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

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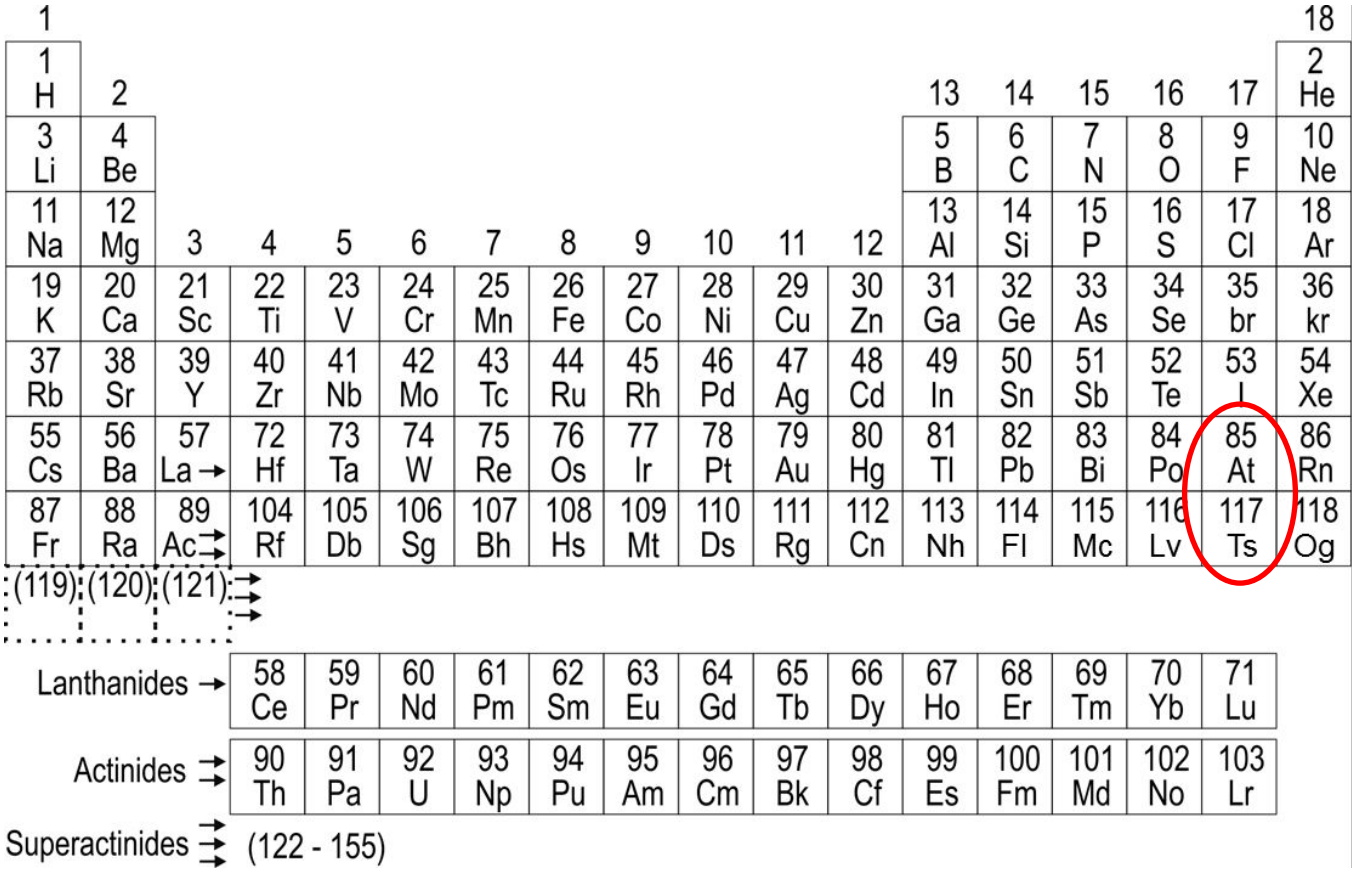
with the support of JINR, Dubna

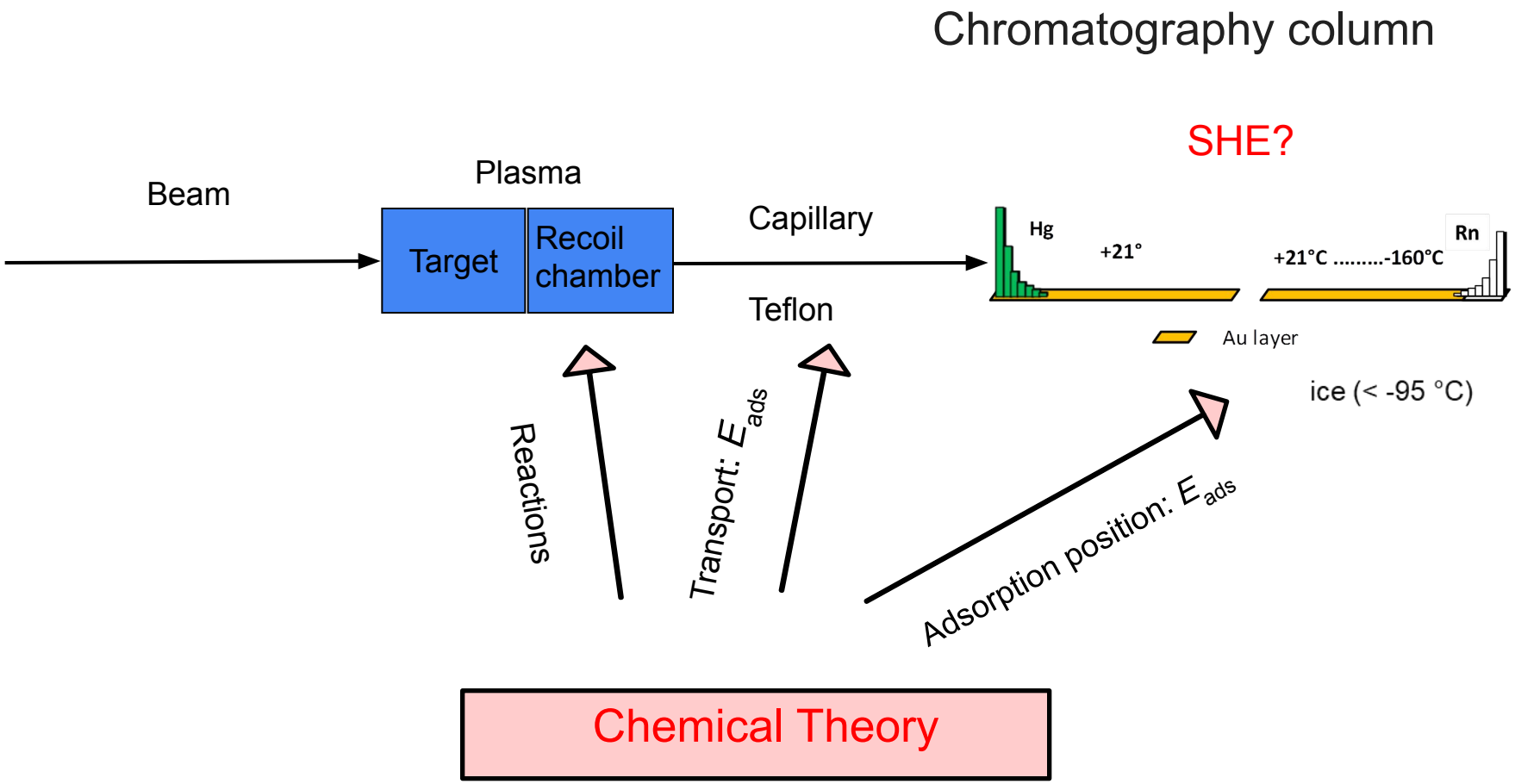
Superheavy Elements to be Chemically Studied



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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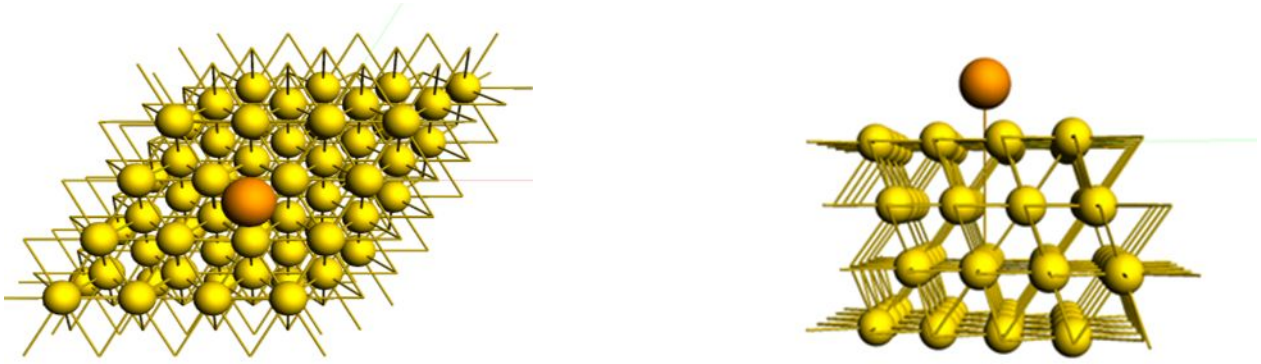
Method for Periodic Calculations

- 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

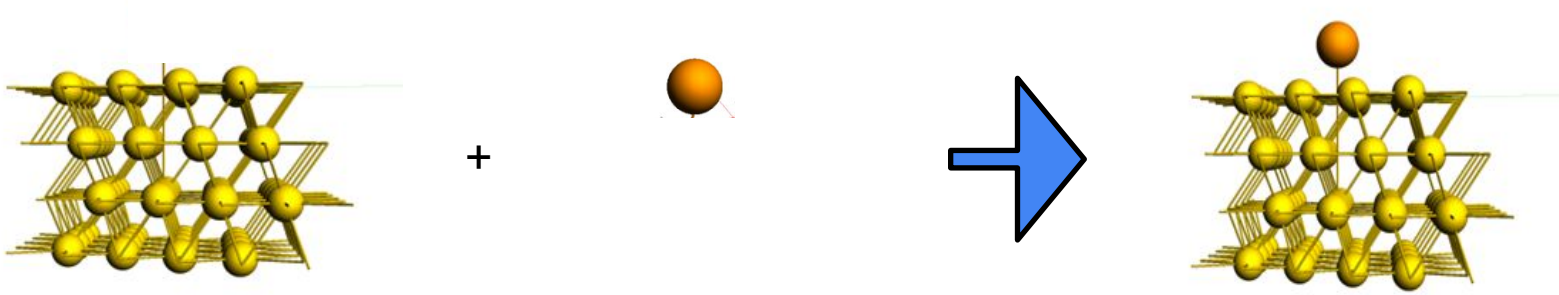
- Modeling gold surfaces
  - calculating structure of gold bulk
  - Au(111) geometrical cut plane – most stable
  - constructing the (4 x 4) supercell to avoid interaction of ad-atoms (for single species of SHEs)



„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

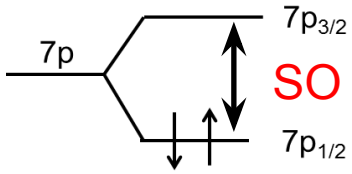


E_f(Au-sc) | E_f (atom/molecule) | E_f(atom/molecule-Au$_{sc}$)

-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]]

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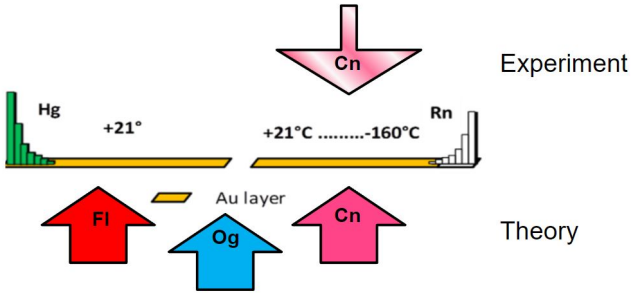
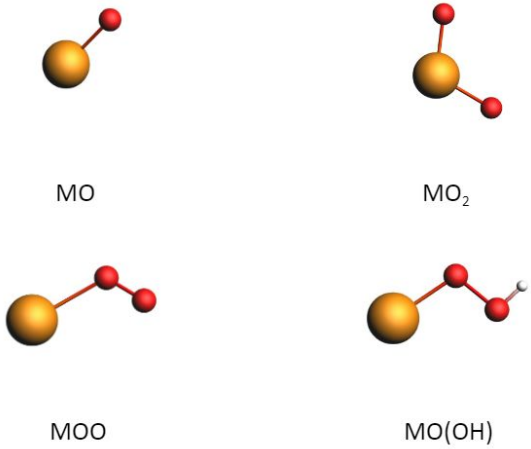
Summary of Previous Studies

- 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
  - oxyhydrides AtOH/TsOH, RnOH/OgOH



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

- Present work
  - oxydes AtO/TsO, AtO_2/TsO_2, AtOO/TsOO
  - oxyhydrides AtO(OH)/TsO(OH)



- Work in progress
  - oxydes PoO/LvO, PoO_2/LvO_2
  - oxyhydrides BiO(OH)/McO(OH), $Po(OH)_2$/$Lv(OH)_2$
  - hydrides PoH_2/LvH_2, BiH_3/McH_3

Formation of Compounds of SHEs

Formation of compounds in the in the atmosphere of O_2 and in the recoil chamber (reactions with O, H and OH radicals)

- $At + O = AtO$ $E_r = -2.679$ eV
- $O + AtO = AtO_2$ $E_r = -2.586$ eV
- $At + O_2 = AtOO$ $E_r = -0.139$ eV
- $AtO + OH = AtO(OH)$ $E_r = -1.730$ eV
- $AtOO + H = AtO(OH)$ $E_r = -3.150$ eV

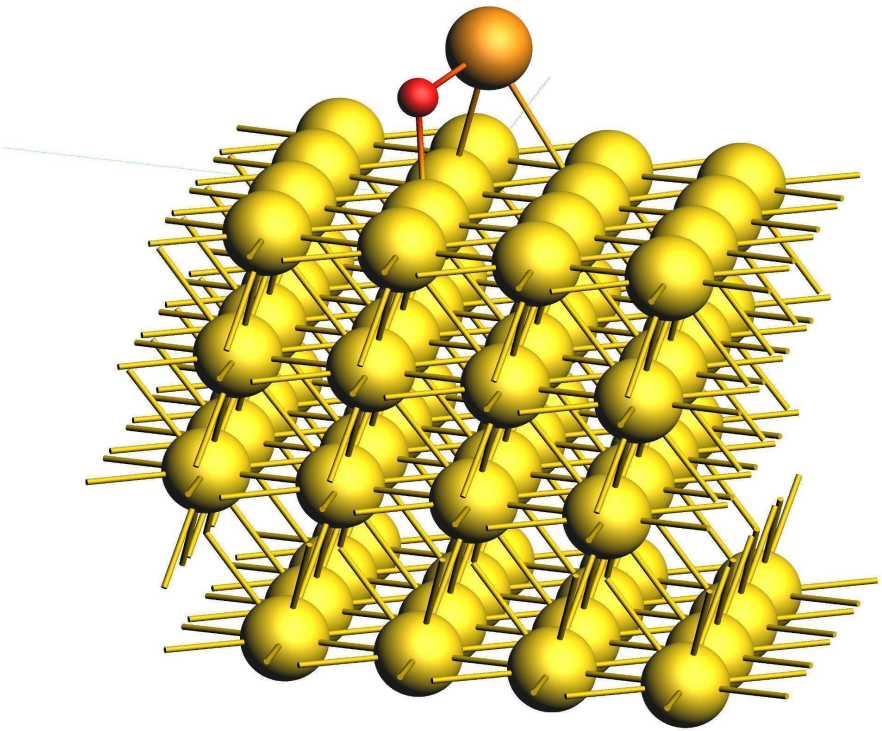
- $Ts + O = TsO$ $E_r = -2.748$ eV
- $O + TsO = TsO_2$ $E_r = -2.335$ eV
- $Ts + O_2 = TsOO$ $E_r = -0.302$ eV
- $TsO + OH = TsO(OH)$ $E_r = -1.830$ eV
- $TsOO + H = TsO(OH)$ $E_r = -3.160$ eV

Adsorption of MO (M = At/Ts) on Au(111)

Results:

SR E_{ads}(AtO) = 186 kJ/mol
SO E_{ads}(AtO) = 168 kJ/mol

SR E_{ads}(TsO) = 204 kJ/mol
SO E_{ads}(TsO) = 213 kJ/mol



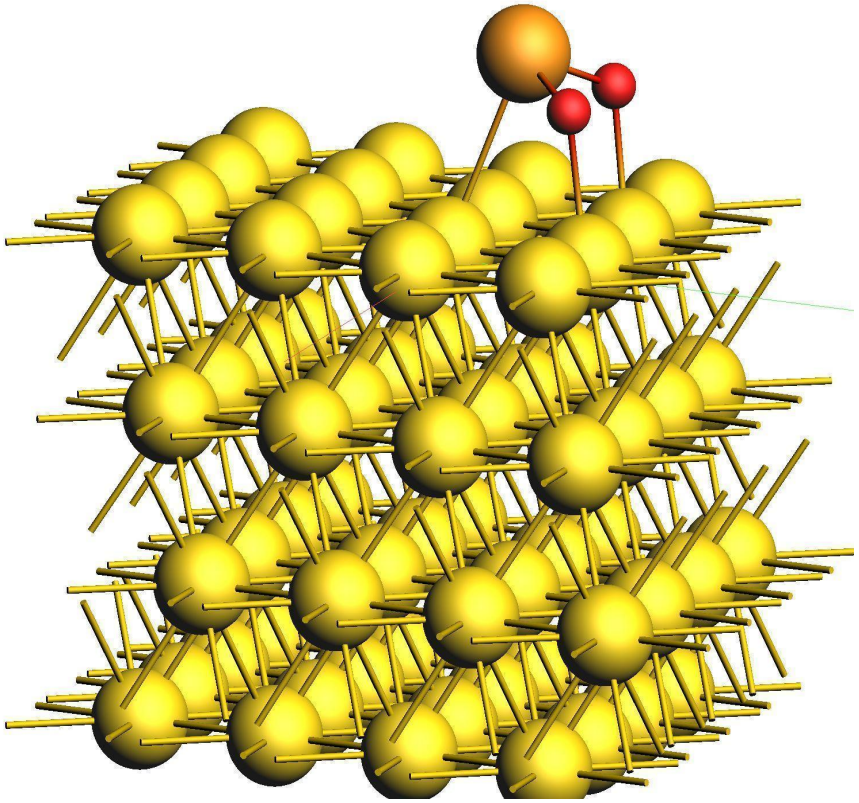
Adsorption of the MO molecules on the Au(111) surfaces takes place via interaction of the both M and O with the surface Au atoms.

Adsorption of MO_2 (M = At/Ts) on Au(111)

Results:

SR $E_{ads}(AtO_2)$ = 179 kJ/mol
SO $E_{ads}(AtO_2)$ = 198 kJ/mol

SR $E_{ads}(TsO_2)$ = 193 kJ/mol
SO $E_{ads}(TsO_2)$ = 271 kJ/mol



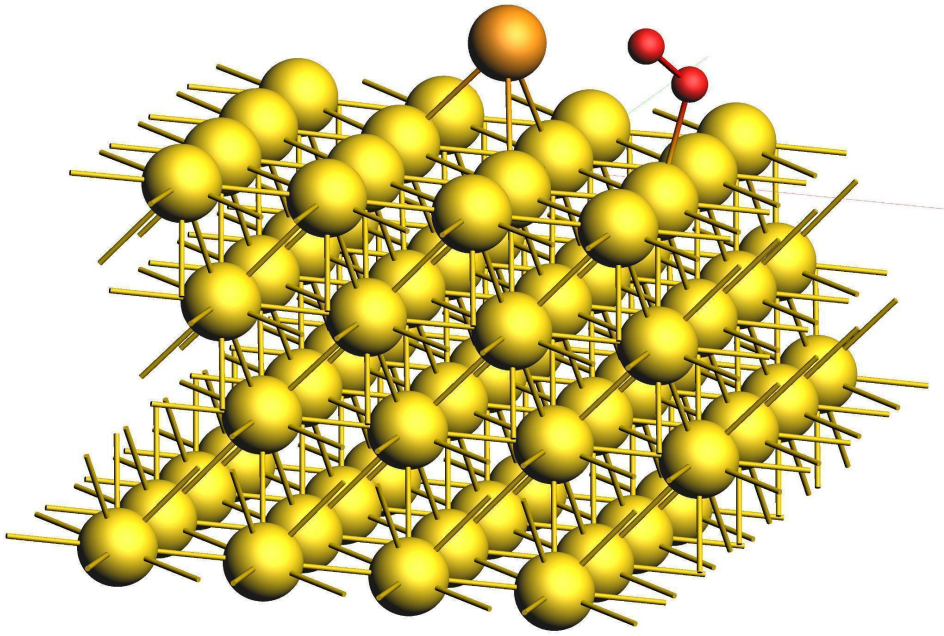
Adsorption of the MO_2 molecules on the Au(111) surfaces takes place via interaction of both oxygen atoms and M atom with the surface Au atoms.

Adsorption of MOO (M = At/Ts) on Au(111)

Results:

SR E_{ads}(AtOO) = 183 kJ/mol
SO E_{ads}(AtOO) = 160 kJ/mol

SR E_{ads}(TsOO) = 192 kJ/mol
SO E_{ads}(TsOO) = 184 kJ/mol



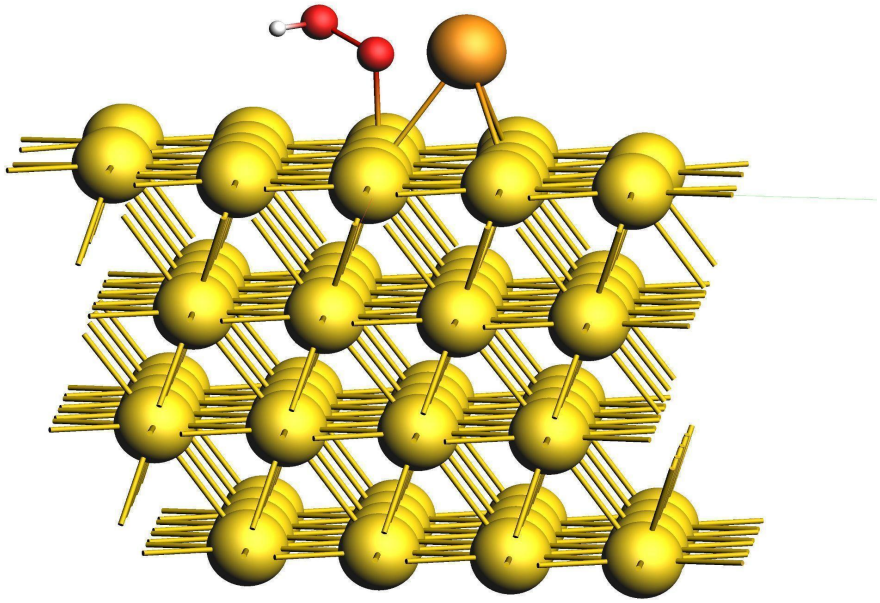
The MOO molecules become rather stretched upon adsorption, so that the M atom and OO group are attached almost separately to the surface.

Adsorption of MO(OH) (M = At/Ts) on Au(111)

Results:

SR E_{ads}(AtO(OH)) = 233 kJ/mol
SO E_{ads}(AtO(OH)) = 217 kJ/mol

SR E_{ads}(TsO(OH)) = 266 kJ/mol
SO E_{ads}(TsO(OH)) = 232 kJ/mol



Adsorption of these molecules occurs similarly to the MOO molecules, where the species become stretched upon adsorption.

Results

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

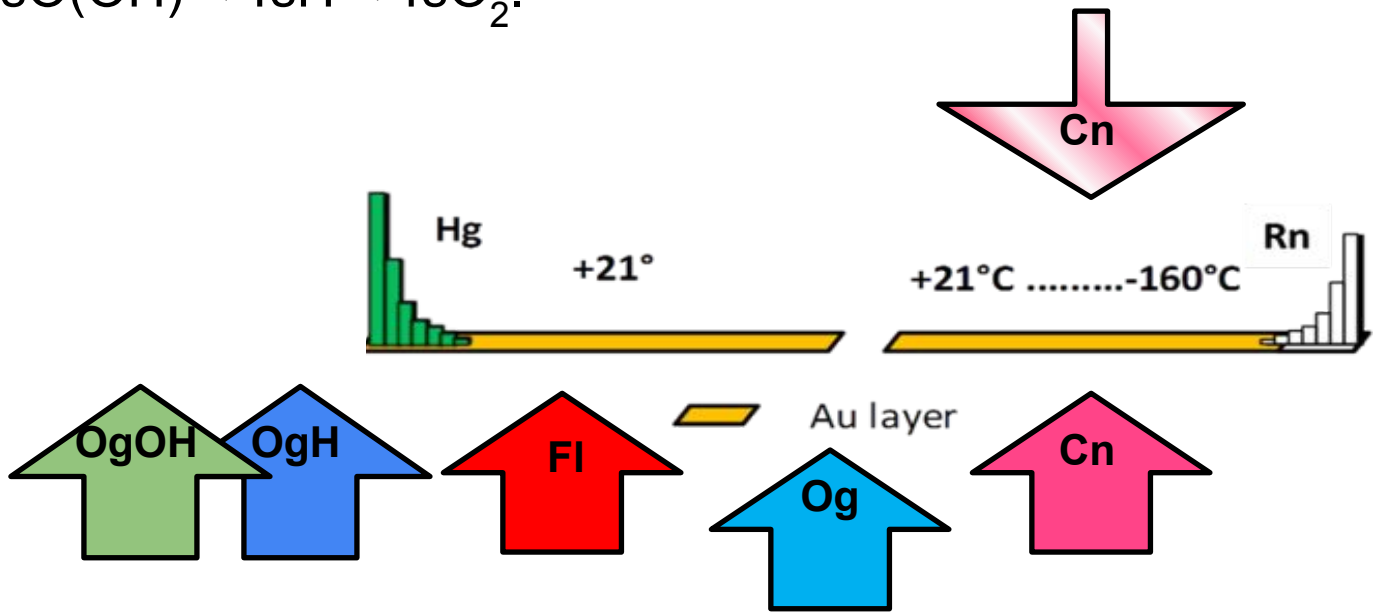
	M[a]	MH[a]	MOH[a]	MO	MO_2	MOO	MO(OH)
M=At	184	164	185	168	198	160	217
M=Ts	203	236	193	213	271	184	232
exp. (At)	154[b]				124[b]		

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

[b]A. Serov et al. *Radiochim. Acta,* 2011, **99**, 593-600.

Conclusions for Experiments with Gold Surface of Detectors

- The E_{ads} values for the At species are similar, with the sequence AtOO < AtH < AtO < At < AtOH < AtO_2 < AtO(OH)
- The E_{ads} values for the Ts species are all larger than for the corresponding At ones with the sequence TsOO < TsOH < Ts < TsO < TsO(OH) < TsH < TsO_2.



Acknowledgment of the Laboratory of Information Technologies of JINR