

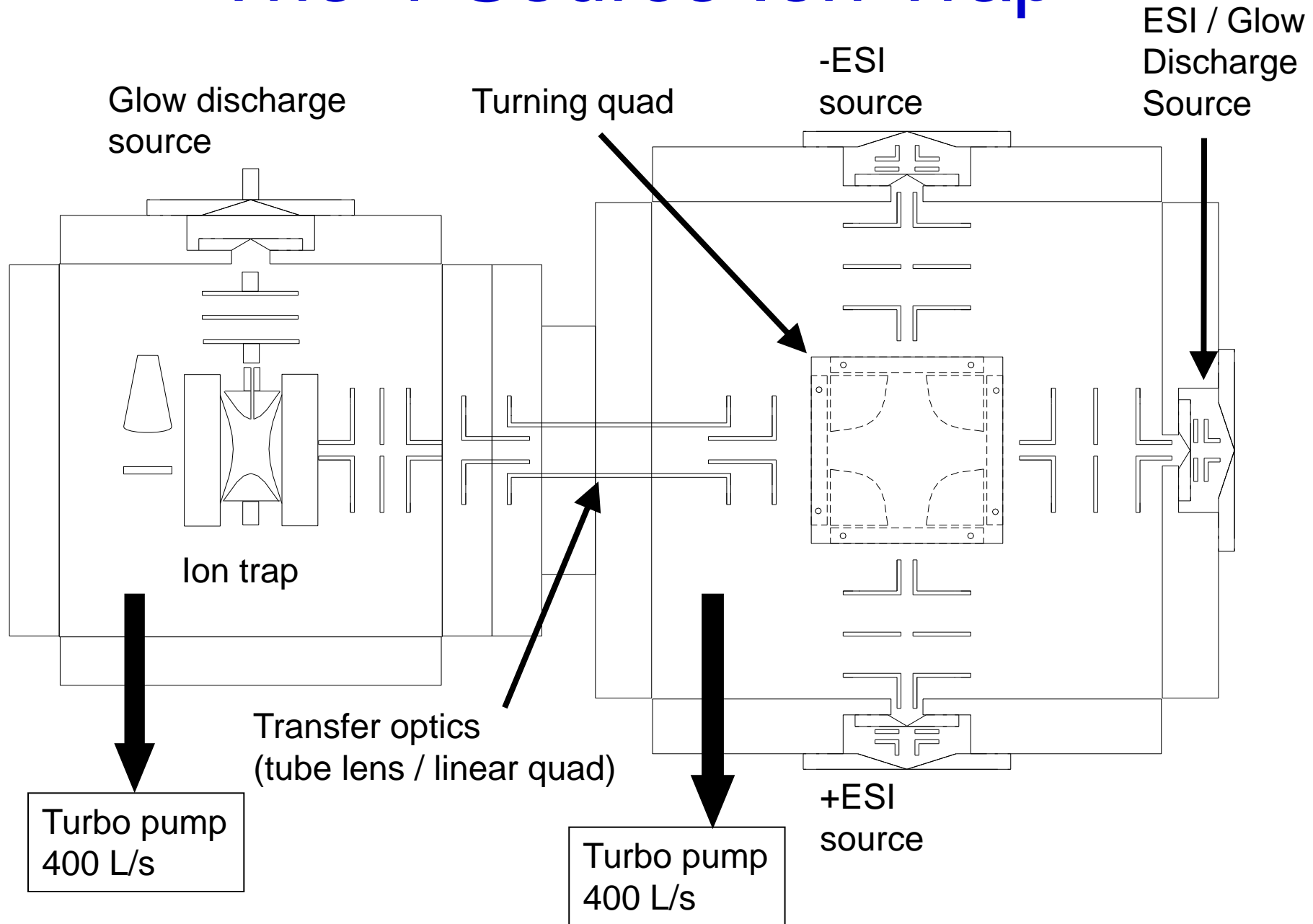
Introduction

- ☯ Our research program is devoted to the study of **gaseous macro-ions** applied within the context of **mass spectrometry** to challenging analysis problems.
- ☯ Our work involves **instrument development**, **ion chemistry studies**, and **applications** to analytical problems. This poster summarizes our recent activities in these areas.

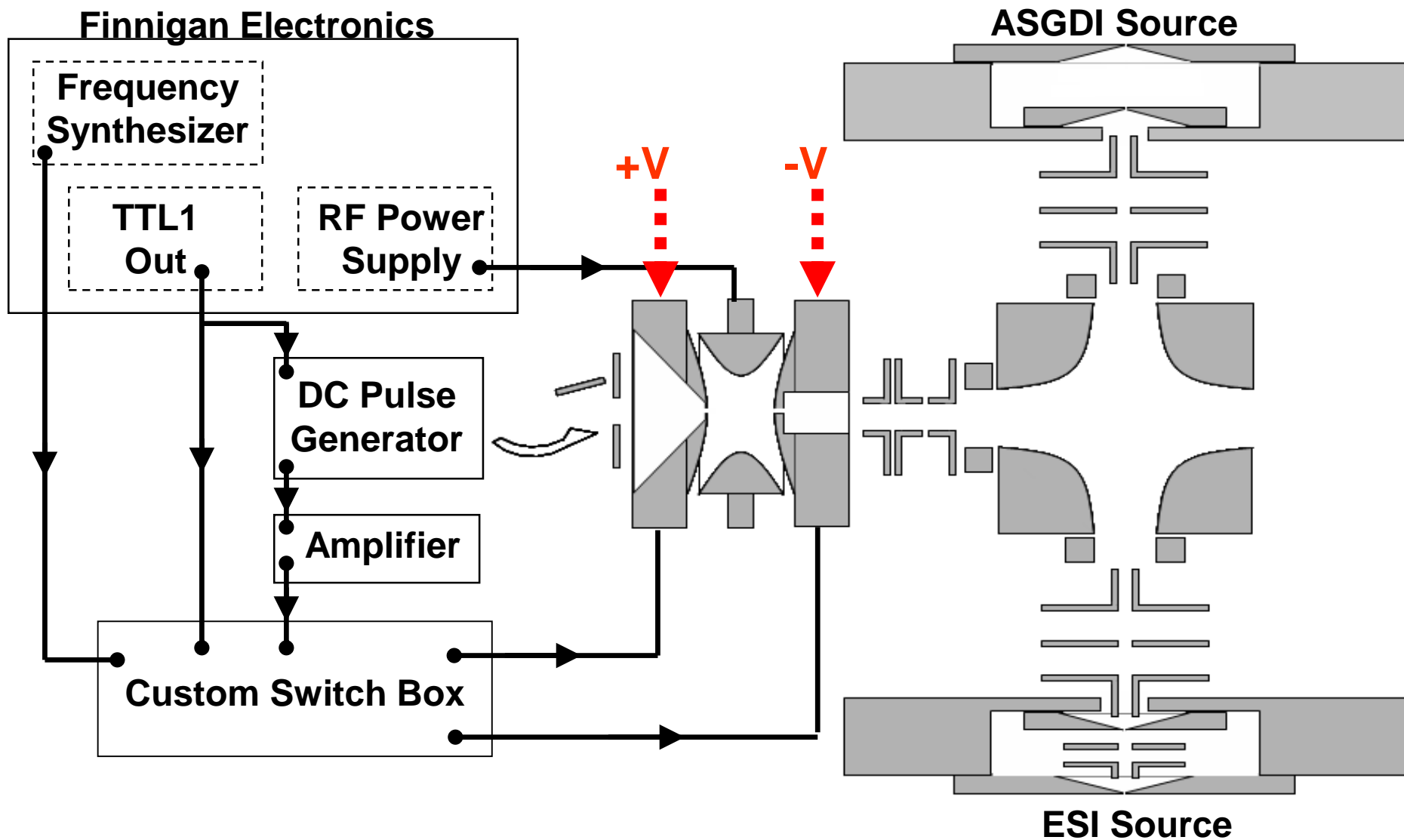
Instrumentation

- ☯ Finnigan (ITMS™) dual source ion trap mass spectrometer
- ☯ Finnigan (ITMS™) 4-source ion trap mass spectrometer
- ☯ Modified Q STAR quadrupole time-of-flight mass spectrometer
- ☯ Two modified Q TRAP linear ion trap mass spectrometers
- ☯ Multi-Source linear ion trap
- ☯ Cold-ion spectroscopy tandem mass spectrometer

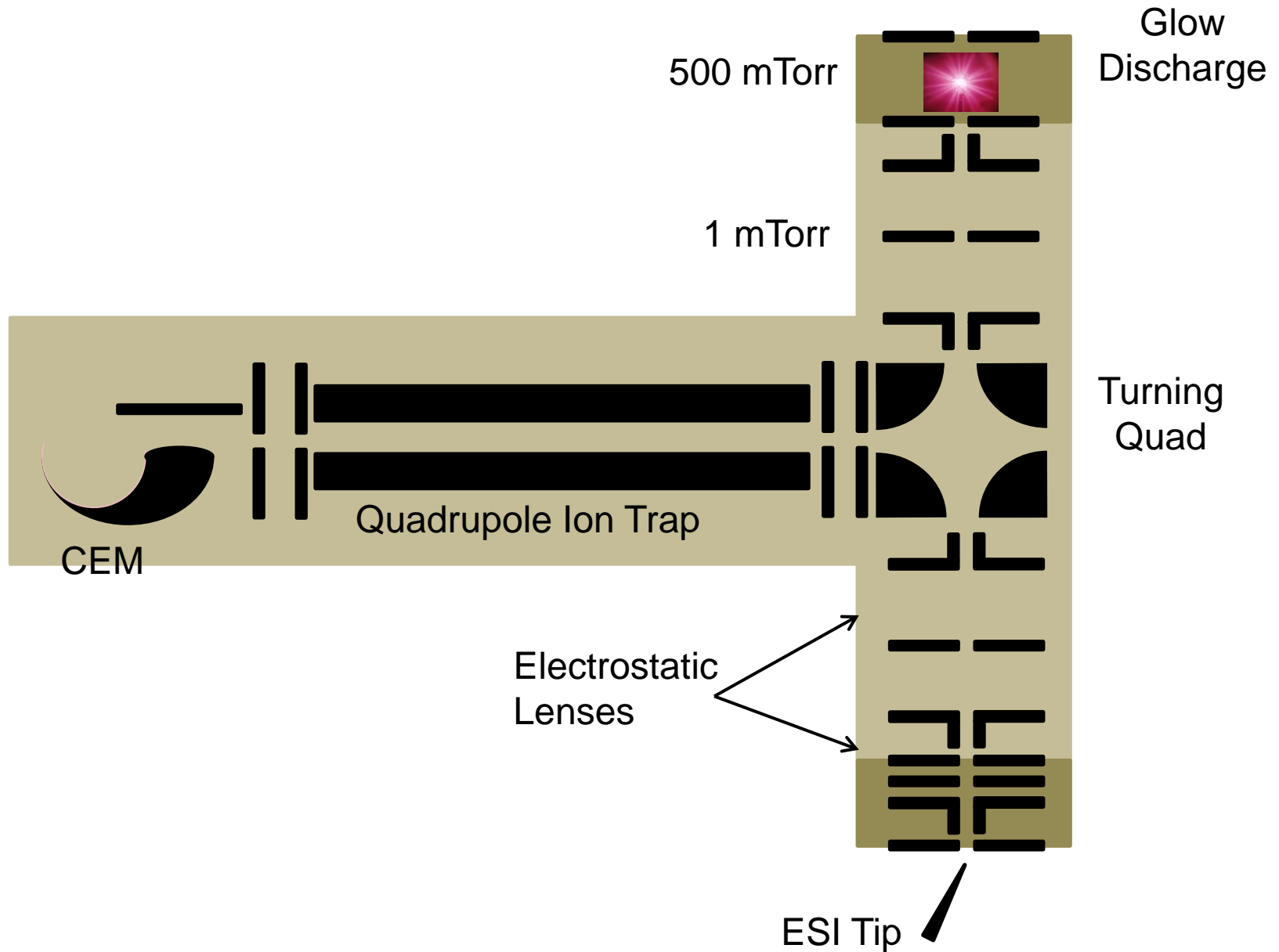
The 4-Source Ion Trap



Modified Dueling Source 3D Ion Trap

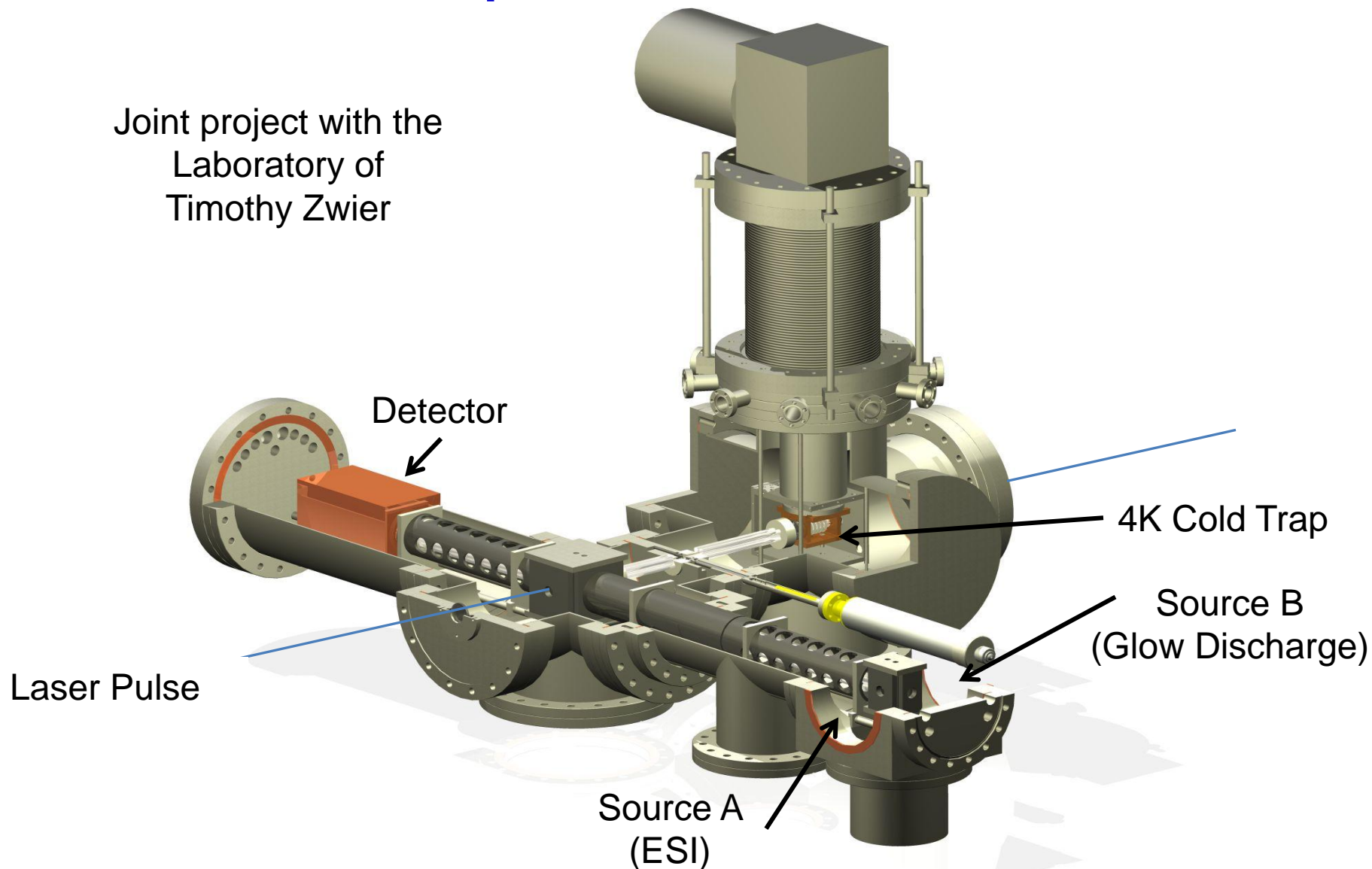


Multi-Source Linear Ion Trap

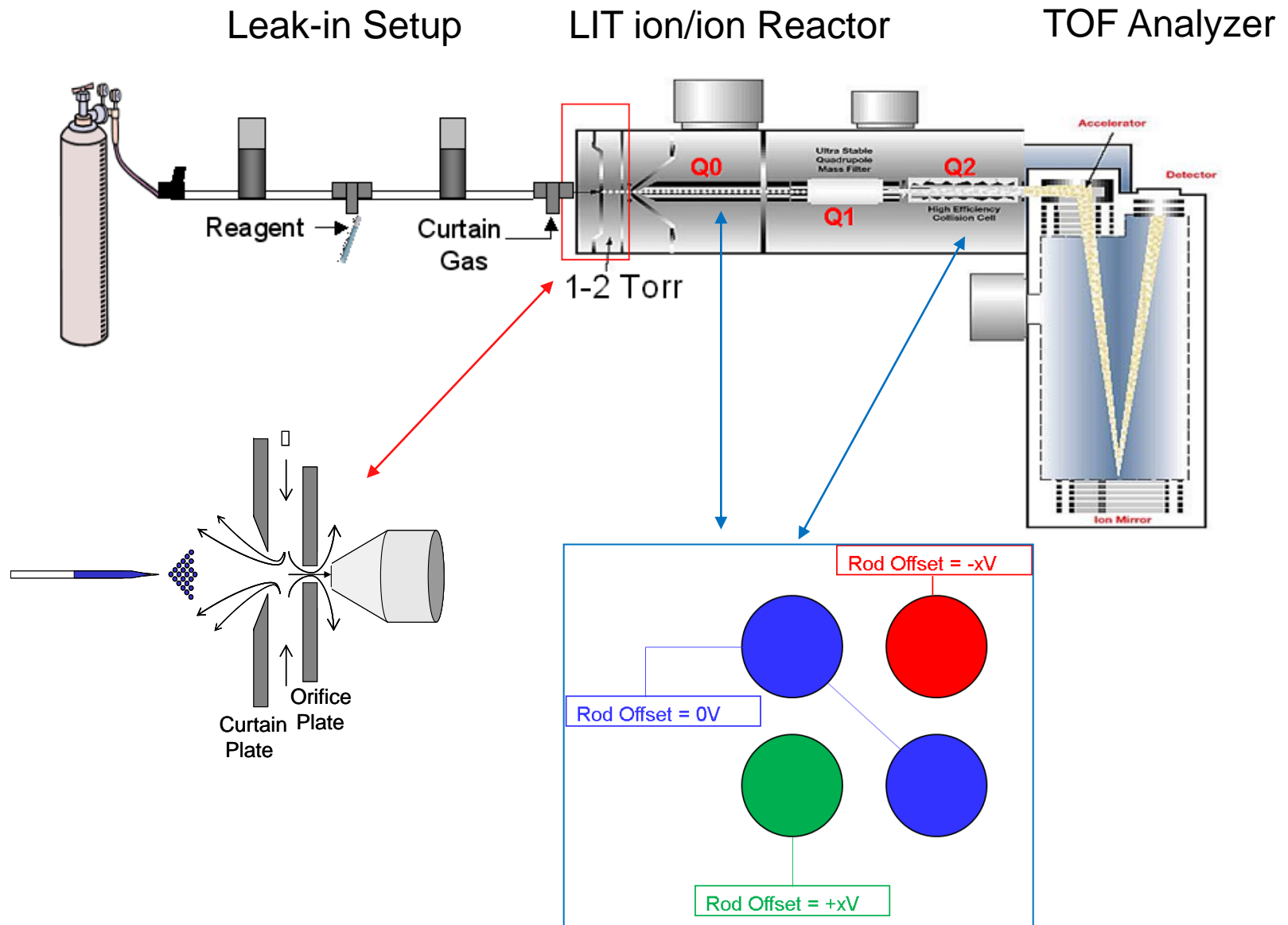


Cold-Ion Spectroscopy Tandem Mass Spectrometer

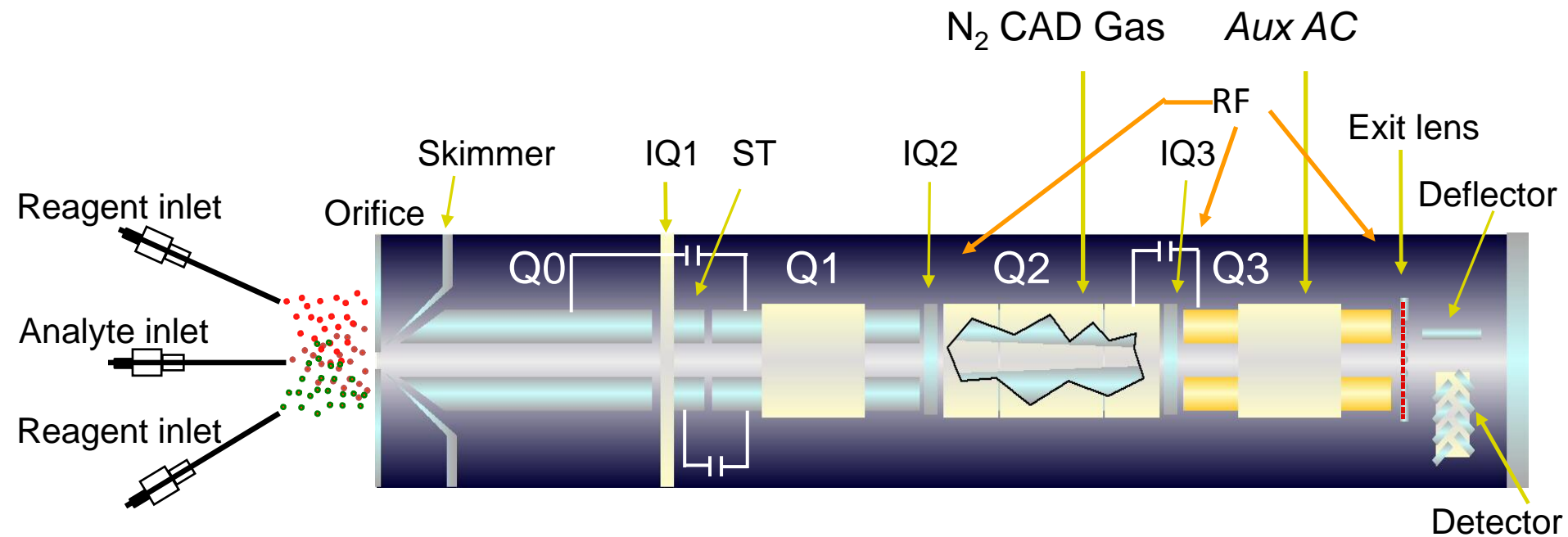
Joint project with the
Laboratory of
Timothy Zwier



Modified Q Star Quadrupole Time-of-Flight

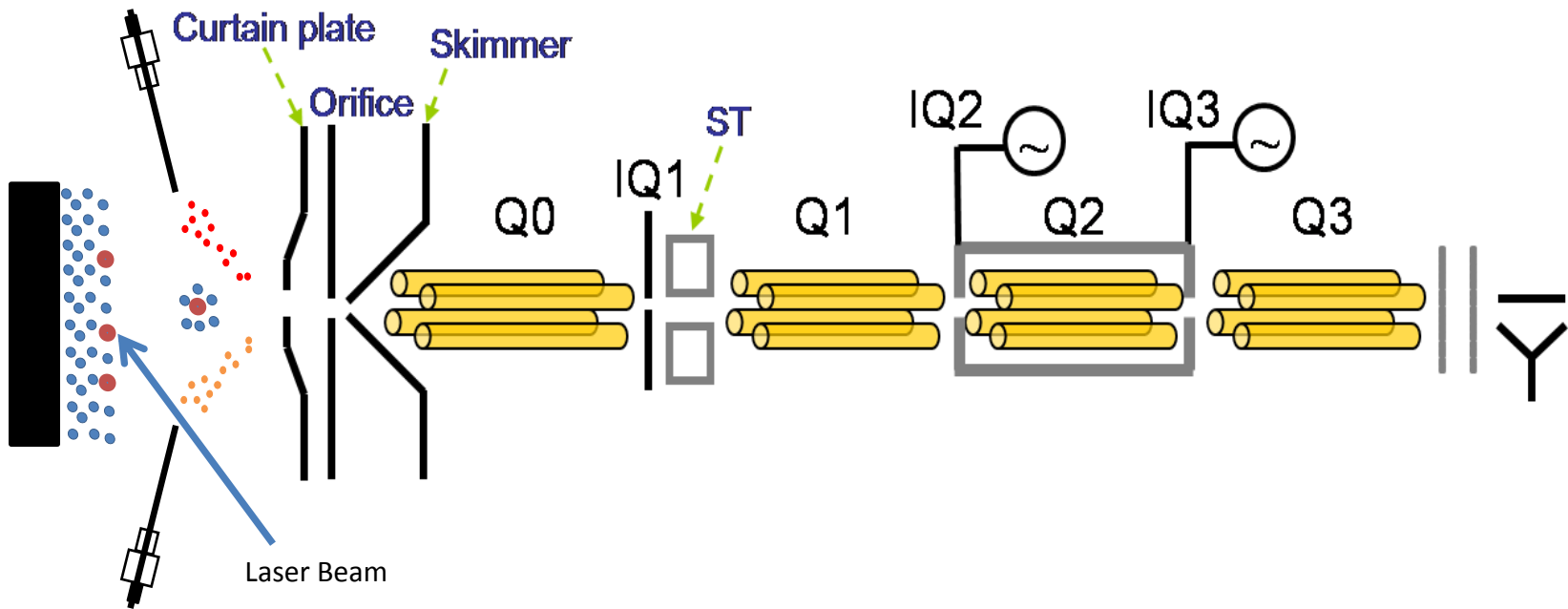


Modified *QTRAP* Linear Ion Trap



Pulsed Triple
Ionization Source

Modified MALDI-Q TRAP4000 Linear Ion Trap



Custom Components

☯ High power rf supplies

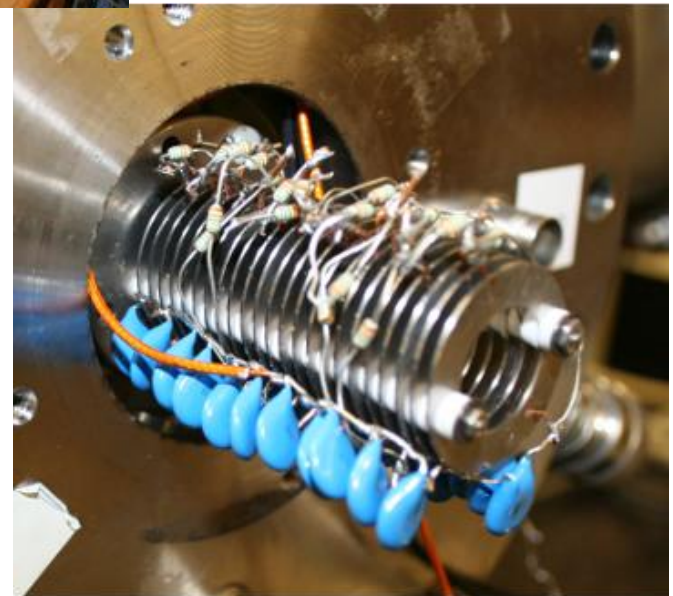
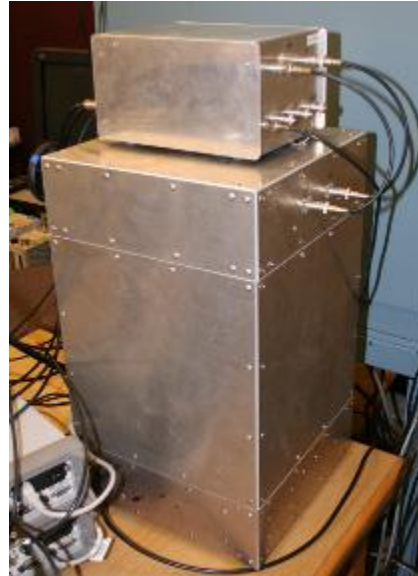
- Able to drive LITs, QIT, and mass resolving Quadrupoles

☯ Low power rf supplies

- Durable tube-based design for ion optical devices
- Scannable transistor supplies for simple mass analysis

☯ Ion funnel

- Small, simple design
- Significant signal gains on homebuilt interface
- Robust interface



Chemistry

Unimolecular Dissociation Reactions

- Peptides
- Proteins
- Nucleic Acids
- Carbohydrates

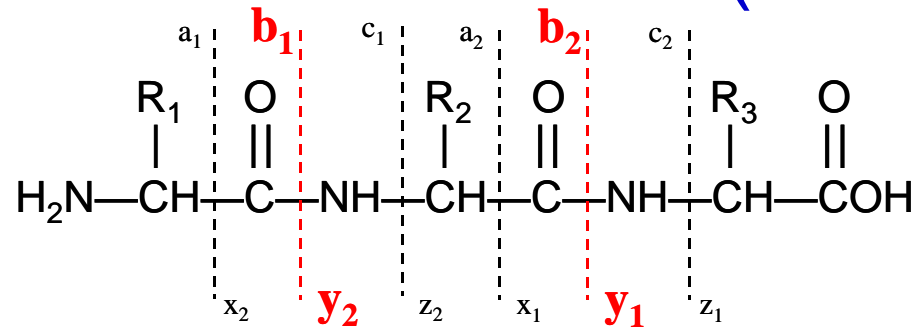
Ion/Ion Reactions

- Proton Transfer (PT)
- Electron Transfer (ET)
- Specific Covalent Chemistry

Ion/Molecule Reaction

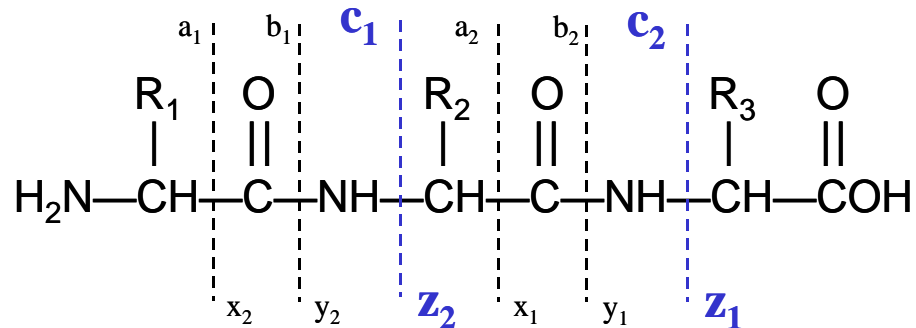
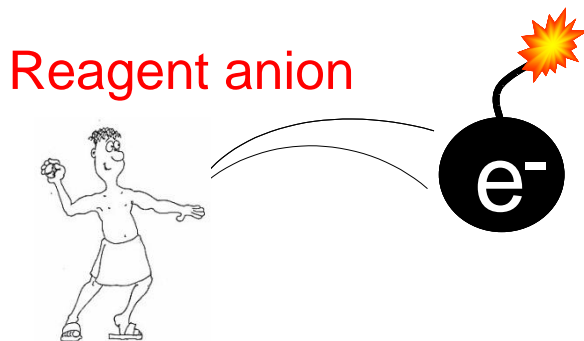
- Treatment of Electrosprayed Droplets

Collision-Induced Dissociation (CID)



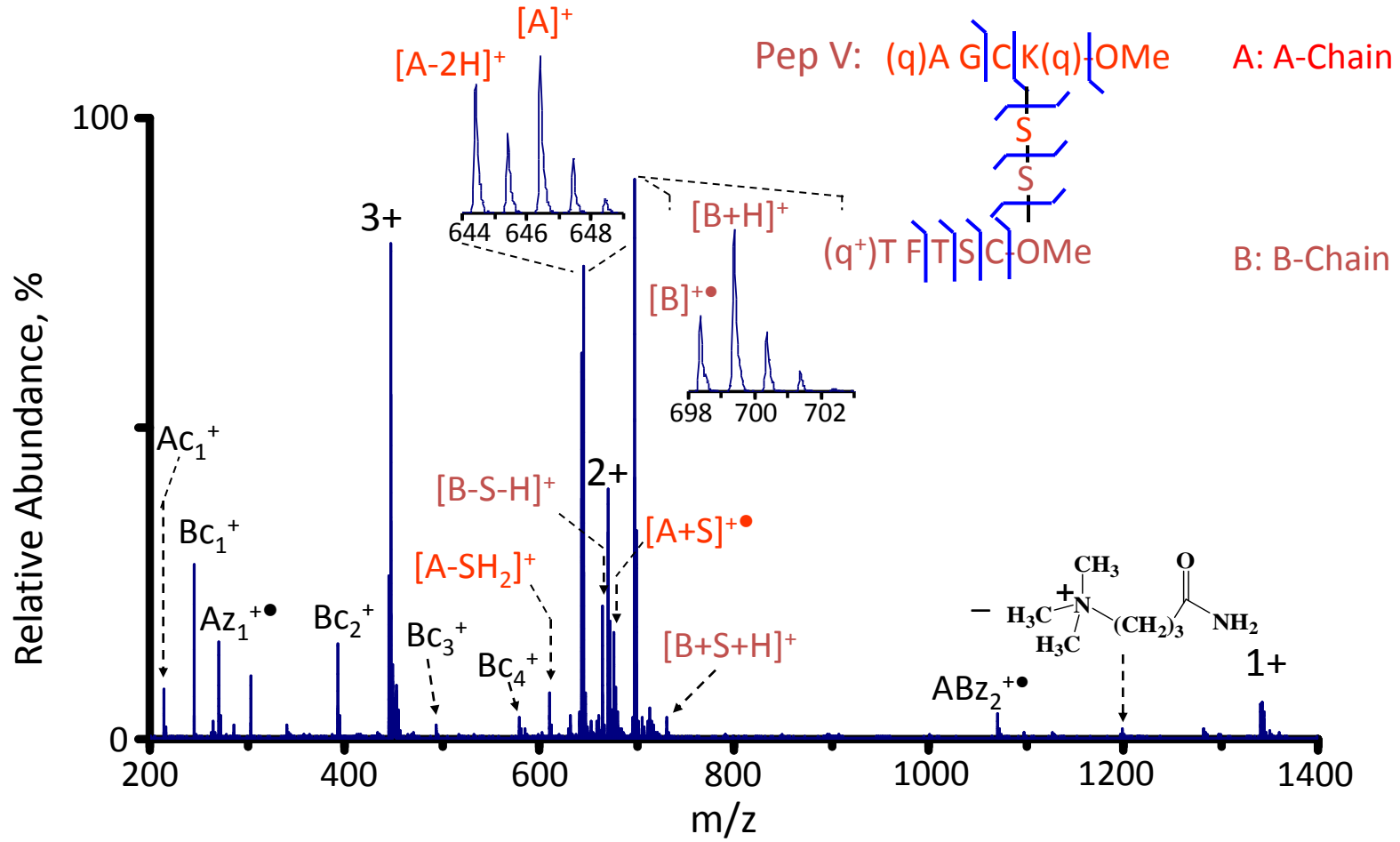
- Excitation increases ion displacement from the trap center, whereby ions undergo increases in kinetic energy. Collisions with the bath gas convert kinetic energy to internal energy (slow heating).

Electron Transfer Dissociation (ETD)

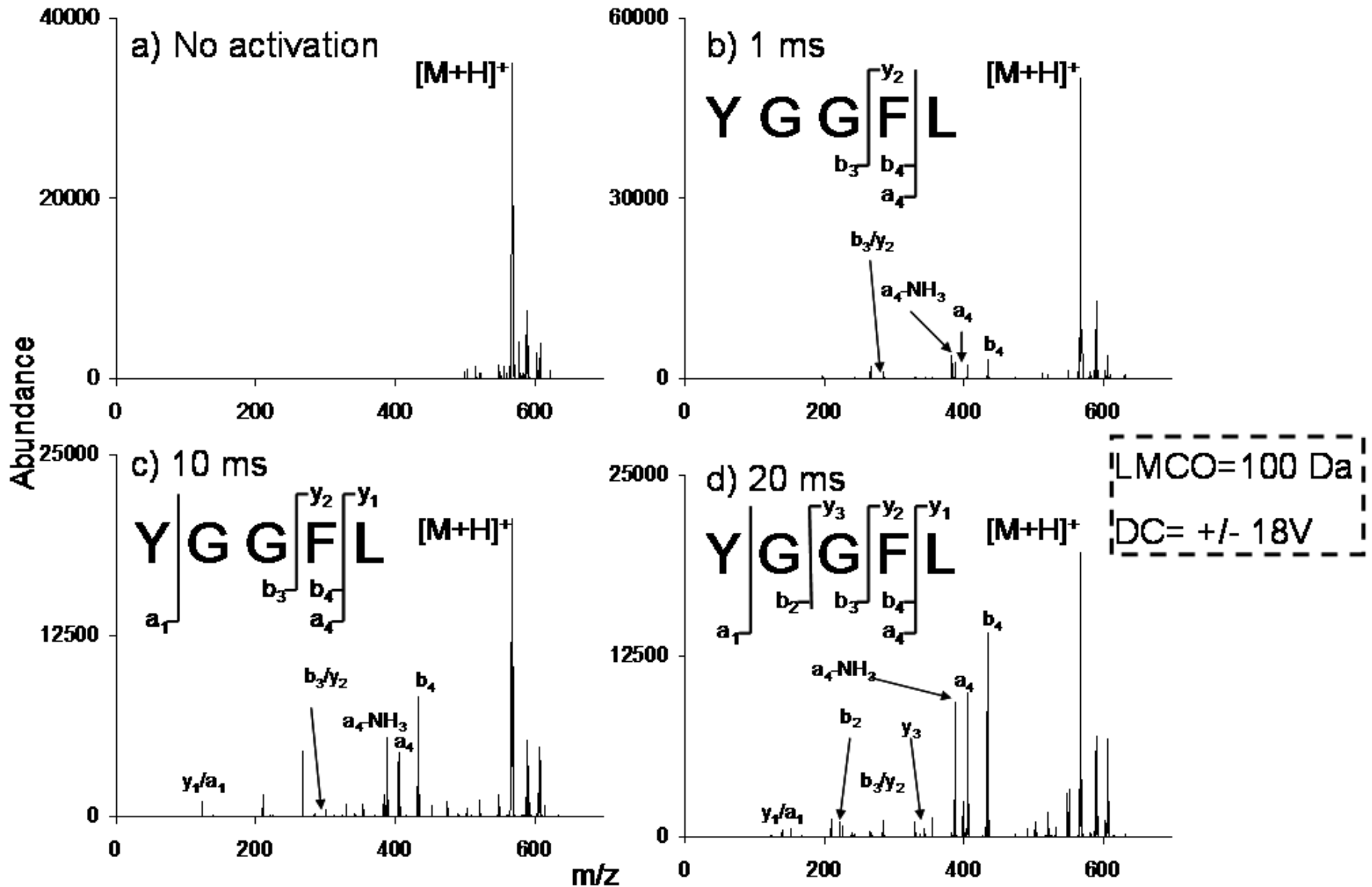


- Less sequence dependence than CID (wider sequence coverage)
- Does not cleave labile post translational modifications

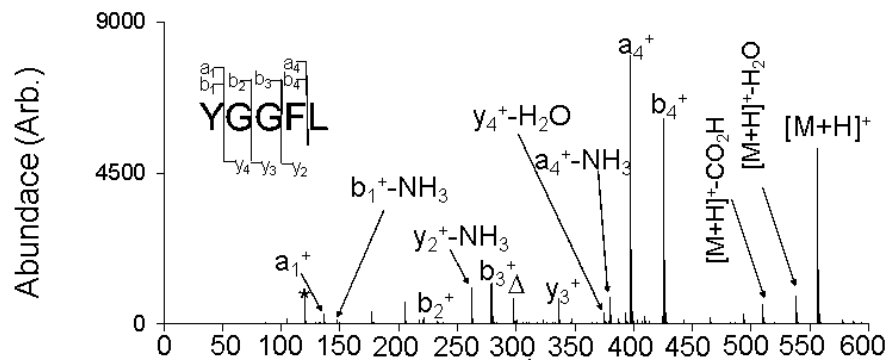
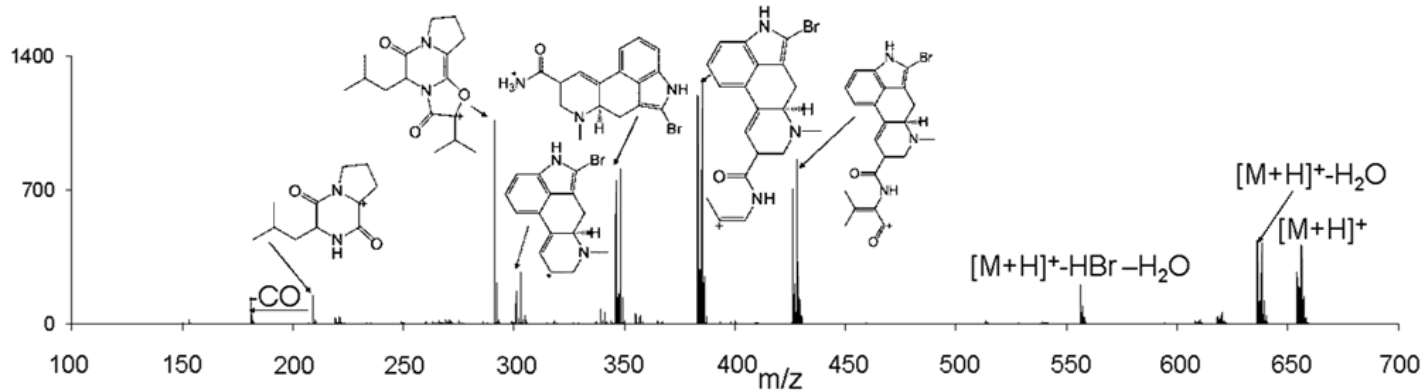
Electron Transfer Reaction between Azobenzene and Disulfide-linked Peptide $[M+3H]^{3+}$



DC CID: Fragmentation vs Time



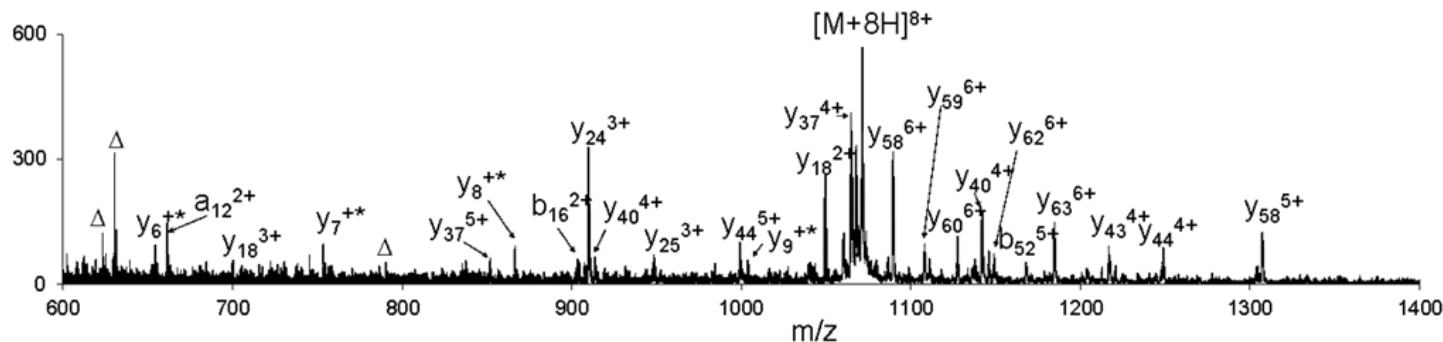
DC CID: A Broadband Application



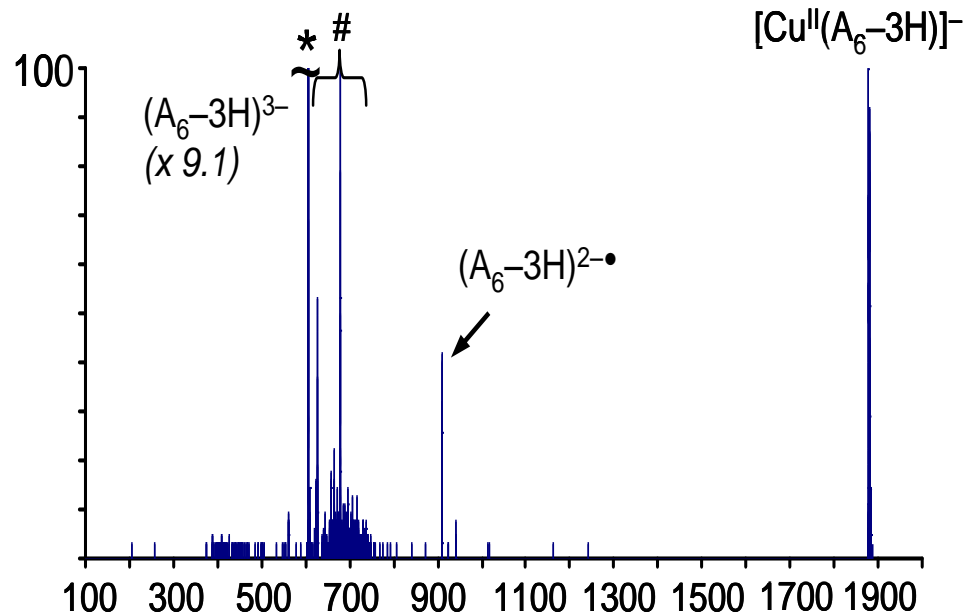
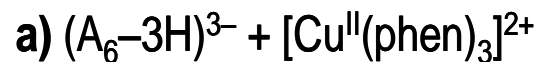
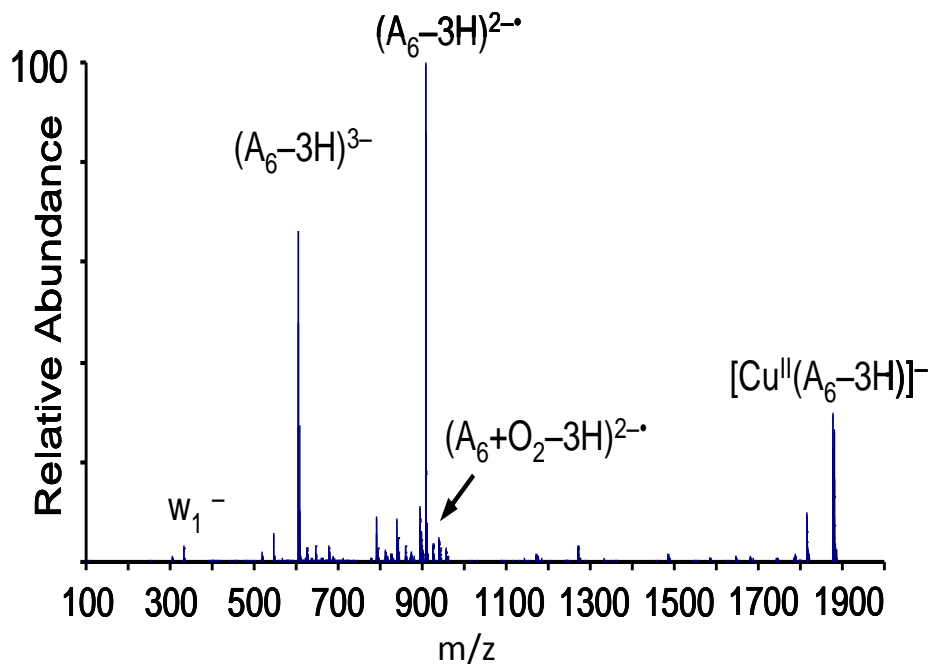
Top: DC CID of bromocriptine. 40 V_{DCC}, 7.5 ms, low mass cutoff = 117 m/z.

Middle: DC CID of YGGFL. 12.8 V_{DCC}, 10 ms, low mass cutoff = 51 Th.

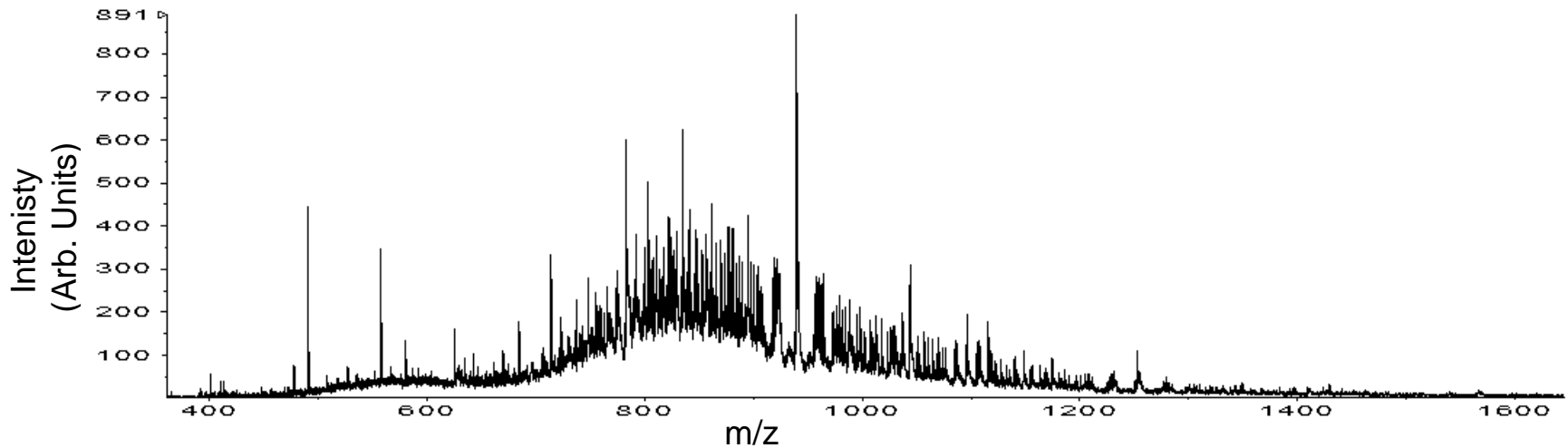
Bottom: DC CID of ubiquitin 8+. 76 V_{DCC}, 10 ms, low mass cutoff = 234 Th.



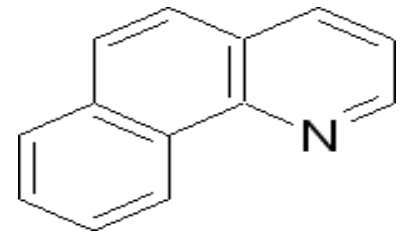
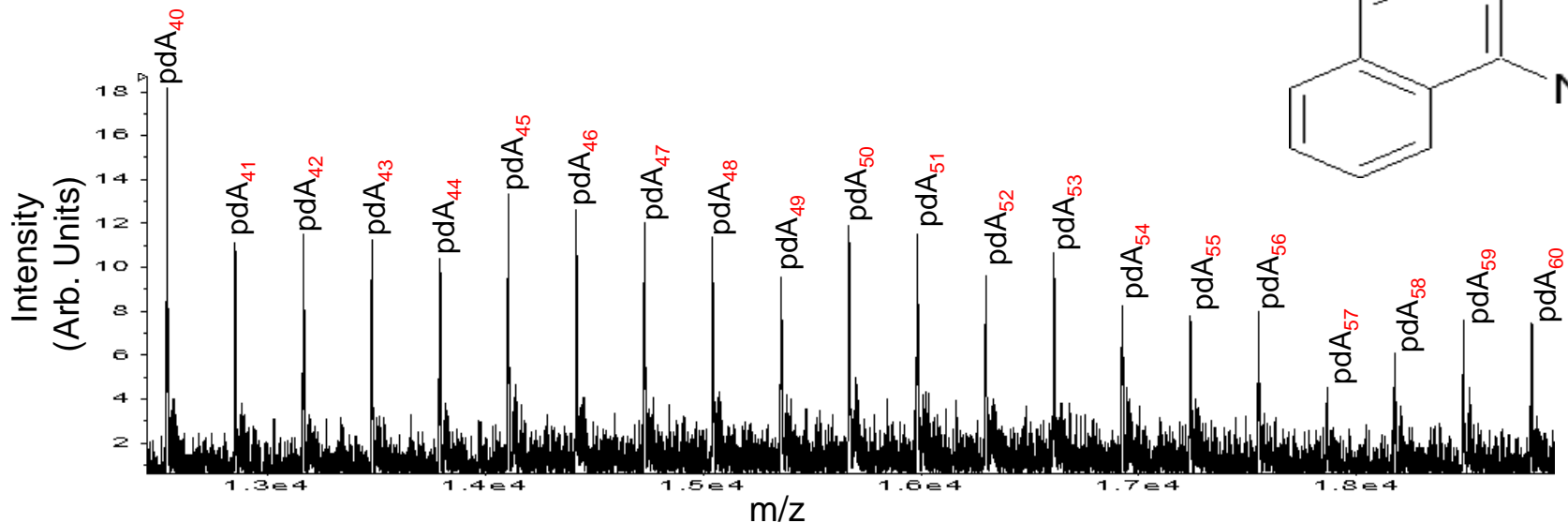
Ion/Ion Reactions of Transition Metal Complex Cations with Multiply Charged Oligodeoxynucleotide Anions



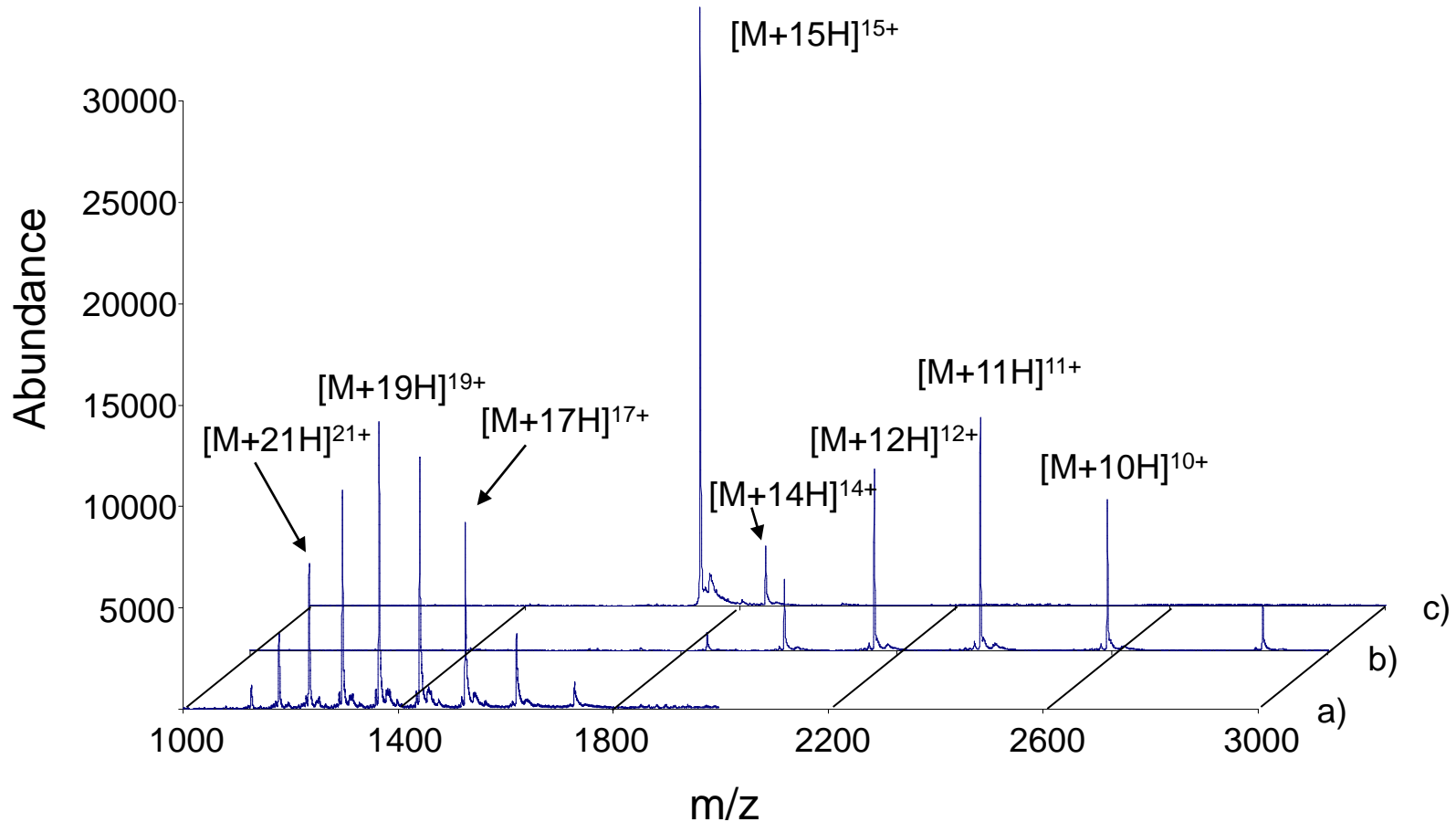
ESI of a DNA Mixture, pd(A)40-60



Proton Transfer Charge Reduction of Multiply-Charged pd(A)40-60 Anions

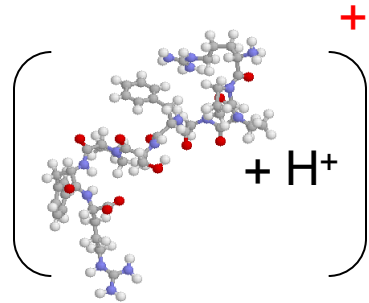


Ion Parking



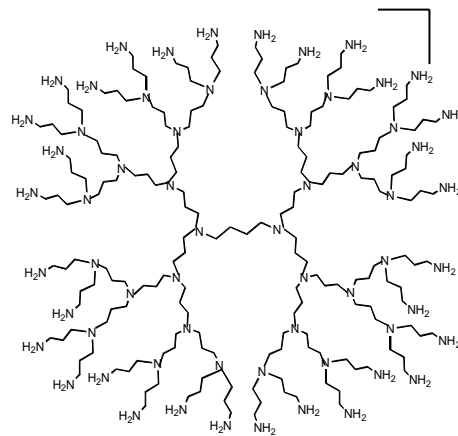
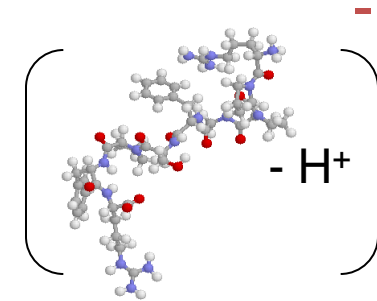
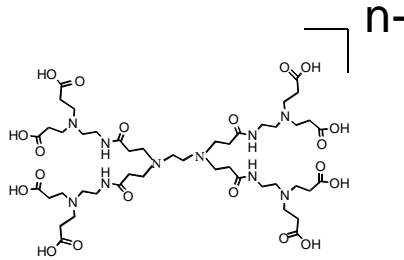
Mass Spectra of Porcine Elastase Acquired in
(a) Pre Ion/Ion, (b) Post Ion/Ion and (c) Ion Parking Modes

Charge Inversion Process

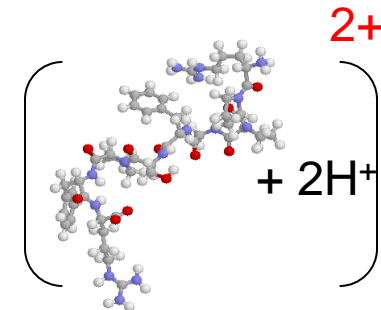
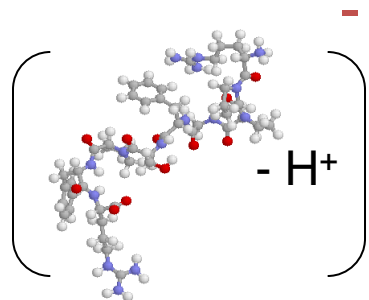


Peptide Ion
(Bradykinin)

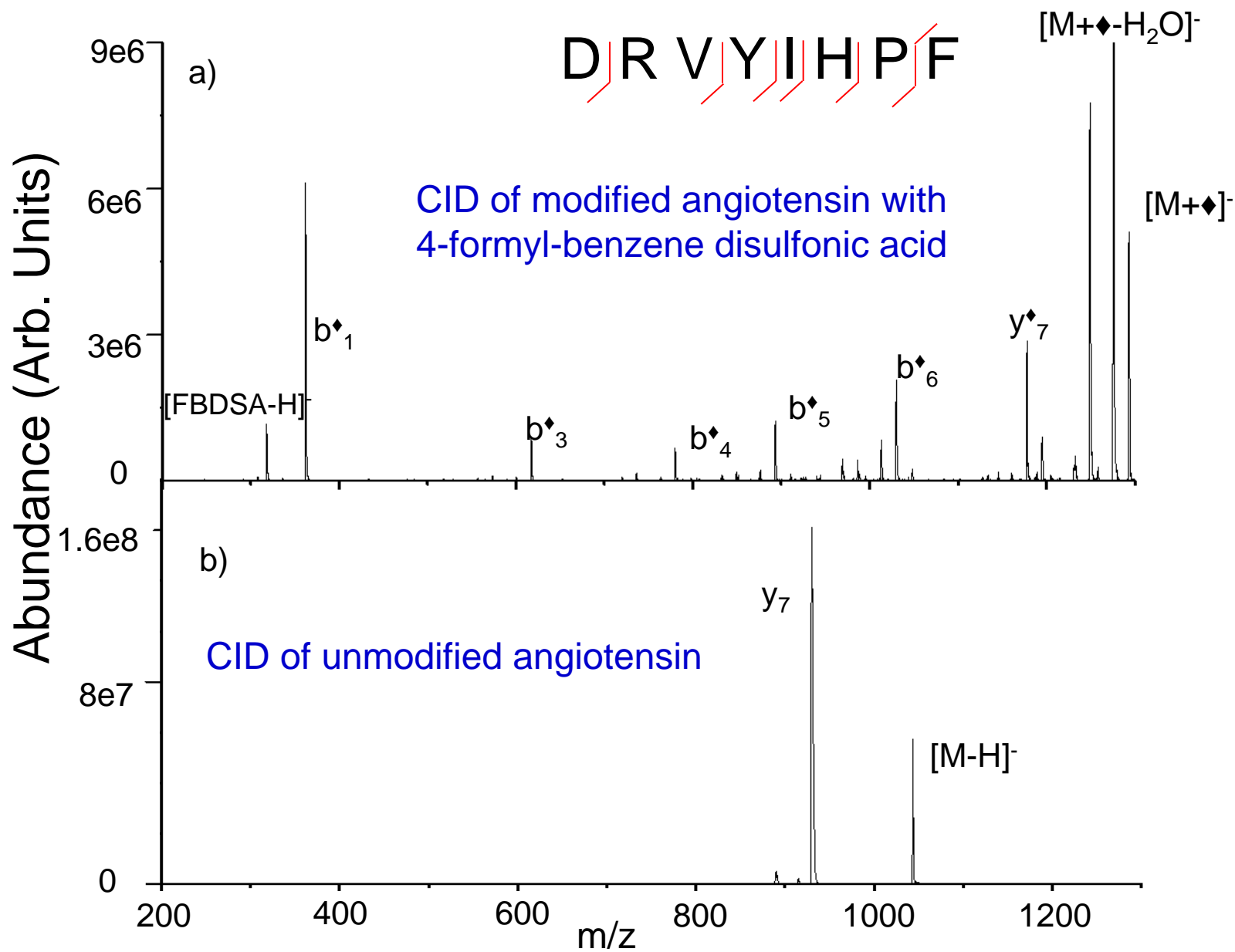
Polyamidoamine (PAMAM)
Dendrimer Anion



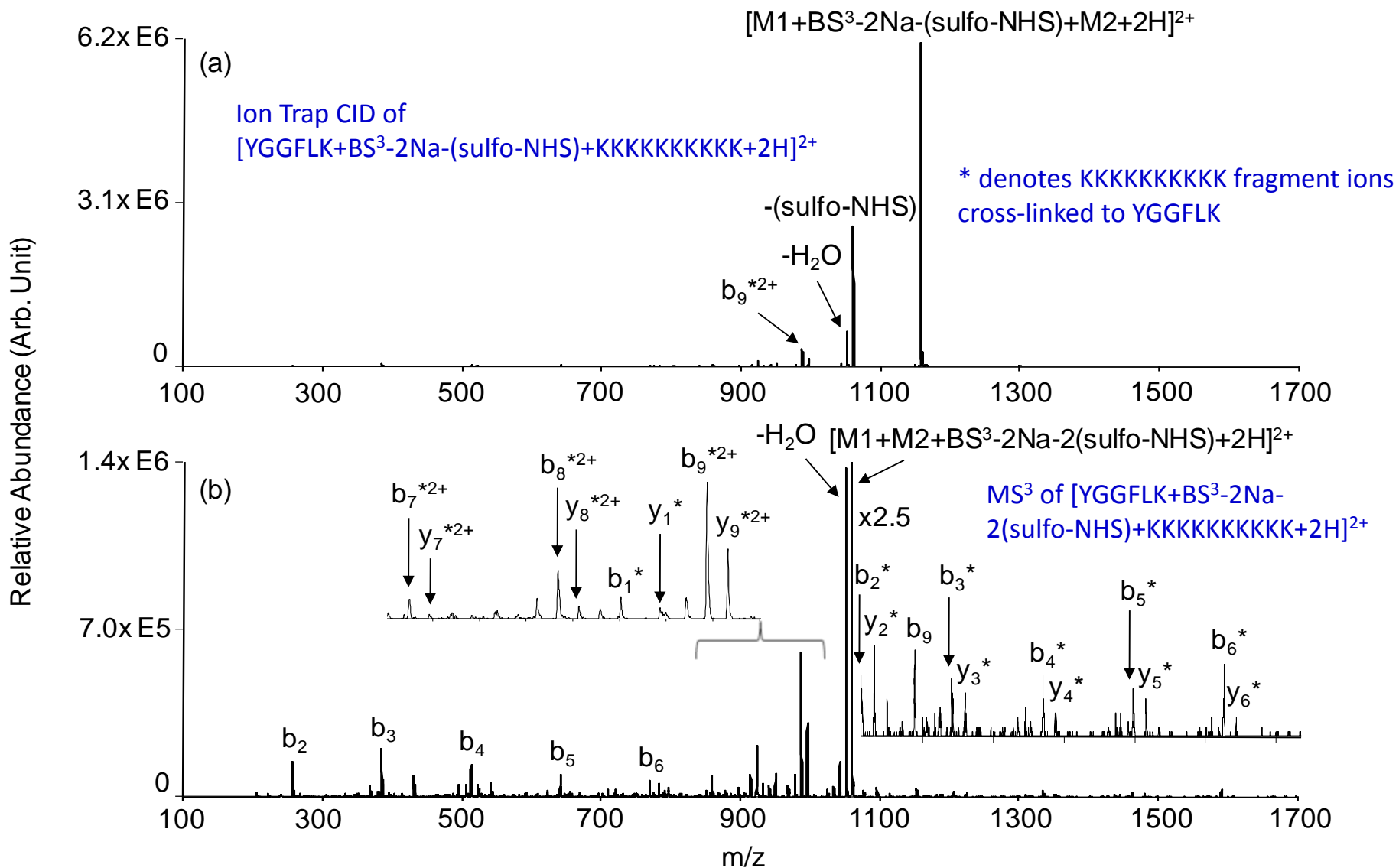
1,4-Diaminobutane (DAB)
Dendrimer Cation



Sequential Information via Covalent Modification made in the Gas Phase

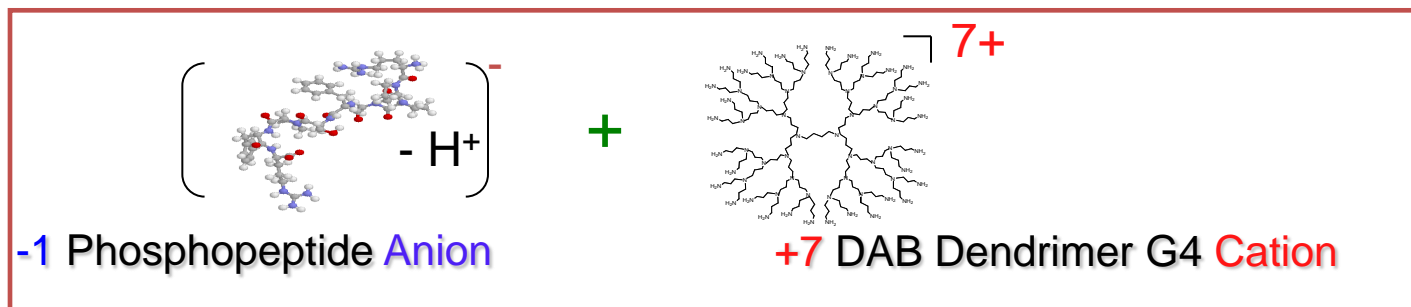


Inter-Molecular Cross-Linking in the Gas-Phase

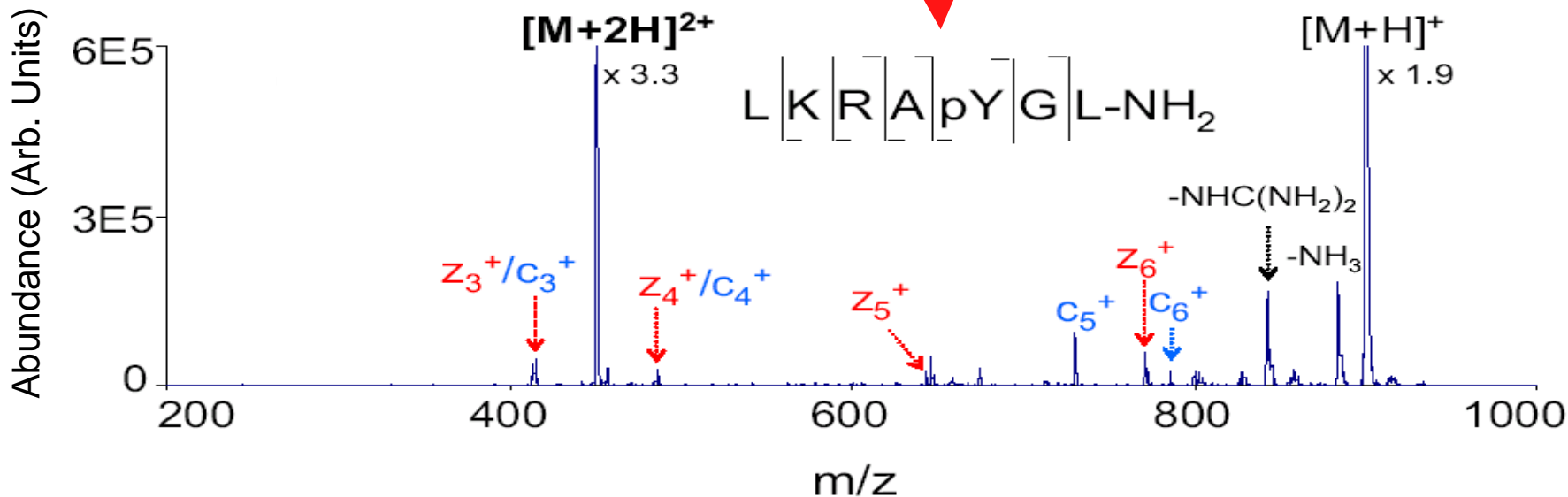
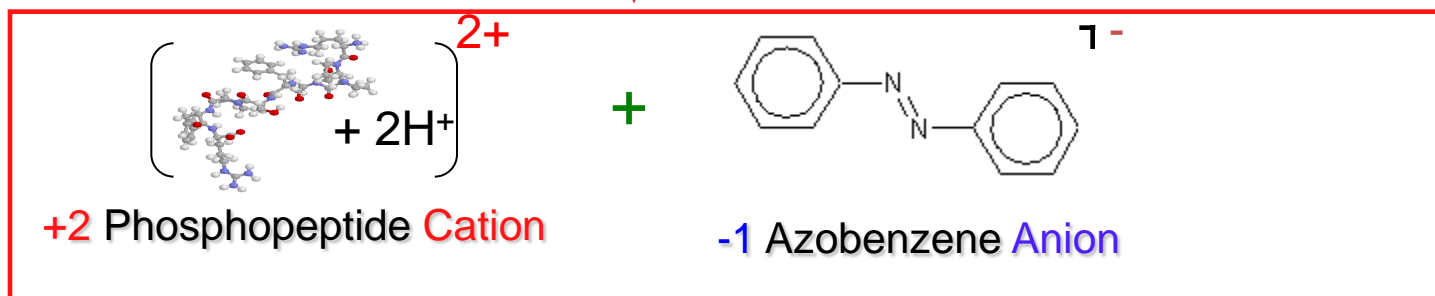


Charge Inversion/ETD of a Phosphopeptide

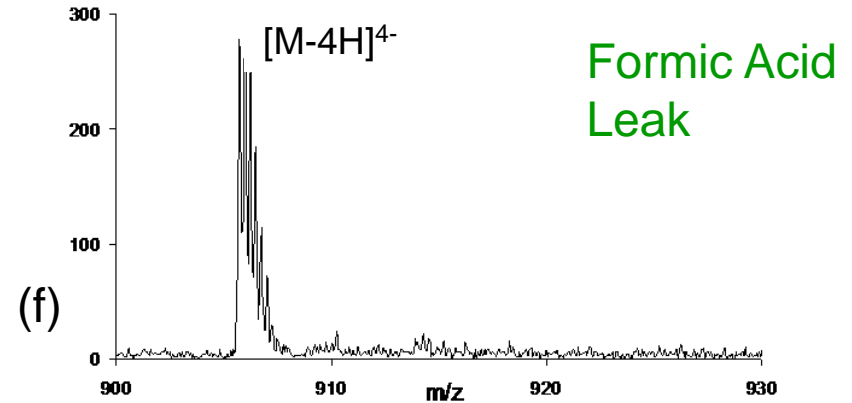
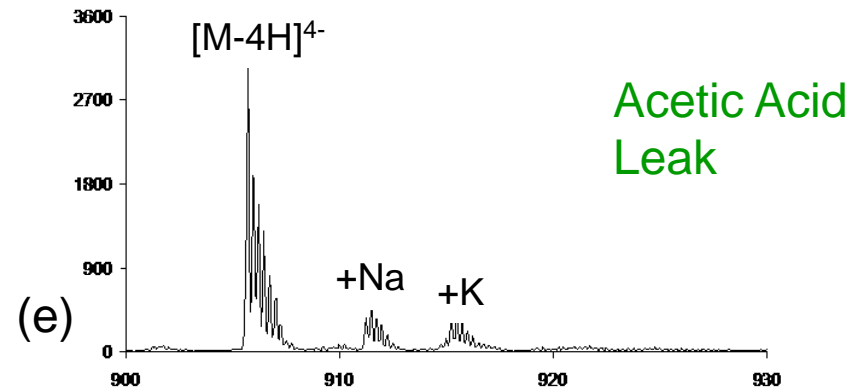
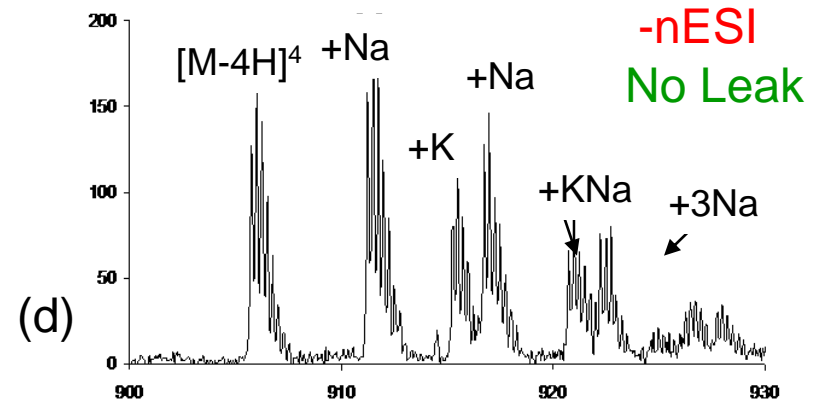
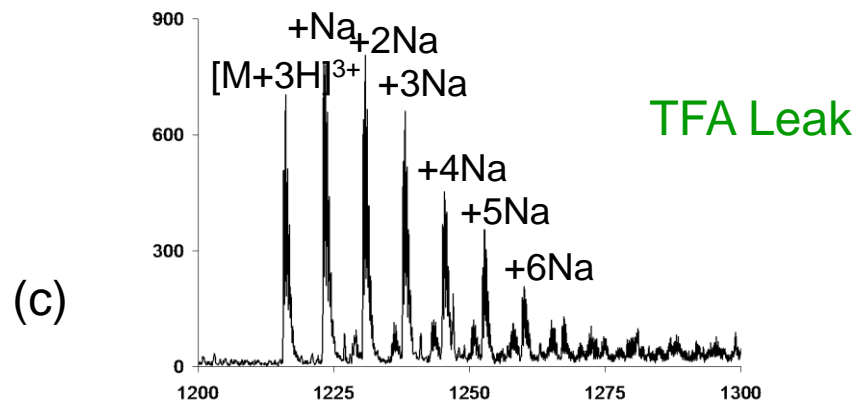
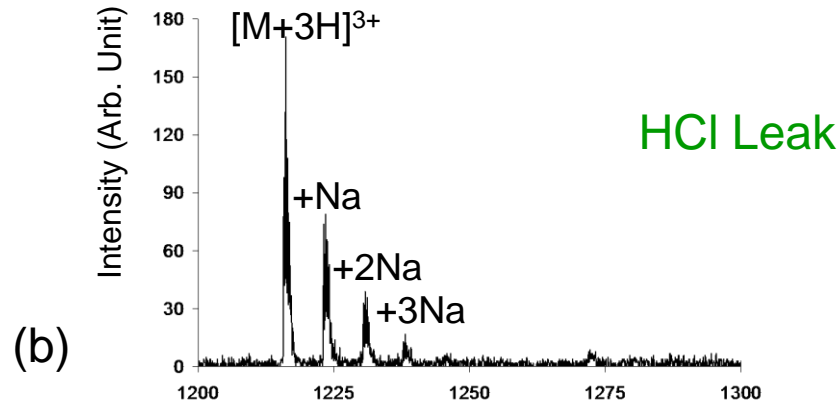
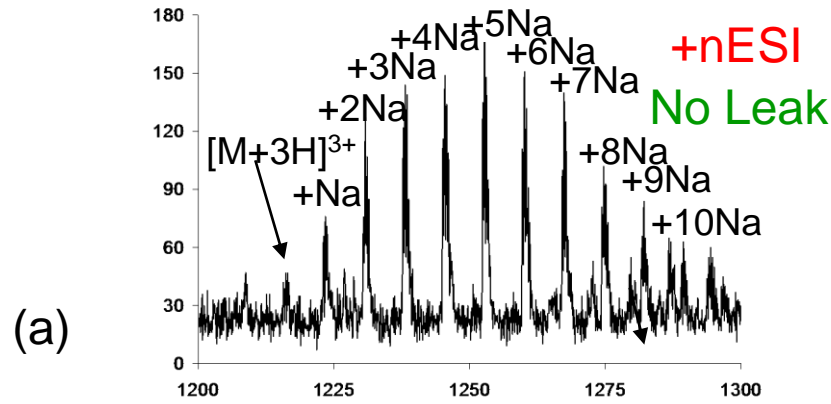
Charge Inversion



ETD




Acid Vapor Introduction for Removal of Metal Counter-Ions of Various DNA 12mers



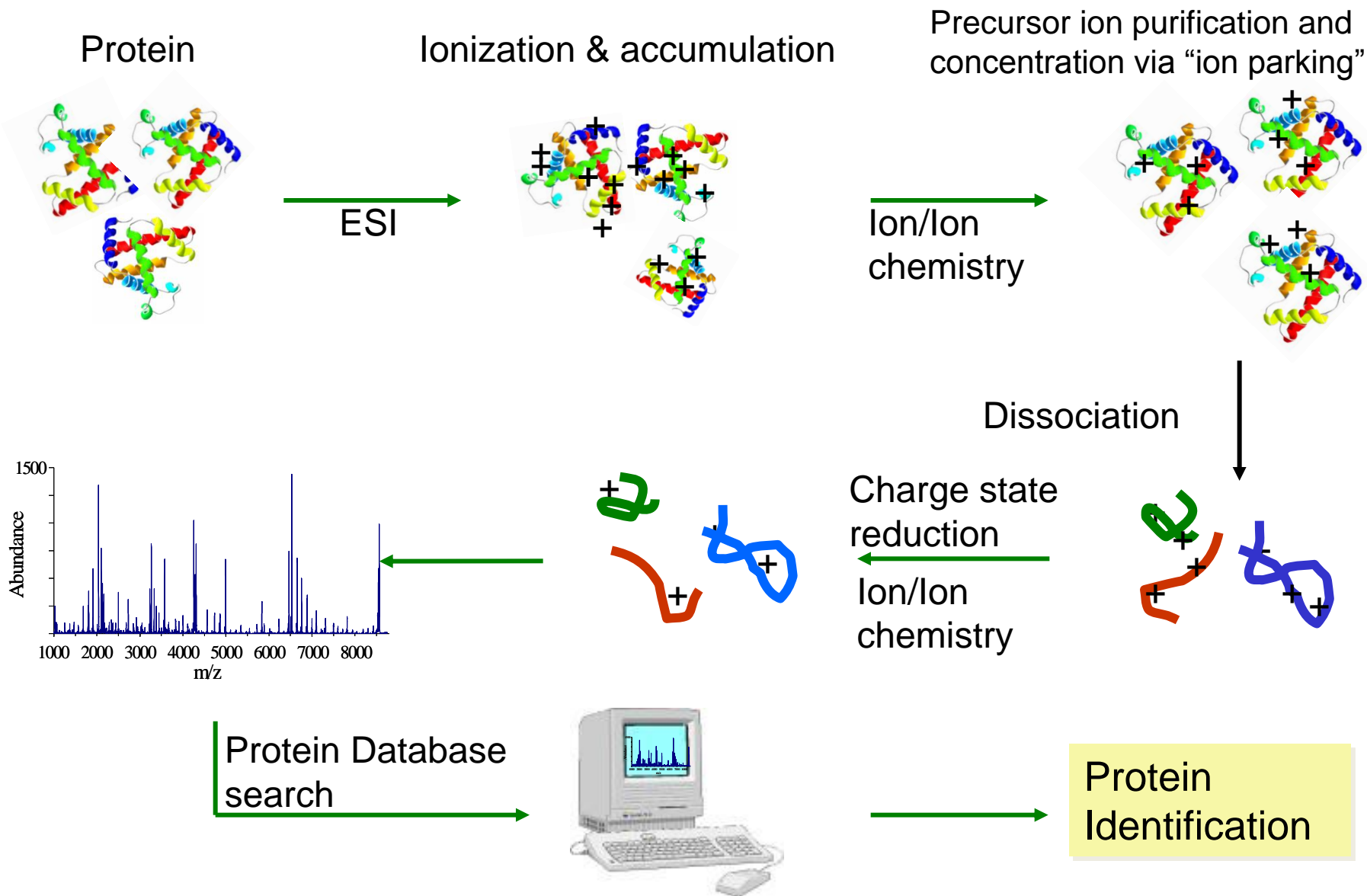
Applications

 Protein Mixture Analysis

 Database-Assisted Protein Identification

 Post-Translational Modification (PTM)
Analysis

“Top-Down” Protein Identification



Relative Informing Power of ESI Based Top-down Approaches



m/z

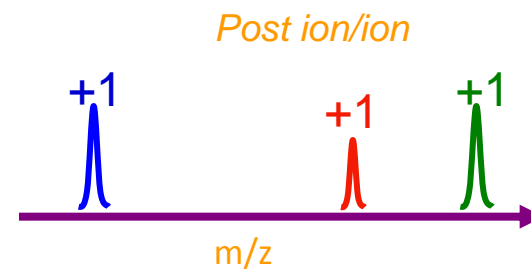
ESI

Ion/Ion reaction



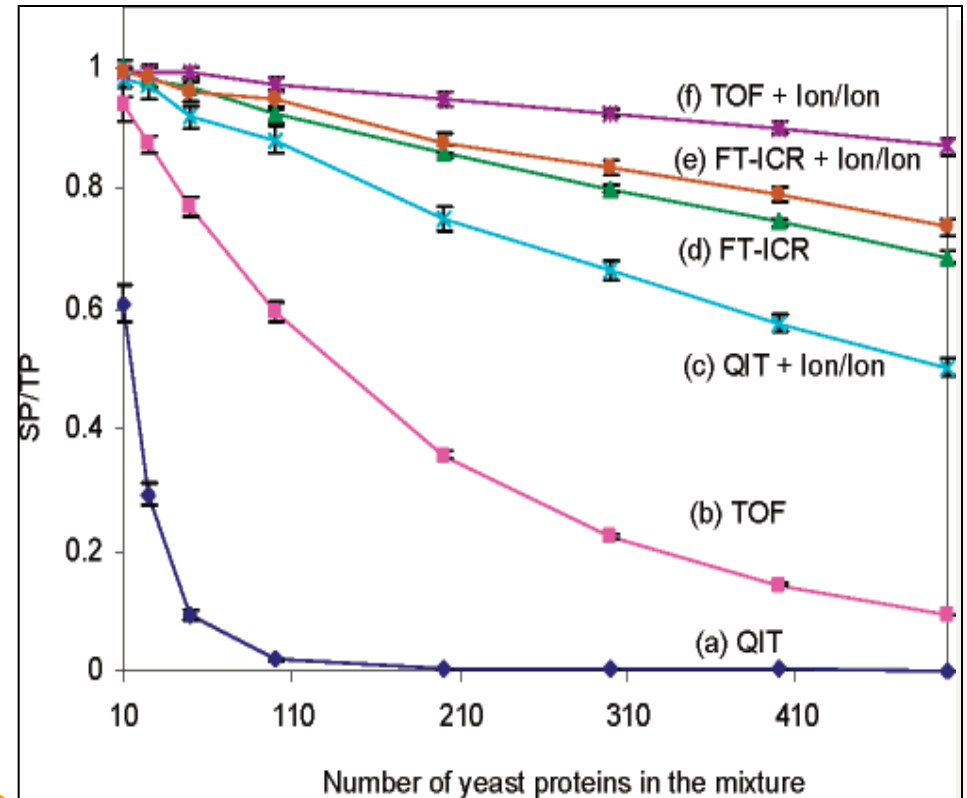
High resolution

m/z

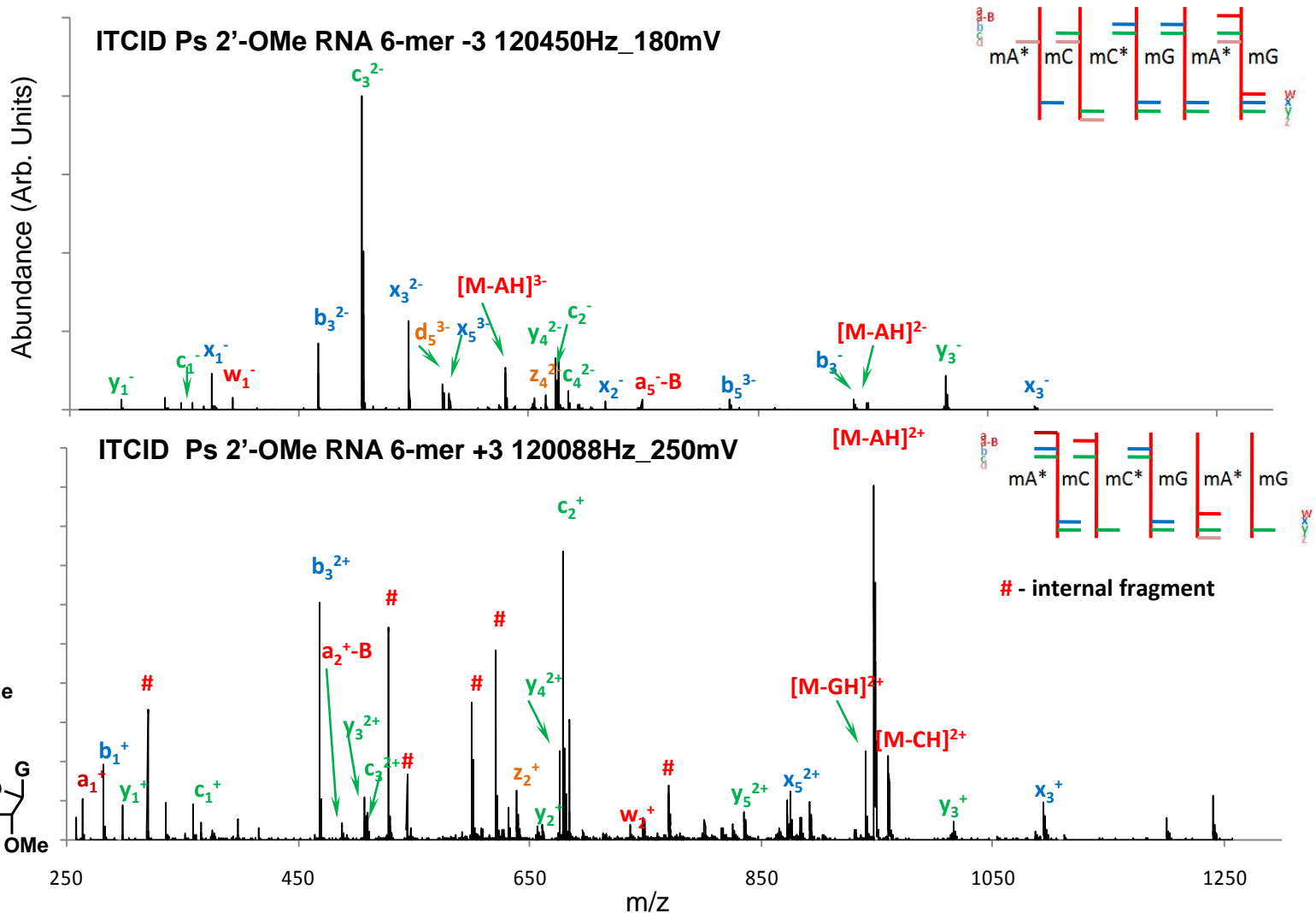
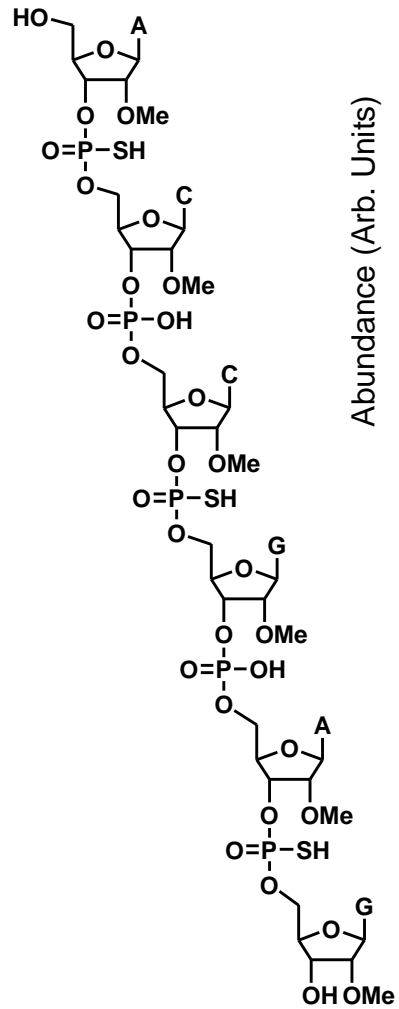


Post ion/ion

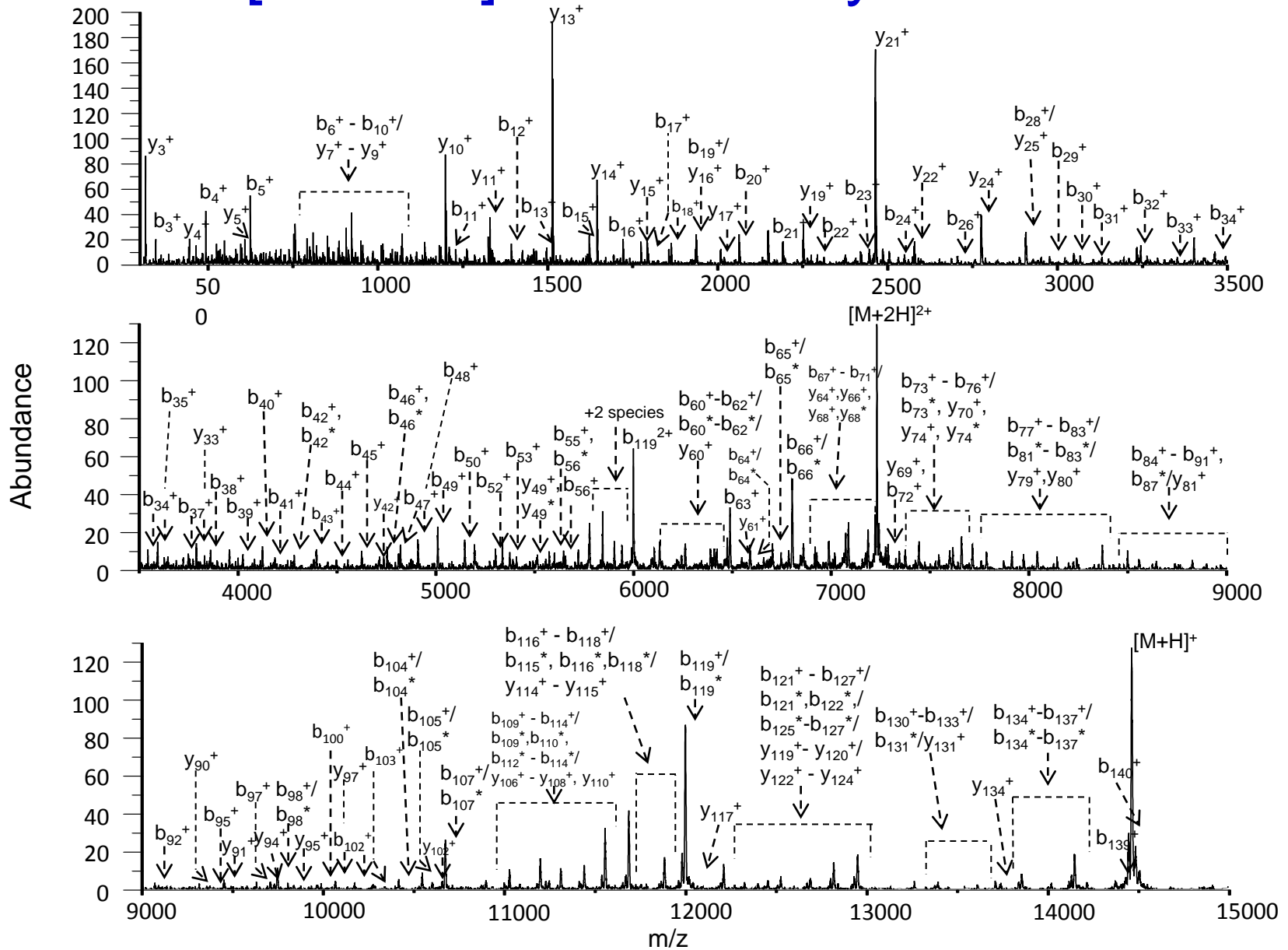
m/z



Modified DNA Sequencing



Post Ion-Ion Reaction MS/MS Spectra of the $[M + 9H]^{9+}$ Ion of α -synuclein



“Macro-Ionophiles”

From N-terminus to
C-terminus:

🌐 **Scott A. McLuckey**

- Ken Chanthamontri
- Corrine DeMuth
- Christine Fisher
- Yang Gao
- Josh Gilbert
- Kerry Hassell
- Ryan Hilger
- Anastasia Kharlamova
- Carl Luongo
- Marija Mentinova
- William McGee
- Boone Prentice
- James Redwine
- Jessica Espy
- John Stutzman
- Ian Webb

