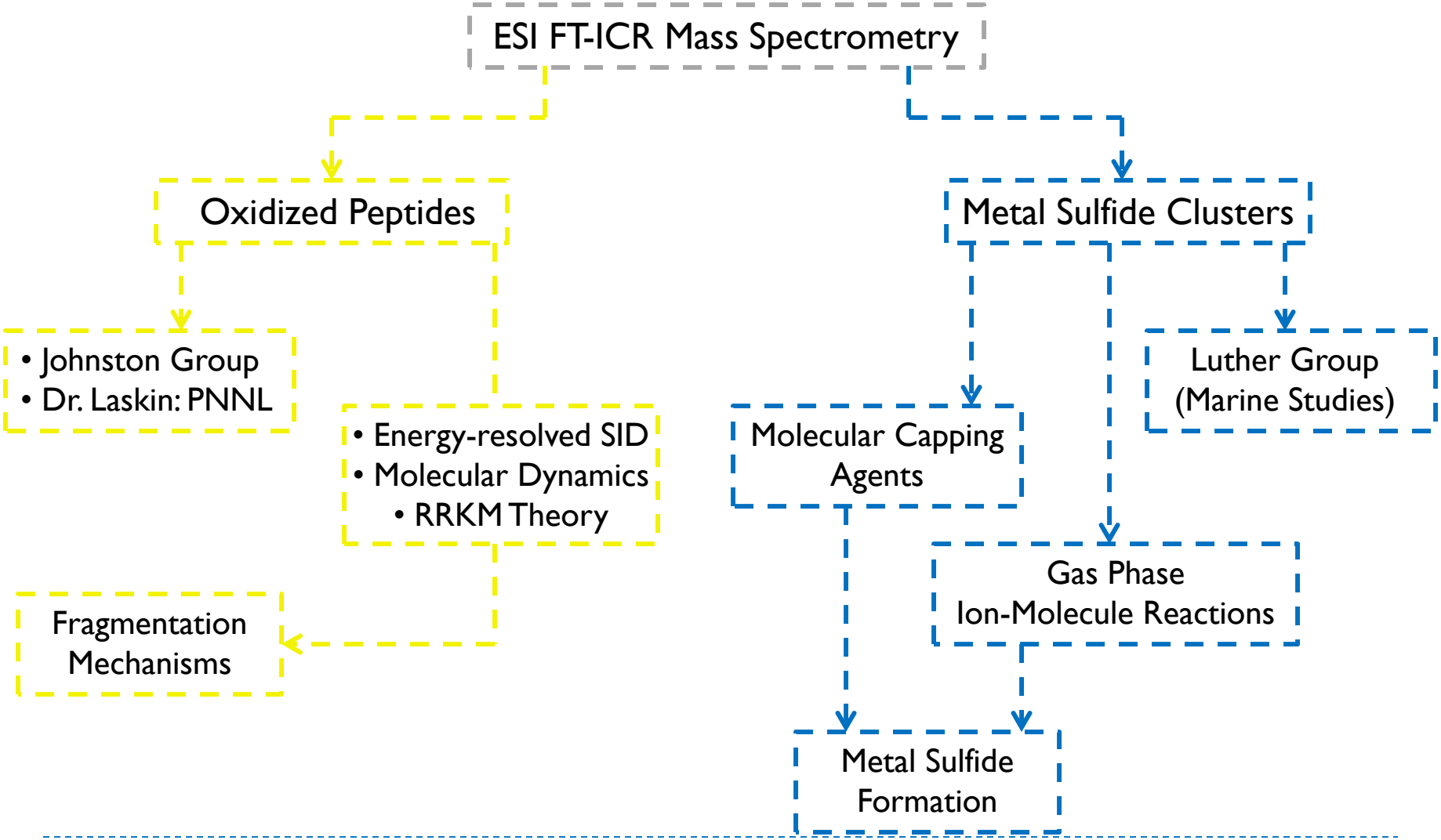
Dissertation Defense
January 7, 2010

Environmental Applications of FT-ICR Mass Spectrometry

Oxidized Peptide and Metal Sulfide Clusters

Jeffrey M. Spraggins
University of Delaware
Department of Chemistry & Biochemistry
Advisor: Douglas Ridge, Ph.D.

Overview


ESI FT-ICR Mass Spectrometry
Oxidized Peptides
Metal Sulfide Clusters
• Johnston Group
• Dr. Laskin: PNNL
• Energy-resolved SID
• Molecular Dynamics
• RRKM Theory
Molecular Capping Agents
Luther Group (Marine Studies)
Fragmentation Mechanisms
Gas Phase Ion-Molecule Reactions
Metal Sulfide Formation

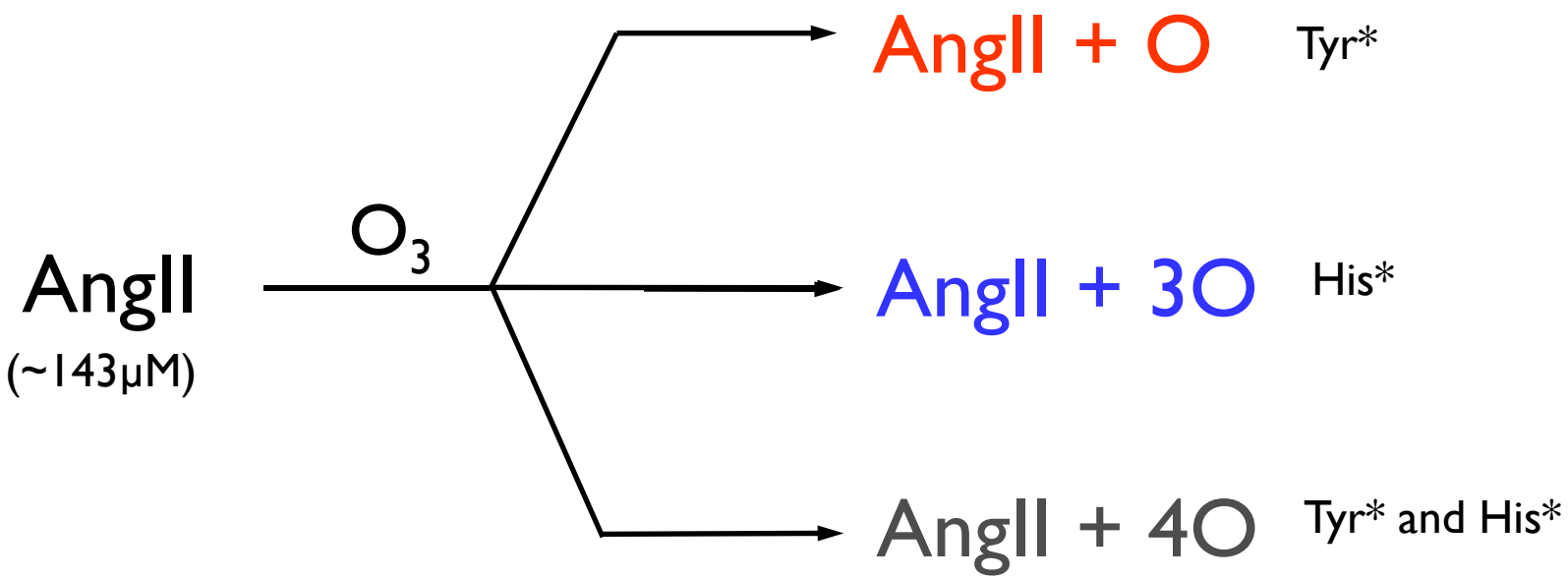
ESI FT-ICR Mass Spectrometry

Oxidized Peptides

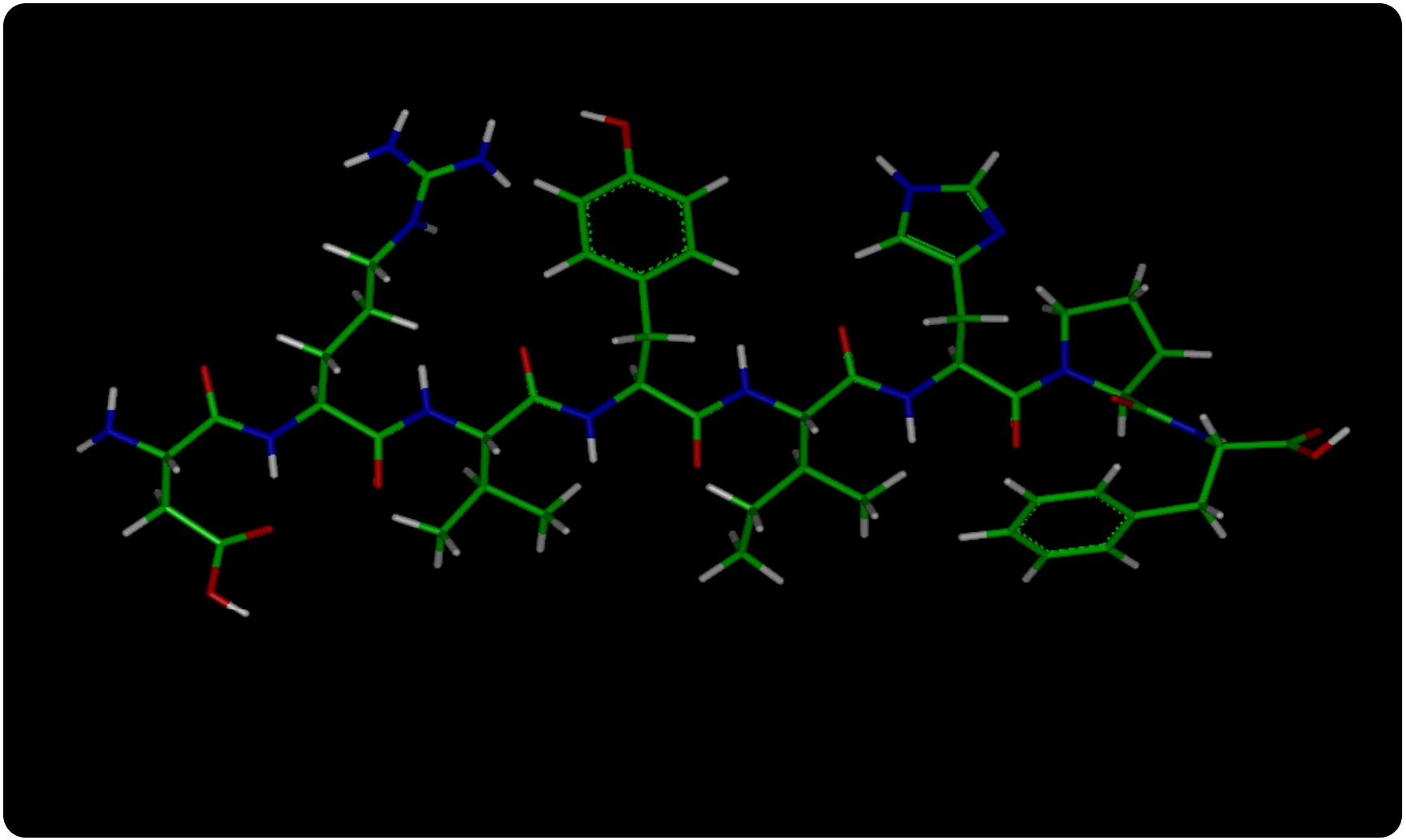
Jeffrey M. Spraggins, Julie A. Lloyd, Murray V. Johnston, Julia Laskin, Douglas P. Ridge *J.Am. Soc. Mass Spec.* (2009), Accepted for puplication.

Julie A. Lloyd, Jeffrey M. Spraggins, Murray V. Johnston, Julia Laskin, *J.Am. Soc. Mass Spec.* (2006), 17(9), 1289-1298

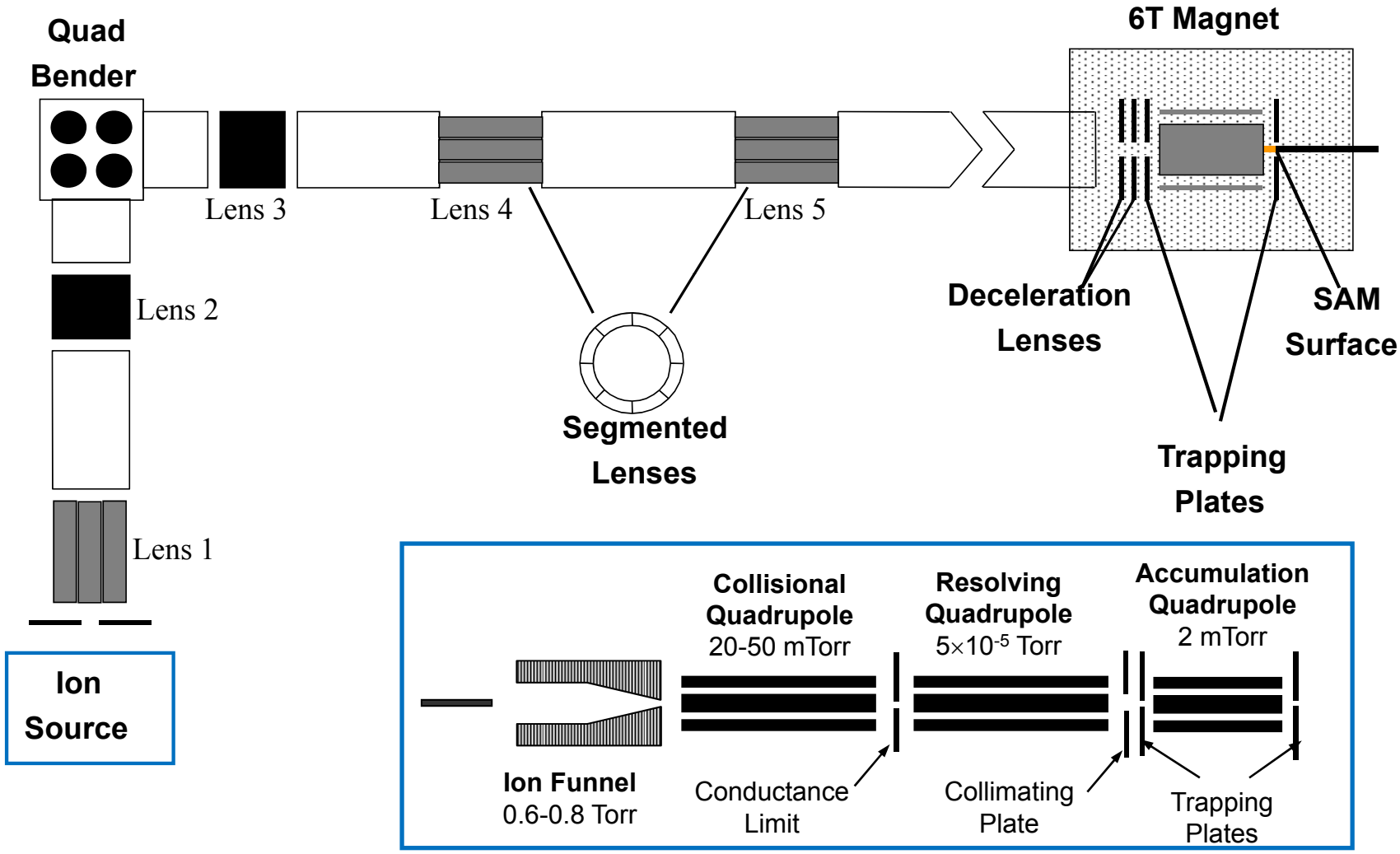
Oxidation Reaction



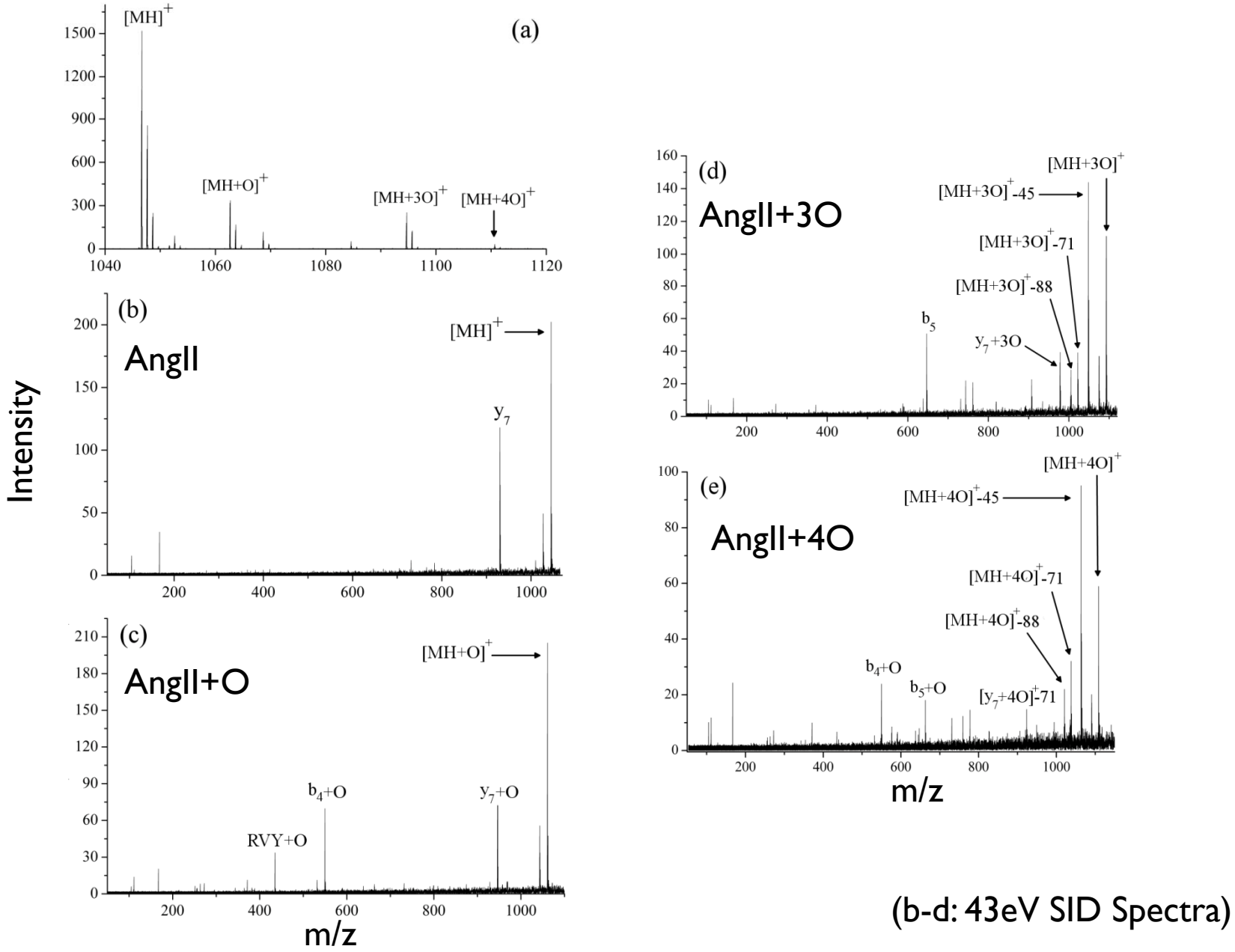
Asp-Arg-Val-Tyr-Ile-His-Pro-Phe



6 T FT-ICR MS: PNNL

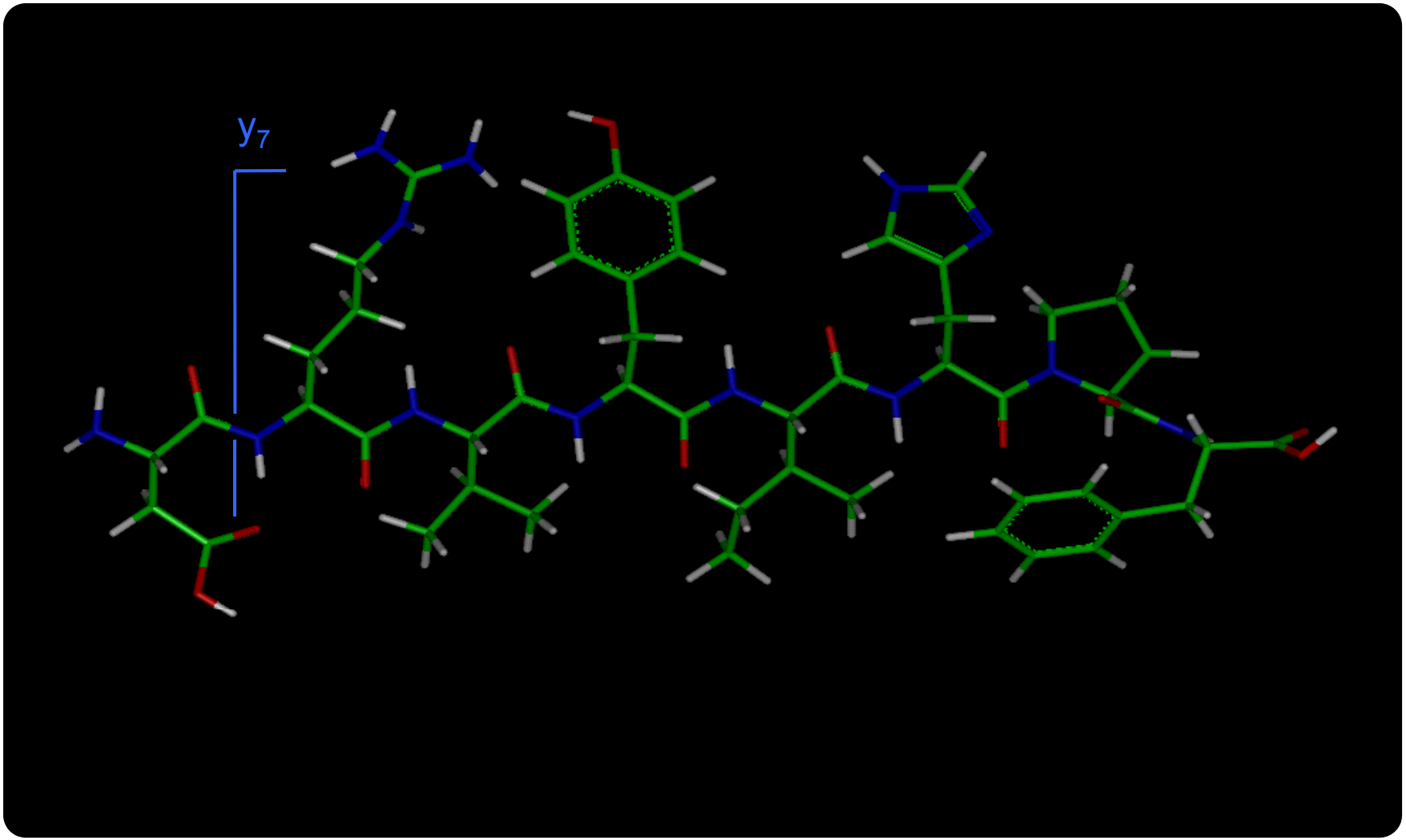


Laskin J.; Denisov E.V.; Shukla A. K.; Barlow S. E.; Futrell J. H. *Analytical chemistry* 2002, 74, 3255-61.

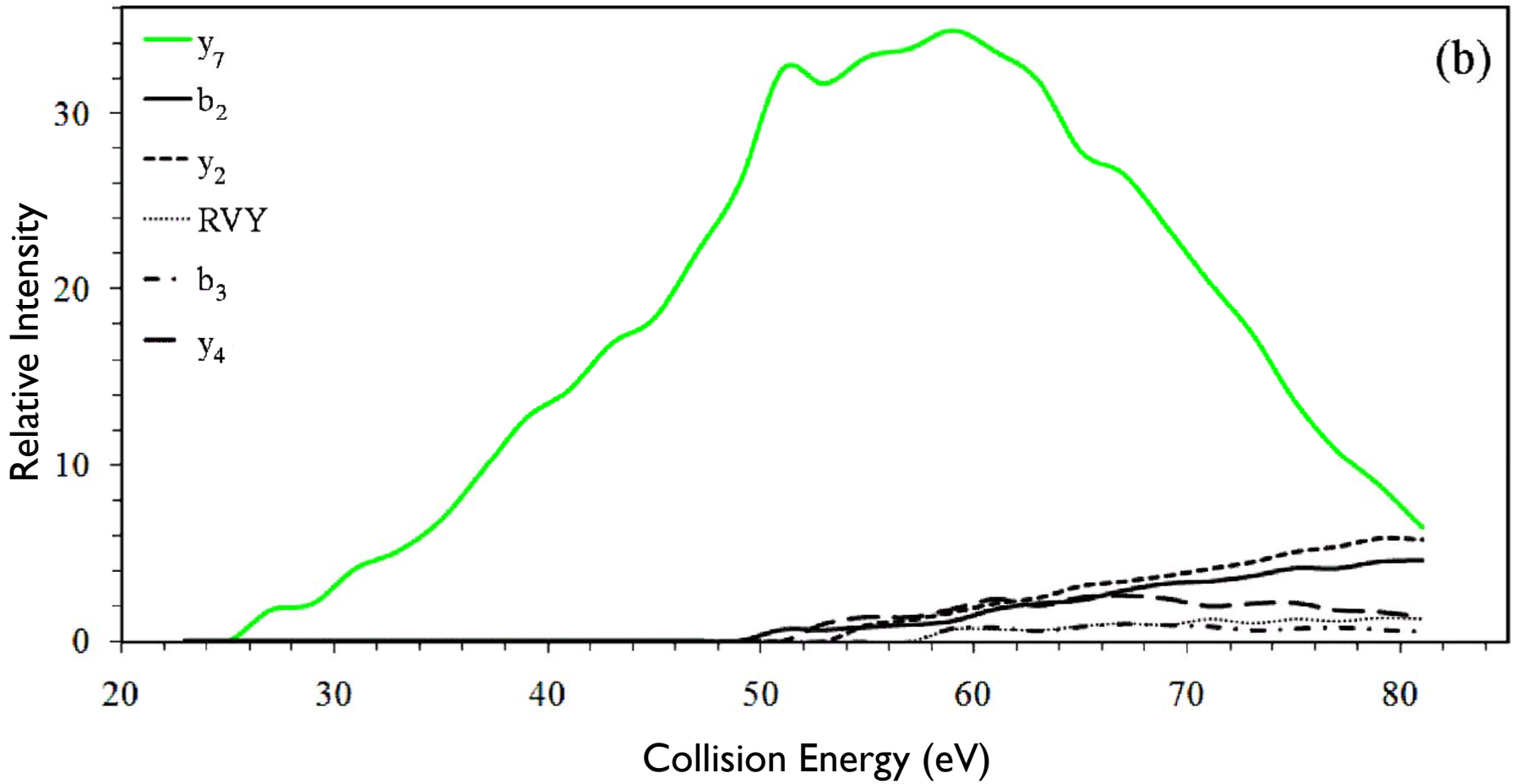


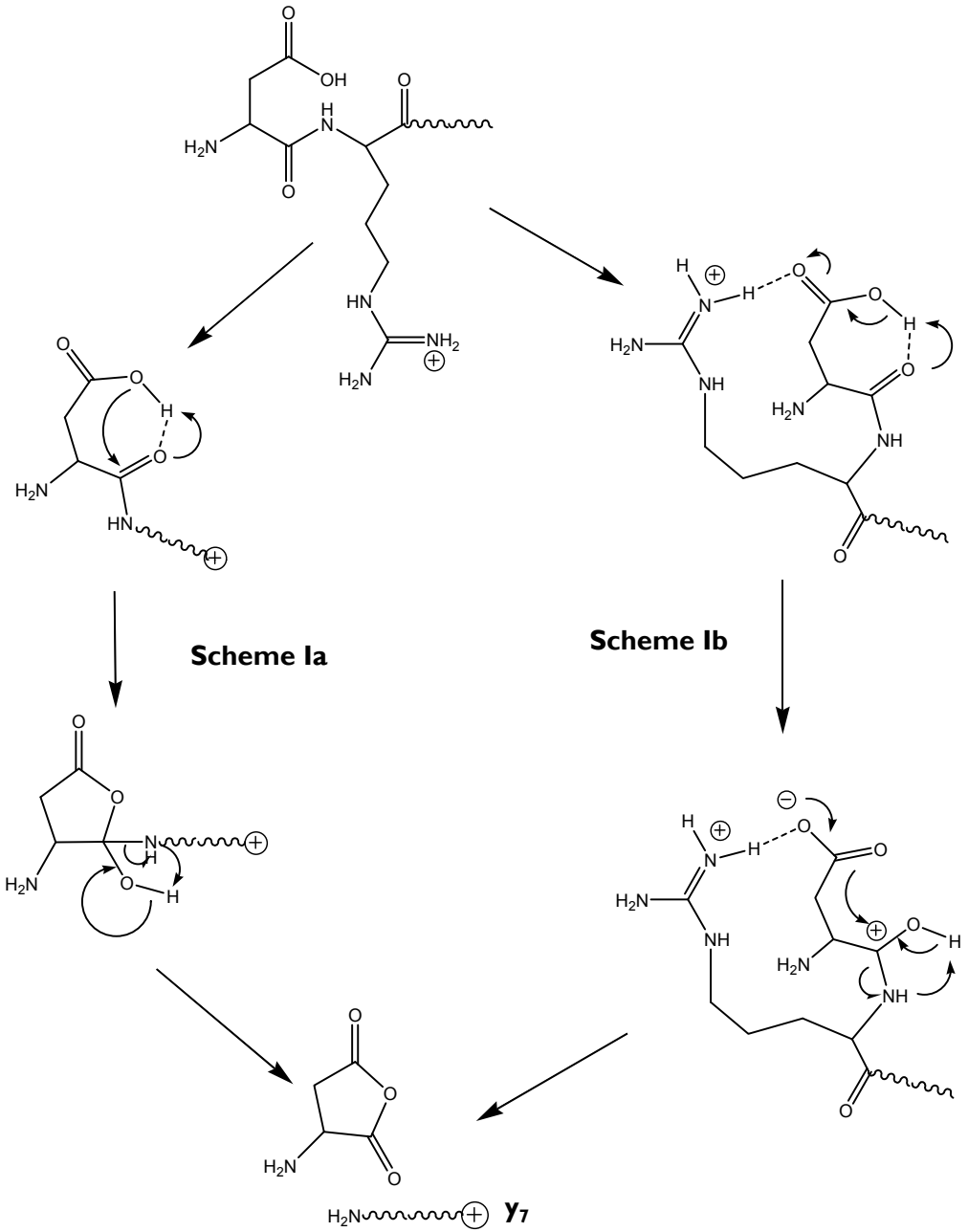
(b-d: 43eV SID Spectra)

Asp-Arg-Val-Tyr-Ile-His-Pro-Phe



Energy Resolved FECs: AngII





Acidic Amino Acids

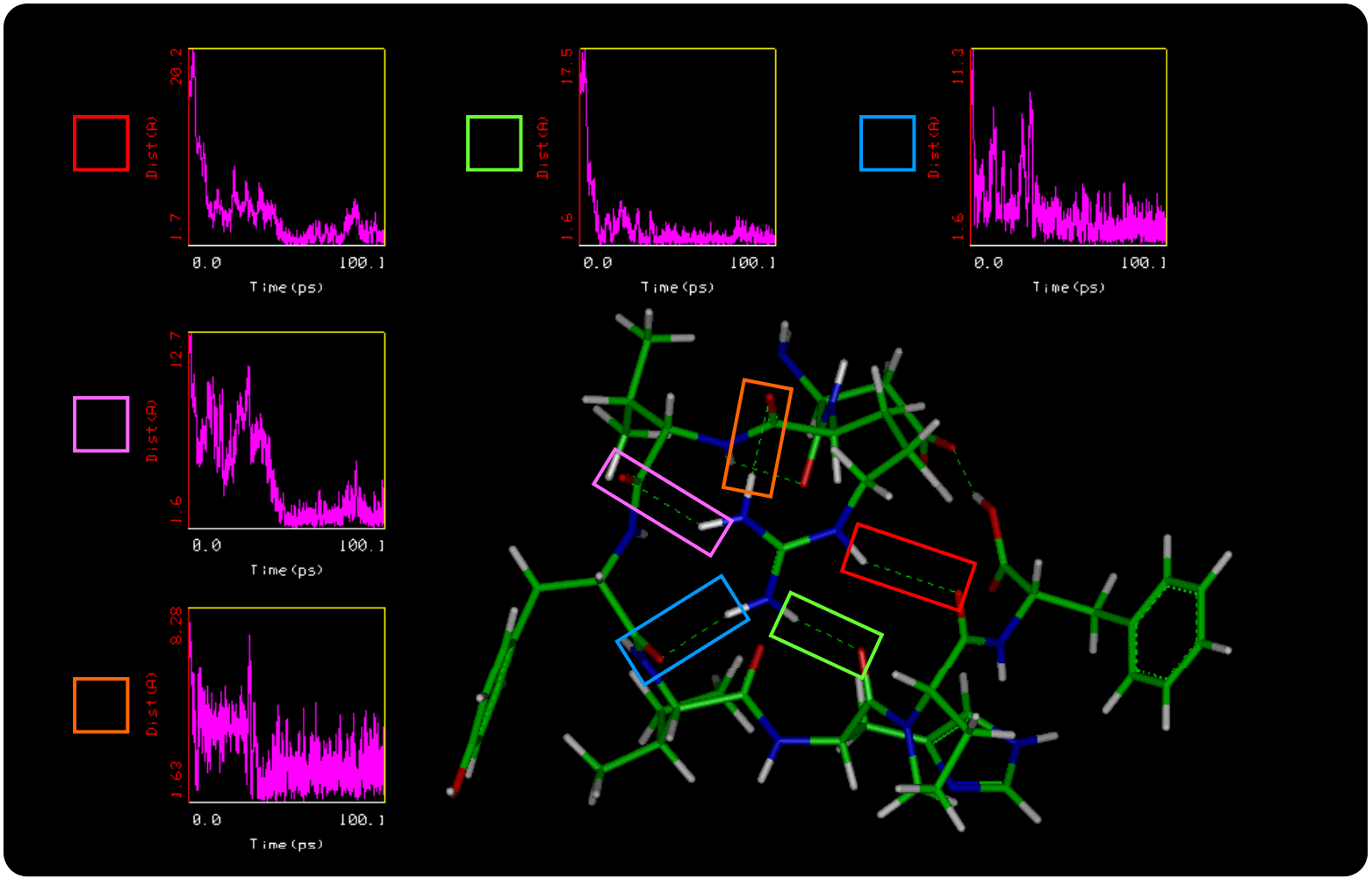
J. Laskin

J. Futrell

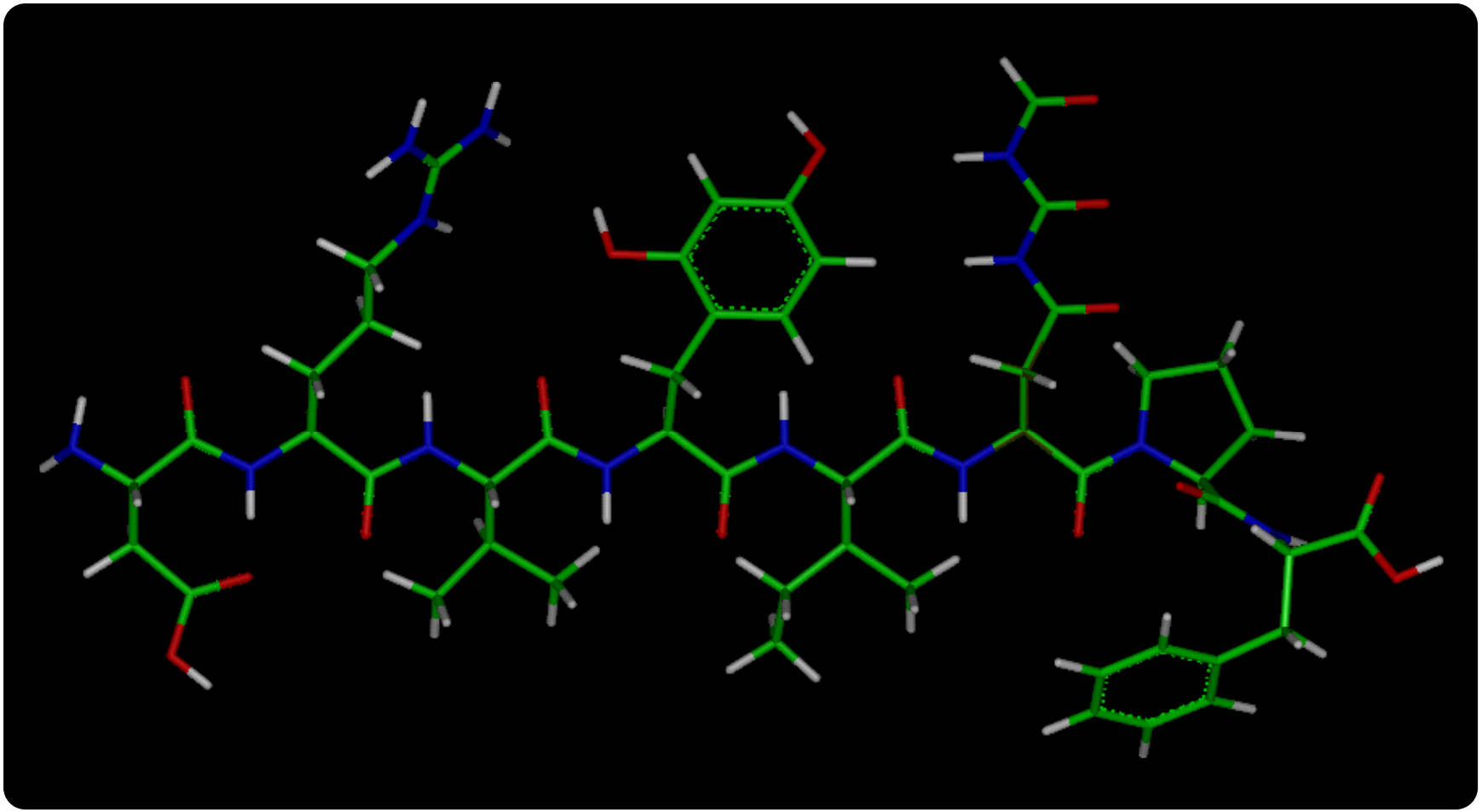
V. Wysocki

J. Beauchamp

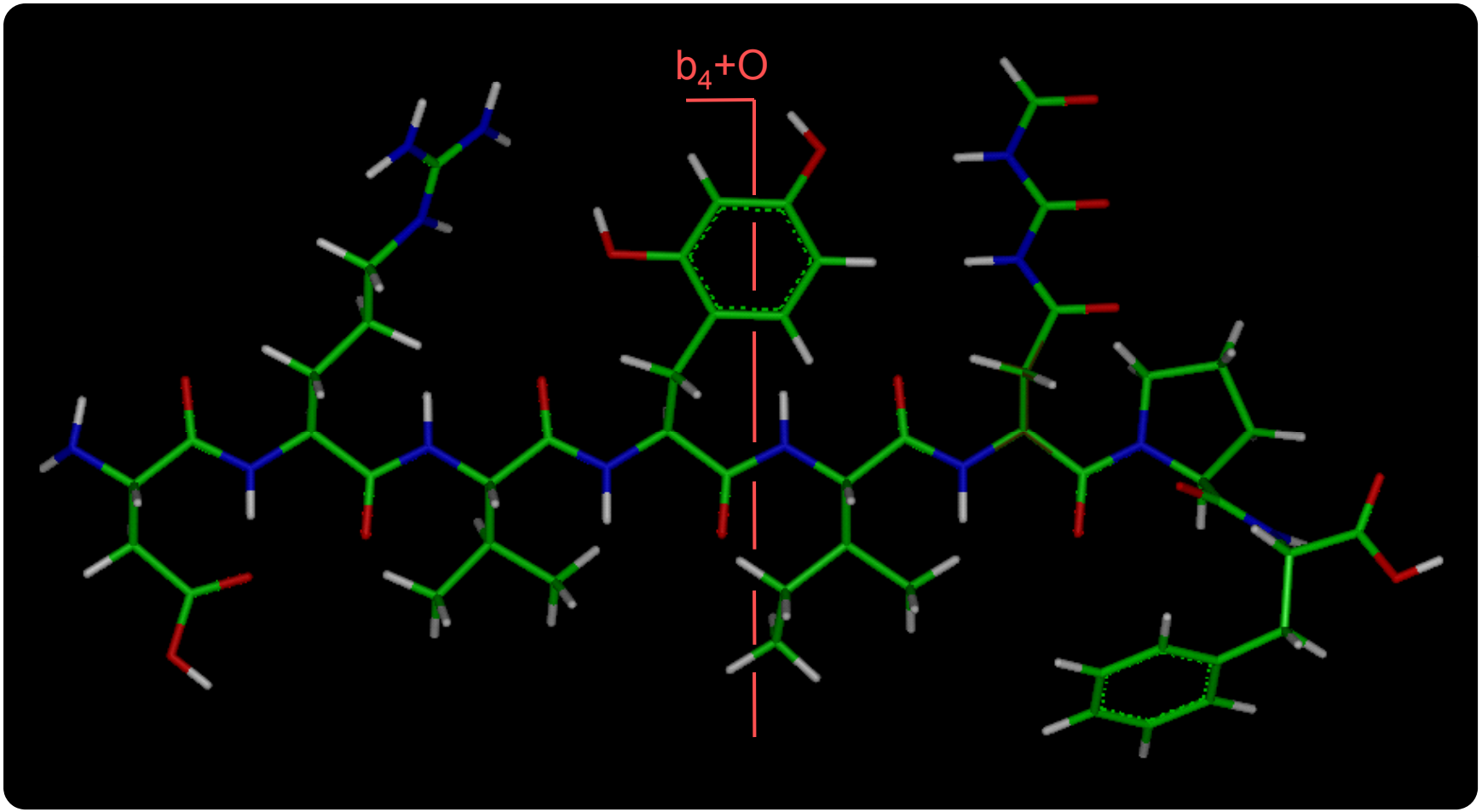
AngII: charge delocalization



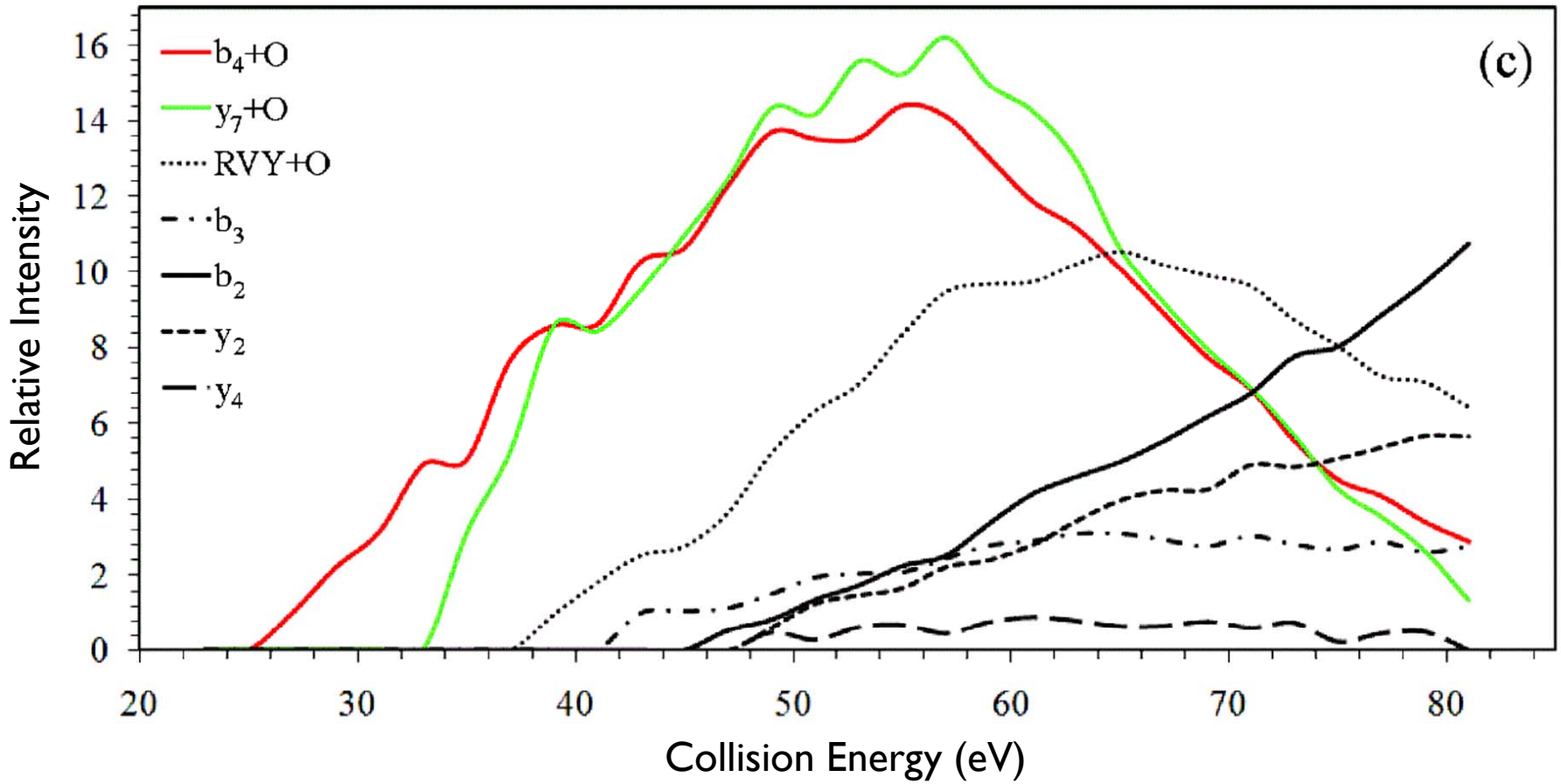
Asp-Arg-Val-*Tyr(+O)*-Ile-*His(+3O)*-Pro-Phe



Asp-Arg-Val-*Tyr(+O)*-Ile-*His(+3O)*-Pro-Phe

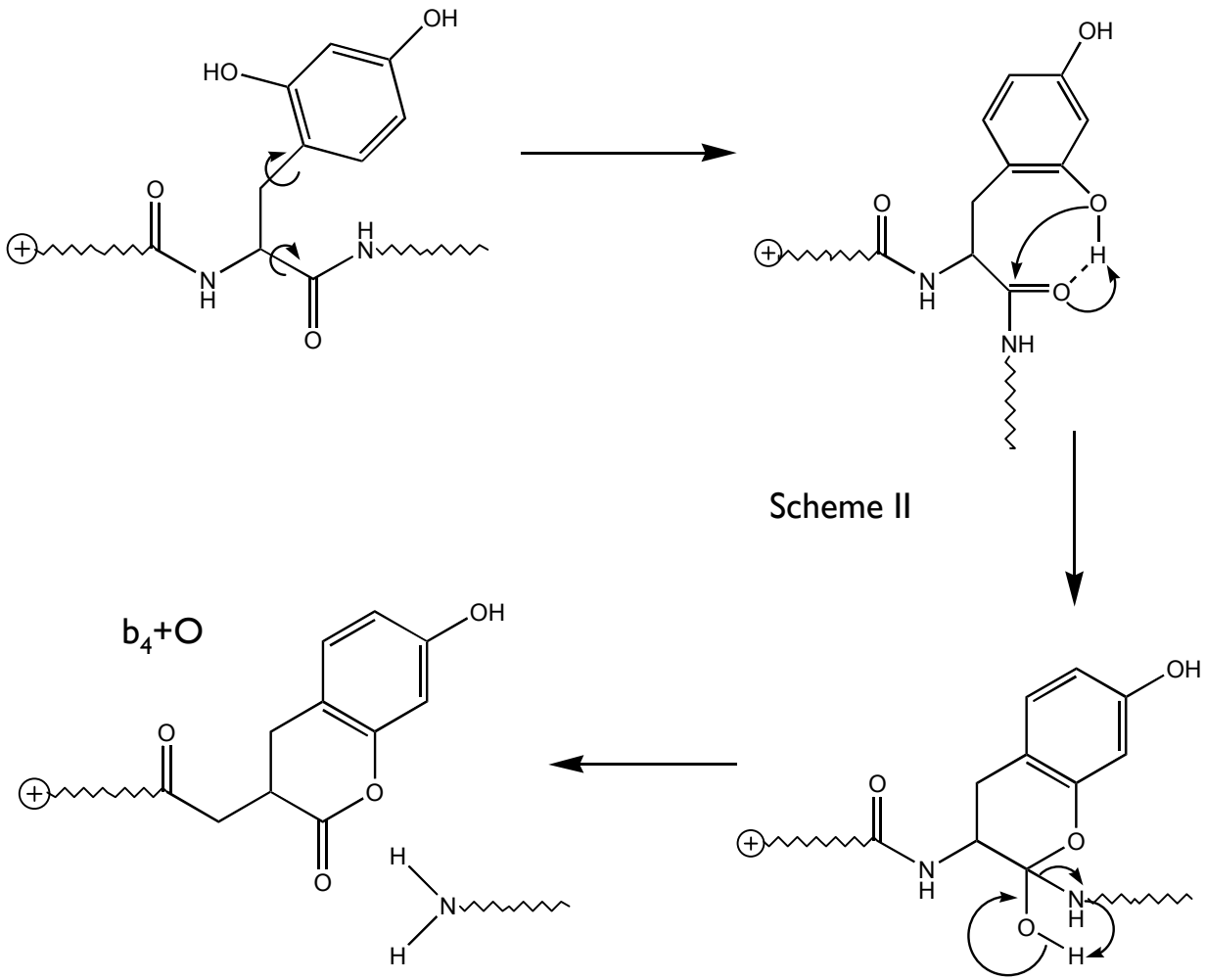


Energy Resolved FECs: AngII+O

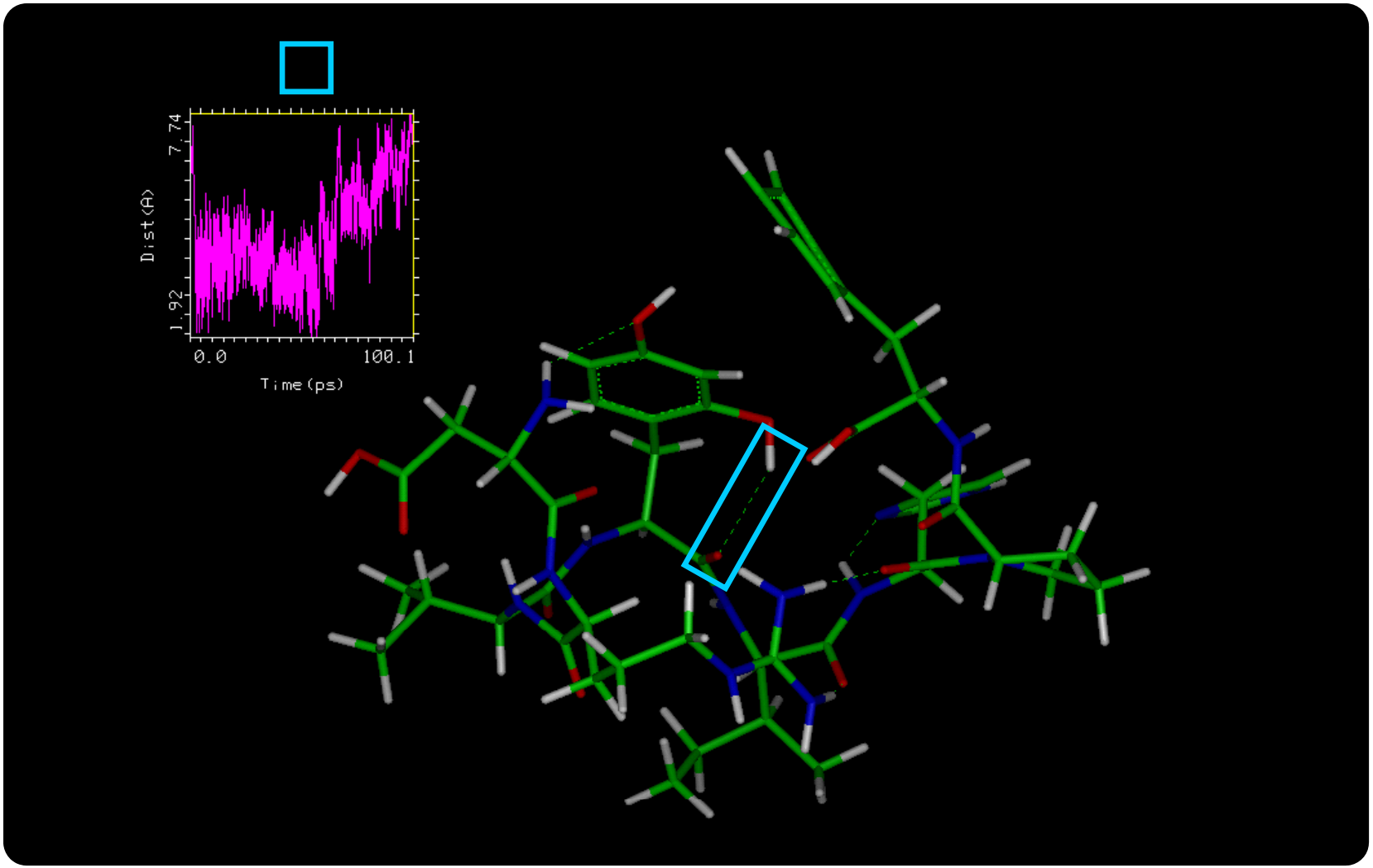


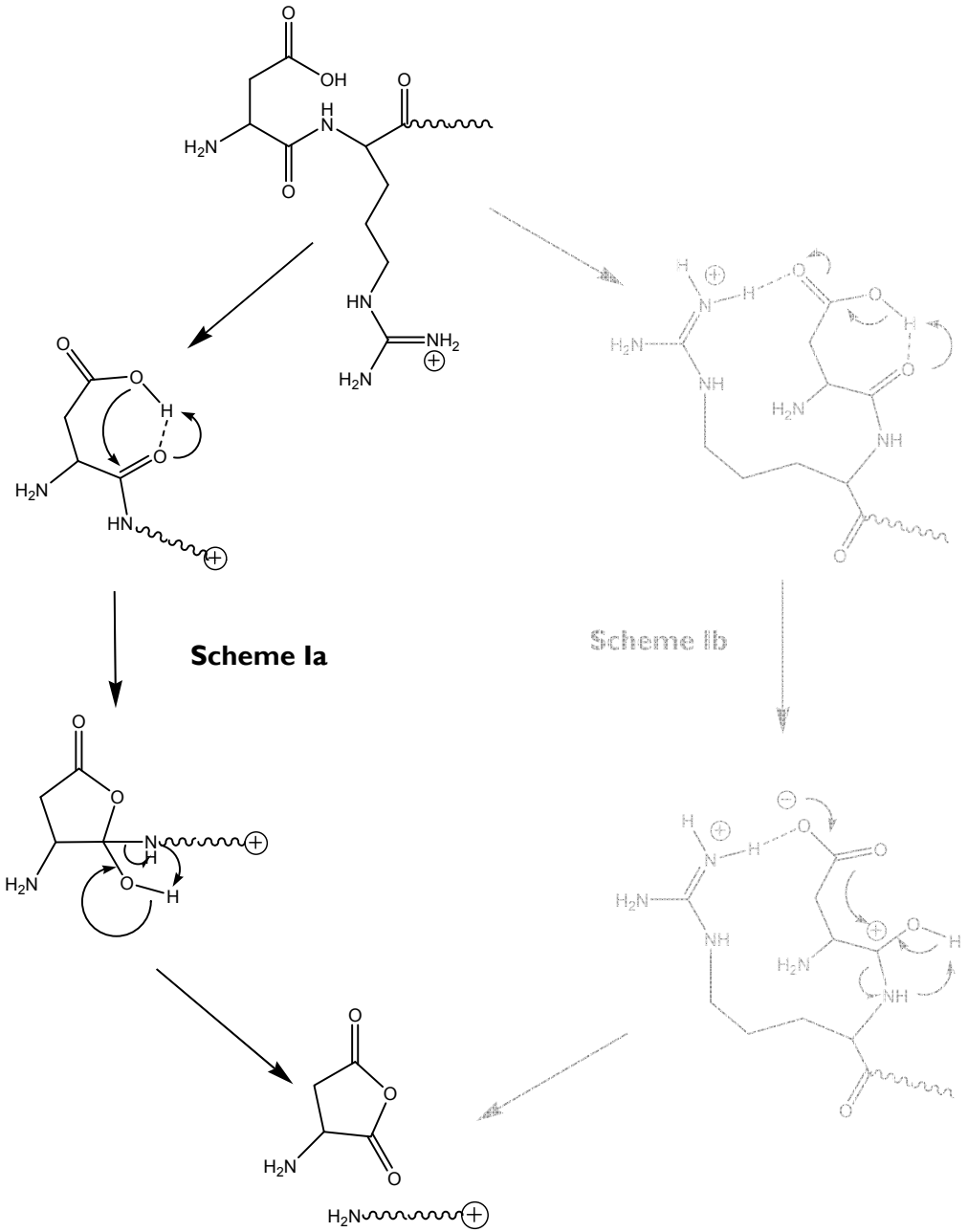
AngII+O

b_4 fragmentation pathway



AngII+O: b_4 fragment





Acidic Amino Acids

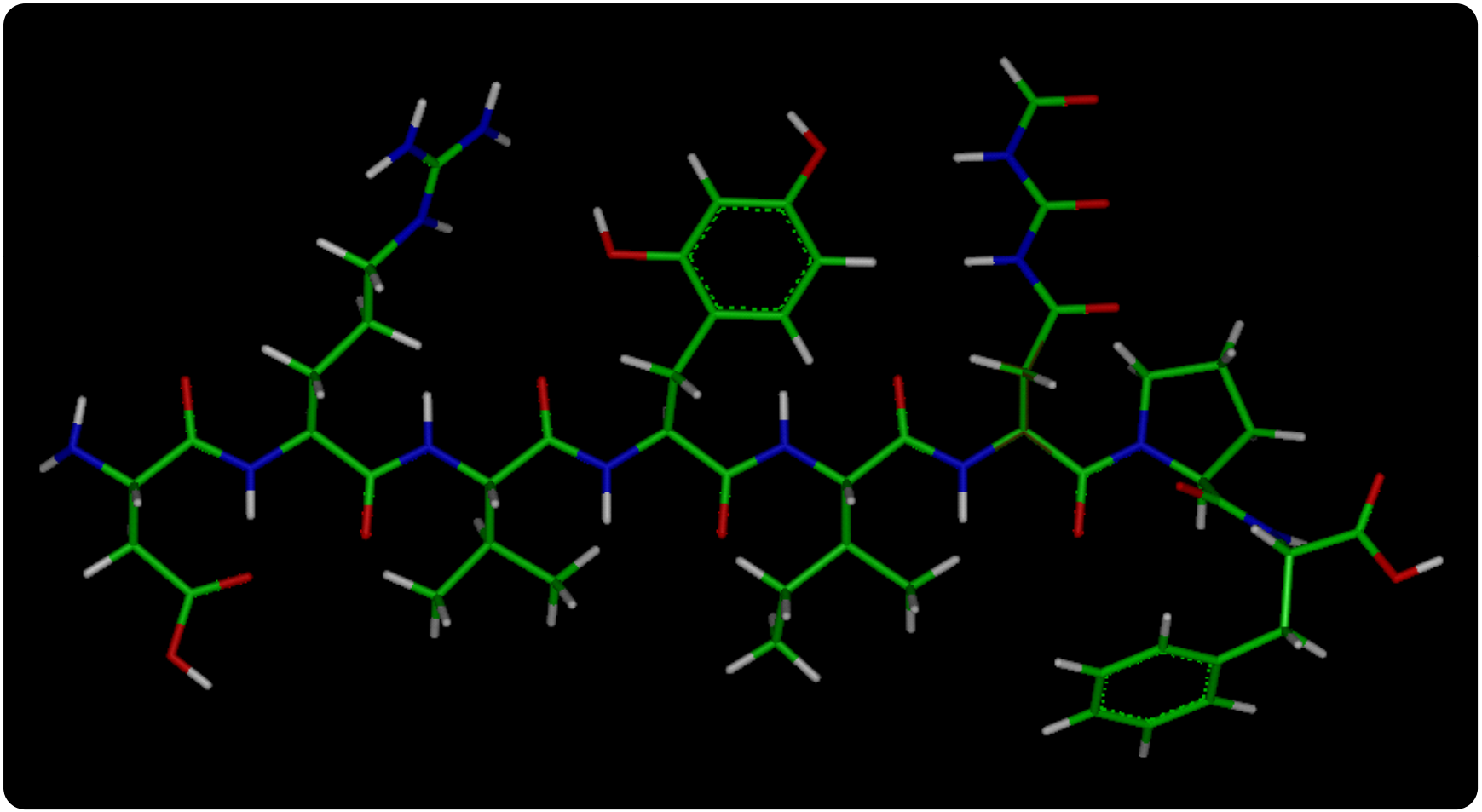
J. Laskin

J. Futrell

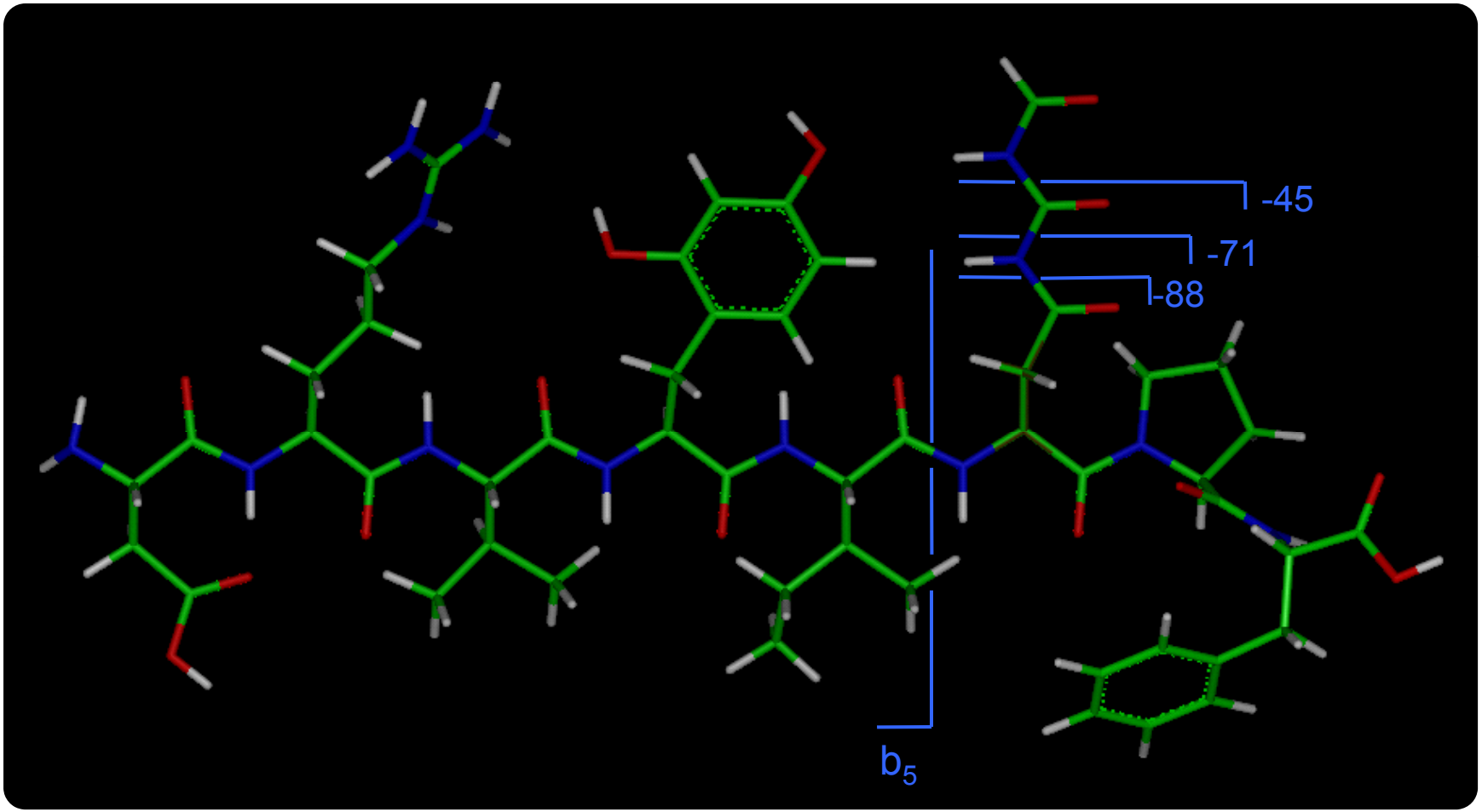
V. Wysocki

J. Beauchamp

Asp-Arg-Val-*Tyr(+O)*-Ile-*His(+3O)*-Pro-Phe

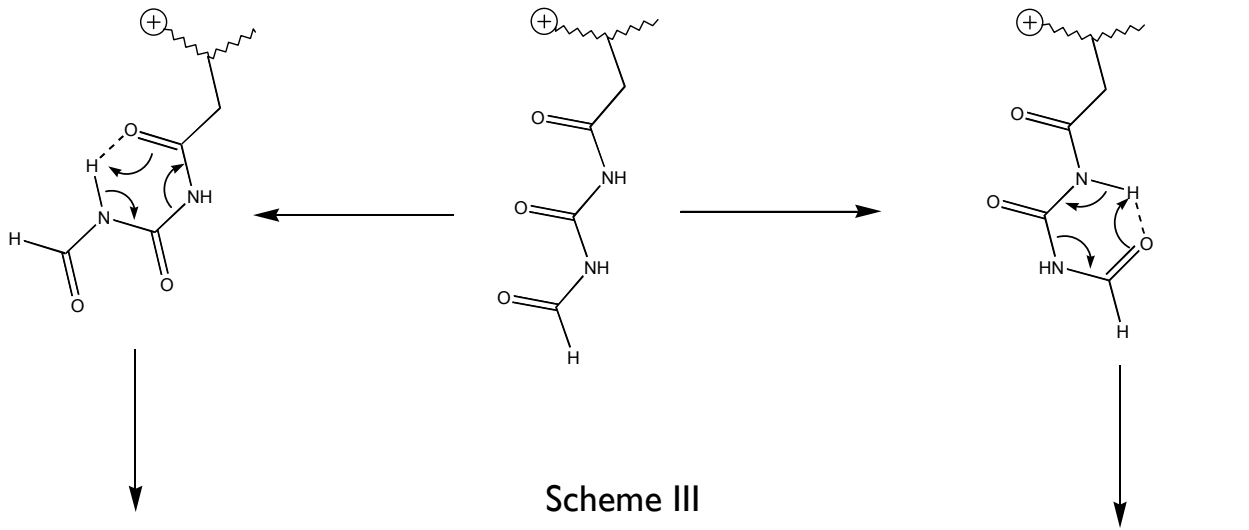


Asp-Arg-Val-*Tyr(+O)*-Ile-*His(+3O)*-Pro-Phe



AngII+3O

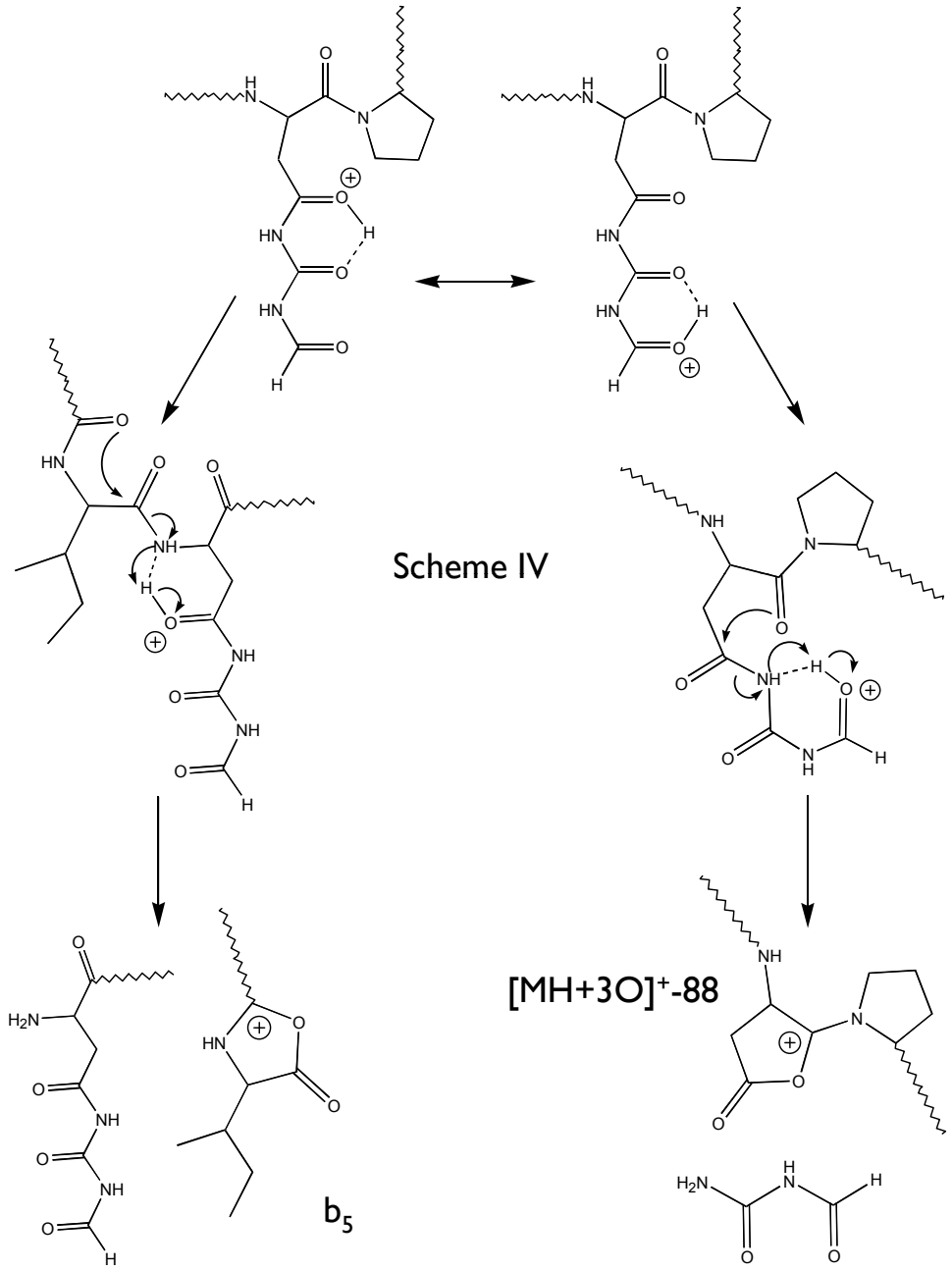
[MH+3O]$^+$-45 &
[MH+3O]$^+$-71



Scheme III

[MH+3O]$^+$-71

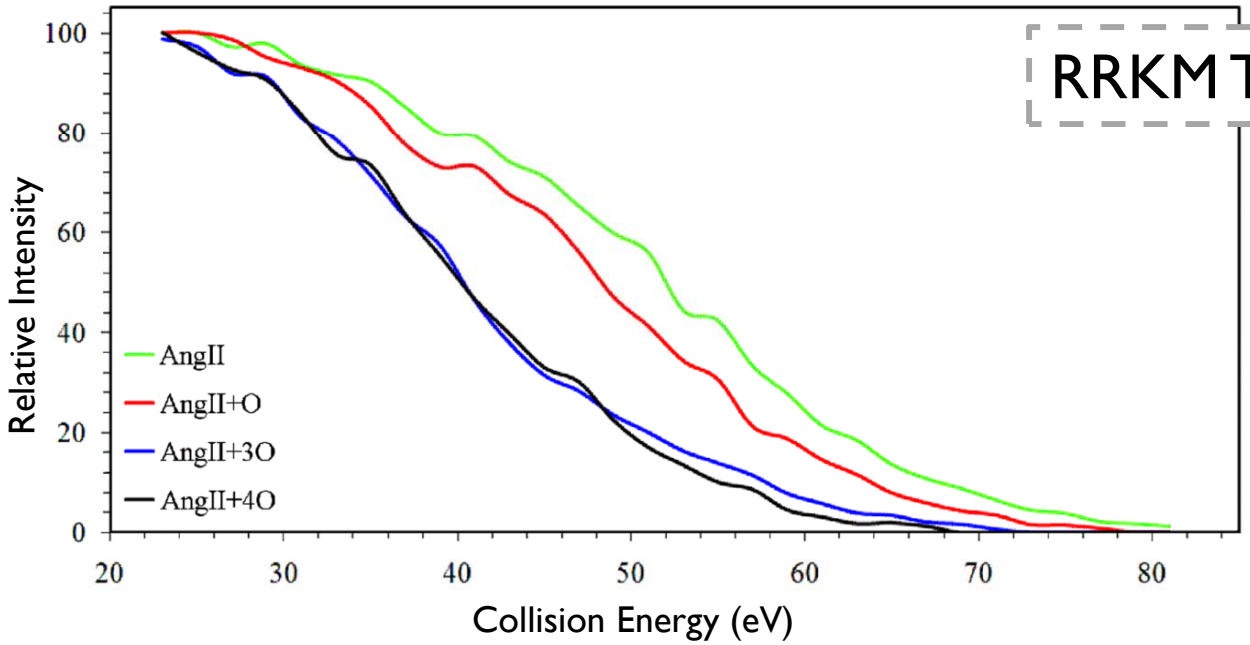
[MH+3O]$^+$-45



AngII+3O

[MH+3O]$^{+}$-88 & b_5 fragmentation pathway

Transition States

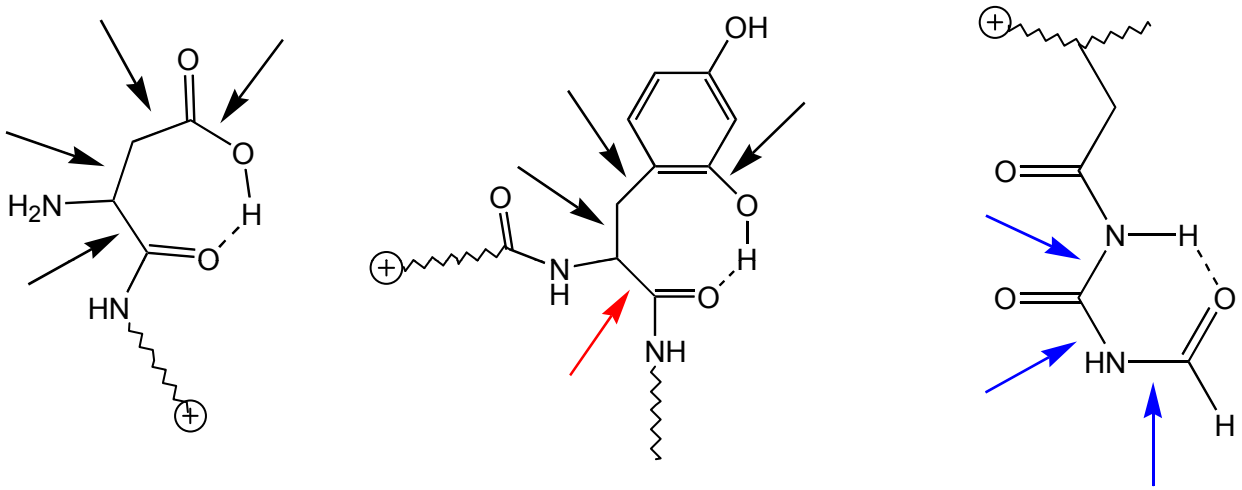


RRKM Theory

$[MH+nO]^+$	*DRVYIHPF*	*DRVY*IHPF*	*DRVYIH*PF*	*DRVY*IH*PF*
M/Z	1046	1062	1110	1126
E_0(eV)	1.14	1.20	1.21	1.24
$\Delta S^{\ddagger}$(cal/mol K)	-25.9	-21.6	-17.0	-15.3
Relative E_0	0	0.06	0.07	0.11
A, s^{-1}	5.6×10^{7}	4.8×10^{8}	4.8×10^{9}	1.2×10^{10}
Log (A)	7.7	8.7	9.7	10.1

$\Delta S^{\ddagger}$(cal/mol K)

-25.9 -21.6 -17.0



(a) **(b)** **(c)**

Side Chain

Backbone

Amide Bond

Entropic Considerations

(a) y_7 fragment

(b) b_4+O fragment

(c) [AngII+3O]-45

Conclusions

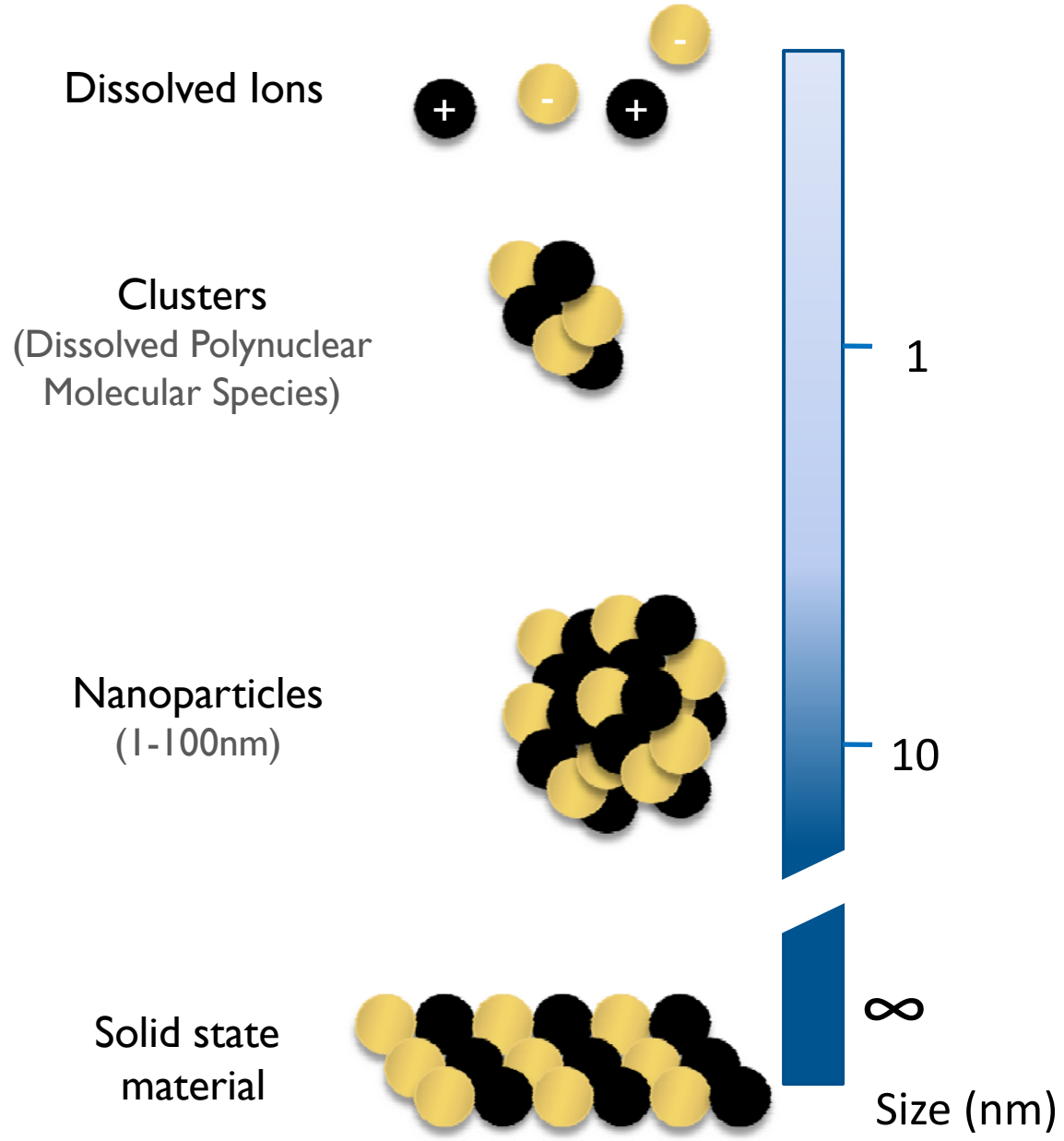
- ***Unmodified Ang II***
  - Charge-remote selectivity towards y_7 fragment
- ***M+O adduct*** *FECs* suggest that the b_4 pathway is a charge-remote process.
  - C-term Tyr* - Backbone interaction leads to b_4 fragment ion.
- ***M+3O product*** *FECs* show both charge-remote and charge-directed selective fragmentation channels are opened with the oxidation of the His residue.
  - Loss of 45m/z and 71m/z driven by strong H-bonding within the His* side chain.
  - His* is thought to compete with Arg for the lone proton leading to the b_5 and $[MH+3O]^+$-88 charge-directed fragments.
- ***RRKM results*** imply destabilization due to entropic effects.
  - Consistent with proposed fragmentation mechanisms for oxidation products

The Big Picture

- ***Structurally characterize peptide degradation*** by ozone exposure
- ***Contribution to Fundamental MS/MS Literature***
- ***Understanding oxidized peptide fragmentation*** could benefit MS protein structural research
- ***Method for increasing fragmentation sequence coverage*** for proteomic studies

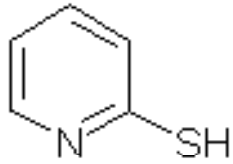
ESI FT-ICR Mass Spectrometry

Metal Sulfide Clusters



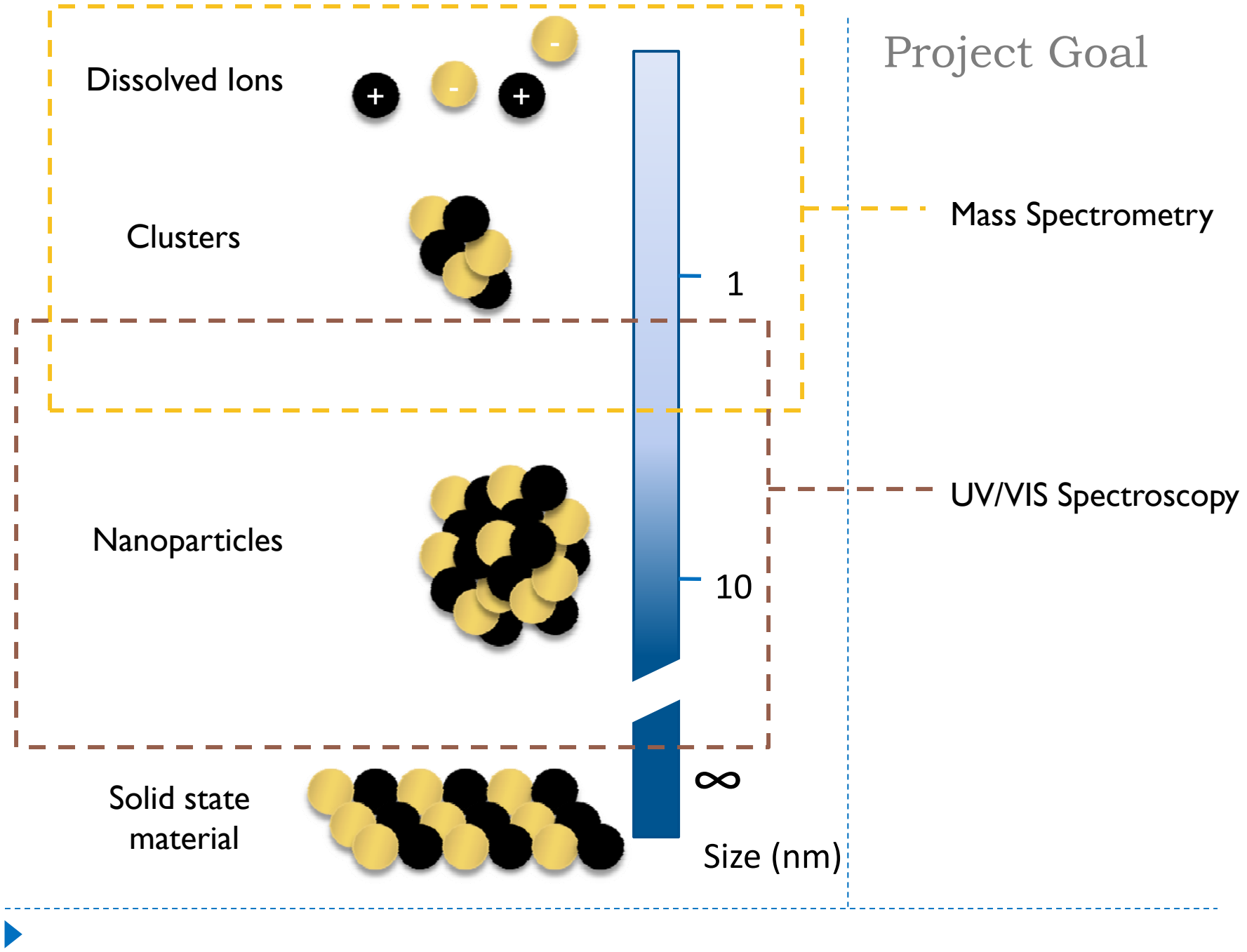
Project Goal

- Metal Sulfide Precipitation
  - Cluster Aggregation†
- Experimental Approach
  - Capping Agents

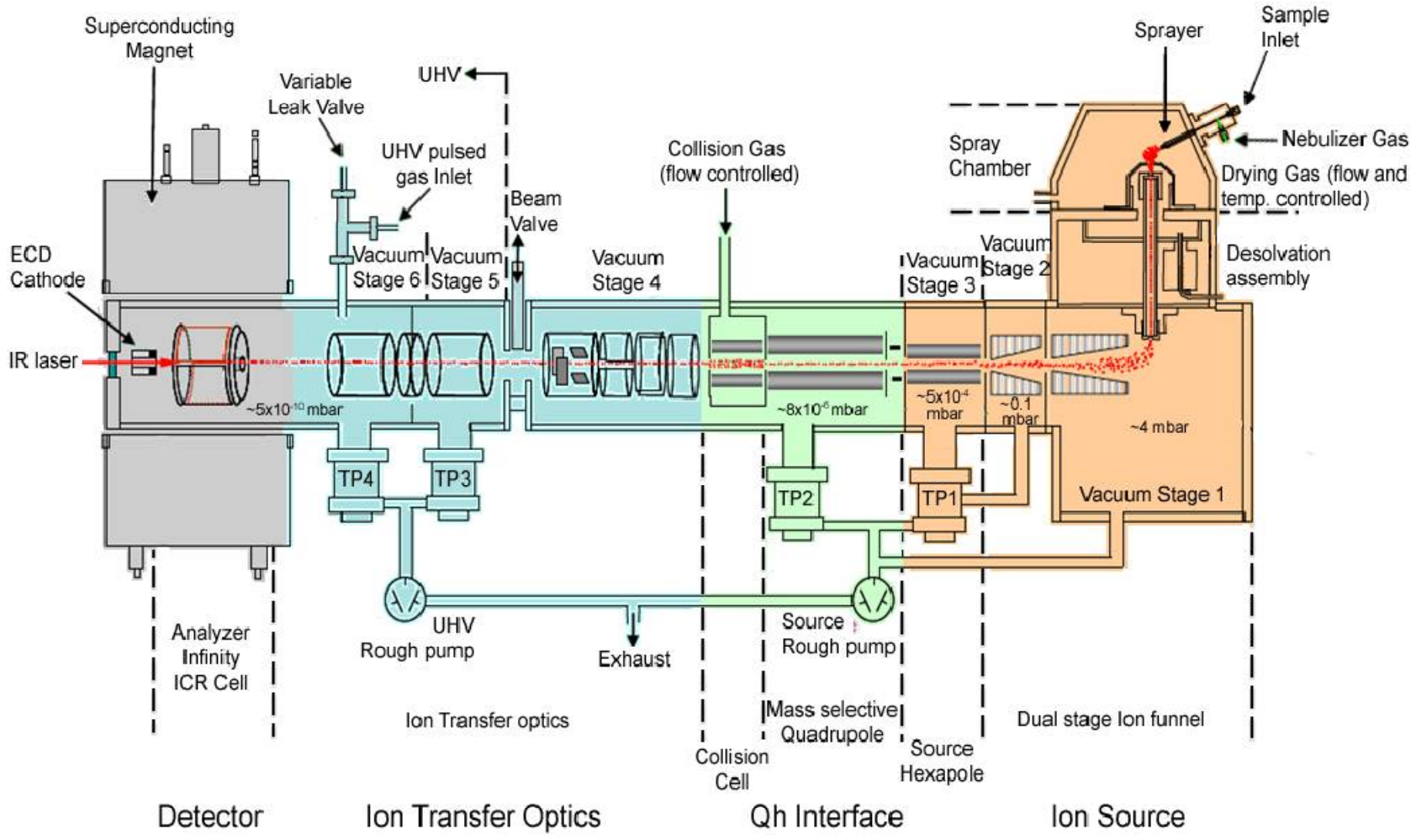


  - Ion-Molecule Reactions

†T. F. Rozan, M. E. Lassman, D. P. Ridge, G.W. Luther. **Evidence for iron, copper and zinc complexation as multinuclear sulphide clusters in oxic rivers.** *Nature*, 2000, *406*, 879-882.


Project Goal
Dissolved Ions
Clusters
Nanoparticles
Solid state material
Mass Spectrometry
UV/VIS Spectroscopy
1
10
∞
Size (nm)

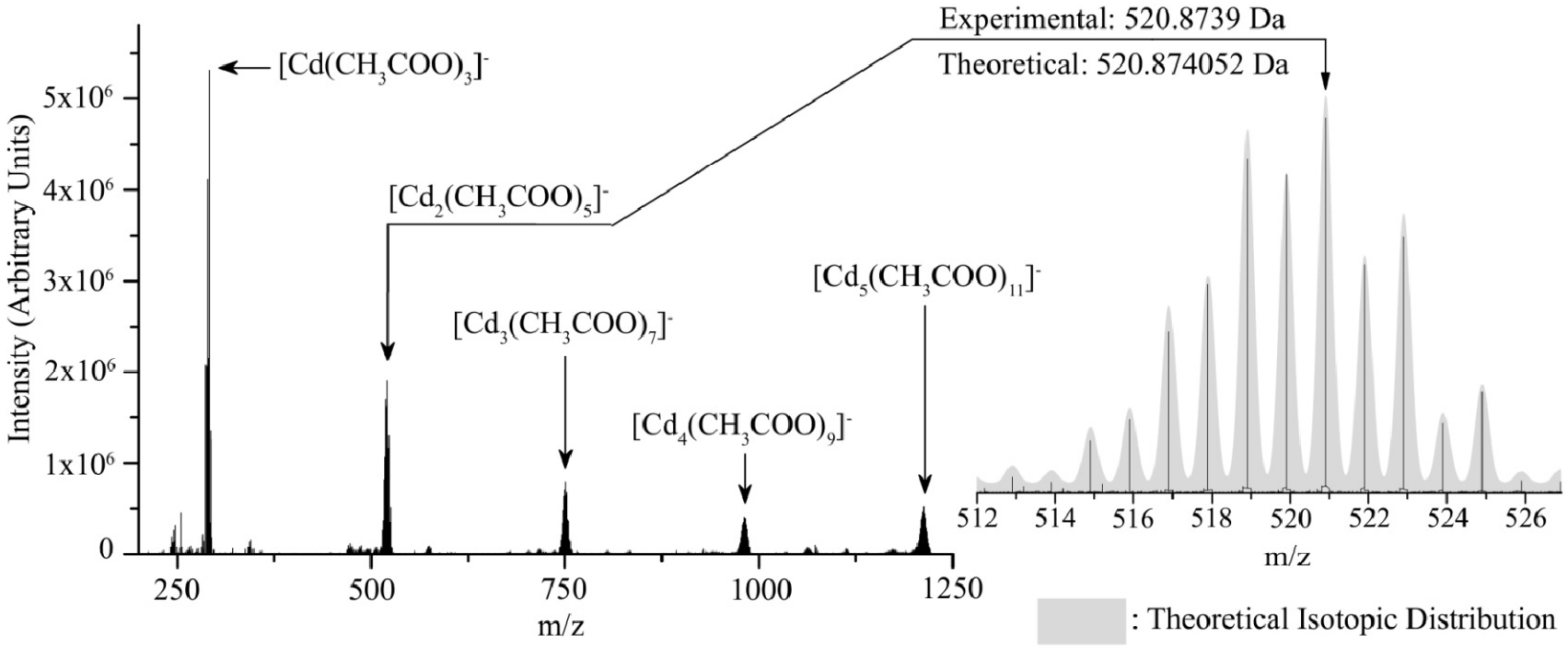
7T FT-ICR MS: UD

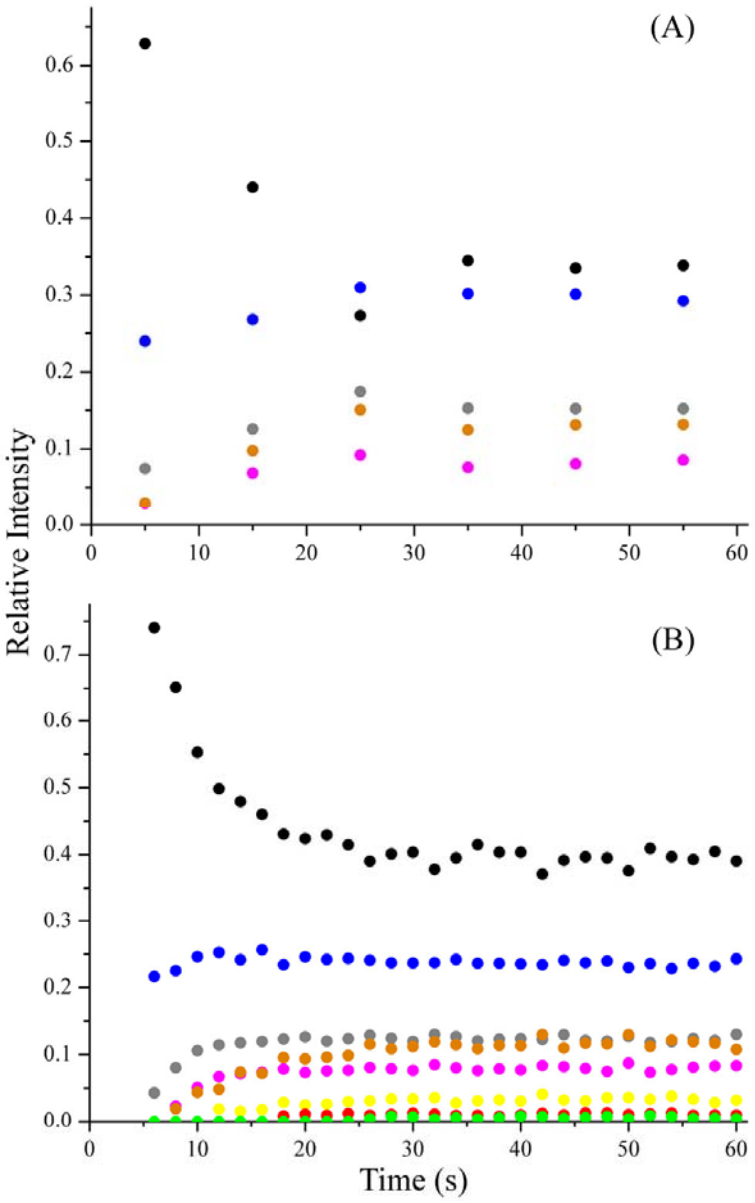


ESI of Metal Salt Solutions

Observed Nucleation Processes

Salt Clusters Observed using ESI FT-ICR MS





Sampling was done using separate aliquots for each spectrum and

A single aliquot was continually injected as spectra were repeatedly taken.

Signal Variance

- $[Cd(CH_3COO)_3]^-$
- $[Cd_2(CH_3COO)_5]^-$
- $[Cd_3(CH_3COO)_7]^-$
- $[Cd_4(CH_3COO)_9]^-$
- $[Cd_5(CH_3COO)_{11}]^-$
- $[Cd_6(CH_3COO)_{13}]^-$
- $[Cd_7(CH_3COO)_{15}]^-$
- $[Cd_8(CH_3COO)_{17}]^-$

0.3 mM cadmium acetate water/MeOH solution (1:1)

Important Points

- Variance in signal over time suggests that clusters observed using ESI are forming in solution.

- Results highlight processes taking place in low dielectric constant solvents
  - Water/MeOH (ε=66[†])
  - Hydrothermal Fluids (ε=10-23[‡])

[†]Akerlof, G. Dielectric Constant of some Organic Solvent-Water Mixtures at various Temperatures. *J. Am. Chem. Soc.* **1932**, *54*, 4125-4139.
[‡]Weingartner, H.; Franck, E. U. Supercritical Water as a Solvent. *Angew Chem Int Ed Engl.* **2005**, *44*, 2672-2692.

Making Metal Sulfide Clusters

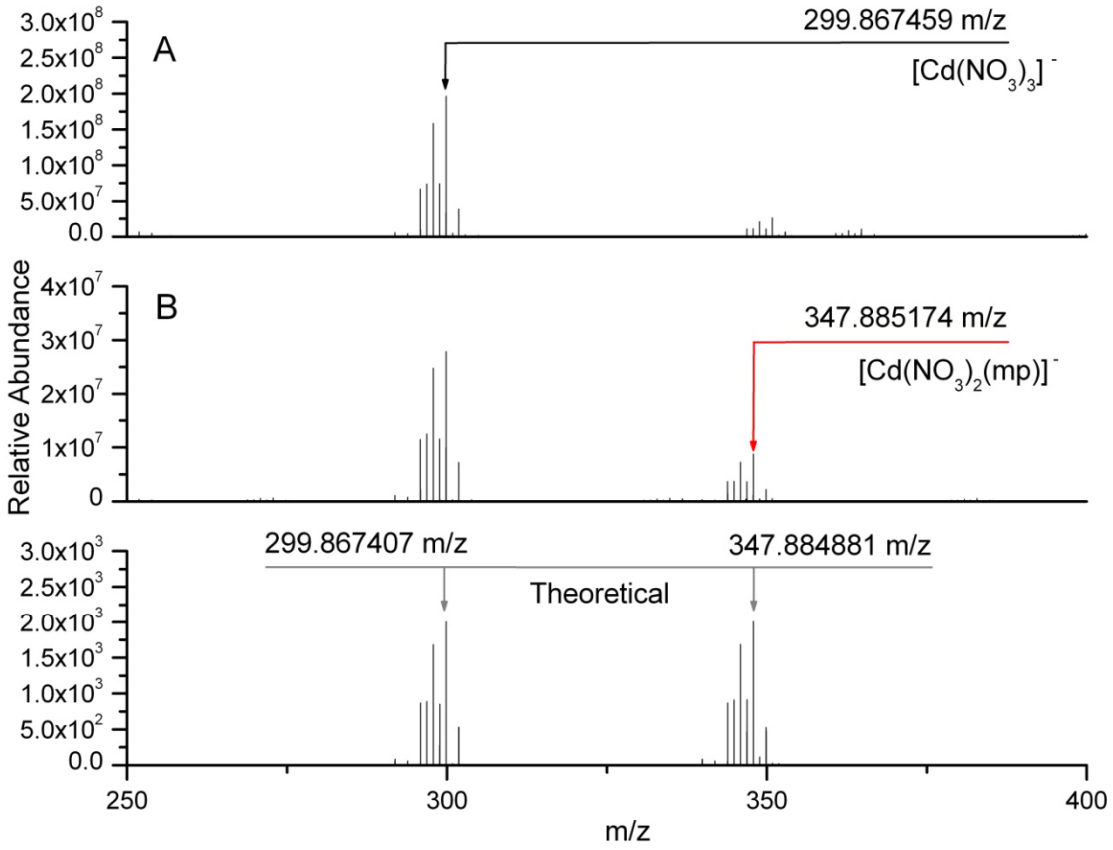
Molecular Capping Agents

Solution Chemistry: Mononuclear Anions

A) 3 mM aqueous solution of $Cd(NO_3)_2 \cdot 4H_2O$ diluted 50/50 with MeOH.

B) 1.5 mM aqueous solution of $Cd(NO_3)_2 \cdot 4H_2O$ and 2-mercaptopyridine (1:1) diluted 50/50 with MeOH.

C) $H_2S(g)$ bubbled through a 3 mM aqueous solution of $Cd(NO_3)_2 \cdot 4H_2O$ followed by addition of 2-mercaptopyridine (1:1), then diluted 50/50 with MeOH.

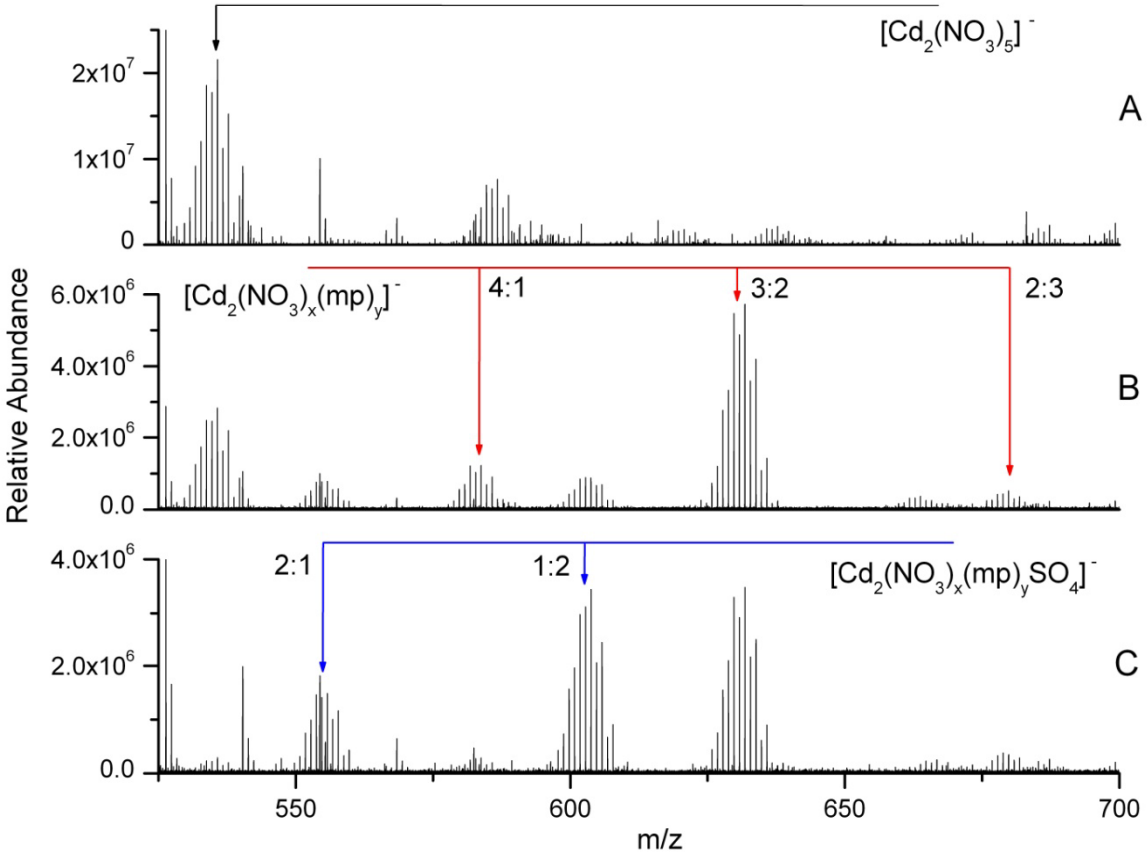


Solution Chemistry: Binuclear Anions

A) 3 mM aqueous solution of $Cd(NO_3)_2 \cdot 4H_2O$ diluted 50/50 with MeOH.

B) 1.5 mM aqueous solution of $Cd(NO_3)_2 \cdot 4H_2O$ and 2-mercaptopyridine (1:1) diluted 50/50 with MeOH.

C) $H_2S(g)$ bubbled through a 3 mM aqueous solution of $Cd(NO_3)_2 \cdot 4H_2O$ followed by addition of 2-mercaptopyridine (1:1), then diluted 50/50 with MeOH.

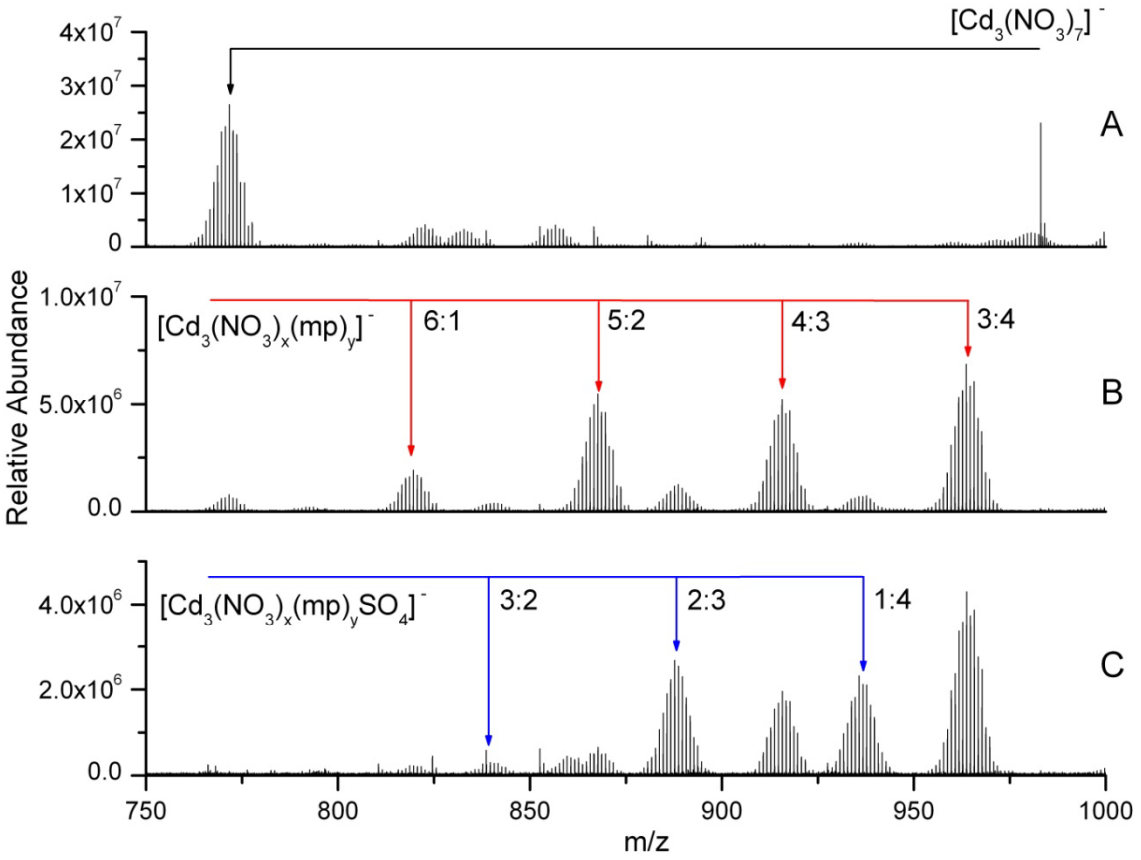


Solution Chemistry: Trinuclear Anions

A) 3 mM aqueous solution of $Cd(NO_3)_2 \cdot 4H_2O$ diluted 50/50 with MeOH.

B) 1.5 mM aqueous solution of $Cd(NO_3)_2 \cdot 4H_2O$ and 2-mercaptopyridine (1:1) diluted 50/50 with MeOH.

C) H_2S(g) bubbled through a 3 mM aqueous solution of $Cd(NO_3)_2 \cdot 4H_2O$ followed by addition of 2-mercaptopyridine (1:1), then diluted 50/50 with MeOH.



Important Points

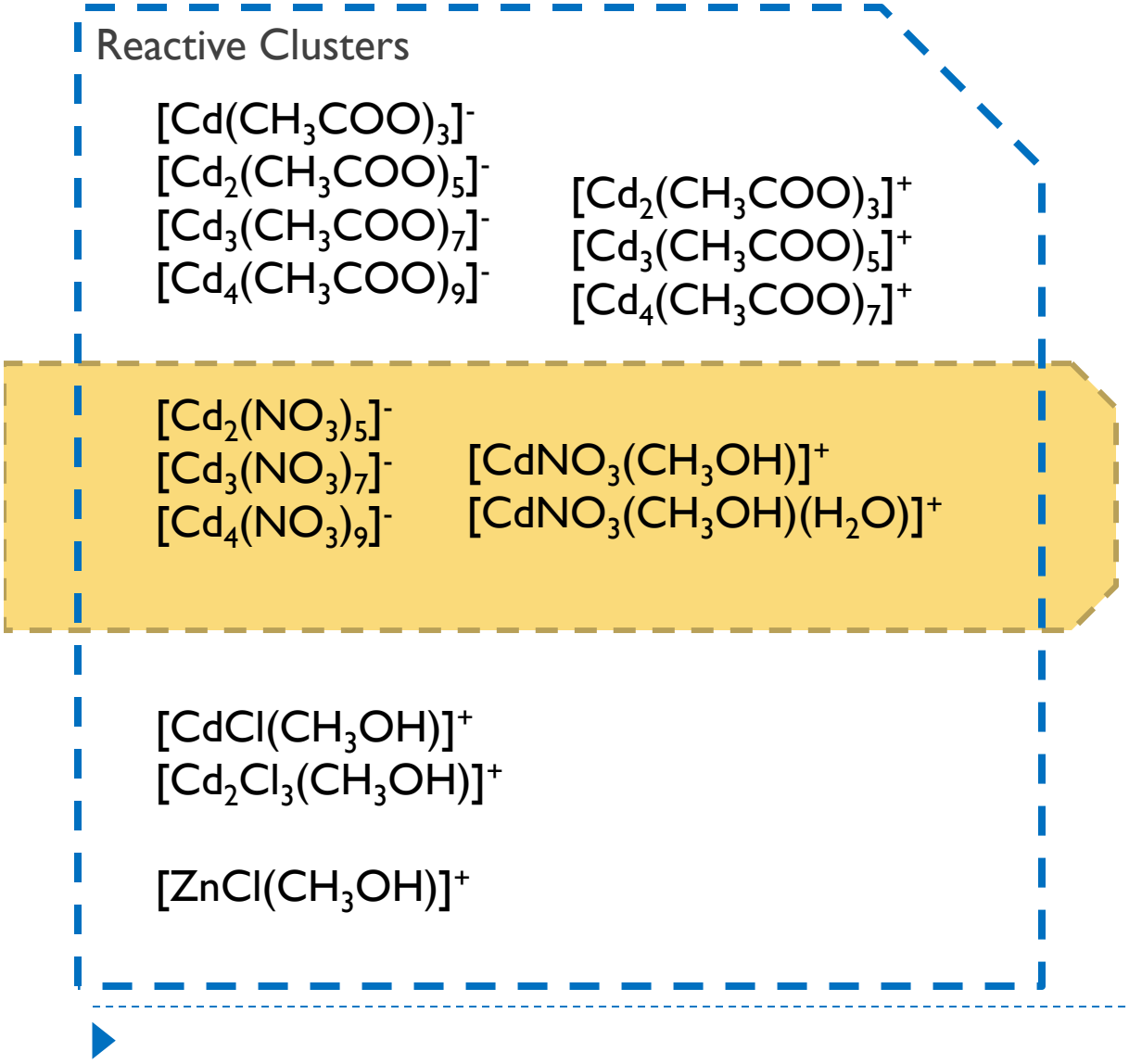
- Sulfidic clusters are observed when 2-mercaptopyridine is introduced.

- Reactivity with H_2S is selective based on cluster size for $[Cd_x(NO_3)_{2x+1}]^-$ species.
  - Sampling a solution based process
  - Gas phase ion-molecule reactions

Making Metal Sulfide Clusters

Gas Phase Ion-Molecule Reactions

Cadmium Salt Clusters

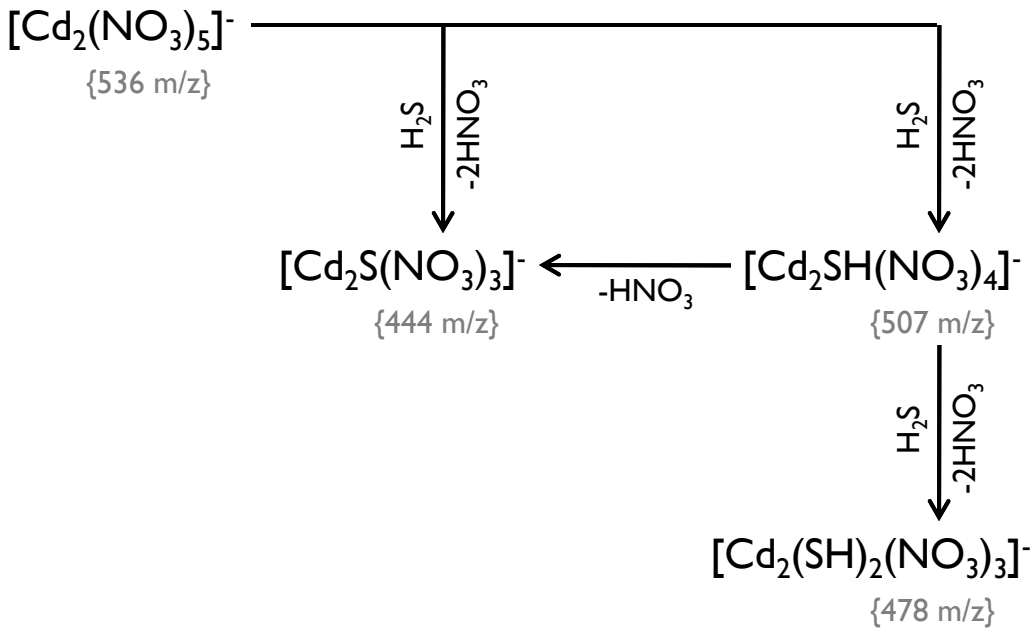


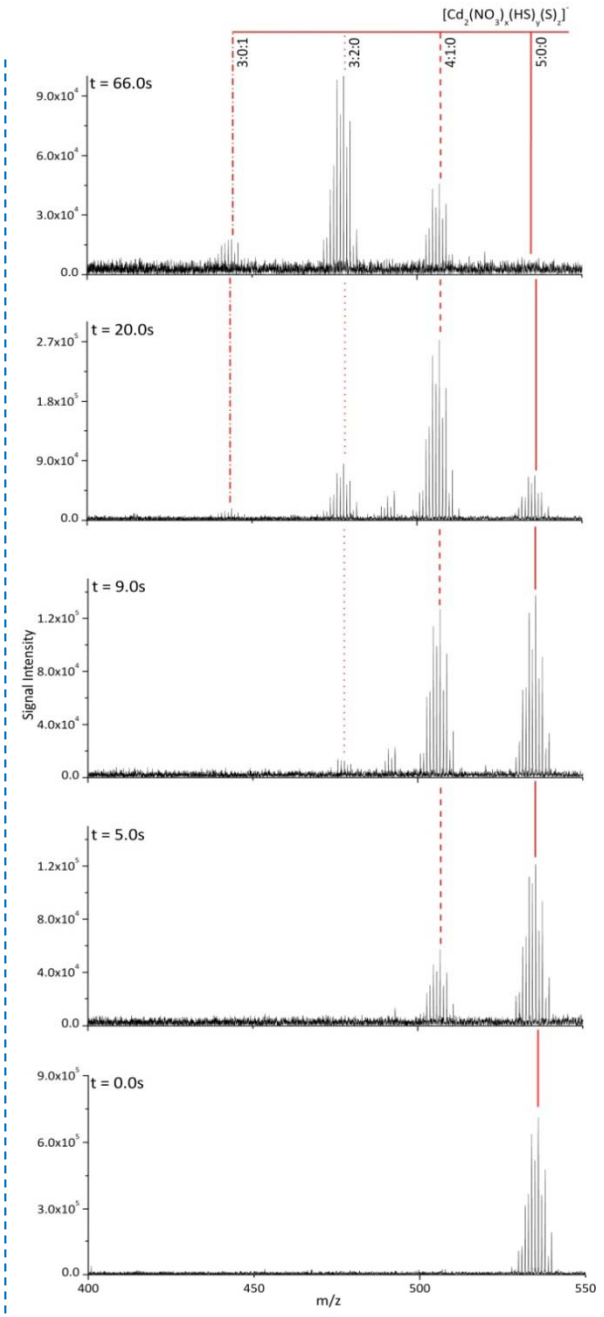
Non-Reactive Clusters

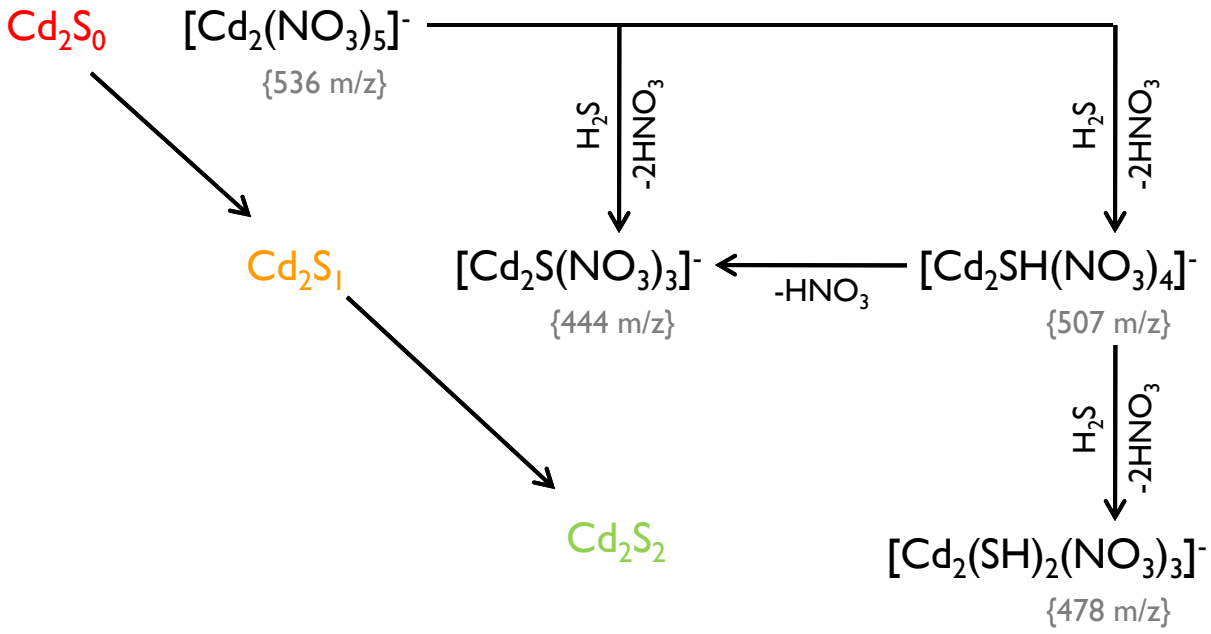
$[Cd(NO_3)_3]^-$

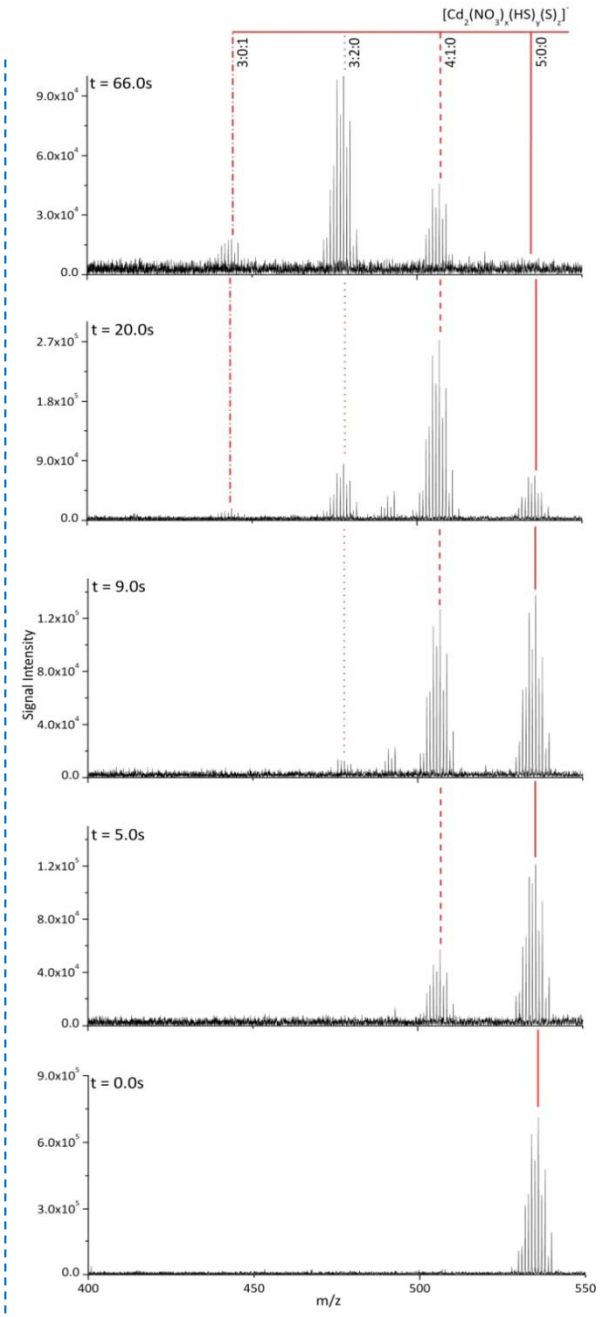
$[Cd_xCl_{2x+1}]^-$

$[Zn_xCl_{2x+1}]^-$


[Cd2(NO3)5]-
{536 m/z}
H2S
-2HNO3
H2S
-2HNO3
[Cd2S(NO3)3]-
{444 m/z}
-HNO3
[Cd2SH(NO3)4]-
{507 m/z}
H2S
-2HNO3
[Cd2(SH)2(NO3)3]-
{478 m/z}


[Cd2(NO3)x(HS)y(S)z]-
3:0:1
3:2:0
4:1:0
5:0:0
t = 66.0s
t = 20.0s
t = 9.0s
t = 5.0s
t = 0.0s
Signal Intensity
m/z
400
450
500
550


Cd2S0
[Cd2(NO3)5]-
{536 m/z}
H2S
-2HNO3
H2S
-2HNO3
Cd2S1
[Cd2S(NO3)3]-
{444 m/z}
-HNO3
[Cd2SH(NO3)4]-
{507 m/z}
H2S
-2HNO3
Cd2S2
[Cd2(SH)2(NO3)3]-
{478 m/z}


[Cd2(NO3)x(HS)y(S)z]-
3:0:1
3:2:0
4:1:0
5:0:0
t = 66.0s
t = 20.0s
t = 9.0s
t = 5.0s
t = 0.0s
Signal Intensity
m/z
400
450
500
550

$r = k[\text{Cluster Family}][H_2S]$

$r = k[\text{Cluster Family}]$

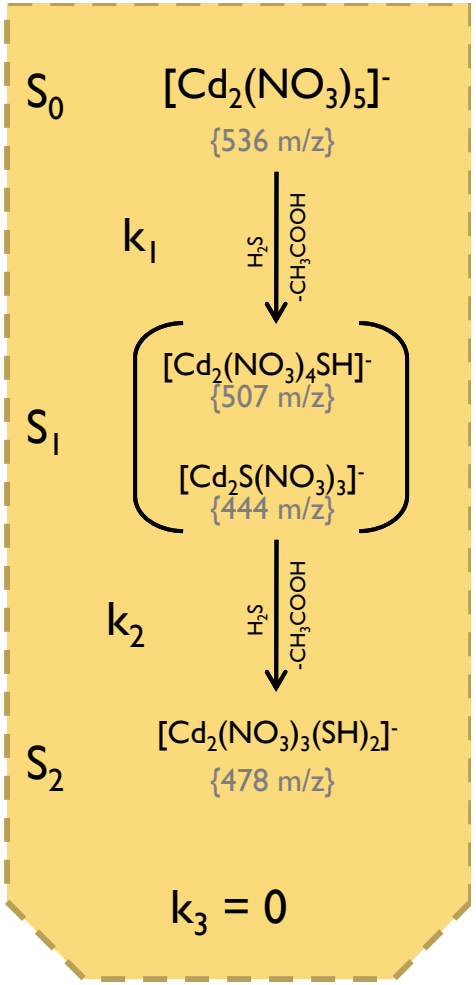
H_2S is in excess

- Pseudo First Order kinetics

$$\frac{d[S_0]}{dt} = -k_1[S_0]$$

$$\frac{d[S_1]}{dt} = k_1[S_0] - k_2[S_2]$$

$$\frac{d[S_2]}{dt} = k_2[S_1]$$



Integrated Rate Equations

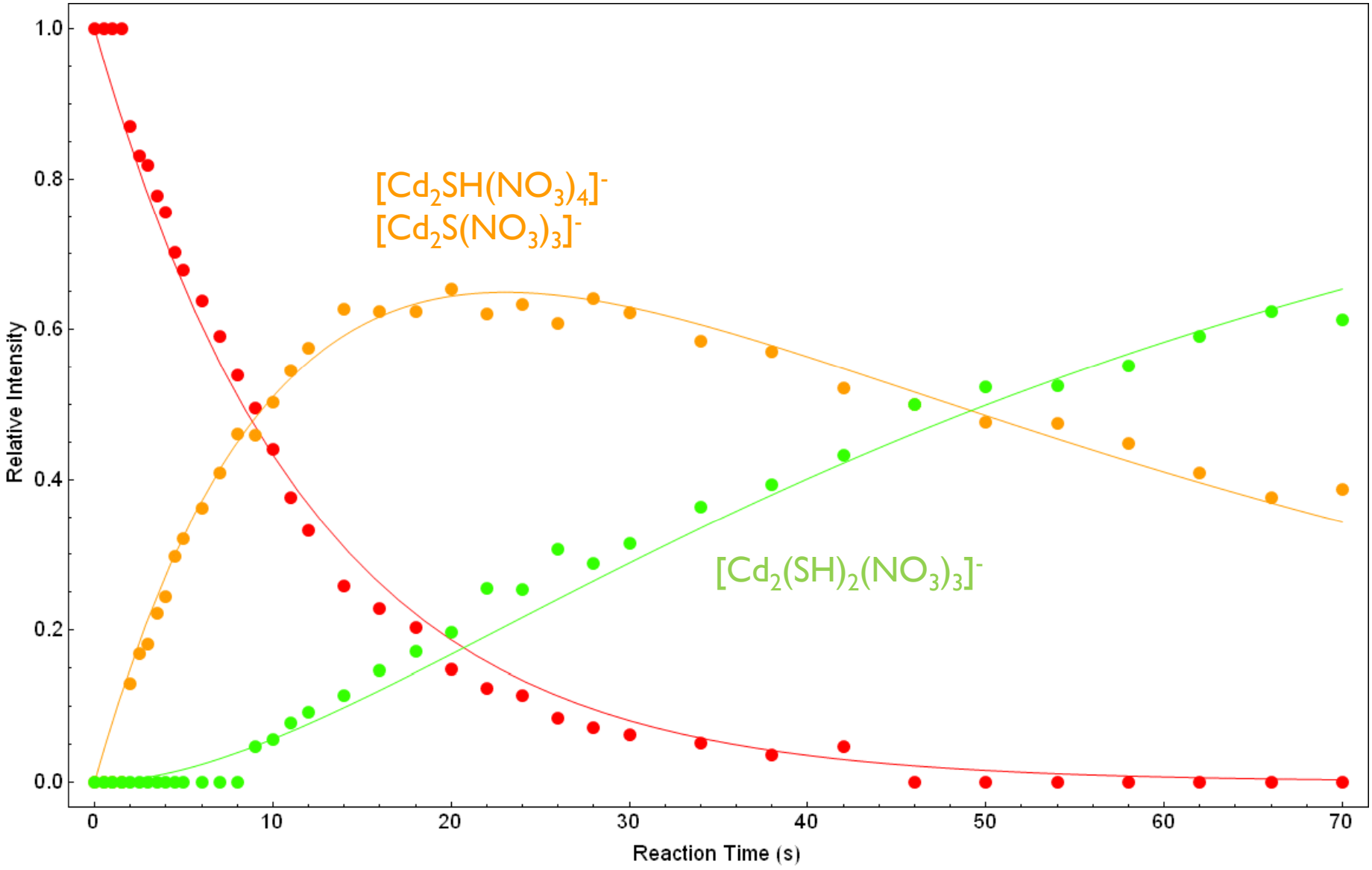
$$[S_0] = [A]_0 \, e^{-k_1 t}$$

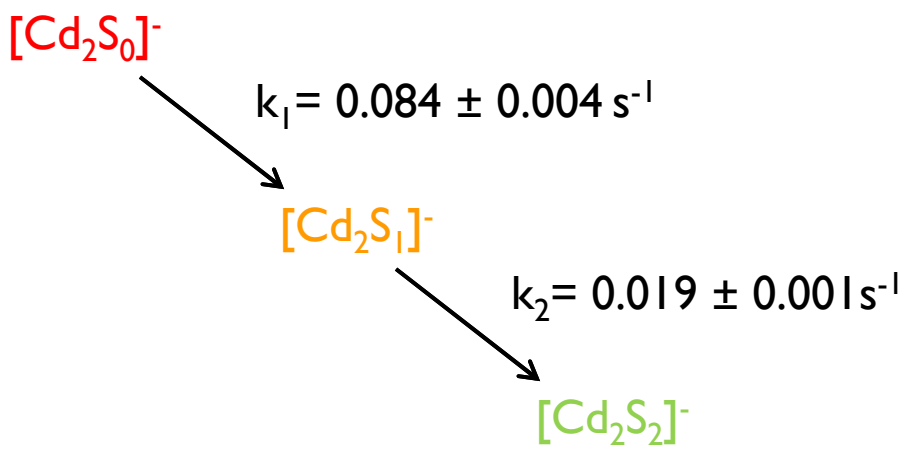
$$[S_1] = [A]_0 \frac{k_1}{k_2 - k_1} \left(e^{-k_1 t} - e^{-k_2 t}\right)$$

$$[S_2] = k_1 k_2 \left(\frac{e^{-k_1 t}}{(k_2 - k_1)(k_3 - k_1)} + \frac{e^{-k_2 t}}{(k_1 - k_2)(k_3 - k_2)} + \frac{e^{-k_3 t}}{(k_1 - k_3)(k_2 - k_3)} \right)$$

$[Cd_2(NO_3)_5]^-$ +H_2S (g)

$4x10^{-9}$ torr



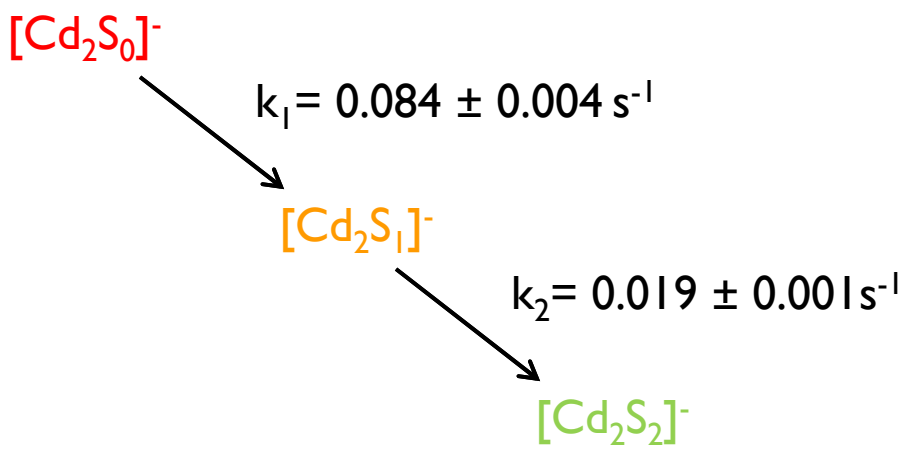


$[Cd_2(NO_3)_5]^- + H_2S$

$[Cd_2SH(NO_3)_4]^-$
$[Cd_2S(NO_3)_3]^-$

$[Cd_2(SH)_2(NO_3)_3]^-$

H_2S: 4×10^{-9} torr



H_2S: 4×10^{-9} torr

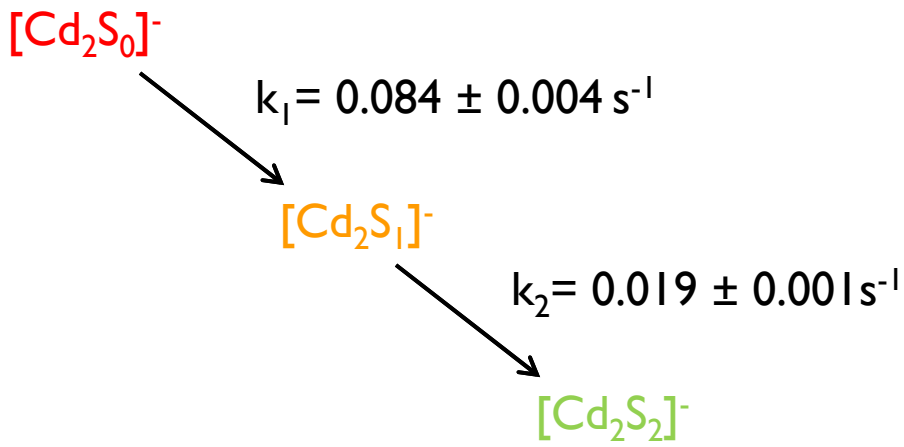
Reaction Efficiency

- Assume fastest RXN is collision rate limited

$[Cd(NO_3)(CH_3OH)]^+$

$k_1 = 2.85 \pm 0.27\ s^{-1}$

- Capture Collision Theory†



Reaction Efficiency

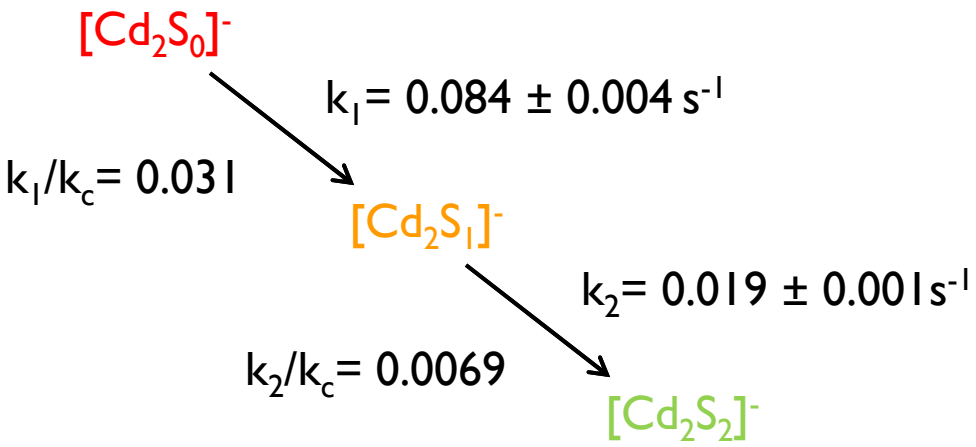
- Assume fastest RXN is collision rate limited

$[Cd(NO_3)(CH_3OH)]^+$
$k_1 = 2.85 \pm 0.27\ s^{-1}$

- Capture Collision Theory†

$$\frac{k}{k_c} = \frac{k_x^1}{2.85 s^{-1}} \left(\frac{\mu_x}{29.19 Da} \right)^{\frac{1}{2}} \left(\frac{4 \times 10^{-9}\ Torr}{P_x} \right)$$

H_2S: 4×10^{-9} torr



$$\frac{k}{k_c} = \frac{k'_x}{2.85 s^{-1}} \left(\frac{\mu_x}{29.19 Da} \right)^{\frac{1}{2}} \left(\frac{4 \times 10^{-9} Torr}{P_x} \right)$$

H_2S: 4×10^{-9} torr

Reaction Efficiency

- Assume fastest RXN is collision rate limited

$[Cd(NO_3)(CH_3OH)]^+$
$k_1 = 2.85 \pm 0.27\ s^{-1}$

- Capture Collision Theory†

Anionic Cadmium Clusters

Reactant	P (10^{-9} torr)	ΔH (kcal/mol)	k_1/k_c	k_2/k_c	k_3/k_c	k_4/k_c	k_5/k_c	k_6/k_c	k_7/k_c
$[Cd(CH_3COO)_3]^-$	4	-6.236082	0.032	0.034	0.023				
$[Cd(CH_3COO)_3]^-$	9	-6.236082	0.035	0.042	0.030				
$[Cd_2(CH_3COO)_5]^-$	4		0.018	0.015	0.010	0.0020			
$[Cd_2(CH_3COO)_5]^-$	9		0.019	0.015	0.0095	0.0034			
$[Cd_3(CH_3COO)_7]^-$	4		0.015	0.14	0.038	0.011	0.019	0.0073	
$[Cd_3(CH_3COO)_7]^-$	9		0.016	0.24	0.061	0.012	0.035	0.0082	
$[Cd_4(CH_3COO)_9]^-$	4		0.013	0.034(24)	1.00*	1.00*	1.00*	0.0079	0.0097(15)
$[Cd_4(CH_3COO)_9]^-$	9		0.013	0.042(15)	1.00*	1.00*	1.00*	0.0080	0.015
$[Cd(NO_3)_3]^-$	4 & 9	9.710921	No RXN						
$[Cd_2(NO_3)_5]^-$	4		0.031	0.0069					
$[Cd_3(NO_3)_7]^-$	4		0.046	0.035	0.00090				
$[Cd_4(NO_3)_9]^-$	4		0.0094	0.0090	0.017				
$[CdCl_3]^-$	4 & 9	8.8245642	No RXN						
$[Cd_xCl_{2x+1}]^-$	4 & 9		No RXN						

Anionic Cadmium Clusters

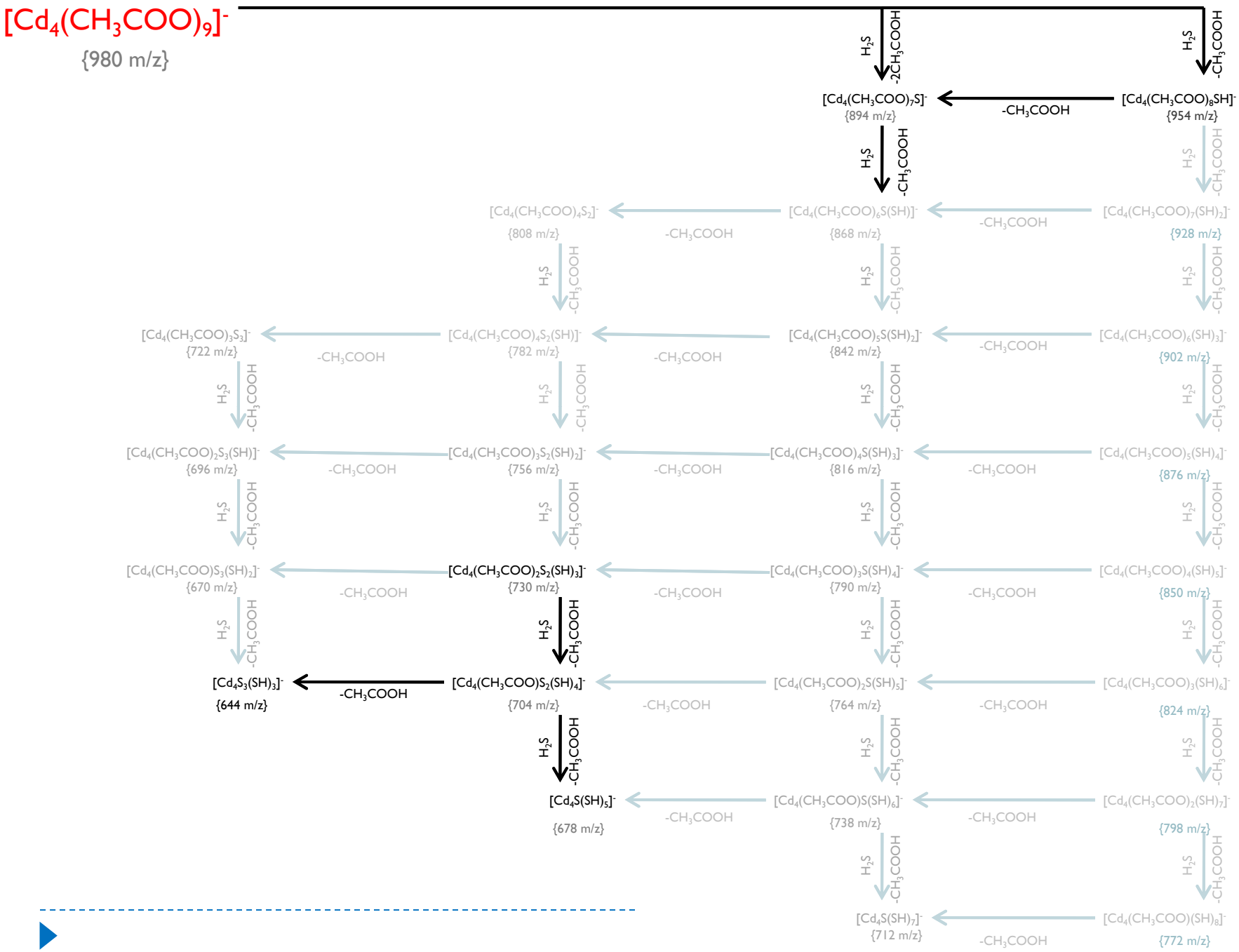
Reactant	P (10^{-9} torr)	ΔH (kcal/mol)	k_1/k_c	k_2/k_c	k_3/k_c	k_4/k_c	k_5/k_c	k_6/k_c	k_7/k_c
$[Cd(CH_3COO)_3]^-$	4	-6.236082	0.032	0.034	0.023				
$[Cd(CH_3COO)_3]^-$	9	-6.236082	0.035	0.042	0.030				
$[Cd_2(CH_3COO)_5]^-$	4		0.018	0.015	0.010	0.0020			
$[Cd_2(CH_3COO)_5]^-$	9		0.020	0.025	0.012	0.0034			
$[Cd_3(CH_3COO)_7]^-$	4		0.015	0.14	0.038	0.011	0.019	0.0073	
$[Cd_3(CH_3COO)_7]^-$	9		0.016	0.24	0.061	0.012	0.035	0.0082	
$[Cd_4(CH_3COO)_9]^-$	4		0.013	0.034(24)	1.00*	1.00*	1.00*	0.0079	0.0097(15)
$[Cd_4(CH_3COO)_9]^-$	9		0.013	0.042(15)	1.00*	1.00*	1.00*	0.0080	0.015
$[Cd(NO_3)_3]^-$	4 & 9	9.710921	No RXN						
$[Cd_2(NO_3)_5]^-$	4		0.031	0.0069					
$[Cd_3(NO_3)_7]^-$	4		0.046	0.035	0.00090				
$[Cd_4(NO_3)_9]^-$	4		0.0094	0.0090	0.017				
$[CdCl_3]^-$	4 & 9	8.8245642	No RXN						
$[Cd_xCl_{2x+1}]^-$	4 & 9		No RXN						

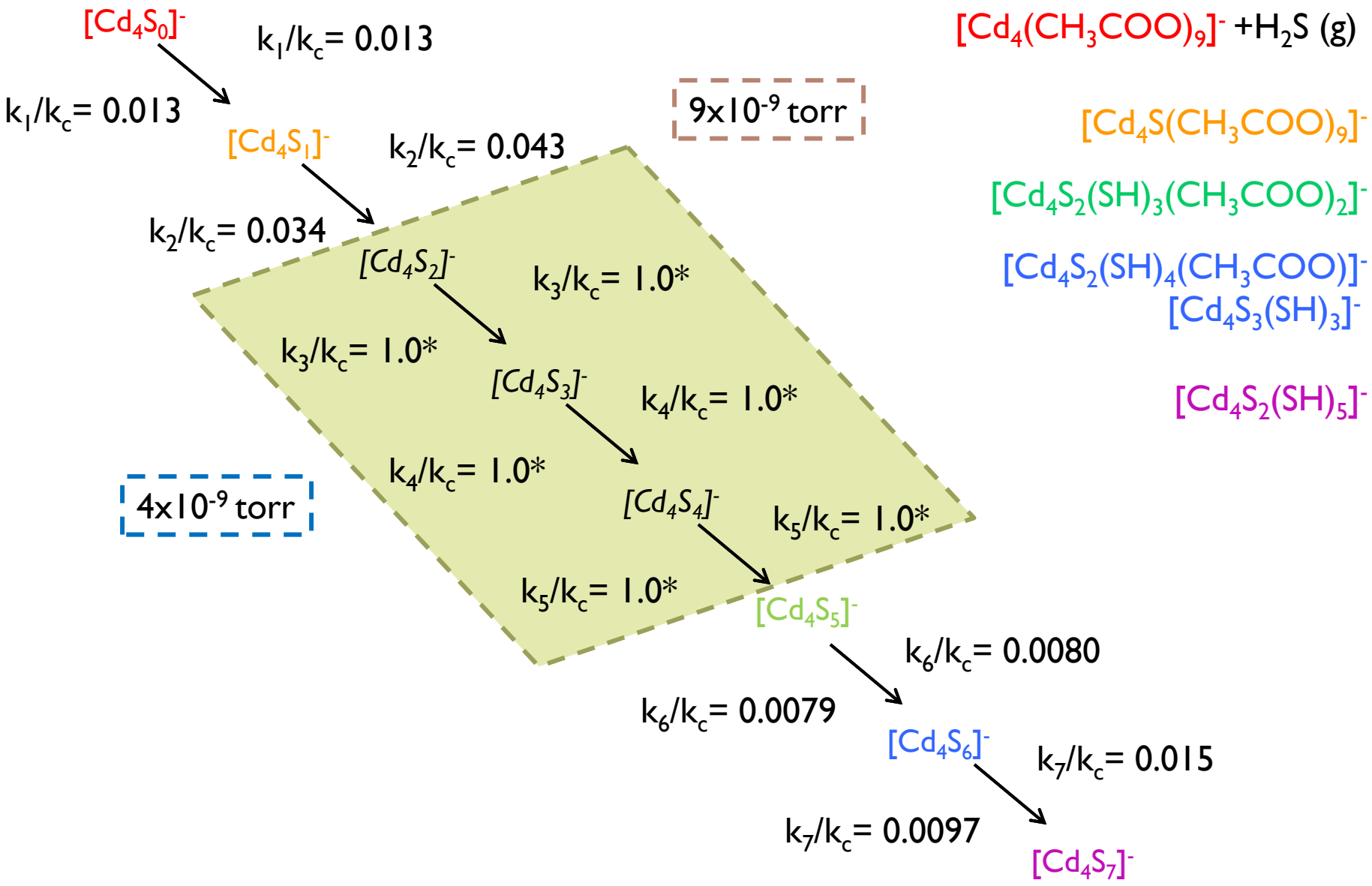
Most Anionic Metal Cluster reactions are < 5% efficient.

Anionic Cadmium Clusters

Reactant	P (10^{-9} torr)	ΔH (kcal/mol)	k_1/k_c	k_2/k_c	k_3/k_c	k_4/k_c	k_5/k_c	k_6/k_c	k_7/k_c
$[Cd(CH_3COO)_3]^-$	4	-6.236082	0.032	0.034	0.023				
$[Cd(CH_3COO)_3]^-$	9	-6.236082	0.035	0.042	0.030				
$[Cd_2(CH_3COO)_5]^-$	4					0.0020			
$[Cd_2(CH_3COO)_5]^-$	9		0.019	0.015	0.0095	0.0034			
$[Cd_3(CH_3COO)_7]^-$	4		0.015	0.14	0.038	0.011	0.019	0.0073	
$[Cd_3(CH_3COO)_7]^-$	9		0.016	0.24	0.061	0.012	0.035	0.0082	
$[Cd_4(CH_3COO)_9]^-$	4		0.013	0.034(24)	1.00*	1.00*	1.00*	0.0079	0.0097(15)
$[Cd_4(CH_3COO)_9]^-$	9		0.013	0.042(15)	1.00*	1.00*	1.00*	0.0080	0.015
$[Cd(NO_3)_3]^-$	4 & 9	9.710921	No RXN						
$[Cd_2(NO_3)_5]^-$	4		0.031	0.0069					
$[Cd_3(NO_3)_7]^-$	4		0.046	0.035	0.00090				
$[Cd_4(NO_3)_9]^-$	4		0.0094	0.0090	0.017				
$[CdCl_3]^-$	4 & 9	8.8245642	No RXN						
$[Cd_xCl_{2x+1}]^-$	4 & 9		No RXN						

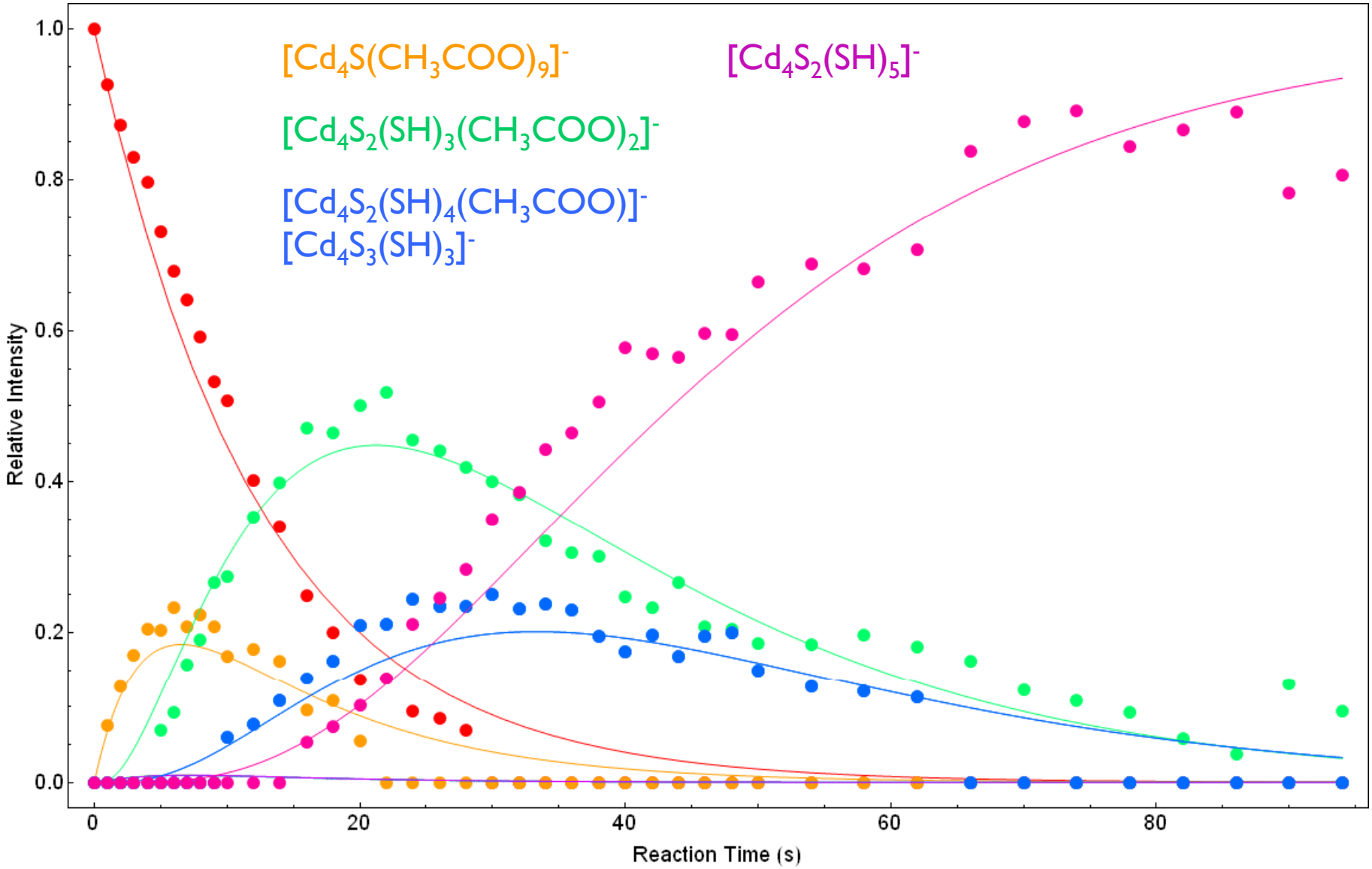
The Exception…


[Cd4(CH3COO)9]-
{980 m/z}
H2S
-2CH3COOH
-CH3COOH
[Cd4(CH3COO)7S]-
{894 m/z}
[Cd4(CH3COO)8SH]-
{954 m/z}
[Cd4(CH3COO)6S(SH)]-
{868 m/z}
[Cd4(CH3COO)7(SH)2]-
{928 m/z}
[Cd4(CH3COO)4S2]-
{808 m/z}
[Cd4(CH3COO)5S(SH)2]-
{842 m/z}
[Cd4(CH3COO)6(SH)3]-
{902 m/z}
[Cd4(CH3COO)3S3]-
{722 m/z}
[Cd4(CH3COO)4S2(SH)]-
{782 m/z}
[Cd4(CH3COO)5(SH)4]-
{876 m/z}
[Cd4(CH3COO)2S3(SH)]-
{696 m/z}
[Cd4(CH3COO)3S2(SH)2]-
{756 m/z}
[Cd4(CH3COO)4S(SH)3]-
{816 m/z}
[Cd4(CH3COO)S3(SH)2]-
{670 m/z}
[Cd4(CH3COO)2S2(SH)3]-
{730 m/z}
[Cd4(CH3COO)3S(SH)4]-
{790 m/z}
[Cd4(CH3COO)4(SH)5]-
{850 m/z}
[Cd4S3(SH)3]-
{644 m/z}
[Cd4(CH3COO)S2(SH)4]-
{704 m/z}
[Cd4(CH3COO)2S(SH)5]-
{764 m/z}
[Cd4(CH3COO)3(SH)6]-
{824 m/z}
[Cd4S(SH)5]-
{678 m/z}
[Cd4(CH3COO)S(SH)6]-
{738 m/z}
[Cd4(CH3COO)2(SH)7]-
{798 m/z}
[Cd4S(SH)7]-
{712 m/z}
[Cd4(CH3COO)(SH)8]-
{772 m/z}


[Cd4S0]-
k1/kc= 0.013
k1/kc= 0.013
[Cd4S1]-
k2/kc= 0.043
k2/kc= 0.034
[Cd4S2]-
k3/kc= 1.0*
k3/kc= 1.0*
[Cd4S3]-
k4/kc= 1.0*
k4/kc= 1.0*
[Cd4S4]-
k5/kc= 1.0*
k5/kc= 1.0*
[Cd4S5]-
k6/kc= 0.0080
k6/kc= 0.0079
[Cd4S6]-
k7/kc= 0.015
k7/kc= 0.0097
[Cd4S7]-
9x10-9 torr
4x10-9 torr
[Cd4(CH3COO)9]- +H2S (g)
[Cd4S(CH3COO)9]-
[Cd4S2(SH)3(CH3COO)2]-
[Cd4S2(SH)4(CH3COO)]-
[Cd4S3(SH)3]-
[Cd4S2(SH)5]-

$[Cd_4(CH_3COO)_9]^-$ +H_2S (g)

$9x10^{-9}$ torr

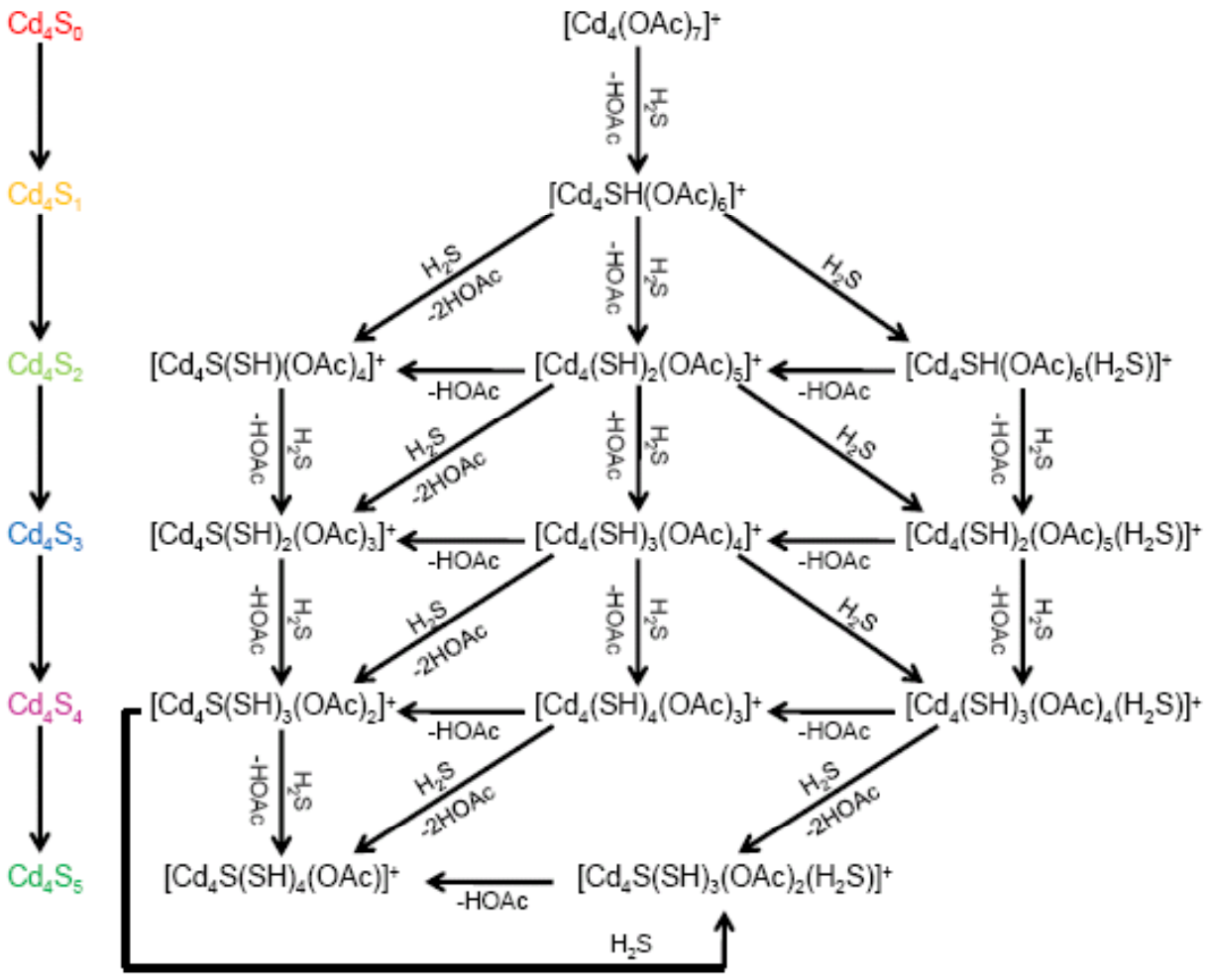


Anionic Cadmium Clusters

Reactant	P (10^{-9} torr)	ΔH (kcal/mol)	k_1/k_c	k_2/k_c	k_3/k_c	k_4/k_c	k_5/k_c	k_6/k_c	k_7/k_c
$[Cd(CH_3COO)_3]^-$	4	-6.236	0.032	0.034	0.023				
$[Cd(CH_3COO)_3]^-$	9	-6.236	0.035	0.042	0.030				
$[Cd_2(CH_3COO)_5]^-$	4		0.018	0.015	0.010	0.0020			
$[Cd_2(CH_3COO)_5]^-$	9		0.019	0.015	0.0095	0.0034			
$[Cd_3(CH_3COO)_7]^-$	4		0.015	0.14	0.038	0.011	0.019	0.0073	
$[Cd_3(CH_3COO)_7]^-$	9		0.018	0.24	0.061	0.012	0.035	0.0082	
$[Cd_4(CH_3COO)_9]^-$	4		0.013	0.034(24)	1.00*	1.00*	1.00*	0.0079	0.0097(15)
$[Cd_4(CH_3COO)_9]^-$	9		0.013	0.042(15)	1.00*	1.00*	1.00*	0.0080	0.015
$[Cd(NO_3)_3]^-$	4 & 9	9.711	No RXN						
$[Cd_2(NO_3)_5]^-$	4		0.031	0.0069					
$[Cd_3(NO_3)_7]^-$	4		0.046	0.035	0.00090				
$[Cd_4(NO_3)_9]^-$	4		0.0094	0.0090	0.017				
$[CdCl_3]^-$	4 & 9	8.825	No RXN						
$[Cd_xCl_{2x+1}]^-$	4 & 9		No RXN						

Calculated reaction enthalpies are consistent with observed reactivity.

Cationic Metal Sulfide Clusters



$[Cd_4(CH_3COO)_7]^+$

+

H_2S

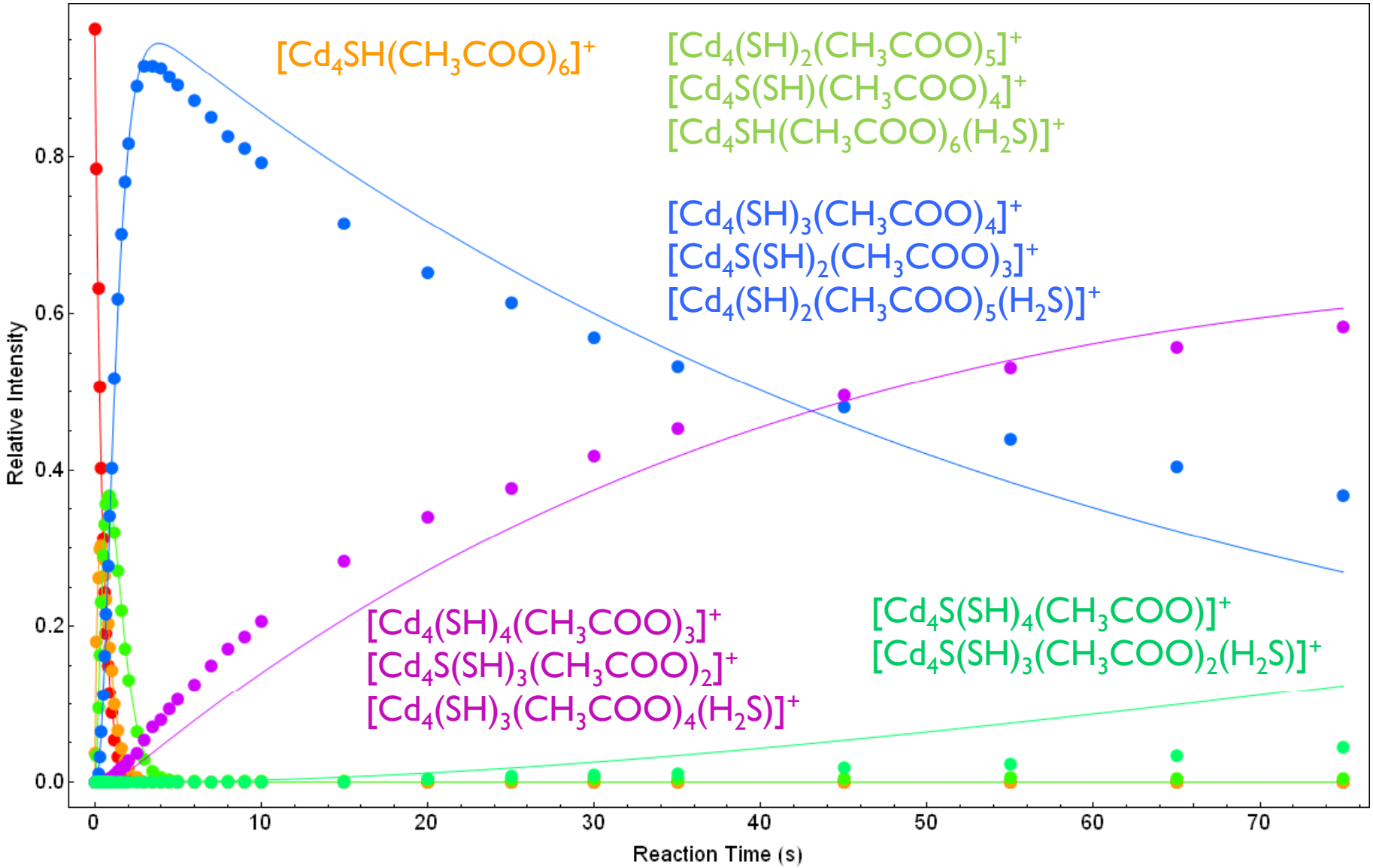
SH^- Substitution

CH_3COOH Elimination

H_2S Addition

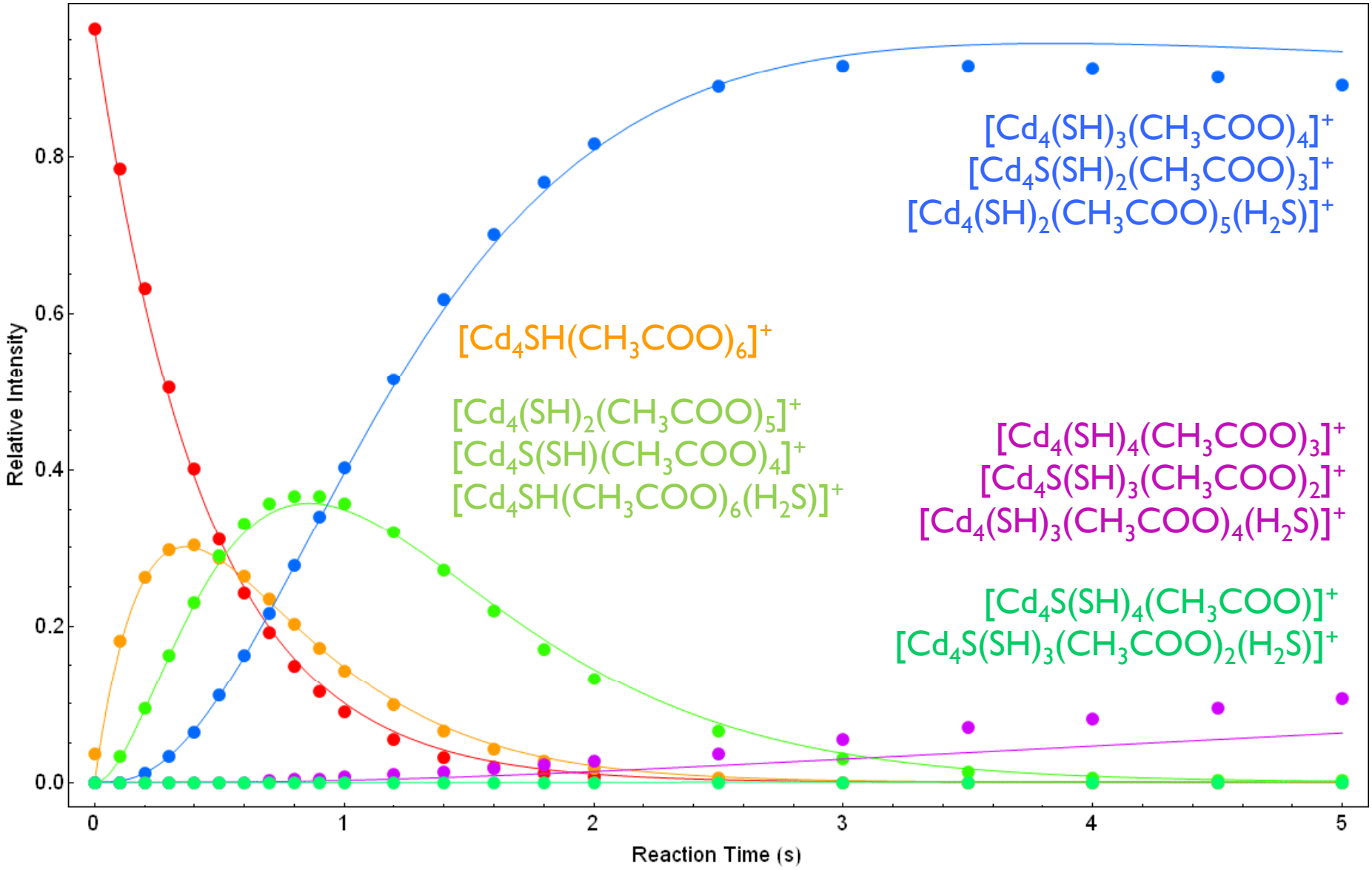
$[Cd_4(CH_3COO)_7]^+ + H_2S$ (g)

9×10^{-9} torr



$[Cd_4(CH_3COO)_7]^+ + H_2S$ (g)

9×10^{-9} torr



Cationic Cadmium Clusters

Reactant	P (10^{-9} torr)	ΔH (kcal/mol)	k_1/k_c	k_2/k_c	k_3/k_c	k_4/k_c	k_5/k_c
$[Cd(CH_3COO)]^+$		-3.759	Not Obs				
$[Cd_2(CH_3COO)_3]^+$	4		0.77	0.0033	0.0045		
$[Cd_3(CH_3COO)_5]^+$	4		0.923	0.0722	0.0045	0.0013	
$[Cd_3(CH_3COO)_5]^+$	9		0.88	0.073	0.0062	0.0066	
$[Cd_4(CH_3COO)_7]^+$	9		0.37	0.54	0.28	0.0029	0.0016
$[Cd(NO_3)]^+$		-17.442	Not Obs				
$[Cd(NO_3)(CH_3OH)]^+$	4		1.00				
$[Cd(NO_3)(CH_3OH)(H_2O)]^+$	4		0.61				
$[CdOH]^+$		-27.183	Not Obs				
$[CdOH(CH_3OH)]^+$	4		0.77				
$[CdCl]^+$		-11.163	Not Obs				
$[CdCl(CH_3OH)]^+$	4		0.16	0.0062			
$[ZnCl]^+$		-11.903	Not Obs				
$[ZnCl(CH_3OH)]^+$	4		0.037				

Cationic Cadmium Clusters

Reactant	P (10^{-9} torr)	ΔH (kcal/mol)	k_1/k_c	k_2/k_c	k_3/k_c	k_4/k_c	k_5/k_c
$[Cd(CH_3COO)]^+$		-3.759478	Not Obs				
$[Cd_2(CH_3COO)_3]^+$	4		0.77	0.0033	0.0045		
$[Cd_3(CH_3COO)_5]^+$	4		0.923	0.0722	0.0045	0.0013	
$[Cd_3(CH_3COO)_5]^+$	9		0.88	0.073	0.0062	0.0066	
$[Cd_4(CH_3COO)_7]^+$	9		0.37	0.54	0.28	0.0029	0.0016
$[Cd(NO_3)]^+$		-17.441937	Not Obs				
$[Cd(NO_3)(CH_3OH)]^+$	4		1.00				
$[Cd(NO_3)(CH_3OH)(H_2O)]^+$	4		0.61				
$[CdOH]^+$		-27.182772	Not Obs				
$[CdOH(CH_3OH)]^+$	4		0.77				
$[CdCl]^+$		-11.162765	Not Obs				
$[CdCl(CH_3OH)]^+$	4		0.16	0.0062			
$[ZnCl]^+$		-11.902944	Not Obs				
$[ZnCl(CH_3OH)]^+$	4		0.037				

Cationic Metal Clusters show much higher reaction efficiencies.

Cationic Cadmium Clusters

Reactant	P (10^{-9} torr)	ΔH (kcal/mol)	k_1/k_c	k_2/k_c	k_3/k_c	k_4/k_c	k_5/k_c
$[Cd(CH_3COO)]^+$		-3.759	Not Obs				
$[Cd_2(CH_3COO)_3]^+$	4		0.77	0.0033	0.0045		
$[Cd_3(CH_3COO)_5]^+$	4		0.923	0.0722	0.0045	0.0013	
$[Cd_3(CH_3COO)_5]^+$	9		0.88	0.073	0.0062	0.0066	
$[Cd_4(CH_3COO)_7]^+$	9		0.37	0.54	0.28	0.0029	0.0016
$[Cd(NO_3)]^+$		-17.442	Not Obs				
$[Cd(NO_3)(CH_3OH)]^+$	4		1.00				
$[Cd(NO_3)(CH_3OH)(H_2O)]^+$	4		0.61				
$[CdOH]^+$		-27.183	Not Obs				
$[CdOH(CH_3OH)]^+$	4		0.77				
$[CdCl]^+$		-11.163	Not Obs				
$[CdCl(CH_3OH)]^+$	4		0.16	0.0062			
$[ZnCl]^+$		-11.903	Not Obs				
$[ZnCl(CH_3OH)]^+$	4		0.037				

Cationic Cadmium Clusters

Reactant	P (10^{-9} torr)	ΔH (kcal/mol)	k_1/k_c	k_2/k_c	k_3/k_c	k_4/k_c	k_5/k_c
$[Cd(CH_3COO)]^+$		-3.759478	Not Obs				
$[Cd_2(CH_3COO)_3]^+$	4		0.77	0.0033	0.0045		
$[Cd_3(CH_3COO)_5]^+$	4		0.923	0.0722	0.0045	0.0013	
$[Cd_3(CH_3COO)_5]^+$	9		0.88	0.073	0.0062	0.0066	
$[Cd_4(CH_3COO)_7]^+$	9		0.37	0.54	0.28	0.0029	0.0016
$[Cd(NO_3)]^+$		-17.441937	Not Obs				
$[Cd(NO_3)(CH_3OH)]^+$	4		[illegible]				
$[Cd(NO_3)(CH_3OH)(H_2O)]^+$	4		0.61				
$[CdOH]^+$		-27.182772	Not Obs				
$[CdOH(CH_3OH)]^+$	4		0.77				
$[CdCl]^+$		-11.162765	Not Obs				
$[CdCl(CH_3OH)]^+$	4		0.16	0.0062			
$[ZnCl]^+$		-11.902944	Not Obs				
$[ZnCl(CH_3OH)]^+$	4		0.037				

Reaction rates vary significantly with successive sulfide addition.

Cationic Cadmium Clusters

Reactant	P (10^{-9} torr)	ΔH (kcal/mol)	k_1/k_c	k_2/k_c	k_3/k_c	k_4/k_c	k_5/k_c
$[Cd(CH_3COO)]^+$		-3.759478	Not Obs				
$[Cd_2(CH_3COO)_3]^+$	4		0.77	0.0033	0.0045		
$[Cd_3(CH_3COO)_5]^+$	4		0.923	0.0722	0.0045	0.0013	
$[Cd_3(CH_3COO)_5]^+$	9		0.88	0.073	0.0062	0.0066	
$[Cd_4(CH_3COO)_7]^+$	9		0.37	0.54	0.28	0.0029	0.0016
$[Cd(NO_3)]^+$		-17.441937	Not Obs				
$[Cd(NO_3)(CH_3OH)]^+$	4		1.00				
$[Cd(NO_3)(CH_3OH)(H_2O)]^+$	4		0.61				
$[CdOH]^+$		-27.182772	Not Obs				
$[CdOH(CH_3OH)]^+$	4		0.77				
$[CdCl]^+$		-11.162765	Not Obs				
$[CdCl(CH_3OH)]^+$	4		0.16	0.0062			
$[ZnCl]^+$		-11.902944	Not Obs				
$[ZnCl(CH_3OH)]^+$	4		0.037				

$NO_3 > OH > Cl$

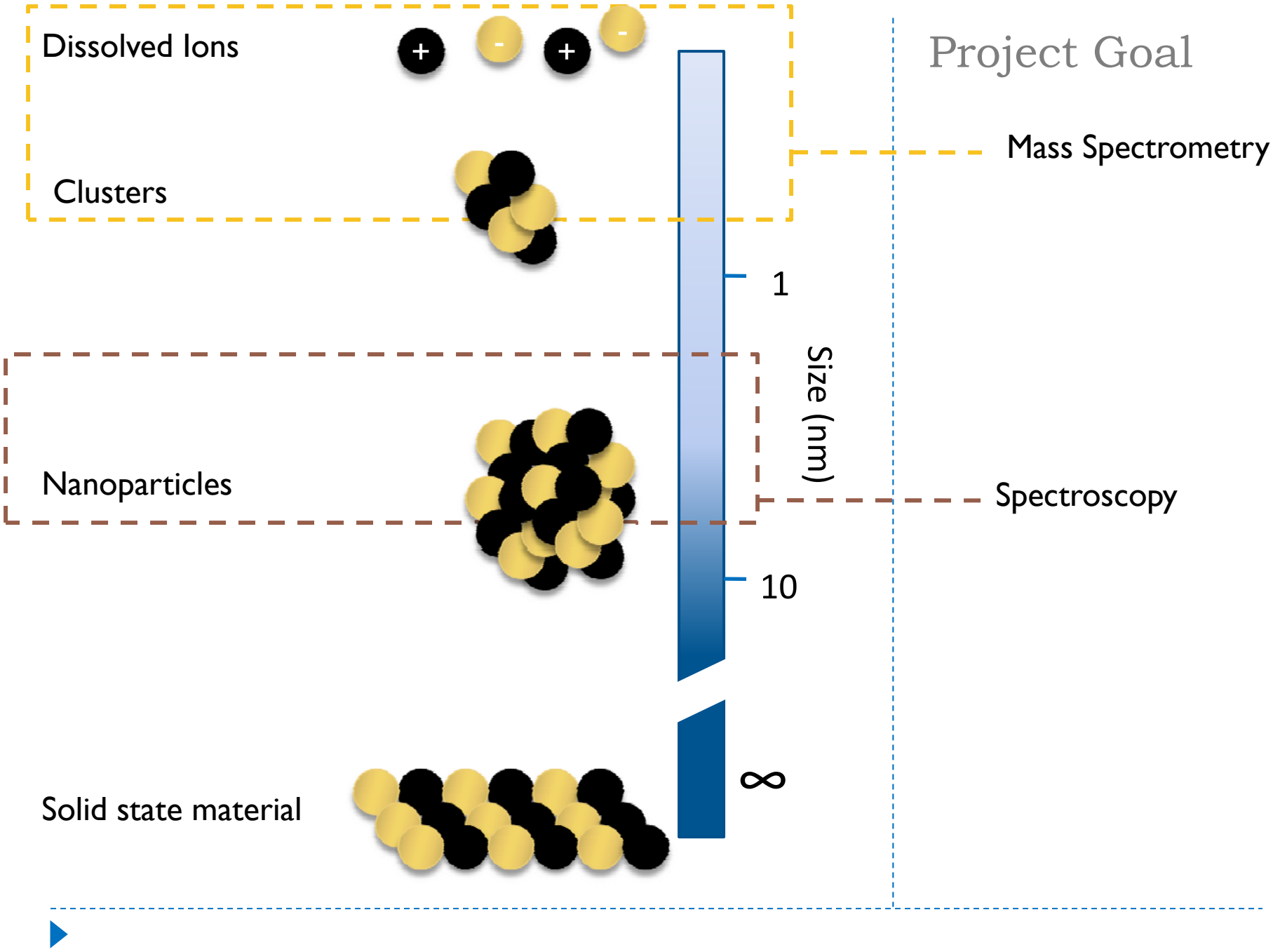
Cationic Cadmium Clusters

Reactant	P (10^{-9} torr)	ΔH (kcal/mol)	k_1/k_c	k_2/k_c	k_3/k_c	k_4/k_c	k_5/k_c
$[Cd(CH_3COO)]^+$		-3.759478	Not Obs				
$[Cd_2(CH_3COO)_3]^+$	4		0.77	0.0033	0.0045		
$[Cd_3(CH_3COO)_5]^+$	4		0.23	0.0722	0.0045	0.0013	
$[Cd_3(CH_3COO)_5]^+$	9		0.88	0.073	0.0062	0.0066	
$[Cd_4(CH_3COO)_7]^+$	9		0.37	0.54	0.28	0.0029	0.0016
$[Cd(NO_3)]^+$		-17.441937	Not Obs				
$[Cd(NO_3)(CH_3OH)]^+$	4		1.00				
$[Cd(NO_3)(CH_3OH)(H_2O)]^+$	4		0.61				
$[CdOH]^+$		-27.182772	Not Obs				
$[CdOH(CH_3OH)]^+$	4		0.77				
$[CdCl]^+$		-11.162765	Not Obs				
$[CdCl(CH_3OH)]^+$	4		0.16	0.0062			
$[ZnCl]^+$		-11.902944	Not Obs				
$[ZnCl(CH_3OH)]^+$	4		0.037				

Calculated reaction enthalpy is consistent with observed reactivity.

Conclusions

- ***ESI of salt solutions*** show variation of cluster size vs. time.
  - Data suggests that both % methanol and concentration play a role.
- ***Solution experiments*** show successive substitutions of ***mp*** for NO_3
  - Treatment with H_2S leads to replacement of $(NO_3)_2$ with SO_4 for larger clusters.
- ***Gas phase ion-molecule reactions*** between metal salt clusters and H_2S result in the formation of a variety of metal sulfide species.
  - Anionic clusters display < 5% reaction efficiency with the exception of $[Cd_4(CH_3COO)_9]^-$
  - Cationic metal clusters show higher initial reaction efficiencies which decreases significantly with successive SH^- substitution.
  - DFT calculations are consistent with gas phase reactivity (Kaitlin Papson).
- ***Similarities between gas and condensed phases*** highlighted by salt nucleation in binary solvents, spectator solvent molecules, and similarities in $[Cd_x(NO_3)_{2x+1}]^-$ reactivity.


Project Goal
Dissolved Ions
+
-
+
-
Clusters
Mass Spectrometry
1
Size (nm)
Nanoparticles
Spectroscopy
10
Solid state material
∞

The Big Picture

- ***Elucidation of initial steps*** for metal sulfide formation
- ***Gas phase ion-molecule reactions as models*** for aqueous metal sulfide reactions
- ***The Next Step:*** high pressure source-side reactions.
  - Structural characterization
  - Surface deposition

Tying it all together….

- The technique: FT-ICR MS
- Understanding environmental chemical processes
  - Atmospheric: Biomolecules
  - Aquatic: Inorganic clusters
- Analytical Chemistry
  - Mass Spectrometry

Acknowledgements

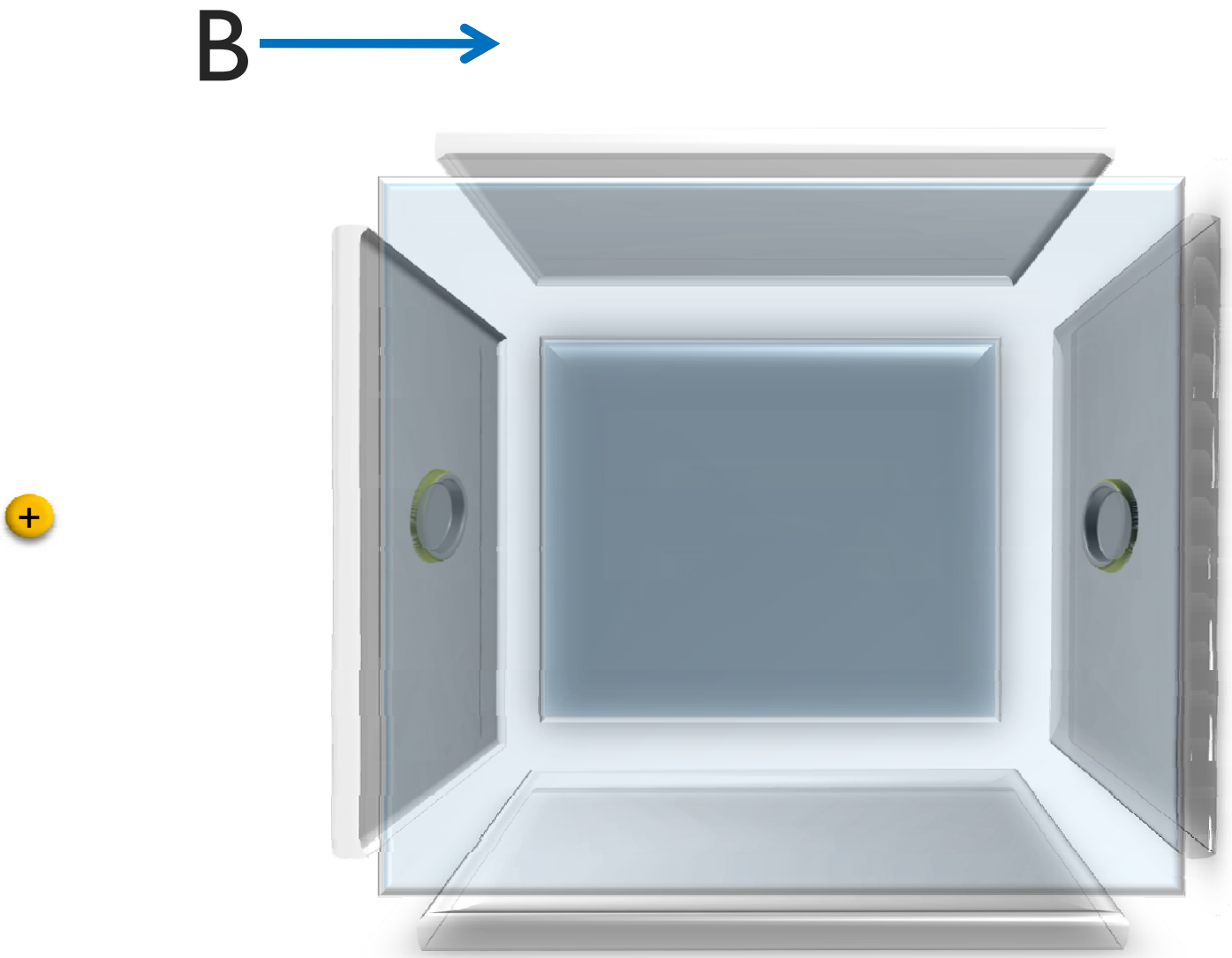
- Dr. Ridge
- Our Research Group
  - Kaitlin Papson
  - Nick Zeringo
  - Una Kim
  - Scott Robinson
- Collaborators
  - George Luther
    - Kate Mullaugh
  - Murray Johnston
    - Julie Lloyd
  - Julia Laskin (PNNL)
- Funding
  - UD GK-12
  - NSF
  - Delaware EPSCoR
  - UD IGERT

Environmental Perspective

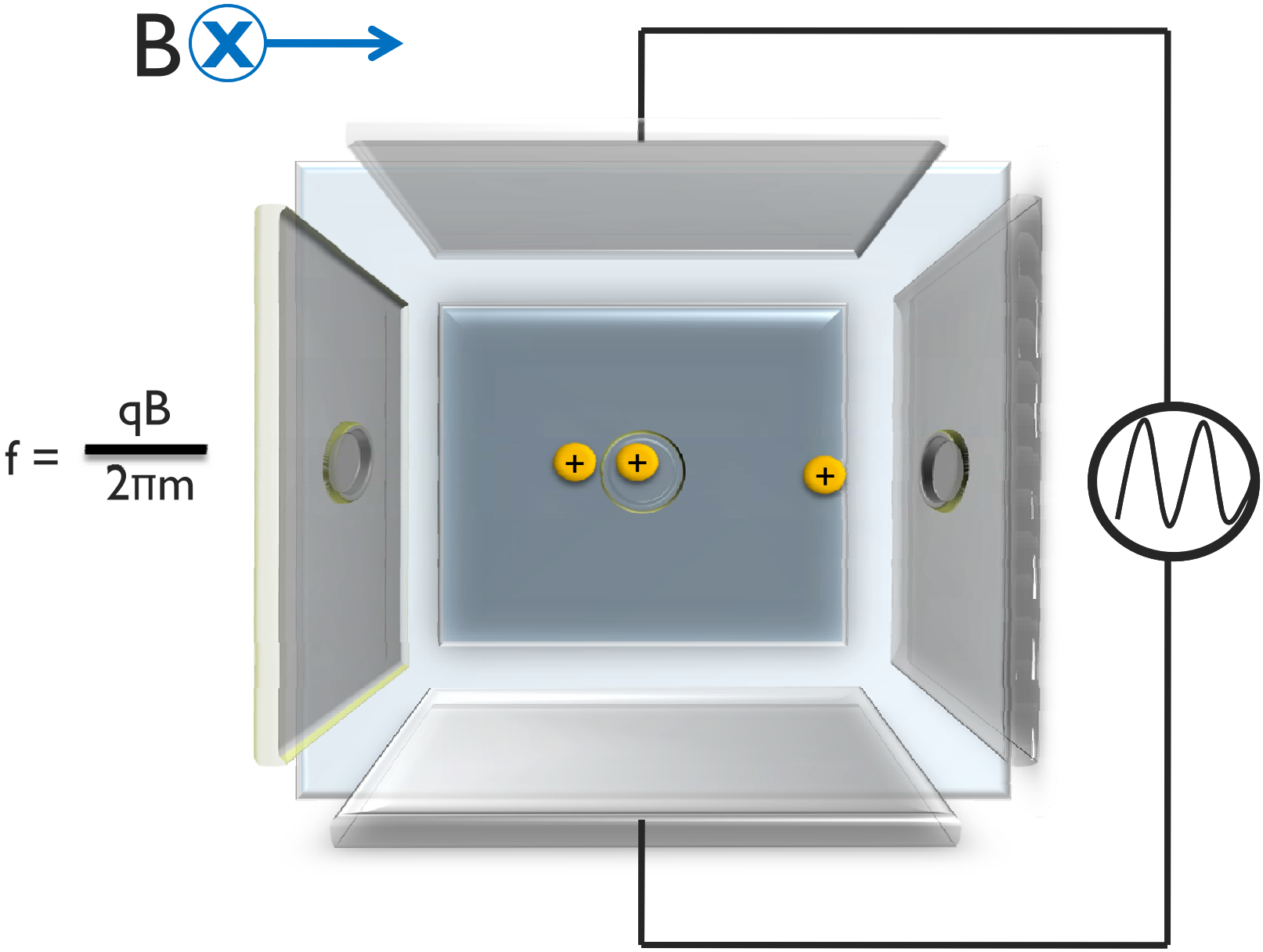
- Evidence of Salt Nucleation at Hydrothermal Sites
  - Salt deposits†
  - gyser-like brine discharges†
  - 'salt diapirs‡' (*dī · ə · pîr*)
    - Buoyant/Mobile salt layer piercing the brittle overlying rock

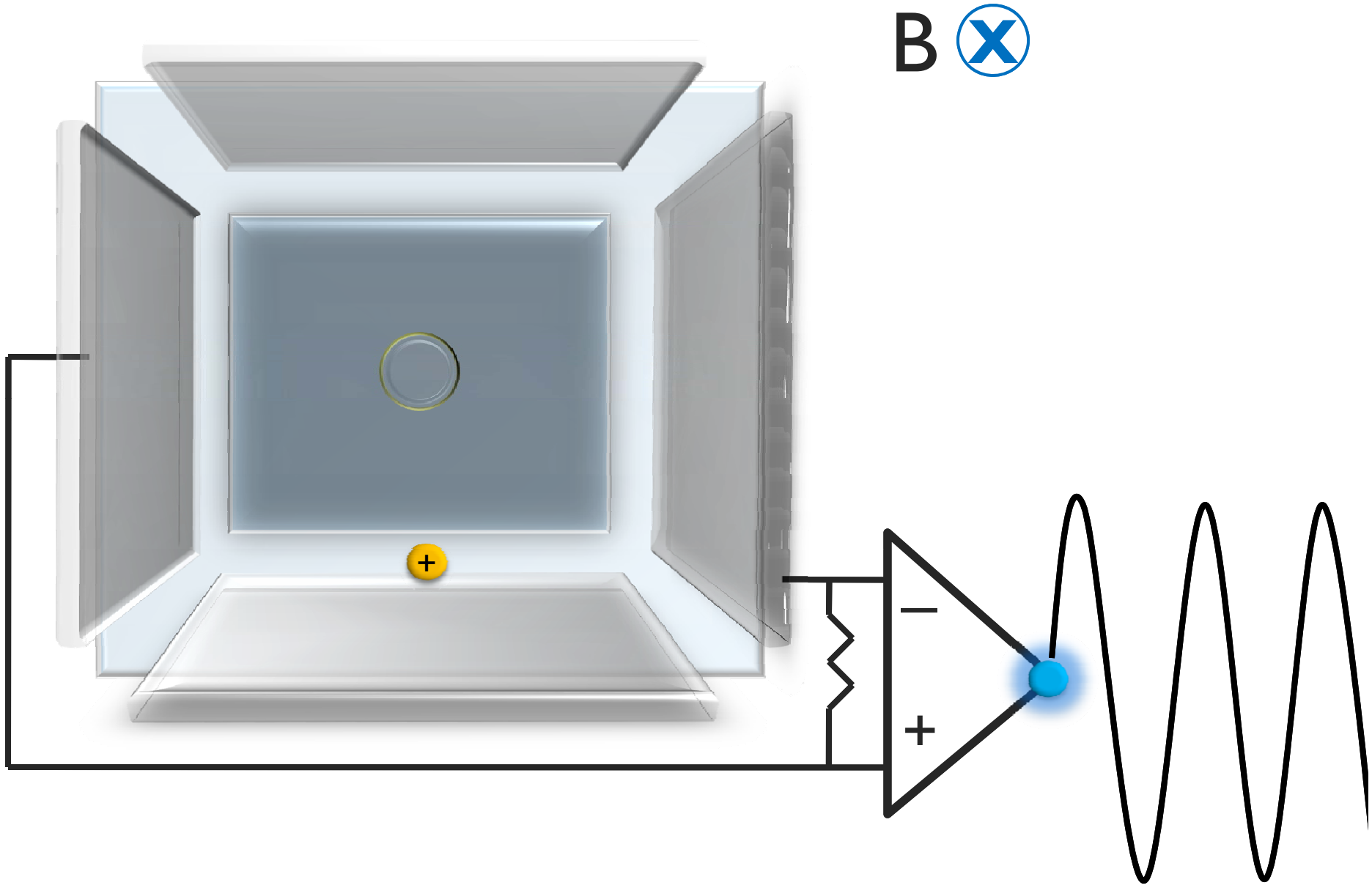
†Hovland, M.; Rueslatten, H. G.; Johnsen, H. K.; Kvamme, B.; Kuznetsova, T. Salt Formation Associated with Sub-Surface Boiling and Supercritical Water. *Mar. Pet. Geol.* **2006**, *23*, 855-869.

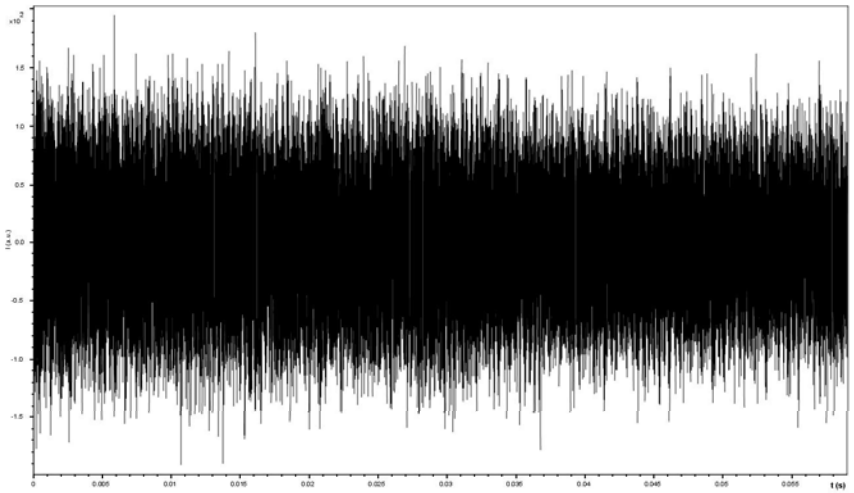
‡Hovland, M.; Fichler, C.; Rueslatten, H.; Johnsen, H. K. Deep-Rooted Piercement Structures in Deep Sedimentary Basins - Manifestations of Supercritical Water Generation at Depth? *J. Geochem. Explor.* **2006**, *89*, 157-160.



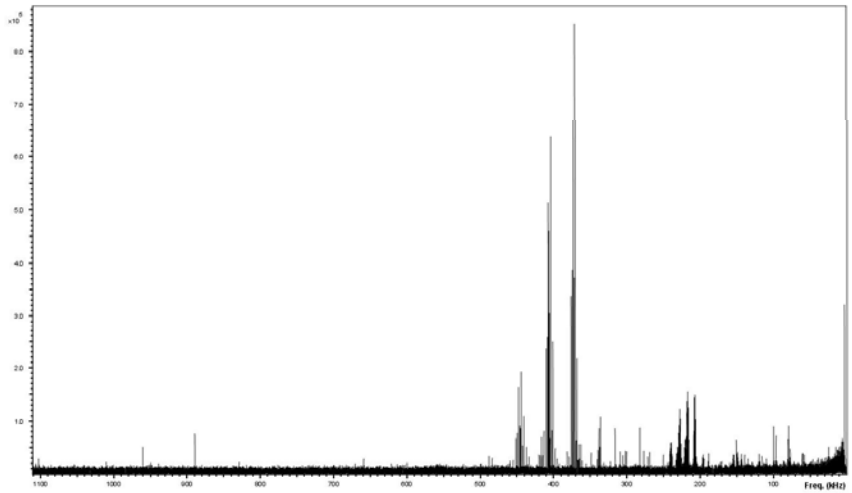
FT-ICR MS

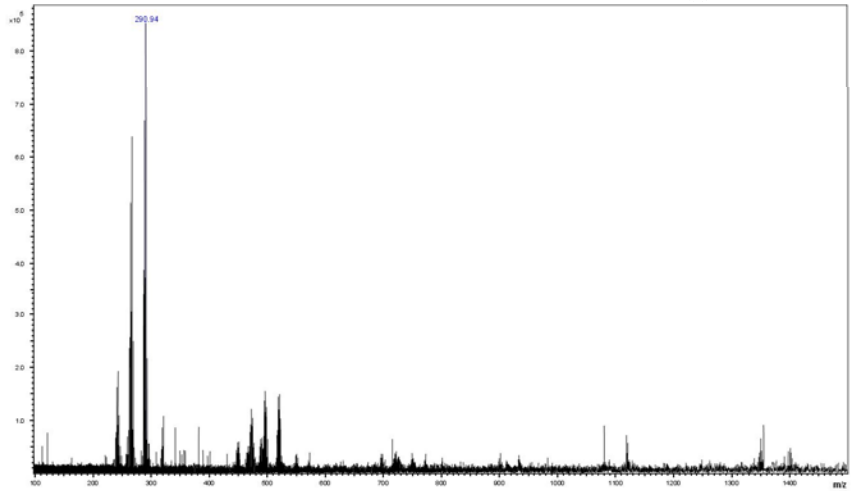

B
f = qB / 2πm


B
+
−
+



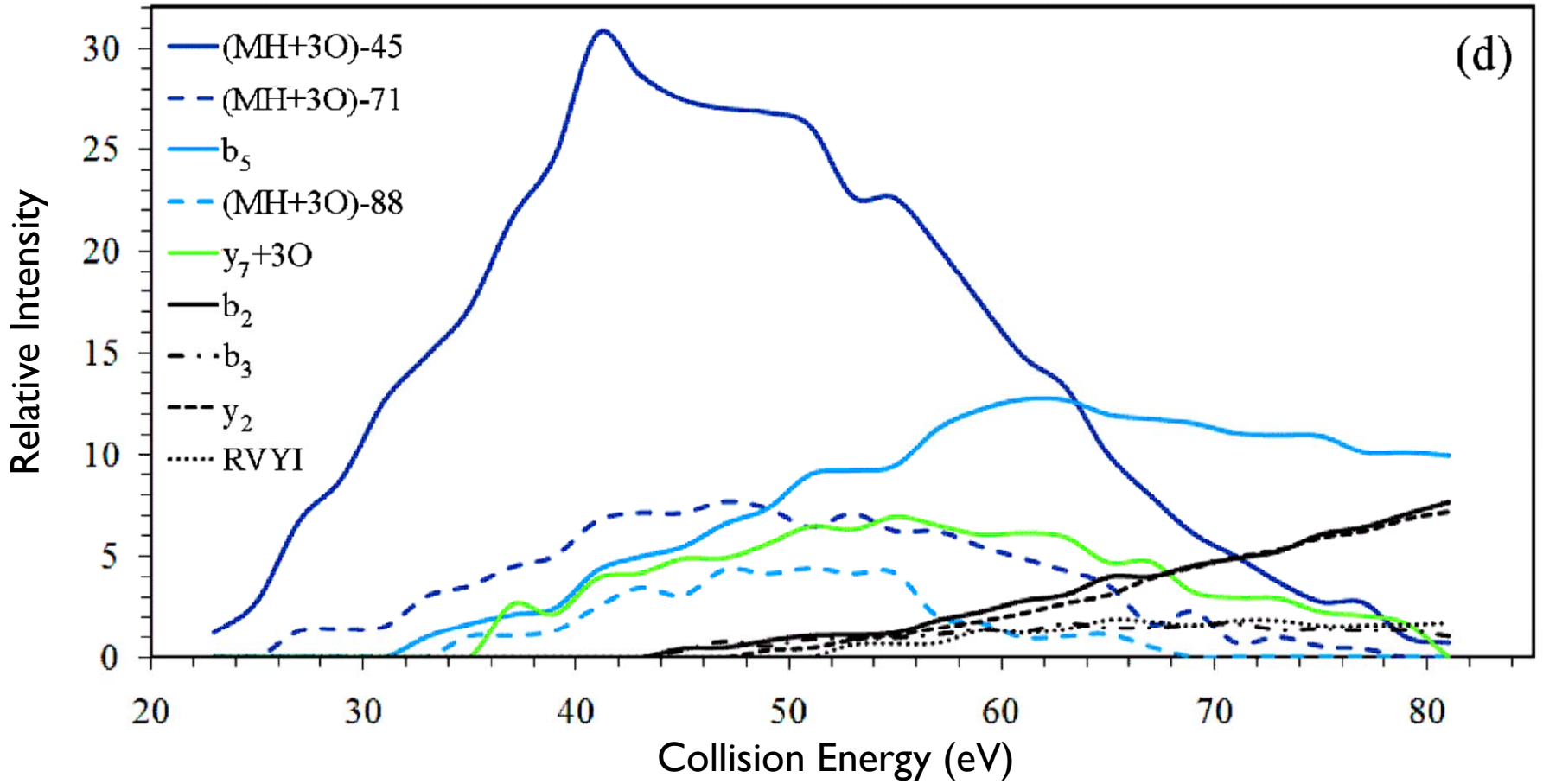
Fourier Transform



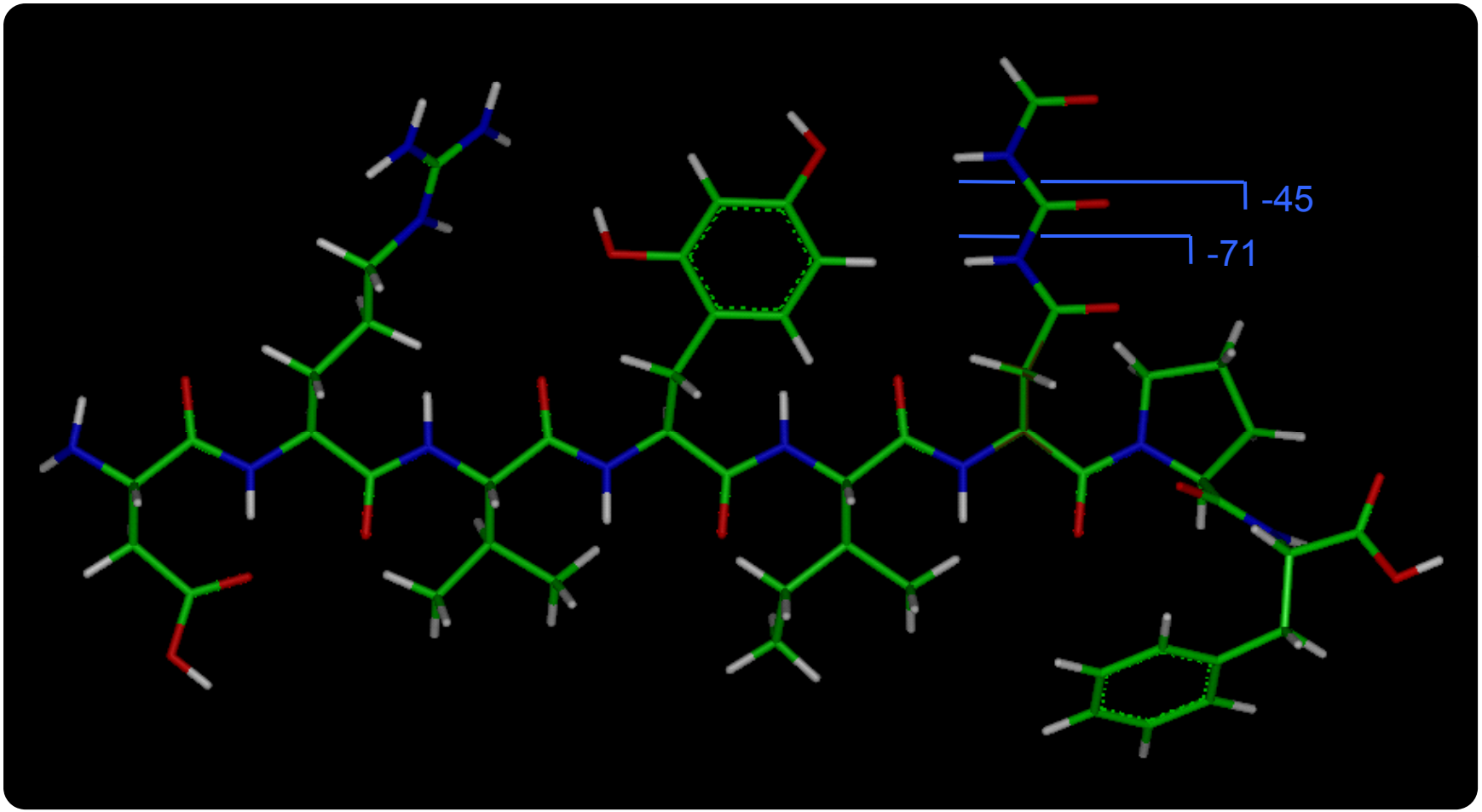


$$f = \frac{qB}{2\pi m}$$

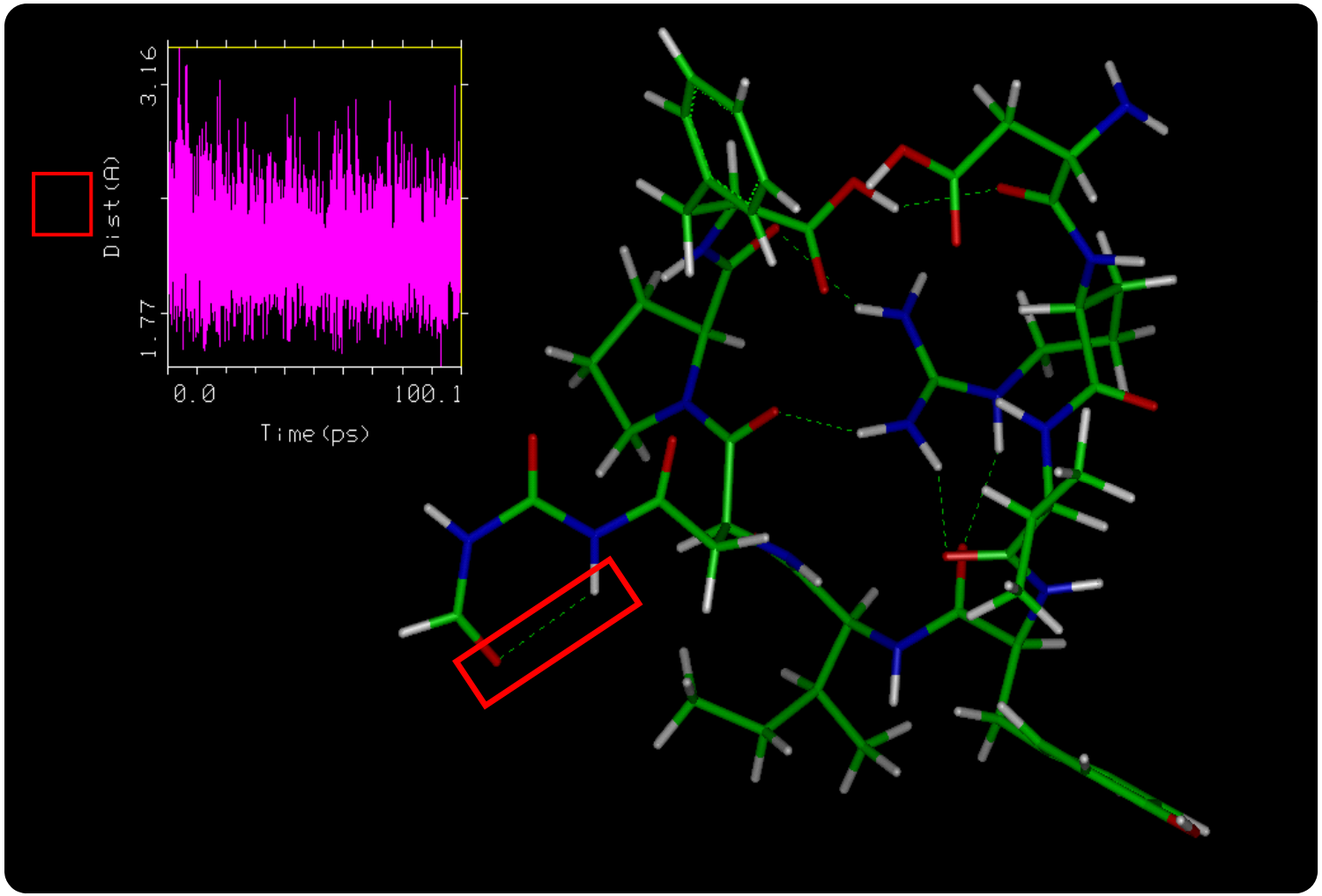
Energy Resolved FECs: AngII+3O



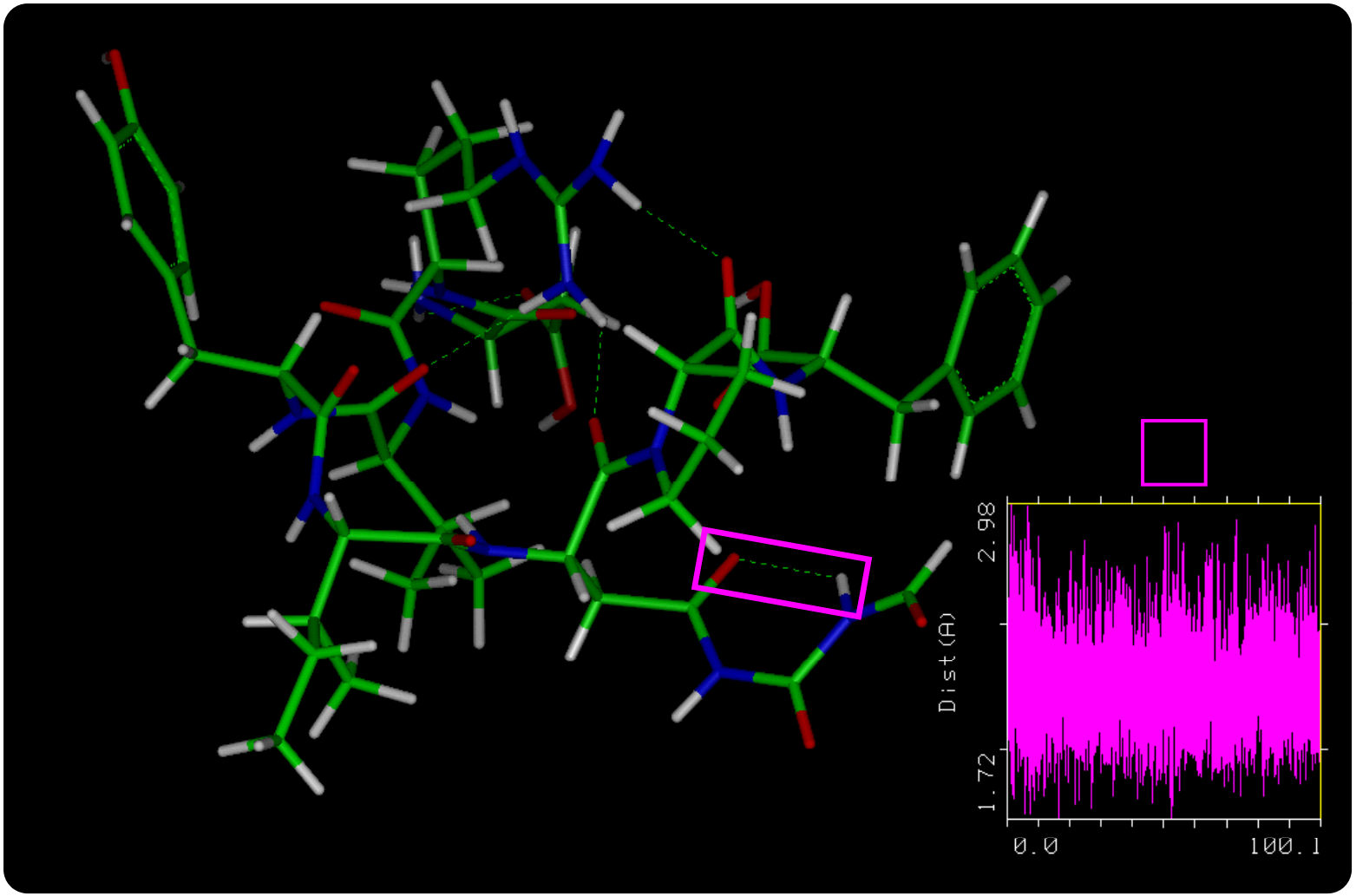
Asp-Arg-Val-*Tyr(+O)*-Ile-*His(+3O)*-Pro-Phe



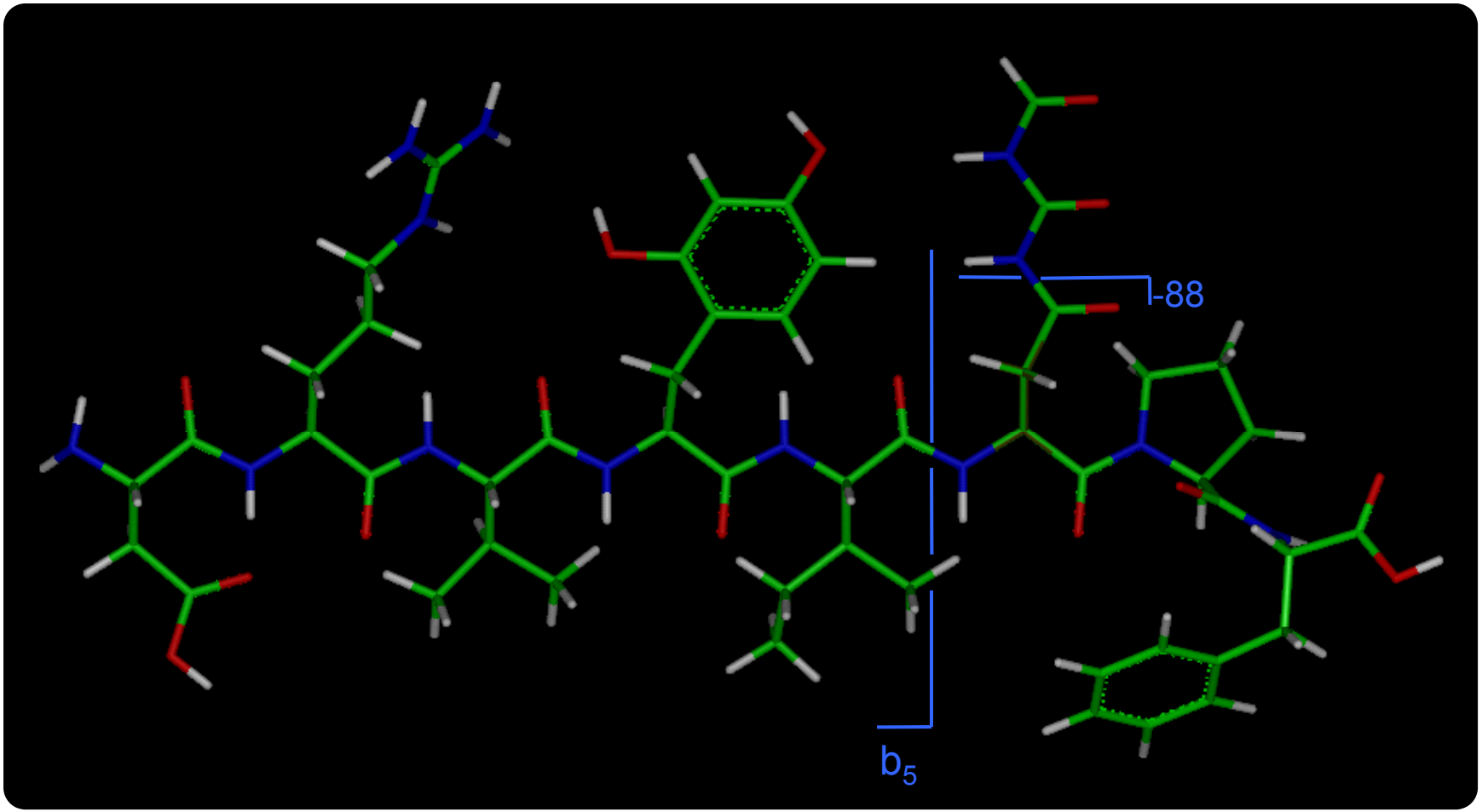
[AngII+3O]-45



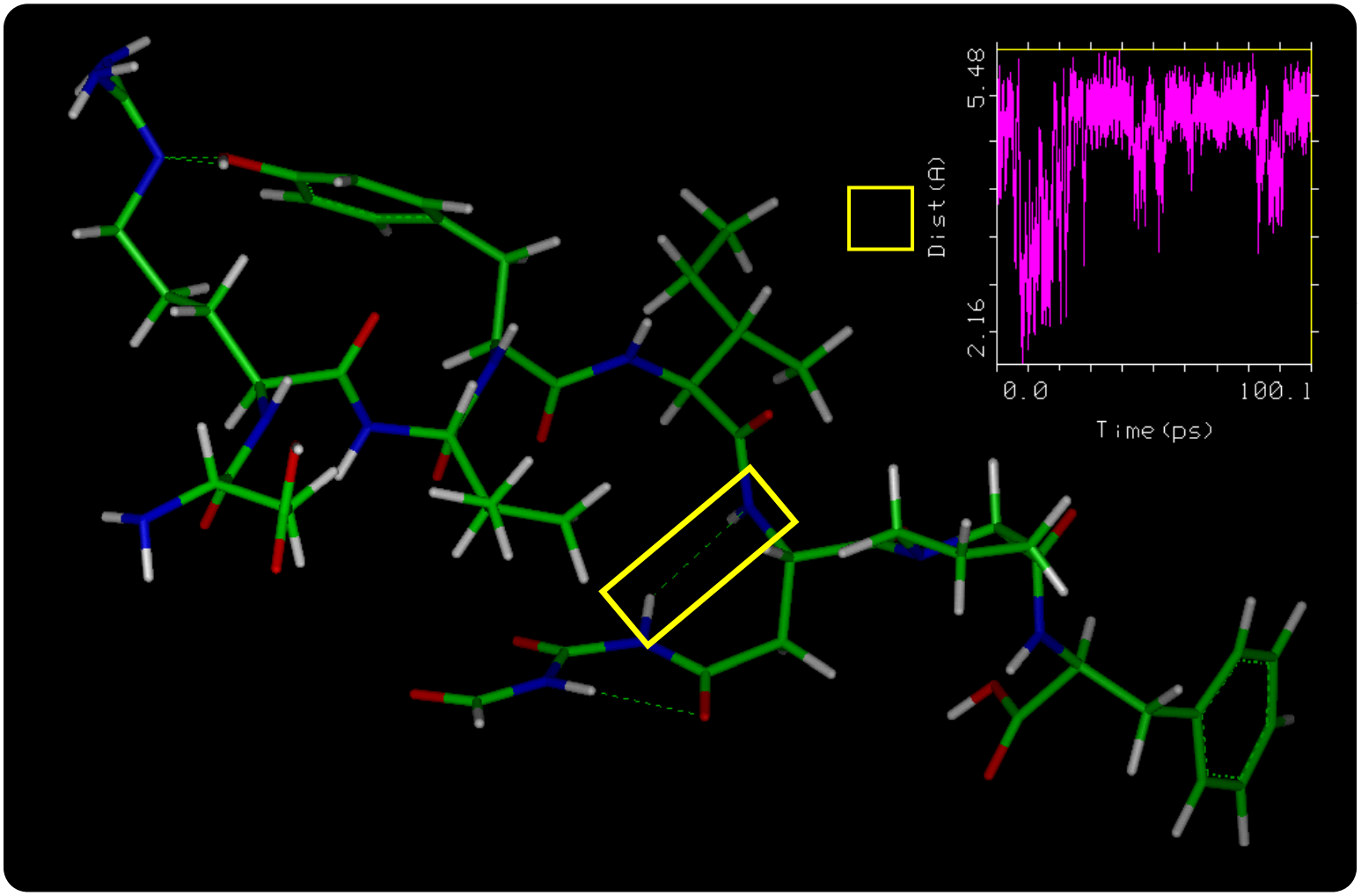
[AngII+3O]-71



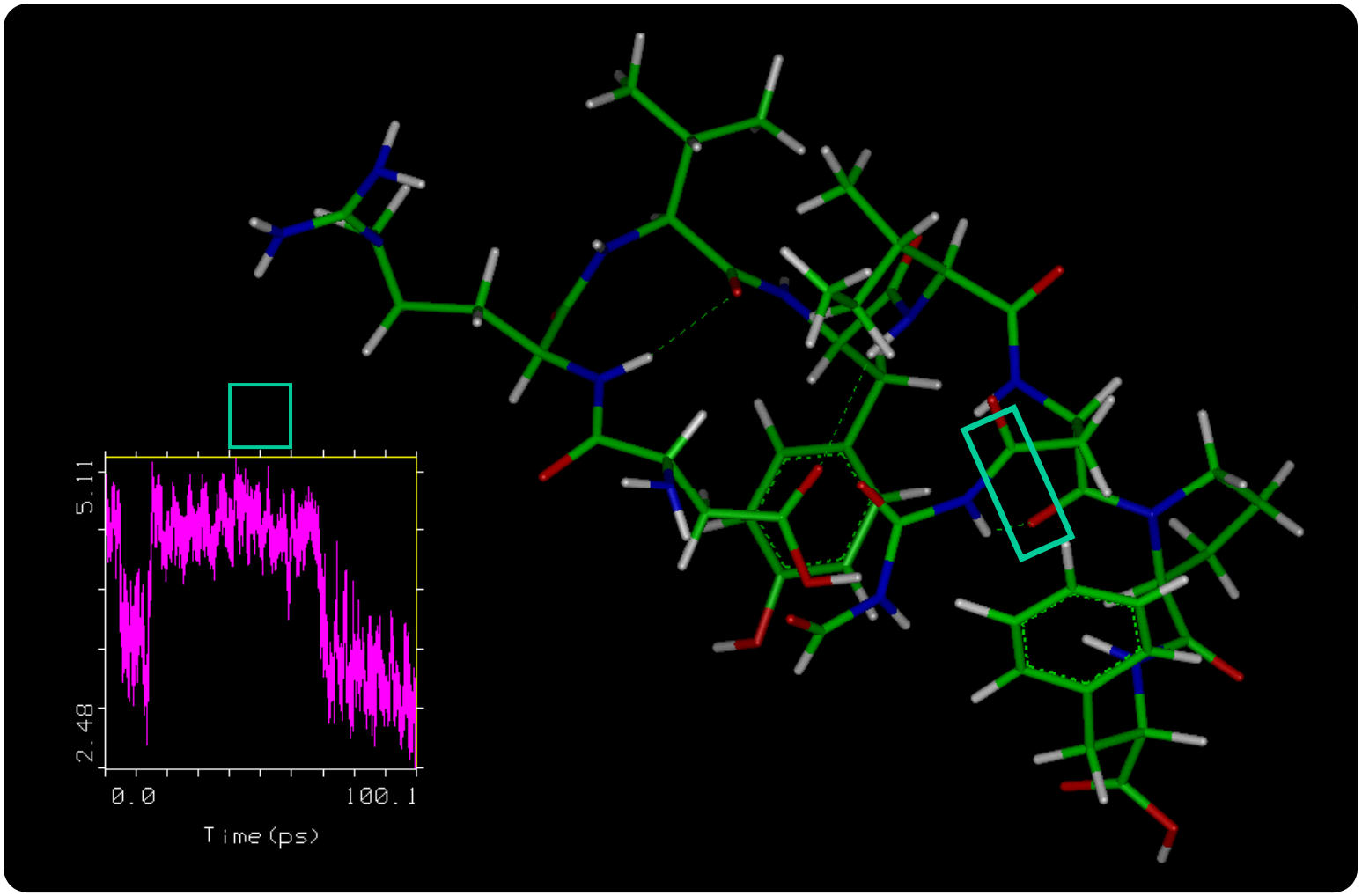
Asp-Arg-Val-*Tyr(+O)*-Ile-*His(+3O)*-Pro-Phe



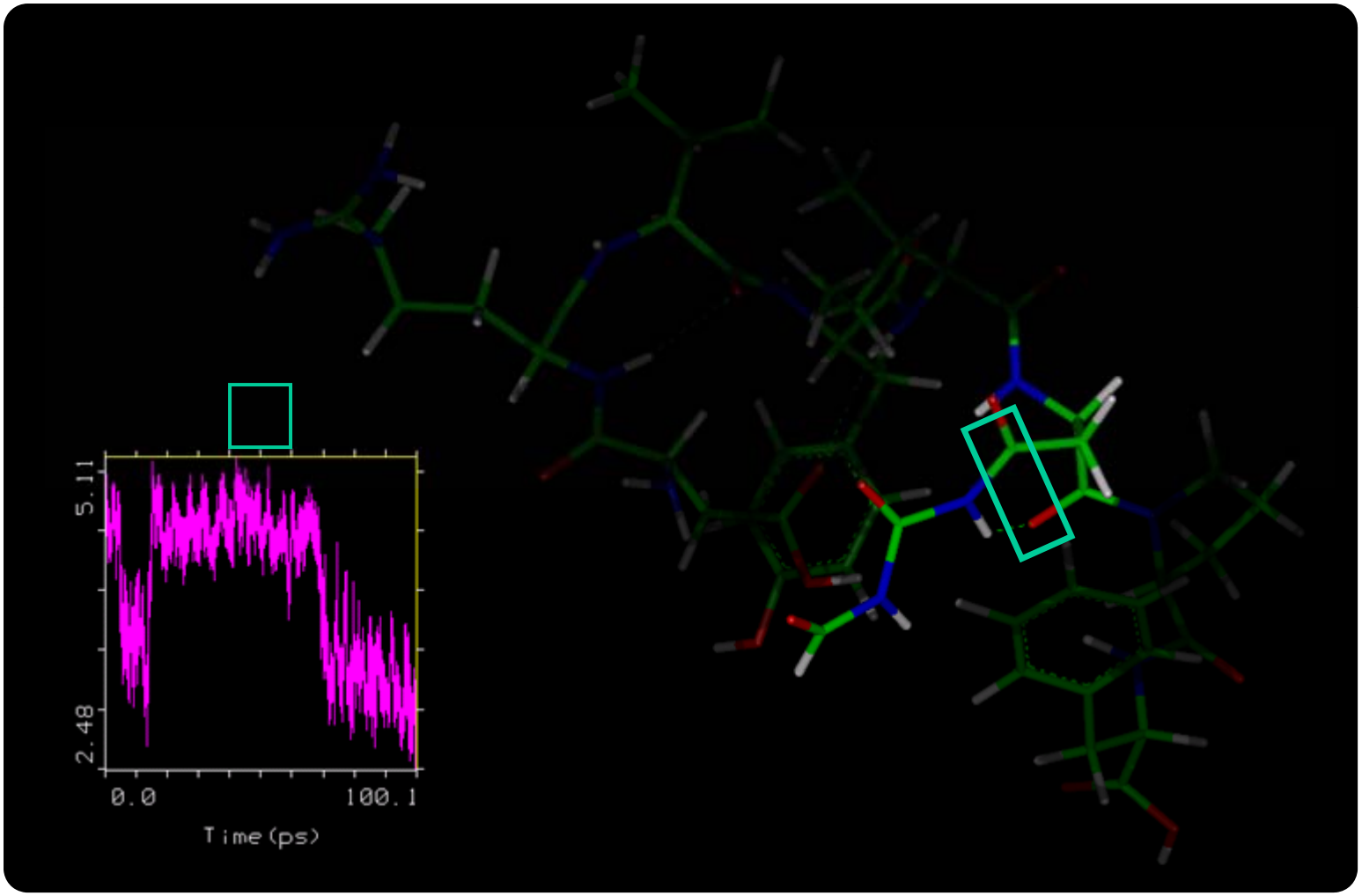
AngII+3O: b_5 fragment



$[AngII+3O]^{+}$-88 fragment



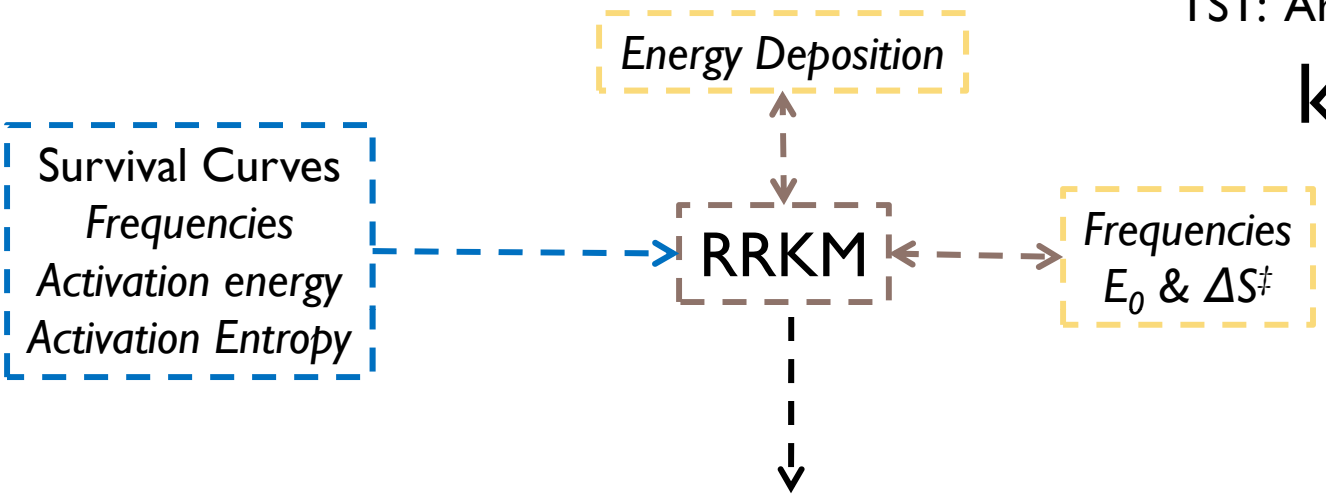
[AngII+3O]$^{+}$-88 fragment



RRKM Modeling: Dr. Julia Laskin

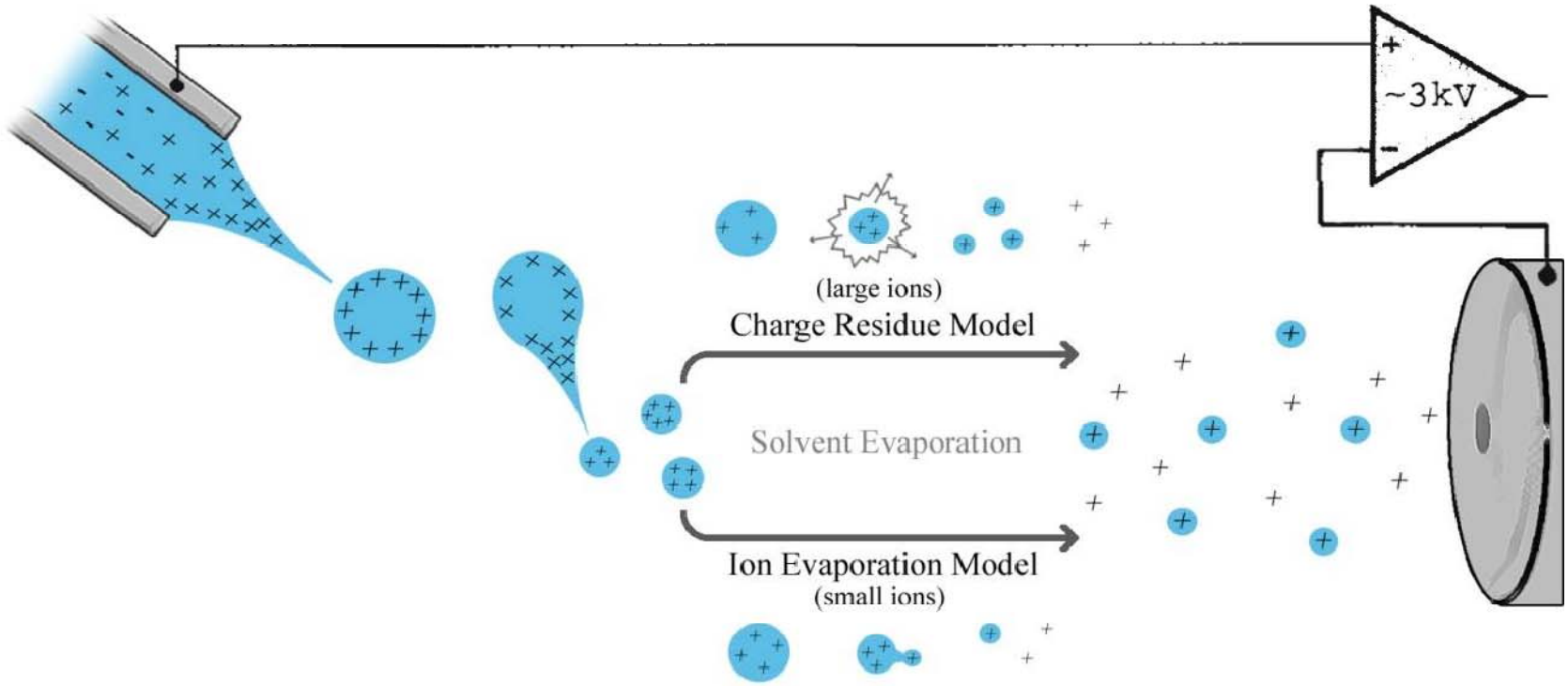
TST: Arrhenius Equation

$$k = Ae^{-E/RT}$$



$[MH+nO]^+$	*DRVYIHPF*	*DRVY*IHPF*	*DRVYIH*PF*	*DRVY*IH*PF*
M/Z	1046	1062	1110	1126
E_0(eV)	1.14	1.20	1.21	1.24
$\Delta S^{\ddagger}$(cal/mol K)	-25.9	-21.6	-17.0	-15.3
Relative E_0	0	0.06	0.07	0.11
A, s^{-1}	5.6×10^7	4.8×10^8	4.8×10^9	1.2×10^{10}
Log (A)	7.7	8.7	9.7	10.1

Electrospray Mechanism

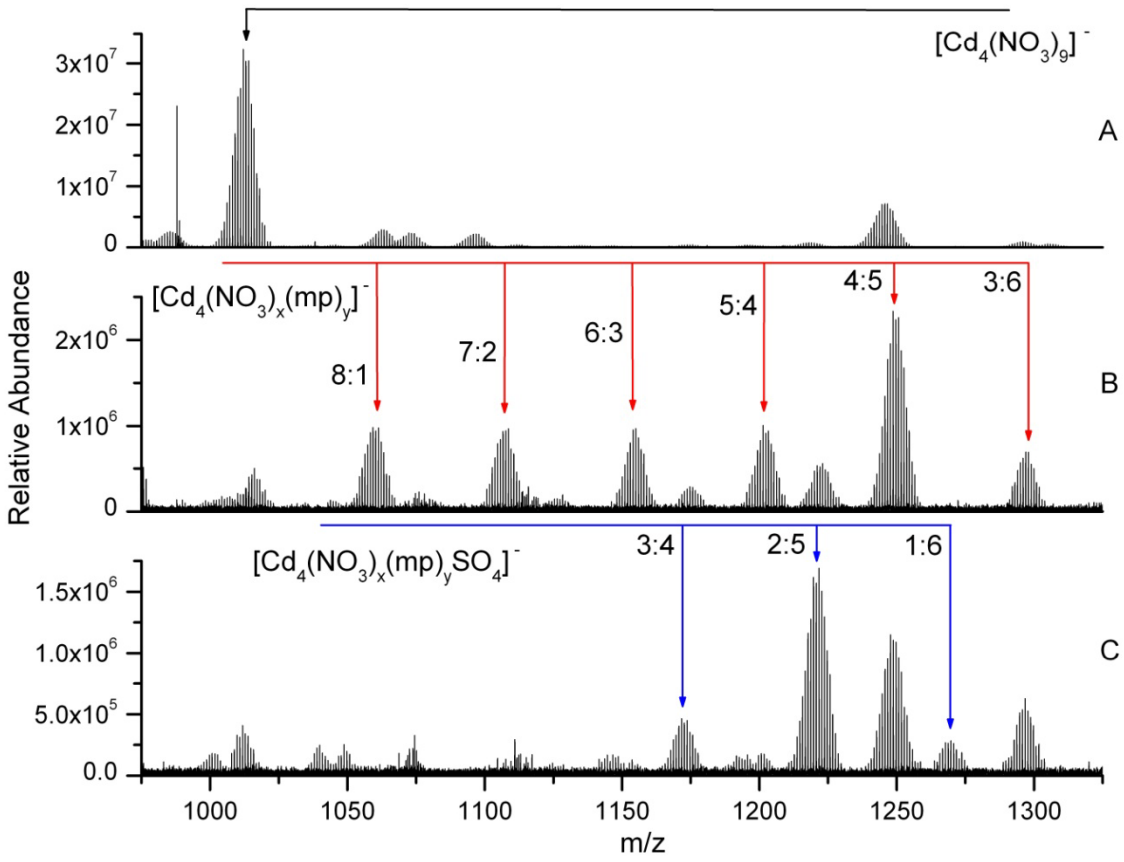


Solution Chemistry: Tetranuclear Anions

A) 3 mM aqueous solution of $Cd(NO_3)_2 \cdot 4H_2O$ diluted 50/50 with MeOH.

B) 1.5 mM aqueous solution of $Cd(NO_3)_2 \cdot 4H_2O$ and 2-mercaptopyridine (1:1) diluted 50/50 with MeOH.

C) H_2S(g) bubbled through a 3 mM aqueous solution of $Cd(NO_3)_2 \cdot 4H_2O$ followed by addition of 2-mercaptopyridine (1:1), then diluted 50/50 with MeOH.

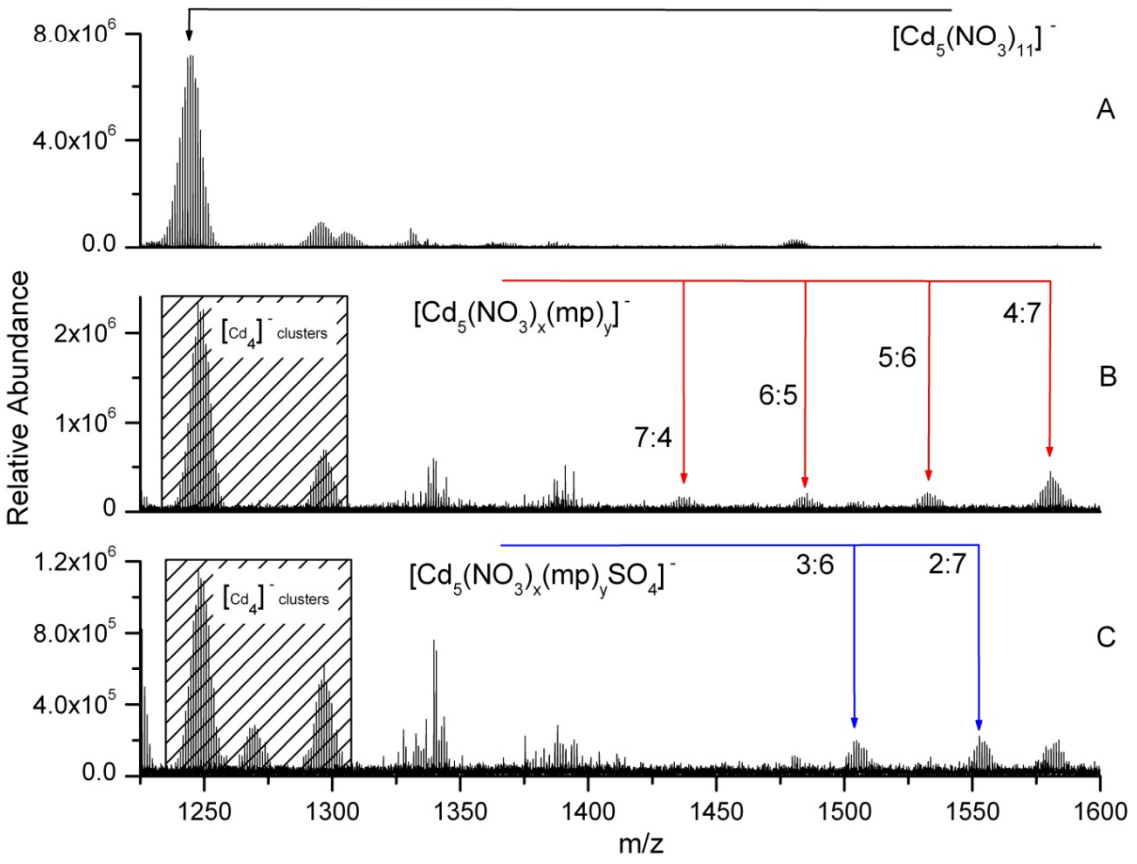


Solution Chemistry: Pentanuclear Anions

A) 3 mM aqueous solution of $Cd(NO_3)_2 \cdot 4H_2O$ diluted 50/50 with MeOH.

B) 1.5 mM aqueous solution of $Cd(NO_3)_2 \cdot 4H_2O$ and 2-mercaptopyridine (1:1) diluted 50/50 with MeOH.

C) $H_2S(g)$ bubbled through a 3 mM aqueous solution of $Cd(NO_3)_2 \cdot 4H_2O$ followed by addition of 2-mercaptopyridine (1:1), then diluted 50/50 with MeOH.



Bimolecular Rate Constants

- Determine $[H_2S]$
  - Assume fasted measured *k* is collision rate limited.
  - Capture Collision Theory

$[Cd(NO_3)(CH_3OH)]^+$

$k_1 = 2.85 \pm 0.27\ s^{-1}$

4×10^{-9} Torr

$$\frac{k}{k_L} = 0.9754 + \frac{\left(\tau/\sqrt{2} + 0.509\right)^2}{10.526} \qquad 0 < \tau < 2\sqrt{2}$$

$$\tau = 85.11\mu_D' \left(\frac{1}{\alpha' T}\right)^{1/2}$$

μ_D' dipole moment (0.97 D)

α' volume polarizability (3.67 Å^3)

$\tau = 2.49$ $\qquad \frac{k}{k_L} = 1.464$

$$k_L = 2.342Z\left(\frac{\alpha'}{\mu'}\right)^{1/2} 10^{-9}\ cm^3 molecule^{-1} s^{-1}$$

μ' reduced mass (29.193 Da)

$k_L = 8.304 \times 10^{-10}\ cm^3 molecule^{-1} s^{-1}$

$k = 1.216 \times 10^{-9}\ cm^3 molecule^{-1} s^{-1}$

Theoretical collision rate

Bimolecular Rate Constants

- Determine $[H_2S]$
  - Assume fasted measured *k* is collision rate limited.
  - Capture Collision Theory

$[Cd(NO_3)(CH_3OH)]^+$

$k_1 = 2.85 \pm 0.27\ s^{-1}$

4×10^{-9} Torr

$k = 1.216 \times 10^{-9}\ cm^3 molecule^{-1} s^{-1}$

Theoretical collision rate

$$k_1^2 = 1.216 \times 10^{-9}\ cm^3 molecule^{-1} s^{-1} = \frac{k_1^1}{[H_2S]}$$

$[H_2S] = 2.34 \times 10^9$ molecules cm^{-3}

$[H_2S] = 6.62 \times 10^{-8}$ Torr

Slowest reaction observed $\longrightarrow$ $k_3^1 = 0.0024 \pm 0.0007 s^{-1}$

$k_1^2 = 1.21 \pm 0.12 \times 10^{-9}\ cm^3 molecule^{-1} s^{-1}$ ——— $k_3^2 = 1.03 \pm 0.31 \times 10^{-12}\ cm^3 molecule^{-1} s^{-1}$

Fastest Slowest

Reaction Efficiency

$$\frac{k}{k_c} = \frac{k_x^1}{2.85 s^{-1}} \left(\frac{\mu_x}{29.19 Da} \right)^{\frac{1}{2}} \left(\frac{4 \times 10^{-9} Torr}{P_x} \right)$$

$[Cd(NO_3)(CH_3OH)]^+$

$k_1^1 = 2.85 \pm 0.27 s^{-1}$

$k_1^2 = 1.21 \pm 0.12 \times 10^{-9} cm^3 molecule^{-1} s^{-1}$

$\frac{k}{k_c} = 1.0$

$k_1^1 = 2.85 \pm 0.27 s^{-1}$ ——— $k_3^1 = 0.0024 \pm 0.0003 s^{-1}$

$k_1^2 = 1.21 \pm 0.12 \times 10^{-9} cm^3 molecule^{-1} s^{-1}$ ——— $k_3^2 = 1.03 \pm 0.13 \times 10^{-12} cm^3 molecule^{-1} s^{-1}$

$\frac{k}{k_c} = 1.0 \pm 0.1$ ——— $\frac{k}{k_c} = 0.000896 \pm 0.0001$

Fastest

Slowest