Towards the carbonyl chemistry of Bh (Z = 107) – studies of carbonyl complexes with ^{259}Sg

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for the TASCA carbonyl chemistry collaboration

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TASCA Workshop 2025, April 23-24, 2025, GSI Darmstadt

Outline

- Motivation
- Previous studies of carbonyl complexes with 4d- and 5d- elements
- First synthesis of the $^{265}Sg(CO)_6$ carbonyl complex, its adsorption and stability
- Preparations for Bh carbonyl complex studies
- Recent study on carbonyl complexes with ^{259}Sg
- Outlook – study of carbonyl complexes with ^{262}Bh

Current status of SHE gas-phase chemistry

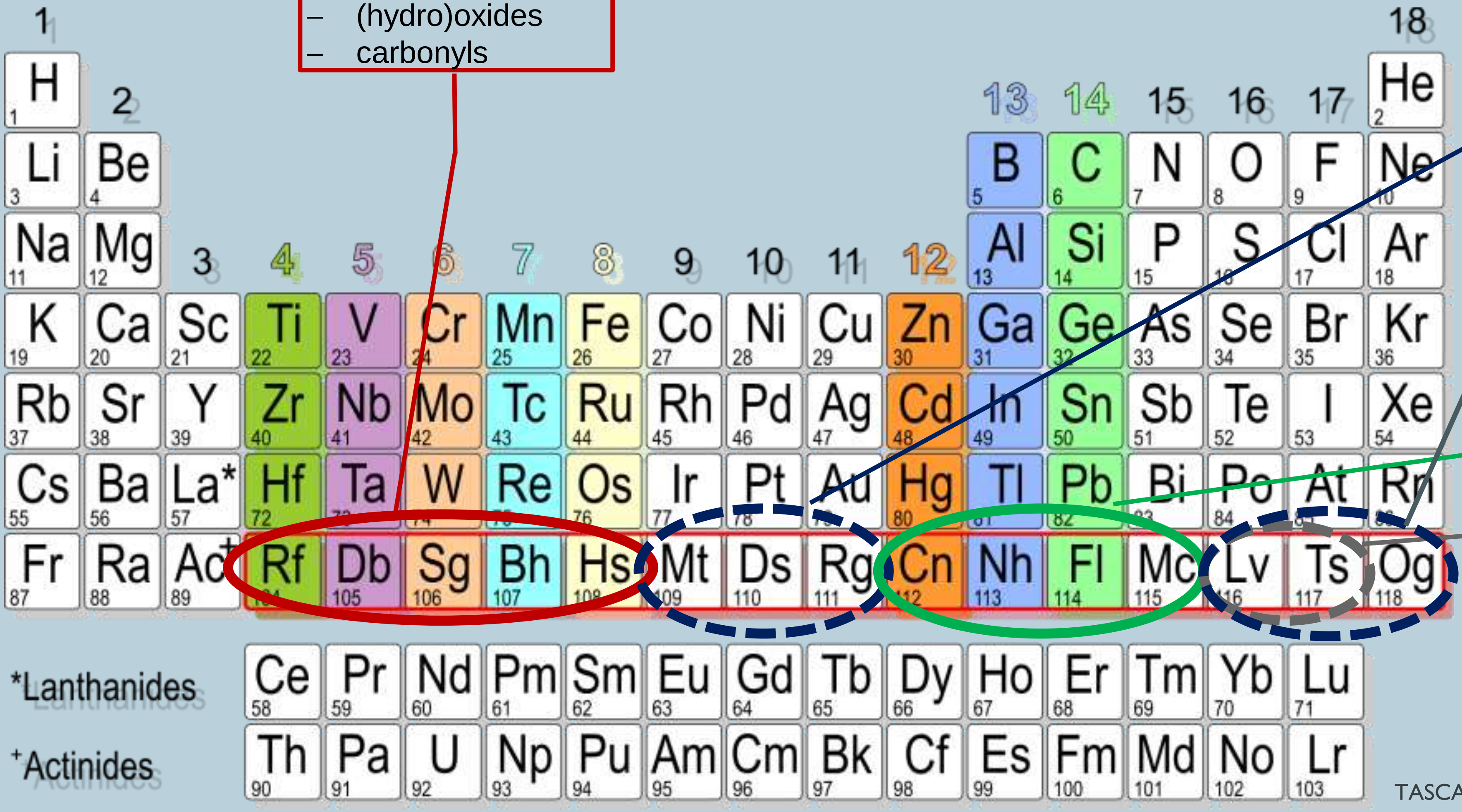
SHE – SuperHeavy Elements (Z > 103)

Volatile compounds have been studied:
- (oxo)chlorides
- (oxo)bromides
- (hydro)oxides
- carbonyls

No chemical studies

Chemical studies with metals in elemental state

Goals for the next future



Chemical systems for superheavy element studies

Table I.1 Place of the Transactinoid/Superheavy Elements in the Mendeleev Periodic Table of the Elements. Emphasized are the **calculated** and just **expected** ground state electronic configurations

Group 3	*4*	*5*	*6*	*7*	*8*	*9*	*10*
Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd
$4d5s^2$	$4d^25s^2$	$4d^45s$	$4d^55s$	$4d^75s$	$4d^85s^2$	$4d^55s^2$	$4d^{10}$
Lu	Hf	Ta	W	Re	Os	Ir	Pt
$5d6s^2$	$5d^26s^2$	$5d^36s^2$	[illegible]	[illegible]	[illegible]	$5d^76s^2$	$5d^96s$
Lr 103	**Rf 104**	**Db 105**	**Sg 106**	**Bh 107**	**Hs 108**	**Mt 109**	**Ds 110**
$7s^2p$	$6d7s^2p$	$6d^37s^2$	$6d^47s^2$	$6d^57s^2$	$6d^67s^2$	$6d^77s^2$	$6d^87s^2$

Transactinoids ——————————————>

11	*12*	*13*	*14*	*15*	*16*	*17*	*18*
Ag	Cd	In	Sn	Sb	Te	J	Xe
$4d^{10}5s$	$4d^{10}5s^2$	$5s^2p$	$5s^2p^2$	$5s^2p^3$	$5s^2p^4$	$5s^2p^5$	$5s^2p^6$
Au	Hg	Tl	Pb	Bi	Po	At	Rn
$5d^{10}6s$	$5d^{10}6s^2$	$6s^2p$	$6s^2p^2$	$6s^2p^3$	$6s^2p^4$	$6s^2p^5$	$6s^2p^6$
Rg 111	**Cn**	**Nh**	**Fl**	**Mc**	**Lv**	**Ts**	**Og**
$6d^97s^2$	$6d^{10}7s^2$	$7s^2p$	$7s^2p^2$	$7s^2p^3$	$7s^2p^4$	$7s^2p^7$	$7s^2p^6$

Superheavies - >

1966- 2000:

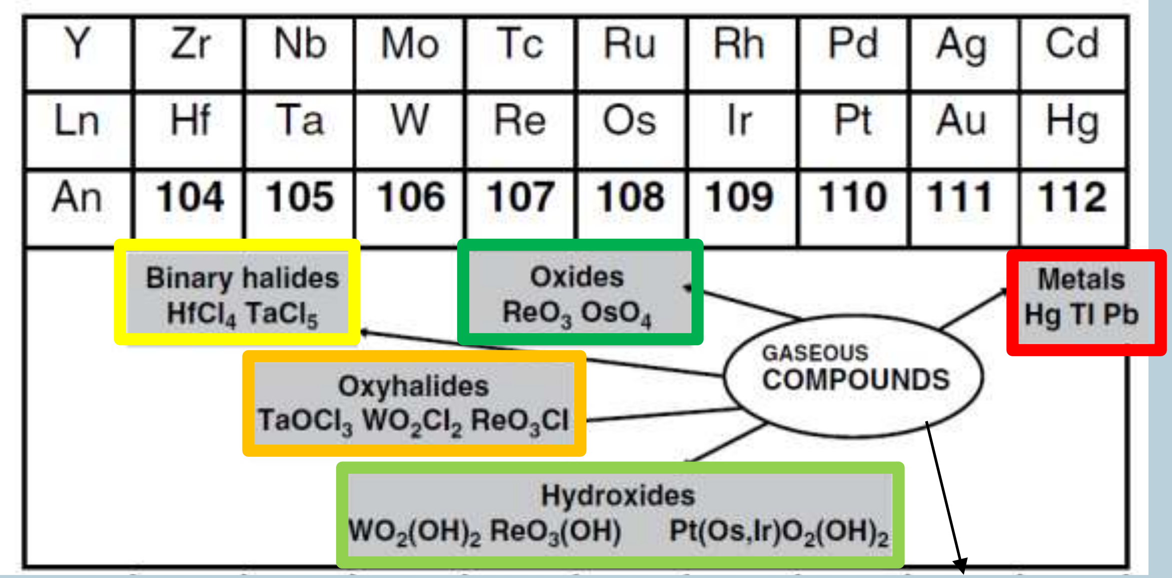
$RfCl_4$, $DbOCl_3$, SgO_2Cl_2, BhO_3Cl

2001-2008: **HsO_4**

2001-2022: **Cn, Nh, Fl, Mc**

2013-2015: **$Sg(CO)_6$**

new: Carbonyls

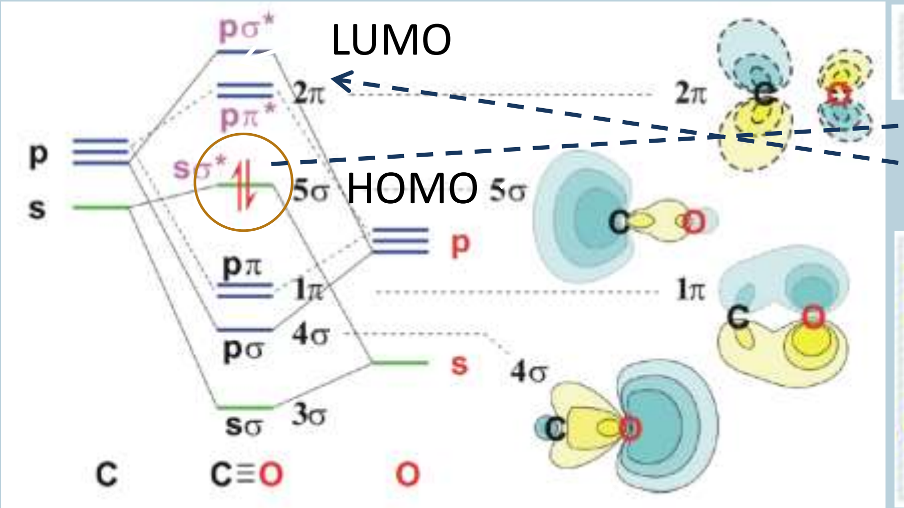


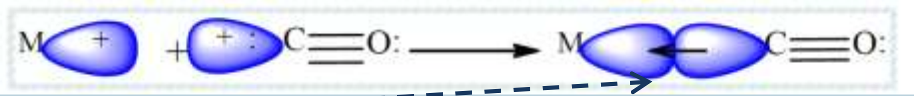
A few chemical compound classes are known for SHE

Carbonyls – the new SHE compound class

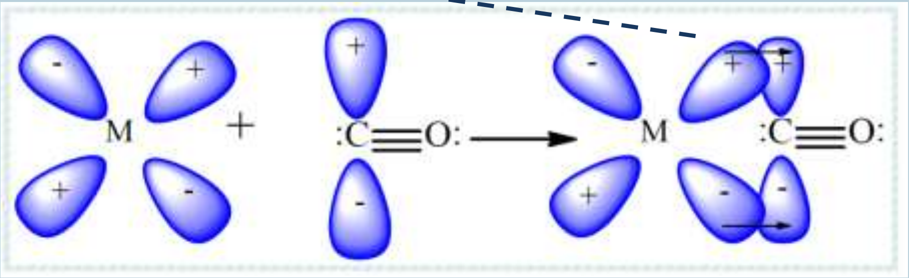
Stable carbonyl complexes are predicted for Sg (Z=106), Bh (Z=107), Hs (Z=108) and Mt (Z=109)

Carbonyl complexes – compounds with zero valence

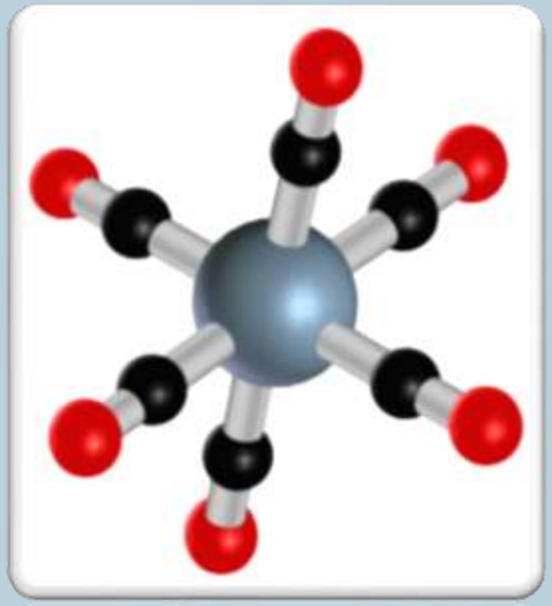




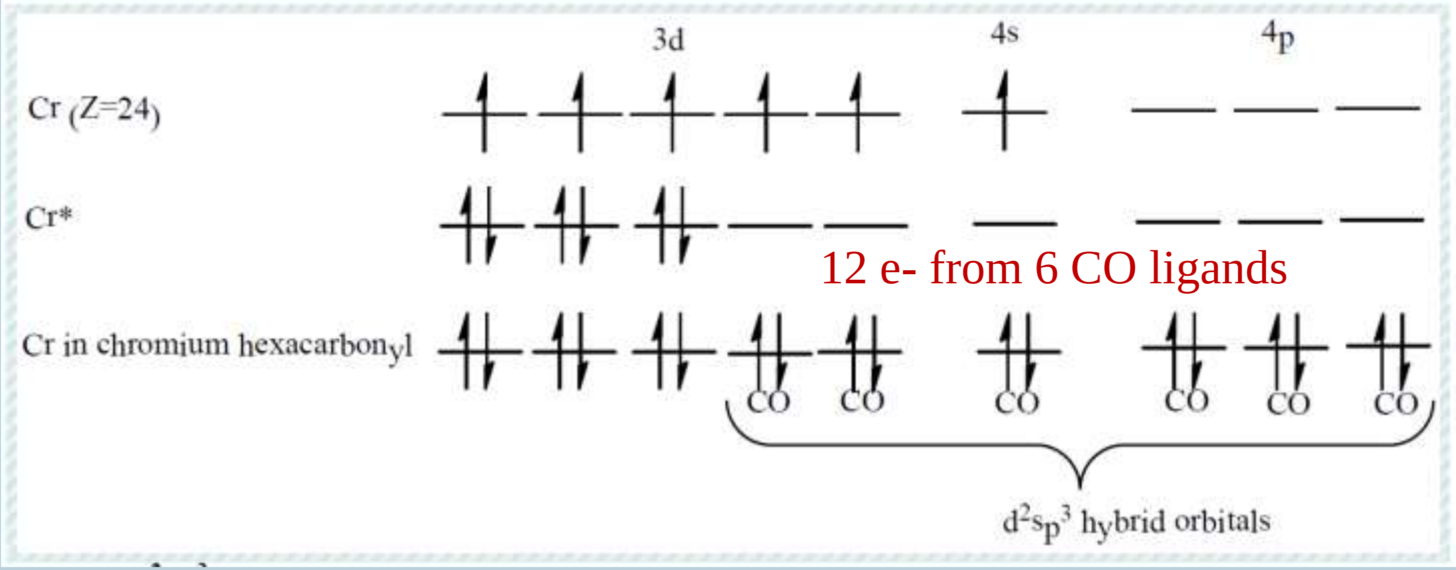
σ-bonds between M and CO



π-backbonding



O_h – octahedral geometry



Neutral metal atom is surrounded with neutral CO molecules – Carbonyl complexes are unique compounds for understanding the relativistic effects

Carbonyl complex studies worldwide

J. Even *et al.*, *Inorg. Chem.* **51,** 6431 (2012)

J. Even *et al.*, *Radiochim. Acta* **102**, 1093 (2014)

J. Even et al., *Science* **345**, 1491 (2014)

J. Even *et al.*, *J. Radioanal. Nucl. Chem.* **303**, 2457 (2015)

Y. Wang *et al.*, Radiochim. Acta **102**, 69 (2014)

Y. Wang, *Phys. Chem. Chem. Phys.* **17**, 13228 (2015)

Y. Wang, *Phys. Chem. Chem. Phys.* **21**, 7147-7154 (2019)

S. Cao, *Phys. Chem. Chem. Phys.* **18**, 119-25 (2016)

R. Eichler et al., *EPJ Web of Conferences* **131**, 07005 (2016)

I. Usoltsev et al., *Radiochim Acta* **104**, Part I and Part II (2016)

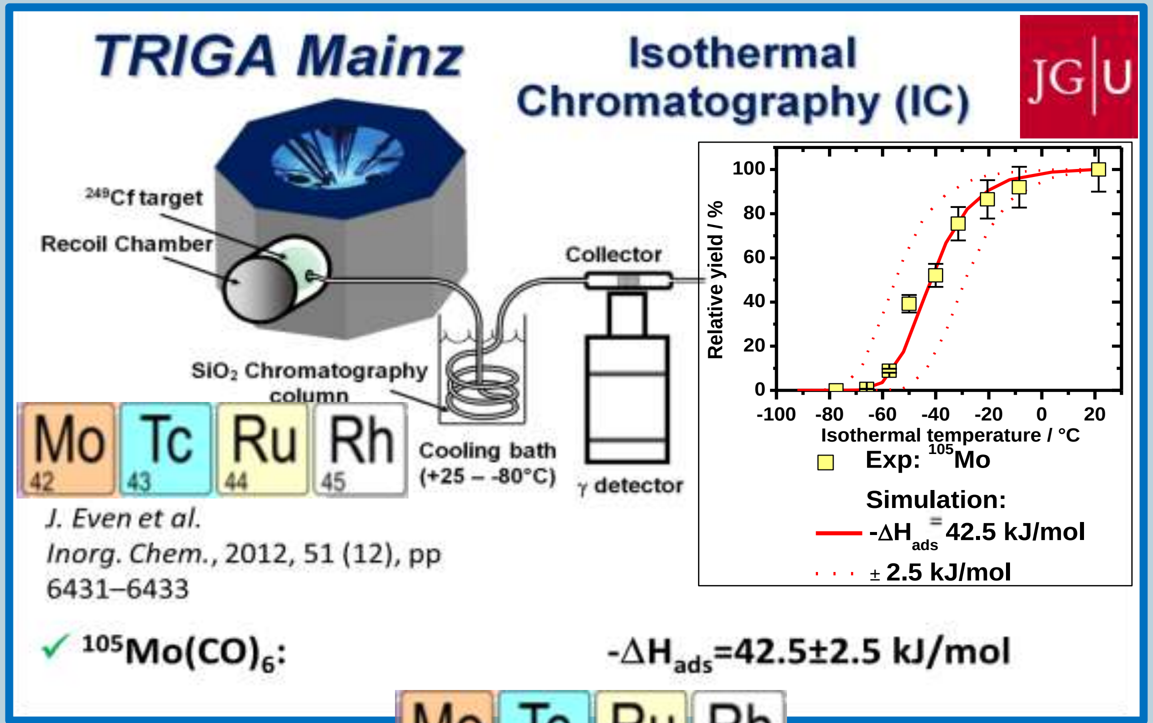
Y. Wittwer et al., *Radiochimica Acta* **109(4)**, 243-260 (2021)

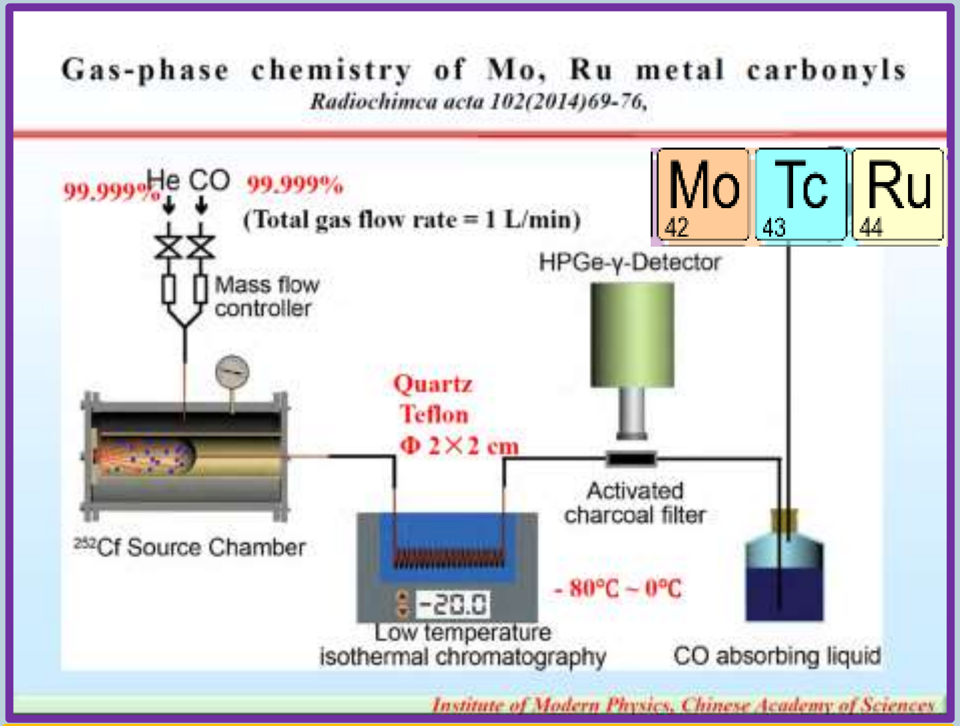
Y. Wittwer et al., *Radiochimica Acta* **109(11**), 799-821 (2021)

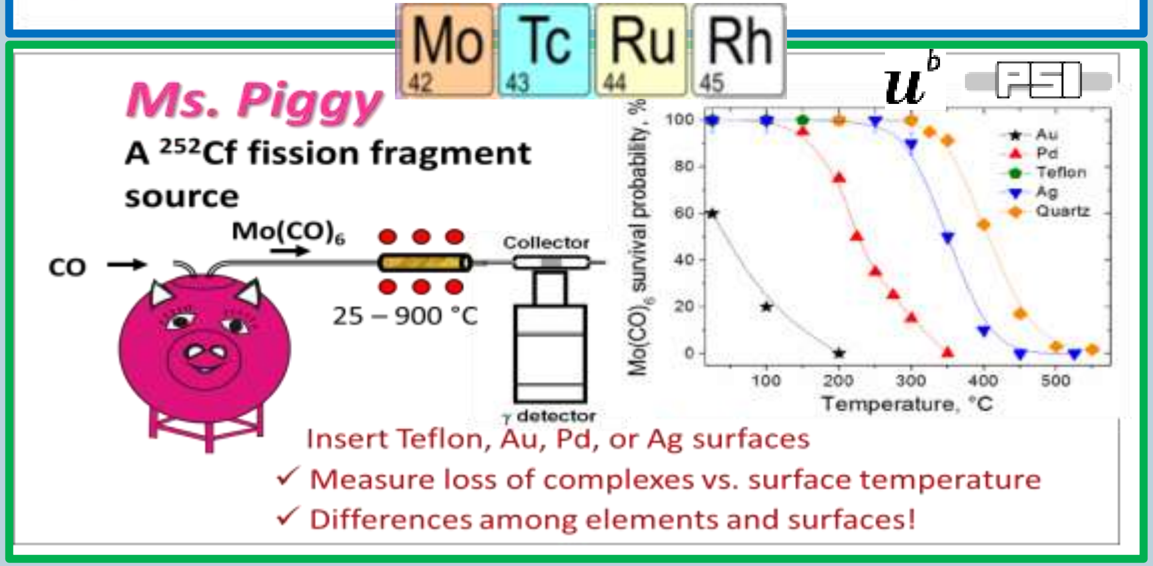
M. Götz et al., *Radiochimica Acta* **109(3)**, 153-165 (2021)

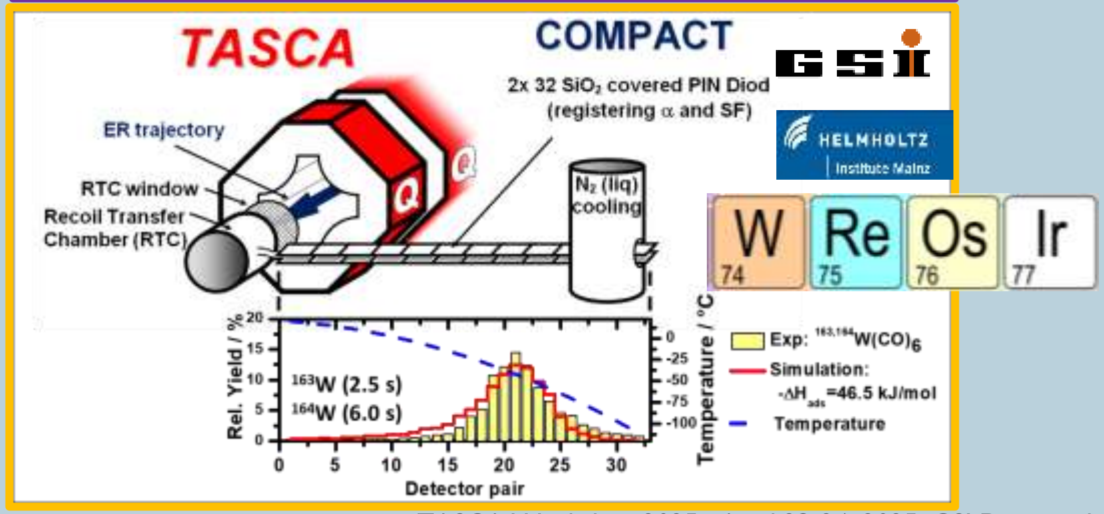
M. Götz et al., *Radiochim. Acta* **110**(2): 75–86 (2022)…

Carbonyl studies with SHE homologues – some examples



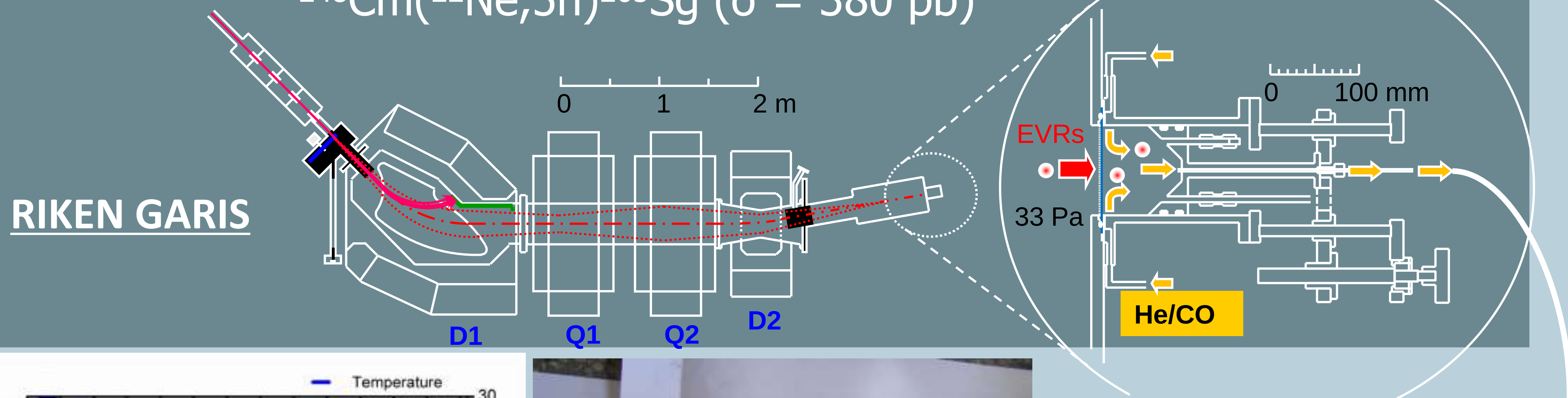




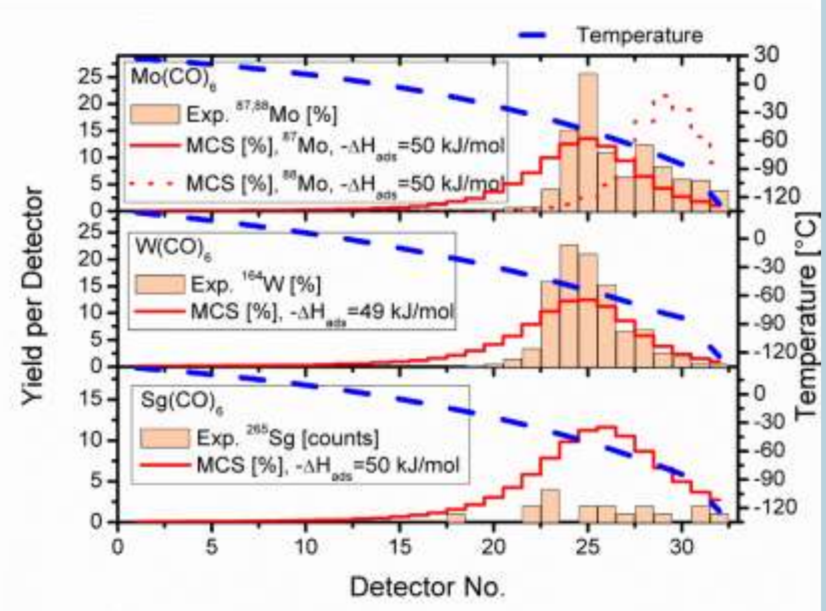


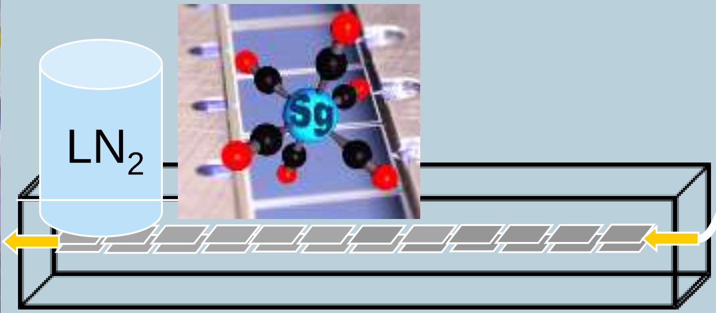
The first sinthesis and adsorption study of $Sg(CO)_6$

$^{248}Cm(^{22}Ne,5n)^{265}Sg$ (σ = 380 pb)



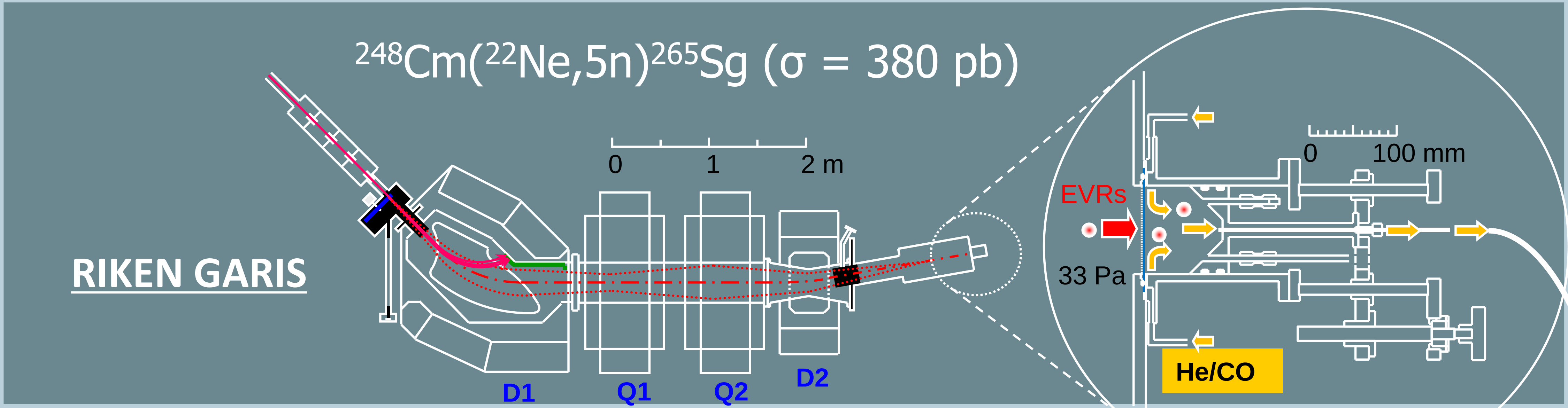
18 Sg atoms

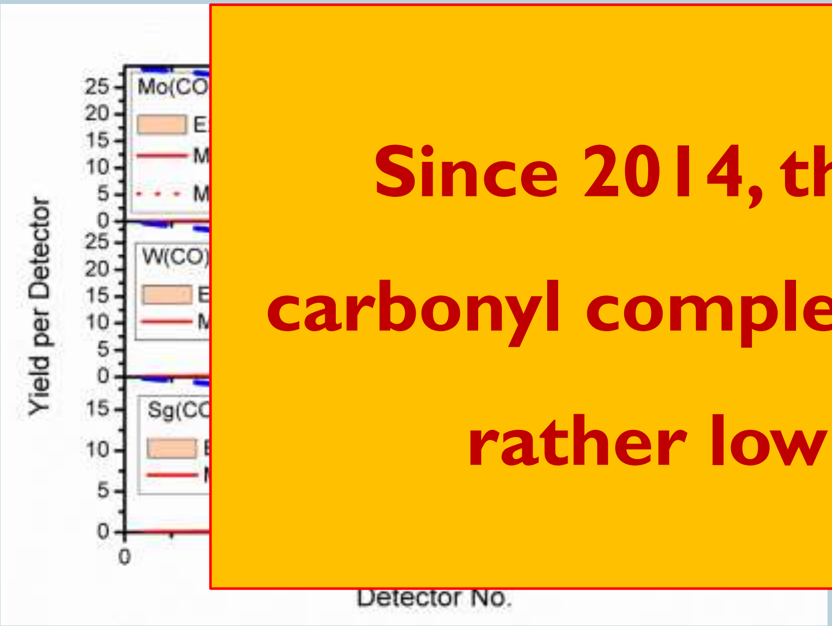




J. Even et al. **Synthesis and detection of a seaborgium carbonyl complex**
Science *Vol. 345 no. 6203 pp. 1491-1493*

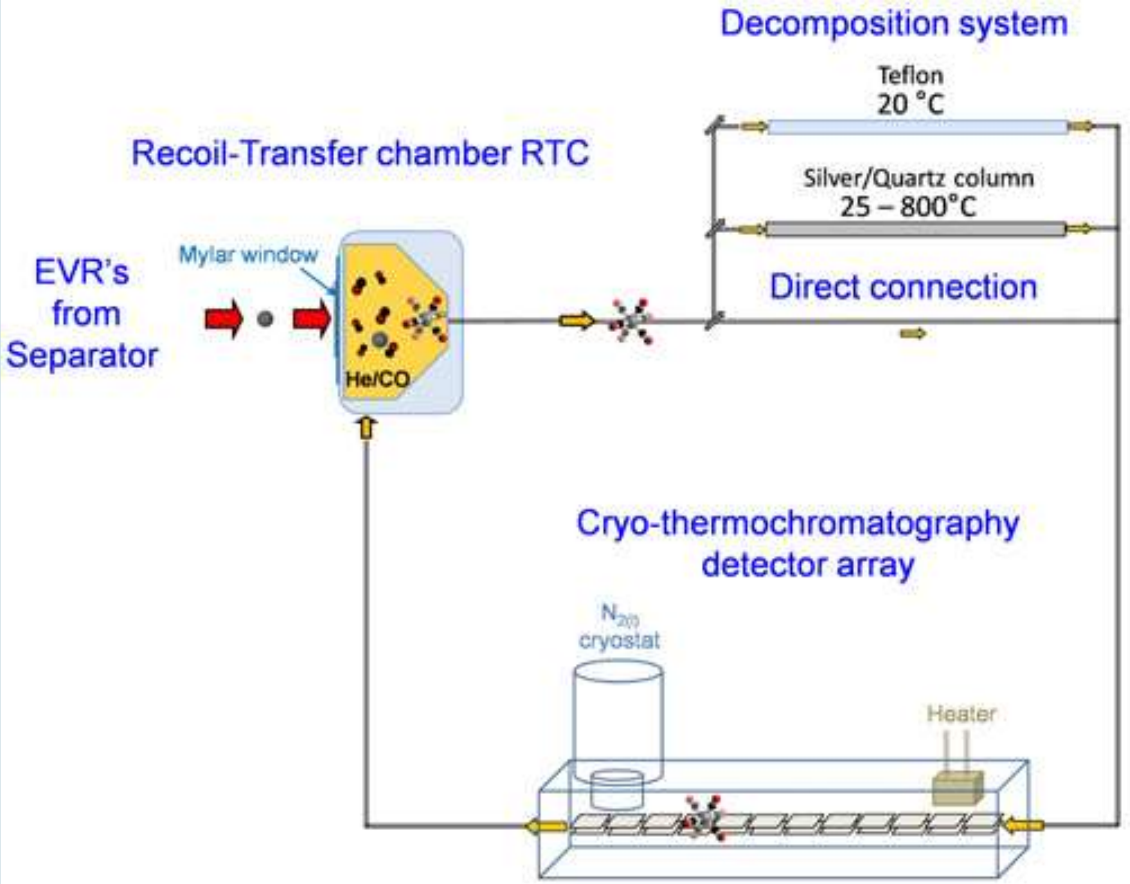
The first sinthesis and adsorption study of $Sg(CO)_6$

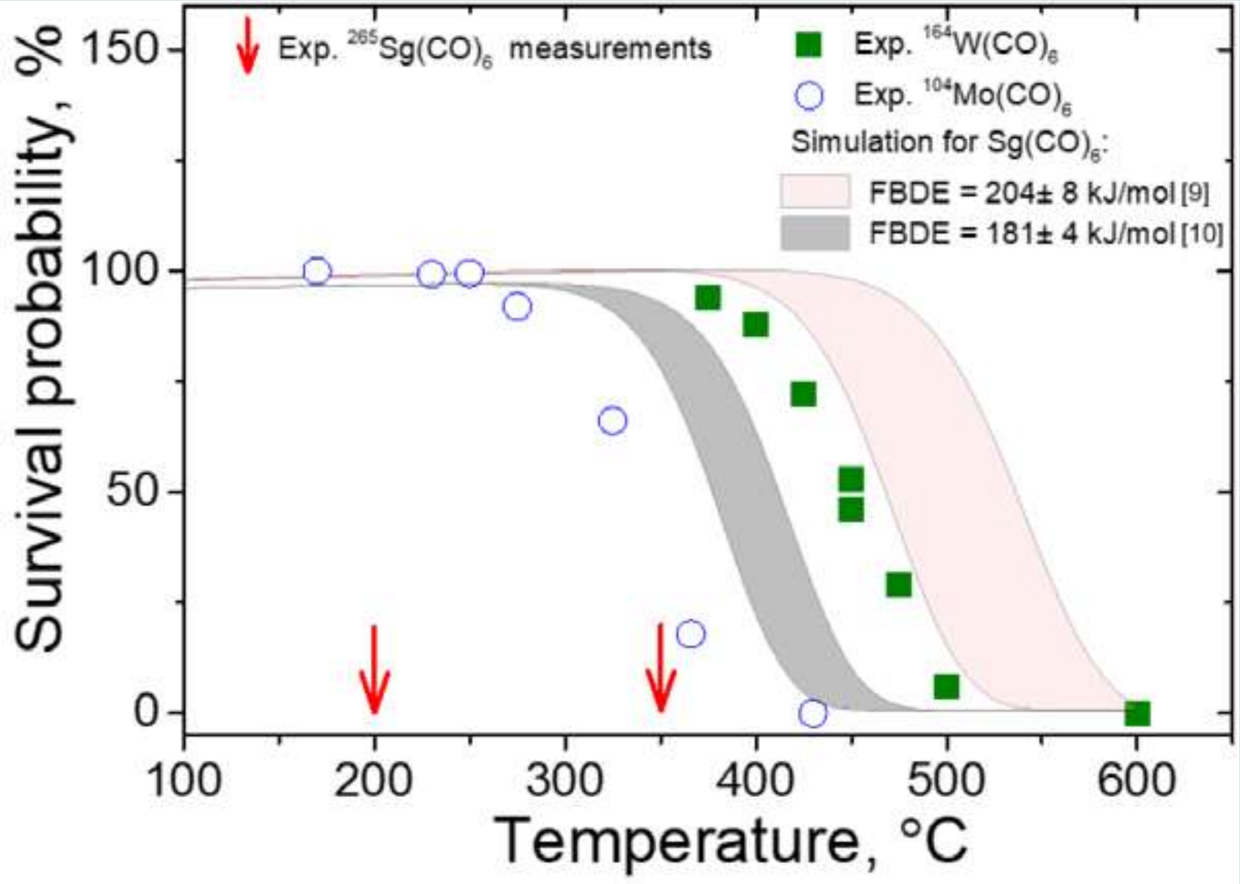




Since 2014, the next goal is synthesis of the Bh carbonyl complex, but it was not yet achieved due to rather low production rate and efficiency

Measurements of the stability of $Sg(CO)_6$



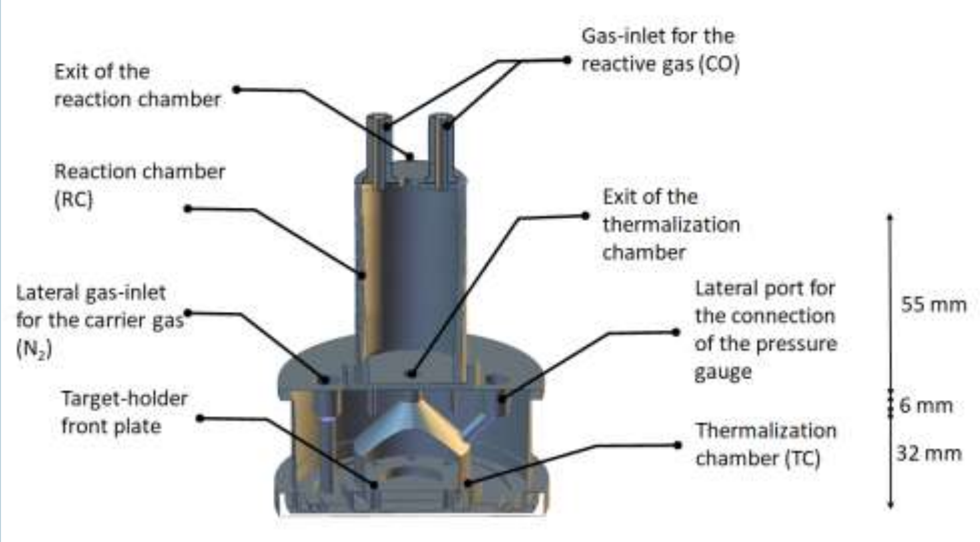


Unpublished experiment: Determination of the First Bond Dissociation Energy (FBDE) for $Sg(CO)_6$

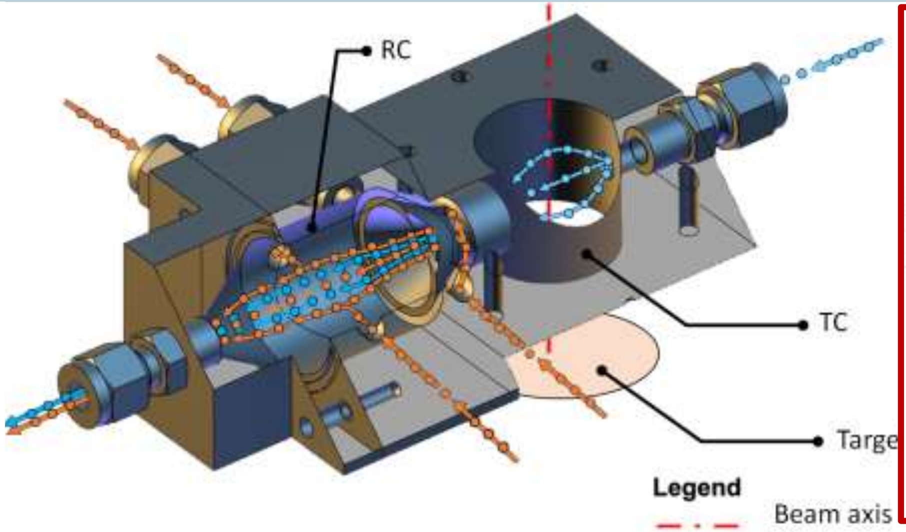
The $Sg(CO)_6$ FBDE value was not given due to low statistics

The chemical yield for $Sg(CO)_6$ is determined on a level of a few percent in both studies

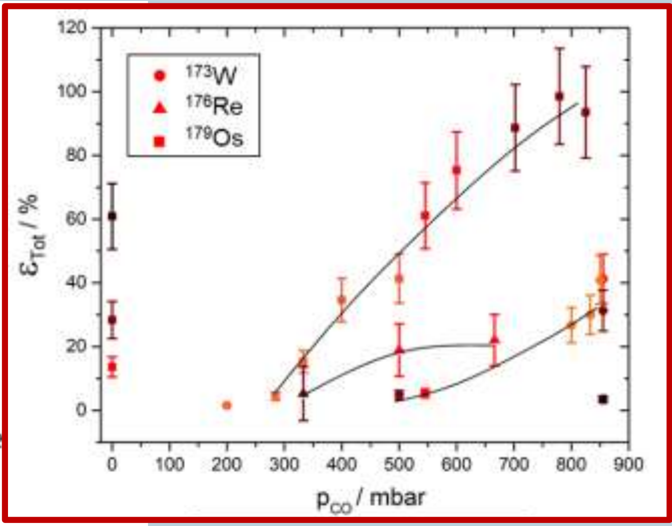
Attempts for carbonyl complex studies w/o preseparation



TRIGA Mainz, Germany



JAEA, Tokai, Japan



Reaction	ε_{Flush} / %	ε_{Chem} / %	ε_{Tot} / %
$^{159}Tb(^{19}F, 5n)^{173}W$	46(5)	85(16)	39(6)
$^{165}Ho(^{19}F, 5n)^{179}Os$	98(10)	96(14)	94(10)
$^{nat}Dy(^{19}F, 5n)^{175-178}Re$	(-)	(-)	(>20)
$^{235}U(n,f)^{101}Mo$	57(5)	83(8)	49(2)

Transmission in a separator for products of asymmetric reactions is low

→ double-chamber approach

M. Götz et al., Radiochim. Acta, 110, 2022; PhD thesis, Mainz 2020

New carbonyl complex studies with Sg and Bh

GSI Research Proposals G-22-00034 and G-24-00248
Chemical studies of carbonyl complexes of the superheavy elements Sg (Z = 106) and Bh (Z = 107)
Spokesperson: Alexander Yakushev

Co-spokespersons H. Haba (RIKEN, Wako-shi, Japan; haba@riken.jp); Ch. E. Düllmann (U. of Mainz, HI Mainz, GSI; duellman@uni-mainz.de)

A. Yakushev[1,2], Ch. E. Düllmann[1,2,3], J. Khuyagbaatar[1], H. Haba[4], M. Block[1,2,3], R. A. Cantemir[1], D. Dietzel[1,3], F. Giacoppo[1,2], J. Krier[1], N. Kurz[1], P. Mosat[1], S. Raeder[1,2], J. Runke[1,3], B. Schausten[1], M. Schädel[1], M. Asai[5], K. Auranen[6], P. Bartl[7], C. M. Folden III[8], R.-D. Herzberg[9], J. John[7], D. Judson[9], L. Lens[10], M. Maiti[11], Y. Nagame[5], J. P. Omtvedt[12], P. Papadakis[13], T. K. Sato[5], U. Scherer[10], E. Tereshatov[8], K. Tsukada[5], J. J. W. van de Laar[10], J. Uusitalo[6], Y. Wei[1,3]

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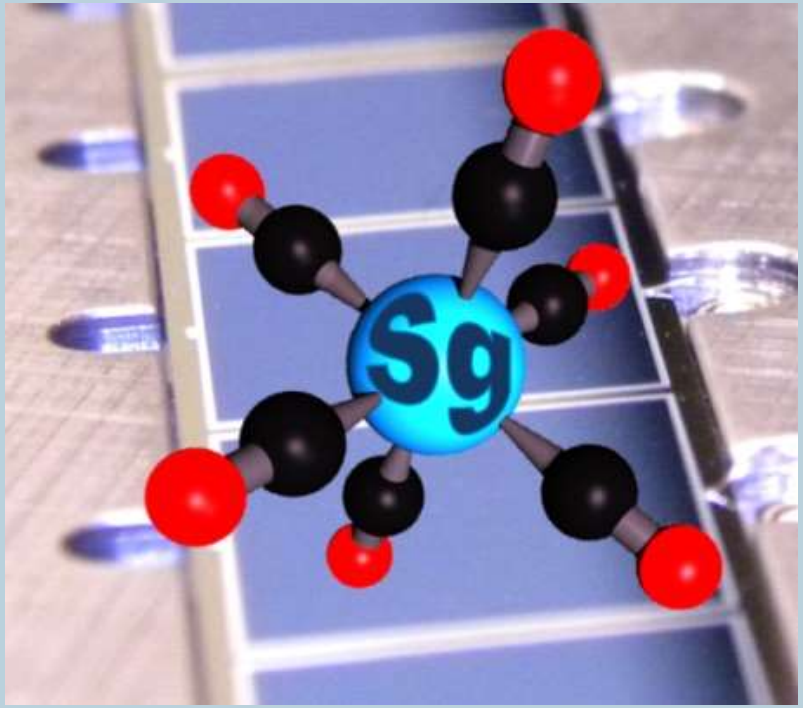
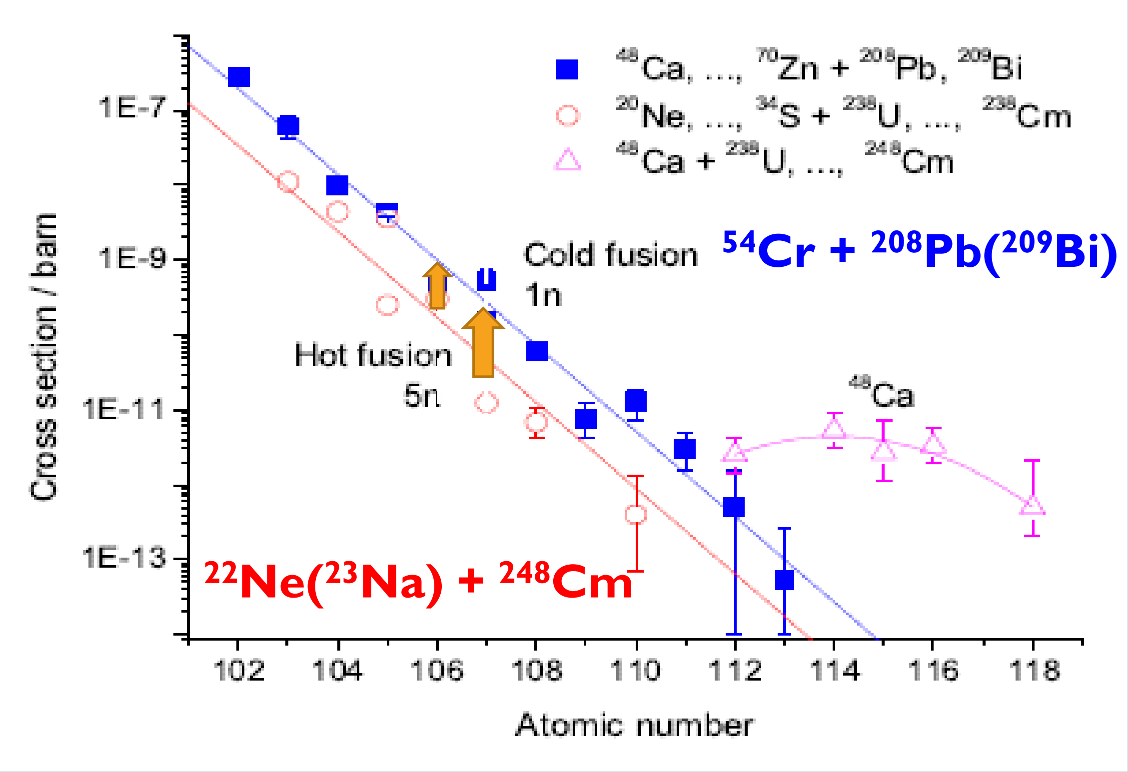
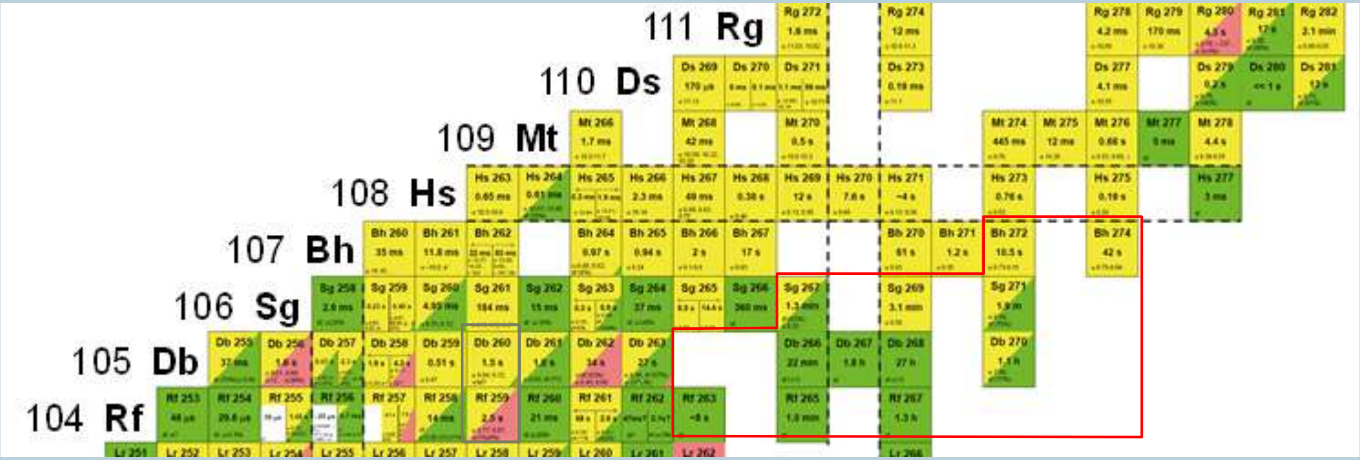
[12]University of Oslo, Oslo, Norway
[13]STFC Daresbury Laboratory, Warrington, UK



Production of Sg and Bh isotopes in hot and cold fusion





Hot fusion

^{266}Bh	2 s	50 pb
^{265}Sg	15 s	380 pb

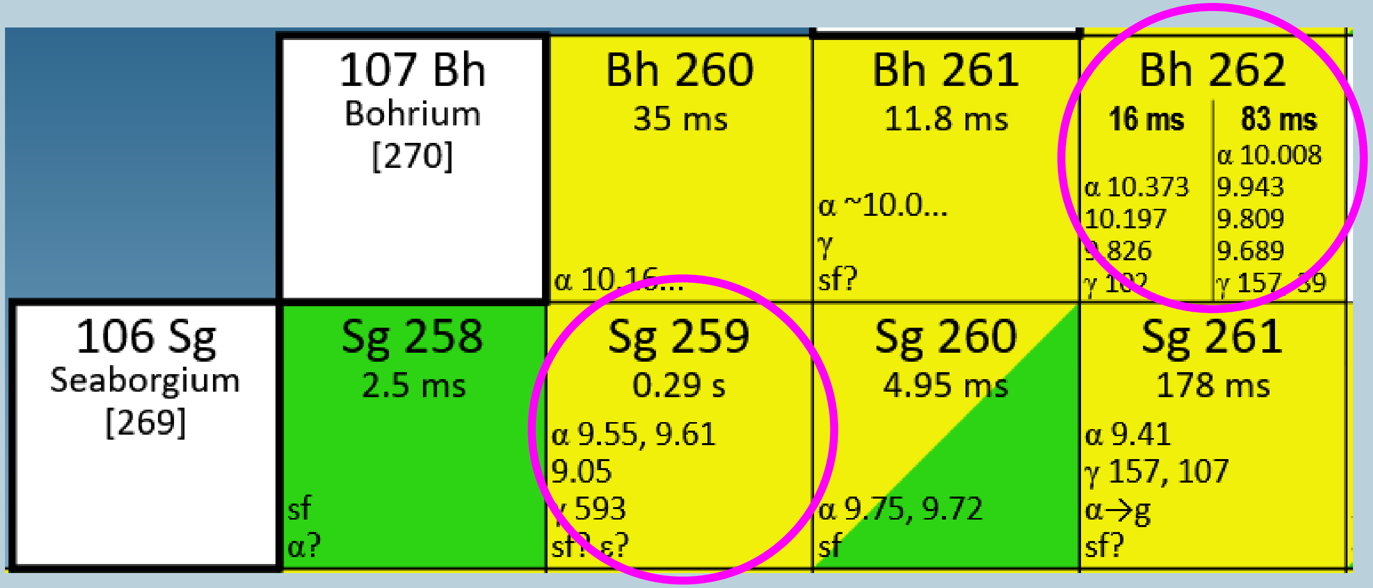
Cold fusion

^{262g}Bh	135 ms	290 pb
^{261}Sg	178 ms	2190 pb

	^{265}Sg → ^{261}Sg	^{266}Bh → ^{262}Bh
Gain in production rate:	x 5	x 6
Gain in separation efficiency:	x 5	x 5
Losses due to short half-lives:	x 0.25	x 0.15
Total gain:	**x 6**	**x 4.5**

☹ Technical problem @ UNILAC:
a low beam intensity of ^{54}Cr ion beam

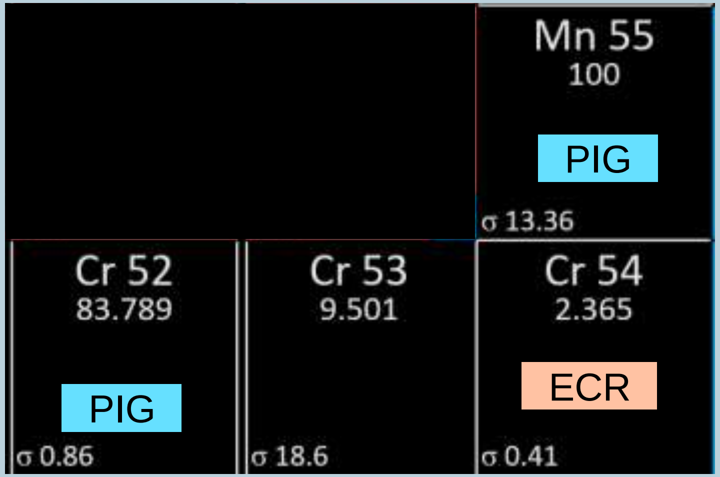
Production of Sg and Bh isotopes – alternatives



$^{54}Cr + ^{209}Bi$ (440^{+440}_{-240} pb)

$^{55}Mn + ^{208}Pb$ (590^{+170}_{-140} pb)

C.M. Folden III et al.,
Phys. Rev. C **73**, 014611 (2006)



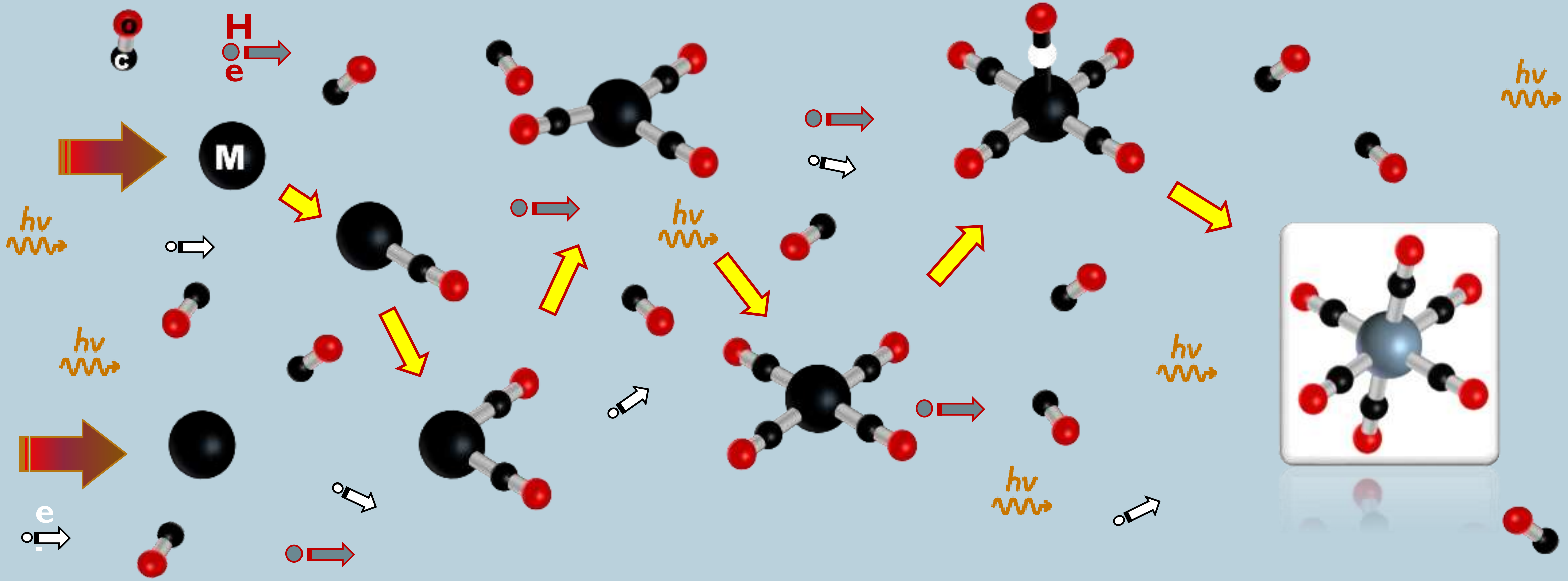
$^{52}Cr + ^{208}Pb$ (320^{+110}_{-100} pb)

C.M. Folden III et al.,
Phys. Rev. C **79**, 027602 (2009)

$^{54}Cr + ^{208}Pb$ (2100 pb)

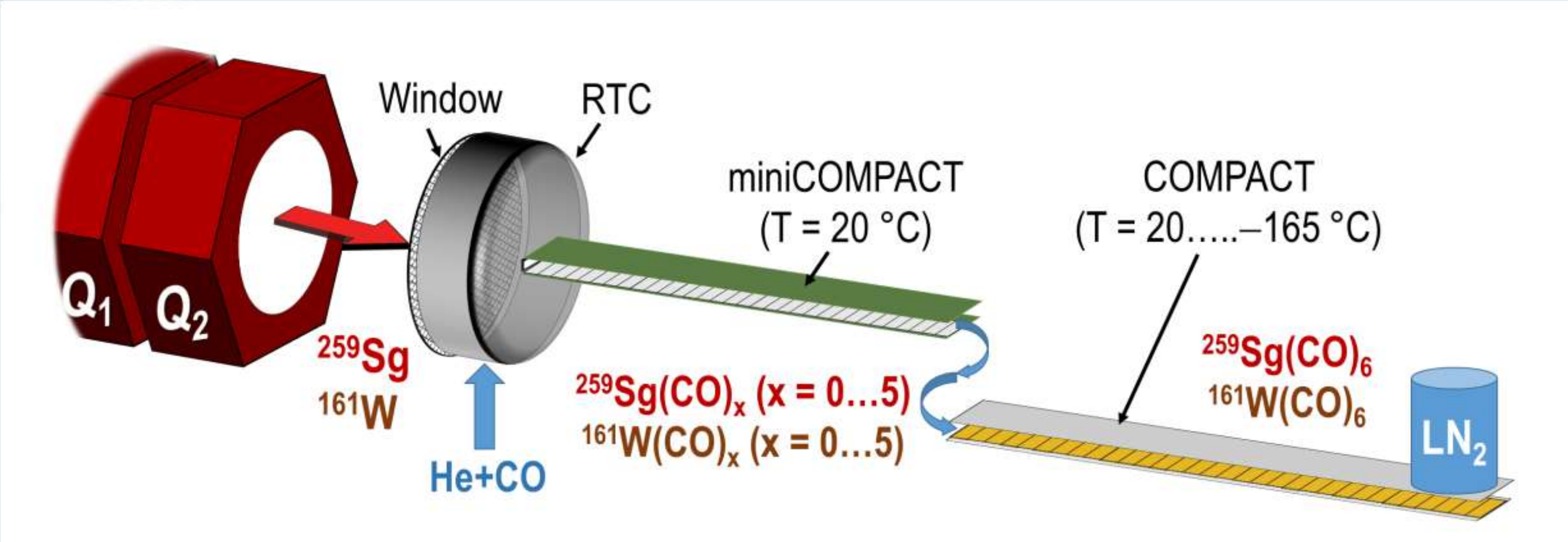
B. Streicher et al.,
Eur. Phys. J. A **45**(3), 275 (2010)

Carbonyl complex formation



- Carbonyl complex formation is a multi-step process
- The final products and all intermediate products exist in the reaction mixture
- All steps are revirsible

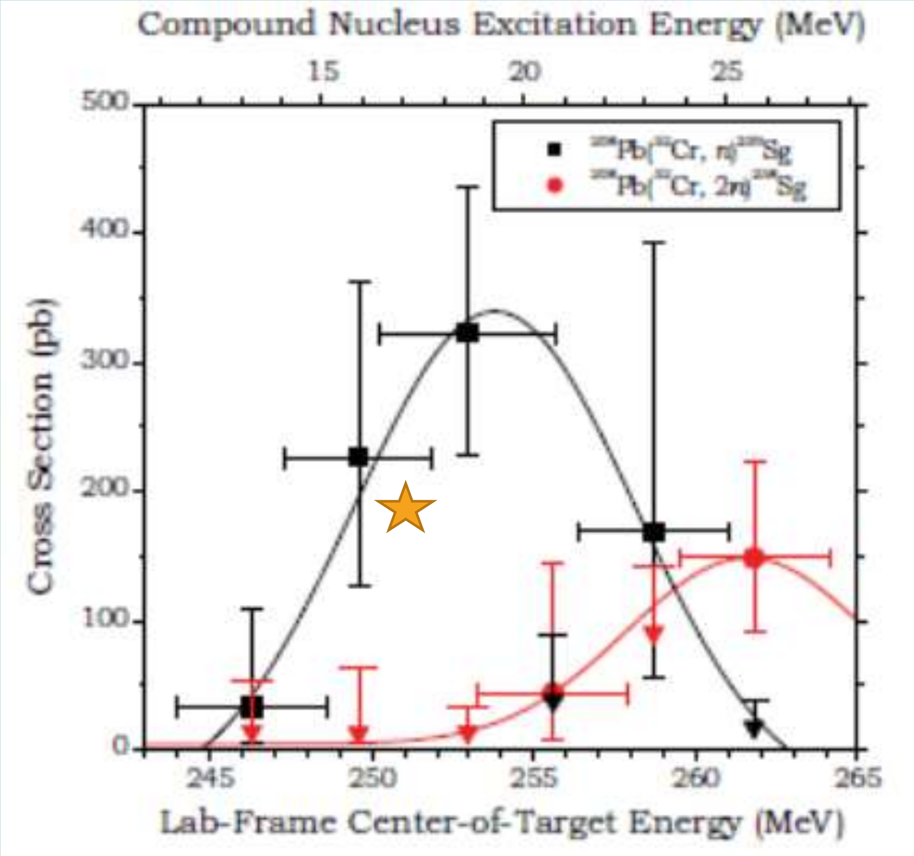
$^{259}Sg(CO)_6$ study – experimental setup



The experimental setup is similar to that used for Mc/Nh studies

$^{259}Sg(CO)_6$ study – experimental results

$^{52}Cr^{14+}$ (4.95 MeV/amu) + ^{208}Pb (800 μg/cm^2), Beam dose ≈ 4 E18 (2 weeks)

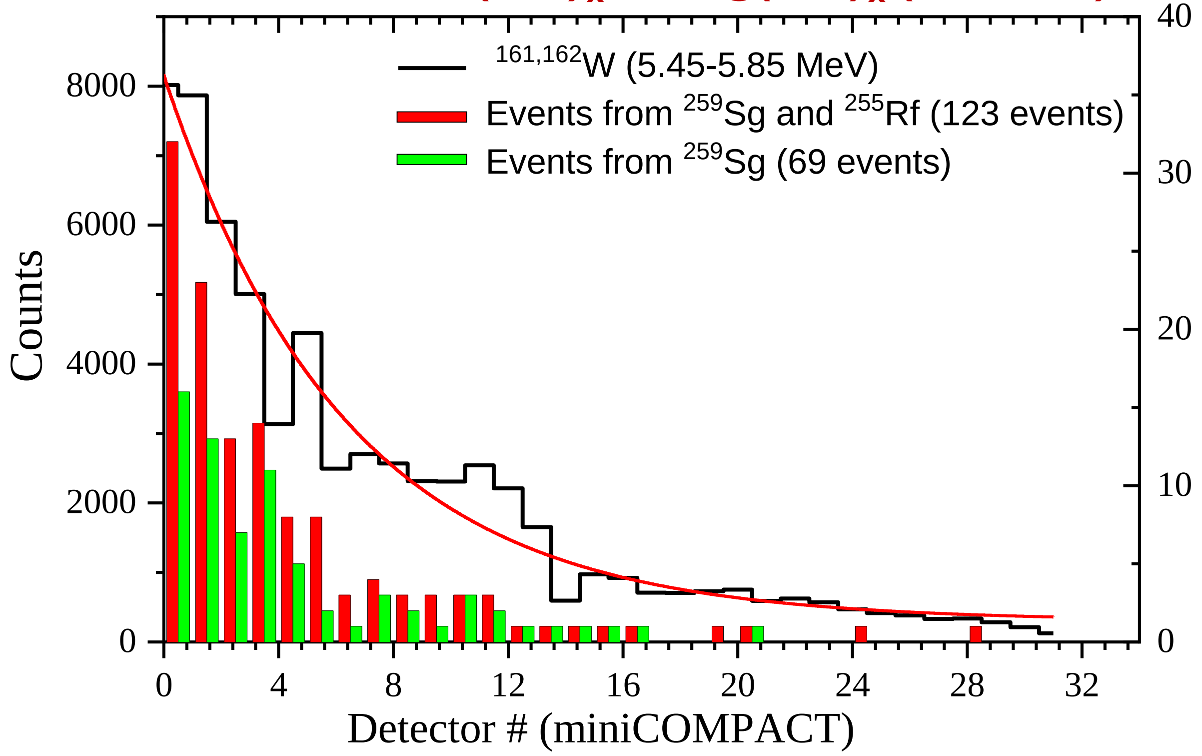


Target thickness	2 E18
TASCA transmis. to RTC window	0.4
Window grid	0.8
Flush-out efficiency	0.35

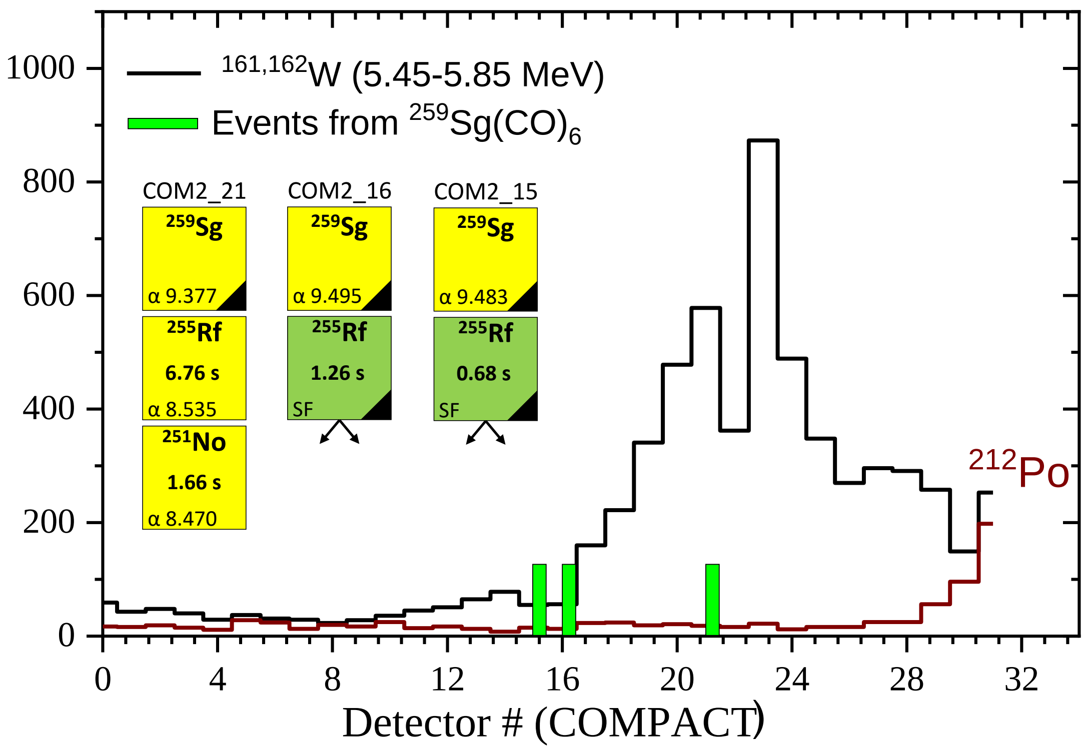
Number of Sg/Rf events	126
Detection efficiency	0.8
Cross section estimation	~200 pb

$^{259}Sg(CO)_6$ study – experimental results

$^{161,162}W(CO)_x$ / $^{259}Sg(CO)_x$ (x = 0…5)



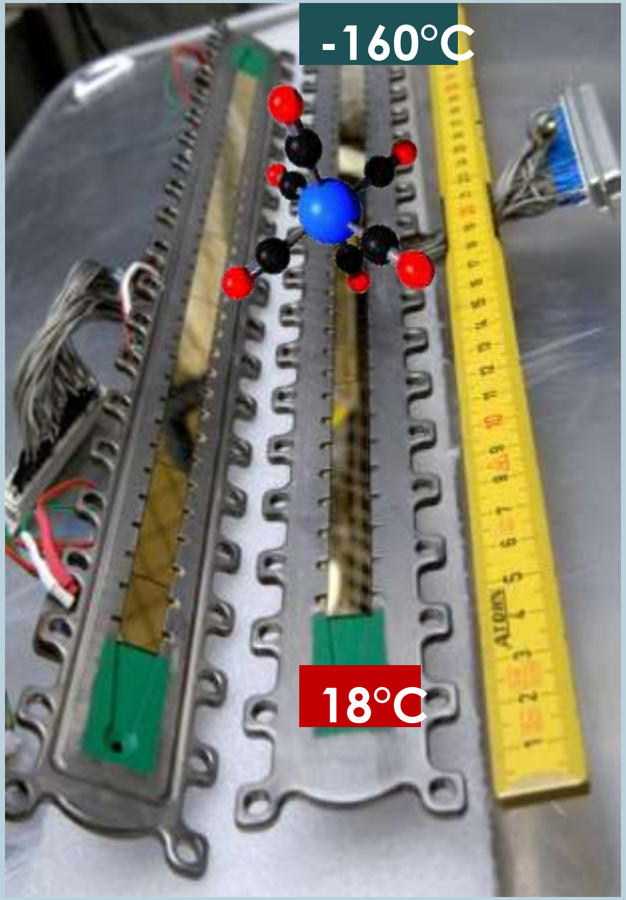
$^{161,162}W(CO)_6$ / $^{259}Sg(CO)_6$

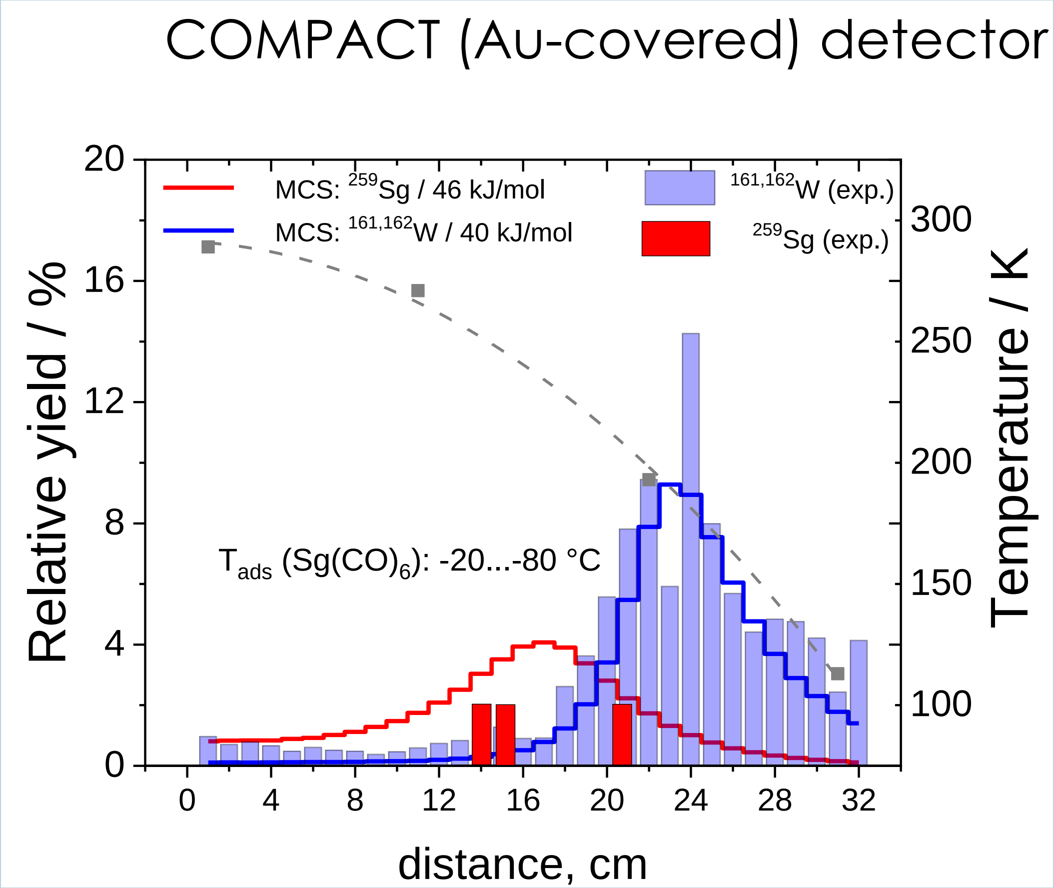


Diffusion-controlled deposition of non-volatile species in miniCOMPACT

Adsorption of volatile $M(CO)_6$ complex (M = W or Sg) at a low temperature on Au

$^{259}Sg(CO)_6$ study – experimental results





Monte Carlo Simulations

$Sg(CO)_6$
$-\Delta H_{ads}$ = 46 kJ/mol

$W(CO)_6$
$-\Delta H_{ads}$ = 40 kJ/mol

(preliminary)

Group	Complex	IC SiO_2	COMPACT SiO_2	COMPACT Au
6	$Mo(CO)_6$	42.5±2.5		
6	$W(CO)_6$		46.5±2.5	41^{+3}_{-4}
7	$Re(CO)_yX$	43±3		
8	$Os(CO)_5$		$43.5^{+3.5}_{-2.3}$	39±4
9	$Ir(CO)_yX$	37±3		

J.Evenet al., Radiochim. Acta, 102, 2014

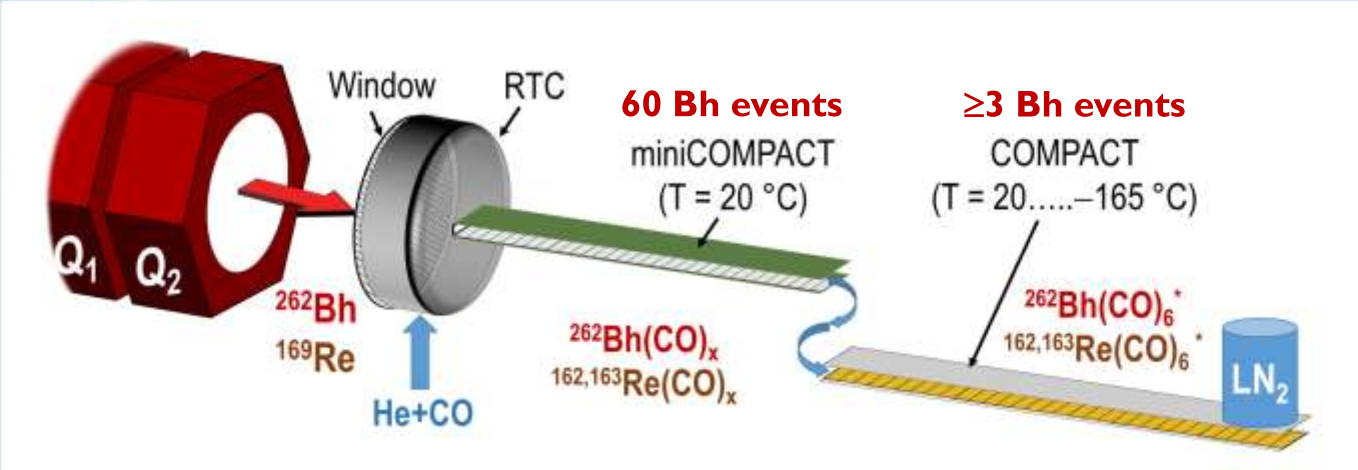
Chemical yield:	$^{161,162}W(CO)_6$	~ 20%
	$^{259}Sg(CO)_6$	~ 4%

$^{262}Bh(CO)_x$ study – a new proposal

$^{55}Mn + ^{208}Pb$
(590 $^{+170}_{-140}$ pb)
(PIG)

Bh 262	
16 ms	83 ms
	α 10.008
α 10.373	9.943
10.197	9.809
9.826	9.689
γ 102	γ 157, 39

^{55}Mn beam (105 shifts)
(~4.9 MeV/amu, 0.8 particle μA)



<u>Beam time request and expected results</u>:

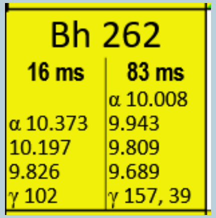
12 shifts of main ^{55}Mn beam -
measurements of the of ^{262}Bh in the focal plane detector
9 shifts of main ^{55}Mn beam - study of the Re carbonyl complex formation with short-lived $^{162,163}Re$ isotopes

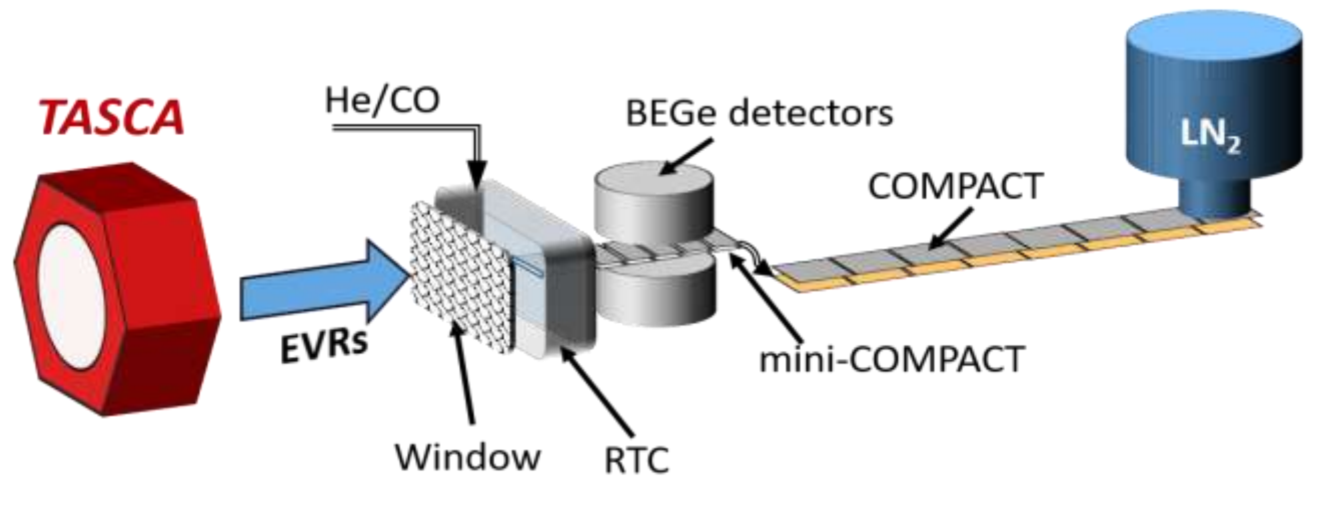
84 shifts of main ^{55}Mn beam (short half-life of ^{262}Bh is a biggest challenge)
First study of the formation of a Bh carbonyl complex, its surface interaction and stability
70 shifts of parasitic beams (^{50}Ti, ^{52}Cr, ^{55}Mn, ^{56}Fe)
for optimization of the experimental setup and flush-out time with short-lived $^{213,214}Th$ isotopes

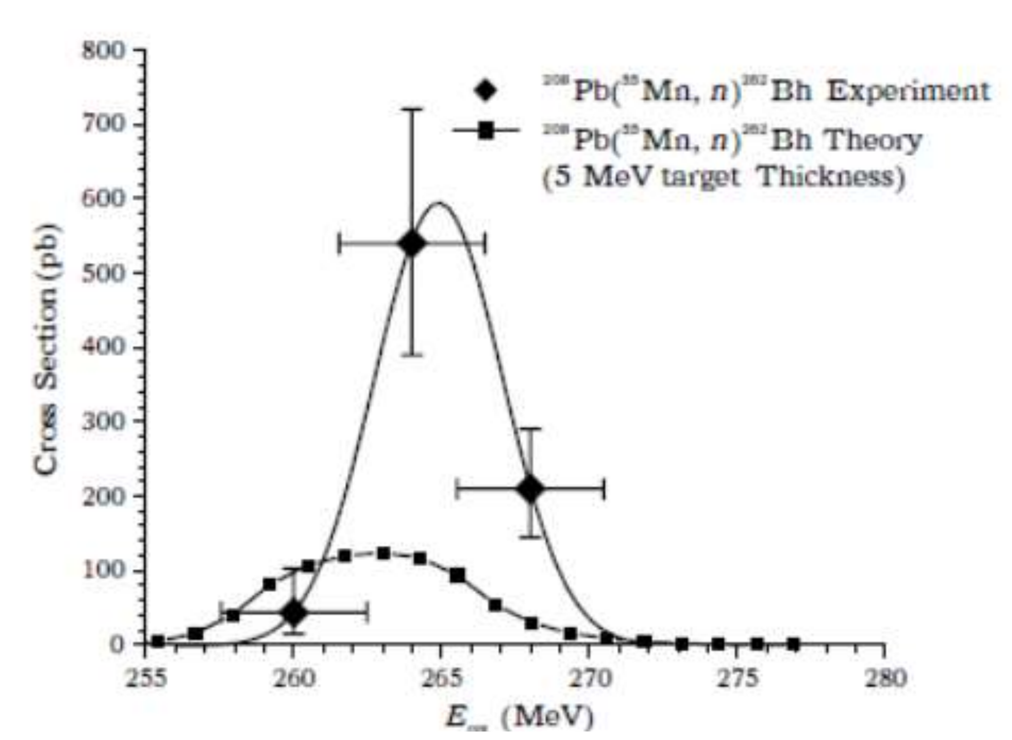
G-PAC decision: 21(main) + 21 (parasitic) shifts for the cross section measurement and optimization of chemistry with Re

^{262}Bh(CO)$_x$ study – a new proposal

^{55}Mn + ^{208}Pb
(σ= 590 $^{+170}_{-140}$ pb)







C.M. Folden III et al., Phys. Rev. C 73, 014611 (2006)

^{55}Mn + ^{112}Sn

A faster gas flow rate in the gas loop will allow for

a transport time ~ 100 ms

Chemical yield optimization

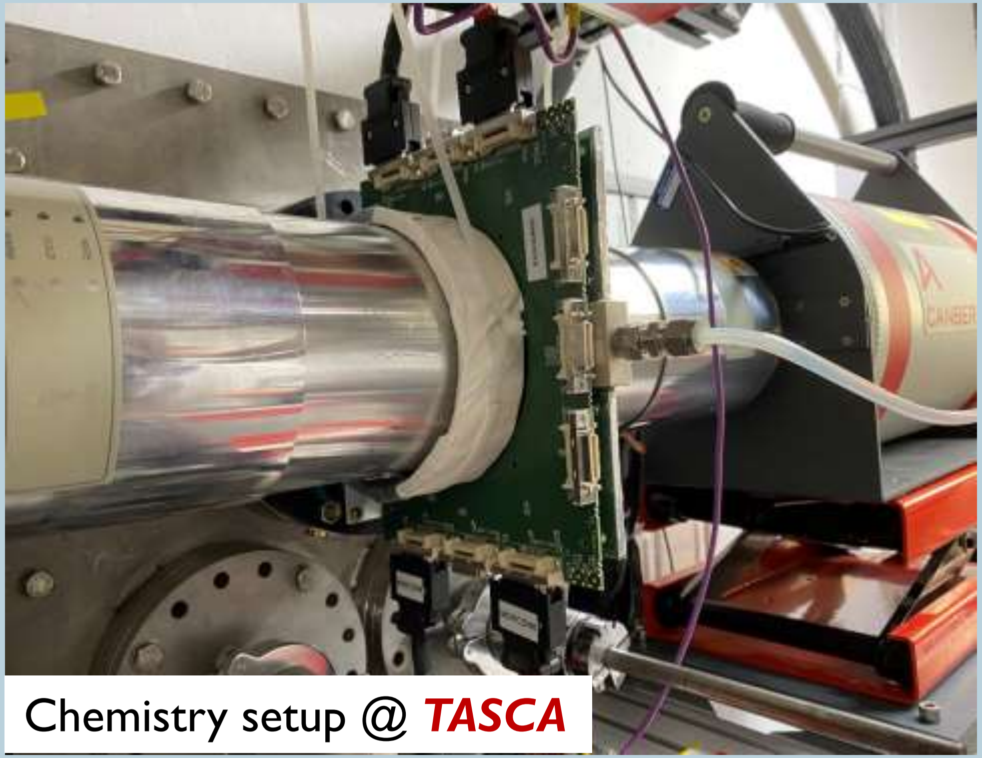
Determination of adsorption enthalpy value

The new focal plane detector will be used

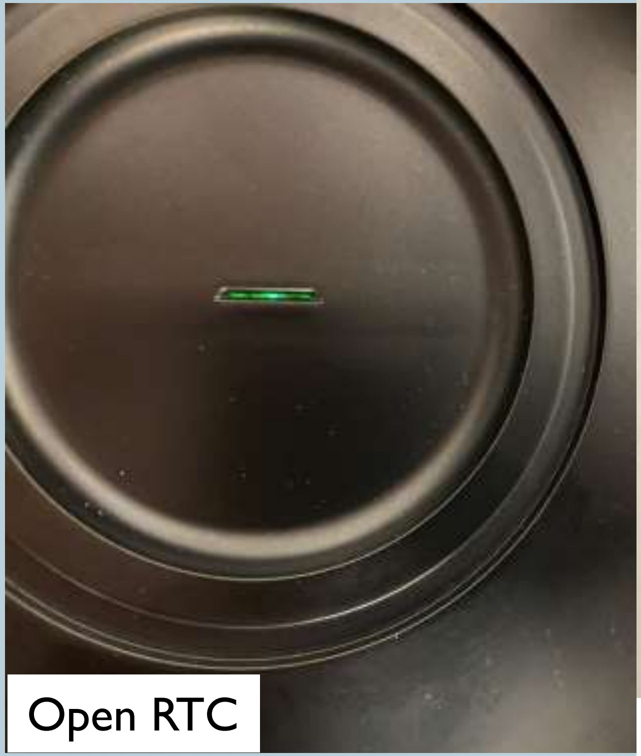
Summary and Outlook

- „Fast“ gas-chromatography setup allows for chemical studies with $^{259,261}Sg$ and ^{262}Bh
- Study of carbonyl complex formation with ^{259}Sg produced in a cold fusion reaction
- Comparative studies of carbonyl formation for W and Sg
  - $Sg(CO)_6$ carbonyl has a higher adsorption enthalpy value
  - Chemical yield for $Sg(CO)_6$ is lower, on the same level as in the first study
- Study of carbonyl complexes with ^{262}Bh is visible, just needs a month of beam time

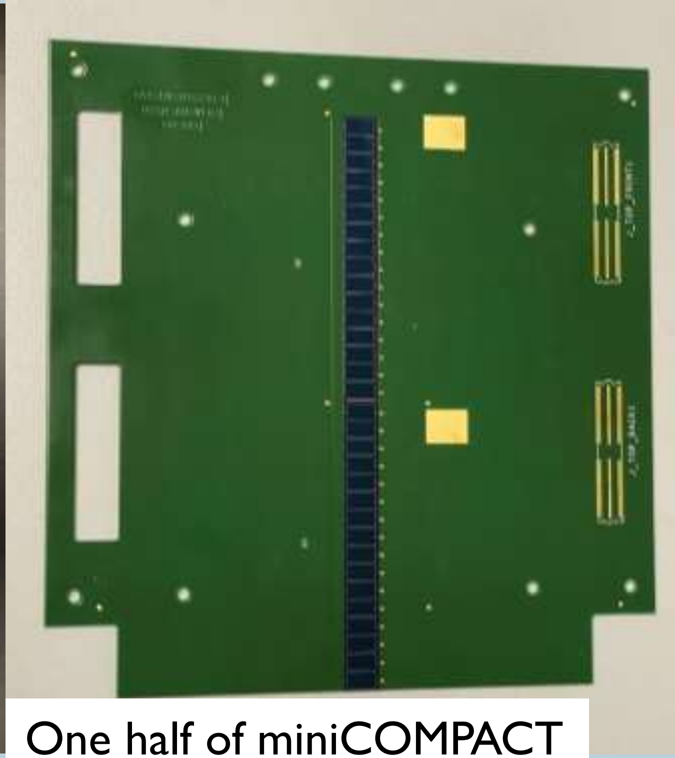
Thanks to all collaborators
Thank you for attention



Chemistry setup @ ***TASCA***



Open RTC



One half of miniCOMPACT

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