Adsorption behavior of superheavy 7p elements and their compounds on gold surface: periodic DFT calculations

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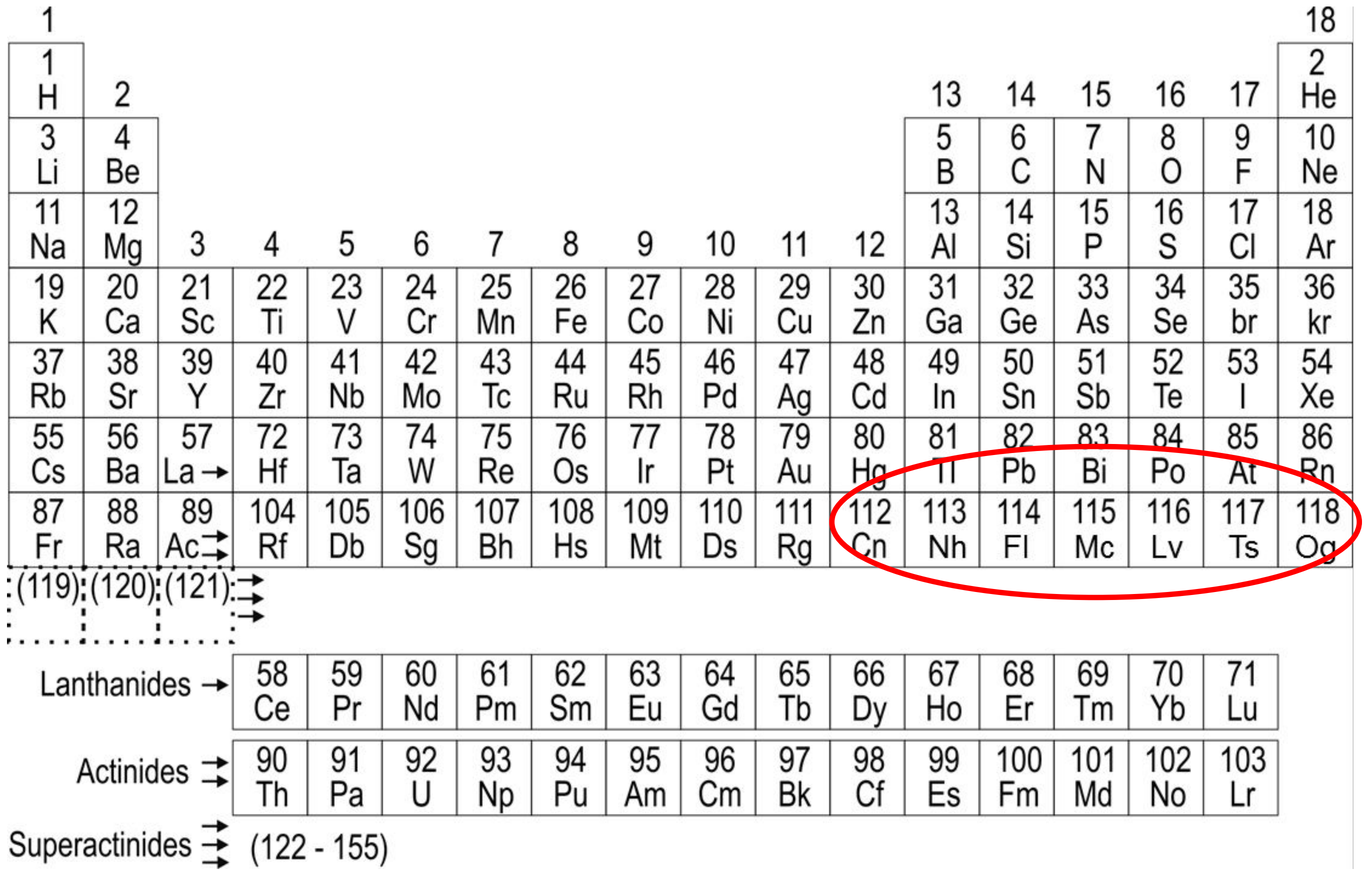
with the support of JINR, Dubna

Superheavy Elements to be Chemically Studied



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

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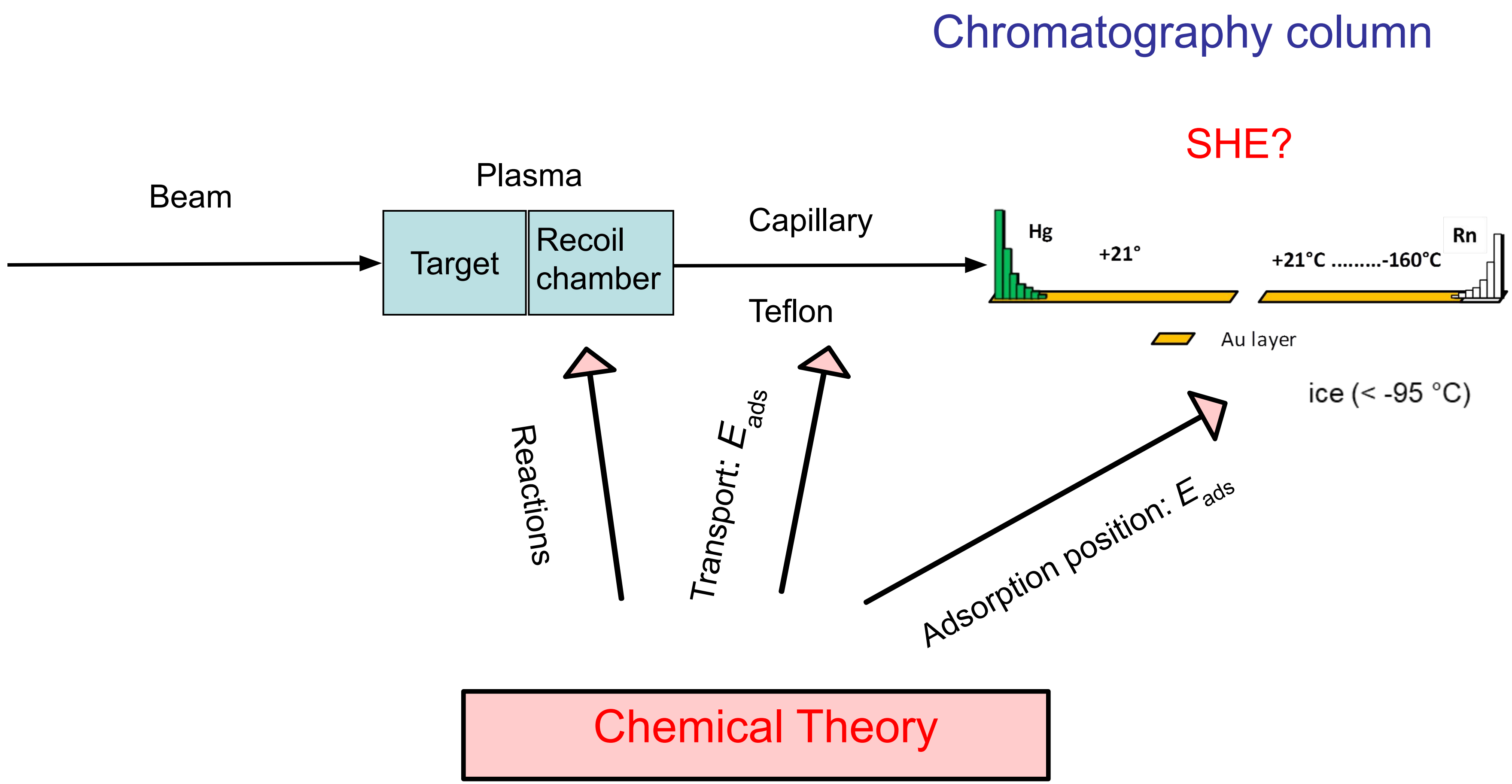
Gas-Phase Chromatography Experiments on SHEs at JINR, Dubna



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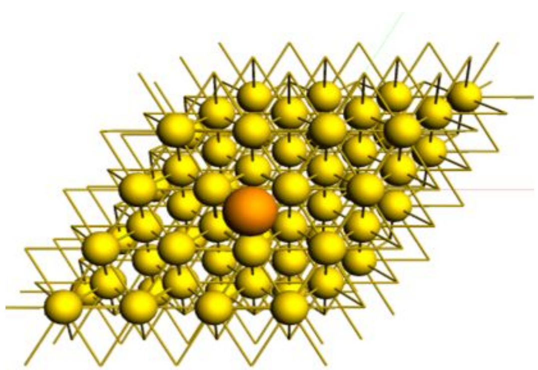
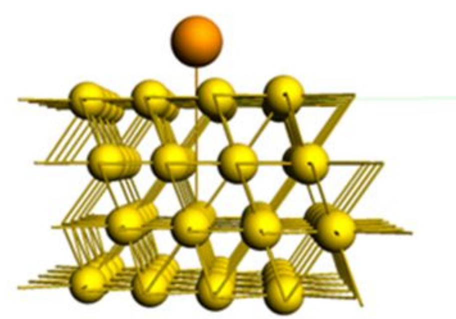
Method for Periodic Calculations

- 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)

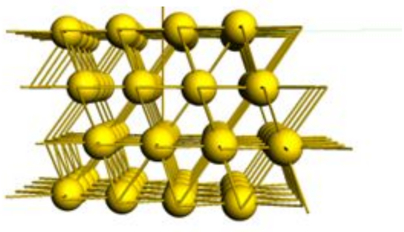




„hollow-2“ is most stable position

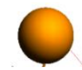
Periodic Calculations of E_{ads}(Pb/Fl) on Au(111)

Au(111) s-cell

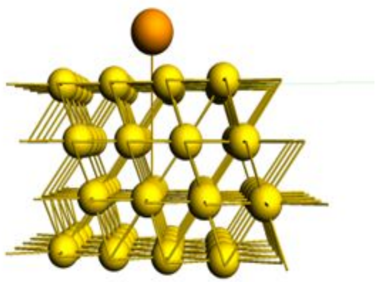


+

Atom/Molecule



M/MO/Au-s-cell



E_f(Au-sc)

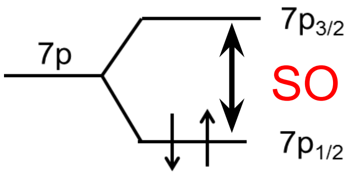
-199.5 eV

E_f (M(/MO)

Pb: -1.88 eV
Fl: -5.12 eV

E_f(M-Au_{sc})

-203.8 eV
-205.1 eV



SO stabilization of Fl atom makes it less reactive than Pb

$$E_{ads} = E_f[\text{M-Au(111)sc}] - E_f(\text{M}) - E_f[\text{Au(111)sc}]$$

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Results for E_{ads}(M) for Hg/Cn - Rn/Og on Au(111) Surface

- Eads: SR and SO in comparison with experimental ones

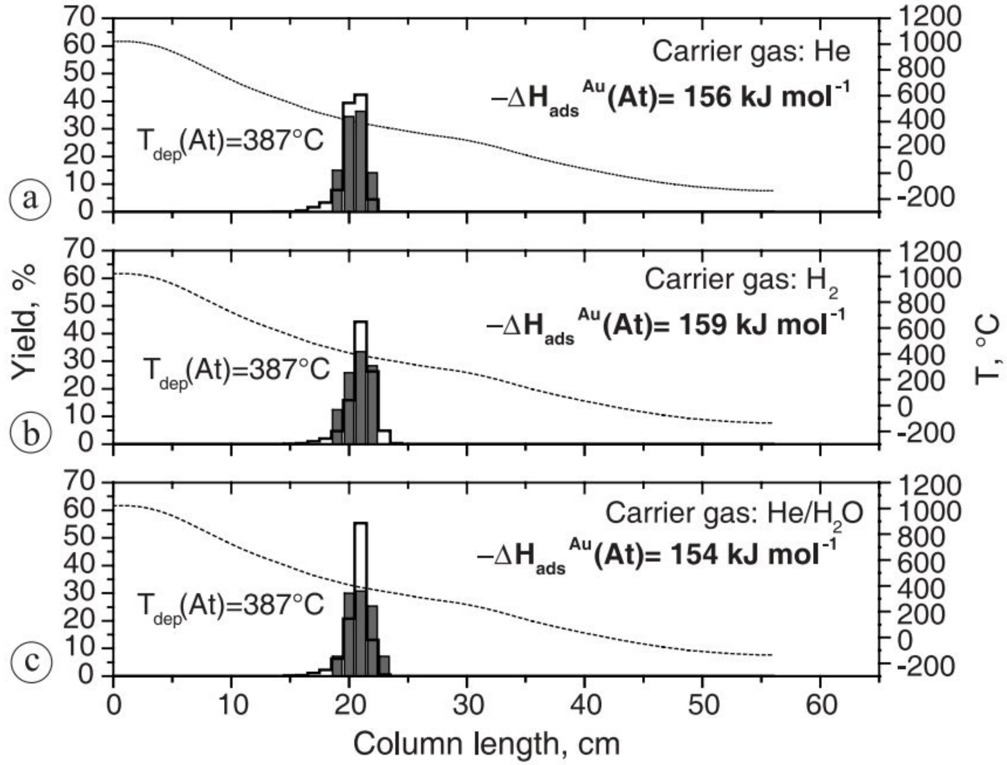
	SCM BAND (revPBE-D3BJ)		Exp.
Element	SR	SO	
6th row			
Hg	73	78[a]	98±3[b]
Tl	359	254[a]	270±10[c]
Pb	367	268[a]	234[d]
Bi	317	280[a]	268/273±7[e]
Po	332	260	250±7[e]
At	232	184	153±5[g]
Rn	42	45	20±1[f]

	SCM BAND (revPBE-D3BJ)		Exp.
Element	SR	SO	
7th row			
Cn	57	68	52^{+4}_{-3} [f]
Nh	351[a]	162[a]	
Fl	355	87	34^{+54}_{-11} [h] >48 [i]
Mc	312[a]	205[a]	
Lv	323	240	
Ts	231	203	
Og	50	78	

[a]Pershina, V. et. al. // *Inorg. Chem.* 60, 9796-9804 (2021);
[b]Lens, L. et. al. // Radiochim. Acta 2018, 106, 949-962;
[c]Serov, A. R. et. al. // Radiochim. Acta 2013, 101, 421-425;
[d]Haenssler, F. et. al. // PSI Annual Report 2005 (2006), p 3;
[e]Maugeri, E. A. et. al. // Radiochim. Acta 2016, 104, 757-767;
[g]Serov, A. et. al. // *Radiochim. Acta,* 99, 693-599 (2011).

[f]Eichler, R. et. al. // Nature 2007, 447, 72-75;
[h]Eichler, R. et. al. // Radiochim. Acta 2010, 98, 133-139;
[i]Yakushev, A. et. al. // Inorg. Chem. 2014, 53, 1624-1629.

Experimental value of At



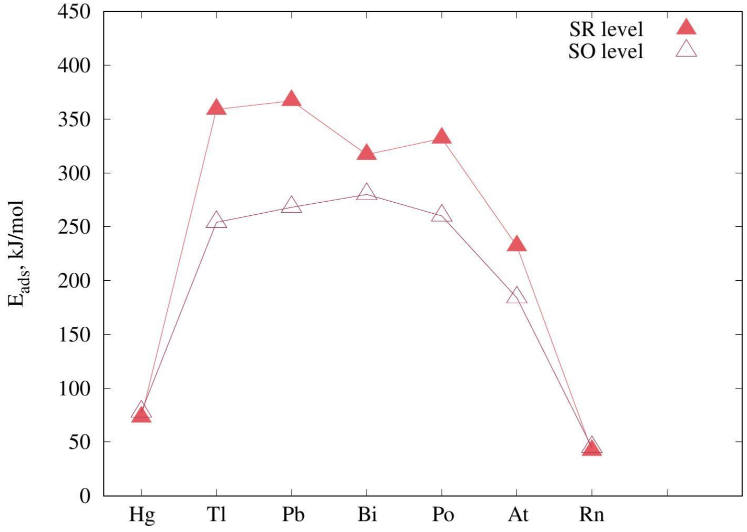
Theoretical results:

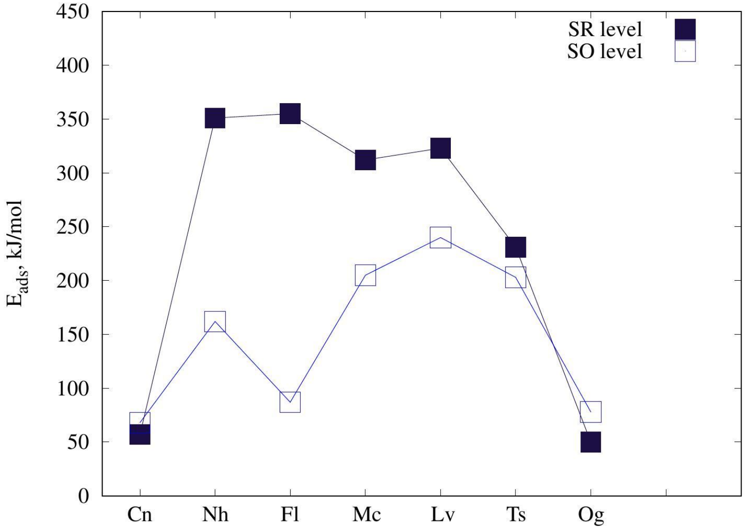
E_{ads}(At) = 184 kJ/mol
E_{ads}(AtOH) = 185 kJ/mol

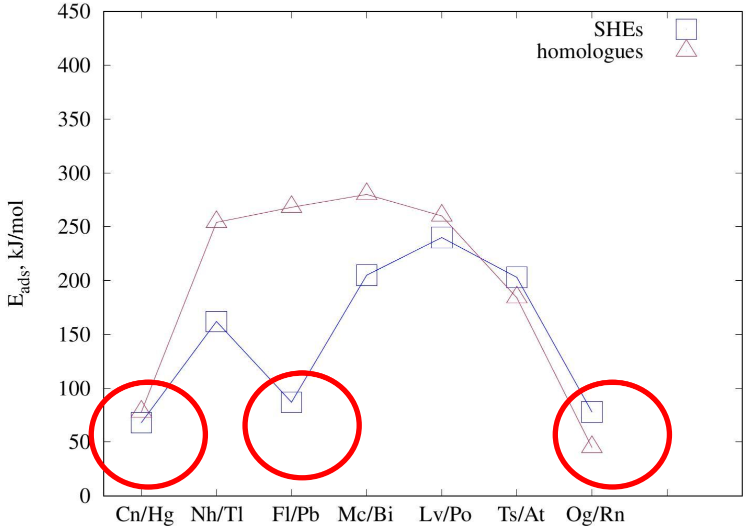
E_{ads}(Ts) = 203 kJ/mol
E_{ads}(TsOH) = 193 kJ/mol

Serov, A. et. al. // *Radiochim. Acta,* 99, 693-599 (2011).

Results for E_{ads}(M) for Hg/Cn - Rn/Og







Distribution of events can be observed in the column at T < room one (i.e. for E_{ads} < 80-90 kJ/mol)

Formation of Compounds of SHEs

- Formation of MH and M(OH) in the atmosphere of O_2, H_2O and H_2

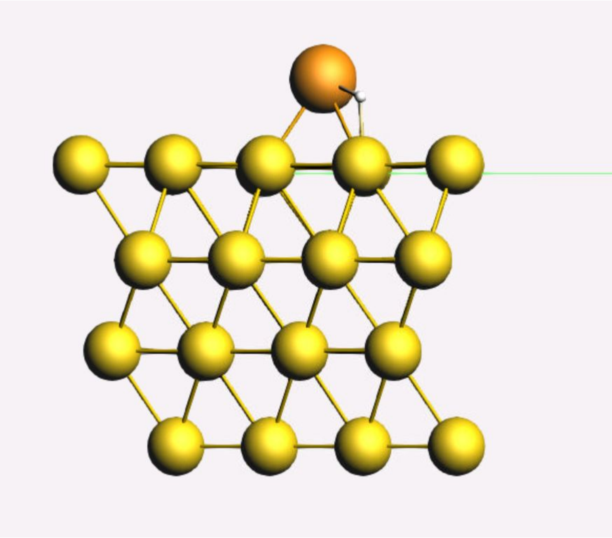
Group 17:

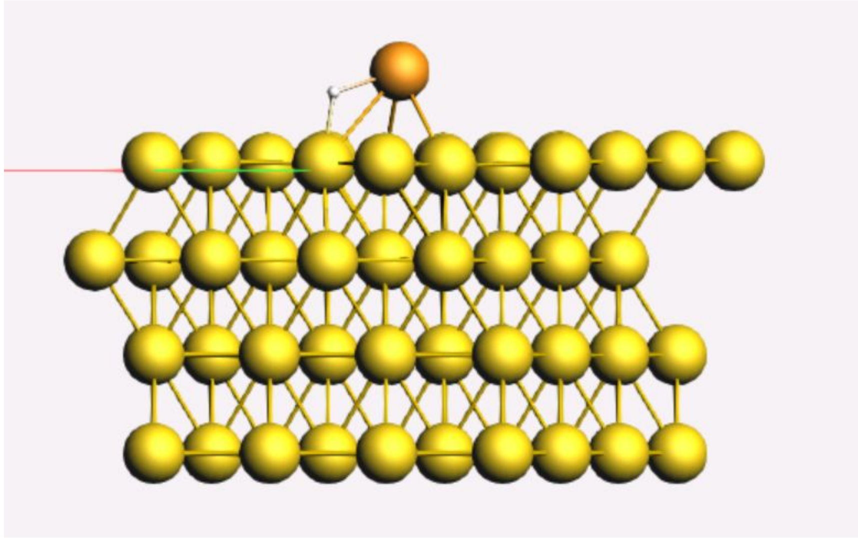
$Ts + O_2 = TsOO$	Er = -0.302 eV
$Ts + O = TsO$	Er = -2.748 eV
$TsO + H_2 = Ts + H_2O$	Er = -2.691 eV
$TsOO + H_2 = TsOH + OH$	Er = -0.832 eV
$TsOO + H_2 = TsO + H_2O$	Er = -1.949 eV

Group 18:

$Og + O_2 = OgOO$	Er = -0.0034 eV
$OgOO + H_2 = OgO + H_2O$	Er = -0.454 eV

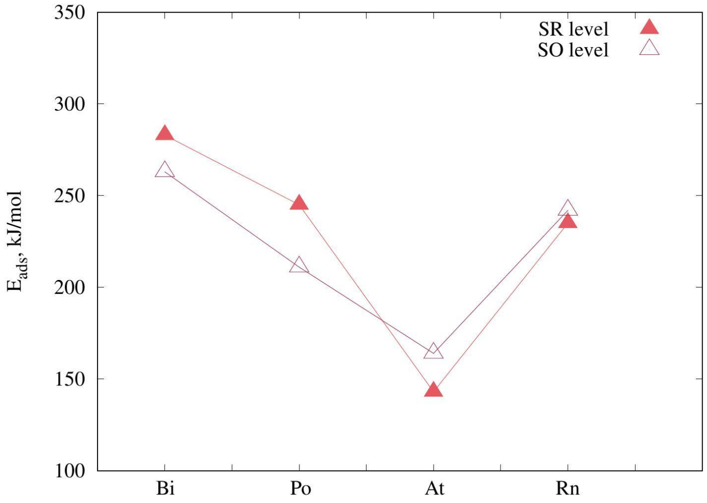
Geometrical Configurations of MH/Au(111) (M = Mc/Bi, Lv/Po, Ts/At, Og/Rn)

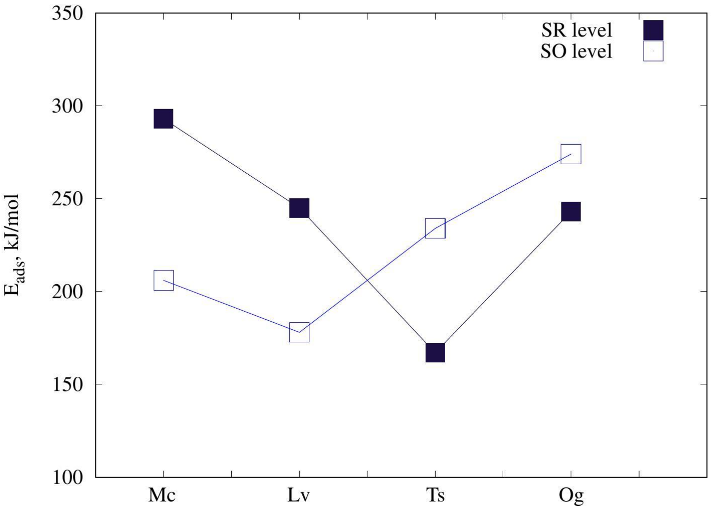


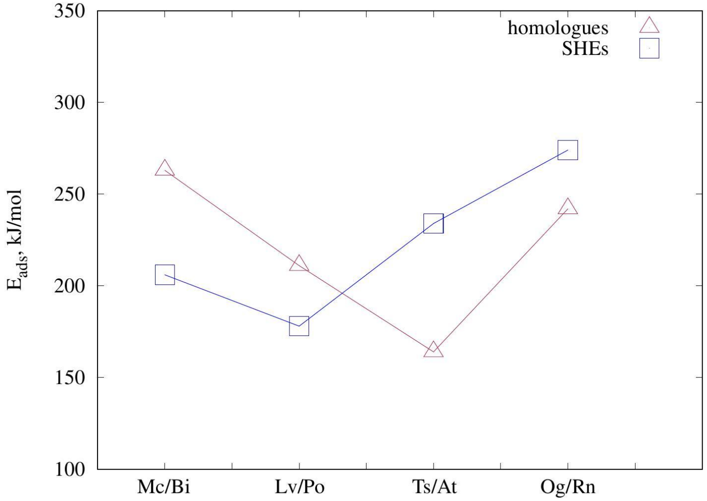


Adsorption of the MH molecules on the Au(111) surfaces takes place via interaction of the both M and H with the surface Au atoms

Adsorption of MH (M = Mc/Bi, Lv/Po, Ts/At, Og/Rn) on Au(111)





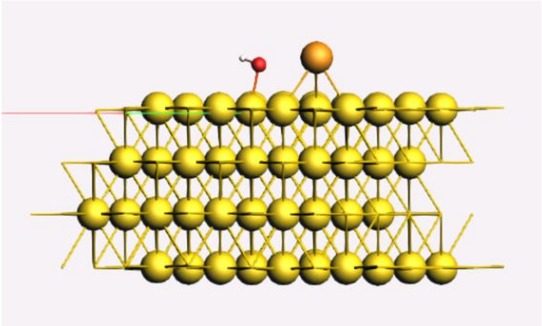


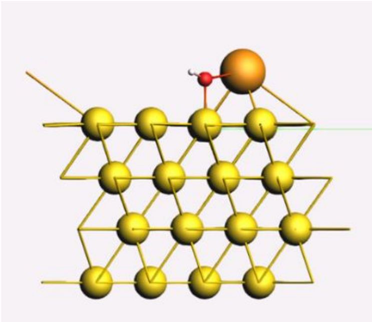
OgH should adsorb on gold much more strongly than RnH and Og: it should be possible to distinguish experimentally between Og and OgH by adsorption on gold

Geometrical Configurations of MOH (M = At/Ts and Rn/Og) on Au(111)

<u>Group 17</u>

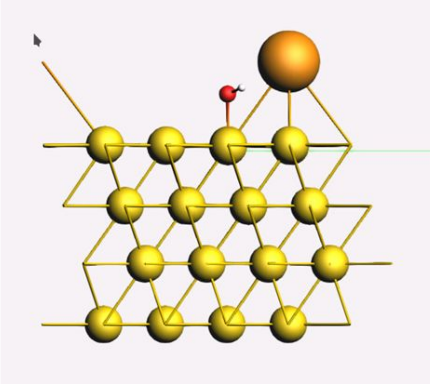
AtOH and TsOH

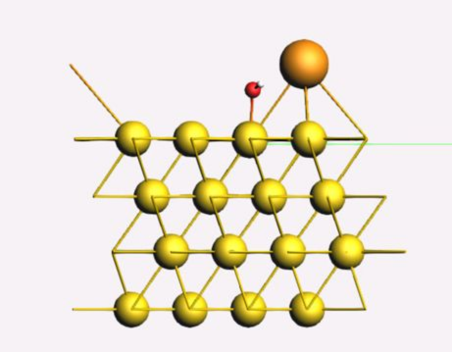




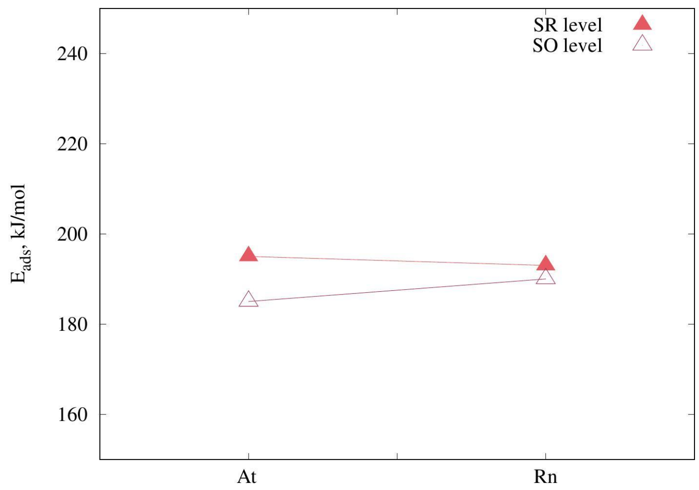
<u>Group 18</u>

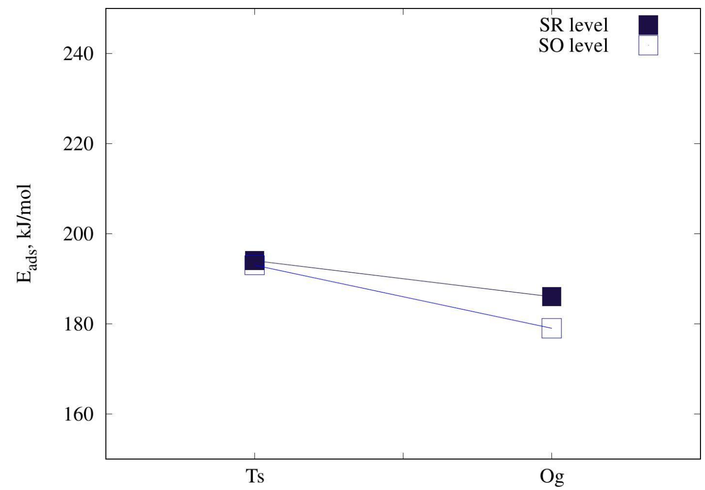
RnOH and OgOH

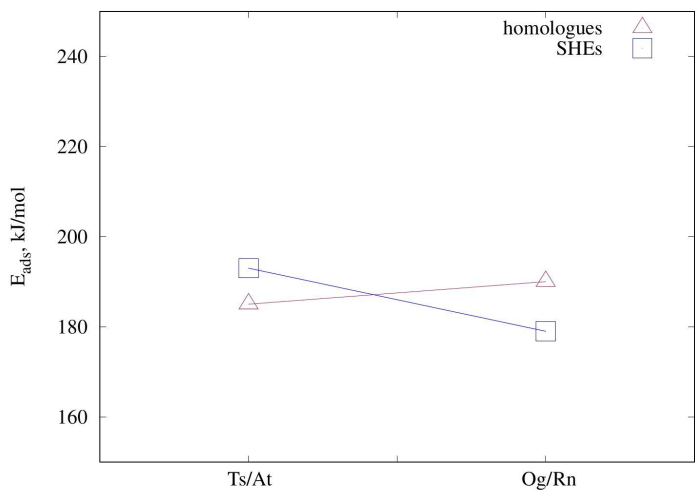




Adsorption of MOH
(M = Ts/At, Og/Rn) on Au(111)

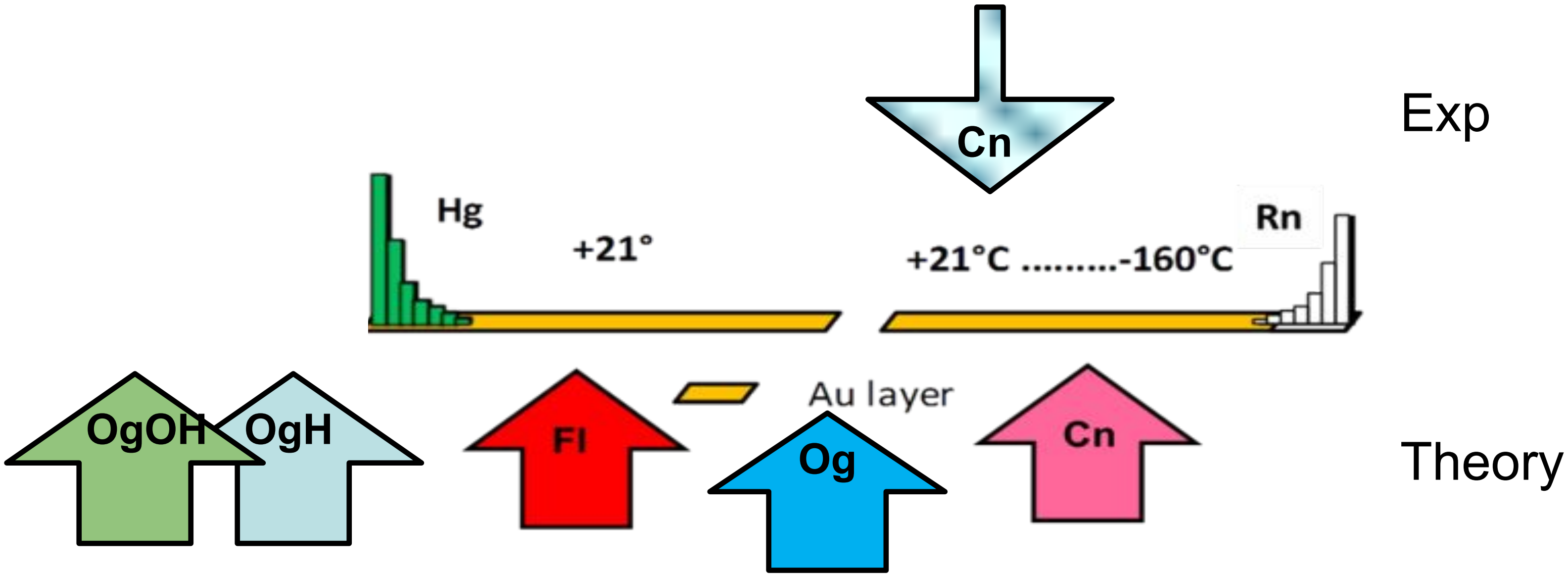






Adsorption of the hydroxides is too high to observe distribution of events at the room temperature or lower ones

Conclusions for Experiments with Gold Surface of Detectors



Acknowledgment of the Laboratory of Information Technologies of JINR