Molecular properties of monoxides, hydrides, and oxyhydrides of superheavy elements

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Calculations are carried out at LIT JINR

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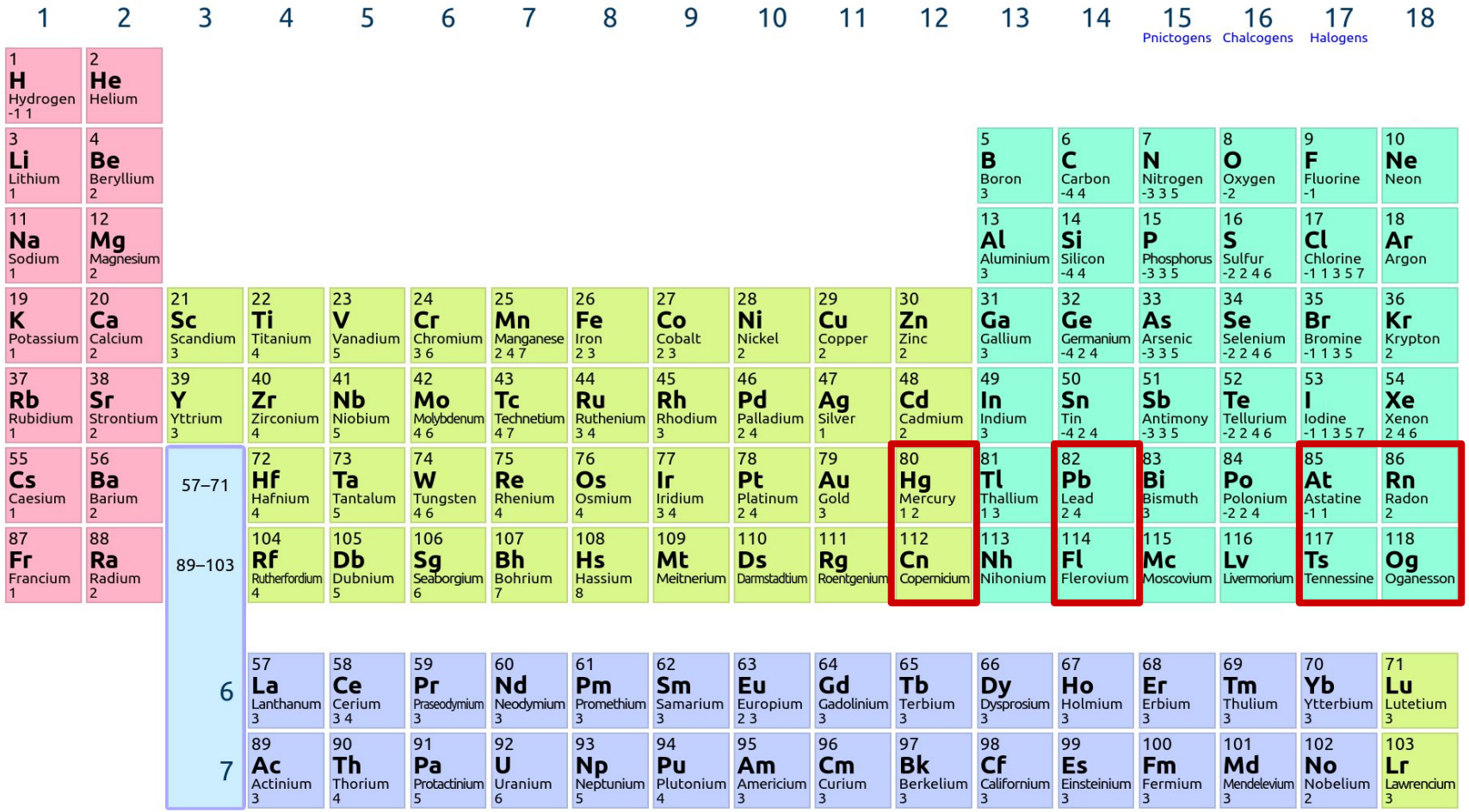
Introduction



Chemical properties

- Formation energies of MO, MO_2, M(OH)
- Molecular properties of MO, MH, MOH:
  - geometry, R
  - Ionization potential, IP
  - dipole moment, μ
  - polarizability, α
  - dissociation energy
- Adsorption properties of MO, MH, MOH:
  - Teflon
  - Quartz
  - Gold
- DFT: ADF BAND
- $E_{ads}(\mu, \alpha, IP_{mol}, IP_{surf}, \varepsilon, x)$

Formation of HgO, CnO и FlO

- Hg
  - $Hg + O_2 = HgO + O \Rightarrow E = 5.322$ eV
  - $Hg + O_2 = HgOO \Rightarrow E = 0.014$ eV
  - **$Hg + O = HgO \Rightarrow E = -0.618$ eV**
- Cn
  - $Cn + O_2 = CnOO \Rightarrow E = 0.005$ eV
  - **$Cn + O = CnO \Rightarrow E = -0.733$ eV**
- Fl
  - $Fl + O_2 = FlO + O \Rightarrow E = 3.993$ eV
  - $Fl + O_2 = FlOO \Rightarrow E = -0.044$ eV
  - $Fl + O_2 = OFlO \Rightarrow E = -0.003$ eV
  - **$Fl + O = FlO \Rightarrow E = -1.947$ eV**
  - $Fl + O_3 = FlO + O_2 \Rightarrow E = -0.348$ eV

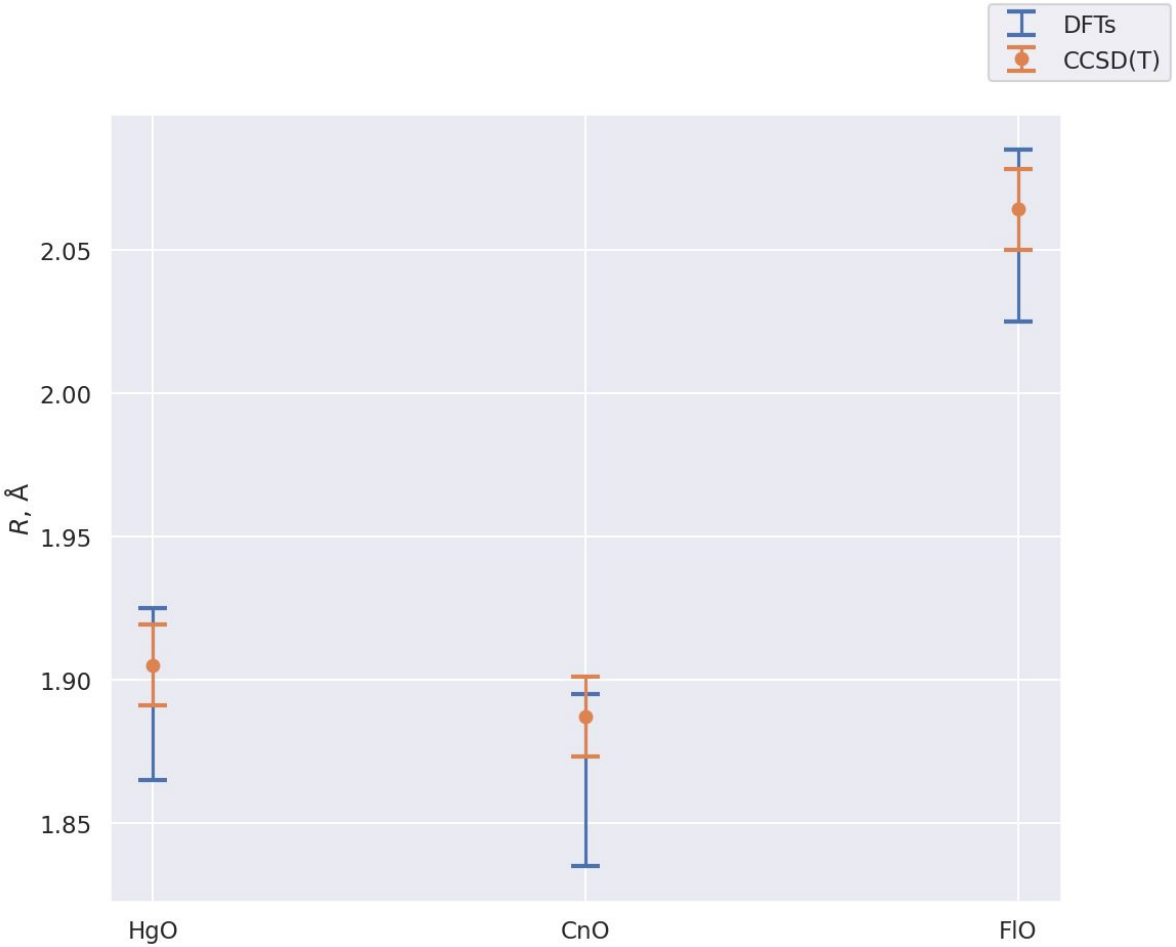
V. Pershina и M. Iliaš, TASCA 2022

Coupled-cluster approach

$$\Psi_{CC} = (1 + T_1 + \frac{1}{2}T_1^2 + T_2 + \frac{1}{3!}T_1^3 + T_1T_2 + T_3 + \ldots)\Phi$$

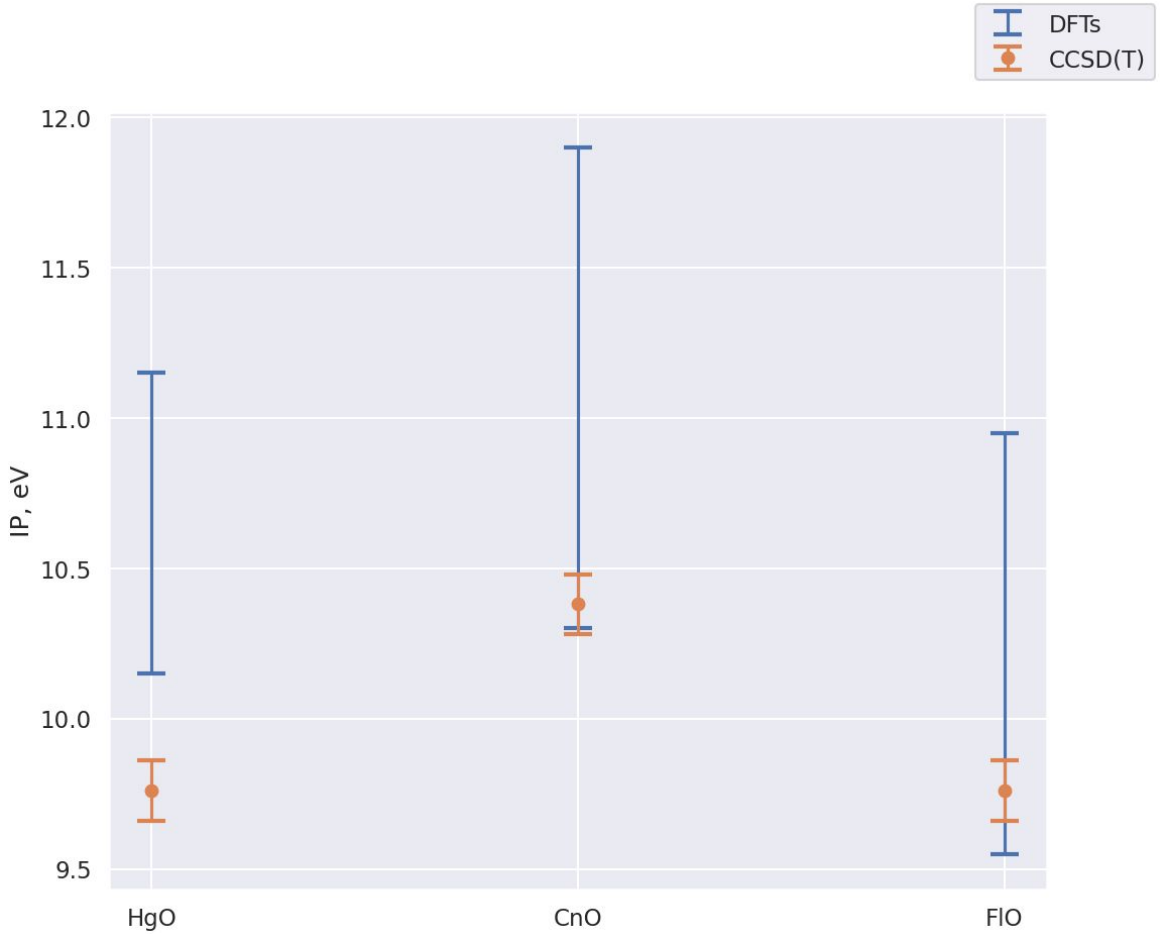
- Approximations:
  - eXact 2-Component vs. Dirac-Coulomb Hamiltonians
  - relativistic effects
- Quality of the basis functions
  - completeness
  - diffuse functions
  - higher orbital momentum
- Size of the correlation space
  - number of electrons and virtual orbitals accounted in the CC procedure
- Order of excitations
  - fully accounted Single and Double
  - Triples via perturbation theory (T)
  - and beyond: A. V. Oleynichenko, A. Zaitsevskii, E. Eliav, Towards High Performance Relativistic Electronic Structure Modelling: The EXP-T Program Package. Commun. Comp. Inf. Sci. 1331, 375-386 (2020) `github.com/aoleynichenko/EXP-T`

Geometry of FlO, CnO, and HgO



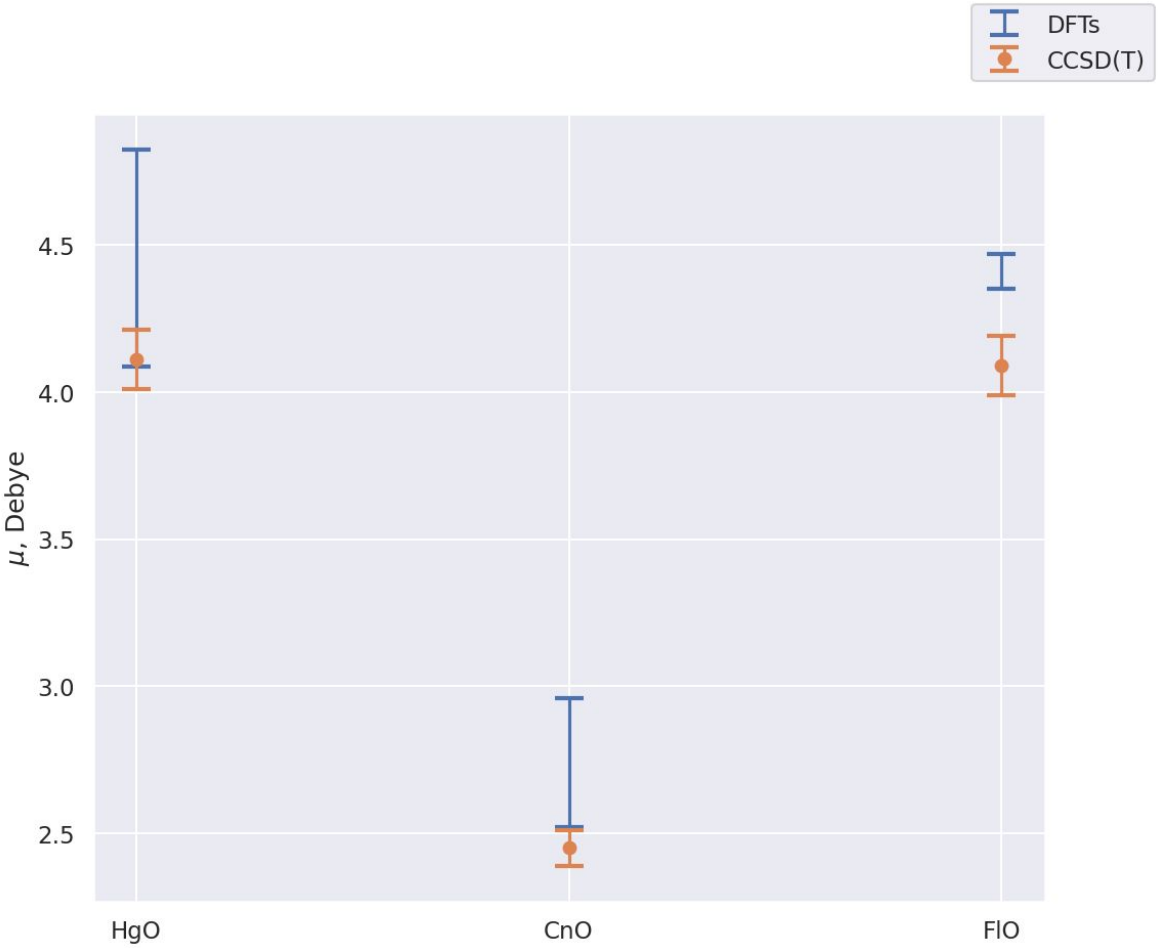
Contrib.	Value
X2C vs. DC	-0.00028 (0.01%)
relativity	-0.00023 (0.01%)
(3+)-excitations	**±0.013 (0.6%)**
gh orbitals	±0.0054 (0.3%)
diffuse functions	±0.0015 (0.07%)
correlation space	±0.00091 (0.04%)

Ionization potential (IP)



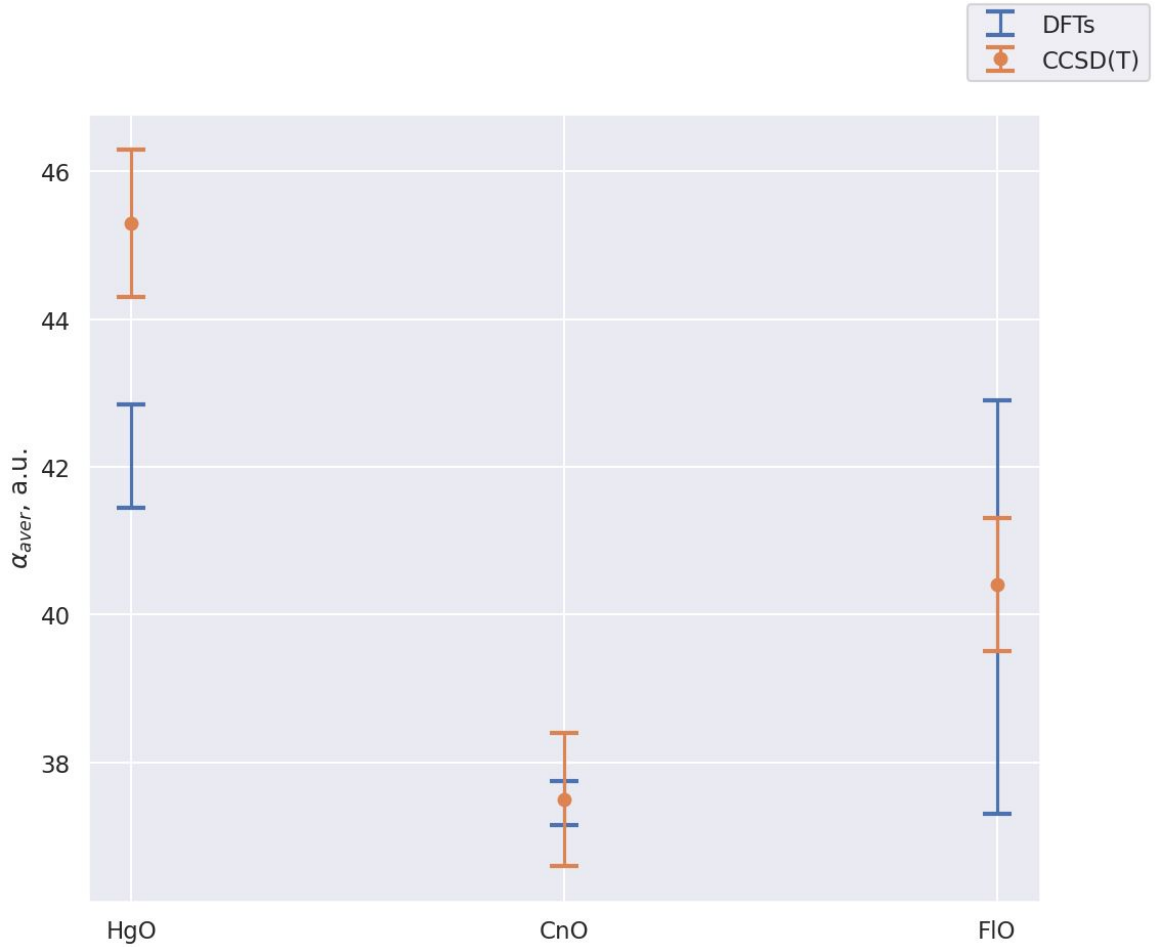
Contrib.	Value
X2C vs. DC	+0.01 (0.1%)
relativity	-0.0084 (0.09%)
3-excitations	**±0.098 (1%)**
geometry	±0.024 (0.3%)
diffuse functions	±0.0005 (0.005%)
correlation space	±0.0002 (0.002%)

Dipole moment μ



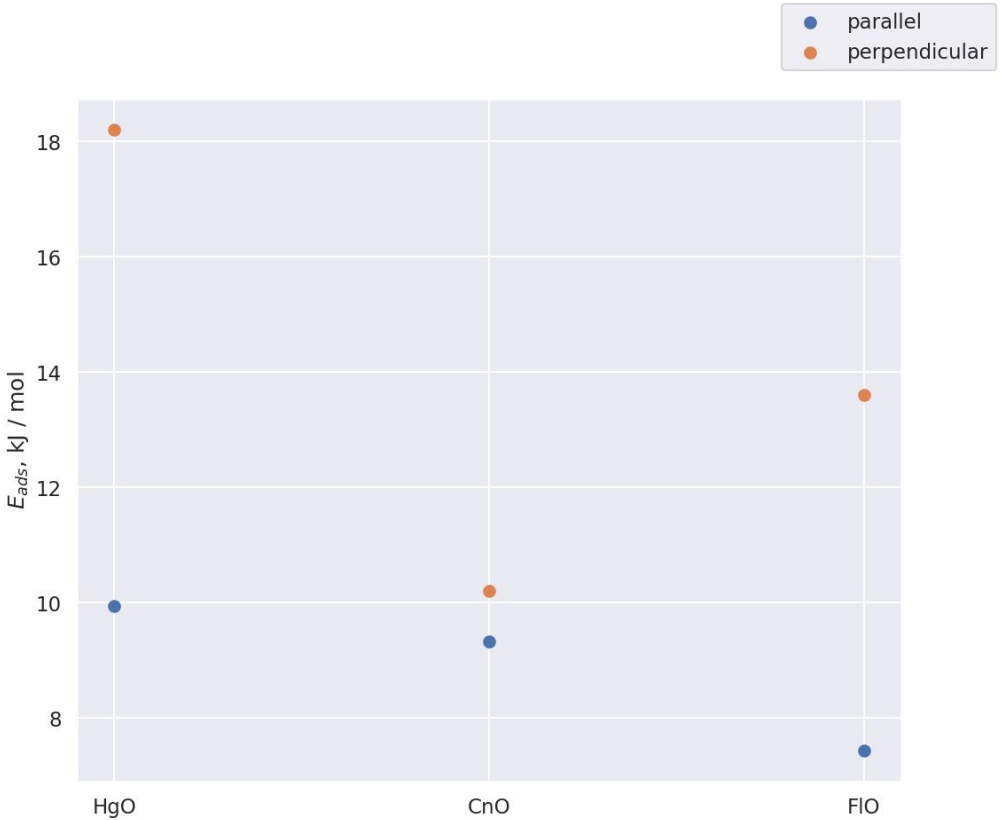
Contrib.	Value
X2C vs. DC	-0.016 (0.4%)
relativity	-0.014 (0.3%)
(3+)-excitations	±0.05 (1.2%)
geometry	±0.036 (0.9%)
gh orbitals	±0.088 (2.2%)
diffuse functions	±0.018 (0.4%)
correlation space	±0.009 (0.2%)

Polarizability α_{aver}, a.e.



Contrib.	Value
X2C vs. DC	-0.11 (0.2%)
relativity	+0.12 (0.2%)
(3+)-excitations	±0.52 (0.9%)
geometry	±0.58 (1%)
gh orbitals	±0.33 (0.6%)
diffuse functions	±0.04 (0.07%)
correlation space	±0.3 (0.5%)

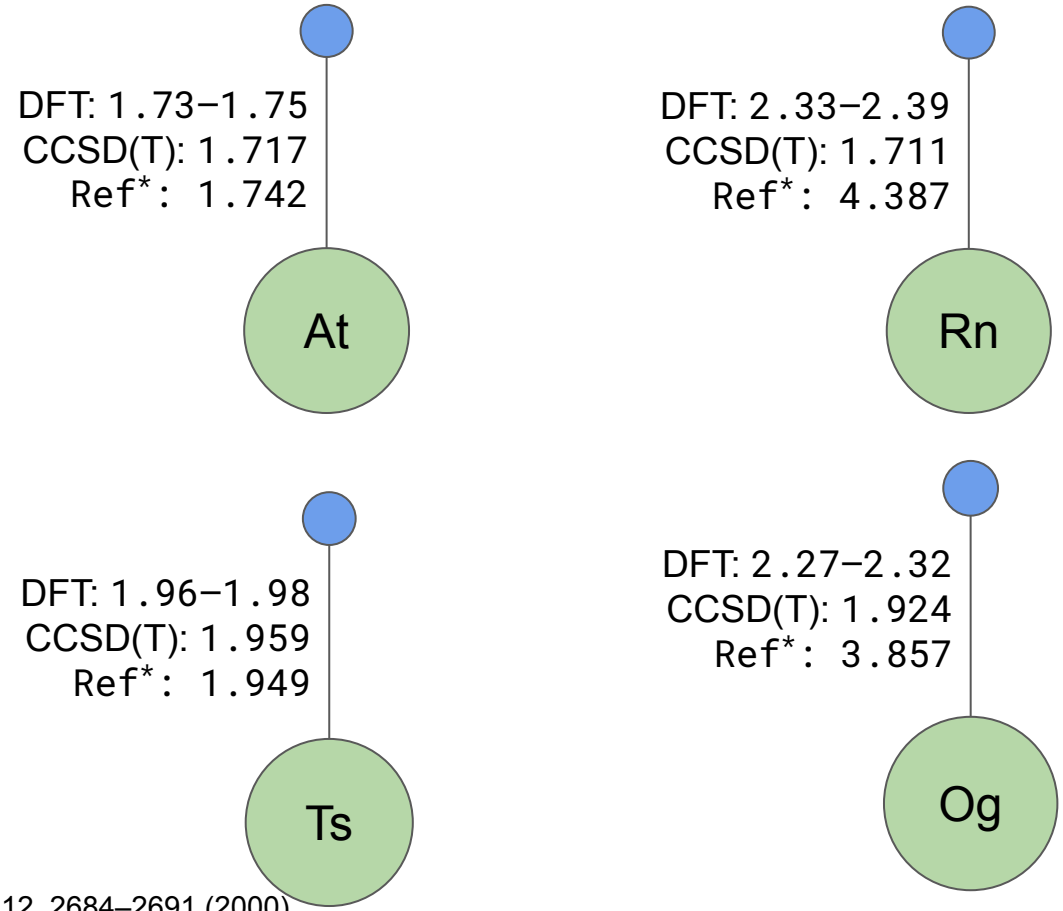
Adsorption energy on Teflon



Molecule	R, Å	d_{par}, Å	d_{per}, Å
HgO	1.905	2.27	3.103
CnO	1.887	2.252	3.076
FlO	2.064	2.429	3.341

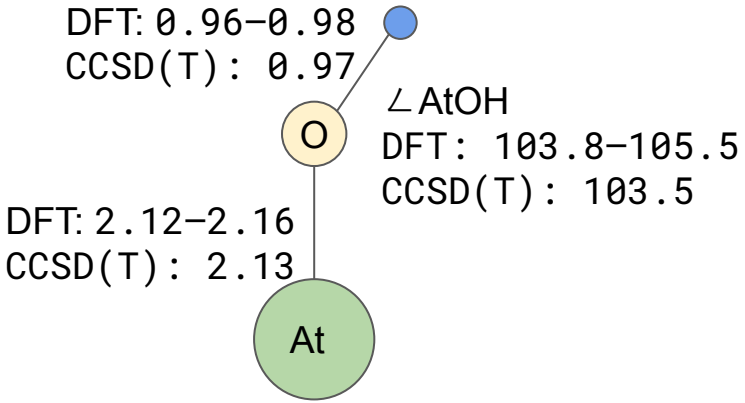
The low E_{ads}(MO) values should guarantee delivery of the molecules from the recoil chamber to the chemistry setup.

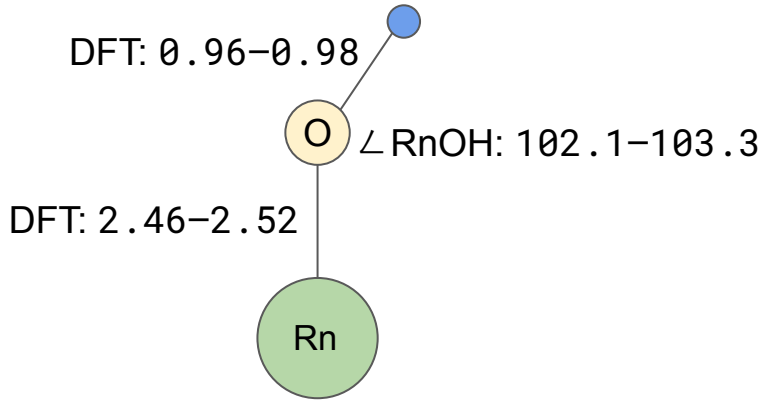
Geometry of hydrides from 17th and 18th groups

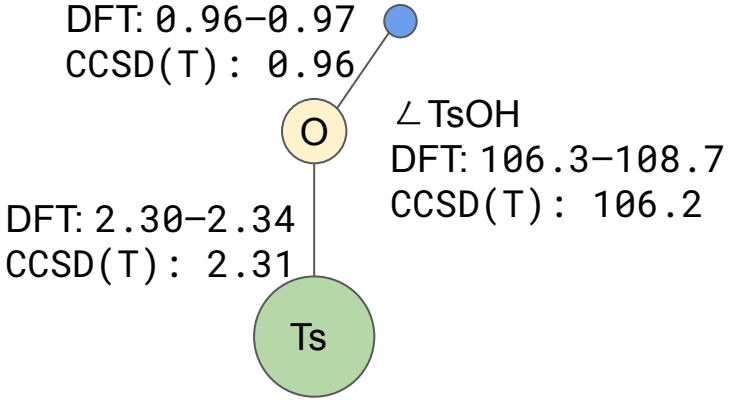


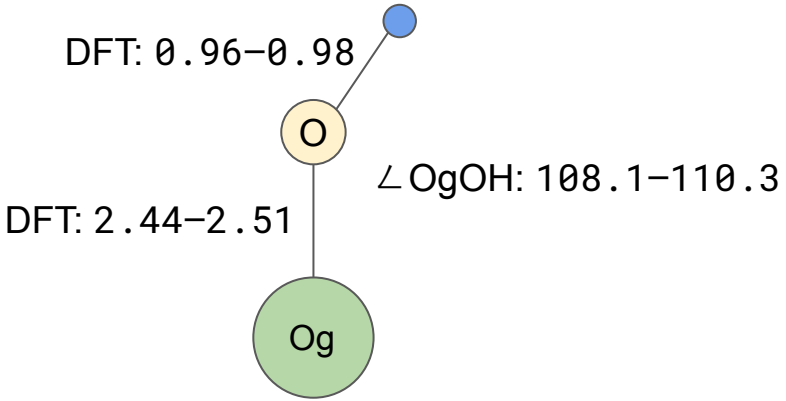
Ref*: Han et al., J. Chem. Phys. 112, 2684–2691 (2000)

Geometry of oxyhydrides from 17th and 18th groups









Conclusion

- Ab-initio calculations of molecular properties of SHEs with oxygen and hydrogen within CCSD(T) approach:
  - The bond lengths of HgO and CnO are quite similar,
  - Dipole moment of FlO is more similar to HgO than CnO's is.
- Low value of E_{ads} with Teflon for oxydes should guarantee delivery of the molecules from the recoil chamber to the chemistry setup
- Evaluation of the reliability of the DFT application in comparison with the strong baseline calculation via CCSD(T).
  - For the geometry calculation DFT works well,
  - For properties (especially IP) DFT may yield erroneous values.
- Large deviation in the geometry of the hydrides of the 18^{th} group between DFT and CCSD(T).

Many thanks to the LIT JINR for their comprehensive assistance in carrying out calculations on the GOVORUN supercomputer.

Geometry R [Å] of FlO, CnO, and HgO

Molecule	DFT	CCSD(T)
HgO	1.88–1.91	1.905(14)
CnO	1.85–1.88	1.887(14)
FlO	2.04–2.07	2.064(14)

Contrib.	X2C vs. DC	relativity	(3+)-excitations	*gh* orbitals	diffuse functions	correlation space
Value	−0.00028 (0.01%)	−0.00023 (0.01%)	**±0.013 (0.6%)**	±0.0054 (0.3%)	±0.0015 (0.07%)	±0.00091 (0.04%)

Contributions and uncertainties for FlO

Ionization potential (IP), eV

Molecule	DFT	FS-CCSD
HgO	10.4-10.9	9.76(10)
CnO	10.7-11.5	10.38(10)
FlO	9.9-10.6	9.76(10)

Contrib.	X2C vs. DC	relativity	(3+)-excitations	geometry	diffuse functions	correlation space
Value	+0.01 (0.1%)	-0.0084 (0.09%)	**±0.098 (1%)**	±0.024 (0.3%)	±0.0005 (0.005%)	±0.0002 (0.002%)

Dipole moment μ, Debye

Molecule	DFT	CCSD(T)
HgO	4.27-4.64	4.11(10)
CnO	2.63-2.85	2.45(6)
FlO	4.38-4.44	4.09(10)

Contrib.	X2C vs. DC	relativity	(3+)-excitations	geometry	*gh* orbitals	diffuse functions	correlation space
Value	-0.016 (0.4%)	-0.014 (0.3%)	**±0.05 (1.2%)**	**±0.036 (0.9%)**	**±0.088 (2.2%)**	±0.018 (0.4%)	±0.009 (0.2%)

Polarizability α_{aver}, a.e.

Molecule	DFT	CCSD(T)
HgO	41.8-42.5	45.3(10)
CnO	37.3-37.6	37.5(9)
FlO	38.7-41.5	40.4(9)

Contrib.	X2C vs. DC	relativity	(3+)-excitations	geometry	*gh* orbitals	diffuse functions	correlation space
Value	-0.11 (0.2%)	+0.12 (0.2%)	**±0.52 (0.9%)**	**±0.58 (1%)**	**±0.33 (0.6%)**	±0.04 (0.07%)	±0.3 (0.5%)

Adsorption energy on Teflon

Molecule	R, Å	d_{par}, Å	d_{per}, Å	μ_z, D	IP, eV	<α>, a.e.	α_{xx}, a.e.	α_{zz}, a.e.	$E_{ads}^{(par)}$, kJ/mol	$E_{ads}^{(per)}$, kJ/mol
HgO	1.905	2.27	3.103	4.109	9.76	45.31	33.9	68.13	9.94	18.2
CnO	1.887	2.252	3.076	2.451	10.38	37.45	30.08	52.19	9.32	10.2
FlO	2.064	2.429	3.341	4.086	9.76	40.36	31.09	58.9	7.44	13.6

The low E_{ads}(MO) values should guarantee delivery of the molecules from the recoil chamber to the chemistry setup.

Polarizability α [a.e.] of FlO, CnO, and HgO

		DFT			
Molecule	component	B3LYP	PBE0	BP86	CCSD(T)
HgO	α_{xx}	33.6	33.5	34.2	33.9(10)
	α_{zz}	59.2	60.4	57.1	68.1(10)
	α_{aver}	**42.1**	**42.5**	**41.8**	**45.3(10)**
CnO	α_{xx}	30.9	30.5	31.6	30.1(9)
	α_{zz}	51.1	51.1	50.8	52.2(9)
	α_{aver}	**37.6**	**37.4**	**37.3**	**37.5(9)**
FlO	α_{xx}	30.2	29.5	32.0	31.1(9)
	α_{zz}	58.1	57.1	60.4	58.9(9)
	α_{aver}	**39.5**	**38.7**	**41.5**	**40.4(9)**

Contrib.	Value
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