A Two Step Dissociative Ionization and Desorption Mechanism for Water Ion Cluster Emission from a Pt Field Emitter Tip

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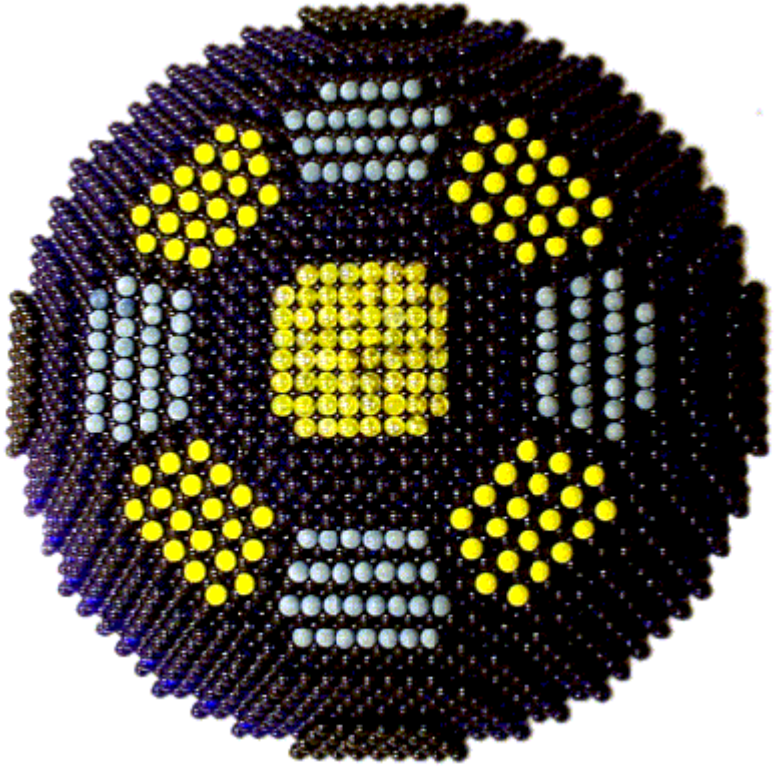

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OVERVIEW

EXPERIMENTAL INTENT

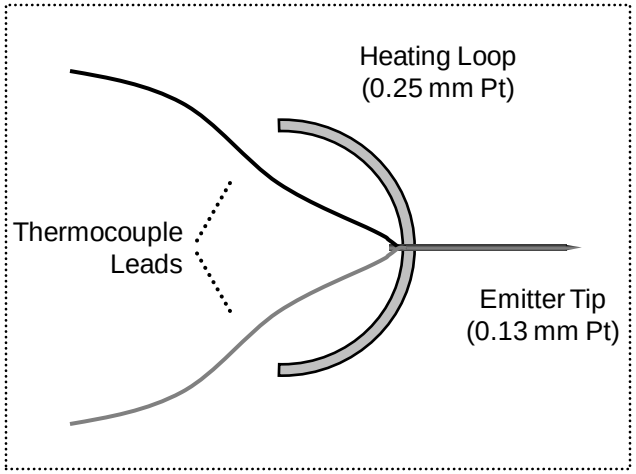
- Study Behavior of Water in High Electric Fields
  - Electrochemical Interfaces (Pt)
  - Double Layer
  - Basic Water Energetics
- Proton Solvation
- Mechanisms for Ionization

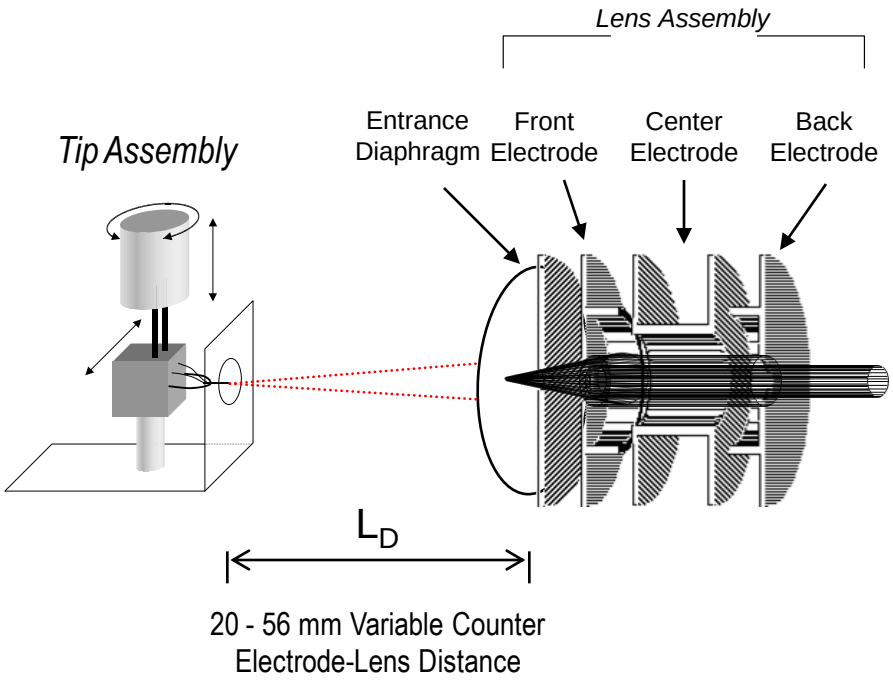
OUTLINE OF DISCUSSION

- Experimental Apparatus and Methods
- 2-Step Ion Dissociation and Emission Mechanism for Protonated Water Clusters
  - Mass Resolved Ion Cluster Formation
    - Field Dependence
    - Temperature Dependence
  - Separation of Dissociation and Emission
  - Role of Proton Solvation
  - Cluster Formation Mechanism

EXPERIMENTAL SETUP

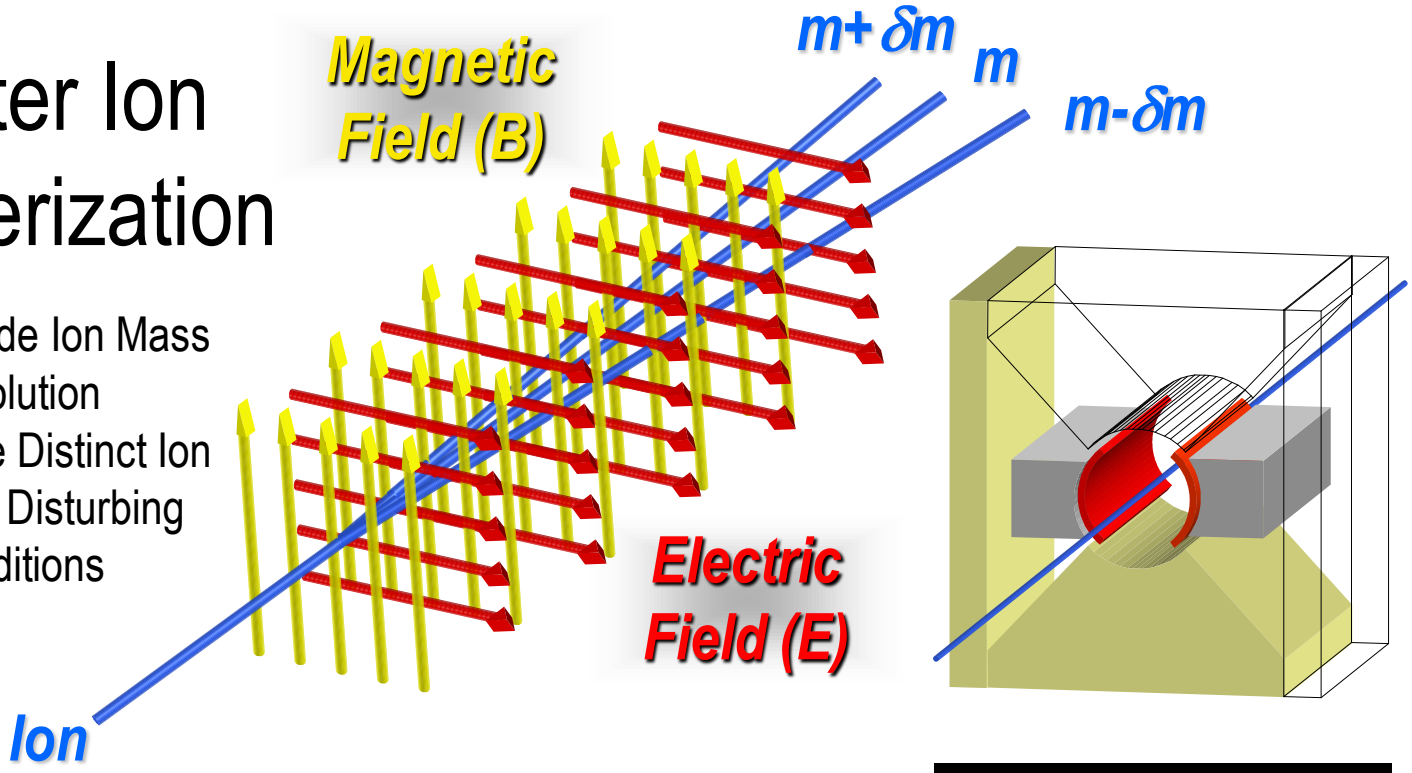
- Pt Field Emitter Tip
  - In UHV 10 $^{-10}$ Torr
  - Radius ~ 350 Å
  - Potential 0 – 5000 (+ or -) V
- Counter Electrode
  - Potential 0 – 5000 (+ or -) V
  - Fields > 4 V/ Å
- Field Desorption Spectroscopy
  - Application of H_2O to Tip Surface
    - Ice Deposition < ~ 150 K
    - Field Adsorption > ~165 K
  - Uniform Tip Potential 3000 V
  - Set CE Potential for Field
  - Emitted Ions
    - Focused w/ Einsel Lens
    - Mass Resolved w/ Wien Filter

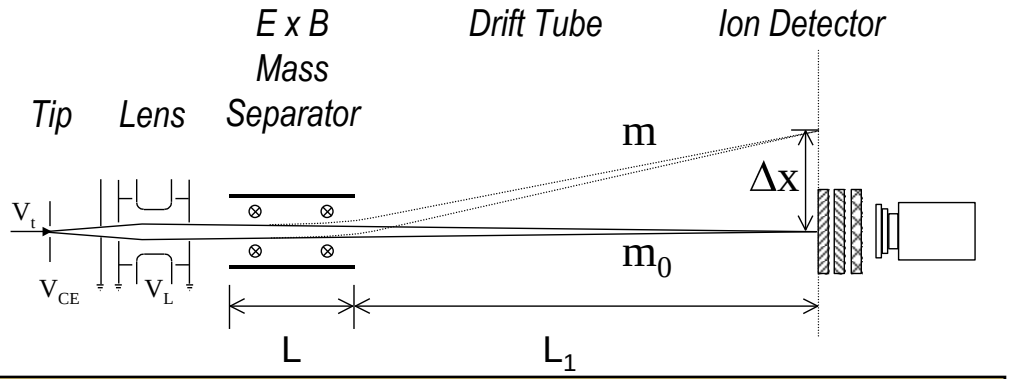




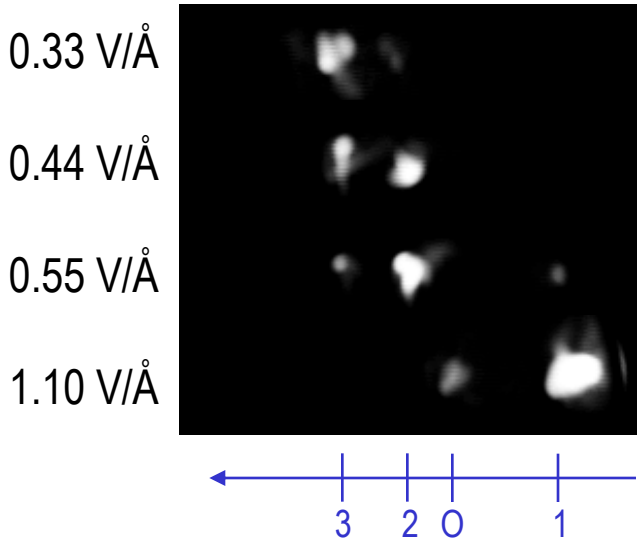
Wien Filter Ion Characterization

- Continuous Mode Ion Mass to Charge Resolution
- Easily Separate Distinct Ion Signals without Disturbing Formation Conditions





$$eE_0 = e\nu B_0 \qquad E_0 = B_0\sqrt{\frac{2e\phi_0}{m_0}} \qquad \Delta x = \frac{E_0}{2\phi_0}\left[\frac{L^2}{2} + LL_1\right]\left(1-\sqrt{\frac{m_0}{m}}\right)$$

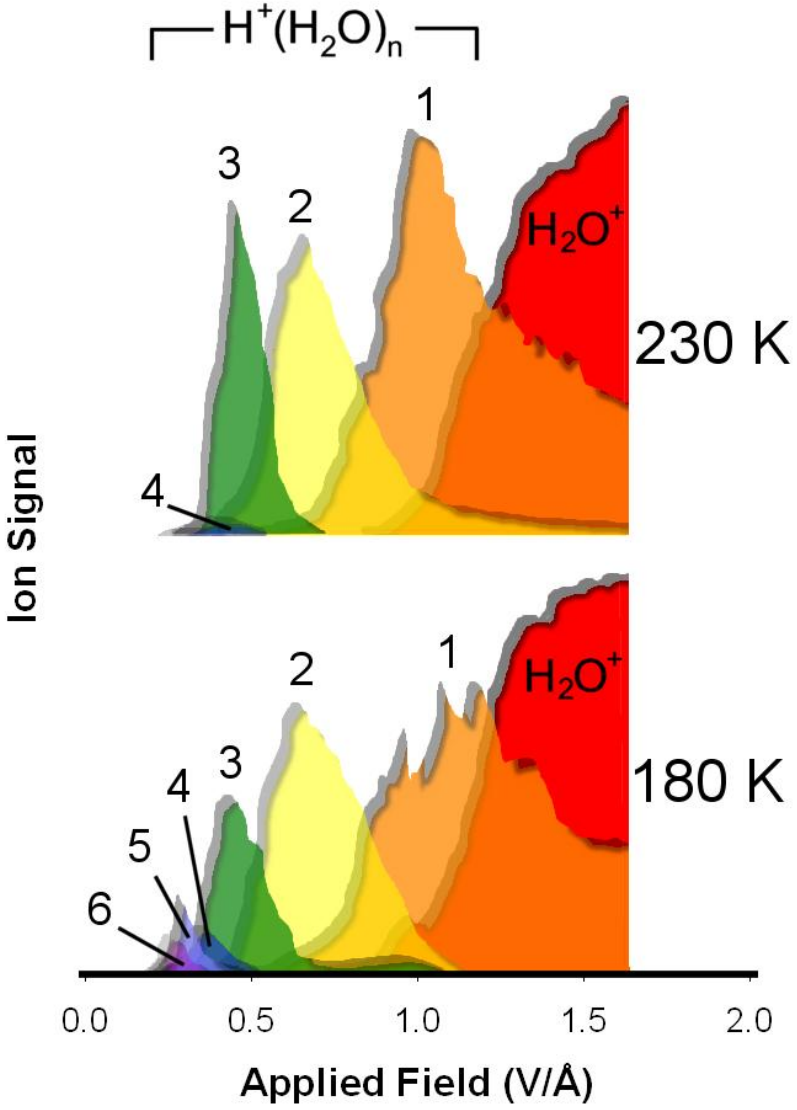


$H^+(H_2O)_n$ Separation by Field

Lens: G.F. Rempter, J. Appl. Phys. **57** (1985) 2385.

E x B Mass Separator: M. Kato and K. Tsuno, Nucl. Instr. Methods **A298** (1990) 296.

Mass Resolved Water Ion Cluster Formation

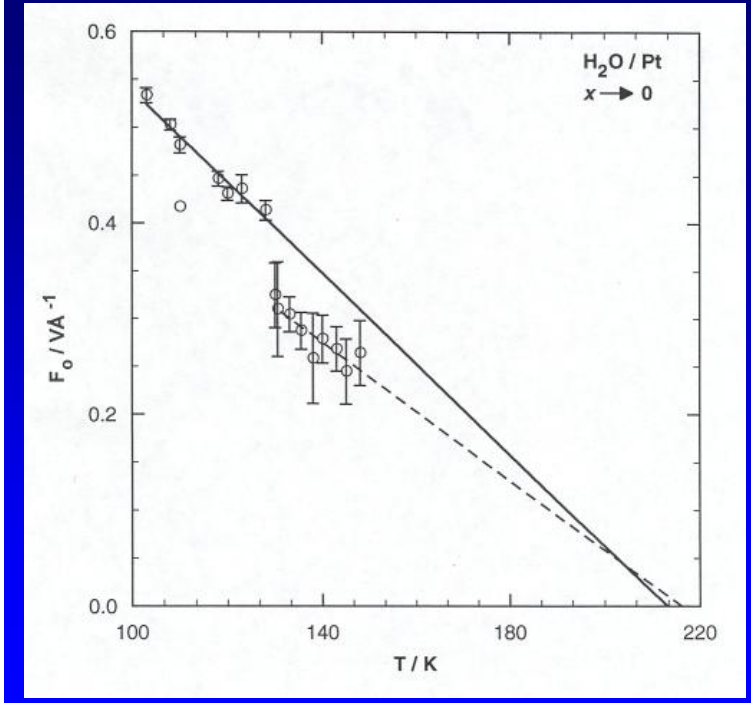


PROCEDURE

- Wien Filter tuned to selected $H^+(H_2O)_n$
- P_{H20}= 5*10^{-6} Torr
- V_{tip} set to 3000V; V_{CE} ramped 3000V to 0V at 10V/s

RESULTS

- Ion Cluster Emission
  - Low Field: Large *n* Clusters (Energetically Favorable)
  - High Field: Small *n* Clusters (Kinetically Favorable)
- Temperature Dependence
  - Onset not Temperature Sensitive
  - High *n* Clusters not Present at Higher Temperatures

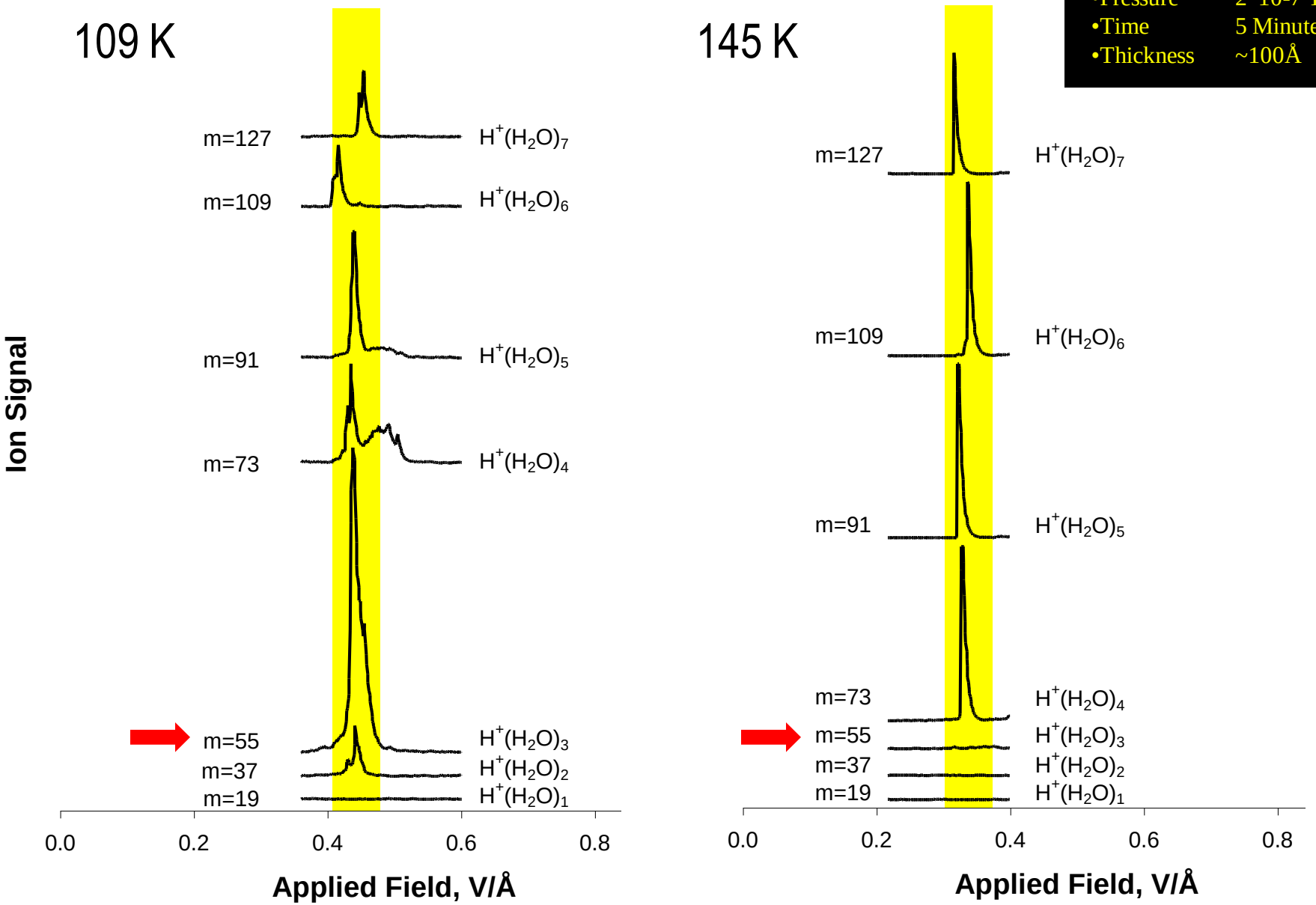


Disagrees with expected trend from previous low temperature data? (Scovell, et al)

Low Temperature Ion Cluster Formation

Tip Radius = ~330Å

H_2O Deposition :
- Temperature 145K
- Pressure 2*10-7 Torr
- Time 5 Minutes
- Thickness ~100Å



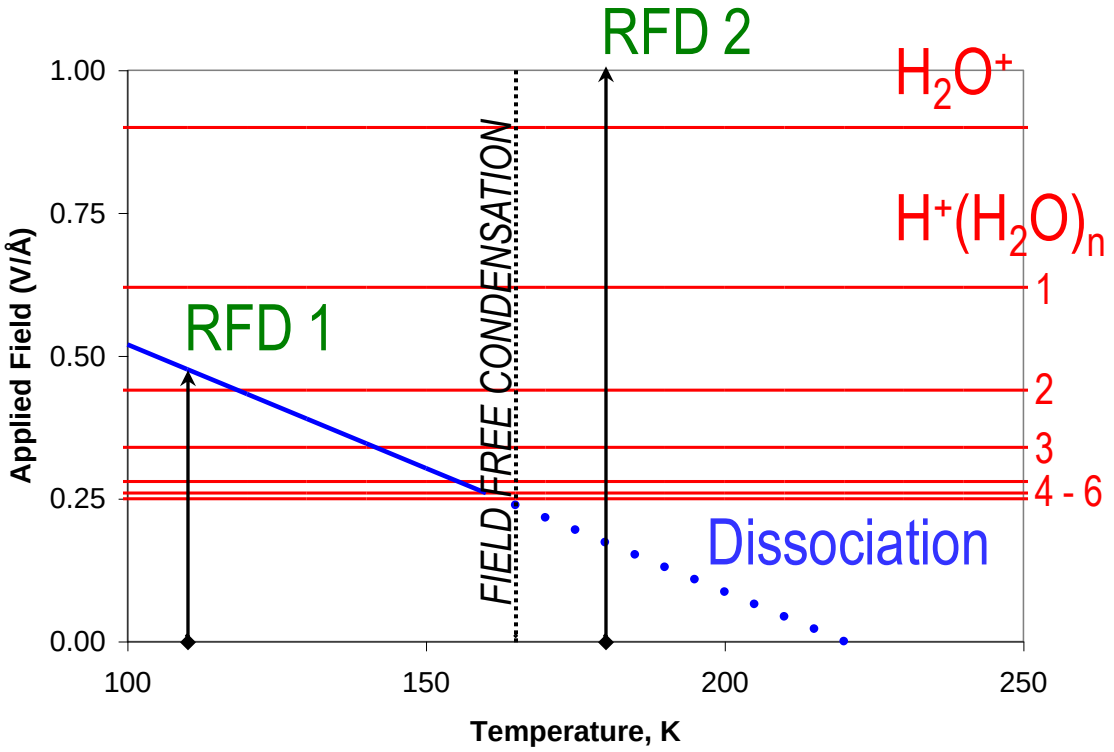
Separating Ion Dissociation and Ion Emission

Ramped Field Desorption 1

- Crystalline Ice Deposition
- Field Ramp passes through Emission Fields for all clusters n ≥ 2 *before* Dissociation
- When Ramp reaches Dissociation Field, clusters n ≥ 2 are Emitted *simultaneously*.

Ramped Field Desorption 2

- Field Adsorbed Layer
- Field Ramp activates Dissociation *before* Emission
- Cluster n emission observed, each *in turn*.



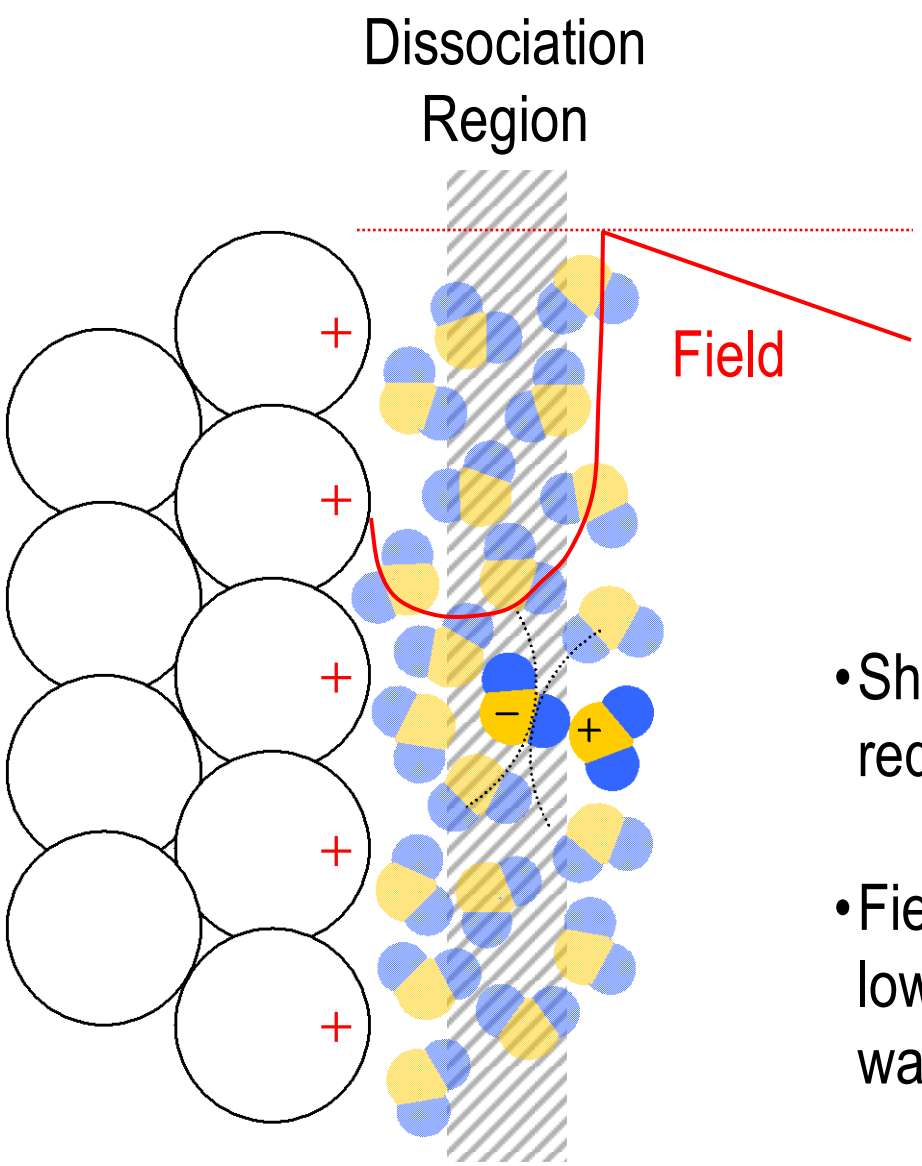
Field Dissociation (~ 0.7 eV)

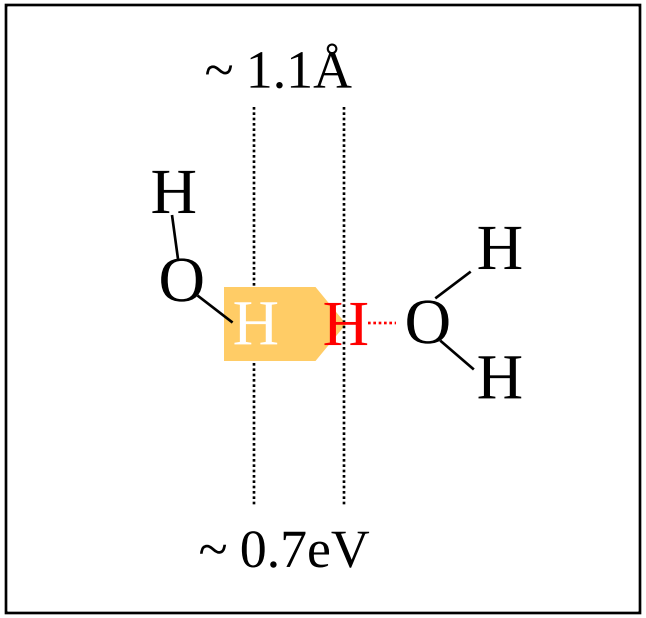
- Strong Temperature Dependence
- Field Free Dissociation at ~ 220K (Extrap)

Field Ion Emission (~ 4-5 eV)

- Not Significantly Temperature Dependent

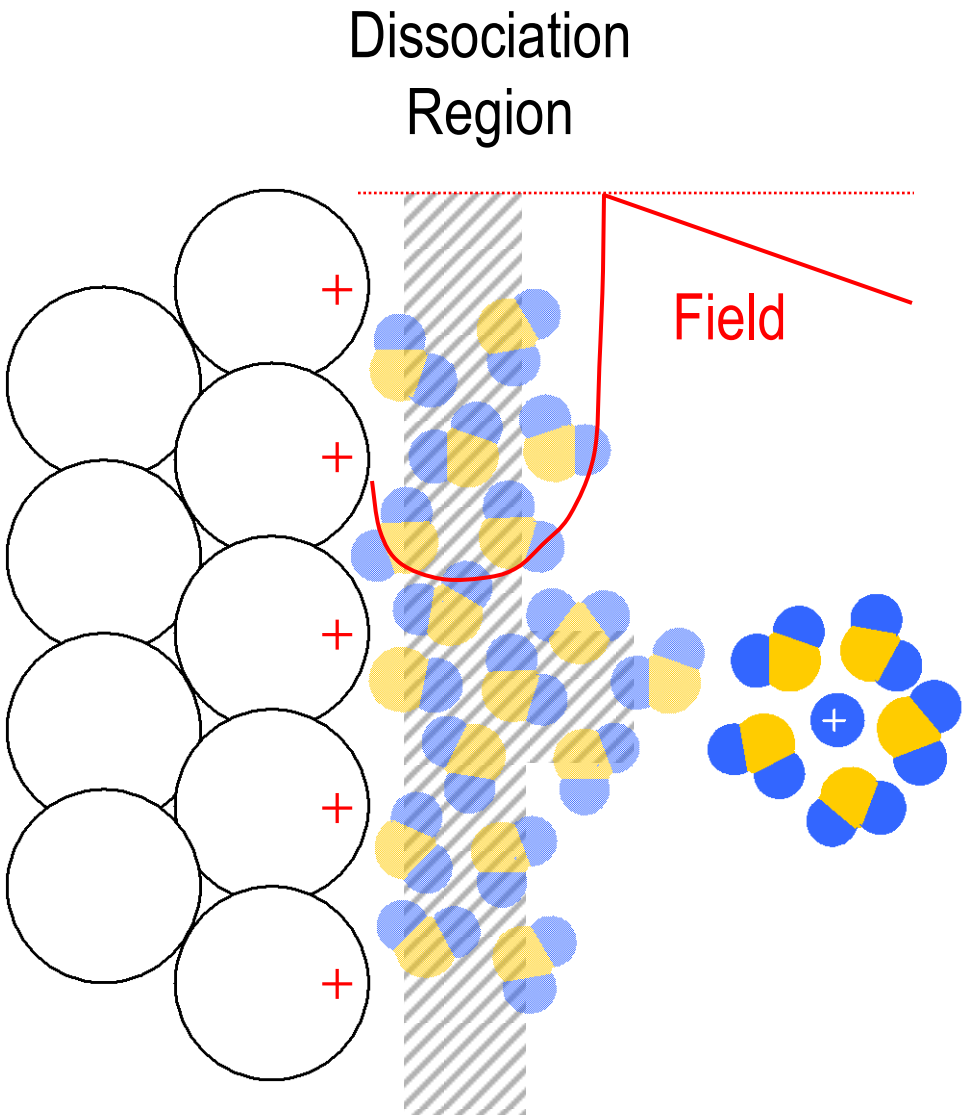
Field Induced Ion Dissociation





- Shifting the Proton along the H bond requires ~0.6 V/Å
- Field in *Dissociation Region* is much lower than applied field or field at water vacuum interface.

Field Induced Ion Emission



- Emission of Ion Cluster from water covered surface requires

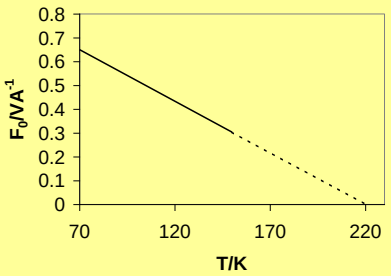
ΔE_{emit}(eV)	$H^+(H_2O)_n$
5.77	1
4.83	2
4.45	3
4.12	4
4.07	5

- Ion cluster can protrude near surface and experience enhanced local field
- Protrusion results in extended local Dissociation Region

Ion Dissociation and Emission Reaction Path

DISSOCIATION

- Thermally Activated
  - Field Free ~0.7eV
- Field Enhanced
  - Dipolar Interaction
  - Charge Separation
- RDS at Low Temp



SOLVATION

- Energy Depends on Extent of Solvation
- Cluster Desolvation Thermally Activated

EMISSION

- Barrier Height Varies with Cluster
  - Field Free ~4-5 eV
- Strongly Field Dependent

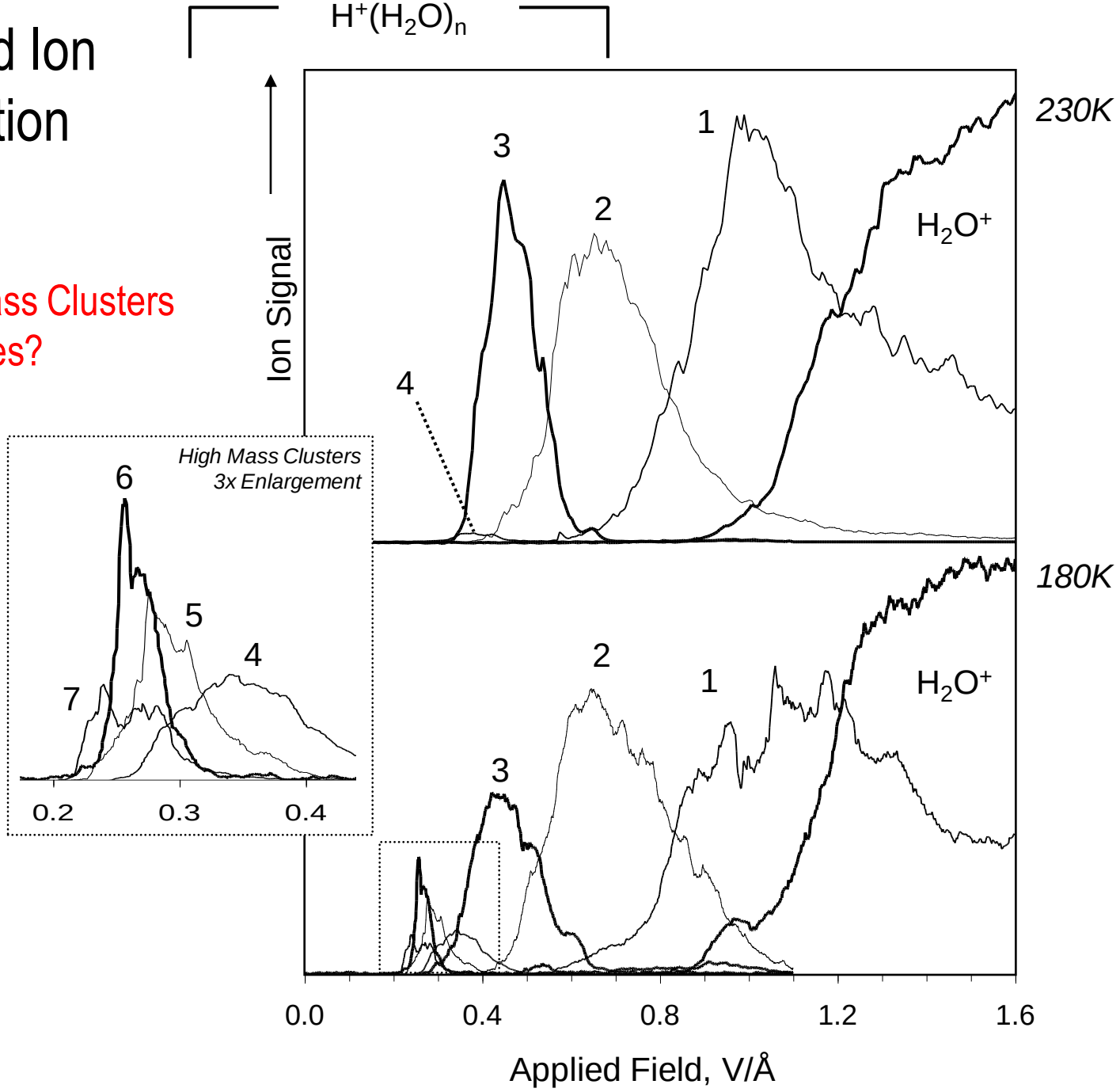
Conclusions

- Dissociation
  - Barrier ~ 0.7eV
  - Field Enhanced, Thermally Activated
  - Rate Determining at Low Temperatures (<~150K)
- Ion Emission
  - Barrier ~ 4 - 5 eV Depending on Cluster Type
  - Field Dependent
  - Rate Determining at High Temperatures (>~170K)

Questions ?

Mass Resolved Ion Cluster Formation Revisited

Absence of High Mass Clusters at High Temperatures?



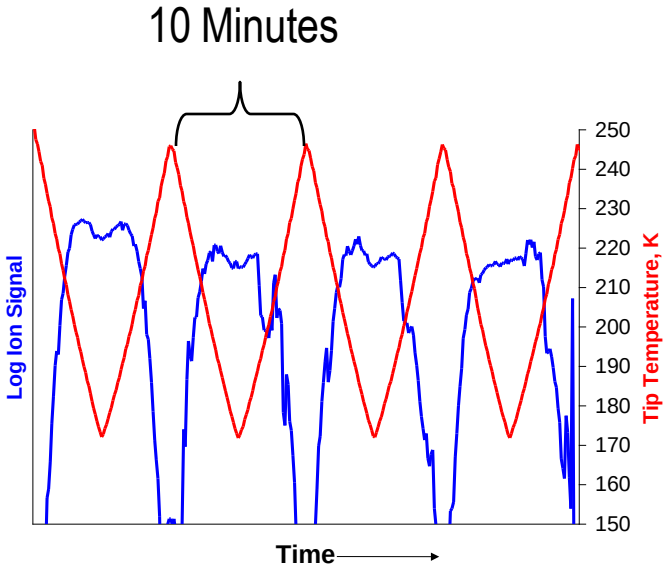
Ion Cluster Formation with Temperature Cycling

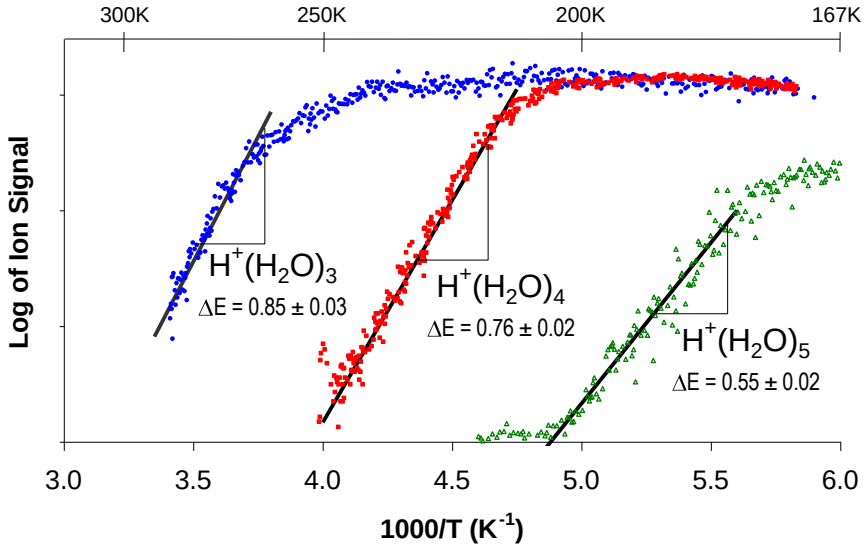
PROCEDURE

- Tip at Optimum Potential for Desired Cluster
- Background H_2O Pressure at $5*10^{-6}$ Torr
- Temperature Cycled Linearly with Time, Remaining Above 165K To Avoid Condensation
- Mass Selected Ion Signal Measured and Imaged with MCPs; for mass 73 $[H^+(H_2O)_4]$...

RESULTS

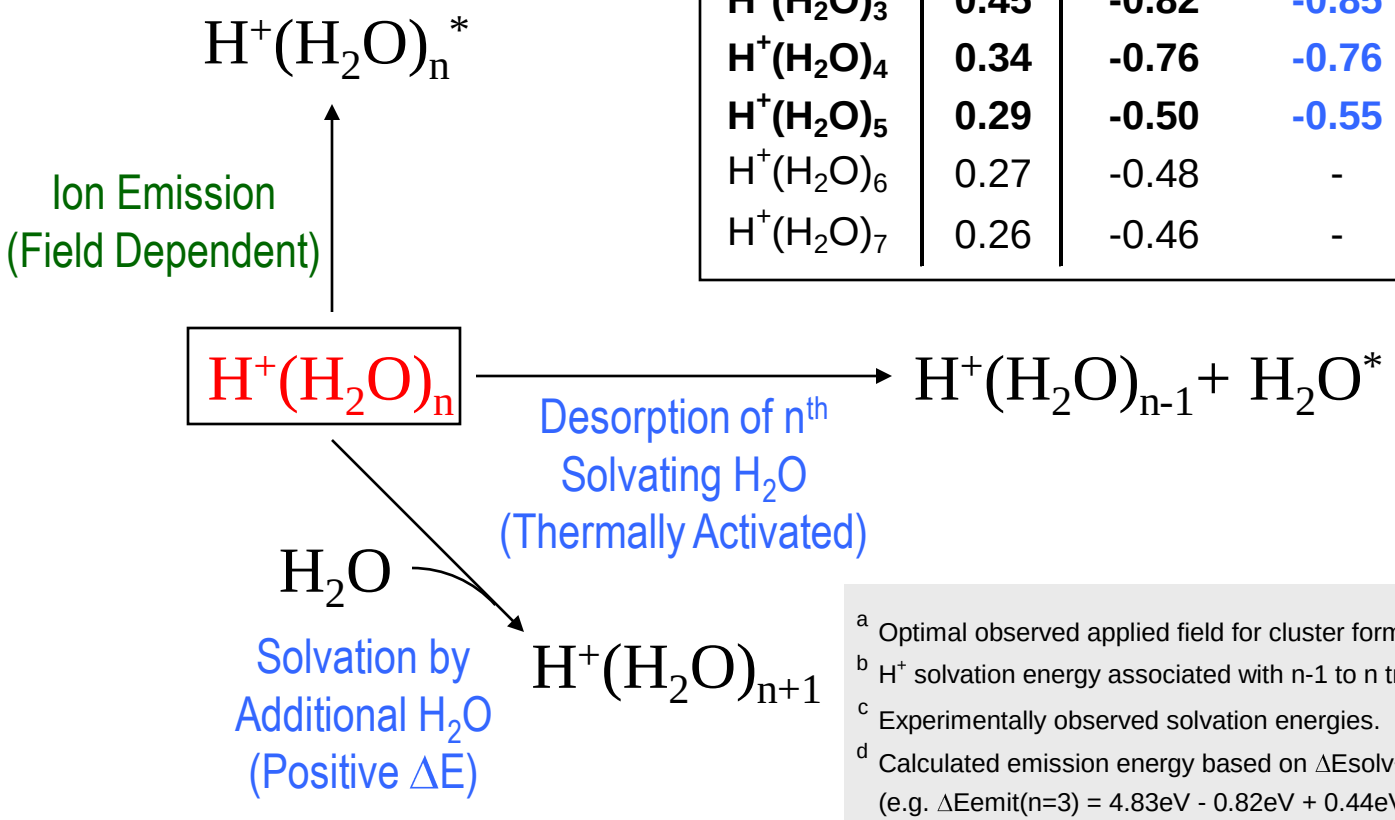
- Ion Cluster emission appears to be a thermally *deactivated* process for a given cluster size.
- Termination of cluster n emission coincides with the beginning of *n*-1 decay.
- Process deactivation energies are comparable to proton solvation energies for the nth solvating water molecule.





Thermal Deactivation of Ion Cluster Emission

	F_{app} [a] V/Å	Lit ΔE_{solv} [b] eV	Exp ΔE_{solv} [c] eV	ΔE_{emit} [d] eV
H^+	n/a	n/a	-	12.55
$H^+(H_2O)$	1.00	-7.22	-	5.77
$H^+(H_2O)_2$	0.64	-1.38	-	4.83
$H^+(H_2O)_3$	**0.45**	**-0.82**	**-0.85**	**4.45**
$H^+(H_2O)_4$	**0.34**	**-0.76**	**-0.76**	**4.12**
$H^+(H_2O)_5$	**0.29**	**-0.50**	**-0.55**	**4.07**
$H^+(H_2O)_6$	0.27	-0.48	-	4.02
$H^+(H_2O)_7$	0.26	-0.46	-	4.00



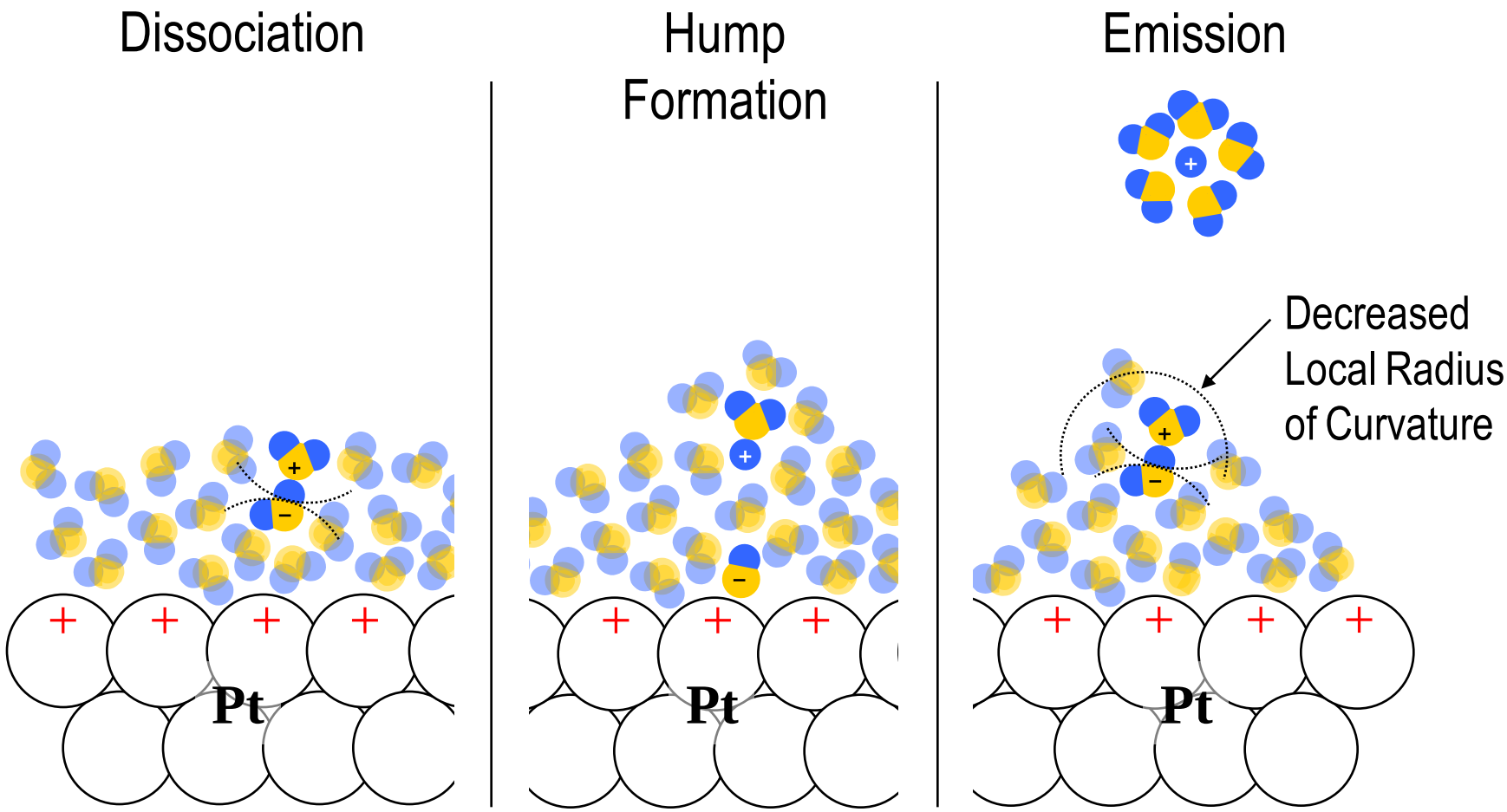
[a] Optimal observed applied field for cluster formation.

[b] H^+ solvation energy associated with n-1 to n transition. [Meot-Ner]

[c] Experimentally observed solvation energies.

[d] Calculated emission energy based on ΔEsolv+Ivap
(e.g. ΔEemit(n=3) = 4.83eV - 0.82eV + 0.44eV = 4.45eV)

Water Ion Cluster Formation
Proposed Mechanism



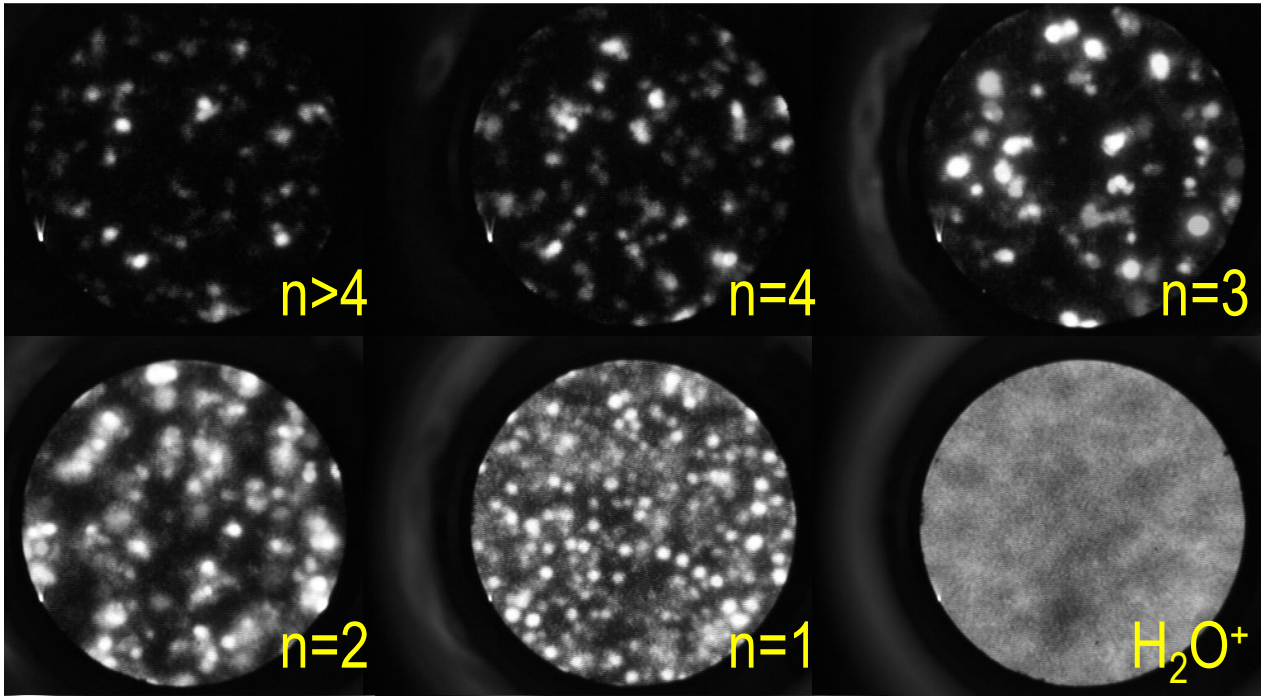
Direct Imaging of Ion Cluster Formation

PROCEDURE

- Ion signal directly imaged by FIM
- P_{H20}= 5*10^{-6} Torr
- Tip at Optimum Potential for Desired Cluster
- 10 second linearly averaged pixel intensity

180K

230K



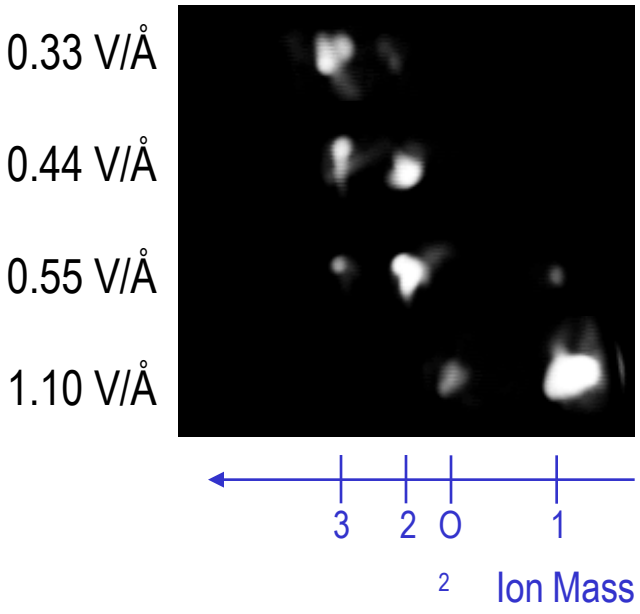
Field Ionization of Water and Methanol

PROCEDURE

- Tip Temperature = 180 K
- Tip Radius ≅ 370 Å
- Wien Filter Resolution of Ions
- 300 Frame Linear Averages

H_2O Only

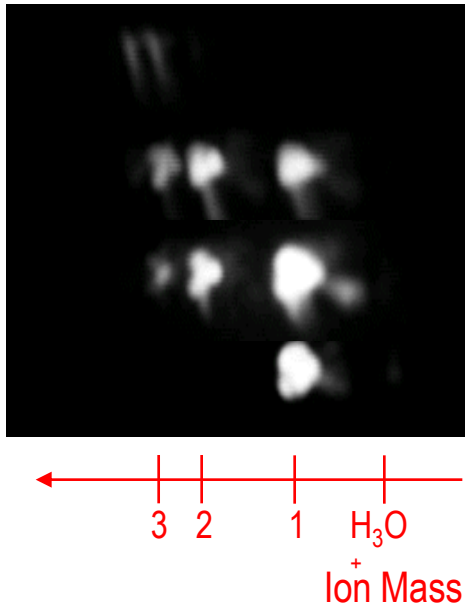
$P_{H_2O} = 4 \cdot 10^{-6}$ Torr



$H^+(H_2O)_n$

MeOH Only

$P_{MeOH} = 4 \cdot 10^{-6}$ Torr

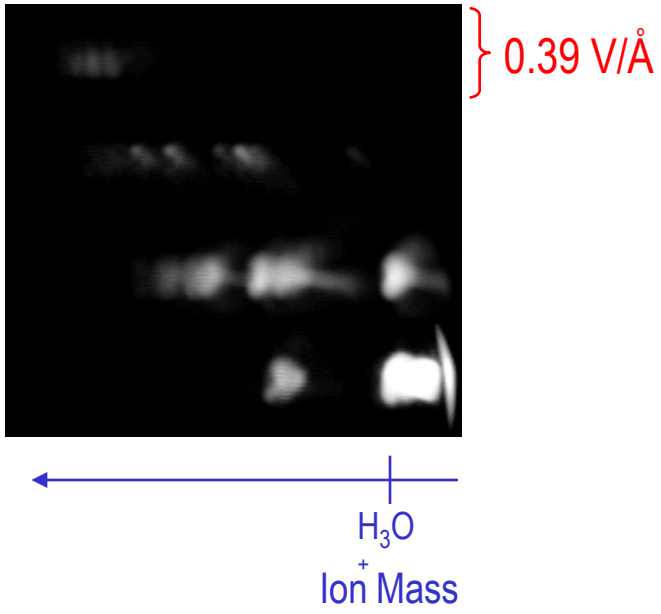


$H^+(CH_3OH)_m$

H_2O + MeOH

$P_{H_2O} = 2 \cdot 10^{-6}$ Torr

$P_{MeOH} = 2 \cdot 10^{-6}$ Torr



$H^+(CH_3OH)_m(H_2O)_n$

Field Effect on Ion Emission

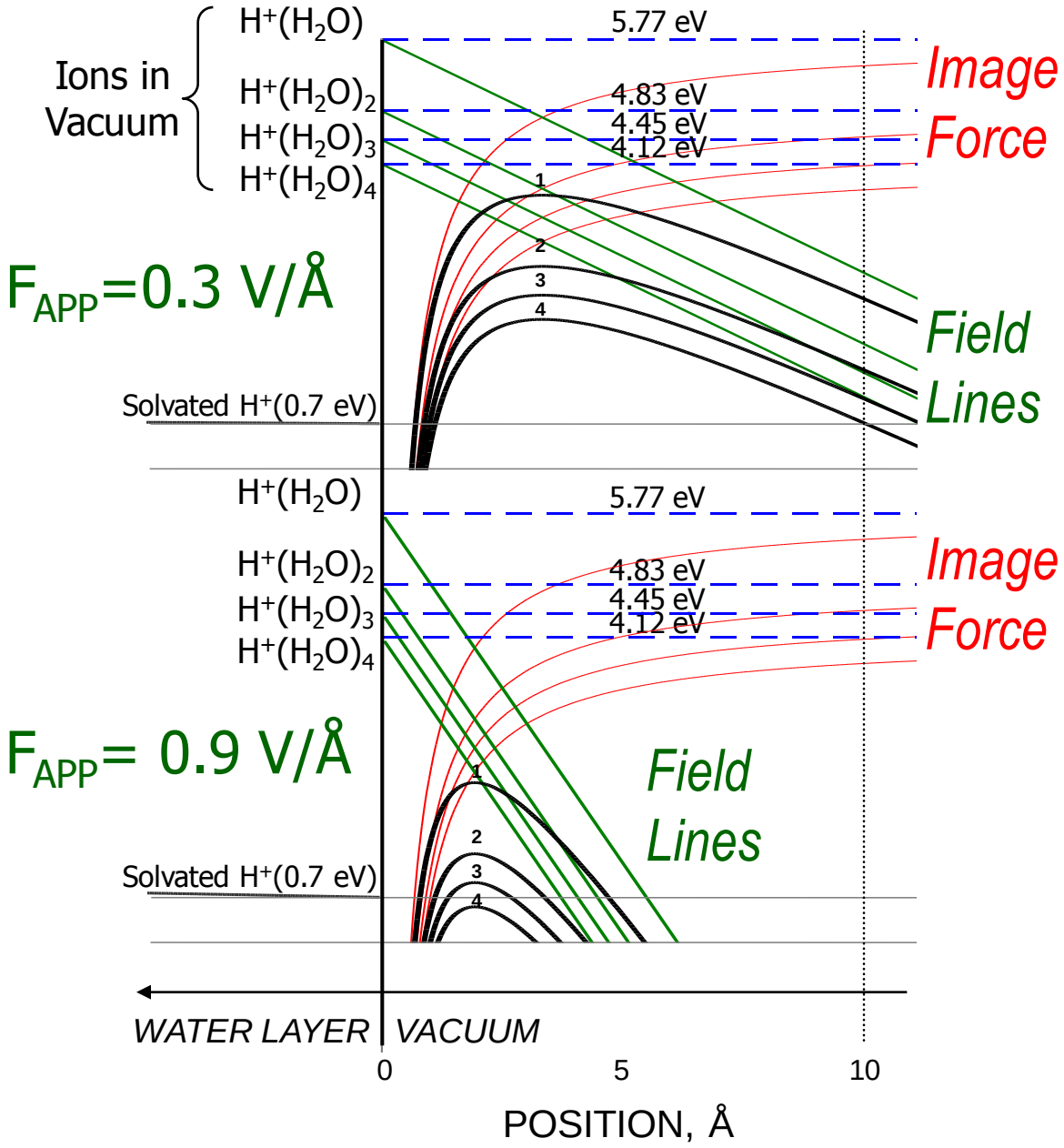
Idealized Energy Barriers for Emission

Potential Taken Relative to Uncharged Water on Uniform Surface

CALCULATION

- Ion Energies Calculated by Thermodynamic Cycle
- Field Assumed Constant
- Image Force Equation for Flat Uniform Surface

$$V_I = \frac{e^2}{4x} \cdot \left[\frac{\varepsilon - 1}{\varepsilon + 1} \right]$$



MeOH Cluster Formation:

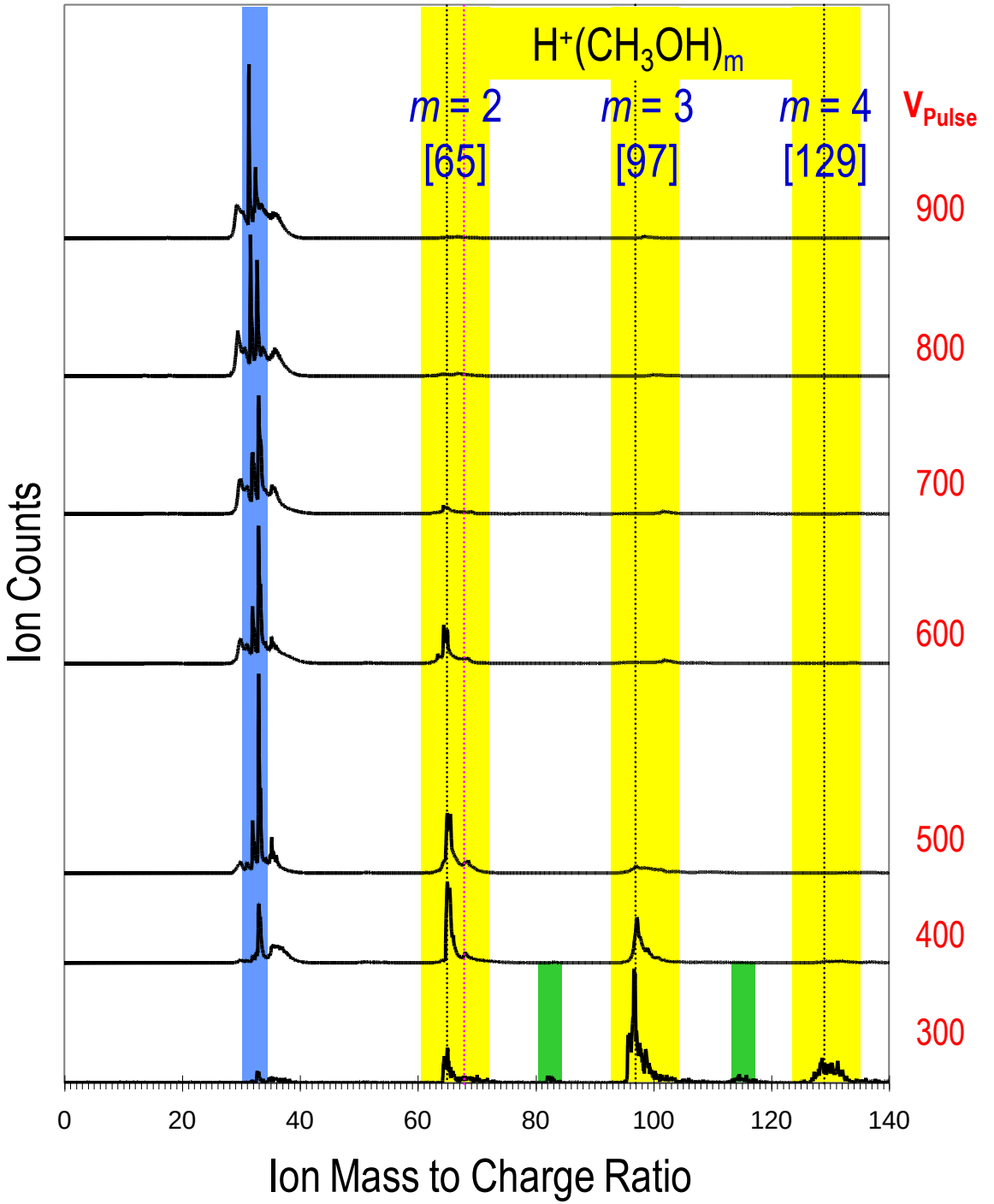
PULSE HEIGHT

PROCEDURE

- Tip Temperature = 165 K
- V_{Tip} at 3000 V; V_{CE} at 2600 V
- V_{CE} pulsed negative by V_{Pulse}
- P_{MeOH}= 6*10^{-6} Torr
- Resolved with ToF

RESULTS

- Protonated Methanol Clusters
- Behavior Similar to H_2O
  - Large Clusters at Low Fields
  - Cluster Size ↓ with Field ↑
- Complicated Spectra Near m = 1
  - Mass 33 to 32 Shift with Field ↑
- Presence of masses 83 and 115
  - $H^+(CH_3OH)_m(H_2O)$ for m = 2,3
  - Contamination?



MeOH / H_2O Cluster Formation:

MIXTURE RATIO

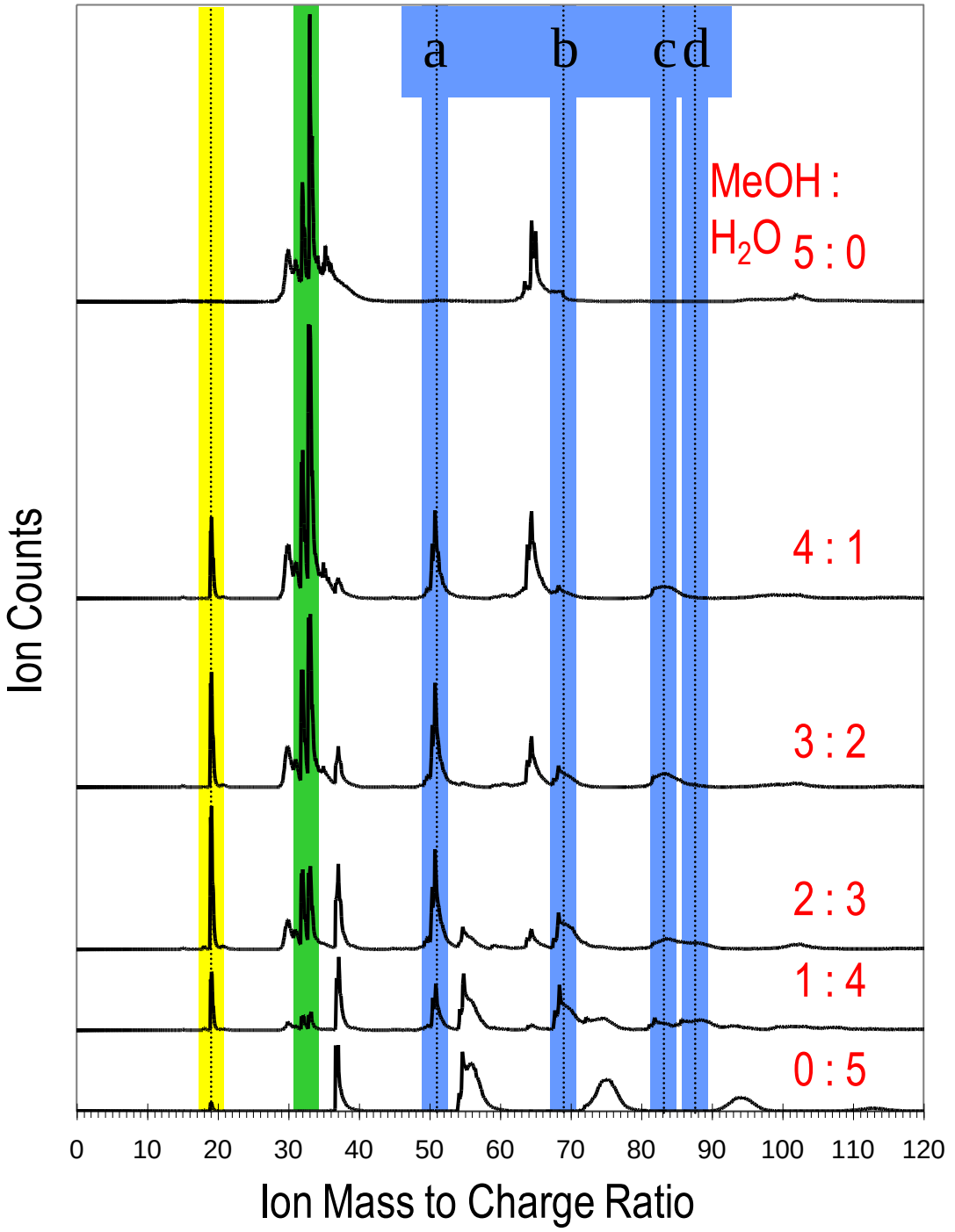
PROCEDURE

- Tip Temperature = 165 K
- V_{Tip} at 3000 V; V_{CE} at 2600 V
- V_{CE} pulsed negative by 600 V
- $P_{MeOH} + P_{H2O} = 5*10^{-6}$ Torr
- Resolved with ToF

RESULTS

- $H^+(CH_3OH)_m(H_2O)_n$ Observed
- H_3O^+ Emission Enhancement
  - MeOH Lowers Emission Barrier?
- 33 to 32 ratio ↑ with H_2O ↓
- Mixed Cluster Formation (m,n)

(a)	1 , 1	mass 51
(b)	1 , 2	mass 69
(c)	2 , 1	mass 83
(d)	1 , 3	mass 87



$MeOH / H_2O$ Cluster Formation:

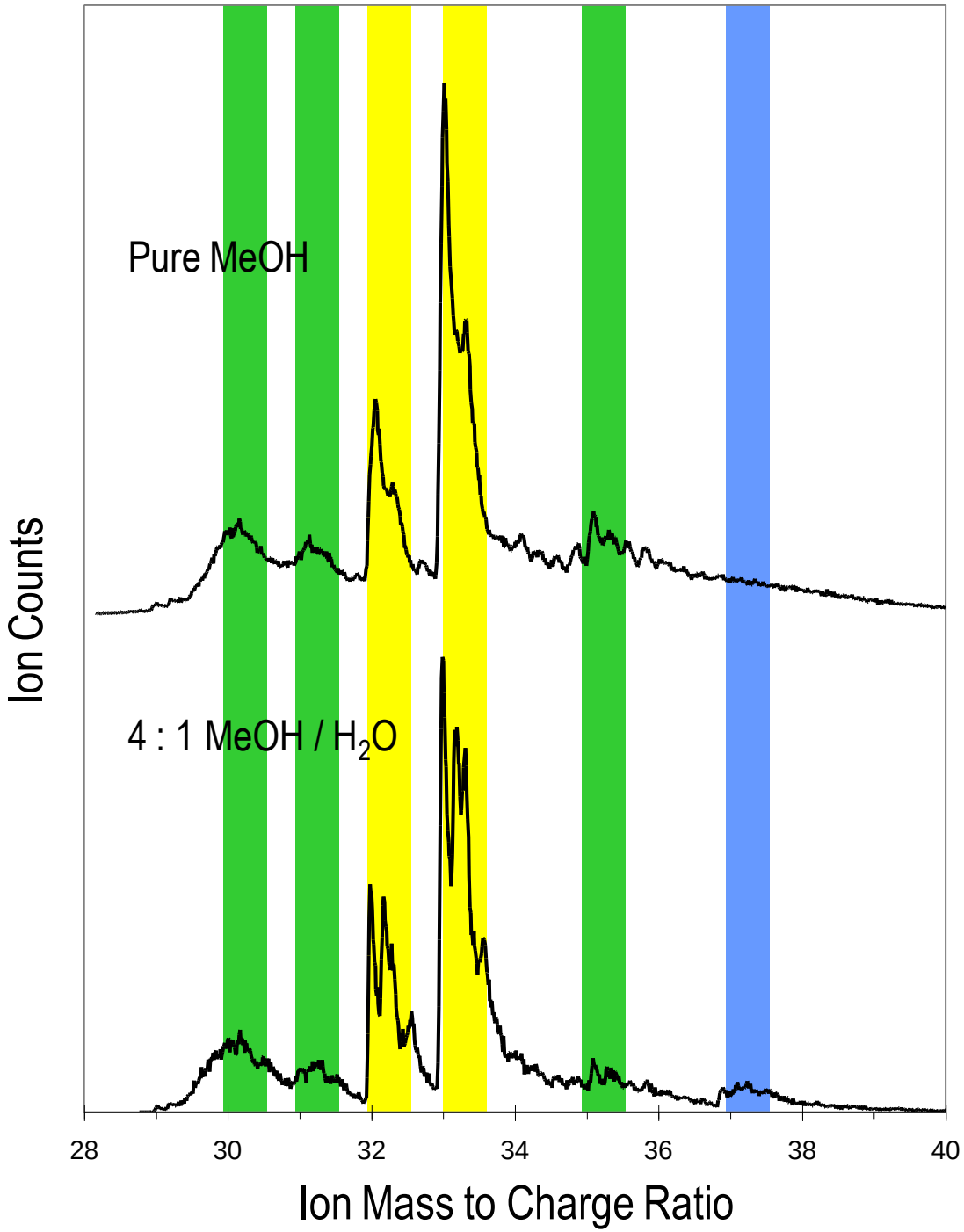
RESOLVED *m* = 1

PROCEDURE

- Tip Temperature = 165 K
- V_{Tip} at 3000 V; V_{CE} at 2600 V
- V_{CE} pulsed negative by 600 V
- Resolved with ToF

RESULTS

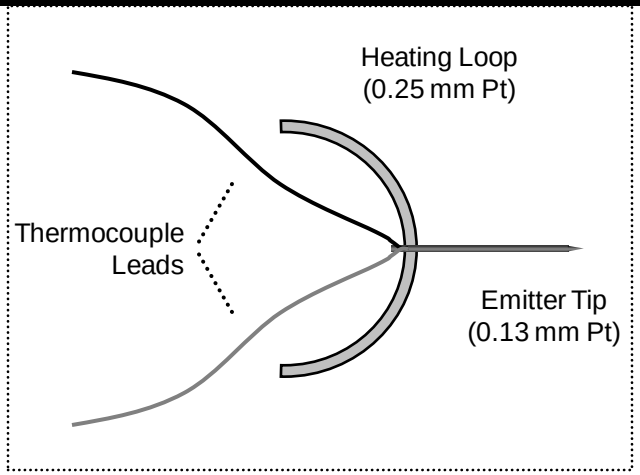
- Diversity of Peaks Near *m* = 1
- $H^+(H_2O)_2$ Peak at 37
- Primary Peaks at 32 and 33
- Other Peaks at 30, 31 and 35
- Secondary Peak Characteristics?
  - ~100 bins between 32 and 33
  - 1600 Ion Count Maximum



Summary of Results II

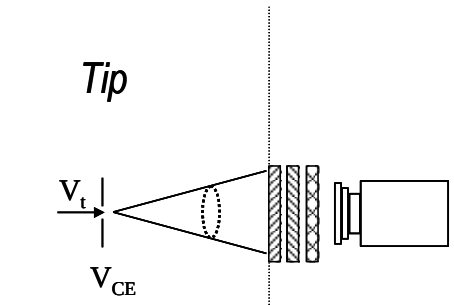
- Methanol Clusters Behave Similarly to Water
  - Protonated clusters: $H^+(CH_3OH)_m$
  - Size determined by pulse height (Field)
- Complicated Emission Spectra Near *m* = 1 Cluster
  - Mass 32 favored over 33 at high fields and low MeOH / H_2O
- Methanol / Water Clusters
  - Mixture enhances mass 19 signal
  - Mixed clusters emitted

FIELD EMITTER TIPS

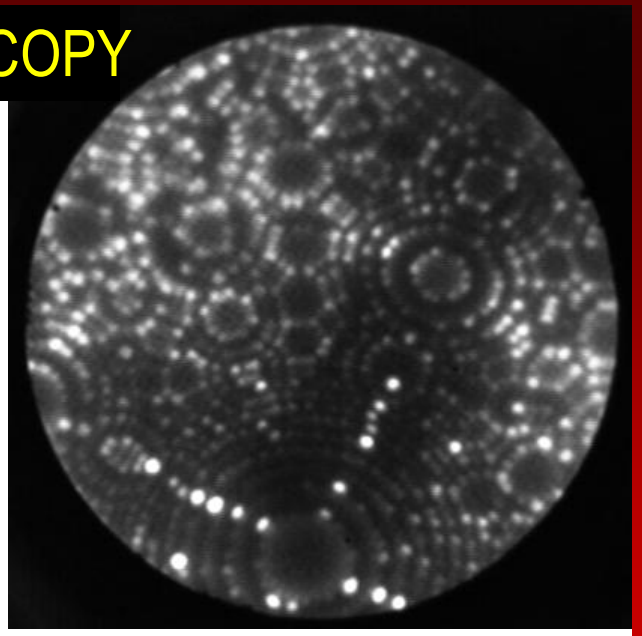


- Tip Radius ~ 370 Å
- Allows Application of High Field (Up to ~ 4 V/ Å)

FIELD ION MICROSCOPY



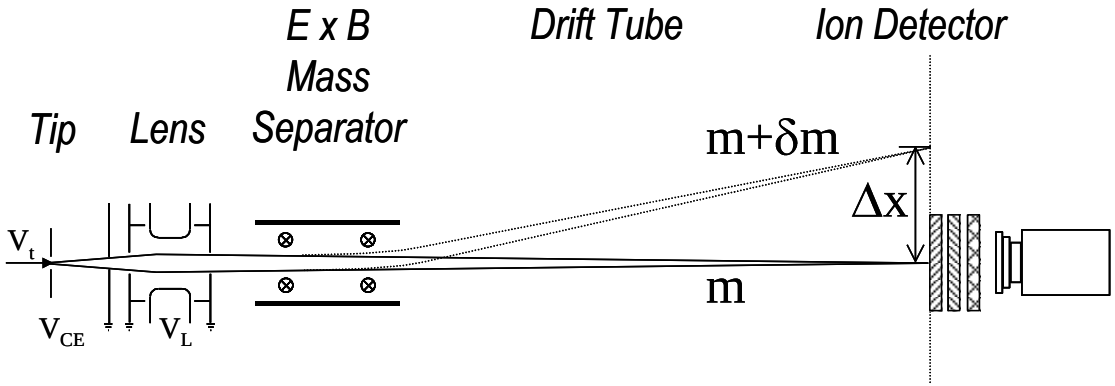
- Spatial Resolution of Ion Emission
- Field Clean Pt Surface to Prevent Possible Contamination

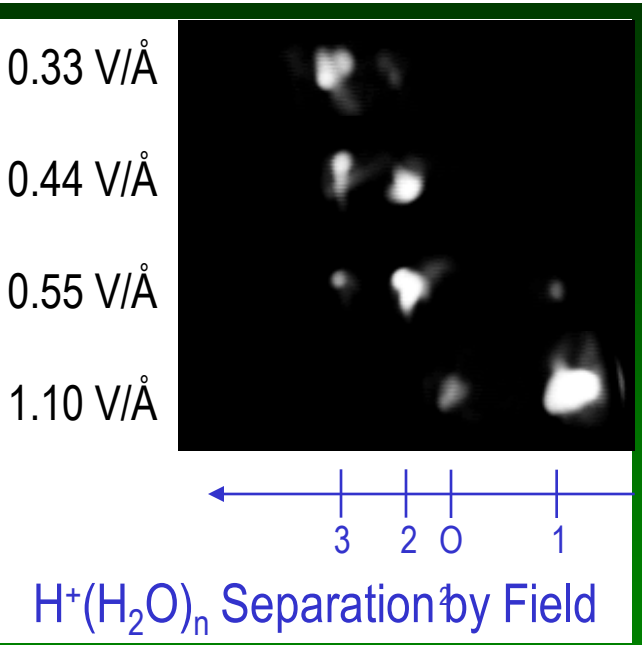


Pt Imaged w/ Ne (107 K, 3.75 V/ Å)

WIEN FILTER MASS SPECTROMETRY

- Continuous Mode Ion Mass to Charge Resolution
- Easily Separate Distinct Ion Signals without Disturbing Formation Conditions





$H^+(H_2O)_n$ Separation by Field

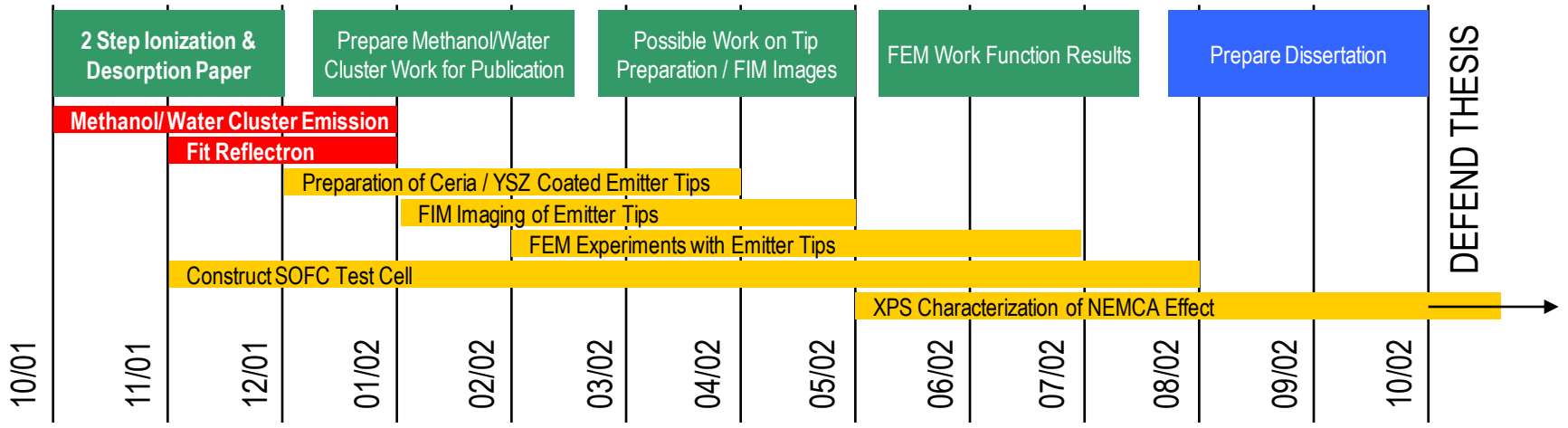
FUTURE WORK

Methanol/Water Cluster Emission

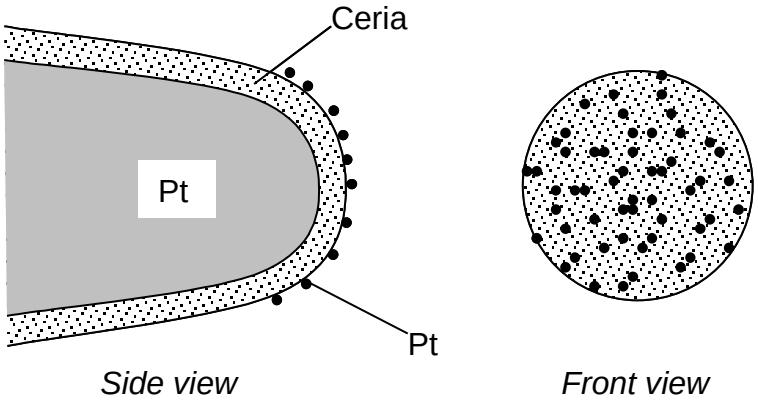
- Low Magnetic Field Wien Filter Experiments
  - Simultaneously resolve masses 30 through 37
  - Continuous mode mass resolution
  - Field dependence of cluster formation: RFDs
  - Temperature cycling to obtain solvation energies
- Time of Flight Using Reflectron
  - More accurate resolution of peaks and energy deficit work

Fit Chamber with Reflectron

- More Accurate Time of Flight Data
- Energy Deficit Resolution



FUTURE WORK



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Ceria / YSZ Coated Emitter Tips

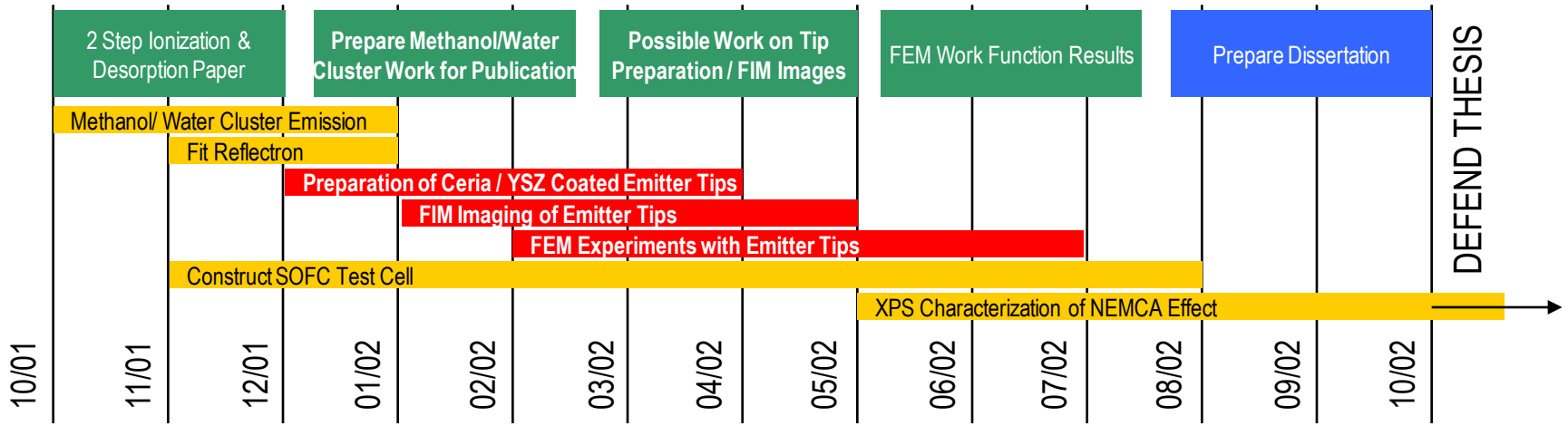
- Base emitter tip made of Tungsten or Pt
- Tip coated with ceria or YSZ
- Possibly apply sub-monolayer of Pt (or other metal)
- Designed to model Solid Oxide Fuel Cell electrode
  - Study oxidation and dehydrogenation reactions
  - Study aromatics, alcohols, aldehydes, etc.
  - Oxygenated fuels such as methanol

FIM Imaging of Emitter Tips

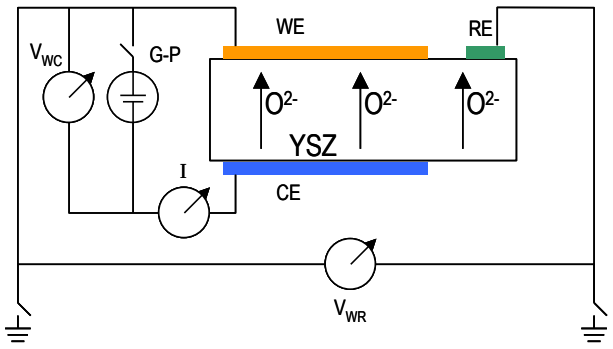
- Characterize structure of tip

FEM Experiments with Emitter Tips

- Get work function data
- Investigate NEMCA effect and three phase boundary



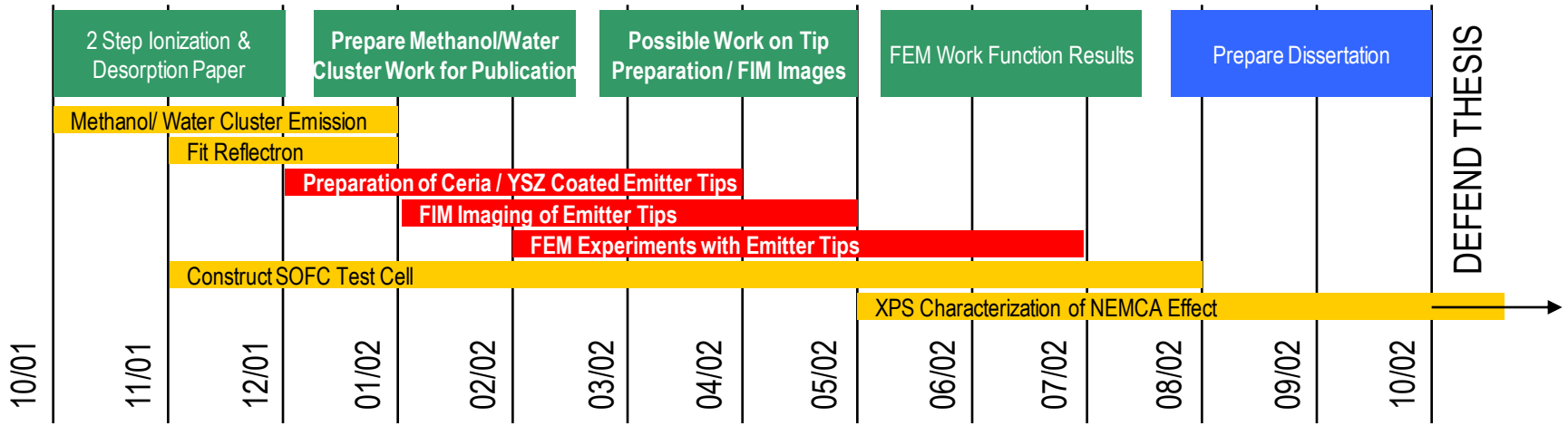
FUTURE WORK



Schematic of Vayenas' experimental setup for NEMCA. WE, RE, and CE are working (Pt), reference (Pt) and counter (Ag) electrodes, respectively; G-P is a galvanostat-potentiostat. [Taken from Vayenas 1993]

NEMCA Effect

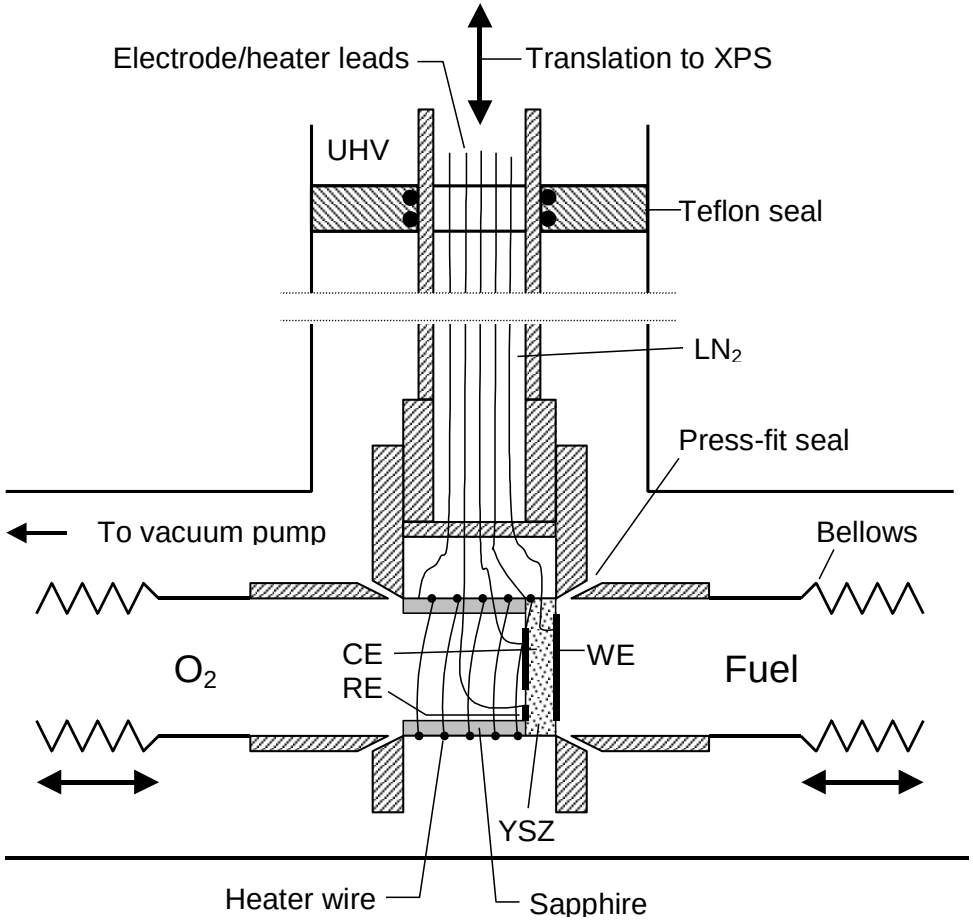
- Non-faradaic electrochemical modification of catalytic activity
- Achieved by applying potential between working and counter electrodes
  - Electrochemically pump ions through solid electrolyte
  - Ions spillover onto working electrode
  - e.g. O^{2-} through YSZ onto Pt
- Results in an increased reaction rate beyond increase in ion supply (e.g. O^{2-})
- Work function of working electrode reversibly changed
  - $\Delta e\Phi = e\Delta V_{WR}$
- May be due to electrochemical polarization at three phase boundary (YSZ / Pt / O) [Janek]

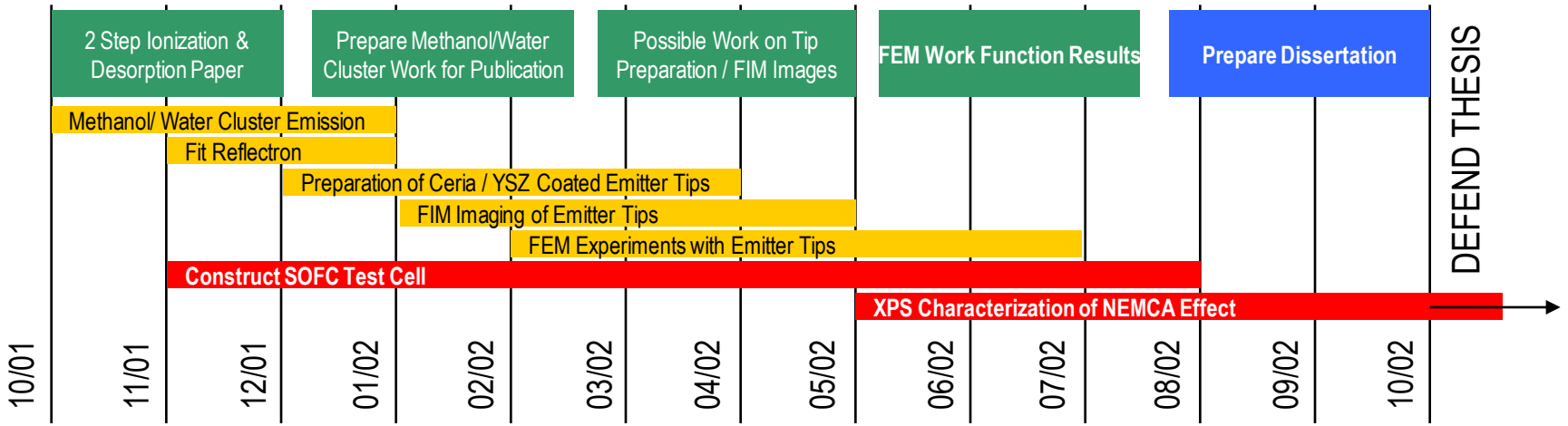


FUTURE WORK

Construct SOFC Test Cell

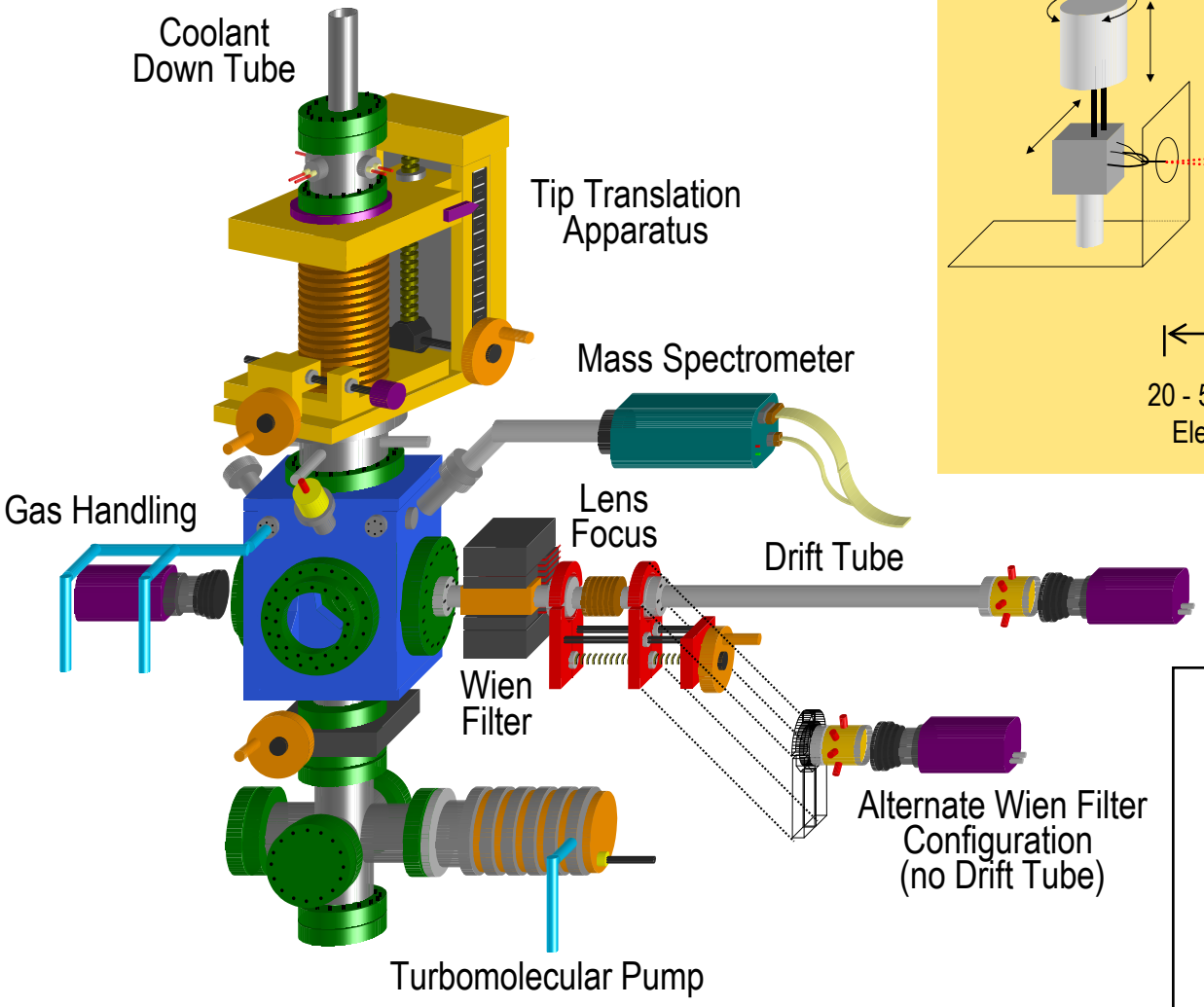
XPS Characterization of NEMCA Effect

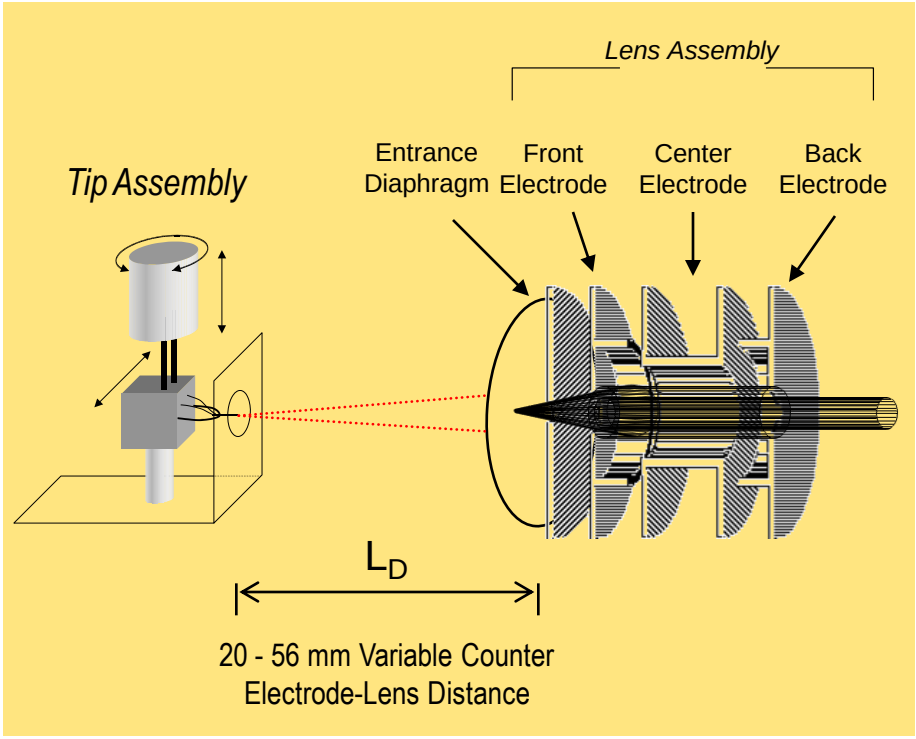




Questions ?

UHV Chamber Configuration





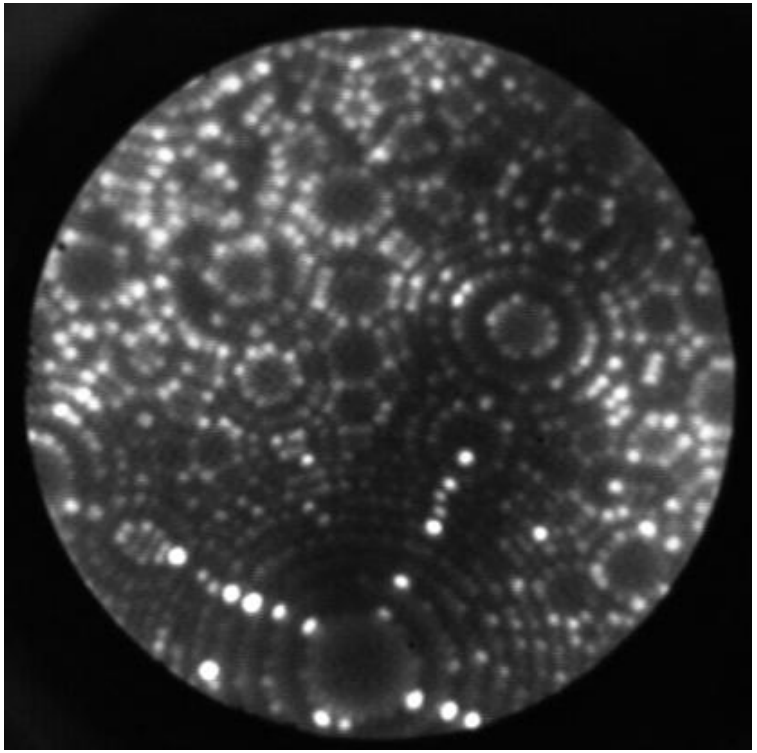
Analytical Equipment

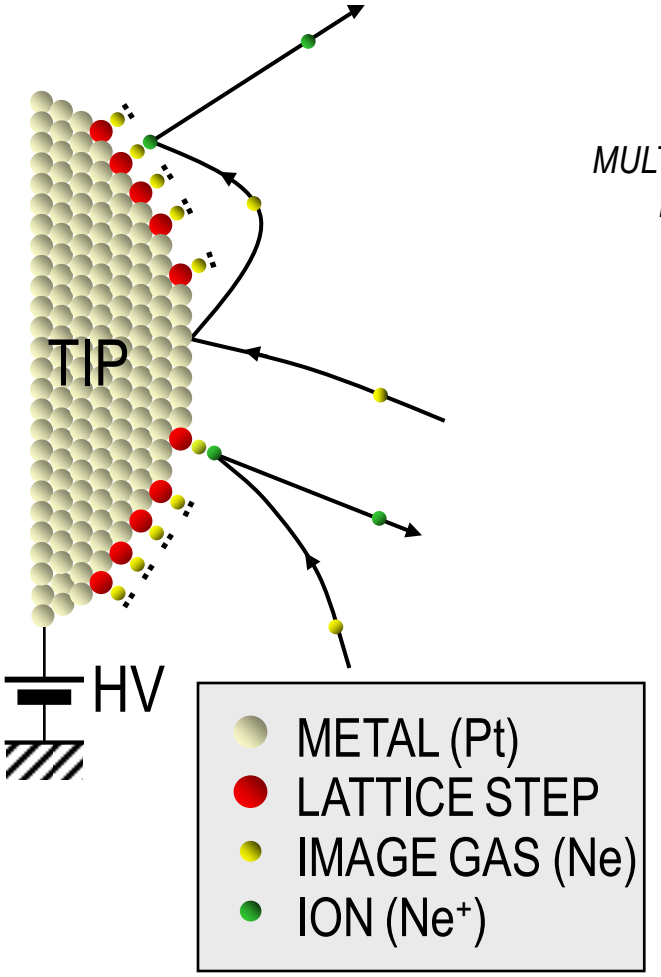
- Rotatable Tip Assembly
- FIM/FEM Imaging
- Wien Filter
- Pulsed Potential Time of Flight
- Quadrupole Mass Spectrometer

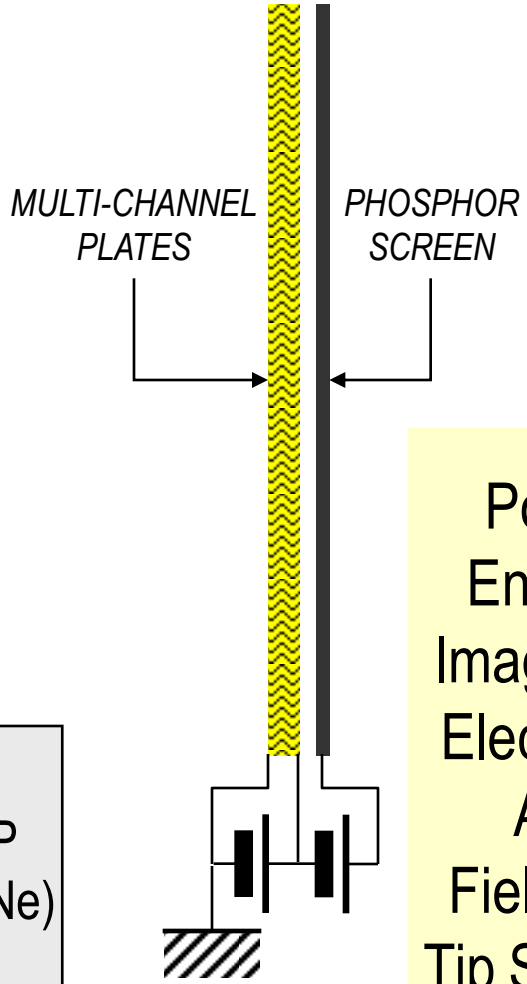
Field Ion Microscopy

- Spatial Resolution of Ion Emission
- Field Clean Pt Surface to Prevent Possible Contamination

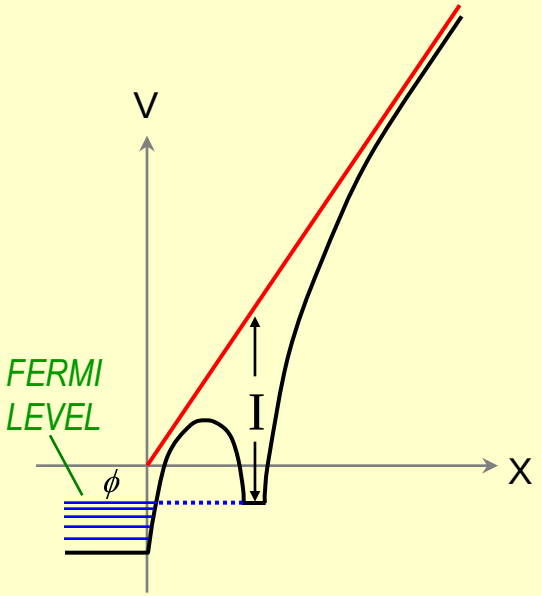
Neon on Pt
107 K
1×10^{-4} Torr
~3.75 V/Å





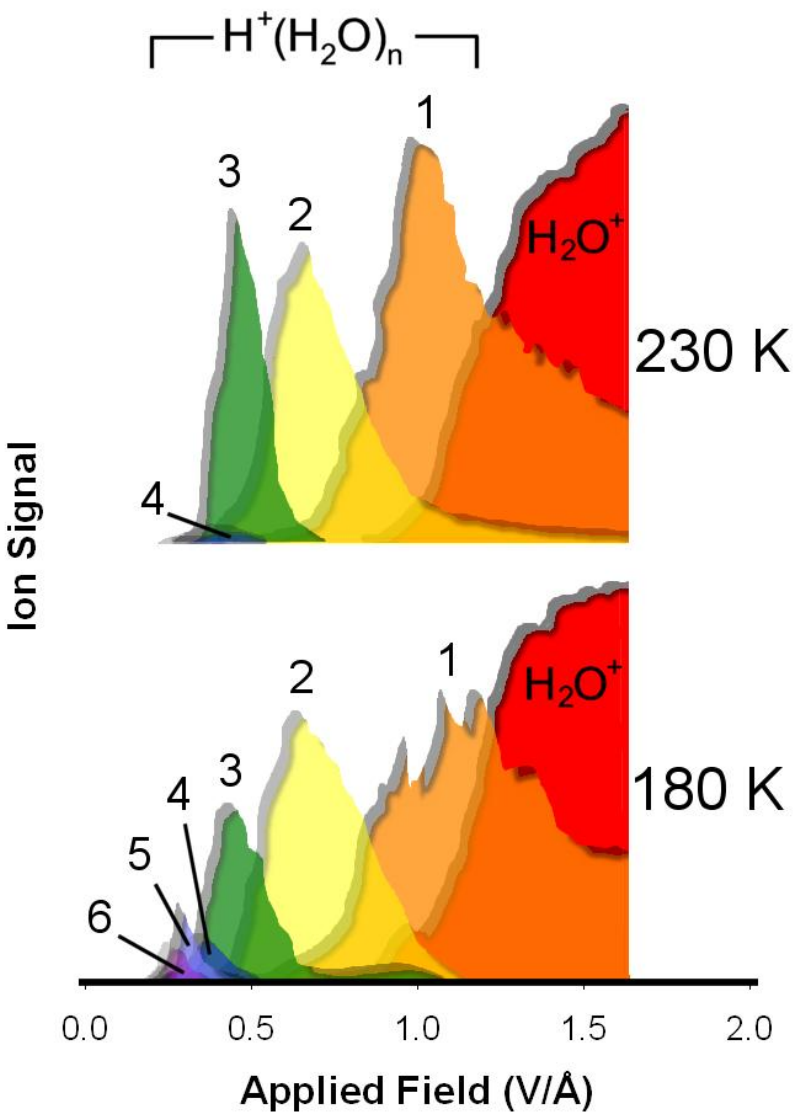


Potential Energy of Image Gas Electron In Applied Field Near Tip Surface



Adapted from Tsong,1990.

Mass Resolved Ion Cluster Formation

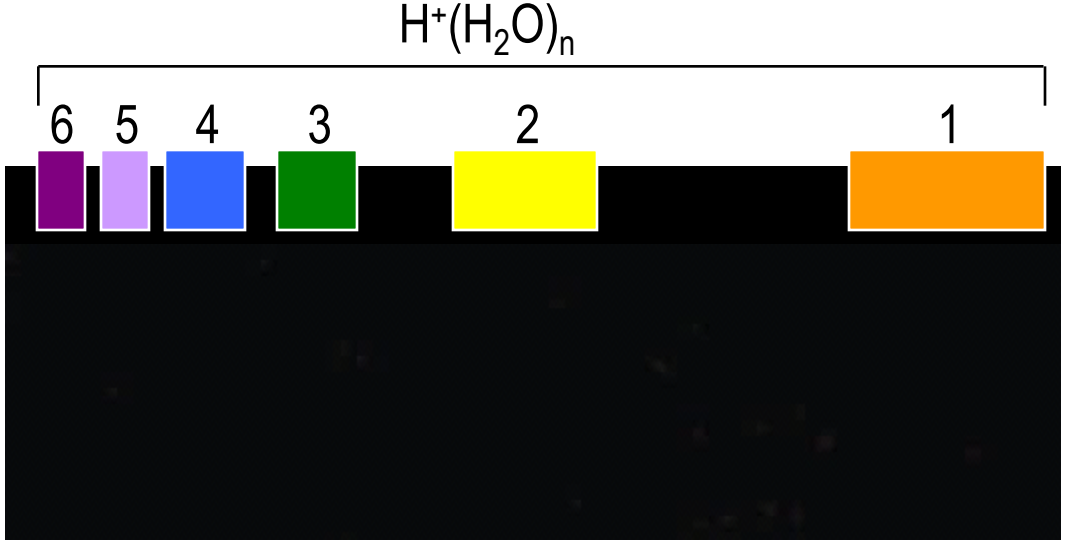


PROCEDURE

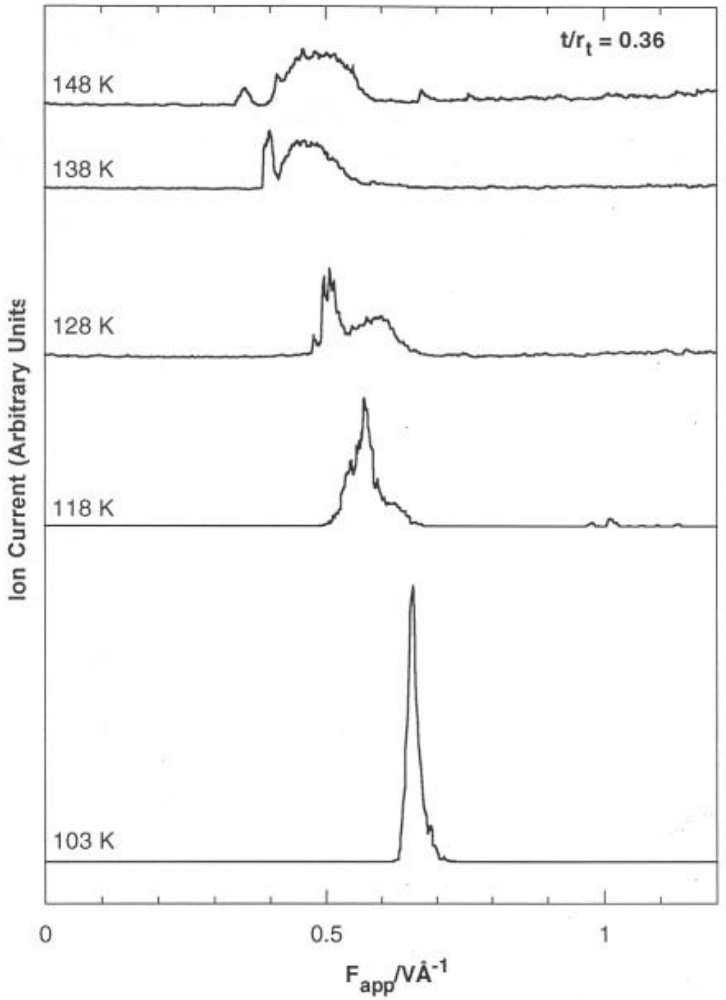
- Wien Filter tuned to selected $H^+(H_2O)_n$
- Tip Potential (V_t) set to 3000V
- P_{H20}= 5*10^{-6} Torr
- V_{CE} ramped from 3000V to 0V at 10V/s
- Ion Signal on MCPs recorded versus potential

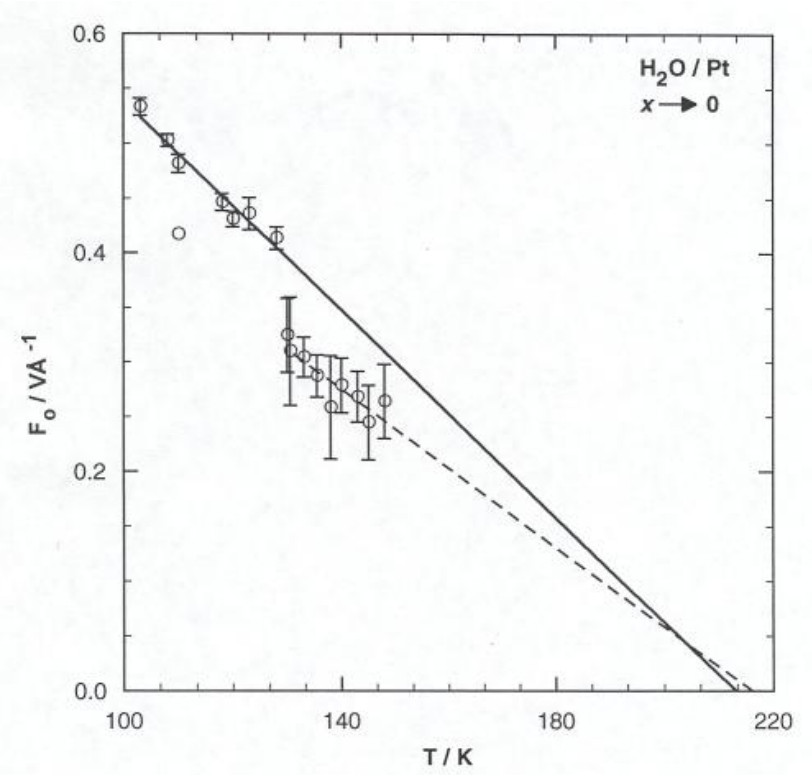
RESULTS

- Ion Cluster Emission
  - Low Field: Large n Clusters (Energetically Favorable)
  - High Field: Small n Clusters (Kinetically Favorable)
- Temperature Dependence
  - Onset not Temperature Sensitive
  - High n Clusters not Present at Higher Temperatures



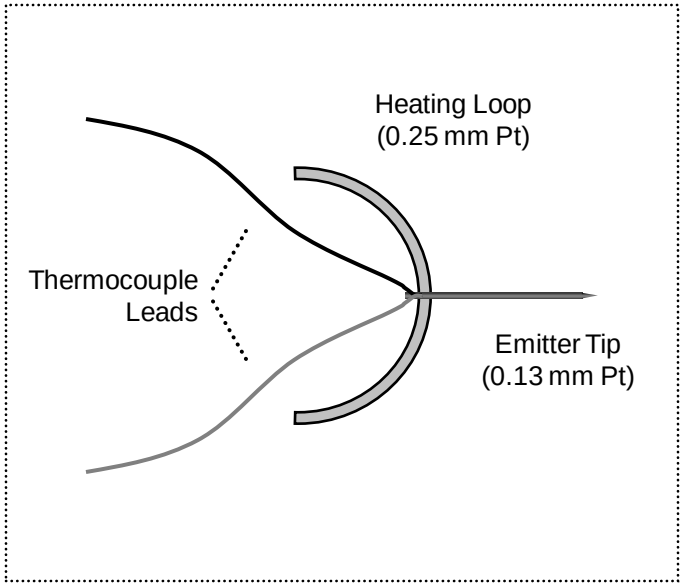
Low Temperature Ion Emission Thresholds

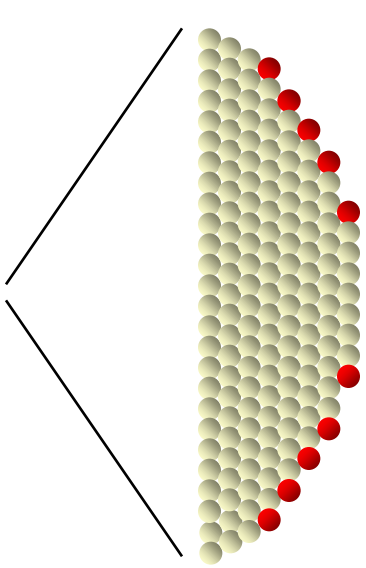


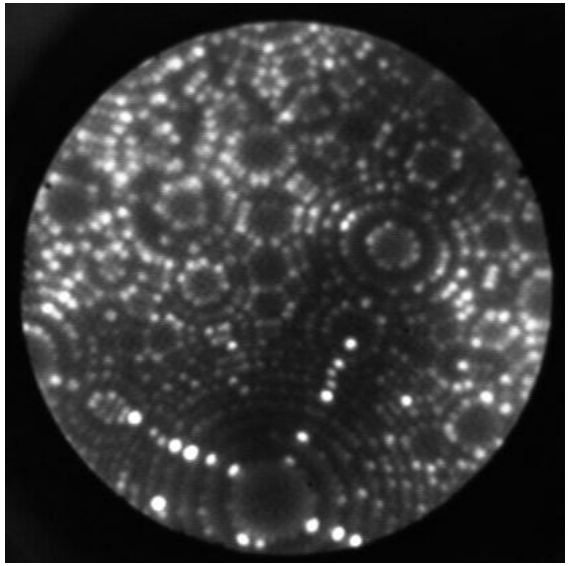


From Scovell et al.

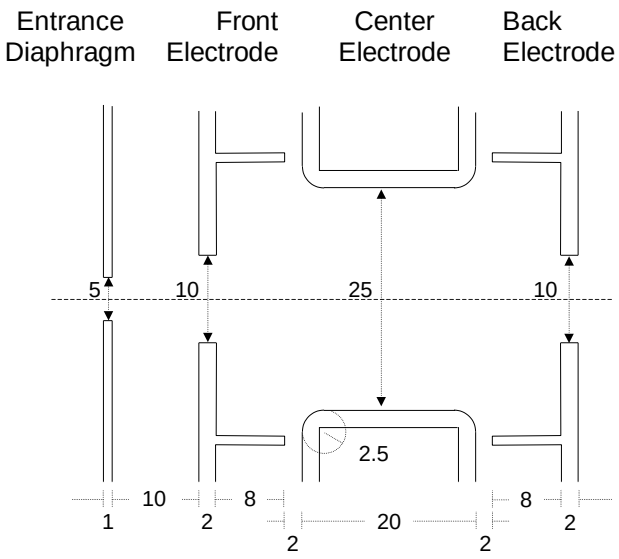
EMITTER TIP


Heating Loop
(0.25 mm Pt)
Thermocouple
Leads
Emitter Tip
(0.13 mm Pt)



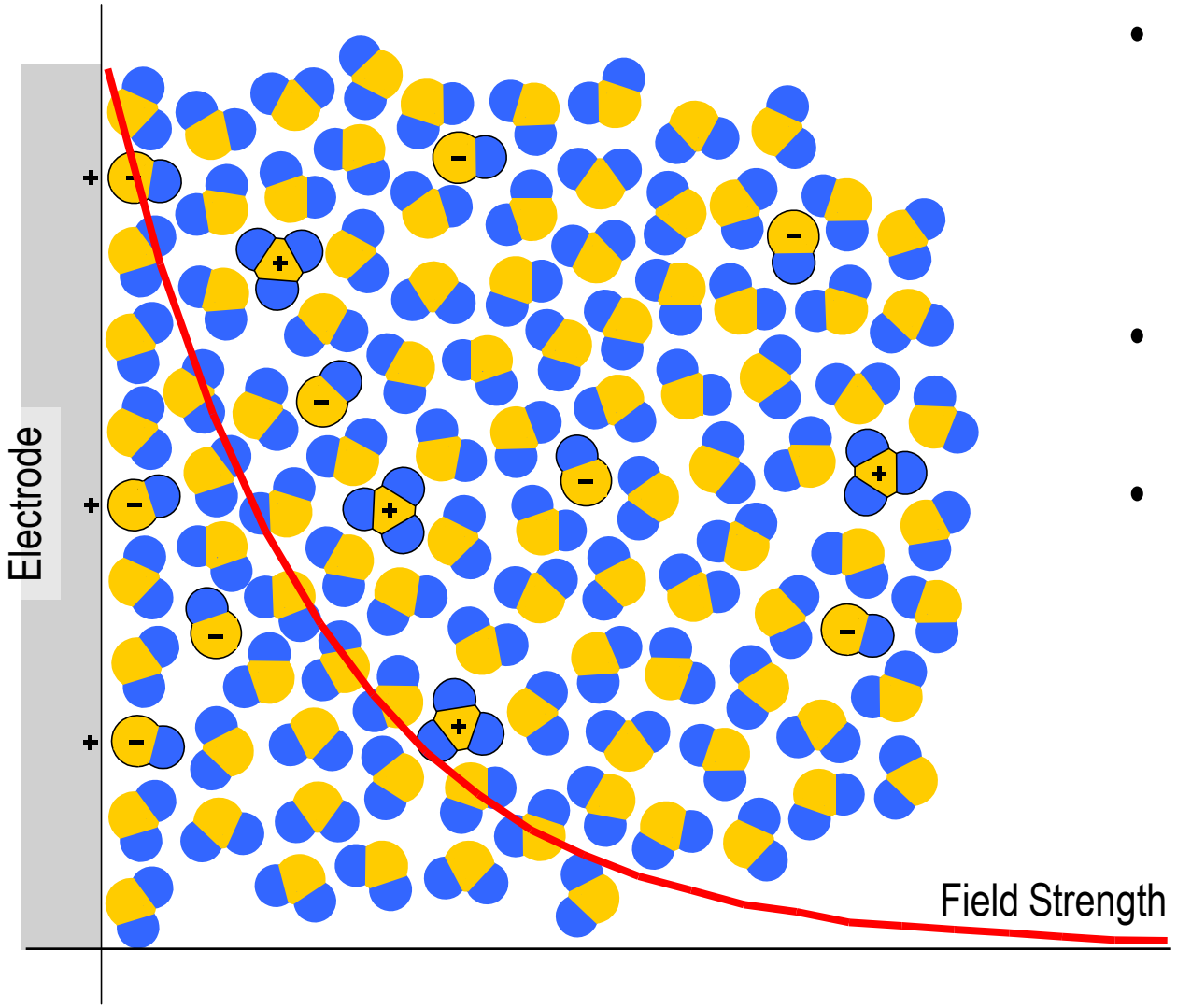


LENS ASSEMBLY

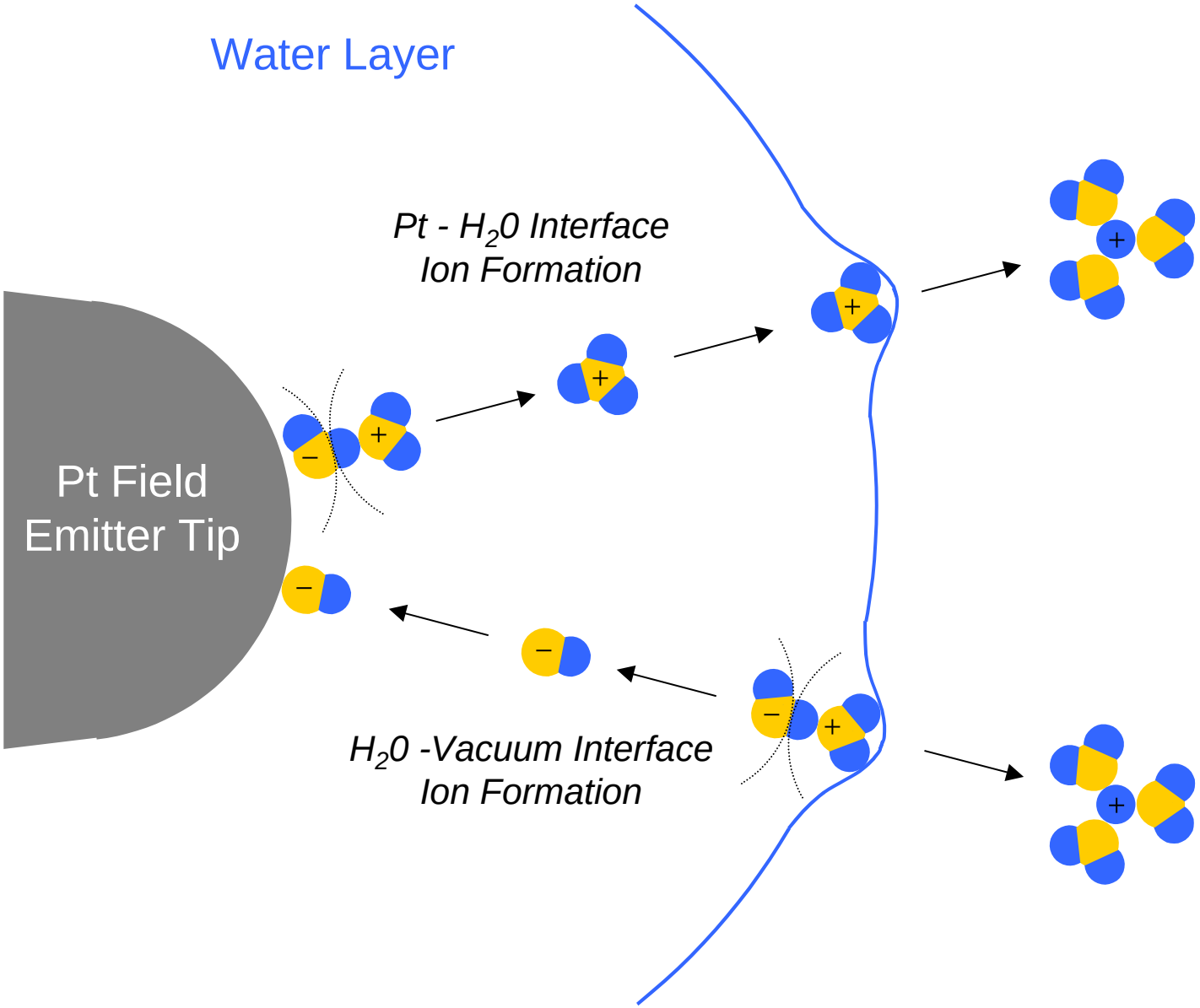


(Dimensions in mm)

High Electric Fields in Electrochemistry

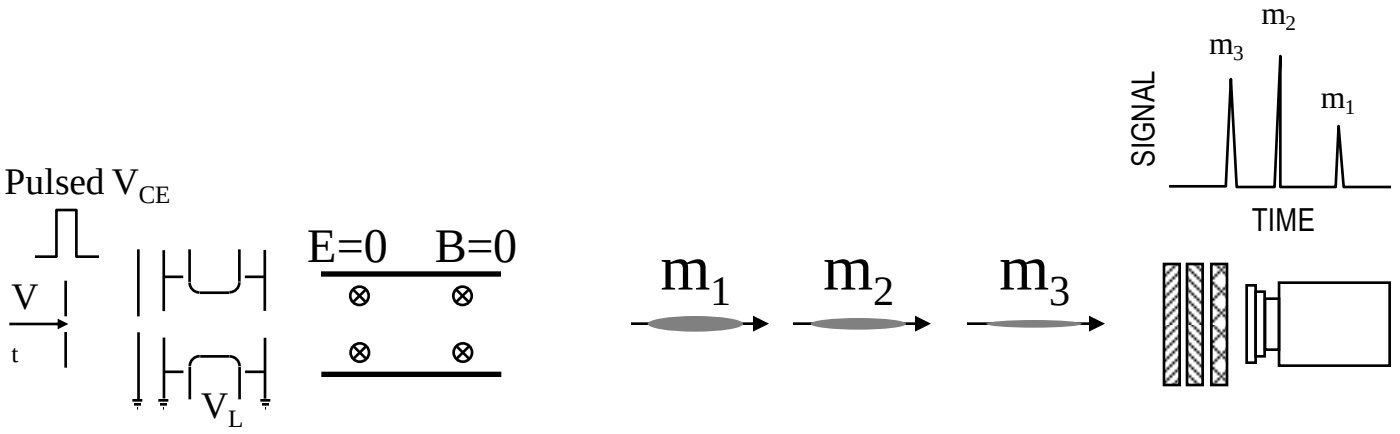


- Caused by screening charges in electrolyte near electrode surface (Double Layer)
- High only near electrode surface
- Field effects influenced by surface details
  - Defects
  - Protruding atoms
  - Adsorbed Particles

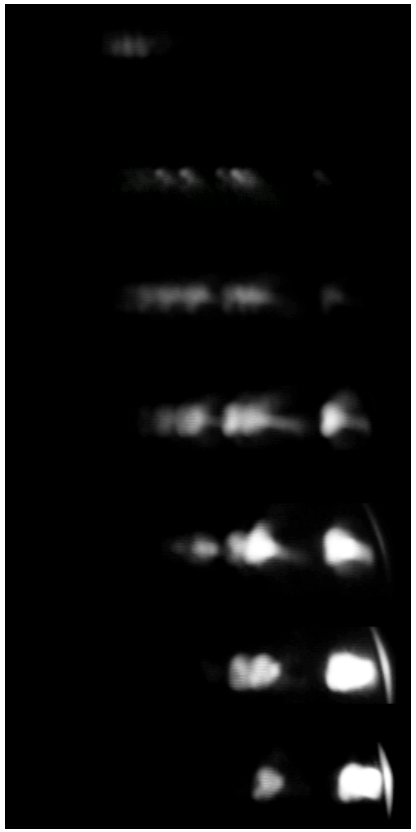

Water Layer
Pt - H_20 Interface
Ion Formation
Pt Field
Emitter Tip
H_20 -Vacuum Interface
Ion Formation

Pulsed Field Desorption with ToF Analysis

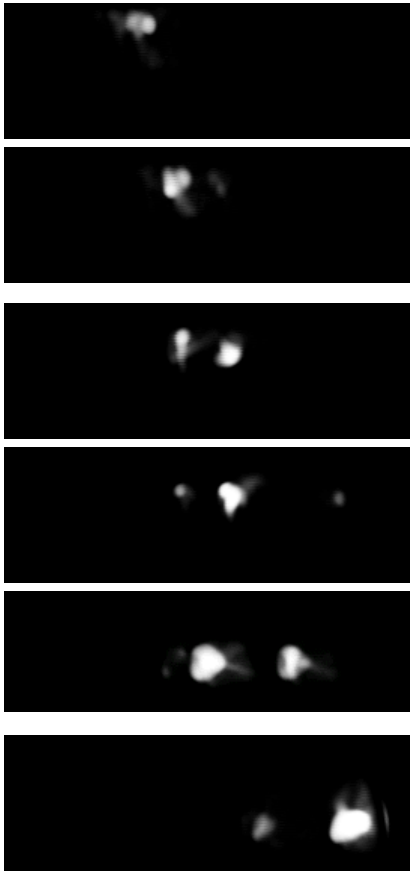
- All Ion Species Analyzed Simultaneously
- High Resolution Allows Analysis of Ion Energy Distribution



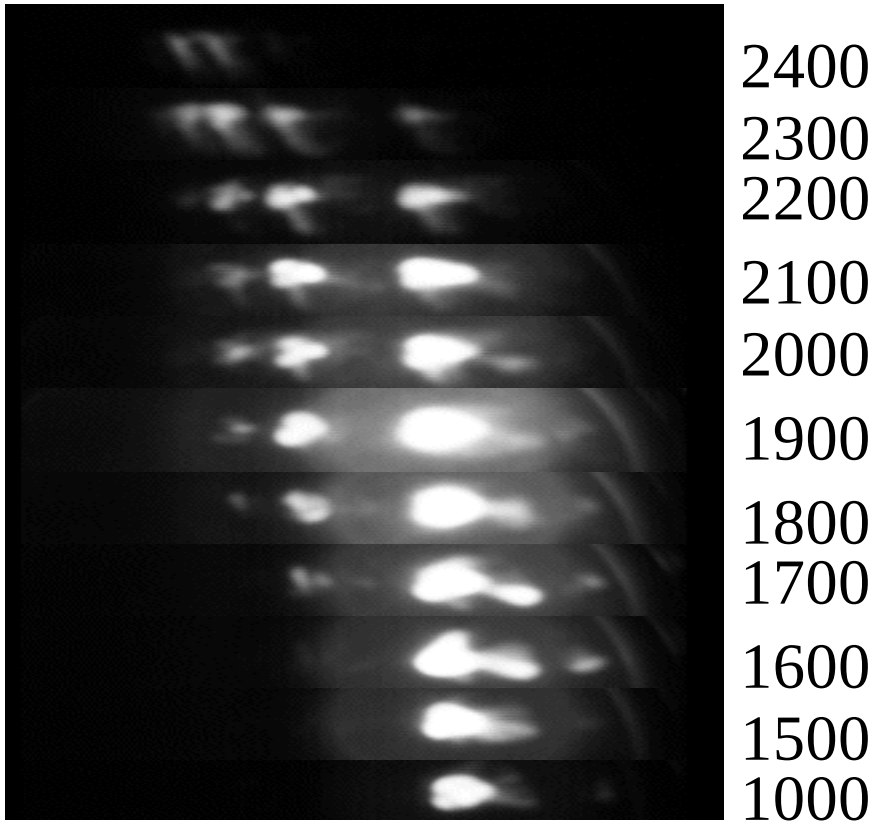
MeOH + Water



Water



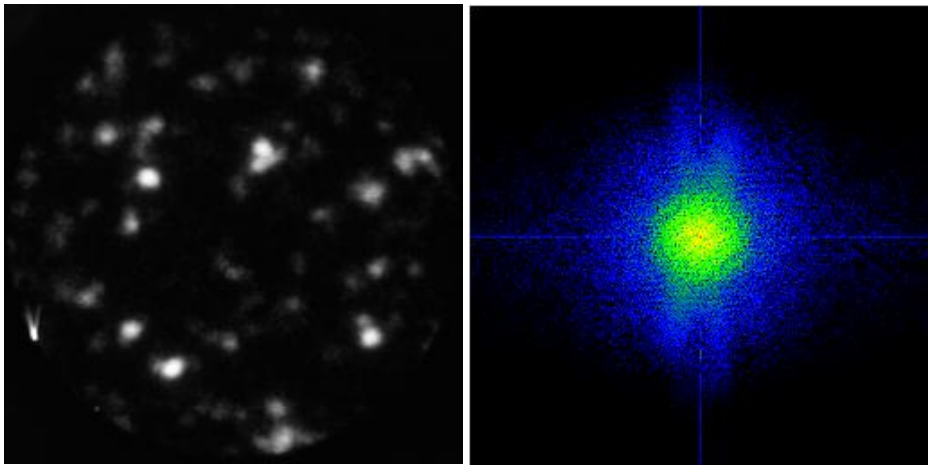
MeOH



180 K

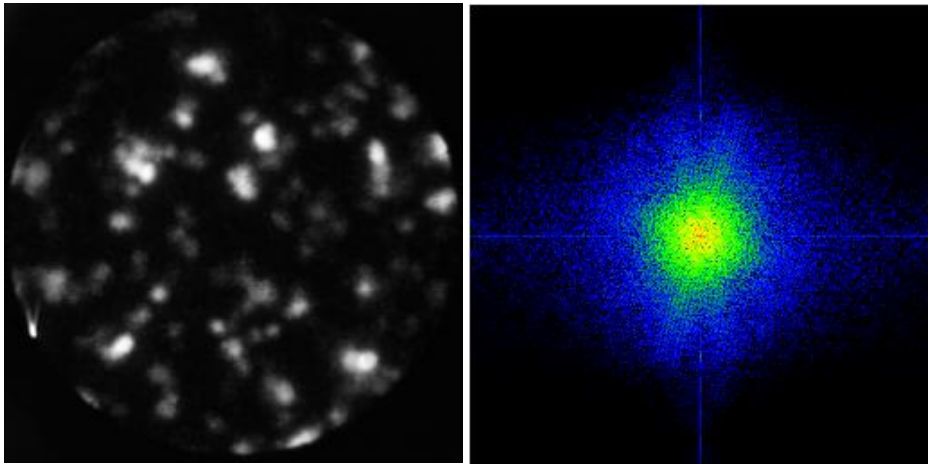
$F_{app} \cong 0.29$ V/Å

n>4



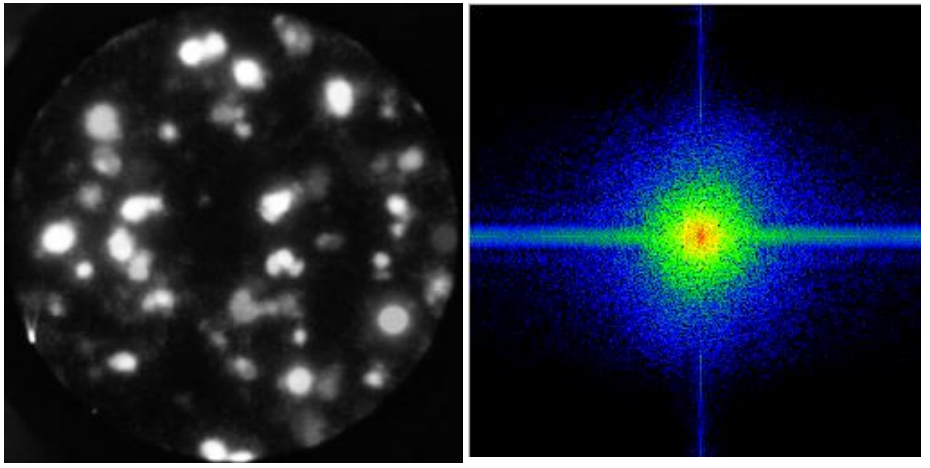
$F_{app} \cong 0.36$ V/Å

n=4

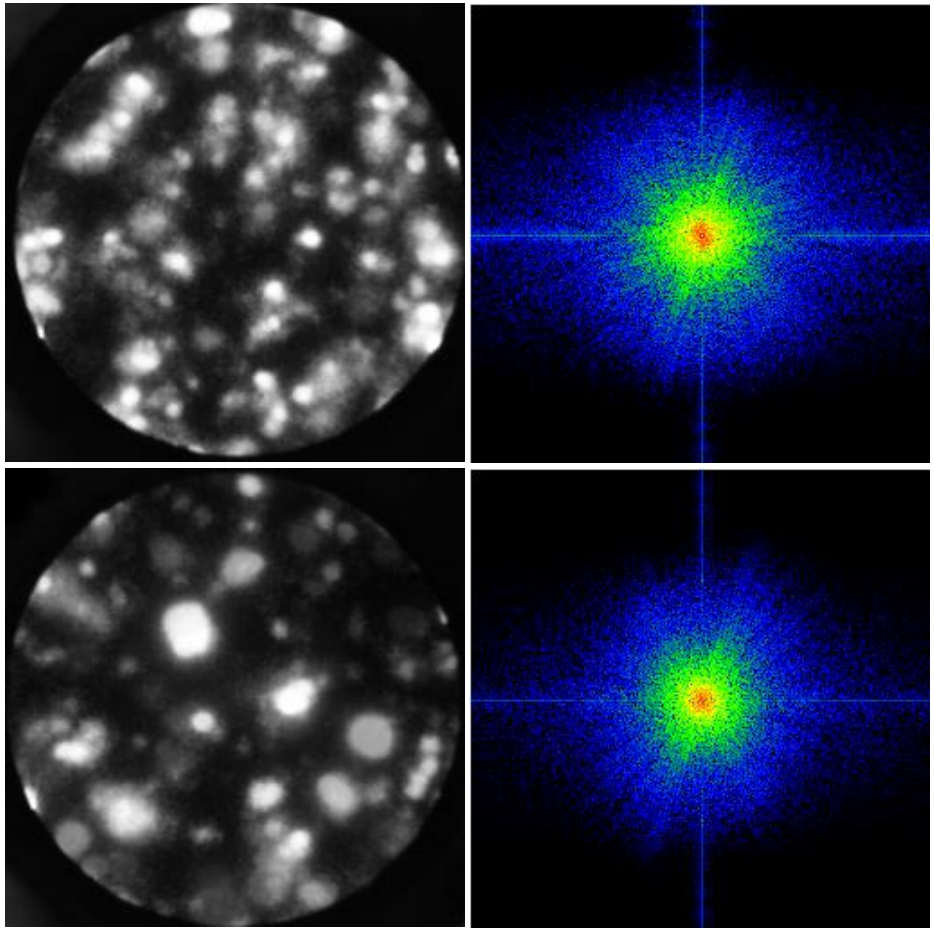


$F_{app} \cong 0.49$ V/Å

n=3



$F_{app} \cong 0.69$ V/Å (n=2)



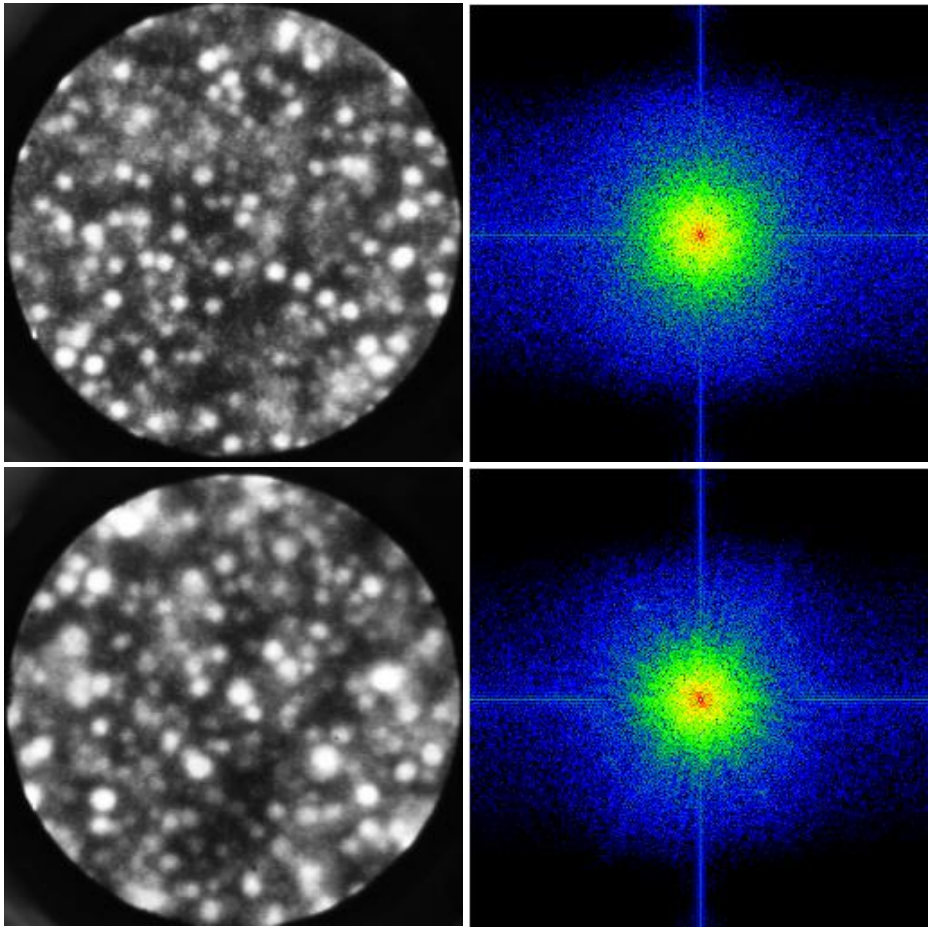
180 K

230 K

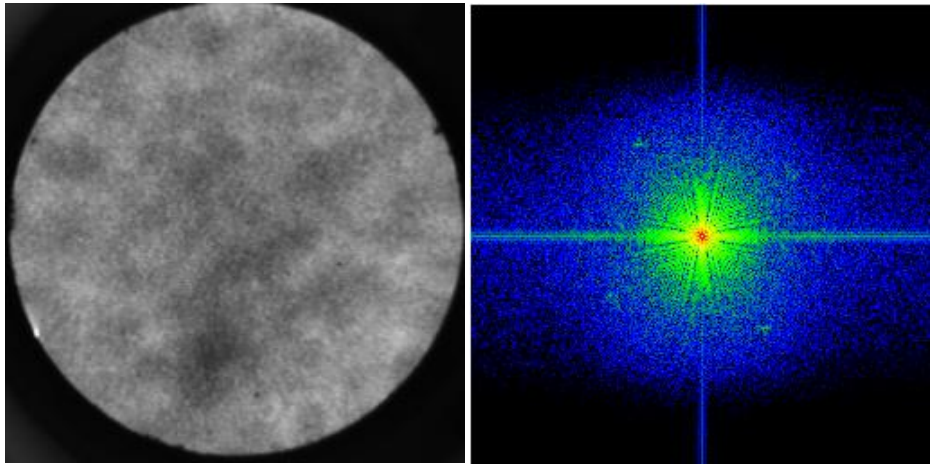
$F_{app} \cong 1.06$ V/Å (n=1)

180 K

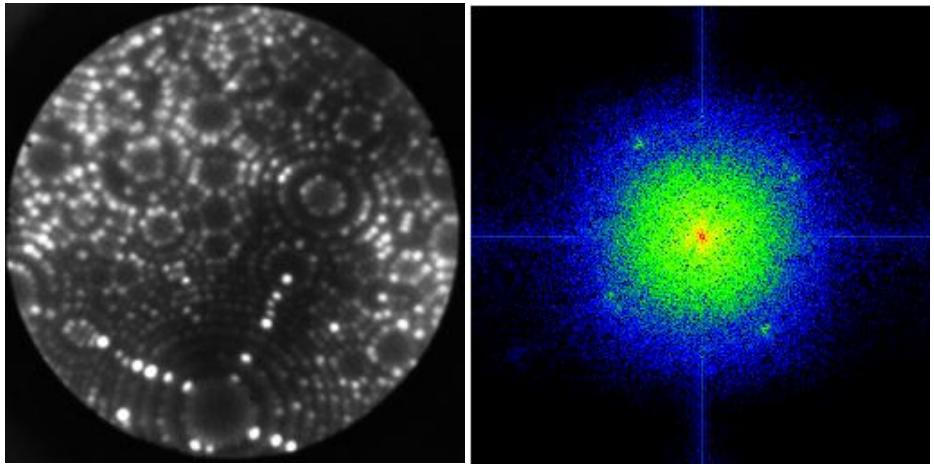
230 K

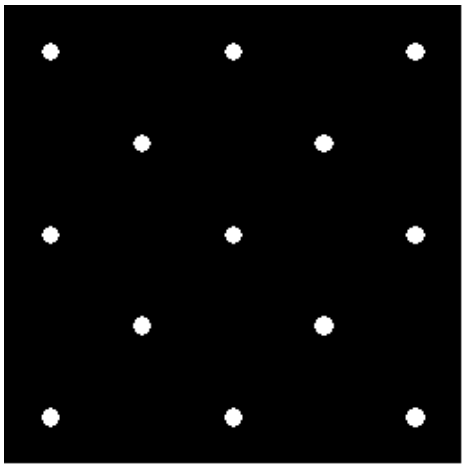


$F_{app} \cong 1.71$ V/Å
180K
n=0 [H_2O^+]

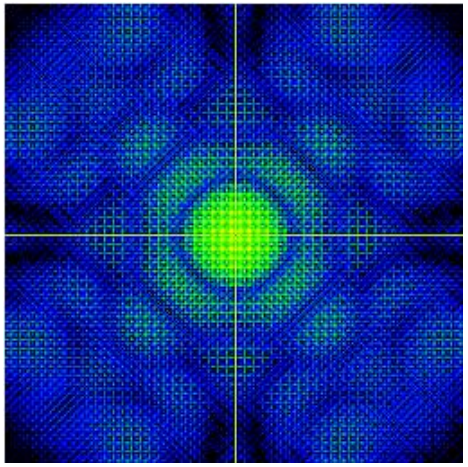


$F_{app} \cong 3.75$ V/Å
107K
Neon

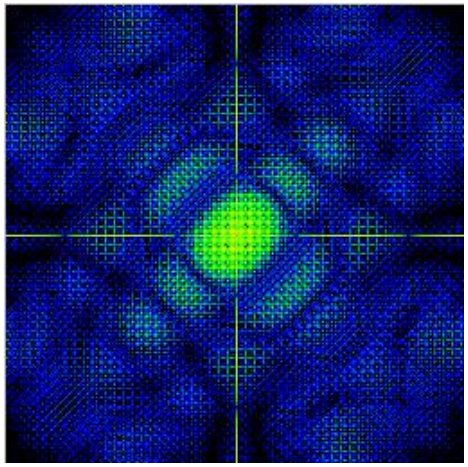




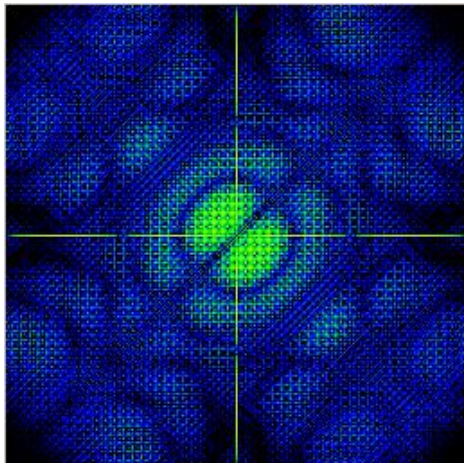
Input Image f(x,y)



Magnitude Spectra |F(u,v)|



Transform Real F(u,v)



Transform Imaginary F(u,v)