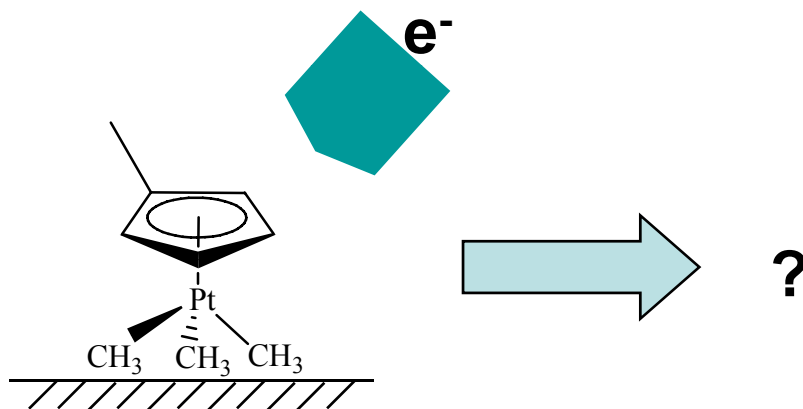


A Molecular Level Investigation of the Electron Beam Induced Deposition of Methylcyclopentadienylplatinum(IV)-trimethyl



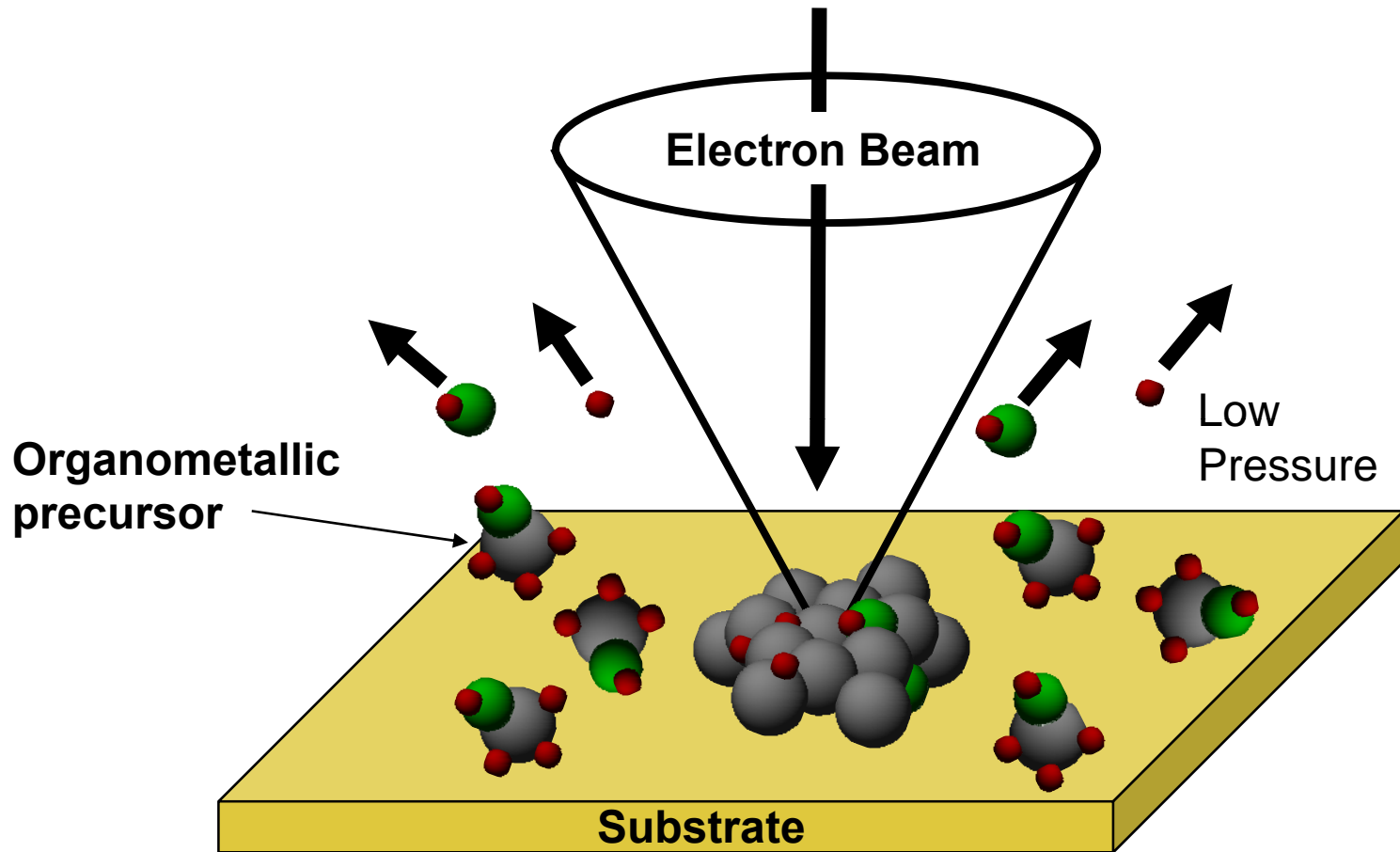
47th Eastern Analytical Symposium
Somerset, NJ

Joshua D. Wnuk
Johns Hopkins University
Baltimore, MD, USA

Outline

- **Background / Motivation**
- Experimental Approach
- Surface Chemistry and Kinetics (500eV)
- Incident Energy Dependence ($\sigma(E)$)
- Summary

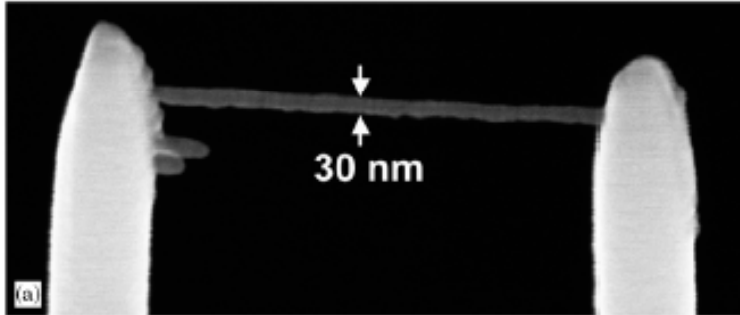
Electron Beam Induced Deposition



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

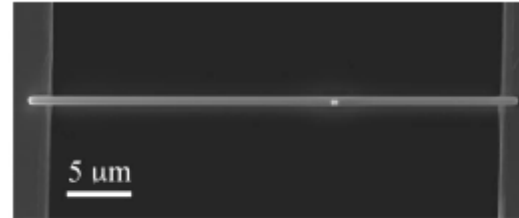
Examples of EBID

Freestanding Pt wire grown from MeCpPtMe₃



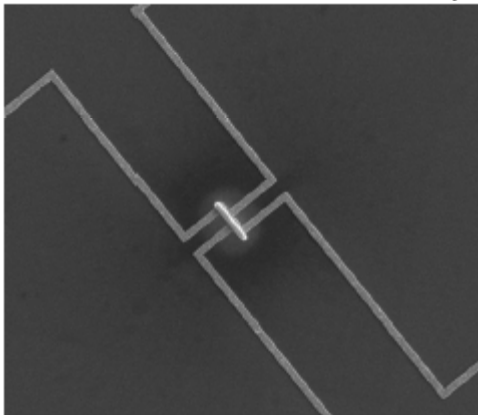
Frabboni et al., *Physica E*, **2007**, 265.

Pt wire grown on SiO₂ from MeCpPtMe₃



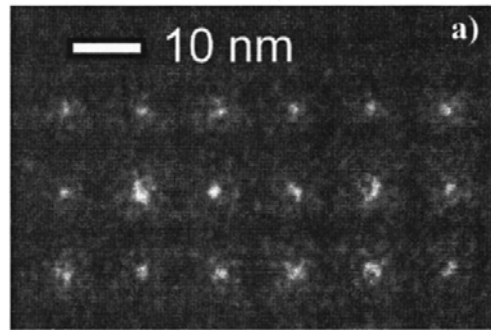
Gopal et al., *Appl. Phys. Lett.*, **2005**, 49.

Pt wire, 4 μm long, grown between Au electrodes on Si / SiO₂ substrate from MeCpPtMe₃



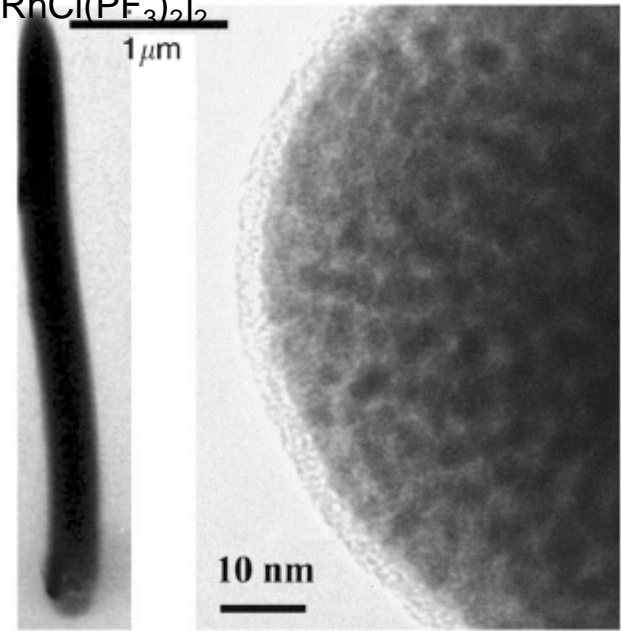
Botman et al., *Nanotechnology*, **2006**, 3779.

W(CO)₆ on C films



van Dorp et al., *JVST B*, **2007**, 2210.

Rh grown on graphite from [RhCl(PE₃)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 reaction at the surface?
 - Incident electron energy dependence?
- 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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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

Experimental Notes

Substrate

- Chemically un-reactive towards precursor

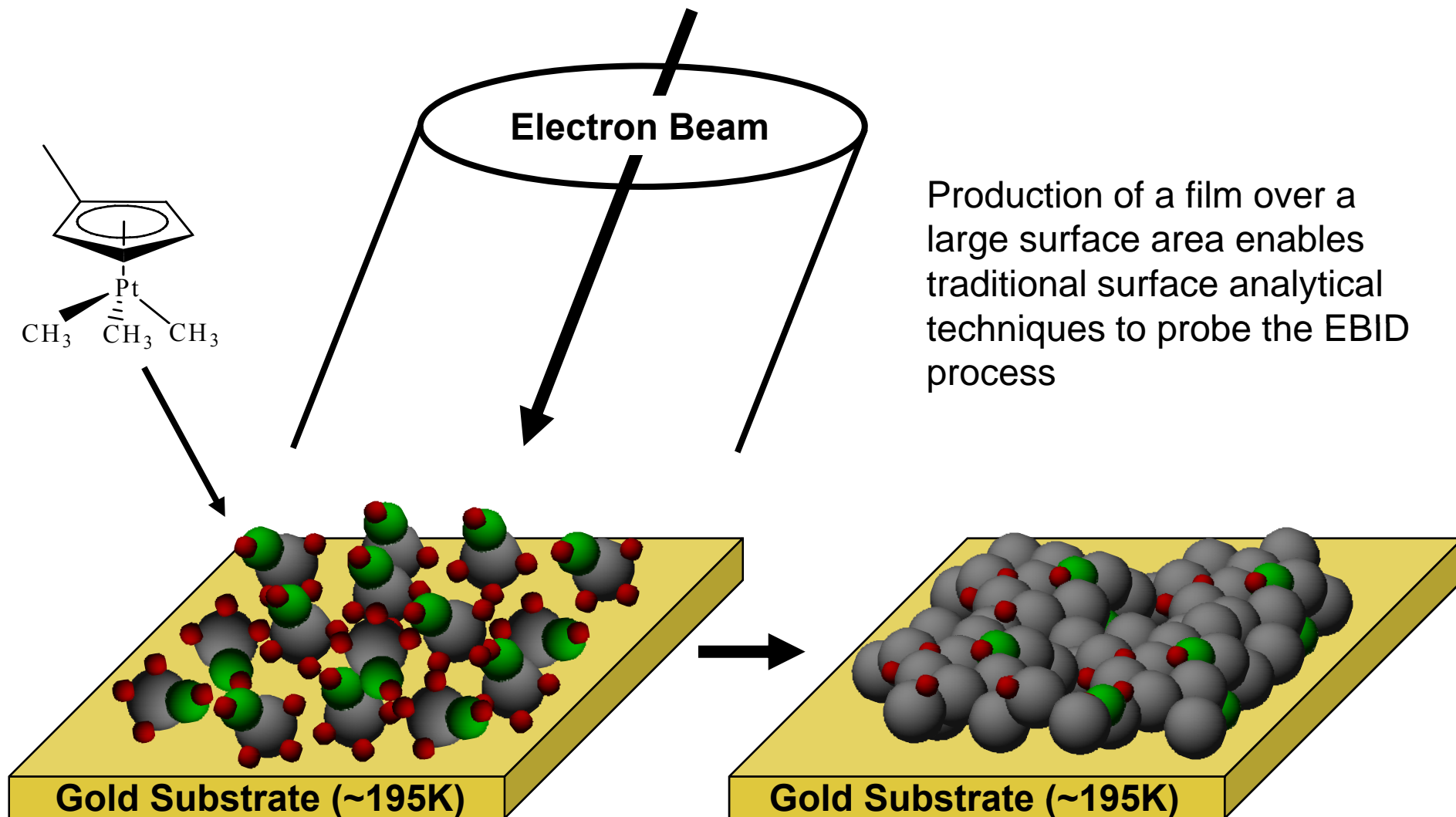
Film

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

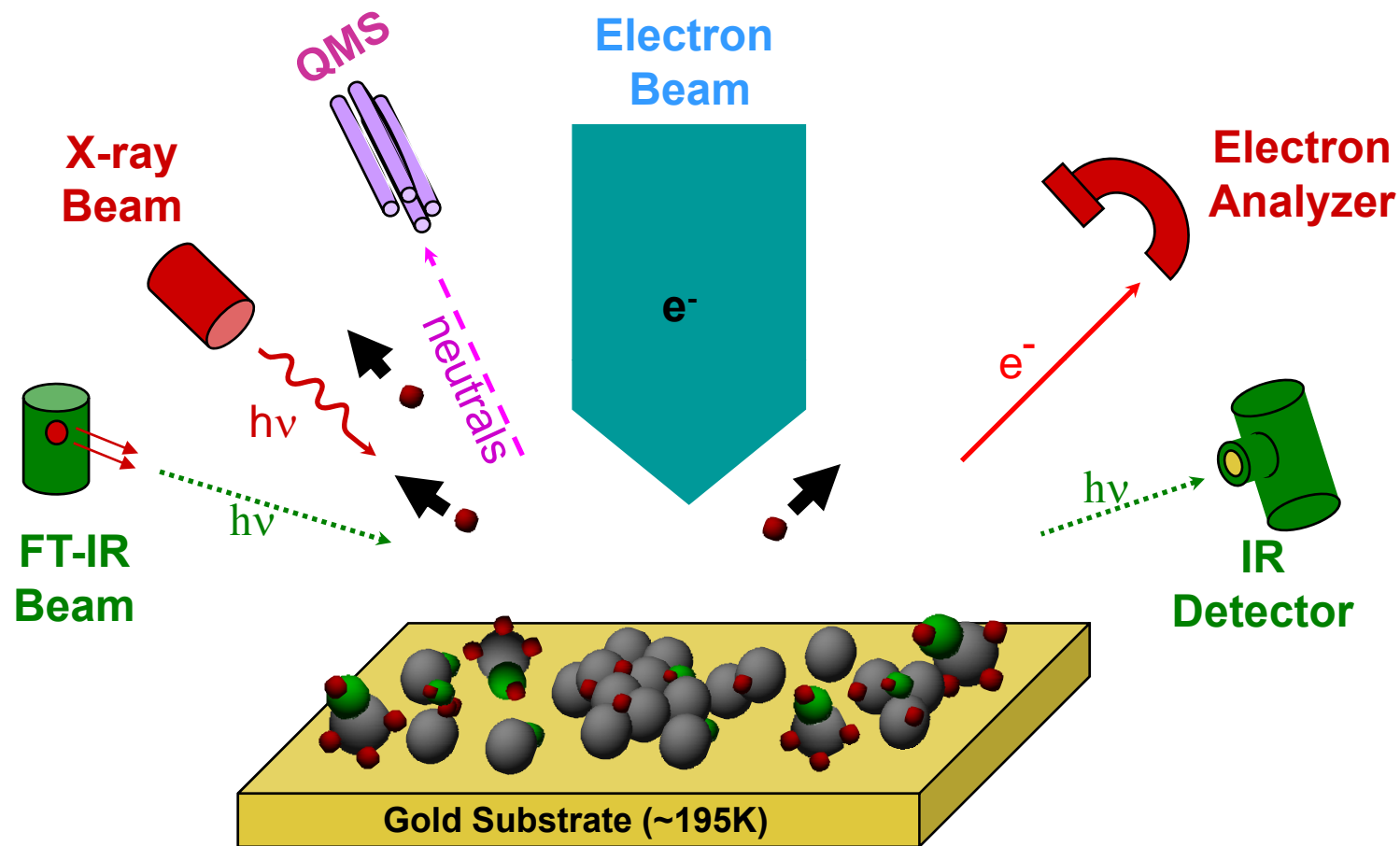
Electron Beam

- Broad and defocused (uniform irradiation)

Broad Beam Surface Irradiation



Instrumental Techniques



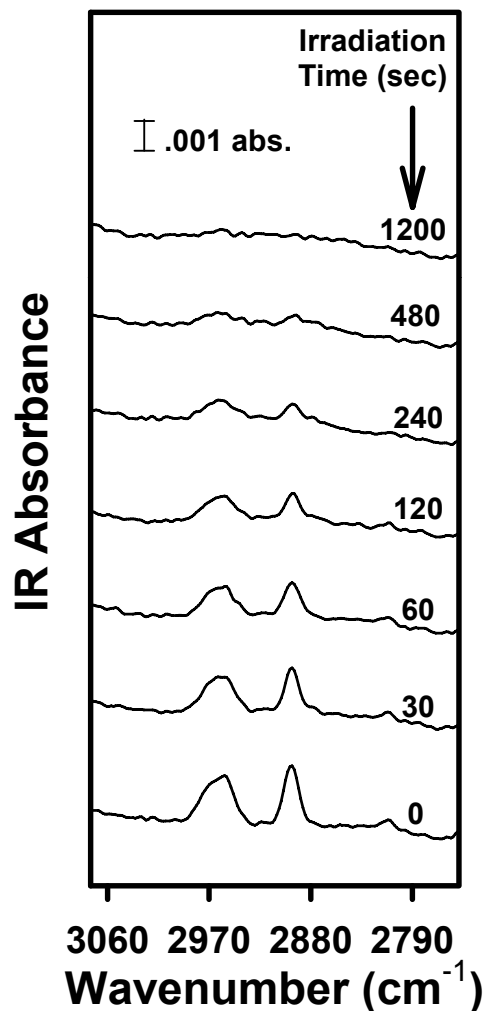
- We have studied the electron stimulated reactions of the well-known Pt precursor, Trimethyl(methylcyclopentadienyl)-platinum(IV), adsorbed onto gold using the above techniques:

Outline

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RAIRS Analysis of Dissociation Kinetics

- Time resolved *in situ* RAIRS analysis shows loss of $\nu(\text{C-H})$ intensity with increasing electron beam irradiation



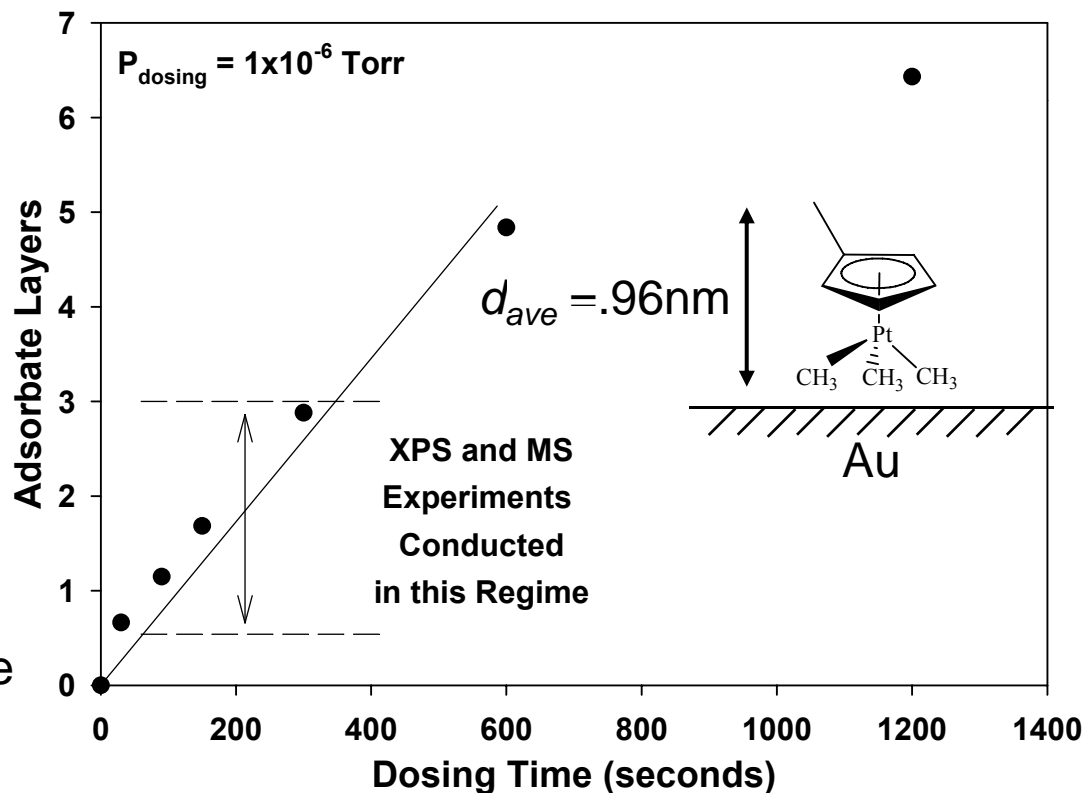
Adsorption of MeCpPt(IV)Me₃ onto Gold Substrate – Controlling film thickness

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

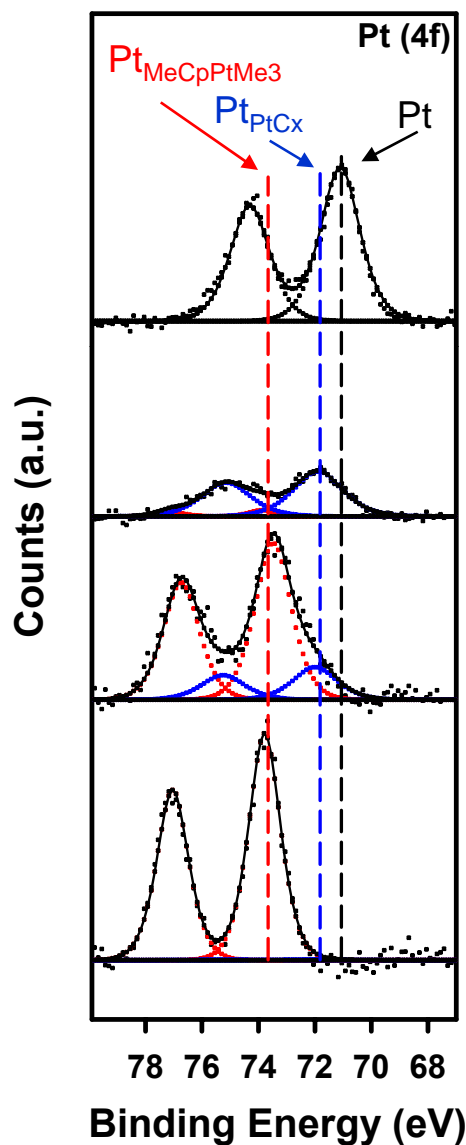
$$d = \lambda * \cos(\theta) * \ln\left(\frac{I}{I_0}\right)$$

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

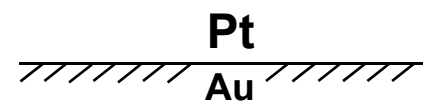
Influence of Dosing Time on Film Thickness



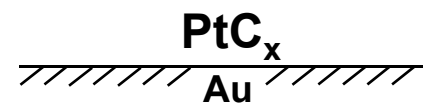
Production of Amorphous Platinum/Carbon Film



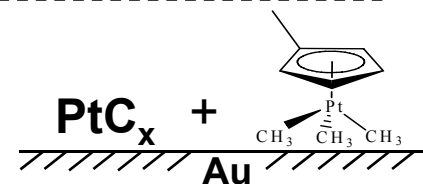
XP spectra of sputter deposited platinum on gold



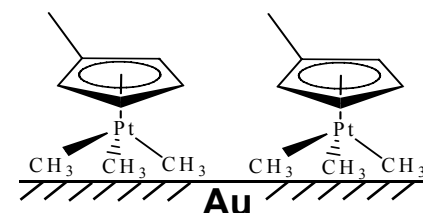
Substrate heated to room temperature leaving electron beam irradiation product



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



MeCpPt(IV)Me₃ adsorbed onto gold substrate (~195K)

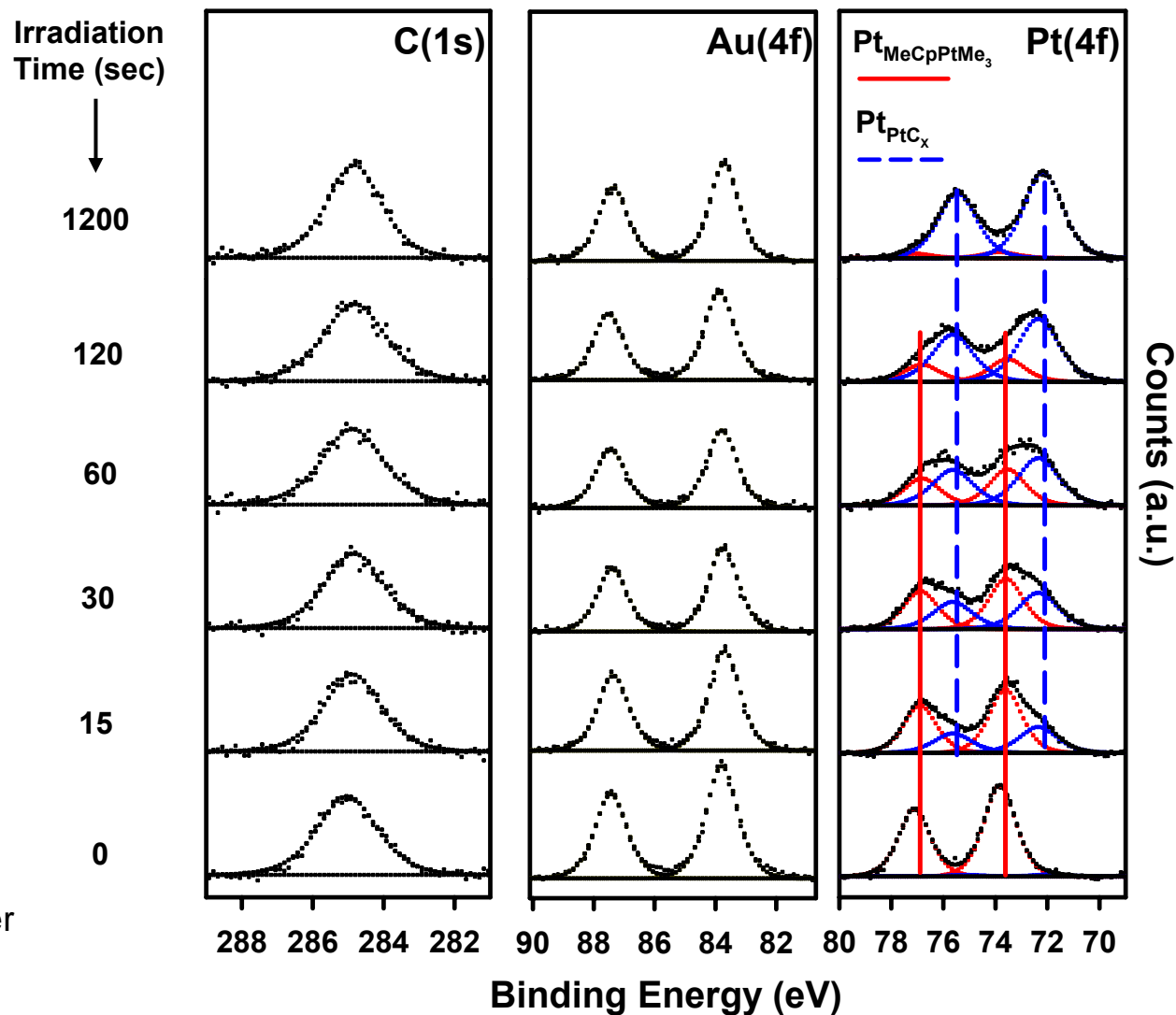


Influence of e^- Beam Irradiation on Surface Composition of Adsorbate Layer

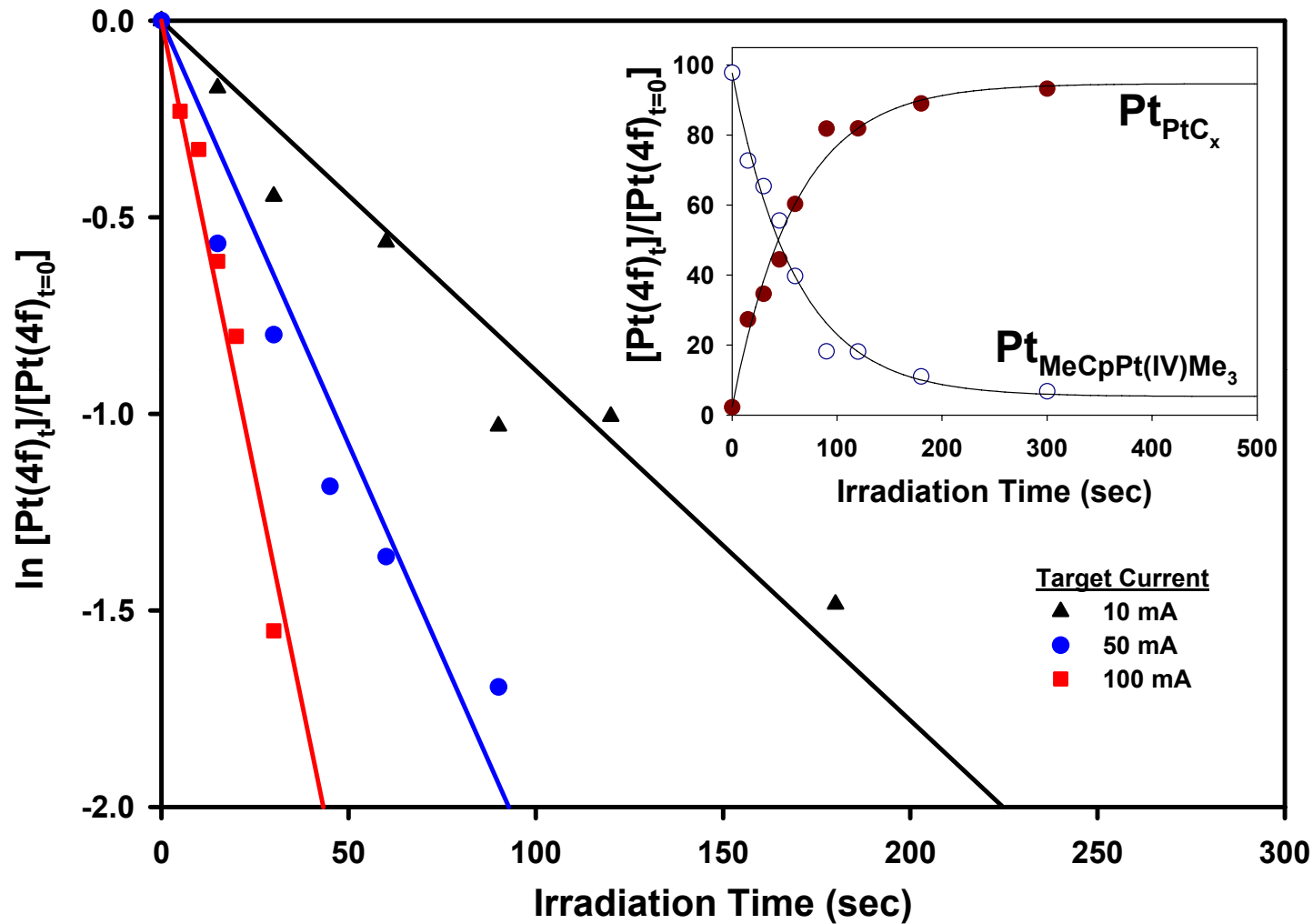
The XP spectra of the C(1s), Au(4f), and Pt(4f) regions shows:

- No loss of platinum from surface
- Shift in platinum environment from precursor to product

MeCpPt(IV)Me₃ is stable under x-ray irradiation for >2hrs



XPS Analysis of Dissociation Kinetics

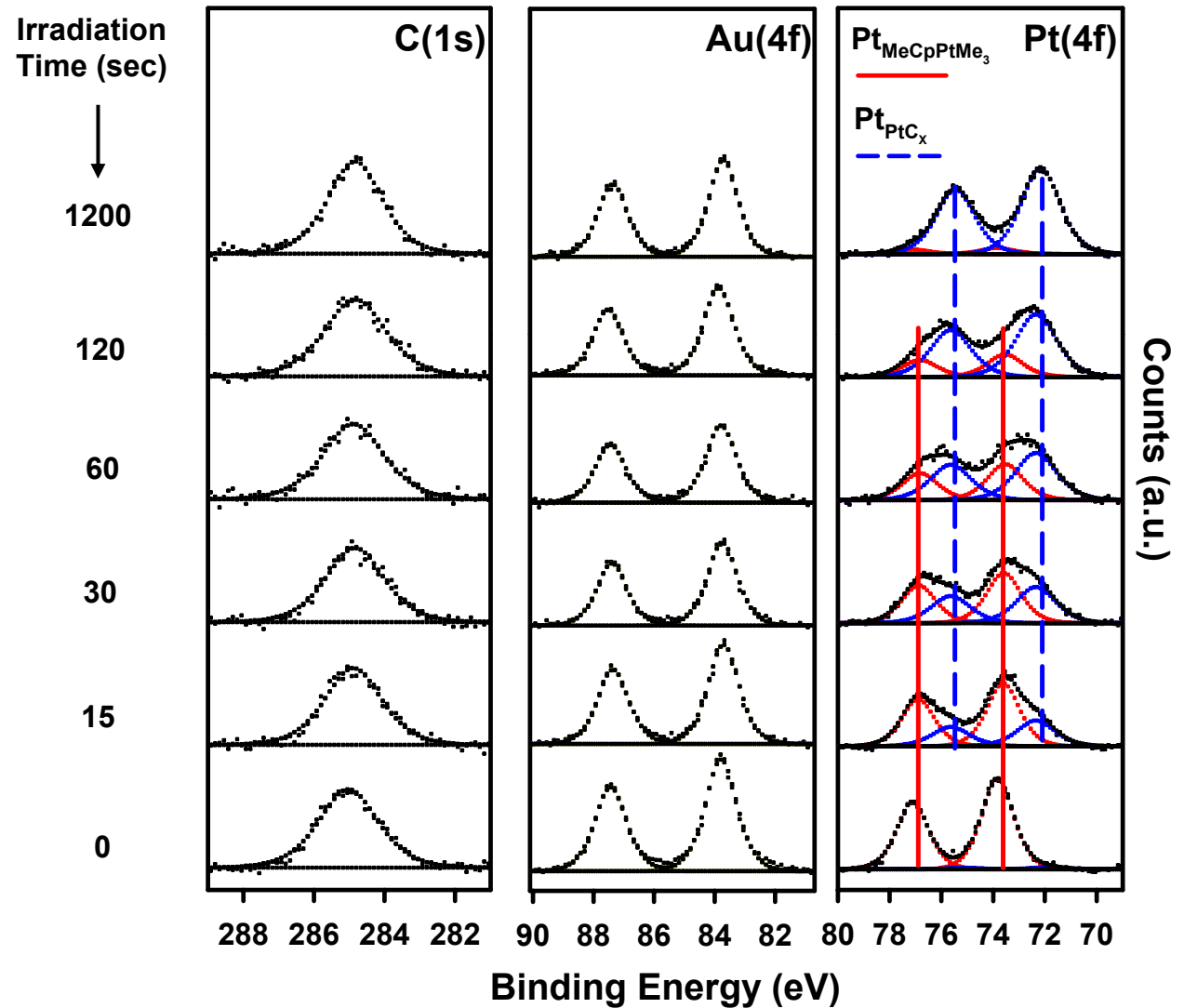


Quantification of the deconvoluted Pt(4f) region fit to exponential decay shows first order kinetics

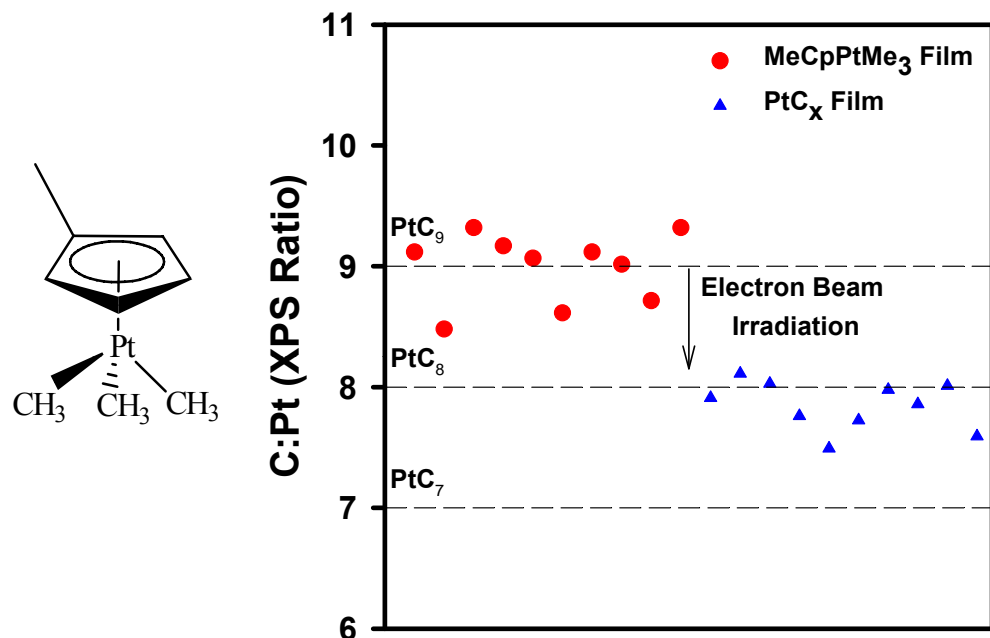
Decay profiles show that the observed rate constant increases with increasing target current.

Signal Resolution vs. Signal Intensity

- High resolution / low intensity emphasizes elemental environment
- 22eV Pass Energy



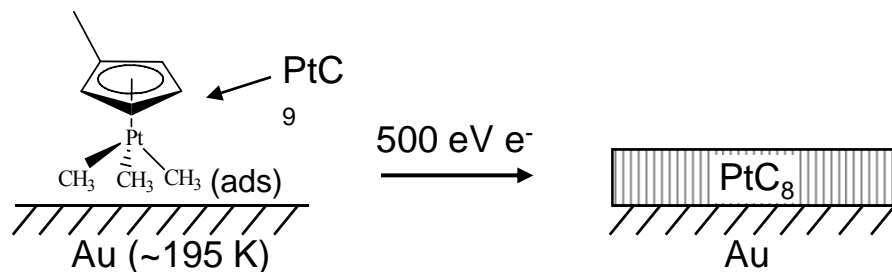
Carbon Loss During Irradiation



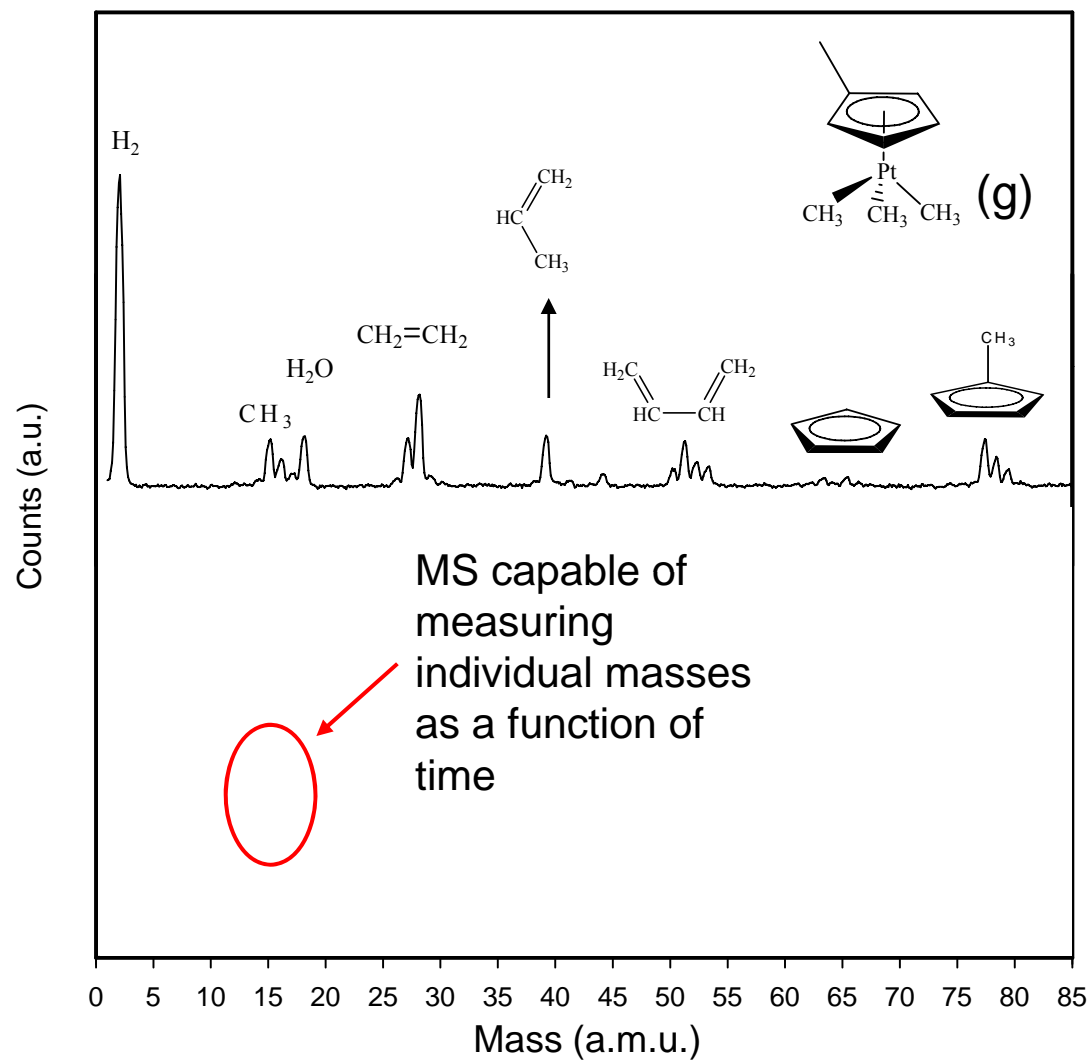
- The C:Pt ratio of 10 XP spectra of the MeCpPt(IV)Me₃ prior to e⁻ beam irradiation is representative of the initial stoichiometric ratio of 9 carbon atoms to 1 platinum atom

The stoichiometric loss of 1

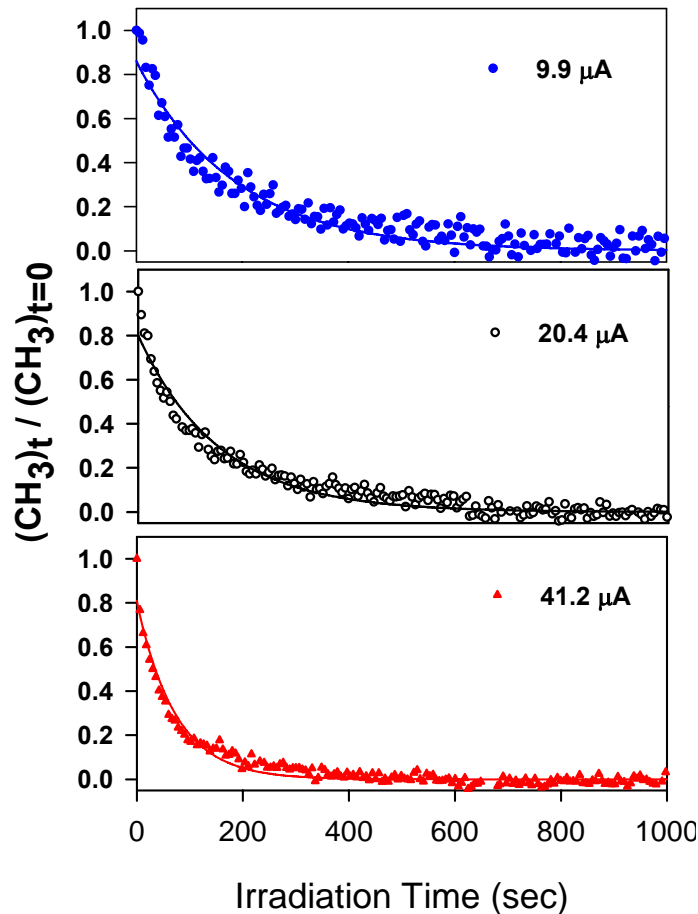
- The C:Pt ratio after e⁻ beam irradiation is independent of film thickness, indicating the loss of 1 carbon atom per molecule as a result of irradiation



Gas Phase Products Analysis

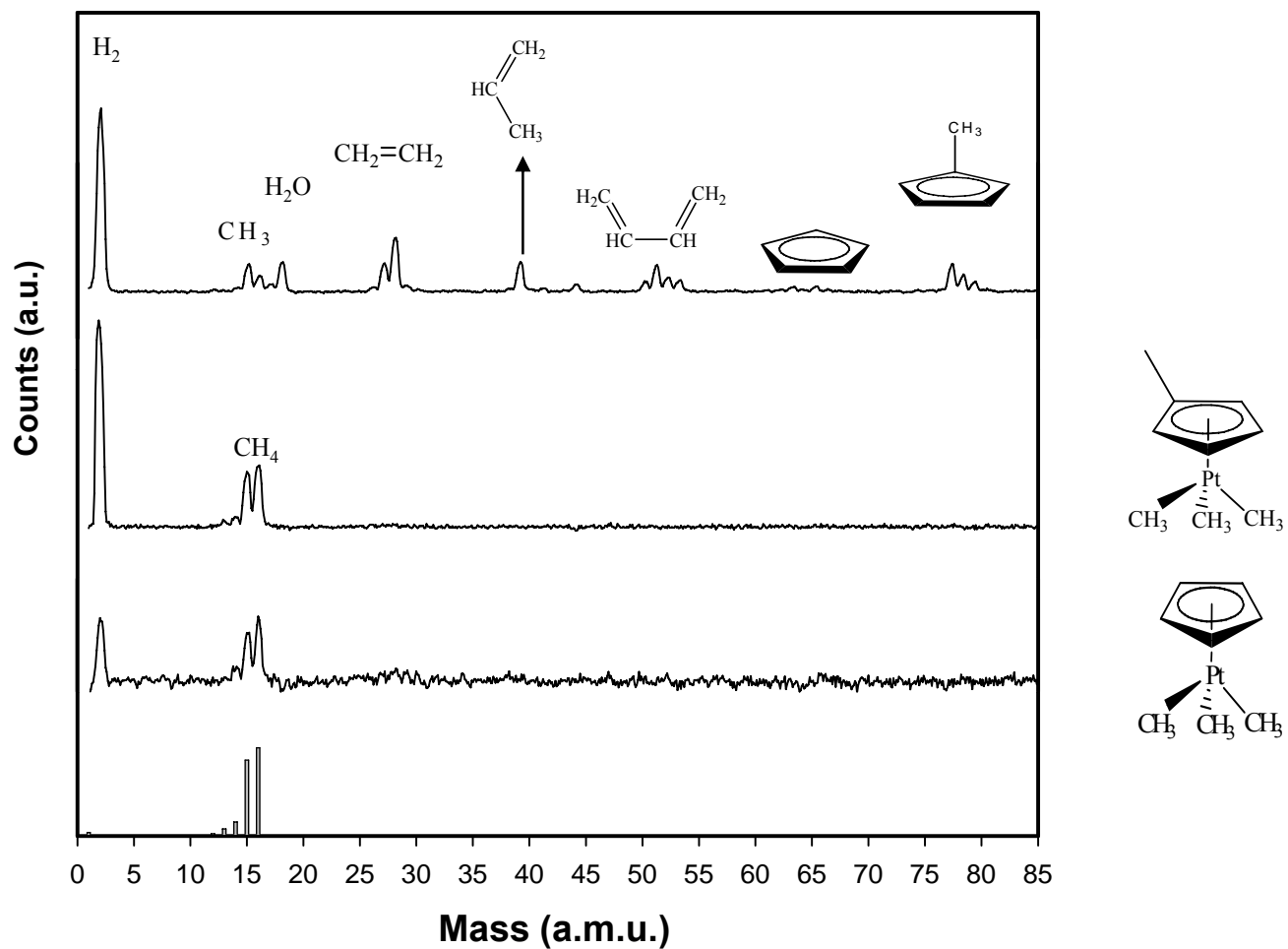


Kinetic Analysis of Methane Production



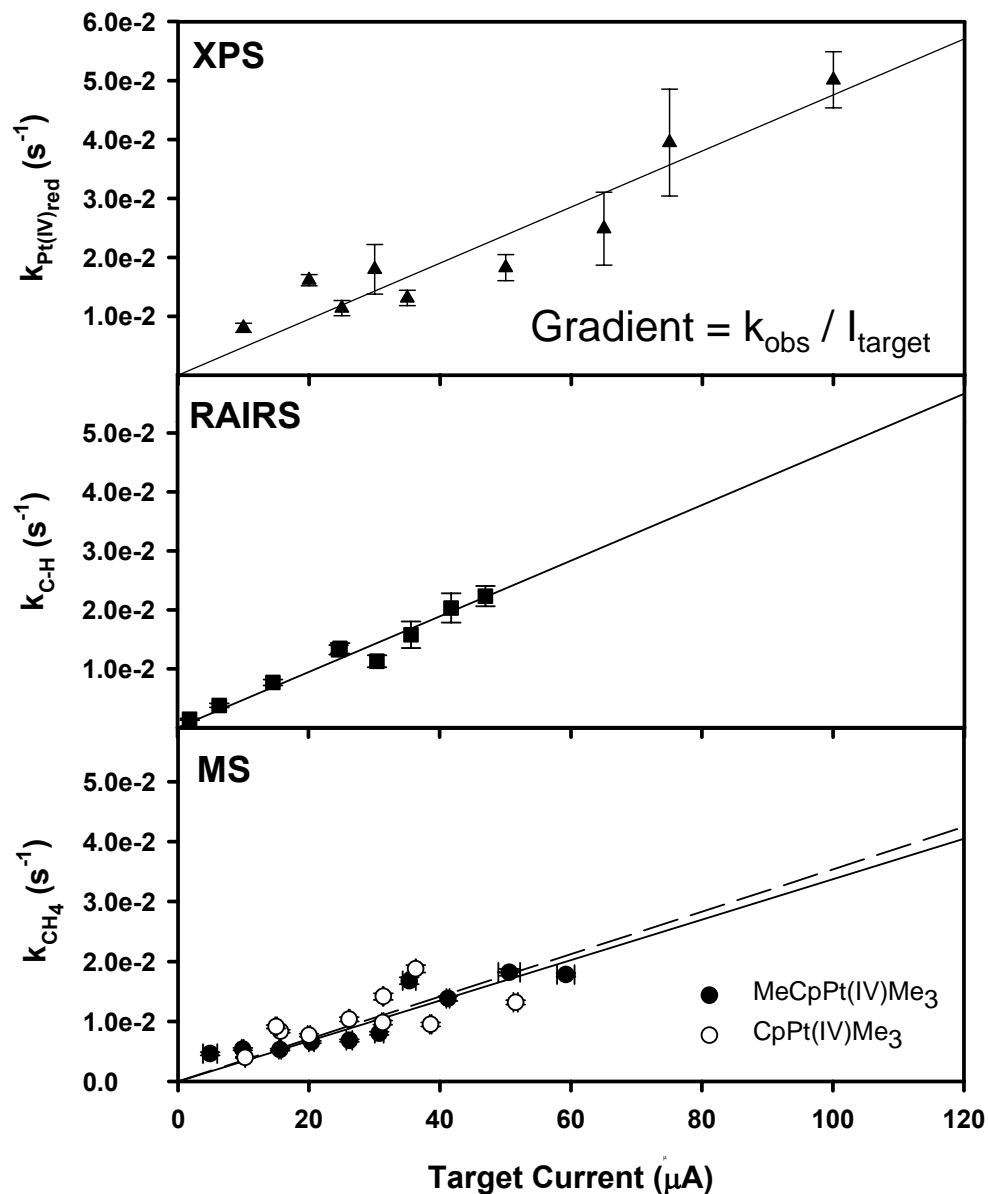
- Tracking methane production during electron beam irradiation fit to exponential decay
- $m/z = 15$ is a unique mass representative of methane
- Methane loss fit to first order kinetics indicates an increase in the observed rate constant with increasing target current

Dissociation by Pt-CH₃ Cleavage



Analogous compound decomposes via production of identical gas phase products

Complementary Techniques



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

	(σ) cm ²
XPS	1.37E-16
RAIRS	4.32E-16
MS (MeCpPtMe ₃)	9.75E-17
MS (CpPtMe ₃)	1.02E-16

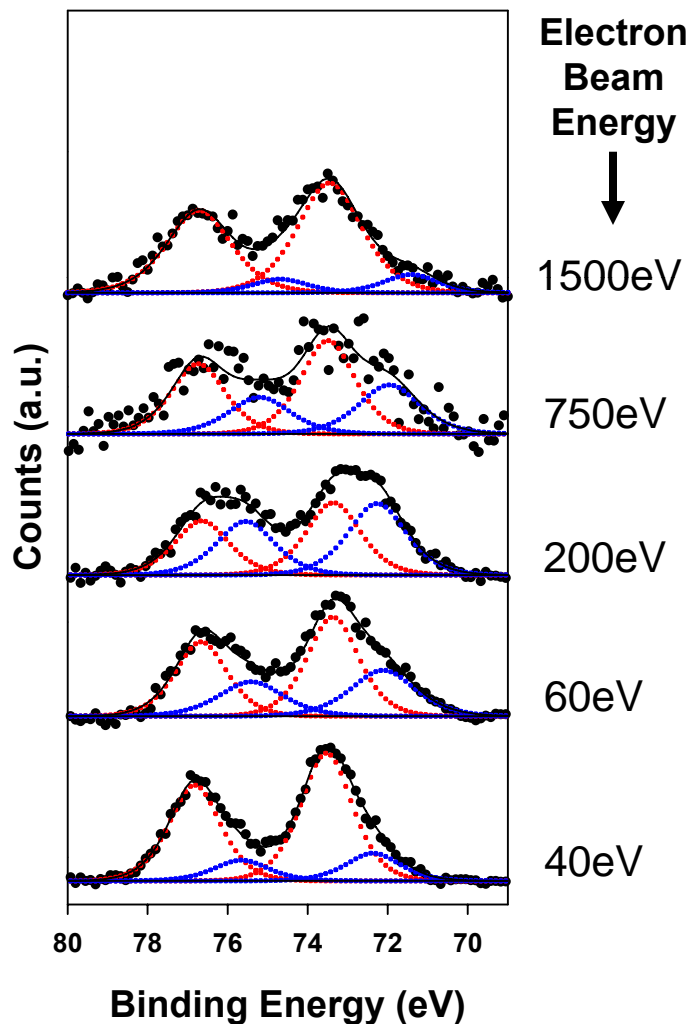
$$\sigma_{ave, 500eV} = 2.2 \text{ E-16 cm}^2$$

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

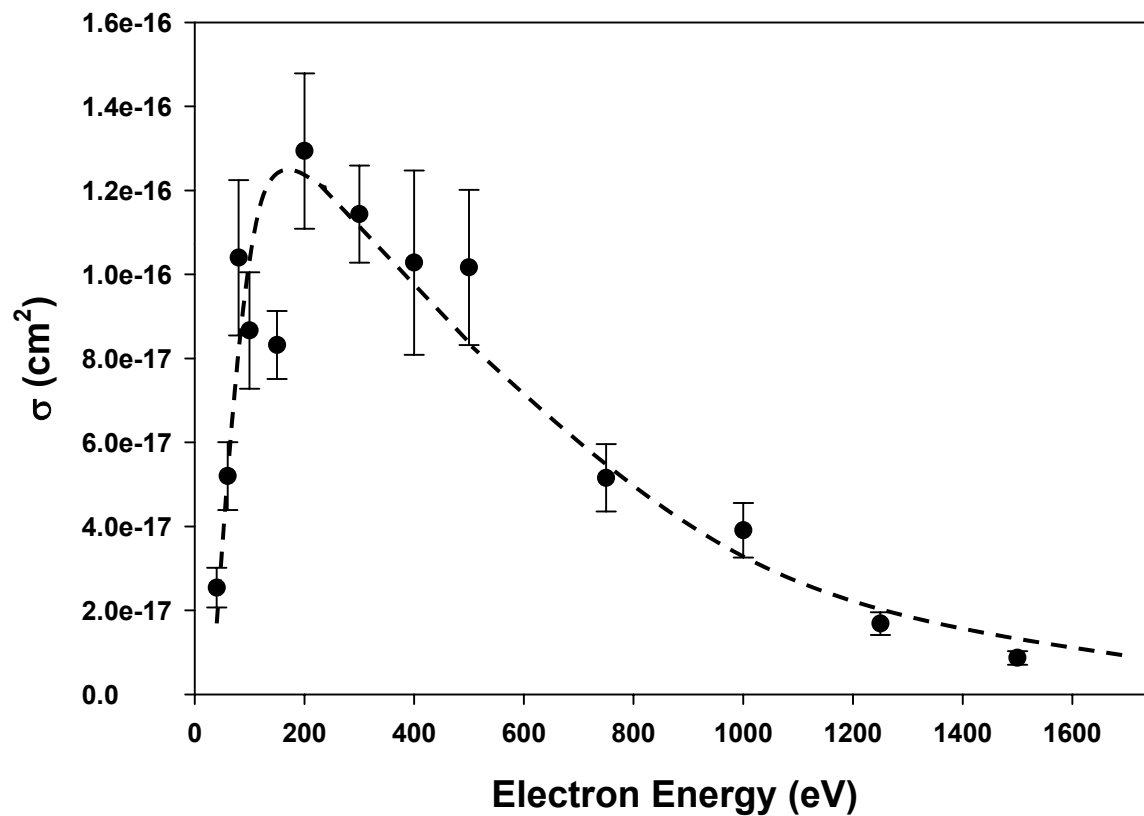
Outline

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Dependence on Incident Electron Energy Observed Using XPS

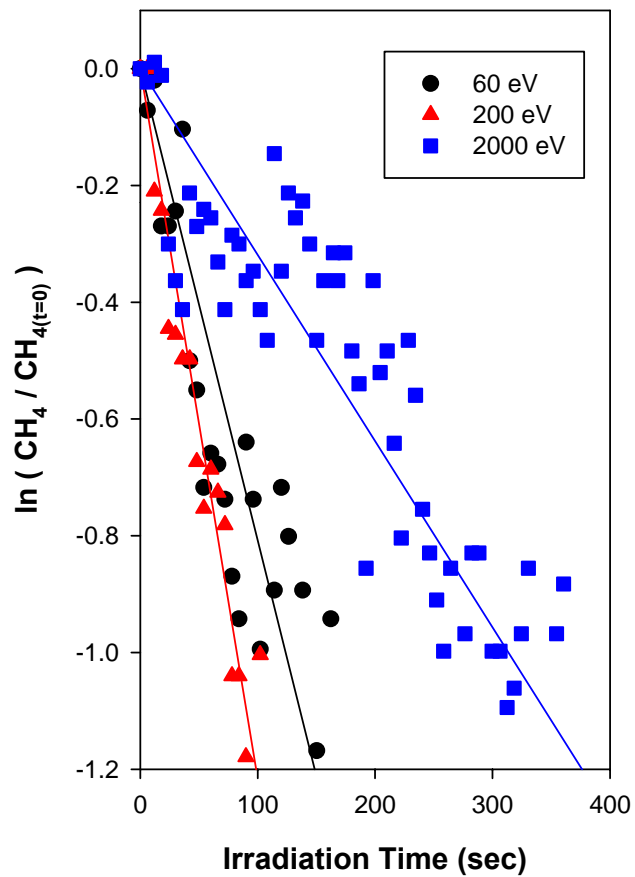


Above XP spectra: 25 μ A, $t=60$ sec

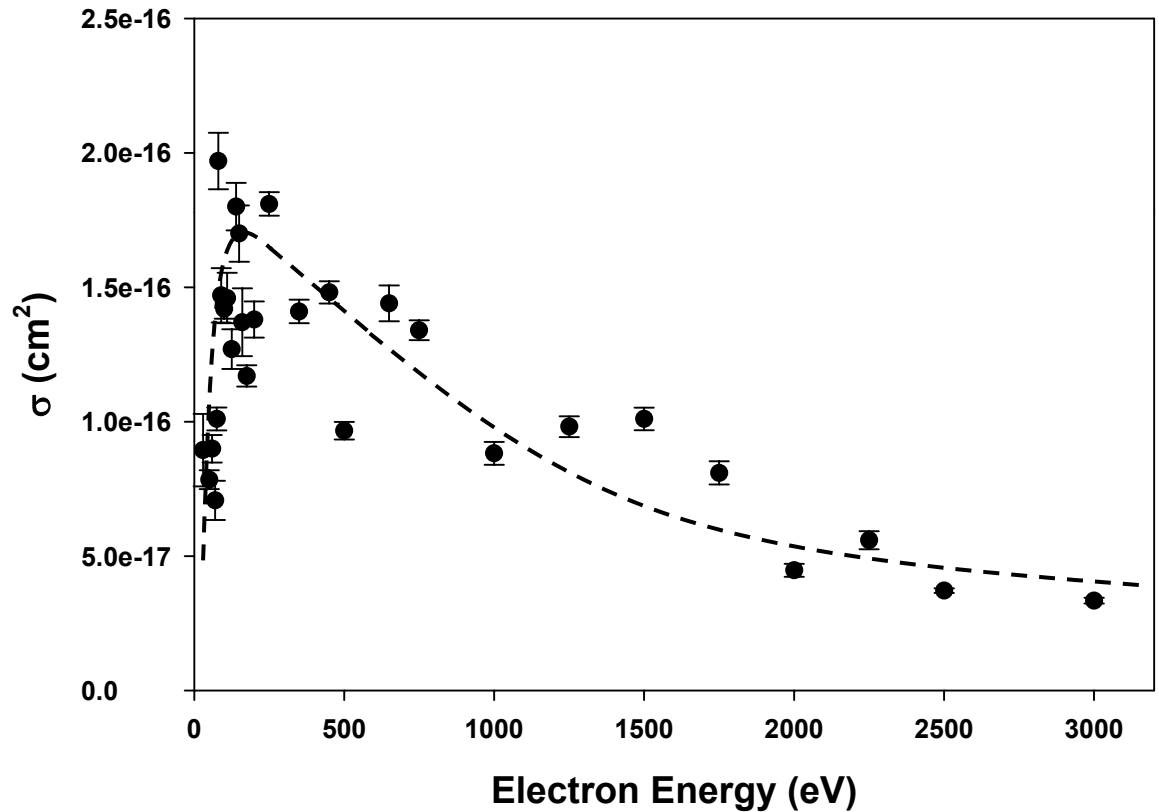


Optimal σ between 100-200eV suggests electron impact ionization process

Dependence on Incident Electron Energy Observed Using MS



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

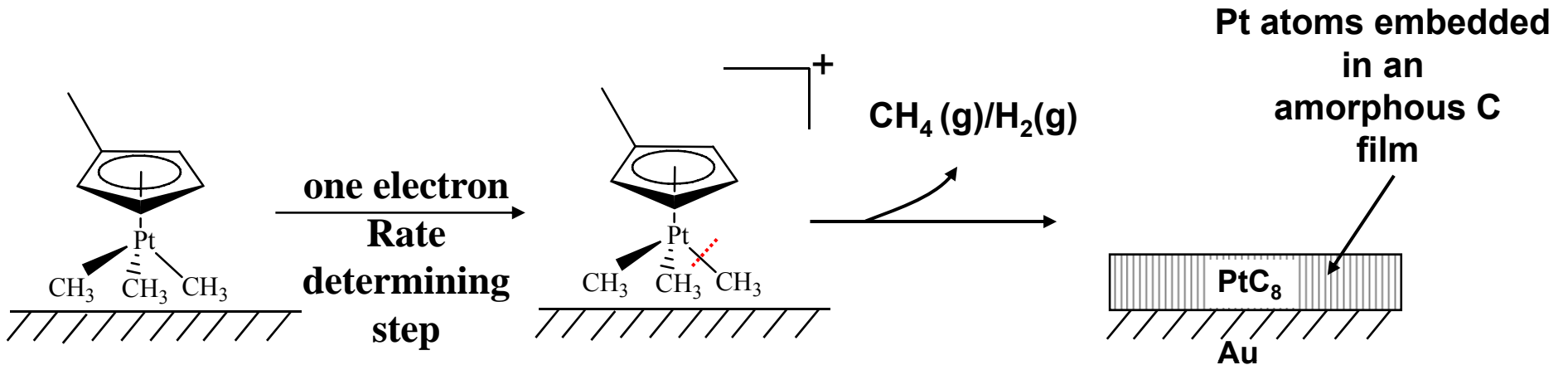


MS supports XPS results

Outline

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- **Summary**

Summary



- Electron beam irradiation of surface adsorbed MeCpPt(IV)Me₃ 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 provide valuable information on reaction rates and fundamental chemical processes involved in EBID

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

(b) Analysis of desorbing species

Simple
reasonable quantification

Decomposition may compete with desorption

Indirect monitor of surface processes

IR (reflection)

Parent can easily be monitored

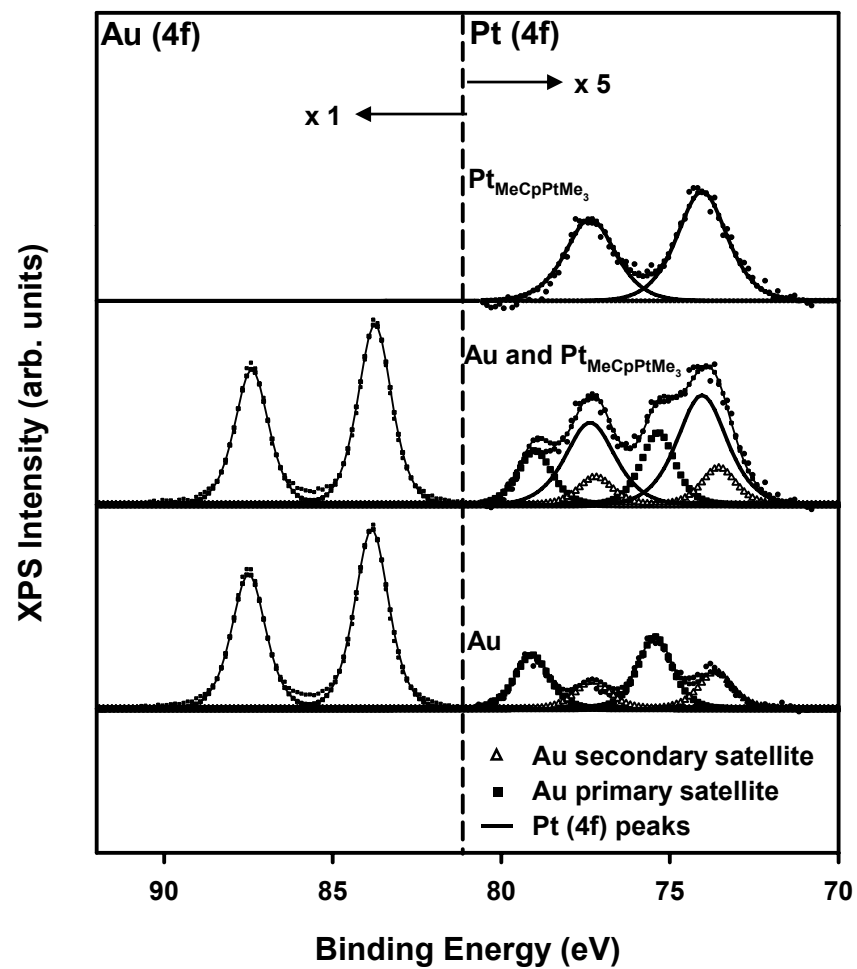
Poor Sensitivity
Modest Quantification

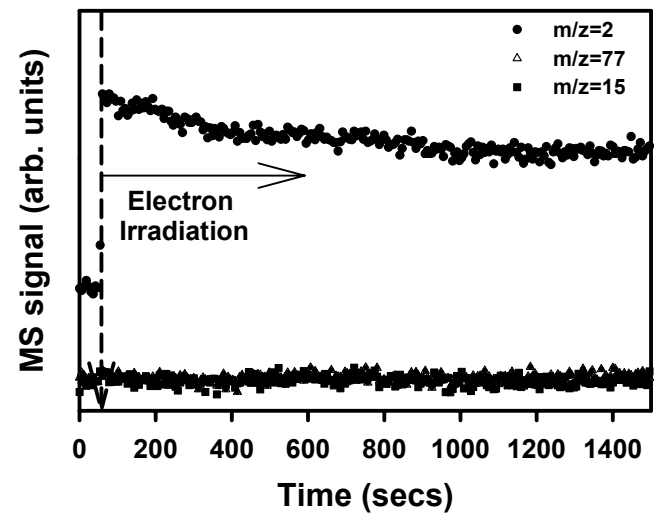
Acknowledgements

- Howard Fairbrother, Johns Hopkins University
- Justin Gorham, Johns Hopkins University
- Samantha Rosenberg, Johns Hopkins University
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- Shimon Zalkind, Rutgers University
- Boris Yakshinskiy, Rutgers University
- Ted Madey, Rutgers University
- Kees Hagen, Delft University of Technology

Thank you

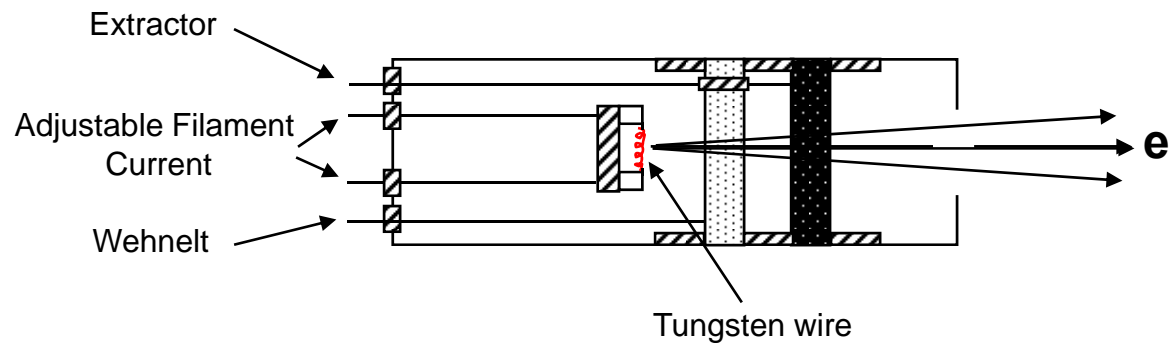
Solution to Au satellites





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)

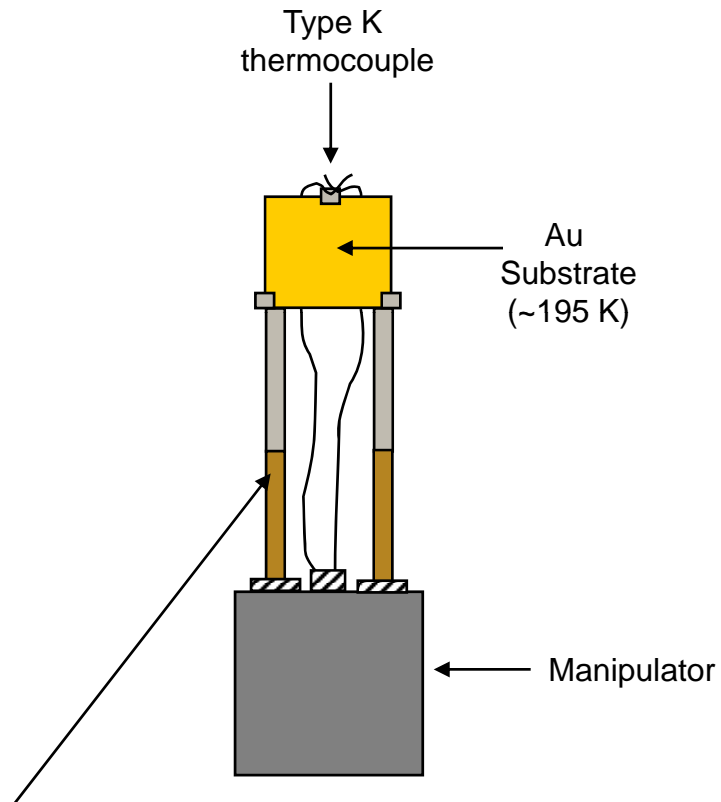


Electron Flood Gun can produce:

(a) 40 - 500 eV electrons

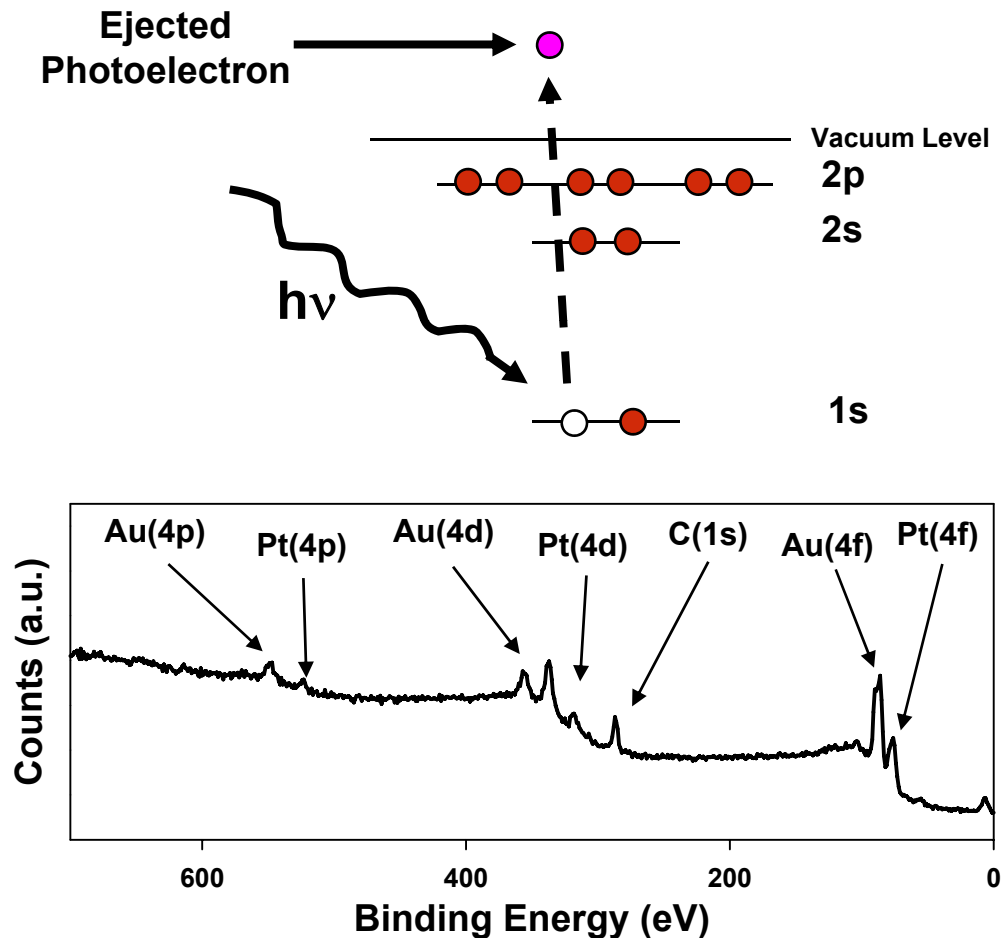
(b) 5 -150 μA target currents

Sample

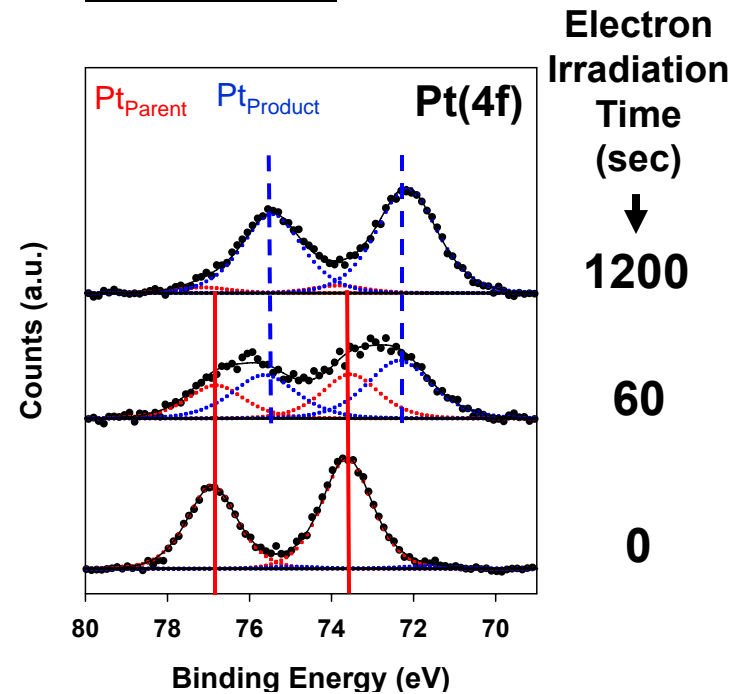
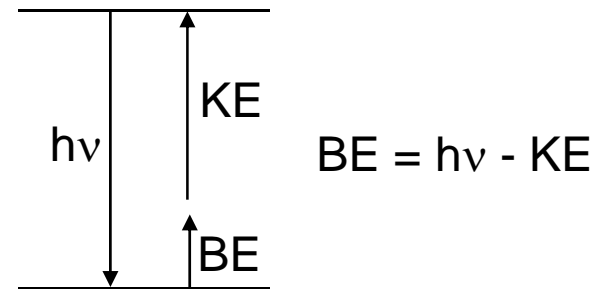


Cu leads provide for heating and cooling
(100K-450K)

X-ray Photoelectron Spectroscopy (XPS)

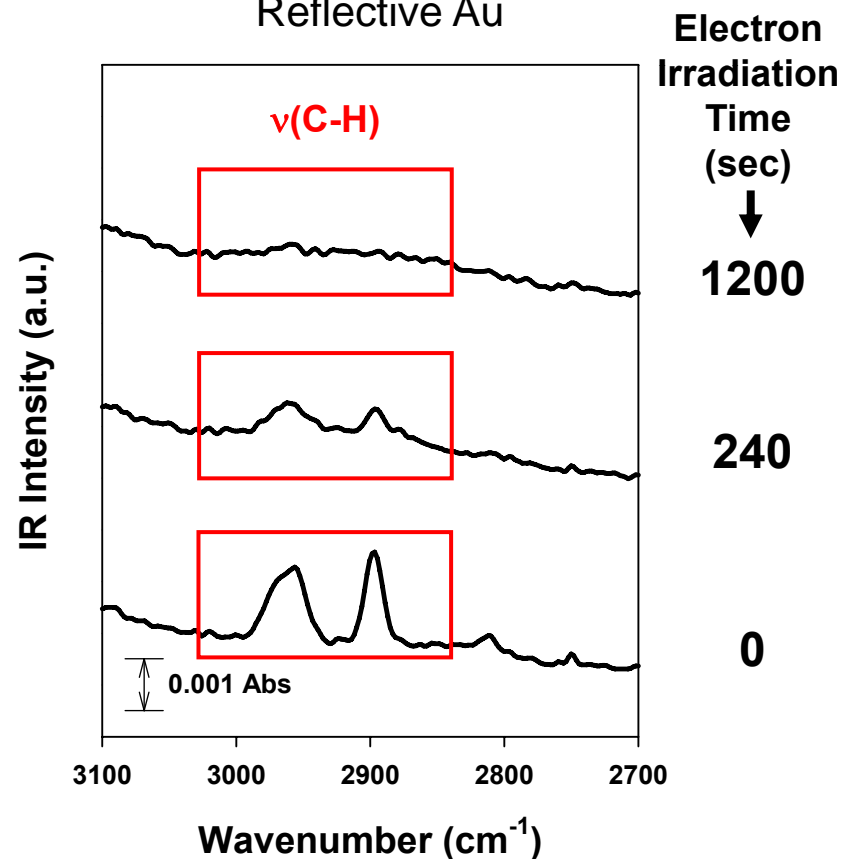
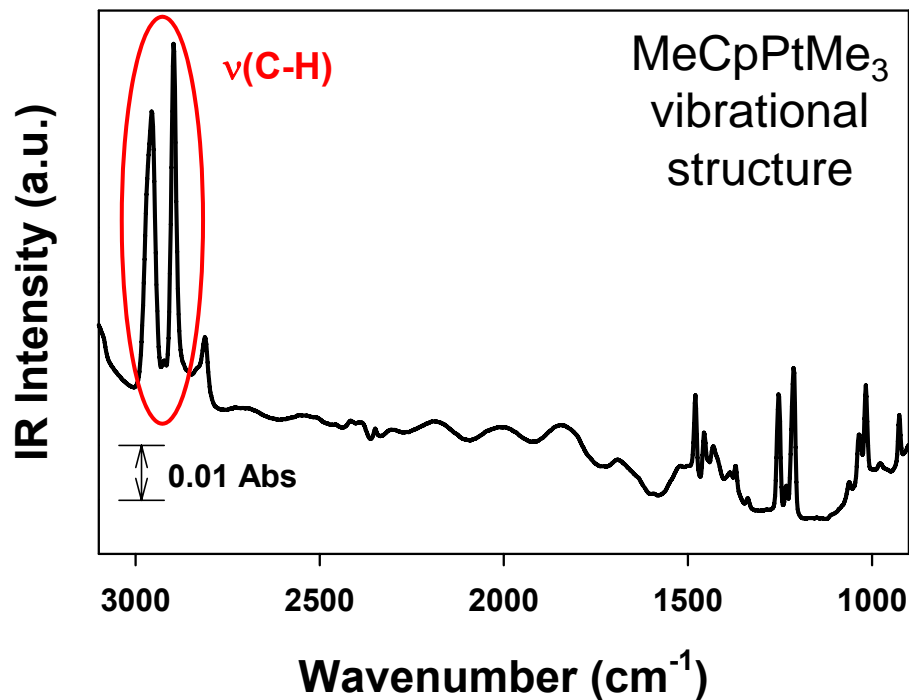
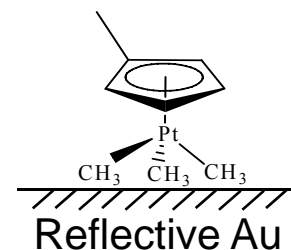
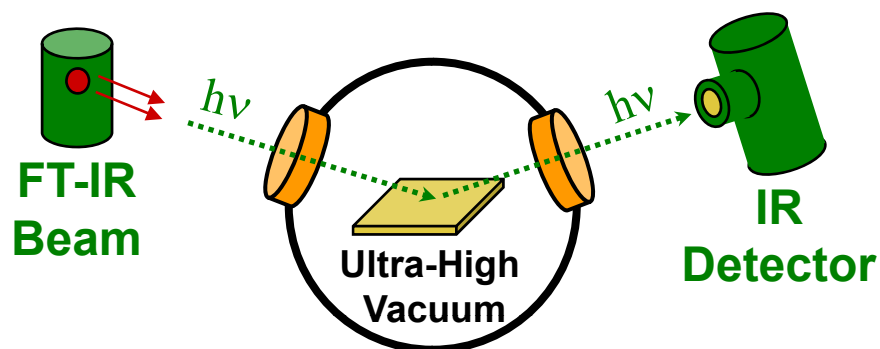


XPS enables quantitative determination of chemical composition and effective oxidation state



Reduction of Pt indicated by peak shift to lower BE

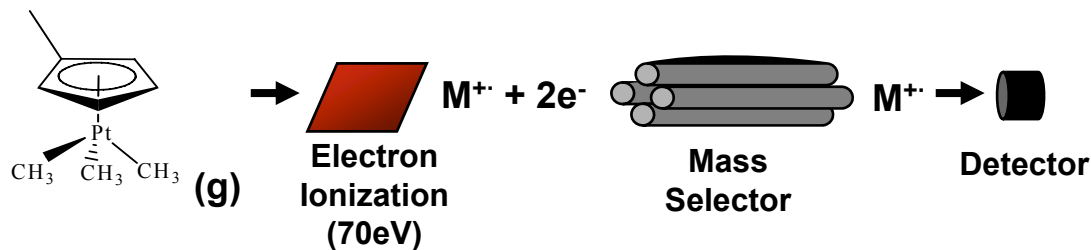
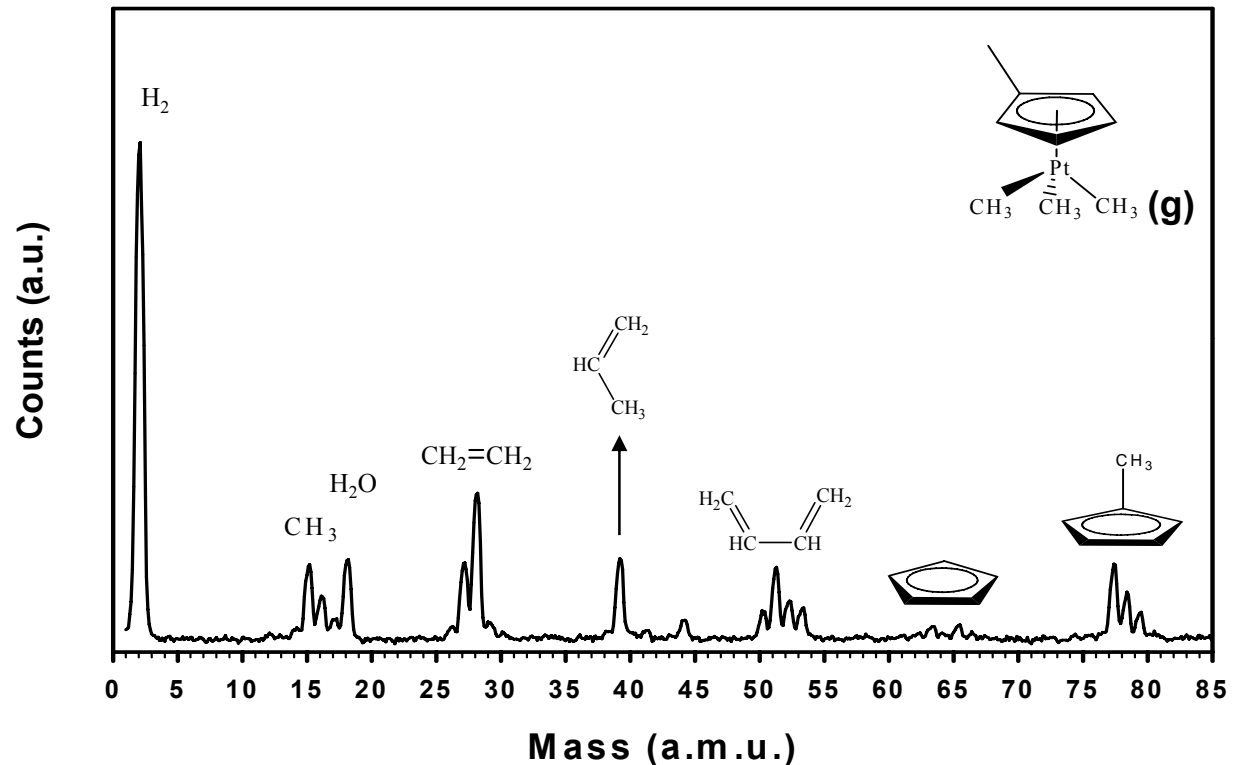
Reflection Absorption Infrared Spectroscopy (RAIRS)



Mass Spectrometry (MS)

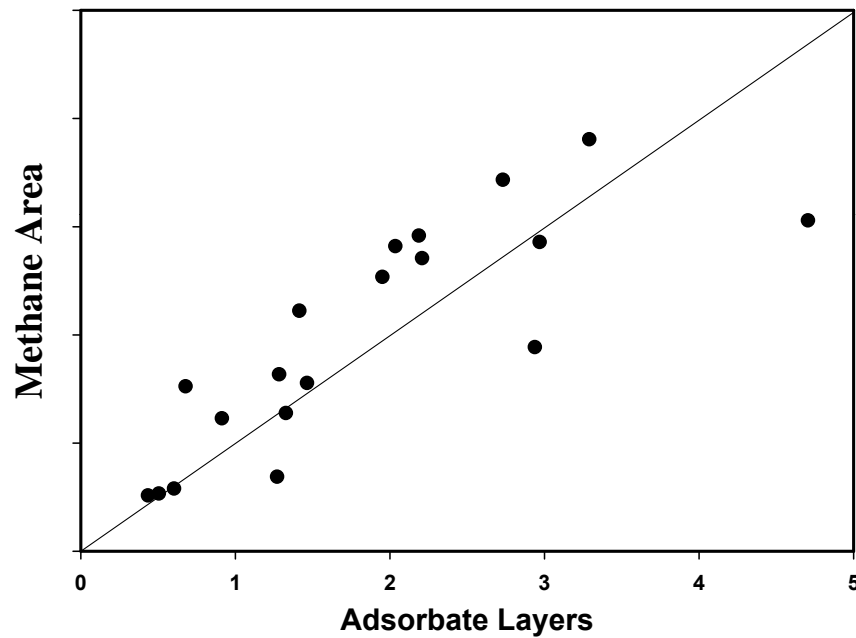
MS was used to:

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

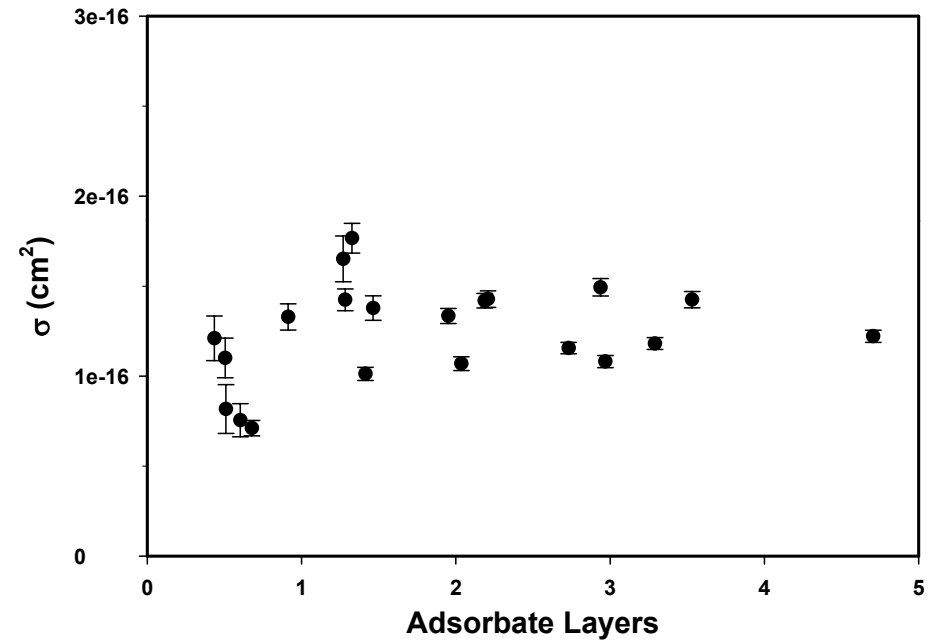


Electron bombardment within the MS creates ionized fragments representative of species present in the gas phase

How does Film Thickness Influence the Process?

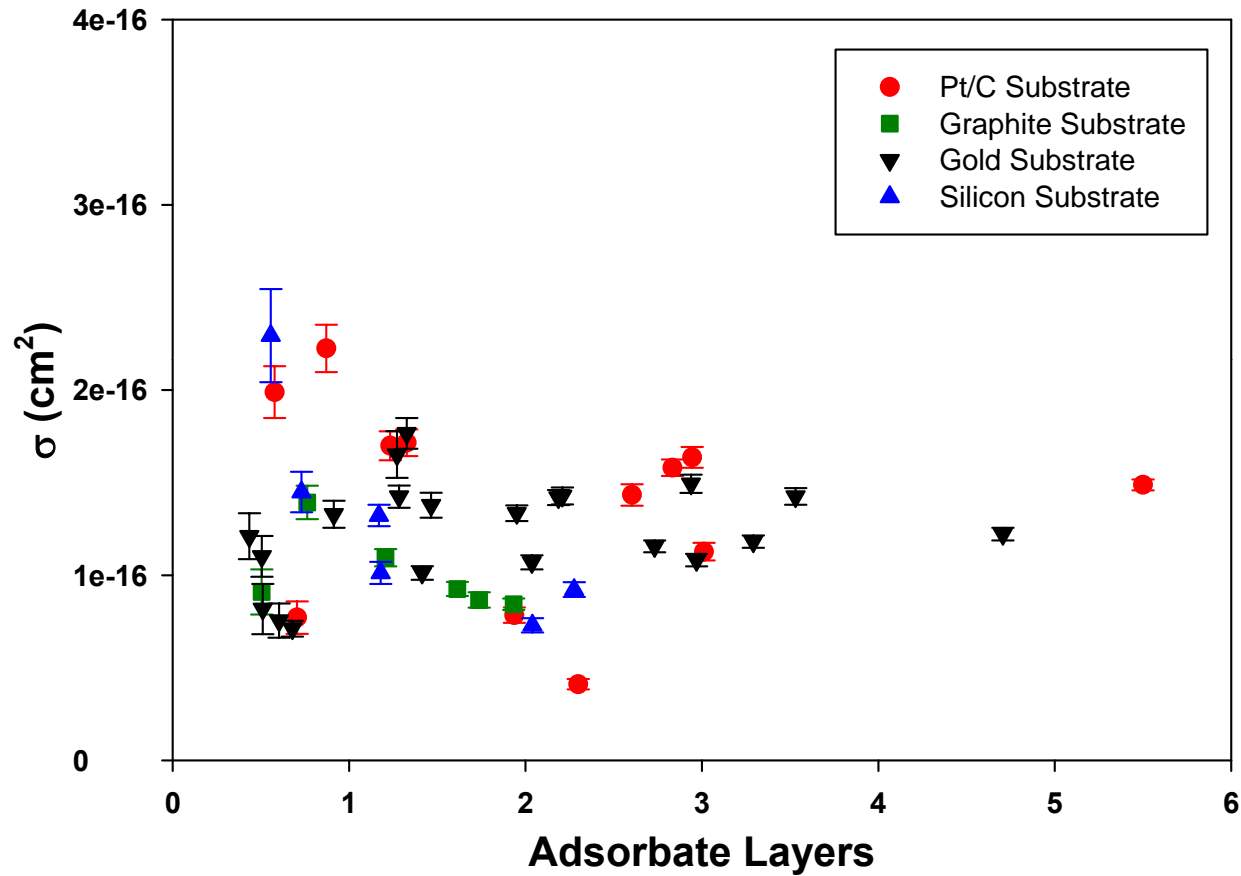


Methane area independent of film thickness



σ independent of film thickness

Substrate Dependence?



NO

All experiments conducted at $\sim 195\text{K}$ with $20\mu\text{A}$ target current and 200eV electron energy