# Molecular Studies of Surfaces under Reaction Conditions; Sum Frequency Generation Vibrational Spectroscopy, Scanning Tunneling Microscopy and Ambient Pressure X-ray Photoelectron Spectroscopy

Gabor A. Somorjai

Department of Chemistry and
Lawrence Berkeley National Laboratory
University of California, Berkeley

# Evolution of Surface Science

**Nanosciences**

Monodispersed nanoparticles 2D and 3D

**Applications in Catalysis, Tribology, Polymers, Biointerfaces, Microelectronics, Energy Conversions, Environmental Chemistry, Electrochemistry, Corrosion**

**Surface Instruments at High Pressures, Liquid Interfaces**

(STM, SFG, AFM, QCM, RAIRS)

**Surface Dynamics**

Rapid energy transfer between incident and product molecules
Mobility of the adsorbed molecules along surfaces during catalytic turnover

**Surface Thermodynamics**

Adsorbate coverage dependent heats of adsorption
Coadsorption induced ordering
Surface segregation

**Surface Structure and Bonding**

Clean surface reconstruction
Adsorbate induced restructuring
Surface defects (steps, kinks) are chemically active

**Model Surfaces - Single Crystals, (Metals, Semiconductors)**

**Surface Instruments in Vacuum (XPS, AES, LEED, SIMS)**

# Surface Science Techniques for Gas/Solid or Liquid/Solid Interfaces

**Photon-in and Photon-out:**

IR spectroscopy, Raman spectroscopy, Sum-frequency generation vibrational spectroscopy, X-ray emission spectroscopy, Surface X-ray diffraction, X-ray absorption fine structure

**Surface probe microscopy:**

Scanning Tunneling Microscopy, Atomic Force Microscopy

**Photon-in and Electron-out:**

Ambient pressure X-ray Photoelectron Spectroscopy

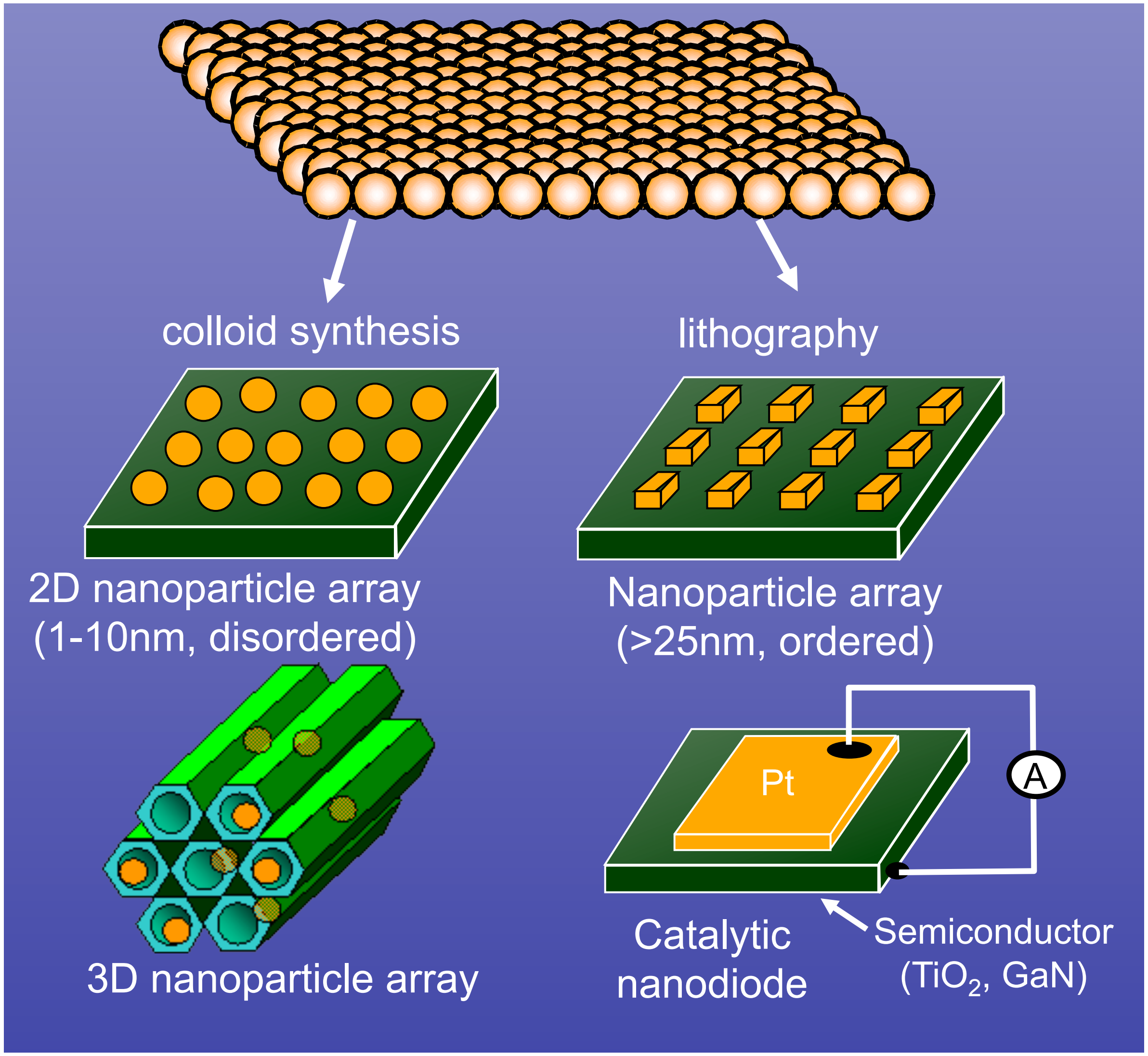
**Electron-in and Electron-out:**

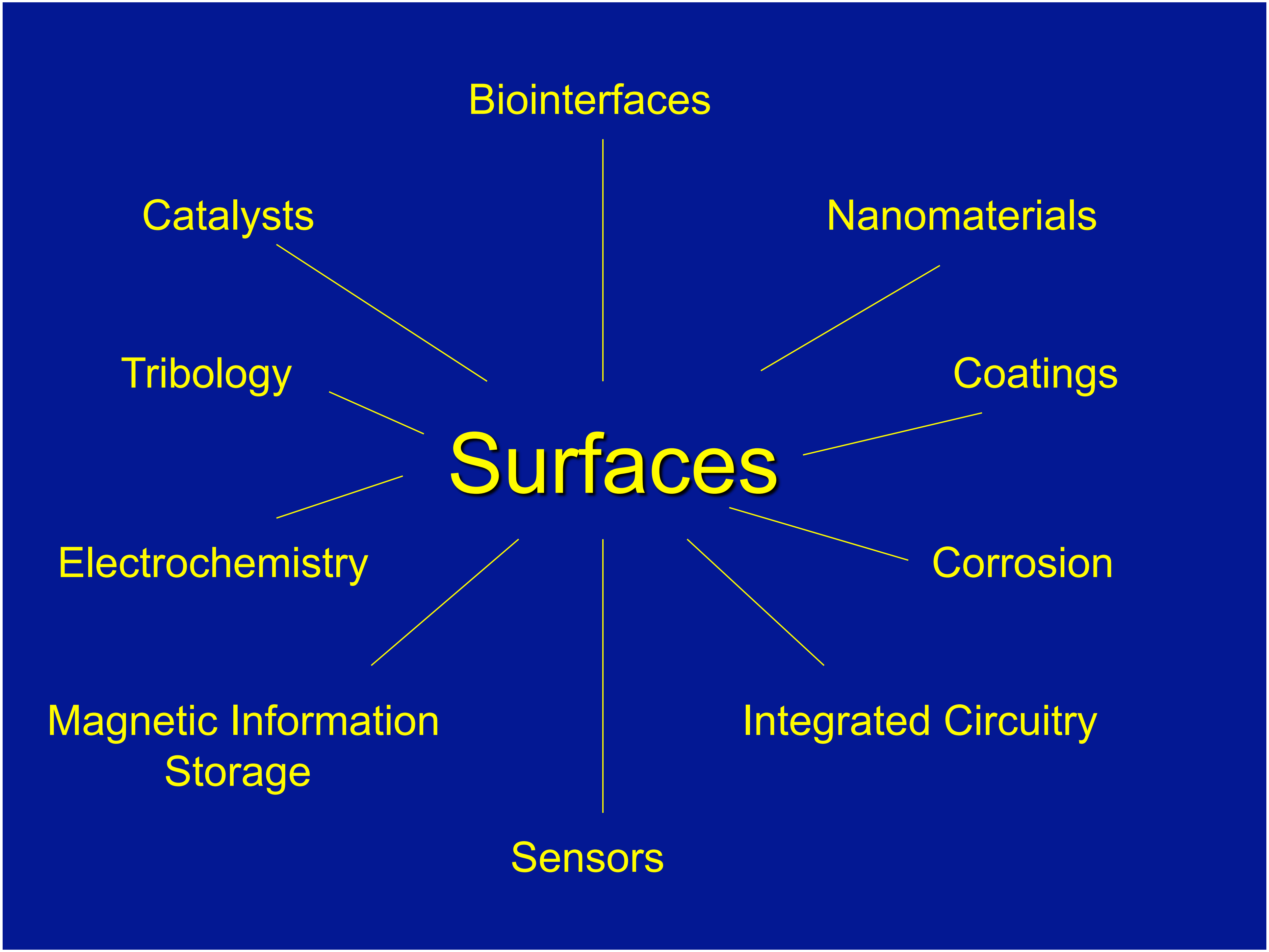
Transmission Electron Microscopy

Electron Flow During Catalytic Reactions

# Model Catalytic Surfaces for Identifying Active Sites

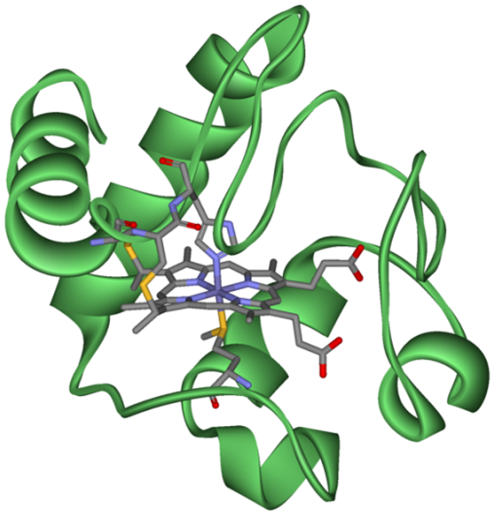
From Single Crystal Surfaces to Monodispersed Nanoparticles




Biointerfaces
Catalysts
Nanomaterials
Tribology
Coatings
Surfaces
Electrochemistry
Corrosion
Magnetic Information Storage
Integrated Circuitry
Sensors

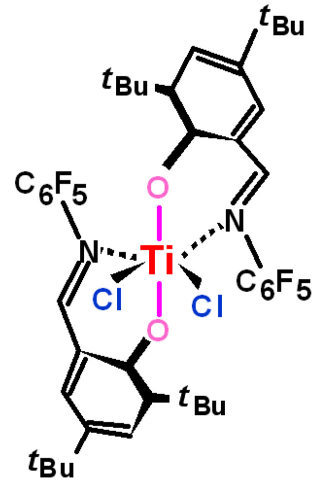
# Catalysts are Nanoparticles

**(a) Enzyme**



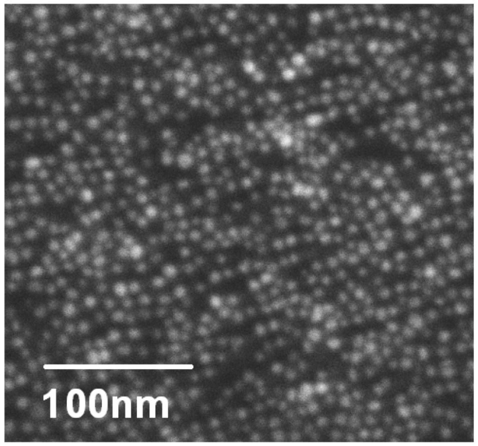
**Cytochrome C**
Size: ~4 nm, 100 amino acids
Molecular weight: ~12,000 daltons

**(b) Homogeneous catalysis**




**Single-site olefin polymerization catalyst**
Size : ~1.6 nm

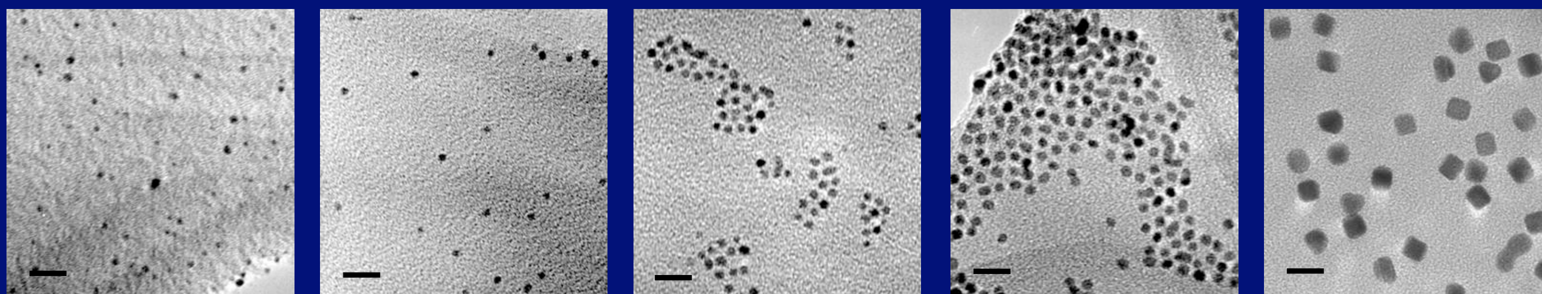
**(c) Heterogeneous catalysis**



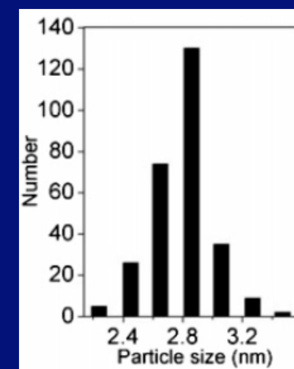

**Pt/Rh bimetallic nanoparticles**
Size : 8 nm

# Synthesis of Pt Nanoparticles with Size and Shape Control

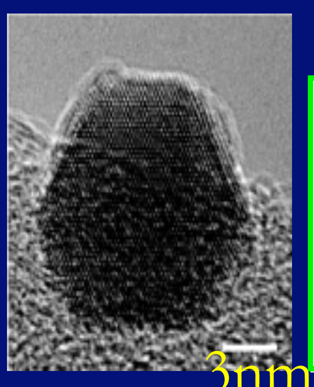
- PVP: Poly(vinylpyrrolidone), surface regulating polymer
- Particle size control in the range of 1.7 ~ 7.1 nm

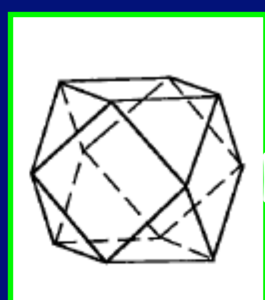


1.73 ± 0.26 nm    2.48 ± 0.22 nm    2.80 ± 0.21 nm    3.39 ± 0.26 nm    7.16 ± 0.37 nm



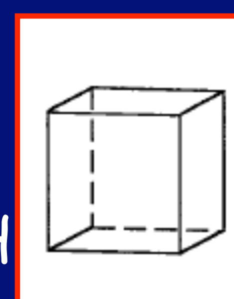

$$K_2PtCl_4 \xrightarrow[50^\circ C]{C_{14}TABr} (C_{14}TA^+)_2PtBr_4^{2-}$$

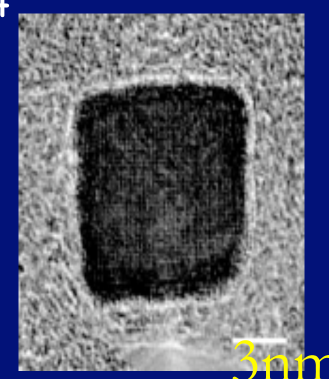


$NaBH_4 + H_2$ low pH → Cuboctahedra

$NaBH_4$ high pH → Cubes {100}






Cuboctahedra

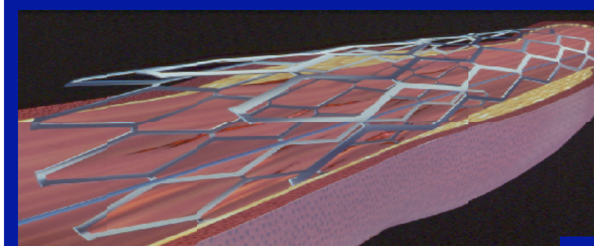
Cubes {100}

Lee, H.*et al., Angewandte Chemie,* **2006,** 45, 7824.

# Biointerfaces and Medical Devices

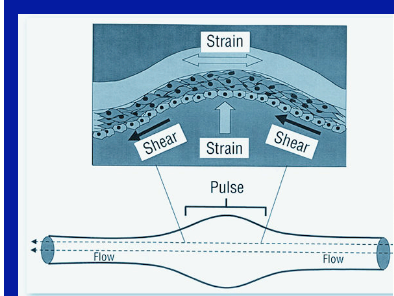
- Biomaterials improve our everyday quality of life
  - NIH estimates 8-10% of Americans have medical implants[1]
- Biological Compatibility of Materials
  - Non-Specific Protein Adsorption[2]

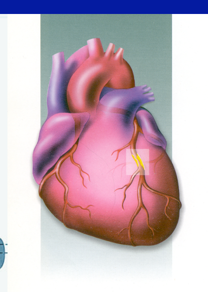
## Heart Stent



Polyurethane Under Reversible Loading (Fatigue Test)

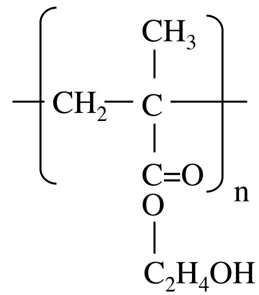
3.2 billion heart valve loading cycles in ~80 years of normal heart function



## Soft Contact Lens

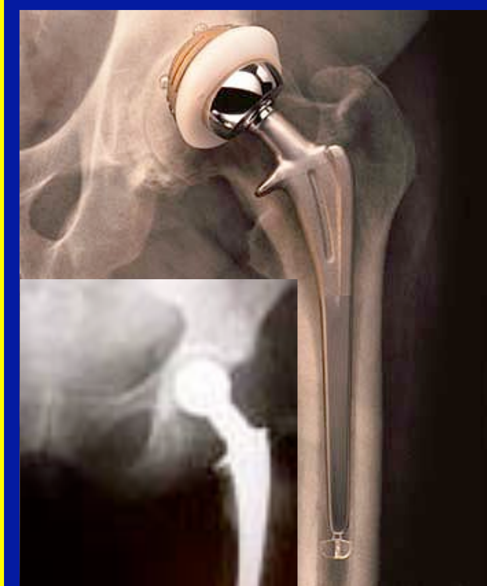
**Soft contact lens: crosslinked pHEMA**




**In water, pHEMA swells & forms hydrogel**

pHEMA = poly(2-hydroxyethyl methacrylate)

## Prosthesis

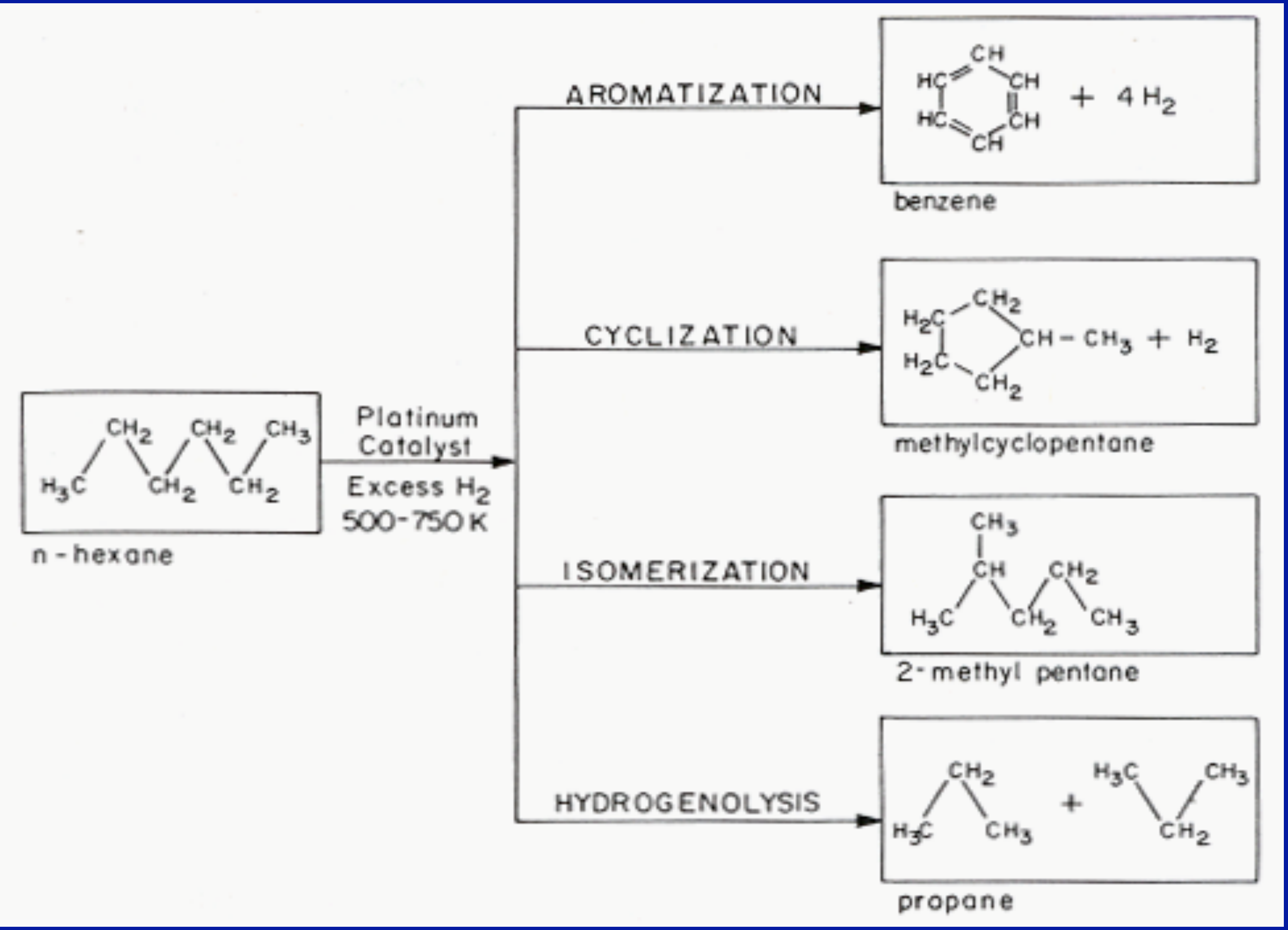


http://www.biotronik.de/sixcms/detail.php/346

1. http://consensus.nih.gov/2000/2000MedicalImplantsta019html.htm
2. Ratner, B.D., Bryant S.J., *Annu. Rev. Biomed. Eng.* (6) 41-75, 2004.

# Catalysis by Metals

**Industrial Hydrocarbon Reforming with Pt Catalyst**



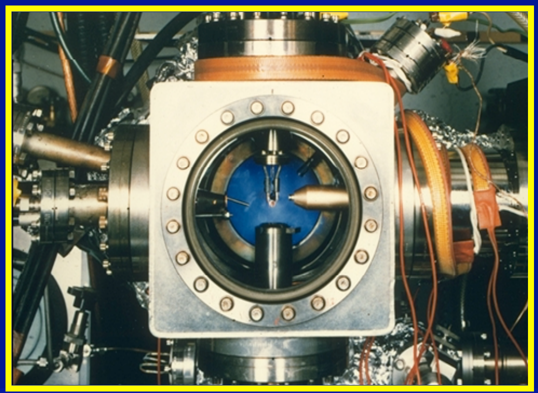

| Octane Rating |
|---|
| 110 |
| 93 |
| 78 |
| N/A |

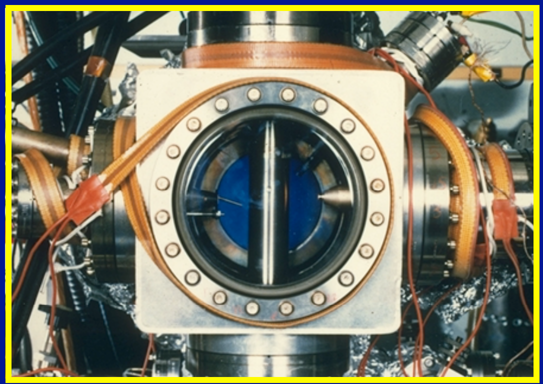
Reaction Selectivity Minimizes Waste Byproducts → **Green Chemistry**

# Prenatal and Postmortem Studies of Metal Catalysis Before SFG Techniques

## Ultra High Vacuum (UHV) Reactor Combined w/ High Pressure Reaction Cell

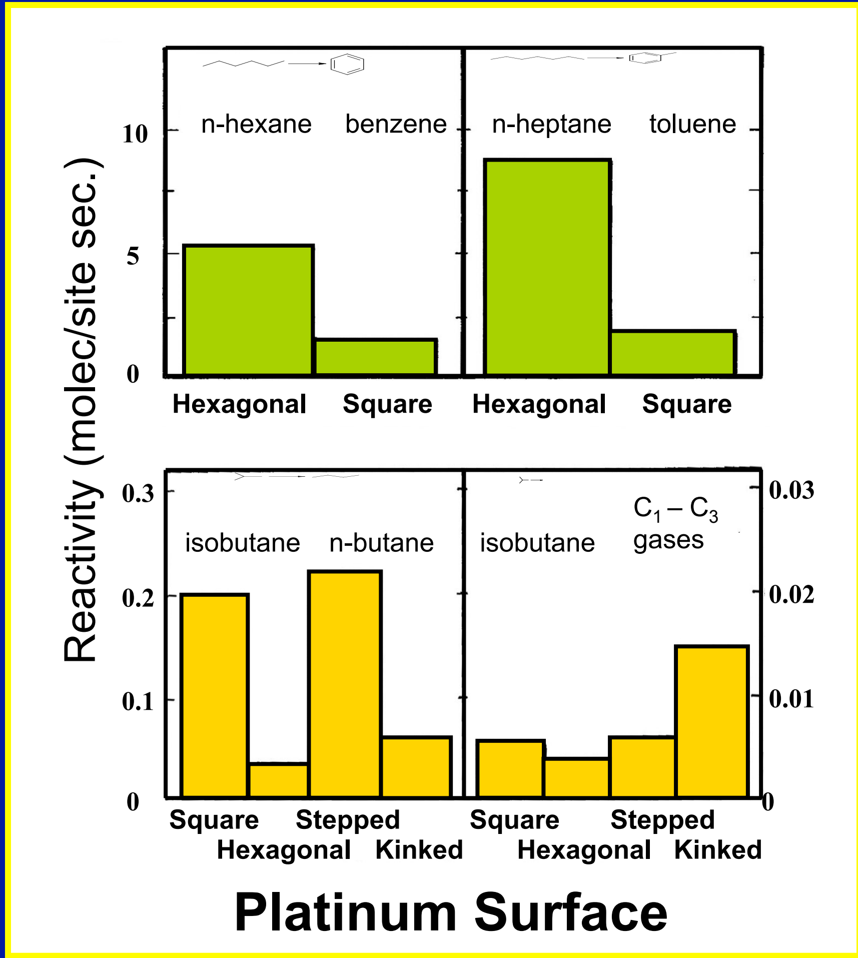
**1. Low Pressure Catalyst Characterization**





**2. High Pressure Catalyst Reaction**

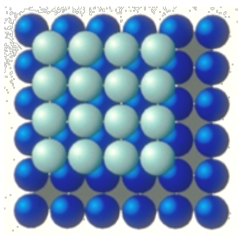
**3. Selectivity & Reaction Product Study**



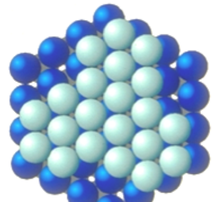
# Benzene Hydrogenation on Pt Nanoparticles

**Pt(111) & Cuboctahedra Nanoparticles show similar selectivity**

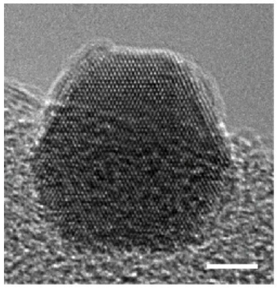
**Pt(100) & Cubic Nanoparticles show similar selectivity**



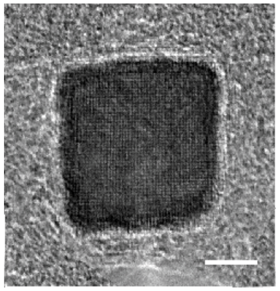
**Pt (100)**



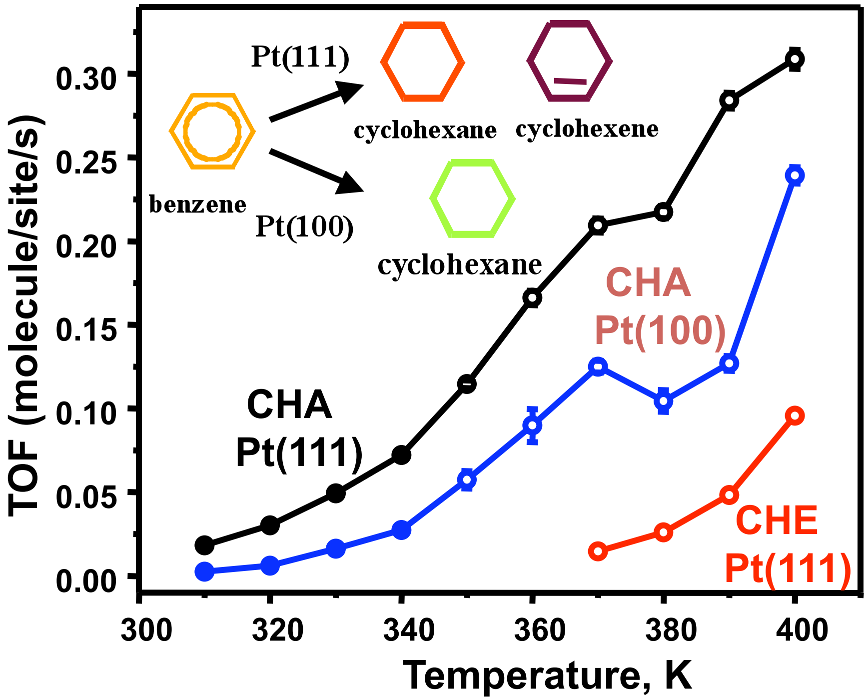
**Pt (111)**

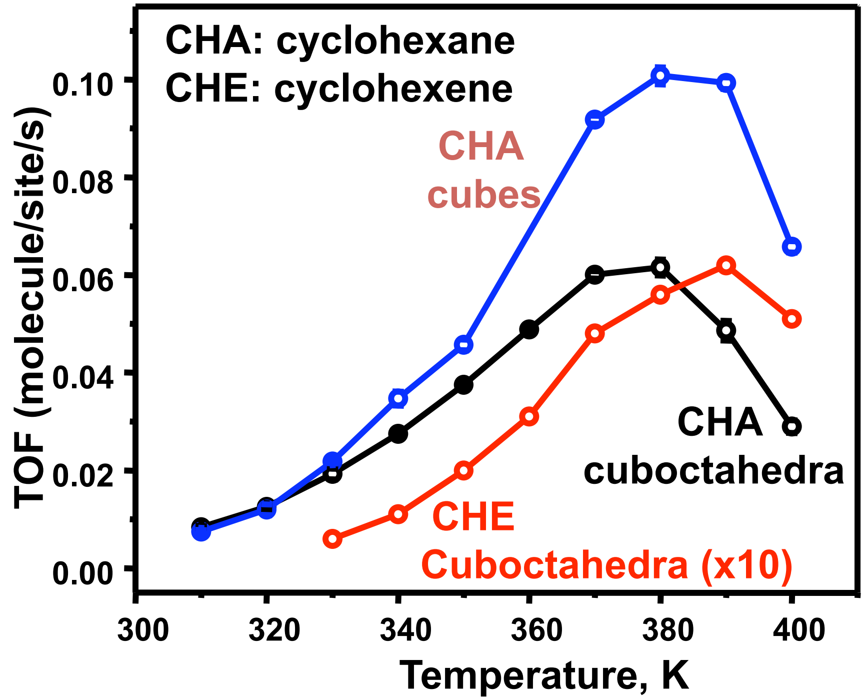


**Cuboctahedra (12.6 nm)**

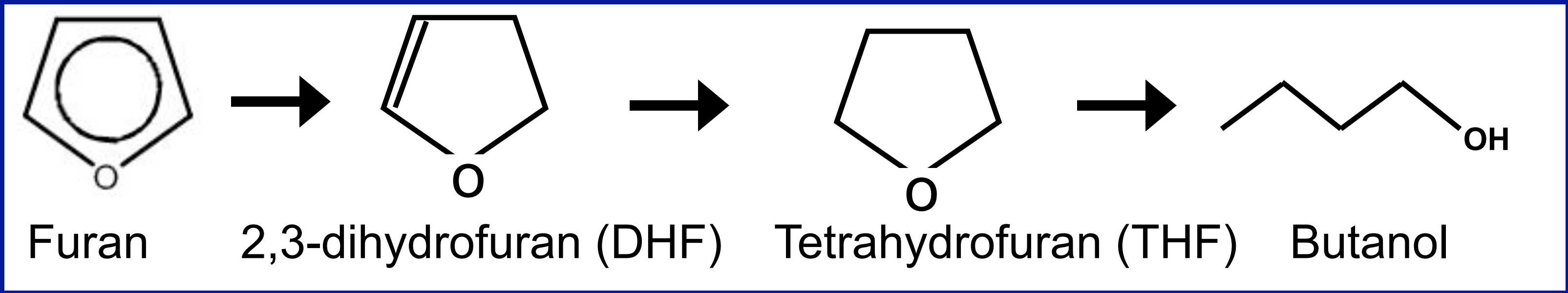


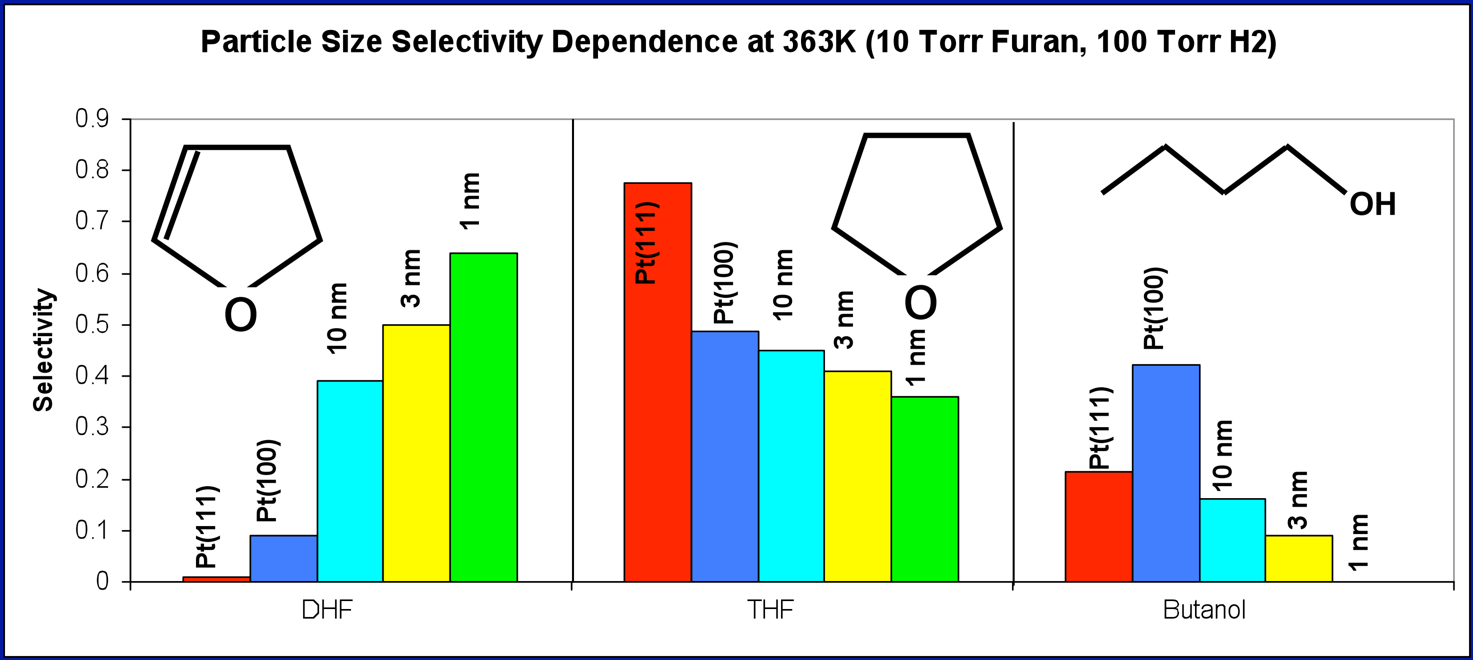
**Cube (13.4 nm)**



# Using SFG to Investigate Furan Hydrogenation: Selectivity Dependence on Pt Nanoparticle Size




**All Runs: 10 Torr Furan, 100 Torr Hydrogen, 363K**

# Why are Catalytic Selectivity and Turnover Rates Nanoparticle Size and Shape Sensitive?

# Prenatal and Postmortem Studies of Metal Catalysis

# Revolution in Molecular Studies of Catalysts During Reactions

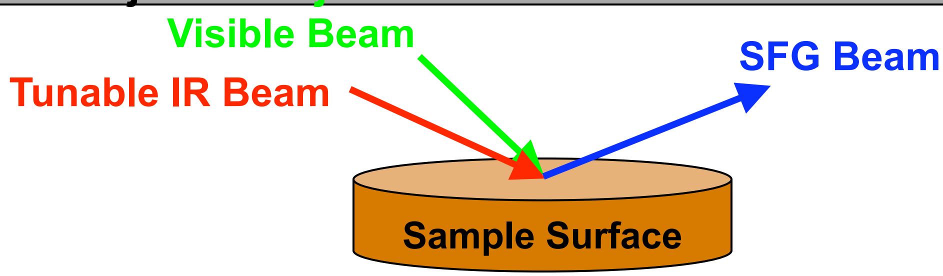
# High Pressure In-situ Surface Techniques

- Sum Frequency Generation Vibrational Spectroscopy (SFG)
- High Pressure Scanning Tunneling Microscopy (HPSTM)
- X-ray Absorption Spectroscopies (XAS)
- Ambient Pressure X-ray Photoelectron Spectroscopy (APXPS)
- Catalytic Nanodiode (CND)

# Sum Frequency Generation Vibrational Spectroscopy

# SFG: Surface-Specific Vibrational Spectroscopy

▶ **Two Laser Beams Overlapped:**
$E = [E_j\cos(\omega_j t) + E_k\cos(\omega_k t)]$




▶ **Intense E-field Induces 2nd Order Non-linear Polarization:**

$P = P^{(0)} + P^{(1)} + P^{(2)} + \ldots$

$P^{(0)} = \chi^{(0)}$ Permanent Dipole

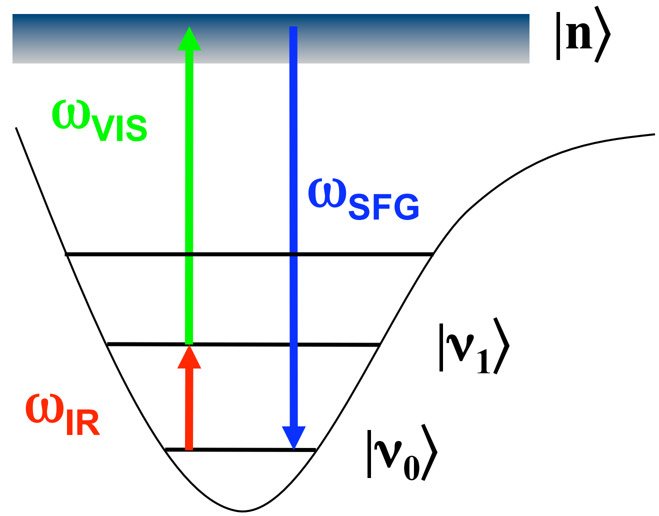
$P^{(1)} = \chi^{(1)}[E_j\cos(\omega_j t) + E_k\cos(\omega_k t)]$ Linear (Raman, IR)

$P^{(2)} = \chi^{(2)}[E_j\cos(\omega_j t) + E_k\cos(\omega_k t)]^2$ Non-linear (SFG, SHG,....)

↓

$P^{(2)} = \chi^{(2)}[E_j E_k[\cos(\omega_j + \omega_k)t] + \ldots\ldots ]$

(SFG)




$\omega_{SFG} = (\omega_{VIS} + \omega_{IR})$

▶ **Total SFG intensity:**
$I(\omega_{SFG}) \propto |\chi^{(2)}|^2 I(\omega_{VIS}) I(\omega_{IR})$

# SFG: Surface-Specific Vibrational Spectroscopy

**Centrosymmetric Distribution:**

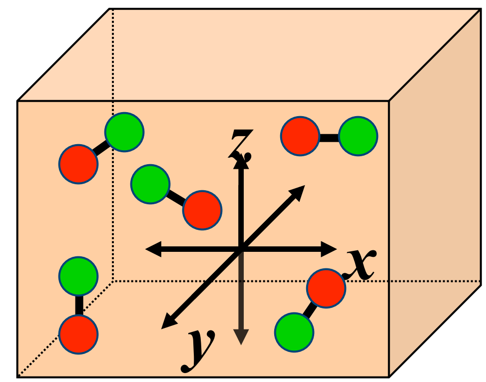
Selection Rule: $\chi^{(2)}_{xyz} = -\chi^{(2)}_{(-x)(-y)(-z)}$

**BUT ……**

x = -x
y = -y
z = -z

$\rightarrow \chi^{(2)}_{xyz} = \chi^{(2)}_{(-x)(-y)(-z)}$

$\longrightarrow \chi^{(2)}_{xyz} = 0$




**$\chi^{(2)}$ is zero → *No SFG Signal!*****

**Chemical Species at Interface:**

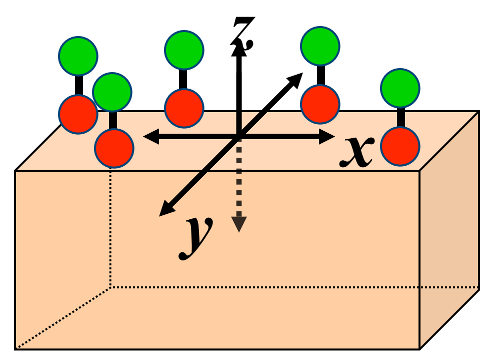
Selection Rule: $\chi^{(2)}_{xyz} = -\chi^{(2)}_{(-x)(-y)(-z)}$

**AND ……**

x = -x
y = -y
z ≠ -z

$\rightarrow \chi^{(2)}_{xyz} \neq \chi^{(2)}_{(-x)(-y)(-z)}$

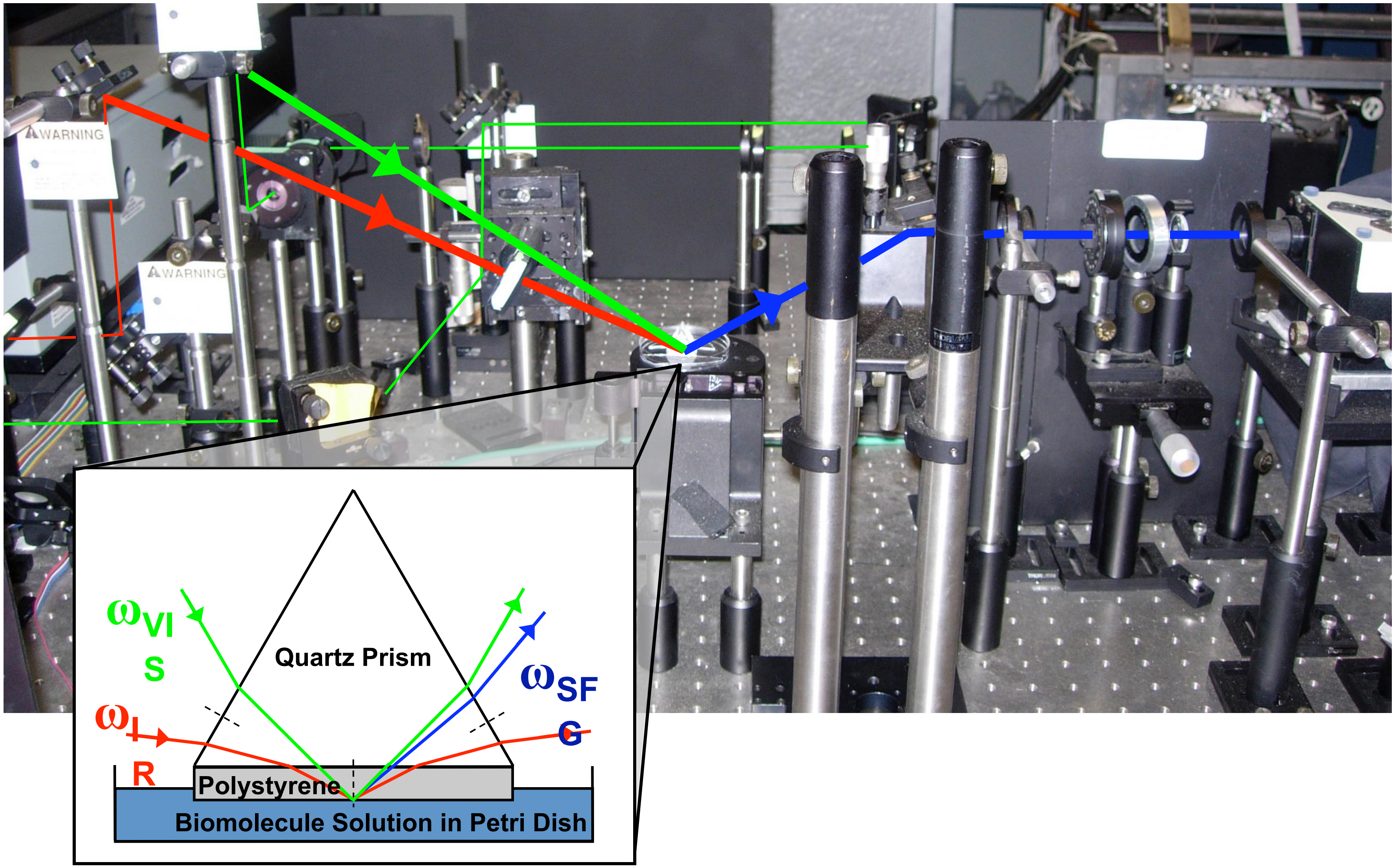
$\longrightarrow \chi^{(2)}_{xyz} \neq 0$



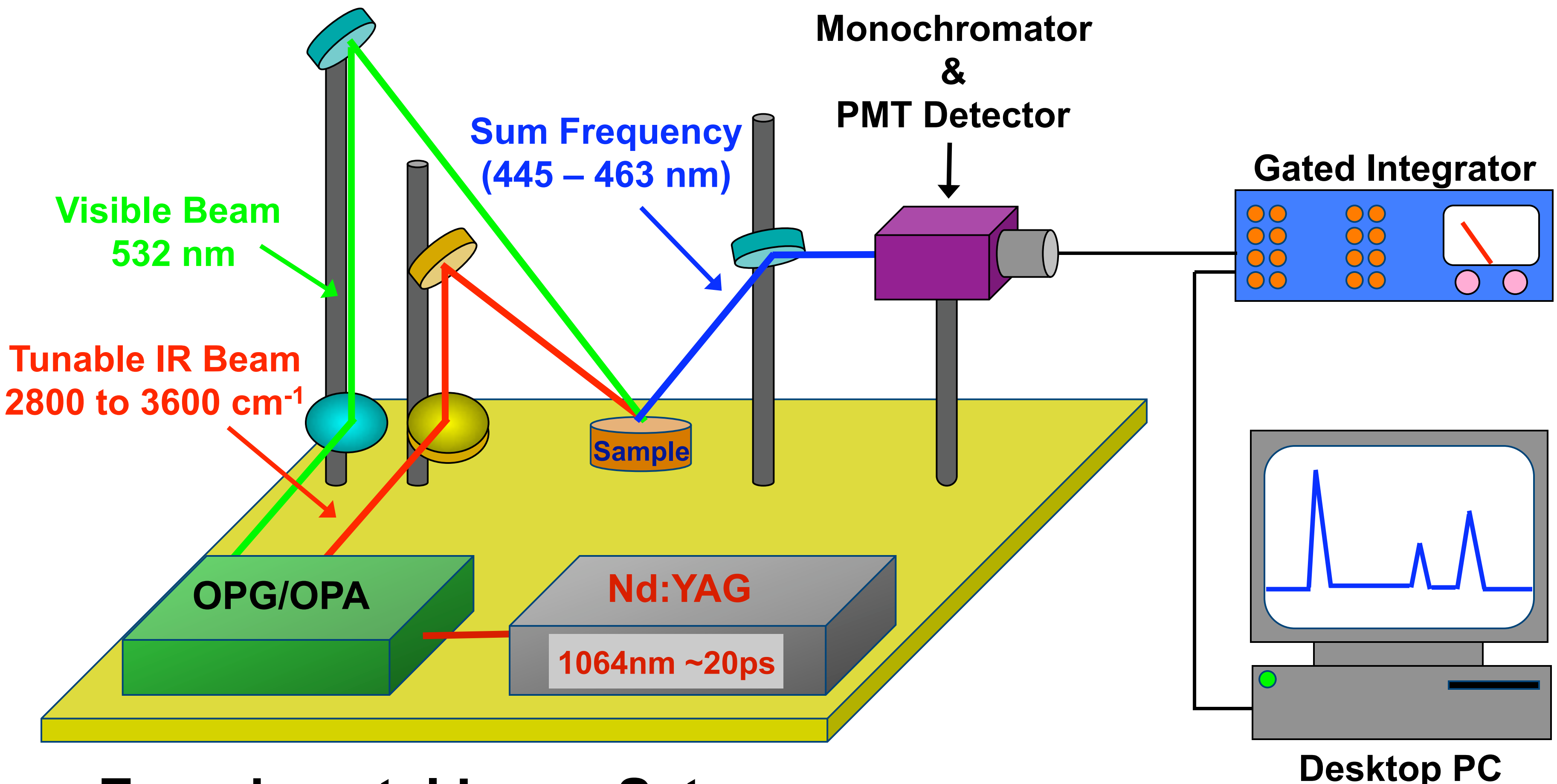

**$\chi^{(2)}$ is nonzero → *Surface-Specific SFG Signal!***

# Experimental SFG Setup

— Visible (532 nm) — IR (2800-3600 cm$^{-1}$) — SFG (445-463 nm)



# SFG: Surface-Specific Vibrational Spectroscopy

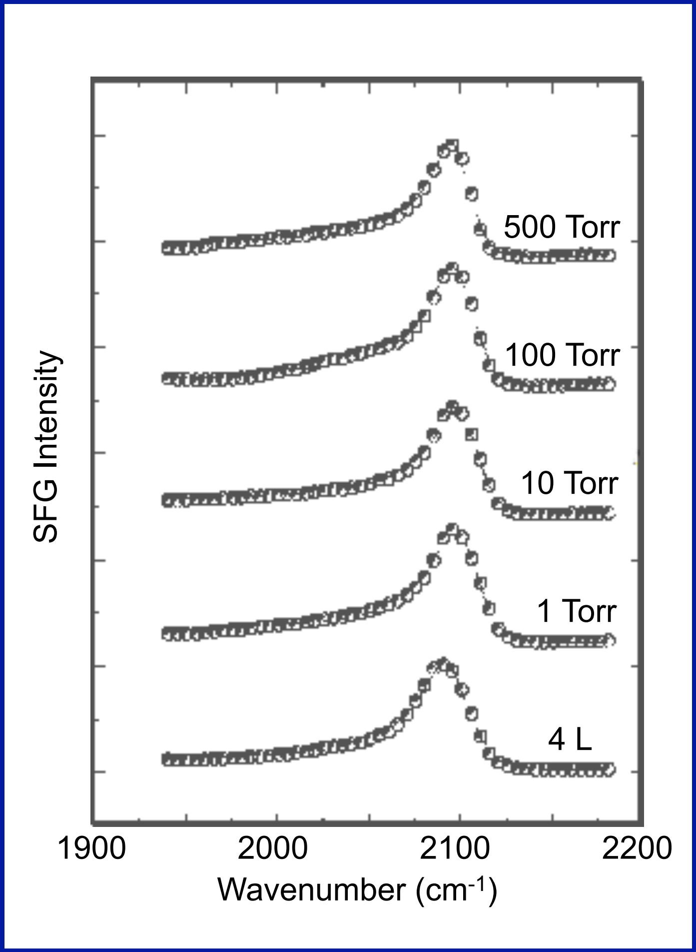



**Experimental Laser Setup**

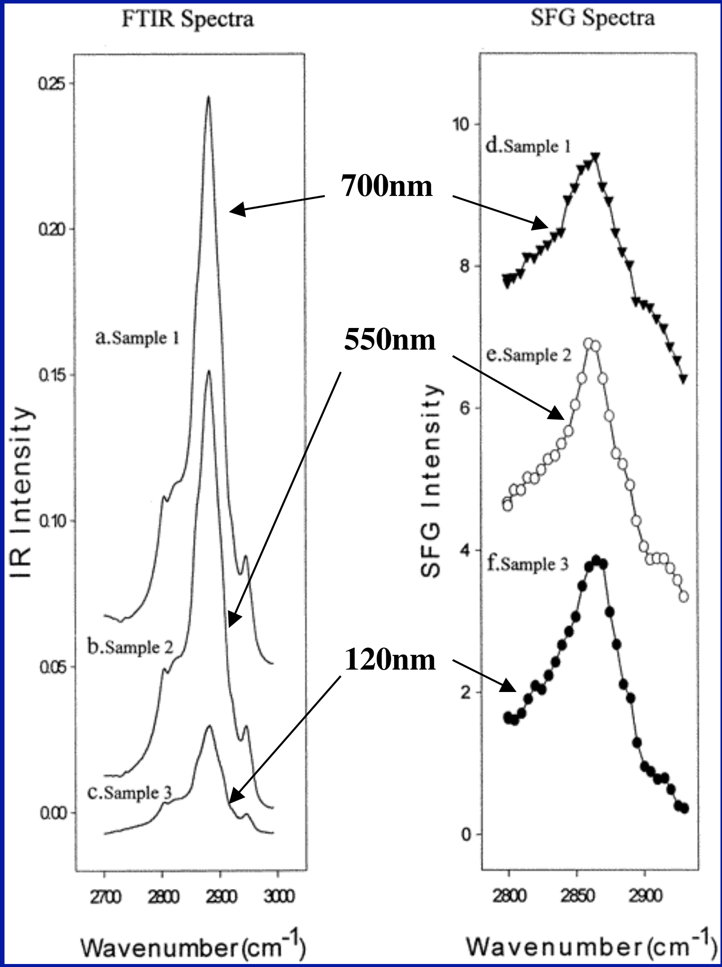
# Surfaces Under Pressure and at Liquid Interfaces

# Experimental Evidence for the Surface Sensitivity of SFG

**The pressure independence of the SFG spectra of CO on Pt (557)**

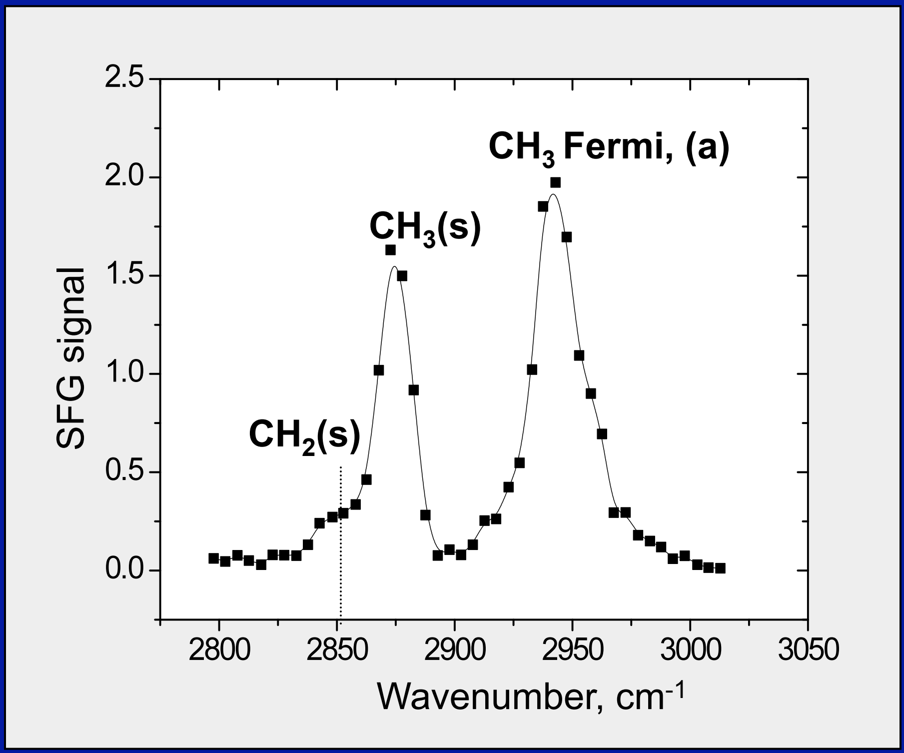


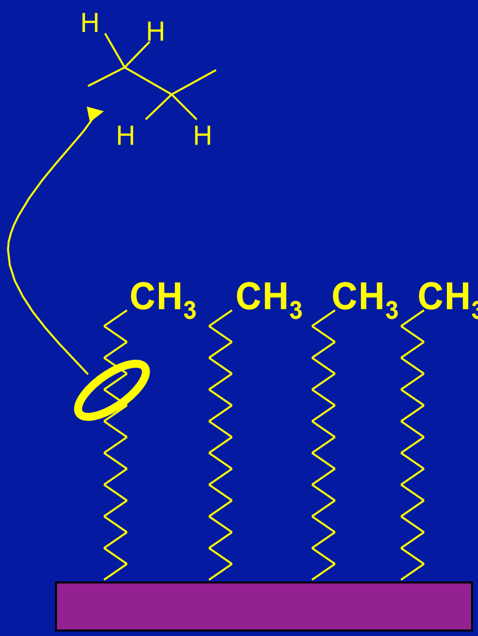

**The thickness independence of the SFG spectra of polyethylene glycol films**



# Example of SFG Surface Sensitivity: Alkanethiol self-assembled monolayer (SAM)

## SFG spectra: C-H stretching region



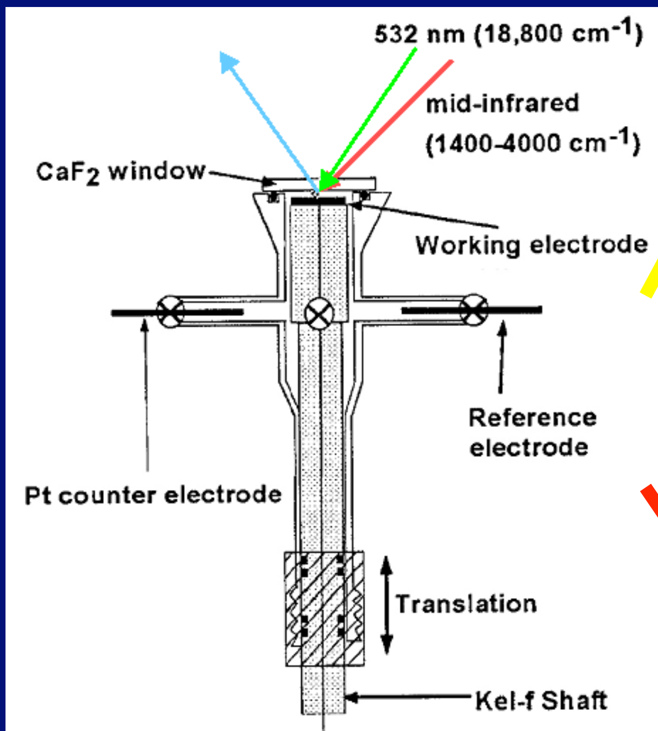



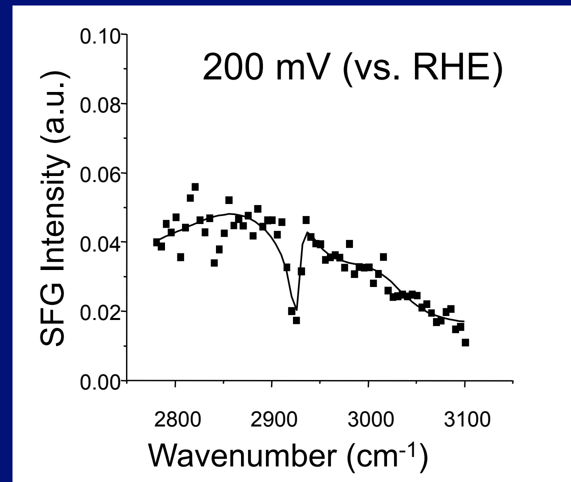
# Surface Science at Liquid Interfaces

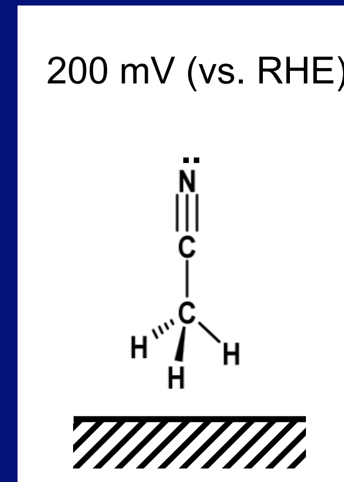
- Surface Electrochemistry
- Biointerfaces

# SFG Sensitive to Orientation of Acetonitrile on Pt(111) with Varying Surface Potential

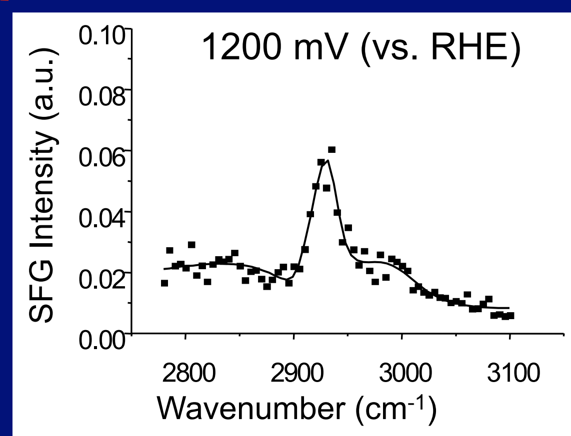
## SFG Electrochemical Cell

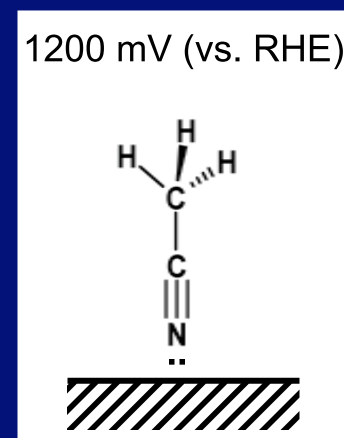



**Low (+) Potential**
**vs.**
**High (+) Potential**



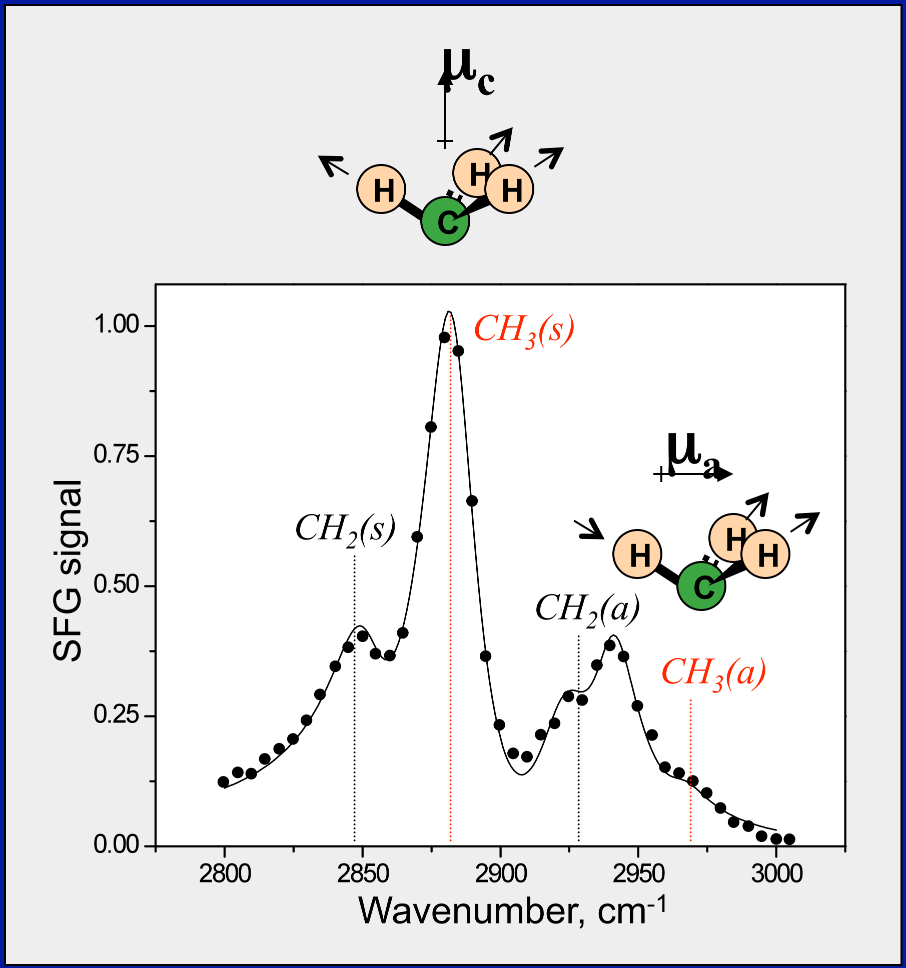



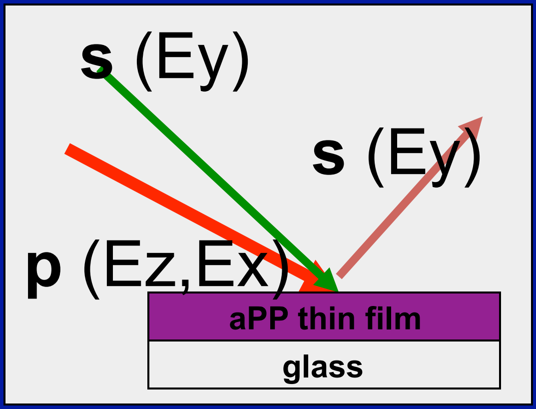


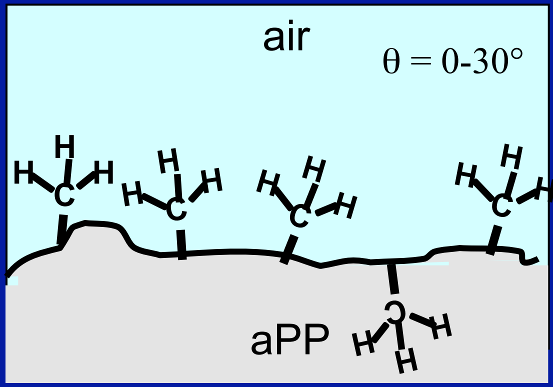
Baldelli S, Mailhot G, Ross PN, and Somorjai GA.
*J. Am. Chem. Soc.* (123) 31, 2001

# Changes of Polymers at Solid-Gas and Solid-Liquid Interfaces

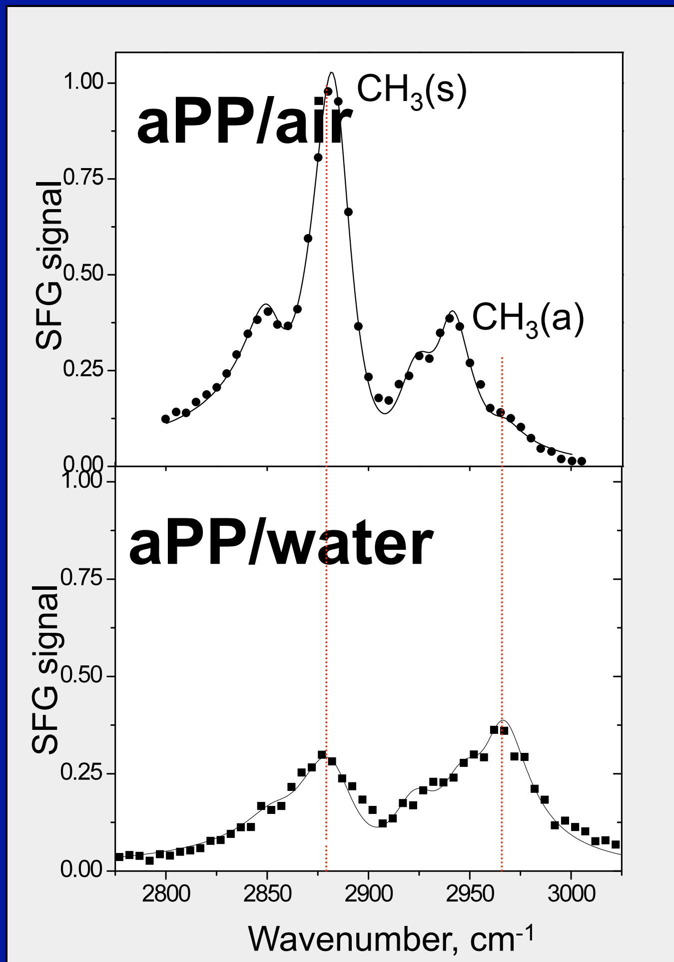
# SFG spectrum of atactic polypropylene

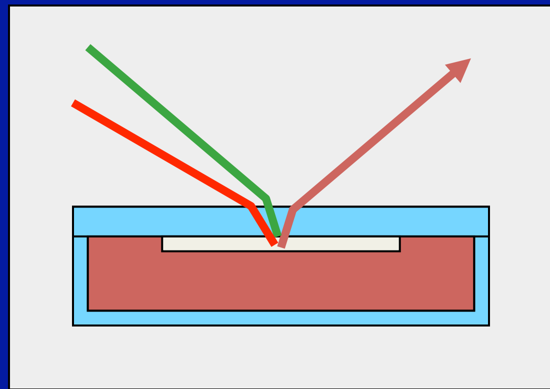


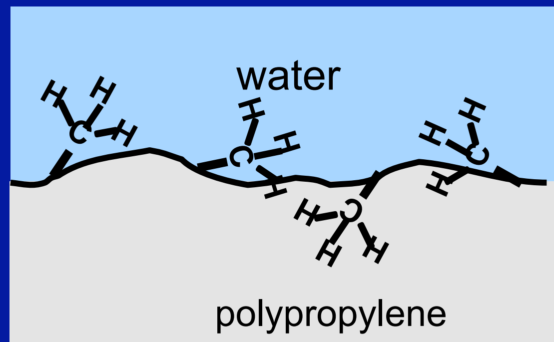



# Polypropylene/water interface

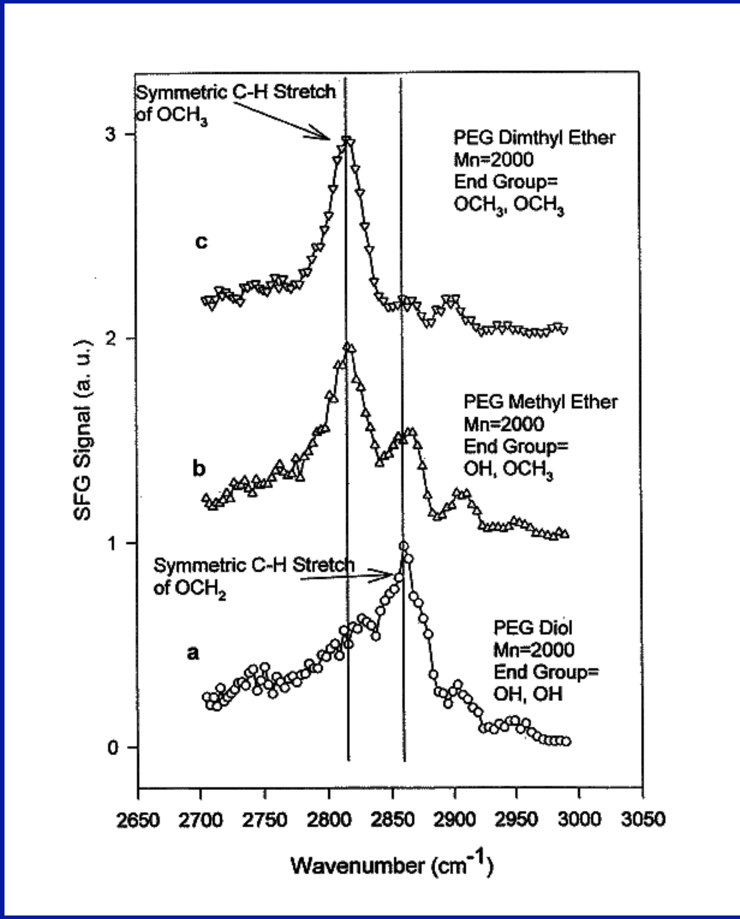


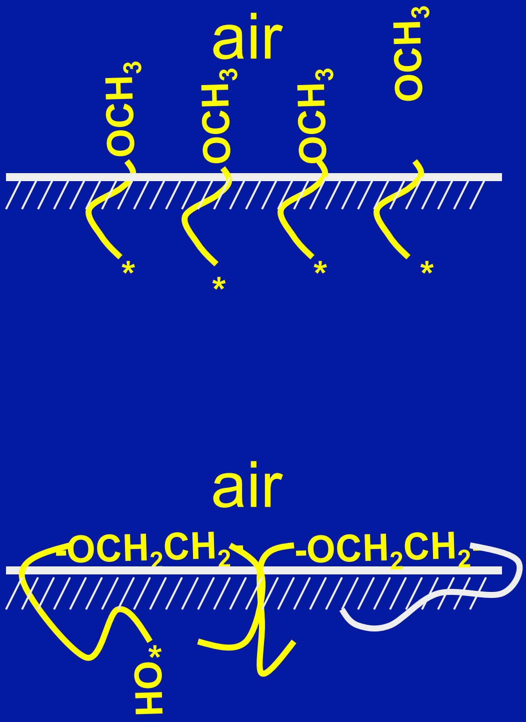






Polypropylene $CH_3$ side branches tilt and/or disorder

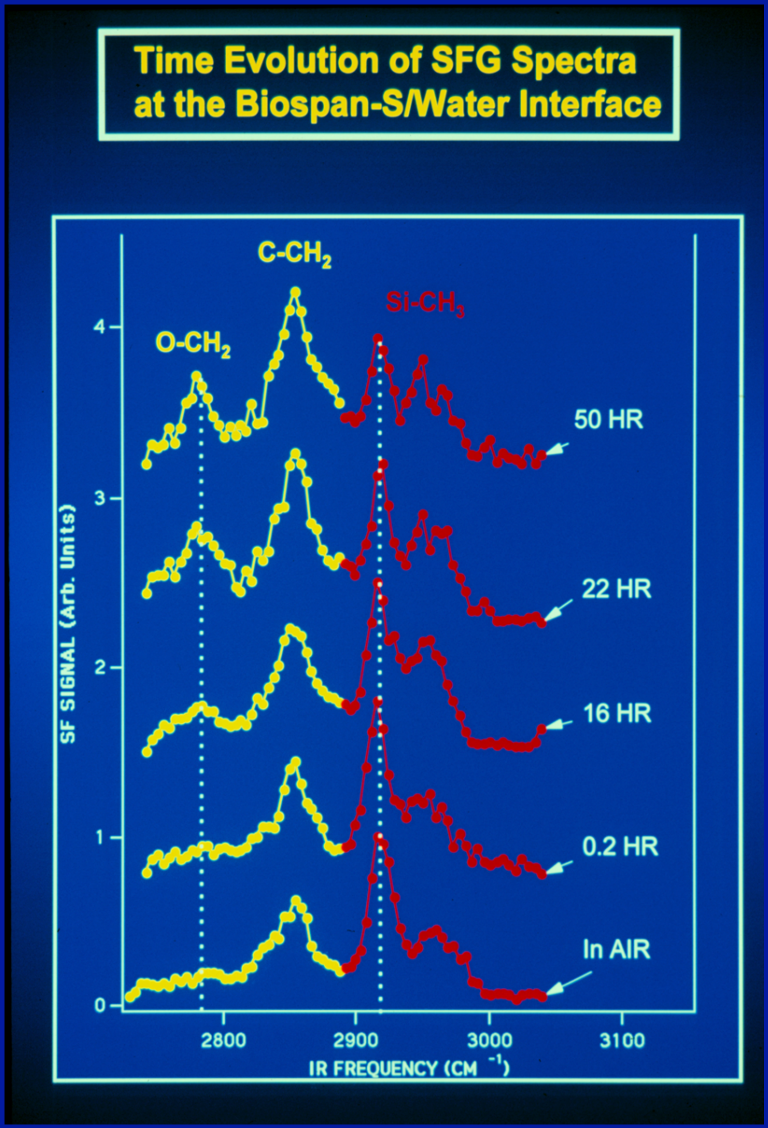
# Hydrophobic endgroup segregation at the air interface in polyethylene glycol (PEG) oligomers

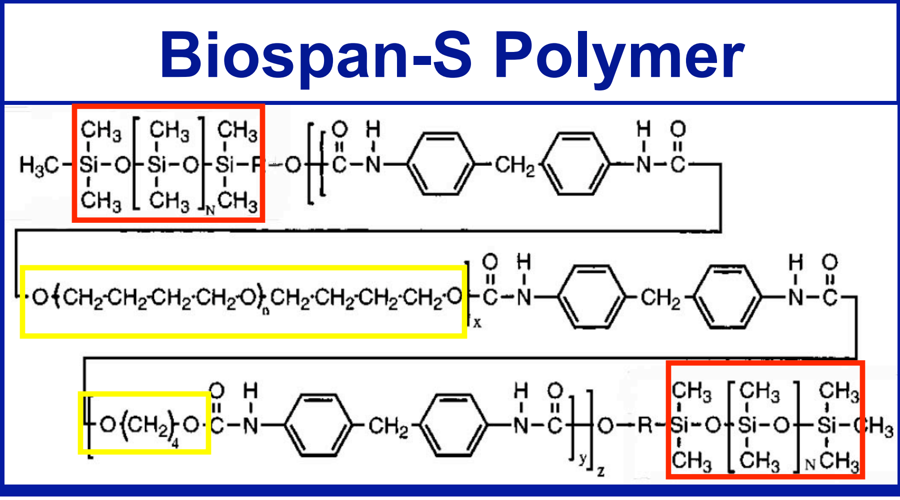


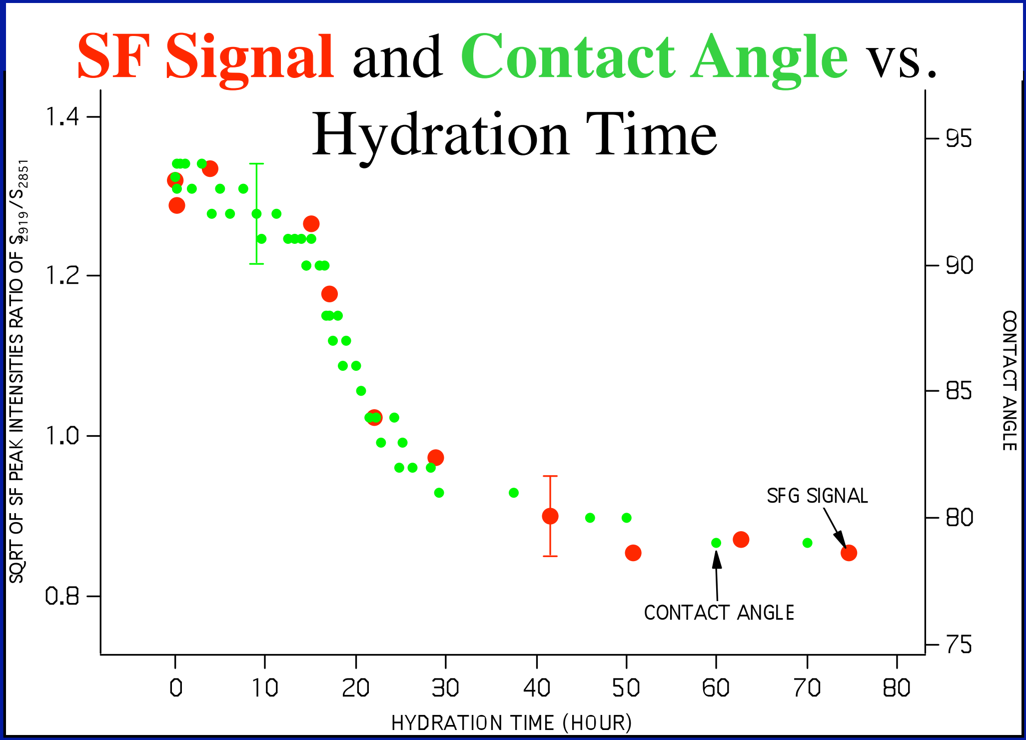




**Detection of Hydrophobic End Groups on Polymer Surfaces by Sum-Frequency Generation Vibrational Spectroscopy**
Chen, Z.; Ward, R.; Tian, Y.; Baldelli, S.; Opdahl, A.; Shen, Y.-R.; Somorjai, G. A.;
*J. Am. Chem. Soc.;* **2000;** *122*(43); 10615-10620.

# SFG Sensitivity to Polymer Surface Hydration



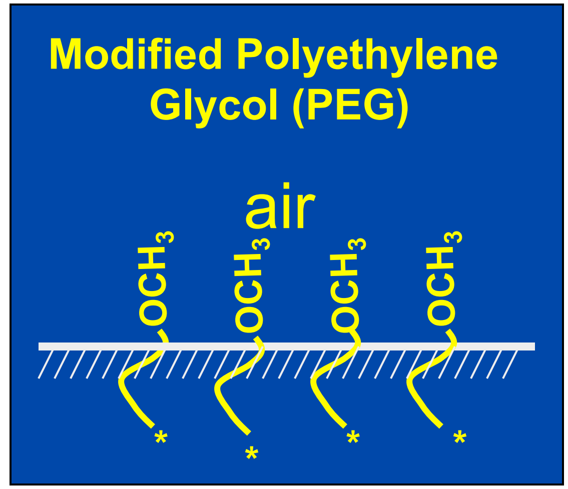



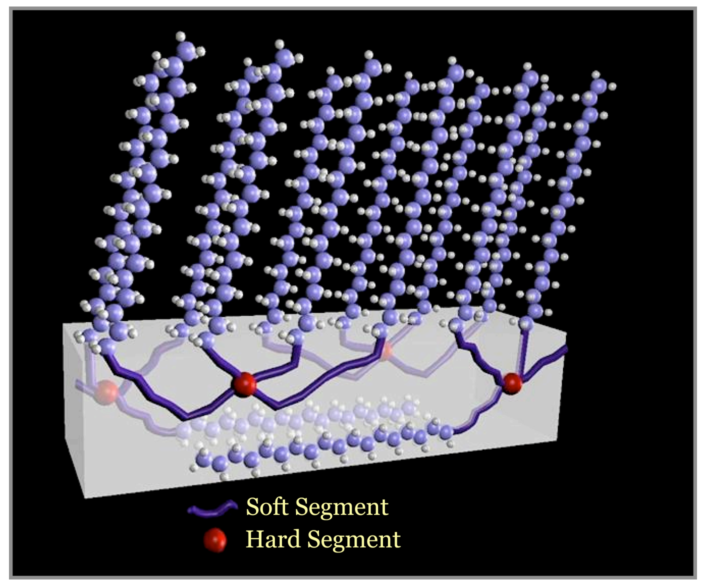

Zhang D, Ward RS, Shen YR, and Somorjai GA. *J. Phys. Chem. B* (101) 44, 1997

# Surface Modification Technology

- **SME™ = Surface Modifying End Group**
  – Surface-active end group covalently bonded to a base polymer during synthesis




- **SAME™ = Self Assembling Monolayer End Group**
  – Self-assembling end group covalently bonded to a base polymer during synthesis



# Utilizing End Groups to Modify Surface Chemistry

1. **Antimicrobial Activity**

$$SAME = HO\text{-}R_1\text{-}N^+(CH_3)_2\text{-}R_2$$

2. **Enhanced Thrombo-resistance**

$$SAME = HO\text{-}(CH_2)_{17}\text{-}CH_3$$

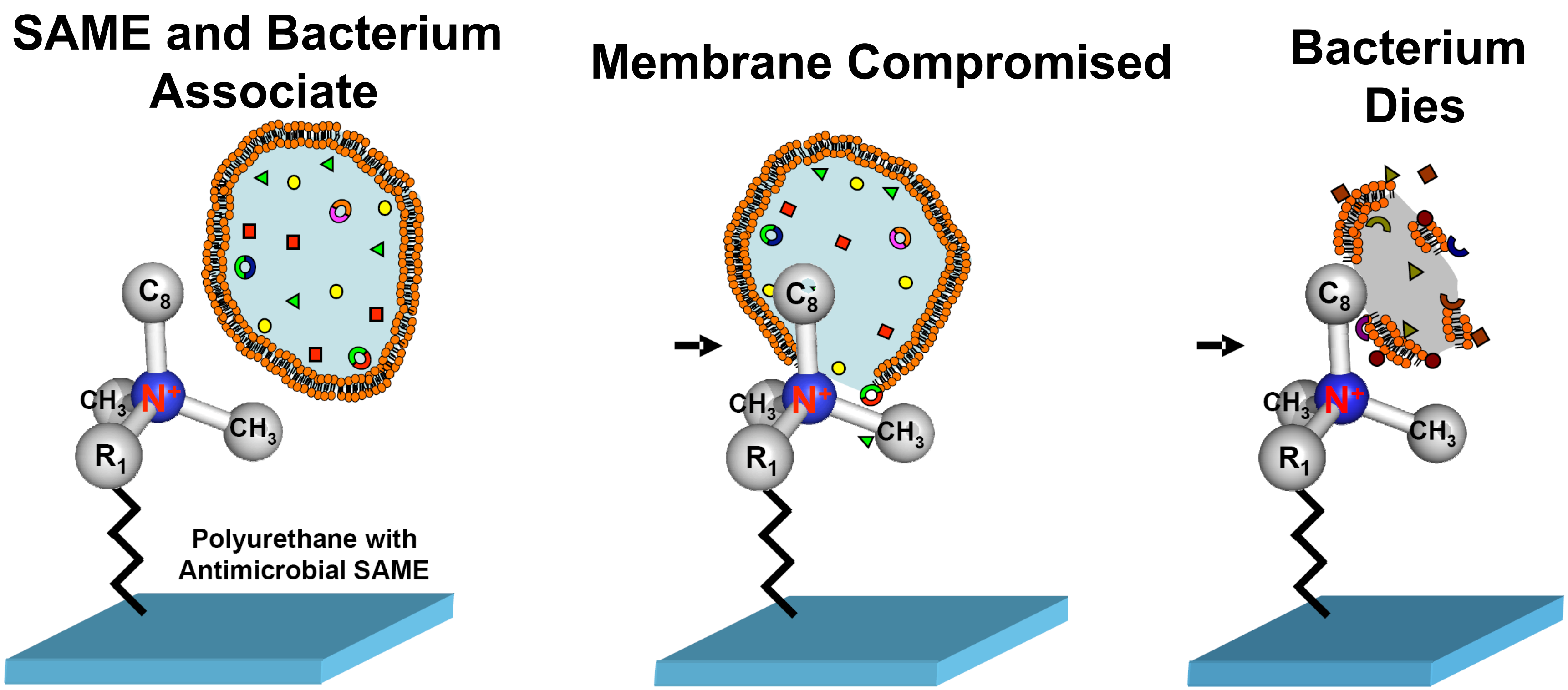
3. **Improved Biostability**

SME = HO-Fluorocarbon

*Unlimited.* DSM

# Example 1: Antimicrobial SAME Surfaces

- Ionic Interaction with Bacterium Cell Membranes[1]
  - Membranes Disrupted
  - Permeability Increased

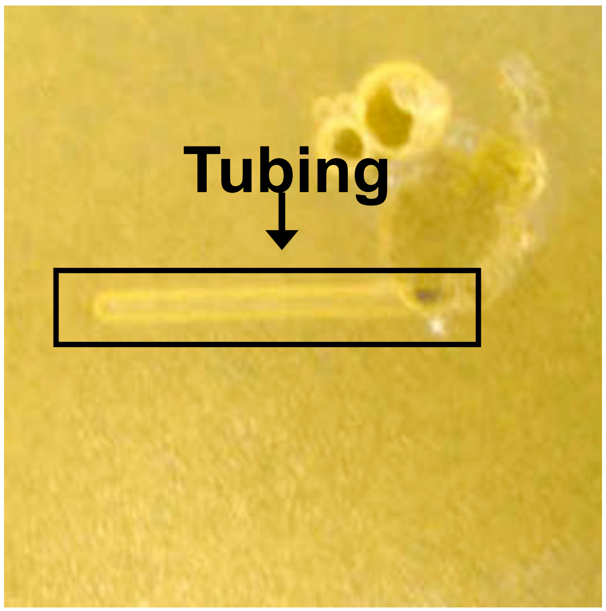



1. Denyer, S. P. and Stewart, G. S. A. B., *Int. Biodet. Biodegrad.* (41) 261-268, 1998.

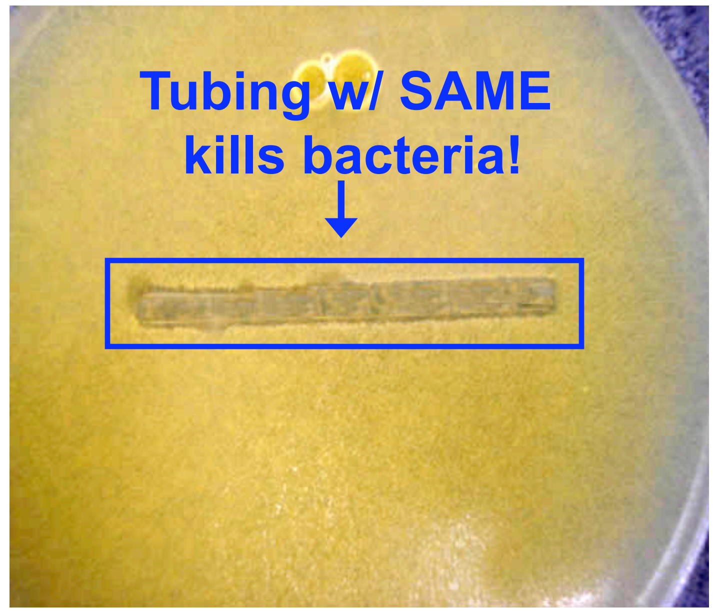
Unlimited. DSM

# Antimicrobial SAME Resists Staphylococcus Bacteria

**PU Tubing Control**



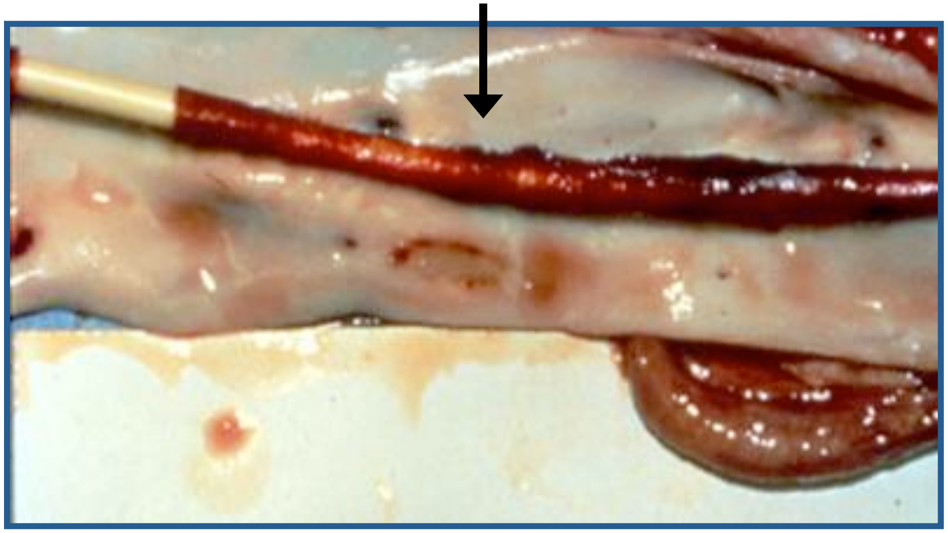

**PU tubing with 0.5 wt% Antimicrobial SAME**




**Test Organism: *Staphylococcus aureus* (ATCC 6538)**

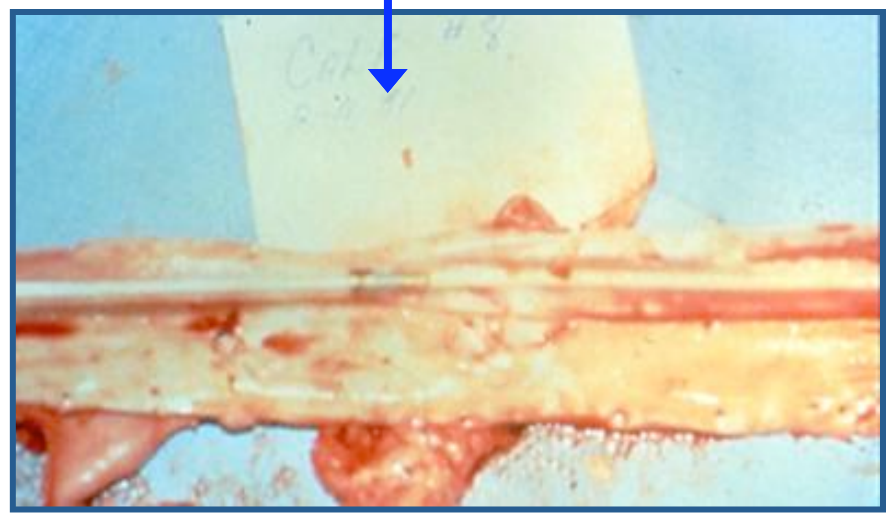
# Enhanced Thrombo-resistance

**<u>Without</u> surface modifier/wax**



**Blood clots line balloon surface**

**<u>With</u> surface modifier/wax**



**Enhanced thrombo-resistance**

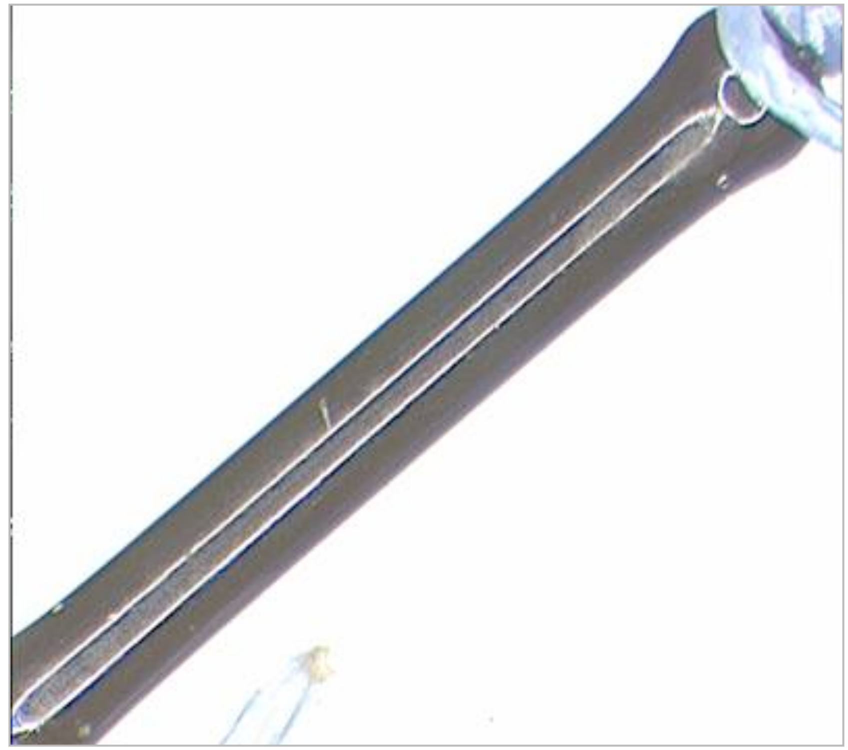
*Unlimited.* **DSM**

# Example 3: Biostability of Fluorocarbon SMEs

**Polyether-urethane control**
**no fluorocarbon**

**Polymer Degradation**

**Polyether-urethane**
**with fluorocarbon SME**



**No Polymer Degradation**

Ward, R. *et al*. *J. Med. Biomed. Res*. (79A) 836-845, 2006

*Unlimited.* **DSM**

# SFG Molecular Studies of Metal Catalysts and Reaction Intermediates

# Catalysis in the 20th Century

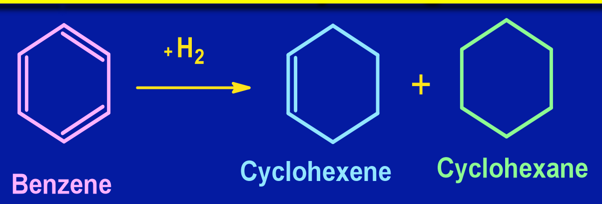
Focus on Catalytic Activity

# Catalysis in the 21th Century

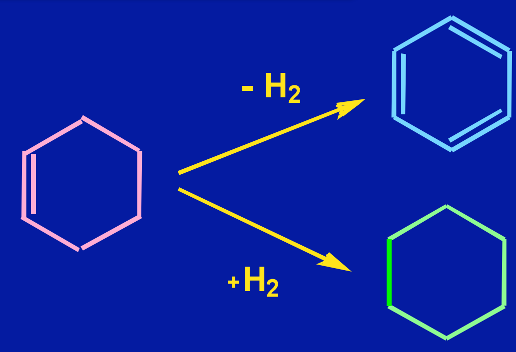
Focus on Catalytic Selectivity

# Catalytic Reactions Studied By SFG

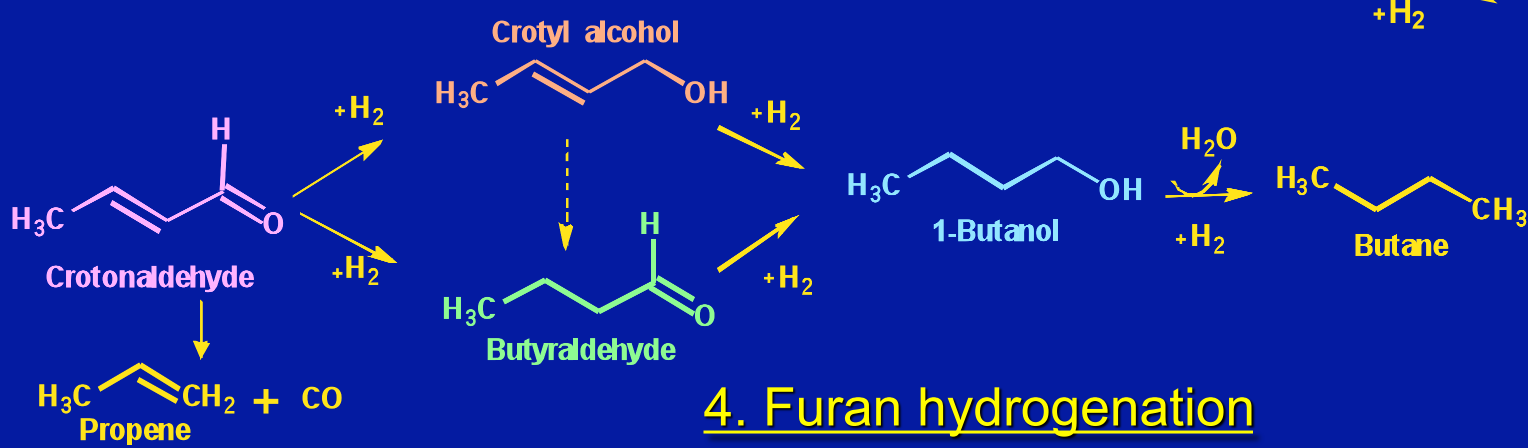
## 1. Benzene hydrogenation



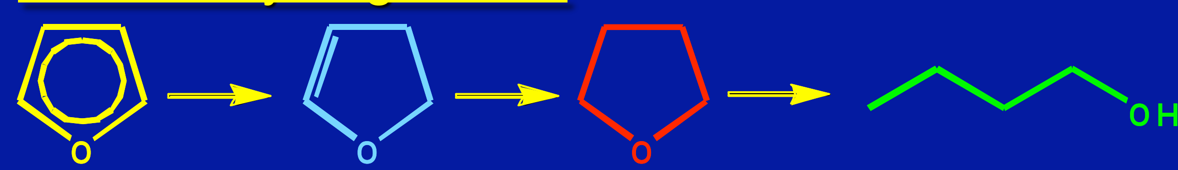

## 2. Cyclohexene hydrogenation/ dehydrogenation



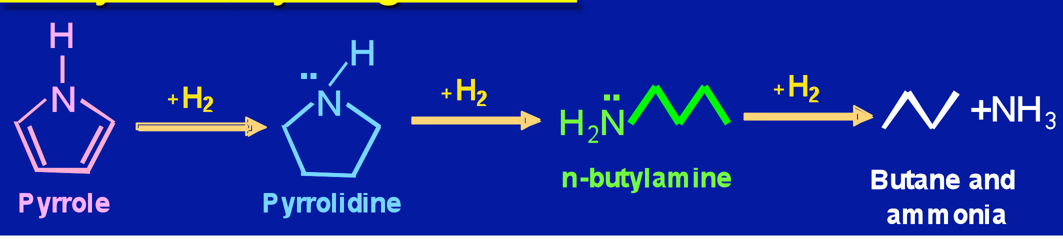

## 3. Crotonaldehyde hydrogenation

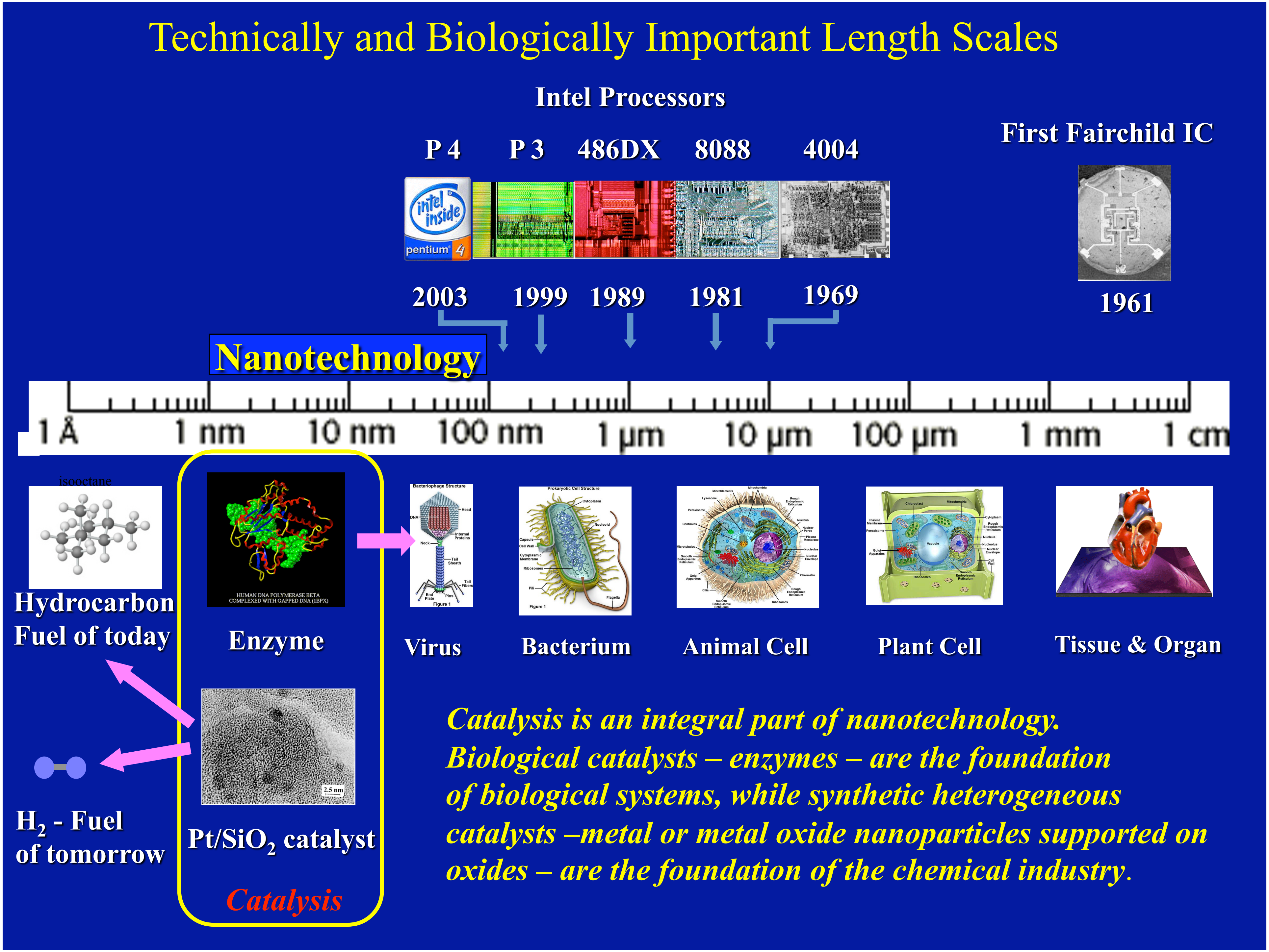



## 4. Furan hydrogenation



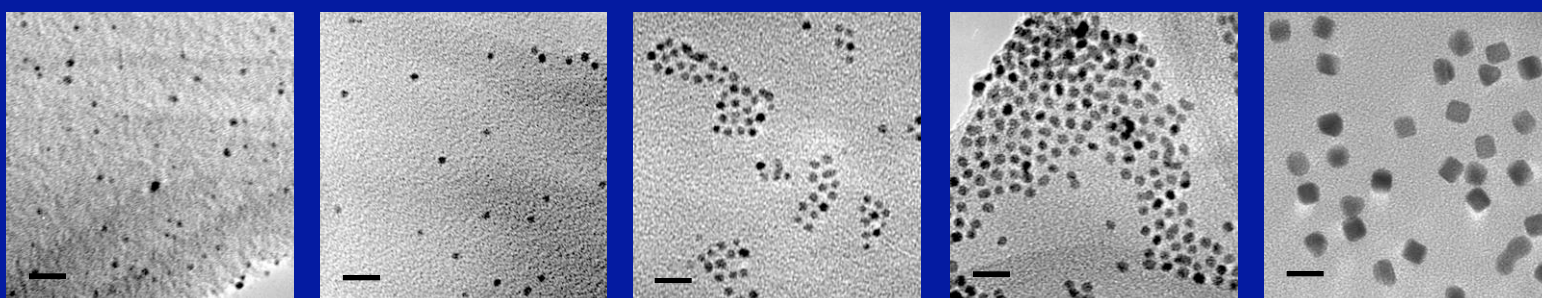

## 5. Pyrrole hydrogenation



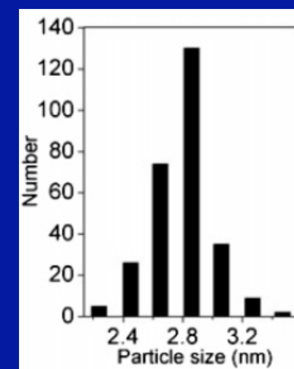

Technically and Biologically Important Length Scales
Intel Processors
P 4
P 3
486DX
8088
4004
2003
1999
1989
1981
1969
First Fairchild IC
1961
Nanotechnology
1 Å
1 nm
10 nm
100 nm
1 μm
10 μm
100 μm
1 mm
1 cm
isooctane
Hydrocarbon
Fuel of today
HUMAN DNA POLYMERASE BETA COMPLEXED WITH GAPPED DNA (1BPX)
Enzyme
Virus
Bacterium
Animal Cell
Plant Cell
Tissue & Organ
2.5 nm
$H_2$ - Fuel
of tomorrow
Pt/$SiO_2$ catalyst
Catalysis
Catalysis is an integral part of nanotechnology.
Biological catalysts – enzymes – are the foundation
of biological systems, while synthetic heterogeneous
catalysts –metal or metal oxide nanoparticles supported on
oxides – are the foundation of the chemical industry.

# Synthesis of Pt Nanoparticles with Size and Shape Control

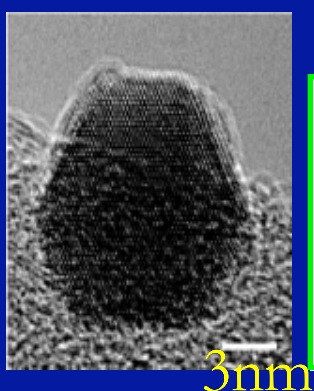
- PVP: Poly(vinylpyrrolidone), surface regulating polymer
- Particle size control in the range of 1.7 ~ 7.1 nm

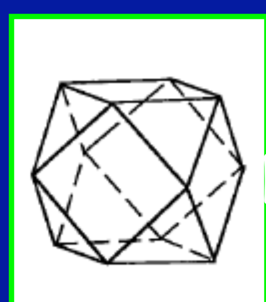


1.73 ± 0.26 nm   2.48 ± 0.22 nm   2.80 ± 0.21 nm   3.39 ± 0.26 nm   7.16 ± 0.37 nm



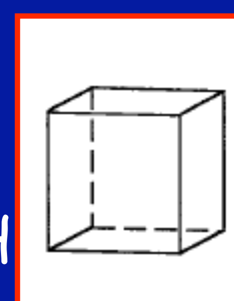

$$K_2PtCl_4 \xrightarrow[50°\,C]{C_{14}TABr} (C_{14}TA^+)_2PtBr_4^{2-}$$

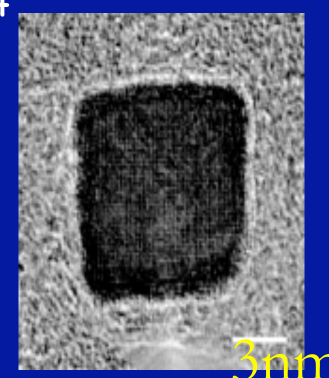


$NaBH_4 + H_2$ low pH

$NaBH_4$ high pH





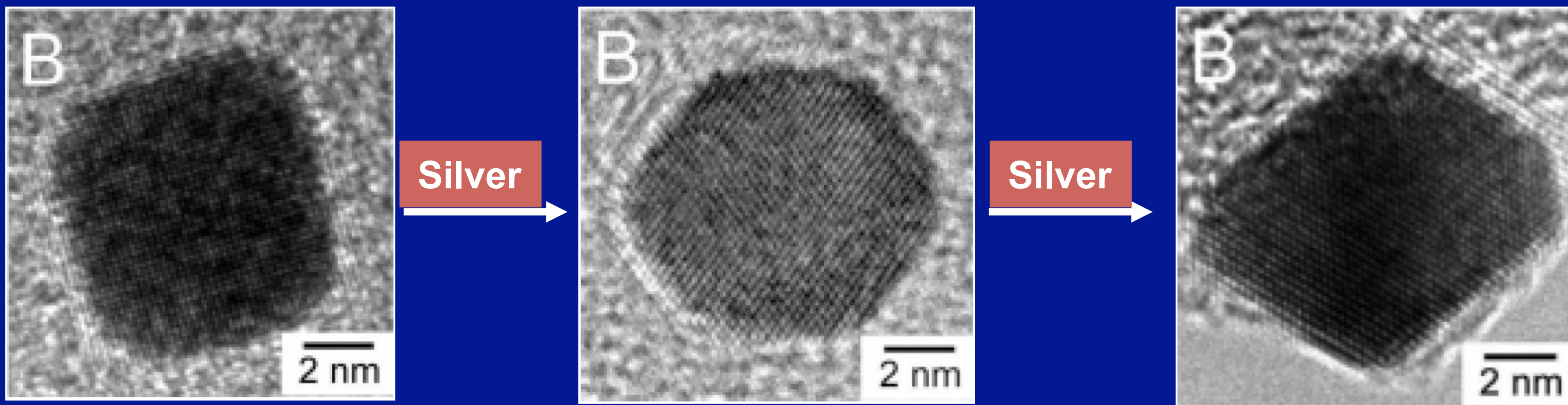

Cuboctahedra

Cubes {100}

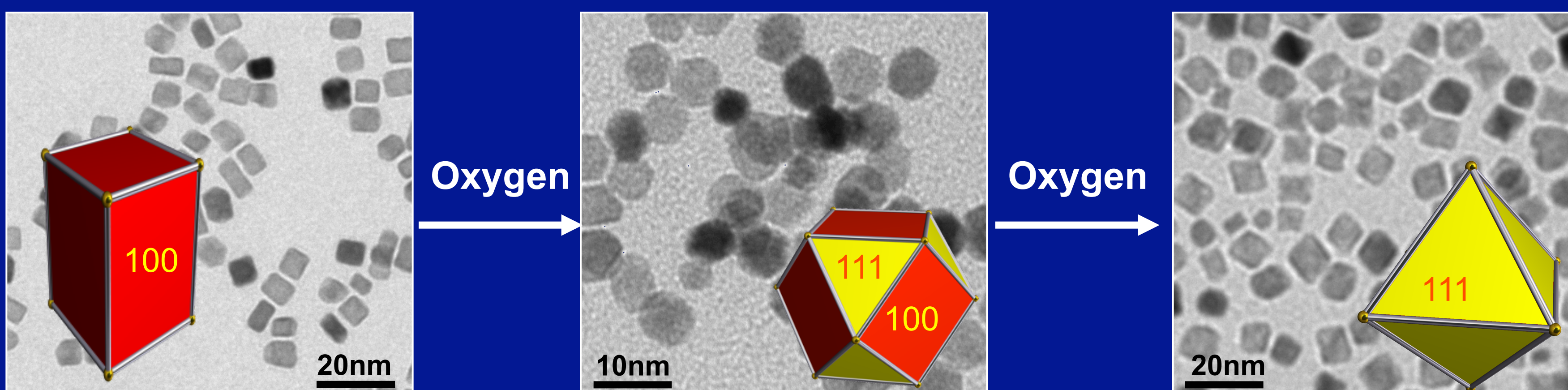
Lee, H.*et al., Angewandte Chemie,* **2006,** 45, 7824.

# Pt and PdPt Alloy Nanocrystal Shape Control

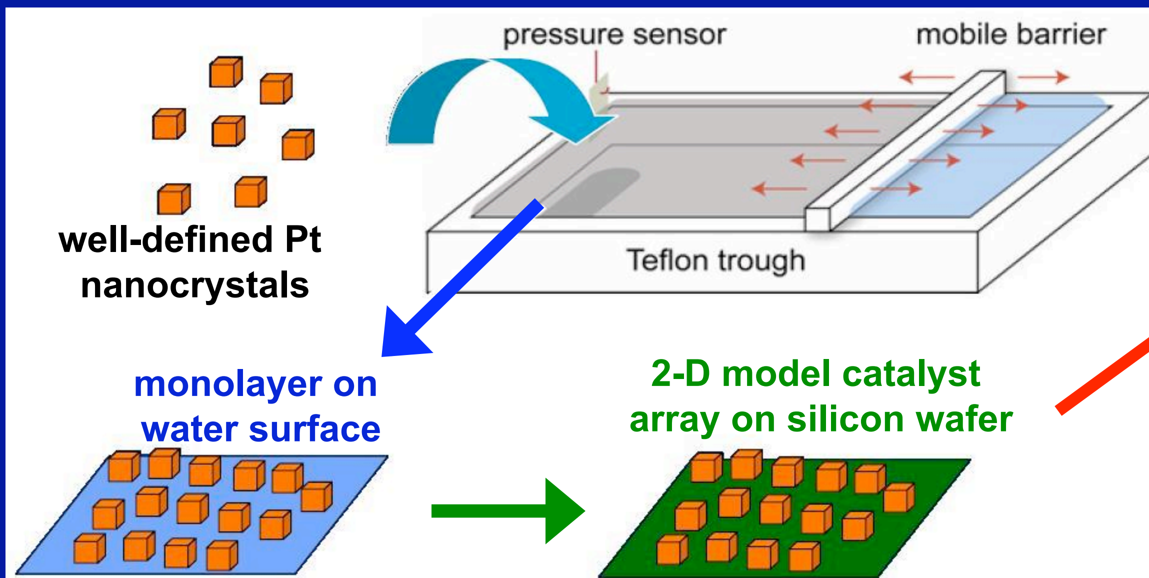
## Pt nanocrystal shape control – silver ion

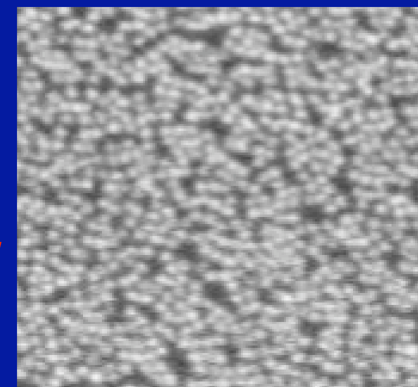



## PdPt alloy nanocrystal shape control – oxygen

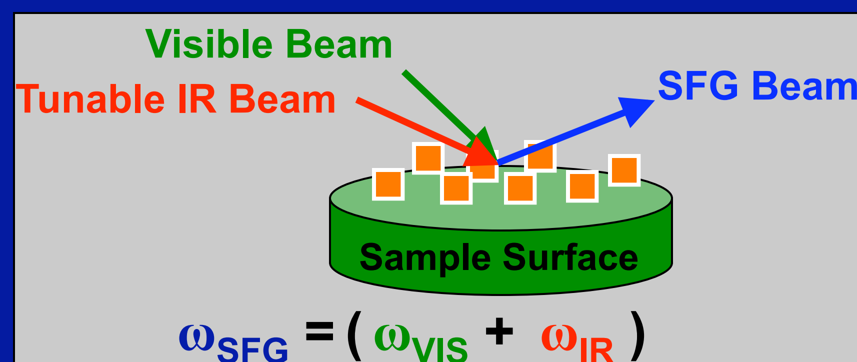


# SFG Catalysis Study of 2-Dimensional Pt Nanoparticle Array



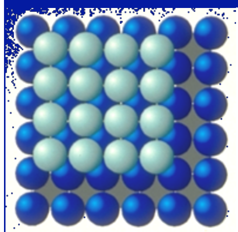



2-D Pt nanoparticles on Silicon Oxide

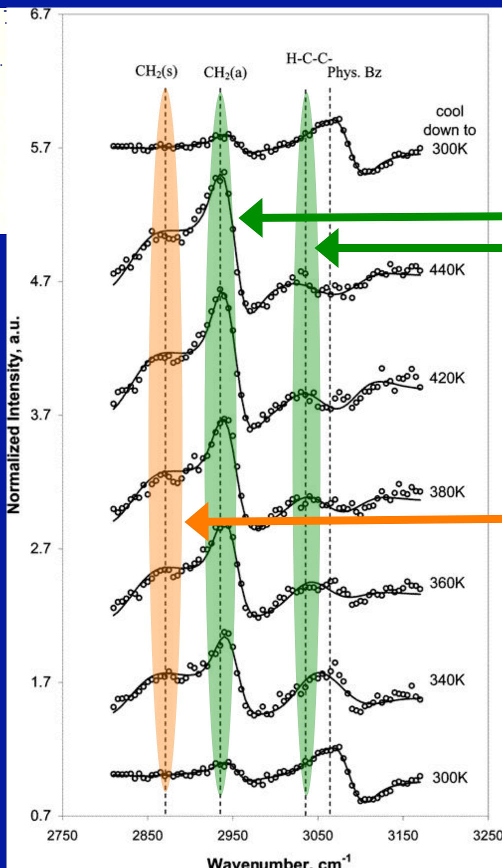


# SFG of Benzene Hydrogenation on Pt(111) and Pt (100)

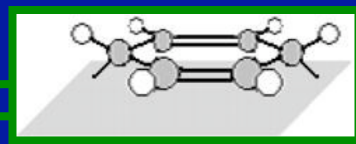
## SFG of Pt (100)

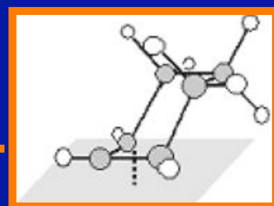


Pt (100)



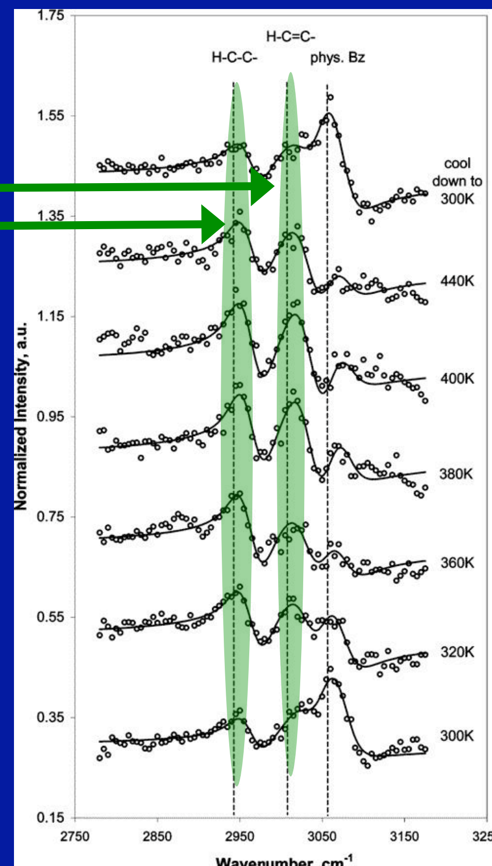

*dienyl* $C_6H_6$

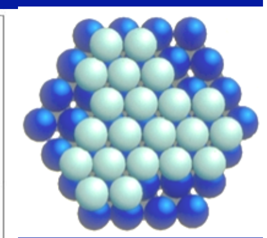




π-allyl *c*-$C_6H_9$

## SFG of Pt (111)



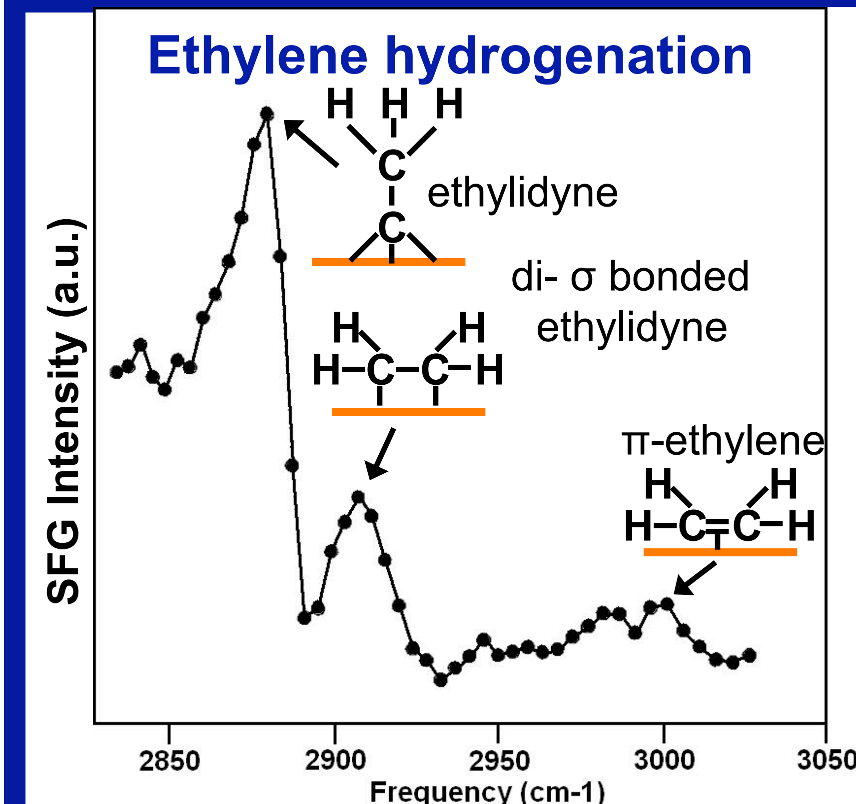
Pt (111)

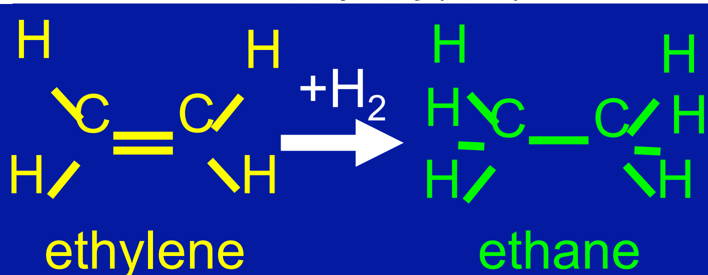
- SFG shows **π-allyl *c*-$C_6H_9$** benzene hydrogenation intermediate on Pt(100) only at high temperatures

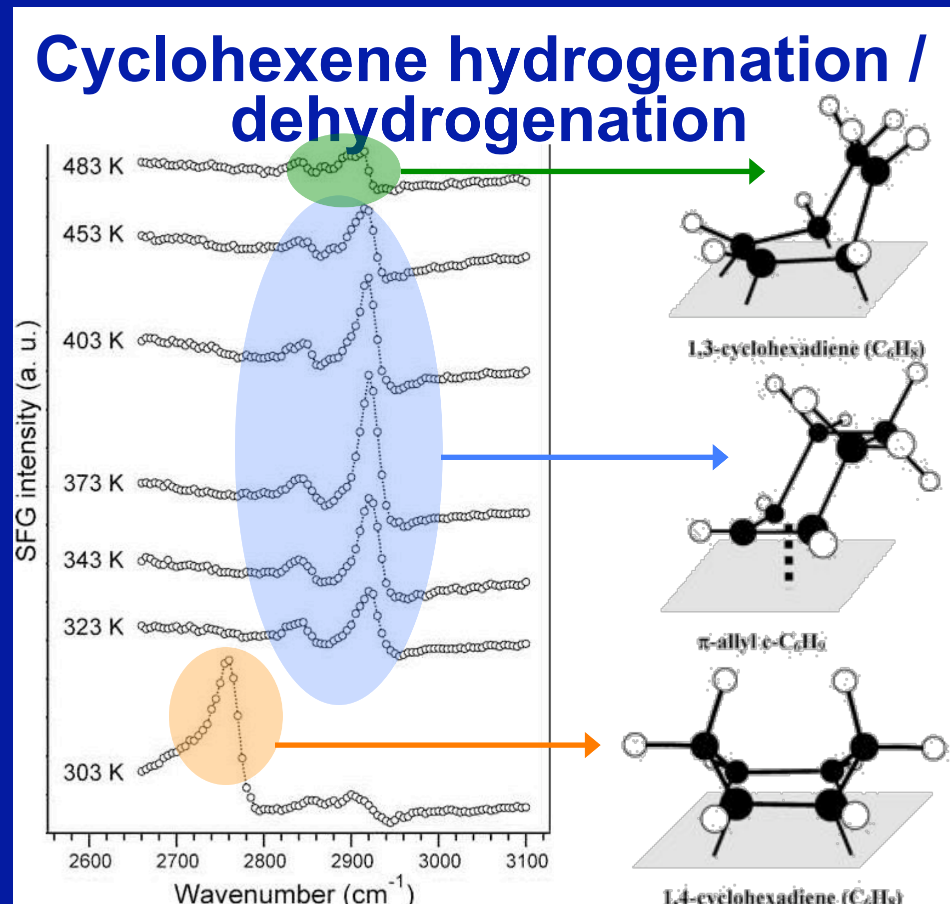
Bratlie KM, Kliewer CJ, Somorjai GA. *J. Phys. Chem. B* (2006), 110, 17925

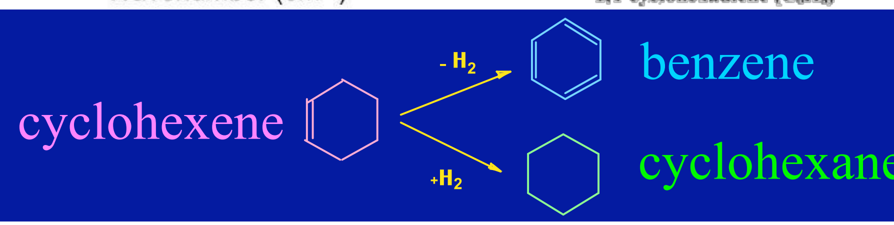
# SFG Allows Study of Single Crystal Metal Catalysts *In-Situ*

## SFG of Catalytic Reaction Intermediates <u>During Reaction</u> on Platinum



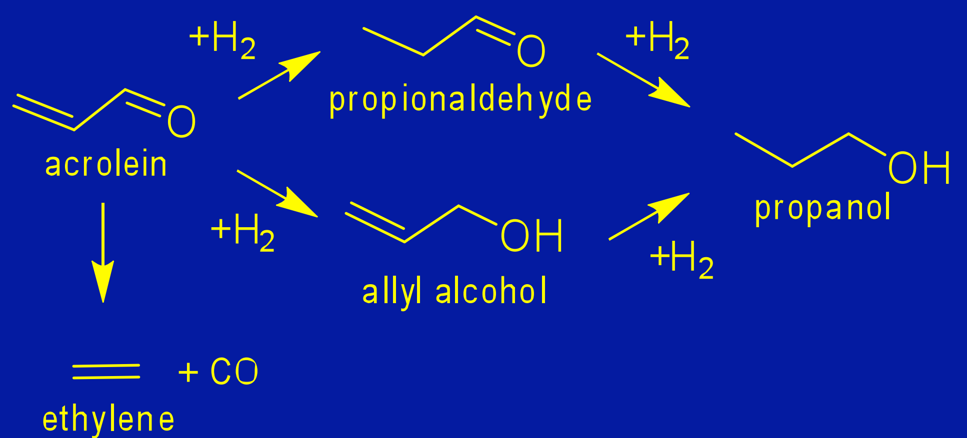



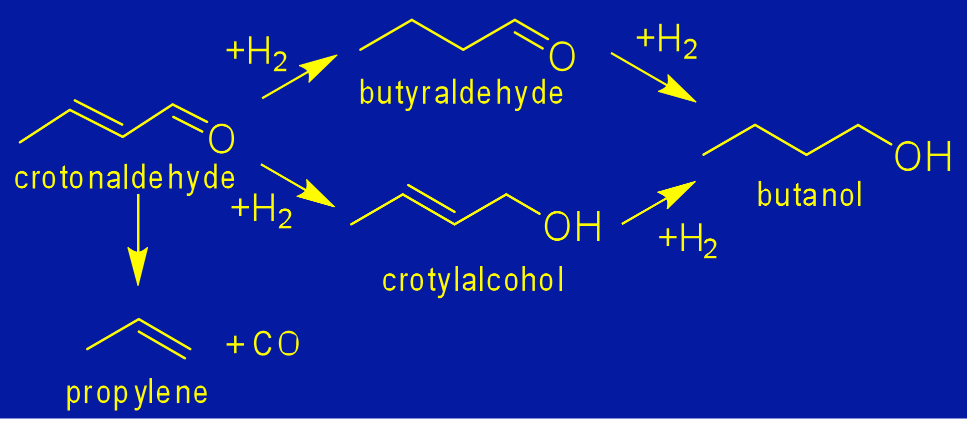



# SFG of Hydrogenation of Bifunctional Molecules over Pt(111)

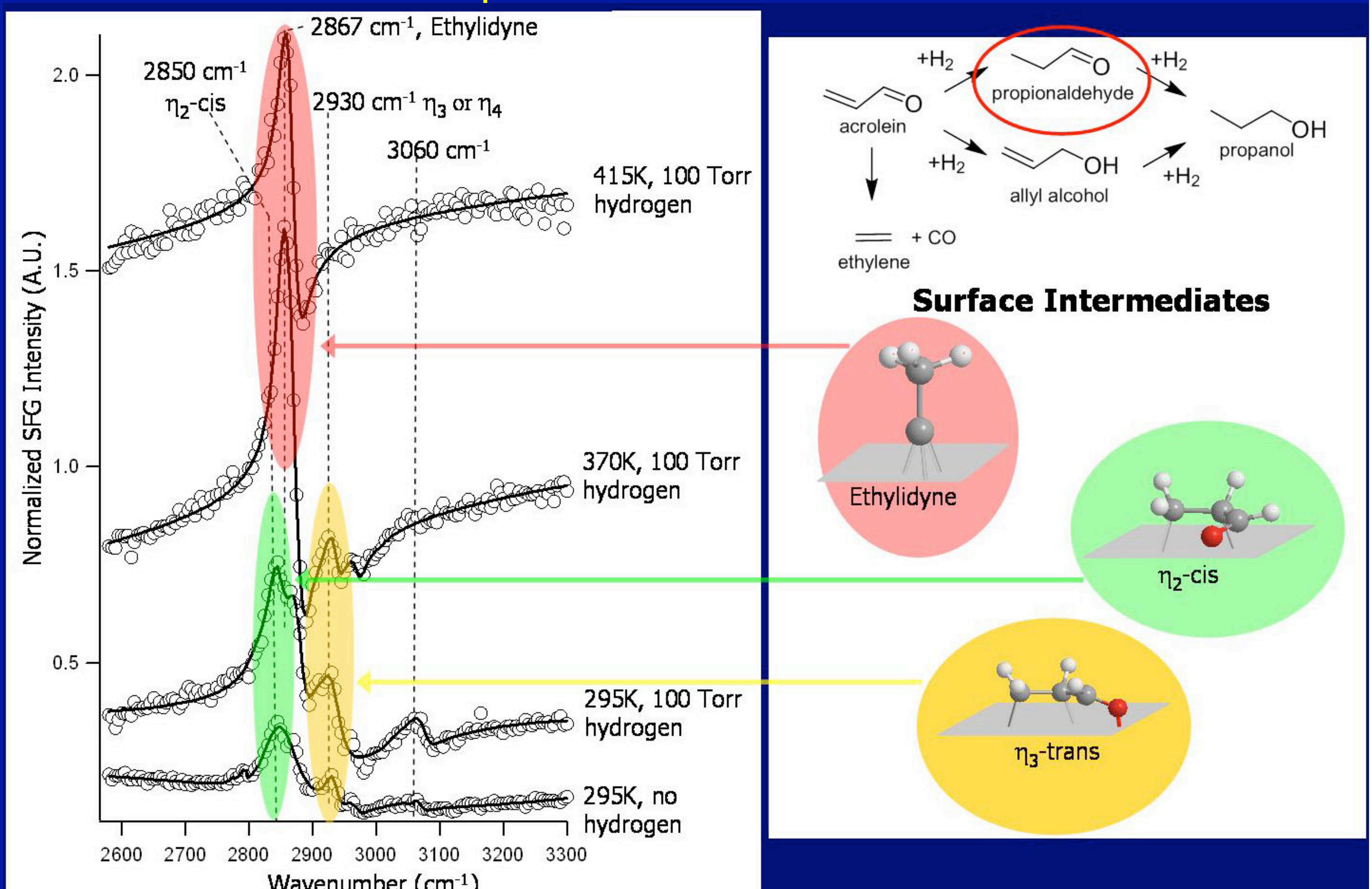
## Acrolein Hydrogenation



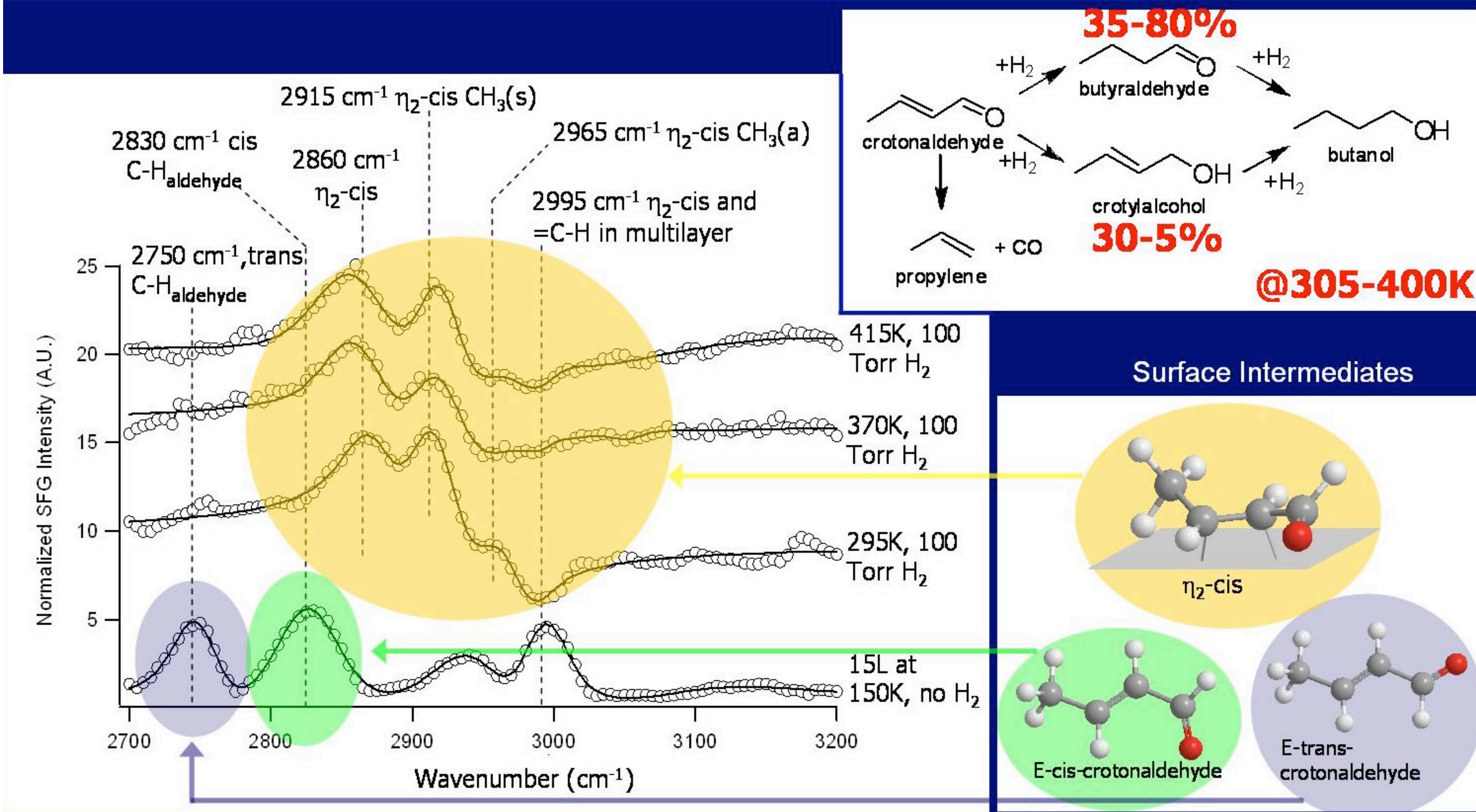

## Crotonaldehyde Hydrogenation



# Acrolein Hydrogenation over Pt(111) Temperature Dependence

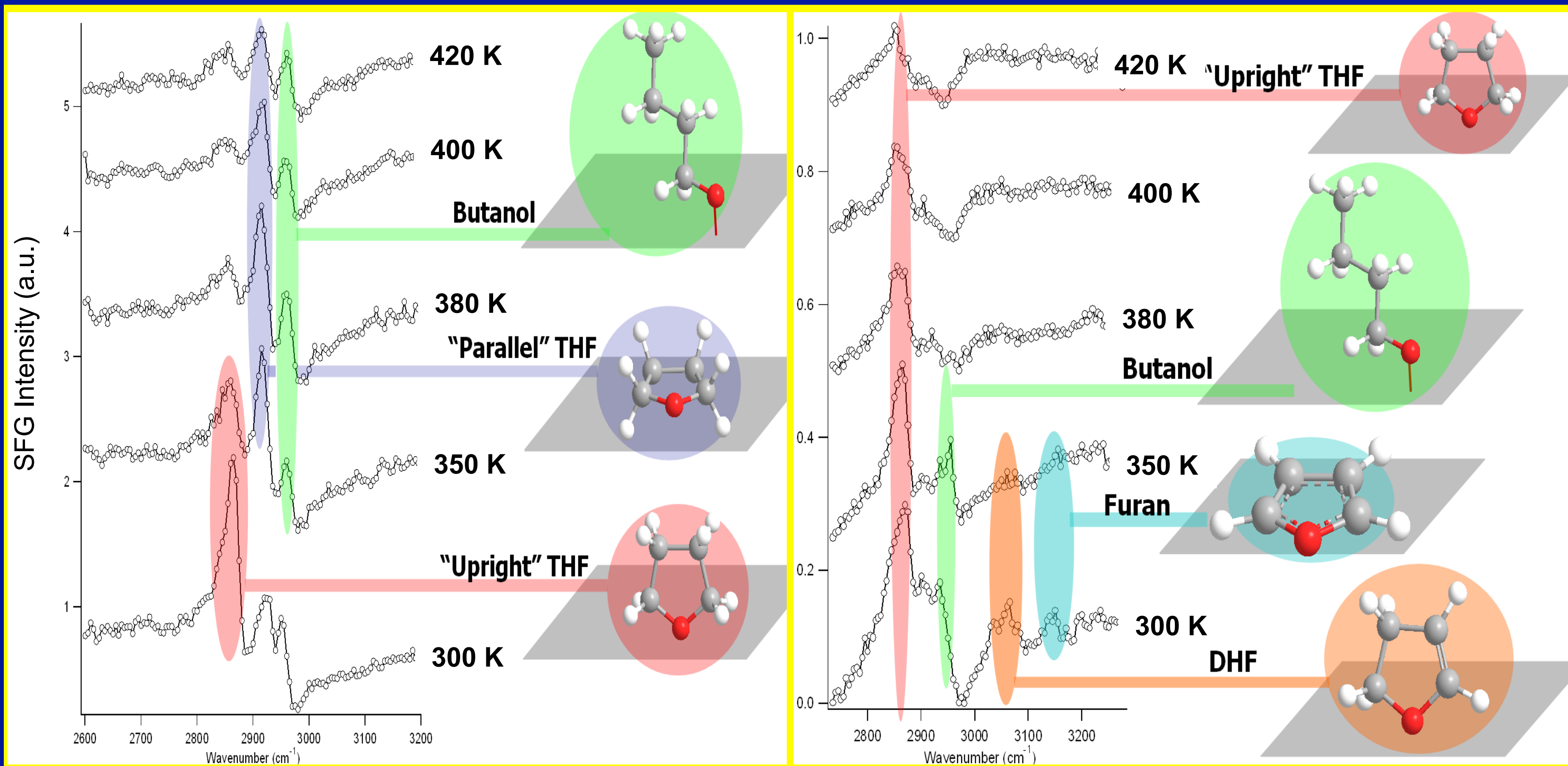


# Crotonaldehyde Hydrogenation on Pt(111)
# (1 Torr Crotonaldehyde)



# Furan Hydrogenation over Pt(111) vs 10 nm Pt Nanoparticles

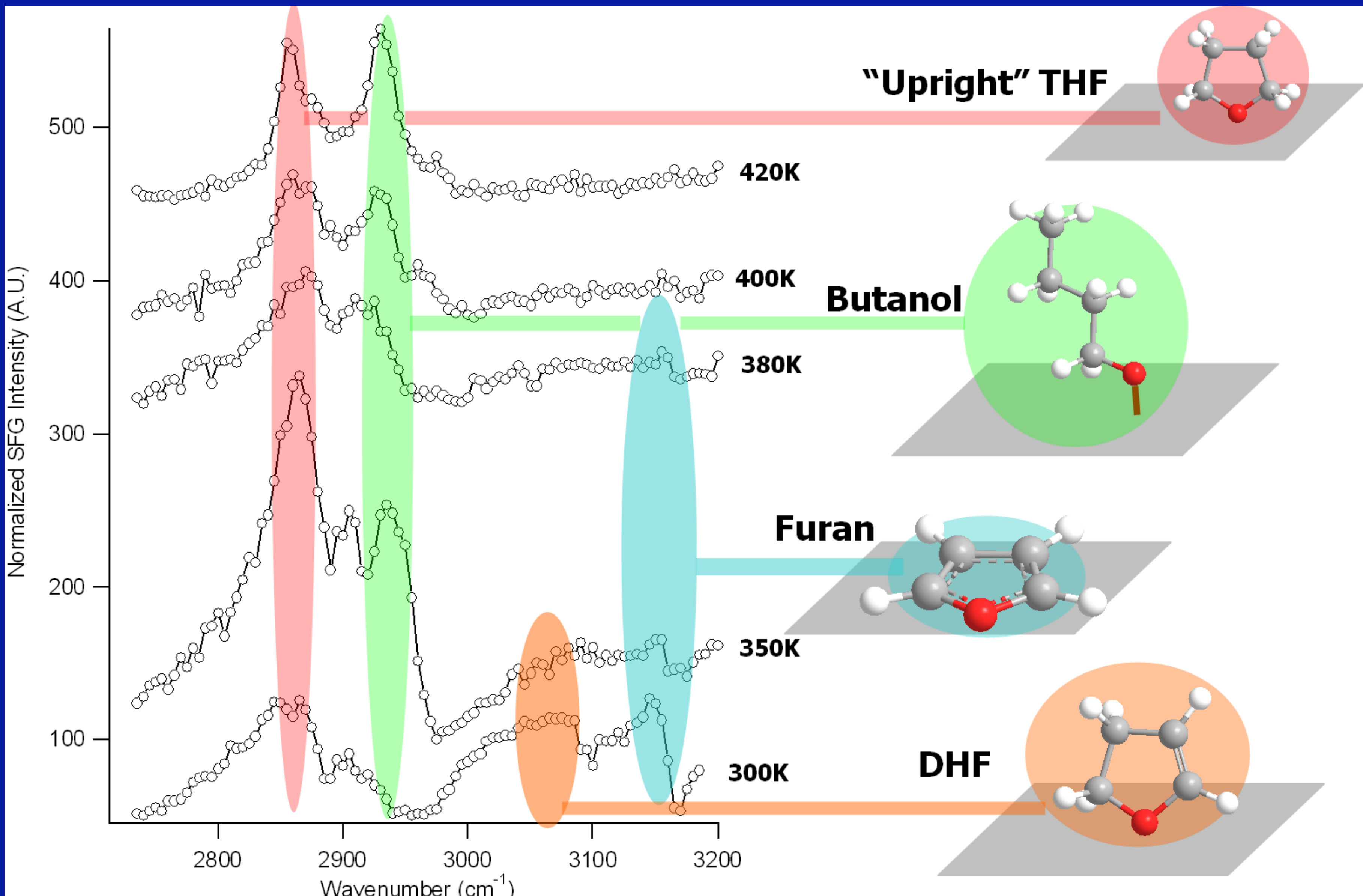
10 Torr Furan and 100 Torr Hydrogen




**Pt(111) Single Crystal** | **10 nm Pt Nanoparticles**

# Furan Hydrogenation on 1 nm Pt Nanoparticles

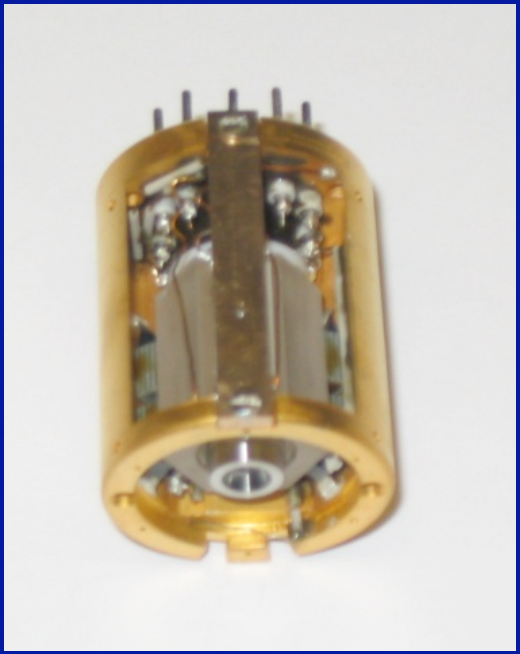
10 Torr Furan / 100 Torr $H_2$

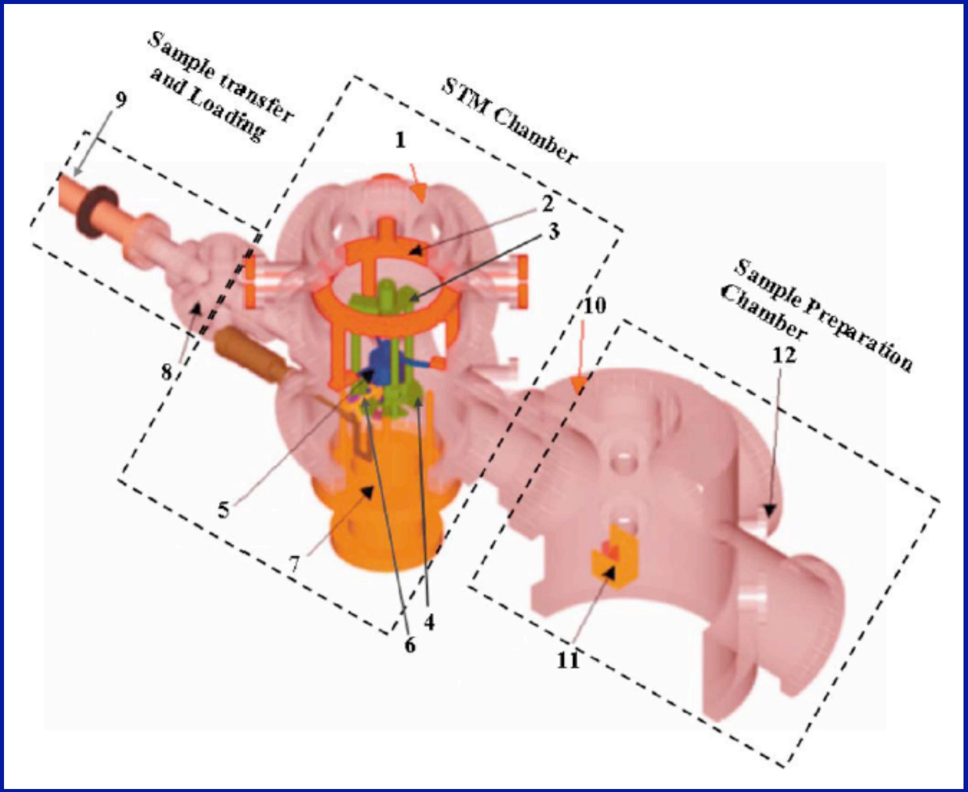


# High Pressure STM

## Substrate Mobility

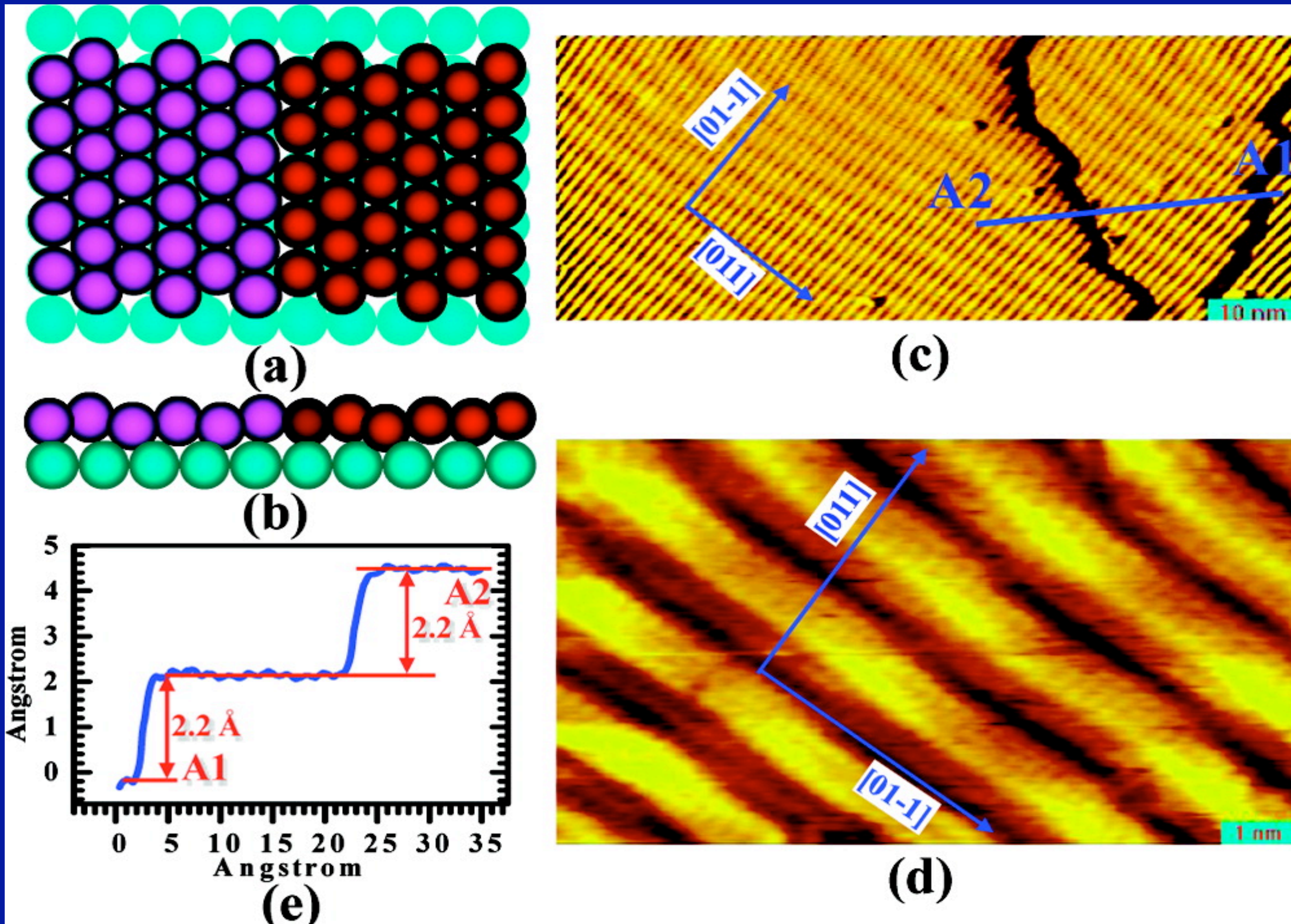
# Scanning tunneling microscopy working under high pressure conditions





# CO on $Pt(100)$

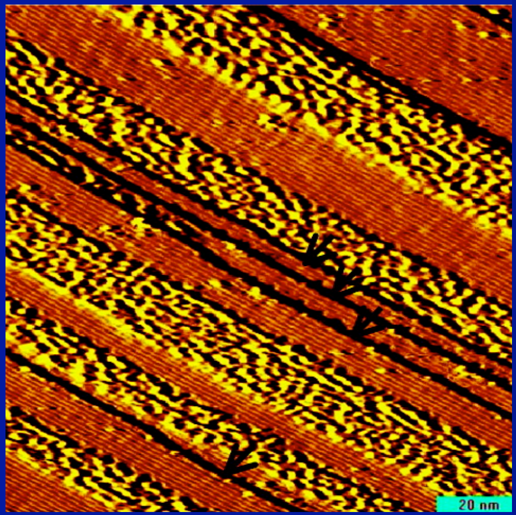
# STM of Pt(100) Hex Reconstruction



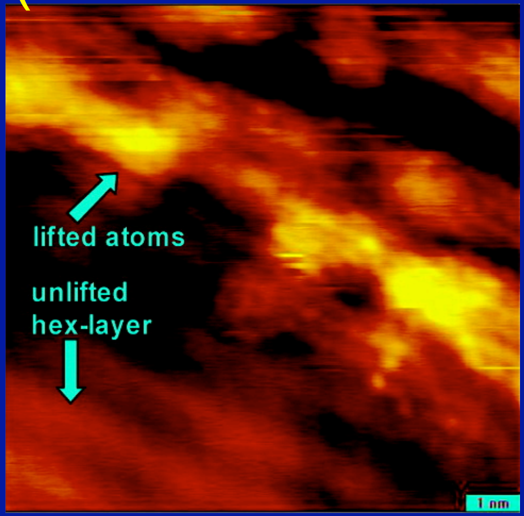

Feng Tao; Sefa Dag; Lin-Wang Wang; Zhi Liu; Derek R. Butcher; Miquel Salmeron; Gabor A. Somorjai; *Nano Lett.* **2009,** 9, 2167-2171.

# Pt(100) Restructuring

10$^{-9}$ Torr CO

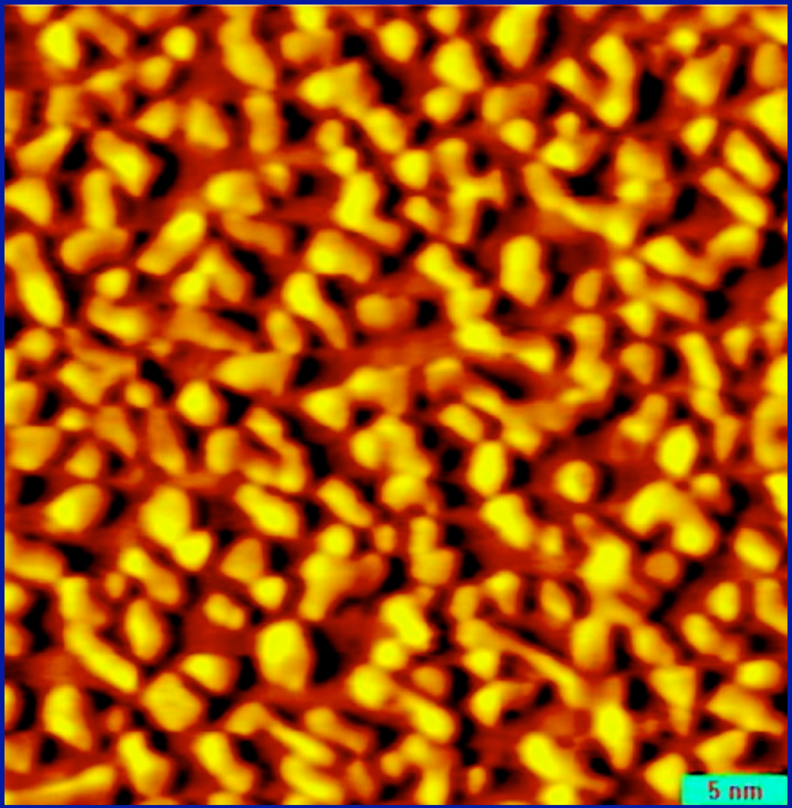



(100 nm x 100 nm)




(10 nm x 10 nm)

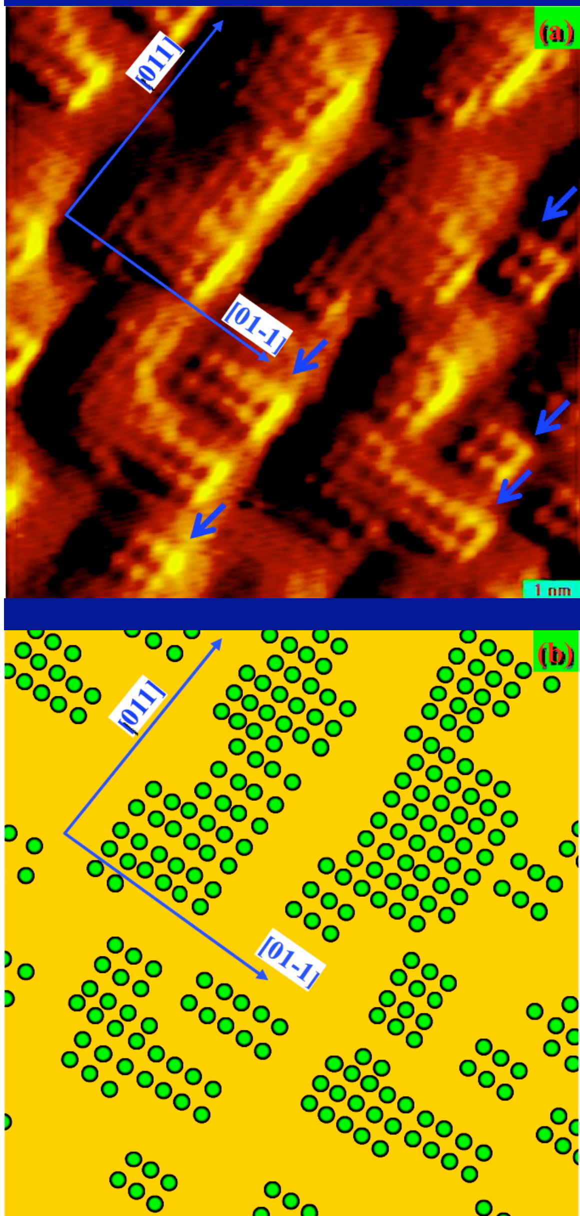
10$^{-5}$ Torr CO




(38 nm x 36 nm)

CO lifts the hex Reconstruction resulting in clusters

# CO/Pt(100) Cluster Structure




**Atomic resolution images**

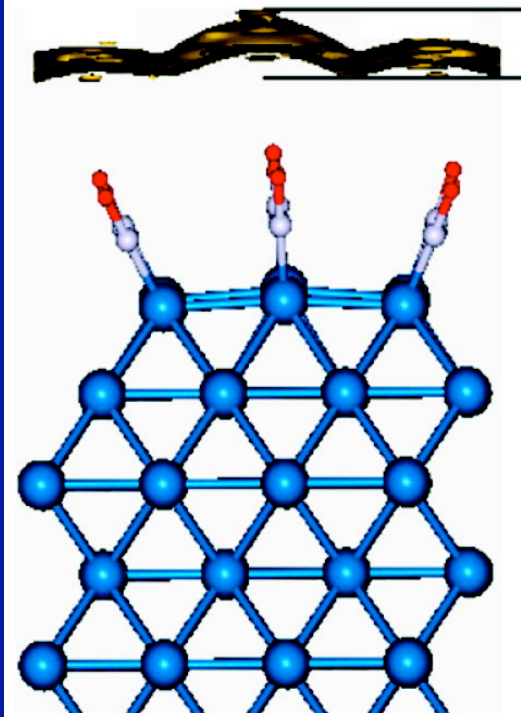
CO nearest neighbor O-O distance: 3.7-4.1 Å

Compared to Pt-Pt 2.75 Å

**DFT Calculations**

CO-CO repulsion results in tilting expanding CO-CO distance.

Energy gain 3.2 eV per Pt-CO pair

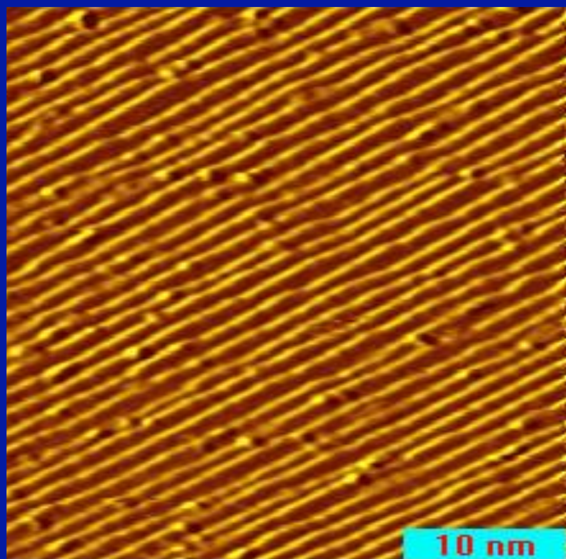


**DFT calculations show tilted CO geometry on (6x3) Pt cluster on a 4 layer slab.**

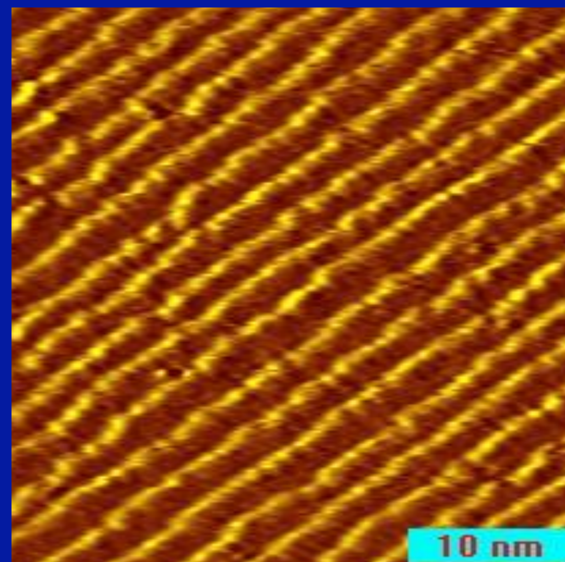
# CO on Stepped Pt

# Reversible Cluster Formation on Pt(557)

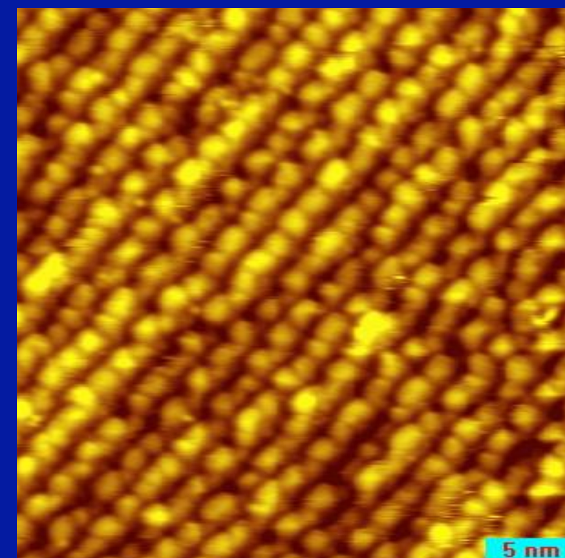
**30 nm x 30 nm**




**$10^{-10}$ Torr**

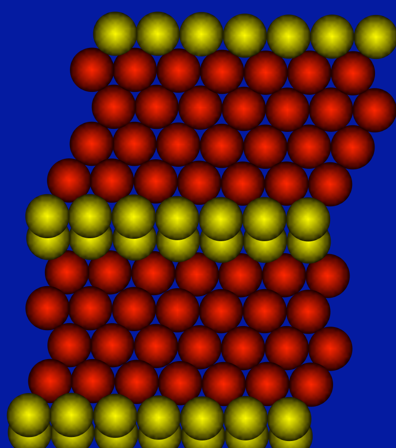



**5 x $10^{-8}$ Torr CO**



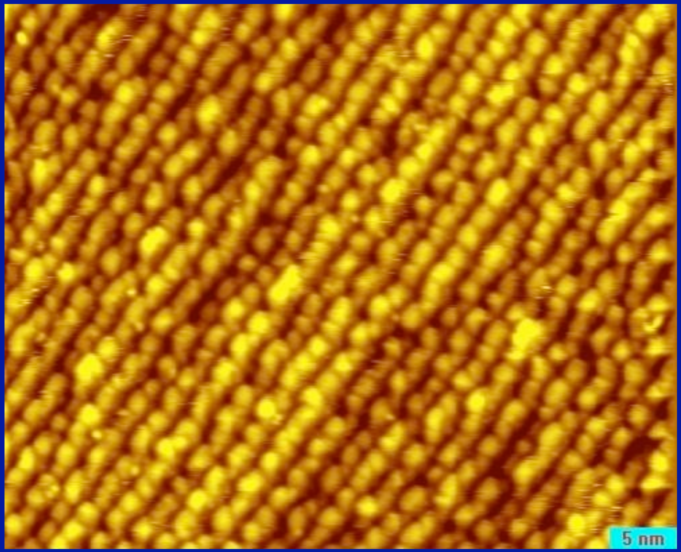

**1 Torr CO**

**Pt(557):**
**6(111)x(100)**



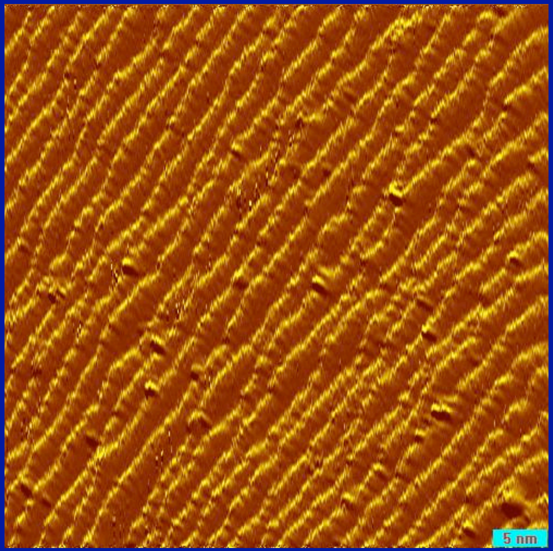
- Low pressure CO induces step doubling
- High pressure CO causes the step terraces to break up into ~2nm clusters

# Reversible CO-induced Restructuring of Pt(557)




1 Torr CO

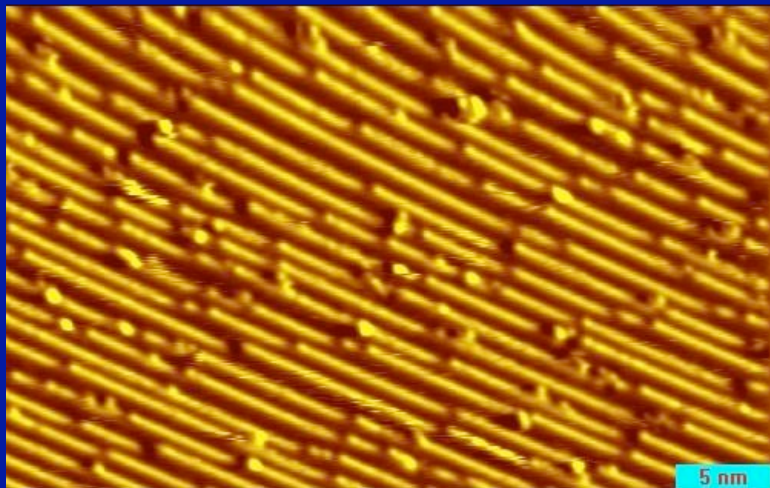
Pump out to $10^{-8}$ Torr CO



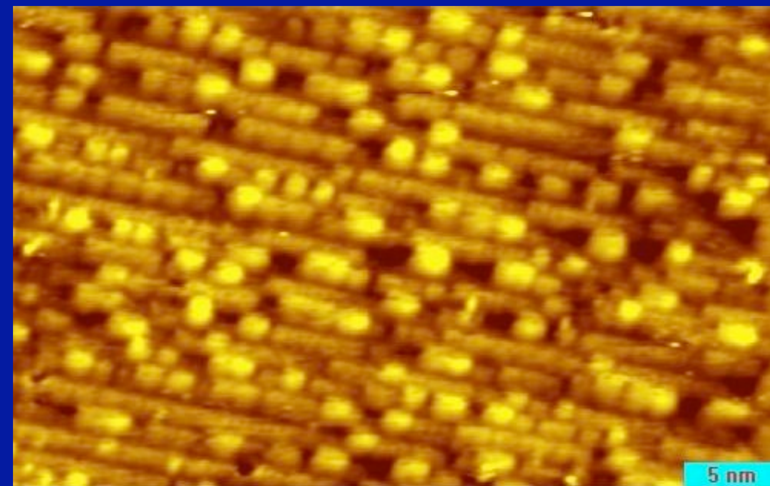

~$10^{-8}$ Torr CO

- Low pressure structure has regular terraces
- High pressure CO causes the step terraces to break up into ~2nm clusters
- Cluster formation is reversible: Pump out reforms terraces with increased kink sites
- CO-CO repulsion causes clustering

# Reversible CO-induced clustering on Pt(332)

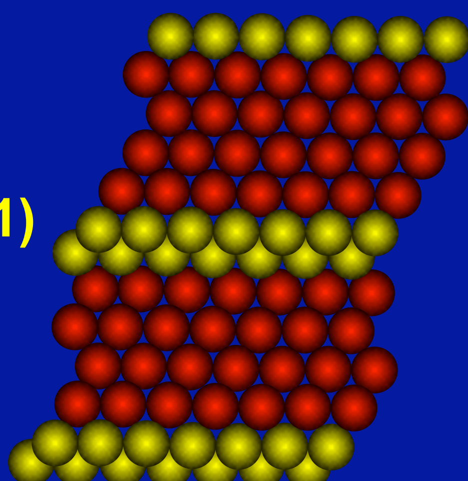



$10^{-8}$ Torr CO




1 Torr CO

**Pt(332):**
**6(111)x(111)**

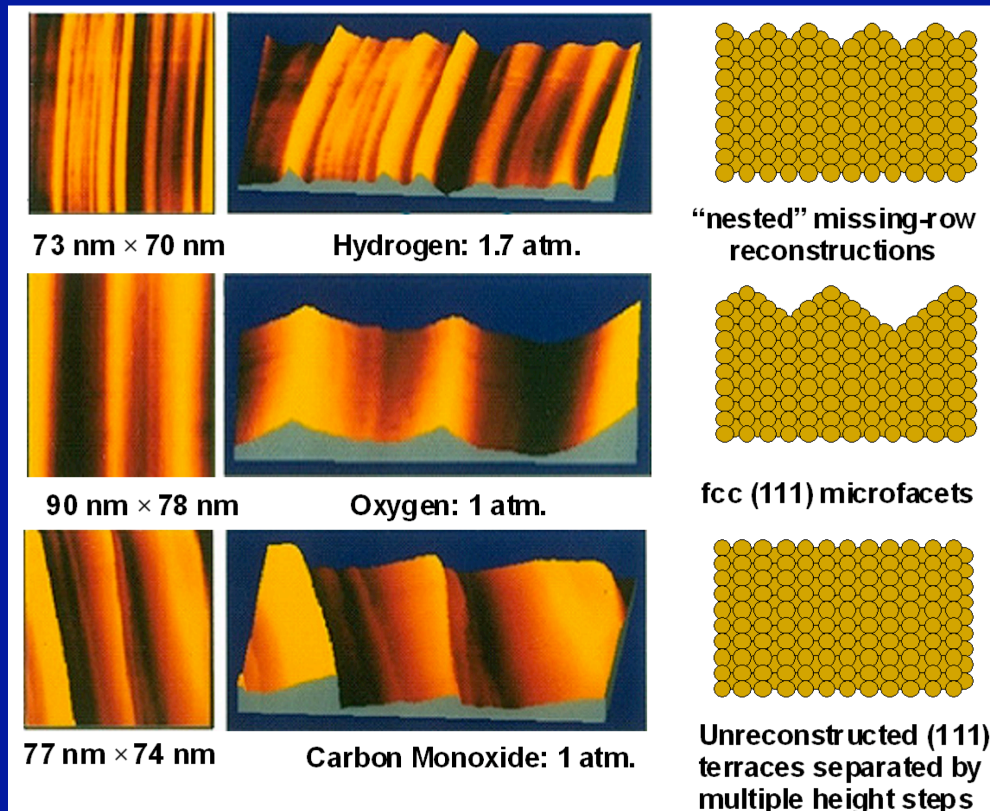


- Cluster Structure on (332) consists of rectangular blocks and depressions
- Clustering is also reversible upon pump out.

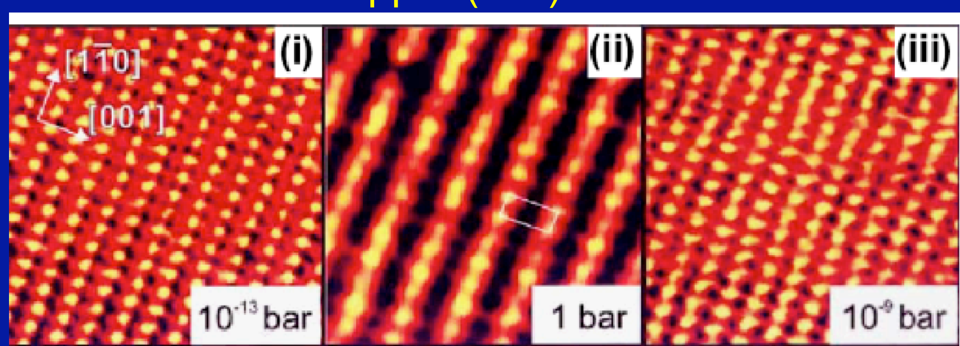
# Pressure Enhanced

## Adsorbate-Induced Restructuring

## Platinum (110)



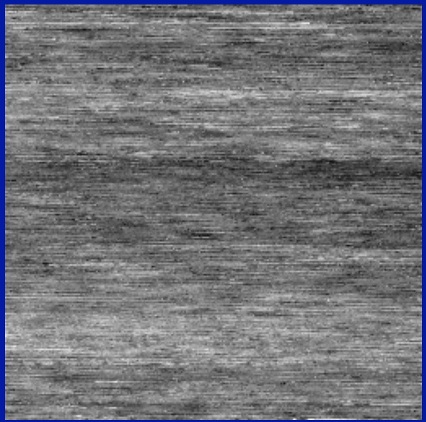

## Copper (110)

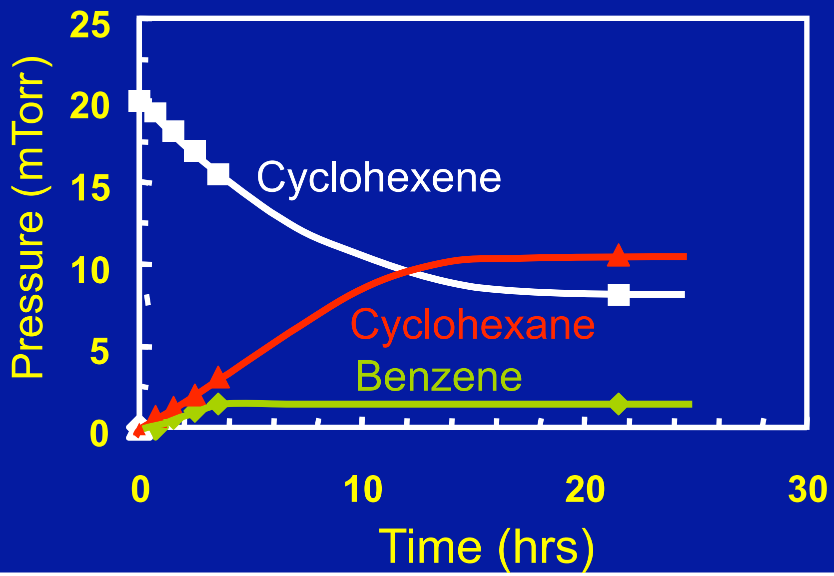


# Adsorbate Mobility

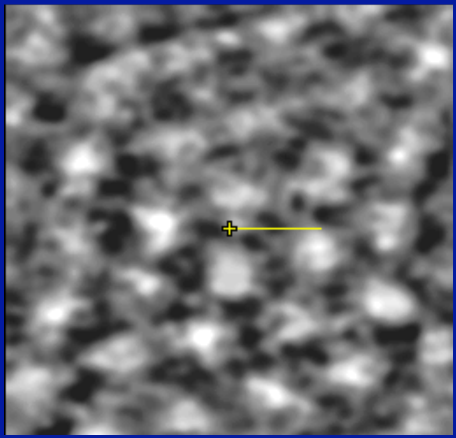
# High pressure STM Reaction Studies: the role of surface mobility

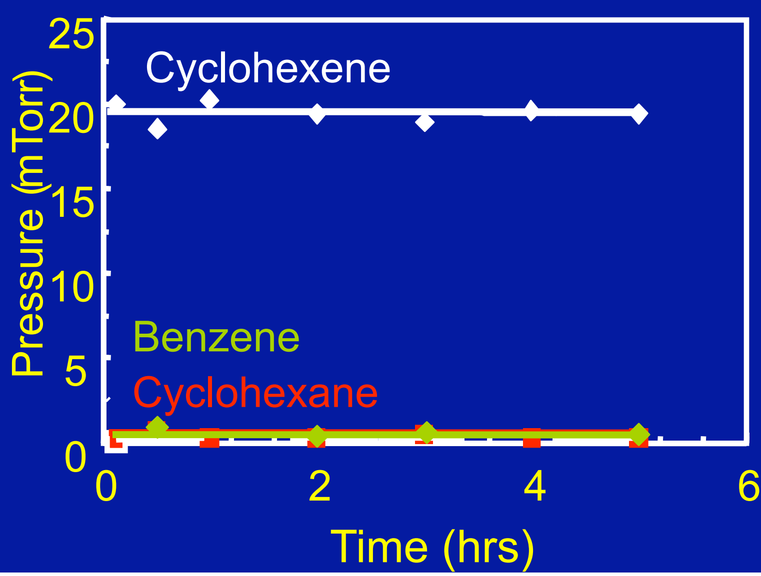
75Å x 75Å image of catalytically active Pt(111) at 25C. 200 mTorr $H_2$ and 20 mTorr cyclohexene



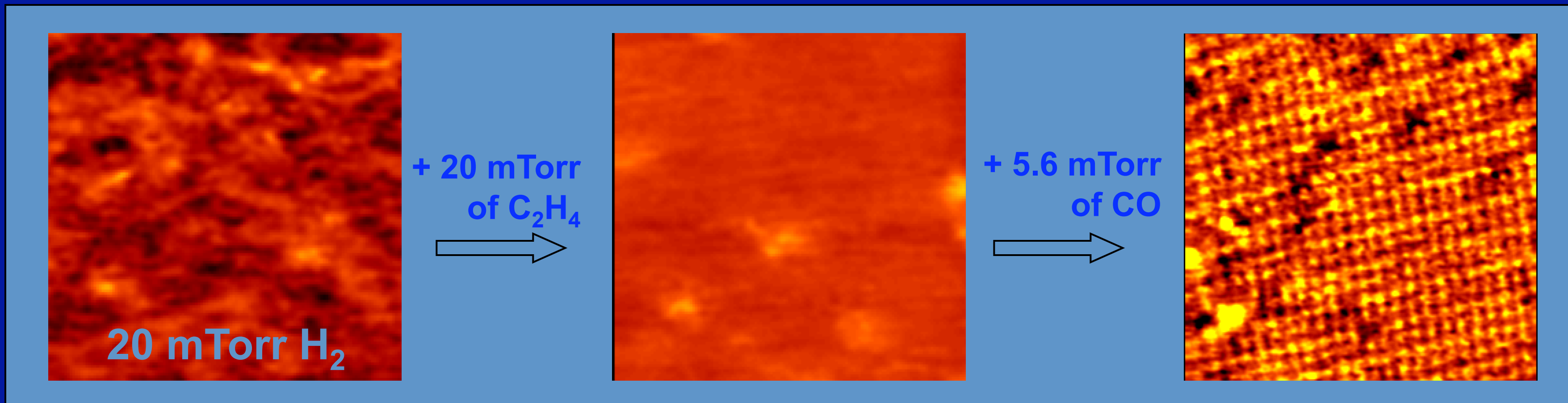



70Å x 70Å image of CO poisoned Pt(111) at 25C. 200 mTorr $H_2$, 20 mTorr of cyclohexene, and 5 mtorr CO

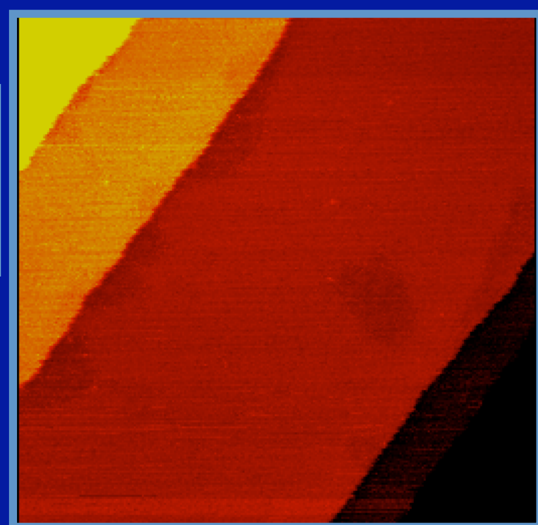


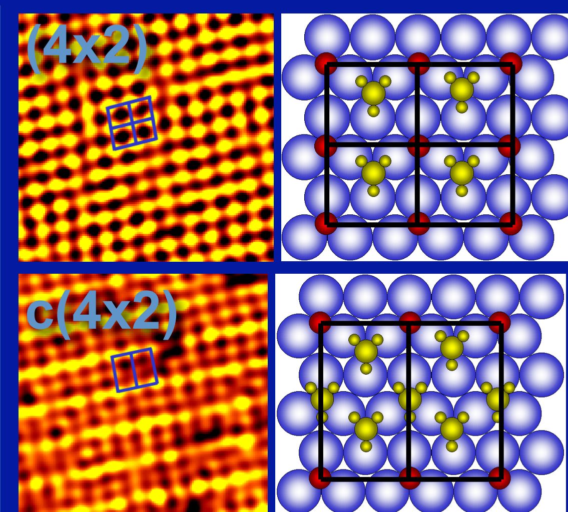


## Blocking of adsorbate ($C_2H_3$, H) mobility by CO poisons catalytic reaction on Rh and Pt(111)



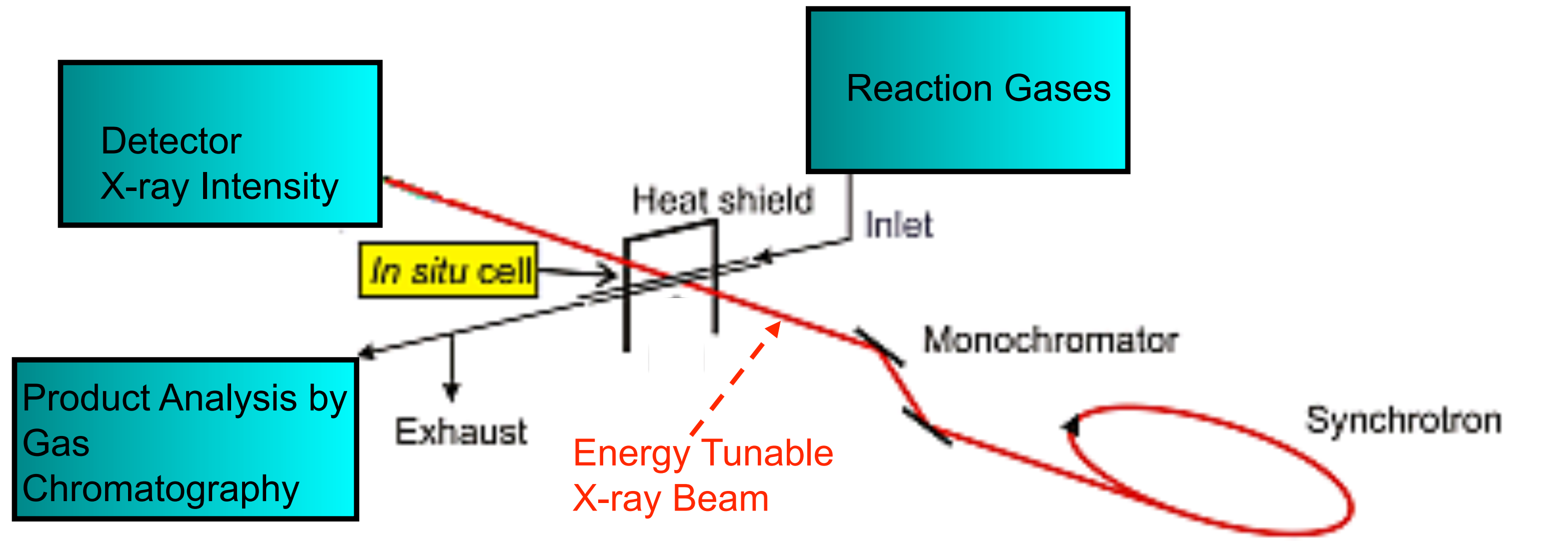

CO induces the formation of immobile crystaline coadsorbed structures





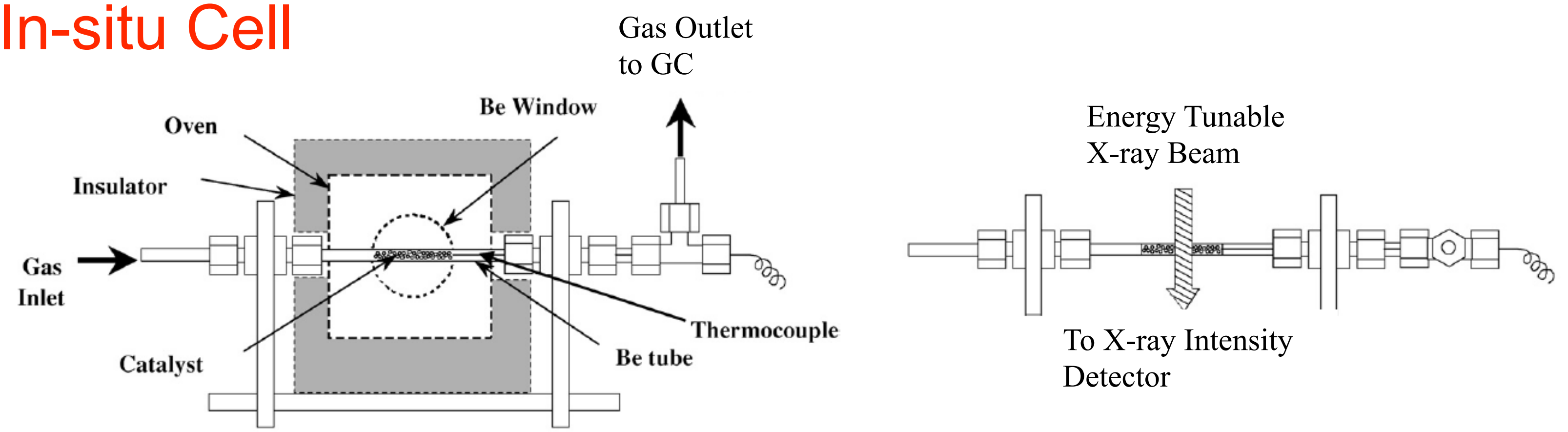

*High pressure scanning tunneling microscopy study of CO poisoning of ethylene hydrogenation on Pt(111) and Rh(111) single crystals*. D.C. Tang, K.S. Hwang, M. Salmeron and G.A. Somorjai. **J. Phys. Chem. B** 108,13300 (2004)

# X-ray Absorption Spectroscopies (XAS)



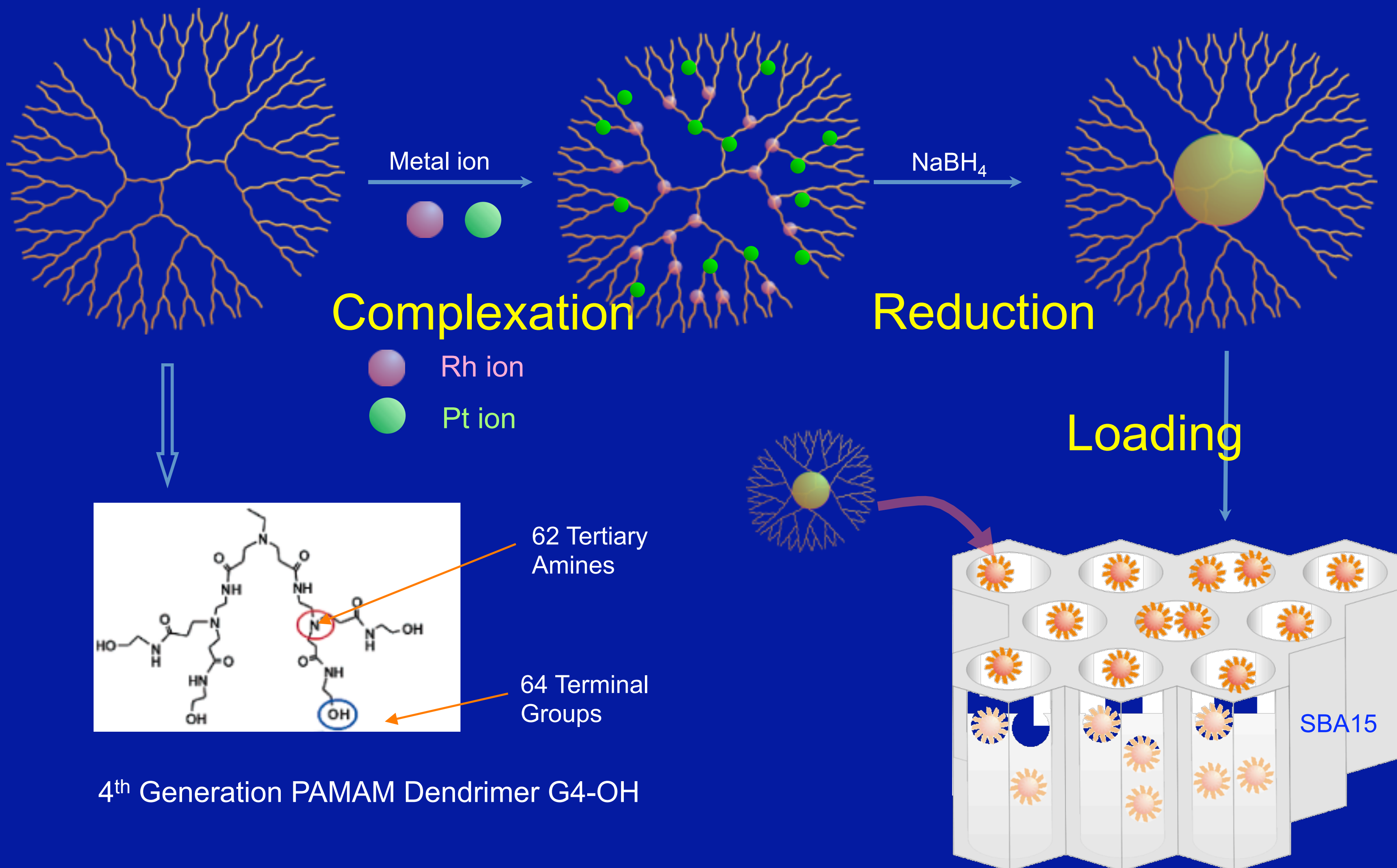

http://hasylab.desy.de/e77/e106/e122/e4410/e4413/fig11_eng.png

## In-situ Cell

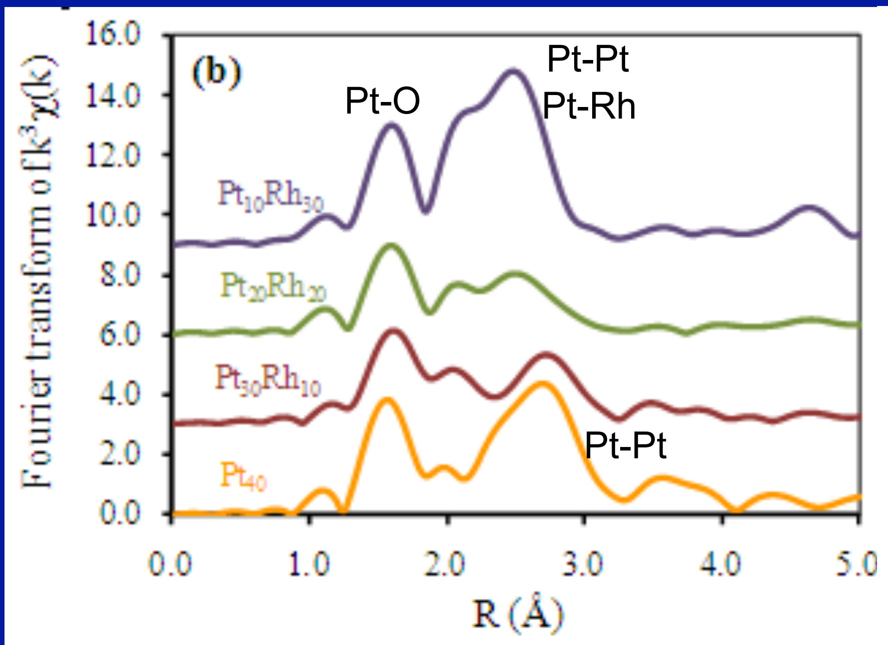



Bare, S. R. et al., *Catal. Today* 2007, 126, (1-2), 18-26.

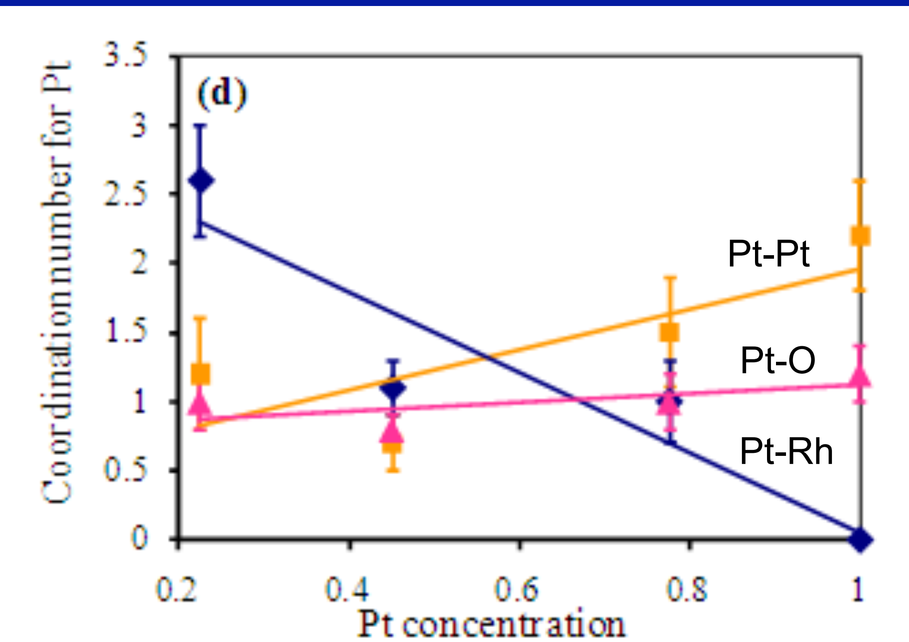
# Synthesis and Immobilization of Dendrimer Encapsulated Bimetallic PtRh Nanoparticles



# Coordination Environment of Dendrimer Encapsulated ~ 1 nm PtRh Bimetallic Nanoparticles Measured by EXAFS at Pt Edge

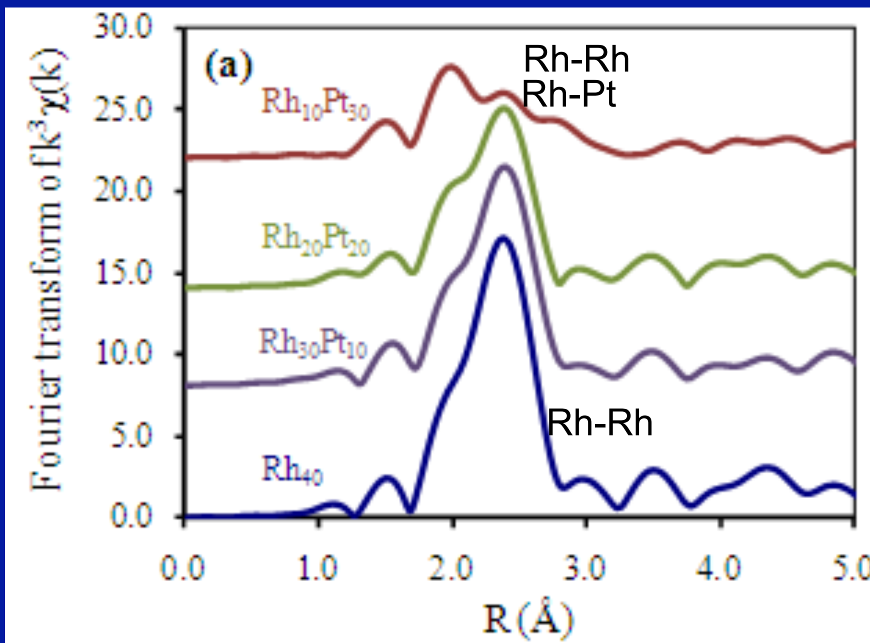



$k^3$-weighted Fourier transform of Pt $L_3$ edge EXAFS spectra of the dendrimer $Pt_xRh_{40-x}$ nanoparticles.

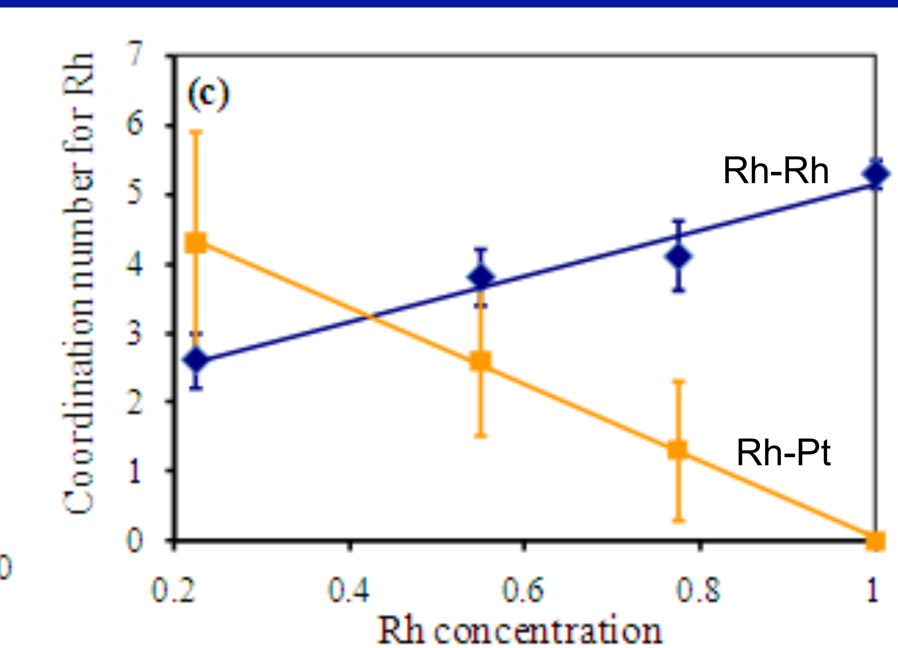



Local coordination numbers for Pt of the dendrimer bimetallic catalysts.

# Coordination Environment of Dendrimer Encapsulated ~ 1 nm PtRh Bimetallic Nanoparticles Measured by EXAFS at Rh Edge




$k^3$-weighted Fourier transform of Rh *K* edge EXAFS spectra of the dendrimer $Pt_xRh_{40-x}$ nanoparticles.




Local coordination numbers for Rh of the dendrimer bimetallic catalysts.

# Degree of Alloying in the $Pt_xRh_{40-x}$ Nanoparticles

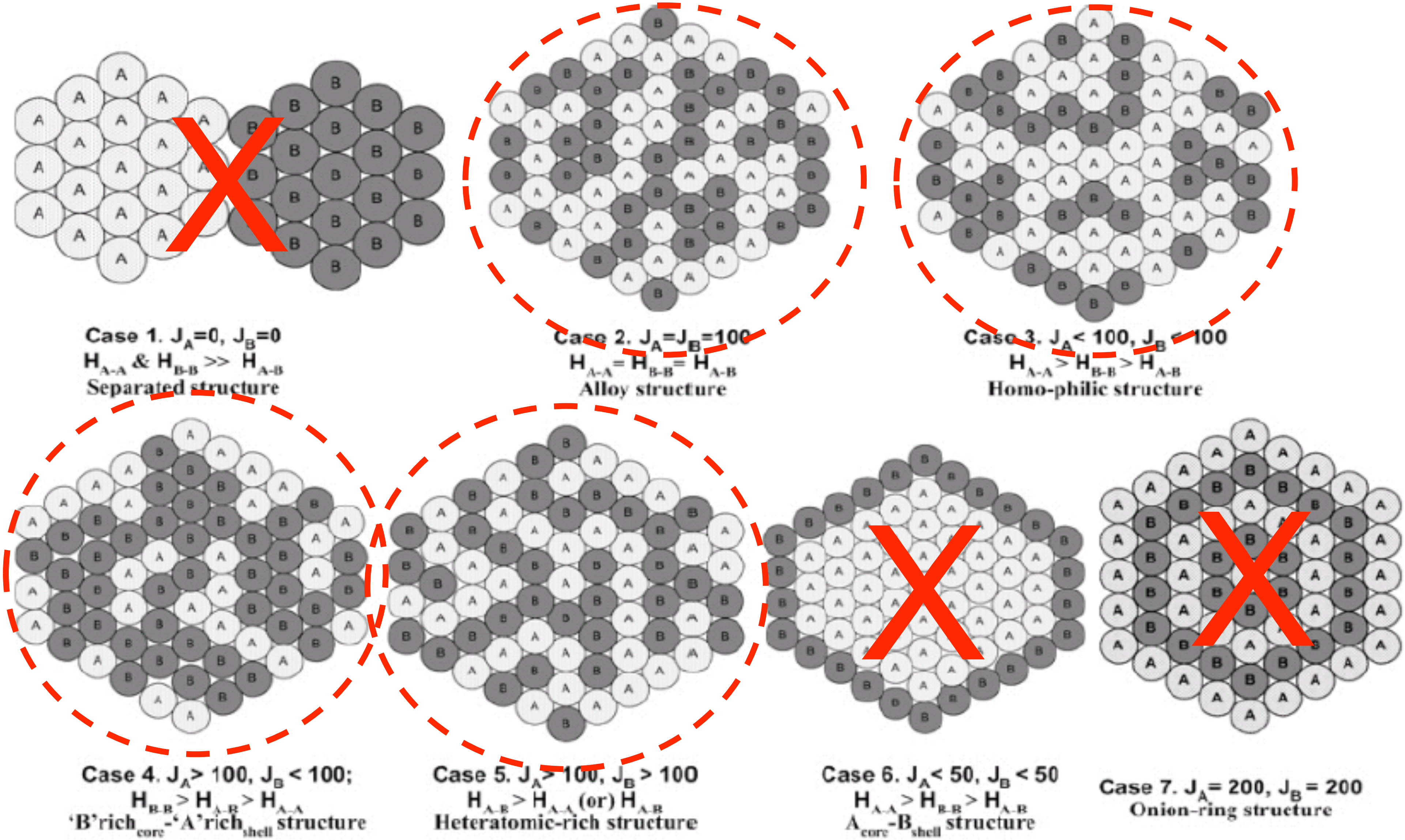
The two quantities determining the degree of alloying are given by

$$J_{Pt} = \frac{N_{Pt\text{-}Rh} / N_{Pt,total}}{c_{Rh}} \times 100\% \qquad J_{Rh} = \frac{N_{Rh\text{-}Pt} / N_{Rh,total}}{c_{Pt}} \times 100\%$$

In above equations, $c_{Pt}$ and $c_{Rh}$ are the concentrations of Pt and Rh in the alloy nanoparticles, respectively. $N_{Pt,total}$ and $N_{Rh,total}$ are the total coordination numbers of the absorber atom Pt and Rh in the nanoparticles, respectively. The calculated $J_{Pt}$ and $J_{Rh}$ for the $Pt_xRh_{40-x}$ samples are

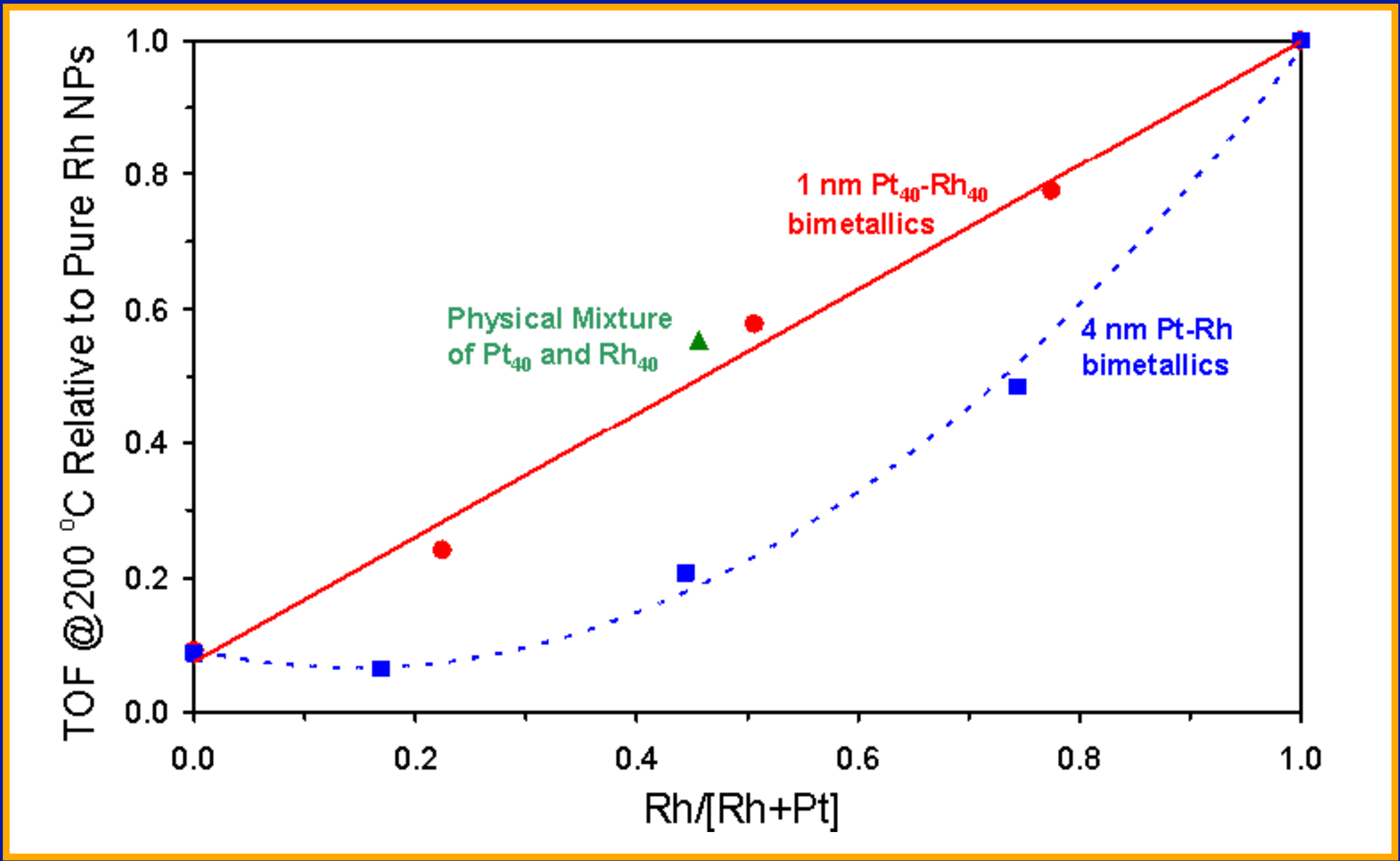
| | $J_{Pt}$ % | $J_{Rh}$ % |
|---|---|---|
| $Pt_{30}Rh_{10}$ | 128 | 80 |
| $Pt_{20}Rh_{20}$ | 77 | 90 |
| $Pt_{10}Rh_{30}$ | 70 | 107 |

# Schematics of bimetallic nanoparticles at various degrees of alloying



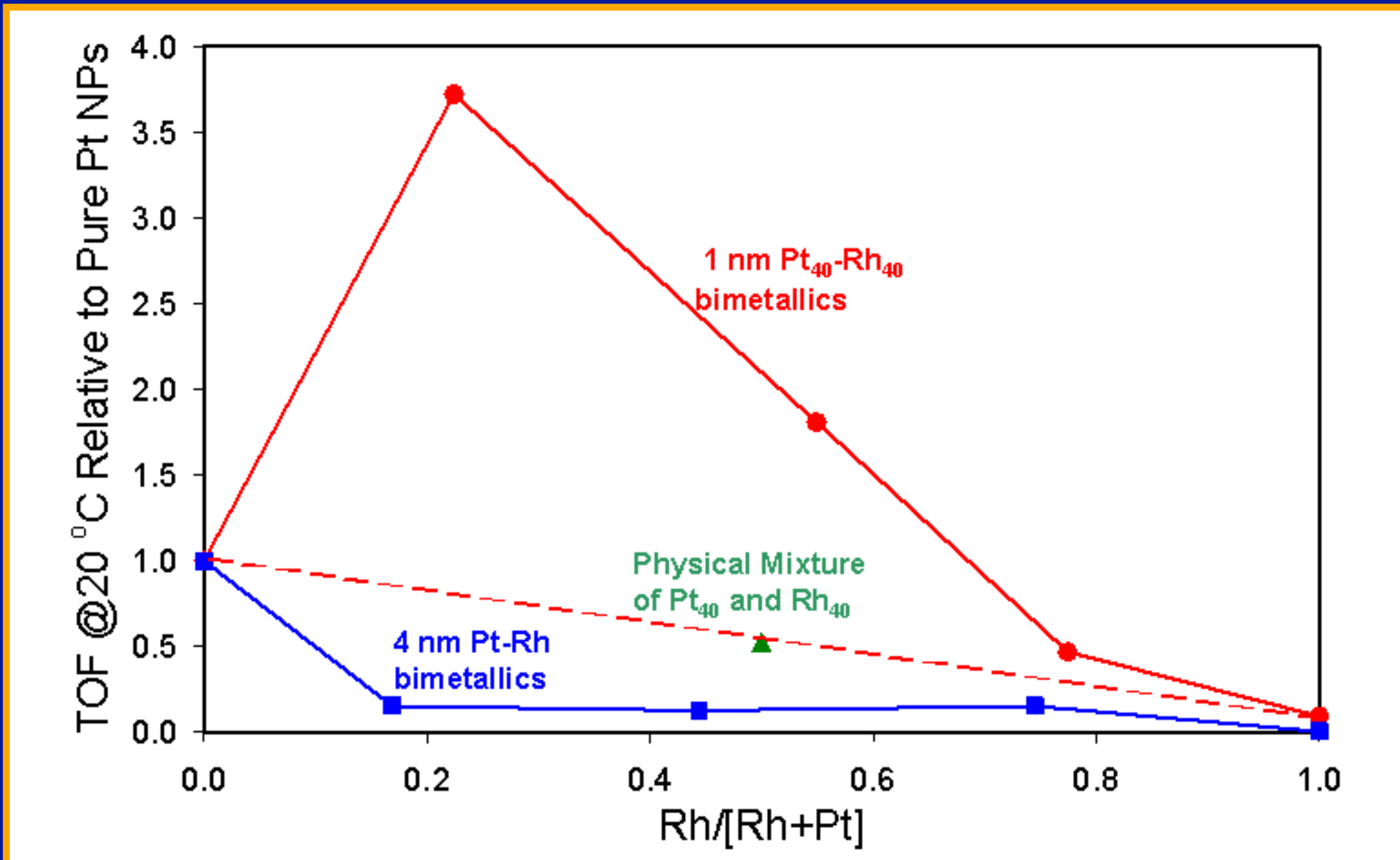

Hwang, B. J. et. al. *J. Am. Chem. Soc.* 2005, 127, (31), 11140-11145.

# CO Oxidation of Dendrimer Encapsulated 1 nm and PVP Capped 4 nm PtRh Bimetallic Nanoparticles




Reaction conditions were 10 Torr $C_2H_4$, 100 Torr $H_2$.
TOF was calculated based on 100 % metal dispersion.

# Ethylene Hydrogenation of Dendrimer Encapsulated 1 nm and PVP Capped 4 nm PtRh Bimetallic Nanoparticles

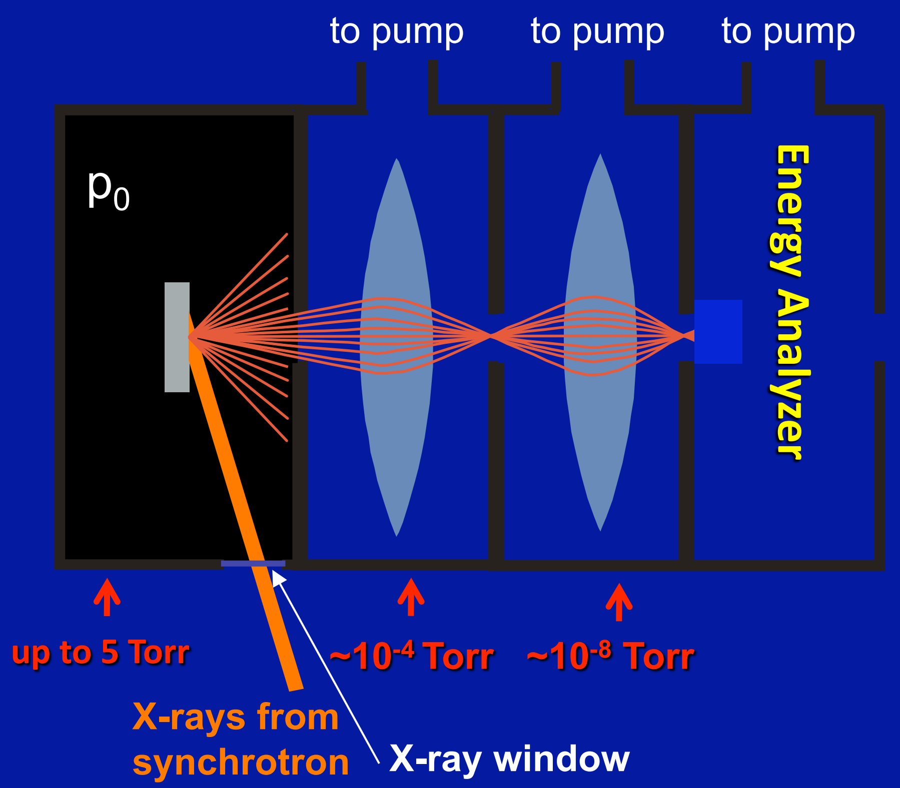


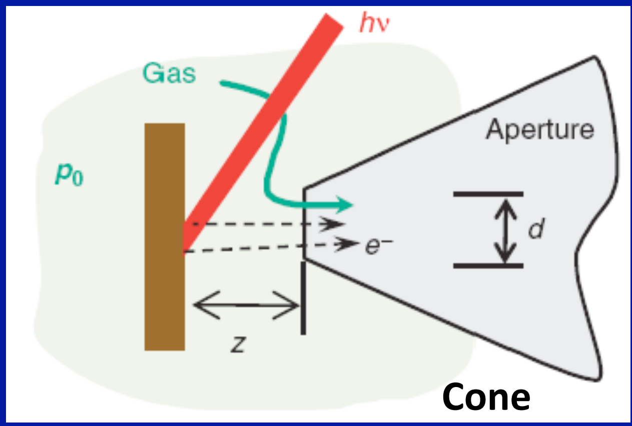

Reaction conditions were 10 Torr $C_2H_4$, 100 Torr $H_2$.
TOF was calculated based on 100 % metal dispersion.

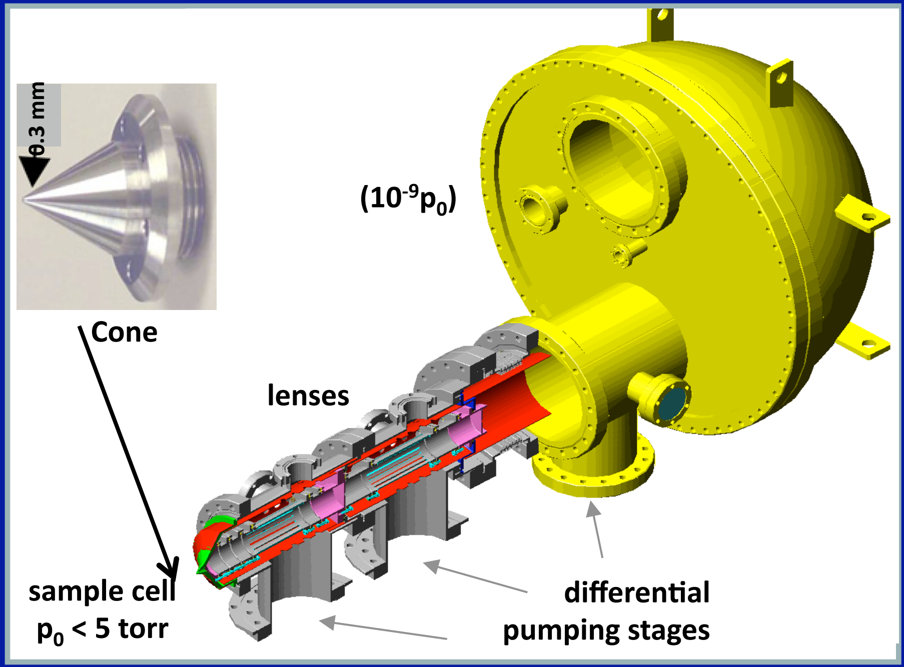
# Ambient Pressure X-Ray Photoelectron Spectroscopy

# High Pressure XPS

**Solutions:** Capture electrons before they collide with gas molecules by means of differential pumping stages and focusing lenses

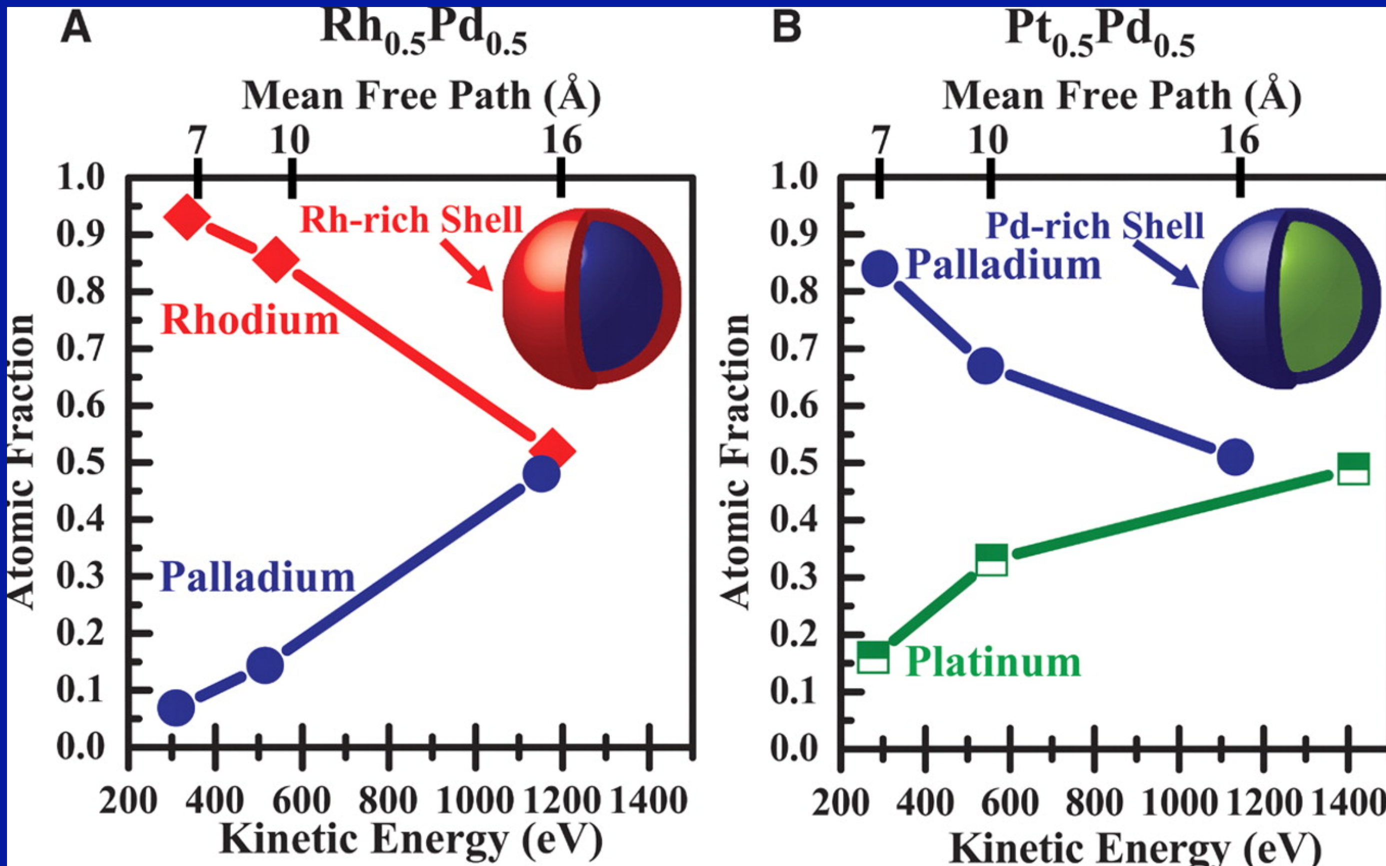


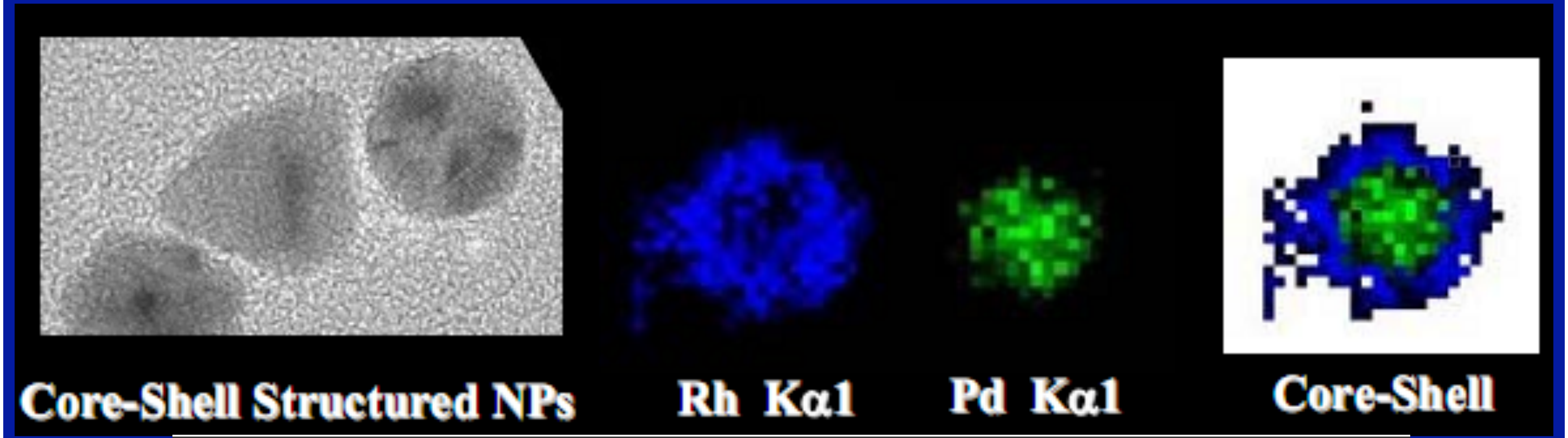
# Surface Composition of Nanoparticles

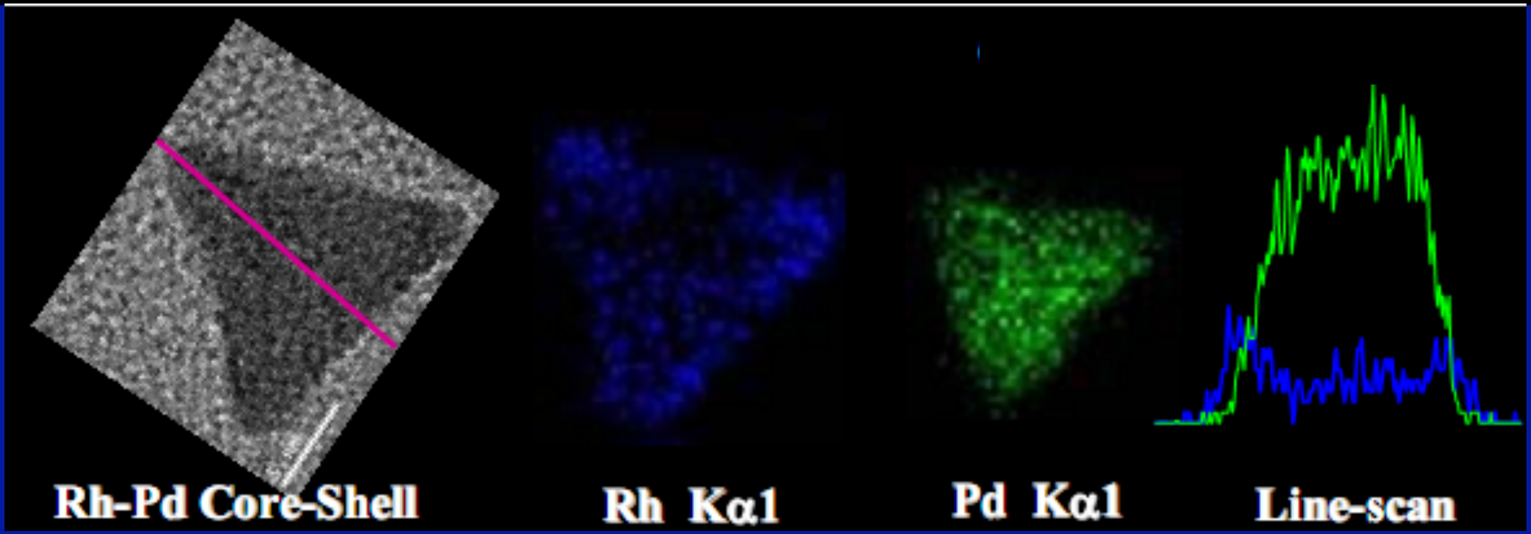
# Core-Shell Structure Probed by Synchrotron XPS




- 16 nm $Rh_{0.5}Pd_{0.5}$ nanoparticles form with a Rh rich shell
- 16 nm $Pt_{0.5}Pd_{0.5}$ nanoparticles form with a Pd rich shell
- XRD reveals only a single 50/50 alloy phase for both systems

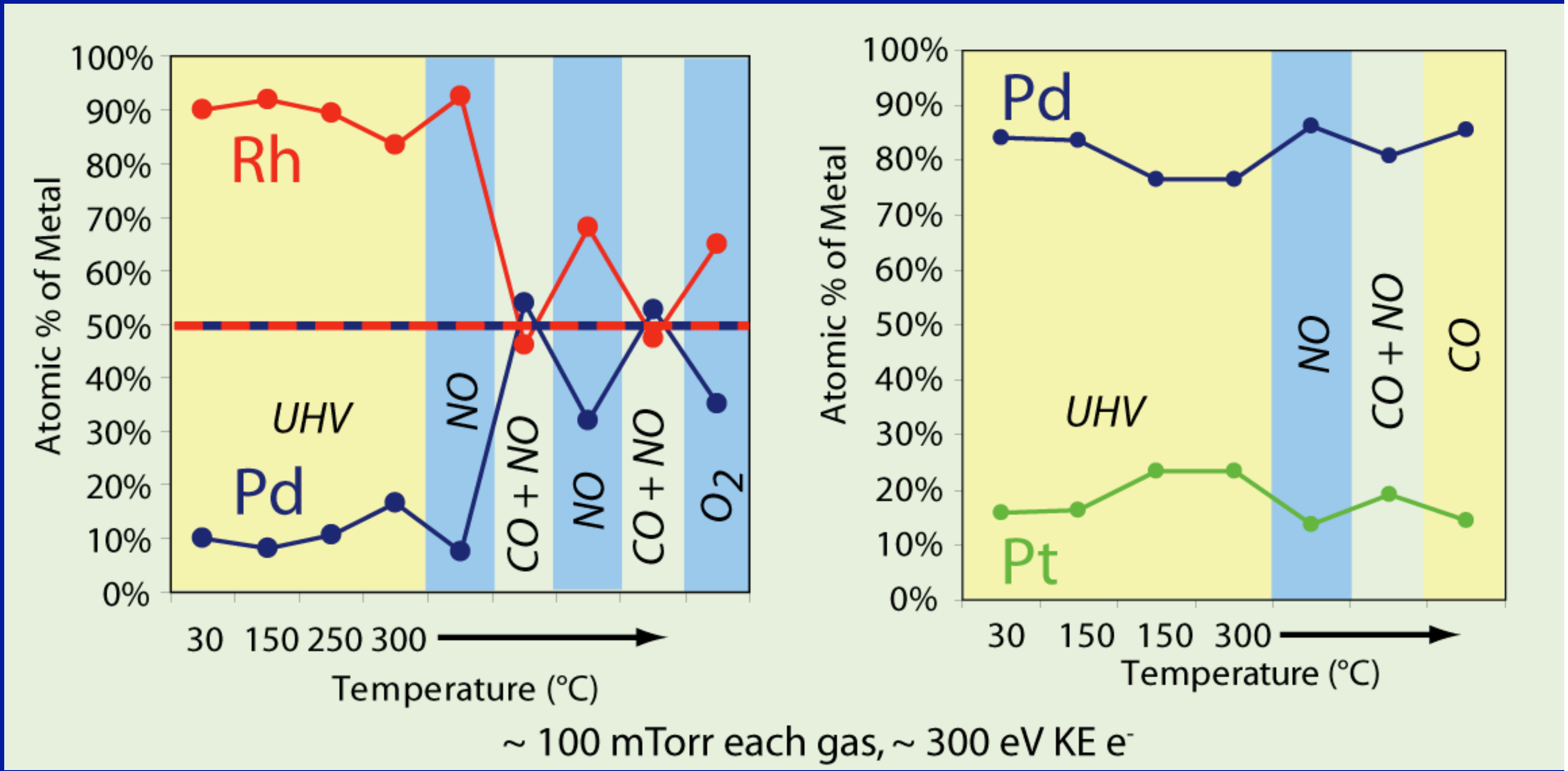
# High Resolution TEM




- Core-Shell structure confirmed with EDS mapping using STEM

# Core-Shell Restructuring Probed by Ambient Pressure XPS



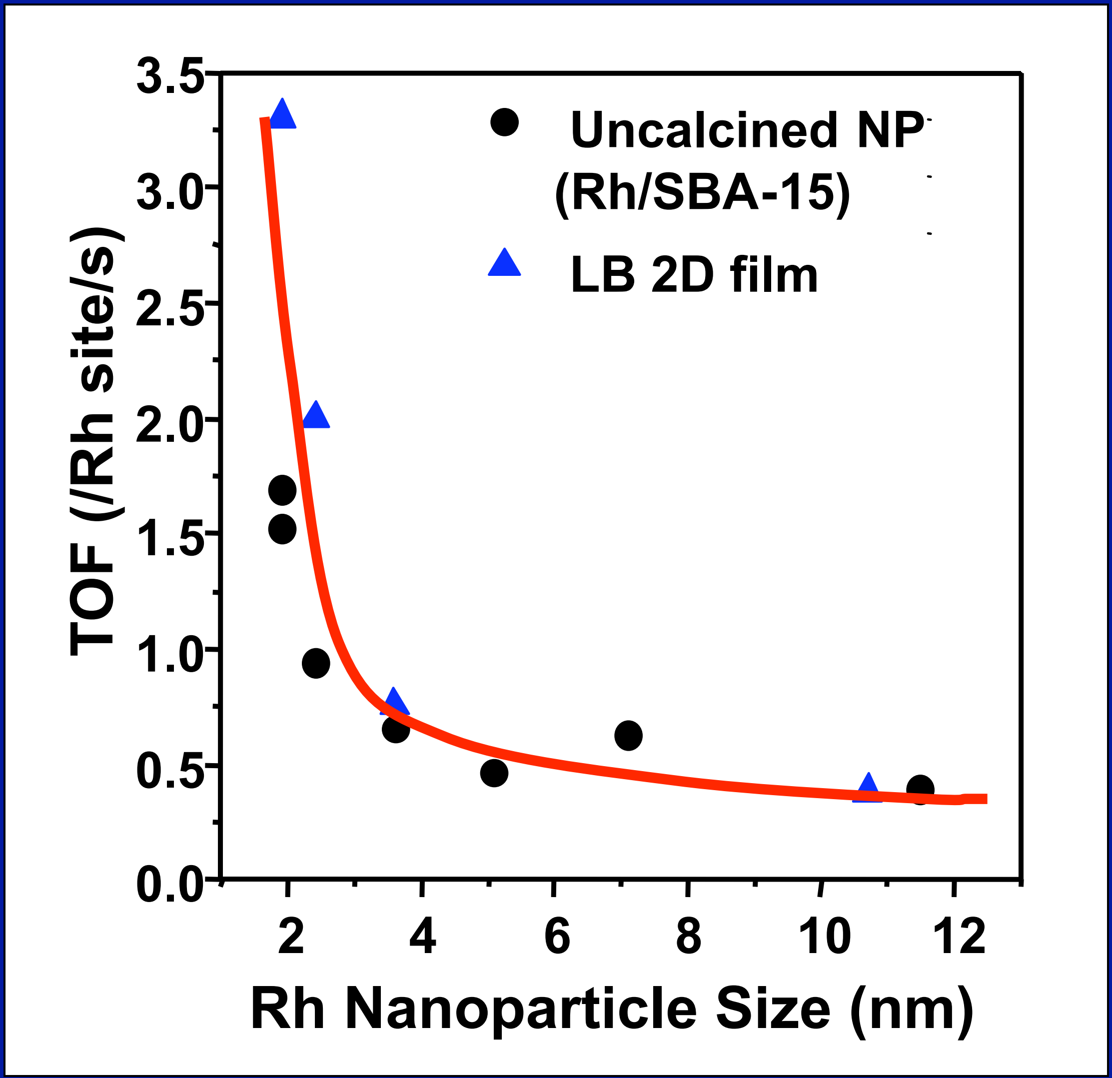

- Atomic diffusion within the nanoparticles results in surface composition changes as a function of ambient pressure
- Oxidation and Reduction at the nanoparticle surface is important

# Molecular Factors of Catalytic Activity and Selectivity

- Surface Structure (Size, Shape)
- Surface Composition
- Reaction Intermediates
- Adsorbate-induced Restructuring
- Adsorbate Mobility
- Oxidation State
- Charge Transport

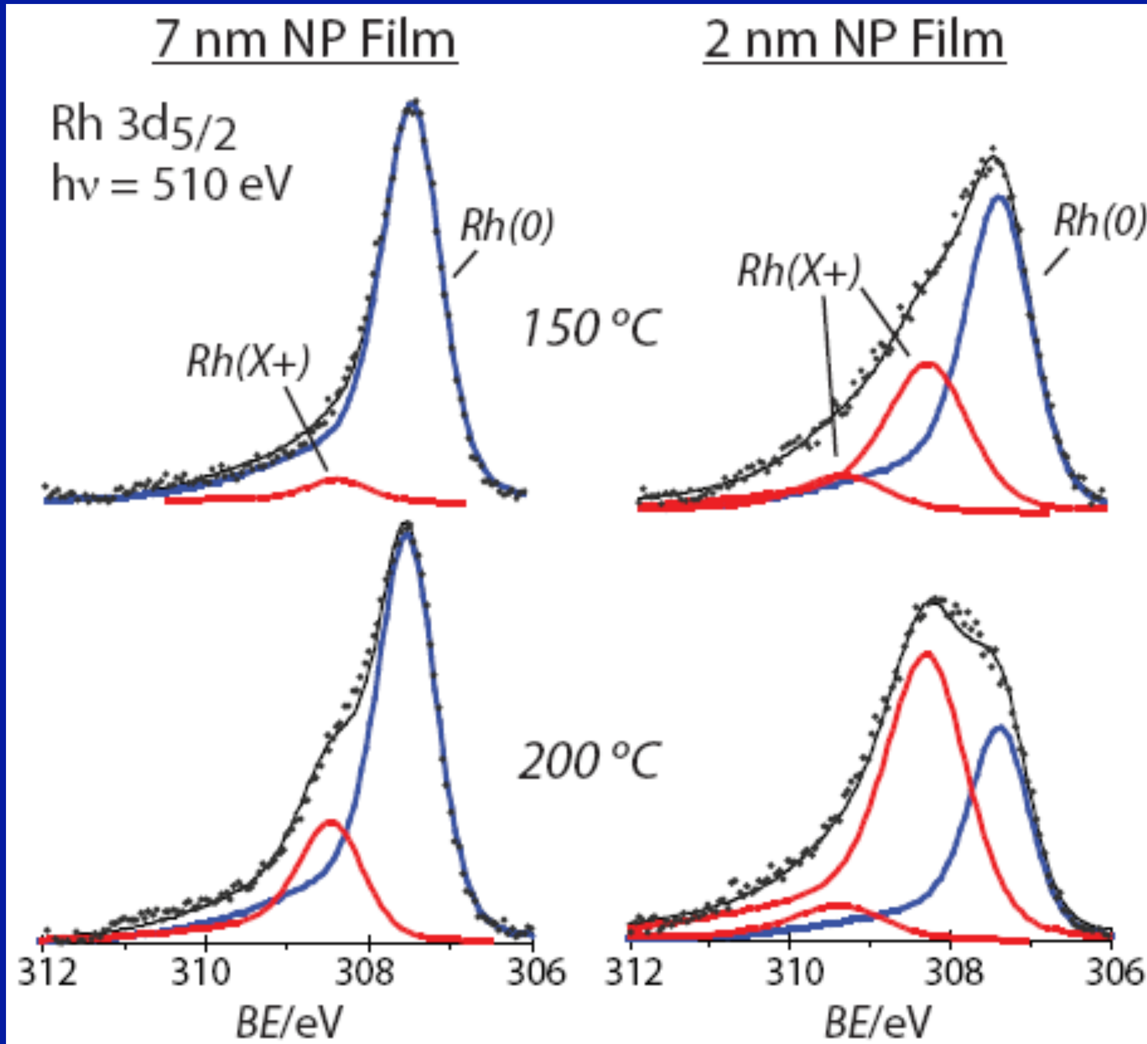
# Size Dependence of CO Oxidation Activity

## (100 Torr of O2,  40 Torr of CO, and 443K)

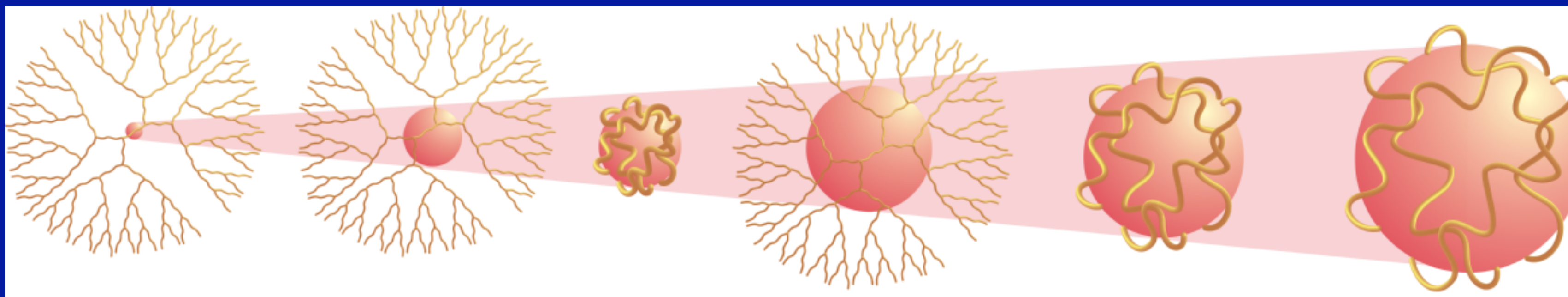



Rh Nanoparticles with size of 2-11 nm were used in this study

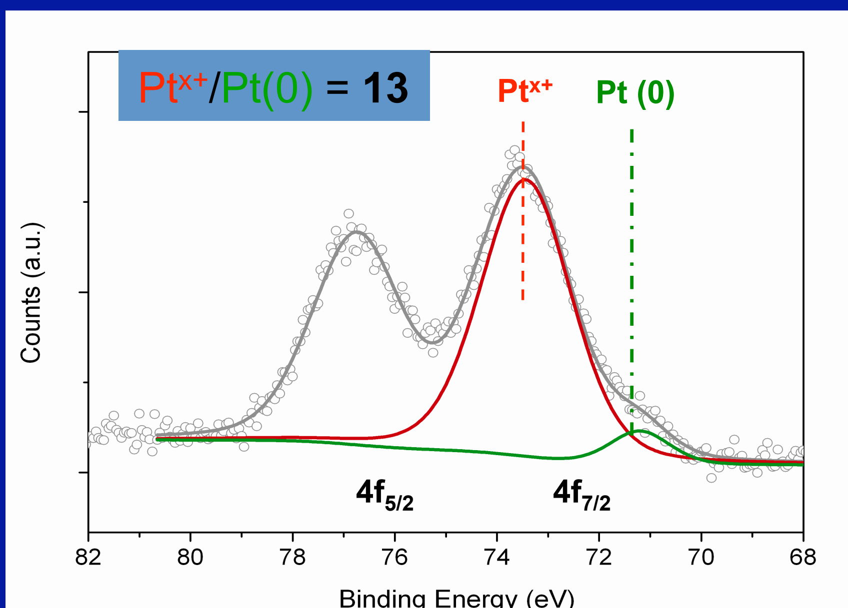
3D Rh nanoparticle catalysts (uncalcined Rh/ SBA 15) exhibit particle size dependence, similar to Rh 2D LB (Langmuir–Blodgett) film


7 nm NP Film
2 nm NP Film
Rh 3d5/2
hν = 510 eV
Rh(0)
Rh(X+)
150 °C
200 °C
312
310
308
306
BE/eV

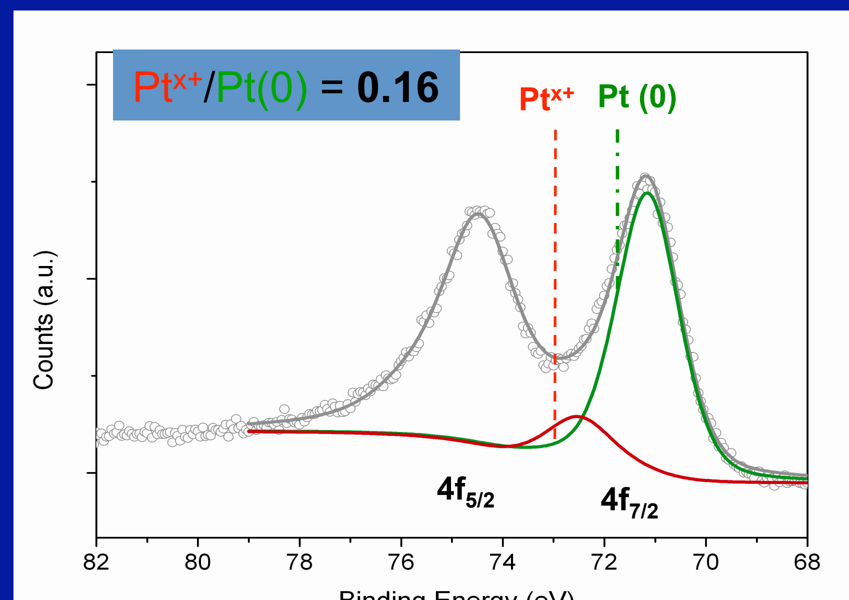
# The Effect of Oxidation State Changes With the Size of Pt Nanoparticles



**Size (nm):**
**0.8 1.1 1.5 2.0 2.9 5.0**



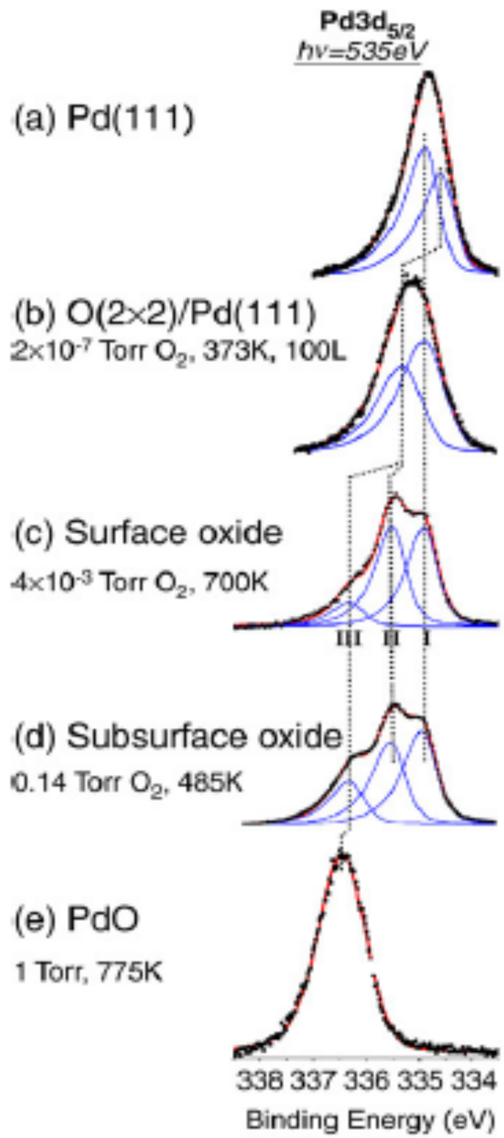

**0.8 nm Pt Nanoparticles**




**1.5 nm Pt Nanoparticles**

For clarity, the deconvoluted peaks for Pt $4f_{5/2}$ are not shown in the XPS spectra.

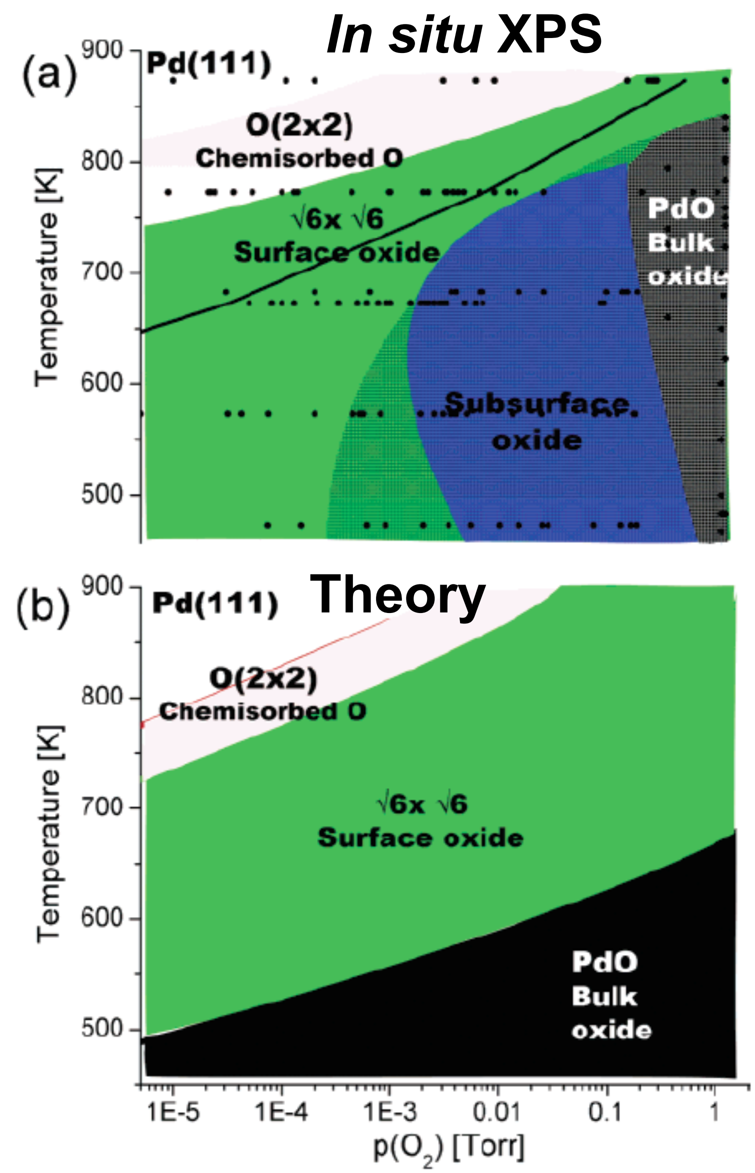
# Oxidation of Pd(111)




I. Bulk Pd

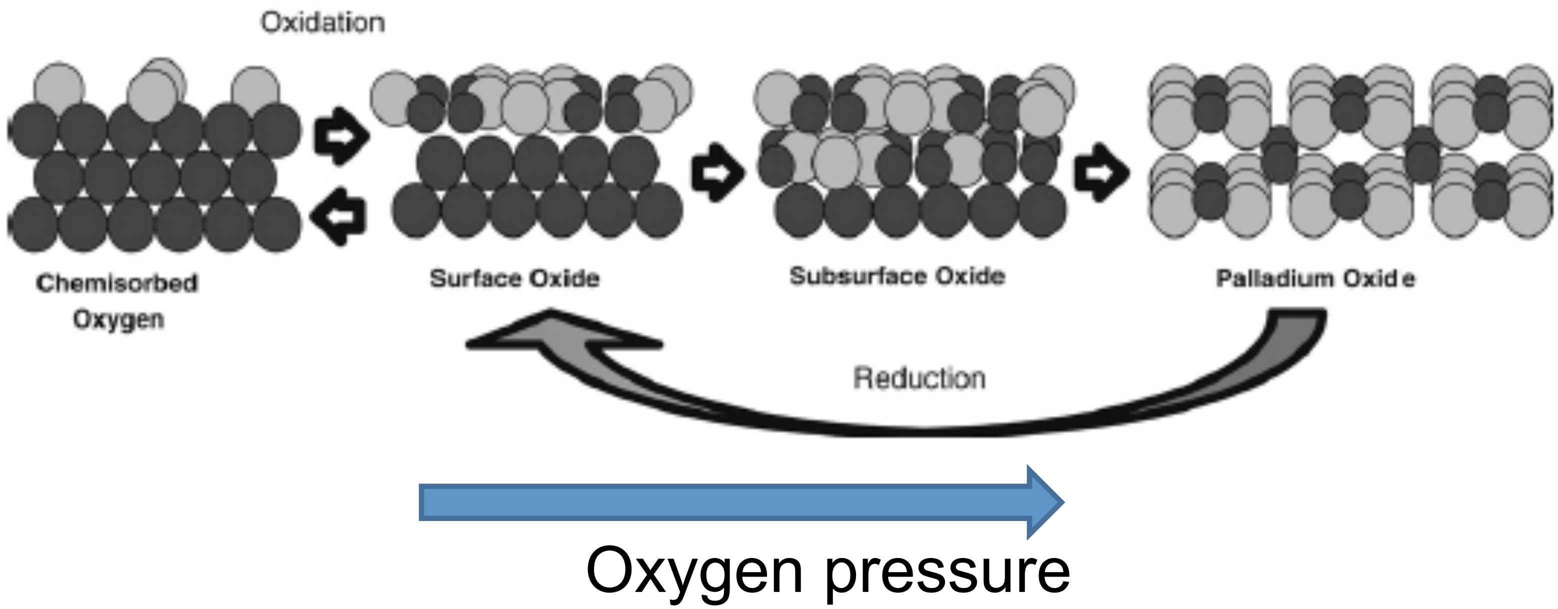
II. Pd atom with two O neighbors

III. Pd atom with four O neighbors




Ketteler, et al, JACS, 2005

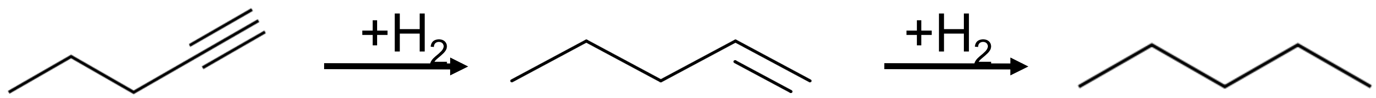
# Oxidation of Pd(111) (Contd.)



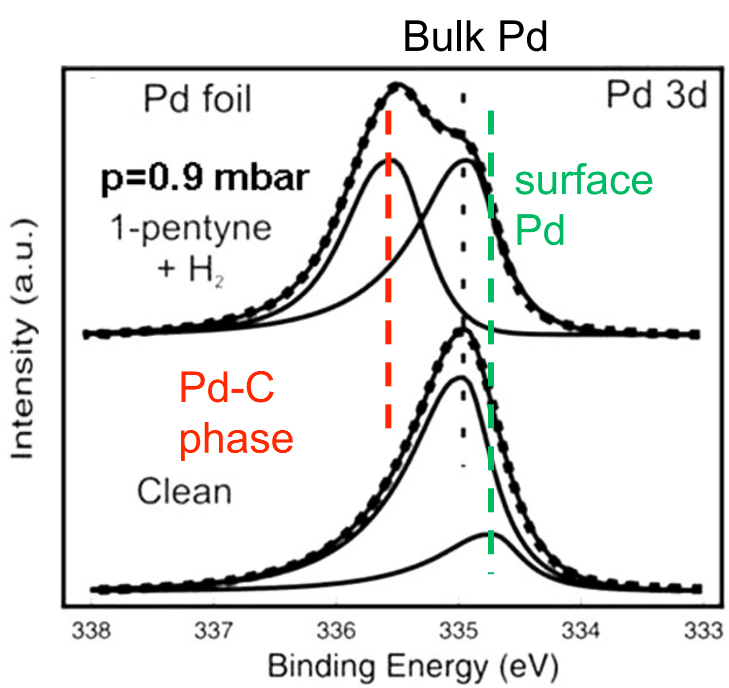

**The subsurface oxide is a metastable phase.**

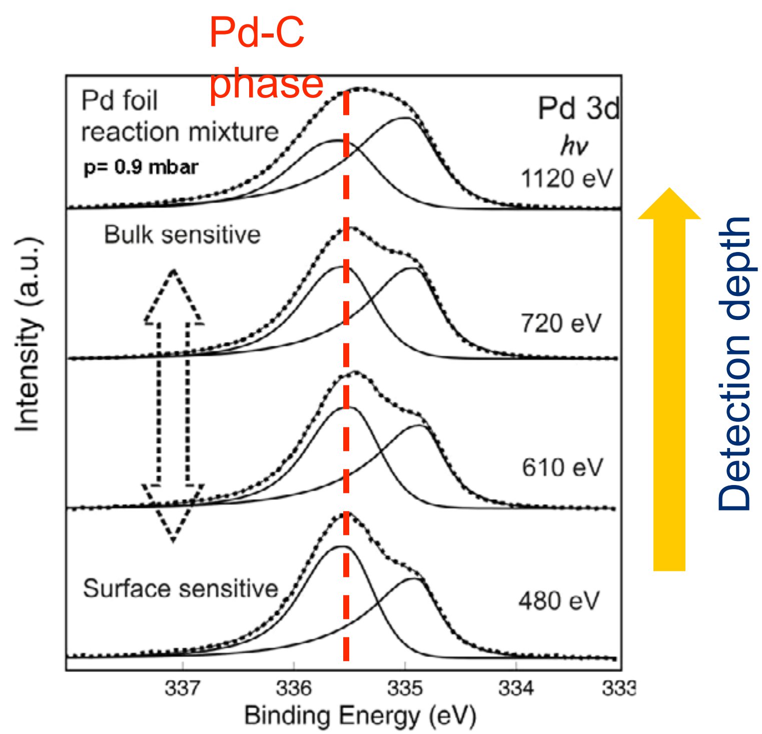
# The role of Carbon Species in Heterogeneous Catalytic Processes

0.85 mbar H +0.05 mbar 1-pentyne at 358 K over Pd foil



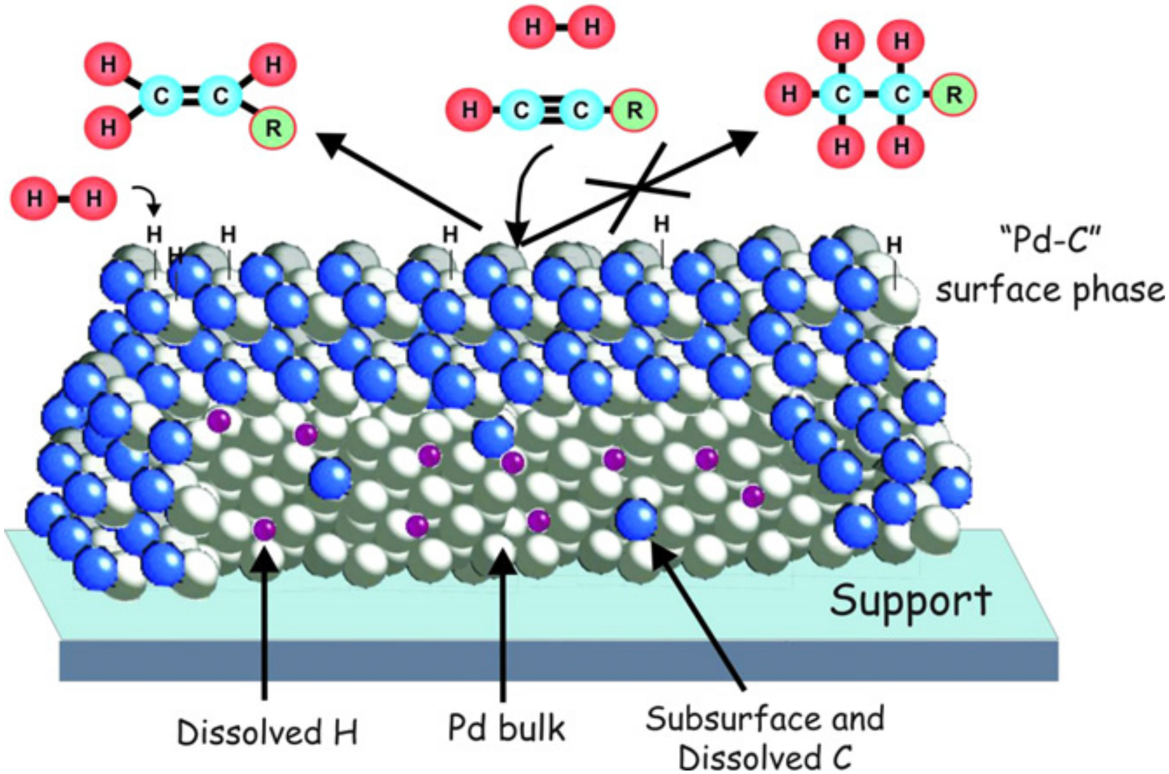

| 1-pentyne | 1-pentene | pentane |
|---|---|---|
| Selectivity: | 98% | 2% |




Teschner D, et al, J. Catal. 242, 26 (2006)

# The role of Carbon Species in Heterogeneous Catalytic Processes (contd.)




Formation of a carbon diluted Pd surface phase inhibited total hydrogenation of pentyne by the elimination of subsurface hydrogen participating in the reaction.

Teschner D, et al, J. Catal. 242, 26 (2006)

# Molecular Factors of Catalytic Activity and Selectivity

- Surface Structure (Size, Shape)
- Surface Composition
- Reaction Intermediates
- Adsorbate-induced Restructuring
- Adsorbate Mobility
- Oxidation State
- Charge Transport

# Metal-Semiconductor Nanodiode

# The Role of Hot Electrons in Catalysis Science

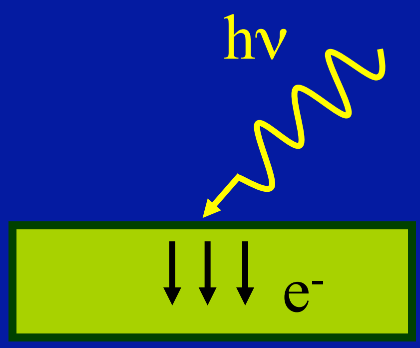
# Hot Electron

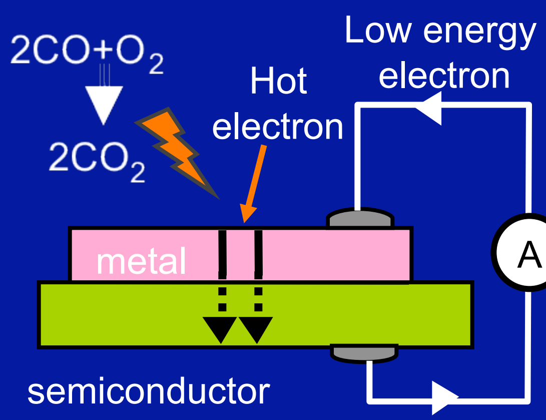
A hot electron is not in thermal equilibrium with the lattice

Creation of hot electrons

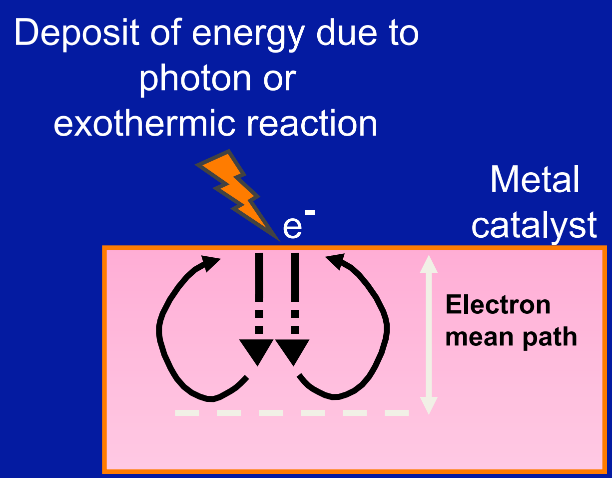
- Energy transfer from photon, energetic ions, exothermic chemical processes – through non-adiabatic energy dissipation

- Injection of hot electron with metal-insulator-metal junctions or STM tip



# Mean Free Path of Hot Electrons in Metal Surfaces



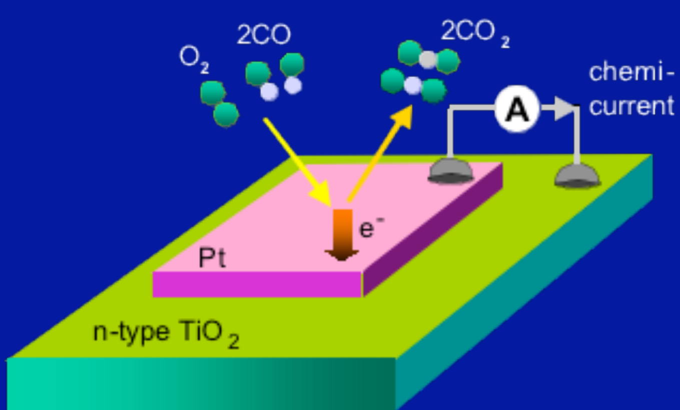

Ballistic Mean Free Path of Electrons at 1eV above $E_f$

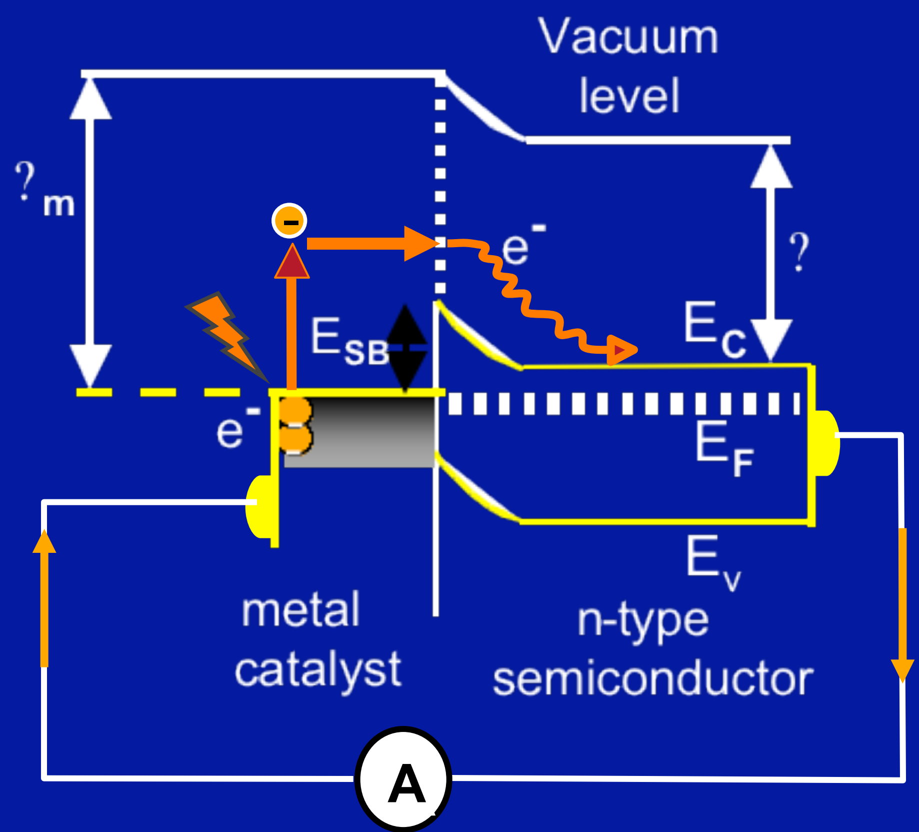
| | |
|---|---|
| • Gold | 10-100 nm |
| • Copper | 10-75 nm |
| • Palladium | 3-9 nm |
| • Platinum | 5-10 nm |

Inelastic mean free path at low energies given by $L \propto E^{-2}$

# Hot electron generation by exothermic catalytic reactions

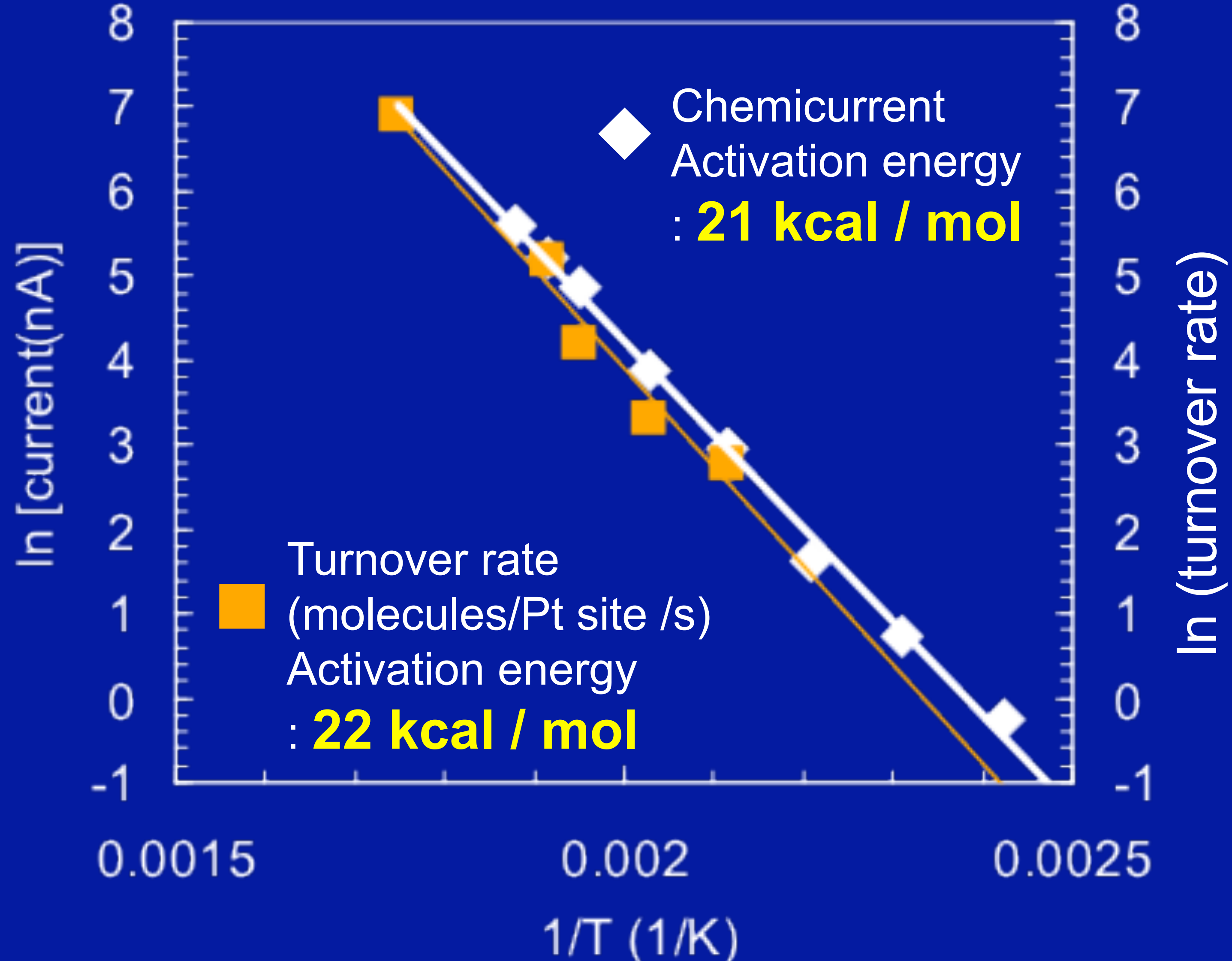
(detection with Schottky diode under CO oxidation)



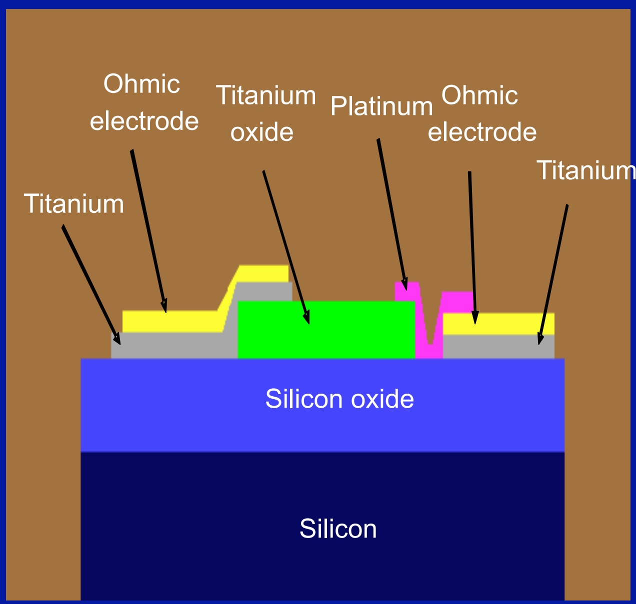

Schematic and energy diagram of catalytic nanodiode

# Chemicurrent and Turnover Rate Measured under Carbon Monoxide Oxidation

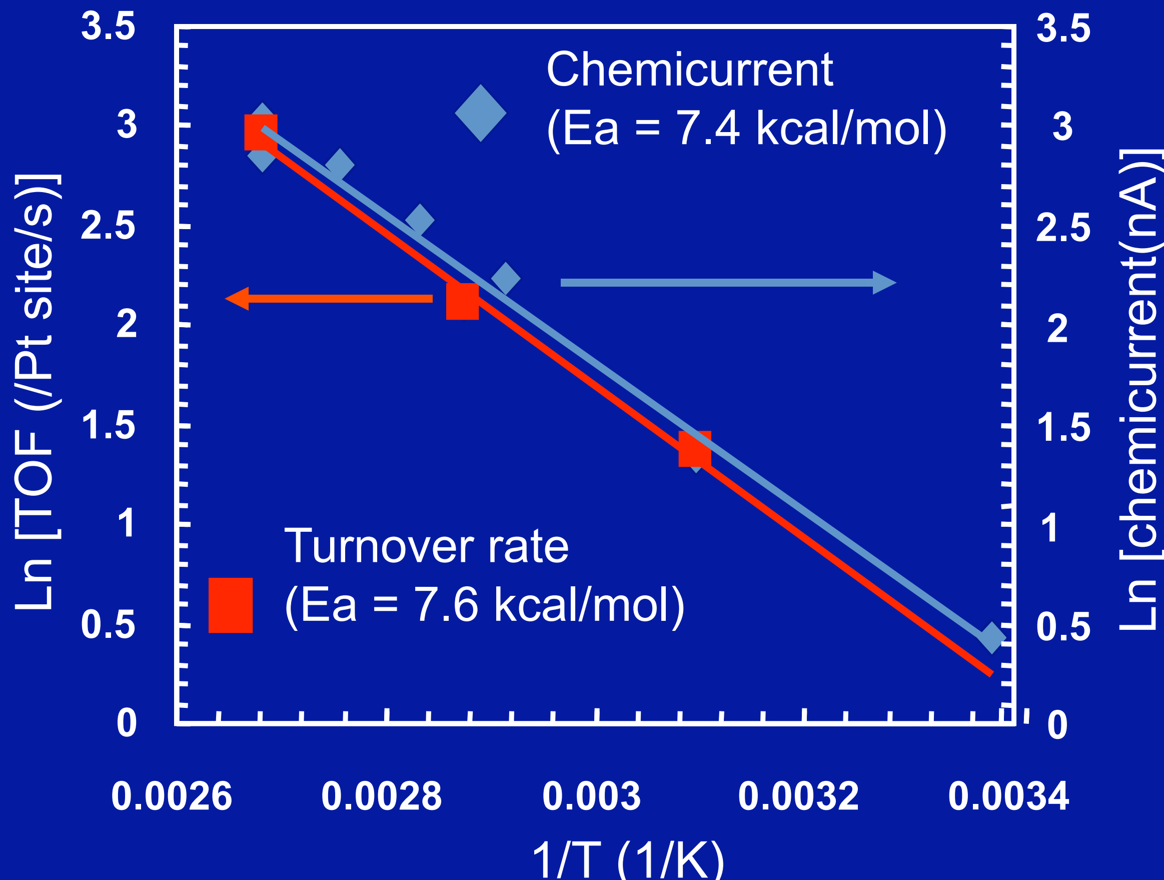


# Chemicurrent and Turnover Rate Measured under Hydrogen Oxidation

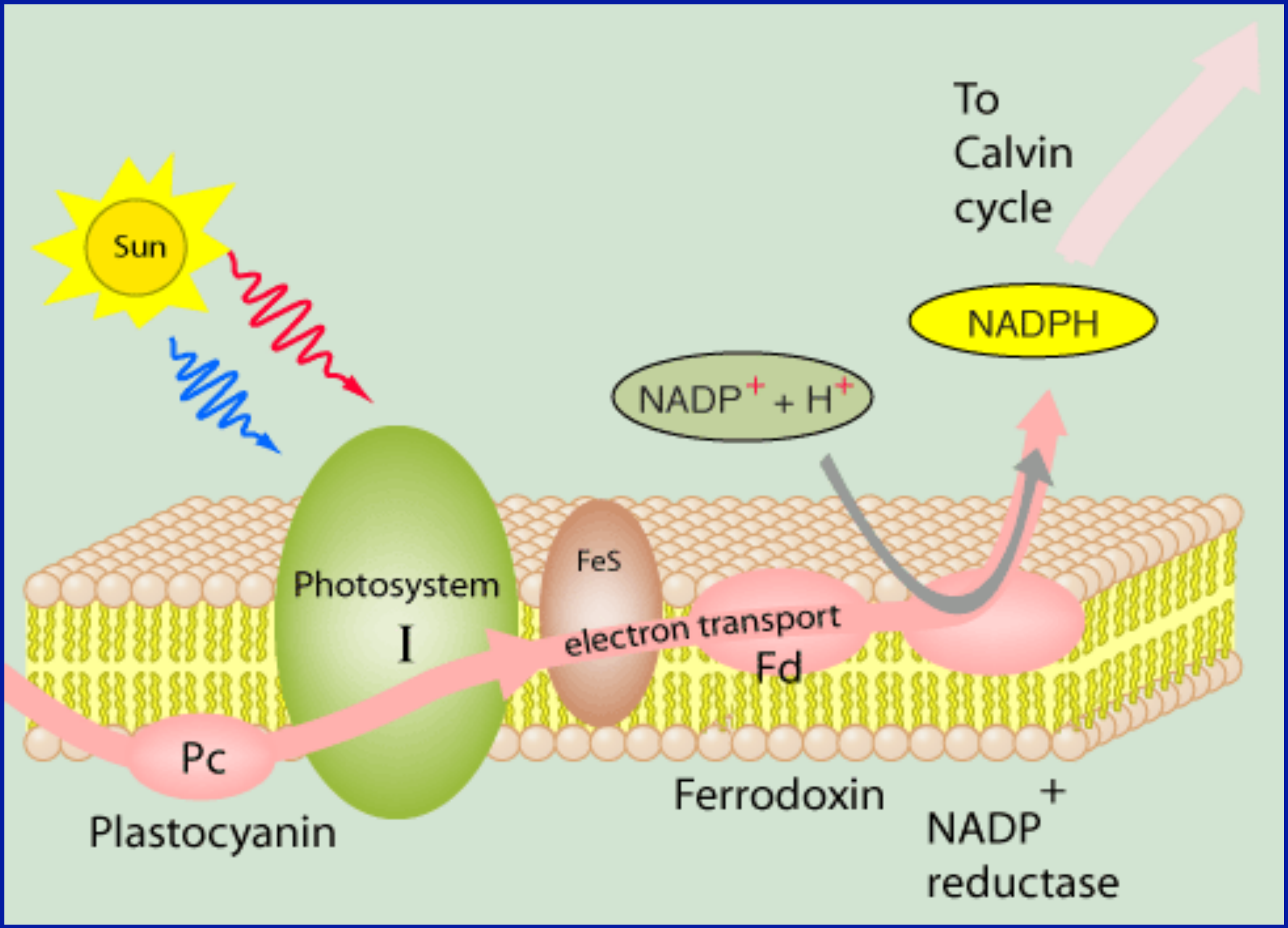
(with Pt/$TiO_2$ nanodiode and 700 Torr of $O_2$ and 6 Torr of $H_2$)




Scheme of Pt/$TiO_2$ nanodiode



# Electron transport in Photosynthesis





http://hyperphysics.phy-astr.gsu.edu/Hbase/Biology/psetran.html

**Moore R, Clark WD, Kingsley RS, and Vodopich D, Botany, Wm. C. Brown, 1995**

**Karp G, Cell and Molecular Biology, 5th Ed., Wiley, 2008**

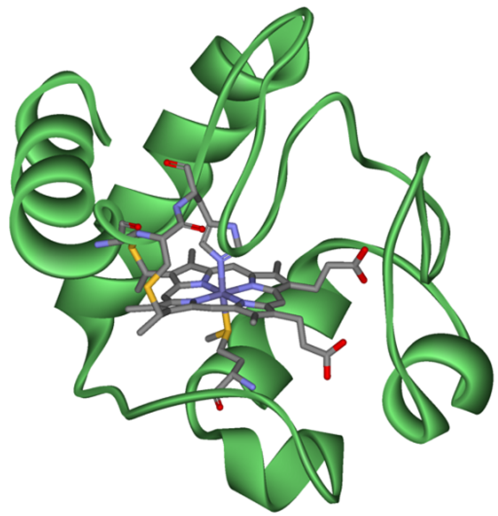
# Molecular Factors of Catalytic Activity and Selectivity

- Surface Structure (Size, Shape)
- Surface Composition
- Reaction Intermediates
- Adsorbate-induced Restructuring
- Adsorbate Mobility
- Oxidation State
- Charge Transport

# Future Challenges

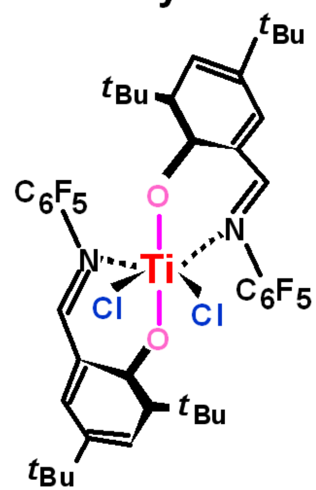
# Catalysts are Nanoparticles

**(a) Enzyme**



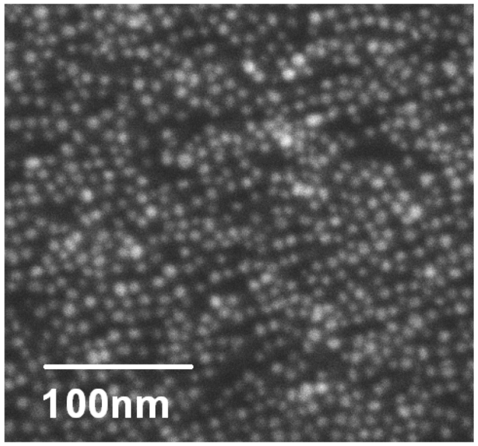
**Cytochrome C**
Size: ~4 nm, 100 amino acids
Molecular weight: ~12,000 daltons

**(b) Homogeneous catalysis**




**Single-site olefin polymerization catalyst**
Size : ~1.6 nm

**(c) Heterogeneous catalysis**




**Pt/Rh bimetallic nanoparticles**
Size : 8 nm

# Hybrid Systems

- Homogeneous – Heterogeneous
- Enzyme – Homogeneous
- Enzyme – Heterogeneous

# Chemistry (Catalysis) of 10-40 Atom Clusters

(No Bulk Atoms)


MATERIALS AND CHEMICAL
SCIENCES DIVISION

Acknowledgement

| | |
|---|---|
| Selim Alayoglu | Jim Krier |
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| Wenyu Huang | Chia-Kuang (Frank) Tsung |
| Sang Hoon Joo | **Professor Dean Toste** |

Department of Energy