Theoretical Study of Molecular Properties of Group-VI, VII and VIII Heavy and Super-heavy Metal Carbonyls

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Aims

- Verify previous calculated data (Group VI carbonyls)

- Apply the established methodology for predicting molecular (and adsorption) properties of new carbonyl compounds (Group VII,VIII and IX)

Metal-carbonyl compounds of interest:

- species stable in the gas phase
- 18-electrons rule

	Group VI Mo, W, Sg	Group VII Tc, Re, Bh	Group VIII Ru, Os, Hs	Group IX Rh, Ir, Mt
	$M(CO)_6$	$MX(CO)_{n1}^{z1}$ **?**	**$M(CO)_5$**	$MX(CO)_{n2}^{z2}$ **?**
$-\Delta H_{ads}$ ($kJ.mol^{-1}$)[a]	Mo	Tc	Ru	Rh
Quartz	39 (38)	39 (38)	35	36
Teflon	38 (37)	39	37	36

[a]Wang, Y., et al. (2014), Radiochimica Acta **102**(1-2): 69-76.

Calculated properties

- Thermodynamical stability
- First CO bond dissociation energy, FBDE, $M(CO)_n$ --> $CO + M(CO)_{n-1}$
- Optimized geometry structures, $E=E_{min}$(geometry coordinates)
- Vertical first ionization potential, IP1=E(0)-E(+)
- Static dipole polarizability, α

Computational methods

- Theory : relativistic quantum chemistry, many-body electronic-structure theory
- Relativistic Hamiltonians: four-component Dirac-Coulomb, transformed two-component (ZORA, IOTC)
- Relativistic DFT methods with relativistic Hamiltonians; relativistic wave-function (WF) theory methods

Suitable software to reach our aims:

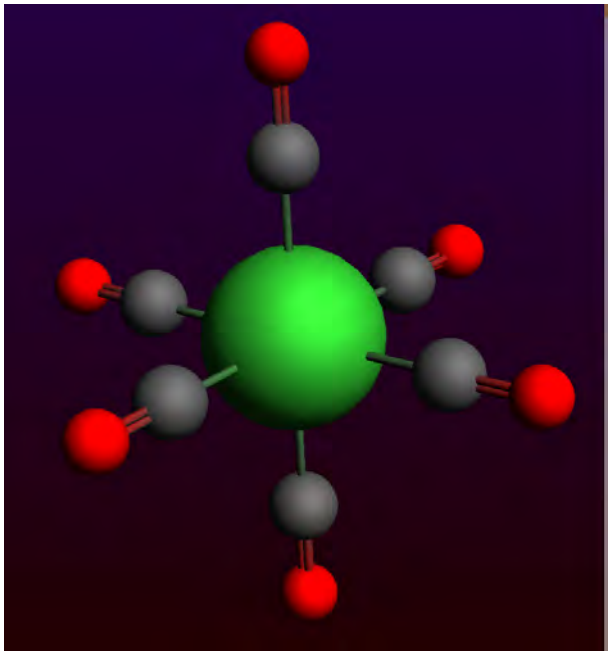
- ADF (state of art commercial software, DFT-only with many properties) *E.J. Baerends et al. (2016). ADF2016. Theoretical Chemistry, Vrije Universiteit, Amsterdam, The Netherlands, SCM.*

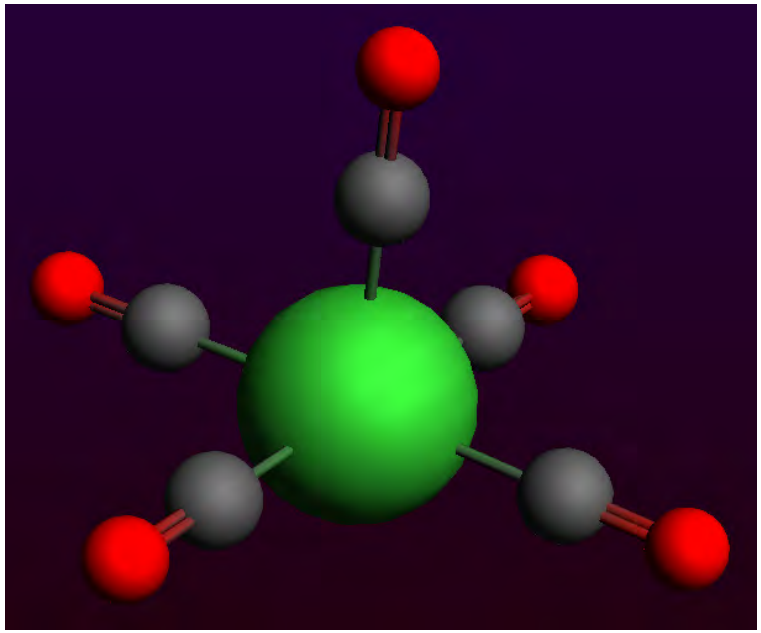
- DIRAC (2c/4c KR DFT with properties, poor geometry optimizer; plenty of WF-based methods) *R. Bast ., et al. (2016). DIRAC, a relativistic electronic structure program.*

- ReSpect (DC-KU-DFT, no electric properties, no geometry optimization) *Repisky, M., et al. (2015). ReSpect: Relativistic Spectroscopy DFT program.*

Group VI Carbonyls

- Closed shell systems, $M(CO)_{5\text{-}6}$, M = Mo, W, Sg
- $M(CO)_6$ *(Oh)* --> CO + $M(CO)_5$ *(C4v)* FBDE – first CO bond dissociation energy





First Bond Dissociation Energies of Group VI $M(CO)_6$ (in kJ/mol)

Molecule	$Mo(CO)_6$	$W(CO)_6$	$Sg(CO)_6$	Reference
RECP-MP2	214.2	243.9	246.4	Nash et al, JACS (1999)
RECP-CCSD	178.7	206.7	214.6	Nash et al, JACS (1999)
RECP-CCSD(T)	190.0	217.6	221.8	Nash et al, JACS (1999)
RECP-CCD	147.3	174.9	182.0	Nash et al, JACS (1999)
SR-ZORA		187.7		van Lenthe et al. (1999)
ZORA-DFT **DC-DFT**	**163.5** **163.2**	**190.8** **192.3**	**180.2** **177.4**	This work, ADF This work, ReSpect
Experiment	167.4±8	192.5±8		Lewis, K. E., et al. (1984).

Group VI – $M(CO)_6$ results

Molecule	M-C/Å	C-O/Å	IP1/eV	α / a.u.
$Mo(CO)_6$				
ZORA-DFT[a]	2.071	1.153	8.986	142.58
DC-DFT[b]	2.067	1.152	9.003	156.41
Exp.	2.063	1.145	(8.12)	
$W(CO)_6$				
ZORA-DFT[a]	2.062	1.154	8.938	144.09
DC-DFT[b]	2.062	1.153	8.925	151.54
Exp.	2.058	1.148	(8.18)	
$Sg(CO)_6$				
ZORA-DFT[a]	2.122	1.155	8.640	153.97
DC-DFT[b]	2.123	1.154	8.631	159.43

[a]This work, ADF [b]Pershina, V. and J. Anton, JCP (2013)

Group VII carbonyl compounds

M=Tc, Re, Bh	Macrochemistry – aq phase
$M(CO)_5(.)$	$Re_2(CO)_{10} \rightarrow 2\ Re(CO)_5(.)$ (pulse photolysis)
$M(CO)_5(-)$	$Tc_2(CO)_{10} \rightarrow [Tc(CO)_5](-)$; $Re_2(CO)_{10} \rightarrow [Re(CO)_5](-)$
$M(CO)_5H$	$[Tc(CO)_5](-) \rightarrow HTc(CO)_5$; $[Re(CO)_5](-) \rightarrow HRe(CO)_5$
$M(CO)_6(+)$	$Tc(CO)_6^{(+)}\ L^{(-)}$

Group VII carbonyls – possible reactions

(1) g: $Re + 5CO = Re(CO)_5$, ΔE=-11.86 eV

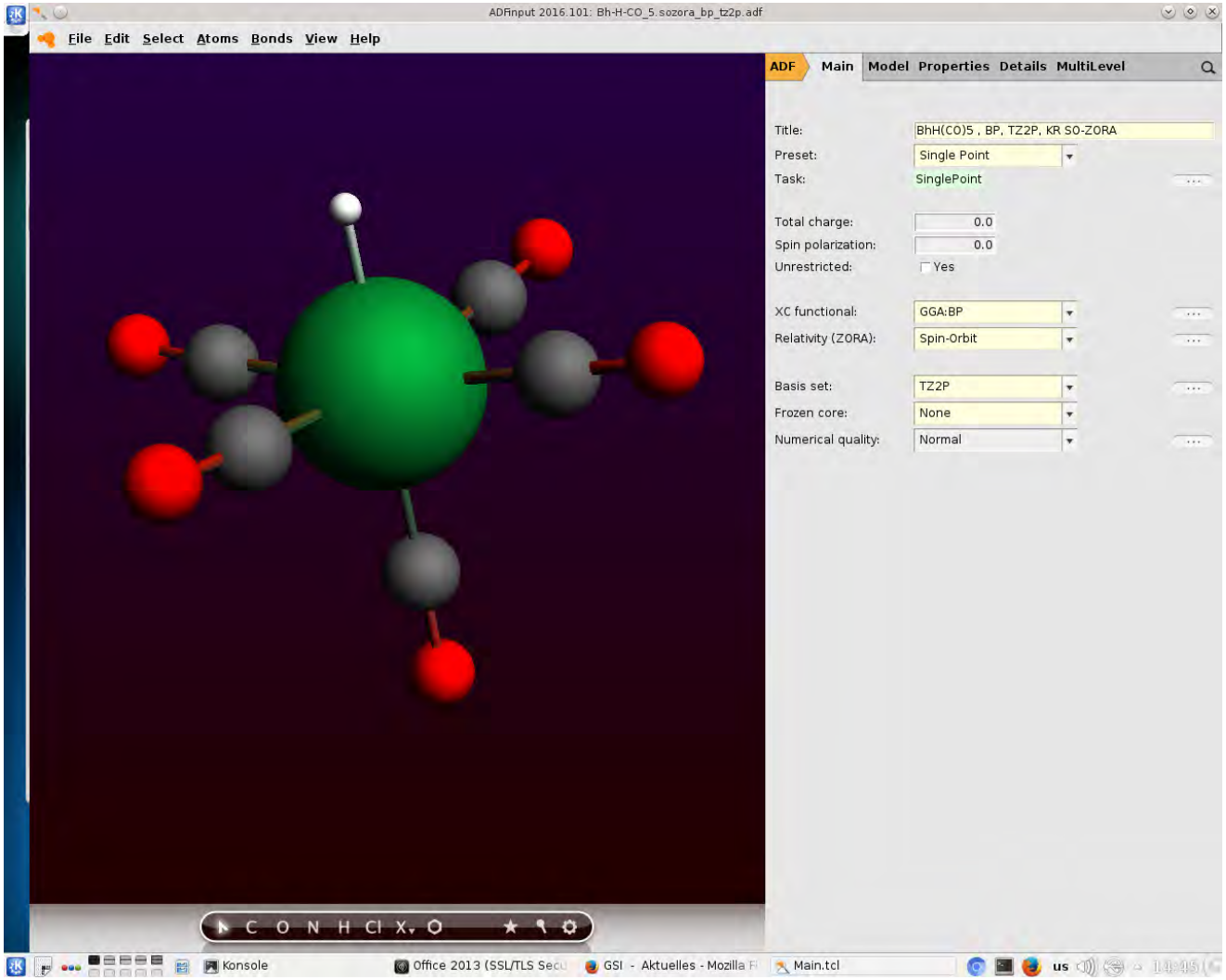
(2) g: $Re(CO)_5 + H_2O = ReH(CO)_5 + OH$, ΔE=+2.20 eV

(3) aq: $Re(CO)^-_5 + H_2O = ReH(CO)_5 + OH^-$, ΔE=-6.98 eV

(1)+(2) g: $Re + 5CO + H_2O = ReH(CO)_5 + OH$, ΔE=-9.48 eV

Based on the macrochemistry, we decided to theoreticaly investigate pentacarbonylhydridometals, **$M(CO)_5H$**

Group VII Carbonyls – preferred $MH(CO)_5$ (C_{4v})

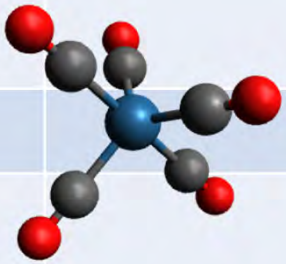


Group VII Carbonyls, $MH(CO)_5$, properties

	$M\text{-}C_{ax}$ /Å	$M\text{-}C_{eq}$/Å	$M\text{-}H_{ax}$/Å	IP1/eV	μ/D	α/ a.u.
$TcH(CO)_5$	2.013	2.000	1.709	9.52	0.30	117.90
$ReH(CO)_5$	2.002	2.003	1.729	9.45 (9.40[c])	0.174	119.92
B3LYP-DFT[a]	2.00	2.00	1.73			
FSCC[a]				8.81		
exp.[b]	2.00	2.00	1.79	8.94		
$BhH(CO)_5$	2.079	2.076	1.790	9.09	0.243	131.05

[a]Ref. Nikoobakht et al. (2015) [b]Measured by Kukolich et al. (1993) [c]ReSpect DC-DFT, this work

Row similarity in Groups VI-VII-VIII

	$W(CO)_6$		$ReH(CO)_5$		$Os(CO)_5$	
$M\text{-}C_{ax}$ / Å $M\text{-}C_{eq}$ / Å	2.062		2.002 2.003		1.968 1.952	
$C\text{-}O_{ax}$ / Å $C\text{-}O_{eq}$ / Å	1.154		1.156 1.152		1.151 1.158	
IP1/eV	8.938		9.45		8.922	
α/ a.u. μ /D	144.09 0.000		119.92 0.174		114.41 0.000	
$-\Delta H_{ads}$ kJ.mol^{-1} [b]	46.5±2.5		43±3		43.5±2	

[a]This work [b]Even et al. RA (2014)

Conclusions and perspectives

- Group VI carbonyls: FBDE for Sg is lower than for W - check it with DC CC method
- Group VII carbonyls: we decided for $MH(CO)_5$ compounds, IP1 to be recalculated with ab-initio methods, predict also ΔH_{ads}
- Group VIII carbonyls: calculations are in progress
- Group IX carbonyls: molecular and adsorption properties to be calculated, $MX(CO)_4$

Thank you for your attention

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