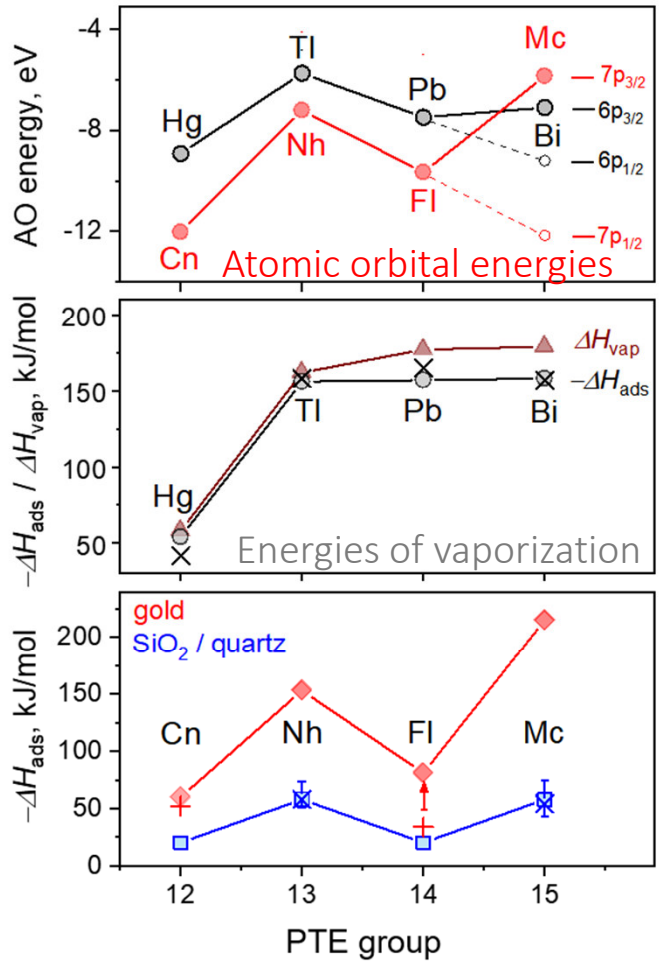
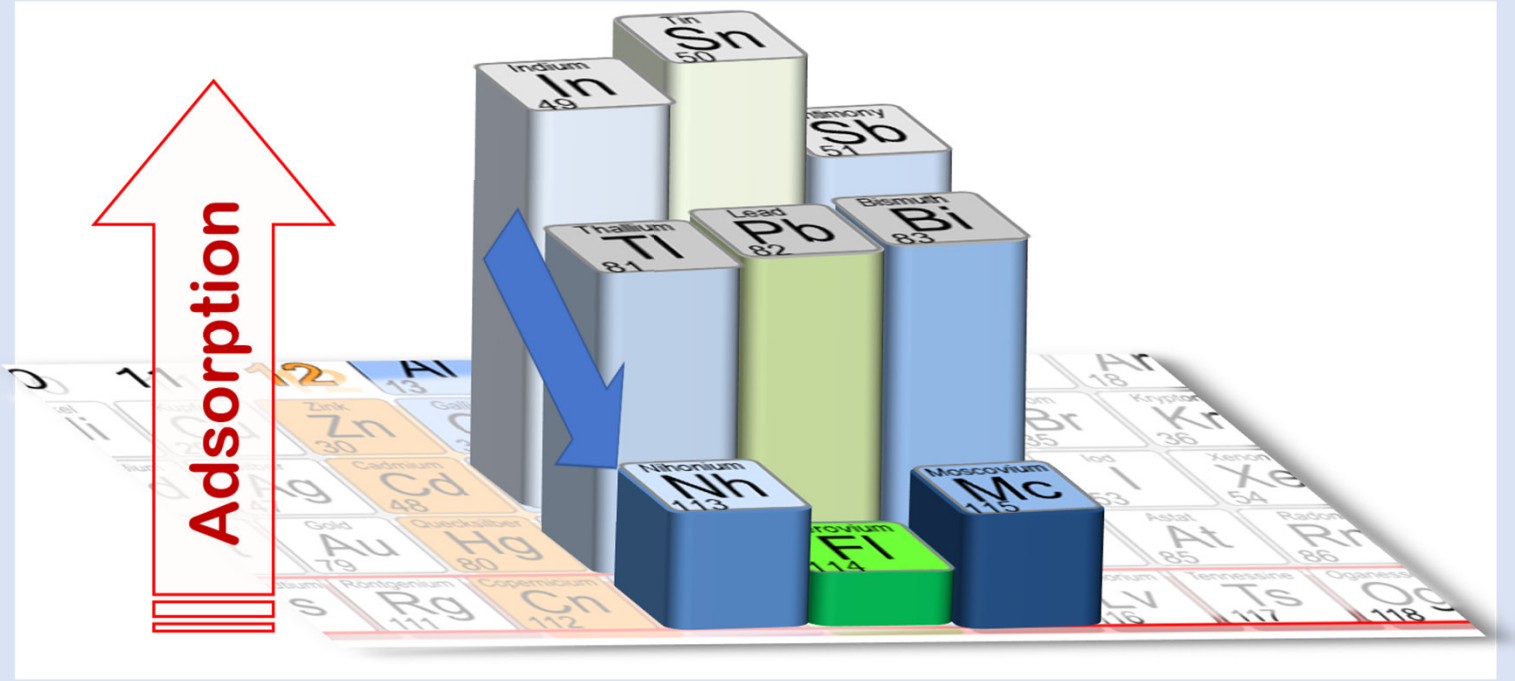
Recent achievements in superheavy element chemistry at GSI Darmstadt

On the stability of the $^{259}Sg(CO)_6$ complex

A. Yakushev, J. Khuyagbaatar, Ch.E. Düllmann, J. Ballof, R.-A. Cantemir, D. Dietzel, K. Hermainski, J. Krier, N. Kurz, S. Löchner, P. Mošať, V. Pershina, M. Schädel, B. Schausten, P. Wieczorek, P. Bartl, M. Block, F. Giacoppo, R.-D. Herzberg, J. John, M. Maiti, S. Raeder, T.K. Sato, J. Uusitalo

Chemical studies with Nh (Z = 113), Fl (Z = 114) and Mc (Z = 115) completed





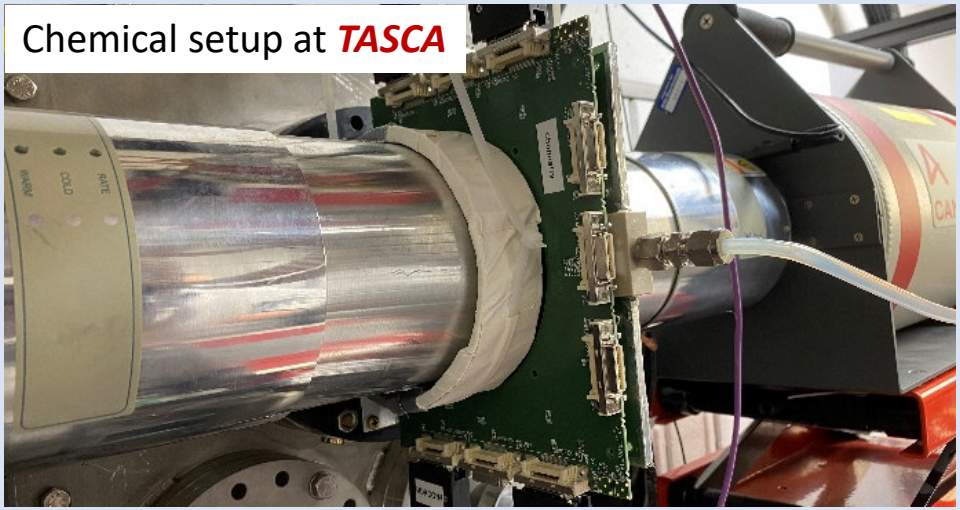
The strong relativistic effects, i.e., the large energy splitting in the *7p* shell and the stabilization of the $7p_{1/2}^2$ subshell, cause

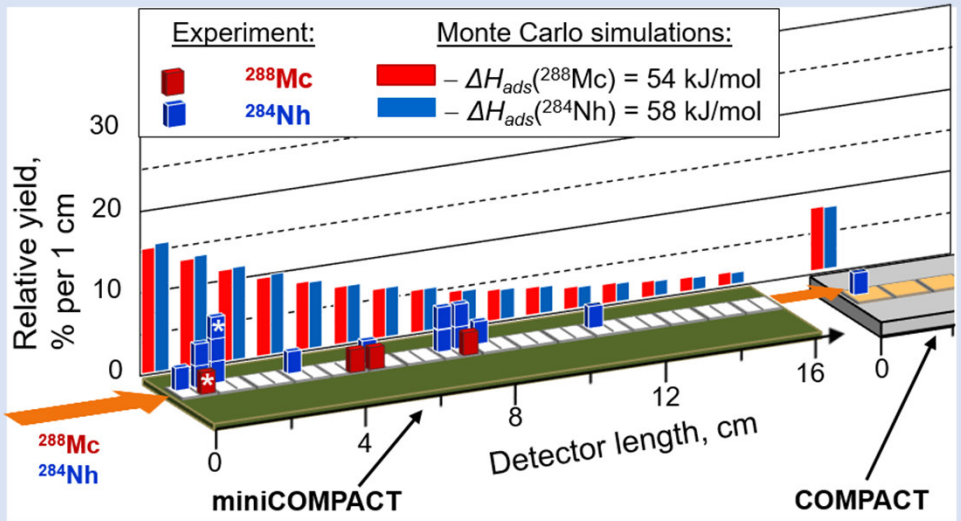
- the high inertness of volatile metals Cn and Fl and
- the lowest chemical reactivity of Nh and Mc in groups 13 and 15,

which now is confirmed experimentally.

A. Yakushev et al. Front. Chem. 12:1474820 (2024)

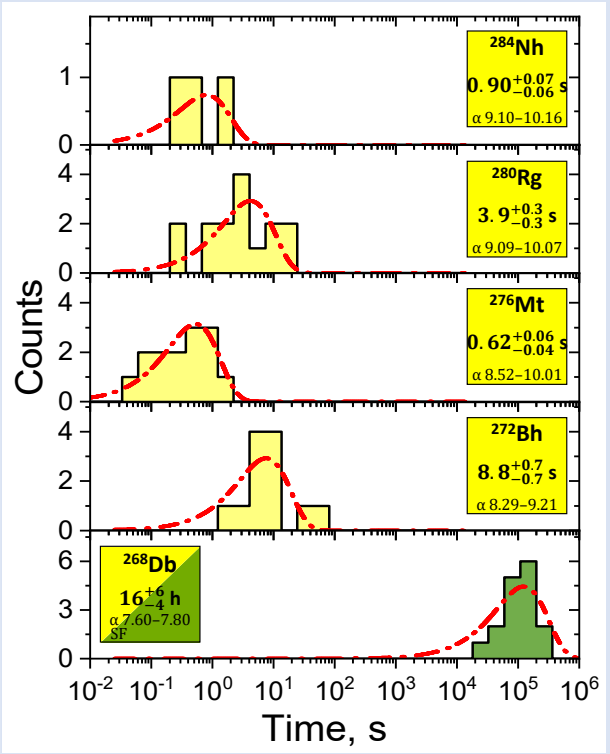
Adsorption of Nh and Mc studied on SiO_2 and Au surfaces





A. Yakushev et al. Front. Chem. 12:1474820 (2024)





Adsorption enthalpies (68% c.i.):

$-\Delta H_{ads}^{SiO_2}(\mathrm{Mc}) = 54^{+11}_{-5}$ kJ/mol $-\Delta H_{ads}^{SiO_2}(\mathrm{Nh}) = 58^{+8}_{-3}$ kJ/mol

Chemical studies beyond Mc are challenging due to short $T_{1/2}$

$^{249}Cf \rightarrow {}_{118}Og$

$^{249}Bk \rightarrow {}_{117}Ls$

$^{248}Cm \rightarrow {}_{116}Lv$

$^{243}Am \rightarrow {}_{115}Mc \xrightarrow{\alpha} {}_{113}Nh$

$^{244}Pu \rightarrow {}_{114}Fl \xrightarrow{\alpha} {}_{112}Cn$

($^{237}Np \rightarrow {}_{113}Nh$)

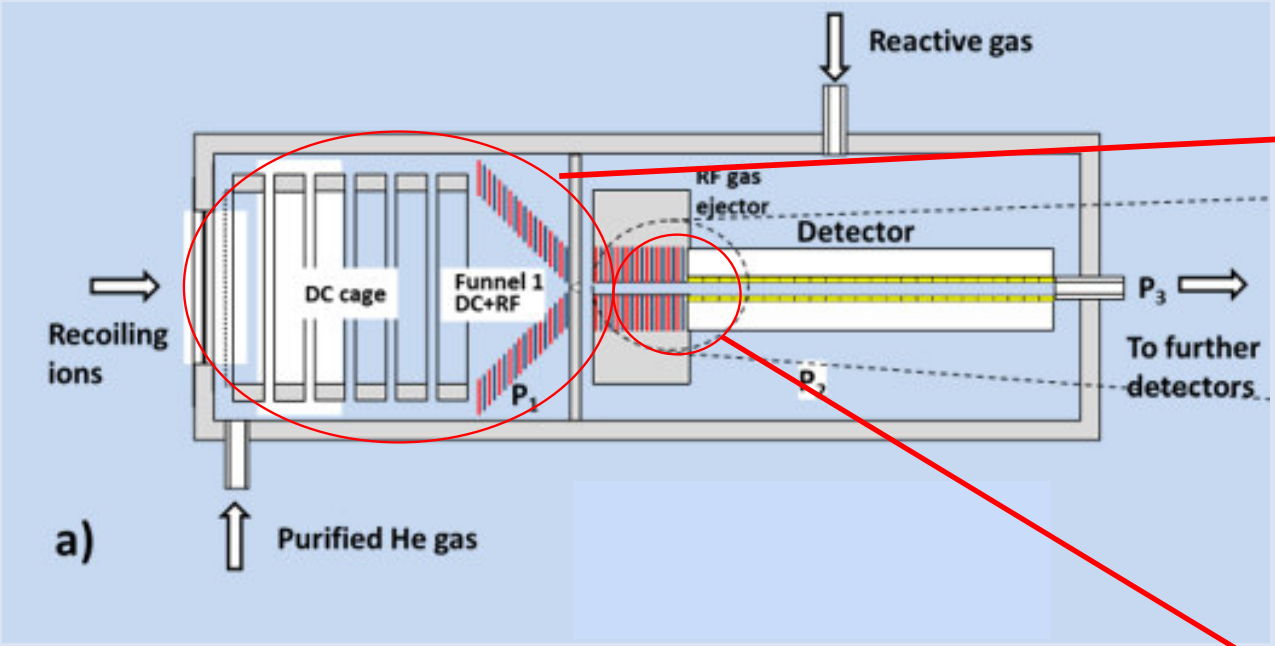
($^{238}U \rightarrow {}_{112}Cn$)

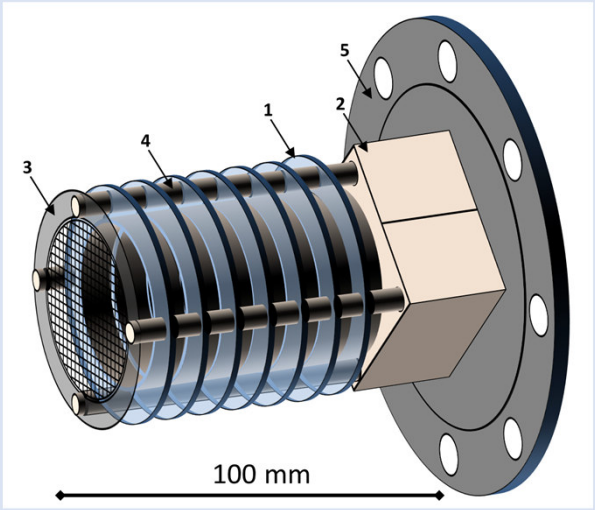
$T_{1/2}$ falls to <100 ms

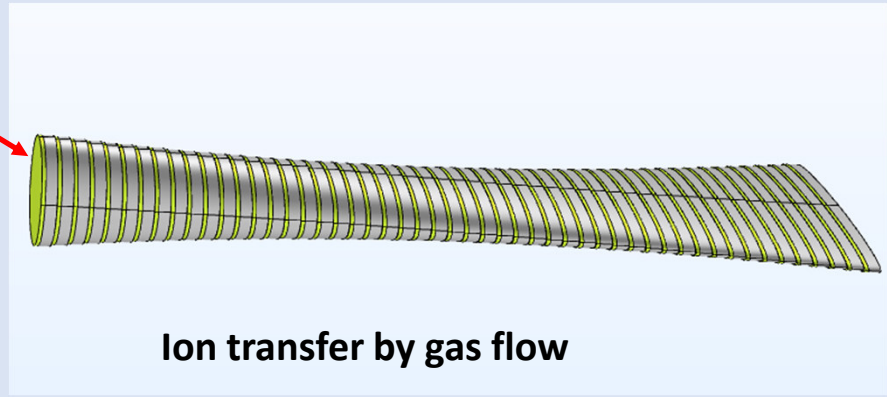
				Og 118	Og 294 0.58 ms α 11.65; (sf≤50%)	
				Ts 117	Ts 293 22 ms α 10.60-11.20	Ts 294 51 ms α 10.81-11.05
			Lv 116	Lv 290 7.1 ms α 10.84	Lv 291 18 ms α 10.74	Lv 292 13 ms α 10.64	Lv 293 61 ms α 10.54
	Mc 115	Mc 286 20 ms α 10.71	Mc 287 42 ms α 10.60	Mc 288 0.18 s α 10.33-10.58 (ε<0.5%)	Mc 289 2.35 s α 10.37	Mc 290 0.75 s α 9.78-10.31
Fl 114	Fl 284 2.5 ms sf	Fl 285 0.15 s α 10.41	Fl 286 105 ms α 10.19; 9.57 sf (45%); e⁻	Fl 287 360 ms α 10.02	Fl 288 0.65 s α 9.92	Fl 289 ~2 s α 9.82
Nh 113	Nh 282 73 ms α 10.63	Nh 283 82 ms α 10.17	Nh 284 0.92 s α 9.7-10.1 ε (3.7%)	Nh 285 22.6 s α 9.58 sf (18%)	Nh 286 7.9 s α 9.3-9.75	
Cn 112	Cn 281 0.13 s α 10.30	Cn 282 0.83 ms sf	Cn 283 3.81 s α 9.53; sf (~40%)	Cn 284 121 ms sf (98%) α 9.33	Cn 285 29 s α 9.15	

Chemical studies with Cn, Nh, Fl and Mc were performed @
FLNR (Dubna)
GSI (Darmstadt)
IMP (Lanzhou)

Chemical studies beyond Mc – a new technique is required







Ion transfer by gas flow

Contents lists available at ScienceDirect

Nuclear Inst. and Methods in Physics Research, A

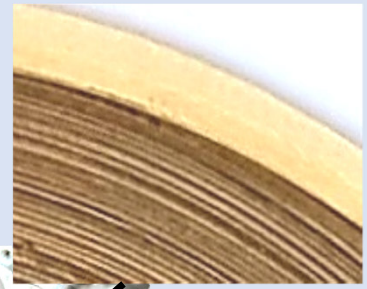
journal homepage: www.elsevier.com/locate/nima

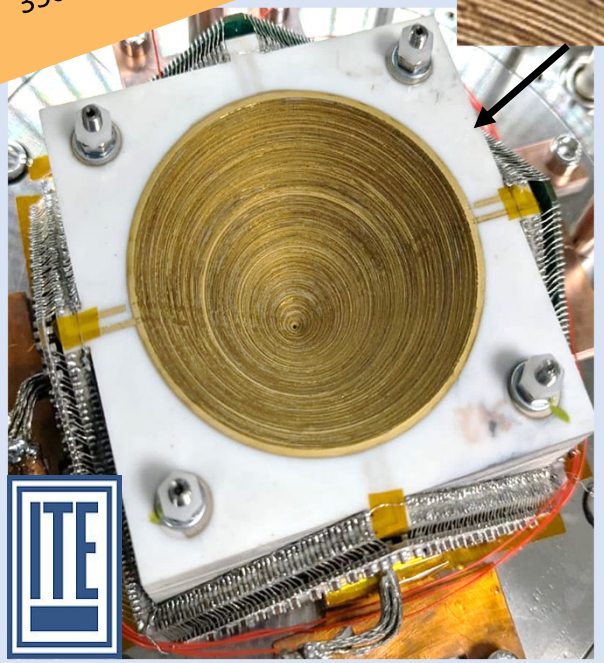
Concept of a new **Uni**versal High-Density Gas Stopping **Cell** Setup for study of gas-phase chemistry and nuclear properties of Super Heavy Elements (**UniCell**)

Victor Varentsov [a,b,*], Alexander Yakushev [c,d]

UniCell – the buffer gas cell for future chemistry experiments

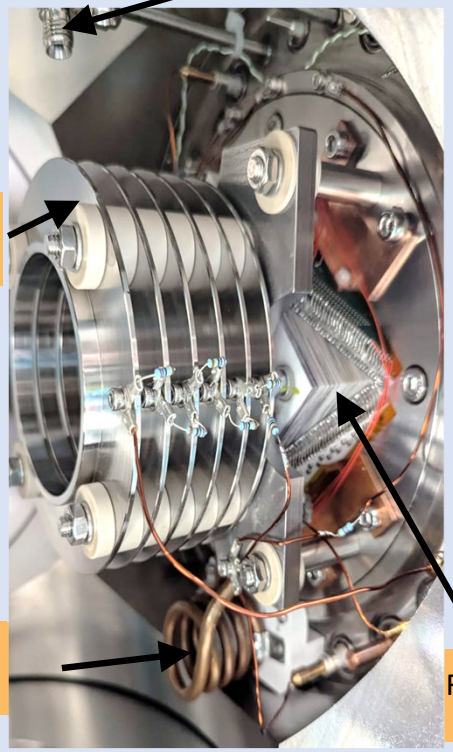
Funnel made of ca. 350 ZrO_2 sheets





DC cage

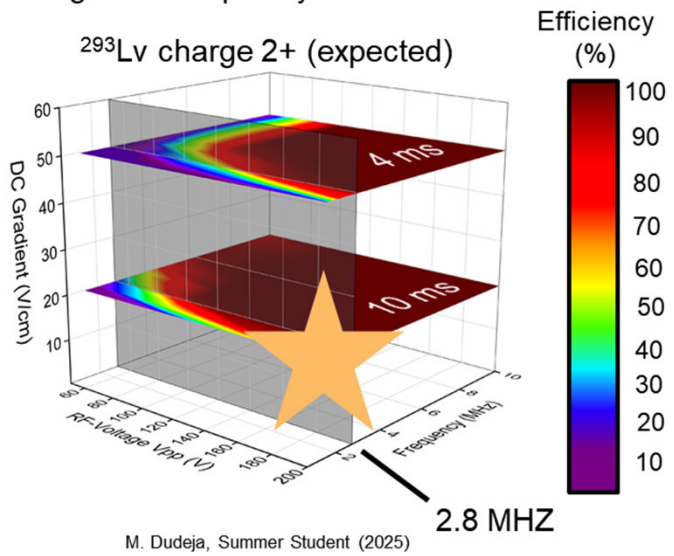
gas inlet



Copper coil

RF + DC funnel

SIMION simulations: extraction time and efficiency depends on DC-gradient, RF-Voltage and frequency



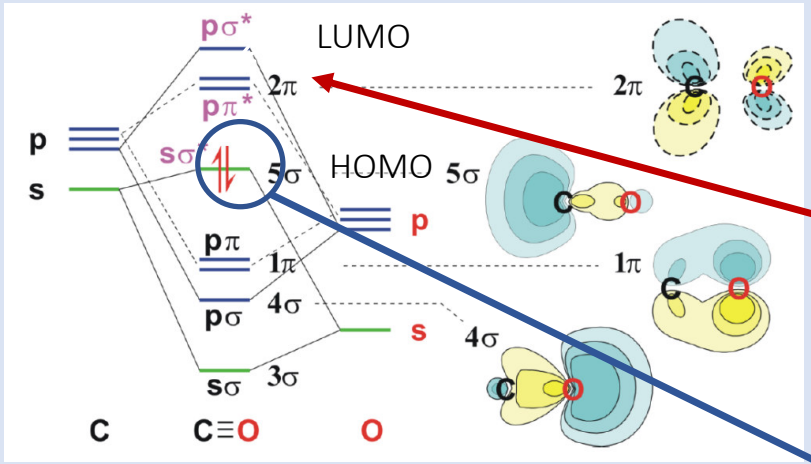
M. Dudeja, Summer Student (2025)

Chemical systems in 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
$5d6s^2$	$5d^26s^2$	$5d^36s^2$					$5d^96s$
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**
$6d^97s^2$	**$6d^{10}7s^2$**	**$7s^2p$**	**$7s^2p^2$**	**$7s^2p^3$**	**$7s^2p^4$**	**$7s^2p^5$**	**$7s^2p^6$**
	Superheavies - - -

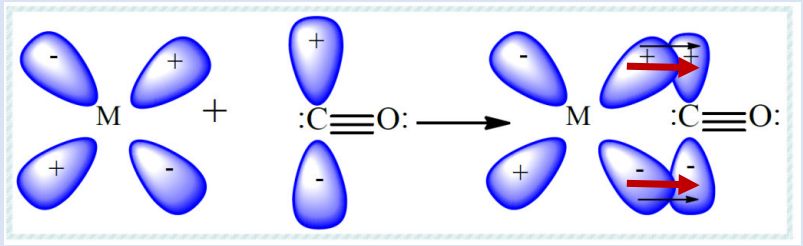
Carbonyl complexes – compounds with zero valence

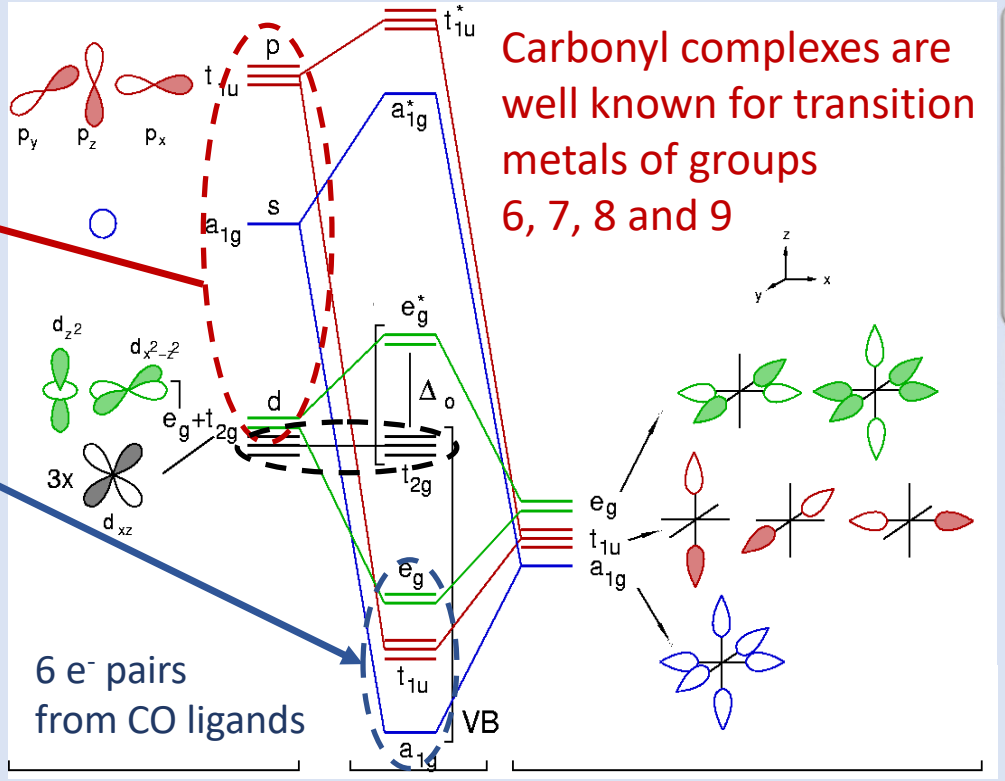


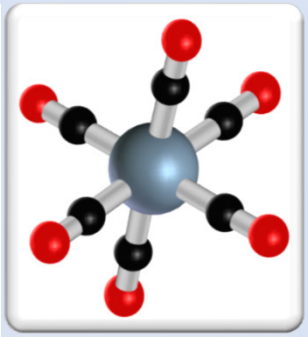
σ-bonds between M and CO



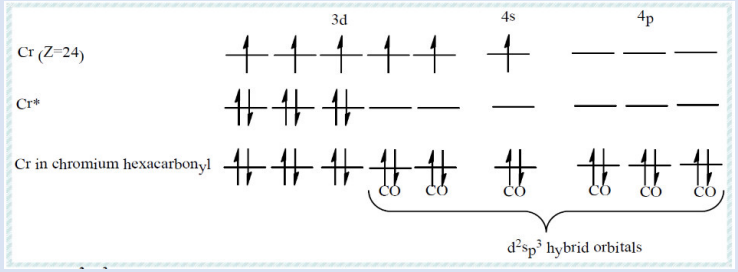
π-backbonding





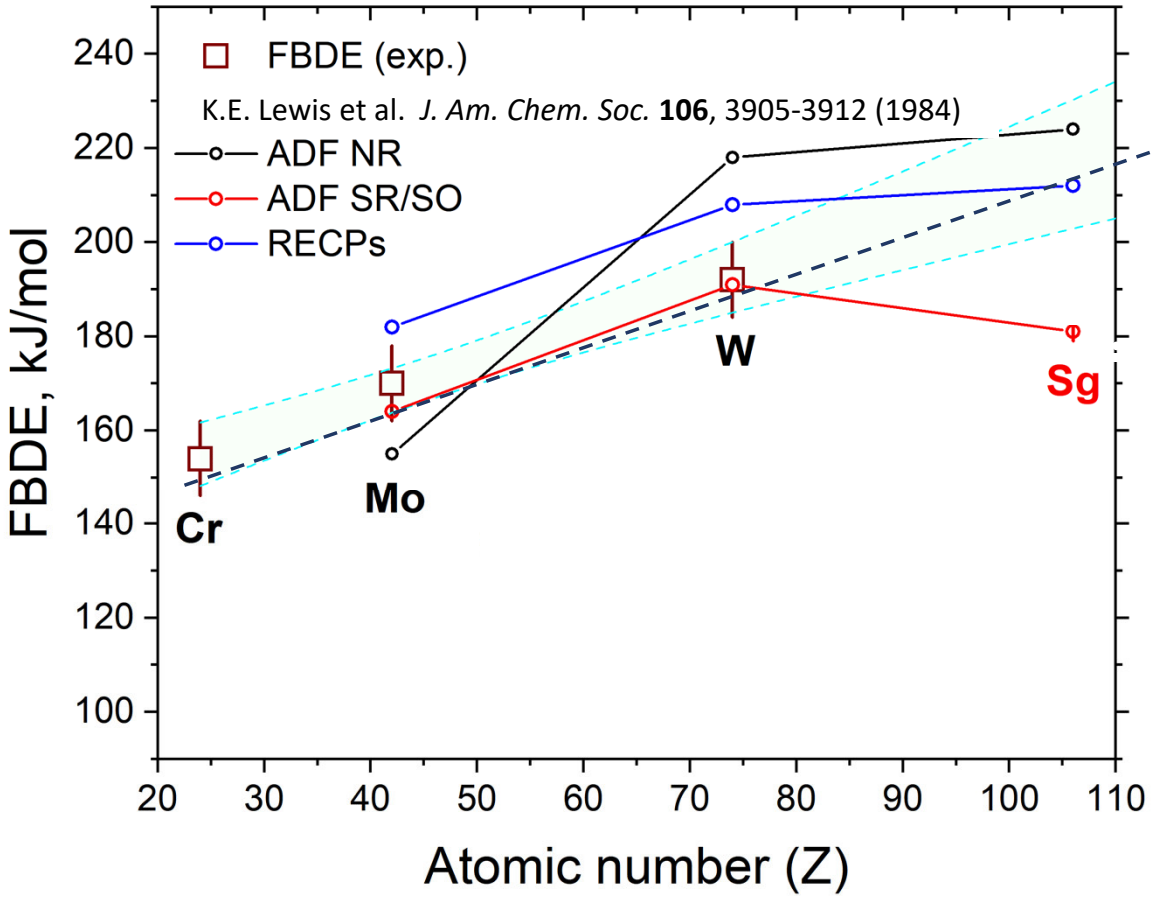


$M(CO)_6$
M = Cr
Mo
W
Sg

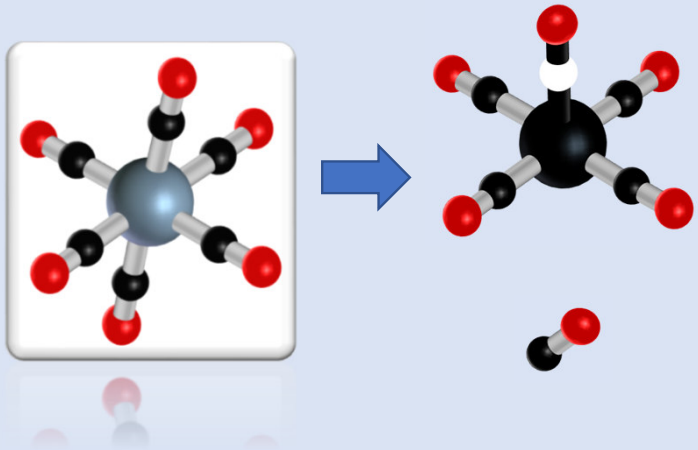


M: $ns^2(n-1)d^4$ 6e⁻
CO ligands: 6 x 2 = 12e⁻
$M(CO)_6$: d^2sp^3 hybrid 18e⁻
O_h – octahedral geometry

The first bond dissociation energy – the measure of stability

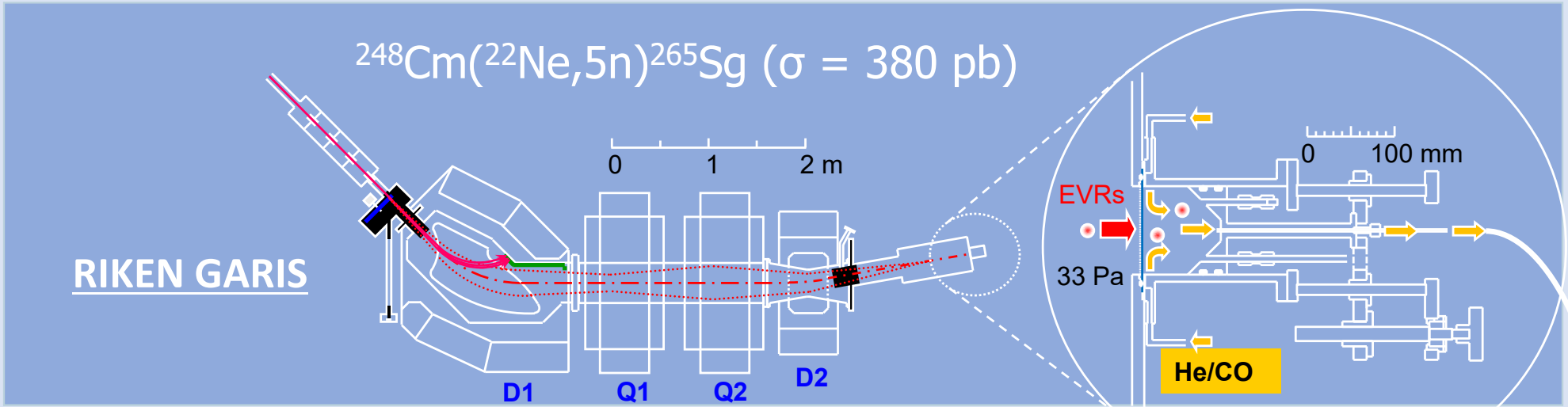


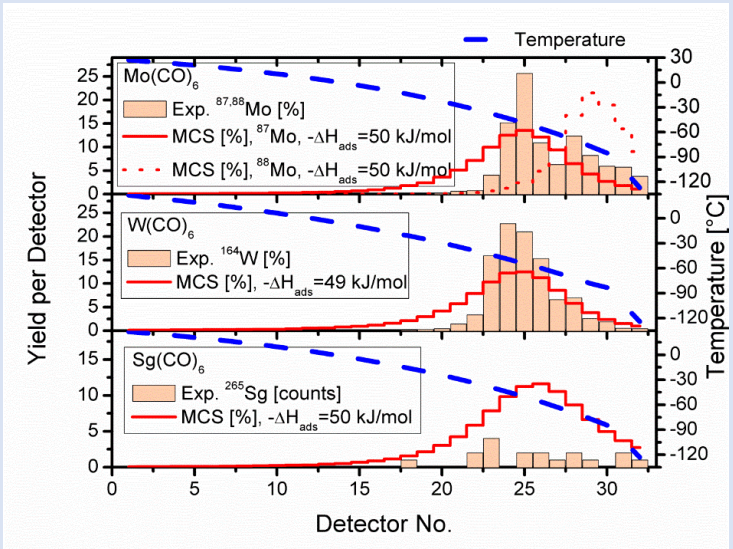
FBDE – First Bond Dissociation Energy

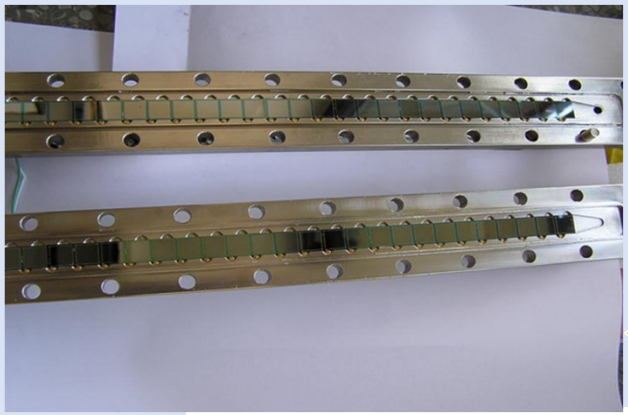


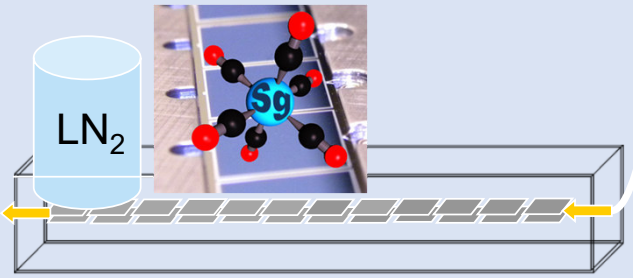
Theory:
Nash, C. S. & Bursten, B. E.
J. Am. Chem. Soc. **121**, 10830−10831 (1999)
Iliaš M. & Pershina V.
Inorg. Chem. **56**, 1638-1645 (2017)

$Sg(CO)_6$ - synthesis and adsorption study of the first SHE carbonyl





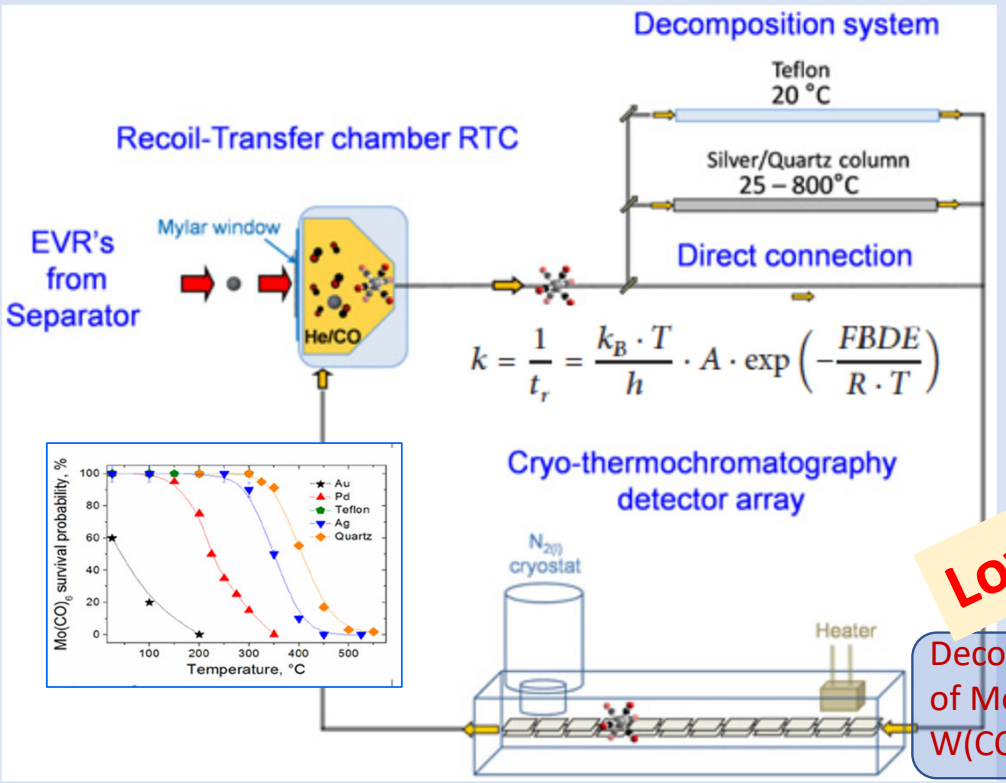


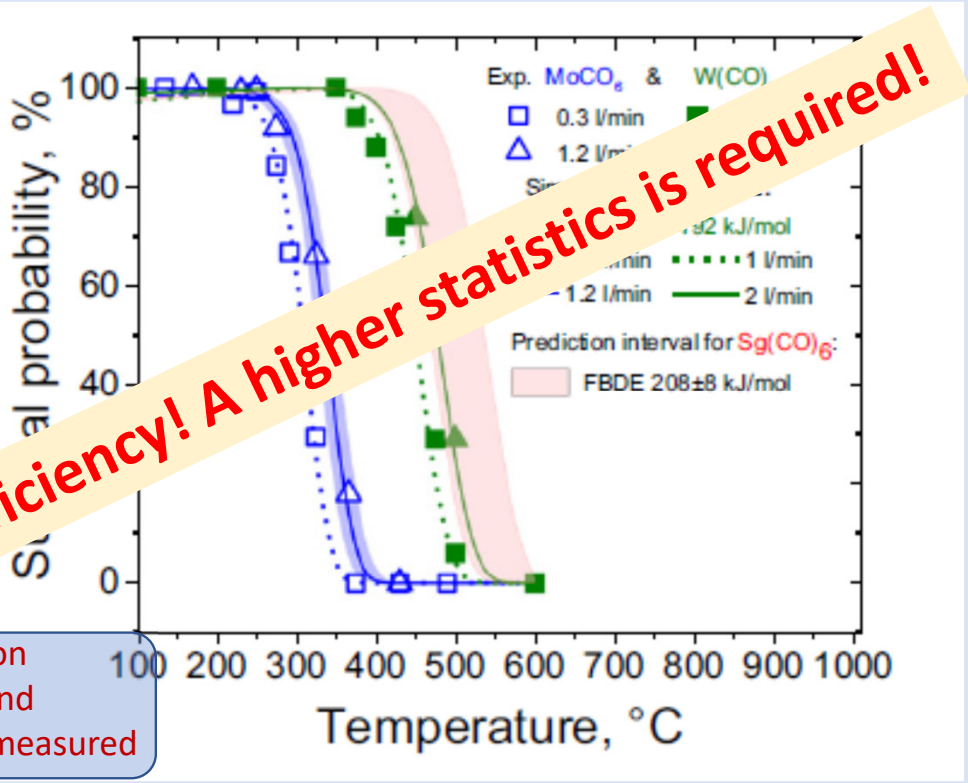


18 $^{265}Sg(CO)_6$ molecules
(only volatile species were measured)

J. Even et al. **Synthesis and detection of a seaborgium carbonyl complex**
Science *Vol. 345 no. 6203 pp. 1491-1493 (2014)*

First attempt to measure stability of the $Sg(CO)_6$ complex





Low efficiency! A higher statistics is required!

Decomposition of $Mo(CO)_6$ and $W(CO)_6$ was measured

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

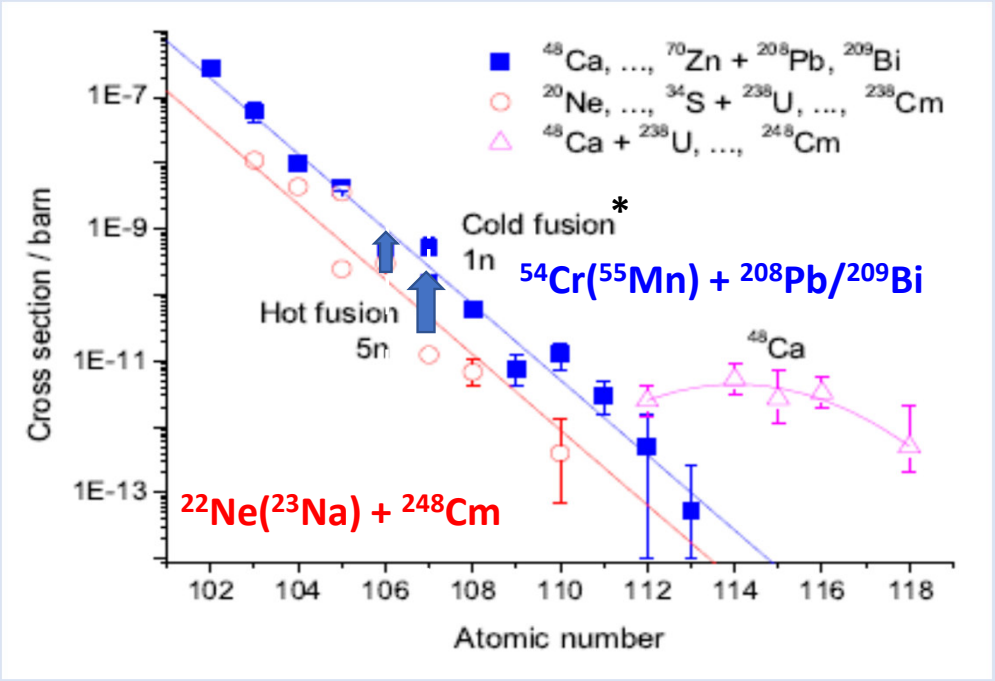
R. Eichler et al., *EPJ Web of Conferences* **131**, 07005 (2016)

Carbonyl complex decomposition on a hot Ag surface

Attempt to measure the FBDE value for $Sg(CO)_6$

No FBDE value for $Sg(CO)_6$ was determined

Production alternatives of SHE isotopes for carbonyl studies

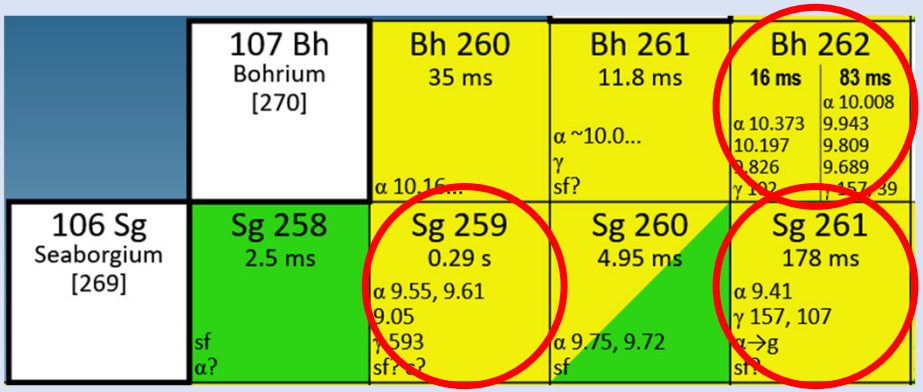


^{288}Mc

190^{+15}_{-13} ms

α 10.21–10.67

* Studied chemically



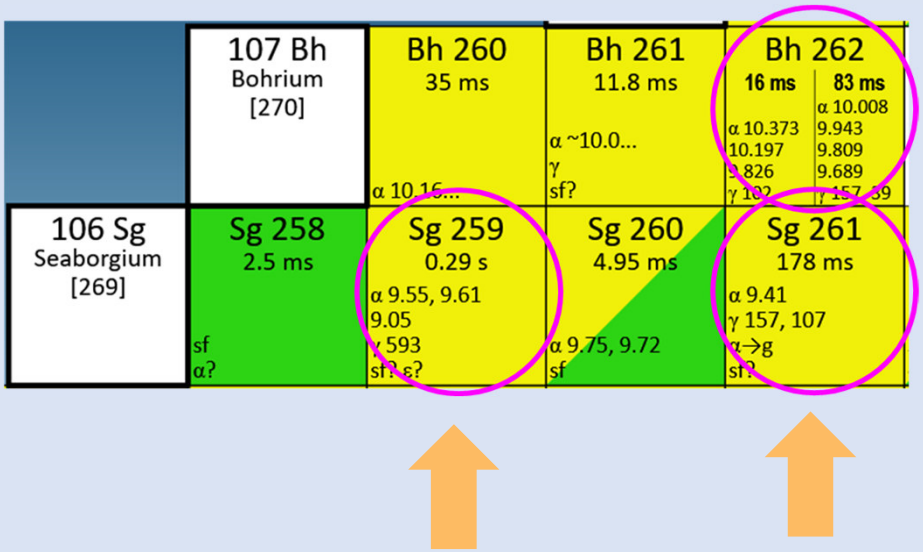
	^{265}Sg → ^{261}Sg	^{266}Bh → ^{262}Bh
Gain in production rate:	x 5	x 6
Gain in separation efficiency:	x 5	x 5
Losses due to short half-lives:	x 0.25	x 0.1
Total gain:	**x 6**	**x 3**

This is a chance for the study of Bh carbonyls!

	Hot fusion		Cold fusion	
Bh (Z = 107)	^{266}Bh 2 s	50 pb	^{262g}Bh 83 ms	290 pb
Sg (Z = 106)	^{265}Sg 15 s	380 pb	^{261}Sg 178 ms	2190 pb

*From all SHE isotopes produced in cold-fusion reactions only ^{257}Rf ($T_{1/2}$ ≈ 4 s) was used for chemistry

Aternatives for production of SHE isotopes for carbonyl studies



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

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

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

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

new:

$^{54}Cr + {}^{209}Bi \quad (703^{+261}_{-246}\ pb)$

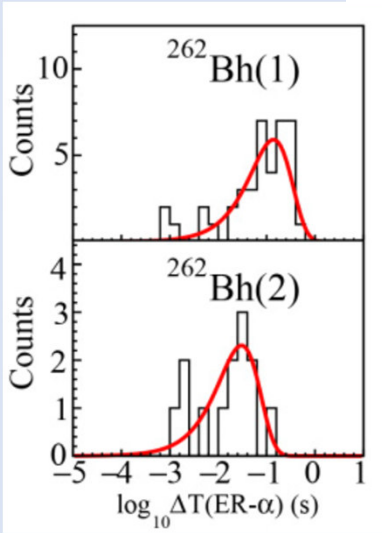
Z. Zhao *et al. Phys. Rev. C* **109**, 034314 (2024)

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

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

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

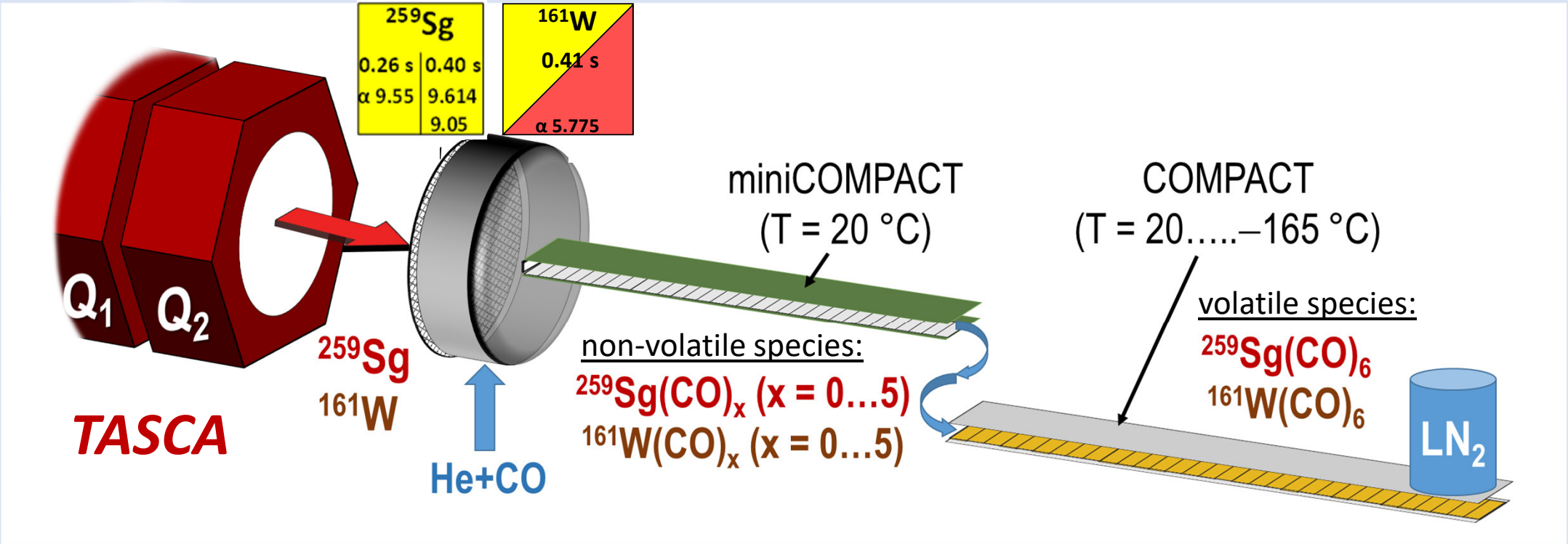
B. Streicher et al.,
Eur. Phys. J. A **45**(3), 275 (2010)



$T_{1/2} = 96^{+18}_{-13}$ ms

$T_{1/2} = 21^{+8}_{-5}$ ms

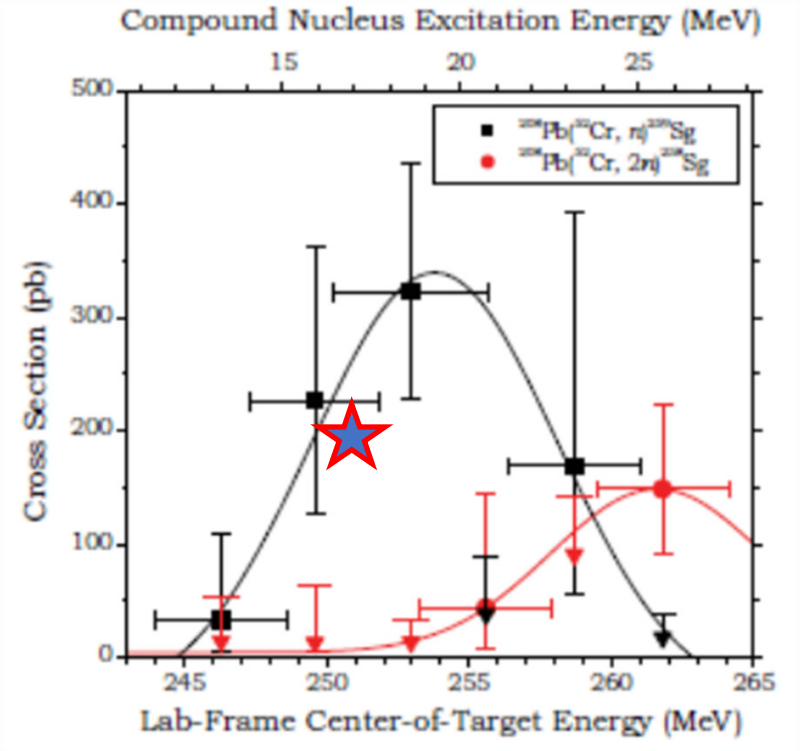
Recent $^{259}Sg(CO)_6$ study at GSI – experimental setup



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

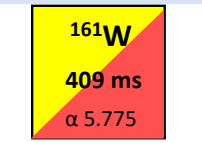
Recent $^{259}Sg(CO)_6$ study at GSI – experimental results

$^{52}Cr^{14+}$ (4.95 MeV/amu) + ^{208}Pb (800 μg/cm^2), Beam dose ≈ 4 x10^{18} (14 d)

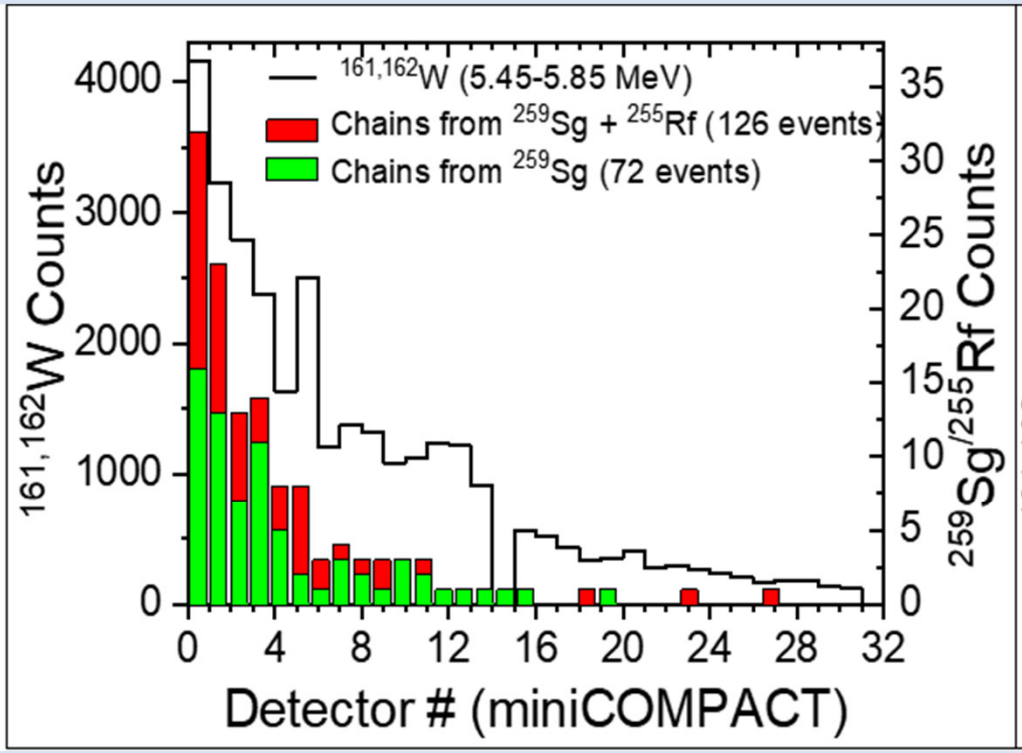


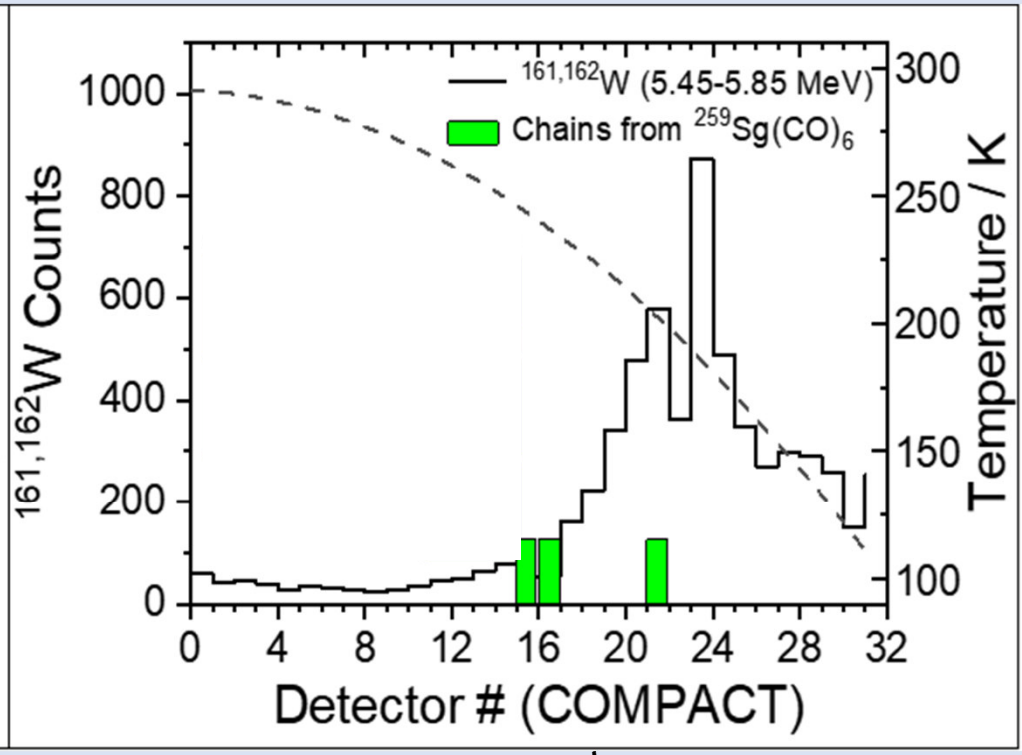
Target thickness	2 x10^{18}
TASCA transmis. to RTC window	0.4
Window grid	0.8
Flush-out efficiency	0.35
Number of (Sg + Rf) events	**126**
Detection efficiency	0.8
Cross section estimation	**~200 pb**

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









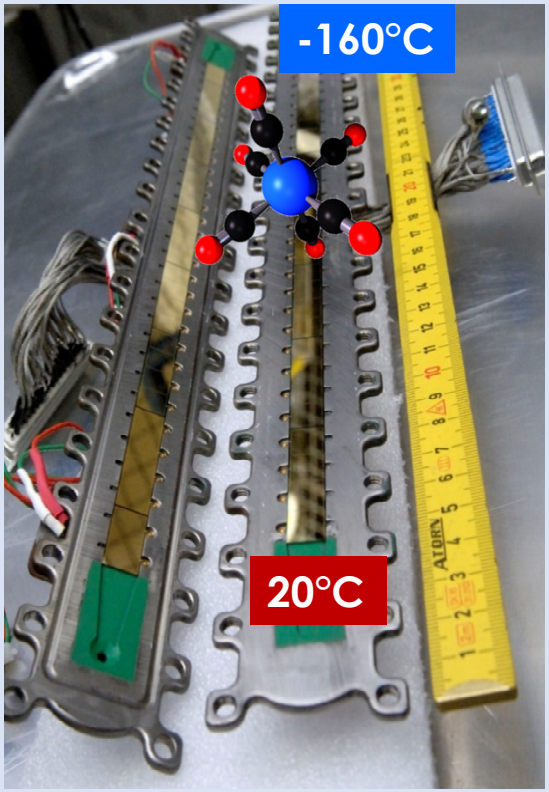
miniCOMPACT: Diffusion-controlled deposition of non-volatile species $M(CO)_x$ at room temperature

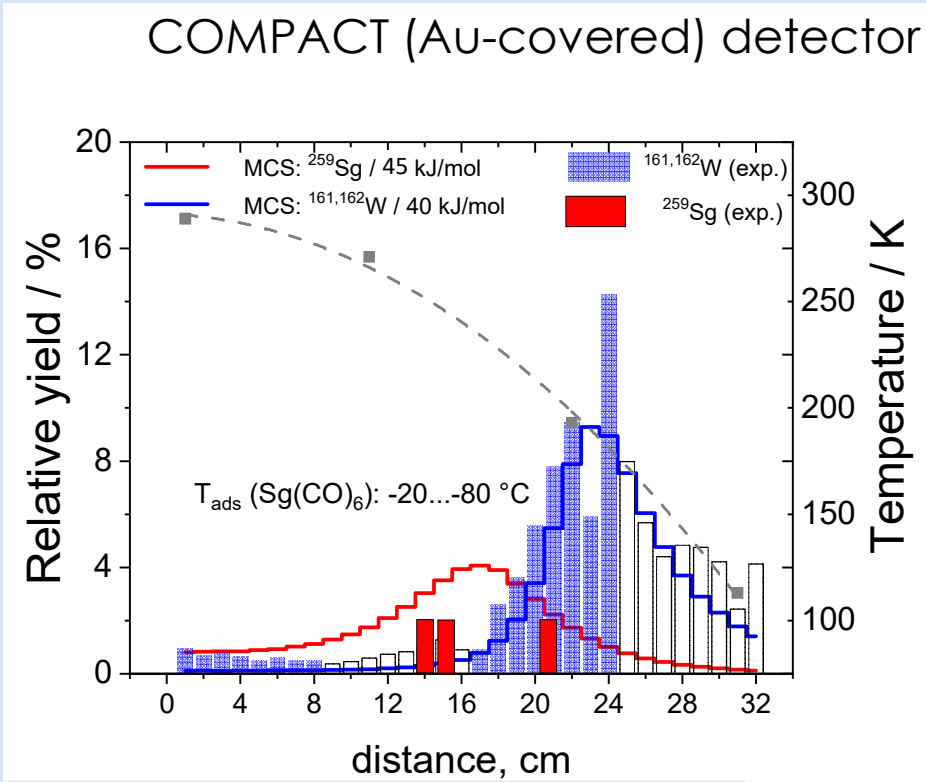
COMPACT: Adsorption of volatile $M(CO)_6$ complex on Au at a low temperature

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

$^{259}Sg(CO)_6$ ~ 4%

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





Monte Carlo Simulations:

$Sg(CO)_6$

$-\Delta H_{ads} = 45^{+4}_{-6}$ kJ/mol

$W(CO)_6$

$-\Delta H_{ads} = 40^{+5}_{-5}$ kJ/mol

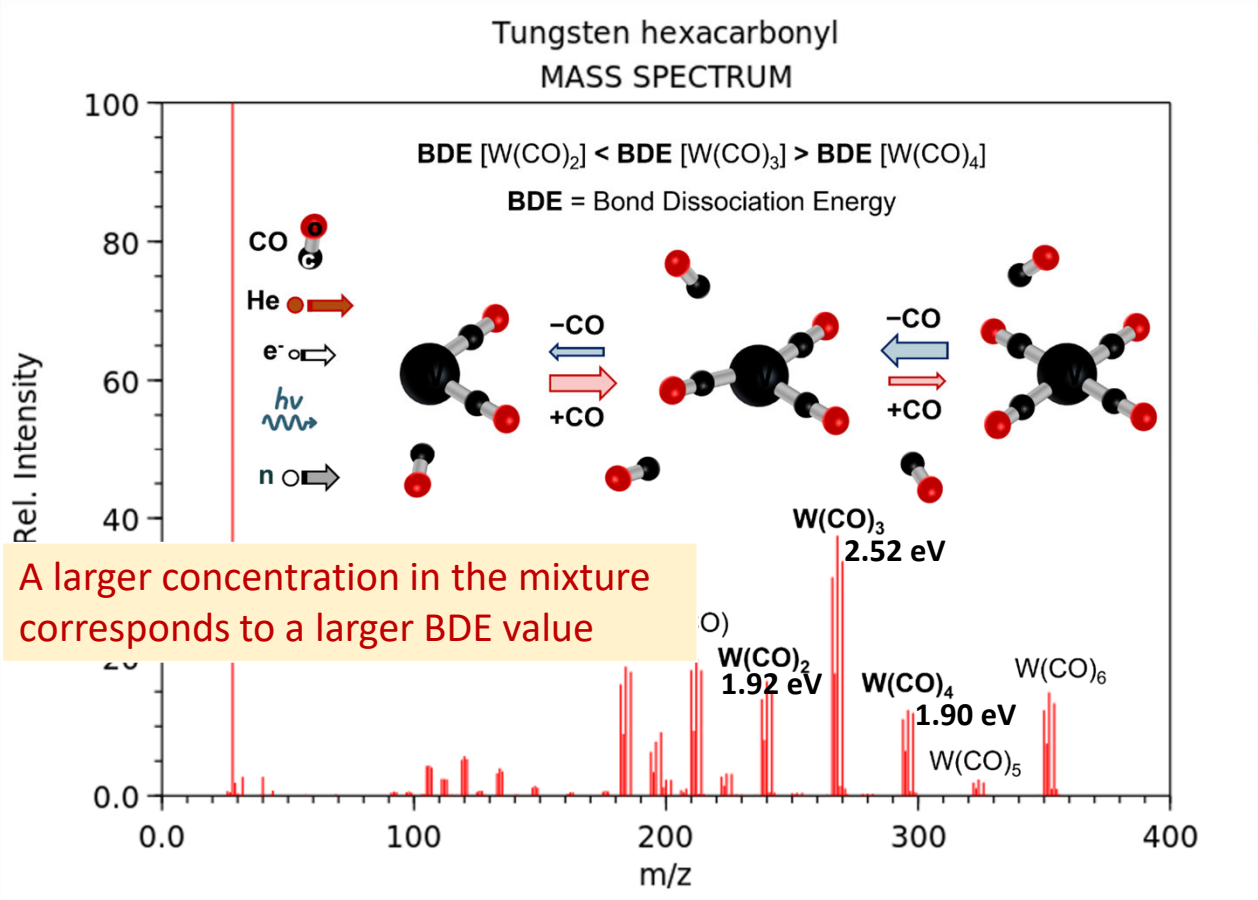
Complex	IC SiO_2	COMPACT SiO_2	COMPACT Au
$Mo(CO)_6$	42.5±2.5		
$W(CO)_6$		46.5±2.5	41^{+3}_{-4}
$Re(CO)_yX$	43±3		
$Os(CO)_5$		$43.5^{+3.5}_{-2.5}$	39±4
$Ir(CO)_yX$	37±3		

J.Even et al., Radiochim. Acta, 102, 2014

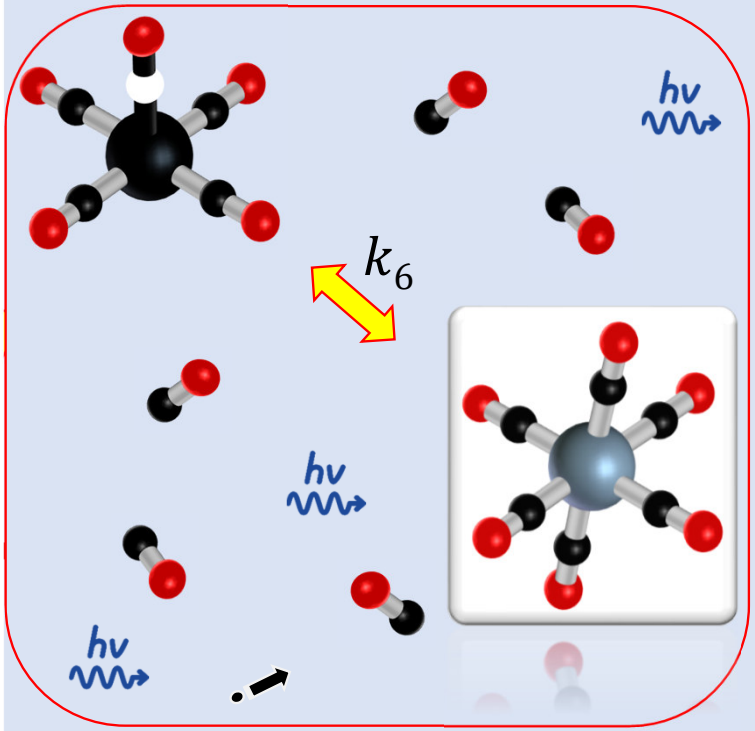
The first measurement of the adsorption enthalpy of the $Sg(CO)_6$ on gold

→ the $-\Delta H_{ads}$ on Au is lower than on SiO_2 for both, $W(CO)_6$ and $Sg(CO)_6$

Carbonyl complex formation



A larger concentration in the mixture corresponds to a larger BDE value



$$k_6 = A\, e^{\frac{-FBDE}{RT}}$$

- Carbonyl complex formation is a multi-step process
- All intermediate products exist in the reaction mixture
- In macrochemistry, it is studied by decomposition of $M(CO)_6$

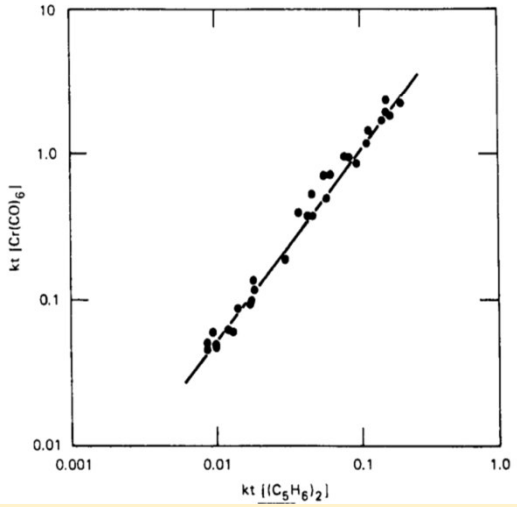
First bond dissociation energy of $Sg(CO)_6$

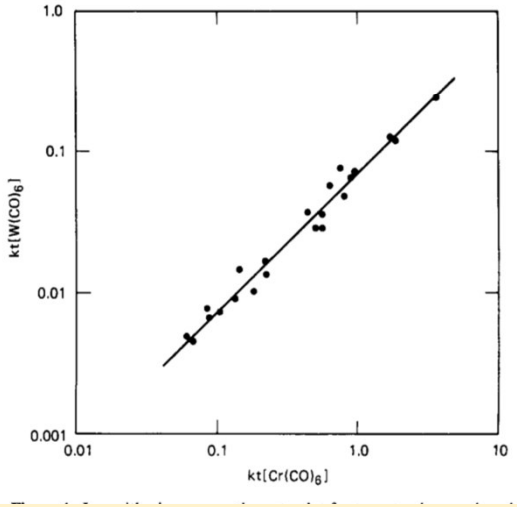
Organometallic Bond Dissociation Energies — *J. Am. Chem. Soc., Vol. 106, No. 14, 1984* 3907

Table I. Summary of Laser Pyrolysis Results

compd	T, K	E_a, kcal/mol	log A	k/k_∞	log A_∞	E_a^∞, kcal/mol	$\Delta H°_{298}$, kcal/mol
$Cr(CO)_6$	740–820	45.5 ± 1.8 (35.3)[a]	17.2 (15.4)	(0.75)	(15.5)	(35.3)	(36.8)
$Mo(CO)_6$	670–760	38.9 ± 2.4	15.4 ± 0.8	0.80–0.79	15.6	39.0	(40.5)
$W(CO)_6$	745–810	44.3 ± 2.8	15.5 ± 0.7	0.90–0.86	15.6	44.5	(46.0)
$Fe(CO)_5$	670–780	39.6 ± 2.3	15.7 ± 0.8	0.88–0.80	15.8	40.0	(41.5)

[a] See text.

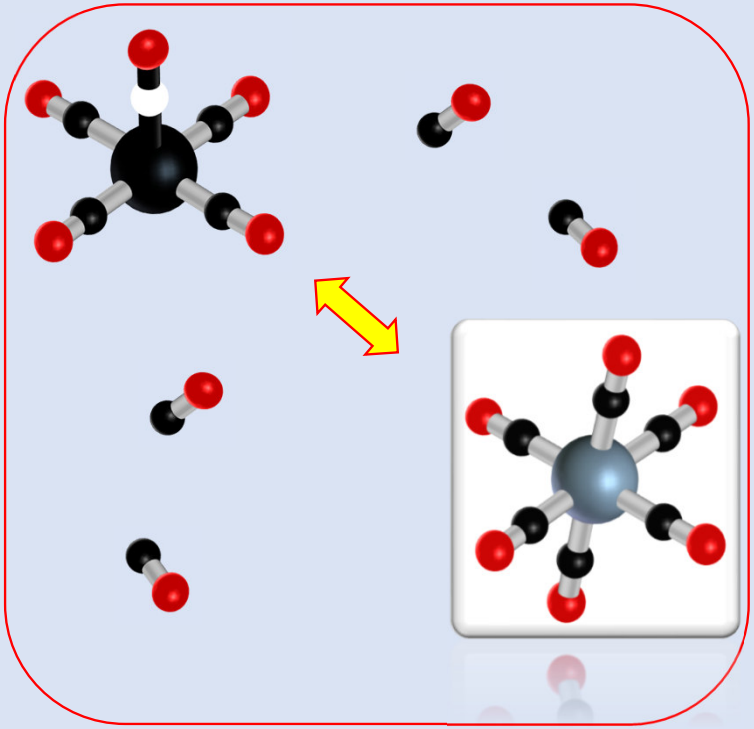




Lewis, K. E. et al. *J. Am. Chem. Soc.* **106**, 3905-3912 (1984)

FBDE $[W(CO)_6]$ = 192(8) kJ/mol

FBDE $[Sg(CO)_6]$ =188(9) kJ/mol



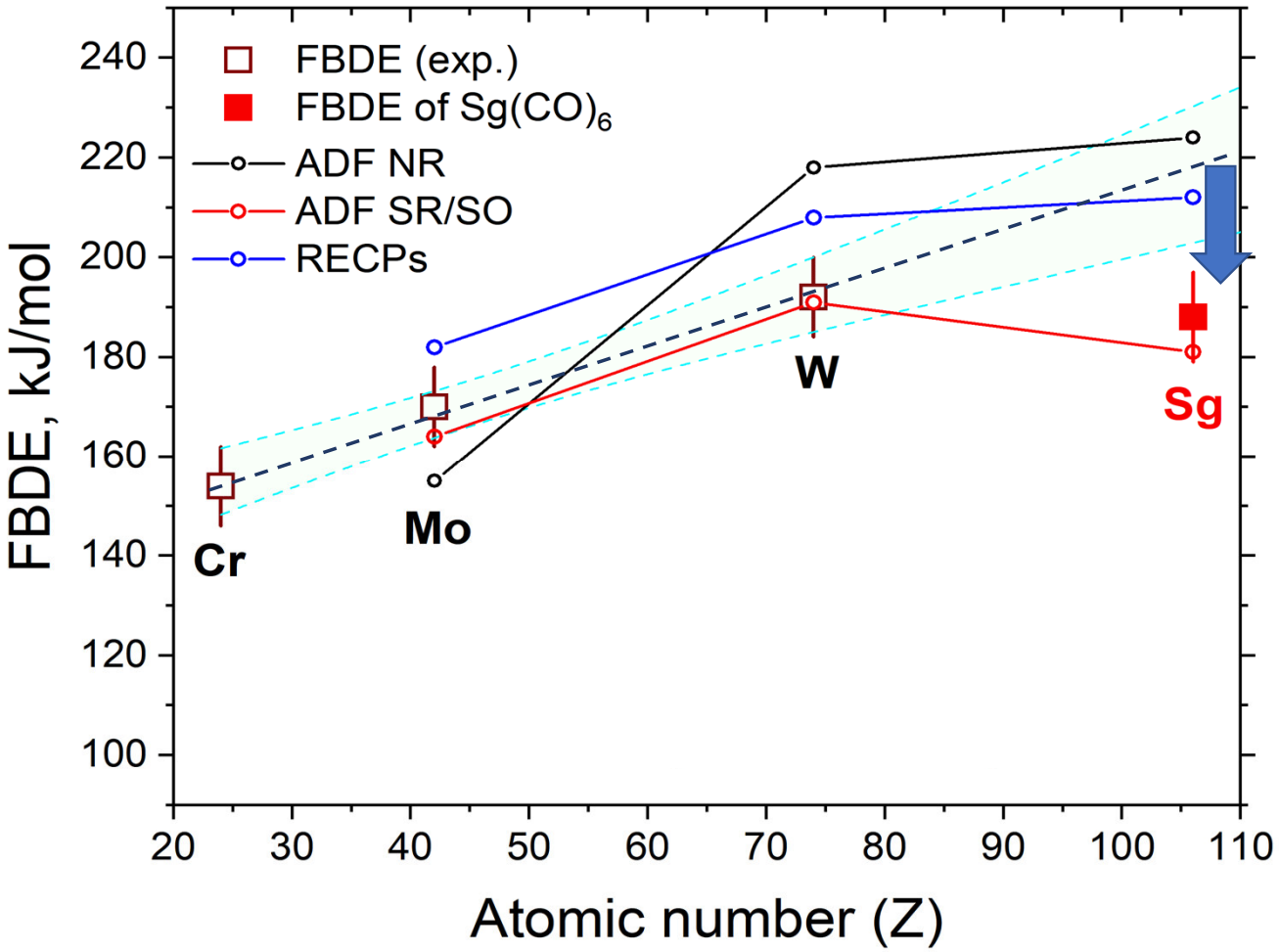
$k = A\, e^{\frac{-FBDE}{RT}}$;

$[M(CO)_6] = k \cdot \tau_r$; τ_r - reaction time,

A – Arrhenius pre-factor, are const. for W and Sg

$$\frac{[W(CO)6]}{[Sg(CO)6]} = \frac{k_W * \tau_r{=}0.20}{k_{Sg} * \tau_r{=}0.04} = \frac{A_W\, e^{\frac{FBDE_W}{RT}}}{A_{Sg}\, e^{\frac{FBDE_{Sg}}{RT}}} \rightarrow \text{FBDE } [W(CO)_6] - \text{FBDE } [Sg(CO)_6] = 4 \text{ kJ/mol}$$

First bond dissociation energy trend for $M(CO)_6$



Experiment:
K.E. Lewis et al. *J. Am. Chem. Soc.* **106**, 3905-3912 (1984) and this work
Theory:
Nash, C. S. & Bursten, B. E. *J. Am. Chem. Soc.* **121**, 10830−10831 (1999)
Iliaš M. & Pershina V. *Inorg. Chem.* **56**, 1638-1645 (2017)

The FBDE value of $Sg(CO)_6$ is lower than that of $W(CO)_6$, and thus, the increasing trend reverses from W to Sg, in agreement with relativistic theory

A. Yakushev et al. accepted for publication

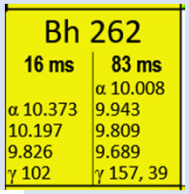
Summary

- „Fast“ gas-chromatography is suitable for chemical studies with short-lived isotopes
- Intramolecular bonding strength of a SHE compound was determined for the first time
- The trend of increasing FBDE values within group 6 reverses from W to Sg
- Relativistic bond weakening of σ-forth and π-back bond between Sg and CO ligands
- Adsorption interaction of $Sg(CO)_6$ on Au is stronger than that of $W(CO)_6$
- Both hexacarbonyls show a weaker interaction with Au compared ti SiO_2

Outlook: chemical study of $^{262}Bh(CO)_x$

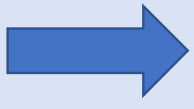
$^{55}Mn + {}^{208}Pb$
($\sigma = 590^{+170}_{-140}$ pb)

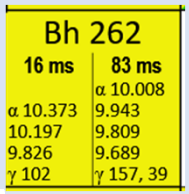




C.M. Folden III et al., Phys. Rev. C 73, 014611 (2006)

or $^{54}Cr + {}^{209}Bi$
($\sigma = 703^{+261}_{-246}$ pb)

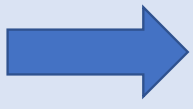


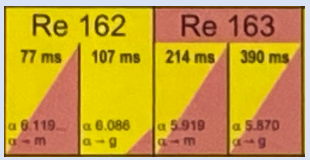


Z. Zhao *et al. Phys. Rev. C* **109**, 034314 (2024)

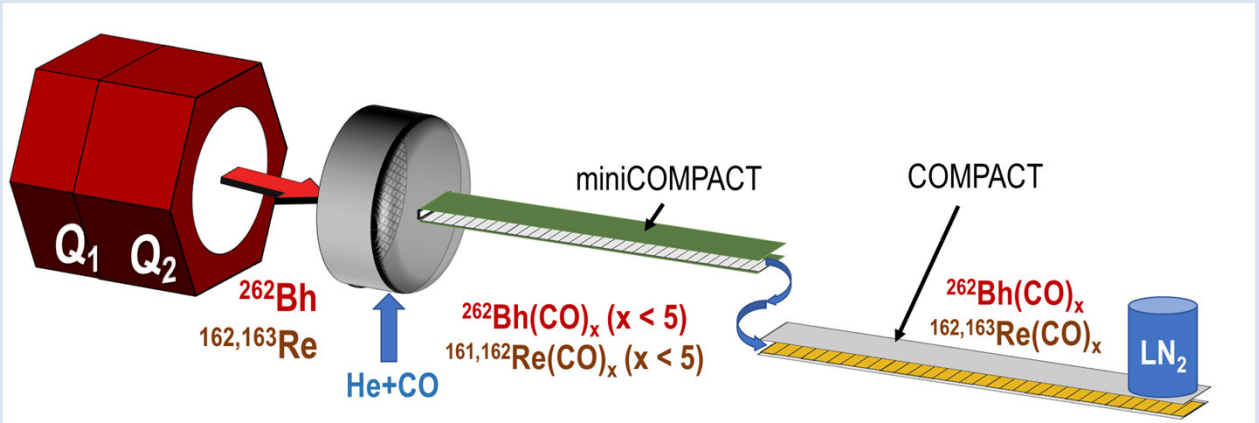
Homolog studies:

$^{55}Mn + {}^{112}Sn$





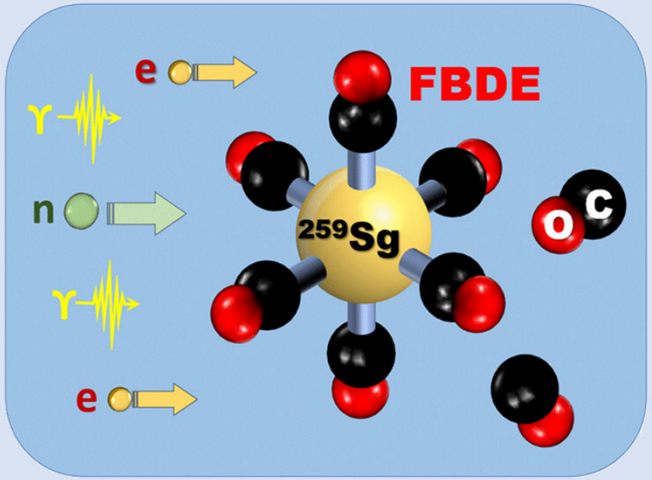
GARIS @ RIKEN (Japan)

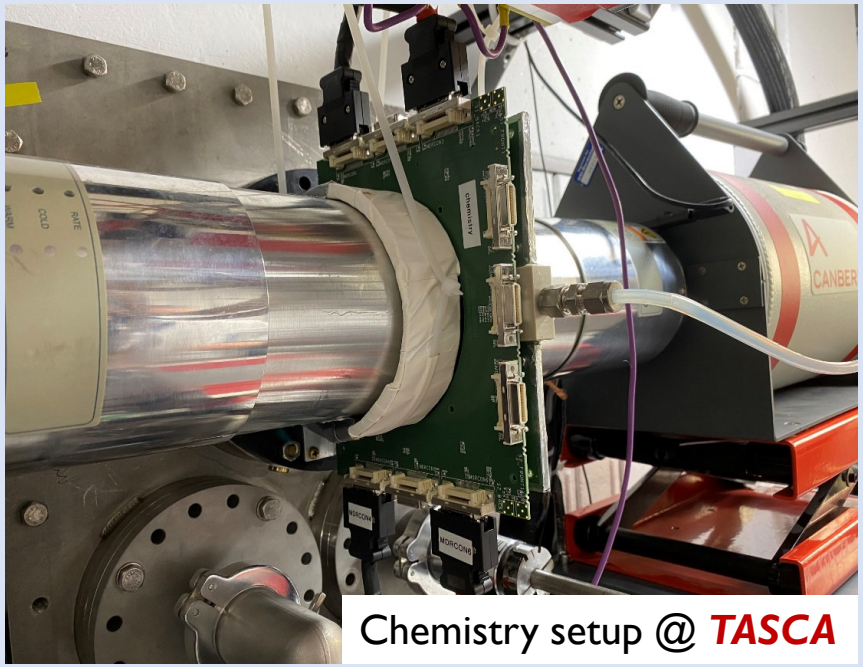


- Studies on the complex formation, adsorption properties and the stability of Bh carbonyl complex

- ✓ An improved gas flow regime will allow for a transport time of ~ 100 ms

Thanks to all collaborators





Chemistry setup @ ***TASCA***

Thank you for attention

Bundesministerium für Bildung und Forschung