Investigating catalyst design strategies for selective reaction of cyclic C4 oxygenates from Biomass

Clay Horiuchi and Dr. Will Medlin

Department of Chemical and Biological Engineering
University of Colorado at Boulder
Boulder, Colorado, USA

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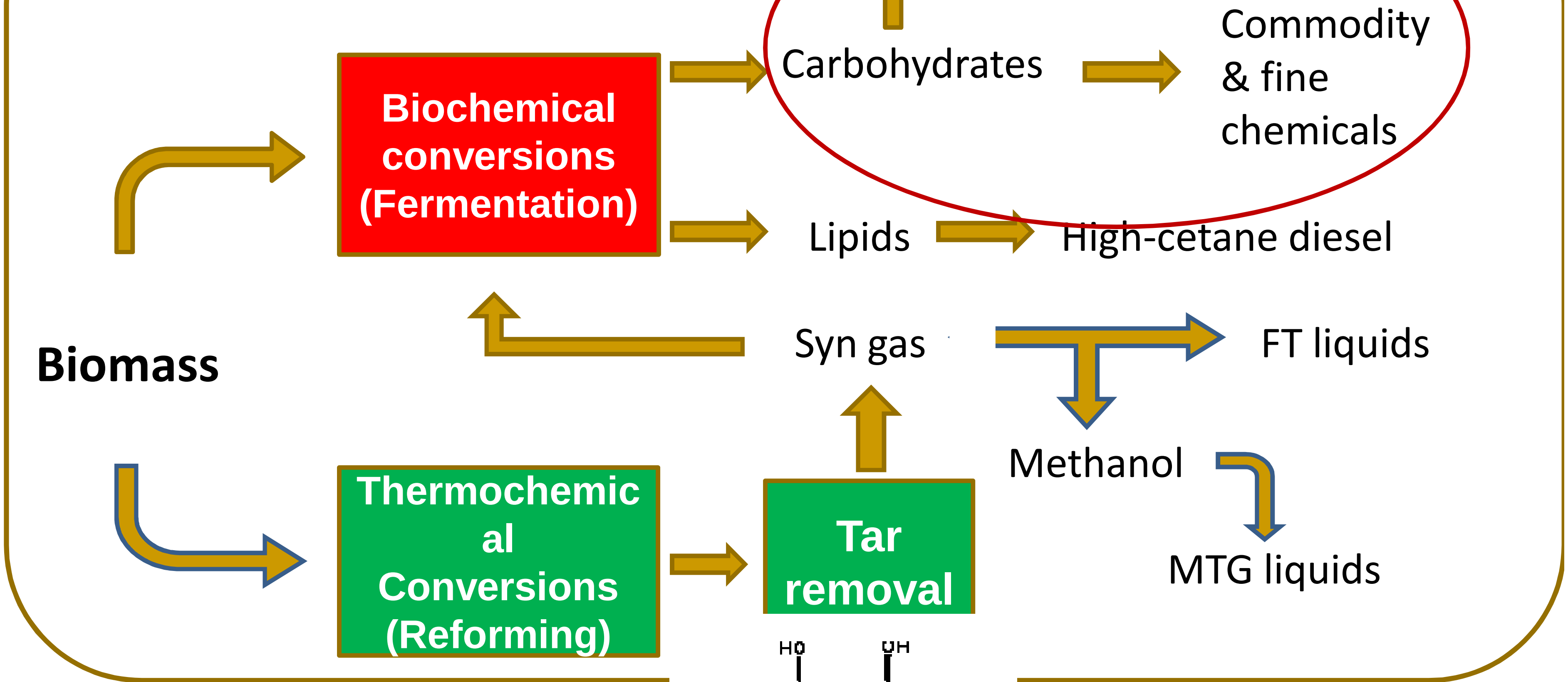
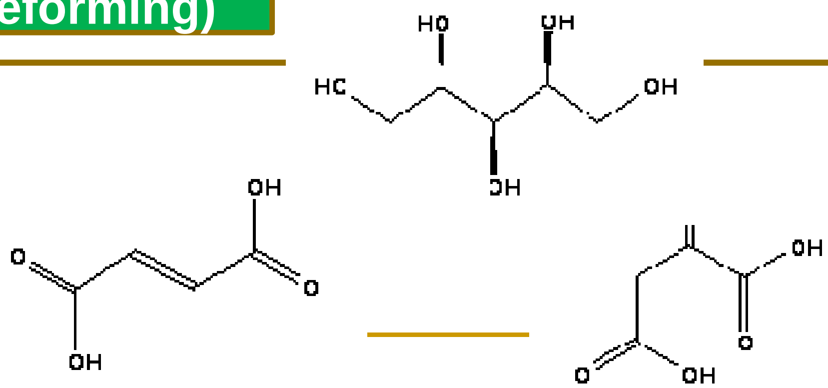
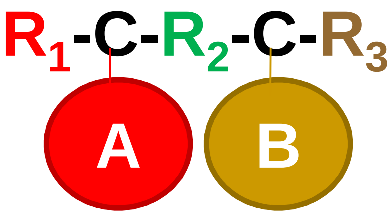
Biorefinery overview

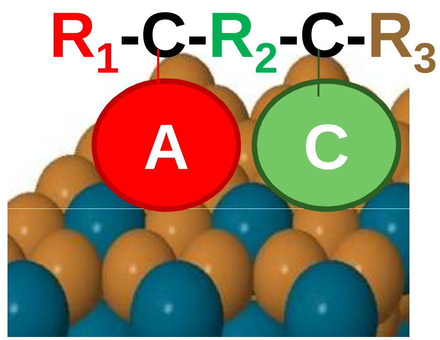




Carbohydrate “Building Blocks”

The goal of this project is to design catalysts that are highly selective for reactions of multifunctional molecules

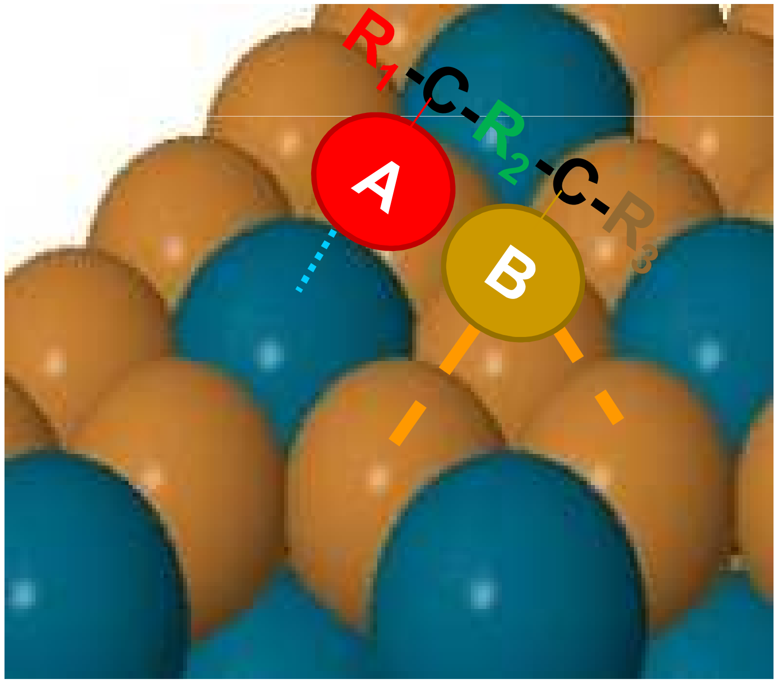




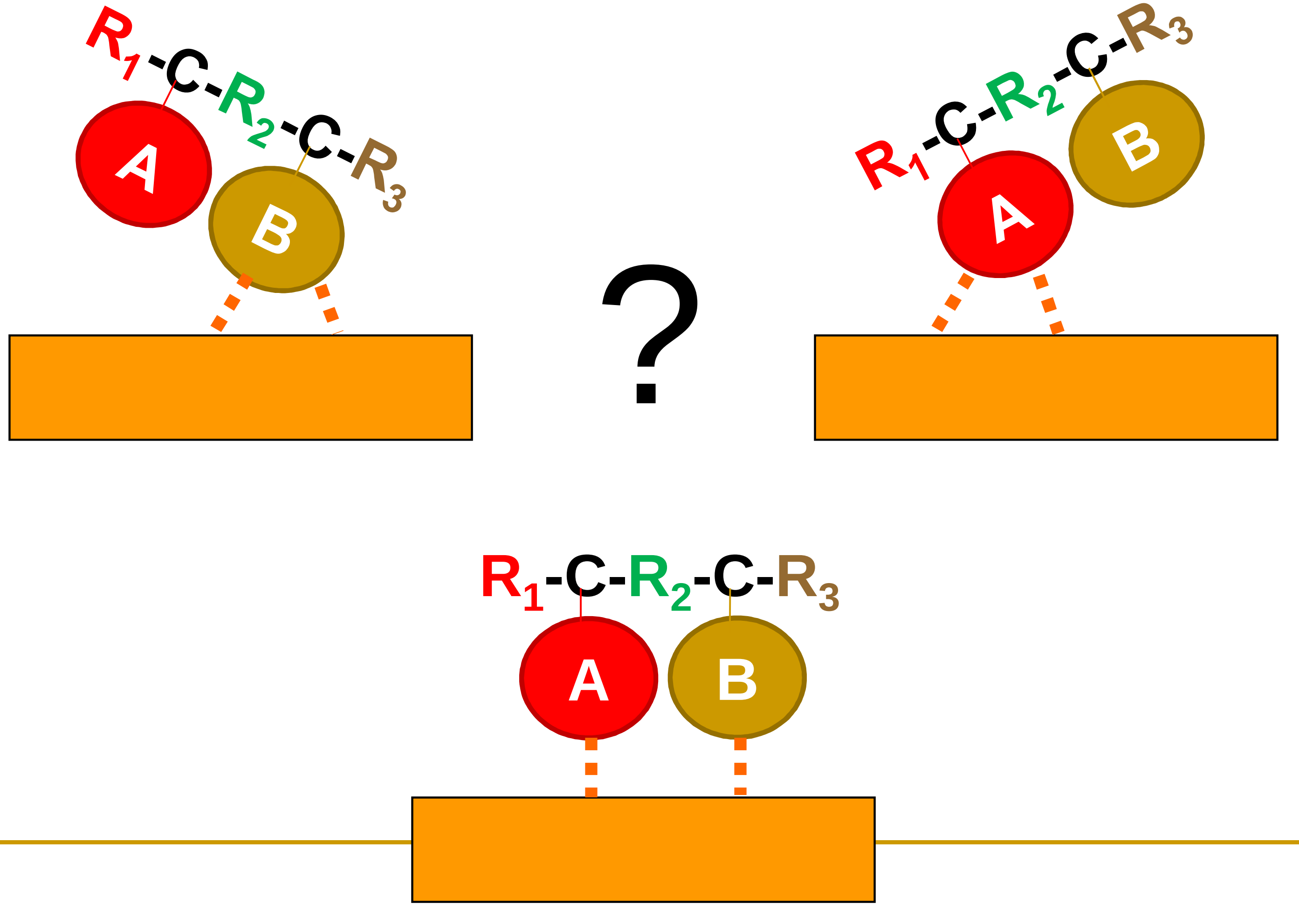
- Applications throughout heterogeneous catalysis and huge potential in biorefining

Catalyst selectivity might be improved by using a bimetallic catalyst

- Degree of interaction between each functional group and the catalyst surface will determine reactivity

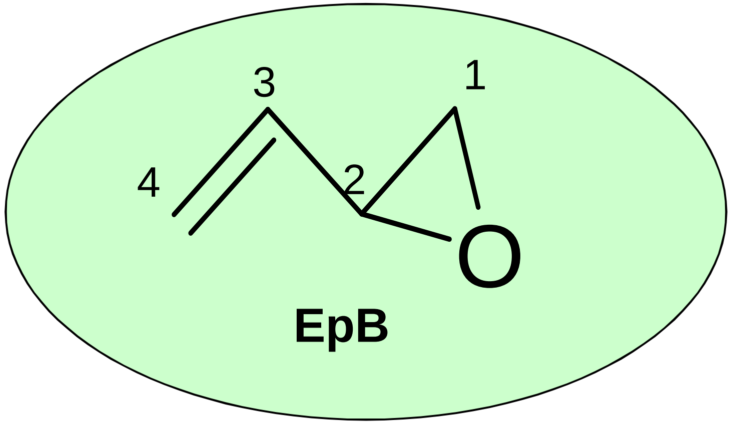


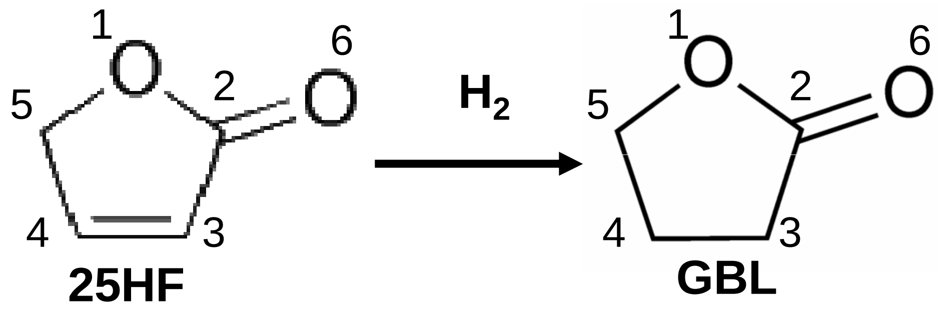
Must first develop molecular-level understanding of surface-adsorbate interactions on individual metals



This work focuses on surface studies of cyclic multifunctional probe molecules

- Multifunctional species:
  - 3-membered ring
    - 1-Epoxy-3-butene (EpB)
  - 5-membered rings
    - 2(5H)-Furanone (25HF)
    - γ-butyrolactone (GBL)





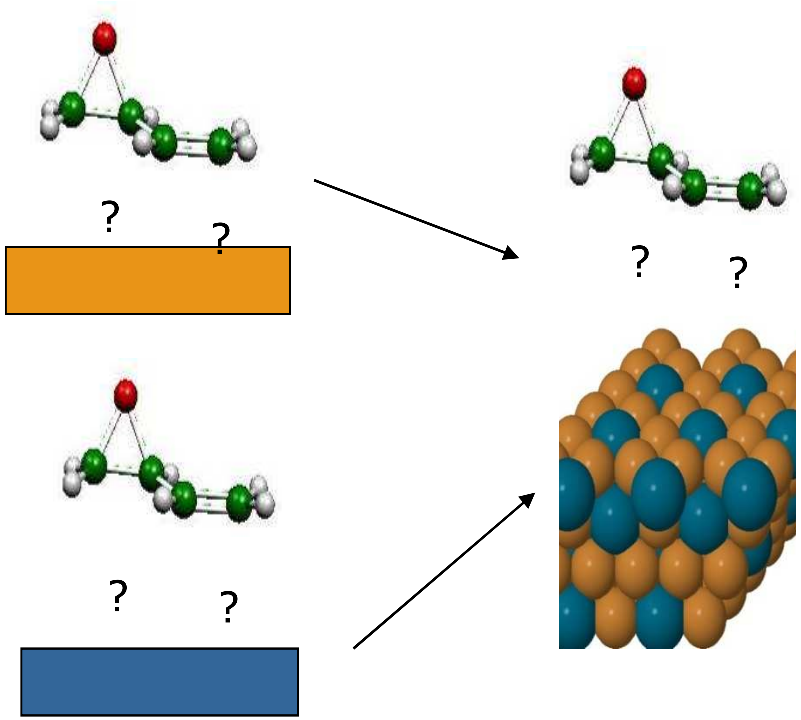
“Furanone”

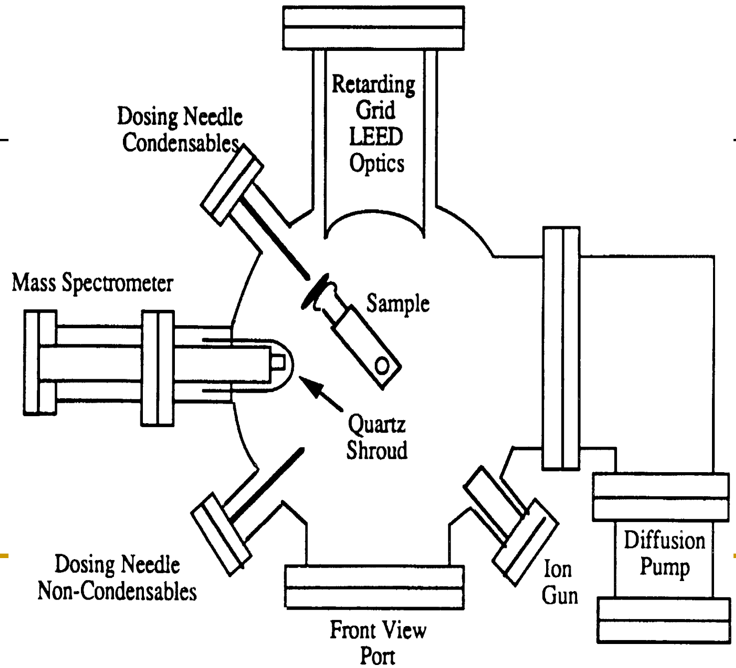
- Contain four carbons, multifunctional oxygenates
- Useful model molecules for complex biorefining “building blocks”

Surface science approaches used to develop molecular-level understanding

Methods for studies on single crystals

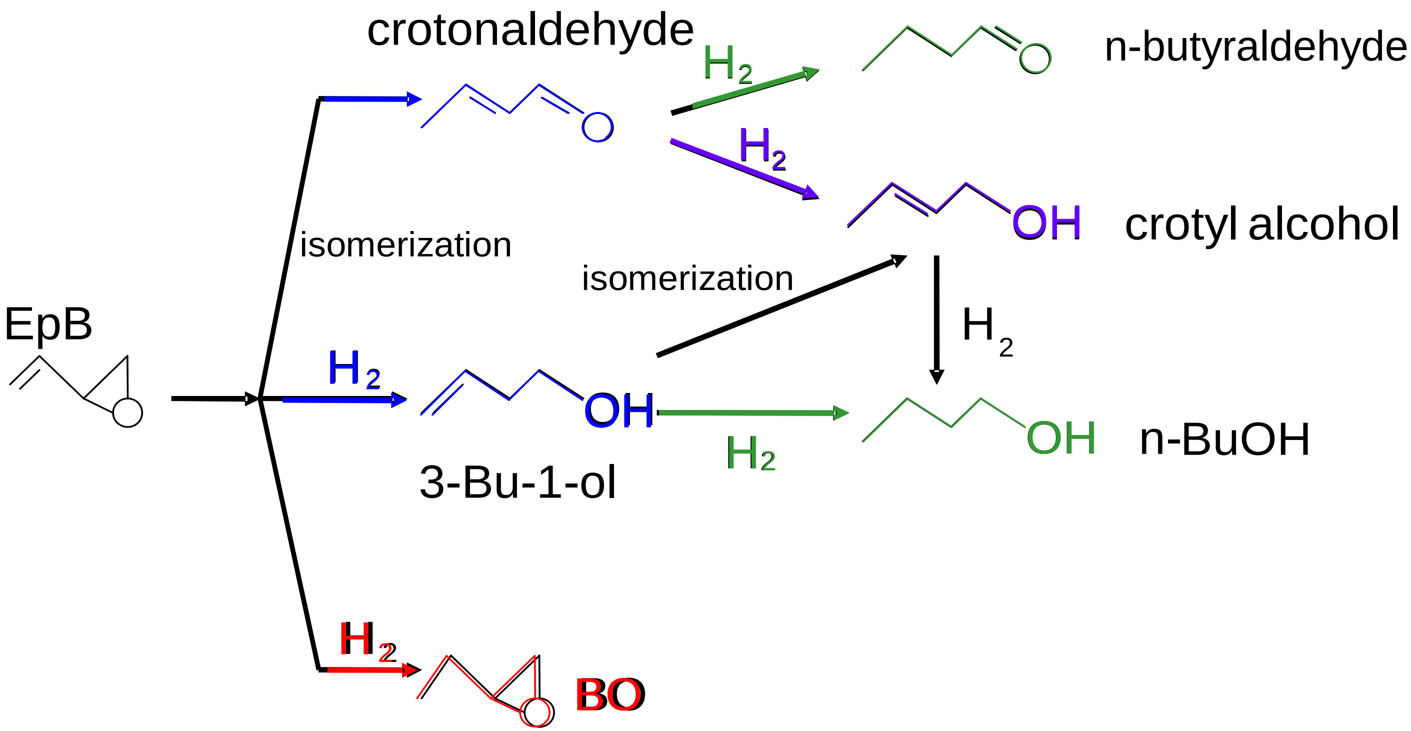
- High Resolution Electron Energy Loss Spectroscopy (HREELS)
- Temperature Programmed Desorption (TPD)
- Density functional theory (DFT)





Pt(111) | **Pd(111)** | **Ag(110)**

Use EpB to refine strategy for designing a selective catalyst

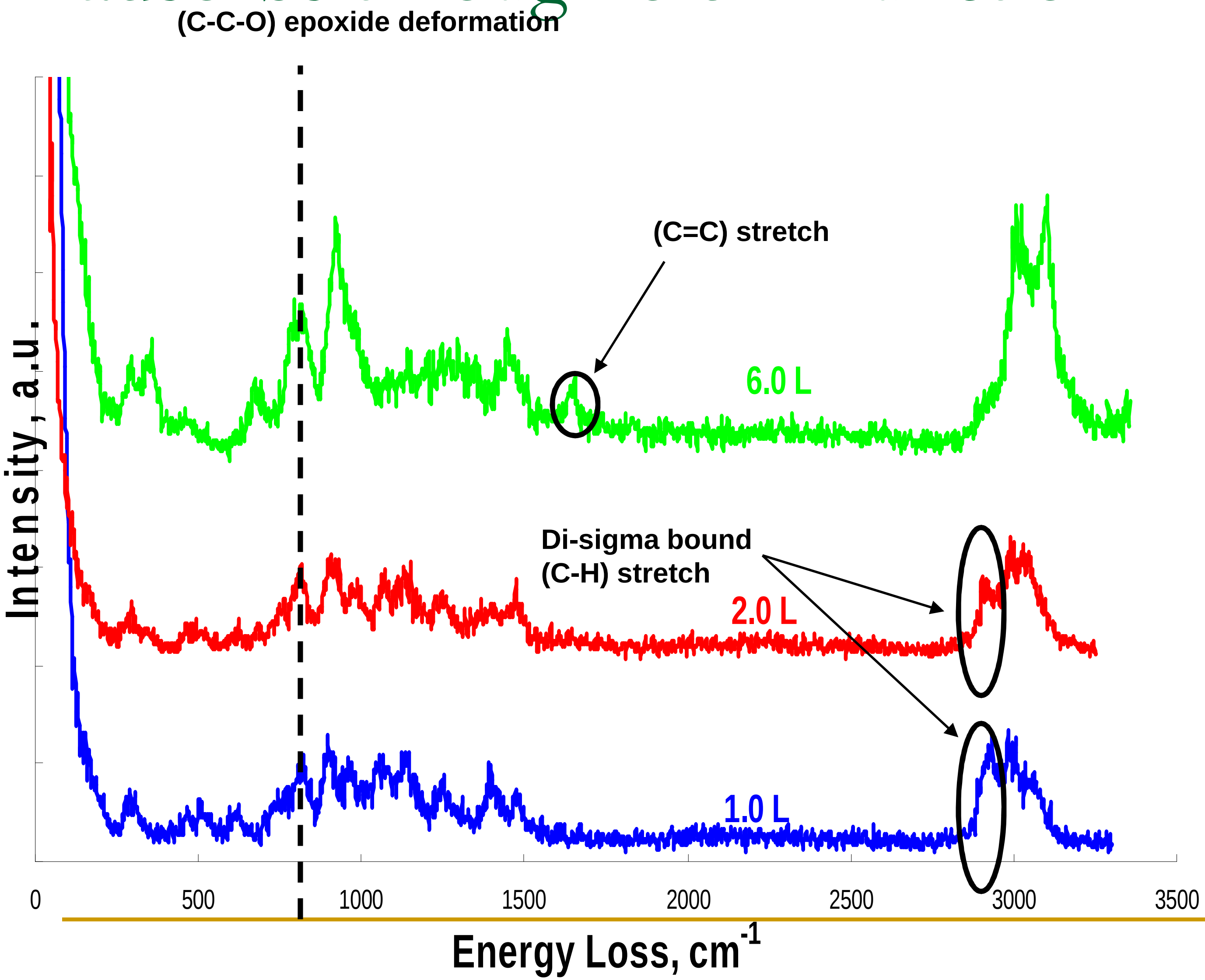


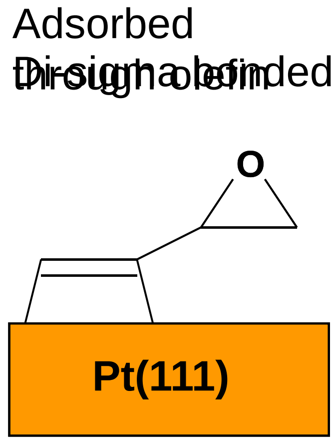
EpB = 3,4 epoxy-1-butene
crotonaldehyde = 2-buten-1-al
crotyl alcohol = 2-buten-1-ol
3-Bu-1-ol = 3-buten-1-ol

n-butanal = n-butyraldehyde
n-BuOH = n-butanol
BO = butylene oxide (epoxybutane)

Schaal et al, *J Catalysis* 254 (2008) 131

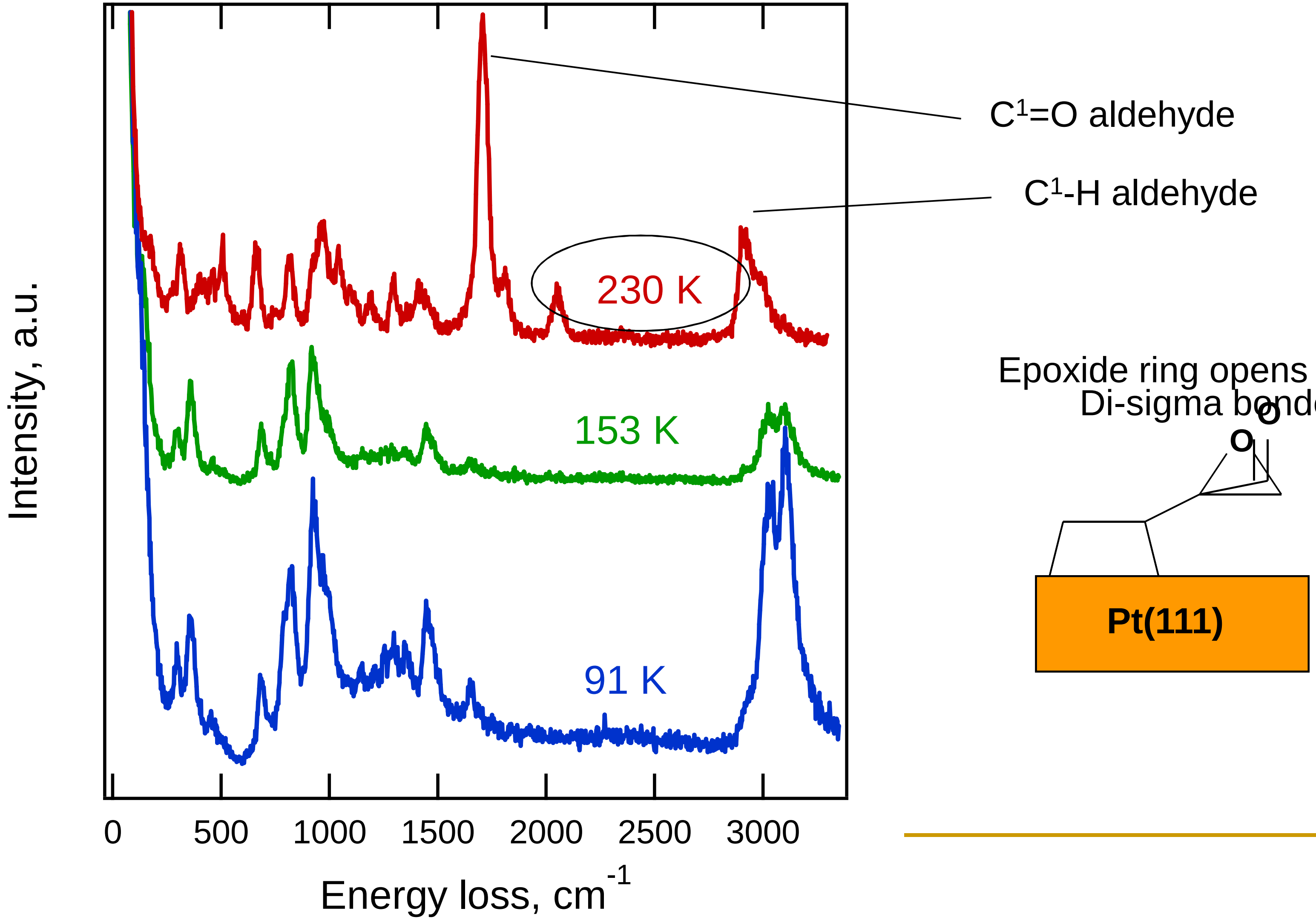
At low temperatures, EpB on Pt(111) adsorbs through olefin function





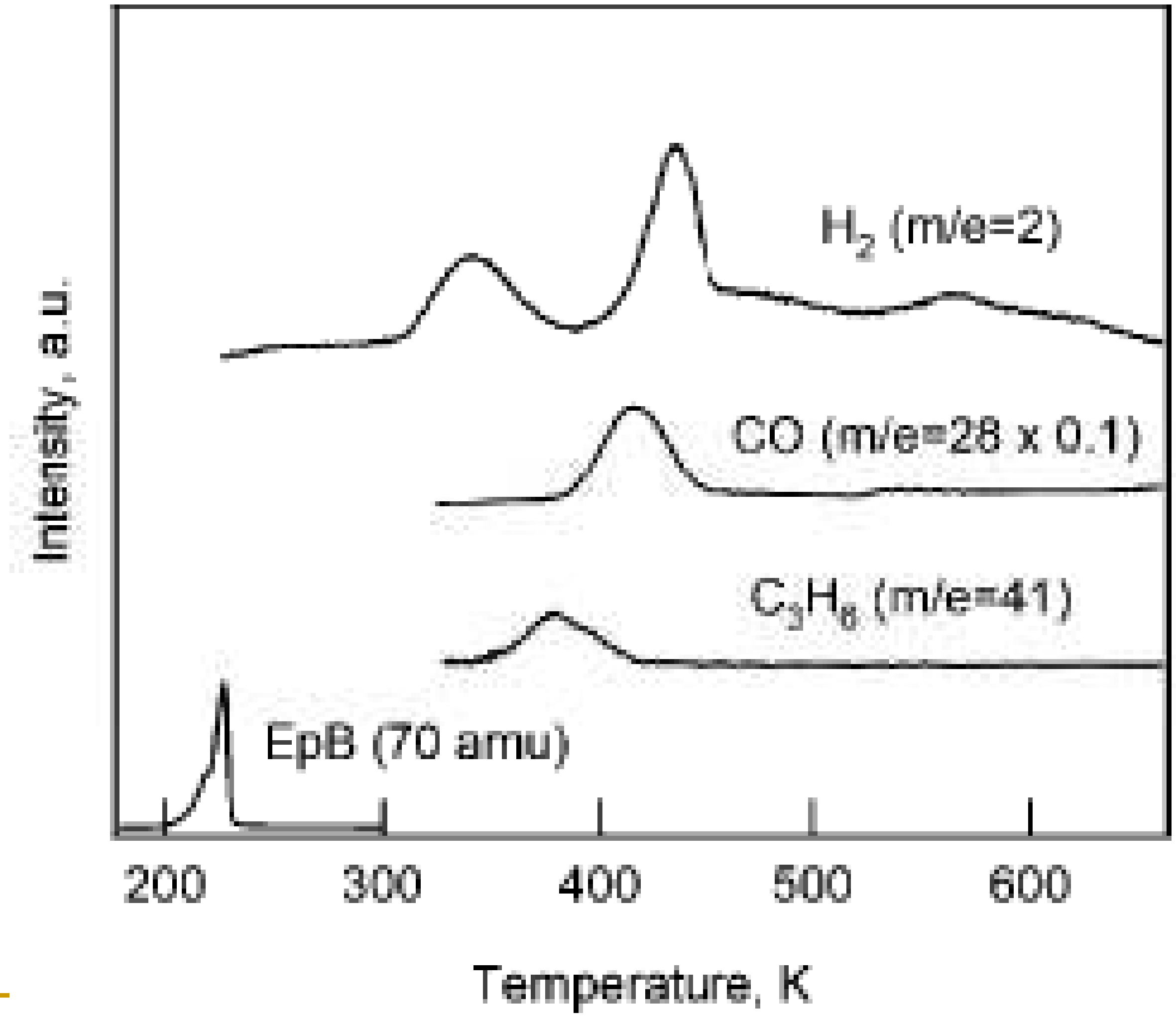
Loh, Davis, Medlin, *JACS* 130 (2008) 5507

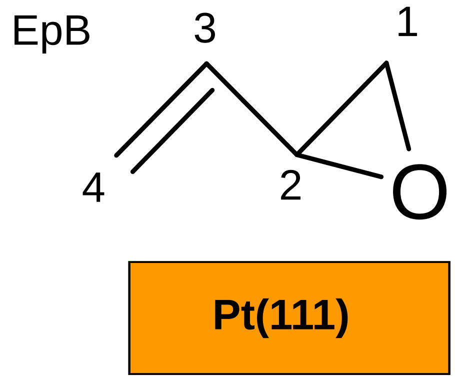
EpB undergoes irreversible ring-opening to form an aldehyde on Pt(111) by 230 K

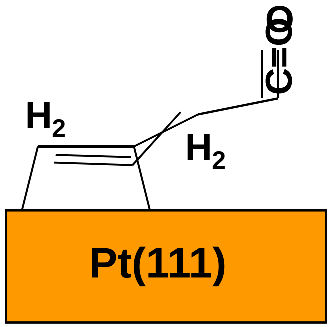


Loh, Davis, Medlin, *JACS* 130 (2008) 5507

EpB / Pt(111) TPD: EpB decomposes by decarbonylation and dehydrogenation



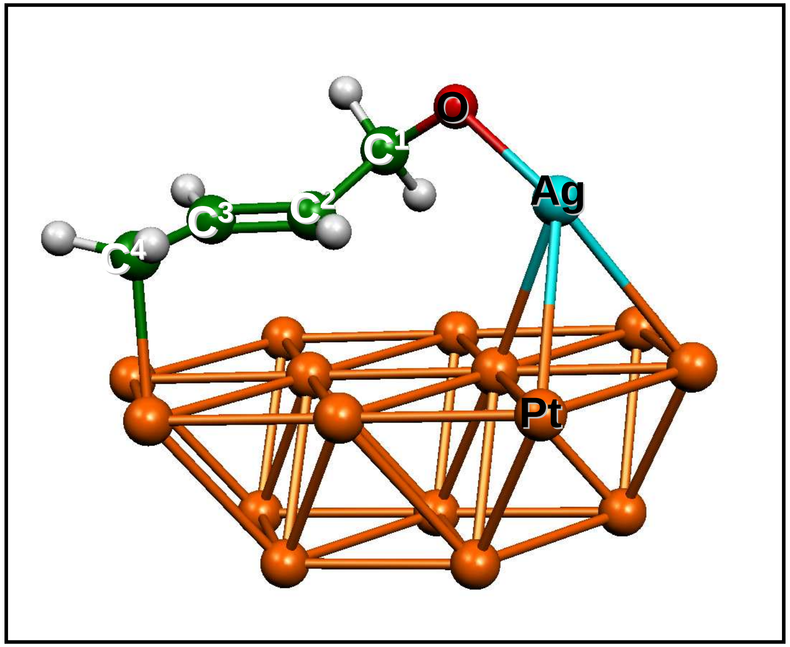


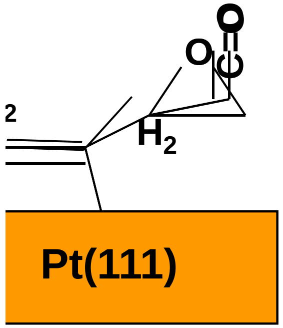


Loh, Davis, Medlin, *JACS* 130 (2008) 5507

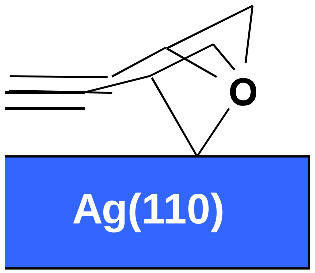
To summarize EpB results:

- On Pt(1
  - Binds p
  - Ring o
  - Underg
- On Ag(1
  - Forms
  - Ring o
  - Can de





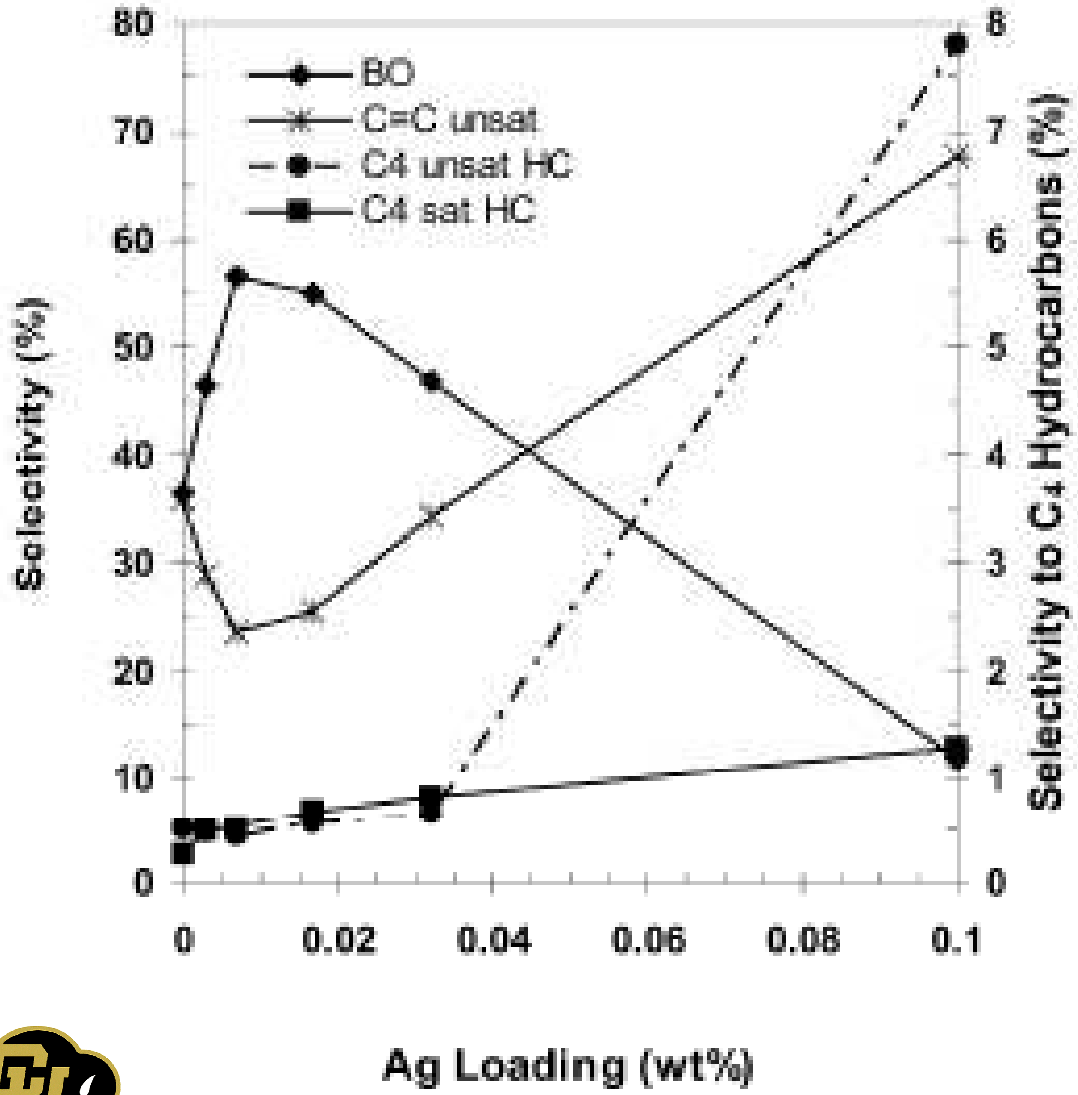
rogenation



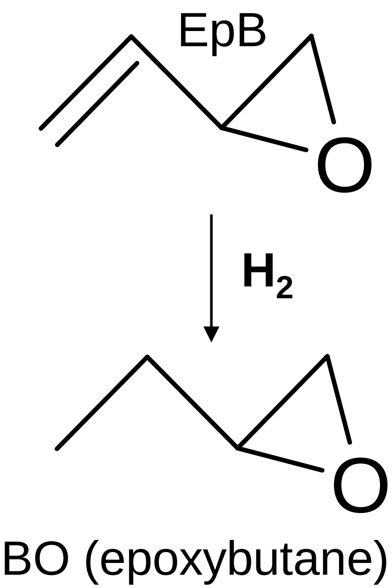
Medlin, Barteau, Vohs, *J. Molec. Cat. A*: *Chem* 163 (2000) 129

Loh, Davis, Medlin, *JACS* 130 (2008) 5507

Selectivity to various products is a sensitive function of surface composition

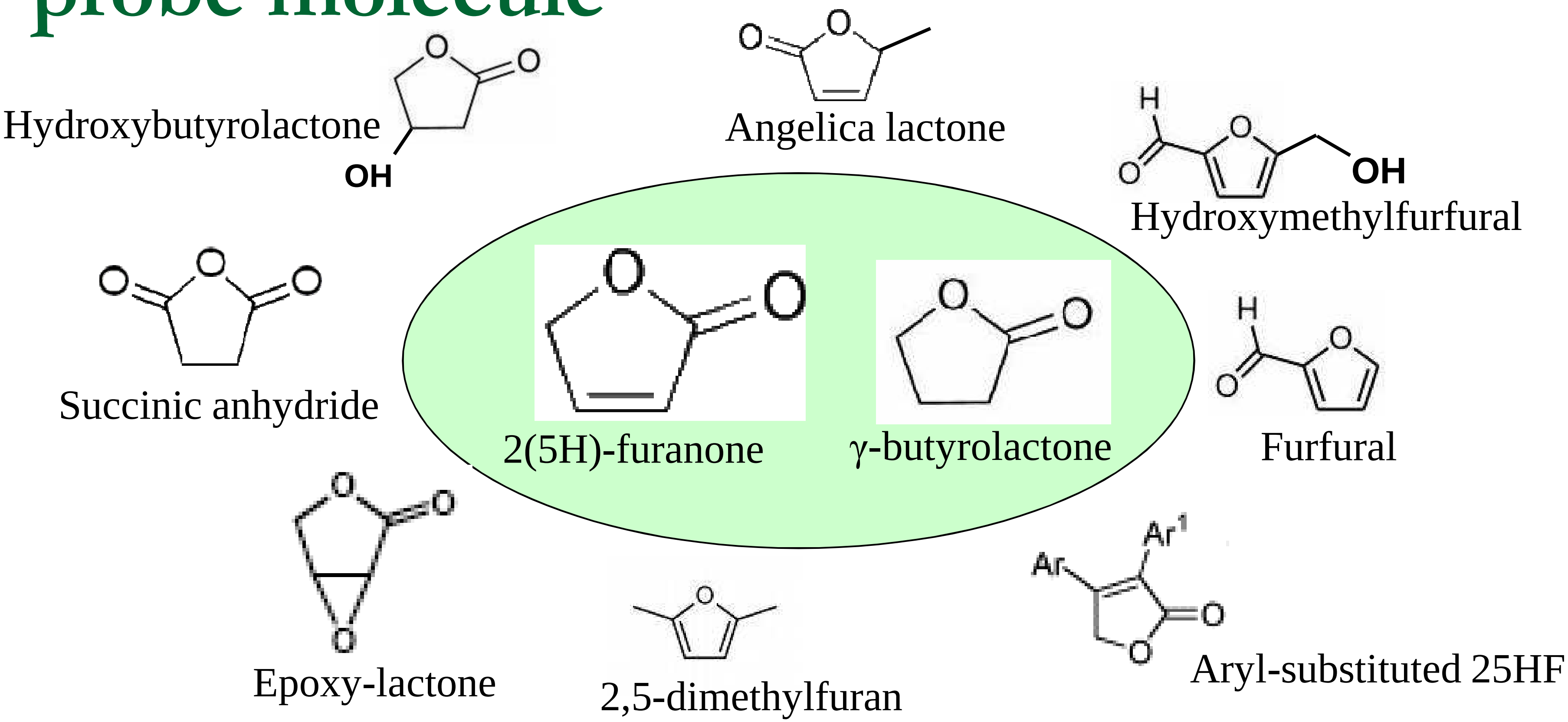


- Supported bimetallic catalyst (Ag-Pt/SiO_2) improves selectivity



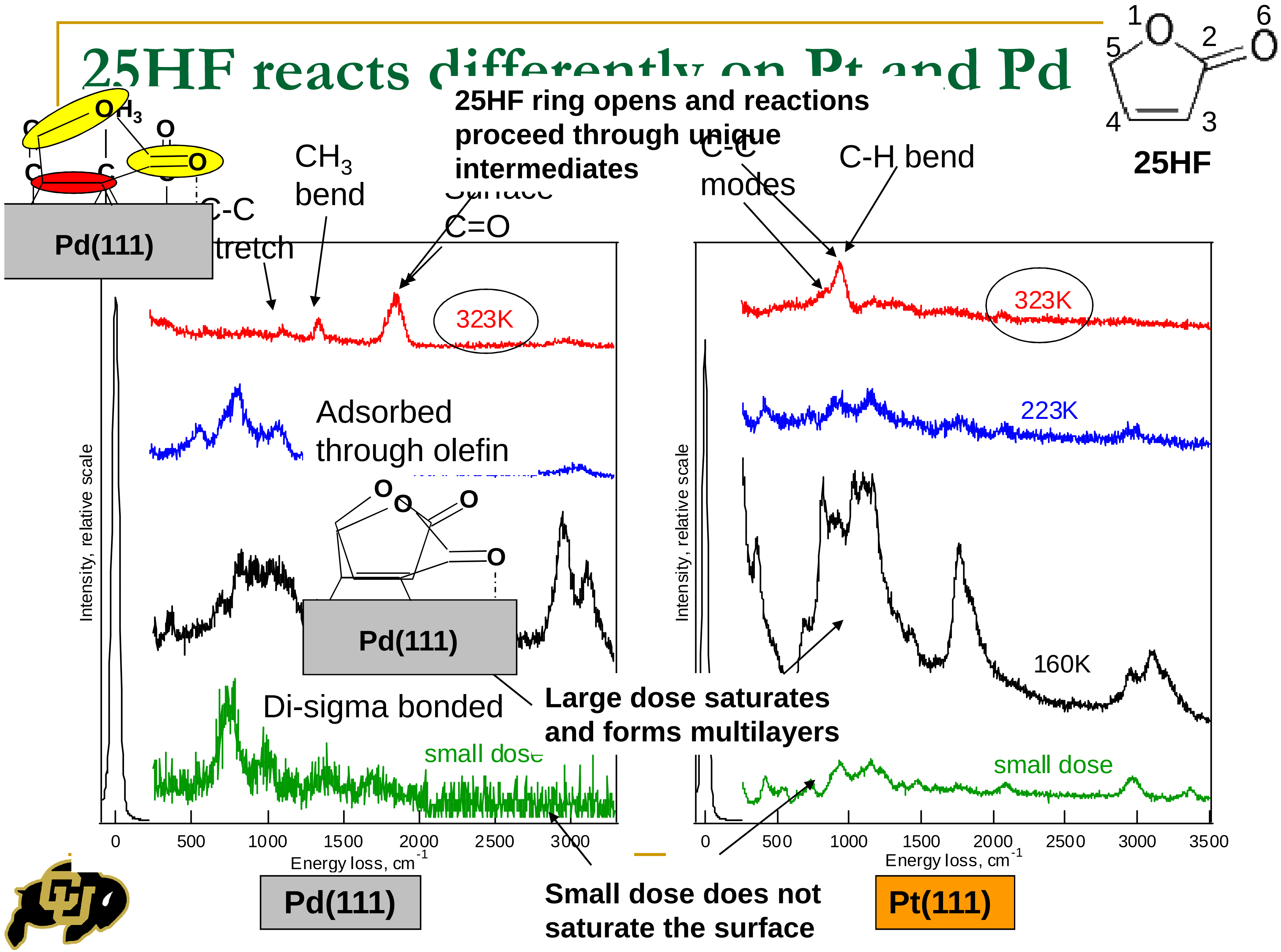
Schaal et al, *J Catalysis* 254 (2008) 131; Schaal et al, *Catalysis Today* 123 (2007) 142

Now progress to more complicated probe molecule

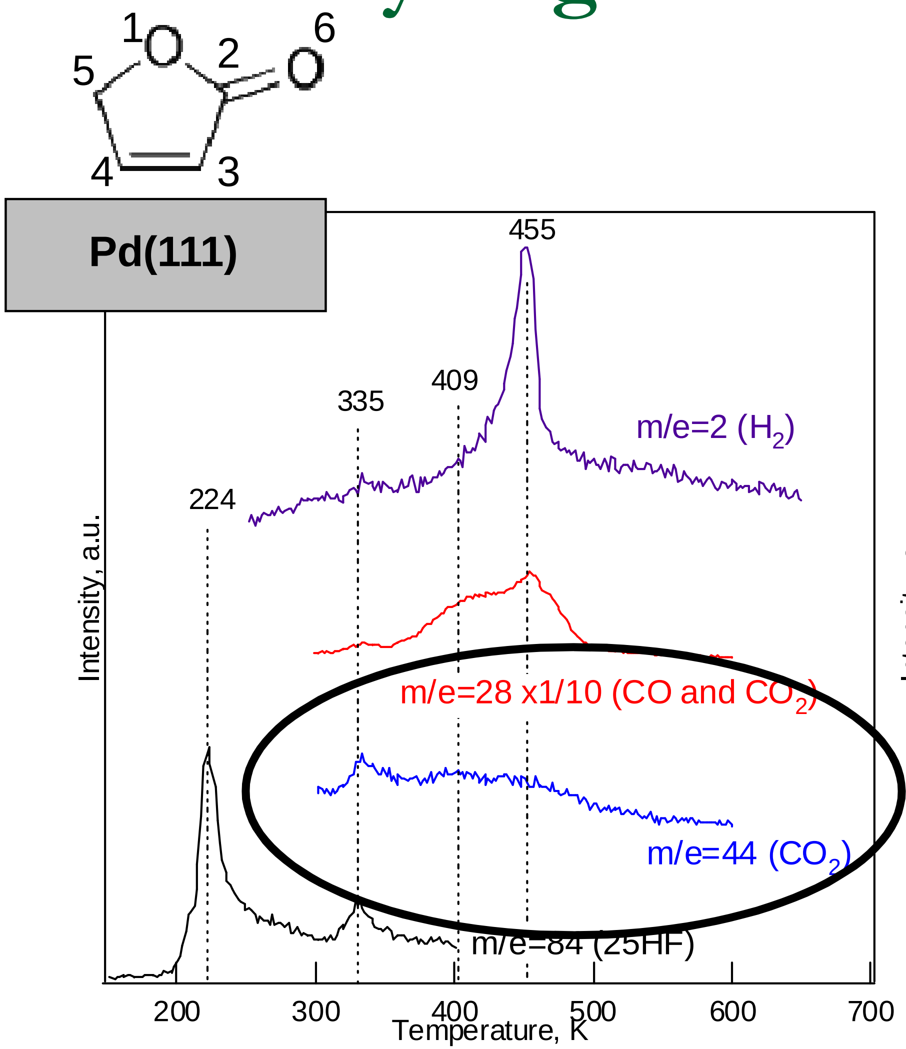


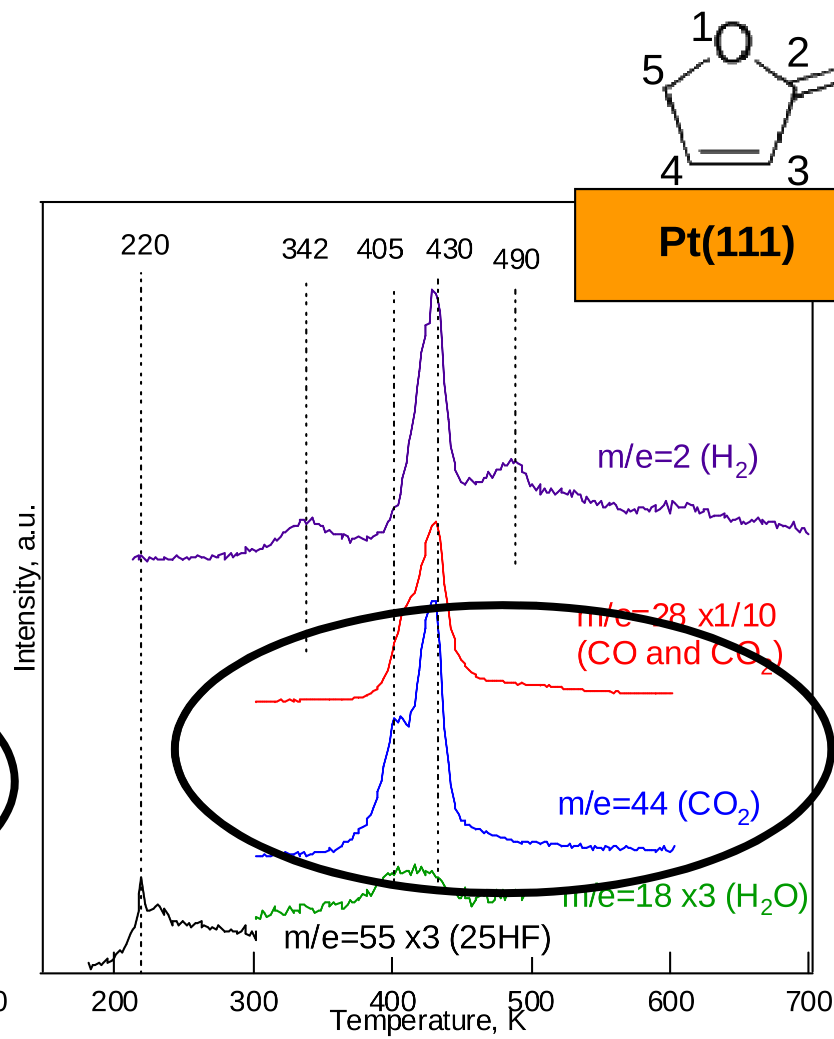
- Start by studying the probe molecules on Pd(111) and Pt(111)

25HF reacts differently on Pt and Pd



25HF TPD results show decarbonylation and dehydrogenation

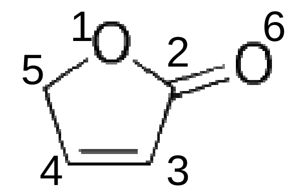


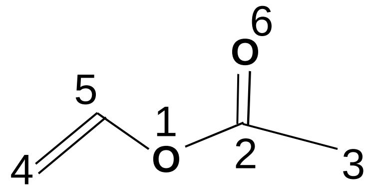


Reaction schemes for 25HF

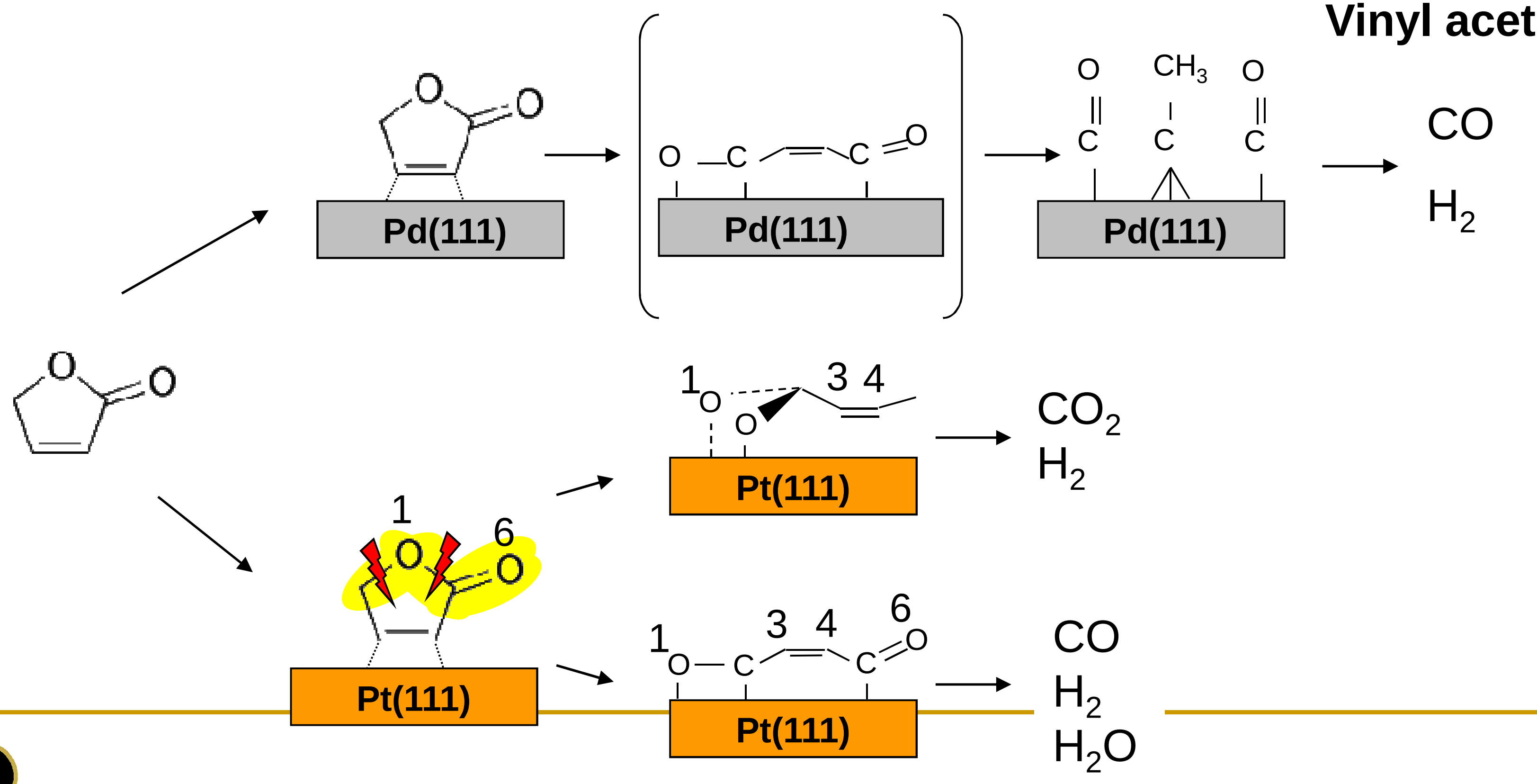
- 25HF proceeds through distinct intermediates on Pd(111) and Pt(111)

25HF

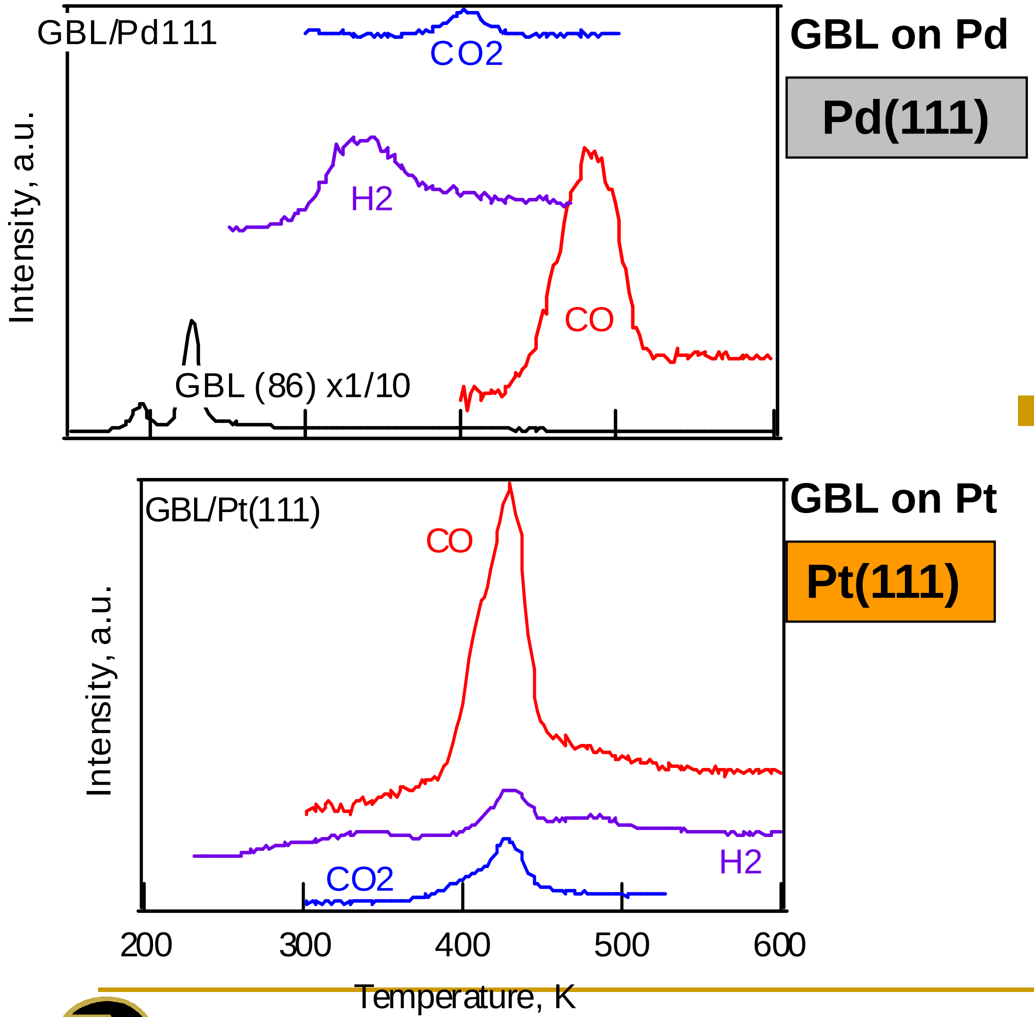


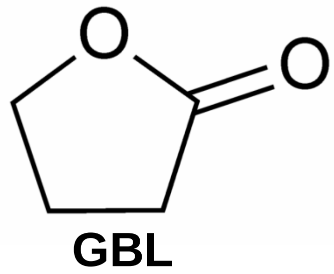


Vinyl acetate



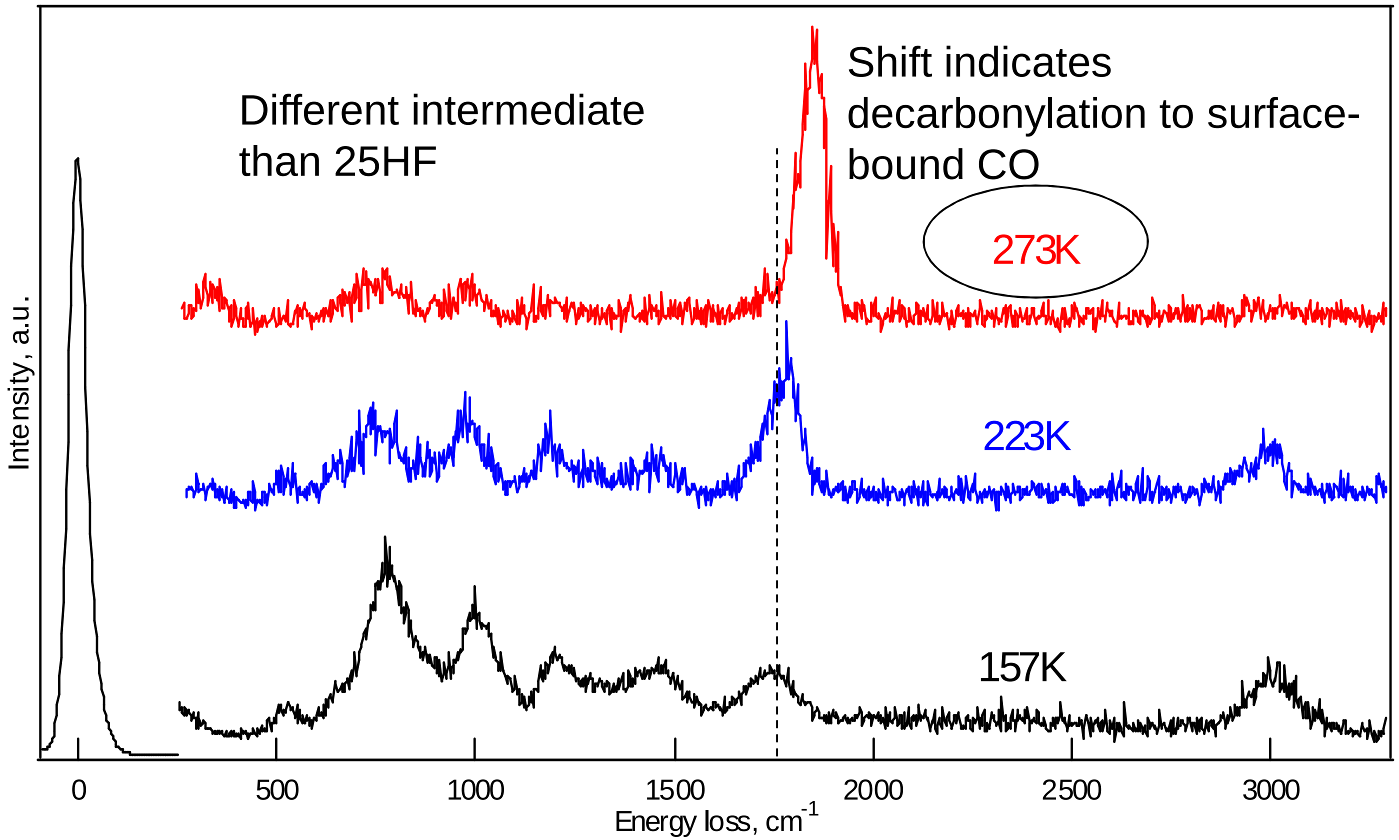
TPD results for GBL show decarbonylation and dehydrogenation



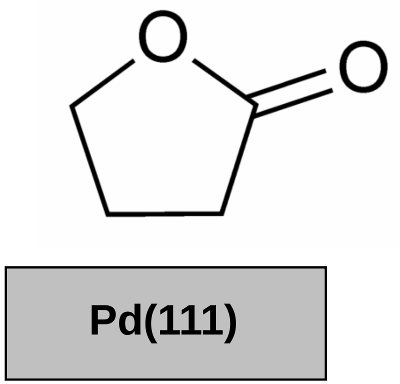


- Unlike 25HF, CO_2 is produced from both Pt and Pd

HREELS GBL on Pd(111)



GBL



- Ring-opening reaction occurs at lower temperature for GBL

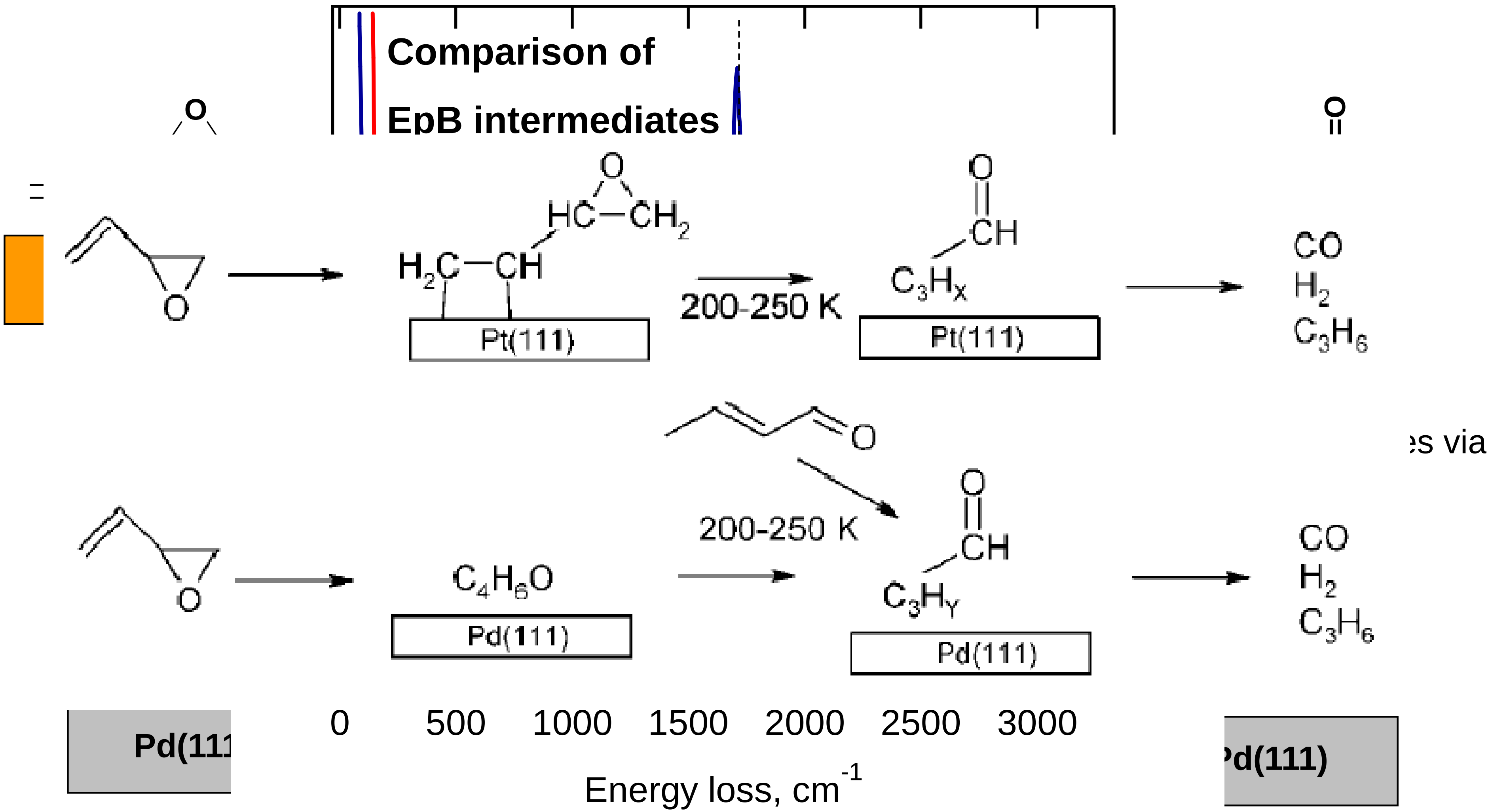
Conclusion slide

- Surface science approaches facilitate an understanding of trends in *adsorption* and *reaction* of unsaturated cyclic oxygenates
  - Adsorption on *Pd* and *Pt* dominated by adsorption through *olefin*
  - Activated ring-opening reactions dependent on structure of the ring
- Combining observations from *different surfaces* allows design of catalysts for selective oxygenate conversions

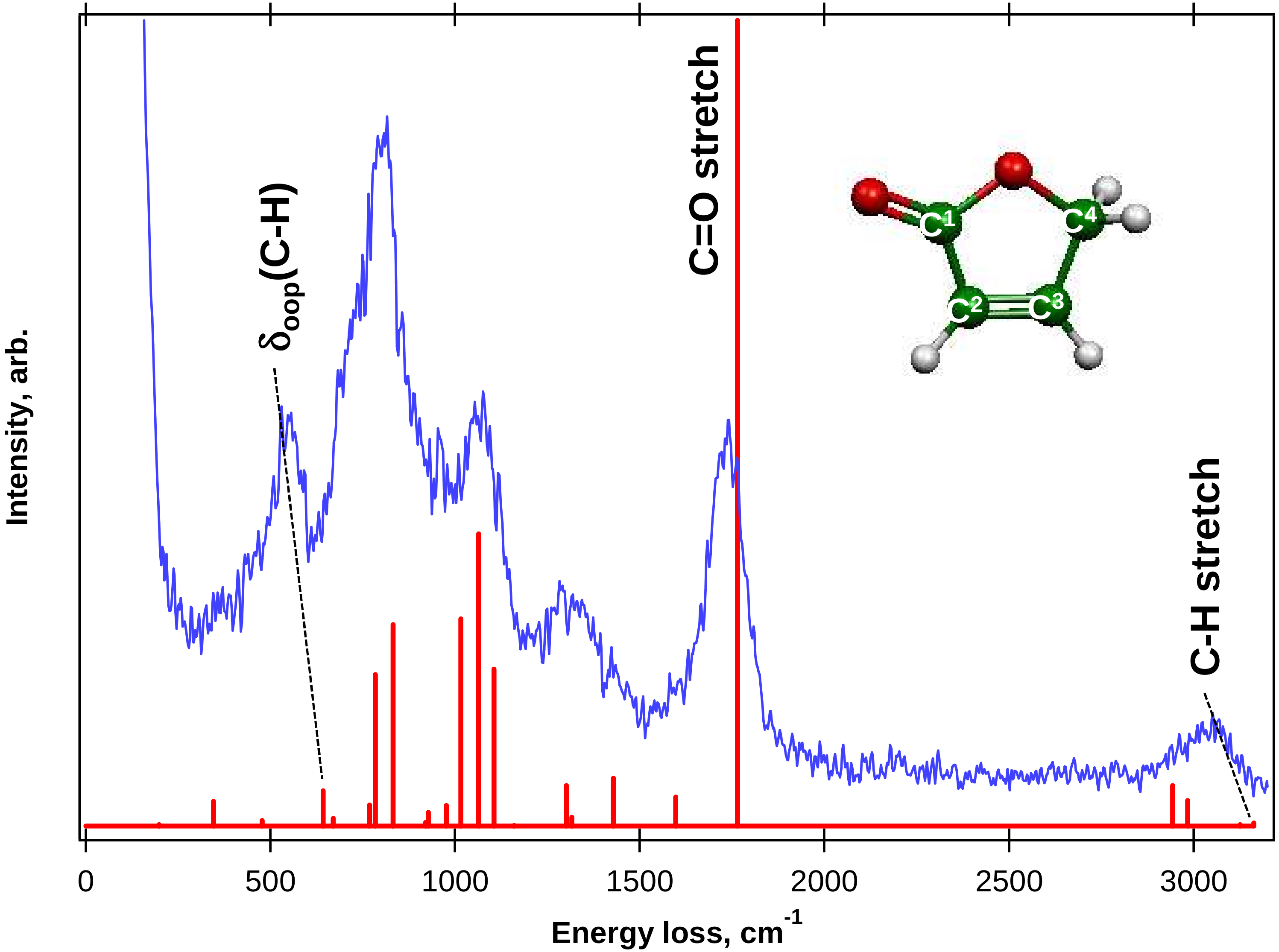
“Knowledge is in the end based on acknowledgement.” - Ludwig Wittgenstein

- Medlin group members
  - In particular:
    - Dr. Dylan Kershner
    - Steve Marshall
    - Meghana Rangan
    - Wenyu Zhang
    - Ben Israel
- Funding sources
  - NSF
  - U.S. Dept of Ed. GAANN
  - CU Graduate School

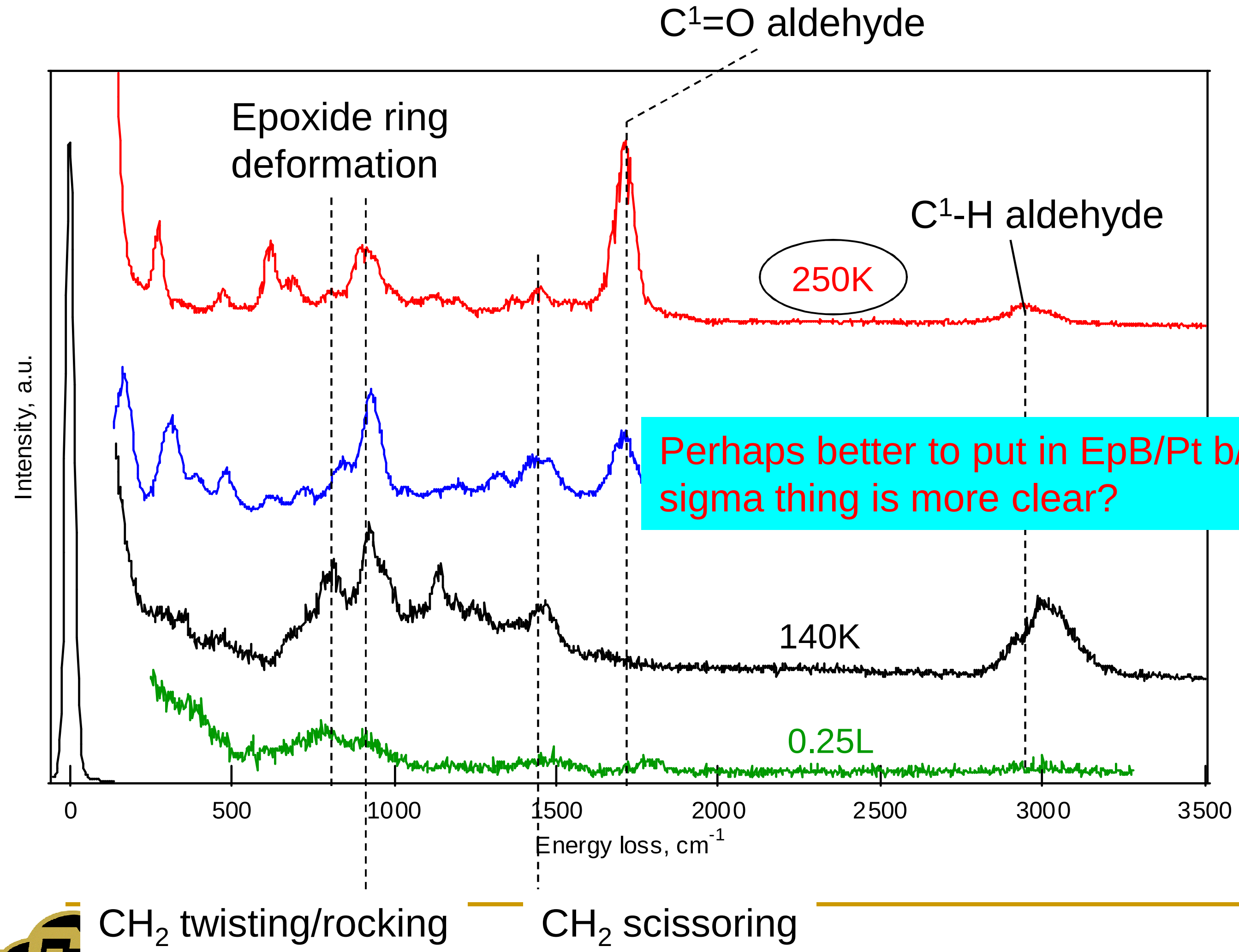
Results of surface science studies



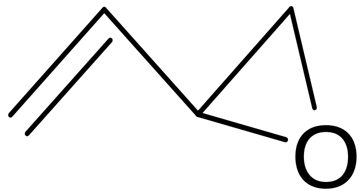
DFT helps in assigning vibrational modes, suggests furanone adsorbed in tilted configuration through olefin



Adsorption and reaction of EpB on Pd(111)

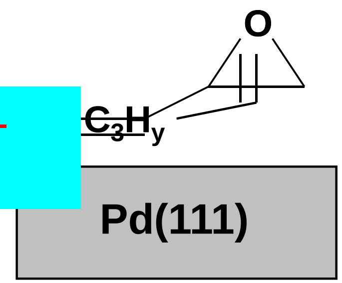


Perhaps better to put in EpB/Pt b/c the di-sigma thing is more clear?



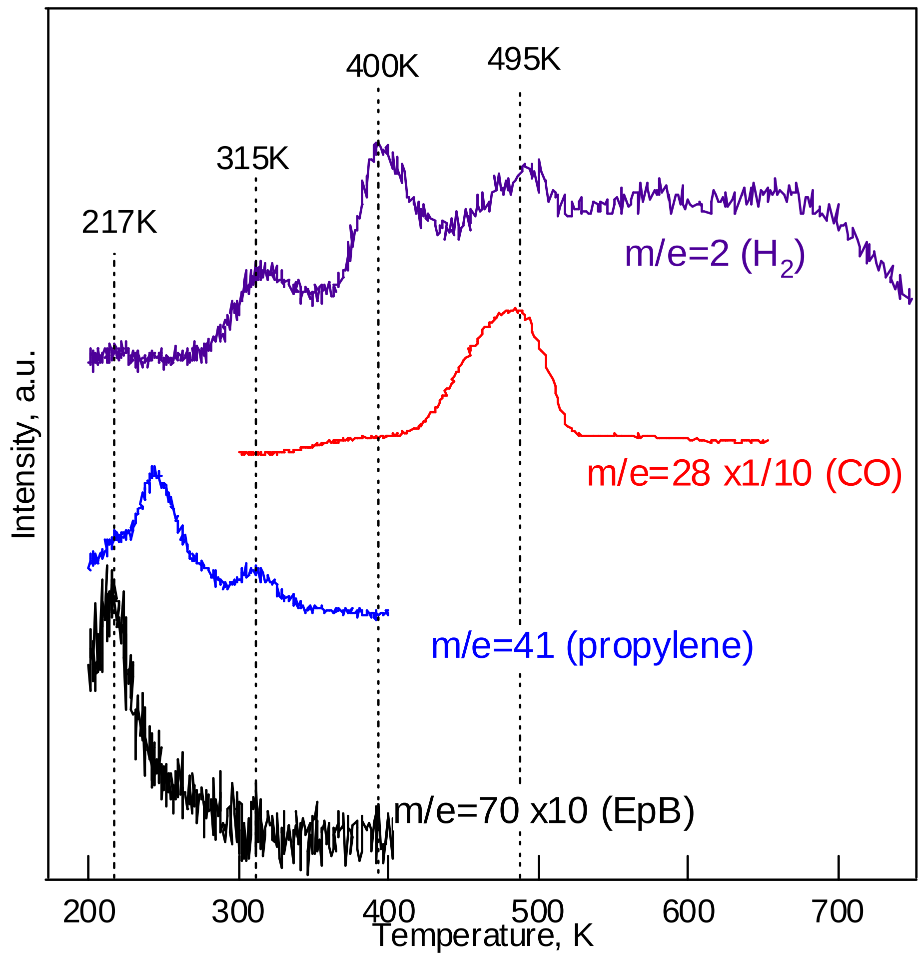
EpB

EpB adsorbs through olefin group

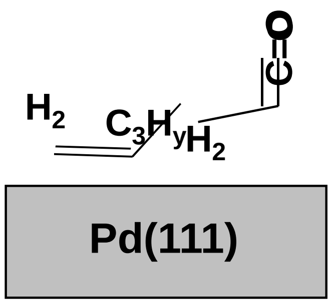


Epoxide ring opens

TPD results for EpB on Pd(111) indicate decarbonylation and dehydrogenation reactions



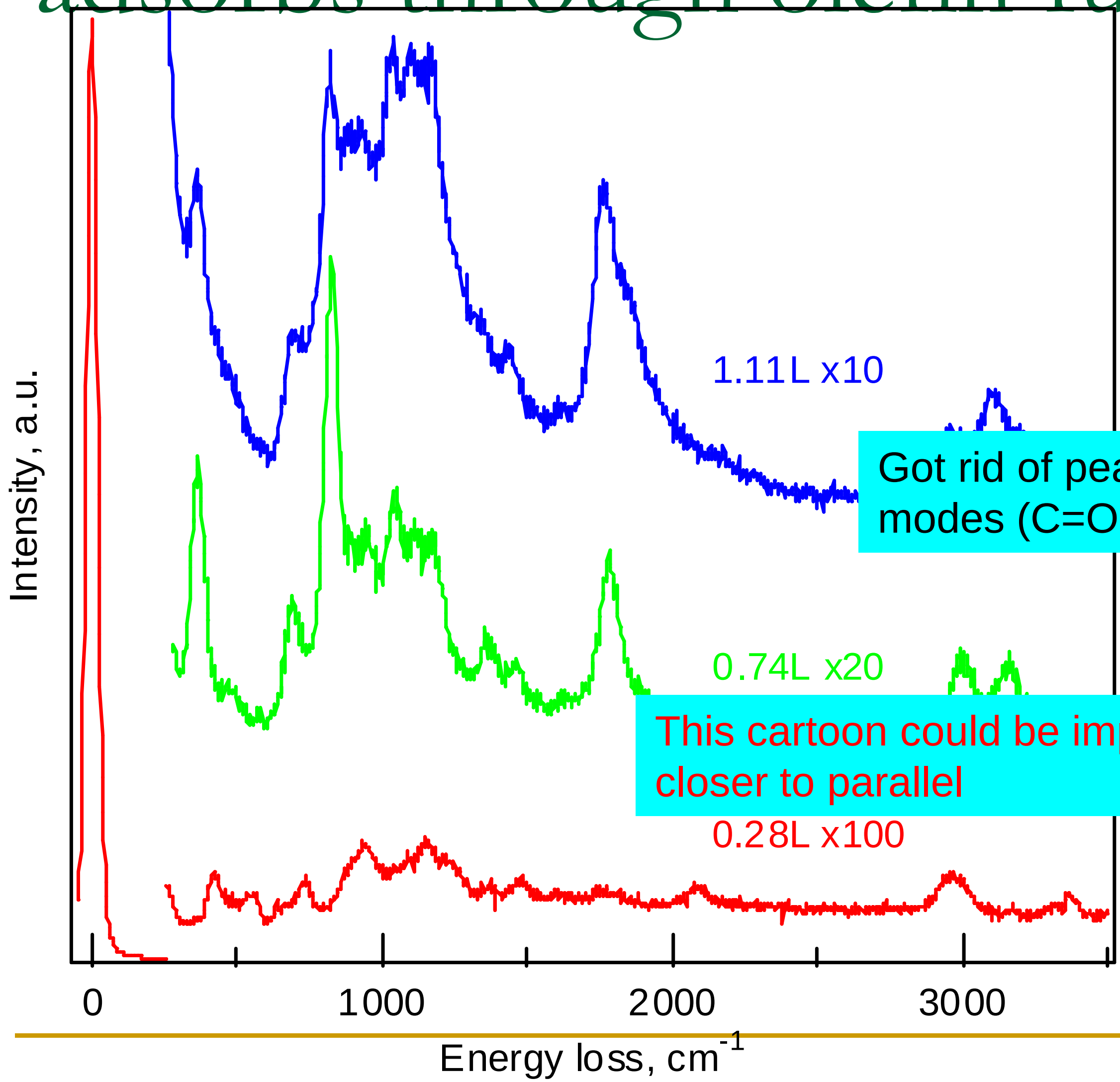
- CO and H_2 are major products
- Small amounts of propylene (m/e=41)
- **NO EpB re-forms**



Summary of "design" cues for EpB and 25HF

- Low temperature adsorption on Pt and Pd occurs (primarily) through olefin function, suggesting potential for selective C=C hydrogenation.
- Irreversible ring-opening occurs by 200 K for EpB and by 300 K for 25HF on Pd and Pt.
- Ring-opening of epoxides on Ag

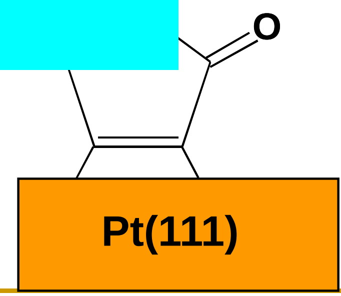
At low temperature, 25HF on Pt111 adsorbs through olefin functionality



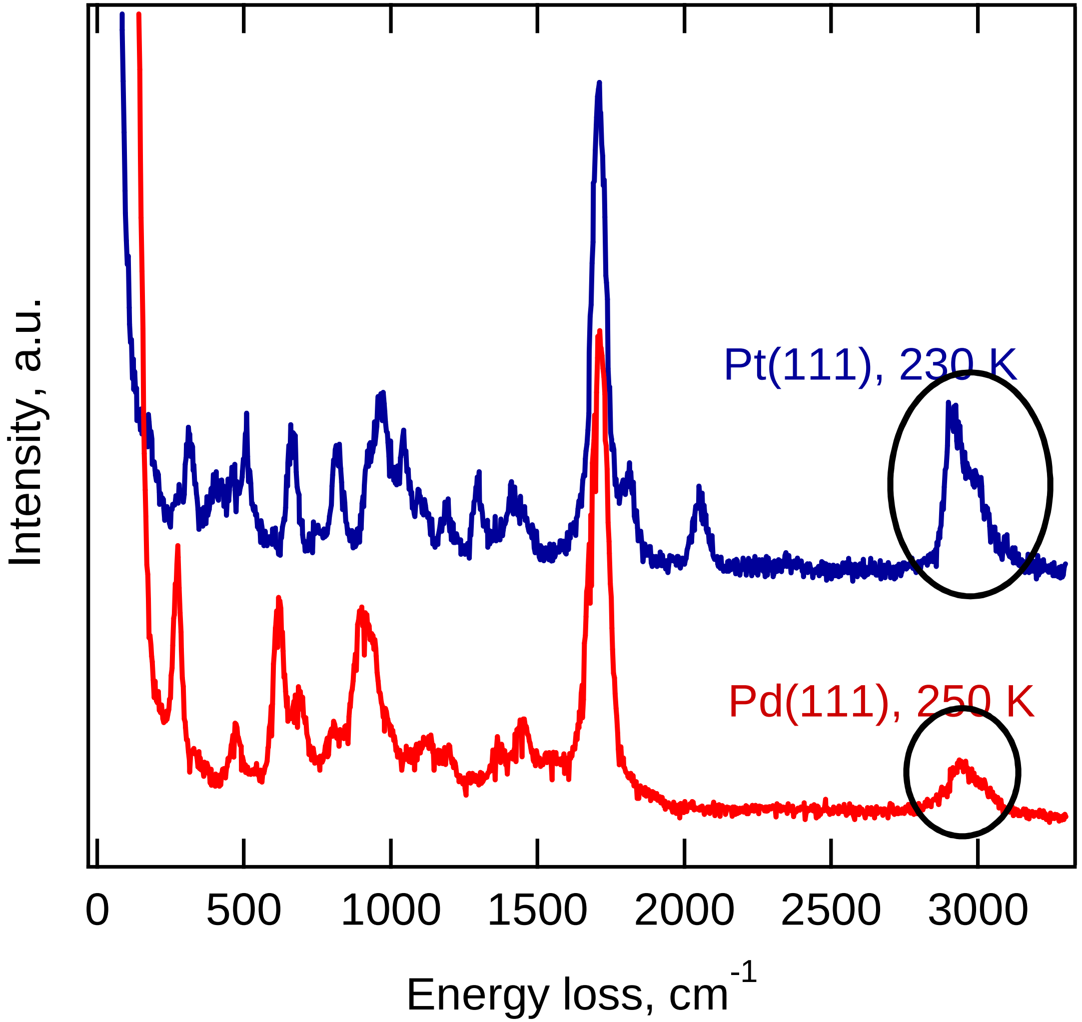
25HF

Got rid of peak labels. Now identify major modes (C=O, C-H, etc). OK, sounds great.

This cartoon could be improved – C=O closer to parallel



HREEL spectra show clear differences between ring-opened EpB on Pt vs. Pd (111)



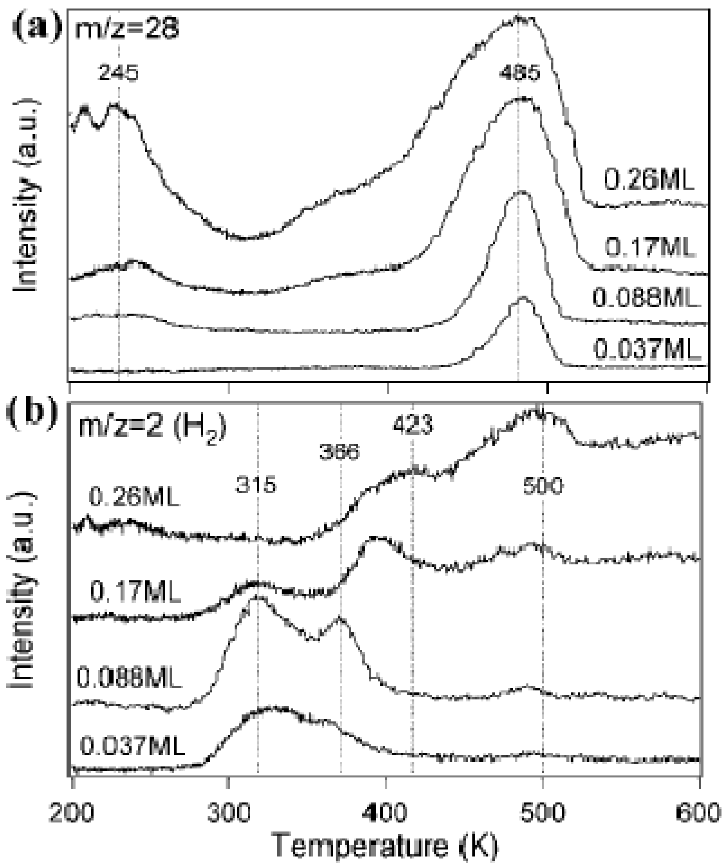
Aldehyde formation and decarbonylation clearly observed on both surfaces….

… but intermediate on Pd(111) is likely to be more dehydrogenated

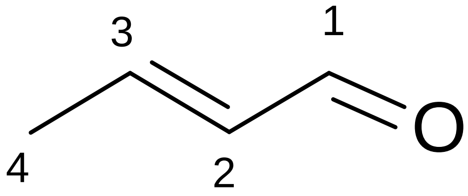
Loh, Davis, Medlin, **JACS** (2008)

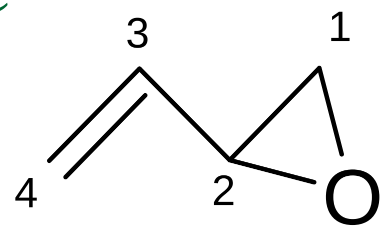
TPD results for EpB on Pd(111)

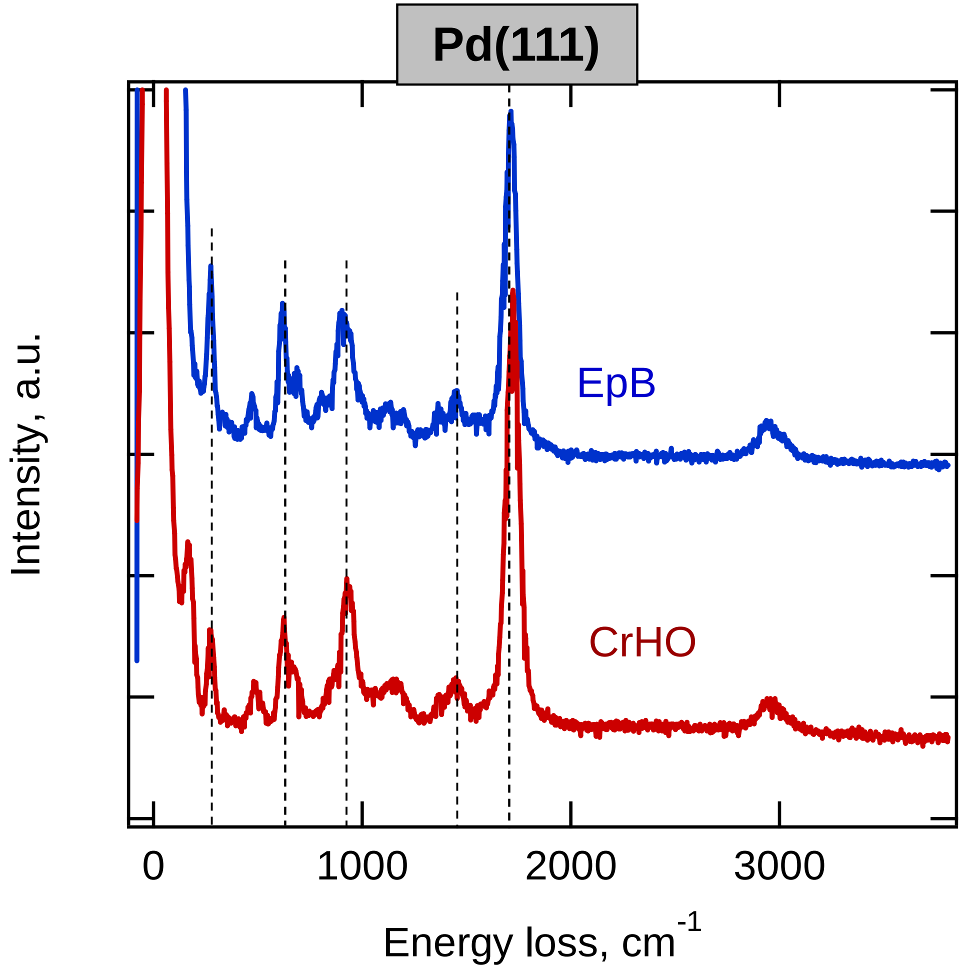
- H_2 desorption becomes more activated at higher coverage (harder for C-H scission to occur as surface gets more crowded)

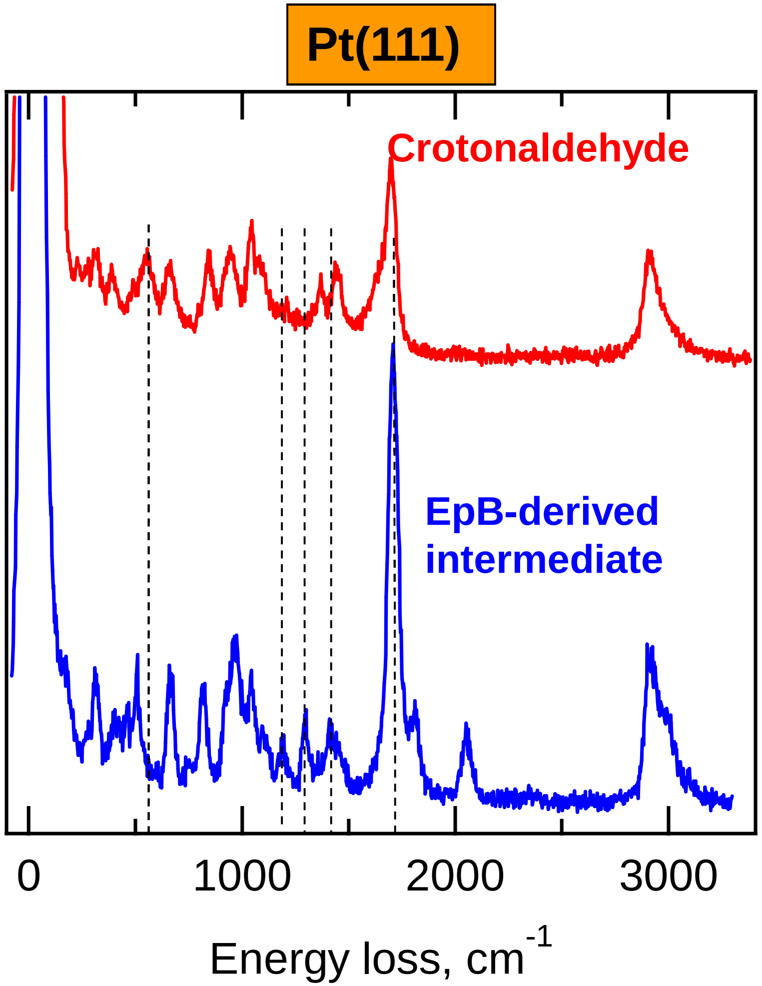


Compare EpB and Crotonaldehyde





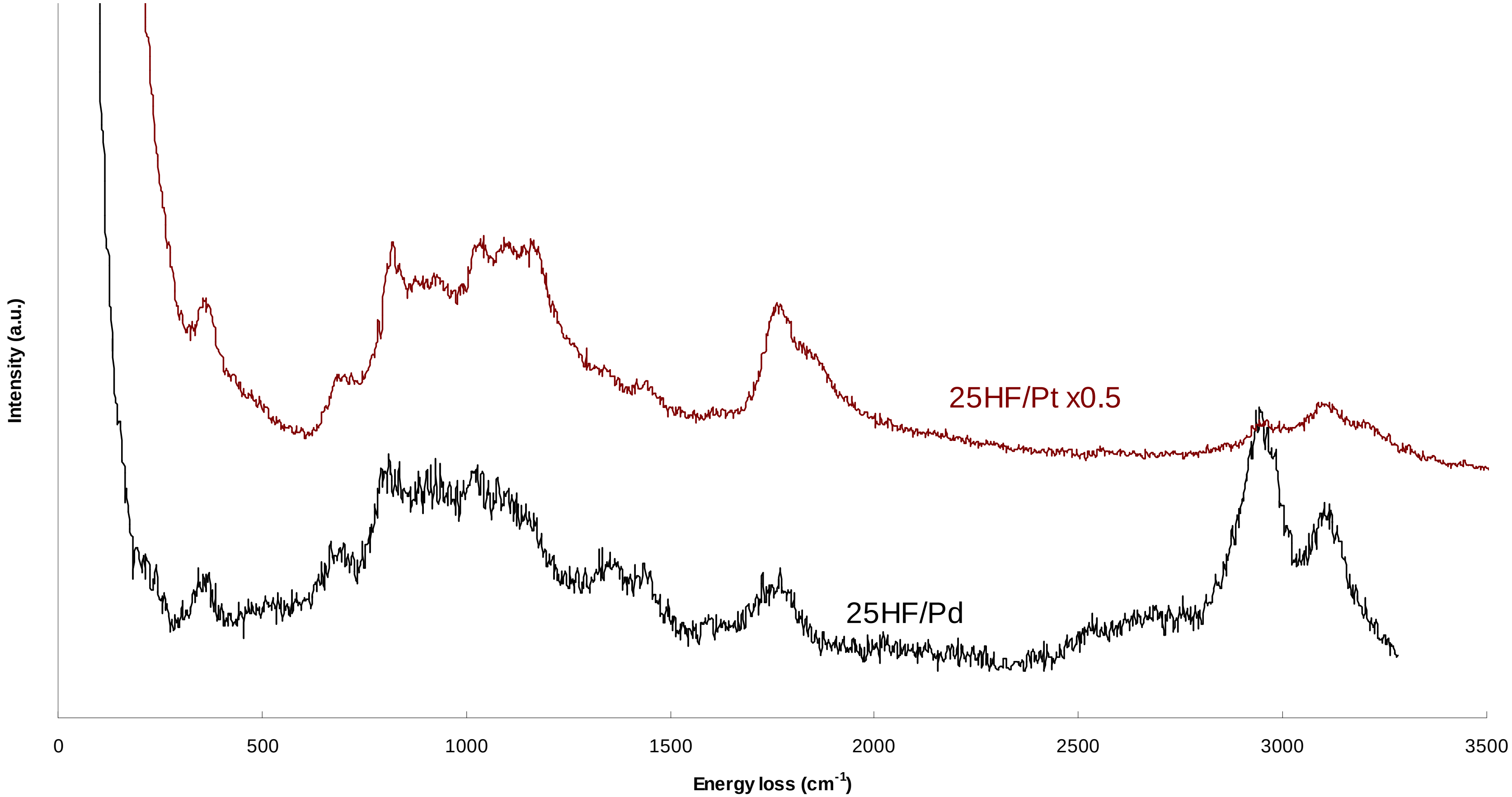




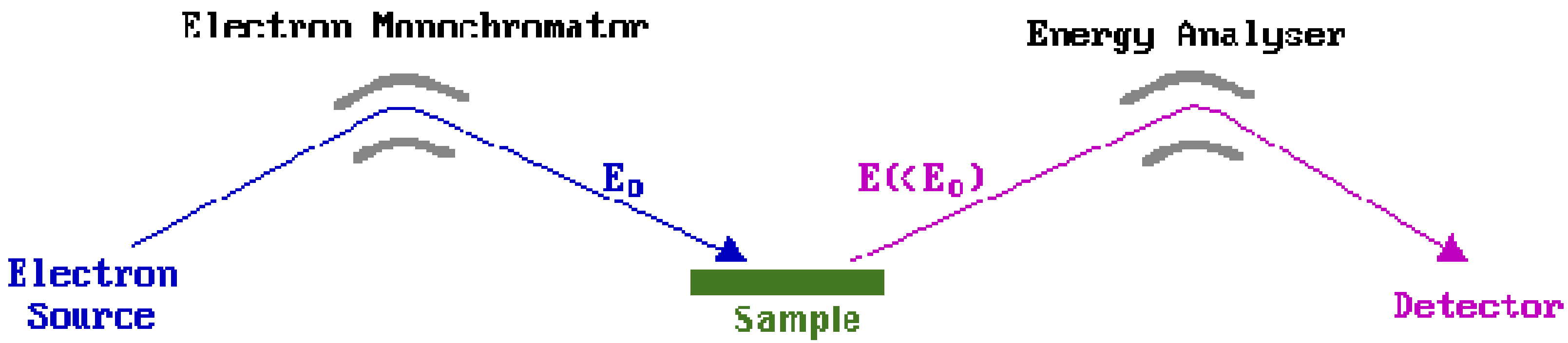
Virtually identical on Pd(111).

Similar but not identical on Pt(111).

25HF multilayers on Pd and Pt



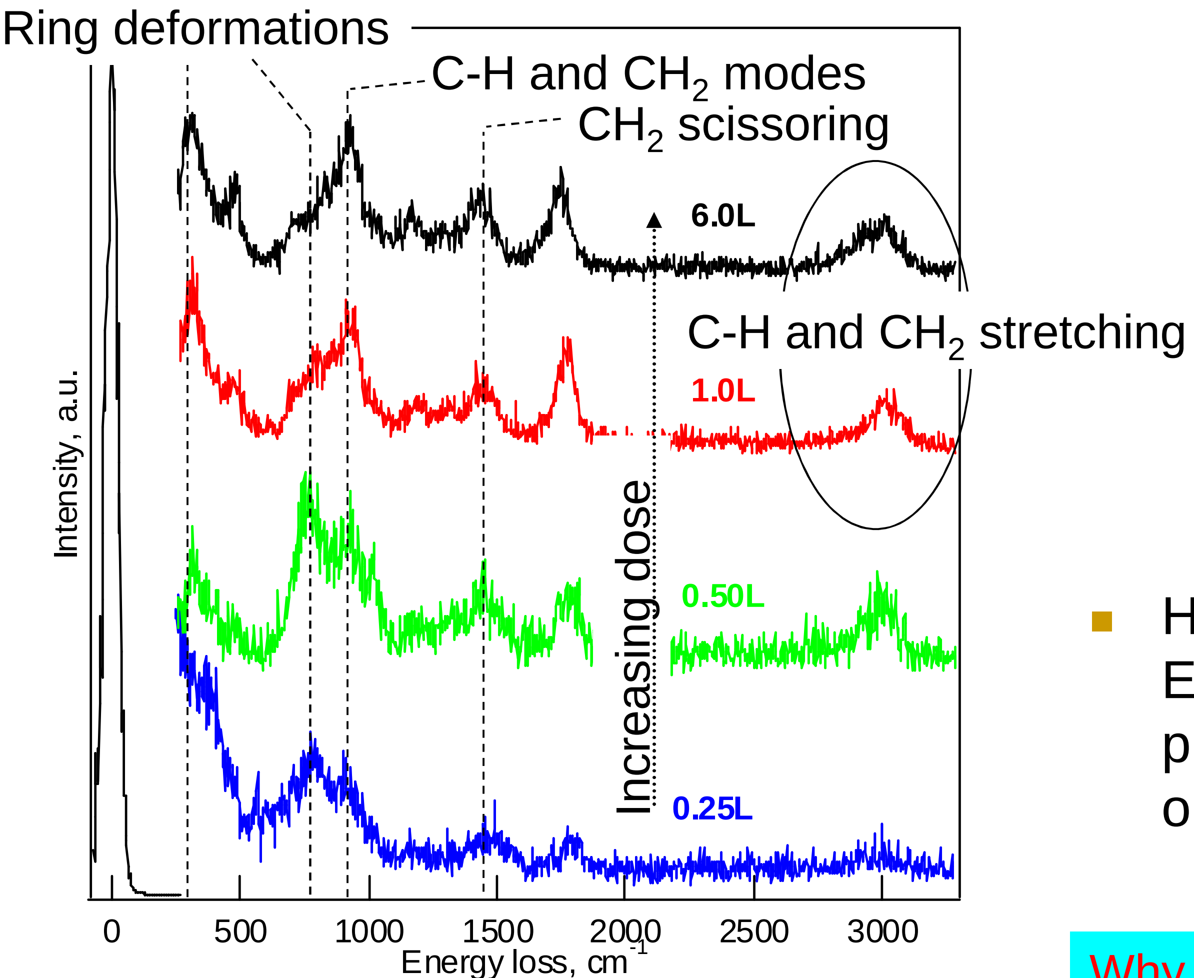
How HREELS works

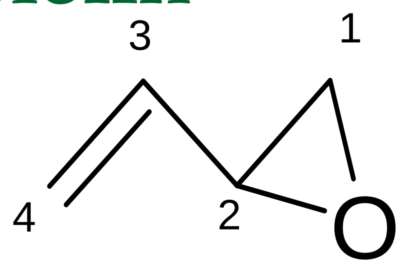


Selection Rules

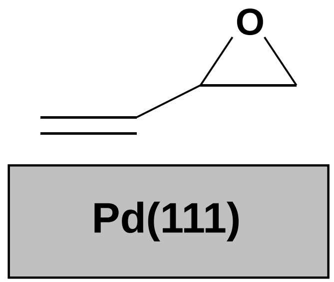
- Long-range dipole scattering and short-range impact scattering
- Dipole scattering:
  - ~3 nm
  - Electric field of moving electron interacts with scatterer; electron acts as a wave
  - Electrons are reflected specularly
- Impact scattering:
  - ~0.2 nm
  - Electron exchanges momentum with scatterer; electron acts as a particle
  - Electrons are reflected diffusely

EpB on Pd(111) adsorbs through olefin functional group





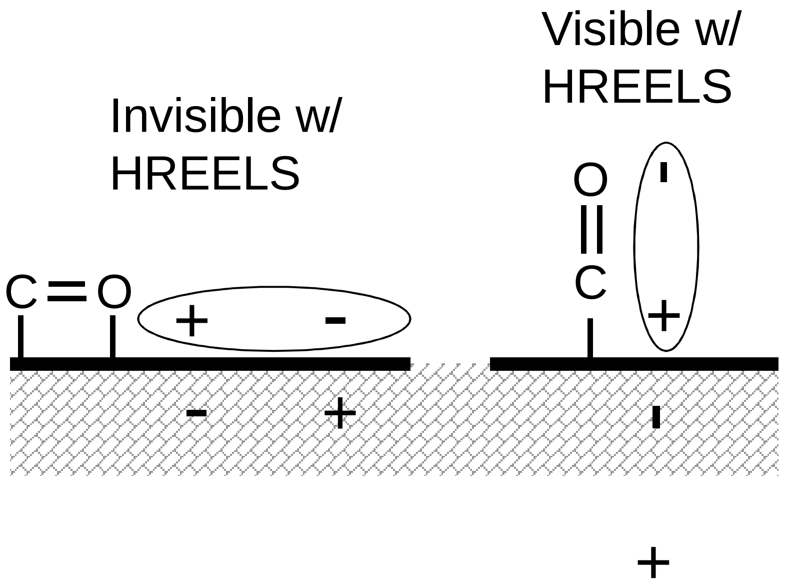
EpB

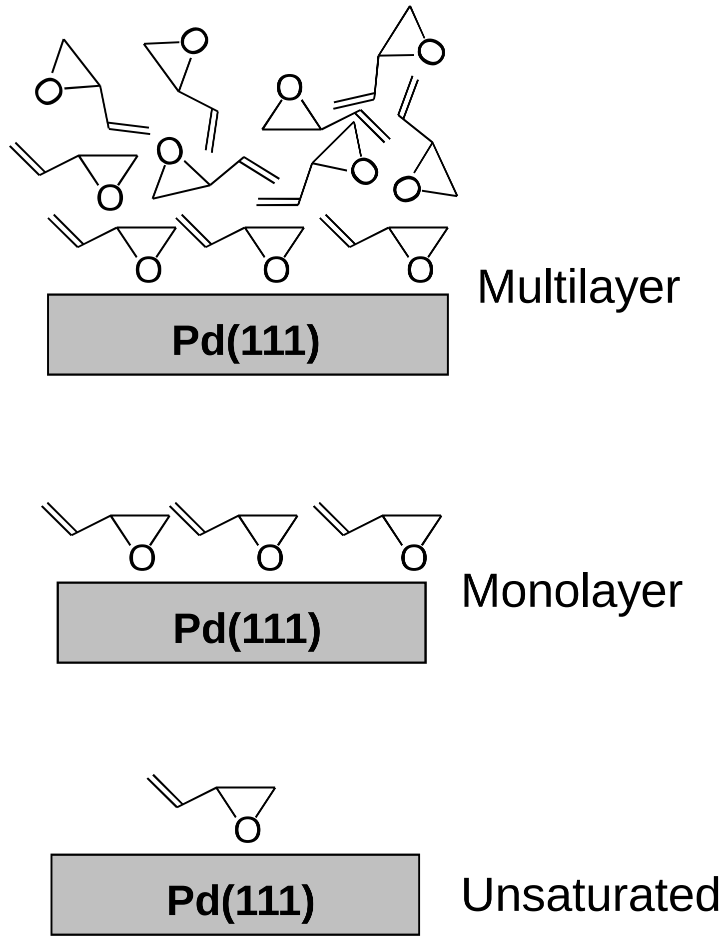


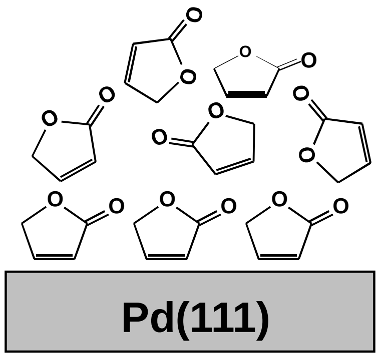
- HREELS indicates EpB is bound preferentially through olefin group

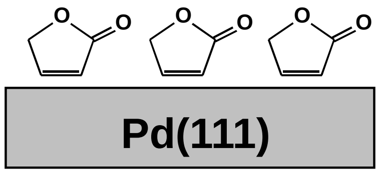
Why don't I see a C=C at high coverage? And why is there a C=O stretch?

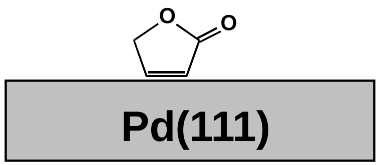
Illustration of HREELS vibrational modes and multilayer formation






Pd(111)


Pd(111)


Pd(111)