Theoretical Studies of Adsorption Properties of Group 15, 16 and 17 Elements, Bi/Mc, Po/Lv and At/Ts, on Surfaces of Gold and Quartz

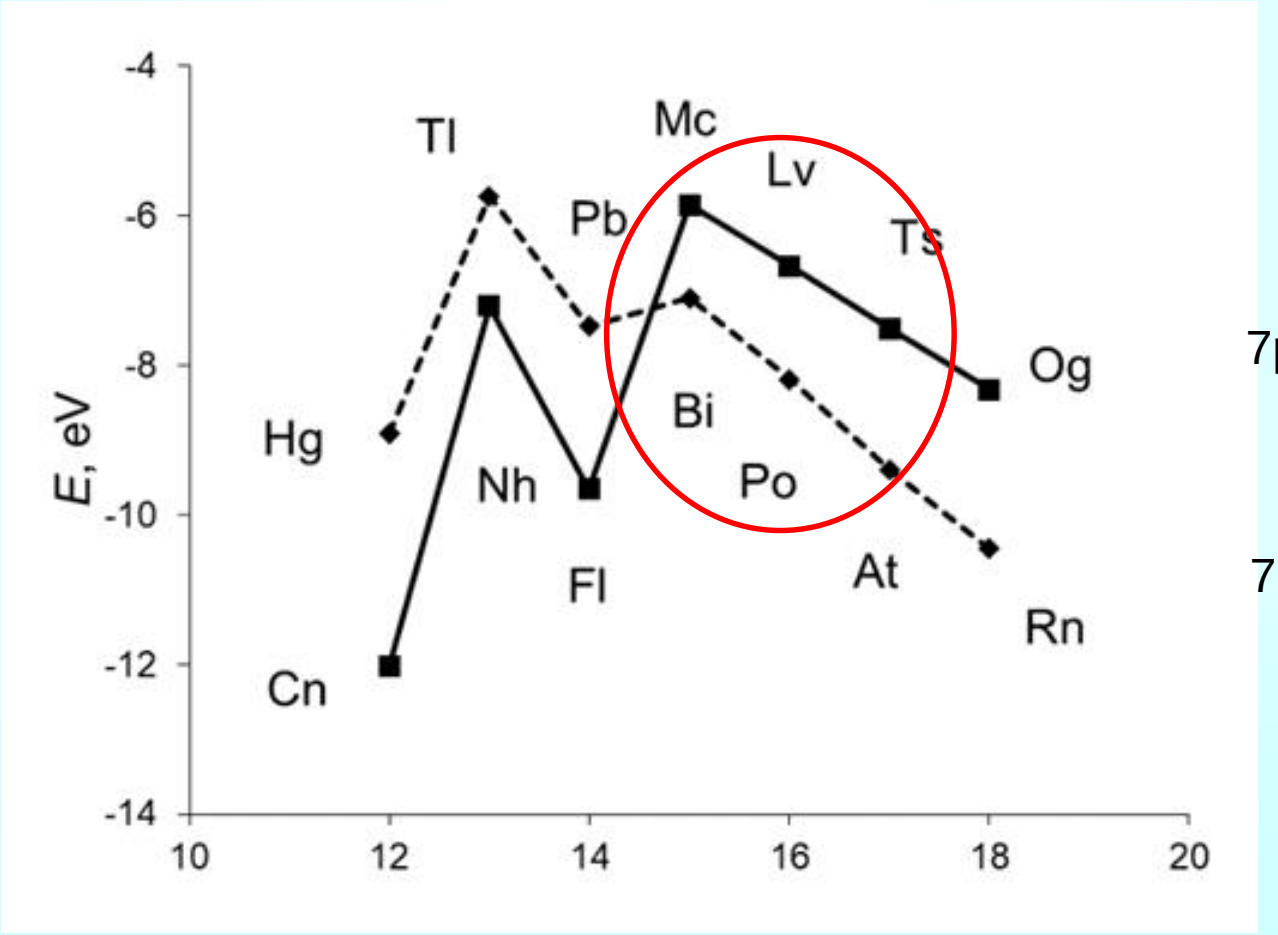
V. Pershina

GSI, Darmstadt, Germany

M. Iliaš

HIM, Universität Mainz, Germany

Valence AO Orbitals



Theoretical Studies of Properties and Volatility of SHEs

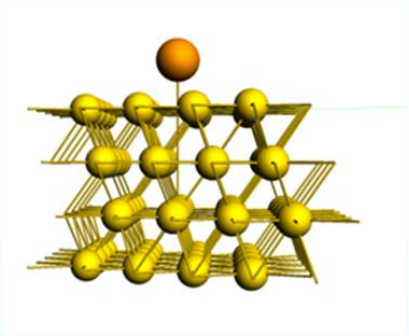
- Formation of MO, MO_2 and M(OH), etc. in the atmosphere of O_2, H_2O and H_2
  - reaction energies
  - properties of atoms/molecules (geom., IP, α, μ)
- Predictions of adsorption properties of M, MO, M(OH) on surfaces of quartz and gold
  - structures
  - adsorption energies
  - analysis of bonding

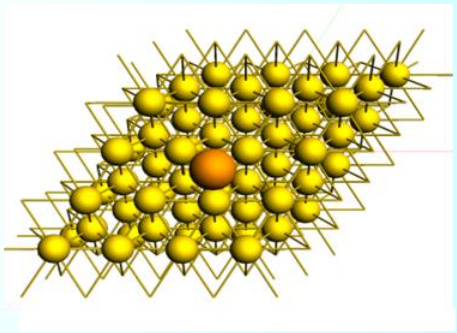
Methods and Softwares – Molecular Codes

- Molecular
  - ADF (SCM)
    - 2c-DFT; SR and SO relativity; all-electron; various E^{xc}; STO basis sets for SHEs
    - energy, properties, fast geometry optimization
    - *commercial & host-locked*
  - DIRAC
    - 2c/4c-DFT + CC – *ab-initio*; all electron, Gaussian orbitals; poor geometry optimization, *free-of-charge*
- Solid state - periodic
  - SCM BAND
    - 2c-SR and SO relativity, all electron, fast geometry optimization, full relaxation, dispersion-corrected Exc , - *commercial & host-locked*

Modeling of Gold and Quartz Surfaces

- Au(111)

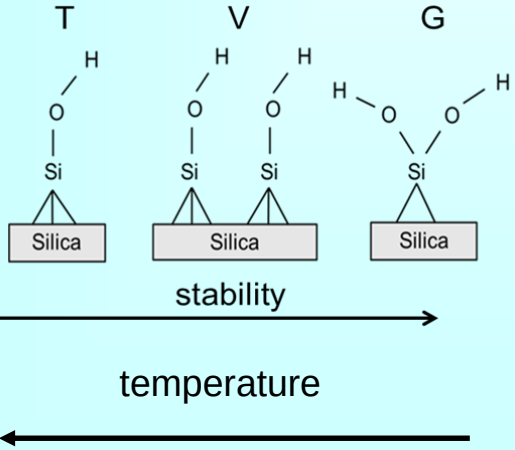


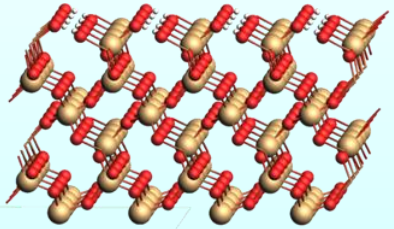


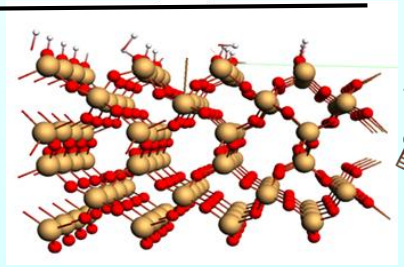
room T

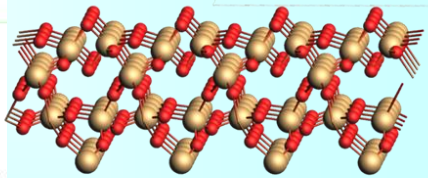
T = 127 C

- Quartz







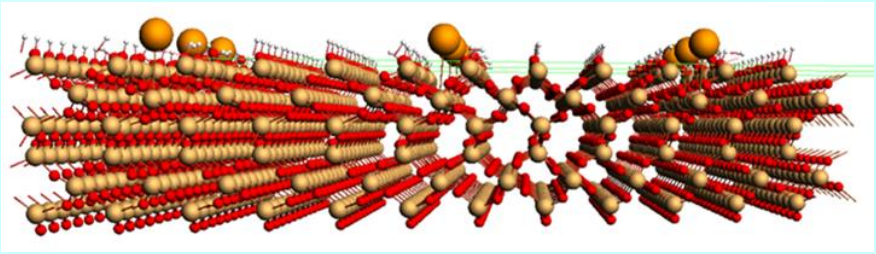


geminal

vicinal (80%)

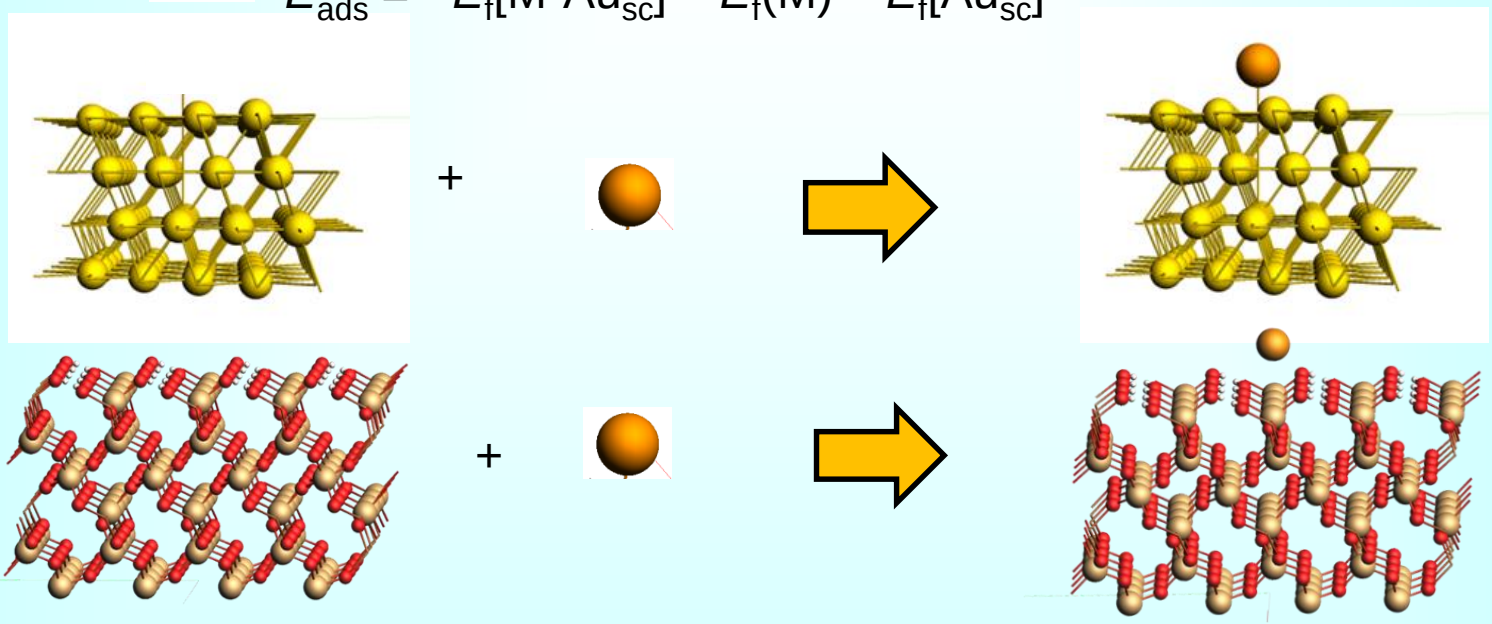
bridged

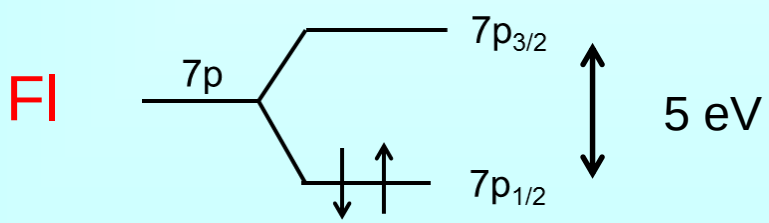
(4 x 4)
supercell

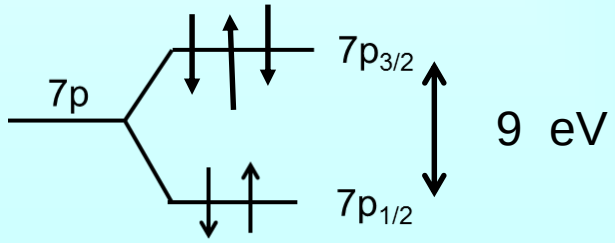


Calculations of E_{ads} (in eV) of M on Au(111) and Quartz Surfaces

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



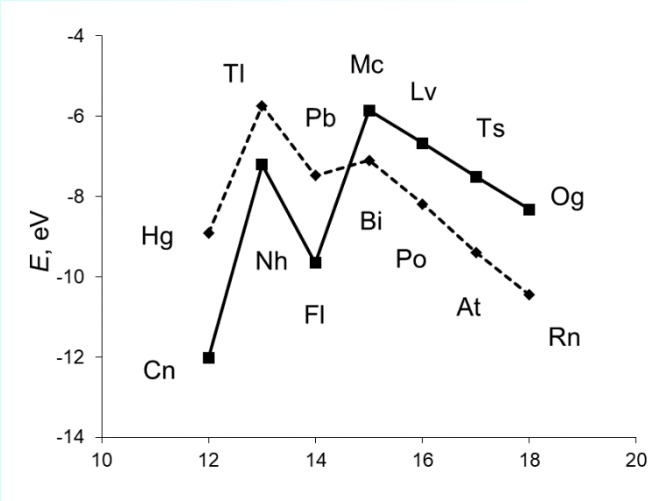




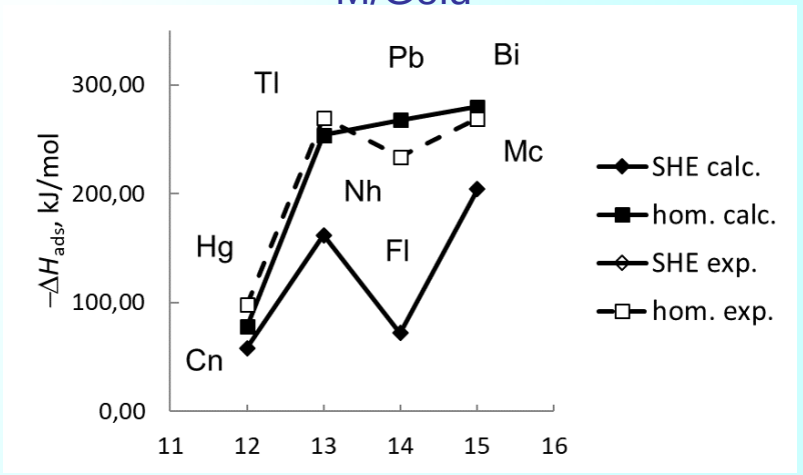
	Fl	Ts
SR	3.68	2.39
SO	0.90	2.10

Calculations of E_{ads} of Group 12-15 Elements on Gold and Quartz

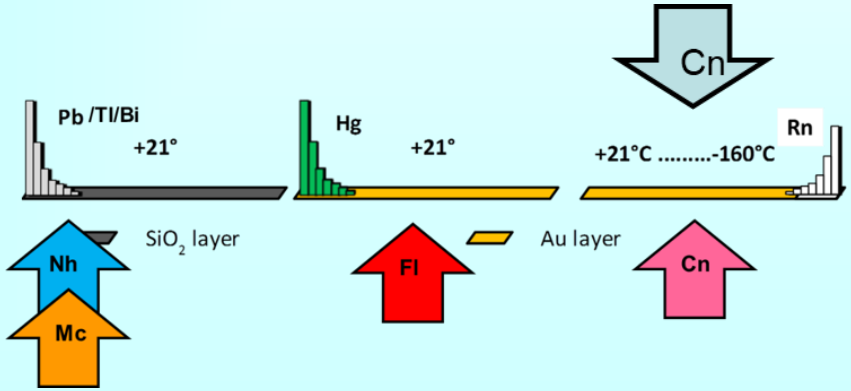
AOs



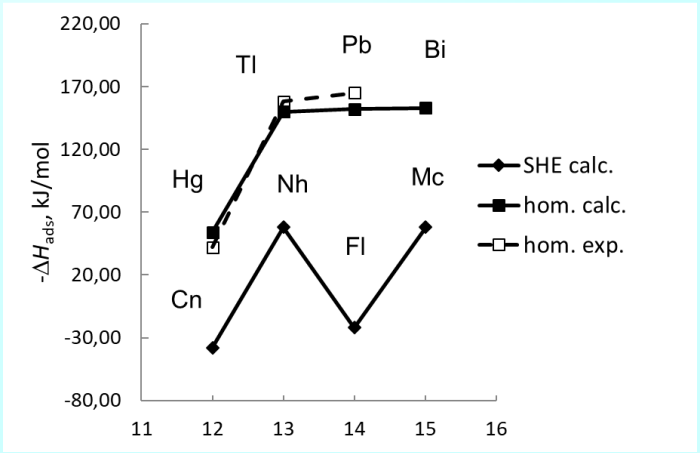
M/Gold



(revPBE-D3BJ)



M/Quartz



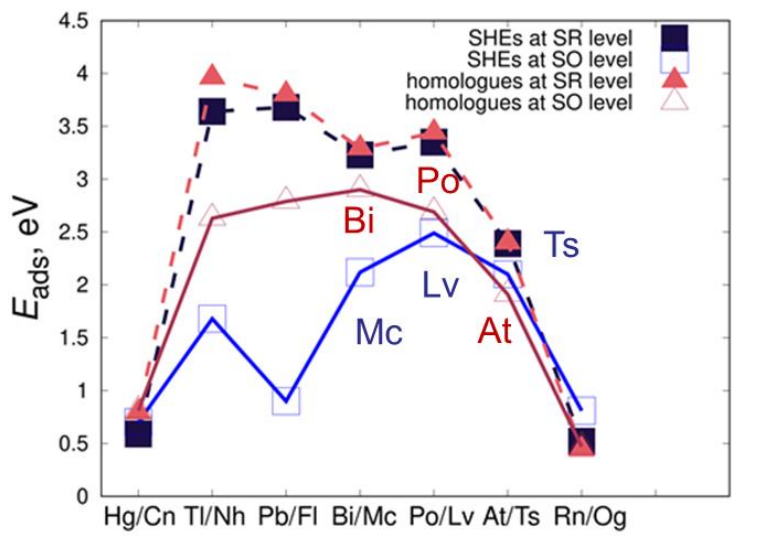
$-\Delta H_{ads}(Nh) = -\Delta H_{ads}(Mc) = 58$ kJ/mol

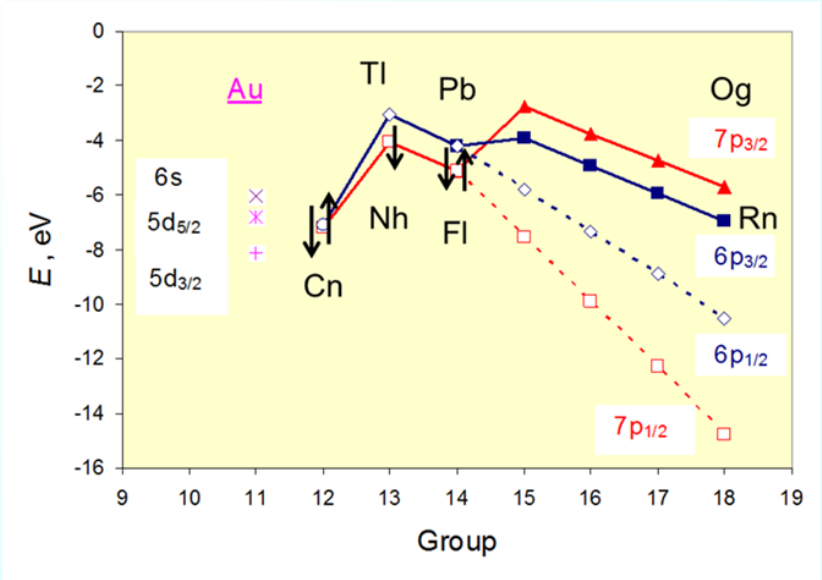
V. Pershina, M. Ilias, A. Yakushev, *Inorg. Chem*. **60**, 9796 (2021)

Experiment; A. Yakushev, et al. *Frontiers*, 2024

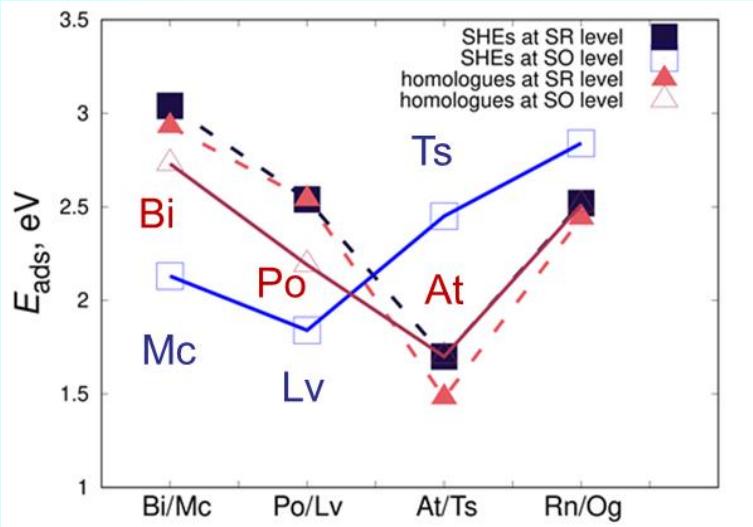
Adsorption of SHEs on Au(111) Surface

M





MH



E_{ads}, eV

Bi	2.90	>	Mc	2.12
Po	2.69	>	Lv	2.49
At	1.91	<	Ts	2.10
BiH	2.73	>	McH	2.13
PoH	2.19	>	LvH	1.84
AtH	1.70	<	TsH	2.45
AtOH	1.92	<	TsOH	2.00

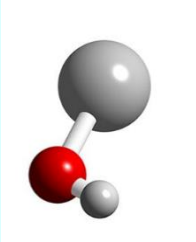
[A. Rhyzhkov, V. Pershina, M. Ilias, *et al*. PCCP 2023]

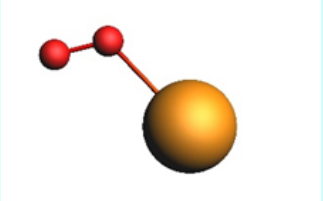
Adsorption of Po Species on Quartz

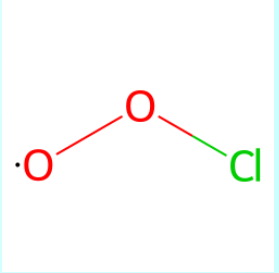
Species	Po		
	Experiment		
	Quartz	Conditions	Ref.
M	85 ± 3	$Ar/H_e/N_2$	Gärtner 2001
	85	He	Vogt 1996
	85 ± 9	H_2	B. Eichler 1976
	125 - 133 ± 5	H_2	Maugeri 2014
	133 ± 5	H_2	Maugeri 2014
	124 - 137 ± 5	He	Mauger 2014i
MO	236	O_2	Maugeri 2014
MO_2	123	He	Gäggeler 1985
	215 ± 5	O_2	Maugeri 2014

Reaction Energies (in eV) for Group 17 Elements with O_2 and H_2O (n/o)

At		Ts	
Reaction	Energy	Reaction	Energy
At + O = AtO (known for Br)	**-2.679**	**Ts + O = TsO**	**-2.748**
At + 1/2 O_2 = AtO	0.289	Ts + 1/2 O_2 = TsO	0.345
At + O_2 = AtOO (R)	**-0.139**	**Ts + O_2 = TsOO (R)**	**-0.302**
At + O_2 = OAtO	0.671	Ts + O_2 = OTsO	0.853
At + OH = AtOH	**-2.115**	**Ts + OH = TsOH**	**-2.272**
AtO + H_2O = AtOH + OH	1.204	TsO + H_2O = TsOH + OH	1.117







At and Ts should not react with O_2 and H_2O forming MO and MO_2 at normal conditions. MOO is a radical.

Ref.

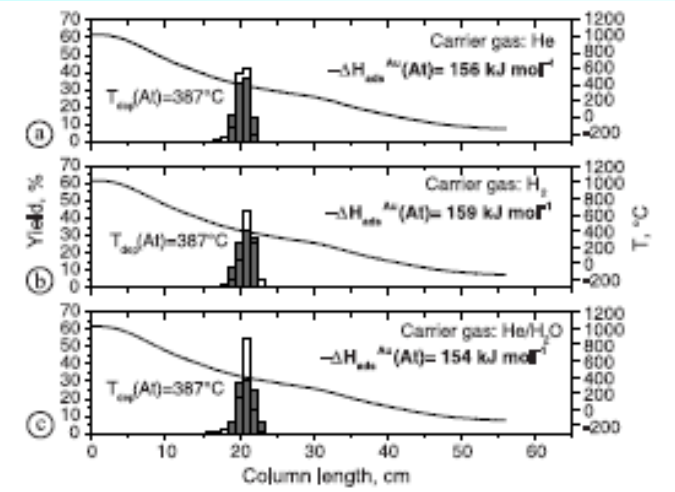
Reaction Energies (in eV) for Group 17 Elements with H_2

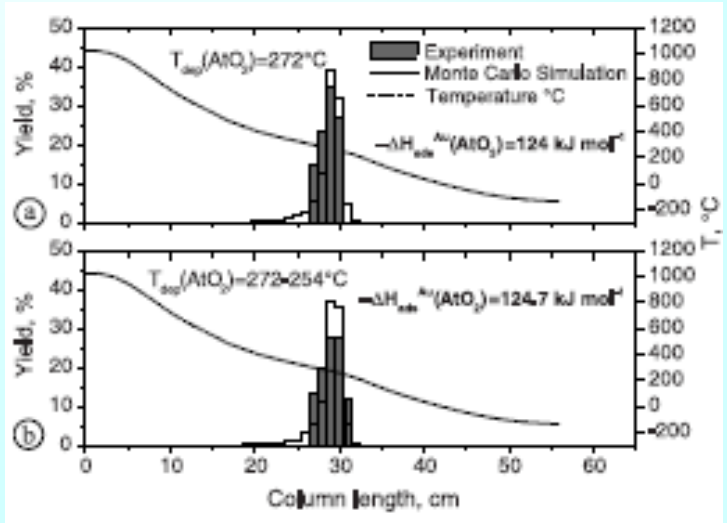
At		Ts	
Reaction	Energy	Reaction	Energy
At + H = AtH	**-2.58**	**Ts + H = TsH**	**-1.99**
At + 1/2H_2 = AtH	**-0.178**	Ts + 1/2H_2 = TsH	0.353
AtO + H_2 = At + H_2O	-2.760	TsO + H_2 = Ts + H2O	-2.691
AtOO + H_2 = AtO + H_2O	**-2.042**	**TsOO + H_2 = TsO + H2O**	**-1.949**
AtOO + H_2 = AtOH + OH(.)	-0.838	TsOO + H_2 = TsOH + OH(.)	-0.832
OAtO + H_2 = AtO + H2O	-2.853	OTsO + H_2 = TsO + H2O	-2.834

Formation of MH, MOH and MO is possible

E_{ads} (in kJ/mol) of At, AtH and AtOH on Gold

	At		AtH		AtOH		AtO_2 (?)	
	Theory	Exp.	Theory	Exp.	Theory	Exp.	Theory	Exp.
Au(111)	184	156 (He) 159 (H_2) 154 (He/H_2O)	164	-	185	-	No reaction with O_2 and H_2O	124 (O_2) 125 (O_2/H_2O)





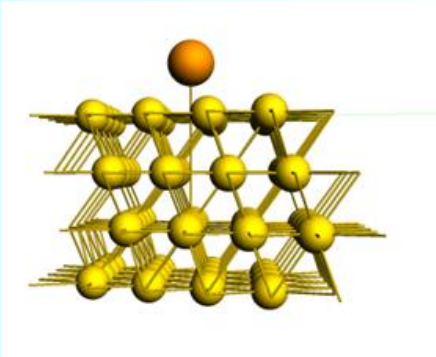
Theory: AtH < At = AtOH

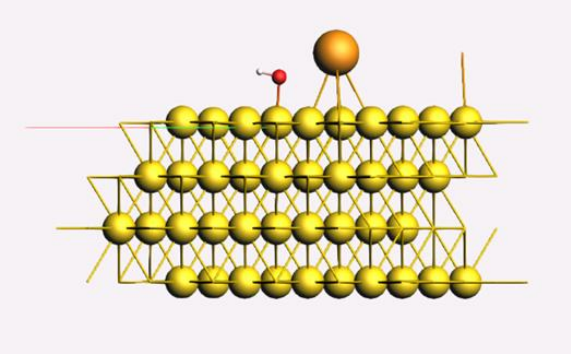
[A. Rhyzhkov, V. Pershina, M. Ilias, *et al*. PCCP 2023]

Exper.: AtO_2 (?) < At

[A. Serov *et al*. RA **99**, 593 (2011)]

E_{ads} (in kJ/mol) of At on Gold





	At		AtH		AtOH		AtO_2 (?)	
	Theory	Exp.	Theory	Exp.	Theory	Exp.	Theory	Exp.
Au(111)	184	156 (He) 159 (H_2) 154 (He/H_2O)	164	-	185	-	No reaction with O_2 and H_2O	124 (O_2) 125 (O_2/H_2O)

Theory: AtH < At = AtOH

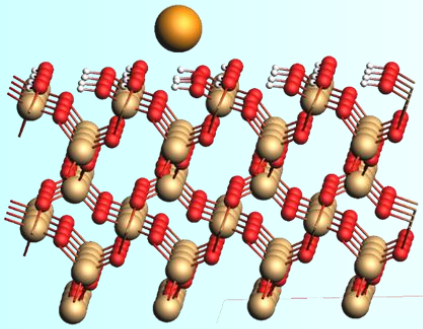
[A. Rhyzhkov, V. Pershina, M. Ilias, *et al*. PCCP 2023]

Exper.: AtO_2 (?) < At

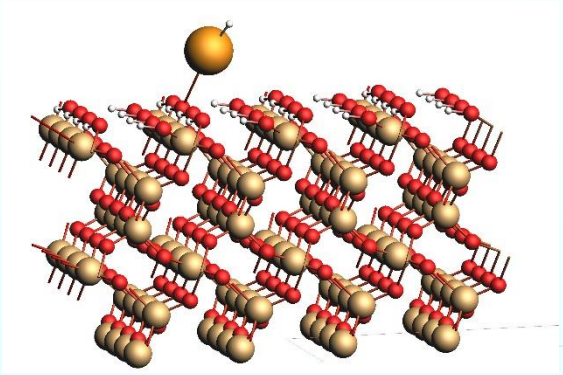
[A. Serov *et al*. RA **99**, 593 (2011)]

E_{ads} (in kJ/mol) of M, MH and MOH (M = At and Ts) on Quartz

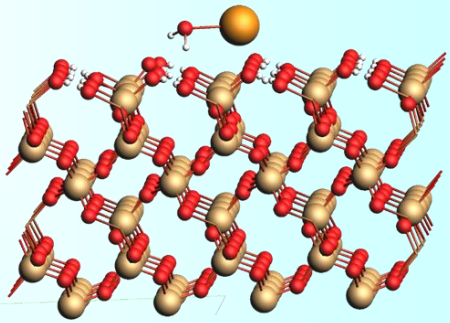
M



MH



MOH

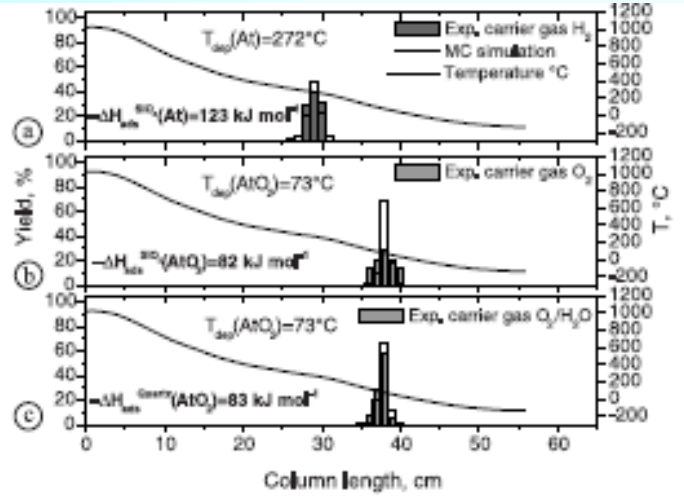


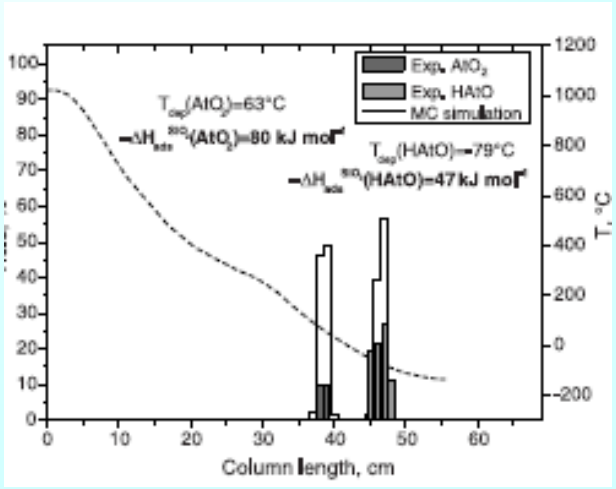
	App.	At	AtH	AtOH
Q(G)	SR	26.1	31.5	38.5
	SO	26.3	31.0	35.5
Q(V)	SR	19.6	40.4	45.0
	SO	19.6	40.3	41.0

At << AtH < AtOH

E_{ads} of At, AtH and AtOH on Quartz

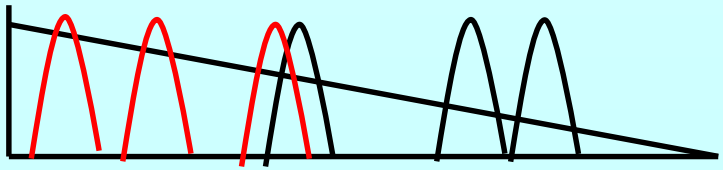
	At		AtH		AtOH		AtO_2 (?)	
	Theory	Exp.	Theory	Exp.	Theory	Exp.	Theory	Exp.
Quartz	20-26	123 (H_2)	27-31	-	35-41	47 (He/H_2O)	No reaction with O_2 and H_2O	82 (O_2) 83 (O_2/H_2O) 80 (He/H_2O)





At AtO_2 AtOH AtOH AtH At

1000 C



Theory: At < AtH < AtOH (At < AtO_2)

Exper.: AtOH << AtO_2 (?) < At

At and Ts on Quartz

MOLECULAR PHYSICS e2363408
https://doi.org/10.1080/00268976.2024.2363408

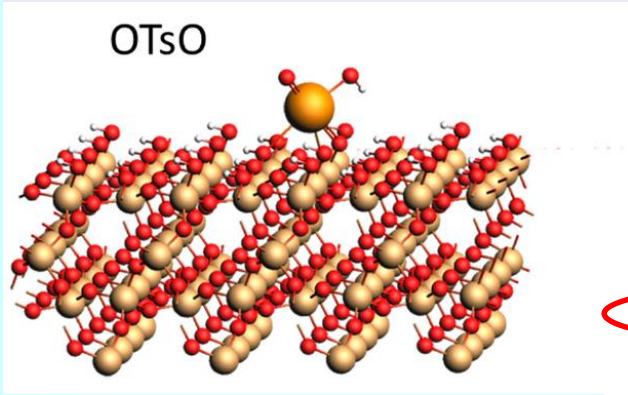
Taylor & Francis
Taylor & Francis Group

RESEARCH ARTICLE

Check for updates

Theoretical predictions of properties and adsorption behaviour of a superheavy element Ts and its lighter homolog At, and of their various gas-phase compounds, on hydroxylated quartz surfaces from periodic DFT calculations

Miroslav Iliaš [a,b] and Valeria Pershina [b]



At < Ts

Table 9. Summary of the calculated adsorption energies of the At and Ts species on the Q(G) and Q(V) surfaces in comparison with experimental $-\Delta H_{ads}$ (in kJ/mol). (The radicals are marked with a star).

Adsorbed species	At				Ts	
	Theory		Experiment		Theory	
	Q(G)	Q(V)	Quartz	Conditions	Q(G)	Q(V)
M	26	20	123 ± 10^{a}	H_2	23	20
MH	31	41			32	48
MOH	36	42	47 ± 5^{a}	He/H_2O	29	47
			$< 65^{b}$	He/Ar		
MO*	39	77			105	125
MOO*	34	34	$80 \pm 5^{a,c}$	$He/O_2/H_2O$	35	49
OMO*	76	98	$80 \pm 5^{a,c}$	$He/O_2/H_2O$	135	158
OMOH	43	99			96	109
MO(OH)	59	83			52	69

Experiment: [a] A. Serov, RA (2011) ; [b] N. Chiera, Mol. Phys. (2023).

E_{ads} (in kJ/mol) of Ts vs At on Gold and Quartz

- Gold

At < Ts	AtH < TsH	AtOH < TsOH
(184 < 203)	(164 < 239)	(185 < 193)

Ts is more reactive

- Quartz

At ≈ Ts	AtH ≈ TsH	AtOH ≈ TsOH
(24 ≈ 23)	(27-31 ≈ 19-32)	47 ≈ 47-50

Preliminary: Ts is about similarly reactive as At.
Adsorption of MO_2 or MO(OH) can also be considered.

Further Theory Tasks

- Temperature dependent thermodyn. properties
- Reconstracted surfaces, e.g. fused silica (Car Parinello method)
- MD process
- Other types of hydroxylated quartz surfaces
- Reactions on the surface
- New surfaces (silicon nitride, Se)
- Kinetics of reactions
- General: „bulk“ Og (not solid).

Acknowlegements

Thanks to

- Katharina Hermaínski, Uni Mainz
- Sasha Yakushev, GSI Darmstadt
- Dominik Dietzel, Uni Mainz

and to you for attention!