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

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with the support of JINR, Dubna

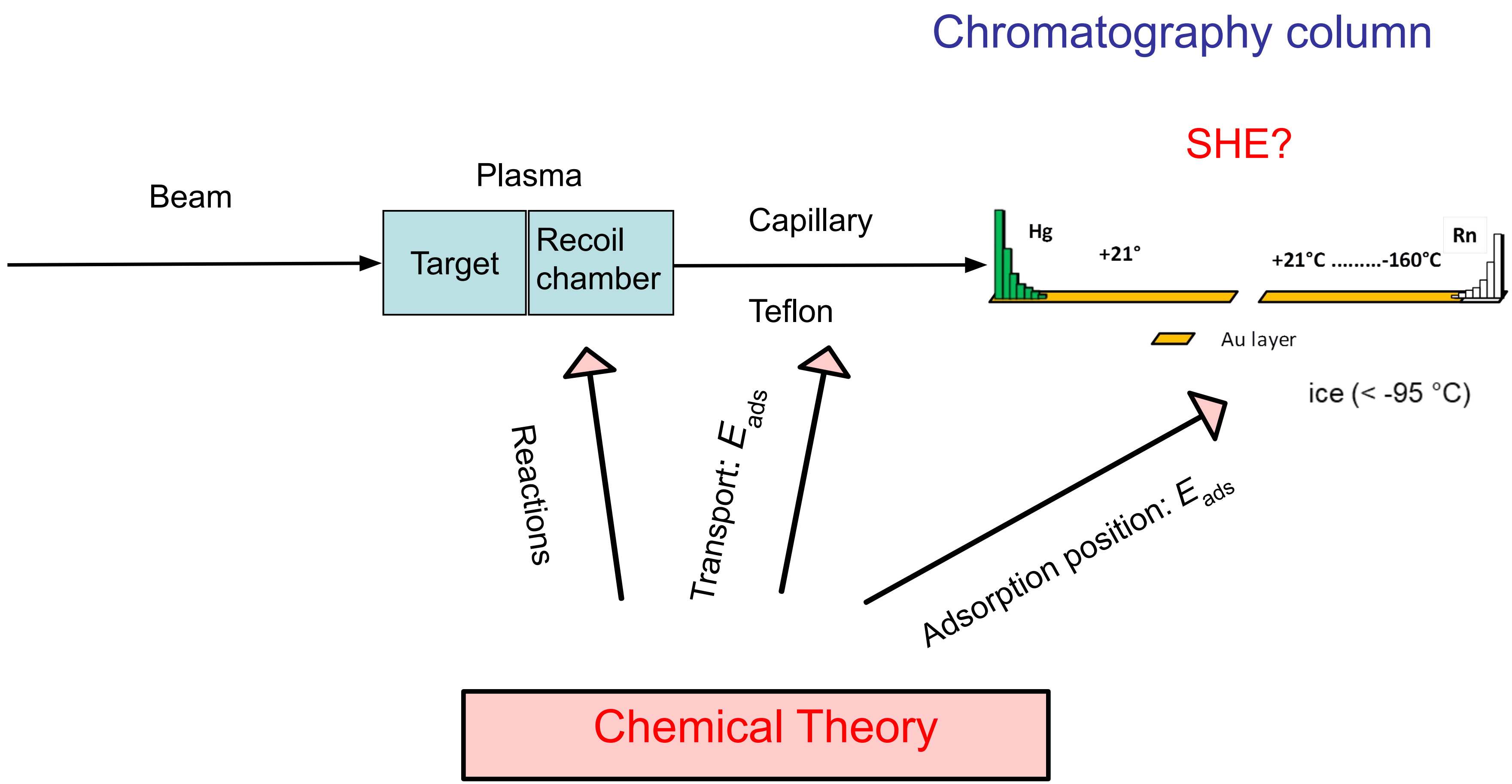
Superheavy Elements to be Chemically Studied

1																	18
1 H	2											13	14	15	16	17	2 He
3 Li	4 Be											5 B	6 C	7 N	8 O	9 F	10 Ne
11 Na	12 Mg	3	4	5	6	7	8	9	10	11	12	13 Al	14 Si	15 P	16 S	17 Cl	18 Ar
19 K	20 Ca	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 br	36 kr
37 Rb	38 Sr	39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe
55 Cs	56 Ba	57 La →	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn
87 Fr	88 Ra	89 Ac →	104 Rf	105 Db	106 Sg	107 Bh	108 Hs	109 Mt	110 Ds	111 Rg	112 Cn	113 Nh	114 Fl	115 Mc	116 Lv	117 Ts	118 Og
(119)	(120)	(121) →															
Lanthanides →			58 Ce	59 Pr	60 Nd	61 Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb	71 Lu	
Actinides →			90 Th	91 Pa	92 U	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No	103 Lr	
Superactinides →			(122 - 155)														

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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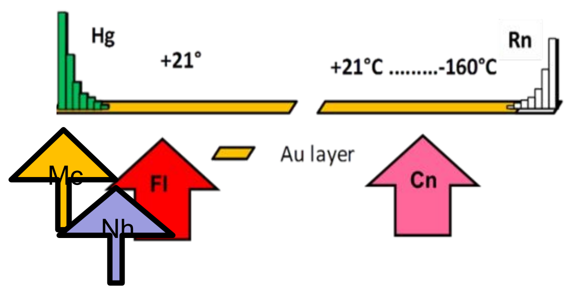
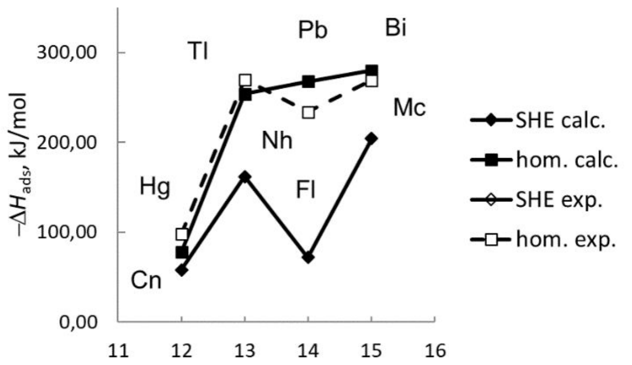
Summary of Previous Studies on E_{ads} of M and MO on Au(111) Surface

- Previous studies
  - Hg/Cn, Tl/Nh,Pb/ Fl and Bi/Mc





V. Pershina. et al., *Inorg. Chem*. **60**, 9796 (2021)

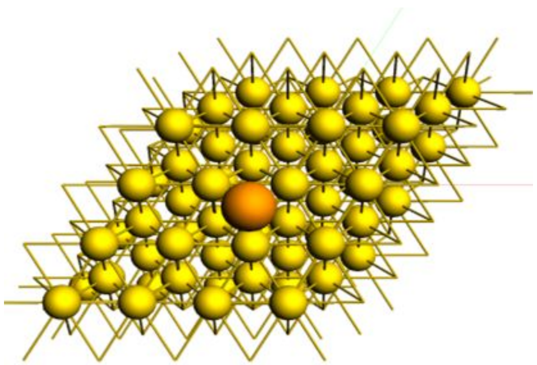
- Present work
  - Entire series of SHE and 6th row: Hg/Cn, Tl/Nh, Pb/Fl, Bi/Mc, Po/Lv, At/Ts, Rn/Og
  - hydrides BiH/McH, PoH/LvH, AtH/TsH, RnH/OgH
  - hydroxides AtOH/TsOH, RnOH/OgOH
- Work in progress
  - BiH_3/McH_3; PoH_2/LvH_2

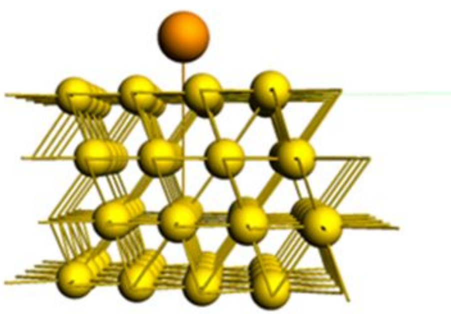
Method for Periodic Calculations

- 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)

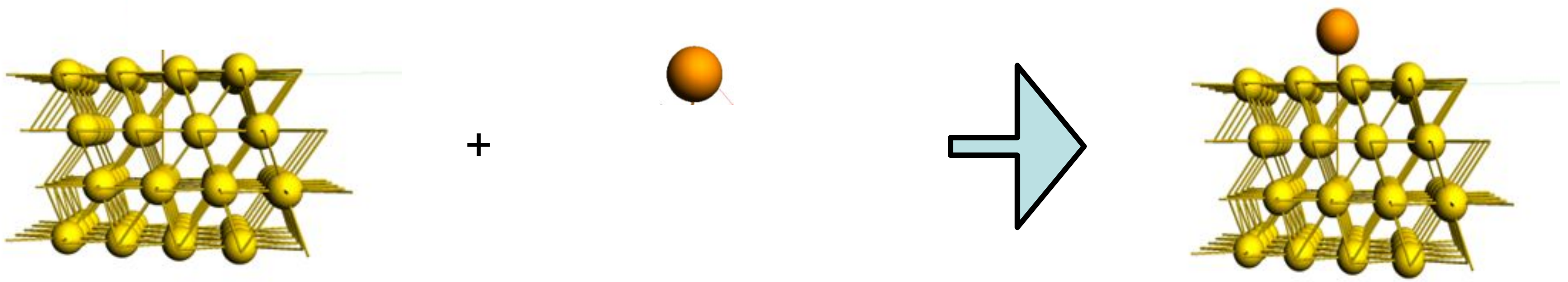




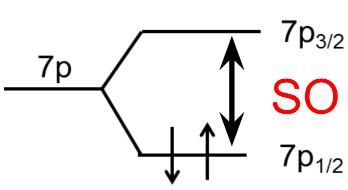
„hollow-2“ is most stable position

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)	E_f (M(/MO)	E_f(M-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

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

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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 ones from the [3]

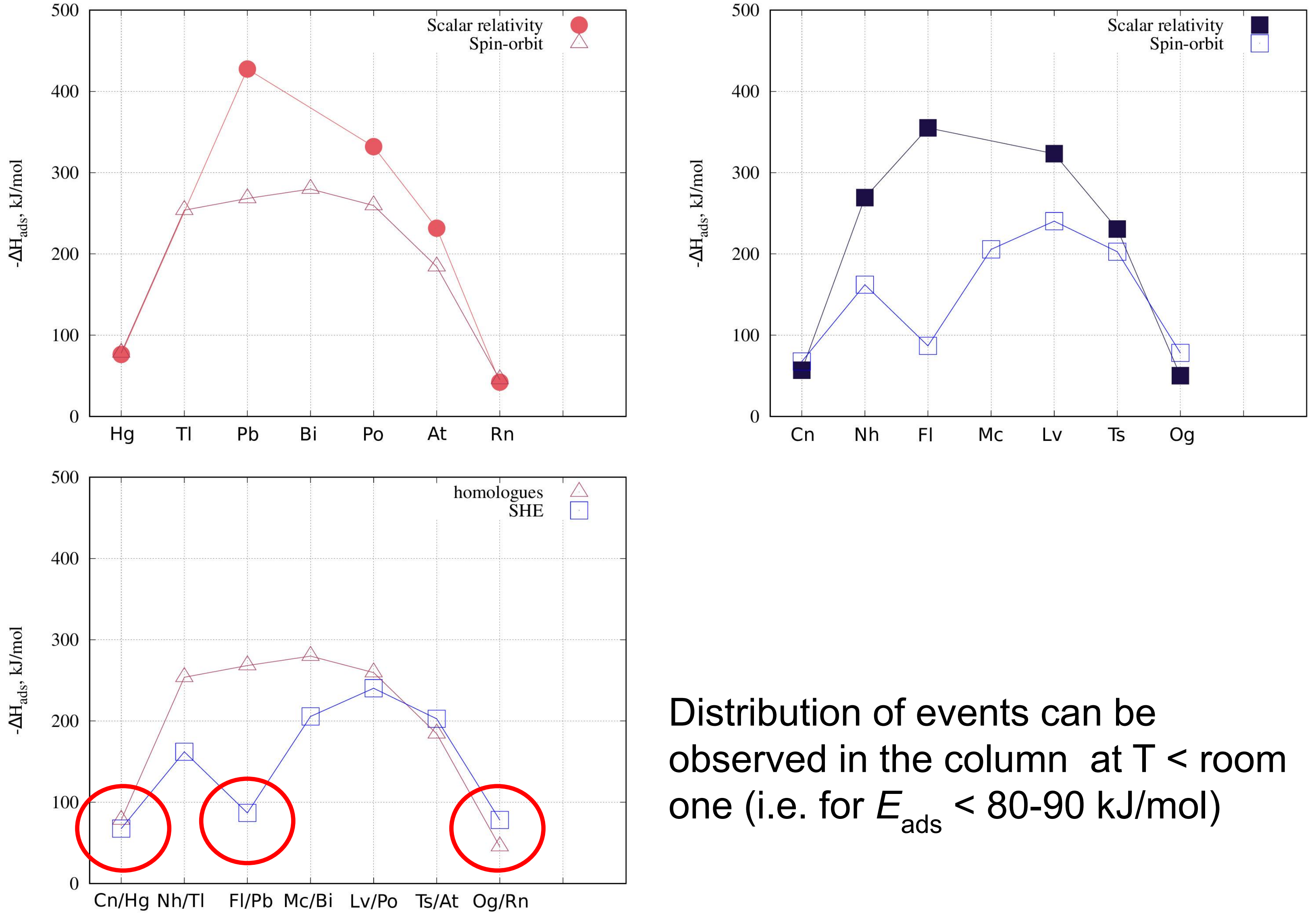
M	SR	SO	SR [3]	SO [3]
	kJ/mol	kJ/mol	kJ/mol	kJ/mol
Hg	76.2	78.15	66.58	72.36
Tl	-	253.76	279.81	231.57
Pb	427.43	268.23	358.93	271.12
Bi	-	279.81	325.16	290.42
Po	331.91	259.55	338.66	267.26
At	231.56	184.29	237.35	189.11
Rn	42.16	45.43	30.86	34.73

M	SR	SO	SR [3]	SO [3]
	kJ/mol	kJ/mol	kJ/mol	kJ/mol
Cn	56.93	67.54	47.28	74.29
Nh	269.19	162.10	281.74	141.83
Fl	355.07	86.84	341.56	75.26
Mc	-	205.51	309.72	225.78
Lv	323.23	240.25	329.02	242.18
Ts	230.60	202.62	250.86	211.30
Og	50.17	78.15	55.96	89.73

[1] Pershina, V.; Iliaš , M.; Yakushev, A. Inorg. Chem., 2021, 60, 9796−9804
[2] Pershina, V. Inorg. Chem., 2018, 57, 3948−3955
[3] Trombach, S.; Ehlert, S.; Grimme, S.; Schwerdtfeger, P.; Jan-Michael Mewes. Phys. Chem. Chem. Phys., 2019, 21, 18048-18058

Og can be deposted on gold with $-\Delta H_{ads}$ = 89 kJ/mol
(at the beginning of the column at room temperature)

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

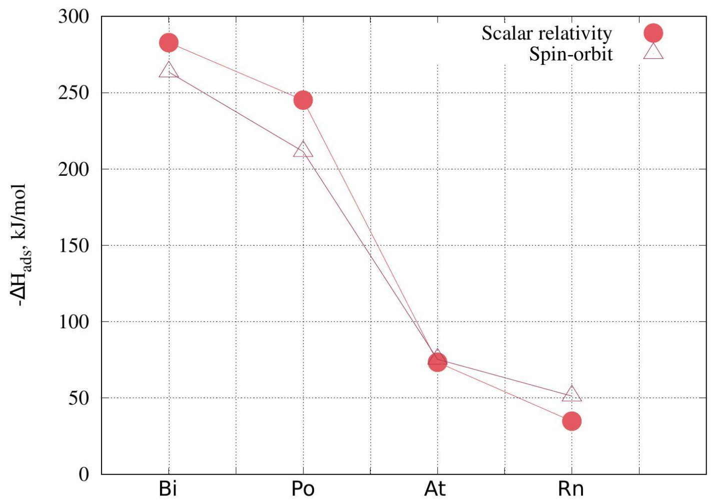
Group 17:

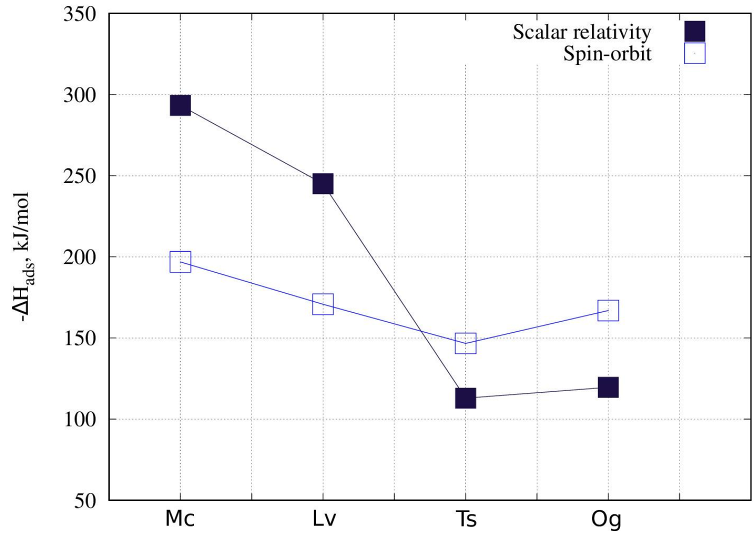
$Ts + O_2 = TsOO$	Er = -0.302 eV
$Ts + O = TsO$	Er = -2.748 eV
$TsO + H_2 = Ts + H_2O$	Er = -2.691 eV
$TsOO + H_2 = TsOH + OH$	Er = -0.832 eV
$TsOO + H_2 = TsO + H_2O$	Er = -1.949 eV

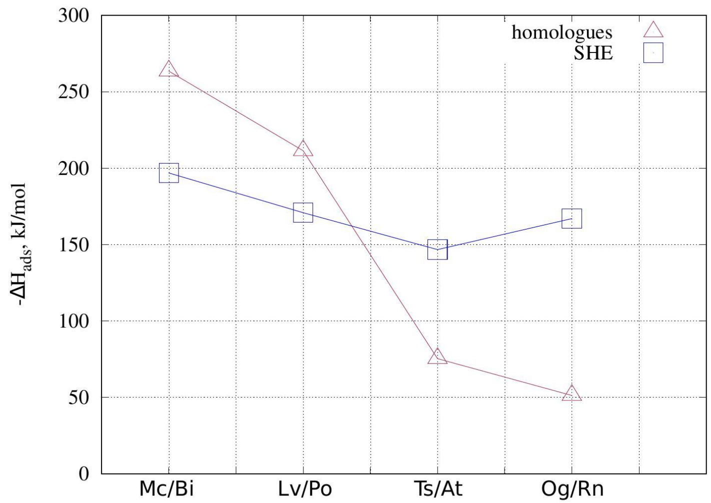
Group 18:

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

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





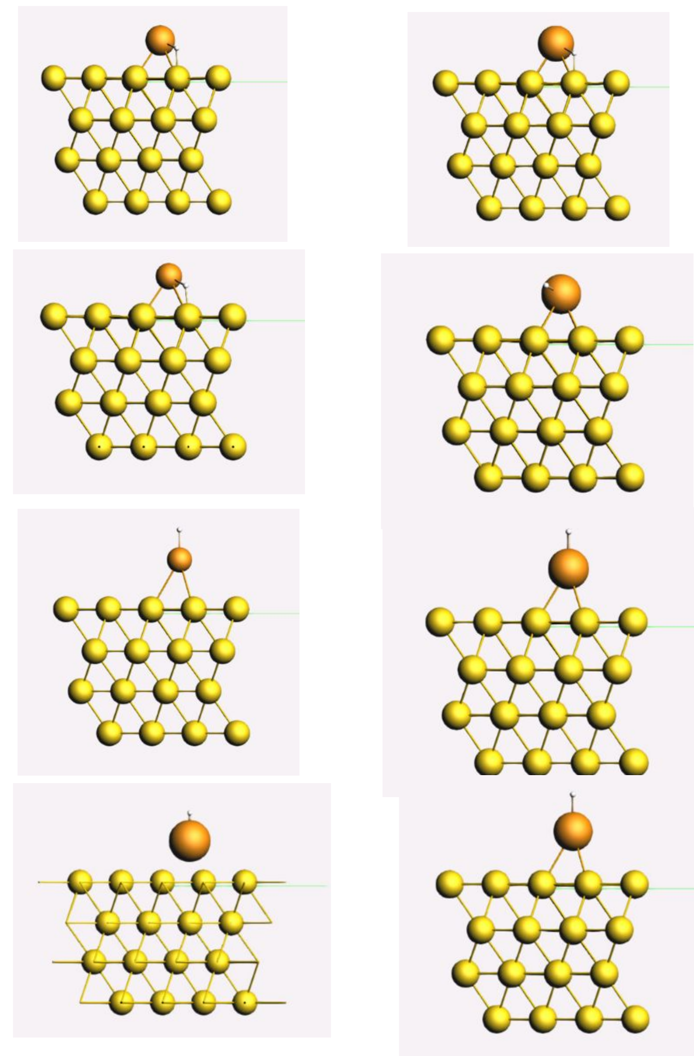


OgH should adsorb on gold much more strongly than RnH and Og: it should be possible to distinguish experimentally between Og and OgH by adsorption on gold

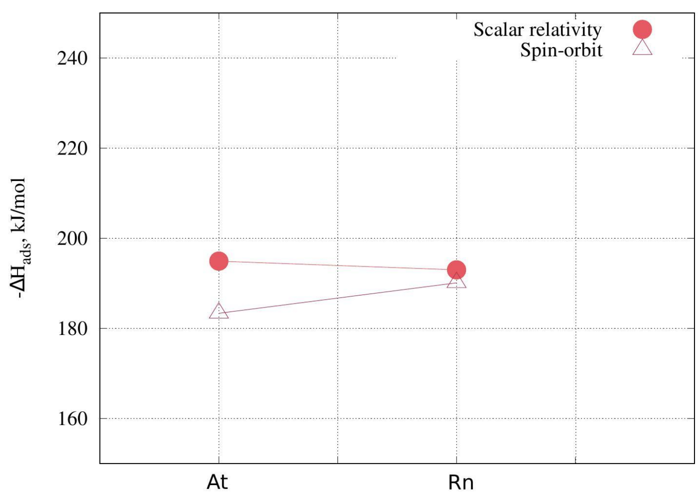
Geometrical Configurations of MH/Au(111)

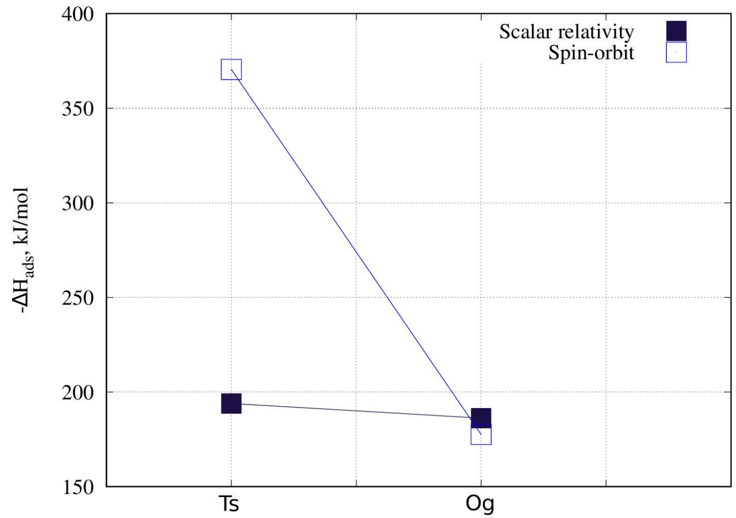
- Group 15
  - BiH and McH
- Group 16
  - PoH and LvH
- Group 17
  - AtH and TsH
- Group 18
  - RnH and OgH

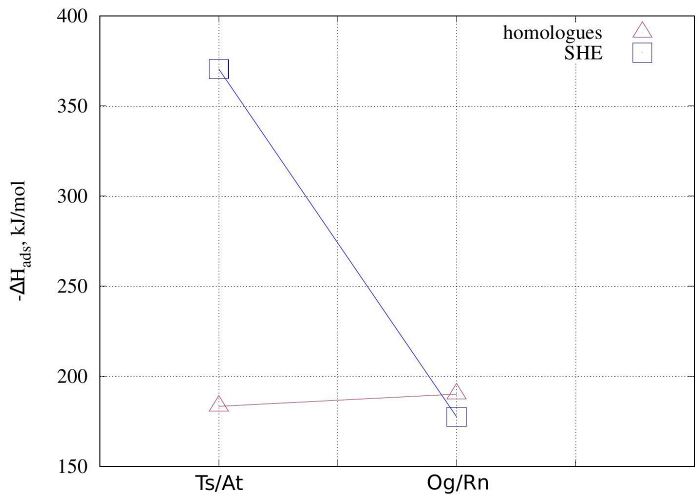
Different structures for group 15/16 and 17/18



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







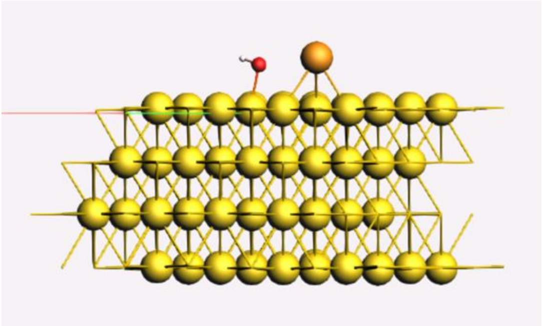
TsOH and OgOH adsorbs on gold much more strongly than TsH and OgH: E_{ads} are too big to observe distribution of events at room and lower temperatures.

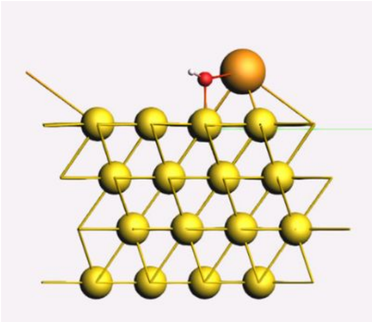
Explanation: ionic compounds interacting strongly with the surface

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

<u>Group 17</u>

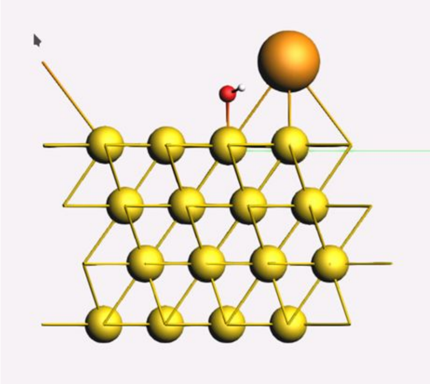
AtOH and TsOH

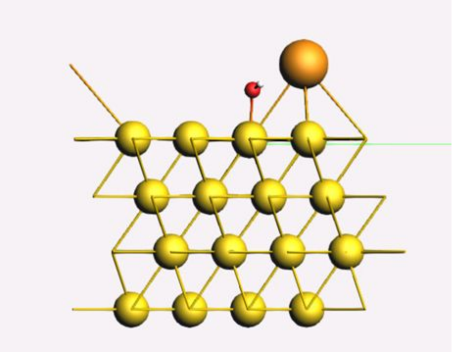




<u>Group 18</u>

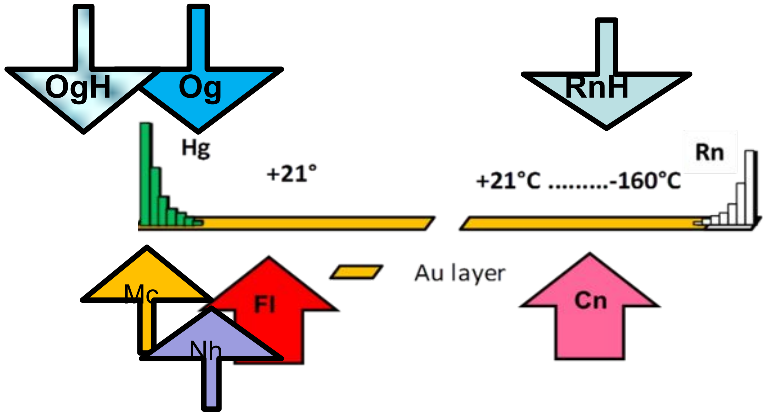
RnOH and OgOH





Conclusions for Experiments with Gold Surface of Detectors

- Distribution of events Hg/Cn, Fl and Rn/Og will be observed at room and lower temperatures in the column
- E_{ads}(Og) ≈ E_{ads}(Hg) at the beginning, while Rn at the cold end of it
- RnH will be observed at T_{ads} below zero, while OgH is much more reactive and should adsorb at the beginning of the column
- MOH (M = Ts and Og) are very reactive: ionic compounds
- For $-\Delta H_{ads}$ > 80-90 kJ/mol, much higher T_{ads} are needed to observe a distribution of events



Acknowledgment of the Laboratory of Information Technologies of JINR