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

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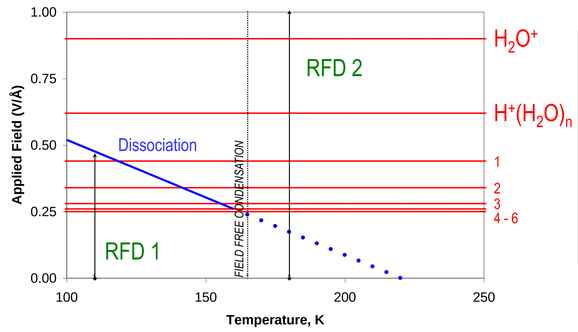
Separating Ion Dissociation and Ion Emission

Ramped Field Desorption 1
- –Amorphous 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*.

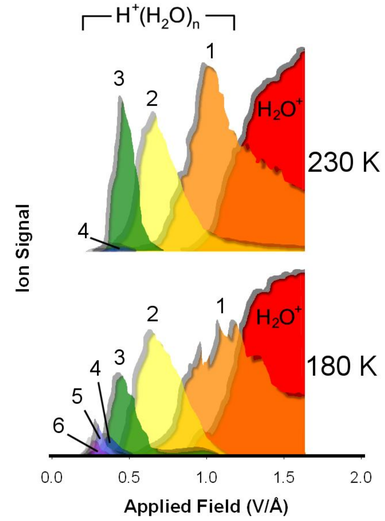


Ramped Field Desorption 2
- –Field Adsorbed Layer
- –Field Ramp activates Dissociation *before* Emission
- –Cluster n emission observed, each *in turn*.

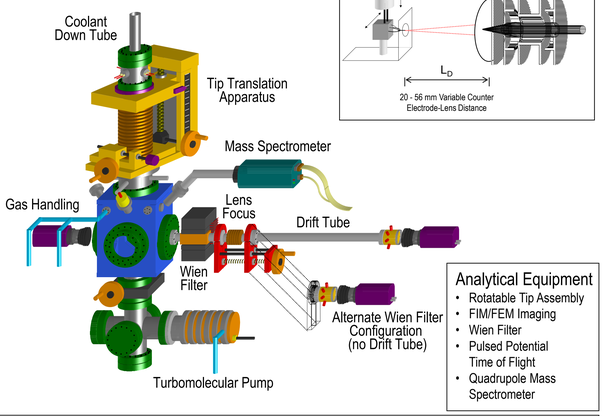
Mass Resolved Ion Cluster Formation

PROCEDURE
- Wien Filter tuned to selected $H^+(H_2O)_n$
- Tip Potential (V_t) set to 3000V
- P_{H2O}= 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

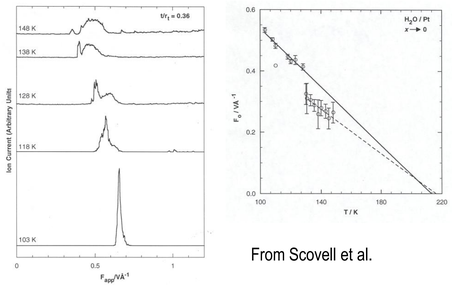


UHV Chamber Configuration



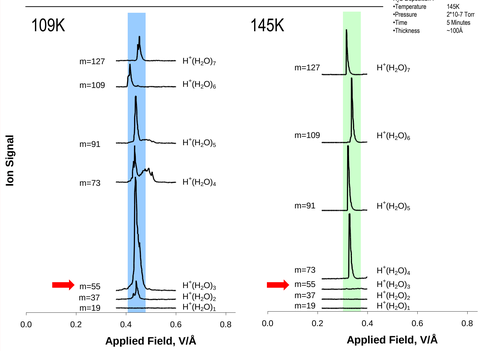
Analytical Equipment
- Rotatable Tip Assembly
- FIM/FEM Imaging
- Wien Filter
- Pulsed Potential Time of Flight
- Quadrupole Mass Spectrometer

Ion Emission Thresholds

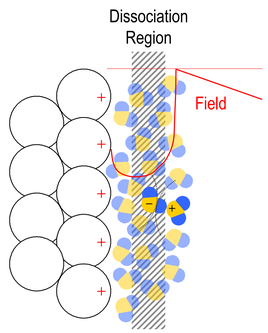


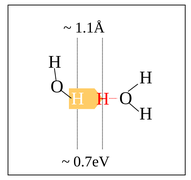
From Scovell et al.

Mass Resolved Cluster Formation



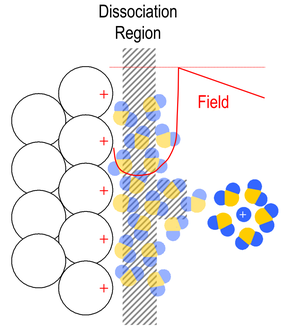
Field Induced Ion Dissociation





- 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

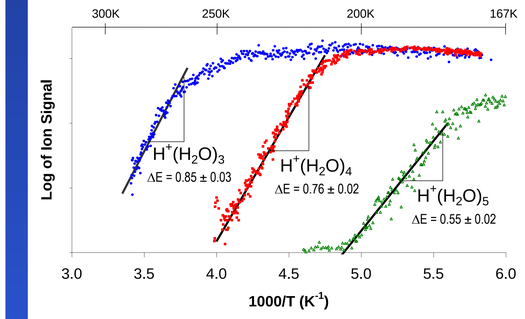


- Emission of Ion Cluster from water covered surface requires

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

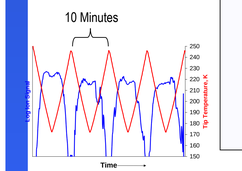
- Ion cluster can protrude near surface and experience enhanced local field
- Protrusion results in extended local Dissociation Region

Ion Cluster Formation with Temperature Cycling

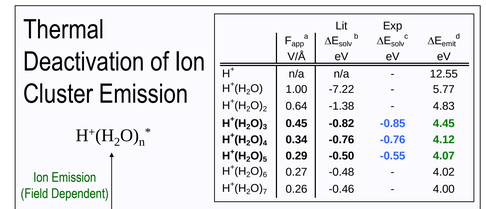


RESULTS
- Ion Cluster emission appears to be a thermally *deactivated* process for a given cluster size.
- Termination of cluster n emission coincides with the beginning of n-1 decay.
- Process deactivation energies are comparable to proton solvation energies for the nth solvating water molecule.

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 [$H^+(H_2O)_4$]...



Thermal Deactivation of Ion Cluster Emission

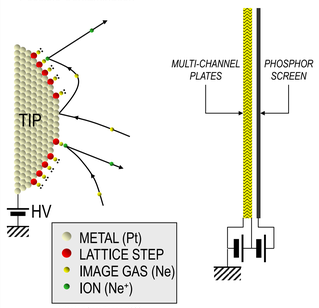


	F_{app}[a] V/Å	Lit ΔE_{solv}[b] eV	Exp ΔE_{solv}[c] eV	ΔE_{emit}[d] eV
H^+	n/a	n/a	-	12.55
$H^+(H_2O)$	1.00	-7.22	-	5.77
$H^+(H_2O)_2$	0.64	-1.38	-	4.83
$H^+(H_2O)_3$	**0.45**	**-0.82**	**-0.85**	**4.45**
$H^+(H_2O)_4$	**0.34**	**-0.76**	**-0.76**	**4.12**
$H^+(H_2O)_5$	**0.29**	**-0.50**	**-0.55**	**4.07**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

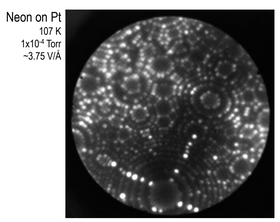
[a] Optimal observed applied field for cluster formation.
[b] H^+ solvation energy associated with n-1 to n transition. [Meot-Ner]
[c] Experimentally observed solvation energies.
[d] Calculated emission energy based on ΔEsolv+ΔEvap (e.g. ΔEemit(n=3) = 4.83eV - 0.82eV + 0.44eV = 4.45eV)

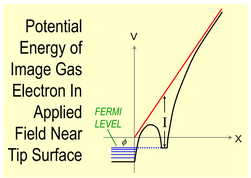
Field Ion Microscopy

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



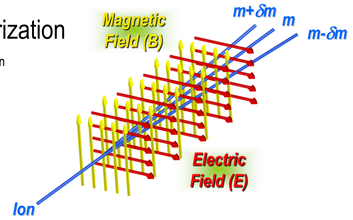
Adapted from Tsong,1990.

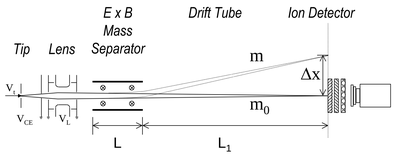


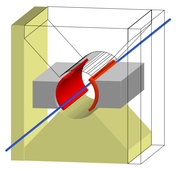


Wien Filter Ion Characterization

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

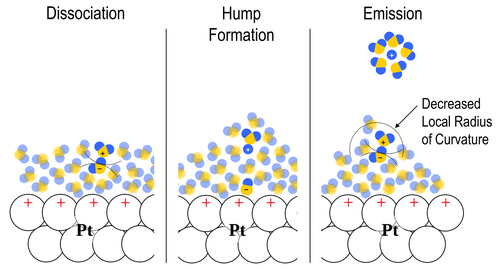






Lens: G.F. Rempter, J. Appl. Phys. **57** (1985) 2385.
E x B Mass Separator: M. Kato and K. Tsuno, Nucl. Instr. Methods **A298** (1990) 296.

Water Ion Cluster Formation Proposed Mechanism

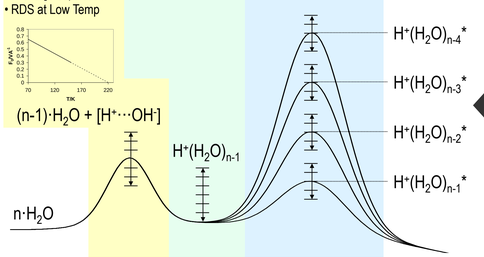


Ion Dissociation and Emission Reaction Path

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



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

