Water / Methanol Ion Cluster Formation on Pt Surfaces at High Electric Fields

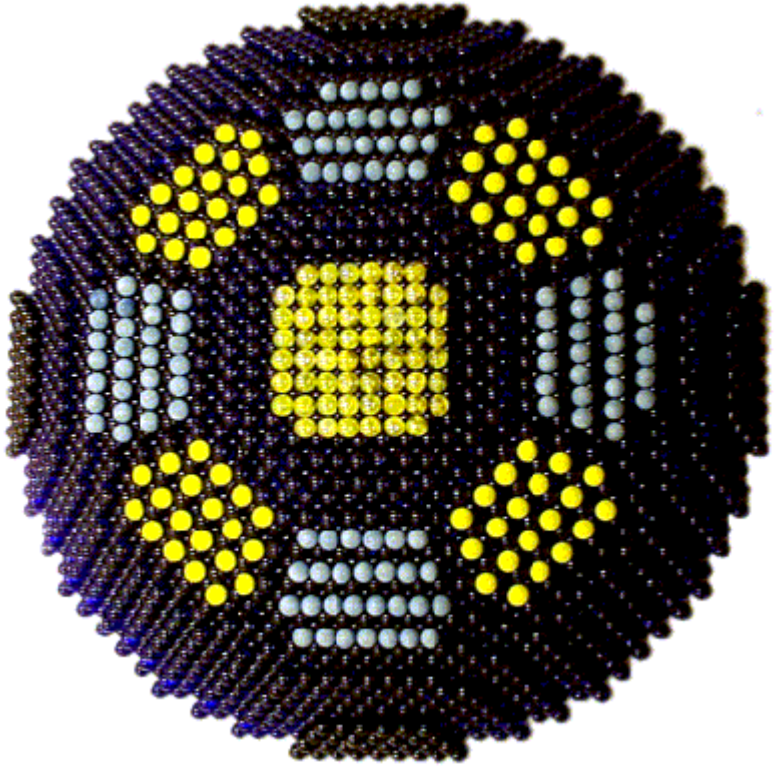
Christopher Rothfuss

Valentin Medvedev

Eric Stuve

Department of Chemical Engineering

University of Washington



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OVERVIEW

Experimental Intent

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

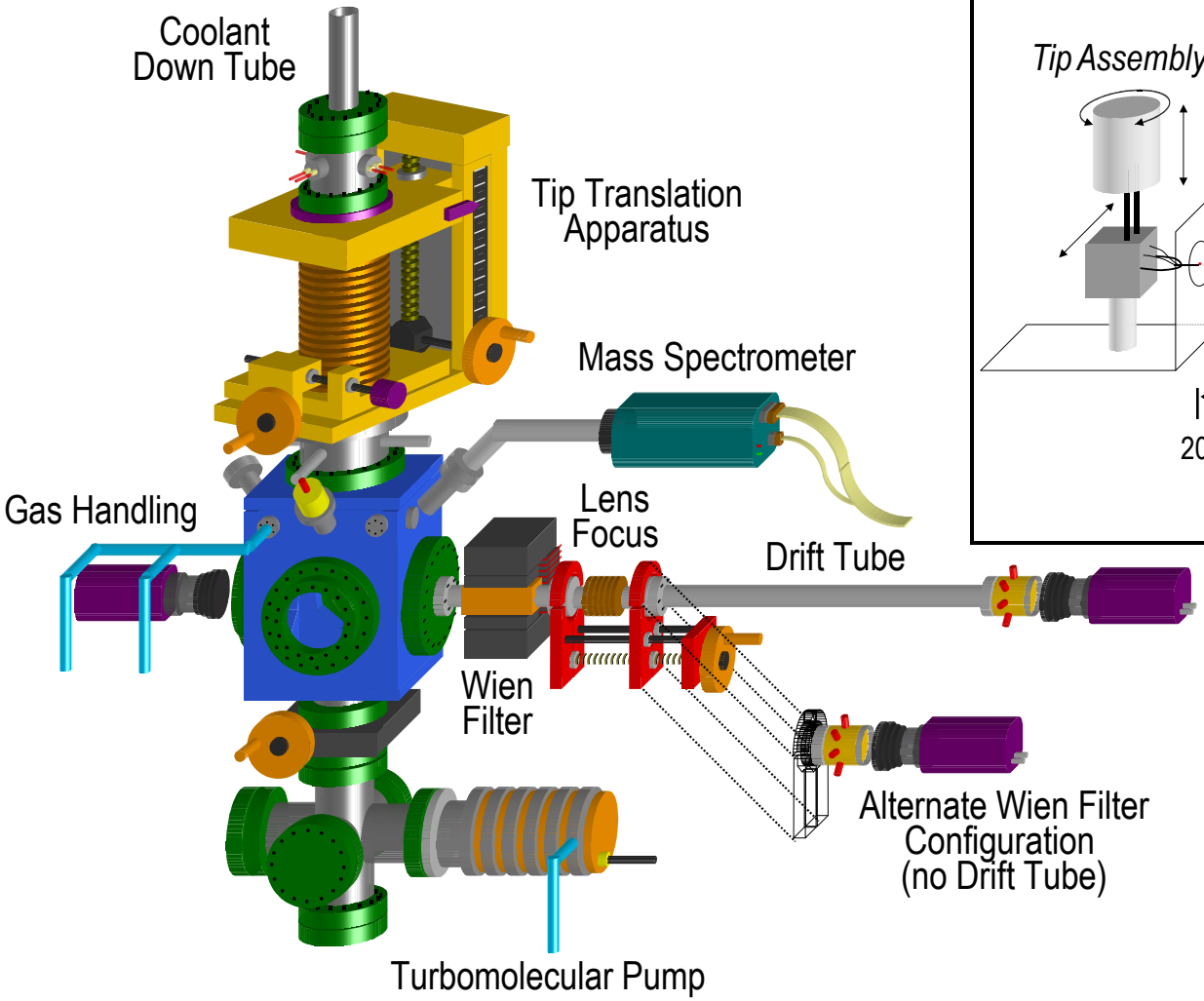
Outline of Discussion

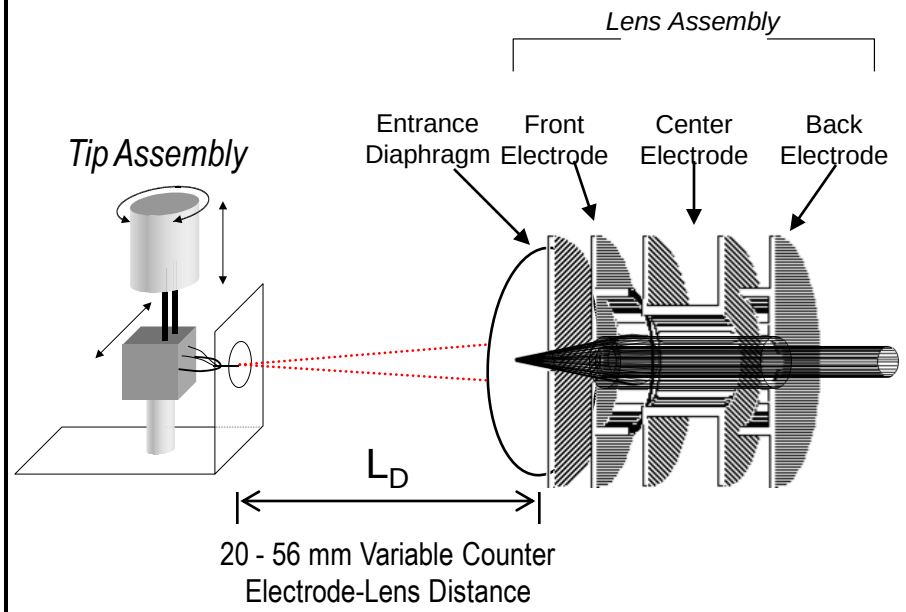
- Experimental Apparatus and Methods
- 2-Step Ion Dissociation / Emission Mechanism for Protonated Water Clusters
- Field Dependent Ion Formation for Methanol and Mixed Water / Methanol Systems
  - Wien Filter spectra
  - Time of Flight results

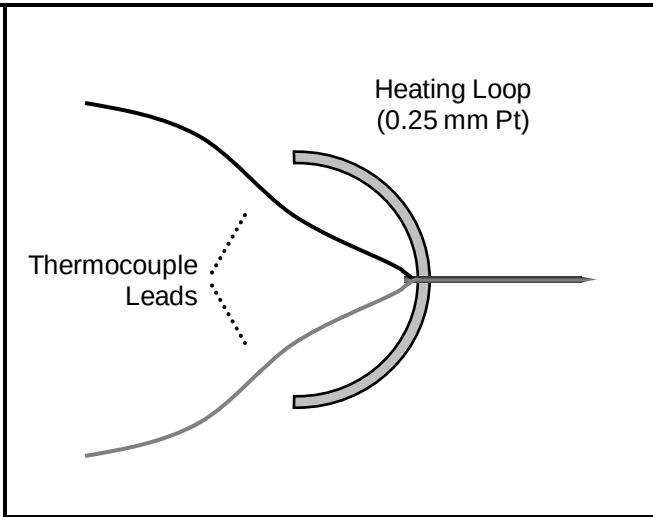
UHV Chamber Configuration

ANALYTICAL EQUIPMENT

- Rotatable Tip Assembly
- FIM/FEM Imaging
- Pulsed Potential ToF
- Quadrupole Mass Spec
- Wien Filter (ExB)

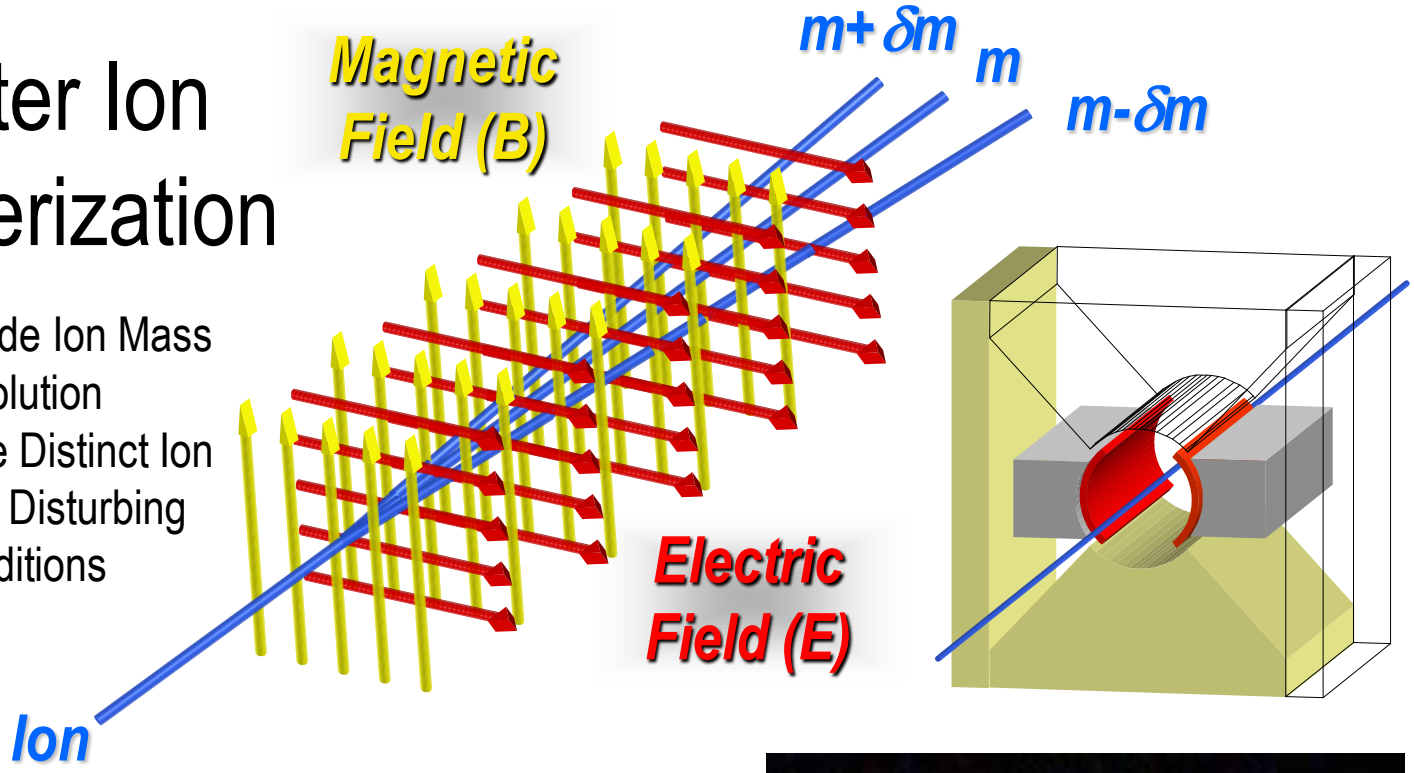


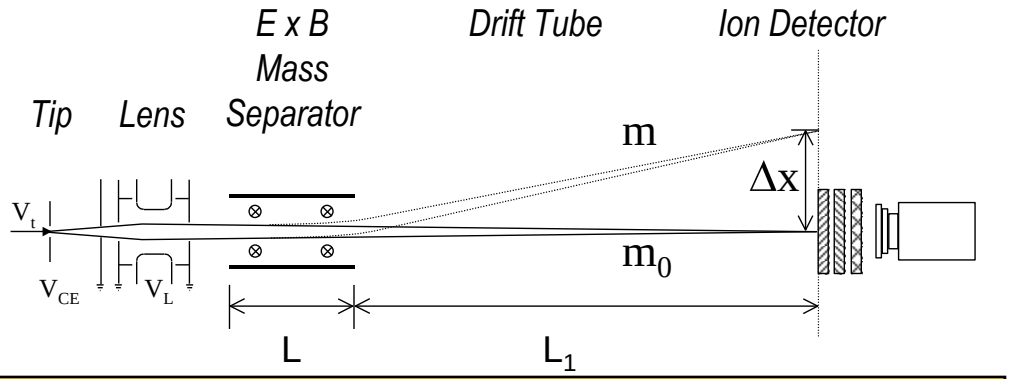




Wien Filter Ion Characterization

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





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



WIEN SEPARATION Masses 19 and 37

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.

PREVIOUS PURE WATER WORK

Water Ion Cluster Formation

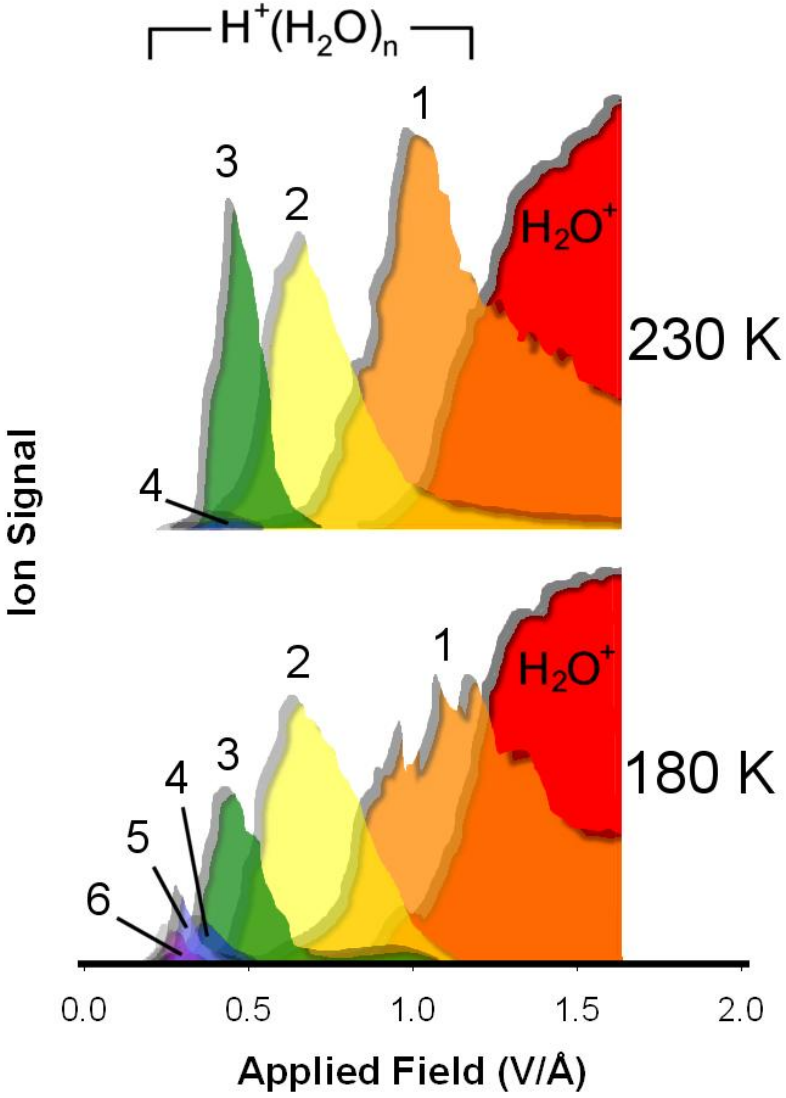
Field Ion Emission from Field Adsorbed Water Layers (>165 K)

Low Temperature (<150 K) Field Desorption from Adsorbed Ice Layers (Amorphous and Crystalline)

Developed 2-Step Ion Dissociation / Emission Mechanism

1) Dissociation
   - Barrier ~ 0.7eV
   - Field Enhanced, Thermally Activated
   - Rate Determining at Low T (<~150K)

2) Ion Emission
   - Barrier ~ 4 - 5 eV Dep on Cluster Type
   - Field Dependent
   - Rate Determining at High T (>~170K)



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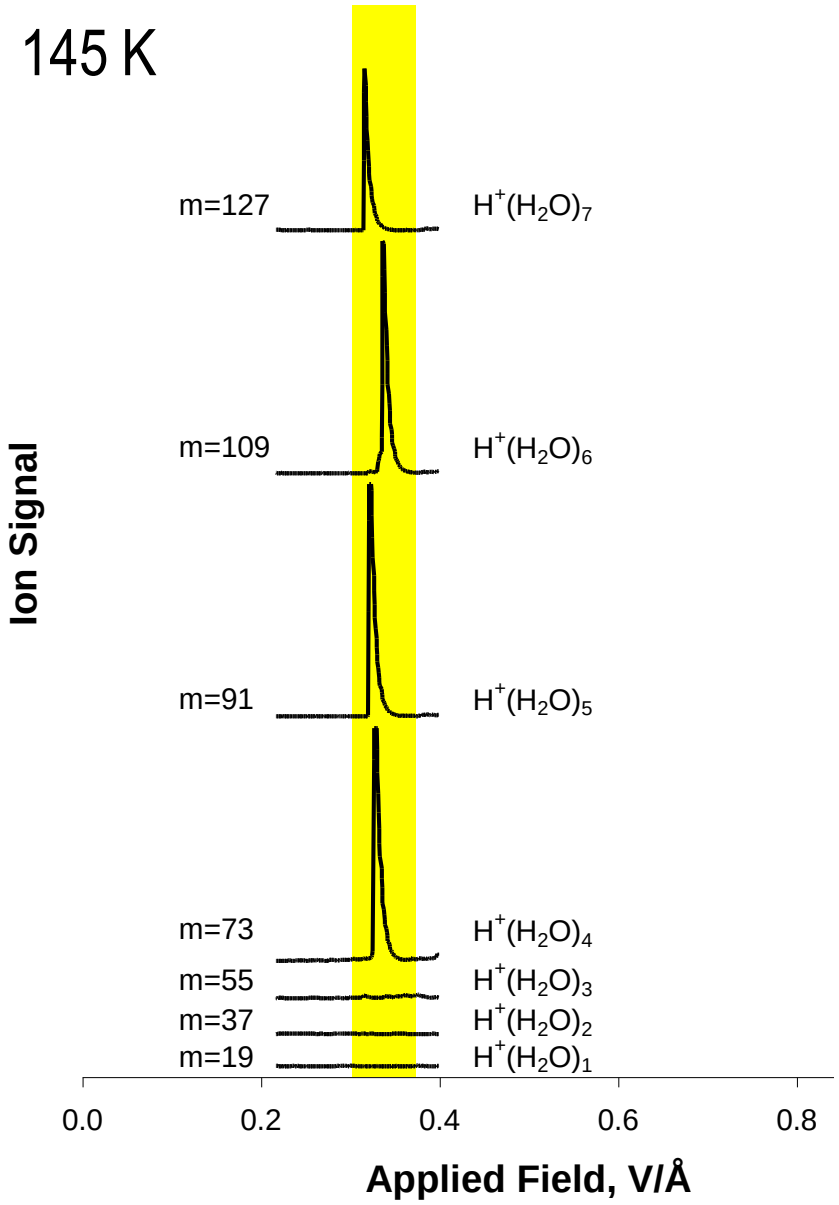
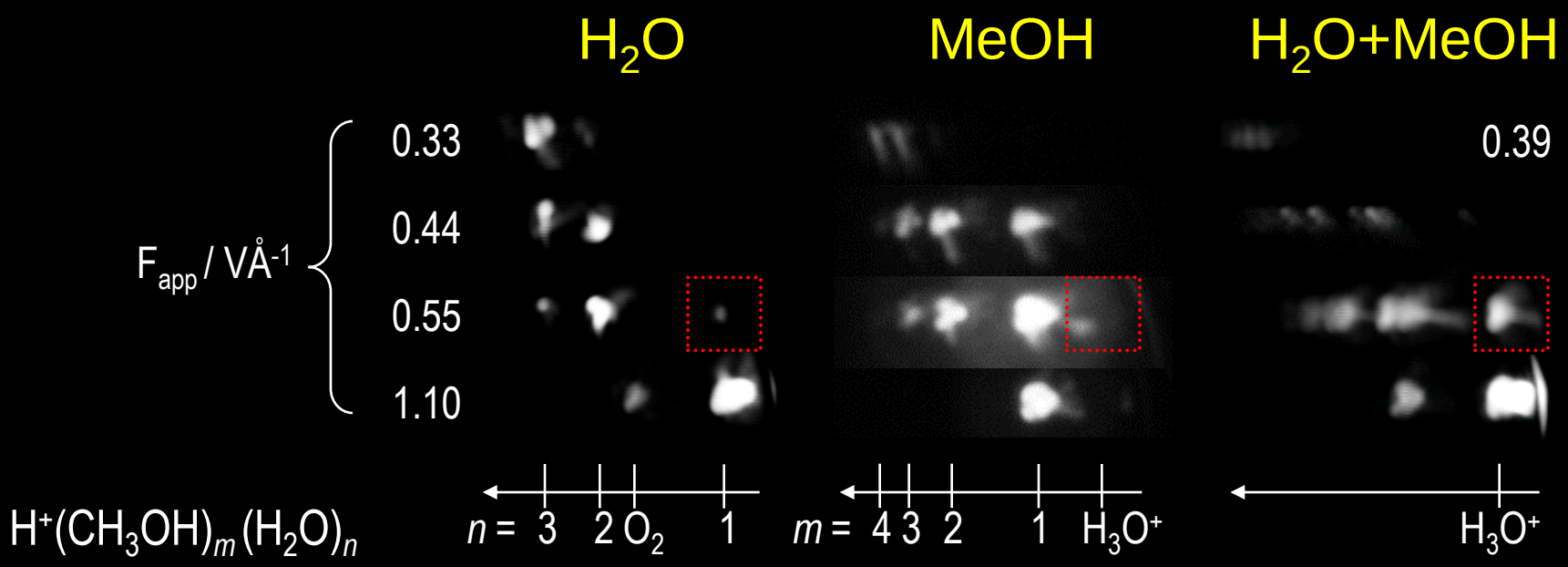


Wien Filter Mass Spectra Comparison



Experimental Conditions

- –Pt Emitter Tip at 180 K
- –V_{tip} = 3000 V
- –Field applied by changing V_{CE}
- –P_{H2O} + P_{MeOH} = 4x10^{-6} Torr

Results

- –Protonated ion clusters observed.
- –Low fields favor larger clusters.
- –Rich spectra for mixed system.
- –Enhanced H_3O^+ emission for mixed system.

MeOH Cluster Formation:

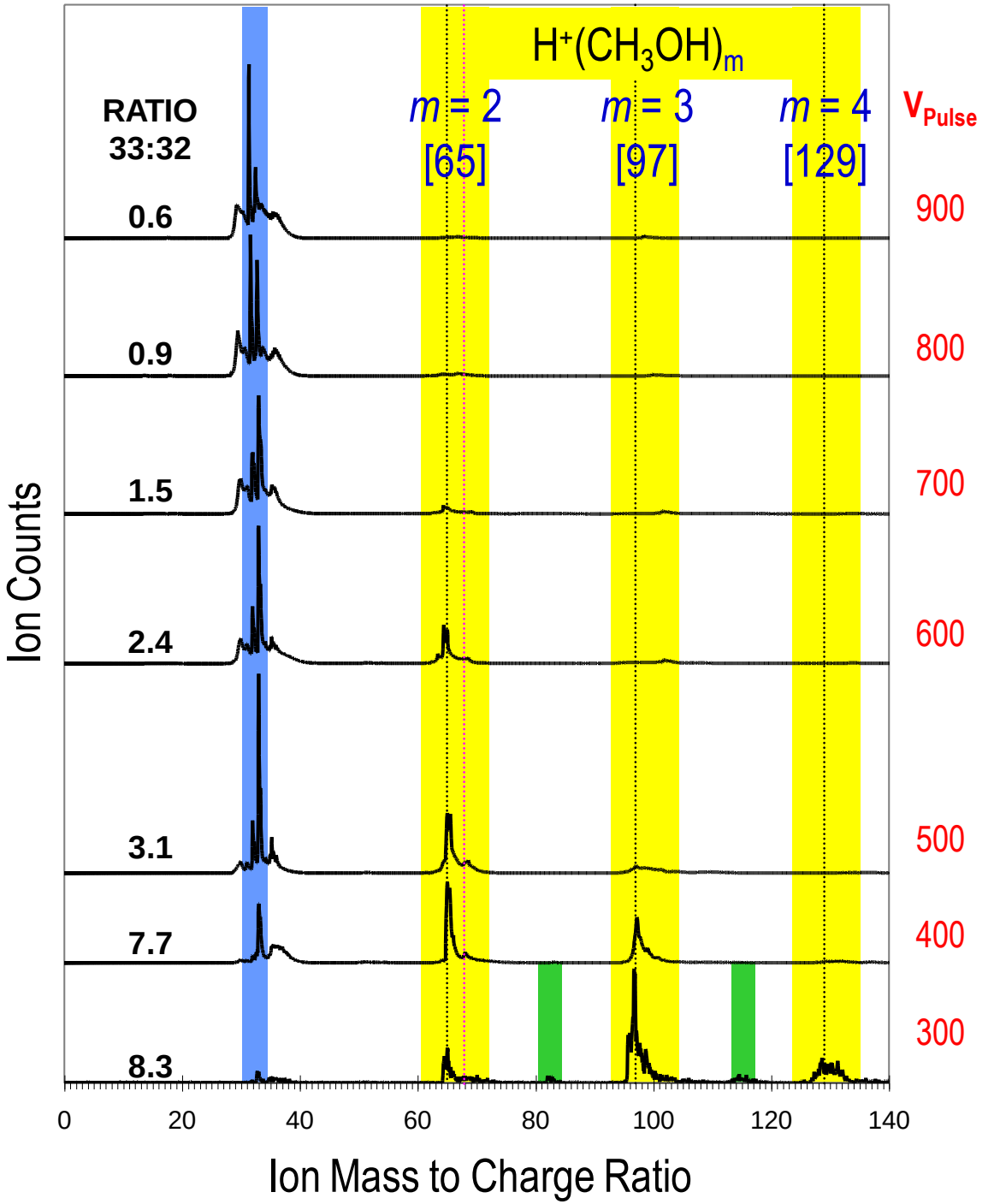
PULSE HEIGHT

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



MeOH / H_2O Cluster Formation:

MIXTURE RATIO

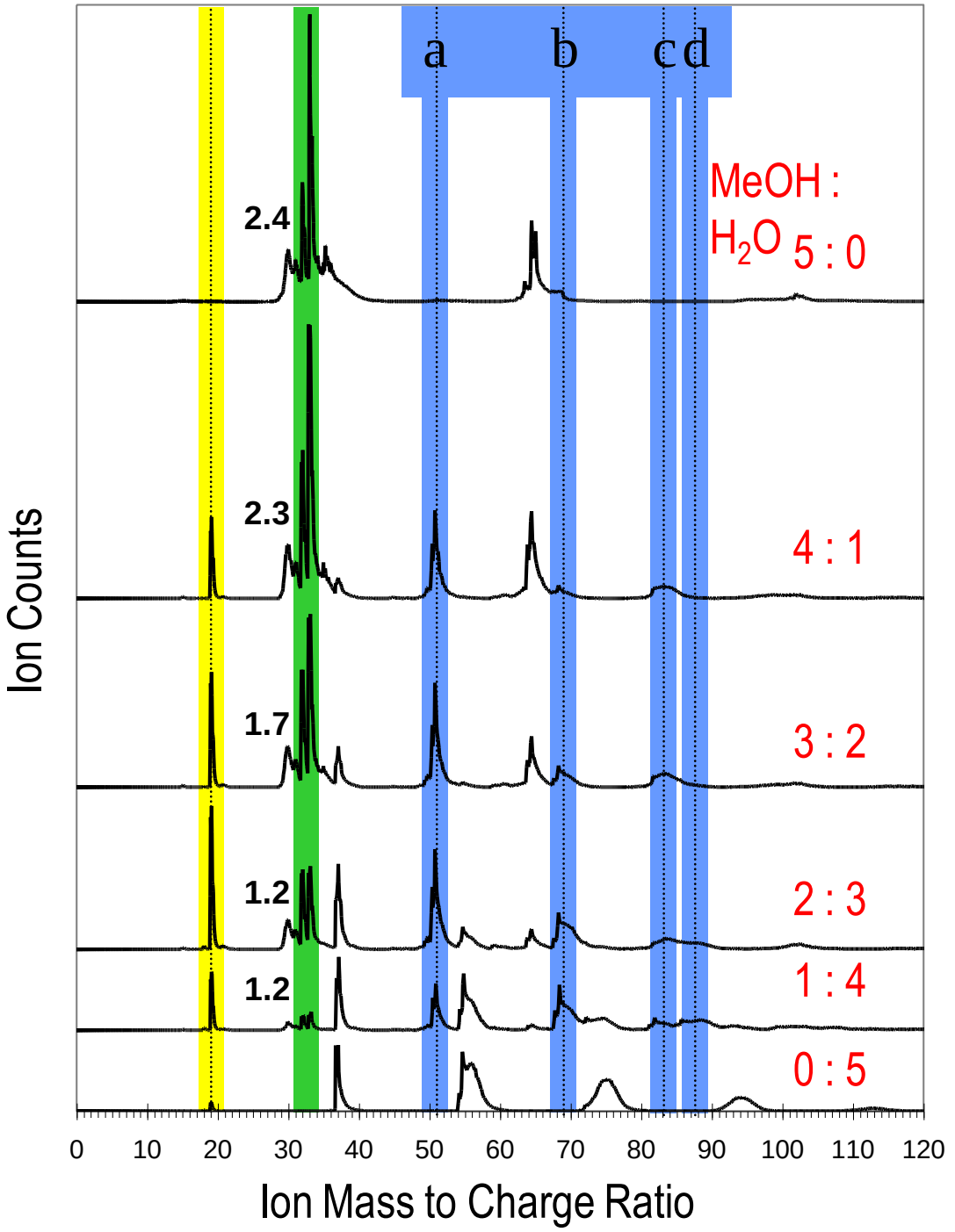
PROCEDURE

- 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:

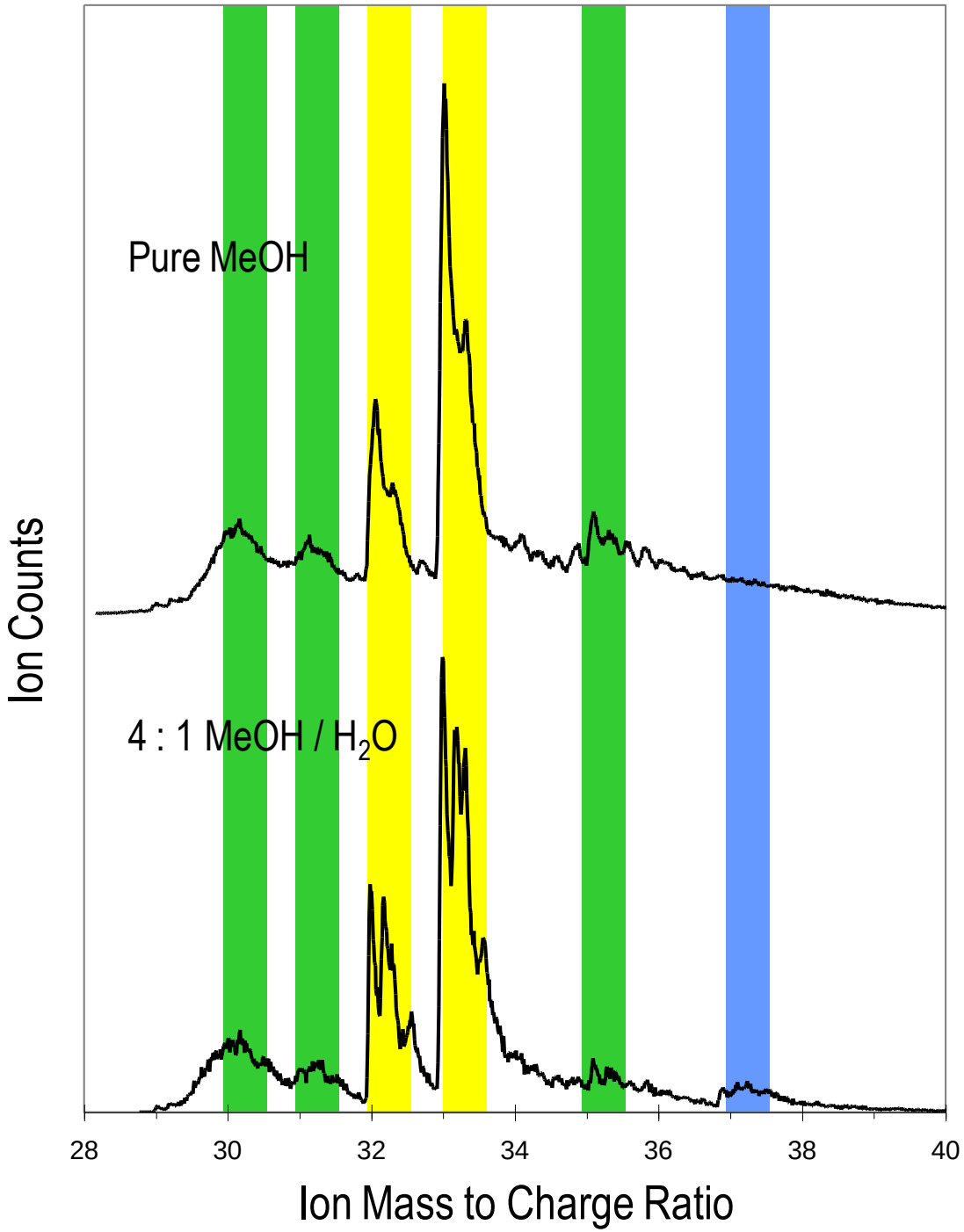
RESOLVED *m* = 1

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

Conclusions

–Protonated MeOH and H_2O / MeOH clusters emitted from Pt tip

–MeOH ion cluster behavior similar to previous H_2O results

–Mixed $H^+(CH_3OH)_m(H_2O)_n$ clusters observed

–Presence of methanol alters emission and solvation

Unanswered Questions

–Identities of masses near m=1?

–Why is mass 19 (H_3O^+) enhanced for mixed systems?

QUESTIONS?

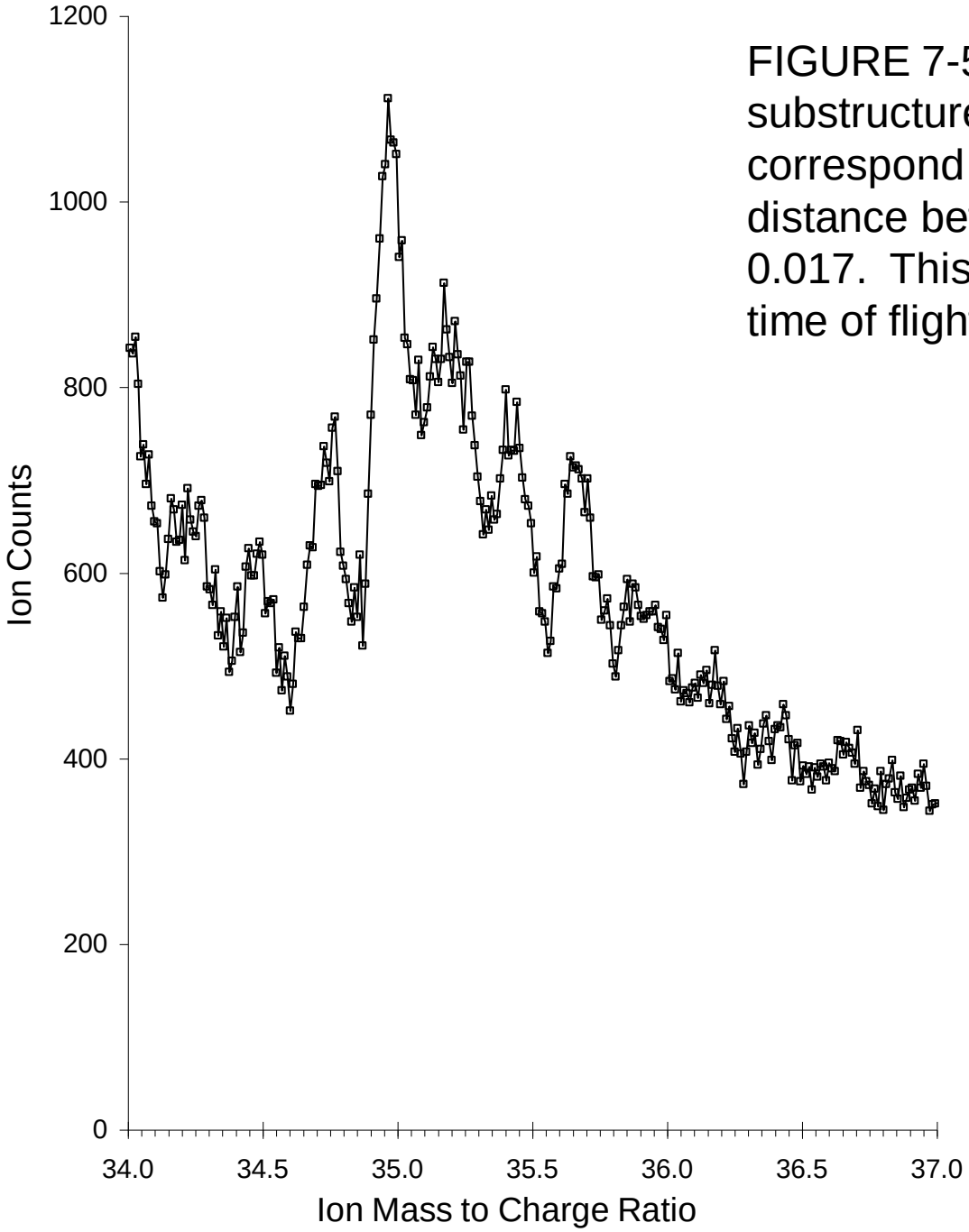
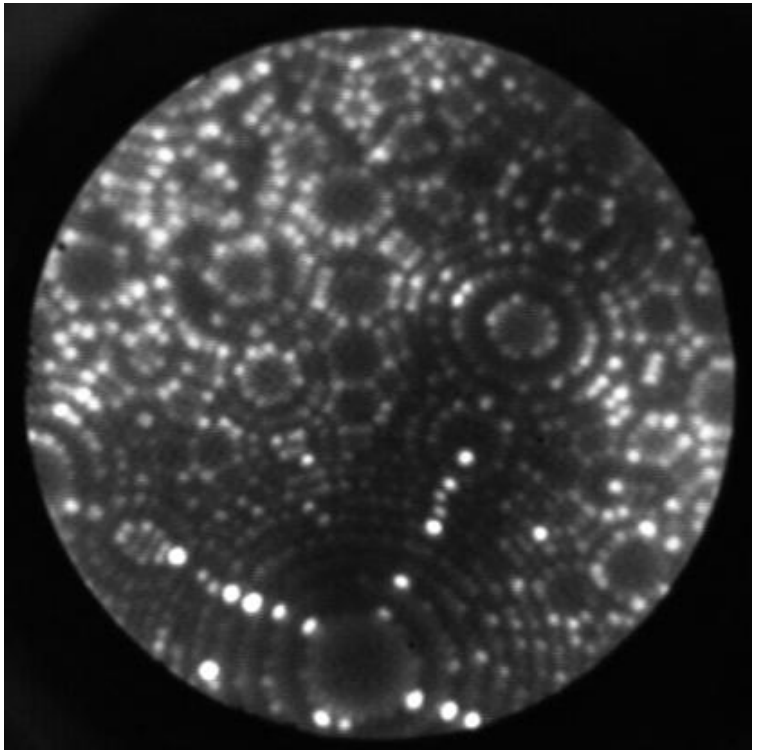


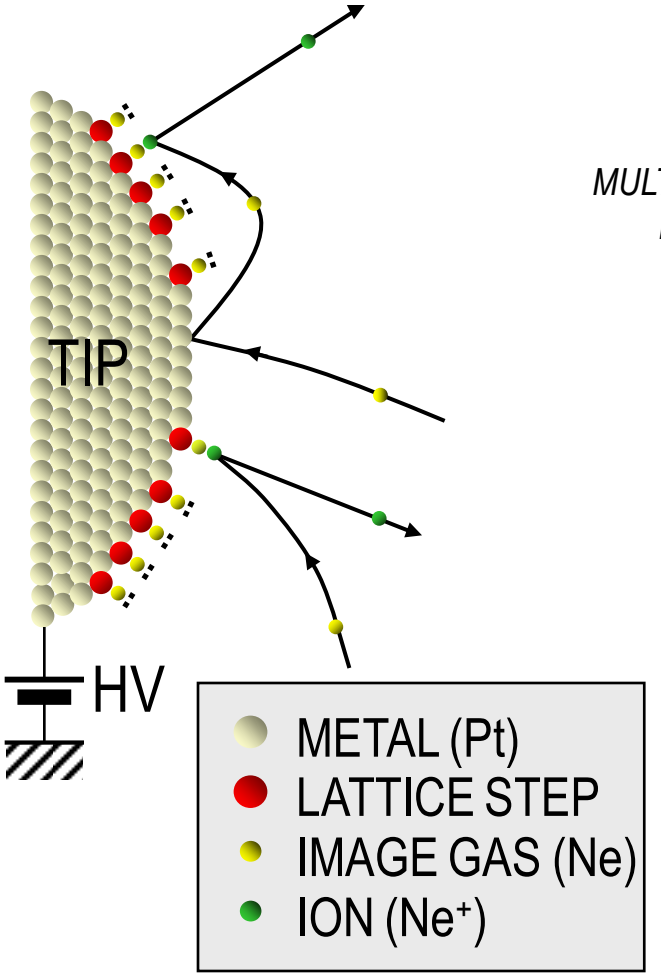
FIGURE 7-5: Mass to charge substructure near mass 35. Drop lines correspond to local minima. Average distance between minima is 0.239 0.017. This corresponds to an average time of flight difference of 29 2 ns.

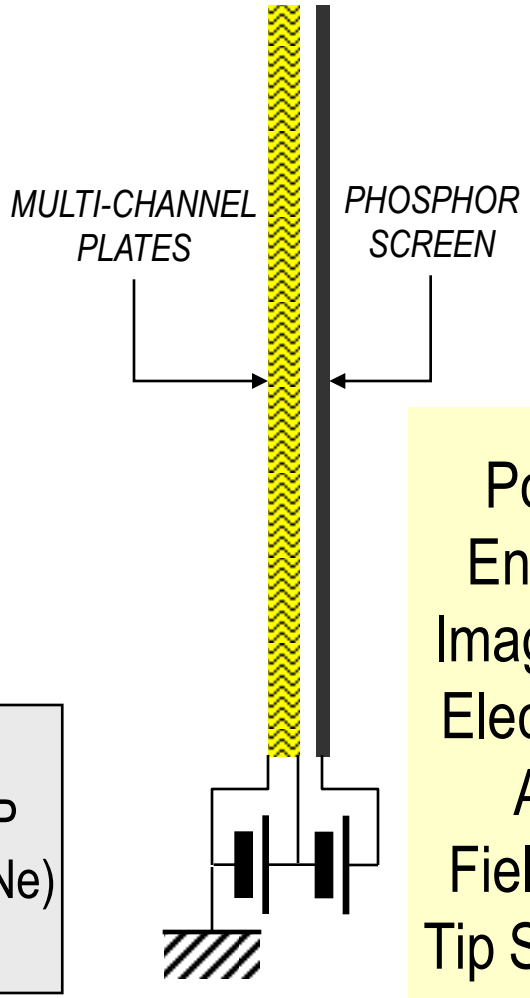
Field Ion Microscopy

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

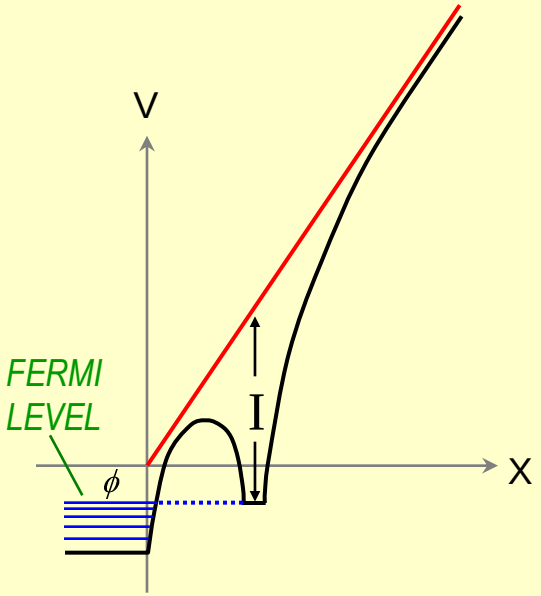
Neon on Pt
107 K
1×10^{-4} Torr
~3.75 V/Å







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

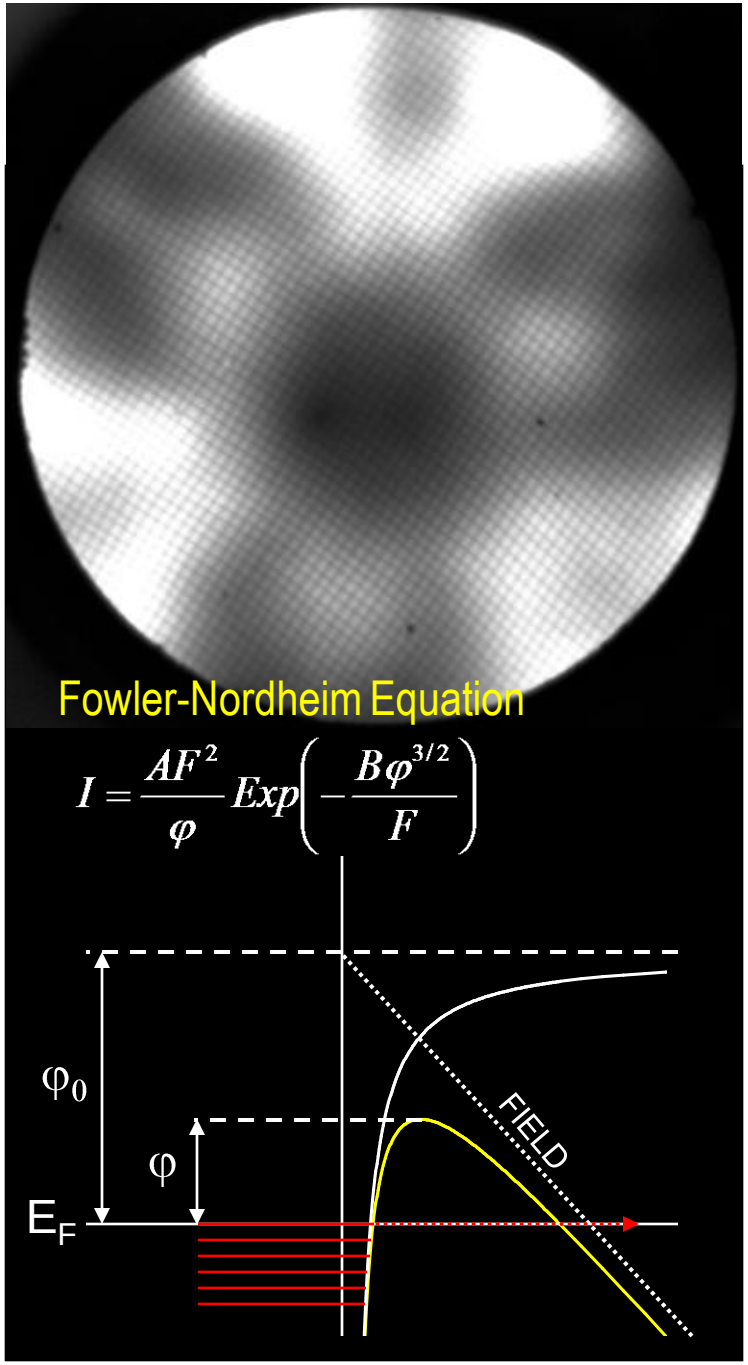


Adapted from Tsong,1990.

Field Emission Microscopy

- Negative Tip Potential
- Electron Tunneling From Tip to Vacuum
- Spatial Resolution of Local Work Function, φ

Pt FEM
298 K
~0.43 V/Å
φ ~ 5.65eV



Fowler-Nordheim Equation

$$I = \frac{AF^2}{\varphi} Exp\left(-\frac{B\varphi^{3/2}}{F}\right)$$

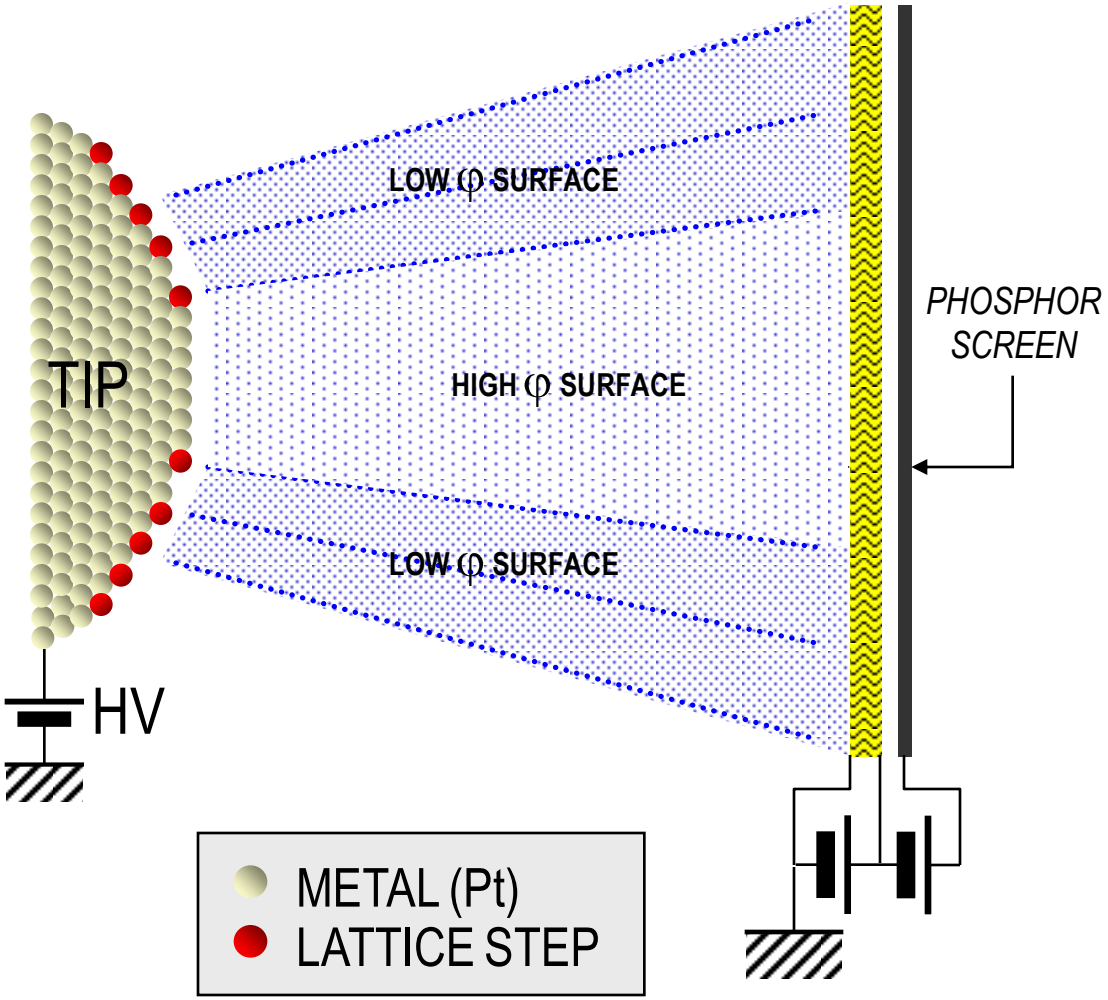


TABLE 7-1: Ion cluster emission energies for protonated methanol clusters.

Ion Cluster	ΔE_{emit} (eV)
H^+	14.19
$H^+(CH_3OH)$	6.81
$H^+(CH_3OH)_2$	5.91
$H^+(CH_3OH)_3$	5.49
$H^+(CH_3OH)_4$	5.28
$H^+(CH_3OH)_5$	5.19
$H^+(CH_3OH)_6$	5.13
$H^+(CH_3OH)_7$	5.11

TABLE 7-2: Excess emission energy $X^{m,n}$ for protonated water / methanol clusters. Values represent the ion cluster emission energy $\Delta E^{m,n}$ minus the proton emission energy ΔE^{H+}. Values are in eV.

water (*n*) \ methanol (*m*)	0	1	2	3	4	5	6	7
0	0.00	-7.38	-8.28	-8.70	-8.91	-9.00	-9.06	-9.08
1	-6.77	-8.04	-8.64	-8.86	-8.99	-9.00		
2	-7.70	-8.51	-8.80	-8.93	-8.93			
3	-8.09	-8.71	-8.85	-8.89	-8.88			
4	-8.41	-8.78	-8.86	-8.85				
5	-8.47	-8.73	-8.84					
6	-8.51	-8.71						
7	-8.53							

TABLE 7-3: Possible ions near mass 32.

Mass	Possible Molecules
30	CH_2O^+, $C_2H_6^+$
31	CH_3O^+, $C_2H_7^+$
32	CH_3OH^+, O_2^+
33	$H^+(CH_3OH)$, $CH_3^+(H_2O)$, HO_2^+
35	$H_3O_2^+$

Ion Counts by Mass

$MeOH:H_2O$	32	33	Ratio
1:4	2677	3308	0.81
2:3	14077	16581	0.85
3:2	20754	35109	0.59
4:1	24667	55461	0.44
5:0	70391	169199	0.42

Ion Counts by Mass

V_P	32	33	Ratio
300	9	73	0.12
400	1376	10693	0.13
500	63416	196751	0.32
600	70391	169199	0.42
700	109915	166171	0.66
800	245423	214381	1.14
900	263153	162437	1.62