Water Ion Cluster Formation in High Electric Fields at and near a Pt Emitter Tip

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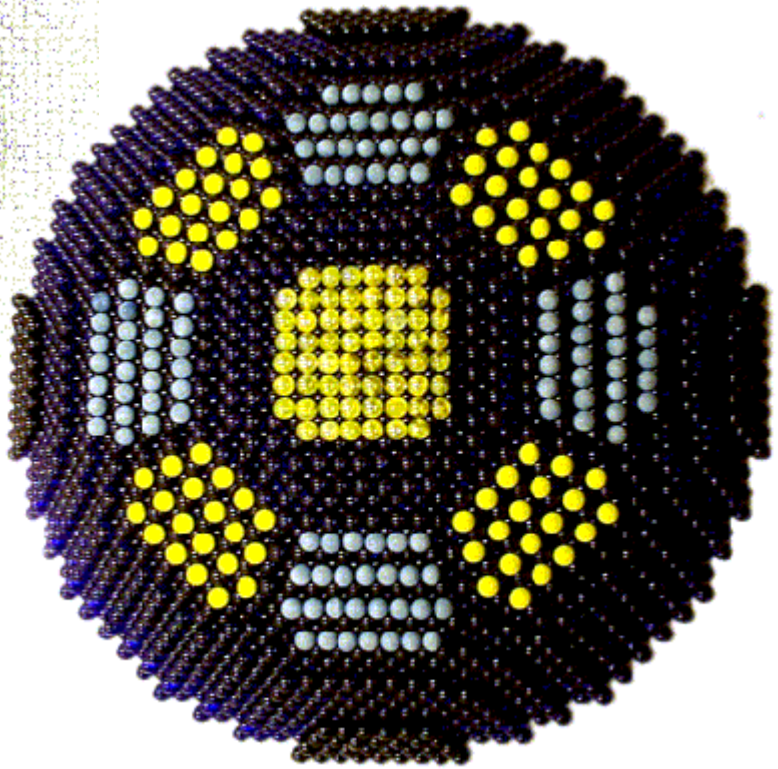

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Overview

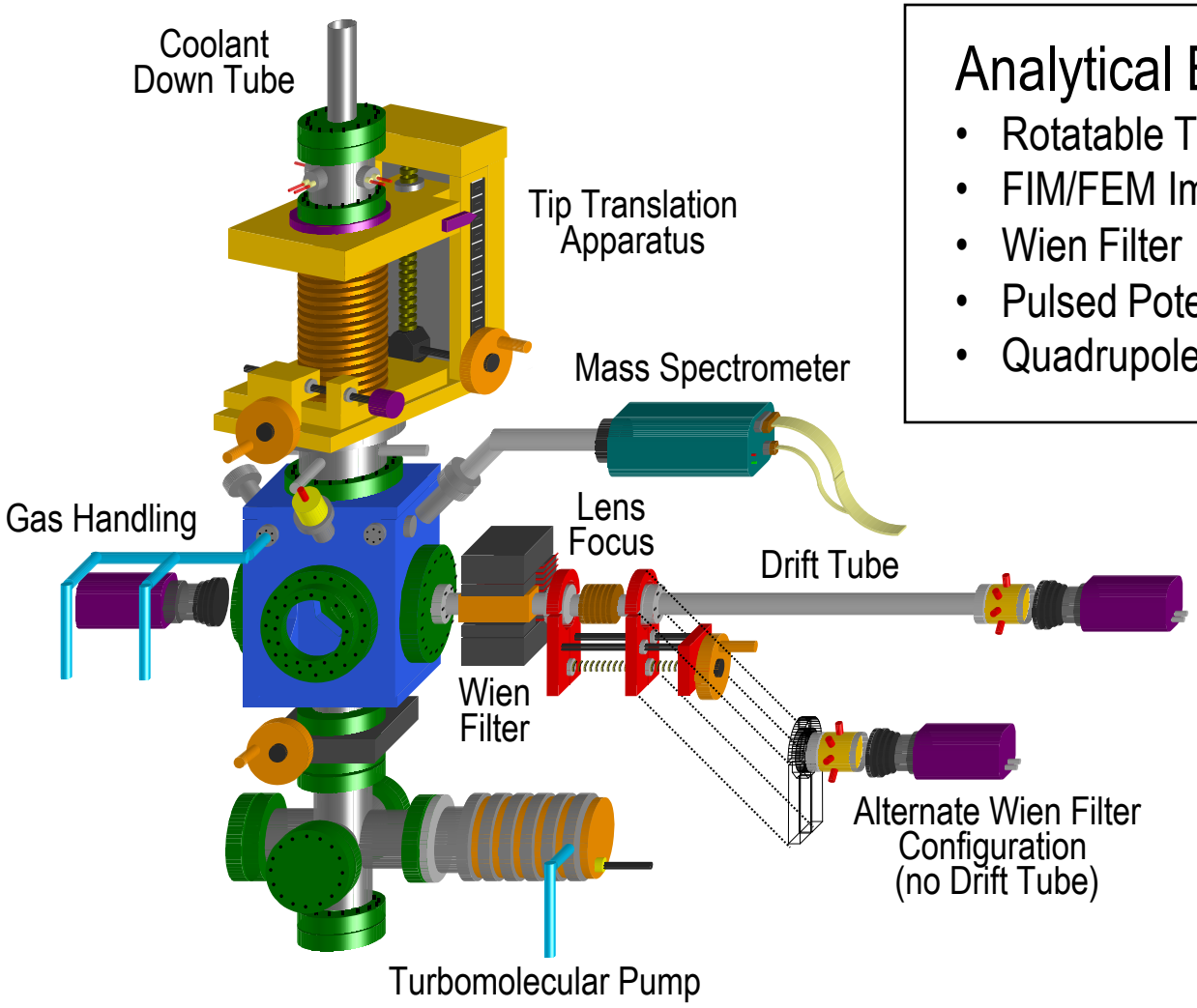
EXPERIMENTAL INTENT

- Study Behavior of Water in High Electric Fields
  - Electrochemical Interfaces
  - Field Emitter Arrays
  - Basic Water Energetics
- Proton Solvation
- Mechanisms for Ionization

OUTLINE OF DISCUSSION

- Experimental Apparatus and Methods
- Mass Resolved Ion Cluster Formation
  - Field Dependence Results
  - Temperature Dependence Results
- Cluster Formation Mechanism

UHV Chamber Configuration

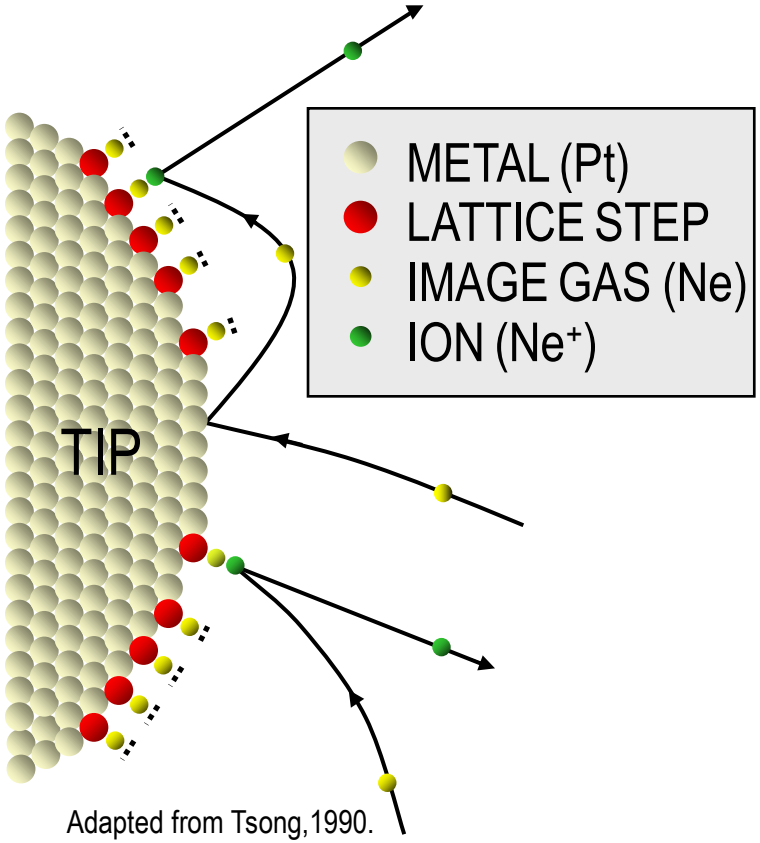


Analytical Equipment

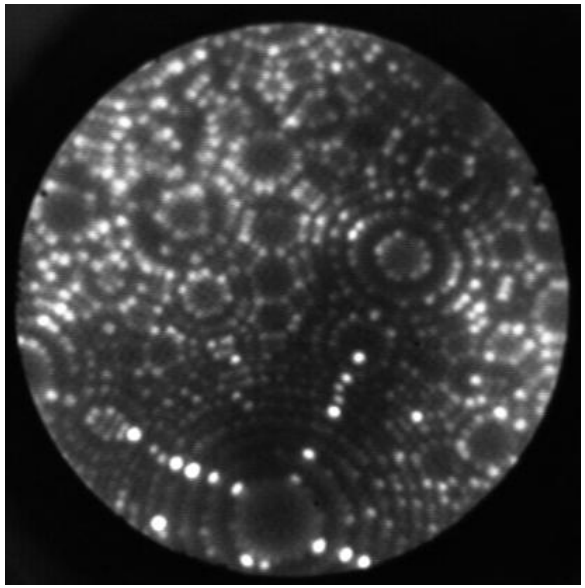
- Rotatable Tip Assembly
- FIM/FEM Imaging
- Wien Filter
- Pulsed Potential Time of Flight
- Quadrupole Mass Spectrometer

Field Ion Microscopy

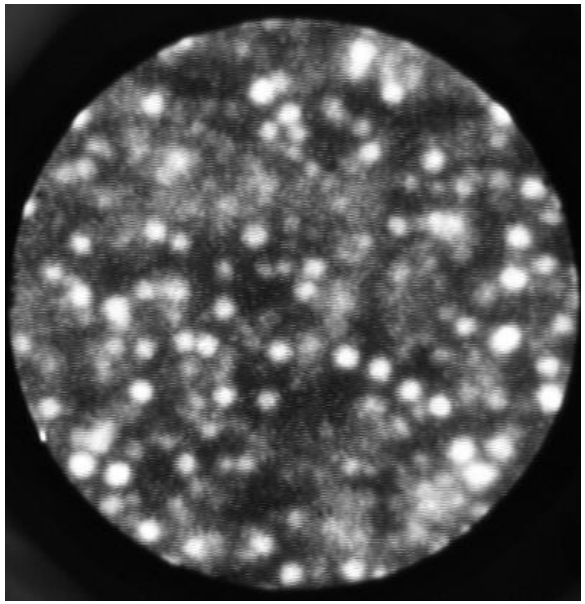
- Spatial Resolution of Ion Emission
- Field Clean Pt Surface to Prevent Possible Contamination



Adapted from Tsong,1990.



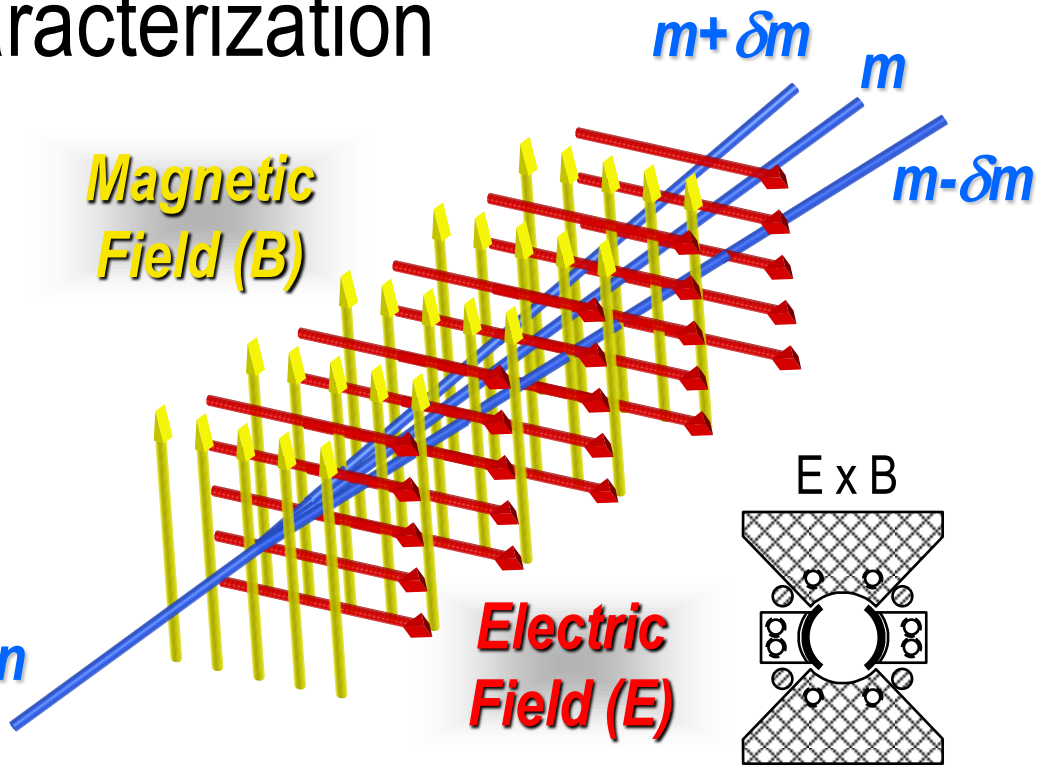
Neon on Pt
107 K
$1x10^{-4}$ Torr
~3.75 V/Å

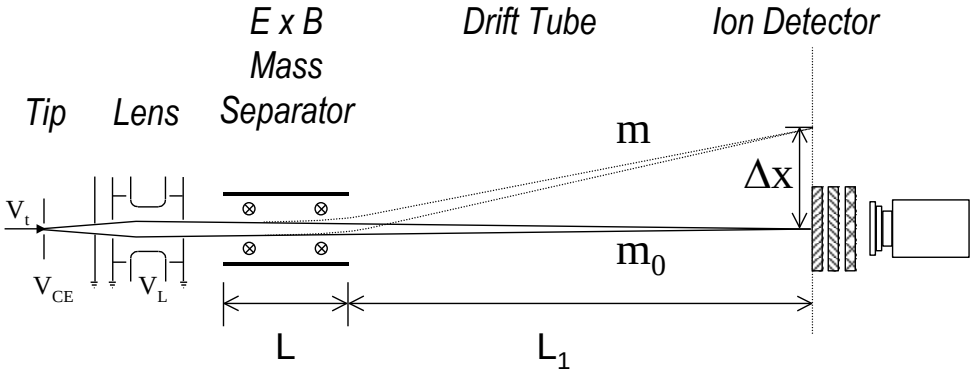


H_2O on Pt
180 K
$5x10^{-6}$ Torr
~1.0 V/Å

Wien Filter Ion Characterization

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





GOVERNING EQUATIONS

$$eE_0 = e\nu B_0 \qquad E_0 = B_0\sqrt{\frac{2e\phi_0}{m_0}}$$

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

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.

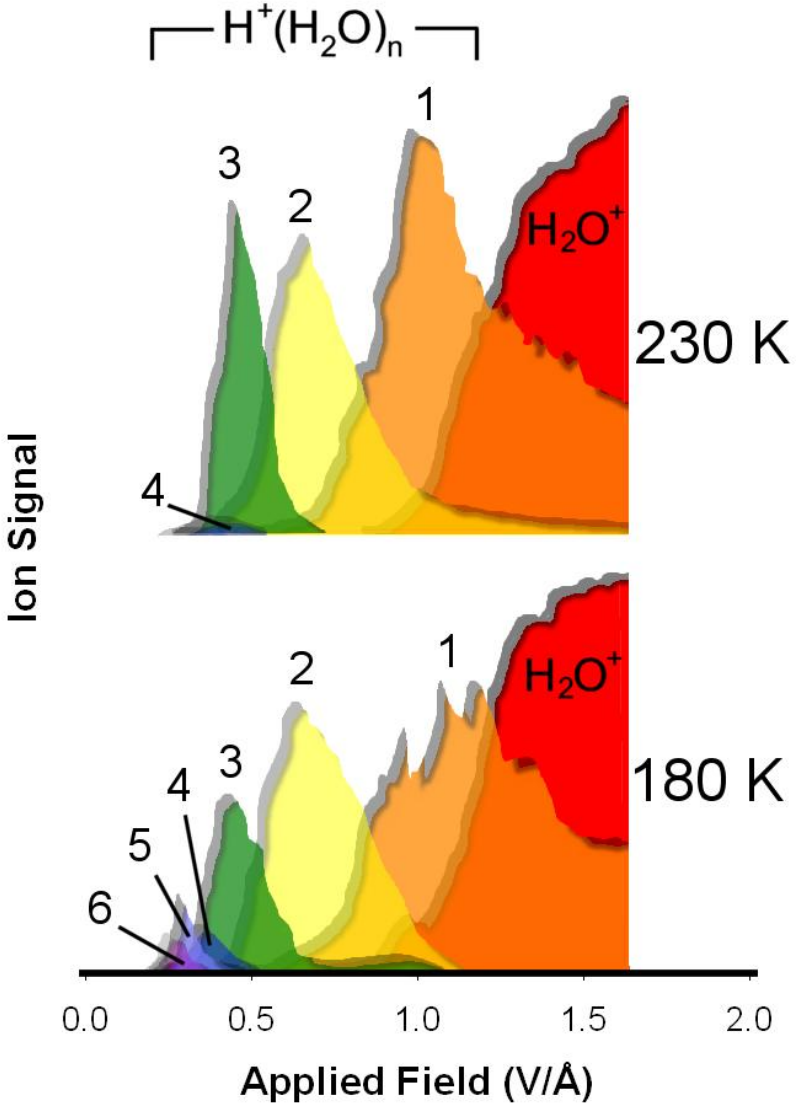
Mass Resolved Ion Cluster Formation

PROCEDURE

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

RESULTS

- Field condensed water layer on tip
- Ion Cluster Emission
  - Low Field Large n Clusters (Energetically Favorable)
  - High Field Favors Small n Clusters (Kinetically Favorable)



Field Effect on Ion Emission

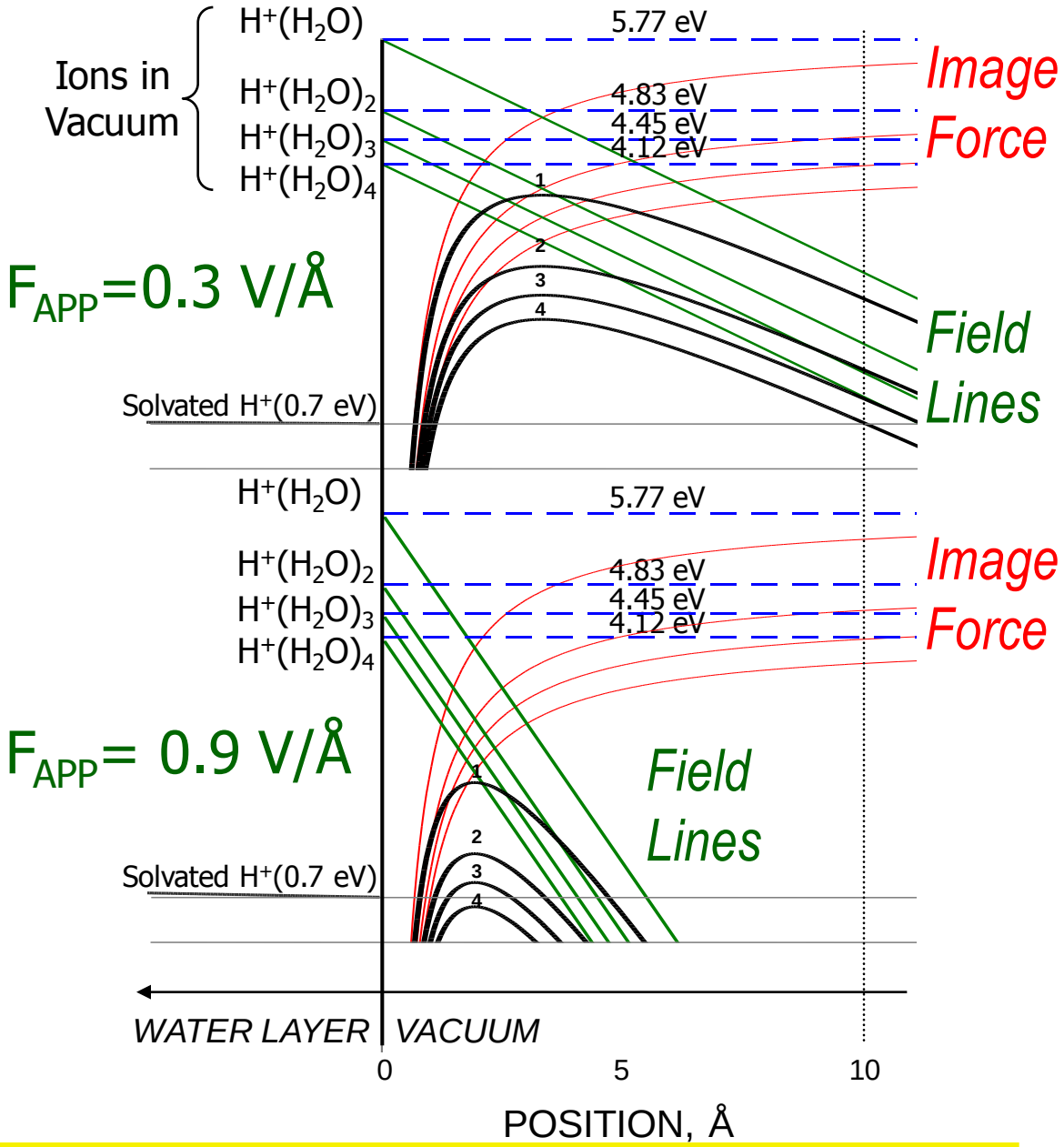
Idealized Energy Barriers for Emission

Potential Taken Relative to Uncharged Water on Uniform Surface

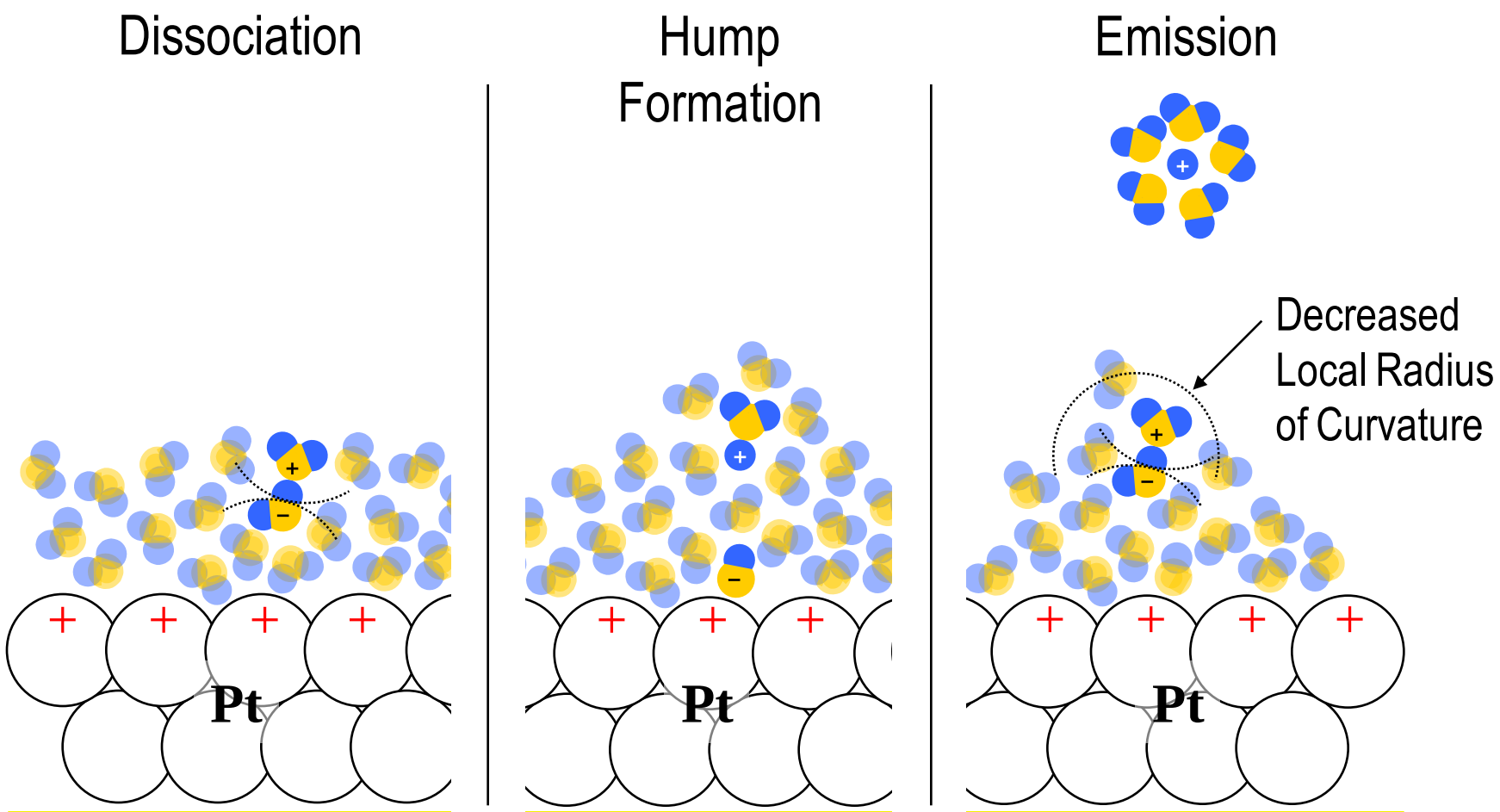
CALCULATION

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

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



Water Ion Cluster Formation
Proposed Mechanism



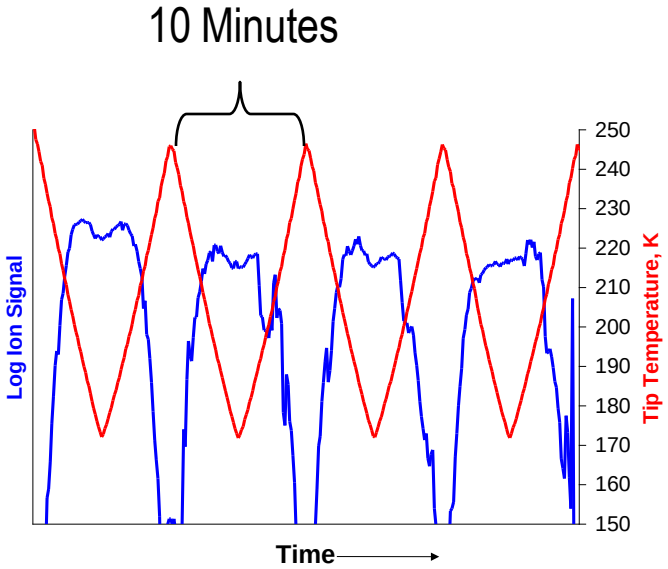
Ion Cluster Formation with Temperature Cycling

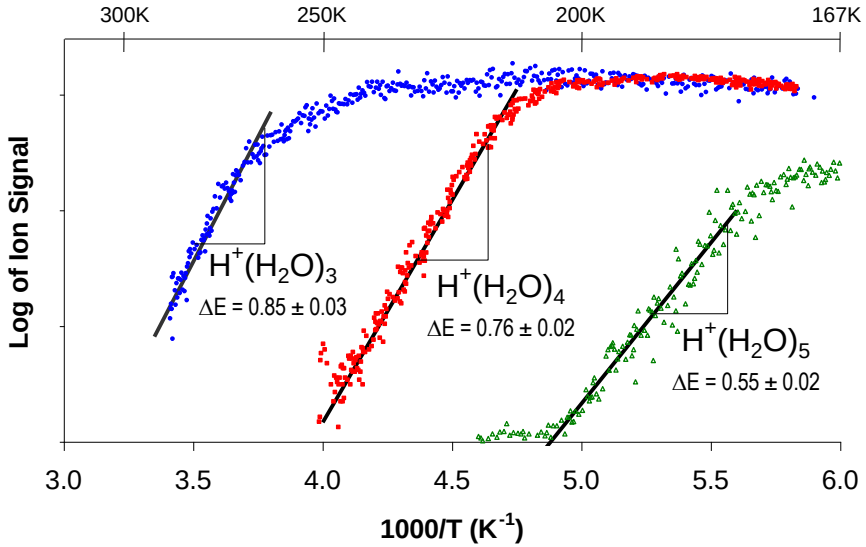
PROCEDURE

- 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.





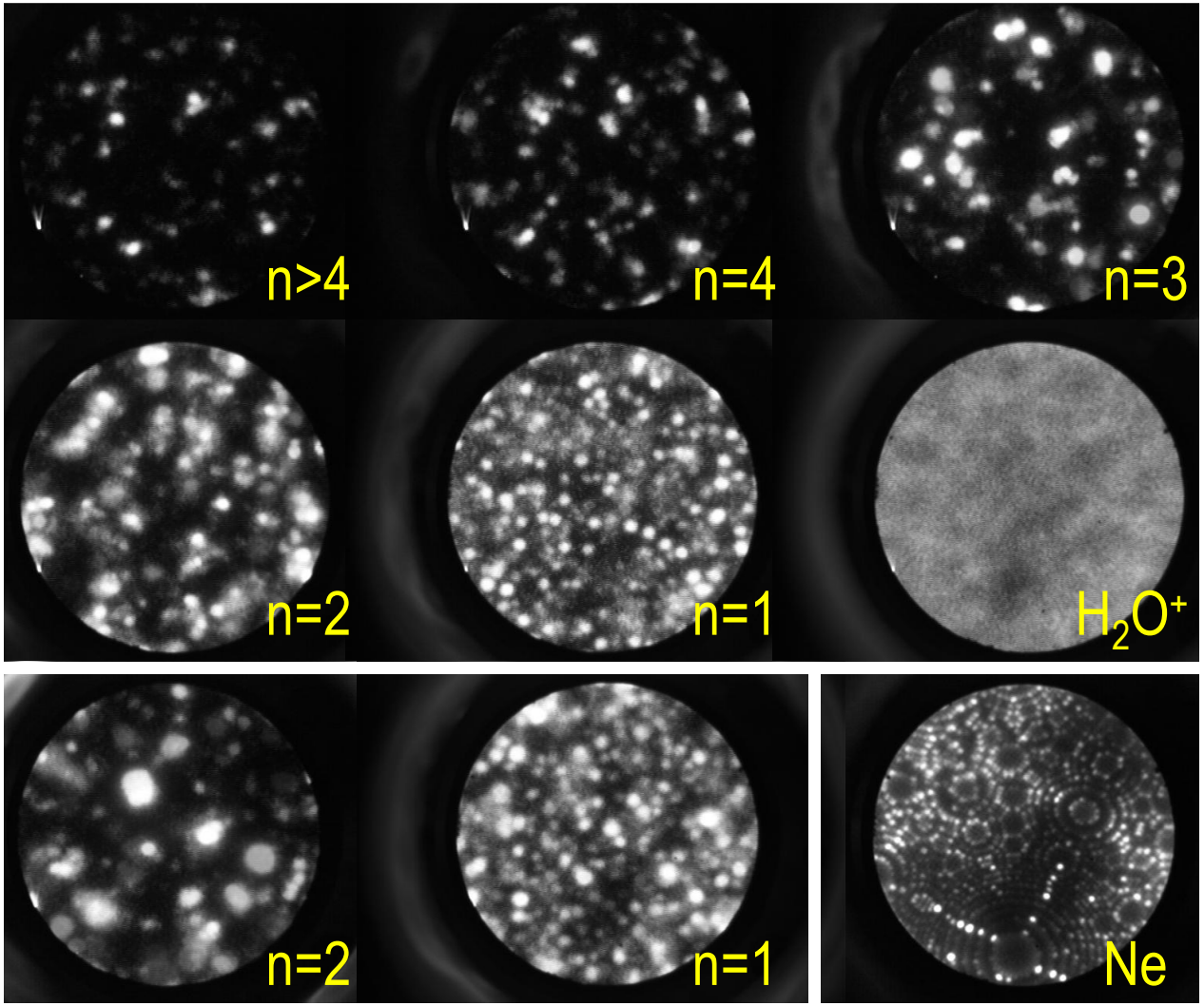
Direct Imaging of Ion Cluster Formation

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

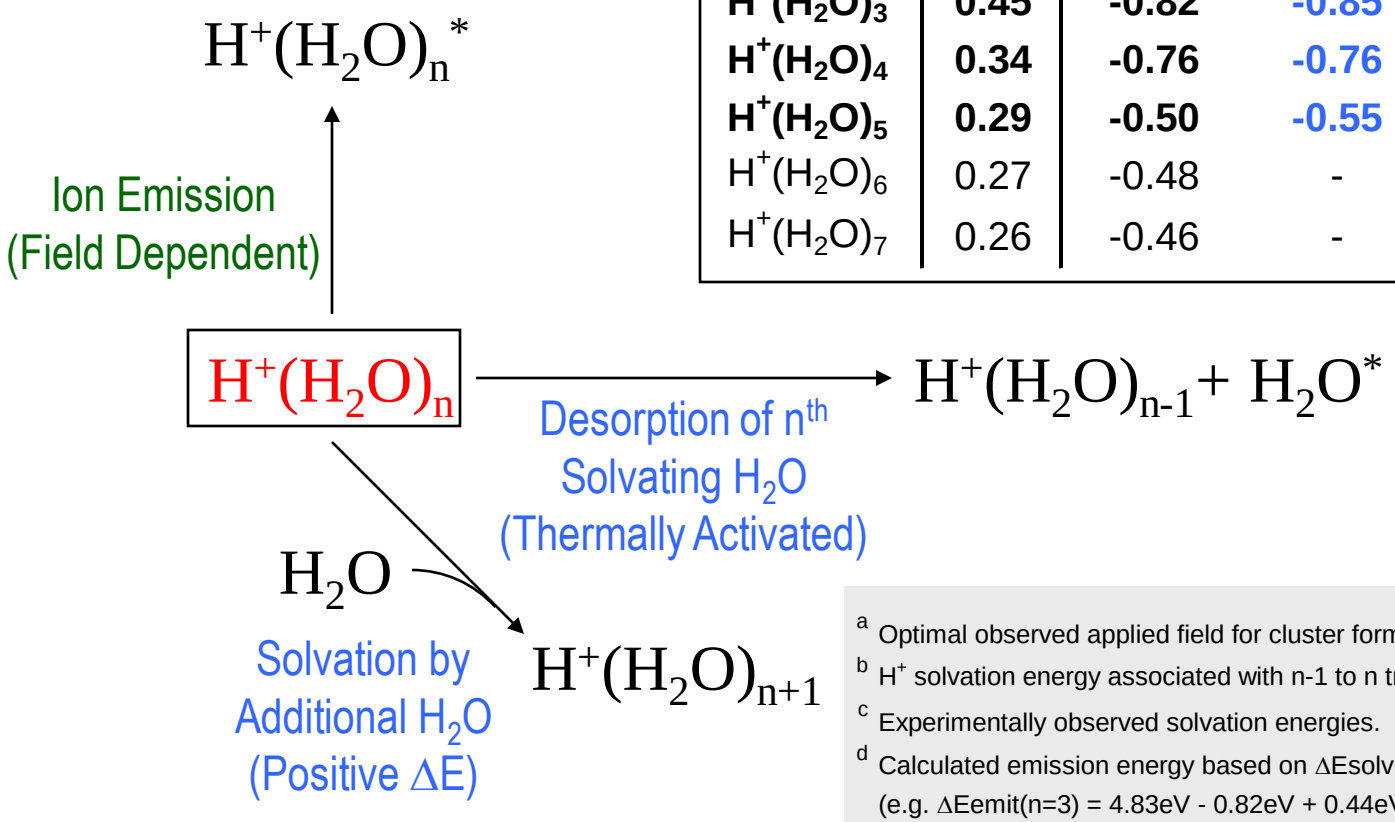
180K

230K



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)

Summary

- Water Ion Clusters $H^+(H_2O)_n$ were detected for n up to 7
  - Field Adsorbed layer on Pt
  - Temperatures 170 K - 300 K
- Low fields favored large clusters (Energetically favorable)
- High fields favored small clusters (Kinetically favorable)
- Ion emission of large clusters was deactivated at high temperatures (Desorption of solvating molecules)
- Ion emission is locally enhanced, possibly due to hump formation.

University of Washington

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ELECTROCHEMICAL
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