Isolated metal molecules for hydrogen storage: predicted MH_{12} species

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Outline

- What is quantum chemistry about?
- What can we do nowadays with quantum chemistry?
- Prediction of metal-hydride species
- Going beyong MH_{12}
- Metal-hydrides @C_{60}

The Early Days

- The Nature of the chemical bond.
- Hybridization, delocalization, lone-pairs, covalent and ionic bonds.. (Pauling, Mulliken, Hückel, Slater and others).
- Ligand field theory for transition metal complexes (Bethe, Van Vleck, Mulliken, etc).
- Hückel theory for unsaturated hydrocarbons. Theoretical electronic spectroscopy (Hückel, Goepper-Mayer, Mulliken, etc).
- The central field model for atoms. Numerical solutions for atoms. Hartree-Fock theory (Hartree, Fock, Slater).
- The Born-Oppenheimer Approximation.

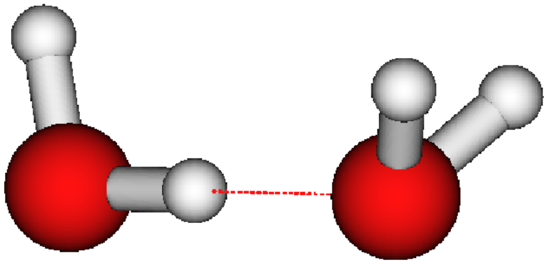
Computational Quantum Chemistry: THE COMPUTERS

- Building of models for computation around 1960:
- based on methods, partly formulated already in the 30ies (Hartree, Fock, Slater etc.),
- but which could in those days be applied only to simple systems (like atoms) or with severe approximations.
- 1960-70: First Methods: Closed Shell HF for molecules, open shell for atoms.
- First Codes: IBMOL (Clementi), POLYATOM (Czismadia, Harrison, Sutcliffe, Moskowitz, etc), 1970 GAUSSIAN (J. Pople)

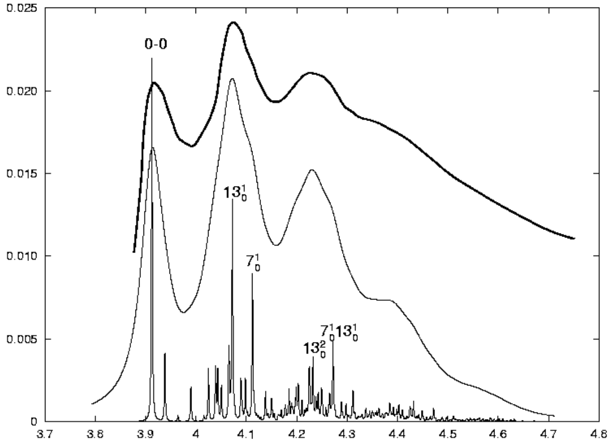
Quantum Chemistry 1990-2005

- Density Functional Theory!
- Larger molecules, biochemistry!
- Multiconfigurational Perturbation Theory.
- Excited states for larger molecules.
- TD-DFT and CC-EOM (excited states). Linear scaling methods.
- Quantum Chemistry conquers chemistry the Gaussian era.
- 1998: Nobel prize in Chemistry to John Pople and Walter Kohn.

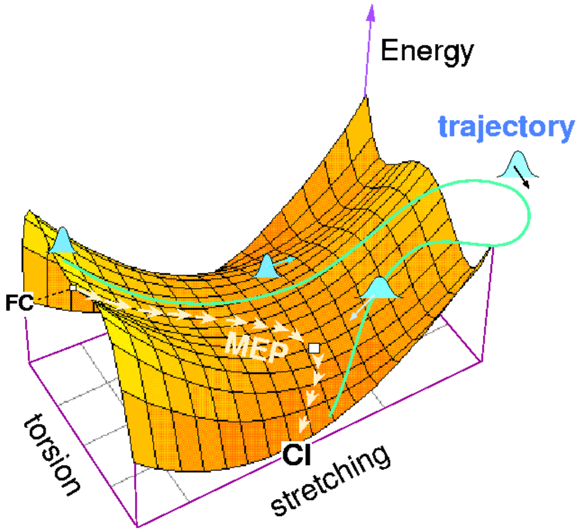
Quantum Chemistry and Chemistry today



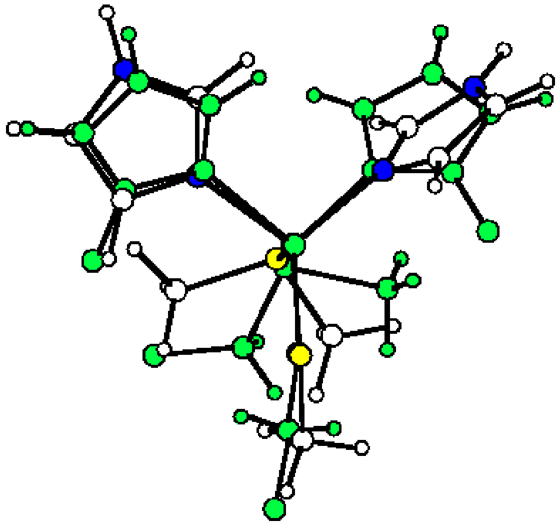
Intermolecular forces



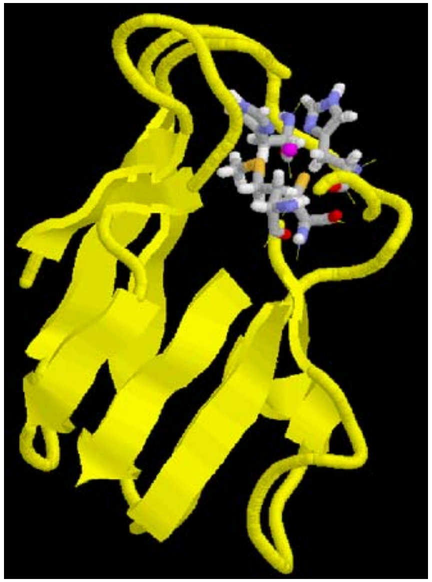
Electronic Spectroscopy



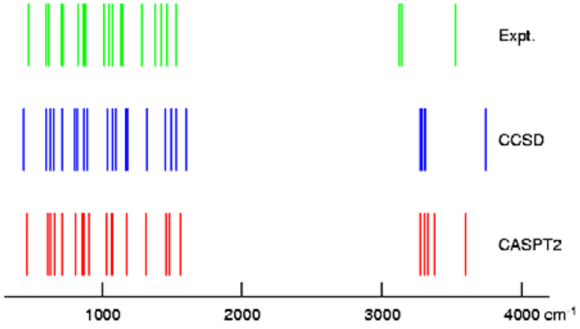
Photochemistry



Molecular Structure



Enzymatic Catalysis



Molecular Spectroscopy

Metal Hydrides

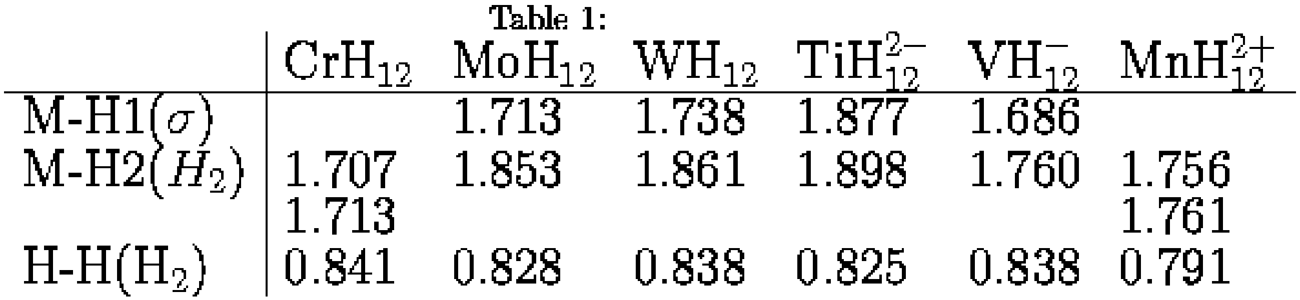
- Interesting as potential hydrogen storage systems (*Chem. Rev.* **104** 1283 (2004)).
- A design target of 6.5 wt% H has been regarded as adequate.
- Molecular-level calculations show that MH_{12} potential species are stable.
- M=Cr, Mo, W, V, Ti, Mn
- The previous MH_n species had n=9 in ReH_9^{2-} Wang, Andrews *Phys. Chem. A* **108** 1103 (2004)
- MH_{12} are a new record for metal hydrides.

Details of the calculations

- B3LYP and CASPT2 calculations.
- 6-31g** basis set on H (2s1p).
- Energy-adjusted Stuttgart ECPs on Ti (12 valence electrons), V (13), Cr, Mo, W(14) and Mn(15). Accompanying valence basis set 6s5p3d.
- Geometry optimization and frequency calculation: B3LYP.
- CASSCF/CASPT2 calculations at the B3LYP geometry: 12 electrons in 12 orbitals.

The structure of the MH_{12} species

Table 1:

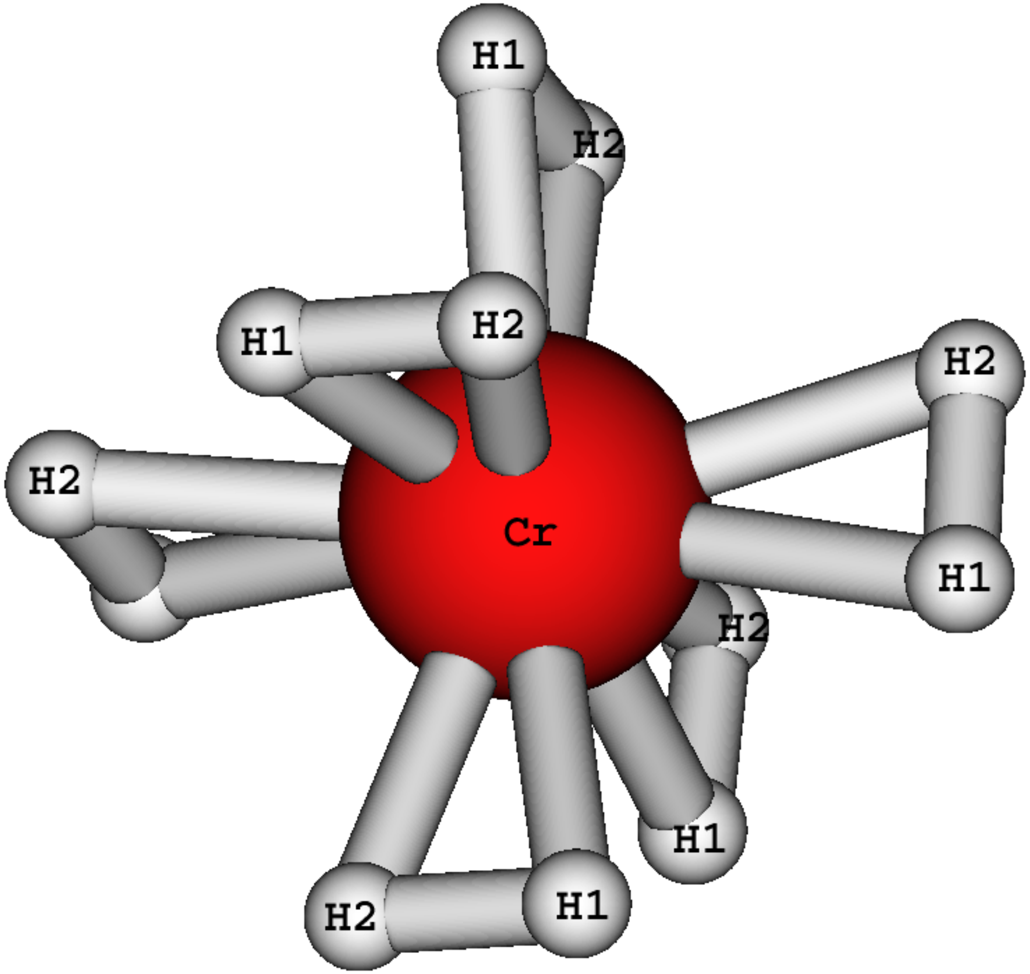


	CrH_{12}	MoH_{12}	WH_{12}	TiH_{12}^{2-}	VH_{12}^{-}	MnH_{12}^{2+}
M-H1(σ)		1.713	1.738	1.877	1.686	
M-H2(H_2)	1.707 1.713	1.853	1.861	1.898	1.760	1.756 1.761
H-H(H_2)	0.841	0.828	0.838	0.825	0.838	0.791

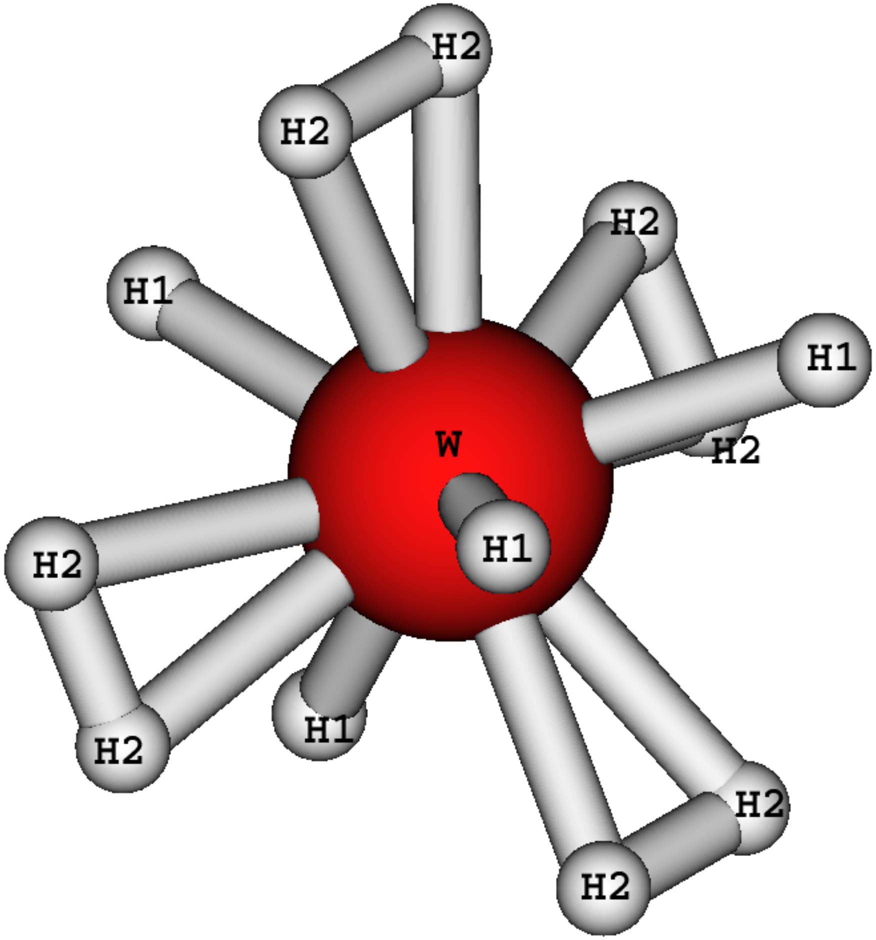
B3LYP bond distances (Å) for the MH_{12} species.
H-H is the distance in the H_2 moiety.
M-H1(σ) is the distance between M and a nonbound H atom.
H-H2(H_2) is the distance between M and H forming a H_2 molecule

CASSCF/CASPT2: singlet ground state (the lowest triplet lies 60 kcal/mol higher in energy).
12 Active Orbitals: linear combination of Cr 3d and H 1s.

CrH$_{12}$ and WH$_{12}$



D$_3$ symmetry



D$_{2d}$ symmetry

Predicted MH_{12} species

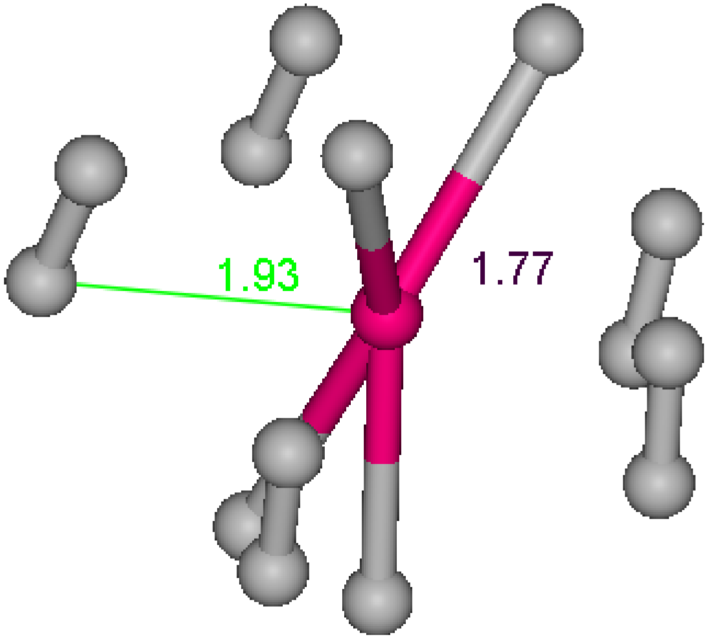
- The MH_{12} compounds have either a mixture of M-H and $M(\eta^2\text{-}H_2)$ bonds or only dihydrogen bonds .
- The formation reaction $6H_2+M \rightarrow MH_{12}$ is 15 kcal/mol endothermic for M=Cr and 55, 89 kcal/mol exothermic for M=Mo,W, respectively.
- The MH_{12} clusters are more stable than the corresponding MH_4 and MH_6 clusters.
- Lester Andrews has recently detected some MH_{12} species in his matrix.

Gagliardi and Pyykkö *J. Am. Chem. Soc.* **126** 15014-15015 (2004); Chem. & Eng. News 82 p 54 Nov. 22 (2004)

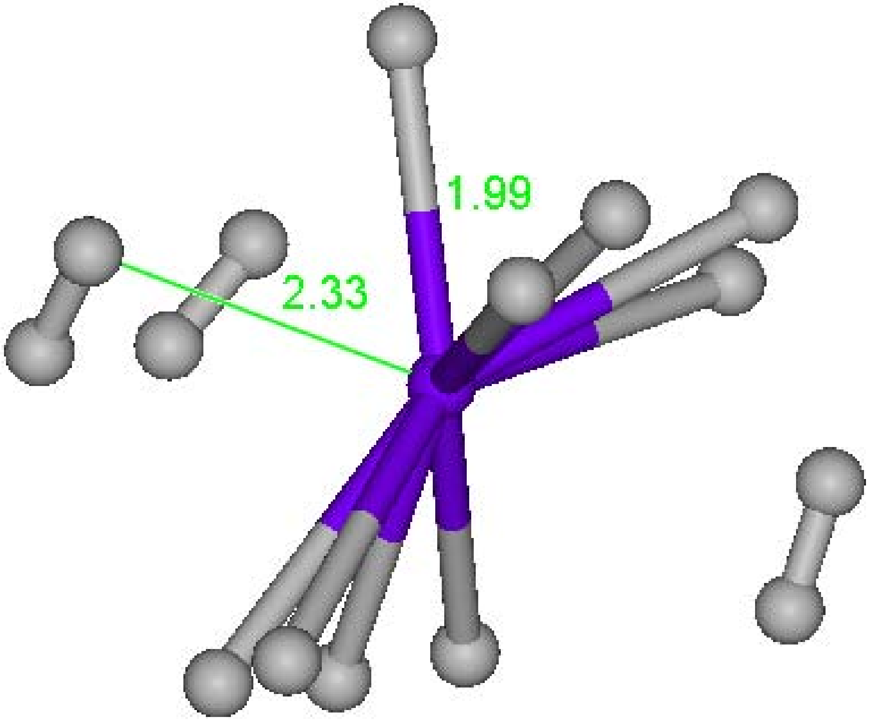
Beyond n=12

- Can we make clusters with a larger number of H atoms?
- Are species like TiH_{14} and YH_{15} also stable?
- 18-electron rule still fulfilled.
- In C_s symmetry all real frequencies.
- However, very long M-H bonds.
- They are not more stable than $TiH_4 + 5H_2$ and so on.

The structure of TiH_{14} and YH_{15}



TiH_{14}



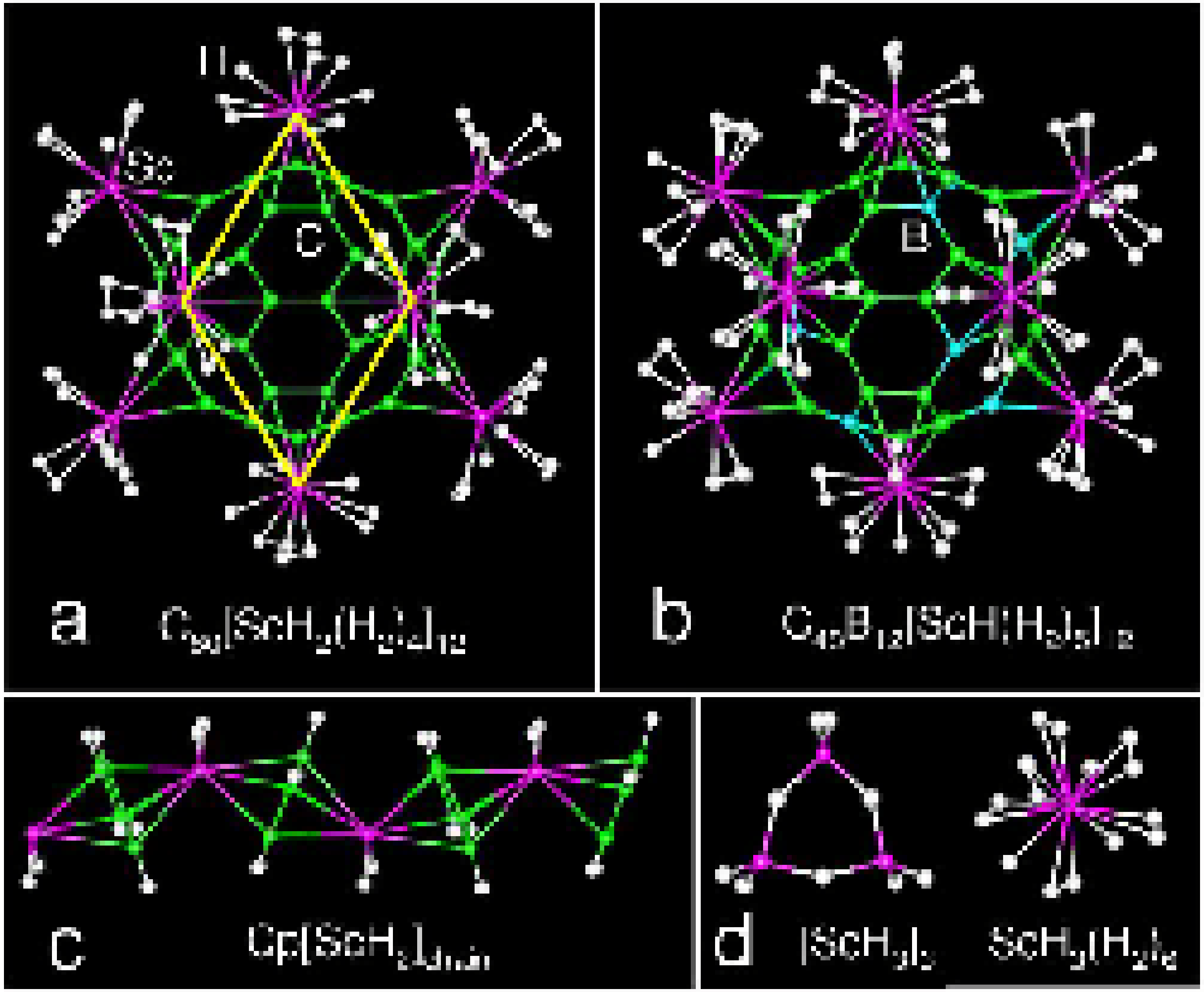
YH_{15}

How can MH_n species be stabilized?

- Make the MH_n species inside a C_{60} cage.
- ZrH_4, ZrH_{14}, ScH_{15} and ZrH_{16} are stable inside C_{60} and have shorter M-H bond distances than as isolated molecules.
- All real frequencies.
- What is the synthetic route to put MH_n inside C_{60}?

L. Gagliardi Angew. Chem. Int. Ed. Submitted (2005)

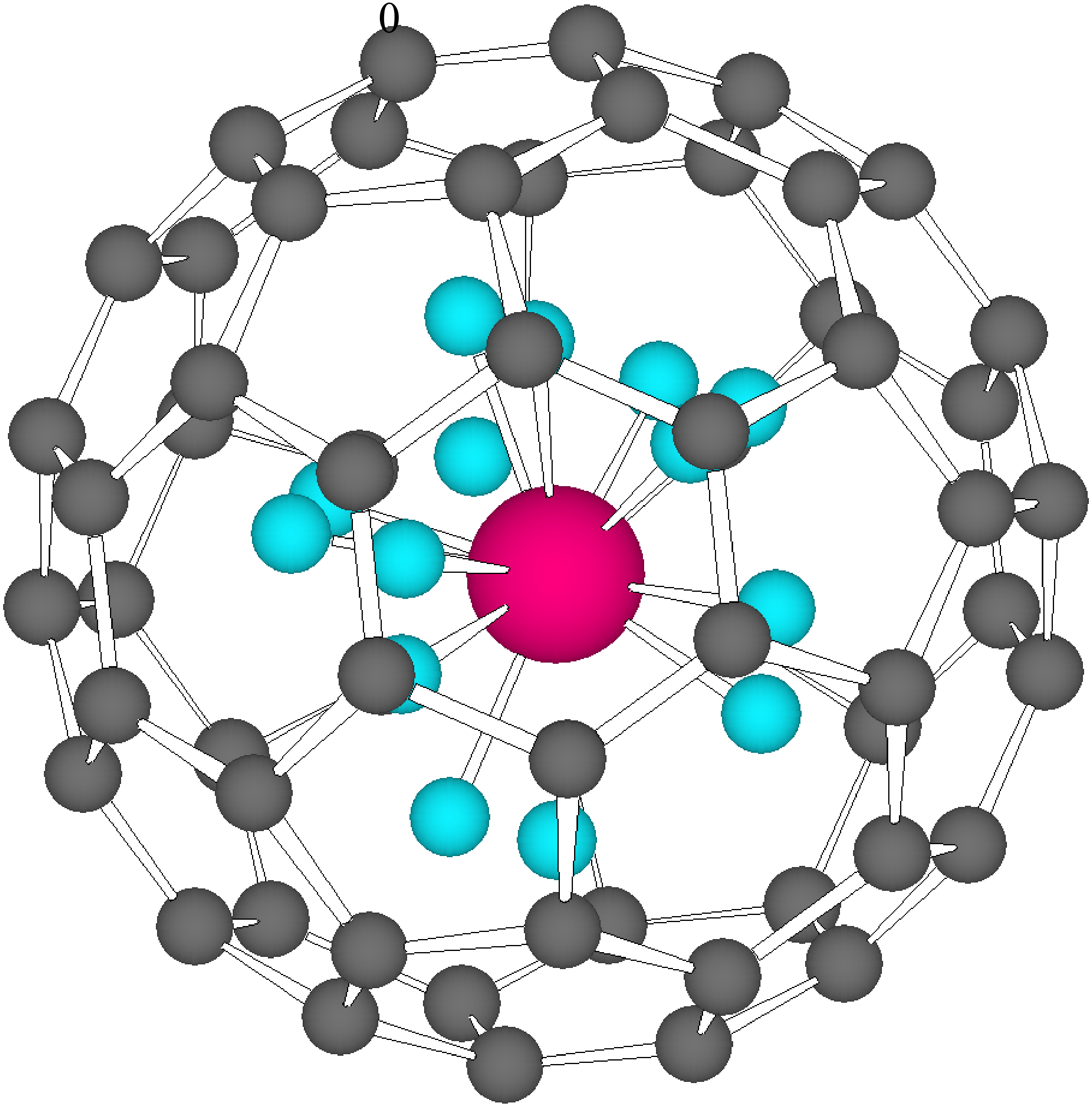
Hydrogen Storage in Novel Organometallic Buckyballs



Zhao, Kim, Dillon, Heben and Zhang PRL **94** 155504 (2005)

$ZrH_{14}@C_{6}$

0



$ZrH_{16}@C_{60}$

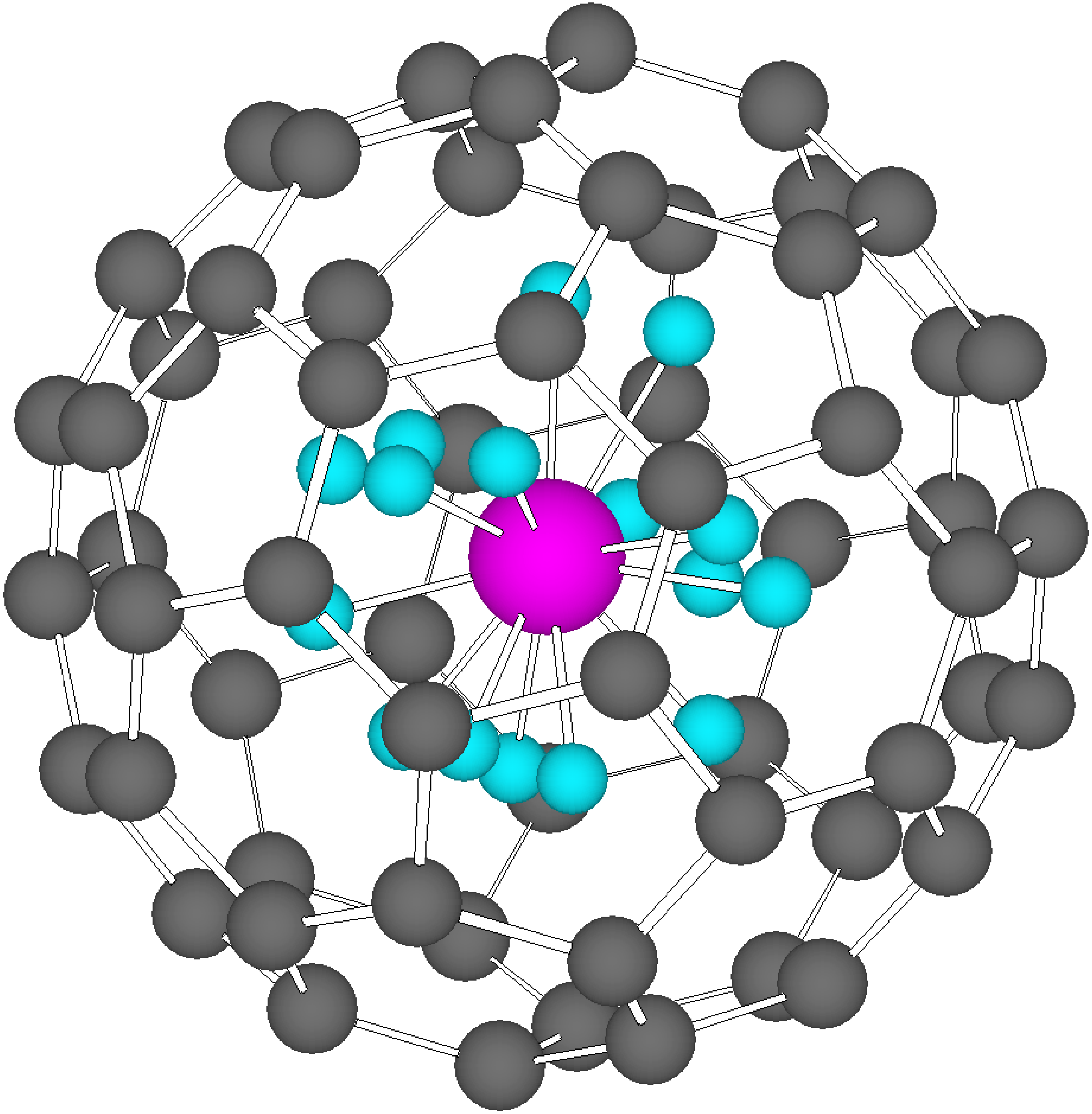


Table 1: Typical bond distances (Å) for the MH_n species. M-H(σ) is the distance between M and a nonbound H atom. M-H(H_2) is the distance between M and H forming a H_2 molecule. H-H is the distance in the H_2 moiety. (See Figures 1, 2, 3)

	M-H(σ)	M-H(H_2)	H-H(H_2)	H-C
ZrH_4	1.859			
ZrH_4@C_{60}	1.706			2.095-2.633
ScH_{15}	1.865	2.018-2.232	0.806-0.861	
ScH_{15}@C_{60}	1.739	1.775-1.891	0.802-0.875	1.848-2.643
ZrH_{16}^{a}	1.87-1.88	2.124-2.136	0.827-0.829	
ZrH_{16}@C_{60}	1.753	1.807-1.853	0.807-0.917	1.841-2.635

[a] ZrH_{16} is ZrH_{12} +2 H_2

In progress

- Synthetic route has to be understood.
- May it be easy to make molecules inside a nanotube than inside C_{60}?
- May other species exist inside C_{60}?
- Preliminary calculations indicate that $CH_4@C_{60}$ is also stable.
- Formation reactions are endothermic.

Collaborators

- My group in Palermo: F. Ferrante, R. Cortese, C. Prinzivalli and E. D'Anna
- Pekka Pyykkö Helsinki
- Björn O. Roos and MOLCAS group:
- http://www.teokem.lu.se/molcas
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Future Collaborations

- I am here to learn from all of you!