Adsorption behavior of superheavy element compounds and their homologs on gold surface: periodic DFT calculations

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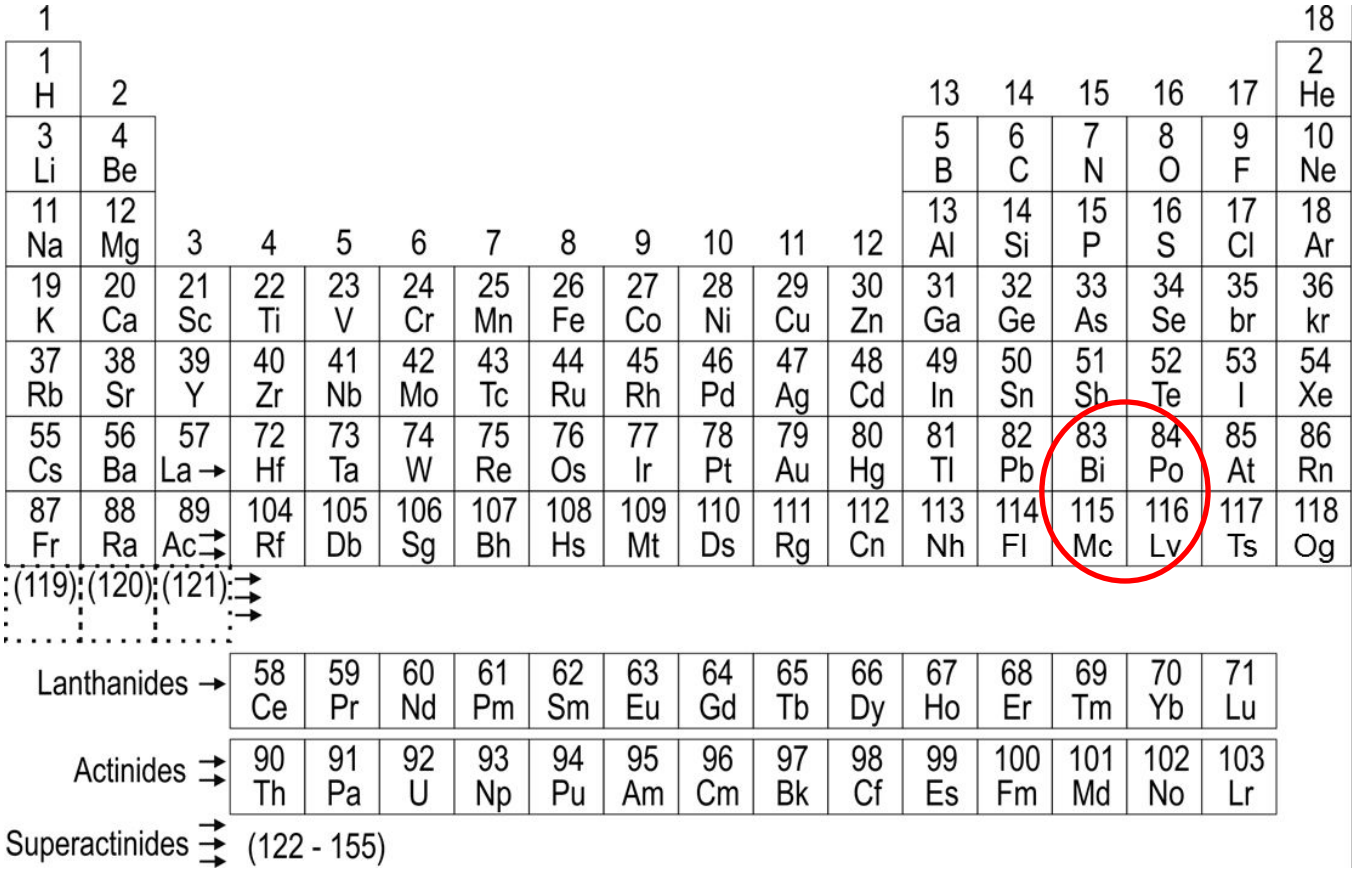
with the support of JINR, Dubna

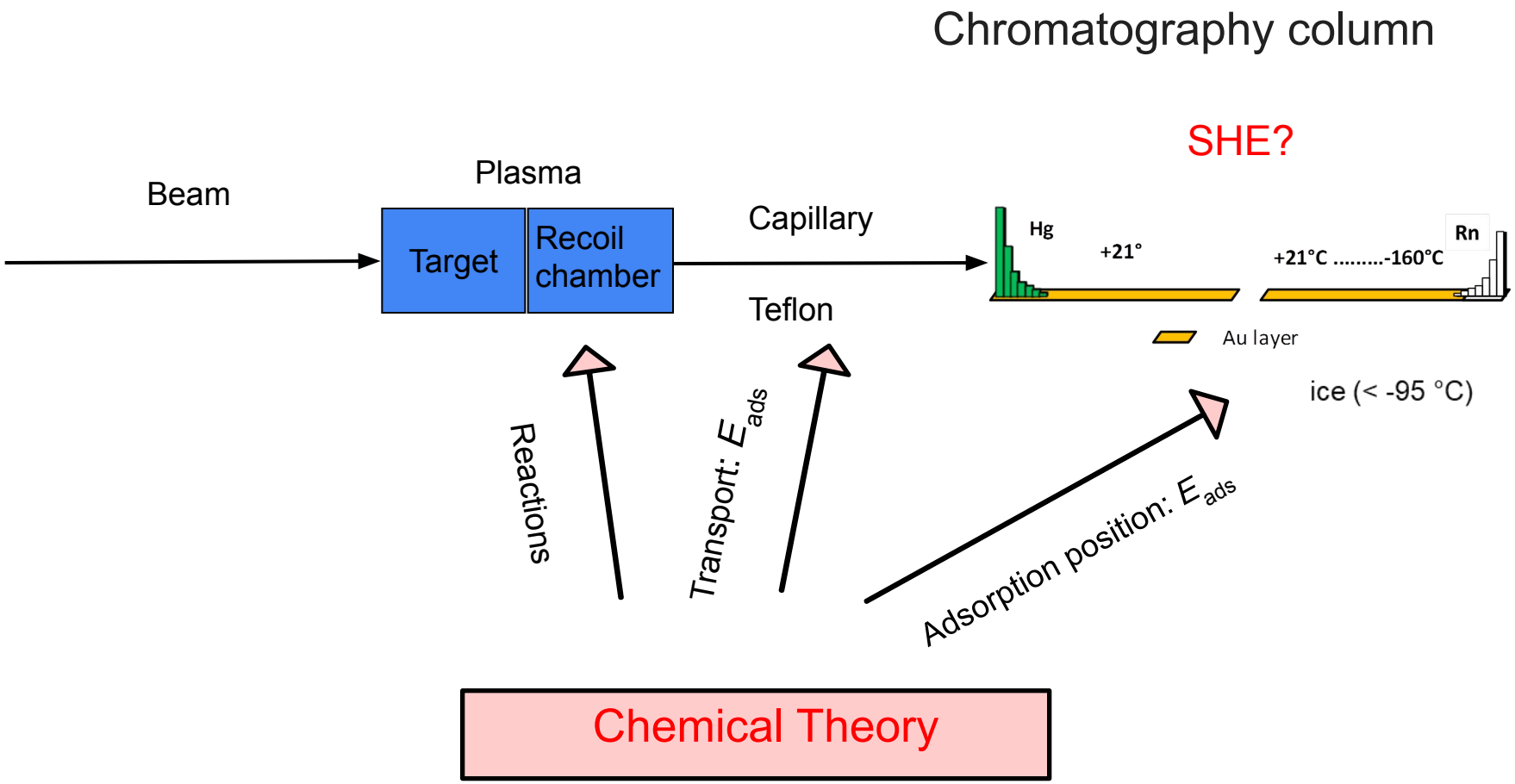
Superheavy Elements to be Chemically Studied



Chemical separation is relatively slow technique –
now SHE isotopes with $t_{1/2}$ > 1 s can be studied

V. Pershina, Dubna Meeting 2021

Gas-Phase Chromatography Experiments on SHEs at JINR, Dubna



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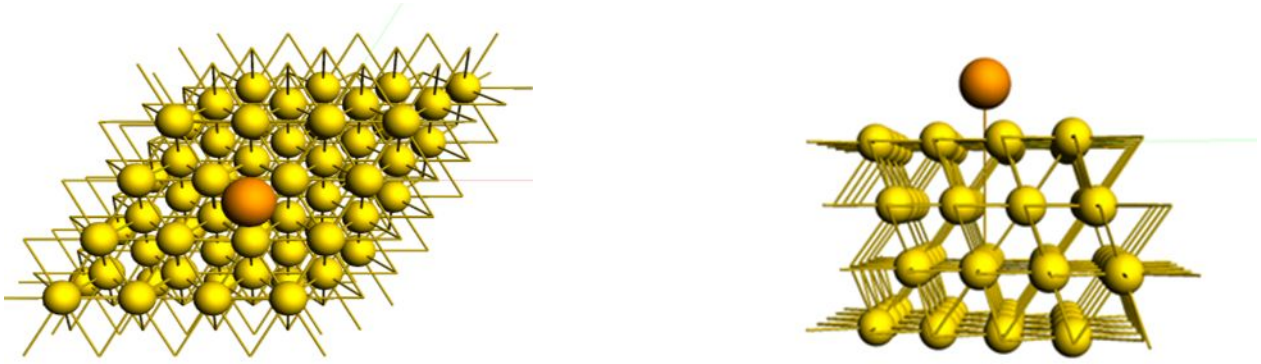
Method for Periodic Calculations

- SCM BAND
  - 2 component: SR and SO relativity
  - all electron
  - STO basis sets till Z=120
  - geometry optimization (up to 300 iterations)
  - full relaxation
  - various E^{xc} including dispersion-corrected
  - checking all adsorption positions (hollow-2 is most stable)
    - (for molecules: Force Field method – *M. Ilias*)
  - *commercial & host-locked*

Modeling Gold Surface

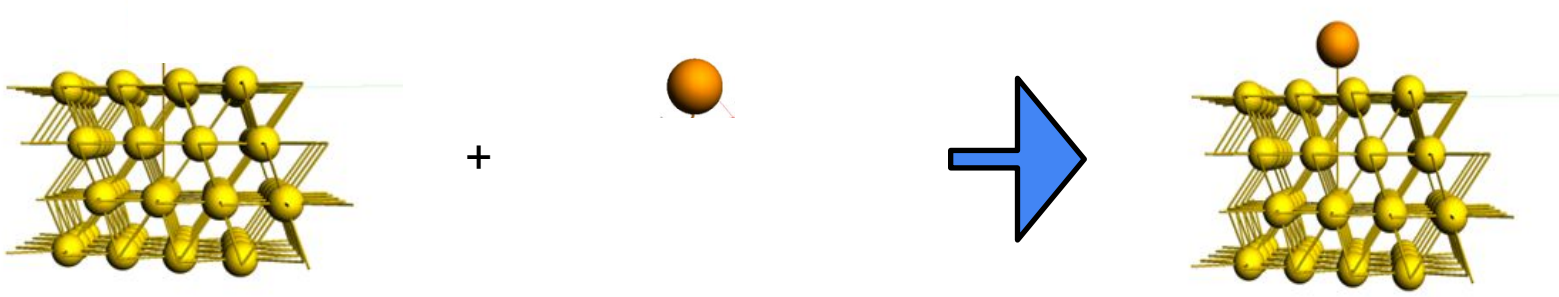
- Modeling gold surfaces
  - calculating structure of gold bulk
  - Au(111) geometrical cut plane – most stable
  - constructing the (4 x 4) supercell to avoid interaction of ad-atoms (for single species of SHEs)



„hollow-2“ is most stable position

Periodic Calculations of E_{ads}(Pb/Fl) on Au(111)

Au(111) s-cell | Atom/Molecule | Atom/Molecule on Au-s-cell

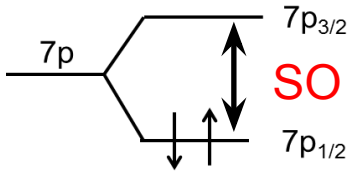


E_f(Au-sc) | E_f (atom/molecule) | E_f(atom/molecule-Au$_{sc}$)

-199.5 eV

Pb: -1.88 eV
Fl: -5.12 eV

-203.8 eV
-205.1 eV



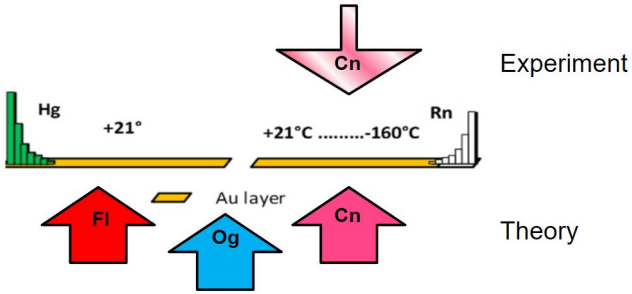
SO stabilization of Fl atom makes it less reactive than Pb

E_{ads} = – [E_f[atom/molecule-Au(111)sc] – E_f(atom/molecule) – E_f[Au(111)sc]]

V. Pershina, Dubna Meeting 2021

Summary of Previous Studies

- Previous studies
  - **Atoms**
    - Hg/Cn, Tl/Nh, Pb/Fl, Bi/Mc, Po/Lv, At/Ts, Rn/Og
  - **Compounds**
    - hydrides BiH/McH, PoH/LvH, AtH/TsH, RnH/OgH
    - oxydes AtO/TsO, AtO_2/TsO_2, AtOO/TsOO
    - oxyhydrides AtOH/TsOH, AtO(OH)/TsO(OH), RnOH/OgOH

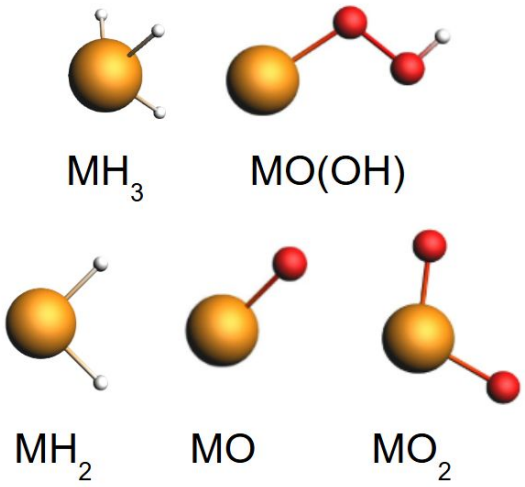


A. Ryzhkov, V. Pershina, M. Ilias and V. Shabaev, Phys. Chem. Chem. Phys., 25 (2023).

- Present work
  - 15^{th} group

    BiH_3/McH_3, BiO(OH)/McO(OH)
  - 16^{th} group

    PoH_2/LvH_2, PoO/LvO, PoO_2/LvO_2



Formation of Compounds of SHEs

Reactions at standard conditions

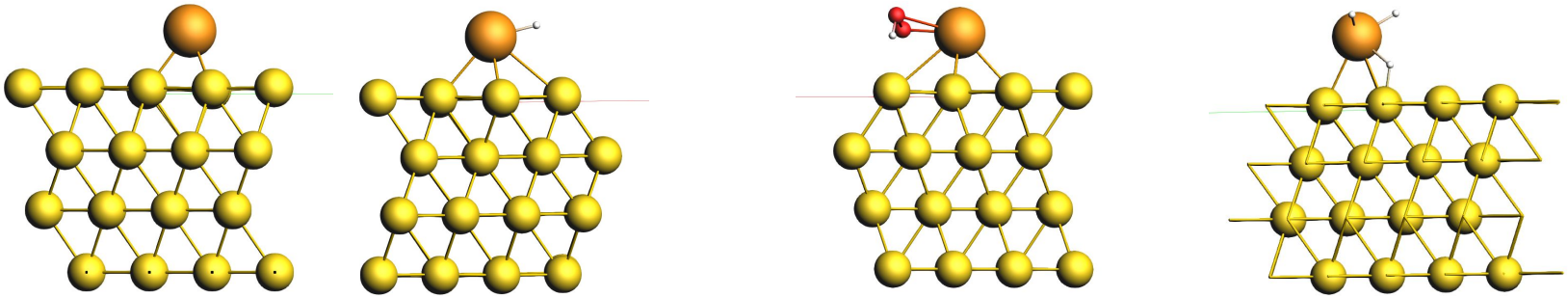
- $M + O_2 \rightarrow MOO$
- $M + O_2 \rightarrow OMO$
- $M + H_2 \rightarrow MH_2$
- $MOO + H_2 \rightarrow MO + H_2O$

Reactions with radicals

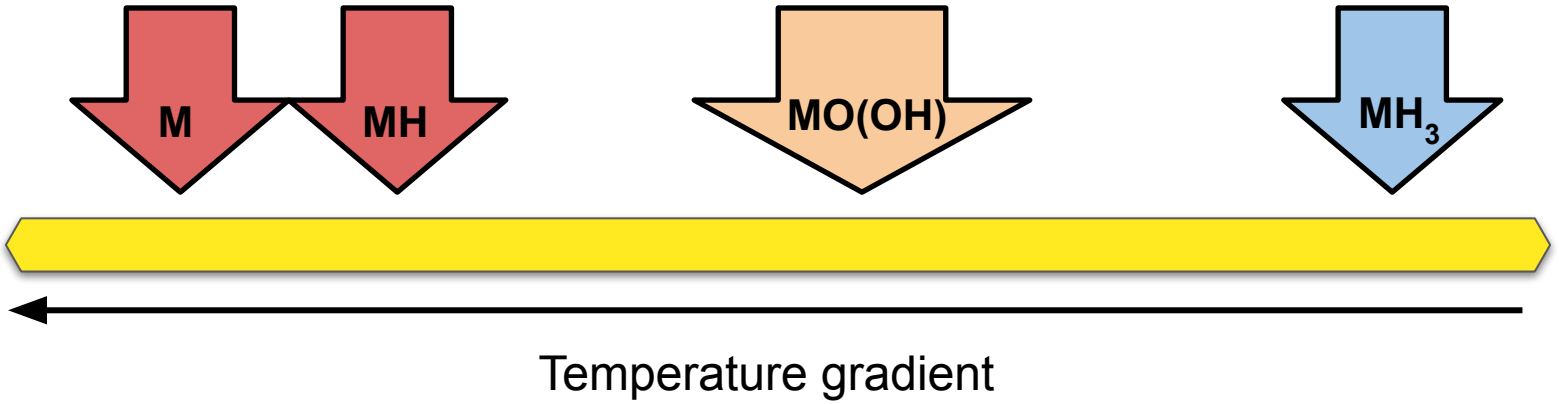
- $M + O \rightarrow MO$
- $MO + OH \rightarrow MO(OH)$
- $M + 3\,H \rightarrow MH_3$
- $MOO + H_2 \rightarrow MO + H_2O$

Adsorption of 15th group element compounds on Au(111)

Adsorption positions



Adsorption strength



Adsorption of 15th group element compounds on Au(111)

Summary of the calculated E_{ads} values of the Bi and Mc compounds on the Au(111) surface at the SO level of theory in comparison with the experimental $-\Delta H_{ads}$ values (in kJ/mol)

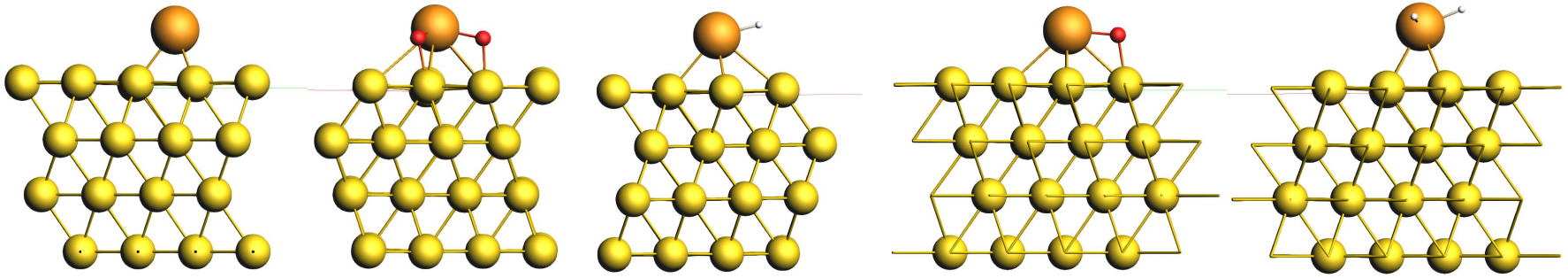
	M[a]	MH[a]	MH_3	MO(OH)
M=Bi	280	263	95	253
M=Mc	205	206	136	140
exp. (Bi)	271± 10[b]			

[a]A. Ryzhkov, V. Pershina, M. Ilias and V. Shabaev, *Phys. Chem. Chem. Phys.*, 2023, **25**, 15362-15370.

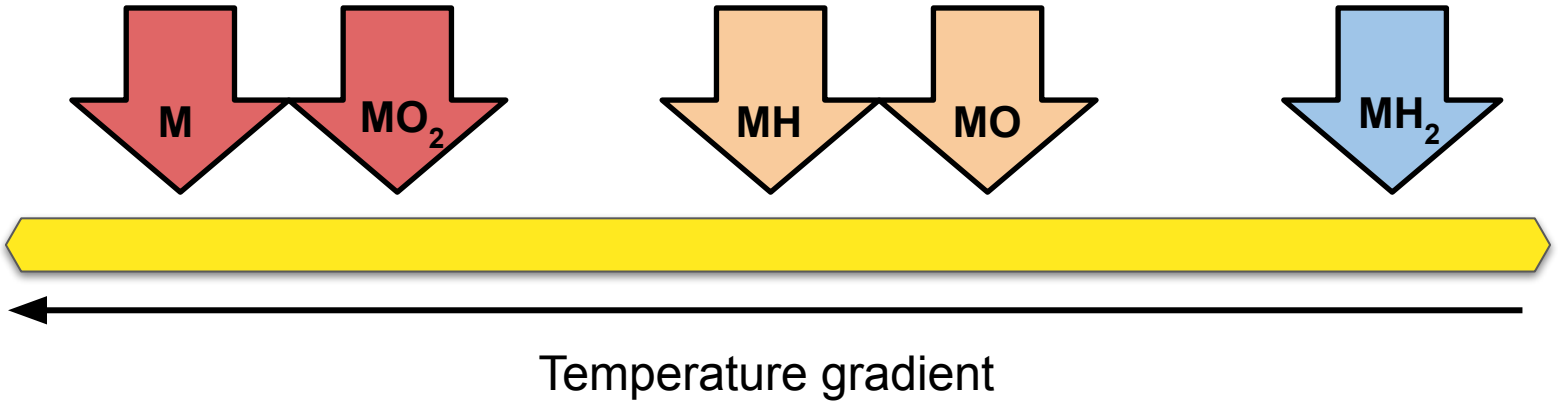
[b]E. A. Maugeri, J. Neuhausen, R. Eichler, R. Dressler, K. Rijpstra, S. Cottenier, D. Piguet, A. Vögele, D. Schumann, Radiochim. Acta, 2016, **104**, 757-767.

Adsorption of 16th group element compounds on Au(111)

Adsorption positions



Adsorption strength



Adsorption of 16th group element compounds on Au(111)

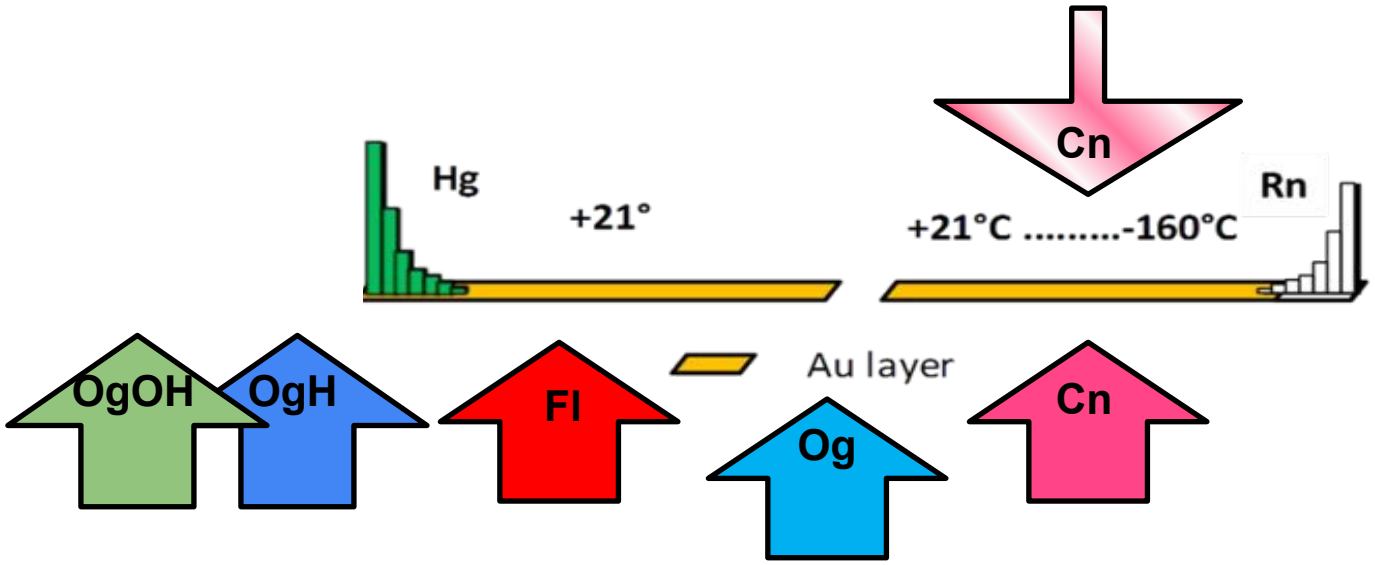
Summary of the calculated E_{ads} values of the Po and Lv compounds on the Au(111) surface at the SO level of theory in comparison with the experimental $-\Delta H_{ads}$ values (in kJ/mol)

	M[a]	MH[a]	MH_2	MO	MO_2
M=Po	260	211	105	208	219
M=Lv	240	178	110	188	286
exp. (Po)	250± 10[b]				228± 10[b]

[a]A. Ryzhkov, V. Pershina, M. Ilias and V. Shabaev, *Phys. Chem. Chem. Phys.*, 2023, **25**, 15362-15370.

[b]E. A. Maugeri, J. Neuhausen, R. Eichler, R. Dressler, K. Rijpstra, S. Cottenier, D. Piguet, A. Vögele, D. Schumann, Radiochim. Acta, 2016, **104**, 757-767.

Conclusions for Experiments with Gold Surface of Detectors



Acknowledgment of the Laboratory of Information Technologies of JINR