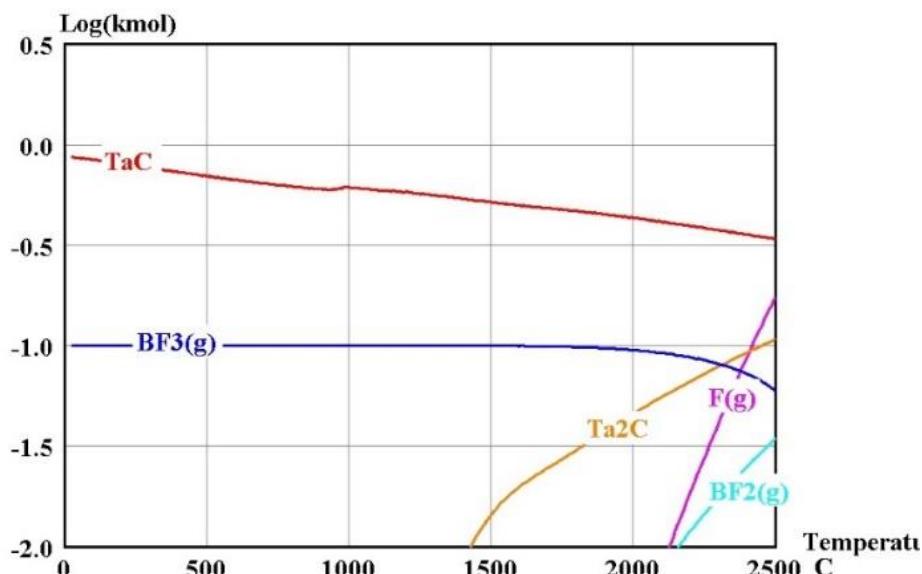
In-Target Chemistry



In-Target Chemistry

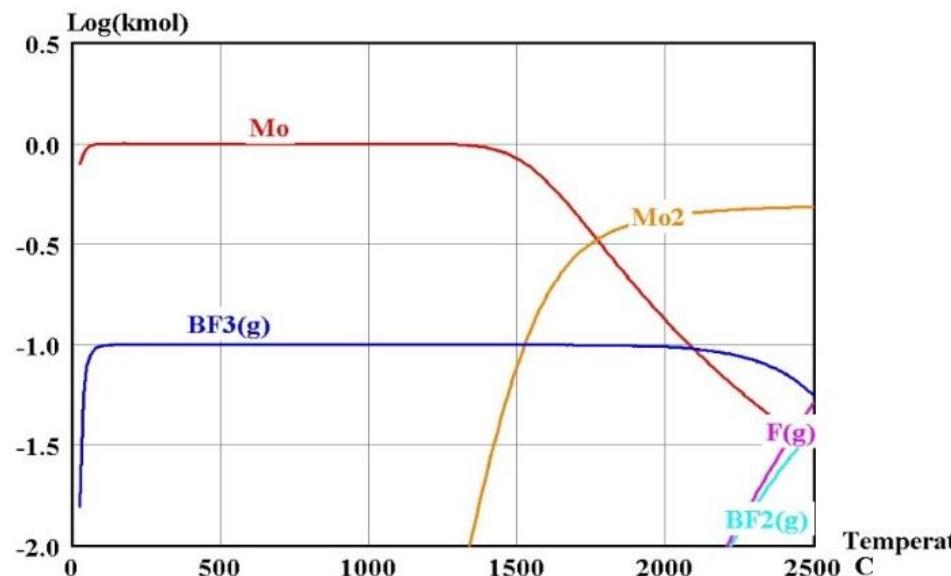
Formation of molecules

Graphite: C+B+SF₆



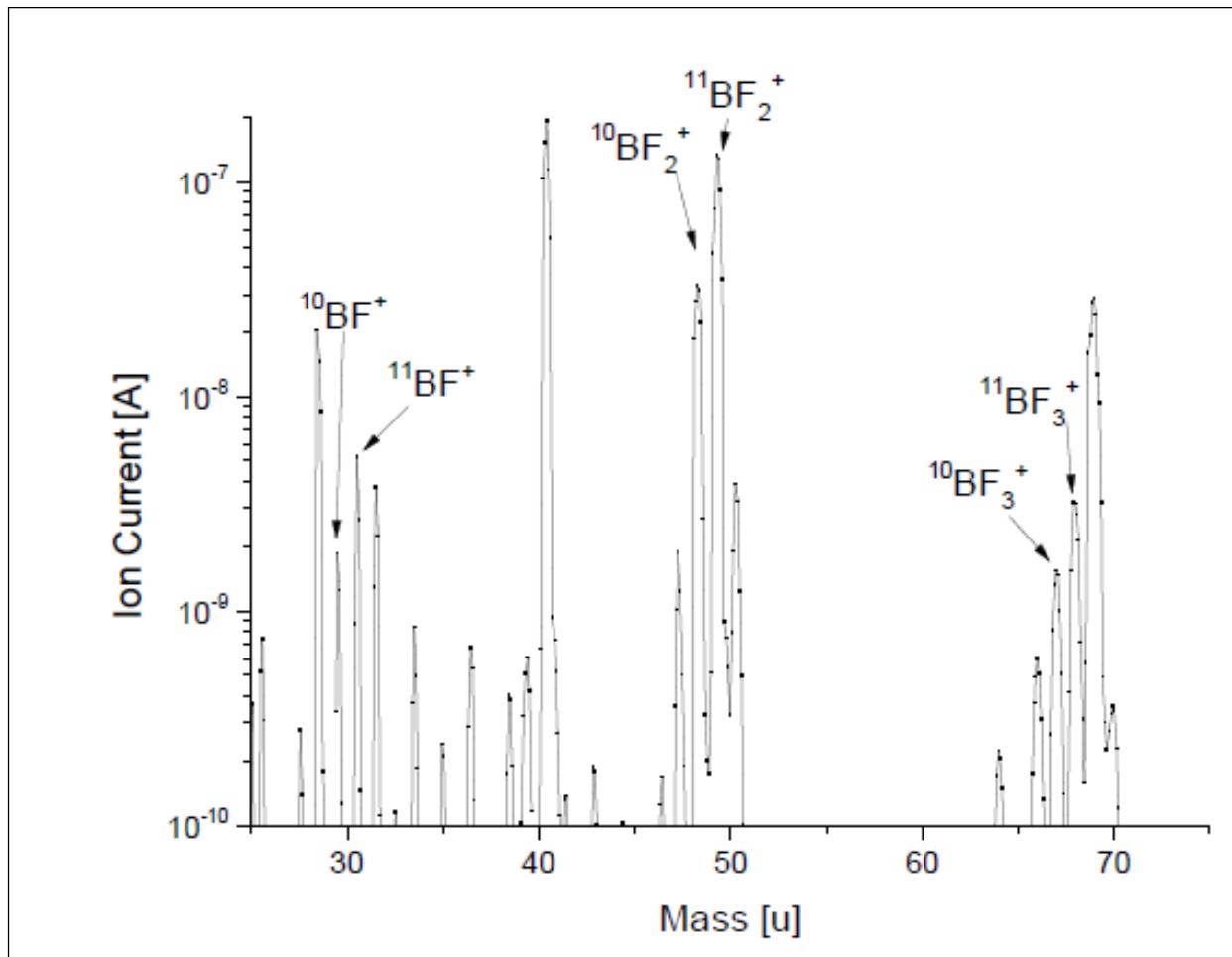
Transport of molecules

Molybdenum: Mo+BF₃



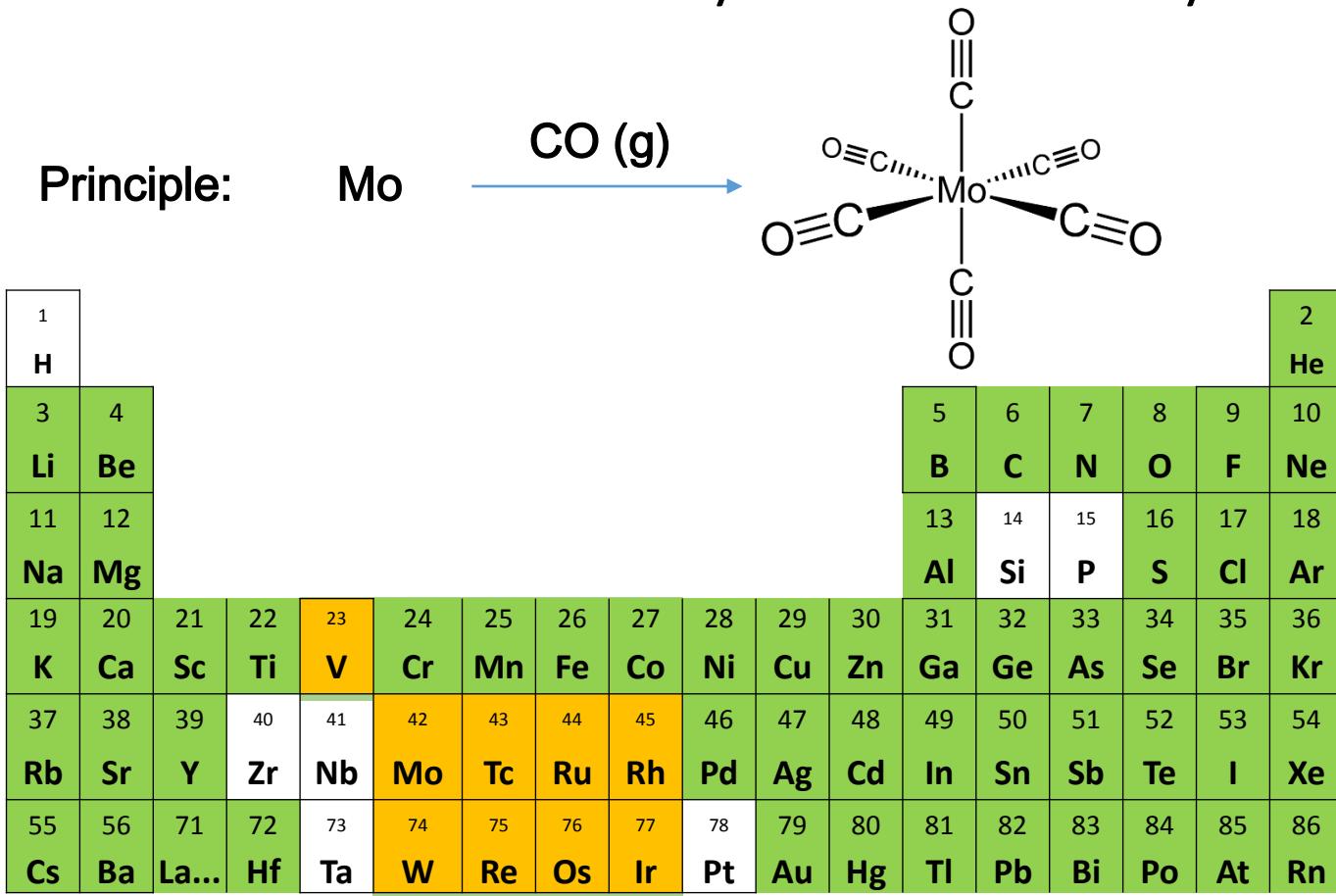
- Calculated helped to identify carbon as a suited target material for extraction of boron
- First ISOL ⁸B beam as ⁸BF_n⁺ at ISOLDE in 2014

- Efficiency loss due to distribution of fragments



Next step: Extraction of refractory elements

- PhD project of Jochen Ballof (TISD team ISOLDE):
 - Extraction of refractory metals as carbonyl compounds



Carbonyle
compounds

V(CO)₆

Cr(CO)₆

Mo(CO)₆

W(CO)₆

Tc₂(CO)₁₀

Re₂(CO)₁₀

Ru(CO)₅

Os(CO)₅

Co₂(CO)₈

Rh₂(CO)₈

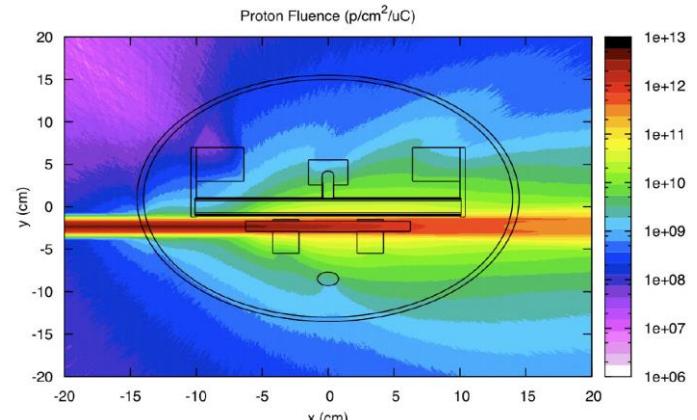
Ir₄(CO)₁₀

Ni(CO)₄

Next step: Extraction of refractory elements

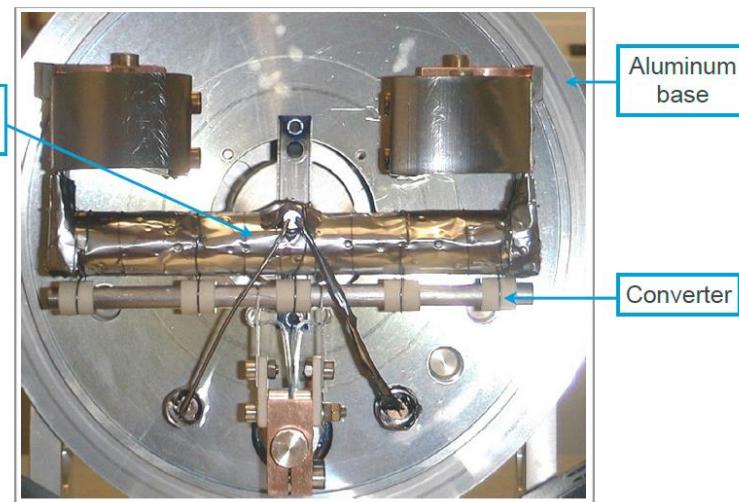
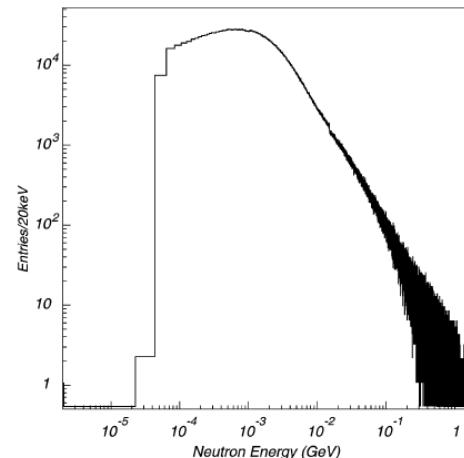
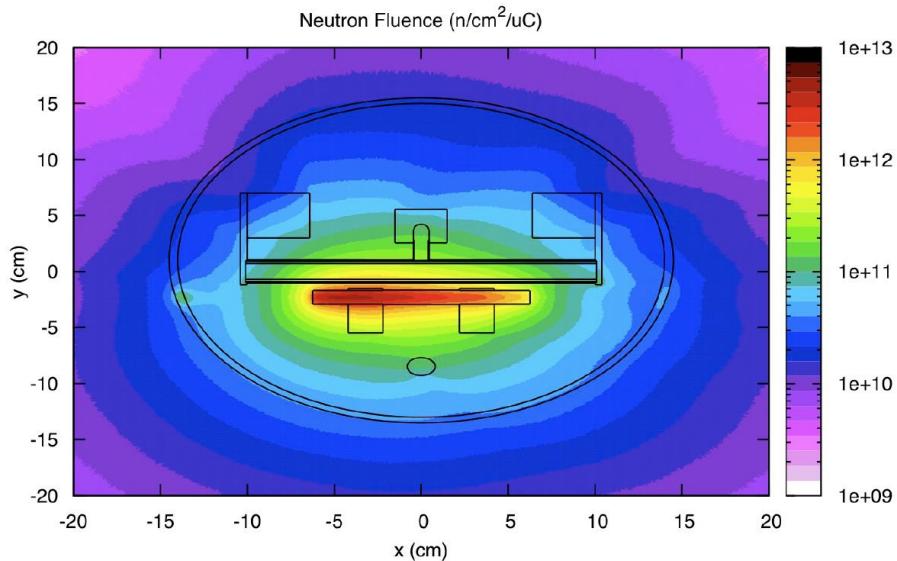
Challenges

- Thermal instability
 - Decomposition at ~ 200 C
 - Slow diffusion inside target materials at low temperatures
- Radiation stability
 - Decomposition due to proton impact on target container
 - Avoid direct irradiation with protons
- High pressure gradient needed
 - High pressure of CO in target needed
 - Ion source only accepts low pressure



Next step: Extraction of refractory elements

- Use neutron converter
- Neutron energy \sim 0.1-10MeV

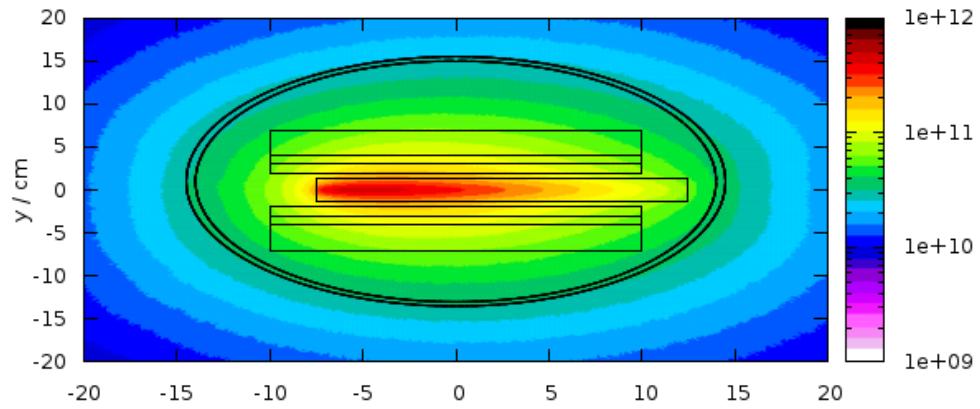
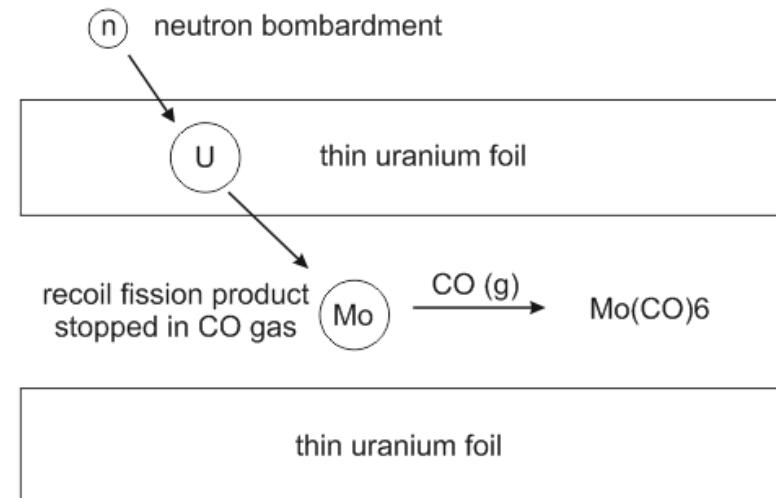
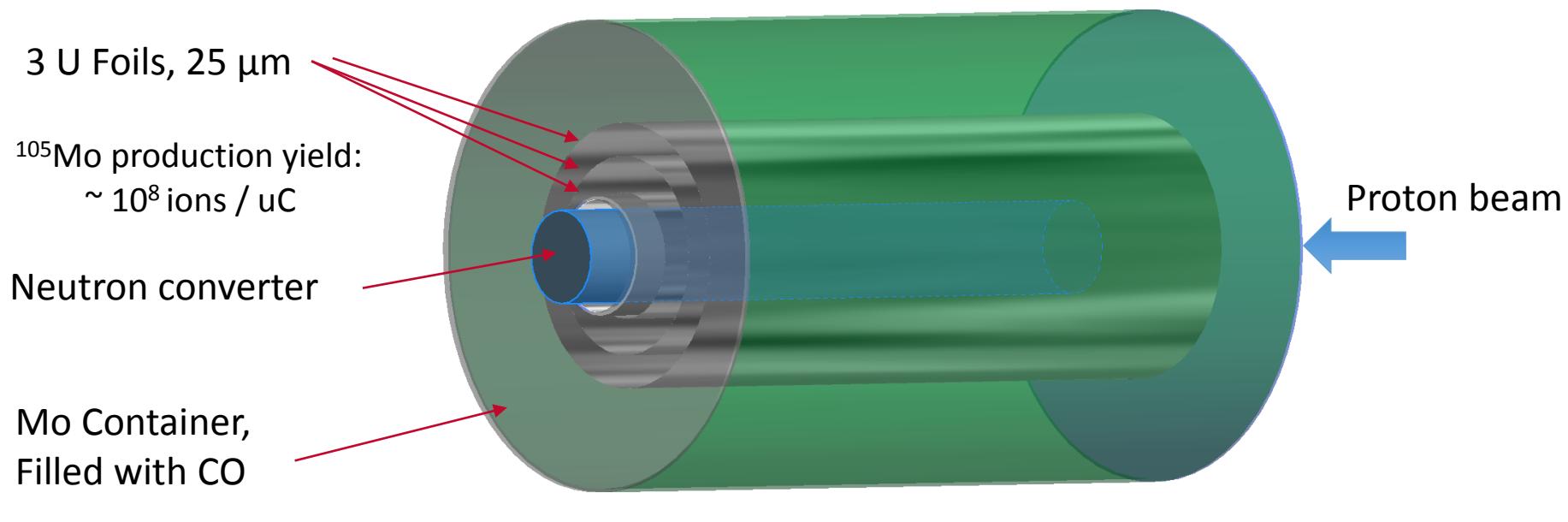


R.Luis, 2013, Radiological Protection and Nuclear Engineering Studies in Multi-MW Target Systems, Phd Thesis
R. Catherall et al, NIMB, 2003, 235-239

Slide: courtesy of Jochen Ballof, Jochen.Ballof@cern.ch
LA³NET Laser Ion Sources Workshop 2016

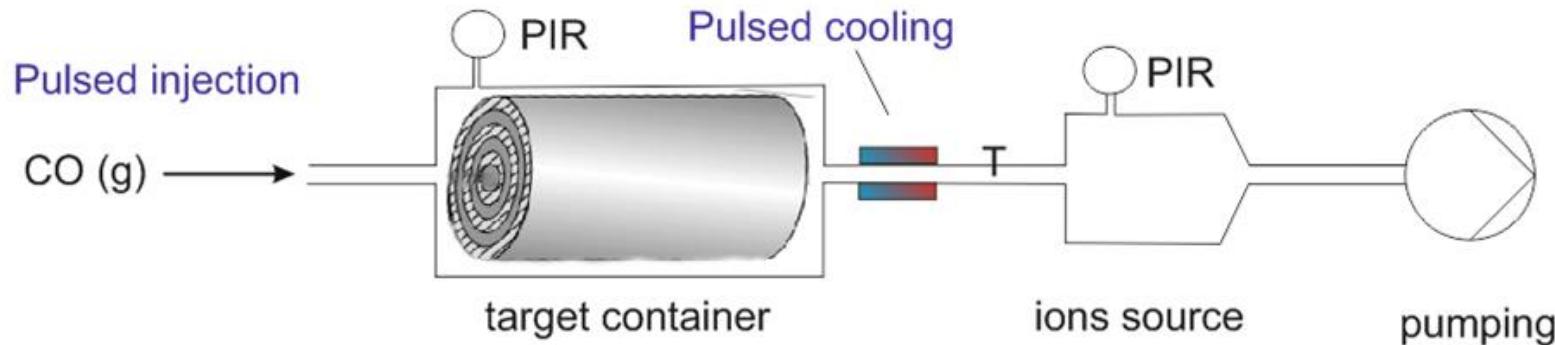
Christoph.Seiffert@Cern.ch

Next step: Extraction of refractory elements

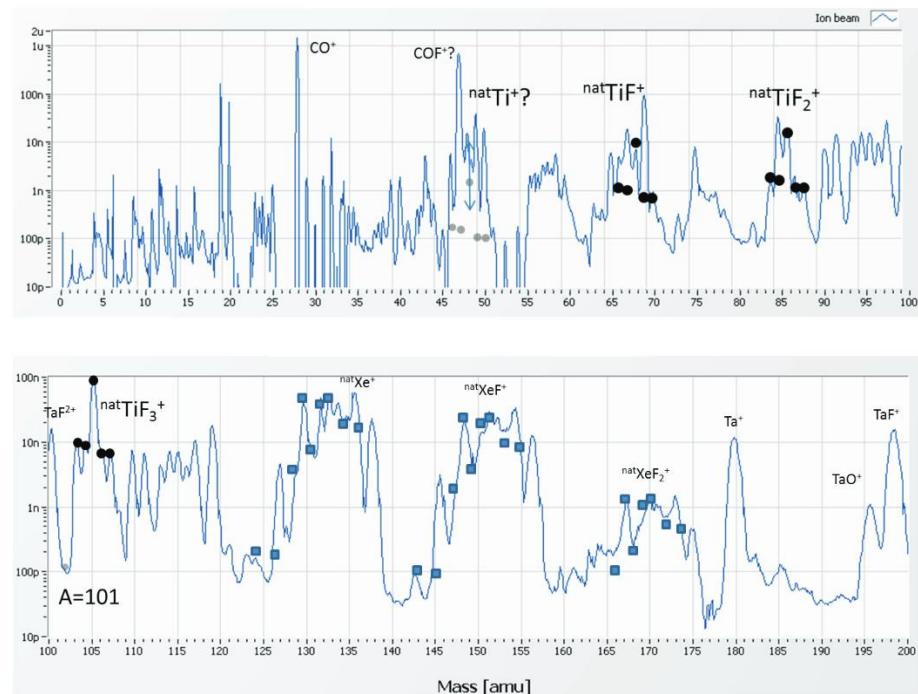
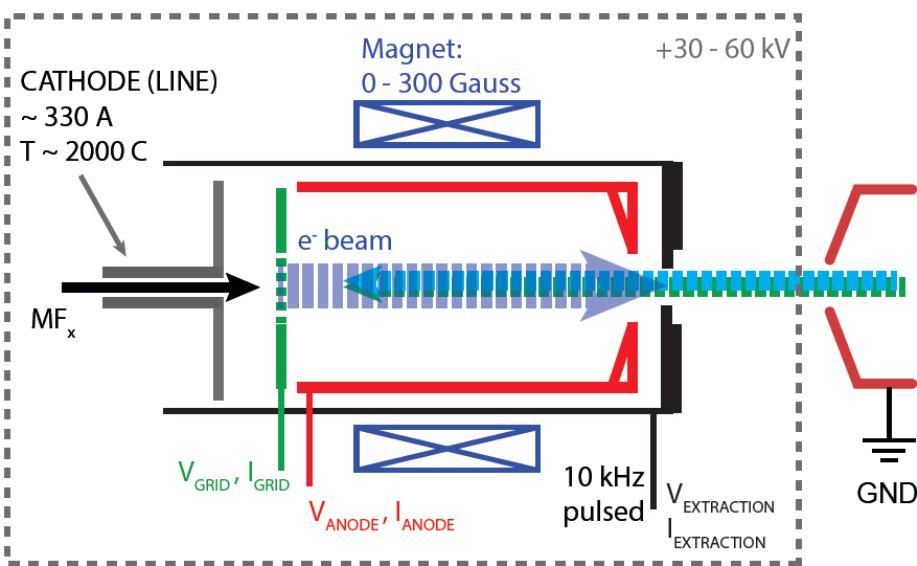


Next step: Extraction of refractory elements

- High and low pressure regimes can be overcome by pulsed operation
- The carbonyls are retained on a cold surface, while the CO is pumped
- After pumping the system, the trap will be heated up to release the carbonyls

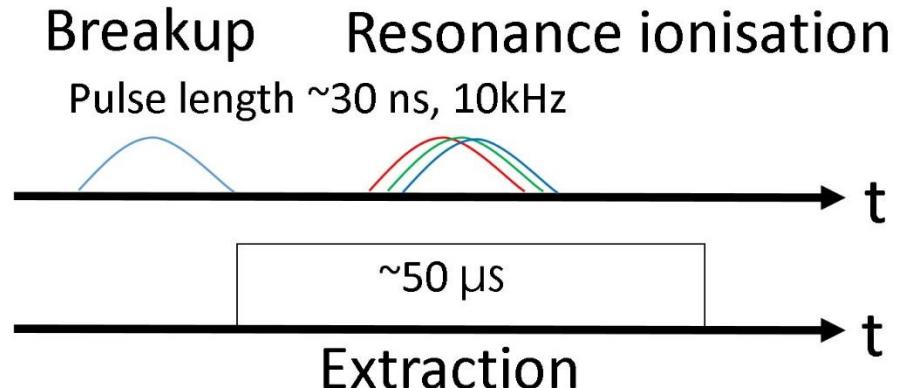
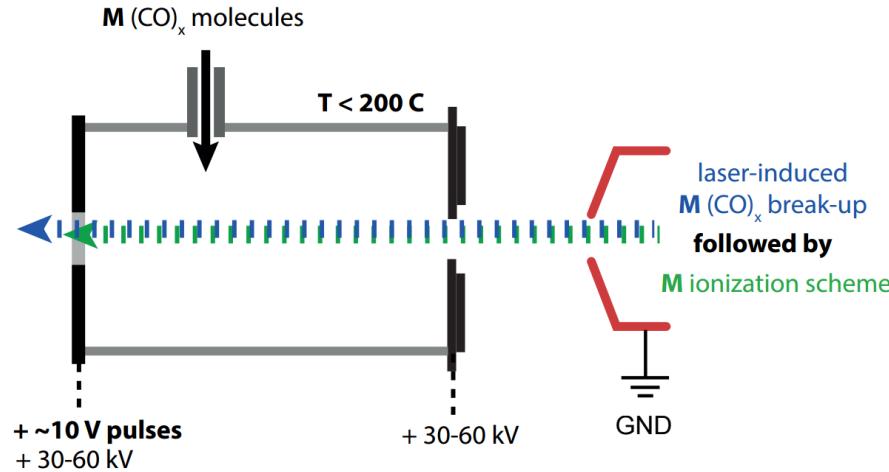


Electron-impact induced molecular breakup



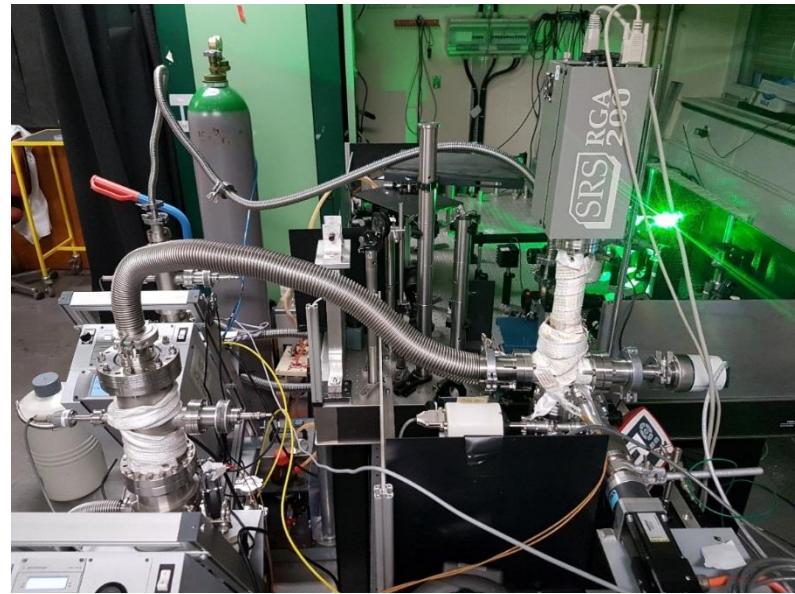
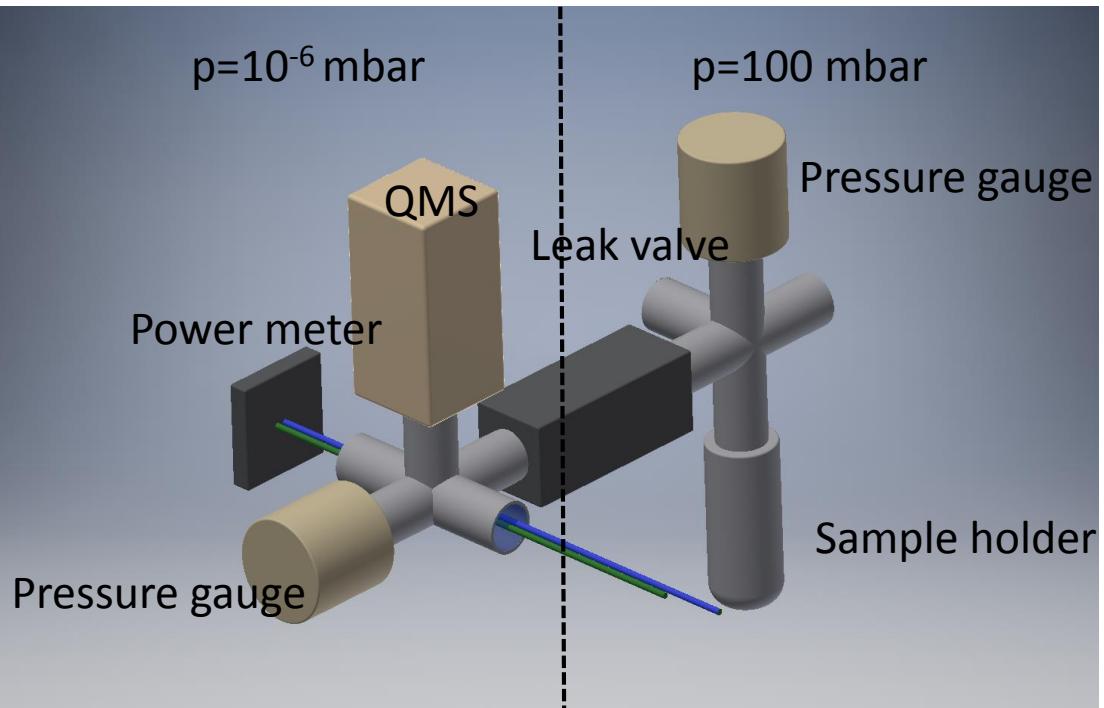
- Use of FEBIAD or RF ion source for molecular breakup
- Dissociation by e^- impact followed by resonance laser ionisation in a pulsed regime
- Ionisation and extraction has to happen before fragments touch the wall
- hot surfaces, partial dissociation

Laser induced molecular breakup

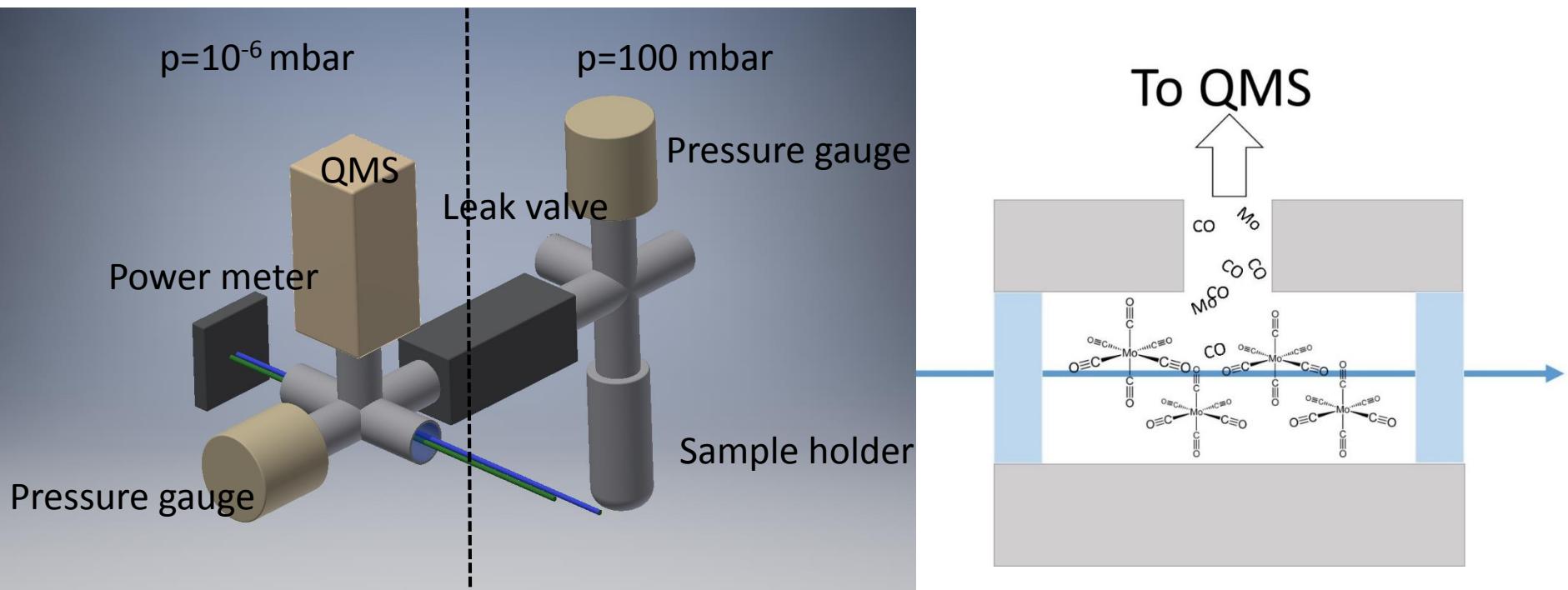


- Use of cold ion source
- Chemically inert materials e.g. PTFE, Quartz
- Laser induced breakup of weakly bound molecules
- Add-on resonance laser ionisation
- Pulsed extraction to enhance beam purity
- Challenge: dissociation cross section?

Laser induced molecular breakup

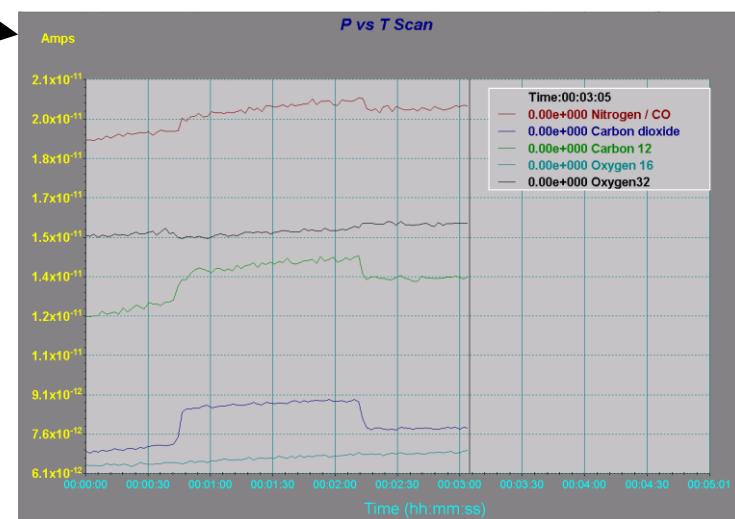
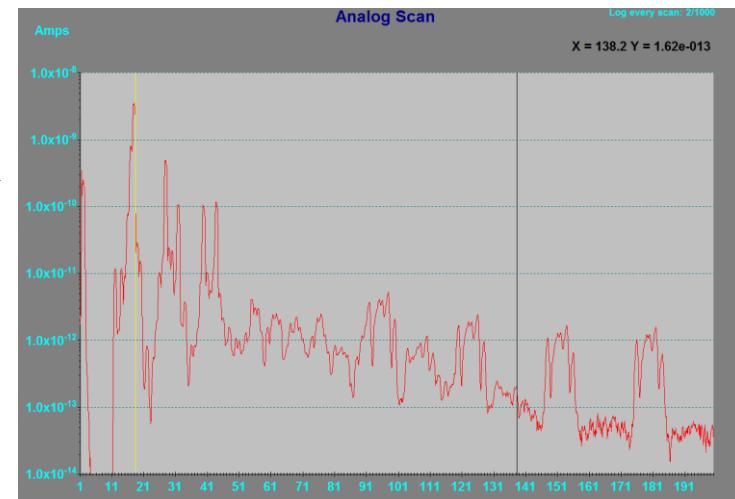
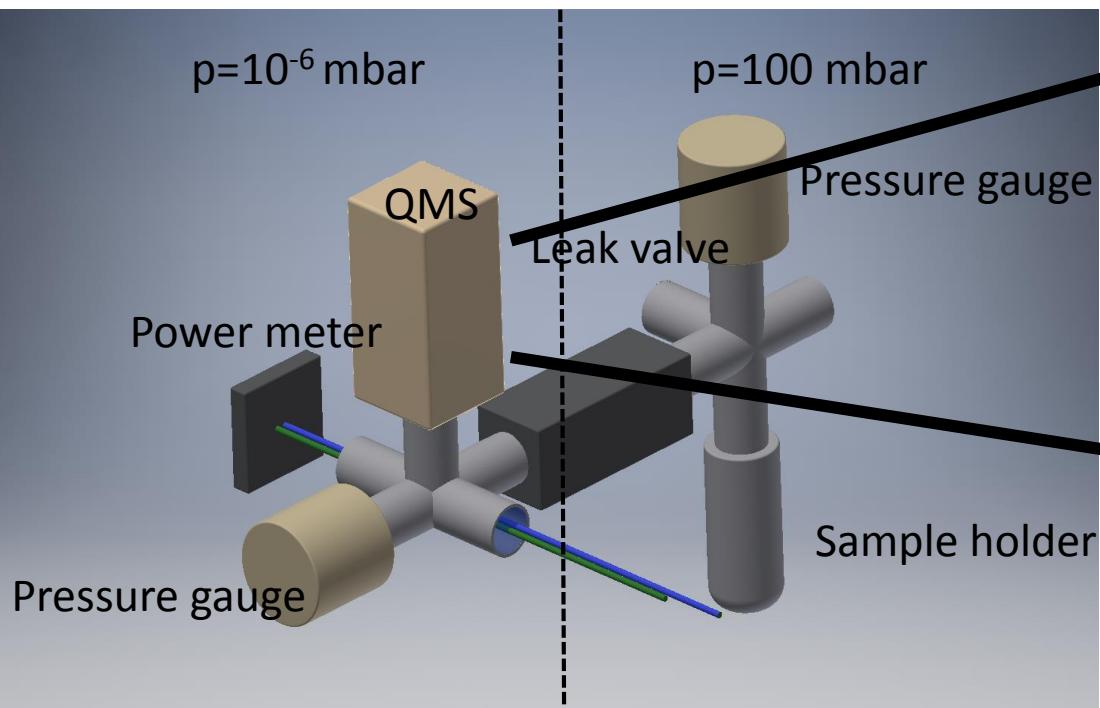


Laser induced molecular breakup



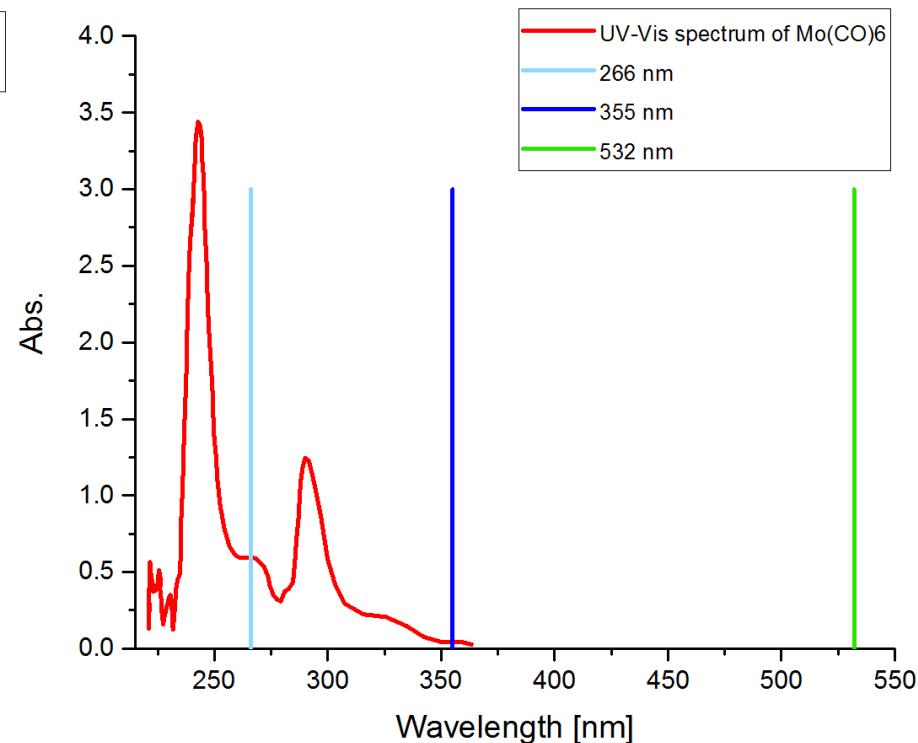
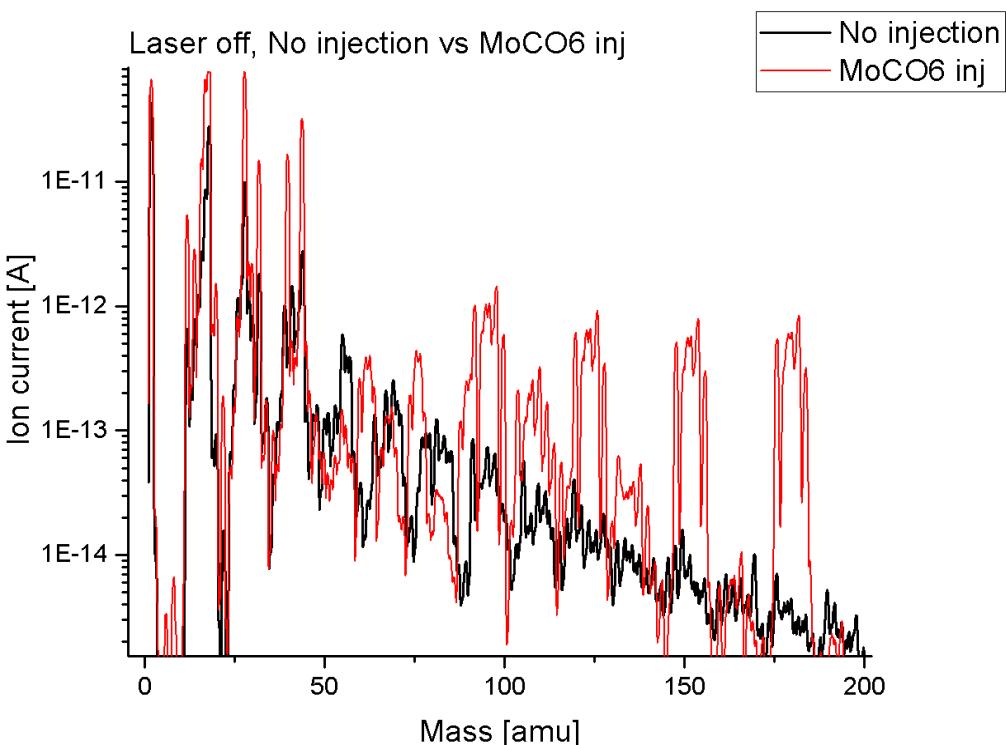
- Detection of $\text{Mo}(\text{CO})_x$ and other fragments

Laser induced molecular breakup



Laser induced molecular breakup

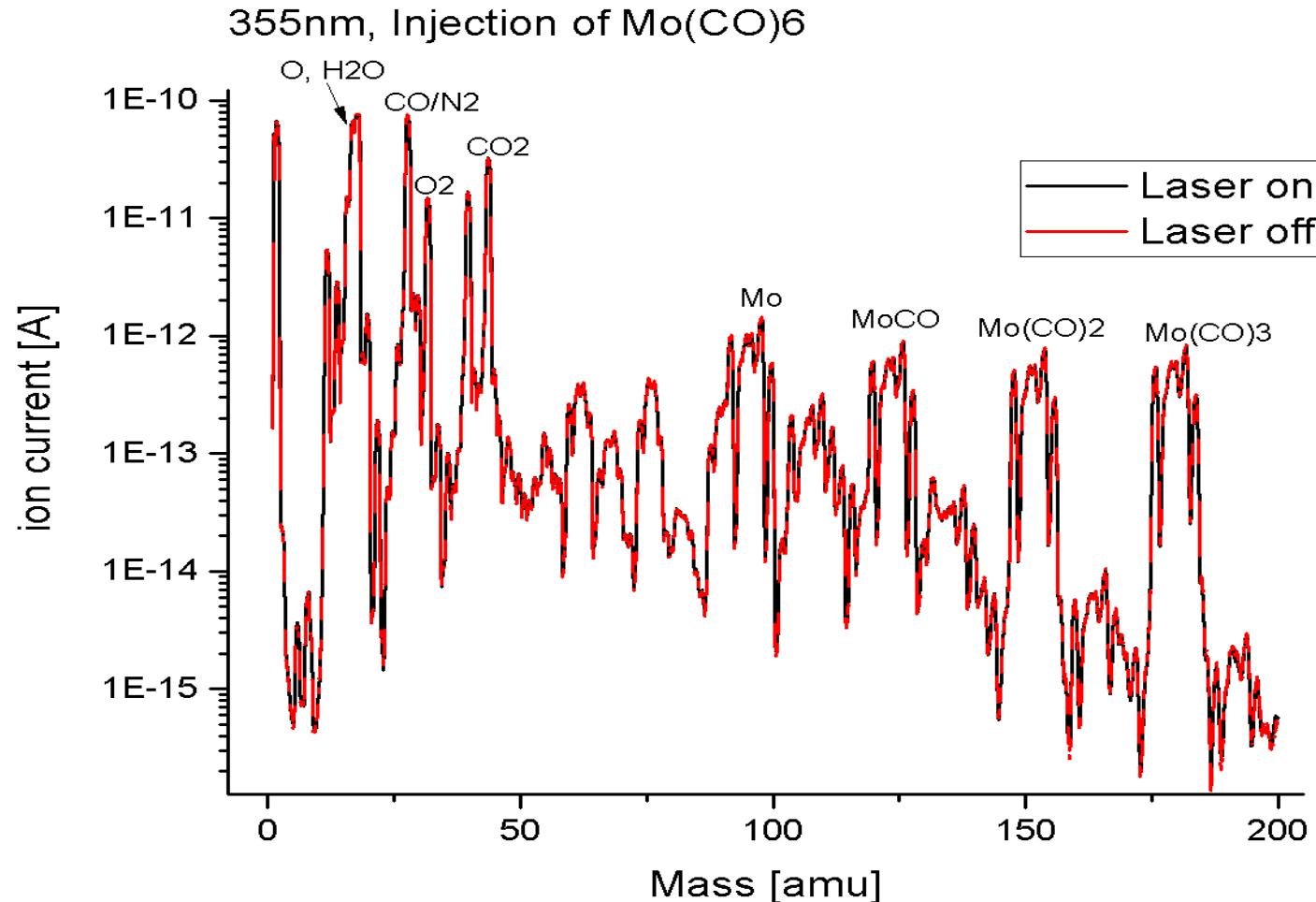
- Binding energy CO group in Mo(CO)₆: ~1.7 eV
(doi 10.1021/j100373a080)



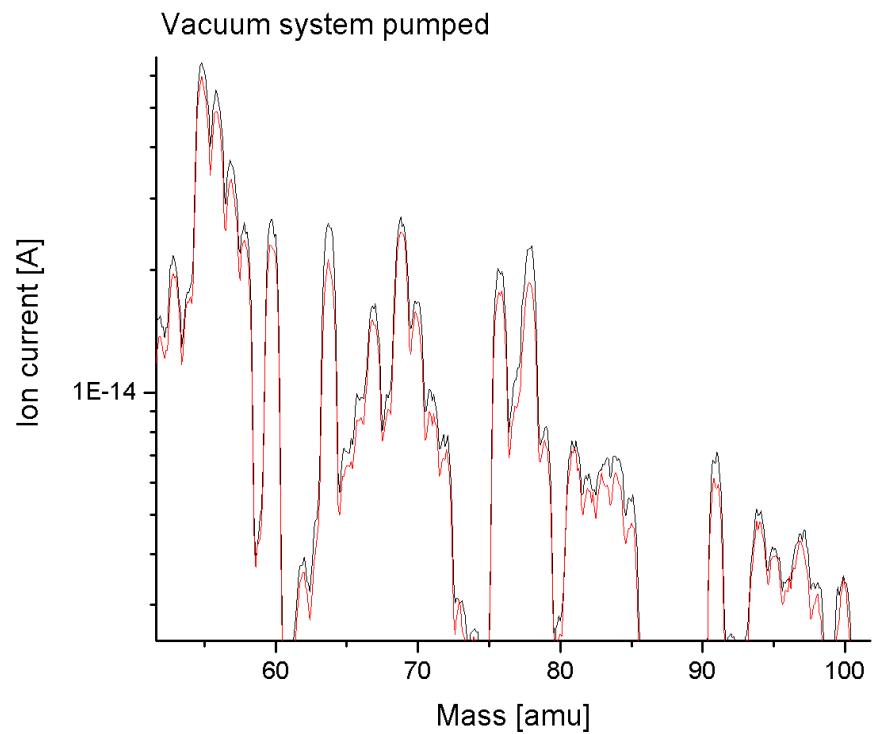
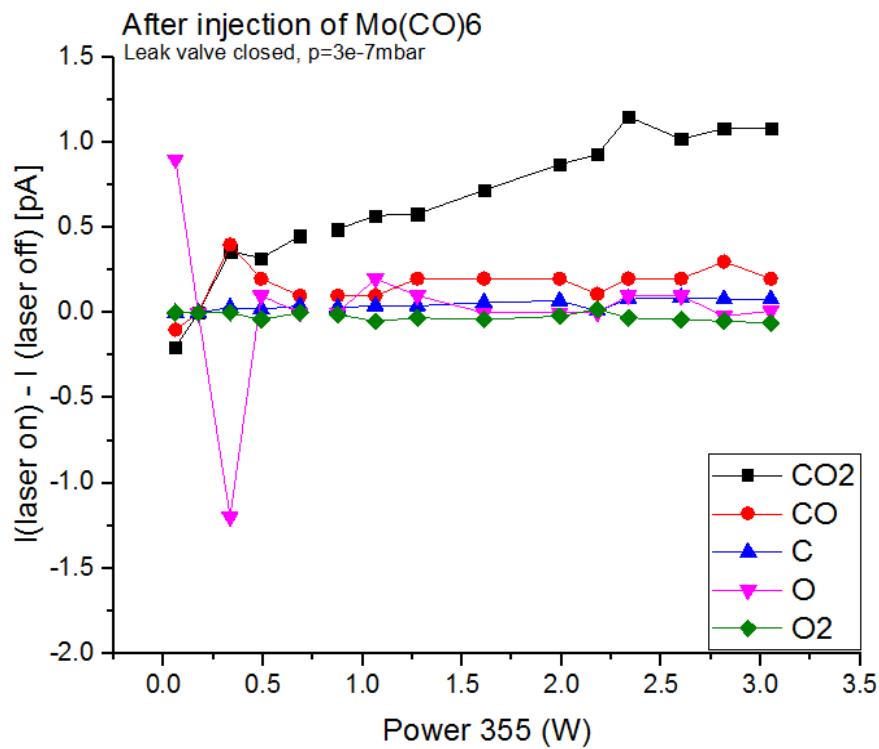
Molybdenum hexacarbonyl supported on functionalized multi-wall carbon nanotubes: Efficient and highly reusable catalysts for epoxidation of alkenes with tert-butyl hydroperoxide

Majid Moghadam ^{a,b,*}, Shahram Tangestaninejad ^{b,*}, Valiollah Mirkhani ^a, Iraj Mohammadpoor-Baltork ^a, Naghmeh Sadat Mirbagheri ^a

Laser induced molecular breakup



Laser induced molecular breakup



• Outlook

- Extend measurement to 255 nm
- Extend measurements to other carbonyls ($\text{Fe}(\text{CO})_5$, $\text{Cr}(\text{CO})_6$,..)
- Efficiency measurements
- Increase laser\gas interaction volume
- Development of laser ionization scheme
- Combined offline tests in ion source

