https://ntrs.nasa.gov/search.jsp?R=20180007719 2020-02-11T06:19:54+00:00Z

A COMPACT TWO-STEP LASER TIME-OF-FLIGHT MASS SPECTROMETER FOR *IN SITU* ANALYSIS OF PLANETARY SURFACES

Stephanie A. Getty and William B. Brinckerhoff
NASA Goddard Space Flight Center

Timothy J. Cornish
C&E Research, Inc.

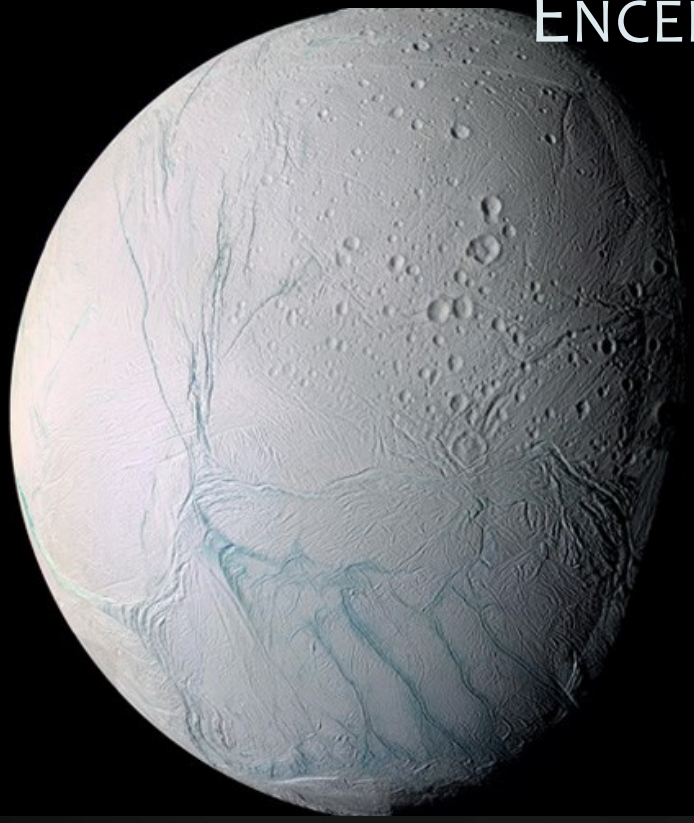
Andrej Grubisic
University of Maryland, College Park

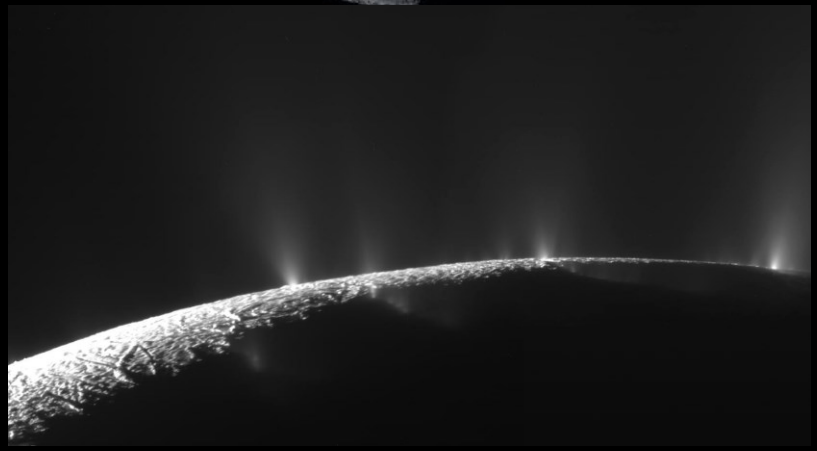
Xiang Li
University of Maryland, Baltimore County

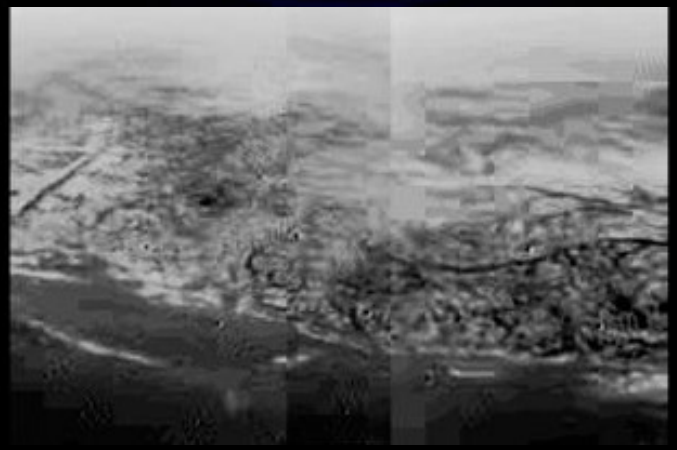
Kyle Uckert
New Mexico State University

Solar System Destinations…
that are just begging to be analyzed!

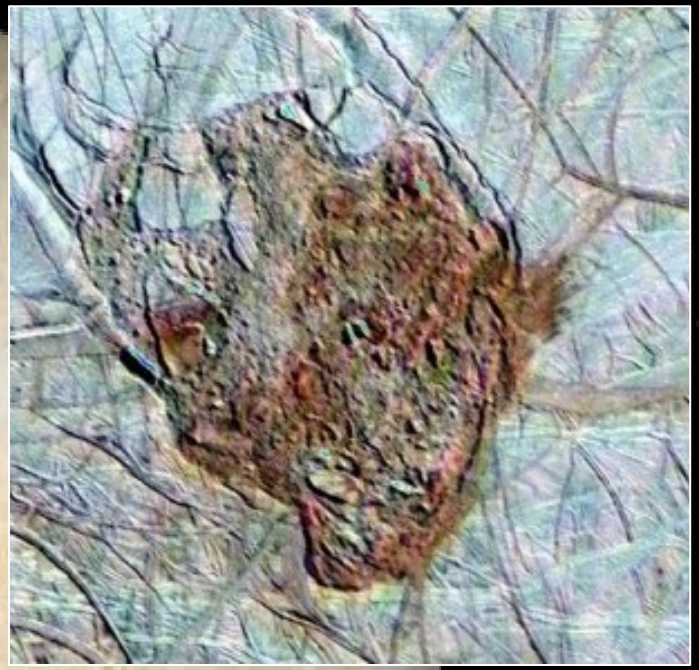
Enceladus & Titan

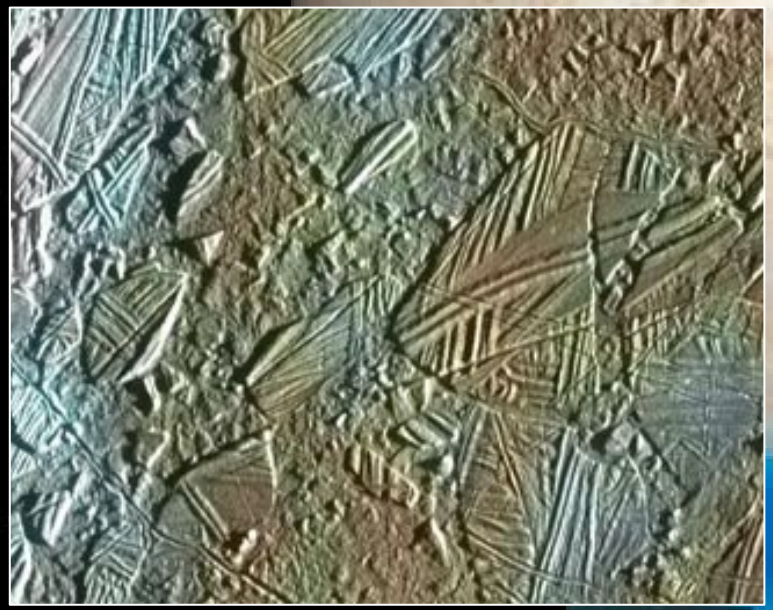




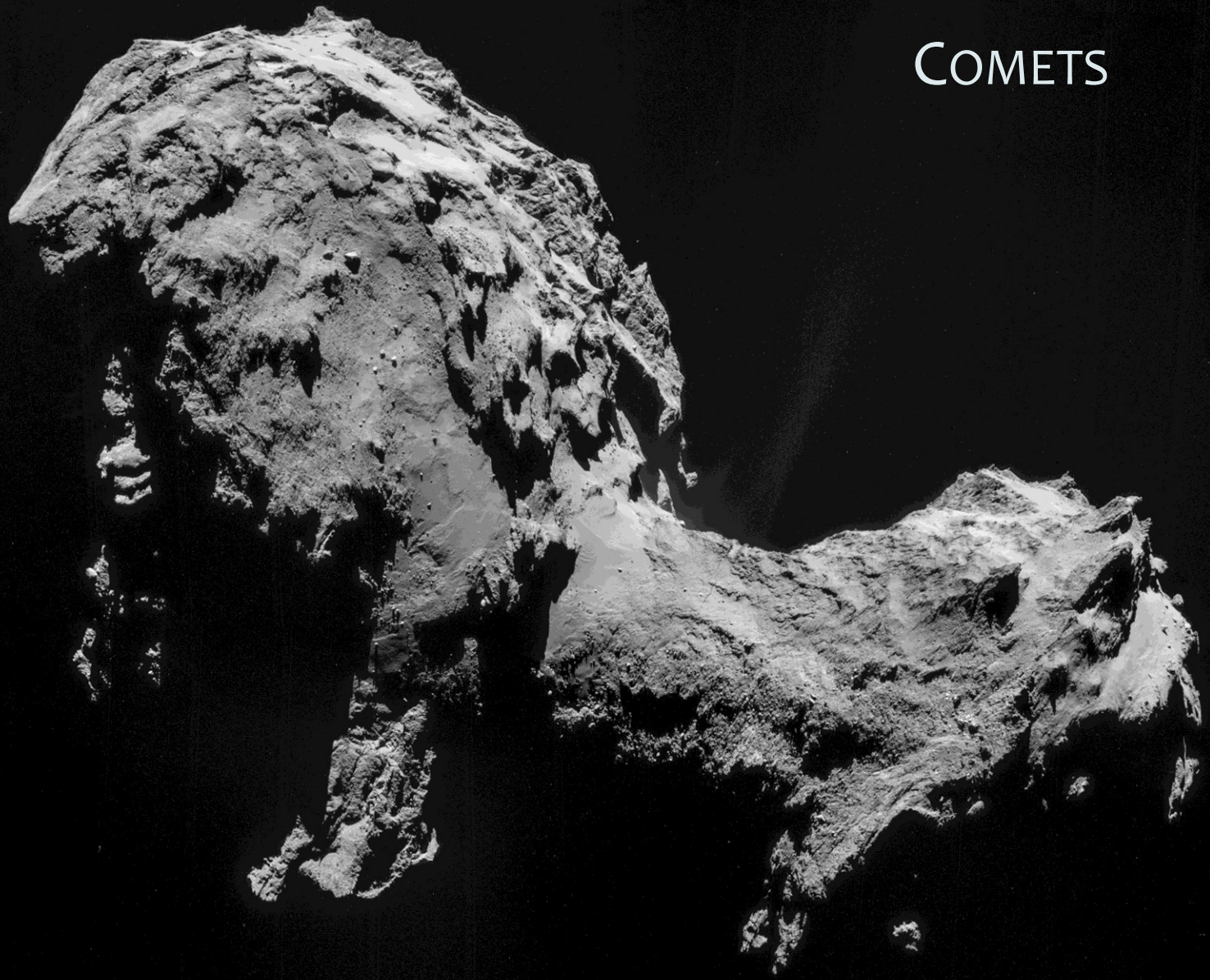


Europa

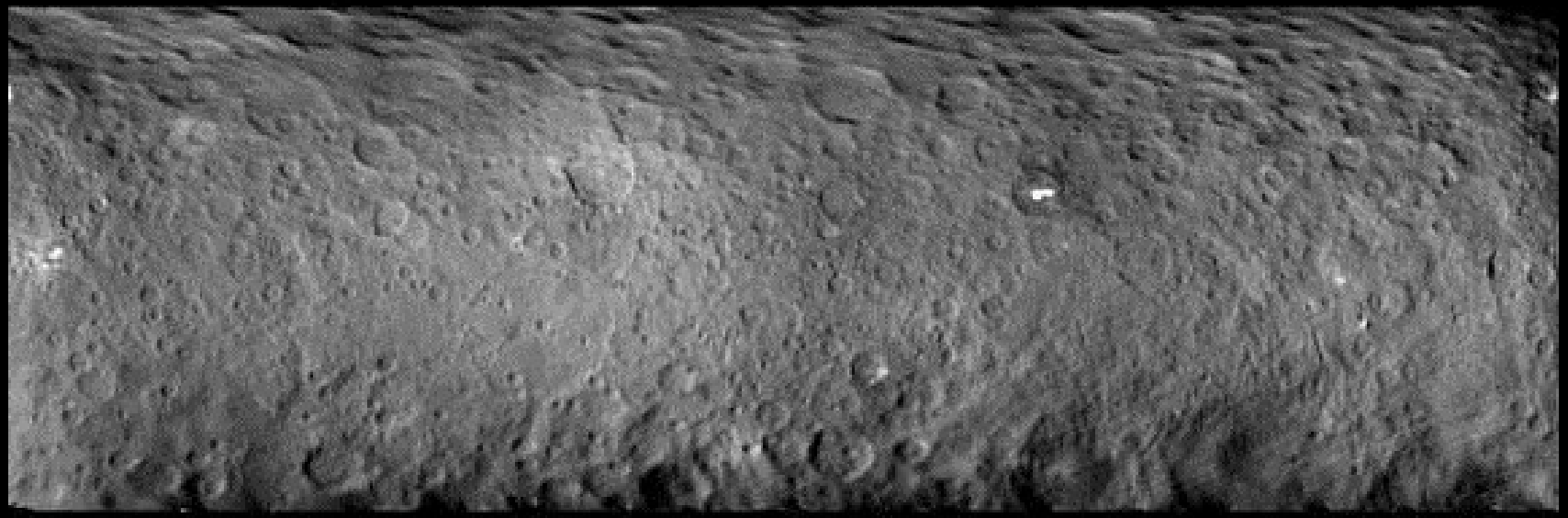




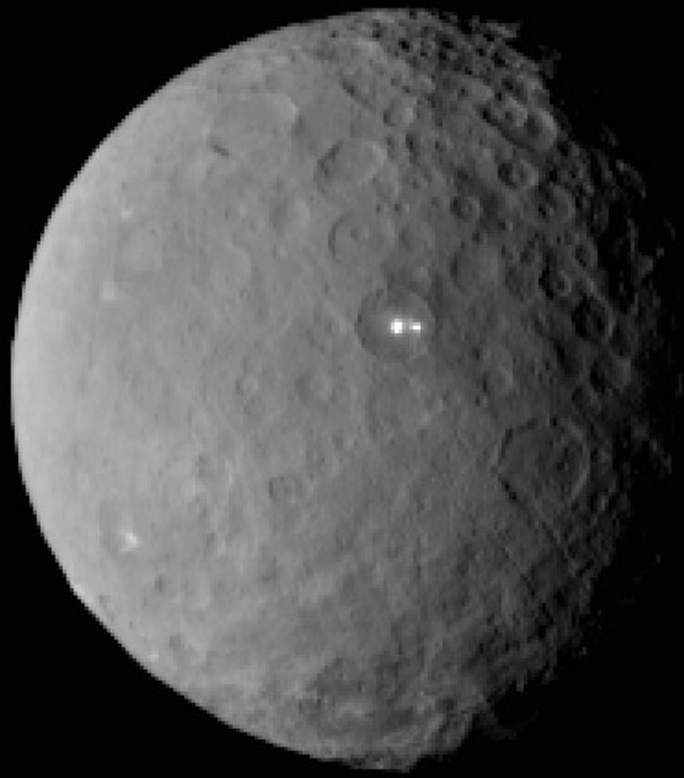
Comets



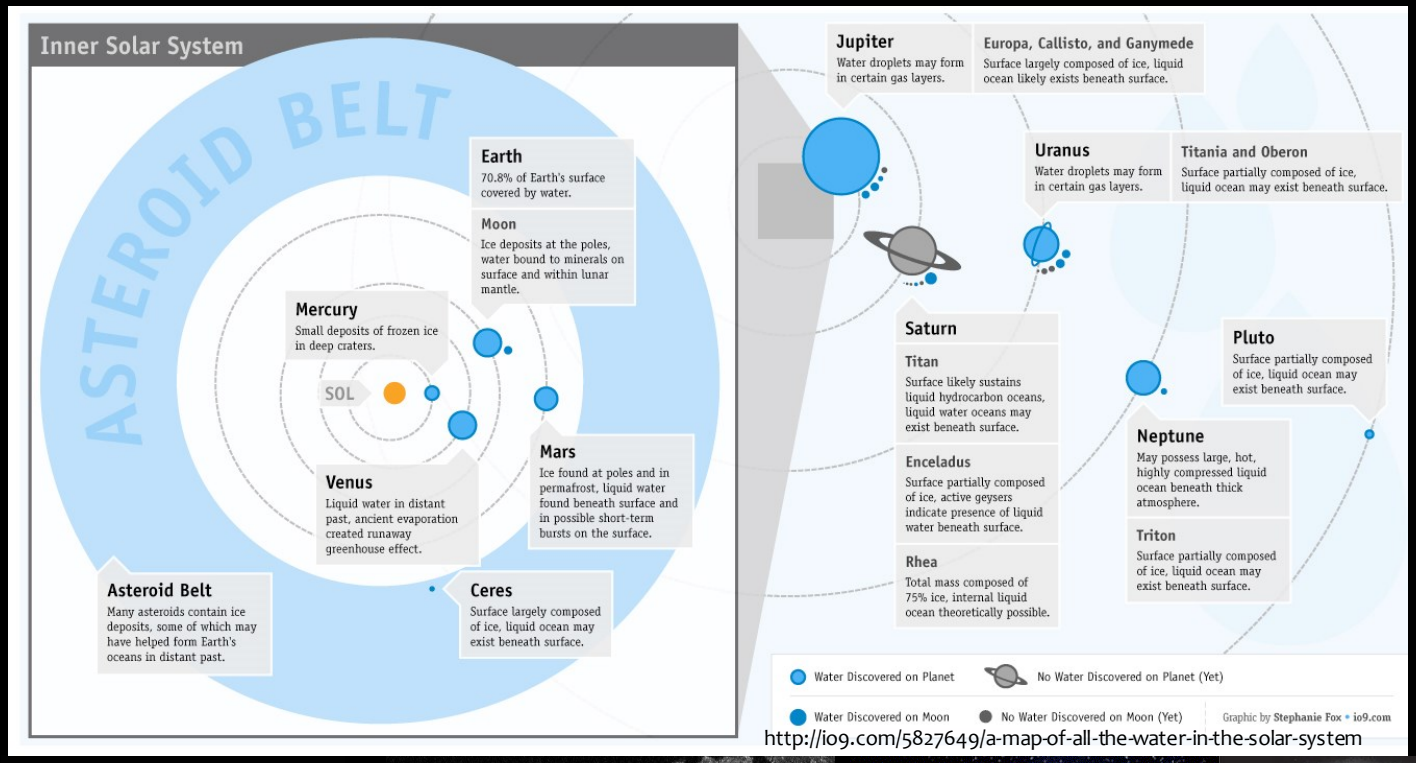
(e.g., 67P Churyumov-Gerasimenko)



Ceres

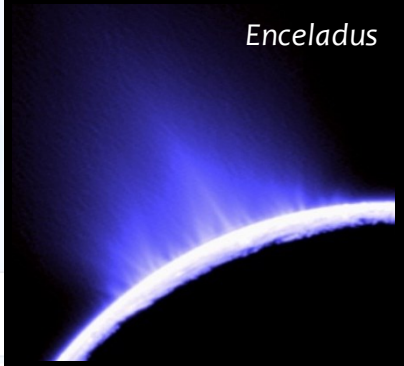


What do these bodies have in common? Volatiles, including water!

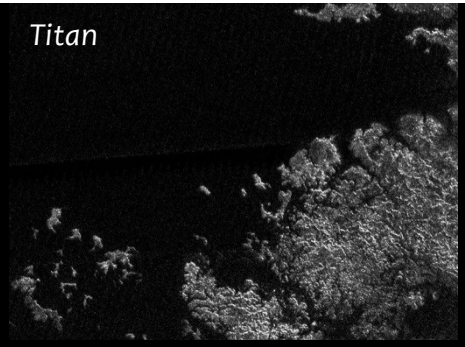


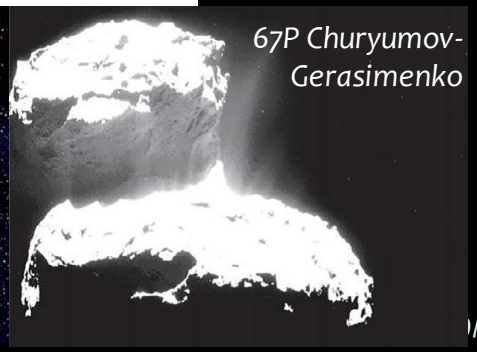
http://io9.com/5827649/a-map-of-all-the-water-in-the-solar-system

Europa


Enceladus

Ceres


Titan

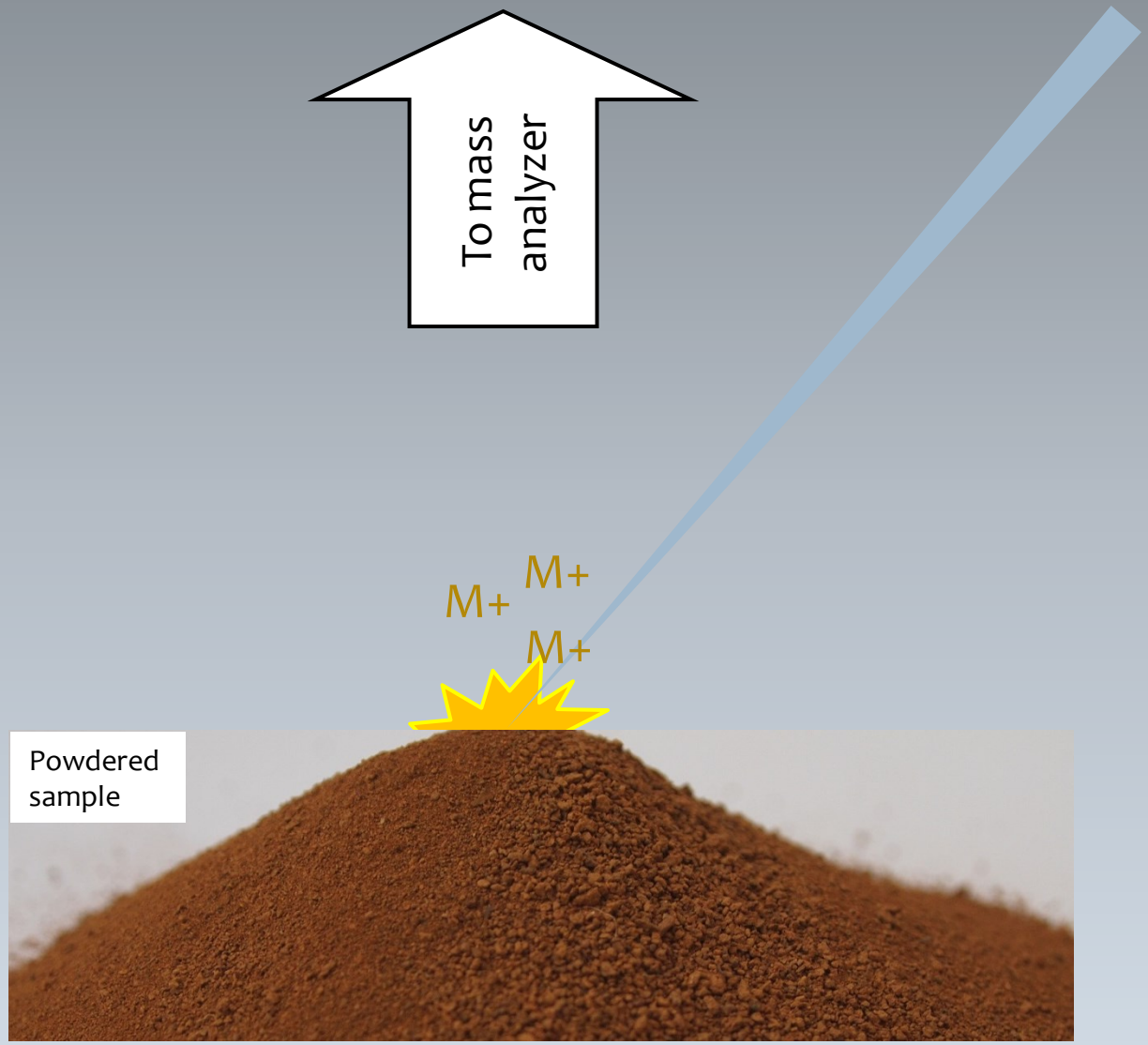

67P Churyumov-Gerasimenko

S. Getty/HEMS 2015

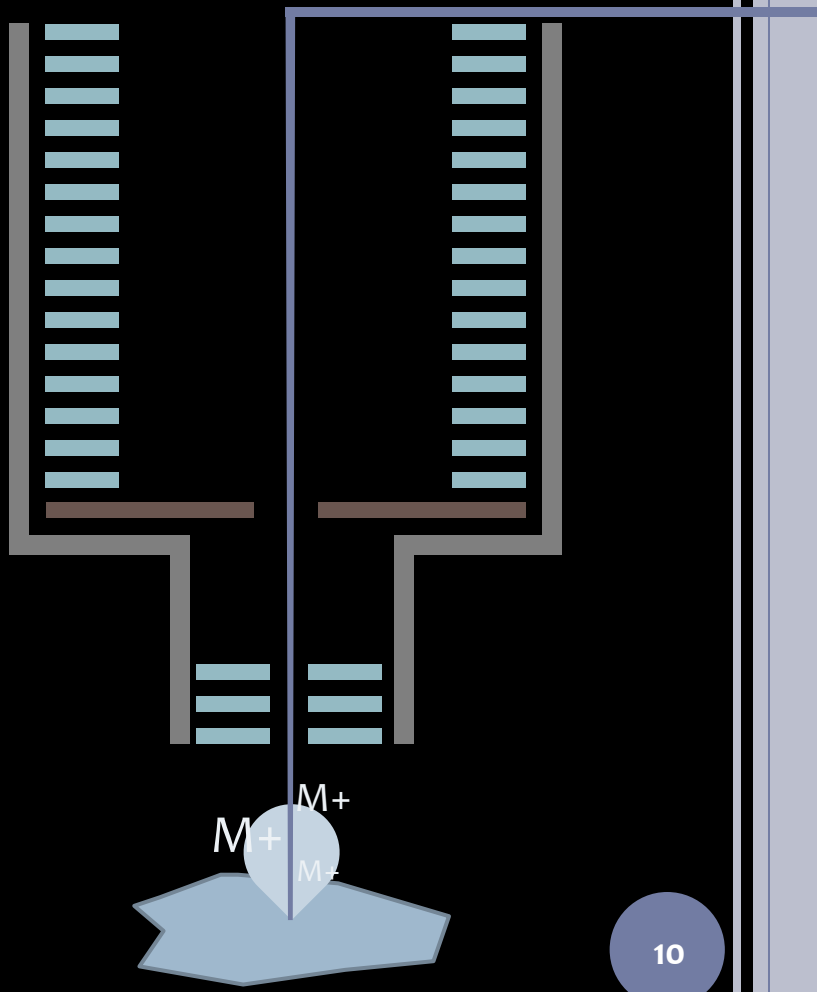
Why Mass Spectrometry for Planetary Missions?

- 'Universal' Detector
- Comprehensive Sample Analysis: compatible with various front-end analytical techniques
- Flexible to mission architecture: flybys, orbiters, landers, rovers

Laser Desorption/Ionization for Direct Analysis of Planetary Surface Materials



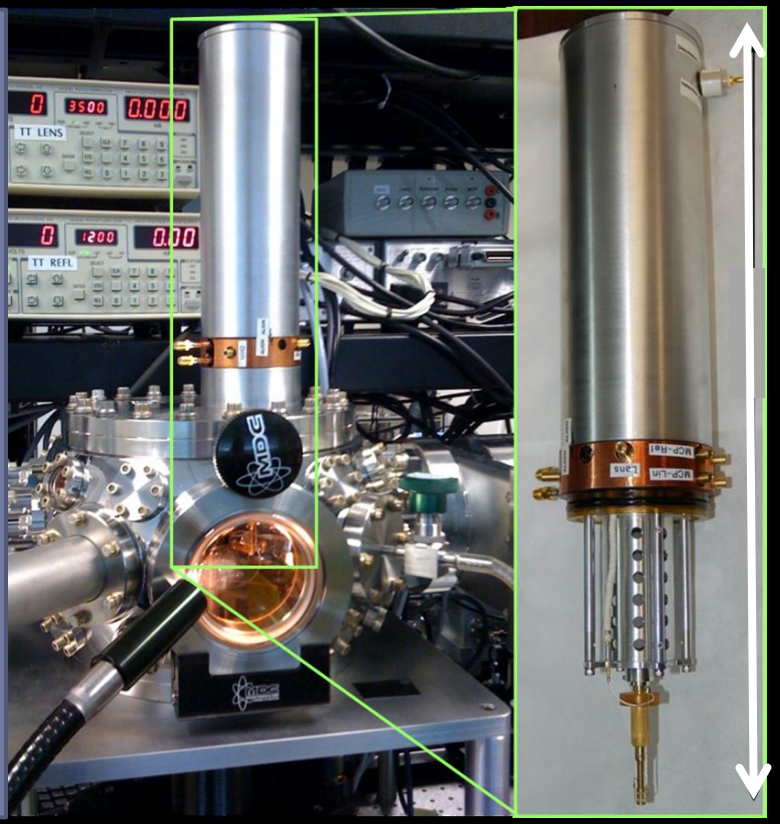
Commercial LD-TOF-MS (or MALDI) is a gold-standard technique for the analysis over a wide range of molecular weight, including large biomolecules



LD-TOF-MS as a compact instrument

is capable of analyzing broadband composition directly from a solid sample

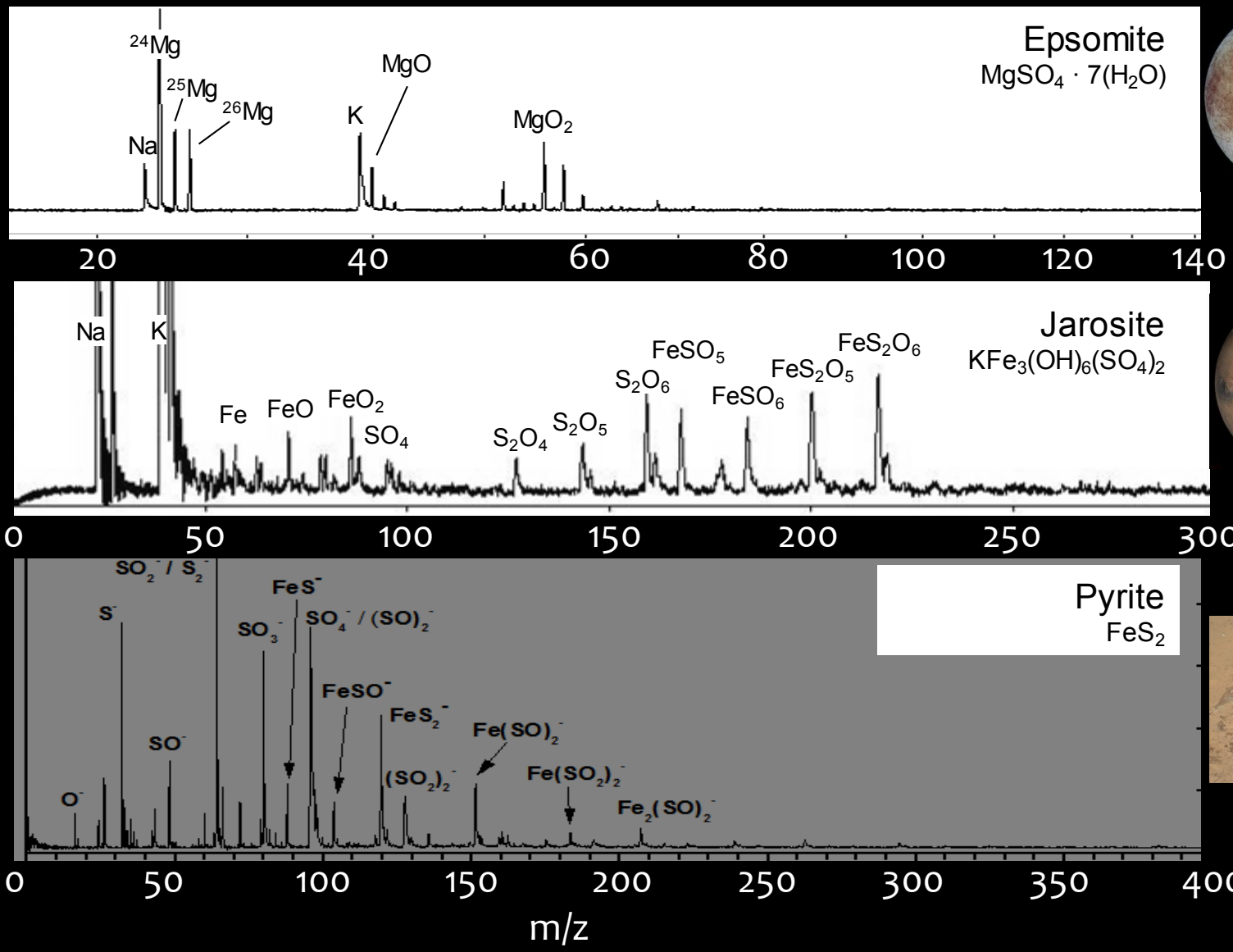
- Minerals
- Small organics:
  amino acids, carboxylic acids, polycyclic aromatics, etc.
- Intermediate organics:
  molecular fossil precursors, conjugated polymers, etc.
- Large organics:
  peptides, biopolymers, informational polymers, etc.
- Can resolve isotopes
  elemental & $^{12}C/^{13}C$ patterns



DUAL POLARITY ION MODE:

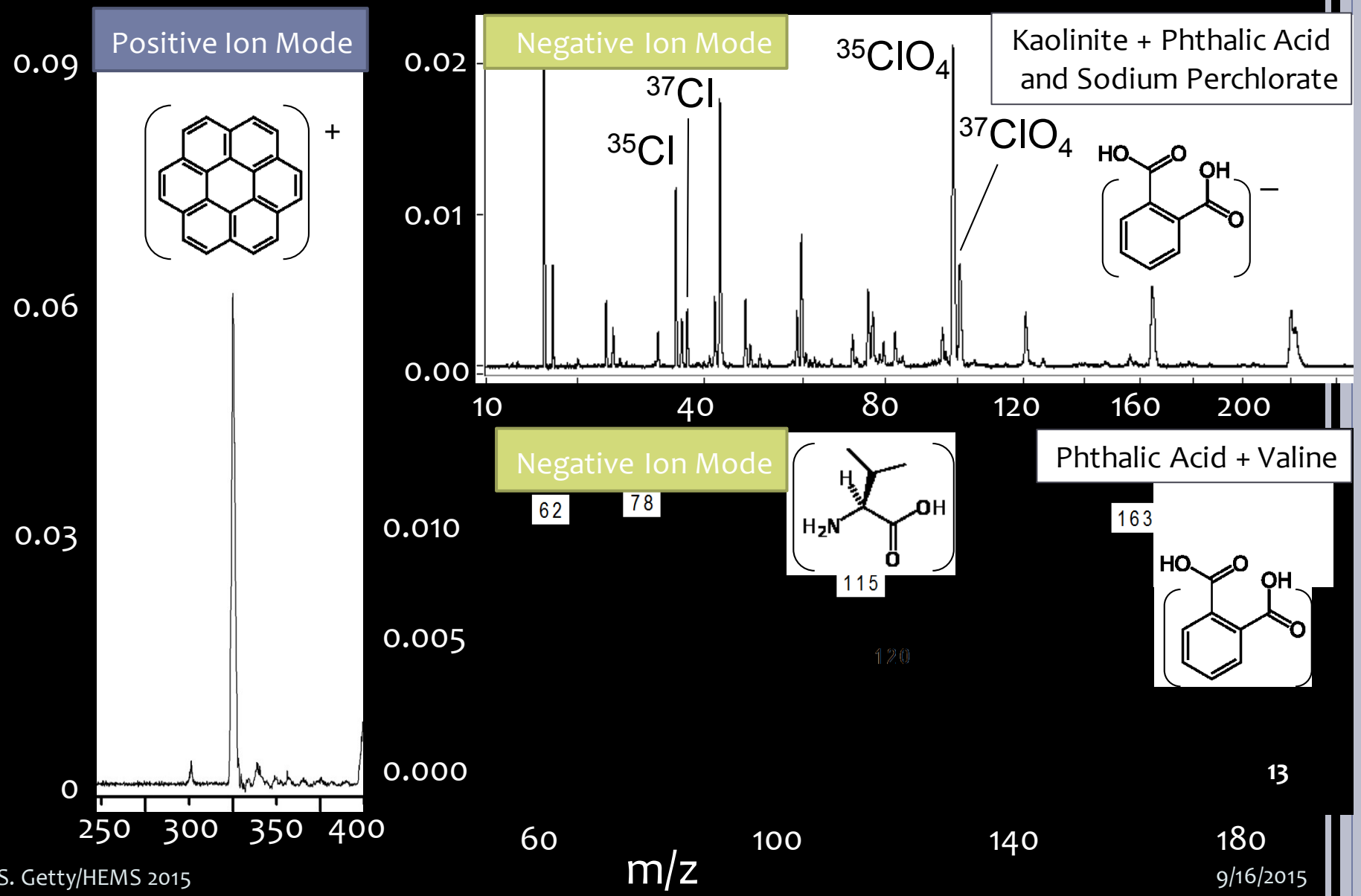
INORGANIC COMPOSITION

SEDIMENTARY AND AQUEOUSLY ALTERED MINERALS

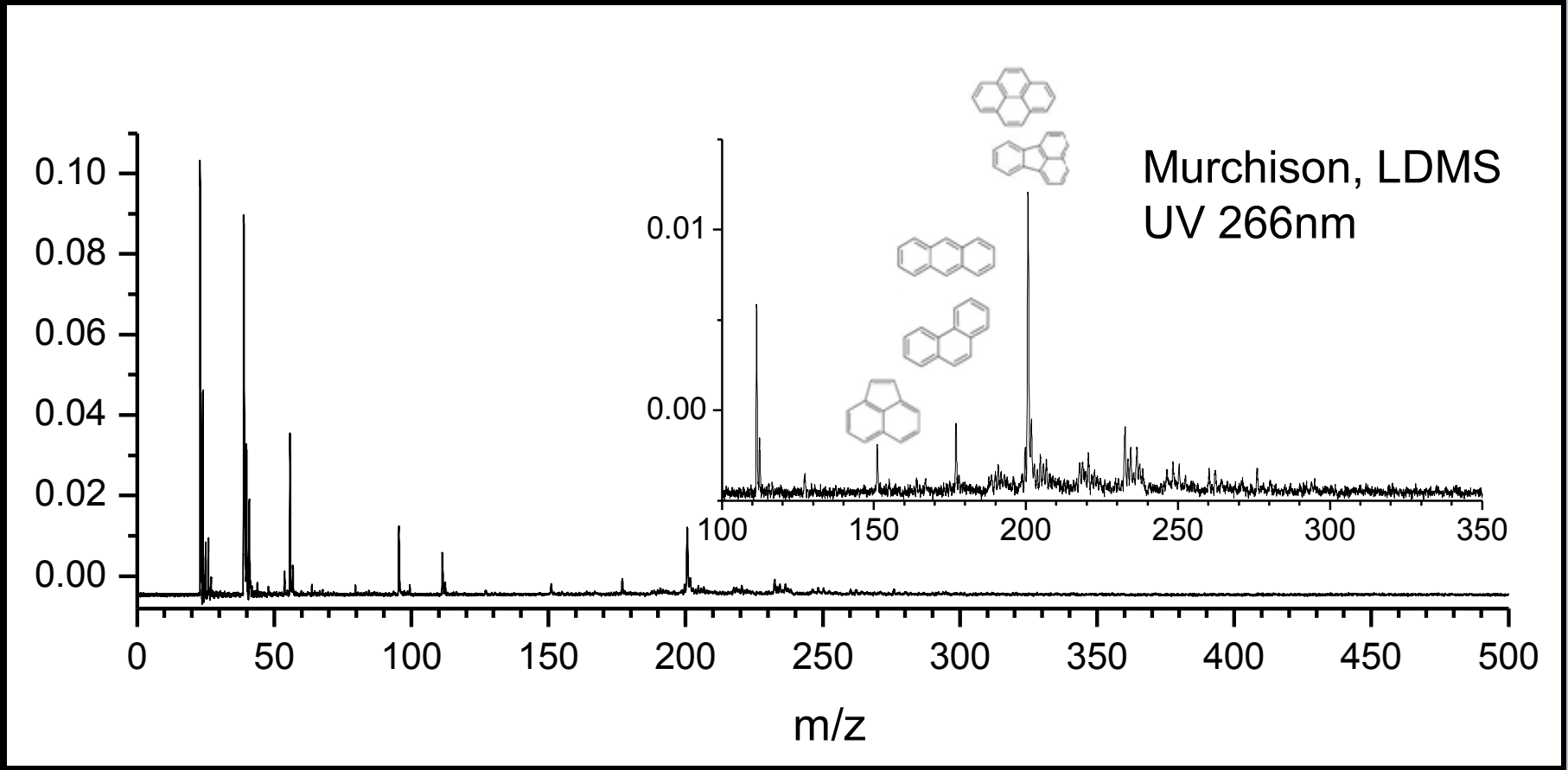


COMPLEMENTARY POSITIVE AND NEGATIVE ION DETECTION:

DETECTING ORGANICS ACROSS CLASSES

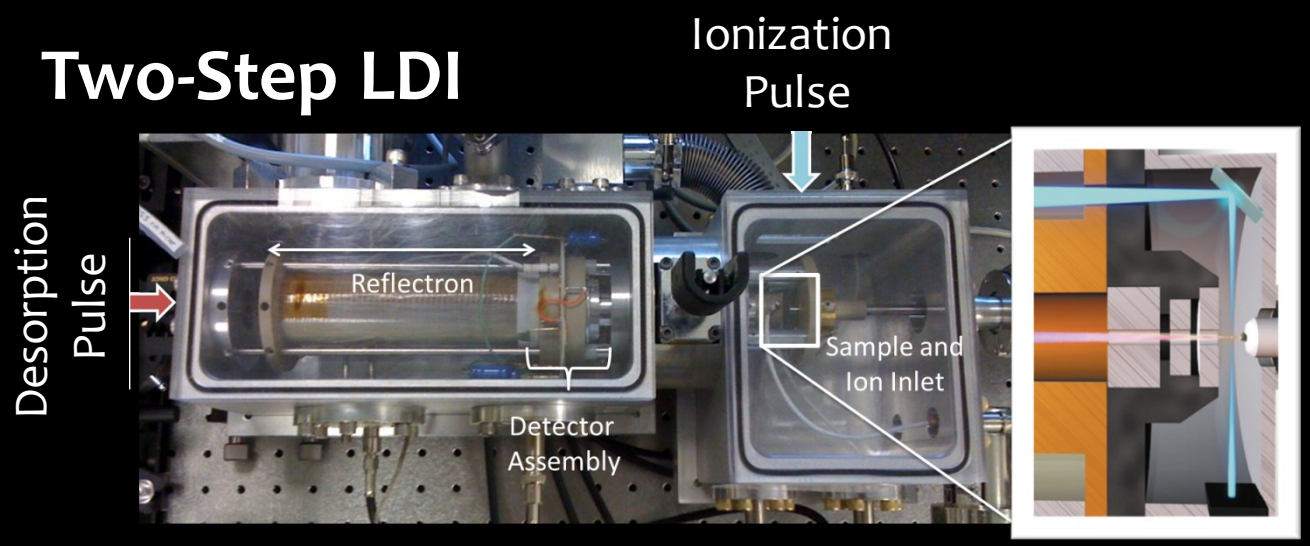


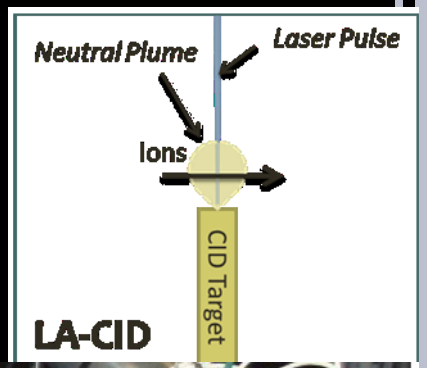
BUT IN REALITY WE COULD GET A SPECTRUM LIKE…



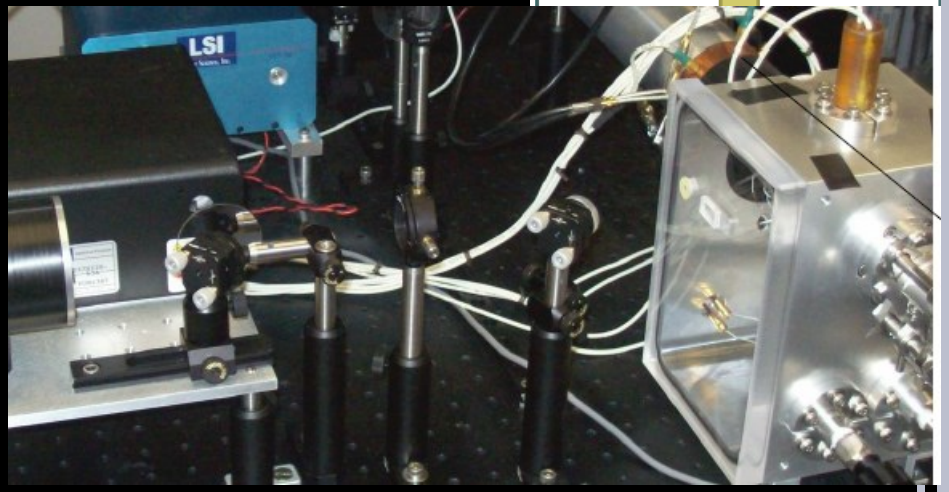
Tandem Two-Step Laser Mass Spectrometer

Two-Step LDI





Precision Ion Gating

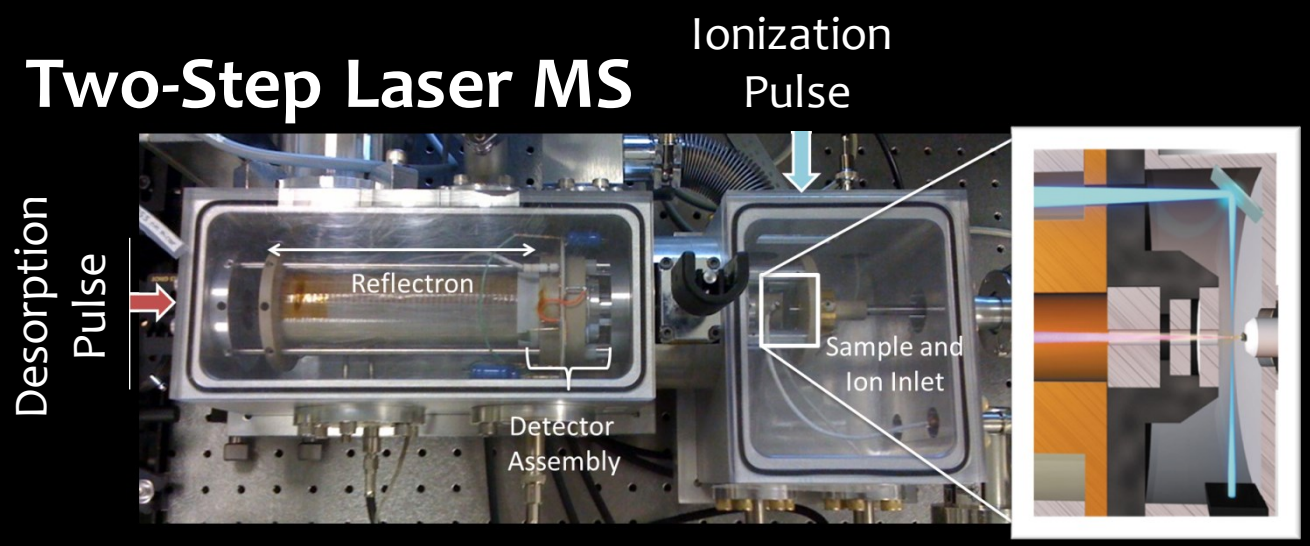


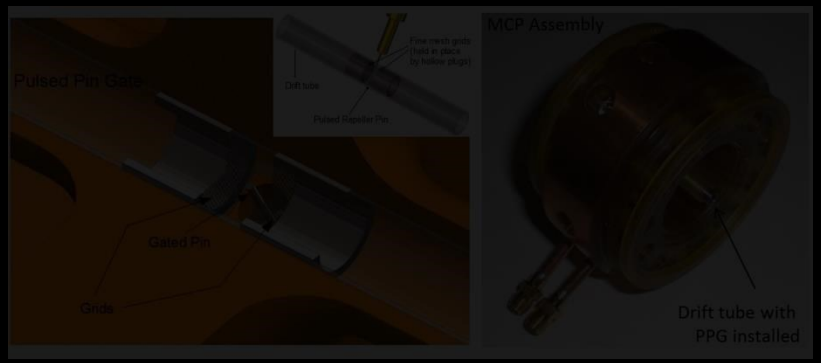
Fragment Analysis

L2MS PROTOTYPE:

FEATURES AND OPERATING PRINCIPLES

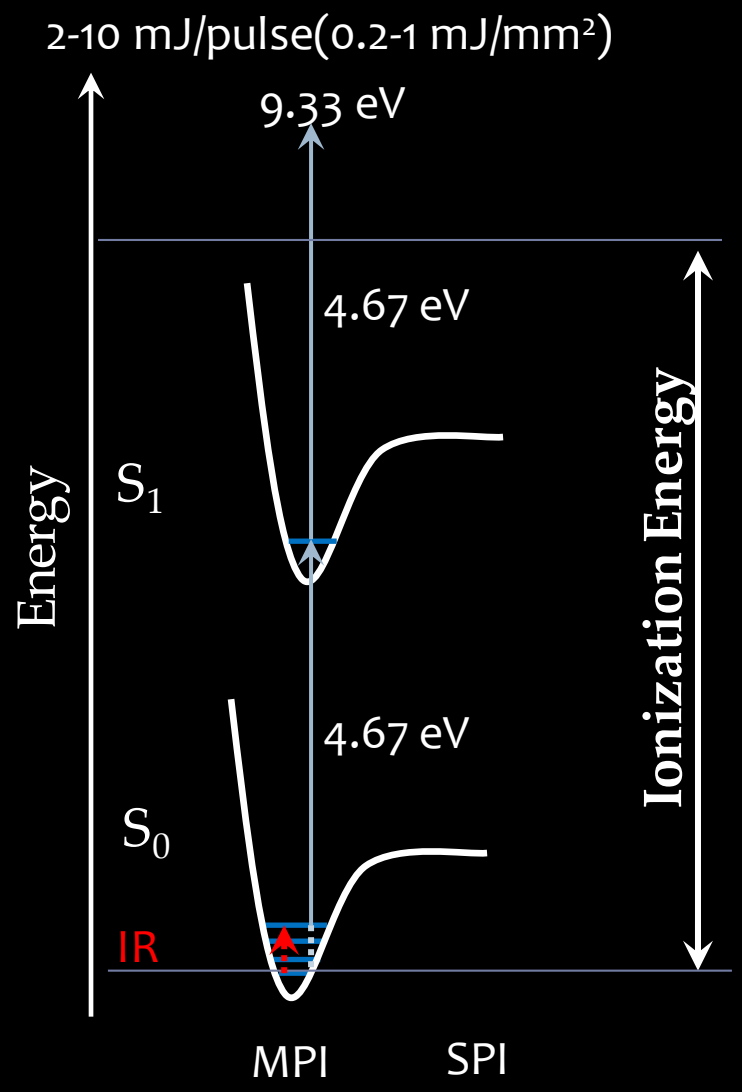
Two-Step Laser MS





Precision Ion Gating

Fragment Analysis

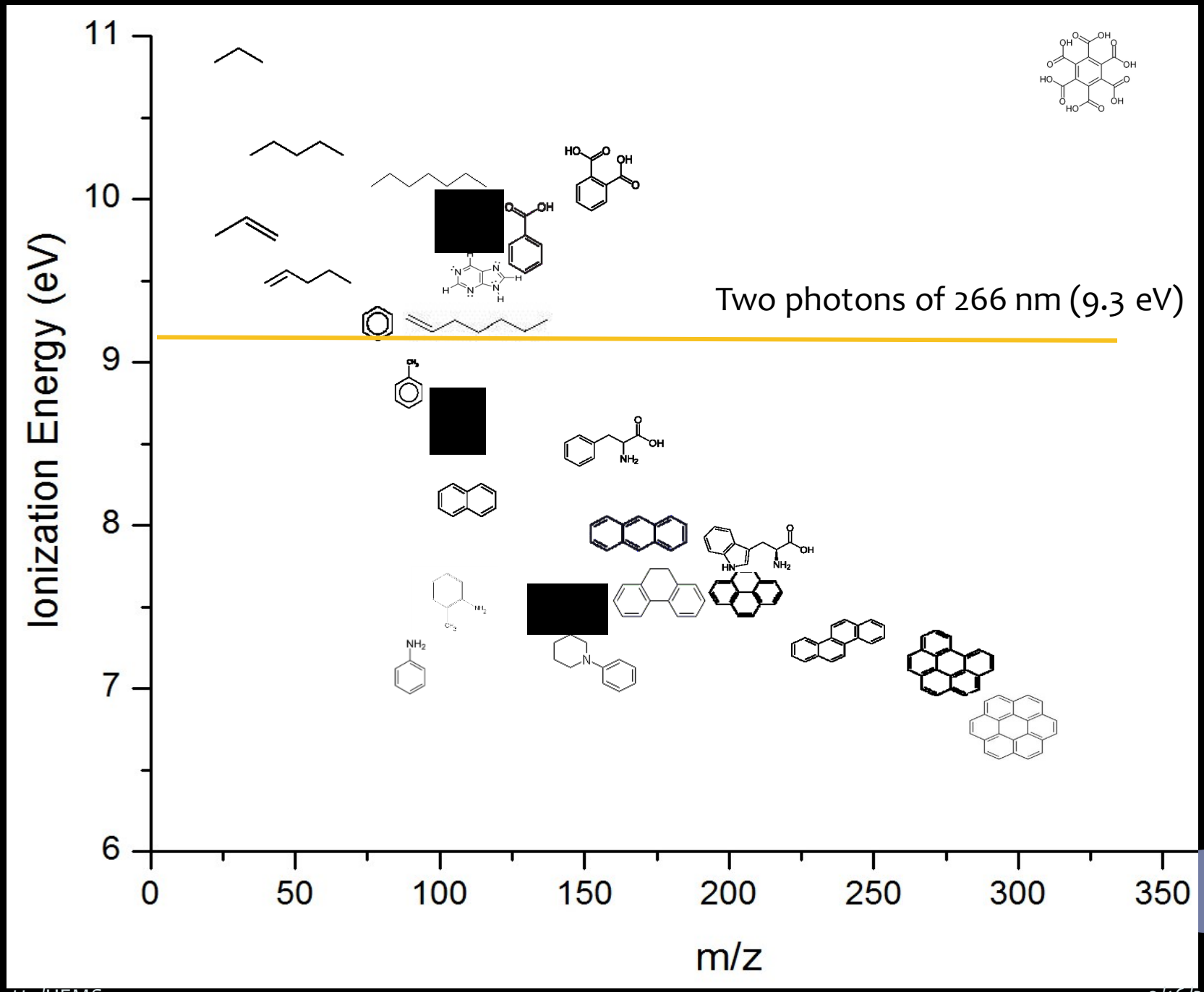


Resonance Enhanced Multiphoton Ionization
Selective ionization:

A. molecules ionization energy is lower than the two-photon energy
B. intermediate state can be pumped by one-photon absorption

Absorption of IR photons (0.12 eV):
Molecules may be at a higher state

Annu. Rev. Phys. Chem. 2007. 58:585–612

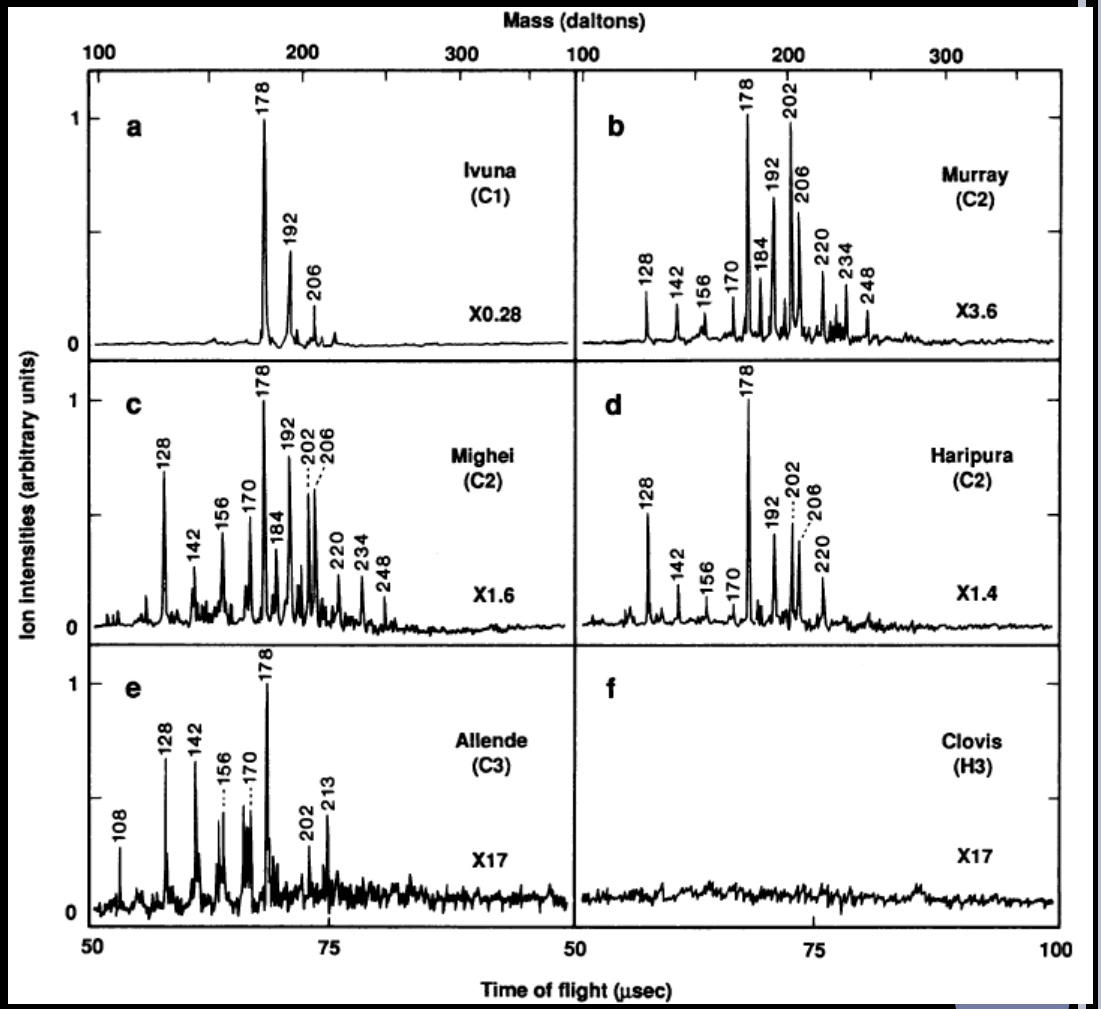

Ionization Energy (eV)
m/z
Two photons of 266 nm (9.3 eV)
11
10
9
8
7
6
0
50
100
150
200
250
300
350

Motivation for L2MS:

Molecular Specificity

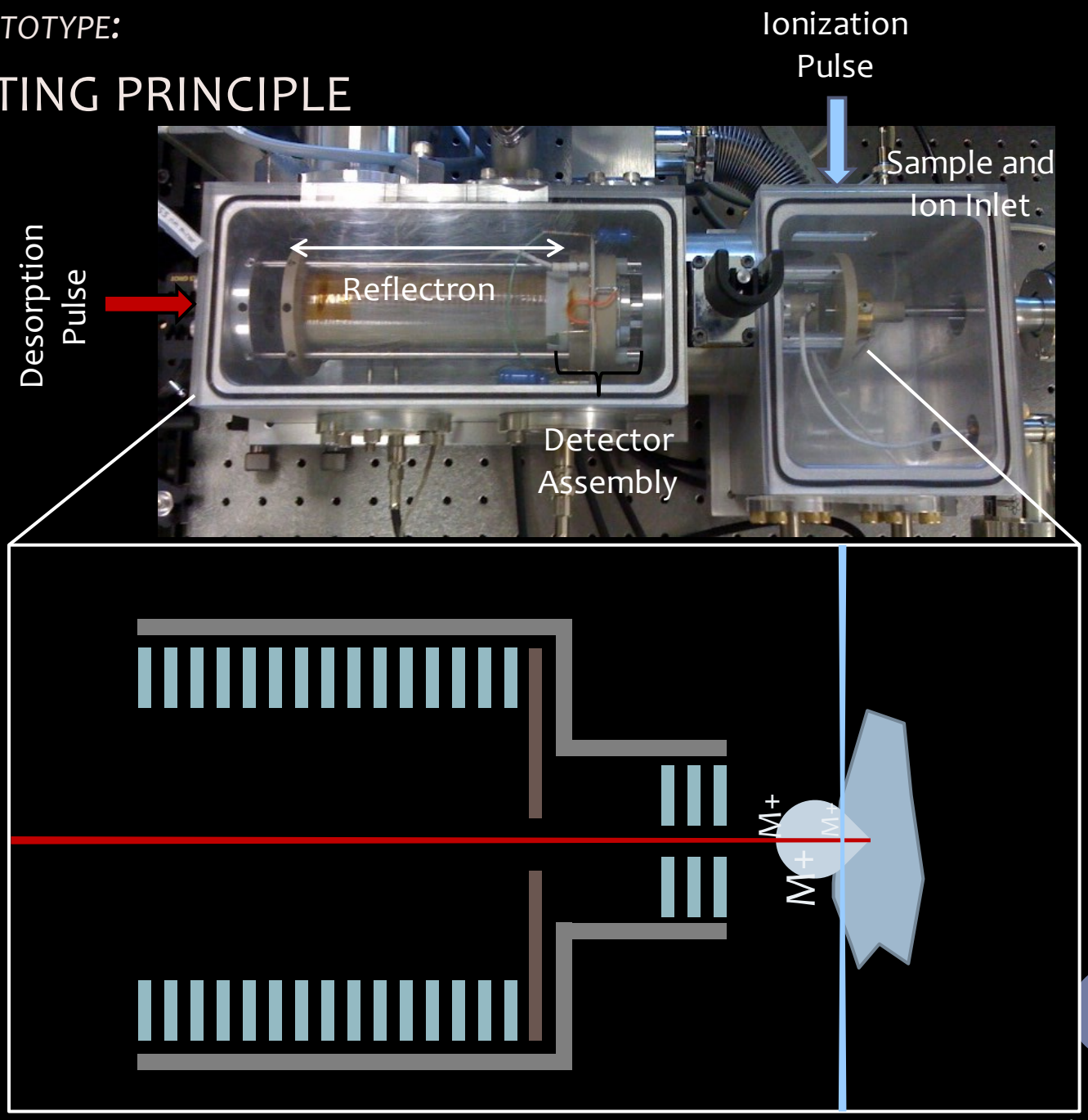
Hahn *et al.* 1998

- L2MS has been an informative technique used in the analysis of extraterrestrial materials, such as meteorites and Stardust samples
- The ionization laser can be chosen to be selective to a subset of organic species, such as polycyclic aromatic hydrocarbons
- Comparison between the single-laser baseline and L2MS spectra can allow separation of aromatic contributions



L2MS PROTOTYPE:

OPERATING PRINCIPLE



L2MS PROTOTYPE:

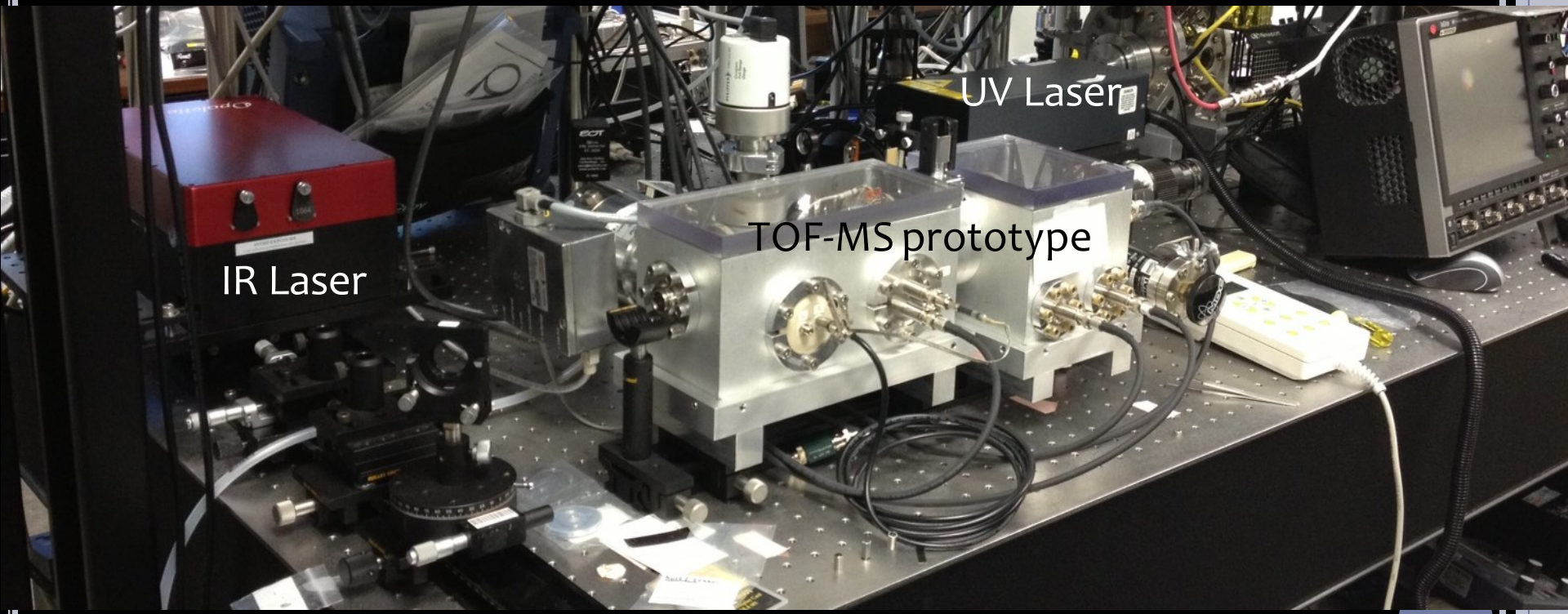
LABORATORY EXPERIMENT

IR Laser:

- 1064 nm Nd:YAG
- 2.7 to 3.1 um tunable OPO
- 10 um CO_2

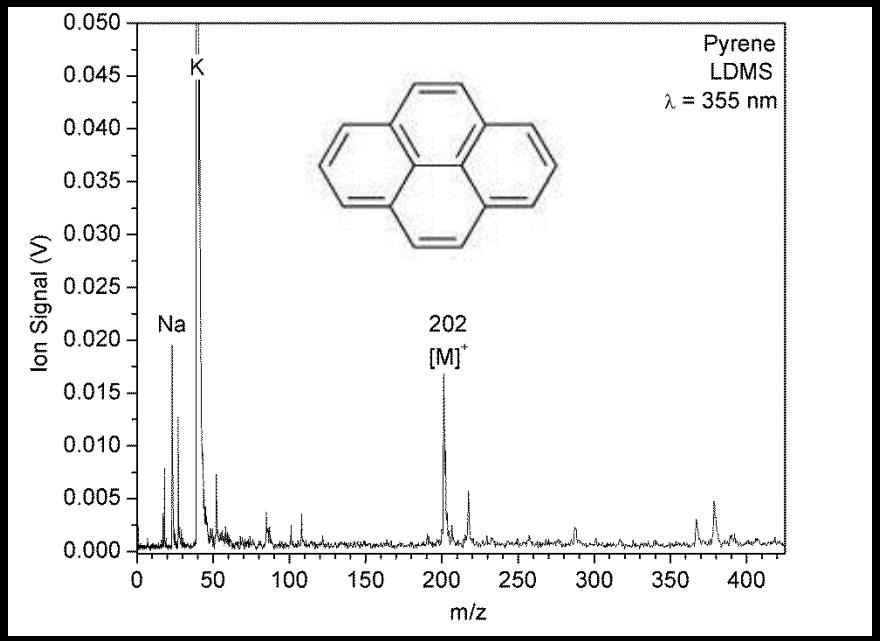
UV Laser:

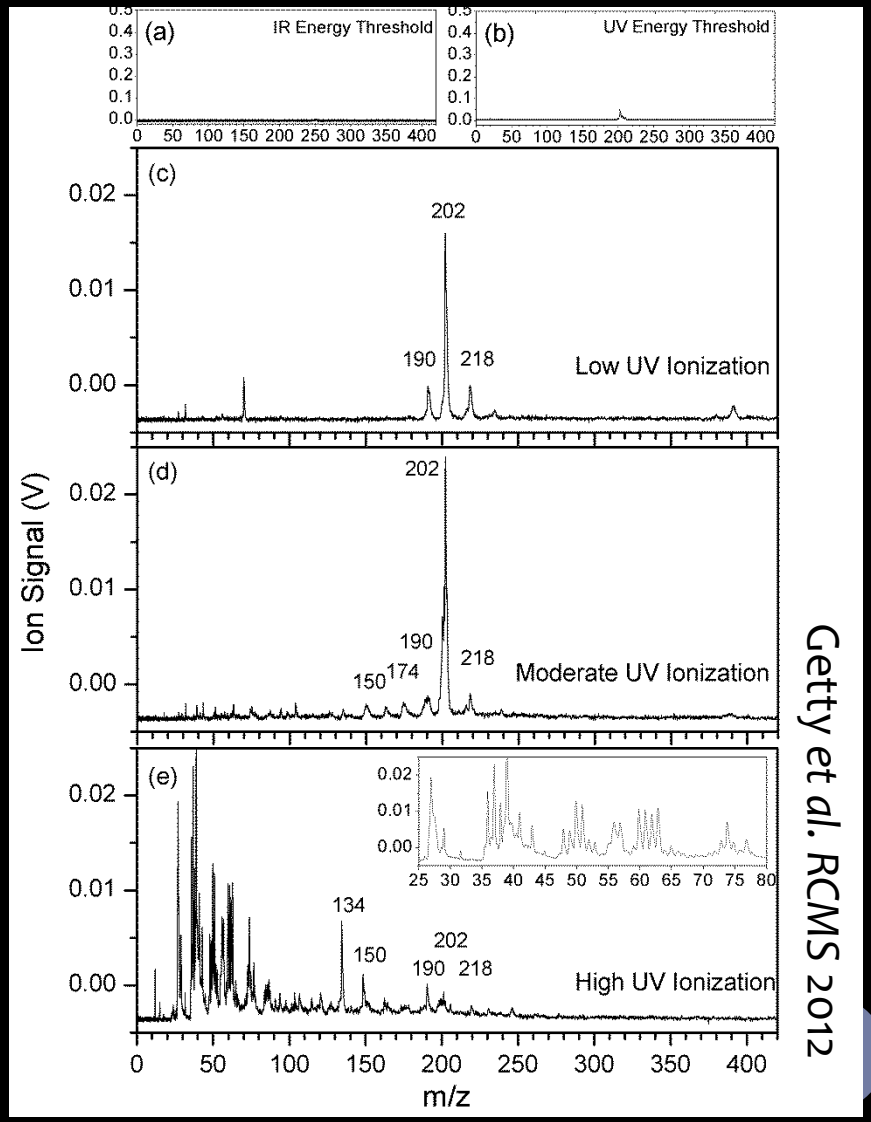
- 266 nm harmonic Nd:YAG
  4-7 ns pulse width
  focused to 50-100 um spot



L2MS PROTOTYPE:

SELECTIVITY TO AROMATICS



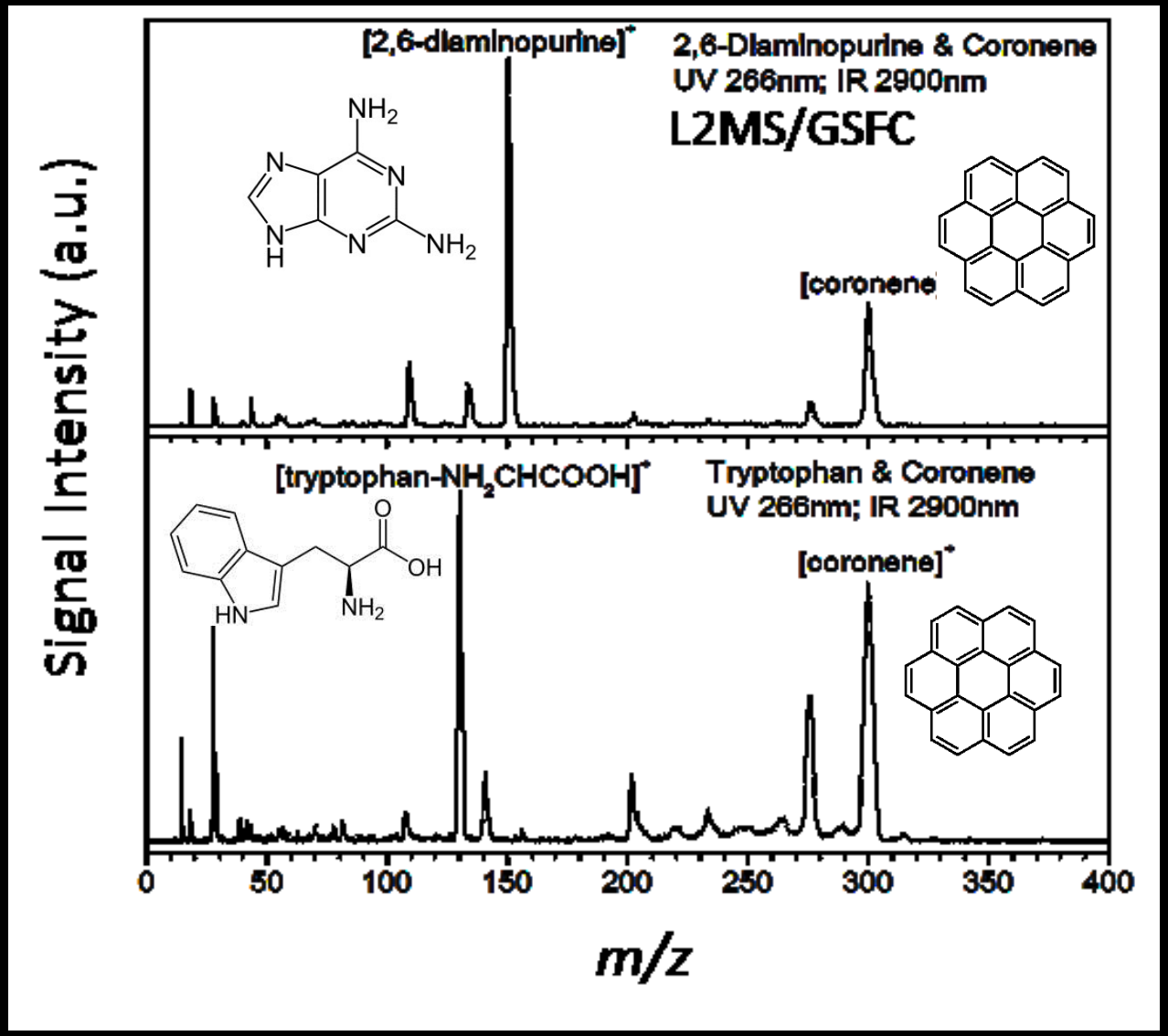


Getty *et al.* RCMS 2012

Model aromatic: pyrene
m/z 202

L2MS PROTOTYPE:

SELECTIVITY TO AROMATICS

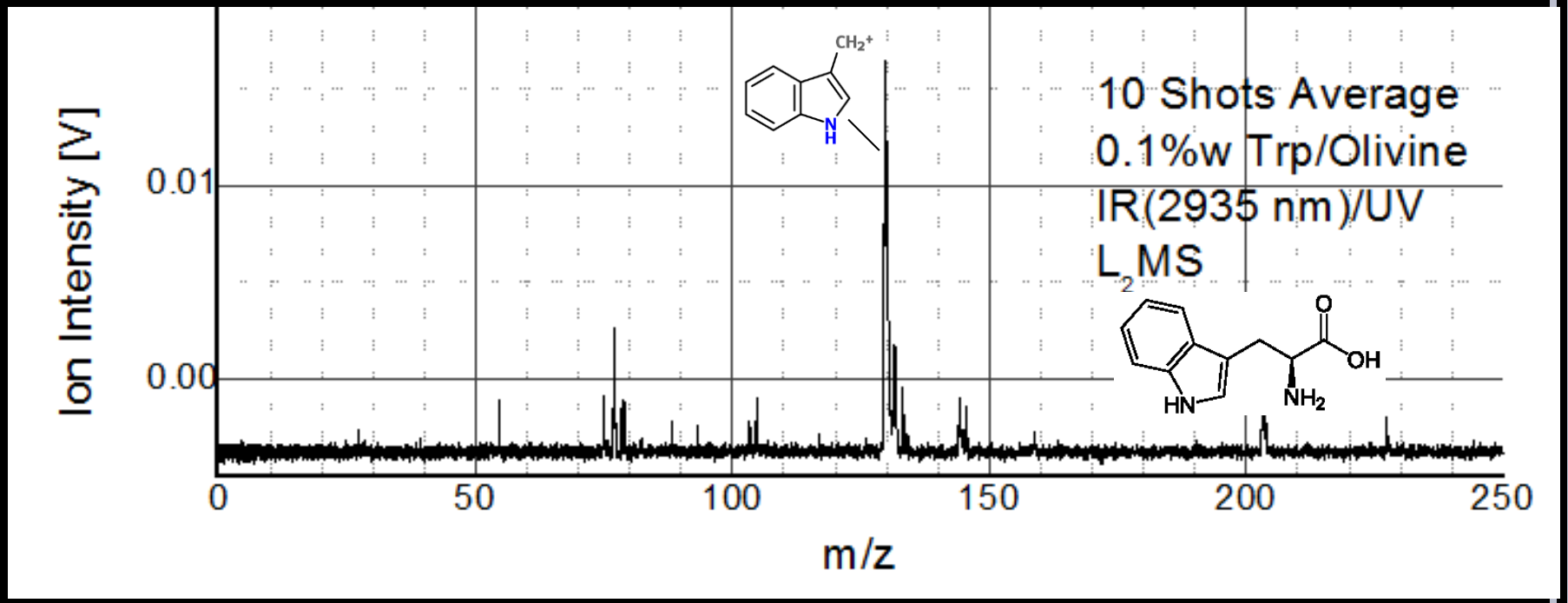


Getty *et al.* IEEE AeroConf 2014

L2MS PROTOTYPE:

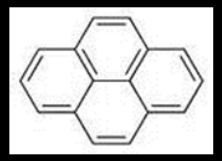
SENSITIVITY TO PREBIOTIC SPECIES

IN THE PRESENCE OF A MINERAL MATRIX

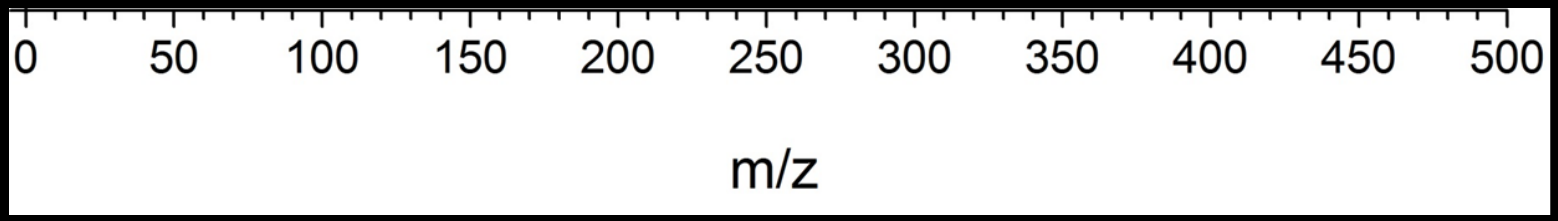


L2MS – Selectivity in Ionization Step

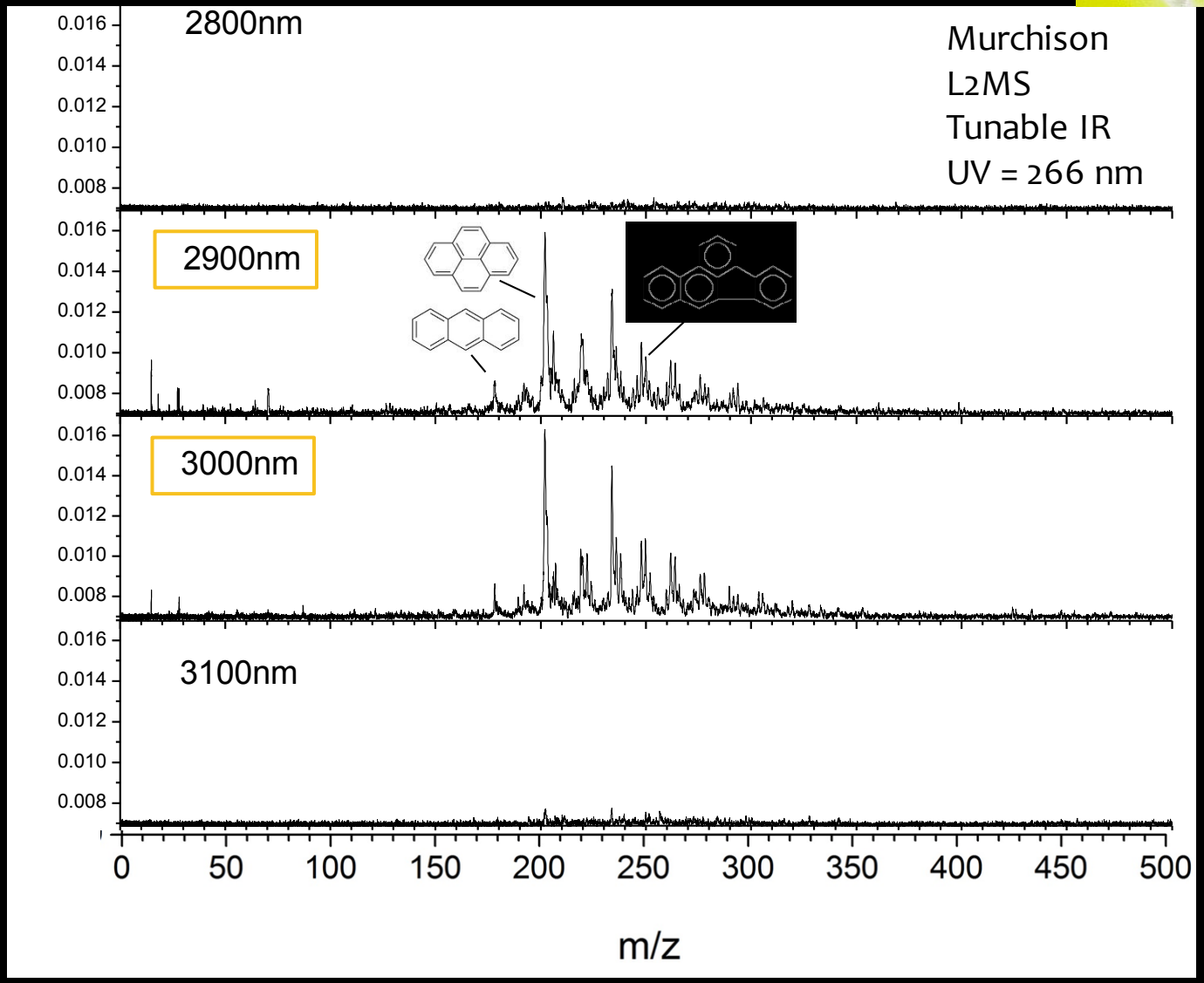
Murchison powder
L1DMS mode

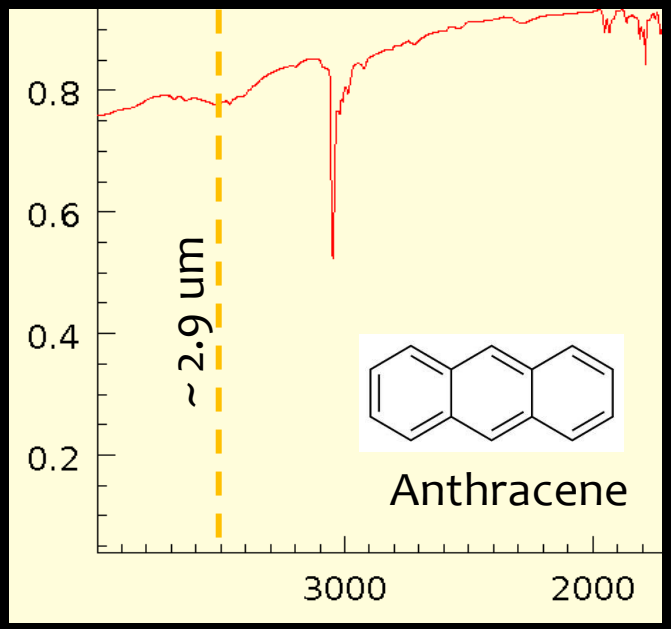


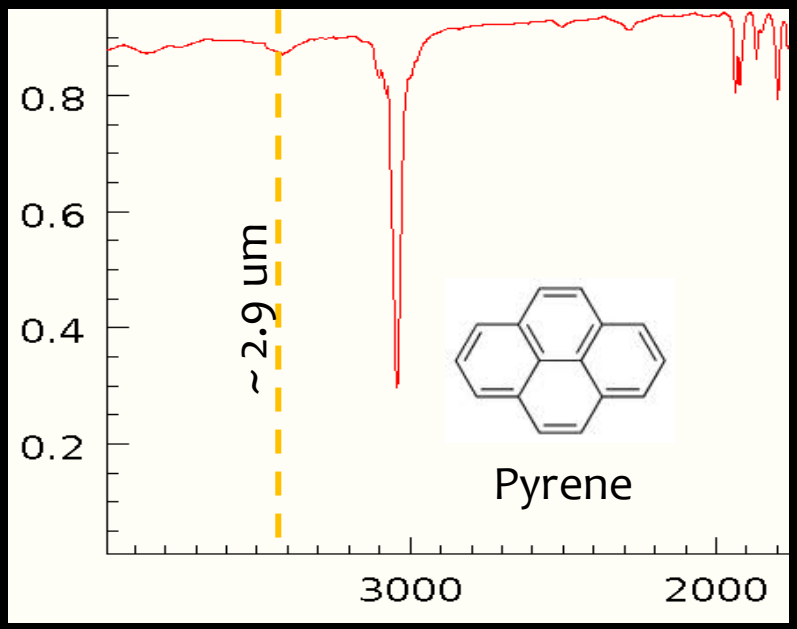
Murchison
L2MS mode



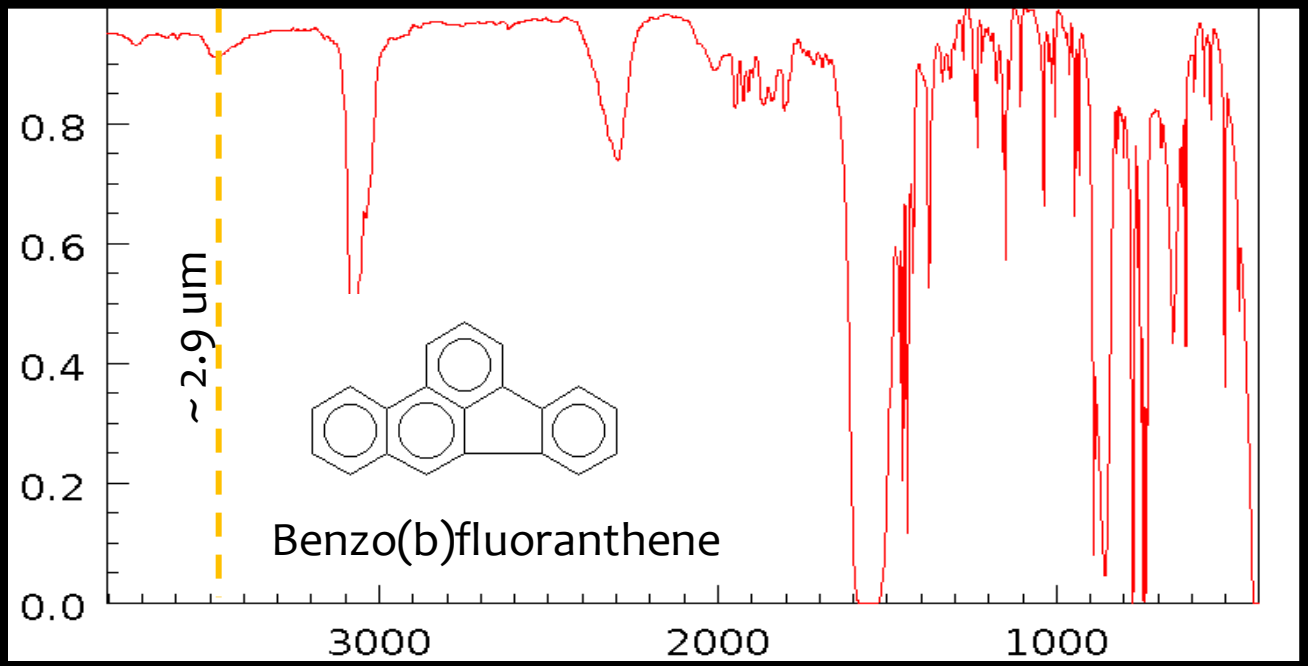
L2MS – Selectivity in Desorption Step







Transmittance

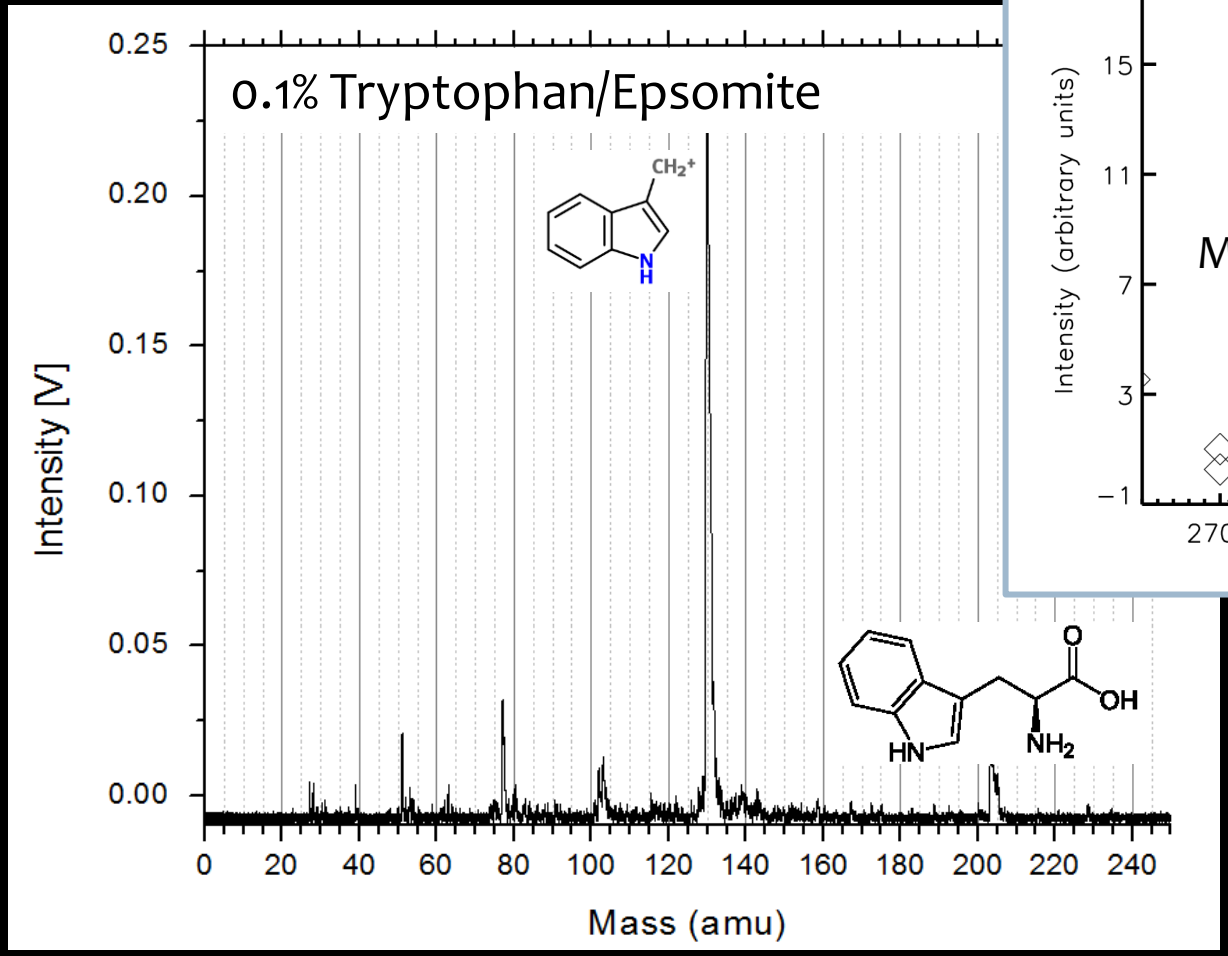


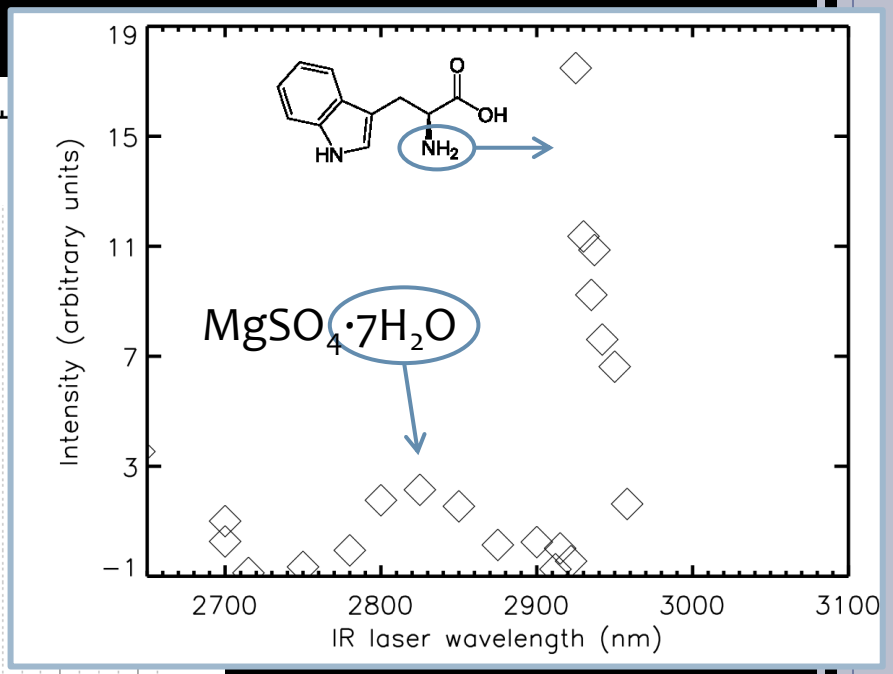
Wavenumbers (cm-1)

L2MS PROTOTYPE:

IR TUNABILITY CAN EXPLOIT RESONANCES

FOR HIGH SENSITIVITY

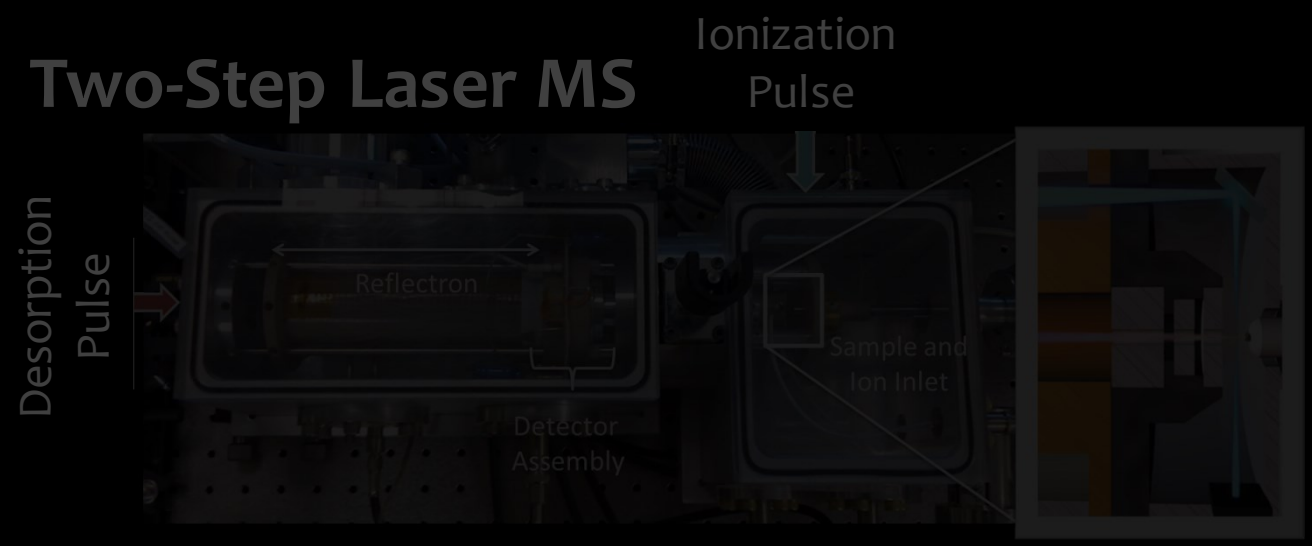


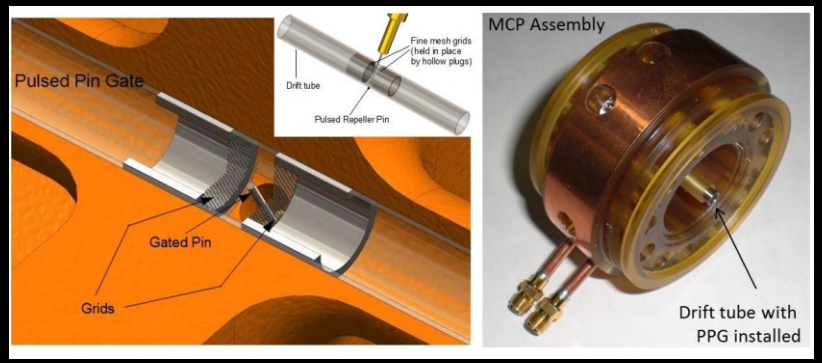


L2MS PROTOTYPE:

FEATURES AND OPERATING PRINCIPLES

Two-Step Laser MS





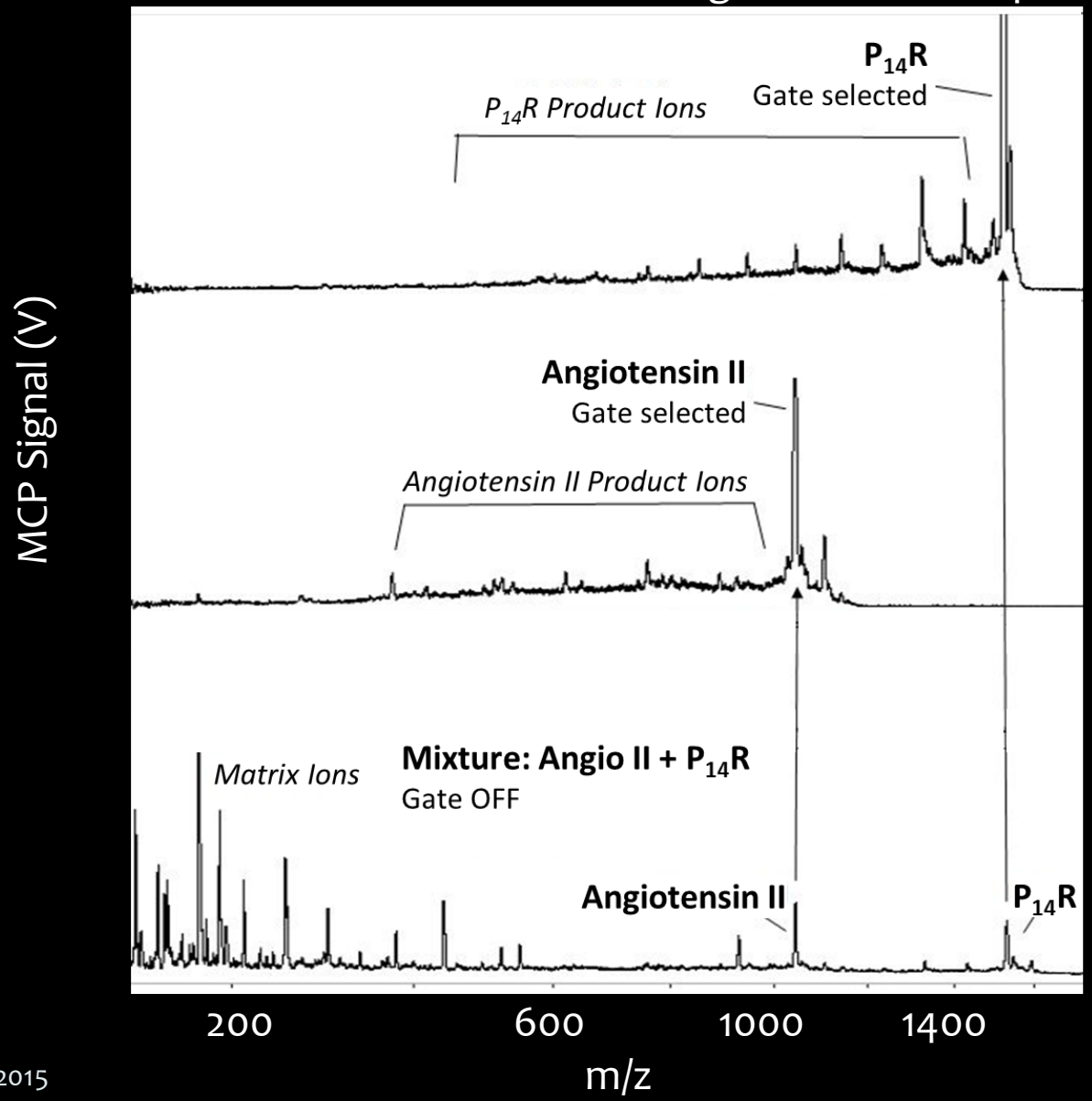
Precision Ion Gating

Fragment Analysis

L2MS PROTOTYPE:

PRECISION ION GATING AND TANDEM MS

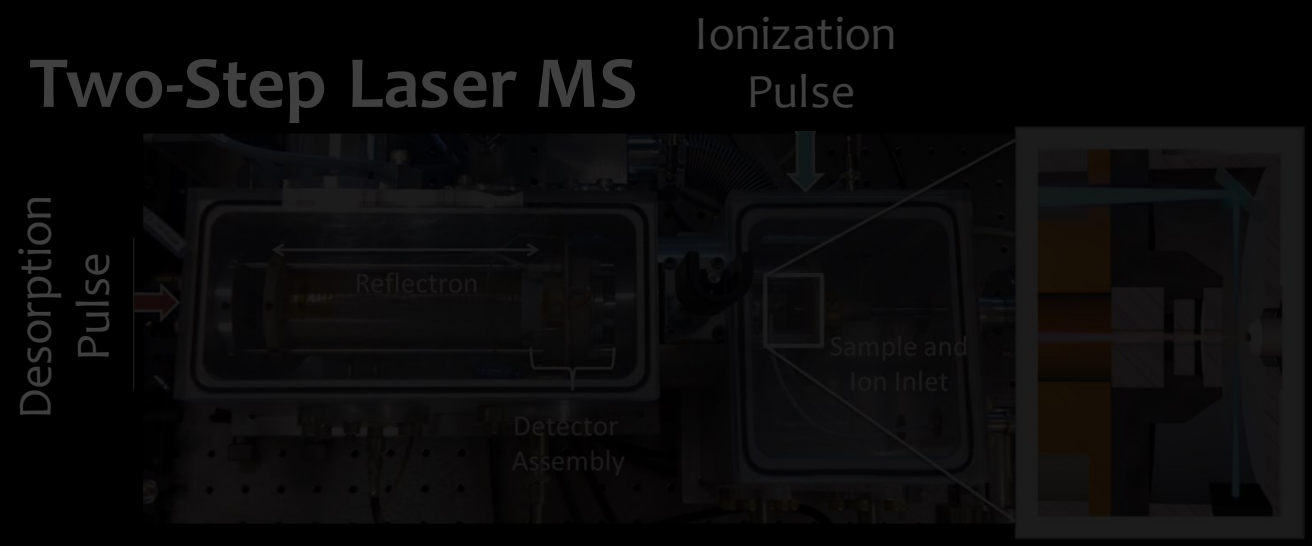
Structural determination using MS/MS techniques

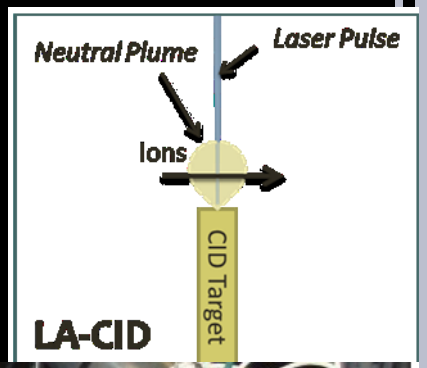


L2MS PROTOTYPE:

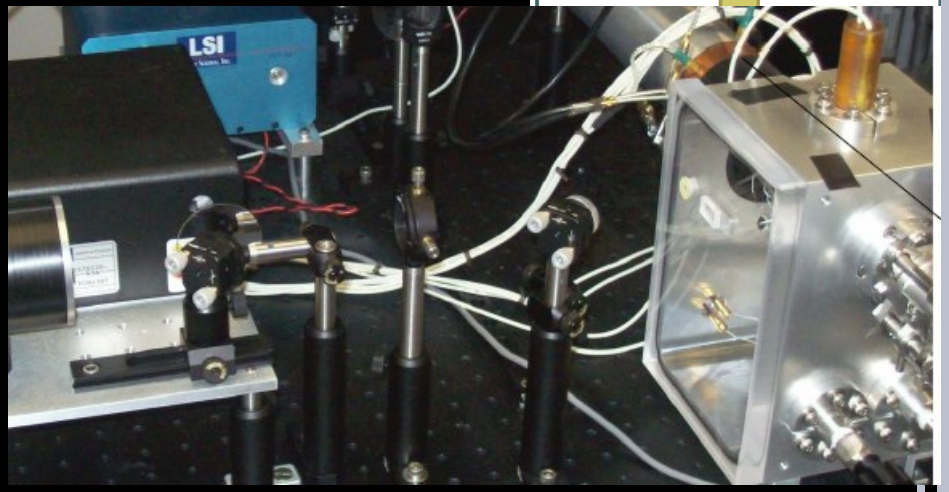
FEATURES AND OPERATING PRINCIPLES

Two-Step Laser MS





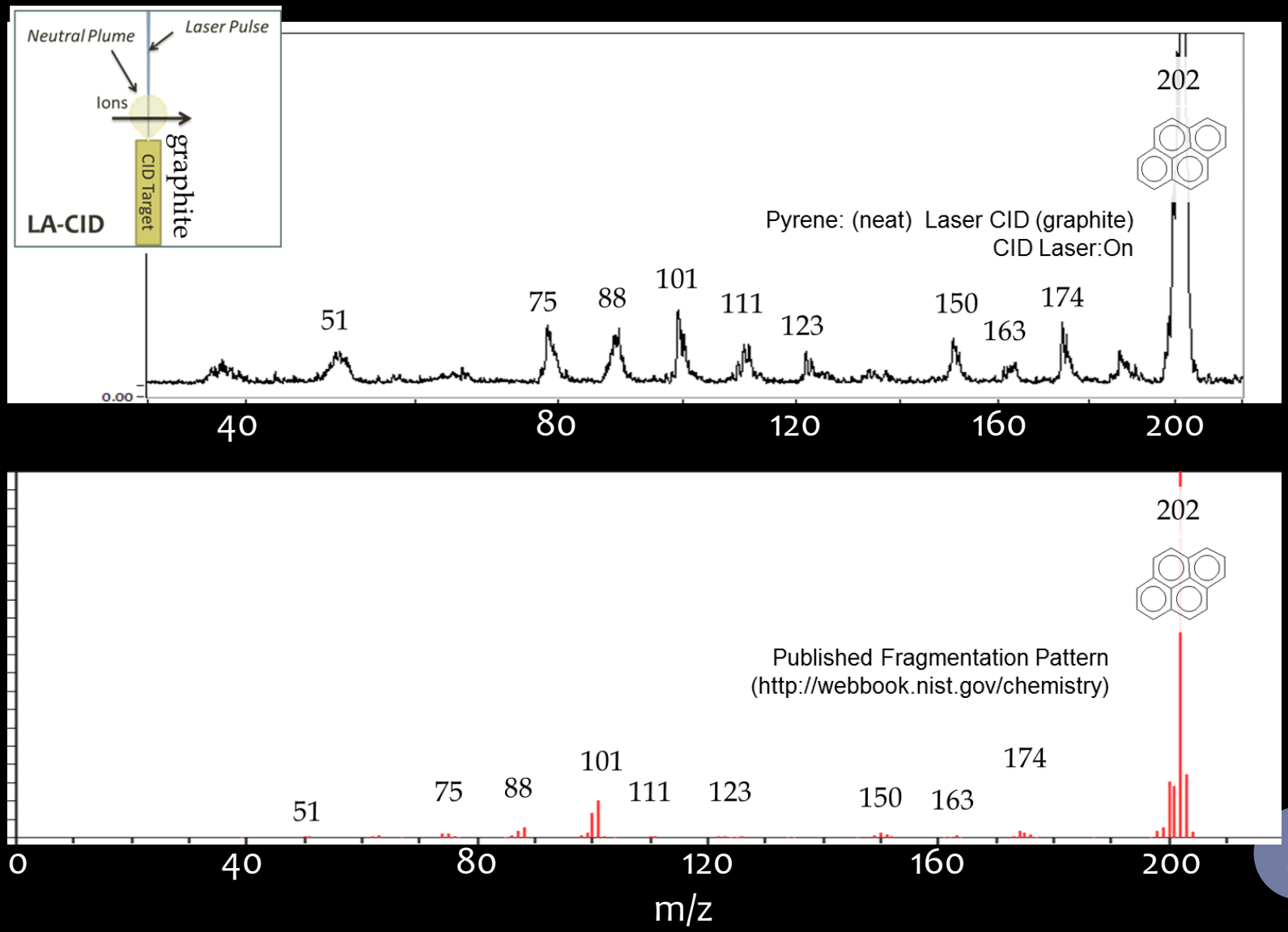
Precision Ion Gating



Fragment Analysis

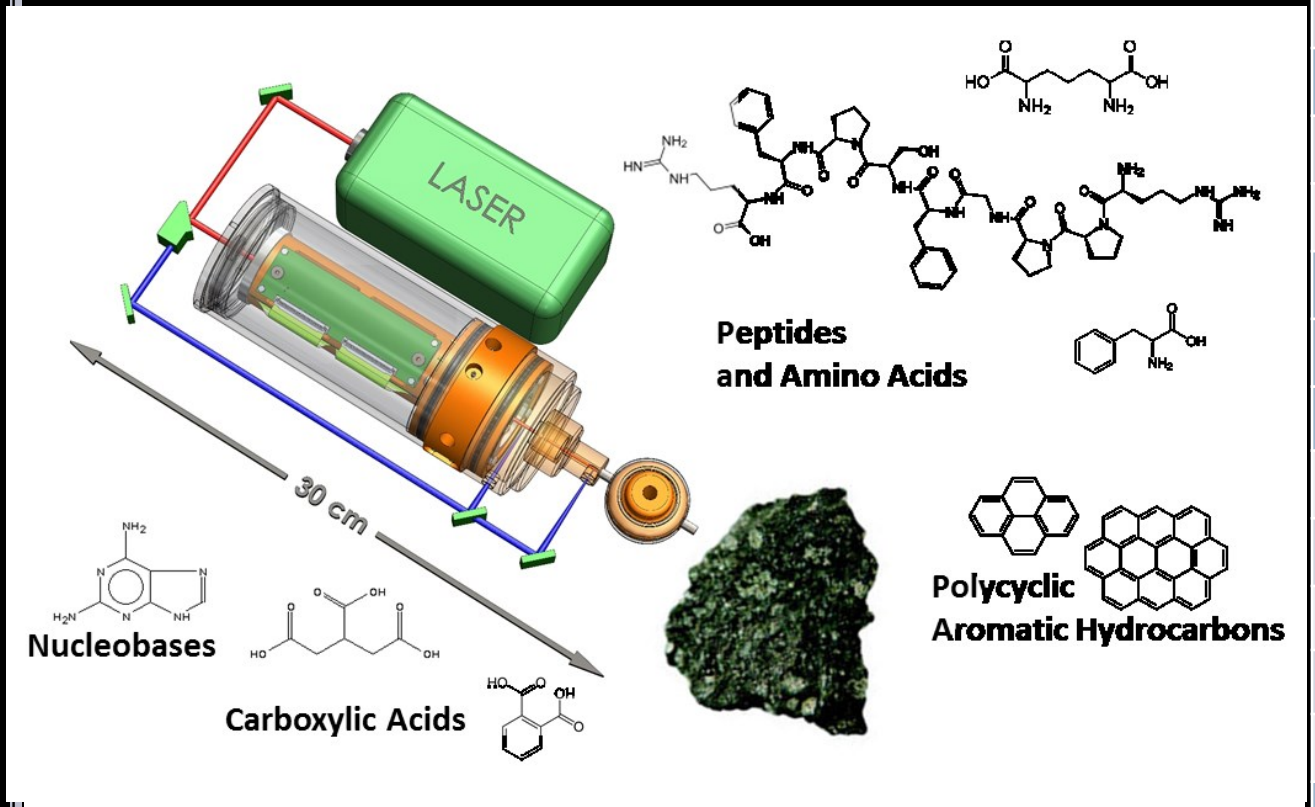
L2MS PROTOTYPE:

LASER-ASSISTED COLLISION-INDUCED DISSOCIATION FOR PSEUDO-TANDEM MASS SPECTROMETRY



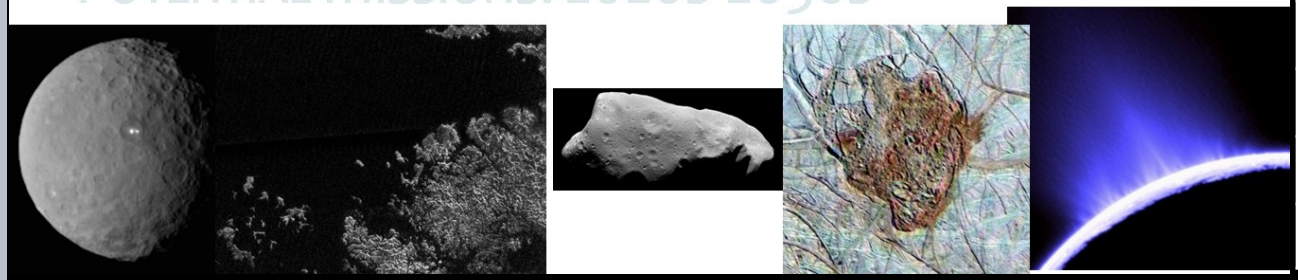
L2MS Instrument Design:

5 kg-class in situ analyzer



L2MS Mass Estimate	
Subsystem	Mass/g
1. TOF-MS	700
1.1 Mass Analyzer	330
1.2 Housing	370
2. Laser	1693
3. Optical	380
4. Electronics	1826
4.1 Comm/Data	291
4.2 Power Supply	585
4.3 Pulsed HV	440
4.4 Detector	260
4.5 Harness	250
SUBTOTAL (airless body)	4599
5. Turbo Pump*	550
5.1 Pump, 200 krpm	200
5.2 Controller	350
TOTAL	5149

Potential Missions: 2020s-2030s



Our Team

GSFC Planetary Environments Lab

- Will Brinckerhoff
- Xiang Li
- Andrej Grubisic
- Rick Arevalo
- Melissa Floyd

GSFC Astrochemistry Lab

- Jamie Elisila
- Mike Callahan

C&E Research, Inc

- Tim Cornish
- Scott Ecelberger

GSFC Laser and Electro Optics Branch

- Tony Yu

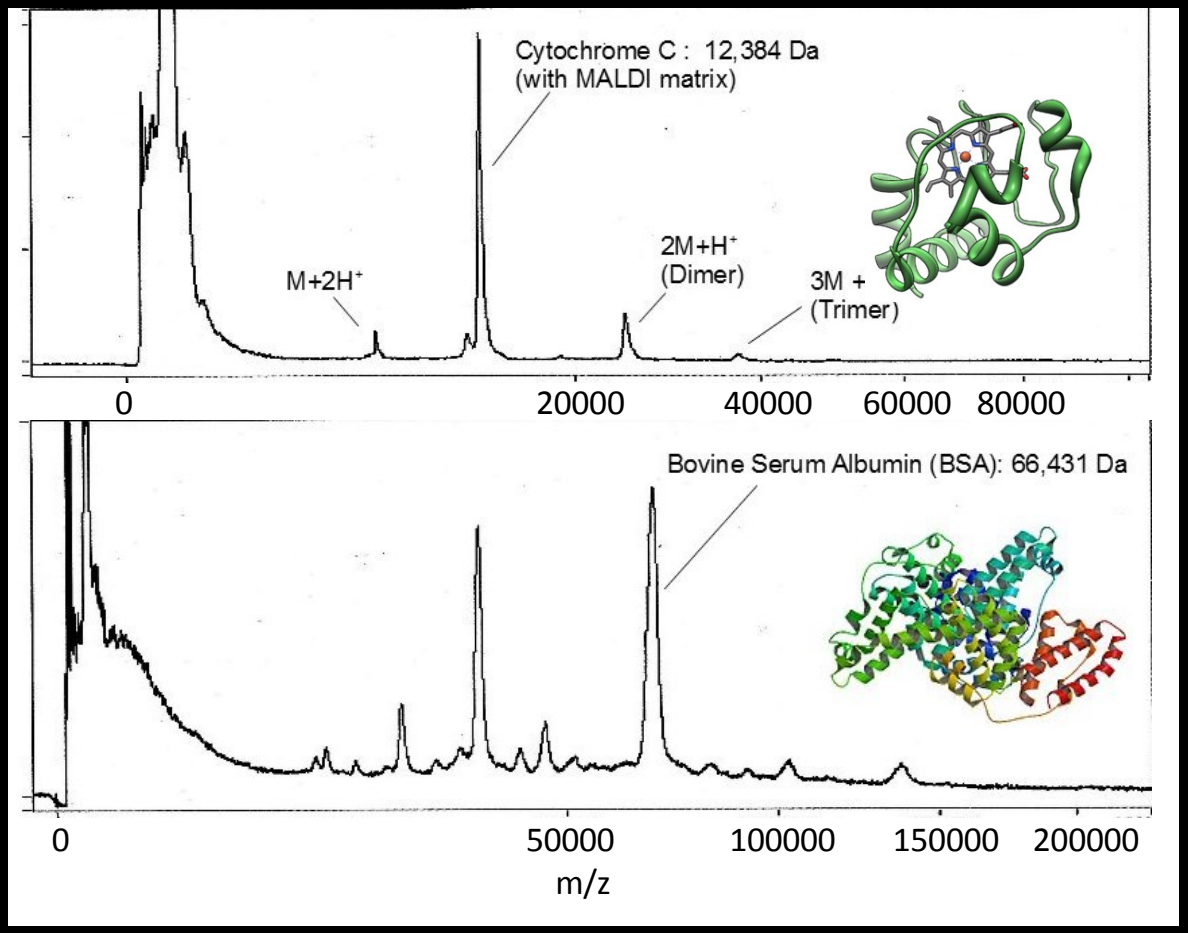
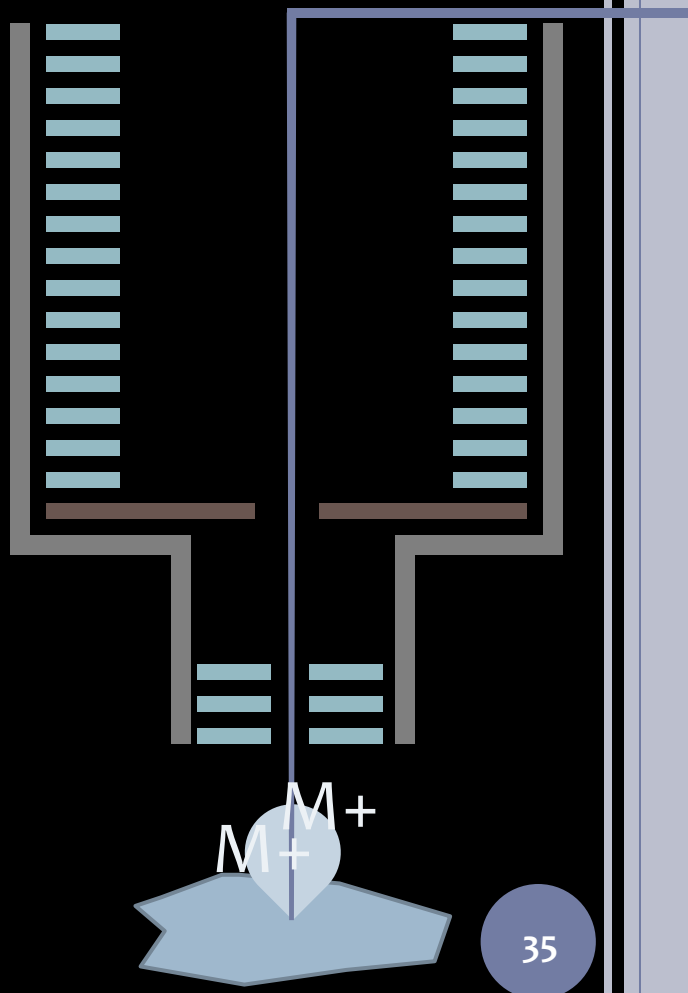
Stanford University

- Dick Zare
- Qingaho Wu

New Mexico State University

- Kyle Uckert (NASA Space Technology Research Fellow)

Supported by

- Planetary Instrument Definition and Development Program
- Astrobiology Science and Technology for Instrument Development Program

High Sensitivity Mode