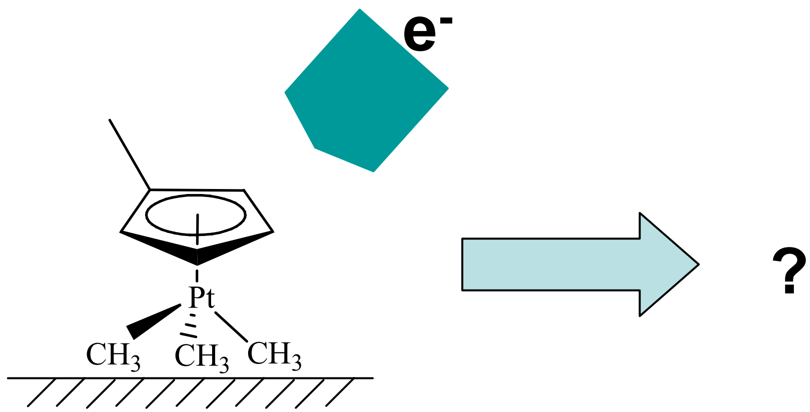
Surface Chemistry and Reaction Dynamics of Electron Beam Induced Deposition Processes



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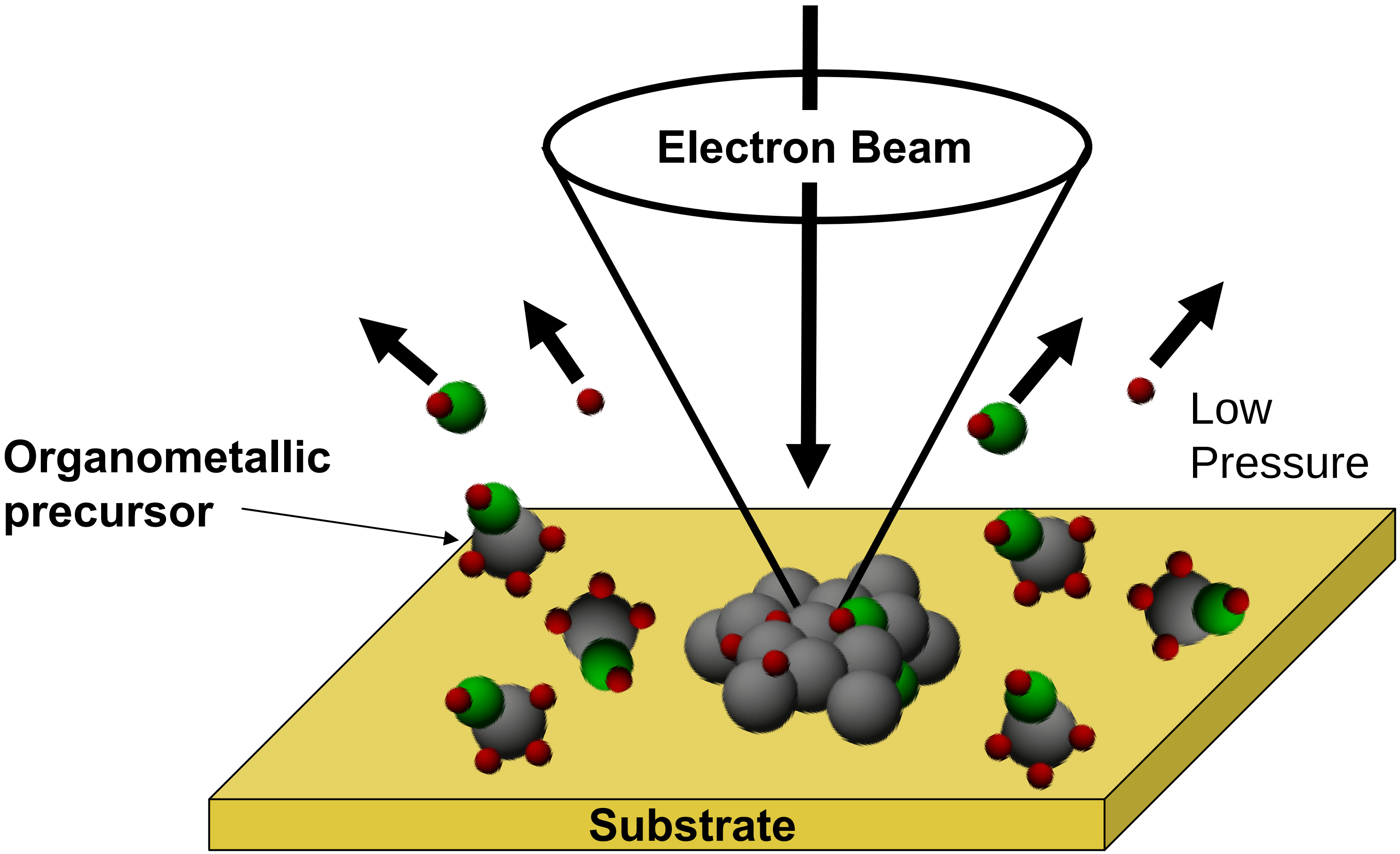
Howard Fairbrother
Johns Hopkins University
Baltimore, MD, USA

Outline

- Background / Motivation
- Experimental Approach
  - Analytical techniques and electron source
- Surface Chemistry and Kinetics
- Electron Stimulated Dissociation Mechanism
- Summary & Outlook

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

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?
  - $\sigma_{reaction}(E)$?

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

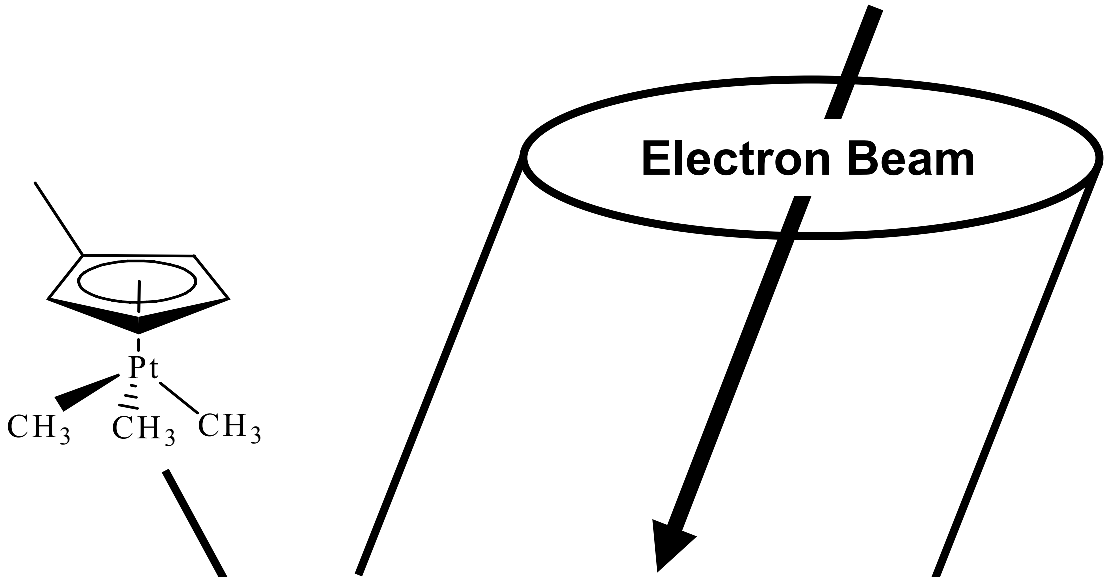
Outline

- Background / Motivation
- Experimental Approach
- Surface Chemistry and Kinetics (500eV)
- Electron Stimulated Dissociation Mechanism
- Summary

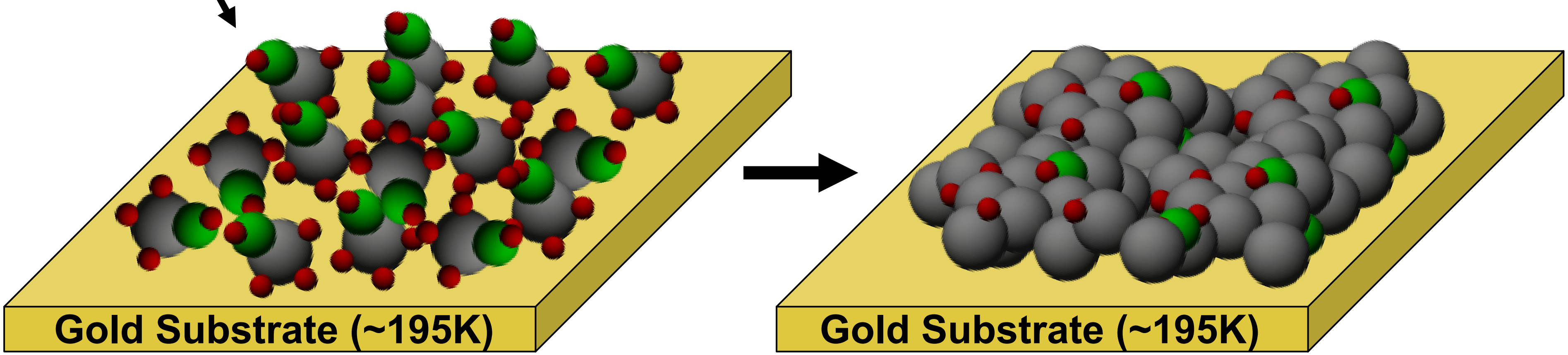
Our Approach

- 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



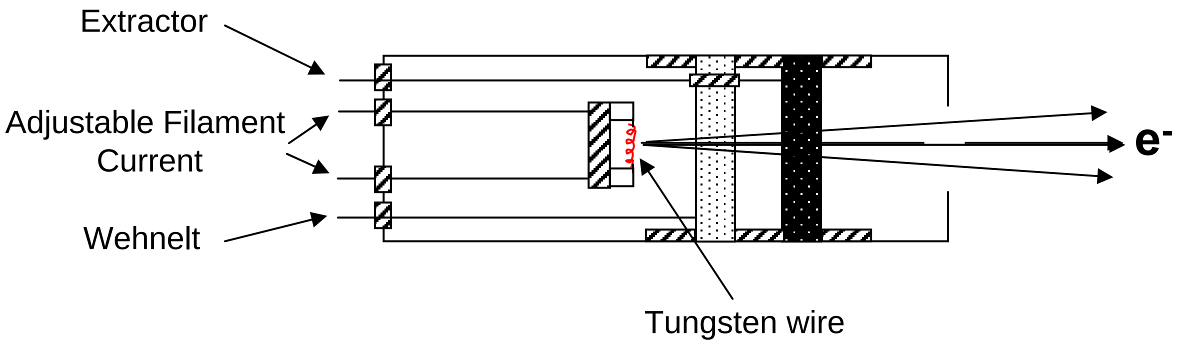
Production of a film over a large surface area enables traditional surface analytical techniques to probe the EBID process



Why gold?

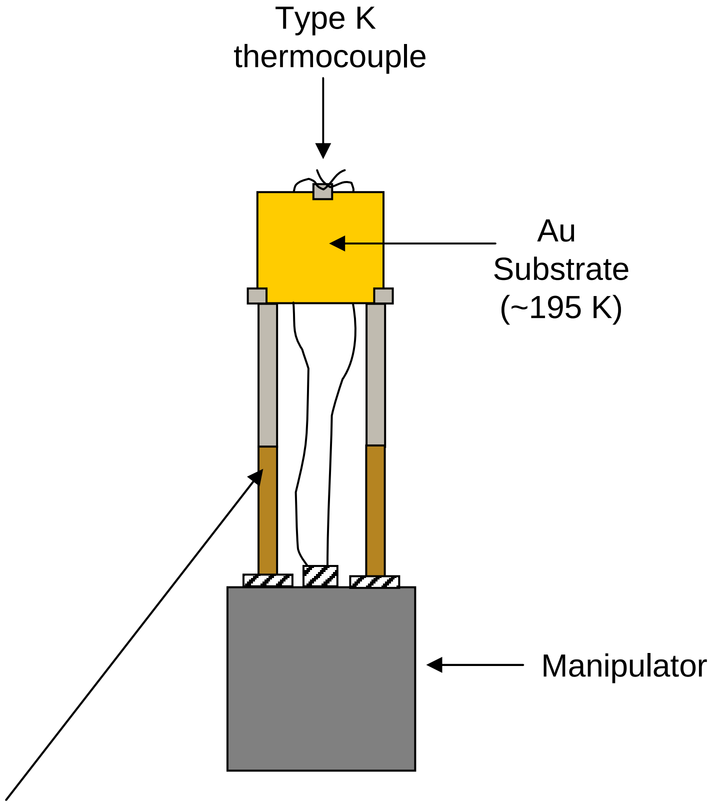
Electron Source: Flood Gun

- 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)



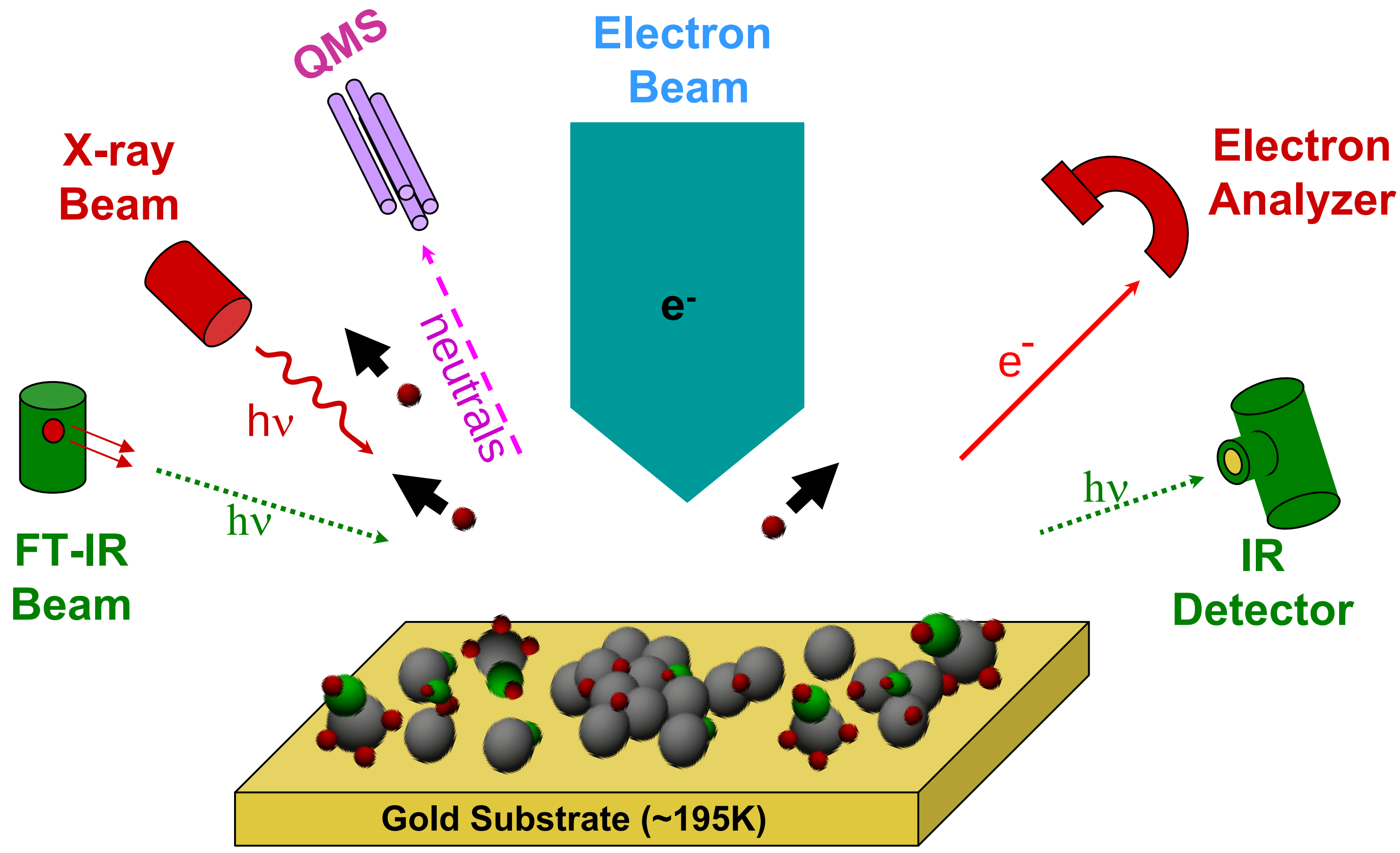
Electron Flood Gun can produce:
(a) 40 - 500 eV electrons
(b) 5 -150 μA target currents

Sample



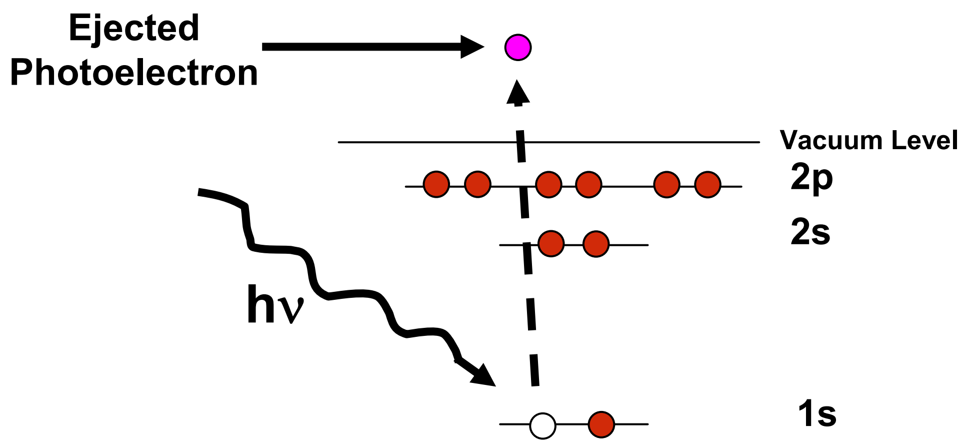
Cu leads provide for heating and cooling (100K-450K)

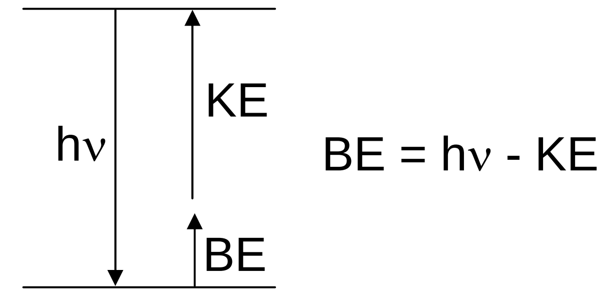
Instrumental Techniques

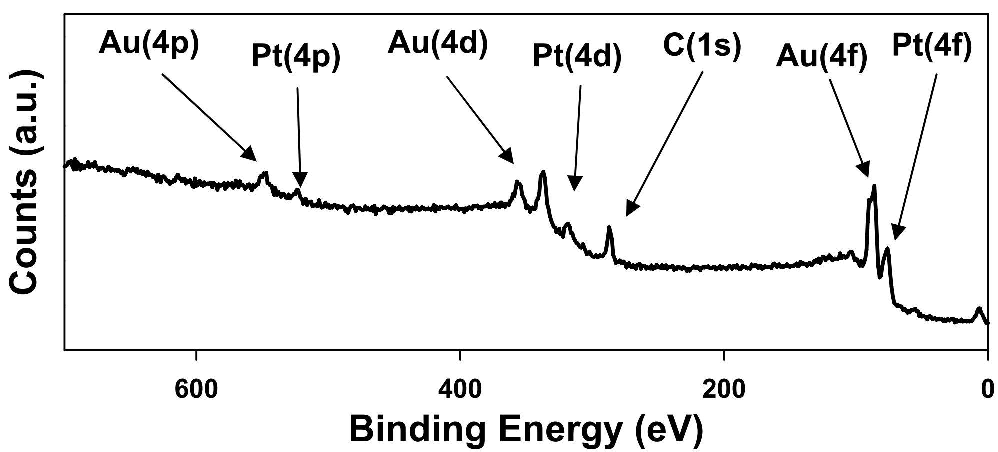


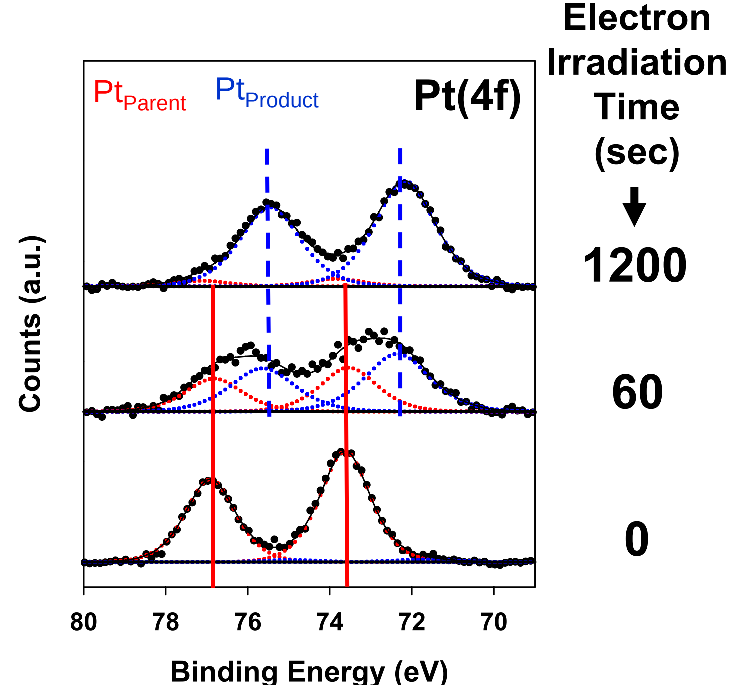
- We have studied the electron stimulated reactions of the well-known Pt precursor, Trimethyl(methylcyclopentadienyl)-platinum(IV), adsorbed onto gold using the above techniques:

X-ray Photoelectron Spectroscopy (XPS)





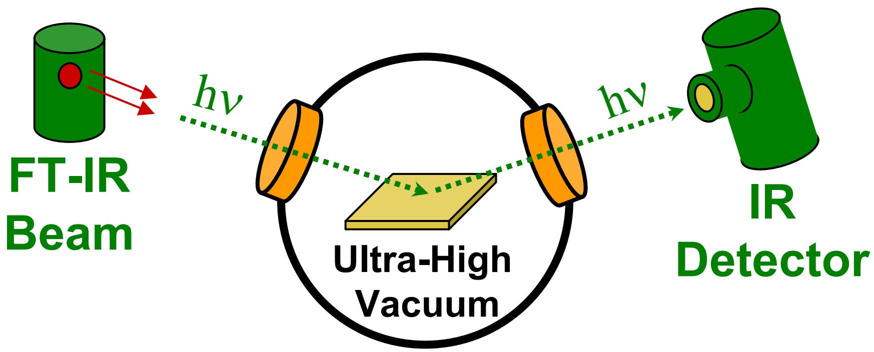


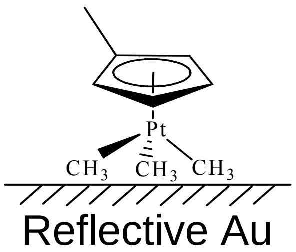


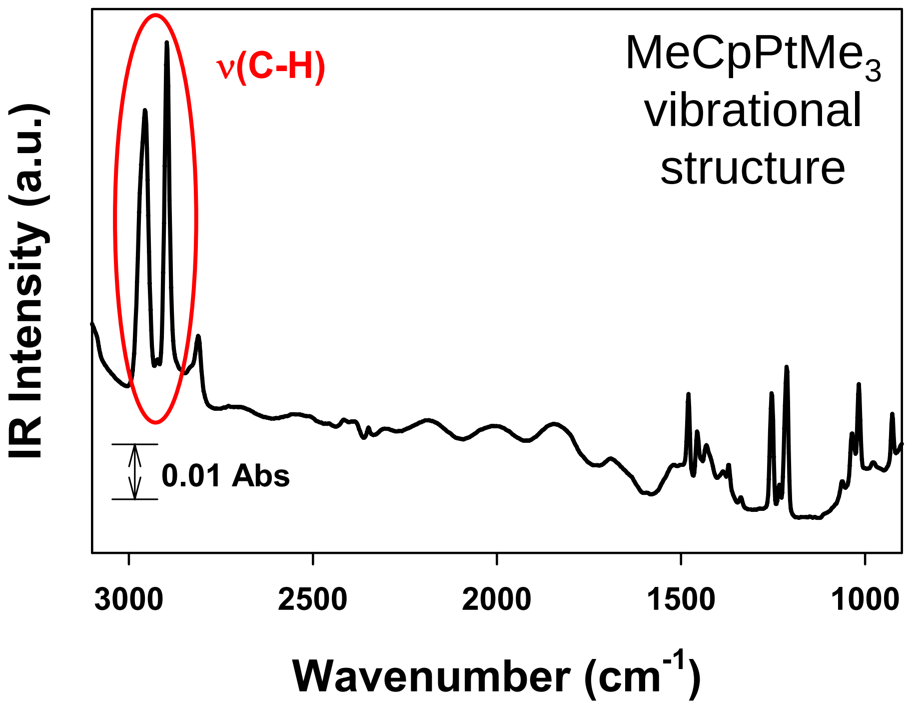
XPS enables quantitative determination of chemical composition and effective oxidation state

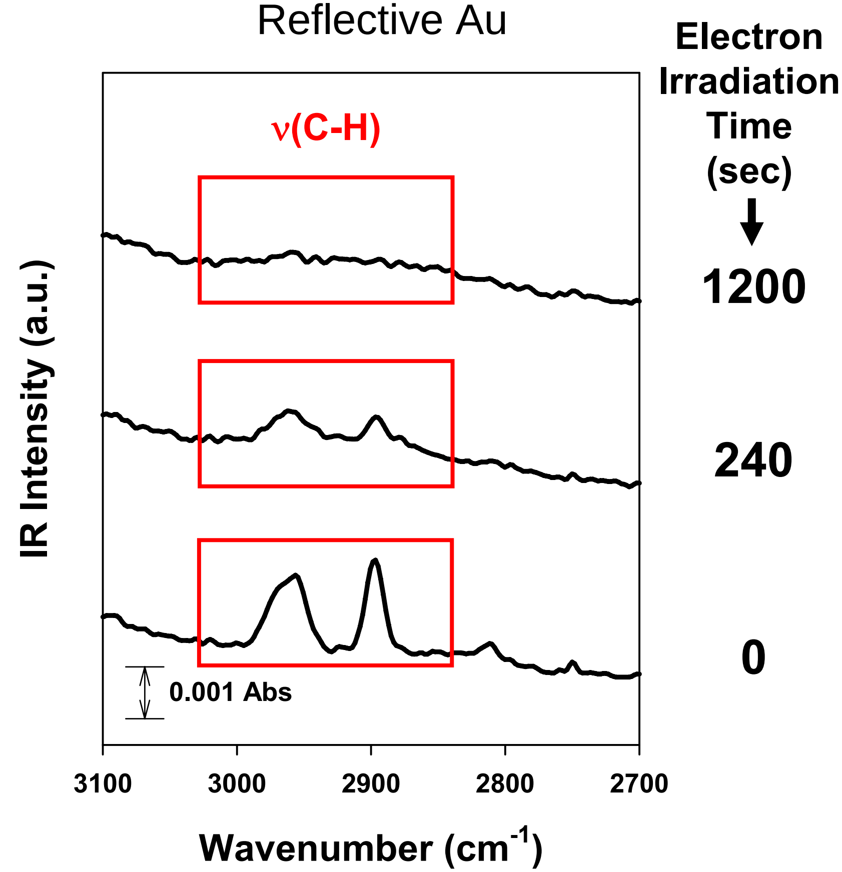
Reduction of Pt indicated by peak shift to lower BE

Reflection Absorption Infrared Spectroscopy (RAIRS)





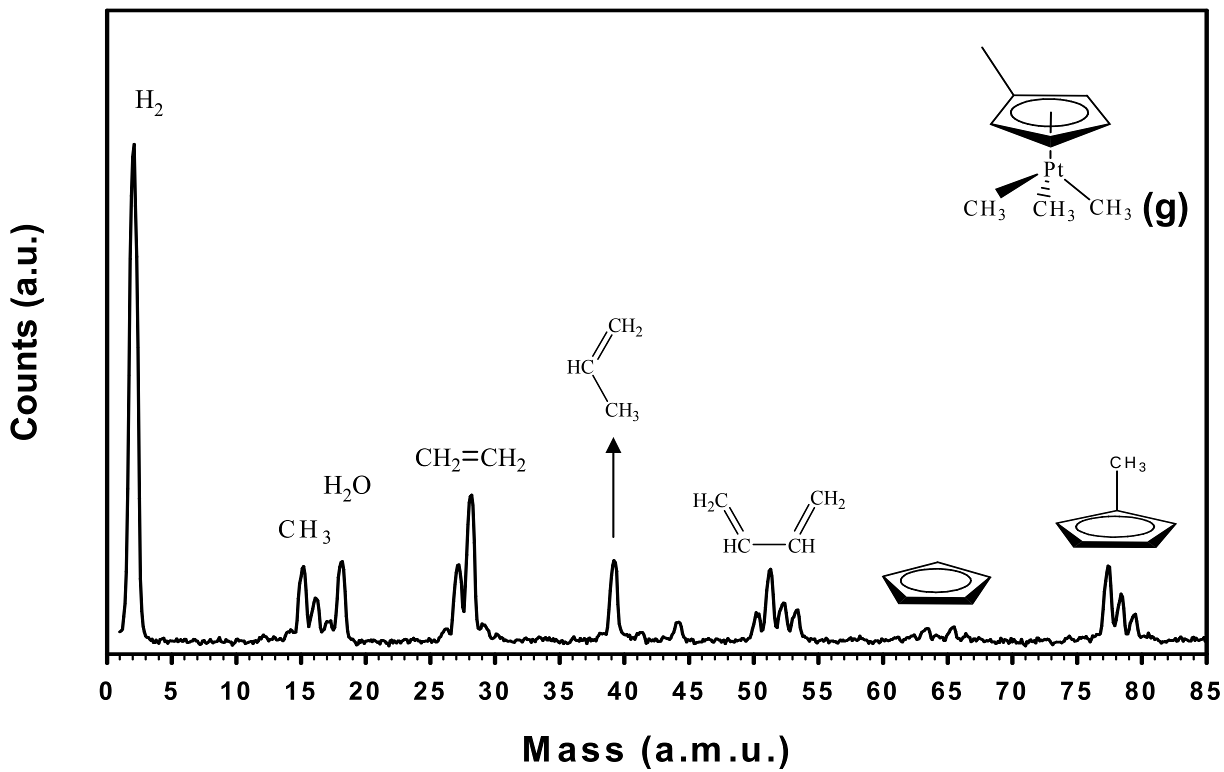


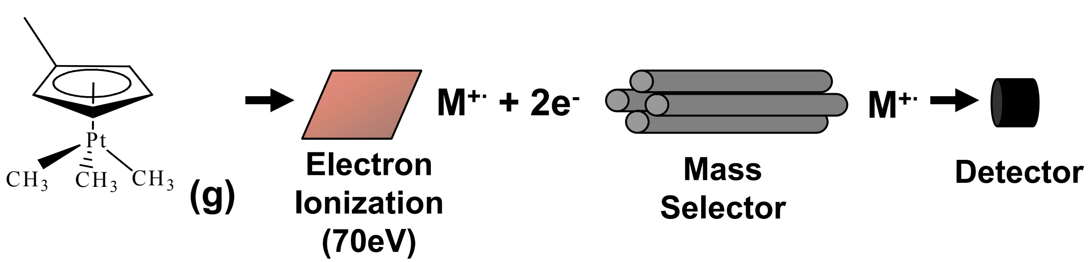


Mass Spectrometry (MS)

<u>MS was used to:</u>

- 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

Outline

- Background / Motivation
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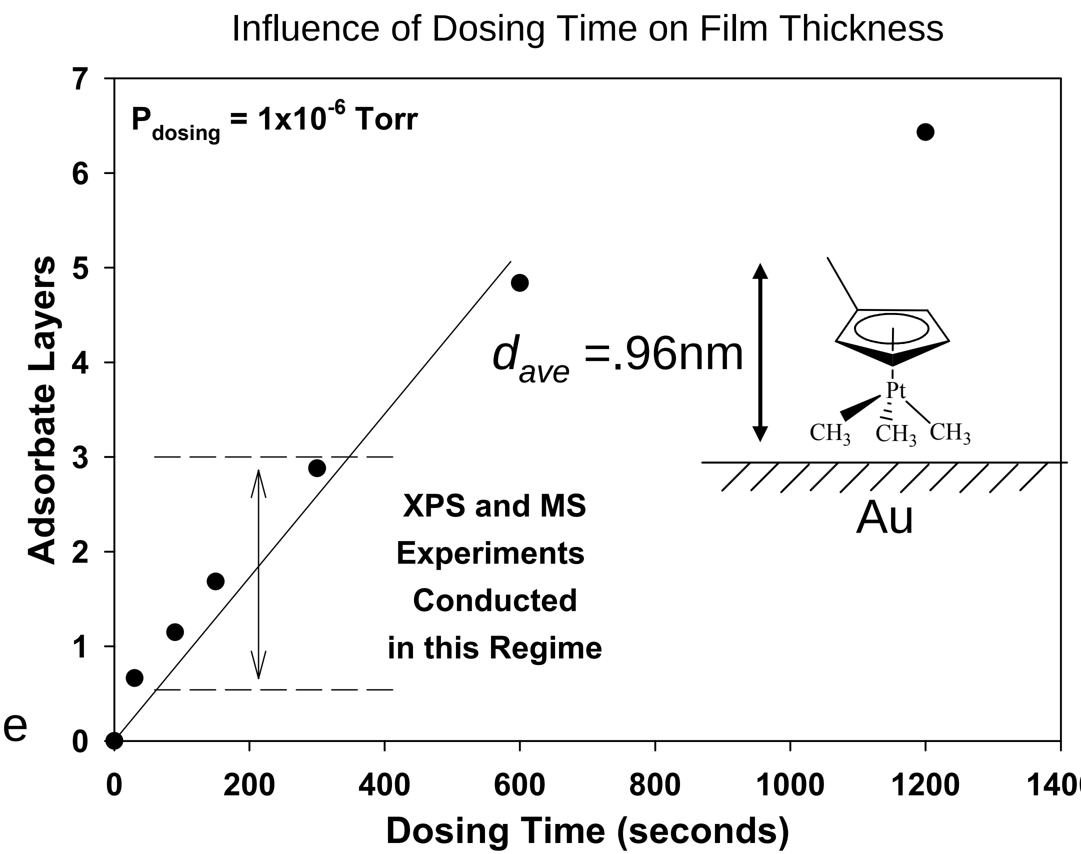
- Surface Chemistry and Kinetics (fixed electron energy = 500eV)
- Electron Stimulated Dissociation Mechanism
- Summary

Adsorption of $MeCpPt(IV)Me_3$ onto Gold Substrate – Controlling film thickness

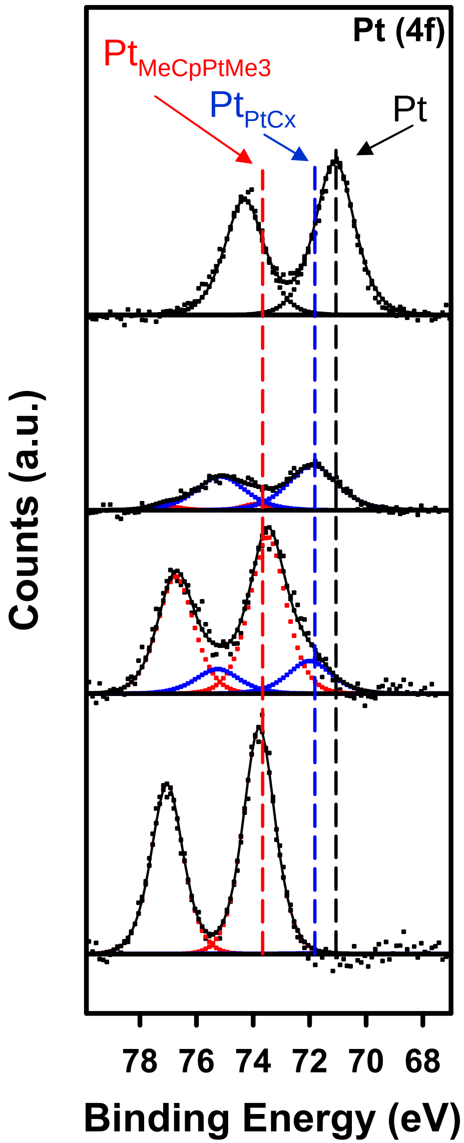
Film thickness, *d*, calculated from attenuation of Au(4f) signal

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

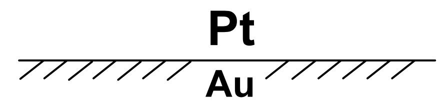
d = adsorbate thickness
λ = ~2nm for Au(4f) photoelectron
θ = 54° photoelectron take-off angle
I = Au(4f) area



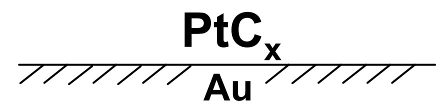
Production of Amorphous Platinum/Carbon Film



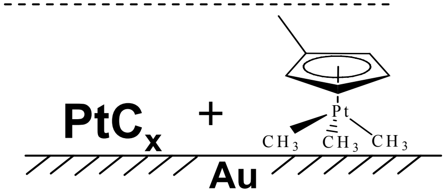
XP spectra of sputter deposited platinum on gold



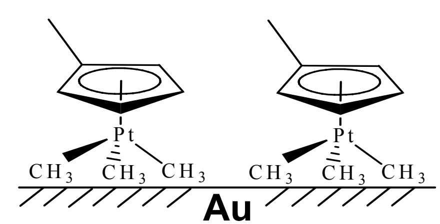
Substrate heated to room temperature leaving electron beam irradiation product



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



$MeCpPt(IV)Me_3$ adsorbed onto gold substrate (~195K)

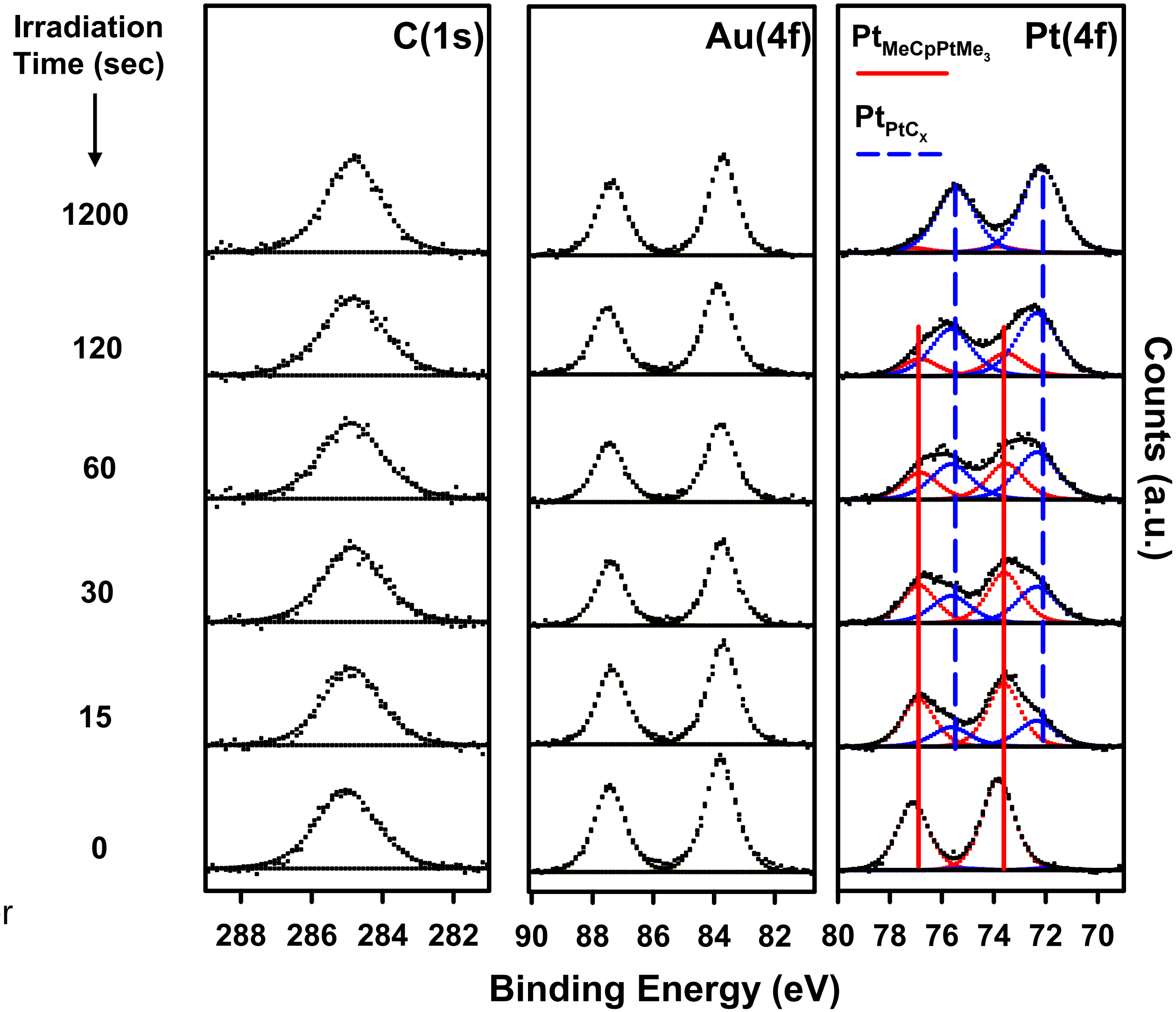


Influence of e^- Beam Irradiation on Surface Composition of Adsorbate Layer

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

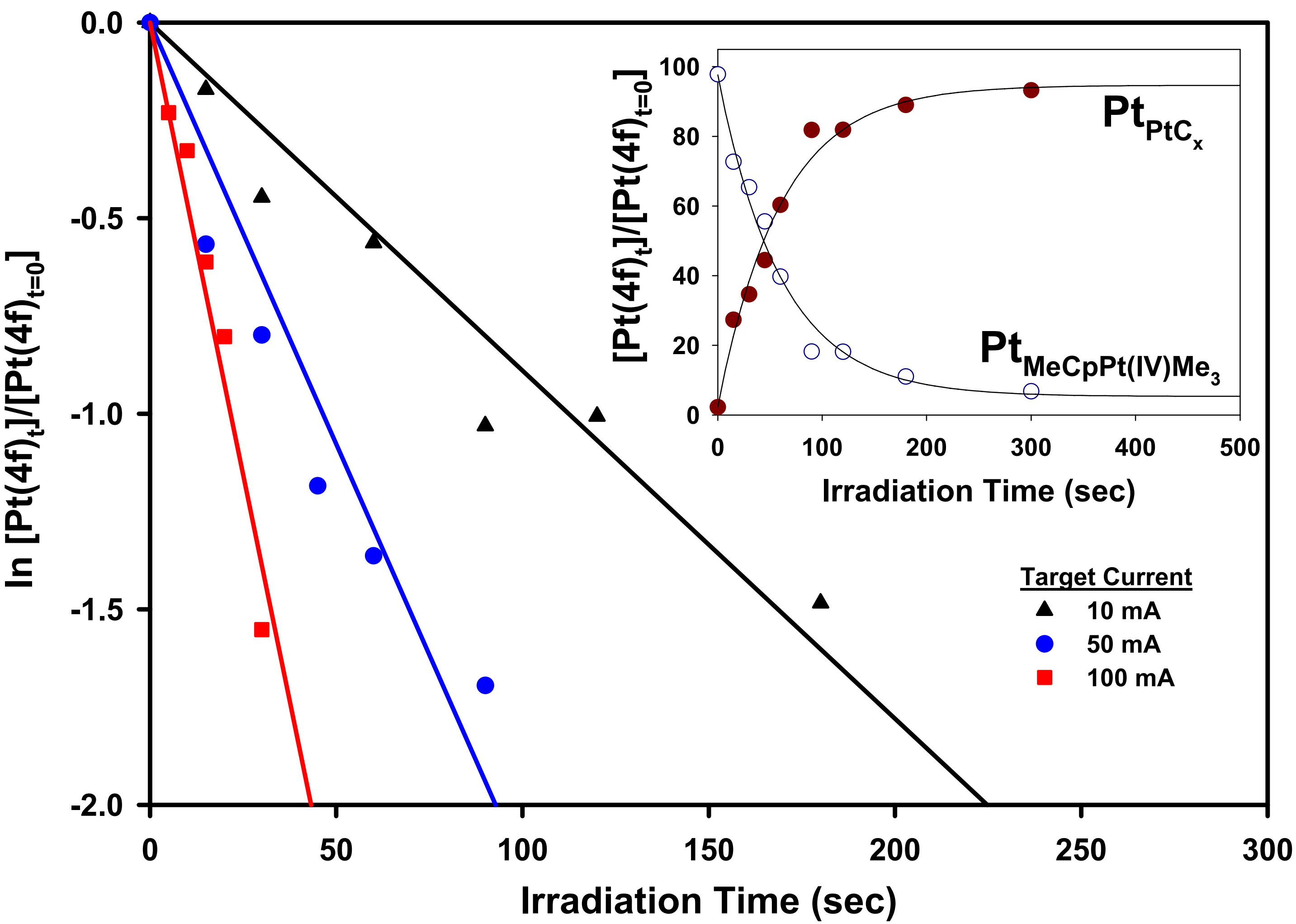
•No change in film thickness as determined by Au(4f) attenuation

•Shift in platinum environment from precursor to product



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

XPS Analysis of Deposition Kinetics



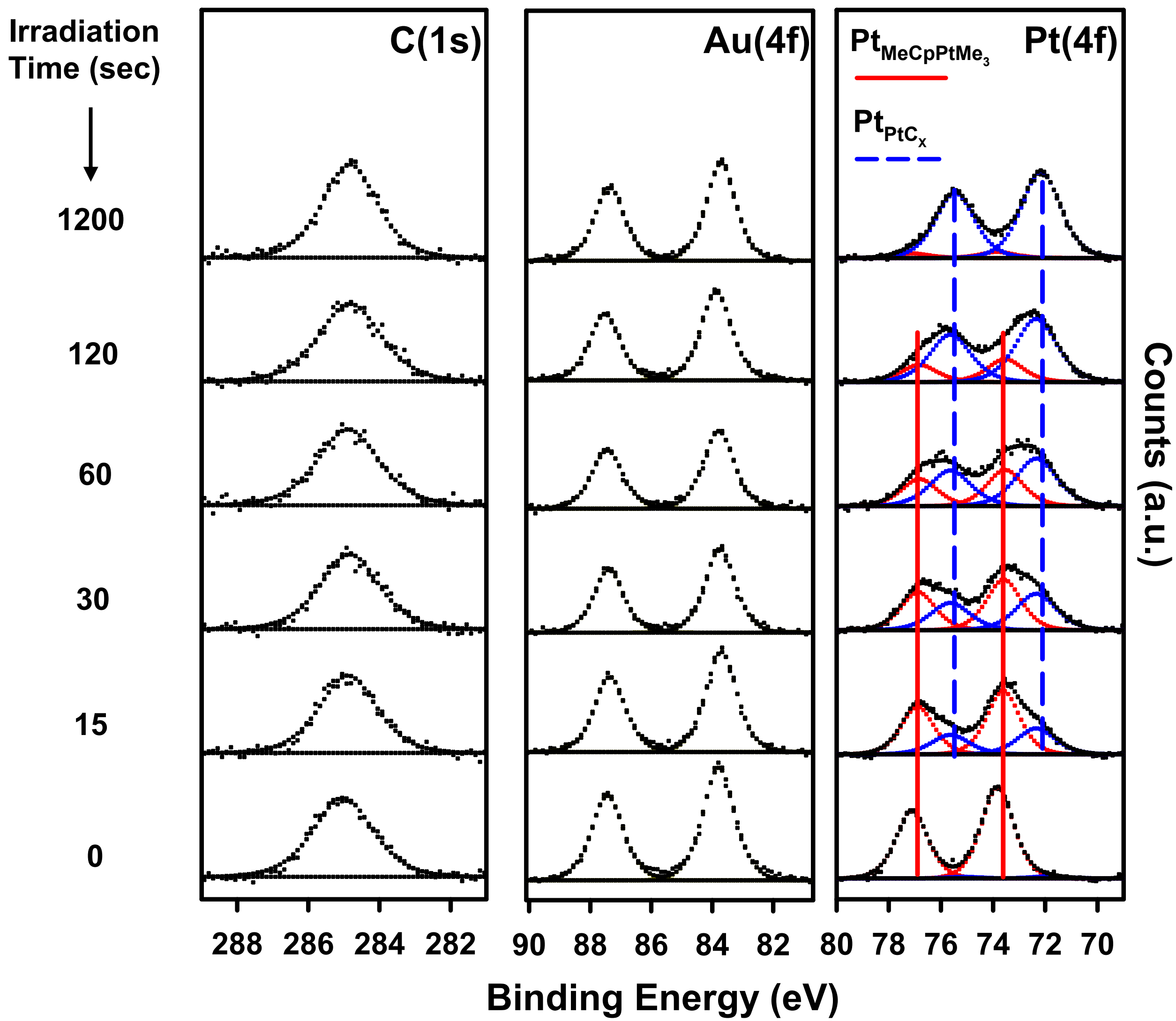
Quantification of the deconvoluted Pt(4f) region fit to exponential decay shows first order kinetics

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

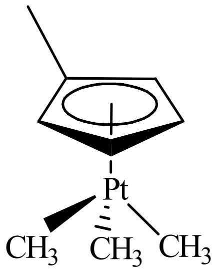
Signal Resolution vs. Signal Intensity

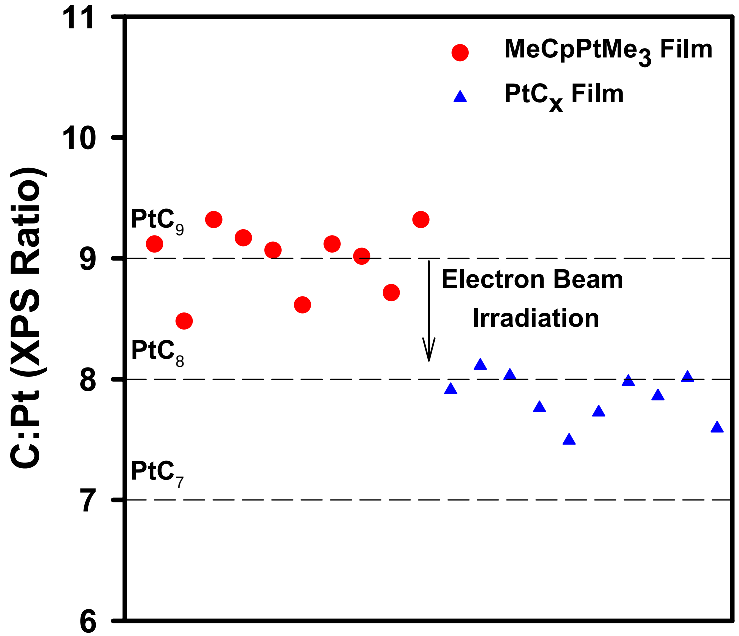
- High resolution / low intensity emphasizes elemental <u>environment</u>

- Low resolution / high intensity emphasizes <u>stoichiometry</u>



Evidence for Carbon Loss During Irradiation

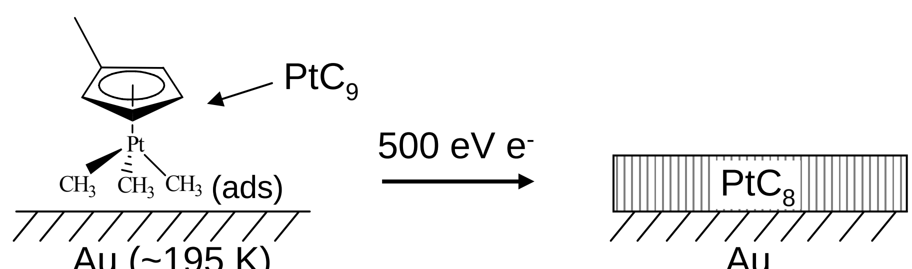




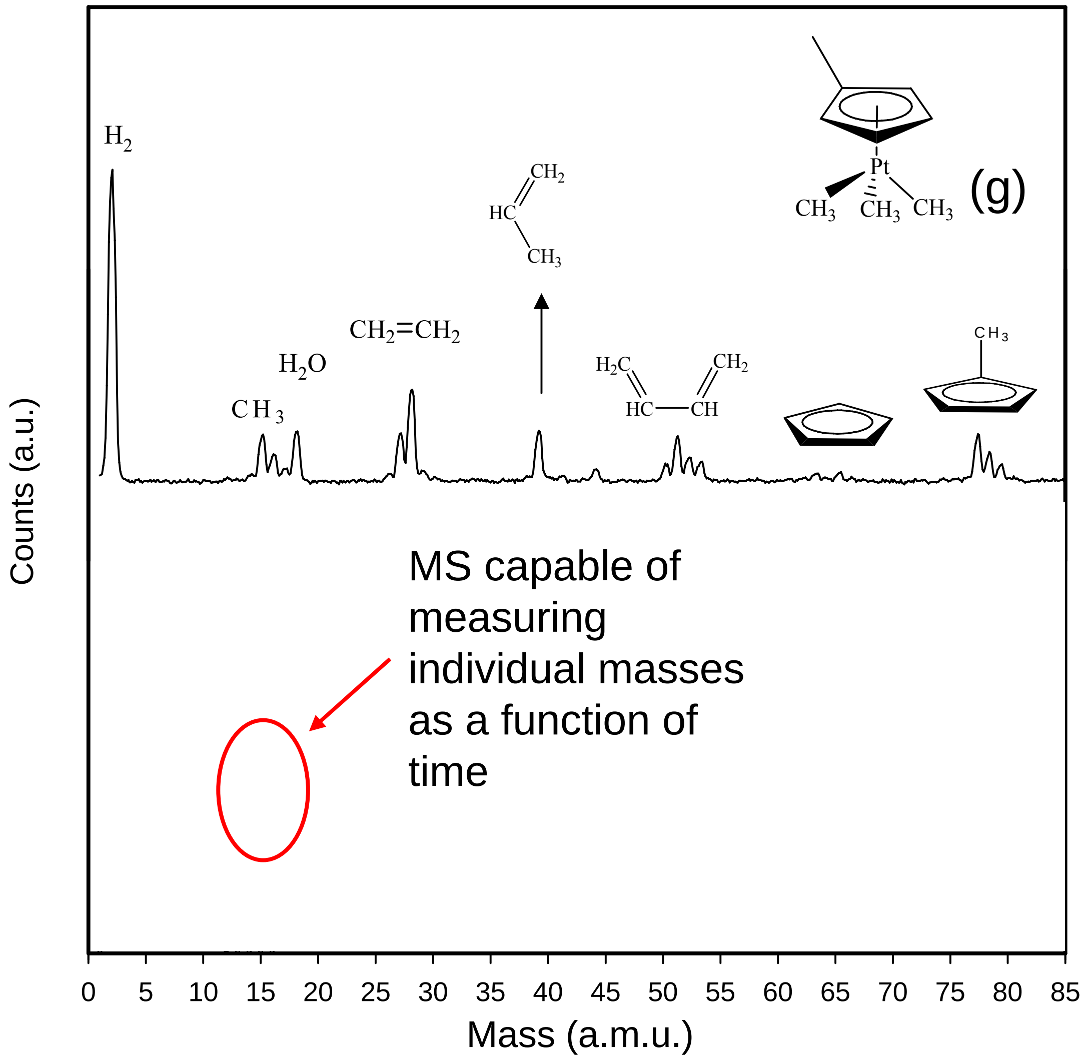
• The C:Pt ratio of 10 XP spectra of the MeCpPt(IV)Me_3 prior to e^- beam irradiation is representative of the initial stoichiometric ratio of 9 carbon atoms to 1 platinum atom

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

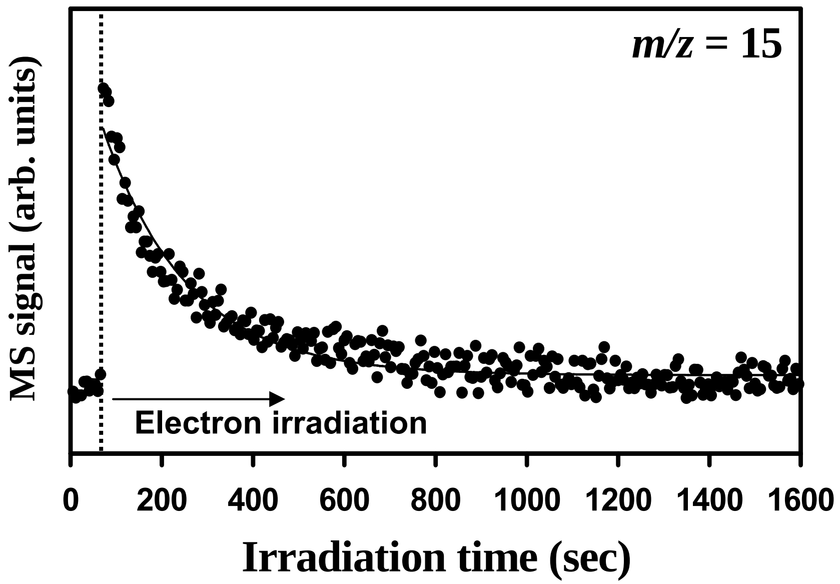
• The C:Pt ratio after e^- beam irradiation decreases to a ratio of 8:1, indicating the loss of 1 carbon atom per molecule as a result of irradiation



Gas Phase Products



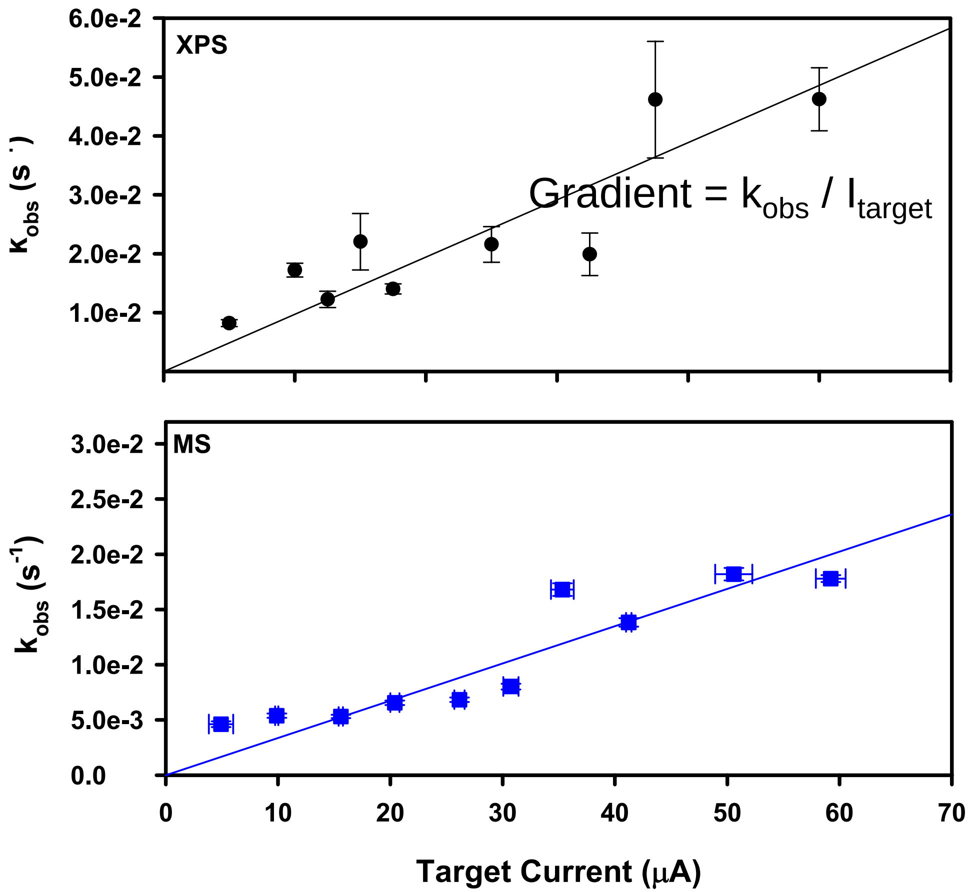
Kinetic Analysis of Methane Production



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

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

Complementary Techniques



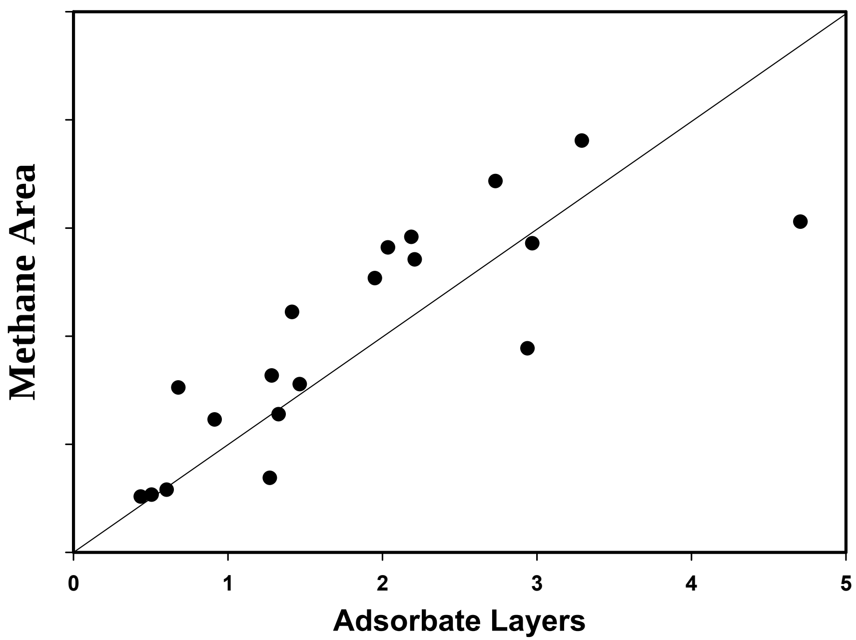
$$\sigma = \frac{k_{obs}}{I_{target}} \times A$$

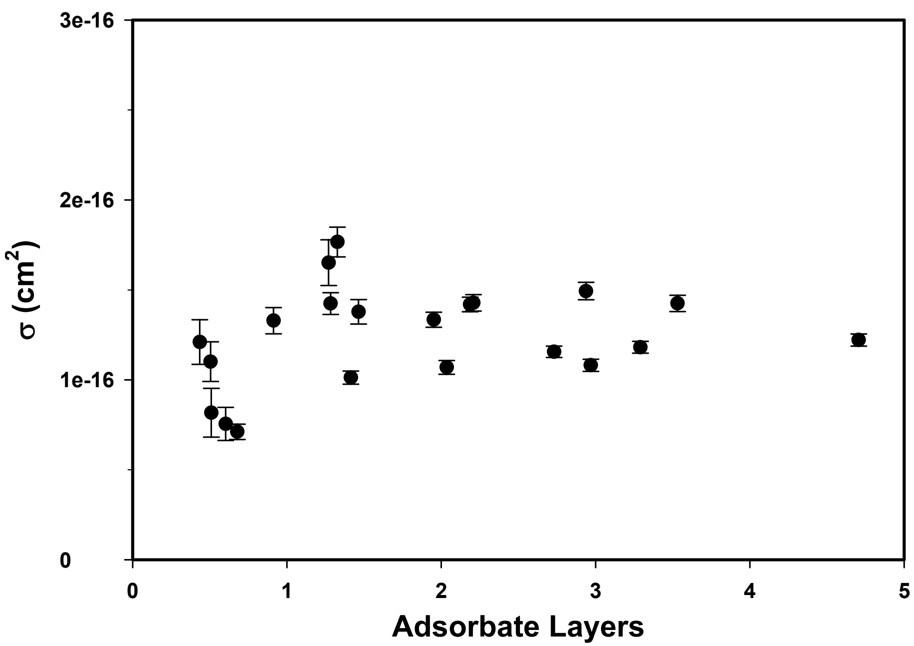
	σ (cm²)
XPS	1.40E-16
MS (m/z=15)	9.75E-17

$\sigma_{ave,\ 500eV}$ **= 2.28E-16 cm²**

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

How does Film Thickness Influence the Process?

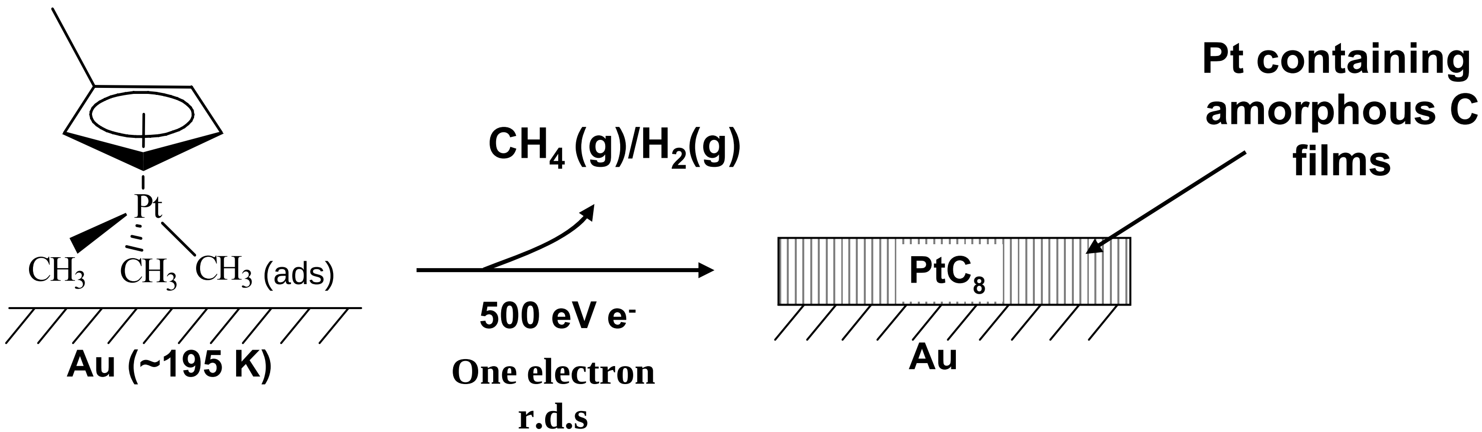




Methane area independent of film thickness

σ independent of film thickness

Surface Chemistry



•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.

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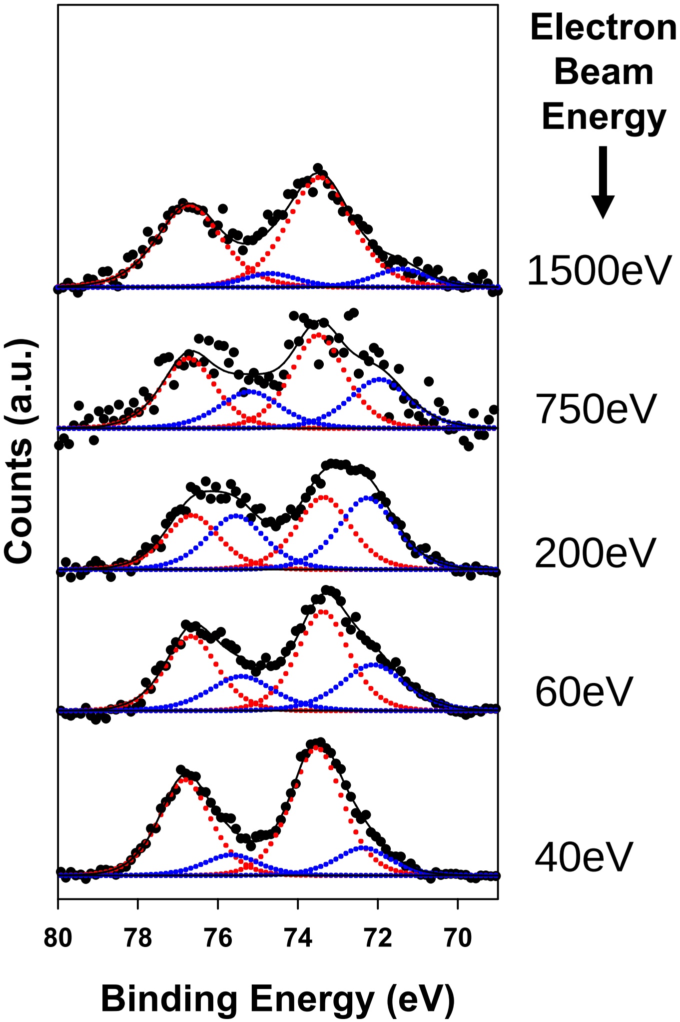
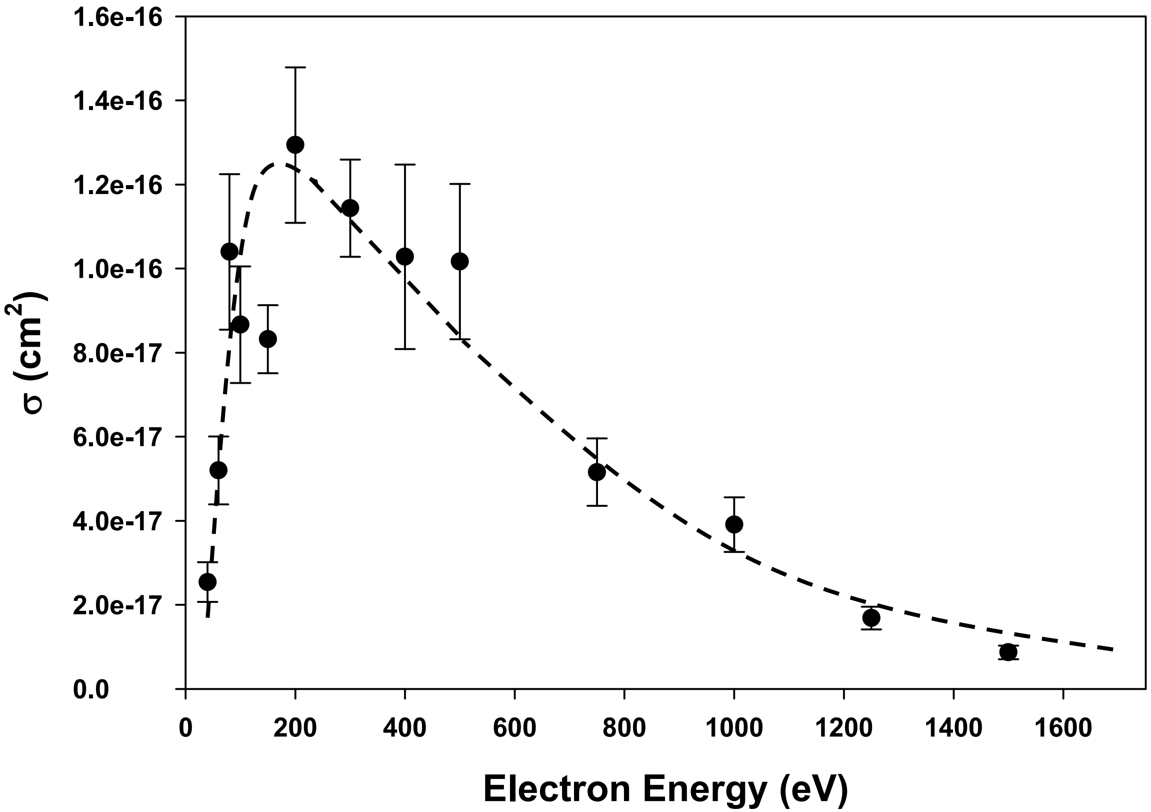
Dependence on Incident Electron Energy Observed Using XPS

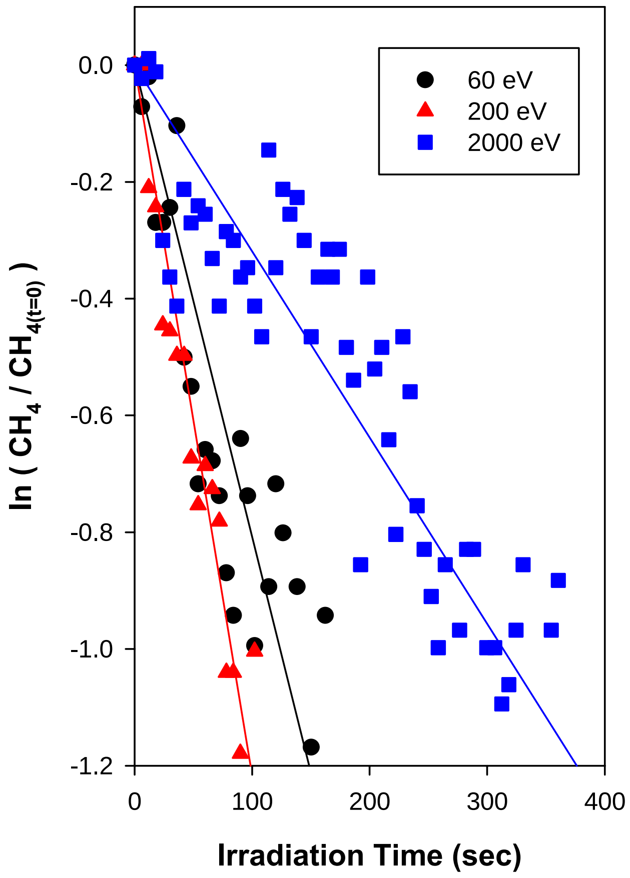


Above XP spectra: 25μA, *t=60* sec

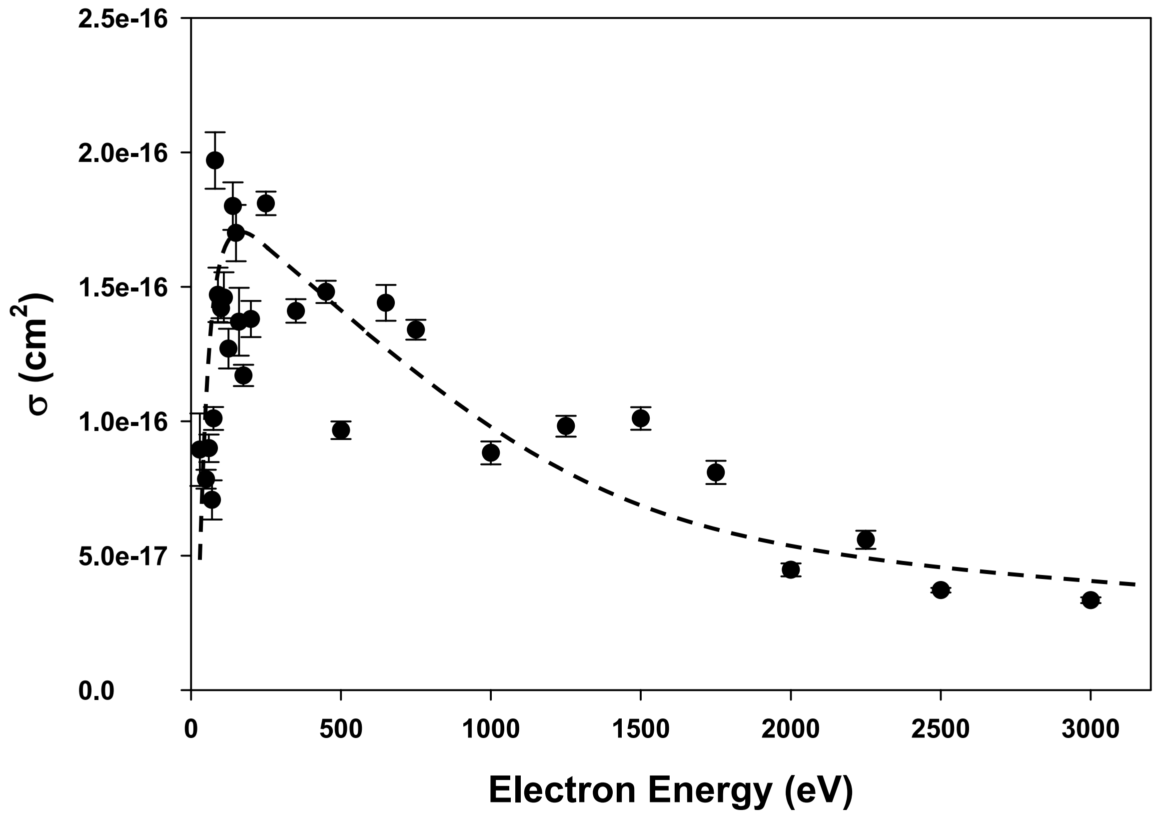


Optimal σ between 100-200eV suggests electron impact ionization process

Dependence on Incident Electron Energy Observed Using MS

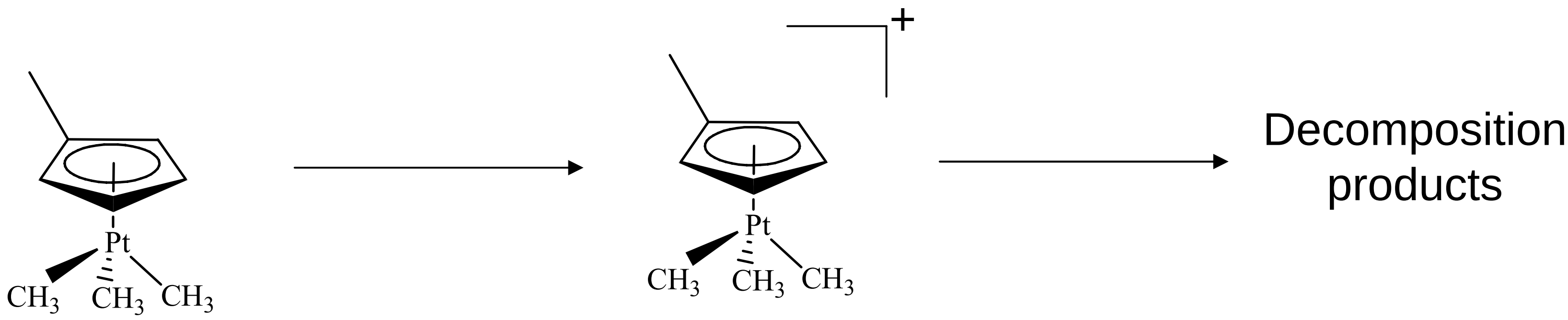


$\sigma_{60eV} < \sigma_{200eV} > \sigma_{2000eV}$

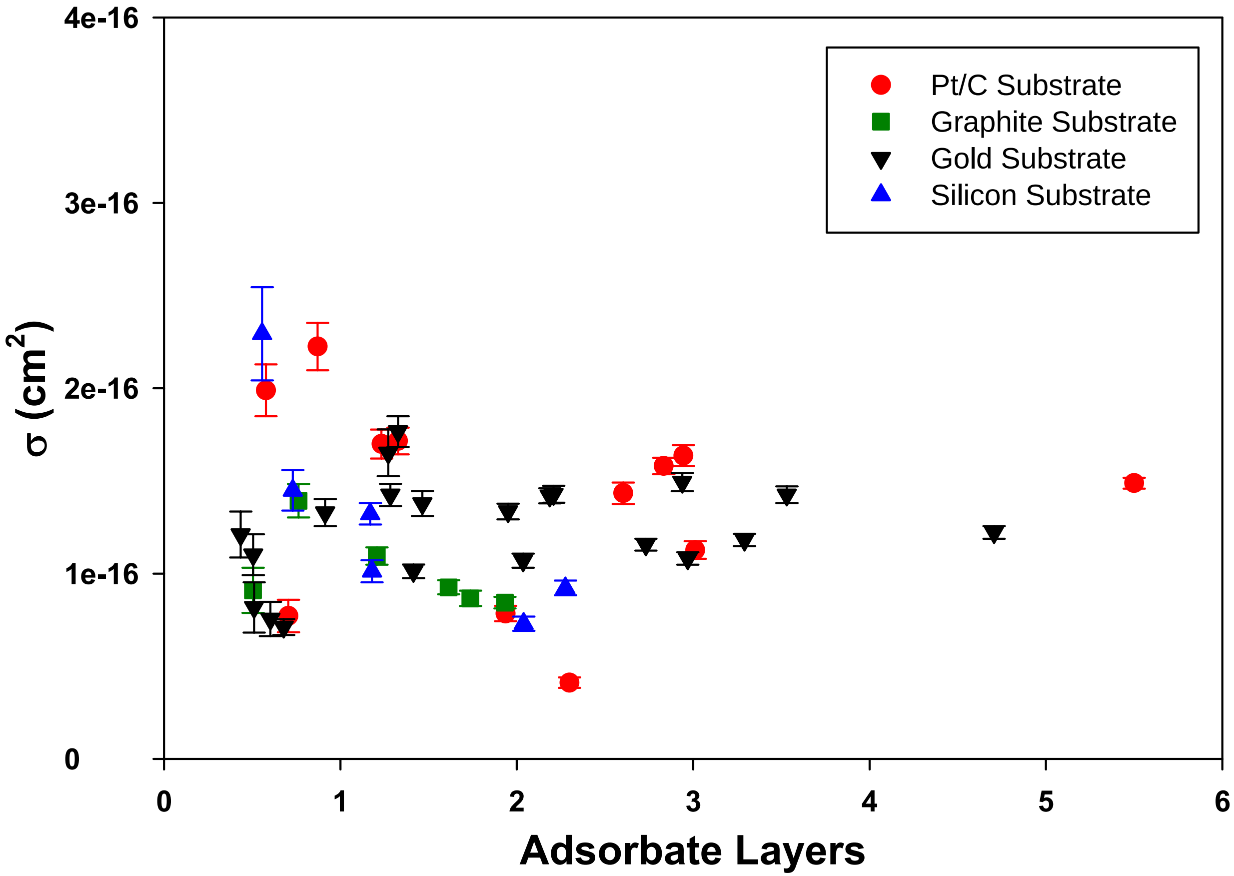


MS supports XPS results

Dissociative Ionization Process



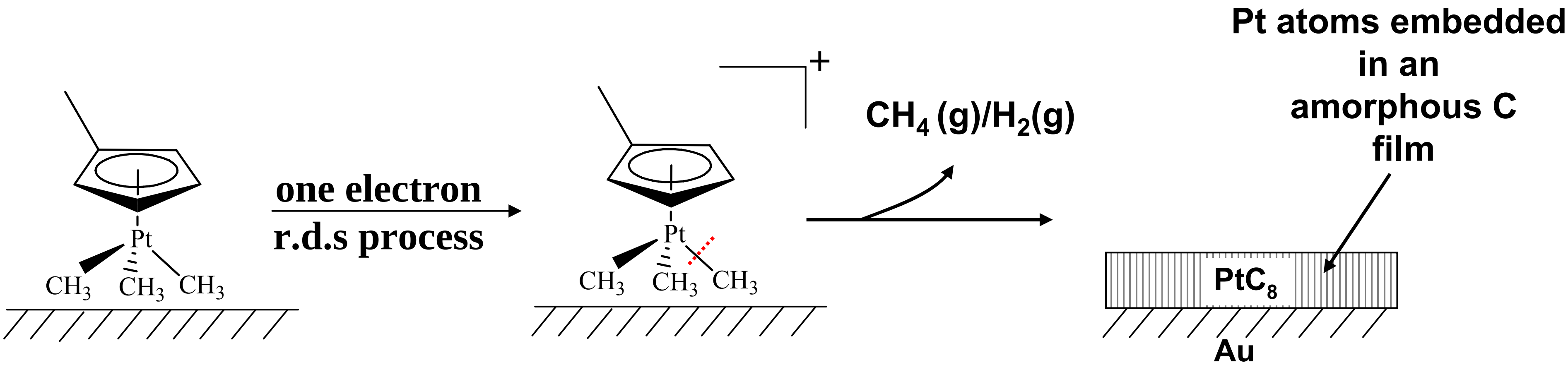
Substrate Dependence?



NO

All experiments conducted at ~195K with 20μA target current and 200eV electron energy

Summary



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

Exptl. Requirements

Substrate

- Chemically unreactive towards precursor

Film

- Thin!!! (1-3 Monolayer regime so that each precursor molecule experience the same electron flux)

Electron Beam

– Broad and defocused (uniform irradiation)

Methods?

Technique	Pros	Cons
XPS	Reasonable quantification	Central atom must change oxidation state
AES	Destructive (Not applicable)	
Mass Spectrometry (a) TPD	Good Quantification	Duty Cycle Slow Decomposition may compete with desorption
(b) Analysis of desorbing species	Simple reasonable quantification	Indirect monitor of surface processes
IR (reflection)	Parent can easily be monitored	Poor Sensitivity Modest Quantification

Acknowledgements

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