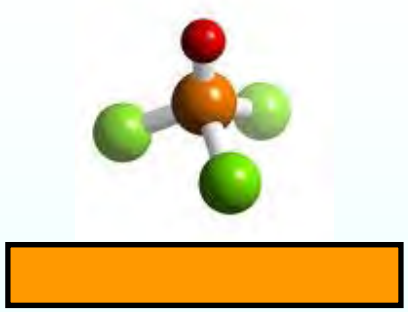
Recent achievements in theoretical studies on SHE

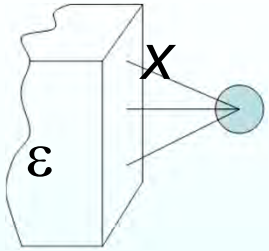
GSI, Darmstadt, Germany

V. Pershina

Calculations of Adsorption Energy on Surfaces

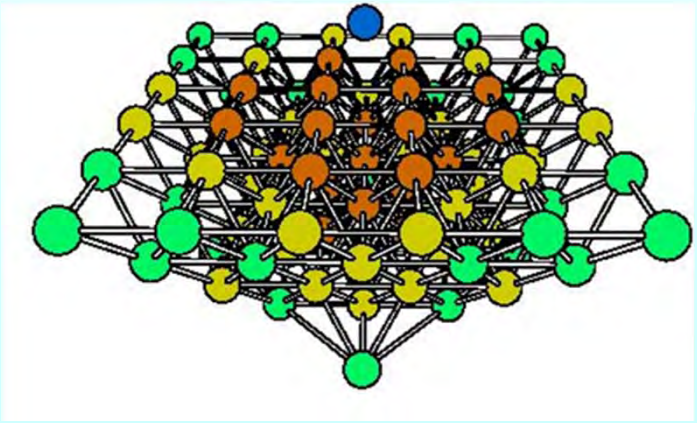
- Inert surfaces, weak interactions: adatom-slab model



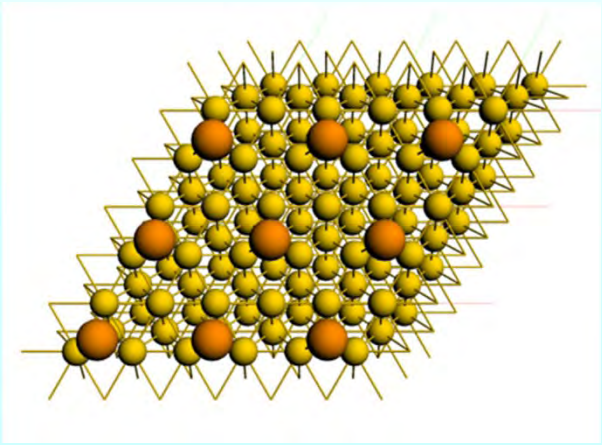


$$E(x) = -\frac{3}{16}\left(\frac{\varepsilon - 1}{\varepsilon + 2}\right)\frac{\alpha_{mol}}{\left(\frac{1}{IP_{slab}} + \frac{1}{IP_{mol}}\right)x^3}$$

- Reactive surfaces: direct calculations



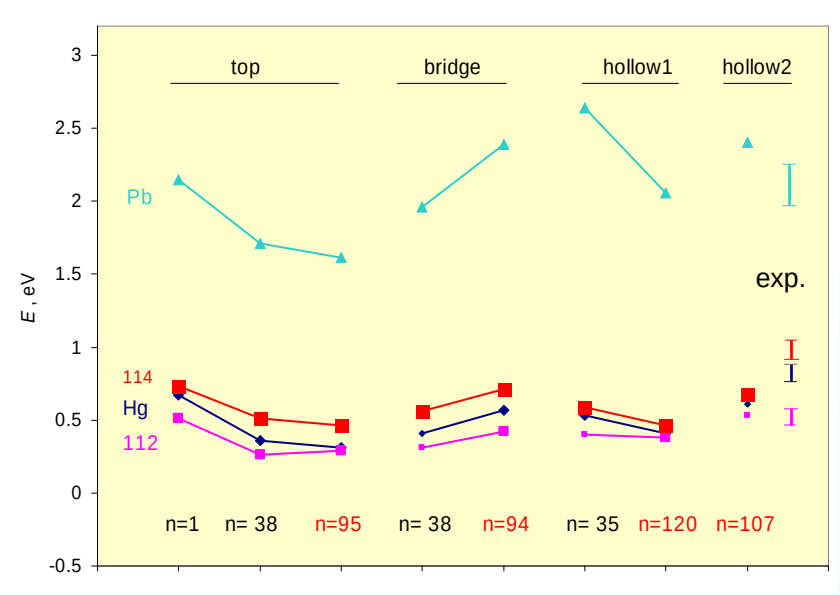
cluster model

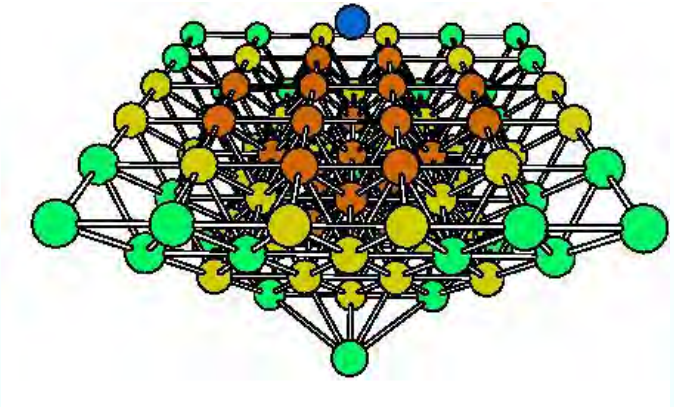


periodic codes

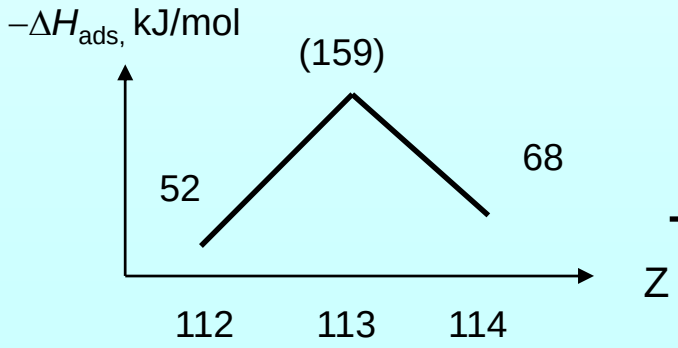
Previous Results on Adsorption of Cn, Nh and Fl on Gold

M-Au$_n$ binding energies





M	position, n	E_b, eV	ΔH_{ads}, eV	Ref. (exp.)
Hg	bridge n=94	**0.56**	**0.92**	Eichler
Cn	hollow n=107	**0.46**	**$0.54^{+0.4}_{-0.03}$**	Eichler
Pb	bridge n=94	**2.40**	**2.43**	Haennsler
114	bridge n=94	**0.71**	**$0.36^{+0.5}_{-0.1}$**	Eichler
			≥ 0.5	Yakushev
Tl	bridge n=16	**2.65**	**2.48**	Serov
113	bridge n=16	**1.34**	**(1.65)**	-



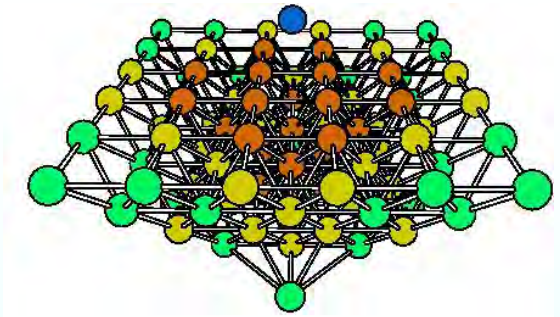
→ like HOAO

[Pershina, Anton, Jacob, JCP, 2009]

Predictions of Adsorption of Cn, Nh and Fl on Au(111) Surface

- cluster approach (4c-DFT)
  - all electron
  - B88/P86

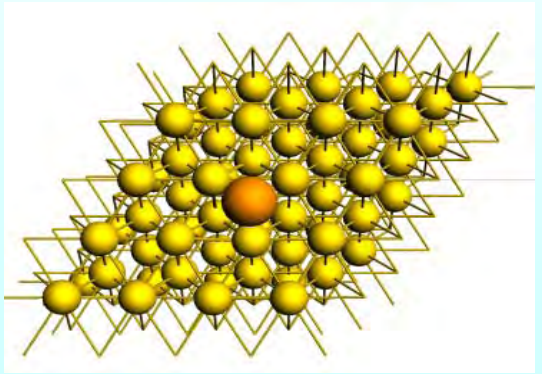
($M\text{-}Au_n$)



[Pershina, Anton, Jacob, J. Chem Phys., 2009]

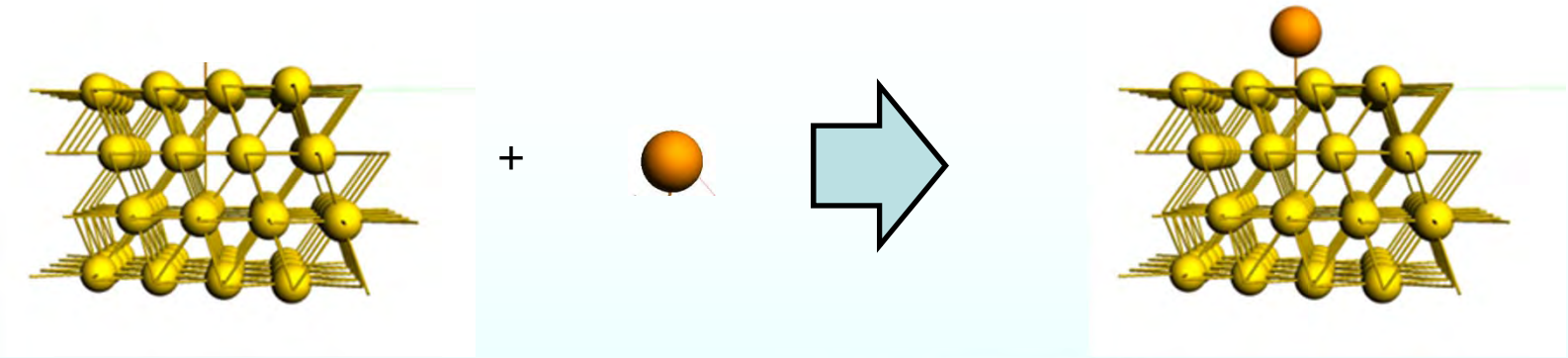
(n x n)M/(Au(111) supercell)

- ADF BAND calculations (ZORA)
  - revPBE, PW91, revPBE D3(BJ)
  - small core
  - TZ2P
  - SR, SO(atoms relaxed, full geometry optim.)
  - difference coverage: slab, (2 x 2) and (4 x 4) supercells

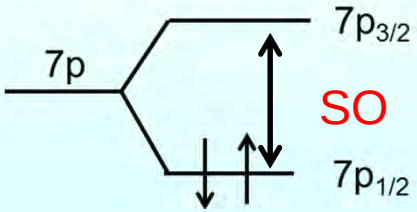


[V. Pershina, PCCP, PC A, JCP, submitted]

Adsorption of M on Gold Surface
Influence of SO Effects

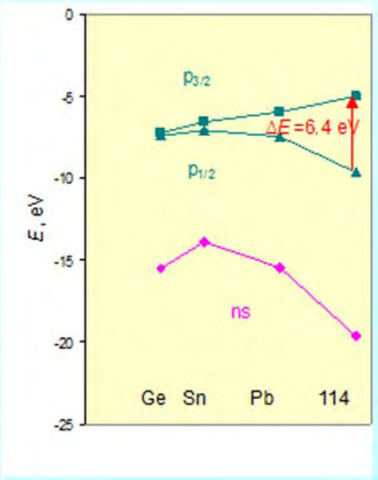


E_f(Au111-supercell) E_f (M-atom) E_f(M-Au111sc)



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

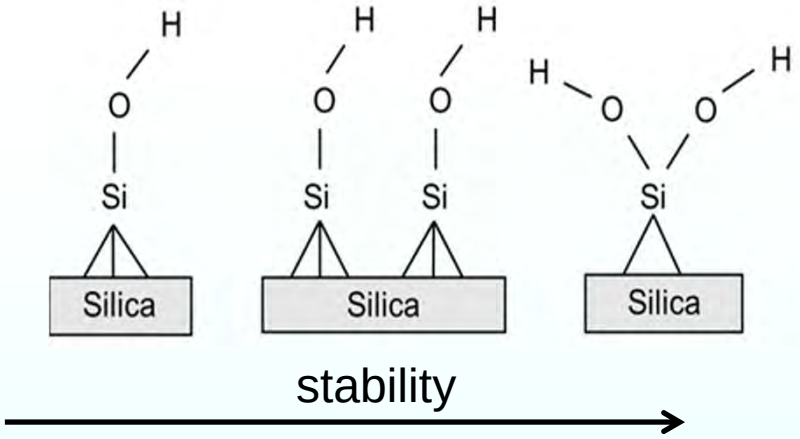
E_f(SO): Cn: 0 eV
Nh: 2.01 eV (194 kJ/mol)
Fl: 5.12 eV (494 kJ/mol)

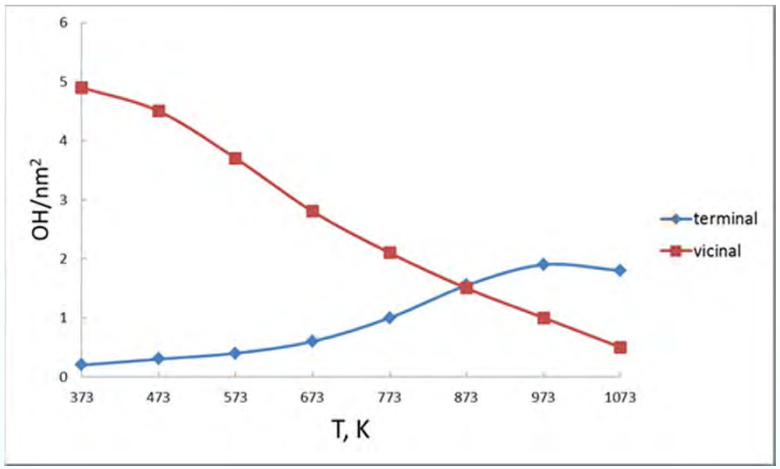


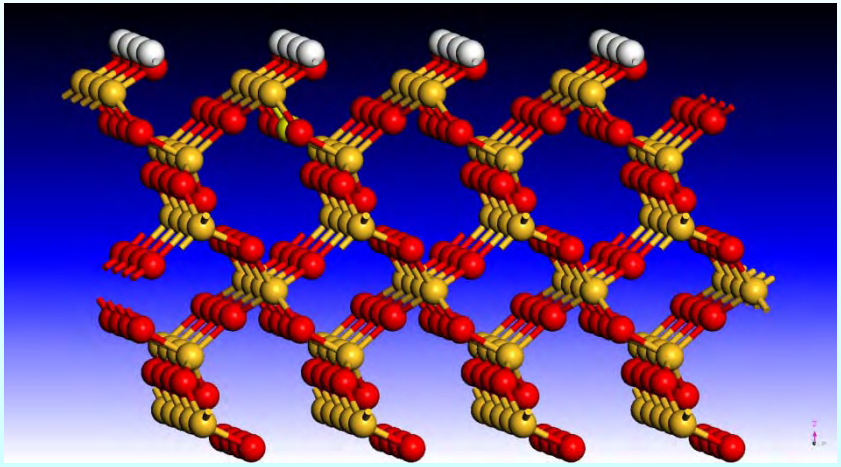
Comparison of Various Calculations of E_{ads} of Group 12-14 Elements on Gold

Method	V^{xc}	Model	Hg	Cn	Tl	Nh	Pb	Fl	Ref.
DFT-SO	PW91	Period.	41	-	-	-	-	-	Lim, 2012
	PBE	Period.	34						Steckel, 2008
4c-DFT[d]	B88/P86	M-Au_n	54	45	-	-	232	68	Pershina, 2009
2c-DFT[e]	B3LYP	M-Au_n	-	-	256	129	-	-	Fox-Beyer, 2012
RECP/DFT	B88/P86	M-Au_n	-	-		116	-	47	Rusakov, 2013
RECP/DFT[h]	B88/PW91	M-Au_n	31	23	-	-	-	-	Rykova, 2006
Exp.		$-\Delta H_{ads}$	> 65	52^{+4}_{-3}	240	-	234	34^{+54}_{-11}	Eichler, 2009
			98±3					≥ 48	Yakushev, 2014

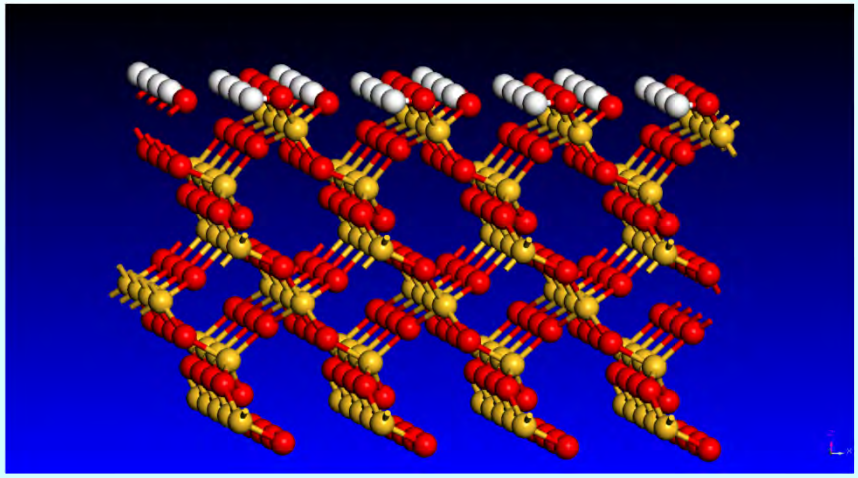
Hydroxylated Quartz (Silanols)





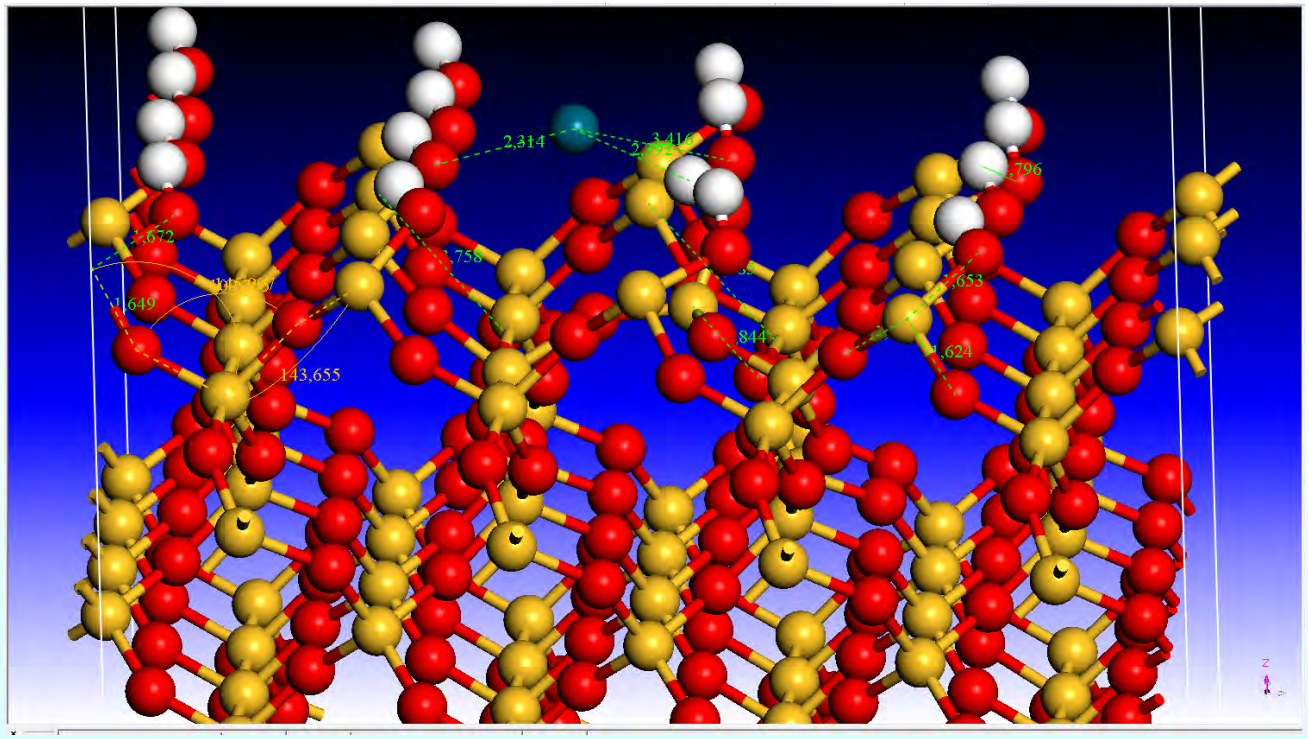


25 °C: vicinal (80%)



geminal (10%)

Adsorption of M on Vicinal Silanols

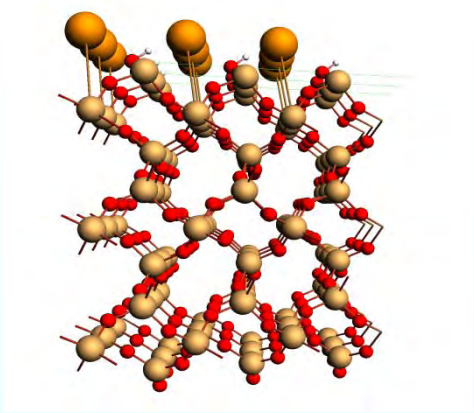


ADF BAND (SHE) + CASTEP calculations
preferential position: hollow

V. Pershina, PCCP (2017), JPC A (2017)

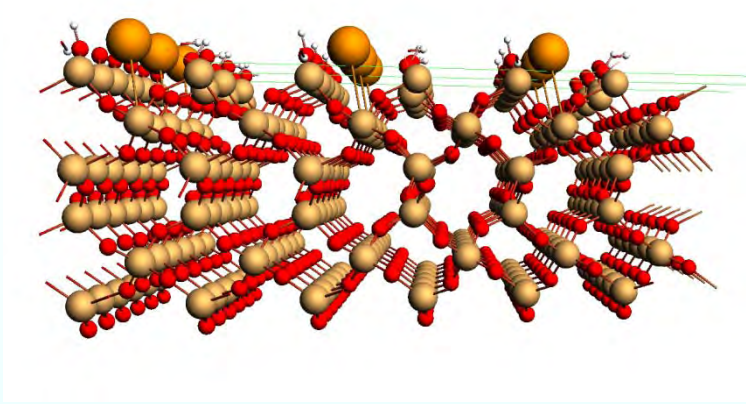
Influence of Coverage on E_{ads} of Pb (revPBE)

full



1.28 eV (d=1.48 Å)

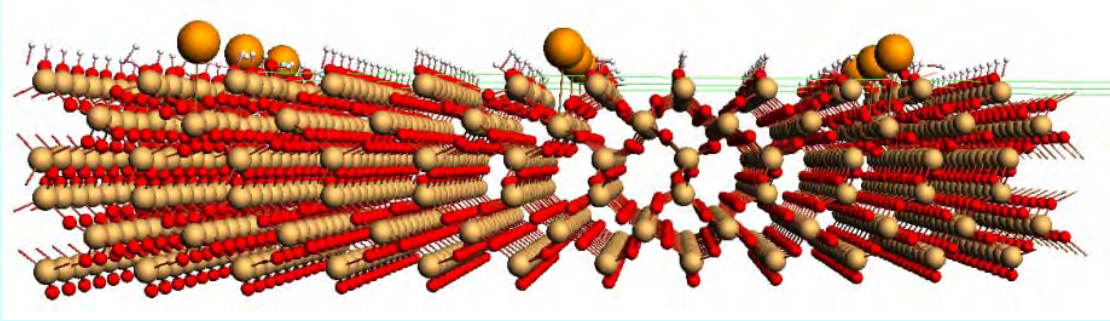
(2 x 2)



2.31 eV (d=1.07 Å)

Exp:
2.12 eV

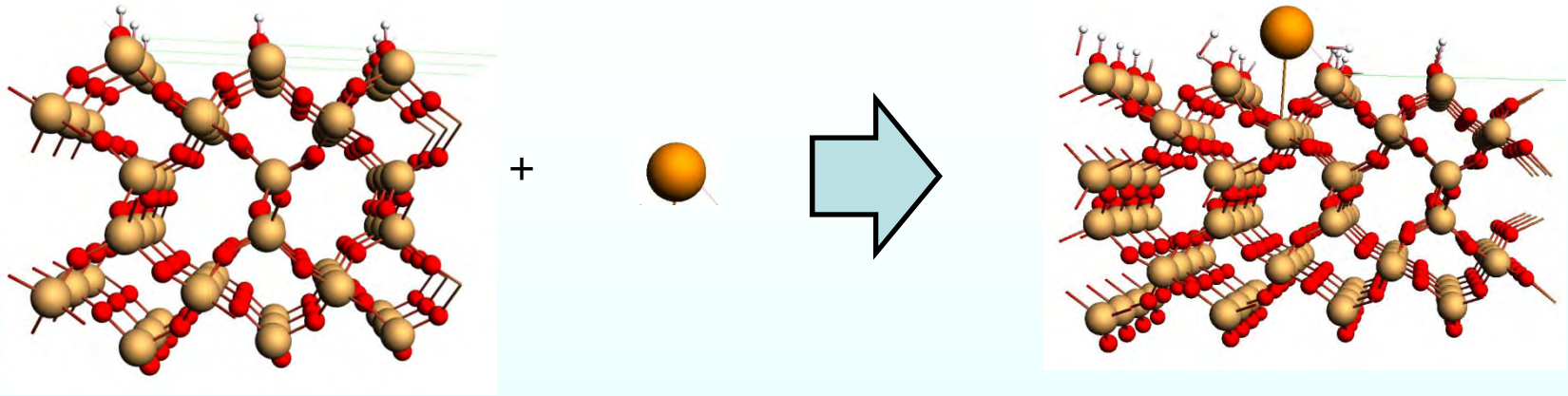
(4 x 4)



1.58 eV (*d*=1.16 Å)

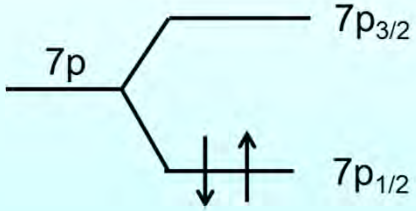
Exp:
1.66±0.1 eV

Adsorption of Pb/Fl on Hydroxylated Quartz: Influence of SO Effects



E_f(SO): 2107.4

Pb: -1.87
Fl: -5.08



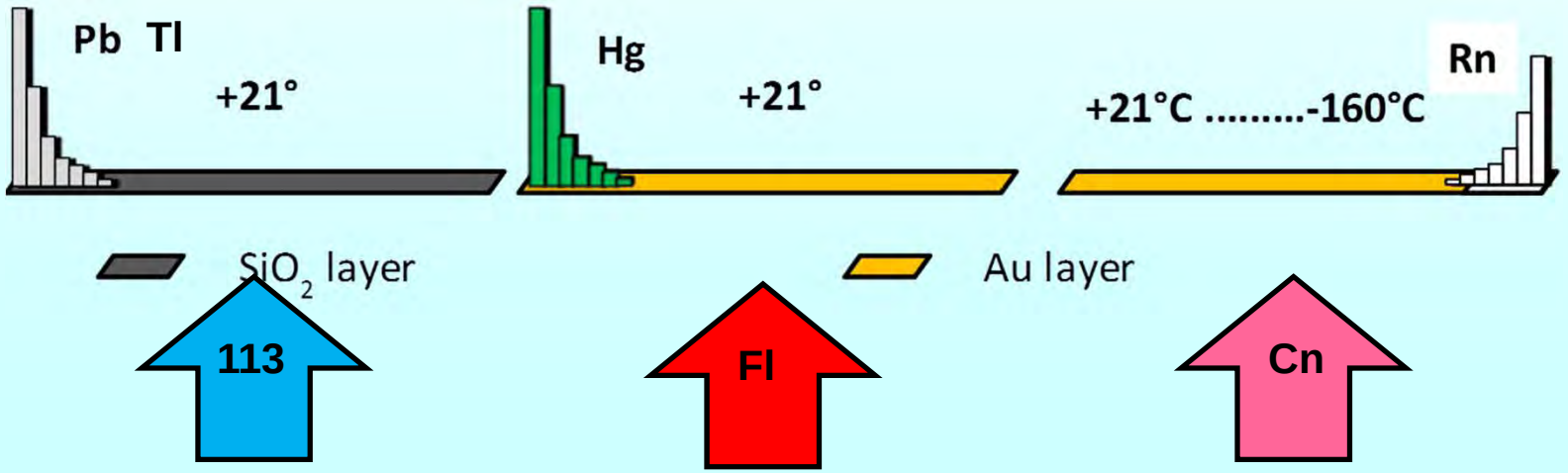
Pb: -2110.0
Fl: -2112.3

$-\Delta H_{ads}$(Pb) = 3.79 eV (SR) = 1.57 eV (SO) (exp. 1.66 eV)

$-\Delta H_{ads}$(Fl) = 3.86 eV (SR) = -0.23 eV (SO)

Adsorption of Group 12, 13 and 14 Elements on Quartz and Gold ($-\Delta H_{ads}$, kJ/mol)

Surf.	Hg	Cn	Tl	Nh	Pb	Fl	Method
SiO_2	54	-38(26)	150	58	152	-22 (21)	BAND (revPBE)
	42 ± 2	-	158 ± 3	-	165 ± 4	-	Exp.
Au	54	45	-	-	232	68	4c-DFT
	98 ± 3	52^{+4}_{-3}	240 ± 5	-	234	34^{+54}_{-11} ≥ 48	Exp.



Thank you for your attention!