Storage of hydrogen in transition metal decorated carbon nanostructures

and

Overview of nano-modelling activities at the ICMAB (and the CIN^2)

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ICMAB

Laboratory of Electronic Structure of Materials

CSIC

Current nano-modelling at the ICMAB

- Electronic transport in nanostructures
  - Nanowires and nanocontacts, including inelastic

!! COMING SOON !!

A new nanomaterials research center in Barcelona: CIN²

(Centro de Investigación en Nanociencia y Nanotecnología)

CSIC + DURSI + ICN + UAB

Pablo Ordejón and **Nicolas Lorente** → **CIN²**

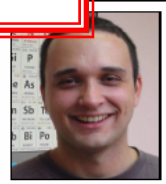
- Multilayered oxide heterostructures
  - Size effects in ultra-thin layers (~ 1-2 nm)
  - Tuning/combination of properties, multifunctionality
- Carbon nanostructures for hydrogen storage


Enric Canadell


Pablo Ordejón


nández


Maged Elhajal


F.D. Novaes


J.M. A. Pruneda

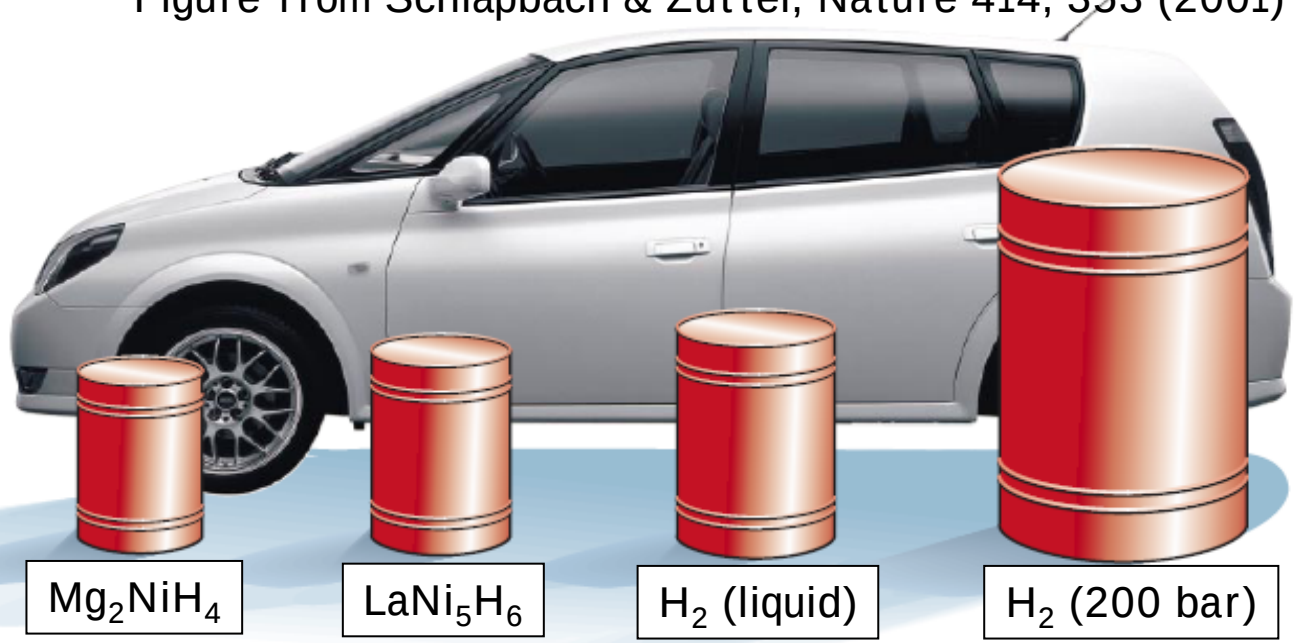

O.N. Bedoya

The problem of storing hydrogen

- Main difficulty for the use of fuel cells in automotive appliations
- Storage "method": volumetric, gravimetric (6%wt), safety requirements.

Figure 1 Volume of 4 kg of hydrogen compacted in different ways, with size relative to the size of a car. (Image of car courtesy of Toyota press information, 33rd Tokyo Motor Show, 1999.)

Figure from Schlapbach & Züttel, Nature 414, 353 (2001)



Volume of 4 kilograms of H (energy-equivalent to ~ 12 (or 24) kg of gasoline)

- Complex, chemical hydrides:
  - Much energy involved in hydrogen desorption
  - **Bad kinetics of H_2 adsorption & desorption (i.e. high T needed)**

Raise and fall of carbon nanotubes for H-storage

- In 1997, CNT's seemed to be the solution to the problem...
  - A.C. Dillon **et al**., Nature **386** , 377 (1997)

    Reported **5-10 wt%** of H per SWNT at 300 K

    CNT's should be ideal regarding sorption and desorption kinetics.

    Acceptable hydrogen density. Thus, the problem is solved !

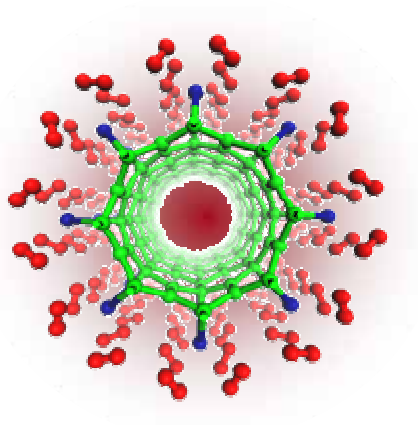
- Unfortunately, the experiments were wrong.
  - M. Hirscher *et al*., Applied Physics A **72**, 129 (2001)

    H stored in Ti-alloy particles present in samples.

H_2 in Nanotubes

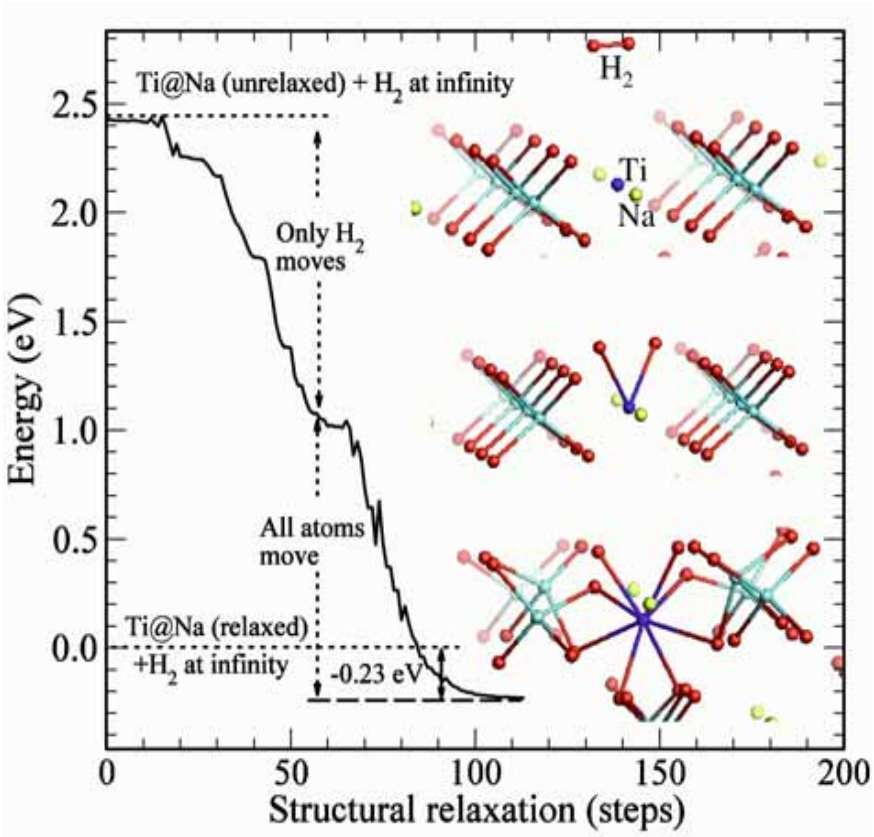
HYDORGEN STORAGE FACTS FOR NANOTUBES

- **Because vdW interactions are very weak (~ 0.1 eV), physisorption on SWNT's is hopeless for hydrogen storage.**
- **Because the C--H bonding is too strong (~ 1 eV), chemisorption of hydrogen on SWNT is not an option for storage either.**
- **We need a new mechanism for SWNT-hydrogen interaction with strength between chemi and phisisorption? HOW CAN WE DO THIS?**



Prediction: light transition metal-coating of "carbons" could provide such a mechanism !

In the study of Ti-doped $NaAlH_4$ surfaces...



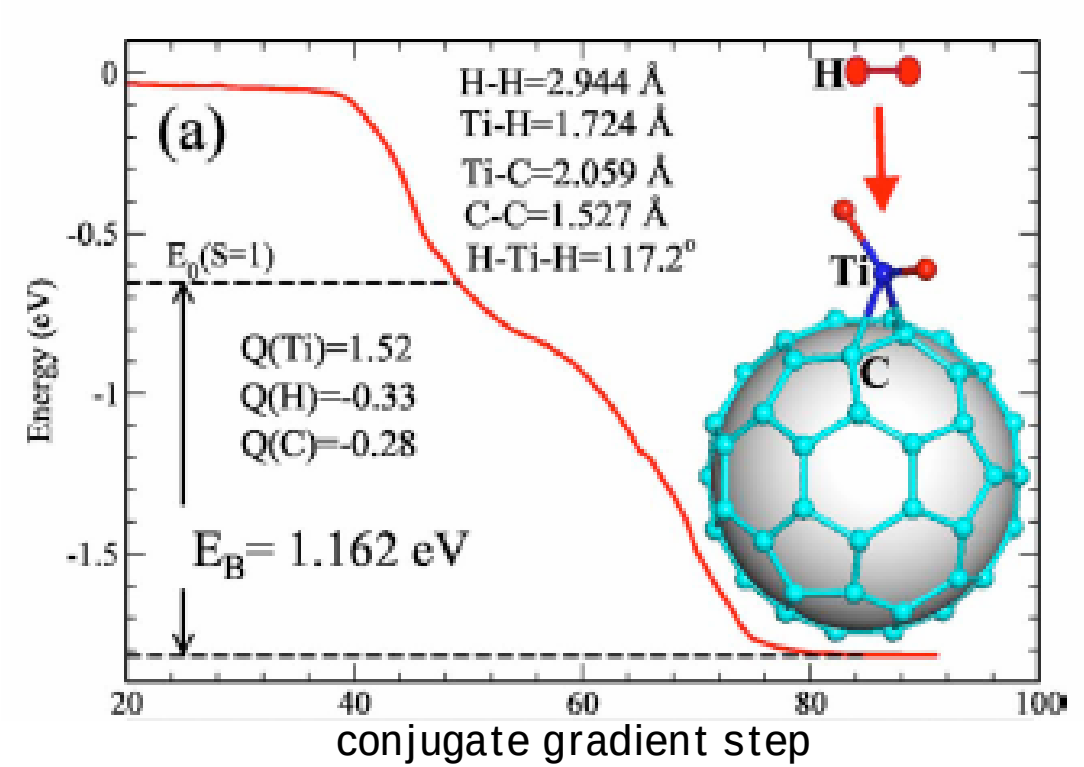
- Iñiguez and Yildirim, submitted (cond-mat/0604472)
- GGA, Troullier-Martins pseudopotentials, DZP optimized basis (SIESTA)

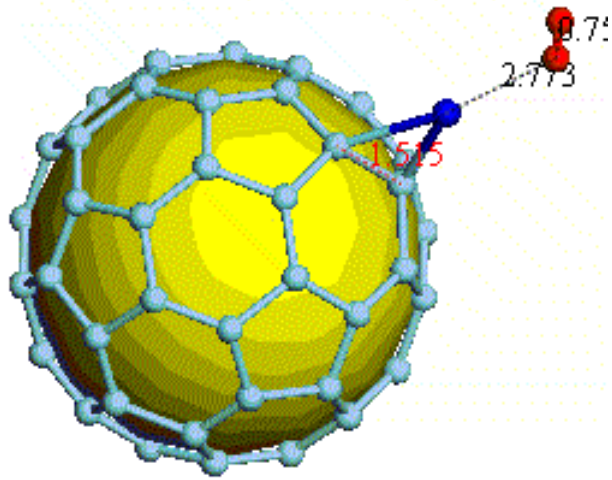
Titanium attracts an external H_2 molecule with a binding energy of ~ 0.23 eV

- **Idea**: **Find model systems to study this H adsorption in more detail**
- Need a light, large surface area, material on which Ti can be deposited
- We (T. Yildirim, NIST) had experience with Ti-coated nanotubes for use as nanowires...

Ti adsorbed on C_{60}

Model system to study H adsorption by transition metals



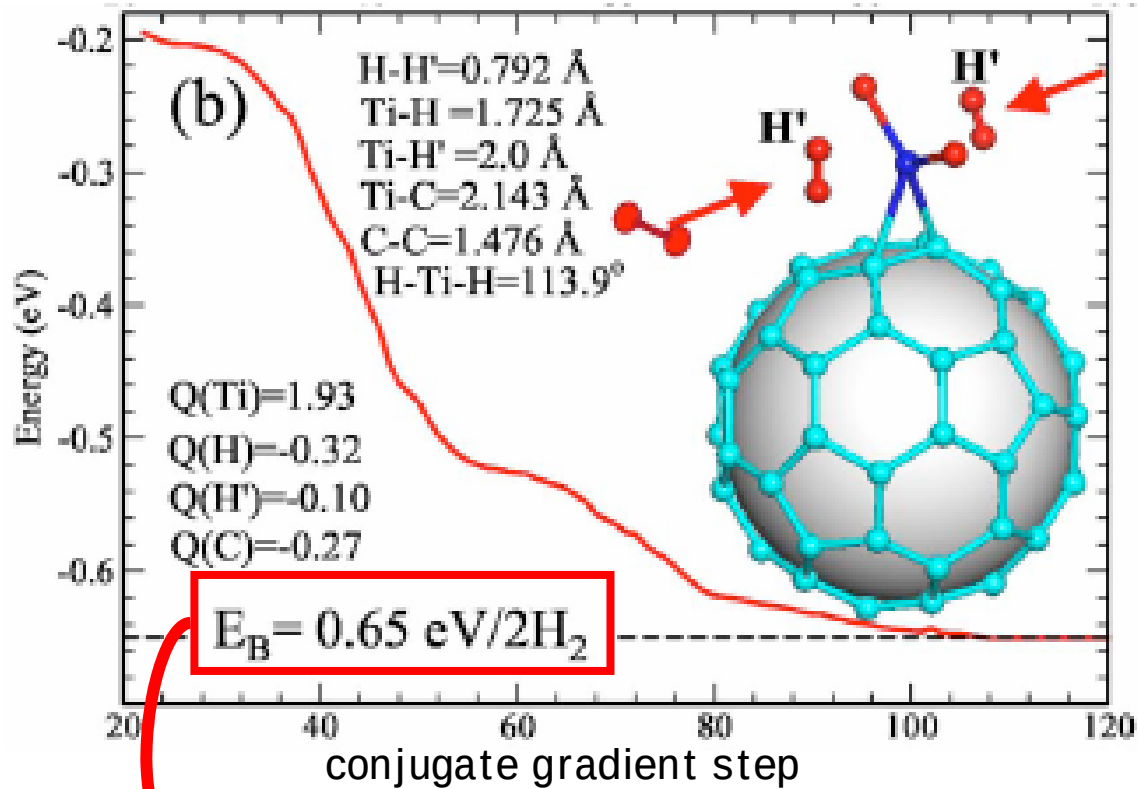


- Yildirim, Íñiguez and Ciraci, PRB 72, 153403 (2005)
- GGA, plane waves, ultrasoft pseudopotentials (CASTEP).

Energy versus structural minimization step (reaction path) for the dissociative adsorption of H_2. H_2 first approaches Ti while H-H bond distance increases to 0.9 A (CG step 44). Then the Ti-H distance rapidly decreases to 1.75 A (CG step 50) and the H_2 molecule dissociates to form TiH_2 group (H-Ti-H angle increases from 35 to 117 between CG steps 50-80). The binding energy is 1.162 eV.

C_{60} + Ti(D) + H_2 + $4H_2$

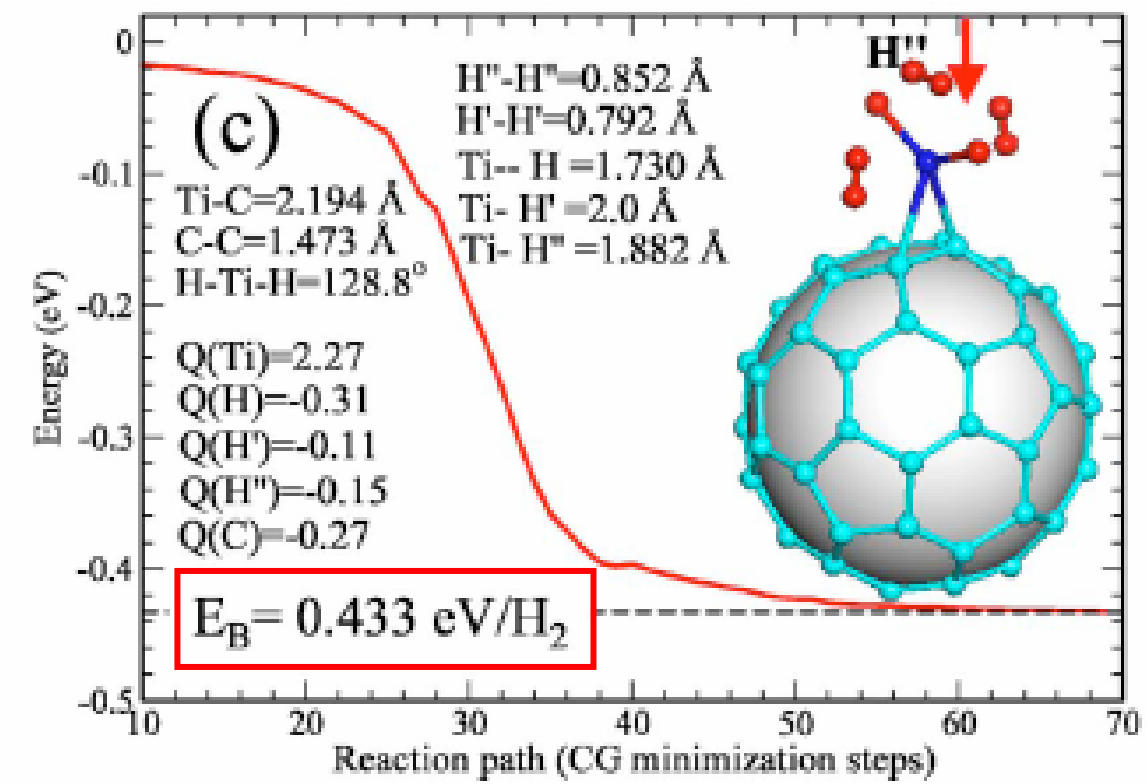
Molecular Adsorption of 3 H_2 molecules on $C_{60}Ti(D)H_2$

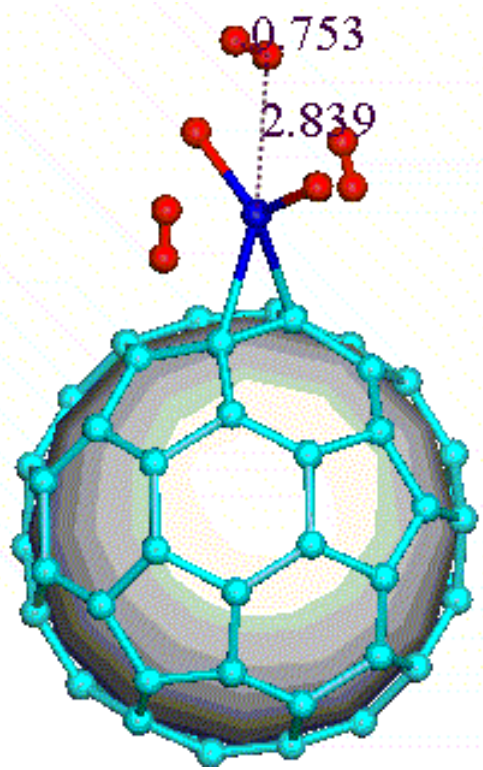


This is the *right* binding energy !

C_{60} + Ti(D) + H_2 + 3H_2

Molecular Adsorption of 3 H_2 molecules on $C_{60}Ti(D)H_2$





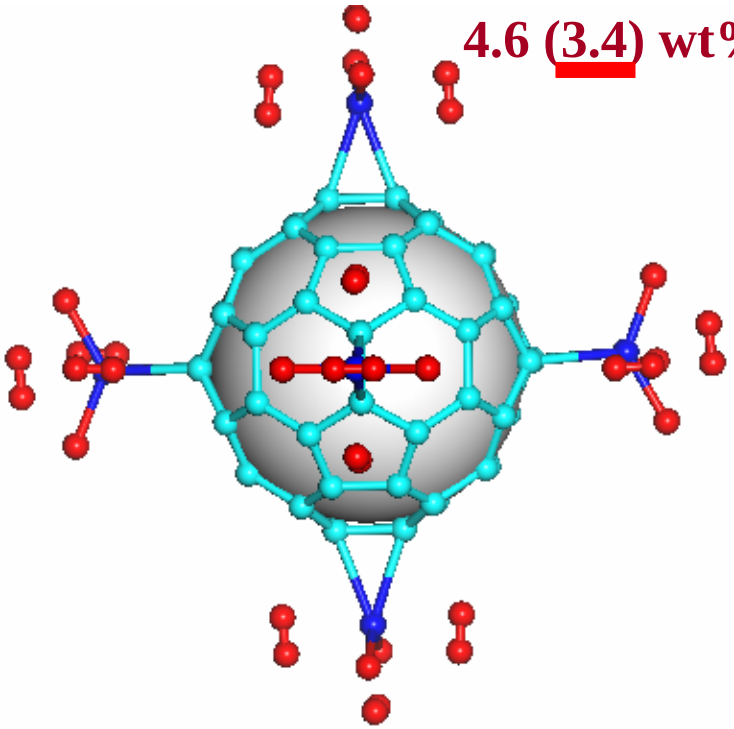
In summary:

- First H_2 binds strongly (> 1 eV)
- Then, binding energy ~ 0.5 eV/H_2
- **It should be possible to desorb 3 H_2 molecules at moderate T**

$C_{60}(Ti(B)H_2\text{-}3H_2)_6 + (Ti(H)\text{-}4H_2)_8$
High Coverage Cases

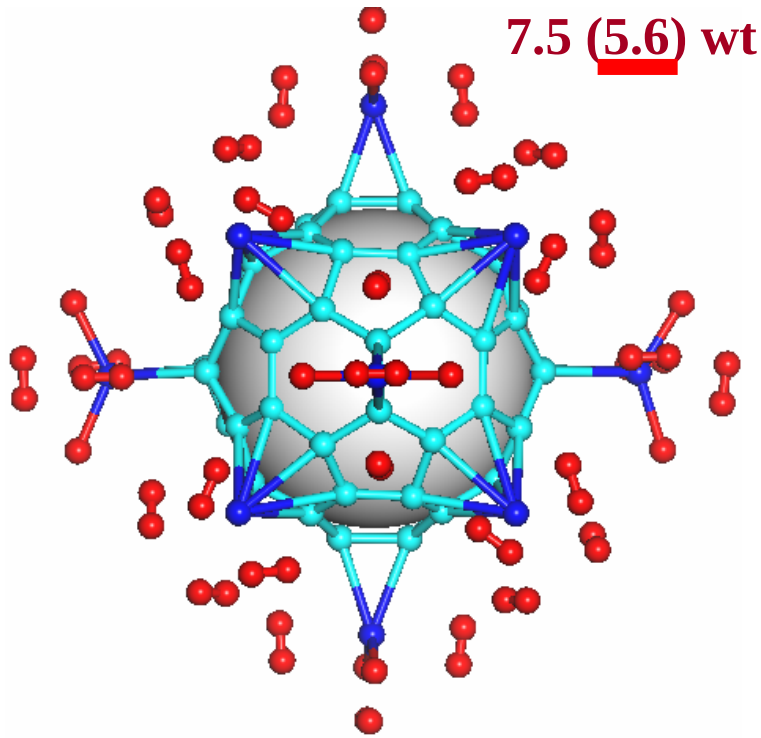
(a) $C_{60}[Ti(B)H_2\text{-}3H_2]_6$

4.6 (3.4) wt% H_2



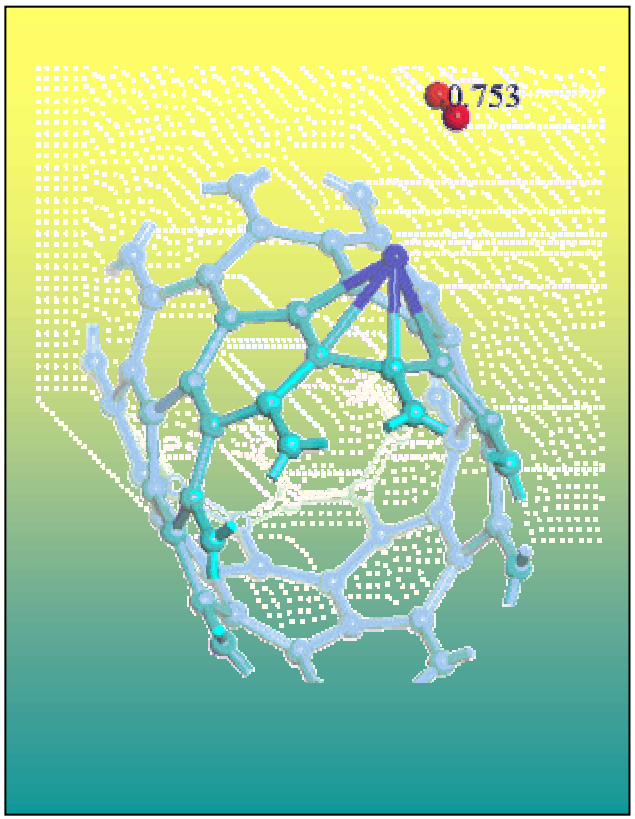
(b) $C_{60}[Ti(B)H_2\text{-}3H_2]_6\text{-}[Ti(H)\text{-}4H_2]_8$

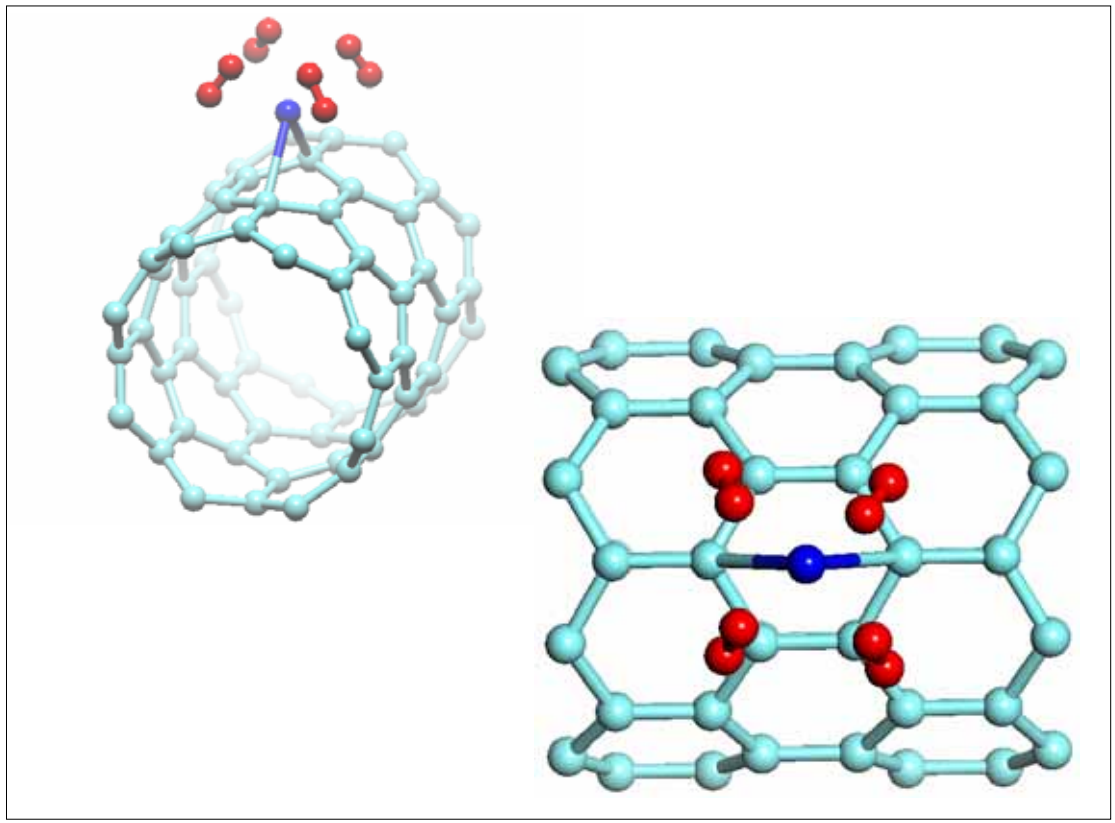
7.5 (5.6) wt% H_2



- Possible to load system with more Ti atoms, each of which can take eight hydrogen atoms.
- Loaded systems are (meta-)stable.
- Binding energy is about 0.5 eV per H_2, very similar to single-Ti case.

Dissociative adsorption of hydrogen on SWNT + Ti





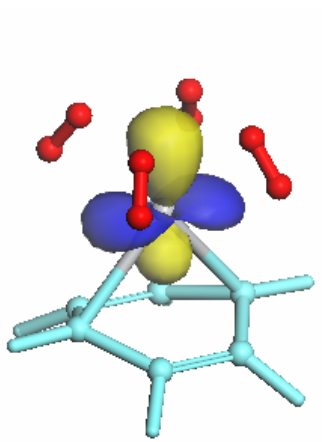
Left: Dissociative adsorption of H_2 on SWNT+Ti. H_2 first approaches Ti, then it dissociates, and then TiH_2 group rotates so that H comes over C atoms.
Right: Side and top views of most stable configuration with 4 H_2 molecules adsorbed. H2 molecules locate over C atoms; remaining 2 carbons are bonded (ionic) to Ti.

SWNT (8,0) + Ti + $4H_2$
WHAT IS THE BONDING MECHANISM?

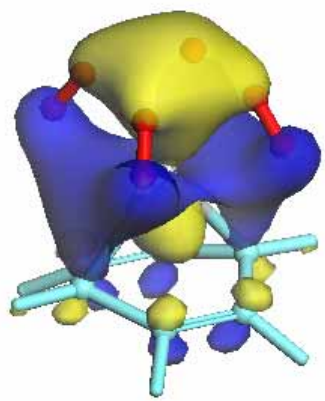
Projected DOS of involved atoms and bond analysis indicate:

1. Significant charge transfers; bonds have strong ionic character.
2. Ti-4*s* electrons alomst completly gone, probably promoted to 3*d* orbitals in analogy to C's sp^3 hybridization.
3. Carbon 2*p* dangling bonds play important role in Ti-H bonding

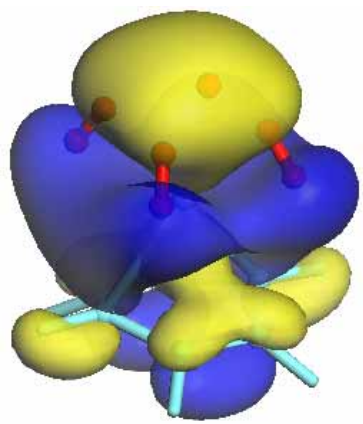
State just below E_F:



ψ=0.08



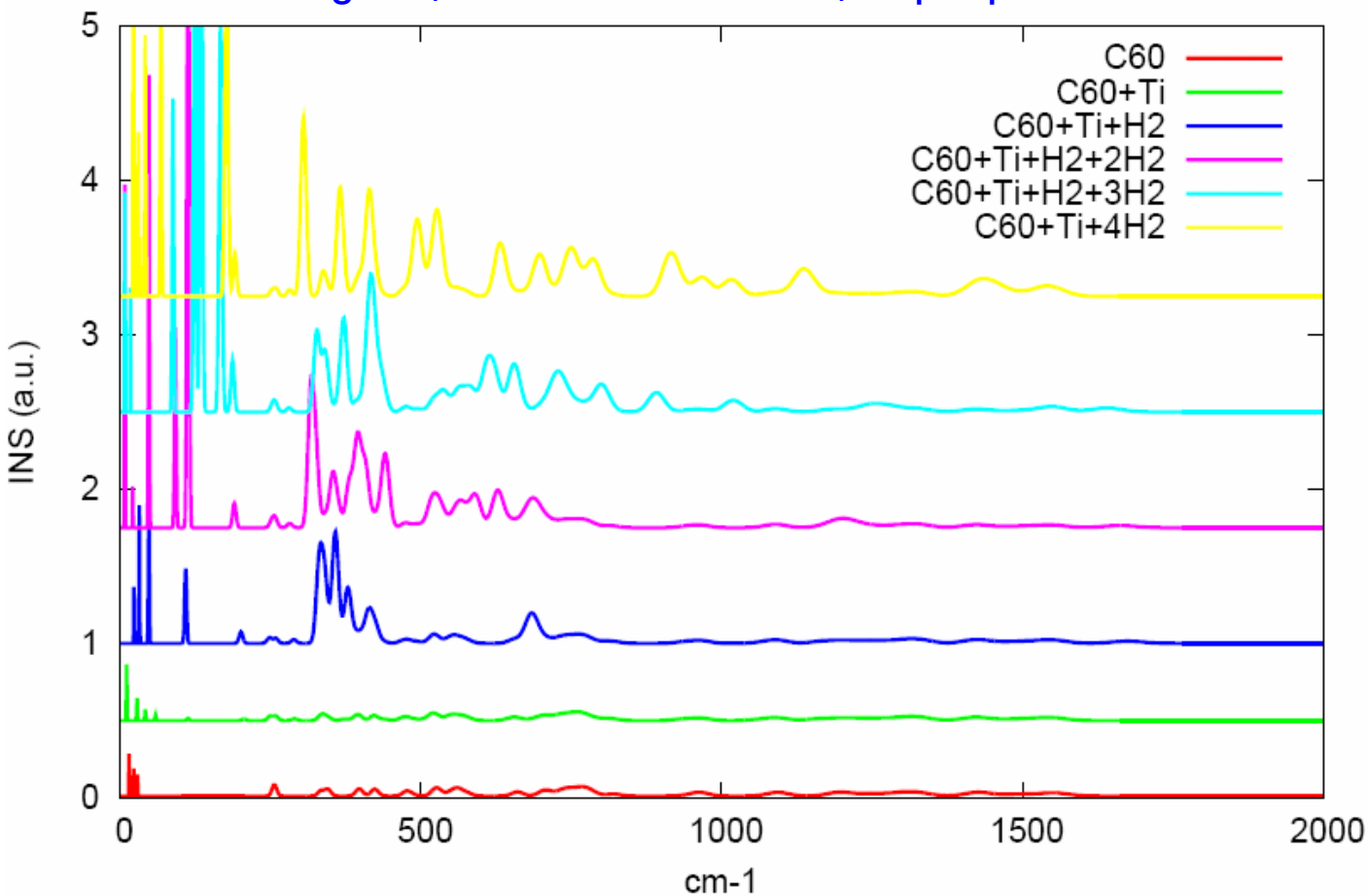
ψ =0.04



ψ =0.02

Calculated vibrational spectrum of $C_{60}TiH_x$

Iñiguez, Zhou and Yildirim, in preparation



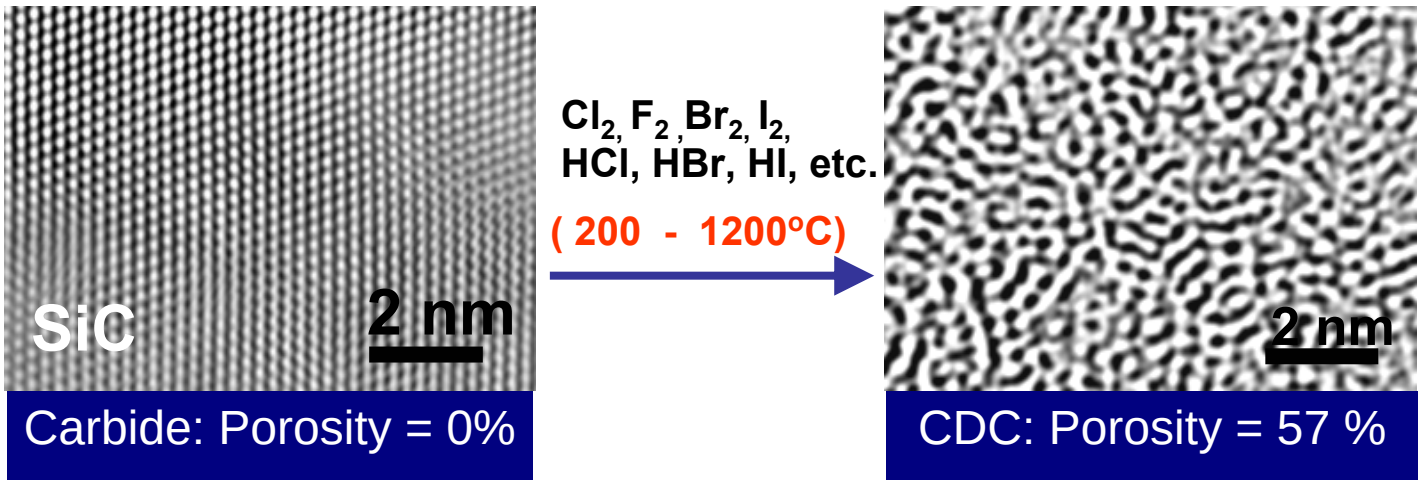
GGA, PAW, plane waves (VASP)

Vibrational spectra (neutron, Raman or IR) for different isomers of TiH_x on C_{60} are different enough to characterize the samples that may have the proposed TiH_x-bonding !

Some experimental attempts at realizing this idea

- Work with Carbide Derived Carbons (CDC's) -- Fischer, Yildirim *et al.*

  $M_aC_b(s) + (c/2)Cl_2(g) \rightarrow aMCl_c(g) + bC(s)$, where M represents metal or metalloid



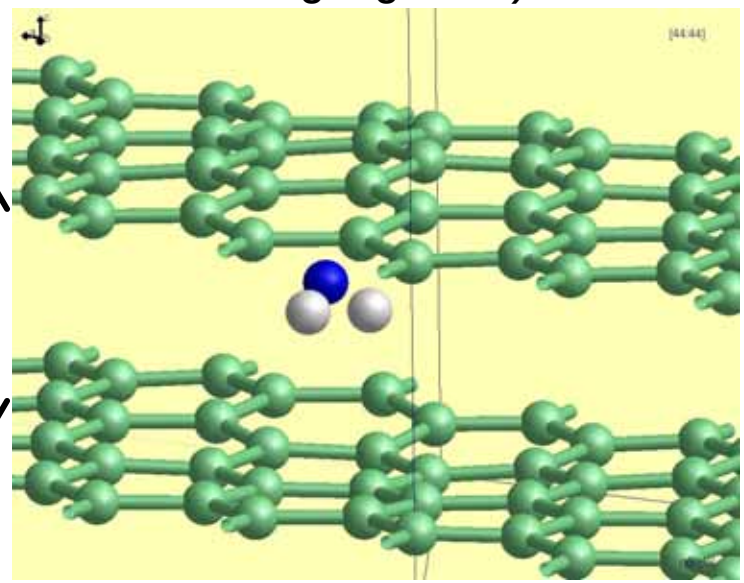
  - Over 30 CDC materials synthesized and evaluated
  - Best results obtained when starting from Ti_3SiC_2
  - No evidence yet of predicted Ti-H bonding

- Attempts using nanoporous carbons and CNT bundles with Ti as T.M.: many problems with oxygen contamination (and expected segregation)

Current work (Manuel Cobian, ICMAB)

- Simplified model of activated carbon
- Test the concept for hydroge storage and identify metals that avoid problems that Ti has (undesired oxidation, segregation)

distance between graphenes can be experimentally controlled by appropriate cation intercalation



- In collaboraion with experimental groups of Gavin Walker (Nottingham) and Richard Chaine (U. Quebec)

Conclusions

- Still some hope for the hydrogen - carbon marriage
- Transition-metal "decoration" may lead to good figures of merit (gravimetric, volumetric, kinetic, safety) for hydrogen storage
- We still need to demonstrate (experimentally) that the idea works ...

- Bousquet & Ghosez (Liege), private communication