SCIENTIFIC CHALLENGES IN HYDROGEN STORAGE: BREAKTHROUGH AT UVa

Adam Phillips and Bellave Shivaram

University of Virginia

- Introduction
- Background and Calculations
- Experimental Results
- Outlook and Broader Impact

Experimental Methods

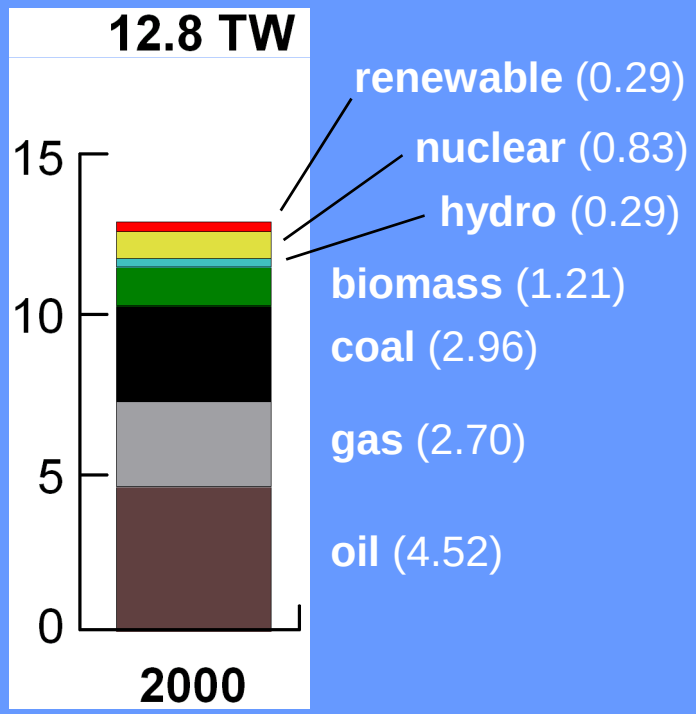
National Science Foundation
WHERE DISCOVERIES BEGIN

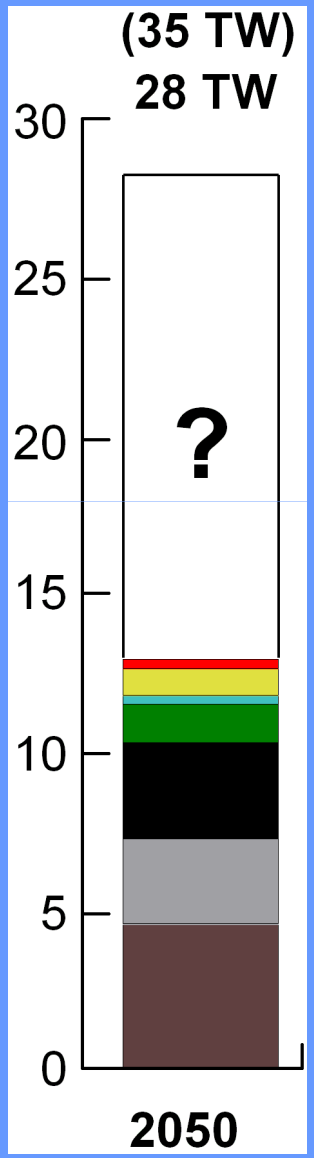
UNIVERSITY of VIRGINIA

ERSITIES RESEARCH ASSOCIATION SURA

Global Energy Inventory

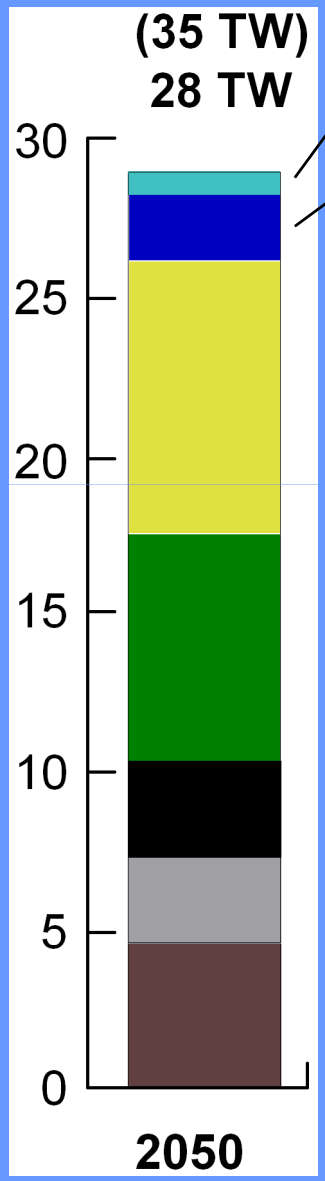
Lewis (Caltech) and Nocera (MIT)
PNAS Perspective, **2006**





Future Global Energy Inventory?

Nocera, *Daedalus*, 2006



hydro…limit (0.7 TW)

wind…theoretical limit
all class 3 (5.1 m/s
10 m above ground) (2.1 TW)

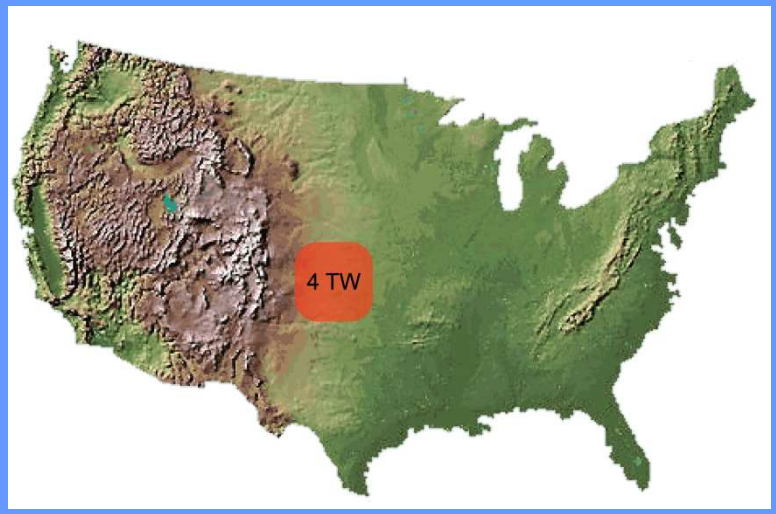
nuclear...
8000 new nuclear
power plants (8 TW)

biomass...
1.28×10^{13} m^2
20% earth's surface
all cultivatable land
used for biomass
(7-10 TW)

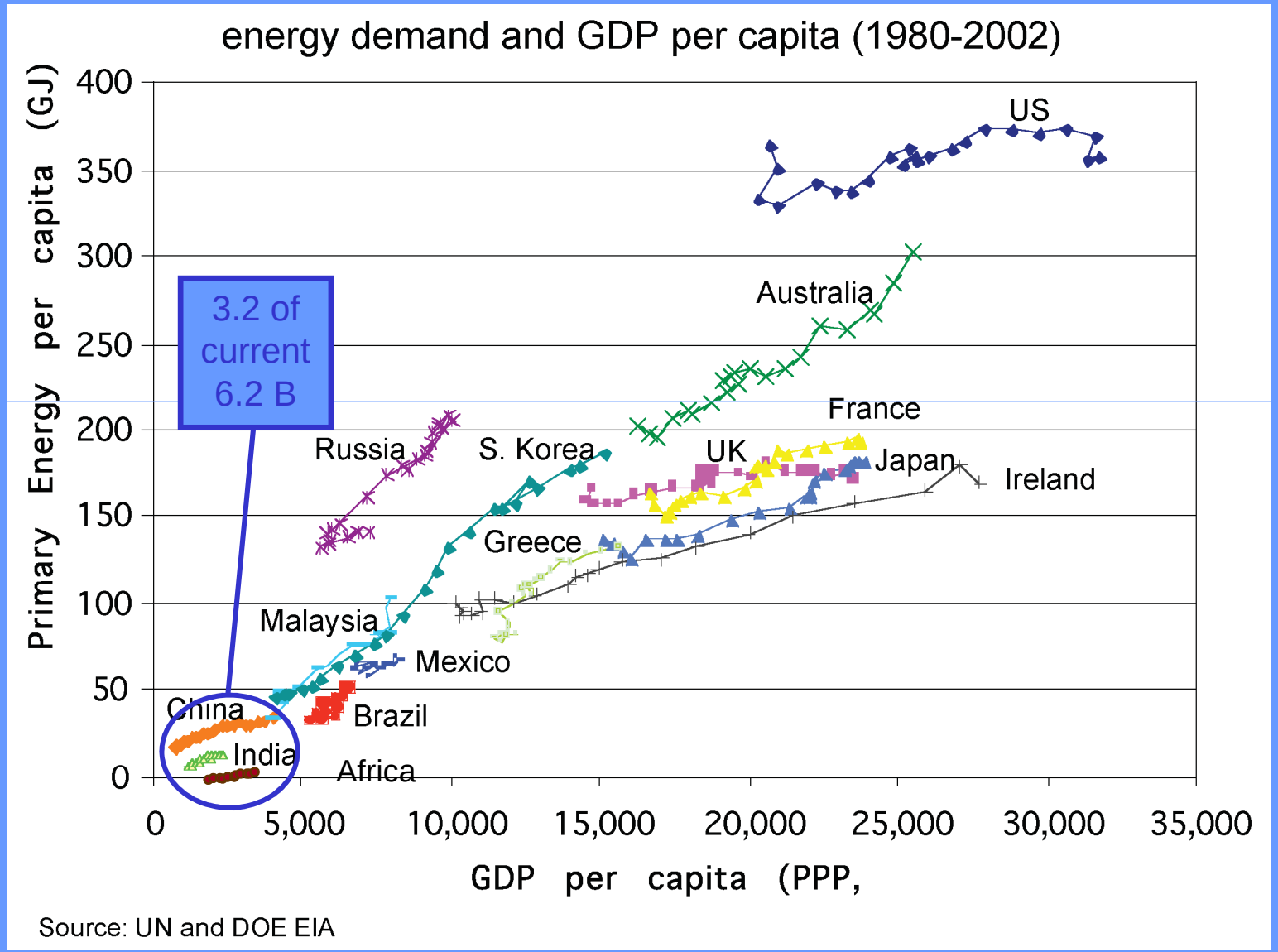
…BUT there is hope

Solar energy is a source of sufficient scale to meet global future energy needs

solar energy
- more sun hits surface in 1 hr, than energy used in one year



Energy Use Per Person in Different Countries



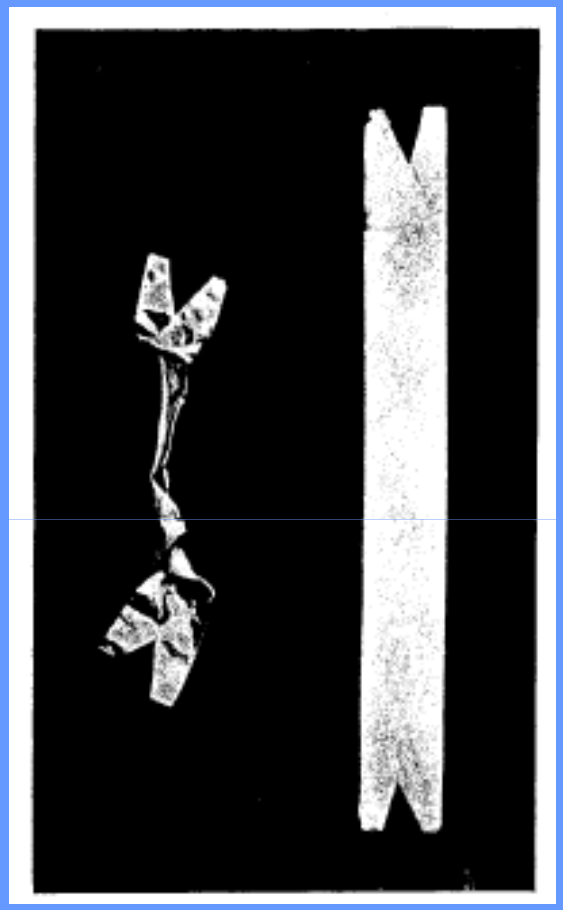
Nocera, *Dædalus*, Fall **2006**

Some “Sociological” Remarks

- **Need for energy is so enormous that conventional, long-discussed sources will not be enough**
- **Current technologies not enough, need new science to take care of the future energy demands**
  - **renewable energy research is not an engineering problem…needs to be tackled as a basic science problem…materials, catalysis and new modes of reactivity or chemical bonds**
- **Physics and Chemistry are THE central sciences of energy (light capture, conversion and storage in bonds or new materials).**

The “Basic Physics” of Hydrogen in Materials

- Hydrogen Embrittlement: Pd-Ag
- Metal Insulator Transition: Y_2O_3-H
- Superconductivity: Pd-H
- Ortho - Para conversion rates
- Spin Polarized Hydrogen – BEC in
- High Pressure Hydrogen – Metallic H_2



Pure Pd and Pd-25%Ag alloy same size specimens after 30 cycles of heating and cooling in H_2 atmosphere.

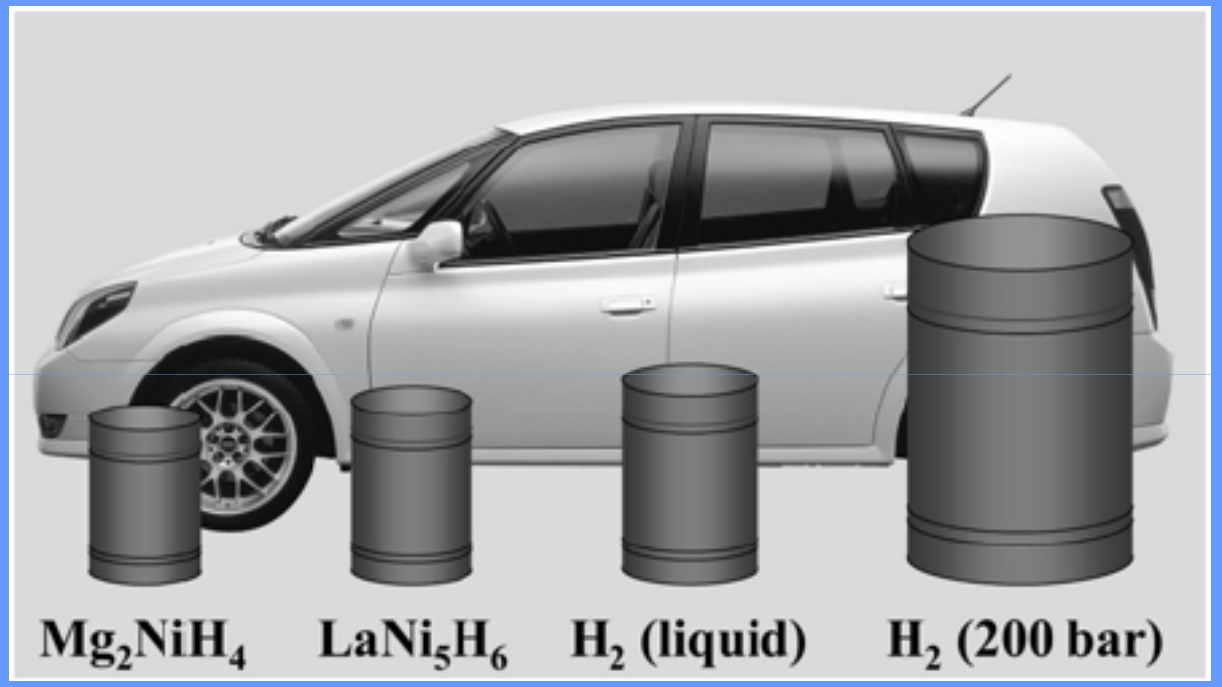
Hydrogen Storage: The "Grand Challenge"

Goal: On-board hydrogen storage for > 300 mile driving range and meet all performance (wt, vol, kinetics, etc.) , safety and cost requirements.

These Are System Targets

Examples of Targets	2010	2015
System Gravimetric Capacity (net)	6 wt.% (2.0 kWh/kg)	9 wt.% (3.0 kWh/kg)
System Volumetric Capacity (net)	1.5 kWh/L (45 g/L)	2.7 kWh/L (81 g/L)
Storage System Cost	$4/kWh (~$133/kg H_2)	$2/kWh ($67/kg H_2)
Min. Full Flow Rate	0.02 g/s/kW	0.02 g/s/kW
Refueling Time (for 5 kg)	3 min	2.5 min
Cycle Life (Durability)	1000 cycles	1500 cycles

QUIZ #1: What is it that is striking about the following picture ?



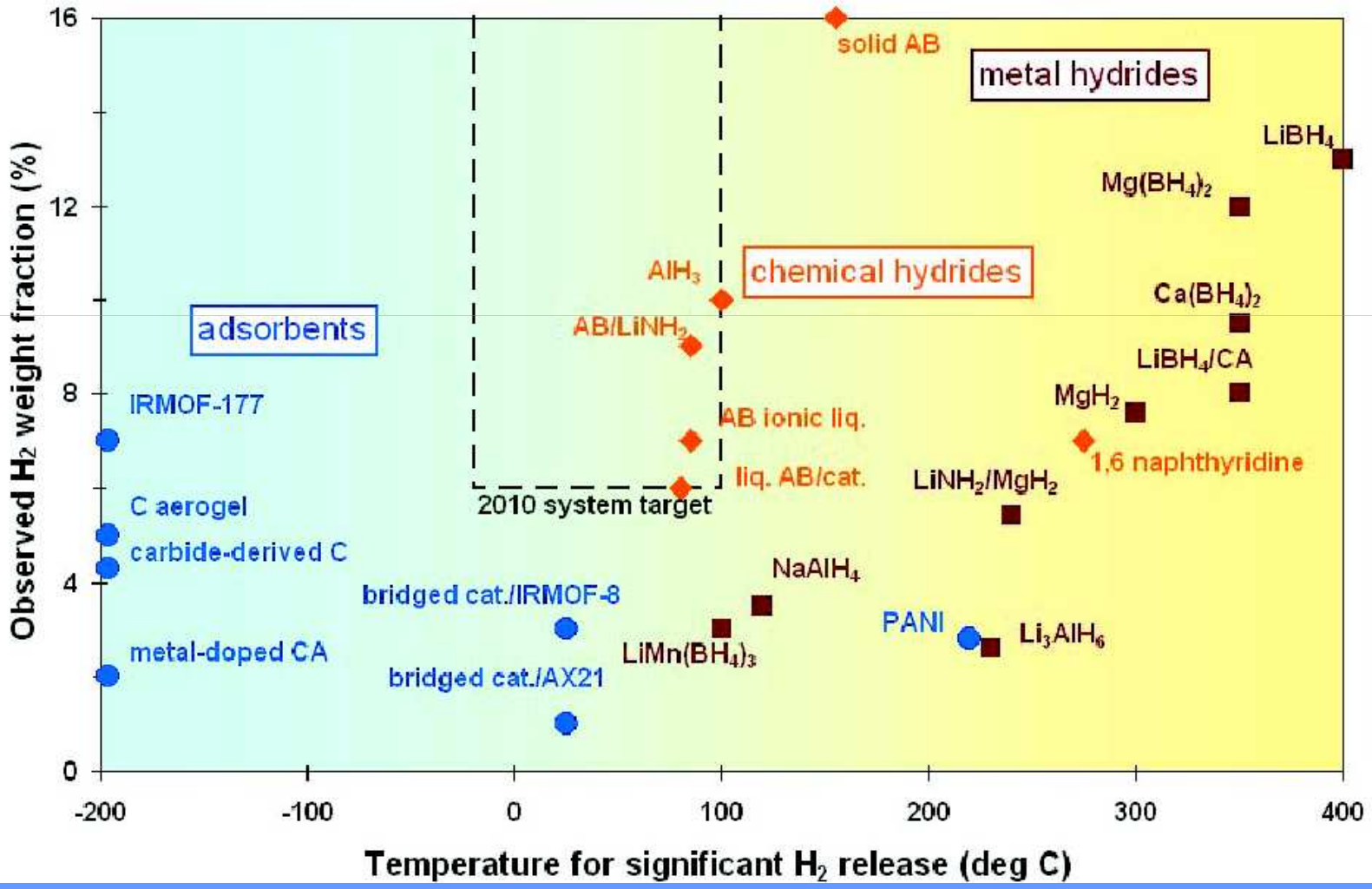
Desirable Characteristics of an Ideal Material

- High capacity absorption at room temperature (volumetric as well as gravimetric).
- Desorption at moderate temperatures
- Rapid kinetics
- Zero degradation with repeated cycling.

SUCH A MATERIAL DOES NOT EXIST TODAY !

SO, WHAT ARE THE MATERIALS THAT DO EXIST AN HOW GOOD ARE THEY ?

Progress: Material Capacity vs. Temperature



Originally Posted: Sat, 2 Aug 20:33 EDT

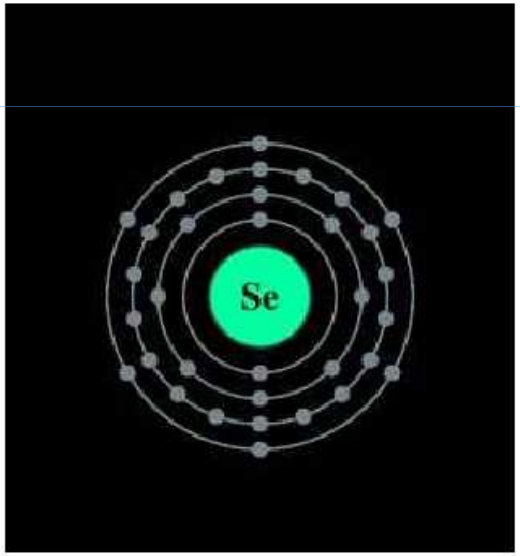
Fill My Valence Electron Shell

Date: 2008-08-02, 8:33PM EDT

A little about me: My name is ~~Selenium~~ Hydrogen, but you can just call me ~~Se~~ H2. I take good care of myself--~~78.96~~ 2.0 amu and disease free. I've been ionized before, but I'm not really into that anymore. but I am not interested in that.

I'm looking for someone to really bond with. Covalently. I ~~want to~~ can be in a truly stable relationship. Do you have what I need?

I'm not just looking for another Bromine. I want someone who will treat me ~~like a princess~~ with high energy and together we can ~~become noble~~ save the world.



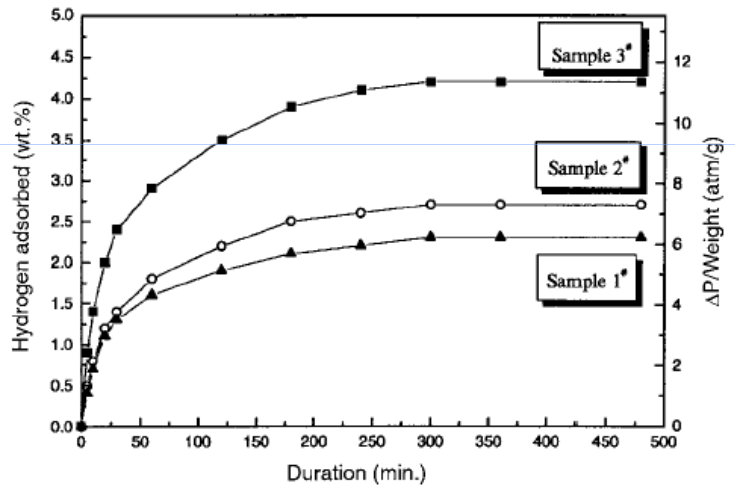
- Location: Unknown
- it's NOT ok to contact this poster with services or other commercial interests

PostingID: 780731449

“Coloring” Research

Hydrogen Storage in Single-Walled Carbon Nanotubes at Room Temperature

C. Liu,[1] Y. Y. Fan,[1] M. Liu,[1] H. T. Cong,[2] H. M. Cheng,[1]*
M. S. Dresselhaus,[3]*

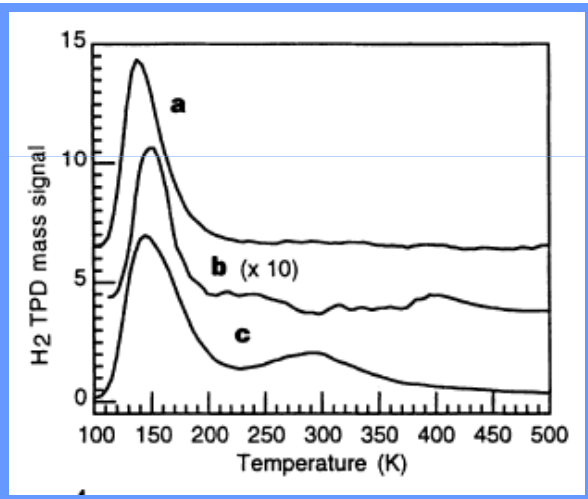


Science, **286**, 1127, 1999.

Storage of hydrogen in single-walled carbon nanotubes

A. C. Dillon*, K. M. Jones*, T. A. Bekkedahl*,
C. H. Kiang†, D. S. Bethune† & M. J. Heben*

* *National Renewable Energy Laboratory, 1617 Cole Boulevard, Golden, Colorado 80401-3393, USA*
† *IBM Research Division, Almaden Research Center, 650 Harry Road, San Jose, California 95120-6099, USA*



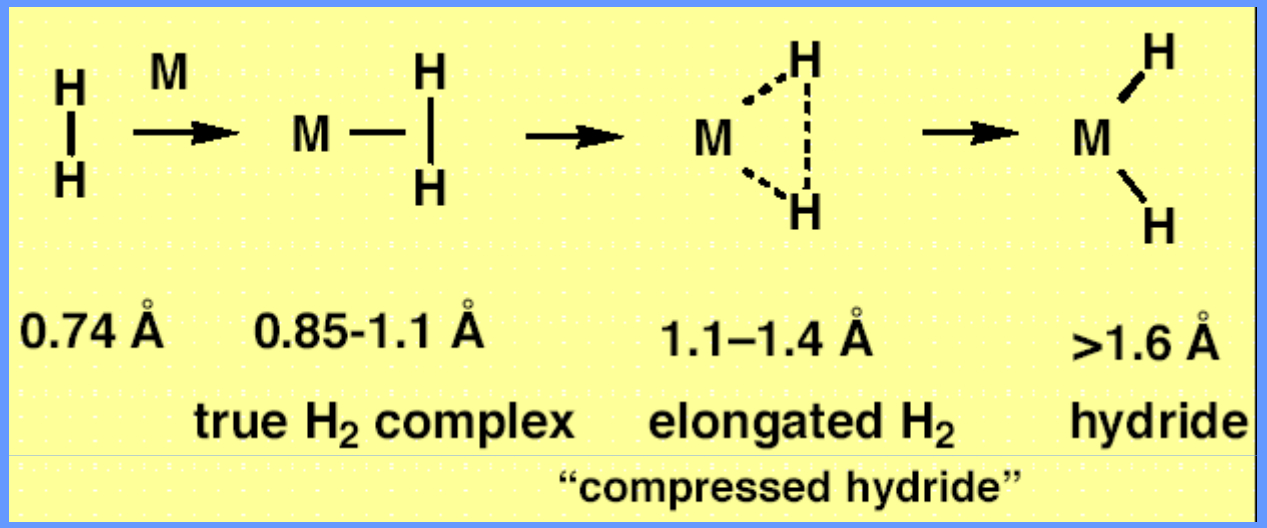
Nature, **386**, 377, 1997

But Co is used as catalyst for making CNT’s.

Some More Sociological Remarks

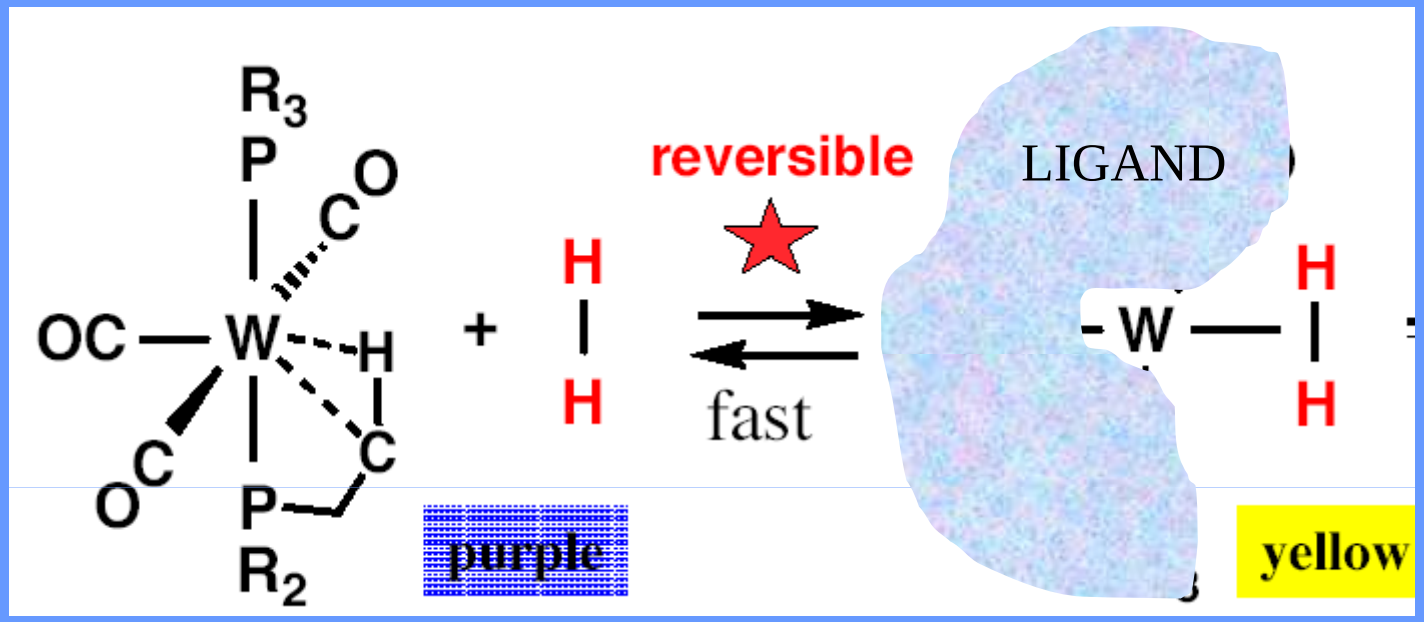
- "NANO" – is highly interdisciplinary.
- Involves interplay of physics, chemistry, materials science etc.
- Hydrogen storage research is a good example of this interplay (as you will see).

H-H Bond distances



- Continuous range possible
- Another way to characterize the "ideal" storage material

Kubas Complex - 1984

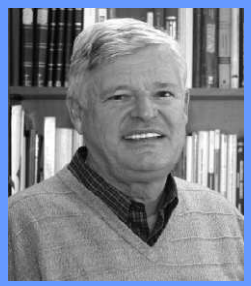


What is a "complex"?

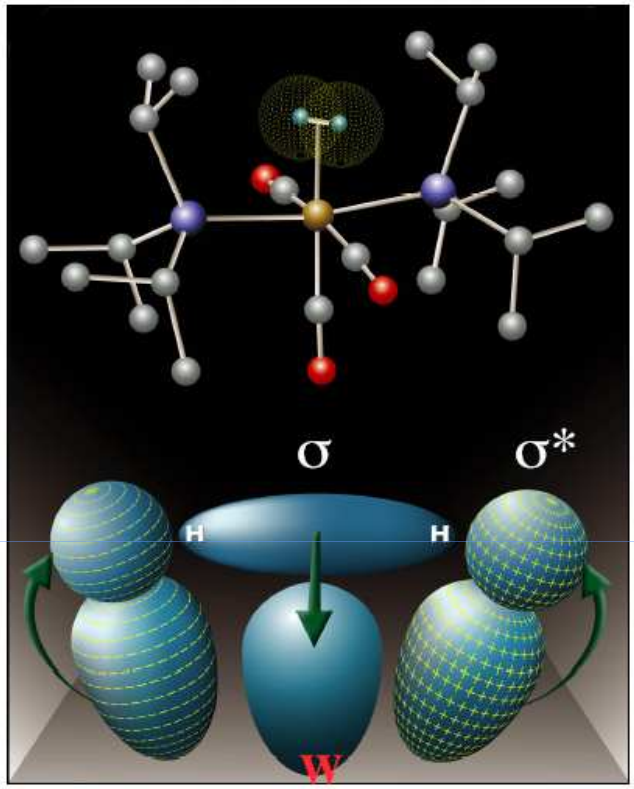
Some 562 of these "complexes" are known today

In all of them only 1 H_2 is reversibly absorbed – with the exception of one where 2 H_2 molecules participate…

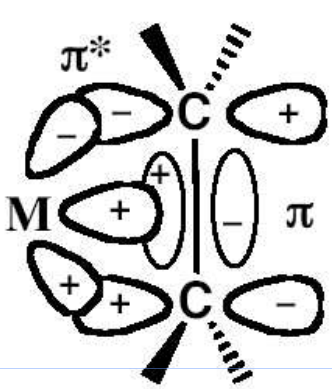
SPECIAL BRANCH OF ORGANO-METALLIC CHEMISTRY



backdonation is critical in stabilizing H_2 and other σ complexes

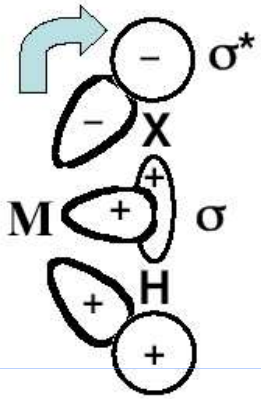


Bonding in $W(CO)_3(P^iPr_3)_2(H_2)$: *donation of the bonding σ electrons in H_2* to a filled metal d orbital and backdonation to the antibonding orbital (σ*) of H_2



M–π bond

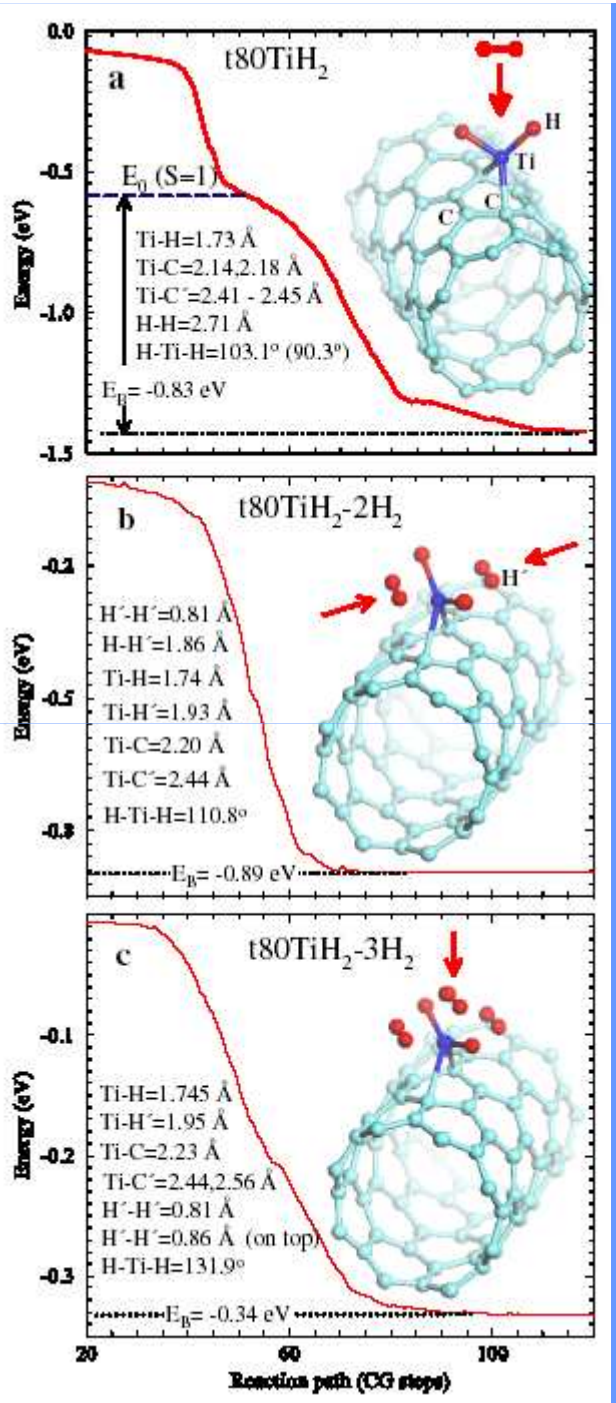
olefin complex



M–σ bond

X = H, C, Si, etc

Hay, P. J. *Chem. Phys. Lett.* **1984**, *103*, 466.



PRL 94, 175501 (2005) PHYSICAL REVIEW LETTERS week ending 6 MAY 2005

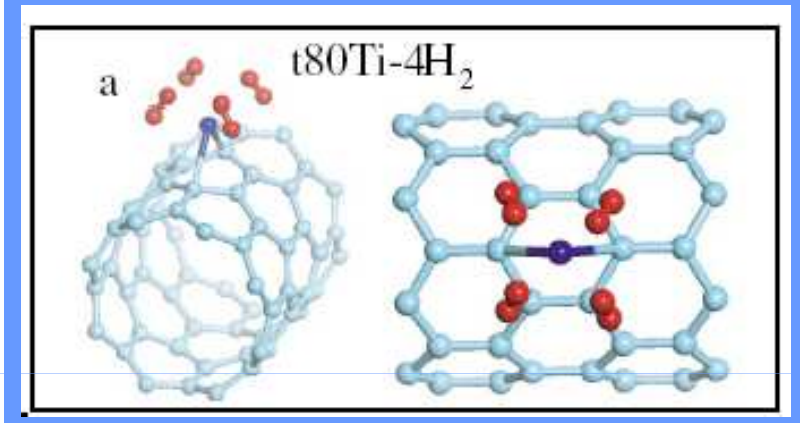
Titanium-Decorated Carbon Nanotubes as a Potential High-Capacity Hydrogen Storage Medium

T. Yildirim[1] and S. Ciraci[2]

[1]*NIST Center for Neutron Research, National Institute of Standards and Technology, Gaithersburg, Maryland 20899, USA*

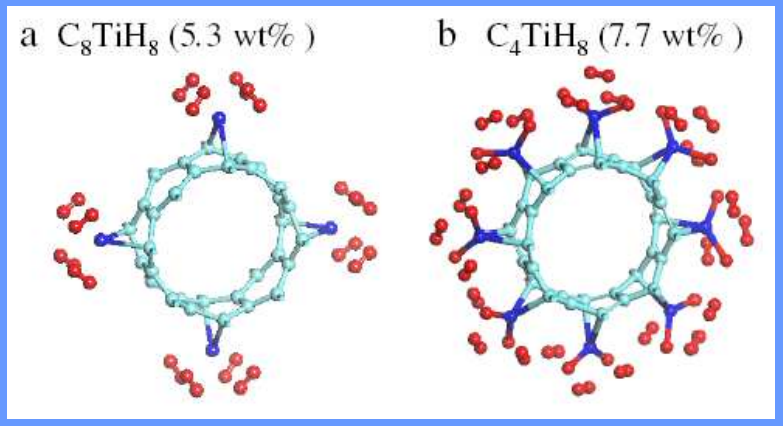
[2]*Physics Department, Bilkent University, 06800 Bilkent, Ankara, Turkey*

(Received 5 November 2004; published 5 May 2005)



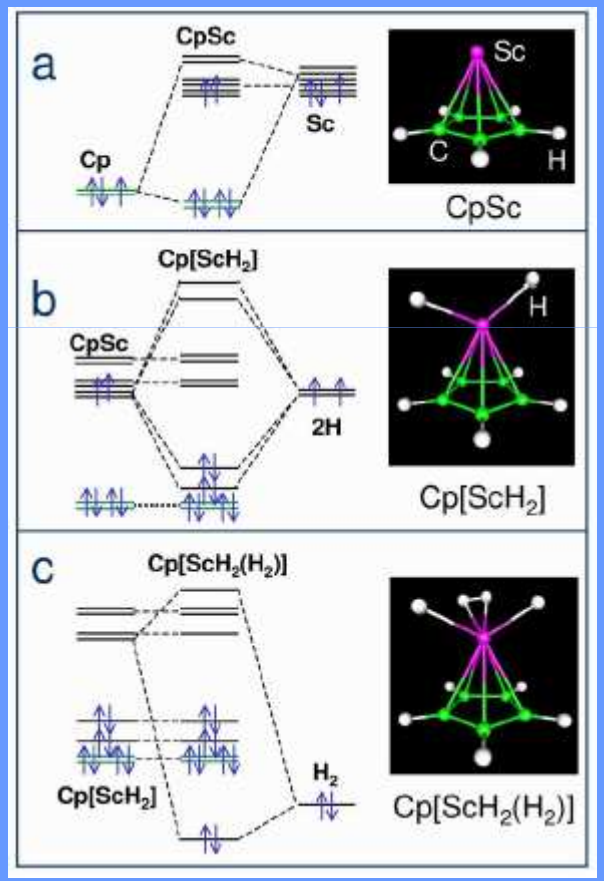
t80Ti-$4H_2$.

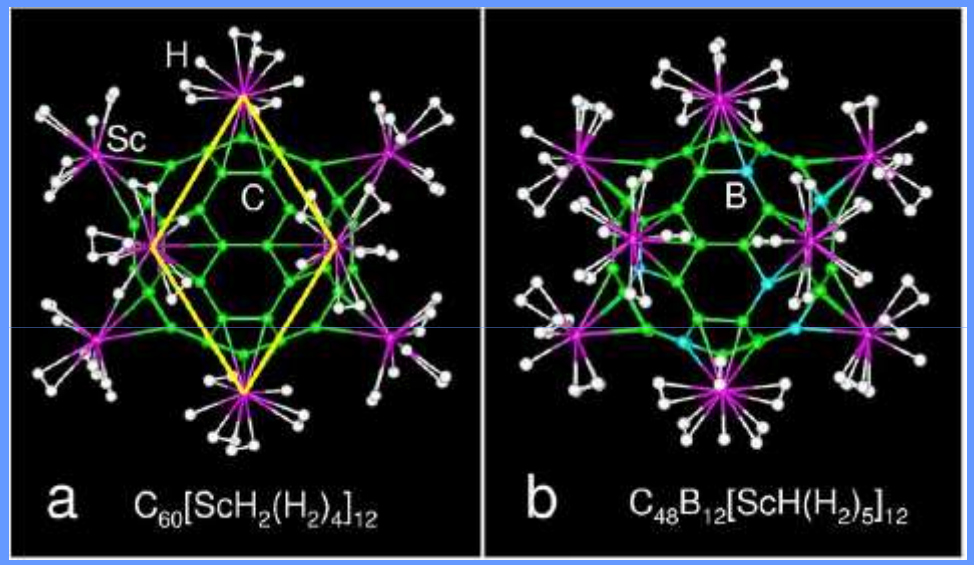
H-H 0.84 A
Ti-H 1.9 A
Ti-C 2.17 A
Ti-C' 2.4 A



Hydrogen Storage in Novel Organometallic Buckyballs

Yufeng Zhao, Yong-Hyun Kim, A. C. Dillon, M. J. Heben, and S. B. Zhang
National Renewable Energy Laboratory, Golden, Colorado 80401, USA
(Received 8 December 2004; published 22 April 2005)





C_{60} ~7 %

$C_{48}B_{12}$ ~8.7 %

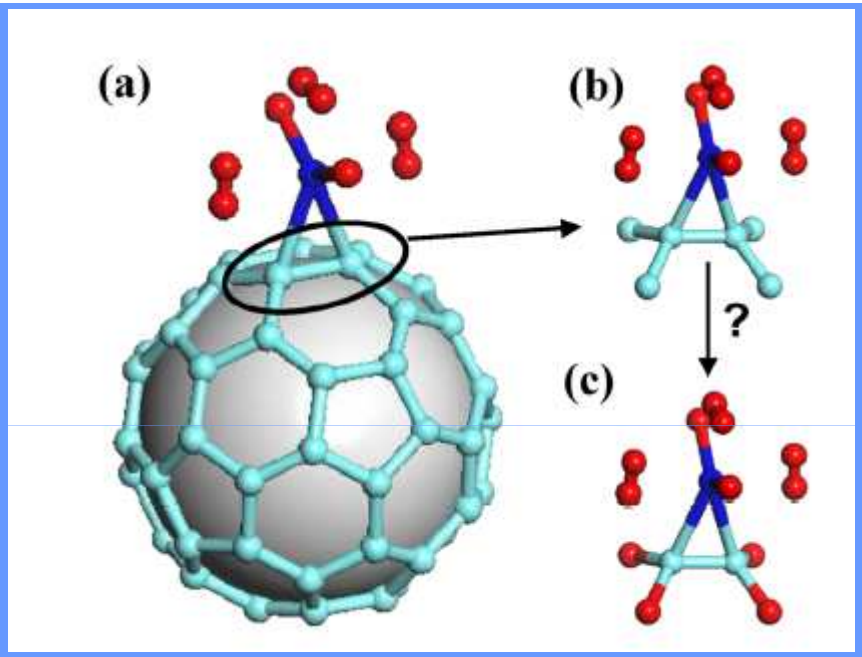
TABLE I. Calculated consecutive binding energies of H_2 molecules (in eV/H_2). In the case of buckyballs, twelve H_2 were added per calculation. A similar trend with the Cp ring case in the table suggests that the procedure is justified.

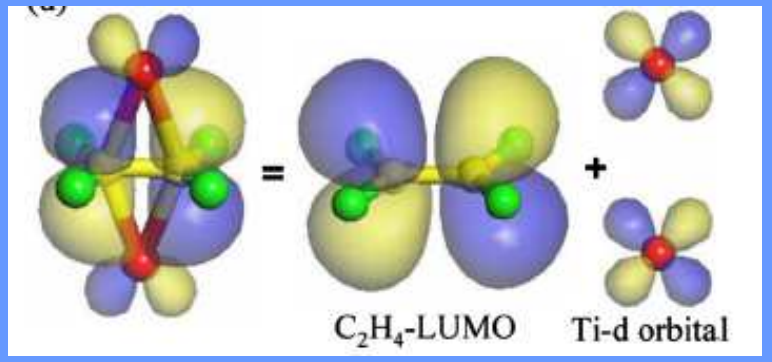
	1st H_2	2nd H_2	3rd H_2	4th H_2	5th H_2
$Cp[ScH_2]$	0.29	0.28	0.46	0.23	
$C_{60}[ScH_2]_{12}$	0.30	0.35	0.42	0.26	
$C_{48}B_{12}[ScH]_{12}$	0.31	0.35	0.30	0.33	0.24

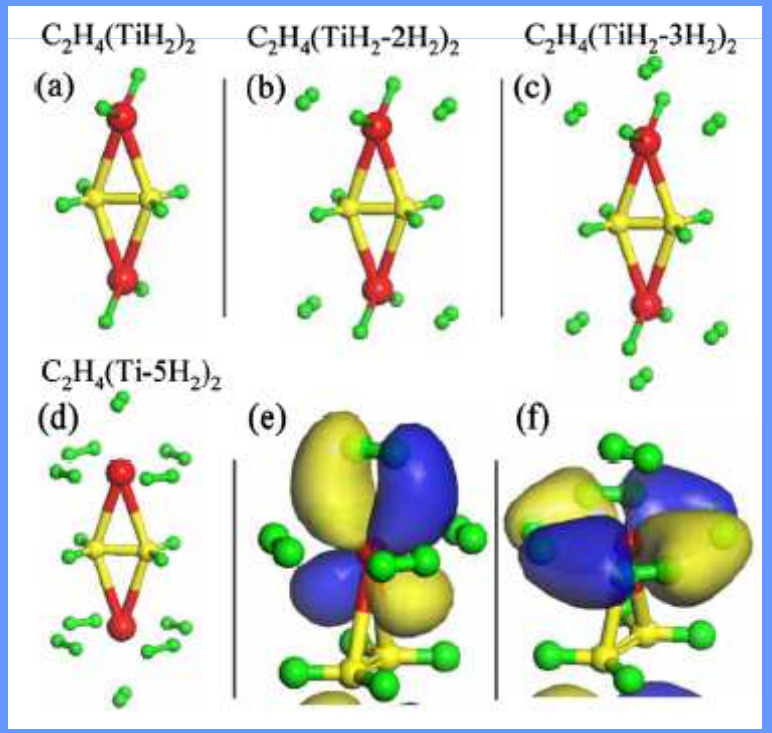
PRL 97, 226102 (2006) PHYSICAL REVIEW LETTERS week ending 1 DECEMBER 2006

Transition-Metal-Ethylene Complexes as High-Capacity Hydrogen-Storage Media

E. Durgun,[1,2] S. Ciraci,[1,2,*] W. Zhou,[3,4] and T. Yildirim[3,4]





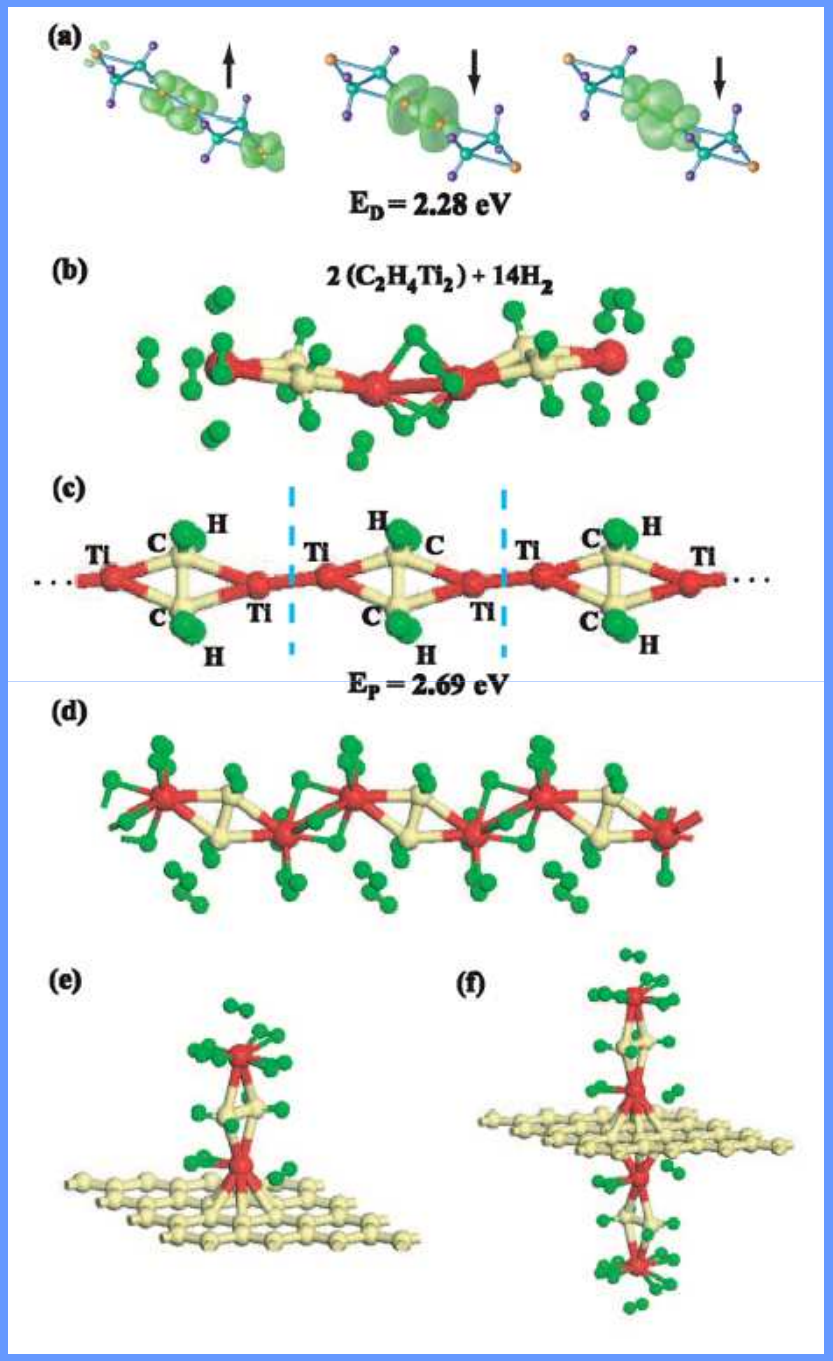


Bonding of single Ti to C_2H_4 – no energy barrier.

First H_2 adsorbed dissociatively

Add 4 more molecularly

H-H ~ 0.85 A



Dimerization and polymerization of Ti_2-C_2H_4

REDUCES # H_2 ADSORBED!

Proposals to prevent dimerization

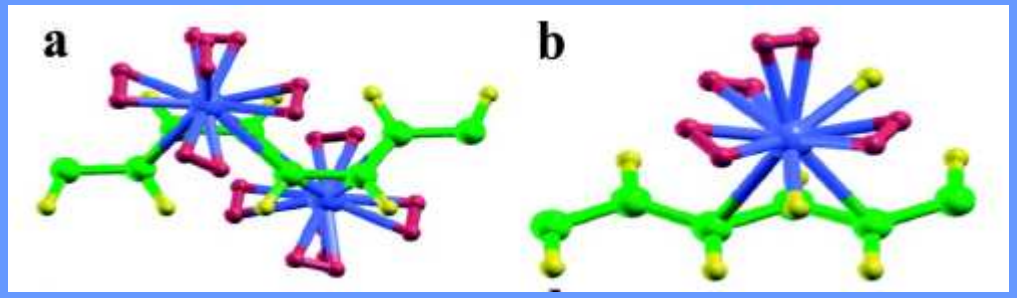
PRL 97, 056104 (2006) PHYSICAL REVIEW LETTERS week ending 4 AUGUST 2006

Combinatorial Search for Optimal Hydrogen-Storage Nanomaterials Based on Polymers

Hoonkyung Lee, Woon Ih Choi, and Jisoon Ihm*

Department of Physics and Astronomy, FPRD, and Center for Theoretical Physics, Seoul National University, Seoul 151-747, Korea

(Received 24 March 2006; published 4 August 2006)

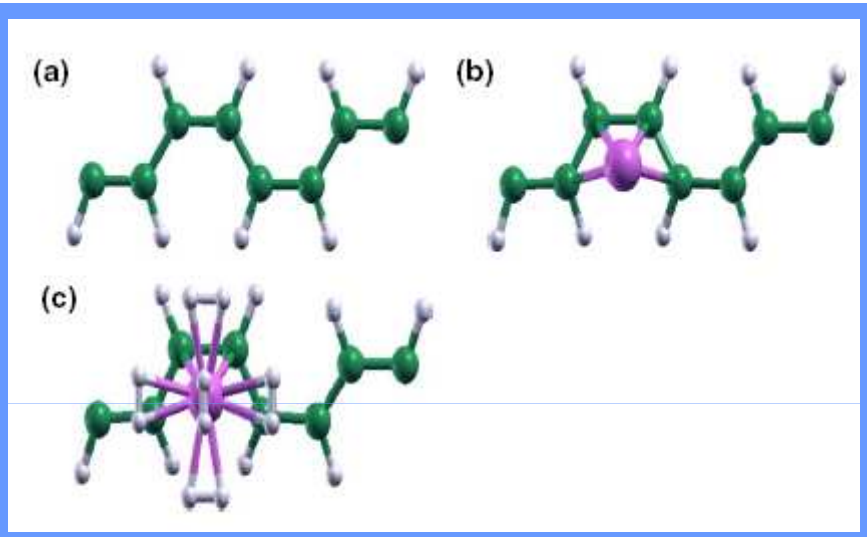


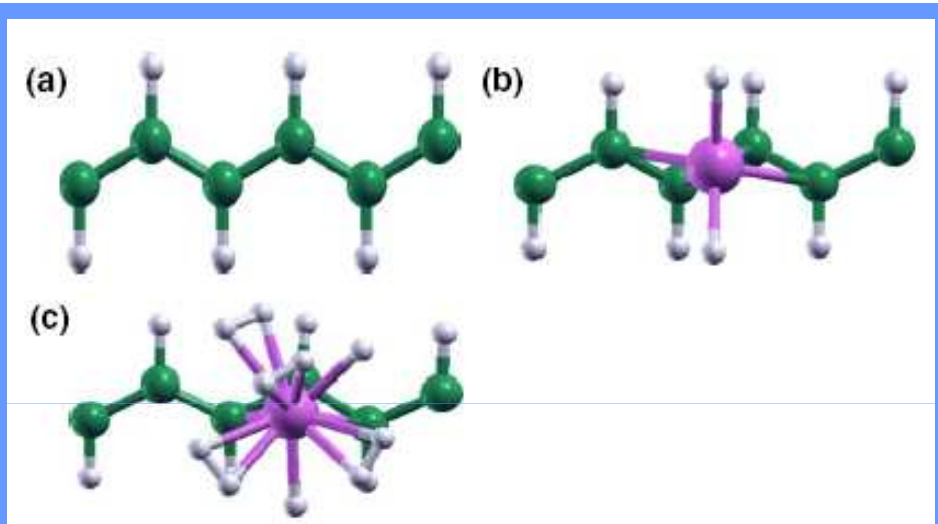
Materials	$N_{ads} - N_{des}$	N_{use}/N_{max}	G_{use}/G_{max} (wt %)	V_{use}/V_{max} (kg/m^3)
cis-PA	5.00 − 1.84	3.16/5	7.6/12	63/100
PPY	3.00 − 0.05	2.95/3	4.9/5	33/34
PANI-out	3.00 − 0.96	2.04/3	4.1/6	31/46
$C_{48}B_{12}Sc_{12}$	2.68 − 0.02	2.66/5	4.7/8.8	23/43
CNT	1.95 − 0.35	1.60/3	4.1/7.7	Not available

PHYSICAL REVIEW B **76**, 195110 (2007)

Ab initio study of dihydrogen binding in metal-decorated polyacetylene for hydrogen storage

Hoonkyung Lee, Woon Ih Choi, Manh Cuong Nguyen, Moon-Hyun Cha, Eungook Moon, and Jisoon Ihm*





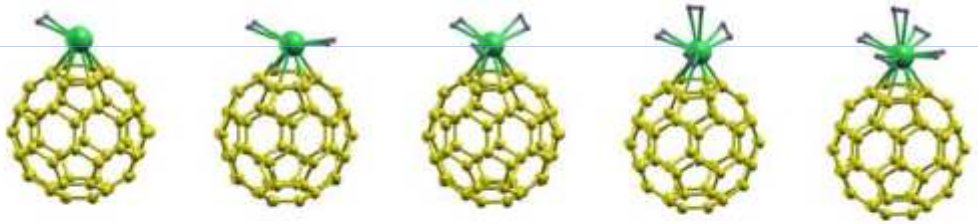
Materials	ZPE	$N_{ads}-N_{des}$	N_{use}/N_{max}	G_{use}/G_{max} (wt %)
Ti-decorated *cis*-PA	Yes	5.00–1.91	3.09/5	7.4/12
Sc-decorated *cis*-PA	Yes	0.86–0.00	0.86/5	2.1/12
Ti-decorated *trans*-PA	Yes	2.57–0.10	2.47/4	6.2/10
Sc-decorated *trans*-PA	Yes	1.90–0.05	1.85/5	4.4/12

PRL 100, 206806 (2008) PHYSICAL REVIEW LETTERS week ending 23 MAY 2008

Calcium as the Superior Coating Metal in Functionalization of Carbon Fullerenes for High-Capacity Hydrogen Storage

Mina Yoon,[1,2] Shenyuan Yang,[3,2] Christian Hicke,[4] Enge Wang,[3] David Geohegan,[1] and Zhenyu Zhang[1,2]

TABLE I. Hydrogen binding energies (in eV) for MC_{60} (M = Ca, Sr). For Ca, the GGA and LDA results are also compared.



Ca	0.222	0.214	0.233	0.206	0.204
(LDA)	0.413	0.396	0.415	0.376	0.385
Sr	0.200	0.192	0.202	0.181	0.179

Even More Sociological Remarks

- How come all these PRLs are only “theory” ?
- Is it yet another “quirk” of our funding system ?

Encouraging Predictions from calculations!

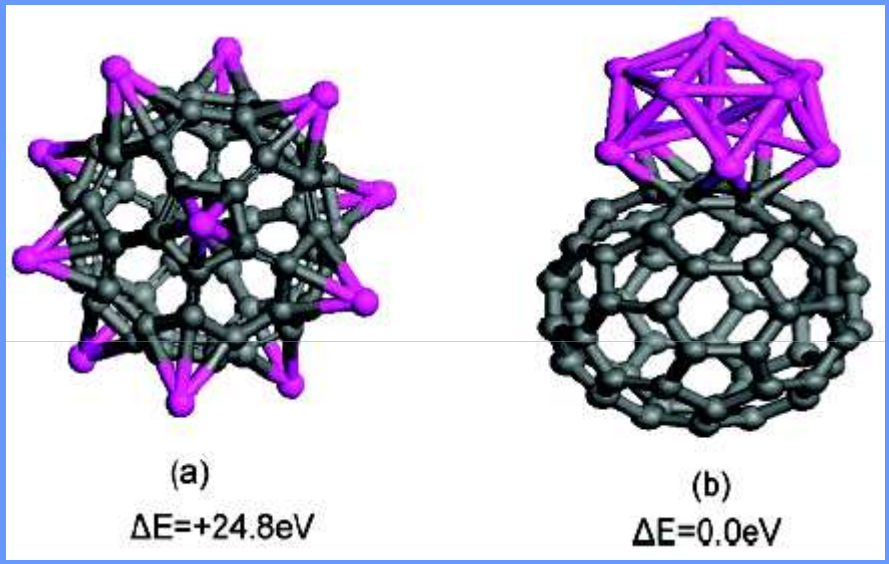
But tempered, again by theorists…..

Agglomeration or Clustering Problems – Guidelines from Theory

Clustering of Ti on a C_{60} Surface and Its Effect on Hydrogen Storage

Qiang Sun,† Qian Wang,† Puru Jena,*,† and Yoshiyuki Kawazoe‡

Physics Department, Virginia Commonwealth University, Richmond, Virginia 23284, and Institute for Material Research, Tohoku University, Sendai 980-8577, Japan



The clustering of Ti atoms on the carbon nanostructures not only significantly changes the nature of hydrogen bonding but also greatly reduces the weight percentage of hydrogen storage.

Clustering of Sc on SWNT and Reduction of Hydrogen Uptake: *Ab-Initio* All-Electron Calculations

Pavel O. Krasnov,† Feng Ding,† Abhishek K. Singh, and Boris I. Yakobson*

Department of Mechanical Engineering & Materials Science, and Department of Chemistry, Rice University, Houston, Texas 77005

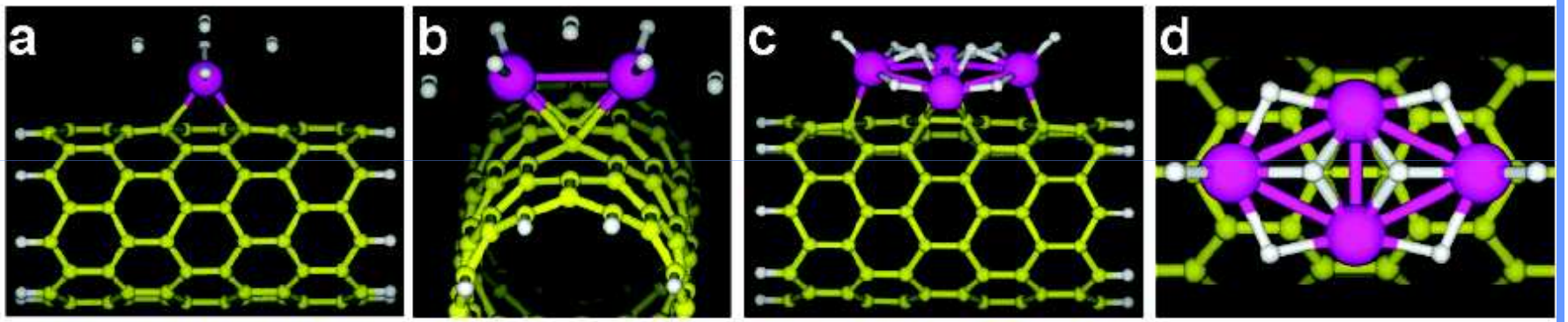
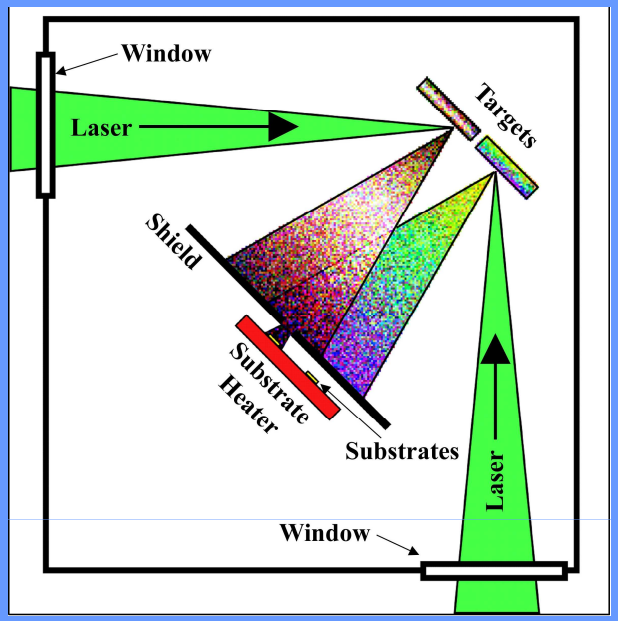


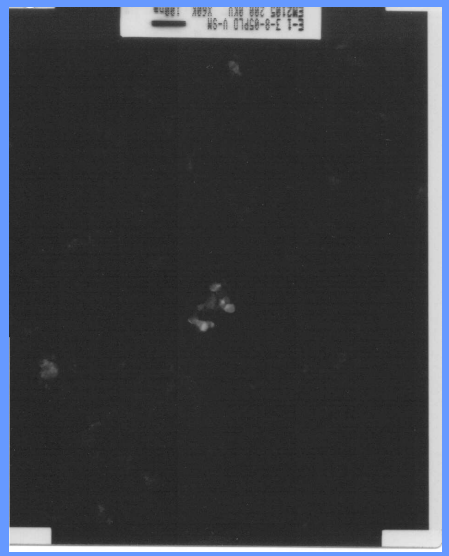
Figure 4. Hydrogen uptake on aggregated Sc_n ($n = 1, 2, 4$) clusters on (8,0) SWNT. (d) is the top view of (c).

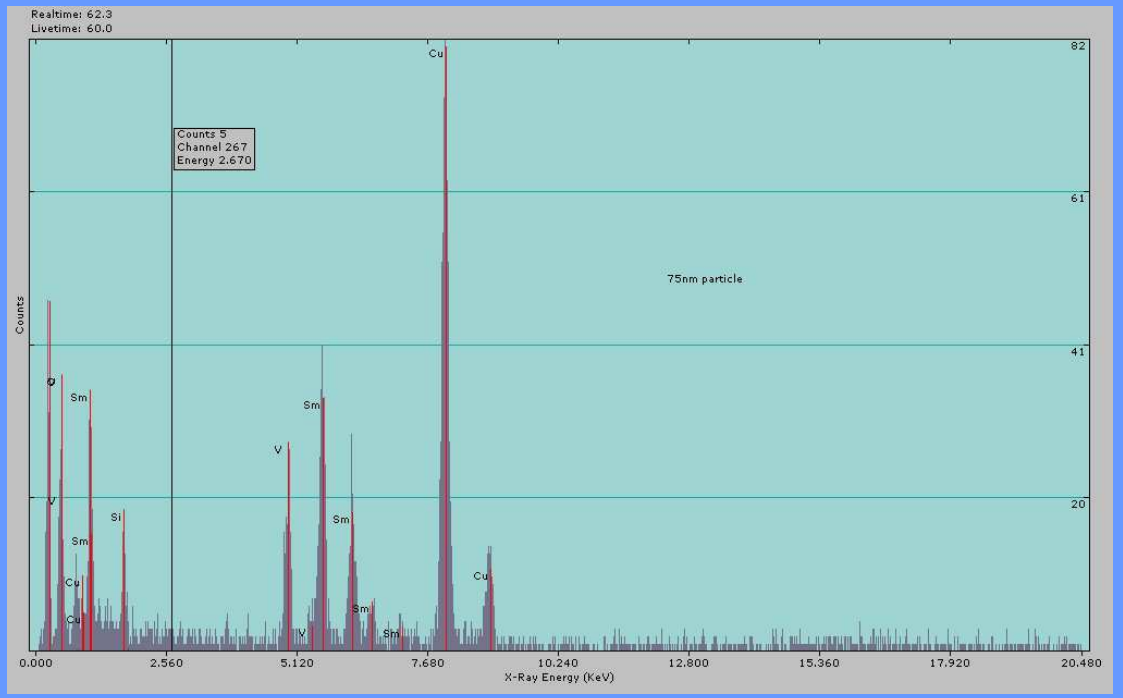
DIGRESSION ON EXPERIMENTAL METHODS

Synthesis of Nanoparticles - PLD

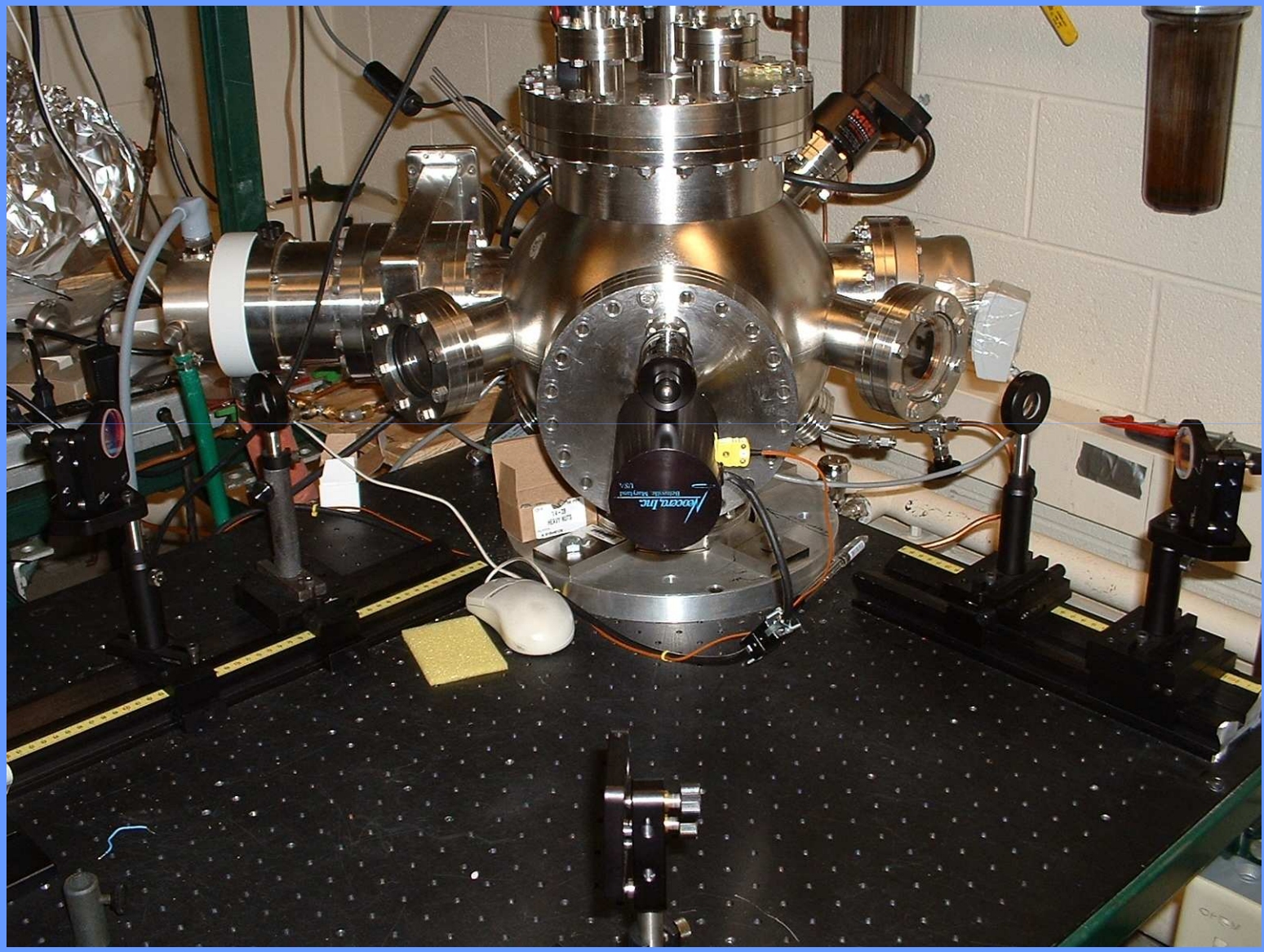


Sm-V, V, Nb, Nb-Al etc.

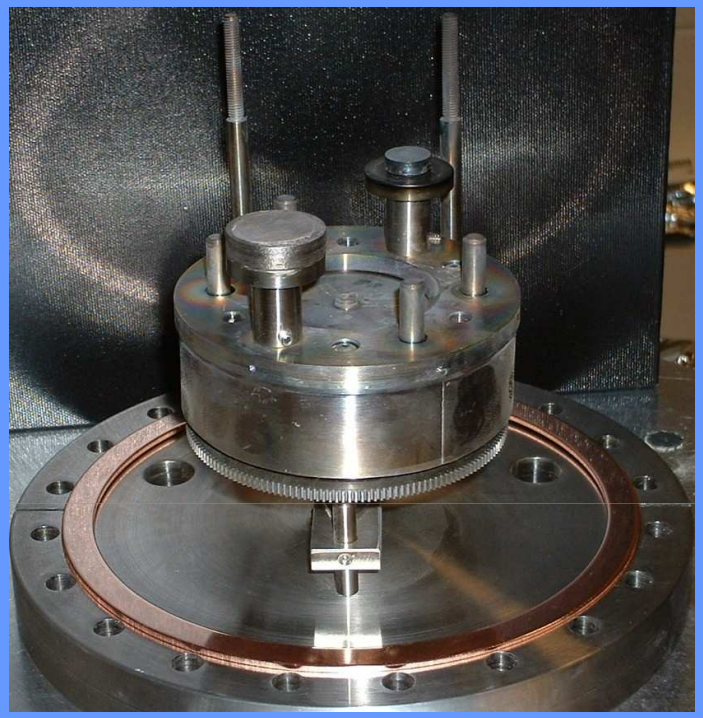


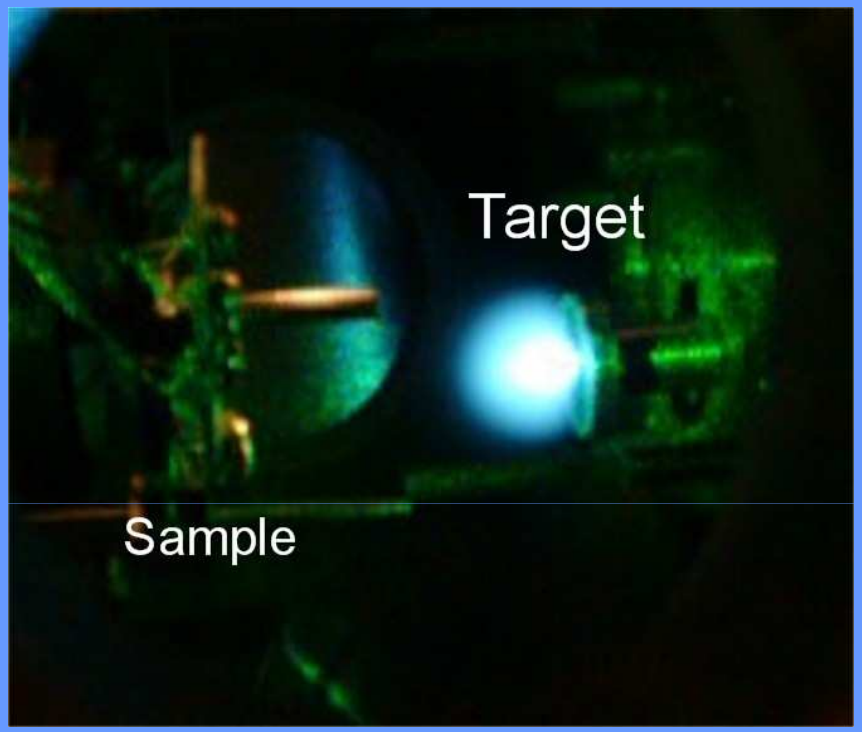


Pulsed Laser Deposition Apparatus



P.L.D. Basics





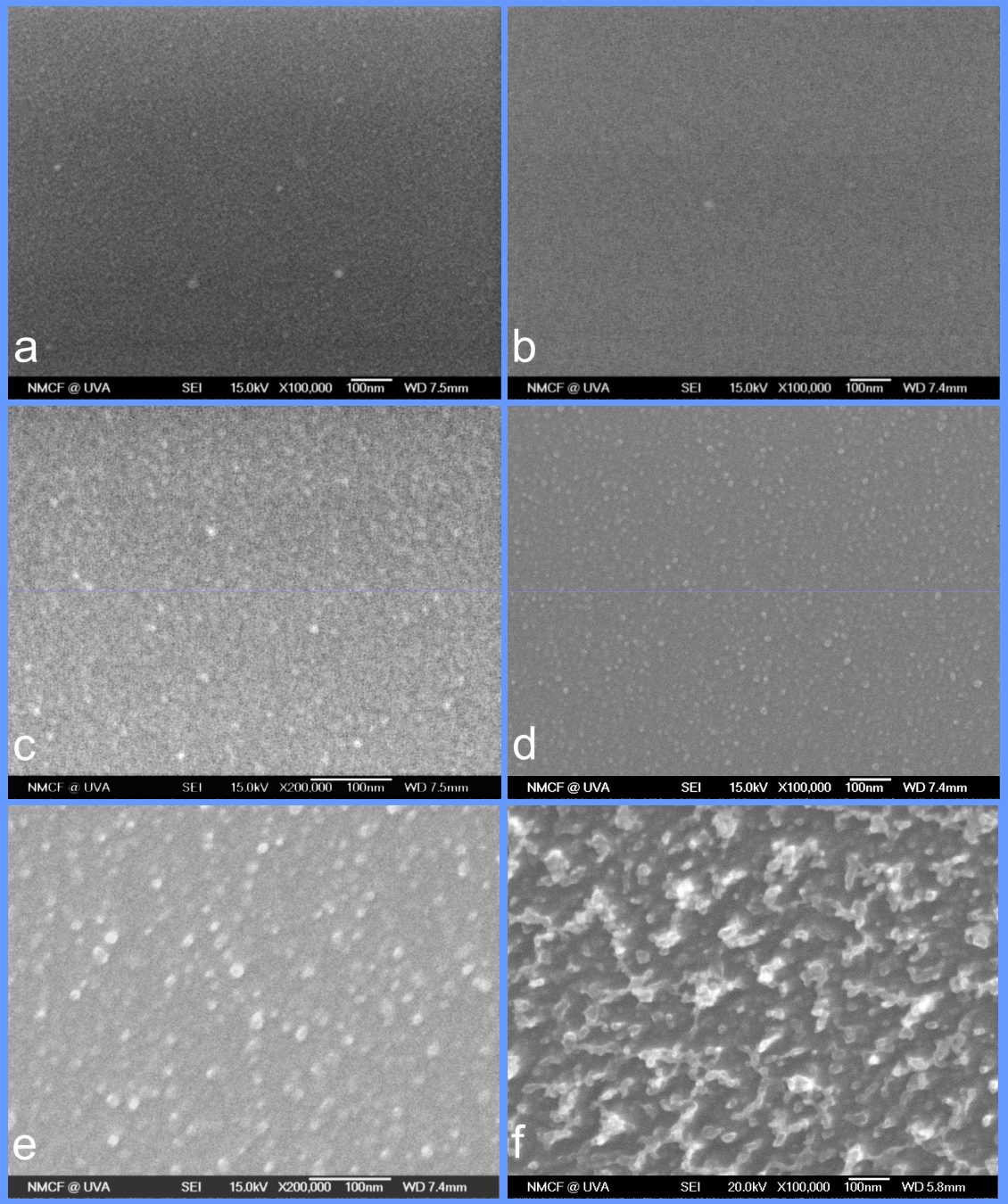
Rotating Target

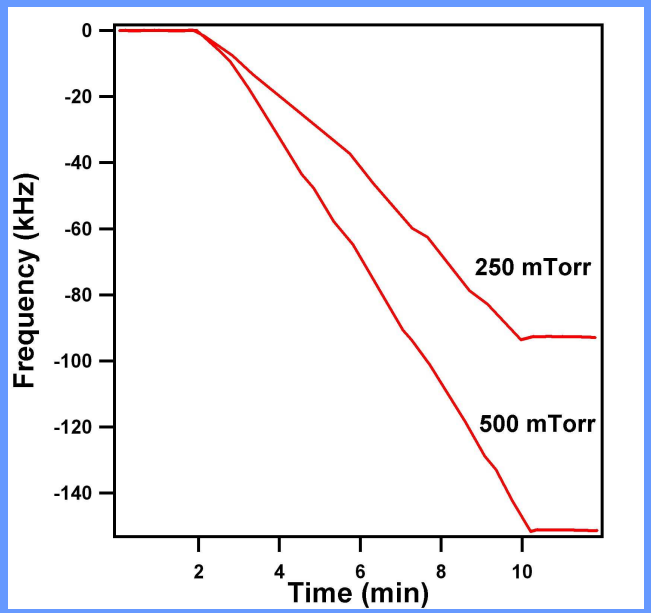
Visible Plume

Mostly Neutrals – but also some ions are produced

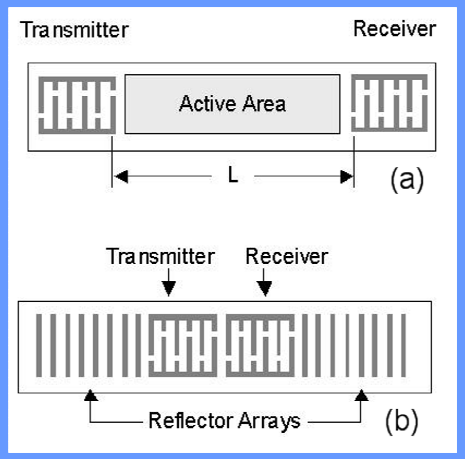
Nd – YAG laser, 10 Hz., 15-60 kJ/m^2

PLD “denominations”

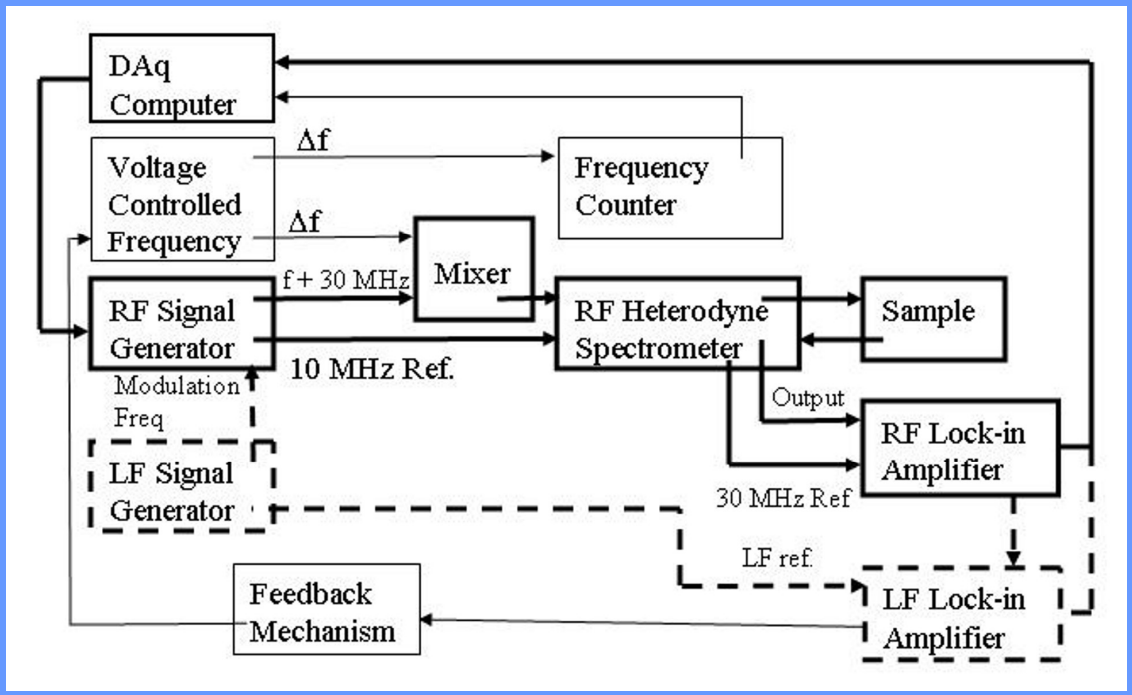

a
NMCF @ UVA SEI 15.0kV X100,000 100nm WD 7.5mm
b
NMCF @ UVA SEI 15.0kV X100,000 100nm WD 7.4mm
c
NMCF @ UVA SEI 15.0kV X200,000 100nm WD 7.5mm
d
NMCF @ UVA SEI 15.0kV X100,000 100nm WD 7.4mm
e
NMCF @ UVA SEI 15.0kV X200,000 100nm WD 7.4mm
f
NMCF @ UVA SEI 20.0kV X100,000 100nm WD 5.8mm


0
-20
-40
-60
-80
-100
-120
-140
Frequency (kHz)
250 mTorr
500 mTorr
2
4
6
8
10
Time (min)

Sensing with Surface Acoustics

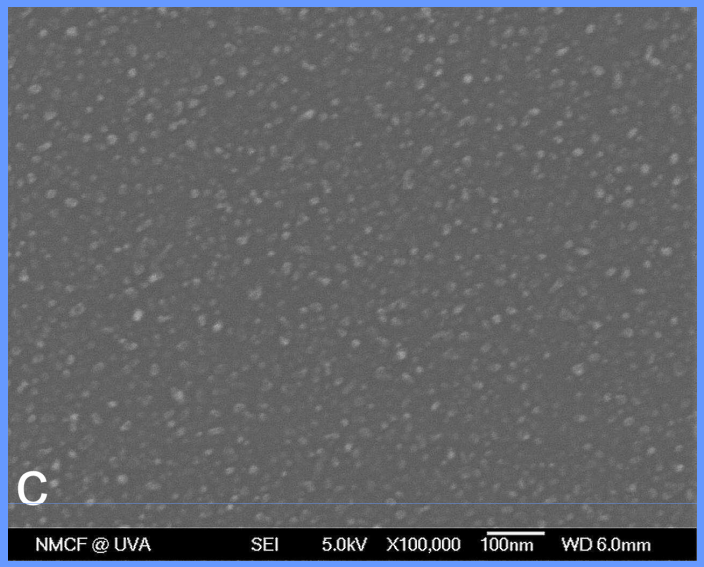


$$\frac{\Delta f}{f_0} = -c_m f_0 \frac{\Delta m}{A} + \text{part from conductivity changes}$$

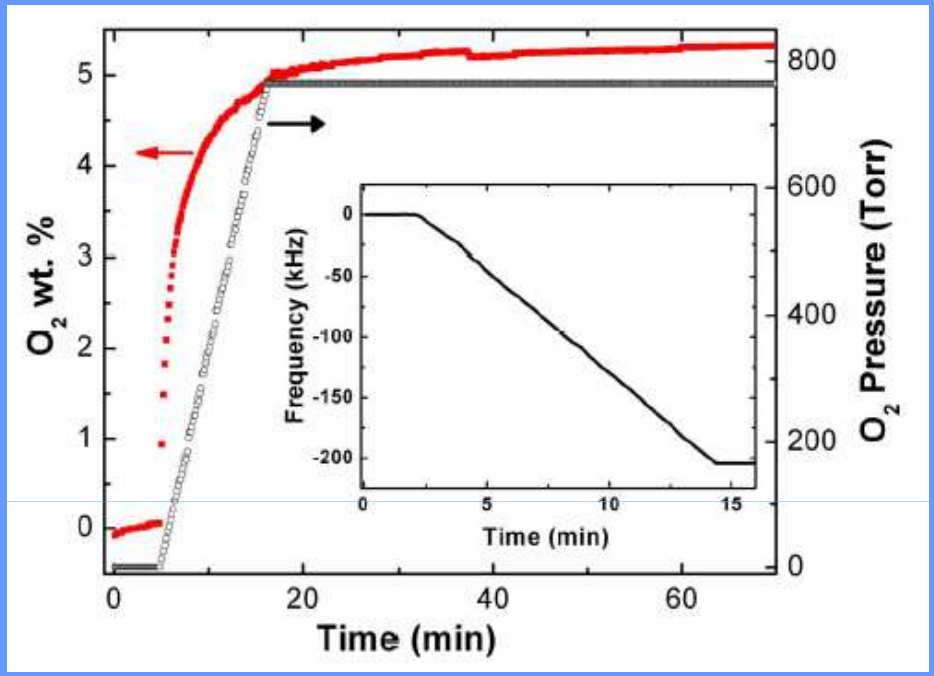


A.B. Phillips and B.S. Shivaram, Rev. Sci. Inst., **79**, 013907, 2008

Sensing with Surface Acoustics



Through SEM measurements of nanoparticles on Si and TEM grids we measure directly the average radius r = 7.32 +/- 1.09 nm.

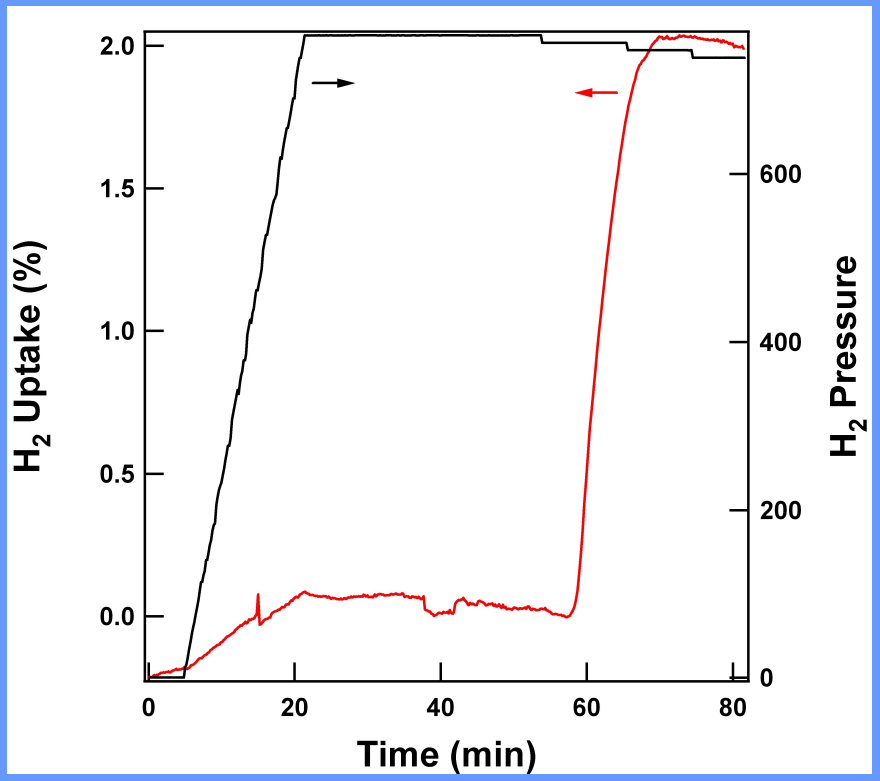


r = 7.63 +/- 0.18 nm for V_2O_5

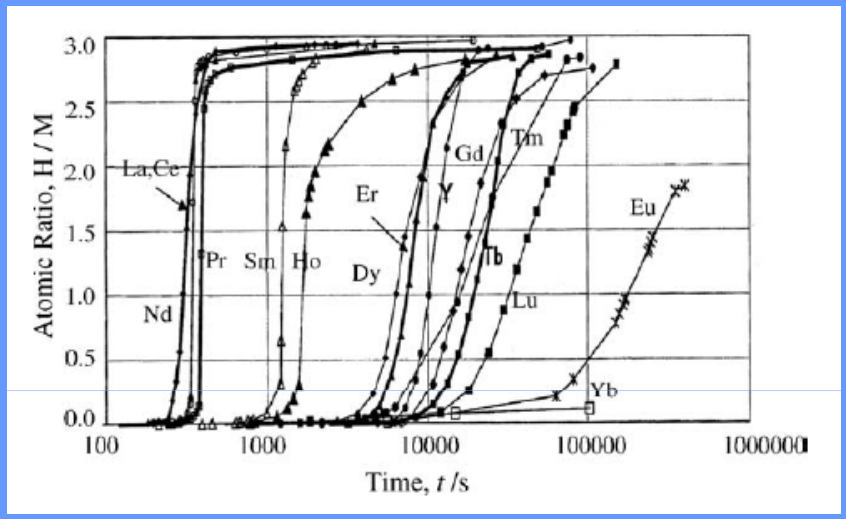
c_m=4.42 x10^{-9} cm^2 / MHz ng

A.B. Phillips and B.S. Shivaram, Appl. Phys. Lett., **91**, 153109, 2007.

Sensing with Surface Acoustics

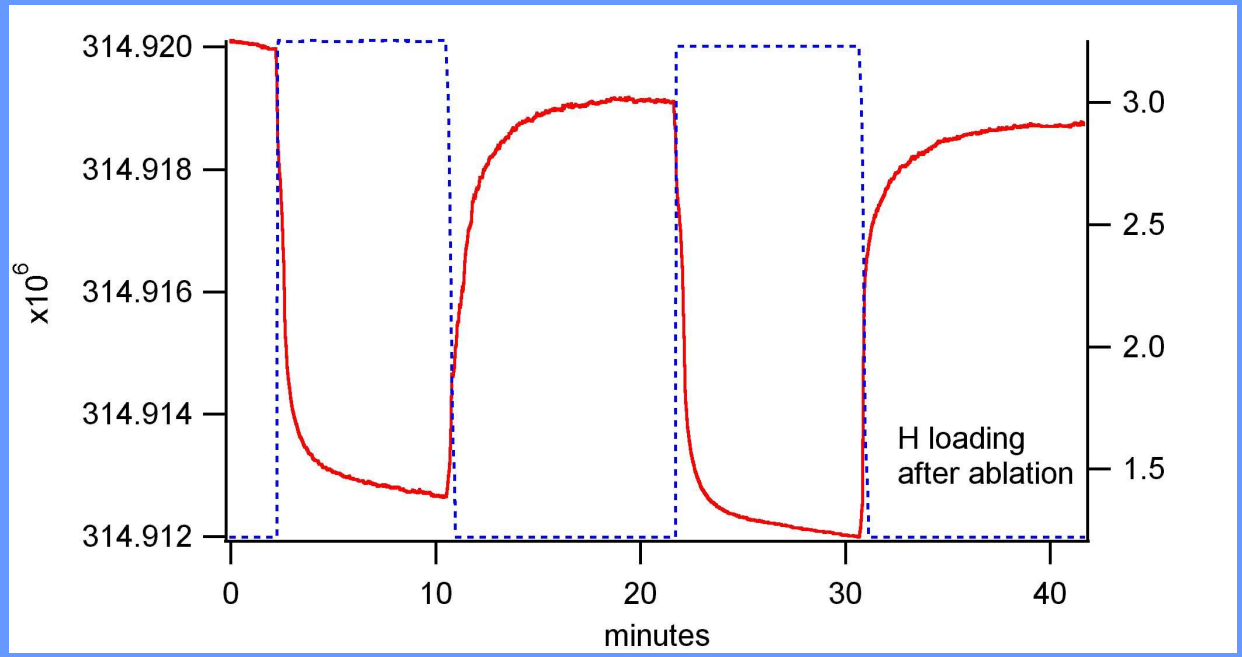


H_2 absorption in Sm nanoparticles
Phillips & Shivaram, RSI, 2007.



K. Hirano et al. / Journal of Alloys and Compounds, ***408–412,*** *351–354 (2006).*

Hydrogen Cycling in Vanadium Nanoparticles

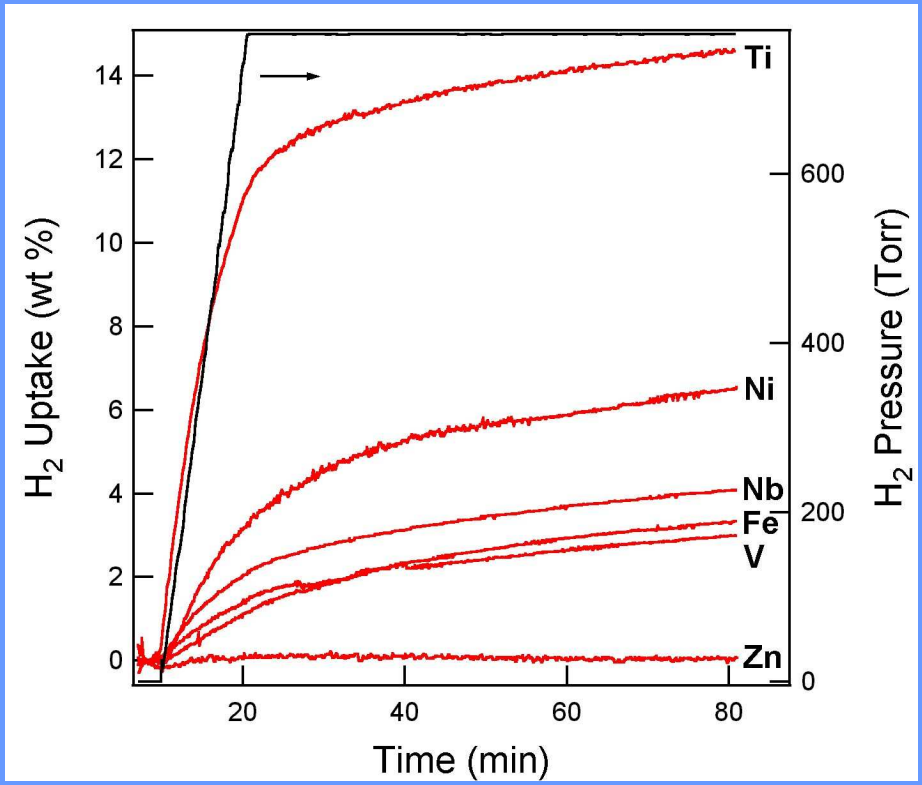


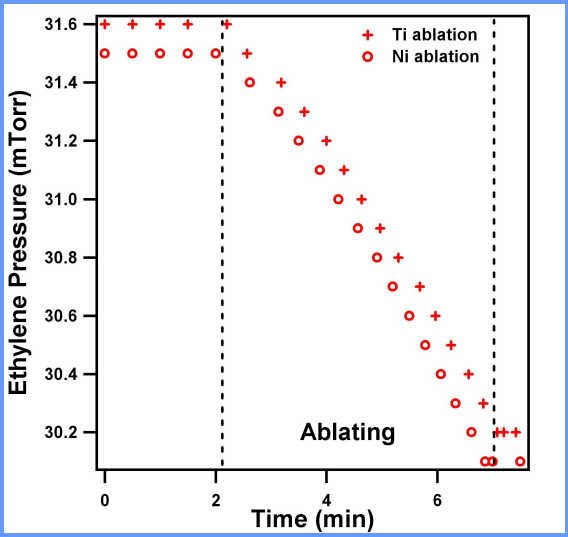
A.B. Phillips, G. Myneni and B.S. Shivaram, AIP. Proc., 2003.

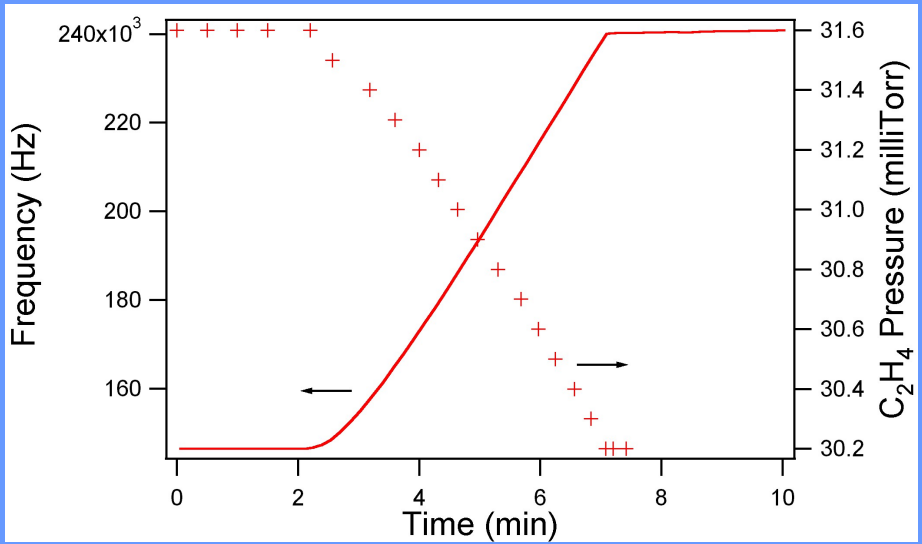
END OF
DIGRESSION ON
EXPERIMENTAL
METHODS

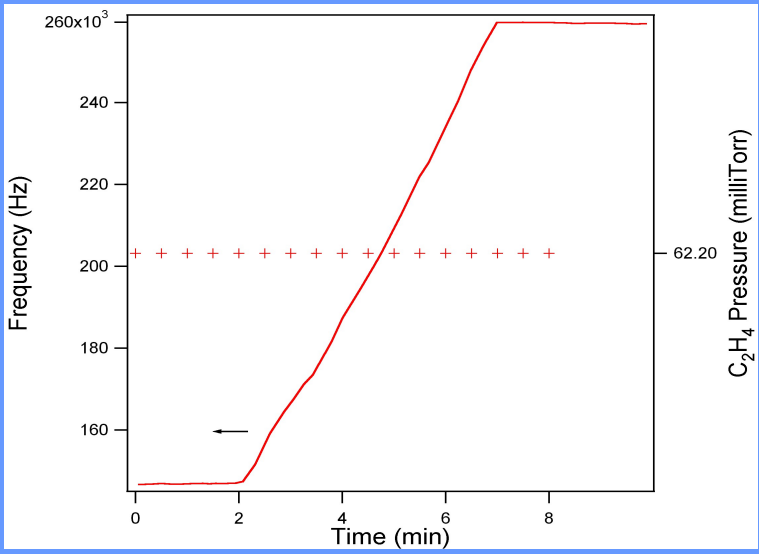
Adam's experiments

Ti and other TM ablated by laser in a UHV chamber in the presence of ethylene (C_2H_4).

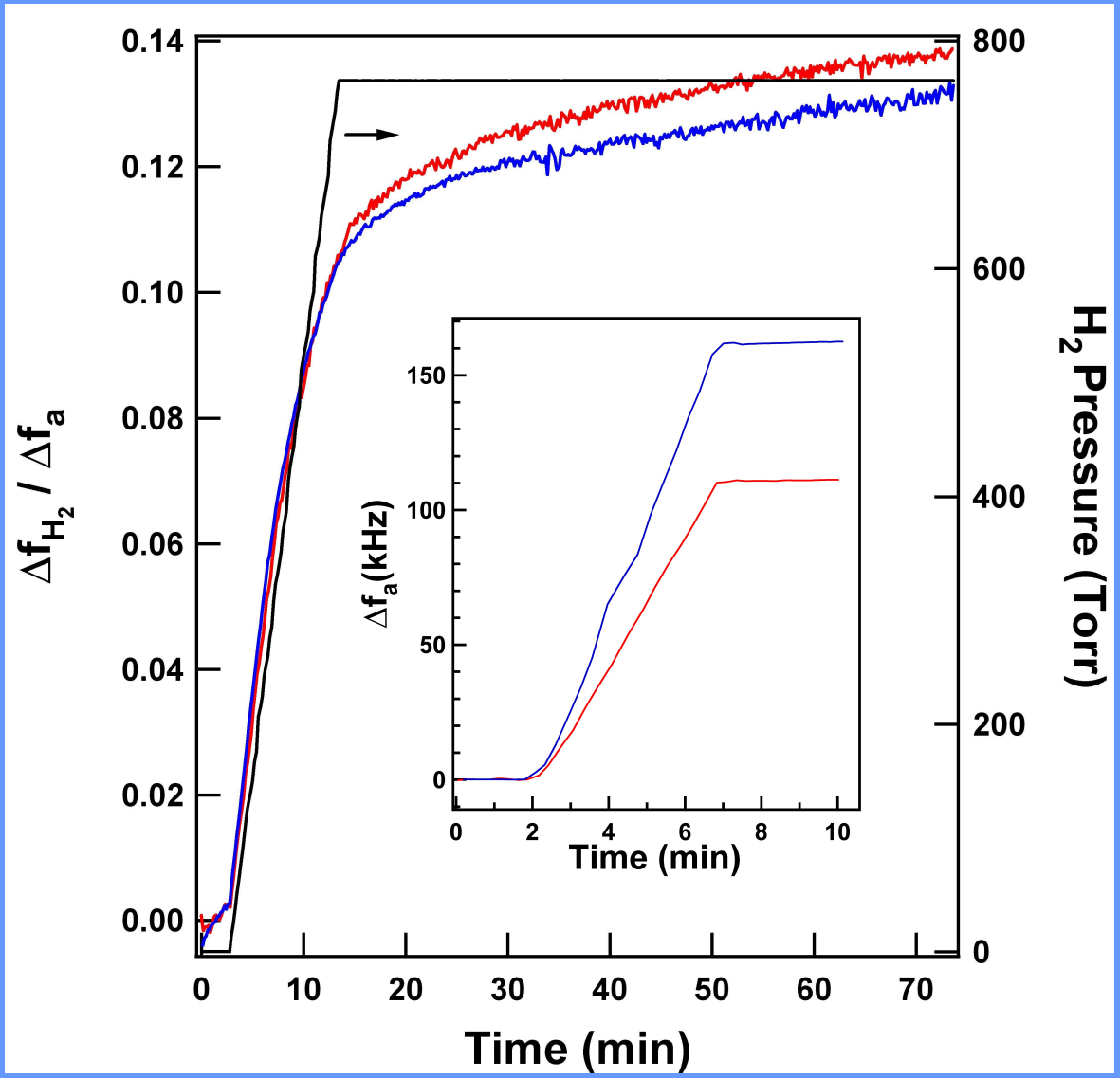




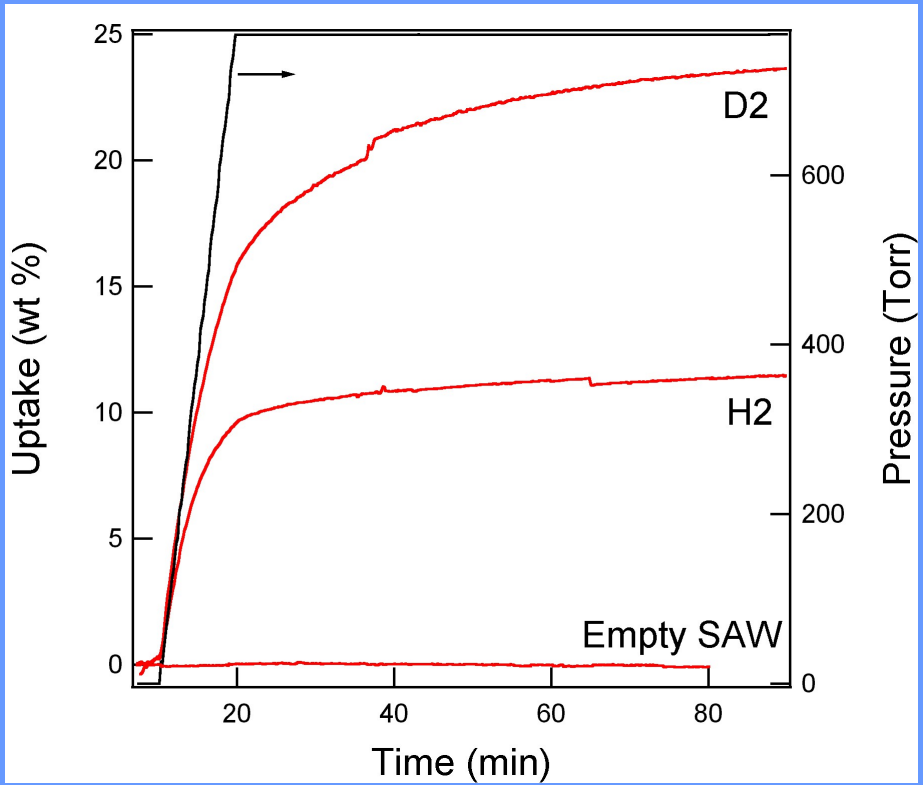




Acoustic Sensors at Different Frequencies Give The Same Result for H_2 Uptake

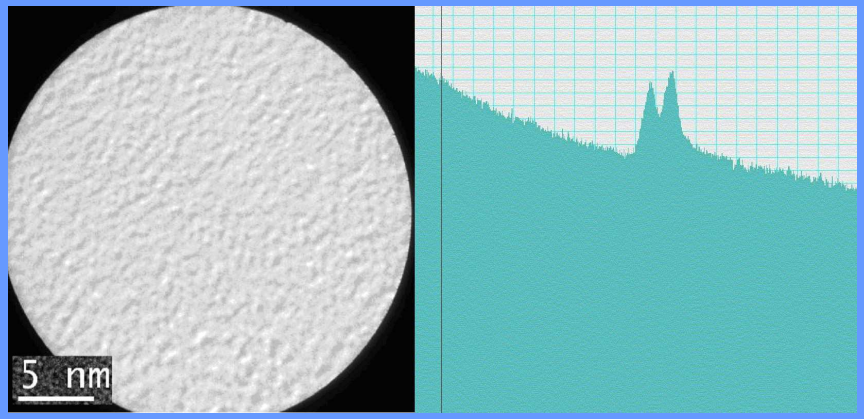


How do we know it really is hydrogen (H_2) that is getting in ?

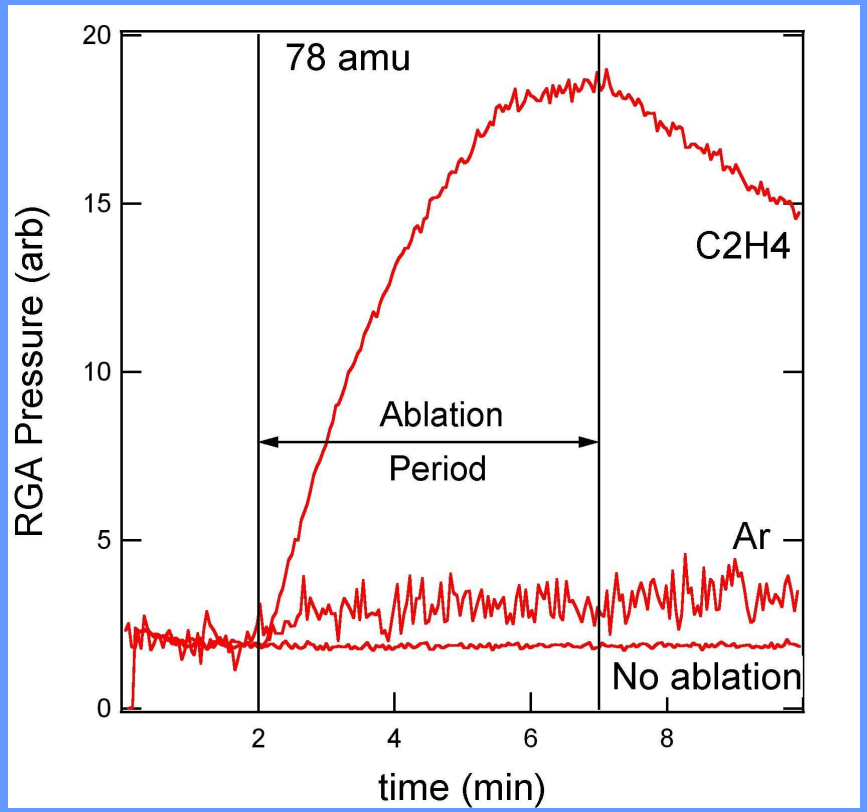


Independent exposure to D_2 indicates doubling of mass accumulated on sensor.

Other characterization experiments.



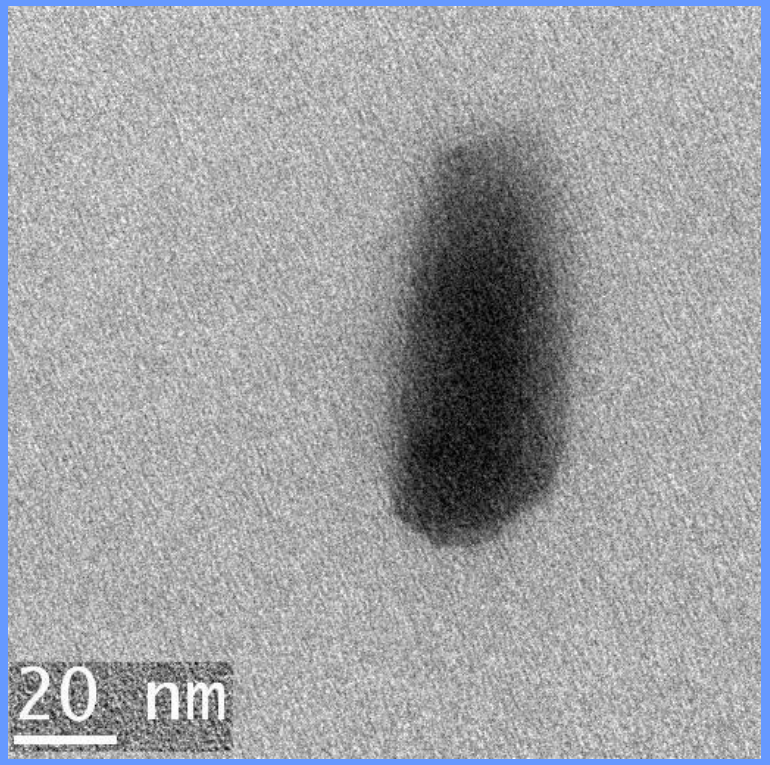
TEM characterization – $Ti(C_2H_4)$

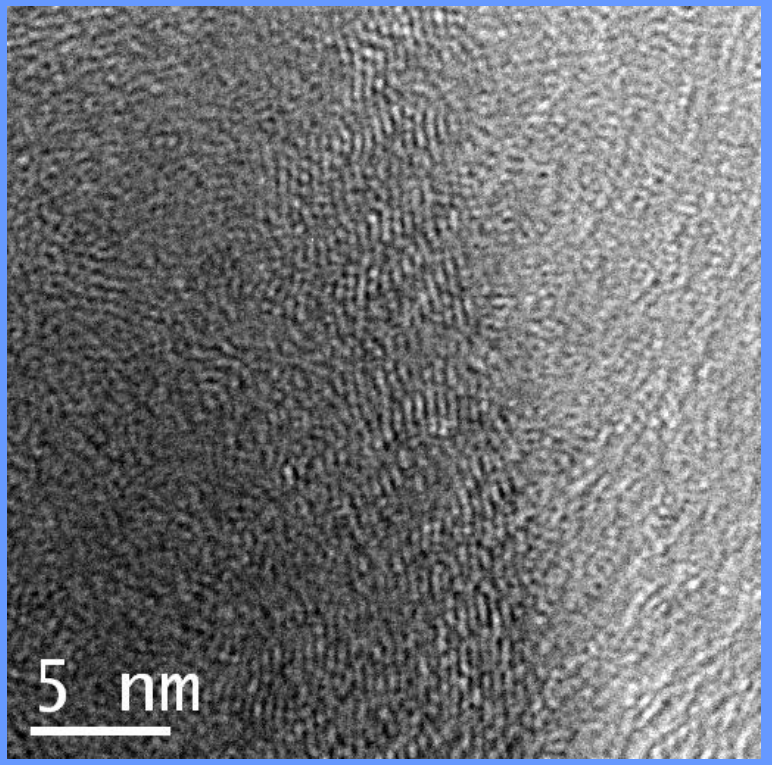


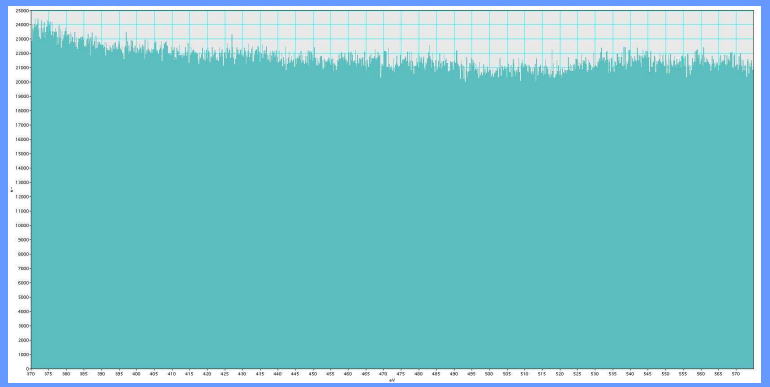
Gas phase characterization

$Ti\ (C_2H_4) \equiv 76$ amu

HRTEM & EELS Spectra – $Ti(C_2H_4)$ Complex



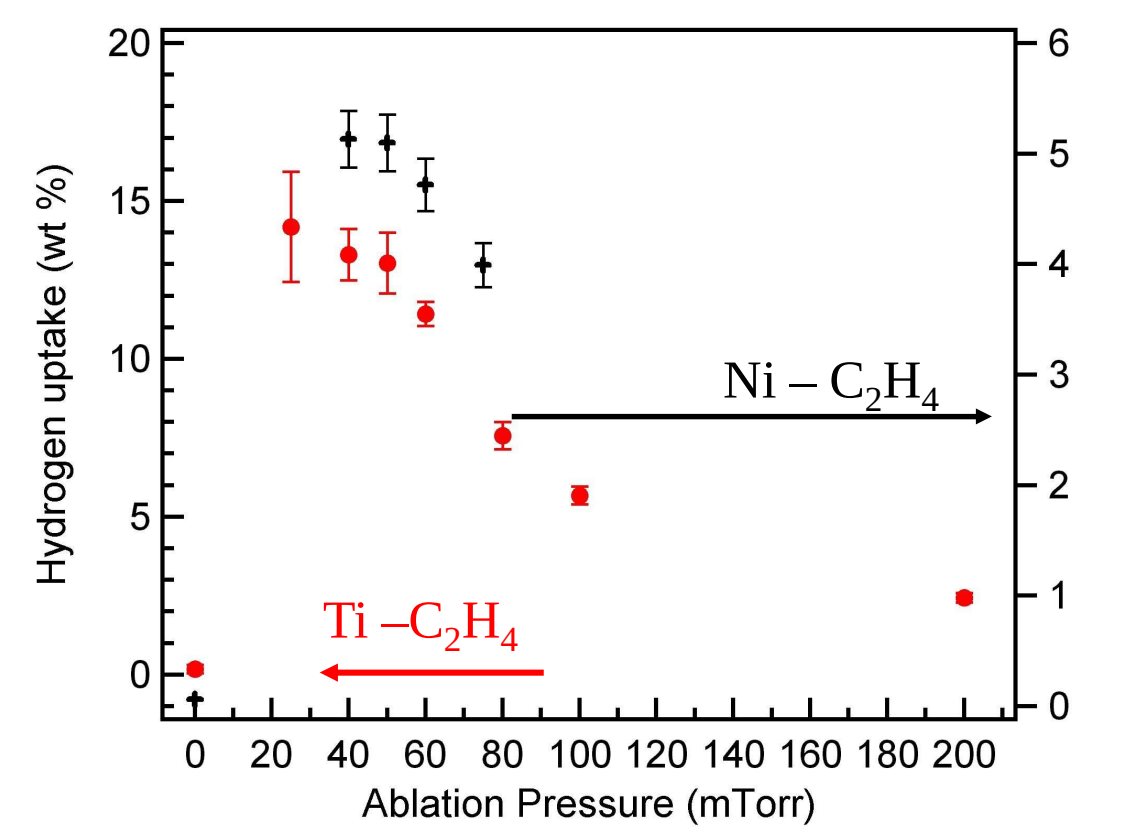




OUTSIDE THE PARTICLE

INSIDE THE PARTICLE

Pressure Dependence of H_2 Uptake



T.E.M. indicates that nanoparticles (and hence clustering of metal atoms) are formed for ablations at ethylene pressures above 100 mtorr.

Reduced hydrogen uptake is consistent with cluster formation.

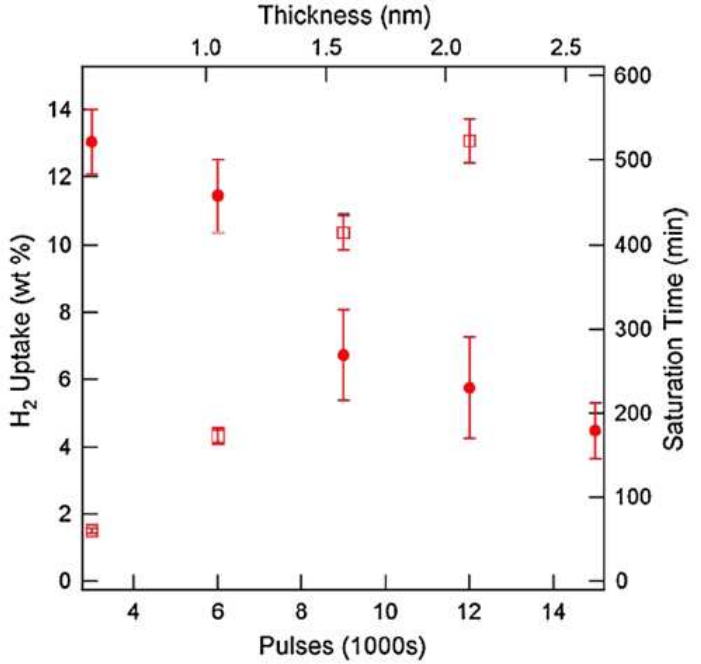
Element	Nb	V	Fe	Zn	Ti	Ni
Experiment	2 ± 0.3	1 ± 0.3	2.0 ± 0.3	0	5 ± 0.4	2 ± 0.3

Experiment

TABLE I. The binding energies (in eV) with respect to atomic and bulk energies of various metals (M). The last two rows indicate the maximum number of H_2 molecules bonded to each metal and its average binding energy (in eV).

Property/M	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Zr	Mo	W	Pd	Pt
E_B (M-atomic)	1.39	1.47	1.27	0.05	0.37	0.83	1.30	0.70	1.41	none	1.69	0.37	1.18	1.56	1.78
E_B (M-bulk)	−2.72	−3.66	−4.13	−3.57	−3.20	−1.74	−2.53	−2.19	−2.25	-	−4.44	−5.84	−7.18	−2.24	−3.56
max H_2/M	5	5	5	5	5	5	3	2	2	-	5	5	5	2	2
E_B (per H_2)	0.39	0.45	0.43	0.35	0.34	0.26	0.41	0.87	0.14	-	0.57	0.77	0.90	0.58	0.95

Th.



The samples we study are very thin – roughly a monolayer !

All of the numbers are based on the **assumption** that we are making purely $Ti(C_2H_4)$.

But there is a problem – we measure the majority species in our gas phase experiments as 78 amu not 76 amu !

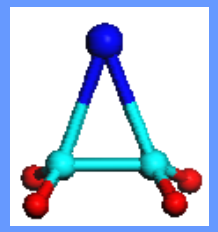
What is it that we are making in our chamber ?

DOES IT MATTER ?!

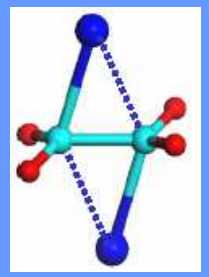
It is better that samples that are not “pure” and that they also exhibit large H_2 absorption !

Follow Up work from NIST group….

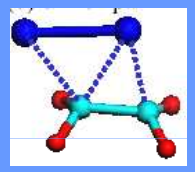
Zhou et. al., PRB, Oct., 2007.



C_2H_4 - M

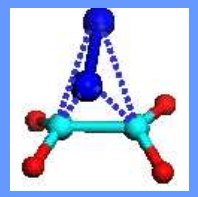


$C_2H_4 – M_2$ (sandwich)



$C_2H_4 – M_2$ (dimer parallel)

$CH_2M – MCH_2$

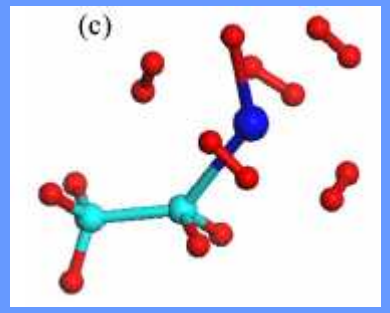


$C_2H_4 – M_2$ (dimer perpendicular)

dissociated

W. Zhou et. al., PRB, Oct 2007.

$CH_3 – CH_2$ -MH

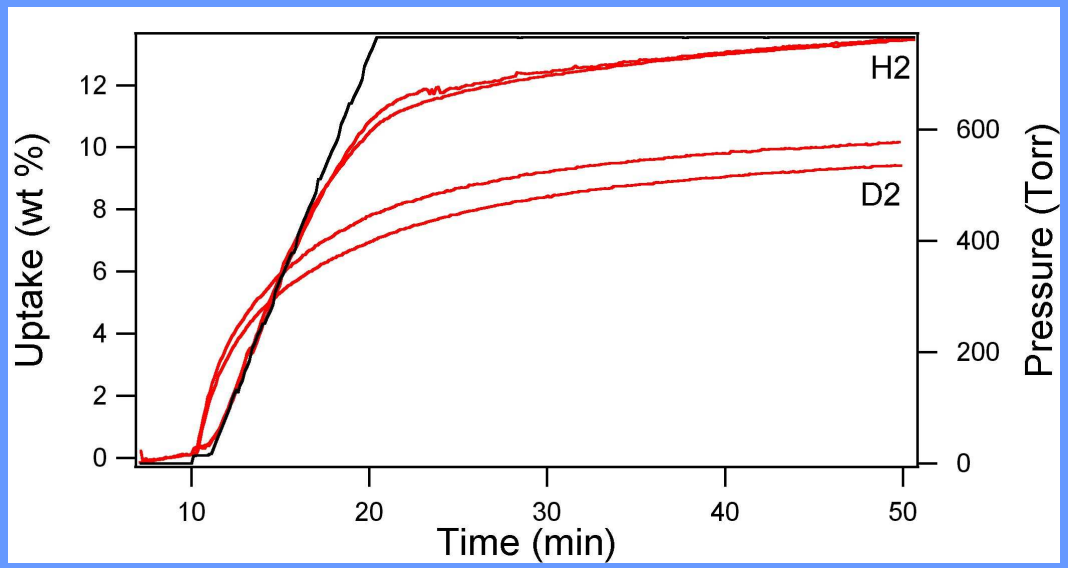


“Titanol”

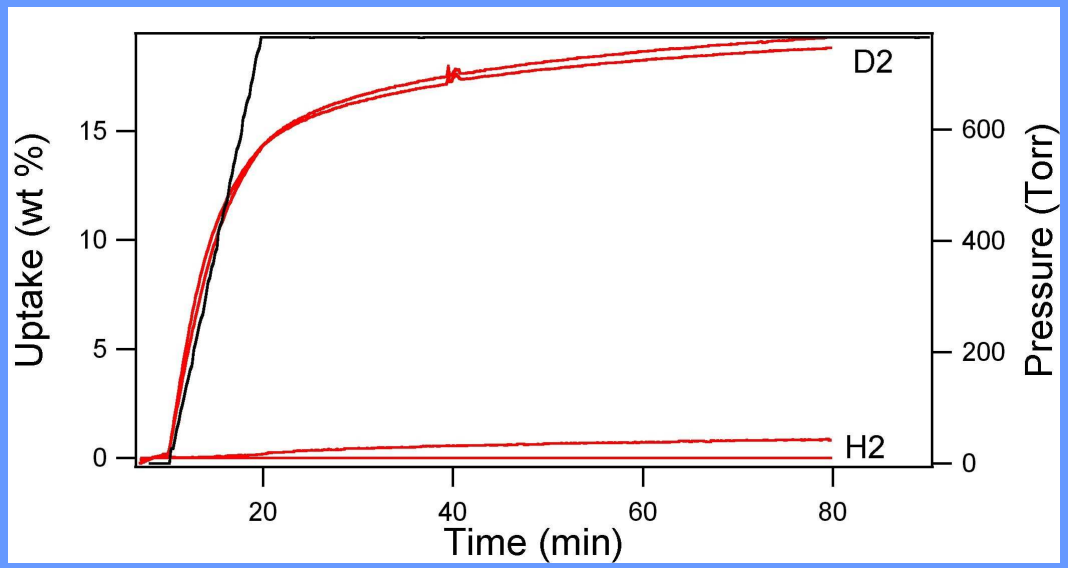
What about desorption ?

Is the H_2 going to come out?

D_2 exchange reactions



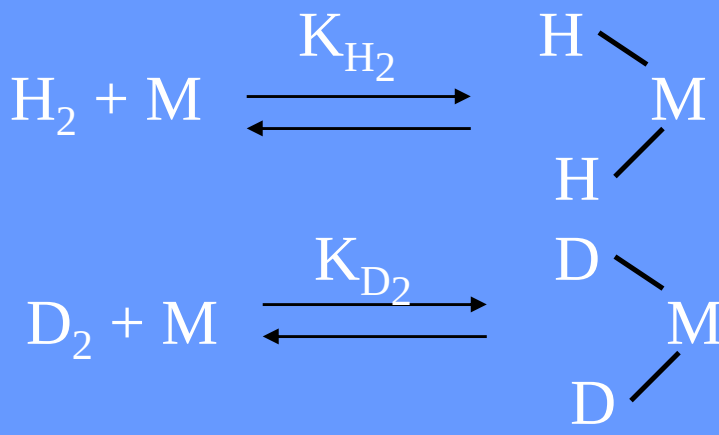
← H_2 then D_2

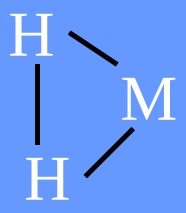


← D_2 then H_2

Equilibrium Isotope Effect

- Free D-D bond is 1.8 kcal/mol stronger than free H-H bond.





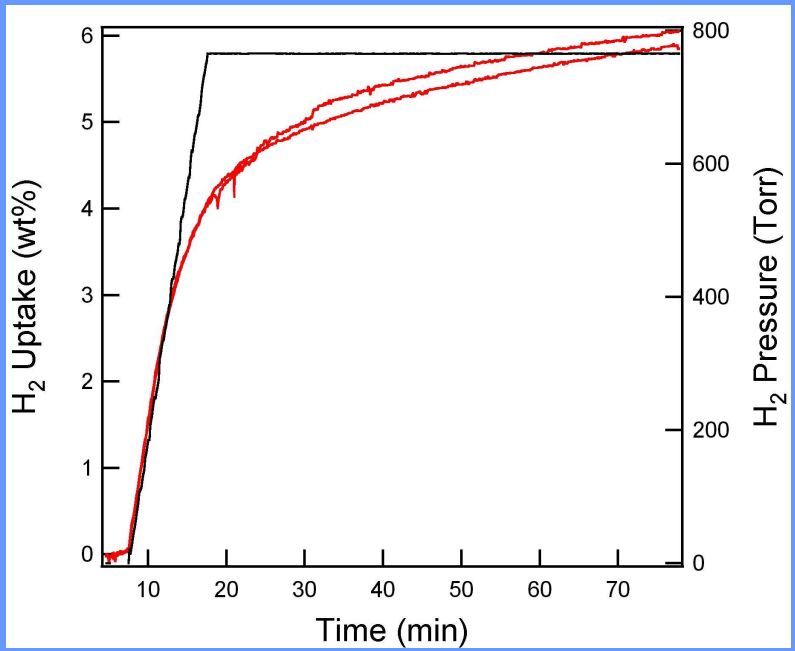
$$\frac{K_{H_2}}{K_{D_2}} = \frac{[MD_2]}{[MH_2]}$$

Bender & Kubas, 2000

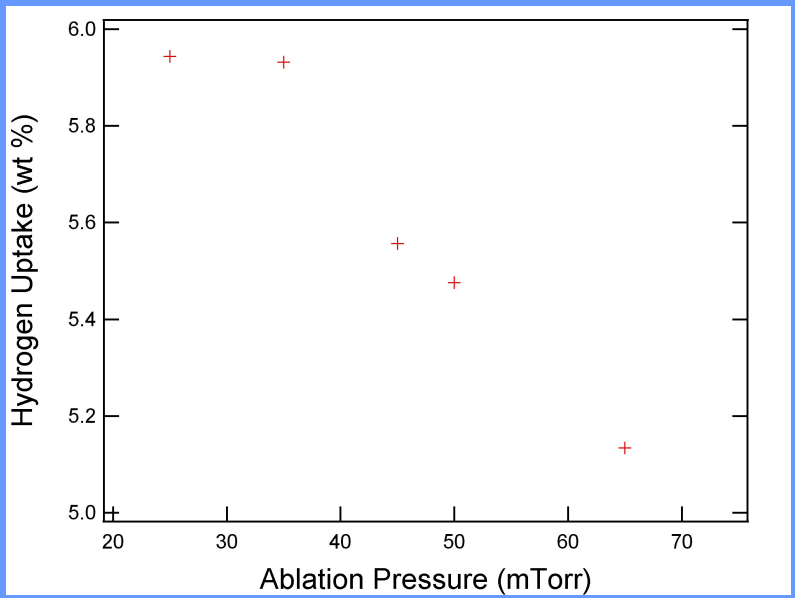
Metal Complex	Product $M(H)_2$ or $M(\eta^2\text{-}H_2)$	K_{H_2}/K_{D_2} = EIE	Temp (°C)
$W(PMe_3)_4I_2$	$W(H)_2$	0.63	60
$W(CO)_3(PCy_3)_2(N_2)$	$W(\eta^2\text{-}H_2)$	0.70	22
$Cr(CO)_3(PCy_3)_2(N_2)$	$Cr(\eta^2\text{-}H_2)$	0.65	22

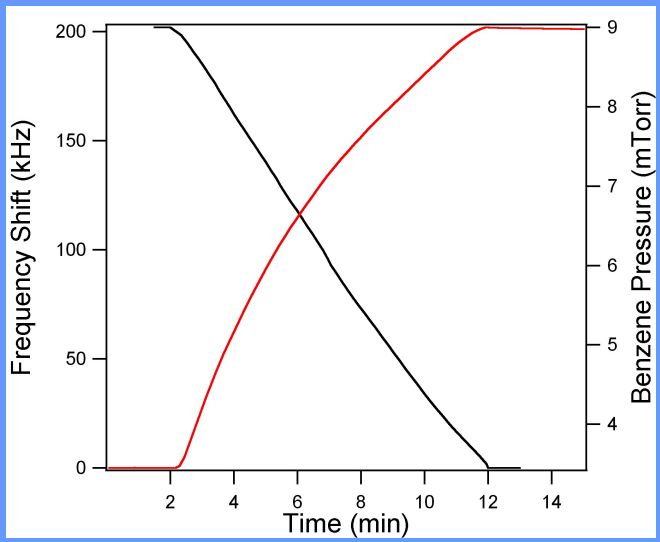
ORGANICS OTHER THAN ETHYLENE

Hydrogen Absorption in Transition Metal – Benzene (Ring) Complexes

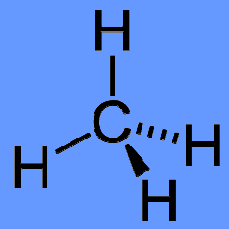


Benzene predicted to absorb ~ 6% by weight of hydrogen (Wecka et. al., J. Phys. Chem., 2008)



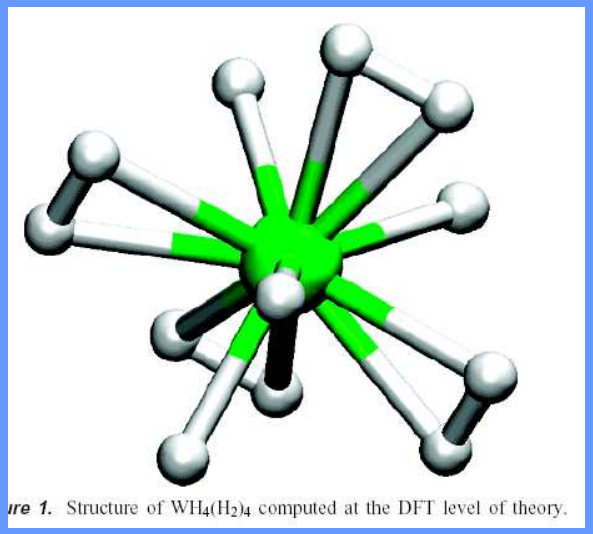


OTHER RESULTS



- Methane runs - small ~1.8% immediate uptake of H_2
- Furthermore there is a very small increase in pressure when ablating (~0.2 mtorr at 250 mtorr).
- Ti-C_2H_4 complexes also absorb methane (~27%).
- TM-$C_2H_4(H_2)$n complexes – unstable to O_2. But exposure to CH_4 appears to prevent oxidation.

CON-CURRENT IMPORTANT WORK AT UVa



ure 1. Structure of $WH_4(H_2)_4$ computed at the DFT level of theory.

Prof. Lester Andrews' Laboratory - Chemistry

Xuefeng Wang, Lester Andrews,Ivan Infante, and Laura Gagliardi, **J. AM. CHEM. SOC. 2008**, 130, 1972-1978.

Wt% ~ 8/188

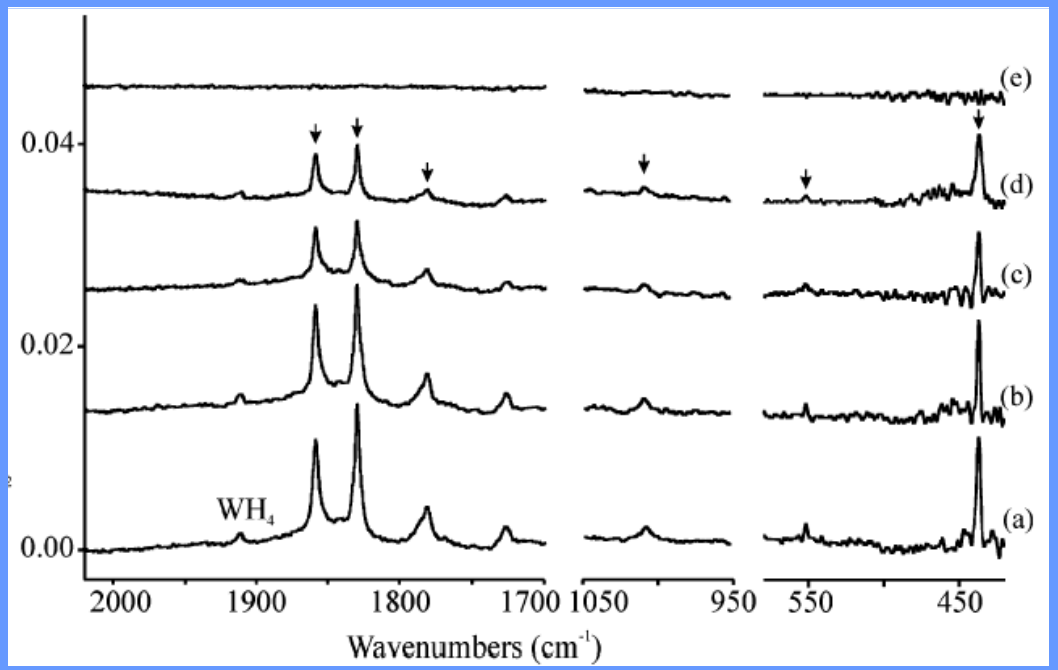


Table 3. Frequencies (cm^{-1}) Calculated at the DFT/BP86/TZVPP Level of Theory for $WH_4(H_2)_4$ (Singlet State, D_{2d} Symmetry)

obs freq[a]	calc freq	int[b]	symm[c]	mode description
	351	0	b_1	
437.2	414	171	b_2	bending H_2-W-H_2
	428	6 × 2	e	bending H_2-W-H_2
	499	0	a_1	
	539	0	a_2	
551.5	565	38 × 2	e	bending H−W−H
	681	0	b_1	
	748	8 × 2	e	bending $H-W-H_2$
	775	0	a_2	
	816	16 × 2	e	bending $H-W-H_2$
	842	0	b_2	
	871	0	a_1	
	897	0	b_1	
1007.6	1065	172 × 2	e	bending H_2-W-H_2
	1160	3	b_2	bending H_2-W-H_2
	1284	0	a_1	
	1741	0	b_1	asym stretch $W-H_2$
	1767	0	a_2	stretch $W-H_2$
1782.0	1790	40 × 2	e	asym stretch $W-H_2$
1830.6	1844	212	b_2	sym stretch W−H
1859.3	1868	53 × 2	e	asym stretch W−H
	1903	0	a_1	totally sym stretch W−H
2500	2657	208 × 2	e	stretch H−H
	2683	11	b_2	stretch H−H
	2740	0	a_1	totally sym stretch H−H

The Infrared Spectrum of Al_2H_6 in Solid Hydrogen

Lester Andrews* and Xuefeng Wang

Science, **299,** 2049, 2003.

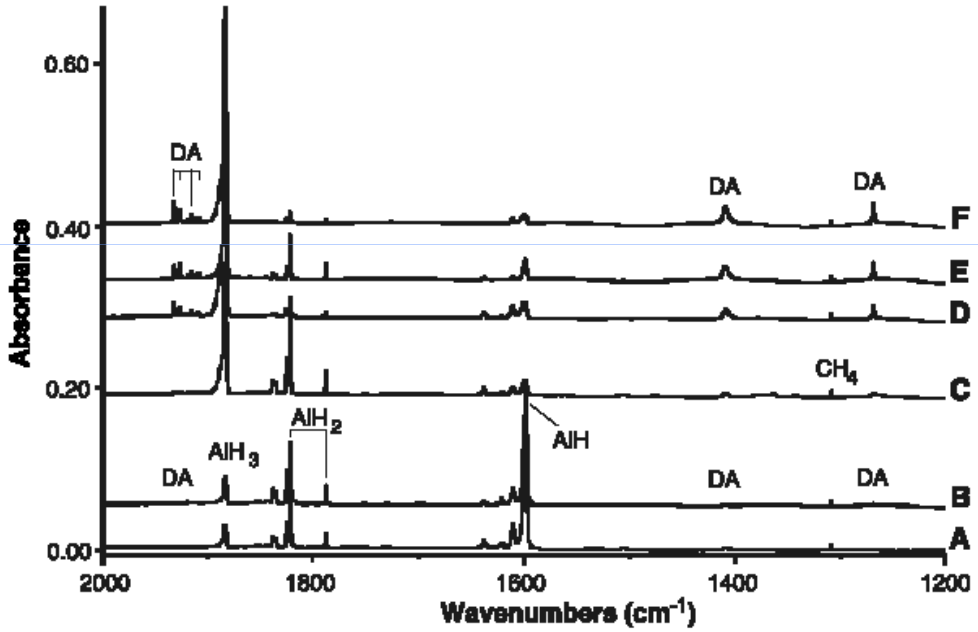
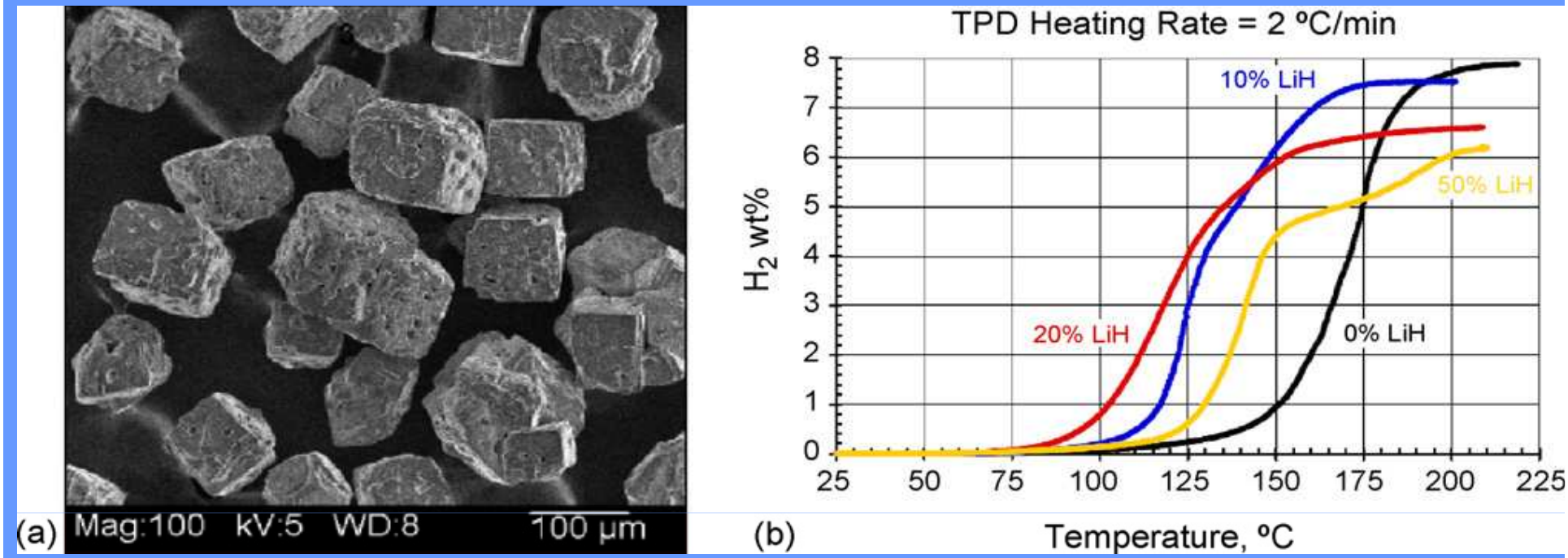


Fig. 1. IR spectra in the 2000 to 1200 cm^{-1} region for laser-ablated Al atoms codeposited with pure hydrogen at 3.5 K. (**A**) Spectrum obtained from initial deposited sample. (**B**) Spectrum after annealing to 6.0 K. (**C**) Spectrum after irradiation at $\lambda > 290$ nm. (**D**) Spectrum after irradiation at $\lambda > 240$ nm. (**E**) Spectrum after annealing to 6.5 K. (**F**) Spectrum after a second irradiation at $\lambda > 240$ nm.

Table 1. IR absorptions (in cm^{-1}) observed from codeposition of laser-ablated Al atoms and pure H_2 or D_2 at 3.5 K. –, not observed.

H_2	D_2	Identification
1932.3	1414.9	DA
1927.2	1413.4	DA site
1915.1	1402.9	DA
1909.1	1401.0	DA site
1883.7	1378.7	AlH_3
1838.4	1346.1	Al_2H_4
1835.8	1343.9	Al_2H_4
1825.5	1306.4	Al_2H_4
1821.9	1337.2	AlH_2
1787.8	1293.1	AlH_2
1638.1	1183.2	AlH_4^-
1610.7	1169.6	AlH site
1598.7	1163.1	AlH
1408.1	1028.5	DA
1268.2	919.7	DA
835.6	607.5	DA
777.9	561.8	AlH_3
711.3	522.0	AlH_3
702.4	510.6	DA
631.9	–	DA

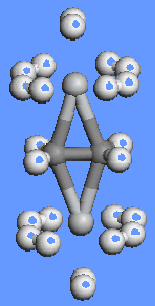
Wt% ~ 6/54~12%



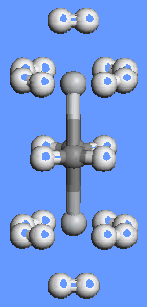
AlH_3 metal hydride particles and (b) H_2 desorbed vs. temperature for AlH_3 doped with LiH. The doped samples (yellow, blue, and red curves) show significantly lower temperatures of desorption than the undoped samples (black curve).

$C_2H_4Ti_2+10H_2$: Distinctive Modes

H-H stretching modes

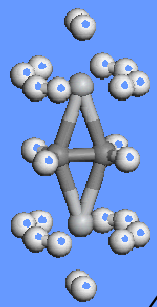


2881 cm^{-1}

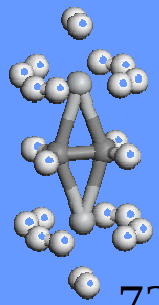


3343 cm^{-1}

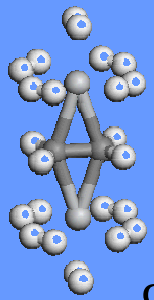
Ti-H_2 stretching modes



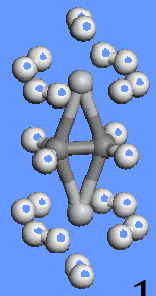
455



726

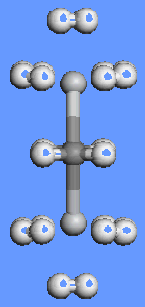


949

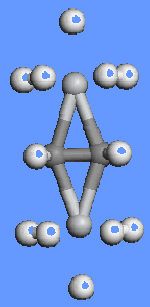


1466

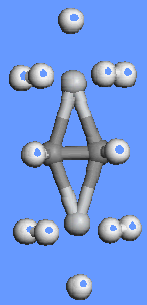
Quasi-rigid modes



Tang. ⊥C=C: 78 cm^{-1}

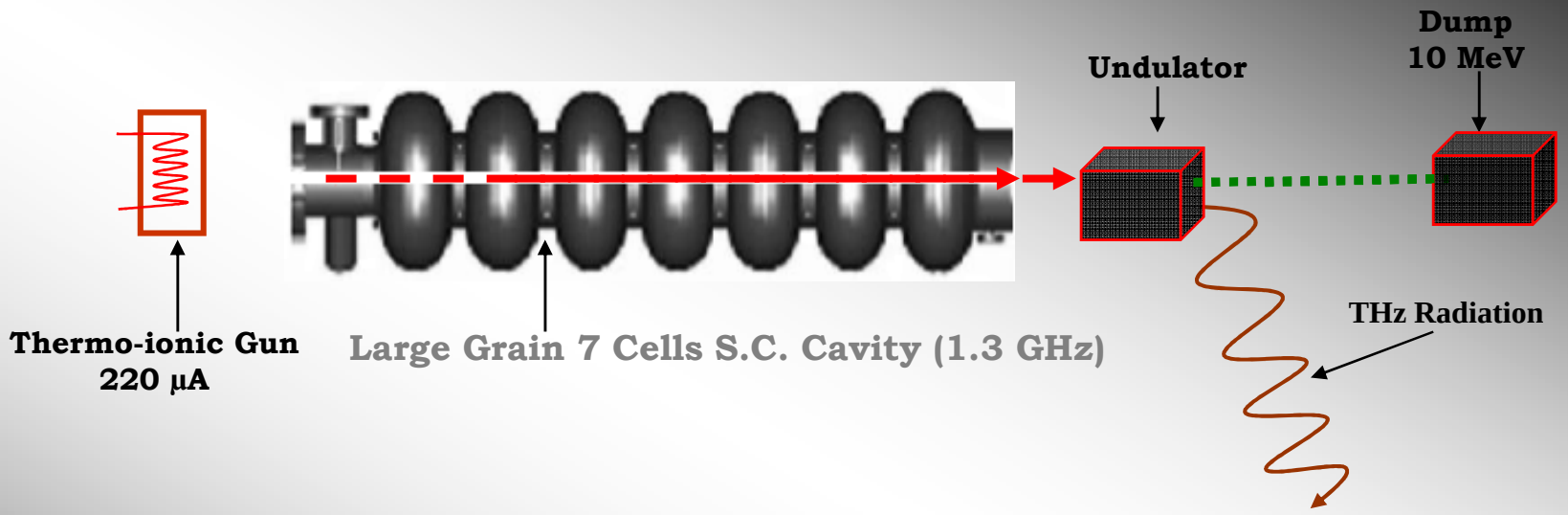


Tang. // C=C: 151 cm^{-1}



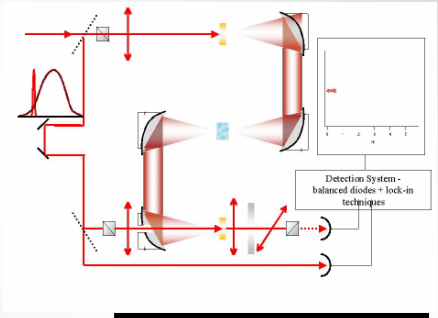
Radial: 240 cm^{-1}

Compact-Intense-Wideband Pilot THz Source



Large Grain Niobium Ingot Slice

Jefferson Lab
Exploring the Nature of Matter



Typical Application

FUTURE WORK

- Spectroscopy – urgently needed !
- Test other predicted materials – there are lots of them - replace C with B etc.
- Size selection of ablated species – “magic numbers”
- Lighter elements – Li , B ?
- Compositionally Challenged Metal Alloys
- Desorption
- Recyclability ?
- Large scale production ???

BROADER IMPACT OF OUR WORK

- Hydrogen Storage - of course !
- Astro-chemistry – “Chemistry of the Universe”.
- Testing DFT – refinements needed to handle D_2 vs H_2 (biggest isotopic effect you can find).
- H_2 and D_2 targets for nuclear physics
- Quantum Impurity Solids
- Alternate route towards metallic hydrogen

ACKNOWLEDGEMENTS

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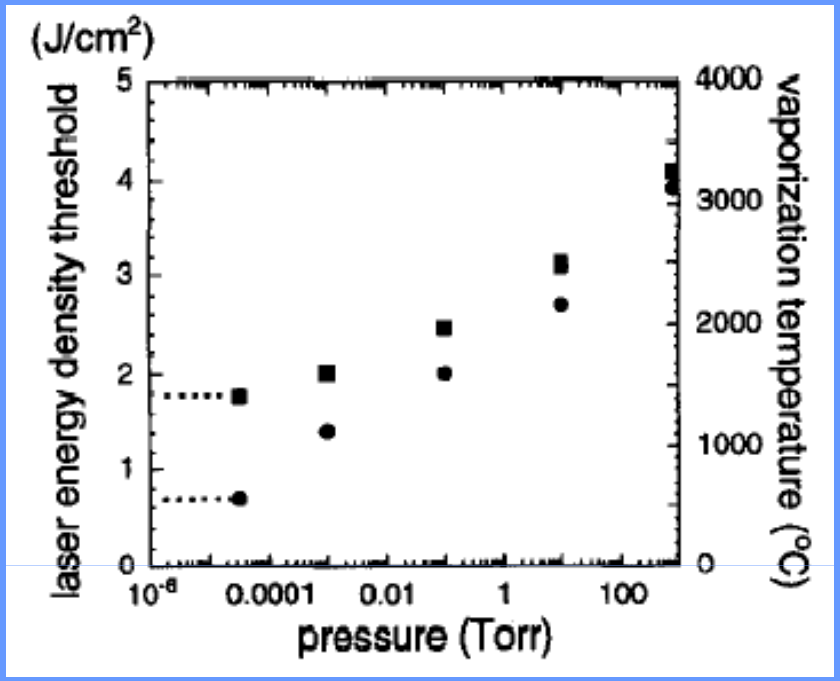
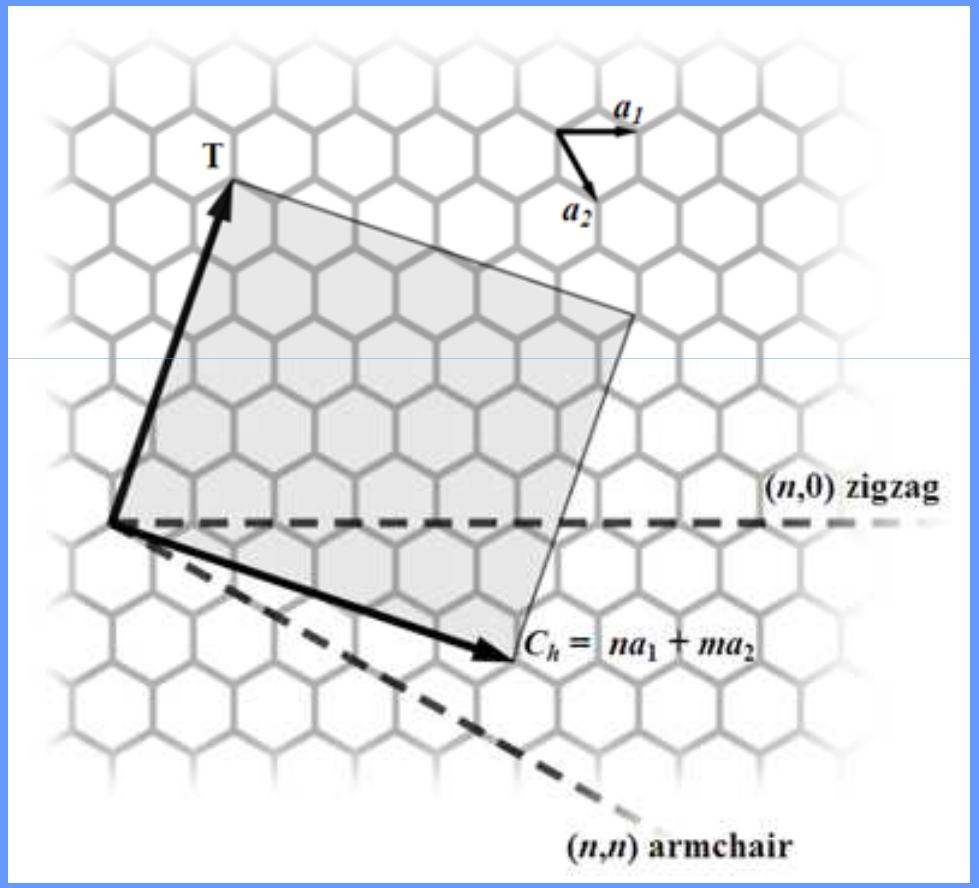
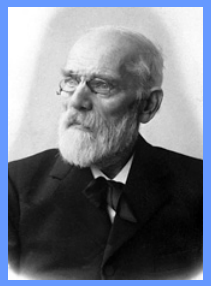


Laser-energy-density threshold (circle) and vaporization temperature (square) versus pressure for silicon.

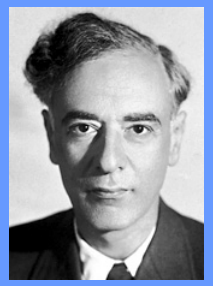
Carbon Nanotube Nomenclature



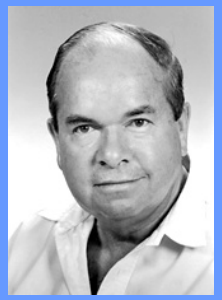


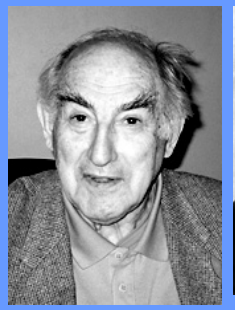
1910 - "for work on the equation of state for gases and liquids"

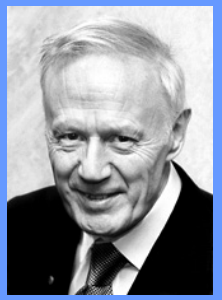
1918 - "in recognition of the services he rendered to the advancement of Physics by his discovery of energy quanta"



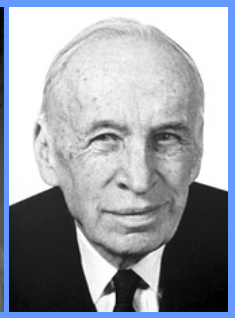
1962- **Lev Davidovich Landau** "for his pioneering theories for condensed matter, especially liquid helium"



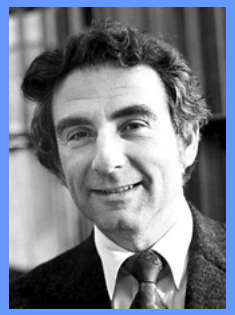


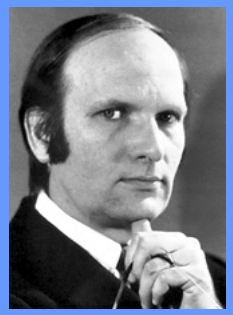


2003 -"for pioneering contributions to the theory of superconductors and superfluids"



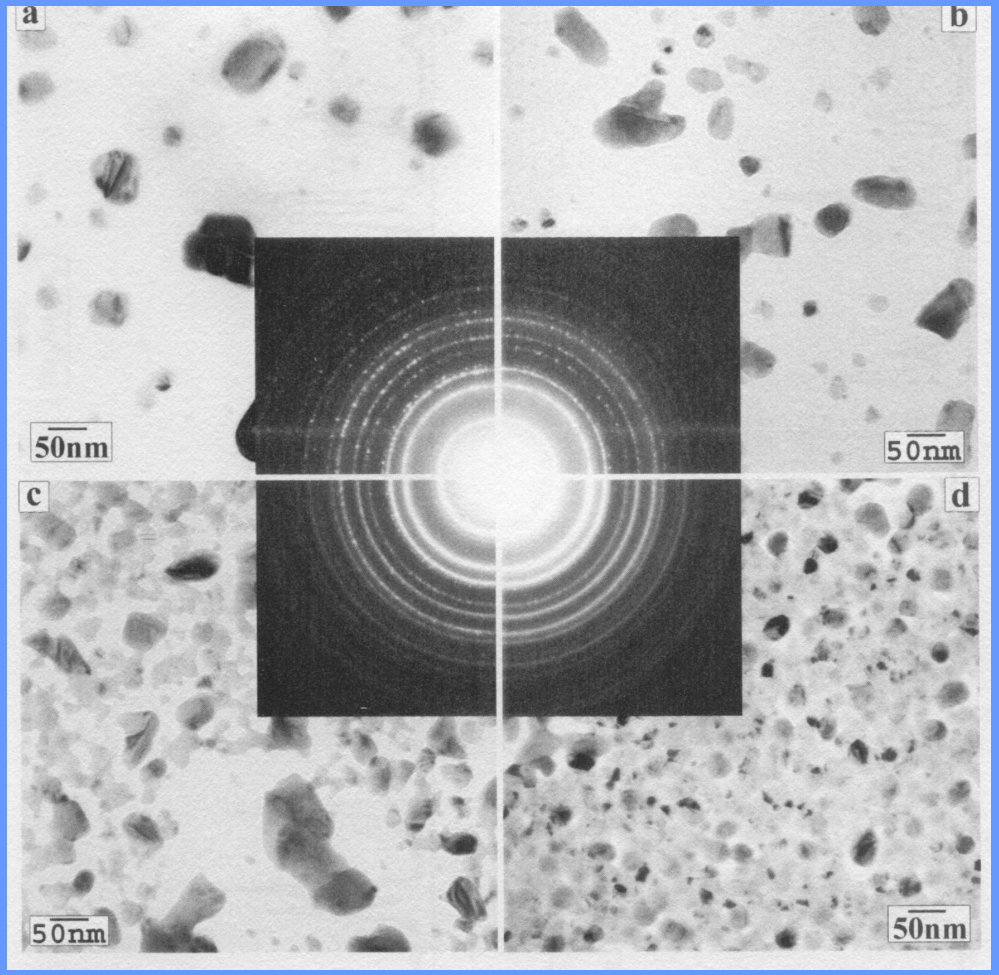
1977 -"for their fundamental theoretical investigations of the electronic structure of magnetic and disordered systems"





1972 "for their jointly developed theory of superconductivity, usually called the BCS-theory"

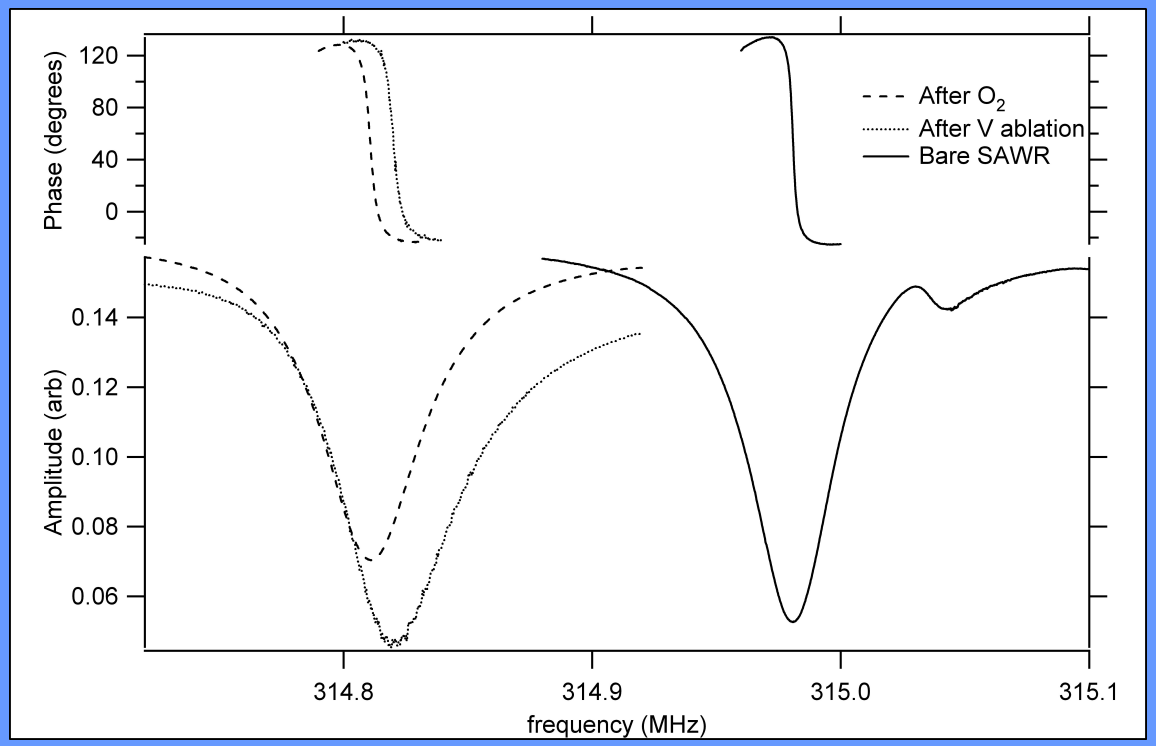
Exposing nanoparticles to air does not destroy the original crystal structure

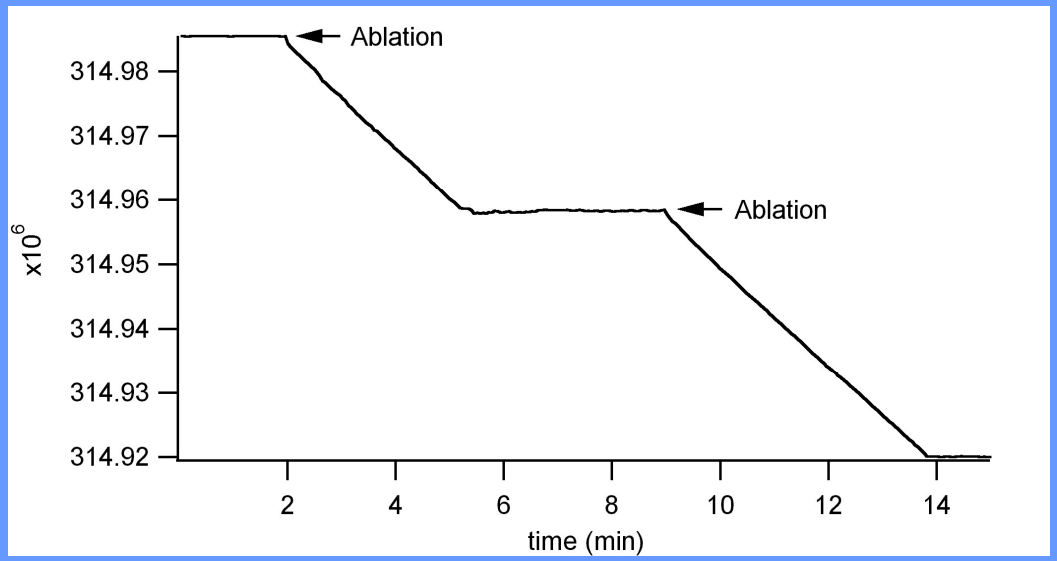


GaAsSb alloy nanoparticles, 550 ^{0}C.

0.7 J/cm2 to 1.6 J/cm2 and 600 to 900 pulses.

Frequency Response of the Surface Acoustic Wave Sensor





J. Phys. Chem. **1992**, *96*, 4879–4883

Chemistry and Kinetics of Primary Reactions of Ti^+ with H_2O, NH_3, CH_3OH, C_2H_4, and C_3H_6 at Thermal Energies

B. C. Guo, K. P. Kerns, and A. W. Castleman, Jr.*

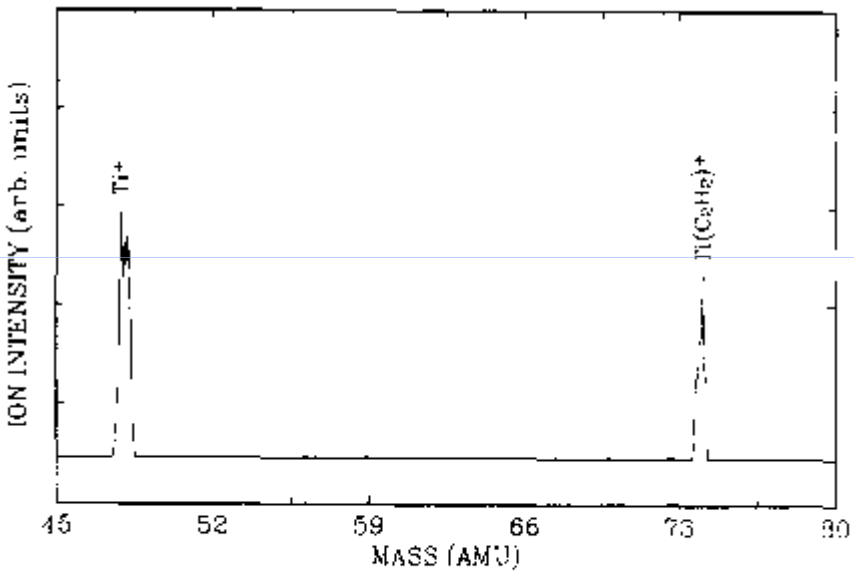


Figure 2. Mass spectrum resulting from the primary reaction of Ti^+ with the ethylene molecule at an ethylene partial pressure of 0.08 mTorr. The peaks labeled are Ti^+ and $Ti(C_2H_2)^+$ from the primary reaction.

$$Ti^+ + C_2H_4 = Ti^+(C_2H_2) + H_2$$