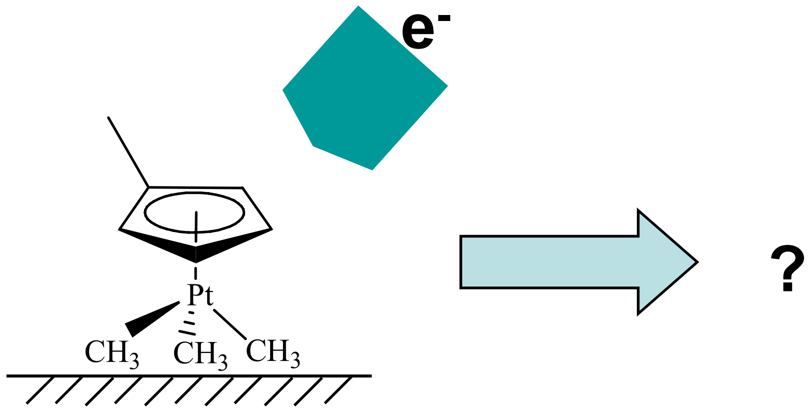
Low Energy Electron Induced Decomposition of Adsorbed Methylcyclopentadienylplatinum(IV)-trimethyl



American Vacuum Society 55th Annual Meeting
Boston, Massachusetts

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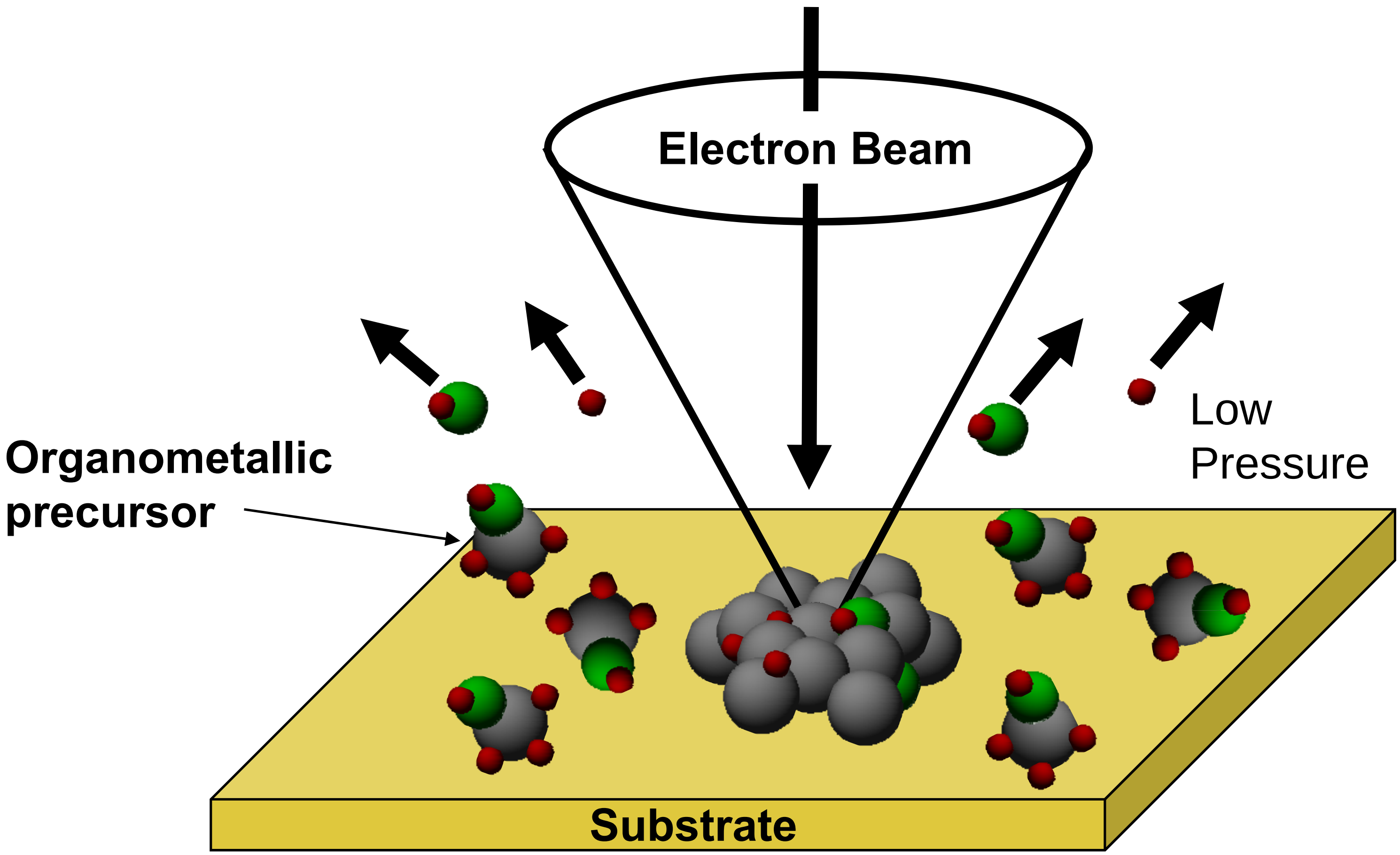
Baltimore, MD, USA

Outline

- Background / Motivation
- Experimental Approach
- Surface Chemistry and Kinetics
- Summary

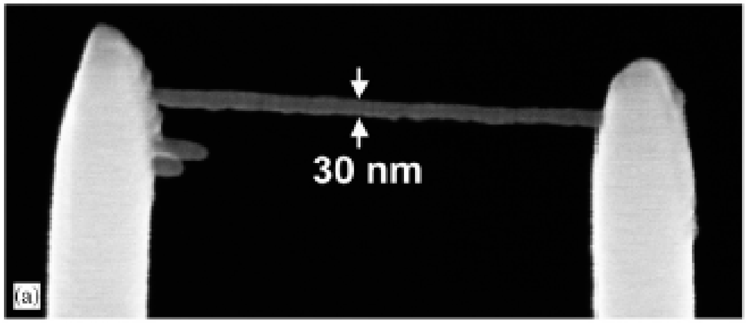
Electron Beam Induced Deposition



The ability to focus electron beams into small spots, control electron beam fluence and raster the beam makes EBID an ideal method for growing a wealth of different nanostructures

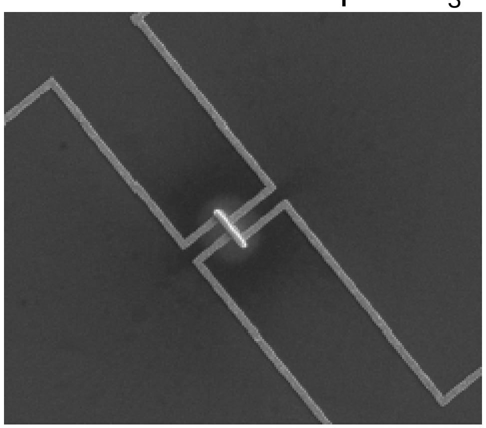
Examples of EBID

Freestanding Pt wire grown from $MeCpPtMe_3$



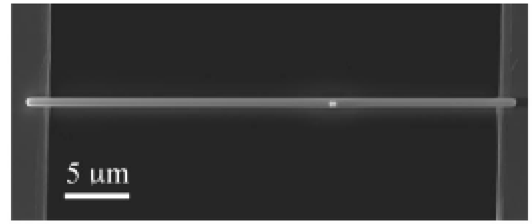
Frabboni et al., *Physica E*, **2007**, 265.

Pt wire, 4μm long, grown between Au electrodes on Si / SiO_2 substrate from $MeCpPtMe_3$



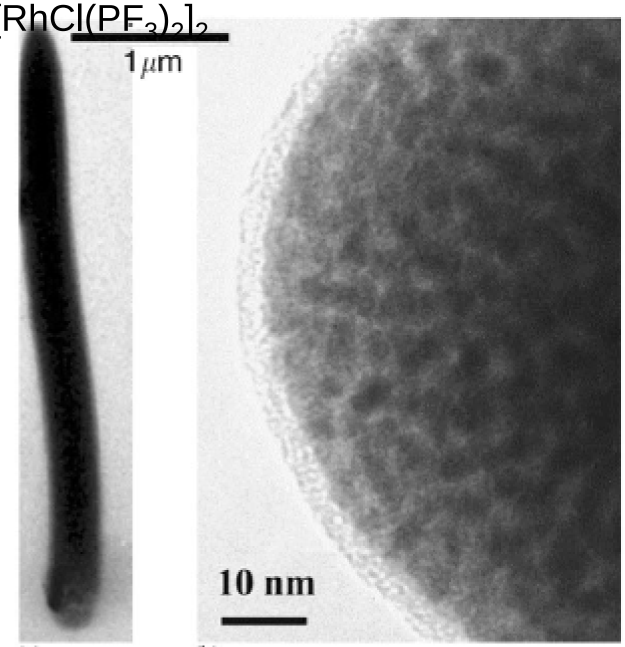
Botman et al., *Nanotechnology*, **2006**, 3779.

Pt wire grown on SiO_2 from $MeCpPtMe_3$



Gopal et al., *Appl. Phys. Lett.,* **2005,** 49.

Rh grown on graphite from $[RhCl(PF_3)_2]_2$



Cicoira et al., *J. Cryst. Growth*, **2004**, 619.

Motivation

The fundamental surface processes that are responsible for electron beam induced deposition of nanostructures are not well understood

↓

- Many questions about EBID process
  - Chemical reactions at the surface?

- If we can better understand the chemistry, we can:
  - Choose precursors more selectively
  - Improve deposition purity (carbon)
  - Improve purification techniques
  - Increase metallic characteristics

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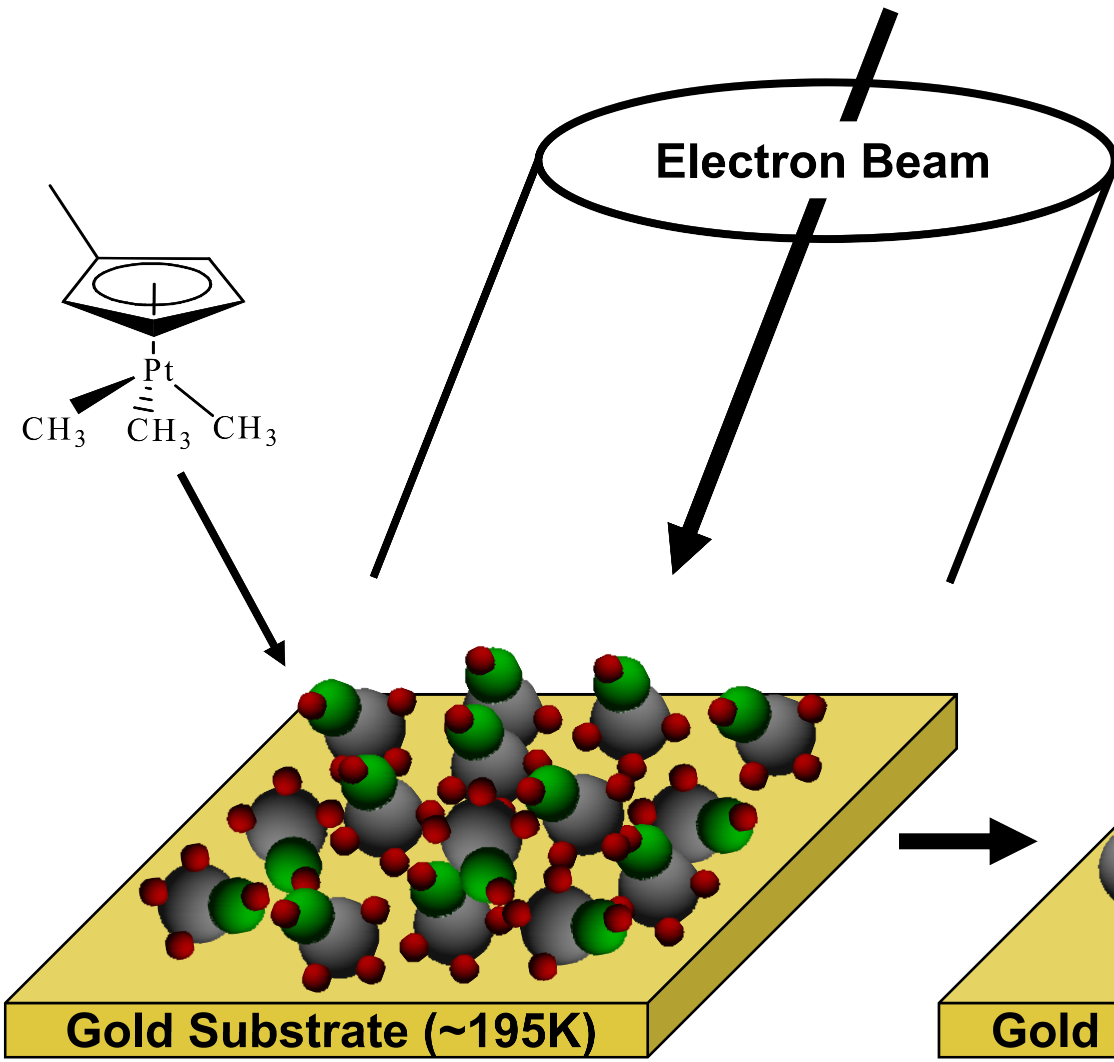
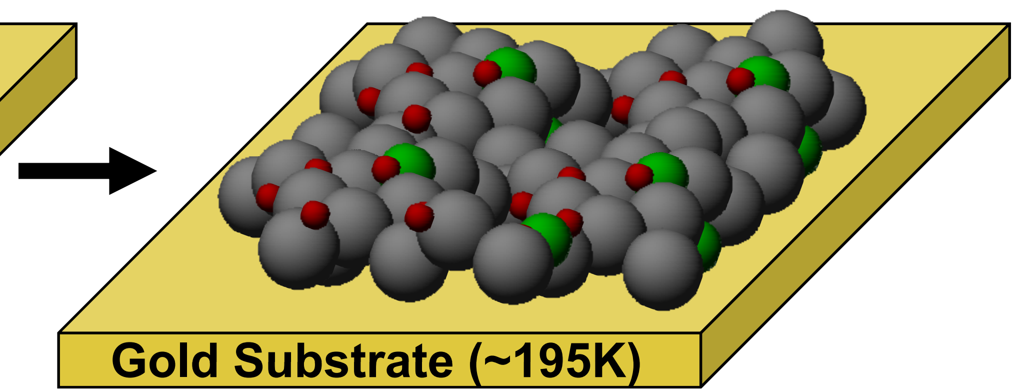
- Experimental Approach
- Surface Chemistry and Kinetics (500eV)
- Summary

Our Approach

- To understand the EBID process using well established surface analytical techniques
  - Adsorbing a nanometer scale film of EBID precursor to a substrate provides a “clean” environment for *in situ* observation
  - Surface coverage can be controlled
  - An UHV environment enables analysis of gas phase products
  - A film, on the order of cm^2 in area, can be analyzed using common surface analytical techniques

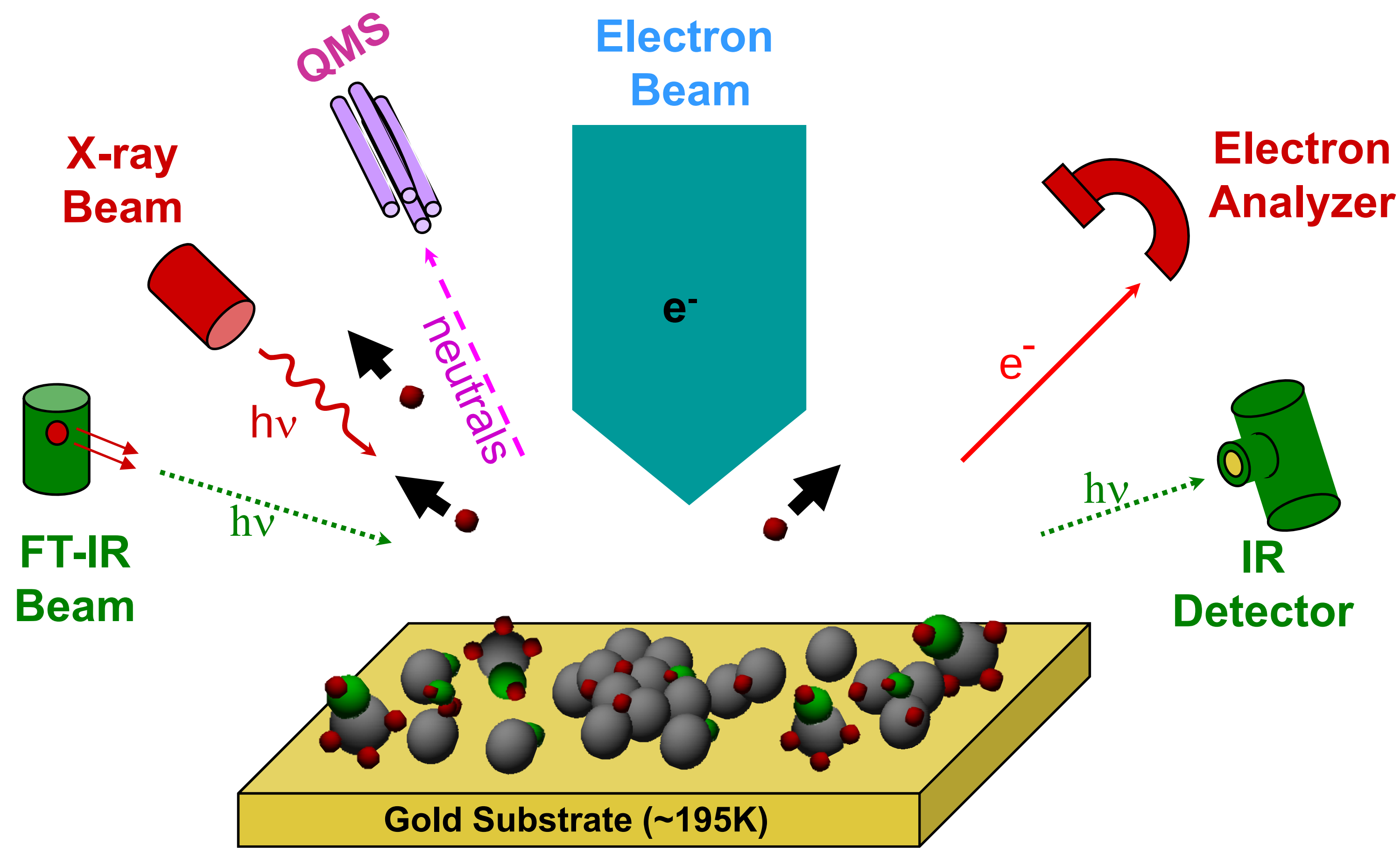
Broad Beam Surface Irradiation





Production of a film over a large surface area enables traditional surface analytical techniques to probe the EBID process

Instrumental Techniques



- We have studied the electron stimulated reactions of the well-known Pt precursor, Trimethyl(methylcyclopentadienyl)-platinum(IV), adsorbed onto gold using the above techniques:

Outline

- Background / Motivation
- Experimental Approach
- Surface Chemistry and Kinetics (fixed electron energy = 500eV)
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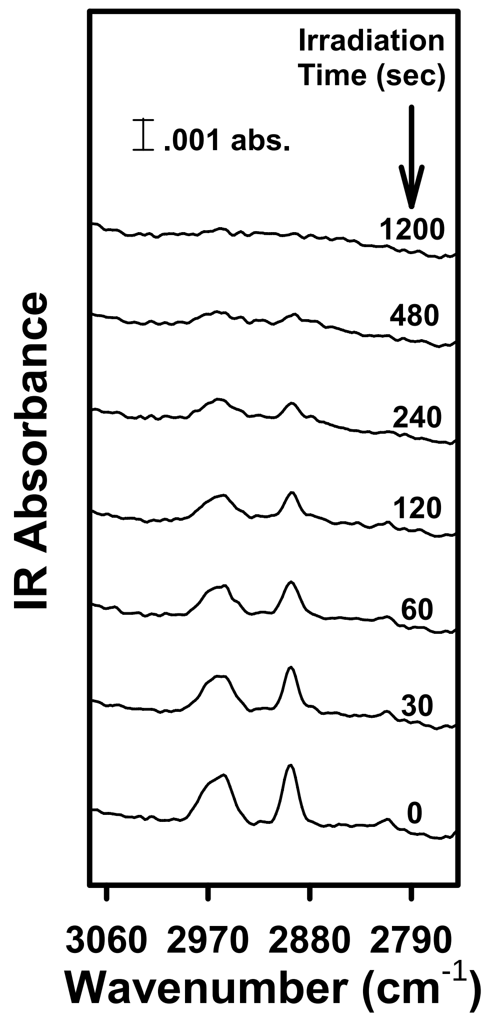
RAIRS Analysis of Dissociation Kinetics

- Time resolved *in situ* RAIRS analysis shows loss of ν(C-H) intensity with increasing electron beam irradiation

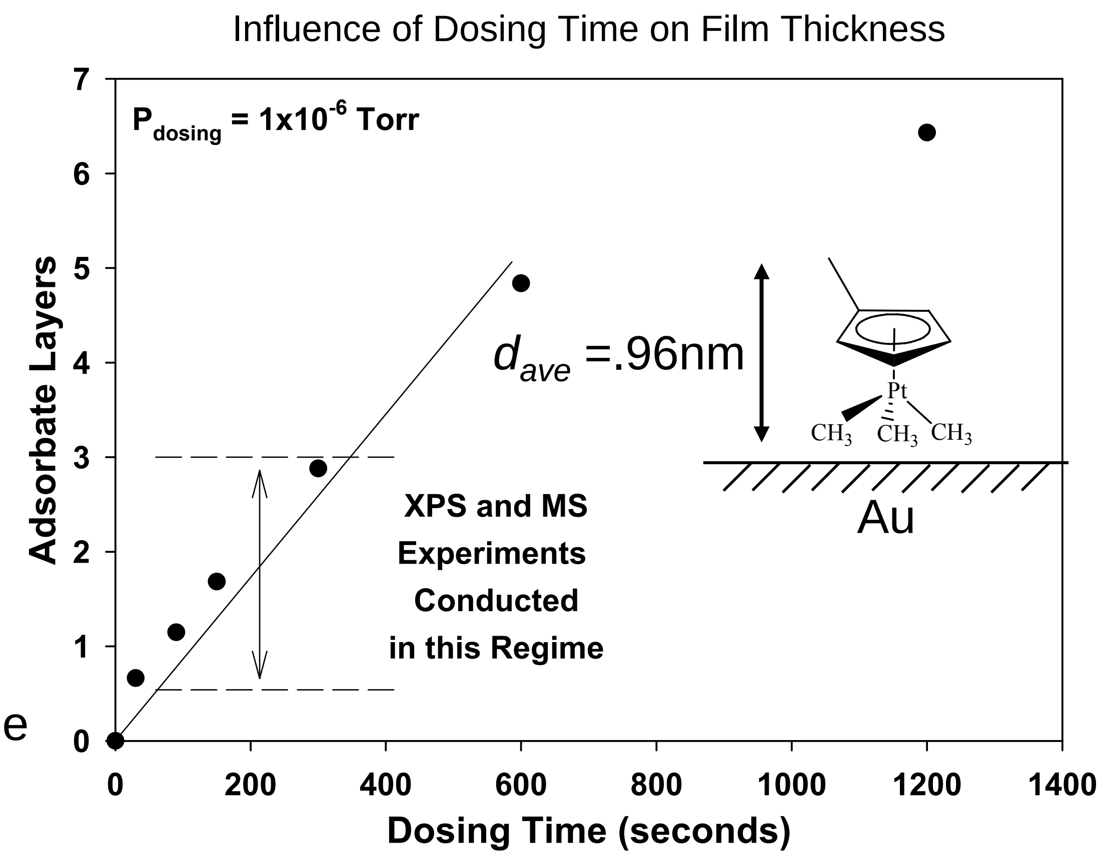


Adsorption of MeCpPt(IV)Me$_3$ onto Gold Substrate – Controlling film thickness

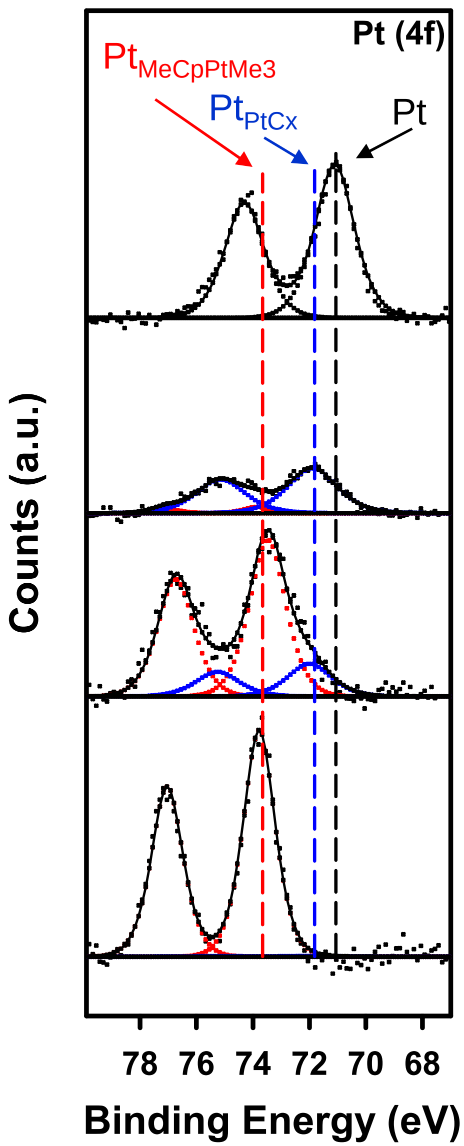
Film thickness, *d*, calculated from attenuation of Au(4f) signal

$$d = \lambda * \cos(\theta) * \ln(\frac{I}{I_0})$$

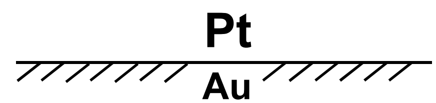
d = adsorbate thickness
λ = ~2nm for Au(4f) photoelectron
θ = 54° photoelectron take-off angle
I = Au(4f) area



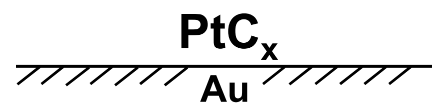
Production of Amorphous Platinum/Carbon Film



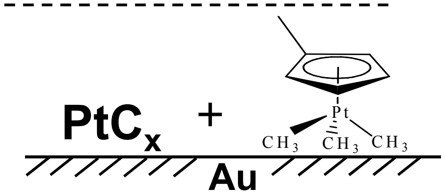
XP spectra of sputter deposited platinum on gold



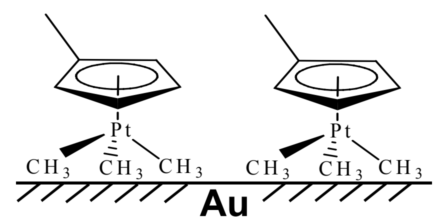
Substrate heated to room temperature leaving electron beam irradiation product



Electron beam irradiation for 20 sec (20μA, 500eV)



MeCpPt(IV)Me$_3$ adsorbed onto gold substrate (~195K)

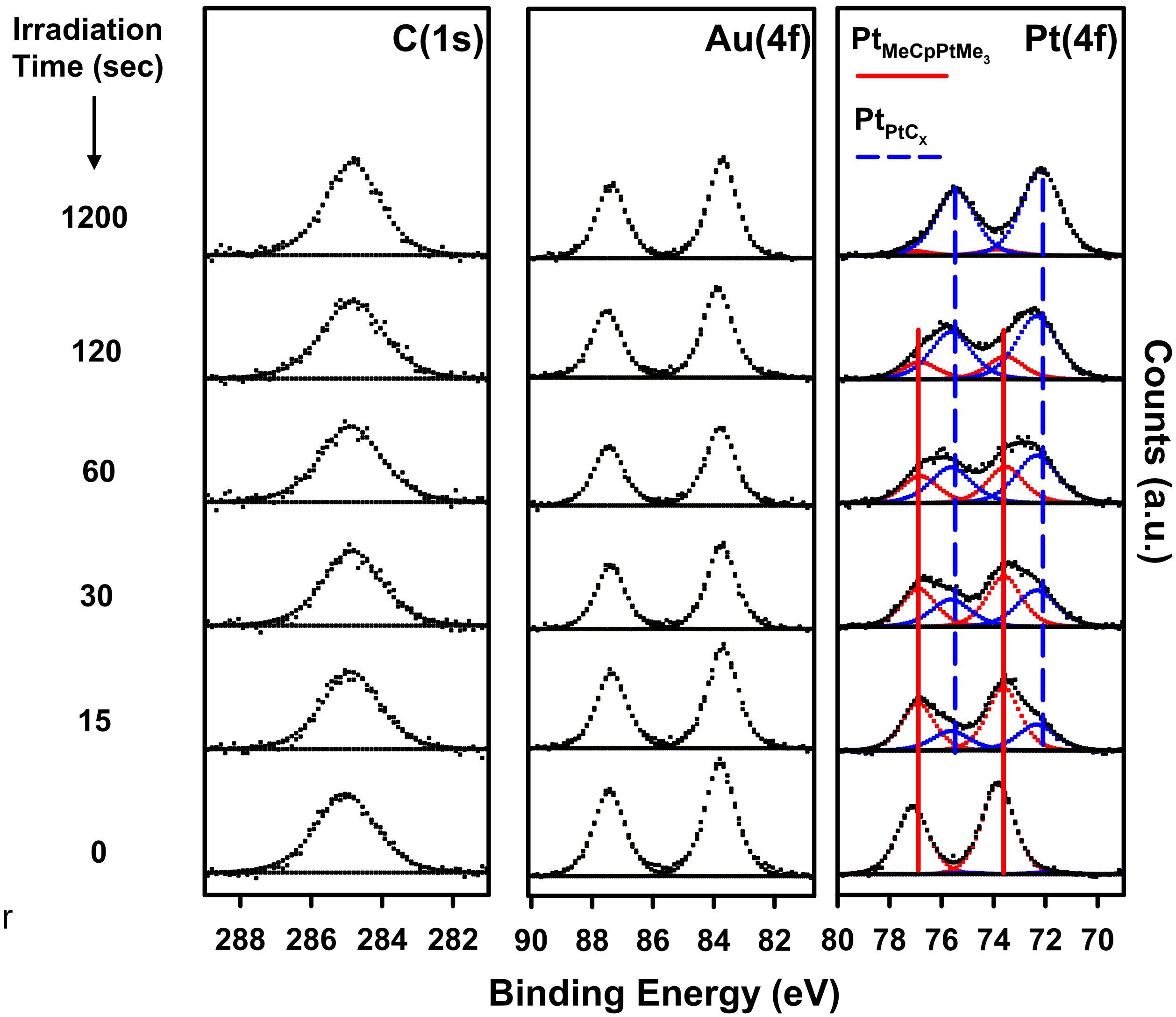


Influence of e⁻ Beam Irradiation on Surface Composition of Adsorbate Layer

The XP spectra of the C(1s), Au(4f), and Pt(4f) regions shows:

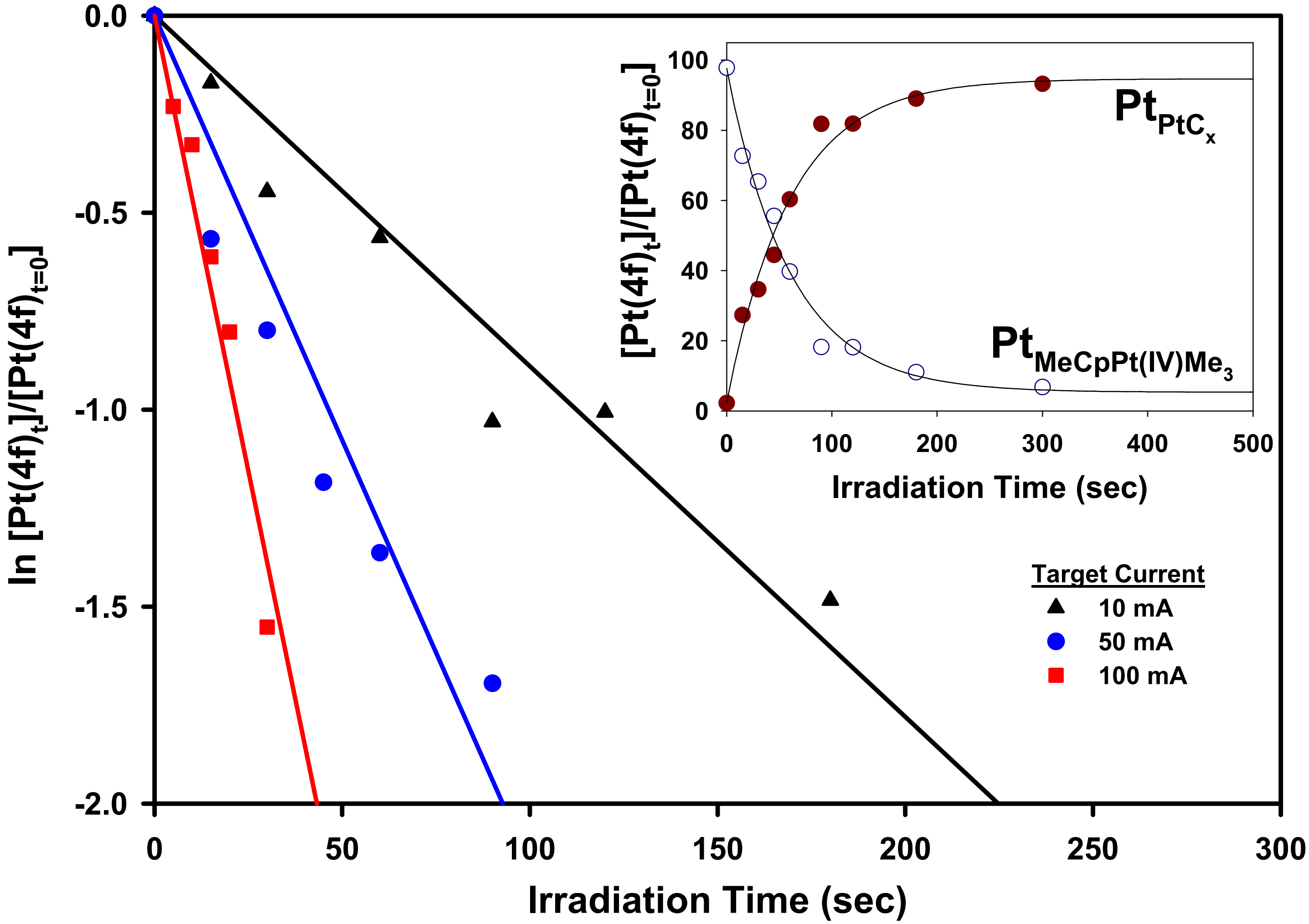
•No loss of platinum from surface

•Shift in platinum environment from precursor to product



$MeCpPt(IV)Me_3$ is stable under x-ray irradiation for >2hrs

XPS Analysis of Dissociation Kinetics



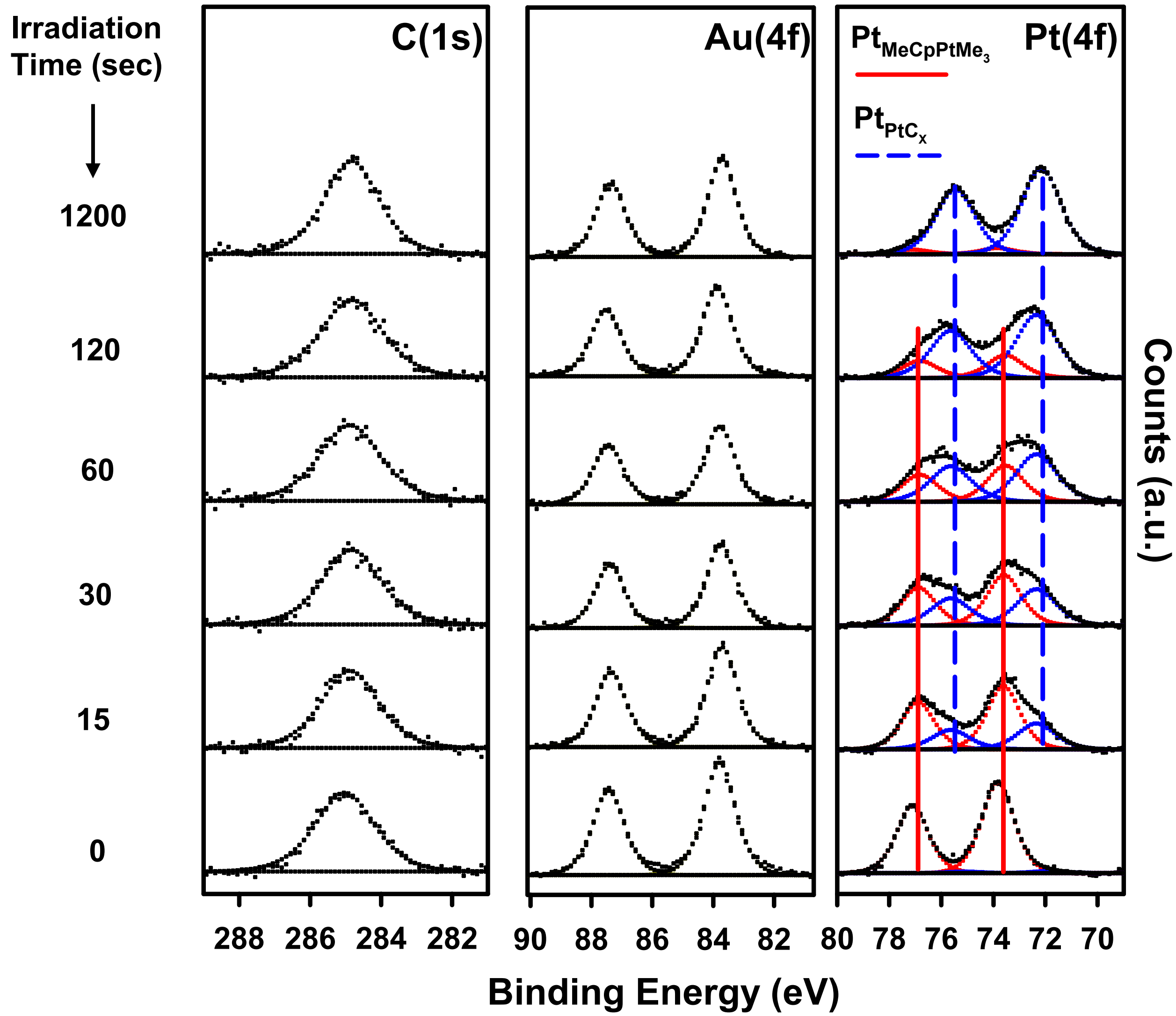
Quantification of the deconvoluted Pt(4f) region fit to exponential decay shows first order kinetics

Decay profiles show that the observed rate constant increases with increasing target current.

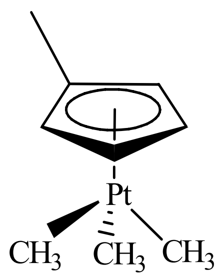
Signal Resolution vs. Signal Intensity

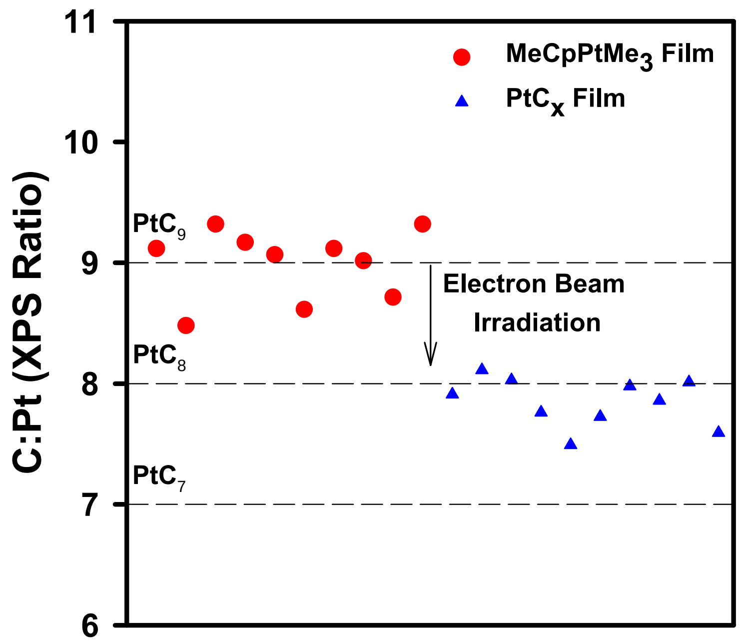
•High resolution / low intensity emphasizes elemental <u>environment</u>

•22eV Pass Energy



Carbon Loss During Irradiation

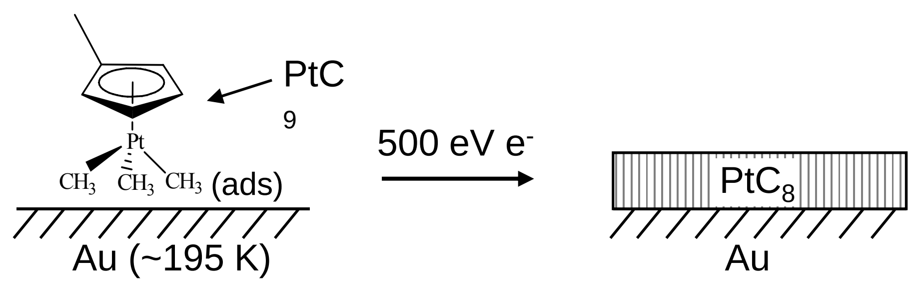




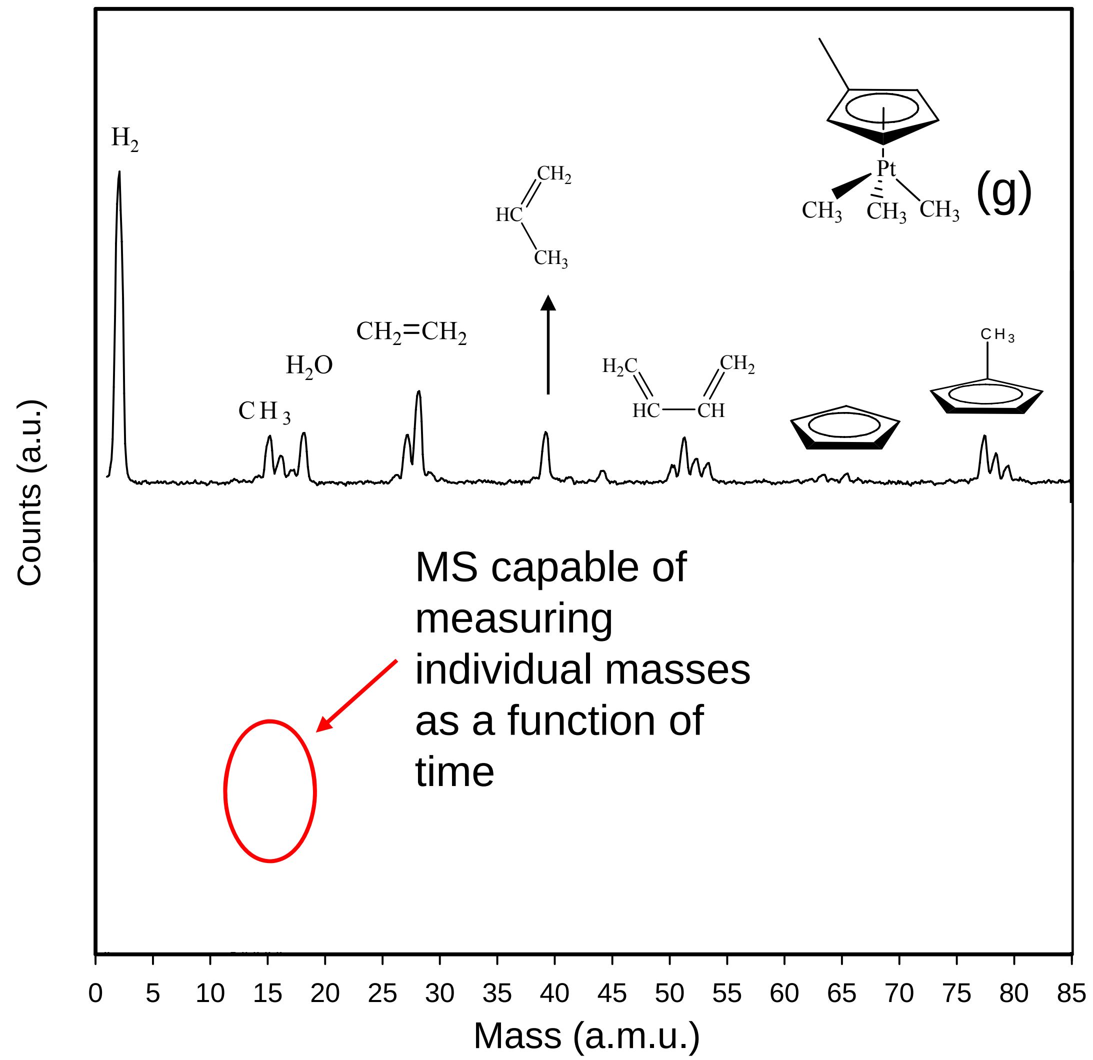
• The C:Pt ratio of 10 XP spectra of the MeCpPt(IV)Me_3 prior to e^- beam irradiation is representative of the initial stoichiometric ratio of 9 carbon atoms to 1 platinum atom

The stoichiometric loss of 1 carbon atom as a result of irradiation is independent of film thickness

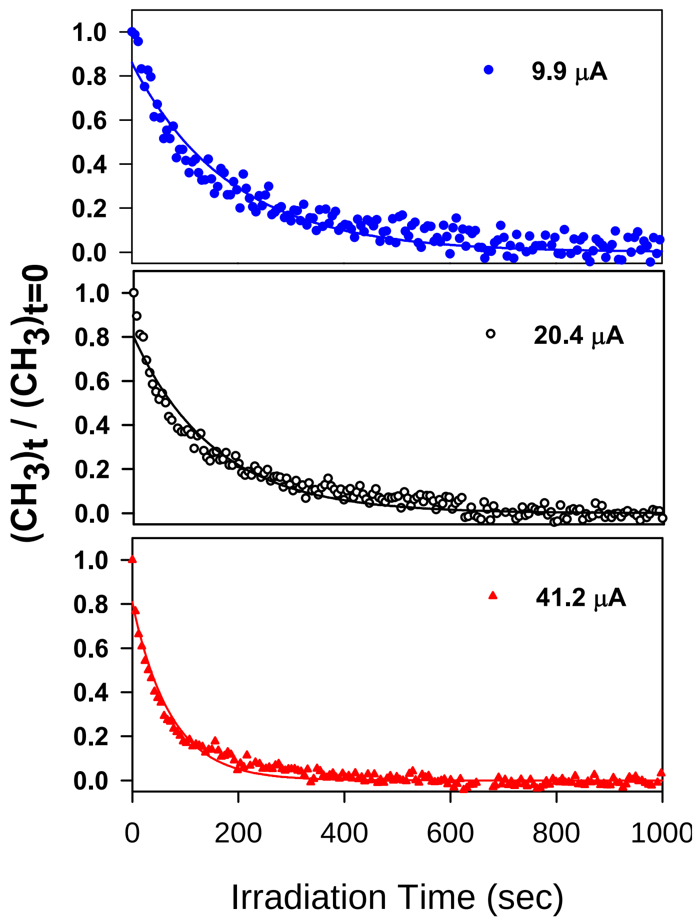
• The C:Pt ratio after e^- beam irradiation decreases to a ratio of 8:1, indicating the loss of 1 carbon atom per molecule as a result of irradiation



Gas Phase Products Analysis



Kinetic Analysis of Methane Production

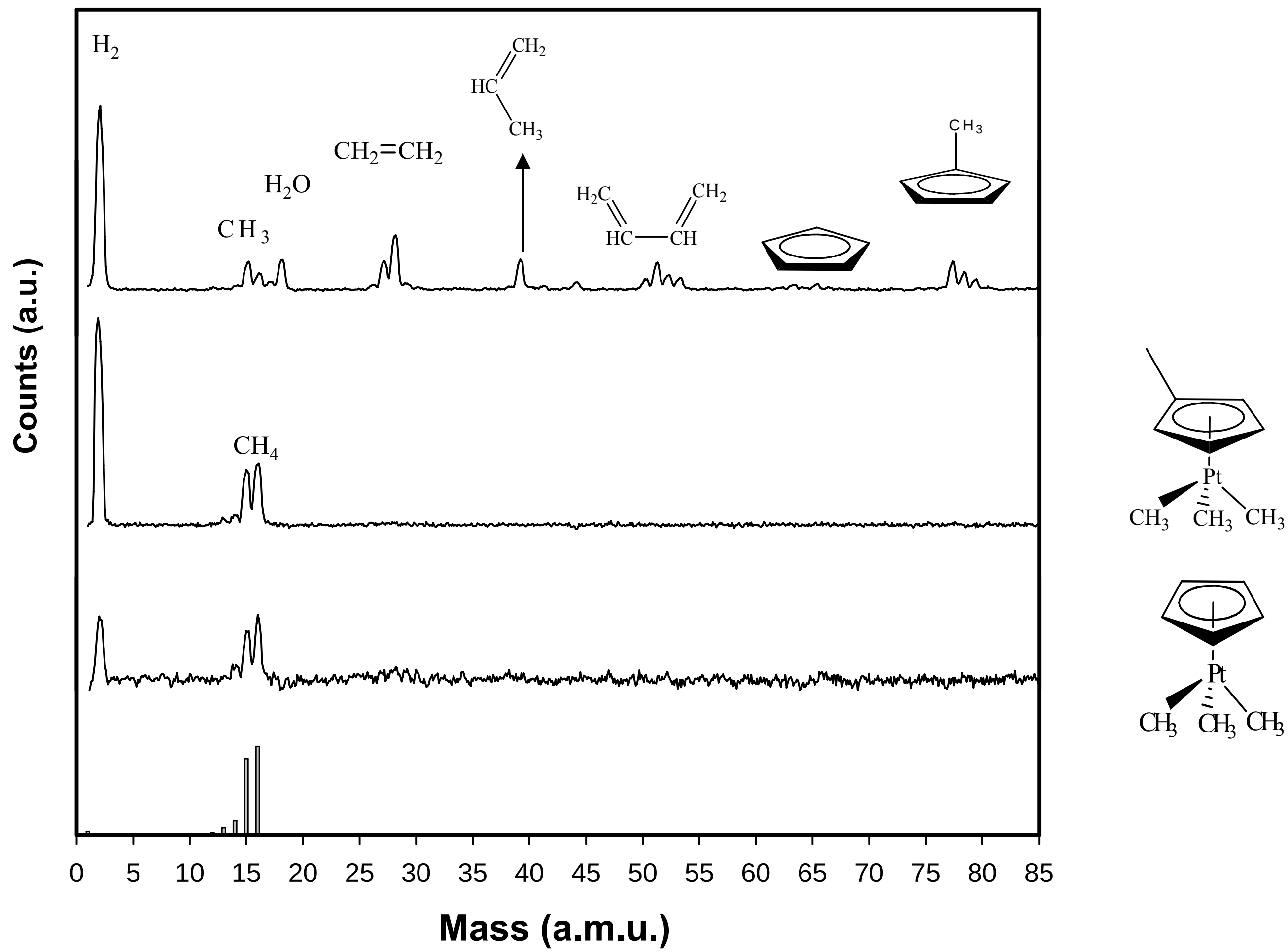


•Tracking methane production during electron beam irradiation fit to exponential decay

•*m/z* = 15 is a unique mass representative of methane

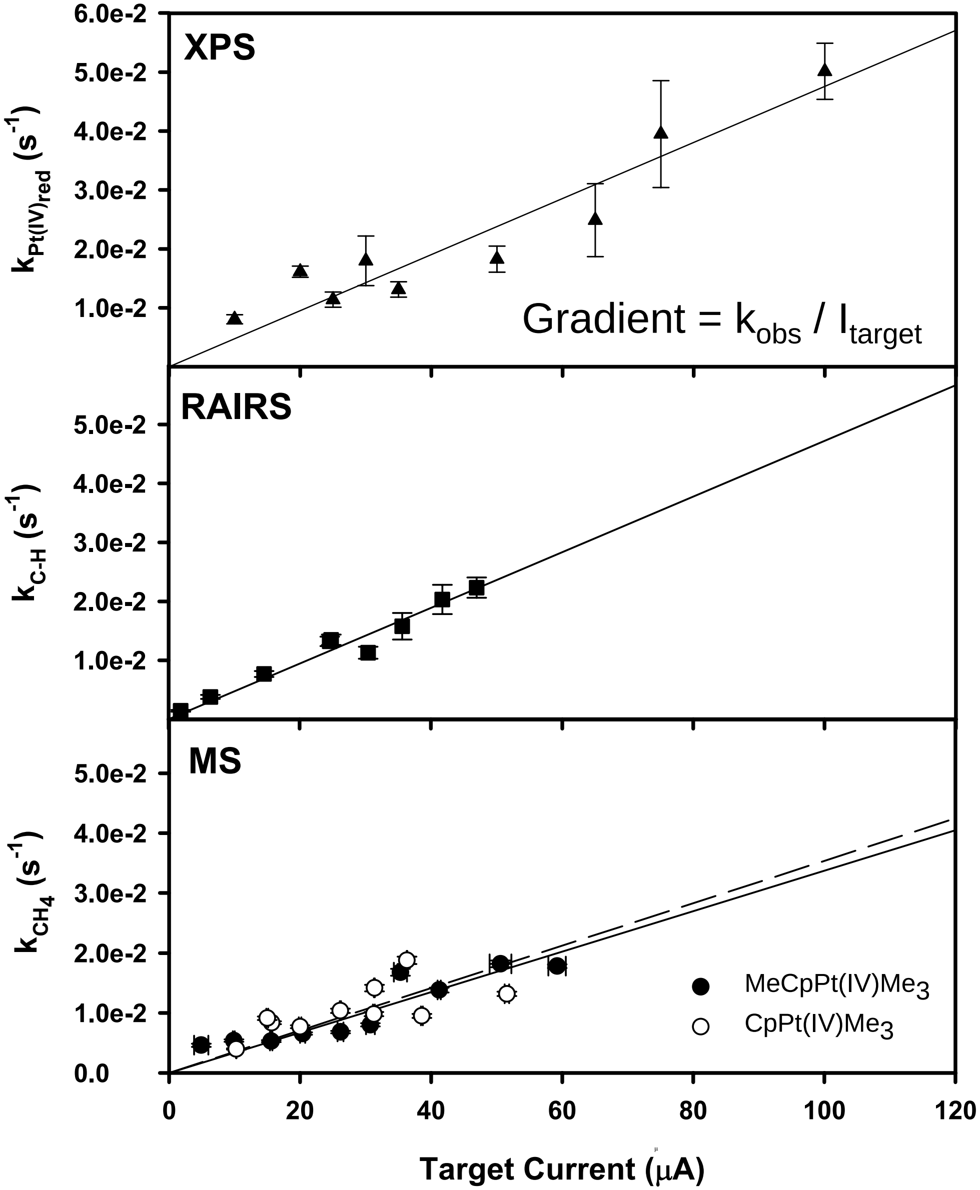
•Methane loss fit to first order kinetics indicates an increase in the observed rate constant with increasing target current

Dissociation by Pt-CH_3 Cleavage



Analogous compound decomposes via production of identical gas phase products

Complementary Techniques



$$\sigma = \frac{k_{obs}}{I_{target}} \times A$$

	(σ) cm²
XPS	1.37E-16
RAIRS	4.32E-16
MS ($MeCpPtMe_3$)	9.75E-17
MS ($CpPtMe_3$)	1.02E-16

$\sigma_{ave,\ 500eV}$ **= 2.2 E-16 cm²**

XPS, RAIRS, and MS provide comparable σ values though they measure different processes

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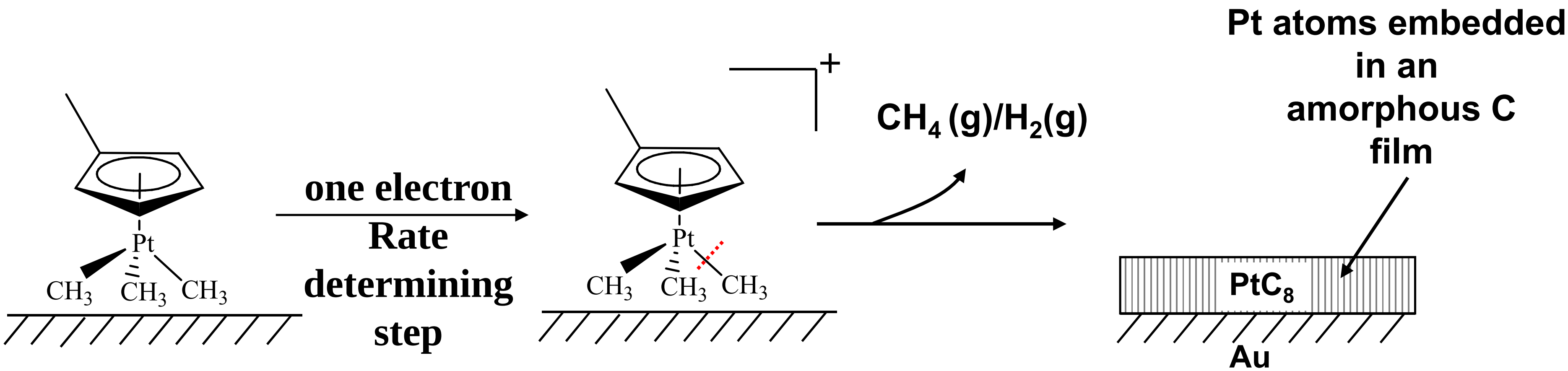
Summary



•Electron beam irradiation of surface adsorbed MeCpPt(IV)Me_3 results in the formation of platinum atoms embedded in an amorphous carbon film via an electron impact process in which bond cleavage releases hydrogen and methane.

•Each precursor molecule that undergoes electron stimulated decomposition losses exactly one carbon atom.

A UHV surface science approach can provided valuable information on reaction rates and fundamental chemical processes involved in EBID

Acknowledgements

- Howard Fairbrother, Johns Hopkins University
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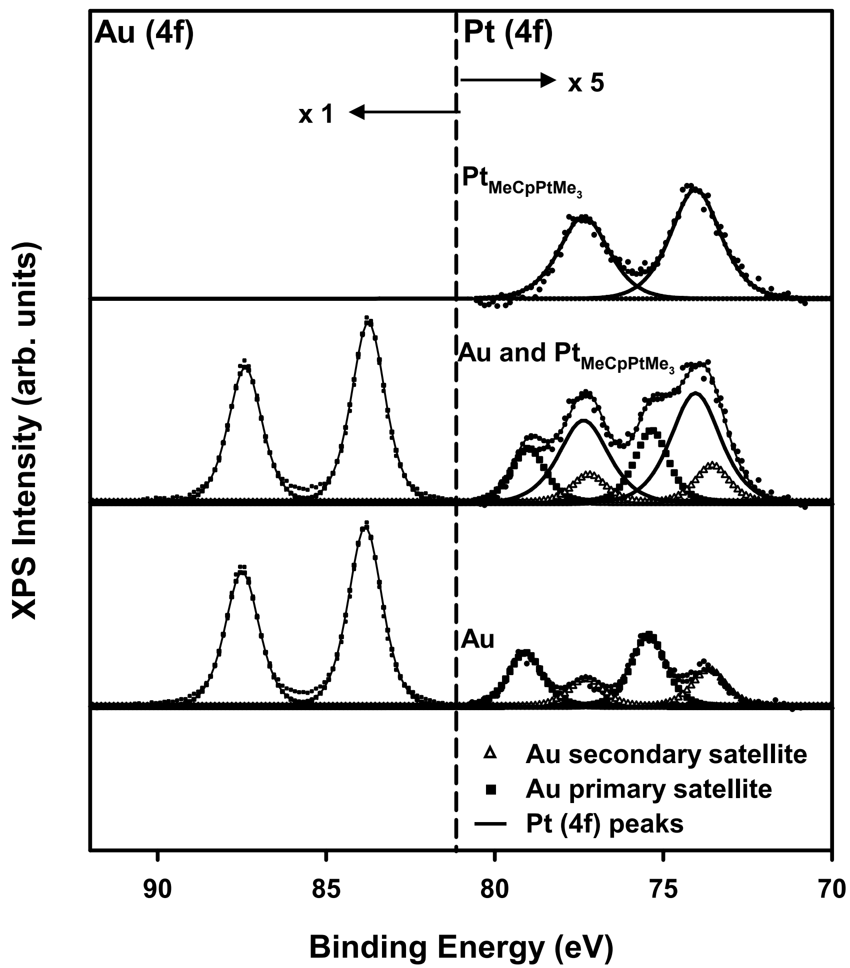
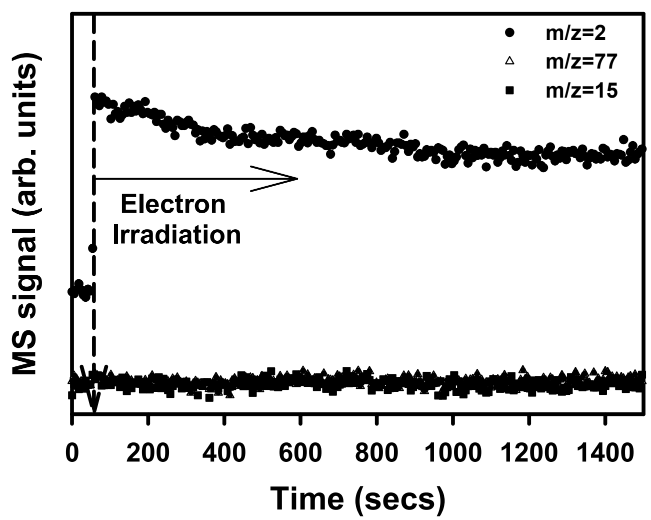
- Ted Madey, Rutgers University
- Kees Hagen, Delft University of Technology

Thank you

Solution to Au satellites

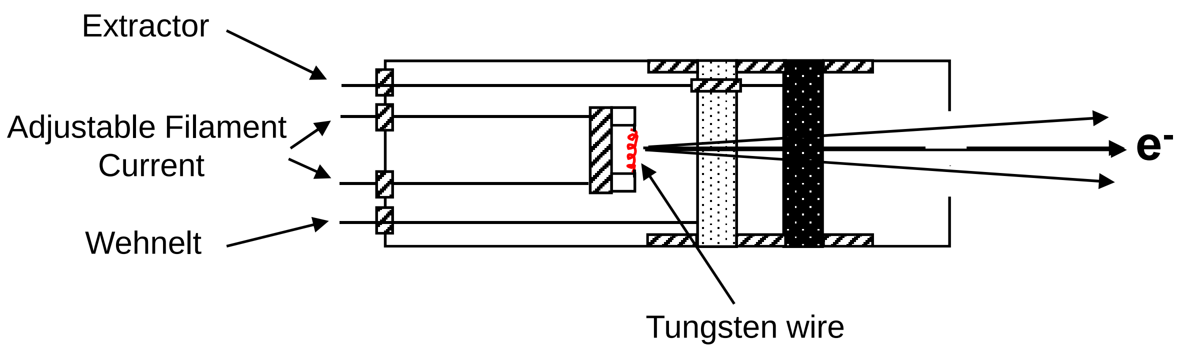




m/z=2
m/z=77
m/z=15
Electron
Irradiation
MS signal (arb. units)
0
200
400
600
800
1000
1200
1400
Time (secs)

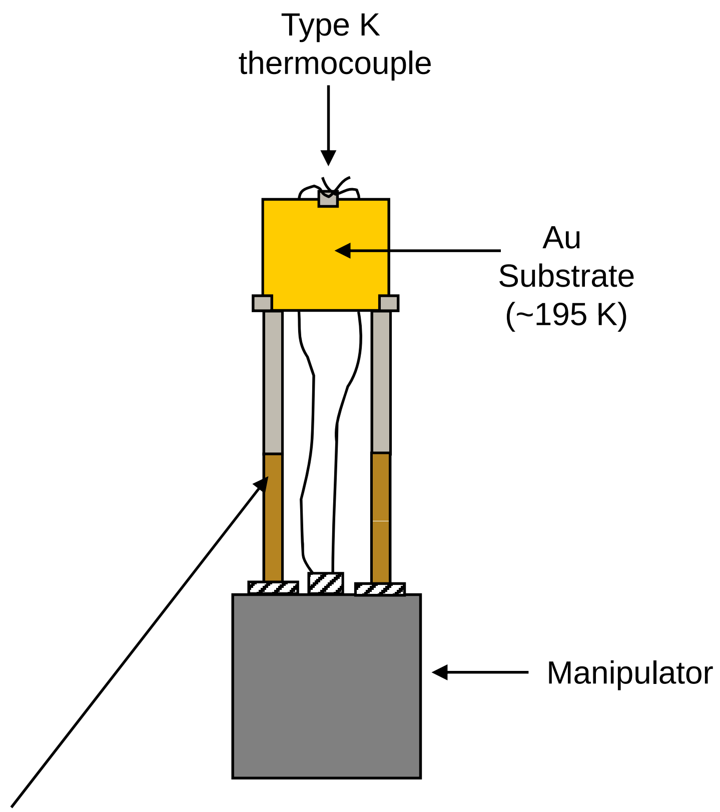
Electron Source: Flood Gun

- Why use a flood gun?
  - Uniform electron beam over a wide area (necessary for XPS and RAIRS)
  - High target current
  - Relatively broad range of Energies (40 – 500eV)



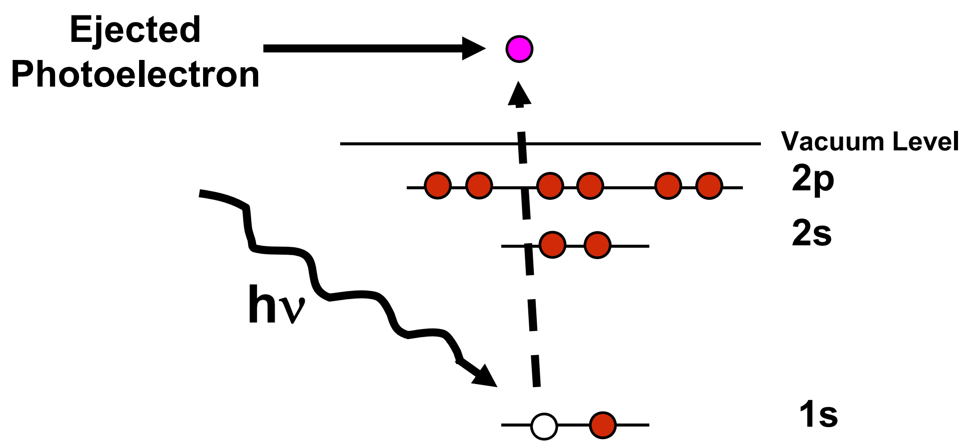
Electron Flood Gun can produce:
(a) 40 - 500 eV electrons
(b) 5 -150 μA target currents

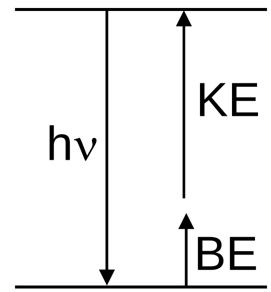
Sample



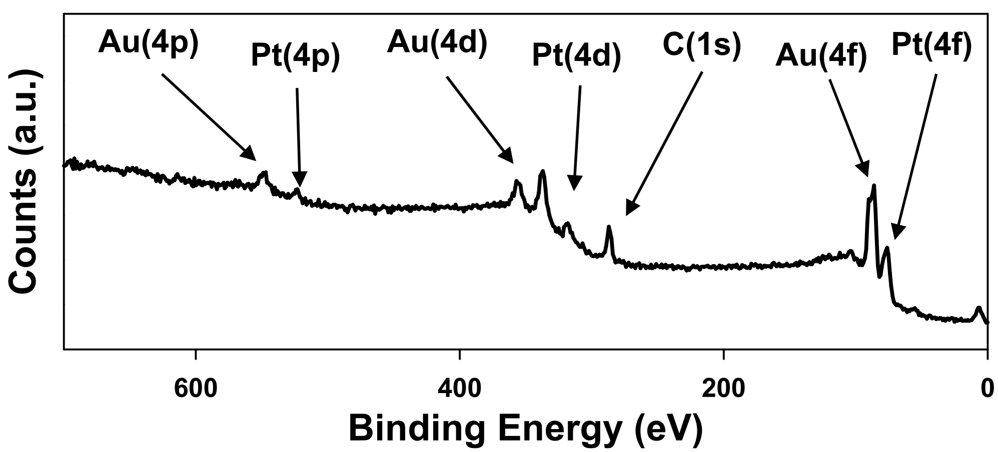
Cu leads provide for heating and cooling
(100K-450K)

X-ray Photoelectron Spectroscopy (XPS)

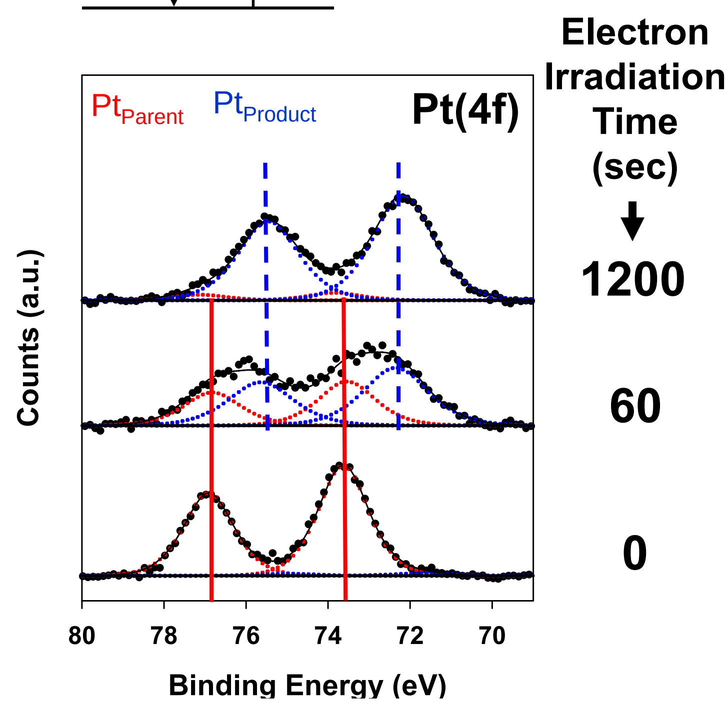




$$BE = h\nu - KE$$

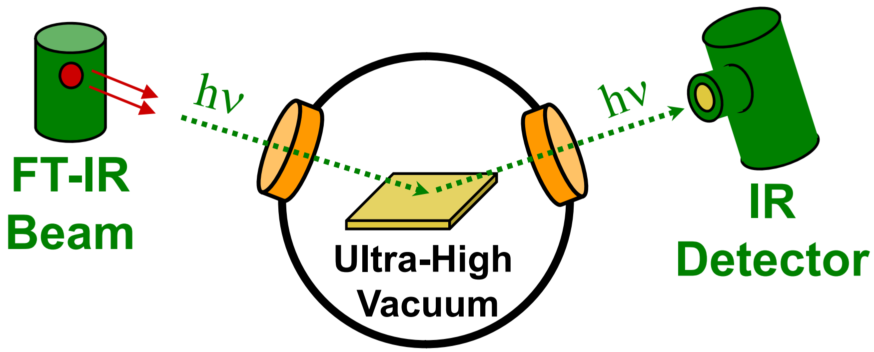


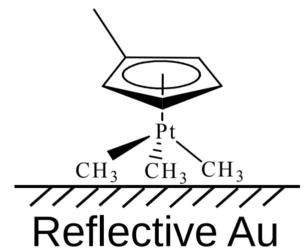
XPS enables quantitative determination of chemical composition and effective oxidation state

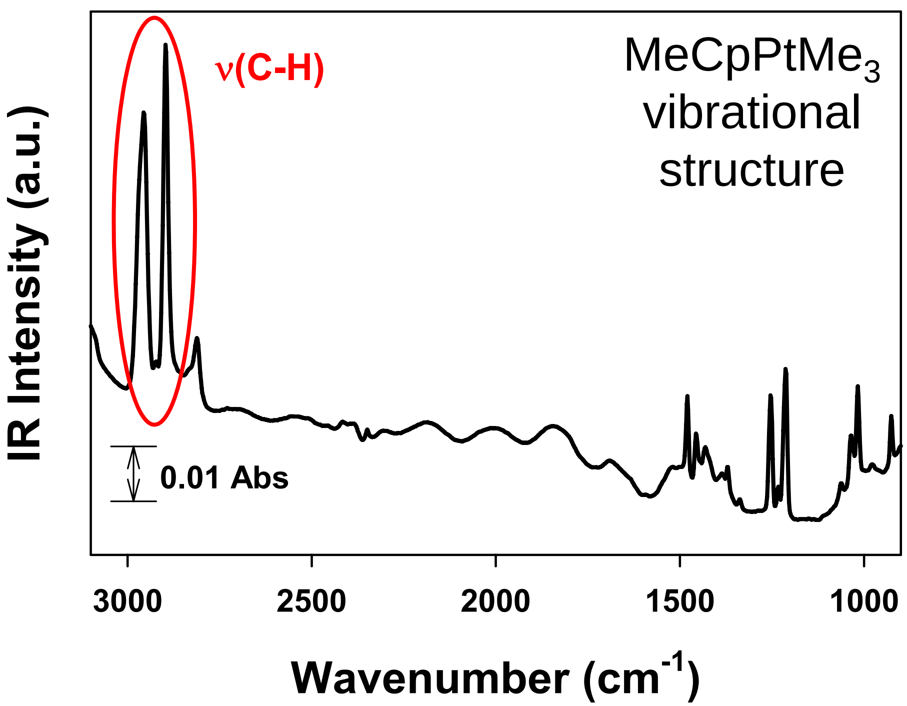


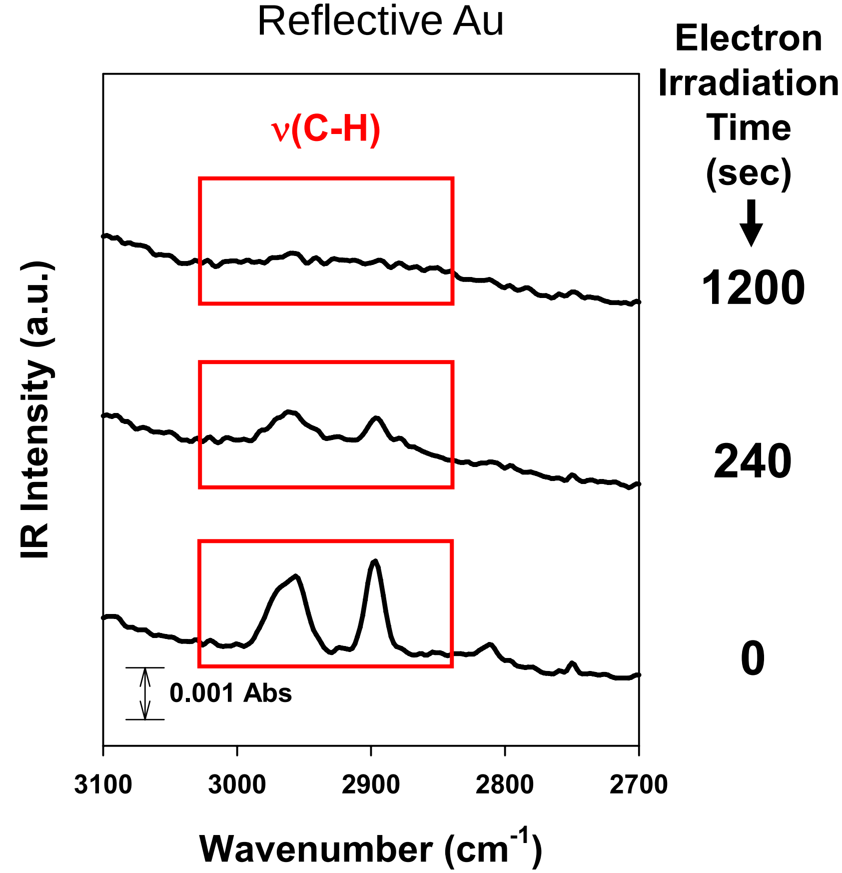
Reduction of Pt indicated by peak shift to lower BE

Reflection Absorption Infrared Spectroscopy (RAIRS)





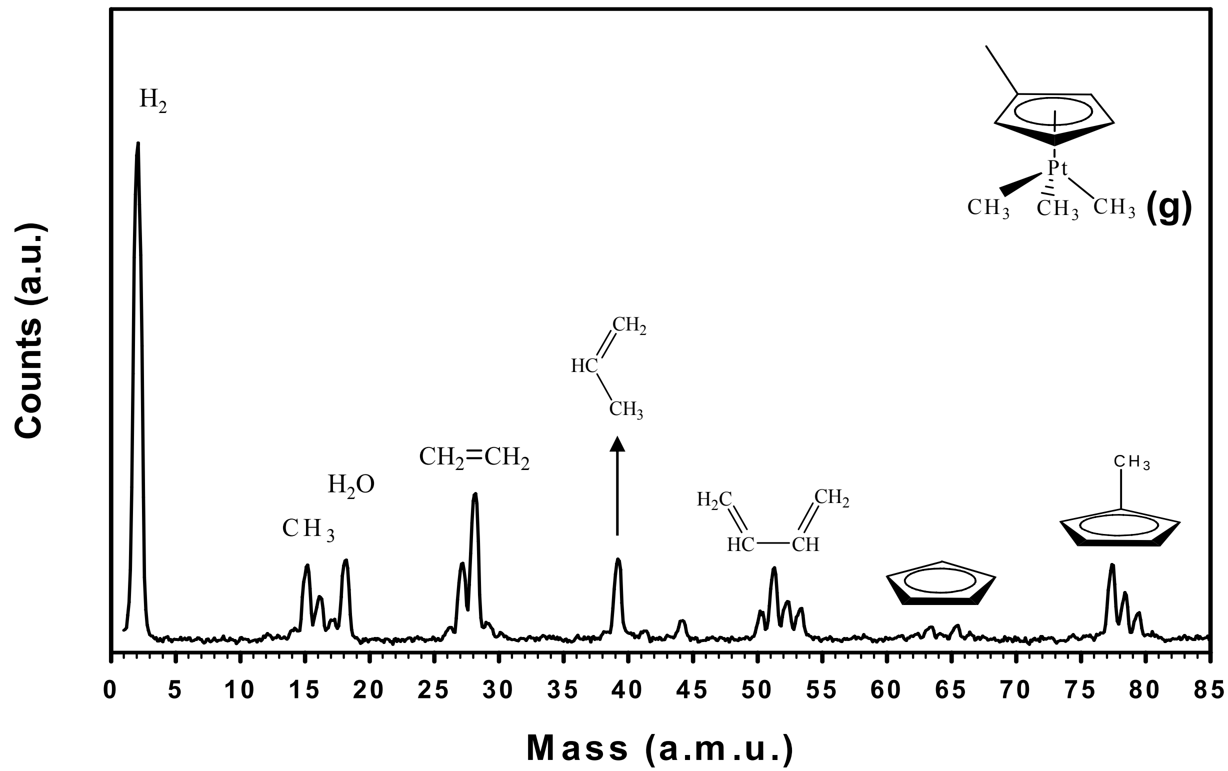


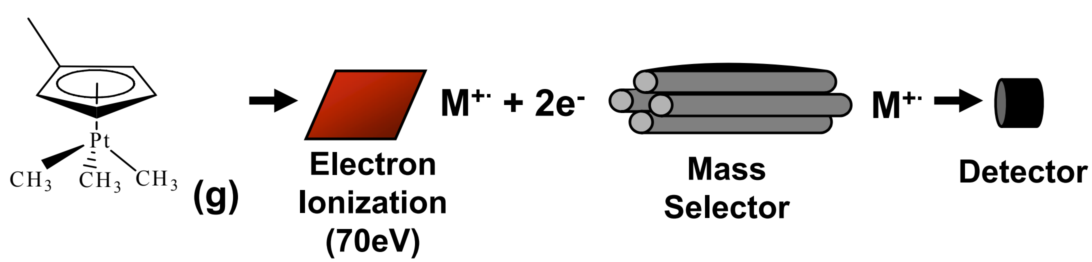


Mass Spectrometry (MS)

MS was used to:

- Verify purity of organometallic precursor
- Observe gaseous products of EBID
- Ensure cleanliness of UHV





Electron bombardment within the MS creates ionized fragments representative of species present in the gas phase